COMPREHENSIVE ORGANOMETALLIC CHEMISTRY III

Editors-in-Chief
Robert H. Crabtree & D. Michael P. Mingos

Volume
6

COMPOUNDS OF GROUP 8

Volume Editor
Michael Bruce

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CHEMISTRY III

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University of Oxford, Oxford, UK

Robert H. Crabtree

Yale University, New Haven, CT, USA

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University of Adelaide, Adelaide, SA, Australia

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Preface

The availability of remarkably efficient search engines has made the access to the relevant literature and specific facts remarkably quick and efficient, but the information retrieved is not always refereed, checked or placed in its appropriate context. As Henry Kissinger [1] has remarked: "The computer has solved the problem of storing knowledge and making a vast amount of data available. Simultaneously, it exacts the price of shrinking [one's] perspective". In this latest edition of Comprehensive Organometallic Chemistry we have tried to engage the best minds in the field to sift the literature in their area of expertise and distill it down to produce a readable summary of the essential material. We have instructed them to be comprehensive in their coverage and authoritative in their approach and thereby maintain the standard and reputation of the original Comprehensive Organometallic Chemistry published in 1982 and the Second Edition published in 1995. Both editions were edited by Professors Abel, Stone and Wilkinson. This Third Edition of Comprehensive Organometallic Chemistry (COMC-III) builds on the two previous collections and incorporates a vast amount of new knowledge published since 1993, and simultaneously interprets the developments by providing general and significant insights by leading experts in the field.

Those seeking a structured entry into the impressive field of organometallic chemistry will find, either the desired information itself, or at least a reference to the primary or secondary literature that covers the point at issue. In the COMC tradition, we hope that this work will be useful not only to experts, but also to workers in allied fields who need to turn to organometallic chemistry to solve some pressing problem. With this in mind we have devoted the first volume to fundamental principles in order to provide a helpful entry into this important field for graduate students and scientists whose primary expertise lies in other areas. We also hope that readers will dip into this work and develop numerous research ideas or encounter a myriad of surprising results. Indeed, the applications of organometallic chemistry continue to expand at a prodigious rate, hence the significant increase in the number of volumes devoted to applications in COMC-III (to organic synthesis, to functional materials, as well as environmental and biological applications). Organic chemists have edited the volumes on organometallic chemistry towards organic synthesis now organized by reaction type so as to be readily accessible to the organic community. The new volume on applications covers a wide range of topics from optoelectronics to clusters and nano-particles.

The forthcoming availability of the whole COMC (1982), COMC-II (1995) through to COMC-III series in a web format will further enhance the utility of the series, providing a truly comprehensive data source and an unparalleled depth of coverage. With these new features, we hope that the combined efforts of the volume editors and individual authors have not only expanded the database of the subject but also provided an expanding perspective for all who use it.

The authors of individual chapters, the editors of the volumes and the editorial staff at Elsevier have made a tremendous effort to produce such a monumental work on schedule. We should like to thank them all most sincerely for working so well together as a team and we are sure the readership will appreciate the mature perspective and insight which they have provided for them.

D. Michael P. Mingos
Robert H. Crabtree

[1] H. Kissinger, Does America Need a Foreign Policy?, Touchstone Press, NY, 2002.

Editors-in-Chief

Michael Mingos has published more than 400 papers in inorganic, organometallic and theoretical chemistry. He has received numerous awards including the Corday-Morgan (1980) and Tilden (1988) Medals of the Royal Society of Chemistry, the Wilhelm Manchott Prize in 1995, the Michael Collins Award for Microwave Chemistry (1996) and was elected a Fellow of the Royal Society in 1992. He is perhaps best known for his contributions to the development of the polyhedral skeletal electron approach for inter-relating the structures of cluster compounds and their valence electron counts – commonly described as the Wade-Mingos Rules, but he has also developed a strong synthetic programme in cluster and supramolecular chemistry. He also pioneered the applications of microwave dielectric heating in organometallic and inorganic chemistry.

Currently Principal of St Edmund Hall and Professor of Inorganic Chemistry at the University of Oxford. He gained his B.Sc. at the University of Manchester (1965) and his D.Phil. at the University of Sussex (1968). He has subsequently received Honorary Degrees from both institutions. He became a Lecturer at Queen Mary College in 1971, before becoming a Fellow at Keble College, Oxford (1976–1992). In 1992 he moved to the Sir Edward Frankland BP Chair in Chemistry at Imperial College where he was elected Dean of the Royal College of Science in 1996.

His Editorial activities include a monograph on cluster chemistry, three undergraduate textbooks and many published reviews. He has also edited several books and served on the editorial boards of a number of international journals. He was Regional Editor of the Journal of Organometallic Chemistry from 1996 to 2006 and is Managing Editor of Structure and Bonding.

Robert Crabtree has published more than 400 papers in inorganic, organometallic and bioinorganic chemistry. He has received numerous awards including the Corday-Morgan (1984) Medal and Organometallic Chemistry Award (1991) of the Royal Society of Chemistry, the Organometallic Chemistry Award (1993) of the American Chemical Society, the Bailar Medal (U of Illinois, 2001), the Dow Lectureship (Berkeley, 2004) and the ISI Highly Cited Author Award (2000). He was chair of the inorganic chemistry division of the American Chemical Society (1998). He is known for the 'Crabtree catalyst' and contributions in alkane activation, sigma complexes, dihydrogen bonding, and molecular recognition in catalysis.

Currently Professor of Inorganic Chemistry at Yale University, he earned his B.A. at the University of Oxford (1970) and his D.Phil. at the University of Sussex (1973). He then became an Attaché de Recherche at the CNRS laboratory at Gif-sur-Yvette before moving to Yale in 1977.

His book, 'The Organometallic Chemistry of the Transition Metals' is now in its fourth edition (2005). He has also served on the editorial boards of a number of international journals. He was Regional Editor of the New Journal of Chemistry from 1998 to 2003 and is Editor-in-Chief of the 'Encyclopedia of Inorganic Chemistry'.

Editor of Volume 6

Michael Bruce was born in London and educated at the Universities of Oxford (MA, 1967; Honours with the late Luigi Venanzi) and Bristol (Ph.D., 1967, under the direction of Gordon Stone; D.Sc., 1977). After a period as lecturer at Bristol, he took up the Chair of Inorganic Chemistry at the University of Adelaide, South Australia. In 1982, he became the Angas Professor of Chemistry, and between 1988–1990 was Dean of Science at the same university. He has received awards from the Royal Australian Chemical Institute (H.G. Smith and Burrows) and was elected Fellow of the Australian Academy of Science in 1989. Most recently, he received the David Craig Medal from the Academy and an Honorary Doctorate from the Université de Rennes 1. He has occupied visiting appointments at the Universities of Cambridge, British Columbia, Neuchâtel, and Rennes 1, and at Louis Pasteur Université, Strasbourg, and the Institute of Organo-Element Compounds, Moscow.

His research has been mainly in (i) molecules with unusual architectures (rods, squares, rectangles); (ii) development of the chemistry of homo- and hetero-metallic cluster compounds with particular relevance to reactions of cluster-bound molecules; (iii) complexes containing metal-carbon σ bonds, particularly those containing unsaturated groups and long chains; (iv) the chemistry of fluoro-organic complexes and cyclometallated derivatives of transition metals; (v) applications of mass spectrometry to the analysis and characterisation of inorganic and organometallic compounds using electron impact and fast atom bombardment techniques. Studies of natural and synthetic plant cell-division inducers (cytokinins) were initiated at CSIRO's Division of Plant Industry, Canberra (1962–64), and led to the discovery of an extensive new class of synthetic materials of this type.

Contributors to Volume 6

M Akita
Tokyo Institute of Technology, Yokohama, Japan

I R Butler
University of Wales – Bangor, Bangor, UK

V Cadierno
Universidad de Oviedo, Oviedo, Spain

M P Cifuentes
Australian National University, Canberra, ACT, Australia

P Crochet
Universidad de Oviedo, Oviedo, Spain

P J Dyson
Institut des sciences et ingénierie chimiques, Lausanne, Switzerland

J Gimeno
Universidad de Oviedo, Oviedo, Spain

C Hofmann
Rice University, Houston, TX, USA

G Hogarth
University College London, London, UK

M G Humphrey
Australian National University, Canberra, ACT, Australia

A L Johnson
University of Bath, Bath, UK

C H Kaschula
University of Cape Town, Rondebosch, South Africa

A T Kelly
Rice University, Houston, TX, USA

M Knorr
Université de Franche-Comté, Besançon, France

B K L Leong
Simon Fraser University, Burnaby, BC, Canada

J S McIndoe
University of Victoria, Victoria, BC, Canada

J R Moss
University of Cape Town, Rondebosch, South Africa

R K Pomeroy
Simon Fraser University, Burnaby, BC, Canada

P R Raithby
University of Bath, Bath, UK

E Sappa
Universita' del Piemonte Orientale, Alessandria, Italy

G S Smith
University of Cape Town, Rondebosch, South Africa

H Suzuki
Tokyo Institute of Technology, Tokyo, Japan

T Takao
Tokyo Institute of Technology, Tokyo, Japan

D Thomas
University of Wales – Bangor, Bangor, UK

K H Whitmire
Rice University, Houston, TX, USA

M K Whittlesey
University of Bath, Bath, UK

J D Wilton-Ely
University of Oxford, Oxford, UK

W-T Wong
University of Hong Kong, Hong Kong, People's Republic of China

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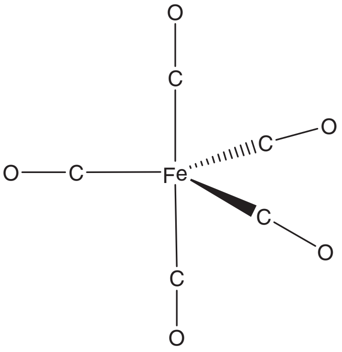
6.01
Mononuclear Iron Carbonyls without Hydrocarbon Ligands

K H Whitmire, A T Kelly, and C Hofmann, Rice University, Houston, TX, USA

6.01.1 Simple Mononuclear Iron Carbonyls

6.01.1.1 Structure of $Fe(CO)_5$

Pentacarbonyliron has long been known to possess a highly fluxional, trigonal-bipyramidal geometry, **1**. While there is no dispute over the D_{3h}-symmetry of the molecule, there is some discussion as to whether the axial or equatorial Fe–CO bonds are longer.[1–3] Different theoretical approaches result in different conclusions and so the question remains somewhat in dispute.[1] A more recent gas-phase electron-diffraction study[2] indicated that the equatorial bonds were longer than the axial ones, in contrast to results obtained from a previous single crystal X-ray diffraction study. These differences were attributed to crystal-packing effects on the solid-state structure. Because of the various ambiguities in the structure of $Fe(CO)_5$, CO stretching frequencies could not be determined with high accuracy by a method based upon a local density approximation at various reference geometries.[4] The assignment of the various vibrational bands in the 300–800 cm^{-1} region has been in dispute, and two recent theoretical studies tend to support the original assignments.[3,4]

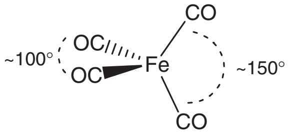


1

6.01.1.2 Photochemistry of $Fe(CO)_5$ and Its Fragments

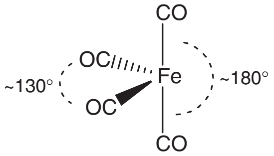
$Fe(CO)_5$ serves as a simple source of neutral, cationic, and anionic fragments: $Fe(CO)_n$ ($n = 1$–4), $[Fe(CO)_n]^+$ ($n = 1$–5), and $[Fe(CO)_n]^-$ ($n = 1$–4). A number of studies focusing on the photodissociation of pentacarbonyliron into these various fragments and the resulting properties of those fragments have been undertaken in the past decade.

The first bond-dissociation energy from neutral $Fe(CO)_5$ was calculated to be 45.7 kcal mol^{-1} by DFT methods,[5] while the coupled-cluster theory model yielded a value of 46.5 kcal mol^{-1}. These are slightly higher than the experimental value (41 kcal mol^{-1}).[1] The optimized triplet state of $Fe(CO)_4$ was found to be tetrahedral **2**, while the singlet state was a see-saw shaped **3** derived from a trigonal-bipyramidal geometry with an equatorial position vacant.[5] The singlet state **3** was 1.8 kJ higher in energy than the triplet state **2**. The structure of $Fe(CO)_4$ was determined with diffraction using ultra-short pulses of electrons.[6] The observed bond distances and angles were in close agreement with those obtained from the *ab initio* calculations for the singlet-state structure **3**.



Triplet (ground) state

2



Singlet (excited) state

3

The gas-phase photochemistry of pentacarbonyliron has received considerable attention on the femtosecond timescale.[7–15] When irradiated in the gas phase with 260 nm radiation for 120 fs, the parent ion $[Fe(CO)_5]^+$ is observed along with dissociation products $[Fe(CO)_{5-x}]^+$ ($x = 1$–5), whereas only Fe^+ was observed using a 10 ns pulse.[8] Similar results were obtained using a pump-probe technique at 400 and 800 nm with a 100 ns pulse.[9] That study concluded that the ions $[Fe(CO)_{5-x}]^+$ occurred with concerted ligand loss, but that the loss of the last CO and formation of neutral Fe occurred in a stepwise fashion.[9,10] These studies showed that $[Fe(CO)_5]^+$ was so short lived that it could not be observed when the timescale of the laser pulse was in the nanosecond regime.

These co-workers also used a feedback loop to maximize the $Fe(CO)_5/Fe$ ratio.[11] A theoretical analysis of the data obtained in these experiments showed that multiple photon processes were necessary to account for the higher order dissociation products.[12] This analysis indicated that the transient behavior of $Fe(CO)_5$ and $Fe(CO)_4$ could be explained by both two- and three-photon processes, but that sequential steps were required to account, at least in part, for the formation of the ions with fewer carbonyl ligands. The authors estimated that 15–45% of the ions subsequently dissociated directly into smaller fragments and that these processes competed with concerted dissociations. Other workers, however, concluded that single CO loss upon irradiation at 267 nm was observed for times less than 100 fs, and that this process already involved relaxation between a number of excited-state surfaces.[13,15] This suggested that the results from previous studies may have been rates for dissociation from the molecular cations rather than the neutral species, the difficulty being that in pumped-probe experiments the products could be derived either from ionization of neutral iron carbonyls or dissociation of the molecular cations.[16] The $Fe(CO)_4$ so produced was generated in a singlet-excited state which decayed to the ground state in about 47 fs, with further dissociation occurring at much longer times. Using 4950 nm mid-IR radiation, multi-photon dissociations of $Fe(CO)_5$ were observed.[14] The fragmentation processes have also been examined by time-resolved photoelectron spectroscopy,[16] and the analysis was consistent with the measurements,[10] suggesting a concerted process.

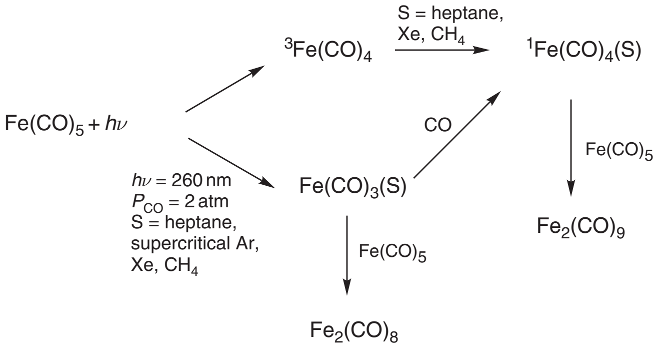
The binding energies of the various $[Fe(CO)_n]^+$ fragments were examined by *ab initio* and DFT calculations.[17] The ground state of $[Fe(CO)_5]^+$ was determined to be a doublet, while those of $[Fe(CO)_n]^+$ ($n = 1$–3) were quartets. The ground state of $[Fe(CO)_4]^+$ could not be determined definitively, with quartet T_d and doublet D_{4h}-geometries being similar in energy. The fragment $[Fe(CO)_2]^+$ was found to be linear. The second CO binding energy was determined to be higher than the first, but addition of a third CO resulted in loss of the $sd\sigma$-hybridization resulting in a lower third binding energy. The optimal geometry of $[Fe(CO)_3]^+$ was C_{3v}, but the fourth CO binding energy was found to be higher than the third even though the average CO binding energy was lower than in $[Fe(CO)_3]^+$. The CO binding energy dropped again upon adding the fifth CO. This effect was attributed to a change in the Fe spin state. The predicted geometry of $[Fe(CO)_5]^+$ is square-pyramidal. These same authors examined the binding energies in the anionic fragments $[Fe(CO)_n]^-$ ($n = 1$–4).[18] The first and second CO binding energies were found to be similar. The addition of the second CO results in lower σ-repulsion and greater π-bonding; however, it comes at the cost of promoting an Fe valence electron into the CO $2\pi^*$-orbital. The third and fourth CO binding energies were found to be significantly greater than the first two, although the fourth was slightly smaller than the third owing to larger ligand–ligand repulsions. The $[Fe(CO)_2]^-$ fragment was found to be linear and $[Fe(CO)_3]^-$ had D_{3h}-symmetry. The ground state for $[Fe(CO)_4]^-$ was determined to be C_{3v} in agreement with previous experimental observations.[18,19] The force constants for $[Fe(CO)_4]^-$ were calculated and found to be in good agreement with those obtained by isotopic enrichment studies.[19]

A DFT study comparing the binding energies, structural parameters, and vibrational frequencies of FeCO, $[FeCO]^+$, and $[FeCO]^-$ was reported.[20] The theoretical ordering of the dissociation energies $D([FeCO]^+) > D([FeCO]^-) > D(FeCO)$ was in agreement with experimental findings. The calculated vibrational bands for FeCO compared satisfactorily with the experimental values (given in parentheses, cm^{-1}): Fe–C stretch, 658 (530), C–O stretch, 1982 (1950); Fe–C–O bend, 368 (330). The pure rotational spectrum of FeCO was measured by microwave spectroscopy.[21] From these data, the Fe–C bond length was determined to be 172.7 pm and the C–O bond length to be 116.0 pm. The Fe–C bond length is about 10 pm shorter than that found in $Fe(CO)_5$ suggesting stronger Fe–CO bonding in FeCO.

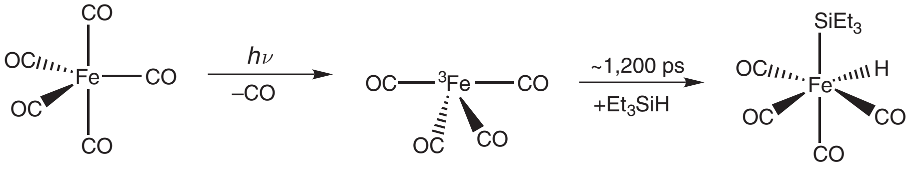
Electron attachment to $Fe(CO)_5$ leads to the formation of a series of cluster anions in the gas phase as determined by time-of-flight mass spectrometry.[22] These clusters had the composition $\{[Fe(CO)_4]^-\}_a[Fe(CO)_5]_b$, where $a = 1, 2$; $b = 0$–8, and these were analyzed as being van der Waals' clusters in which the $[Fe(CO)_4]^-$ fragments function as ion cores. The clusters were examined by photoelectron spectroscopy. The spectra were all very similar with the threshold-binding energies and vertical-detachment energies varying linearly with cluster size. The data were consistent with electron ejection from the encapsulated $[Fe(CO)_4]^-$ unit.

The various photoreactions of $Fe(CO)_5$ dissociation fragments that arise upon irradiation at 260 nm in several solvents using picosecond spectroscopy are presented in Scheme 1.[7] The solvents (S) examined included heptane or supercritical Ar, Xe, and CH_4. The primary initial products $Fe(CO)_4$ and $Fe(CO)_3(S)$ are formed as a mixture within 5 ps. The $Fe(CO)_4$ is produced in a triplet state but decays rapidly to singlet $Fe(CO)_4(S)$, and the production of $Fe(CO)_3(S)$ was found to be a one-photon process. The solvated forms $Fe(CO)_4(S)$ and $Fe(CO)_3(S)$ were not thought to form in supercritical Ar. Both the tetracarbonyl and tricarbonyl solvated forms react with $Fe(CO)_5$ to produce the corresponding dinuclear complexes.

When the photolysis of $Fe(CO)_5$ is performed in the presence of Et_3SiH, the triplet $^3Fe(CO)_4$ species is the observed intermediate before the oxidative addition of the Si–H bond to give $HFe(CO)_4SiEt_3$ (Scheme 2).[23] This work indicated that a complex between singlet $Fe(CO)_4$ and an ethyl group on triethylsilane had to dissociate before going on to products. Similarly, photolysis of $Fe(CO)_5$ in alcohols produces $^3Fe(CO)_4$ followed by rapid decay to a single

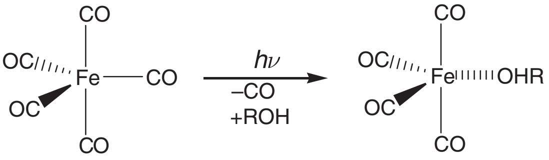


Scheme 1[7]



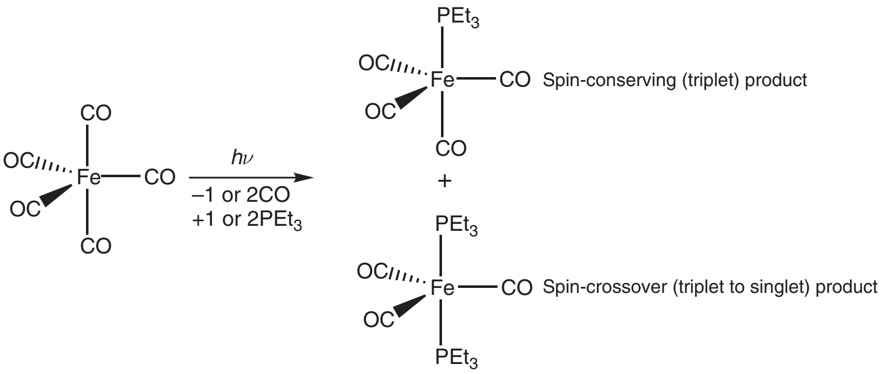
Scheme 2[23]

alcohol-solvated singlet-state complex (Equation (1)),[24] but the intermediate $^3Fe(CO)_4$ was not detected in neat PEt_3 (Scheme 3).[24] Instead, direct formation of $Fe(CO)_4PEt_3$ was observed. A subsequent photolysis product was proposed to be $^3Fe(CO)_3PEt_3$, which reacts further with PEt_3 to give the disubstituted product in a singlet configuration.

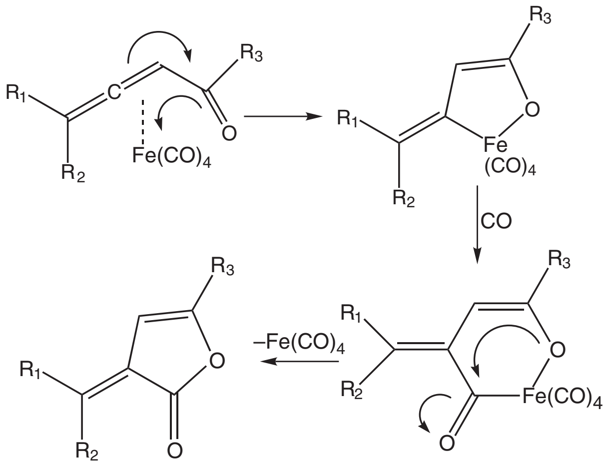


(1)

Pentacarbonyliron catalyzes the [4 + 1]-cycloaddition of CO to allenyl ketones and allenyl aldehydes in high yields and with good stereoselectivity. This reaction was examined in 2-methyltetrahydrofuran (2-MeTHF) matrices where the substituted complex $Fe(CO)_4(2\text{-}MeTHF)$ was found to be produced upon photolysis of $Fe(CO)_5$ at 190–230 K. When $Fe(CO)_5$ was photolyzed at 230 K in 2-MeTHF in the presence of 5-methyl-3,4-hexadien-2-one and CO, the corresponding α-alkylidene butenolide was obtained (Scheme 4).[25] The reaction proceeded via a dissociative process from $Fe(CO)_4(2\text{-}MeTHF)$.[25]



Scheme 3[24]



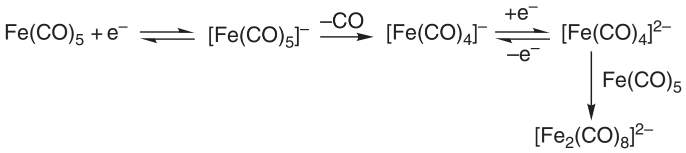
Scheme 4[25]

6.01.1.3 Redox Reactions of $Fe(CO)_5$

The electrochemical reduction of $Fe(CO)_5$ has been examined (Scheme 5).[26] It is found that reduction of $Fe(CO)_5$ is a sequential two-electron process giving ultimately the expected $[Fe(CO)_4]^{2-}$. An overall apparent one-electron consumption is observed when $[Fe(CO)_4]^{2-}$ reacts with unreduced $Fe(CO)_5$ to produce $[Fe_2(CO)_8]^{2-}$.[26] Reduction occurs at $E^p = -2.67$ V (referenced to Ag/Ag^+). Three oxidation steps were observed at −1.89, −1.62, and −0.09 V corresponding to (i) one-electron oxidation of $[Fe(CO)_4]^{2-}$, (ii) one-electron oxidation of $[Fe_2(CO)_8]^{2-}$, and (iii) one-electron oxidation of $[Fe_2(CO)_8]^-$, respectively. The intermediate $[Fe(CO)_5]^-$ was not observed directly during the reduction; however, it could be trapped in the presence of $HSnR_3$ yielding the formyl anion $[Fe(CO)_4C({=}O)H]^-$. This allowed the lifetime of the $[Fe(CO)_5]^-$ species to be bracketed between 10 ns and 5 μs. The data were consistent with CO loss from $[Fe(CO)_5]^-$ having a rate constant between 2×10^5 and $1 \times 10^8\,s^{-1}$.

Oxidation of $Fe(CO)_5$ has also been examined, and salts of the $[Fe(CO)_6]^{2+}$ cation can be prepared by oxidative carbonylation of $Fe(CO)_5$ using XeF_2 in HF/SbF_5 (Equation (2)),[27] HF/BF_3, or AsF_5 or Cl_2 in SbF_5.[27–30] The anions from this synthesis are $[SbF_6]^-$, $[Sb_2F_{11}]^-$, or $[BF_4]^-$. Washing the $[Sb_2F_{11}]^-$ salt with anhydrous HF converts it into the $[SbF_6]^-$ derivative. Heating the $[Sb_2F_{11}]^-$ salt to 170 °C leads to loss of SbF_5 and formation of $[Fe(CO)_6][SbF_6]_2$, followed by decomposition to FeF_2 and $Fe(SbF_6)_2$ at 185 °C, whereas $[Fe(CO)_6][SbF_6]_2$ decomposes directly to those same products at 180 °C. Vibrational properties of $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os) in salts are nearly identical—almost independent of counterion and of metal.[28] The diamagnetic cation $[Fe(CO)_6]^{2+}$ shows a slightly elongated tetragonal distortion from octahedral in all of its crystallographically characterized salts. DFT calculations were performed on the cation to determine the dissociation energies, vibrational frequencies, and ^{13}C NMR data.[31] The bond-dissociation energy was calculated to be 53 kcal mol^{-1}, which was greater than that of the Ru compound but less than that of the Os analog. The calculated ^{13}C NMR shift for the carbonyl ligands of 179.0 ppm compared well to the observed value of 182.3 ppm.

$$Fe(CO)_5 + XeF_2 + CO + 4SbF_5 \xrightarrow[HF/SbF_5,\ 2\,d]{50\,^{\circ}C,\ 1\,atm\ CO} \underset{50\%}{[Fe(CO)_6][Sb_2F_{11}]_2} + Xe \qquad (2)$$



$$\begin{tikzcd} Fe(CO)_5 + e^- \arrow[r, shift left] & {[Fe(CO)_5]^-} \arrow[l, shift left] \arrow[r, "-CO"] & {[Fe(CO)_4]^-} \arrow[r, shift left, "+e^-"] & {[Fe(CO)_4]^{2-}} \arrow[l, shift left, "-e^-"] \arrow[d, "Fe(CO)_5"] \\ & & & {[Fe_2(CO)_8]^{2-}} \end{tikzcd}$$

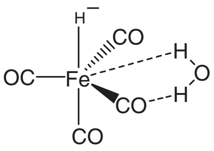
Scheme 5[26]

6.01.1.4 Other Reactions of $Fe(CO)_5$

Iron carbonyls serve as catalysts for the isomerization of allylic alcohols to saturated carbonyl complexes as well as the conversion of allylic alcohols and formaldehyde to aldols.[32,33] These processes were examined theoretically and the authors proposed that intermediate $Fe(CO)_3$ was responsible for converting coordinated allyl alcohol into coordinated enol via two successive 1,3-hydride shifts.[25] Several pathways for the subsequent reaction with formaldehyde were examined, but the most favorable involved direct attack of H_2CO on the decomplexed enol.[26]

$Fe(CO)_5$ has long been known to serve as a catalyst for the water–gas shift reaction (WGSR, Equation (3)) and this is attributed to the attack of hydroxide ion on the carbon atom of a coordinated CO ligand in basic solution. Carbon dioxide elimination from this intermediate leads to the stable hydride $[HFe(CO)_4]^-$. This reaction was re-examined theoretically using DFT calculations for hydroxide ion attack on $Fe(CO)_5$.[34] The study supported the previously proposed initial attack of hydroxide ion on coordinated CO as well as the proposal that CO_2 elimination occurred via a four-centered transition state in a concerted process. The study also proposed two new species as being involved in the catalytic cycle. One of these was a water adduct of $[HFe(CO)_4]^-$ **4**. The second was a trigonal-bipyramidal isomer of $H_2Fe(CO)_4$ **5**, in which the two hydrogen atoms formed an equatorial dihydrogen ligand.

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{3}$$



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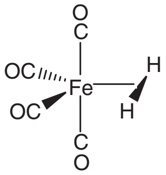
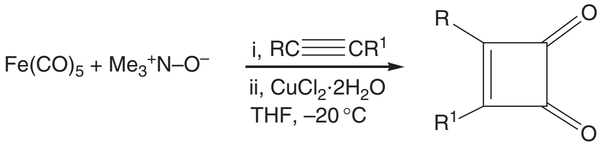


5

Unsaturated "$Fe(CO)_4$" was generated from $Fe(CO)_5$ and Me_3NO and reacted with alkynes to give corresponding cyclobutenediones or the anhydrides in yields of 50–75% after $CuCl_2{\cdot}2H_2O$ oxidation (Equation (4)).[35]



R	*R*^{1}	*Yield* (%)
H	Ph	72
H	C_5H_{11}	68
Ph	Ph	80
C_3H_5	C_8H_{17}	60
Ph	Ph	75

(4)

Syntheses and magnetic studies of iron nanorods and nanospheres have been reported using pentacarbonyliron. Spherical nanostructures formed by thermal decomposition of $Fe(CO)_5$ in the presence of stabilizing surfactant trioctylphosphine oxide (TOPO) at 340 °C were reported to give small spherical and rod-shape iron nanostructures.[36] However, in the presence of both TOPO and trioctylphosphine (TOP) at 300 °C, FeP nanoparticles are obtained.[37] Presumably, the coordination of the phosphorus of the TOP molecule directly to Fe activates it to loss of the organic substituents.

Pentacarbonyliron is involved in the conversion of the $[Te_4]^{2+}$ into the polymeric $[Te_7]^{2+}$ cation (Equation (5)).[38] The fate of the iron carbonyl was not clear; however, evidence suggested the formation of iron carbonyl–tellurium cations in solution.

$$[Te_4][AsF_6]_2 \xrightarrow[SO_2]{Fe(CO)_5} [Te_7][AsF_6]_2 \tag{5}$$

6.01.2 Simple Iron Carbonyl Hydrides

The simplest neutral iron carbonyl hydride is the eighteen-electron $H_2Fe(CO)_4$. The molecule has long been known to be fluxional, which is unusual for the octahedral configuration. The hydride ligands are *cis* to each other. Theoretical calculations using *ab initio* methods have shown the transition state is a dihydrogen complex, adopting a square-pyramidal configuration with the H_2 ligand in an apical position.[39] The fluxional process was found to be similar to that for the ethene complex $Fe(CO)_4(C_2H_4)$.

Time-resolved IR spectroscopy was used to study the oxidative addition and reductive elimination of H_2 from $H_2Fe(CO)_4$.[40] The activation barrier to reductive elimination was found to be 20.5 ± 2.1 kcal mol^{-1}, while the rate constant for addition of H_2 to $Fe(CO)_4$ was found to be insensitive to temperature indicating a very small activation barrier for that process (<4 kcal mol^{-1}). The addition of H_2 was also found to be smaller than for similar unsaturated metal fragments, and this was attributed to required intersystem crossing from the triplet ground state of $Fe(CO)_4$ before addition could occur. From the kinetic data, the average dissociation energy for the Fe–H bonds was calculated to be 62 ± 2 kcal mol^{-1}. These excited states and photodissociation processes of $H_2Fe(CO)_4$ were also examined theoretically.[41,42] The authors found that there were two excited states for photodecomposition. One of these leads to loss of H_2 on a very short time scale (Equation (6),[42] <40 fs), while the second leads primarily to fast H_2 loss, but is accompanied by some CO dissociation (~4%, in 100 fs). These same authors calculated the lowest excited states for $H_2Fe(CO)_4$.

$$H_2Fe(CO)_4 \xrightarrow[254\ \text{nm}]{h\nu} H_2 + Fe(CO)_4 \tag{6}$$

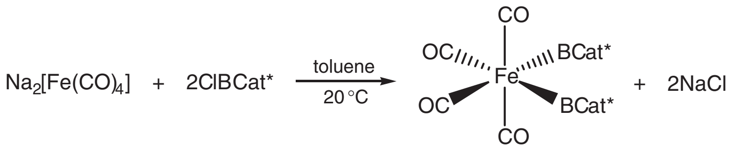
The slow step in the iron carbonyl-catalyzed water gas shift reaction (Equation (3)) is the proton transfer from water to the iron hydride anion (Equation (7)). *Ab initio* calculations have been made on this process.[43] It was found that in solution, the proton transfer was still endothermic (as in the gas phase); however, there was a reduction in the reaction energy of about 50 kcal mol^{-1}.

$$[HFe(CO)_4]^- + H_2O \longrightarrow H_2Fe(CO)_4 + OH^- \tag{7}$$

6.01.3 Iron Carbonyl with Group 13 Ligands

6.01.3.1 Boron

Iron carbonyl fragments have been incorporated into many heterometallic borane and carborane compounds. Those compounds are covered in Chapter 3.05 and will not be discussed here. Simple boryl adducts have been reported from the reaction of $Na_2Fe(CO)_4$ and ClBCat* (Cat* = catecholate or a ^{t}Bu-substituted derivative, Equation (8)).[44] The same products can be obtained upon irradiating $Fe(CO)_5$ and Cat*B–BCat* in toluene at 0 °C. Reaction of the diboryl **6** with 1 equiv. of lithium bis(trimethylsilyl)amide in toluene solvent leads to removal of one boryl unit and the formation of an anionic iron boryl complex (Equation (9)).[44] The anionic species can also be obtained by stoichiometric addition of the ClBCat* complex to $Na_2Fe(CO)_4$. Reaction of $[Fe(CO)_4\{B(3,5\text{-}t\text{-}Bu_2\text{-}Cat)\}]^-$ with $ClSnMe_3$ gives the stannylated derivative $Fe(CO)_4\{B(3,5\text{-}t\text{-}Bu_2\text{-}Cat)\}(SnMe_3)$.



(8)

6

BCat* = $B(O_2C_6H_4)$, $B(O_2\text{-}4\text{-}t\text{-}BuC_6H_3)$, $B(O_2\text{-}3,5\text{-di-}t\text{-}BuC_6H_2)$

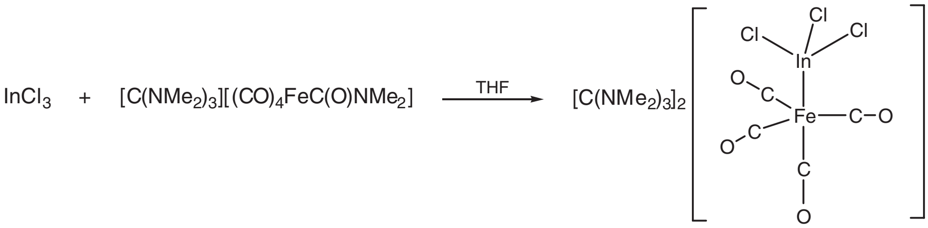
$$\mathbf{6} + LiN(SiMe_3)_2 \xrightarrow[20\ ^\circ C]{\text{toluene}} Li[(OC)_4Fe^-BCat^*] + (Me_3Si)_2NBCat^* \tag{9}$$

BCat* = $B(O_2C_6H_4)$, $B(O_2\text{-}4\text{-}t\text{-}BuC_6H_3)$, $B(O_2\text{-}3,5\text{-di-}t\text{-}BuC_6H_2)$

6.01.3.2 Al, Ga, In, and Tl

6.01.3.2.1 Iron carbonyl complexes with formally trivalent E substituents

The $[Fe(CO)_4]^{2-}$ ion, which has been known for sometime to form the Lewis acid–base adduct **7** with $InCl_3$, was also obtained via reaction of $[C(NMe_2)_3][Fe(CO)_4\{C(O)NMe_2\}]$ with $InCl_3$ in THF in about 30% yield (Equation (10)).[45] The product was structurally characterized, showing a trigonal-bipyramidal iron center with the $InCl_3$ unit occupying an axial position. The Fe–In distance was found to be 251.7(2) pm. DFT calculations suggest that the molecule is best viewed as an $InCl_3$ adduct of $[Fe(CO)_4]^{2-}$, since the Fe–In interaction has a strong ionic character. When the compound is treated with hot water, the diiron compound $[C(NMe_2)_3]_2[(CO)_4Fe(\mu\text{-}InCl_2)_2Fe(CO)_4]$ **8** results.[46]



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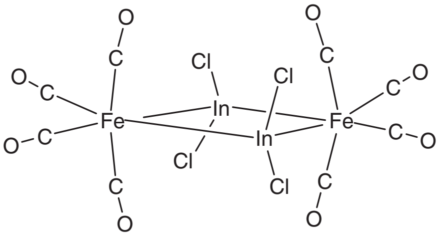
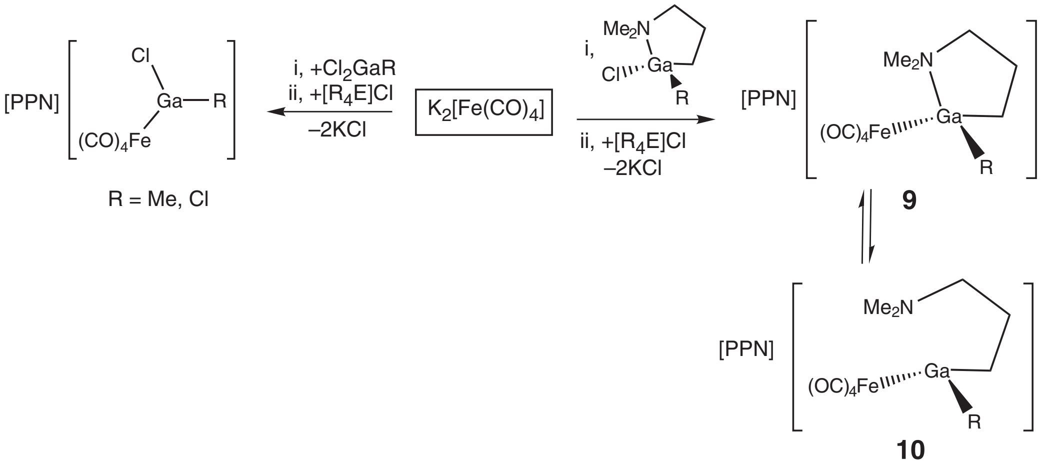
(10)

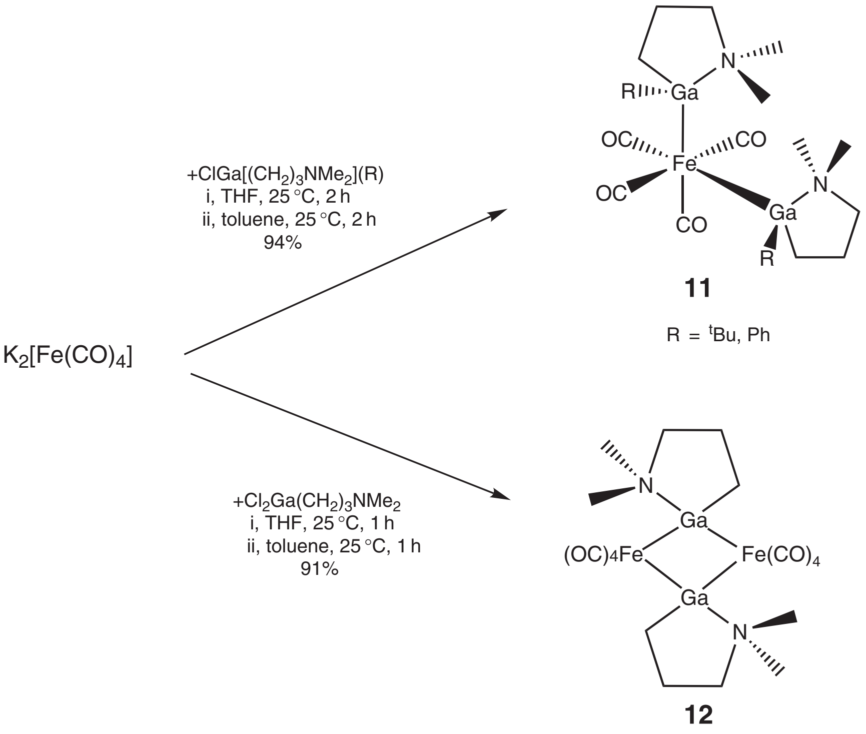


8

Gallium halides can undergo replacement of a halide by $[Fe(CO)_4]^{2-}$ to produce simple substituted complexes as shown in Scheme 6.[47] If the gallium reagent is a monohalide, then the products are most often viewed as a substitution process in which an $[Fe(CO)_4]^{2-}$ replaces the halide and there is no change in oxidation number of the gallium. This is illustrated by $[PPN]_2[MeGa\{Fe(CO)_4\}_2]$ whose crystal structure shows a distorted trigonal-planar Ga atom in which chloride ions have been replaced by $[Fe(CO)_4]^{2-}$ groups.[47] If the organogallium complex is a dihalide, then the resulting product $(OC)_4FeGaR$ can be viewed as either a Ga^{3+} center coordinated to Fe^{2-}, or as a Ga^{+} coordinated to Fe(0). The latter is a formal reduction process and, as will be seen in the next section, these same complexes can be obtained by substitution of neutral iron carbonyls by neutral E–R fragments. Calculations on



Scheme 6[47]



11

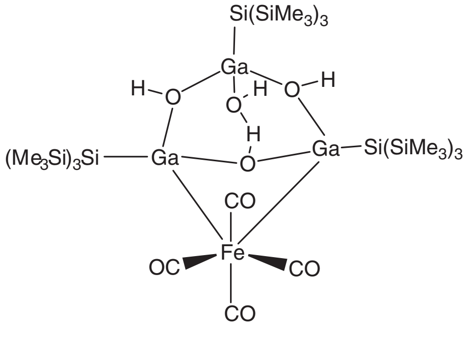
R = ^{t}Bu, Ph

12

Scheme 7[48]

this class of molecules indicate that a substantial M–E charge separation remains in these complexes. The Ga centers can act as Lewis acids to bind an internally bound donor ligand,[47,48] as illustrated in Schemes 6 and 7. The coordinating base may be intramolecularly bound to the Ga atom. All of these compounds have been prepared by salt metathesis from a suitable organogallium halide reagent and a salt of $[Fe(CO_4)]^{2-}$. The chelating arm can come off reversibly, as illustrated by **9** and **10** in Scheme 6. Scheme 7 illustrates that these compounds can form disubstituted complexes **11** as well as bridging species **12**. The latter can be viewed as a Ga^{+} compound instead of Ga^{3+}. This illustrates the ambiguity of assigning oxidation numbers in these compounds, which will be discussed further below.

A more complicated disubstituted derivative of $Fe(CO)_4$ was obtained from the reaction of $\{ClGaSi(SiMe_3)_3\}_4$ with $Na_2[Fe(CO)_4]\cdot(3/2)$dioxane in Et_2O. It has the form shown in **13**.[49] A complex ligand $[Ga_3R_3(OH)_4]^{2+}$ is produced, presumably because of the NaOH impurity present in the iron carbonyl reagent, and chelates the iron tetracarbonyl fragment through two of the gallium atoms.



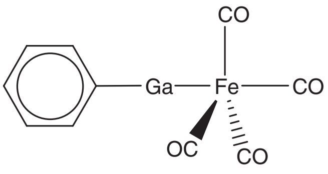
13

Some additional compounds with In or Ga bonds to iron that are prepared from silyliron carbonyl complexes are described in Section 6.01.4.2.

6.01.3.2.2 Iron carbonyl complexes with formally monovalent E substituents

The most common derivatives encountered between simple iron carbonyl fragments and the heavier group 13 elements in the past decade are those that can be classified as R–E: derivatives of $Fe(CO)_4$.[50] Here, the E atom is formally in the +1 oxidation state, and retains a lone pair of electrons. If R is an anionic species (usually an organic function), then the overall complex is neutral, and on a very simple level the RE–$Fe(CO)_4$ species can be viewed as simple substitution products of $Fe(CO)_5$. However, the system is really more complicated than that, and there is some merit considering these compounds as trivalent R–E^{2+} derivatives of $[Fe(CO)_4]^{2-}$. The very short E–Fe distances and the availability of an empty orbital on the E atom led researchers to propose initially the presence of E–Fe multiple bonding. This issue turns out to be quite complicated and is more extensively discussed in Chapter 3.08.4. where it will be seen that a very wide range of metal carbonyl and cyclopentadienyl metal carbonyl fragments may support R–E: ligands.

A number of theoretical calculations examining the bonding in the simple E–R iron carbonyl derivatives have been reported.[50–53] If the R group is a bulky σ-bonded group, then the E atom is linear and has only two bonds, one to Fe and the other to R (Table 1). If R is small, then the complexes are generally stabilized by adduct formation with a base, usually a nitrogen donor, to the E atom. A theoretical study has examined the bonding in a series of E–R complexes for E = B, Al, Ga, In, Tl.[50] That work concluded that $Fe \leftarrow ER$ σ-donation is the major cause for attractive orbital interactions between Fe and ER in $(CO)_4Fe$–ER. When R is a poor π-donor, there is slightly stronger π-back donation. The covalent and electrostatic interactions are similar in strength for the series E = Al–Tl, where R is a good π-donor substituent. DFT calculations on $[PhGaFe(CO)_4]$ **14** and $[CpGaFe(CO)_4]$ **15** predict a higher degree of $Ga \leftarrow Fe$ π-backbonding in the phenyl derivative than in π-complex.[53] Compound **14** has a much stronger Ga–Fe bond ($D_e = 54.9\,\text{kcal mol})^{-1}$ than **15** ($D_e = 32.8\,\text{kcal mol}^{-1}$).



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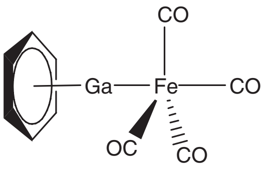
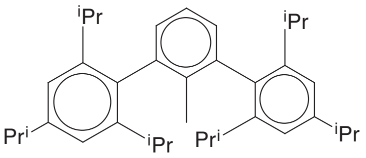
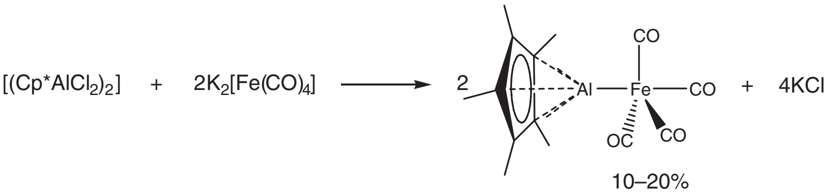


15

The iron carbonyl complexes are most easily obtained via reaction of a suitable salt of $[Fe(CO)_4]^{2-}$ and an appropriate dihalo–group 13 element complex X_2ER,[52,54] but reaction of a neutral iron carbonyl compound with $(RE)_x$ may also be used.[52,55] The syntheses of the known $Fe(CO)_4$ compounds are presented in Equations (11)–(14).[52,54,55–57] The R group attached to E can also be a donor ligand such as tris(pyrazolyl)borate (Equation (14)).[56,57]

Table 1 Compounds of the type $(CO)_4$Fe–E–R

E	*R*	$d_{\text{Fe–E}}$ (pm)	*References*
Al	Cp*	223.1(3)	52
Ga	Cp*	227.31(4)	55
Ga		222.48(7)	54
Ga	$HB(3,5\text{-}Me_2Pz)_3$	231.5(3)	56
In	$HB(3,5\text{-}Me_2Pz)_3$	246.3(2)	57



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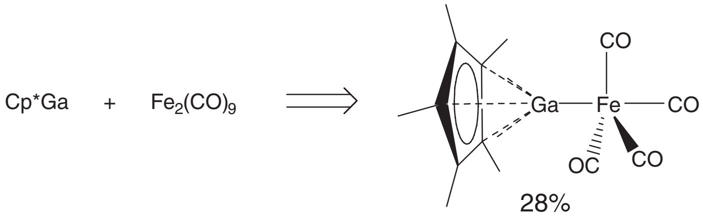

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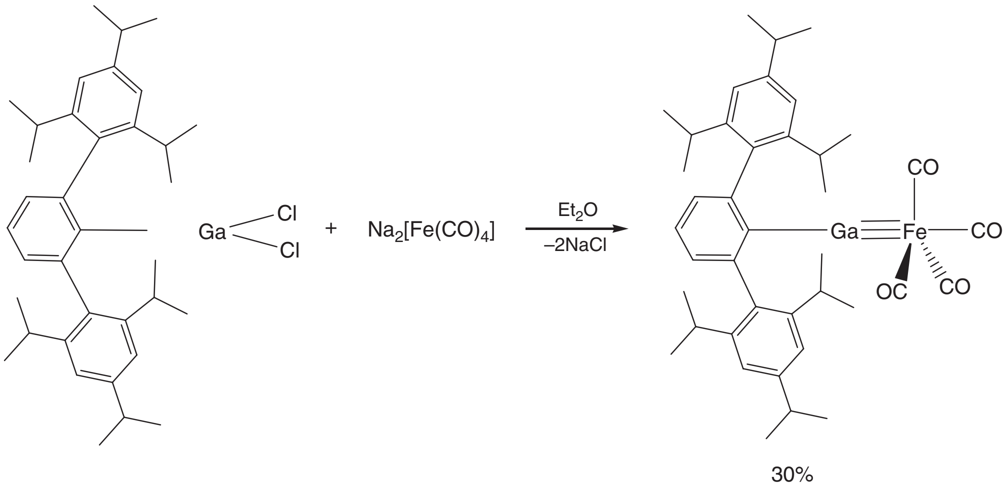

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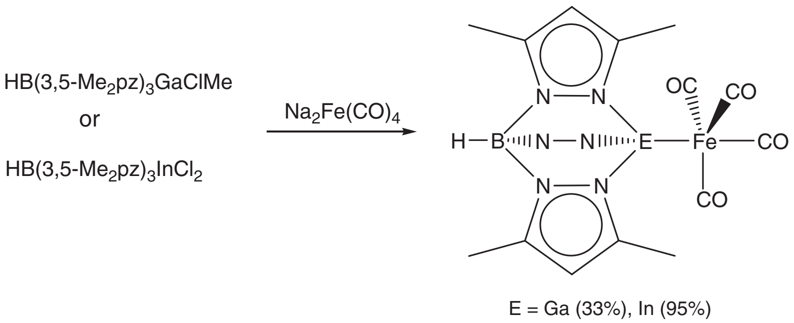


(14)

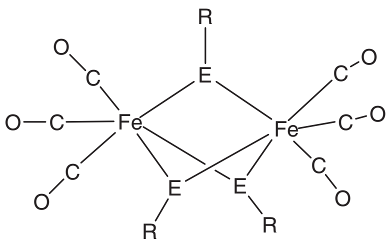
Higher nuclearity derivatives that can be viewed as substitution products of $Fe_2(CO)_9$ have been prepared for $GaCp^*$, $GaSi(SiMe_3)_3$, and $InC(SiMe_3)_3$ (Equations (15)–(17)).[49,55,58] All of these adducts show a preferential replacement of the μ-CO groups by the E–R fragments **16**. In the $GaCp^*$ derivative, there is some asymmetry in the bonding of the Cp^* groups to the Ga atoms. Two of these are bound in the pentahapto fashion, but one is trihapto. The Fe–Fe distances in these molecules are long (290.8(6), 287.6(2), and 299.2(2) pm for the $GaCp^*$, $GaSi(SiMe_3)_3$, and $InC(SiMe_3)_3$ compounds, respectively), which is consistent with the absence of a direct Fe–Fe bond. The bonding is better described viewing these as cluster compounds with delocalized bonding. Theoretical calculations on the In derivative[59] support this view as do related studies on the isoelectronic

$[Fe_2(CO)_6\{\mu\text{-}TlFe(CO)_4\}_3]^{3-}$ where E–R = $\{TlFe(CO)_4\}^-$.[60] The crystal structure of $[PPN]_3[Fe_2(CO)_6\{\mu\text{-}TlFe(CO)_4\}_3]$ showed it to be monomeric with structure **16**, in contrast to the $[Et_4N]^+$ salt which had previously been reported to be dimeric **17** via additional interactions between the μ-Tl atoms and Fe atoms on an adjacent molecule in the solid state.[60]

$$2Fe(CO)_3(\text{cycloheptatriene}) + 3GaCp^* \xrightarrow[\substack{-2\ \text{cycloheptatriene}\\ 59\%}]{\text{toluene}} Fe_2(CO)_6(\mu\text{-}GaCp^*)_3 \tag{15}$$

$$Na_2[Fe(CO)_4]\cdot 3/2\text{dioxane} + \{ClGaSi(SiMe_3)_3\}_4 \xRightarrow[41\%]{Et_2O} Fe_2(CO)_6\{\mu\text{-}GaSi(SiMe_3)\}_3 \tag{16}$$

$$8Fe(CO)_3(COT) + 3\{InC(SiMe_3)_3\}_4 \xrightarrow[60\%]{-8COT} 4Fe_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_3 \tag{17}$$



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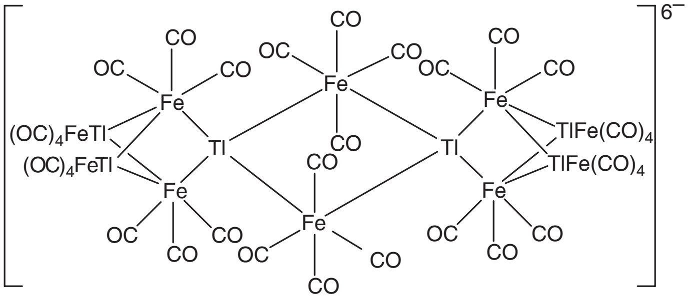
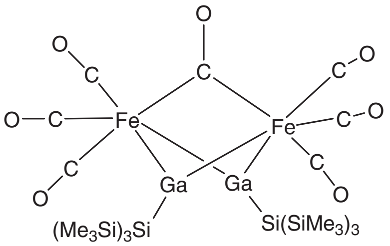


17

In the case of the $GaSi(SiMe_3)_3$ compounds, $Fe_2(CO)_9$ analogs with two of the bridging CO's replaced by the E–R fragments were also prepared.[49] These derivatives have the form $Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}GaSi(SiMe_3)_3\}_2$ **18** and $[Na(Et_2O)_2(THF)][Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}GaSi(SiMe_3)_3\}_2(\mu\text{-}Cl)]$ **19**. Compound **19** can be viewed as a Lewis-base addition of Cl^- ion to the Ga centers of **18**, with a simultaneous Lewis acid–base interaction formed between the Na^+ counterion and the basic oxygen atom of the bridging carbonyl. The Fe–Fe distances in these molecules are shorter than those for the trisubstituted derivatives, with little difference observed between **18** (268.04(8) pm) and the chloride adduct **19** (267.9(2) pm).[49]



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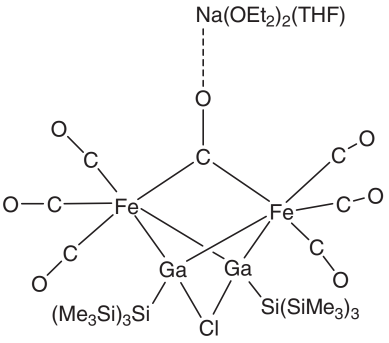
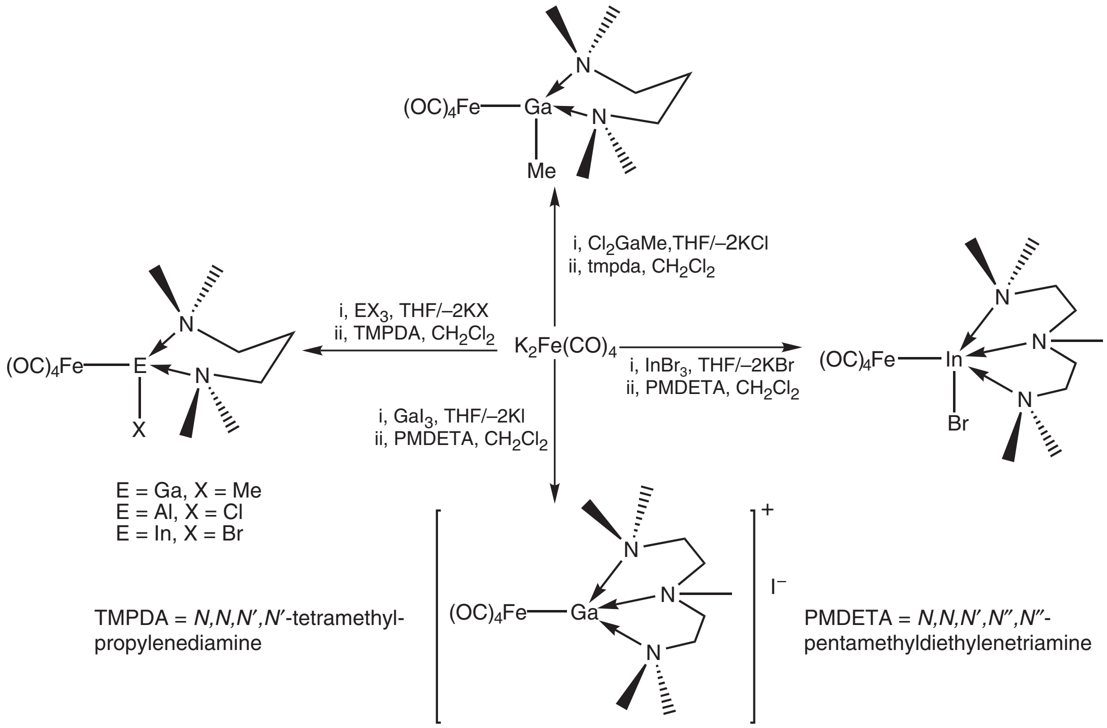


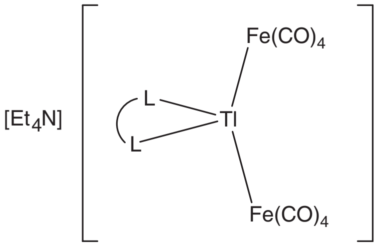
19

The main group atoms in the formally E^+ derivatives of $Fe(CO)_4$ can act as Lewis acids as illustrated in Scheme 8.[61] These compounds are prepared by carrying out the reaction of REX_2 or EX_3 with $[Fe(CO)_4]^{2-}$ in the presence of the appropriate chelating base.



Scheme 8[61]

Base adducts **20** of $[Et_4N][Tl\{Fe(CO)_4\}_2]$ have been prepared.[62] The only stable ones found were those of chelating bases including ethylenediamine (en), bipyridine, phenanthroline (phen), tetramethylethylenediamine, and diethylenetriamine (trien). The en derivative reacts in acetone solution to form what is believed to be the diimine derivative $[Et_4N][(Me_2C{=}NCH_2CH_2N{=}CMe_2)Tl\{Fe(CO)_4\}_2]$, but attempted isolation of that compound produced **21** instead. This complex is apparently an oxidation product and shows the presence of two of the diimine ligands. Tl NMR proved to be a valuable tool to study these complexes because of the large chemical-shift range as well as the presence of two stable spin-(1/2) nuclei (^{205}Tl and ^{203}Tl). Electron-deficient three-coordinate thallium centers in these complexes were found in the range of 6,000–6,800 ppm, while four-coordinate thallium centers were between 4,400 and 5,800 ppm. Further information on dimer formation/dissociation in solution for related complexes could be obtained from the ^{203}Tl–^{205}Tl coupling found in isotopomers containing more than one thallium atom. The equilibria studied are given in Equations (18)–(21).[62] The data indicated that the Tl_2Fe_6 compound in Equation (20) did not dissociate in solution, whereas dissociation into the monomeric units appeared likely in Equations (18), (19), and (21). The dimerization processes appear to occur to satisfy the electron demand of the Lewis-acidic thallium atoms.



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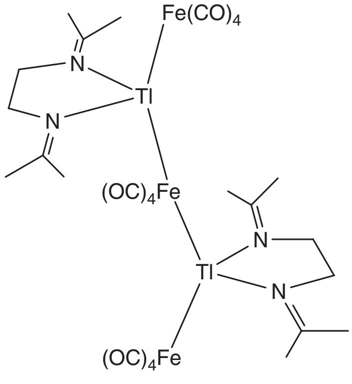

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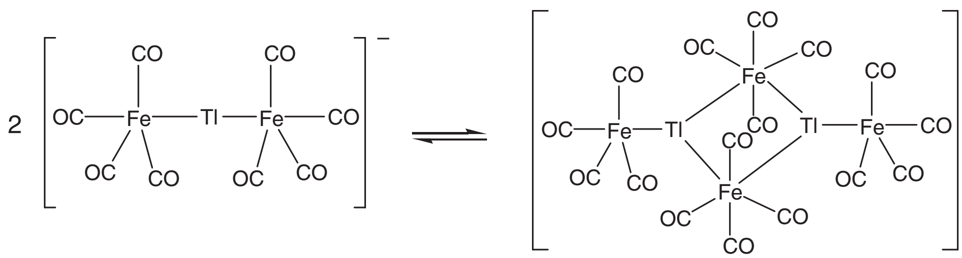

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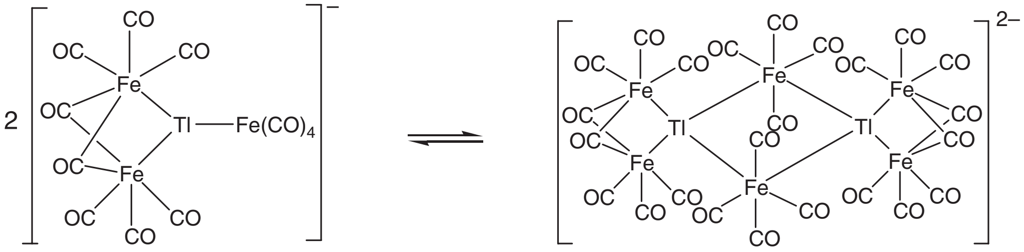

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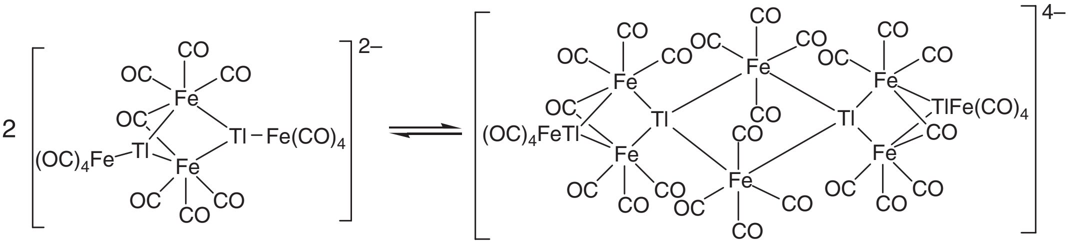

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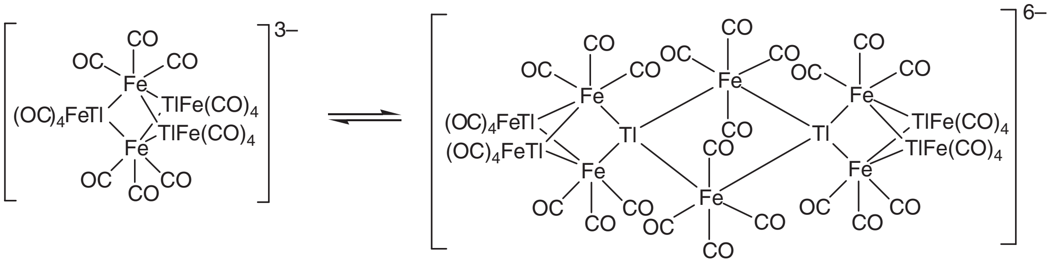
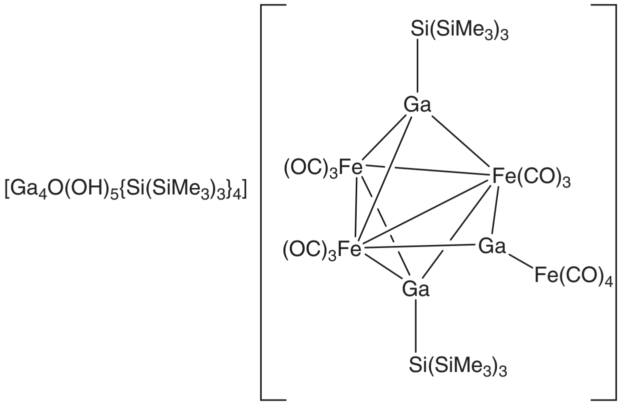


(21)

6.01.3.3 Cluster Compounds with Gallium Ligands

Some cluster compounds also arise from the reactions of organogallium halides with iron carbonyl anions.[49] We have already encountered some products from reaction of $[\{Ga(Cl)Si(SiMe_3)_3\}_4]$ with $Na_2Fe(CO)_4$ that fall into the molecular classes discussed above. The product $[Ga_4O(OH)_5\{Si(SiMe_3)_3\}_4][Fe_3(CO)_9\{\mu_3\text{-}GaSi(SiMe_3)_3\}_2]\text{-}\{\mu\text{-}GaFe(CO)_4\}$ 22 was also obtained from that reaction, while use of $Na_2Fe_2(CO)_8$ instead of the mononuclear iron carbonyl dianion produced $[Na(triglyme)][HFe_3(CO)_9\{GaSi(SiMe_3)_3\}_2]$ 23. These molecules are related structurally—the $GaFe(CO)_4^-$ fragment in 22 being replaced by a bridging H^- ligand in 23. Considering the Ga atoms as two-electron donors, they both exhibit 48 cluster electrons, and are thus isoelectronic to other Fe_3 clusters such as $Fe_3(CO)_{12}$.



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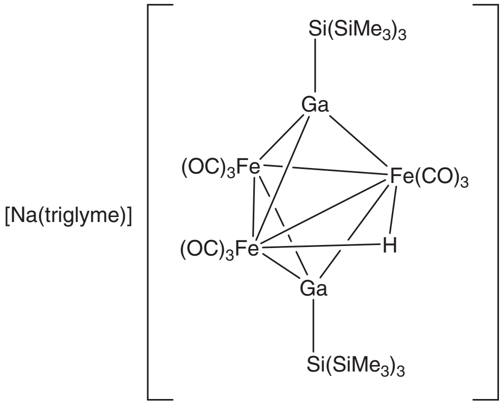


23

6.01.4 Iron Carbonyl with Group 14 Ligands

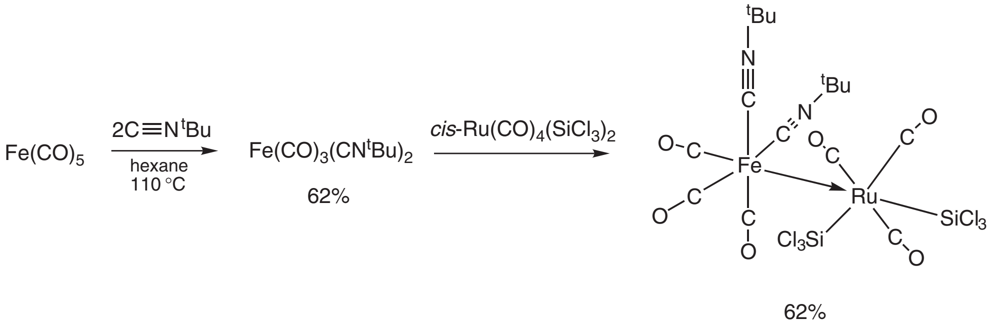
6.01.4.1 Cyanide and Isocyanide Complexes

Cyano–iron carbonyl complexes have received attention recently for their relationship to the active sites in hydrogenases. Some of this work will be discussed in the section on iron carbonyl complexes with thiolate ligands (see Section 6.01.6.2).[63–67]

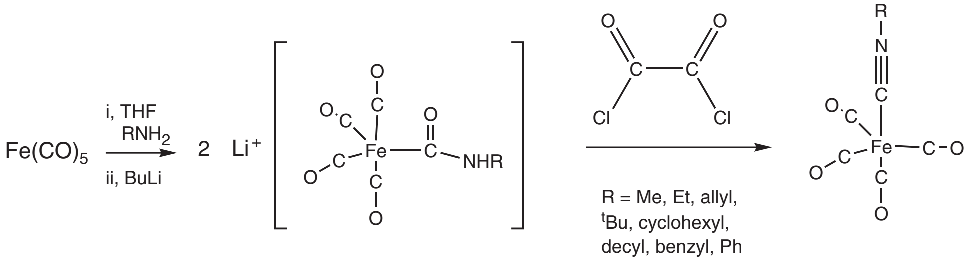
The complex $Fe(CO)_3(CN^tBu)_2$ was prepared directly via a thermal reaction between $Fe(CO)_5$ and CN^tBu in hexane (Scheme 9).[68] Upon cooling to liquid nitrogen temperature, crystals of the desired compound crystallized. This material reacts with *cis*-$Ru(CO)_4(SiCl_3)_2$ to give a complex with a dative $Fe \rightarrow Ru$ bond.

A new route to monosubstituted isonitrile complexes $Fe(CO)_4(CNR)$ has been reported (Scheme 10).[69] It takes advantage of the reaction of oxalyl chloride with carbamoylferrates (produced *in situ* by addition of a primary amine to $Fe(CO)_5$ followed by addition of BuLi in THF) and gives yields of approximately 60–70%.

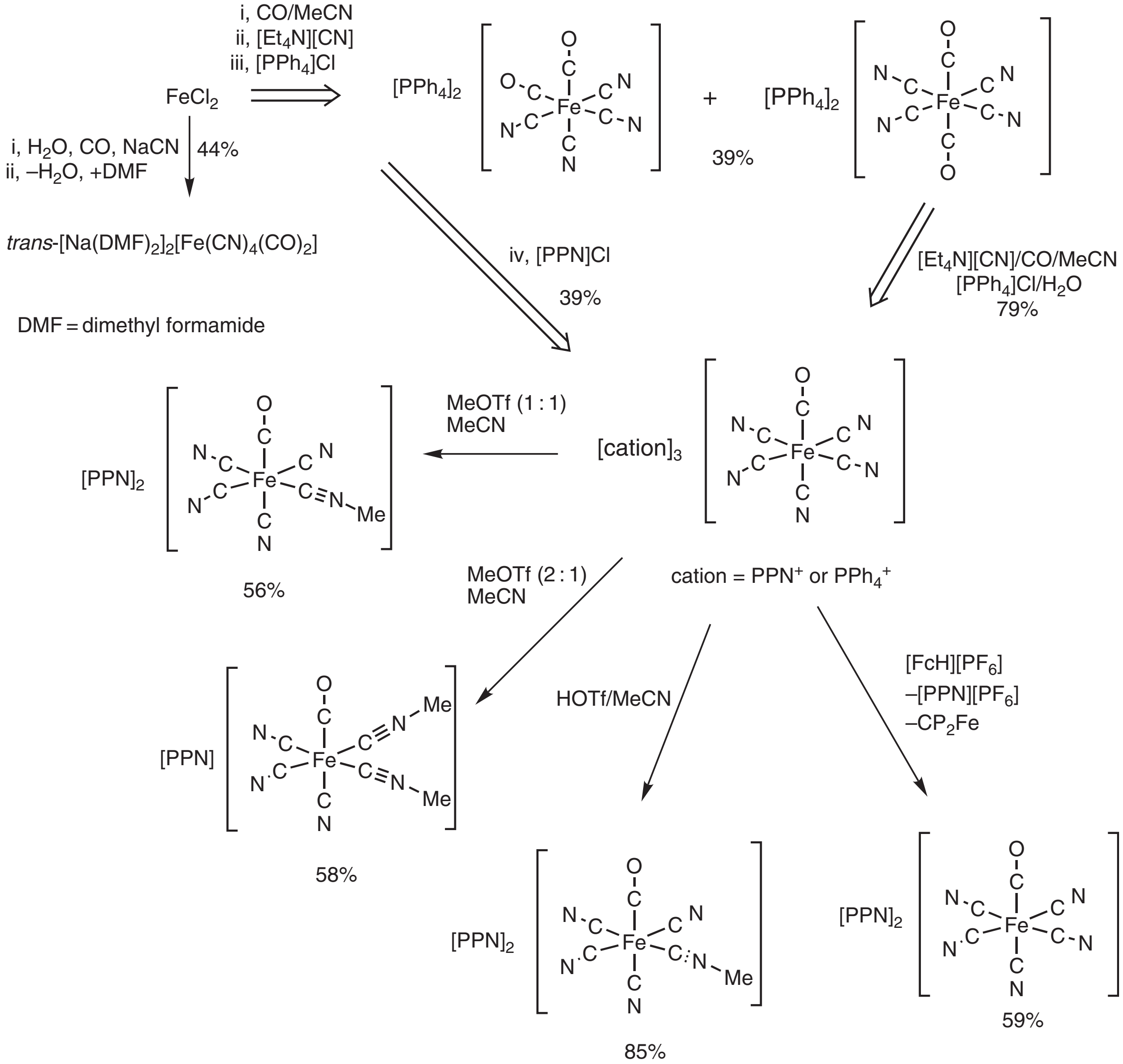
Reaction of ferrous chloride with cyanide ions in the presence of CO produces a mixture of cyano–carbonyl ions including *cis*-$[Fe(CN)_4(CO)_2]^{2-}$, *trans*-$[Fe(CN)_4(CO)_2]^{2-}$, and $[Fe(CN)_5(CO)]^{3-}$ (Scheme 11).[63,70,71] The *cis*-dicarbonyl compound was also prepared via the reaction of $Fe(CO)_4I_2$ with 4 equiv. of MCN ($M = Na$, K) in MeOH (Scheme 12).[71] Treating $[Fe(CN)_3(CO)_3]^-$ with NaCN also produced the *cis*-derivative.[71] As with the previous work reviewed in COMC II (1982) and COMC (1995), alkylation of these anionic cyano complexes leads to isocyanide derivatives. Similarly, protonation leads to the formation of the bound isocyanic acid. Oxidation of the $[Fe(CN)_5(CO)]^{3-}$ ion gives $[Fe(CN)_5(CO)]^{2-}$. Two-dimensional polymeric networks were obtained when $[Na(DMF)_2]_2$[*trans*-$Fe(CN)_4(CO)_2$] was treated with divalent metal salts in agar gels (Equation (22)).[72]



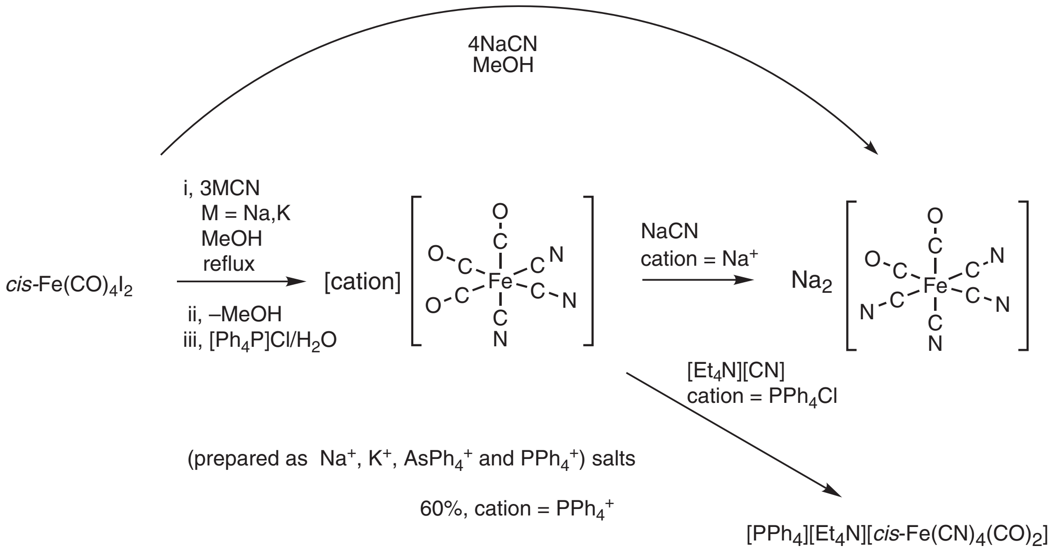
Scheme 9[68]



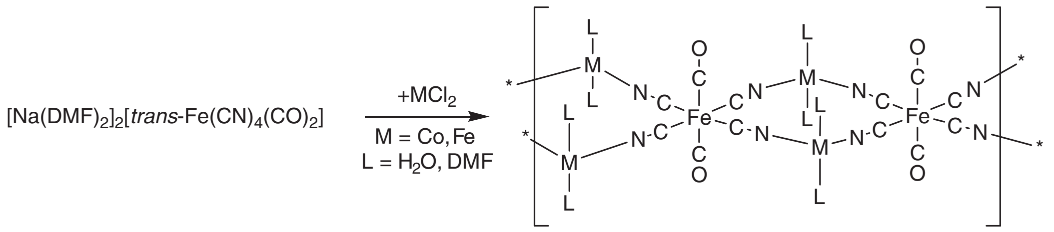
Scheme 10[69]



Scheme 11[63,70,71]



Scheme 12[70,71]



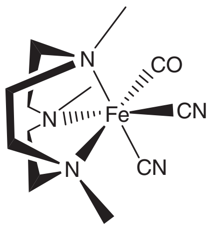
(22)

The dicyanotricarbonyl complex $[Et_4N]_2[Fe(CO)_3(CN)_2]$ has been produced by photochemical reaction of iron pentacarbonyl with $[Et_4N][CN]$ (Scheme 13).[64] The complex, which is air sensitive, adopts a D_{3h}-configuration with *trans*-axial cyanide ligands. Upon protonation, a mixture of the three possible hydride derivatives $[Et_4N][HFe(CO)_3(CN)_2]$ results, with the two isomers having both cyanide ligands *cis* to the hydride ligand predominating.

The complex $[Fe(CN)_2(CO)_3(Br)]^-$ is created via the reaction of cyanogen bromide with $[Fe(CN)(CO)_4]^-$ (Equation (23)), and the product was used to synthesize dicyanodicarbonylthiolate derivatives (see Section 6.01.6.2).[67]

$$[Fe(CO)_4(CN)]^- \quad + \quad BrCN \longrightarrow [Fe(CN)_2(CO)_3Br]^- \qquad (23)$$

A nitrogen-substituted iron carbonyl–cyanide complex **24** has been prepared from $(Me_3TACN)FeCl_2$ by adding cyanide ions in the presence of CO ($Me_3TACN = N,N',N''$-trimethyl-1,4,7-triazacyclononane).[73]



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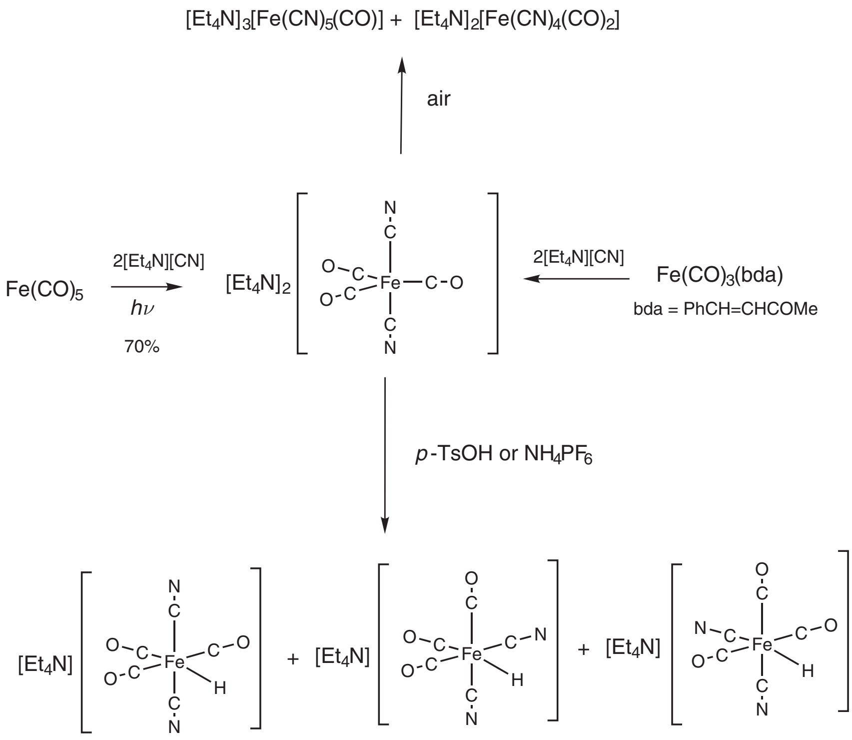


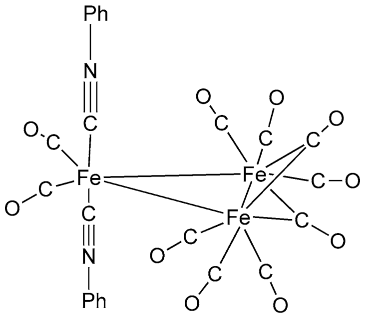
Scheme 13[64]

Quantum calculations of equilibrium structures and vibrational frequencies of $[Fe(CN)_x(CO)_y]^q$ (for the series $x=0$–6, $y=0$–5, $q=2-x$) as well as the Fe^0 compounds (where $x=1$, $y=4$, $q=-1$) and the Fe^{3+} compounds (where $x=5$, $y=1$, $q=-2$) are known.[74] The compounds were studied because of the relationship to the catalytic centers in hydrogenases. Calculated bond lengths agree with experimental values for the Fe–CO bonds (slightly shorter), but are longer than experimental for Fe–CN. The calculated vibrational frequencies were higher for CN^- and lower for CO than the experimental values. The expected correlation between the amount of π-backdonation and the calculated vibrational mode of the CO was seen. The Fe → L π-backdonation affects the stretching frequencies of CO more than those of CN^-. Finally, the Fe–CN^- bonds have less π-character than the Fe–CO bonds.

The complexes $Fe(CO)_{5-n}({}^tBuCN)_n$ ($n=1$, 2) form 1 : 1 adducts with HgX_2 (X = Cl, I) in acetone (Equation (24)).[75]

$$Fe(CO)_{5-n}({}^tBuNC)_n + HgX_2 \xrightarrow[X = Cl, I]{n = 1, 2} Fe(CO)_{5-n}({}^tBuNC)_n(HgX_2) \tag{24}$$

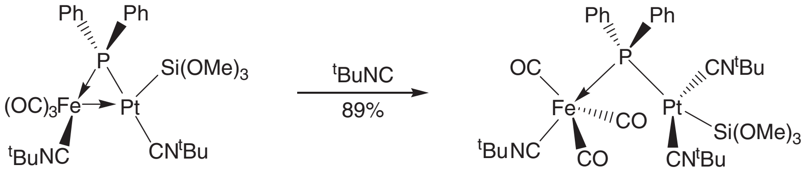
The reaction of the trinuclear cluster $Fe_3(CO)_{12}$ with isocyanides RNC (R = Ph, C_6H_4OMe-*p*, or $CH_2SO_2C_6H_4Me$-*p*) has been investigated by electrospray mass spectrometry producing $Fe_3(CO)_{12-n}(CNR)_n$.[76] For R = Ph, $n=1$–6; for R = C_6H_4OMe-*p*, $n=3$–5, and for $CH_2SO_2C_6H_4Me$-*p*, $n=1$–5. For R = Ph, only the $n=1$, 2 derivatives could be isolated and characterized. The disubstituted compound was shown to have the structure **25**, which retains the core geometry of $Fe_3(CO)_{12}$ with substitution occurring in the axial positions on the unique Fe atom. This contrasts with the previously determined structure of CN^tBu derivative, where the ligands are also found on the unique Fe atom but one in an axial and the other in an equatorial site. Thermolysis of the mono- and disubstituted isocyanide derivatives for R = Ph, C_6H_4OMe-*p* in toluene at about 75 °C led to loss of CO and more complex binding of one isonitrile ligand to the cluster. In this fashion, the complexes $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNR)$ and $Fe_3(CO)_8(\mu_3\text{-}\eta^2\text{-}CNR)(CNR)$ were obtained.



25

The liquid-crystal behavior of iron carbonyl–isocyanide complexes has been examined for $Fe(CO)_4(CNR)$ (where $R = C_6H_4O(O)CC_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_4C(O)OC_6H_4C_6H_4OC_nH_{2n+1}$, or $C_6H_4C_6H_4O(O)CC_6H_4OC_nH_{2n+1}$).[77] The free isocyanides produce nematic and/or smectic phases for short chains, while the longer chain derivatives only produced smectic A phases. When coordinated to the iron carbonyl unit, the isocyanides gave similar behavior but the transition temperatures were slightly lower. All of the iron complexes described undergo severe decomposition near 120 °C.

An isocyanide-substituted iron–platinum complex **26** undergoes Fe–Pt bond cleavage to give **27** upon further treatment with ^{t}BuNC (Equation (25)).[78] The ease with which the bond was opened was attributed to the dative character of the Fe–Pt bond.



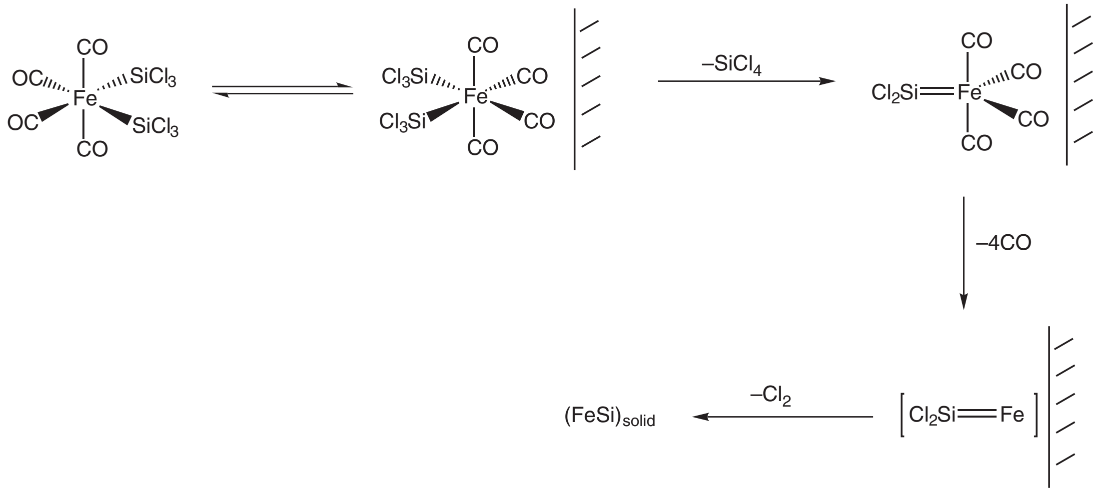
26 **27** (25)

6.01.4.2 Silicon Complexes

The compound *cis*-$Fe(CO)_4(SiCl_3)_2$ was prepared via reaction of $Fe_3(CO)_{12}$ and $HSiCl_3$.[79] Photoelectron studies of $Fe(CO)_4(SiCl_3)_2$ showed the *cis*-isomer predominated in the gas phase. From a comparison with data for $H_2Fe(CO)_4$, it was concluded that the Fe–H orbitals were approximately 1.3 eV higher in energy than the Fe–Si orbitals.[79]

The formation of iron silicides from a single source precursor, *cis*-$Fe(SiCl_3)_2(CO)_4$, via chemical vapor deposition was studied using *in situ* photoelectron spectroscopy.[80] $SiCl_4$ was detected as a byproduct of that process, suggesting that the decomposition proceeded via the formation of reactive silylene species, $[Fe(CO)_4{=}SiCl_2]$ (Scheme 14). This species is proposed to lose CO and Cl_2 and then undergo nucleation to form the iron silicide. The mechanism was supported by DFT calculations. The conversion of *cis*-$Fe(CO)_4(SiCl_3)_2$ to the $Fe(CO)_4({=}SiCl_2)$ molecule was calculated to have an activation barrier of 47 kcal mol^{-1}, and the Fe=Si bond-dissociation energy was determined to be 52 kcal mol^{-1}.

The formation of $Fe(CO)_4({=}SiR_2)$ complexes has continued to receive attention. In most cases, the mononuclear products formed are stabilized by the presence of a donor ligand coordinated to Si: $Fe(CO)_4({=}SiR_2L)$. Thus, the irradiation of an alkoxyhydrosilane with $Fe(CO)_5$ in the presence of HMPA resulted in the formation of the silylene complex $(CO)_4Fe{=}SiMe_2{\cdot}HMPA$ (HMPA = hexamethylphosphoramide) (Equation (26)).[81] Yields decreased as the size of the R group increased. The reaction was also performed without HMPA, in which case hydrido–iron silyl complexes were obtained instead (Equation (27)).[81] When R = 2-pyridyloxy, the product formed (Equation (28))[81] was different, exhibiting a chelating bis(silyl) ligand.



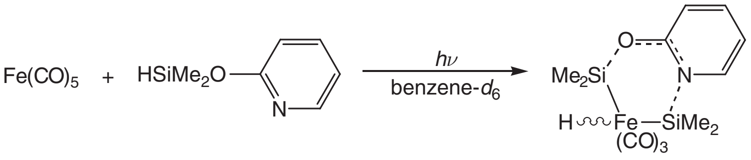
Scheme 14[80]

$$Fe(CO)_5 + HSiMe_2OR + HMPA \xrightarrow[\text{benzene-}d_6]{h\nu} (CO)_4Fe{=}SiMe_2{\cdot}HMPA + SiMe_2(OR)_2 \tag{26}$$

$$R = Me\ (19\%),\ Et\ (9\%),\ {}^{i}Pr\ (3\%),\ Ph\ (6\%)$$

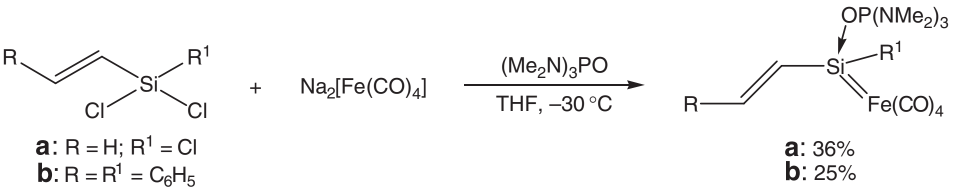
$$Fe(CO)_5 + HSiMe_2OR \xrightarrow[\text{benzene-}d_6]{h\nu} HFe(CO)_4SiMe_2OR + SiMe_2(OR)_2 \tag{27}$$

$$R = Me\ (49\%),\ Et\ (45\%),\ {}^{i}Pr\ (41\%),\ {}^{t}Bu\ (24\%),\ Ph\ (48\%)$$



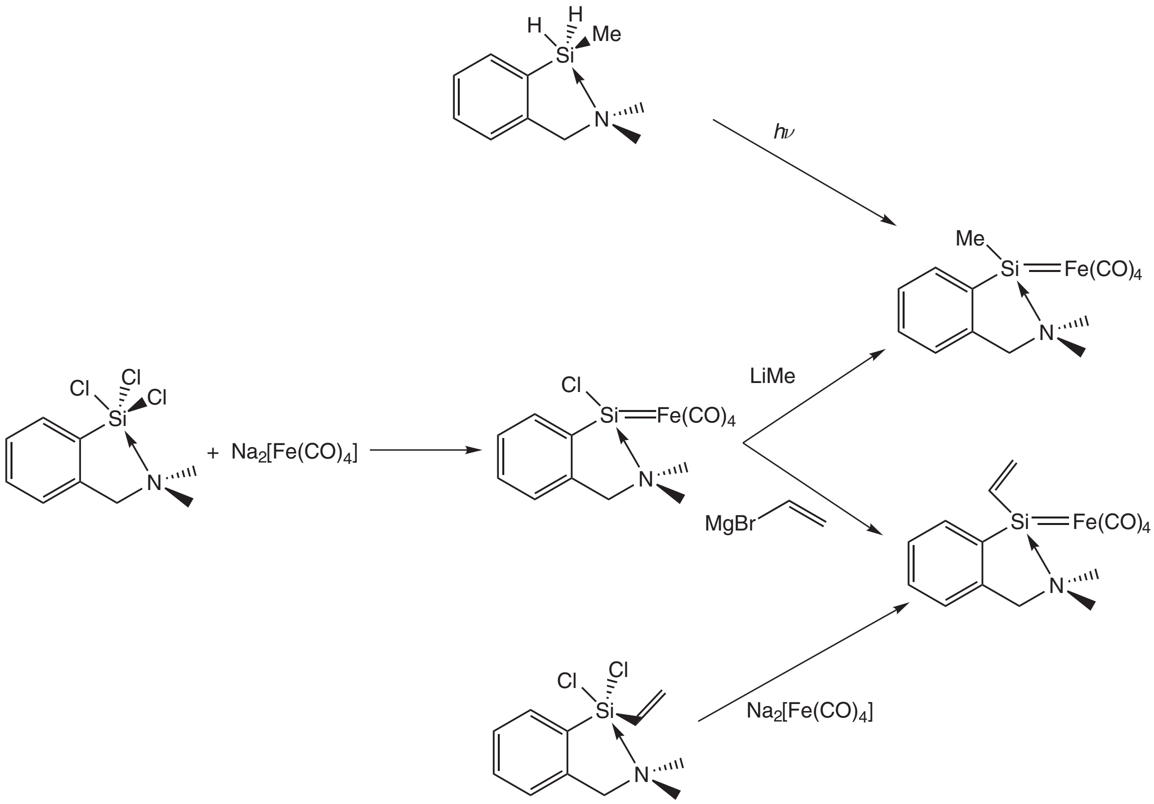
(28)

Reaction of the tetracarbonylferrate dianion with a dichlorosilane in the presence of HMPA also produced base-stabilized silylene complexes (Equation (29)),[82,83] but the donor group could also be intramolecularly bound (Scheme 15).[82]

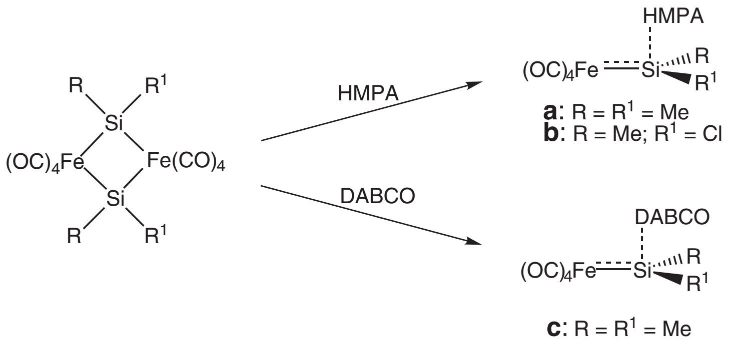


(29)

For small R groups, the formation of a stable mononuclear silylene of the type $Fe(CO)_4({=}SiR_2)$ is not favored, but dimeric species $Fe_2(CO)_8(\mu\text{-}SiR_2)_2$ (Scheme 16)[84] have been observed. Reaction of these four-membered ring structures with Lewis bases disrupts the Fe_2Si_2 framework and produces base-stabilized iron–silylene complexes.[84] In contrast to the reactions with HMPA and 1,4-diazabicyclo-[2.2.2]-octane (DABCO), addition of PMe_3 gave only *trans*-$Fe(CO)_3(PMe_3)_2$ in 90% yield.

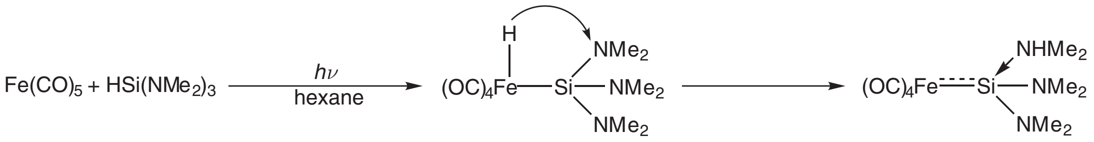


Scheme 15[82,83]

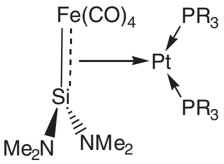


Scheme 16[84]

A base-stabilized silylene complex was synthesized via oxidative addition of $HSi(NMe_2)_3$ to photochemically generated $Fe(CO)_4$ (Scheme 17).[85] It was thought that the presence of the $HFe(CO)_4\{Si(NMe_2)_3\}$ tautomer would allow reaction with other metal complexes to produce heterobimetallic species, which proved to be the case for $[Pt(C_2H_4)(PR_3)_2]$ (R = Ph, *p*-tolyl) 28,[85] although the reaction is believed to have taken place via the displacement of one of the amine ligands rather than by an oxidative addition reaction.[85] Addition of a phosphine was attempted to stabilize the iron–silicon bond of the silylene.[85] The expected product was not formed, but rather a complex resulting from the exchange of two ethoxy groups on phosphorus with two of the dimethylamino groups on silicon was formed (Equation (30)).[85] Deprotonation of this product followed by reaction with metal complexes of Cu, Ag, and Au led to heterobimetallic complexes.[85]



Scheme 17[85]



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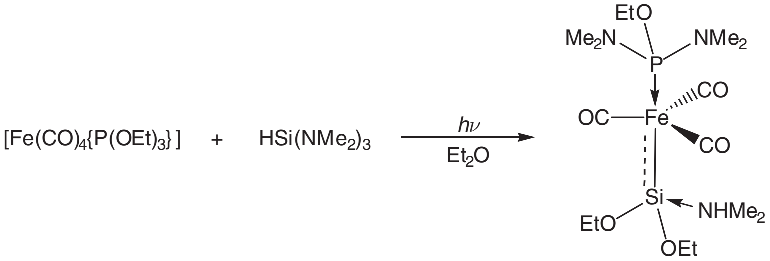
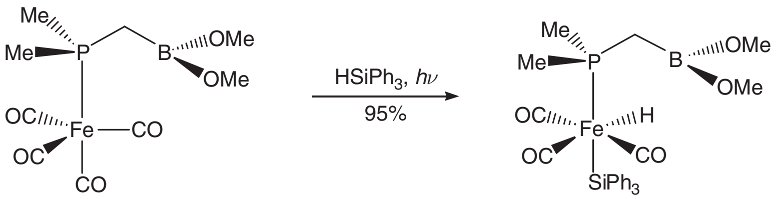


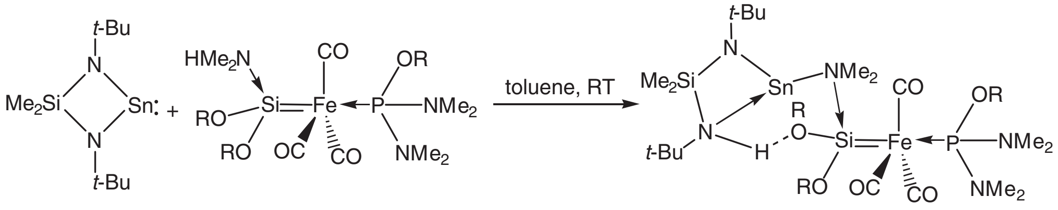
(30)

Similarly, the complex $HFe(CO)_3(SiPh_3)\{Me_2PCH_2B(OMe)_2\}$ resulted from photolysis of $Fe(CO)_4\{Me_2PCH_2B(OMe)_2\}$ with $HSiPh_3$ (Equation (31)).[86]



(31)

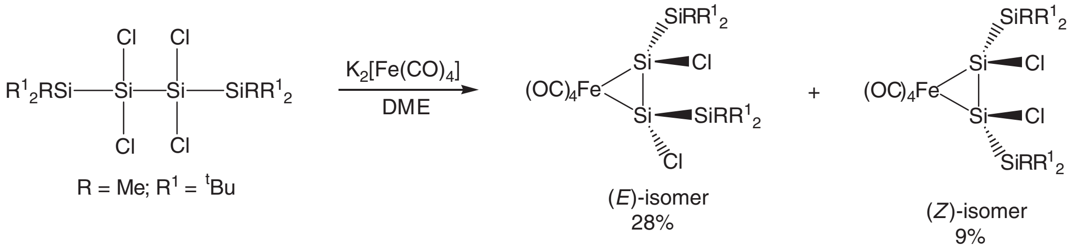
The reaction of a methylamine-stabilized alkoxysilyl iron complex with a cyclic stannylene gave insertion of the stannylene into the N–H bond of the methylamine (Equation (32)).[87]



(32)

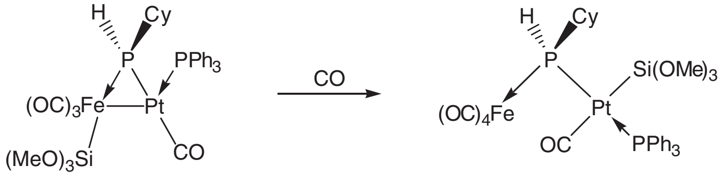
a: R = Et, 78%
b: R = Me, not isolated

The reaction between $K_2Fe(CO)_4$ and a tetrachlorotetrasilane resulted in the formation of an iron complex with a disilene ligand (Equation (33)).[88] Both the (*E*)- and (*Z*)-isomers were formed. The reaction, when monitored by ^{1}H NMR spectroscopy, indicated the initial formation of the (*Z*)-isomer with isomerization to the more stable (*E*)-isomer over time. Kinetic studies were also performed, and suggested that the (*E*)-isomer is $>3\,\text{kcal mol}^{-1}$ more stable than the (*Z*)-isomer. Theoretical calculations for similar molecules with varying R groups indicated that the stability of the molecule is dependent on the bulkiness of the R group.

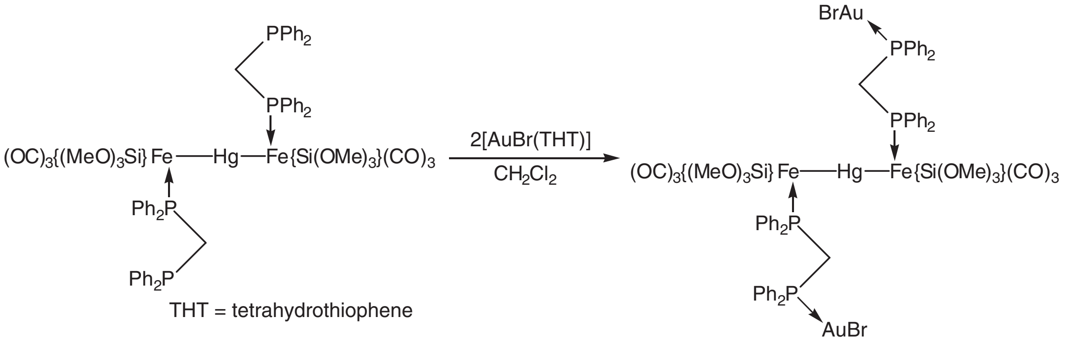


(33)

An extensive series of compounds based upon tris(alkoxy)silyl iron complexes has been prepared and the reaction chemistry examined for both transition metals (Equation (34)[78], Schemes 18–22[89–96,98]) and main group elements (Equations (35)–(41),[97,99,100,102,103] Schemes 19,[89–95] 23–26).[101,104] The goal of much of that work has been to prepare heterobimetallic complexes, which is discussed in more depth elsewhere (see Chapter 6.04), and, as such, these reports will only be briefly examined here for those cases in which a compound without an iron–metal bond is either used or produced.



(34)



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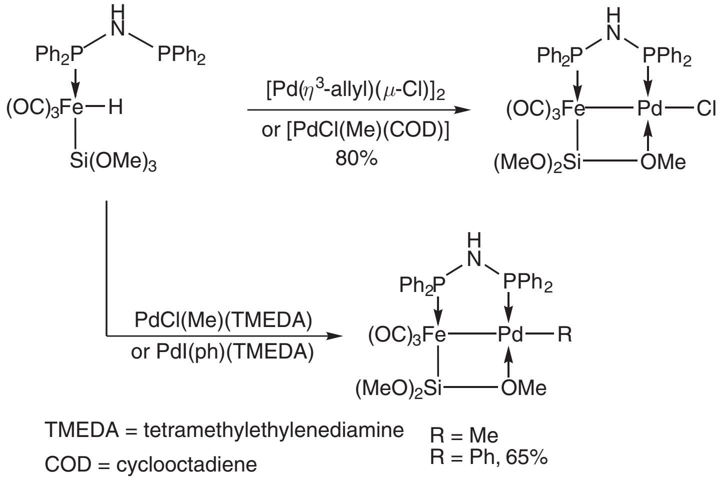
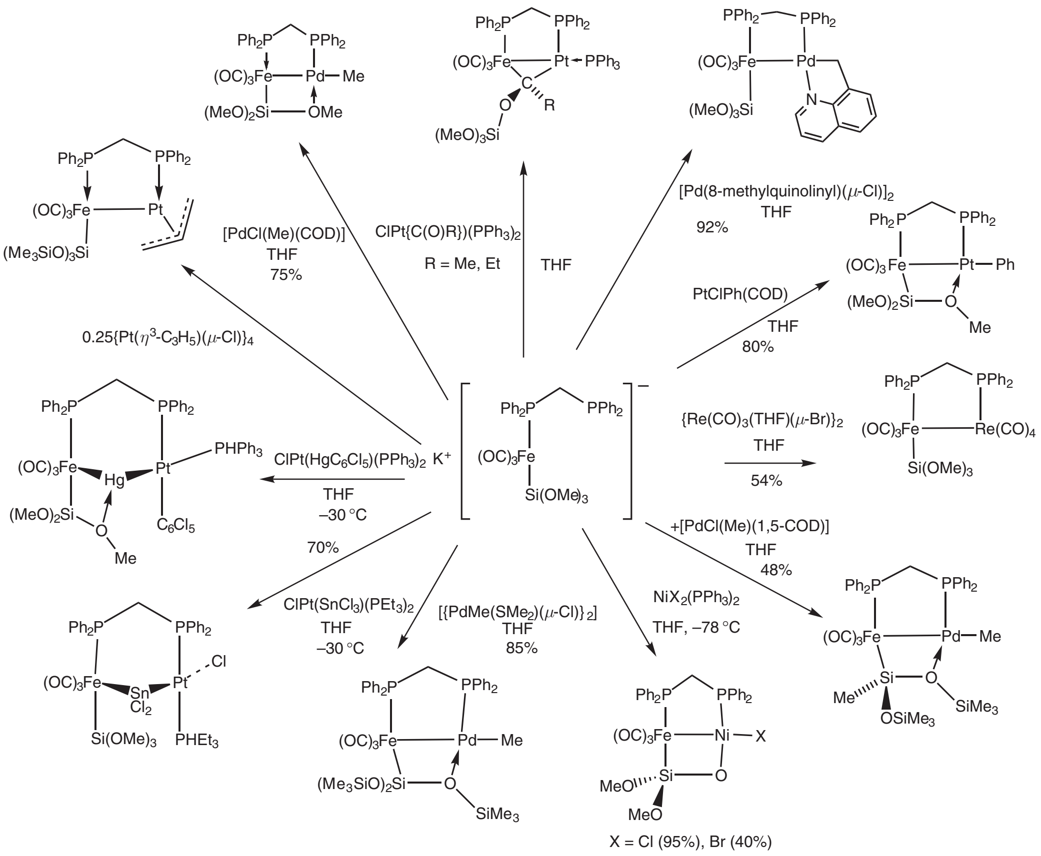
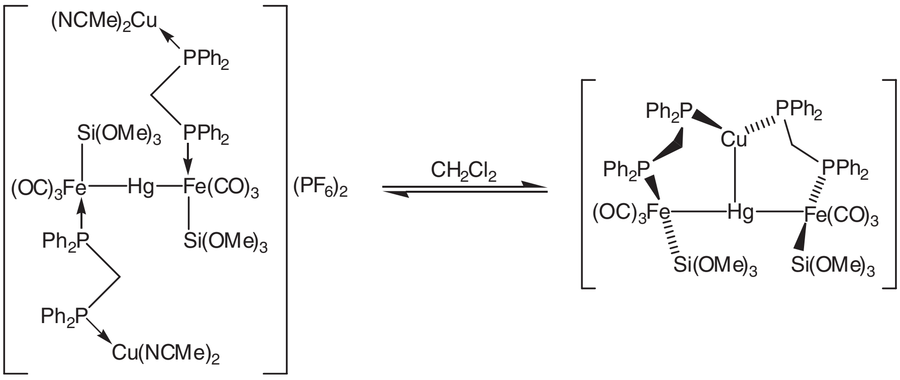


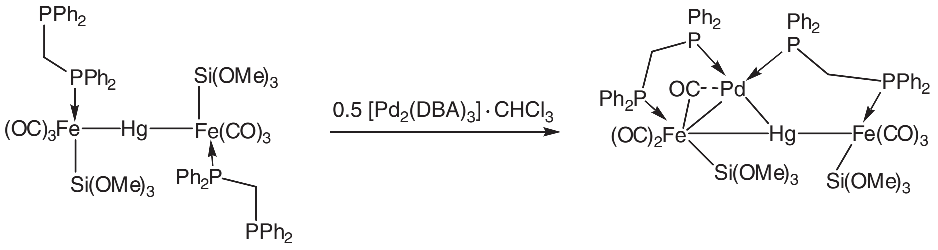
Scheme 18[89]



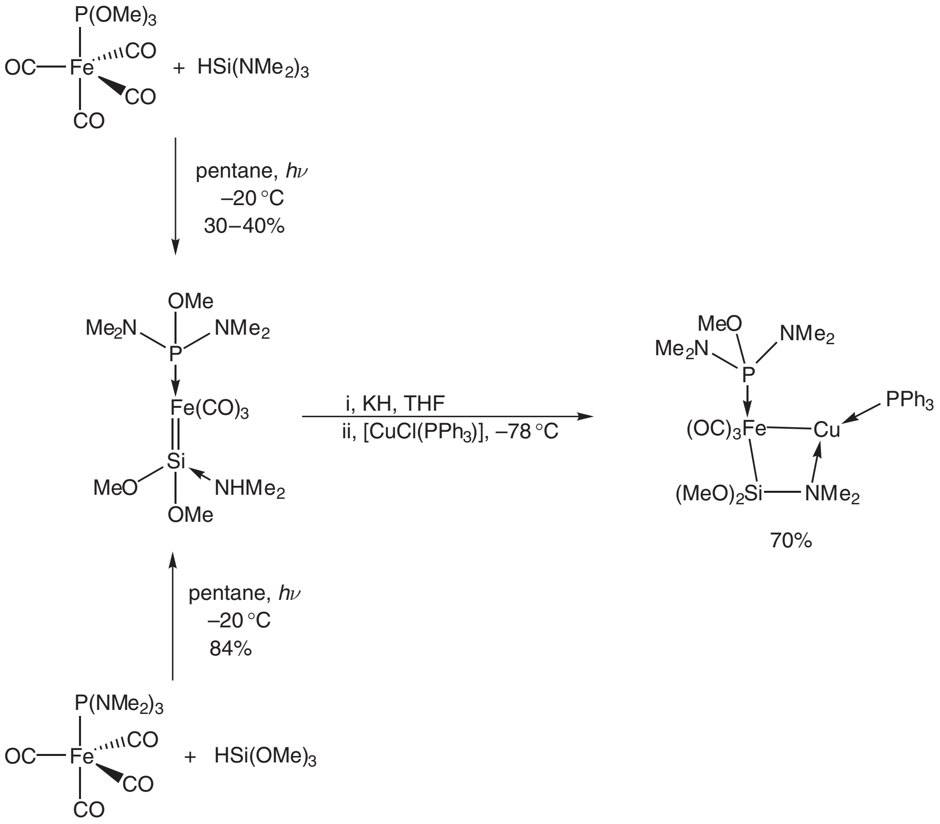
Scheme 19[89–95]



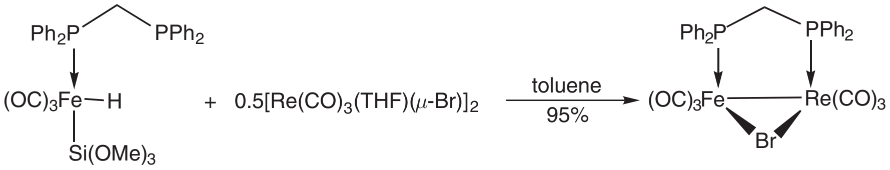
(36)



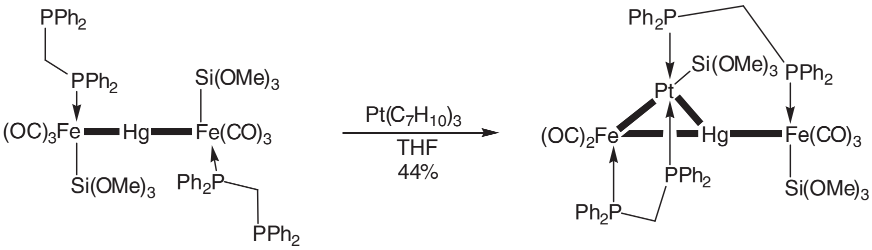
(37)



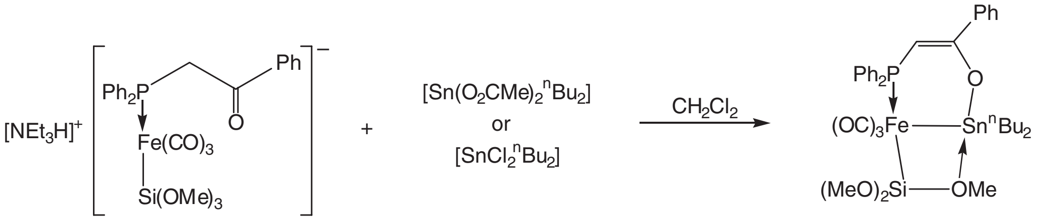
Scheme 20[96]



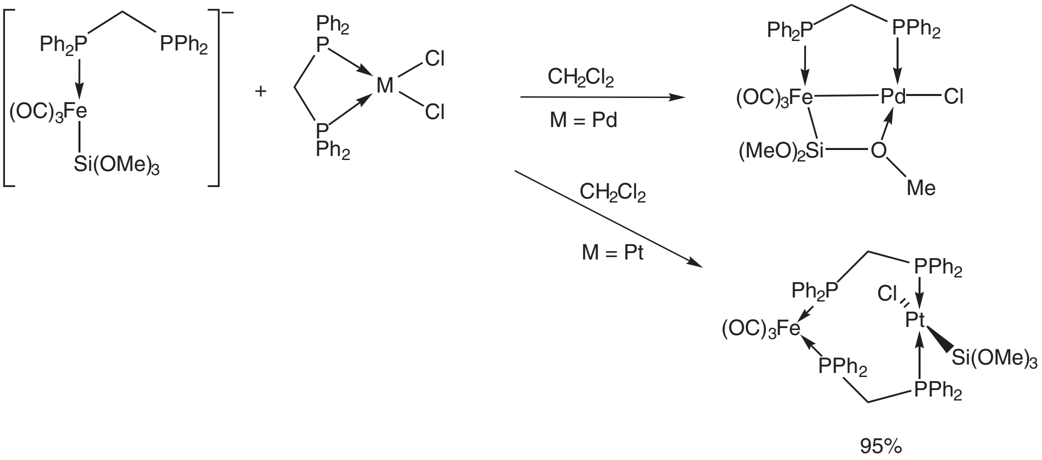
Scheme 21[95]



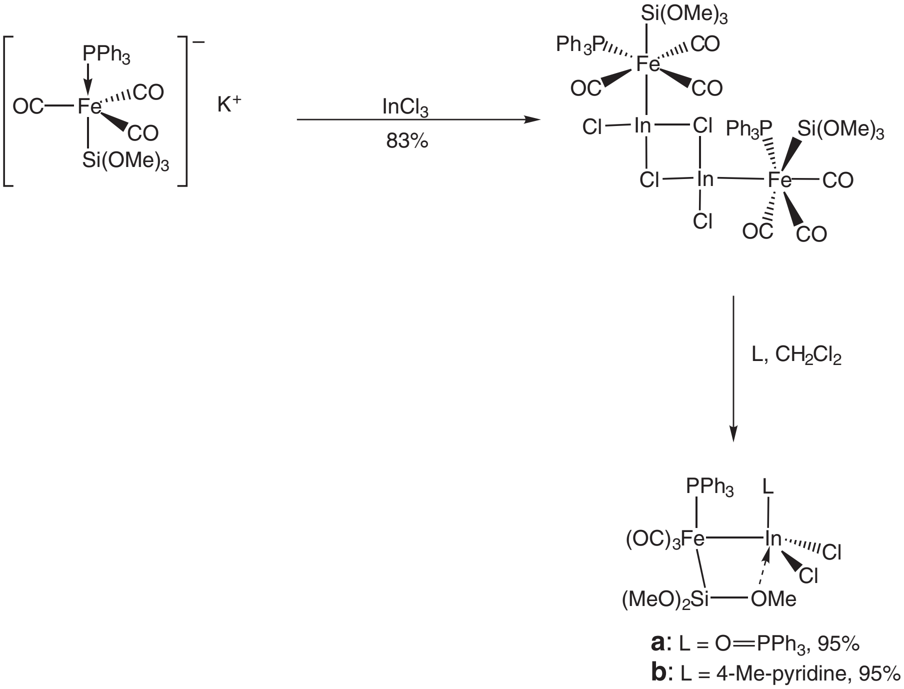
(38)



(39)

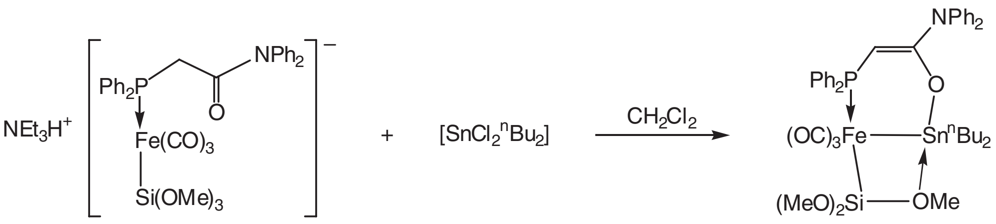


Scheme 22[98]



a: L = O═PPh$_3$, 95%
b: L = 4-Me-pyridine, 95%

Scheme 23[101]



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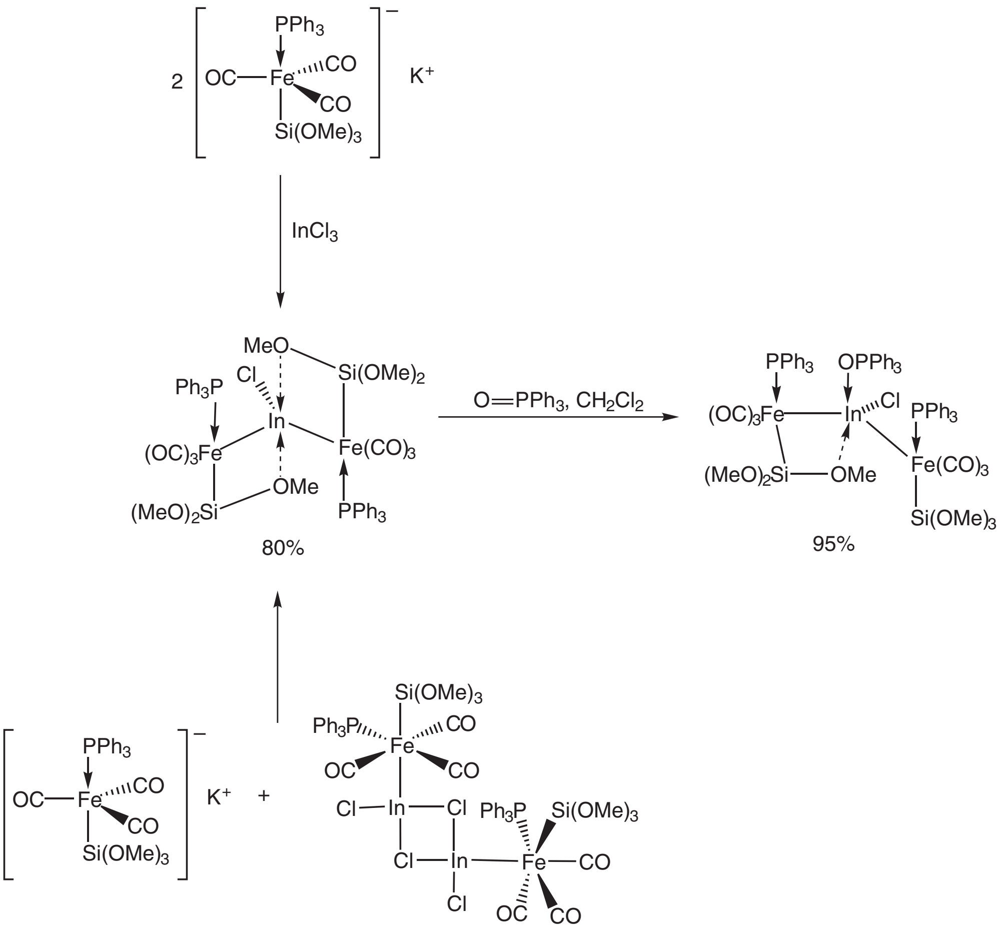
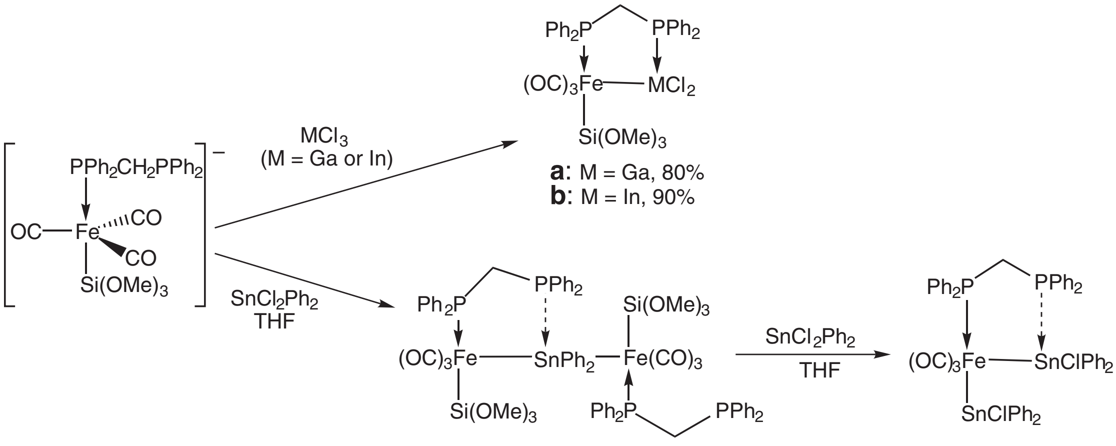
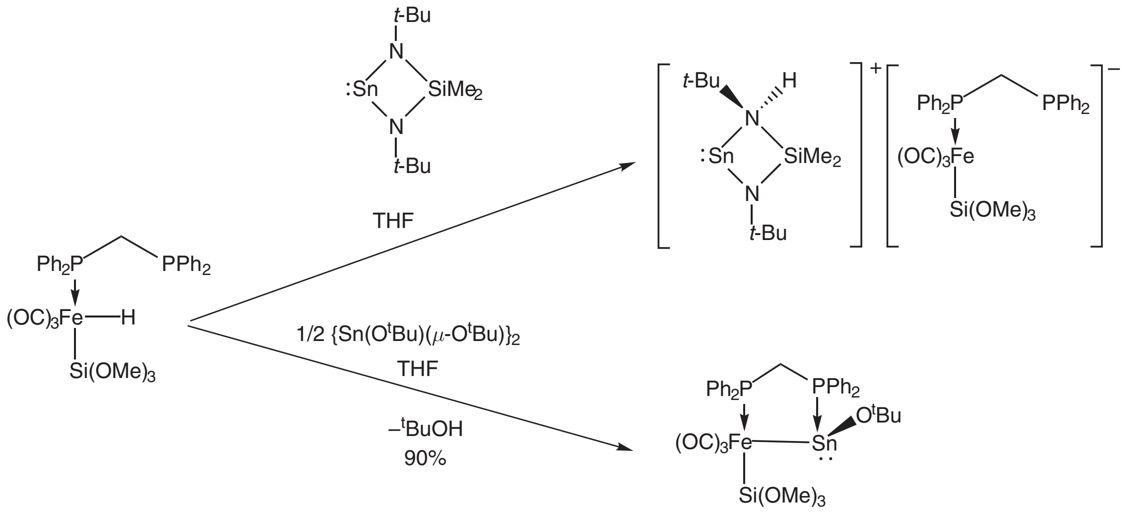


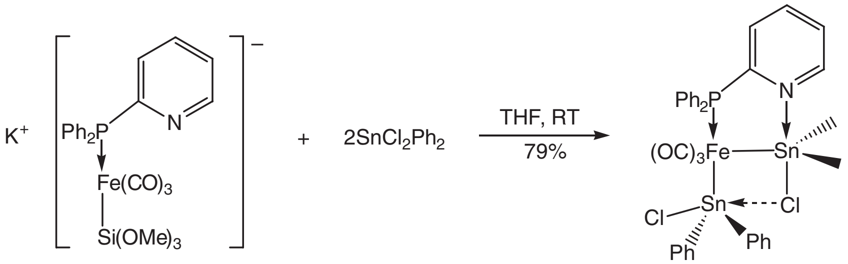
Scheme 24[101]



Scheme 25[101]



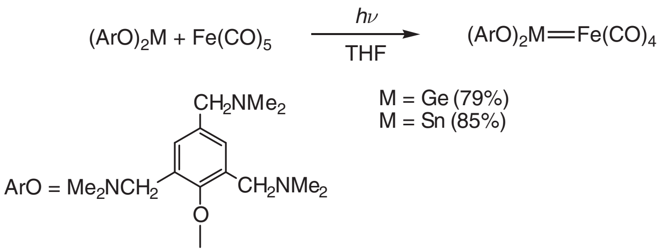
Scheme 26[104]



(41)

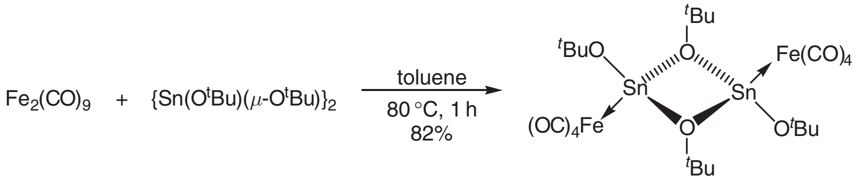
6.01.4.3 Germanium, Tin, and Lead Complexes

Some iron carbonyl complexes containing Fe–Sn bonds as well as Fe–Si bonds have been described in Section 6.01.4.2 (Equations (39)–(41), Schemes 19 and 25).[101–104] These were prepared by reaction of a siloxyiron carbonyl anion with a suitable halo tin complex or a tin(II) alkoxide with an iron hydride (Scheme 26). Reactions in Equations (42)–(46)[104–107] demonstrate the reactions of neutral iron carbonyl complexes with E(II) reagents to introduce terminal or bridging stannylene and germylene ligands. The M–Fe bond distances in **29** (Equation (45))[105] are among the shortest of such bonds known (Ge–Fe: 2.298(2) and Sn–Fe: 2.440(1) Å). Calculations indicated that the ligands are good σ-donors and poor π-acceptors.[105] The bonding here is similar to that studied for the group 13 E^+ complexes (see Section 6.01.3.3 and Chapter 3.08.4). The Sn(salen) ligand (Equation (46))[106] was found to be in an axial position of the $Fe(CO)_4$ trigonal bipyramid, indicating that it is a better σ-donor than π-acceptor ligand.[106]

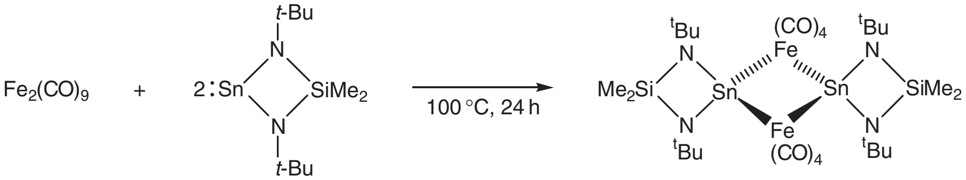


$$(ArO)_2M + Fe(CO)_5 \xrightarrow[THF]{h\nu} (ArO)_2M{=}Fe(CO)_4$$

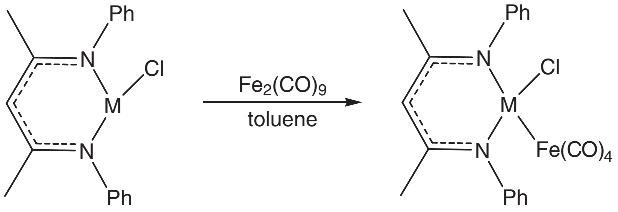
(42)



(43)



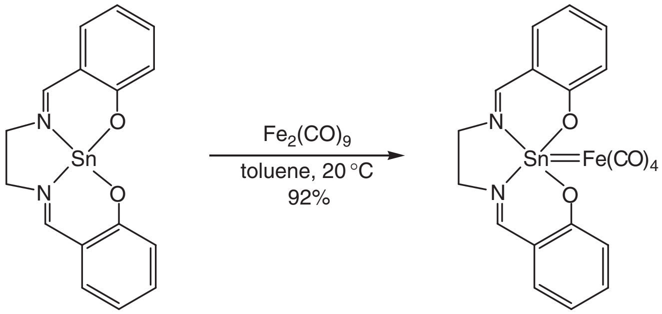
(44)



(45)

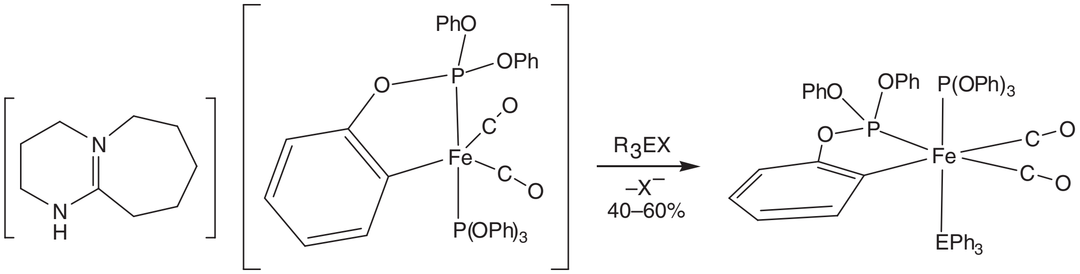
M = Ge, Sn

29



(46)

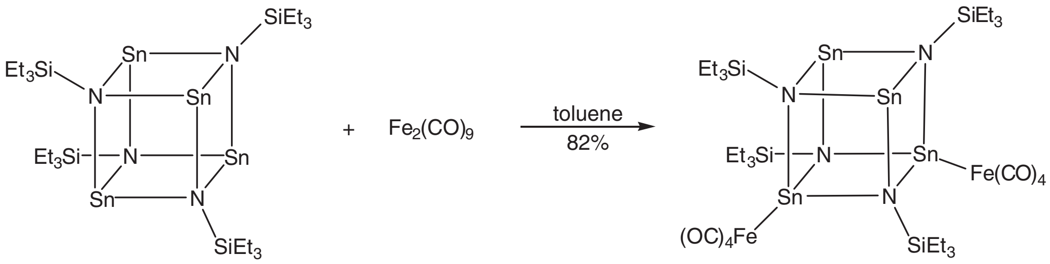
The anionic orthometallated compound $[Fe(CO)_2\{P(OPh)_3\}\{(PhO)_2POC_6H_4\}]^-$ reacts with organotin and -lead halides to form Fe–Sn and Fe–Pb bonds (Equation (47)).[108]



(47)

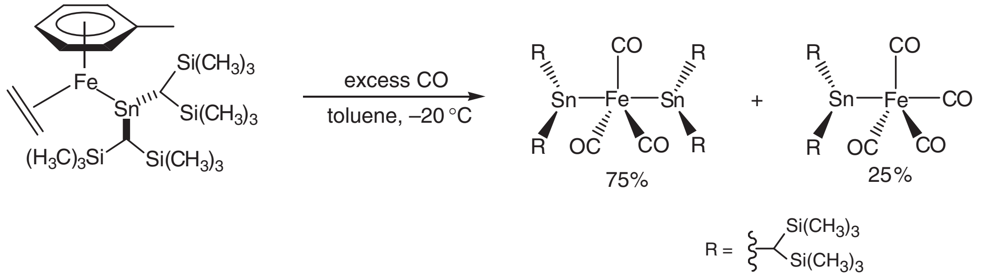
E = Sn, R = Ph, Me, X = Cl
E = Pb, R = Ph, X = Cl; R = Me, X = OAc

A new silyl-substituted heterocubane of tin and nitrogen was synthesized, and reaction with $Fe_2(CO)_9$ led to the addition of $Fe(CO)_4$ fragments to two of the tin atoms (Equation (48)).[109]

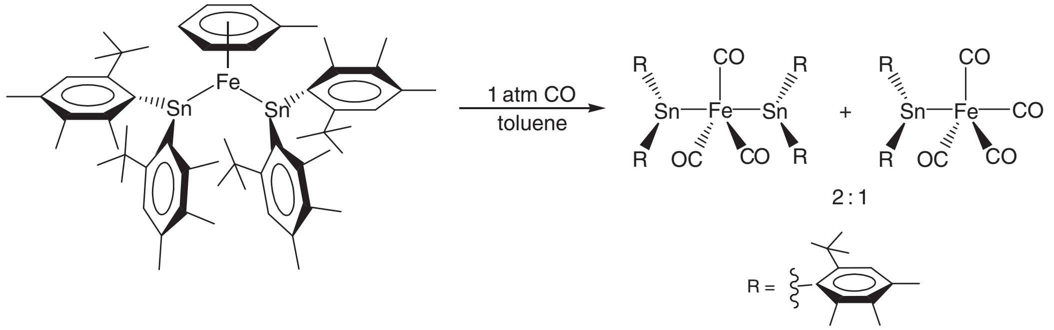


(48)

Iron carbonyl complexes containing tin(II) ligands could also be obtained starting from arene iron complexes by displacement of the arene (Equations (49)[110] and (50)).[112] Reactions of (arene)Fe(SnR$_2$)(ethene) or bis{{bis(2-*tert*-butyl-4,5,6-trimethylphenyl)}Sn}Fe(η^6-toluene) with carbon monoxide led to the substitution of the ethene and toluene ligands (Equation (49)).[110,111] The complex bis{{bis(2-*tert*-butyl-4,5,6-trimethylphenyl)}Sn}Fe(η^6-toluene) was synthesized and reacted with 1 atm of carbon monoxide (Equation (50)). Attempts to synthesize the product in which only the toluene is substituted were unsuccessful.[112]

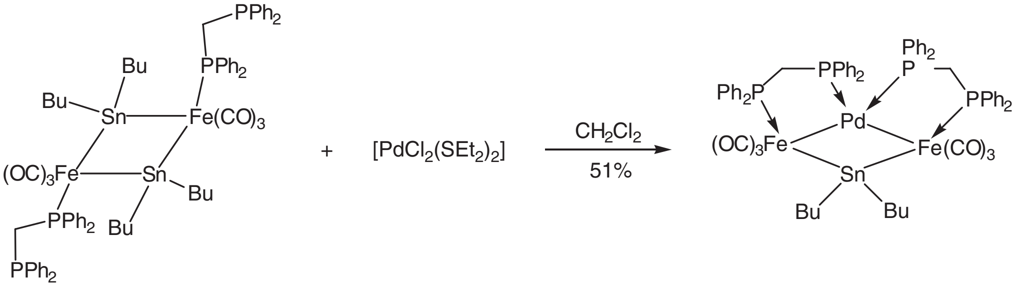


(49)



(50)

The cyclic Fe$_2$Sn$_2$ complex reacts with PdCl$_2$(SEt$_2$)$_2$ to substitute one of the Sn atoms by Pd (Equation (51)).[113]



(51)

6.01.5 Iron Carbonyls with Group 15 Ligands

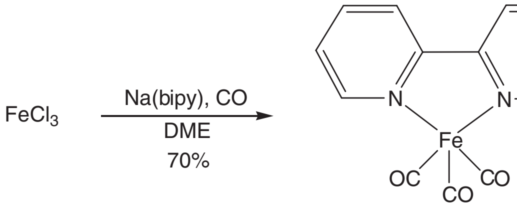
6.01.5.1 Nitrogen Donor Ligands

Computational studies were carried out to determine how the presence of iron carbonyl fragments would influence the hydrogenation of dinitrogen to ammonia in terms of reaction enthalpies (Scheme 27).[114] It was discovered that the only significant difference between the catalyzed and non-catalyzed reactions occurred for the first step of the hydrogenation—the reaction enthalpy for $(CO)_4Fe–N_2$ to $(CO)_4Fe–N_2H_2$ was 16.1 kcal mol^{-1} lower than the metal-free hydrogenation. The same step involving the dinuclear species $(CO)_4Fe–N_2–Fe(CO)_4$ was found to be lower than that of the mononuclear species by 13.1 kcal mol^{-1}.

The reaction of iron pentacarbonyl with 1,4-diazabicyclo[2.2.2]-octane with UV irradiation produced the mononuclear iron carbonyl complex **30** (Scheme 28).[115] Subsequent irradiation of **30** with additional $Fe(CO)_5$ resulted in a complex with two $Fe(CO)_4$ fragments **31**.

The chelating diimines 2,2′-bipyridine and 1,10-phenanthroline react with $Fe(CO)_3(BDA)$ with substitution of the BDA to give $Fe(CO)_3(bpy)$ and $Fe(CO)_3(phen)$, which were structurally characterized (Scheme 29).[116] The same complexes could be obtained using $Fe_2(CO)_9$, but $Fe_2(CO)_7(L)$ (L = bipy, phen) was the predominant product of those reactions.

The synthesis of $Fe(CO)_3(bipy)$ was also achieved by reducing iron(III) chloride with Na(bipy) in the presence of CO (Equation (52))[117] or by reaction of CO with $FeR_2(bipy)_2$ (R = Me, Et) (Scheme 30). The outcome of the latter reaction was dependent on the solvent in which the reaction was performed, giving $Fe(CO)_3(bipy)$ in toluene but $Fe_2(bipy)_2(CO)_5$ in heptane.[117]



(52)

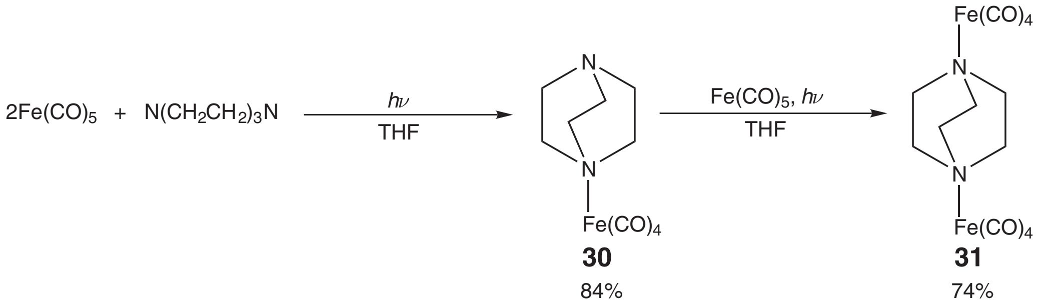
A. Non-catalyzed pathway

1. $N_2 + H_2 \longrightarrow N_2H_2$
2. $N_2H_2 + H_2 \longrightarrow N_2H_4$
3. $N_2H_4 + H_2 \longrightarrow 2\ NH_3$

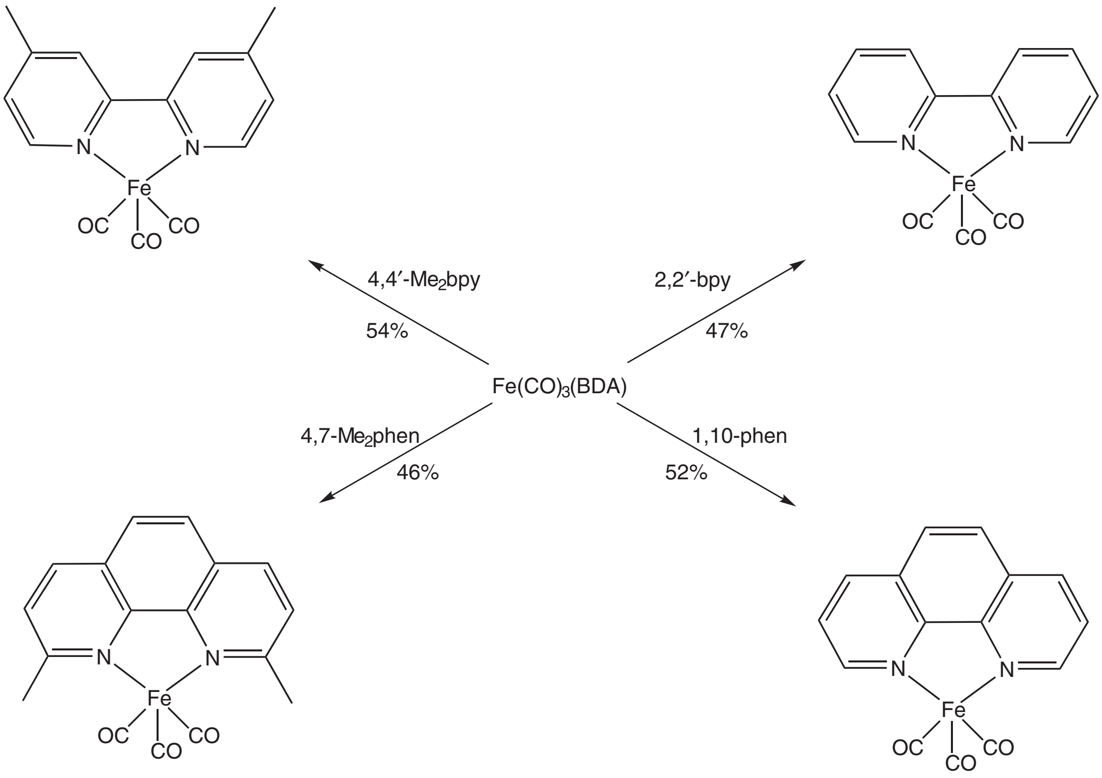
B. Iron carbonyl-catalyzed pathway

1. $(OC)_4Fe\text{-}N_2 + H_2 \longrightarrow (OC)_4Fe\text{-}N_2H_2$
2. $(OC)_4Fe\text{-}N_2H_2 + H_2 \longrightarrow (OC)_4Fe\text{-}N_2H_4$
3. $(OC)_4Fe\text{-}N_2H_4 + H_2 \longrightarrow (OC)_4Fe\text{-}NH_3 + NH_3$

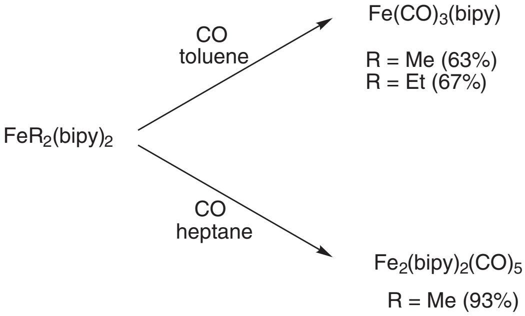
Scheme 27[114]



Scheme 28[115]



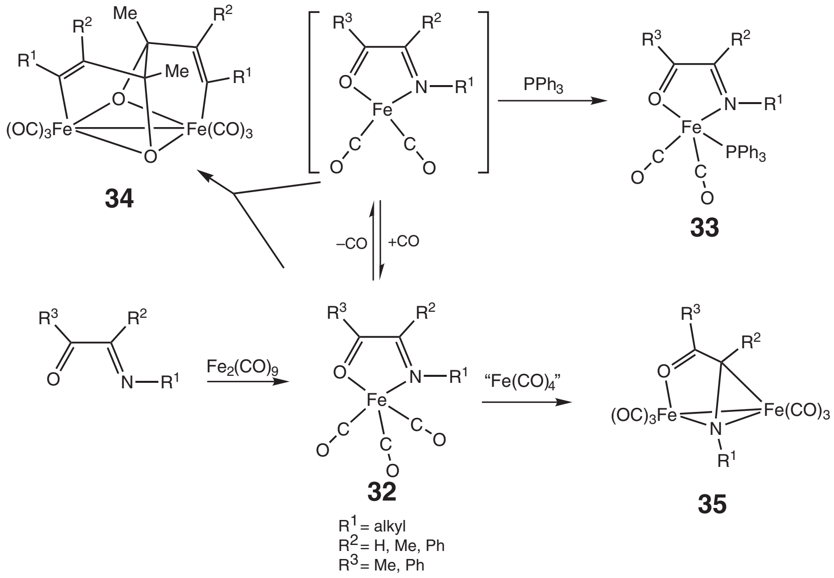
Scheme 29[116]



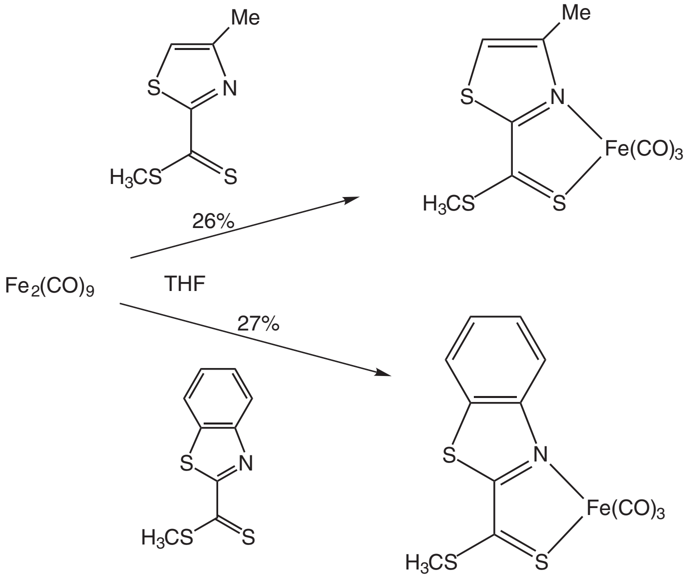
Scheme 30[117]

The reactions of $Fe_2(CO)_9$ with $R^1N{=}CR^2C(R^3){=}O$ (R^1 = alkyl; R^2 = H, Me, PH; R^3 = Me, Ph) lead to complexes with both the imine and carbonyl groups attached to the iron center (Scheme 31).[118] The product **32** undergoes CO loss which permits substitution **33** or dimerization **34**. Additional iron carbonyl fragments that are present can also add to the compound to produce dinuclear complex **35**.

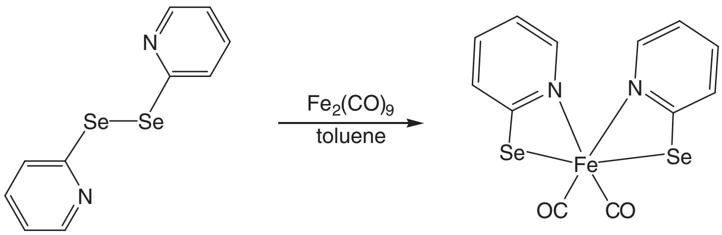
Pyridine-based ligands that also contain a sulfur or selenium donor atom can form chelate complexes when treated with $Fe_2(CO)_9$ (Scheme 32).[119,120] The X-ray structure of the *S*-derivative shows a trigonal-bipyramidal configuration, unlike the square-pyramidal geometry often seen in $[Fe(CO)_3(L\text{–}L)]$ complexes.[119] The compound 2,2′-dipyridyl diselenide reacts via reductive cleavage of the selenium–selenium bond (Equation (53)).[120]



Scheme 31[118]

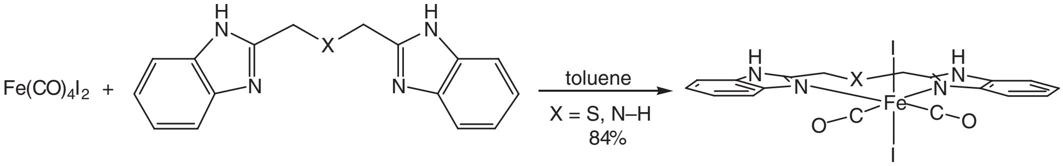


Scheme 32[119]



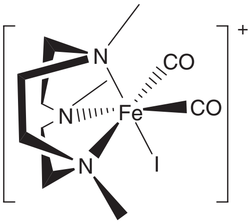
(53)

When $Fe(CO)_4I_2$ was reacted with bis(benzimidazolyl-2-ylmethyl)amine or bis(benzimidazolyl-2-methyl)thioether, a substituted iron(II) dicarbonyl complex resulted (Equation (54)).[121] Based upon their infrared spectra, the complexes were proposed to have *cis*-carbonyl ligands, with the two iodide ligands *trans* to each other. Other related benzimidazolyl ligands led to complete CO loss and formation of $FeI_2(L)$ with no observed carbonyl-containing intermediates.



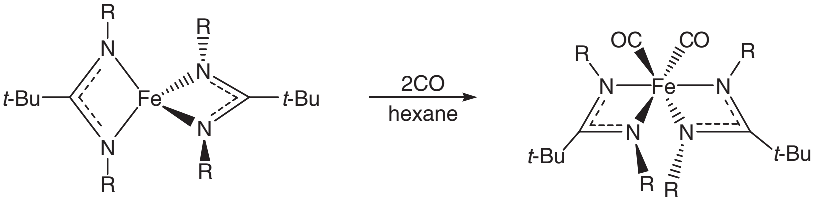
(54)

Similarly, the cyclic ligand Me_3TACN reacts with $Fe(CO)_4I_2$ to give $[(Me_3TACN)FeI(CO)_2]I$ **36** in 90% yield.[73] This compound can be compared to derivative $(Me_3TACN)Fe(CO)(CN)_2$ **24** described in Section 6.01.4.1.[73]



36

Another iron(II) dicarbonyl complex is formed when a bis(amidinate) iron(II) complex was treated with carbon monoxide in hexane (Equation (55)).[122] The product is diamagnetic. The X-ray structure for the *i*-propyl derivative was reported.[122]



R = cyclohexyl (69%)
R = *i*-propyl (28%)

(55)

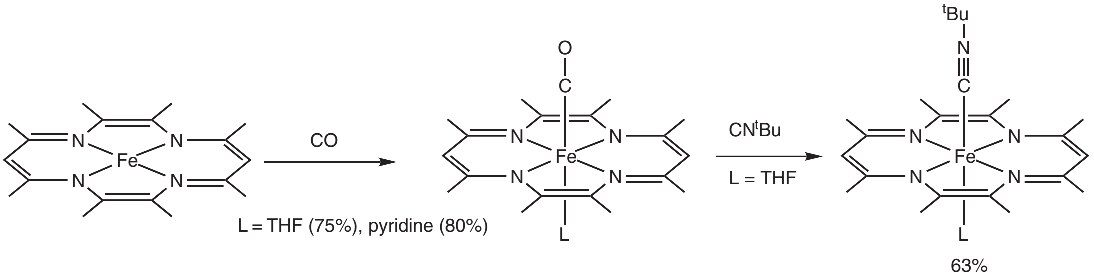
An iron(II) monocarbonyl derivative was obtained by addition of CO to Fe(TMTAA) in the presence of THF or pyridine (TMTAA = dibenzotetramethyltetraaza[14]annulene dianion) (Scheme 33).[123] The carbonyl ligand could be displaced by isocyanides.

Similarly, synthesis and characterization of new monocarbonyl iron(II) complexes with macrocylic borylated bis(dimethylglyoximato) ligands has been reported (Scheme 34). These have the general formula, $Fe(DMGBR_2)_2(pyridine)(CO)$ ($BR_2 = BH_2$, BPh_2, or 9-borabicyclo[3.3.1]-nonane),[124] and were studied due to their similarity to heme. Kinetics of ligand-exchange reactions were reported and compared to the previously reported BF_2 derivative.

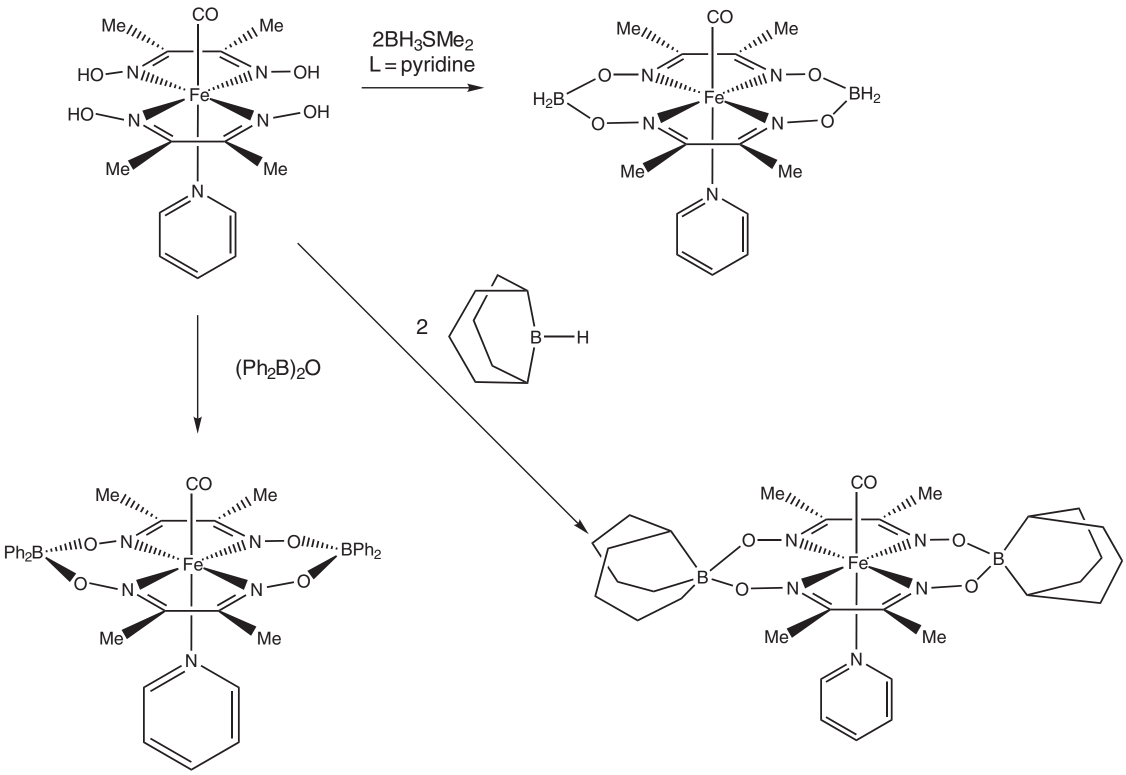
The porphyrin complex **37** with 2,6-difluorophenyl substituents binds two molecules of THF **38**, but even in THF solution, one of these is displaced by carbon monoxide (**39**, Scheme 35).[125] Flash photolysis of the carbonyl complex in cyclohexane or CO-saturated THF resulted in elimination of the CO ligand. With 1 atm CO, the carbonyl complex was regenerated in THF with a rate constant k_{obs} of $1.6\ (\pm 0.2) \times 10^4\ s^{-1}$. The X-ray structure of **39** showed that the Fe(II) atom lies in the plane of the porphyrin.

6.01.5.2 Phosphorus Donor Ligands

Phosphorus very readily forms complexes with iron carbonyl fragments to give mono- and disubstituted $Fe(CO)_4L$ and $Fe(CO)_3L_2$ complexes. These are common derivatives to prepare and may be made directly from $Fe(CO)_5$ or from the higher nuclearity carbonyls $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. Dinuclear $Fe_2(CO)_9$ is not known to be soluble in any common organic solvents with retention of its composition but it does dissolve in coordinating solvents, THF being



Scheme 33[123]



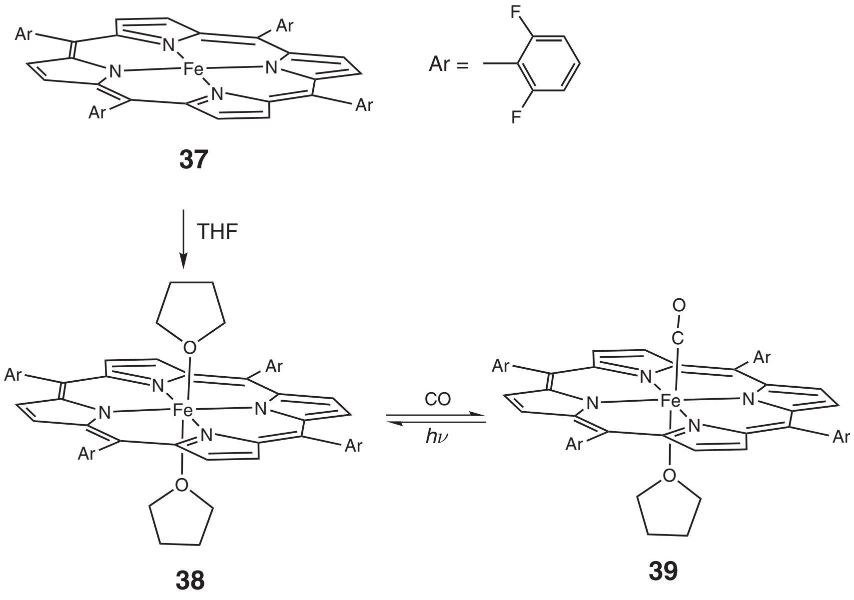
Scheme 34[124]

the most commonly employed, to give solvated mononuclear iron carbonyl fragments. Substitution of $Fe_3(CO)_{12}$ may lead to substituted trinuclear complexes, but under forcing conditions substituted mononuclear compounds are often obtained instead. These compounds will be discussed in order of the degree of substitution of the iron carbonyl fragment.

6.01.5.2.1 $Fe(CO)_4L$ complexes

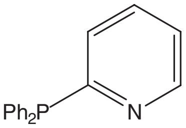
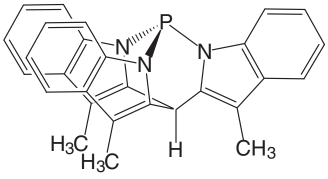
Preparation of $Fe(CO)_4L$ derivatives continues to be a common methodology. New compounds are given in Table 2. Various $Fe(CO)_4PR_3$ complexes were studied to determine steric and electronic factors affecting the iron–phosphorus bond. After being examined, the phosphines were divided into three groups: σ-donor [PMe_3, PPh_3, P(*i*-Pr)$_3$], σ-donor/π-acceptor [PF_3, $P(NC_4H_4)_3$], and intermediate ligands [PH_3, $P(OMe)_3$].[126]

The photolytic production of substituted iron carbonyls in neat PEt_3 has been examined (Scheme 36).[24] The product is a mixture of $Fe(CO)_4(PEt_3)$ and $Fe(CO)_3(PEt_3)_2$. Triplet state $^3Fe(CO)_3PEt_3$ was determined to be an intermediate based upon the spectroscopic data.



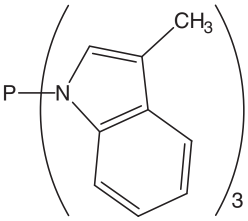
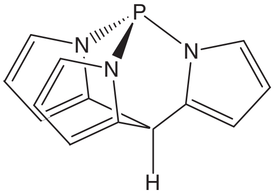
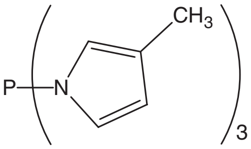
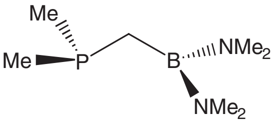
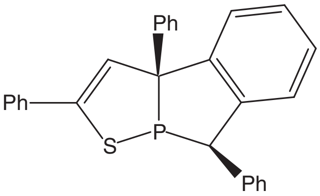
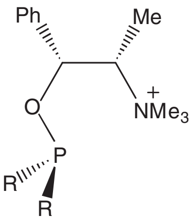
Scheme 35[125]

Table 2 $Fe(CO)_4L$ Complexes

Ligand	*Method of production*	*Crystal structure known*	*Yield (%)*	*References*
	Me_3NO	No	86	127
$[Ph_2P(CH_2)_nPMe_3]X$ ($n = 2, 3, 6, 10$; $X = NO_3, PF_6, BPh_4$)	$Fe_2(CO)_9$, THF	No	[a]	128
PAr_3 ($Ar = 3\text{-}CF_3C_6H_4$, $4\text{-}CF_3C_6H_4$, $3,5\text{-}(CF_3)_2C_6H_3$)	$Fe_2(CO)_9$, Et_2O	Yes	[a]	129
$PAr_3(Ar = 2\text{-}CH_3C_6H_4$, $4\text{-}FC_6H_4)$	$Fe_2(CO)_9$, Et_2O	No	[a]	129
$(R_1R_2N)_2PH$ a: $R_1 = R_2 = Me$ b: $R_1 = R_2 = {}^iPr$ c: $R_1 = Et$; $R_2 = Ph$ d: $R_1 = R_2 = Ph$	$K[HFe(CO)_4]$, THF	No (a–c) Yes (d)	90 (a) 90 (b) 70 (c) 32 (d)	130
	$Fe_2(CO)_9$, toluene	Yes	77	131

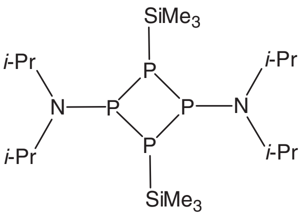
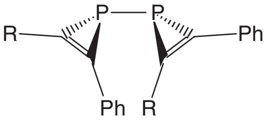
(Continued)

Table 2 (Continued)

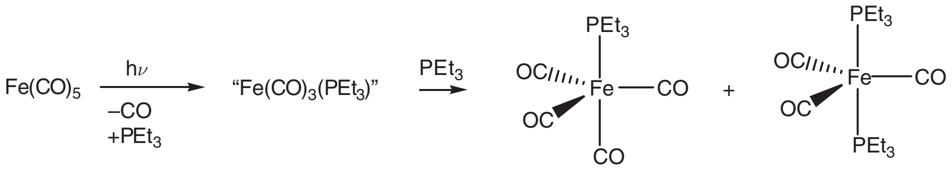
Ligand	*Method of production*	*Crystal structure known*	*Yield (%)*	*References*
	$Fe_2(CO)_9$, Et_2O	No	60	131
	$Fe_2(CO)_9$, toluene	Yes	90	131
	$Fe_2(CO)_9$, toluene (originally synthesized in 1982)	Yes	*	131
	$Fe_2(CO)_9$, THF	No	80	86
	$Fe_2(CO)_9$, toluene	No	17	132
 **a**: R = NMe_2 **b**: R = Ph	$K[HFe(CO)_4]$, THF	No (a) Yes (b)	56 (a) 100 (b)	133

(*Continued*)

Table 2 (Continued)

Ligand	*Method of production*	*Crystal structure known*	*Yield (%)*	*References*
	$Fe_2(CO)_9$, hexane	Yes	44	134
P_4O_6	[a]	Yes	[a]	135
 **a**: R = ^{t}Bu **b**: R = ^{t}Pen	$Na_2[Fe(CO)_4]$, Et_2O	No	58 (a)60 (b)	136

[a]Not given.



Scheme 36[24]

$$Fe(CO)_4 + PH_3 \xleftarrow{h\nu} Fe(CO)_4PH_3 \xrightarrow{h\nu} Fe(CO)_3PH_3 + CO$$

Scheme 37[137]

Time-dependent DFT was used to study the photochemistry of $Fe(CO)_4PH_3$. The aim of the study was to determine whether the complex would expel PH_3 or CO.[137] Results indicated that the excited $Fe(CO)_4PH_3$ complex was more inclined to phosphine rather than CO dissociation (Scheme 37).

Various mononuclear iron carbonyl complexes with a single water-soluble phosphine ligand were synthesized of the form $Fe(CO)_4L$, $L = [Ph_2P(CH_2)_nPMe_3]^+$ ($n = 2$, 3, 6, 10). Small amounts of the disubstituted complexes were also formed, as shown in Equation (56).[128]

$$Fe_2(CO)_9 + [Ph_2P(CH_2)_nPMe_3]X \xrightarrow{THF} [Fe(CO)_4(Ph_2P(CH_2)_nPMe_3)]X + trans\text{-}[Fe(CO)_3(Ph_2P(CH_2)_nPMe_3)_2]X_2 + Fe(CO)_5 \qquad (56)$$

$n = 2$; $X = NO_3^-$, PF_6^-
$n = 3$; $X = BPh_4^-$
$n = 6$; $X = PF_6^-$
$n = 10$; $X = BPh_4^-$

A number of triarylphosphines PAr_3 ($Ar = 2\text{-}C_6H_4CF_3$, $3\text{-}C_6H_4CF_3$, $4\text{-}C_6H_4CF_3$, $3,5\text{-}C_6H_3(CF_3)_2$) gave monosubstituted $Fe(CO)_4L$ complexes when treated with $Fe_2(CO)_9$.[129] A small amount of $[Fe(CO)_3\{P(4\text{-}CF_3C_6H_4)_3\}_2]$ was also formed during the recrystallization of $Fe(CO)_4P(C_6H_4CF_3\text{-}p)_3$; the structure showed the conventional trigonal-bipyramidal arrangement with the phosphine ligands in *trans*-positions.[129]

The photochemical reactions of thin amorphous films of $Fe(CO)_4PPh_3$ on silicon surfaces were studied. Photolysis of the films was monitored by IR and indicated complete loss of $Fe(CO)_4PPh_3$. The proposed reaction is shown in Scheme 38.[138] Evidence for the intermediate $Fe(CO)_3PPh_3$ was obtained by addition of PPh_3 to the film. This addition resulted in the trapping of the intermediate to form $Fe(CO)_3(PPh_3)_2$. Quantum yield studies were performed, indicating a dependence of the reaction on film thickness. With thicker films, lower quantum yields are observed, presumably because the intermediate may react with CO trapped in the film to reform the starting material.

The formation of an acylated phosphine was accomplished via the reaction of chlorodiphenylphosphine with a carbonylferrate. The proposed pathway is shown in Scheme 39.[139] Similarly, reactions employing $ClP(NR_2)_2$ led ultimately to insertion of the $P(NR_2)_2$ fragment into the Fe–H bond (Equation (57)).[130] Reactions between $KHFe(CO)_4$ and amino-substituted phosphines were reported. Reactions with tris(amino)phosphines, proceeding via activation of a P–N bond, are shown in Equation (58).[130] Reactions of these products with an excess of potassium hydride resulted in the formation of phosphido complexes (Equation (59)),[130] which react with either methyl iodide or acetyl chloride to alkylate/acylate the phosphorus atom.

$$K[HFe(CO)_4] + (R^1R^2N)_2PCl \xrightarrow[-KCl]{THF,\ RT} [(R^1R^2N)_2PH]Fe(CO)_4 \tag{57}$$

c: $R^1 = Et$; $R^2 = Ph$ (72%)
d: $R^1 = R^2 = Ph$ (32%)

$$2K[HFe(CO)_4] + P(NR^1R^2)_3 \xrightarrow[-R^1R^2NH]{THF,\ RT} [(R^1R^2N)_2PH]Fe(CO)_4 + K_2[Fe(CO)_4] \tag{58}$$

a: $R^1 = R^2 = Me$ (90%)
b: $R^1 = R^2 = {}^iPr$ (90%)
c: $R^1 = Et$; $R^2 = Ph$ (70%)

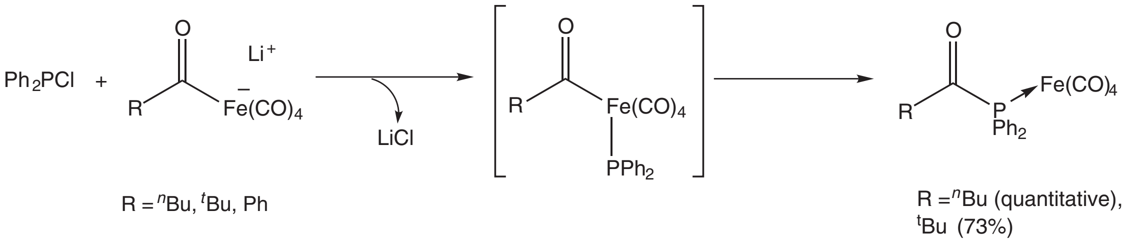
$$[(R^1R^2N)_2PH]Fe(CO)_4 + KH \xrightarrow{Et_2O,\ RT} K^+[\{(R^1R^2N)_2P\}Fe(CO)_4]^- \tag{59}$$

a: $R^1 = R^2 = Me$
c: $R^1 = Et$; $R^2 = Ph$ (70%)
d: $R^1 = R^2 = Ph$

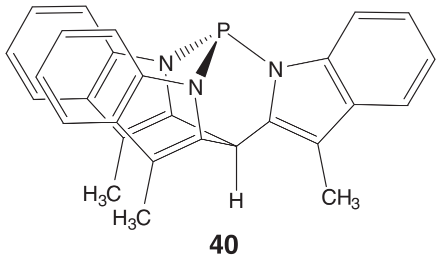
Tris(amido)phosphines **40–43** react with $Fe_2(CO)_9$ to give mononuclear iron carbonyl complexes $Fe(CO)_4(PR_3)$.[131] IR data collected from these complexes, combined with data from similar complexes, revealed the π-acidity of the phosphines to be: **41** $\approx$ **40** $>$ **43** $> P(OPh)_3 >$ **42** $> PPh_3 > P(NMe_2)_3$. Variable-temperature ^{13}C NMR on the $Fe(CO)_4$ complexes of **41–43** showed rapid exchange of axial and equatorial carbonyls from −80 to 20 °C, while complex **40** showed slow axial–equatorial carbonyl exchange even at room temperature, attributed to the steric bulk and rigidity of the ligand.[131]

$$Fe(CO)_4PPh_3 \xrightarrow[-CO]{h\nu} Fe(CO)_3PPh_3 \xrightarrow{\text{rapid decomposition}} Fe + 3CO + PPh_3$$

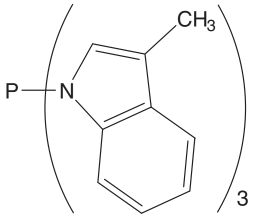
Scheme 38[138]



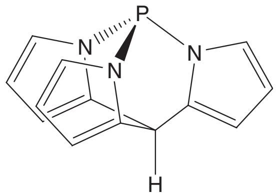
Scheme 39[139]



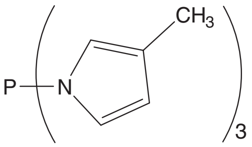
40



41



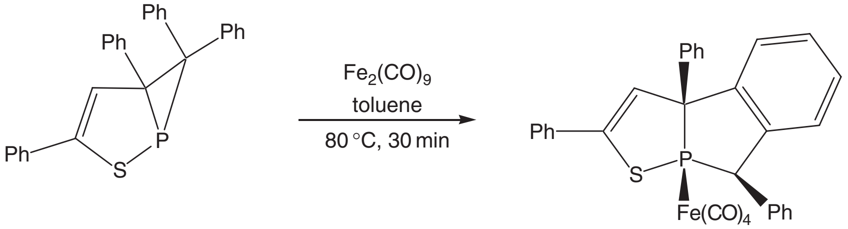
42



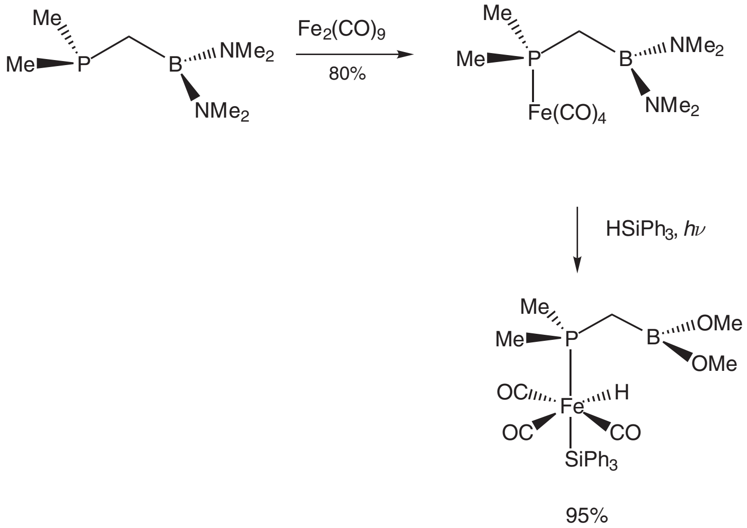
43

Reaction of $Me_2PCH_2B(NMe_2)_2$ with $Fe_2(CO)_9$ yielded a phosphine-bound $Fe(CO)_4L$ complex (Scheme 40).[86] The NMe_2 substituents bound to boron underwent substitution and/or addition by a variety of donors. In this way, the complexes $(OC)_4FeL$ with $L = Me_2PCH_2B(OMe)_2$, $Me_2PCH_2B(NMe_2)Cl$, $Me_2PCH_2B(NMe_2)_2(NHMe_2)$, $Me_2PCH_2B(NMe_2)_2(NHMe_2)$, $Me_2PCH_2BCl_2(NHMe_2)$, and $Me_2PCH_2BH_2(2,4,6\text{-}C_5H_2N)$, as well as the anionic complex $Li[Fe(CO)_4Me_2PCH_2BH_3]$, were prepared. Photolysis of $(OC)_4Fe\{Me_2PCH_2B(OMe)_2\}$ with $HSiPh_3$ led to oxidative addition and the formation of $HFe(CO)_3(SiPh_3)\{Me_2PCH_2B(OMe)_2\}$.

The reaction of a 1,2-thiaphospholo[*a*]phosphirane with diiron nonacarbonyl resulted in a complex in which the phosphirane underwent a rearrangement (Equation (60)).[132] The product was not very stable and was only isolated in 17% yield.[132]

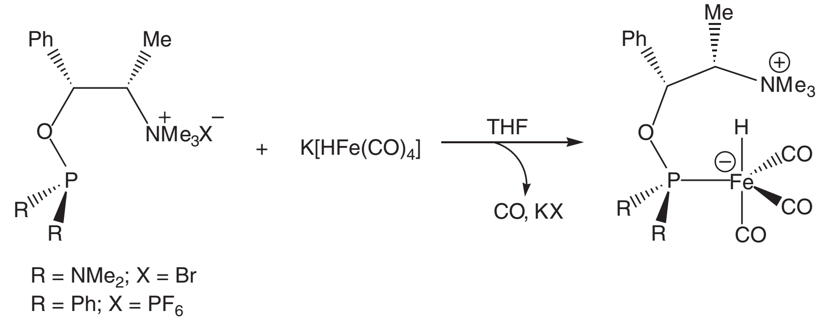


(60)



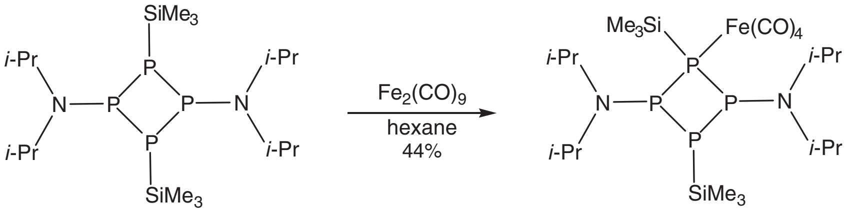
Scheme 40[86]

"Ephosiums," chiral phosphorus ligands with ammonium side chains, were synthesized and reacted with $KHFe(CO)_4$ to form zwitterionic complexes (Equation (61)).[133]



(61)

A new polyphosphorus ring compound was synthesized and reacted with $Fe_2(CO)_9$ to form a monometallic complex having an $Fe(CO)_4$ fragment bound to one of the phosphorus atoms (Equation (62)).[134]

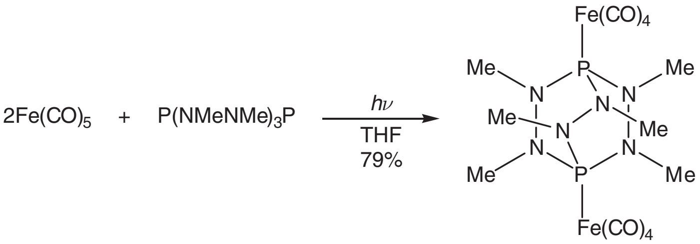


(62)

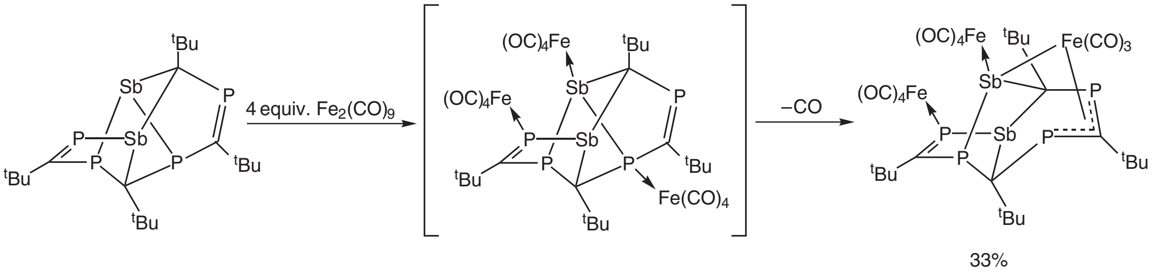
A previously synthesized cage compound containing phosphorus and antimony, $P_4Sb_2C_4{}^tBu_4$, was reacted with $Fe_2(CO)_9$.[140] The intermediate complex depicted in Scheme 41 was proposed, but no evidence for it was observed by NMR. The authors propose the insertion of an $Fe(CO)_4$ moiety into the Sb–P bond with loss of a carbonyl to form the final product.[140]

The crystal structure of $[Fe(CO)_4(P_4O_6)]$ was reported—the first single crystal X-ray data for a transition metal complex containing P_4O_6. The iron atom possesses the usual trigonal-bipyramidal geometry, with the P_4O_6 cage occupying an axial position.[135]

A related cage-like phosphine ligand $P(NMeNMe)_3P$ was found that binds two $Fe(CO)_4$ groups upon UV photolysis with iron pentacarbonyl in THF (Equation (63)).[115]

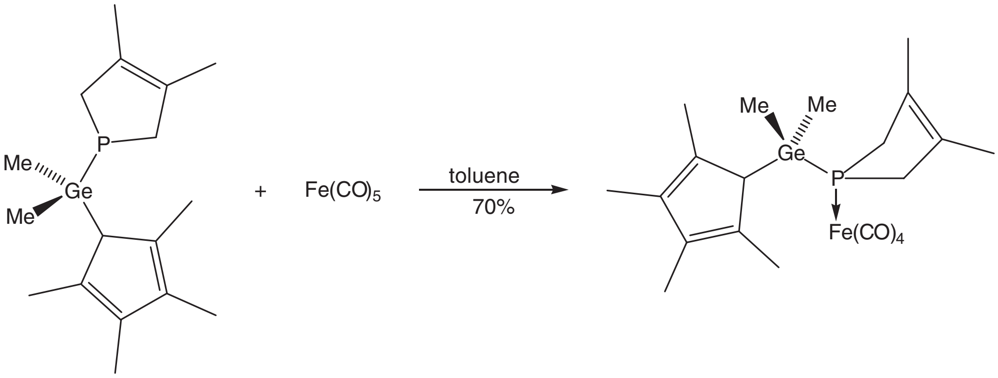


(63)



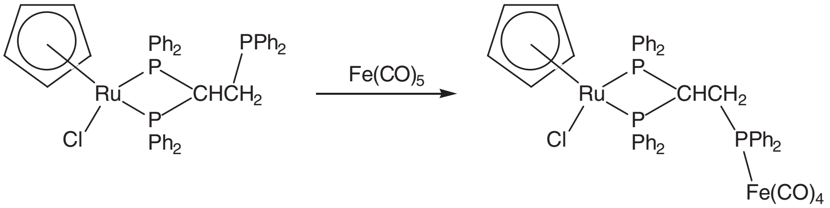
Scheme 41[140]

Other complex phosphine ligands such as the germanium-containing species shown in Equation (64) also form simple $Fe(CO)_4$ derivatives.[141]



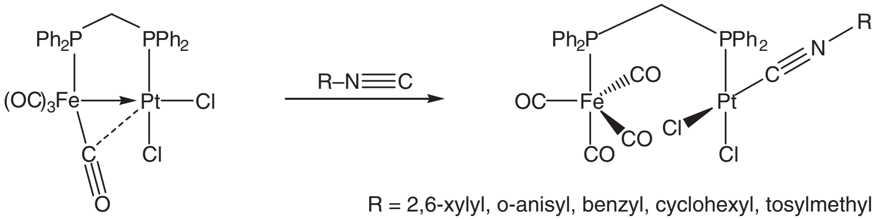
(64)

The ruthenium complex $[RuCl\{(PPh_2)_2CHCH_2PPh_2\}(C_5H_5)]$ contains a "dangling" phosphine which reacts with $Fe(CO)_5$ (Equation (65)) without the formation of an Ru–Fe bond.[142]



(65)

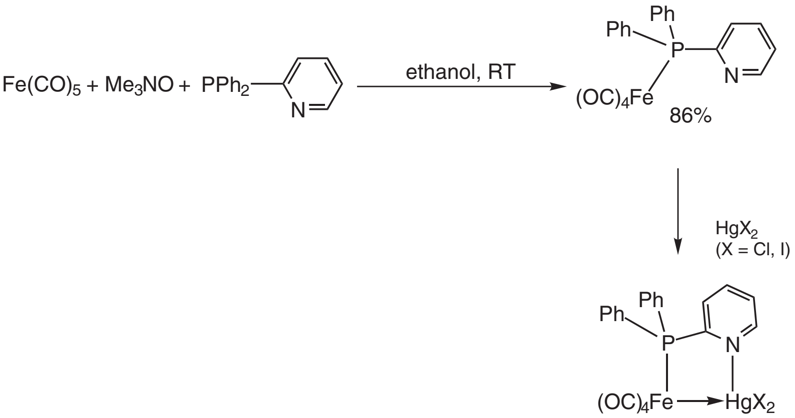
Metal–metal bonds can be opened to give complexes with isolated iron carbonyl functions. An attempt to form a bridging CNR group between the iron and platinum atoms resulted in opening of the iron–platinum dative bond, with binding of CNR to platinum (Equation (66)).[143]



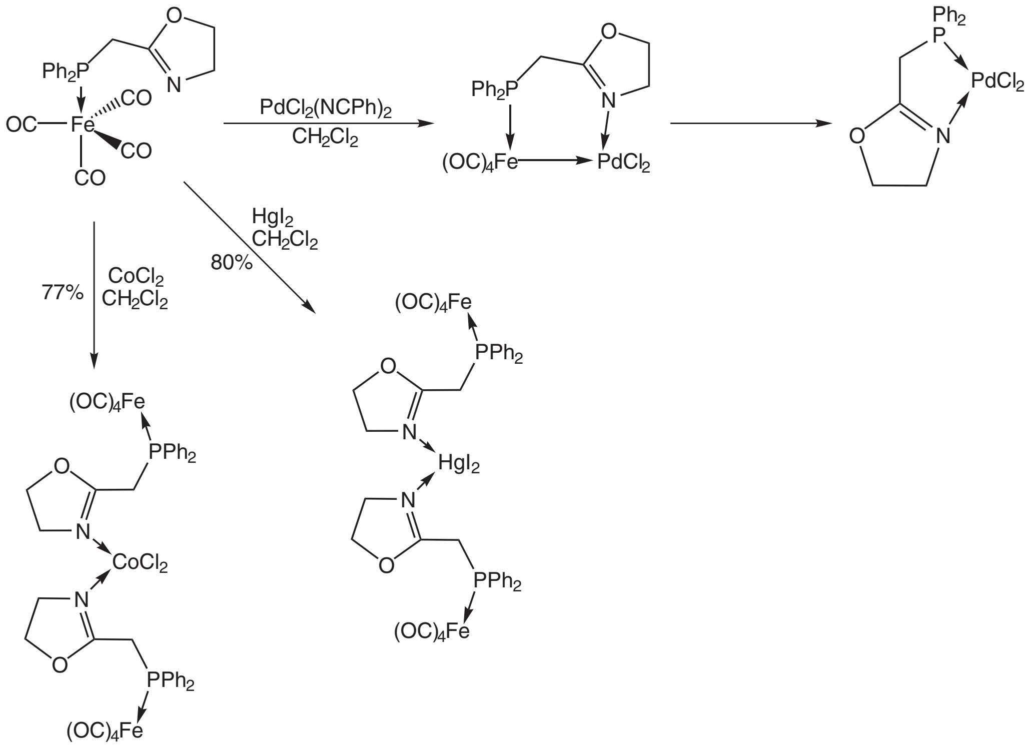
(66)

R = 2,6-xylyl, o-anisyl, benzyl, cyclohexyl, tosylmethyl

The mononuclear iron complex $Fe(CO)_4(Ph_2PC_5H_4N)$ (Scheme 42) is prepared directly from $Fe(CO)_5$ and the ligand in the presence of Me_3NO. Trimethylamine-*N*-oxide was previously established as a reagent for activating



Scheme 42[127]

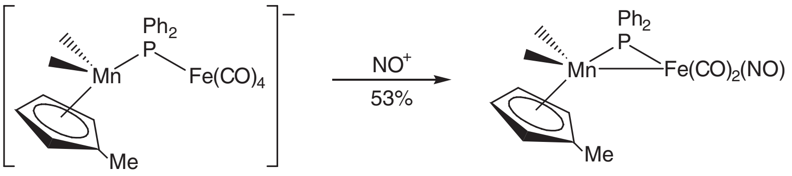


Scheme 43[144]

metal carbonyls to substitution by attacking a carbonyl ligand giving rise to $\mathrm{Me_3N}$ and $\mathrm{CO_2}$. The complex reacts with $\mathrm{HgX_2}$ forming a binuclear complex with a dative Fe → Hg bond.[127]

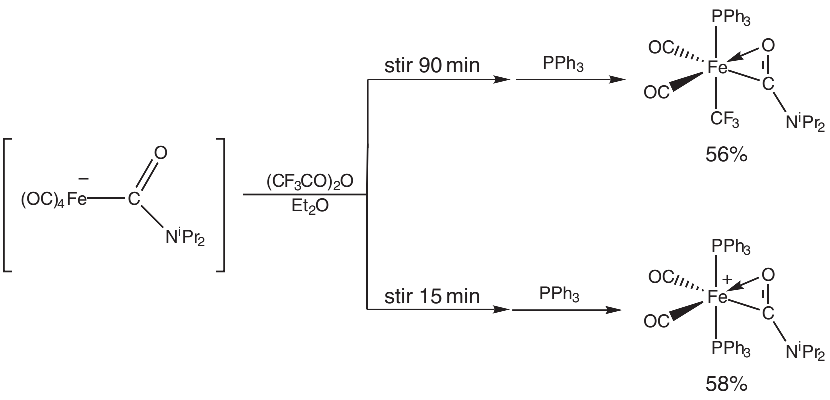
A heterometallic complex of iron and palladium with one phosphino-oxazoline ligand was synthesized (Scheme 43).[142] The complex had limited stability, and ultimately formed the product in which the ligand had been completely transferred from iron to palladium. In reactions with $\mathrm{CoCl_2}$ or $\mathrm{HgI_2}$, the phosphino-oxazoline complex serves only as a nitrogen donor ligand. The product obtained from $\mathrm{CoCl_2}$ was found to oligomerize ethylene, resulting in α-olefins in the range $\mathrm{C_4}$–$\mathrm{C_{26}}$.[144]

The complex $\mathrm{(OC)_4FePPh_2Mn(CO)_2(C_5H_4Me)}$ forms a complex with an Fe–Mn bond when treated with $\mathrm{NO^+}$ (Equation (67)).[145]

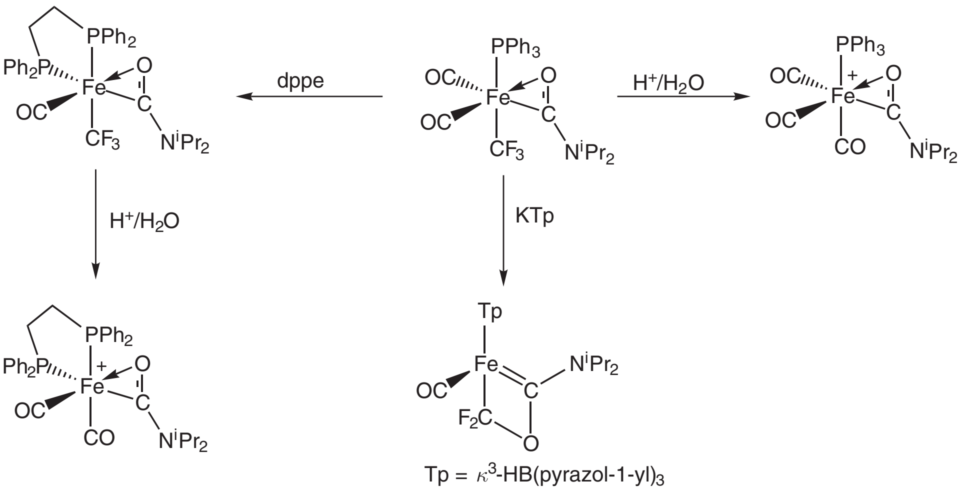


(67)

Various carbamoyl complexes were studied, all of which displayed a bidentate binding of the carbamoyl moiety (Schemes 44–47).[146,147] As seen in Scheme 44, varying the reaction time produced different products.[147] Treatment of $[\mathrm{Fe}(\eta^2\text{-}\mathrm{OCN^iPr_2})(\mathrm{CO})_2(\mathrm{CF_3})(\mathrm{PPh_3})]$ with 1,2-bis(diphenylphosphino)ethane (dppe) was performed in an attempt to achieve monodentate coordination of the carbamoyl; however, the product formed retained bidentate coordination. An alternate attempt to change the binding of the carbamoyl involved the use of the strongly chelating ligand, hydrotris(pyrazolyl)borate, resulting in the formation of a ferraoxetene (Scheme 45). The $\mathrm{CF_3}$ moiety in these complexes is easily replaced by CO upon addition of aqueous $\mathrm{HBF_4}$. A variety of ligand-exchange reactions for these products were carried out and are depicted in Scheme 45. The reaction of $[\mathrm{Fe}(\eta^2\text{-}\mathrm{OCN^iPr_2})(\mathrm{SnPh_3})(\mathrm{CO})_2(\mathrm{PPh_3})]$ with iodine was intended to be used as a means of cleaving an Sn–Ph bond; however, as depicted in Scheme 47, the reaction resulted in the cleavage of the Sn–Fe bond.



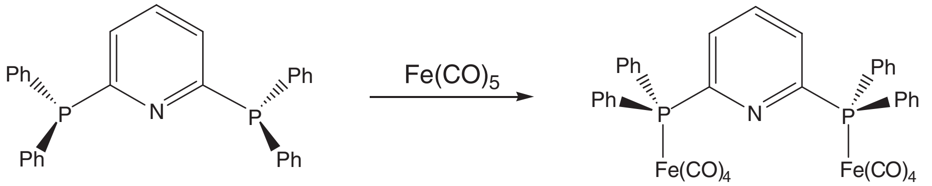
Scheme 44[147]

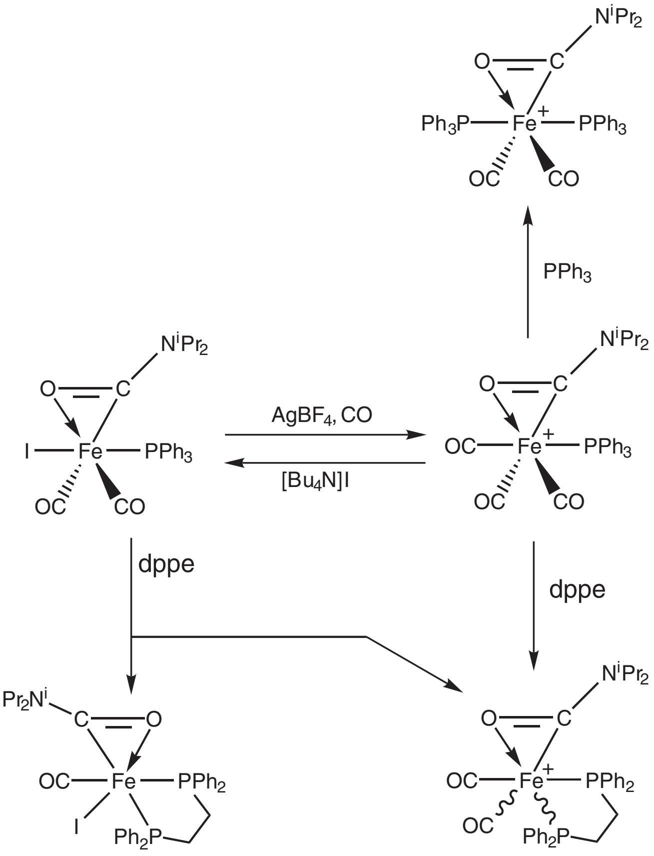


Scheme 45[147]

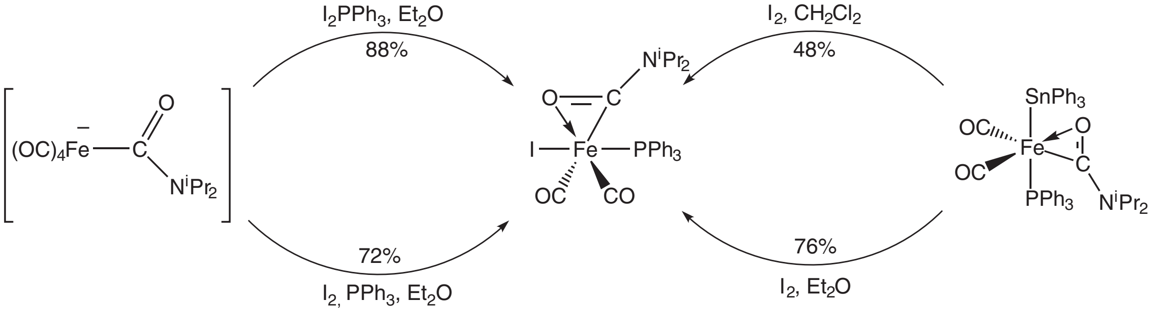
Reaction of disodium tetracarbonylferrate with 2 equiv. of a chlorophosphirene resulted in coupling of two of the phosphirine units and complexation to $Fe(CO)_4$ (Scheme 48). Subsequent reaction with diiron nonacarbonyl gave the di-complexed phosphirene.[136,148]

The ligand 2,6-bis(diphenylphosphino)pyridine was metallated at both phosphorus atoms using $Fe(CO)_5$ (Equation (68)).[149] X-ray crystallography demonstrated the presence of both eclipsed and staggered conformations.[149] Further reactions of the ligand to synthesize various heterometallic complexes with silver and mercury were also performed.

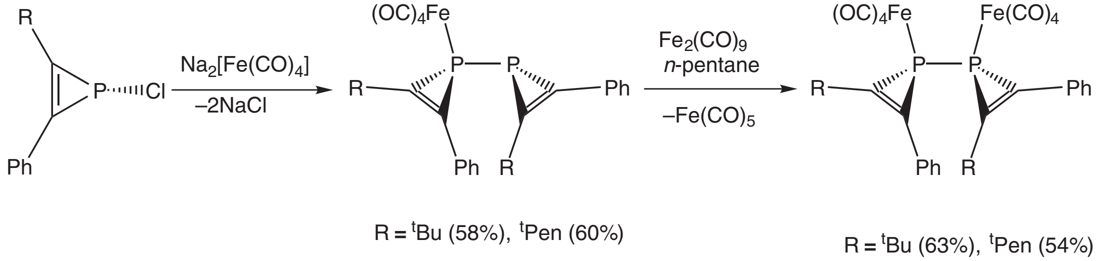
 (68)



Scheme 46[146]



Scheme 47[146]

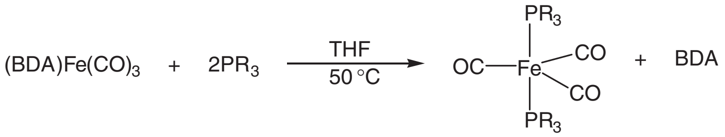


Scheme 48[136,148]

6.01.5.2.2 $Fe(CO)_3L_2$ and $Fe(CO)_3LL'$ complexes

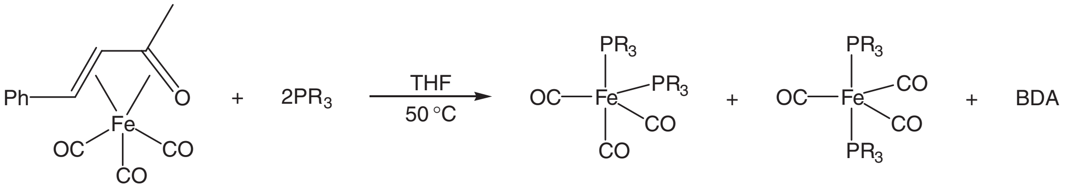
The crystal structure of *trans*-$Fe(CO)_3(PPh_3)_2$ was reported and compared to $Ru(CO)_3(PPh_3)_2$, $Os(CO)_3(PPh_3)_2$, $Fe(CO)_2(CS)(PPh_3)_2$, *trans*-$Fe(CO)_3(PR_3)_2$ (R = NMe_2, OMe), and $Fe(CO)_4PR_3$ (R = Ph, NMe_2, CMe_3, $SiMe_3$).[150] Theoretical calculations indicated that differences in Fe–P bond distances and non-linear P–Fe–P angles in X-ray crystal structures were due to packing effects rather than intrinsic properties of the molecules.[150] Similar results were obtained for the PPh_2Me complex.[151]

The BDA ligand in $Fe(CO)_3(BDA)$ is readily displaced by two phosphine ligands, and the thermochemistry of these reactions with various sterically demanding phosphines was studied using solution calorimetry for trialkyl- and triphenylphosphine (PR_3, Equation (69)),[152] for $PPh_{3-x}(pyrrolyl)_x$ ($x = 1$–3) and $P(pyrrolidinyl)_3$ (Equation (70)),[154] and for a series of substituted aryl phosphines $P(C_6H_4X)_3$ (Equation (71)).[153] The enthalpies of substitution were calculated and compared. The overall relative order of stability was found to be (ΔH, kcal mol^{-1}): $PPh_3 < PCy_2Ph$ {27.1(0.1)} $< PCyPh_2$ [27.5(0.1)] $< PCy_3$ [30.7(0.2)] $< P^iPr_3$ [31.6(0.1)] $< PPh_2Et$ [32.7(0.1)] $< PBz_3$ [32.8(0.2)].[152] Enthalpies of reaction (kcal mol^{-1}) for $P(C_6H_4X)_3$ showed a strong dependence on the electronic nature of the phosphine ligand (kcal mol^{-1}): $X = CF_3$ 22.4(0.3) $<$ Cl 25.0(0.1) $<$ F 25.8(0.2) $<$ H 26.9(0.2) $< CH_3$ 28.2(0.3) $< CH_3O$ 30.1(0.2).[153] The pyrrolyl derivatives give a mixture of *trans*- and *cis*-(axial/equatorial) isomers with the following diaxial/axial-equatorial product ratios: $x = 3$, 81 : 19; $x = 2$, 72.5 : 27.5; $x = 1$, 86.7 : 13.3. The equilibria were examined and the interconversion was determined to have an extremely low energy barrier, so that the isomerization did not affect the enthalpy of formation measurements. For the related complex with L = $P(pyrrolydinyl)_3$, only the *trans*-form was observed. The enthalpies of reaction for this series gave a good linear correlation to the CO stretching frequency of the diaxial isomer, a measure of the electronic properties of the phosphine ligands.



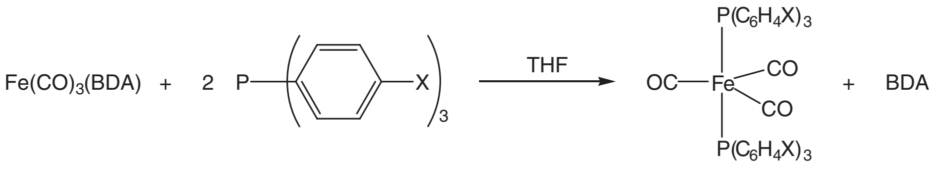
(69)

$PR_3 = PCy_2Ph, PCyPh_2, PCy_3, P^iPr_3, PPh_2Et, PBz_3$



(70)

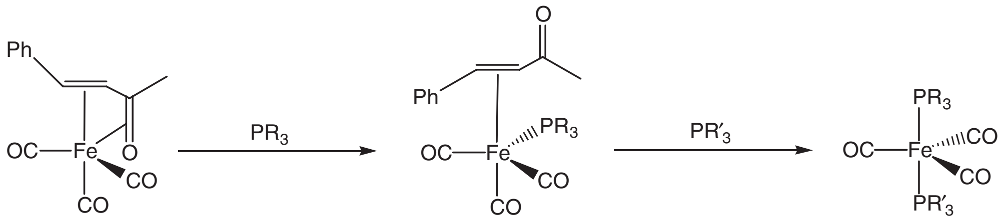
$PR_3 = P(pyrrolyl)_{3-x}Ph_x$
$x = 1$–3



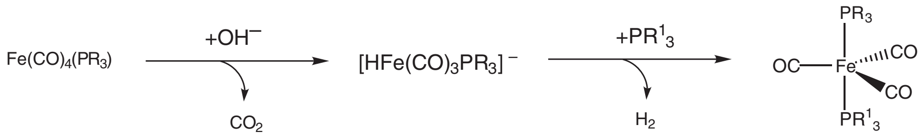
(71)

$X = H, CH_3O, CH_3, Cl, F, CF_3$

Asymmetric *trans*-$Fe(CO)_3LL'$ complexes (L, L′ = phosphine) were prepared by (i) displacement of BDA from $Fe(CO)_3(BDA)$ (Scheme 49), (ii) reaction of $Fe(CO)_4L$ (L = phosphine) with another phosphine in the presence of a base (Scheme 50), and (iii) displacement of $AsPh_3$ from $Fe(CO)_3(AsPh_3)_2$.[155] Table 3 lists the various combinations of L and L′ that have been produced. The $^2J_{PP}$ values of the $^{31}P\{^1H\}$ NMR spectra exhibited a strong negative correlation with the sum of the phosphine pK_a values. This allows for the prediction of $^2J_{PP}$ values for *trans*-$Fe(CO)_3L_2$ complexes. The first crystal structure of an iron carbonyl having two different phosphine ligands, *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$, was reported.[155]



Scheme 49[155]



Scheme 50[155]

Table 3 Disubstituted $Fe(CO)_3LL'$ complexes[155]

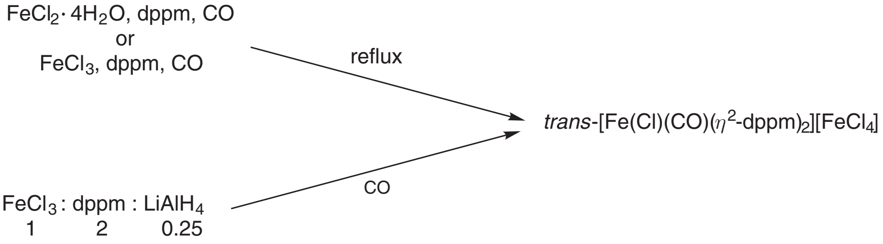
L	L'
PPh_3	PPh_2Me, $PPhMe_2$, PMe_3, PPh_2Et, PEt_3, $PPh_2CH{=}CH_2$, PPh_2H, $AsPh_3$, $P(OPh)_3$
PMe_3	PEt_3, PPh_2Et, PCy_3, PPh_2Me, $PPhMe_2$
PEt_3	PPh_2Me
PPh_2H	$PPh_2CH{=}CH_2$, PPh_2Et
$AsPh_3$	$PPhMe_2$, $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$

The series of complexes $[Fe(CO)_3\{PPh_{3-x}(C_6H_4OMe\text{-}p)\}_x]$ ($x = 0$–3) was prepared by conventional methods and studied by electrospray mass spectrometry.[156] While the *all*-Ph derivative did not give a spectrum, the methoxy derivatives did produce $[M+H]^+$ ions, presumably because of the presence of the basic OMe functions.

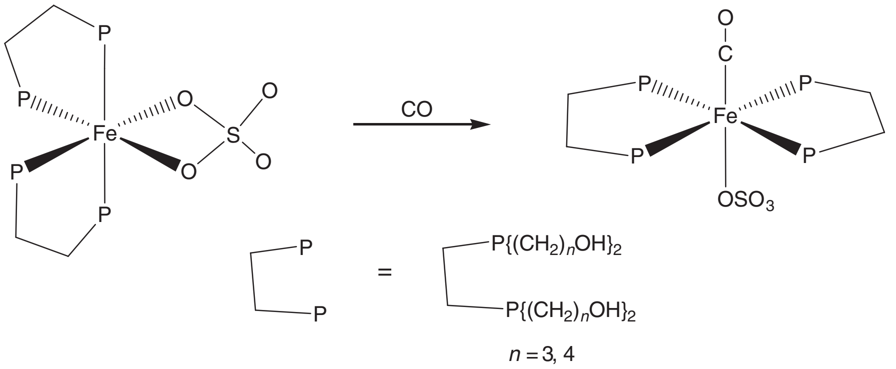
When Fe(III), dppm, and $LiAlH_4$ were reacted in the presence of CO, various iron carbonyl–halide complexes were formed. Reactions are depicted in Scheme 51 and Equation (72).[157]

$$trans\text{-}[Fe(H)_2(\eta^2\text{-dppm})_2] \xrightarrow[CH_2Cl_2]{CO} trans\text{-}[Fe(CO)_3(\eta^1\text{-dppm})_2] \qquad (72)$$

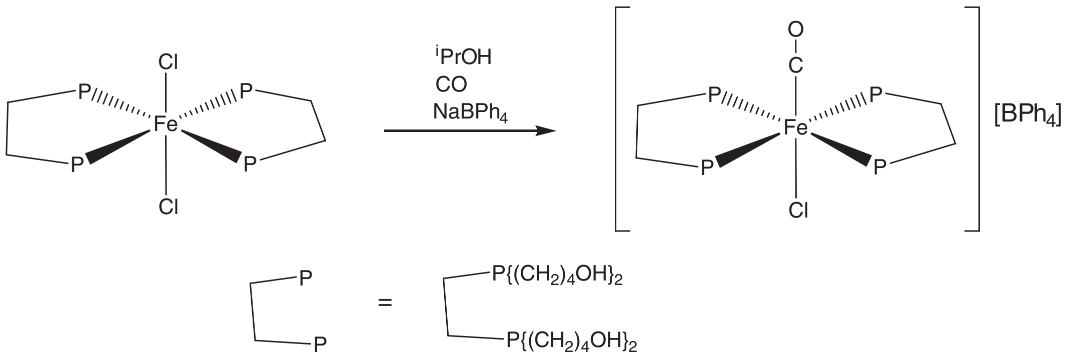
Water-soluble iron carbonyl complexes with hydroxyalkyl bis(phosphino)ethane ligands $\{HO(CH_2)_n\}_2PCH_2CH_2P\{(CH_2)_nOH\}_2$ ($n = 3$, 4) were prepared by addition of CO to the iron(II) precursor complexes (Equations (73) and (74)).[158]



Scheme 51[157]

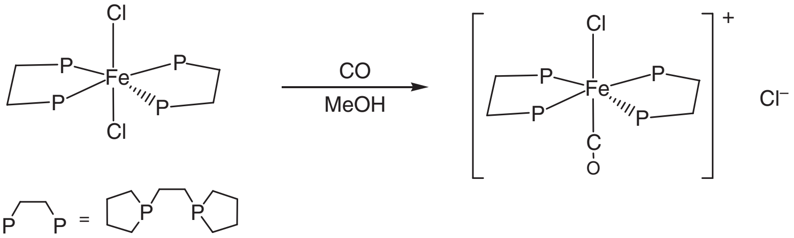


(73)

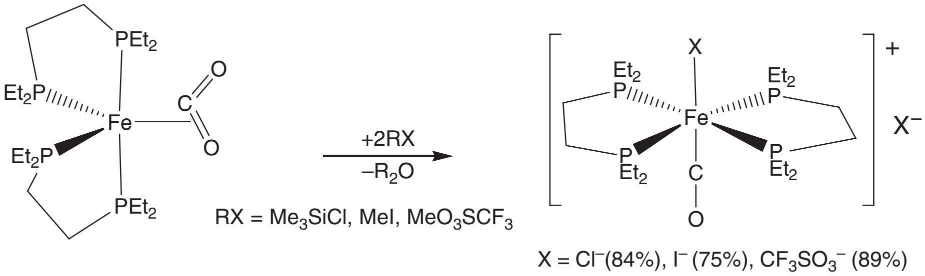


(74)

The cyclic bis(phosphine) dichloride complex shown in Equation (75) underwent substitution of a chloride with CO in MeOH to give a cationic complex.[159] Related cationic carbonyl halide complexes of iron with bis(chelating phosphine) ligands can also be accessed by reactions of the corresponding CO_2 complex as shown in Equation (76).[160]

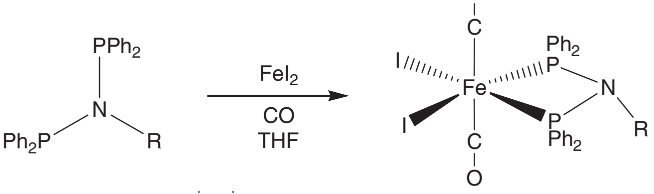


(75)



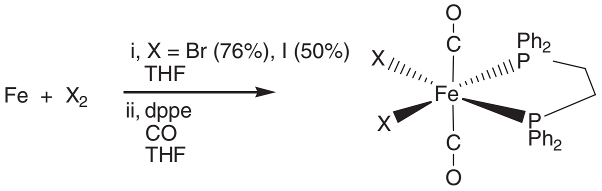
(76)

Iron(II) halides react with bidentate chelating phosphine ligands in the presence of CO to give the dicarbonyl dihalide complexes (Equations (77)[161–163] and (78)).[162] The *N*,*N*-bis(diphenylphosphino)amino acid–methyl ester complex in Equation (77) was used to label biological molecules.[163] Reaction of $FeCl_2·4H_2O$ with dppe in the presence of CO leads to isolation of a compound formulated as $[Fe(dppe)_2Cl_2][FeCl_2(CO)]_2$ (Equation (79)).[162] The compound is stable in the solid state but decomposes rapidly in solution. The remarkable $\{FeCl_2(CO)\}_2$ exhibits a C–O stretching frequency at 1,938 cm^{-1}, which the authors attribute to the binding of the O atom to a metal center. The authors base their characterization of this unit, which may be viewed as a dimerization of $FeCl_2(CO)$, upon the crystallographic data and the CO stretching frequency and attribute its unexpected stability to the Fe(dppe)$_2$Cl$_2$ lattice. More characterization of this compound is needed, however, before one can take confidence in this assignment, as normally M–C–O–M′ linkages would have linear M–C–O with either linear or bent C–O–M′. One would also not expect a carbonyl complex of FeCl$_2$ to show much stability. When Fe$_2$(CO)$_9$ is treated with the phosphorus(V) compound I$_2$Ph$_2$PCH$_2$CH$_2$PPh$_2$I$_2$, the product is [Fe(CO)$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)I]I$_3$, in which the phosphorus centers have been reduced to phosphorus(III).[164]

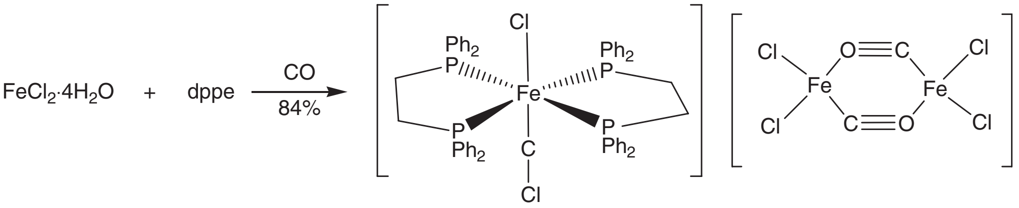


R = ^{i}Pr, ^{i}Bu, –CH(R)CO$_2$Me

(77)



(78)



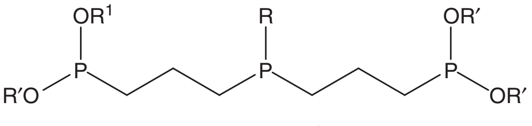
(79)

Reduction of the diphosphine dihalo complexes Fe(CO)$_2$(PR$_3$)$_2$X$_2$ (R = Et, OMe, O^{i}Pr; X = Br, I) has been explored (Scheme 52).[165] Reduction using Zn or LiPh produces the Fe(I) complexes Fe(CO)$_2$(PR$_3$)$_2$X **44**, but reduction with Na/Hg or LiBu/THF gave the Fe(0) anions **45**, which could not be isolated. Conproportionation of Fe(CO)$_2$(PR$_3$)$_2$X$_2$ with [Fe(CO)$_2$(PR$_3$)$_2$X]$^-$, the dinitrogen complexes Fe(CO)$_2$(PR$_3$)$_2$N$_2$ or [Fe(CO)$_2$(PR$_3$)$_2$]-(μ-N$_2$) could also be used to produce **44**.

The compound Fe(CO)$_3${P(OPh)$_3$}$_2$ undergoes orthometallation of one of the phenyl rings with loss of CO. This process is reversible upon addition of an isocyanide ligand to give a substituted bis(phosphine)–bis(carbonyl) complex (Scheme 53).[166]

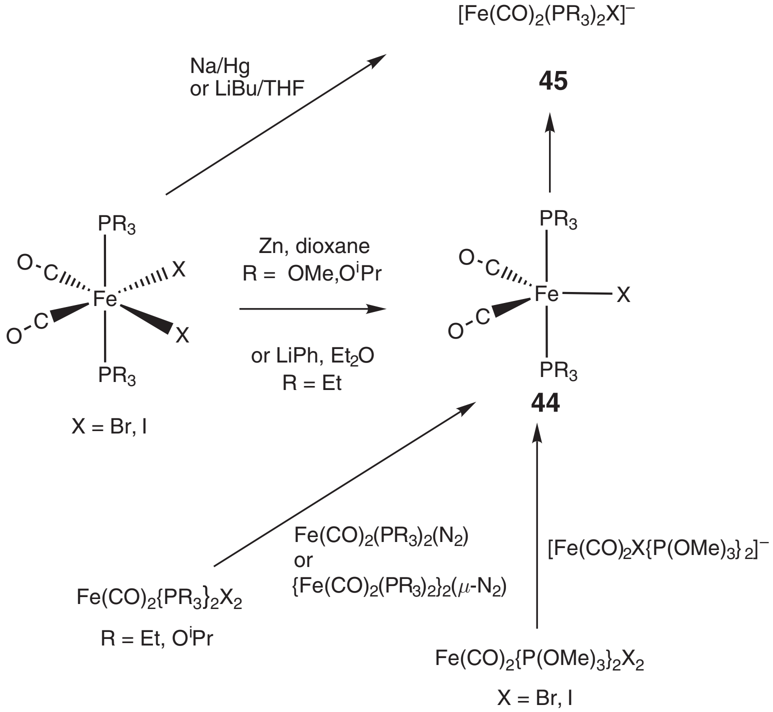
The complex Fe(CO)$_2$(PPh$_3$)$_2$(η^2-CS$_2$) (L = PPh$_3$), synthesized previously, was reacted with cobalt complexes as an entry into a series of trinuclear FeCo$_2$ cluster complexes.[167] Reactions of Fe(CO)$_2${P(OPh)$_3$}$_2$(η^2-CS$_2$) with PBu$_3$ were solvent dependent. With polar solvents such as MeCN or DMSO, the desulfurization product was formed, while with non-polar solvents (e.g., CH$_2$Cl$_2$ or C$_6$H$_6$), a substitution reaction took place (Scheme 54).[168] The structure of Fe(CO)$_2${P(OPh)$_3$}$_2$(CS) is very similar to that of Fe(CO)$_3${P(OPh)$_3$}$_2$, both having a trigonal-bipyramidal geometry with the phosphite ligands in the apical positions.[168] The derivatives Fe(CO)$_2$L$_2$(η^2-CS$_2$) [L = P(OPh)$_3$, P(OEt)$_3$, P(O^{i}Pr)$_3$, PPh(OEt)$_2$, and PPh$_2$(OEt)] were found to produce dithiolene complexes upon heating (Scheme 55). The stabilities of the complexes were dependent on the cone angles of the phosphorus ligands, with the most stable being those with L = P(OPh)$_3$ and P(O^{i}Pr)$_3$.[169] This reaction did not occur for L with cone angles smaller than 109°.

New tridentate phosphine ligands **46** were synthesized and reacted to form iron carbonyl complexes having the ligands bound in either a tridentate or bidentate fashion (Scheme 56).[170] Reactions of these complexes with alkyl iodides were performed.

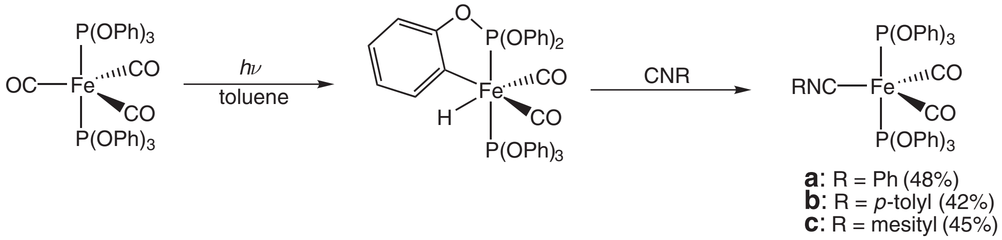


R = Ph, Cy; R^1 = ^{i}Pr, Me

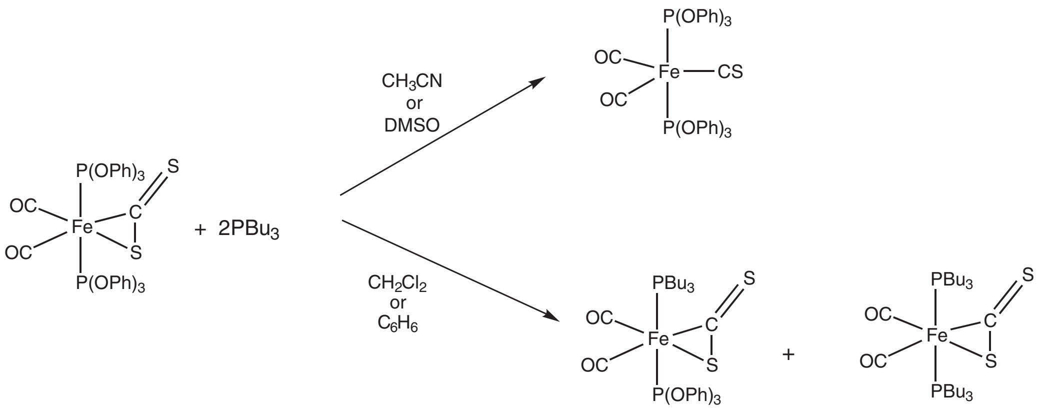
46



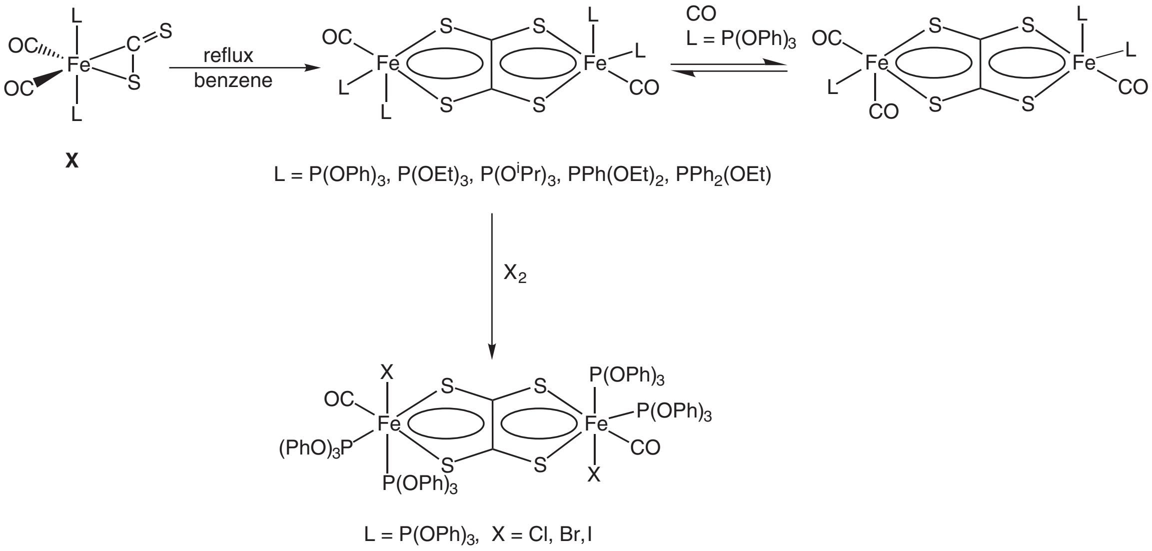
Scheme 52[165]



Scheme 53[166]

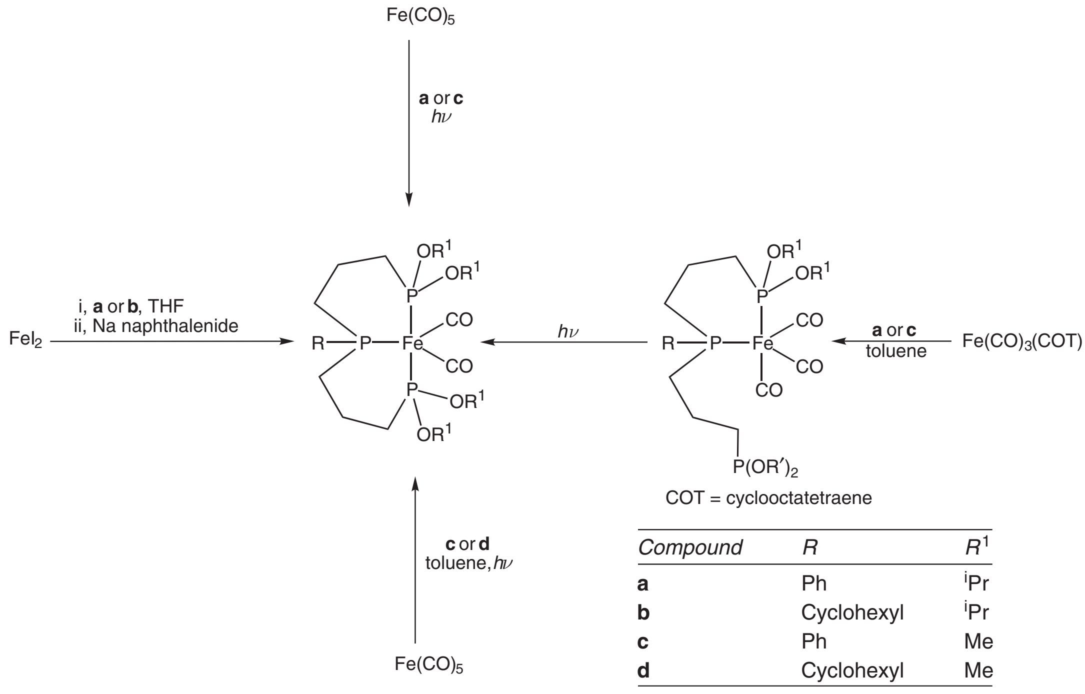


Scheme 54[168]



X

Scheme 55[169]

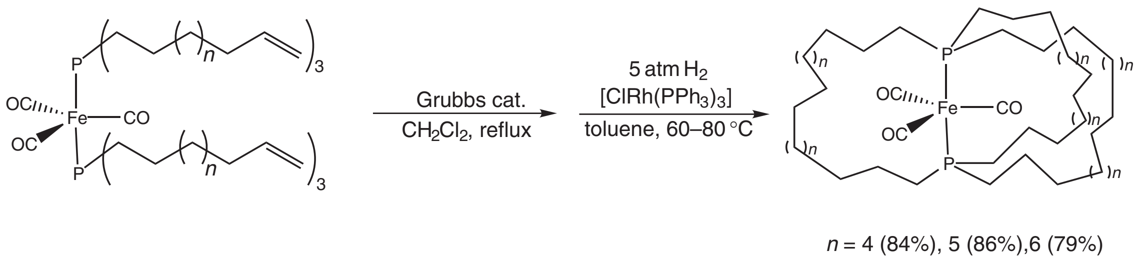


Compound	*R*	*R*^{1}
a	Ph	^{i}Pr
b	Cyclohexyl	^{i}Pr
c	Ph	Me
d	Cyclohexyl	Me

Scheme 56[170]

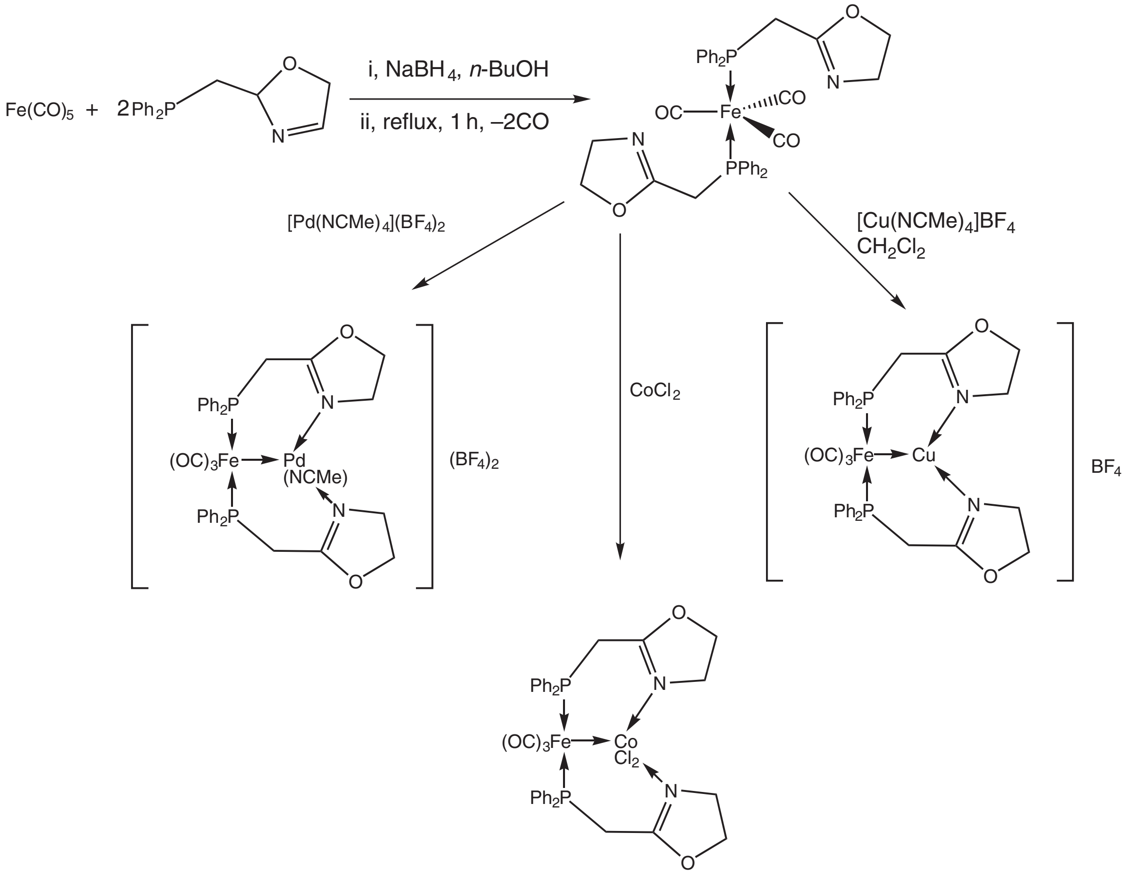
Molecular gyroscopes were synthesized in which an $Fe(CO)_3$ unit is bound axially to two phosphorus atoms (Scheme 57).[171] Reaction with NO^+ to form an $Fe(CO)_2(NO)$ rotator led to the introduction of a dipole moment, which opens up the possibility of unidirectional rotation.[171]

Several disubstituted complexes were prepared that have additional donor functions attached so that bimetallic complexes can be prepared and, conversely, complexes with an Fe–metal bond can undergo bond cleavage to give products with isolated $Fe(CO)_xL_y$ units.[95,98,127,144,172,173] Examples are given in Equations (80)[98] and (81)[172] and

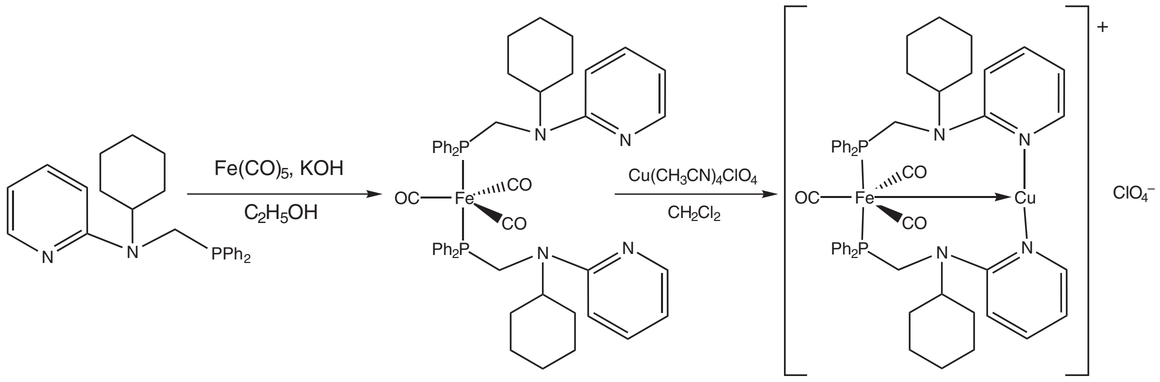


Scheme 57[171]

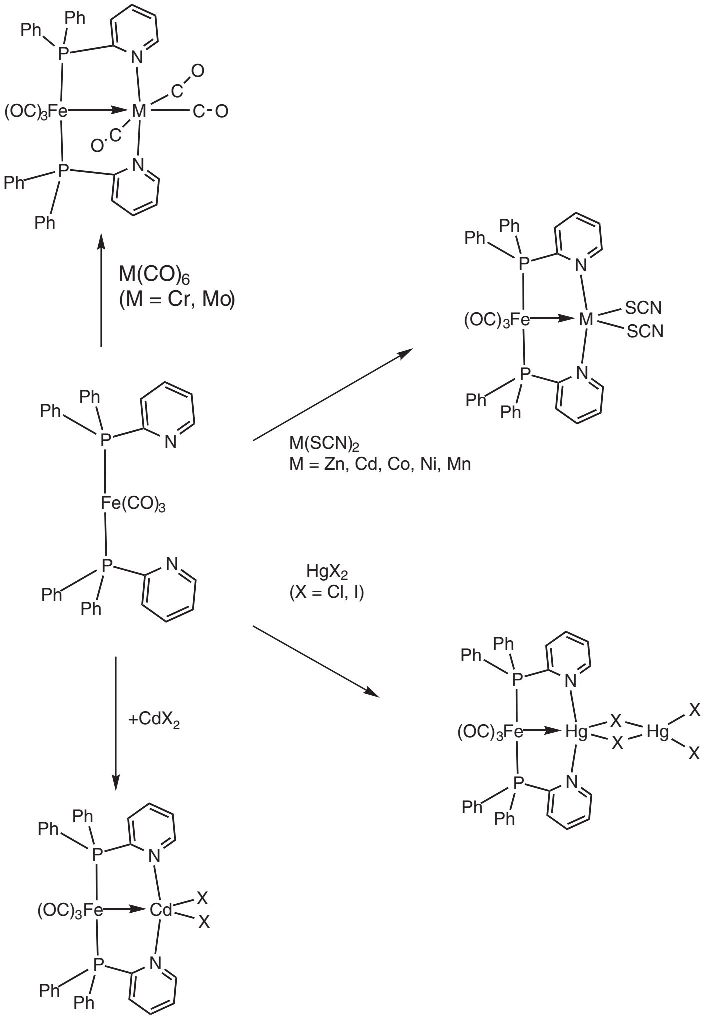
Schemes 58–62. A new non-rigid phosphine ligand was synthesized and reacted with $Fe(CO)_5$ to form the mononuclear iron complex (Equation (81)).[172] Phosphino-oxazoline ligands were used as assembling ligands for heterometallic complexes, where the phosphorus atom binds to iron and the nitrogen atoms act as donor atoms to copper, cobalt, or palladium (Scheme 58).[144,174] The copper complex catalyzes cyclopropanation and Diels–Alder reactions.[174] When 2-(*N*-diphenylphosphinomethyl-*N*-cyclohexyl)aminopyridine (NNP) reacts with $Fe(CO)_5$ in ethanol, *trans*-$(OC)_3Fe(NNP)_2$ is formed (Scheme 59). This monometallic complex can then be reacted with a copper salt in CH_2Cl_2 to form a complex having an Fe–Cu dative bond.[173] The complex was demonstrated to be an efficient catalyst for the cyclopropanation of styrene by ethyl diazoacetate and for the Diels–Alder reaction of cyclopentadiene and methacrolein. No other heterometallic complexes have been shown to have such reactivity. Previously known



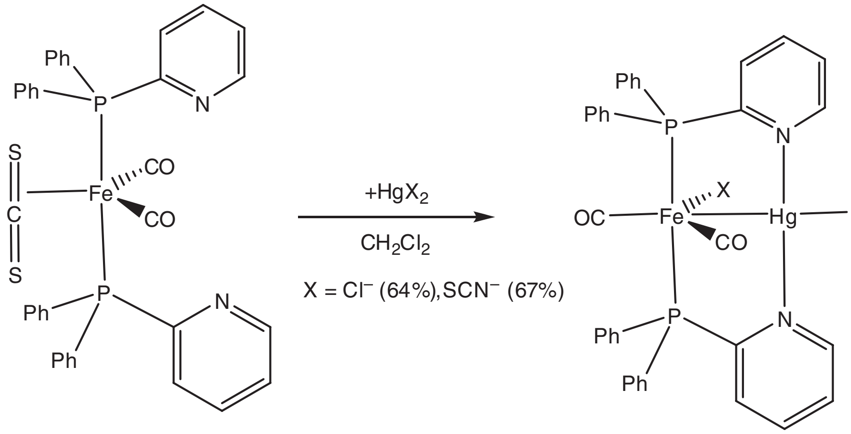
Scheme 58[144,174]



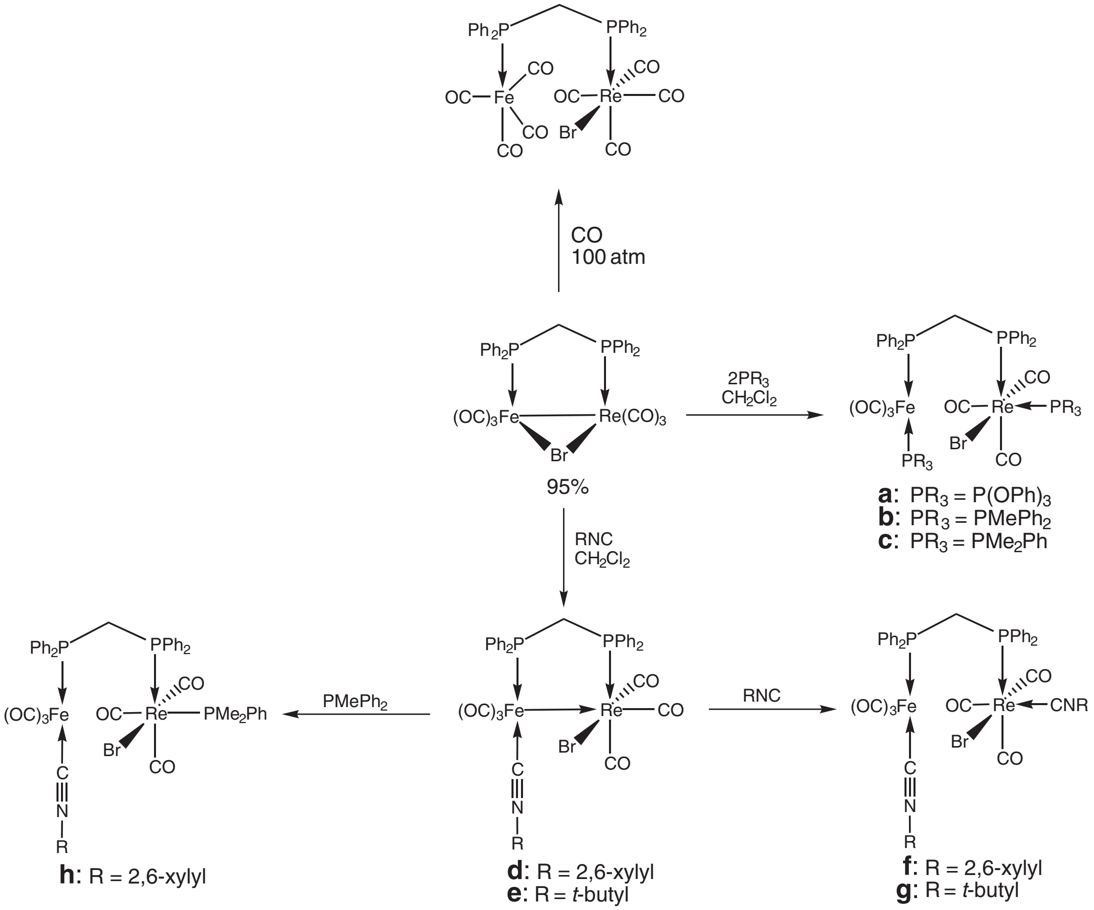
Scheme 59[173]



Scheme 60[127,175]

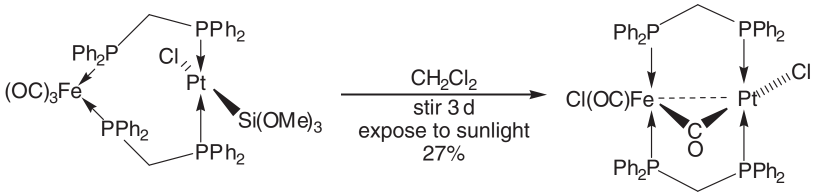


Scheme 61[176]

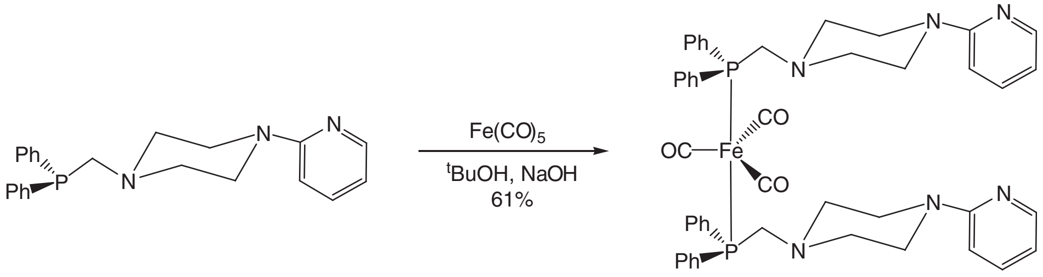


Scheme 62[95]

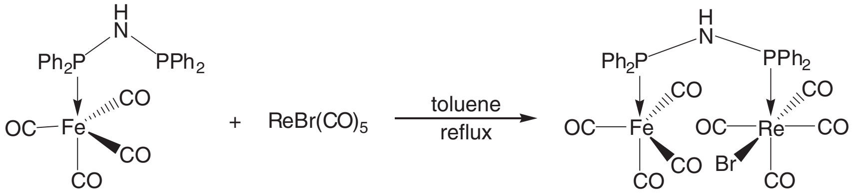
$Fe(CO)_3(Ph_2PC_5H_4N)_2$ was treated with various metal complexes (i.e., $M(CO)_6$, $M(SCN)_2$ (M = Zn, Co, Mn), MCl_2 (M = Co, Ni, Sn, Cd, Hg), HgI_2, $AgClO_4$) to form binuclear complexes (Schemes 60 and 61).[127,175] Dimetallic complexes can be prepared from $Fe(CO)_4L$ (L = dppm or bis(diphenylphosphino)amine) (Equations (82) and (83)).[95] In the case of dppm, the product possesses an Fe–Re bond, but this is not the case for the amine derivative. The metal–metal bonded product $FeRe(CO)_6(\mu\text{-dppm})(\mu\text{-Br})$, however, makes a convenient starting point for a variety of $Fe(CO)_4L$ complexes that have a tethered Re carbonyl fragment attached, but with no Fe–Re bond (Scheme 62).[95]



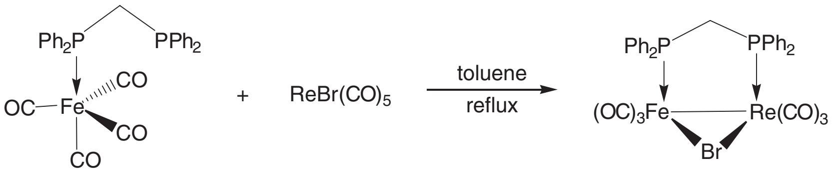
(80)



(81)



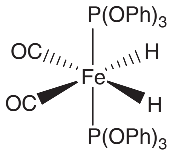
(82)



(83)

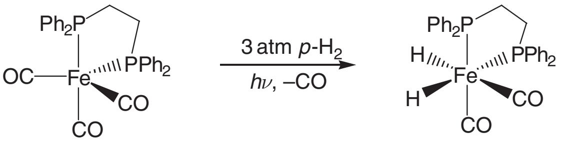
6.01.5.2.3 Phosphine hydrides

The first X-ray characterization of a mononuclear iron carbonyl dihydride has been reported. The compound studied, $H_2Fe(CO)_2\{P(OPh)_3\}_2$, was shown to have the *cis*-dihyride, *cis*-carbonyl structure **47**.[177] Neutron diffraction data have also been reported.[178]



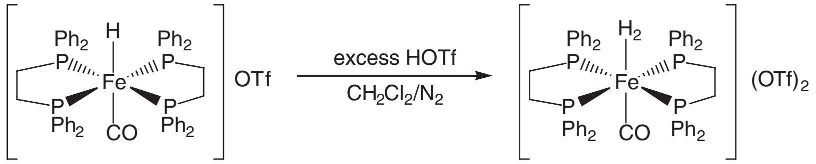
47

In situ photolysis of the reaction between $Fe(CO)_3(dppe)$ and *para*-hydrogen was used to study the reaction intermediates formed (Equation (84)).[179] NMR data combined with theoretical studies were used to investigate the fluxionality of the complex. A calculated reaction coordinate revealed two possible routes for ligand exchange: (i) phosphorus and carbonyl interchange with no hydride exchange, and (ii) interchange of all three ligands.[179]

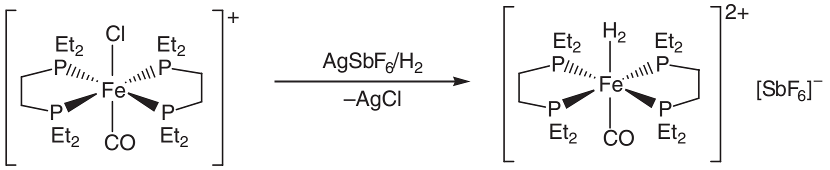


(84)

A bis(dppe) dihydrogen iron complex was formed via the reaction of $HFe(dppe)_2(CO)$ with triflic acid (Equation (85)).[180] The product has "strong three-center ($Fe–H_2$), two-electron σ-bonding," as was deduced by the stability of the complex under reduced pressure. Other products identified, but not isolated, from this reaction were $[\textit{trans}\text{-}Fe(H_2O)(CO)(dppe)_2]^{2+}$ and $[\textit{trans}\text{-}Fe(OTf)(CO)(dppe)_2]^{+}$. A similar complex with depe was prepared by treating $[Fe(depe)_2(CO)Cl]^{+}$ with $AgSbF_6$ in the presence of H_2 (Equation (86)).[180] Reactivity of the two complexes was compared, and they found that the dppe complex was more reactive toward nucleophiles than the depe complex. This was believed to be a result of the steric differences between the dppe and depe ligands.[180]



(85)



(86)

The dihydrogen complex $[Fe(H)(H_2)(dppm)_2]BF_4$ undergoes displacement of the H_2 ligand by CO (Equation (87)).[157]

$$\textit{trans}\text{-}[Fe(H)(\eta^2\text{-}H_2)(\eta^2\text{-dppm})_2]BF_4 \xrightarrow{CO} \textit{trans}\text{-}[Fe(H)(CO)(\eta^2\text{-dppm})_2]BF_4 \qquad (87)$$

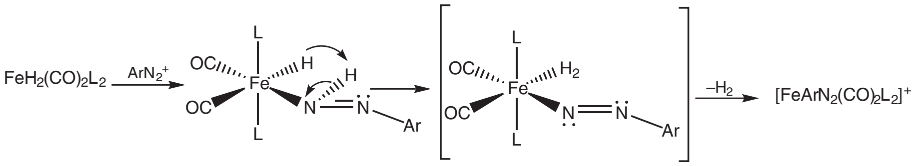
Syntheses of $[Fe(ArN_2)(CO)_2L_2]BPh_4$ and $[\{Fe(CO)_2L_2\}_2(\mu\text{-}N_2Ar\text{-}ArN_2)](BPh_4)_2$ [L = (P(OEt)$_3$, PPh(OEt)$_2$, PPh$_2$OEt, P(OPh)$_3$; Ar = Ph, 2-CH$_3$C$_6$H$_4$; Ar–Ar = 4,4′-C$_6$H$_4$C$_6$H$_4$, 4,4′-(2-MeC$_6$H$_3$C$_6$H$_3$-2-Me), 4,4′-C$_6$H$_4$-CH$_2$C$_6$H$_4$] are given in Equations (88) and (89).[181] NMR studies suggested that the reaction proceeds with initial insertion of the $ArN_2{}^{+}$ group into the Fe–H bond (Scheme 63).

$$H_2Fe(CO)_2L_2 + [ArN_2]BF_4 \xrightarrow{\substack{\text{i, CH}_2\text{Cl}_2 \\ \text{ii, EtOH/NaBPh}_4}} [Fe(ArN_2)(CO)_2L_2]BPh_4 \qquad (88)$$

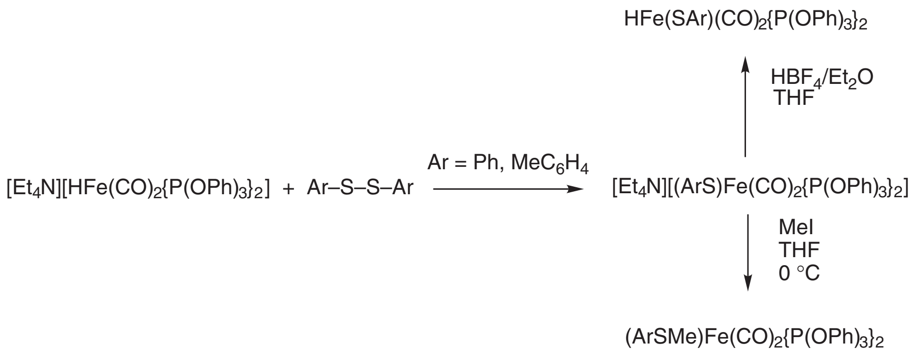
L = P(OEt)$_3$, PPh(OEt)$_2$, PPh$_2$(OEt), P(OPh)$_3$
Ar = Ph, 2-MeC$_6$H$_4$

$$2H_2Fe(CO)_2L_2 + [N_2Ar\text{–}ArN_2][BF_4]_2 \xrightarrow{\substack{\text{i, acetone} \\ \text{ii, EtOH/NaBPh}_4}} [\{L_2(CO)_2Fe\}_2(\mu\text{-}N_2Ar\text{–}ArN_2)(CO)_2L_2][BPh_4]_2 \qquad (89)$$

L = P(OEt)$_3$, PPh(OEt)$_2$, PPh$_2$(OEt), P(OPh)$_3$
Ar = Ph, 2-MeC6H4



Scheme 63[181]



Scheme 64[182]

Reaction of $[Et_4N][HFe(CO)_2\{P(OPh)_3\}_2]$ with aryl disulfides produces $HFe(SAr)(CO)_2\{P(OPh)_3\}_2$ (Scheme 64).[182]

6.01.5.3 Arsenic, Antimony, and Bismuth Donor Ligands

Substituted iron carbonyl complexes including $Fe(CO)_3\{As(C_6H_4OMe\text{-}p)_3\}_2$ and $Fe(CO)_4\{As(C_6H_4OMe\text{-}p)_3\}$ were examined by electrospray mass spectrometry (ESMS).[156] Whereas the related compound $Fe(CO)_3(AsPh_3)_2$ did not give an ESMS spectrum, the methoxy-substituted compounds did. This was attributed to the presence of protonatable methoxy groups. Both the monosubstituted and disubstituted compounds were observed in a crude preparation of these compounds.[183]

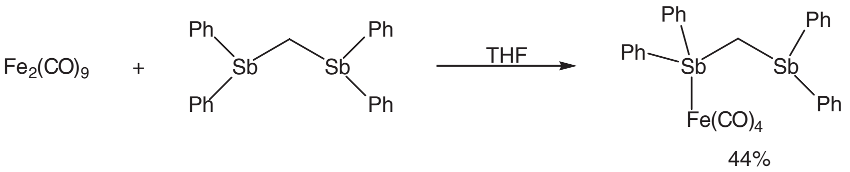
Various distibines were synthesized and reacted with $Fe_2(CO)_9$ to determine what type of coordination the ligand would adopt with the iron carbonyl fragment.[183] All of the complexes had the same conformation, with the distibine ligand bonding to two $Fe(CO)_4$ fragments (Equation (90)[183], Table 4). The crystal structure of $[\{Fe(CO)_4\}_2\{1,3\text{-}C_6H_4(CH_2SbMe_2)_2\}]$ was reported; the distibine ligand was bound axially to the iron carbonyl fragments as is normally observed.

(90)

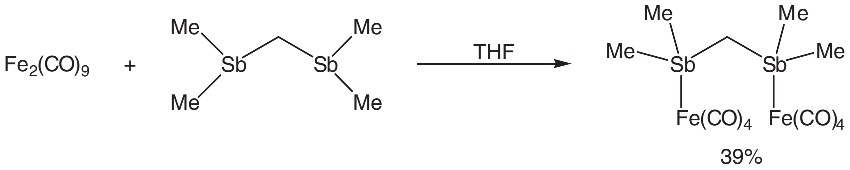
The reaction of bis(diphenylstibino)methane with $Fe_2(CO)_9$ resulted in a complex in which one of the stibine ligands occupied an axial site of $Fe(CO)_4$ group (Equation (91)).[184] A similar reaction involving bis(dimethylstibino)-methane (Equation (92))[184] or 1,3-bis(diphenylstibino)propane (Equation (93))[185] resulted in a complex with two $Fe(CO)_4$ fragments.

Table 4 Organoantimony complexes with $Fe(CO_4)$ fragments[183]

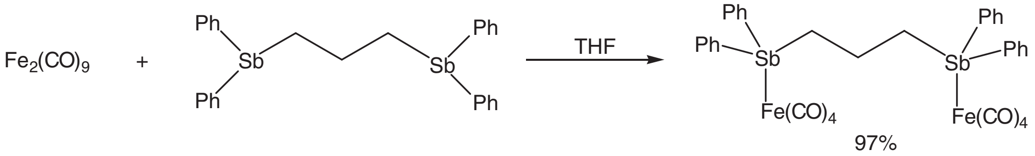
Aryl ring substitution	*X*	*Yield* (%)
1,2	CH_2SbMe_2	40
1,3	CH_2SbMe_2	48
1,4	CH_2SbMe_2	30
1,3	$SbMe_2$	33
1,4	$SbMe_2$	51



(91)

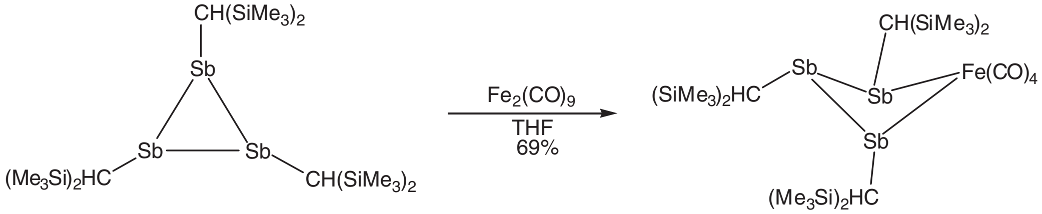


(92)



(93)

A heterocyclic complex of iron and antimony was synthesized via insertion of an $Fe(CO)_4$ fragment into a cyclic antimony compound (Equation (94)).[186]



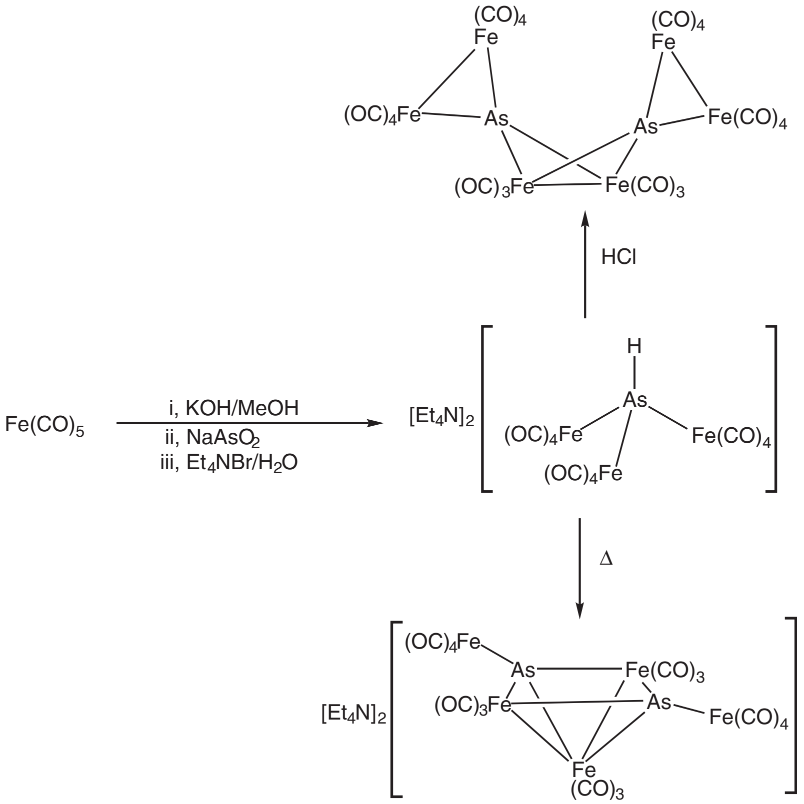
(94)

When $Fe(CO)_5$ is treated with $NaAsO_2$, As_2O_3, or Sb_2O_3 in methanolic alkali metal hydroxide solutions, triiron anions $[HE\{Fe(CO)_4\}_3]^{2-}$ (E = As, Sb) with no Fe–Fe bonds are obtained (Scheme 65).[187,188] The As–Fe bond had an average length of 2.460(7) Å, which is longer than those for other clusters having As–Fe single bonds (2.32–2.38 Å). Studies were performed to determine the reactivity of $[HAs\{Fe(CO)_4\}_3]^{2-}$, including pyrolysis, photolysis, and protonation.[189]

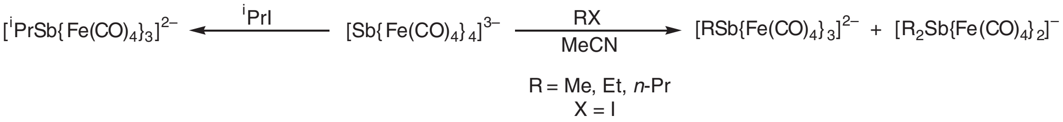
Various reactions of $[Et_3N]_3[Sb\{Fe(CO)_4\}_4]$ were performed with R–I (R = Me, Et, ^{n}Pr, or ^{i}Pr) (Scheme 66) and dihalides (Scheme 67).[190] The products from the R–I reactions contained four-coordinate SbR or SbR_2 fragments with the other coordination sites occupied by $Fe(CO)_4$ groups, whereas the reactions with the organic dihalides were more complicated. For 1,2-dibromoethane, a halogenated antimony complex was observed. With $Cl(CH_2)_3Br$, a monoalkylation product as observed for the R–I reactions was obtained along with a dialkylation product in which both the antimony and the iron were bonded to carbon ($SbFeC_3$ ring). In contrast, with $Br(CH_2)_4Br$, a monoalkylation product as well as one in which the antimony was dialkylated were observed. When the starting compound was the antimony hydride $[PPN]_2[HSb\{Fe(CO)_4\}_3]$, however, a different reaction with alkyl iodides was observed (Scheme 68). With methyl iodide, oxidative addition of MeI occurs at the antimony center giving a dimetallated organoantimony halide. Reaction with ethyl iodide resulted in $[PPN]_2[ISb\{Fe(CO)_4\}_3]$, similar to the reaction of 1,2-dibromoethane with $[Sb\{Fe(CO)_4\}_4]^{3-}$.[191]

The synthesis of a polymer having a Bi–Fe chain was accomplished via the ultrasonication of previously reported ring compound $[\{n\text{-}BuBiFe(CO)_4\}_2]$ (Scheme 69).[192]

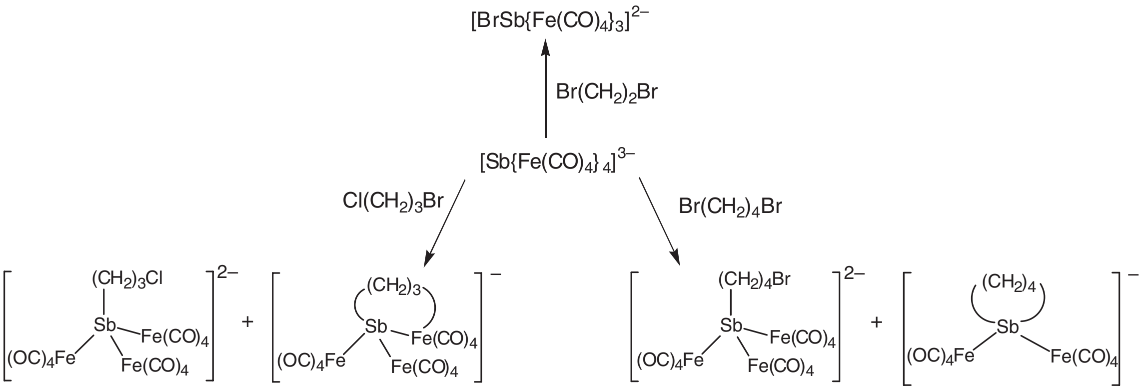
Bismuth chloride forms a simple bis(adduct) **48** with $[Fe(CO)_4]^{2-}$ (Equation (95)).[193] The Lewis-acidic bismuth atoms expand their coordination environments by sharing chloride ions. The bismuth atoms are distorted square pyramids attached to a distorted octahedral iron carbonyl fragment. Calculations on these structures indicated that a substantial charge separation remains in the products.



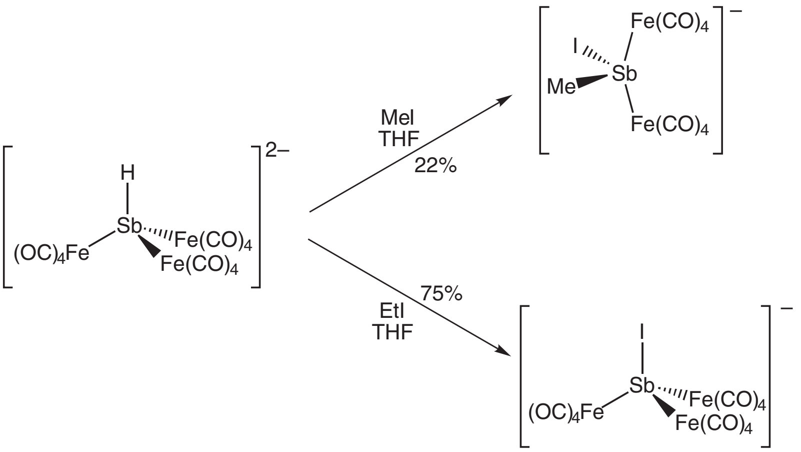
Scheme 65[187]



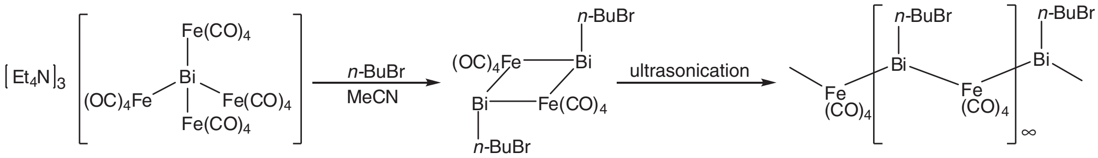
Scheme 66[190]



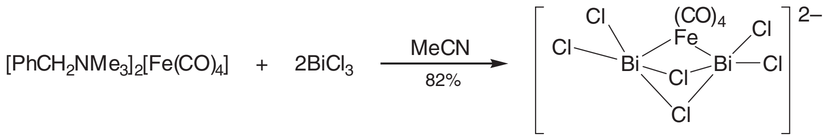
Scheme 67[190]



Scheme 68[191]



Scheme 69[192]



48

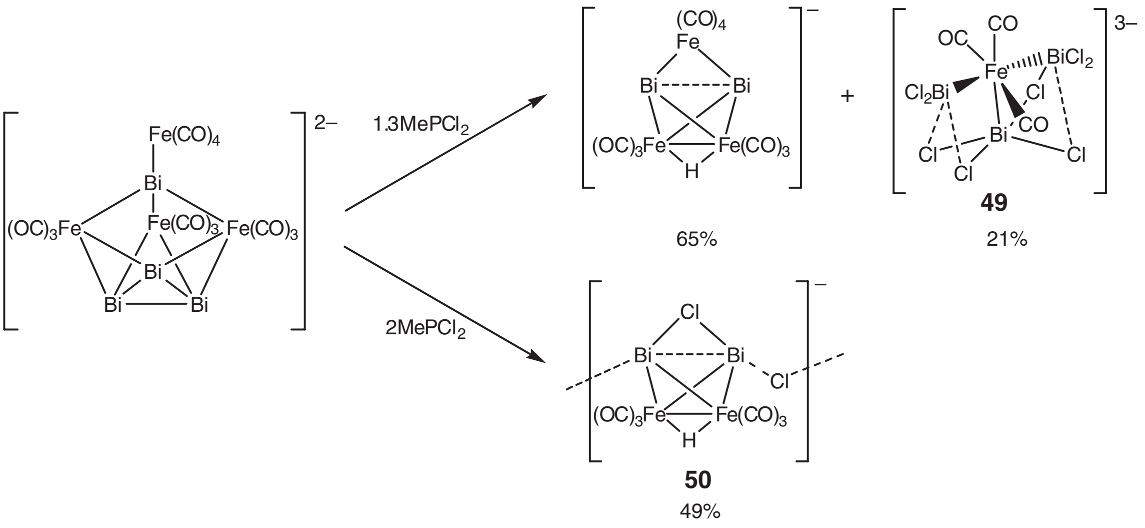
(95)

Various complexes resulted from the reaction of $[Bi_4Fe_4(CO)_{13}]$ with $MePCl_2$.[194] The product obtained was dependent on the amount of $MePCl_2$ used in the reaction (Scheme 69). Compound **49** can be viewed as a derivative of **48**, in which a CO ligand is replaced by a $BiCl_2^-$ group (Scheme 70). Calculations on **49** showed that substantial charge separation remained and that all of the bismuth atoms were in approximately the same oxidation state. Two cluster products based upon Fe_2Bi_2 tetrahedral units were also observed in these reactions. One of these, **50**, was polymeric with chloride ions bridging between bismuth atoms of adjacent cluster molecules.

6.01.6 Oxygen, Sulfur, Selenium, and Tellurium Donor Ligands

6.01.6.1 Oxygen

Little work has been reported on complexes with both carbonyl and oxygen donor ligands. Iron carbonyl fragments are known to be stabilized by bonding to alcohol and ether solvents, although these complexes are not often stable enough to isolate (see Equation (1)).[24,25] As seen in Scheme 4, organic fragments containing oxygen donor atoms may also show bonding of the oxygen atom to the iron center. This is seen in Schemes 31 and 44–47, where iminoketone-derived ligands and carbamoyl derivatives bond to iron through O as well as through N or C.[146, 147]



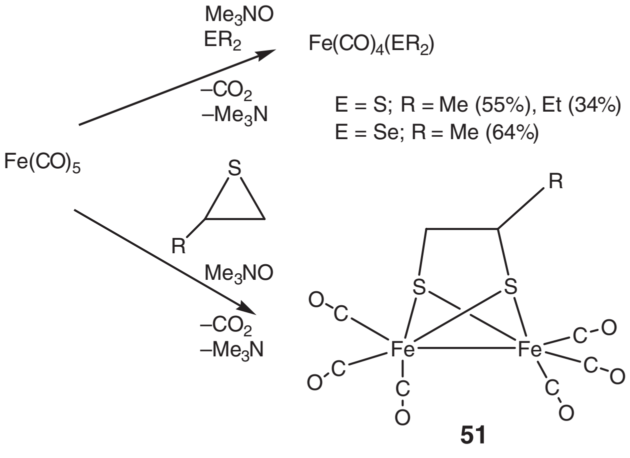
Scheme 70[194]

6.01.6.2 Sulfur

6.01.6.2.1 Iron carbonyls containing S-donor ligands

In the past decade there has been a renewed interest in iron carbonyl complexes with sulfide, thiolate, and thiol ligands owing to the discovery that the active center in hydrogenases possess dinuclear centers with these ligands as well as cyanide and nitrogen donor ligands. Complexes with only S-based ligands and CO will be covered first, followed by a discussion of those complexes that also possess cyanide and/or CNR ligands. Complexes with nitrogen donor ligands as well will be presented last. Since this section is focused on mononuclear iron carbonyl complexes, those compounds which possess M–M bonds will only be covered in so far as they are produced from or react to form a species with no metal bonds to the iron carbonyl fragment. For compounds with M–M bonding, see Chapters 6.02 and 6.03.

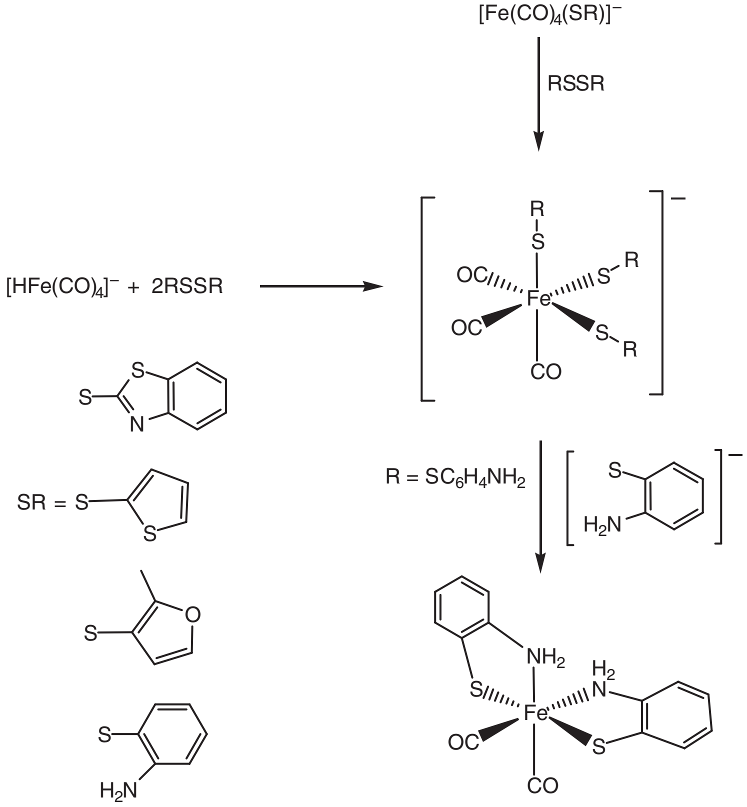
Reaction of $Fe(CO)_5$ with dialkyl sulfides in the presence of trimethylamine–*N*-oxide leads to simple, monosubstituted $Fe(CO)_4(SR_2)$ complexes (Scheme 71), whereas this reaction performed with cyclic thioethers gave dinuclear complexes.[195] Dinuclear complexes related to **51** with a variety of groups bridging between the two sulfur atoms have been derivatized with cyanide and organic isocyanides.[66,196–198]



51

R = H, (39%), Me (63%)

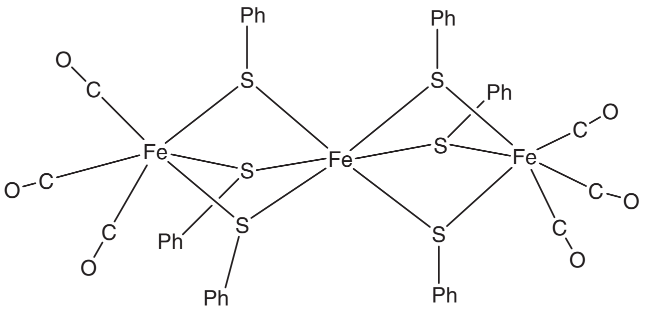
Scheme 71[195]



Scheme 72[199]

The iron carbonyl hydride $[HFe(CO)_4]^-$ reacts with disulfides to produce $[fac\text{-}Fe(CO)_3(SR)_3]^-$ (Scheme 72).[199] The reaction proceeds through the intermediacy of $[RSFe(CO)_4]^-$. When the R group is $–C_6H_4\text{-}o\text{-}NH_2$, the reaction proceeds with the elimination of one thiolate ligand and one carbonyl to give $Fe(CO)_2(SC_6H_4NH_2)_2$, which chelates the iron center using both the S and N atoms ($SC_6H_4\text{-}o\text{-}NH_2$).

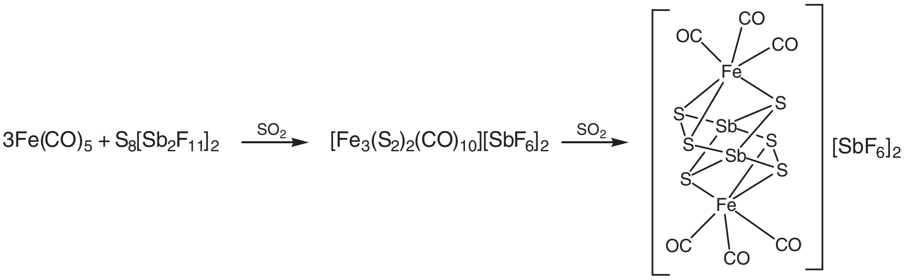
Temperature- and field-dependent Mössbauer studies were performed on $Fe_3(SPh)_6(CO)_6$ **52**.[200] All Fe atoms are Fe(II) with the two $Fe(CO)_3$ units having low spin, while the central Fe(II) is high spin ($S = 2$).[200]



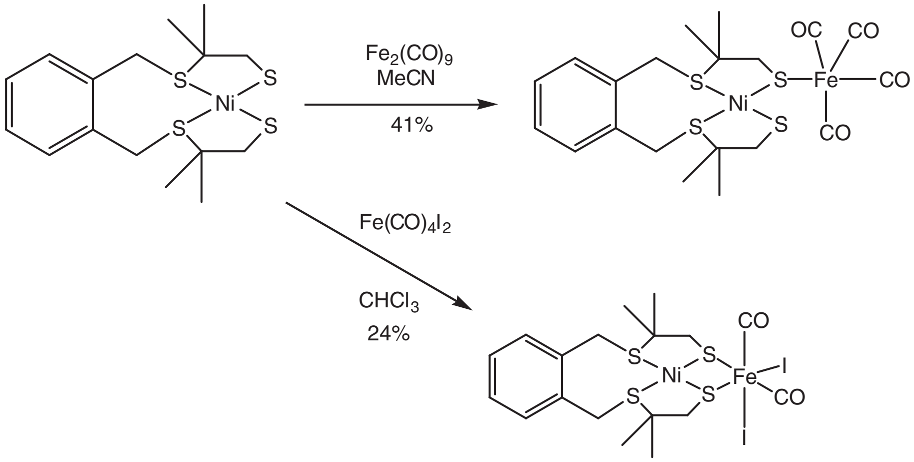
52

The first metal carbonyl compound bound to a mixed main group (15/16) cationic complex, $[Fe_2(Sb_2S_6)(CO)_6][SbF_6]_2{\cdot}2SO_2$, was reported (Scheme 73).[201] This cationic cluster possesses an Sb_2S_6 cage that is attached to the $Fe(CO)_3$ units only by bonds to sulfur.

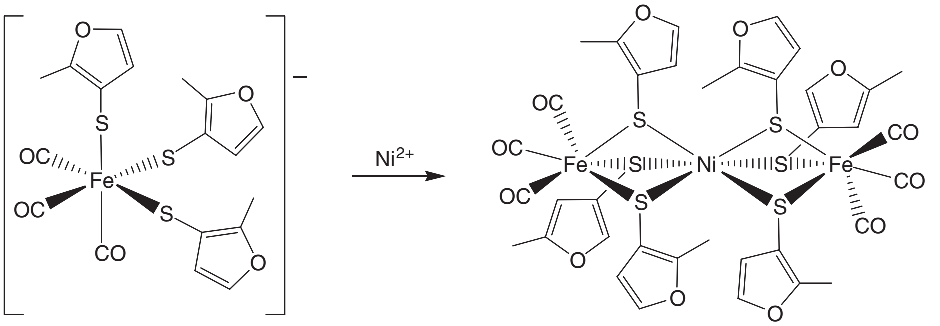
Several bimetallic complexes have been prepared beginning with mononuclear iron carbonyl–thiolate species or via reaction of an iron carbonyl with another thiolate complex (Equations (96)–(98),[199,202,203] Scheme 74).[204]



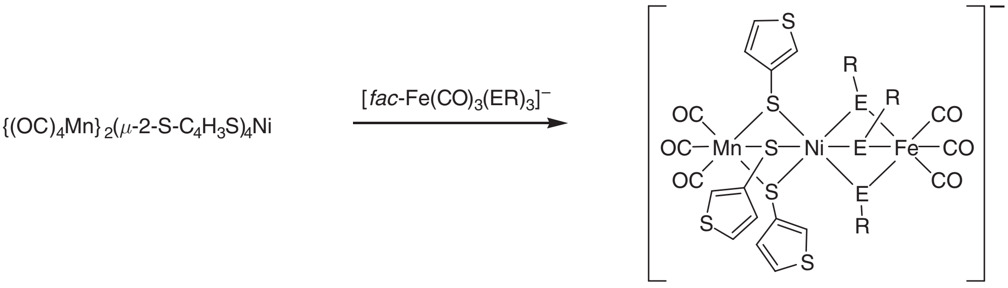
Scheme 73[201]



Scheme 74[204]

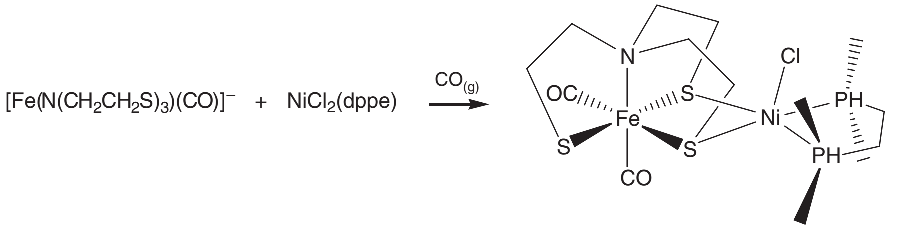


(96)



(97)

E = S; R = C_4H_3S
E = Se; R = Ph (85%)



(98)

In addition to these mononuclear complexes, the chemistry of the diiron compounds of the type $Fe_2(CO)_6(\mu\text{-}SR)_2$, $Fe_2(CO)_6(\mu\text{-}ER)(\mu\text{-}ER)$, $[Fe_2(CO)_6(\mu\text{-}ER)(\mu\text{-}E)]^-$ (E = S, Se), and related complexes has been thoroughly examined.[149,205–241] Since these compounds have Fe–Fe bonds, the reader is referred to Chapter 6.02.

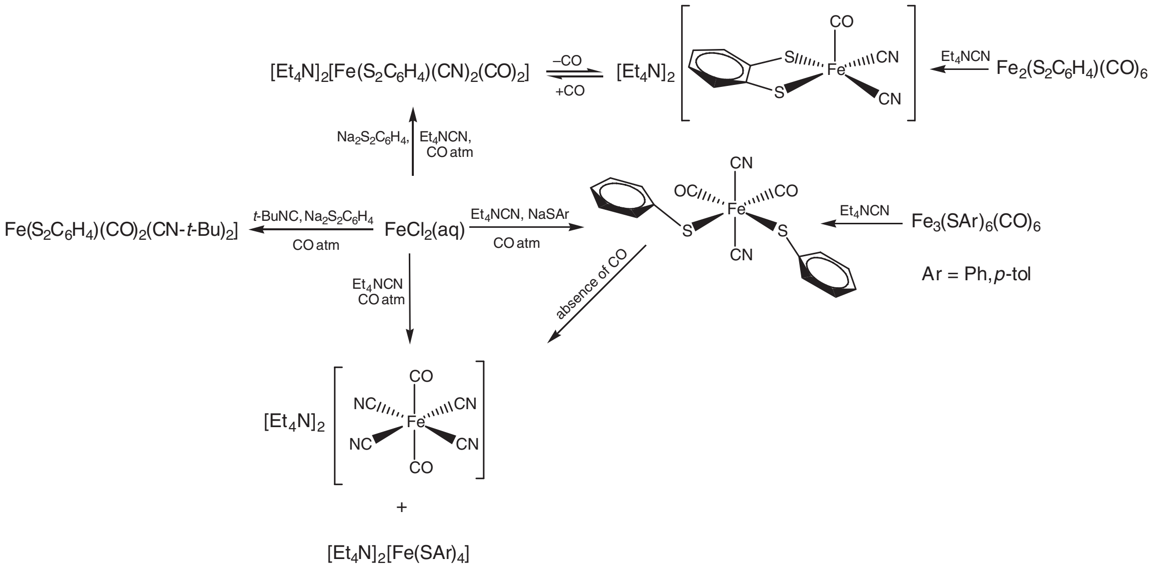
6.01.6.2.2 Iron carbonyls containing S-donor ligands and cyanide or organic isocyanide ligands

Iron carbonyl complexes with cyanide or organic isocyanide ligands have been presented in Section 6.01.4.1. The chemistry of those compounds is related to the preparation of compounds which contain both cyanide and S-donor ligands. Reaction of $FeCl_2$ with $[Et_4N]CN$ or organic isocyanides in the presence of CO and thiolate ligands is a convenient entryway into this class of compounds (Scheme 75).[242]

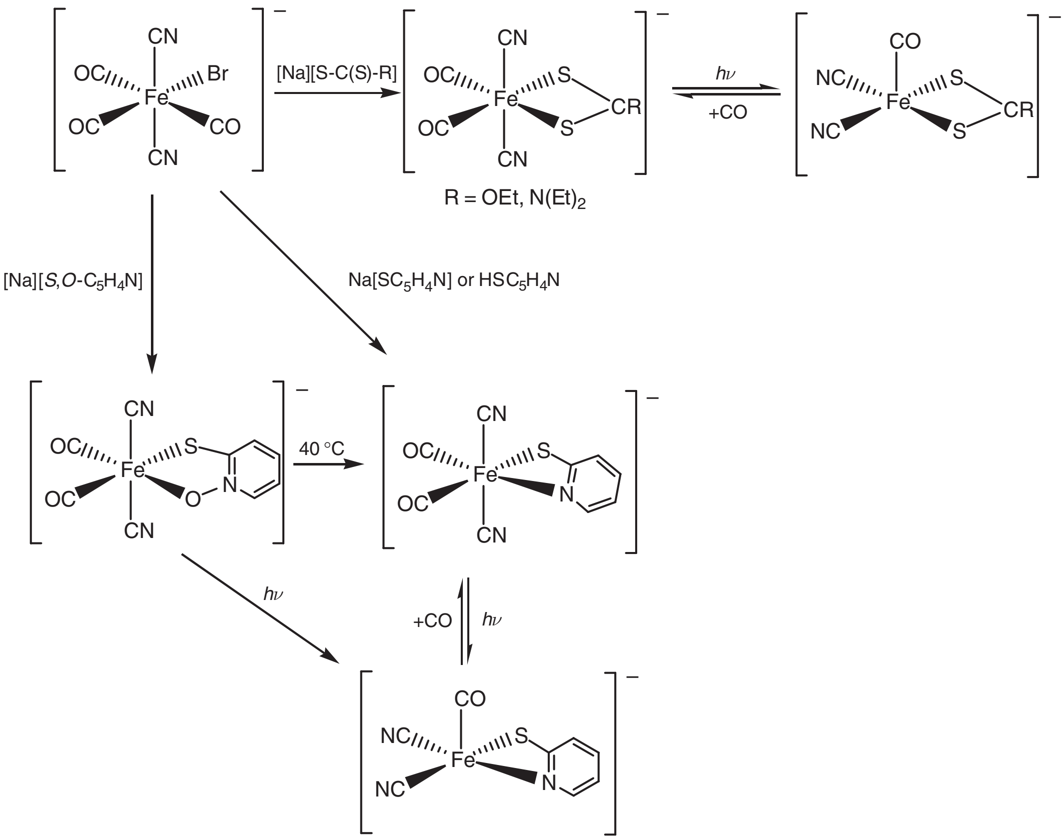
Compounds with both cyanide and S-donor ligands can be prepared from thiolates, dithiocarbamates, or alkyl dithiocarbonates and $[Fe(CN)_2(CO)_3(Br)]^-$ by metathesis of Br^- (Schemes 76[67] and 77).[65] An important feature of some of these compounds is their ability to bind CO reversibly.

6.01.6.2.3 Iron carbonyls containing S- and N- or P-donor ligands

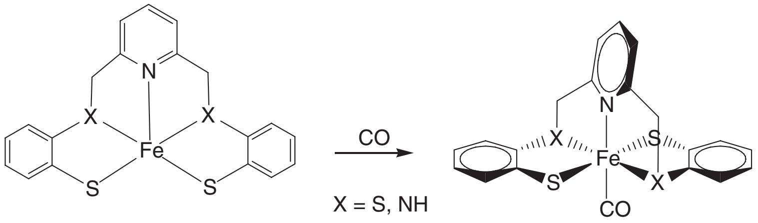
New transition metal complexes with ligands containing several sulfur donor atoms were obtained by addition of CO to the corresponding non-carbonyl-containing iron–ligand complex (Equation (99)).[243] The structure of these ligands forced *trans*-coordination of the thiolate groups. For the X = NH derivative, the ν_{CO} indicates strong Fe–CO (π-backbonding) bond, but the CO dissociates readily in solution. The complex with X = S was obtained from alkylation of $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$ with $[py(CH_2OTs)_2]$ or from reaction of $FeCl_2{\cdot}4H_2O$ with the free ligand in the presence of CO. This product is stable toward dissociation of CO.



Scheme 75[242]

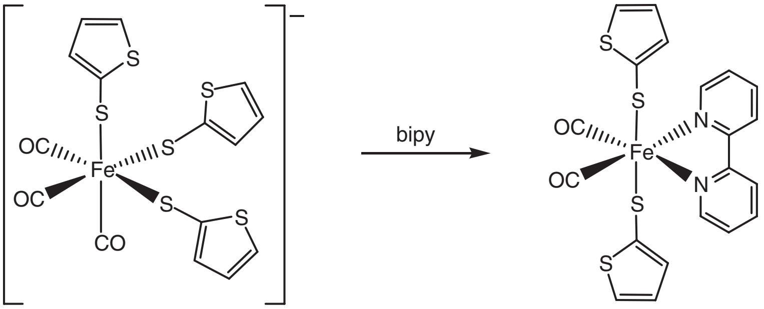


Scheme 76[67]

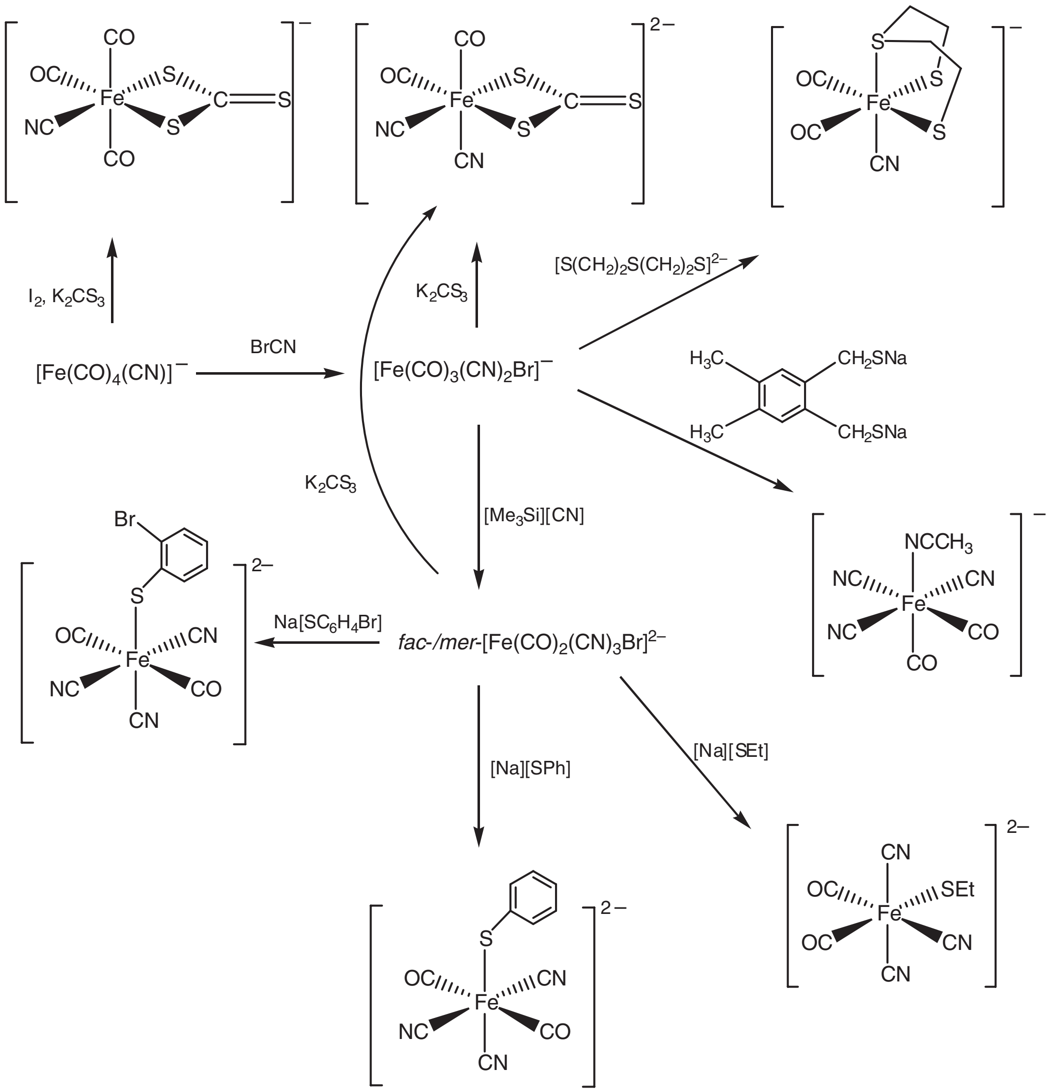


(99)

The complex $[Fe(CO)_3(SC_4H_3S)_3]^-$ reacts with bipyridine to eliminate one ligand and produce neutral $Fe(CO)_2(SC_4H_3S)_2$(bipy) (Equation (100)).[199] The interconversion of the pyridine-2-thiolate complexes $[Fe(CO)_4(SC_5H_4N)]^-$, *cis*-$[Fe^{II}(CO)_2(SC_5H_4N)_2]$, and $[Fe^{II}(SC_5H_4N)_3]^-$ has been studied (see Scheme 72).[199, 244] The *S*,*N*-chelating pyridine-2-thiolate ligand binds to Fe(0) in a monodentate fashion, while it prefers a bidentate, chelating mode for Fe(II).



(100)

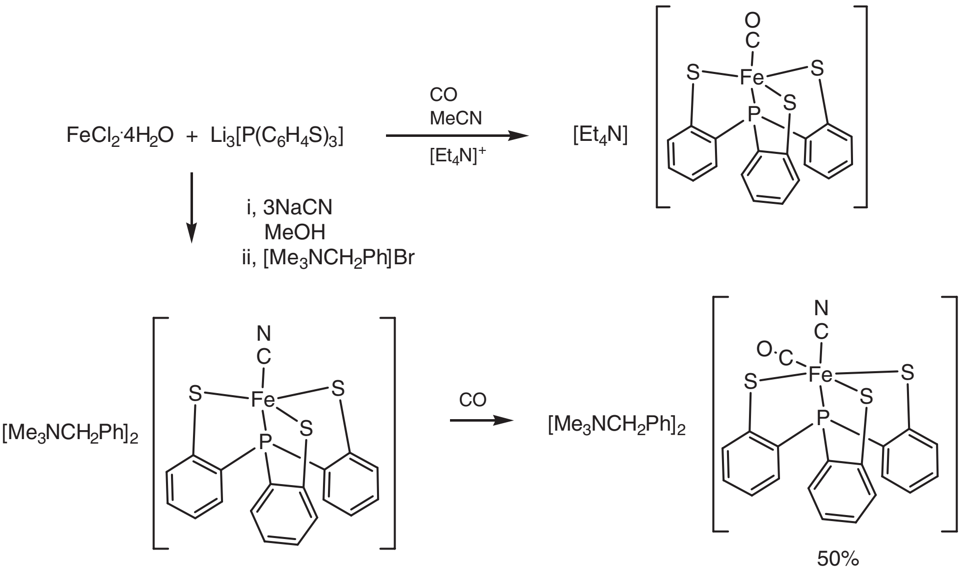


Scheme 77[65]

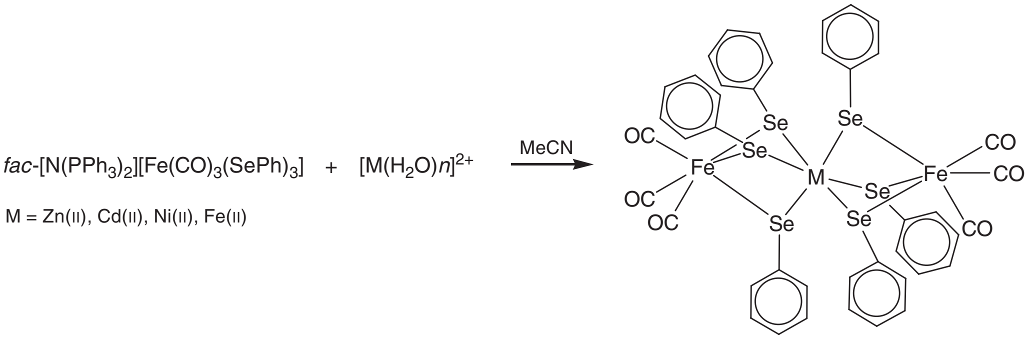
The thiol-substituted triphenylphosphine ligand $[P(C_6H_4S)_3]^{3-}$ has been used to prepare iron carbonyl, cyano, and cyano-carbonyl complexes (Scheme 78).[245,246] The trigonal-bipyramidal arrangement of ligands in $[Et_4N][Fe\{P(C_6H_4S)_3\}CO]$ prevents the formation of a diamagnetic ground state and the compound is the only example of a paramagnetic iron(II) carbonyl complex. The cyano carbonyl complex tends to lose CO in solution. Both carbonyl compounds undergo reversible oxidation in solution, with oxidation of the carbonyl complex occurring at +0.83 V and the cyano carbonyl species at −0.476 V (vs. SCE).

6.01.6.3 Iron Carbonyls with Se-donor Ligands

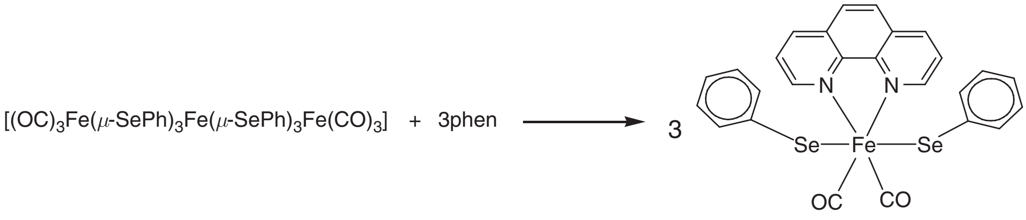
The chemistry of iron carbonyls with organoselenium ligands has many parallels to the chemistry of the related thiolates. For example, the *fac*-anion $[Fe(CO)_3(SePh)_3]^-$ is known and is a starting material for making other iron carbonyl selenato derivatives (Equations (101) and (102)).[247] Synthesis and structural characterization of $[(OC)_3Fe(\mu\text{-}SePh)_3M(\mu\text{-}SePh)_3Fe(CO)_3]$ (M = Zn(II), Cd(II), Ni(II), Fe(II)) have been reported.



Scheme 78[245,246]



(101)

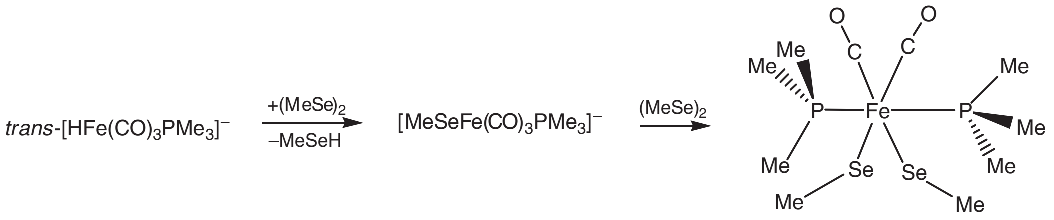


(102)

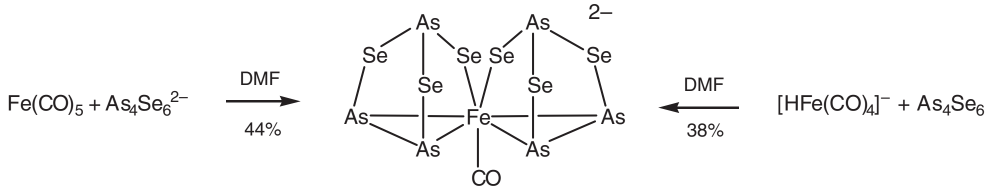
Reaction of the iron carbonyl–hydride anion $[HFe(CO)_3(PMe_3)]^-$ with diselenides leads to formation of iron carbonyl selenolate complexes and elimination of RSeH (Scheme 79).[248] The *cis*,*cis*,*trans*-configuration of the final product was established by single crystal X-ray diffraction.

Reaction of pentacarbonyl iron with $K_2As_4Se_6$ or of $[PPN][HFe(CO)_4]$ with As_4Se_6 produced a monocarbonyl iron complex with two $As_3Se_3^-$ ions bonded to the metal through both As and Se (Scheme 80).[249]

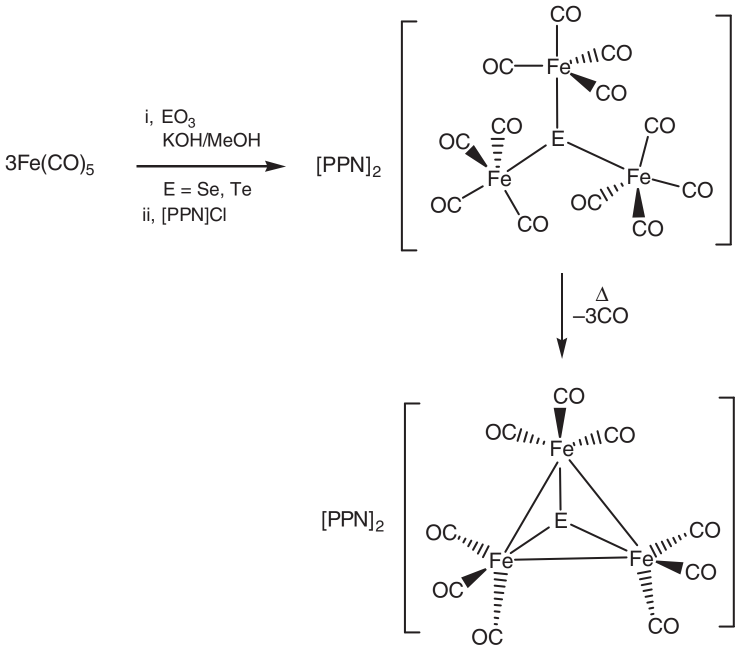
Iron carbonyl clusters incorporating Se or Te have been synthesized by reacting methanolic KOH solutions of $Fe(CO)_5$ with the main group element oxides (Scheme 81).[250] Both complexes $[E\{Fe(CO)_4\}_3]^{2-}$ lose CO at room temperature in THF solution to form the closed tetrahedral clusters, but in the case of selenium, the loss is so rapid that isolation of the pure complex without Fe–Fe bonds is very difficult.



Scheme 79[248]



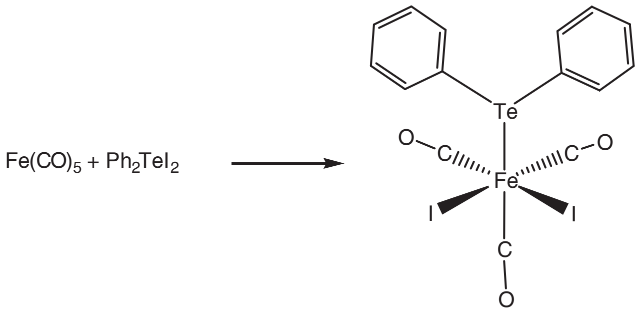
Scheme 80[249]



Scheme 81[250]

6.01.6.4 Tellurium

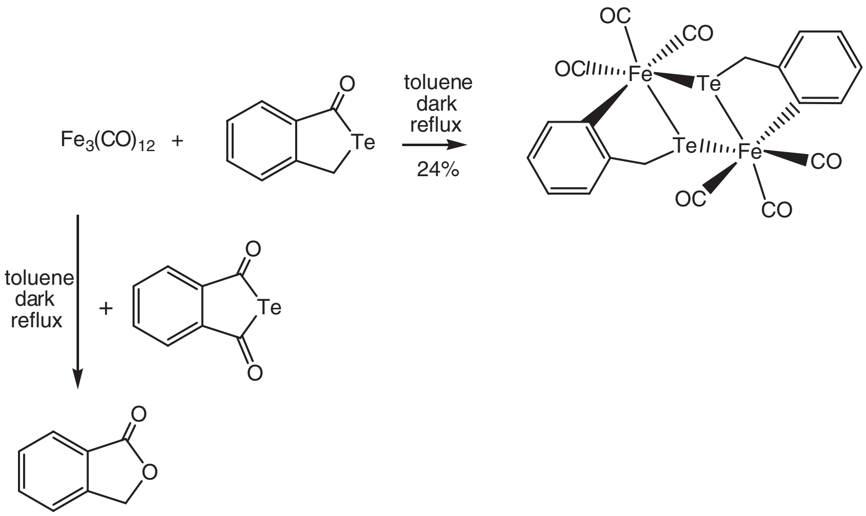
New iron carbonyl complexes with both organotellurium and naked tellurium atoms have been prepared (Schemes 82–84). This section will cover only those compounds that have iron centers without bonds to other metals. Reaction of $Fe(CO)_5$ with Ph_2TeI_2 leads to formation of $PhTeFe(CO)_3I_2$ via oxidative addition to the iron center.[251] In this process, the tellurium is reduced to Te(0), giving the first characterized example of a telluroether complex. The analogous $(MeTePh)Fe(CO)_3I_2$ was prepared by an indirect route as shown in Scheme 83. Organotellurium derivatives could also be prepared starting from $Fe_3(CO)_{12}$ (Scheme 84).[252] Reaction of 2-telluraphthalide with $[Fe_3(CO)_{12}]$ gave $\{C_6H_4CH_2TeFe(CO)_3\}_2$. The product shows that an iron atom has inserted into the



Scheme 82[251]

$$[HFe(CO)_4]^- \xrightarrow{(PhTe)_2} [PhTeFe(CO)_4]^- \xrightarrow{MeI} (MeTePh)Fe(CO)_4 \xrightarrow{I_2} (MeTePh)Fe(CO)_3I_2$$

Scheme 83[251]



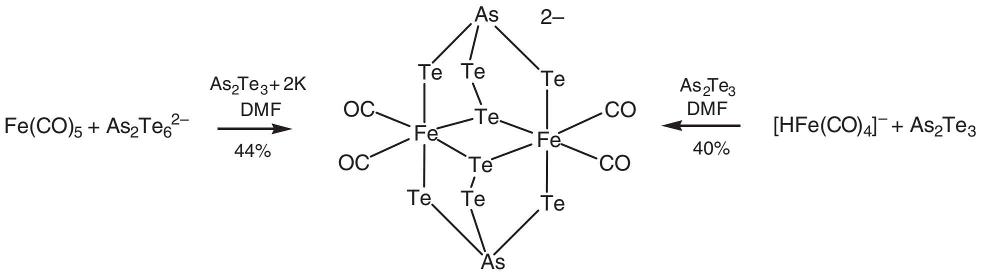
Scheme 84[252]

tellurium–carbon ring system, and the organic carbonyl has been eliminated. The product has a distorted square-shaped Fe_2Te_2 core. The dimerization is apparently driven by fulfilling the 18-electron rule at the iron center.

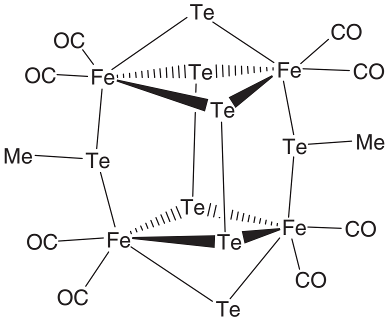
The trigonal-planar tellurium complex $[PPN]_2[Te\{Fe(CO)_4\}_3]$ analogous to the selenium analog described in the previous section also has no metal–metal bonds and has been obtained from the reaction of TeO_3 with pentacarbonyliron in methanolic KOH (Scheme 81). As with the selenium analog, the tellurium compound loses CO to give the closed tetrahedral dianion $[Fe_3(CO)_9E]^{2-}$ cleanly and in good yield.[250]

Similar to reactions with arsenic selenide anions described in the previous section, pentacarbonyliron or the hydrido–iron tetracarbonyl anion react with arsenic tellurides to produce complex iron carbonyl-bound tellurium arsenic anions (Scheme 85).[249] Unlike the selenium analogs, the isolated complex for Te does not exhibit Fe–As bonds.

Other complex iron carbonyl tellurides can be obtained by solvothermal reactions.[253] Compound **53**, $(Me_4N)_2[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$, is produced when $Fe_3(CO)_{12}$, Na_2Te_2, and Me_4NBr are mixed with a small amount of methanol and heated at 110 °C. This complex exhibits solvent-derived methylation of Te^{2-} ions, which was not expected.

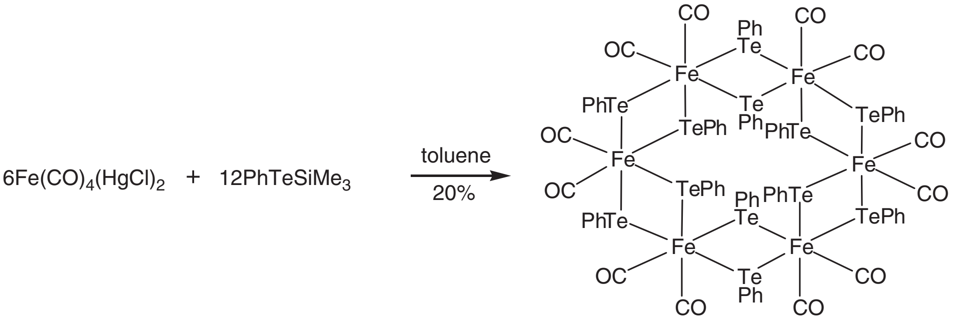


Scheme 85[249]



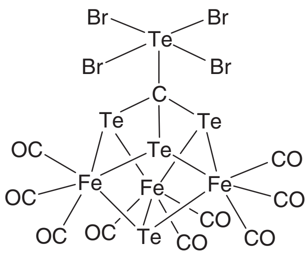
53[253]

Reaction of $Fe(CO)_4(HgCl)_2$ with $PhTeSiMe_3$ gives an interesting ring structure composed of six iron and 12 tellurium atoms (Equation (103)).[254]



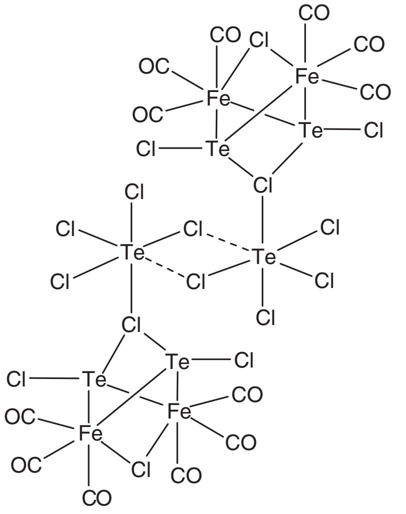
(103)

The long-known square-pyramidal complex $Te_2Fe_3(CO)_9$ reacts with CBr_4 in a 2 : 1 ratio to give the unusual species $Fe_3(CO)_9Te_4(\mu_3\text{-}CTeBr_4)$ **54**.[255] The cluster is unusual in that it possesses Te(0) and Te(IV) in the same molecule. The formation of the CTe_4 unit is also noteworthy. The structure is best described as an Fe_3Te_4C cubane with no direct Fe–Fe bonding.

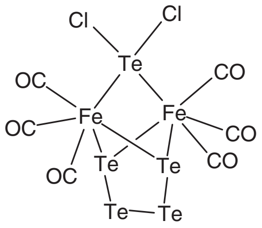


54[255]

Reaction of $Te_2Fe_3(CO)_9$ with $SOCl_2$ or SO_2Cl_2 led to the production of $[Fe_2(CO)_6(\mu\text{-Cl})(\mu\text{-TeCl})_2]_2\{\mu_2,\mu_1\text{-}\eta^2\text{-}Te_2Cl_{10}\}$ **55**, and its decomposition to $[Fe_2(CO)_6(\mu_2,\mu_2\text{-}\eta^2\text{-}Te_4)(\mu\text{-}TeCl_2)]$ **56**.[256] The thionyl and sulfuryl chlorides were intended as mild oxidants to convert the square-pyramidal cluster $Te_2Fe_3(CO)_9$ to a cationic species that would be isoelectronic to the trigonal-bipyramidal $Bi_2Fe_3(CO)_9$. Compound **55** was obtained in 89% yield based on Te. Upon standing, **55** decomposed into **56** in 73% yield based on Te. Compound **56** is unusual in having both low-valent Te (the Te_4 unit) and higher-valent Te (the $TeCl_2$ fragment) in the same molecule.

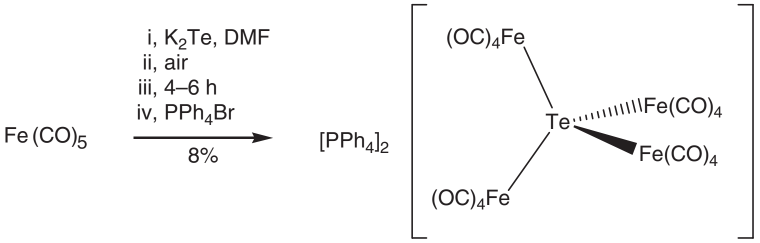


55[256]

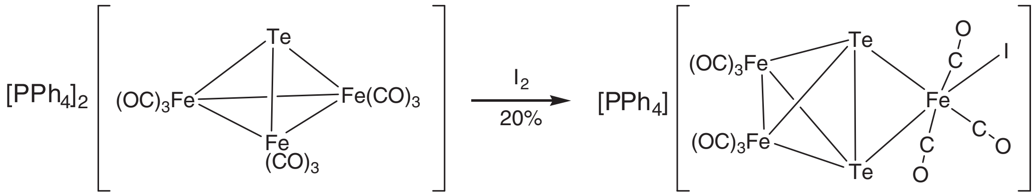


56[256]

In studies of the reaction of Te^{2-} with $Fe(CO)_5$, which led to nearly quantitative yields of $[Fe_3(CO)_9Te]^{2-}$, it was discovered that air oxidation of the reaction mixture led to $[Te\{Fe(CO)_4\}_4]^{2-}$ (Equation (104)).[257] Oxidation of $[Fe_3(CO)_9Te]^{2-}$ with I_2 instead led to a cluster compound with an $Fe(CO)_3I$ unit bridging between two tellurium atoms (Equation (105)).[257]



(104)



(105)

6.01.7 Fluoride, Chloride, Bromide, and Iodide Complexes

Iron carbonyl halides have not been extensively examined in the past decade for their own sake, but rather most studies where both CO and halide ions are bound to iron have focused on preparing derivatives with other ligand types bound to Fe. Examples of these have already been described in the appropriate sections above. The reader is referred to Equations 54, 75, 76, 78, 79, 105, Schemes 21, 46, 51, 55, 74, 75, 82, 83, and structure **36**. General routes to these compounds include substitution reactions of $Fe(CO)_4X_2$ complexes and carbonylation of iron halide coordination compounds.

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6.02
Mononuclear Iron Compounds with η^1-Hydrocarbon Ligands

M Knorr, Université de Franche-Comté, Besançon, France

6.02.1 Introduction

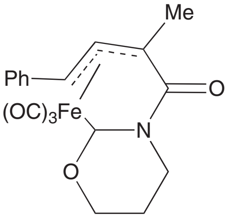
This section surveys the developments concerning synthesis and reactivity of iron complexes having η^1-metal–carbon bonds from 1993, where COMC (1995) ended, through September 2005. A few references dating from 1992 and not cited in COMC (1995) are also included. Coverage of this section corresponds roughly to that of section 31.2 of COMC (1982) and section 2.3 of COMC (1995). The material is organized here according to the kind of organic ligand attached to iron: after hydrocarbyl ligands with an sp^3-hybridized α-carbon atom such as alkyl, σ-allyls and their formal derived insertion products (acyls, iminoacyls) follow sp^2-type ligands such as σ-vinyls and σ-aryls and finally σ-acetylides, whose α-carbon is considered as sp-hybridized. Besides, two subsections are devoted to the chemistry of carbenoid complexes, regardless of the bonding interaction between the metal center and the carbenoid ligand (purely dative with a formal $Fe \leftarrow C$ single bond, or with σ-donor/π-acceptor propensities with a formal $Fe{=}C$ double bond). The important class of η^5-C_5R_5 iron compounds with η^1-hydrocarbon ligands is covered separately in Chapter 6.04.

Several statements, still valid in COMC (1995), have been now overtaken by the recent progress since 1993 and need revision. For example, it was stated in section 2.1.2 that, "As a central transition metal, iron slavishly follows the 18-electron rule in forming isolable organometallic compounds, although electrochemical and photochemical methods of generation and detection have revealed many reactive intermediates having between 16 and 20 electrons by conventional count." As will be shown, the conception of novel ligand systems like β-diketiminates, amidodiphosphines, "second-generation" tripodal ligands such as $[PhB(CH_2P^iPr_2)_3]^-$, or electron-rich *N*-heterocyclic pincer carbenes has allowed the isolation and structural characterization of numerous highly unsaturated, but thermally stable 12-electron and 14-electron species and odd 15-electron and 17-electron compounds. Moreover, due to the advances in design of sterically crowded alkyl and aryl groups, even the synthesis of homoleptic 10-electron iron alkyls and aryls could be achieved. In COMC (1995), isolable diorganyliron compounds were still considered "more the exception than the rule." The growing number of structurally characterized bis(alkyls) and bis(aryls) makes this statement, which was entirely justified in the 1980s and early 1990s, now obsolete.

Organoiron compounds (as reaction intermediates) are becoming more and more competitive as efficient low-cost alternatives to established catalytic processes, such as Pd-catalyzed cross-coupling reactions. A real breakthrough in the field of olefin oligo- and polymerization was the discovery that bis(imino)pyridine-based iron halides can rival metallocenes after activation by alkylating agents as co-catalyst. Although catalysis is beyond the scope of this article, this catalytic activity has initiated intensive experimental work on the preparation and reactivity of iron hydrocarbyl model compounds, supposed to be involved in the catalytic process. Organoiron chemistry is far and away from being "established routine chemistry;" exciting novel aspects and perspectives are emerging!

6.02.2 Synthesis and Reactivity of Alkyls, Acyls, Iminoacyls, and Carbamoyls

This section covers developments concerning synthesis and reactivity of organometallic iron complexes having a η^1-bound hydrocarbyl ligand, whose α-carbon atom is considered as sp^3-hybridized, and their formal derived insertion products (acyls, iminoacyls). Iron complexes ligated both by η^1- and η^n- ($n = 2$–4) hydrocarbyl ligands such as the η^1-alkyl–η^3-allyl compounds **1–3**[1–3] or the benzene-coordinated acyl complex [Fe{PhCH(=O)}(CO)$_3$] **4**[4] will be treated in Chapter 6.03, since their higher hapticity predominates.



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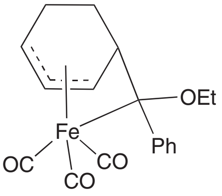

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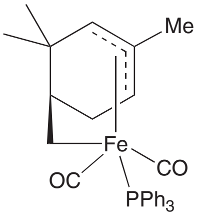

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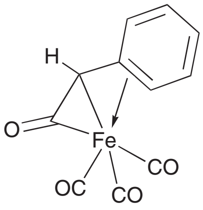

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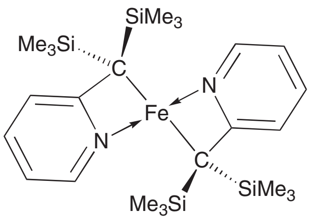
The application of the non-stabilized homoleptic iron alkyls Me_2Fe, Bu_2Fe, Me_3FeLi, Bu_3FeLi, or Me_4FeLi_2 as powerful reagents for cross-coupling reactions with organic halides, conversion of acyl chlorides into ketones, and rearrangement of aliphatic terminal epoxides to methyl ketones has been further developed since COMC (1995). The precise composition of these species, prepared *in situ* by reduction of $FeCl_3$ to $FeCl_2$, and subsequent alkylation with MeLi, MeMgBr, BuLi, or BuMgBr, or direct stoichiometric treatment of $FeCl_2$ with RLi, remains speculative.[5–7] The thermal stability of the paramagnetic THF solutions decreases in the order Me_4FeLi_2 (+40 °C) > Me_3FeLi (+25 °C) > MeFeCl (0 °C) > Me_2Fe (−10 °C) > Bu_4FeLi_2 (−25 °C). Closely related cyano–ate complexes of unknown structure (the following formulas are based only on the stoichiometry of the starting materials) are produced *in situ* in the form of black paramagnetic suspensions by the action of 1–4 equiv. of MeLi or BuLi on $Fe(CN)_2$ at −78 °C.[8] These new reagents are very favorable for cross-coupling with organic halides: coupling with 1-bromononane can be achieved by $Me_4Fe(CN)_2Li_4$ in 83–90% yield. $Me_2Fe(CN)_2Li_2$ and $Me_3Fe(CN)_2Li_3$ couple with α-bromostyrene with similar yields (89 and 84%, respectively), as does the homoleptic complex Me_4FeLi_2 couple (81%) with 1-bromo-2-phenylethyne. Mechanistic aspects of the C–C coupling reaction and the potential of these Fe(II)-alkyls and alkyl cyanoferrate species for organic synthesis, which offer various advantages over classical alkyllithium, alkylmagnesium, and organocopper reagents, have been reviewed.[9]

With the exception of [Fe(norbornyl)$_4$],[10] reported in COMC (1982), no stable, base-free simple homoleptic iron alkyls had been isolated. Therefore, the recent isolation and structural characterization of the remarkable stable homoleptic complex [Fe{C(SiMe$_3$)$_3$}$_2$], substituted with two bulky tris(trimethylsilyl)methyl groups, may be considered as one of the highlights of the past decade in the chemistry of iron alkyls. This red-violet, two-coordinate paramagnetic compound possessing a linear C–Fe–C skeleton (C–Fe–C 180.0°) with d(Fe–C) of 204.5(4) pm has been independently synthesized by reaction of $FeCl_3$ with 3 equiv. of Li[C(SiMe$_3$)$_3$] in toluene with concurrent reduction, or in an alternative synthesis, by treatment of $FeCl_2$ with 2 equiv. of Li(THF)$_2$[C(SiMe$_3$)$_3$] in THF.[11,12] The ESR spectrum recorded at 4 K indicates a configuration with two unpaired electrons. Despite its unsaturation, this formally 10-electron species does not react with an excess of pyridine, PMe_3, or phenol. Due to its steric protection, [Fe{C(SiMe$_3$)$_3$}$_2$] is even air and water stable in the solid state.

The synthesis of the thermally stable homoleptic dialkyl [Fe{C(SiMe$_3$)$_2$C$_5$H$_4$N-2}$_2$] **5** has been independently reported by two groups.[13,14] Paramagnetic **5** is isolated in 80% yield from the reaction of $FeCl_2$ with the sterically demanding reagent Li[C(SiMe$_3$)$_2$C$_5$H$_4$N-2]. An X-ray diffraction study of this distorted tetrahedral compound reveals that the alkyl substituents [d(Fe–C) = 215.4(8) pm; C–Fe–C = 160.4(3)°] are bonded in a chelating manner via coordination of the pyridine nitrogens to iron. In an analogous manner, treatment of $FeCl_2$ in a 1 : 2 ratio with the *N*-functionalized alkyls Li[{CPh(SiMe$_3$)C$_5$H$_4$N-2}(TMEDA)$_2$] and Li[{CH(SiMe$_3$)C$_9$H$_6$N-8}(TMEDA)] furnished [Fe{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$] **6** and [Fe{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$] **7**, respectively.[15] These 14-electron species have magnetic moments in the range of 4.24–4.96μ_B that are characteristic of a high-spin d^6-electronic configuration with four unpaired electrons. The redox behavior of **5–7** has been studied by cyclic voltammetry (CV) in THF; the Mössbauer spectrum of **5** has been obtained at 80 °K.



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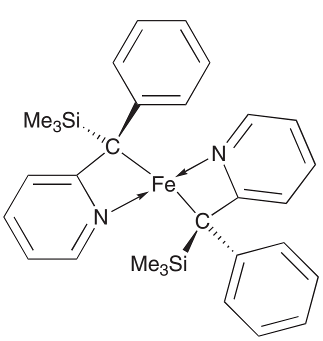

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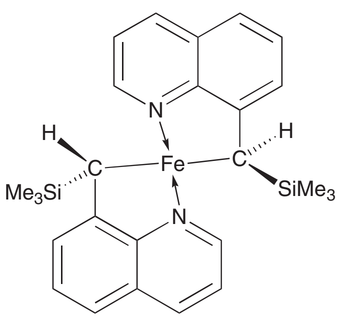
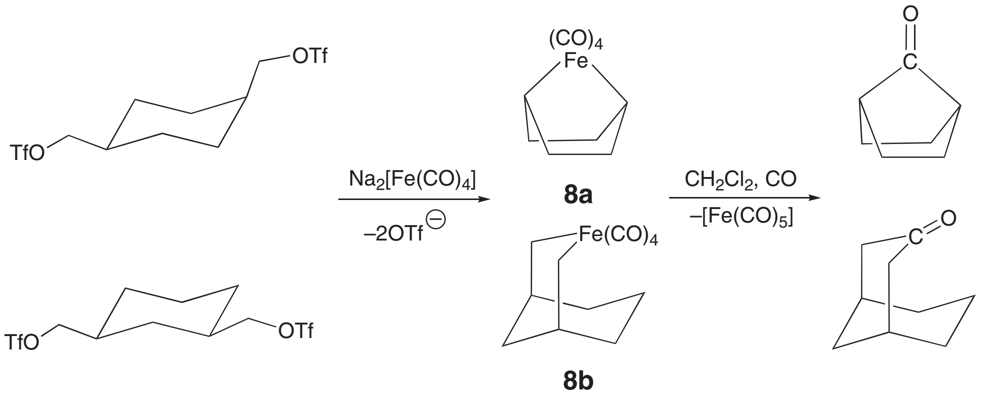


7

The dimeric bis(alkyl) complex $[Fe\{CH(Si^tBuMe_2)C_5H_4N\text{-}2\}_2]_2$ is obtained from alkylation of $FeCl_2$ with $Li[\{CH(Si^tBuMe_2)C_5H_4N\text{-}2\}(TMEDA)_2]$. Its eight-membered stair-like conformation of the dinuclear $Fe_2(C\cap N)_2$ core results from intermolecular *N*-bonding of one $CH(Si^tBuMe_2)C_5H_4N$ ligand to the second iron center. To account for the magnetic moment of only $2.92\mu_B$ per iron atom, an anti-ferromagnetic coupling between the two iron(II) centers is proposed. Alkylation of $FeCl_2$ with 1 molar equiv. of the organolithium reagent $Li[\{CPh(SiMe_3)C_5H_4N\text{-}2\}(TMEDA)]$ gave the monomeric monoalkyliron(II) complex $[Fe\{CPh(SiMe_3)C_5H_4N\text{-}2\}(Cl)(TMEDA)]$, in which the five-coordinate Fe center is surrounded by the *C,N*-chelating organic substituent [*d*(Fe–C) = 221.2(6) pm] and a chelating TMEDA ligand, the chloro atom occupying the apical position of the distorted square-planar structure. Addition of 2 equiv. of the sterically hindered phenol $2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2OH$ or thiophenol $2,4,6\text{-}^tBu_3C_6H_2SH$ to hexane solutions of 4 cleaves the Fe–C bonds, yielding the unusual three-coordinated iron(II) bis(phenoxide) $[Fe(OAr)_2\{CH(SiMe_3)_2C_5H_4N\text{-}2\}]$ and dithiolate $[Fe(SAr)_2\{CH(SiMe_3)_2C_5H_4N\text{-}2\}]$, respectively. A neutral $py\text{-}CH(SiMe_3)_2$ ligand stemming from protonation by ArOH or ArSH remains coordinated via its pyridyl nitrogen atom, thus conferring a 12-electron count to iron.[15]

Meanwhile, a classical method for the synthesis of monoalkyls and dialkyls of type $[RFe(CO)_4]^-$ and $[R_2Fe(CO)_4]$, for which many examples have been referenced in COMC (1982) and COMC (1995), consists in reaction of Collman's reagent $Na_2[Fe(CO)_4]$ with organohalides RX. Alternatively, treatment of $Na_2[Fe(CO)_4]$ with $[MeMn(CO)_5]$ and $[MeMoCp(CO)_3]$ cleanly provides within seconds $[MeFe(CO)_4]^-$ with formation of $[Mn(CO)_5]^-$ or $[CpMo(CO)_3]^-$, respectively. These formal CH_3^+ transfer reactions are first order in $[Fe(CO)_4]^{2-}$ and in the concentration of methyl complex.[16] Reaction of $Na[RC({=}O)Fe(CO)_4]$, prepared *in situ* by bubbling CO through a solution of $[RFe(CO)_4]^-$, with CuCl allows the synthesis of 1,2-diketones RCOCOR in high yield. It is proposed that the diketone formation takes place through oxidation of intermediate $Cu[RC({=}O)Fe(CO)_4]$ to the radical species $[RC({=}O)Fe(CO)_4]^{\cdot}$.[17] With the objective of preparing *meso*- and macrocyclic ketones, which are otherwise hardly accessible via "classical" organic synthesis, a series of ferracycles has been prepared using a slight variation of the above-mentioned method employing alkyl bis(triflates). Upon exposure to a carbon monoxide atmosphere, these unstable compounds rapidly insert CO into an Fe–alkyl bond. Subsequent reductive elimination of $[Fe(CO)_5]$ furnishes the desired cycloalkanones with excellent yields under mild conditions (Scheme 1). For example, the constitutionally isomeric



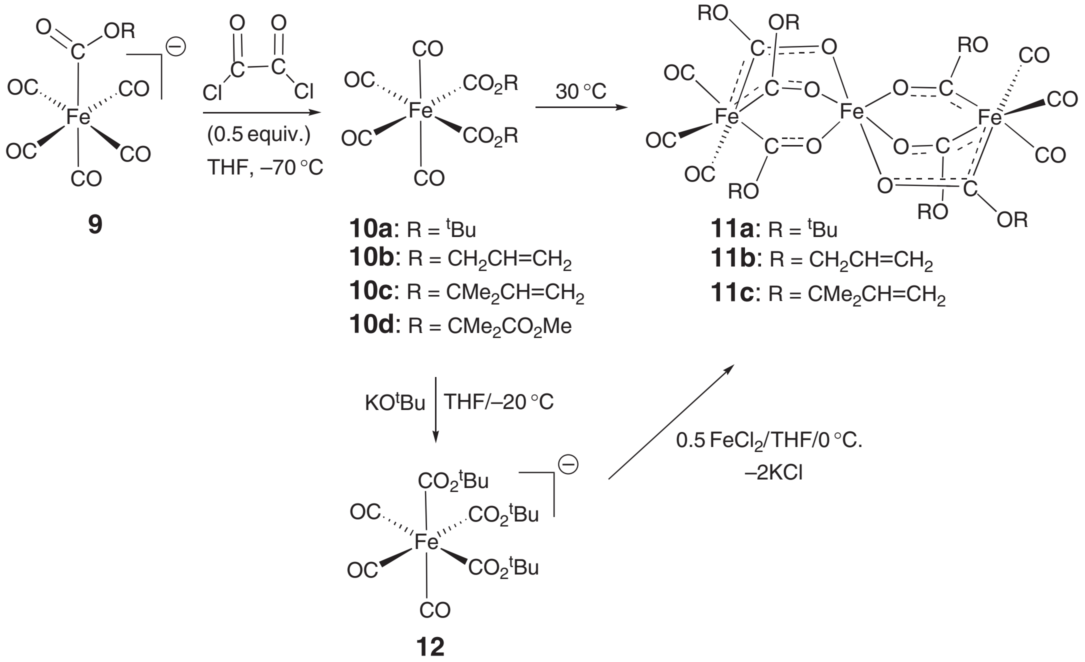
Scheme 1

ferrabicyclo[3.2.2]nonanes **8a** and **8b** have been obtained by reactions of the bis(triflates) $Z(CH_2OSO_2CF_3)_2$ (Z = *cis*-1,4- and *cis*-1,3-cyclohexane) with $Na_2[Fe(CO)_4]$. In the presence of CO, the ketones bicyclo[3.2.2]nonane-3-one and bicyclo[3.2.1]nonane-3-one are formed from these cyclic dialkyls.[18]

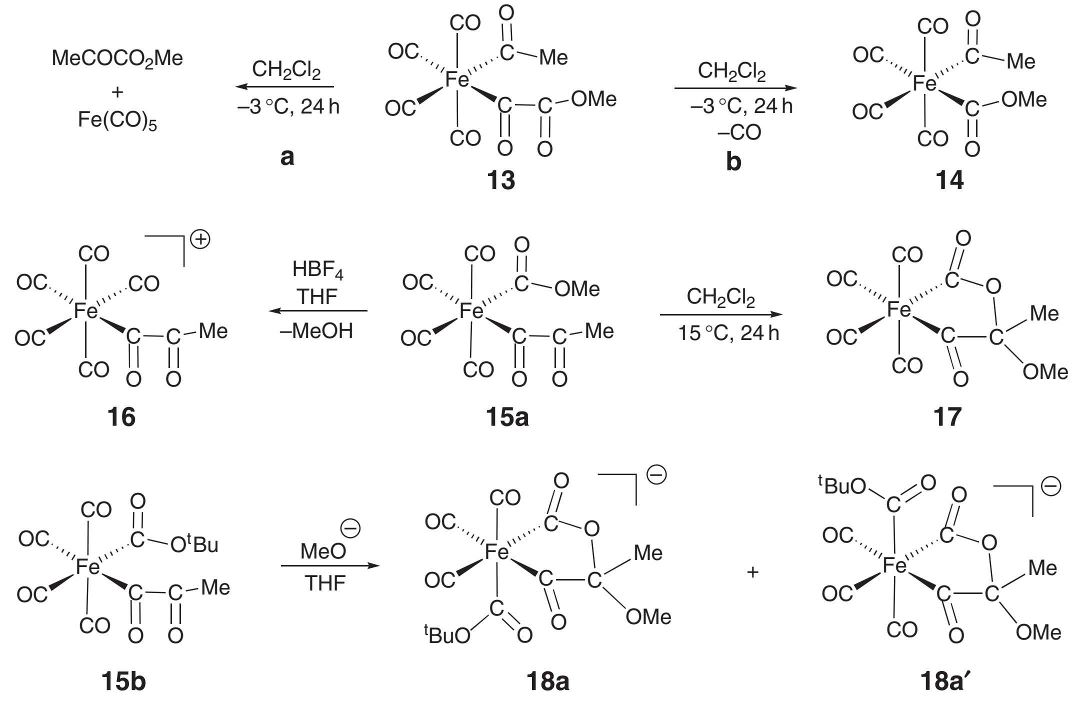
In an analogous manner, reaction of 1,2-bis[2-(trifluoromethylsulfonyloxy)ethyl]benzene and 1,2-bis[3-(trifluoromethylsulfonyloxy)propyl]benzene with $[Fe(CO)_4]^{2-}$ gave the corresponding ferracyclophanes. After CO insertion into the Fe–C σ-bonds of the ferracycles, the ketones 3-oxo[5]*ortho*-cyclophane and 3-oxo[5.2]*ortho*-cyclophane were formed.[19] This bis(triflate) route offers also an easy approach for macrocycles functionalized with two keto groups, such as 1,10-cyclooctadecanedione.[20–22] Based on an analogy with Collman's sequence for converting alkyl halides and triflates (see above) to ketones, chlorodiphenylphosphine was reacted with $Li[RC({=}O)Fe(CO)_4]$ (R = ^{n}Bu, ^{t}Bu) to give the corresponding acylphosphine complexes $[Fe\{PPh_2C({=}O)R\}(CO)_4]$, most probably via formation of a phosphido intermediate *cis*-$[Fe(PPh_2)\{C({=}O)R\}(CO)_4]$ undergoing a reductive coupling of the acyl and phosphido moieties.[23] The outcome of the reaction of $[NEt_4][CH_3C({=}O)Fe(CO)_4]$ with CH_3I and diphenylacetylene depends on the stoichiometry: carrying out the reaction of the acylferrate with 0.5 equiv. of CH_3I and PhC≡CPh yields the dinuclear compound $[NEt_4][Fe_2(CO)_6(\mu_2\text{-}CPh{=}CPhOCH_3)]$, while employing an excess of methyl iodide affords both the dinuclear complex $[Fe_2(CO)_6\{\mu\text{-}CPhCPhCCH_3(OCH_3)\}]$ and, as major product, the ferracyclopentendione $[NEt_4][IFe(CO)_3\{C({=}O)CPh\}_2]$.[24] The molecular structure determination of this maleoyl salt reveals the iodo ligand being perpendicular to the five-membered ferracycle, which stems from C–C coupling between two carbonyls with the alkyne. Extremely unstable bis(carbamoyl) complexes $[Fe(CO)_4\{C({=}O)NR_2\}_2]$ result from reactions of carbamoylferrates $Li[Fe(CO)_4\{C({=}O)NR_2\}]$ with oxalyl chloride.[25] The same reaction, performed with $Li[Fe(CO)_4\{C({=}O)N(H)R\}]$, bearing a primary carbamoyl, is supposed to yield as first intermediate *cis*-$[Fe(CO)_4\{C({=}O)N(H)R\}_2]$, which rearranges under extrusion of CO_2 and RNH_2 to afford finally the isocyanide complexes $[Fe(CO)_4(CNR)]$ (R = Me, Et, allyl, ^{t}Bu, C_6H_{11}, Ph, benzyl).[26] Treatment of the alkoxycarbonylferrates $Na[Fe(CO)_4\{C({=}O)OR\}]$ **9**, bearing bulky alkoxycarbonyl groups (R = *t*-Bu, $CMe_2CH{=}CH_2$), with 0.5 equiv. of oxalyl chloride at −30 °C leads (via a putative C(=O)–C(=O)-bridged dinuclear intermediate $[Fe\{C({=}O)OR\}(CO)_4\{C({=}O)\}]_2$) to the dimeric Fe–Fe compounds $[Fe(CO)_4\{C({=}O)OR\}]_2$. The existence of a metal–metal bond was confirmed by an X-ray diffraction study conducted on the *t*-Bu derivative.[27,28] When the addition of ClC(=O)C(=O)Cl to the bulky ferrates **9** is performed at −70 °C, the products of the reaction are the mononuclear bis(alkoxycarbonyls) *cis*-$[Fe(CO)_4\{C({=}O)OR\}_2]$ **10**. The crystal structure of octahedral **10a**, revealing rather short Fe–$CO_2{}^t$Bu distances of 200.9(2) pm, has been resolved.[27] The outcome of the alkoxy–amine exchange of **10b** in the presence of PR_3 was found to depend on both the phosphine and the amine used to achieve the process: when performed with $HNEt_2$ and PMe_3, the exchange gave rise to *fac*-$[Fe(CO)_3\{C({=}O)Oallyl\}\ \{C({=}O)NEt_2\}(PMe_3)]$. With HN^nPr_2 and PPh_3, dicarbonyl complex $[Fe(CO)_2\{C({=}O)Oallyl\}\ \{\eta^2\text{-}C({=}O)NEt_2\}(PPh_3)]$ bearing a η^2-carbamoyl ligand was isolated.[25]

Instead of the expected C–C coupling producing oxalates, thermolysis of mononuclear bis(alkoxycarbonyls) **10** at 30 °C was found to afford the novel trimetallic compounds $\{(CO)_3Fe(\mu,\eta^2\text{-}CO_2R)_3\}_2Fe$ **11**.[29] The crystal structure of **11b** shows that the central Fe(II) atom is surrounded by two *fac*-$[(CO)_3Fe(CO_2CH_2CH{=}CH_2)_3]^-$ entities acting as tridentate ligands encapsulating this center, the six μ-alkoxycarbonyls being equivalent with *d*(Fe–C) = 199.1(3) pm. Mössbauer studies revealed a high-spin configuration of the central iron atom and a low-spin configuration of the two lateral iron atoms; the magnetic moments determined by ESR are in the range between 5.20–5.45 μ_B. Complex **11a** has been independently synthesized by addition of $FeCl_2$ to $K[Fe(CO)_3\{C({=}O)O^tBu\}_3]$ **12** in 74% yield (Scheme 2).

The latter salt **12**, as well a series of other derivatives of type $[Fe(CO)_2L(R)(R^1)(CO_2R^2)]^-$, have been obtained quantitatively by nucleophilic attack of OR^- (R = Me, ^{t}Bu) on a terminal carbonyl ligand of *cis*-$[Fe(CO)_3L(R)(R^1)]$ (L = CO, $P(OEt)_3$; R, R^1 = CO_2Me, $CO_2{}^tBu$, CH_2CO_2Me, $COCO_2Me$). The facial arrangement of the three alkoxycarbonyls of **12** was corroborated by an X-ray diffraction study.[30] Two independent strategies were developed to prepare (alkoxycarbonyl)–(alkyloxalyl) complexes *cis*-$[Fe(CO)_4\{C({=}O)OR\}\{C({=}O)CO_2R^1\}]$ (R = R^1 = Me; R = R^1 = Et; R = R^1 = ^{i}Pr; R = Me, R^1 = Et; R = Et, R^1 = Me).[31] The first one consists in addition of $ClC({=}O)CO_2R^1$ to $Na[Fe(CO)_4(CO_2R)]$ in THF at −20 °C. The second one is based on the synthesis of bis(alkyloxalyl) complexes *cis*-$[Fe(CO)_4\{C({=}O)CO_2R\}_2]$ (R = Me, Et) from $Na[Fe(CO)_4\{C({=}O)CO_2R\}]$ and $ClC({=}O)CO_2R$ in THF at −40 °C and subsequent mono-decarbonylation at +12 °C. The complexes *cis*-$[Fe(CO)_4\{C({=}O)OR\}\{C({=}O)CO_2R^1\}]$ thus obtained decompose gradually at +28 °C by two different pathways: further mono-decarbonylation leads to the bis(alkoxycarbonyls) $[Fe(CO)_4\{C({=}O)OR\}_2]$, while reductive elimination gives oxalates $RO_2C\text{–}CO_2R$ and $[Fe(CO)_5]$. Bulky and more electron-donating R or R^1 groups favor the latter thermolysis pathway, and this is the only one observed when the CO *trans* to the alkyloxalyl is substituted by PPh_3. Protonation of *cis*-$[Fe(CO)_4\{C({=}O)OMe\}\{C({=}O)CO_2Me\}]$ with HBF_4 causes elimination of MeOH from the methoxycarbonyl ligand, thus generating the salt $[Fe(CO)_5\{C({=}O)CO_2Me\}][BF_4]$. In a similar manner, the



Scheme 2



Scheme 3

pyruvyl(methoxycarbonyl) complex **15a** is converted to [Fe(CO)$_5${C(═O)C(═O)Me}][BF$_4$] **16** (Scheme 3). Conversely, addition of NaOEt to the cationic complex **16** generates the derivative *cis*-[Fe(CO)$_4$-{C(═O)OEt}{C(═O)-C(═O)Me}] **14b** by nucleophilic attack on a terminal carbonyl ligand.[32] Two competing thermolysis pathways are operating for (alkoxycarbonyl)–(alkyloxalyl) complex **13** at temperatures above

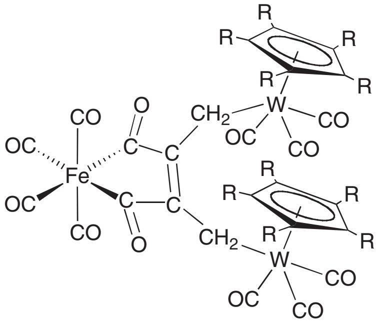
−3 °C.[33,34] The first path (a) is reductive elimination of methyl pyruvate resulting from C–C coupling between the acetyl ligand and the carbon in the β-position on the methyloxalyl entity. The second decarbonylation process (b) produces the (alkoxycarbonyl)–(acetyl) complex **14**. However, the isomeric pyruvyl(methoxycarbonyl) complex **15a**, whose crystal structure has been established,[35] exhibits a completely different reactivity pattern. By analogy to the chain-ring isomerization of organic γ-keto esters, thermolysis at +15 °C induced migration of an alkoxy group and intramolecular cyclization, thus affording quantitatively in an irreversible manner the structurally characterized alkoxy γ-metallalactone **17** (Scheme 3). A similar cyclization leading to substituted metallalactones *cis*-$[(OC)_4Fe\{C({=}O)C(CH_3)(Nu)OC\text{-}({=}O)\}]$ was induced upon addition of protic nucleophiles Nu-H such as ROH, EtSH, and HPR_2 to **15a**. An X-ray structure determination of a $P(C_6H_{11})_2$-functionalized derivative confirmed the existence of the five-membered metallacycle.[32] On the other hand, anionic trifunctionalized metallalactones $[(OC)_3Fe\{C({=}O)C(CH_3)\text{-}(Nu)OC({=}O)\}(CO_2CH_3)]^-$ **18** were obtained as isomeric mixtures after addition of anionic reagents ($Nu^- = MeO^-$, EtO^-, MeS^-, PPh_2^-) to pyruvyl(alkoxycarbonyl) complexes **15**, as exemplified for the reaction of **15b** with methanolate leading to **18a/18a′** (Scheme 3).[35]

When the stronger base $^tBuO^-$ is added to **15a** or **15b**, the major product of the process, after acidification with HCl, is the structurally characterized methylene-substituted metallalactone *cis*-$[(OC)_4Fe\{C({=}O)C({=}CH_2)\text{-}OC({=}O)\}]$. The synthesis and reactivity of complexes *cis*-$[Fe(CO)_4\{(CO)_xR\}\{(CO)_yR^1\}]$ ($x + y = 0, 1, 2, 3, 4$), including thermolysis, double carbonylation, and detailed mechanistic discussions, have been reviewed.[36,37]

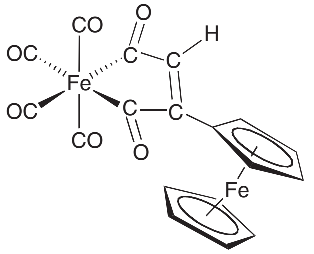
Reaction of the carbamoyl(trifluoromethyl) complex $[Fe(CO)_2\{\eta^2\text{-}C({=}O)N^iPr_2\}(CF_3)(PPh_3)]$[38] with potassium hydridotris(pyrazol-1-yl) borate provides the four-membered ferraoxetene $[Fe(CO)\{CF_2OC(N^iPr_2)\}\{HB(pz)_3\}]$, presumably via coupling of the carbamoyl ligand with a difluorocarbene intermediate.[39] The crystal structure reveals rather short metallacycle Fe–C bonds of 192.1 and 190.8 pm, indicating a partial carbenoid character. The ferraoxetene undergoes an unusual acid hydrolysis with aqueous HPF_6 under CO atmosphere to provide the isonitrile salt $[Fe(CO)_2(CN^iPr)\{HB(pz)_3\}][PF_6]$.[40] Halogenation of the carbamoylferrate $Li[Fe(CO)_4\{C({=}O)N^iPr_2\}]$ with I_2 or Br_2 in the presence of triphenylphosphine led to $[Fe(CO)_2(X)\{\eta^2\text{-}C({=}O)N^iPr_2\}(PPh_3)]$ (X = Br, I), which was finally converted under a CO atmosphere to the stable salt $[Fe(CO)_3\{\eta^2\text{-}C({=}O)N^iPr_2\}(PPh_3)][BF_4]$ by halide abstraction with $AgBF_4$.[41] One carbonyl ligand is labile and readily replaced by PPh_3 to yield structurally characterized *trans*-$[Fe(CO)_2\{\eta^2\text{-}C({=}O)N^iPr_2\}(PPh_3)_2][BF_4]$, while addition of dppe led to substitution of one CO and the PPh_3 ligand to provide the chelate complex $[Fe(CO)_2\{\eta^2\text{-}C({=}O)N^iPr_2\}(dppe)][BF_4]$ (dppe = 1,2-bis-(diphenylphosphino)ethane).[42]

Since COMC (1995), no new reports on isolable mononuclear formyls $[L_nFe\{C({=}O)H\}]$ have appeared. However, stable heterodinuclear formyl-bridged Mo(μ-OCH)Fe bimetallics have been isolated in high yields by rapid insertion of $[Fe(CO)_5]$ into the Mo–H bond of *mer*-$[Mo(CO)H(NO)(PMe_3)_3]$ and *trans*-$[Mo(H)(NO)(dmpe)_2]$, respectively (dmpe = 1,2-bis(dimethylphosphino)ethane).[43,44] In the crystal structures of μ-formyl complexes $[(Me_3P)_3(ON)\text{-}(OC)Mo(\mu\text{-}OCH)Fe(CO)_4]$ and $[Mo(dmpe)_2(NO)(\mu\text{-}OCH)Fe(CO)_4]$, the formyl groups occupy axial positions of trigonal-bipyramidal iron moieties. The relatively short Fe–C bond distances of 191.7(3) and 195.3(11) pm may be indicative of a partial carbenoid contribution involved in the Fe–C(formyl) interactions. In an analogous manner, the μ-formyl compound $[(Me_3P)_4(ON)W(\mu\text{-}OCH)Fe(CO)_4]$ was obtained.[45]

Several examples of neutral maleoyl complexes (ferracyclopentendiones) have been prepared via different synthetic routes, despite their common cyclic core structure (for an example of anionic ferracyclopentendione, see above): the heterotrinuclear compounds **19** have been assembled in excellent yield by treatment of the dinuclear 2-butyne-1,4-diyl tungsten complexes $[(\eta^5\text{-}C_5R_5)(OC)_3W\text{–}CH_2C{\equiv}CCH_2\text{-}W(CO)_3(\eta^5\text{-}C_5R_5)]$ (R = H, Me) with $[Fe_2(CO)_9]$ under flowing CO.[46] According to the crystal structure, the alkyne function of **19b** has undergone a double carbonylation and becomes symmetrically linked to the $Fe(CO)_4$ fragment. Photolysis of $[Fe(CO)_5]$ in the presence of ethynylferrocene led, albeit in low yield, to the structurally characterized ferracyclopentendione **20**.[47] The orthometallated hydride $[FeH(CO)_2\{P(OPh)_3\}\{P(OPh)_2OC_6H_4\}]$, generated *in situ* by UV irradiation of $[Fe(CO)_3\{P(OPh)_3\}_2]$, reacts with internal alkynes to give the maleoyls $[Fe(CO)_2\{P(OPh)_3\}_2\{\eta^1{:}\eta^1\text{-}C({=}O)C(R^1)C(R^2)C({=}O)\}]$ (**21a**, $R^1 = Ph$, $R^2 = Me$; **21b**, $R^1 = R^2 = Me$; **21c**, $R^1 = Me$, $R^2 = CH(OEt)_2$; **21d**, $R^1 = Me$, $R^2 = CH_2OH$; **21e**, $R^1 = R^2 = CH_2OH$). The *trans*-arrangement of the two phosphite ligands has been crystallographically ascertained.[48] A modification of this synthetic route employs the alkyne complex $[Fe(CO)_2\{\eta^2\text{-}PhC{\equiv}CPh\}\{P(OPh)_3\}_2]$ as starting material.[49] A mixture of the two ferracycles $[Fe(CO)_3\{P(OPh)_3\}\ \{C({=}O)CPh\}_2]$ **21f** and $[Fe(CO)_2\{P(OPh)_3\}_2\{C({=}O)CPh\}_2]$ **21g** arises from rapid insertion of an axial CO ligand into the Fe–alkyne bonds of the latter precursor. To account for the observation that ^{13}CO is incorporated into Fe–CO as well as maleoyl CO sites, the intermediacy of a five-coordinate 16-electron maleoyl species has been suggested. Similarly, conversion of $[Fe(CO)_2\{\eta^2\text{-}PhC{\equiv}CPh\}\{P(OMe)_3\}_2]$ afforded as sole product the derivative **21h**.



19a: R = H
19b: R = Me



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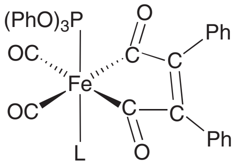
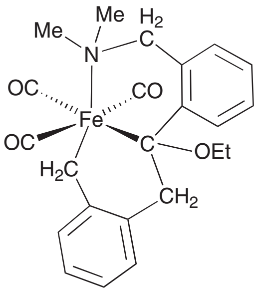


21f: L = CO
21g: L = P(OPh)$_3$
21h: L = P(OMe)$_3$

Since COMC (1995), use of (π-vinylcarbene)iron compounds as precursors for ferracyclopentenone derivatives has further evolved. Thus, [{1–3-η-l-methoxy-2,3-bis(trifluoromethyl)prop-2-en-l-ylidene}Fe(CO)$_3$] reacts with 2 molar equiv. of CO to give [tetracarbonyl-3-methoxy-4,5-bis(trifluoromethyl)ferracyclopent-3-en-2-one].[50] Likewise, treatment of [{1–3-η-1-methoxy-2,3-bis(methoxycarbonyl)-prop-2-en-1-ylidene}Fe(CO)$_3$] with 2,2′-bipyridyl or 1,10-phenanthroline gave the corresponding ferracyclopentenones, ligated by the chelating diamines.[51] The crystal structure of octahedral [dicarbonyl(bipy)-3-methoxy-4,5-bis(methoxycarbonyl)ferracyclopent-3-en-2-one] reveals that the two carbonyl groups are in *cis*-configuration; the acyl group and one of the bipy nitrogens are *trans*-arranged. Nucleophilic addition of *o*-lithiobenzyldimethylamine to a carbonyl ligand of [Fe{*o*-(CH$_2$=)$_2$C$_6$H$_4$}(CO)$_3$], followed by alkylation of the acylmetallate intermediate with [Et$_3$O][BF$_4$], led to formation of a new C–C bond in the bicyclic Fe(II)-chelate **22**.[52]

The unusual zwitterionic complexes **23** and **24** were obtained as an isomeric mixture upon treatment of [Fe$_3$(CO)$_{12}$] or [Fe$_2$(CO)$_9$] with the ylide reagent 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete in a 1 : 1 ratio in THF.[53] Noteworthy is the rather long Fe–C(diphosphete) bond length of 213.0(3) pm. Surprisingly, the composition of the isolated products depends in a sensible manner on the stoichiometry of the reactants. Conducting the same reaction in THF with [Fe$_3$(CO)$_{12}$] or [Fe(CO)$_5$] in the presence of an excess of the diphosphete yields the zwitterionic acylferrate **25** (together with the phosphonio–acetylide compound **147**, see Section 6.02.6).[54] The allyl groups of [(η^3-allyl)Fe(CO)$_3$(NO)] undergo dppe-promoted regioselective carbonylation at the less-substituted carbon of the π-allyl ligand, with retention of configuration of the allylic double bond, to give β,γ-unsaturated acyls of type [{C$_3$R$_5$C(=O)}Fe(CO)(NO)(dppe)].[55,56] A characteristic substituent effect of the η^3-C$_3$R$_5$ ligands on the rate of the CO migratory insertion was noticed on testing a series of 15 derivatives, functionalized by a range of R groups with quite divergent stereoelectronic propensities. A trigonal-bipyramidal geometry with the acyl group located at an axial position has been ascertained by X-ray analysis for [{CH$_2$=CHCH$_2$C(=O)} Fe(CO)(NO)(dppe)]. Unsaturated carboxylic acid esters and amides were prepared upon treatment of the acyl iron complexes with alcohols or amines in the presence of iodine.



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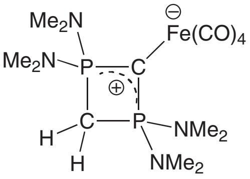

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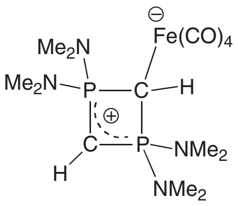

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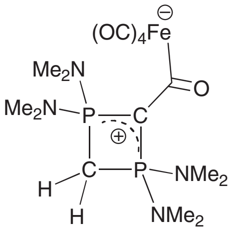
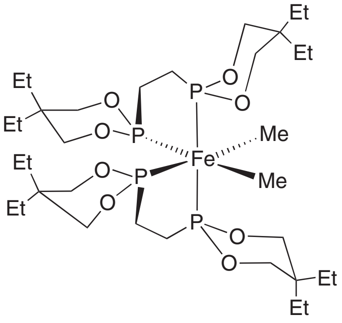


25

The energetics and mechanism of the decarboxylation of the hydroxycarbonyl compound [Fe(CO$_2$H)(CO)$_4$]$^-$, and its reactivity toward SO$_2$ has been investigated using the flowing afterglow–triple quadrupole technique.[57] The gas-phase reaction of C_2H_5I with photogenerated $[Fe(CO)_4]$ was followed using time-resolved IR in conjunction with kinetic measurements.[58] C_2H_5I oxidatively adds to $[Fe(CO)_4]$ to produce first $[FeI(C_2H_5)(CO)_4]$, which inserts CO to yield unsaturated $[FeI\{\eta^1\text{-}C({=}O)C_2H_5\}(CO)_3]$. This intermediate then undergoes acetyl "slippage" to produce the η^2-complex $[FeI\{\eta^2\text{-}C({=}O)C_2H_5\}(CO)_3]$. In the presence of CO, $[FeI\{\eta^1\text{-}C({=}O)C_2H_5\}(CO)_3]$ is converted to $[FeI\{\eta^1\text{-}C({=}O)C_2H_5\}(CO)_4]$, which is stable enough to survive for minutes. The relative stability of the η^1- and η^2-acyl isomers of $[Fe(X)\{C({=}O)R\}(CO)_3]$ (R = Me, Et, ^{t}Bu; X = I, H, Me) was investigated using DFT calculations. The compound $[Fe(CH_3)\{\eta^2\text{-}C({=}O)C(CH)_3\}(CO)_3]$ is the most stable of the acyls studied.[59] The bonding and geometries of $[(H_2)Fe(CO)_3]$, $[(H_2)Fe(CO)_3(C_2H_4)]$, and $[HFe(CO)_3(C_2H_5)]$, which are species relevant to iron carbonyl-catalyzed olefin–hydrogenation, were analyzed using DFT calculations. The dihydrogen complex $[(H_2)Fe(CO)_3(C_2H_4)]$ can rearrange to form hydride $[HFe(CO)_3(C_2H_5)]$. Reductive elimination of C_2H_6 from $[HFe(CO)_3(C_2H_5)]$ is exothermic, whether it is accompanied by or precedes ethylene addition.[60]

Several papers deal with the synthesis and reactivity of simple dileptic, electron-rich mono- and bis(alkyls) coordinated by chelating bi-, tri-, and tetradentate phosphite and phosphine ligands. The principal route implies alkylation of a halogeno precursor $(P{\cap}P)_nFeX_2$ by RLi, RMgX or Me_2Mg. For instance, methylation of the tied-back diphosphonite ligated starting compound *cis*-$[FeCl_2(P{\cap}P)_2]$ ($P{\cap}P$ = 1,2-bis(2,2-diethyl-1,3-propanedioxyphosphino)ethane) with Me_2Mg afforded complex **26**, for which a molecular structure was obtained.[61] As a synthon for the organometallic chemistry of *o*-phenylenebis(dimethylphosphine) (pdmp)-containing iron complexes, *trans*-$[FeCl_2(pdmp)_2]$ has been prepared and this reacts with an excess of MeLi affording **27b**, isolated as *cis*/*trans* mixture.[62] One of the methyl groups is cleaved after addition of 1 equiv. of HCl to give **27a**. The ethylene in $[Fe(\eta^2\text{-}CH_2{=}CH_2)(pdmp)_2]$ is readily protonated by $HBF_4{\cdot}Et_2O$ to afford the salt $[Fe(C_2H_5)(pdmp)_2][BF_4]$, in which the ethyl group may be agostic.



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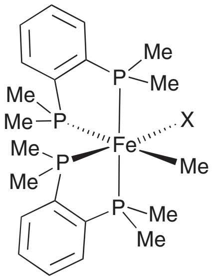
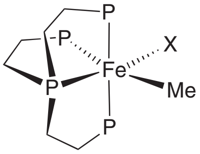


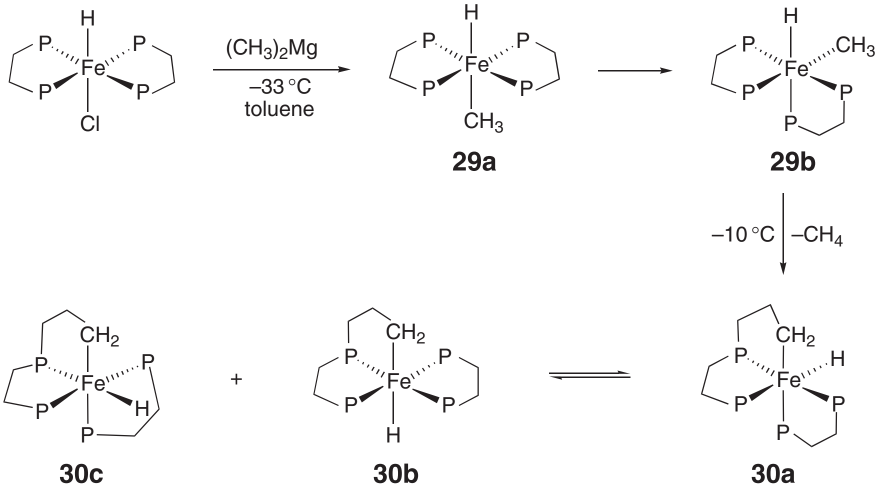
27a: X = Cl
27b: X = Me



28a: X = Cl
28b: X = Me

A number of complexes of the tripodal tetraphosphine $P(CH_2CH_2PMe_2)_3$ (pp_3) has been synthesized, including $[FeCl_2(pp_3)]$, $[FeClH(pp_3)]$, $[FeMeCl(pp_3)]$ **28a**, and $[FeMe_2(pp_3)]$ **28b**.[63] Complex $[FeClH(pp_3)]$ reacts with acetaldehyde in EtOH to give the methyl carbonyl salt $[FeMe(CO)(pp_3)]^+$.[64] The latter compound was also obtained independently by carbonylation of **28a** in THF; the structure determination confirms that the methyl group is *cis*- to the central phosphorus atom [d(Fe–C) = 214.0(3) pm]. Further information on *trans*-$[FeCl(CH_3)(dmpe)_2]$ and *trans*-$[FeCl(CH_3)(depe)_2]$ as precursors for the preparation of corresponding acetylido (methyl)iron(II) complexes is given in Section 6.1.2.1.5 (depe = 1,2-bis(diethylphosphino)ethane).[65] The transient photochemistry in solution and low-temperature matrix photochemistry of $[Fe(dmpe)_2H_2]$ has been investigated. Pulsed-laser photolysis (308 nm) of alkane solutions of the dihydride at ambient temperature generates unsaturated $[Fe(dmpe)_2]$ within 30 ns. In the absence of added quenchers, the latter decays by reaction with the alkane solvent. UV irradiation in a methane matrix generates the alkyl hydride $[FeH(CH_3)(dmpe)_2]$.[66] The closely related methyliron hydride *trans*-$[FeH(CH_3)\ (dprpe)_2]$ **29a** (dprpe = 1,2-bis(dipropylphosphino)ethane) isomerizes slowly at −33 °C to *cis*-$[FeH(CH_3)(dprpe)_2]$ **29b**.[67]

At −10 °C, **29b** undergoes reductive elimination accompanied by quantitative conversion into the cyclometallated hydride **30a** by C–H activation of a propyl group. Raising the temperature to ambient causes partial isomerization of **30a** to produce two new isomeric cyclometallated complexes **30b** and **30c** (Scheme 4). After 30 min at room temperature, an equilibrium mixture was established with **30a**, **30b**, and **30c** present in a 70 : 22 : 8 ratio. Elimination of H_2 and concomitant C–H activation generating **30a** was also induced by photolysis of $[FeH_2(dprpe)_2]$ at −80 °C.

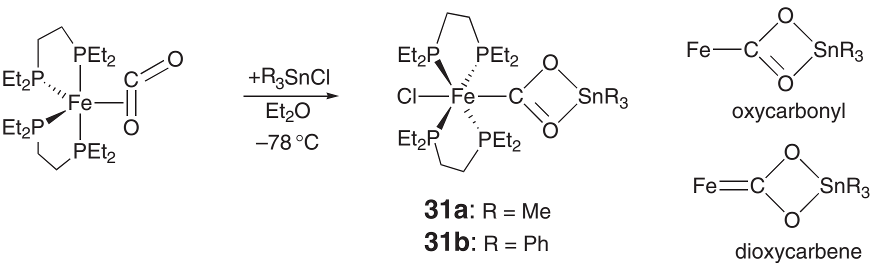


Scheme 4

The enhanced nucleophilicity of coordinated CO_2 in complex $[Fe(CO_2)(depe)_2]$ allowed reaction with organotin chlorides. In the resulting carboxylate complexes **31**, the CO_2 unit links the two metals via a μ-$\eta^1(C)$:$\eta^2(O,O')$ bonding mode.[68] Although the X-ray data of **31b** exclude the contribution of a carbenoid form in the solid state, chemical shifts of μ-CO_2 in the ^{13}C NMR spectra indicate a borderline case between oxycarbonyl and dioxycarbene character (Scheme 5).

Attempts to isolate stable 14-electron high-spin dialkyls of stoichiometry $[FeR_2(dippe)]$ by reaction of $[FeBr_2(dippe)]$ with $MgEt_2$ or Mg^tBu_2 in aromatic solvents failed (dippe = 1,2-bis(diisopropylphosphino)ethane). Presumably, the species $[FeR_2(dippe)]$ are first generated, but undergo β-elimination to give iron(II) hydrides. These unstable intermediates then reductively eliminate H_2 to afford finally the iron(0) arene compounds $[Fe(\eta^6\text{-arene})(dippe)]$.[69] Alternatively, $[Fe(\eta^6\text{-}p\text{-xylene})(dippe)]$ was isolated after hydrogenation of paramagnetic $[Fe(CH_2C_6H_4\text{-}p)_2(dippe)]$[38] in Et_2O by addition of a hydrogen atom to the α-carbon of the p-methylbenzyl substituent.

The design of new chelating phosphine ligands incorporating heteroelements has allowed the isolation of a range of novel, relatively stable paramagnetic iron alkyls. The preparation of $[FeR\{N(SiMe_2CH_2PPh_2)_2\}]$ containing an amidodiphosphine ligand was examined: compounds containing small alkyl groups such as R = Me or CH_2Ph were found to be thermally labile, whereas for bulky R = CH_2SiMe_3 and $CH(SiMe_3)_2$, stable yellow solids could be obtained.[70] A structural determination of the $CH(SiMe_3)_2$ derivative established a tetrahedral geometry around the iron(II) center and an Fe–C bond distance of 206.9(2) pm. From the magnetic moment of 5.3 μ_B, an electronic configuration with four unpaired electrons with a second-order orbital contribution was concluded. Several coordinatively unsaturated pseudotetrahedral complexes $[FeR\{PhB(CH_2P^iPr_2)_3\}]$ (R = Me, CH_2Ph, CH_2CMe_3), supported by a second-generation tripodal $\{PhB(CH_2P^iPr_2)_3\}^-$ ligand, have been prepared from $[FeCl\{PhB(CH_2P^iPr_2)_3\}]$.[71] These paramagnetic 14-electron species were structurally characterized, their solution magnetism indicating four unpaired electrons ($S = 2$) and CV revealing a reversible wave at low potential assigned as an Fe(II/I) redox process. These



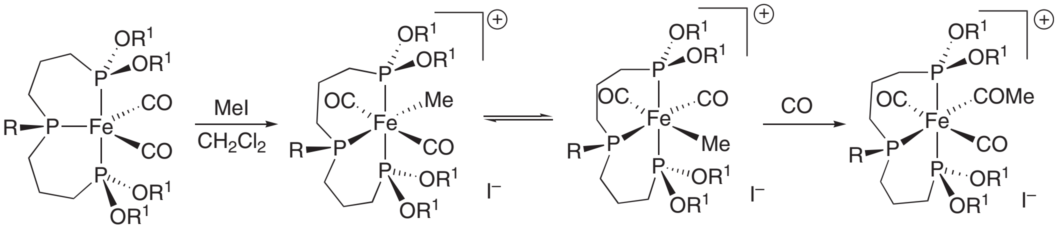
Scheme 5

alkyls can each be hydrogenated to liberate RH in the presence of PR_3 to afford diamagnetic iron(IV) trihydrides $[FeH_3(PR_3)\{PhB(CH_2P^iPr_2)_3\}]$. Insertion of ethylene into Fe–H bond of the latter hydrides produces cleanly the stable ethyl complex $[FeEt(PR_3)\{PhB(CH_2P^iPr_2)_3\}]$ along with an equivalent of ethane. Likewise, the insertion product $[Fe(C_2H_4Ph)(PR_3)\{PhB(CH_2P^iPr_2)_3\}]$ is detected as intermediate during catalytic styrene hydrogenation.

An extensive number of papers reports also on the synthesis and reactivity, including kinetic and mechanistic investigations, of phosphine- and phosphite-substituted iron carbonyls with σ-bound alkyl, acyl, and iminoacyl groups. Oxidative addition of CH_3I to $[Fe(CO)_2\{MeP(CH_2CH_2CH_2PMe_2)_2\}]$ proceeds instantaneously yielding the octahedral cationic complexes *mer,trans*-$[FeMe(CO)_2\{MeP(CH_2CH_2CH_2PMe_2)_2\}]I$ and *mer,cis*-$[FeMe(CO)_2$-$\{MeP(CH_2CH_2CH_2PMe_2)_2\}]I$. In contrast to their Ru counterparts, both isomers are resistant toward CO migratory insertion.[72] Similarly, oxidative addition of CH_3I to **32** yielded an isomeric mixture of the methyls **33** according to Scheme 6. Derivative **33d** (as the BPh_4 salt) was structurally characterized.[73]

Unexpectedly, efforts to alkylate **32** with EtI, ^iPrI, or ^nPrI afforded rather the cationic iodo complexes *mer,cis*-$[FeI(CO)_2(triphos)]I$. Reaction of **33** with CO produced the acetyl compounds **34a–d**. In an attempt to prepare ketene complexes, **34** was treated with bases. Indeed, deprotonation of the acyl group was achieved, but instead the hoped-for ketene compound, only starting material **32** was formed. However, functionalized ketene complexes were accessible from carbonyl coupling reactions using PEt_3-ligated iron acyl precursors.[74] The latter result from oxidative addition of XCH_2CO_2R substrates bearing electron-withdrawing ester functionalities onto $[Fe(CO)_2(PEt_3)_2(N_2)]$. In Scheme 7, it is suggested that the alkyls **35a–c** thus formed partially isomerize into η^2-acyls **36**. Subsequent deprotonation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or lithium diisopropylamide (LDA) should generate an equilibrium mixture of anionic species **37** and **38**. Trapping of **38** with Me_3SiCl, isolation of the *O*-silylated metallacycles **39a–c**, and structural characterization of **39a** support this hypothesis. Another possibility for trapping **37** and **38** is replacement of X by CO, allowing both the isolation of the ketene complexes **40′** and their isomers **41a** and **41b**. Exemplary X-ray diffraction studies have been carried out on **40a′** and **41b**. In a comparable manner, $[Fe(CH_2R)Br(CO)_2(PEt_3)_2]$ (R = 1,3-dioxolan-2-yl, 2,4,10-trioxoadamantan-3-yl) were prepared and converted in the presence of CO and DBU to *E,Z* mixtures of the corresponding stable ketene complexes $[Fe\{\eta^2(C,O)$-$COCHR\}Br(CO)_2(PEt_3)_2]$.[74]

No ketene conversion could be achieved using $[Fe(CH_2Y)X(CO)_2(PEt_3)_2]$ (Y = Cl, I, CN; X = Cl, I) as starting material, while in the case of $[Fe(CH_2R)I(CO)_2(PEt_3)_2]$ (R = H, CH_3, $SiMe_3$), only IR detection of the resulting labile ketene complexes was possible. The structural determination of *trans,cis*-$[Fe(CH_2Cl)Cl(CO)_2(PEt_3)_2]$ is worth mentioning, which represents a rare example of a structurally characterized iron halomethyl complex [d(Fe–C) = 204.8(6) pm].[74] A number of other methyl complexes $[FeMe(X)(CO)_2(PR_3)_2]$ ($PR_3 = PMe_3$, $PPhMe_2$, PPh_2Me, $P(OMe)_3$, P^nBu_3) has been prepared, the photochemical isomerization of *cis,trans*-$[FeMe(I)(CO)_2(PMe_3)_2]$ to *trans,trans*-$[FeMe(I)(CO)_2(PMe_3)_2]$ effectuated in the solid state being noteworthy.[75] The thermodynamics and kinetics of migratory CO insertion into the Fe–Me bond of that series has been studied. The formation rates and the equilibrium constants of *cis,trans*-acetyl with respect to *cis,trans*-methyl follow the order NCS > CN > Cl > Br > I and are determined by the electron-withdrawing propensity of X, while the equilibrium constants of *trans,trans*-acetyl as compared to *cis,trans*-acetyl follow the order I > Br > Cl >> CN > I and are influenced by the steric hindrance of the



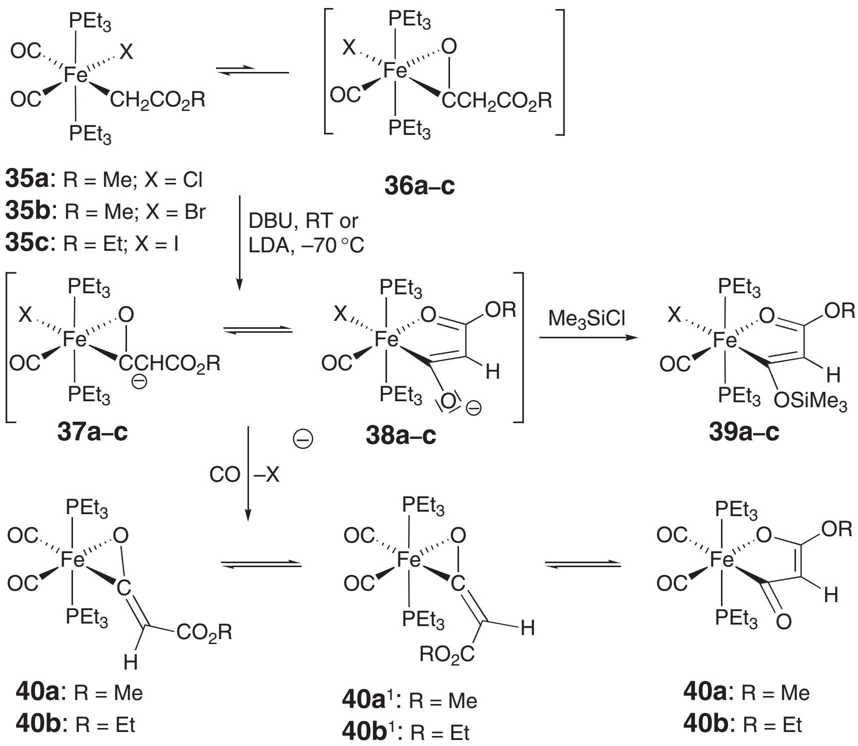
32a: R = Ph; $R^1 = {}^iPr$
32b: R = Cy; $R^1 = {}^iPr$
32c: R = Ph; R^1 = Me
32d: R = Cy; R^1 = Me

33a: traces
33b: 95%
33c: traces
33d: 100%

33a′: 100%
33b′: 5%
33c′: 100%
33d′: traces

34a
34b
34c
34d

Scheme 6



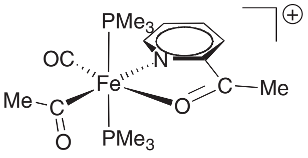
Scheme 7

ligands. A comparison of NMR data and thermodynamic results with related alkylosmium and alkylruthenium complexes has been made.[76]

The carbonylation reaction of *cis,trans*-[FeMeI(CO)$_2$(PMe$_3$)$_2$] to *cis,trans*-[Fe{C(=O)Me}I(CO)$_2$(PMe$_3$)$_2$] and isomerization to *trans,trans*-[Fe{C(=O)Me}I(CO)$_2$(PMe$_3$)$_2$] was studied in polar and apolar solvents.[77] The results suggest that the first step of the carbonylation is the formation of the ionic intermediate [Fe(CH$_3$)(CO)$_3$(PMe$_3$)$_2$]I; the acetyl complexes are both formed from this intermediate but at different rates due to the differential cooperative effect of the anion. Further information was obtained from structural studies of complexes *cis,trans*-[Fe(CH$_3$)I(CO)$_2$(PMe$_3$)$_2$] and *trans,trans*-[Fe(CH$_3$)I(CO)$_2$(PMe$_3$)$_2$]. Nucleophilic substitution of iodide in *cis,trans*-[Fe(CH$_3$)I(CO)$_2$(PMe$_3$)$_2$] was studied in CH$_2$Cl$_2$ using bromide salts with different structure and solvation. Analysis of the rate constants suggests that the reaction takes place via two reaction paths: the principal path involves the free ion (Br$^-$), whereas the second path involves the ion pair (A$^+$Br$^-$), and its rate generally increases as the dissociation constants of the salt increase.[78] [Fe(CH$_3$)I(CO)$_2$(PMe$_3$)$_2$] and [Fe(CH$_3$)(CO)$_3$(PMe$_3$)$_2$][BPh$_4$] react with borohydrides via a putative formyl intermediate to give *cis,trans*-[FeH$_2$(CO)$_2$(PMe$_3$)$_2$]; upon treatment with MeLi, the bis(alkyl) *cis,trans*-[Fe(CH$_3$)$_2$(CO)$_2$(PMe$_3$)$_2$] was isolated.[79] Reaction of *fac*-[Fe(CH$_3$)(CO)$_2$(PMe$_3$)$_2$][BPh$_4$] with MeLi produces first *cis,trans*-[Fe{C(=O)Me}(CH$_3$)(CO)$_2$(PMe$_3$)$_2$], which then decarbonylates to give the dimethyl complex. Upon exposure to CO, the latter reductively eliminates CH$_3$C(=O)C(=O)CH$_3$. The dimethyl compound was otherwise synthesized by action of MeLi on *cis,trans*-[FeCl$_2$(CO)$_2$(PMe$_3$)$_2$] and possesses rather long average Fe–Me bond distances of 213.5 pm.[80] The reaction of *cis,trans*-[Fe(CH$_3$)$_2$(CO)$_2$(PMe$_3$)$_2$] with B(C$_6$F$_5$)$_3$ involves Me abstraction from the metal with formation of decomposition products along with generation of redistribution products *fac*-[Fe(CH$_3$)(CO)$_3$(PMe$_3$)$_2$][MeB(C$_6$F$_5$)$_3$] and *fac*-[Fe(CH$_3$)(CO)$_2$(PMe$_3$)$_3$][MeB(C$_6$F$_5$)$_3$].[81]

Insertion of ethylene into an Fe–H bond of the dinuclear [Fe]H$_2$-ase model complex [Fe(μ-H)(CO)$_2$(PMe$_3$)$_2$-(μ-SCH$_2$CH$_2$CH$_2$S)]$_2$ leads to an Fe–ethyl intermediate.[82] Intramolecular oxidative addition of an Sn–Me group of [Fe(CO)$_4$(Ph$_2$PCH$_2$CH$_2$SnMe$_3$)] allowed the isolation of the five-membered chelate complex *mer*-[Fe(CH$_3$)(CO)$_3$(Ph$_2$PCH$_2$CH$_2$SnMe$_2$)] with *cis*-disposition of the Fe–Me and Fe–SnPh$_2$R ligands.[83]

In continuation of previous studies on the isocyanide insertion into Fe–alkyl bonds described in COMC (1995), the equilibrium and kinetics of ^{t}BuNC insertion of *cis,trans*-[FeMe(CN^{t}Bu)(CO)$_2$(PMe$_3$)$_2$]X (X$^-$ = I$^-$, BPh$_4$$^-$, BF$_4$$^-$) affording iminoacyls [Fe(η^2-CMe=N^{t}Bu)(CO)$_2$(PMe$_3$)$_2$]X were investigated in various solvents.[84] The reaction proceeds via an associative mechanism with preliminary formation of contact ion pairs. The structure of the contact ion pair, which is independent of the nature of the solvent and of the counterion, was studied by ^{1}H-NOESY and ^{19}F{^{1}H}-HOESY NMR spectroscopy. In the BPh_4^- and BF_4^- salts, the counterion is located between the CO and the isocyanide ligands; in the iminoacyl complexes, the counterions BPh_4^- and BF_4^- are located near the dihapto iminoacyl ligand. The reaction rate increases with the charge density and the coordinating propensity of the anions, the effect of the solvent also being explained on the basis of its coordinating power. The compound *cis,trans*-$[Fe(CH_3)I(CO)_3(PMe_3)_2]$ also offers a convenient entry into the chemistry of iron alkyls containing bi- and tridentate nitrogen donors. With the objective of coordinating potentially hemilabile *N,O* ligands with a hard O function and a softer *N* function, *cis,trans*-$[Fe(CH_3)I(CO)_3(PMe_3)_2]$ was reacted with 2-acetylpyridine, 2-benzoylpyridine, and 2,2′-dipyridylketone in the presence of $NaBPh_4$ to give the salts *trans*-$[Fe\{C(=O)CH_3\}(CO)(N\cap O)(PMe_3)_2][BPh_4]$ **42–44**.[85] These complexes are present in solution as equilibrium mixtures of two stereoisomers having the *N* arm *cis* (minor isomer) or *trans* (major isomer) relative to the acetyl group. The ion-pair structures in solution and the localization of the counterion (in front of the face determined by PMe_3 and the two arms of the *N,O* ligand) were investigated by the detection of interionic contacts in the ^{1}H-NOESY NMR spectra.



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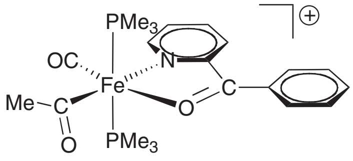

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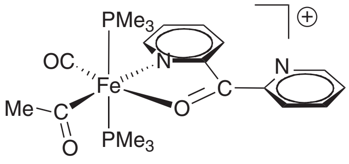


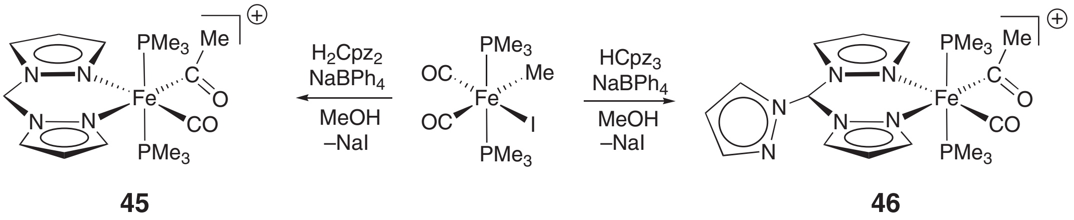
44

Relatively scarce in the past, the number of pyrazol-1-yl-containing iron alkyls has grown considerably. Apart from the above-mentioned ferraoxetene $[Fe(CO)\{CF_2OC(N^iPr_2)\}\{(pz)_3BH\}]$,[39] a number of iron methyls and acetyls has been prepared, starting from *cis,trans*-$[Fe(CH_3)I(CO)_3(PMe_3)_2]$ as precursor. For instance, addition of bis(pyrazol-1-yl)- and tris(pyrazol-1-yl)methane in the presence of $NaBPh_4$ allows the synthesis of the cationic acetyls *trans*-$[Fe\{C(=O)CH_3\}(CO)(pz_2CH_2)(PMe_3)_2][BPh_4]$ **45** and *trans*-$[Fe\{C(=O)CH_3\}(CO)(\eta^2\text{-}pz_3CH)(PMe_3)_2][BPh_4]$ **46**, respectively.[86] It was not possible to coordinate the third dangling pz cycle even after heating (Scheme 8).

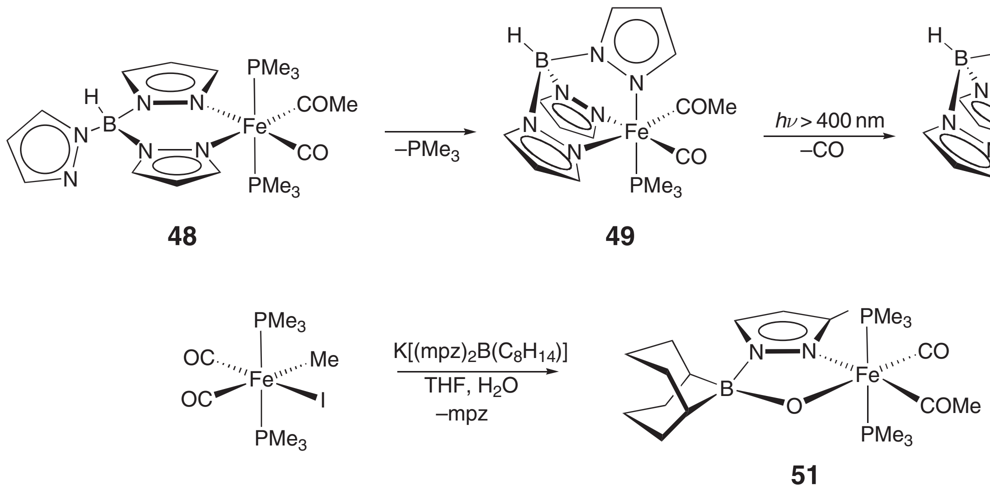
Related neutral bis- and tris(pyrazol-1-yl)borate acetyl complexes *trans*-$[Fe\{C(=O)CH_3\}(CO)(pz_2BH_2)(PMe_3)_2]$ **47** and *trans*-$[Fe\{C(=O)CH_3\}(CO)(\eta^2\text{-}pz_3BH)(PMe_3)_2]$ **48** were obtained after coordination of $K[pz_2BH_2]$ or $Na[pz_3BH]$ to *cis,trans*-$[Fe(CH_3)I(CO)_3(PMe_3)_2]$ and concomitant CO insertion.[87] In this case, the pendant pyrazolyl arm of **48** easily displaces a coordinated PMe_3 ligand upon refluxing in hexane solution to yield $[Fe\{C(=O)CH_3\}(CO)(\kappa^3\text{-}pz_3BH)(PMe_3)]$ **49** (Scheme 9). Alternatively, the acyls **47** and **48** are accessible by replacement of the coordinated isosteric poly(pyrazol-1-yl)methanes of **45** and **46** with the borates.

The synthesis of *trans*-$[Fe(CH_3)(CO)(\eta^2\text{-}pz_3BH)(PMe_3)_2]$ **50**, which represents the first example of a structurally characterized octahedral hydrotris(pyrazolyl)borate methyl complex, was achieved by visible light irradiation of **49** for 1 h.[88] The determination of the crystal structure of complex *trans*-$[Fe\{C(=O)CH_3\}(CO)(\kappa^2\text{-}mpz\text{-}OBC_8H_{14})(PMe_3)_2]$ **51** reveals an oxygen incorporation, originating from partial hydrolysis of the methylpyrazolyl ligand $K[(mpz)_2B(C_8H_{14})]$. The aroyl compound $[Fe\{C(=O)C_6H_3Me_2\}(CO)_2(\kappa^3\text{-}pz_3BH)]$ results from reaction of $[Fe(CO)_2(I)\{\eta^2\text{-}C(=O)C_6H_3Me_2\}(PPh_3)]$ with $K[pz_3BH]$.[89]

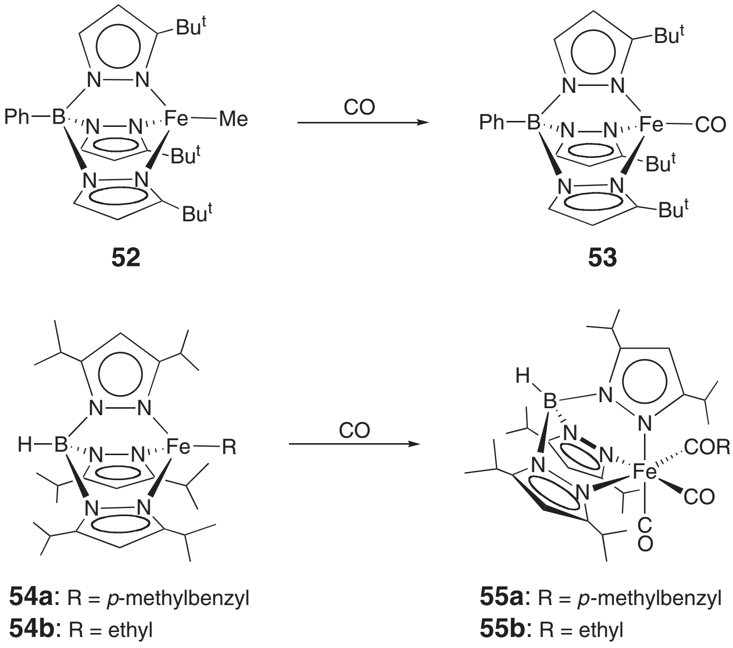
An exciting recent development, initiated almost simultaneously by several groups, is the isolation of stable, unsaturated four-coordinate tris(pyrazolyl)borate-containing iron alkyls, allyls, and acetylides. It seems that steric shielding by bulky ^{t}Bu or ^{i}Pr substituents on the pz rings is a prerequisite for the stabilization of these species. The



Scheme 8



Scheme 9



Scheme 10

14-electron complex $[\mathrm{Fe(CH_3)}\{\kappa^3\text{-}(^t\mathrm{Bupz})_3\mathrm{BPh}\}]$ **52** was obtained via reaction of $[\mathrm{FeCl}\{\kappa^3\text{-}(^t\mathrm{Bupz})_3\mathrm{BPh}\}]$ with either MeLi or $\mathrm{MgMe_2}$ (Scheme 10).[90] Structurally characterized **52**, having an unexceptional Fe–$\mathrm{CH_3}$ bond distance of 207.9(3) pm, reacts with MeI to afford $[\mathrm{FeI}\{\kappa^3\text{-}(^t\mathrm{Bupz})_3\mathrm{BPh}\}]$; surprisingly, cleavage of the Fe–$\mathrm{CH_3}$ bond occurs also during reaction with CO, producing the novel 15-electron iron(I) carbonyl complex $[\mathrm{Fe(CO)}\{\kappa^3\text{-}(^t\mathrm{Bupz})_3\mathrm{BPh}\}]$ **53**. The 17-electron dinitrosyl compound $[\mathrm{Fe(NO)_2}\{\eta^2\text{-}(^t\mathrm{Bupz})_3\mathrm{BPh}\}]$ was isolated after treatment of **52** with NO.[90]

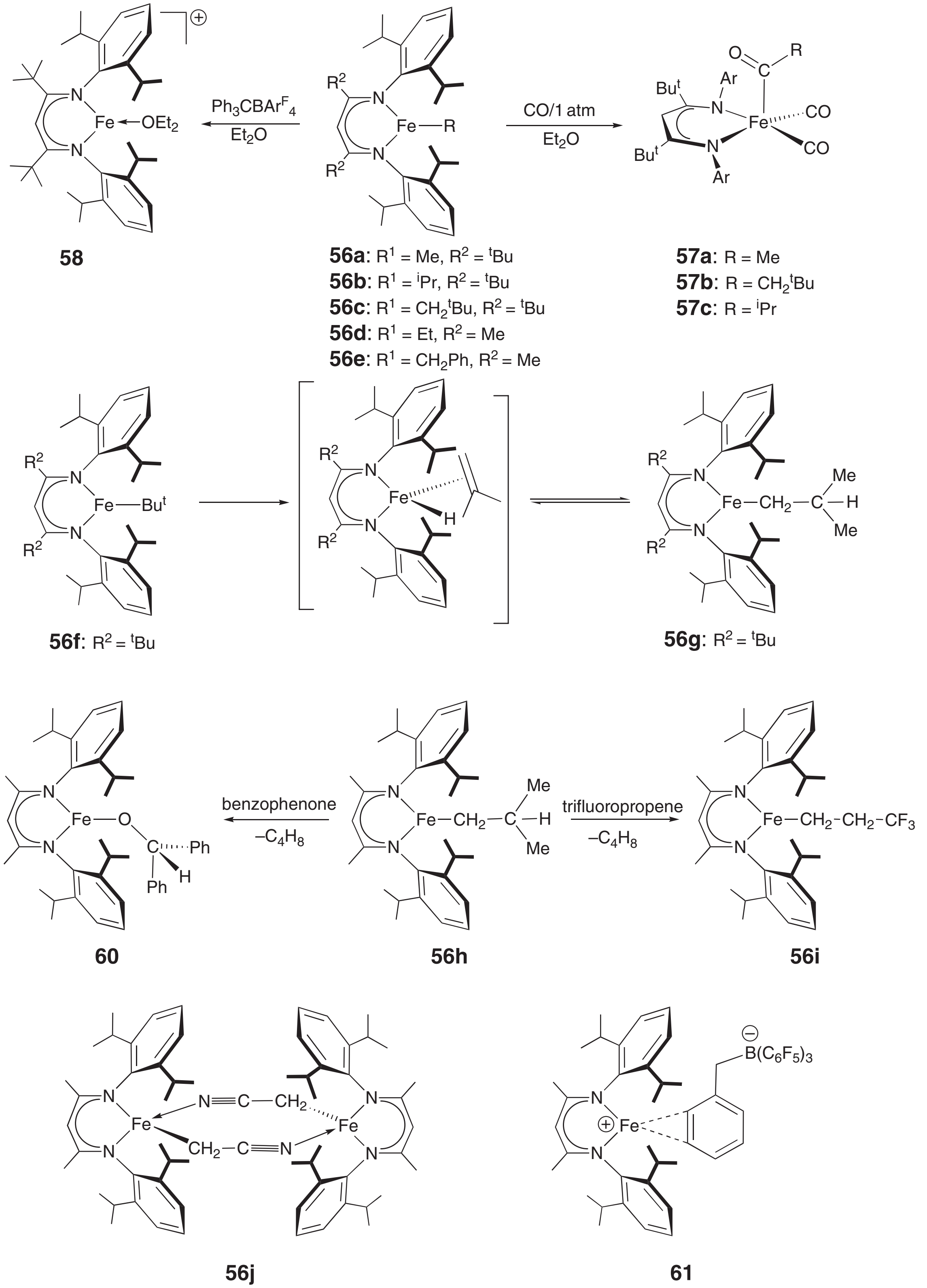
In a similar manner, coordinatively unsaturated benzyl and ethyl iron complexes $[\mathrm{FeR}\{\kappa^3\text{-}(3,5\text{-}^i\mathrm{Pr_2pz})_3\mathrm{BPh}\}]$ **54**, supported with the hydrotris(3,5-diisopropylpyrazolyl)borate ligand, have been prepared and characterized by X-ray crystallography.[91–93] Particularly noteworthy is the observation that the ethyl derivative **54b** is resistant to β-elimination up to 110 °C: after 5 h under reflux in heptane, only small amounts of ethane and ethene were detected. As depicted in Scheme 10, the outcome of the carbonylation of **54a**, **54b** differs significantly from that of **52**. In addition to CO insertion into the Fe–R bond, two further carbonyls are bound terminally to afford the diamagnetic acetyls **55**, which are isoelectronic with their well-known [CpFe{C(═O)R}$(CO)_2$] counterparts. Exposure of **54a** to O_2 resulted in instantaneous oxygenation and formation of *p*-tolualdehyde, most probably via an alkylperoxo intermediate Fe–O–O–R. The magnetic susceptibility of these η^1-hydrocarbyl complexes, combined with the results of EHMO calculations for the model complex [Fe$(CH_3)(\kappa^3$-$pz_3BH)$], reveals the high-spin configuration of the *d*-electrons, which leads to occupation of all five frontier orbitals by one electron pair and four unpaired electrons ($S = 2$). The lack of a vacant *d*-orbital is concluded to be the origin of the thermal stability of the electron-deficient hydrocarbyl complexes.[93] Theoretical calculations on the metathesis process $[(\kappa^3\text{-}pz_3BH)(PH_3)MR(\eta^2\text{-}H\text{–}CH_3)] \rightarrow [(\kappa^3\text{-}pz_3BH)(PH_3)MCH_3(\eta^2\text{-}H\text{–}R)]$ (M = Fe, Ru, Os; R = H, CH_3) have been carried out. In the case of iron, a one-step process with a four-membered transition state is preferred.[94]

Another class of iron compounds which has attracted much attention are alkyl, vinyl, and acetylide complexes containing sterically-demanding β-diketiminate ligands.[95] The first example of a thermally stable, 12-electron three-coordinate iron(II) methyl complex **56a** has been prepared by reaction of its chloro precursor with MeMgBr.[96] The ethyl derivative **56d**, which is resistant toward β-elimination, was obtained similarly.[97] Their crystal structures reveal the absence of agostic interactions and the existence of rather short Fe–CH_3 and Fe–Et bonds of 200.9(3) and 203.3(3) pm, respectively. The bulky β-diketiminate provides the steric protection for these low coordinate complexes. Further information on the electronic structure was obtained by means of DFT calculations. Moreover, the Mössbauer and EPR spectra of **56a** having a large orbital angular momentum were recorded and a crystal field analysis was performed.[98] Future studies of this compound and other three coordinate derivatives may give some insight into the low-coordinate metal sites present in some metalloenzymes.[99] The ^{t}Bu derivate **56f** undergoes reversible β-elimination upon heating to generate a hydrido–alkene intermediate, isomerization of which leads to the isobutyl derivative **56g** (Scheme 11).[97] In the presence of ethylene, olefin exchange occurs with concomitant liberation of isobutylene to produce the corresponding ethyl complex by insertion into the Fe–H bond. The activation parameters for this reaction have been ascertained. Competition experiments and DFT calculations demonstrate an enthalpic preference for alkyl isomers with iron bound to the terminal carbon of the alkyl chain. Generalization of the hydride transfer reaction also allows isolation of structurally characterized **56i** after addition of trifluoropropene to **56h**; upon treatment with benzophenone, the alkoxide **59** has been obtained.[100] Formation of the dinuclear system **56j**, which results from reaction of **56h** with acetonitrile, may be considered as an acid–base reaction. X-ray crystallography shows that in the dimer the fragments are linked by two deprotonated acetonitrile ligands. Carbonylation of **56a–c** produces the diamagnetic acetyls **57a–c**.[101] In the crystalline state, the geometry around the iron center of **57a** is square pyramidal. The acetyl group is in the apical position, with the acyl methyl pointed away from the diketiminate backbone.

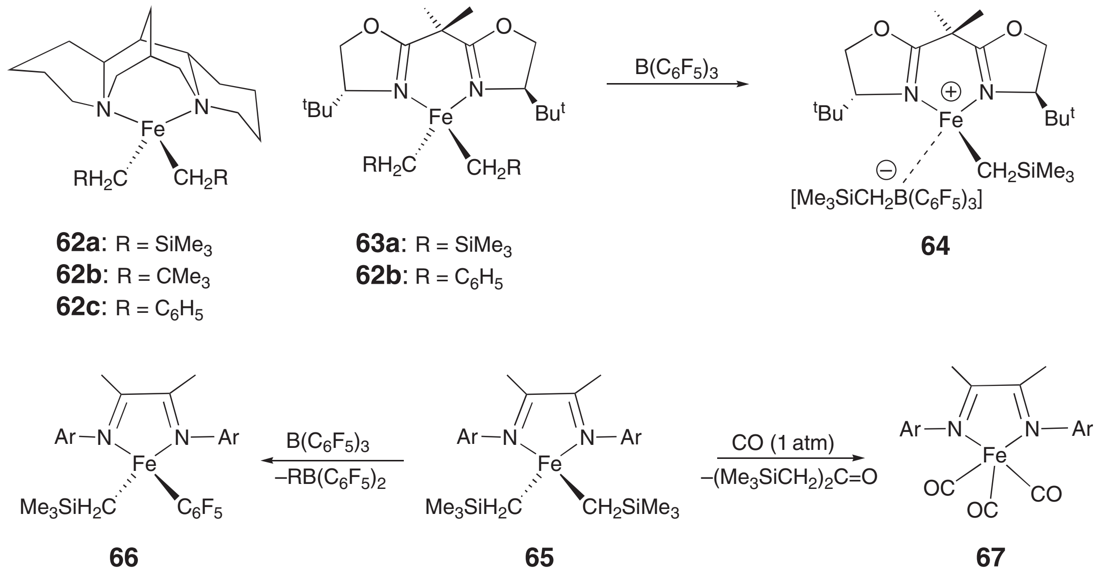
The methyl group of **56a** is abstracted after addition of $Ph_3CBAr^F{}_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) to produce the salt **58**; after abstraction of the benzyl group of **56e** with $B(C_6F_5)_3$, the arene adduct **61** is formed.[102,103] **56e** forms also a stable, tetrahedral 14-electron compound with pyridine. This adduct formation with the Lewis base causes a noticeable elongation of the Fe–C bond length compared to that of parent compound **56e** [210.7(2) vs. 204.14(18) pm].[103a] Furthermore, alkyl complexes **56** serve as precursors for discrete iron(II) fluorides by reaction with trimethyltin fluoride.[104]

The reactivity of paramagnetic chelate complex [(TMEDA)Fe$(CH_2Ph)_2$] towards organic halides has been investigated.[105] The coupling product $PhCH_2CH_2Ph$ was formed upon addition of $PhCH_2X$, a mixture of $PhCH_2CH_2CH{=}CH_2$ and 1,5-hexadiene resulted from addition of allyl bromide. The intermediacy of organic radicals has been evidenced. More stable paramagnetic four-coordinate iron bis(alkyls) **62** and **63**, containing enantiopure (−)-sparteine and 2,2-bis{2-[4(*S*)-(R)-1,3-oxazolinyl}propane as bidentate nitrogen ligands, were obtained by treatment of the corresponding dichloro complexes with RLi.[106] The α-diimine-chelated compound **65** was prepared in an analogous manner. Solution magnetic susceptibility measurements and X-ray diffraction studies revealed each of the novel bis(trimethylsilyl) derivatives **62a**, **63a**, and **65** to be high-spin, $S = 2$, tetrahedral molecules. Alkyl abstraction from **63a** with $B(C_6F_5)_3$ generates the contact ion pair **64**, whereas in case of **65** aryl group transfer was noticed to produce the alkyl aryl complex **66**. Carbonylation of **65** causes immediate reduction to the Fe(0) tricarbonyl compound **67** with ketone elimination according to Scheme 12.

The chemistry of diamagnetic iron carbonyl complexes chelated by 1,4 diazabutadiene (α-diimine) ligands, which was initiated in 1980s,[38] has considerably progressed during the past decade. The propensity of this ligand system to undergo oxidative, metal-mediated 1,3-dipolar cycloaddition to the M–N═C fragment (M = Fe, Ru) has been reviewed.[107,108] For example, a 1,3-dipolar cycloaddition of dimethyl acetylenedicarboxylate (DMAD) to an Fe–N═C fragment of diimine complex [Fe(^{i}PrN═CH–CH═N^{i}Pr)(CNR)$(CO)_2$] produces the two ferra-[2.2.2]


58
$Ph_3CBAr^F_4$
Et_2O
$Fe \leftarrow OEt_2$
CO/1 atm
Et_2O
56a: R^1 = Me, R^2 = ^{t}Bu
56b: R^1 = ^{i}Pr, R^2 = ^{t}Bu
56c: R^1 = $CH_2{}^tBu$, R^2 = ^{t}Bu
56d: R^1 = Et, R^2 = Me
56e: R^1 = CH_2Ph, R^2 = Me
57a: R = Me
57b: R = $CH_2{}^tBu$
57c: R = ^{i}Pr
56f: R^2 = ^{t}Bu
56g: R^2 = ^{t}Bu
benzophenone
$-C_4H_8$
trifluoropropene
$-C_4H_8$
$Fe-CH_2-CH_2-CF_3$
60
56h
56i
56j
61
$B(C_6F_5)_3$

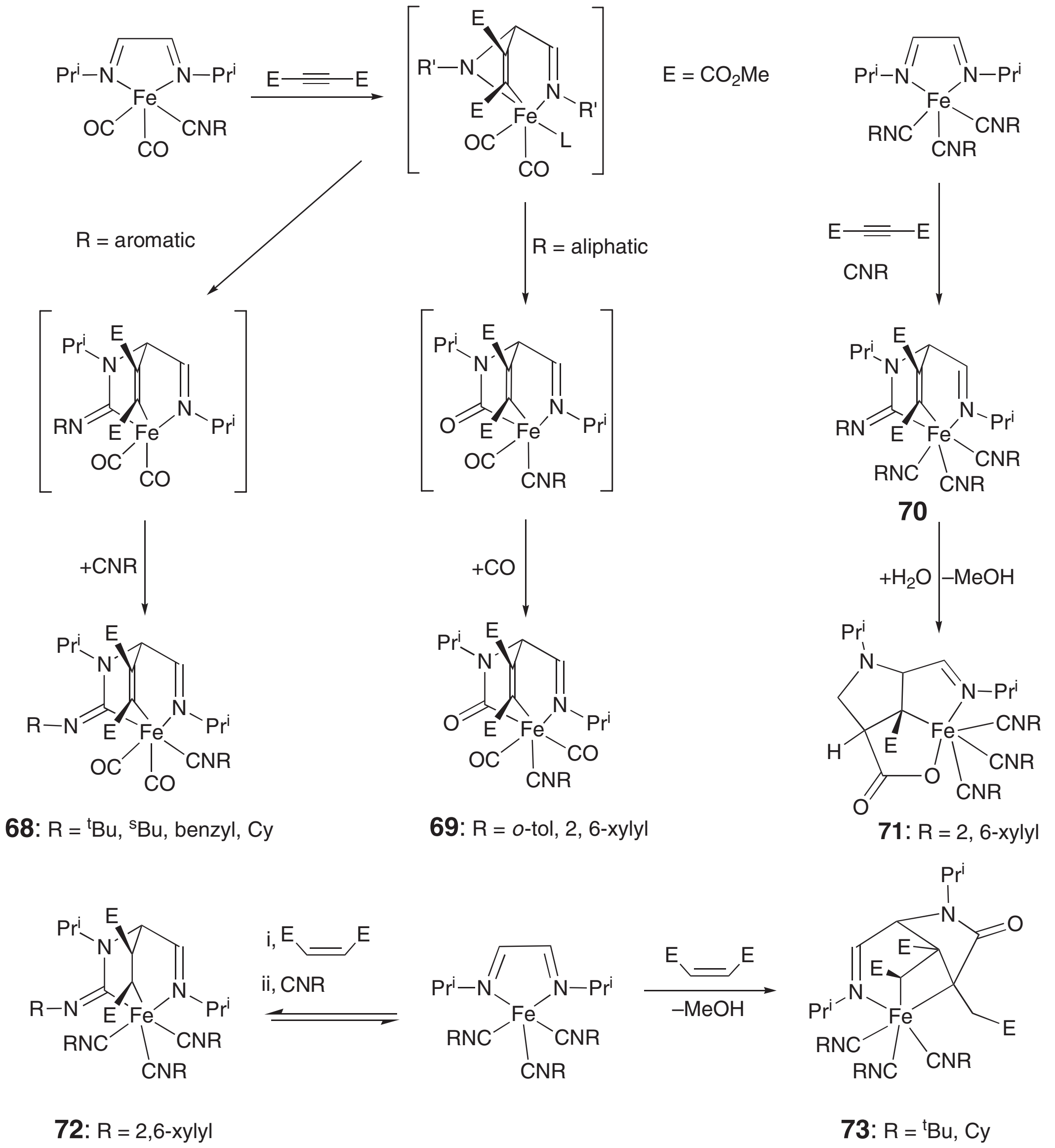
Scheme 11



Scheme 12

bicyclic compounds **68** and **69**, which are the result of a competition between subsequent CO and isocyanide insertion.[109] The trend for preferred insertion is aromatic CNR > CO > aliphatic CNR. Stereochemical aspects of the cycloaddition of DMAD and MP (MP = methyl propiolate) using chiral *N*-substituted α-diimine backbones have also been thoroughly investigated.[110] The distribution of products is governed by the electronic properties of the isocyanides. The combination of $[Fe(^iPrN{=}CHCH{=}N^iPr)(CNXy)_3]$ with DMAD, followed by isocyanide insertion, affords the structurally characterized compound **70** (Scheme 13).[111] In the presence of water, this ferra-[2.2.2] bicycle undergoes a cyclometallation reaction with one of the ester groups to form metallacycle **71**. The molecular structure consists of three five-membered rings, with the metal incorporated into two of them and an Fe–C bond length of 207.0(1) pm. In the cycloaddition of $[Fe(^iPrN{=}CHCH{=}N^iPr)(CNR)_3]$ (R = Xy, ^{t}Bu, cyclohexyl) with dimethyl maleate, two totally different pathways are followed, depending on the type of isocyanide used.[112] With the aromatic isocyanide, 1,3-dipolar cycloaddition of the alkene across the Fe–N=C unit and isocyanide insertion occurs, forming ferra-[2.2.2] bicycle **72**. When this mixture is warmed above room temperature, the reaction is reversed, disassembling **72** into its starting components. The adducts coordinated with aliphatic isocyanides react with dimethyl maleate to give tricyclic **73**, in which two alkenes are coupled and bonded to the metal and the α-diimine ligand (Scheme 13). The crystal structure reveals that in the cyclization reaction a γ-lactam ring has been formed with loss of a methoxy group from one of the ester functions, the metal being incorporated in the six- and four-membered rings.

The cycloaddition of DMAD has also been extended to $[Fe(^tBuN{=}CHCR{=}O)(CO)_3]$ systems.[113] When these iminoketone complexes are treated with 2 equiv. of MP, the tricyclic complexes **74a** and **74b** are formed in moderate yield.[114] The molecular structure of **74a** contains three five-membered rings, with the two fused metallacycles sharing three common carbon atoms with the third γ-lactone ring. The fact that complexes **74** can also be obtained in high yield by irradiation of **75** in the presence of an excess of MP strongly supports a reaction mechanism in which the second alkyne is initially π-coordinated and subsequently coupled with the π-coordinated double bond of the butenolide heterocycle (Scheme 14). Quite similar tricyclic iron alkyls also resulted from the reactions of DMAD or MP with $[Fe\{^iPrN{=}CHC(OR){=}O\}(CO)_3]$, containing α-iminoester chelates susceptible for cycloaddition reactions.[115,116] Conversion of these α-iminoester compounds to σ-alkyls is also possible without additional unsaturated substrate. In a reaction not yet understood mechanistically, **76**, prepared *in situ* in THF solution, are converted to bis(alkyls) **77** in low yield.[117] In the presence of water, the reaction in THF leads to formation of monoalkyls **78**. The unusual $\sigma(N):\sigma(C)$ bonding mode of the newly formed ligands in **77** and **78** was confirmed by determination of the crystal structures. Even heteroallenes such as S=C=O or S=C=S are suitable reagents for 1,3-dipolar cycloaddition across an Fe–C=N motif. An X-ray diffraction study has been conducted on a ferra-[2.2.2] bicyclic compound originating from CS_2 addition across $[Fe(^iPrN{=}CHCH{=}N^iPr)(CNXy)_3]$ and subsequent isocyanide insertion.[118] The cycloaddition reaction of $[Fe(^iPrN{=}CHCH{=}N^iPr)(CNXy)_3]$ with *para*-substituted phenyl isothiocyanates p-$RC_6H_4N{=}C{=}S$ (R = H, Me, OMe, NO_2) is followed by one or two isonitrile insertions. Depending

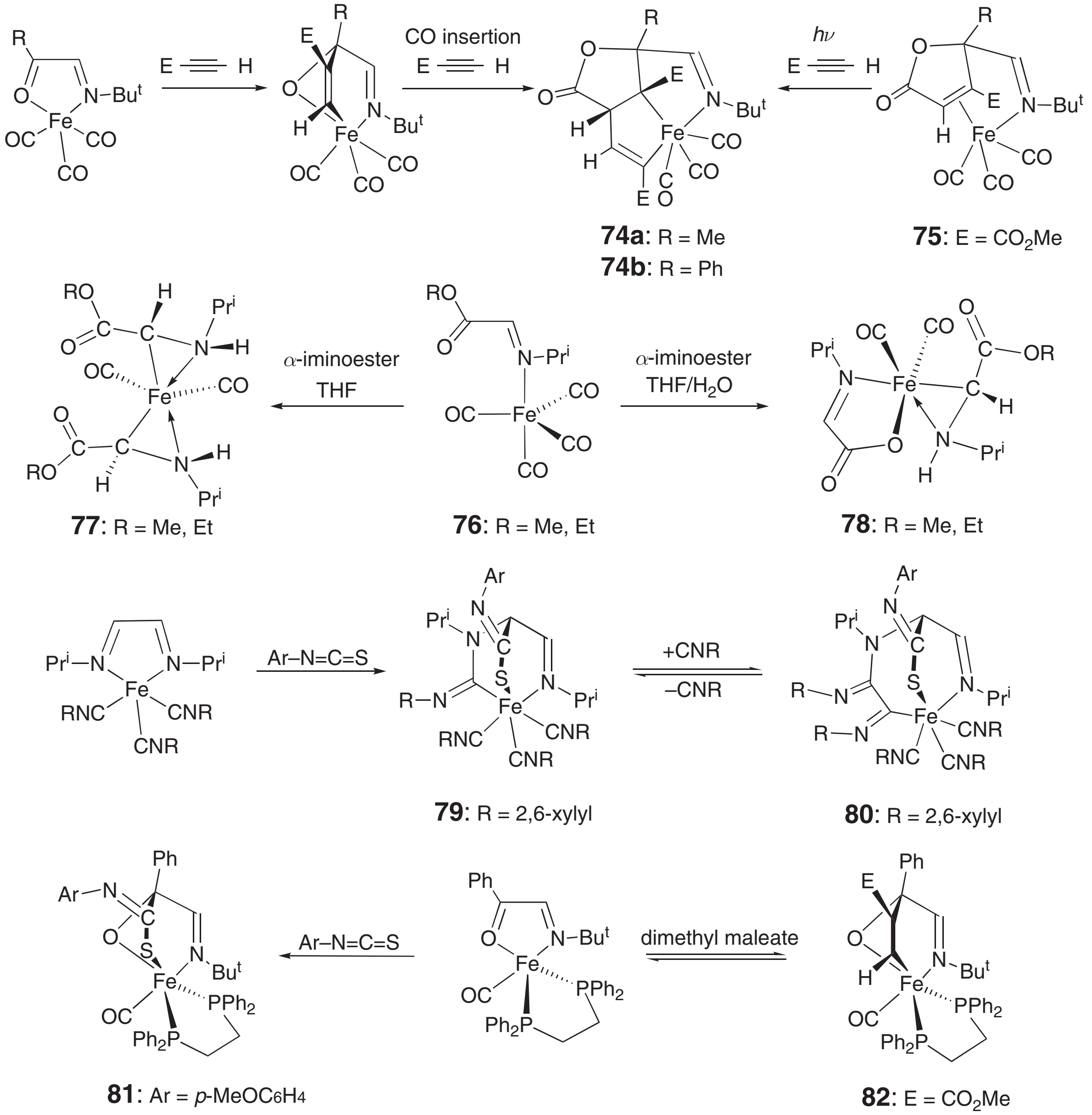


Scheme 13

on the solvent and type of isothiocyanate used, [2.2.2]- and [3.2.2]-bicyclic products 79 and 80 are isolated according to Scheme 14.[119] This second insertion is cleanly reversible and the thermodynamic parameters for this insertion/de-insertion process could be assessed. The interaction of [Fe(^{i}PrN=CHCH=N^{i}Pr)(CNR)$_3$] (R = ^{t}Bu, cyclohexyl), containing stronger σ-donating aliphatic isocyanides, with p-RC$_6$H$_4$N=C=S has also been investigated.[120]

With the objective of stabilizing the initial intermediates formed after addition of dipolarophiles, a huge series of mono- and diphosphine-containing α-iminoketone starting compounds [Fe(RN=CHCR=O)(PR$_3$)(CO)$_2$] and [Fe(RN=CHCR=O)(dppe)(CO)] has been synthesized and subjected to cycloaddition with DMAD, MP, phenylacetylene, dimethyl maleate, and ArNCS.[121] As can be inferred from the structures of the bicyclo[2.2.1]-adducts 81 and 82 depicted in Scheme 14, oxidative cycloaddition across the Fe–O=C dipole is preferred over Fe–N=C addition.

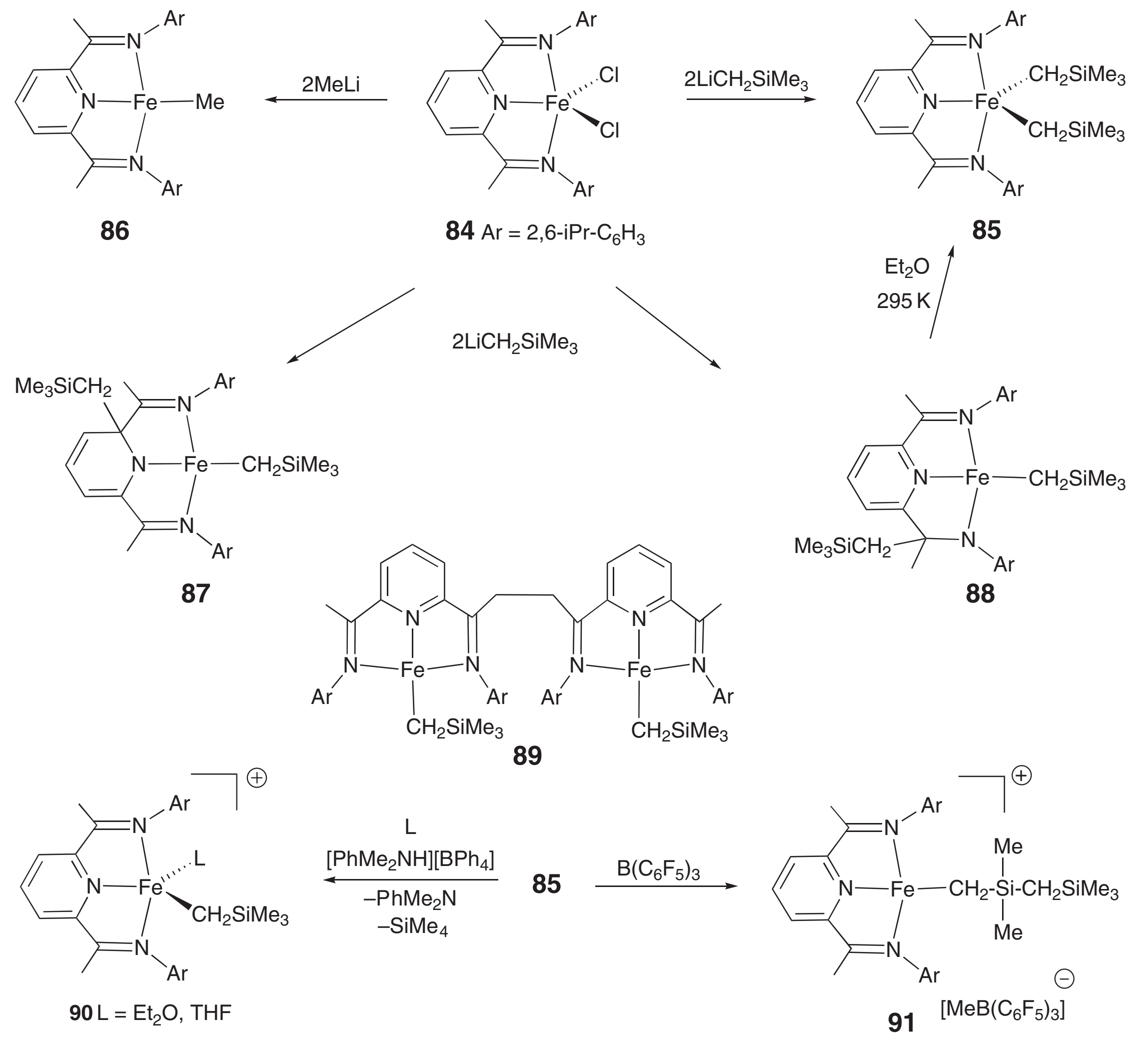
One of the most important discoveries in the domain of iron chemistry in the late nineties was the discovery by Brookhart's and Gibson's groups that bis(imino)pyridine-based cobalt and iron halides are extremely efficient catalysts for olefin oligo- and polymerization. These low-cost systems, which rival metallocenes in efficiency, are transformed into active species by addition of methylalumoxane (MAO) or related alkylating agents as



Scheme 14

co-catalysts.[122–129] Although catalysis is beyond the scope of this article, this important innovation deserves some additional comments, since formation of an Fe–hydrocarbyl bond is involved after action of MAO and in the chain-propagation process. A proposed pathway for the activation of 2,6-bis(imino)pyridine iron(II) chloride pre-catalysts, such as $[\{2,6\text{-}(2\text{-Br-4-CH}_3\text{C}_6\text{H}_3\text{N{=}CCH}_3)_2(\text{C}_5\text{H}_3\text{N})\}\text{FeCl}_2]$ 83[130] or 84 involves (i) abstraction of one of the chlorides followed by (ii) transmetallation with an alkylaluminum species, leading to the cationic monomethylated iron catalyst.[131] Both monochloro and monoalkyl cationic species are considered to be present in the solution.

Meanwhile, a large number of five-coordinate iron(II) complexes with 2,6-bis(imino)pyridyl or related ligands has been synthesized[132–136] and supported on silica.[137,138] Similar complexes with amine rather than imine donor atoms have been synthesized and studied as catalysts.[139] Mechanisms of chain-propagation and β-hydride-transfer chain-termination steps have been investigated theoretically and the effect of factors such as ligand design upon the mechanism discussed.[140–142] Modification with heteroatoms can lead to higher catalytic activities, co-polymerization of ethene with hexene being achieved.[143] Because of their lower oxophilicity, these "post-metallocene" catalysts are even well-suited for co-polymerization of α-olefins with polar monomers.[144] Modification of the ligand system also allows catalytic olefin dimerization and oligomerization.[130,145,146,147]



Scheme 15

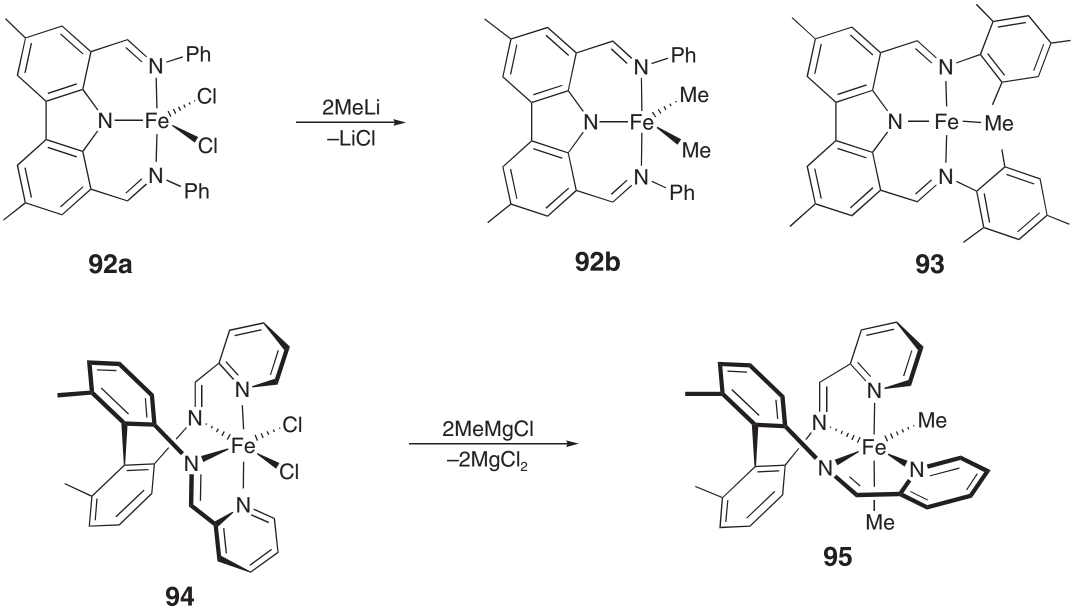
In order to get a better understanding of the structure and stability of the supposed alkyl species, much work has been devoted to the synthesis and characterization of well-defined bis(imino)pyridyl and related complexes bearing η^1-hydrocarbyl groups, which may serve as model compounds. Alkylation of the starting bis(imino)pyridyl complex 84 with 2 equiv. of $LiCH_2SiMe_3$ yielded the structurally characterized Fe(II) bis(alkyl) 85, whose magnetic moment of $4.8\,\mu_B$ is consistent with a spin-only value of four unpaired electrons (Scheme 15). However, using the smaller alkyllithium MeLi produced the Fe(I) monoalkyl 86 by reductive methylation.[148] The determination of the solid-state structure revealed a square-planar coordination sphere with an Fe–C bond distance of 200.1(6) pm, which is slightly shorter than the mean distance of 205.8(3) pm encountered in 85. Complex 86, as well some other methyl derivatives with bulky Ar substituents, were also accessible by methylation of the corresponding Fe(I) monochloro precursors. Solution magnetometry of these methyl compounds indicates an electronic configuration with three unpaired electrons. Shortly after publication of these results, another research group reinvestigated the alkylation of 84 with $LiCH_2SiMe_3$ and MeLi.[149,149a] Depending on the reaction conditions, apart from 85 as major component, other alkyl species in which alkylation occurred also at the pyridine ring *ortho*-position 87, and at the imine C atom 88, have been isolated and structurally characterized (Scheme 15). Dissolution of isolated 88 in Et_2O at ambient temperature causes migration of the imine-bound CH_2SiMe_3 group to the iron center to yield bis(alkyl) 85. Moreover, the reaction mechanism leading to the dinuclear Fe(I) alkyl catalyst 89 has been elucidated. All of these high-spin species have been shown to have high catalytic activity for olefin polymerization, producing polyethylenes of two distinct natures (low molecular weight PE with narrow distribution or high molecular weight PE with broad dispersion), depending on the formal oxidation state of the metal center.[149] Upon addition of 3 equiv. of MeLi to **84**, the formally zerovalent salt $[Li(THF)_4][2,6\text{-}\{2,6\text{-}^iPr_2C_6H_3[N{=}C(CH_3)]_2\}(C_5H_3N)FeMe]$ is formed in 64% yield. The anionic moiety of the paramagnetic complex is nearly isostructural with the monovalent counterpart **86**; interestingly, evidence for a noncationic ethylene-polymerization pathway (see below for a cationic-polymerization pathway) in the presence of MAO is provided.[149a]

Experimental evidence for a possible intermediacy of cationic iron alkyl species after activation of Fe(II) bis(imino)pyridine halides by MAO was provided by the abstraction of an alkyl group of **85**.[150] In the presence of neutral donors, cationic Lewis base adducts **90** could be isolated. Attempts to induce alkyl abstraction with $B(C_6F_5)_3$ resulted in silicon methide abstraction followed by rearrangement to give the base-free cation **91**. The distorted square-pyramidal geometries of **90** with $L = Et_2O$ and THF, as well as the distorted square-planar geometry of **91** have been ascertained by X-ray crystallography. In an evaluation of the ethylene-polymerization productivity, **91** proved to be the most efficacious system producing linear polyethylene with olefinic end groups.

The existence of cationic alkyl species by the action of MAO was attested by means of electrospray-ionization tandem mass spectrometry. After activation of **84** with MAO in THF, the cationic complex $[\{bis(imino)pyridyl\}FeCH_3]^+$, similar to the THF adduct **90**, was identified.[151] In addition, the monochloride iron(II) complex $[\{bis(imino)pyridyl\}FeCl]^+$ and the cationic iron hydride complex $[\{bis(imino)pyridyl\}FeH]^+$ were identified. Furthermore, the generation of $[\{bis(imino)pyridyl\}FeCH_2AlMe_2]^+$, resulting from α-H transfer from $[\{bis(imino)pyridyl\}FeCH_3]^+$ to trimethylaluminum was evidenced. Experimental proof for the existence of hetero-dinuclear iron–aluminum alkyl species after mixing with different AlR_3 activators came also from ^1H and ^2H NMR experiments.[152,152a] In conditions approaching real polymerization, neutral species of the type $[\{bis(imino)pyridyl\}FeCl(\mu\text{-}R)_2AlR_2]$ or $[\{bis(imino)pyridyl\}FeR(\mu\text{-}R)_2AlR_2]$ dominate in the reaction solution in $LFeCl_2 + AlR_3$ systems, whereas in $LFeCl_2$/MAO systems, ion pairs $[\{bis(imino)pyridyl\}Fe(\mu\text{-}Me)(\mu\text{-}Cl)AlMe_2]^+$–$[Me\text{–}MAO]^-$ and $[\{bis(imino)pyridyl\}Fe(\mu\text{-}Me)_2AlMe_2]^+$–$[Me\text{–}MAO]^-$ are the predominant species. Formation of similar alkyl-bridged iron–zinc heterobimetallics occurs after combining **84** with MAO and $ZnEt_2$.[153]

The synthesis of a new family of monoanionic, tridentate bis(imino)carbazolide ligands and their iron complexes has been reported.[154] Treatment of **92a** with MeLi affords the Fe(III) dialkyl species **92b**, whose magnetic moment of 1.8 μ_B suggests a low-spin configuration (Scheme 16). Alkylation of the Fe(II) bis(imino)carbazolide monochloride precursor leads to four-coordinate monoalkyl **93**, displaying a magnetic moment of 3.0 μ_B.

The chiral C_1-symmetric, diamagnetic octahedral dimethyl complex **95**, ligated by a tetradentate bis(pyridylimine) ligand, was obtained after methylation of its paramagnetic C_2-symmetric chloro precursor **94**.[155] Two independent



92a **92b** **93**

94 **95**

Scheme 16

reinvestigations appeared of mechanistic problems of the $[Fe(bipy)_2Et_2]$-catalyzed polymerization of acrylonitrile. A Ziegler-type insertion mechanism is unlikely; it seems that the initiating species is a transient hydrido–ethyl compound generated by β-hydride elimination.[156,157]

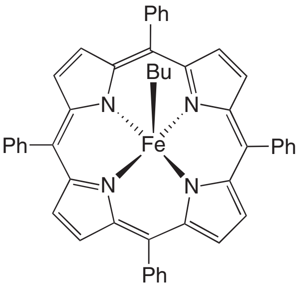
The carbonylation of $[Fe(bipy)_2R_2]$ (R = Me, Et) in THF or toluene proceeds with formation of acetone or diethyl ketone, as the iron(0)-containing species resulting from this reductive elimination, $[Fe(bipy)(CO)_3]$, has been isolated and structurally characterized.[158] Paramagnetic bis(pyridine) dialkyl complexes $[Fe(py)_2R_2]$ (R = CH_2Ph, CH_2CMe_2Ph, CH_2SiMe_3) were isolated after treatment of $[Fe(py)_4Cl_2]$ with RMgCl.[159] A crystal-structure determination conducted on the four-coordinate neophyl derivative reveals a distorted tetrahedral coordination with mean Fe–C bond distances of 209 pm. The derivative $[Fe(py)_2(CH_2SiMe_3)_2]$ reacts rapidly with bis(imino)pyridine ligands to afford bis(alkylated) high-spin 2,6-bis(imino)pyridine iron complexes quite similar to compound **85**. The crystal structure of five-coordinate $[\{2,6\text{-}(2,4,6\text{-trimethyl-}C_6H_2N{=}CCH_3)_2C_5H_3N\}Fe(CH_2SiMe_3)_2]$ was determined and the catalytic potential for ethylene polymerization was probed. The formation of a catalytically active 1 : 1 Fe/Al adduct upon addition of $AlMe_3$ was detected by ^1H and UV–VIS spectroscopies.

The metal–ligand interactions in iron compounds supported with porphyrins or related ligands such as phthalocyanines and corroles confer unique physicochemical properties to these systems. This fact, combined with the emergence of catalytic applications and the ever growing importance of bioinorganic iron chemistry, may explain the continuing interest. Therefore, it is not surprising that since COMC (1995), numerous papers on organoiron porphyrins with alkyl, aryl, allyl, acetylide, and carbene ligands were published. Three reviews and accounts on the organometallic chemistry of transition metal porphyrins appeared in 2001 and 2005.[160–162]

Despite the successful determination of the crystal structures of some alkyliron porphyrins (see below), these compounds are in general, and notably in solution, quite fragile due to facile Fe–C bond homolysis (Equation (1)). Alkyliron(III) porphyrin Fe–C bond cleavage at ambient temperature yields therefore a putative steady-state concentration of alkyl radicals.

$$[(por)Fe^{III}\text{-}R] \rightleftharpoons [(por)Fe^{II}] + \cdot R \qquad (1)$$

Homolytic decomposition by radical coupling and other reactions becomes auto-limiting due to competitive capture of subsequently formed alkyl radicals by the Fe(II) porphyrin product. This reaction sequence is supported by radical-transfer crossover reactions in which the alkyl ligands of $[(TTP)Fe(C_4H_9)]$ **96** and $[(F_{20}TPP)Fe(C_4H_9)]$ is transferred to another Fe(II) porphyrin of different structure such as $[(F_{20}TPP)Fe^{II}]$ (TTP = dianion of tetra-*p*-tolylporphyrin; TPP = dianion of tetraphenylporphyrin).[163] Addition of an excess of tributyltin hydride to [(tetra-*p*-anisyl-por)FeR] (R = ^nPr, ^nBu) produces paramagnetic [(tetra-*p*-anisyl-por)Fe($SnBu_3$)] with spin state $S = 1/2$. This formation of the tributyltin complex is consistent with a free-radical process initiated by homolysis of the alkyliron(III) Fe–C bond. The resulting alkyl radical abstracts an H atom from Bu_3SnH to yield the alkane and a Bu_3Sn radical that subsequently adds to the Fe(II) porphyrin.[164] The *n*-butyl derivative **96** was also evaluated as a suitable catalyst for free-radical olefin polymerization.[165] Dissociation of butyl radicals initiated the polymerization reaction, but the ratio of the propagation was low. Analysis of the reaction mixture of *n*-butyliron(III) porphyrin and styrene has revealed several products containing two Bu groups, while traces of β-hydrogen-abstracted products were also observed. The crystal structure of five-coordinate **96** exhibits an Fe–C distance of 203.0(2) pm. The tetraphenyl oxaporphyrin **97**, which is stable at 205 K, resulted from titration of [(tetraphenyl-oxapor)Fe^{II})Cl] with BuLi. At higher temperatures, the iron(II) species **97** decomposes via homolytic cleavage of the Fe–Bu bond to produce [(tetraphenyl-oxapor)Fe^I].[166]



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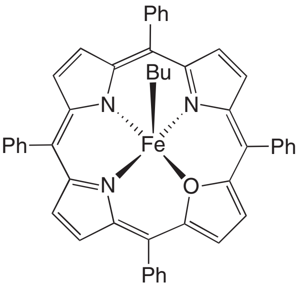

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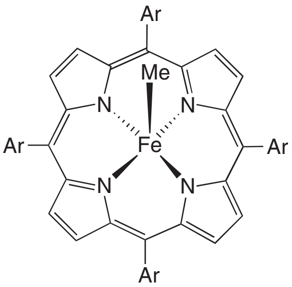


98 Ar = *p*-anisyl

Overall, the Fe–C bonds are 10–15 kcal mol^{-1} weaker than the corresponding organocobalt porphyrin Co–C bonds. The kinetics of Fe–C bond homolysis were investigated using Ph_3SnH as a radical trap, which captures R· released by thermolysis of [(OEP)FeR] and [(TTP)FeR] (OEP = dianion of octaethylporphyrin) (Equation (2)).[167] The bond-dissociation activation enthalpies were measured to be 31 kcal mol^{-1} for R = Ph, 21 kcal mol^{-1} for Me, 17 kcal mol^{-1} for Et, and 17 kcal mol^{-1} for neopentyl, also taking into account diffusion-limited recombination. For both aromatic and aliphatic derivatives, decreasing D_{Fe-R} correlates with the increasing steric requirements of R. Addition of the donors PEt_3 or pyridine, acting as axial ligands, accelerates the rate of Fe–C bond homolysis of the resulting six-coordinate adducts.

$$[(\mathrm{por})\mathrm{Fe}^{\mathrm{III}}\text{-R}] + \mathrm{HSnPh_3} \rightleftharpoons [(\mathrm{por})\mathrm{Fe}^{\mathrm{II}}] + \mathrm{RH} + 1/2\ \mathrm{Sn_2Ph_6} \qquad (2)$$

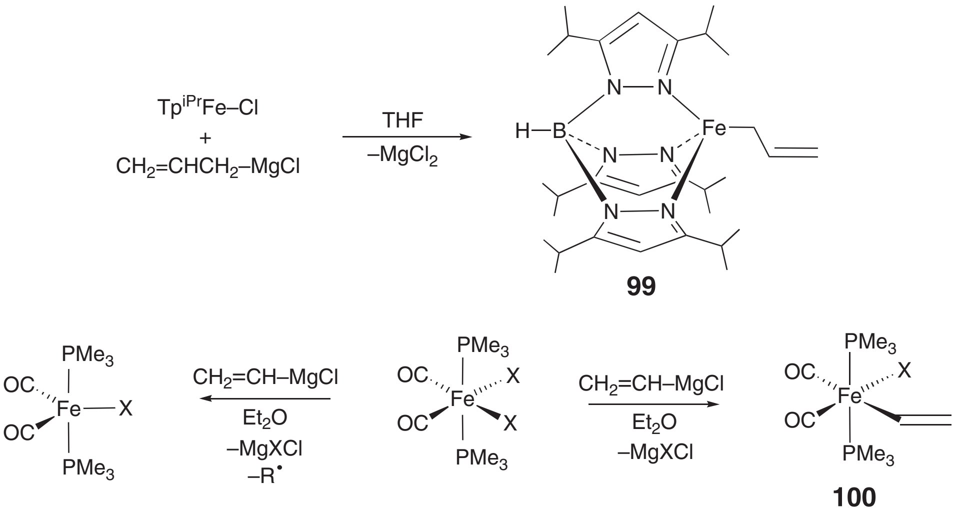
The electron-transfer redox chemistry for the alkyl derivatives of [(por)Fe^{III}–R] has been characterized on the basis of cyclic voltammetric and controlled-potential electrolysis measurements. The electrogenerated anions $[(por)Fe]^-$ and $[(por\cdot)Fe]^-$ are strong nucleophiles that react with alkyl halides via a nucleophilic displacement process to form metal–carbon bonds [(por)Fe–R] and [(por$^{\cdot}$)Fe–R]. The difference in the reduction potentials for RX and (por)Fe(II) provides an approximate measure of the Fe–R bond-formation free energy ($-\Delta G_{BF}$). The $-\Delta G_{BF}$ values for iron porphyrins (14–35 kcal mol^{-1}) depend on the electron density of the porphyrin ring (OEP > TPP > Cl_8TPP > F_{20}TPP) and the structure of the alkyl group (1° > 2° > 3°). The apparent metal–carbon bond energy for [(OEP)Fe(C_4H_9)] determined by this technique is 28 ± 2 kcal mol^{-1}.[168]

The crystal structure of the five-coordinate low-spin iron(III) complex [(tetra-*p*-anisyl-por)Fe(CH_3)] **98** has been resolved, the Fe–C distance of the axial-bound methyl group being 197.9(9) pm.[169] The analogous *n*-butyl derivative readily inserts CO to afford the acyl compound [(tetra-*p*-anisylpor)Fe{C(=O)^{n}Bu}] with $S = 1/2$. Despite the electron-deficient nature of the five-coordinate 15-electron complex, the acyl is η^1-bound with an Fe–C bond distance of 196.5(12) pm. ^{2}D NMR monitoring at low temperature shows that in the presence of O_2, the labeled acyl [(tetramesitylpor)Fe{C(=O)C_2D_5}] is converted to the high-spin carboxyl [(tetramesitylpor)Fe{OC(=O)C_2D_5}]. The reactions of reduced iron porphyrins with alkyl-containing supporting electrolytes used in electrochemistry has been observed with CV and spectroelectrochemistry, in which the tetraalkylammonium ions can act as the source of the R group in electrogenerated [(TTP)FeR].[170] Low-temperature spectroelectrochemistry was also performed to generate highly reduced iron σ-alkyls containing halogenated porphyrin cores, which underwent homolytic Fe–C bond breaking at room temperature. Under anaerobic conditions, it was thus possible for the first time to detect highly reduced σ-ethyl Fe(I) porphyrins.[171] σ-Alkyliron complexes are assumed to be intermediates in the (porphinato)iron-mediated reduction of alkenes and alkynes with $NaBH_4$ and in the (porphinato)iron-catalyzed addition of thiols to alkenes.[172,173] Mechanisms have been proposed for the (porphinato)iron-catalyzed oxidation of styrene by O_2 in the presence of $NaBH_4$. The product analysis suggests that the σ-alkyliron(III) complex, [(TTP)Fe{CH(C_6H_5)CH_3}], is formed as an intermediate. Insertion of O_2 into the (σ-alkyl)Fe(III) complex having a radical character yields a (peroxy)iron(III) complex, [(TTP)Fe{OOCH(C_6H_5)CH_3}].[174]

6.02.3 Synthesis and Reactivity of σ-Allyls and σ-Vinyls (σ-Alkenyls)

In contrast to iron complexes with π-bound allyl ligands, those containing an η^1-bound allyl are quite scarce. One of the rare examples is the 14-electron tris(pyrazol-1-yl)borate complex **99**, whose crystal structure determination evidences the η^1-bonding mode of the allyl ligand (Scheme 17).[91,175] Paramagnetic Fe(III) porphyrin complexes with axial σ-allyl and vinyl ligands were prepared by the addition of the appropriate Grignard reagent to [(TTP)FeCl] for *in situ* observation by ^{1}H NMR spectroscopy.[176,177] The products are considerably less stable than their alkyl counterparts. The spectral data indicate that the allyl and vinyl groups are coordinated in an η^1-fashion at low temperatures (−80 to −40 °C). Dioxygen reacts with [(TTP)Fe(allyl)] at −80 °C to produce [(TTP)Fe^{III}(OH)] and acrolein, CH_2=CHCHO, the expected products of insertion of O_2 into an Fe–C σ-bond.

The salt-elimination route using vinyllithium or vinyl-Grignard reagents was also applied to prepare the stable carbonyl complexes *cis,trans*-[Fe(CH=CH_2)(X)$(CO)_2$$(PMe_3)_2$] **100** (X = Cl, Br) starting from [$FeX_2$$(CO)_2$-$(PMe_3)_2$].[178] With both reagents, the reaction proceeds following two parallel pathways: the dominating one is metallation yielding the iron vinyl, the second one affords 17-electron species $[FeX(CO)_2(PMe_3)_2]^{\cdot}$ via monoelectron reductive elimination. Addition of an excess of vinyllithium yields the bis(vinyl) complex *cis,trans*-[Fe$(CH{=}CH_2)_2$$(CO)_2$$(PMe_3)_2$], whose crystal structure shows a *cis*-arrangement of the vinyl ligands.[80] A comparison of the mean Fe–C bond lengths with those of [$Fe(CH_3)_2(CO)_2(PMe_3)_2$] clearly shows a significant shortening

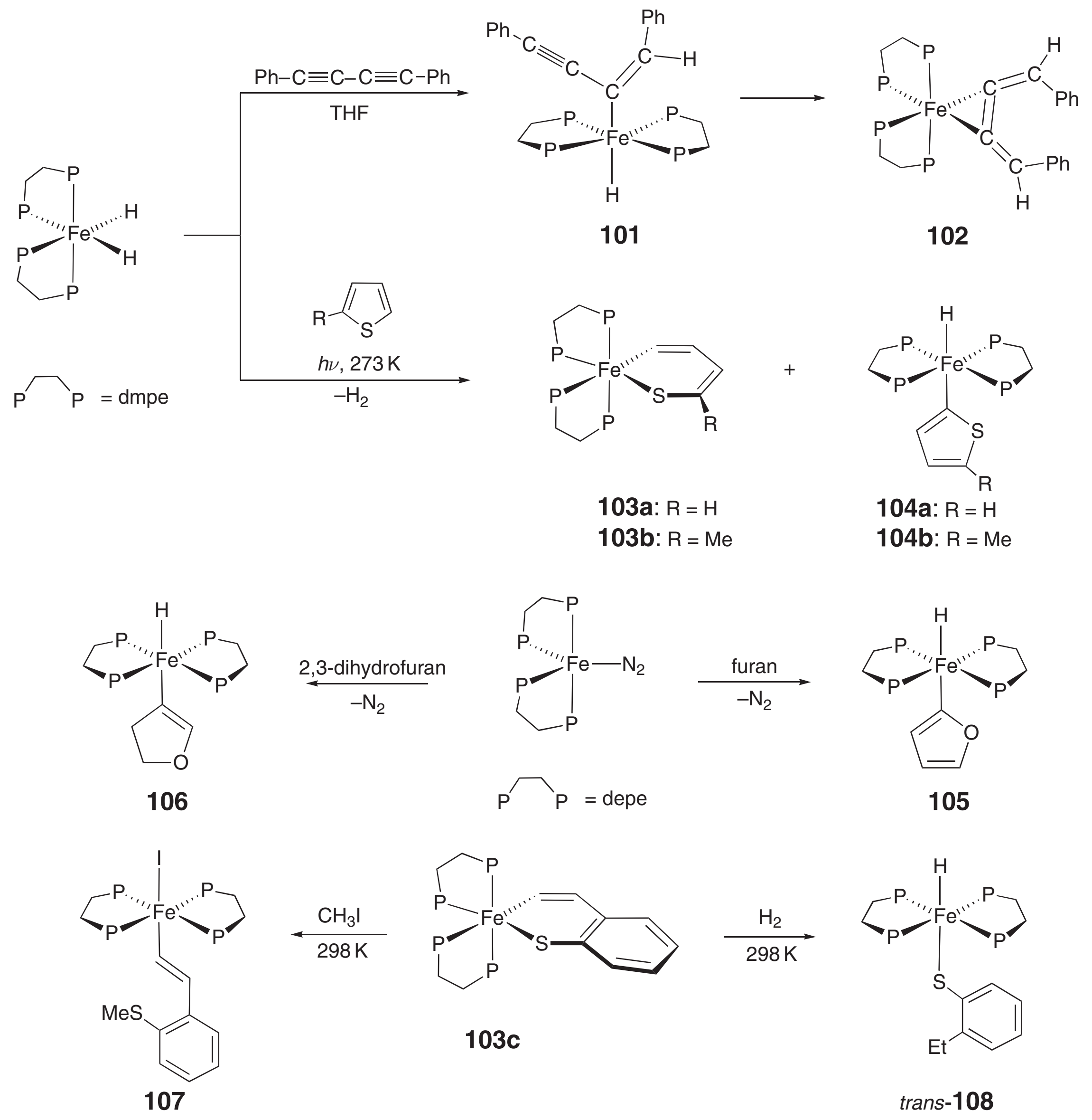


Scheme 17

(201.5 vs. 213.5 pm), in agreement with π-electron delocalization. In solution, gradual transformation to [Fe(η^4-butadiene)(CO)$_2$(PMe$_3$)$_2$] via reductive coupling of the vinyl groups is noticed.

Another strategy allowing to form iron vinyl units involves insertion of alkynes into the Fe–H bond of a hydride precursor complex. Thus, treatment of *trans*-[FeH(Cl)(dppe)$_2$] with MP in the presence of TlBF$_4$ yields five-membered metallacyclic *cis*-[Fe(CH═CHCO$_2$Me)(dppe)$_2$][BF$_4$].[179] A crystal-structure analysis indicates bonding of the chelating vinyl unit through the α-carbon [Fe–C, 196.0(2) pm] and the carbonyl oxygen of the ester function. The quite similar complex *cis*-[Fe(CH═CHCO$_2$Me)(dmpe)$_2$][BPh$_4$] was reported as product of the reaction of MP with [FeCl$_2$(dmpe)$_2$] in the presence of NaBH$_4$.[180] Its formation was interpreted in terms of alkyne insertion into the Fe–H bond of *in situ*-generated [Fe(H)(H$_2$)$_2$(dmpe)$_2$]$^+$. Likewise, insertion of HC≡CSiMe$_3$ into the Fe–H bond of [FeH(H$_2$)$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$}][BPh$_4$] allowed the isolation of the paramagnetic alkenyl [Fe(CH═CHSiMe$_3$)-{P(CH$_2$CH$_2$PPh$_2$)$_3$}][BPh$_4$].[181] After mixing of [FeH(H$_2$)$_2${P(CH$_2$CH$_2$PMe$_2$)$_3$}][BPh$_4$] or [FeHCl{P(CH$_2$CH$_2$PMe$_2$)$_3$}] (in the presence of NaBPh$_4$) with HC≡CCMe$_3$ or HC≡CPh, the butenynyl complexes [Fe(η^3-RC≡C–C═CR){P(CH$_2$CH$_2$PMe$_2$)$_3$}][BPh$_4$] are formed via carbon–carbon coupling of two alkynes.[182] To account for the reversible interconversion between two isomeric forms, in which the but-1-en-3-yn-2-yl fragment is bound as σ-vinyl/π-acetylenic ligand, the intermediacy of a species with an exclusively η^1-bound vinyl unit is suggested. Reaction of [FeH$_2$(dmpe)$_2$] with diphenylbutadiyne results in insertion into both of the Fe–H bonds to form the metallacycle **102** chelated by a 1,4-diphenylbutatriene ligand.[183] The insertion proceeds via intermediate formation of the hydrido–vinyl complex **101**, the overall reaction being greatly accelerated by application of high pressure (Scheme 18). Remarkably stable 12-electron three-coordinate iron(II) vinyls, similar to their alkyl counterparts **56**, have been prepared by insertion of 2-butyne or 3-hexyne into the iron–hydride bond of the β-diketiminato–hydrido precursor. The crystal structure of the hexyne insertion product, with (*Z*)-conformation of the ethyl groups about the alkenyl fragment, as well as rate and activation parameters for the alkyne insertion have been determined.[184]

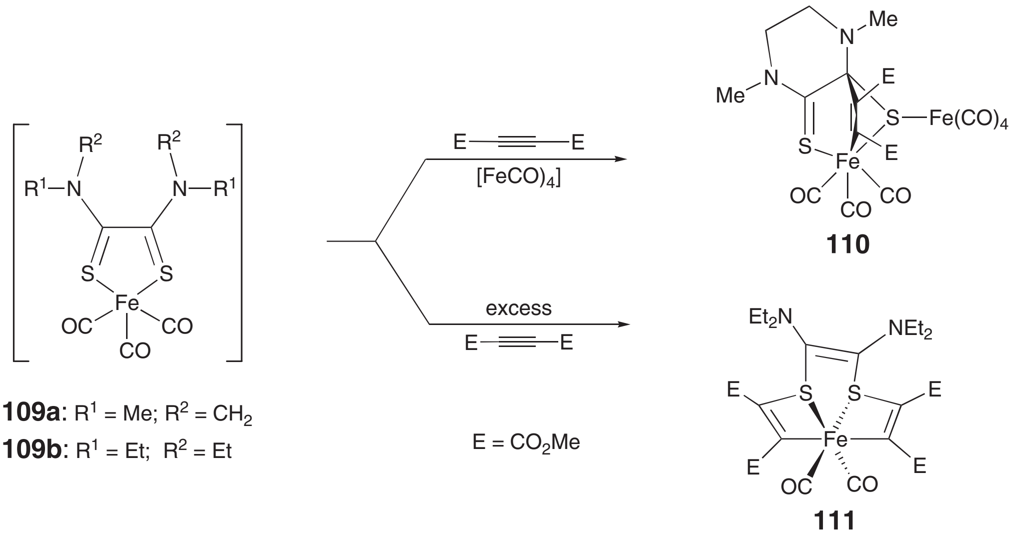
A third route to iron σ-alkenyls is based on the activation of olefinic C–H bonds. With the objective of measuring heteronuclear coupling constants using two-dimensional NMR techniques, a number of hydrido–alkenyl [FeHR{P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$}] (R = *E*-pentenyl, *E*-2-methyl-1-pentenyl, cyclopentenyl, *E*-3,3-dimethyl-1-butenyl) were prepared *in situ* by low-temperature photolysis of [FeH$_2${P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$}] in neat alkene solvent.[185] ^{1}H–^{1}H NOE experiments indicate a *trans*-arrangement of the alkenyl groups to the central apical phosphorus atom of the tripodal ligand. Upon photolysis of [FeH$_2$(dmpe)$_2$] in the presence of simple thiophenes, alkenyl products **103** and **104** stemming from insertion of the transient unsaturated [Fe(dmpe)$_2$] fragment into both C–H and C–S bonds are formed (Scheme 18).[186] The existence of an almost planar six-membered ferrathiacycle was authenticated by a single crystal X-ray analysis of **103b**. Using the bulkier dibenzothiophene as substrate afforded exclusively the C–H insertion product. [Fe(depe)$_2$(N$_2$)] has also been examined for its ability to activate olefinic C–H bonds. The complex loses N$_2$ readily and olefinic C–H activation of 2-methylstyrene under thermal conditions leads quantitatively to a mixture of *cis*- and *trans*-[FeH(CH═CHC$_6$H$_4$CH$_3$)(depe)$_2$].[187] Further heating gives η^6-coordination of the arene



Scheme 18

and dissociation of one diphosphine ligand leading to [Fe{η^6-$C_6H_4(Et)CH_3$}(depe)]. The activation of the C–H bonds of furan, benzo[*b*]furan, and 2,3-dihydrofuran by [Fe(depe)$_2$(N_2)] led to hydrido–alkenyl complexes such as **105** and **106** according to Scheme 18.[188] In contrast, competing C–H and C–S activation was encountered using various thiophenes as substrates. A series of ferrathiacyclic and hydrido–alkenyl derivatives, which are structurally related to **103** and **104**, was isolated. Structurally characterized **103c** undergoes immediate ring opening with CH_3I to afford the iodo–alkenyl complex **107**. The X-ray structure determination of **107** demonstrates that electrophilic attack of CH_3I took place at the S atom, followed by Fe–S bond cleavage giving a (*E*)-configuration about the styrenyl fragment with an Fe–C bond length of 200.0(2) pm. Exposure of **103c** to 50 atm of H_2 produces a mixture of hydrido thiolates *cis*- and *trans*-[FeH(SC_6H_4-2-Et)(depe)$_2$] **108** by hydrogenation of the vinylic C=C bond.

The alkenyl complexes *trans*-[Fe(X)(CH=CHC$_6$H$_5$)(dmpe)$_2$] (X = Cl, N_3, SCN), which resemble **107**, were obtained by a completely different synthetic method. This consists in quantitative anion-induced rearrangement of the hydrido–acetylide complex *trans*-[FeH(C≡CC$_6$H$_5$)(dmpe)$_2$] in methanol solution containing chloride, azide, or



109a: R^1 = Me; R^2 = CH_2
109b: R^1 = Et; R^2 = Et

E = CO_2Me

110

111

Scheme 19

thiocyanate.[189] The crystal structure of *trans*-$[Fe(N_3)(CH{=}CHC_6H_5)(dmpe)_2]$ shows an (*E*)-configuration about the styrenyl ligand.

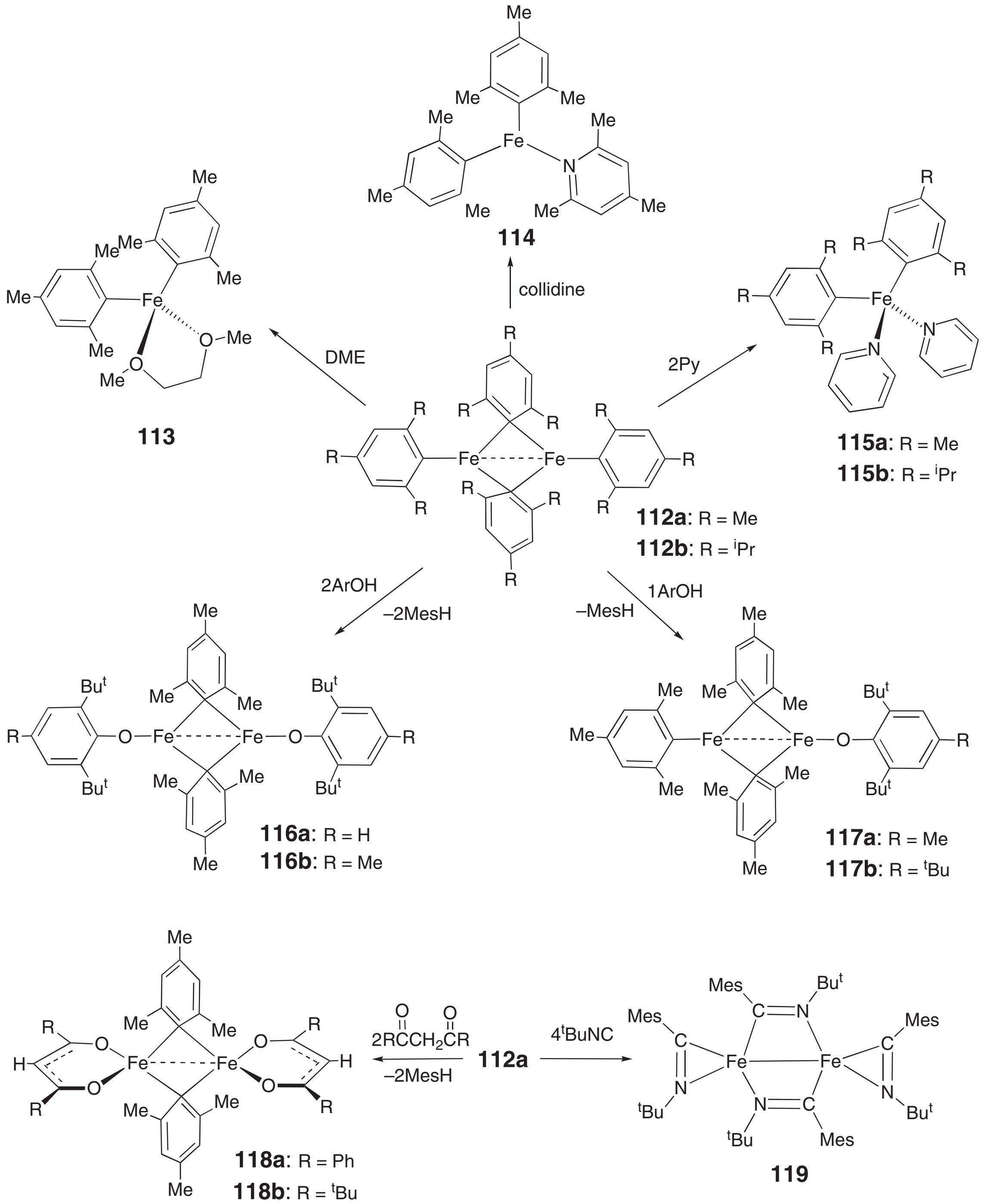
The outcome of the addition of DMAD to *in situ*-prepared iron(0) compounds **109a and 109b** depends on the nature of the chelating dithiooxamide ligand.[190] **109a** reacts with 1 equiv. of DMAD in an oxidative 1,3-dipolar cycloaddition to give the stable ferra-[2.2.1] bicyclic system **110**. A crystal-structure determination evidences the coordination of an additional $Fe(CO)_4$ fragment to the sulfido S atom of the cycloadded Fe–S=C fragment. In contrast, treatment of **109b** with 2 equiv. of DMAD provides the bis(alkenyl) complex **111** as the result of two [2+2] cycloaddition reactions (Scheme 19), as established by an X-ray diffraction study. Five-membered metallacyclic vinyl complexes $[Fe\{\eta^3\text{-}SC(R){=}CHCHSMe\}(CO)(PMe_3)_2]$ (R = Ph, H) were also obtained by insertion of alkynes into the coordinated C–S bond of the corresponding dithioformate precursors.[190a]

The gas-phase reactions of photogenerated $[Fe(CO)_3]$ and $[Fe(CO)_4]$ with $Cl_2C{=}CCl_2$ have been followed by transient IR spectroscopy.[191] With the latter species, the olefin complex $[Fe(C_2Cl_4)(CO)_4]$ is formed, which isomerizes via an oxidative addition to yield the vinyl compound $[FeCl(CCl{=}CCl_2)(CO)_4]$. The activation energy for this process has been determined to be $21 \pm 2\,\text{kcal mol}^{-1}$. The iron–olefin bond energies for complexes $[Fe(C_2X_4)(CO)_4]$ (X = hal, CN) have been determined by means of DFT calculations. The increase in the C–X bond length upon bonding of the olefin to $[Fe(CO)_4]$ correlates well with the exothermicity of the oxidative addition leading to vinyls $[FeX(C_2X_3)(CO)_4]$.[192]

6.02.4 Synthesis and Reactivity of σ-Aryls

The compound formerly reported as a homoleptic iron(0) species $[Li(OEt_2)]_4[FePh_4]$[38] is now believed to be the iron(II) dihydride compound $[Li(OEt_2)]_4[FeH_2Ph_4]$ after reinvestigation of the crystal-structure data.[193] Several groups continued the exploration of the chemistry of the venerable compound dimesityliron **112a**, first synthesized in 1976.[10,38] The determination of the crystal structure of $[Mes_2Fe]_2$ **112a** reveals that this homoleptic aryl is dimeric in the solid state.[194] Each iron center has a terminal mesityl ligand, the two moieties being bridged by μ-mesityl groups. The mean Fe–C bond distances of the terminal and bridging mesityl groups amount to 202.3 and 212.8 pm, respectively. The dimesityliron dimer is cleaved in polar solvents to yield solvated monomers. An adduct with dimethoxyethane **113** was isolated and characterized by an X-ray structure determination (Scheme 20).[195] The iron mesityl anion $[Mes_3Fe]^-$ has been reported to be three-coordinate with an Fe–C bond length of 211.7(6) pm.[196]

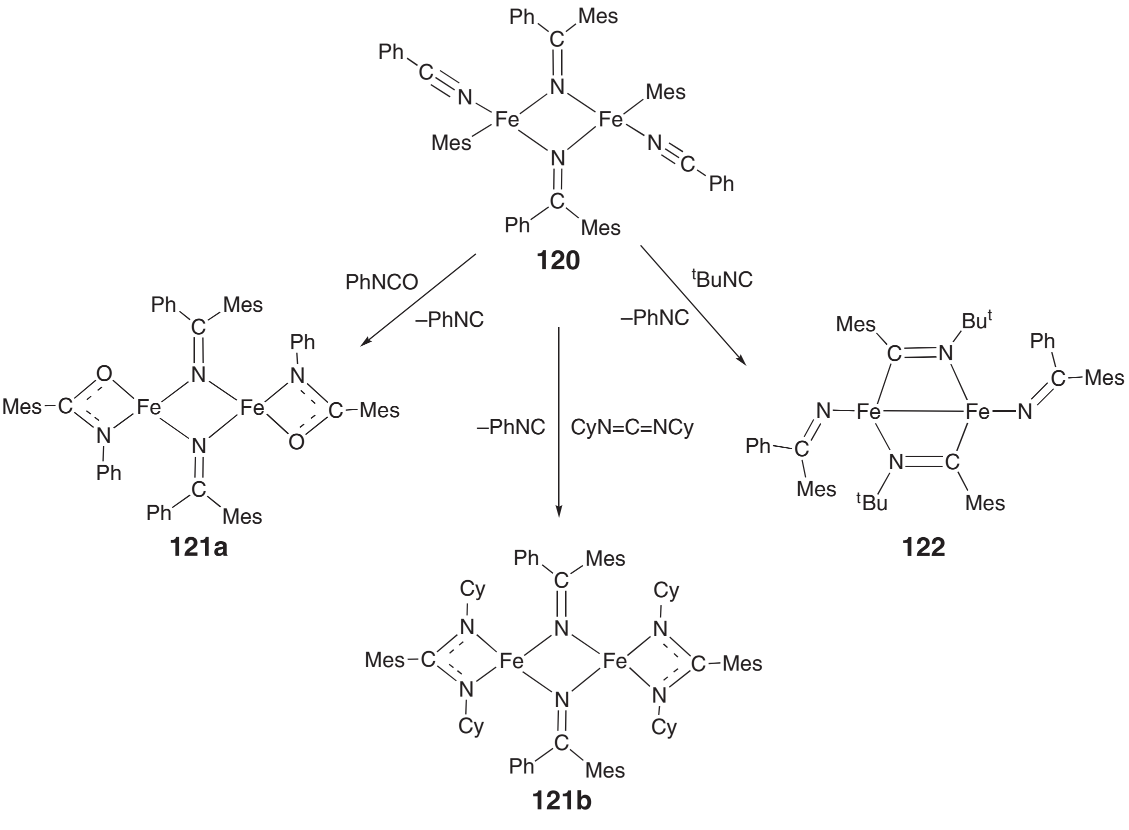
The coordination number around iron upon complexation of pyridine-type ligands depends on their steric requirements. X-ray structure analysis of the collidine adduct **114** confirmed a trigonal-planar geometry with an Fe–C bond length of 211.7(6) pm, whereas in the case of pyridine, the tetrahedral bis(adduct) **115a** having an



Scheme 20

averaged Fe–C bond distance of 214.8(5) pm was isolated.[197,198] Based on solution magnetic measurements showing a magnetic moment of 5.1 μ_B, a tetrahedral geometry with spin state $S = 2$ was also deduced for [Mes$_2$Fe(*N*,*N*-dimethylaminopyridine)$_2$] and [Mes$_2$Fe(TMEDA)$_2$].[199] The dimeric complexes **116** with a coordination number of three are obtained from **112a** by partial acidolyses with 2,6-di-*tert*-butyl-substituted phenols.[200] Reaction with HOAr in the molar ratio of 1 : 1 gives [Fe$_2$(μ-Mes)$_2$Mes(OAr)] **117**. These findings demonstrate the enhanced reactivity of the terminal aryls compared to the bridging ones. Electrophilic attack of 1,3-diketones in a molar ratio of 1 : 2 affords the dinuclear diketonate compounds **118**. A central $[Fe_2(\mu\text{-}Mes)_2]$ unit with short Fe–Fe separations of 256.7(1), 258.9(1), and 262.4(1) pm is found in **116a**, **117b**, and **118b**, respectively. The mixed ligand complexes react with an excess of phenol or β-diketone to $[Fe(OAr)_2]$ or $[Fe(diketonate)_2]$, respectively. After addition of bipy to **116a**, the tetracoordinate chelate complex $[FeMes(OC_6H_2\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}Me)(bipy)]$ is formed. Arylation of $FeCl_2(THF)_{1.5}$ with MesMgBr in the presence of 9,10-phenanthroline led to crystalline $[FeMes_2(phen)]$, which contains a tetrahedral Fe(II) with two σ-bonded mesityl groups with Fe–C bond lengths of 206.3(4) pm.[201] They can be removed by a variety of protic amino acids HA such as proline to afford $[Fe(phen)(A)_2]$. Homoleptic metal–sugar complexes were obtained as iron(II)–diacetoneglucose derivatives.[202] The protolysis of **112a** with DAGH (diacetoneglucose) led to monomeric $[Fe(DAG)_2]$. An interesting organometallic functionalization was achieved via a ligand-redistribution reaction by mixing $[Fe(DAG)_2]$ with **112a**. This reaction gave the trinuclear mixed alkoxo aryl complex $[(Mes)_2Fe_2(\mu\text{-}DAG)_2Fe(\mu\text{-}Mes)_2]$ having a linear trimetallic skeleton with non-bonding Fe···Fe average distances of 288 pm. Each iron center possesses a distorted tetrahedral coordination sphere. The magnetic analysis shows a strong antiferromagnetic coupling between the Fe(II) centers, with spin frustration leading to an overall $S = 2$ ground state. The magnetic moment is strongly temperature dependent and rises from 2.95 μ_B at 1.9 K to 4.39 μ_B at 295 K.

The reactions of **112a** with isocyanates and PhNCS proceed with insertion into all Fe–mesityl bonds.[203] Migratory insertion into all of the Fe–aryl bonds also occurs with ^tBuNC leading to the thermally stable dimeric iminoacyl compound $[\{\eta^2\text{-}C(Mes){=}{}^tBuFe\}_2\{\mu\text{-}C(Mes){=}N^tBu\}_2]$ **119** containing both terminal and bridging iminoacyl functionalities.[198] **119** has a very short Fe–Fe distance of 236.6(2) pm and a low magnetic moment (3.40 μ_B per iron at 250 K). A twofold insertion was observed with PhCN to give dimeric $[\{(PhCN)(Mes)Fe\}_2\{\mu\text{-}N{=}CPhMes\}_2]$ **120**, in which the iron centers are bridged at a distance of 286.0(2) pm from each other by two imino anions. Homoleptic complex **120** has a magnetic moment of 2.82 μ_B at 250 K, suggesting a strong magnetic coupling between the two iron atoms. Further reaction of **120** with PhN=C=O led to insertion into the residual Fe–Mes bond and formation of **121a** with conservation of the bimetallic core and the bridging imino functions (Scheme 21). In a similar manner,

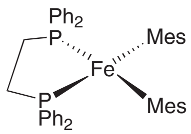


Scheme 21

insertion of CyN=C=NCy furnishes dinuclear $[\{(\mathrm{CyNC(Mes){=}NCy})\}_2\mathrm{Fe}_2\{\mu\text{-N}{=}\mathrm{CPhMes}\}_2]$ **121b**, chelated by two bidentate diamido ligands. In contrast, treatment of **120** with ^{t}BuNC replaces the bridging imino functions by bridging iminoacyl groups to yield the dinuclear complex **122**.

Despite the increased steric bulk of the isopropyl substituents, $[\mathrm{Fe}\{(2,4,6\text{-}^i\mathrm{Pr}_3\mathrm{C}_6\mathrm{H}_2\}_2]_2$ **112b** is isostructural with **112a**, as witnessed by an X-ray diffraction study.[198] A structurally characterized monomeric bis(pyridine) adduct **115b** is isolated after coordination of pyridine.[197] However, treatment of FeBr_2 with Mes*MgBr (Mes* = 2,4,6-$^t\mathrm{BuC}_6\mathrm{H}_2$) allowed isolation of mononuclear homoleptic $[\mathrm{FeMes}^*{}_2]$. Two independent crystallographic studies show that in this two-coordinate high-spin species (4.77 μ_B), the angle C–Fe–C is 158.9(3)°, the Fe–C bond distance being comparable with the terminal Fe–aryl bond distances of **112b** [205.1(5) *vs*. 208.3(9) pm].[204,205] Due to its steric protection, this thermally stable 10-electron species does not react with an excess of pyridine or other bases.

With the objective of evaluating the parameters decisive for square planar *vs*. tetrahedral in four-coordinate Fe(II) complexes, **112a** was reacted with PR_3, $\mathrm{P(OR)}_3$, and chelating diphosphine ligands.[199] Identification of the geometry has been accomplished by a combination of magnetometry, X-ray crystallography, and Mössbauer spectroscopy. Whereas in the case of the afore-mentioned nitrogen-supported derivatives $[\mathrm{FeMes}_2(\mathrm{L_N})_2]$ ($\mathrm{L_N}$ = nitrogen donor) a tetrahedral geometry was encountered, coordination of monodentate PR_3 and $\mathrm{P(OR)}_3$ furnished square-planar derivatives *trans*-$[\mathrm{FeMes}_2(\mathrm{PR}_3)_2]$ with spin state $S = 1$. Alternatively, structurally characterized *trans*-$[\mathrm{FeMes}_2(\mathrm{PMe}_3)_2]$ was obtained in an exchange reaction by treatment of **115a** with PMe_3. In contrast, addition of dmpe or depe to **112a** affords the tetrahedral chelate complexes $[\mathrm{FeMes}_2(\mathrm{dmpe})]$ and $[\mathrm{FeMes}_2(\mathrm{depe})]$, the latter being crystallographically authenticated. However, chelation with the less electron-donating dppe ligand furnishes square-planar *cis*-$[\mathrm{FeMes}_2(\mathrm{dppe})]$ **123**, as corroborated by SQUID magnetometry and Mössbauer spectroscopy. Abstraction of a mesityl group in $\mathrm{CH}_2\mathrm{Cl}_2$ solution converted **123** to crystallographically studied tetrahedral **124**. The crystallographic verification of the diaryl **125**, first reported in 1961, confirmed its square-planar coordination.[199,206]



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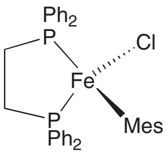

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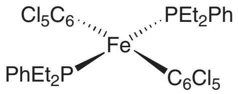

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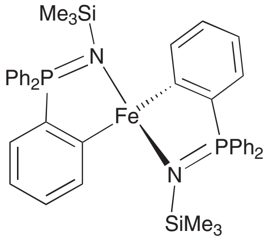
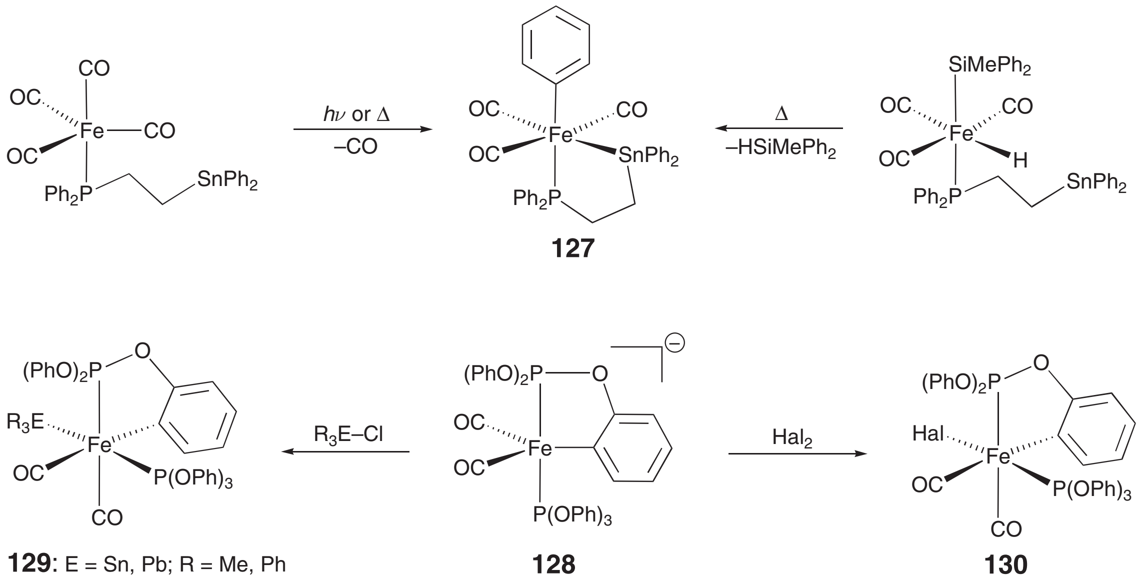


126

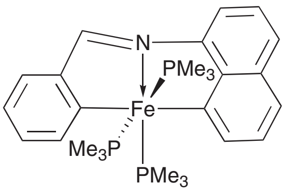
The chelate complex **126** results from treatment of FeCl_2 with the *ortho*-lithiated iminophosphorane $[\mathrm{Li}(o\text{-}\mathrm{C}_6\mathrm{H}_4\mathrm{PPh}_2\mathrm{NSiMe}_3)]_2\cdot\mathrm{Et}_2\mathrm{O}$.[207] The crystal structure of this distorted tetrahedral 14-electron species displays quite short Fe–C bond distances of 207.1(3) pm. The salt-elimination route using PhLi or Grignard reagents p-Y-$\mathrm{C}_6\mathrm{H}_4\mathrm{MgBr}$ (Y = H, OMe, Cl, F, Me) also allowed the synthesis of a number of stable octahedral aryl complexes *cis,trans*-$[\mathrm{Fe(Ar)(X)(CO)}_2(\mathrm{PMe}_3)_2]$ starting from $[\mathrm{FeX}_2(\mathrm{CO})_2(\mathrm{PMe}_3)_2]$.[178] Several X-ray structure determinations performed on $[\mathrm{FePh(X)(CO)}_2(\mathrm{PMe}_3)_2]$ (X = Cl, Br, I) showed that the aryl ligand is *cis*-orientated relative to the halide ligand, with Fe–Ph bond lengths in the range between 205.7 and 209.3 pm.

The structurally characterized phenylstannyl complex **127** is accessible by thermal silane elimination and concomitant oxidative addition of an Sn–Ph group from *mer*-$[\mathrm{FeH(SiMePh}_2)(\mathrm{CO})_3(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{CH}_2\mathrm{SnPh}_3)]$. A second route to (phosphinoalkyl)stannyl complexes of this type is the chelate-assisted thermal or photochemical activation of an Sn–Ph bond of $[\mathrm{Fe(CO)}_4\{\mathrm{Ph}_2\mathrm{P(CH}_2)_n\mathrm{SnPh}_3\}]$ ($n = 1$–3), as shown in Scheme 22.[83,208] Cyclometallated stannyl and plumbyl complexes **129** result from nucleophilic attack of orthometallated anion $[\mathrm{Fe(CO)}_2\text{-}\{\mathrm{P(OPh)}_3\}\{\mathrm{P(OPh)}_2\mathrm{OC}_6\mathrm{H}_4\}]^-$ **128** on ClSnR_3 and ClPbR_3. This metallate was generated *in situ* by deprotonation of the hydride $[\mathrm{FeH(CO)}_2\{\mathrm{P(OPh)}_3\}\{\mathrm{P(OPh)}_2\mathrm{OC}_6\mathrm{H}_4\}]$.[209] A mixture of geometric isomers was obtained upon treatment of **128** with halogens or PhICl_2. Crystal-structure determinations confirmed that the major isomer (Hal = I) has the ligand arrangement illustrated in Scheme 22, the minor isomeric form being related to **130** by exchange of the $\mathrm{P(OPh)}_3$ and CO positions. Irradiation of the thiocarbonyl compound $[\mathrm{Fe(CS)(CO)}_2\{\mathrm{P(OPh)}_3\}_2]$ is thought to generate first the orthometallated hydride $[\mathrm{FeH(CS)(CO)}_2\{\mathrm{P(OPh)}_3\}\{(\mathrm{PhO})_2\mathrm{POC}_6\mathrm{H}_4\}]$. Subsequent CS insertion into the Fe–aryl bond, followed by hydride shift, produces finally the cyclic η^2(*C*,*S*)-bonded thioaldehyde complex $[\mathrm{Fe(CO)}_2\{\mathrm{P(OPh)}_3\}\{(\mathrm{PhO})_2\mathrm{P(OC}_6\mathrm{H}_4\mathrm{CHS})\}]$.[210]



Scheme 22

A novel meridional bicyclometallation was achieved by methane extrusion from $[Fe(CH_3)_2(PMe_3)_4]$ with *N*-benzylidene-1-naphthylamine and (1-naphthyl)(2-pyridyl)ethene. In the crystal structures of isomeric **131** and **132**, the iron center bears three meridional PMe_3 ligands.[211] C–H activation of aromatic imines in the presence of $[Fe(CH_3)_2(PMe_3)_4]$ or $[Fe(PMe_3)_4]$ led to the orthometallated methyl and hydride compounds **133** and **134**, respectively.[212]



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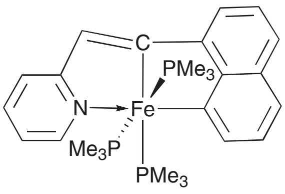

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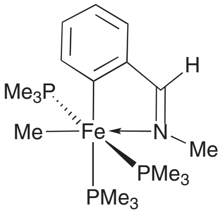

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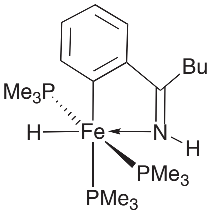
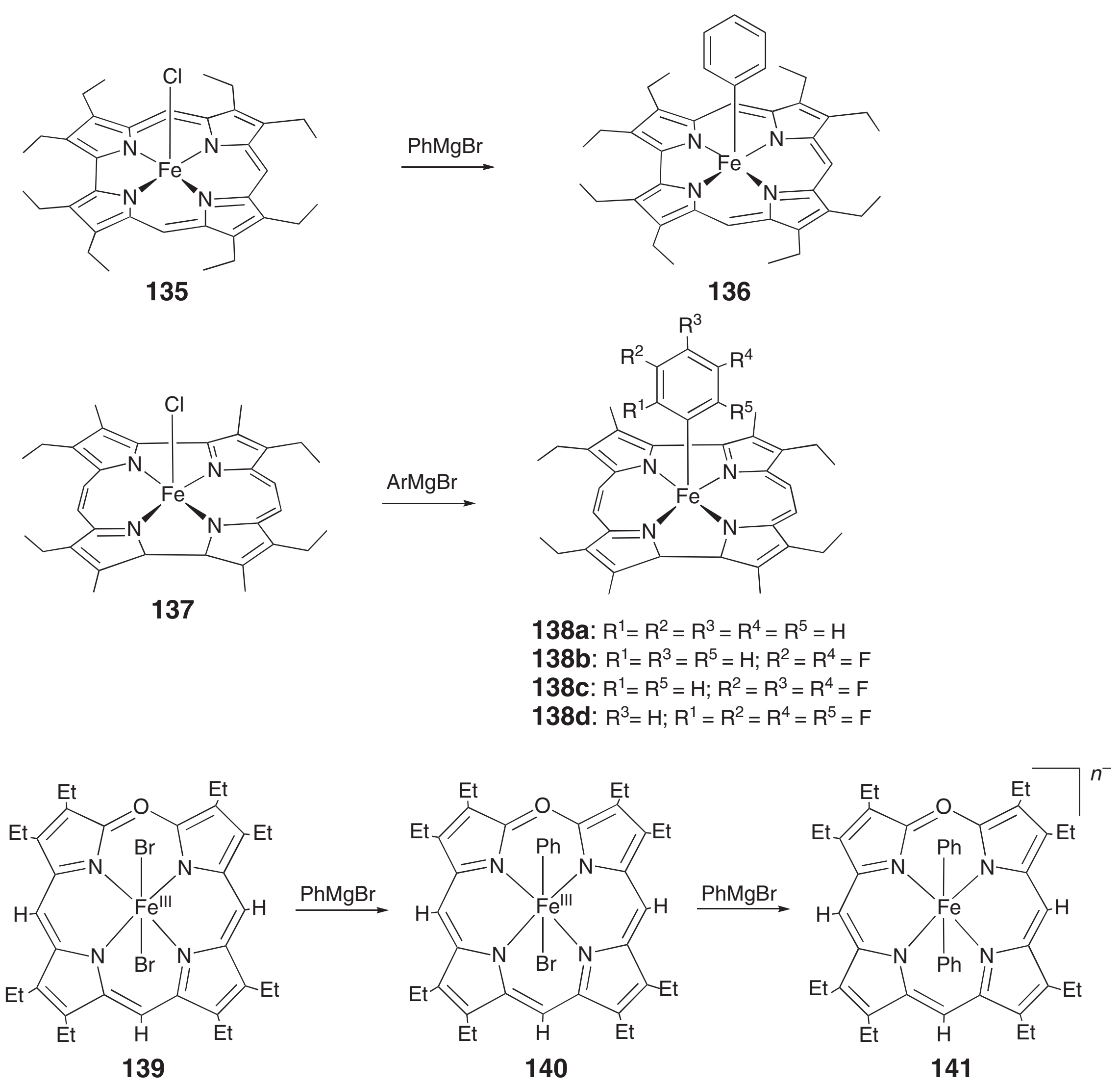


134

The major product from *N*-methyl-*N*-nitrosoaniline and $[Fe_2(CO)_9]$ is the orthometallated compound *cis*-$[Fe\{C({=}O)C_6H_4NCH_3\}(CO)_4]$. This crystallographically characterized five-membered ferracycle, tetracarbonyl(1-methyl-3-ferra-2-oxindole), undergoes *N*-oxide-induced or photochemically promoted alkyne insertions.[213]

Treatment of the corrole chloro complex **135** with PhMgBr allowed the structural characterization of $[(octaethylcorrole)Fe(C_6H_5)]$ **136**, which represents the first example of an air-stable Fe(IV) compound containing a tetrapyrrole ligand (Scheme 23).[214] This paramagnetic compound with $S = 1$ can be oxidized either chemically or electrochemically to give cationic $[(octaethylcorrole)Fe(C_6H_5)][ClO_4]$ with a spin state $S = 1/2$. The complex contains a five-coordinate iron with an Fe–C bond distance slightly shorter than that of **136** [196.5(5) vs. 198.4(3) pm]. The formulation of the electron distribution in this Fe(IV) corrole π-cation radical was confirmed by Mössbauer, X-ray crystallographic, and magnetic susceptibility data, as well as by EPR spectroscopy, which gives evidence for strong antiferromagnetic coupling between the iron(IV) center and the singly oxidized corrole macrocycle. In an attempt to determine the electronic configuration, $[(7,13\text{-}Me_2Et_6corrole)Fe(C_6H_5)]$ has been studied by temperature-dependent magnetic susceptibility, Mössbauer, and ^1H NMR spectroscopy, and the results have been compared to those determined on the basis of spin-unrestricted DFT calculations.[215]

In a similar manner, the first examples of iron metalloporphycenes [(EtioPc)FeAr] **138** with σ-bonded aryl groups have been synthesized (EtioPc = dianion of 2,7,12,17-tetraethyl-3,6,13,16-tetramethylporphycene) (Scheme 23).[216,217] Since the porphycene macrocycle is isomeric with the porphyrin cycle, a comparison of the electrochemical behavior to



138a: $R^1 = R^2 = R^3 = R^4 = R^5 = H$
138b: $R^1 = R^3 = R^5 = H$; $R^2 = R^4 = F$
138c: $R^1 = R^5 = H$; $R^2 = R^3 = R^4 = F$
138d: $R^3 = H$; $R^1 = R^2 = R^4 = R^5 = F$

Scheme 23

that of the corresponding porphyrin counterpart was possible. Derivative 138a undergoes two one-electron reductions at the conjugated π-ring system, which is the first reported example where a iron(III) porphyrin-like molecule is reduced at the ring rather than at the metal center. 138a also undergoes three one-electron oxidations. The first oxidation occurs at the iron center to give $[(\mathrm{EtioPc})\mathrm{Fe}^{\mathrm{IV}}\mathrm{Ph}]^+$. Subsequent migration of the phenyl group and demetallation gives then (N-C_6H_5EtioPc)H as final product. ESR measurements show that the porphycenes 138 can be high or low spin, depending upon the axial ligand and temperature. An X-ray structure of the low-spin derivative 138b shows that the iron atom is nearly in the basal plane, *d*(Fe–C) being 195.0(4) pm.

The iron verdoheme 139 was treated with PhMgBr to give the σ-phenyl complex 140, which was further reacted with PhMgBr to produce the bis(phenyl) system 141. The paramagnetic nature of these 5-oxaporphyrins was studied extensively by NMR.[218] Several neutral five-coordinate and anionic six-coordinate tetraphenyloxaporphyrin-supported iron(II) complexes bearing one or two σ-bonded aryl groups resulted from titration of [(tetraphenyloxapor)Fe$^{\mathrm{II}}$Cl] with ArMgBr (Ar = C_6H_5, p-$CH_3C_6H_4$, C_6F_5). The electronic structure of these paramagnetic 21-oxaporphyrins was examined by ^{1}H NMR spectroscopy.[219] The addition of aryl Grignard reagents to the iron(III) tetraphenylporphyrin π-cation radical [(TTP$^{\cdot}$)FeCl][SbCl$_6$] was reported to generate a mixture of [(TTP)Fe$^{\mathrm{IV}}$Ar][SbCl$_6$] and [(TTP)Fe$^{\mathrm{III}}$Ar], which was analyzed by ^{1}H NMR.[220] Stable low-spin σ-aryliron(III) complexes were obtained by reaction of [(octaphenyltetraazapor)FeCl] with aryl Grignard reagents (Ar = Ph, p-tolyl).[221]

[(TTP)FeCl] was also reported to catalyze the formation of aryl and heteroaryl Grignard reagents via the intermediacy of ArFe(MgCl) species.[222]

Several papers have been devoted to the chemistry of OEP- and OETPP-supported iron porphyrin systems (OETPP = dianion of octaethyl-tetraphenylporphyrin). The electrochemical behavior of [(OEP)Fe^{III}(Pyr)] bearing a σ-bonded pyrrole and its electrocatalytic activity for the reduction of O_2 were investigated.[223] The generation of the cationic iron(IV) porphyrin [(OETPP)Fe(C_6H_5)]$^+$, which is stable at room temperature, in non-aqueous media was reported.[224] [(OETPP)Fe(C_6H_5)] is the first monomeric iron(III) porphyrin to undergo three reversible oxidations, and represents the first example where migration of a σ-bonded axial ligand to a porphyrin nitrogen occurs from a doubly oxidized iron porphyrin. A self-consistent mechanism for the reduction of [(OETPP)Fe(C_6F_5)], [(OETPP)Fe(C_6F_4H)], and other σ-bonded fluorophenyl iron(III) porphyrins was elucidated using electrochemical and spectroelectrochemical techniques.[225] An unusual feature of these fluoroaryl OETPP compounds is that they are low spin, in contrast to the corresponding OEP and TPP complexes, which are high spin. In contrast to the oxidized species [(OEP)Fe^{IV}(C_6H_5)]$^+$, [(OETPP)Fe^{IV}(C_6H_5)]$^+$ is quite stable and does not undergo phenyl group migration. However, iron-to-nitrogen phenyl migration is induced after a second oxidation.[226]

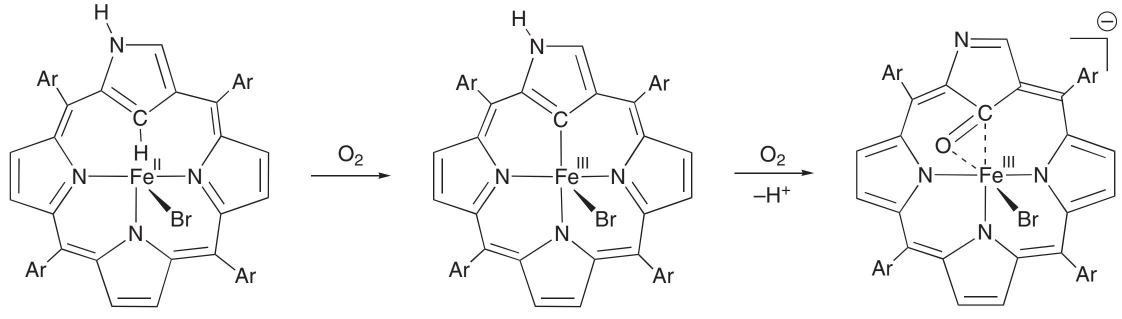
A kinetic and thermodynamic study on series of aryl porphyrins [(OEP)FeAr] in several oxidation states shows that neither the iron(III) spin state nor the ligand-field strength of the σ-bonded organic ligand are in themselves key factors in the occurrence of this aryl migration. Kinetic measurements both in the absence and presence of pyridine as sixth ligand indicate that the donor ability of Ar accelerates, while an increased electron donation from a coordinated pyridine decelerates, the migration rate.[227] Homogeneous electron-transfer kinetics for the oxidation of a number of [(OEP)Fe^{III}Ar] and [(OETTP)Fe^{III}Ar] porphyrins using three different oxidants were examined, and the resulting data were evaluated in light of the Marcus theory of electron transfer to determine reorganization energies of the rate-determining oxidation of Fe(III) to Fe(IV).[228] Iron-to-nitrogen migration rates of aryl porphyrins [(OETPP)Fe^{IV}Ar]$^{n+}$ ($n = 1, 2$) were also examined as function of the compound's oxidation state.[229] They were determined for both the one-electron and two-electron oxidized species produced in the electron-transfer oxidation with different oxidants in acetonitrile at 298 K. The migration rate of the aryl group in [(OETPP)FeAr]$^+$ is about 10^4 times slower than that of the corresponding two-electron oxidized species, [(OETPP)FeAr]$^{2+}$. Five-coordinate [(OETPP)FePh], whose crystal structure has been determined [d(Fe–C) = 196.0(3) pm], was oxidized with [phenoxathiinylium][$SbCl_6$] to generate quite stable [(OETPP)FePh][$SbCl_6$].[230] The latter iron(IV) species with spin state $S = 1$ was investigated by Mössbauer spectroscopy.

The six-coordinate nitrosyl–aryl porphyrin complex [(OEP)Fe(NO)(p-C_6H_4F)] was synthesized.[231] An X-ray structure determination reveals an unprecedented bending and tilting of the Fe–NO unit as well as significant lengthening of *trans*-axial bond distances. The Fe–N–O angle is 157.4(2)°, the nitrosyl N atom is tilted off of the normal to the heme plane by 9.2°, the bond distances Fe–N(NO) and Fe–C(aryl) being 172.8(2) and 204.0(3) pm, respectively. Calculations reproduce the structural distortions and show that the observed bending and tilting of the Fe–NO group indeed represents a low-energy conformation. The aryl ligand also affects the Fe–NO π-bonding as measured by IR and ^{57}Fe Mössbauer spectroscopy.

The reactions of cytochrome P450$_{cam}$ with aryldiazenes (ArN=NH) yield σ-bonded iron–aryl complexes, whose oxidation causes regioselective migration of the aryl group from the iron to the porphyrin nitrogens. The influence of high pressure on the formation and rearrangement of these Fe–aryl complexes was studied. The aryls are stable at atmospheric pressure but decompose in a pressure-dependent manner at pressures above 1,500 (Fe–phenyl) or 2,500 bar (Fe–(2-naphthyl) or Fe–(p-biphenyl)) under formation of the *N*-aryl protoporphyrin adducts.[232]

Another interesting recent research area in the field of organometallic porphyrin chemistry concerns the formation and reactivity of core-modified carba- and benziporphyrins.[161,162] One-electron oxidation of the inverted 2-aza-21-carbaporphyrin **142** with O_2 is accompanied by deprotonation of C(21) and formation of an Fe–C bond yielding **143** (Scheme 24).[233] In the solid state, the Fe–C bond distance to the trigonal pyrrolic carbon in five-coordinate **143** amounts to 198.1(8) pm. In the subsequent step, insertion of an O atom into the Fe–C bond produces anionic **144**, whose crystallographic data suggest an η^2-interaction between iron and the carbonyl function. The existence of agostic C···H···Fe interactions was evidenced in related carba- and benziporphyrin systems.[162,234,235]

The iron-catalyzed cross-coupling of Grignard reagents with aromatic organic substrates becomes more and more an efficient and low-cost alternative to well-established Ni- and Pd-catalyzed carbon–carbon coupling strategies.[236–238] The advances and scope of these promising coupling reactions involving the intermediacy of iron aryl species have been reviewed.[239,240] Last but not least, an organometallic modification of iron surfaces was achieved by electrochemical reduction of aromatic diazonium salts.[241] Covalently σ-bound nitrophenyl groups were also surface-grafted with formation of an organic layer by dipping a metallic iron sample into a solution of [p-$NO_2C_6H_4N_2$][BF_4].[242]



142 **143** **144**

Scheme 24

6.02.5 Synthesis and Reactivity of σ-Alkynyls (Acetylides)

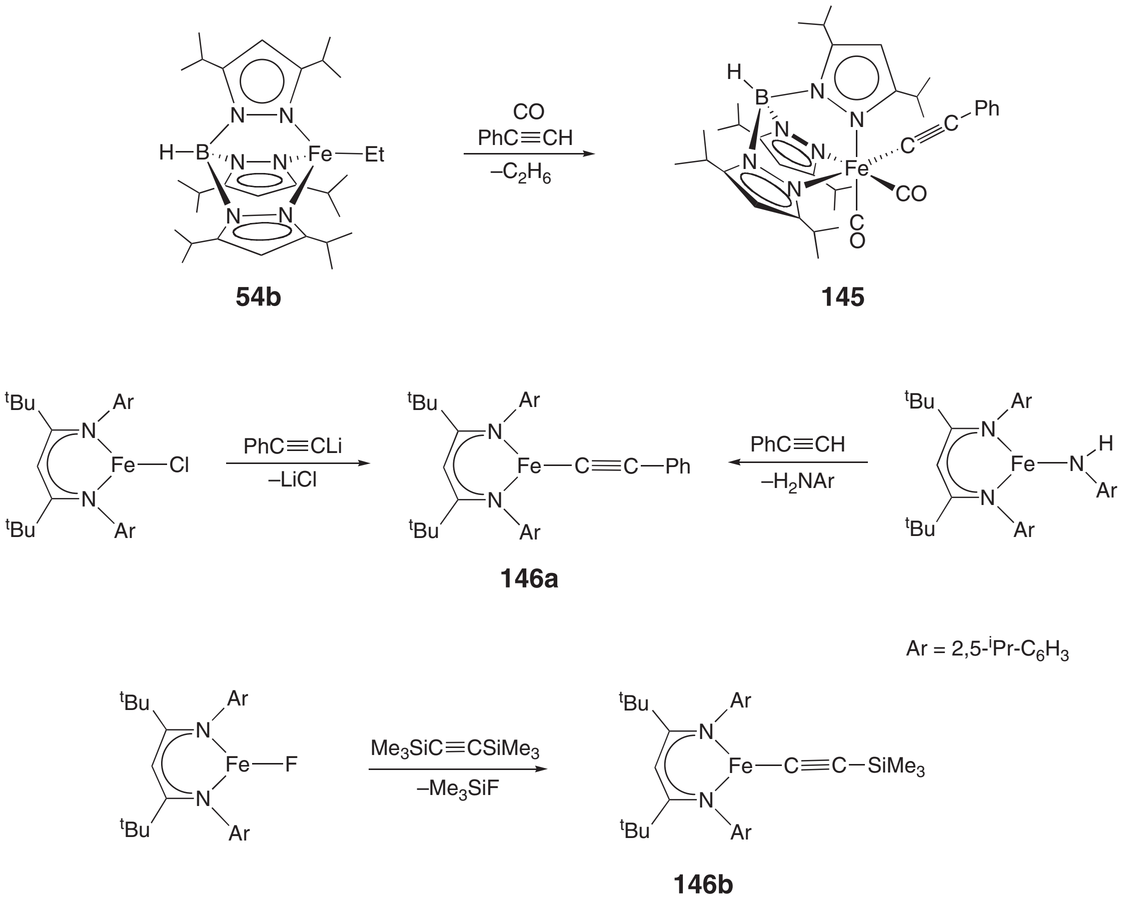
The interest in transition metals with σ-bound alkynyl ligands continues, since metal acetylides are potential nonlinear optical, conducting, or liquid crystalline materials. Their chemistry and applications have been reviewed in 2003 and 2004.[243,244] Another review dealing on organoiron polymers includes also rigid-rod iron acetylides.[245] The chemistry of metal complexes with 1,3-diynes and polyynes was surveyed in 2001.[245a]

The preparation of dilithium[*trans*-bis(3,3-dimethyl-1-butynyl)phthalocyaninato)iron(II)] and dilithium[*trans*-bis(phenylethynyl)phthalocyaninato)iron(II)], regarded as model compounds for one-dimensional conductors, was reported.[246] The high-spin ($S=5/2$) five-coordinate porphyrins [(TTP)Fe(C$\equiv$CR)] (R = ^{n}Pr, Ph), obtained by titration of [(TTP)FeCl] with the appropriate lithium acetylide, were converted to six-coordinate low-spin adducts by axial ligation of THF or pyridine.[246a] The homoleptic salt $Li_4[Fe(C{\equiv}CSiMe_3)_6]\cdot 4LiCCSiMe_3\cdot 4Et_2O$, whose crystal structure shows mean Fe–C bond distances of 193.0(9) pm, results from treatment of $Fe(CF_3SO_3)_2$ with an excess of $LiC{\equiv}CSiMe_3$ in Et_2O as solvent.[246b]

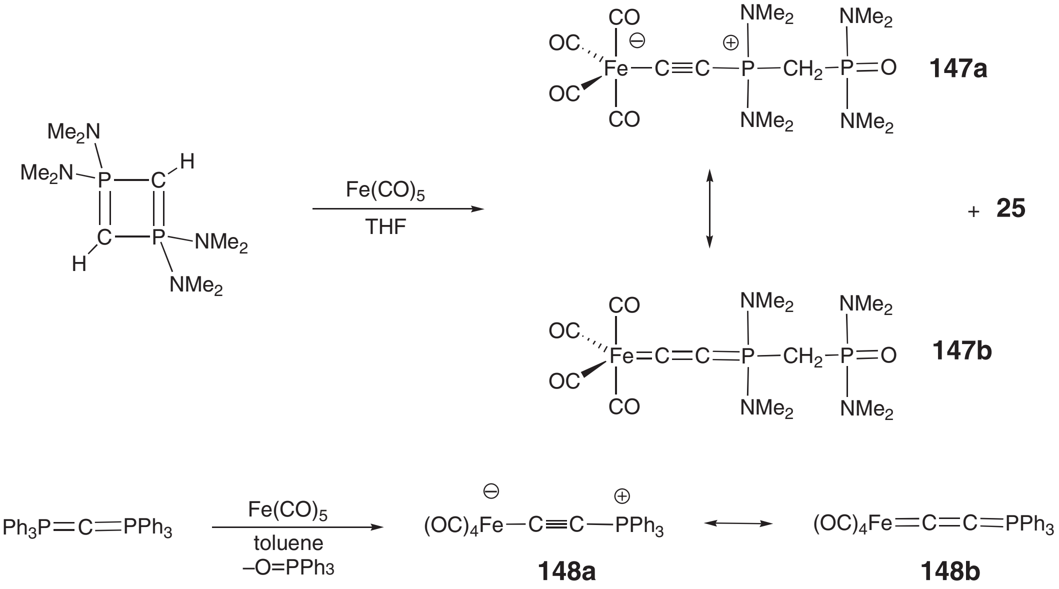
The hydrotris(3,5-diisopropylpyrazolyl)borate-containing acetylide **145** stems from protonolysis of the ethyl precursor **54b** with phenylacetylene in the presence of CO (Scheme 25).[93] Several synthetic routes leading to β-diketiminate-supported σ-alkynyls **146** are presented in Scheme 25. Treatment of the chloro precursor with LiC$\equiv$CPh produces crystallographically characterized **146a**. Alternatively, this trigonal-planar compound is accessible by protonolysis of the amido precursor with phenylacetylene.[247] The silaphilic Fe–F starting complex reacts readily with bis(trimethysilyl)acetylene to yield **146b**, whose Fe–C bond distance is slightly shorter than that of **146a** [196.1(6) vs 200.0(2) pm].[105]

As already mentioned in Section 6.02.1, reaction of $[Fe(CO)_5]$ with a diphosphete reagent provides via an initial [2 + 2] cycloaddition the phosphonio–acetylide **147** as major product, together with acylferrate **25** (Scheme 26).[54] ^{13}C NMR data and a crystal structure determination show that this compound may be considered as a zwitterionic phosphonio–acetylide **147a** with a C$\equiv$C separation of 120.9(6) pm characteristic for an acetylenic triple bond, but the quite short Fe–C bond distance of 191.2(5) pm suggests also a certain degree of an allenylidene-like contribution **147b** (see Section 6.02.1). Another borderline case is phosphonio–acetylide **148**, obtained from reaction of $[Fe(CO)_5]$ with a carbodiphosphorane.[248] NMR and crystallographic data [d(Fe–C) = 190.2(2) pm] indicate that the allenylidene character of **148b** is even more pronounced than for **147**.

Most iron alkynyls are supported by mono- or bidentate phosphorus donors. The bis(alkynyl) derivatives *trans*-$[Fe(C{\equiv}CR)_2\{PPh(OEt)_2\}_4]$ and *trans*-$[Fe(C{\equiv}CR)_2\{P(OR^1)_3\}_4]$ (R = Ph, *p*-tolyl, ^{t}Bu; R^1 = Me, Et) were synthesized by treating lithium acetylides with a phosphite-containing $FeCl_2$ solution in THF.[249] Protonation of $[Fe(C{\equiv}CPh)_2\{P(OR^1)_3\}_4]$ with HBF_4 converted these bis(alkynyls) to alkynyl vinylidene cations *trans*-$[Fe(C{\equiv}CPh)({=}C{=}CHPh)\{P(OR^1)_3\}_4][BF_4]$, as ascertained by an X-ray diffraction study. A number of alkynyl methylvinylidene cations *trans*-$[Fe(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OR^1)_3\}_4][CF_3SO_3]$ and $[Fe(C{\equiv}CBu^t)\{{=}C{=}C(Me)Bu^t\}\{P(OEt)_3\}_4][CF_3SO_3]$ were also generated by alkylation with methyl triflate. Electrophilic attack of $[p\text{-}CH_3C_6H_4N_2][BPh_4]$ on $[Fe(C{\equiv}CPh)_2\{P(OEt)_3\}_4]$ produces the alkynyl diazovinylidene salt *trans*-$[Fe(C{\equiv}CPh)\{{=}C{=}C(N{=}N\text{-}p\text{-tolyl})Ph\}\{P(OEt)_3\}_4][BPh_4]$. The vinylidene unit of $[Fe(C{\equiv}CPh)({=}C{=}CHPh)\{P(OEt)_3\}_4]$ $[BF_4]$ is replaced by CO in the presence of $NaBPh_4$ to afford $[Fe(C{\equiv}CPh)(CO)\{P(OEt)_3\}_4][BF_4]$. Treatment of $[FeHCl\{PPh(OEt)_2\}_4]$ with LiC$\equiv$CR (R = Ph, *p*-tolyl, ^{t}Bu) gives the alkynyl hydrides



Scheme 25



Scheme 26

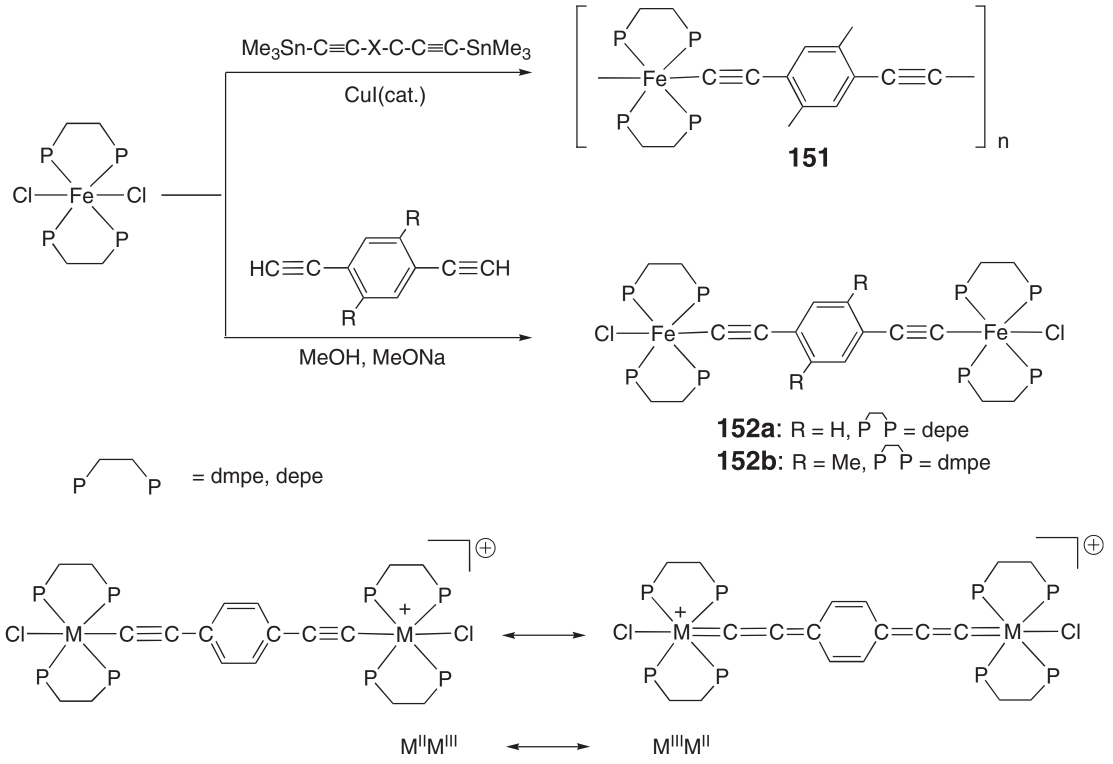
trans-$[FeH(C\equiv CR)\{PPh(OEt)_2\}_4]$.[250] Cationic alkynyl compounds $[Fe(C\equiv CR)\{P(OEt)_3\}_5]^+$ were also formed upon reaction of $P(OEt)_3$-containing $FeCl_2$ solutions with propargylic alcohol $HC\equiv CCMePh(OH)$ in the presence of NEt_3 or with $HC\equiv CPh$.[251] The binuclear complex $[\{Fe[P(OEt)_3]_5\}_2(\mu\text{-}1,4\text{-}C\equiv CC_6H_4C\equiv C)][BPh_4]_2$ resulted from addition of 1,4-diethynylbenzene.

The coupling of MP with $[Fe(CO)_2(PEt_3)_2(N_2)]$ affords an equilibrium mixture of $[Fe(CO)_2(PEt_3)_2(\eta^2\text{-}HC\equiv CCO_2Me)]$ and alkynyl hydride *cis,trans*-$[FeH(C\equiv CCO_2Me)(CO)_2(PEt_3)_2]$. This mixture is irreversibly converted to the vinylidene species $[Fe({=}C{=}CHCO_2Me)(CO)_2(PEt_3)_2]$ **156c** (see Section 6.02.6) in the presence of silylated silica.[252] With acetylene itself, a mixture consisting of $[Fe(CO)_2(PEt_3)_2(\eta^2\text{-}HC\equiv CH)]$, $[FeH(C\equiv CH)(CO)_2(PEt_3)_2]$, and $[Fe({=}C{=}CH_2)(CO)_2(PEt_3)_2]$ is formed. Again, chromatography over silylated silica induced transformation of all species to the vinylidene isomer.[253] However, exclusive alkynyl hydride formation was noticed upon oxidative addition of $HC\equiv CSiMe_3$ to $[Fe(CO)_2\{P(OPr^i)_3\}_2(N_2)]$ to give $[FeH(C\equiv CSiMe_3)(CO)_2\{P(O^iPr)_3\}_2]$ **149**. A number of hydride complexes $[FeH(C\equiv CR_2OH)(CO)_2(PEt_3)_2]$ **150a-f** were also obtained as sole products after reactions of $HC\equiv CCR_2(OH)$ with $[Fe(CO)_2(PEt_3)_2(N_2)]$ (Scheme 28).[254] Treatment of $[FeH(N_2)\{P(CH_2CH_2PPh_2)_3\}][BPh_4]$ or $[Fe(H)(H_2)_2\{P(CH_2CH_2PPh_2)_3\}][BPh_4]$ with an excess of terminal acetylenes allowed the isolation of a series of stable paramagnetic d^6-alkynyls $[Fe(C\equiv CR)\{P(CH_2CH_2PPh_2)_3\}][BPh_4]$. CV shows that all iron(II) derivatives undergo electron-transfer reactions encompassing the Fe(I), Fe(II), and Fe(III) oxidation states.[255] Reduction of $[Fe(C\equiv CPh)\{P(CH_2CH_2PPh_2)_3\}][BPh_4]$ with $[CoCp_2]$ provides the d^7-low-spin compound $[Fe(C\equiv CPh)\{P(CH_2CH_2PPh_2)_3\}]$. A comparison of the crystal structures of this redox couple reveals an elongation of the Fe–C bond length after reduction [188.0(2) vs. 192.0(1) pm].

Under high-pressure conditions, $[FeH_2(dmpe)_2]$ reacts with $HC\equiv CPh$ to form almost quantitatively *trans*-$[FeH(C\equiv CPh)(dmpe)_2]$ within 30 min.[256] In contrast, a methanolic solution of $[FeH_2(dmpe)_2]$ reacts with the conjugated alkyne $HC\equiv CCMe{=}CH_2$ to afford the bis(acetylide) *trans*-$[Fe(C\equiv CCMe{=}CH_2)_2(dmpe)_2]$, whose crystal structure reveals an Fe–C bond distance of 190.5(4) pm.[257] A similar Fe–C bond distance of 191.8(3) pm has been reported for *trans*-$[FeCl(C\equiv CPh)(dmpe)_2]$, stemming from treatment of $[FeCl_2(dmpe)_2]$ with $HC\equiv CPh$ in $NaBH_4$ containing EtOH.[180] The acetylido–methyl iron complexes, *cis/trans*-$[Fe(C\equiv CR)(CH_3)(dmpe)_2]$ and *trans*-$[Fe(C\equiv CR)(CH_3)(depe)_2]$ were synthesized by transmetallation with $Mg(C\equiv CR)_2$ ($R = C_6H_5$, C_6H_4OMe) from the corresponding methyl halide complexes. Alternatively, they were formed by transmetallation from the chloride complexes $[FeCl(C\equiv CR)(dmpe)_2]$ and $[FeCl(C\equiv CR)(depe)_2]$ with $Mg(CH_3)_2$.[65] The crystal-structure determination of $[Fe(C\equiv CC_6H_5)(CH_3)(dmpe)_2]$ reveals $Fe–CH_3$ and $Fe–C\equiv C$ bond lengths of 214.4(3) and 192.3(3) pm, respectively.

The methyl acetylides $[Fe(C\equiv CR)(CH_3)(dmpe)_2]$ are thermally stable in the presence of acetylenes, but under UV irradiation, methane extrusion produces iron bis(acetylides). Photochemical metathesis of *cis*- or *trans*-$[Fe(C\equiv CR)(CH_3)(dmpe)_2]$ ($R = Ph$, $p\text{-}C_6H_4OCH_3$) with terminal acetylenes was used to selectively synthesize a number of unsymmetrical bis(acetylides) of the type *trans*-$[Fe(C\equiv CR)(C\equiv CR^1)(dmpe)_2]$. The structure of *trans*-$[Fe(C\equiv Ph)(C\equiv CC_6H_4OCH_3)(dmpe)_2]$ was determined by single crystal X-ray diffraction. The photochemical metathesis of 1,7-octadiyne with $[Fe(CH_3)(C\equiv CPh)(dmpe)_2]$ was utilized to synthesize the bridged binuclear species *trans,trans*-$[(dmpe)_2(PhC\equiv C)Fe\{\mu\text{-}C\equiv C(CH_2)_4C\equiv C\}Fe(C\equiv Ph)(dmpe)_2]$. The trinuclear species *trans, trans,trans*-$[(dmpe)_2(PhC\equiv C)Fe\{\mu\text{-}C\equiv C(CH_2)_4C\equiv C\}Fe(dmpe)_2\{\mu\text{-}C\equiv C(CH_2)_4C\equiv C\}Fe(C\equiv CPh)(dmpe)_2]$ was synthesized by the photochemical reaction of $[Fe(C\equiv CPh)\{C\equiv C(CH_2)_4C\equiv CH\}(dmpe)_2]$ with $[Fe(CH_3)_2(dmpe)_2]$. Extended irradiation of the bis(acetylides) with phenylacetylene resulted in insertion of the terminal alkyne into one of the metal acetylide bonds to give acetylide–butenyne complexes, as confirmed by an X-ray diffraction study of *trans*-$[Fe(C\equiv CC_6H_4OCH_3)\{\eta^1\text{-}C(Ph){=}CH(C\equiv CC_6H_4OCH_3)\}(dmpe)_2]$. As expected, the Fe–alkynyl bond is shorter than the Fe–alkenyl bond [193.7(2) vs. 206.7(2) pm].

The synthetic utility of (trimethylstannyl)alkynyls in the preparation of *trans*-$[Fe(C\equiv C\text{–}Ph)_2(dmpe)_2]$ has been demonstrated. A polymeric rigid-rod σ-acetylide $[\text{–}Fe(dmpe)_2\text{–}C\equiv C\text{–}X\text{–}C\equiv C\text{–}]_n$ **151** results from reaction of $[FeCl_2(dmpe)_2]$ with $Me_3SnC\equiv C\text{–}X\text{–}C\equiv CSnMe_3$ ($X = 2,5$-xylene) in the presence of catalytic amounts of CuI.[258] Electrochemistry evidences a metal–metal interaction across the linking acetylide in dinuclear systems of the type **152**, prepared according to Scheme 27. Coulometry in combination with optical absorbance spectroscopy shows the presence of mixed-valence oxidized species which possess a delocalized allenylidene structure. Calculations on the optimized geometric structure of the bridging acetylide of this Fe complex $CPh{=}CH_2$, **152** and related Ru and Os bimetallics indicate that the conjugated system undergoes a structural change upon oxidation to give a quinoid-like geometry.[259] The behavior of the alkynyl complexes *trans*-$[FeBr(C\equiv CR)(depe)_2]$ ($R = CPh_2H$) was studied by CV and the electrochemical P_L and E_L ligand parameters for the alkynyl ligands were estimated, showing that they behave as very strong net electron donors.[260]



Scheme 27

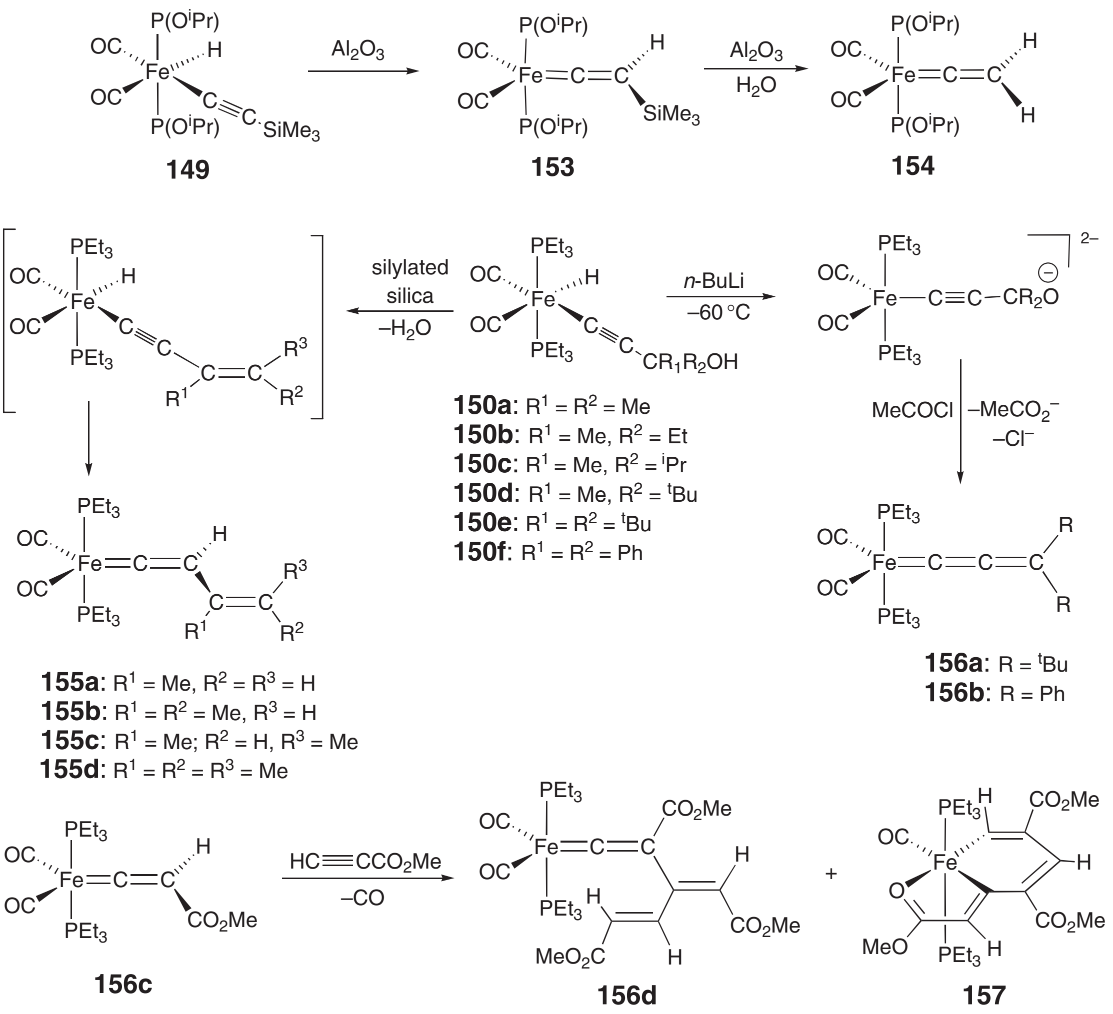
The synthesis of *trans*-[FeCl(C$\equiv$CC$_6$H$_4$NO$_2$)(diph)$_2$], containing the optically active 1,2-bis(methylphenyphosphino)benzene ligand (diph), has been reported. The electrochemical behavior and the NLO properties of this complex were investigated and compared with those of related Ru and Os derivatives.[261] A comparative DFT study on trends in back-bonding in the series *trans*-[MCl(C$\equiv$CR)(PH$_3$)$_4$] (M = Fe, Ru, Os; R = H, Ph, *p*-C$_6$H$_4$NO$_2$) indicates that the π-acceptor character of the acetylide ligand increases with the electron-withdrawing ability of R. The inclusion of relativistic effects in the calculation results in a metal dependence of Fe $\sim$ Ru $<$ Os for the backbonding, consistent with the observed trend in quadratic hyperpolarizabilities, β.[262]

6.02.6 Synthesis and Reactivity of Vinylidenes and Allenylidenes

Little information on iron vinylidene and allenylidene complexes without stabilizing Cp ligands was available in COMC (1995), allowing them to be considered along with simple carbene complexes. Because of the increasing number of articles on iron vinylidenes and allenylidenes, it seemed necessary to devote a separate subsection on the chemistry of these compounds. Some recent reviews on transition metal-containing vinylidene, allenylidene, and cumulenylidene ligands have appeared.[263–265] As seen in the preceding subsection, the chemistry of vinylidenes and cumulenes is often closely allied to that of metal acetylides. Therefore iron complexes containing this class of ligands are covered before presentation of simple carbene complexes in Section 6.02.7.

Treatment of acetone solutions of [FeH(H$_2$)$_2$(dmpe)$_2$][BPh$_4$] with HC$\equiv$CR was reported to produce the alkynyl vinylidene cations *trans*-[Fe(C$\equiv$CR){=C=C(H)R}(dmpe)$_2$][BPh$_4$] (R = Me, ^{i}Pr).[266] The formation of these crystallographically characterized salts proceeds via intermediate generation of the corresponding neutral bis(acetylides). These acetylides *trans*-[Fe(C$\equiv$CR)$_2$(dmpe)$_2$] were also obtained by deprotonation of the alkynyl vinylidene cations with KOBu^t in THF solution. Based on the crystallographic data, showing a rather short C=C and a quite long Fe=C bond of 185.3(9) pm, the NMR spectra, and the Mössbauer isomer shift, a bonding mode with partial Fe $\leftarrow$ C$^-$=C$^+$HR character was suggested for the vinylidene unit.

Contact of hydrido–acetylide **149** with Al$_2$O$_3$ induces isomerization to vinylidene **153**, while in the presence of water, cleavage of the silyl group occurs, leading finally to **154**.[253] Dehydration of alkynyls **150** during

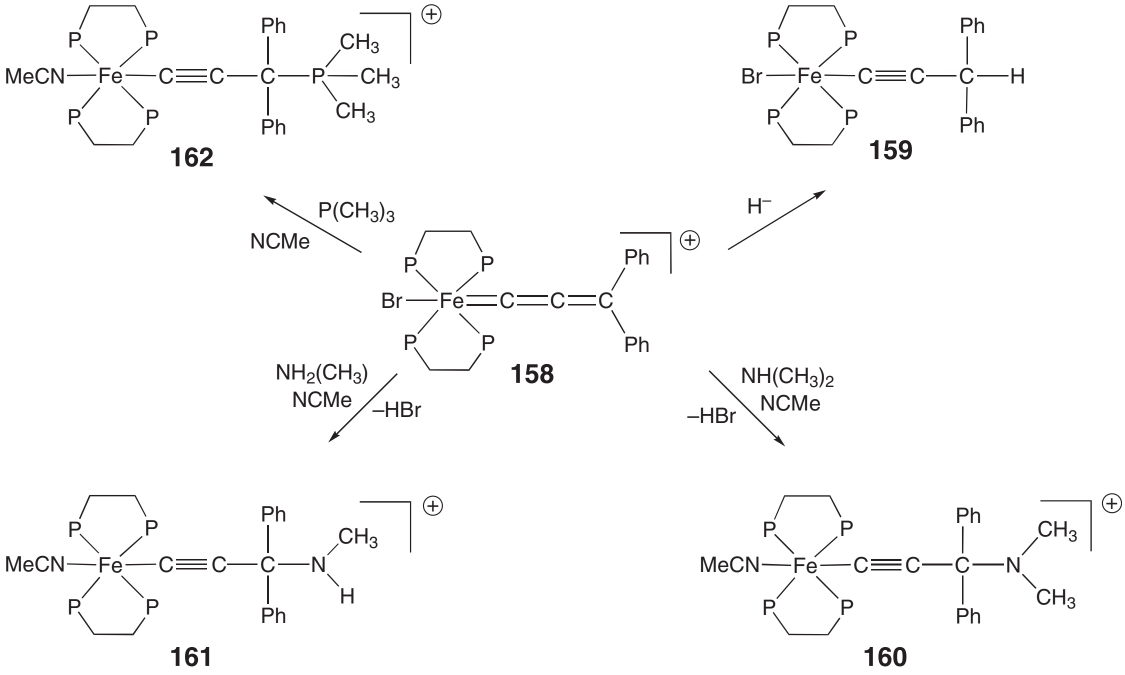


Scheme 28

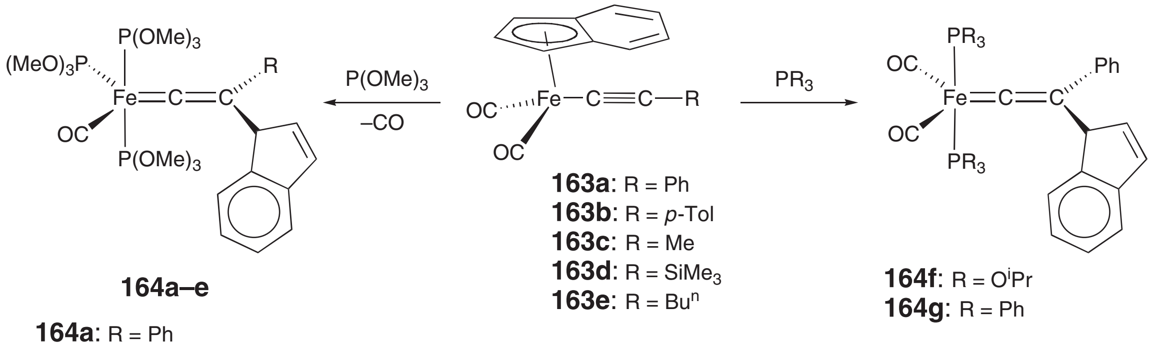
chromatography over silylated silica affords the vinyl-substituted vinylidenes **155a–d**. However, double deprotonation with BuLi and subsequent deoxygenation with acetyl chloride ultimately produced the formal products of dehydration **156a and 156b**.[254] Coupling of **156c** with further equivalents of MP leads to isolation of the structurally characterized vinylidene **156d** [d(Fe–C) = 173.0(8) pm] and metallacycle **157** (Scheme 28).[252] Reaction of $[Fe(CO)_2\{P(OMe)_3\}_2(N_2)]$ with the diyne $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ affords an equilibrium mixture of a π-alkyne complex with vinylidene $[Fe\{{=}C{=}C(SiMe_3)C{\equiv}CSiMe_3\}(CO)_2\{P(OMe)_3\}_2]$. The latter hydrolyzes upon chromatography on silica to yield finally $[Fe\{{=}C{=}CHC{\equiv}CSiMe_3\}(CO)_2\{P(OMe)_3\}_2]$.[253] An alternative route to allenylidene $[Fe({=}C{=}C{=}CPh_2)\ (CO)_2\{P(OMe)_3\}_2]$, quite similar to **156b**, starts from $Na[FeI(CO)_2\{P(OMe)_3\}_2]$ and $HC{\equiv}CCPh_2OAc$. This high-yield synthesis passes presumably through vinylidene intermediate $[Fe\{{=}C{=}CHCPh_2OAc\}(CO)_2\{P(OMe)_3\}_2]$, which eliminates acetic acid.[254] The crystal-structure determination of the trigonal-bipyramidal derivative $[Fe({=}C{=}C{=}C^tBu_2)(CO)_2\{P(OMe)_3\}_2]$ shows an Fe═C bond length of 183.3(4) and C═C intrachain distances of 126.6(5) and 134.4(6) pm.

Treatment of an MeOH solution of *trans*-$[FeBr_2(depe)_2]$ with alkynol $HC{\equiv}CC_6H_{10}OH$ in the presence of $NaBPh_4$ forms the cyclic allenylidene *trans*-$[FeBr({=}C{=}C{=}C_6H_{10})(depe)_2][BPh_4]$.[267] The cyclic voltammetric behavior of the allenylidene series *trans*-$[FeBr({=}C{=}C{=}CR_2)(depe)_2][BF_4]$ (R = Me, Et, Ph) was examined and the electrochemical P_L and E_L ligand parameters for the allenylidene ligands were estimated, showing that they behave as slightly weaker net-electron donors than organonitriles.[268] Further allenylidene complexes *trans*-$[FeBr({=}C{=}C{=}CRPh)(depe)_2][BPh_4]$ (R = Me, Ph) were obtained by treatment of a methanolic solution of *trans*-[$FeBr_2(depe)_2$] with $HC{\equiv}CC(R)Ph(OH)$ in the presence of Na[BPh_4]. The methylallenylidene ligand undergoes reversible deprotonation by NaOMe to yield the enynyl complex *trans*-[FeBr{$C{\equiv}CC({=}CH_2)Ph$}$(depe)_2$]. In an analogous manner, [FeBr($=C=C=CEt_2$)$(depe)_2$][BF_4] was converted to [FeBr{$C{\equiv}CC({=}CHMe)Et$}$(depe)_2$].[269,270] The diphenylallenylidene ligand of **158** undergoes regioselective hydride γ-addition on reaction with K[$BH(CHMeEt)_3$] to afford the alkynyl complex **159**. This compound is also formed upon electrochemical reduction of **158**. The neutral alkynyls *trans*-[FeBr{$C{\equiv}CC(Y)Ph_2$}$(depe)_2$] ($Y = MeO^-$, CN^-), originating from nucleophilic attack of methoxide and cyanide, were crystallographically characterized. The crystal structure of the cationic compound **160**, resulting from nucleophilic addition of $HNMe_2$, has also been determined. In a similar manner, addition of H_2NMe and PMe_3 gives the cationic alkynyls **161** and **162**, respectively (Scheme 29).

An unexpected migration of the indenyl ligand of alkynyl(η^5-indenyl) complexes **163** is induced by addition of a large excess of $P(OMe)_3$, leading to novel vinylidenes **164a–e** (Scheme 30).[271] When the bulkier ligands $P(O^iPr)_3$ or



Scheme 29



164a: R = Ph
164b: R = *p*-Tol
164c: R = Me
164d: R = $SiMe_3$
164e: R = Bu^n

Scheme 30

PPh_3 react with **163a**, only dicarbonyl vinylidenes **164f and 164g** are obtained. Mechanistic studies indicate that the intermolecular migration proceeds by a radical pathway.

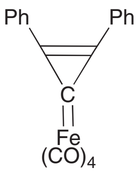
Photolysis of the porphyrin-supported vinylidene $[(TTP)Fe\{{=}C{=}C(p\text{-}C_6H_4Cl)_2\}]$ is reported to generate quantitatively $[(TTP)Fe^{II}]$ and bis(*p*-chlorophenyl)acetylene.[272] A combined photoelectron spectroscopic and DFT study deals with the Fe–C multiple-bonding character of the species $[FeC_n]^-$ and $[FeC_nH]^-$ ($n = 3, 4$).[273] The $n = 3$ species can be best characterized by cumulenic types of bonding with $[FeC_3H]^-$ also having an acetylenic isomer. The latter isomer $[Fe{\equiv}C\text{–}C{\equiv}C\text{–}H]^-$ is assumed to be linear with the H atom bonded to a *sp*-hybridized C atom and the Fe–C bond length close to that of a triple bond, whereas in the cumulenic isomer $[Fe{=}C{=}C{=}C\text{–}H]^-$, the H atom is off-linear by 20°. Both forms are almost degenerate in energy.

6.02.7 Synthesis and Reactivity of Simple Carbenes $L_nFe{=}CR_2$ and Carbynes $L_nFe{\equiv}CR$

In addition to the classical Fischer method and action of diazo compounds on metal complexes, extensively described in COMC (1982) and COMC (1995), several new synthetic routes toward iron carbenes have emerged during the past decade. Some are serendipitous, but the introduction of stable so-called Arduengo carbenes[274–275a] as ligands in transition metal chemistry also offers promising perspectives for the synthesis and catalytic reactivity of novel *N*-heterocyclic iron carbenes. Regardless of their bonding mode, which is essentially purely dative, these cyclic carbenes are treated together with iron carbenes possessing both σ-donor/π-acceptor properties within this chapter. Furthermore, no differentiation is made from Schrock-type alkylidenes. This section deals only with carbene complexes which lack ligands of higher hapticity. The chemistry of carbon–transition metal double and triple bond has been annually surveyed in *Coordination Chemistry Reviews* since 1997.[276,276a–276f]

Coupling of $Na_2[Fe(CO)_4]$ with 2,3-diphenyldichlorocyclopropene yields the cyclic carbene **165**.[277] A large number of aminocarbene complexes $[(CO)_4Fe\{{=}C(R)NR^1{}_2\}]$, without hydrogen atoms at the position α to the carbene carbon, was obtained by reaction of formamides or aromatic/heteroaromatic tertiary amides with $Na_2[Fe(CO)_4]$ and Me_3SiCl in THF solution.[278] This strategy has also been extended to synthesize homodinuclear bis(carbene) complexes. The crystal structure of the heterodinuclear bis(carbene) complex **166** reveals an Fe=C bond distance of 178.0(2) pm.[279] The thermal coupling of derivatives $[Fe\{{=}C(Ar)NMe_2\}(CO)_4]$ bearing an aromatic substituent with electron-deficient alkenes furnishes after demetallation 1,4-dicarbonyl compounds.[280] Aminocarbene complexes containing a C=C bond in the *N*-substituent were obtained after mixing $Na_2[Fe(CO)_4]/Me_3SiCl$ with *N*-(3-buten-1-yl)-*N*-methylbenzamide or *N*-(3-buten-2,2-dimethyl-1-yl)-*N*-methylbenzamide.[281] The preparation of *N*-allylaminocarbene compounds of type **167** and their thermolysis leading to η^3-1-azaallyltricarbonyl complexes was studied both experimentally and theoretically.[282] Thermolysis of $[(OC)_4Fe{=}C(NMe_2)_2]$ is reported to give a mixture containing the bridging aminocarbyne complexes $[(OC)_3Fe(\mu\text{-}CNMe_2)_2Fe(CO)_3]$ and trinuclear $[(OC)_3Fe_3(\mu_3\text{-}CNMe_2)_2]$. Other products stemming from the intermediacy of a putative aminocarbyne $[(OC)_4Fe{\equiv}C\text{–}NMe_2]$ include the dinuclear μ-carbamoyl compound $[(OC)_3Fe(\mu\text{-}CNMe_2)(\mu\text{-}OCNMe_2)Fe(CO)_3]$ and μ-amide $[(OC)_3Fe(\mu\text{-}NMe_2)(\mu\text{-}CNMe_2)Fe(CO)_3]$.[213]

Formal insertion of $Ti(NMe_2)_4$ into coordinated carbonyl groups of $[Fe(CO)_5]$ gives heterometallic aminocarbene complexes. Whereas with a 1 : 1 ratio of the reactants, heterodinuclear $[(CO)_4Fe{=}C(NMe_2)\{OTi(NMe_2)_3\}]$ is formed quantitatively, longer reaction times and an excess of $[Fe(CO)_5]$ lead to the trimetallic carbene **168**.[283] A pentanuclear multicarbene complex resulted from carbonyl insertion of $[Fe(CO)_5]$ into Zr–N bonds of $[Zr(NMe_2)_4]_2$.[284] The ylide $CH_2{=}P(NMe_2)_3$ attacks $[Fe(CO)_5]$ to produce the acylferrate $[MeP(NMe_2)_3]$ $[(OC)_4FeC({=}O)\{CH{=}P(NMe_2)_3\}]$. Reaction of this salt with Me_3SiCl or $MeSO_3CF_3$ results in formation of the carbenes $[(OC)_4Fe{=}C(OSiMe_3)\{CH{=}P(NMe_2)_3\}]$ and $[(OC)_4Fe{=}C(OMe)\{CH{=}P(NMe_2)_3\}]$, respectively. The occupation of the axial position of the latter trigonal-pyramidal compound by the carbene unit [$d(Fe{=}C) = 200.1(3)$ pm] was evidenced by X-ray crystallography.[285]



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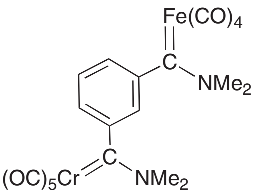

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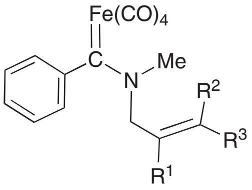

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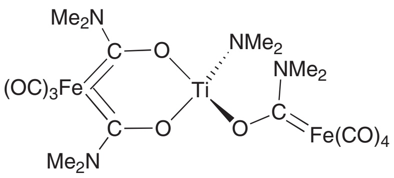
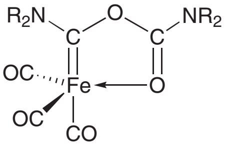
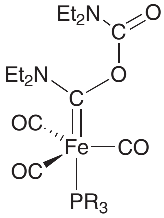


168

Nucleophilic addition of the lithiated aldimine BuN=C(^{t}Bu)Li to [Fe(CO)$_5$] generates first the acylferrate Li[(OC)$_4$FeC(=O)(C^{t}Bu=NBu^t)], which is converted to Fischer carbene [(OC)$_4$Fe=C(OMe)(C^{t}Bu=NBu^t)] after *O*-alkylation with [Me$_3$O]BF$_4$.[286] The outcome of the reaction of the alkynyl(ethoxy)carbene [(OC)$_4$Fe=C(OEt)(C≡CBu^t)] with HNMe$_2$ is temperature dependent: at −78 °C, substitution at the carbene gives exclusively [(OC)$_4$Fe=C(NMe$_2$)(C≡CBu^t)]. However, at 25 °C, an η^3-{2-(*tert*-butylcarbonyl)vinyl}carbene complex is formed.[287] The bis(carbamoyls) [Fe(CO)$_4${C(=O)NR$_2$}$_2$] undergo a rapid carbon–oxygen coupling of their two carbamoyl ligands to afford, after decarbonylation, the stable metallacyclic carbenes **169**.[288] Addition of PR$_3$ (R = Me, Ph) to the structurally characterized derivative **169b** [*d*(Fe=C) = 191.1(5) pm] causes ring opening, leading to carbenes **170**.[25] The cyclometallated carbene **171** results from transformation of *cis,trans*-[Fe(CH$_3$)(I)(CO)$_3$(PMe$_3$)$_2$] by aqueous B(C$_6$F$_5$)$_3$.[81] The formation involves interaction of this reagent with a CO ligand, which facilitates methyl migration. The existence of a five-membered cycle incorporating a B(C$_6$F$_5$)$_2$ unit and a carbenic Fe=C bond of 184.0(2) pm was established by X-ray diffraction. The cyclic Fe(II) carbene–thiolato complex **172** originates from insertion of carbon monoxide into an Si–C bond of its precursor. The Fe=C bond length of 198.1(4) pm of this distorted octahedral compound is at the long end of known Fe=C bonds.[289] An original synthetic pathway has been developed to obtain the ferrabicyclobutenone **174**.[290] Treatment of [Fe(CO)$_5$] with alkyne Me$_2$NC≡CNMe$_2$ affords first ferracyclobutenone **173**, which decarbonylates above −30 °C to yield **174**. Further decarbonylation in refluxing toluene leads quantitatively to **175**. Cyclic carbene **174** readily inserts MeNC to yield the 1,4-diaza-1,3-diene complex **176**, and the aminocarbene complex **177** results from protonation with CF$_3$SO$_3$H. The structures of compounds **174–177** in Scheme 31 were authenticated by X-ray crystallography.



169a: R = Me
169b: R = Et
169c: R = Pr



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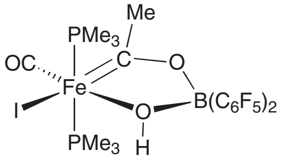

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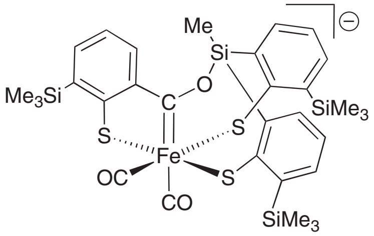

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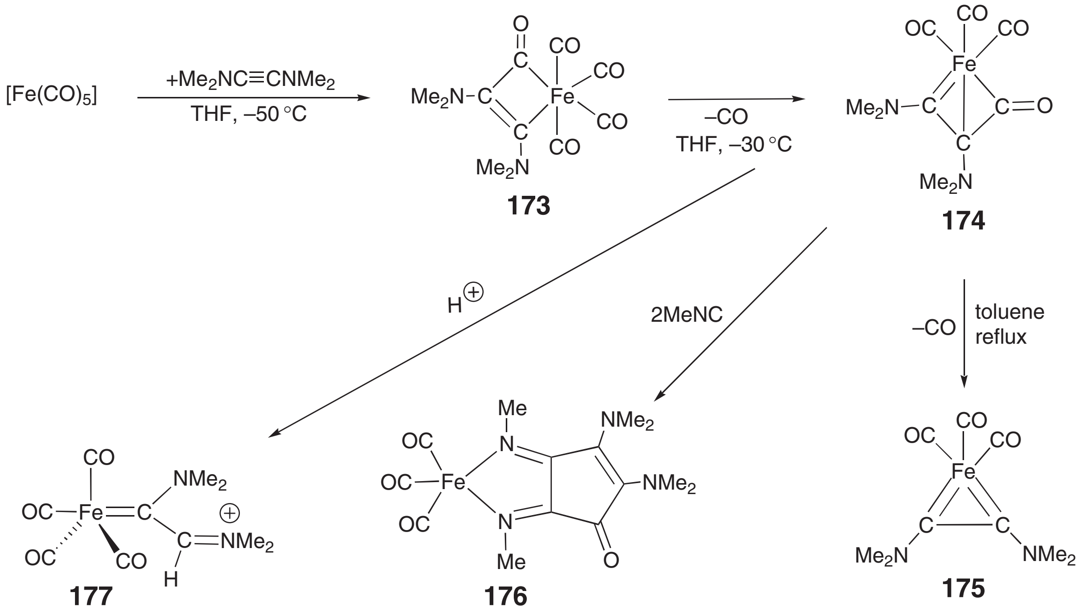
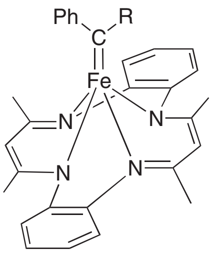


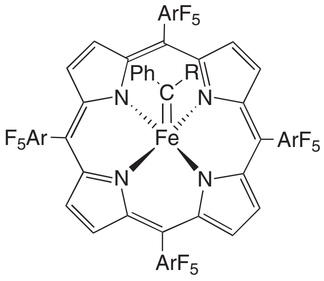
Scheme 31

A crystal-structure determination shows that upon treatment of the unsaturated Fe(II) calixarene [{calix[4]$(OMe)_2(O)_2$}Fe] with diphenyldiazomethane, the stable paramagnetic complex [{calix[4]$(OMe)_2(O)_2$} Fe=CPh_2] is formed, in which the carbene ligand is ligated [*d*(Fe=C) = 194.6(8) pm] to a almost planar tetraoxo–Fe surface.[291] Other derivatives, displaying an unusual high-spin state due to formation of a weak π-interaction between the metal and the carbene carbon, were studied by means of X-ray crystallography, CV, and EHMO calculations.[292] An entry to low-spin tetramethyldibenzotetraazaannulene-supported carbene complexes **178** consists of reactions of [Fe^{II}(tmtaa)] with Ph_2CN_2 or $PhCHN_2$. In contrast to **178b**, five-coordinate **178a** is very stable and possesses a particularly short Fe=C bond distance of only 179.4(3) pm.[293] The Fe=C interaction was also theoretically investigated.[294]

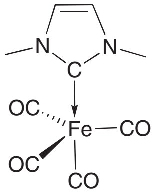
The remarkably stable porphyrins **179** result from reaction of [(F_{20}TPP)Fe^{II}] with the corresponding diazo compounds $PhCRN_2$.[295] Treatment of **179a** with *N*-methylimidazole gave the hexacoordinate adduct [(F_{20}TPP)Fe(=CPh_2)(MeIm)]. This adduct formation lengthens the Fe=CPh_2 bond from 176.7(3) **179a** to 182.7(5) pm. Stoichiometric cyclopropanation is achieved by addition of styrenes to **179b**, while catalytic intermolecular cyclopropanation of styrenes in presence of ethyl diazoacetate is catalyzed by **179a**. A direct comparison among related Fe, Ru, and Os carbene compounds has been made.[296]



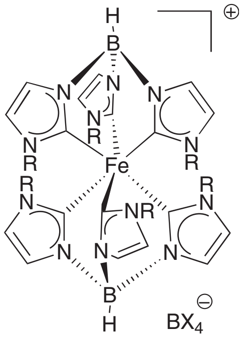
178a: R = Ph
178b: R = H



179a: R = Ph
179b: R = CO_2Et
179c: R = $CO_2CH_2CH{=}CH_2$



180



181a: R = Me; X = Ph
181b: R = Et; X = Ph

Several other studies deal with the syntheses and catalytic activity of tetraazaannulene and porphyrin complexes bearing carbene ligands.[297–299] Apart from cyclopropanation, these carbenes also catalyze the olefination of carbonyl compounds with ethyl diazoacetate in the presence of triphenylphosphine. The intermediacy of carbenoid species has been suggested in the catalytic electrochemical reduction of CO_2 by iron(0) porphyrins.[300,301] According to FT-IR and theoretical studies, the M–C bond in d^6-porphyrin Fe and Ru carbenes is a double bond in the singlet state, while the M–C bond is a single bond in the multiplet state.[302] The photolysis of the porphyrin-supported carbenes [(TPP)Fe=CX_2] (CX_2 = CClF, CCl_2, CBr_2, CClCN) is reported to produce free carbenes CX_2 and [(TTP)Fe^{II}]. The liberated halogenated carbenes were trapped by addition of alkenes to form dihalogenated cyclopropanes.[303] [(TTP)Fe=CCl_2] serves also as starting material for preparation of a dinuclear heteroleptic μ-carbido Fe=C=Fe compound, containing both porphyrin and phthalocyanine macrocycles, by reaction with phthalocyaninato ferrate.[304] In a similar manner, the dinuclear porphyrin [$\{Fe(OEP)\}_2(\mu\text{-}C)$] was prepared and crystallographically characterized.[305]

The synthesis of **180** bearing an essentially σ-donating nucleophilic carbene ligand, which may be considered as a phosphine analog, was achieved by treatment of [$Fe(CO)_5$] with the heterocyclic carbene 1,3-dimethyl-4-imidazolin-2-ylidene.[306] Deprotonation of [hydridotris(imidazolium)borate][BF_4]$_2$ by BuLi and reaction with $FeCl_2$ gave the homoleptic bis[hydridotris(imidazolyl)borato]iron(III) complexes **181**. These paramagnetic 17-electron salts, which represent the first hexacarbene–iron complexes, were characterized by X-ray crystallography and studied by CV.[307,308] The steric bulk of the carbene ligand seems to have an important impact on the molecular structure of the resulting chelate complex: transfer of the sterically more demanding "second-generation" tris(imidazol-2-ylidene)borate ligand from **182** to $FeBr_2$ yields the four-coordinate carbene complex **183** with spin state $S = 2$.[309]

Six- and five-coordinate Fe(II) complexes with the pincer ligand 2,6-bis(imidazolylidene)pyridine (C–N–C), [(C–N–C)Fe$(MeCN)_3$][BPh_4]$_2$ **184** and [(C–N–C)$FeBr_2$] **186**, respectively, were synthesized. Substitution of TMEDA in [$FeCl_2$(TMEDA)]$_2$ by C–N–C gave the six-coordinate chelate {[Fe(C–N–C)(C–N–C^*)][$FeCl_4$]} **185**, in which one of the pincer ligands is bound to the metal via the 2- and 5-imidazole carbons.[310] Reduction of **186** with Na(Hg) allowed the synthesis of the first bis(dinitrogen) complex of iron, [(C–N–C)$Fe(N_2)_2$] **187**. One of the side-on-bound N_2 ligands of diamagnetic **187** may be substituted by PR_3 (R = Me, C_6H_{11}) or ethylene to afford **188a and 188b**, respectively. Under a CO atmosphere, the distorted square-pyramidal dicarbonyl complex **189** is formed.[311] Complex **186** and related pincer carbene complexes have been evaluated as catalysts for ethylene oligomerization and polymerization in combination with a variety of co-catalysts. While titanium and vanadium complexes of this bis(imidazolylidene)pyridine ligand give rise to highly active ethylene polymerization catalysts, complexes of Fe are inactive.[312] In contrast, the structurally characterized tetrahedral complexes [(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)$_2$FeX$_2$] (X = Br, Cl), possessing strongly electron-donating carbene ligands, were found to be remarkably active and efficient catalysts for the atom-transfer radical polymerization of styrene and methyl methacrylate (Scheme 32).[313]

The electronic structure and properties of Fe=CH$_2$ were investigated using density functional methods.[314] A theoretical study of iron complexes [(OC)$_4$Fe=CX$_2$], including the vinylidene, methylene, and CF$_2$ derivatives, shows that in all cases the carbene ligand prefers the equatorial position. Studies focus on the bond lengths, bond-dissociation energies, and donor–acceptor properties of the carbene ligands. The bond-dissociation energies decrease from (=CH$_2$, 87.4) > (=C=CH$_2$, 83.8) > (=CF$_2$, 64.3 kcal mol^{-1}).[315] Note that [(OC)$_4$Fe=CF$_2$] is most probably formed upon treatment of Na$_2$[Fe(CO)$_4$] with Br$_2$CF$_2$, but then dimerizes to afford dinuclear [(OC)$_3$Fe(μ-CF$_2$)$_2$(μ-CO)Fe(CO)$_3$].[315a]

Quantum chemical calculations carried out for the carbon complex [(OC)$_4$FeC] suggest that the terminal carbon ligand is a strong π-acceptor and an even stronger σ-donor.[316] Lewis acid-stabilized carbon complexes such as [(OC)$_4$FeC(BCl$_3$)] might be isolated under appropriate conditions and the intermediacy of [(OC)$_4$FeC] has been suggested in the reaction between [(OC)$_4$FeCS] and P(NMe$_2$)$_3$.[317] The bonding situation has been compared with those of [(OC)$_4$Fe=CH$_2$] and carbyne [(OC)$_3$(I)Fe≡CH].

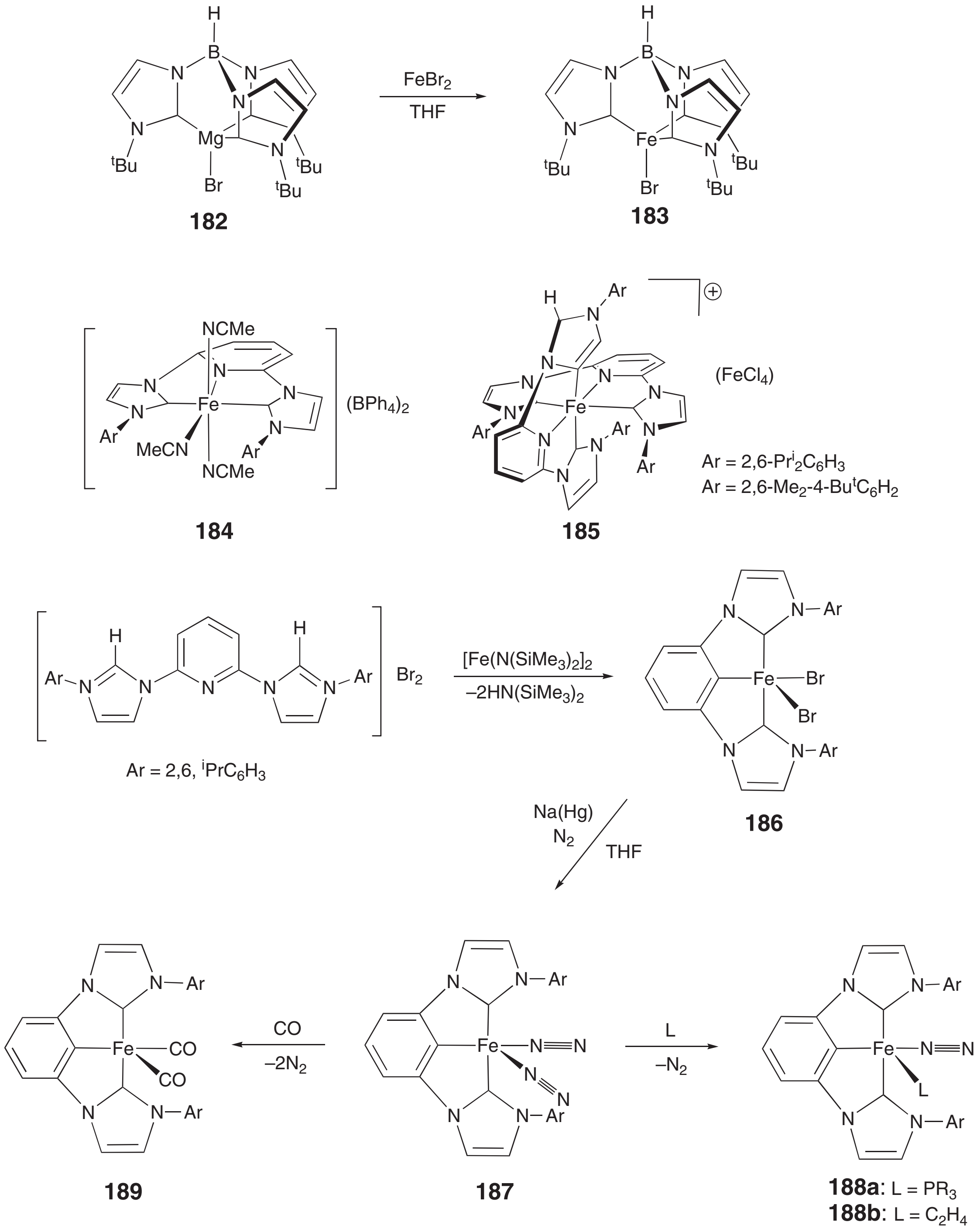
In contrast to homo- and heterodinuclear iron compounds bearing μ-carbyne ligands,[318–320] mononuclear carbynes without Cp ligands remain extremely rare. Since Fischer's report dating from 1984 on the aminomethylidyne complex [(OC)$_3$Fe(≡CN^{i}Pr$_2$)(PPh$_3$)][BCl$_4$],[38] no further information on other stable iron carbynes is available. However, the cationic derivatives [(OC)$_3$Fe(≡CN^{i}Pr$_2$)(PPh$_3$)]I and [(OC)$_3$Fe(≡CN^{i}Pr$_2$)(PPh$_3$)][O$_2$CCF$_3$] have been obtained in a less sophisticated manner by two novel unexpected routes: (i) iodination of the carbamoyl complex [(OC)$_2$Fe{η^2-C(=O)N^{i}Pr$_2$}(CF$_3$)(PPh$_3$)] and (ii) *O*-trifluoroacetylation of the carbamoylate Li[(OC)$_4$Fe{C(=O)N^{i}Pr$_2$}].[41]

6.02.8 Gas Phase and Matrix Studies

The activation of the C–H bond of allene by ground-state atomic iron has been observed in solid argon at 10 K. The new matrix-isolated product, propadienyliron hydride [HFe(CH=C=CH$_2$)], was characterized via FTIR spectroscopy. The photochemistry of the metal atom and allene was studied and revealed the isomerization of allene into propyne via the formation of the σ-bonded iron–propyne adduct [Fe(HC≡CCH$_3$)].[321] [HFe(CH=C=CH$_2$)] is also formed upon co-condensation of iron vapors with methylacetylene and subsequent photolysis in an Ar matrix. Excitation with shorter-wavelength visible light leads to formation of 1-propynyliron hydride. After photolysis with UV light, competing C–H and C–C bond activation generates 3-propynyliron hydride and ethynyl(methyl)iron, respectively.[322] Atomic iron forms first a weakly bound adduct with cyclopropanes in an Ar matrix at 15 K. C–C bond activation then provides, via a putative ferracyclobutane intermediate, the carbene [(H$_2$C=CH$_2$)Fe=CH$_2$] and a species in which FeH$_2$ is complexed with allene. UV photolysis of the matrix resulted in C–H activation to give methyl(vinyl)iron and ethynyliron hydride [FeH(C≡CH)].[323] The reaction of highly excited laser-evaporated iron atoms with methane gas was investigated using a matrix-isolation technique. Detection by IR and Mössbauer spectroscopy revealed that [FeH(CH$_3$)] is produced in a CH$_4$/Ar mixture, whereas both [FeH(CH$_3$)] and the dinuclear hydride-bridged species [(CH$_3$)$_2$Fe(μ-H)$_2$Fe(CH$_3$)$_2$] are generated in a pure CH$_4$ matrix.[324]

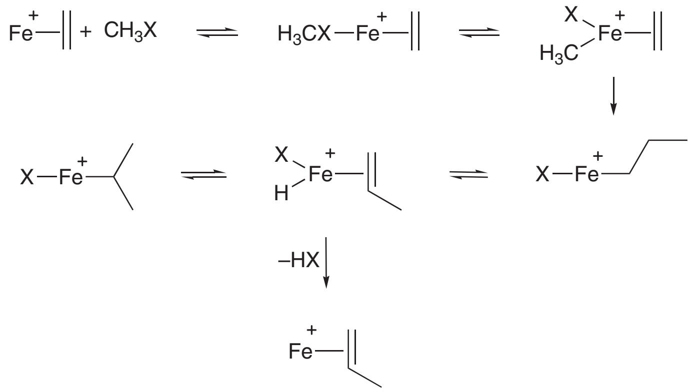
Investigations of the interaction of organic substrates with iron anions or with bare cationic Fe$^+$, FeO$^+$, or FeR$^+$ species in the gas phase may also provide valuable thermodynamic information and mechanistic insights for the synthetic chemist. The theoretical principles and experimental techniques associated with that domain of organometallic iron chemistry have been described in detail in section 2.2 of COMC (1995).[38] A review article dating from 1998 deals on the gas-phase reactivity of ionic iron complexes and makes comparisons with solution chemistry. A survey of experimental methods and a summary of bond energies of iron complexes is also included.[325]

Rate constants for successively ligated anions [Fe(CO)$_n$]$^-$ (n = 0–4) reacting with CH$_3$X (X = F, Cl, Br, I) were measured using a selected-ion flow-tube apparatus. Information on the bond strengths, D[Fe(CO)$_n$–CH$_3$], was deduced. The homolytic Fe–Me bond energies were calculated to be $0.13\ \text{eV} \leq D[\text{Fe–CH}_3] \leq 1.76\ \text{eV}$, $D[\text{Fe(CO)–CH}_3] = 1.2 \pm 0.2\ \text{eV}$, $D[\text{Fe(CO)}_2\text{–CH}_3] = 1.3 \pm 0.3\ \text{eV}$, $D[\text{Fe(CO)}_3\text{–CH}_3] < 1.4\ \text{eV}$, and $D[\text{Fe(CO)}_4\text{–CH}_3] < 2.1\ \text{eV}$.[326]



Scheme 32

The gas-phase chemistry of [Fe(olefin)]$^+$ complexes with CH$_3$X (X = OH, F, Cl, Br, I) was investigated by means of Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrometry. C–C bond formation between the alkene and CH$_3$X occurs via initial insertion of Fe$^+$ into the C–X bond of [FeX(CH$_3$)]$^+$ (Scheme 33). A combination of subsequent β-H shift and reductive elimination of HX completes the reaction.[327]



Scheme 33

Sigma-bound alkyl and aryl iron species are also involved in the gas-phase reactions of [Fe(benzyne)]$^+$ and [Fe(arene)]$^+$ with simple alkyl halides and halobenzenes.[328,329] Evidence is presented that the encounter complexes of [FeCX_3]$^+$ (X = H, D) with 1-octyne, prior to C–H and C–C bond activation, undergo interligand C–C bond coupling as well as extensive hydrogen exchange. In distinct contrast, in the related complexes formed by gas-phase reaction of [FeCX_3]$^+$ with 1-octene, the metal–Me group retains its identity, while the alkene ligand is subject to extensive hydrogen scrambling presumably by β-hydrogen shift to and from the metal centers.[330] The remote C–H bond activation of aliphatic nitriles by [FeCH_3]$^+$ has been investigated by FT–ICR mass spectrometry.[331] The gas-phase reactions of [FeCF_3]$^+$, generated from Fe$^+$ and CF_3I, with a series of alkanes and alkenes were also studied by this technique. Calculated bond energies matched the experimental results.[332] A combined FT–ICR and DFT study was employed to assess the interconversion of [FeC_2H_3]$^+$ and [Fe(H)C_2H_2]$^+$.[333] The reactions of several ligated [Fe(L)]$^+$ cations (L = H_2O, CO, CH_2O, C_2H_4, CH_3CHO, C_3H_6, C_2H_2, ${}^iC_4H_8$, MeCN, C_4H_6) with 4-heptanone were examined by MS. In general, the ion–molecule reactions of the ligated [Fe(L)]$^+$ cations differ substantially from the behavior of bare Fe$^+$ itself in that C–C bond activation as well as consecutive fragmentations are suppressed in favor of exclusive C–H bond activation for [Fe(L)]$^+$ cations.[334] A number of papers have also addressed to the activation of C–C and C–H bonds of organic substrates by bare Fe(I)$^+$ and FeO$^+$ cations in the gas phase.[335–345]

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6.03
Mononuclear Compounds with Hydrocarbon Ligands: Compounds with η^2–η^4 Hydrocarbon Ligands

J R Moss, G S Smith, and C H Kaschula, University of Cape Town, Rondebosch, South Africa

6.03.1 Introduction

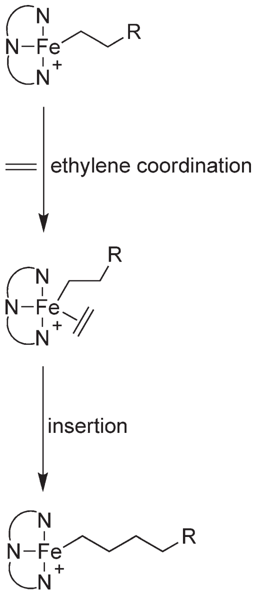
The main types of iron compounds with η^2-hydrocarbon ligands are alkene and alkyne complexes typified by $Fe(CO)_4(\eta^2\text{-}C_2H_4)$ and $Fe(CO)_4(\eta^2\text{-}C_2R_2)$. The synthesis of many such compounds is well described in COMC (1982) (section 31.3) and COMC (1995) (section 2.4). The interaction of η^2-ligands with iron is of crucial importance in catalytic oligomerization and polymerization reactions, particularly in the polymerization of alkenes. The first iron-based polymerization catalysts were reported in 1998 by the groups of Brookhart[1] and Gibson,[2] and since then many other iron-based polymerization catalysts have been described. Due to the potential commercial applications of these catalyst systems, much of this work has been published in the patent literature. The catalysts can also be adapted to yield low molecular weight oligomers including α-olefins as well as high molecular weight polymers. Many of these catalytic reactions are believed to occur through key intermediates where there is an η^2-alkene iron interaction of the type shown in Scheme 1.

Since the unsaturated organic group is activated on coordination to iron, complexes or intermediates of this type have been used extensively in organic synthesis and this trend is likely to continue.

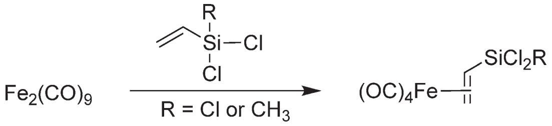
6.03.2 Alkene Complexes

The reactions of iron group metal carbonyls with functionally substituted alkenes have been reviewed.[3] It was found that the reactions of the iron carbonyls with alkenes differ from those of the Ru and Os analogs. For Os, in particular, unsaturated ligands raise their hapticity to form unusual structures.[3]

The reactions of diiron nonacarbonyl with $SiCl_2(CH{=}CH_2)R$ ($R = Cl$ or CH_3) yield mononuclear complexes, where the vinyl unit is η^2-coordinated to iron (see Scheme 2).[4]



Scheme 1



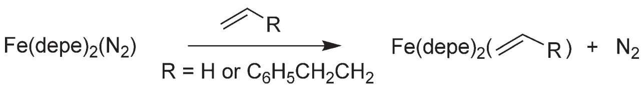
Scheme 2

Iron–olefin bond energies (in kcal/mol) for the monoolefin complexes $Fe(CO)_4(C_2X_4)$ (X = H (35), F (38), Cl (25), Br (29), I (22), CN (33)) have been calculated using density functional theory (DFT).[5] The net iron–olefin bond energy, is made up of the attractive electronic interactions as well as the deformation energy which is the energy needed to deform the $Fe(CO)_4$ and olefin moieties. As a result of this deformation energy the bond energies for the substituted olefins are similar or even smaller than that for the Fe–C_2H_4 bond.[5]

DFT has also been used to calculate energies of structures for the singlet and triplet states of $Fe(CO)_3(\eta^2\text{-}C_3H_6)$, either pseudo-axial or pseudo-equatorial isomers, and for three isomers of $HFe(CO)_3(\eta^3\text{-}C_3H_5)$. This and other evidence suggest that the reaction (Equation (1)) is expected to occur from the triplet state *pseudo*-axial mono-olefin isomer to either or both of the facial-*exo* and *endo*-allyl product isomers.[6]

$$Fe(CO)_3(\eta^2\text{-}C_3H_6) \rightarrow HFe(CO)_3(\eta^3\text{-}C_3H_5) \qquad (1)$$

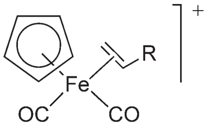
Reaction of $Fe(depe)_2(N_2)$ with C_2H_4 (1 atm) yields the ethylene complex $Fe(depe)_2(C_2H_4)$ (where depe = 1,2-bis(diethylphosphinoethane))[7] as shown in Scheme 3. A similar N_2 substitution reaction initially occurs with 4-phenyl-1-butene but this product rearranges to the iron arene complex, $Fe(depe)(C_6H_5CH{=}CHCH_2CH_3)$.[7]



Scheme 3

Cationic alkene iron compounds of the type **1** have been used in a variety of experimental and theoretical studies.

Compound **1** (where R = H) has been used as a synthon to prepare a range of heterobimetallic hydrocarbon-bridged complexes (e.g., as shown in Scheme 4).[8]



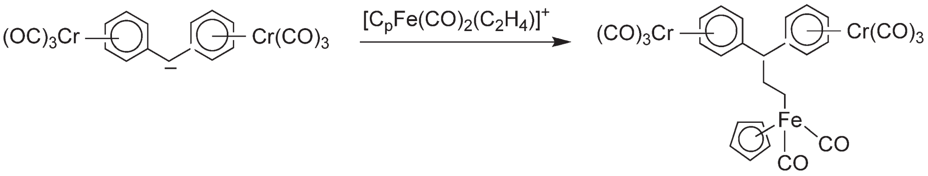
1

The η^1-allyl compound, $CpFe(CO)_2(\eta^1\text{-}C_3H_5)$, has been shown to react with organic carbonyl compounds in the presence of Lewis acids to give η^2-alkene cations. These alkene cations can then rearrange to yield tetrahydrofuran esters via a formal [3 + 2]-cycloaddition (see Scheme 5).[9]

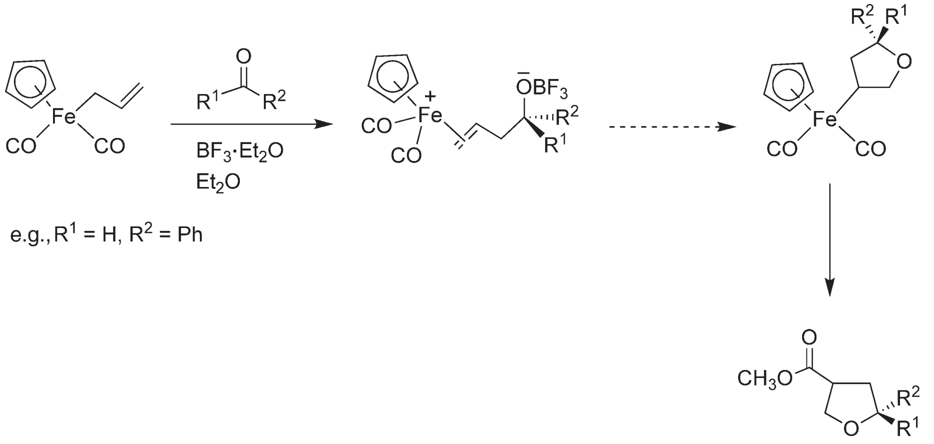
Similarly zwitterionic iron alkene complexes are intermediates in the production of homoallylic alcohols and related products. The zwitterionic iron alkene complexes **1** (where $R = CH_2CH(OBF_3)Ph^-$, $CH_2CH(OBF_3)PhNO_2^-$ for example) were isolated as yellow precipitates and characterized by IR and ^1H NMR spectroscopy.[10]

An extensive series of alkene cations **1** (R = Me to $n\text{-}C_{14}H_{29}$) has been prepared and fully characterized by analytical and spectroscopic methods.[11] Some analogous Cp* complex cations have also been prepared.[11] Some of the Cp-iron cations have been reacted with the isopropoxide ion to give new ether derivatives $CpFe(CO)_2\{CH_2CH[OCH(CH_3)_2]R\}$ (R = Me, Et, *n*-Bu, or $n\text{-}C_{13}H_{27}$).

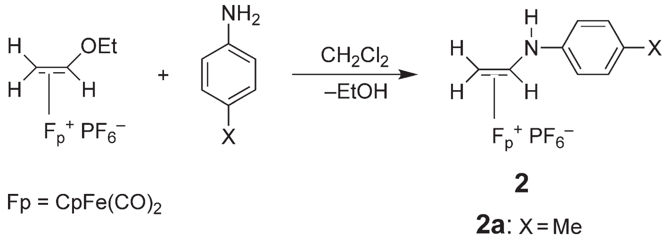
Matchett and co-workers have reported a series of nucleophilic substitution reactions of $[CpFe(CO)_2(\eta^2\text{-}CH_2CH(OEt))]PF_6$ with *para*-substituted anilines (Scheme 6). Correlation of the Hammett σ-parameters with the ^{13}C NMR shifts of the metal-coordinated vinyl carbons demonstrated the ability to control the position of Fp^+ along the face of the olefin. Thus, as the electron-donating character of the *para* substituent was increased, the Fp^+ moiety was displaced from the nitrogen-bearing carbon, increasing the asymmetry of the metal–olefin bonding.



Scheme 4



Scheme 5



2

2a: X = Me
2b: X = COMe

Scheme 6

These conclusions are supported by the X-ray crystal structures of compounds **2a** and **2b**.[12] The X-ray structures of the PF_6^- salts of the cations **1** (where R = OEt and NMe_2) have been determined. These studies show a very long Fe–C_β distance for R = NMe_2 of 2.823(11) Å compared to R = OEt of 2.402(10) Å (where C_β is the carbon with the substituent). These results, combined with DFT calculations, are rationalized in terms of increased localization of nucleophilicity on the C_α of the olefin as the π-donor ability of R strengthens. Thus it appears that not all olefins will show η^2-binding.[13]

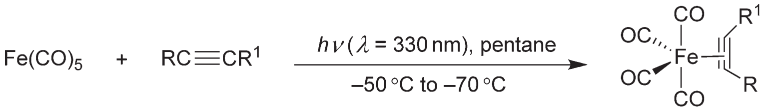
The olefin bond rotation barriers have also been determined for the vinylaniline complexes **2** using several ^1H NMR techniques, namely: selective inversion, total line shape analysis, and $T_1\rho$ measurements (i.e., spin-lattice relaxation rate in the rotating frame).[14]

The competitive alkylidene transfer to olefins and alkylidene to olefin interconversion of the electrophilic carbene complexes $[CpFe(CO)L({=}CHR)]^+$ (where L = CO or PH_3; R = Me or Et) has been studied theoretically. These transformations are believed to involve cationic olefin complexes of the type $[CpFe(CO)L(olefin)]^+$.[15]

6.03.3 Alkyne Complexes

The iron–alkyne interaction is important because there are practical applications in organic synthesis, such as the iron carbonyl-mediated coupling of alkynes and CO. As a result, the reactions of alkynes with iron carbonyls have thus been the subject of many studies since the first report in 1953. Surprisingly, up until 1997, however, there was only one well-documented example of an $Fe(CO)_4(\eta^2\text{-alkyne})$ species **3** (see Scheme 7). This is in part because complexes of this type are highly sensitive to the preparative conditions. Takats and co-workers have prepared a series of complexes of this type **3a–3e** from $Fe(CO)_5$ (see Scheme 7) under carefully controlled photolysis conditions.[16] The complexes $Fe(CO)_4(\eta^2\text{-alkyne})$ are shown to react with an excess of alkyne and CO, thus confirming early proposals that they are key intermediates in the coupling of alkynes with CO.[16]

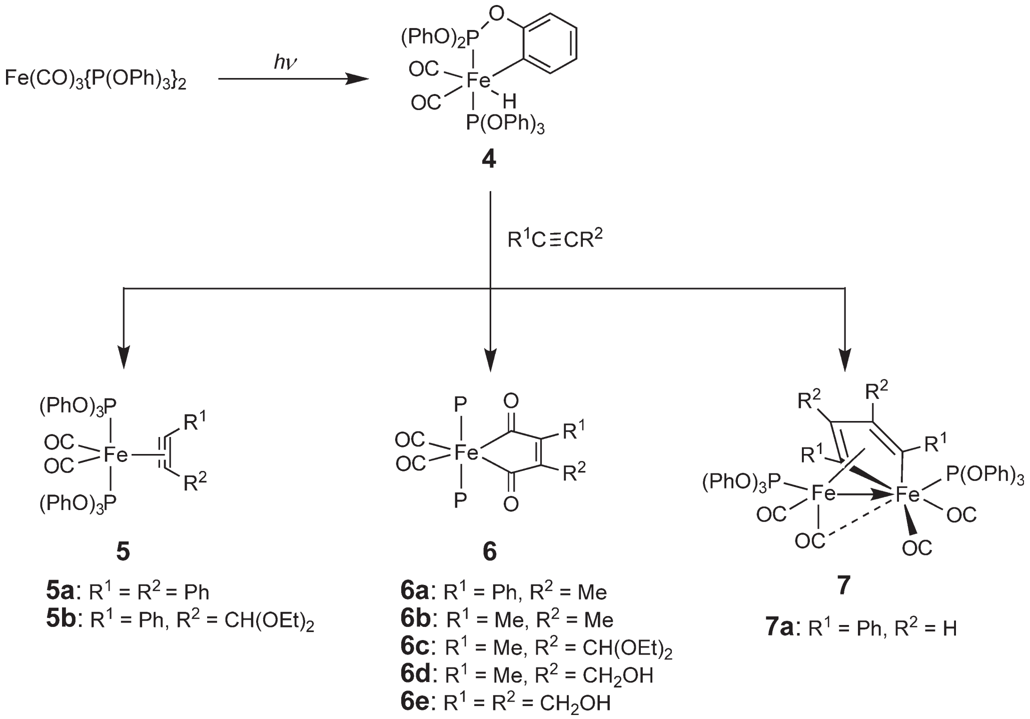
It is interesting to note that the alkyne ligand in $Fe(CO)_4(\eta^2\text{-alkyne})$ can enhance CO substitution in the complex. Thus, similar substitution reactions were compared for $M(CO)_5$ and $M(CO)_4(\eta^2\text{-alkyne})$ (where M = Fe, Ru, or Os). It is known that for $M(CO)_5$, the reactivity is Ru ≫ Os > Fe whereas for the alkyne complexes the order changes to



3

3a: R, $R^1 = CF_3$, 84%
3b: R, R^1 = H, 75%
3c: R, R^1 = Me, 57%
3d: R = H, $R^1 = CF_3$, 65%
3e: R = H, R^1 = Me, 63%

Scheme 7



4

5

5a: $R^1 = R^2 = Ph$
5b: $R^1 = Ph, R^2 = CH(OEt)_2$

6

6a: $R^1 = Ph, R^2 = Me$
6b: $R^1 = Me, R^2 = Me$
6c: $R^1 = Me, R^2 = CH(OEt)_2$
6d: $R^1 = Me, R^2 = CH_2OH$
6e: $R^1 = R^2 = CH_2OH$

7

7a: $R^1 = Ph, R^2 = H$

Scheme 8

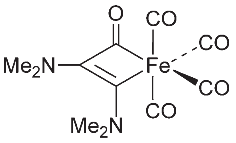
Fe ≫ Ru > Os. Thus the presence of the alkyne in $Fe(CO)_4(\eta^2\text{-alkyne})$ has a dramatic effect on CO substitution reactions, as shown in Equation (2). Compared to $Fe(CO)_5$, there is a spectacular increase in reaction rate for $Fe(CO)_4(\eta^2\text{-alkyne})$ of 13 orders of magnitude![17]

$$Fe(CO)_4(\eta^2\text{-HFB}) + PR_3 \rightarrow Fe(CO)_3(\eta^2\text{-HFB})(PR_3) + CO \ (\text{HFB} = \text{hexafluorobut-2-yne}) \qquad (2)$$

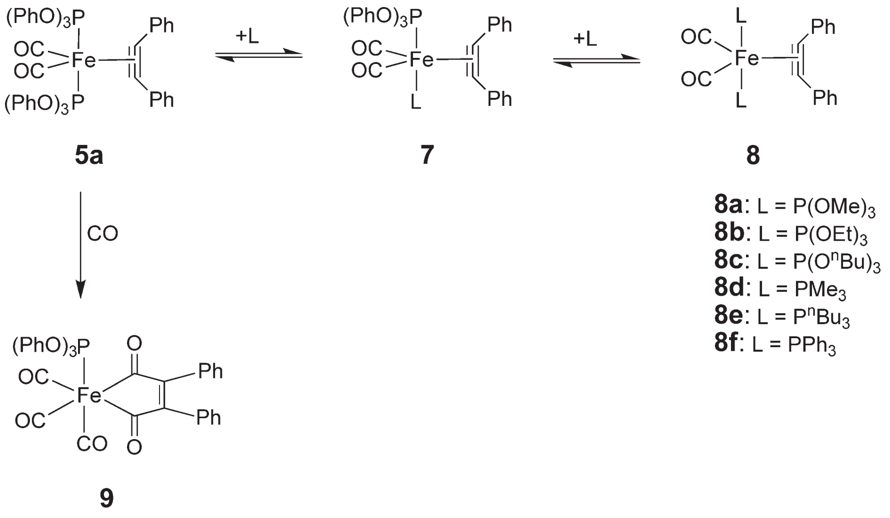
The reactions of iron carbonyls with alkynes however can often lead to a range of products that are difficult to separate. Manning and co-workers[18] have found that photolysis of $Fe(CO)_3\{P(OPh)_3\}_2$ with alkynes gives products $Fe(CO)_2\{P(OPh)_3\}_2(\eta^2\text{-alkyne})$ **5** via the orthometallated iron–hydride intermediate $HFe(CO)_2\{P(OPh)_3\}\{(PhO)_2POC_6H_4\}$ **4**. Maleoyl complexes **6** are also formed with internal alkynes. However, the ferrole derivative **7** is obtained by reaction with the terminal alkyne $HC{\equiv}CPh$ (see Scheme 8). Crystal structures of the complexes **5a** and **6c** have been determined and confirm their formulations. The alkyne carbon–carbon distance in **5a** is 1.274(4) Å which lies toward the shorter end of the range of reported carbon–carbon distances of coordinated diphenylacetylene (1.24–1.35 Å).

Enhanced substitutional lability of $P(OPh)_3$ by PR_3 is found for the η^2-alkyne complex $Fe(CO)_2\{P(OPh)_3\}_2(\eta^2\text{-}PhC{\equiv}CPh)$ **5a** to give **8a–8f**. Reaction of **5a** with CO yields the maleoyl complex **9** (Scheme 9). The structure of this CO derivative **9** was confirmed by X-ray crystallography.[19]

The reaction of $Fe(CO)_5$ with $Me_2NC{\equiv}CNMe_2$ at −50 °C has been reported to yield a thermolabile associative product, which was characterized as the ferracyclobutenone **10**; this product decarbonylates above −30 °C.[20]

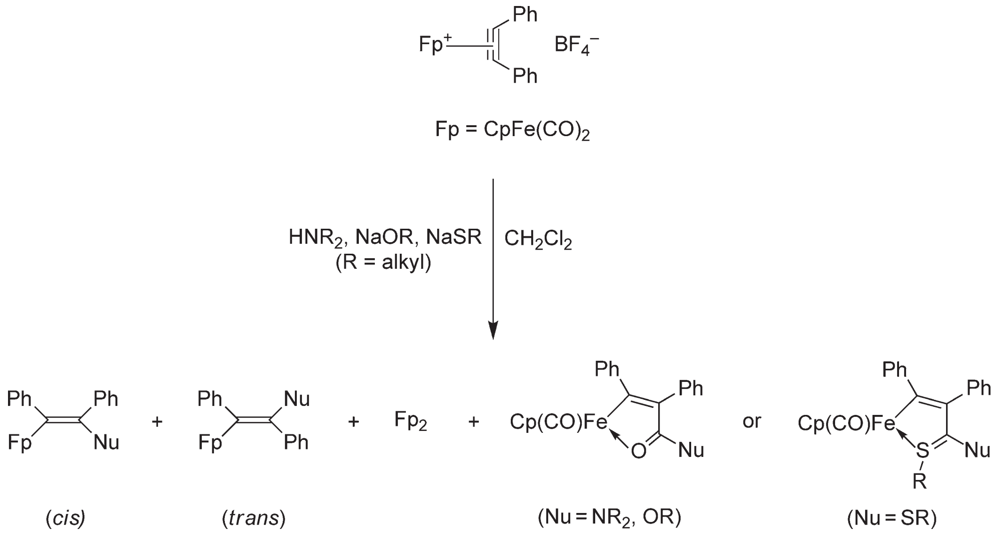


10



8a: L = $P(OMe)_3$
8b: L = $P(OEt)_3$
8c: L = $P(O^nBu)_3$
8d: L = PMe_3
8e: L = P^nBu_3
8f: L = PPh_3

Scheme 9



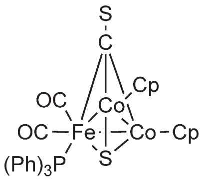
Scheme 10

In complexes of the type $[CpFe(CO)_2(\eta^2\text{-}C_2R_2)]^+$, the alkyne ligand is susceptible to attack by *O*-, *N*- and *C*-nucleophiles (Nu) to yield *cis*- or *trans*-alkenyl products of the type $CpFe(CO)_2(RC{=}CRNu)$ as well as metallacycles (see Scheme 10). Crystallographic determination of the stereochemistry of the products revealed that basic nucleophiles bearing alkyl substituents produced the *cis*-alkenyl complex and/or metallacycles, whereas less basic nucleophiles bearing aryl substituents afforded the *trans*-alkenyl complex.[21]

The chiral-at-metal Fischer carbene complexes, $[CpFe(PPh_3)(NO)(CCH_2CH_2CH_2O)]X$ ($X = SbF_6$, CF_3SO_3), are prepared by reaction of coordinatively unsaturated $[CpFe(CO)(PPh_3)]^+$ with hydroxyalkynes.[22]

6.03.4 Heteroalkene Complexes

There have been only a few studies on heteroalkene complexes of iron in the last 10 years. Manning and co-workers have explored the reactions of $Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)$ with $CpCo(PPh_3)_2$ which results in C–S bond cleavage to give the heterobimetallic cluster complex $FeCo_2(\mu_3\text{-}S)(\mu_3\text{-}CS)(CO)_2(PPh_3)Cp_2$ **11** in good yield. A similar reaction occurs with the $Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CSMe)$.[23]



11

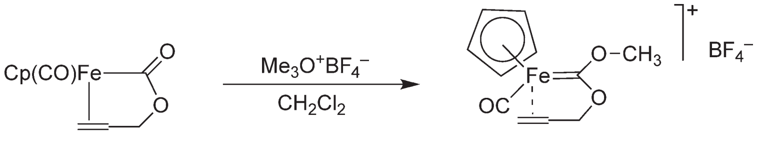
6.03.5 Chelated Alkene Complexes

Novel ferracyclic (η^2-alkene)carbene complexes, for example, **12** have been prepared in good yield (see Scheme 11) and characterized by analytical and spectroscopic methods. The structure of **12** has been determined by X-ray crystallography.[24]

The related ferracyclic carbene complexes **13a** has been shown to react with carbon nucleophiles such as lithium enolates and organocuprates to give 4-substituted-(3*E*)-diene tricarbonyl iron complexes for example **13c** (Scheme 12).[25] Decomposition of **13a** with formal loss of CO and MeOH can also occur to give **13b**.

Reactions of the chelate alkene complex **14** with a range of alkenes results in CO substitution by the added alkene to give **15** (see Scheme 13).[26] The structure of **15** where alkene = maleic anhydride has been confirmed by X-ray crystallography.[26]

The alkenylcarbene complex **16** has been prepared using the $[Fe(CO)_4]^{2-}$ nucleophile (see Scheme 14). Other related complexes were prepared in a similar way. Tethering the η^2-alkene ligand to the carbene carbon changes the reactivity of these complexes substantially.[27]



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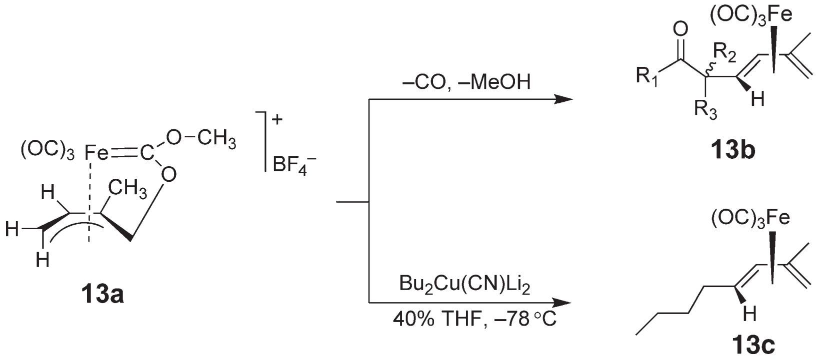
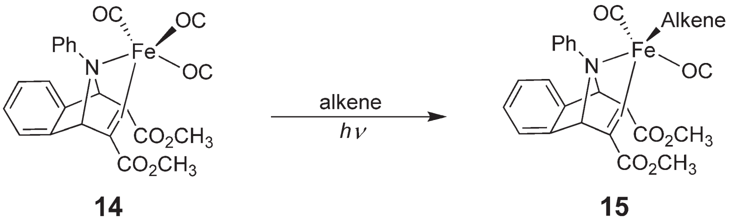
Scheme 11

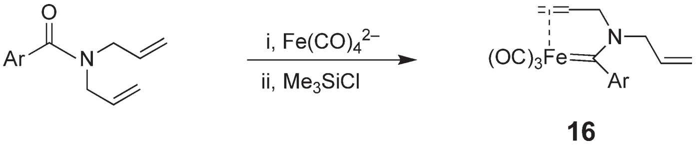


Scheme 12



Alkene = ethyl acrylate, dimethyl malonate, dimethyl fumerate, maleic anhydride, etc.

Scheme 13



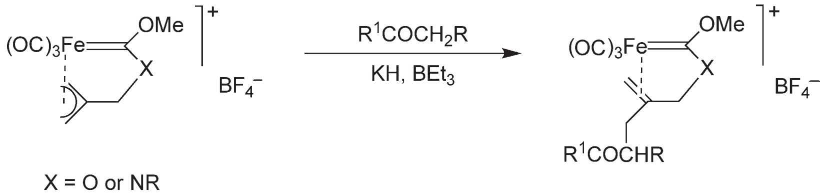
Scheme 14

6.03.6 $\eta^2 \rightarrow \eta^3$ Interconversions

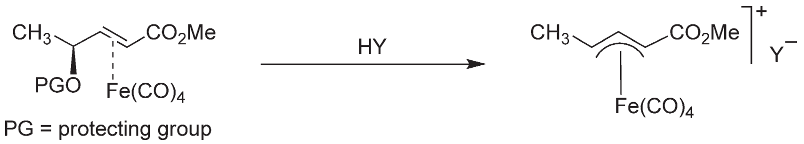
Schobert and co-workers have performed a study on η^2-alkene and η^3-allylcarbene complexes of transition metals. This particularly includes studies on the chemistry of metallacyclic alkenyl complexes of iron, which are reviewed in this chapter.[28] An example of the $\eta^3 \rightarrow \eta^2$ transformation is shown in Scheme 15. Iron-mediated allylic substitution reactions involve $\eta^2 \rightarrow \eta^3$ interconversion and can show chirality transfer.[29] A working hypothesis involves the reaction shown in Scheme 16.

6.03.7 η^2-Alkene Intermediates in Catalytic Polymerization and Other Reactions

One of the major areas of application of iron alkene complexes that has been discovered in recent years is their use as catalyst precursors for alkene polymerization and oligomerization reactions. There has been great interest in this area with a very large number of papers published in the last 10 years.[30] This trend is likely to continue, with more efficient and selective catalysts being discovered in the future.



Scheme 15



Scheme 16

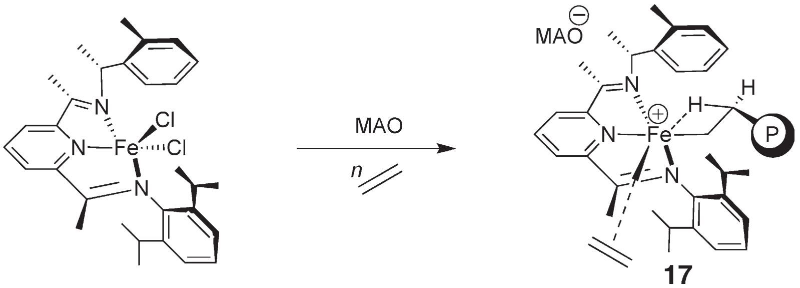
Although the iron η^2-alkene interaction is the key to many of these catalytic reactions, discrete organometallic complexes have not been isolated in most cases. Thus, for example, the activation of the complexes (2,6-bis(arylimino)pyridyl)iron dichloride with MAO (methylaluminoxane) yields an ethylene oligomerization catalyst which is likely to involve an intermediate η^2-C_2H_4 iron species such as **17** (Scheme 17).[31] The iron catalysts of this type yield α-olefins with a Schulz–Flory distribution as well as linear homopolymers. This is the first time that the simultaneous production of both products has been reported.[31] Iron–alkene intermediates are also important in addition reactions. Thus, the reactions of some aminocarbene iron complexes with electron-deficient alkenes lead to 1,4-dicarbonyl compounds via iron–alkene intermediates as shown in Scheme 18.

The photolysis of $Fe(CO)_5$ with different types of polyethylene that contain some residual alkene unsaturation in the polymer chain results in the impregnation of iron into the polymer via species of the type $Fe(CO)_4(\eta^2\text{-alkene})_{PE}$.[32] Extended photolysis can lead to isomerization of the alkene moieties.

Three-coordinate iron alkyl compounds can be stable with bulky ligands. They can coordinate ethylene as shown in Scheme 19 and undergo isomerization and exchange reactions of the alkyl group through β-H elimination.[33]

Iron salts can catalyze the allylic orientation of alkenes by arylhydroxylamines and this reaction is envisaged to go via alkene intermediates as shown in Scheme 20.[34]

A new family of 2,6-bis(imino)pyridyl iron complexes has been prepared and used as catalyst precursors for ethylene oligomerization to give linear α-olefins, via η^2-alkene intermediates.[35] The use of $Fe(CO)_5$ as a catalyst precursor in the hydrogenation of cyclohexene and l-hexene is believed to go via the intermediates $Fe(CO)_4$(alkene) and $HFe(CO)_3(\eta^3\text{-allyl})$ **18**.[36]



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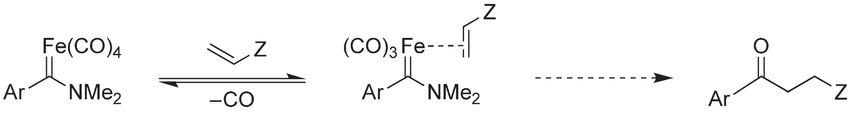
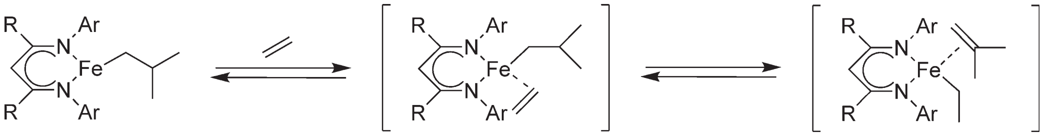
Scheme 17

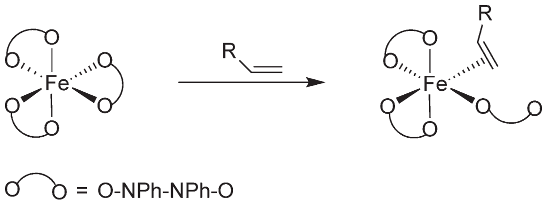


Ar = Ph, Z = CO_2Me; Ar = 2-pyridyl, Z = CO_2Me, etc.

Scheme 18



Scheme 19



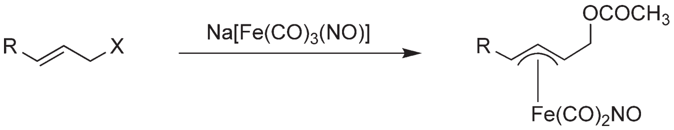
Scheme 20

6.03.8 Allyl Complexes

The chemistry of η^3-allyliron complexes as versatile allylating agents in organic synthesis is well recognized.[37] These complexes can function as either electrophilic or nucleophilic allylating agents, depending on the properties of the metal and the coordinated ligands. This subsection reviews isolated and well-defined compounds that contain an η^3-hydrocarbon moiety bonded to iron.

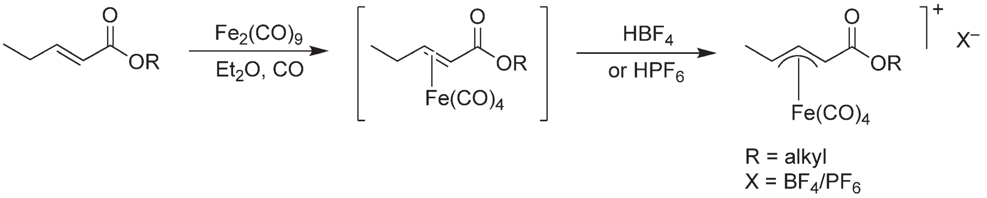
η^3-Allyliron complexes can be divided into three types: cationic, neutral, and anionic complexes. Cationic tetracarbonyl (π-allyl)iron complexes are generally prepared from appropriate η^4-diene tricarbonyl iron complexes by protonation with HBF_4 under a CO atmosphere.[37] Recent literature shows a slight variation of this method, by converting enolates into tetracarbonyl(η^3–allyl)iron(1+) complexes[38] (Scheme 21). The mechanism is thought to entail initial complexation of nonacarbonyldiiron [$Fe_2(CO)_9$] to give neutral tetracarbonyl(η^2-alkene)iron(0) species, followed by subsequent protonation with anhydrous HPF_6 or HBF_4 in diethyl ether (under an atmosphere of CO). Complexes were obtained in good yields as moderately air- and moisture-sensitive pale yellow solids.[38–44]

Another method of preparation is the one-pot reaction of allyl halides with $[NBu_4][Fe(CO)_3(NO)]$ to form neutral (η^3-allyl)dicarbonylnitrosyliron complexes as products (Equation (3)).[45]

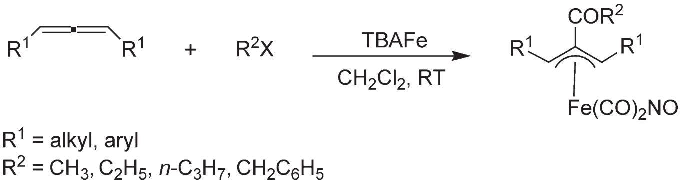


(3)

Reactions of this nature have been used extensively to form an array of substituted (η^3-allyl)$Fe(CO)_2NO$ complexes.[45,46] [η^3-1-(Acetoxymethyl)allyl]$Fe(CO)_2NO$ complexes can be formed by the reactions of alkenyloxiranes with $NBu_4[Fe(CO)_3NO]$, in the presence of acetyl chloride and pyridine.[45] The tricarbonylnitrosylferrate also reacted with tosylates, trifluoroacetates and phosphonates of allylic alcohols, and with allylic halides to produce [Fe(η^3-allyl)$(CO)_2$(NO)] complexes.[47] Acetates and carbonates of the allylic alcohols proved to be ineffective. The efficiency is proportional to the leaving ability of the allylic substrates. If the pK_a of the conjugate acids of the leaving group is less than 3, the allylic substrates are useful for preparing the complex. Reacting $NBu_4[Fe(CO)_3NO]$ with (η^3-allyl)bromopalladium complexes produces the (η^3-allyl)dicarbonylnitrosyliron complex in good yield.[48] This provides a new route to complexes of this type via transmetallation of the η^3-allyl ligand from palladium to iron. An alternative method of preparing neutral (η^3-allyl)dicarbonylnitrosyliron complexes entails the acylmetallation of allenes with acyliron complexes $RC(O)Fe(CO)_2NO$.[49] This reaction provides a high-yielding and convenient method for the preparation of di- and trisubstituted η^3-allyliron complexes with acyl groups at the central carbon of allylic ligands (Equation (4)).



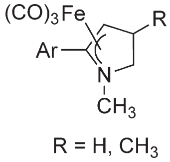
Scheme 21



(4)

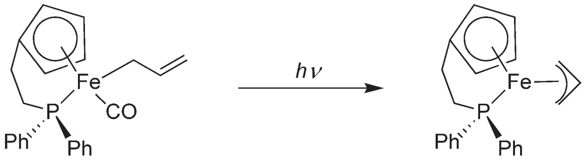
$[CpFe(CO)_2]^-$ anions (Fp^- anions) also react with allenic electrophiles in an S_N2 fashion to generate Fp-substituted 1,3-dienyl complexes.[50] Thermal and photochemical reactions with these Fp complexes result in the formation of η^3-butadienyl complexes.

New η^3-iron tricarbonyl complexes of 2,3-dihydropyrrole were formed by the thermolysis of iron *N*-methyl-*N*-allylaminocarbene complexes in toluene at 100 °C.[51] Attempts to prepare **19** by direct complexation of independently prepared 1-methyl-2-phenyl-4,5-dihydropyrrole with $Fe(CO)_5$ or $Fe_2(CO)_9$ were unsuccessful.



19

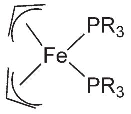
Photoexcitation of cyclopentadienylirondicarbonyl (Fp) allyl complexes normally leads to cleavage of the Fe–CO bond. Upon irradiation of a related phosphine-chelated iron-allyl complex, the known (η^3-allyl)iron complex was isolated as one of the major products (Equation (5)).[52] The mechanism also proceeds via Fe–CO bond cleavage, to yield the η^3-allyl complex in 77% yield.



(5)

Treatment of ((3,3-dimethylbutynyl)ethoxymethylene)$Fe(CO)_4$ with diethylamine at 25 °C in diethyl ether yielded (η^3-(β-(*tert*-butylcarbonyl)vinyl)carbene)$Fe(CO)_3$ in 96% yield in 2 min.[53] This product was produced through a Michael-type addition of the amine to the metal alkynylcarbene complex and is predominant over substitution at the carbene carbon above room temperature (RT).

There are rather few cases of bis(η^3-allyl)iron(II) complexes.[54–56] Complexes **20** and **21** were synthesized by conventional reactions between allylmagnesium chloride and either preformed $Fe(PR_3)_2Cl_2$, $Fe\{R_2P(CH_2)_nPR_2\}Cl_2$ or $Fe(THF)_nCl_2$ in the presence of a monodentate phosphine.[56] Some of the complexes were also made by the reactions between tris(η^3-allyl)iron and bis(dimethylphosphino)ethane. The products of these reactions were shown to be a mixture of two isomers that differ in the mutual arrangement of the two allyl groups.



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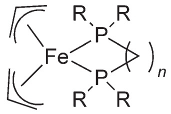
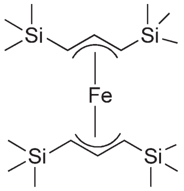


21

Complex **22** represents the first bis(π-allyl)iron(II) complex. The parent bis(allyl)iron(II) is unknown. The reaction between 1,3-bis(trimethylsilyl)allyl anion and $FeCl_3$ in THF at −78 °C produced **22** in good yield.[54] The complex shows good solubility in ethers, and both aliphatic and aromatic hydrocarbons, and is stable under an N_2 atmosphere at RT. The presence of trimethylsilyl groups confers an increased thermal stability on the allyl complexes. The iron complex melts at 72 °C, in contrast to $(\eta^3\text{-}C_3H_5)_2Fe(PR_3)_2$ species, which decompose above 0 °C. Trimethylenemethane tricarbonyliron complexes containing olefinic side groups were oxidized by Me_3NO in boiling benzene to produce new dibridged dicarbonyl bis(π-allyl) complexes.[55]



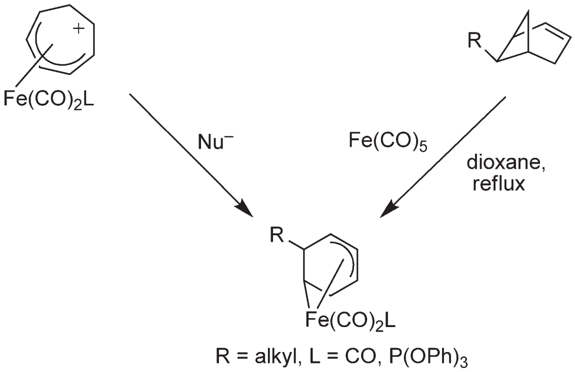
22

Iron carbonyl complexes containing η^1-alkyl-η^3-allyl coordinated hydrocarbon ligands are obtained in several ways. Nucleophilic addition to cationic iron complexes containing η^5-pentadienyl ligands yields (pentenediyl)iron complexes. Oxidatively-induced reductive elimination of these complexes can be utilized as a means to generate 1,2,3-trisubstituted cyclopropanes.[57] The reaction of cationic cycloheptadienyl complexes (Scheme 22) with appropriate nucleophiles also yields the alkyl–allyliron carbonyl complexes.[58,59] $Fe(CO)_5$ also reacts with α- or β-pinene in refluxing dioxane (Scheme 22) to produce an alkyl–allyliron complex.[60] Recently, 1,2- and 1,4-disubstituted $[(\text{pentadienyl})Fe(CO)_3]^+$ cations were shown to react with carbon nucleophiles, such as sodium dimethylmalonate, to yield η^1,η^3-allyl complexes as products.[61]

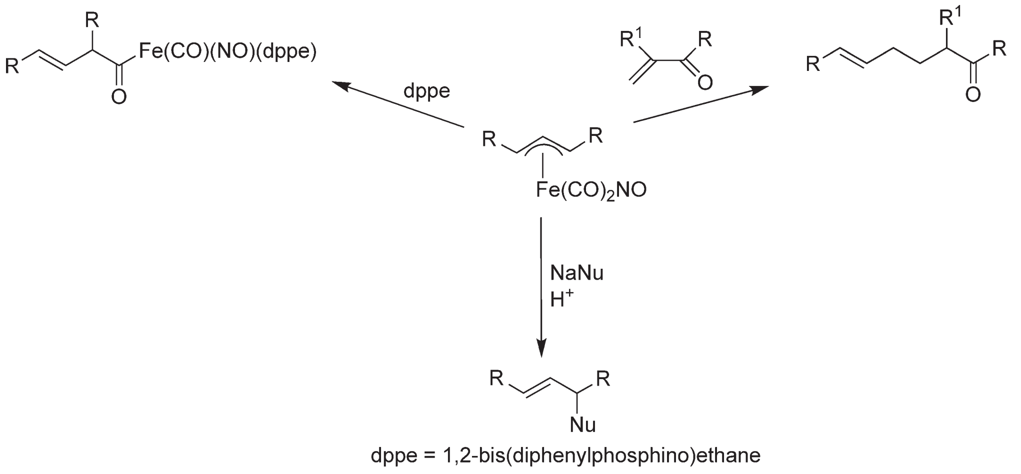
Anionic (η^3-allyl)iron tricarbonyl complexes are easily prepared by the hydride reduction of (butadiene)iron tricarbonyl or (1-phenylbutadiene)iron tricarbonyl complexes with $Li[BHEt_3]$ in THF.[62] Tricarbonyl(η^4-1,3-diene)-iron(0) complexes undergo addition reactions with reactive carbanions, such as $LiCHPh_2$, to form anionic tricarbonyl(η^1,η^2-but-3-en-1-yl)iron(0) complexes.[63,64]

X-ray crystal structures of several (η^3-allyl)iron complexes have been reported.[46,47,51,54,60,62,65–70] Apart from crystal structure data, several reports of the analytical characterization of the allyl complexes are given. The first solution characterization of the highly reactive iron η^3-allyl hydrido complex, $[HFe(CO)_3(\eta^3\text{-}CH_2CHCH_2)]$, by ^1H and ^{13}C NMR spectroscopy, has been reported.[71] Long *et al.* used near-UV photolysis to produce the complex, and using time-resolved infrared spectroscopy studied the mechanism of iron carbonyl-catalyzed isomerization.[72,73] Photoelectron spectra of $(\eta^3\text{-}C_3R_5)Fe(CO)_2(NO)$ have been reported.[74] Density functional calculations have been reported for two structural isomers of η^3-allyltricarbonyliron bromide and for $[HFe(CO)_3(\eta^3\text{-}C_3H_5)]$.[6,65]

η^3-Allyl complexes of iron are widely used in organic synthesis, in particular, as allylating reagents. η^3-Allyltetracarbonyl iron complexes serve only as electrophiles, and η^3-allyldicarbonylnitrosyl iron complexes as ambiphiles. Allylic ligands of the complexes react with carbon electrophiles, such as allylic halides and acyl halides. Complexes with allyl ligands act as stabilized carbon equivalents and show enhanced reactivity toward nucleophiles, that is, in the reaction with $Na[CH(CO_2Et)_2]$ which occurs at the less-hindered site (Scheme 23). Reaction of the



Scheme 22



Scheme 23

(η^3-allyl)Fe(CO)$_2$NO complex with 1,2-bis(diphenylphosphino)ethane (dppe) led to the formation of a β,γ-unsaturated acyliron complex.[75,76] The allyliron precursors undergo regioselective carbonylation at the less substituted carbon of the η^3-allyl ligand.

Cationic η^3-allyltetracarbonyliron complexes undergo addition reactions with several nucleophiles at the terminal carbon atom of the allyl group. The chemistry of these complexes is highlighted by their reactions with silylenol ethers,[38,77,78] allyltrimethylsilane,[42] chiral enamines,[40] metal imines,[40] silylketone derivatives,[40] and various functionalized copper–zinc reagents.[39] Carbonylmetallates $[L_m(OC)_nM]^-$ react with the cationic complex $[Fe(CO)_3(\eta^2{:}\eta^3\text{-1,2,3-bicyclo[3.2.1]octadienyl})]^+$ to give hetero- di-, tri-, and tetrametallic hydrocarbon-bridged complexes.[79] Functionalization of the allyl unit, in the synthesis of alkenyl sulfones, proceeds normally with regio- and stereocontrol.[39,43] Synthesis of γ-amino enolates by the reactions of cationic η^3-allyltetracarbonyl iron complexes with amines has been reported. A key step in the synthesis of myoporone, a hepotoxic furanosesquiterpene diketone, involved the regio- and stereocontrolled addition of a silyl enol ether to a planar chiral $[(\eta^3\text{-allyl})\text{tetracarbonyliron}]^+$ complex.[41]

Conjugate addition of (η^3-allyl)Fe(CO)$_2$NO complexes to α,β-unsaturated carbonyl compounds yields the corresponding δ,ε-unsaturated carbonyl compounds in high yields.[80] (η^3-1- and 2-trimethylsiloxyallyl)Fe(CO)$_2$NO and (η^3-1-acetonylallyl)Fe(CO)$_2$NO complexes react regioselectively with α,β-unsaturated carbonyl compounds to give 1,5-, 1,6-, and 1,8-dicarbonyl compounds.[80] Treatment of (η^3-allyl)Fe(CO)$_2$NO complexes with carbon nucleophiles yields 3-substituted 4-acetoxy-1-butene derivatives.[45]

The (η^3-allyl)Fe(CO)$_2$NO complex was also shown to undergo rotameric transformations in several RT photochemical studies.[81] These transformations include allyl rotation, CO loss, and nitrosyl linkage isomerism.

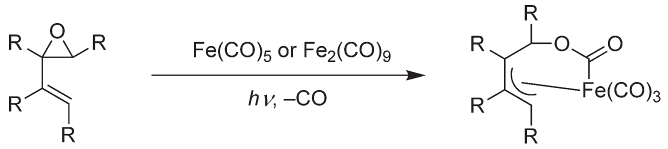
Asymmetric carbon–carbon and carbon–nitrogen bond-forming reactions via planar chiral η^3-allyldicarbonylnitrosyl iron complexes have been reported.[82,83] The planar iron complexes react with various amines regio- and stereoselectively to give γ-amino-α,β-unsaturated carboxylic acid derivatives. When electron-withdrawing substituents, such as ester and amide groups, are introduced into the allyl ligands, the allyliron complexes show enhanced reactivity and high regioselectivity in amination reactions.[82]

Bicyclo[4.1.1] or [3.2.1]octenones[58,59] and cyclopropanes[57] have resulted from decomplexation of the iron tricarbonyl group from the alkyl–allyliron tricarbonyl complex, using oxidative (i.e., CO atmosphere) or carbonylative methods for the bicyclooctenones and ceric ammonium nitrate (CAN) for the cyclopropanes. Photolysis of analogous tricarbonyl iron complexes leads to monoolefinic hydrocarbons or aldehydes.[60] The kinetics of CO substitution in reactions of η^3-cyclopropenyl complexes of iron is also reported.[84] A number of comprehensive reviews[85–89] have appeared since 1992, illustrating the chemistry of η^3-allyliron complexes.

Anionic (η^3-allyl)tricarbonyliron complexes react with Me$_3$SnCl to produce (allyl)Fe(CO)$_3$(SnMe$_3$) complexes in good yields.[62] Reaction of anionic cycloheptatrienyltricarbonyliron complexes with $[(\eta^3\text{-C}_8\text{H}_{12})\text{PdL}]^+$ yields bridging heterobimetallic complexes of the type, $[Fe(CO)_3(\mu\text{-C}_7H_7)PdL]$.[90]

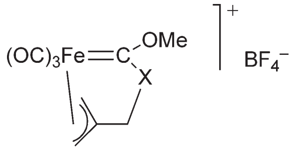
6.03.9 Chelated Allyl Complexes

The chemistry of chelated allyl complexes is dominated by ferralactones or η^3-allyltricarbonyliron lactone complexes. These complexes are used extensively in organic synthesis[91] and are obtained by the reaction of an α,β-unsaturated lactone with $Fe(CO)_5$ (Equation (6)). Oxidation of the ferralactone complex with CAN yields the β-lactone as the major product.[66,67,92–94]



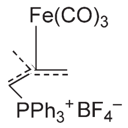
(6)

The reactions of various iron carbonyl complexes, such as $Fe(CO)_4(NMe_3)$, with allene compounds under photolytic conditions, yield chelated η^3-allyliron complexes.[95] Two brief reviews discussing the chemistry and application to organic synthesis of these (π-allyl)tricarbonyl iron lactone complexes have appeared recently.[96,97] Reaction of the iron lactone complexes with trimethyloxonium tetrafluoroborate yields the carbene complex **23** in good yields.[70,98] Treatment of the cationic carbene complex with triphenylphosphine results in substitution at the terminal end of the allyl ligand of the trimethylenemethane complex **24**.



X = O, NR

23

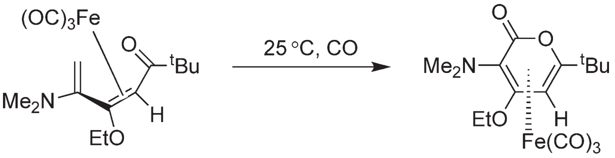


24

Decomplexation reactions, using H_2O_2/NaOH, give rise to the corresponding allylic alcohols in good yields. The electrophilic cationic (η^3-allyl)carbene complexes also react with certain carbon and heteroatom nucleophiles, such as lithium enolates, potassium enoxyborates, and organocuprates.[68] Attack normally occurs on the allyl terminus of the metallacycle. In a related study, primary amines were found to react with neutral ferralactones at the terminal position of the allyl ligand.[69] Cationic η^3-allyl iron lactone complexes are attacked by nucleophiles either on the allylic terminus or on the vinyl residue that forms part of an activated Michael system. Various organometallic reagents have been reported to react with carbonyl groups in the side chains of acyclic π-allyltricarbonyliron lactone complexes.[99] η^3-Allyltricarbonyliron lactones are also important reagents in the synthesis of the β-lactone cholesterol synthase inhibitor 1233A.[100]

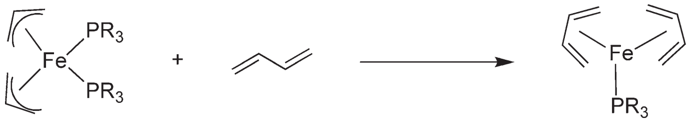
6.03.10 η^3–η^4 Interconversions

The conversion of an η^3-(2-(*tert*-butylcarbonyl)vinyl)carbene iron complex into the (η^4-α-pyrone)$Fe(CO)_3$ complex has been reported (Scheme 24).[53] This reaction was performed under moderate CO pressure at 25 °C to give the product in high yield. The yield decreased significantly with increasing reaction temperature, as well as with decreasing CO pressure.



Scheme 24

The reaction of $(\eta^3\text{-}C_3H_5)_2Fe(PR_3)_2$ with 1,3-butadiene gave $(\eta^4\text{-}1,3\text{-}C_4H_6)_2Fe(PR_3)$ as a result of butadiene-induced reductive coupling of the allyl groups followed by diene exchange (Equation (7)).[56]



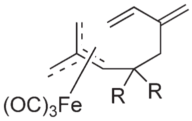
(7)

Reactions of allyliron tricarbonyl anions with carbon electrophiles, such as alkyl halides, followed by treatment with PPh_3, yield η^4-$\{CH_3CH{=}CHC(O)R\}Fe(CO)_2(PPh_3)$ complexes.[101]

6.03.11 Complexes of Cyclobutadiene and Trimethylenemethane

1,3-Disubstituted and 1,2,3-trisubstituted (cyclobutadiene)tricarbonyliron complexes have been prepared using traditional synthetic methods. Selective alkylations on diisopropyl squarate and subsequent complexation with $Fe_2(CO)_9$ afford the corresponding (cyclobutadiene)tricarbonyliron complexes.[102] Bunz and Enkelmann coupled the cyclobutadiene complex, $(C_4I_4)Fe(CO)_3$, with a variety of stannylbutadiynes to prepare new $\{C_4(C{\equiv}CC{\equiv}CR)_4\}Fe(CO)_3$ complexes.[103] Crystal structures for these star-shaped tricarbonyl(cyclobutadiene)iron complexes have also been reported. New carbon–carbon bond-forming reactions were shown by the reaction of tricarbonyl(η^4-cyclobutadienyl)iron complexes with various nucleophilic alkenes, such as silyl enol ethers.[104] Cyclobutadiene tricarbonyliron complexes undergo intramolecular cycloadditions with olefins to produce highly functionalized cyclobutene-containing products.[105]

Oxidation of tricarbonyl(trimethylenemethane)iron complexes **25** containing an olefinic side chain, with Me_3NO in boiling benzene, affords dibridged dicarbonyl (bis-π-allyl)iron complexes.[106]

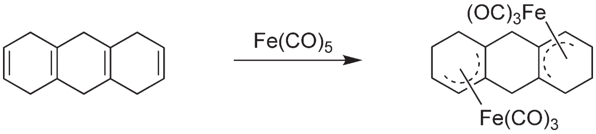


25

6.03.12 Complexes of Stable Dienes

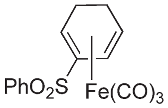
Complexes of this type are dominated by tricarbonyl (η^4-1,3-diene)iron complexes. The irontricarbonyl moiety serves as a protecting group for conjugated dienes. It directs the formation of chiral centers and stabilizes positive charge adjacent to the complexed diene. Traditional methods for the synthesis of tricarbonyliron–diene complexes are based on the direct reaction of carbonyliron compounds, such as pentacarbonyliron,[107–116] nonacarbonyldiiron,[117–130] or dodecacarbonyltriiron,[118] with dienes, under thermal or photolytic conditions. Four comprehensive reviews detailing the synthesis of various diene iron complexes and their applications to organic synthesis have been published since 1992.[131–134]

The reaction of enantiomerically pure sulfinyl dienes with $Fe(CO)_5$ yields (η^4-(1*Z*)-sulfinyl diene)iron(0) tricarbonyl complexes.[113,114] Planar and axial chirality are introduced upon complexation of similar ligands with $(dba)Fe(CO)_3$ (dba = dibenzylideneacetone).[135] Complexation of sorbic acid with $Fe(CO)_5$ in acetone upon irradiation with UV light produced the (η^4-2,4-hexadienoic acid)$Fe(CO)_3$ complex in good yields.[112] Stobart *et al.* reported the reaction of 1,4,5,8,9,10-hexahydroanthracene with $Fe(CO)_5$ under UV irradiation[107] to form a complex in which two tricarbonyliron moieties are bound in an η^4-fashion to the ends of the isolated conjugated diene units (Equation (8)).



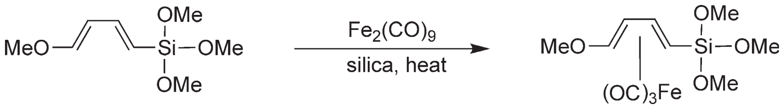
(8)

Reports on the synthesis of diene complexes using $Fe_2(CO)_9$ are more common. Reaction of 2-phenylsulfonyl-1,3-cyclohexadiene with 2 equiv. of $Fe_2(CO)_9$ in refluxing ether formed the [1-(phenylsulfonyl)-1,3-cyclohexadiene]iron(0)tricarbonyl isomer **26**.[119] The reaction is catalyzed by 1-aza-1,3-butadiene. In a separate study, 1-aza-1,3-butadienes were shown to effect a quantitative catalytic complexation of cyclohexadienes with $Fe_2(CO)_9$.[136] Activities are greatly enhanced in the presence of aryl rings bonded to nitrogen.



26

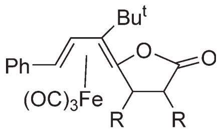
Complexation of dienols with $Fe_2(CO)_9$ in benzene at 50 °C yielded the corresponding (dienol)irontricarbonyl complexes.[121] Subsequent reaction with hexafluorophosphoric acid produced the tricarbonyl(pentadienyl)iron(+1) cations as their PF_6^- salts. Treatment of two azadienes and four dienamides having chiral auxillaries with $Fe_2(CO)_9$ yielded an equimolar mixture of diene–$Fe(CO)_3$ diastereomeric complexes.[128] (Diene)$Fe(CO)_3$ complexes may also be formed by ring-opening of strained cyclic compounds. The reaction of 3-vinyl-1-cyclopropene with $Fe_2(CO)_9$ proceeds via ring expansion to afford (η^4-cyclohexadienone) iron complexes.[124] Nucleophilic addition of primary and secondary amines to the tricarbonyl(η^5-methylnopadienyl)iron(+1) cation affords optically active η^4-(aminodiolefin) tricarbonyliron complexes.[125] Pauson *et al.* reported a novel route for the more efficient, rapid synthesis of (diene)$Fe(CO)_3$ complexes.[120] This was achieved through the action of mild heat, in the absence of solvent, on a mixture of the diene and a preformed mixture of $Fe_2(CO)_9$ and silica gel (Equation (9)). The yields of the diene iron complexes compare well with those already reported in the literature.



(9)

Stephenson and co-workers used sonication to effect the reaction of alkenyloxides with $Fe_2(CO)_9$ to afford ferralactones. Treatment of the ferralactones with barium hydroxide yields the η^4-diene irontricarbonyl complex.[117] Attachment of a (tricarbonyl)iron adjunct to an acyclic diene has been shown to effect diastereoselective bond formation at unsaturated centers adjacent to the diene. Here, the enantiomers of tricarbonyl(methyl 6-oxo-2,4-hexadienoate)iron, generated by complexation of dienoates with $Fe_2(CO)_9$, have proved to be especially useful in asymmetric synthesis.[122] The reaction of 1,2-(3,5-cyclohexadieno)buckminsterfullerene with $Fe_3(CO)_{12}$ gives the complex [η^4-1,2-(3,5-cyclohexadieno)buckminsterfullerene]iron tricarbonyl[118] in 14% yield, and is the first structurally characterized iron-containing C_{60} compound.[118]

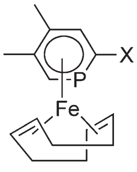
Alternative methods for the synthesis of (η^4-diene)iron complexes include nucleophilic attack on tricarbonyl(η^5-cyclohexadienyl)iron cations to afford tricarbonyl(η^4-cyclohexadiene) complexes.[137–140] Tricarbonyl-(pentadienyl)iron(1+) cations also undergo nucleophilic addition to yield the corresponding acyclic (diene)$Fe(CO)_3$ complexes.[141,142] The reactions of tricarbonyl(vinylketene)iron(0) complexes with alkynes produce chelated allyliron tricarbonyl complexes. Further heating under a CO atmosphere gives the lactone complex **27** as one of the products.[143]



27

The incorporation of organometallic fragments into biomolecules has attracted attention in recent years. The addition of $[Ph_2C{=}NCHCO_2Me]^-$ to $[(C_6H_7)Fe(CO)_3]^+$ and $[(C_7H_9)Fe(CO)_3]^+$ gives derivatives of α-amino acids with organometallic side chains. This leads to the formation of an organometallic-substituted α-amino acid whose structure is supported by X-ray crystallographic data. The structure of $[(\eta^4\text{-}C_6H_7)CH(N{=}CPh_2)CO_2Me]Fe(CO)_3$ has been determined by X-ray diffraction.[144] Beck *et al.* have introduced the iron tricarbonyl moiety into barbituric acid, using cationic iron complexes.[145] An application of this study is the ability to label biologically important molecules.

(η^4-1,5-Cyclooctadiene)(η^6-phosphinine)iron(0) complexes 28 were prepared by the reaction of iron vapor with COD (COD = cyclooctadiene) and 2-(trimethylsilyl)-4,5-dimethylphosphinine.[146] This complex was used as a catalyst for cyclization of alkynes and nitriles to pyridines.



28

X = $SiMe_3$, Cl

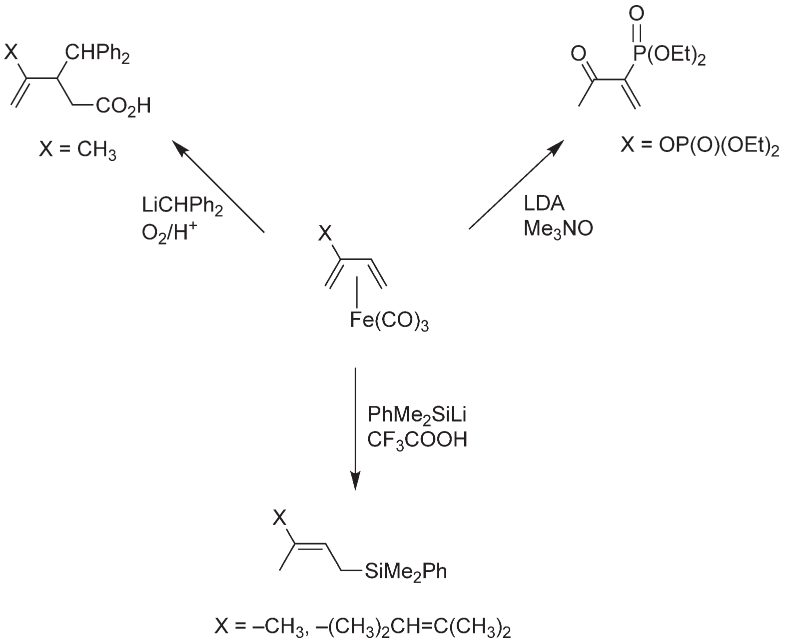
Structural characterization of (butadiene)tricarbonyliron complexes has been carried out by microwave spectroscopy,[147,148] solution calorimetry,[149] pulsed-electron high pressure mass spectrometry,[150] infrared spectroscopy,[151,152] and vibrational overtone spectroscopy.[153] Theoretical investigations using DFT have also been reported.[154–156] Extended Hückel calculations have been employed to study structure and stereodynamic relationships in a variety of (η^4-diene)iron carbonyl complexes.[157,158]

There has been a prolific interest in the application of (diene)iron complexes in organic synthesis. Donaldson has extensively reviewed synthetic applications of these types of complexes.[131] Tricarbonyl [1-(methoxycarbonyl)-pentadienyl]iron(1+) hexaflurophosphate was used to prepare a racemic 5-HETE methyl ester and a 5-HETE lactone (5-HETE = 5-hydroxyeicosatetraenoic acid).[159] In a separate study, an acyclic (pentadienyl)iron(1+) cation was used to synthesize the 8(*E*),10(*Z*),16(*E*),18(*E*)-tetraene segment of macrolactin A, a 24-membered polyene macrolide that exhibits antiviral activity.[160,161] New methodology for the preparation of tetrahydrothiopyrans[162] and oxocenes[163] via intramolecular trapping of pentadienylcations complexed to $Fe(CO)_3$ has been reported. Utilizing organoiron methodology, via an η^4-diene iron tricarbonyl complex, the synthesis of the *as*-indacene unit of ikarugamycin, a polycyclic lactam, is described.[164] Ikarugamycin is reported to display antibiotic activity. The planarity of $[Fe(diene)(CO)_3]$ complexes imparts the potential as chiral auxiliaries for the asymmetric synthesis of natural products. This is ascribed to the ability of the iron tricarbonyl units to control the regio- and stereochemistry of nucleophilic addition. Using various $Fe(diene)(CO)_3$ complexes, the asymmetric synthesis of (+)- and (−)-frontalin, a piperidine alkaloid (SS20846A), and *N*-Boc-*O*-Me-(2*R*,3*S*,5*E*,7*E*)-2-aminotetradeca-5,7-diene–3-ol has been reported.[165] α-Lipoic acid, used for the treatment of diabetic polyneuropathy, was prepared using a tricarbonyl(diene)iron complex.[166] This highly yielding route is favorable as the acid is only available in small quantities from natural resources. The synthesis of 11(*Z*)-retinal, a chromophore of photosensitive pigments is reported from the β-ionylideneacetaldehyde–tricarbonyliron complex.[167] Apart from biologically important molecules and natural products, (η^4-diene)$Fe(CO)_3$ complexes have been utilized to prepare an array of organic molecules, including γ,δ-unsaturated acids and allylic alcohols,[168] γ- and δ-lactones,[169] α-phosphono-α,β-unsaturated ketones,[170] and 1-dimethyl(phenyl)silylcyclohex-1-enes and other dienylsilanes (Scheme 25).[171]

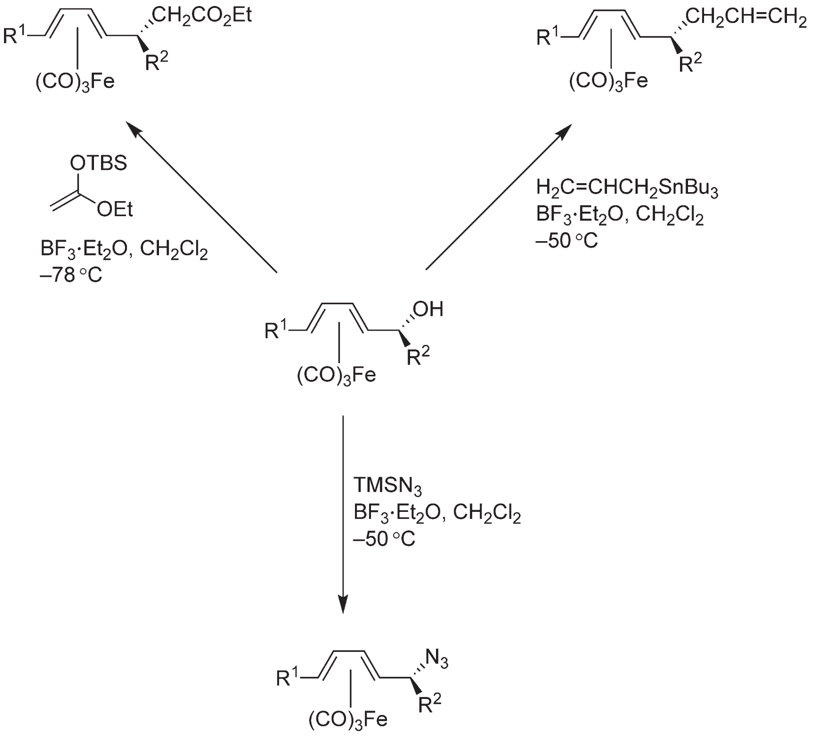
Oxidative cyclization of alkylamines tethered to tricarbonyl–cyclohexadiene complexes facilitates an easy route to synthesis of indole derivatives.[172] The ring closure is brought about using a single-electron-transfer (SET) agent, such as ferricenium hexafluorophosphate. Yeh *et al.* reported the first intramolecular radical cyclization of (η^4-diene)$Fe(CO)_3$ complexes, to afford racemic cyclic tertiary alcohols.[173]

(Diene)tricarbonyliron complexes are able to react with a variety of nucleophiles, mediated by a Lewis acid. The Darzens–Nenitzescu reaction was utilized to prepare η^4-dienetricarbonyliron complexes containing carbonyl groups.[174] Lewis acid-catalyzed nucleophilic additions have been reported to occur at carbonyl functionalities adjacent to an iron-complexed diene.[175–178] In a separate study, facile racemization or epimerization was observed in solution, for complexes containing aldehyde or ketone functionalities adjacent to the diene moiety.[179,180] This seems to indicate a new role for the $Fe(CO)_3$ moiety in (diene)tricarbonyliron complexes. Other examples of bond formation at centers adjacent to the coordinated diene include alkylations,[181] osmylation,[182] and reactions with boron trifluoride.[183] Substituted η^4-(3(*E*),5(*E*)-heptadien-2-ol]$Fe(CO)_3$ complexes undergo Lewis acid-mediated nucleophilic substitution reactions with AlR_3 reagents, ketene silyl acetals, allyltributylstannane, allyltrimethylsilane, and trimethylsilyl azides (Scheme 26).[184]

Cyclic and acyclic $[(pentadienyl)Fe(CO)_2L]X$ complexes (L = CO, PPh_3) react with nucleophiles to form the corresponding complexes containing terminal acyloxy or alkoxy substituents.[185] The synthesis of the first (diene)$Fe(CO)_3$ complex functionalized with a fluorine atom in the allylic position has been reported.[186] Reactions



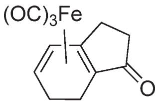
Scheme 25



Scheme 26

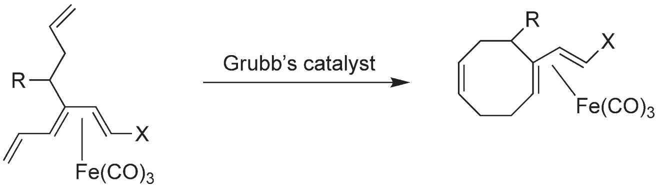
of cationic tricarbonyl(η^5-pentadienyl)iron(1+) complexes with hetero- and carbon-atom nucleophiles yielded neutral tricarbonyl(η^4-diene)iron(0) complexes.[187] Nucleophilic attack by heteroatom nucleophiles on *O*-acyl and *O*-phosphoryl cyanohydrin–Fe(CO)$_3$ complexes resulted in substituted hepta-2,4-dienonitrile Fe(CO)$_3$ complexes.[188] Studies on the reactions of η^4-(diene)Fe(CO)$_3$ complexes with nucleophilic organometallic reagents have also been reported.[189–193] Tricarbonyl [(1-4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron is shown to react with both nucleophiles and electrophiles.[194] Friedel–Crafts reactions of acyclic diene iron tricarbonyl complexes with alkoxychloromethanes produce alkoxypenta-2,4-diene complexes.[195] Diels–Alder reactions of planar chiral η^4-(diene)Fe(CO)$_3$ with α,β-unsaturated ketones adjacent to the diene react with cyclopentadiene to afford the *endo*-adducts stereoselectively.[196] New 4-substituted-tricarbonyl(η^4-cyclohex-2,4-dien-1-one)Fe(CO)$_3$ complexes were prepared by the oxidation of cyclohexadiene iron tricarbonyl complexes with thallium trifluoroacetate.[197] The reaction of (dienal)iron tricarbonyl complexes with allyldiisopinocampheylborane yields (1,4,6-trien-3-ol)iron complexes.[198]

Studies of cyclization reactions of (η^4-diene)Fe(CO)$_3$ complexes are sparse. (η^4-Cyclohexadiene)Fe(CO)$_3$ complexes containing an acid chloride in the side chain react with Lewis acids, such as aluminum chloride, to afford cyclic keto complexes of a type similar to complex **29**.[199,200]



29

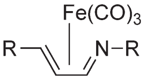
(Diene)Fe(CO)$_3$ complexes have been used to construct 2-azaspiro[5.5]undecane and tricyclic ring systems.[201,202] Intramolecular coupling reactions between diene–Fe(CO)$_3$ complexes and a pendant olefinic group or pendant alcohols have been studied.[203–205] The cyclization of allylic thioester-functionalized cyclohexadiene iron tricarbonyl complexes, via intramolecular coupling, leads to the formation of *spiro*-thialactone derivatives.[206,207] Enantiopure η^4-(1-sulfinyldiene)iron(0) tricarbonyl complexes containing bis-olefins, have been cyclized in the presence of Grubb's ruthenium carbene catalyst to afford medium-sized carbocycles (Equation (10)).[208] Iron tricarbonyl systems containing diazoketones tethered to the terminal position of the acyclic coordinated diene have been utilized to effect ring formation, via inter- and intramolecular carbene reactions, affording new cyclohexa-2,4-dienone and cyclopent-2-enone tricarbonyl iron complexes.[209]



(10)

6.03.13 Complexes of Heterodienes

The majority of heterodiene complexes continue to be dominated by the synthesis of 1-azadiene **30**[110,111,210–212] and 1-oxadiene complexes **31**, of the type shown below.[210,213]



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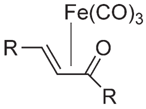
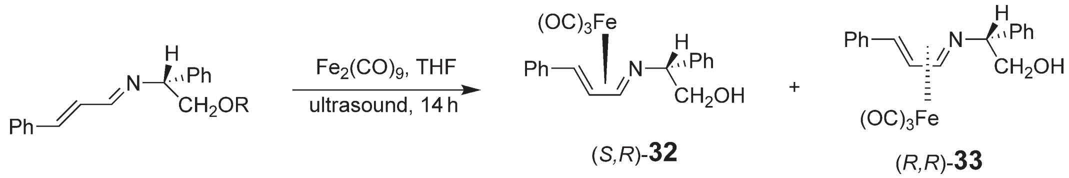
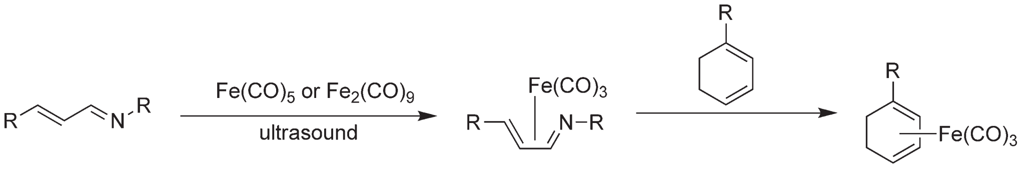


31

Chiral 1-aza-1,3-butadienes react with nonacarbonyldiiron in THF at RT using ultrasound, to yield a 5 : 1 mixture of the (*S*,*R*)-**32** and (*R*,*R*)-**33** diastereoisomers, respectively. The crystal structure of **32** has been reported (Scheme 27).[211] The free ligands of 1-aza-1,3-dienes are reported to be efficient catalysts for the complexation of 1,3-dienes with either pentacarbonyliron or nonacarbonyldiiron.[111,212] In this respect, the heterodiene complexes serve as useful tricarbonyliron transfer reagents, to yield free 1-azabuta-1,3-dienes (Scheme 28).

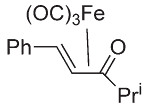


Scheme 27

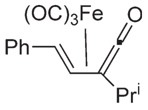


Scheme 28

The reaction of vinyl ketones with pentacarbonyliron affords the corresponding η^4-oxadiene tricarbonyliron complex 34, which can easily be converted into the vinyl ketene iron tricarbonyl complexes 35 upon reaction with alkyllithium reagents under an atmosphere of carbon monoxide.[213]



34

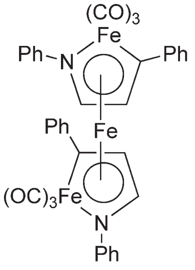


35

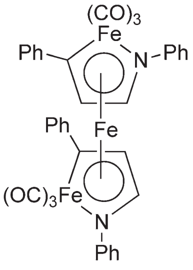
Tricarbonyl(vinylketene)iron(0) complexes were shown to react with dimethyl maleate, dimethyl fumarate, (*E*)-methyl 4-oxopent-2-enoate and (*E*)-ethyl 4,4,4-trifluorobut-2-enoate to give decarbonylated adducts.[214] New (η^4-azadiene)Fe(CO)$_3$ complexes containing furan, thiophene or ferrocenyl moieties at the C terminus of the heterodiene complexes have been prepared.[215] X-ray crystal structures and extended Hückel calculations of the new materials have been reported. Complexation of Fe$_2$(CO)$_9$ with *N*,*N*′-bis(3-phenylallylidene)hydrazine in refluxing THF affords new (η^4-azadiene)Fe(CO)$_3$ complexes.[216] Molecular structures of the new complexes have been confirmed by X-ray diffraction studies.

(1–Heterodiene)tricarbonyliron(0) complexes are generally known to react with alkyllithium reagents. Recent reports describe the reactions of heterodiene complexes with lithium aluminum deuteride affording 1,2,3-trideutero alcohols and amines.[217] The reactions of (1-azadiene)tricarbonyliron(0) complexes with lithiated amines to produce (2-aminohomodiene)tricarbonyliron(0) complexes have also been reported.[217]

(η^4-1-Azabuta-1,3-diene)tricarbonyliron complexes can act as substitutes for cyclopentadiene. To this end, two diastereomeric bis(azaferracyclopentadienyl)iron(II) compounds 36 and 37 have been isolated by refluxing the azabutadiene tricarbonyliron complex in toluene.[218] These compounds react with {CpFe(CO)$_2$}$_2$ to afford half-sandwich iron complexes.



36



37

Kinetic studies show that bond-shift isomerization of heterodiene tricarbonyliron complexes hinders the application of these complexes in stereoselective and/or asymmetric synthesis.[219]

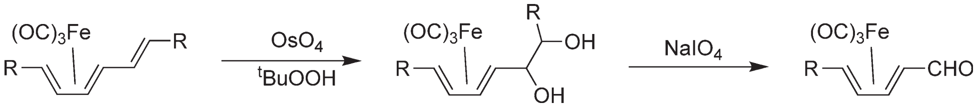
6.03.14 Complexes of Trienes and Tetraenes

Various reports on the synthesis and reactivity of iron complexes of trienes and tetraenes have been reported in the past 10 years. Reactivity studies of various triene and tetraene complexes predominate in the recent literature. (η^4-Triene)Fe(CO)$_3$ complexes have been reported to undergo osmylation reactions with OsO$_4$ to yield the corresponding glycols (Scheme 29).[220] Subsequent reaction with NaIO$_4$ in THF/H$_2$O/23 °C affords (dienal)Fe(CO)$_3$ complexes.

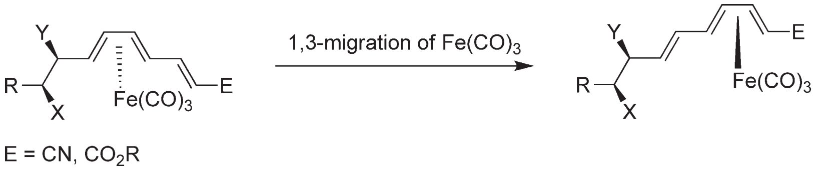
Acyclic conjugated (η^4-4-7)-triene Fe(CO)$_3$ complexes bearing an electron-withdrawing group at the terminal position undergo 1,3-migration of the Fe(CO)$_3$ group on the triene to afford (η^4-2-5)-triene Fe(CO)$_3$ complexes when treated with a base such as KN(SiMe$_3$)$_2$ and NaH (Scheme 30).[221]

Cycloheptatrienes in protic solvents are reported to react with Fe(CO)$_5$ and a catalytic amount of NaBH$_4$ to produce (η^4-1,3-diene)iron tricarbonyl complexes.[222] Pearson and Ghidu have demonstrated that stereospecific cyclization of iron tricarbonyl diene complexes with pendant alkenes and arenes proceeds via protonation of a double bond vicinal to the iron tricarbonyl diene moiety.[223] This methodology has been used to diastereoselectively produce polycycles from iron tricarbonyl-stabilized pentadienyl carbocations.[224]

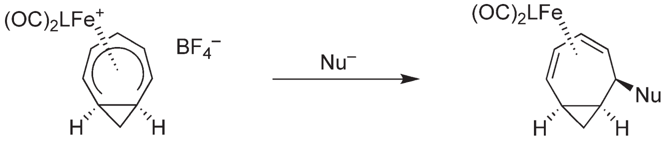
The trienes 3-methylene-1,6-heptadiene (MHD) and 3-methylene-1,7-octadiene react with zerovalent [Fe(Pr$^i{}_2$P(CH$_2$)$_n$ PPr$^i{}_2$)] species ($n=1, 2, 3$) to produce acyclic triene complexes bonded in an η^2,η^4-fashion to iron, confirmed by X-ray diffraction for (η^2,η^4-3-MHD)Fe(Pr$^i{}_2$P(C$_2$H$_4$)PPr$^i{}_2$)[225] Similar reactions of the tetraene 3,6-dimethylene-1,7-octadiene (DMOD) with trialkylphosphine–iron complexes, produce (η^4,η^4-DMOD)Fe(PR$_3$) complexes. Crystallographic data for these complexes are reported. (η^4-Cycloheptatriene)Fe(CO)$_2${P(OPh)$_3$} was converted into (ketocycloheptadiene)Fe(CO)$_2${P(OPh)$_3$} by hydroboration followed by Swern oxidation.[226] Protonation of (cyclooctatetraene)Fe(CO)$_3$ by noncoordinating acids affords a bicyclic cation **38**, which shows enantiofacial selectivity toward nucleophiles which attack from the face opposite to iron, to give 6-substituted (bicyclo-[5.1.0]octa-1,4-diene)iron complexes **39** (Scheme 31). This methodology, which presents a unique route to



Scheme 29



Scheme 30

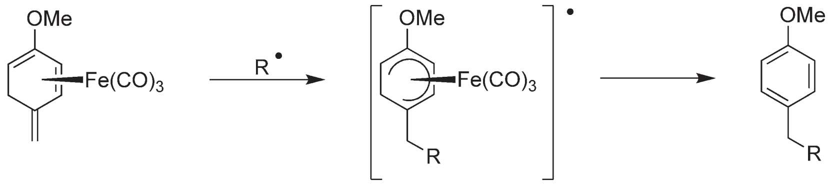


38

L = CO$_2$, PPh$_3$

39

Scheme 31



Scheme 32

synthesizing substituted cyclopropanes, has been applied to the synthesis of *cis*-2-(2′-carboxycyclopropyl)glycine.[227] Methodology has been developed for the stereospecific preparation of cyclopropanes which represent key structural features in many naturally occurring compounds, that is, *cis*-2-(2′-carboxycyclopropyl)glycine. Here protonation of (cyclooctatetraene)Fe(CO)$_3$ by non-coordinating acids affords a bicyclic cation possessing a *cis*-disubstituted cyclopropane ring.

Tricarbonyl [(1-4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron was found to undergo facile radical addition regioselectively at the exocyclic methylene group to yield an aromatized product upon demetallation (Scheme 32).[228]

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6.04
Mononuclear Compounds with C_5 and C_6 Ligands

J R Moss, C H Kaschula and G S Smith, University of Cape Town, Rondebosch, South Africa

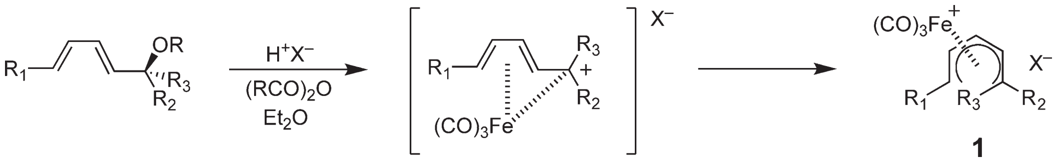
6.04.1 Acyclic Pentadienyls

Over the past 20 years, there has been a growing interest in the use of acyclic (or open) (η^5-pentadienyl)iron cations 1 (Scheme 1) as synthetic tools for C–C bond formation. Complexation of $Fe(CO)_3$ to a diene distinguishes between two enantiotopic faces of the ligand and directs diastereoselective bond formation at unsaturated centers adjacent to the coordinated diene. In addition, the electron-donor ability of the carbonyliron group allows for the generation of cationic centers adjacent to the coordinated diene.[1,2]

Dehydration of (pentadienol)- or (pentadienylether)$Fe(CO)_3$ complexes with a strong acid is the most common method used for the preparation of acyclic (η^5-pentadienyl)iron cations.[3] It has been demonstrated that ionization of the hydroxyl group occurs with anchimeric assistance from iron, and that isomerization of the initially generated *transoid* pentadienyl cation to the more stable *cisoid* cation occurs with retention of configuration about the C1–C2 bond.[4]

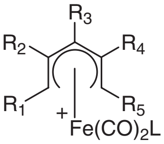
Since 1993, a large number of new acyclic (η^5-pentadienyl)iron cations (**2**–**38**) have been prepared and isolated (Table 1). These include the stereoselectively labeled cations **33** and **34** and cations that have been prepared both in an optically enriched and optically pure form **13**, **14**, **18**, **19**, **28**–**31**, **37**, and **38**.

The first crystal structure of an acyclic (η^5-pentadienyl)iron cation 39 has been reported.[5] Compound 39 was found to have the expected piano-stool geometry, except that one of the carbonyl ligands is tilted toward the dienyl ligand by about 25° relative to the other carbonyl ligands. The central C–C–C bond angle is significantly larger (129.1°) than the terminal C–C–C bond angles (122.2°) of the open dienyl ligand, and the Fe–C bond lengths were found to be longest for the terminal C atoms (average 2.177 Å), intermediate for the formally uncharged atoms in the 2- and 4-positions (average 2.145 Å), and shortest for the central C atom (2.109 Å).

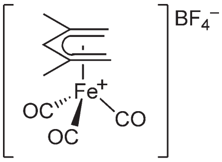


Scheme 1

Table 1 Acyclic (η^5-pentadienyl) cations prepared since 1933

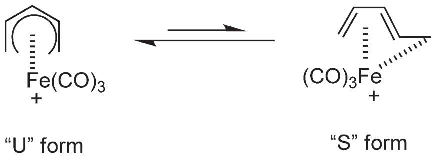


No.	R_1	R_2	R_3	R_4	R_5	*L*	*References*
2	Me				OCOMe	CO	178
3	Me					CO	15
4	Me					PPh_3	178,15
5	OMe					PPh_3	178
6	OCOMe					PPh_3	178
7	OCOPh					PPh_3	178
8	OMe					CO	178
9	OCOMe					CO	178
10	OCOPh					CO	178
11	$PhCO_2$				Me	CO	178
12	HO				Me	CO	178
13	Me (*syn*)				Me (*syn*)	CO	178
14	Me (*syn*)				Me (*anti*)	CO	178
15	PhCOO					PPh_3	178
16	MeCOO					PPh_3	178
17	MeCOO				Me	CO	178
18	PhCOO (*syn*)				Me (*syn*)	CO	178
19	PhCOO (*syn*)				Me (*anti*)	CO	178
20	Me	Me				CO	7
21	Ph	Me				CO	7
22	Me			Me		CO	7
23	Ph			Me		CO	7
24	EtO_2C	Me				CO	14
25	Me					CO	15
26	CO_2Me					CO	10
27	Me					CO	10
28	Me, (1R)					CO	179
29	Me, (1R)					PPh_3	179
30	Me, (1R)					$P(OMe)_3$	179
31	MeO_2C (rac and 2R, 5S)					CO	22
32				Me	Me	PPh_3	35
33	CO_2Me				D	CO	29
34	Me				D	CO	180,19
35	C_6H_4OMe					CO	11
36	CO_2Me					PPh_3	11
37	CH_3 (1S)				SO_2Ph (1S)	CO	21
38	CH_3 (1R)				SO_2Ph(1R)	CO	21



39

In a theoretical investigation,[6] two minimum energy structures for the acyclic (η^5-pentadienyl)Fe(CO)$_3$ cation (**40** and **41**, Scheme 2) were found. The calculated geometry of **40** indicates an η^4-mode of coordination with an additional attractive interaction between Fe and C5. Complex **41** was found to exhibit C_s-symmetry with the metal



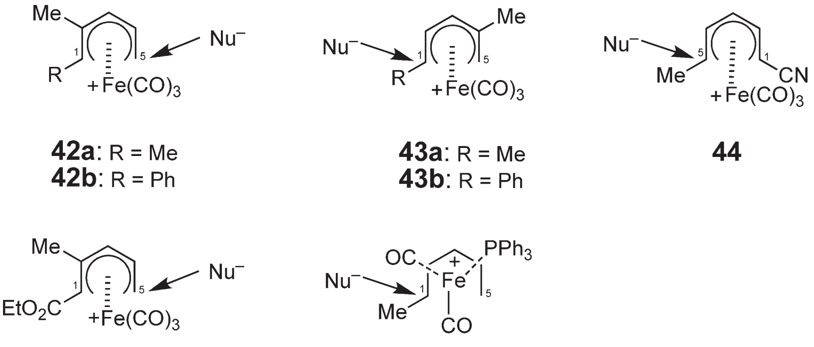
41 **40**

Scheme 2

interacting with the pentadienyl ligand in an η^5-manner. Compound **41** was calculated to be 9.2 kcal mol^{-1} more stable than **40**.

The regioselectivity of nucleophilic attack for the formation of C–C bonds depends on the nature of the nucleophile as well as the substituents attached to the dienyl ligand. Reactions of 1,2-disubstituted **42a** and **42b** and 1,4-disubstituted **43a** and **43b** cations with methanol, triphenylphosphine, lithium dimethylcuprate, and sodium dimethylmalonate nucleophiles have been investigated.[7,8] It was found that cations **42a** and **42b** direct nucleophilic attack regiospecifically to the unsubstituted C5 position whereas cations **43a** and **43b** undergo C1 addition, although in a less predictable manner (Scheme 3). Weak nucleophiles such as methanol,[7] allyltrimethylsilane, furan,[9] and allylic organozirconiums[10] are found to attack exclusively at the less substituted pentadienyl terminus and on the less stable, but more reactive, *transoid* pentadienyl form. Malonate anion attack on 1-substituted acyclic (η^5-pentadienyl)-iron cations is directed to an internal pentadienyl position by a strongly electron-withdrawing group, and to the terminal pentadienyl position by a strongly electron-donating group.[11] In a study on 1-methyl-5-cyano-(η^5-pentadienyl)iron cations **44**, highly diastereoselective C5 substitution was found to occur using a wide range of heteroaromatic nucleophiles to generate a mixture of both *cis*- and *trans*-dienes with 1,2-migration of the $Fe(CO)_3$ moiety.[12] This 1,2-shift has also been observed in the preparation of *trans*-2-disubstituted 1,4-dioxanes.[13] The 1,2-disubstituted acyclic (η^5-pentadienyl)iron cation **45**, which contains a strongly electron-withdrawing group at the 1-position, was found to undergo nucleophilic attack exclusively at the unsubstituted 5-position with a wide range of nucleophiles.[14] Replacement of CO by a phosphine ligand was found to alter the regioselectivity of nucleophilic attack on the 1-methyl(η^5-pentadienyl)iron cation to the substituted C1 position.[15] This observation is based on the existence of a single rotamer **46** where a bulky phosphine ligand, situated in a basal position *trans* to the methyl substituents, directs nucleophilic attack to the opposite diene terminus.

Addition of amines[16,17] and phosphines[18,19] to acyclic (η^5-pentadienyl)iron cations is reversible in some cases. In a representative example (Scheme 4),[19] kinetically controlled nucleophilic attack by phosphine occurs on the more abundant *cisoid* cation to generate an *E*,*Z*-diene **47**. Since significant steric interactions exist between the phosphine nucleophile and substituents present on the pentadienyl ligand, nucleophilic attack in this case is reversible. At higher temperatures and longer reaction times, the thermodynamically more stable *E*,*E*-diene **48** is formed via nucleopilic attack on the less abundant *transoid* form of the (η^5-pentadienyl)iron cation. Amine nucleophiles add regioselectively to the unsubstituted terminus of the (η^5-pentadienyl)iron cation.[16,17]



42a: R = Me
42b: R = Ph

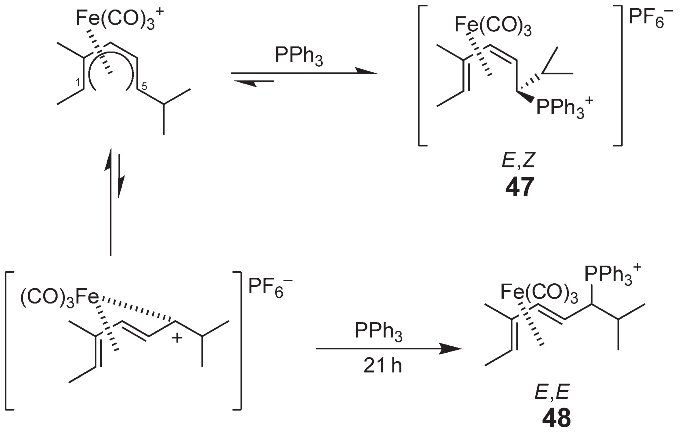
43a: R = Me
43b: R = Ph

44

45

46

Scheme 3

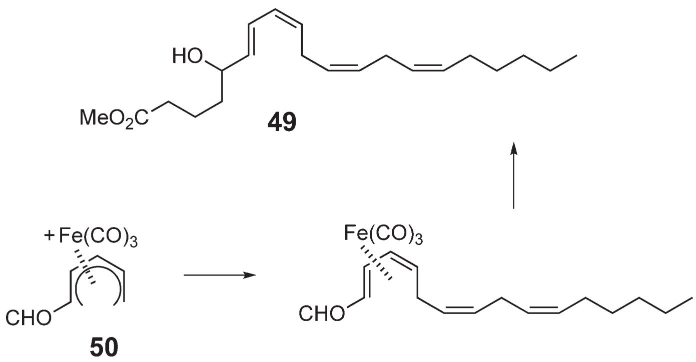


Scheme 4

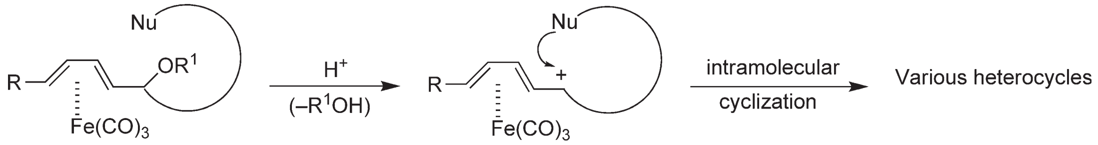
Nucleophilic addition of primary and secondary alcohols to an acyclic 1-butyl-(η^5-pentadienyl)iron cation was found to proceed exclusively at the unsubstituted C5 position.[20] Here, a "one-pot" reaction system has been developed for *in situ* generation of the acyclic (η^5-pentadienyl)iron cation followed by etherification.

Starting from a single and stereochemically well-defined diene, it is possible to generate enantiomerically pure acyclic (η^5-pentadienyl)iron complexes[16,21] that provide a route to enantiomerically enriched substituted dienes. The optically active leukotriene **49** has been synthesized from the acyclic [1-methoxycarbonyl-(η^5-pentadienyl)]iron cation **50** in a key step that involves nucleophilic addition of an organocuprate to the C5 position (Scheme 5).[22]

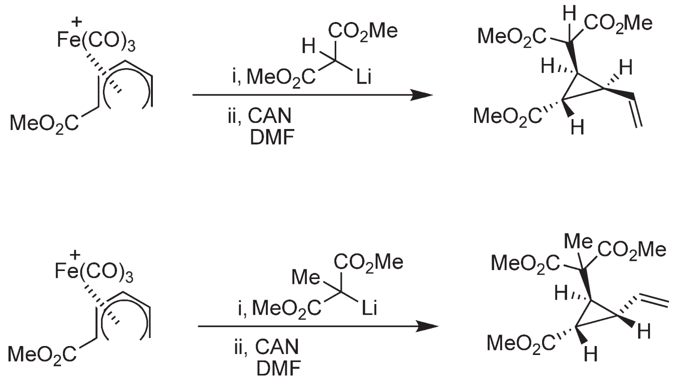
Bridged and fused bicyclic[23] and tricyclic[24] carbon-containing ring systems have been synthesized by addition of functionalized carbon nucleophiles to the acyclic (η^5-pentadienyl)iron cation, followed by stereocontrolled intramolecular cyclization onto the diene–iron complex (general Scheme 6). This methodology has been used to synthesize fused bicyclic bicyclo[3.3.0]octanone and bicyclo[4.4.3]nonanone,[23] as well as the tricyclic tricyclo[6.3.0.0]undecane, tricyclo[6.4.0.0]dodecane, tricyclo[7.3.0.0]dodecane, and tricyclo[7.4.0.0]tridecane ring systems.[24] In both papers, excellent stereocontrol at four stereogenic centers in the fused bicyclic and heterotricyclic compounds is achieved. This methodology has been extended to the diastereoselective synthesis of nitrogen-containing heterobicyclic and



Scheme 5



Scheme 6



Scheme 7

tricyclic compounds. Here, a secondary amine nucleophile adds to the (η^5-pentadienyl)iron cation which then cyclizes to give the 6-azatricyclo[6.3.0.0]undecane and 7-azatricyclo[7.3.0.0]dodecane ring systems.[25] Stereoselective *O*-heterocyclization involving (η^5-pentadienyl)iron cations generated *in situ* provided useful access to chiral-functionalized *trans*-2,3-disubstituted 1,4-dioxanes[13] and oxocenes.[26] Stereoselective synthesis of chiral tetrahydrothiopyrans has been achieved based on the intramolecular trapping of acyclic (η^5-pentadienyl)iron cations by sulfur nucleophiles.[27] Chiral optically pure 2-substituted-4-piperidones[28] have been synthesized using an acyclic (η^5-pentadienyl)iron cation to direct formation of C–C bonds by an intramolecular Mannich reaction.

An interesting route to the synthesis of cyclopropane rings makes use of the acyclic (η^5-pentadienyl)iron cation as a starting material. The addition of lithium dimethylmalonate or lithium dimethylmethylmalonate to the tricarbonyl(1-methylcarbonylpentadienyl)iron cation proceeds exclusively via attack at the C2 carbon.[11,29] Oxidation of the resulting complexes affords vinylcyclopropanecarboxylates in good yield.[29–31] In general, the relative stereochemistry about the cyclopropane ring reflects reductive elimination with retention of configuration, but in cases where the C2 substituent is bulky, the major cyclopropane product represents ring closure with inversion at C3 (Scheme 7).[29]

Acyclic (η^5-pentadienyl)iron cations have been used to stereochemically control C–C bond formation in the syntheses of numerous types of products. This methodology has been used in the synthesis of (*R*)-5-HETE methyl ester,[22] α-lipoic acid,[32] various segments of the 24-membered polyene macrolactin,[33–37] the polycyclic lactam ikarugamycin,[37] and an amino alcohol that is structurally related to sphingosines.[38]

6.04.2 Dicarbonyl(cyclopentadienyl)hydridoiron (FpH) and Related Compounds

The cyclopentadienyliron dicarbonyl group is abbreviated as Fp and the iron pentamethylcyclopentadienyldicarbonyl group as Fp*. These groups form complexes with electron donors to give the half-sandwich complexes FpX and Fp*X. These complexes are very stable, due in part to the strong bonding that exists between the Cp or Cp* ligand and iron. The chemistry of these complexes is often localized at the iron center and the η^1-ligands. This section describes the chemical properties of $CpFe(CO)_2H$ (FpH) and related systems. It also covers the chemistry of some coordinatively unsaturated half-sandwich iron compounds with fewer than 18 electrons. The section then covers new FpX complexes, where X = halogen, phosphenium, borane, and silane groups.

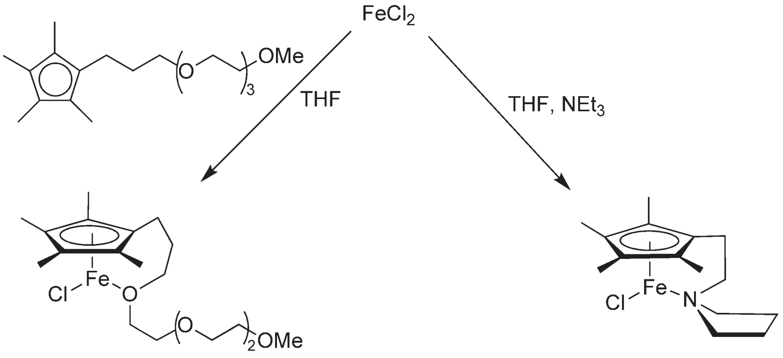
Dihydrogen complexes are a unique class of hydride complex in which the H–H bond is retained. Complexes of the formula $[CpFeH_2L_2]^+$ can exist in the pure dihydrogen (H_2) form, or as mixtures of the dihydrogen with the *trans*- and *cis*-dihydride species.[39] Reported dihydrogen and dihydride complexes produced since 1993 are listed in Table 2.

Compounds **51**, **52**, **55**, **56** were all produced by protonation of the respective monohydride complexes.[40,41] Compounds **53** and **54** were produced by reaction of CpFeCl(dippe) or Cp*FeCl(dippe) with methanol followed by addition of $Na[BPh_4]$.[42] Here, iron is proposed to exist as an iron(IV) dihydride species.

The monohydride Cp*FeH(dppp) was prepared by treatment of the corresponding chloro-derivative Cp*FeCl(dppp) with an excess of $LiAlH_4$ in THF at low temperature.[43] The monohydrides CpFeH(dippe), Cp*FeH(dippe),[42] and Cp*FeH(dppp)[43] undergo a one-electron oxidation with $[FeCp_2][PF_6]$ to yield the 17-electron hydrides, which were isolated as tetraphenylborate $[CpFeH(dippe)][BPh_4]$, $[Cp^*FeH(dippe)][BPh_4]$,[42] and hexafluorophosphate $[Cp^*FeH(dppp)][PF_6]$ salts.[43]

Table 2 Dihydrogen and dihydride complexes prepared since 1993

No.	*Compound*	*References*
51	$[CpFe(H_2)(dppe)][BF_4]$	40
52	$[CpFe(H_2)(dppp)][BF_4]$	40
53	*trans*-$[CpFe(H_2)(dippe)][BPh_4]$	42
54	*trans*-$[Cp^*Fe(H_2)(dippe)][BPh_4]$	42
55	$[CpFe(H_2)CO(PPh_3)_2][BAr_4]$	41
56	$[CpFe(H_2)CO(PEt_3)_2][BAr_4]$	41

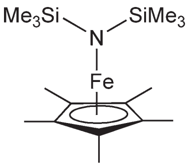


57 **58**

Scheme 8

A number of coordinatively unsaturated half-sandwich iron compounds have been synthesized, characterized, and reviewed.[44] Neutral iron complexes include compounds 57 and 58 which are prepared by reaction of $FeCl_2$ with $Li[C_5Me_4(CH_2)_2N(C_4H_8)]$ in THF/NEt_3[45] or with $Li[C_5Me_4(CH_2)_3(OCH_2CH_2)_3OMe]$ in THF.[46,47] At low temperature, these reactions yield the neutral 16-electron complexes that are stabilized by intramolecular coordination of the pendant amine or glycol ether moiety to iron (Scheme 8). Whereas 57 appears to be stable only in solution,[46,47] 58 has been isolated in the crystalline state.[45]

The diamagnetic 14-electron complex, $Cp^*Fe\{N(SiMe_3)_2\}$ 59, has been synthesized by reaction of $FeCl_2$ with 1 equiv. of $K[N(SiMe_3)_2]$ in THF and subsequent addition of $LiCp^*$.[48] The compound has been characterized in the crystalline state and was shown to have a "pogo-stick" structure.



59

Paramagnetic 16-electron half-sandwich iron complexes have been prepared and are summarized in Table 3. The first X-ray structure for this class of compounds was obtained for $[Cp^*Fe(dippe)][BPh_4]$ **60**.[49] This complex was prepared by halide abstraction from $Cp^*Fe(dippe)Cl$ in methanol under an argon atmosphere, using $NaBPh_4$ as a chloride scavenger. A similar complex, $[Cp^*Fe(dppe)][PF_6]$ **62**, was prepared by oxidation of the 17-electron radical complex $Cp^*Fe(dppe)$ by $[Cp_2Fe][PF_6]$.[50] Dissociation of N_2 from $[CpFe(N_2)(dippe)]^+$ under an argon atmosphere gives the paramagnetic, 16-electron complex $[CpFe(dippe)][BPh_4]$[49] **61**. A related analog $[Cp^*Fe(dppp)][CF_3SO_3]$ **63** has been obtained by hydride abstraction from $Cp^*FeH(dppp)$ using $MeOSO_2CF_3$ as a hydride scavenger.[43]

All the 16-electron coordinatively unsaturated half-sandwich iron compounds reported to date are paramagnetic species with magnetic moments consistent with a triplet state configuration.[43,49,51] The structures of these complexes have been analyzed by Hückel methodology,[52] density functional theory (DFT),[53] and the through-space coupling (TSC) concept.[54,55]

Table 3 Paramagnetic 16-electron half-sandwich iron complexes prepared since 1993

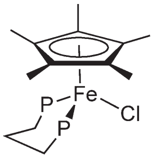
No.	*Compound*	*X-ray crystal structure*	*References*
60	$[Cp^*Fe(dippe)][BPh_4]$	√	49
61	$[CpFe(dippe)][BPh_4]$		49
62	$[Cp^*Fe(dppe)][PF_6]$	√	50
63	$[Cp^*Fe(dppp)][CF_3SO_3]$	√	43

dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dippe = 1,2-bis(diisopropylphosphino)ethane.

A number of 17-electron complexes have been prepared. Pentaarylcyclopentadienyl compounds $(\eta^5\text{-}C_5Ph_4Ar)Fe(CO)_2$ (Ar = Ph, *p*-tolyl) have been generated from $[(\eta^5\text{-}C_5Ph_4Ar)Fe(CO)_2H]$ (Ar = Ph, *p*-tolyl) compounds by hydride abstraction using a trityl radical.[56] These dicarbonyl complexes are stabilized by bulky substituents on the cyclopentadienyl ring and exist in equilibrium with their 18-electron dimers $[(\eta^5\text{-}C_5Ph_4Ar)Fe(CO)_2]_2$. The 17-electron complexes [CpFeCl(dippe)] **64** and $[Cp^*FeCl(dippe)]$ have been prepared by oxidation of $[CpFeCl(dippe)][BPh_4]$ and $[Cp^*FeCl(dippe)][BPh_4]$, respectively, under an oxygen atmosphere in alcoholic solution.[49]

A series of $[(\eta^5\text{-pentadienyl})Fe(CO)_2]^-$ anions (pentadienyl = MeCp, Cp^*, C_5Ph_5, and C_9H_7) have been prepared in THF from the corresponding dimers $[(\eta^5\text{-pentadienyl})Fe(CO)_2]_2$ and $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2Br$.[51]

Various new $CpFeL_2X$ (X = halogen) complexes have been reported. Included is the iron chloro complex $Cp^*Fe(dppp)Cl$ 65, prepared by reaction of $FeCl_2(dppp)$ with Cp^*Li. This complex has been characterized in the solid state.[43] Experiments aimed at trapping the thermally sensitive, 14-electron half-sandwich compound $Fe\{C_5H_2(SiMe_3)_3\}X$ (X = Cl, Br, I) using tetramethylethylenediamine (TMEDA) or triphenylphosphite have yielded the 18-electron complexes 66 and 67, respectively.[57]



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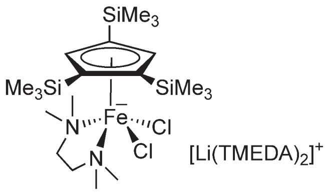

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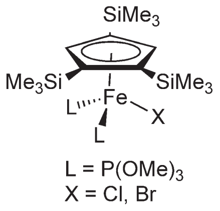

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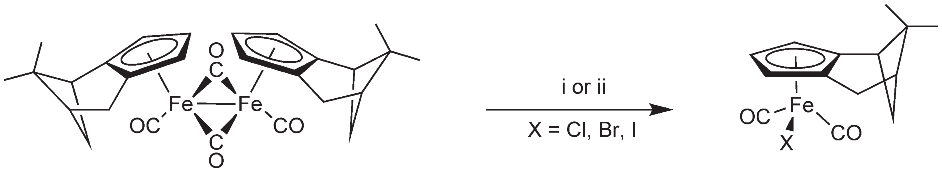
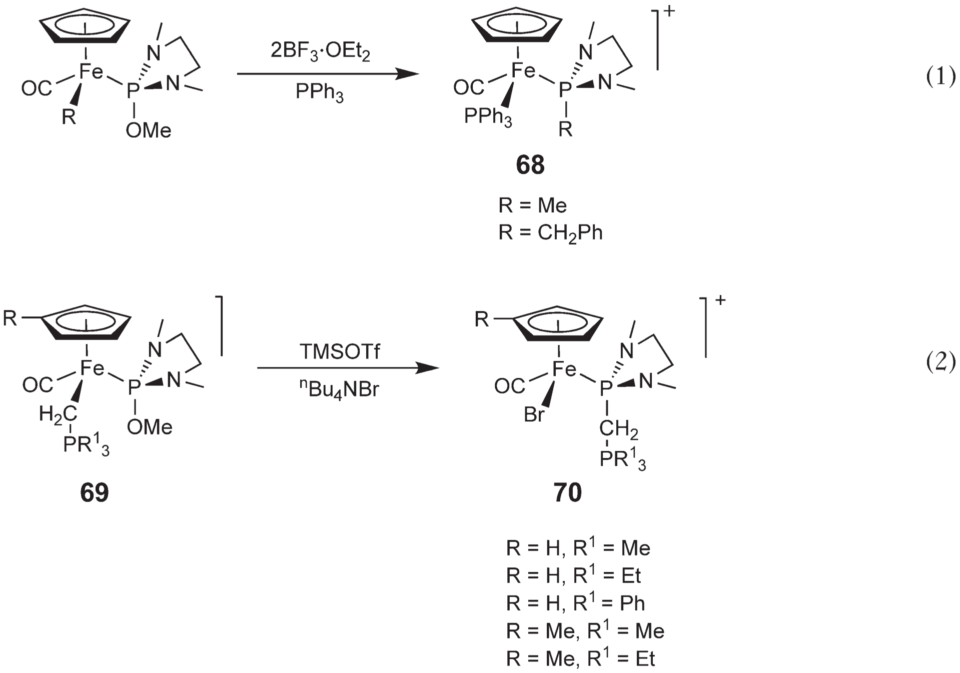
The optically active complex $\{PCpFe(CO)_2\}_2$ (PCp = pinene-fused cyclopentadiene) is converted into the half-sandwich complexes $PCpFe(CO)_2X$ (X = Cl, Br, I) by iodine oxidation,[58] or photochemical reduction with CX_4 (X = Cl, Br, I)[59] (Scheme 9). Ligand exchange of one of the diastereotopic carbonyl ligands for a tertiary phosphine or phosphite then generates diastereomeric complexes PCpFeL(CO)X with pseudo-tetrahedral chirality at the metal center. Here, diastereomeric ratios were found to increase with increasing size of L (L = tertiary phosphine or phosphite).[59]

Various new $CpFeL_2X$ (X = P, B, Si) complexes have been prepared since 1993. Treatment of $Cp(CO)(R)Fe(PNMeCH_2CH_2NMe)$ (R = Me, CH_2Ph) with $BF_3{\cdot}OEt_2$, and then PPh_3 yields $[Cp(CO)(PPh_3)Fe\{PN(Me)CH_2CH_2NMe(R)\}]^+$ complexes (R = Me **68**, CH_2Ph) (Scheme 10, (Equation (1)).[60,61] This reaction is proposed to

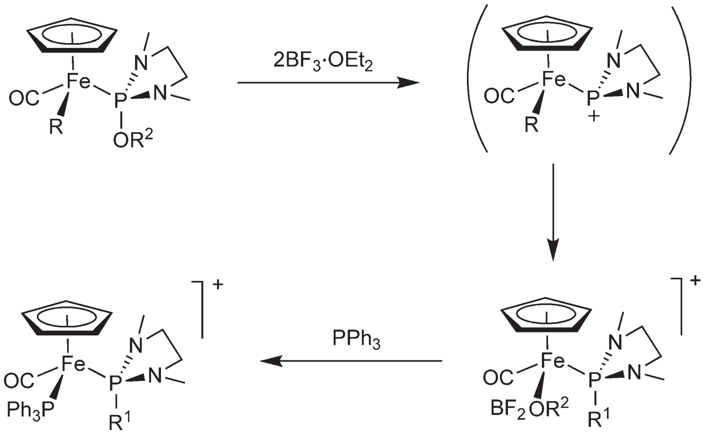


i, I_2; ii, CX_4, $h\nu$

Scheme 9



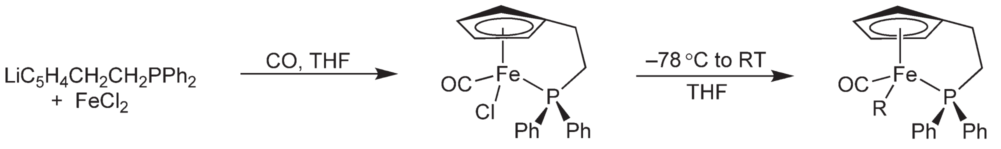
Scheme 10



Scheme 11

proceed via migratory insertion of the phosphenium ligand into an iron–alkyl bond (i.e., alkyl migration from a transition metal to a phosphenium ligand, Scheme 11). Complex **69**, which is a phosphorus ylide complex of iron, reacts with a Lewis acid ($Me_3SiOSO_2CF_3$ (TMSOTf)) followed by $[NBu_4]Br$ to give **70** (Scheme 10, Equation (2)).[61,62] This reaction is proposed to proceed via the same alkyl migration mechanism proposed in Scheme 11. The crystal structure of the iron phosphorus ylide complex, $Cp(CO)(CH_2OMe)Fe\{PN(Me)CH_2CH_2NMe(OEt)\}$, has been reported.[60]

Very stable complexes of the general formula $[CpFe(CO)_x\{Ph_2P(dmpz)\}][BF_4]$ ($x = 1, 2$) (dmpz = 3,5-dimethylpyrazolyl) are prepared by reaction of $PPh_2(dmpz)$ with $\{Fe(CO)_2Cp\}_2$ in the presence of $[FeCp_2]BF_4$ at room temperature. When $[CpFe(CO)_2\{Ph_2P(dmpz)\}][BF_4]$ is treated with Me_3NO, one coordinated CO is lost to form a four-membered ring in which a pyrazoyl ligand is coordinated to the iron.[63] The novel chelate iron half-sandwich complex **72**, with a ligating phosphine connected to the Cp ring, has been prepared by reacting $LiC_5H_4CH_2CH_2PPh_2$

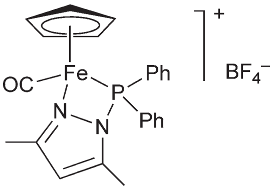


72 **73**

73a: R = CH_3–
73b: R = C_6H_5-CC–
73c: R = $(CH_3)_3$Si-CC–

Scheme 12

with $FeCl_2$, followed by addition of CO.[64] Reaction of 72 with *sp*-, *sp*^{2}-, and *sp*^{3}-hybridized carbon nucleophiles provided various substitution products 73, of which complexes (73a–c) have been characterized in the solid state (Scheme 12). A diastereomeric mixture of an asymmetric Lewis acid catalyst, $[\{\eta^5:\eta^1\text{-}C_5H_4CH(Ph)(OPPh_2)\}\text{-}Fe(CO)(THF)][BF_4]$ 74, featuring a novel cyclopentadienyl ring that is tethered to a terminal diphenylphosphine moiety, has been synthesized.[65] Complex 74 is an effective catalyst in an aziridine-forming reaction and produces *cis*-aziridines in low ee.



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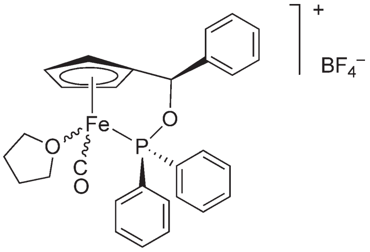
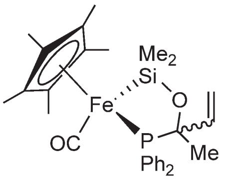


74

Treatment of $Cp^*(CO)Fe\{\kappa^2(Si,P)\text{-}SiMe_2PPh_2\}$ or $Cp^*(CO)_2Fe(SiMe_2PPh_2)$ with methyl vinyl ketone gives 1,2-addition products, $Cp^*(CO)Fe\{\kappa^2(Si,P)\text{-}SiMe_2OCMe(CH{=}CH_2)PPh_2\}$ 75 and $Cp^*(CO)_2Fe\{\kappa^1(Si)\text{-}SiMe_2O\text{-}C(Me){=}CHCH_2PPh_2\}$ 76, respectively.[66] Complex 76 was further converted into the cyclic $Cp^*(CO)Fe\{\kappa^2(Si,P)\text{-}SiMe_2\text{-}OCMe{=}CHCH_2PPh_2\}$ 77 upon photolysis. The salt $K[CpFe(CN)_2(PTA)]$ (PTA = 1,3,5-triaza-7-phosphaadamantane) has been synthesized by photolysis of $K[CpFe(CN)_2CO]$ and PTA in methanol.[67] Protonation of this salt by hydrogen exchange employing DOWEX 50 WX8-100 ion exchange resin yields a protonated complex $CpFe(CN)_2(PTAH)$.



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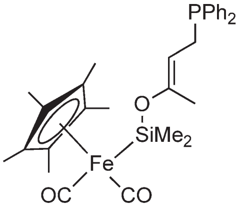

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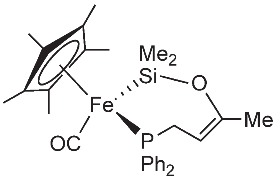

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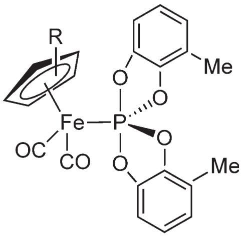
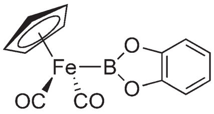
The catalytic substitution of a halide in the series of complexes, $CpFe(CO)_2X$ (X = Cl, Br, I), by a phosphine (PR_3) is shown to proceed through an electron chain catalysis mechanism.[68] The reaction is initiated by $CpFe(CO)_2(PR_3)^\cdot$, which is generated by photochemical or thermal cleavage of $\{CpFe(CO)_2\}_2$, or by addition of catalytic amounts of other strong reductants. Two iron complexes bearing a phosphorane fragment with two 3-methylcatecholate substituents, $Cp^1(CO)_2Fe\{P(OC_7H_6O)_2\}$ ($Cp^1 = \eta^5\text{-}C_5H_5$ 78 and $\eta^5\text{-}C_5Me_5$ 79), have been prepared.[69] These compounds were used to study the apical–equatorial rearrangement of ligands about the five-coordinate phosphorus center (Berry pseudorotation) using variable-temperature ^{31}P NMR.



78: R = H
79: R = Me

A new C_2-symmetric bidentate phosphorus ligand derived from (*R*,*R*)- or (*S*,*S*)-hydrobenzoin has been complexed to $CpFe(CO)_2Me$ to form a highly enantioselective Fe Lewis acid catalyst capable of catalyzing Diels–Alder reactions between α,β-enals and dienes.[70]

Transition metal boryl complexes have been the subject of considerable recent research effort. These compounds find application as synthetically useful reagents in organic transformations such as hydroboration and diboration of carbon–carbon multiple bonds.[71] More recently, the involvement of cyclopentadienyl transition metal boryl complexes in both stoichiometric and catalytic functionalization of alkanes and arenes has been demonstrated, notably by Hartwig *et al.*[72–78] Complexes $CpFe(CO)_2(Bcat)$ ($cat = O_2C_6H_4$) 80, and $CpFe(CO)_2(BPh_2)$, which have been characterized in the solid state,[72,75] were synthesized by addition of *B*-chlorocatecholborane or diphenylboron bromide to a benzene suspension of $Na[CpFe(CO)_2]$.[72] It was found that irradiation of 80 in the presence of arenes and alkenes leads to the selective, high yield formation of aryl- and vinylboranes.[73] An analog of 80 containing blocked *sp*^{2}-hybridized positions, $Cp^*Fe(CO)_2(Bcat^1)$ ($cat^1 = 1,2\text{-}O_2C_6H_2\text{-}3,5\text{-}(CH_3)_2$) 81, was found to catalyze the formation of alkylboronate esters from alkanes (Scheme 13).[74] It was found that the second- and third-row transition metal complexes catalyzed the alkane functionalization reaction with higher efficiency in the order (W > Ru > Fe).[74,76]



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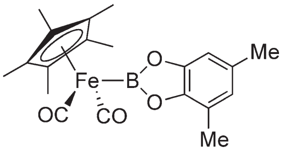


81

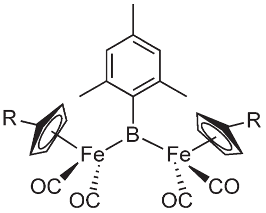
It has been suggested that the unusual regiochemistry and activity of the $Cp^*Fe(CO)_2(Bcat)$ catalysts may be due to the Lewis acid properties of the boryl ligand, which provides favorable kinetics for the formation of the boron–carbon bonds.[76] The functionalization of alkanes with terminal regiospecificity begins with photodissociation of one CO ligand to generate a coordinatively unsaturated 16-electron intermediate which readily cleaves and functionalizes the terminal alkane C–H bond.[75,78] A combination of experimental and theoretical evidence has shown that the formally unoccupied *p*-orbital of the dioxaboryl ligand is intimately involved in the C–H activation step, and that this step occurs in σ-bond metathesis.[78] Analysis of the bonding in transition metal boryl complexes of the type $(C_5R_5)M(CO)_2(Bcat)$, carried out using density functional methods, has shown that the relative contributions from σ- and π-symmetry covalent interactions emphasize the description of boryl ligands as good σ-donors and poor π-acceptors.[79]

Scheme 13

The iron Lewis acid complex, $[CpFe(CO)_2(THF)][BF_4]$, has been shown to catalyze the reaction of ethyl diazoacetate[80] and phenyldiazomethane[81] with olefins to form cyclopropanes. The selectivity of the reaction suggests the involvement of an intermediate iron carbene $[Cp(CO)_2Fe\{{=}CH(CO_2Et)\}]^+$.

Families of $CpFe(CO)_2$-substituted *closo*-carboranes have been synthesized and characterized.[82,83] The bimetallic complex, 1,12-Fp_2-1,12-$C_2B_{10}H_{10}$, exhibits through-cage communication between the iron centers as evidenced by UV–VIS measurements and cyclic voltammetry. X-ray structures have been determined for complexes 1-$\{CpFe(PPh_3)(CO)\}$-1,12-$C_2B_{10}H_{11}$, 1,12-$\{CpFe(CO)_2\}_2$-1,12-$C_2B_{10}H_{10}$, and 1,10-$\{CpFe(CO)_2\}_2$-1,10-$C_2B_8H_8$.

The synthesis, spectroscopic and structural characterization of bromo–boryl complexes have been reported, and they have been shown to be versatile substrates for the synthesis of both asymmetric boryl complexes and bridging borylene complexes, for example, $\{(\eta^5\text{-}C_5H_4R)Fe(CO)_2\}_2(\mu\text{-}BMe)$ where R = H **82** and R = Me **83**, via substitution chemistry with retention of the metal–boron bond.[84] Complexes **82** and **83** are the first reported examples of structurally characterized bridging borylene complexes without a supporting M–M bond.



82: R = H
83: R = Me

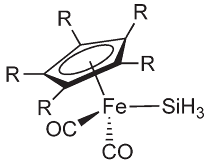
A novel 3-borane–1-alkylimidazol-2-ylidene complex has been obtained by reaction of a 3-borane-1,4,5-trimethylimidazole-2-ylidene anion with $CpFe(CO)_2Br$.[85] A newly developed route to terminal borylene complexes makes use of halide abstraction to generate the first example of a cationic $[L_nMBR]^+$ species.[86] The compound so generated, $[Cp^*Fe(CO)_2(BMes)]^+[BAr^f_4]$ ($Ar^f = C_6H_3(CF_3)_2$-3,5), contains the shortest M–B distance yet reported, a feature indicative of a novel Fe═B double bond.

A number of interesting Fp–silane complexes have appeared in the literature since 1993. Sharma and Pannell have reviewed the literature covering the activation of an Si–Si bond by Fe and other transition metal complexes.[87]

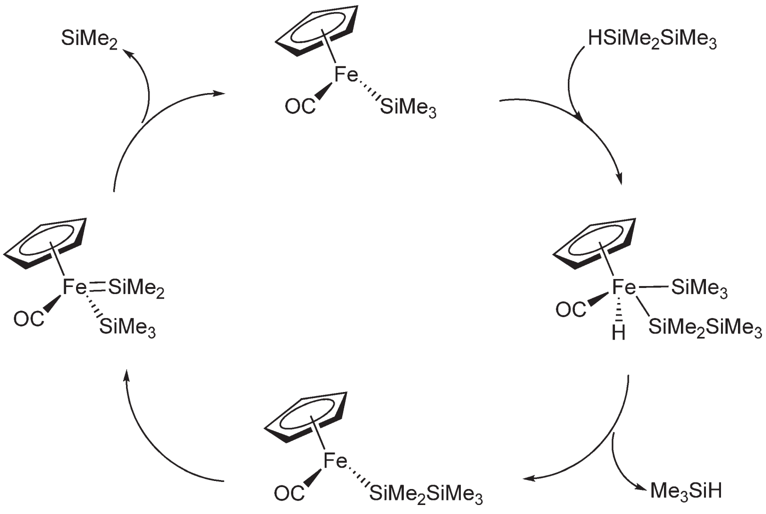
The transition metal–Si bond is photochemically labile and exhibits two primary types of chemical transformation, namely, silylene expulsion and/or isomerization. The photolysis of $FpSiMe_2SiMe_2H$ in methanol produces an interesting mix of products which implies the transient formation of a disileneiron $(\eta^5\text{-}C_5H_5)FeH(CO)$-$(SiMe_2{=}SiMe_2)$, and a methoxy-bridged bis(silylene)iron, $(\eta^5\text{-}C_5H_5)FeH(CO)$–$(SiMe_2\cdots OMe\cdots SiMe_2)$, complex.[88] Photochemical treatment of disilyl complexes $FpSiMe_2SiMe_2Ar$ and $FpSiMeArSiMe_3$ in inert hydrocarbon solvents leads to the expulsion of $SiMe_2$ and/or SiMeAr fragments to yield $FpSiMe_3$ and/or $FpSiMe_2Ar$.[89] Trisilyliron complexes of the type $FpSi_3Me_6R$ (R = Me, Ph) are all photochemically labile with respect to silylene elimination; however, prior to SiR_2 loss, isomerization occurs.[90] Photochemical treatment of a series of triphenyl(dimethyl)disilanyl isomers substituted with indenyliron dicarbonyl, $(\eta^5\text{-}C_9H_7)$-$Fe(CO)_2Si_2Me_2Ph_3$, results in the formation of monosilyl complexes $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_nPh_{3-n}$ ($n = 0$–2) via the elimination of silylene fragments.[91]

The silylene, Me_2Si, can be generated catalytically from a photochemically generated $[CpFe(CO)(SiMe_3)]$ species and pentamethyldisilane (Scheme 14).[92]

The ferrotrihydridosilanes $[(\eta^5\text{-}C_5R_5)(OC)_2Fe(SiH_3)]$ (R = H **84**, Me **85**) were prepared by reaction of the corresponding ferrodichlorosilane $[(\eta^5\text{-}C_5R_5)(OC)_2Fe(SiHCl_2)]$ with $LiAlH_4$ in Et_2O.[93] Photoinduced substitution of CO by L in **84** was achieved leading to the phosphane-substituted ferrotrihydridosilanes $[Cp(CO)(L)Fe(SiH_3)]$ ($L = Me_3P$ or Ph_3P).

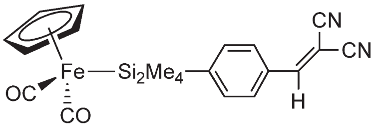


84: R = H
85: R = Me



Scheme 14

The Fe–disilanes $CpFe(CO)_2(Si_2Me_4Ar)$ ($Ar = C_6H_4X$; X = H, *p*-Cl, *m*-CF_3, *o*-Me, *p*-OMe, *p*-NMe_2) have been synthesized by standard methods and characterized.[94] Reaction of the ferriodisilanes (η^5-C_5R_5)$(OC)_2Fe(Si_2H_5)$ (R = H, Me) with dimethyldioxirane leads to selective insertion of oxygen into the α-Si–H bonds to yield the corresponding ferridihydroxydisilanes (η^5-C_5R_5)$(OC)_2Fe\{Si(OH)_2SiH_3\}$.[94] Treatment of pentachloroirondisilane $Cp(OC)_2Fe(Si_2Cl_5)$ with water results in the regiospecific hydroxylation of the β-silicon atom to generate a metallodisilanetriol $Cp(OC)_2Fe\{SiCl_2Si(OH)_3\}$. A study on the electron donor–acceptor interactions in the disubstituted disilane $CpFe(OC)_2\{Si_2Me_4C_6H_4CH{=}C(CN)_2\}$ **86** using UV absorption spectroscopy, cyclic voltammetry, and X-ray crystallography has been presented.[95]



86

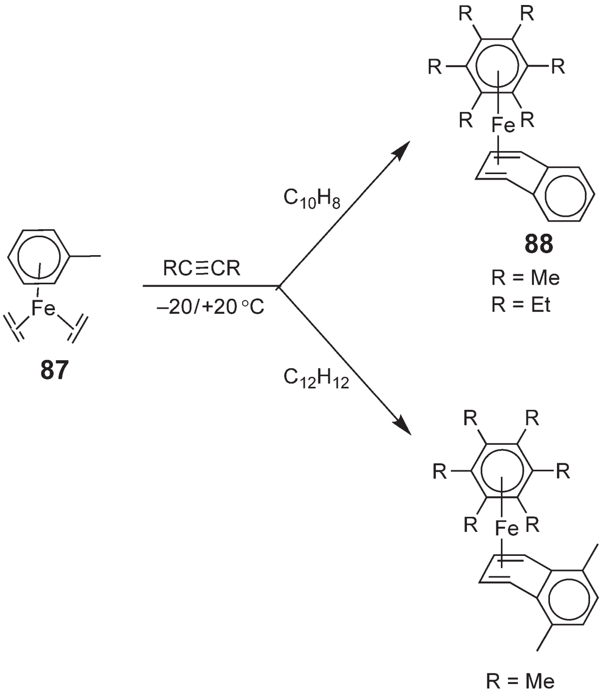
6.04.3 Arene FeL$_2$ Complexes

The interaction of aromatic hydrocarbons with iron cations has been studied in the gas phase.[96] The results of these studies provide information useful in the proposal that polycyclic aromatic hydrocarbons undergo efficient reactions with iron and other transition metals in the interstellar medium. $Fe(\eta$-$C_2H_4)_2(\eta$-PhMe) **87** is a useful precursor for a range of arene iron complexes. Thus, reaction of **87** with the desired naphthalene derivative and three molecules of butyne or hexyne leads to the (hexaalkylbenzene)naphthalene iron complexes, as shown in Scheme 15.[97]

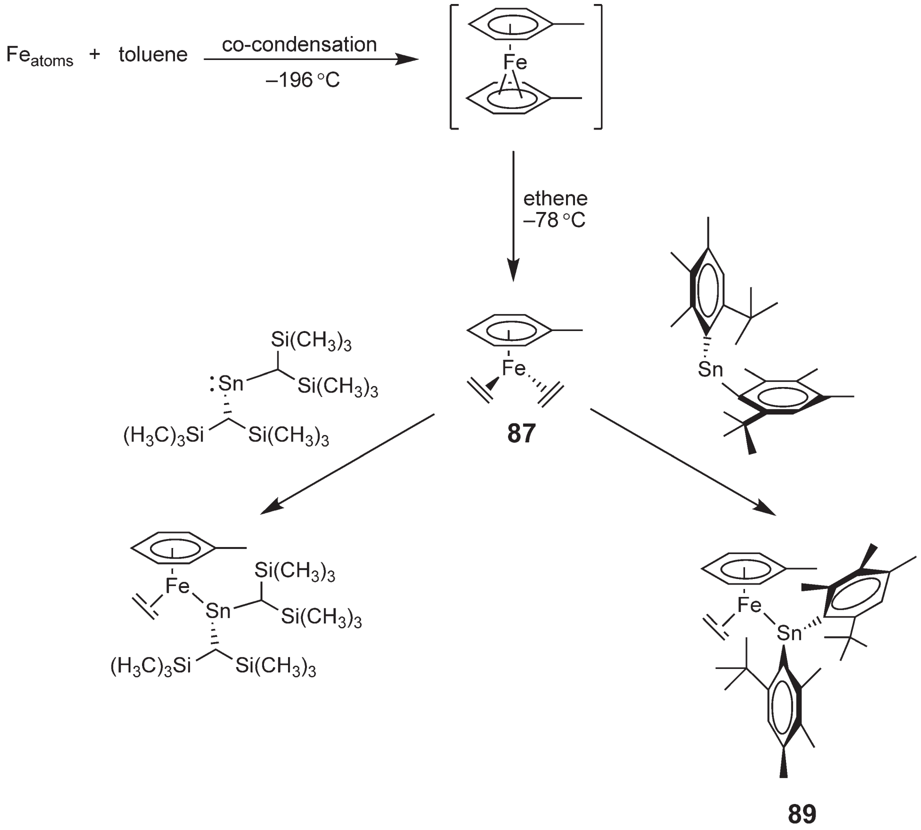
The crystal structure of compound **88** (R = Me) has been determined. It confirms the formulation and shows that the naphthalene group is bonded to Fe via only four carbon atoms (Fe–C = 1.998–2.088 Å).

Co-condensation of iron atoms and toluene at −196 °C, then warming up to −30 °C in an atmosphere of ethylene, leads to **87**. The resulting solution of **87** has been reacted *in situ* with SnR_2 to yield novel stannanediyl compounds (Scheme 16). The crystal structure of compound **89** confirms the formulation, with an Fe–Sn bond of 2.4362(10) Å being one of the shortest Fe–Sn bonds reported.[98]

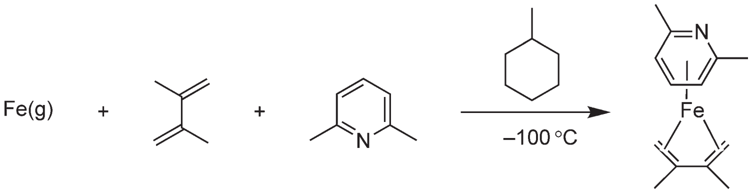
Other (arene)FeL_2 complexes have also been prepared directly from iron atoms. This method has led to a number of novel derivatives. Thus, the (η^6-2,6-dimethylpyridine)iron complex **90** has been prepared albeit in low yield (Scheme 17). In contrast, the (arene)iron diazadiene complex **91**, which has been characterized by X-ray crystallography, has been isolated in 48% yield from **87** (Scheme 18).



Scheme 15

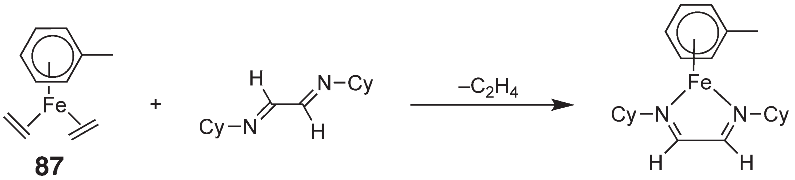


Scheme 16



90

Scheme 17



87

91

Scheme 18

Compound **91** and related compounds have been evaluated for catalytic activity in the cyclodimerization of 1,3-butadiene in the presence of $\{AlEt_2(OEt)\}_2$ as co-catalyst.[99] These results show that yields of 1,5-cyclooctadiene (COD) of up to 92% can be obtained and that almost quantitative conversion of butadiene can be achieved with less than 0.1% catalyst.[99]

Other routes have also yielded FeL_2(arene) complexes. Thus, the reaction of hydrogen with the bis-benzyl complex **92** has yielded compound **93** (Scheme 19) which is believed to form from the hydride intermediate **I**. The *p*-xylene derivative **93** was isolated as red-orange prisms in 50% yield.[100]

The reactions of **87** with compounds containing the RC≡P bond have also been investigated and lead to novel neutral bis(arene)-type complexes (Scheme 20). The compound **94a** was obtained in 55% yield and its formulation confirmed by X-ray crystallography.[101]

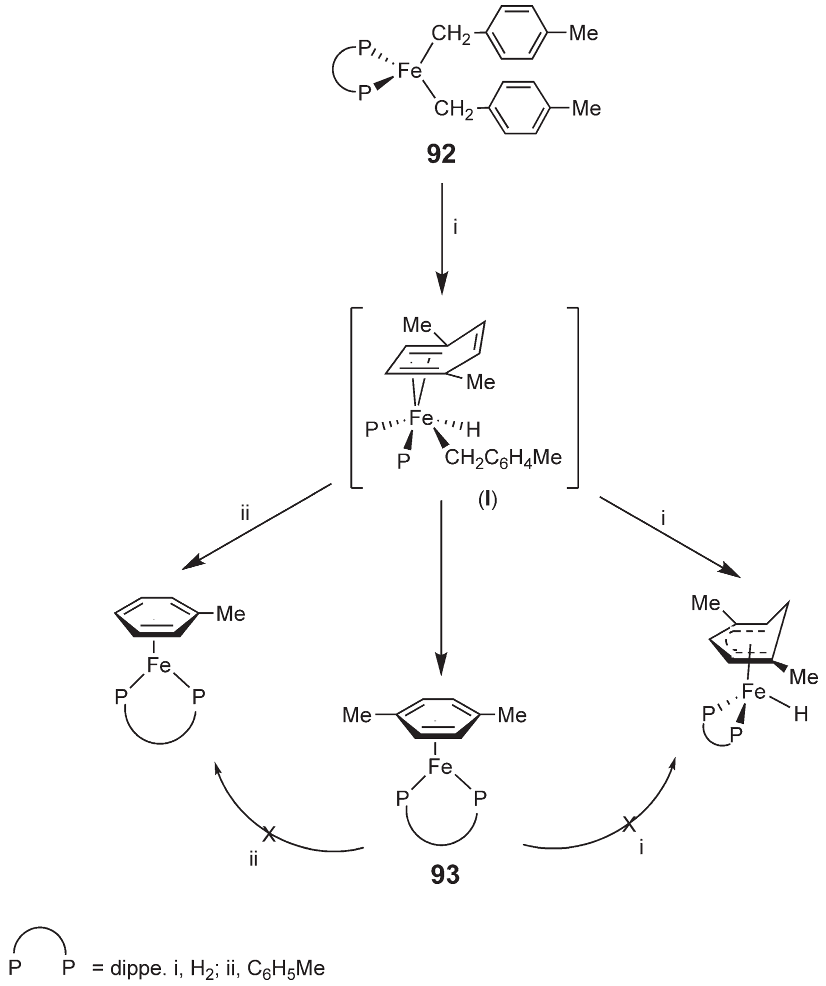
The η^6-cyclohepta-1,3,5-triene complex Fe(η^6-CHT)(η^4-COD) has been evaluated as a catalyst precursor in several reactions, including hydroformylation of 1-hexene and cyclotrimerization of acetylenes. It is found to be more active than other iron catalysts.[102]

6.04.4 Fe(Arene)(Cyclopentadienyl) Cations and Related Compounds

There have been many studies on this important class of arene iron compound, in part, because they can be used in organic synthesis, polymer synthesis, and for the preparation of a range of new organoiron derivatives that are both mononuclear and polynuclear. Kündig has written a review on the synthesis of transition metal η^6-arene complexes, which includes a section on $[Fe(arene)Cp]^+$ cations.[103]

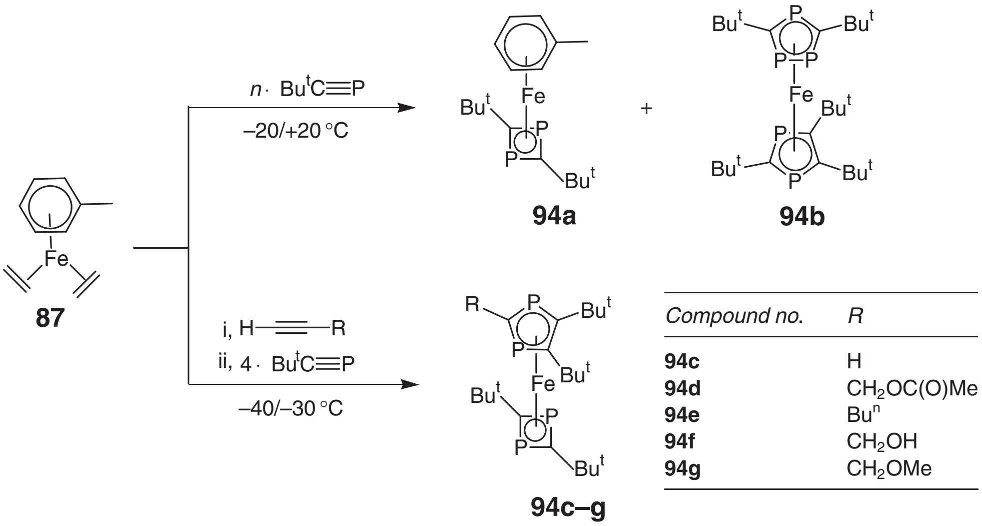
Abd-El-Aziz and Bernardin have written an extensive review (314 references) describing the synthesis and reactivity of mono- and polyiron arene complexes.[103a] Examples of some polyiron complexes where polyaromatic ethers and thioethers are coordinated to pendant CpFe cationic moieties have been reported by Abd-El-Aziz and de Denus.[103b]

Fernando and Roberts have reported the synthesis of a series of derivatives of the type $[Fe(arene)Cp][PF_6]$ where a range of indole-related substituents are bonded to the arene moiety via nitrogen.[104] For example, the reaction of compound **95** with potassium indolate gives the new arene derivative **96** in 47% yield (Scheme 21). Using this procedure, a range of new arene derivatives **97–104** (Table 4) has been prepared and fully characterized by analytical and spectroscopic methods.



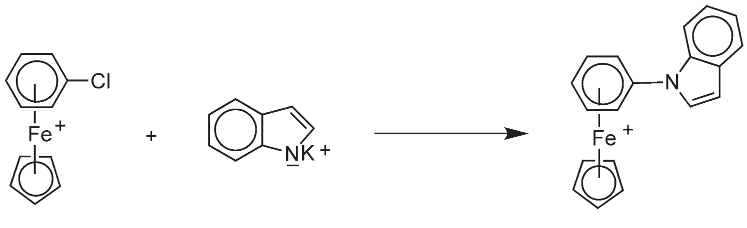
P P = dippe. i, H_2; ii, C_6H_5Me

Scheme 19



Compound no.	*R*
94c	H
94d	$CH_2OC(O)Me$
94e	Bu^n
94f	CH_2OH
94g	CH_2OMe

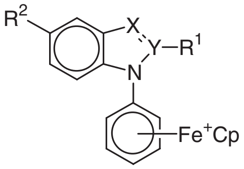
Scheme 20



95 **96**

Scheme 21

Table 4 New Fp arene derivatives prepared using the method illustrated in Scheme 21



Compound no.	*X*	*Y*	*R^1*	*R^2*
97	CH	C	C_6H_5	H
98	CH	N	–	H
99	N	C	H	H
100	N	C	2-Pyridyl	H
101	N	N	–	H
102	N	N	–	CH_3
103	N	N	–	Cl
104	NH	C	=O	–

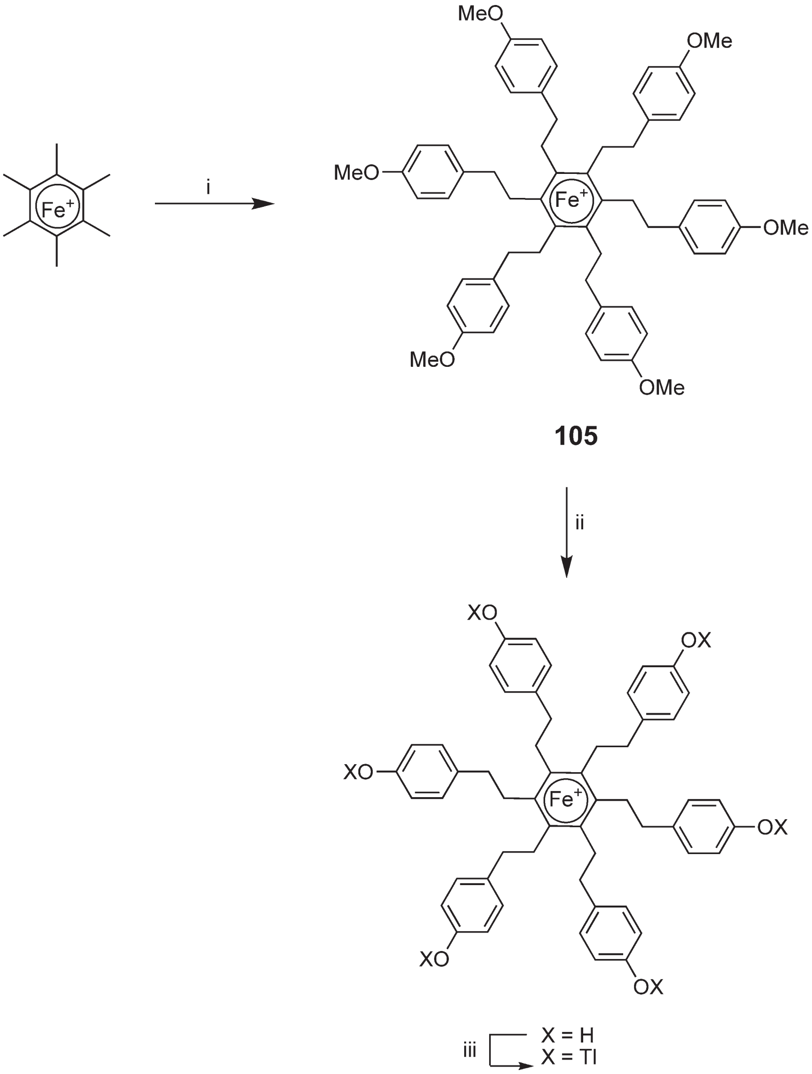
In a similar way, a range of cationic (arene)Fe complexes with amino acid side chains of the type [Fe{η^6-PhNHCH(R^1)CO_2R}Cp][PF_6] have been prepared. Decomplexation can be accomplished with light in the presence of 1,10-phenanthroline. This provides a useful method for the *N*-arylation of amino acids.[103,105]

The π-complexation of an arene to iron facilitates nucleophilic reactions. Astruc and co-workers have made use of this to prepare a spectacular array of new organometallic and organic compounds. For example,[106,107] the reaction of [Fe(C_6Me_6)Cp][PF_6] with Bu^tOK and $BrCH_2C_6H_4OMe$*p* in DME yields the dendrimer compound **105** (Scheme 22).

Perallylation of arenes containing benzylic hydrogens can also be accomplished (see, e.g., Schemes 23–25). Ring-closing metathesis (RCM) on the allyl tails can be achieved with Grubbs catalyst and decomplexation accomplished to give free arenes. Polyiron derivatives can also be obtained from these reactions. The synthesis of a number of $[Fe(arene)Cp]^+$ cations has also been accomplished from ferrocene using the ambient-temperature[108] ionic liquid system [1-butyl–3-methylimidazolium]Cl/$AlCl_3$. The ionic liquid acts as both solvent and a Lewis acid. The X-ray structure of [Fe(η^6-PhC_6H_4Br)Cp][PF_6], prepared in this way, has been determined and shows π–π stacking interactions between neighboring cations.

NMR spectroscopy, in particular, has been very useful in providing information about the structure of Fe(arene)(Cp) cations, and an overview of some of this work has been published.[109]

The synthesis of 12 new complexes of type **106** has been reported (Scheme 26), and the X-ray structure of compound **106g** has been determined and confirms this formulation. Cyclic voltammetry studies for compounds **106a–c** show an irreversible one-electron reduction step, and the redox potential indicates that the reduction occurs at the cationic electron-acceptor mixed-sandwich unit.[110]



i, Bu^{t}OK, $BrCH_2C_6H_4OMe$-*p*, DME, 40 °C, 24 h; ii, (a) BBr_3, CH_2Cl_2, –78 °C to room temperature, 20 h; (b) H_2O, 0 °C; iii, TlOEt, 7 equiv.

Scheme 22

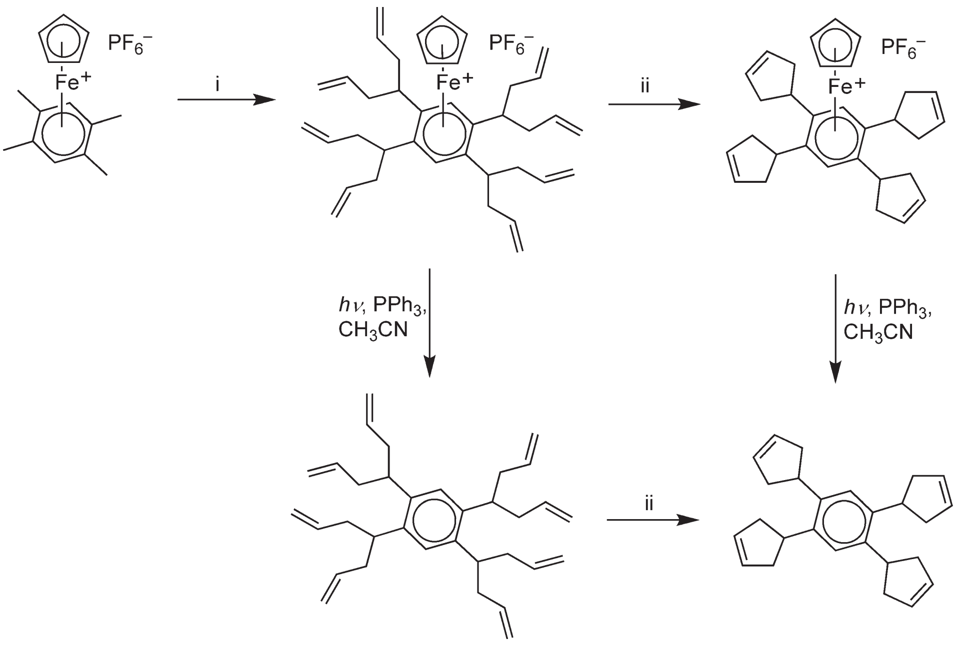
Arene exchange is another useful and efficient method which has been used to prepare a series of complex cations of the type $[Fe(arene)Cp]^+$.[111] A related method using the readily available ferrocene starting material has also been described (Scheme 27).[112]

The X-ray crystal structures of the two isomeric naphthalene cations **107** and **108** as PF_6^- salts have been determined, and represent the first reported X-ray structures of $[Fe(naphthalene)Cp]^+$ cations.

Reactions of some $[Fe(arene)Cp]^+$ cations **109** with $LiC(N_2)CO_2Et$ produce neutral adducts, for example, **110**, which on reaction with a catalytic amount of $Rh_2(OAc)_4$ in CH_2Cl_2 yields a metallocarbene that further reacts by 1,2-hydrogen migration to give **111** (Scheme 28).[113]

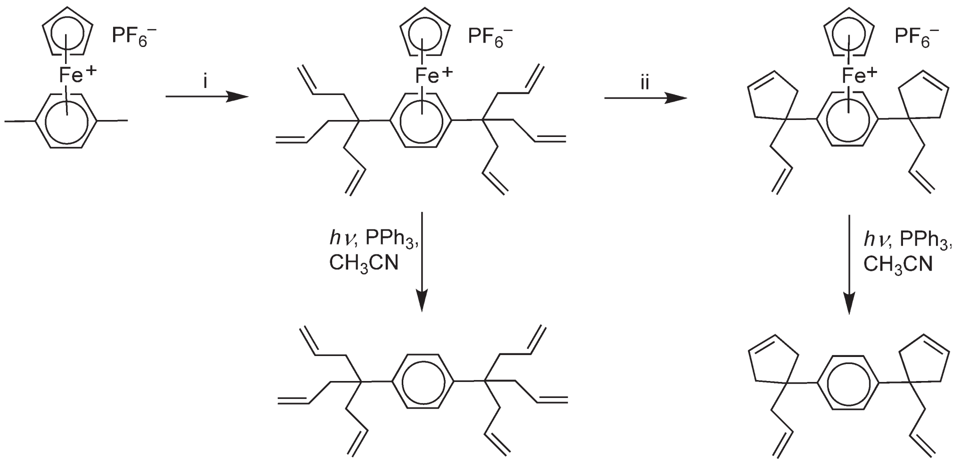
The reactions of $[Fe(arene)Cp]^+$ with CN^- can be monitored by voltammetry. With electron-withdrawing groups such as NO_2, COR, SO_2R, and N_2R bonded to the arene, a rapid reaction occurs to give the hexadienyl species, for example, **112**, in good yields.[114] Nucleophilic addition of hydride and cyanide to a series of other $[Fe(arene)Cp]^+$ cations has also been reported.[115]

$[Fe(arene)Cp]^+$ cations are important in metal-mediated organic synthesis, but the success of this approach depends on the efficient removal of the modified arene from the complex. Brown and co-workers[116] have made a study of the relative merits of a range of decomplexation reagents in the demetallation of $[Fe(arene)Cp]PF_6$ compounds. K^tBuO in pyridine or DMSO was found to be an excellent demetallating agent, even with sterically crowded complexes.



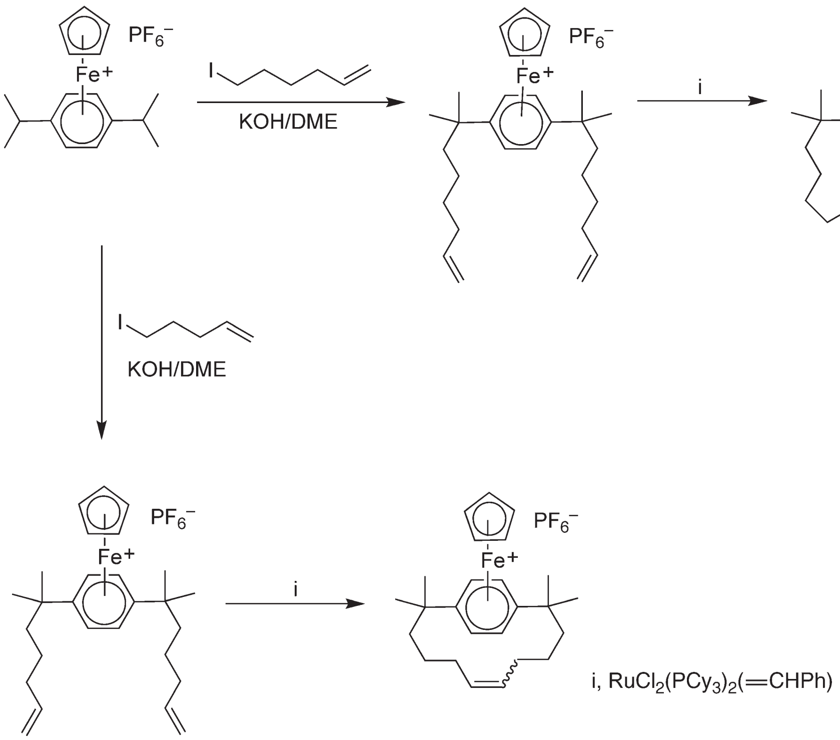
i, allyl bromide, KOH, THF; ii, $[Ru(PCy_3)_2Cl_2(=CHPh)]$

Scheme 23

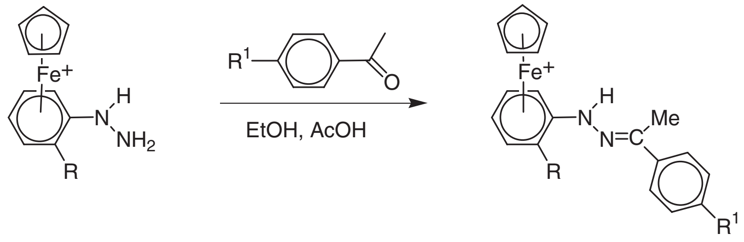


i, allyl bromide, KOH, THF; ii, $[Ru(PCy_3)_2Cl_2(=CHPh)]$

Scheme 24



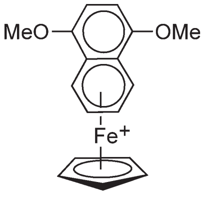
Scheme 25



106

Compound no.	*R*	*R*¹
106a	H	Me
106b	H	OMe
106c	H	NMe_2
106d	Me	Me
106e	Me	OMe
106f	Me	NMe_2
106g	OMe	Me
106h	OMe	OMe
106i	OMe	NMe_2
106j	Cl	Me
106k	Cl	OMe
106l	Cl	NMe_2

Scheme 26



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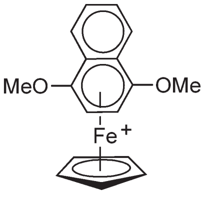

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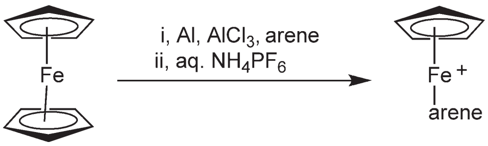
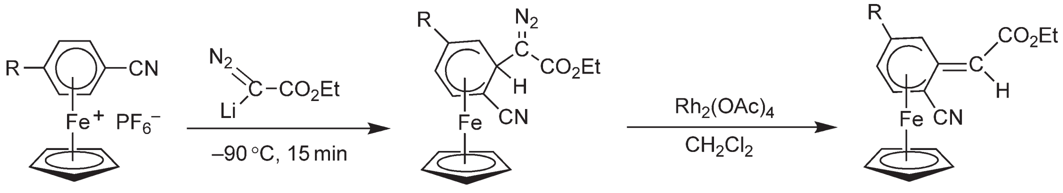


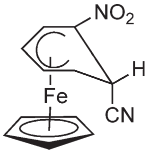
Scheme 27



109 **110** **111**

R = H, Me

Scheme 28

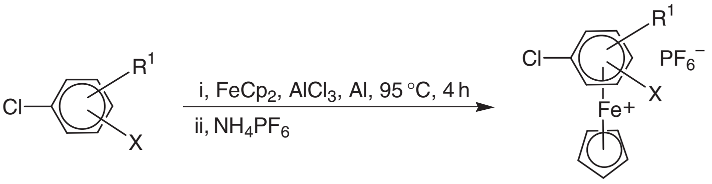


112

The photochemical displacement of arenes from $[Fe(arene)Cp]^+$ complexes in CH_2Cl_2 solutions has been compared with arene displacement from the Ru and Os analogs. It is found that the reactivity of the complexes decreases in the order Fe > Ru > Os for simple methyl-substituted arenes.[117]

A laser flash photolysis study has been carried out by Burget and Foussier to investigate the interaction of Rose Bengal with $[Fe(\eta^6\text{-}C_6H_5CMe_2)Cp]PF_6$. This interaction leads to a semi-oxidized Rose Bengal and a 19-electron iron arene complex $[Fe^I(arene)Cp]$.[118] Photolysis of [Fe(arene)Cp][X] complexes is important since this can lead to photoinitiators with applications in polymerization reactions. Thus, $[Fe(arene)Cp]^+$ (where arene = toluene, naphthalene, and $X = PF_6^-$ or SbF_6^-) are shown to be effective cationic photoinitiators for the polymerization of dicyanate esters.[119] The [Fe(arene)Cp][X] complexes (where arene = $C_6H_5CMe_2$, C_6H_5OMe or $p\text{-}C_6H_4(OMe)_2$ and $X = PF_6^-$ or SbF_6^-) have also been used for photopolymerization of cyclohexene oxide.[120] The decomposition of $[Fe(cumene)Cp]PF_6$ **113** has been investigated by singlet and triplet sensitization.[121] It was found that **113** quenched the excited state of various sensitizers, and decomposition of **113** took place efficiently in CH_2Cl_2.

A recent and important new development in the application of $[Fe(arene)Cp]^+$ chemistry is that iron-assisted S_NAr reactions have, for the first time, been performed in the solid phase. A library of 36 unsymetrically substituted phenylpiperazines and phenyl-1,4-diazepanes was synthesized using this novel strategy. Scheme 29 shows some of the iron complexes **114a–d** that were prepared. Decomplexation of resin-bound iron complexes was achieved with 1,10-phenanthroline under irradiation.[121]



Compound no.	*R*^{1}	*X*	*Yield* (%)
114a	H	2-Cl	38
114b	H	3-Cl	20
114c	H	4-Cl	28
114d	2-Me	3-Cl	33

Scheme 29

The mechanism of the photochemical decomposition of $[Fe(C_6H_6)Cp]^+$ in solution has been studied using electrospray ionization mass spectrometry with millisecond time resolution.[122,123] In acetonitrile solution, photolysis of $[Fe(C_6H_6)Cp]^+$ yields the short-lived half-sandwich compound $[FeCp(CH_3CN)_3]^+$. If the irradiation is carried out in the presence of cyclohexene oxide, $[Fe(arene)Cp]^+$ generates photoproducts that are capable of initiating the cationic polymerization of the epoxide monomer.

6.04.5 Bis(Arene)iron Dications and Related Compounds

Very few compounds in this class have been described in recent years. Timms and co-workers have used metal atoms to prepare a series of metal arene complexes. These have included the co-condensation of iron vapor with toluene and iodine at −95 °C to yield the bis(arene) complex $[Fe(C_6H_5CH_3)_2][I_3]_2$. This was converted into the PF_6^- salt and identified spectroscopically.[124]

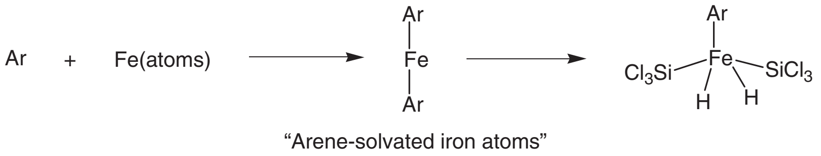
Klabunde and co-workers have reported that co-condensation of iron atoms with an excess of arene at −196 °C forms "arene-solvated iron atoms," which react with $HSiCl_3$ to produce a series of arene Fe(IV) compounds (Scheme 30),[125] as crystallographically confirmed for **115a**.

6.04.6 Complexes with η^1- and C_5 Ligands

There has been much recent interest in compounds of the type Fe–R (mononuclear) and Fe–R–Fe (binuclear) where R = acyl (Fe–COR), alkyl (Fe–R), alkenyl (Fe–CH═CR), alkynyl (Fe–C≡CR), diynyl (Fe–C≡C–C≡CR), allenyl (Fe–CH═C═CR), cumulenylidenyl (Fe–CH═C═C═CR), carbenyl (Fe═CR), or allenylidenyl (Fe═C═C═CR). Review articles that cover much of this material have appeared in the literature over the last few years.[126,127] In this chapter, mononuclear compounds of this type are summarized in Section 6.04.6.1. and binuclear compounds are summarized in Section 6.04.6.2.

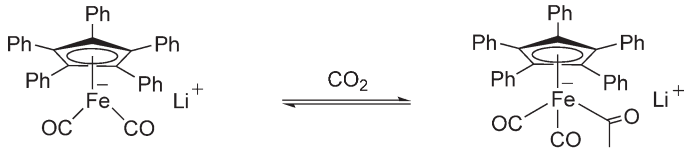
6.04.6.1 Mononuclear Fp Complexes Bearing η^1- and C_5 Ligands

Various new Fp–acyl complexes have been described. Fp anions are useful synthons for a wide range of products. Ion-pairing thermodynamics has been studied for a series of anions $[Cp^xFe(CO)_2]^-$ (where $Cp^x = C_5H_4Me$, C_5Me_5, C_5Ph_5, and C_9H_7).[51] The X-ray crystal structure of $[(C_5Ph_5)Fe(CO)_2][PPN]$ has been determined and shows the five phenyl groups arranged in a paddle wheel fashion about the C_5 ring. Bond lengths are in keeping with those found in related structures.[51] The compound $[(C_5Ph_5)Fe(CO)_2]Li$ **116** reacts reversibly with CO_2 via nucleophilic attack to give a metallocarboxylate anion, as shown in Scheme 31.[51]



Compound no.	*Ar*
115a	C_6H_6
115b	C_6H_5Me
115c	*p*-xylene

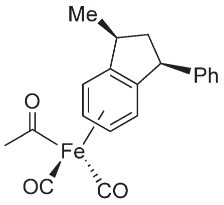
Scheme 30



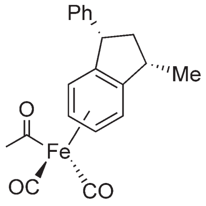
116

Scheme 31

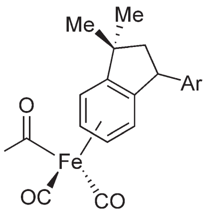
The new half-sandwich acetyl compounds with tetrahydropentalenyl ligands (**117a** and **117b**, **118a** and **118b**) have been prepared by the reaction of the iron nucleophiles with acetyl chloride.[93] Iron carboxyalkyls of type **119** are obtained by adding 1 equiv. of NaOMe to an equimolar mixture of FpI and PPh_3 after addition of a few drops of *n*-BuLi. This takes advantage of the catalytic formation of $[Fp(PPh_3)]I$ which then reacts with the methoxide anion.[128]



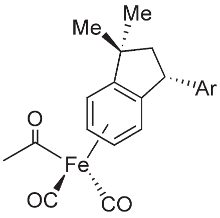
117a



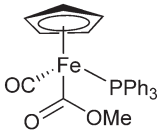
117b



118a



118b

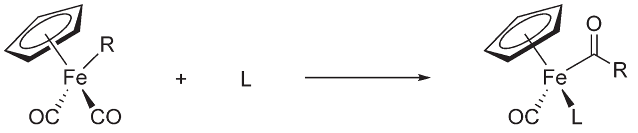


119

A wide range of Fp–alkyl compounds has been prepared and studied over many years (see COMC (1982) and COMC2 (1995)). The reaction of $FpCH_3$ with a chiral fluorophenyl diphosphine ligand under photolytic conditions in toluene leads to the substitution of both CO groups by the diphosphine ligand. Methyl abstraction in the presence of a ligand L results in the chiral cation $[CpFe(diphos)L]^+$ (where L = CO, CH_3CN, $CH_2{=}CHCHO$). These cations have been shown to be active catalysts for asymmetric Diels–Alder reactions.[129]

The alkyl migration reaction shown in Scheme 32 has been used as a model reaction for the key step in many important catalytic reactions. A kinetic study of the reaction shown in Scheme 32, where $R = CH_3$ and $L = P(4\text{-}FC_6H_4)_3$ or $P(4\text{-}MeC_6H_4)_3$, has been reported as well as the crystal structures of **121a** and **121b**.[130] This study shows that $P(4\text{-}MeC_6H_4)_3$ reacts faster than $P(4\text{-}FC_6H_4)_3$. There is also an increase in the reactivity of the migratory carbonyl insertion for the ligand $P(4\text{-}MeC_6H_4)_3$ when the solvent is changed from CH_2Cl_2 to MeCN.

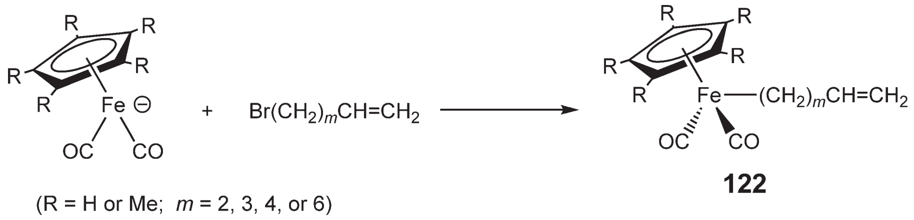
The hydroxyalkyl compounds of the type **120** (where $R = CH_2(CH_2)_nCH_2OH$ and $n = 2,3,4$, or 6) have been prepared as well as the Cp* analogs by the oxidative hydroboration of the η^1-alkenyl compounds $Cp^xFe(CO)_2\{(CH_2)_nCH{=}CH_2\}$ (where $Cp^x = Cp$ or Cp^* and $n = 2,3,4$, or 6). These new ω-hydroxy-alkyl compounds were isolated as low-melting yellow solids or yellow-brown oils and characterized by IR, NMR, and mass spectrometry.[131]



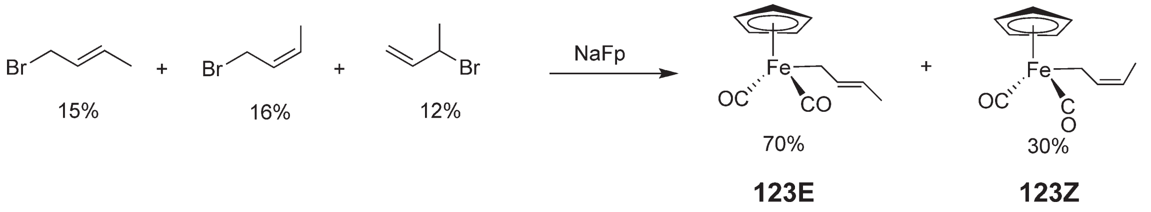
120

121a: R = Me; L = $P(4\text{-}FC_6H_4)_3$
121b: R = Me; L = $P(4\text{-}MeC_6H_4)_3$

Scheme 32



Scheme 33



Scheme 34

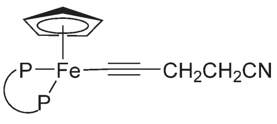
The photoreaction of the iron silyl compound $Fp(SiMe_3)$ with $P(NMeCH_2)_2OMe$ (L) in CH_3CN yields the iron alkyl product (CO)FeCpL(Me) as well as $CpFeL_2(Me)$ and $CpFeL_2(CN)$. The presence of a silyl group allows for C–C bond cleavage of CH_3CN to occur.[132] The Fp–alkyl cation $[Fp(CH_2SPh_2)]BF_4$ has been shown to react with cyclooctene in CH_2Cl_2 to yield bicyclo[6.1.0]nonane. The kinetics of this reaction have been studied and suggest that $[Fp(CH_2SPh_2)]^+$ undergoes a reversible, dissociative loss of Ph_2S followed by competitive capture of the methylene iron complex by cyclooctene.[133]

The new Fp–alkenyl complexes $Cp^xFe(CO)_2\{(CH_2)_mCH{=}CH_2\}$ ($x = H$, CH_3; $m = 2$ and 3) **122** have been prepared by the reactions of the iron nucleophiles $[Cp^xFe(CO)_2]^-$ with the appropriate n-bromo-1-alkene (Scheme 33).[134,135] These compounds were fully characterized by IR, ^1H and ^{13}C NMR, and mass spectrometry. They are among the few examples of ω-alkenyl compounds known and characterized at this time.

Various reactions have been carried out on the compounds $Fp(CH_2)_mCH{=}CH_2$ ($m = 2$ or 3) including hydrogenation, hydroboration, and hydroformylation. Some of these reactions lead to functionalized Fp–alkyl compounds.[134]

Commercially available crotyl bromide was used to prepare the (E)-, (Z)-mixture shown in Scheme 34, that is, **123*E* and 123*Z***. The diastereoselectivity of the [3 + 2]-cycloaddition of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron with **123*E* and 123*Z*** has been studied. This reaction is both regio- and stereoselective.[136]

The reaction of $HC{\equiv}CCH_2CH_2CN$ with $FeCl(CO)_2Cp$ yielded the Fp–alkynyl complex, $Fe(C{\equiv}CCH_2CH_2CN)(CO)_2Cp$. Further reaction with dppe under UV irradiation resulted in substitution of the CO ligands affording the complex $Fe(C{\equiv}CCH_2CH_2CN)(dppe)Cp$ **124**.[137]

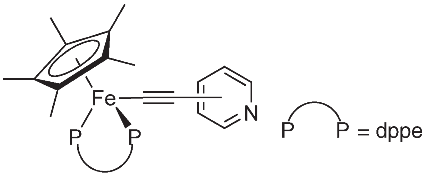


124

Protonation of **124** using either HBF_4 or $NH_4[PF_6]$ gives the cationic vinylidene complexes, $[Fe({=}C{=}CHCH_2CH_2CN)(dppe)(Cp)]X$ ($X = BF_4$ or PF_6). The dimeric complex, $[(Cp)(dppe)[Cp(dppe)Fe(C{\equiv}CCH_2CH_2CN)Fe(dppe)Cp][PF_6]$, formed by the reaction of **124** with $[Fe(NCMe)(dppe)(Cp)][PF_6]$ was unstable compared to its mononuclear analog.

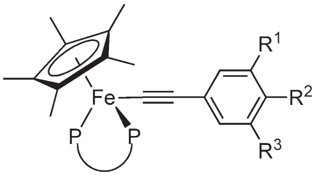
Iron alkynyl complexes containing aromatic moieties are of particular interest as building blocks for molecular devices. Second-order non-linear optical properties have been investigated for various Fe(II) and Fe(III) complexes of the type $[(dppe)Cp^*Fe(C{\equiv}C–Ar)]^{n+}$ where Ar = pyridine, $C_5H_4N(CH_3)^+$, or p-C_6H_4X ($X = NO_2$, CN, CF_3, H, OMe, and NH_2).[138] These compounds have shown significant quadratic redox-switchable polarizabilities. Further examples of redox-active iron alkynyl synthons containing aromatic units have been reported, where the iron alkynyl unit is bonded to various substituted bromo-aromatics.[139] A crystal structure of the fluoro analog has been published. The bonding of metal–alkynyl complexes has also been described.[140]

The synthesis and characterization of three iron–alkynyl complexes [(dppe)Cp*Fe(C$\equiv$C–L)] (L = 4-Py **125a**, 3-Py **125b**, 2-Py **125c**) have been reported.[141] Coordination of the pyridyl group on these complexes to another metal center such as W, Pd, or Pt results in modifications of the electronic properties of the ligands which is indicative of good communication within the ligand. A series of papers have described the synthesis and characterization of organometallic molecules containing one **126**, two **127 and 128**, and three **129** electron-rich Cp*(dppe)Fe units linked to a connecting arene group through an ethynyl spacer.[142–145] All these compounds can be prepared and isolated with multiple oxidation states, since each metal center can be oxidized stepwise.[144,145] The first-order hyperpolarizabilities of these compounds have been determined using hyper-Rayleigh scattering at 1.06 μm.[146] It was found that the molecular non-linear optical (NLO) responses for these complexes can be controlled by a one-electron redox processes for the mixed-valence iron(II)/iron(III) complexes.

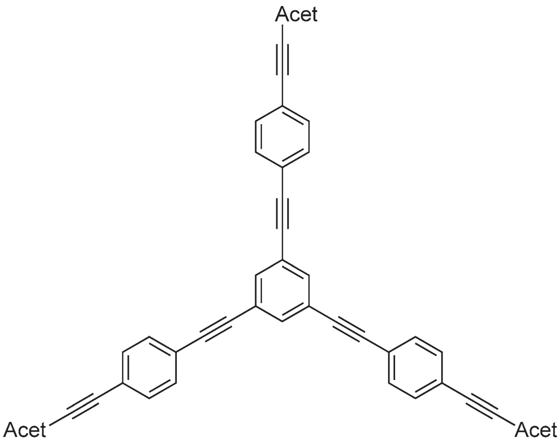


125a: 4-Py
125b: 3-Py
125c: 2-Py

The syntheses of 1,3,5-{(dppe)Cp*FeC$\equiv$C-4-C_6H_4C$\equiv$C}$_3$$C_6H_3$ **130** and (dppe)Cp*Fe(C$\equiv$C-1,4-C_6H_4C$\equiv$CPh) **131** are reported along with an X-ray diffraction study of **131**.[147] The linear optical spectra of these compounds reveal characteristic low-energy transitions at 430 and 436 nm, respectively, and are significantly red-shifted in comparison to those recorded for **126 and 129**. Cubic non-linear optical response data are also recorded for **130, 131**, and **126**.



	R^1	R^2	R^3
126	H	H	H
127	Acet	H	H
128	H	Acet	H
129	Acet	H	Acet



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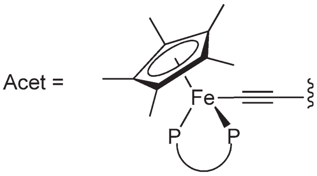
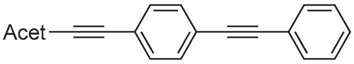
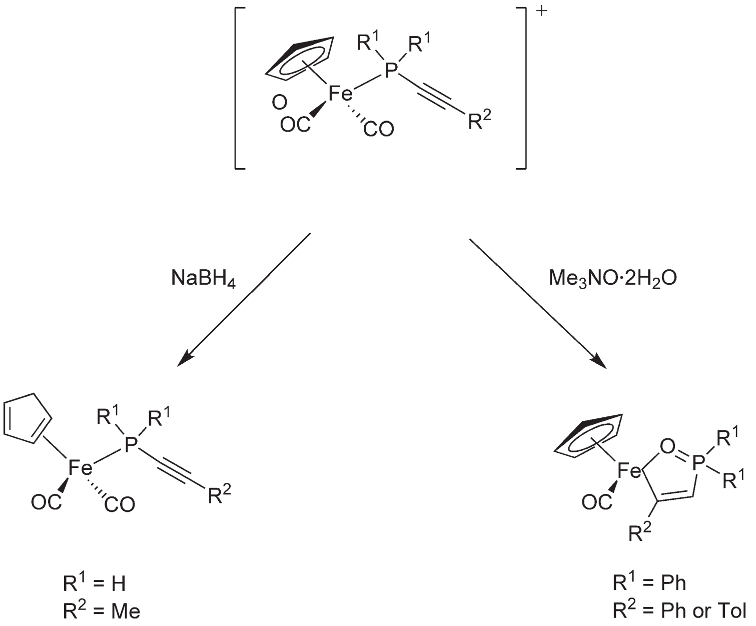




131

Examples of phosphorus-coordinated Fp–alkynyls have been reported.[148,149] These complexes may be easily obtained by the reaction of an uncoordinated *P*-alkene with {CpFe(CO)$_2$}$_2$ to yield the corresponding cationic



Scheme 35

complex. The complex reacts with sodium borohydride to yield a neutral iron complex, or with $Me_3NO{\cdot}H_2O$ to give a coordinated $\eta^2(O,C)$-vinyldiphenylphosphine oxide (Scheme 35).

A novel diynyl Fe compound, $Fe(C{\equiv}CC{\equiv}CSiMe_3)(dppe)Cp^*$, has been reported[150,151] and characterized by X-ray diffraction. Three signature IR bands are present in this compound that lie between $\nu = 2181$ and $1990 cm^{-1}$, arising from the presence of the $C{\equiv}C$ bond.[152]

The chemistry of transition metal complexes containing alkylidene, allenylidene, and cumulenylidene ligands, $[L_mM]{=}C({=}C)_n{=}CRR^1$ ($n \geq 2$), has been reviewed.[153–155] An extensive series of Cp^*(dppe)Fe compounds with an end-bound hydrocarbon ligand have been synthesized, and the iron–carbon bonding studied using ^{57}Fe Mössbauer spectroscopy.[156]

Fp–vinylidene complexes represent an important class of compounds which have been the subject of several recent review articles.[157–160] A major driving force behind the interest in this class of compounds is application of certain types of terminal vinylidene complexes in olefin metathesis reactions. Lapinte *et al.* reported on the synthesis of a series of vinylidene and allenylidene iron complexes.[161] The allenylidene complex $[Cp^*(dppe)Fe({=}C{=}C{=}CPh_2)][PF_6]$ can be obtained by the reaction of Cp^*(dppe)FeCl with 1,1-diphenylprop-2-yn-l-ol at 20 °C in the presence of KPF_6. The hydroxyvinylidene $[Cp^*(dppe)Fe\{{=}C{=}CHC(OH)Ph_2\}][BPh_4]$ was isolated as a byproduct when KPF_6 was replaced with $NaBPh_4$. The synthesis of the iron allenylidene complex $[Cp^*(dppe)Fe\{{=}C{=}C{=}C(OCH_3)CH_3\}][BPh_4]$ has been achieved in one step from the reaction of Cp^*(dppe)FeCl with 1 equiv. of $Me_3SiC{\equiv}CC{\equiv}CH$.[156] The acyl(oxy) carbene complex $[Fe(SnPh_3)(CO)\{{=}C(OCOR)Ph\}(\eta\text{-}C_5H_5)$ is formed through the low-temperature reaction of acid chlorides RCOCl with $[Fe(SnPh_3)(CO)(COPh)(\eta\text{-}C_5H_5)]^-$.[162] This reaction, if carried out at ambient temperature, yields neutral vinylidenes of the type $Fe(SnPh_3)(CO)({=}C{=}CHR)(\eta\text{-}C_5H_5)$ (R = H, Pr, Me, Ph). The crystal structure of $Fe(SnPh_3)(CO)({=}C{=}CHR)$-$(\eta\text{-}C_5H_5)$ has been reported.[163] Redox-induced reactions of transition metal vinylidene complexes have been summarized in a recent review by Valyaev *et al.*[159]

Isomerizations of acyclic $Cp(CO)_2Fe$ disubstituted η^1-vinylidene complexes to η^2-acetylene complexes have also been reported.[164] Here, $[Cp(CO)_2Fe({=}C{=}CR^1R^2)][TfO]$ (R^1, $R^2 = Me$; $R^1 = Ph$, $R^2 = Me$; R^1, $R^2 = Ph$) isomerizes to non-terminal η^2-acetylene complexes, $[Cp(CO)_2Fe(\eta^2\text{-}R^1C{\equiv}CR^2)][TfO]$, in CD_2Cl_2 above −50 °C. These isomerizations are intramolecular and apparently reversible.

The alkoxycarbene complex, $[FeCp^*(CO)_2\{{=}C(OMe)Me\}][CF_3SO_3]$, undergoes substitution of one or two carbonyl ligands to produce various mono- and disubstituted methoxycarbene complexes, providing a convenient method for the generation of cationic iron–carbene complexes.[165]

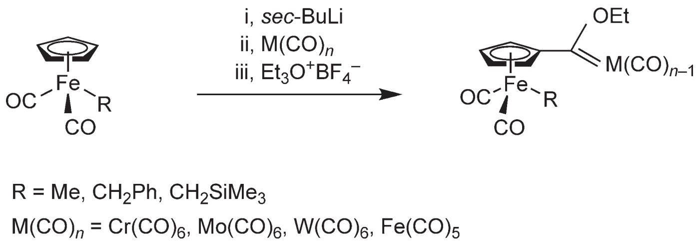
6.04.6.2 Binuclear Fp Complexes Bearing η^1- and C_5 Ligands

Binuclear and polynuclear heterometallic compounds, where there are no direct metal–metal bonds, have been prepared by functionalization of the Cp ligand in mononuclear iron complexes of the type FpR (where R = CH_3 or CH_2Ph) (Scheme 36).[166] Polynuclear complexes have also been prepared using the same methodology but starting with the binuclear complexes $Fp(CH_2)_3Fp$ (Scheme 37).[166] The complexes were generally isolated as low-melting crystalline solids in reasonable to good yields and characterized by spectroscopic and analytical methods. The binuclear complex in Scheme 36 (where R = CH_2Ph and M = Cr) was further characterized by X-ray crystallography. Cyclic voltammetry studies on all the binuclear complexes were carried out and compared to related ferrocene derivatives.[166]

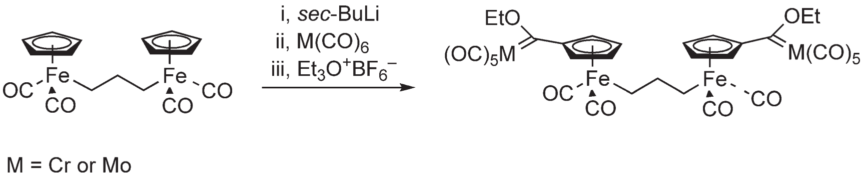
A series of new metal aminocarbene-substituted Fp complexes have also been prepared starting from the above ethoxycarbene complex.[167] Some examples of these binuclear aminocarbene complexes are shown in Scheme 38. The complexes were characterized by analytical and spectroscopic methods. Cyclic voltammetry was also used to investigate these binuclear aminocarbene compounds, and two complexes were structurally characterized by X-ray crystallography.[167]

An extensive series of binuclear CpFe complexes has been prepared where the metal centers are linked by unsaturated carbon chains. Binuclear compounds containing iron as one of the metals, with bridging carbide or unsaturated hydrocarbon ligands and no metal–metal bond, can be prepared by reactions of the appropriate mononuclear iron compounds. This topic has been recently reviewed by Selegue.[160] Iron is an important metal in binuclear compounds with bridging carbon atom chains. This is clearly demonstrated in the review of Bruce and Low that describes transition metal complexes containing all-carbon ligands.[126] The bonding in metal–alkynyl compounds, including those of the types M–C≡CR and M–C≡C–M, has also been reviewed.[140]

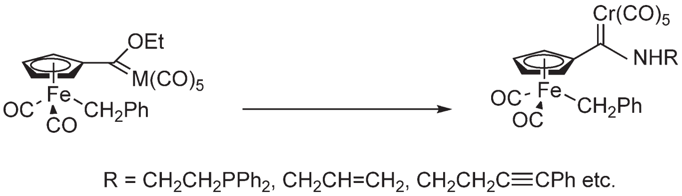
There has been considerable interest shown recently in the synthesis, structure, and properties of binuclear complexes bridged by long chains of carbon of the type $L_nM–(C{\equiv}C)_n–ML_n$. Such oligomers may exhibit novel properties such as one-dimensional conductivity, non-linear optical properties, or bulk spin alignment. Dinuclear



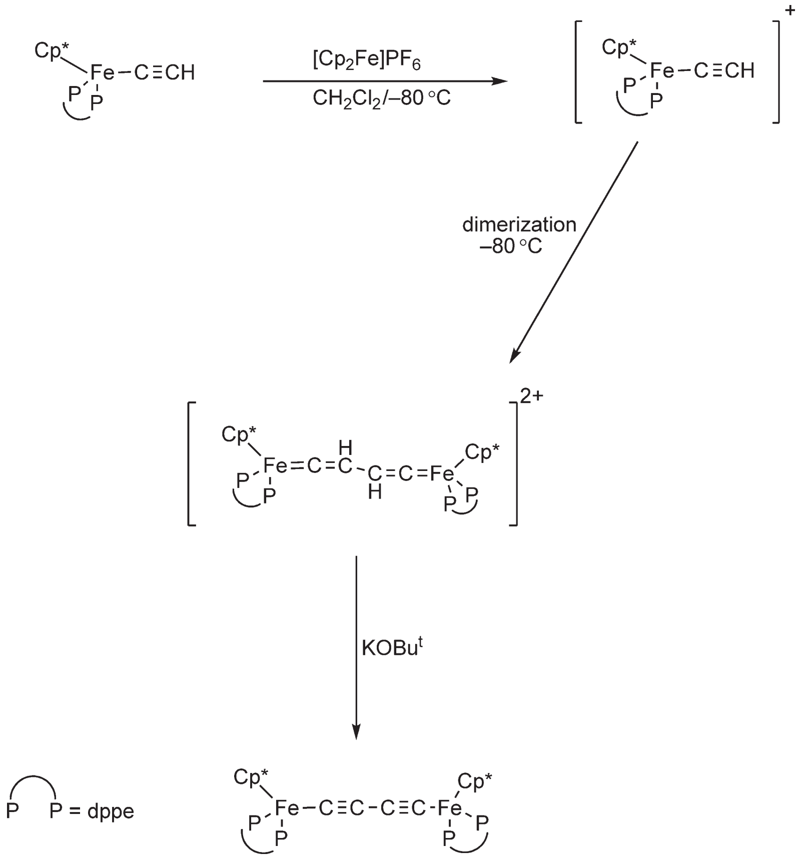
Scheme 36



Scheme 37



Scheme 38

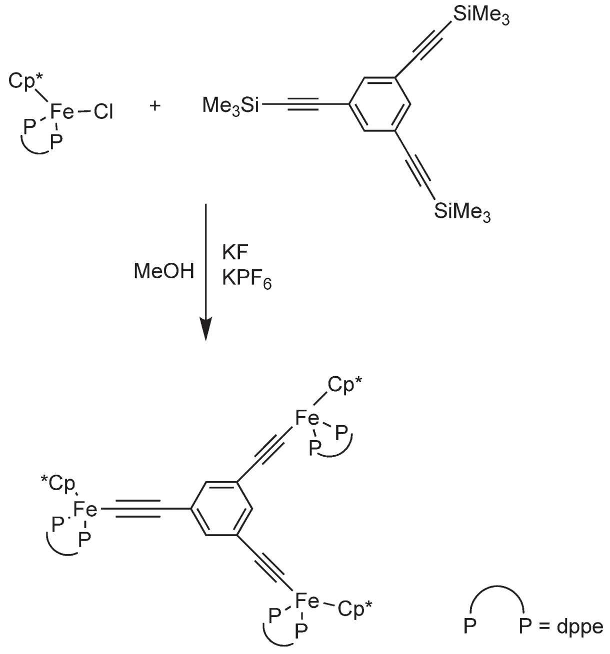


Scheme 39

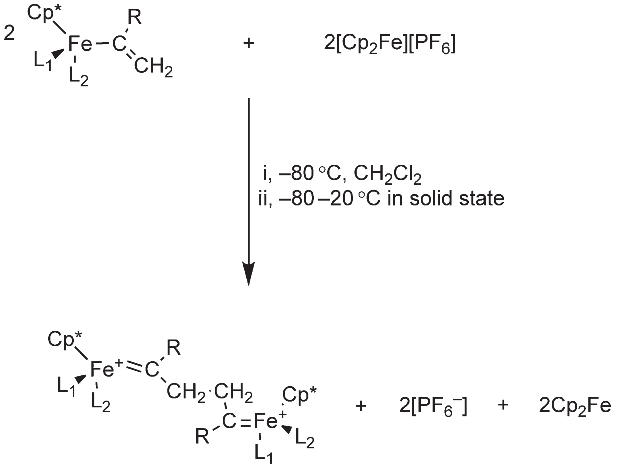
iron complexes have featured prominently in these studies. Thus, Lapinte and co-workers have prepared the complex $Cp^*(dppe)FeC_4Fe(dppe)Cp^*$ in high yield, as shown in Scheme 39.[168] CV analysis of this butadiyne-bridged complex shows two reversible one-electron oxidation waves. The mixed-valence Fe(II)–Fe(III) cation can be isolated by chemical oxidation of the butadiyne-bridged complex, and this air-stable cationic compound has been characterized by X-ray crystallography.[168] Mixed-valence Fe(II)–Fe(III) compounds can also be obtained with a 1,4-diethynylbenzene-bridging group. This mixed-valence intermediate can be further oxidized to the Fe(II)–Fe(III) dication.[169]

$Cp^*Fe(dppe)$ is a good end-capping group for long carbon chains, and Lapinte and co-workers have prepared the C_8 chain $Cp^*(dppe)FeC_8Fe(dppe)Cp^*$ by the oxidative coupling reaction of $Cp^*(dppe)Fe(C{\equiv}CC{\equiv}CH)$. The C_8 chain compound has been structurally characterized and is shown to act as a molecular wire between the iron centers.[170,171]

Carbon chain compounds with two different end-capping groups can also be synthesized. Thus, Sato and co-workers[172] have prepared a series of compounds of the type $Cp'L_2Fe–C{\equiv}C–Fc$ (where $Cp' = \eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5Me_5$; $L_2 = (CO)_2$ or dppe, dppm, or dmpe; Fc = ferrocenyl). These complexes have been studied by cyclic voltammetry and can also be chemically oxidized to the mixed-valence compounds which show considerable electron delocalization.[172] Carbon chains have also been prepared with two different iron end-capping groups. Thus, the compound $Cp^*(dppe)FeC_4Fe(CO)_2Cp^*$ has been prepared in 69% yield by the reaction of $Cp^*Fe(CO)_2(C{\equiv}CC{\equiv}CH)$ with $Cp^*Fe(dppe)Cl$ in the presence of KPF_6 and $KOBu^t$ in methanol.[150] The structure of the binuclear compound has been confirmed by X-ray crystallography. Related complexes were also prepared in a similar way. The complexes were studied by cyclic voltammetry and Mössbauer spectroscopy. The latter technique showed that the electron density of the two different iron atoms is quite different.[173] This synthetic methodology has also been used by Akita *et al.* to prepare a series of symmetrical end-capped carbon



Scheme 40



R = OMe; L_1 = CO; L_2 = PPh_3
R = OMe; L_1 = CO; L_2 = PMe_3
R = OMe; L_1, L_2 = dppe
R = H; L_1, L_2 = dppe

Scheme 41

chains of the type Fp*–(C≡C)$_n$–Fp* (where $n = 2$ or 4).[173] X-ray crystallography confirmed the linear structure of the C_4 chain and its mononuclear precursor.[173] Binuclear and trinuclear σ-acetylide complexes have also been prepared in 80% yield, as shown for the trinuclear compound in Scheme 40.[143] CV studies show that there is significant electronic communication between the metal centers.[144] Carbon chains with different metals as end-capping groups have also been prepared.[174]

Thus, Bruce *et al.* have prepared the compounds $Cp(CO)_3M–C{\equiv}C–C{\equiv}C–Fp$ (where M = Mo or W), and these compounds are shown to react further with $Co_2(CO)_8$ at the least sterically hindered C≡C bond to give adducts.[174] Electron transfer and electron exchange in conjugated carbon-rich systems is of much current interest. An anthracene-bridged complex has been structurally characterized and the oxidized forms have also been synthesized and studied by CV.[175]

The mixed metal C_4-chain compound $[Cp^*(dppe)Fe(C{\equiv}CC{\equiv}C)Ru(dppe)Cp^*]$ and related compounds have been prepared, characterized, and studied by cyclic voltammetry. Dramatic changes in electronic structure are observed when compared to the analogous diiron analog.[176] Thus, the nature of the metal in these binuclear carbon chain compounds has a pronounced role in tuning the electronic and magnetic properties.[176] New dinuclear bis-carbene compounds have been prepared from mononuclear iron vinyl precursors (Scheme 41) and their reactivity explored.[177]

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6.05
Mononuclear Iron Compounds: Ferrocenes

I R Butler and D Thomas, University of Wales Bangor, Bangor, UK

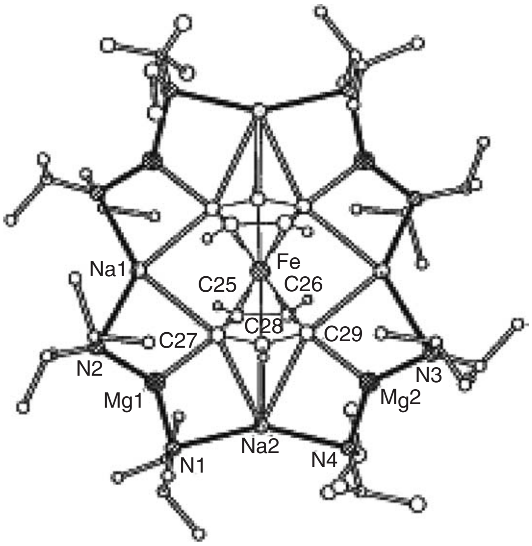
6.05.1 Introduction

The use of ferrocene in organometallic chemistry has dramatically increased since the publication of COMC (1995). Since then, there are at least 7,000 primary references in major journals in which ferrocene plays a central role. The sheer publication volume means that there are no longer comprehensive annual reviews available; however, there are several key sources which may be used to obtain pertinent information. Many of the papers published refer specifically to the electrochemistry of ferrocene and its derivatives or to applications of ferrocene only indirectly related to organometallic chemistry, which are clearly beyond the scope of this overview. The most important primary sources of reference materials come with the publication of two books on the subject.[1,2] Additionally, brief annual reviews of ferrocene chemistry may be found in the Royal Society of Chemistry series *Organometallic Chemistry*, "Transition metal complexes of cyclopentadienyl ligands."[3–11] There are additionally a number of reviews on ferrocene chemistry which relate to synthesis or directly to its organometallic chemistry. These will be referred to in the detailed sections, which follow. It should be noted that the 50th anniversary of the first synthesis of ferrocene was marked by the publication of a specific volume in the *Journal of Organometallic Chemistry* to mark the event. Key papers in this were first-hand accounts by some researchers directly involved in the discovery and characterization of ferrocene.[12–16]

6.05.2 Synthesis

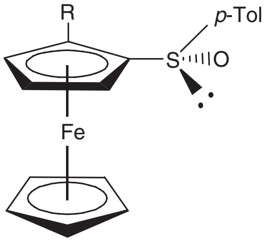
6.05.2.1 Metallation Reactions

Metallation reaction chemistry of ferrocene has been used as the most prevalent route to the preparation of substituted ferrocenes, even more so than Friedel–Crafts methodology. The lithiation of ferrocene with *n*-butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) remains the method of choice for the preparation of 1,1′-dilithioferrocene, whereas the direct lithiation of ferrocene with *t*-butyllithium, when ferrocene is present in excess, is the most practical method for the preparation of monolithioferrocene. An improved monolithiation procedure which uses *t*-butyllithium and potassium *t*-butoxide mixtures (the superbase method) has been devised, which achieves yields of 90%.[17] However, where absolutely pure samples of lithioferrocene are required, either tri-*n*-butylstannylferrocene or bromoferrocene are the precursors of choice. Kagan *et al.* have re-investigated these basic lithiation methods, and although the results essentially concur with the previous accumulated literature data, the paper serves as a useful summary.[18] The *ortho*-lithiation of 1,1′-dibromoferrocene has proved to be useful for the preparation of a range of substituted ferrocenes including ferrocenylphosphines. 1,2-Dilithioferrocene has also been prepared directly from the 2-sulfinylbromoferrocene.[19] One of the most interesting results in this area is the observation that ferrocene can be transformed into a 1,1′,3,3′-tetraanion by the fourfold deprotonation of a 16-membered Na_4Mg_4(amide) ring, **1**.[20–22]



1

It has been difficult to quench this tetrametallated species to gain the maximum benefit in synthesis, as mixed products are generally obtained when common electrophilic quenching reagents are used. The general approach to this method may be found in a general text.[23] *o*-Methylephedrine has been used as a chiral auxiliary in the *ortho*-metallation of ferrocenes.[24] In addition, (−)-sparteine has been successfully used as a chiral auxialiary in the asymmetric metallation of ferrocene sulfonates,[25] carboxamides,[26,27] and planar chiral ferrocene diamides.[28] Sparteine may also be used in the asymmetric synthesis of ferrocenyl alkylamines beginning with dimethylamino fulvene.[29] Interestingly, the products obtained on the lithium diisopropylamide (LDA)-assisted dilithiation of 1,1′-dibromoferrocene indicate a preference in dilithiation for the formation of the 1,3-disubstituted products.[30] It is also possible to prepare 1,3-disubstituted ferrocenes using a method described by Brown where ferrocene–*p*-tolyl sulfide is the precursor compound. Using *sec*-butlylithium as the metallating agent up to 94% regioselectivity toward the 3-position may be obtained in this metallation.[31] The selective monolithiation of 1,1′-dibromoferrocene may also be used to obtain a range of unsymmetrically substituted ferrocenes,[32] whereas the lithiation of *N*-BOC-protected ferrocenyl alkylamines (BOC = *t*-butyloxycarbonyl) has been used to obtain 1,1′-unsymmetrically disubstituted ferrocenes.[33] Solvent effects and the effect of the lithiating reagent have also been examined in the lithiation of chiral 1,1′-bis(oxazolinyl)ferrocenes.[34] A series of articles on the use of ferrocenecarboxaldehyde as a precursor, in which it is reacted with *N*-methylpiperazide, has described substitution at the 1′-position[35] and, in addition, the development of a chiral lithiation strategy based on the formation of chiral acetals.[36–38] One of the most useful synthetic procedures developed is the preparation of enantiopure ferrocenyl sulfoxides, of the type shown in **2**, via LDA lithiation of the starting ferrocenyl *p*-tolyl sulfoxide.[39]

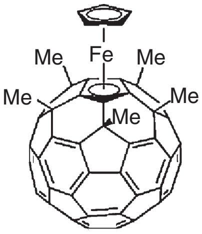


2

A typical example of the use of ferrocenyllithium is in the synthesis of ferrocenylquinones (initial reaction with diisopropyl squarate).[40]

6.05.2.2 General Synthetic Methods

So-called “buckyferrocenes and ruthenocenes” of the types Fc($C_{60}Me_5$)Cp, Ru($C_{60}Me_5$)Cp, and Fc($C_{70}Me_3$)Cp, for example 3, have been prepared by what are very simple synthetic procedures, which involve the thermolysis of metal cyclopentadienyl precursors.[41,42] The first planar-chiral stable carbene has also been prepared, which is shown as 4.[43]



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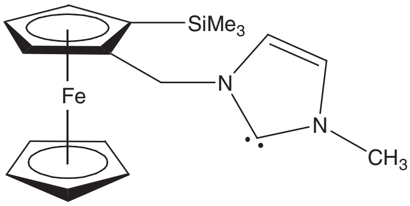
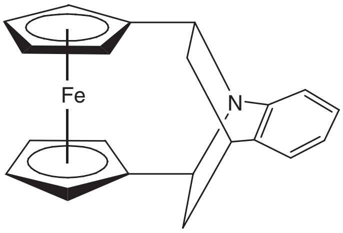


4

New strained 2-aza[3]ferrocenophanes 5, have also been obtained, and these have been used as metal ion sensors.[44] An excellent paper describes the synthesis, structure, and the electrochemistry of pentamethylferrocenes, which interestingly undergo acylation reactions etc; however, the metallation reaction requires the use of quite forcing conditions.[45]



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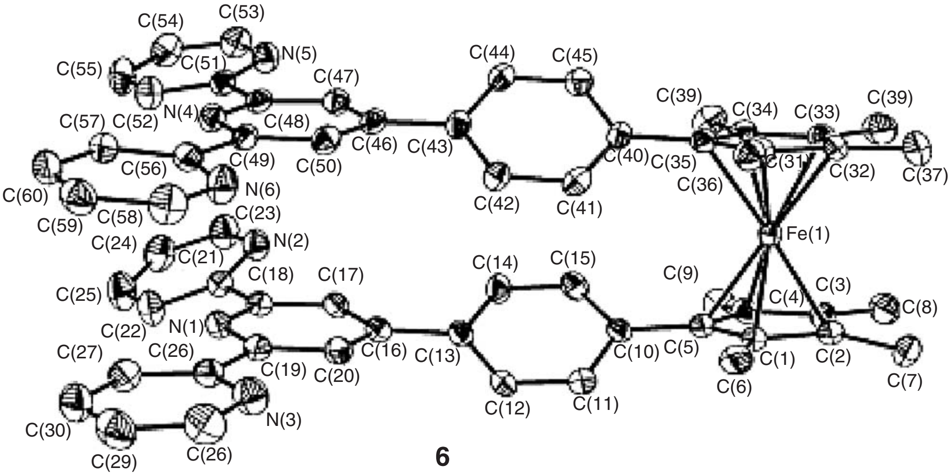
A new practical synthesis of 1,1′-diaminoferrocene which is based on the reaction of 1,1′-dibromoferrocene with sodium azide, followed by H_2 reduction, has been developed. It is found that the 1,1′-diaminoferrocene, previously thought to be quite unstable, is reasonably easy to handle.[46] Titanium complexes of the trimethylsilyl (TMS) part protected bis-amine were subsequently prepared and crystallographically characterized.[47,48] Ferrocenylamine serves as a useful precursor to isocyanoferrocene, when reacted in two steps with PhOCHO/phenol and $POCl_3/^iPrNH_2$.[49] An alternative synthesis of aminoferrocene (72%) by quenching lithioferrocene with α-azidostyrene, followed by acidification and base precipitation, is reported in a paper describing an alternate synthesis of 1,1′-diisocyanoferrocene.[50]

An interesting ferrocenophane containing an N–Si–C–C–Si–N bridge may be obtained from the 1,1′-diaminoferrocene on treatment with 1,2-bis(dimethylchlorosilyl)ethane.[51] Another useful compound is 1-aminoferrocene-1′-carboxylic acid, which has been obtained by three different routes.[52,53] The first procedure used 1,1′-dibromoferrocene as a convenient precursor.[52] Alternatively, it may be obtained from 1-azodicarbonylferrocene–1′-carboxylate[53] or from

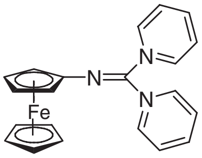
1-(acetylamino)ferrocene.[54,55] Ferrocene-based olefin polymerization catalysts may be obtained from the zirconium complexes of silyl-protected 1,1′-ferrocenyldiamine.[56] These silyl-protected ferrocenylamines are readily obtained from reactions of ferrocenylamines with chlorosilanes in the presence of triethylamine.[57]

A range of phenyl-spaced ferrocenyl terpyridyl compounds have also been prepared from the appropriately substituted cyclopentadienyl derivative. A typical example is as shown in 6.[58]



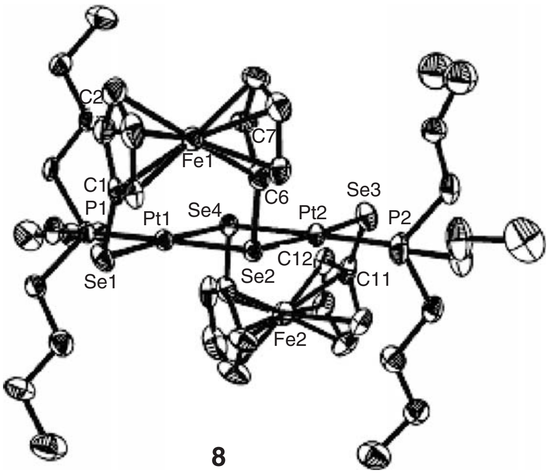
6

The formation of 1,1,12,12-tetramethyl[1,1]silaferrocenophane has been achieved from the salt of dimethyldicyclopentadienylsilane on treatment with iron(III) chloride.[59] Ferrocenylamine condenses with 2,2′-dipyridylketone to give the imine 7, which is efficient in the complexation of Cu(I).[60] The self-assembly of new copper–ferrocene Schiff base ligands has also been achieved.[61] The reaction of CpFe(CO)$_2$I in the presence of 2 equiv. of triphenylphosphine and 1,1′-dilithioferrocene results in the formation of CpFe(CO)(PPh$_3$)[μ-C : η^5-C(O)C$_5$H$_4$]Fe[μ,η^5 : η^4-5-*exo*-(1′-C$_5$H$_4$)C$_5$H$_5$]Fe(CO)$_2$(PPh$_3$), which is obtained in 50% yield.[62] The use of Wittig olefination has provided a useful route to (*E*)-2-(1′-formylruthenocenyl)ethenyl-1′,2,2′,3,3′,4,4′,5-octamethylferrocene and (*all-E*)-2,5-bis[2-[1′-[2-(1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)ethenyl]ruthenocenyl]ethynyl] thiophane.[63]



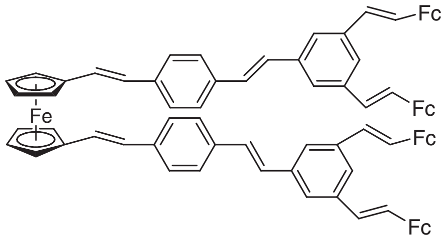
7

A series of palladium and platinum complexes of ferrocenylselenolates has been obtained from 1,1′-bis(trimethylsilylseleno)ferrocene, an example of which is shown as 8.[64]



8

Charge transfer between two ferrocenyl units separated by oligothiophenes has also been examined in an investigation looking at possible applications in molecular electronics.[65] Further use of Wittig coupling chemistry has been made in the preparation of compounds such as **9**.[66] An *in situ* generated acylation agent, obtained from a carboxylic acid and phosphorus trichloride, in the presence of a sacrificial aluminum anode, has been described. While the method is reasonably efficient in the production of monoacyl ferrocenes, low yields of diacyl compounds were obtained.[67] A series of ferrocenylanthracenes and anthraquinones have been prepared such as 1- and 2-ferrocenyl(9,10-phenylethynyl)anthracene in addition to ferrocenylanthraquinones with ethenyl spacers such as **10**.[68]



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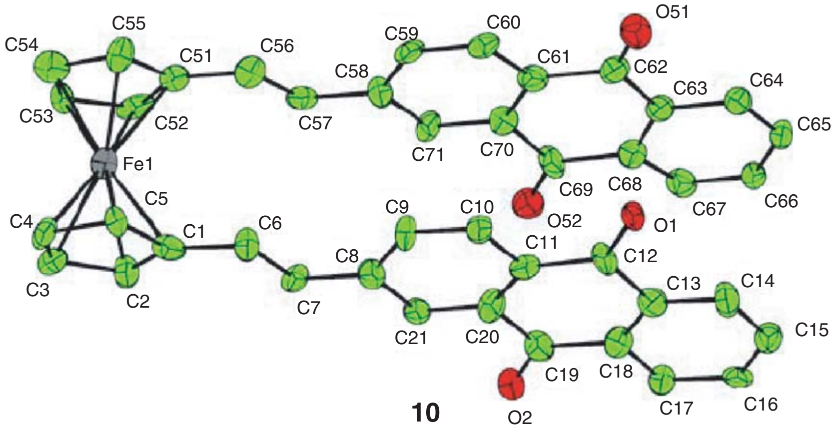
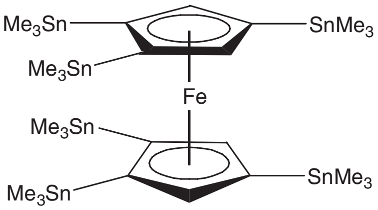


10

Similarly, a series of ferrocene-substituted anthracenes has been prepared, in which the link group is a phenyl alkyl ether.[69] An interesting variation on the theme is the reduction of 1,8-dichloroanthracene in the presence of aluminum trichloride and ferrocene to afford $[(\eta^6:\eta^6\text{-1,8-dichloro-9,10-dihydroanthracene})(\text{FeCp})_2](\text{PF}_6)_2$.[70] A useful synthesis of mixed-ring ferrocenes in which the salt $[(\text{fluorene})\text{FeCp}]\text{PF}_6$ is used as a cyclopentadienyl iron-transfer reagent.[71] Jutzi's research group has continued their work on the preparation of multiply stannylated ferrocenes, such as **11**, beginning with the appropriately substituted cyclopentadienyl compound.[72]



11

They have also prepared tetra-3-butenyl-substituted ferrocenes as core compounds for the preparation of polynuclear compounds[73] and a number of 1,1′-digallylferrocenes[74] such as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{GaMe}_2)_2]$. The same research group has also prepared octamethylferrocenylethynyl groups for use as peripheral groups in rigid molecular structures[75] and functionalized silicon-bridged compounds with pentamethylcyclopentadienylalkyl ligands for use in ferrocene-containing polymer preparation.[76]

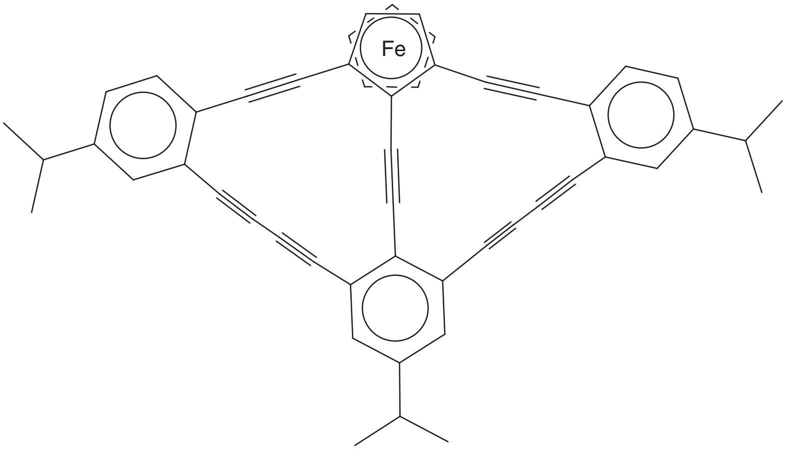
A series of ferrocene polyaromatic dyads of the type Fc–C═C–Ar, *trans*-Fc–CH═CH–Ar, and Fc–CH═CH–CH═CH–Ar have been prepared and characterized.[77] Tetrapyrrole derivatives substituted with ferrocenylethynyl groups have also been prepared and used to make zinc phthalocyanins appended with eight peripheral ferrocenylalkynes.[78] Similarly, star-shaped polyferrocenes based on thiophene have been prepared where tetrabromothiophene has been reacted with a range of ferrocene-substituted ethynes.[79]

6.05.2.3 Mechanisms of Synthesis

There are three useful mechanistic papers, the first of which is on the mechanism of electrophilic substitution, specifically mercuration, which concludes that the initial mercuration takes place on the cyclopentadienyl ring without the involvement of the metal center.[80] The other papers, by the same author, were on the acetylation of 1,1′-bis(trimethylsilyl)- and 1,1′-bis(tributylstannyl)ferrocenes, where it was concluded through mechanistic experiments using deuterium labeling that the attack of the acetyl chloride–aluminum trichloride complex occurred at the *exo*-face of the cyclopentadienyl ring followed by a proton transfer from carbon to iron.[81,82]

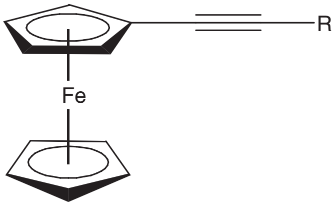
6.05.2.4 Ferrocenyl Alkynes

In a series of the synthetic papers exploring “carbon-rich” structures, the chemistry of alkynated ferrocenes has been described, an example of which is shown in **12**.[83] These multiply-substituted ferrocenes are prepared by metallation, formylation, and Ohira alkynation chemistry.



12

Following this strategy, it has been possible to obtain the first 1,2,3,4,5-pentaalkynylferrocene derivative (the 4′-tolyl ethynyl derivative).[84] Previously, as part of this synthetic program, the synthesis of 1,2,3-triformylferrocenes[85] was described, which ultimately led to the preparation of the 1,2,3,4,5-pentaformylferrocene.[86] 1,2-Diethynylferrocene[87] has also successfully been used in the synthesis of organometallic dehydroannulenes with fused ferrocenes.[88,89] A broad range of ferrocenyl alkynes **13** has been prepared by two routes: metathesis of (lithioethynyl)ferrocene with electrophiles or *trans*-metallation of the same compound with $ZnCl_2$ followed by coupling.[90]



R = H, Me, Ph, CMe_3, $SiMe_3$, $GeMe_3$, $SnMe_3$, I, $C(OH)Ph_2$, $C(OMe)Ph_2$, CHO, C(O)Me, CO_2H, CO_2Et

13

A simple and effective synthesis of ethynylferrocene beginning with ferrocenecarboxaldehyde using Wittig chemistry has been described, and the crystal structure of 1,4-diferrocenyl-1,3-butadiyne has been determined.[91] Again, aromatic ethynyl-bridged ferrocenes of the type $\mathrm{FcC{\equiv}C{-}R{-}C{\equiv}CFc}$ have been obtained by palladium-catalyzed coupling of iodoferrocene with dialkynes or alternatively by coupling ethynylferrocene with di(haloaryl) reagents.[92]

6.05.2.5 Miscellaneous Synthetic Reports

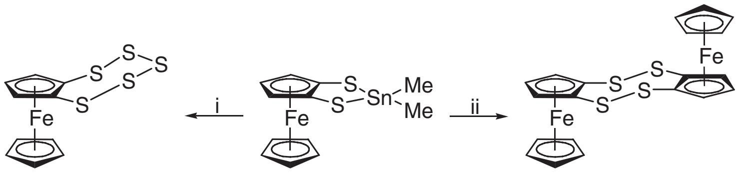
Synthesis of a stable pentathiepin fused to a single cyclopentadienyl ring of ferrocene was performed by treatment of the corresponding dithiastannole, a synthetic equivalent of the unstable ferrocene-1,2-dithiol, with a sulfur source. On the other hand, deprotection of the dithiastannole gave a novel tetrathiocin comprised of two ferrocene units (Scheme 1).[93]

Other general synthetic reports of note include the cyclodextrin inclusion complex of $\mathrm{[(Fc\text{-}4\text{-}pyr)ReO_3Me_3]}$;[94] ferrocene-substituted 5-alkylidenesulfuranones and 4-cyclopentene-1,3-diones;[95] 1,1′-bis(*N*-*tert*-butyl)-*N*-hydroxyamino)ferrocene;[96] 2-ferrocenylindoles and 1-ferrocenyl-2-aryl(heteroaryl)acetylenes;[97] 4-ethynyl-benzonitrile-substituted ferrocenes, $\mathrm{[FcC{\equiv}CC_6H_4C{\equiv}N\text{-}1,4]}$, and related palladium complexes;[98] peptide synthesis using ferrocenylamino acids;[99] a dehydrogenation route to ferrocenylsiloxanes;[100] synthesis of 1,3-(*t*-butyl)alkyltin-substituted ferrocenes;[101] synthesis of triferrocenylmethanes;[102] $\mathrm{[Li(FcBH_3)][Li_2\{1,1'\text{-}Fc(BMe_3)_2\}]}$, $\mathrm{[Li_2\{1,1'\text{-}Fc(BMe_2P_2)_2\}]}$;[103] ferrocenyldicarboxamide linkers as DNA probes;[104] [pyridazin-3(2H)-one-6-ylferrocenes];[105] ferrocene-endcapped bis(butadiynyl)fluorenes;[106] ferrocenyl tropones from diferrocenylbutadiyne dicobalt hexacarbonyl adducts;[107] *N*,*N*-dimethylferrocenylmethylhexadecylammonium bromide;[108] *N*-*para*-ferrocenylbenzoylamino acid ethyl esters;[109] ferrocenylenone synthesis using $\mathrm{EtAlCl_2{-}Me_3Al}$ Friedel–Crafts methods;[110] rhenium complexes of 1,1′-(ferrocene)bispyrazoylmethane;[111] ferrocene-substituted triarylmethyl dye molecules;[112] improved synthetic method for ferrocenylcarbene complexes of Cr, Mo, W;[113] gold and silver complexes of ferrocenyl–pyrazolate ligands;[114] preparation and structures of copper(II) and zinc(II) complexes with 5-ferrocenylpyrimidine;[115] face-to-face fused ferrocenes; synthesis and properties of 2,10-diferrocenyl- and 2,5,7,10-tetraferrocenyl–1, 6-methano[10]annulenes;[116] and the synthesis of ferrocene-substituted 2-azetidinones.[117]

6.05.3 Materials

Ferrocene derivatives have been used in a wide number of material science applications—so diverse are they that it is difficult to compartmentalize these into a coherent text. Thus, this is a general overview of some specific applications. At the outset, it is worth noting that in many cases ferrocene acts as a reagent in synthesis, specific examples would be in the preparation of nanotubes and iron-containing nanotubes which is not reviewed here,[118,119] or the vapor-phase insertion of ferrocene into zeolites.[120]

Another particularly interesting area of research is the use of ferrocenes in luminescent systems, which again has been systematically reviewed,[121] which relates to the intramolecular quenching of excited singlet states by ferrocenyl derivatives.[122] Ethynylferrocenes have also been attached to phthalocyanins[123] and porphyrins,[124] which augments the previously known non-conjugated ferrocene-linked systems.[125–130] Again, 2,5-diethylpyridine has been used to bridge ferrocenes in the construction of a molecular diode.[131] Ferrocene–oligothiophene-fullerene triads have also been prepared, and the emission and fluorescence spectra observed.[132] Also, lithium ion sensors have been prepared using an anthracene–ferrocene dyad, even though ferrocene is a recognized fluorescence quencher.[133] Ultrafast intramolecular electron transfer from a ferrocene donor to a nile blue dye acceptor covalently bound to the ferrocene has been observed.[134] Ferrocene nanotubes have been attached to β-cyclodextrin self-assembled monolayers for use in cavity size molecular recognition.[135] Self-assembly of ferrocenylpyridines has been re-examined in several cases, with combinations of organic acids.[136]

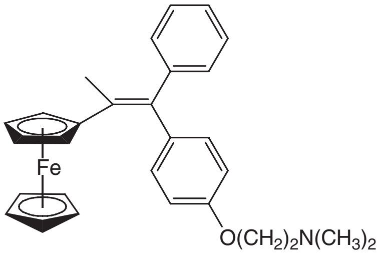


i, $\mathrm{SCl_2}$, THF; ii, $\mathrm{I_2}$, $\mathrm{CHCl_3}$

Scheme 1

6.05.4 Medicine

A general review has examined the bio-organometallic chemistry of ferrocene,[137] in which the focus is on 1,1′-bis-amino acid and 1,1′-bis-peptide-substituted ferrocenes. Clearly, the most significant work in this area is the preparation of ferrocifen, **14**, which is the ferrocene analog of tamoxifen[138] and its related compounds.[139–141] Ring modifications of the Cp′ ring in ferrocifen have also been carried out, and the data correlated with the influence of the estrogen receptor recognition.[142] In addition to the parent ferrocene compounds, several complexes of ferrocene ligands have also been investigated such as the rhodium–ferrocene complex [Rh(fctfa)(COD)],[143] rhodium and iridium complexes and ferrocene-polymer conjugates,[144–147] and Pd and Pt complexes of ferrocene-based ligands.[148]



14

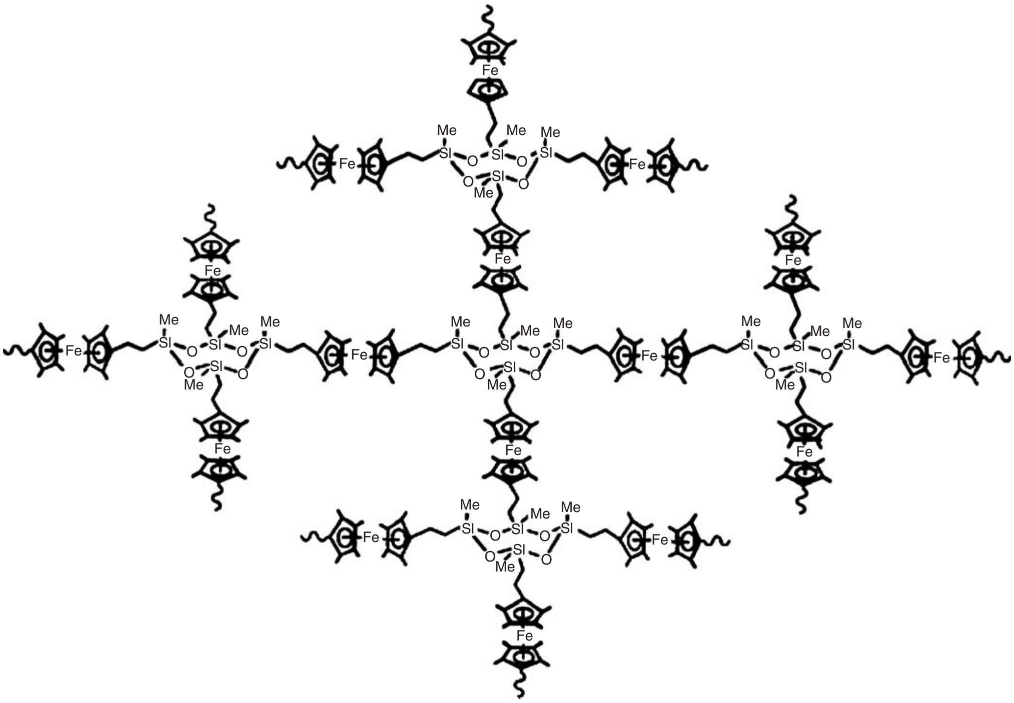
The fungicidal properties of ferrocenyltriazoles have also been investigated intensively.[149] The antifungal activity of ferrocene–fluconazole analogs has been evaluated, in which the ferrocene replaces the difluorophenyl substituent, and it has been observed that surprisingly the ferrocene analog had no effect on fungal growth.[150] Ferrocene–triazacyclononane quinoline conjugates have also been used in antiplasmodial trials, and it was observed that one particular derivative 7-chloro-4-[4-(7-chloro-4-quinolyl)-7-ferrocenylmethyl-1,4,7-trazacyclononan-1-yl]quinoline exhibits "potent" antimalarial activity.[151] In a study of the ferrocene in chloroquine, it was observed that 7-chloro-4-*N*-[(4-*N*′-ethyl-*N*′-ferrocenylmethyl)amino-1-methylbutylamino]quinolin-1-ium bitartrate also exhibited good antimalarial activity.[152] Other noteworthy papers in this field include ferrocene–cobaltocenium derivatives in amperometric enzyme electrodes for glucose sensing;[153] DNA sensors using a ferrocene-modified oligonucleotides;[154] DNA sensors using a ferrocene–oligonucleoside conjugate;[155] bonding patterns in ferrocenyl peptides;[156] 2′-ribose ferrocene oligonucleotides for electronic detection of nucleic acids;[157,158] immunoglobulin G labeled with ferrocenecarboxaldehyde;[159] soft X-ray spectroscopy of ferrocene–proline conjugates.[160]

6.05.5 Dendrimers

A review article examines the literature up to 1999 on silicon- and amine-based ferrocene dendrimers and polymers and those immobilized on electrodes. In these dendrimers the ferrocene itself may be at the core, the periphery, or be used as a spacer molecule. Some examples of these molecules are shown as **15–17**.[161]

Such materials are obtained by standard synthetic routes, the diversity of which is beyond the scope of this review. Electroactive films may also be obtained.[162] Mixed ferrocene–cobaltocinium dendrimers[163] also find applications in glucose monitoring[164] and anion sensing.[165] Another review article covers the synthesis and properties of phenyl–ethenylferrocenyl oligomers and dendrimers such as the one shown as **18**.[166] The background synthetic methods appear in a related article.[167]

Chiral phosphorus-containing dendrimers which have ferrocene molecules at the periphery have been the subject of work by Majoral and co-workers. These materials will have obvious applications in catalysis.[168] Layer-by-layer dendrimers, which are built up containing chiral ferrocenylphosphine molecules, have also been prepared, and their chiroptical and electrochemical properties have been investigated.[169,170] A recent article covers the basic chemistry of ferrocene-containing liquid-crystalline polymers which stems from the extensive work of Deschenaux, who essentially pioneered the area.[171] A ferrocene end-capped dendrimer has also been used in carbon monoxide sensing. The actual dendrimer, shown as **19**, has 48 ferrocene molecules on the periphery.[172]



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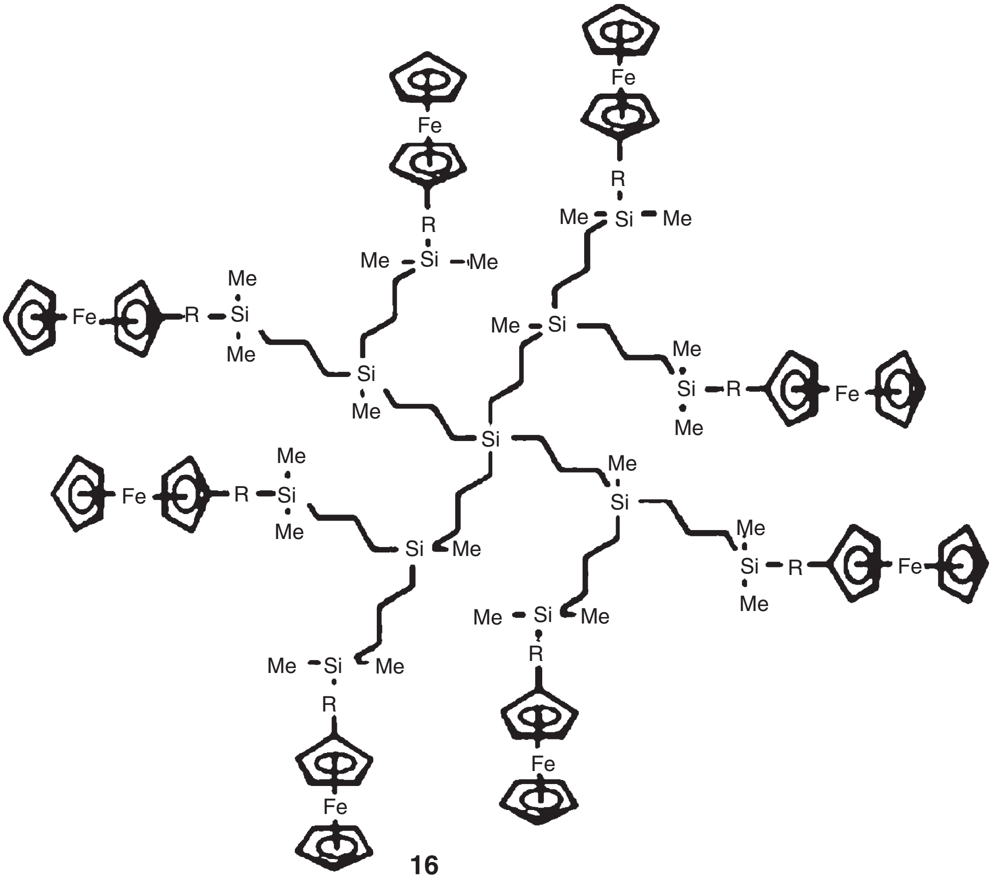

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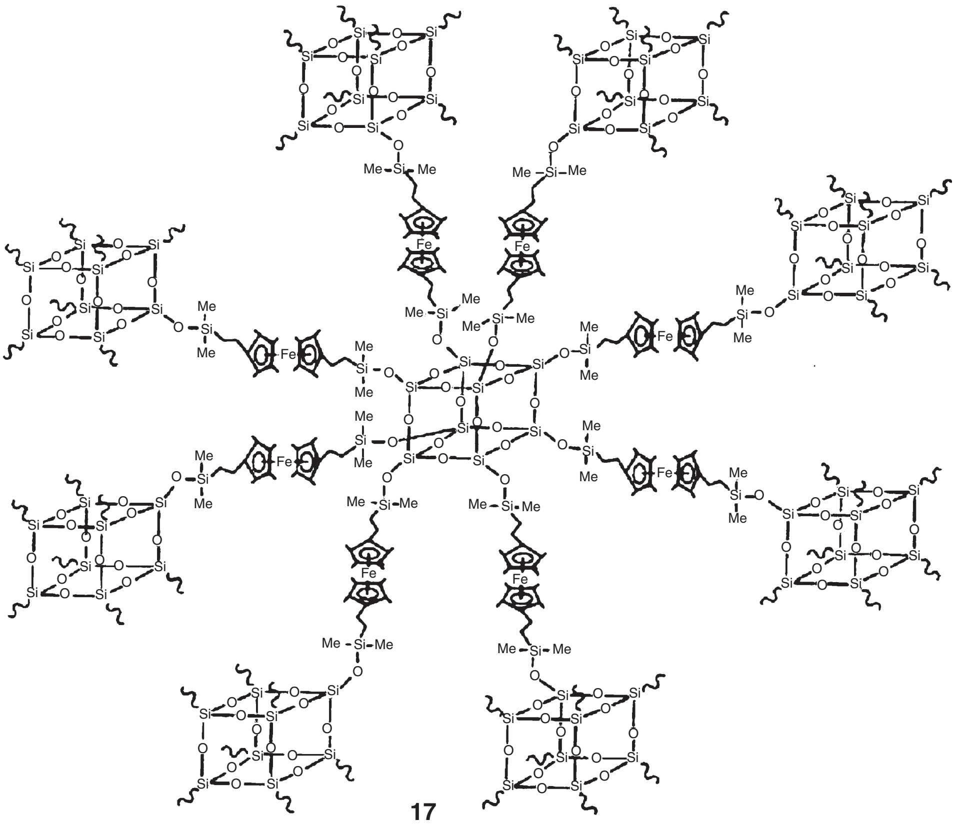

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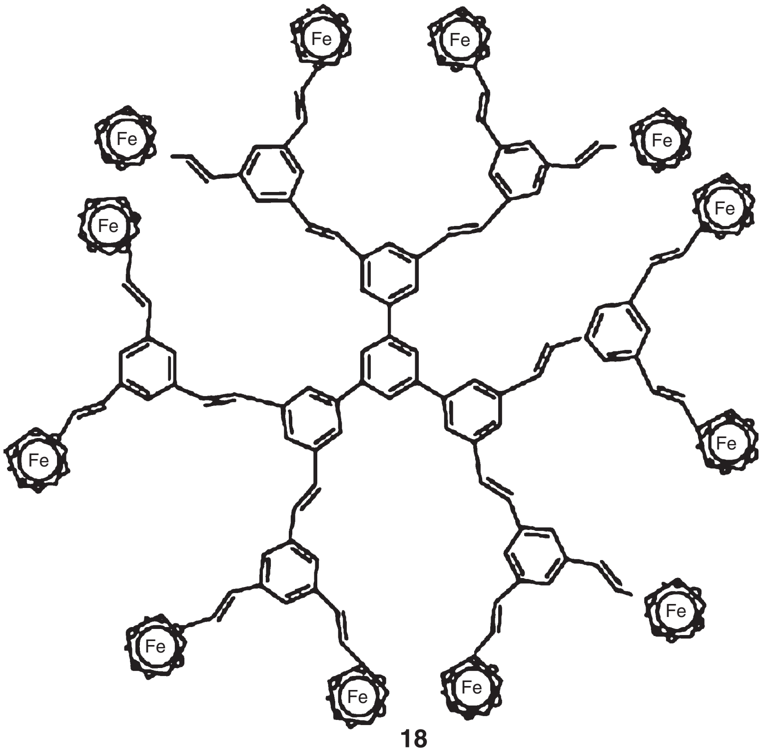

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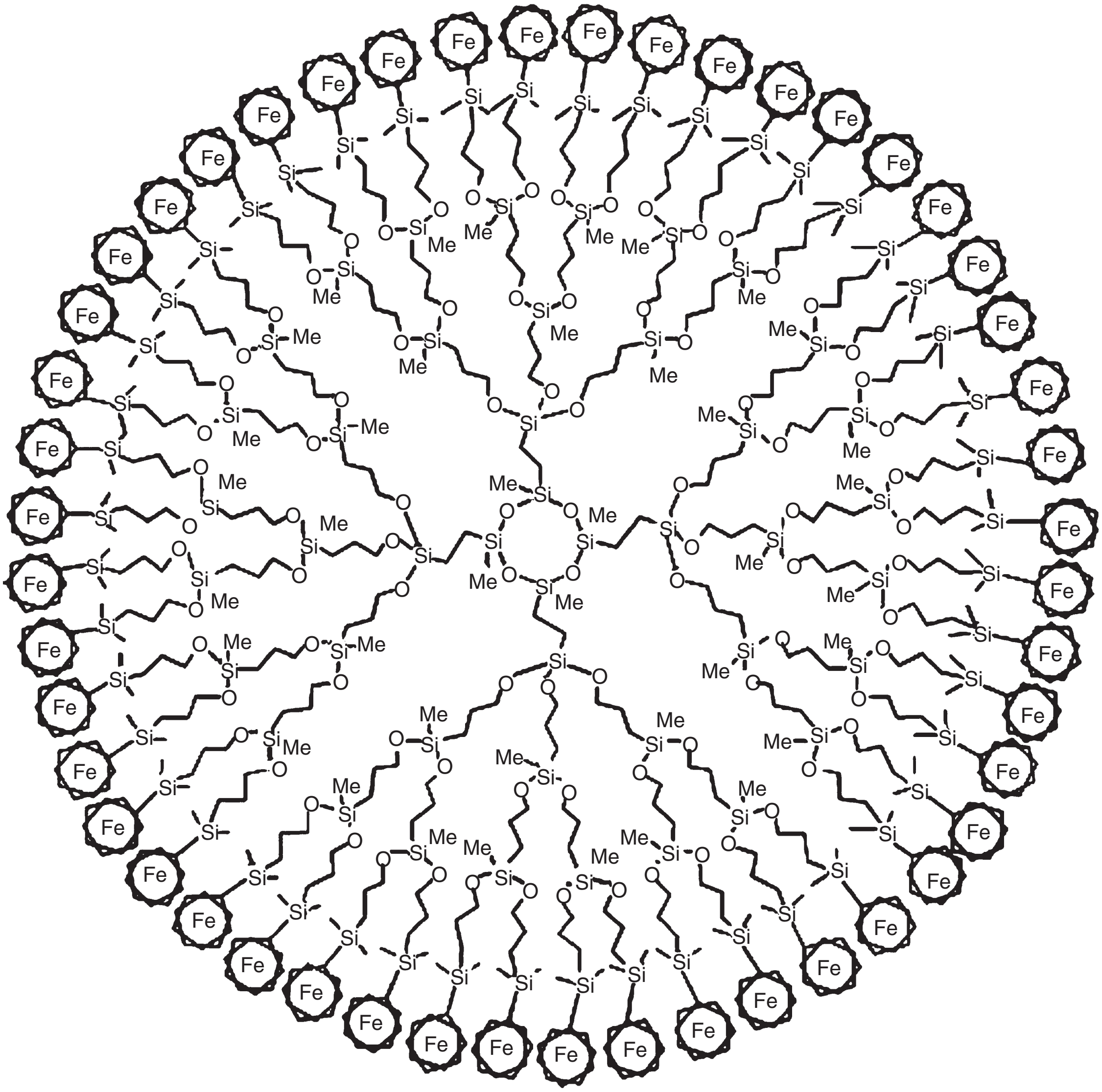
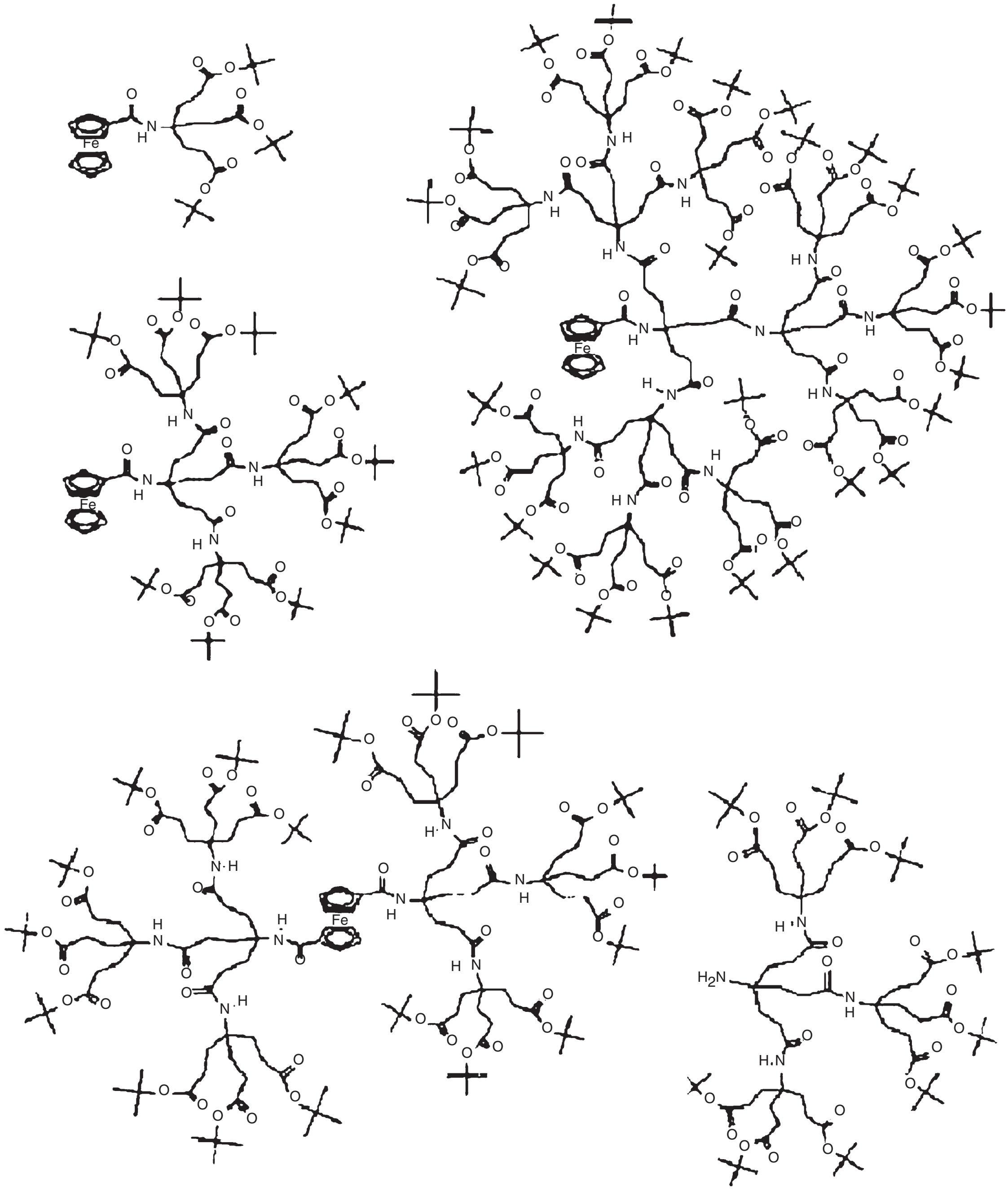


19

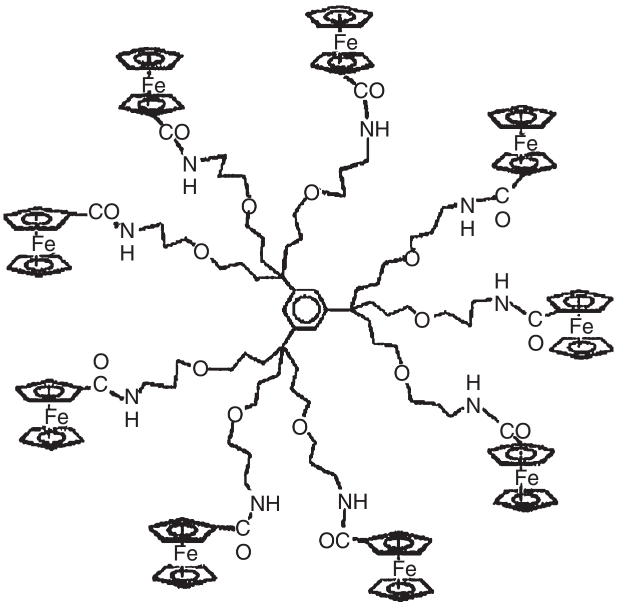
Ferrocene has also been encapsulated inside a symmetric ether–amide shell—the synthesis again begins with the use of 1,1′-bis(chlorocarbonyl)ferrocene at the core,[173] and these dendrimers have been examined in relation to their anion-binding ability.[174] Ferrocene dendrimers have also been prepared with cyclotriphosphazene cores,[175] trisubstituted benzene cores,[176,177] and oligo-alkylamine cores.[178] Ferrocene has been used as the central subunit in a number of dendritic structures such as the series of dendrimers shown as **20**; again, the initial synthesis begins with chlorocarbonylferrocene.[179] It has also been used in many cases as the peripheral group on molecules such as those shown in **21**.[180]

Polyamidoferrocenylalkylthiolate–Au nanoparticles (AuNP), AuNP-cored polyferrocenyl dendrimers, and AuNPs containing a nonasilylferrocenyl dendron have been synthesized. These AuNPs selectively recognize the anions $H_2PO_4^-$ and adenosine–5′-triphosphate (ATP^{2-}) with a positive dendritic effect, when monitored by cyclic voltammetry.[181] There are numerous examples with ferrocene as an end group.[182] The synthesis of three families of phosphorus-containing dendrimers having chiral ferrocene subunits precisely placed at one individual shell within their skeleton has been reported, and the influence of the progressive "burying" of the chiral ferrocene derivatives upon their electrochemical and chiroptical properties discussed.[183] The first synthesis of a series of glutamic acid-based dendrimers having a central ferrocene core has been described. The redox properties of the ferrocene core are attenuated by the increase in the peptide dendritic sphere.[184] Water-soluble multiferrocenyl ammonium compounds, which are dendritic, have been prepared by condensation of dendritic primary amines with ferrocenecarboxaldehyde, and tetranuclear ferrocenes, shown as 22, have been obtained by quaternization of dimethylaminoethylferrocene with a range of multifunctional benzylic bromides.[185]



20

Unsymmetrical aryl alkyl ether dendrimers with a ferrocene core which are based on the (3,5-dihydroxybenzylalcohol) unit have been prepared: essentially, these species are prepared by condensation of ferrocenoyl fluoride with a benzyl alcohol at the center of the dendrimer.[186]



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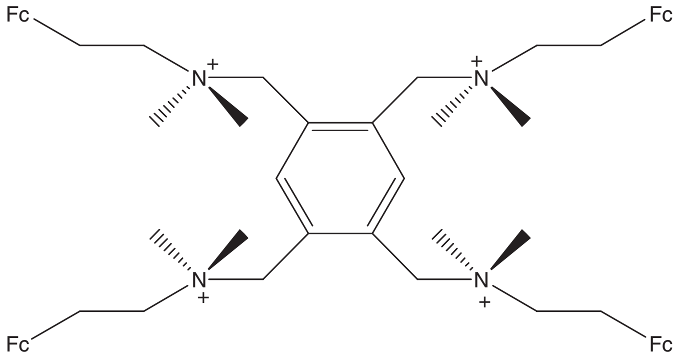

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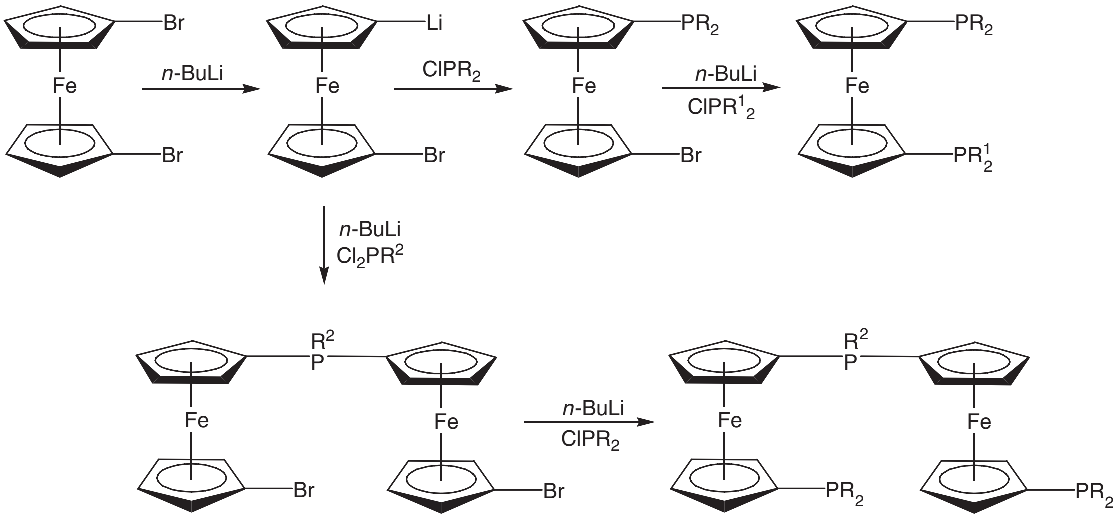
6.05.6 Ligands Based on Ferrocene

The ferrocene core continues to be used as a useful template for the design of an ever-increasing number of ligands. The most frequently used of these are the ferrocenylphosphines, which are now one of the most common ligand families used in transition metal-based catalysis. A significant volume of literature is also dedicated to the use of chiral ferrocene ligands for use in asymmetric synthesis. However, there are many more families of ferrocene-based ligands, based on the substitution of the cyclopentadienyl rings. These will briefly be reviewed here.

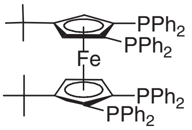
As discussed, ferrocenylphosphines are now one of the most important ligand classes used in transition metal-catalyzed processes. The most well known remains the widely used ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf), which has been used in a vast array of organometallic complexes. Since the publication of COMC (1995), a review has been published which covers the structures of complexes.[187] There follows a brief review of typical examples of the complexes of dppf and its derivatives and analogs; however, the sheer volume of literature on these complexes of dppf is again beyond the scope of this present review.



Scheme 2

Methoxycarbonylation of styrene to methylarylpropanates has been catalyzed by palladium complexes of dppf and its ruthenocenyl and osmocenyl analogs.[188] Both dppf and dippf, and its isopropylphosphine-substituted analogs have been used in ruthenium-catalyzed transfer hydrogenations of ketones,[189,190] and they have been used as ligands in ruthenium alkylidene chemistry.[191] Chiral cyclopalladated complexes containing dppf have also been used as antitumor agents,[192] as have platinum complexes of ferrocene-derived phosphonate ligands.[193] This general area of research has been reviewed recently as part of a broader review article.[194] A simple and effective methodology has been used to obtain unsymmetric 1,1′-disubstituted ferrocenylphosphines. This is based on the monolithiation of 1,1′-dibromoferrocene (Scheme 2).[195] A simple adaptation allows the synthesis of diferrocenyltriphosphines, which possess interesting coordination chemistry.[196,197]

Chiral ligands have been obtained by quenching the lithium salt intermediates using chiral phosphine-quenching reagents.[198,199] Again, further adaptation allows for the synthesis of a range of triferrocenylphosphines.[200] A simple synthesis has been developed for the preparation of ferrocenylmethylphosphines, which have proved highly effective ligands in the palladium-catalyzed formation of methylpropionate from methanol, carbon monoxide, and ethene.[201] An alternate synthetic methodology for these phosphines is to prepare the ferrocenes directly from the appropriately substituted cyclopentadienyl salts; for example, 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene, **23**, was obtained from 1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyllithium on reaction with $FeCl_2$. The *t*-butyl group is used to sterically direct the lithiation to the 2-position in the cyclopentadienyl precursor by blocking the 3-position.[202,203] In the absence of the *t*-butyl group, 1,3-diphosphines are obtained as the major products. The coordination chemistry of these ligands has been explored in detail.[204,205] The ligands $[\{C_5Me_3\text{-}1,2\text{-}(PPh_2)_2\}_2Fe]$ and $[\{C_5Me_3\text{-}1,2\text{-}(PPh_2)_2\}Fe\{C_5Me_4(PPh_2)\}]$ have also been obtained using the same strategy.[206] Mixed phosphine–phosphonate ferrocene ligands have also been prepared by the ring-opening reaction of ferrocene–diylphenylphosphine—for example, an enantiopure phosphine–menthylphosphonite ferrocene compound, **24**, has been obtained, and this ligand has been used in Rh-catalyzed hydroformylations and Pd-catalyzed Heck reactions.[207,208] The asymmetric ring-opening reaction also allows for the one-step preparation of chiral ferrocenyl phosphines.[209]



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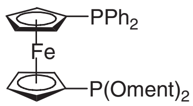
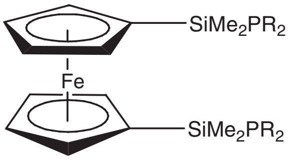


24

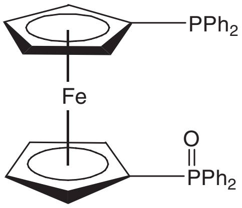
Hydroxylmethylphosphine synthesis has been a feature of the Henderson group. On reaction with formaldehyde, the ferrocenyl phosphines $FcPH_2$ and 1,1′-$Fc(PH_2)_2$ produce the hydroxymethylphosphines $FcP(CH_2OH)_2$ and

1,1′-Fc{P($CH_2OH)_2\}_2$.[210] Some other papers involving the use of dppf and its analogs with only a brief explaination of each are as follows: substitution reactions on [Au_2Cl_2(μ-dppf)];[211] chloride substitution of [CpRu(dppf)Cl];[212,213] the crystal structure of *cis*-Pd(κS-SOCMe$)_2$(dppf),[214] platinum complexes of the type [{Pt(dppf)(C=CPh$)_2\}_2M]_2BF_4$, M = Cu, Ag.[215] Silicon-containing ferrocenylphosphine ligand **25** has also been prepared directly from {Fe(η-$C_5H_4SiMe_2Cl)\}_2$ on reaction with lithium phosphides.[216]



25

The palladium complex of 1,1′-bis(diphenylphosphino)ferrocene oxide (dppfo), **26**, has been prepared from $Na_2[PdCl_4]$ in a dichloromethane–methanol mixture, and the complex found to have the *trans*-configuration. The solution chemistry of the complex was investigated for a range of solvents.[217]



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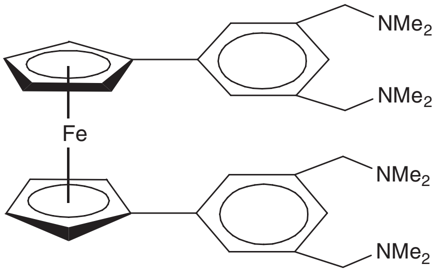
There are several pincer ligand designs based on the ferrocenyl backbone either with a spacer such as the ligands shown as **27**,[218] or without, such as the ligand shown as **28**.[219–222]



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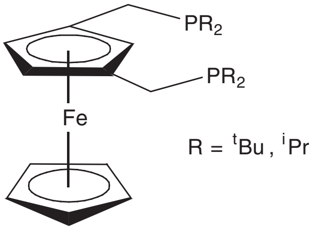

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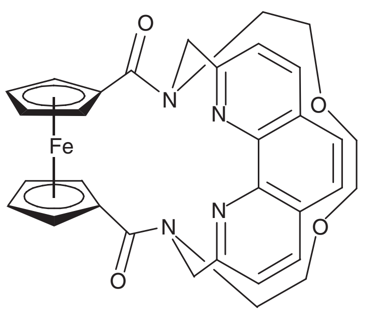
Cyclotrimerizations of phenylethynes using palladium-dppf complexes have been studied,[223] and the coordination chemistry of 1,1′-bis(diphenylselenophosphoryl)ferrocene with gold and silver has been investigated.[224] The novel 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene-type phosphines may be used as ligands in palladium-catalyzed Suzuki cross-coupling and Heck alkylation of aryl halides.[225]

A series of papers has been devoted to the palladium-catalyzed methoxycarbonylation of alkenes using ferrocene-based ligands, which are based on dppf-type derivatives. Interestingly, in the methoxycarbonylation of ethene, when 1,1′-bis(diphenylphosphino)octamethylferrocene (dppomf) is used as a ligand, the derived catalyst results in the selective production of methyl propanoate, whereas when dppf is used as a ligand, the derived catalyst leads to the formation of a series of low molecular weight oligoketones.[226] The similar methoxycarbonylation of styrene gave primarily 3-phenylpropanoate, with up to 85% regioselectivity.[227,188] The hydroformylation of styrene using platinum catalysts has also benefited from the use of heterobidentate ferrocenyldiphosphine ligands.[228] Di-*t*-butyl(ferrocenylmethyl)phosphine when used as a ligand is effective in the palladium-catalyzed cross-coupling reactions;[229] however, its 1,2-disubstituted analog is one of the most effective ligands in the methoxycarbonylation of ethene to selectively give methyl propionate with high turnover numbers.[230]

There have been a significant number of papers published in ferrocenes containing pyridine-related side-groups, which follows the early work on ferrocenylpyridines published in the early 1960s. The 1,1′-bis(4-pyridyl)ferrocene ligand gives a family of coordination complexes which are typically dimeric. The metals used were Ag, Cd, Cu, and Zn in this particular investigation.[231] A redox-active cryptand which contains both aromatic and phenanthrolinyl units in the macrocyclic structure, shown as **29**, has been prepared.[232] An interesting preparation of 1,3,1′,3′-tetrasubstituted bipyridylborane has been effected in the reaction of ferrocenylboranes[233] with bipyridine. An example is shown as **30**.[234]



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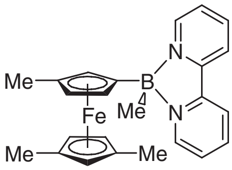
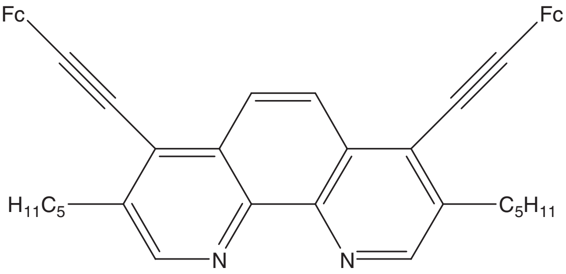


30

Another ligand prepared in this series has a 1,10-phenanthroline ligand tethered to ethynylferrocene and is shown as **31**.[235] Again a number of "rigid rod" type ferrocenylpyridines and bipyridines have been obtained by coupling 1,1′-diiodoferrocene with a range of ethynylpyridines and bipyridines.[236]

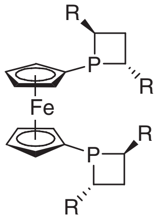


31

Other papers that have been published in this general area include ferrocenylphosphine-based amine-free Sonogashira coupling reactions;[237] the cross-coupling of thiols with aryl halides using Pd catalysis with bdipf (bdipf = 1,1′-bis(diisopropyl)ferrocene);[238] chiral ferrocene-based phosphine-imine ligands in palladium-catalyzed allylic alkylation of cycloalkenyl esters;[239] palladium-catalyzed coupling of bis(ferrocenyl)mercury with aryl iodides;[240] *P*,*N*-donor ferrocene ligands in asymmetric allylic alkylation;[241] an investigation on the role of planar chiral ligands with *S*,*N*- or *P*,*N*-ferrocene ligands in palladium–catalyzed allylic substitutions;[242] palladium-catalyzed arylation of malonates using ferrocenyldialkyl phosphine ligands.[243]

The preparations and structures of 1,1′-diphenylphosphinoferrocenecarboxaldehyde and 1,1′-diphenylphosphinoferrocenylmethanol and 1,1′-diphenylphosphinoferrocene carboxylic acid all use the approach used by Butler *et al.*[195,244,245] An extremely useful synthesis which has been developed is the one-pot method using ferrocenecarboxaldehyde which is protected *in situ* with *N*-methylpiperazide which is then used to direct lithiation into the 1′-position.[246]

Chiral 1,1′-diphosphetanylferrocenes such as **32** have been synthesized and have been found to be efficient ligands for use in hydrogenation chemistry.[247] The ferrocene analog of the BIPNOR ligand, **33**, has been produced and its use in catalysis has been examined.[248] The reaction of 1-(R-aminoalkyl)-2-diphenylphosphinoferrocenes with glyoxals gave 1,2-ferrocenediylazaphosphinines of the general type **34** as a new class of planar-chiral ferrocenes via an unusual heterocyclization.[249]



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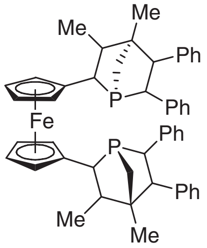

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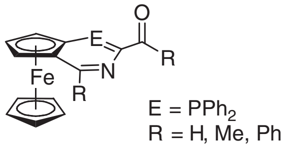

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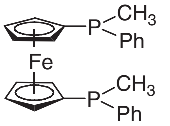
The discovery that it is possible to ortholithiate dibromoferrocene with LDA has allowed the synthesis of a range of new ligands.[19,30] In very elegant synthetic work, the asymmetric synthesis of (*S*,*S*)-(+)-1,1′-bis(methylphenylphosphinoferrocene) shown as **35** has been achieved.[250] The same synthetic methodology allowed the synthesis of the ligands of the type shown in **36** which have been structurally characterized and their use in catalytic systems examined.[251]



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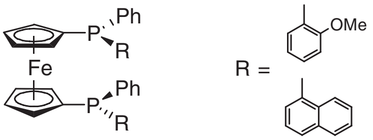

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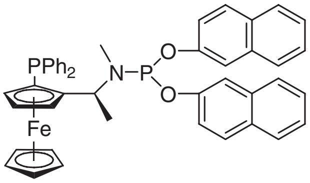
A series of ferrocene-based chiral dinuclear complexes of Pd(II) and Pt(II), containing the deprotonated form of the ligand (*R*)-1-[(*S*)-diphenylphosphino)ferrocenyl]ethyl mercaptan, have been prepared, which further extends the utility of this ligand class.[252]

Other work involving complexation of ferrocenylphosphines include: the preparation of silver complexes of diferrocenylphosphine;[253] a trinuclear dirhenium complex;[254] dppf as a spacer ligand between rhenium centres;[255] dppf in gold complexes;[256] palladium and platinum complexes from the carboxylation of [(dppf)MCl$_2$], M = Pd, Pt complexes;[257] technetium and rhenium heterometallic complexes;[258] mixed silver/nickel complexes;[259] manganese and rhenium complexes;[260] the photo-oxidation of bis(dppf)PdCl$_2$;[261] electrospray mass spectrometric characterization of ferrocenylphosphines;[262] the structure determination of *trans*-[PdMeCl(PPh$_2$Fc)$_2$]·2C$_6$H$_6$;[263] [Pt(dppf)-(H$_2$O)][OTf]$_2$ structure;[264] dppf in ruthenium clusters;[265] the crystal structure of [PdCl$_2$(dppfo$_2$)];[266] modified Pt(dppf)Cl$_2$ complexes and their interactions with L-cys and L-met;[267] osmium complexes of dppf;[268] dpopf as a ligand in silver(I) complexes;[269] transition metal clusters containing dppf ligands;[270] Ag(I) triflate dppf complexes;[271] a re-examination of the redox behavior of the 1,1′-bis(diphenylphosphino)ferrocenium monocation;[272] fullerene palladium and platinum complexes;[273] cobalt nitrosyl complexes;[274] the oxidation of iron versus ruthenium in dppf ruthenium complexes;[275] dimeric ruthenium(II) and rhodium(III) complexes bridged by dppf;[276] (η^6-arene)ruthenium (II) complexes of dppf;[277] [Rh(dppf)$_2$] and [Na(THF)$_5$][Rh(dppf)$_2$]·THF complexes;[278] copper–ruthenium carbonyl cluster complexes of dppf;[279] two solid forms of [(dppf)Rh]BPh$_4$;[280] the solid-state structure of dppf oxide and sulfides;[281] carboxylate Pd(II)(dppf) complexes;[282] a study of the thermal behavior of (dppf)MCl$_2$, M = Ni, Pd, Pt;[283] silver adducts of the type AgX : dppf (1 : 1) (X = halide or oxyanion);[284] indium–palladium and silver–palladium complexes;[285] gold(I and II) complexes of 1,1′-bis(diphenylthiophosphoryl) ferrocene;[286] mass spectrometric studies on homoleptic and mixed aryl dichalcogenide bis(diphenylphosphino)ferrocene nickel, palladium, and platinum complexes;[287] gold–manganese carbonyl clusters containing dppf;[288] dppf platinum dithiolate complexes.[289]

6.05.6.1 Chiral Phosphines

Most syntheses continue to use the chiral-directing group approach or the use of chiral-protecting groups for metallation. The synthesis and application of a new family of air-stable, highly unsymmetrical ferrocene-based phosphine–phosphoramidites, exemplified by **37**, has been described, and their use in Rh-catalyzed asymmetric hydrogenation reactions examined.[290] The synthesis of phosphine–chiral hydrazone ligands of the type **38** has also been reported, and their application to the palladium-catalyzed asymmetric allylic alkylation examined.[291]



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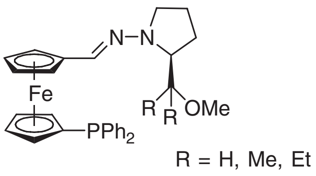
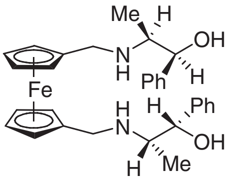


38

The synthesis of novel 1,1′- and 1,2-disubstituted ferrocenyl amino alcohols of the type shown in **39** has been developed, and their application as catalysts in the enantioselective alkylation of benzaldehyde investigated.[292] The catalytic behavior of **40** in palladium-catalyzed allylic alkylation reactions was also investigated, and the experimental results obtained rationalized with a computational study.[293]



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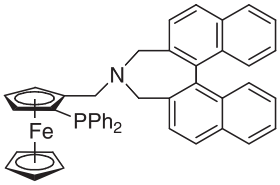
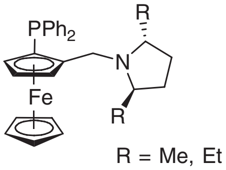


40

The preparation of 2-(S_p)-[(*trans*-(2*R*,5*R*)-2,5-dialkylpyrrolidinyl)methyl] ferrocenyldiphenylphosphines, **41**, new ferrocenylphosphinamine ligands possessing one site of planar chirality and two stereogenic centers, has been described, and their application in palladium-catalyzed asymmetric allylic alkylation reaction has been investigated.[294]



41

A series of new chiral (iminophosphoranyl)ferrocenes have been synthsized, and their coordination chemistry and catalytic properties in rhodium-catalyzed asymmetric hydrogenation investigated.[295,296]

6.05.6.1.1 Ferrocenyl oxazolines

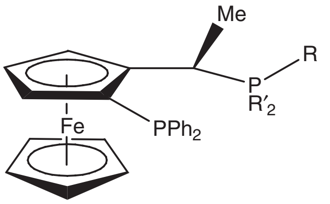
Ferrocenyloxazolines have become a useful class of ligands in their own right. The general research area of ferrocenyloxazoline chemistry,[297] which was tentatively developed in the early 1980s, has been taken forward by Sammakia,[298–300] Richards,[301–304] and Uemura[305–309] with their more detailed synthetic work. The focus was and still is on the synthesis of asymmetric ligands for use in catalysis. Today, a considerable number of these exist, and for research purposes, the reader is directed to a pertinent review which covers the literature on planar chiral 2-ferrocenyloxazolines and 1,1′-bis(oxazolinyl)ferrocenes to 2002.[310] The synthetic methods available typically begin with ferrocenylcarbonitrile, ferrocenecarboxaldehyde, or ferrocenylcarbonyl chloride. The oxazoline function is typically used as an *ortho*-directing reagent, and thus a large number of compounds are accessible by the use of the broad range of quench reagents available in organo-lithium chemistry. A number of bis-oxazolines are also accessible as well as unsymmetrically substituted ferrocenyloxazolines. There are many research papers on the substitution chemistry of such ferrocenyloxazolines, which are presented here.[311–371]

Further examples of papers are 4-ferrocenyl-1,3-oxazoline ligands in asymmetric allylation reactions;[372] *ortho*-silylation of 2,2,′-bis(oxazolinyl)-1,1′-bis(diphenylphosphino)ferrocenes in palladium-catalyzed asymmetric allylic alkylations;[373] polymer-supported ferrocenyl oxazalines for asymmetric phenyl-transfer reactions;[374] 1′-substituted ferrocenyl oxazolines in enantioselective diethylzinc transfer reactions[375] and in asymmetric allylic substitution reactions.[376] Ferrocenyloxazolines have also been used in the preparation of planar chiral phosphinoferrocenylcarboxylic acids,[377] and oxazolines have been used as ligands in Pd-catalyzed allylic substitution reactions,[378,379] lithiation and phosphorylation,[380] synthesis of the first C_2-symmetric diphosphine with only planar chirality from ferrocenyloxazoline precursors.[381]

6.05.6.1.2 Chiral synthesis

There are also a number of review articles which document the use of chiral ferrocene ligands in general asymmetric catalysis.[382,383] A range of chiral phosphines of the general type **42** have been prepared beginning with (*N*,*N*′-dimethylamino)ethyl ferrocene (Scheme 3).[384]

Related ligands of the type represented by **43** have been successfully used in asymmetric hydrogenation reactions of dehydro-α-amino acid derivatives.[385] A *trans*-chelating bis-phosphine **44** derived from the TRAP ligand,[386] which only possesses planar chilarity, has been prepared in seven steps beginning with a ferrocenyloxazoline.[387] A new series of planar chiral ligands of the general type **45** have also been prepared beginning with *N*,*N*-diisopropylferrocenecarboxamide.[388]



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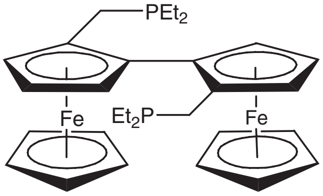

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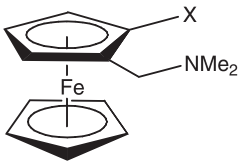
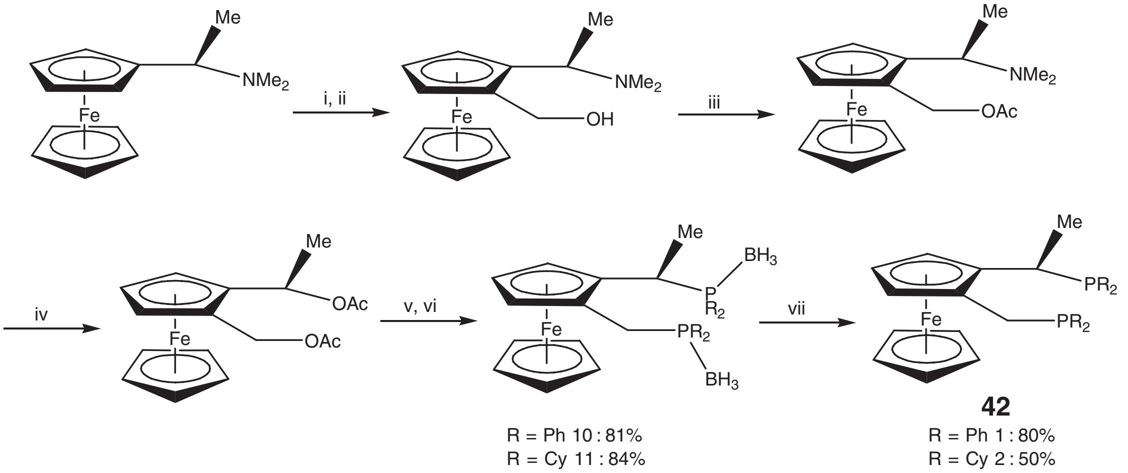


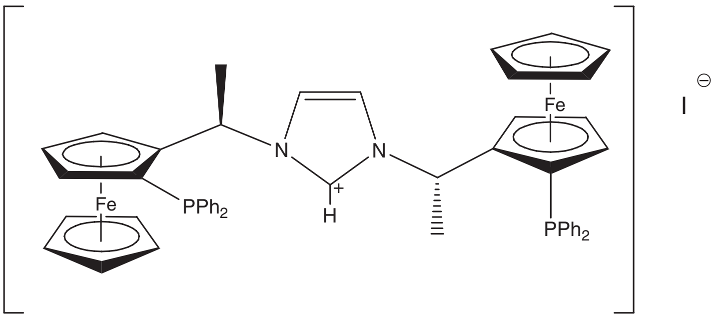
X = SPh, SMe, PPh_2, OMe

45

A related chiral imidazolium salt, 1,3-bis[(*R*)-1-(*S*)-2-(diphenylphosphinoferrocenyl)ethyl]-imidazolium iodide, **46**, has also been prepared in three steps from (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine.[389]



Scheme 3 Reagents and conditions: i, *t*-BuLi, Et_2O, then DMF; ii, $NaBH_4$, MeOH; iii, Ac_2O, DMAP, Et_3N, RT, 1 h; iv, Ac_2O, 100 °C, 45 min; v, HBF_4, CH_2Cl_2, then HPR_2, CH_2Cl_2, RT; vi, BH_3Me_2S, THF, RT, 1 h; vii, morpholine for 1 or HBF_4EOEt_2, RT for 2, 12 h.



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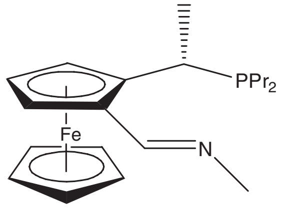
In work by the same research group, the synthesis of chiral ferrocenyl-iminophosphines of the type **47** has been described, and the authors have used them in palladium-catalyzed allylic alkylation reactions,[390] and related pyridine ligands have also been prepared where pyridine is a substituent on the carbon of a chiral ferrocenylimine.[391]



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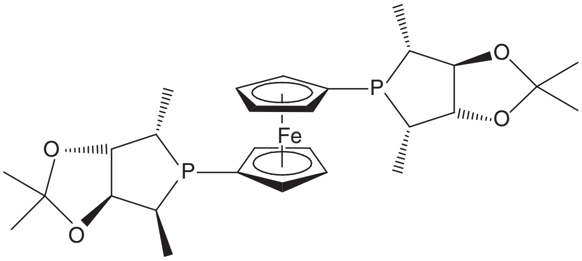
A new borohydride reduction, which is catalyzed by an optically active β-ketoiminato Co (II) complex, has been used in the preparation of chiral ferrocenyl diols from 1,1′-dibenzoyl- and dialkanoylferrocenes with ee's greater than 99% (with dl : *meso* ratios from 81 : 19 to 89 : 11).[392] A novel chiral ferrocene ligand has been obtained in the reaction of 1,1′-bis(phosphino)ferrocene with an optically active 1,4-diol cyclic sulphate **48**.[393] Also, the asymmetric synthesis of chiral α-ferrocenylalkylamines has been developed using an imine reduction methodology to give as products molecules such as **49**.[394]



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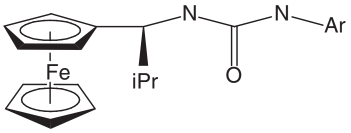

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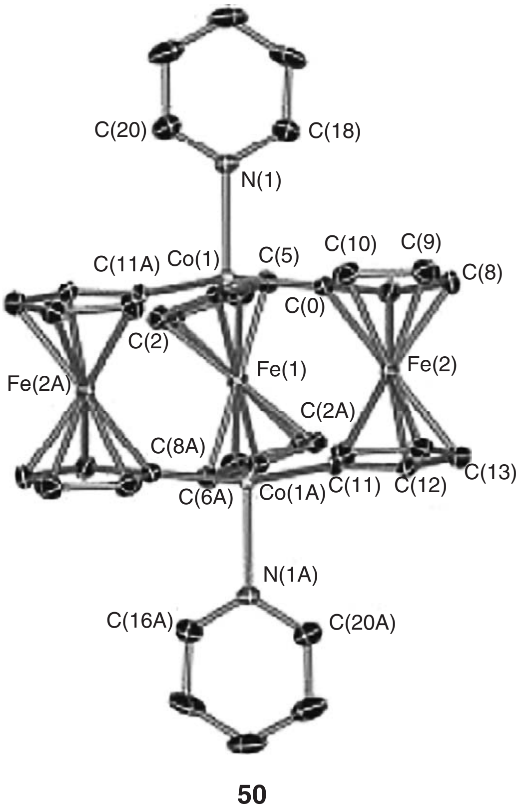
A series of chiral C_1- and C_2-symmetry ferrocenyl-Schiff bases, aminoalcohols, and phosphine-amides for asymmetric diethylzinc addition to aldehydes has also been prepared.[395]

6.05.6.2 Ferrocenophanes

The ring-opening polymerization (ROP) of ring-strained ferrocenophanes has progressed over the past decade or so from basic synthesis in the early stages to more sophisticated preparations of tailored polymers to the stage where the emphasis has latterly been on applications. There are several review articles covering this area of research which are detailed as follows: neutral and cationic macromolecules based on iron sandwich complexes;[396] the synthesis of polymetallocenes with predictable optical properties;[397] polyferrocenylsilanes for electronic and photonic applications;[398] toward the synthesis of supramolecular inorganic polymers;[399] polyferrocenylsilanes—general article;[400] ROP of strained metallophanes;[401] organometallic polymers with transition metals in the main chain;[402] ROP of strained metallocenophanes: the discovery and development of new routes to high molecular weight poly(metallocenes);[403] ROP of silicon-bridged [1]-ferrocenophanes;[404] route to polymers with skeletal transition metal atoms;[405] general synthesis of [1]- and [2]-ferrocenophanes with sterically demanding trimethylsilyl groups on the cyclopentadienyl ring;[406] general review on ROPs;[407,408] short general review of ring-opening metathesis polymerization (ROMP) of metallocenophanes.[409]

A summary of individual papers follows. The syntheses of a range of [2]-ferrocenophanes with carbon–germanium and carbon–tin bridges have been described. These are obtained from the reactions of $[(\eta\text{-}C_5H_4Li)Fe(\eta\text{-}C_5H_4Li)CH_2Li]\cdot TMEDA$ with Cl_2ER_2, E = Ge, Sn, R = aryl, alkyl.[410] Digalla[1,1]ferrocenophane has also been prepared by the Jutzi research group,[411] together with a trinuclear gallium-bridged ferrocenophane **50**, which is described as a ferrocenophane with a carousel structure.[412] The same group has prepared [3]-ferroceneophanes with tetramethyldisiloxane bridges,[413] and they have exploited the use of dimethylsilandiyl-bridged dicyclopentadienyl ligands in the synthesis of ferrocenophanes.[414] A general article by the same group has documented their research strategies for cyclopentadienyl ligand modification.[415]



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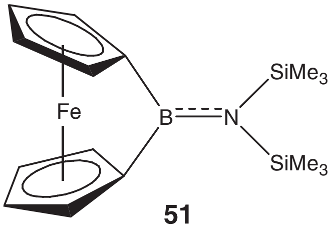
Ferrocenophanes may also be obtained by ring-closing metathesis.[416] Related to this is the preparation of the ring-strained 1,2-(1,1′-ferrocenediyl)ethane, which may be obtained in a six-step synthesis.[417] *ansa*-Ferrocenes have also been prepared with both trisulfide and hydrocarbon straps, that is, with both a C_2-bridge and S_3-bridge.[418]

6.05.6.2.1 Silicon-bridged ferrocenophanes

The reaction of dichlorodiferrocenylsilane with 1,1′-dilithioferrocene gave the trimetallic ferrocenophane, $FcSiFc_2$, in high yield.[419] The insertion of a platinum(0) fragment into the silicon–carbon bond of a silicon-bridged ferrocenophane has been achieved to give the ferrocenophane $[Fe(\eta\text{-}C_5H_4)_2Pt(PEt_3)_2SiMe_2]$ which may then be used in further synthetic transformations.[420,421] Again related to this was a general study of the Pt(II) or Pt(0)-catalyzed ring-opening reactions of [1]-ferrocenophanes.[422] A [2]-platinasilaferrocenophane $[Fe(\eta\text{-}C_5H_4)_2Pt(COD)SiMe_2]$, which functions as a pre-catalyst for the ROP of [1]-ferrocenophane was isolated on reaction of the $SiMe_2$-bridged ferrocenophane with $[Pt(COD)_2]$.[423] The first [1,1]-ferrocenophane $[\{Fe(\eta\text{-}C_5H_4)_2SiMe_2\}_2]$ was obtained in a five-step synthetic procedure.[424] Interestingly, it is also possible to polymerize [1]-ferrocenophane with γ irradiation.[425]

The basic ring-opening reactions of ferrocenophanes have developed into a mature research area, the most significant work has been carried out by the Manners' research group. The essential synthetic methodology is to react a ring-strained ferrocenophane with a alkyllithium reagent or a metal salt to initiate polymerization. There now exists a broad literature based on the subject, and several reviews have been published.[426–432]

The ROP of a series of [2]-ferrocenophanes with unsymmetrical C–E bridges (where E = substituted Si, P, or S) has been investigated. These compounds were prepared by reaction of the dilithium salt $[(\eta\text{-C}_5\text{H}_4\text{Li})\text{Fe}(\eta\text{-C}_5\text{Me}_4\text{CH}_2\text{Li})]$ with the relevant Cl_2ER_x species.[433] The first tin-bridged ferrocenophanes $[\text{Fe}(\eta\text{-C}_5\text{H}_4)_2\text{SnR}_2]$ ($\text{R} = {}^t\text{Bu}$, mesityl) were obtained as orange crystalline solids which could be polymerized despite their smaller ring tilt angles in comparison with other [1]-ferrocenophanes.[434] The first boron-bridged [1]-ferrocenophane was also reported, which is shown as **51**.[435]



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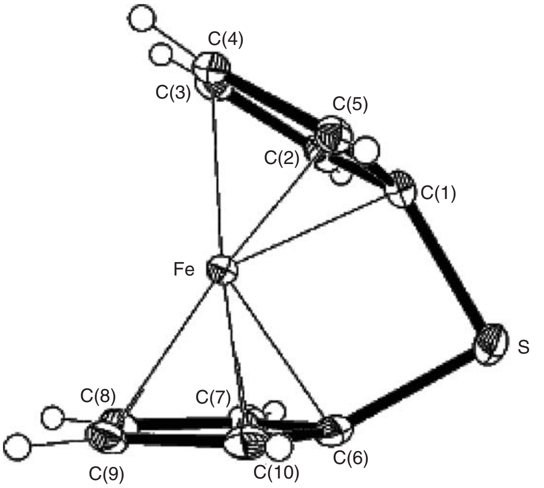
Similarly [1]-thia- and [1]-selena-ferrocenophanes may be obtained and polymerized. These S- and Se-bridged species are shown as **52** and **53**.[436,437]



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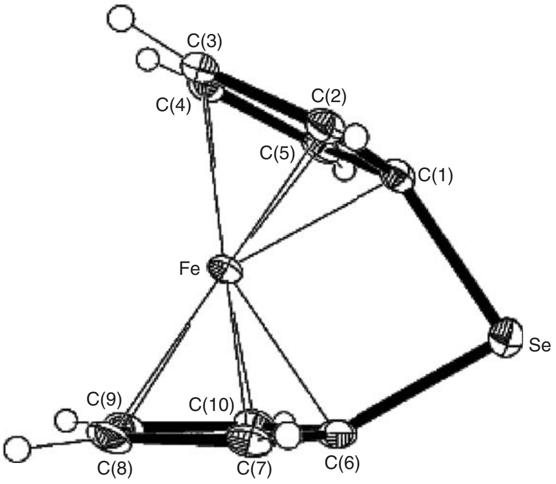

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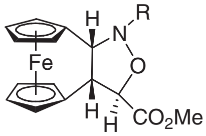
The transition metal-catalyzed ROP of silicon-bridged [1]-ferrocenophanes, when carried out in the presence of methylphenylsilane or chlorosilanes, facilitates the synthesis of polymers of controlled molecular weights, which are capped by an end-group silane derived from the added silane or chlorosilane.[438] There are many documented synthetic methods for the formation of ferrocenophanes based on Si in the bridge.[439] The synthesis of miktoarm (heteroarm) star co-polymer using anion polymerization with SiCl_4 has been reported. The polymerization essentially proceeds to form micellar polymers.[440] The platinum-catalyzed ring opening of silicon-bridged ferrocenophanes, in which the silicon has been substituted with acetylene groups, has been effected and shown to give high molecular weight polymers in addition to a cyclic dimer $[\text{Fe}(\eta\text{-C}_5\text{H}_4)_2\text{SiMe}(\text{C}{=}\text{CPh})]_2$ in one instance.[441] Related to this is an investigation of the nature of the catalyst involved in these platinum-catalyzed ring-opening polymerizations.[442] The ring-opening reaction may be effected by boron halides.[443]

Unsymmetrically disubstituted ferrocenes have been prepared also from ferrocene carboxaldehyde by first converting the aldehyde to the β-(methoxycarbonyl)ethenylferrocene which may be formylated at the 1′-position. A series of ferrocenophanes such as **54** were then obtained in two steps from the formylated products.[444]



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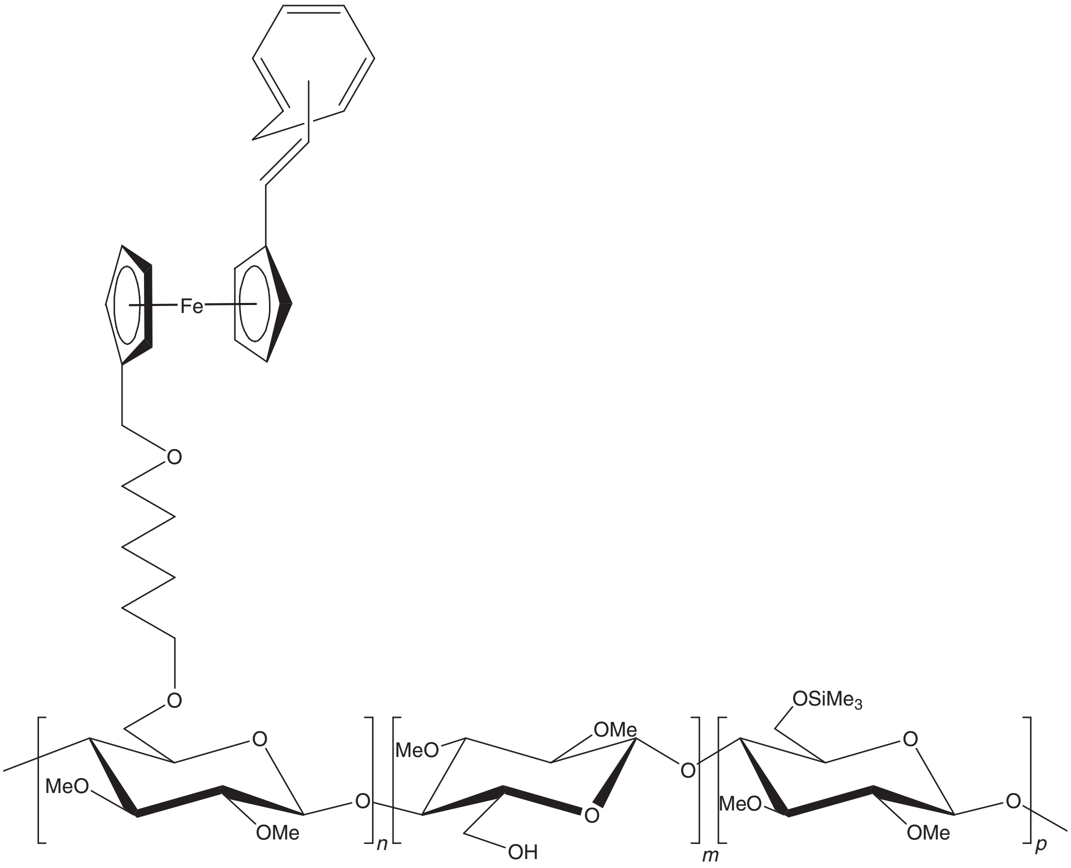
6.05.6.2.2 Polymer applications

A general review outlines the general features of ferrocene polymers.[445] Polymers with ferrocene in the backbone have been prepared by ROMP from 1,1′-((1-*t*-butyl)-1-3-butadienyl)ferrocene. These polymers are highly soluble, high molecular weight species.[446] Inorganic co-polymers which are based on poly(ferrocenyl)silanes have been used as precursors for nanostructured ceramics.[447] Photocurable ferrocene-containing poly(2-hydroxylethylmethacrylide) films have been developed for use in the medialert amperometric glucose biosensor; these were prepared by the incorporation of vinylferrocene into the polymerization of 2-hydroxyethyl methacrylate monomers.[448] A series of polymers based on ferrocene-substituted thiophene and terthiophene have been used as biosensors.[449] Polyanionic water-soluble poly(ferrocenylsilanes) have been prepared by the incorporation of sodium acetate in the polymer backbone by a simple and effective reaction of an alkyl iodide built into the polymer with the anion derived from methyl trimethylsilyl methylmalonate.[450] Similarly, thin-film water-soluble poly(ferrocenylsilanes) have been prepared by the combination of polyanions and polycations of the ferrocenylsilanes.[451] The palladium-catalyzed polycondensation has been used to obtain a series of poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylenes).[452] Polymers with [2.2]-paracyclophane and ferrocenes have also been prepared by palladium-catalyzed polycondensation; in this case, 1,1′-diiodoferrocene has been used as the precursor compound.[453] Cellulose-based polymers with long-chain pendant-substituted ferrocenes have been prepared by using the desymmetrization of 1,1′-tributylstannylferrocene as a precursor.[454] A typical section of polymer is shown as 55.



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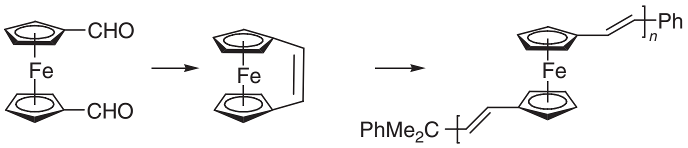
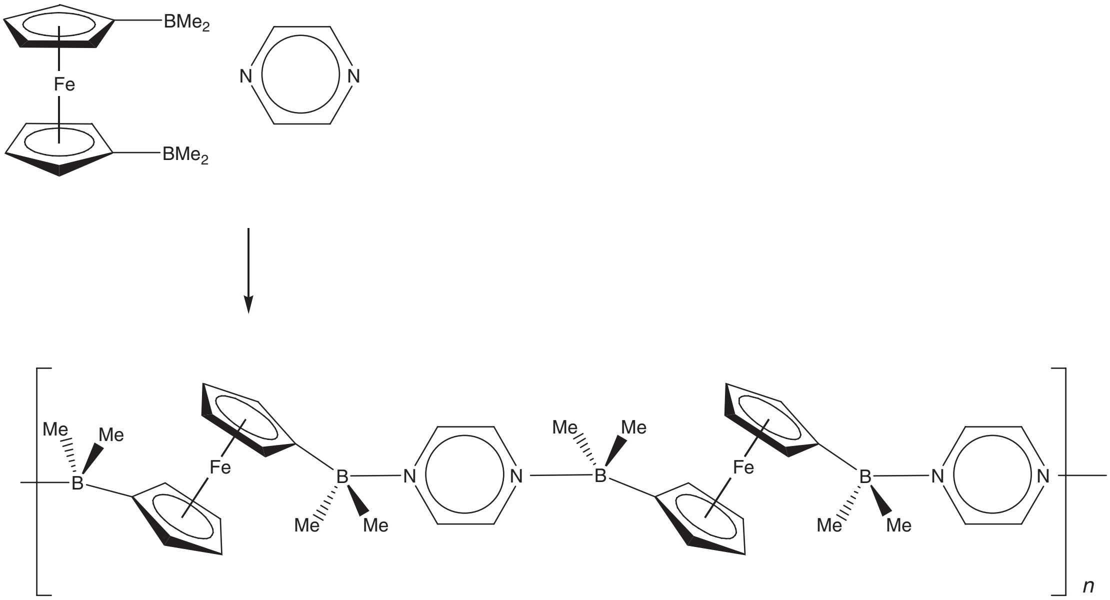


Scheme 4

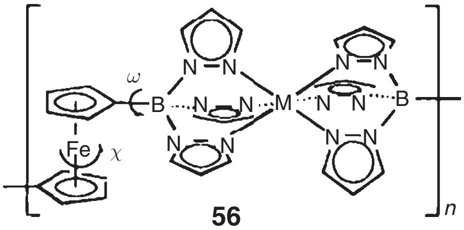


Scheme 5

One of the most elegant synthetic reports is based on the ring-opening metallocene polymerizations of *ansa*-(vinylene)ferrocene (see Scheme 4).[455]

Boron–nitrogen coordination polymers with ferrocene in the main chain have also been obtained by reacting 1,1′-$\mathrm{Fc(BMe_2)_2}$ with pyrazine (see Scheme 5).[456]

Another condensation of 1,1′-diiodoferrocene with a series of dialkynes has led to the formation of a series of poly(arylene-ethynylene) type polymers.[457,458] Bifunctional ferrocene-based tris(1-pyrazolyl)borates have been used to obtain a range of inorganic polymers with ferrocene in the backbone—see **56**.[459]



56

The living anionic polymerization of phosphorus-bridged [1]-ferrocenophanes initiated using *n*-BuLi has been studied. In this work, $\{(\eta\text{-}C_5H_4)_2FePPh\}_5$ has been isolated and reacted with sulfur.[460] The phosphonium-bridged ferrocenophane $[(\eta\text{-}C_5H_4)_2FePPhMe][OTf]$ was obtained by simple reaction of the corresponding phosphorus-bridged ferrocenophane with methyl triflate—this compound could be polymerized either by metal-induced or by thermal polymerization.[461] Poly(ferrocenyldimethylsilanes) have been used in reactive ion etch barrier applications.[462] Thermotropic liquid crystalline polymers have been made from poly(ferrocenylsilanes).[463] Table 1 describes the work carried out by the Manners group on ferrocene-based polymers.

Table 1 Studies on ferrocene-based polymers by the Manners research group

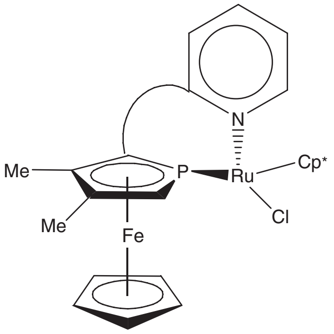
Description of publication	*References*
Diblock co-polymers from ethylmethylsila[1]ferrocenophane	464
Functionalization of polyferrocenylsilanes by hydrosilation	465
Ring-opening protonolysis of sila[1]ferrocenophanes to give silylium ions	466
The structure of (4-*t*-butylphenyl)phospha[1]ferrocenophane	467
The structure of methylchlorosila[1]ferrocenephane	468
Graft co-polymers of polystyrene-polyferrocenylsilane	469
Polyferrocenylsilane-based redox-active organometallic vesicles	470
Polyferrocenes with tunable refractive indexes	471
Lithographic applications of metallized polyferrocenylsilanes	472
Self-assembly of coil-crystalline polyferrocenylphosphine–polyferrocenyl silane–polysiloxane triblock co-polymers	473
Polyferrocenyl silane microspheres	474
Water-soluble cationic and anionic polyferrocenylsilane polyelectrolytes	475
ROPs of tin-bridged [1]-ferrocenophanes	476
Water-soluble polyferrocenylsilane electrolytes	477
Reaction of tin-bridged [1]-ferrocenophanes with metal carbonyls	478
Synthesis of polyferrocenylsilane–poly(aminoalkylmethacrylate)-block co-polymers	479
Poly(ferrocenylsilanes) with chloroalkyl side chains	480
Co-polymers of poly(isoprene-*b*-ferrocenylphenylphosphine)	481
Self-assembly of organometallic block co-polymers containing poly(ferrocenylsilane-*b*-dimethylsiloxane) in *n*-alkane solvents	482
Layer-by-layer self-assembly of organic–organometallic polymer electrostatic superlattices using poly(ferrocenylsilanes)	483
Borane adducts of *P*-phenylphospha[1]ferrocenophane	484
Nucleophilically assisted ROMP of group 14 element-bridged [1]-ferrocenophanes	485
Synthesis and ROP of phosphorus-bridged ferrocenophanes	486
Anionic ROPs of phosphorus-bridged ferrocenophanes	487
Structural characterization of the first mixed-ring [1]-ferrocenophane	488
Mössbauer study of dicarbon bridged [2]-ferrocenophanes	489
Hybrid borazine–phosphazenes and strained ferrocenophanes	490
Ring opening of S-, Se-, and B-bridged [1]-ferrocenophanes	491
Solid-state polymerization of $[Fe(\eta\text{-}C_5H_4)_2SiMePh]$	492
Transition metal-catalyzed ROP of silicon-bridged [1]-ferrocenophanes	493
Living anionic polymerization of phosphorus-bridged [1]-ferrocenophanes	494
Synthesis and ROP of tin-bridged [1]-ferrocenophanes	495
Transition metal-catalyzed ring-opening co-polymerization of silicon-bridged [1]-ferrocenophanes	496
Living anionic ROP of silica-bridged [1]-ferrocenophane	497
ROP of Si-bridged ferrocenophanes with chlorine substituents on silicone	498
Synthesis of poly(ferrocenylgermanes) and their co-polymers with poly(ferrocenylsilanes)	499
Synthesis of (1,1′-ferrocenediyl)methylphenyl silane	500
Synthesis and ROP of [1]- and [2]-metallocenophanes	501
Synthesis of high molecular weight unsymmetrically substituted polyferrocenylsilanes	502
The synthesis of the first [1]-silaferrocenophane with only one substituent on the silica	503
Self-assembly of a poly(ferrocene)-*b*-polysiloxane-*b*-polyferrocene triblock polymer	504
The synthesis of 1-stanna-2-boraferrocenes	505
Poly(ferrocenylsilanes) with alkoxy, amino, and aryloxy substituents at silicon	506
Silicon-bridged ferrocenophanes of methylated ferrocenes	507

6.05.6.3 Azaferrocenes and Phosphaferrocenes

A simple method to prepare 2,5-dimethylazaferrocene has been reported.[508] The lithiation of 2,5-dimethylazaferrocene with *sec*-butyllithium in the presence of TMEDA at low temperature progressed with Cp ring lithiation (54%), methyl group lithiation (38%) and β-pyrrolylaryl lithiation (8%). When benzyl chloride or *p*-methoxybenzaldehyde were used as quench reagents only the products from methyl group lithiation were isolated.[509] However, when other electrophilic quenches were used, such as chlorodiphenylphosphine, products of both methyl group lithiation and Cp ring lithiation were isolated. Tungsten complexes were readily obtained from the azaferrocene ligands by photolysis of the azaferrocene with tungsten hexacarbonyl.[510] Friedel–Crafts acylation of $W(CO)_5$ complexes of azaferrocenes is also possible.[511] The axial coordination of azaferrocene to transition metal centres has been reviewed up to 1995.[512] The electrochemical oxidation of azaferrocenes and the reactivity of azaferrocinium cations with Lewis bases have also been examined. It is concluded that in dichloromethane the cyclic voltammograms of these compounds indicate clean chemical reversibility; however, in more polar of coordinating solvents this is not so.[513,514] Mössbauer studies have also been carried out on the Cr, Mo, and W complexes of azaferrocenes.[515] Related to this is the ^{1}H NMR and Mössbauer study on substituent effects on azaferrocenes.[516] In more applied chemistry, the formation and quenching of the photoexcited triplet state of tetrasulfonated zinc phthalocyanine by azaferrocene quenches the S_1 state and 2,5-dimethylazaferrocene does not quench the S_1 state.[517] Similar work has also been carried out on the quenching of aluminum phthalocyanine complexes by azaferrocenes.[518] In addition, the photoreduction of both zinc- and aluminum-2,3-naphthalocyanine in the presence of azaferrocene has been examined under red light.[519] Pentamethylated and pentaphenylated azaferrocenes and azaruthenocenes have also been prepared and lithiated. Interestingly, these compounds lithiate on the pyrollyl ring relatively easily in contrast to the ferrocene-based analog compounds. Quenching with (−)-(1R, 2S, 5R)-menthyl-(*S*)-*p*-toluenesulfinate gives a separable mixture of enantiopure sulfoxide diastereomers which then may be reacted following separation with *t*-butyllithium and quenched with a range of electrophiles to give enantiopure products.[520,521] Similar sparteine-mediated lithiation has been undertaken to give enantiopure azaferrocenes.[522] A comparative study has also been made of the electronegativity versus lone pair shape in aza- and phosphaferrocenes.[523] Similarly in an earlier paper a comparative study has been carried out on the ^{57}Fe Mössbauer and ^{13}C NMR spectroscopy of aza- and phosphaferrocenes.[524]

A brief review has recounted the discovery and applications of phosphametallocenes.[525] The synthesis and structure of 1,1′-diphospha[2]ferrocenophane have also appeared: these derivatives are obtained starting with 1-phenyl-3,4-dimethylphosphole-2-carboxaldehyde in a six-step synthetic procedure.[526] A general mini-review on phosphorus heterocycles also highlights the synthesis and use of a number of phosphaferrocenes.[527] A phosphaferrocenium compound has also been prepared as its triiodide $[Cp^*Fe(C_{12}H_{20}P)][I_3]$.[528] Borane adducts of phosphaferrocenes have also been obtained simply by treating the appropriate phosphaferrocenes with boron tribromide.[529]

Phosphaferrocenes find increasing use as ligands both chiral and achiral: for example, a number of new P,N-chelate ligands based on pyridyl-substituted phosphaferrocenes have been prepared—the synthesis uses 2-formyl-3,4-dimethylphosphaferrocene as a precursor. A typical complex is shown as **57**.[530] A range of 2-(2′-pyridyl)phosphaferrocenes have also been prepared and used as ligands; an example of which is shown as **58**.[531] A number of chiral ligands such as phosphaferrocene-oxazoline ligands have also been prepared and are used in asymmetric catalysis, for example, **59**.[532]



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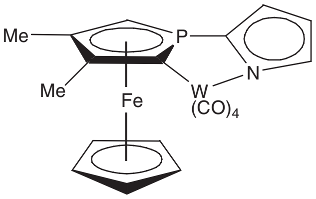

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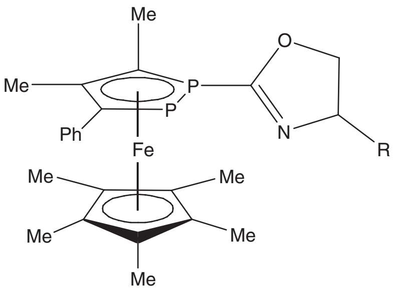
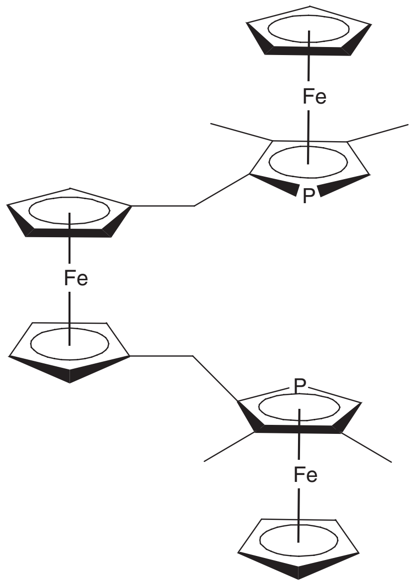


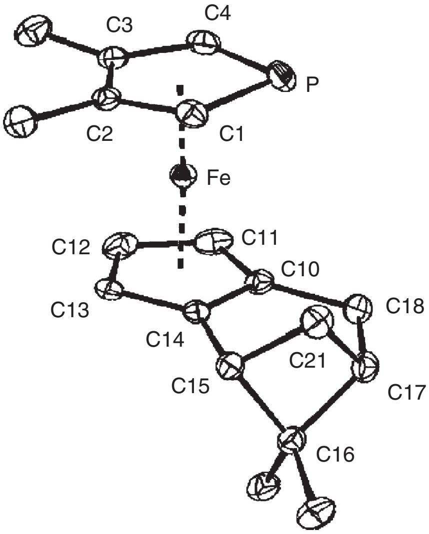
59

Cyclopentadienyl-substituted phosphaferrocenes have been prepared again using 2-formyl-3,4-dimethylphosphaferrocene and these have been elaborated into ferrocenes such as **60**.[533]



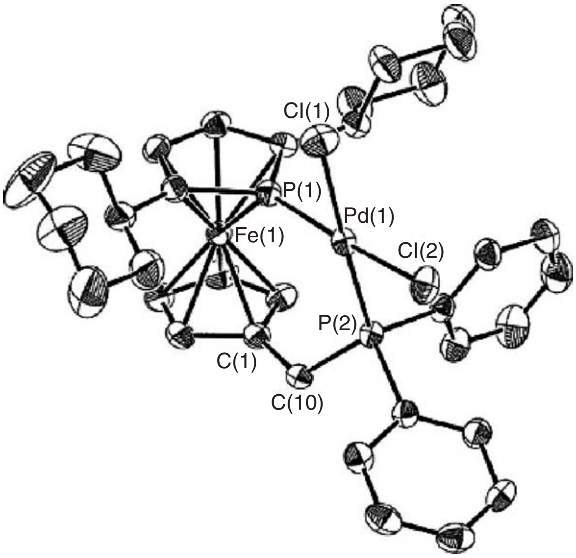
60

Enantiopure 2-formyl-3,4-dimethylphosphaferrocene has been prepared by column chromatography of the aminals from reaction with (*R*),(*R*)-1,2-di(*N*-methylamino)cyclohexane.[534] Chiral pinene-fused cyclopentadienyl-containing phosphaferrocenes have also been prepared directly from the iron tricarbonyl complex $\{PCp\mathrm{Fe(CO)_2}\}_2$ and *t*-butylphosphole, where *PCp* = pinene–fused cyclopentadiene. A crystal structure of the product phosphaferrocene is shown as **61**.[535]



61

In addition, the same research group has carried out the diastereoselective synthesis of α-phospharyl-substituted 2-ethylphosphaferrocenes.[536] New triple-decker complexes $[(\mu,\eta^5:\eta^5:\mathrm{C_4Me_4P})(\mathrm{FeCp^*})(\mathrm{MCp^*})](\mathrm{BF_4})$ (M = Rh, Ir) have been obtained directly from 1,2,3,4-tetramethylphosphaferrocene.[537] (−)-Menthyl-substituted phosphametallocenes have been investigated by variable-temperature NMR spectroscopy to examine the effect of the bulky methyl group on the ring rotation.[538] It has also been observed that phosphaferrocenes react with $[\mathrm{Pd(COD)Cl_2}]$ to afford *cis*-complexes of the type $[\mathrm{Pd(L)Cl_2}]$ which slowly decompose in solution to give dimeric complexes of the type $\{\mathrm{Pd(L)Cl}\}_2$.[539] Related phosphino-phosphaferrocenes have also been treated with $[\mathrm{Pd(COD)Cl_2}]$ to give a mixture of products which have been characterized by NMR spectroscopy.[540] A typical example of this type of ligand is shown as 62. Again chiral phosphino-phosphaferrocenes have been used as ligands in the Pd-catalyzed asymmetric allylic alkylation reaction.[541]



62

In summary the chemistry of ferrocene remains a core of organometallic chemistry as a whole both in terms of synthesis and applications.

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6.06
Dinuclear Iron Compounds with Iron–Iron Bonds

G Hogarth, University College London, London, UK

6.06.1 Introduction

The organization of the material in this review differs from that in COMC(1995) where it was covered in two separate sections, dinuclear iron compounds with and without hydrocarbon ligands. This divide now seems artificial and material from 1993 through 2004 is presented in a single section, subdivided according to the absence or presence of cyclopentadienyl ligands. The scientific content generally follows that in COMC(1995), a major new area being the study of dithiolate-bridged compounds as biomimetic models of the iron hydrogenase active site.

6.06.2 Diiron Carbonyl Complexes without Cyclopentadienyl Ligands

6.06.2.1 Homoleptic Diiron Carbonyls

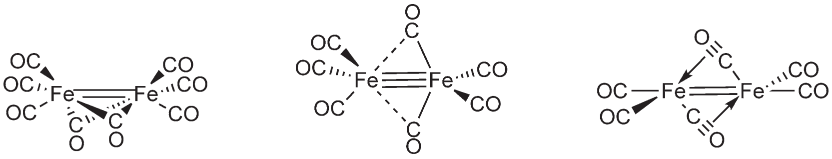
Homoleptic diiron carbonyls continue to be an area of considerable experimental and theoretical interest. It is slightly ironic given the title of this chapter that it now seems clear that there is little direct metal–metal bonding in $Fe_2(CO)_9$. A theoretical analysis based on a population–depopulation of the frontier molecular orbitals approach shows that while there is a weak direct metal–metal interaction as part of the metal-bridge bonding, this is significantly smaller than the strong direct repulsive through-bond iron–iron interactions. Hence, it seems that the co-facial bioctahedra are linked together through the metal-bridge bonding.[1] Other theoretical work on $Fe_2(CO)_9$ supports this idea.[2–5] In contrast to the MP2 approach, DFT analyses give a structure which is in excellent agreement with that seen experimentally and show that compared to the heavier homologs, the more contracted metal orbitals on iron lead to a relatively weak direct metal–metal repulsion.[2] A hybrid Hartree–Fock/DFT approach has been used to calculate the theoretical vibrational frequencies with *ab initio* methods for the first time.[4] A comparison with experimental values suggests that several of the current assignments are dubious and more work is needed in this area. Using ^{13}CO and $C^{17}O$ enriched samples, solid-state NMR measurements have led to the determination of the ^{13}C and ^{17}O shielding behavior and O^{17} nuclear quadrupole coupling constants for $Fe_2(CO)_9$.[6,7] Interestingly, the bridging oxygen shift tensor has its most deshielded component parallel to the C–O axis, behavior akin to that usually observed for organic carbonyl compounds.

A simple and efficient photochemical setup for the preparation of $Fe_2(CO)_9$ from $Fe(CO)_5$ has been described[8] and *ab initio* calculations have been used to understand the formation of $Fe_2(CO)_9$ from the combination of $Fe(CO)_5$ and $Fe(CO)_4$ fragments.[9] The first stage in this process is proposed to be orbital-controlled and involves a square-pyramidal form of $Fe(CO)_5$. Disproportionation of $Fe_2(CO)_9$ in a benzene–THF mixture under vacuum has been shown to slowly afford small red tabular crystals of $Fe(THF)_4\{HFe_3(CO)_{11}\}_2$,[10] behavior that differs from that previously found in benzene alone, where only $Fe(CO)_5$ and $Fe_3(CO)_{12}$ result.

Gradient-corrected DFT theory has been used to probe both the dissociation of the iron–iron and iron carbonyl bonds in $Fe_2(CO)_9$;[11] the calculated iron–iron bond dissociation energy of 29.5 $kcal\,mol^{-1}$ and the first carbonyl loss energy of 27.9 $kcal\,mol^{-1}$ both being consistent with experimental measurements. Loss of a carbonyl gives $Fe_2(CO)_8$, a number of forms of which are possible. Moskovits and co-workers have used the reaction of deposited $Fe_2{}^+$ in CO to prepare an unbridged form of $Fe_2(CO)_8$ characterized by IR spectroscopy.[12] The formation of the octa- rather than the nonacarbonyl is unusual and the authors speculate that this may be linked to an energy barrier associated with the extensive rearrangement in the electronic character of the iron–iron bonding upon CO addition. Jacobsen and Ziegler have carried out a DFT study of $Fe_2(CO)_8$.[3] A number of possible isomers were considered, that with only two bridging carbonyls and staggered terminal carbonyls (C_s symmetry) being identified as the most stable structure, even though the removal of a terminal ligand from $Fe_2(CO)_9$ was found to be energetically favorable. The lowest energy unbridged isomer was found to have C_{2h} symmetry and a relatively long iron–iron bond (2.671 Å) suggesting only a weak π-component, being stabilized by a *trans*-bent distortion. Xie *et al.* have also used DFT theory to probe the structures of the homoleptic diiron carbonyl compounds $Fe_2(CO)_x$ ($x=6$–9).[13] They too find a low energy doubly bridged structure for $Fe_2(CO)_8$, but their most stable unbridged isomer has a significantly shorter iron–iron distance (2.542–2.551 Å) than that of Jacobsen and Zeigler, and also eclipsed carbonyls. Their lowest energy structure of $Fe_2(CO)_7$ has C_s symmetry and that for $Fe_2(CO)_6$ is a distorted dibridged structure with C_{2h} symmetry. Close in energy to the latter is an unbridged isomer with a very short (2.00 Å) iron–iron interaction, leading the authors to suggest a quadruple bond. These results are summarized in Scheme 1. Interestingly, in a mass spectrometric study, Markin and Sugawara have observed the radical cations $[Fe_2(CO)_x]^+$ ($x=1-9$) by energy-resolved collision-induced dissociation (CID), measuring the CID energy thresholds for each CO loss process.[14] Values of the latter suggest that homoleptic diiron carbonyls other than $Fe_2(CO)_9$ are unlikely to be able to be isolated on a preparative scale.[13]

6.06.2.2 $Fe_2(CO)_9$ Derivatives

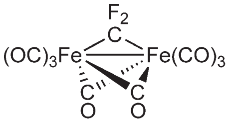
The bridging carbonyls in $Fe_2(CO)_9$ can easily be substituted by a wide range of other ligands with varying σ-donor and π-acceptor capabilities. Petz *et al.* have prepared the μ-CF_2 complexes, $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}CF_2)$ **1** and $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CF_2)_2$ **2**, from the reaction of Br_2CF_2 with $Na_2[Fe(CO)_4]$ and $Na_2[Fe_2(CO)_8]$, a reaction that possibly proceeds via the non-isolable $(CO)_4Fe{=}CF_2$.[15] The structure of **2** closely resembles that of $Fe_2(CO)_9$ **1**, and is best considered as having two semi-bridging carbonyls. Further, addition of 2 equiv. of PPh_3 to **1** affords $Fe_2(CO)_6(PPh_3)_2(\mu\text{-}CF_2)$ which has only a single bridging ligand. The μ-silylene complexes, $Fe_2(CO)_8(\mu\text{-}SiR_2)$ **3** ($R=$ Mes, O-2,6-$Pr^i{}_2C_6H_3$), prepared from a thermal reaction of $Fe_2(CO)_9$ and the relevant secondary silane, adopt similar mono-bridged structures,[16] while in contrast, a crystal structure of $Fe_2(CO)_6(\mu\text{-}SiMe_2)_3$ **4** shows that it



C_{2v} C_s C_{2h}

Scheme 1 The most stable isomers of $Fe_2(CO)_x$ ($x=6$–8) as calculated by Xie *et al*.

contains three μ-silylene ligands.[17] Uhl and co-workers have prepared a series of μ-InC(SiMe$_3$)$_3$-bridged complexes $Fe_2(CO)_8(\mu\text{-InR})$ **5**, $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-InR})_2$ **6**, and $Fe_2(CO)_6(\mu\text{-InR})_3$ **7** from reactions of iron carbonyls with tetrahedral In_4R_4 [$R=C(SiMe_3)_3$].[18,19] Again, **5** contains no other bridging groups, while **7** contains a trigonal-bipyramidal Fe_2In_3 unit with a highly elongated iron–iron interaction (2.992(2) Å). Related μ-GaSi(SiMe$_3$)$_3$ complexes, $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-GaR})_2$ **8**, $Fe_2(CO)_6(\mu\text{-GaR})_3$ **9**, and $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-GaR})_2$.Na(thf) $(OEt_2)_2Cl$ **10**, have been prepared from iron carbonyl anions and $(GaClR)_4$ [$R=Si(SiMe_3)_3$].[20] The latter is related to **9** but contains a bound, solvated, sodium chloride unit, the solvated sodium ion being bound to bridging carbonyl oxygen with the chloride bridging the two gallium atoms. A complex with three Cp*Ga bridging ligands has been prepared from the addition of Cp*Ga to $Fe(CO)_3(C_7H_8)$ and here the iron–iron bond is also elongated (2.908(6) Å).[21]



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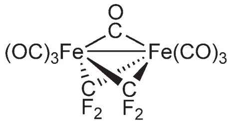

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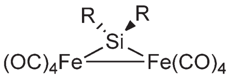

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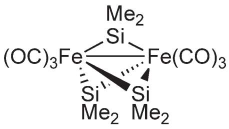

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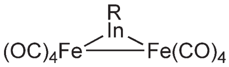

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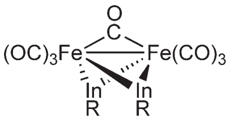

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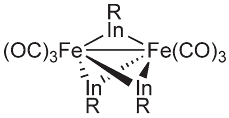

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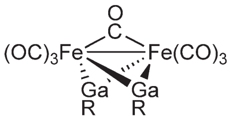

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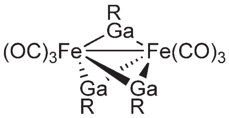

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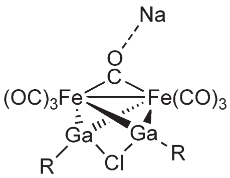


10

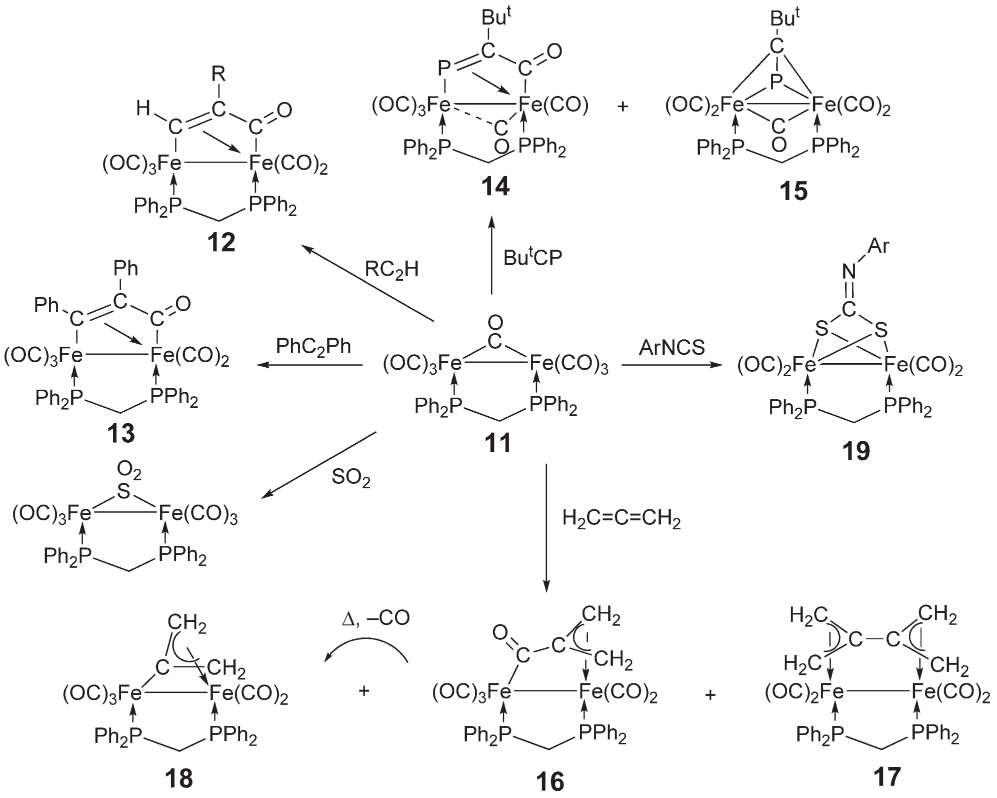
Molecular orbital calculations have been used to gain further insight into the bonding in these complexes,[15,20,22] details of which have been summarized in a recent review.[23] Based on structural data, two types of bridging groups have been identified, those with a bridging carbon atom (group 1) and those with a bridging heteroatom (group 2). Compounds in group 1 typically have shorter iron–iron bonds than $Fe_2(CO)_9$, while those in group 2 have elongated iron–iron vectors. These changes relate to the σ-donor and π-acceptor properties of the bridging ligands, ligands in group 1 as typified by CO being weak σ-donors and strong π-acceptors, the converse being true for group 2. The differences have been ascribed to the nature of the two HOMOs, the strength of the direct attractive iron–iron interaction being modulated by the nature of the bridging groups.[23]

A pair of bridging carbonyls in $Fe_2(CO)_9$ can be replaced by small bite-angle diphosphines such as bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)amine (dppa) to afford $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-dppm})$ **11**[24] and $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-dppa})$[25] respectively, with further reaction giving $Fe_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2$[26] and $Fe_2(CO)_4(\mu\text{-CO})(\mu\text{-dppa})_2$.[25] The photochemically induced reactivity of **11** has been extensively studied (Scheme 2).[24,26–29] Addition of alkynes leads to the formation of fluxional dimetallacyclopentenone complexes **12–14**, while with $P{\equiv}CBu^t$ a second minor product is the parallel phospha-alkyne complex **15**.[26] With allene, three products **16–18** are observed resulting from the simple binding of allene, allene coupling with CO, and coupling of two allene moieties,[29] while with isothiocyanates (ArNCS, Ar = Ph, *p*-Tol) dithiolate-bridged complexes **19** result.[24]

All the $Fe_2(CO)_9$ derivatives discussed above have at least one non-carbonyl bridging group; however, this need not be the case. Reaction of α-diimines with $Fe_2(CO)_9$ affords heptacarbonyl complexes, $Fe_2(CO)_7(\alpha\text{-diimine})$, with $Fe_2(CO)_6(bipy)(\mu\text{-CO})$ and $Fe_2(CO)_5(phen)(\mu\text{-CO})_2$ being crystallographically characterized.[30] Both show π-stacking of the α-diimine ligands and a theoretical study suggests that, in a similar manner to $Fe_2(CO)_9$, there is no significant direct iron–iron interaction.

6.06.2.3 Compounds with Only Hydrocarbon Ligands

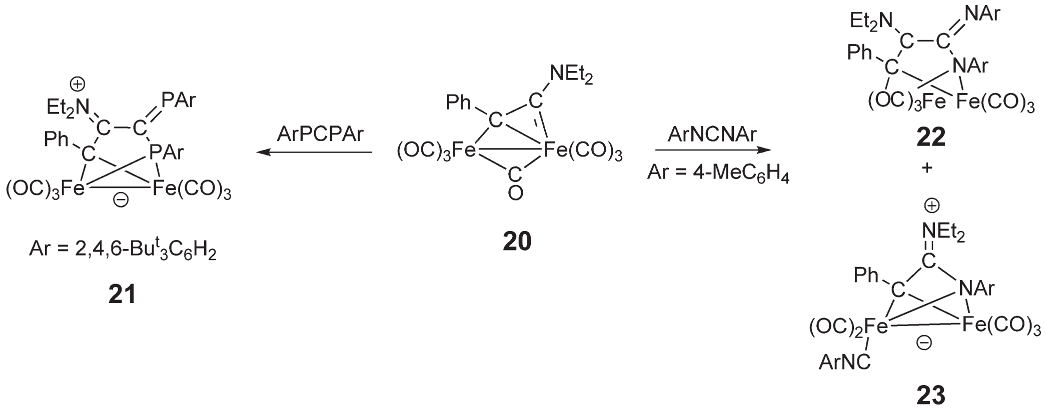
A wide range of hydrocarbon ligands can be stabilized at the diiron centre. In this section, we consider the synthesis and reactivity of those compounds with only bound hydrocarbon and CO ligands. Jeannin and co-workers have continued their



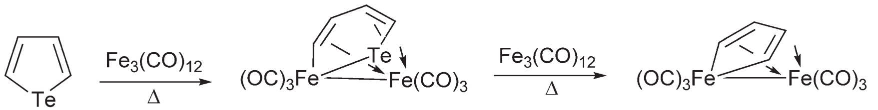
Scheme 2 Some reactions of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)$, **11**.

studies on the reactivity of the ynamine complexes including $Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}PhC{=}C(NEt_2)\}$ **20**.[31–33] Addition of ArPCPAr (Ar = 2,4,6-$Bu^t{}_3C_6H_2$) results in insertion into the iron–carbene bond to give **21**, while with ArCNCAr (Ar = *p*-Tol) a similar product **22** results together with a second species **23** formed upon isocyanide extrusion (Scheme 3).[33]

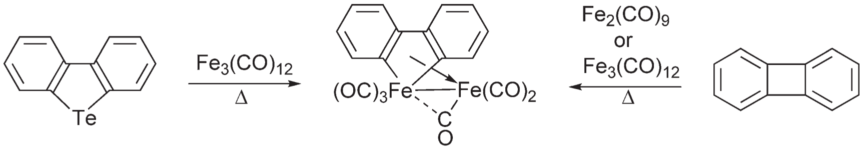
McWhinnie and co-workers have reported that heating $Fe_3(CO)_{12}$ and tellurophene in heptane initially affords the telluraferrole complex **24** which later eliminates tellurium to give ferrole **25** (Equation (1)).[34] A similar reaction with dibenzotellurophene affords the dibenzoferrole complex **26**,[34] also formed upon thermolysis of iron carbonyls with biphenylene (Equation (2)),[35] while thermolysis of 2,2′-biindenyl with $Fe(CO)_5$ in an autoclave at 180 °C affords **27** (Equation (3)).[36]



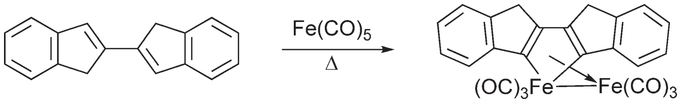
Scheme 3 Reaction of $Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}PhCC(NEt_2)\}$ **20** with ArECEAr (E = N, P).



24 **25** (1)



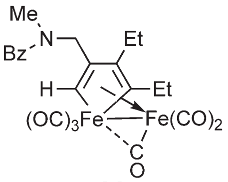
26 (2)



27 (3)

Ferrole complexes have also been prepared upon reaction of ethylthioalkynes, RC≡CSEt (R = Me, Ph) with iron carbonyls, isomeric mixtures being formed,[37] while reaction of $Fe_3(CO)_9(\mu_3\text{-}EtC_2Et)$ with the propargylamine, $HC{\equiv}CCH_2NMeBz$, affords ferrole **28**, and ferrole **29** results from diphenylethyne addition to **11** via an intermediate dimetallacyclopentenone complex.[24]

A number of allyl-type hydrocarbon units have been bound to the diiron centre. McGlinchey and co-workers have reported the formation of **30**, a metal-stabilized disjoint hydrocarbon, from the reaction of tetrabromodurene with iron carbonyls,[38] which is somewhat similar to the coupled product **17** of allene addition to **11** (Scheme 2).[29] Monosubstituted allenes (R = Bu^t, OMe, CO_2Me, CH_2CO_2Et) have also been shown to react with $Fe_2(CO)_9$ to give complexes containing one **31** and two **32** allene moieties.[39]



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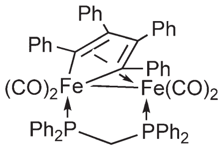

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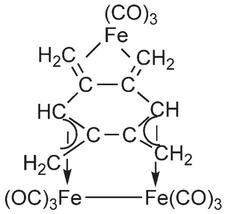

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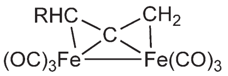

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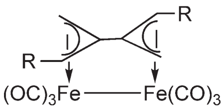
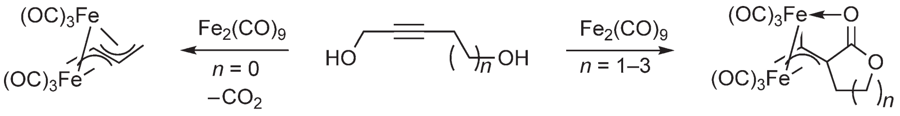


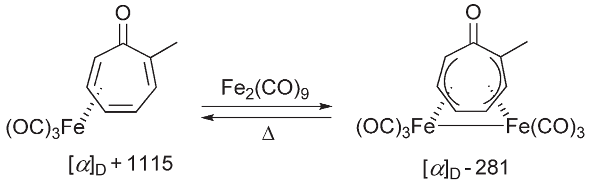
32

Schobert *et al.* have prepared a number of diiron allyl-type complexes from reactions of unsaturated diols with $Fe_2(CO)_9$.[40,41] With 2-butyne-1,4-diol, the butatriene complex **33** is produced after loss of CO_2,[41] while with longer-chain alcohols, 1-lactonyl–allyl complexes **34** result (Equation (4)).[41]



33 **34** (4)

Tropones bind to diiron centres in a bis(allyl) fashion. Osella *et al.* have shown that the known tropone complexes, $Fe_2(CO)_5\{\mu\text{-}(RC_2R)_3CO\}$ (R = Me, Et, Pr), undergo a reversible one-electron reduction on the cyclic voltammetry (CV) timescale; however, electrogenerated anions rearrange smoothly to mononuclear tropone complexes over longer timescales.[42] Morita *et al.* have also prepared the optically active 2-methyltropone diiron complex **36** from the chiral mononuclear 7-methyltropone complex **35** (Equation (5)).[43]

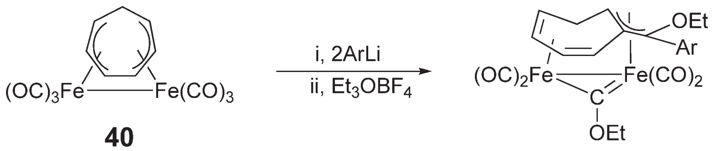


35 **36**

(5)

It has long been known that reaction of $Fe_2(CO)_9$ with ethyne produced tropone as one of the products and using the dppm-stabilized complex, $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)$ **11**, this process has been shown to occur in a stepwise manner. Thus, the tropone complex **39** results upon prolonged photolysis of **11** and ethyne, while over shorter timescales dimetallacyclopentenone **37** and the flyover complex **38** are the major products (Scheme 4).[24]

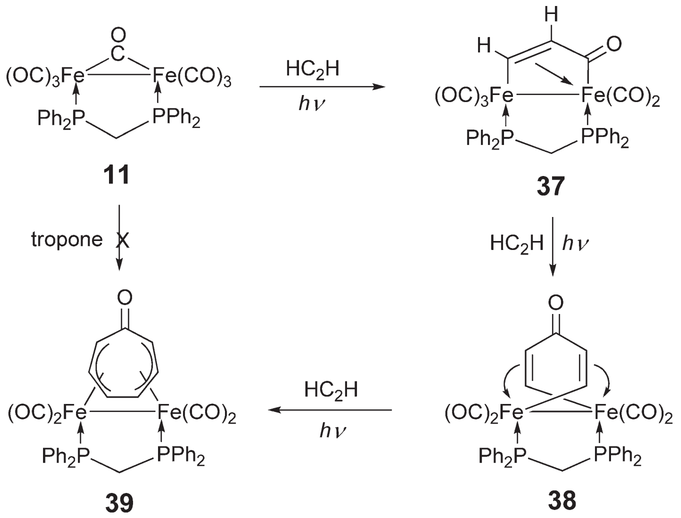
Closely related to **39**, and binding in a similar manner, is the cycloheptatriene complex **40**, which reacts with 2 equiv. of aryllithium reagents to afford novel μ-alkylidyne complexes **41** (Equation (6)).[44] The mode of formation of **41** is complex and involves the coupling of cycloheptatriene and alkylidene fragments, together with cleavage of an aryl group from a second alkylidene ligand.



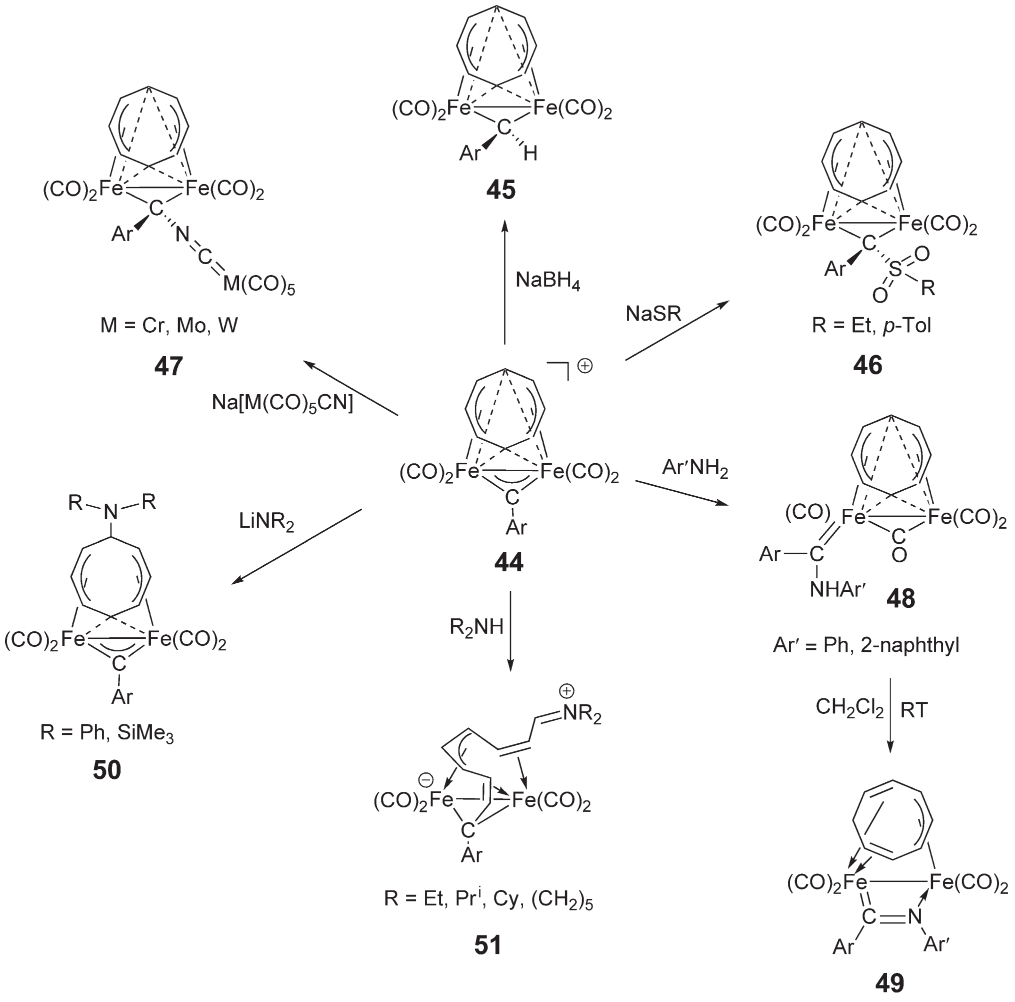
40 **41**

(6)

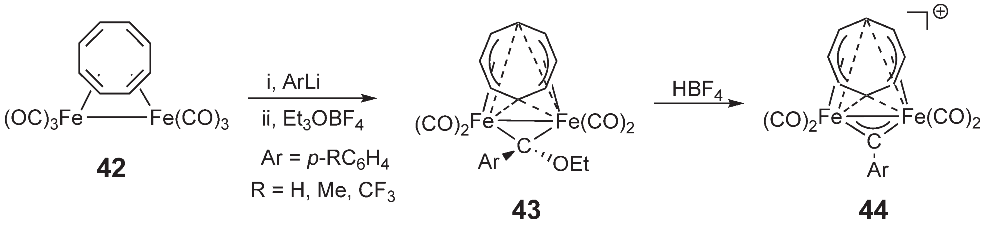
Under similar conditions, the related cyclooctatetraene compound **42** affords μ-alkylidene complexes **43**,[45] which react further with $HBF_4.Et_2O$ to give μ-alkylidyne complexes **44** (Equation (7)).[46] The latter have been shown to react with a wide range of nucleophiles, aspects of which are summarized in Scheme 5.[46–48] Most attack the μ-alkylidyne group to afford new μ-alkylidene complexes such as **45–47**, while certain anilines initially afford terminal alkylidene complexes **48** which rapidly rearrange to give C–N bridged complexes **49**. Certain more basic amines and amides preferentially attack the cyclooctatetraene ligand leading to amino-substituted cyclooctatetraene complexes **50** and, in some instances, to ring-opened products **51** resulting from the coupling of the two hydrocarbon ligands.



Scheme 4 Stepwise synthesis of tropone at the diiron center.

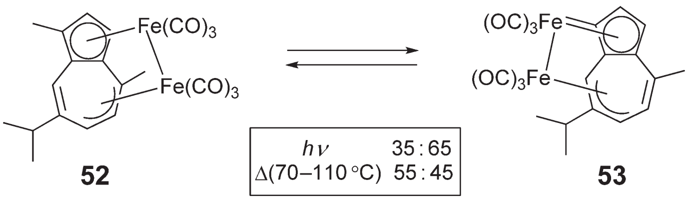


Scheme 5 Some reactions of 44 with nucleophiles.



(7)

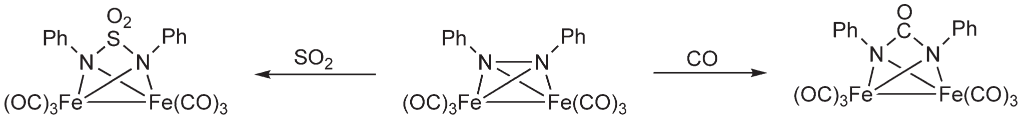
Nagashima and co-workers have studied the thermally and photochemically induced isomerization of bridging guaiazulene complexes 52 and 53 (Equation (8)),[49] along with phosphine- and phosphite-substituted derivatives[49,50] and related acenaphthylene and aceanthrylene complexes.[51]



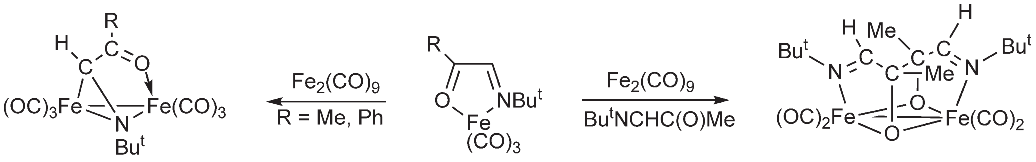
(8)

6.06.2.4 Compounds with Nitrogen-containing Ligands

Vahrenkamp and co-workers have described the synthesis of the azobenzene complex, $Fe_2(CO)_6(\mu\text{-}PhN_2Ph)$, formed by photolysis of $Fe(CO)_3(\eta^2\text{-}PhN_4Ph)$,[52] which further inserts CO and SO_2 into the nitrogen–nitrogen bond affording **54** and **55**, respectively (Equation (9)).[53,54] Frühauf and co-workers have shown that mononuclear imino ketone complexes **56** react further with $Fe_2(CO)_9$ to afford **57**, while in the presence of more free imino ketone complex **58** results (Equation (10)).[55]

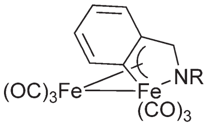


55 **54** (9)



57 **56** **58** (10)

In a large series of papers, Imhof,[56–60] Hwang,[61–69] and their co-workers detail the reactions of $Fe_2(CO)_9$ with a wide variety of imines, predominantly those bound to heterocyclic aromatic groups. For example, Imhof has shown that imines derived from benzaldehyde afford complexes **59** resulting from the intramolecular C–H activation of the bond *ortho* to the imine functionality. Complexes **60–62** represent further examples of products of this type. Hwang's work focuses on reactions of thienyl imines with $Fe_2(CO)_9$ in benzene. Cyclometallated complexes akin to **60** are the major products, although in some cases (R = Ph) a second product type **63** is also obtained resulting from coupling of two imines.[61] Reaction with the *ortho*-fluorinated aldazine, $(2,6\text{-}F_2C_6H_3CH{=}N)_2$, gives a range of products including diiron complexes **64** and **65**.[60] The former is the expected product of C–F activation, while the latter results instead from N–N bond cleavage, a process which also occurs to afford similar products **66** in reactions with diaza compounds with thienyl substituents.[65]



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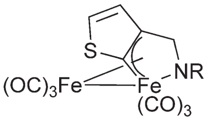

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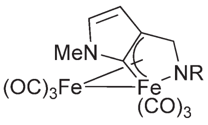

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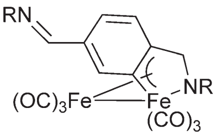

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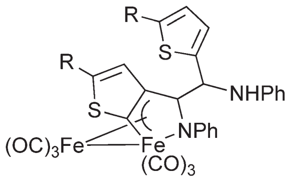
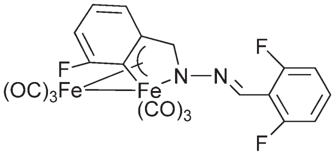


R = H, Me

63



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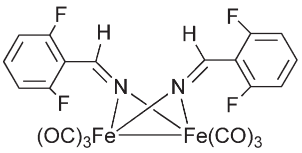

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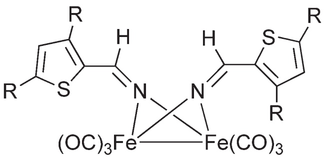
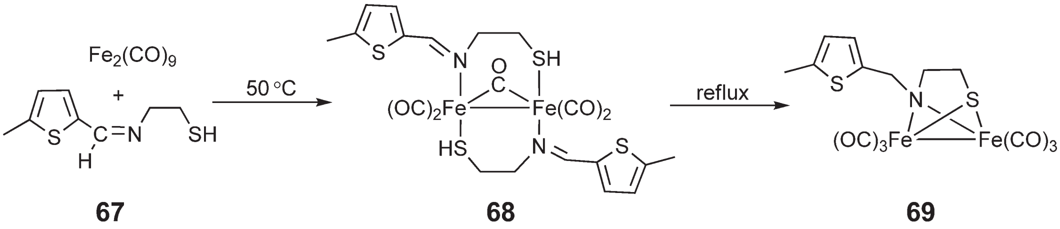


R = H, Me

66

Hwang and co-workers have recently shown that reaction of $Fe_2(CO)_9$ with **67** in MeCN affords quite different products to those discussed above, namely **68** and **69** (Equation (11)) in which the ligand bridges the diiron center.[68]

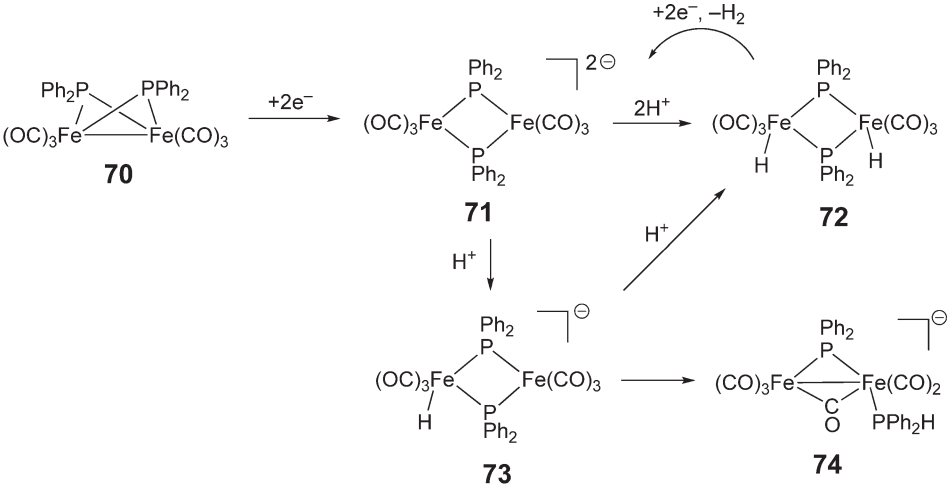


(11)

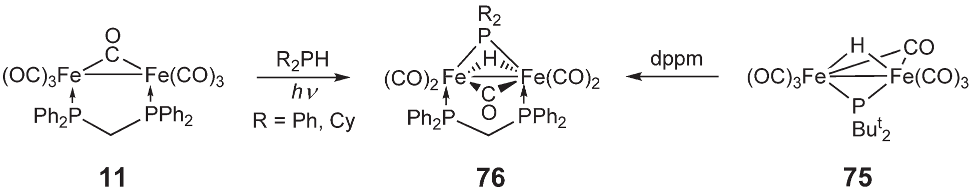
6.06.2.5 Compounds with Phosphido Bridges

Phosphido-bridged diiron complexes continue to be an area of intense research activity, predominantly due to the rich organic chemistry that this center can support. Saturated 34-electron bis(phosphido) complexes, $Fe_2(CO)_6(\mu\text{-}PR_2)_2$, are well known. Böttcher and co-workers have studied the photochemically induced carbonyl substitution of $Fe_2(CO)_6(\mu\text{-}PBu^t{}_2)(\mu\text{-}PR_2)$ (R = Me, Cy) by PBu_3 and $P(OMe)_3$, products being formed in a stepwise fashion with loss of up to three carbonyls, and similar behavior is shown by the unsaturated 32-electron complexes, $Fe_2(CO)_5(\mu\text{-}PBu^t{}_2)(\mu\text{-}PR_2)$ (R = Cy, Bu^t).[70] Best and co-workers have carried out a detailed spectroelectrochemical study of the reduction of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ **70** in the presence of protons.[71] Electrocatalytic proton reduction is noted, a process which involves the initial formation of the dianion, $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^{2-}$ **71**. This in turn is doubly protonated to give $H_2Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ **72**, which then undergoes further reduction and hydrogen elimination. Addition of a single proton to **71** affords $[HFe_2(CO)_6(\mu\text{-}PPh_2)_2]^-$ **73** which subsequently rearranges to iron–iron-bonded $[Fe_2(CO)_5(Ph_2PH)(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ **74** (Scheme 6).

A number of papers deal with the synthesis of phosphido-bridged diiron complexes with a bridging hydride ligand.[72–77] Böttcher and co-workers describe the synthesis of $Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PBu^t{}_2)$ **75** upon protonation of $Na[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PBu^t{}_2)]$, the iron–iron bond unexpectedly becoming shorter upon protonation.[72] Reaction of **75** with PPh_3 and $PBu^t{}_2H$ affords related monosubstituted products, while with dppm the diphosphine-bridged complex $Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PR_2)(\mu\text{-}dppm)$ **76** (R = Bu^t) results.[73] Other complexes of this type (R = Ph, Cy) have also been prepared from the photochemical reaction of the appropriate secondary phosphine with $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)$ **11** (Equation (12)).[76,77] Interestingly, addition of Ph_2PH to $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppa)$ affords $HFe_2(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}dppa)$ in which the hydride occupies a terminal site in the solid state, while in solution interconversion of terminal and bridging forms is proposed.[25]

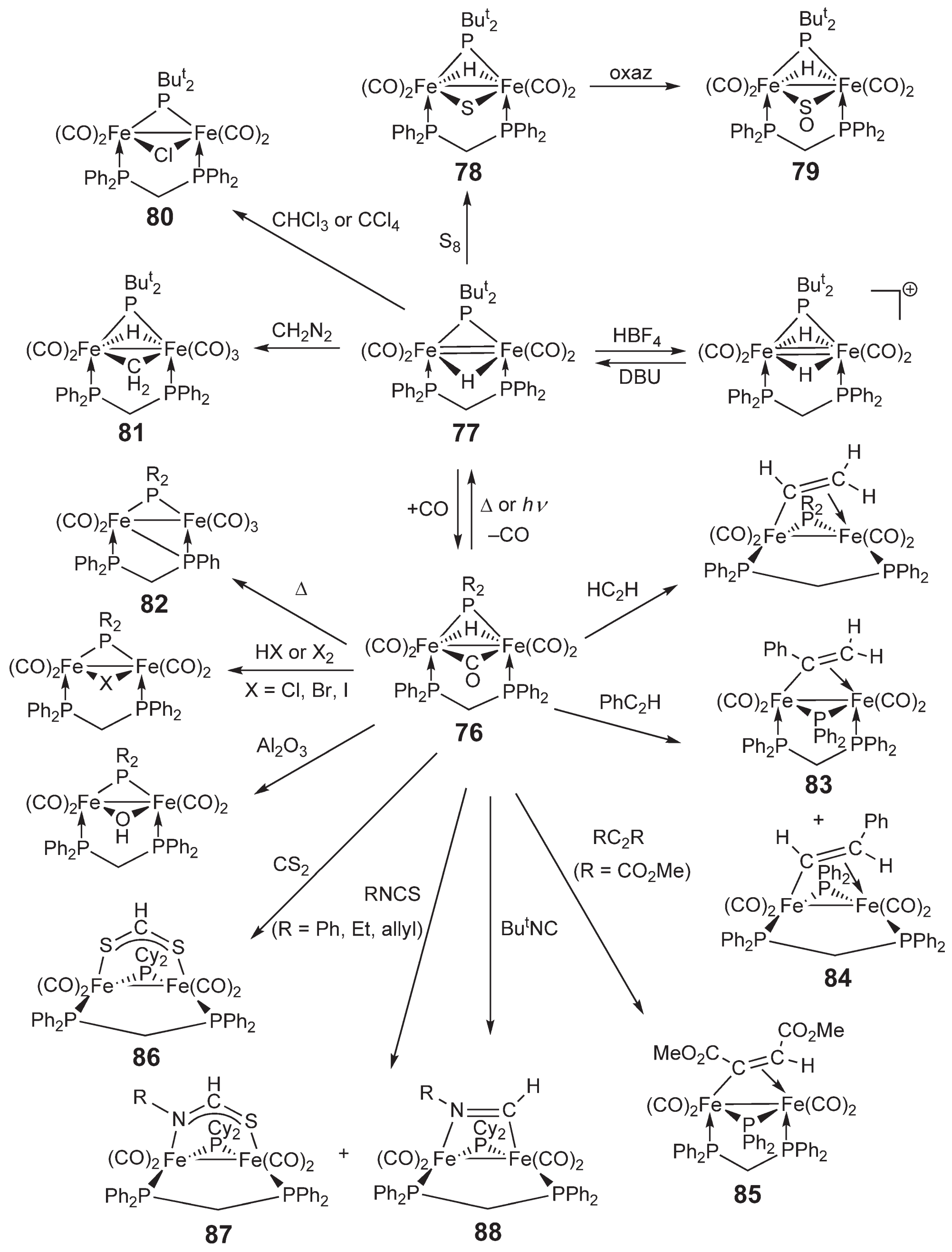


Scheme 6 Reductive chemistry of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$, **70**.



(12)

Hydride complexes **76** have a rich chemistry,[73–79] aspects of which are summarized in Scheme 7. The μ-PBu^t_2 complex reversibly loses CO to afford the unsaturated species $Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}PBu^t_2)(\mu\text{-dppm})$ **77**, a

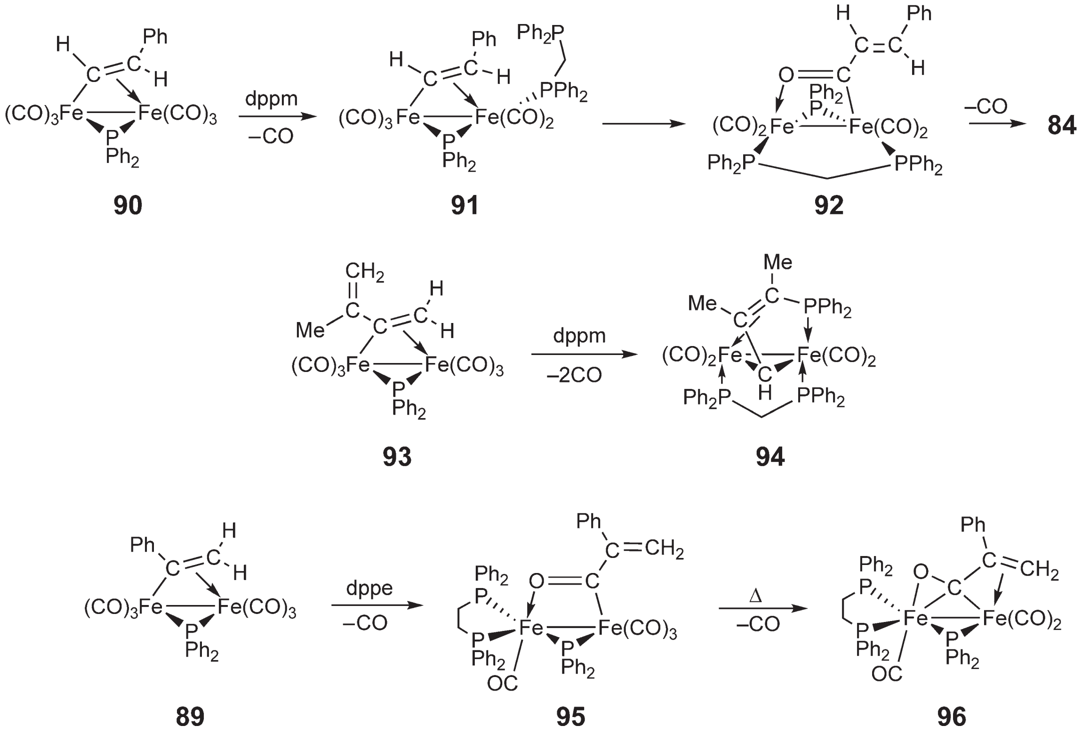


Scheme 7 Reactivity of $Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PR_2)(\mu\text{-dppm})$, **76**.

crystallographic study showing a relatively short iron–iron bond of 2.496(1) Å, suggestive of some double bond character.[73] Certainly **77** behaves as if it is unsaturated reacting with two-electron donor ligands to afford saturated 34-electron complexes **78–81**. For example, elemental sulfur adds across the iron–iron bond to give $Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}S)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)$ **78**, which in turn reacts with the oxidizing agent, 3-phenyl-2(phenylsulfonyl)-oxaziridine (oxaz), to afford the corresponding μ-SO complex **79**.[75] Further oxidation does not occur even under forcing conditions and **77** does not react directly with SO_2. The corresponding $\mu\text{-}PPh_2$ and $\mu\text{-}PCy_2$ derivatives of **76** do not lose CO to form the analogous unsaturated species; they undergo thermolysis instead resulting in benzene elimination and formation of $Fe_2(CO)_5(\mu\text{-}PR_2)(\mu\text{-}Ph_2CH_2PPh)$ **82**.[76,77] Nevertheless, both react with a wide variety of reagents at or near room temperature with loss of CO (Scheme 7). Addition of primary alkynes affords μ-alkenyl complexes, α- and β-isomers (e.g., **83** and **84**) being isolated, which also differ in their relative positioning of the diphosphine and phosphido bridges.[77,79] Disubstituted alkynes are in general unreactive, but the activated alkyne RC_2R ($R = CO_2Me$) does add to form the expected μ-alkenyl complex **85**.[78] Both carbon disulfide and isothiocyanates insert into the bridging hydride of the $\mu\text{-}PCy_2$ complex giving **86** and **87**, respectively, second products in the latter reaction being the formimidoyl complexes **88** resulting from sulfur extrusion, one example of which is directly accessible from the reaction with *tert*-butyl isocyanide.[77]

Some of the μ-alkenyl species described above are also available from thermal reactions of $Fe_2(CO)_6(\mu\text{-alkenyl})(\mu\text{-}PPh_2)$ with dppm; however, these reactions are not always as simple as might be anticipated (Scheme 8).[80] For example, while $Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)$ **89** reacts smoothly to afford the expected dppm-bridged complex **83**, reaction with isomeric $Fe_2(CO)_6(\mu\text{-}HC{=}CHPh)(\mu\text{-}PPh_2)$ **90** to give **84** proceeds via the intermediate formation of a monodentate dppm complex **91** and the α,β-unsaturated acyl **92**. With $Fe_2(CO)_6(\mu\text{-}PhC{=}CHPh)(\mu\text{-}PPh_2)$, only an α,β-unsaturated acyl complex is observed and no further CO loss occurs, while the α-vinyl complex **93** reacts to afford **94** resulting from phosphido-bridge addition to the unsaturated organic moiety. Complex **89** also reacts with dppe leading to the formation of the α,β-unsaturated acyl complex **95** which undergoes further CO loss to afford **96**, which contains a rare example of a π-bound α,β-unsaturated acyl ligand.[81]

As mentioned above, α- and β-isomers **83** and **84** differ not only in the substitution pattern at the alkenyl ligand but also in the relative orientations of the phosphorus-containing ligands. This has a pronounced effect on

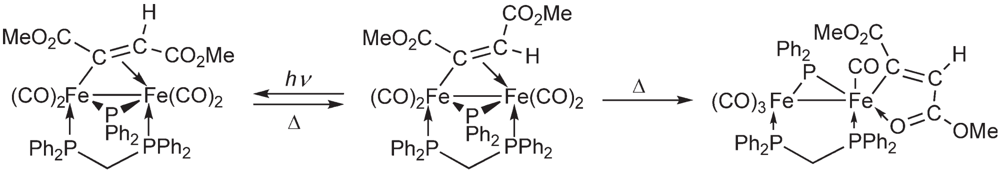


Scheme 8 Examples of the thermal reactions of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-alkenyl})$ with diphosphines.

the rate of the well-known "windshield wiper" fluxionality, free energies of activation varying between 63 ± 1 and $45 \pm 1\,\mathrm{kJ\ mol^{-1}}$ in 83 and 84, respectively.[79] The related hexacarbonyl complexes 89 ($\geq 63 \pm 1\,\mathrm{kJ\ mol^{-1}}$) and 90 ($52 \pm 1\,\mathrm{kJ\ mol^{-1}}$) show a similar, though less pronounced, difference suggesting that it may be a general effect that α-substituted binuclear alkenyl complexes have higher free energies of activation for this process than the corresponding β-isomers. A rationalization for the difference between 83 and 84 comes from crystallographic studies which show that alkenyl bonding to the diiron center is quite different between the two isomers. Thus, while the Fe(σ)–C_α distance does not vary significantly between isomers, Fe π-bonding differs markedly between the two. In 83, Fe is bound almost symmetrically to both C_α and C_β, while in 84 there is a difference of nearly 0.2 Å, the shorter bond being that to C_α. Given that in the proposed transition state for "windshield wiper" fluxionality both the α- and β-carbon atoms symmetrically bridge the diiron vector, it has been proposed that it may be these ground-state differences which lead to the large observed difference in free energies of activation.[79]

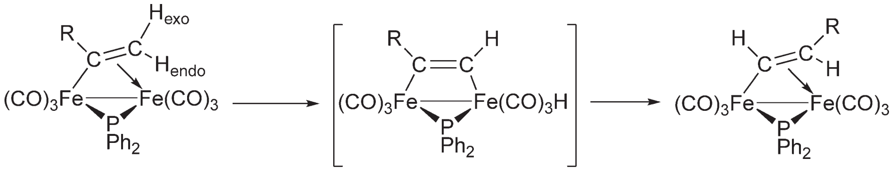
The lower limit measurement of the free energy of activation for "windshield wiper" fluxionality in 89 results from its facile isomerization to 90 upon heating at 110 °C.[82] Indeed, $\alpha \rightarrow \beta$ alkenyl isomerization appears to be general in complexes of this type.[83] Isomerization is accelerated in the presence of tertiary phosphines, and on the basis of labeling studies a mechanism has been proposed in which oxidative addition of the protons on the β-carbon in the α-isomers occurs to afford an intermediate parallel alkyne complex with a terminally bound hydride (Scheme 9), addition of the *trans(exo)* and *cis(endo)* β-protons being in competition.[83]

Isomerization of diiron alkenyl complexes is not limited to that described above. Photolysis of 85, which has a *cis*-arrangement of substituents, results in the formation of the *trans*-isomer 97, a process which is reversed upon heating. Warming 85 above 80 °C, however, leads to the irreversible formation of metallacyclic 98 with metal coordination of an ester carbonyl (Equation (13)).[78] The reactivity of the parent alkenyl complex, $Fe_2(CO)_4(\mu\text{-HC{=}CH}_2)(\mu\text{-PCy}_2)(\mu\text{-dppm})$, toward a range of acids has been assessed.[84] In all cases, protonation leads to the release of ethylene, the diiron product being dependent on the nature of the anion. Coordinating anions produce neutral complexes, $Fe_2(CO)_4(\mu\text{-X})(\mu\text{-PCy}_2)(\mu\text{-dppm})$ (X = F, Cl, Br, HCO_2, CF_3CO_2, CBr_3CO_2), while non-coordinating anions give salts, $[Fe_2(CO)_6(\mu\text{-PCy}_2)(\mu\text{-dppm})]X$ (X = F, BF_4, PF_6, 0.5 SO_4). Closely related to the latter is the neutral complex, $Fe_2(CO)_6(\mu\text{-PPh}_2)(\mu\text{-Ph}_2\text{PNPPh}_2)$, formed upon sequential addition of *n*-BuLi and Ph_2PCl to $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-dppa})$.[25] Addition of Ph_2PCl to $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-dppa})$ in the absence of base affords chloride-bridged $Fe_2(CO)_4(\mu\text{-Cl})(\mu\text{-PPh}_2)(\mu\text{-dppa})$ which exists as a mixture of isomers with varying relative orientations (*cis* or *trans*) of the phosphorus-containing ligands.



97 85 98 (13)

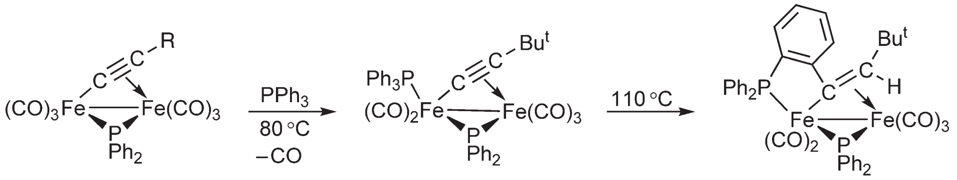
The chemistry of alkynyl complexes, $Fe_2(CO)_6(\mu\text{-alkynyl})(\mu\text{-PPh}_2)$, continues to attract interest. Two groups have independently shown that heating $Fe_2(CO)_6(\mu\text{-C{\equiv}CPh})(\mu\text{-PPh}_2)$ 99 (R = Ph) in toluene results in CO loss and dimerization to give the novel tetranuclear complex, $Fe_4(CO)_8(\mu_4\text{-C{\equiv}CPh})_2(\mu\text{-PPh}_2)_2$, in which the alkynyl ligands cap square faces,[85,86] while addition of a range of metal fragments under similar conditions affords trinuclear complexes with capping alkynyl or alkyne groups.[87] Addition of PPh_3 to $Fe_2(CO)_6(\mu\text{-C{\equiv}CBu}^t)(\mu\text{-PPh}_2)$ 99 (R = t-Bu) at 80 °C affords the phosphine adduct 100, but heating the latter at 110 °C results in the formation of



R = Ph, Me, Pr^n, Bu^n, Bu^t

Scheme 9 $\alpha \rightarrow \beta$ Alkenyl isomerization in $Fe_2(CO)_6(\mu\text{-PPh}_2)(\mu\text{-alkenyl})$ complexes.

μ-alkenyl complex **101** as the major product resulting from C–H addition across the carbon–carbon triple bond (Equation (14)).[88] Phosphine and phosphite addition to $Fe_2(CO)_4(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(\mu\text{-dppm})$ affords substituted complexes $Fe_2(CO)_3L(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(\mu\text{-dppm})$ [$L = Ph_2PC{\equiv}CPh$, $P(OEt_3)$], in which the facile σ–π alkynyl fluxionality exhibited by the parent complex is frozen out at room temperature.[89]



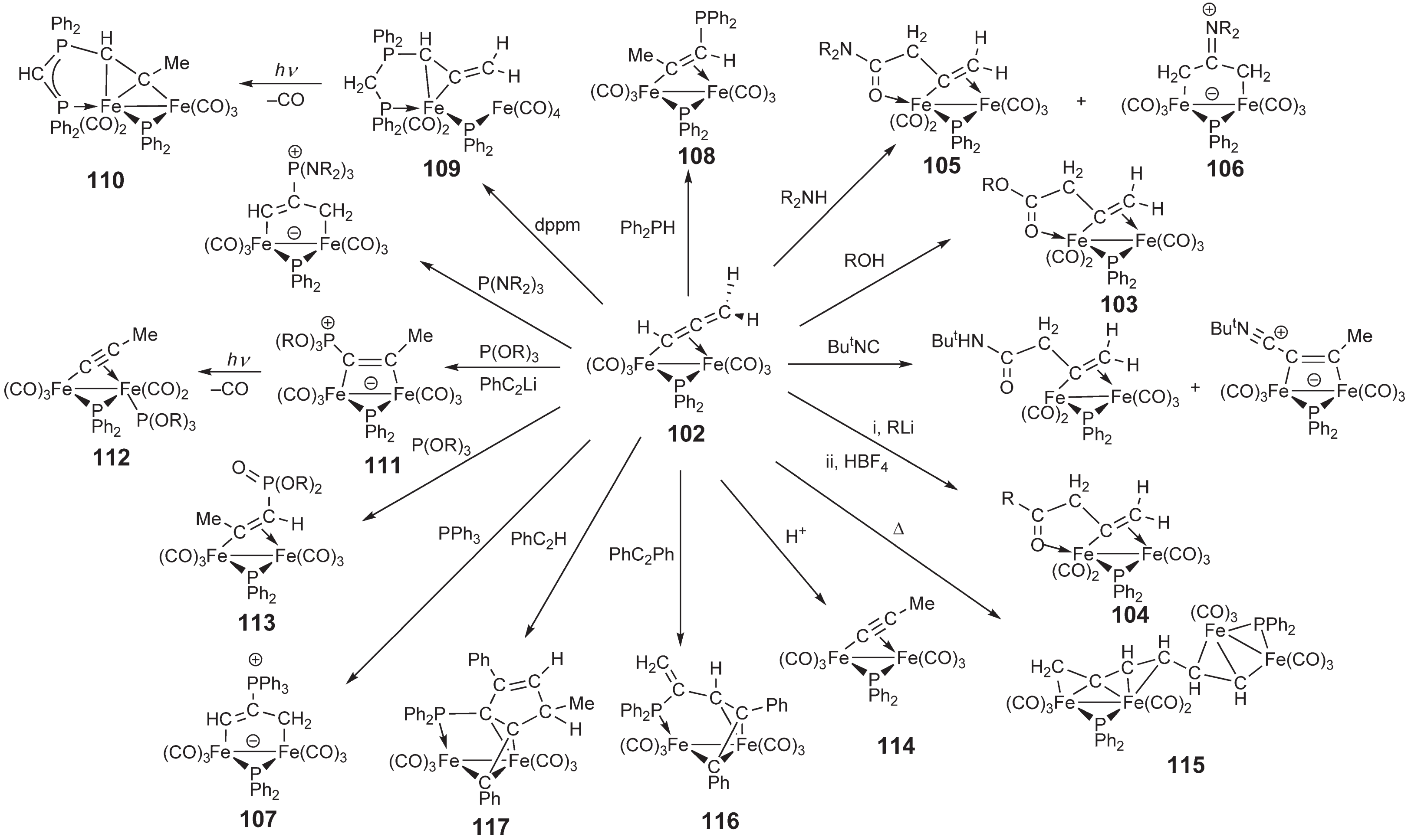
99 **100** **101** (14)

In a series of papers, Doherty and co-workers describe the synthesis and reactivity of allenyl complexes $Fe_2(CO)_6(\mu\text{-}RC{=}C{=}CH_2)(\mu\text{-}PPh_2)$ ($R = H$, Ph) and $Fe_2(CO)_6(\mu\text{-}HC{=}C{=}CMe_2)$ $(\mu\text{-}PPh_2)$. The parent complex, $Fe_2(CO)_6(\mu\text{-}HC{=}C{=}CH_2)(\mu\text{-}PPh_2)$ **102**, prepared from the reaction of $Na[Fe_2(CO)_7(\mu\text{-}PPh_2)]$ with $BrCH_2C{\equiv}CH$, is the most widely utilized, and aspects of this work are summarized in Scheme 10.[90–100] It contains a highly fluxional α,β-coordinated allenyl ligand, the fluxional process interconverting the two iron centers and the methylene protons,[94] and reacts with a wide range of nucleophiles. Addition of alcohols[93] and organolithium[94] reagents occurs at a carbonyl group with subsequent coupling of the generated acyl ligand to the γ-carbon of the allenyl ligand to afford **103** and **104**, respectively. Secondary amines[91,96] behave similarly to give **105**, although a second product **106**, resulting from attack at the β-carbon of the allenyl ligand, is also seen in some instances.

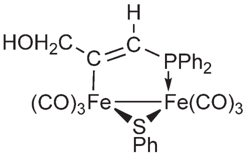
Reactions with a number of phosphines are also reported. Triphenylphosphine initially adds to the β-carbon to give a dimetallacyclopentene **107**, which readily isomerizes to a novel zwitterionic α-phosphonium alkoxide and loses CO upon heating to yield a PPh_3 derivative of **102** (not shown).[97,101] Diphenylphosphine adds across the allenyl fragment to give the μ-alkenyl compound **108**,[90] while dppm attacks the α-carbon to afford **109** which rearranges upon photolysis to give **110** resulting from CO loss and proton migration.[92] The products of phosphite addition are highly dependent upon the reaction conditions employed.[95] In the presence of $PhC{\equiv}CLi$, which acts to remove extraneous water, **111** results from addition of the phosphite to the α-carbon followed by a 1,3-proton shift. These complexes rearrange upon photolysis to give the phosphite-substituted alkynyl complexes **113**, while in the absence of $PhC{\equiv}CLi$ Arbuzov-type dealkylation products **112** result. In the presence of acids, isomerization of **102** to give the μ-alkynyl complex **114** is quantitative, while thermolysis in toluene results in the formation the novel hexa-1,3,5-triene-2,6-diyl complex **115** resulting from coupling of two allenyl diiron fragments.[101] The phosphido bridge is not always innocent. With $PhC{\equiv}CPh$, coupling with both the allenyl and phosphido bridges affords the novel μ-alkylidene complex **116**, while 2 equiv. of $PhC{\equiv}CH$ add to **102** to afford another μ-alkylidene complex **117** resulting from a complex sequence of carbon–carbon and carbon–phosphorus bond formation and hydrogen migration steps.[99]

In a number of other instances, the phosphido bridge has been shown to be non-innocent. Somewhat similar to the reactions with alkynes described above, Mays and co-workers have reported the formation of **118** from the reaction of $Fe_2(CO)_6(\mu\text{-}SPh)(\mu\text{-}PPh_2)$ with propargyl alcohol.[102] While thermolysis of **102** affords the allenyl-linked complex **115**, under similar conditions the dimethylallenyl derivative, $Fe_2(CO)_6(\mu\text{-}HC{=}C{=}CMe_2)(\mu\text{-}PPh_2)$, isomerizes to afford **119** resulting from allenyl-phosphido coupling. Similar behavior is also seen with phosphine-substituted analogs of **102**.[101] For example, thermolysis of $Fe_2(CO)_5(PPh_3)(\mu\text{-}HC{=}C{=}CR_2)(\mu\text{-}PPh_2)$ ($R = H$, Me), which exist as mixtures of isomers, affords coupled products $Fe_2(CO)_5(PPh_3)(\mu\text{-}Ph_2PCHCCR_2)$ in which the two phosphorus atoms bind to different iron centers.

Knox and co-workers have reported the insertion of allene into the phosphido bridge of $Fe_2(CO)_6(\mu\text{-}CH_2PPh_2)$-$(\mu\text{-}PPh_2)$ to give **120**, which subsequently undergoes protonation in the presence of CO to give a novel μ-propenylphosphine complex.[29] The diyndiyl complex, $\{Fe_2(CO)_6(\mu\text{-}PPh_2)\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$, is a low yield product of the reaction of $Ph_2PC{\equiv}CC{\equiv}CPPh_2$ with $Fe_3(CO)_{12}$.[103] It reacts with both $P(OMe)_3$ to afford **121** resulting from phosphite addition to one of the α-carbon atoms followed by coupling to the phosphido bridge.[104] Reaction with Et_2NH proceeds somewhat similarly to give **122**, but now a second product results from carbonyl rather than phosphido-bridge coupling, which contains a trinuclear–mononuclear arrangement of the four iron atoms.



Scheme 10 Reactivity of $Fe_2(CO)_6(\mu\text{-}HC{=}C{=}CH_2)(\mu\text{-}PPh_2)$, **102**.



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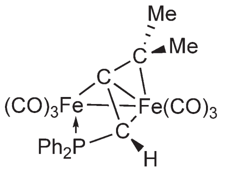

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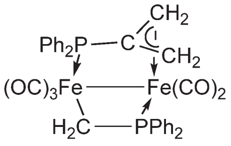

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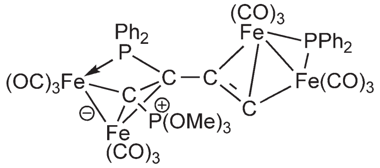

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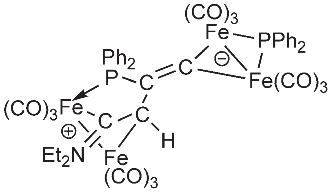

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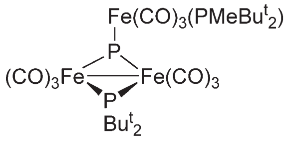
6.06.2.6 Other Phosphorus-containing Compounds

A number of other phosphorus-containing ligands have been stabilized at the diiron centre. Knox and co-workers have reported that upon thermolysis the dimetallacyclopentenone complexes **123** undergo a number of unusual transformations (Scheme 11).[105] Primary alkyne complexes rearrange to give the novel diphosphine complexes **124** resulting from coupling of the organic and dppm ligands through one of the phenyl rings of the latter. For the ethyne adduct (R = H), a second reaction route competes, in which the diphosphine couples to the organic group via formation of a new carbon–phosphorus bond to yield the zwitterionic μ-alkenyl complex **125**, which further transforms as a result of a novel phenyl migration reaction to afford **126**.

Diiron complexes containing μ-RP=CH$_2$ or μ-RPCH$_2$P(R)CH$_2$ bridges are among products of the dehalogenation of RPClCH$_2$Cl by iron carbonyls,[106] while **127** is one of the products of the reaction of Bu$^t{}_2$P–P=PMeBu$^t{}_2$ with Fe$_2$(CO)$_9$.[107] Regitz and co-workers have shown that the unusual diphosphine complexes **128** (R = Bu^t, *t*-pentyl) are formed upon photolysis of the diphosphirene complexes {Fe(CO)$_4$(PCR = CPh)}$_2$ in benzene, as a result of opening of one of the phosphirene rings to produce a 1-phospha-allyl ligand.[108]



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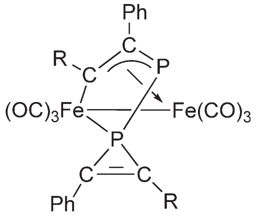

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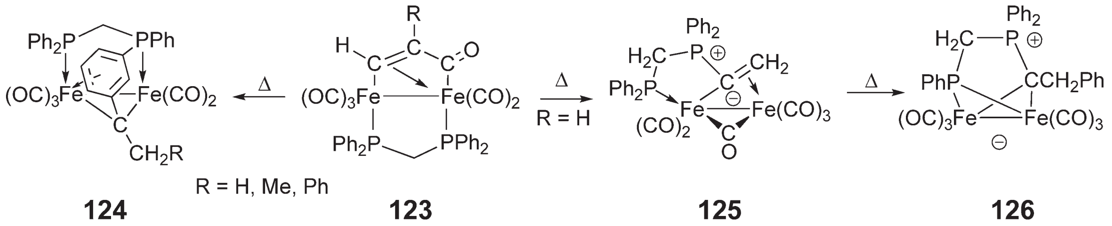


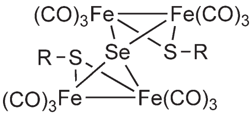
Scheme 11 Thermal rearrangement of metallacyclopentenone complexes.

6.06.2.7 Compounds with a Single Thiolate Bridge

Thiolate-bridged anions, $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SR)]^-$ **129**, previously prepared by Seyferth and co-workers, continue to serve as valuable precursors to a wide range of thiolate-bridged diiron chemistry (Scheme 12).[109–119] Products from their reactions with bis(1-alkynyl)mercury compounds are highly dependent upon the nature of the alkynyl group, μ-alkynyl **130** and vinylalkylidyne **131** complexes being observed, along with cluster compounds in which mercury is incorporated.[109] Ethylthiolato μ-alkynyl complexes $Fe_2(CO)_6(\mu\text{-}SEt)(\mu\text{-}C{\equiv}CR)(R = Me, Ph)$ have also been prepared in low yields from the reaction of $EtSC{\equiv}CR$ with $Fe_2(CO)_9$, while $Fe_2(CO)_6(\mu\text{-}SC{\equiv}CPh)(\mu\text{-}C{\equiv}CPh)$, prepared in a similar manner from $S(C{\equiv}CPh)_2$, has been crystallographically characterized. The reactivity of these μ-alkynyl complexes toward alkynes and phosphines has also been explored.[120] A wide range of products has been isolated, reactions with alkynes leading to unusual new complexes as a result of the coupling of thiolato-alkynyl-alkyne-carbonyl moieties at the diiron center.

Reaction of **129** with $EtOC{\equiv}CH$ followed by addition of acetyl or benzoyl chloride gives novel vinyl alkylidene complexes **132**, while quenching with CF_3CO_2H gives the vinyl–acyl complex **133** which loses CO upon standing to give $Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}EtOC{=}CH_2)$.[110] Aryl–acyl complexes **134** are formed upon addition of chlorobenzoyl chlorides to **98**[111] and related bis(diiron) complexes result when phthaloyl chlorides are used.[112] Iminoacyl complexes **135** are generated from $Ph(Cl)C{=}NAr$ (Ar = Ph, *p*-Tol, *p*-C_6H_4Cl),[114] while closely related **136** (X = O, S, NMe; $R^2 = H$, Me) have also been prepared.[115] Novel phosphido-bridged compounds **137**, which exist as a mixture of three isomers with different relative arrangements of the subsistuents at sulfur and phosphorus, are prepared from phospha-alkene addition,[116] while reaction with $AuCl(PPh_3)$ in the presence of $TlBF_4$ affords novel clusters **138**.[117] Addition of selenium powder or S_8 affords anions **139**;[118,119] CS_2 adds across the diiron center to give **140**,[112] and reaction with S_2Cl_2 leads to the formation of bis(diiron) complexes **141**.[112]

Song *et al*. have prepared a wide range of bis(diiron) complexes such as **141** with anions **139** and **140** being widely utilized precursors.[112,119,121–128] For example, reaction of **139** (E = S) with SO_2Cl_2 provides another route to **141**. In contrast, with the seleno-bridged analog, selenium is extruded to yield **142**, the analogous sulfur-linked complexes being prepared upon reaction of **139** (E = S) with succinoyl or terephthaloyl chloride.[119] Anions **140** also react with SO_2Cl_2, somewhat surprisingly giving dithioformamato-bridged complexes **143**.[121] Reaction of **129** with $Fe_2(CO)_6(\mu\text{-}E_2)$ (E = S, Se) affords bis(diiron) anions **144**,[124–127] which react further with a wide range of organohalides to afford complexes with up to four isolated diiron centers.[124]



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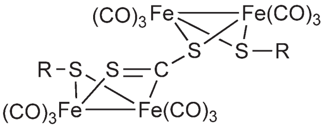

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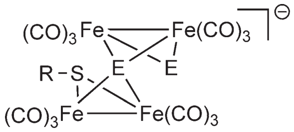
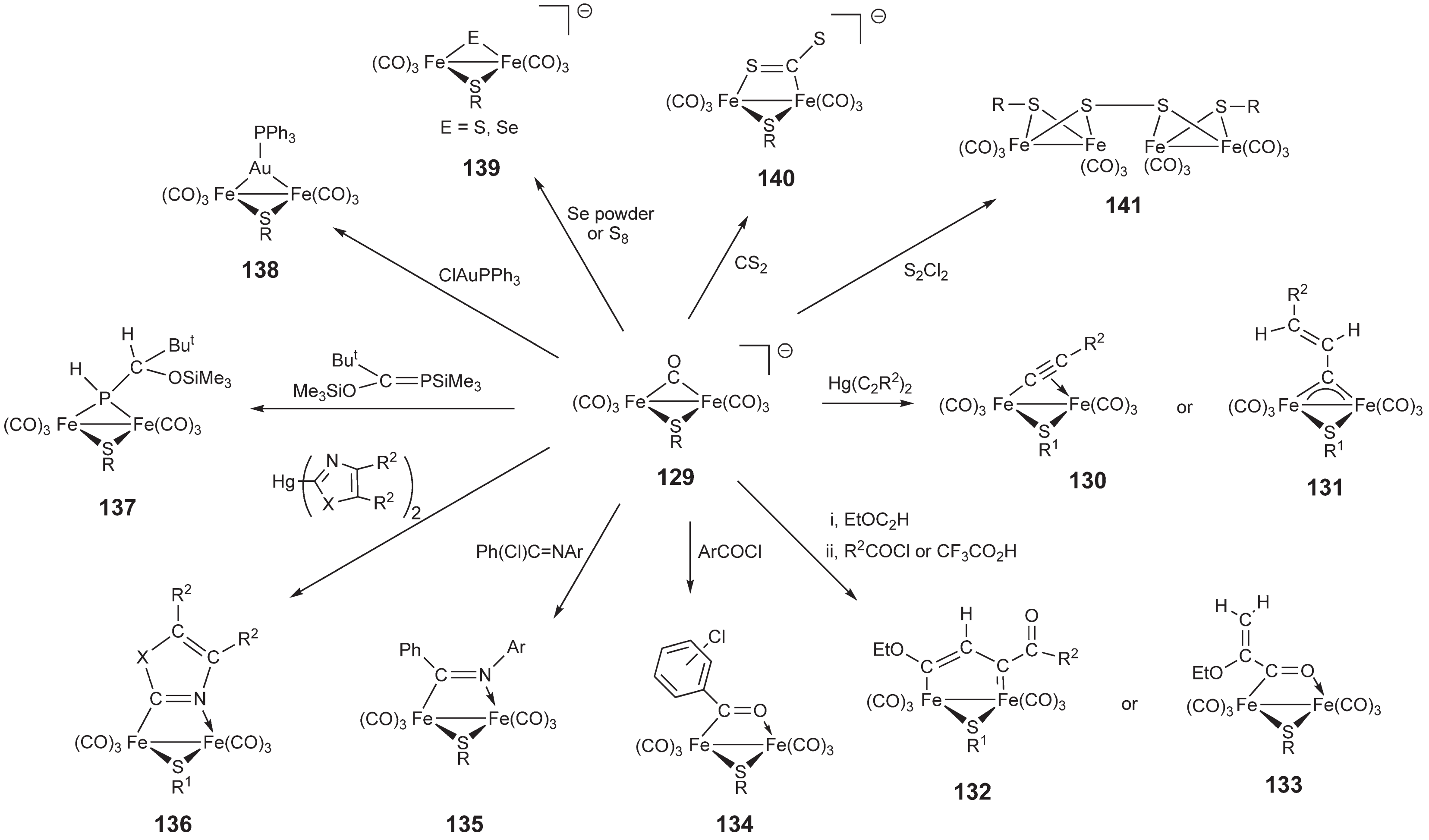


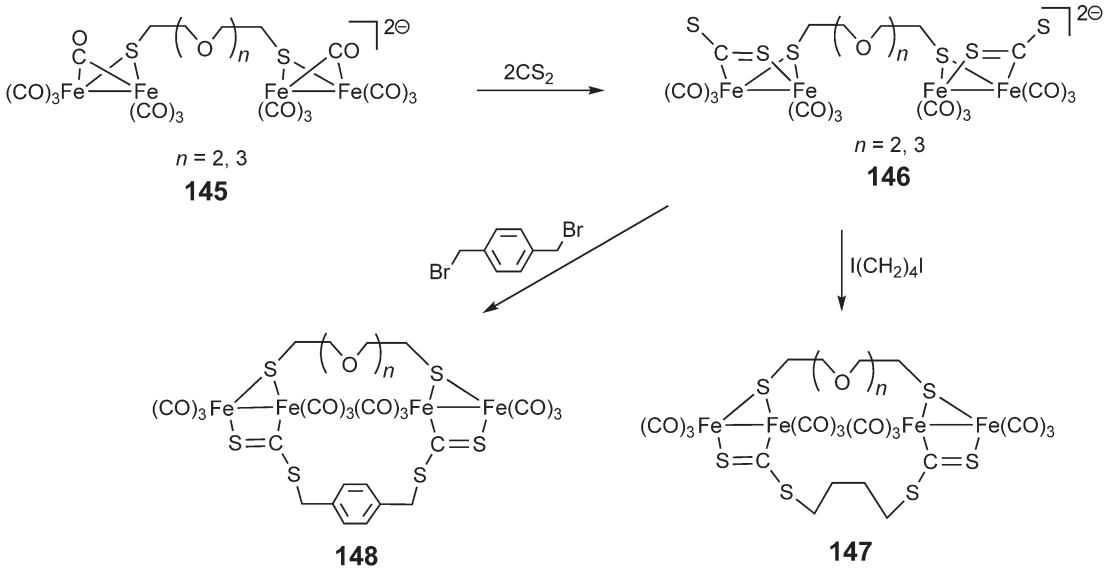
144

In a second approach to preparing clusters with multiple diiron centres, Song *et al*. have utilized the diiron-bridged complexes **145**, prepared from the reactions of $Fe_3(CO)_{12}$ with the appropriate dithiol in the presence of Et_3N, as a building block to synthesize a range of chains and macrocycles containing up to four diiron centers.[129–132] For example, addition of CS_2 to afford **146** or $Fe_2(CO)_6(\mu\text{-}E_2)$ (E = S, Se) occurs in a manner analogous to that discussed for **129**, and when the anions generated are reacted with dihalides macrocycles such as **147** and **148** result (Scheme 13).

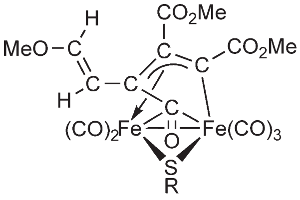
A few papers have focused on the reactivity of thiolate-bridged complexes. Seyferth *et al*. have shown that μ-alkylidyne complexes $Fe_2(CO)_6(\mu\text{-}COEt)(\mu\text{-}SR)$ readily isomerize to the μ-acyl species $Fe_2(CO)_6(\mu\text{-}O{=}CEt)(\mu\text{-}SR)$ and react with activated alkynes such as RC_2R ($R = CO_2Me$) to afford **149** resulting from coupling of the alkyne, alkylidyne, and CO moieties.[133] Hogarth *et al*. have reported that heating $Fe_2(CO)_6\{\mu\text{-}O{=}C\text{–}C(Ph){=}CH_2\}(\mu\text{-}SC_6F_5)$ with dppm yields predominantly **150** and **151** resulting from elimination of pentafluorobenzene,[134] and Petillon and co-workers have described the phosphine and phosphite substitution chemistry of **152**.[135,136] The thiolate ligands in **150–152** and their derivatives are dynamic and their fluxionality has been studied extensively by VT NMR, changes being interpreted as resulting from a tethered "windshield wiper" process.[79,134]



Scheme 12 Reactions of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SR)]^-$, 129.



Scheme 13 Examples of the synthesis of diiron containing macrocycles.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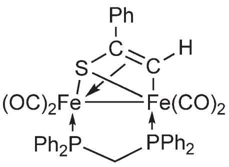
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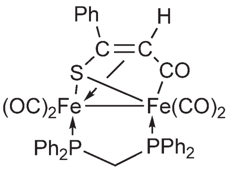
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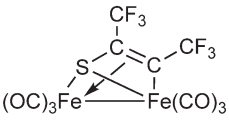
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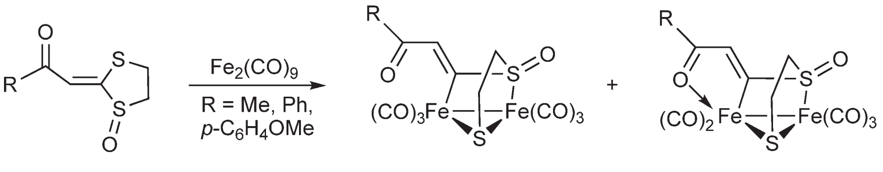
6.06.2.8 Dithiolate-bridged Compounds

Dithiolate-bridged compounds, $Fe_2(CO)_6(\mu\text{-}SR)_2$, have been known for many years but have recently taken on a greater significance due to their structural similarity to the active site of the iron-only hydrogenase enzyme (see following section). Crystallographic studies of a number of phosphine-substituted derivatives have been carried out including $Fe_2(CO)_4(\mu\text{-}SAr)_2(\mu\text{-}dppm)_2$ (Ar = Ph, *p*-Tol),[28] $Fe_2(CO)_5(PPh_3)(\mu\text{-}SEt)_2$,[117] and $Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SEt)_2$;[137] those with aryl groups adopt the *anti*-conformation, while μ-SEt complexes adopt a *syn*-conformation.

A number of hexacarbonyl complexes with linked dithiolate ligands have been prepared, including $Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S)$[138] and $Fe_2(CO)_6\{\mu\text{-}SCH_2CH_2C(S)S\}$,[139] the latter resulting from addition of the cyclic trithiocarbonate to $Fe_2(CO)_9$. Alvarez-Toledano and co-workers have prepared $Fe_2(CO)_6\{\mu\text{-}SCH(CH_2C(O)C_6H_6R)S\}$ (R = Me, OMe, Cl, Br) and $Fe_2(CO)_6\{\mu\text{-}SC({=}CHC(O)C_6H_6R)S\}$ (R = OMe, F) with a single backbone carbon atom from reactions of the appropriate dithiol with $Fe_2(CO)_9$.[140,141] When α,β-unsaturated ketones containing β-sulfoxide groups **153** were reacted with $Fe_2(CO)_9$, products included $Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S)$, **154** (R = Me, Ph, *p*-C_6H_4OMe) and **155** (R = *p*-C_6H_4OMe) resulting from opening of the thiolate ring (Equation (15)).[142]



(15)

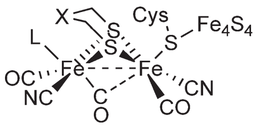
Rauchfuss and co-workers report that UV irradiation of toluene solutions of $Fe_2(CO)_6(\mu\text{-}S_2)$ and C_{60} affords a mixture of addition products, $C_{60}\{Fe_2(CO)_6(\mu\text{-}S_2)\}_n$ ($n = 1$–6), the lighter three members of which have been fully characterized.[143] One ($n = 1$) has been studied crystallographically and closely resembles $Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S)$. Addition of C_{60} to $Fe_2(CO)_5(PPh_3)(\mu\text{-}S_2)$ affords similar adducts ($n = 1$–3) which appear to exist as mixtures of isomers, while the photochemical reaction of $Fe_2(CO)_6(\mu\text{-}S_2)$ with C_{70} at −40 °C also affords similar adducts ($n = 1$–4), four isomers being detected for the bis(adduct).

Reactions of the toluene-dithiolate-bridged complex, $Fe_2(CO)_6(\mu\text{-}SC_6H_4MeS)$, with a range of phosphines and phosphites have been studied.[144] With phosphites, both mono- and disubstituted products are formed at 70 °C, while with Ph_2PH disubstitution occurs at room temperature; however, for dppm only a monosubstituted product is seen even after prolonged heating at 80 °C.

6.06.2.9 Dithiolate-bridged Compounds as Biomimetic Models for Iron-only Hydrogenase

Hydrogenases are enzymes which catalyze dihydrogen metabolism in a wide range of micro-organisms, functioning either as electron sinks or providing organisms with reducing power from the oxidation of hydrogen. They can be divided into two unrelated types: nickel–iron (Ni–Fe) and iron-only (Fe–Fe) hydrogenases, reflecting the different metals present at the active site. In the late 1990s, evidence from crystallographic studies of two organisms, *Clostridium pasteurianum*[145] and *Desulfovibrio desulfuricans*,[146] together with an IR study,[147] led to the realization that the active site of the iron-only hydrogenases contained a dithiolate-bridged diiron center stabilized by carbonyl and cyanide ligands, being anchored to the protein through a single cysteine (Cys) sulfur which bridges to an adjacent Fe_4S_4 cluster **156**. From this early work the nature of the thiolate bridging group (X) was unclear, but later crystallographic[148] and theoretical[149,150] studies have concluded that it is most likely an azapropanedithiolate ligand (X = NH). From both experimental and theoretical work,[150,151] it appears that the oxidized form (H_{ox}) of the enzyme (as isolated in air) is an inactive Fe(II)–Fe(II) species, the site "L" in **156** being occupied by strongly coordinated water which probably leads to the inactivity. In the reduced form of the enzyme (H_{red}), presumed to be Fe(I)–Fe(I), this site is either vacant or occupied by H_2 or H^- which cannot be detected by protein crystallography.[146,148] Catalysis of proton reduction by the iron-only hydrogenases occurs at extremely fast rates, of the order of 10^4 turnovers s^{-1}, suggesting that major structural rearrangements are not occurring during the process.[152,153] In light of these findings, a wide range of dithiolate-bridged diiron complexes have been studied as biomimetic models of iron-only hydrogenases, leading contributions being made by the groups of Darensbourg,[137,154–161] Rauchfuss,[162–169] Pickett,[170–175] Ott,[176–178] and others.[179–183] A number of recent reviews have appeared summarizing the efforts in the area[150,151,184–187] and so here only a relatively brief synopsis will be given.

Early biomimetic models included the hexacarbonyl complexes $Fe_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)$ **157**,[154,162,170] and $Fe_2(CO)_6(\mu\text{-}SCH_2NRCH_2S)$ **158** (R = H, Me),[163,166] and pentacarbonyl **159**.[188] Complexes are generally easily prepared, either from reaction of the appropriate dithiol with iron carbonyls or from $Fe_2(CO)_6(\mu\text{-}S_2)$ or $Fe_2(CO)_6(\mu\text{-}SH)_2$. All undergo relatively facile substitution of two carbonyls for cyanides upon addition of $[Et_4N]CN$,[154,162,163,170] or phosphines,[157] affording tetracarbonyl complexes with close structural similarities to the active site of iron-only hydrogenases. For example, **157** reacts with $[Et_4N]CN$ to afford dianion $[Fe_2(CO)_4(CN)_2(\mu\text{-}SCH_2CH_2CH_2S)]^{2-}$ **160**, a crystal structure showing that each iron atom is bound to a single cyanide.[162] It is interesting to note that the monosubstituted species $[Fe_2(CO)_5(CN)(\mu\text{-}SCH_2CH_2CH_2S)]^-$ **161** is seen only in trace amounts when **157** reacts with 1 equiv. of $[Et_4N]CN$ and it has been shown that **161** is not an intermediate in the formation of **160**, addition probably occurring via a non-metal–metal bonded intermediate **162** (Scheme 14).[155,167]



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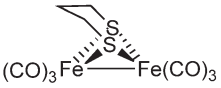

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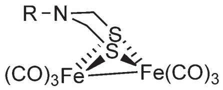

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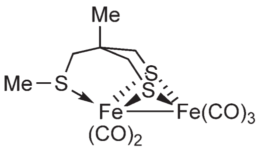
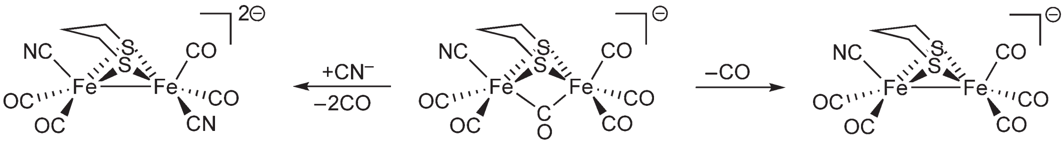


159

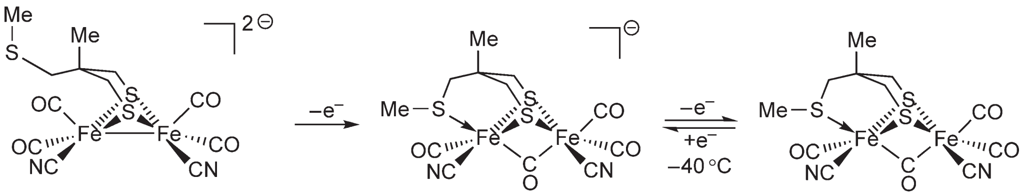
It is noteworthy that in **160** and other disubstituted complexes, all four remaining carbonyls are terminally bonded, while the enzyme active site features a bridging carbonyl, although the degree of bridging depends on the oxidation state of the diiron center. The bridging carbonyl feature has been hard to replicate in the biomimetic Fe(I)–Fe(I)


160 **162** **161**

Scheme 14 Cyanide substitution pathways for $Fe_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)$, **157** via **162**.

models, although thermally unstable intermediates **164 and 165** with bridging carbonyls have been observed upon oxidation of **163** (Scheme 15).[172]

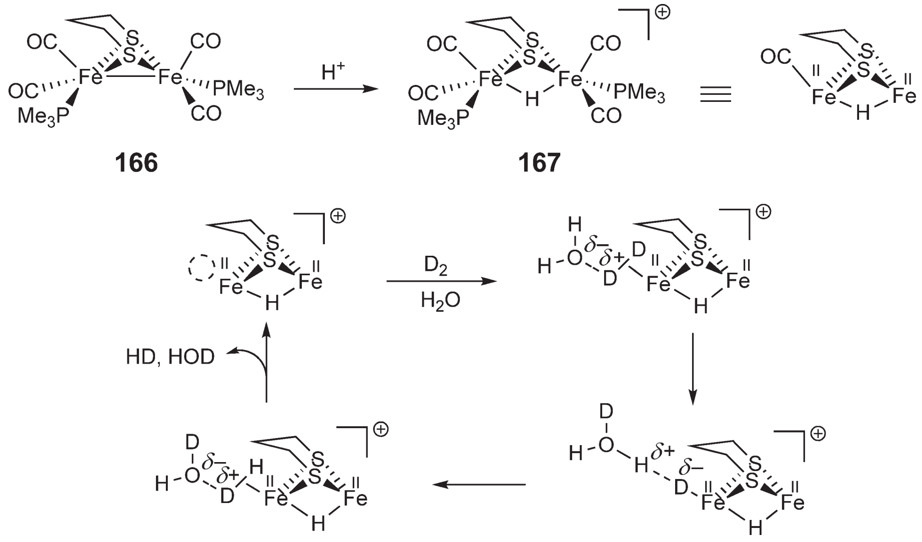
From structural and spectroscopic studies it appears that the reduced Fe(I)–Fe(I) form of the enzyme (H_{red}) has a vacant coordination site capable of substrate binding and can take up a proton. However, no hexacarbonyl model is sufficiently basic to perform this task. Darensbourg and co-workers have shown that the more electron-rich tetracarbonyl complex $Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SCH_2CH_2CH_2S)$ **166** and others are capable of binding H^+ and other electrophiles.[137,157,159] Protonation to afford **167** results in only small changes to the Fe_2S_2 core, the iron–iron bond length increasing from 2.555(2) to 2.578(1) Å. Consistent with the behavior of the enzyme, H/D exchange occurs upon addition of D_2 or D_2O to the Fe(II)–Fe(II) complex **167**, processes that are facilitated by light but inhibited by CO. This suggests that a vacant coordination site is required for the exchange leading to the suggestion of a possible mechanism (Scheme 16).[159,185] Interestingly, Darensbourg and co-workers have also demonstrated that


Fe(I)–Fe(I)
163

Fe(I)–Fe(II)
164

Fe(I)–Fe(II)
165

Scheme 15 Generation of bridging carbonyl complexes upon oxidation of Fe(I)–Fe(I) complex, **163**.

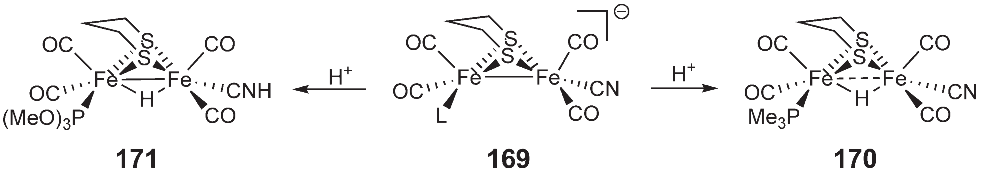

166 **167**

Scheme 16 Protonation of $Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SCH_2CH_2CH_2S)$, **166**, and proposed mechanism for H/D exchange.

H/D exchange occurs between D_2 and terminal alkenes in the presence of **167**, substantial regioselectivity for H/D exchange at the internal vinylic hydrogen being observed.[158]

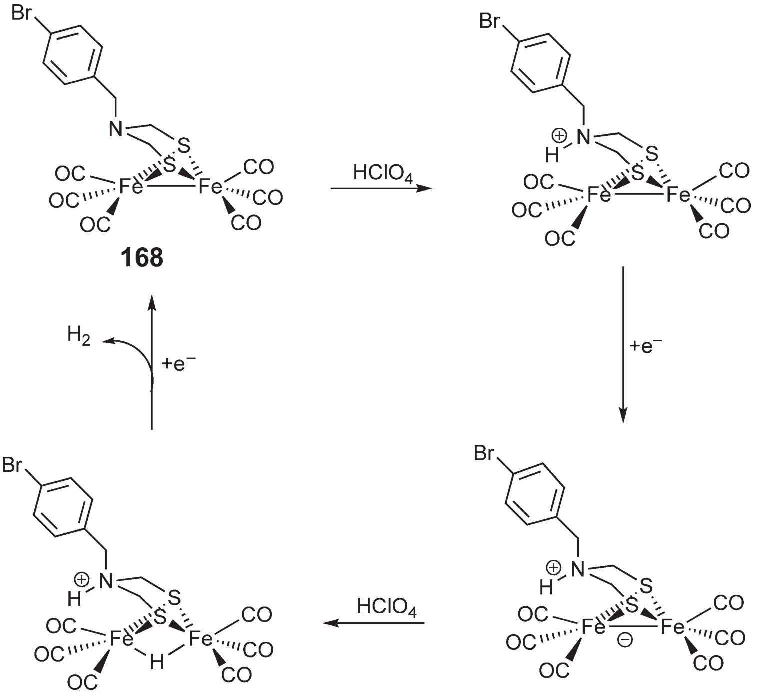
It should be stressed that at no stage does a bridging hydride occur in the enzyme and it is most likely that a one-electron oxidation of the Fe(I)–Fe(I) state yields an Fe(I)–Fe(II) center, and it is the coordinately unsaturated 16-electron iron(II) center which can bind dihydrogen. A number of other publications deal with the protonation of model compounds. Ott and co-workers have shown that the hexacarbonyl azadithiolate compound **168** is protonated at nitrogen by strong acids and under these conditions electrocatalytic reduction of protons occurs to give dihydrogen, a catalytic cycle being proposed (Scheme 17).[177] Best and co-workers have also shown that while $Fe_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)$ **157** does not readily bind protons, electrocatalytic proton reduction can occur in the presence of moderately strong acids, the reduction being about as fast as related cyano- and phosphine-substituted complexes.[175]

Rauchfuss and co-workers report that while protonation of $[Fe_2(CO)_4(CN)_2(\mu\text{-}SCH_2CH_2CH_2S)]^{2-}$ **160** results in generation of some dihydrogen, this is accompanied by the irreversible formation of an intractable solid, probably as a result of protonation of the cyanides.[162] The monoanion **169** ($L = PMe_3$), while being ca. 0.5 V less reducing than **160**, has proved to be an excellent catalyst for proton reduction.[165] Interestingly, while protonation of **169** ($L = PMe_3$) occurs as expected across the iron–iron vector to afford **170**, addition to the analogous phosphite derivative **169** [$L = P(OMe_3)$] occurs at the cyanide ligand to give **171** (Equation (16)).[165,169] DFT calculations have been used to probe this regioselectivity and suggest that the difference in the donor properties of phosphine and phosphite leads to a crossover between the more basic site, being either the iron–iron bond or the cyanide ligand.



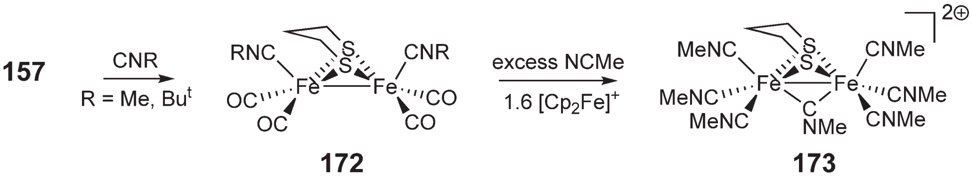
(16)

Nehring and Heinekey have reported that protonation of $Fe_2(CO)_4(CNR)_2(\mu\text{-}SCH_2CH_2CH_2S)$ **172** ($R = Bu^t$) occurs across the iron–iron bond to afford a mixture of four isomeric cationic bridging hydride complexes, differing in the relative orientations of the isonitrile ligands, which react with D_2 upon irradiation leading to the formation of HD.[179] Heating **172** ($R = Me$) with an excess of CNMe at 70 °C in the presence of ferrocenium cation results in



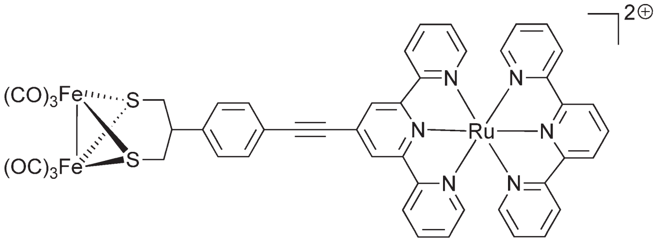
Scheme 17 Proposed catalytic cycle for the electrocataytic reduction of protons by **168**.

complete carbonyl displacement to give the novel dication **173** (Equation (17)), the ethanedithiolate analog being prepared in a similar manner.[168] Both have been characterized crystallographically and, importantly with respect to the iron-only hydrogenases, they contain a bridging isocyanide ligand which is approximately linear, being consistent with little backbonding from the Fe(II)–Fe(II) center, and relatively short iron–iron contacts [2.600(1)–2.634(1) Å].



(17)

In recent work, Ott *et al.* have prepared the biomimetic complex **174** in which the diiron unit is covalently linked to a $[Ru(terpy)_2]^+$ photosensitizer, in a first attempt toward making a light-driven proton reduction system.[176,178] IR spectra of **174** are identical to the parent azadithiolate complex, suggesting that the metal centers are electronically isolated. The observed excited-state lifetime is 6.5 ns, being substantially shorter than related non-iron-containing compounds, and combined with electrochemical measurements this shows that electron transfer from the photogenerated $[Ru(terpy)_2]^{2+}$ excited state to the diiron center is uphill by 0.59 eV.[176]



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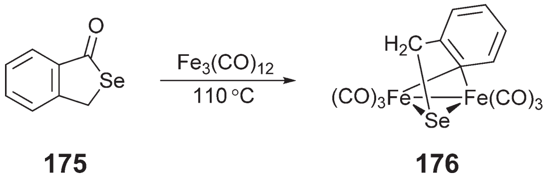
6.06.2.10 Selenolate and Tellurolate-bridged Compounds

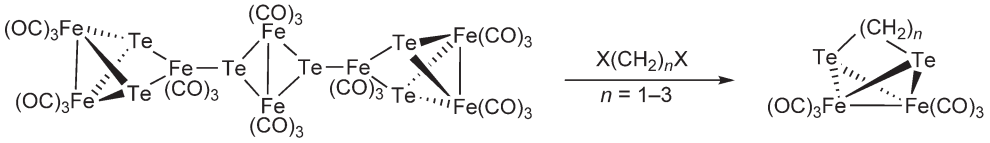
Selenolate-bridged anions $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SeR)]^-$, previously prepared by Seyferth and co-workers, have been extensively utilized by Song *et al.* in a wide range of reactions, the observed chemistry mirroring that of the analogous thiolate-bridged species.[114,116,121,124,189–193] McWhinnie and co-workers have reported that thermolysis of 2-selenaphthalide **175** with $Fe_3(CO)_{12}$ affords binuclear **176** as the major product, resulting from CO extrusion (Equation (18)).[194]



(18)

Bis(selenolate) complexes $Fe_2(CO)_6(\mu\text{-}SeR)_2$ have been prepared in a number of ways. Reduction of $Fe_2(CO)_6(\mu\text{-}Se_2)$ by Bu^{n}Li affords $Li_2[Fe_2(CO)_6(\mu\text{-}Se)_2]$ which in turn reacts with MeI to afford $Fe_2(CO)_6(\mu\text{-}SeMe)_2$,[195] while reaction of PhSeP=CClBu^t with $Fe_2(CO)_9$ affords $Fe_2(CO)_6(\mu\text{-}SePh)_2$.[196] The phosphine substitution chemistry of the latter and the related *p*-tolylselenolate complex has been extensively investigated and a range of penta- and tetracarbonyl derivatives characterized.[197,198]

A number of tellurolate-bridged anions $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}TeR)]^-$ have been prepared by Song *et al.* from the reaction of the *in situ* generated RTeLi or RTeMgX with $Fe_3(CO)_{12}$.[193,199] Their chemistry has been extensively investigated,[124,193,199,200] and again it closely mirrors that of the analogous thiolate and selenolate-bridged species. Shieh *et al.* have prepared the novel cluster **177** from the reaction of K_2TeO_3 and $Fe(CO)_5$/KOH in methanol.[201] It consists of three diiron centers linked via $Te_2Fe(CO)_3Te$ units. Reactions with dihaloakanes result in the formation of ditellurolate-bridged complexes $Fe_2(CO)_6\{\mu\text{-}Te(CH_2)_nTe\}$ **178** ($n = 1–3$) (Equation (19)), while with 1,3-dibromopropane, anionic $[Fe_2(CO)_6(\mu\text{-}BrTe_2)]^-$ is also obtained.[202] Three of the complexes including the latter have been crystallographically characterized, each showing the expected Fe_2Te_2 butterfly core geometry.

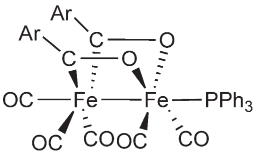


177 **178**

(19)

6.06.2.11 Bis(acyl)-bridged Compounds

A number of acyl-bridged diiron complexes have been detailed above in which phosphido- or thiolate-ligands also bridge the diiron vector. Somewhat different are bis(acyl)-bridged compounds that contain quite different iron atoms, one bound to the two carbons and the second to the two oxygens. A number of synthetic routes have been developed. While addition of organolithium reagents to $Fe(CO)_5$ followed by acidification by CF_3CO_2H in the presence of PPh_3 generally affords a high yielding route to $Fe(CO)_3(PPh_3)_2$, when 2,6-$Me_2C_6H_3Li$ (ArLi) is employed, the phosphine-substituted bis(acyl) complex **179** is the major product.[203] A closely related μ-carbamoyl complex **180** can be prepared by a number of routes including the oxidation of the mononuclear carbamoyl complex $Li[Fe(CO)_4\{C(O)NPr^i{}_2\}]$ with $HgCl_2$ in the presence of PPh_3.[203] In both of these examples, the phosphine is bound to the oxygen-ligated iron center, lying approximately *trans* to the metal–metal bond. The amine-substituted μ-carbamoyl complex **181** is formed upon oxidation of $[C(NMe_2)_3][Fe(CO)_4\{C(O)NMe_2\}]$ with Ag^+.[204] The amine, which again lies on the oxygen-bound center and *trans* to the metal–metal bond, can be readily substituted by a range of phosphines including dppe.[205] The latter gives two products, one in which two diiron centers are bridged by the diphosphine and a second **182** with a chelating diphosphine. The central core of these molecules can be described by a number of resonance forms. A comparison of structural parameters between **179** and **180** led Hill *et al.* to conclude that a resonance form **183** involving delocalization of the nitrogen lone pair onto the diiron center may be important in μ-carbamoyl complexes, and this is supported by NMR measurements which show restricted rotation about the N–C bonds.[203]



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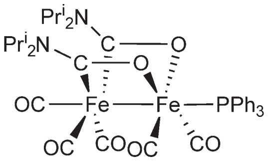

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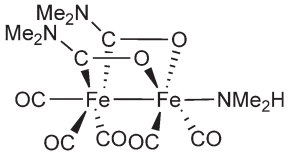

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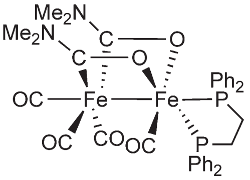

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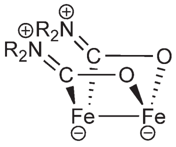
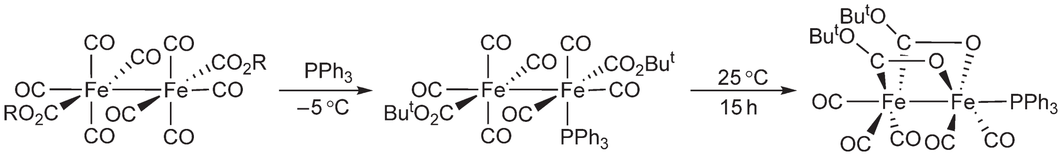


183

Salaün and co-workers have reported that the bis(acyl) complex $Fe_2(CO)_6(\mu\text{-}O{=}CMe)_2$ results from addition of oxalyl chloride to 2 equiv. of $Li[Fe(CO)_4\{C(O)Me\}]$, the analogous carbamoyl complex resulting when $Li[Fe(CO)_4\{C(O)NPr^i{}_2\}]$ is used.[206] In contrast, with the alkoxycarbonyl complexes, $Li[Fe(CO)_4\{C(O)OR\}]$ ($R = Bu^t$, $CMe_2CH{=}CH_2$), unbridged **184** result.[206,207] Addition of PPh_3 to **184** ($R = Bu^t$) at low temperatures initially affords a monosubstituted product **185** but this slowly converts to a μ-alkoxyacyl complex **186** upon standing at room temperature (Equation (20)).



(20)

184 **185** **186**

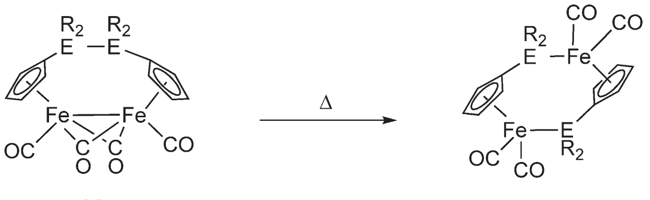
6.06.3 Diiron Carbonyl Complexes with Cyclopentadienyl Ligands

6.06.3.1 $Cp_2Fe_2(CO)_4$ and Related Compounds—Synthesis, Structure, and Photochemistry

Dimeric cyclopentadienyl complexes $Cp_2Fe_2(CO)_4$ have been known for many years and are valuable starting materials for the development of organometallic diiron chemistry. They are readily formed upon heating cyclopentadienes with $Fe(CO)_5$,[208–213] while unsymmetrical complexes can be prepared upon reaction of $Cp^1Fe(CO)_2I$ with $Na[Cp^2Fe(CO)_2]$.[213] They generally exist in solution as interconverting mixtures of *cis*- and *trans*-isomers, the relative amounts of each being dependent on both solvent and substituents, a greater *trans : cis* ratio being achieved upon increasing the number of substituents, the steric limit for an observable amount of the *cis*-isomer being three in the case of methyl substituents.[213]

It has long been known that photolysis of $Cp_2Fe_2(CO)_4$ leads to two disparate processes: metal–metal bond cleavage to give radicals $[CpFe(CO)_2]^{\cdot}$ and CO loss to afford $Cp_2Fe_2(\mu\text{-CO})_3$.[214] Bursten and co-workers have published a detailed resonance Raman study of $Cp_2Fe_2(CO)_4$ and $Cp^*{}_2Fe_2(CO)_4$ leading to a detailed spectroscopic assignment of both tetracarbonyls and also their CO-loss products,[215] while a similar analysis of polycrystalline and matrix-isolated $Cp_2Fe_2(CO)_4$ has been undertaken.[216] A number of groups have used picosecond-resolved spectroscopy to probe the CO-loss process.[217,218] Using UV–VIS detection, Perutz and co-workers have shown the existence of two intermediates en route to $Cp_2Fe_2(\mu\text{-CO})_3$, proposed to be an excited state of *trans*-$Cp_2Fe_2(CO)_4$ which loses CO to afford *trans*-$Cp_2Fe_2(\mu\text{-CO})_2(CO)$.[218] In a significant contribution, Kvietok and Bursten report that extended UV photolysis of $Cp_2Fe_2(CO)_4$ in 3-methylpentane matrices at 98 K leads to the formation of a new species proposed to be $Cp_2Fe_2(CO)_2$, and containing the first example of an unsupported iron–iron triple bond.[219] Structures calculated from DFT calculations are very sensitive to the spin states, the photogenerated triplet state with terminal carbonyls relaxing to a singlet ground state which has bridging carbonyls (Scheme 18).[220] Bursten and co-workers have also examined the matrix photochemistry of $Cp^*{}_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-CH}_2)$[221] and $Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-CHMe})$.[222] With *trans*-$Cp^*{}_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-CH}_2)$, CO loss results to give $Cp^*{}_2Fe_2(CO)_2(\mu\text{-CH}_2)$. This subsequently loses a second CO to afford $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}\eta^1,\eta^1\text{-CO})(\mu\text{-CH}_2)$, which is proposed to contain an iron–iron double bond and a side-bound bridging carbonyl.[221]

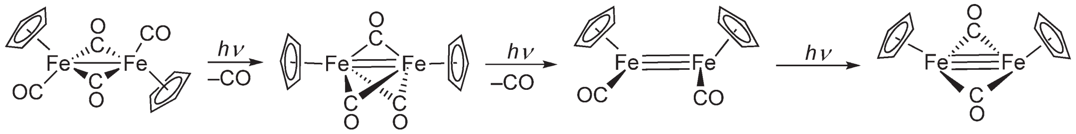
A large number of complexes containing linked cyclopentadienyl ligands have been prepared and structurally characterized. Manning and co-workers have focused their efforts on the preparation of ligands with an asymmetric C_2 backbone, many of which are chiral,[223–226] while Heck and co-workers have prepared the CMe_2-linked complex.[227] In an extensive series of papers, workers at Nankai University in China have detailed the synthesis of disilyl[228–237] and digermyl-bridged[238–240] complexes **187**. These rearrange to the isomeric non-metal–metal bonded complexes **188** upon extended thermolysis in xylene via an intramolecular process which results in the cleavage of both Fe–Fe and E–E (E = Si, Ge) bonds and formation of two new Fe–E bonds (Equation (21)).



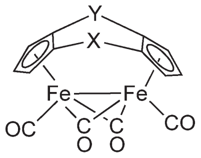
187 **188**

(21)

Very recently a wide range of related doubly bridged complexes **189** have been prepared, although yields are often low.[241,242] Interestingly, they exhibit greater thermal stability than related singly bridged complexes and to date ligand-centered rearrangements have not been noted. Angelici and co-workers have studied the protonation of one example ($X = Y = SiMe_2$), which gives a bridging hydride. The process is reversed upon addition of nucleophiles, which is in contrast to the behavior of the ruthenium analog which undergoes attack at CO.[243]



Scheme 18 Carbonyl loss products of $Cp_2Fe_2(CO)_4$ photolysis.

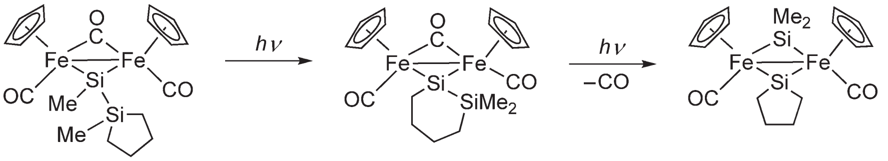


189

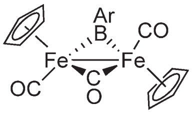
X = Y = $SiMe_2$, $GeMe_2$, $Me_2SiSiMe_2$
X = CH_2; Y = $SiMe_2$, $GeMe_2$
X = CMe_2; Y = $Me_2SiSiMe_2$, $SiMe_2$, $SiPh_2$, $GeMe_2$
X = C_6H_{10}; Y = $SiMe_2$, $GeMe_2$
X = $SiMe_2$; Y = $GeMe_2$, $Me_2SiSiMe_2$

6.06.3.2 Compounds with Group 13 and Heavier Group 14 Ligands

A number of $Cp_2Fe_2(CO)_4$ derivatives with bridging group 13 ligands have been prepared including borylene **190** [Cp = Cp, MeCp, Cp*; Ar = Ph, Mes, $N(SiMe_3)_2$],[244–246] gallylene **191** (Cp = Cp, Cp*; Ar = Mes),[247] and indylene **192**.[248] Borylene and gallylene complexes are prepared either upon photolysis of the corresponding non-metal–metal bonded tetracarbonyls[244,247] or in one case from addition of Na[Cp*$Fe(CO)_2$] to a haloboryl complex,[244] while **192** results upon photolysis of mononuclear $CpFe(CO)_2\{In(CH_2CH_2CH_2NMe_2)_2\}$.[248] A number of silylene complexes **193** have been reported[249,250] including $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiH_2)$[251] formed upon irradiation of the non-metal–metal bonded tetracarbonyl. Ogino and co-workers have also reported related complexes **194** (Ar = Mes, 2,6-$Et_2C_6H_3$, 2,4,6-$Pr^i_3C_6H_2$) formed upon photolysis of $CpFe(CO)_2Me$ and Ar_2SiH_2.[252] All are paramagnetic, as a result of their triplet ground state, and display a short iron–iron interaction of 2.303(2) Å (Ar = 2,4,6-$Pr^i_3C_6H_2$) suggestive of double bond character. Below 10 K, magnetic moments drop sharply to zero, being attributed to an intermolecular antiferromagnetic interaction. Bis(silylene)-bridged complexes **195** have been prepared by Pannell and co-workers by methyl migration in **196** followed by the novel extrusion of an $SiMe_2$ unit from a monosilylene-bridged complex **197** (Equation (22)).[253]



196 **197** **195** (22)



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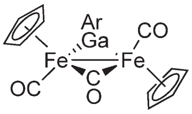

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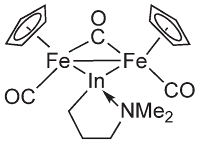

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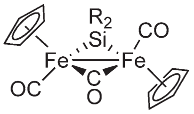

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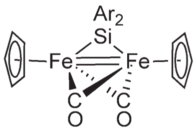

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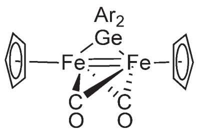

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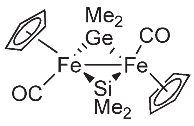

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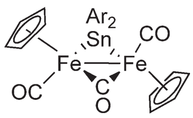

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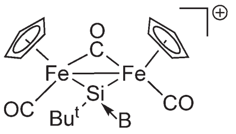

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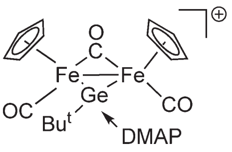


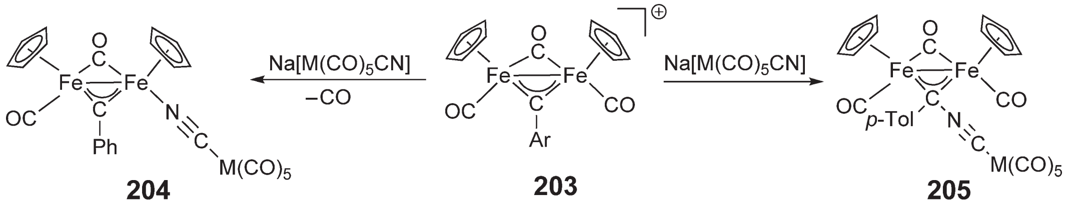
202

Very recently related germylene-bridged complexes **198** (Ar = Mes, 2,4,6-$Pr^i_3C_6H_2$) have been prepared, which again display a triplet ground state.[254] Photolysis of $CpFe(CO)_2SiMe_3$ in the presence of Bu^tGeH_3 affords a mixture of mono- and bisgermylene-bridged complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeHBu^t)$ and $\{CpFe(CO)(\mu\text{-}GeHBu^t)\}_2$ respectively,[255] while extended photolysis of $\{CpFe(CO)_2\}_2(\mu\text{-}Me_2SiGeMe_2)$ affords the mixed silylene–germylene complex $Cp_2Fe_2(CO)_2(\mu\text{-}SiMe_2)(\mu\text{-}GeMe_2)$ **199**.[256] In contrast to the analogous silylene and germylene, photolysis of $CpFe(CO)_2Me$ with Ar_2SnH_2 (Ar = Mes, 2,4,6-$Pr^i_3C_6H_2$) gives only the diamagnetic tricarbonyl complexes **200** and no futher CO loss was noted even when **199** was irradiated under the continuous removal of CO.[254]

Donor-stabilized μ-silylyne and μ-germylyne complexes have been reported. For example, silylenes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHBu^t)$ react with halohydrocarbons to afford μ-halosilylene species $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiBu^tX)$ (X = Cl, Br, I), the iodide complex reacting further with strong Lewis bases, *N*-methylimidazole or 4-(dimethylamino)pyridine (DMAP), to give donor-stabilized μ-silylyne complexes **201**.[250] Other DMAP-stabilized silylyne complexes have also been prepared,[249] as has the germylyne complex **202**.[257]

6.06.3.3 Compounds with Alkylidene and Alkylidyne Ligands

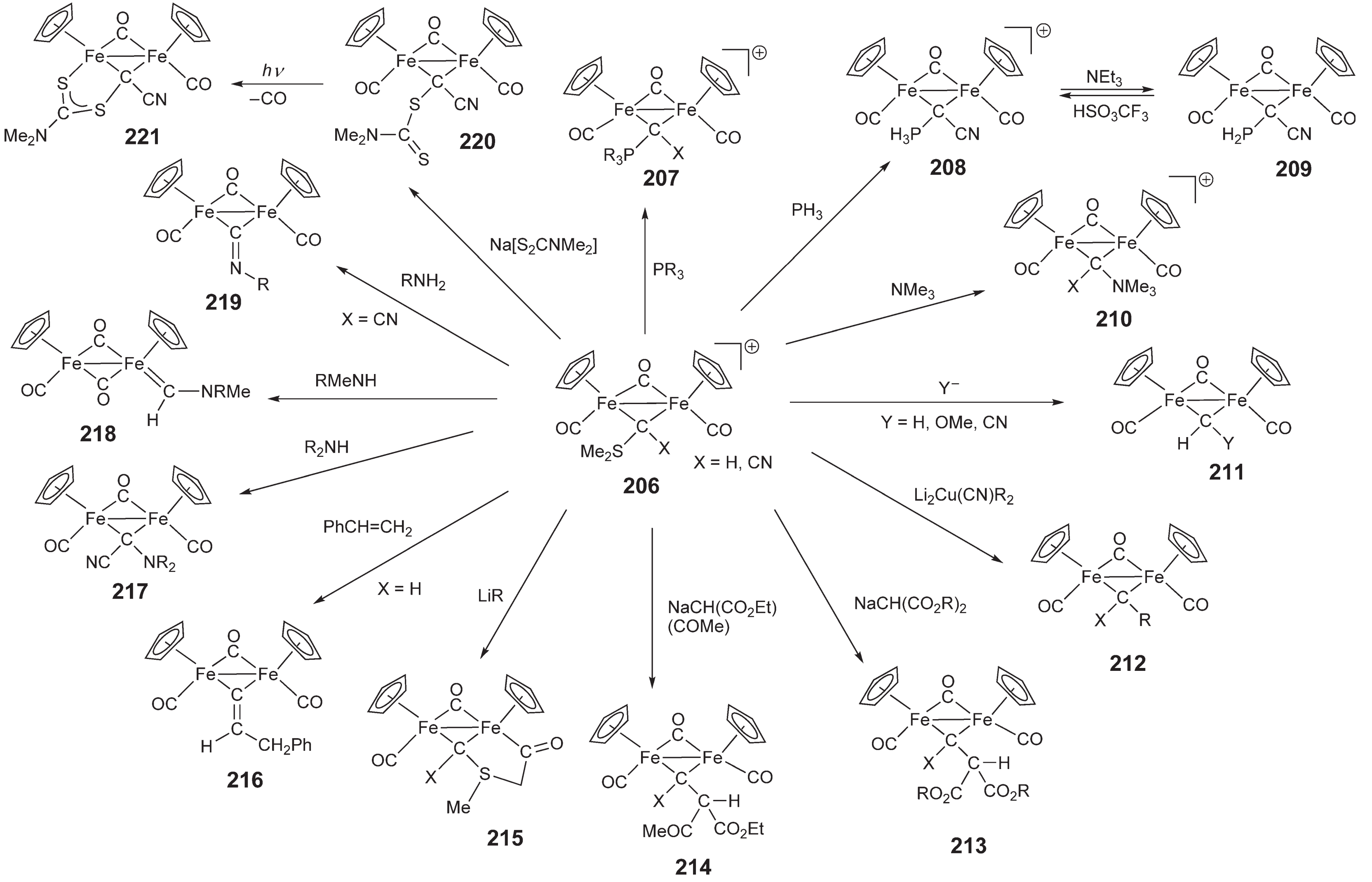
A wide range of diiron alkylidene and alkylidyne complexes have been reported over the past 10 years. In a series of papers, Chen *et al.* have described the synthesis and reactivity of cationic alkylidyne complexes, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CAr)][BBr_4]$ **203** (Ar = Ph, *p*-Tol),[258–260] together with related $SiMe_2$-linked cyclopentadienyl complexes.[261,262] They are formed upon BBr_3 addition to the ethoxy–alkylidene complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CAr(OEt)\}$[258] and react with a range of nucleophiles to yield new heteroatom-substituted alkylidene complexes, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CAr(ER)\}$ (E = S; R = Me, Et, Ph, *p*-Tol, *p*-$C_6H_4NO_2$; ER = OPh, $N(SiMe_3)_2$).[259] With metal carbonyl anions, $Na[M(CO)_5(CN)]$ (M = Cr, Mo, W), the final product is highly dependent upon the nature of the aryl substituent. In one instance (Ar = Ph), carbonyl displacement is observed affording the neutral μ-alkylidyne complexes **204**, while in the second (Ar = *p*-Tol) new μ-alkylidene complexes **205** result from attack at the central carbon (Equation (23)).[260] This difference is considered to be due to the electron-releasing nature of the *p*-tolyl group which leads to the greater π-back-bonding to the carbonyls, thus precluding CO loss. Interestingly, reaction of $Na[Fe(CO)_4(CN)]$ with **203** (Ar = Ph) leads to the formation of the known μ-alkylidene complex, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPh)$.



(23)

Zanotti and co-workers have prepared the base-stabilized μ-methylidyne complex, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CH(SMe_2)\}][SO_3CF_3]$ **206** (X = H), upon treatment of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CH(SMe)\}$ with $MeSO_3CF_3$.[263] The presence of the dimethylsulfide unit not only makes the complex easier to handle than the base-free analog but also reduces the electrophilic character of the methylidyne ligand. Nevertheless, nucleophiles still add to form a range of substituted μ-alkylidene complexes, reactivity which mirrors that of the related cyano–alkylidyne complex, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SMe_2)\}][SO_3CF_3]$ **206** (X = CN).[263–268] Aspects of the chemistry of both are summarized in Scheme 19. Tertiary phosphines readily displace dimethylsulfide to afford phosphonium salts **207**.[263,266] With PH_3 itself (X = CN), an interconvertible mixture of phosphonium salt **208** and the μ-phosphino-alkylidene complex **209** results,[266] similar chemistry being observed for secondary phosphines.[263] Trimethylamine also displaces dimethylsulfide to afford **210**,[263] while neutral μ-methylidene complexes **211** result from addition of various nucleophiles to **206** (X = H).[263] Products of reactions with organometallic compounds are highly dependent upon the nature of the reagent utilized.[267] Thus, while Grignard reagents are unreactive, addition of sodium salts or organocopper reagents $Li_2Cu(CN)R_2$ (R = Ph, Me, Bu, C≡C-*p*-Tol, C_4H_3S) leads to μ-alkylidene complexes **212–214**.[267] In contrast, reactions with alkyllithium reagents give **215**, resulting from deprotonation of a methyl group followed by subsequent attack of the generated carbanion on a metal-bound carbonyl, while vinylidene **216** results from the slow reaction of **206** (X = H) with an excess of styrene.[263]

Reactions of **216** with amines have been extensively studied,[264] addition of tertiary amines resulting in displacement of dimethylsulfide to give adducts akin to **210**. Products of reactions with secondary amines are highly



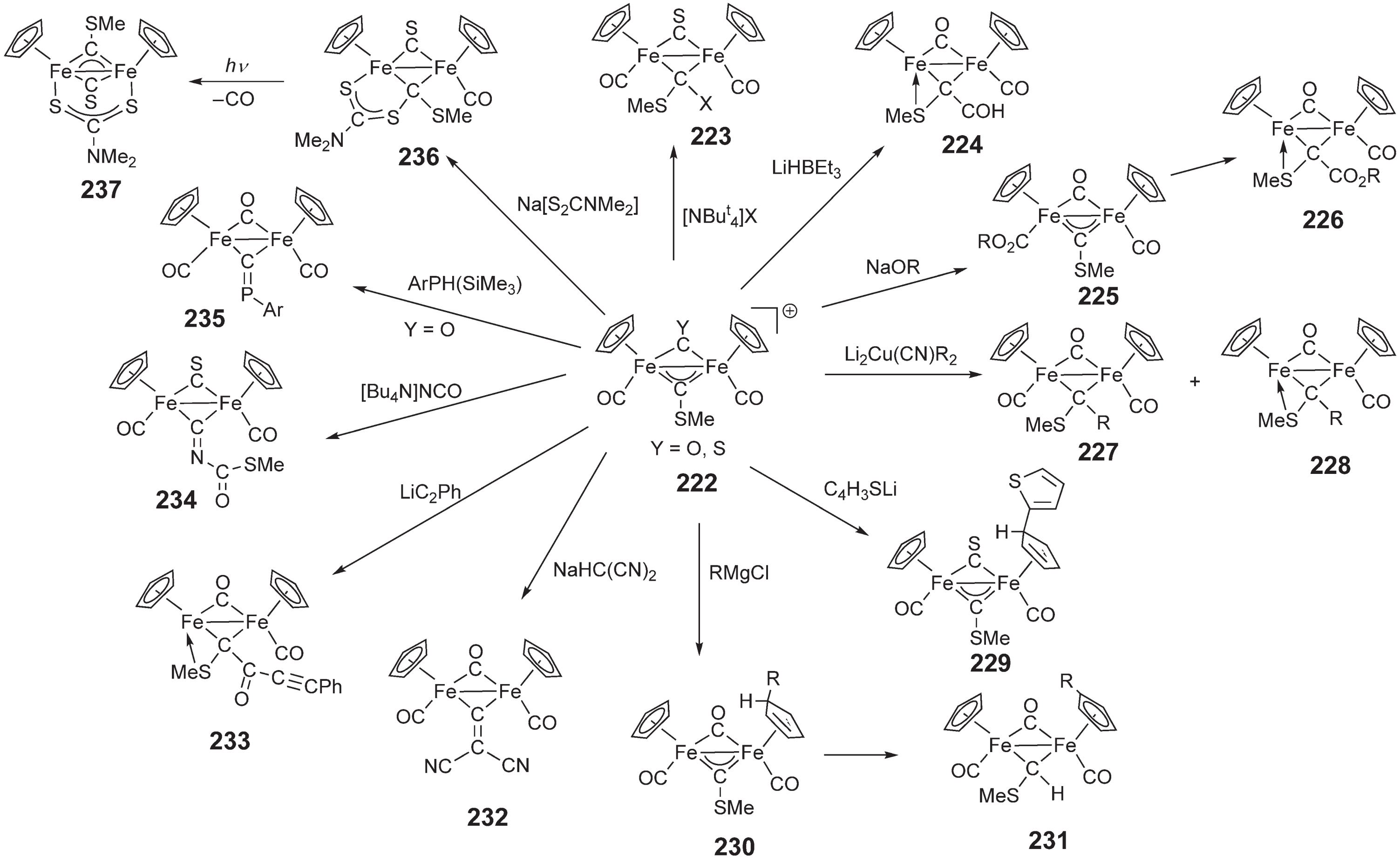
Scheme 19 Aspects of the chemistry of [Cp$_2$Fe$_2$(CO)$_2$(μ-CO){μ-C(X)(SMe$_2$)}][SO$_3$CF$_3$] (X = H, CN), 206.

dependent upon the nature of the alkylidyne substituent ($X = H$, CN). Thus, **206** ($X = CN$) reacts with a wide range of secondary amines to give μ-aminoalkylidene complexes **217**, although the bulky amine Ph_2NH was found to be unreactive. In contrast, secondary amine (MeRNH, $R = Me$, Et) addition to **206** ($X = H$) gives terminal alkylidene complexes **218**,[264] a difference ascribed to the enhanced π-acceptor ability of the cyano-substituted alkylidene group. Interestingly, terminal and bridged isomers of $Cp_2Fe_2(CO)_3\{C(CN)(NEt_2)\}$ are believed to be in thermal equilibrium, suggesting that steric effects are also important.[264] Treatment of **206** ($X = CN$) with a range of primary amines leads to degradation of the bridging alkylidyne unit and formation of isocyanide derivatives **219**, a transformation shown to occur via an aminoalkylidene intermediate. Quite recently, addition of $Na[S_2CNMe_2]$ to **206** ($X = CN$) has been shown to initially afford the simple dithiocarbamate adduct **220**, later photolysis of which leads to carbonyl loss and formation of **221**.[265]

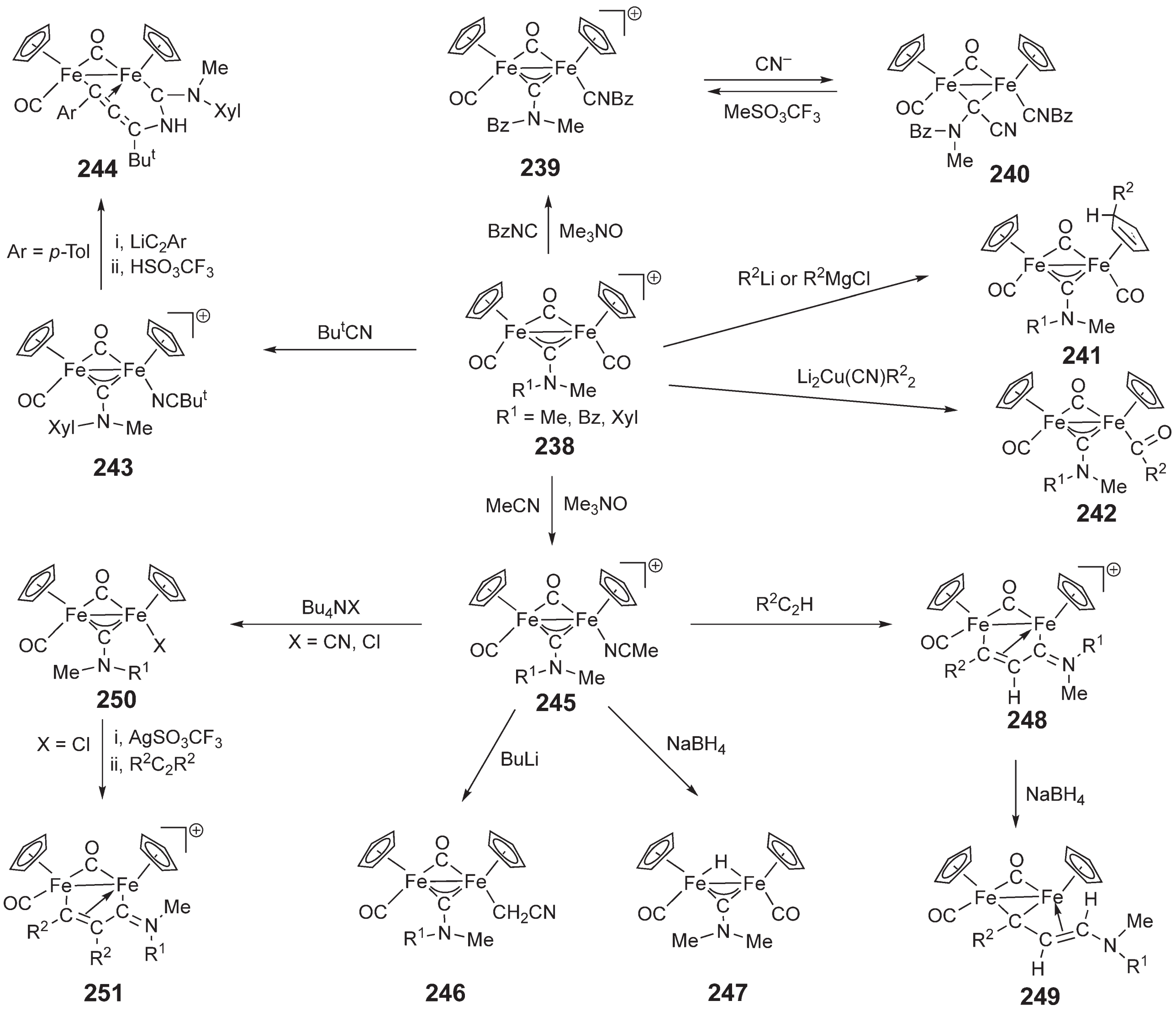
Albano and co-workers have carried out extensive studies of the reactivity of μ-thioalkylidyne complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CY)(\mu\text{-}CSMe)][SO_3CF_3]$ ($Y = O$, S) **222** (Scheme 20).[265,269–274] While their reactivity is dominated by the electrophilic character of the thioalkylidyne ligand, nucleophilic attack has been identified at three sites: the alkylidyne carbon, a carbonyl, or a cyclopentadienyl ligand. Addition of ammonium salts $[NBu^t_4]X$ ($X = H$, CN) affords μ-alkylidene complexes **223** in high yields.[272] With $LiHBEt_3$, the major product is aldehyde **224** proposed to result from hydride addition to a terminal carbonyl followed by subsequent migration of the generated aldehyde moiety to the μ-alkylidyne carbon.[269] Alkoxides also add to a terminal carbonyl affording alkoxycarbonyl complexes **225**, which upon standing rearrange to novel μ-alkylidene complexes **226** via alkoxycarbonyl migration.[269] Addition of organocopper reagents, $Li_2Cu(CN)R_2$ ($R = Me$, Ph), leads to direct attack at the μ-alkylidyne carbon to give μ-alkylidene complexes **227** which readily lose CO to afford **228**.[273] This behavior contrasts markedly with the formation of **229** upon addition of 2-thienyllithium, where attack has clearly taken place at a cyclopentadienyl ligand. With Grignard reagents, nucleophilic attack also initially occurs at a cyclopentadienyl ligand to afford substituted cyclopentadiene complexes **230**, later proton migration to the alkylidyne carbon leading to the formation of μ-alkylidene complexes **231** with a substituted cyclopentadienyl ligand.[271,273] With $NaHC(CN)_2$, attack at the alkylidyne carbon is followed by loss of MeSH to yield the dicyanovinylidene complex **232** which, unlike most diiron vinylidene complexes of this type, exists as a separable mixture of *cis*- and *trans*-isomers.[273] Treatment of **222** ($Y = O$) with $LiC{\equiv}CPh$ at −20 °C affords the new μ-alkylidene complex **233**, presumably formed via initial attack of the acetylide on a terminal carbonyl followed by migration of the unsaturated acyl group to the alkylidyne cartbon.[273] Addition of $[NBu_4]NCO$ to **222** ($Y = S$) leads to an unusual transformation to give **234**, the isocyanate group inserting into the carbon–sulfur bond of the thioalkylidyne ligand,[270] while condensation ($Y = O$) with the secondary phosphines, $ArPH(SiMe_3)$ ($Ar = 2,4,6\text{-}R_3C_6H_2$; $R = H$, Pr^i, Bu^t), affords novel edge-bridging phospha-alkyne complexes **235**.[275] Room-temperature addition of $Na[S_2CNMe_2]$ to **222** ($Y = S$) gives a mixture of **236** and **237**. The latter contains a bridging dithiocarbamate ligand and can also be prepared upon photolysis of **236** or upon addition of $Na[S_2CNMe_2]$ to the bis(acetonitrile) adduct $[Cp_2Fe_2(NCMe)_2(\mu\text{-}CS)(\mu\text{-}CSMe)][SO_3CF_3]$, itself being readily formed upon addition of Me_3NO to **222** ($Y = S$) in acetonitrile.[265] Somewhat surprisingly, all attempts to prepare analogous dithiocarbamate complexes from **222** ($Y = O$) failed, addition of $Na[S_2CNMe_2]$ leading only to $CpFe(CO)(S_2CNMe_2)$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CS)(\mu\text{-}CO)$.

The reactivity of μ-aminoalkylidyne complexes has also been extensively investigated by Albano[276–285] and Manning[286–289] and their co-workers. Cationic complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMeR^1)]^+$ **238** ($R^1 = Me$, Bz, Xyl) display an extensive chemistry (Scheme 21). In a similar manner to the related μ-thioalkylidyne complexes, nucleophilic attack can occur at either the metal-bound carbonyl or cyclopentadienyl ligands; however, in no instance does attack occur directly at the aminoalkylidyne ligand. A key feature of their chemistry is the facile replacement of a carbonyl for an isonitrile or isocyanide in the presence of Me_3NO and the acetonitrile adducts, $[Cp_2Fe_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}CNMeR^1)]^+$ **245**, have been extensively utilized as starting materials for further chemistry. Reactions with butyllithium result in deprotonation of the acetonitrile followed by rearrangement to give neutral cyanomethyl complexes **246**,[280] while in contrast $NaBH_4$ adds to displace acetonitrile and give the μ-hydride complexes **247**.[279] Addition of terminal alkynes leads to the formation of μ-vinyliminium complexes **248** resulting from the regioselective insertion of the alkyne into the metal-aminoalkylidyne unit, which in turn react with $NaBH_4$ to give **249**.[282,284] Insertion of internal alkynes does not occur directly; however, upon removal of chloride from $[Cp_2Fe_2Cl(CO)(\mu\text{-}CO)(\mu\text{-}CNMeR^1)]$ **250** ($X = Cl$), insertion occurs to afford **251** as a mixture of regioisomers. In both instances when non-symmetrical μ-aminoalkylidyne complexes are used ($R^1 = Bz$, Xyl), a mixture of *E*- and *Z*-isomers is possible, although crystallographic studies reveal that complexes derived from terminal alkynes preferentially adopt the *E*-configuration while those from internal alkynes are exclusively *Z*.[284]

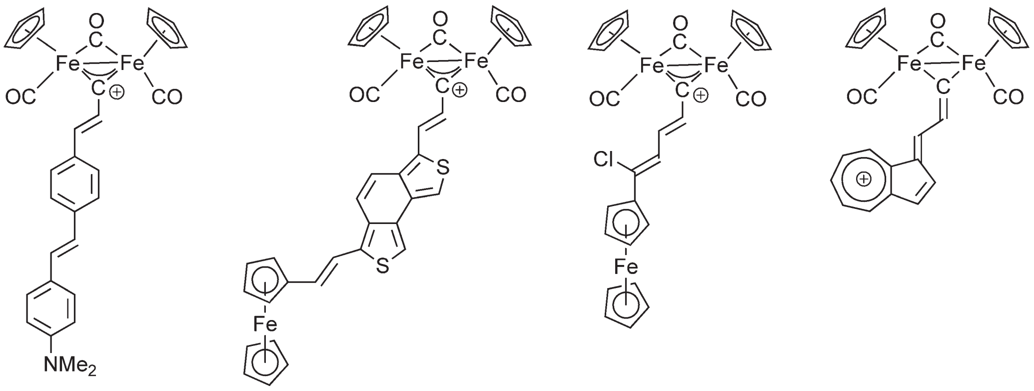
Manning and co-workers have extensively investigated the reactivity of the bis(aminoalkylidyne) complex $[Cp_2Fe_2(CO)_2(\mu\text{-}CNMe_2)_2]^{2+}$ toward a range of hard nucleophiles (OH^-, OR^-, NR_2^-, H^-, Me^-) and found that



Scheme 20 Aspects of the chemistry of [Cp$_2$Fe$_2$(CO)$_2$(μ-CY)(μ-CSMe)][SO$_3$CF$_3$] (Y = O, S), 222.

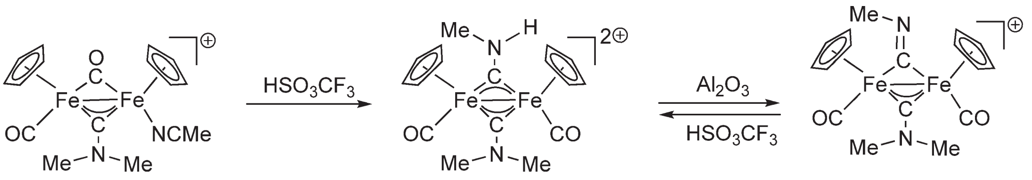


Scheme 21 Aspects of the chemistry of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMeR^1)][SO_3CF_3]$ (R = Me, Bz, Xyl), 238.



Scheme 22 Examples of diiron complexes utilized for non-linear optics.

attack occurs exclusively at a terminal carbonyl.[287,289] They have also reported that the acetonitrile adduct $[Cp_2Fe_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ **252** reacts with trifluoromethanesulfonic acid to give the bis(aminoalkylidyne) complex $[Cp_2Fe_2(CO)_2(\mu\text{-}CNMe_2)(\mu\text{-}CNMeH)]^{2+}$ **253** which in turn can be reversibly deprotonated yielding **254** (Equation (24)).[286,288]



252 **253** **254** (24)

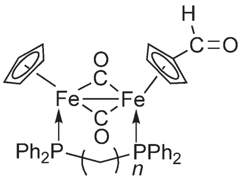
In a series of papers, Manning and co-workers have also reported on the linear and non-linear optical (NLO) properties of a range of μ-vinylalkylidyne and μ-vinylidene complexes, representative examples of which are shown in Scheme 22.[290–296] The cationic diiron moiety, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{-})]^+$, acts as an electron acceptor and conjugation between this moiety and the attached substituted vinyl systems is maintained throughout rotation about the μ-C–vinyl bond.

6.06.3.4 Compounds with Phosphorus Ligands

Phosphido- and phosphinidene-bridged complexes have been prepared from the non-metal–metal bonded $[Cp_2Fe_2(CO)_4(\mu\text{-}PPhR)]^+$ (R = H, Me, Ph, CH_2SiMe_3), photolysis resulting in CO loss and formation of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}PPhR)]^+$, while reaction with $KOBu^t$ at −78 °C (R = H) affords the unstable phosphinidene complex $[Cp_2Fe_2(CO)_4(\mu\text{-}PPh)]^+$.[297]

Shade and co-workers have shown that photolysis of the diphosphine-bridged complexes $Cp_2Fe_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}$ ($n = 1, 2$) in chloroform results in the formation of substituted cyclopentadienyl complexes **255** in which one of the cyclopentadienyl rings has been formylated.[298] Mechanistic studies suggest that the transformation proceeds via a photochemical Reimer–Tiemann reaction in which an irreversible charge transfer occurs to yield a diiron radical cation and a dichloromethyl radical, which after coupling and subsequent hydrolysis afford the observed products. In support of this hypothesis, $[Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}dppm)]^+$ reacts with ICH_2CO_2Et under similar conditions to yield ring-substituted **256**.

While the thermal reaction of $Cp_2Fe_2(CO)_4$ with dppm is known to cleanly afford $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}dppm)$, Ruiz and co-workers have reported that under photochemical conditions seven further products are formed, resulting from a complex series of competing P–C and C–H bond cleavage processes, together with C–C bond formation.[299] The products include a number with novel bridging phosphino-cyclopentadienyl ligands **257, 258** and other phosphido-bridged species **259, 260.** A similar photochemical reaction with $(EtO)_2POP(OEt)_2$ (tedip) affords non-metal-metal bonded $Cp_2Fe_2(CO)_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}OP(OEt)_2\}$ which transforms into $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}tedip)$ in reluxing xylene under a CO atmosphere, a transformation which involves the reductive elimination of the P-O bond.[300]



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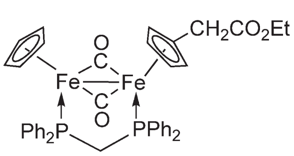

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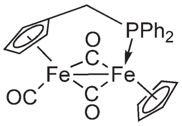

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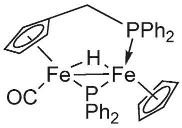

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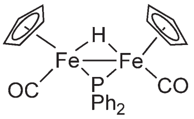

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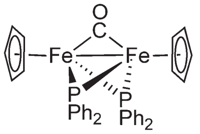

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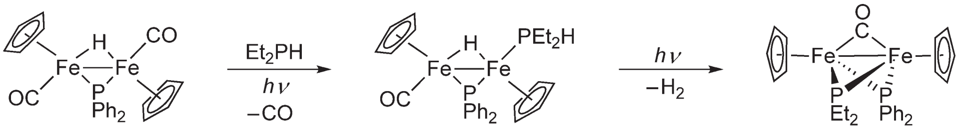
Hydride-bridged $Cp_2Fe_2(CO)_2(\mu\text{-}H)(\mu\text{-}PPh_2)$ is also formed upon thermolysis of $Cp_2Fe_2(CO)_4$ and Ph_2PH, the *trans* isomer **261** initially resulting, which is converted into the *cis* isomer **259** upon photolysis under a CO atmosphere.[301] *Trans* **261** reacts further with Et_2PH upon photolysis to initially afford the carbonyl substitution product **262** which later eliminates hydrogen to yield the asymmetric bis(phosphido)-bridged species **263** (Equation (25)). Complex **261** is also deprotonated upon addition of BuLi to give $Li[Cp_2Fe_2(CO)_2(\mu\text{-}PPh_2)]$ which reacts with MeI yielding $Cp_2Fe_2(Me)(CO)(\mu\text{-}CO)(\mu\text{-}PPh_2)$ and undergoes a reversible one-electron oxidation to the corresponding radical cation upon addition of $[Cp_2Fe][PF_6]$.

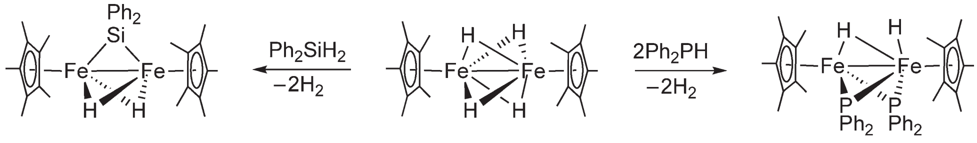


261 **262** **263**

(25)

6.06.3.5 $Cp^*{}_2Fe_2(\mu\text{-}H)_4$ and Compounds with a Single Cyclopentadienyl Ligand

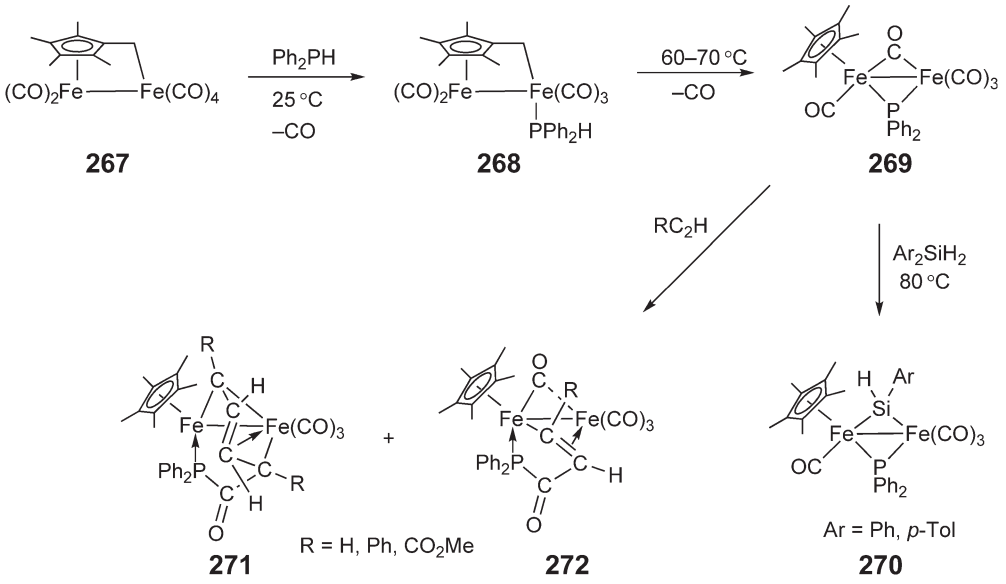
The unstable tetrahydride, $Cp^*{}_2Fe_2(\mu\text{-}H)_4$ **264**, prepared upon reduction of $Cp^*FeCl(tmeda)$ by $LiAlH_4$, contains a short iron-iron bond (2.202(2) Å) suggestive of multiple bond character, although a theoretical analysis of the analogous ruthenium complex suggested the absence of a direct metal-metal interaction.[302] It is highly reactive, addition of Ph_2SiH_2 and Ph_2PH leading to silylene **265** and phosphido-bridged **266** complexes, respectively (Equation (26)), the terminal and bridging hydrides of the latter exchanging at higher temperatures. Borane addition has also been reported, leading to the formation of $Cp^*FeB_4H_{11}$ as a result of metal-metal bond scission.[303]



265 **264** **266**

(26)

Ogino and co-workers have reported the synthesis of the tetramethylfulvene-bridged diiron complex **267** formed from the reaction of tetramethylfulvene with $Fe_2(CO)_9$ in hexane.[304] Thermolysis with CS_2 affords trinuclear and mononuclear products resulting from CS_2 insertion into the iron-carbon bond.[305] With Ph_2PH, the CO-substituted adduct **268** is initially formed at room temperature that transforms into phosphido-bridged **269** after heating at 60–70 °C in benzene.[304] An alternative synthesis of **269** involves the addition of $Li[Fe(CO)_4(PPh_2)]$ to $Cp^*Fe(CO)_2I$ followed by photolysis,[306] and it reacts with silanes Ar_2SiH_2 to give silylene-bridged complexes **270** and $ArSiH_3$,[307] while with primary alkynes and ethyne itself binuclear **271**, **272** (Scheme 23) and mononuclear products result from the coupling of CO, alkyne and phosphido moieties.[306]



Scheme 23 Synthesis and reactions of Cp*$Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$, 269.

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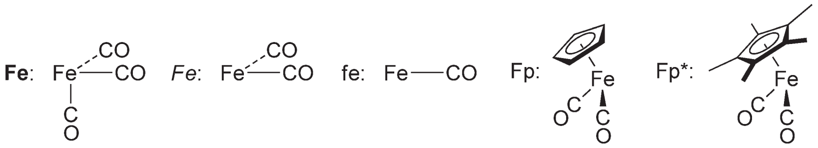
6.07
Iron Cluster Compounds: Compounds without Hydrocarbon Ligands

M Akita, Tokyo Institute of Technology, Yokohama, Japan

6.07.1 Introduction

This chapter covers iron cluster compounds without hydrocarbon ligands reported until early 2005. Previous works were reviewed in COMC (1982) (chapter 31.1, volume 4) and COMC (1995) (chapter 1, volume 7). The first section dealing with iron carbonyl cluster species is followed by sections dealing with polyiron complexes bridged by group 13–16 element ligands, and the contents are organized according to the descending order of the group number of the bridging ligands in the periodic table. Compared with the period covered by the previous versions (−1994), when hydrocarbyl complexes (Chapter 6.08) were the main subject of organometallic cluster chemistry, increasing attention has been focused on cluster compounds containing heteroatoms (main group elements: E) in concert with the rapid development of main group element chemistry. Main group element ligands (E and its functionalized counterparts ER_n), in particular, heavier group 15 and 16 element ligands with lone pair(s) of electrons, readily combine plural iron centers to form polyiron complexes but, in contrast to the robust ruthenium and osmium congeners, a metal–metal bonded cluster structure frequently suffers from fragmentation under the reaction conditions to afford a mixture of di- and mononuclear products. In addition to metal–metal bonded cluster compounds, therefore, condensates or aggregates of di- and/or mononuclear units (e.g., iron–sulfur clusters) are also discussed in this chapter for their relevance to cluster chemistry. The last part is devoted to polyiron complexes consisting of mono- and diiron fragments.

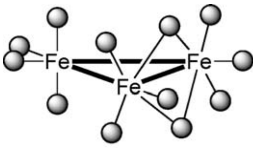
In this chapter the iron carbonyl fragments are abbreviated as shown below and metal–metal bonds are indicated with bold lines. Throughout this chapter, η^5-C_5H_5 and η^5-C_5Me_5 ligands are denoted by Cp and Cp*, respectively.



6.07.2 Iron Carbonyl Clusters

6.07.2.1 $Fe_3(CO)_{12}$

In dodecacarbonyltriiron, $Fe_3(CO)_{12}$ **1**, the Fe_3 triangle adopts a C_{2v}-symmetrical structure with two bridging CO ligands in the solid state in contrast to its heavier congeners of D_{3h}-symmetry only with terminal CO ligands ($Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$). The spectroscopic and structural studies on **1** carried out in the 1990s focused on its complicated dynamic behavior, which equilibrates all 12 CO ligands at higher temperatures (even in the solid state). The dynamic properties have been investigated by means of many techniques including low-temperature X-ray crystallography,[1,2] low-temperature ^{13}C CP-MAS NMR,[3] extended Hückel molecular orbital (EHMO) [4] and DFT calculations,[5–8] molecular mechanics,[9] and Mössbauer spectroscopy.[10] The rotation behavior of the Fe_3 triangle with respect to the icosahedron formed by the 12 CO ligands has been interpreted in terms of several mechanisms including the ligand polyhedral model (LPM) and the bridge-opening–bridge-closing mechanism, which have remained a matter of debate.[11–16] Relevant substituted derivatives have been prepared to simplify the dynamic behavior by blocking some of the possible dynamic motions: $Fe_3(CO)_{12-n}(L)_n$ [17] $[(L)_n = \{P(OMe)_3\}_{1-3}$,[18,19] Bu^{t}NC,[20] (Bu^{t}NC){P(OMe)$_3$},[20] κ^2-dppe,[21] κ^2-dppm,[22] $(Ph_2P)_2NH$,[22] $\{(EtO)_2P\}_2O$,[22] (κ^2-dppm){P(OMe)$_3$},[22] $(PhNC)_2]$,[23] $Fe_3(CO)_8(Bu^tNC)_{4-n}(L)_n$ $[(L)_n =$ none, $\{P(OMe)_3\}_{1,2}$, $\{P(OCH_2)_3CMe\}_{1,2}$, $\{P(OMe)_3\}\{P(OCH_2)_3CMe\}]$,[24] Fe_nM_{3-n}-$(CO)_{12}$ ($n = 1$–3; M = Ru,[25,26] Os),[27] and $Fe_mRu_{3-m}(CO)_{12-n}(L)_n$ (m/L/n = 1,2/Bu^{t}NC/1,2).[28] Several pieces of additional spectroscopic data and physicochemical properties for **1** are reported: photoionization dynamics,[29] absorption spectrum,[30] flash photolysis,[31] negative ion UV laser desorption TOF-MS,[32] and ESI-MS.[33] Formation of **1** is observed upon co-deposition of a mass-selected Fe cluster beam and CO [34] and UV-photolysis of $Fe(CO)_5$ on an Fe film.[35]



1 (●: CO)

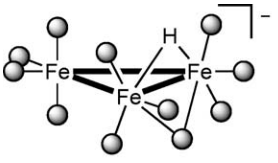
Reactions of **1** with organic compounds frequently result in fragmentation of the triangular Fe_3 core and, therefore, **1** serves as a source of mono- and diiron fragments. Various compounds have been subjected to reaction with **1**, and selected examples are listed – group 13: carborane;[36–38] group 14: alkyne,[39–43] diene,[44–46] cumulene,[47] $HSiCl_3$,[48] stannylene;[49] group 15: diazabutadiene,[50,51] *N*-nitrosamine,[52] tris(cycloheptatrienyl)phosphine,[53] β-ketophosphine,[54] diphosphene,[55] diphosphete,[56] H_2PBu^t and $HPBu^t_2$ complexes,[57,58] Me_2Al-$P(SiMe_3)_2$,[59] PhP–Co complexes,[60] $NaAsO_2$;[61] group 16: propargyl alcohol,[62] thiol and thiolate,[63–72] thiophene,[73,74] acylketene dithioacetal,[75] thioalkyne,[76] selena- and telluracycles,[77,78] tellurophene;[79,80] Yb.[81] (see also each section of this chapter and Chapter 6.08).

The catalytic performance of **1** was examined for hydroformylation of alkyne (as a catalyst additive)[82] and methoxycarbonylation of alkyl halide,[83] and **1** is also used as a stoichiometric reagent for an Ni-catalyzed ketone synthesis from alkyl halide.[84] Heterogeneous catalysts derived from **1** are used for hydrogenation of CO_x [85] and coal tar pitch,[86] crude oil upgrading,[87] and coal liquefaction (preparation of the pyrrhotite catalyst).[88] An Fe–Ru–Se catalyst dispersed on a glassy carbon-supported Nafion film prepared from **1** is reported to be effective for electrocatalytic oxygen reduction.[89]

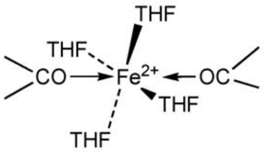
Compound **1** is useful as a starting material or as a catalyst for preparation of new materials, for example, fine metal particles dispersed on cellulose acetate films [90] and a thin film (a CVD process).[91] The former serves as a catalyst for the water-gas-shift reaction, CO oxidation, NO reduction, and olefin hydrogenation. **1** is soluble in liquid or supercritical CO_2,[92] and the solution is used for preparation of metal fine particles [93] and dyeing of PET fibers.[94] Vapor-grown carbon fibers are obtained from a mixture of H_2 and methane under the catalysis of **1**.[95]

6.07.2.2 Other Iron Carbonyl Clusters

Redox disproportionation reactions of carbonylmetal species are a versatile preparative method for carbonylmetallates, and $[Fe_3(CO)_{11}(\mu\text{-H})]^-$ salts **2** are formed by the reaction of $Fe_2(CO)_9$ with THF **a**[96] or *N*,*N′*-diaryltetrahydropyrrolo-[2,1-*c*][1,4]-oxazine-3,4-diylidenediamine **b**.[97] The anion **2** is also obtained by treatment of **1** with 1,3,5-trimethyl-1,3,5-triazacyclohexane via an apparent *β*-hydride elimination **c**[98] and by reaction of $[Fe_2(CO)_8]^{2-}$ with a methylacridinium salt (detected by IR).[99] The cations of the obtained compounds are as shown below.

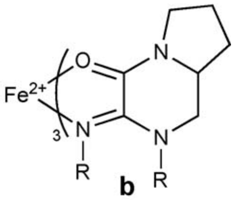


2 (●: CO)



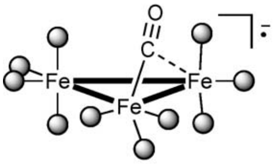
a

(1 : 2 complex)

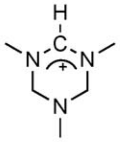


b

(1 : 2 complex)



3



c

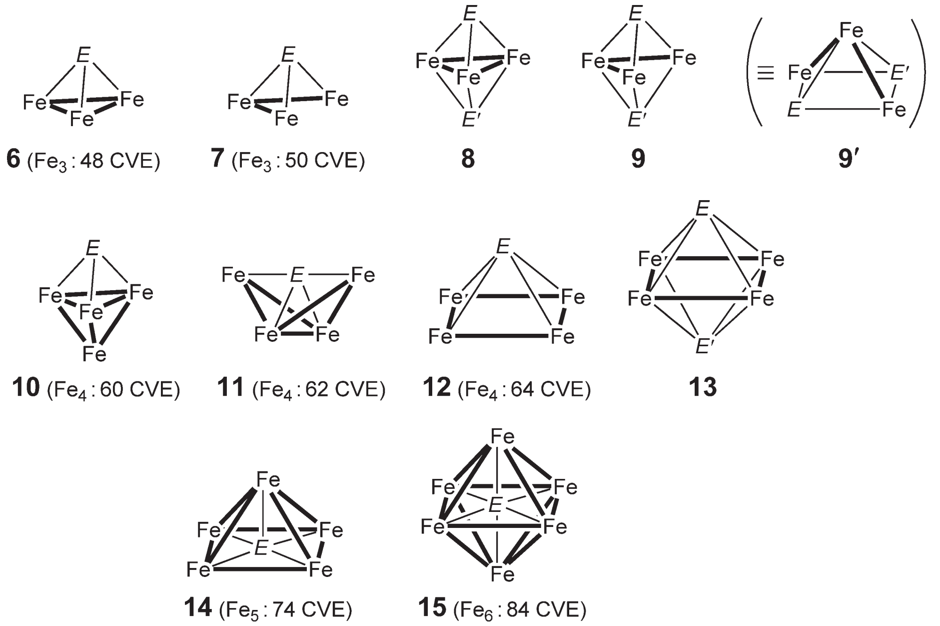
In addition to the electron-precise 48e hydrido cluster anion **2**, the 47e-radical anion, $[Fe_3(CO)_{11}]^{\cdot -}$ **3**, is regarded as a key intermediate in reductive transformation of nitroaromatics to anilines or their carbonylated derivatives. The radical **3** is formed via a redox disproportionation reaction upon treatment of **1** with halide (Cl^-, Br^-, I^-) or pseudohalide (NCO^-) in THF in contrast to the reactions of the Ru and Os derivatives, which afford the diamagnetic substituted anions, $[M_3(CO)_{10}(\mu\text{-X})]^-$.[100,101] Treatment of iron carbonyls such as **1** with trimethylamine *N*-oxide or $[Et_4N]SEt$ produces a mixture of anionic radical species, including **3** as characterized by ESR.[102,103] The anion part in $[PPh_4][$**3**$]$ has 10 terminal and one semi-bridging CO ligands as determined by X-ray crystallography. A THF solution of **3** slowly decomposes over the course of 1–2 days to give $[Fe_3(CO)_{11}(\mu\text{-H})]^-$, $Fe(CO)_5$, and $[Fe_4(CO)_{13}]^{2-}$, and exposure to CO causes immediate decomposition. Reaction of **3** with $ArNO_2$ affords a μ_3-arylimido complex (Section 6.07.6.1).

The dianionic species, $[Fe_3(CO)_{11}]^{2-}$ **4** and $[Fe_4(CO)_{13}]^{2-}$ **5** (see Scheme 10), are used for preparation of heteronuclear cluster compounds.[104–107] Polymer-bound **4** and **5** are obtained by treatment of **1** with aminated polystyrenes in MeOH–H_2O.[108] The ligand polyhedral model (LPM) has been successfully applied to $[M_4(CO)_{13}]^{x-}$ species including **5**.[109] It is claimed that a new neutral binary iron carbonyl formulated as $Fe_4(CO)_{14}$ (characterized by IR) is formed by co-deposition of mass-selected Fe_4^+ and CO.[110]

6.07.3 General Comments on Iron Clusters with Groups 13–16 Bridging Ligands

The following sections deal with iron cluster compounds containing main group elements (groups 13–16). Common structural motifs for them are shown in Scheme 1. *E* stands for a main group element, and functionalized counterparts (*E*R) can also work as the bridging ligands. *E* and *E*R fragments of group 15 and 16 elements have lone pair electrons, which combine plural metal centers to form cluster compounds, and group 13 and 14 elements without such excess lone pair electrons can also be incorporated into a cluster system through hypervalent hybridization of the *E* atom and/or the 3c-2e *E*–H–M interaction(s) in addition to *σ*- and *π*-bonding interactions.

The metal skeleton, of course, depends on the kinds and numbers of the metals and the bridging ligands and, for electron-precise cluster compounds, the structure is basically determined by the number of CVE (cluster valence electrons; shown in parentheses), which is the sum of the numbers of the valence electrons provided by the metal



Scheme 1

centers and the ligands. It is notable that neutral and anionic clusters are much more frequently encountered than cationic counterparts.

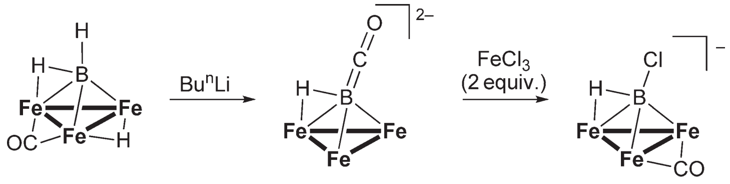
Triiron clusters are based on either an Fe_3 triangle **6** or an open Fe–Fe–Fe linkage **7**, and the μ_3-bridging main group ligand (except group 13 element ligands) provides three electrons to the cluster moiety to form three σ-bonds with the metal skeleton. The corresponding dicapped structures **8** and **9** are also known, and **9** is alternatively regarded as a square-pyramidal species with the Fe_2E_2 basal plane **9′**. Several Fe_4 skeletons including the tetrahedral **10**, butterfly **11**, and square structures **12** have been established. Group 13–16 element ligands can be incorporated into the tetrahedral structure **10**. On the other hand, the butterfly structure **11** is often found for the first-row elements, whereas the square structure **12** is common for heavier congeners, presumably because of the properties of the bridging ligand, that is, the ease of hypervalent hybridization and the atomic size (radius). The dicapped structure **13** is also known. The penta- **14** and hexanuclear structures **15** with the interstitial ligand are limited to the first-row main group elements, presumably because the heavier main group elements are too large to fit into the interstitial void created by iron atoms, a first-row transition metal with a small atomic radius.

Many reactivity studies of anionic cluster compounds toward electrophiles are centered on the reaction site (at E vs. at the Fe_n skeleton), which is dependent on the properties of E as well as the electrophiles to be reacted.

6.07.4 Iron Clusters with Group 13 Ligands (B, Ga, In)

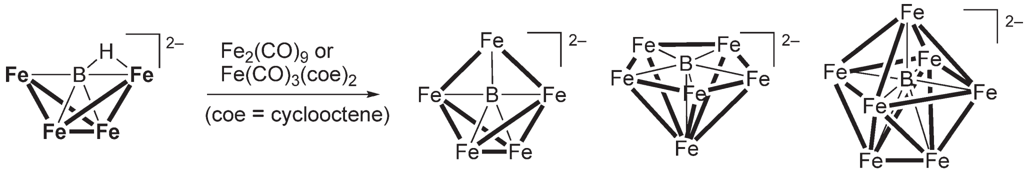
Only a few iron clusters with group 13 ligands were reported during last decade, and according to the author's literature survey, no report on an Al-containing iron cluster compound appeared during that time.

The structure of $M_3(CO)_9(H_3BCO)$ depends on M. In contrast to the Os derivative, $Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}B{=}C{=}O)$, with the B–CO linkage and the μ-H bridges (cf. the triiron ketenylidene cluster; Chapter 6.08.4), the Fe analog is characterized as $Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}BH_2)$ **16** with the B–H and B–H–Fe interactions (Equation (1)).[111] Deprotonation of **16** with Bu^nLi, however, causes a rearrangement of the μ_3-HB=C=O species **17** via a B–CO coupling, which is further converted into $Li[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]$ **18** via a B–C bond cleavage upon treatment with $FeCl_3$.[112] The structures with or without the B–CO linkage should be determined by a balance of energetics of the relevant bonding interactions including M–H, B–H, B–C, C–CO, and M–CO bonds. Reaction of the tetrairon borido cluster compound, $[Fe_4(CO)_{12}(\mu\text{-}BH)]^{2-}$ **19**, with $Fe_2(CO)_9$ or $Fe(CO)_3(cyclooctene)_2$ results in sequential formation of $[Fe_5(CO)_{15}(\mu\text{-}BH)]^{2-}$,**20** $[Fe_6(CO)_{17}(\mu\text{-}B)(H)]^{2-}$ **21**, and $[Fe_7(CO)_{20}(\mu\text{-}B)]^{2-}$ **22**[113] (Equation (2)), and the cluster structure expansion is explained in terms of a radical-anion-mediated cluster-building process, which is initiated by electron-transfer from **19** to $Fe_2(CO)_9$ forming $Fe(CO)_5$ as a by-product.



16 **17** **18**

(1)

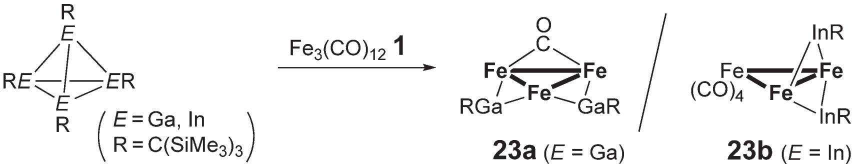


19 **20** **21** **22**

(H and CO ligands are omitted.)

(2)

The tetrahedral compounds, $(ER)_4$ ($E=Ga$, In; $R=C(SiMe_3)_3$), serve as a source of the monomeric ER species, which is isolobal with CO, and reaction with $Fe_3(CO)_{12}$ **1** results in CO replacement to form the di(μ-ER) complexes, $Fe_3(CO)_9(\mu\text{-}ER)_2$ **23** [$E=Ga$ **23a**,[114] In **23b**][115] (Equation (3)). In **23a**, the group 13 bridging ligands span across the different Fe–Fe bonds, whereas those in **23b** bridge the same Fe–Fe bond. The reaction of the In compound affords the two dinuclear products, $Fe_2(CO)_8(\mu\text{-}InR)$ and $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}InR)_2$, in addition to **23b**. Reactions of $\{RGaCl\}_4$ ($R=Si(SiMe_3)_3$; a dimer of R(Cl)Ga–Ga(Cl)R with a unique cage structure) with ferrates ($Na_2[Fe(CO)_4]$, $Na_2[Fe_2(CO)_8]$, $Na_2[Fe_3(CO)_{11}]$ **4**) give the analogous di- and trinuclear complexes, $Fe_2(CO)_6(\mu\text{-}GaR)_3$, $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}GaR)_2$, $[(Et_2O)_2(THF)Na][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}GaR)_2(\mu\text{-}Cl)]$, $[(triglyme)Na][Fe_3(CO)_9(\mu_3\text{-}GaR)_2]$, and $Fe_3(CO)_9(\mu\text{-}GaR)(\mu_3\text{-}GaR)_2$, together with partially hydrolyzed products.[116]



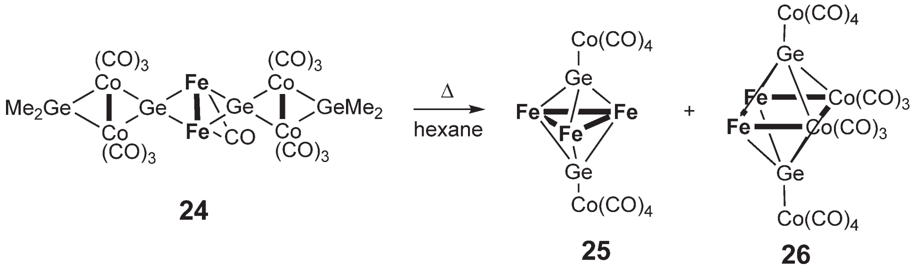
23a (E = Ga) **23b** (E = In)

(3)

6.07.5 Iron Clusters with Group 14 Ligands (Ge, Sn, Pb)

A few iron clusters with the heavier group 14 ligands (Ge, Sn, Pd) were reported during last decade. Compounds containing C ligands are reviewed in Chapter 6.08 but, according to the author's literature survey, no report on an Si-containing iron cluster compound appeared during that period.

Thermal decarbonylation of the heteronuclear di(μ_4-germido) complex **24** gives the di(μ_4-germido) complex with an Fe_3 triangle core, $(OC)_9Fe_3\{(\mu_4\text{-}Ge)Co(CO)_4\}_2$ **25**, as a minor product in addition to the μ_5-germido complex, $(OC)_{12}Fe_2Co_2\{\mu_5\text{-}GeCo(CO)_4\}_2$ **26**(Equation (4)).[117] Isolobal replacement of the $Fe(CO)_4$ part in $Fe_3(CO)_{12}$ **1** by stannylenes bearing bulky aryl groups ($SnAr_2$) affords the di(μ-stannylene)diiron complexes, $Fe_2(CO)_8(\mu\text{-}SnAr_2)$, while the pentamethylphenyl derivative results in Sn–C bond cleavage to produce the *spiro*-μ_4-stannido tetrairon complex, $(\mu_4\text{-}Sn)\{Fe_2(CO)_8\}_2$, with an $SnFe_4$-bow-tie core,[118] which was prepared many years ago by the reaction of Bu_3SnCl and $Fe(CO)_5$. Anionic stannyl- and plumbyl-triiron clusters, $[Fe_3(CO)_9(\mu\text{-}CO)_2(\eta^1\text{-}MPh_3)]^-$ [**27**; M = Sn **27a**, Pb **27b**], are prepared by treatment of $[Fe_3(CO)_{11}]^{2-}$ **4** with the corresponding group 14 metal chloride.[119] Complex **27b** is the first iron cluster with an open Fe–Fe–Pb linkage.



(4)

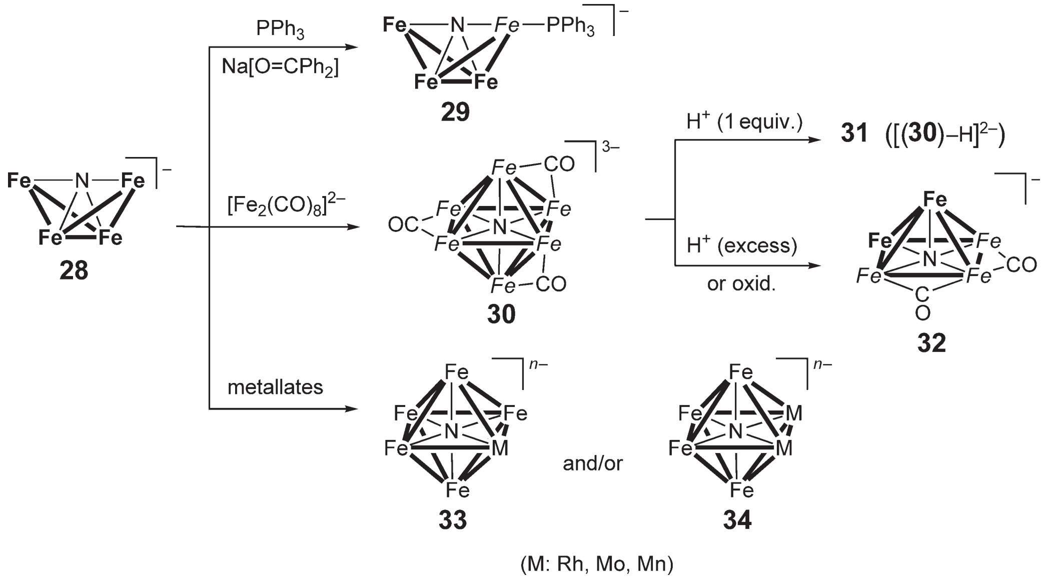
6.07.6 Iron Clusters with Group 15 Ligands

Compared to the limited number of the iron clusters with group 13 and 14 ligands, many more reports have appeared for those with group 15 ligands. For a review see Ref: 120.

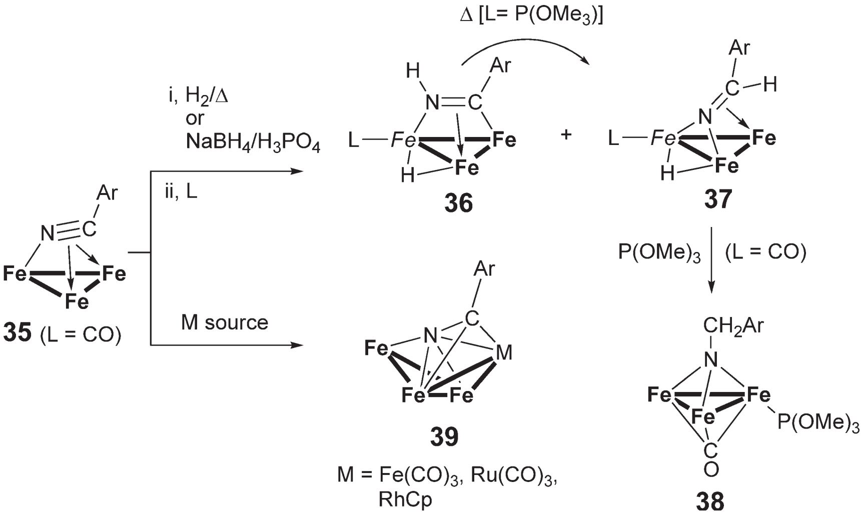
6.07.6.1 Iron Clusters with N Ligands

Organoimido clusters with **6**-, **9**-, and **13**-type structures (Scheme 1) were discussed in COMC (1995). The unprecedented dianionic μ_3-arylimido complex with a **6**-type structure, $[Fe_3(CO)_9(\mu_3\text{-}NC_6Cl_5)]^{2-}$, is obtained by reaction of the monoanionic radical species, $[Fe_3(CO)_{11}]^{\cdot-}$ **3**, with $C_6Cl_5NO_2$ (Section 6.07.2.2), while the protonated complex, $[Fe_3(CO)_9(\mu_3\text{-}NPh)(\mu\text{-}H)]^-$, is formed by reaction of **2** with PhNO.[100]

The tetrairon butterfly μ_4-nitrido complex, $[Fe_4(CO)_{12}(\mu_4\text{-}N)]^-$ **28**, undergoes two consecutive reduction processes, and the initial $-1/-2$ process triggers electrocatalytic CO substitution with PPh_3 giving $[Fe_4(CO)_{11}(PPh_3)(\mu_4\text{-}N)]^-$ **29** (Scheme 2).[121] Redox condensation of **28** with $[Fe_2(CO)_8]^{2-}$ produces the octahedral hexairon cluster compound with an interstitial μ_6-nitrido ligand, $[Fe_6(CO)_{15}(\mu_6\text{-}N)]^{3-}$ **30**, which is protonated to form the hydride, $[Fe_6(CO)_{15}(H)(\mu_6\text{-}N)]^{2-}$ **31**.[122] The hexairon complex **30** has been fully characterized by X-ray crystallographic and spectroscopic methods, which reveal the structure of **30** with three bridging CO ligands of an apparent D_3 symmetry. The metal framework and the ligand architecture of **30** and **31** are very similar but the hydrido ligand of **31** could not be located by X-ray crystallography. Compound **30** loses a mononuclear fragment upon treatment with a large amount of acid or electrochemical oxidation to form the pentairon μ_5-nitrido cluster, $[Fe_5(\mu_5\text{-}N)(CO)_{14}]^-$ **32**. The ν(Fe–N) (IR: 779 (E)



Scheme 2

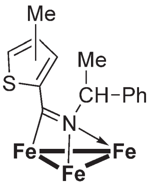


Scheme 3

and 749 cm^{-1} (A$_1$)) and ν(Fe–(μ-CO)) vibrations of **30** (IR: 665 (A$_2$), 624 cm^{-1} (A$_2$); Raman: 662 (E) and 635 cm^{-1} (A$_1$)) are assigned by use of a ^{15}N-enriched sample, and the ^{15}N NMR signals of **30** and **31** are located at δ 565 and 543 (downfield from NH$_3$), respectively, the latter being coupled with the hydrido ligand ($^2J_{\text{N–H}} = 3.1$ Hz). The redox condensation of **28** with metalates is also effective for synthesis of a series of heteronuclear μ_6-nitrido cluster complexes, **33** and **34**,[123–125] and their ^{15}N NMR data are reported: $[\text{Fe}_5\text{Rh(CO)}_{15}(\mu_6\text{-N})]^{2-}$ [δ_N 514 (*d*, $J_{\text{RhN}} = 8$ Hz)], $[\text{Fe}_5\text{Ir(CO)}_{15}(\mu_6\text{-N})]^{2-}$ [δ_N 514 (s)], $[\text{Fe}_5\text{Rh(CO)}_{15}(\mu_6\text{-N})]^{2-}$ [δ_N 470 (*t*, $J_{\text{RhN}} = 8$ Hz)]. The NO-substituted product, $[\text{Fe}_6(\text{CO})_{14}(\text{NO})(\mu_6\text{-N})]^{2-}$, is prepared by reaction of **28** with Mo(CO)$_3$(EtCN)$_3$, and it is concluded that the NO ligand is formed via a formal oxo transfer reaction (μ_6-N + CO → NO + C), although the fate of the liberated carbon atom remains to be clarified.[125] The Rh-containing clusters show catalytic activity for olefin hydroformylation, but Rh fragments of low nuclearity resulting from fragmentation may be responsible for the catalysis.

A series of μ_3-η^2-aromatic nitrile clusters, Fe$_3$(CO)$_8$(L)(μ_3-η^2-NCAr) **35** (L = CO, NCR, PR$_3$), is prepared by hydrogenolysis of Fe$_3$(CO)$_{12}$ **1** in the presence of the nitrile in refluxing cyclohexane followed by treatment with appropriate L (Scheme 3).[126] Complexes **35** (L = CO) are converted into a mixture of isomers, μ_3-η^2-acimidoyl **36** and μ_3-η^2-alkylidenimido complexes **37**, upon: (i) hydrogenolysis or (ii) sequential treatment with H$^-$ and H$^+$ (NaBH$_4$/H$_3$PO$_4$).[127] Thermal conversion of **36** into **37** is noted, and addition of P(OMe)$_3$ to **37** (L = CO) induces an H migration to give the μ_3-benzylimido complex **38**, Fe$_3$(CO)$_9$(μ_3-CO)(μ_3-NCH$_2$Ar). These nitrile cluster transformations have been described already in COMC (1982). Addition of a metal fragment to **35** (L = CO) leads to the tetranuclear butterfly cluster complexes **39** with the unsymmetrically coordinated μ_4-η^2-nitrile ligand.[128] The related CN-bridged complexes, Fe$_3$(CO)$_{11}${κ^1-NC(FeL$_2$Cp)} (L$_2$ = (CO)$_2$, dppe),[129] are also reported.

Thienyl-substituted imine compounds, 3- and 5-methylthien-2-yl–CH═NCH(CH$_3$)Ph, react with Fe$_2$(CO)$_9$ to give a mixture containing the μ_3-imidoyl cluster **40** (3-Me **40a**, 5-Me **40b**) and dinuclear products resulting from C–H bond activation.[130,131] Reaction of 1,4-bis(2,6-dihalophenyl)-2,3-diazabutadiene (azine) with Fe$_2$(CO)$_9$ affords a mixture of di- and trinuclear products, which includes those resulting from an N–N bond cleavage, that is, the bridging alkylideneimido complexes, **41** and **42**, together with the orthometallated products with retention of the N–N bond, for example, **43** and **44**.[132,133]



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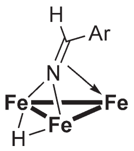

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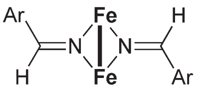

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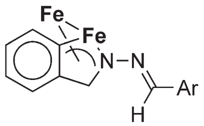

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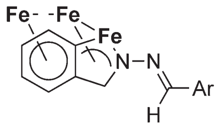

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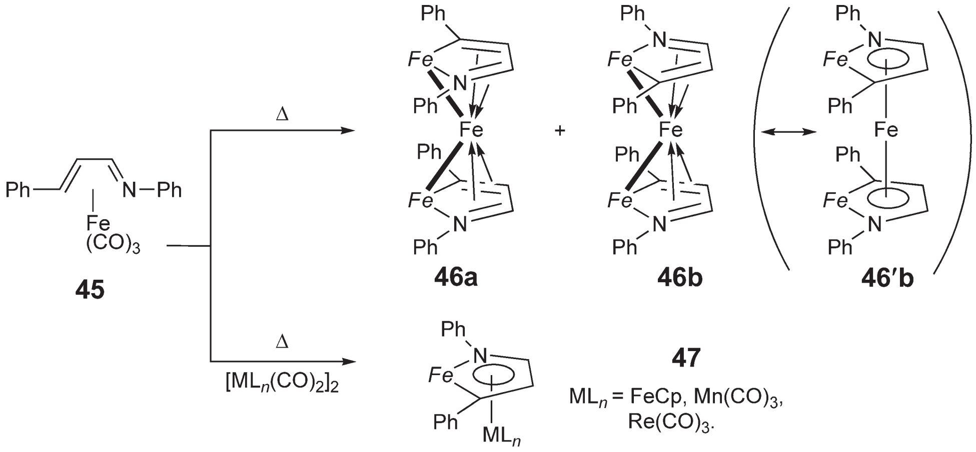


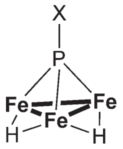
Scheme 4

Thermolysis of the mononuclear (1,4-diphenyl-1-azabutadiene)iron complex **45** gives a diastereomeric mixture of the trinuclear complexes **46a** and **46b**, which are regarded as analogs of ferrocene with the η^5-azaferracyclopentadienyl ligand **46′**.[134] Co-thermolysis of **45** with other metal carbonyl species produces heterodinuclear η^5-azaferracyclopentadienyl complexes **47** (Scheme 4).

6.07.6.2 Iron Clusters with P Ligands

6.07.6.2.1 Phosphinidene clusters

Typical metal frameworks for bridging μ_3-phosphinidene (μ_3-PR) clusters (cf. Scheme 1) involve Fe_3 triangles **48–50**, and an acyclic, folded Fe_3 linkage **51**, and tetrairon μ_4-PR complexes of **12**- and **13**-types (Scheme 1) are also known (COMC (1995)).



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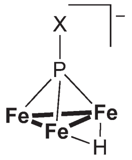

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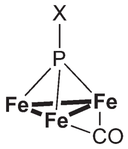

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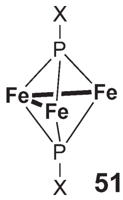
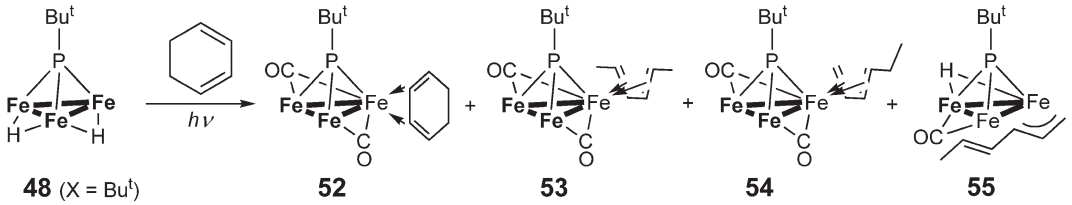


51

6.07.6.2.1.(i) Mono(μ_3-phosphinidene) clusters

UV irradiation of $Fe_3(CO)_9(\mu\text{-}H)_2(PBu^t)$ **48** ($X = Bu^t$) in the presence of 1,3-cyclohexadiene forms, in addition to the η^4-cyclohexadiene complex $Fe_3(CO)_8(\eta^4\text{-cyclohexadiene})$ **52**, minor products with hexadiene ligands, arising from reductive C–C bond cleavage reactions of 1,3-cyclohexadiene, **53–55** (Equation (5)).[135] Complex **52** is also obtained by thermal reaction of $Fe_3(CO)_{10}(\mu_3\text{-}PBu^t)$ **50** ($X = Bu^t$) with 1,3-cyclohexadiene, and UV irradiation of **52** causes dehydrogenation to give the η^6-benzene complex **56** (Equation (6)).



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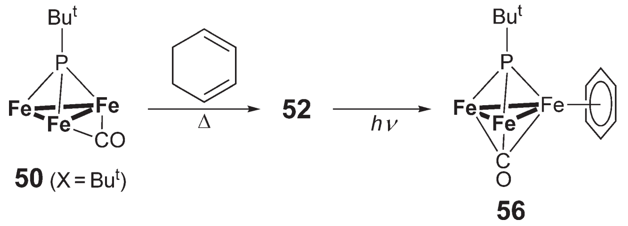
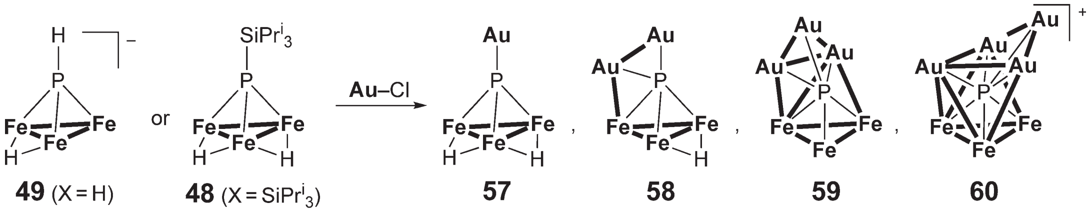


(6)

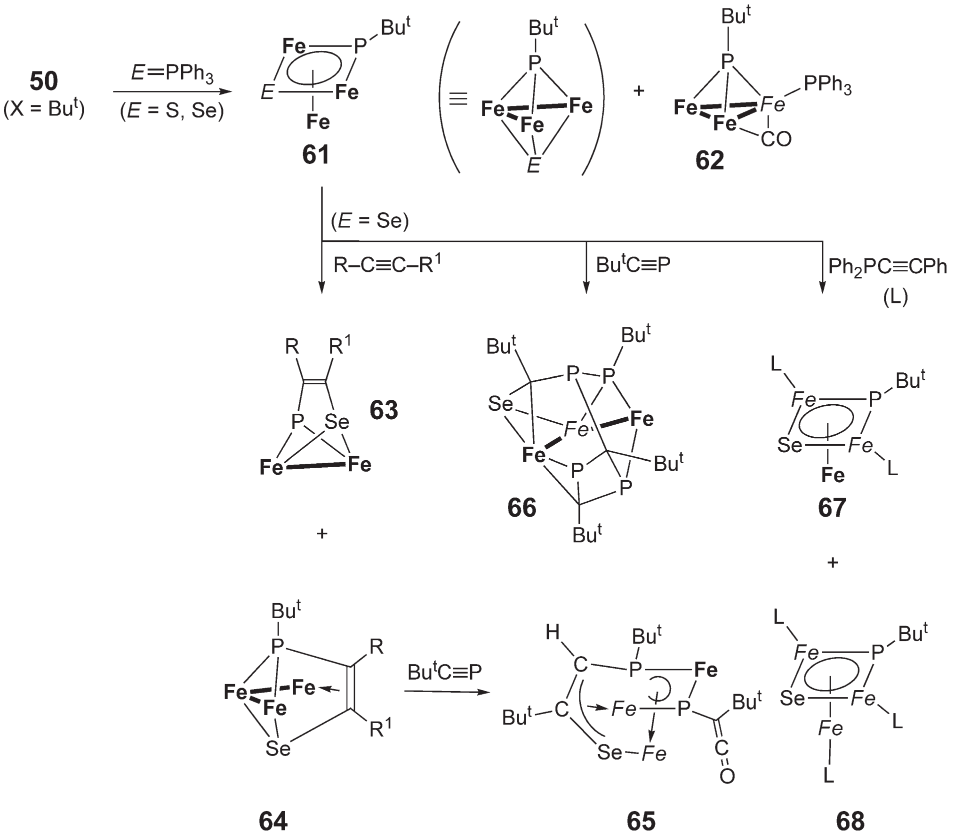
Mono-μ_3-phosphinidene complexes, $[Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}PH)]^-$ **49** (X = H) or $Fe_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}PSiPr^i{}_3)$ **48** (X = SiPr$^i_3$), are converted into a series of Fe_3Au_n-cluster complexes (*n* = 1–4): $Fe_3(CO)_9(\mu\text{-}H)_2[\mu_3\text{-}P\{Au(PPh_3)\}]$ **57**, $Fe_3(CO)_9(\mu\text{-}H)(\mu_5\text{-}P)\{Au_2(PPh_3)_2\}$ **58**, $Fe_3(CO)_9(\mu_6\text{-}P)\{Au_3(PPh_3)_3\}$ **59**, and $[Fe_3(CO)_9(\mu_7\text{-}P)\{Au_4(PPh_3)_4\}]^+$ **60**, by selective, sequential addition reactions of the Au fragment (Equation (7)).[136–138]



(7)

(**Au** = Au(PR$_3$) (R = Ph, Et))

Reaction of **50** (X = Bu^t) with S=PPh$_3$ results in S–P bond splitting followed by interaction with the resultant fragments to give **61** (*E* = S) and **62** (Scheme 5).[139] The (μ_3-phosphinidene) (μ_3-sulfido) cluster **61**, regarded as an



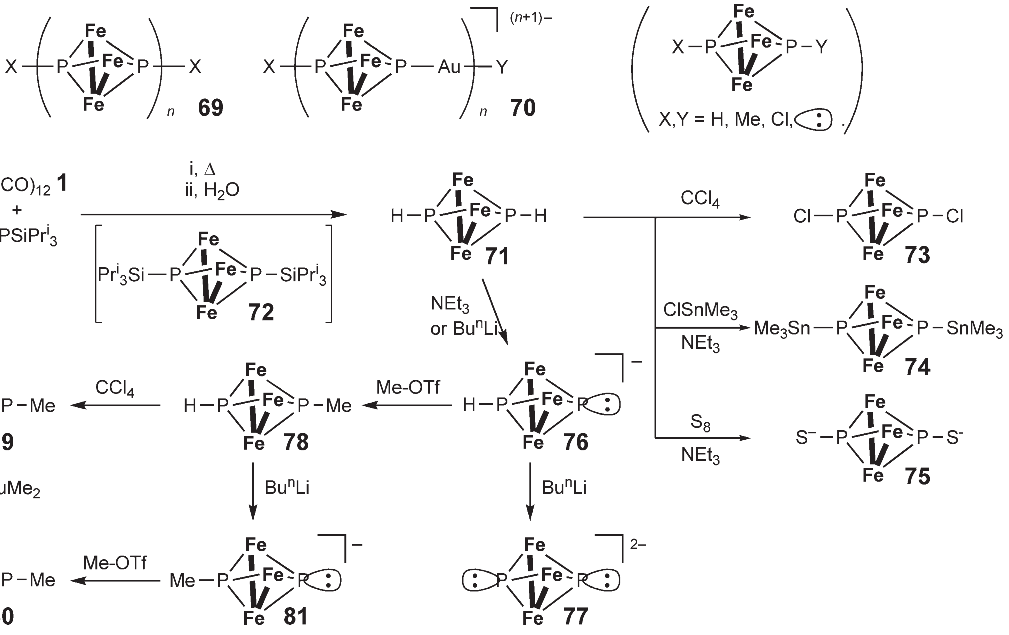
Scheme 5

E-substituted derivative of **51**, was previously obtained by *E*-transfer reactions from ECN^- or thiourea. The reaction with $Se{=}PPh_3$ gives the Se analog **61** ($E = Se$) together with its mono- and di-PPh_3-substituted derivatives. Complex **61** ($E = Se$) undergoes insertion of alkynes between the P and Se atoms to form the di- **63** and trinuclear phosphaselenametallacycles **64**, and the latter complexes **64** further react with phospha-alkyne to form **65**, where the μ-ketenylphosphido group resulting from coupling with a CO ligand bridges the three Fe atoms.[140] On the other hand, reaction of **61** ($E = Se$) with $Bu^tC{\equiv}P$ results in incorporation of three phospha-alkyne molecules as well as P–P, P–C, and Se–C couplings to form the complicated cage compound **66**. In contrast to these coupling reactions, reaction with an alkynylphosphine causes CO substitution to furnish **67** and **68**.

6.07.6.2.1.(ii) Di(μ_3-phosphinidene) clusters

A systematic synthetic study targeting one-dimensional linear cluster chains (e.g., **69** and **70**), based on the di(μ_3-phosphinidene)triiron cluster unit **51**, has been carried out, and for this purpose several versatile building blocks are devised, as summarized in Scheme 6.[136,141–143] The parent di(μ_3-phosphinidene)triiron cluster **71** is prepared by hydrolysis of the di(μ_3-silylphosphinidene) complex **72** *in situ* generated by treatment of $Fe_3(CO)_{12}$ **1** with $H_2PSiPr^i{}_3$. Warming a CCl_4 solution of **71** results in chlorination of the P–H moieties to give the di(μ_3-chlorophosphinidene) complex **73**, whereas deprotonation of **71** with NEt_3 forms the anion **76**, which is isolated as a PPN salt. The dianion **77** can be generated by the action of Bu^nLi. The anion **76** can be trapped by electrophiles as exemplified by the reaction with methyl triflate leading to the unsymmetrical (μ_3-phosphinidene) (μ_3-methylphosphinidene) complex **78**, which is further converted into the di(μ_3-methylphosphinidene) complex **80** either via the chlorination **(79)**–methylation sequence or via the deprotonation**(81)**–methylation sequence. Another nucleophilic Sn species **74** derived from **71** is susceptible to Michael addition with methyl acrylate and acrylonitrile.[143] Condensation of the nucleophilic species (e.g., **74** and **76**) with μ_3-PCl complexes (e.g., **73** and **79**) furnishes oligomers **69** ($n = 2,3$; $X = (\mu_3\text{-P})Fe_3(CO)_9(\mu_3\text{-PMe})$).[144] The Au-bridged analogs **70** ($n = 2$–4; $X = Me$, $Y = (\mu_3\text{-P})Fe_3(CO)_9(\mu_3\text{-PMe})$) are prepared by condensation between **71** and $[Au(tht)_2]PF_6$ in the presence of NEt_3 and the terminal capping reagent **79**.[142] The S-derivative **75** may be also used as a building block for a polymeric one-dimensional chain by a combination with a difunctional bridging electrophile.[143]

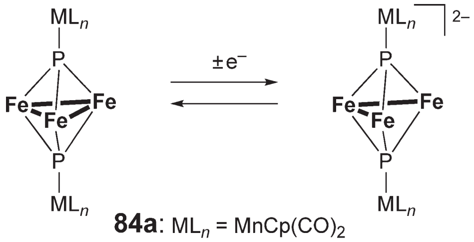
Reaction of a bulky primary phosphine, $AdPH_2$ (Ad = 1-adamantyl), with $Fe_3(CO)_{12}$ **1** in refluxing toluene affords a mixture of **48** (X = Ad), **51** (X = Ad), and stereoisomers of di(μ-phosphido)diiron complex, $Fe_2(CO)_6(\mu\text{-PAd})_2$ **82**,[145] while the reaction with $Fe_2(CO)_9$ at room temperature (RT) produces the η^1-phosphine complex, $Fe(CO)_4(\eta^1\text{-PH}_2Ad)$ **83**, which is converted into **82** upon heating. Complex **83** is the first mononuclear primary phosphine–iron adduct.



Scheme 6

A series of **51**-type symmetrical (X = NMe_2, OMe, CH_3, H, Cl. CF_3, CN) and unsymmetrical di(μ_3-arylphosphinidene) complexes, $(\mu_3\text{-}p\text{-}Me_2NC_6H_4P)_2Fe_3(CO)_9(PC_6H_4\text{-}p\text{-}CN)$, is prepared by reactions between $Na_2[Fe_2(CO)_8]$ and $Cl_2PC_6H_4\text{-}p\text{-}X$. These complexes undergo stepwise two-electron reduction, and no significant substituent effect on the anionic species has been revealed by ESR, CV, IR, and MO studies.[146]

The di(μ-phosphinidene) complexes with the dangling metal fragments, $Fe_3(CO)_9(\mu_4\text{-}P\text{–}ML_n)_2$ **84** (ML_n = $MnCp(CO)_2$ **84a**, $Cr(CO)_5$ **84b**), and their As and Sb analogs are reported (Equation (8)).[147] The iron triangle is opened upon two-electron reduction, and **84a** undergoes electrocatalytic CO substitution on the Fe_3 triangle.[148]

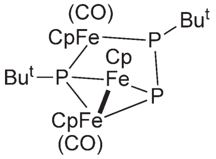


84a: ML_n = $MnCp(CO)_2$

84b: ML_n = $Cr(CO)_5$

(8)

Cyclic oligophosphines, $c\text{-}(PR)_n$, serve as phosphinidene sources via fragmentation. UV irradiation of the 1-Bu^t-2,3,4-triphenylcyclotetraphosphine, $c\text{-}(PPh)_3(PBu^t)$, in the presence of iron precursors produces the following triiron complexes via P–P bond cleavage: an unsymmetrical di(μ_3-phosphinidene) complex, $Fe_3(CO)_9(\mu_3\text{-}PBu^t)(\mu_3\text{-}PC_6H_5)$ (**51**-type, with $Fe(CO)_5$) and $Cp_3Fe_3(CO)_2(\mu_3\text{-}PPBu^t)(\mu_3\text{-}PBu^t)$ **85** (with $Fe_2(CO)_4Cp_2$).[149] Thermal reaction of hexaphenylcyclohexaphosphine, $c\text{-}(PPh)_6$, with $Fe_3(CO)_{12}$ **1** affords a mixture of **51** (X = Ph) and the products with P–P bonds, **86 and 87**, whereas the reaction with the As derivative, $c\text{-}(AsPh)_6$, produces $\{Fe_3(CO)_9(\mu_3\text{-}AsPh)\}_2$ **88** (the As analog of **51** (X = Ph)) in a selective manner.[150] From a mixture of $c\text{-}(PPh)_6$ and $c\text{-}(AsPh)_6$, the mixed P–As derivative of **88**, $Fe_3(CO)_9(\mu_3\text{-}PPh)(\mu_3\text{-}AsPh)$, is obtained together with the symmetrical complexes, **51** (X = Ph) and **88**.



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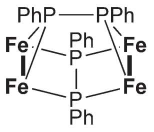

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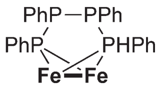
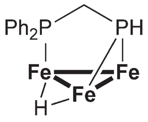


87

6.07.6.2.2 Miscellaneous iron clusters with P ligands

Reaction of $Fe_3(CO)_{12}$ **1** with diphosphines (dppe, dppb, dppf, $o\text{-}(Ph_2P)_2C_6H_4$) in the presence of Me_3NO produces the bridged species, $(\mu\text{-}\kappa^1:\kappa^1\text{-diphosphine})\{Fe_3(CO)_{11}\}_2$ and $(OC)_{11}Fe_3(\mu\text{-}\kappa^1:\kappa^1\text{-diphosphine})Fe(CO)_4$, in addition to the chelated product, $Fe_3(CO)_{10}(\kappa^2\text{-diphosphine})$, and electrochemical properties of the bridged species have been investigated.[151]

Diphosphines bearing P–H functional groups react with iron carbonyls to form μ-phosphido and μ_3-phosphinidene complexes. Reaction of 1,1-diphenyl-1,3-diphosphapropane (L) with $Fe_2(CO)_9$ results in a sequential formation of the simple 1 : 1 adducts, $Fe(CO)_4(\kappa^1\text{-L})$, and the bridged 1 : 2 adduct, $(\mu\text{-}\kappa^1:\kappa^1\text{-L})\{Fe(CO)_4\}_2$ (detected spectroscopically), and then the triiron adduct with a μ-phosphido functional group **89**.[152] The reaction at 80 °C forms the tetranuclear μ_3-phosphinidene complex with a spiked triangular iron array **90**, which is converted into the *spiro*-μ_4-P complex **91** by successive P–C bond cleavage. On the other hand, reaction of related disecondary methylene diphosphines, $R(H)PCH_2P(H)R$ (R = bulky aryl groups), with $Fe_2(CO)_9$ forms a variety of products depending on the reaction conditions and the substituent (R). For example, thermolysis with the 2,4,6-Pr^i_3-phenyl derivative in octane at 60 °C produces the (μ-phosphido)triiron clusters, **92 and 93**, and heating at 120 °C causes P–C and C–H bond cleavage to give the cyclic phosphine complex **94**.[153] It is also reported that thermolysis of **93** causes P–C bond cleavage to give the $\mu_3\text{-}\eta^2$-phospha-alkene complex **95**.



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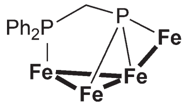

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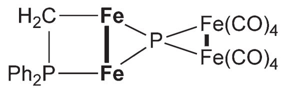

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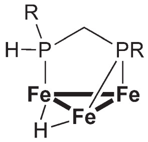

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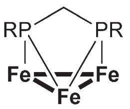

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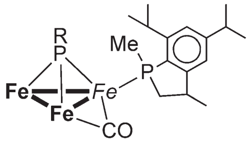
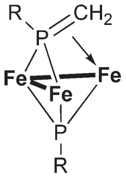


94

Chloro(chloromethyl)phosphines, RPCl(CH$_2$Cl), are readily converted into the mononuclear η^1-adducts, Fe(CO)$_4${κ^1-PRCl(CH$_2$Cl)} **96**, upon treatment with Fe$_2$(CO)$_9$. Further reaction of **96** with Fe$_2$(CO)$_9$ results in dechlorination to give the triiron μ_3-η_2-phosphaalkene complexes **97**, while reaction with Fe$_3$(CO)$_{12}$ **1** affords another type of μ_3-η_2-phospha-alkene complexes **95**.[154]



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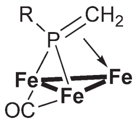
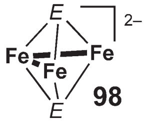


97

6.07.6.3 Iron Clusters with As, Sb, and Bi Ligands

A variety of As-, Sb-, and Bi-containing iron clusters based on the square-pyramidal Fe$_3E_2$ core with an open Fe$_3$ linkage, [Fe$_3$(CO)$_9$(μ_3-E)$_2$]$^{3-}$ **98** (E = As **98a**, Sb **98b**, Bi **98c**), have been reported. The Fe(CO)$_4$-dicapped pentairon–arsenic complex, [Fe$_3$(CO)$_9${μ_4-AsFe(CO)$_4$}$_2$]$^{2-}$ **99a**, is obtained by thermolysis of [HAs{Fe(CO)$_4$}$_3$]$^{2-}$ (Section 6.07.8.1).[155] Photochemical- or thermal- or Me$_3$NO-induced decarbonylation of the tetrahedral [Bi{Fe(CO)$_4$}$_4$]$^{3-}$ species[156] affords the bismuth derivative **99c** together with the monocapped complex, [Fe$_3$(CO)$_9$(μ_3-Bi){μ_3-BiFe$_3$(CO)$_9$}]$^{2-}$ **100**, the dicapped complex **98c**, [Fe$_4$(CO)$_{13}$]$^{2-}$ **5** and [Fe$_2$(CO)$_8$]$^{2-}$ depending on the reaction conditions (Scheme 7).[157] Complex **98c** is also accessible by reduction of the neutral precursor **101** with the triangular Fe$_3$ core or refluxing [Fe$_4$Bi$_4$(CO)$_{13}$]$^{2-}$ **102** in MeCN.[158] Reaction of **102** with MePCl$_2$ results in cluster degradation to give **103** and chlorinated mono- and dinuclear complexes depending on the stoichiometry of **102**/MePCl$_2$ (Scheme 7).[159] The di(μ_3-phenylarsinidene) complex 88 is obtained from hexaphenylcyclohexaarsine, c-(AsPh)$_6$ (Section 6.07.6.2.1.(ii)).



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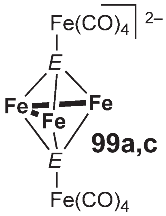
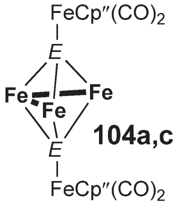
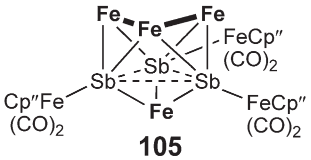


99a,c



104a,c

a: E = As
b: E = Sb
c: E = Bi



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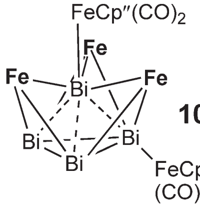

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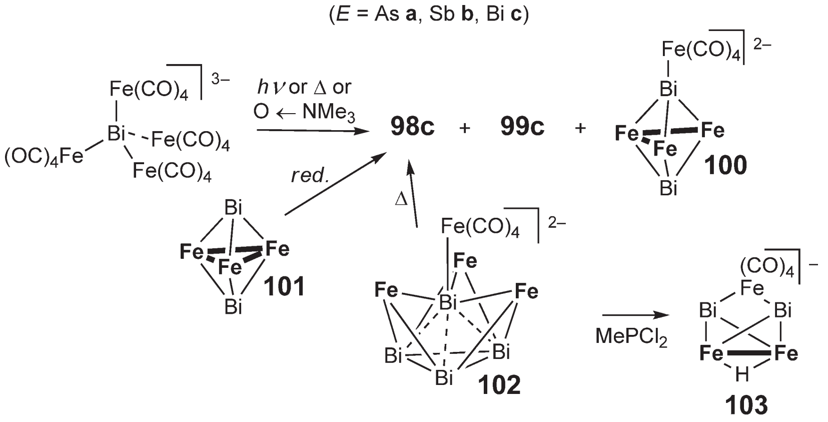


Scheme 7

Complexes **104**, the $FeCp''(CO)_2$ analogs of **99** ($Cp'' = 1,3\text{-}Bu^t{}_2$-cyclopentadienyl), are prepared by reaction of $Cp''(OC)_2FeECl_2$ with $Na_2[Fe(CO)_4]$.[160,161] The products from **104a** and **104c** are accompanied by formation of the hepta- **105** and pentanuclear cage cluster complexes **106** with weak $E\cdots E$ interactions, respectively. The core structure of the latter complex resembles that of **102**.

6.07.7 Iron Clusters with Group 16 Ligands

Of the iron clusters with main group element ligands summarized in this chapter, those with group 16 ligands, in particular, the heavier S, Se, and Te ligands, have been studied most extensively.

6.07.7.1 Iron Clusters with O Ligands

Core expansion of the μ_3-oxotriiron cluster **107** is reported (Scheme 8). Interaction with Mn and Re electrophiles leads to the formation of the heterotetranuclear μ_4-oxo clusters with the butterfly metal array **108**[162] and the μ_3-oxo clusters with expanded metal frameworks **111–113**,[163,164] which arise by Fe_2O **108** and Fe_3 face capping **111–113**, respectively. Interstitial clusters (e.g., **14**- and **15**-type complexes; Scheme 1) are rare for the oxo cluster compounds (see below) in contrast to the related carbido and nitrido clusters.

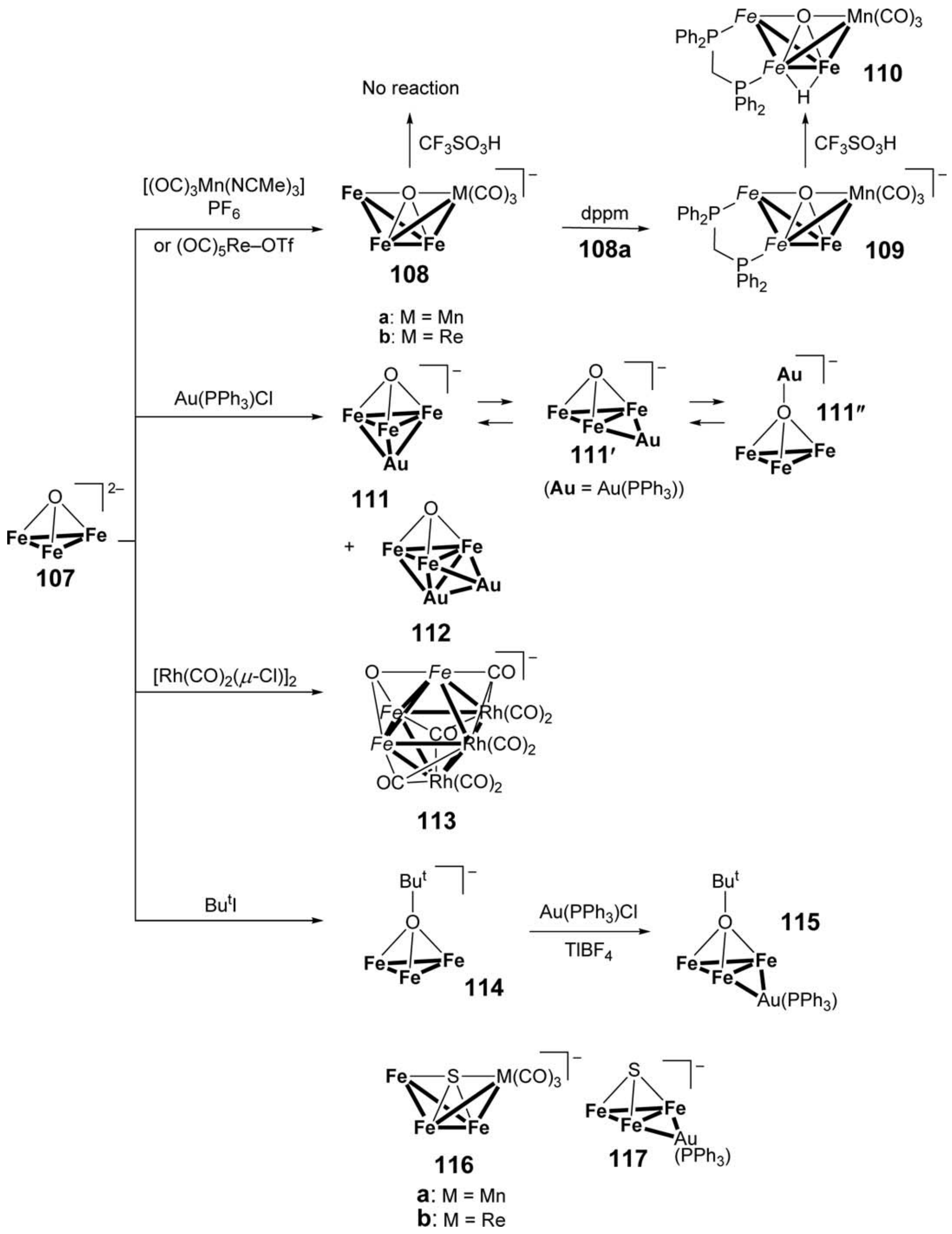
Comparative studies on the related sulfido clusters reveal that the μ_4-S cluster **116**, isostructural with **108**, is obtained from the reaction of $[Fe_3(CO)_9(\mu_3\text{-}S)]^{2-}$ (isostructural with **107**) with the Mn and Re cations, while the reaction with a $[Au(PPh_3)]^+$ fragment affords **117** through edge bridging. In the preparation of **108b** and **116b**, intermediates characterized as the adducts with the dangling metal fragment, $[Fe_3(CO)_9(\mu_4\text{-}S\text{–}ML_n)]^-$ (analogous to **111″**), are detected and subsequent decarbonylation converts them into the Fe_2E face-capped butterfly structure. It is notable that, in the case of the adduct **111** of the $[Au(PPh_3)]^+$ fragment (isolobal with H^+) with the μ_3-oxo cluster **107**, interconversion among three isomers **111**, **111′**, and **111″** in solution is observed by IR, suggesting very similar stabilities of the isomers, although only **111** is isolated as single crystals and characterized by X-ray crystallography.

While complex **108a** cannot be protonated by CF_3SO_3H, protonation of the dppm derivative **109** occurs on the hinge metal–metal bond to give **110**, as observed for the related carbido and nitrido clusters, $[Fe_4(CO)_{12}(\mu_4\text{-}X)]^{n-}$ ($X/n = C/2$, $N/1$).[165] On the other hand, protonation of the μ_4-S-derivative **116a** causes degradation of the tetranuclear structure to give $H_2Fe_3(CO)_9(\mu_3\text{-}S)$ (Section 6.07.7.2.1).[162] Alkylation of **107** with Bu^tI occurs at the capping oxo ligand to furnish the μ_3-alkoxo cluster **114**, which is further converted into the Au derivative **115** (Scheme 8).[166]

A rare example of a heterohexametallic interstitial μ_6-oxo cluster with an octahedral metal array, $Fe_4(CO)_{12}(CrCp)_2(\mu_6\text{-}O)$ (cf. **15**), is obtained by reaction of $Cp(OC)_2Cr{\equiv}S{\equiv}CrCp(CO)_2$ with $Fe_3(CO)_{12}$ **1**, the bridging oxo ligand coming from air during TLC separation.[167]

6.07.7.2 Iron clusters with S, Se, and Te ligands

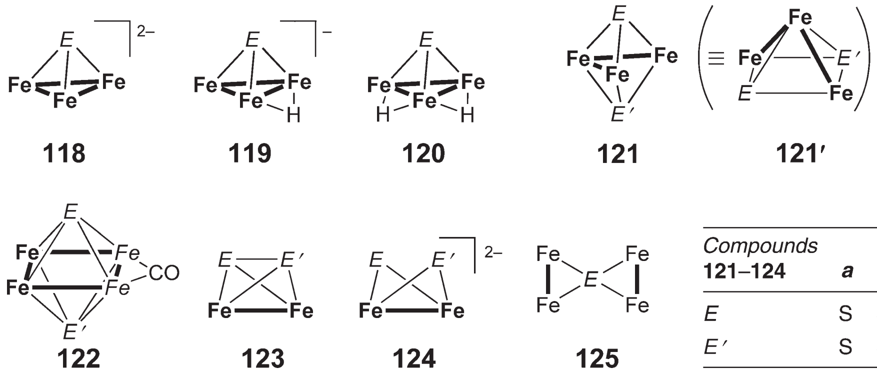
For reviews, see Refs: 168–172.



Scheme 8

6.07.7.2.1 Synthesis of S-, Se-, and Te-containing iron clusters

Typical structural motifs for S-, Se-, and Te-containing iron cluster compounds shown in Scheme 9 (E, $E' =$ S, Se, Te; cf. Scheme 1) involve the tetrahedral monocapped species with the closed iron triangle **118** and the dicapped triiron species with the open Fe_3 framework **121**, which can also be regarded as a square-pyramidal Fe_3EE' skeleton with an Fe_2EE' basal plane **121′**. The protonated forms of **118** (**119** and **120**) and the dicapped octahedral structure **122** based on an Fe_4 square are also known. Butterfly **11** and interstitial structures (**14** and **15**; Scheme 1) are very rare for non-first-row main group elements, and a rare example of the μ_4-S butterfly cluster **116** is discussed in Section



118–120a: $E = S$
118–120b: $E = Se$
118–120c: $E = Te$

Compounds 121–124	a	b	c	d	e	f
E	S	Se	Te	S	S	Se
E′	S	Se	Te	Se	Te	Te

Scheme 9

6.07.7.1 (Scheme 8). Combinations of these structural motifs with the dinuclear units **123** and **124** lead to a variety of unique structures. In addition to these typical core structures, complexes with the twisted bow-tie-shaped *spiro*-Fe_4E core skeleton **125** constitute a large class of chalcogenido clusters. The S-, Se-, and Te-containing clusters are divided into those with and without the bow-tie $Fe_4(\mu_4\text{-}E)$ core **125** as described in the following sections and, throughout Section 6.07.7.2.1, compounds of **a**, **b**, and **c** series denote S-, Se-, and Te homologs, respectively, unless otherwise stated. For the $(\eta^5\text{-}C_5R_5)_4Fe_4S_n$-type cubane cluster compounds, see Section 6.07.8.2.

The Fe–S bond enthalpy for the Fe–SR and Fe–S moieties in **121a**, **123a**, and $(\mu\text{-SEt})_2\{Fe(CO)_3\}_2$ is estimated to be 175 and 156 $kJ\cdot mol^{-1}$, respectively, on the basis of calorimetric measurements.[173]

6.07.7.2.1.(i) Clusters not based on the twisted bow-tie $Fe_4(\mu_4\text{-}E)$ core

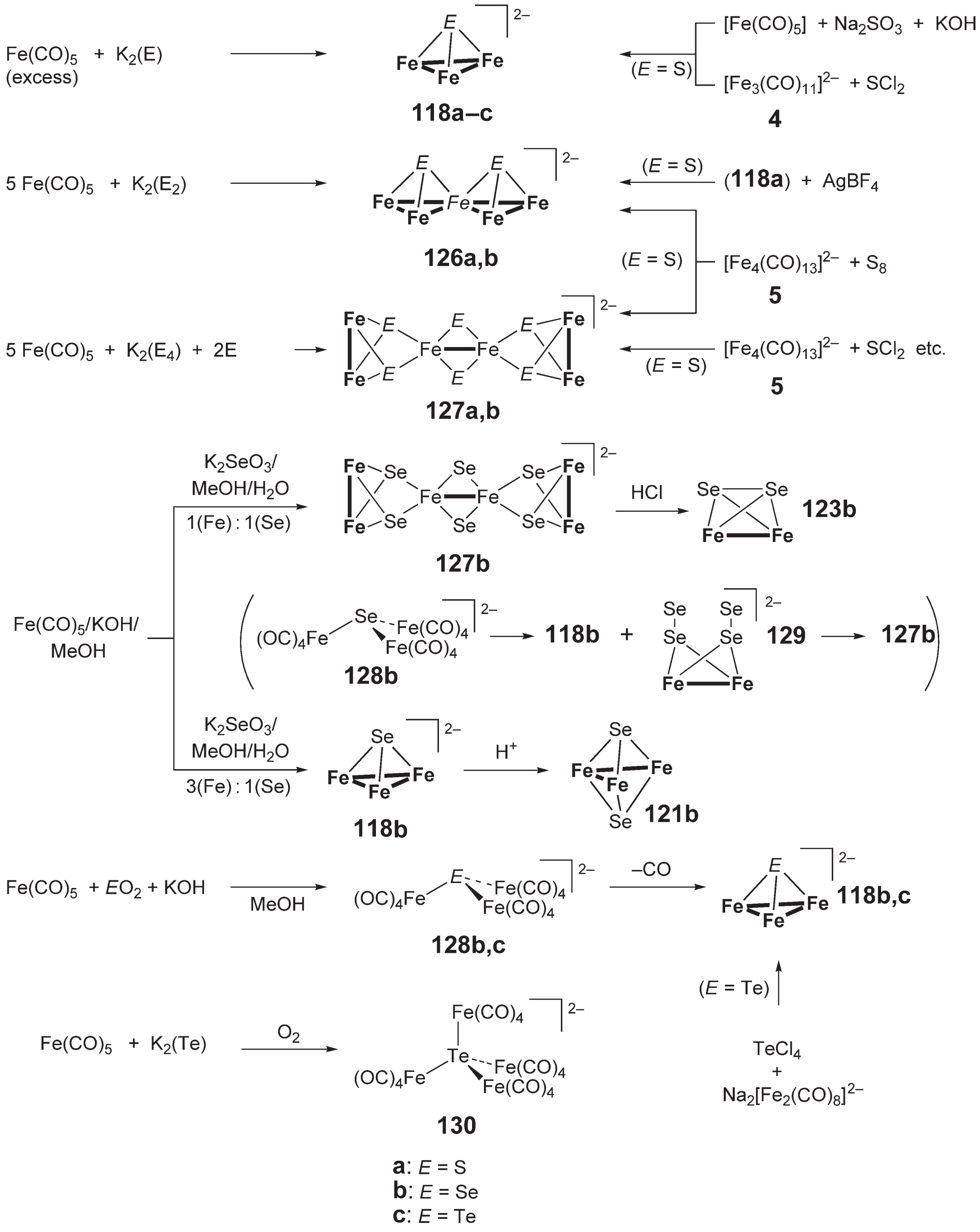
Reactions of $Fe(CO)_5$ with polychalcogenide anions and oxochalcogen species were studied in a systematic manner (Scheme 10) as prompted by the original synthetic reports on chalcogenidoiron carbonyl complexes by Hieber. The structures of the cluster products, which are relevant to the biologically important Fe–S cluster compounds, are dependent on the stoichiometry (iron carbonyl vs. chalcogen reagent) and the type of the chalcogen reagent (e.g., polychalcogenide anion (E_n^{2-}), EO_2, and EO_3^{2-}).

A convenient preparative method for the μ_3-sulfido cluster **118a** has been developed. Refluxing a MeOH solution of $Fe(CO)_5$ in the presence of Na_2SO_3 and KOH followed by precipitation with $[NEt_4]Br$ provides the NEt_4 salt of **118a** in 33% yield (based on S) after simple crystallization (Scheme 10).[174] Unless the reaction is carried out in a basic solution, a mixture contaminated by the protonated species, **119a** and **120a**, is obtained. These species are in turn prepared in pure forms by acidification of **118a** (see below). Treatment of $[Fe_3(CO)_{11}]^{2-}$ **4** with SCl_2 (or the charge-transfer piperidine–sulfur adduct) also provides **118a**.[175]

The reaction of $Fe(CO)_5$ with polychalcogenides, $K_2[E_n]$, depends on n (Scheme 10).[176,177] Interaction of $K_2[E]$ with an excess amount of $Fe(CO)_5$ affords **118a–118c** in excellent yields, while the reactions with $K_2[E_n]$ ($n \geq 2$; $E = S$, Se) give the penta- (**126a** and **126b**) and hexairon complexes **127a** and **127b**.[177] An increase in n causes an increase in the degree of oxidation of the iron centers, as in **126** and **127**. Complex **126a** is also obtained by oxidation of **118a** (with $AgBF_4$ or tropylium cation) or by treatment of $[Fe_4(CO)_{13}]^{2-}$ **5** with SCl_2, and the latter reaction affords **118a** as a by-product.[175] Complex **127a** is often formed as a by-product of related transformations.[175] Electrochemical studies of these Fe–S clusters combined with ESR measurements reveal:

(i) formation of monoanionic species upon oxidation of the dianionic species **118a** and **126a**,
(ii) involvement of the monoanion radical of **118a** in oxidative conversion of **118a** into **126a**, and
(iii) reduction of **126a** resulting in cluster fragmentation.[175]

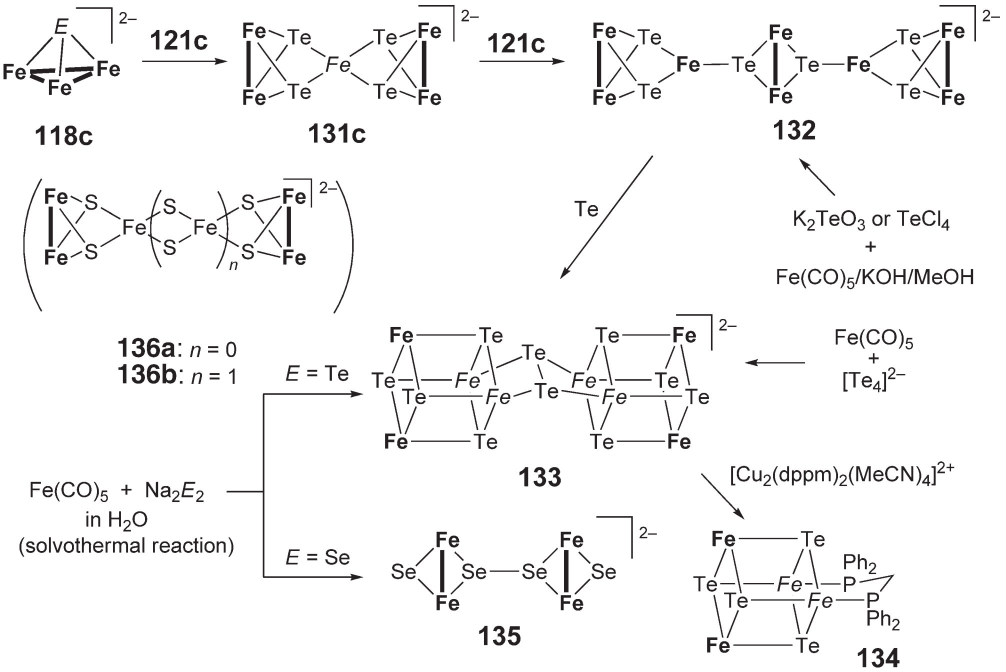
The μ_3-selenidotriiron cluster **127b** is prepared by reaction of K_2SeO_3/H_2O with $Fe(CO)_5$ (1 equiv.)/KOH in MeOH, and subsequent acidification of **127b** leads to **123b**.[178] Monitoring the reaction carried out in MeOH verifies the sequential formation of **128b** → **118b** + **129** (proposed) → **127b**. On the other hand, a 3Fe : 1Se reaction provides **118b**, which is converted into **121b** upon acidification. These results demonstrate that the SeO_3^{2-} (oxidant)/ $Fe(CO)_5$ + KOH (reductant) ratio is the controlling factor in determining the product selectivity, **123b** versus **121b**, and can account for the results of the original synthetic reports on the chalcogenidoiron clusters made by Hieber.



Scheme 10

The non-Fe–Fe-bonded μ_3-selenido- and μ_3-tellurido-triiron complexes **128b** and **128c**[179] are obtained by the reaction of EO_2 with $Fe(CO)_5$/KOH/MeOH, but are readily decarbonylated to the Fe–Fe-bonded species **118b**, **118c** (Scheme 10; see also Scheme 18). The tellurium intermediate **128c** can be isolated and fully characterized, while facile decarbonylation of the selenium derivative **128b** hinders its isolation in a pure form. On the other hand, the reaction of $Fe(CO)_5$ with K_2Te in air gives the tetrahedral (μ_4-tellurido)tetrairon complex **130** in a low yield.[176]

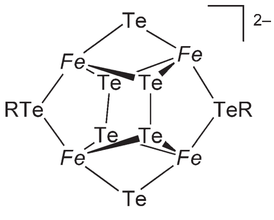
Another network connecting the telluridoiron clusters has been established (Scheme 11).[180] The dicapped species **121c** serves as a source of a "Te_xFe" fragment to convert the monocapped precursor **118c** into the penta- **131** and then to



Scheme 11

the octairon species **132**, and the latter species is finally transformed into the double-cubane species **133** by the action of Te. The first synthesis of **133** involved the reaction of $Fe(CO)_5$ with $Te_4{}^{2-}$,[181] and **133** may serve as a cubic precursor as exemplified by conversion into **134** by treatment with $[Cu_2(dppm)_2(MeCN)_4]^{2+}$.[180] The octanuclear complex **132** is also accessible by treatment of K_2TeO_3 or $TeCl_4$ with $Fe(CO)_5$/KOH/MeOH/H_2O.[182,183] Compound **136a**, $[Fe_5S_4(CO)_{12}]^{2-}$, with the $Fe_5(\mu_3\text{-}S)_4$ core similar to that found for **131c**, being relevant to the biological Mo–Fe–S clusters, is prepared by a 2 : 1 condensation of **124a** with $FeBr_2$.[184] One-electron oxidation of **136a** forms the corresponding monoanionic species, and **136a** is converted into the extended hexairon complex, $[Fe_6S_6(CO)_{12}]^{2-}$ **136b**, upon O_2 oxidation.

Solvothermal reaction is regarded as an effective synthetic method for chalcogenidoiron cluster compounds, and products arising from oxidative decarbonylation of metal carbonyls are dependent on various factors such as the stoichiometry, the chalcogenide source, the counteranion, the solvent, and the reaction conditions. The double-cubane complex **133** is prepared by hydrothermal reaction of $Fe(CO)_5$ with Na_2Te_2/$[PPh_4]Cl$ for 60 h at 110 °C, whereas the analogous reaction of Na_2Se_2 for 96 h at 80 °C forms the tetrairon complex **135** with the μ_4-Se_2 bridge (Scheme 11).[185] Solvothermal reactions of $Fe_3(CO)_{12}$ **1** with Na_2Te_2/$[PPh_4]Br$ (in MeOH) and Cs_2Te_3 (in H_2O) give the tetrairon complexes **137** and **119c**, respectively (Scheme 12).[186] A series of unique ditellurido clusters, **138–141**, is prepared by solvothermal reactions, and the R part (R = Me, Et) in $[Fe_4(\mu_4\text{-}Te_2)(\mu\text{-}Te)_2(\mu\text{-}TeR)_2]^{2-}$ **138** comes from the alcohol solvent.[187,188] The hexairon complex, $[Fe_6(CO)_{12}(\mu_6\text{-}Te_2)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{-}Te_2)_6]^{2-}$ **139**, contains an ethane-like Te_2Fe_6 core, where the six triangular Fe_3 faces are capped by $\eta^1\text{:}\eta^2$-Te_2 ligands, and the dinuclear complex **140** is formed as a by-product.[188] A related heteronuclear cluster, $[Fe_3W_2(CO)_{12}Te_8(TeMe)]^{3-}$ **141**, is prepared by methanothermolysis of $Fe_3(CO)_{12}$ **1**, $W(CO)_6$, and Na_2Te_2.[189]



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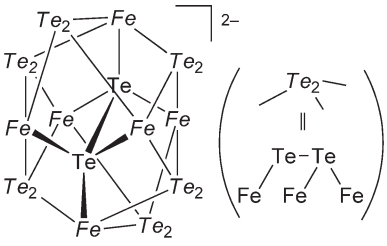

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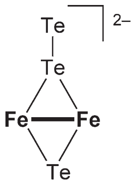

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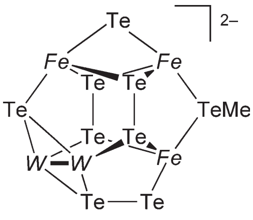
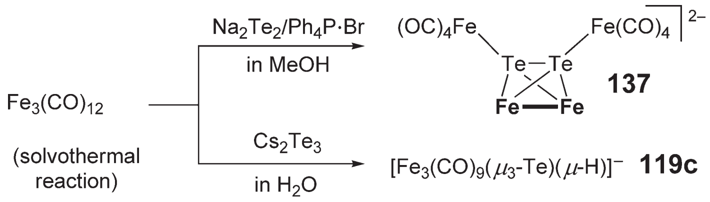


141 W = $W(CO)_3$



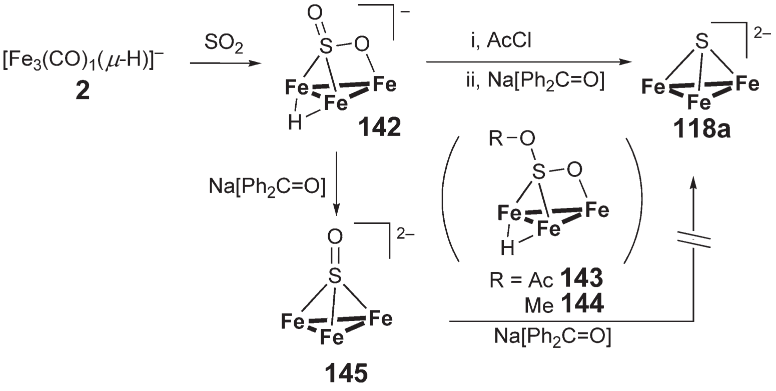
Scheme 12

The μ_3-sulfido cluster **118a** is also accessible via sequential acetylation–reduction of the μ_3-η^2-SO_2 complex **142**, which is obtained by reaction of $[Fe_3(CO)_{11}(\mu\text{-}H)]^-$ **2** with SO_2.[190] The formation mechanism of **118a** may be analogous to that of the carbido iron cluster compound (e.g., $[Fe_3(CO)_9(C{=}C{=}O)]^{2-}$ from $[Fe_3(CO)_{11}]^{2-}$ **4**; $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$ from $[Fe_4(CO)_{13}]^{2-}$ **5**; COMC (1995)), and the acetylated species **143** (R = Ac) is proposed as the intermediate, which should be susceptible to reductive S–O bond cleavage by the action of benzophenone ketyl. The corresponding methyl derivative, $Fe_3(CO)_9(\mu\text{-}H)\{S(O)OMe\}$ **144** (R = Me), is prepared by treatment of **142** with methyl triflate and structurally characterized.[191] On the other hand, reduction of **142** without acetylation affords the rare μ_3-SO complex **145**, which cannot be converted into **118a** by reduction (Scheme 13).

Analogous reaction of $[Fe_4(CO)_{13}]^{2-}$ **5** with SO_2 results in cluster fragmentation to afford the diiron complex, $[Fe_2(CO)_6(\mu\text{-}SO_2)_2]^{2-}$, and a similar fragmentation is noted for the related tetrahedral heterometallic clusters, $[Fe_3M(CO)_{14}]^{2-}$ **146** (M = Cr, Mo, W), leading to a mixture of the heterometal-extruded products, $[Fe_3(CO)_8(\mu_3\text{-}\eta^2\text{-}SO_2)]^{2-}$ **147** (the deprotonated form of **142**), and $[Fe_3(CO)_8(\mu_3\text{-}S)(\mu\text{-}SO_2)]^{2-}$ **148**.[192] CO ligands may serve as a deoxygenating agent as suggested by the formation of CO_2. Furthermore, SO_2 treatment of the homo- and heterotetrametallic μ_4-carbido cluster compounds, $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$ and $[MFe_3(CO)_{14}(\mu_4\text{-}C)]^{2-}$ (M = Cr, W), also results in extrusion of the heterometal to give the ketenylidene triiron clusters, $[Fe_3(CO)_8(\mu_3\text{-}C{=}C{=}O)(\mu\text{-}SO_2)]^{2-}$ and $[Fe_3(CO)_7(\mu_3\text{-}C{=}C{=}O)(\mu\text{-}SO_2)_2]^{2-}$.

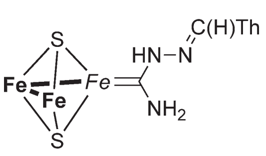
Stepwise protonation of $[Fe_3(CO)_9(\mu_3\text{-}E)]^{2-}$ **118** produces the mono-, $[Fe_3(CO)_9(\mu_3\text{-}E)(\mu\text{-}H)]^-$ **119**, and diprotonated species, $Fe_3(CO)_9(\mu_3\text{-}E)(\mu\text{-}H)_2$ **120**, which have been isolated and fully characterized.[174,176,193,194] The thermodynamically preferred protonation site of the anion turns out to be the Fe–Fe bond rather than the bridging chalcogenide atom, and the same regiochemistry is noted for the interaction with d^{10} metal species (Section 6.07.7.2.2). The reverse deprotonation of **119** and **120** is also feasible.[162] Te derivatives are obtained by a Te transfer reaction from L_2NbTe_2H to **1** ($[LNb(CO)_2]^+$[**119c**]$^-$ (L = η^5-C_5Me_5, η^5-C_5Me_4Et))[195] and the hydrothermal reaction mentioned above (Scheme 12).[186] Solution-phase self-assembly of **118b** and **118c** and its monoprotonated species onto a gold surface forms a bilayer, and binding of the Se atom to the gold is verified by XPS.[196] Second molecular hyperpolarizabilities of **118a** and **118b** are compared with those of mixed metal derivatives.[197] A neutral decacarbonyl species with an Fe_3 triangle, $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}Se)$, is prepared by treatment of **118b** with $BiCl_3$.[198]

C=*E* bond cleavage is an alternative synthetic method for chalcogenido cluster compounds. Treatment of the thiophene-substituted thiosemicarbazone, ThCH=NCHC(=S)NH_2 (Th = 2-thienyl), with $Fe_2(CO)_9$ at RT gives the carbene complex **149** together with the carbene complex **150** with the bow-tie core, **121a**, and a mononuclear complex.[199]



Scheme 13

Reaction of $Fe_3(CO)_{12}$ **1** with $R_3P{=}Se$ results in an analogous Se-transfer reaction to give a mixture of the selenido cluster complexes, **121b** and **123b**, and their mono- and diphosphine-substituted derivatives.[200–205] Mixed element-bridged derivatives **61** are also prepared by E-transfer from $E{=}PPh_3$ (Scheme 5). Formation of **121a** and **123a** from reaction of dithiooxamide, $\{C({=}S)NH_2\}_2$, with $Fe_2(CO)_9$ is reported,[206] and structural comparison of **121b** with a heterometallic derivative, $[Mn_3(CO)_9(\mu_3\text{-}Se)_2]^{2-}$, is made.[207] Irradiation of $Fe_2(CO)_7(dppm)$ with CS_2 brings about C═S bond splitting to form an isomeric mixture of a tetrairon complex **151**, for which an acyclic metal skeleton is proposed.[208]



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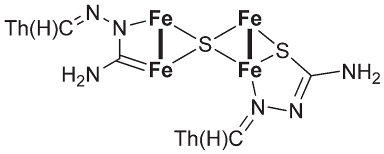

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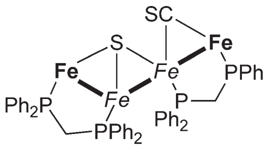

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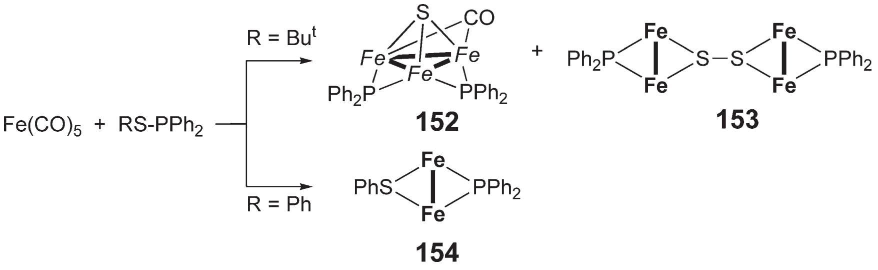
P–S and P–C bond cleavage reactions of Ph_2PSBu^t induced by $Fe(CO)_5$ produce the μ_3-sulfido-capped triiron cluster with two μ-phosphido bridges, $Fe_3(CO)_7(\mu_3\text{-}S)(\mu\text{-}PPh_2)_2$ **152**, together with the tetranuclear complex **153**, while the reaction with Ph_2PSPh gives the dinuclear complex **154** with retention of the SPh linkage (Scheme 14).[209]

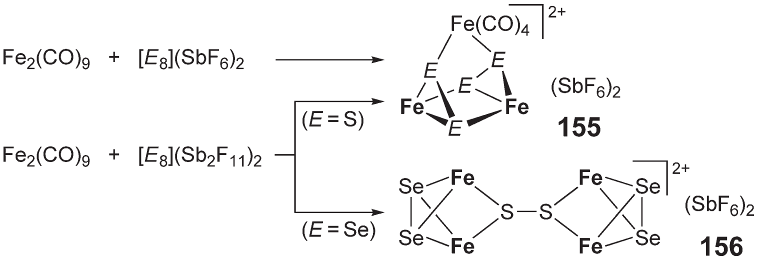
The NO derivatives of the mono-μ_3-sufido-capped complexes with a **118a**-type core, $[Fe_3(CO)_8(NO)(\mu_3\text{-}S)\text{-}(\mu\text{-}H)_n]^{n-1}$ ($n = 0$, 1) and $Fe_3(CO)_7(NO)(\mu_3\text{-}S)$, are prepared by acidifying a MeOH solution containing **119a**, $NaNO_2$, and NaOH with aqueous HCl solution,[210] and this synthetic procedure is applicable to the related thiolato cluster, $Fe_3(CO)_8(NO)(\mu_3\text{-}SBu^t)$. The tellurido derivative, $[Fe_3(CO)_8(NO)(\mu_3\text{-}Te)]^-$, is prepared by treatment of **118c** with $[NO]BF_4$.[176]

The di(μ_4-chalcogenido)tetrairon complexes **122b** and **122c** are accessible by visible light irradiation of a mixture of **121b**, **121c**, and $Fe(CO)_5$ ($E = Se$, Te)[211–213] or by mixing **121c** and $Fe_2(CO)_9$ in toluene or by photolysis of a mixture of **121c** and $Fe(CO)_5$ ($E = Te$).[214]

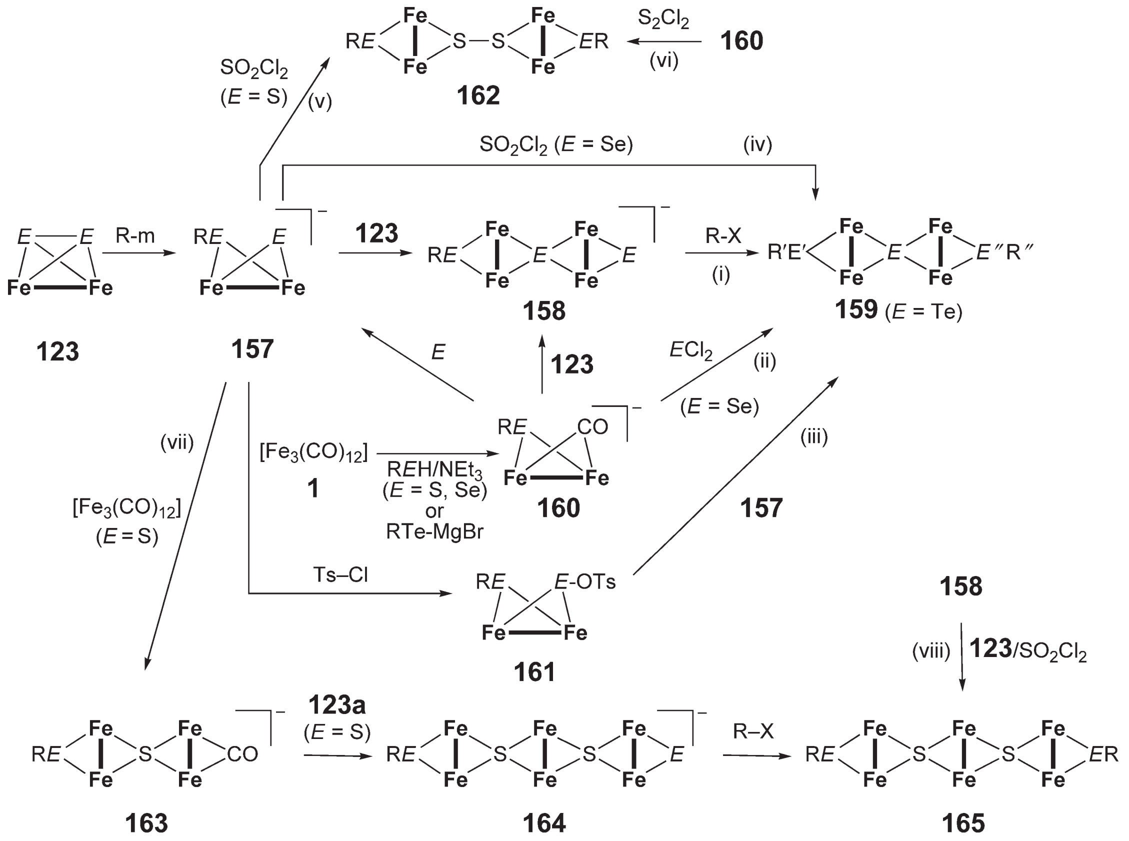
Cationic dichalcogenido cluster compounds are prepared from $E_8{}^{2+}$ cations ($E = S$, Se), and the products obtained depend on E and the counteranion (Scheme 15).[215] The reaction of $Fe_2(CO)_9$ with $[E_8](SbF_6)_2$ or $[S_8](Sb_2F_{11})_2$ gives the picnic basket-like $(E_2)_2Fe_3$ dication **155**, whereas the reaction with $[Se_8](Sb_2F_{11})_2$ affords the $(Se_2)_3Fe_4$ dication **156** with the SbF_6 counteranion. Because of their cationic nature, these complexes are extremely air and moisture sensitive and lack an Fe–Fe bond.



Scheme 14



Scheme 15

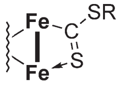


Scheme 16

6.07.7.2.1.(ii) Polyiron complexes based on the twisted bow-tie Fe$_4$(μ_4-E) core

A series of homo- and mixed chalcogenido-bridged polyiron complexes **159** based on the twisted bow-tie *spiro*-Fe$_4$(μ_4-E) core **125** is reported (Scheme 16; Table 1), and these are derived from nucleophilic reactions of the versatile E-centered anionic tetraferrate **158** (route (i) in Scheme 16), which can be generated *in situ* by treatment of the diferrates, **157** or **160**, with **123**. The nucleophilic reactions of **157** and **160** were extensively studied in the 1980s (COMC (1995)). The E-centered anion **157** can be readily obtained by addition of a carbanion (RMgX or RLi) to **123** or treatment of **160** with elemental chalcogen (E = S, Se). On the other hand, the CO-centered anion **160** can be generated by reaction of Fe$_3$(CO)$_{12}$ **1** with REH/NEt$_3$ or RTeMgBr (obtained from RMgX and Te). Various combinations of E, R$^1E'$ and R$^2E''$ lead to symmetrical and unsymmetrical, homo- and mixed chalcogenido derivatives of **159** (Table 1), and organic (e.g., alkyl halide, acyl halide, arene diazonium salt) and organometallic electrophiles (e.g., I–Fp) are used to trap **158**. No example containing Te in the central position has been reported so far. Symmetrical complexes are accessible by condensation between **160** and ECl$_2$ (route (ii)) or by treatment of **157** (E = Se) with SO$_2$Cl$_2$ (route (iv)). The latter reactions of the Se compounds contrast with the reactions of the S analogs (**157** (E = S) + SO$_2$Cl$_2$ (route (v))[216] and **160** + S$_2$Cl$_2$ (route (vi))),[217,218] which give the S–S-bonded species **162**. Coupling between the tosylate **161** and the anion **157** provides unsymmetrical derivatives **159** (E'R$^1 \neq E''$R^2), where the central E atom comes from **157** (route (iii)). The Te analog Fe$_4$(CO)$_{12}$(μ_4-S$_2$)(μ-TeBu)$_2$ **162c** is formed as a minor product on acetylation of Li[Fe$_2$(CO)$_6$(μ-CO)(μ-TeBu)] **160c**.[219] NLO properties of **159** (E = S, E'R^1 = E''R^2 = SPh) were investigated by the Z-scan technique.[220]

Bow-tie complexes with different end structures, **166**,[217,230,232–234] **167**,[216] **168**,[235] **169**,[236–238] and **170**[239] were also reported.[240] The μ-acetylide complex **170** is formed from PhC≡CSC≡CPh and Fe$_3$(CO)$_{12}$ **1** via the dinuclear intermediate Fe$_2$(CO)$_6$(μ-SC≡CPh)(μ-C≡CPh).



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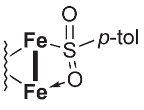

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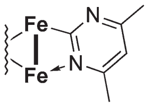

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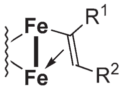

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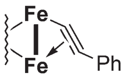
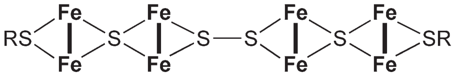


170

Table 1 A list of **159**-type tetrairon complexes

E	*E′*	*E″*	*Synthetic route*	*References*
S	S	S	(i) from **160**	221–223
			(iii)	224
			PhSH + $[Fe_3(CO)_{12}]$	220,225
Se	Se	Se	(i) from **160**	226
			(ii)	216
			(iv)	227
			157 + $Br(CH_2)_3Br$	228
S	S	Se	(i) from **160**	218,229,232
S	Te	Te	(ii)	230
Se	S	S	(i) from **157**	226
			(iv)	216,231
Se	S	Se	(i) from **160**	226
Se	Se	Te	(i) from **160**	226
Se	Te	Te	(ii)	232

Structure expansion of the diiron butterfly unit in **157** has been achieved by a sequential treatment with $Fe_3(CO)_{12}$ **1** and **123** (via **163**), and alkylation of the resultant anionic species **164** gives the triple butterfly structure **165** ($E = S$, Se) (route (vii) in Scheme 16).[223,230,233,234] Another synthetic route to **165** (route (viii)) involves coupling between the dinuclear anion **158** with **123** induced by the action of SO_2Cl_2.[232] An extended octairon complex with the μ_4-S_2 ligand **171**[241] and its Re derivative **172**[242] were also reported.



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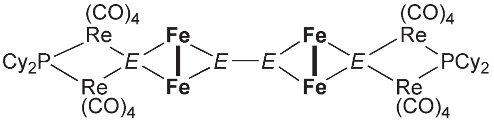


$E = S, Se, Te$

172

6.07.7.2.1.(iii) Organochalcogenato clusters

Compared to the chalcogenido clusters, very few examples of organochalcogenato clusters have been reported except for the bow-tie clusters with the $Fe_2(\mu\text{-}ER)$ end groups, which were discussed in the previous section.

A μ_3-methanethiolato cluster, $[Fe_3(CO)_9(SMe)]^{2-}$, is obtained by methylation of **118a** with MeOTf (Section 6.07.7.2.2.(i), and an unsymmetrical triiron complex containing a μ-SH and a μ_3-SBu^t ligand, $Fe_3(CO)_9(\mu\text{-}SH)(\mu_3\text{-}SBu^t)$ **173**, is formed by treatment of **160** ($ER = SBu^t$) with $Zn(OAc)_2 \cdot H_2O$.[243] Complex **173** contains an acyclic Fe_3 linkage and the μ-SH ligand bridges the terminal Fe atoms. A tetranuclear complex obtained from reaction of ethanedithiol with $Na_2[Fe_2(CO)_8]$ or $Fe_3(CO)_{12}$ **1** is formulated as $Fe_4(CO)_{12}(HSCH_2CH_2SH)_2$, but its structure remains to be characterized.[64]

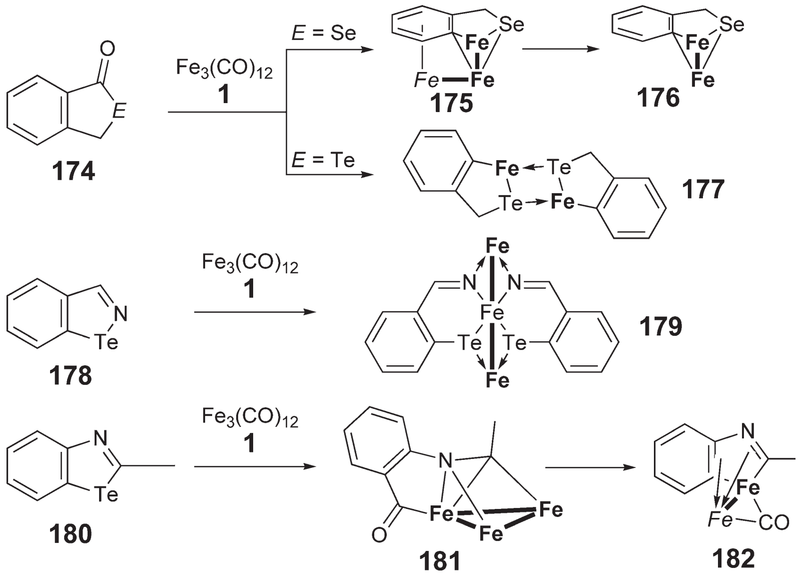
Upon treatment with $Fe_3(CO)_{12}$ **1**, selena- and telluracycles are converted into a variety of products resulting from a combination of *E*–X bond oxidative addition, dechalcogenation and so on (Scheme 17). 2-Chalcogenonaphthalide **174** gives the products **175**–**177** containing a 1-ferra-2-chalcogena-indane skeleton, which results from *E*–C bond oxidative addition and decarbonylation, while 2-telluraphthalic anhydride is converted into phthalide **174** ($E = O$) via a reductive dechalcogenation reaction.[77] Reactions of the N-containing derivatives, benzoisotellurazole **178** and 2-methylbenzotellurazole **180**, furnish an oxidative addition product **179** and dechalcogenated products, **181** and **182**, respectively.[78]

6.07.7.2.2 Reactivity of S-, Se-, and Te-containing Iron Clusters

6.07.7.2.2.(i) Reactions with organic reagents

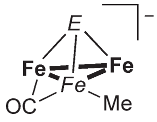
The chalcogenido cluster compounds, in particular, the anionic species, are so nucleophilic as to couple with electrophiles (*El*) to form products with an *E*–*El* bond or an Fe–*El* bond.

Reactions of the monocapped dianion **118** with H^+ and the isolobal d^{10} metal fragments (Hg^{2+}, $Au(PPh_3)^+$, Cu^+) occur on an Fe–Fe bond as suggested by a Fenske–Hall calculation [162] (Sections 6.07.7.2.1.(i) and 6.07.7.2.2.(ii)), while the reaction sites of alkylation are dependent on the μ_3-*E* ligand. Treatment of **118b**, **118c** with MeOTf results in methylation on the Fe_3 triangle to give **183a**, **183b**, rare examples of clusters with an η^1-alkyl group, while the methylation of **118a** occurs at the μ_3-S atom to afford the μ_3-methanethiolato cluster **184**,[174,244] and this regiochemistry

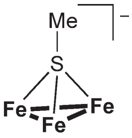


Scheme 17

(on E) is the same as that observed for the protonation and methylation of the oxo analog **107** and the reaction of **118a** with $Re(CO)_5(OTf)$ (Scheme 8).[162] Nucleophilicity of the μ_3-E atom in the series of $[Fe_3(CO)_9(\mu_3\text{-}E)]^{2-}$-type complexes, **107** and **118a–118c**, decreases in the order of O > S > Se > Te, and the order is in accord with the product distributions of protonation and methylation: O (**107**): H^+, Me^+ both on O; S (**118a**): H^+ on Fe_3 and Me^+ on S; Se (**118b**) and Te (**118c**): H^+, Me^+ both on Fe_3. A decrease of electron density on the clusters with the $(\mu_3\text{-}E)Fe_3$ core is correlated with a downfield shift of the ^{77}Se and ^{125}Te NMR signals and a shift of the ν_{CO} vibrations to lower energies.

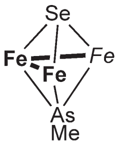


183a: E = Se
183b: E = Te



184

Reaction of **118b** with $MeAsI_2$ or $RSbBr_2$ occurs on the Fe_3 site to give the mixed heavy element-bridged species $Fe_3(CO)_9(\mu_3\text{-Se})(\mu_3\text{-AsMe})$ **185** or $Fe_3(CO)_9(\mu_3\text{-}E)(\mu_3\text{-SbR})$ **186** or **187**.[245–247]



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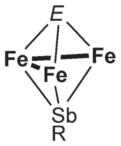

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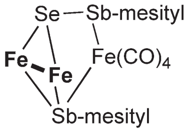
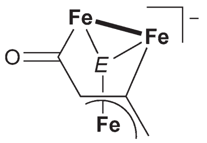


187

a: R = mesityl
b: R = C_6Me_5
c: R = $Fe(CO)_2Cp$

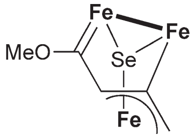
Formation of **188** with the allylcarbonyl ligand from the monocapped anions (**118b, 118c**), and propargyl bromide may involve an initial alkylation on the Fe_3 triangle followed by CO insertion, and subsequent methylation of **188b** with MeOTf gives the Fischer-type carbene complex **189**.[248] Reaction of the neutral selenido complexes **121b** and **123b** with diazomethane results in concomitant fragmentation and alkylation at the Se atom to give a mixture of products, **190–194**.[249–252] The nitrosyl ligands in **194** may come from the precursor for diazomethane, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide. A 2 : 1 reaction of the dicapped tellurido cluster **121c** with CBr_4 affords **123c**, while the addition of more than one additional equivalent of CBr_4 yields the unique carbide cubane cluster

195.[253] The tellurido-octairon complex **132** reacts with haloalkanes to give the μ-alkanetellurido complexes **196** and **197**, which apparently derive from alkylation of **124** formed by fragmentation of **132**.[254,183]



188

E = Se, Te



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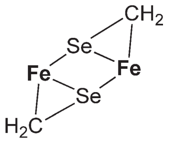

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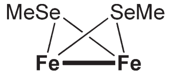

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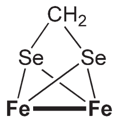

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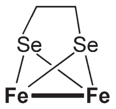

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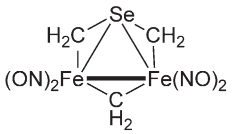

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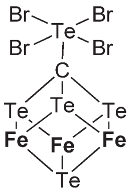

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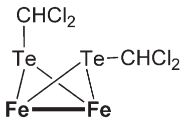

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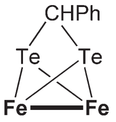
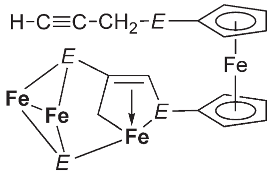


197

The dicapped species **121a** and **121b** react with 1,1′-di(propargylchalcogeno)ferrocenes to yield **198**.[255] The di(μ-phosphido) (μ_3-thiolato) complex **152** (Section 6.07.7.2.1.(i)) undergoes CO substitution at an iron atom coordinated by the μ-CO ligand, and reaction with 1-alkyne results in fragmentation of the Fe_3 triangle to form the dinuclear complexes, **199** and **200**, with a 3-phospha-2*Z*-propene-1-thiolato ligand formed via coupling of the alkyne with the bridging P and S ligands.[209] A phospha-alkyne, Bu^t–C≡P, readily reacts with **123b** upon irradiation to give the pentanuclear complex **201**,[256] while the photolysis in the presence of NaH affords **202**.[257] In **201** the phosphine moiety resulting from incorporation of the phospha-alkyne into the diiron unit is coordinated to a terminal iron center in the **121**-type triiron fragment, while the complicated fused cage structure of **202** results from P–Se bond formation. Nonlinear optical properties of **202** were investigated by the Z-scan technique and compared with related derivatives. An Fe_3Cr_2 complex **203** analogous to **201** is formed by CO substitution of **121b** by $\{Cr(\eta^5\text{-}C_5H_4Me)\}_2(\mu\text{-}Se)(\mu\text{-}SePh)_2$.[258]



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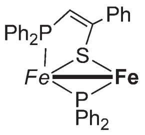

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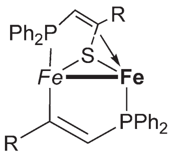

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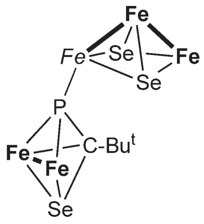

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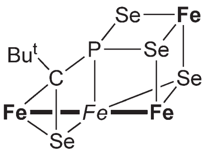

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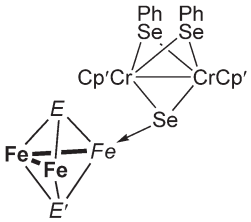


203

Catalytic carbonylation of MeOH giving methyl formate (HCOOMe) is mediated by the monocapped clusters **118a–118c**, and detailed kinetic analyses suggest that: (i) intact (μ_3-*E*)Fe_3 species are the catalytic species and

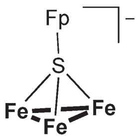
(ii) a plausible reaction mechanism should involve nucleophilic addition of methoxide to a carbonyl ligand as well as reversible opening of the Fe_3 triangle by the action of CO.[259]

In contrast to the reactions with electrophiles hitherto discussed, treatment of **121b** with allyl Grignard reagent, a nucleophile, causes fragmentation of the cluster core, upon quenching with FpCl, to form $Fe_2(CO)_6(\mu$-Se–allyl)(μ-SeFp) with a **124**-type Fe_2S_2 butterfly core.[260]

6.07.7.2.2.(ii) Reactions with organometallic species leading to higher nuclearity clusters

The iron clusters with group 16 ligands serve as versatile precursors for higher nuclearity cluster compounds, in particular, for heterometallic complexes, because the E moiety with a lone pair of electrons shows high affinity toward transition metal fragments. Two types of reactions have been established for organic electrophiles: (i) reaction at E (often leading to an Fe_2E face capping) and (ii) interaction with the Fe_3 core.

A typical example of type (i) reaction is formation of the μ_4-sulfido-bridged cluster with the dangling Fp group **204** by simple coordination of the μ_3-S ligand in **118a** to $[Fp(THF)]BF_4$,[261] and analogs with the Fe_2Co triangular basal core were also reported.[262–264] The heterometallic μ_4-chalcogenido clusters with the butterfly metal array, **116** and **205**, analogous to the μ_4-oxo cluster **108**, are obtained by treatment of **118b and 118c** with the labile cationic species, $[Mn(CO)_3(NCMe)_3]BF_4$ or $Re(CO)_5(OTf)$ [162] or $[MCp^*(NCMe)_3](OTf)_2$ (M = Rh, Ir) (see also Scheme 8).[265] Complexes **116** and **205** are rare examples of butterfly clusters with non-first-row main group elements. On the other hand, d^{10} fragments such as $Au(PR_3)$ and HgX bridge an Fe–Fe bond in triiron clusters (type ii) to form cluster compounds with a fused triangular Fe_2M motif **206** (M = Au,[176] Hg,[176,266,267] Cu [193]), as observed for protonation of **118** (Section 6.07.7.2.1.(i)) and formation of the related oxo cluster **115** (Scheme 1). The methanethiolato complex **184** undergoes auration on an Fe–Fe bond to give **207**, presumably owing to lack of a lone pair of electrons on S.[268]



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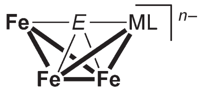
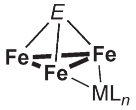
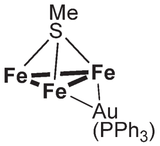


E/ML/*n* =
S/Mn(CO)$_3$/1 **116a**
S/Re(CO)$_3$/1 **116b**
Se, Te/RhCp*/0 **205a**
Se, Te/IrCp*/0 **205b**



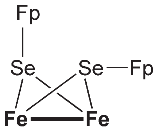
206

M = Au, Hg, Cu



207

The dinuclear dianion **124** readily reacts with metal electrophiles at the E atoms to form the homo- and heterometallic cluster compounds, **208** (with Fp–Cl),[269] **209** (with VCl_3), **210** (with $MnCl_2$),[270] and **211** (with $O{=}MoCl_3(THF)_2$).[271] On the other hand, reaction of the Fe_3 complexes **121** with Pd(II) or Pt(II) species induces fragmentation of the Fe_3 linkage to form the heterotrinuclear Fe_2M complexes **212** (M = Pd, Pt, E = S, Se, Te, $(L)_2 = (PPh_3)_2$, dppf, cod).[272–274] The unique μ_3-PE_3 complexes **213a** (E = S) and **213b** (E = Se) are formed from **121** and the η^3-P_3 complex, $CrCp(CO)_2(\eta^3$-$P_3)$.[275]



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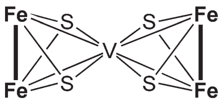

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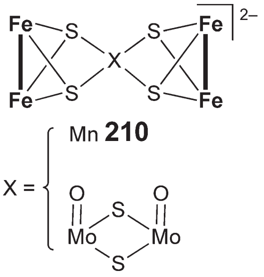

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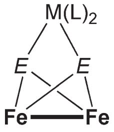

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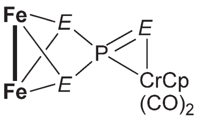
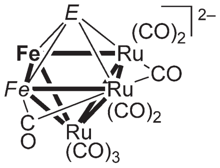


213

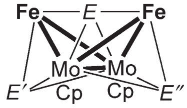
Cluster core expansion of the trinuclear μ_3-chalcogenido clusters, **118 and 121**, has been examined with Ru and Mo species. Upon treatment with $Ru_3(CO)_{12}$, the dianionic mono(μ_3-chalcogenido) species **118a and 118b** are converted into the pentanuclear (μ_4-E)Fe_2Ru_3 complexes **214**, and methylation of the μ_4-sulfido complex **214a** occurs at the S atom to give the corresponding monoanionic μ_4-SMe complex.[174,276] Reaction of the di(μ_3-selenido) complex **121b** with $Ru(CO)_4(CH_2{=}CH_2)$ at ambient temperature results in addition of a mononuclear Ru fragment to give $Fe_3Ru(CO)_{11}(\mu_4\text{-}Se)$ (the Fe_3Ru analog of **122b**), whereas the reaction with $Ru_3(CO)_{12}$ in refluxing benzene results not only in the addition but in replacement of the Fe fragments by the Ru fragments to afford $Ru_4(CO)_{11}(\mu_4\text{-}Se)$ (the Ru_4 analog of **122b**).[211,277]



a: *E* = S
b: *E* = Se

214

In contrast to the reaction with $Ru_3(CO)_{12}$, reactions of **121** with $Mo_2(CO)_6Cp_2$ cause interaction of the added Mo fragments with the bridging chalcogenido ligands to form the cage compound **215** with an Fe_2Mo_2 butterfly core supported by one μ_4- and two μ_3-*E* ligands, and the trinuclear μ_3-*E* cluster **216a** and some other Fe_2Mo_2 complexes (e.g., **217a**) are formed as by-products.[278–281] The formation of **215** apparently involves redistribution of the bridging *E* ligands. Derivatives with a variety of combinations of $E/E'/E''$ were reported.



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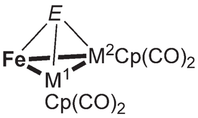
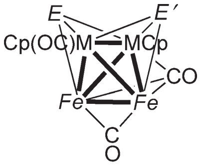
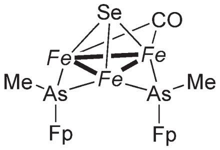


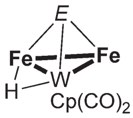
216a: M^1/M^2 = Mo/Mo
216b: M^1/M^2 = W/W
216c: M^1/M^2 = Mo/W

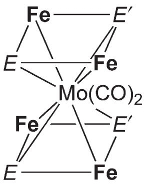


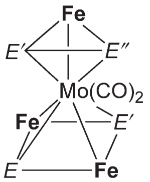
217a: M = Mo
217b: M = W

The mixed heavy element-bridged complex, $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}AsMe)$ **185**, is converted into $Fe_2Mo_2Cp_2(CO)_7(\mu_3\text{-}Se)(\mu_3\text{-}AsMe)$ analogous to **217** upon treatment with $Mo_2(CO)_6Cp_2$.[245] On the other hand, interaction with $Co(CO)_2Cp$ affords the bridging methylarsenido complex **218** via an unknown mechanism, which involves redistribution of the AsMe ligand and the Fe fragments as well as transfer of the Cp ligand from Co to Fe.[282] Isolobal replacement in the Fe_3 core as involved in the formation of **215–217** is observed for the reaction of $Fe_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}E)$ **120b and 120c** with $W_2(CO)_6Cp_2$, producing **219**, **216b**, and **217b**.[283–285] A chiral molecule **216c** (E = Se) is obtained by sequential addition of the two metal sources, though not resolved.[286] Reaction of the Fe_2 complex **123** with $Mo(CO)_5(THF)$ results in oxidative addition of the E–E' bond as well as Fe–Fe bond cleavage to give the hour-glass Fe_4 clusters **220** (E/E' = S/S, S/Se, S/Te, Se/Se), accompanying formation of the partially degraded Fe_3 complexes **221** ($E/E'/E''$ = S/S/S, S/S/Se, S/Se/Se, S/Te/Te, Se/Se/Se).[287,288]



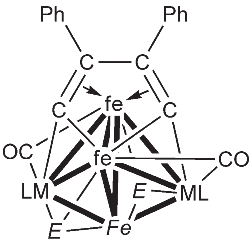






218 **219** **220** **221**

Similar heterometallic cluster formation is induced by treatment of **121** with group 6 metal acetylides, $Cp(OC)_3M$–$C{\equiv}CR$ (M = Mo, W), which usually afford a mixture of products including, for example, the acetylide-coupling products, **222 and 223**.[289–294] When the reaction with $FpC{\equiv}CR$ is carried out in an NEt_3–H_2O mixture under irradiation, the μ_3-$ECCH_2R$ complex **224** is formed, where the CH_2 hydrogen atoms come from H_2O as confirmed by a labeling experiment.[295]



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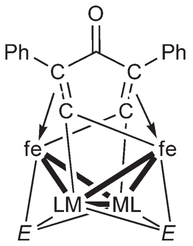

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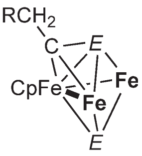


224

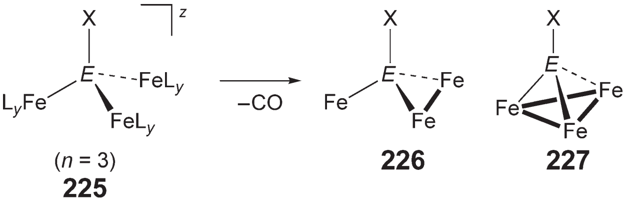
6.07.8 Polyiron Complexes Consisting of Mono- and Dinuclear Iron Fragments

The title compounds are divided into three categories: (i) polyiron compounds consisting of mononuclear fragments, (ii) $Fe_4(\eta^5\text{-}C_5R_5)_2S_4$-type cubane cluster compounds and their derivatives, and (iii) polyiron compounds consisting of dinuclear fragments.

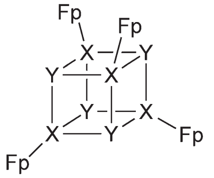
6.07.8.1 Polyiron Complexes Consisting of Mononuclear Fragments

A series of tetrahedral polyiron complexes bridged by group 14–16 elements (E), $[E(FeL_y)_n(X)_{4-n}]^z$ **225**, has been reported (Scheme 18). The Fp and $Fe(CO)_4$ fragments are used as the iron units (FeL_y) as listed below: (group 14) $SnFp_3(OH)$;[296] (group 15) $[HPFp_3]^+$,[297] $S{=}PFp_3$,[298] $[HAs\{Fe(CO)_4\}_3]^{2-}$,[299] $[E\{Fe(CO)_4\}_3]^{2-}$ (E = As, Sb),[155,300] $[SbFp_3(Ph)]^{+1}$,[301] $[SbFp_3(I)]^-$,[302] $Sb\{Fe(\eta^5\text{-}C_5H_4Me)(CO)_2\}_3$,[303] $[Sb\{Fe(CO)_4\}_3(X \text{ or } R)]^{2-}$,[304] EFp_3 (E = Sb, Bi),[305] $[SbFp_2\{Fe(CO)_4\}]^-$,[306] $[Bi\{Fe(CO)_4\}_3(R)]^{-2}$,[307] and (group 16) $[Te\{Fe(CO)_4\}_4]^{2-}$.[176] A group 13 compound, $InFp_3$, contains a trigonal-planar $InFe_3$ core.[308] In some cases, **225** is unstable with respect to decarbonylation and is converted into the Fe–Fe-bonded species with **226**- [298,305,309–311] and **227**-type core structures (Scheme 18).[155]

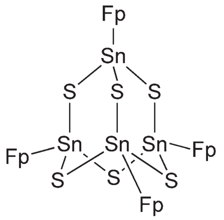
A cage structure is another important core motif for the title compounds. The cage may consist of main group elements, or Fe atoms may be incorporated into the cage as is the case for the Fe_4S_4 cubane clusters, which are discussed in Section 6.07.8.2. The Ga-containing cages, **228**[311] and **229**,[312] are prepared via dechlorosilylation of $Fp_2GaCl/KP(SiMe_3)_2$ and $Fp_2GaCl/E(SiMe_3)_2$, respectively, and the Fe_4Sb_4 cage **230** is formed upon thermolysis of $Et_4N[SbFp_3I]$ in refluxing dioxane.[313] The adamantane-like sesquisulfide **231**[314] and the four-membered Fe_2Sn_2 complex **232**[315] are prepared by condensation of $FpSnCl_3/S(SnBu_3)_2$ and $Fp_2SnCl_2/Te(SiMe_3)_2$, respectively. The metalloxane complexes **233**,[316] **234**,[317] and **235**[318,319] are formed via partial hydrolysis of the E–X linkages in Fp–EX_n, and a hexagonal prismatic Ga_6O_6 intermediate is proposed for **233**. Reaction of Li_3P_7 with Fp–X affords **236** with the nortricyclane-type P_7 core, while a three-component reaction ($FeCl_2 + Cp^*Li + P_7(SiMe_3)_3$) forms the P_6Fe_3 cluster **237**.[320] The phosphorus linkage found in the $P_{11}Fe_3$ complex **238** resembles that found in a substructure of Hittorf's phosphorus,[321] and the core structure of the hexameric complex, $\{Fe(CO)_2(TePh)_2\}_6$ **239**, is akin to a so-called "ferric wheel".[322]



Scheme 18



Str.	X	Y
228	Ga	$PSiMe_3$
229	Ga	S,Se, Te
230	Sb	$Fe(CO)_3$



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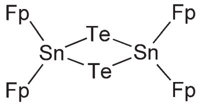

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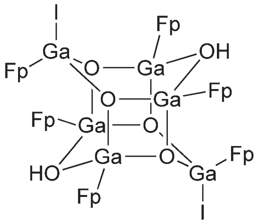

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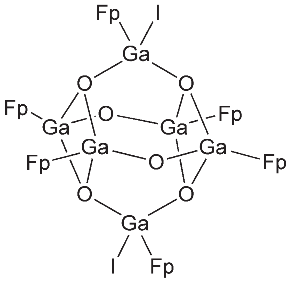

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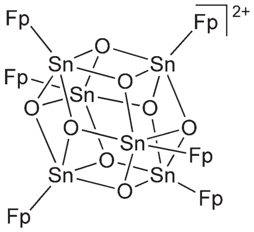

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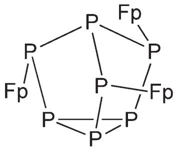

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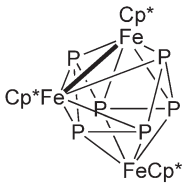

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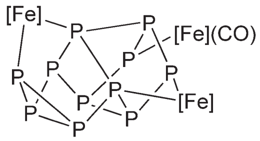
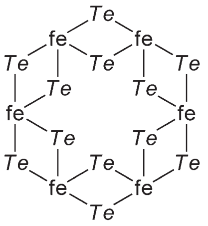


238

[Fe] = Fe(η^5-$C_5Pr^i{}_5$)(CO)



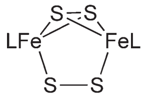
239

(*Te* = TePh)

6.07.8.2 Polyiron Complexes Relevant to Fe_4E_4 Cubane Clusters

Reaction of $Fe_2(CO)_4L_2$ (L = η^5-C_5R_5) with elemental sulfur provides a variety of iron–sulfur complexes depending on the cyclopentadienyl ligand employed (Scheme 19), as already described in COMC (1982) (Chapter 31.5.3.3 Volume 4) and COMC (1995) (Chapter 4.4.2 Volume 7). The selectivity for the di- and tetrairon complexes depends on the size of the cyclopentadienyl ligand, and a bulkier ligand tends to form dinuclear complexes to reduce the mutual steric repulsion. For example, reaction of the η^5-$C_5H_4SiMe_3$ derivative affords a mixture of $Fe_4S_6L_4$ **240**, $Fe_4S_5L_4$ **241**, and $Fe_4S_4L_4$ **242**, while reaction of the bulkier η^5-$C_5H_3(SiMe_3)_2$ derivative gives the dinuclear complex $Fe_2S_4L_2$ **243**.[323] The C_2 chiral cluster with two Fe–Fe bonds **242** (η^5-$C_5H_4SiMe_3$) shows fluxional behavior following a reversible Fe–Fe bond cleavage (Scheme 19).[324]

The di(μ-disulfido)diiron complex **243** (L = Cp*) is converted into the di(μ_3-sulfido)triiron complex **244** by thermal reaction with iron carbonyls.[325] Selective mono-CO substitution of **244** by PPh_3 is accelerated by photolysis or by treatment with reductant (benzophenone ketyl) or oxidant (ferrocenium cation).[326]



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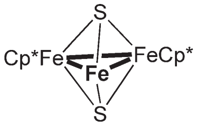

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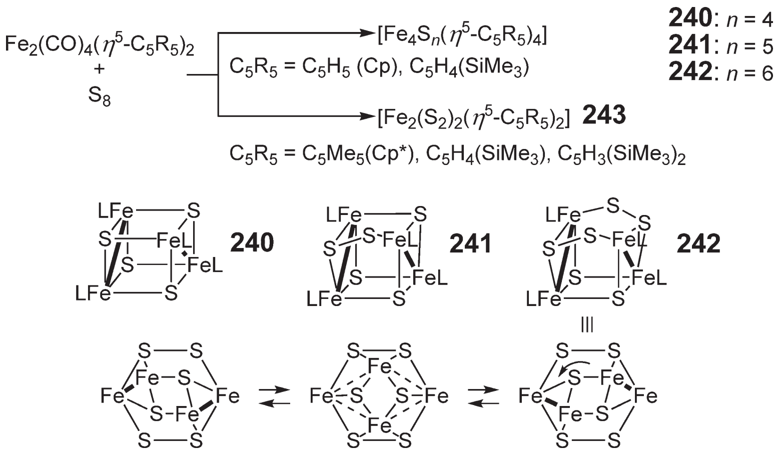
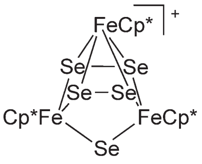
The analogous reaction of $Fe_2(CO)_4Cp^*{}_2$ with Se_8 affords the paramagnetic triiron cluster, $Fe_3Se_5Cp^*{}_3$, which undergoes air oxidation to form the diamagnetic monocationic species **245** with two μ_3-$\eta^1:\eta^1:\eta^2$-Se_2 and one μ-Se



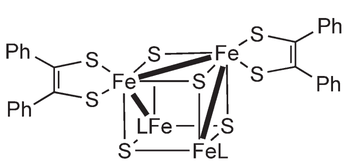
Scheme 19

ligands. Complex **245** serves as a precursor for a variety of complexes including $[Fe_3(CO)Cp^*{}_3Se_4]^+$ (treatment with CO), $[Fe_3Cp^*{}_3Se_2]^+$ (with PBu_3), $[Fe_3(CO)Cp^*{}_3Se_2]^+$ (with PBu_3 followed by CO), and $[Fe_3(CO)Cp^*{}_3(Se_4Me_2)]^+$ (with $LiHBEt_3$ followed by MeI).[327]



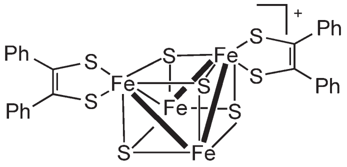
245

Addition of alkyne to the reaction system forms the cubane cluster with the dithiolene ligand. The reaction of the C_5H_5 (Cp) complex with S_8 and PhC≡CPh gives the bis(dithiolene) complex **246a** (L = Cp) in addition to **240a** (L = Cp), while the reaction of the Cp* complex gives the μ-dithiolene complex with the μ_3-S_2 ligand **247** (L = Cp*) together with **246b** (L = Cp*).[328] In the latter reaction, **243** (L = Cp*) is detected as an intermediate. The reaction of $Fe_2(CO)_4Cp^*{}_2$ with dimethyl acetylenedicarboxylate furnishes the dinuclear complex **249** in addition to the **246b**- and **247**-type complexes with two COOMe groups on the dithiolene ligand.[329] The Fe_4S_4 **246b** and Fe_4S_5 clusters **247b** exhibit four reversible redox waves (**246b** : $+2 \leftrightarrow -2$; **247b** : $+3 \leftrightarrow -1$). X-ray crystallography reveals that oxidation induces reorganization of the Fe–Fe bonding interactions, suggesting flexibility of the Fe–S cluster cores.[330,331] Methylation of **247** with MeI occurs at the S_2 ligand to form $\mathbf{248}^+$, which is converted into the neutral species **248** upon treatment with cobaltocene.[332]



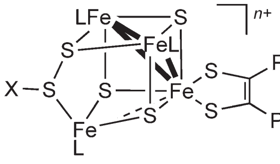
a: L = C_5H_5
b: L = C_5Me_5

246

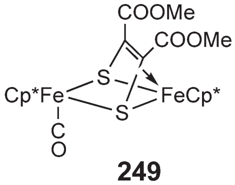


246⁺

a: L = C_5H_5
b: L = C_5Me_5



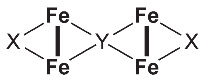
X = none; $n = +3 - -1$ ($\mathbf{247}^{n+}$)
X = Me; $n = 0, 1$ ($\mathbf{248}^{n+}$)



249

6.07.8.3 Polyiron Complexes Consisting of Dinuclear Fragments

A number of tetranuclear complexes consisting of two dinuclear units connected by a bridging ligand, **250–252**, were reported, and many of the structures of the dinuclear unit are based on the Fe_2E_2-butterfly structures discussed in Section 6.07.7.2.1.(ii).



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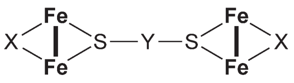

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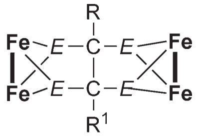

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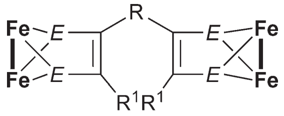
Typical examples are as follows: **250** (X/Y = none/(μ-$\eta^2:\eta^2$-SN)$_2$–R,[333] ER/η^2(C,S)-η^1-CS_2,[334] ER/$AsMe_2$–$AsMe_2$,[183] (μ-CO)(μ-PPh_2)/Cu{μ-$Ph_2P(CH_2)_nPPh_2$}Cu,[335] μ-PPh_2/(μ-$\eta^1:\eta^2$-CH=CH)$_2$PPh,[336] (μ-CO)$_2$/$Tl_2Fe_2(CO)_8$ (dianionic species)),[337,338] **251** (Y = μ-C(=S)SR or μ-C(=O)Ph/alkylene or phenylene),[339–341] **252** (E/R/R′ = Se/H/H,[342,343] S, Se/H/Ph,[344] Se/H/thienyl,[345] Se/H/C≡CR),[346] and **253** (E/R/R′ = Se/none/H,[347] S, Se, Te/CH(OEt)–CH(OEt)/Ph).[348] Cp derivatives of **250**,[349] macrocyclic complexes based on the structure motif **251**,[350,351] related unsymmetrical complexes,[352–355] and diphosphine-bridged complexes [356,357] were also reported.



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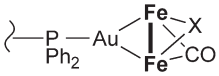

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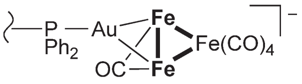

255

The mixed metal Au–Fe cluster compounds containing $(RPh_2P)AuFe_2(CO)_7(\mu\text{-}PPh_2)$[358] and $(RPh_2P)AuFe_3(CO)_{10}]^-$ units[359] are readily prepared by condensation between the corresponding PAuCl complex with $[Fe_2(CO)_7(\mu\text{-}L)]^-$ and $[Fe_3(CO)_{11}]^{2-}$, respectively, and connection of the $AuFe_n$ units by a multidentate phosphine ligand leads to oligomeric species. This strategy has been extended to the synthesis of dendrimers.[360–362] $AuFe_2$ dendrimers with up to 192 iron atoms were prepared.

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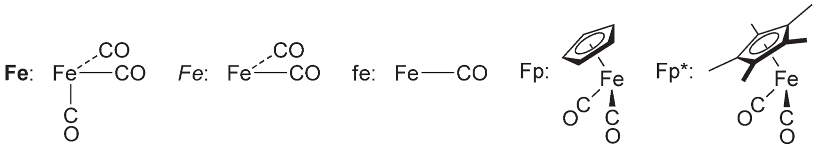
6.08
Iron Cluster Compounds: Compounds with Hydrocarbon Ligands

M Akita, Tokyo Institute of Technology, Yokohama, Japan

6.08.1 Introduction

This chapter covers iron cluster compounds with hydrocarbon ligands reported until early 2005. Previous works were reviewed in the corresponding chapters in COMC(1982) (Chapter 31.5, Vol. 4) and COMC(1995) (Chapter 4, Vol. 7). Although a few novel types of iron cluster compounds have appeared, most of the coordination structures of the hydrocarbyl ligands and many of the prototypes of their reactivity were already established during the period covered by the previous versions. The final part of this chapter is devoted to $Fe_4Cp_4(\mu_3\text{-}CO)_4$ and polyiron complexes consisting of mononuclear fragments bridged by a polyfunctional hydrocarbyl group.

In this chapter the iron carbonyl fragments are abbreviated as shown below and metal–metal bonds are indicated with bold lines. Throughout this chapter, η^5-C_5H_5 and η^5-C_5Me_5 ligands are denoted by Cp and Cp*, respectively.

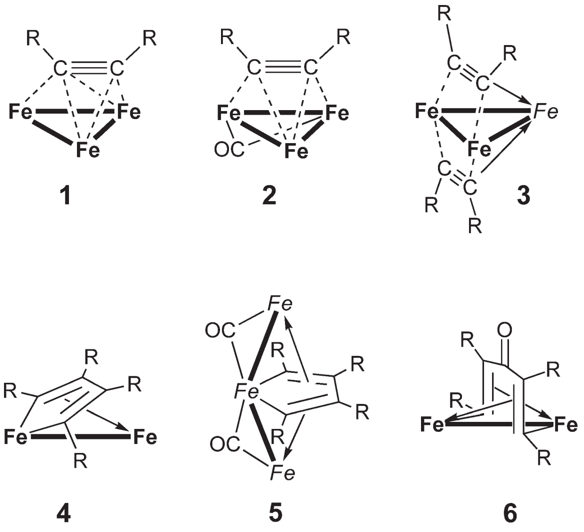


6.08.2 Clusters Derived from Alkynes and Related Compounds

6.08.2.1 Alkyne Clusters

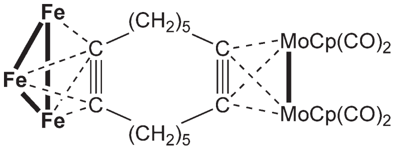
Reactions of alkynes with iron carbonyl species afford a variety of products (usually with a low selectivity) depending on the structure of the alkyne and the reaction conditions as already described in COMC(1982). Major products are the trinuclear μ_3-alkyne clusters with the ⊥- **1** and ‖-coordinated alkyne ligands **2**, the trinuclear di(μ_3-alkyne) complexes **3**, the di- **4** and trinuclear ferrole complexes **5**, and the diiron flyover complexes **6** (Scheme 1).

Additional pieces of information on iron carbonyl alkyne cluster compounds have been reported. Interaction of $Fe_3(CO)_{12}$ with (μ-η^2-cyclotetradeca-1,8-diyne)$Mo_2Cp_2(CO)_4$, the 1 : 1 adduct of the dimolybdenum fragment with the diyne, produces $(CO)_9Fe_3\{\mu_3(Fe_3)$-⊥-;μ-$\eta^2(Mo_2)$-cyclotetradeca-1,8-diyne$\}Mo_2Cp_2(CO)_4$ **7** of the **1**-type coordination.[1] Unsymmetrically substituted alkynes give a mixture of the regioisomers of the products, and it is noted that chromatographic separation of the reaction mixture by silica gel causes degradation to the dinuclear μ-2-alkenoate



Scheme 1

complex, $Fe_2(CO)_6\{\mu\text{-}C(R){=}C(R)\text{–}C({=}O)O\}$ **8**.[2] Catalytic activity of a variety of **1** for alkyne hydrogenation is rather poor because of the concomitant formation of the ferrole complexes **4** and **5**, and a mixture of *E*/*Z*-alkene and alkane is obtained.[3]



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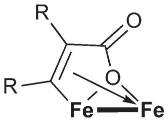

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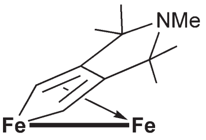
Reactions with hetero-substituted alkynes are also examined. The dipropargylamine, $MeN(CH_2C{\equiv}CH)_2$, reacts with $Fe_3(CO)_{12}$ to provide a mixture of the bicyclic **4**- and **5**-type ferrole complexes, **9** and **10**, as the major products,[4–6] while propargyl alcohols give allenylidene complexes, $Fe_3(CO)_{10}(\mu\text{-}C{=}C{=}CR_2)$ ($R_2 = Me_2$, $(CH_2)_5$, Me/Ph) (see Section 6.08.2.3) via dehydration together with the **2**- and **4**-type complexes.[7–9] For a thiopropargyl system, see Chapter 6.07.7.2.2.1.



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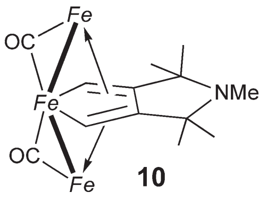

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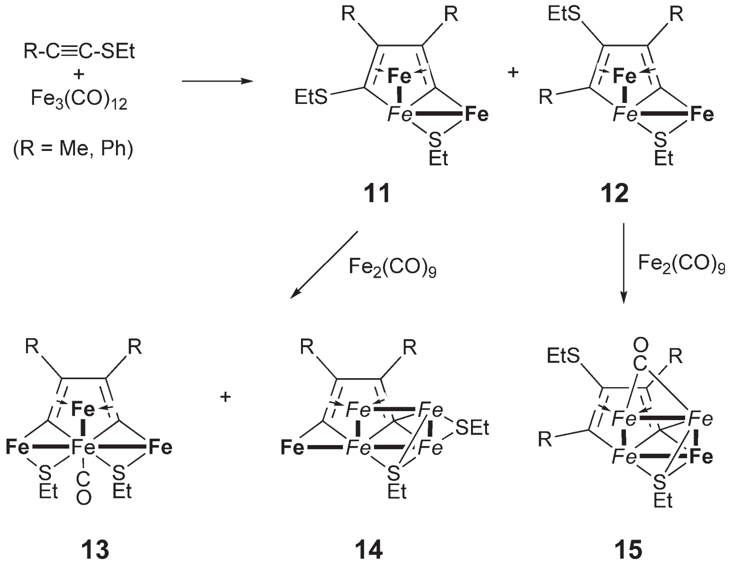
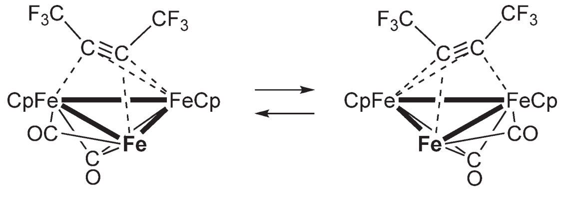
Reactions of thioalkynes with $Fe_3(CO)_{12}$ in refluxing hexane give the trinuclear complexes **11** and **12** via: (i) oxidative metallacyclization giving the ferrole group associated with (ii) C–S bond cleavage giving the μ-thiolato ligand (Scheme 2), in contrast to the reactions with $Fe_2(CO)_9$, which afford isomers of dinuclear ferroles without C–S bond cleavage.[10] The trinuclear complexes **11** and **12** differ in the orientation of one of the two alkyne molecules incorporated in the ferrole moiety. Further reaction of **11** with $Fe_2(CO)_9$ results in C–S bond cleavage to afford the tetranuclear cluster **13** with a T-shaped metal skeleton and the pentanuclear cluster **14** with a spiked-square metal skeleton. The reaction of the other isomer **12** results in addition of an iron fragment to form the tetranuclear cluster **15** with a square metal skeleton.

Alkyne clusters of **1**- and **2**-types (R = H) and the tautomeric vinylidene cluster, $Fe_3(CO)_9(\mu_3\text{-}C{=}CH_2)$, were examined by DFT calculations.[11] Two-electron reduction of **1** (R = Et; 46e) consisting of two consecutive one-electron

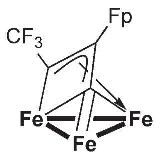


Scheme 2

processes causes isomerization to **1**$^{2-}$ (48e) with the $\|$-oriented alkyne ligand similar to that observed for the 48e cluster **2**.[12] On the basis of simulation of the electrochemical processes, it is proposed that the rearrangement of the alkyne ligand takes place after the two-electron reduction and the reverse reorientation at the stage of the monoanion radical intermediate. The dynamic NMR features of a Cp-containing cluster, (μ_3-$\|$-$CF_3C{\equiv}CCF_3$)$Fe_3Cp_2(CO)_5$ **16**, consistent with an apparent mirror-symmetrical structure are interpreted in terms of an interconversion with another $\|$-coordinated intermediate **16′** (Equation (1)), and the alkyne reorientation is also promoted by redox processes as observed for **1**.[13] Complex **16** is obtained by thermolysis of {(OC)CpFeC(CF_3)=C(CF_3)SMe}$_2$ together with **17**.[14] A **4**-type product **18** is formed via C–C bond cleavage of biphenylene (dibenzocyclobutadiene) with $Fe_3(CO)_{12}$.[15]



16 **16′** (1)



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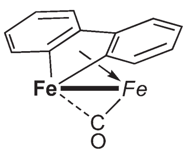

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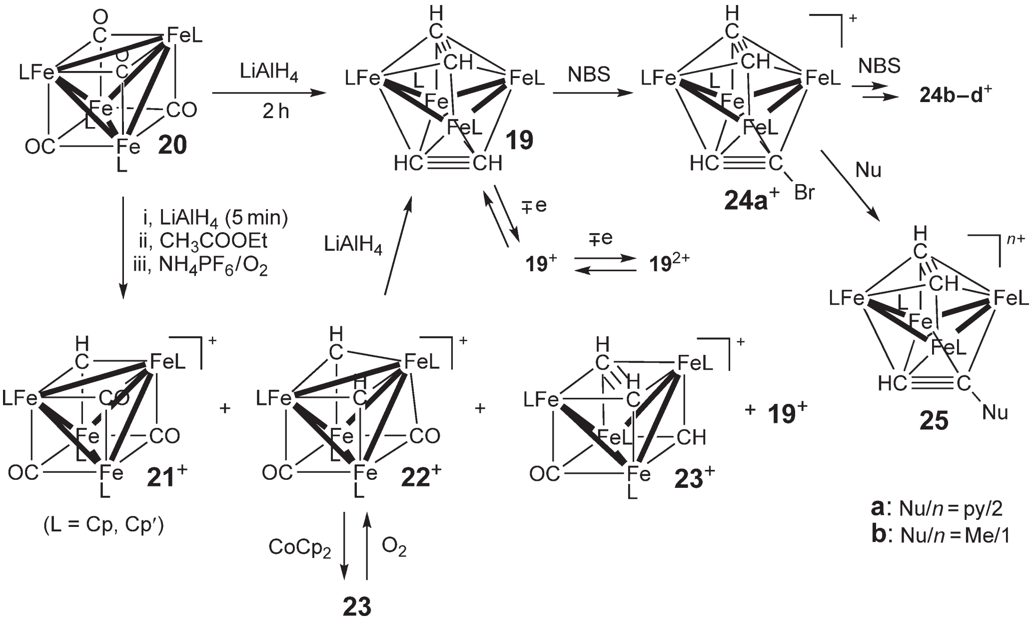
A new type of di(μ_4-$\eta^1:\eta^1:\eta^2:\eta^2$-ethyne) cluster compound **19** is synthesized by treatment of $Fe_4L_4(\mu_3\text{-}CO)_4$ **20** (L = η^5-C_5H_5 (Cp), η^5-C_5H_4Me (Cp′)) with $LiAlH_4$ (Scheme 3)[16] (for **20**, see Section 6.08.5). Shortening the reaction time (2 h → 5 min) and quenching with CH_3COOEt followed by an aerobic workup leads to a series of paramagnetic monocationic tetrairon complexes, which are separated and characterized by X-ray crystallography: the



Scheme 3

$(\mu_3\text{-CH})(\mu_3\text{-CO})_3$ **21**$^+$, $(\mu_3\text{-CH})_2(\mu_3\text{-CO})_2$ **22**$^+$, $(\mu_4\text{-HC}{\equiv}\text{CH})(\mu_3\text{-CH})(\mu_3\text{-CO})$ **23**$^+$, and $(\mu_4\text{-HC}{\equiv}\text{CH})_2$ complexes **19**$^+$.[17,18] The structures of these species suggest that mechanism of formation of the ethyne linkage involves an intramolecular C–C coupling of two methylidyne ligands resulting from deoxygenative reduction of the μ_3-CO ligands in **20**, as evidenced by: (i) redox-induced reversible C–C bond formation and cleavage processes between **22**$^+$ and **23**$^+$, (ii) conversion of **22**$^+$ into **19** induced by LiAlH_4 treatment, and (iii) a crossover experiment using the Cp and Cp′ derivatives.

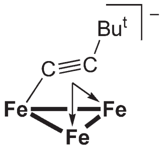
The neutral complex **19** undergoes three reversible or quasi-reversible one-electron oxidation processes and one irreversible one-electron reduction process. Air oxidation and electrochemical oxidation of **19** give the paramagnetic one-electron oxidation product **19**$^+$ and two-electron oxidation product **19**$^{2+}$, respectively.[19] The dicationic species **19**$^{2+}$ contains diamagnetic and paramagnetic components as revealed by an NMR measurement but the detailed behavior in solutions remains to be studied. The three species **19**, **19**$^+$, and **19**$^{2+}$ turn out to be isostructural but the successive shortening of the averaged Fe–Fe bond distances indicates an increase of the total Fe–Fe bond order, while the C–C lengths remain essentially unchanged.

Bromination of **19** with *N*-bromosuccinimide (NBS) produces a series of cationic cluster compounds with μ_4-bromo- and μ_4-dibromo-ethyne ligands, $[(\mu_4\text{-BrC}{\equiv}\text{CH})(\mu_4\text{-HC}{\equiv}\text{CH})\text{Fe}_4\text{Cp}_4]^+$ **24a**$^+$, $[(\mu_4\text{-BrC}{\equiv}\text{CH})_2\text{Fe}_4\text{Cp}_4]^+$ **24b**$^+$, $[(\mu_4\text{-BrC}{\equiv}\text{CBr})(\mu_4\text{-BrC}{\equiv}\text{CH})\text{Fe}_4\text{Cp}_4]^+$ **24c**$^+$, and $[(\mu_4\text{-BrC}{\equiv}\text{CBr})_2\text{Fe}_4\text{Cp}_4]^+$ (**24d**$^+$) in a stepwise manner,[20] and the mono-μ_4-bromoethyne complex **24a**$^+$ is converted into the functionalized derivatives $[(\mu_4\text{-HC}{\equiv}\text{Cpy})(\mu_4\text{-HC}{\equiv}\text{CH})\text{Fe}_4\text{Cp}_4]^{2+}$ **25a** and $[(\mu_4\text{-HC}{\equiv}\text{CMe})(\mu_4\text{-HC}{\equiv}\text{CH})\text{Fe}_4\text{Cp}_4]^+$ **25b** upon nucleophilic substitution of Br.

6.08.2.2 Acetylide Clusters

Some miscellaneous preparative methods for acetylide clusters are reported. Reaction of a vinylideneruthenium complex, $\text{Cp}^*(\text{Ph}_3\text{P})(\text{Cl})\text{Ru}{=}\text{C}{=}\text{CHBu}^\text{t}$, with $\text{Fe}_2(\text{CO})_9$ produces the anionic acetylide cluster complex **26** in a low yield via dehydrochlorination associated with intermolecular transfer of the vinylidene (or acetylide) ligand.[21] Reaction of the double ylide, $\text{Ph}_3\text{P}{=}\text{C}{=}\text{PPh}_3$, with Fe(CO)_5 affords the mononuclear cumulenic complex, $(\text{OC})_4\text{Fe}({=}\text{C}{=}\text{C}{=}\text{PPh}_3)$, which is further converted into the PPh_3-substituted acetylide cluster complex **27**.[22] Propargyl alcohols serve as an equivalent for 1-alkyne via ketone elimination as is exemplified by the reactions with $\text{Fe}_3(\text{CO})_{12}$, which give the pentanuclear di(μ_3-acetylide) cluster complexes with a bow tie-metal core **28** (R = Me, Et) in very low yield in addition to the normal products **2**, **4**, and **6** (Scheme 1).[23] Treatment of the μ_3-alkynylsulfido cluster, $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-SC}{\equiv}\text{CBu}^\text{t})]^-$, with $\text{ClAu}(\text{PPh}_3)$ results in desulfurization to give the mixed metal tetranuclear

μ_4-acetylide cluster compound **29**.[24] Crystallographic and detailed spectroscopic analyses reveal that complex **29** undergoes reversible metal migration, which is relevant to the interconversion between 1-alkyne and (hydrido)(alkynyl) species on a cluster system, when the isolobal H–Au(PR_3) relationship is taken into account (Equation (2)).



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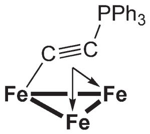
[Cp*(Ph_3P)Ru$(CO)_2$]$^+$



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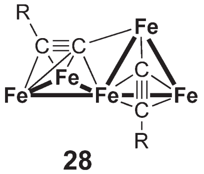

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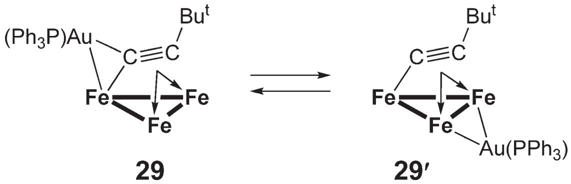
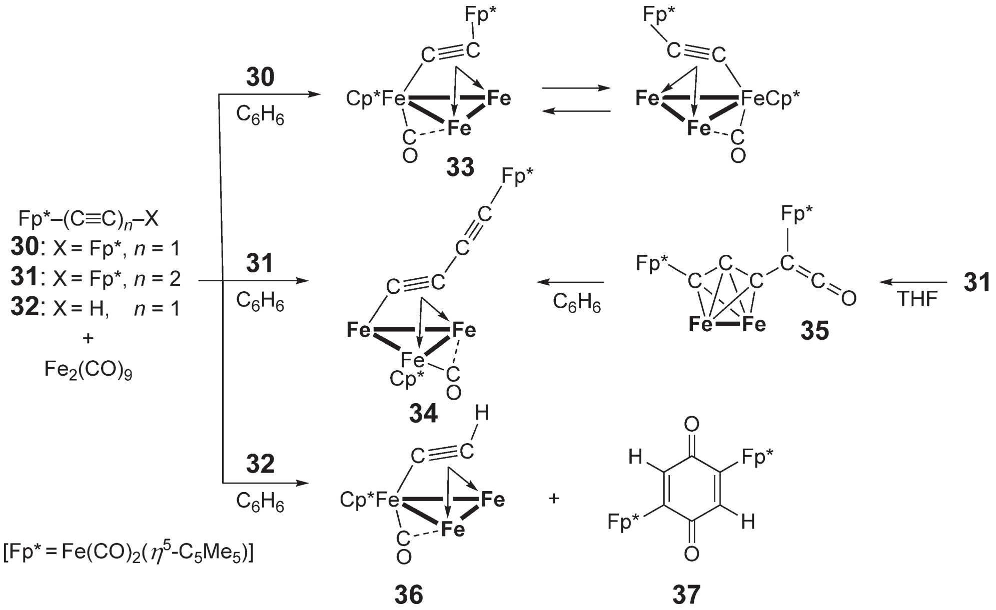


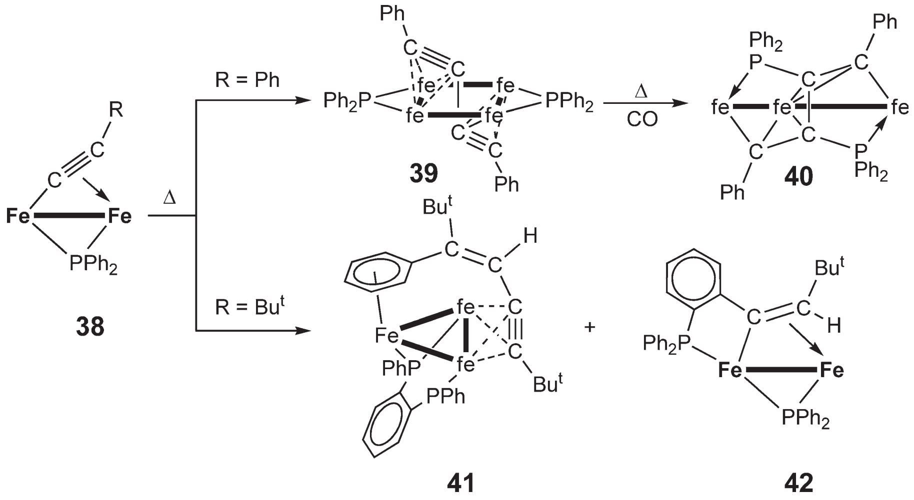
(2)

Ethynediyl (μ-C_2) and butadiynediyl (μ-C_4) diiron complexes of the formulas, Fp^*–$(C{\equiv}C)_n$–Fp^* ($n = 1$ **30**, 2 **31**; $Fp^* = Fe(CO)_2(\eta^5$-$C_5Me_5))$, are converted into the corresponding acetylide cluster complexes **33** and **34**, respectively, in a selective manner, when the reactions are carried out in benzene (Scheme 4).[25] The μ_4-C_2 cluster complex **33** derived from **30** shows dynamic behavior via reversible metal–metal bond cleavage and recombination processes. On the other hand, the reaction of **31** in THF gives the μ-η^3-propargylidene–ketenyl complex **35** as a byproduct, which is converted into **34** via decarbonylation upon dissolution in benzene. Reaction of the related mononuclear ethynyl complex **32** affords a mixture of the trinuclear acetylide cluster complex **36** and the dimetal-substituted quinone complex **37**.

Coupling of two acetylide ligands leading to a C_4 linkage is observed for the μ-phosphido-diiron complexes **38** (Scheme 5). Thermal decarbonylation of **38** (R = Ph) produces the tetranuclear μ_4-diyne complex **39**, and subsequent



Scheme 4



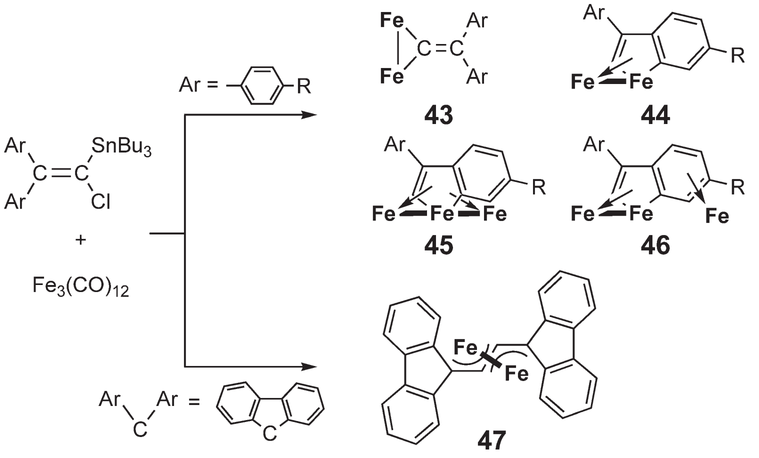
Scheme 5

carbonylation gives the P–C coupled product 40.[26,27] The Bu^t derivative also undergoes acetylide dimerization but a different type of the product 41 results from a complicated mechanism including P–C bond cleavage and C–H bond activation.[28] The dinuclear byproduct 42 is formed via C–H activation and C–C coupling. Nucleophilic addition to the C_4 bridge in the μ_4-C_4 complex, $(\mu_4\text{-}C_4)\{Fe_2(\mu\text{-}PPh_2)(CO)_6\}_2$ 38 ($R = (\mu\text{-}C_2)Fe_2(\mu\text{-}PPh_2)(CO)_6$), has also been investigated and the α-carbon atom is found to be susceptible to the addition.[29]

6.08.2.3 Cumulenylidene and Cumulenyl Clusters

gem-Chlorostannylalkenes ($R_2C{=}C(Cl)SnBu_3$) serve as a source of vinylidene species ($R_2C{=}C$) via dechlorostannylation (Scheme 6).[30] Treatment of acyclic diaryl derivatives with $Fe_3(CO)_{12}$ gives the dinuclear vinylidene complexes 43 in low yields together with the 4- and 5-type fused ferrole complexes, 44–46, arising from orthometallation of an aryl group of μ-vinylidene intermediates, whereas the cyclic fluorenyl derivative affords the μ-butatriene complex 47 via C–C coupling.

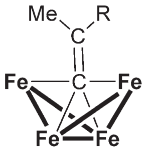
A μ_4-vinylidene cluster compound with the butterfly tetrairon metal array, $Fe_4(\mu_4\text{-}C{=}CHMe)(CO)_{12}$ 48, is prepared by successive treatment of the MeO complex 49 with $LiHBEt_3$ and Me_3SiOTf.[31] In contrast to other derivatives (e.g., 49), the vinylidene α-carbon atom of 48 lies below the Fe(wingtip)–Fe(wingtip) vector owing to strong back-donation from the wingtip Fe atoms as suggested by a Fenske–Hall MO calculation. A heterotetranuclear



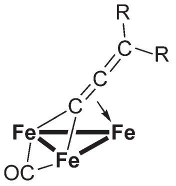
Scheme 6

(Fe_3Pd) μ_4-vinylidene complex with a butterfly metal array has been reported.[32–34] Formation of μ-allenylidene complexes **50** from propargyl alcohols with $Fe_3(CO)_{12}$ may involve a dehydration process.[7–9]

The Fischer-type Cr and W carbene complexes with a PhC≡C substituent, $(OC)_5M{=}C(OEt)C{\equiv}CPh$, react with $[(\mu\text{-H})Fe_3(CO)_{11}]^-$ to give the μ_3-$\eta^1:\eta^2:\eta^2$-allenyl complex, $Fe_3(CO)_9\{\mu\text{-EtOC}=C=CHPh\}$ **51**, via ligand transfer from M to the triiron unit as well as insertion of the C≡C linkage across the Fe–H bond.[35] Oxidation of a (μ-vinylidene)(μ-phosphido) complex, $[Fe_3(CO)_8(\mu\text{-C}{=}CHBu^t)(\mu\text{-PPh}_2)]^-$ **52**, affords the diiron complex **53** via H redistribution and P–C and C–CO coupling, while protonation occurs on an Fe–Fe bond to induce rotation of the vinylidene ligand on the Fe_3 face in **54**.[36]



R = Me **48**
OMe **49**



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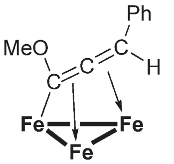

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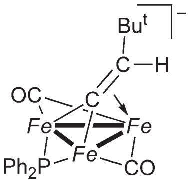

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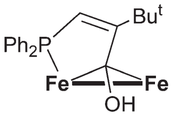

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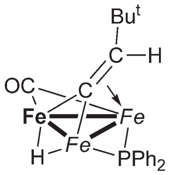

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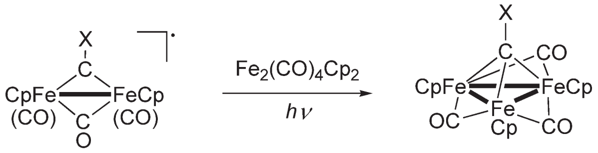
6.08.3 Alkylidyne and Alkyl Clusters

Heteroatom-substituted μ_3-alkylidyne complexes, $[Fe_3(CO)_3(\mu\text{-CX})Cp_3]$ (X = SR **55**, NR_2 **56**), are prepared by photolysis of the paramagnetic μ-alkylidyne complexes, $[Fe_2(CO)_3Cp_2(\mu\text{-CX})]$, in the presence of $Fe_2(CO)_4Cp_2$ (Equation (3)).[37] Methylation of **55a** gives the diamagnetic cationic complex, $[Fe_3(CO)_3Cp_3(\mu_3\text{-CSMe}_2)]^+$.

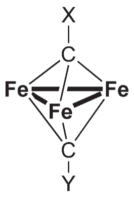


(3)

(X = SR, NMeBz)

55a: X = SMe
55b: X = SEt
56: X = NMeBz

Reaction of the ferrate $[Fe_3(CO)_{11}]^{2-}$ with Cl_2BNR_2 results in double O-borylation to furnish the di(μ_3-boroxymethylidyne) cluster, $Fe_3(CO)_9(\mu_3\text{-COBClNR}_2)_2$ **57** (X, Y = OB(Cl)NR_2).[38] Thermal reaction of EtSC≡CMe with $Fe_2(CO)_9$ in the presence of trimethylamine oxide produces the (μ_3-propylidyne)(μ_3-dimethylaminomethylidyne) cluster compound **57** (X = Et, Y = NMe_2) via activation of the three C–H bonds in one of the three methyl groups in the amine oxide and S–C≡bond cleavage, in addition to the dinuclear complex, $Fe_2(CO)_6(\mu\text{-SEt})_2$ (cf. Scheme 2).[39]



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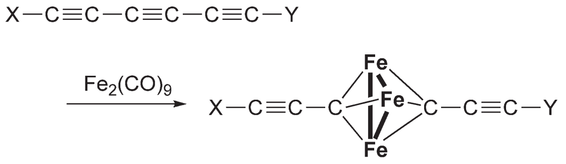
C≡C bond cleavage reactions of hexatriyne- and octatetrayne-diyl dimetal complexes, M–(C≡C)$_n$–M (M = Fp*, RuCp(PPh$_3$)$_2$; n = 3, 4), smoothly proceed at ambient temperature upon treatment with $Fe_2(CO)_9$ to form the di(μ_3-alkylidyne) complexes **57a** and **57b** (X = C≡C–M, Y = (C≡C)$_{n-2}$–M) (Equation (4)).[40,41] It is proposed that the electron-donating metal fragment stabilizes an electron-deficient side-on coordinated intermediate. Accordingly, Fp*–(C≡C)$_3$–SiMe$_3$ also affords **57c** (X = C≡C–Fp*, Y = C≡C–SiMe$_3$), while Me$_3$Si–(C≡C)$_3$–SiMe$_3$ without the Fp* substituent does not undergo the C≡C bond cleavage.



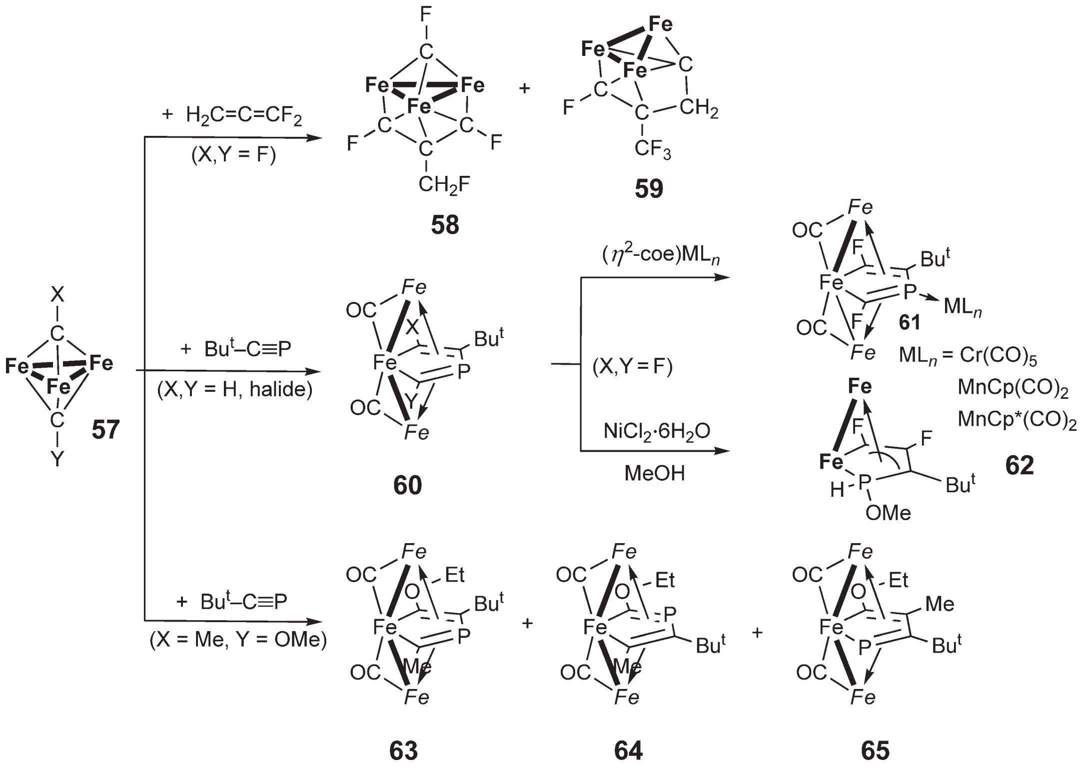
(4)

(No C≡C cleavage when X = Y = SiMe$_3$)

57a: X = Y = Fp*
57b: X = Y = RuCp(PPh$_3$)$_2$
57c: X = Fp*, Y = SiMe$_3$

A series of di(μ_3-alkylidyne) complexes **57** (X = Y = H, F, Cl, Br) undergoes one reversible reduction process and one irreversible oxidation process but C–C bond formation as observed for **21** (Scheme 3) is not noted.[42,43] Photochemical reaction of the di(μ_3-fluoromethylidyne) cluster **57** (X = Y = F) with 1,1-difluoroallene results in C–C coupling to give products with a C$_3$- **58** and C$_4$-linkage **59**, formation of which involves non-destructive activation of the strong C–F bonds (D(C–F) = 109–130 kcal mol^{-1}) (Scheme 7).[44]

The reaction of *t*-Bu–phospha-alkyne, Bu^{t}C≡P, with the di(μ_3-alkylidyne) cluster compound, Fe$_3$(CO)$_9$(μ_3-CX)(μ_3-CY) **57** (X = Y = H, F, Cl, Br), results in a three-component coupling among the C≡P moiety and the two μ_3-alkylidyne groups to form the triiron phosphaferrole complexes **60** (Scheme 7).[45] Upon treatment with labile

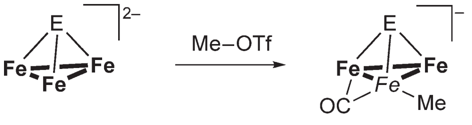


Scheme 7

η^2-cyclooctene species, the P moiety in **60** (X = Y = F) is coordinated to the added metal center to give **61**, whereas attempted coordination to $NiCl_2{\cdot}6H_2O$ in MeOH results in degradation and rearrangement of the five-membered ring to give the dinuclear complex **62**. The reaction with an unsymmetrical di(μ_3-alkylidyne) cluster complex **57** (X = Me, Y = OMe) gives a mixture of three isomers, **63**, **64**, and **65**, with **63** being the major product.

A mono-capped phosphine-substituted μ_3-alkylidyne complex, $[(\mu_3\text{-}CCH_3)Fe_3(CO)_9(\eta^1\text{-}Ph_2PC{\equiv}CPPh_2)]^-$, is prepared by an insertion reaction of the vinylidene hydrido complex, $[(\mu_3\text{-}C{=}CH_2)(\mu\text{-}H)Fe_3(CO)_9]^-$, induced by coordination of $Ph_2PC{\equiv}CPPh_2$.[46]

Rare examples of η^1-alkyl clusters are reported. The η^1-methyl complexes with μ_3-chalcogenido-bridged triiron cores, $[MeFe_3(CO)_9(\mu_3\text{-}E)]^-$ **66** (E = Se, Te), are synthesized by methylation of the corresponding dianion with MeOTf (Equation (5); Chapter 6.07.7.2.2.1).[47]

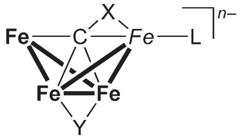


66 (E = Se, Te)

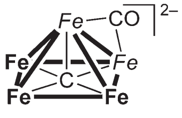
(5)

6.08.4 Carbido and Ketenylidene Clusters

Some structures of typical carbido-iron clusters **67–72** are shown below.



67: X,Y = none, L = CO, *n* = 2
68: X,Y = H, L = PR$_3$, *n* = 0
69: X,Y = H, L = CO, *n* = 0
70: X = none, Y = H, L = CO, *n* = 1



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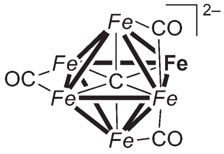

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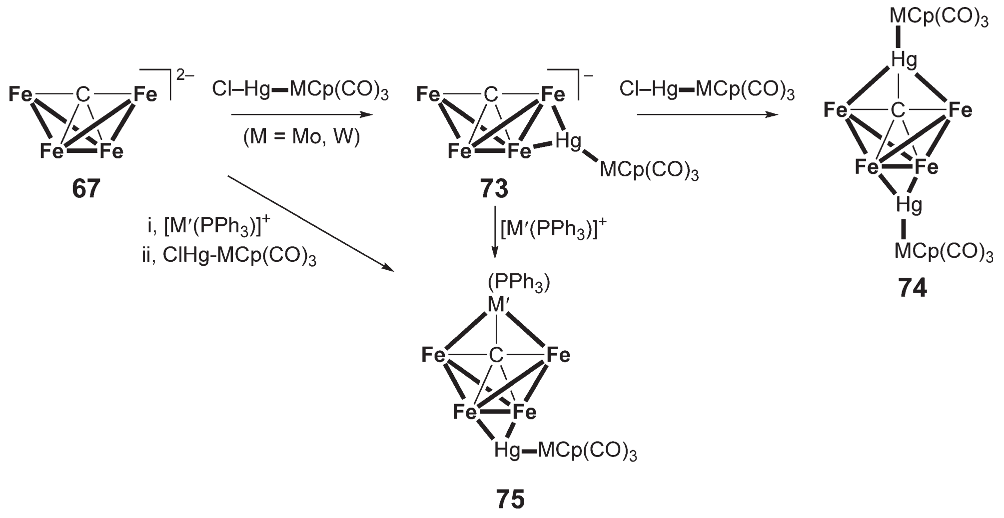
A series of heterometallic carbido cluster complexes, in particular, Au- and Hg-derivatives, is prepared by treatment of anionic carbido clusters ($[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$ **67**,[48,49] $[Fe_5(\mu_5\text{-}C)(CO)_{14}]^{2-}$ **71**,[50–52] and $[Fe_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ **72**[53,54]) with metal electrophiles. Analogous Au- and Hg-derivatives of Fe-containing mixed-metal carbido cluster compounds are also reported.[55–60] A new mode of electrophilic addition to the tetrairon μ_4-carbido cluster **66** is noted (Scheme 8).[48,61] In addition to the interactions with the hinge Fe–Fe bond (e.g., H^+) and the overbridging Fe(wingtip)–C–Fe(wingtip) linkage (e.g., $[Au(PPh_3)]^+$), it is revealed that the Hg–MCp(CO)$_3$ fragments (M = Mo, W) add across the Fe(wingtip)–Fe(hinge) bond to form **73**, and further addition of another equivalent of the Hg reagent causes an Hg migration to give **74**, where the Hg fragments are located on the hinge Fe–Fe bond and over the Fe–C–Fe moiety. Similar migration is induced by the addition of a $[M'(PPh_3)]^+$ fragment (M′ = Au, Cu, Ag) to **73** to give **75**, which is also obtained by initial overbridging with $[M'(PPh_3)]^+$ followed by addition of the Hg reagent. Complex **74** exhibits dynamic behavior which equilibrates the two Hg moieties.

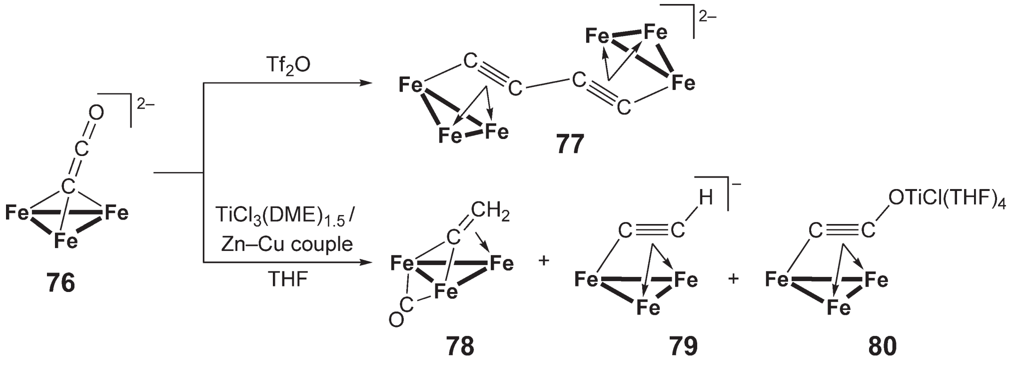
A series of phosphine-substituted tetranuclear μ_4-methylidyne complexes with the butterfly Fe$_4$ linkage, $Fe_4(\mu_4\text{-}CH)(\mu\text{-}H)(CO)_{11}(PR_3)$ **68**, is prepared by substitution of the corresponding dodecacarbonyl complex, $Fe_4(\mu_4\text{-}CH)(\mu\text{-}H)(CO)_{12}$ **69**, with phosphines.[62] The phosphine ligand is introduced on the wingtip Fe center. Dynamic processes including: (i) switching of the C–H moiety between the two wingtip Fe atoms and (ii) exchange of the CH and $Fe_2(\mu\text{-}H)$ hydrogen atoms are examined by means of NMR and MO analyses.

Treatment of the pentairon cluster, $[Fe_5(\mu_5\text{-}C)(CO)_{14}]^{2-}$ **71**, with bipy causes a contraction of the cluster core to afford the tetrairon complex, $[Fe(bipy)_3][Fe_4(\mu_4\text{-}C)(CO)_{12}(\mu\text{-}H)]_2$ ($[Fe(bipy)_3]^{2+}$(**70**$^-$)$_2$), in contrast to the reactions of the binary iron carbonyls, which result in substitution of two CO ligands by bipy.[63]

The trinuclear ketenylidene complex, $[Fe_3(\mu_3\text{-}C{=}C{=}O)(CO)_9]^{2-}$ **76**, serves as a versatile starting compound for: (i) heteronuclear ketenylidene complexes,[64,65] (ii) μ_3-alkylidyne complexes (via C=CO bond cleavage),[64] and (iii) C_2 complexes (via conversion into μ_3-C≡C–OX ligands),[66] as described in COMC(1995). Treatment of **76**

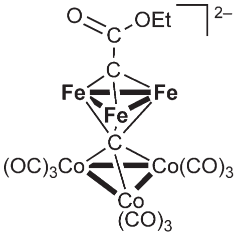


Scheme 8



Scheme 9

with trifluoromethanesulfonic anhydride induces C–C coupling to give the μ_4-C_4 complex, $[(OC)_9Fe_3(\mu_3:\eta^2:\mu_3:\eta^2\text{-}C_4)Fe_3(CO)_9]^{2-}$ **77**,[67,68] while the attempted reductive coupling of **76** with the McMurry reagent $(TiCl_3\cdot(DME)_{1.5}$/Zn–Cu couple) affords a mixture of the μ_3-vinylidene **78**, μ_3-ethynyl **79**, and μ_3-C$\equiv$COTiCl(THF)$_4$ complexes **80**, of which **78** and **79** result from reductive C–O bond cleavage reactions (Scheme 9).[69] On the other hand, condensation of the (μ_3-chloromethylidyne)tricobalt cluster compound, $Co_3(CO)_9(\mu_3\text{-}CCl)$, with **76** produces the heterometallic μ_6-carbido cluster compound, $[Fe_3Co_3(\mu_6\text{-}C)\{\mu_3\text{-}CC({=}O)OEt\}(CO)_{18}]^{-}$ **81** (after treatment with EtOH), with retention of the C–C$=$O linkage in contrast to the reaction with $[Fe_3(CO)_{11}]^{2-}$, which affords the μ-C_2-complex, $Fe_3Co_3(\mu_6\text{-}C_2)(CO)_{17}$ **82**, via a C–C coupling reaction.[70]



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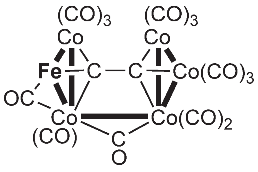

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6.08.5 $Fe_4Cp_4(\mu_3\text{-}CO)_4$ and its Derivatives

An improved synthesis of $Fe_4Cp_4(\mu_3\text{-}CO)_4$ **20** on a gram scale is reported.[71] Cothermolysis of $Fe_2Cp_2(CO)_4$ and PPh_3 provides **20** in 27% yield together with $Fe_4(\eta^5\text{-}C_5H_4Ph)Cp_3(\mu_3\text{-}CO)_4$ and $Fe_3Cp_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu\text{-}PPh_2)$ arising from P–C bond activation of PPh_3.

Functionalization of the Cp ligands in **20** has been examined, and deprotonation with lithium diisopropylamide (LDA) **83** followed by quenching with electrophiles turns out to be a versatile synthetic method for a variety of derivatives **84** containing COOH **85**, CHO, $CH(OH)CH_3$, $CH{=}CH_2$, SPh, PPh_2, and ferrocenyl groups (Scheme 10).[71–74] The COOH compound **85** can be converted into other carbonyl derivatives **87** through the COCl intermediate **86**, which is generated upon treatment of **85** with $(COCl)_2$. Multiple functionalization is also possible. Alkylation can be also achieved by treatment with organolithium reagents (Bu^nLi, PhLi), and the reaction proceeds through the anionic η^4-cyclopentadiene intermediate **88** resulting from nucleophilic addition to a Cp ring, subsequent oxidative workup furnishing the $\eta^5\text{-}C_5H_4R$ ring **89**. The nucleophilic addition to the Cp ring contrasts with the $LiAlH_4$ reduction giving **19** (Scheme 3). Double cubane octairon clusters with two **20** units, $\{\mu\text{-}X(\eta^5\text{-}C_5H_4)_2\}\{Fe_4Cp_3(\mu_3\text{-}CO)_4\}_2$ (X = CH(OH), *p*-phenylene, none), are also prepared by application of these functionalization methods.

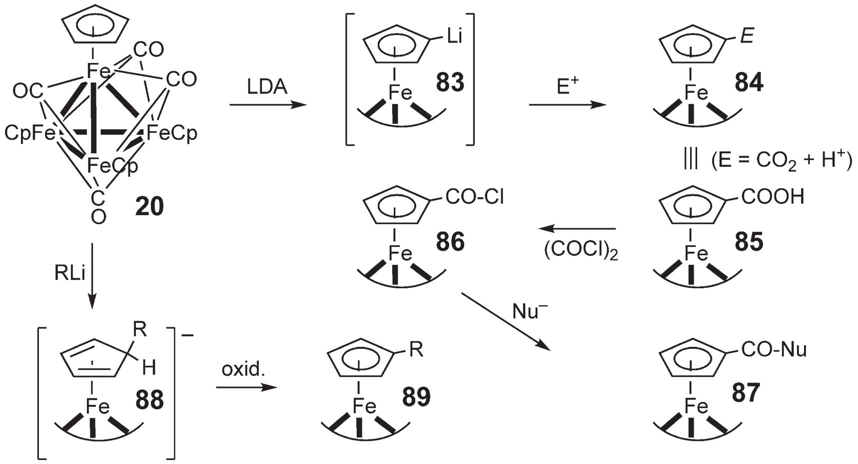
Physicochemical properties of **20** are analyzed (picosecond pump–probe transmission measurements [75] and electrochemistry [76]), and an analogy of the chemical bonding in **20** to that of metallaborane has been noted.[77]

Reduction of **20** with $LiAlH_4$ produces the ethyne cluster via reductive coupling of CO ligands as discussed in Section 6.08.2.1.

6.08.6 Polyiron Complexes Consisting of Mononuclear Fragments

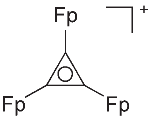
Several typical examples of the title compounds of formula $(\mu_n\text{-}BL)(FeL_x)_n$ (BL = bridging ligand) are discussed in this section. Polynuclear iron complexes, which contain the $\eta^5\text{-}C_5R_5$ groups as the only ancillary hydrocarbyl ligands in the compounds (e.g., $Fe_4(\eta^5\text{-}C_5R_5)_4E_4$-type cubane complexes), are discussed in Chapter 6.07.8, and for ferrocene derivatives, see Chapter 6.01.2.5.

Typical examples of symmetrical $(\mu_n\text{-}BL)(FeL_x)_n$-type complexes (BL = bridging ligand) are shown below. The cyclopropenium complex **90** and its analogs with other metal fragments are prepared by treatment of the trichlorocyclopropenium cation with the corresponding metalate, and the central part adopts a virtual equilateral triangle owing to π-delocalization.[78,79] Complexes with the triethynylbenzene **91**[80] and (tetraethynylcyclobutadiene)$Fe(CO)_3$ bridge **93**[81] are prepared to examine electronic communication among the metal centers. In the tri(cyclobutadieno)benzene complex **92**, prepared by treatment of hexabromotricyclobutabenzene with $Fe_2(CO)_9$, one of the three $Fe(CO)_3$ groups directed to the opposite side owing to the steric repulsion of the metal fragments, and crystallographic and MO analyses indicate that the central C_6 ring should be regarded as three $C(sp^2)$–$C(sp^2)$ single bonds connecting three



Scheme 10

(η^4-cyclobutadiene)Fe(CO)$_3$ complexes.[82] The quadruply bonded species **94** is prepared from an aqueous CrCl$_2$ solution and FpCH$_2$COOH.[83]



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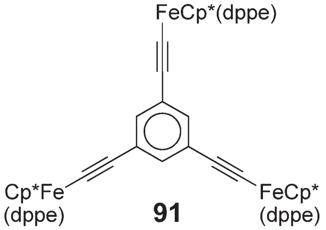

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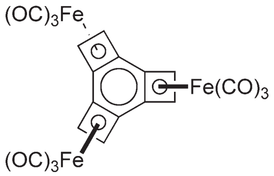

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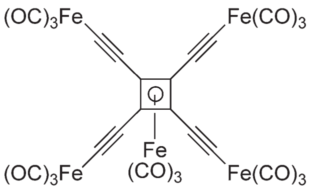

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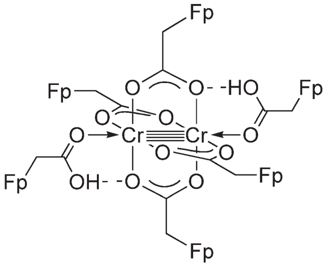

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6.09
Iron Cluster Compounds: Compounds with Fe–C Bonds to Heteroatom Ligands

E Sappa, Universita' del Piemonte Orientale, Alessandria, Italy

6.09.1 Introduction

Although iron and its coordination and organometallic complexes are assuming an increasing importance in metal-promoted organic syntheses,[1] references to tri- and polynuclear clusters substituted with organic ligands containing heteroelements are found in smaller numbers when compared with ruthenium and osmium derivatives (see Chapter 7.03).

An ordering of the complexes, based partly on structural schemes and partly on synthetic approaches, has been adopted. An example of a common structural scheme is the family of the pentagonal bipyramidal clusters. An example of a common synthetic method is the activation of CO (and methanol). When more than one heteroelement is present in the clusters, the collocation of the complexes is decided considering which of the two above-mentioned criteria is prevailing. The complexes have been numbered for ease of reference. In many reactions which afford the complexes described below, binuclear derivatives are also formed; the reader is referred to Section 6.2 for this chemistry. For the more interesting binuclear derivatives only one reference, among the many available for each research group involved, is given and that is usually the more recent and exhaustive one.

6.09.2 Group 16 Ligands

6.09.2.1 Triiron Complexes Bound through Carbon and Oxygen

6.09.2.1.1 Complexes derived from functionalized alkynes

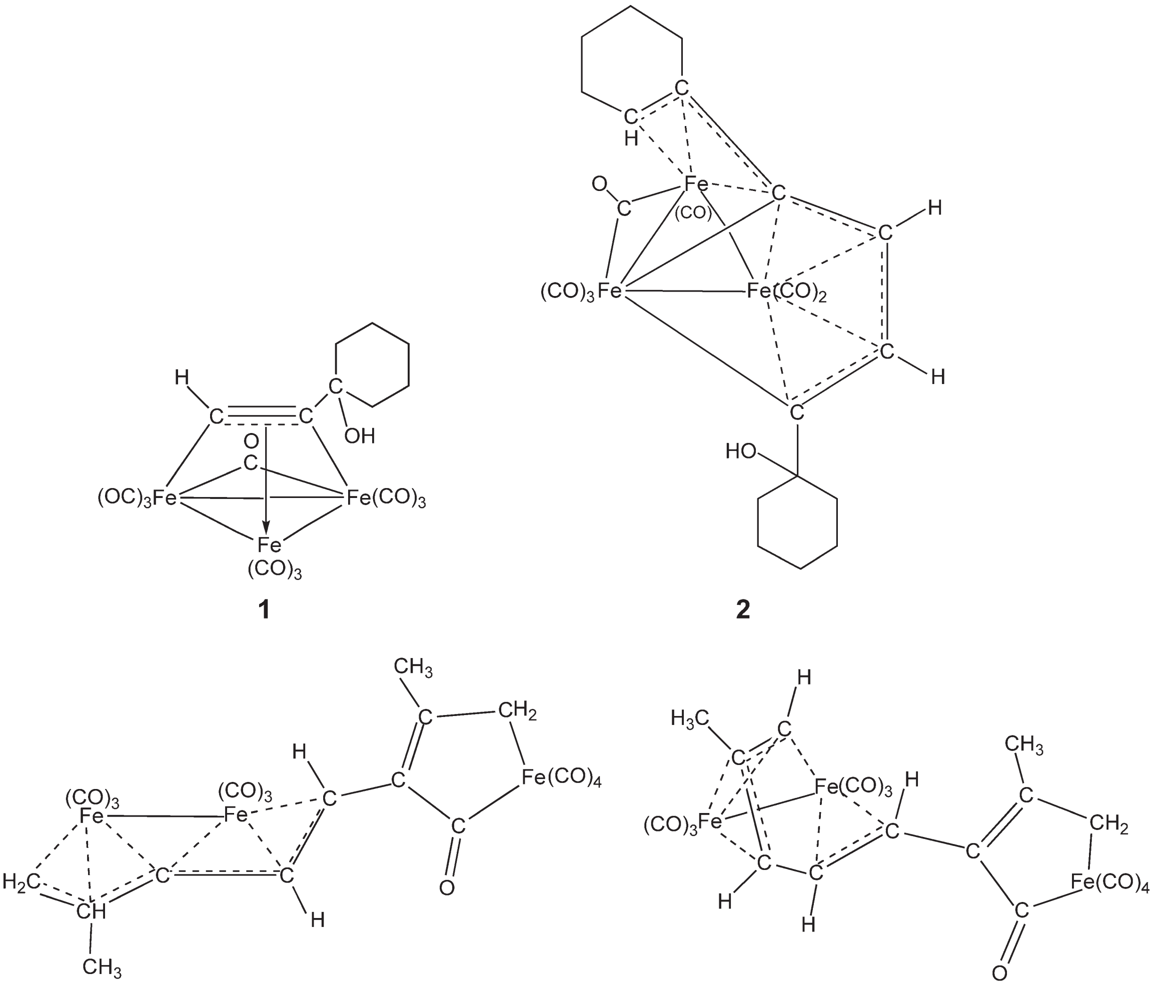
Triiron derivatives substituted with oxygen-containing acetylides or acetylenes have been reported for a long time, for example, by Shriver,[2,2a–2c] Wong[3] and their co-workers. Shriver's group, in particular, has performed the synthesis of ketenylidene derivatives starting from complexes containing parallel or perpendicular functionalized alkynes or acetylides. Complexes with μ_3-apical ligands have also been obtained by both groups.

Complexes with coordinated functionalized alkynes were obtained by Mathieu and co-workers[4] using an indirect reaction pathway: they reduced the methylidyne anion $[Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CMe)]^-$ and obtained the dianion $[Fe_3(CO)_9(MeC{\equiv}CO)]^{2-}$ bearing a "parallel" ligand.[5] This can be further reduced (with loss of OMe^-) to form a ketenylidene species. The two-electron reduction of the bis-methylidyne $Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}COC_2H_5)$ also leads to the allenyl anion $[Fe_3(CO)_9\{(C_2H_5O)\text{-}C{=}C{=}CCHCHC(O)CH_3\}]^-$.[6] A "direct" synthesis is represented by the reaction of $Fe_3(CO)_{11}(MeCN)$ with 1,4-dimethoxy-2-butyne to give the parallel $Fe_3(CO)_9(\mu\text{-}CO)(MeOCH_2C{\equiv}CCH_2OMe)$ and the perpendicular $Fe_3(CO)_9(MeOCH_2C{\equiv}CCH_2OMe)$.[7]

More recent examples of complexes obtained from alkynols are the triiron derivatives containing the intact alkyne (complex **1**) or a partially dehydrated alkyne dimer **2** isolated during the reactions of $Fe_3(CO)_{12}$ (and of $Co_2(CO)_8$) with 1-ethynylcyclohexanol.[8] Their structures were proposed on the basis of spectroscopic analyses.

6.09.2.1.2 Complexes obtained upon CO and methanol activation

Formation of alkyne dimers with a CO inserted was observed in the thermal reactions of $Fe_3(CO)_{12}$ with isopropenylacetylene; two isomeric open clusters **3a** and **3b** were isolated and characterized by X-ray diffraction.[9] In contrast, the thermal reactions of internal propargylic alcohols with $Fe_3(CO)_{12}$ led to pentanuclear acetylide derivatives, obtained upon elimination of aldehydes or chetones from the alkynes (Figure 1).[10]



1 **2**

3a **3b**

Figure 1

Formal insertion of CO_2 into Fe–C bonds is formed in the reaction of $Fe_3(CO)_{12}$ with hex-1-en-3-yne. The reaction consists in the splitting of water into its three components, favored by the "tlc" silica used for purification. The final product is, however, a binuclear complex.[11] Related to this behavior is the reaction of $Fe_3(CO)_{12}$ with 1-phenyl-2-propyn-1-ol where the allenylidene complex $Fe_3(CO)_9(\mu\text{-}CO)\{C{=}C{=}C(H)Ph\}$ **4** is obtained first. It reacts with methanol to form a ferrole-like methoxycarbonyl (or acetate) derivative.[12] It has been also observed that similar binuclear complexes can be obtained by reacting $Fe_3(CO)_{12}$ with propargyl alcohol or propargyl chloride in KOH/CH_3OH solutions followed by acidification with HCl; CO and methanol activation occurs in this instance to form binuclear methoxycarbonyl derivatives and the open cluster $Fe_3(CO)_{10}\{H_2CCC(H)C({=}O)C[CH_2(O)CH_3CCH_2]\}$ **5**.[13]

The stepwise formation of tropones upon insertion of CO into alkyne dimers coordinated to diiron centers is a commonly found process in iron carbonyl chemistry; no triiron complexes are isolated during these processes (e.g., see Refs: 14 and 14a). Finally, CO insertion is observed when diiron dimers linked by diacetylene moieties are reacted with diethylamine to give the complexes **6 and 7** (Figure 2); these complexes also contain iron–carbon–nitrogen and iron–carbon–phosphorus bonds.[15]

The reactions of acylferrate anion $[CH_3COFe(CO)_4]^-$ with methyl iodide and acetylenes have been reported to show that dinuclear alkenyl ketone iron complexes are formed.[16] The reactions of the anion $[Fe_3(CO)_9(\mu_3\text{-}Se)]^{2-}$ with $HC{\equiv}CCH_2Br$ lead first to a product with a CO inserted into an $Fe\text{-}CH_2CCH$ carbon chain; a further reaction with $MeOSO_3CF_3$ results in the addition of Me to the inserted CO.[17] The homologous anion $[(\mu_3\text{-}Te)Fe_3(CO)_9]^{2-}$ shows the same behavior; it reacts with propargyl bromide in MeCN forming complex **8**, a cluster with a CO inserted into an Fe–C bond: the latter reacts with CF_3SO_3Me to form the two isomers **9a and 9b** containing a *cis*- or *trans*-C-OMe group.[18] No Fe–Te–C bonds are found in these complexes. Finally, the complexes $[Et_4N]_2[Fe_3(CO)_9E]$ ($E = S$, Se, Te) catalyze the carbonylation of methanol to methyl formate;[19] a full catalytic cycle that involves the dianionic intermediates **10, 11** has been proposed (Figure 3).

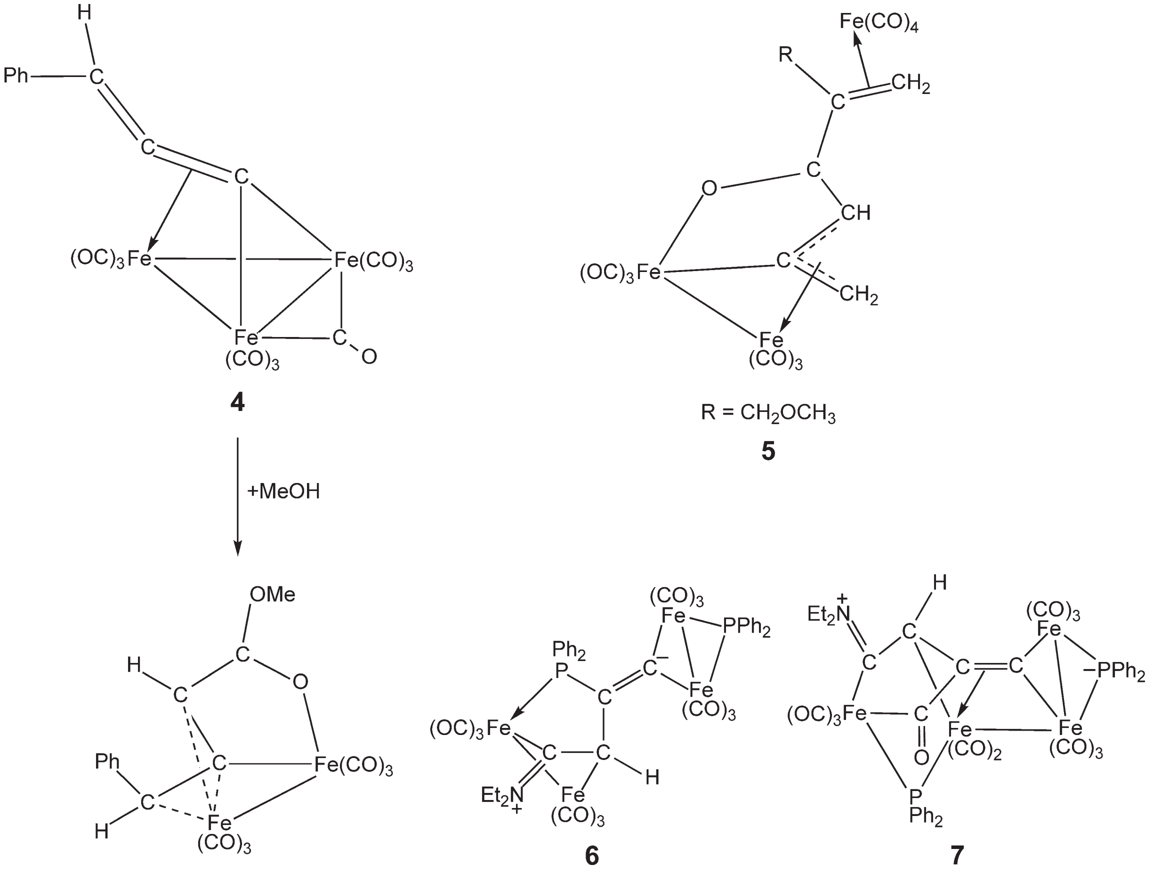
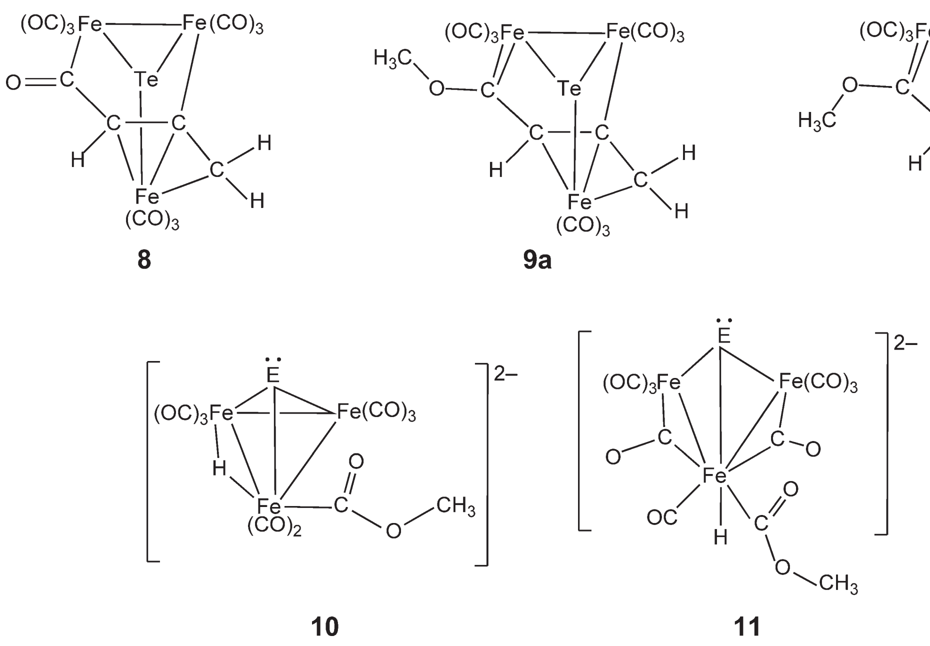


Figure 2



8 **9a** **9b**

10 **11**

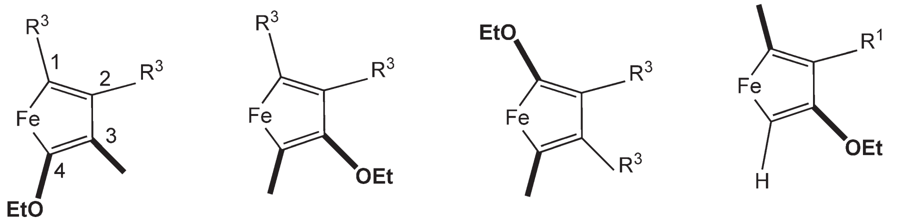
Figure 3

6.09.2.1.3 Pentagonal bipyramidal complexes

This family of triiron derivatives showing characteristic structures has been known for a long time; they were initially obtained from non-functionalized alkynes (e.g., see Refs: 20 and 20a). These structures are also common for triiron complexes containing nitrogen-, sulfur-, and phosphorus-based ligands, as discussed below. However, a good number of these are formed by oxygen-containing acetylides or acetylenes, or by oxygen-containing bis-methylidyne derivatives. Lentz,[21] Mathieu,[22,22a,22b] and their co-workers, in particular, have obtained several complexes showing this structural pattern.

Although not all mechanisms of the above reactions have been determined, there are several examples involving the intermediacy of mono- or mainly of bis-methylidyne trinuclear derivatives. A recent example of this kind of complex is the bicapped triiron acetate complex $Fe_3(CO)_9(\mu_3\text{-CH})\{\mu_3\text{-CC(=O)OCH}_3\}$ **12**; it is obtained from an acetylenic ligand already containing the acetate group.[23] The interaction of similar complexes with alkynes or related ligands leads to isomeric pentagonal bipyramidal derivatives depending on the substitution of the metalla-cyclopentadienyl ring **a–d**.[22b] In addition, the bis-methylidyne capped $Fe_3(CO)_9(\mu_3\text{-CCH}_3)$ $(\mu_3\text{-COC}_2H_5)$ **13** reacts with $Bu^tC\equiv CP$, yielding three pentagonal bipyramidal phosphaferrole derivatives $Fe_3(CO)_6(\mu\text{-CO})_2\{C(OMe)C(OEt)(P)CBu^t\}$ showing the same isomerism as above.[21] The isomerism is due to the different position of the P atom in the phosphaferrole ring with respect to the positions of the other (oxygenated) substituents.

Other recent examples are the reactions of 2-methyl-3-butyn-2-ol with $Fe_3(CO)_{12}$ which afforded, among others, a triiron complex containing a partially dehydrated alkyne dimer **14**[24] and the related pentagonal bipyramidal complex **15** with nitrogen-containing ligands (Figure 4).

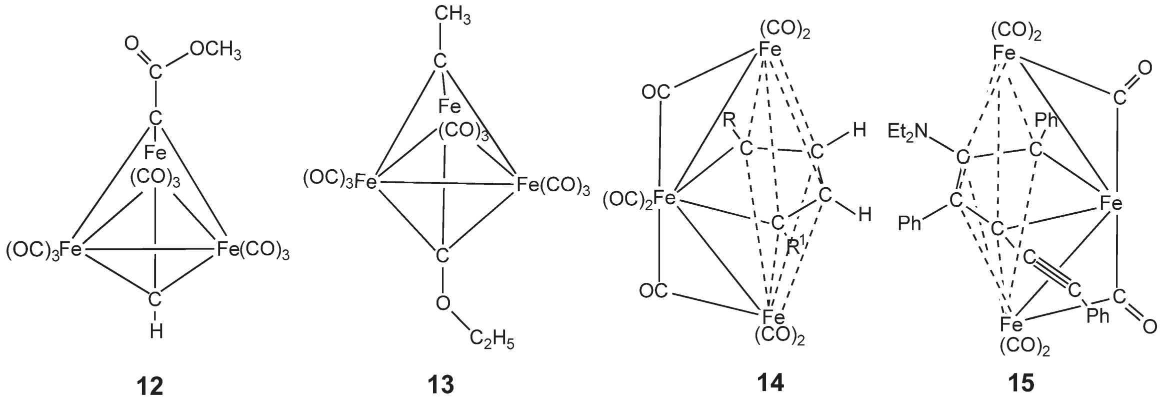


a: R^3 = Ph

b: R^3 = TMS

c: R^3 = H
R^3 = Me

d: etc.
1-alkyne



12 **13** **14** **15**

$R = C(Me)_2OH$

$R^1 = C(Me){=}CH_2$

Figure 4

Electrochemical studies on pentagonal bipyramidal structures (not containing heteroatoms) have been performed.[25] A discussion of the poly- and binuclear pentagonal bipyramidal structures and their isolobal relationships has been given in Ref: 20a. These types of structures have also been found (although less frequently) for ruthenium and osmium.

6.09.2.2 Iron Complexes Bound through Carbon and Sulfur

As previously pointed out, for sulfur-containing iron complexes too, the number of binuclear derivatives is much greater than that of the triiron derivatives (see Section 6.2.n). An interesting group of diiron disulfur complexes has been synthesized and their reactivity explored in a study of the models of the active center of the Fe-only hydrogenases (see, e.g., Refs: 26 and 26a–26e).

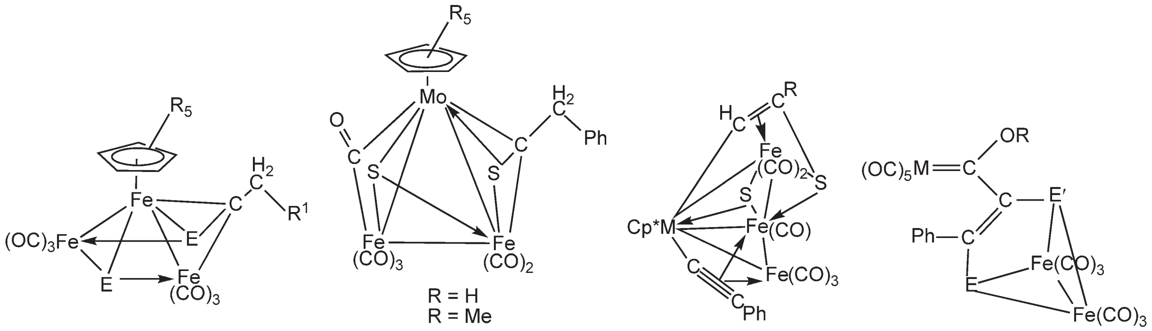
6.09.2.2.1 Reactivity of triiron complexes containing capping chalcogens (and related complexes)

The reactivity of the open, capped $Fe_3(CO)_9(\mu_3\text{-}S)_2$ has been extensively studied by Mathur and co-workers. The complex reacts with $Cp^*Fe(CO)_2(C{\equiv}CR)$ forming the open clusters $Cp^*Fe_3(CO)_6(\mu_3\text{-}E)(\mu_3\text{-}ECCH_2R)$ (**16**, R = Ph,Fc, E = S,Se)[27] and with alkynes and carbynic complexes of molybdenum and tungsten, forming the heterometallic closed $Cp^*MoFe_2(CO)_6(\mu\text{-}CO)(\mu_3\text{-}S)(SCCH_2Ph)$ **17** and open $Cp^*MFe_3(\mu_3\text{-}S)(CO)_6\{\mu_3\text{-}C(H){\equiv}C(R)S\}(\mu_3\text{-}CCPh)$ (**18**, M = Mo, W, R = Ph, Bu^n) clusters.[28] In more forcing conditions, however, polynuclear heterometallic clusters, where the alkynes are not bound through sulfur, are obtained.[29] The same happens for the homolog containing selenium.[30,30a] However, the open derivatives $Fe_2(CO)_6\{EC(Ph){\equiv}C(E)C(OR)M(CO)_4\}$ (**19**, M = Cr,W, E = Se,Te) (Figure 5) have also been synthesized.[31]

More recently, complexes **20** (M = Fe, Ru) (Figure 6) have been obtained[32] from the reactions of ferrocenyl–chalcogeno–propargyl derivatives with the $Fe_3(CO)_9E_2$ clusters (E = S, Se).The reactions of $Fe_3(CO)_9Se_2$ with ferrocene-1,1′-bis(diphenylphosphine selenide) ($dppfSe_2$) have been reported as well.[33] However, only Fe–P–C bonds are observed in these derivatives. A review on selenium- and tellurium-containing iron carbonyl clusters has appeared in the literature.[34]

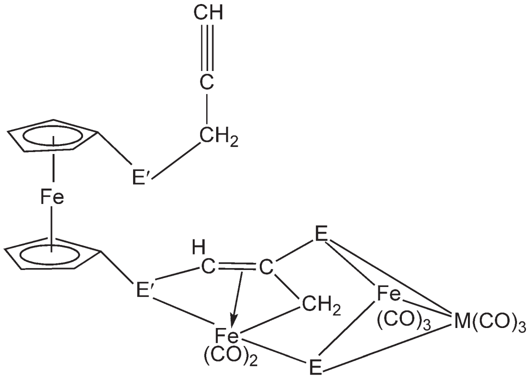
The clusters $Fe_3(CO)_9(\mu_3\text{-}E)_2$ (E = S, Se, Te) have been reacted under various conditions (see, e.g., Refs: 35 and 35a–35c); fragmentation to binuclear complexes which can dimerize (and, in some instances, form E–C bonds) has been usually observed. Diiron complexes containing both C–S and C–N bonds have also been reported (e.g., see Ref: 36, 36a, and 36b). Finally, the trinuclear clusters $Fe_3(CO)_8(\mu\text{-}CO)(\mu_3\text{-}S)(PPh_2C{\equiv}CR)$ and $Fe_3(CO)_8(\mu_3\text{-}S)_2(PPh_2C{\equiv}CR)$ (R = Pr^i, Bu^t) have been reported;[37] these, however, do not contain C–S bonds. Last, but not least, the cluster $Fe_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)$ reacts with alkynes forming diiron derivatives, through the proposed intermediacy of the triiron complexes **21** and **22** (Figure 7) containing both P–C and S–C bonds.[38]

The heterometallic derivative $Fe_2(CO)_6(Se)_2\{\mu\text{-}HCC(CCMe)\}Os_3(CO)_{10}$ and its ruthenium homolog $Fe_2(CO)_6(Se)_2\{\mu\text{-}HCC(CCMe)\}Ru_3(CO)_{10}$ both contain an alkyne bound in parallel fashion to the trinuclear cluster and also show Se–C bonds.[39]



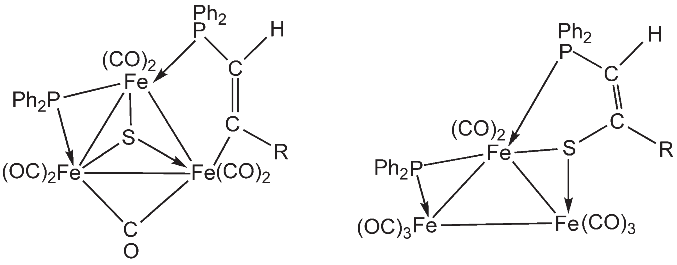
16 **17** **18** **19**

Figure 5



20

Figure 6



21 **22**

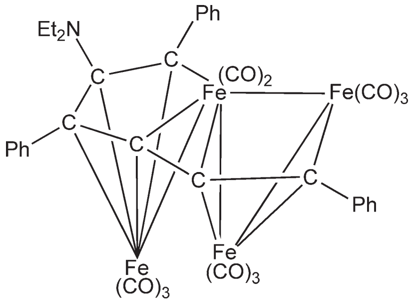
Figure 7

An interesting series of derivatives containing Fe–S–C bonds are the starlike anionic and neutral complexes obtained from $Fe_3(CO)_{12}$ and the ligand $N(CH_2CH_2SH)_3$; these are formed by three diiron complexes linked through the SCH_2CH_2 chains to the nitrogen atom.[40]

6.09.3 Group 15 Ligands

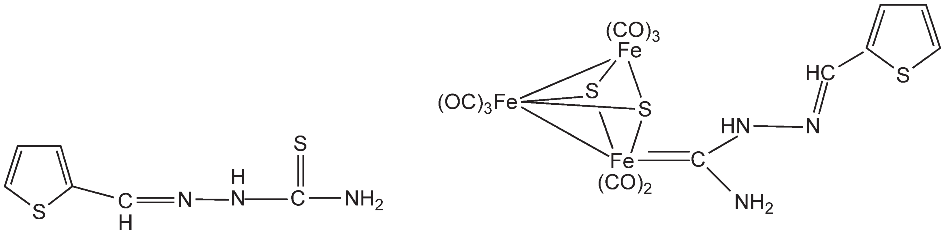
6.09.3.1 Complexes Bound through Carbon and Nitrogen

Vahrenkamp and co-workers have reported on several iron-containing heterometallic complexes with CN bridges;[41] these compounds, however, belong to the class of coordination compounds. The reader is referred to *Comprehensive*



23

Figure 8



a

24

Figure 9

Coordination Chemistry. The synthesis and reactivity of the complexes $Fe_2Ru(CO)_{12-n}(CNBu^t)_n$ and $FeRu_2(CO)_{12-n}(CNBu^t)_2$ have also been reported.[42]

Several diiron complexes containing C–N bonds have been obtained when reacting $Fe_2(CO)_9$ with 2-[2,3-diaza-4-(2-thienyl)buta-1,3-dienyl]thiophene,[43] *N*-(2-thienylmethylidene)-2-thienyl-methylamine,[44] terephthal-bis-imines,[45] naphthyl-imines,[46] and 2-oxo-2-methylethanamine[47](see Section 6.2). In contrast a small number of triiron derivatives is known, one of which is the pentagonal bipyramidal complex $Fe_3(CO)_6(\mu\text{-}CO)_2\{(HC{\equiv}CCMe_2)_2NH\}$.[48] From the reactions of diphenylbuta-1,4-diyne and $Fe_2(CO)_7\{C(Ph)C(NEt_2)\}$, another pentagonal bipyramidal complex **15** has been obtained[49] along with the tetrairon derivative **23** (Figure 8). Finally, another trinuclear example is $Fe_3(CO)_8(\mu_3\text{-}S)_2\{C(NH_2)NHNCH(2\text{-}C_4H_3S)\}$ **24** obtained from $Fe_2(CO)_9$ and thiophene-2-carboxaldehyde thiosemicarbazone (ligand **a**). (Figure 9)[50]

6.09.3.1.1 Complexes with apical ligands

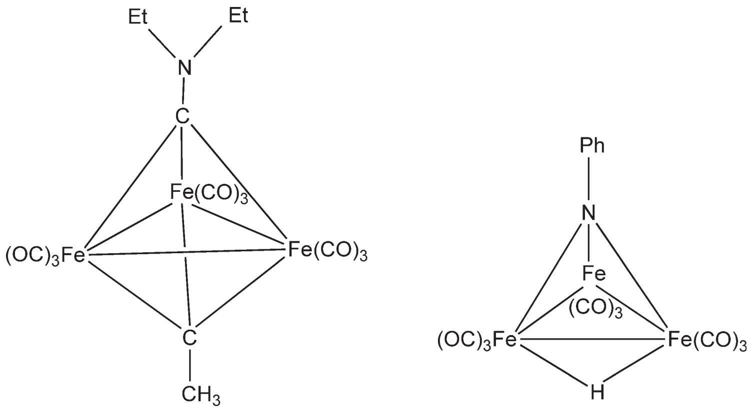
Starting from $Fe_2(CO)_9$ and $MeC{\equiv}CNEt_2$, the bicapped complex $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}CNEt_2)$ **25** was obtained.[51] More recently, the anions $[Fe_3(CO)_9(\mu_3\text{-}NPh)]^{2-}$ and $[HFe_3(CO)_9(\mu_3\text{-}NPh)]^{-}$ **26** have been synthesized and their X-ray structures determined; these anions promote radical processes in the reduction of nitrobenzene (Figure 10).[52]

6.09.3.2 Triiron Complexes Bound through Carbon and Phosphorus

A considerable number of bimetallic iron complexes containing phosphorus exist; again, the triiron derivatives are less frequent. For example, several dialkylaminophosphorus diiron carbonyls have been synthesized (see Ref: 53 and 54) and tested in homogeneous catalysis.[55]

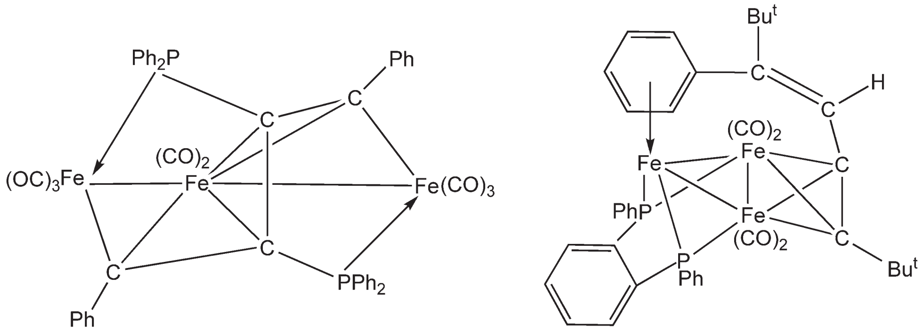
6.09.3.2.1 Complexes obtained through metal fragment condensation

The reactivity of $Fe_2(CO)_6(\mu\text{-}PPh_2)(C{\equiv}CR)$ complexes and of their homologs with coordinated vinylidenes or allenylidenes has been extensively studied.[56,56a,56b] Again, diiron complexes (containing C–P bonds) are obtained. However, in some instances, the parent binuclear derivatives may lead to polynuclear complexes. Thus, for example, the open cluster $Fe_3(CO)_8\{PhCC(PPh_2)C(PPh_2)CPh\}$ **27** is obtained from $Fe_2(CO)_6(PPh_2)(C{\equiv}CPh)$ under thermal



25 **26**

Figure 10



27 **28**

Figure 11

conditions and through the intermediacy of $Fe_4(CO)_9(PPh_2)_2(C{\equiv}CPh)_2$, a square-planar cluster in which the two acetylides are apparently linked by a long C–C bond passing through the cluster plane.[57,57a] Under thermal conditions, $Fe_2(CO)_5(PPh_3)(PPh_2)(C{\equiv}CBu^t)$ yields, among other products, the closed cluster $Fe_3(CO)_4\{PhP(C_6H_4)PPh\}\{Bu^tCCC(H){=}C(Bu^t)Ph\}$ **28** (Figure 11).[58]

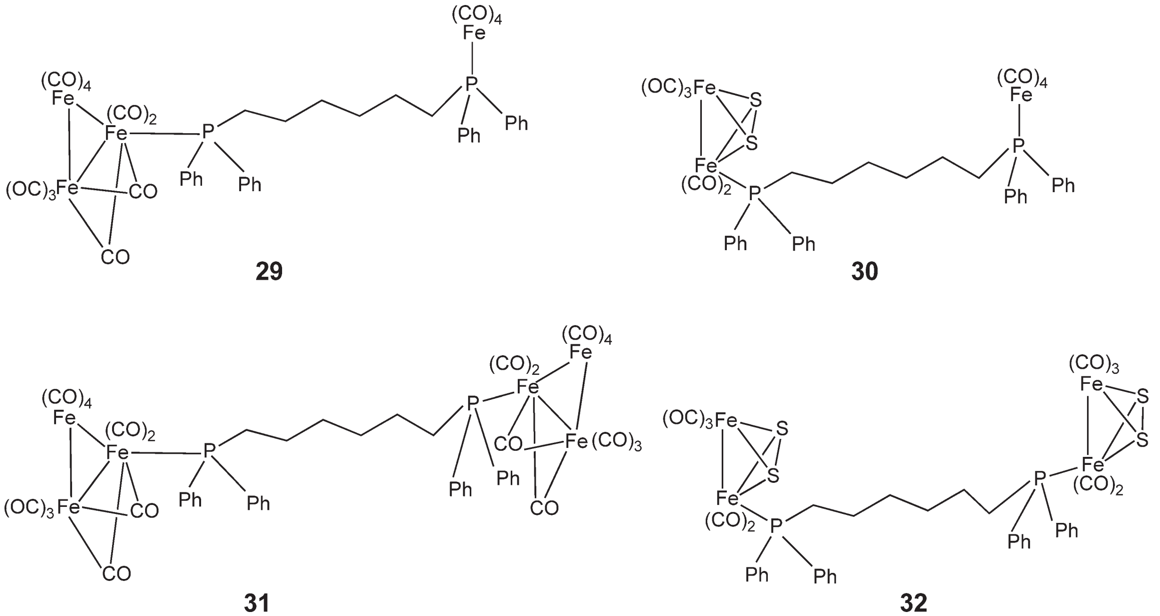
6.09.3.2.2 Bis(diphenylphosphino) alkynes as bridging ligands

Bis(diphenylphosphino) acetylene (DBPA) and bis(diphenylphosphino) butadiyne (DDPB) may bridge trinuclear clusters of several metals (including iron) using the phosphorus atoms. Complexes with BDPA and BDPB are discussed in Refs: 59 and 59a–59c. A relatively recent example of open tri- and tetra-iron clusters kept together by $Ph_2P(CH_2)_nPPh_2$ bridges is represented by complexes **29–32** (Figure 12) (also containing sulfur).[60]

6.09.3.2.3 Miscellaneous complexes

As already mentioned in Section 6.03.1.1.1, isomeric triiron clusters containing P–C bonds are also obtained from bis-methylidyne complexes such as $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ with $Bu^tC{\equiv}P$.[21] Phosphorus–carbon coupling on triiron cores has also been observed: examples are $[Fe_3(CO)_9\{(PPh_2)C{=}CH_2\}]^-$ **33** obtained from $[HFe_3(CO)_{11}]^-$ together with the open cluster $\{Fe(CO)_4\}(PPh_2)CC(H)C(OMe)C\{Fe_2(CO)_6\}$ **34** derived from $Ph_2PC{\equiv}CC(O)OMe$[61]

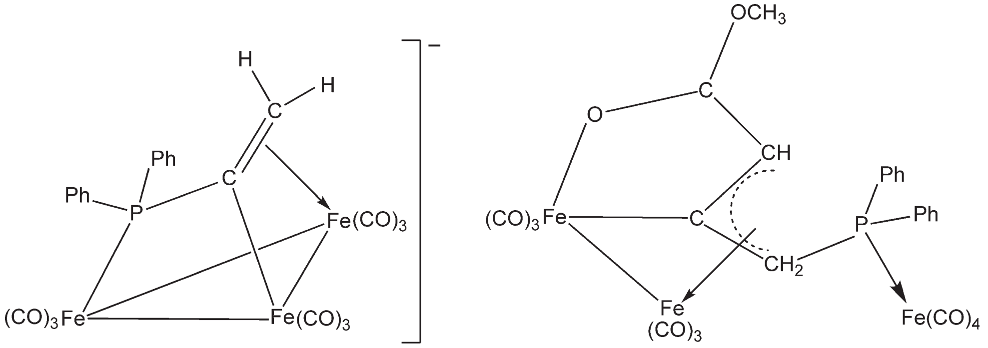
Open clusters such as $Fe_3(CO)_9(\mu_3\text{-}PR)_2$ have also been obtained.[62] The derivative with $R = H$, $R' = Me$ forms the anionic dimer $[\{Fe_3(CO)_9(\mu_3\text{-}PMe)(\mu_3\text{-}P)\}_2Au]^-$.[63] Finally, the complexes $Fe_3(CO)_9(\mu_3\text{-}P\text{-}p\text{-}C_6H_4X)(\mu_3\text{-}P\text{-}p\text{-}C_6H_4X')$ ($X = CN$, NMe_2, $X' = NMe_2$) have been studied under the electrochemical profile as models of the communication between the cluster surface and the $Fe_3(CO)_9$ core (Figure 13).[64]



29 **30**

31 **32**

Figure 12



33 **34**

Figure 13

6.09.4 Concluding Remarks

In the last ten years, developments in the chemistry of iron clusters, and in particular the triiron derivatives, has been much less when compared with the previous decades. That may be due to the following reasons: (i) It has been known for long that polynuclear iron carbonyls undergo fragmentation more easily than the heavier elements of the triad, so the final products of the reactions are mostly binuclear complexes. (ii) Triiron carbonyls show a lesser tendency to form hydridic complexes with respect to ruthenium and osmium; these are particularly important in catalysis. (iii) In recent times fewer attempts at using clusters in homogeneous catalysis have been reported: this may be due to the difficult release of the organic products especially in the case of iron. (iv) It is also possible that oxygenated compounds (and, to a lesser extent, sulfur-containing compounds) oxidize iron (or form iron sulfides) instead of forming organometallic compounds. In the author's opinion, however, there are some signals for a revival of the triiron cluster chemistry.

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6.10
Heterometallic Iron-containing Compounds

W-T Wong, The University of Hong Kong, Hong Kong, People's Republic of China

6.10.1 Introduction

Heteronuclear compounds with an Fe–M bond have received much attention in the past decade. Significant progress has been made both in their synthetic methodologies and in the study of their chemical reactivity. There are more than 300 papers that have reported on the chemistry of this class of compounds, and more than 700 structurally characterized mixed-metal compounds that contain iron have appeared since this area was reviewed in COMC (1995). Clearly, this volume of data and information should be best presented in a systematic way, for which a tabulated form is preferable. All of the heterodinuclear species and mixed-metal clusters with known structures are therefore presented in Tables 1–3 respectively.

This review is intended to highlight any new reaction types that have been discovered, novel structural features that have been encountered, and chemical patterns and principles that have been observed for this class of compounds. Due to space limitations, only very selective examples of reactions are presented. Heterobimetallic species have been prepared and characterized for most combinations of iron and other transition metals. Their potential in the cooperative activation of small molecules, such as CO and unsaturated hydrocarbons, is an important research focus for this class of compounds. For mixed-metal clusters, enormous efforts have been made to develop rational cluster build-up methods and their potential applications in catalysis. Some important reviews that are pertinent to this type of species have appeared in the literature.[1–3]

6.10.2 Dinuclear Compounds

The formation of an Fe–M dative bond in ferrocene-containing compounds was reported for the first time in 1983 by Seyferth *et al.*[4] Since then, a number of related compounds that contain late transition metals have been synthesized and characterized. However, the use of a ferrocene group to stabilize an electron-deficient early transition metal center with an Fe–M dative bond was achieved only recently by Arnold *et al.* The Ti complex **1** supported by a ligand that is based on 1,1′-diaminoferrocene reacted with $B(C_6F_5)_3$ in pentane to give a dark red product **2** in 64% yield. A similar reaction of **1** with more bulky Lewis acid $[Ph_3C][B(C_6F_5)_4]$ gave compound **3**, which was found to extract a chloride from dichloromethane solvent to form a dimeric product **4**. X-ray analysis of **2** and **4** revealed Fe–Ti distances of 3.07 and 2.49 Å, respectively.[5,7]

A systematic study of the Ti and Zr complexes with tripodal amido ligands showed that they are good building blocks for stable bimetallic complexes that contain polar metal–metal bonds. A representative example of this class of compound is the Fe–Ti mixed-metal complex **5**.[8,10] The Fe–Ti distance for this unsupported metal–metal bond is 2.433 Å, which is comparable to that in the supported system **4**.

Iron–zirconium mixed-metal complexes have also been studied, although they are rather rare. The reaction of $[Fe(CO)_5]$ with $[Zr(NMe_2)_4]_2$ yielded the multicarbene complex **6** that contains three Fe and two Zr centers. The insertion of five CO groups into Zr–N bonds to give chelating biscarbene ligands and one terminal carbene ligand has been observed.[12]

Table 1 Heterodinuclear iron-containing compounds with known structure

	References
Fe—Group 4	
$[FeTi\{\eta^3\text{-}N,N',N''–CH_3[SiMe_2N(p\text{-}MeC_6H_4)]_3\}(CO)_2Cp]$	6
$[FeTi\{\eta^3\text{-}N,N',N''–CH_3C(CH_2NSiMe_3)_3\}(CO)_2Cp]$	8
$[FeTi\{\eta^3\text{-}N,N',N''–CH(SiMe_2NTol^p)_3\}(CO)_2Cp]$	9
$[FeTi\{\eta^3\text{-}N,N',N''–SiMe(SiMe_2NTol^p)_3\}(CO)_2Cp]$	10
$[FeZr(\eta^2\text{-}SiMe_3NCH_2CH_2CH_2NSiMe_3)(CO)_2Cp_2]$	11
$[FeZr\{SiMe(SiMe_2NTol^p)_3(CO)_2Cp\}]$	6,10
Fe—Group 5	
$[FeNb(\mu\text{-}CO)_2(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2Cp]$	14
$[FeNb(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_3Cp_2]$	13
$[FeTa(\mu\text{-}As_5)(\eta^5\text{-}1,3\text{-}C_5H_3Bu^t{}_2)Cp^*]$	15
$[FeTa\{\mu\text{-}P(P{=}P)_2\}(\eta^5\text{-}1,3\text{-}C_5H_3Bu^t{}_2)Cp^*]$	16
$[FeTa(\mu\text{-}\eta^2\text{-}C{\equiv}CMe)(\mu\text{-}CO)(CO)_3Cp_2]$	17
Fe—Group 6	
$[FeCr(NO)(\mu\text{-}CO)_2(CO)(\eta^5\text{-}C_5H_4Me)Cp][PPh_3Me]$	18
$[FeCr(\mu\text{-}SiMe_2)(\mu\text{-}\eta^6\text{-}C_6H_5SiMe_2)(CO)_3Cp^*]$	19
$[FeCr(\mu\text{-}\eta^5,\eta^3\text{-}C_8H_8)(CO)_3Cp^*]$	22
$[FeCr(\mu\text{-}\eta^5,\eta^3\text{-}C_8H_8)\{P(OEt)_3\}(CO)_2Cp^*]$	22
$[FeCr(\mu\text{-}\eta^5,\eta^3\text{-}cy\text{-}C_8H_8)(PMe_3)(CO)_2Cp^*]$	22
$[FeCr(\mu\text{-}\eta^5,\eta^3\text{-}C_8H_8)(CO)_3Cp]$	23
$[FeMo(\mu\text{-}3\text{-}Bu^t\text{-}1,2,4\text{-}P_3C)(\mu\text{-}P_2)(\eta^5\text{-}1,2,4\text{-}C_5H_2Bu^t{}_3)Cp^*]$	24
$[FeMo(\mu\text{-}2,3\text{-}Ph_2\text{-}1,4\text{-}C_2P_2)(\mu\text{-}P_2)Cp^*{}_2]$	24
$[FeMo\{\mu\text{-}\eta^2\text{-}(2,4,6\text{-}Bu^t{}_3C_6H_2O)P(CH{=}CHPh)(CH{=}CHPh)\}(CO)_5Cp]$	26
$[FeMo(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_5CpCp^*]$	27
$[FeMo\{\mu\text{-}2\text{-}(PPhEt)C_5H_4N\}_2(CO)_6]$	28
$[FeMo(\mu\text{-}PPh_2)(CO)_7]$	29
$[FeMo(\mu\text{-}PPh_2)\{P(OMe)_3\}(CO)_5Cp]$	30
$[FeMo(\mu\text{-}\eta^4\text{-}P_4)(\mu\text{-}\eta^2\text{-}\eta^2\text{-}P_2)Cp^*{}_2]$	31
$[FeMo(H)(B_5H_7)(PPhMe_2)_3Cp]$	32
$[FeMo\{\mu_2\text{-}(Pr^i{}_2NPO)_4\}(CO)_7]$	33
$[FeW(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5Cp]$	35
$[FeW(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_3H_4)(CO)_3Cp_2]$	36
$[FeW(\mu\text{-}S)_2(\mu\text{-}Me_2PCH_2CH_2S)(S)Cl_2][PPh_4]$	37
$[FeW(\mu\text{-}SiHCHPh_2)(\mu\text{-}CO)(CO)_3CpCp^*]$	38
$[FeW(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(N{=}O)(\mu\text{-}CO)(CO)Cp_2]$	39
$[FeW(\mu\text{-}PPh_2)(PPh_3)(CO)_5Cp]$	40
$[FeW(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5Cp]$	40
$[FeW(\mu\text{-}PPh_2)(PPh_2H)(CO)_5Cp]$	41
$[FeW\{\mu\text{-}PPhN(SiMe_3)_2\}(\mu\text{-}CO)(CO)_5Cp]$	42
$[FeW(\mu\text{-}CPh)(CO)_6Cp]$	43
Fe—Group 7	
$[FeMn(\mu\text{-}SEt)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_3Me)Cp]$	44
$[FeMn\{\mu\text{-}\eta^2,\eta^2,\eta^2\text{-}C_7H_7C(OEt)(Tol^o)\}(CO)_6]$	45
$[FeMn(\mu\text{-}\alpha\text{-}PhSeCPh)(CO)_5Cp]$	46
$[FeMn(\mu\text{-}\eta^2,\sigma^1\text{-}CHCMeCOBu)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_4Me)Cp]$	47
$[FeMn\{\mu\text{-}\eta^2,\eta^2,\eta^2\text{-}C_7H_7C(Ph)(OEt)\}(CO)_6]$	48
$[FeMn(\mu\text{-}CPh)(NO)(CO)_4Cp]$	49
$[FeMn\{\mu\text{-}PhC(SBu)\}(CO)_5Cp]$	50
$[FeMn\{\mu\text{-}PhC(SPh)\}(CO)_5Cp]$	50
$[FeMn\{\mu\text{-}\eta^2\text{-}CHC_6H_5\}(CO)_5Cp]$	51
$[FeMn(\mu\text{-}COEt)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_4Me)Cp]$	52
$[FeMn(\mu\text{-}\eta^5,\eta^4\text{-}C_9H_7)(CO)_5]$	53
$[FeMn\{\mu\text{-}PhCC(Et)(O)\}(CO)_5Cp]$	54
$[FeRe\{\mu\text{-}\eta^2,\eta^2,\eta^2\text{-}C_7H_7C(OEt)(p\text{-}C_6H_4CF_3)\}(CO)_6]$	45
$[FeRe(\mu\text{-}CHPh)(CO)_6Cp]$	55
$[FeRe\{\mu\text{-}PhC(SePh)\}(CO)_5Cp]$	46
$[FeRe\{\mu\text{-}PhC(SeEt)\}(CO)_5Cp]$	46

(*Continued*)

Table 1 (Continued)

	References
[FeRe(μ-dppm){Si(OMe)$_3$}(CO)$_7$]	57
[FeRe(μ-dppm)(μ-Br)(CO)$_6$]	57
[FeRe{μ-PhC(SBu)}(CO)$_5$Cp]	50
[FeRe(μ-CHPh)(PPh$_3$)(CO)$_5$Cp]	51
[FeRe{μ-η^4-C$_4$(COOMe)$_4$}(CO)$_4$Cp]	58
[FeRe(μ-CPh){μ-η^2-CO(C$_2$B$_{10}$H$_{10}$)}(μ-CO)(CO)$_3$Cp]	59
[FeRe(μ-C$_{15}$H$_{13}$NO$_5$S)(μ-CO)(CO)$_4$Cp]	60
Fe—Group 8	
[FeRu(C$\equiv$NBu^t)$_2$(SiCl$_3$)$_2$(CO)$_6$]	61
[FeRu(η^5-7,8-C$_2$B$_9$H$_{11}$)(μ-CO)$_2$(CO)$_2$Cp][K(18-crown-6)]	65
[FeRu(μ-η^3-Ph(CH)$_3$NHPr^i)(CO)$_6$]	66
[FeRu(μ-η^2-PhCCHCHNPr^i)(μ-H)(CO)$_6$]	66
[FeRu{μ-η^3-C,O-(COOMe)$_2$(OMe)C$_3$H}(CO)$_6$]	67
[FeRu{μ-η^3-C,O-(COOMe)$_2$(OMe)C$_3$H}(PPh$_3$)(CO)$_5$]	67
[FeRu(μ-SCPhCPhS)$_2$(SCPhCPhS){η^5-C$_5$H$_4$SiMe$_3$}]	68
[FeRu(μ_2-η^2,η^2,σ^1-C$_3$H$_2$PhCO)(CO)$_4$Cp]	69
[FeRu{μ_2-σ^2,η^2-PhC=CHCH=NPr^i}(μ-CO)(CO)$_3$Cp]	70
[FeRu(μ_2-σ^2,η^2-N,N′-Py-2-CH=NPr^i)(CO)$_6$]	71
[FeRu(μ_2-σ^2,η^3-4-C$_4$H$_4$NPr^i)(CO)$_6$]	72
[FeRu{η^5-2,4-C$_5$H$_5$(Me)$_2$}(μ-CO)$_2$(CO)$_2$Cp*]	73
[FeRu(μ-PBu$^t{}_2$)$_2$(CO)$_5$]	74
[FeRu{μ-η^2-C(CO$_2$Me)=C(CO$_2$Me)C(O)}(Pr^{i}N=CHPy)(CO)$_5$]	315
Fe—Group 9	
[FeCo{μ-η^3,η^2-(Me)$_2$C=C=C(SiMe$_2$F)}(CO)$_6$]	77
[FeCo(μ-η^3,σ^2-H$_2$C=C=CMe)(PPh$_3$)(CO)$_5$]	78
[FeCo{HB(3,5-Pr$^i{}_2$C$_3$HN$_2$)$_3$}](CO)$_4$]	79
[FeCo(μ-CO)$_2$(CO)$_4$Cp*]	80
[FeCo(CO)$_3$(B$_3$H$_7$)Cp*]	81
[FeCo(μ-η^2-PhC=CHCOPPh$_2$){P(OMe)$_3$}(μ-CO)(CO)$_4$]	82
[FeCo{μ-η^2-(MeOOC)C=C(COOMe)PPh$_2$}(PPhMe$_2$)(CO)$_5$]	82
[FeCo{μ-η^2-(MeOOC)HC=C(COOMe)PPh$_2$}(μ-PPh$_2$)(CO)$_5$]	82
[FeCo(μ-CO)(CO)$_7$][PPN]	83
[FeCo{μ-η^3,η^2-(C$_{12}$H$_8$)C=CSiMe$_3$}(CO)$_6$]	84
[FeCo{(μ-η^3,η^2-C$_8$H$_4$Ph$_2$)C=CSiMe$_3$}(CO)$_6$]	84
[FeCo(μ-H)(μ-B$_4$H$_7$)(CO)$_3$Cp*]	85
[FeRh(PPh$_3$)(μ-CO)$_2$(CO)$_3$(η^5-C$_5$H$_4$SiMe$_2$C$_5$HMe$_4$)]	86
[FeRh(μ-dppm)I$_2$(μ-CO)$_2$Cp]	87
[FeRh(μ-dppm)(μ-PBu$^t{}_2$)(μ-CO)(CO)$_3$]	88
[FeRh(μ-PBu$^t{}_2$)(CO)$_6$]	89
[FeRh(μ-dppm)(μ-CO)$_2$Cl$_2$(η^5-C$_5$H$_4$Me)]	90
[FeRh(PMe$_3$)$_3$(μ-CO)$_2$Cp]	91
[FeIr(μ-PBu$^t{}_2$)(PHBu$^t{}_2$)(μ-CO)(CO)$_4$]	93
[FeIr{B$_5$H$_4$(PPh$_3$)}(PPh$_3$)(CO)$_5$]	94
[FeIr(B$_2$H$_5$)(PPh$_3$)$_2$(CO)$_4$]	95
[FeIr(PMe$_3$)$_4$(μ-CO)$_2$Cp]	91
[FeIr(μ_3-Se)$_2$Cl$_2$Cp$^*_2$]	96
Fe—Group 10	
[FeNi(η^5-C$_5$H$_4$S)$_2$(PPhMe$_2$)]	97
[FeNi(μ-dppm){μ-Si(OMe)$_3$}(CH$_3$)(CO)$_3$]	98
[FeNi{η^2-N,N′-(PhCH=CHCH=N)$_2$(CH$_2$)$_3$}(μ-CO)$_2$(CO)$_3$]	99
[FePd{μ-2-(PPh$_2$)C$_5$H$_4$N}(CH$_2$=CH=CH$_2$){SiMe(OSiMe$_3$)$_2$}(CO)$_3$]	104
[FePd{μ-η^5-(C$_5$H$_4$)PPh$_2$}$_2$(PPh$_3$)][BF$_4$]$_2$	105
[FePd(μ-dppa){μ-Si(OMe)$_3$}Cl(CO)$_3$]	106
[FePd(μ-dppa){μ-Si(OMe)$_3$}Ph(CO)$_3$]	106
[FePd(μ-dppm)(C$_{10}$H$_8$N){Si(OMe)$_3$}(CO)$_3$]	106
[FePd(μ-η^3,η^2-C$_7$H$_7$)(CO)$_3$Cp]	108

(Continued)

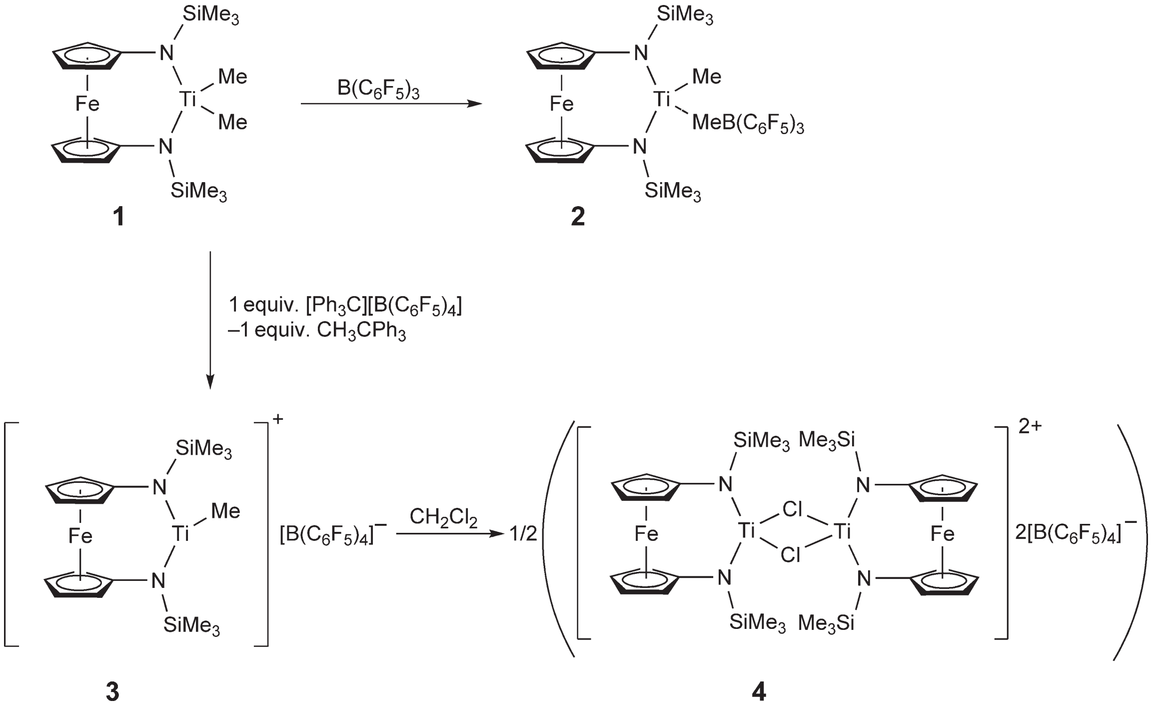
Table 1 (Continued)

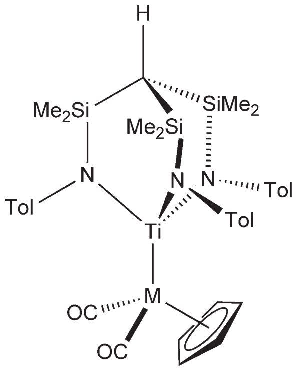
	References
$[FePd(\mu\text{-dppa})\{Si(OMe)_3\}(C_{11}H_{12}NO_4)(CO)_3]$	109
$[FePd\{\mu\text{-}\eta^5\text{-}S(CH_2CH_2CH_2S\text{-}C_5H_4)_2\}][BF_4]_2$	110
$[FePd\{\mu\text{-}\eta^5\text{-}S(CH_2CH_2CH_2S\text{-}C_5H_4)_2\}(NCMe)][BF_4]_2$	110
$[FePd(\mu\text{-dppm})(CH_3)Cl(CO)_4]$	111
$[FePd(\mu\text{-dppa})(MeC{=}N\text{-}2,6\text{-}C_6H_4Me_2)Cl(CO)_4]$	111
$[FePd(\mu\text{-dppa})(\mu\text{-}CH_2CH_2COMe)(CO)_4][BF_4]$	111
$[FePd(\mu\text{-}\eta^3,\eta^2\text{-}C_7H_7)(\eta^3\text{-}C_3H_5)(\mu\text{-}CO)(CO)_2]$	112
$[FePd(\mu\text{-dppm})\{\mu\text{-}Si(OSiMe_3)_3\}(Cl)(CO)_3)$	113
$[FePd(\mu\text{-dppa})\{\mu\text{-}Si(OMe)_3\}(I)(CO)_3]$	114
$[FePd(\mu\text{-dppm})\{\mu\text{-}Si(OMe)_3\}(I)(CO)_3]$	114
$[FePd(\mu\text{-dppm})(\mu\text{-}I)(I)(CO)_3]$	114
$[FePd(\eta^5\text{-}C_5H_4PBu^t{}_2)_2I]$	115
$[FePt(\mu\text{-}PPh_2CHCO(Tol^p))(\mu\text{-}PPh_2)\{Si(OMe)_3\}(CO_3)]$	103
$[FePt(\mu\text{-}\eta^3,\eta^2\text{-}C_7H_7)(\eta^2\text{-}\sigma\text{-}C_8H_{11}\text{-}C_5H_5)(\mu\text{-}CO)(CO)_2]$	117
$[FePt(\mu\text{-dppa})(H)(PPh_3)\{Si(OMe)_3\}(CO)_3]$	118
$[FePt(\mu\text{-dppm})(\mu\text{-}C{=}N\text{-}Xy)(PPh_3)(CO)_3]$	118
$[FePt(\mu\text{-dppm})(\mu\text{-}C{=}NC_6H_4OMe)(PPh_3)(CO)_3]$	118
$[FePt(\mu\text{-}PPh_2)(PPh_3)(SiPh_3)(CO)_4]$	119
$[FePt(\mu\text{-dppm})(\mu\text{-}C{=}NCH_2Ph)(PPh_3)(CO)_3]$	120
$[FePt(\mu\text{-dppm})(C{\equiv}NC_6H_{11})I_2(\mu\text{-}CO)(CO)_2]$	120
$[FePt\{\mu\text{-}N(PPh_2)_2\}(\mu\text{-}CNMe\text{-}2,6\text{-}Xy)(PPh_3)(CO)_3]$	121
$[FePt(\mu\text{-dppa})(\mu\text{-}CNH\text{-}6\text{-}C_6H_4OMe)(PPh_3)(CO)_3][CF_3SO_3]$	121
$[FePt(\mu\text{-dppm})(C{\equiv}NBu^t)\{Si(OMe)_3\}(COMe)(CO)_3]$	122
$[FePt(\mu\text{-dppm})(C{=}CHPh)(PPh_3)(CO)_3]$	122
$[FePt(\mu\text{-dppm})(\mu\text{-}Si(OMe)_3)(C{\equiv}N\text{-}2,6\text{-}Xy)(CO)_3][PF_6]$	123
$[FePt(\mu\text{-}PPh_2)(PMe_3)_2(SiPh_3)(CO)_3]$	124
$[FePt(\mu\text{-}PPh_2)\{(PPh_2)_2C{=}CH_2\}(SiPh_3)(CO)_3]$	124
$[FePt(\eta^5\text{-}C_5H_4SMe)_2(PPh_3)][BF_4]_2$	110
$[FePt(\mu\text{-dppe})(Me)(CO)_2Cp]$	125
$[FePt\{\mu\text{-}P(C_6H_{11})_2\}\{Si(OMe)_3\}(CO)_5]$	126
$[FePt(\mu\text{-}PPh_2)(SiPh_3)(CO)_5]$	126
$[FePt(\mu\text{-}PPh_2)(C{\equiv}NBu^t)_2(SiPh_3)(CO)_3]$	126
$[FePt(\mu\text{-}PPh_2)(C{\equiv}N\text{-}2,6\text{-}Xy)(PPh_3)(SiPh_3)(CO)_3]$	126
$[FePt(\mu\text{-dppm})\{\mu\text{-}EtCOSi(OMe)_3\}(PPh_3)(CO)_3]$	127
$[FePt(\mu\text{-dppm})(\eta^3\text{-}1\text{-}3\text{-}COD)\{Si(OMe)_3\}(CO)_3]$	128
$[FePt(\mu\text{-}PPh_2)(\eta^4\text{-}1,5\text{-}COD)\{Si(OMe)_3\}(CO)_3]$	128
$[FePt(\mu\text{-dppm})\{\mu\text{-}Si(OMe)_3\}(nb)(\mu\text{-}CO)(CO)_2]$	128
$[FePt(\mu\text{-dppm})(\eta^3\text{-}C_3H_5)\{Si(OSiMe_3)_3\}(CO)_3]$	113
$[FePt(\mu\text{-dppm})\{C{=}NCH_2P(OEt)_2O\}(PPh_3)(CO)_3]$	129
Fe—Group 11	
$[FeCu\{\mu\text{-}PPh_2(CH_2mor)\}_2(CO)_3][ClO_4]$	130
$[FeCu(\mu\text{-}2\text{-}Ph_2PC_6H_4N)_2(OCMe_2)(CO)_3][ClO_4]$	131
$[FeCu(\mu\text{-}2\text{-}Ph_2PC_6H_4N)_2(H_2O)(CO)_3][ClO_4]$	131
$[FeCu\{\mu\text{-}2\text{-}Ph_2PCH_2N(C_6H_{11})(C_5H_4N)_2(\mu\text{-}CO)_2(CO)\}[ClO_4]$	132
$[FeCu\{\mu\text{-}(CH_3)_2NSi(OMe)_2\}\{P(NMe_2)_2OMe\}(PPh_3)(\mu\text{-}CO)(CO)_2]$	133
$[FeCu(NH_3)_2(N{=}O)(\mu\text{-}CO)_2(CO)]$	134
$[FeCu(\mu\text{-}Me_2NCH_2CH_2NMe_2)(NH_3)(N{=}O)(\mu\text{-}CO)_2(CO)]$	134
$[FeCu(\mu\text{-}2\text{-}Ph_2PCH_2C{=}NCH_2CH_2O)_2(CO)_3][BF_4]$	135
$[FeCu(\mu\text{-}NH_2CH_2CH_2NH_2)(N{=}O)(\mu\text{-}CO)_2(CO)]$	136
$[FeCu(\eta^3\text{-}N,N',N''\text{–}H_2NCH_2CH_2NHCH_2CH_2NH_2)(N{=}O)(\mu\text{-}CO)_2(CO)]$	136
$[FeAg\{\mu\text{-}2\text{-}\ Ph_2PC_5H_4N\}_2(2\text{-}Ph_2PC_5H_4N)(CO)_3]$	131
Fe—Group 12	
$[FeZn(\mu\text{-}\eta^5\text{-}C_5H_4\text{–}C_9H_6N)_2Cl][Zn_2Cl_6]_2$	139
$[FeCd(\mu\text{-}2\text{-}Ph_2PC{=}NCH{=}CHS)_2I_2(CO)_3]$	140

(Continued)

Table 1 (Continued)

	References
$[FeCd(\mu\text{-}N{-}Ph_2PCH_2NCH_2CH_2OCH_2CH_2)(Ph_2PCH_2mor)I_2(CO)_3]$	130
$[FeCd(\mu\text{-}2\text{-}PhEtP{-}C_5H_4N)_2(NCS)_2(CO)_2]$	28
$[FeCd(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2Cl_2(CO)_3]$	141
$[FeCd(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2Br_2(CO)_3]$	141
$[FeCd(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2I_2(CO)_3]$	141
$[FeCd(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2(NCS)_2(CO)_3]$	141
$[FeCd(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2(NCMe)(H_2O)(CO)_3][ClO_4]$	141
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_{10}H_8N)_2I(CO)_3][HgI_3]$	142
$[FeHg(\mu\text{-}2\text{-}PhEtP{-}C_5H_3N)Cl_2(CO)_4]$	143
$[FeHg(\mu\text{-}PPh_2{-}C{=}NCH{=}CHS)_2(SCN)_2(CO)_3]$	140
$[FeHg(PPh_2CH_2mor)I_2(CO)_3]$	130
$[FeHg(dppm)\{Si(OMe)_3\}(C_6Cl_5)(CO)_3]$	144
$[FeHg(\mu\text{-}2\text{-}(Ph)_2P{-}C_5H_4N)_2(SCN)_2(CO)_2]$	145
$[FeHg\{\mu\text{-}2\text{-}(Ph)_2P{-}C_5H_4N\}_2(Cl_2)(CO)_2]$	145
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2Cl_2(CO)_3]$	146
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)(2\text{-}Ph_2P{-}C_4H_3N_2)Cl_2(CO)_3]$	146
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2Br_2(CO)_3]$	146
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)_2I_2(CO)_3]$	146
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_4H_3N_2)(2\text{-}Ph_2P{-}C_4H_3N_2)(SCN)_2(CO)_3]$	146
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_5H_4N)_2(ClO_4)(H_2O)(CO)_3][ClO_4]$	131
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_5H_4N)_2I_2(CO)_3]$	147
$[FeHg(\mu\text{-}2\text{-}Ph_2P{-}C_5H_4N)_2(SCN)_2(CO)_3]$	148





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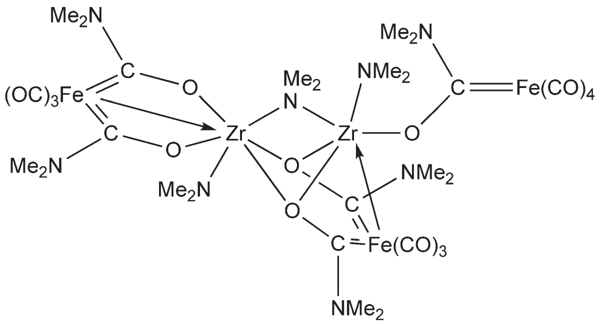
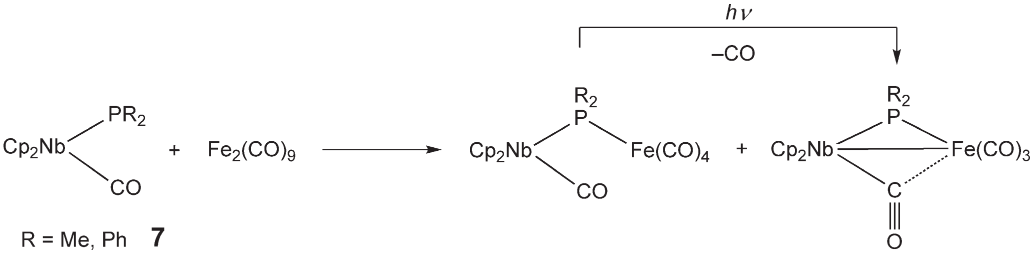


6

Treatment of $[Fe_2(CO)_9]$ with the terminal phosphido complexes, $[Cp_2Nb(CO)PR_2]$ 7 (R = Ph, Me), resulted in a mixture of monobridged and dibridged compounds $[FeNb(\mu\text{-}PR_2)(CO)_5Cp_2]$ and $[FeNb(\mu\text{-}PR_2)(CO)_4Cp_2]$. Photolysis of the monobridged compound led to CO dissociation and the dibridged compound in quantitative yield. The dibridged compound reacted with the phosphine ligand to give phosphido-monobridged compounds.[13]

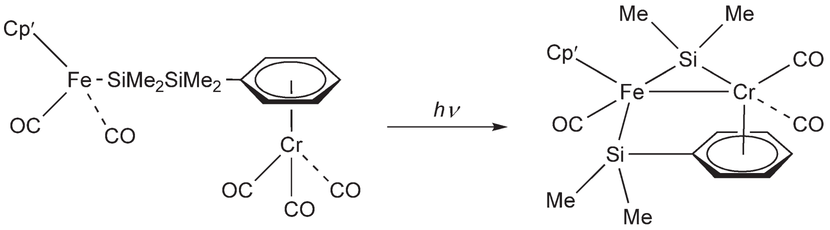


7

Another useful Nb reagent for the synthesis of mixed-metal compounds is $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(CO)\}_2Hg$. Upon thermolysis or photolysis, the homolysis of the Nb–Hg bond generated short-lived Nb(II) radicals $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(CO)]$ that can be trapped with dimeric metal complexes such as $[CpFe(CO)_2]_2$, $Co_2(CO)_8$, and $[CpNi(CO)]_2$ to give the corresponding dinuclear mixed-metal complexes. The Fe–Nb compound $[FeNb(CO)_3(\eta^5\text{-}C_5H_4SiMe_3)_2Cp]$ has been characterized by both X-ray and variable temperature (VT) NMR techniques.[14]

An improved synthesis for the bimetallic Fe–Cr complexes that contain μ-cyclooctatetraene as a bridging ligand was described by Heck *et al.* The reaction of $[Cp'Cr(\eta^6\text{-cot})]$ ($Cp' = Cp$ or Cp^*) with $[Fe(CO)_3(\eta^5\text{-cot})_2]$ gave the dinuclear complexes $[FeCr\{\mu\text{-}\eta^5(Cr){:}\eta^3(Fe)\text{-cot}\}(CO)_3Cp']$ in good yields. These compounds are substitutionally labile with respect to phosphines. X-ray analyses of Cp^*-containing species and its phosphine derivatives showed the exclusively *syn*-facial coordination of the two metal ligand moieties and an Fe–Cr distance close to 3.0 Å.[22,23] The electronic structure of these cyclooctatetraene-bridged dinuclear species has been a subject of intensive theoretical calculations. They can be regarded as being composed of a chromocene-like subunit $CpCr(\eta^5\text{-}C_5H_5)$ and the fragment $Fe(CO)_3(\eta^3\text{-}C_3H_3)$ with a direct metal–metal bond between them.[20,21]

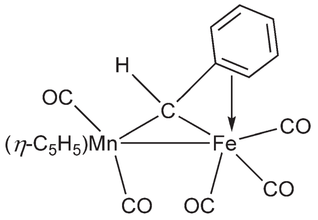
The bimetallic disilyl complexes that contain iron and chromium, $[Cp'Fe(CO)_2SiMe_2SiMe_2\{\eta^6\text{-}C_6H_5Cr(CO)_3\}]$ ($Cp' = Cp, Cp^*$), were found to undergo photolysis in C_6D_6 solution to give the silylene-bridged complexes 8 and 9 in moderate yields. X-ray analysis of 9 revealed an Fe–Cr distance of 3.095 Å, which is significantly longer than the previously reported Fe–Cr distances.[19]



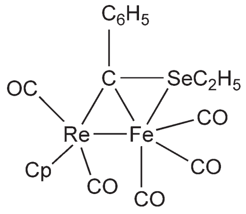
8: Cp′ = Cp
9: Cp′ = Cp*

The synthesis of Fe–Mo and Fe–W dinuclear complexes is often assisted by bridging phosphido ligands,[29,30,40–42] although it is also known that a number of tungsten acetylides[39,43] and related complexes[34] provide effective building blocks for the creation of heterobimetallic Fe–W complexes.

Chen *et al.* successfully employed the cationic metal carbyne complexes $[Cp(CO)_2M{\equiv}CPh][BBr_4]$ (M = Mn and Re) to generate heterobimetallic complexes with a bridging carbene ligand.[55] The carbonyl iron salts, such as $Na_2[Fe(CO)_4]$, $[Me_4N][HFe(CO)_4]$,[51] $[Et_4N]_2[Fe_2(CO)_8]$,[54] $Na_2[Fe_3(CO)_{11}]$, and $[Et_3NH][Fe_2(\mu\text{-SeR})(CO)_7]$,[46] were used to give the corresponding Fe–M (M = Mn and Re) complexes in moderate to good yields. However, these compounds, such as **10** and **11**, are very sensitive to air and are unstable in solution.

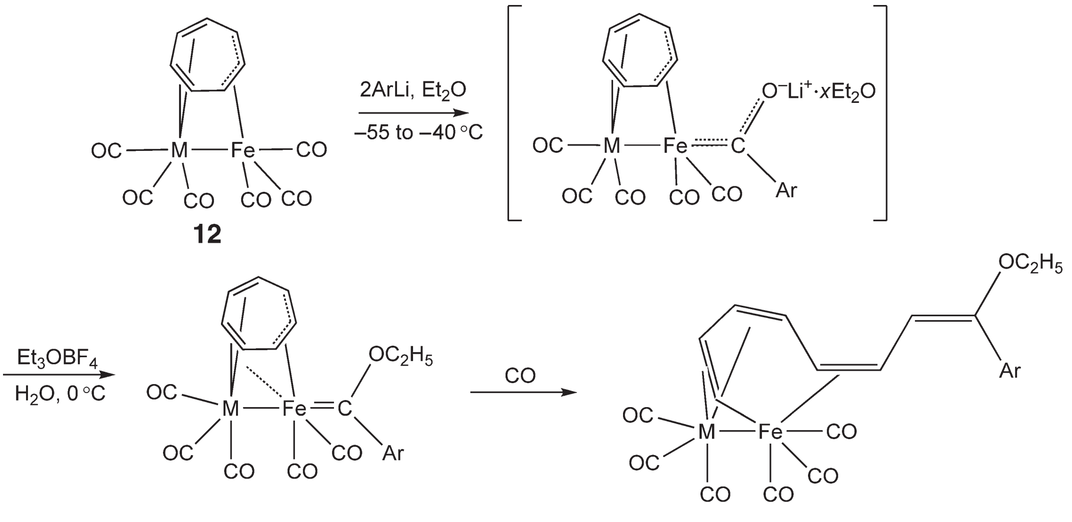


10



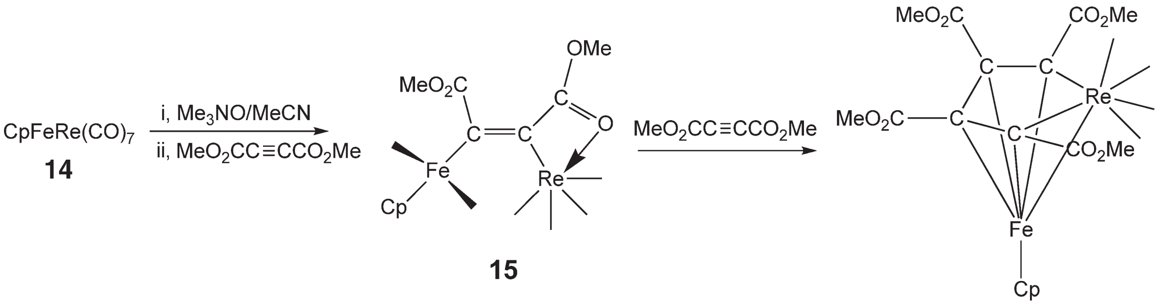
11

A novel ring-opening reaction of the cycloheptatrienyl ring to give polyene complexes was observed in the mixed-metal complex $[FeMn(C_7H_7)(CO)_6]$ **12**. The reaction of **12** with aryllithium reagents ArLi (Ar = Ph, *o*-, *m*-, *p*-MeC_6H_4) in diethyl ether at a low temperature, followed by alkylation with $[Et_3O]BF_4$ in aqueous medium at 0 °C, gave the ring-opened polyene compounds $[FeMn\{C_8H_7(OEt)Ar\}(CO)_6]$ **13**.[48] Analogous reactions have also been reported for the Re system.[45]



M = Mn, Ar = Ph **13**

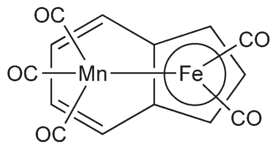
Adams *et al.* reported that the activation of Fe–Re complex **14** by Me_3NO followed by the addition of $MeO_2CC{\equiv}CCO_2Me$ afforded the (*Z*)-dimetalated olefin complex **15** in good yield. Further reaction with $MeO_2CC{\equiv}CCO_2Me$ in heptane at reflux gave the metallacyclic complex **16**, in which the two alkynes coupled to each other and to the Re atom to form a metallacycle that is π-coordinated to the iron center.[58]



15

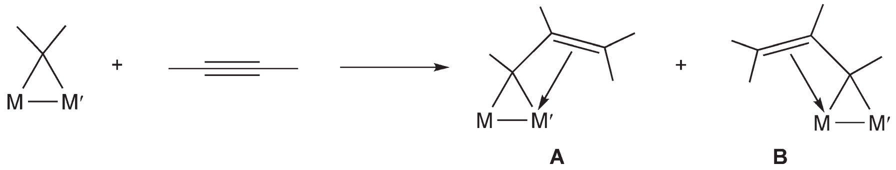
16

Sweigart *et al.* developed a novel synthetic method to derive polyarene complexes that contain two *syn*-facial metal atoms. A representative example is the reaction of [Mn(1-methylnaphthalene) $(CO)_3]BF_4$ **17** with [Fe(indenyl) $(CO)_3]BF_4$ in CH_2Cl_2 to give bimetallic complex **18** in 72% yield. The capacity of **17** as an $Mn(CO)_3$ transfer reagent in these reactions was demonstrated.[53]

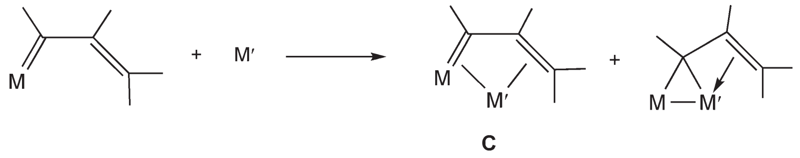


18

Heterobinuclear vinylcarbene complexes have been well explored.[62] The mixed-metal (μ-vinylcarbene) complexes are usually prepared by either the reaction of (μ-methylene) bimetallic complexes with alkynes (Equation (1)) or the reaction of 1-metallabutadienes with another metal reagent (Equation (2)). Mitsudo *et al.* established a selective synthetic route to the type B product in good yield. The reaction of Fe complex **19** with $[Ru(CO)_3(COD)]$ led to the formation of heterometallic complex **20**, which is slowly oxidized in air. It is interesting to note that no transmetallated complex (type A product) was formed.[67]



(1)



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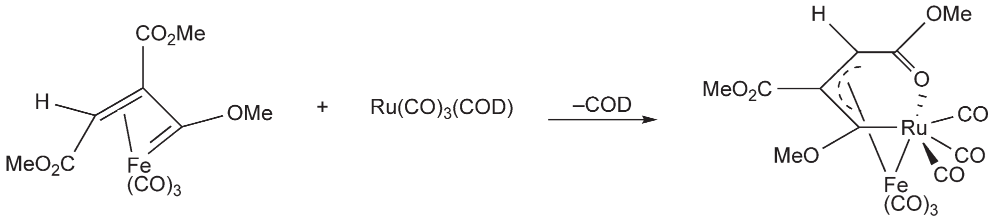
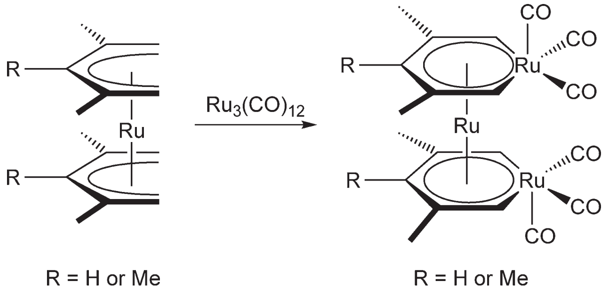


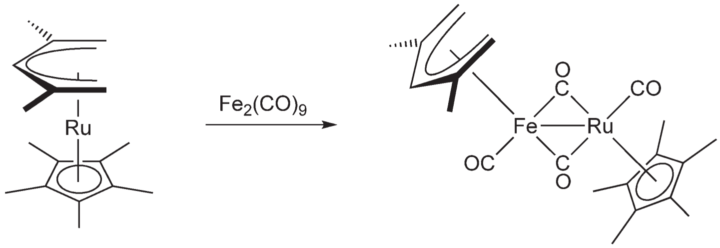
19

20

The chemistry of metallabenzenes has been extensively investigated.[63] However, their synthesis by the insertion method is poorly understood and difficult to predict. Salzer *et al.* recently reported an excellent method to generate bis(metallabenzene) ruthenium complexes (Equation (3)). With this strategy, heterometallic compounds can also be obtained. However, these reactions are sometimes more complicated than one would anticipate. For example, the reactions of the pentadienyl sandwich complex **21** with [$Fe_2(CO)_9$] afforded the heterometallic complex **22** in 80% yield, which clearly involved a relatively complicated process to allow the transfer of the pentadienyl group from Ru to the Fe center.[73]

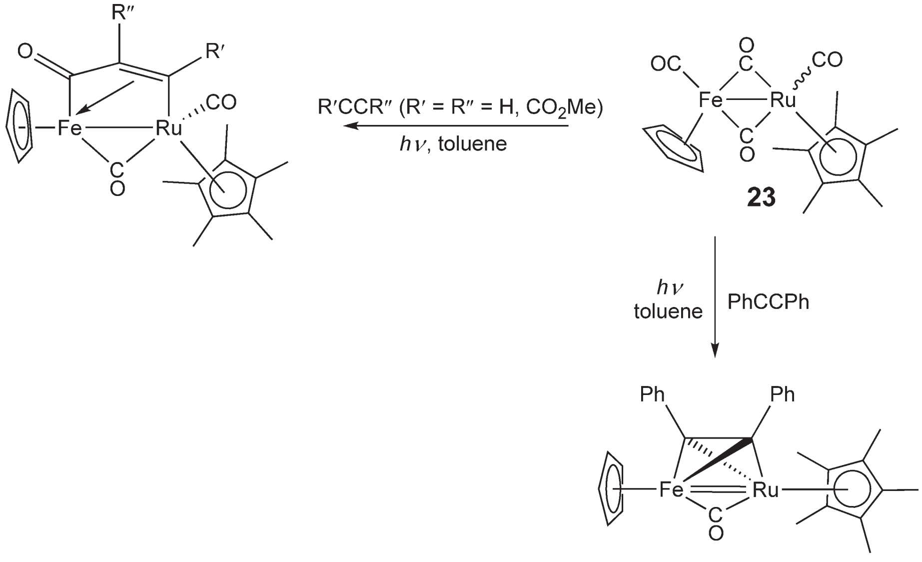


(3)



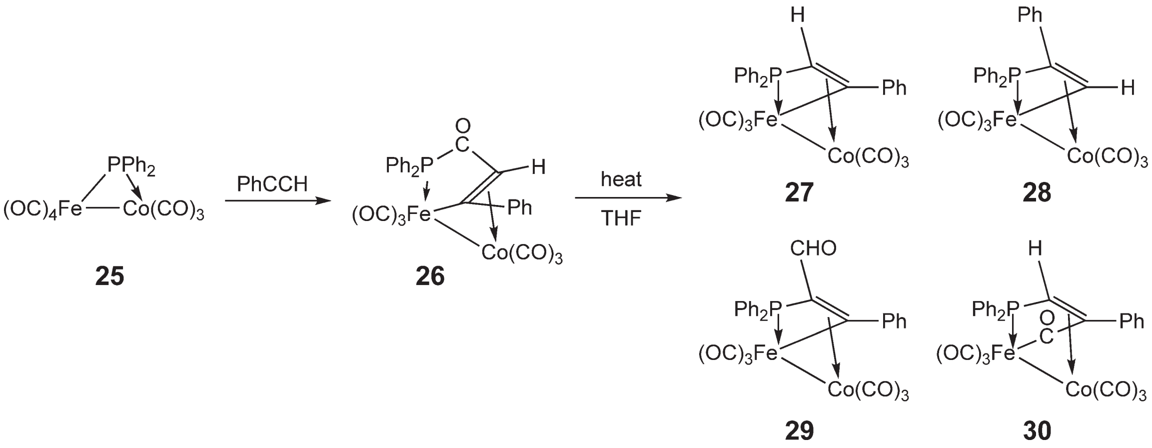
21 **22**

The chemistry of the heterobimetallic complex [$FeRu(CO)_4CpCp^*$] **23** was extensively studied by Knox. It was shown that complex **23** displayed enhanced photolytic reactivity to alkynes compared to its homometallic analogs, and formed the dimetallacyclopentenone complexes. It is interesting to note that on prolonged photolysis of **23** with diphenylacetylene, a novel dimetallatetrahedrane complex **24** was formed that contains an iron–ruthenium double bond with a bond length of 2.4018(9) Å. Related complexes that contain a variety of organic fragments, such as alkenylidene, allenyl, and vinyl groups, have also been investigated for their reactivity and solution dynamics.[64]



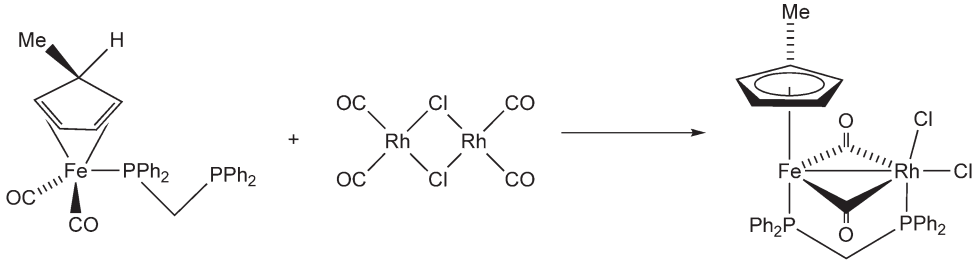
24

The bridging phosphido group in bimetallic transition metal complexes appeared to participate in a transformation, rather than behave as an inert spectator ligand. This is particularly obvious in homobimetallic iron[75] and cobalt systems.[76] Mays *et al.* showed that the reactions of iron–cobalt phosphido-bridged complex **25** with both symmetrical and unsymmetrical alkynes gave five-membered ferracycle-containing compounds, such as **26**, in which a CO and an alkyne were inserted regiospecifically into a Co–P bond in **25**. Subsequent decarbonylation led to a set of four-membered ferracyclic species **27–30** in low yields.[82]



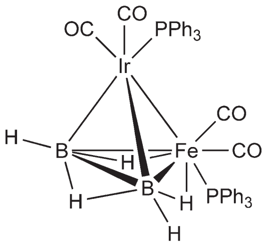
25 **26** **27** **28** **29** **30**

The monodentate dppm complex [Fe(η^4-MeC$_5$H$_5$)(η^1-dppm)(CO)$_2$] **31** reacted with [Rh(CO)$_2$Cl]$_2$ in THF/*n*-hexane at room temperature (RT) to give a novel heterobimetallic Fe–Rh complex **32**.[90]

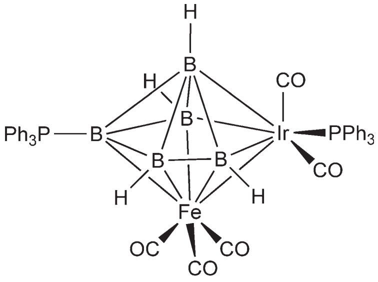


31 **32**

Barton *et al.* established synthetic methods for the derivation of heterobimetallaborane compounds, such as **33** and **34**, which have *nido*- and *closo*-structures, respectively.[92,94,95]



33

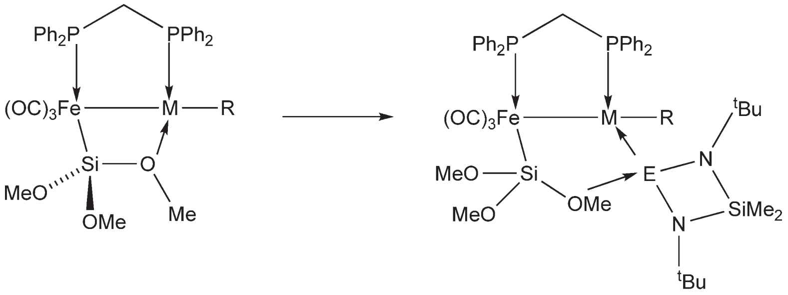


34

The chemistry of heterodinuclear Fe–M (M = Ni, Pd, Pt) complexes has been systematically studied by a number of research groups. New synthetic routes to these complexes were developed, and their interesting reactivity examined. Braunstein *et al.* reported a series of heterodinuclear Fe–M (M = Ni, Pd, Pt) complexes that contain a bridging alkoxysilyl ligand with a skeleton that is exemplified by complex **35**, for which the molecular structure was established by X-ray crystallography.

Treatment of **35** with an excess of C_3H_5MgCl led to bimetallic allyl complex **37**. A rapid η^3-allyl-η^1-allyl interconversion was observed. The CO insertion reaction into the Ni–C bond to give the acyl complex **39** was also studied.[98]

The addition of isocyanides yielded the labile σ-allyl complexes for both the Pd and Pt analogs of **35**.[113,123] The insertion of cyclic amides $[E(NBu^t)_2SiMe_2]$ (E = Ge, Sn) into the Pd–O or Pt–O bonds to give **40** and related species was observed. However, no similar reaction was observed for a plumbylene reagent.[116] The palladium analog of **37** and the chloride derivatives are both effective catalysts for the dehydrogenative coupling of triorganotin hydrides $HSnR'_3$ ($R' = Ph$, ^nBu). The elementary transformations during catalysis appeared to take place at the palladium center. However, the iron fragment provides the Pd atom with the appropriate coordination environment via metal–metal bonding and the Si-containing ligand.[100] Other bidentate phosphine ligands, such as $Ph_2PCH_2PPh_2$[109,114] and $Ph_2PNHPPh_2$,[111] and phosphine–pyridine-type ligands,[104] have also been used to construct binuclear analogs of **35**. Their reactivity to phosphine substitution,[101] CO insertion, and isonitrile insertion has also been reported.[122]

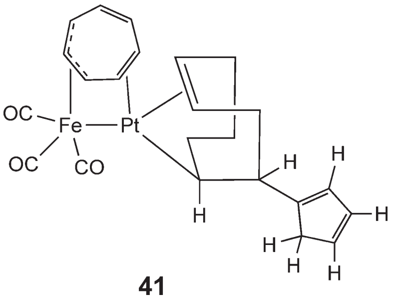


35: M = Ni, R = Me
36: M = Ni, R = Ph
37: M = Ni, R = C_3H_5
38: M = Ni, R = CH_2Ph
39: M = Ni, R = C(O)Me

M = Pd, R = Me, E = Ge
M = Pd, R = Me, E = Sn
M = Pt, R = Me, E = Sn

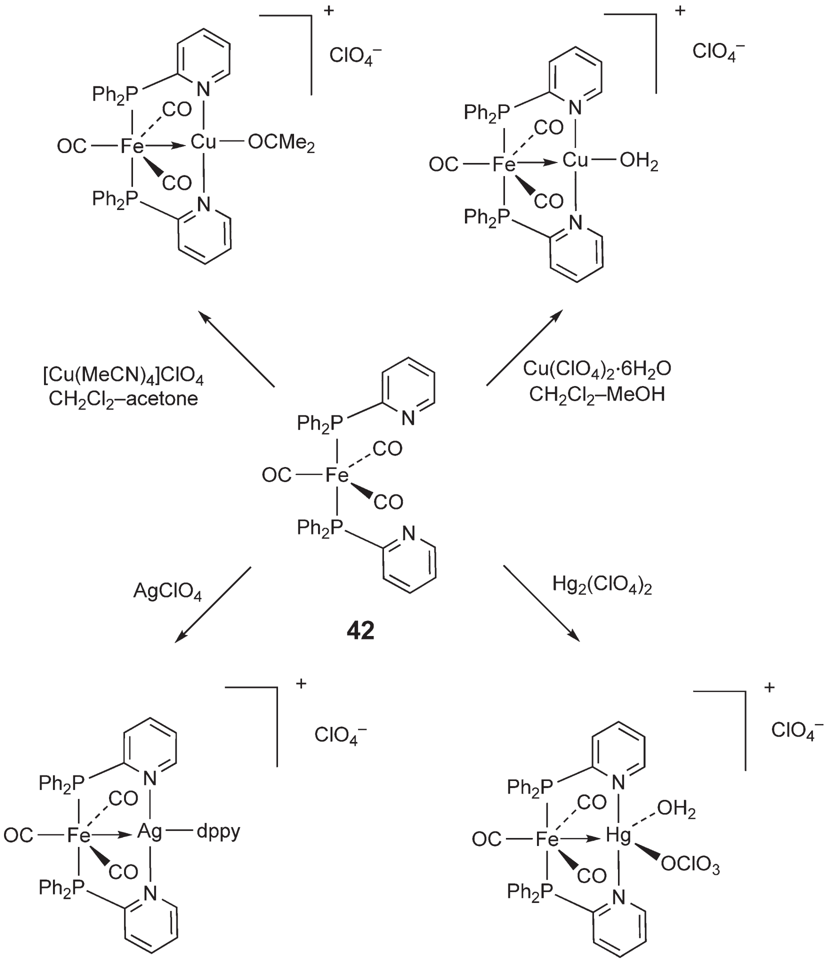
40

Closely related heterobimetallic Fe–Pd and Fe–Pt complexes that are bridged by the PR_2 group instead of bidentate phosphine chelates were also reported by Braunstein.[102,103,119,124] It is interesting to note that novel intramolecular metal-to-metal silyl ligand migration reaction on these phosphido-bridged Fe–Pt complexes can be effected by the addition of nucleophiles, such as CO and phosphines.[126] Ionic coupling between $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$ and $[(\eta^4\text{-}C_8H_{12})CpPt]^+$ led to the formation of the binuclear complex *syn*-$[FePt(\mu\text{-}\eta^3;\eta^2\text{-}C_7H_7)(\eta^2\text{-}\sigma\text{-}C_8H_{12}C_5H_5)(CO)_3]$ **41**, which contains a cyclopentadienyl unit that is linked to the C_8H_{12} ring through an *sp*^{2} carbon. Such a C_5H_5 transfer that is mediated by platinum metal is useful for the synthesis of the skeletons of natural products.[117]

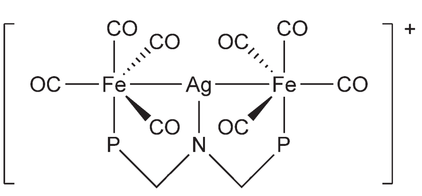


41

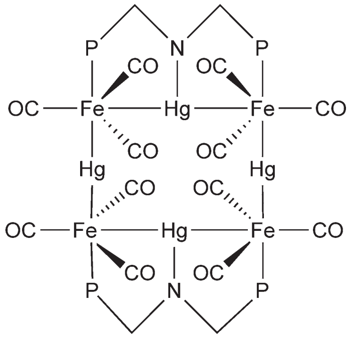
Mak *et al.* employed $[Fe(CO)_4(Ph_2PPy)_2]$ **42** (Ph_2PPy = 2-(diphenylphosphino)pyridine) to construct a series of heterobimetallic compounds with an Fe–M dative bond. The iron center in **42** is zero-valent and electron rich and, together with the two pendant pyridyl groups, can be viewed as a structural analog of terpyridine. A rather comprehensive series of metal salts were incorporated, including Cu(I), Ag(I), Zn(II), Cd(II), Hg(II), and other first-row transition elements, such as Fe, Co, and Ni.[28,131,140,141,143,145,146,147,149]



An extension of this strategy, with the bridging phosphine ligand 2,6-bis(diphenylphosphino)pyridine (PNP), was used to generate the metallo-ligand {Fe(CO)$_4$}$_2$(μ-PNP). Both the Ag and Hg metal complexes **43 and 44** were synthesized and structurally characterized.[150]

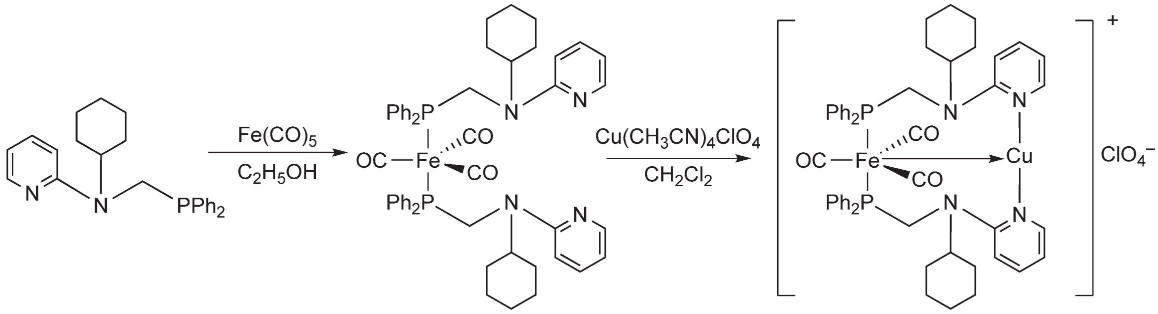


43



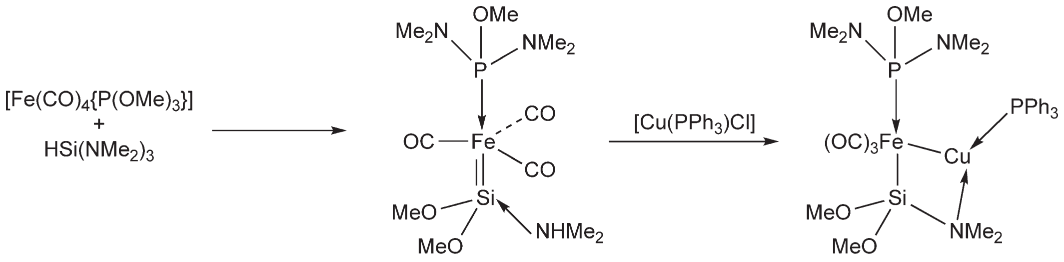
44

In addition, the modification of the phosphine ligand to allow flexibility has also been introduced. 2-(*N*-Diphenylphosphinomethyl-*N*-cyclohexyl)aminopyridine (NNP) was used to build up the novel cationic complex **45**, which has two seven-membered macrocycles and an Fe(0) → Cu(I) dative bond.[132]



45

Braunstein *et al.* showed that the bridging aminosilyl ligand could be used to stabilize a novel four-membered bimetallic ring structure, as in 46, in addition to the novel structure that was established for the metal complex. It is also interesting to note that a remarkable exchange of OMe and NMe$_2$ groups on the phosphorus and silicon occurred.[133]



46

6.10.3 Cluster Compounds

Tremendous developments in the chemistry of mixed-metal cluster complexes that contain iron have been made in the past 10 years. Over 600 compounds with known structures were reported in this review period (see Tables 2 and 3). New synthetic methods, chemical reactivity, and structural properties remain the major areas of research for

Table 2 Heterometallic iron cluster compounds containing two different metals with known structure

	References
Fe—Group 4	
[$Fe_2Ti_2(\eta^5$-$C_5H_4NSiMe_3)_4(\mu$-$Cl)_2][B(C_6F_5)_4]_2$	5
[$FeZr_6(Cl)_{18}][1$-Et-3-Me-$C_3H_3N_2$]	155
[$Fe_2Zr(SiMe_3NCH_2CH_2CH_2NSiMe_3)(CO)_4Cp_2$]	156
[$Fe_3Zr_2(\mu$-C,O-$NMe_2CO)_2(\mu$-O,O-$NMe_2CO)_2(\mu$-$NMe_2)(NMe_2CO)(NMe_2)_2(CO)_{10}$]	12
Fe—Group 5	
[$FeV_2(\mu_3$-$S)_4(Medtc)_5][NEt_4$]	157
[$Fe_3V(\mu_3$-$S)_4Cl_3(HB(pz)_3)][NMe_4$]	158
[$Fe_4V(\mu_3$-$S)_3(\mu$-$S)_3(PEt_3)_4(SPh)$]	159
[$Fe_4V(\mu_3$-$S)_4(CO)_{12}$]	160
Fe—Group 6	
[$FeCr_2(\mu_3$-$B_4H_8)(CO)_3Cp^*_2$]	163,191

(*Continued*)

Table 2 (Continued)

	References
$[FeCr_2(\mu_3\text{-}S)_2(SBu^t)Cp_3]$	164
$[FeCr_2(\mu_3\text{-}S)_2(SPh)Cp_3]$	164
$[FeCr_2(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_9][PPN]$	165
$[FeCr_2(\mu_3\text{-}Te)_2(\mu\text{-}CO)(CO)_9][PPN]$	165
$[FeCr_4(\mu_3\text{-}S)_4(SBu^t)_2(\eta^5\text{-}C_5H_4Me)_4]$	166
$[Fe_4Cr_2(\mu_6\text{-}O)(CO)_{12}Cp_2]$	167
$[FeMo_2(\mu_3\text{-}BH_3)(\mu_3\text{-}B_4H_6)(CO)_3Cp^*{}_2]$	191
$[FeMo_2(\mu_3\text{-}PPh)(CO)_7Cp_2]$	192
$[FeMo_2(\mu_3\text{-}S)(CO)_7\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(O)(CH_2)_2C(O)C_5H_4)\}]$	193
$[FeMo_2(\mu_3\text{-}S)(CO)_7\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH(OH)(CH_2)_2CH(OH)C_5H_4\}]$	193
$[FeMo_2(\mu_3\text{-}S)(CO)_7Cp_2]$	194
$[FeMo_2(\mu_3\text{-}S)(CO)_7(\eta^5\text{-}C_5H_4Me)]$	184
$[FeMo_2(\mu_3\text{-}S)(\mu\text{-}CO)(CO)_6\{\mu\text{-}\eta^5,\eta^5\text{-}1,1'\text{-}C_5H_4(CH_2CH_2O)_3CH_2CH_2C_5H_4\}]$	195
$[FeMo_2(\mu_3\text{-}S)(\mu\text{-}CO)_3(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}1,5\text{-}C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)]$	196
$[FeMo_2(\mu_3\text{-}S)\{\mu\text{-}CO)_3(CO)_4\{\mu\text{-}\eta^5,\eta^5\text{-}1,8\text{-}C_5H_4(CH_2CH_2O)_2CH_2CH_2C_5H_4\}]$	196
$[FeMo_2(\mu_3\text{-}S)_4(\eta\text{-}SEtS)_2S_2][NEt_4]$	166
$[FeMo_2(\mu_3\text{-}\sigma^3,\eta^2\text{-}C{\equiv}CH)(\mu\text{-}CO)(CO)_4Cp_3]$	197
$[FeMo_2(\mu_3\text{-}Se)(CO)_7Cp_2]$	198
$[FeMo_2(\mu_3\text{-}Te)(CO)_7Cp_2]$	199
$[FeMo_2(\mu\text{-}S)_4\{\eta\text{-}S_2C(NMe_2)\}_2(O)_2][NEt_4]$	200
$[FeMo_2(\mu\text{-}SPh)_4(CO)_8]$	201
$[FeMo_3(\mu_3\text{-}S)_4(H_2O)_{10}][OTs]_4$	202
$[FeMo_3(\mu_3\text{-}S)_4(SH)(\eta^5\text{-}C_5H_4Me)_3]$	203
$[FeMo_3(\mu_4\text{-}P)(CO)_{10}Cp_3]Cl_2$	204
$[Fe_2Mo(\mu_3\text{-}\eta^2,\eta^2,\eta^1\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5Cp]$	172
$[Fe_2Mo(\mu_3\text{-}\eta^2,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_5Cp_2]$	172
$[Fe_2Mo(\mu_3\text{-}O)(\mu_2\text{-}SBu^t)(CO)_8(\eta^5\text{-}C_5H_4COOMe)]$	205
$[Fe_2Mo(\mu_3\text{-}S)(\mu\text{-}SCCH_2Ph)(\mu\text{-}CO)(CO)_5Cp^*]$	206
$[Fe_2Mo(\mu_3\text{-}S)_2(\eta^2\text{-}C_6Cl_4O_2)_2(PEt_3)_2(CO)_4]$	207
$[Fe_2Mo(\mu_3\text{-}\sigma^2,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_6Cp]Cl_2$	172
$[Fe_2Mo(\mu_3\text{-}Se)_2(CO)_{10}]$	208
$[Fe_2Mo(\mu_3\text{-}Se)(\mu\text{-}\eta^2,\sigma\text{-}COPh)(\mu\text{-}SePh)_2(CO)_4(\eta^5\text{-}C_5H_4COMe)]$	209
$[Fe_2Mo(\mu_3\text{-}Se)_2(C{\equiv}CPh)(CO)_7Cp]$	210
$[Fe_2Mo_2(\mu_3\text{-}H)(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu\text{-}CO)(CO)_4Cp_2]$	213
$[Fe_2Mo_2(\mu_3\text{-}O)(\mu_3\text{-}S)_3(\eta^2\text{-}C_6Cl_4O_2)_2(PEt_3)_3Cl][Fe(NCMe)_4(PEt_3)_2]$	214
$[Fe_2Mo_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(C{\equiv}NPr^i)(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_4Cp_2]$	217
$[Fe_2Mo_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}CO)(CO)_6Cp_2]$	199
$[Fe_2Mo_2(\mu_3\text{-}S)_2(CO)_8(\eta^5\text{-}C_5H_4COOMe)_2]$	218
$[Fe_2Mo_2(\mu_3\text{-}S)_4(NO)_2(\eta^5\text{-}C_5Me_4Et)_2]$	219
$[Fe_2Mo(\mu\text{-}S)_4(SSiPh_3)_4][PPh_4]$	220
$[Fe_2Mo_2(\mu_3\text{-}S)_4Cl_2Cp^*{}_2]$	221
$[Fe_2Mo_2(\mu_3\text{-}Se)(\mu_3\text{-}CH_3As)(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_5Cp_2]$	222
$[Fe_2Mo_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)(\mu\text{-}CO)(CO)_6Cp_2]$	223
$[Fe_2Mo_2(\mu_3\text{-}Se)_2(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_5Cp_2]$	198
$[Fe_2Mo_2(\mu_3\text{-}Te)_2(C{\equiv}NBu^t)(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_4Cp_2]$	217
$[Fe_2Mo_2(\mu_4\text{-}P)(\mu\text{-}H)(CO)_{11}Cp_2]$	204
$[Fe_2Mo_2(\mu_4\text{-}Se)(\mu_3\text{-}Se)(\mu\text{-}S)(CO)_6Cp_2]$	223
$[Fe_2Mo_2(\mu_4\text{-}Se)(\mu_3\text{-}Se)_2(CO)_6Cp_2]$	255
$[Fe_2Mo_2(\mu_4\text{-}Te)(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_6Cp_2]$	199
$[Fe_2Mo_2(\mu_4\text{-}Te)(\mu_3\text{-}S)_2(CO)_6Cp_2]$	199
$[Fe_2Mo_2(\mu_4\text{-}Te)(\mu_3\text{-}Te)(\mu_3\text{-}S)(CO)_6Cp_2]$	199
$[Fe_2Mo_2(\mu_4\text{-}Te)(\mu_3\text{-}Se)_2(CO)_6Cp_2]$	223
$[Fe_2Mo_2(\mu_4\text{-}Te)(\mu_3\text{-}Te)_2(CO)_6Cp_2]$	199
$[Fe_2Mo_2(\mu\text{-}S)_4Br_2Cp^*{}_2]$	224
$[Fe_2Mo_2\{\mathit{cis}\text{-}(\mu_3\text{-}Se)\text{-}(\mu_3\text{-}S)\}(CO)_8Cp_2]$	226
$[Fe_2Mo_2\{\mathit{trans}\text{-}(\mu_3\text{-}Se)\text{-}(\mu_3\text{-}S)\}(CO)_8Cp_2]$	226
$[Fe_3Mo(\mu_3\text{-}\eta^2\text{-}C{=}CPhS)(\mu_3\text{-}\eta^2,\eta^2\text{-}C{\equiv}CPh)(\mu_3\text{-}S)(CO)_6Cp^*]$	229
$[Fe_3Mo(\mu_3\text{-}S)(\mu_3\text{-}Se)(\mu\text{-}Se_2)(CO)_{11}]$	230

(Continued)

Table 2 (Continued)

	References
$[Fe_3Mo(\mu_3\text{-}S)_4(\eta^2\text{-}C_6Cl_4O_2)(SPEt_3)_2(PEt_3)Cl]$	207
$[Fe_3Mo(\mu_3\text{-}S)_2(\mu\text{-}S_2)(CO)_{11}]$	230
$[Fe_3Mo(\mu_3\text{-}S)_2(\mu\text{-}S\text{-}Se)(CO)_{11}]$	230
$[Fe_3Mo(\mu_3\text{-}S)_3(\eta^2\text{-}C_6Cl_4O_2)(PEt_3)_2(CO)_6]$	231
$[Fe_3Mo(\mu_3\text{-}S)_3(\eta^2\text{-}C_6Cl_4O_2)\{P(Pr)_3\}_2(Py)(CO)_6]$	232
$[Fe_3Mo(\mu_3\text{-}S)_3(\eta^2\text{-}C_6Cl_4O_2)\{P(Pr)_3\}_3(CO)_6]$	232
$[Fe_3Mo(\mu_3\text{-}S)_3\{P(C_3H_7)_3\}_3(Py)(\eta^2\text{-}C_6Cl_4O_2)(CO)_4]$	233
$[Fe_3Mo(\mu_3\text{-}S)_3(PEt_3)_2(Py)(\eta^2\text{-}C_6Cl_4O_2)(CO)_6]$	233
$[Fe_3Mo(\mu_3\text{-}S)_4(\eta^2\text{-}C_6Cl_4O_2)(Pz)Cl_3][NEt_4]$	234
$[Fe_3Mo(\mu_3\text{-}S)_4(\eta^2\text{-}C_2O_4)Cl_4][NEt_4]_3$	235
$[Fe_3Mo(\mu_3\text{-}S)_4(\eta^2\text{-}C_2O_4)(CN)Cl_3][NEt_4]_3$	236
$[Fe_3Mo(\mu_3\text{-}S)_4(NH_2Me)Cl_3(\eta^2\text{-}C_6Cl_4O_2)][NEt_4]_2$	237
$[Fe_3Mo(\mu_3\text{-}S)_4\{S(CH_2COO)_2\}Cl_3][NEt_4]_2$	238
$[Fe_3Mo(\mu_4\text{-}S)(\mu_3\text{-}S)_2(\eta^2\text{-}C_6Cl_4O_2)(PEt_3)_3(O)(CO)_5]$	231
$[Fe_3Mo(\mu_4\text{-}S)(\mu_3\text{-}S)_2(\eta^2\text{-}C_6Cl_4O_2)\{P(Pr)_3\}_2(O)(CO)_6]$	232
$[Fe_3Mo(\mu_4\text{-}S)(\mu_3\text{-}S)_2(\eta^2\text{-}C_6Cl_4O_2)\{P(Pr)_3\}_3(O)(CO)_5]$	232
$[Fe_3Mo(\mu_4\text{-}S)(\mu_3\text{-}S)_2(PEt_3)_2(O)(\eta^2\text{-}C_6Cl_4O_2)(CO)_6]$	233
$[Fe_3Mo_2(\mu_4\text{-}S)(\mu_3\text{-}S)_4(\eta^2\text{-}C_6Cl_4O_2)(PEt_3)_5]$	214
$[Fe_3Mo_2\{\mu_5\text{-}\eta^3\text{-}2,3\text{-}CC(Ph)C(Ph)C\}(\mu_3\text{-}S)_2(CO)_7Cp_2]$	239
$[Fe_3Mo_2\{\mu_5\text{-}\eta^3\text{-}2,3\text{-}CC(Ph)C(Ph)C\}(\mu_3\text{-}Se)_2(CO)_7Cp_2]$	239
$[Fe_3Mo_2(\mu_5\text{-}\eta^2,\eta^2,\eta^2\text{-}PhC\equiv CPhC=C)(\mu_3\text{-}S)_2(CO)_8Cp_2]$	239
$[Fe_3Mo_3(\mu_6\text{-}N)(\mu\text{-}CO)(CO)_{17}][N(tol)Me_3]_2[NEt_4]$	240
$[Fe_4Mo(\mu_3\text{-}S)_2(\mu_3\text{-}Te)_2(CO)_{14}]$	230
$[Fe_4Mo(\mu_3\text{-}S)_3(\mu\text{-}S)_3(PEt_3)_4SPh]$	159
$[Fe_4Mo(\mu_3\text{-}S)_3(\mu\text{-}S)_3(PEt_3)_4(S\text{-}p\text{-}C_6H_4OMe)]$	159
$[Fe_4Mo\{(\mu_3\text{-}Se)(\mu_3\text{-}Te)\}_2(CO)_{14}]$	25
$[Fe_3Mo_2(\mu_4\text{-}\eta^2,\eta^2\text{-}C\equiv CPh)(\mu_4\text{-}\eta^2\text{-}C\equiv CPh)(\mu_3\text{-}S)_2(CO)_9Cp_2]$	239
$[Fe_4Mo_3(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}C\equiv CPh)(\mu\text{-}S)\{(\mu\text{-}S)_2(\mu\text{-}O)(CO)_6\}_2Cp^*]$	212
$[Fe_5Mo(\mu_6\text{-}N)(\mu\text{-}CO)_3(CO)_{11}Cp][PPh_4]_2$	240
$[Fe_6Mo_2(\mu_3\text{-}S)_8\{\mu\text{-}SCH(Me)COO\}_2Cl_6][NEt_4]$	238,244
$[Fe_6Mo_2(\mu_3\text{-}S)_8(\mu\text{-}depe)(\eta\text{-}depe)_4(\eta^2\text{-}C_6Cl_4O_2)_2Cl_2]$	245
$[Fe_6Mo_2(\mu_3\text{-}S)_8(\mu\text{-}dmpe)(\mu\text{-}S)(\eta^2\text{-}dmpe)_4(\eta^2\text{-}C_6Cl_4O_2)_2]$	245
$[Fe_6Mo_2(\mu_3\text{-}S)_8(\mu\text{-}H_2NNH_2)(\eta^2\text{-}C_6Cl_4O_2)_2Cl_6][NEt_4]$	234
$[Fe_6Mo_2(\mu_3\text{-}S)_8(PEt_3)_6(C_6Cl_4O_2)_2]_4[NEt_4]_4$	246
$[Fe_6Mo_2(\mu_4\text{-}S)_2(\mu_3\text{-}S)_6(PEt_3)_6(C_6Cl_4O_2)_2][NEt_4]$	246
$[Fe_6Mo_2(\mu\text{-}N,N\text{-}pz)(\mu_3\text{-}S)_8(\eta^2\text{-}C_6Cl_4O_2)_2Cl_6][NEt_4]$	234
$[Fe_6Mo_2\{(\mu_3\text{-}S)_4(\eta^2\text{-}OCOCOO)Cl_2\}_2(\mu\text{-}C\equiv N)(\mu\text{-}S)][NEt_4]_5$	236
$[Fe_6Mo_2\{(\mu_3\text{-}S)_4Cl_3\}_2(SCH_2COO)_2][NEt_4]_4$	238
$[Fe_6Mo_2\{(\mu_4\text{-}S)(\mu_3\text{-}S)_3(PEt_3)_3(\eta^2\text{-}C_6Cl_4O_2)\}_2][NEt_4]$	246
$[Fe_6Mo_6\{(\mu_3\text{-}S)_4\}_3(\mu\text{-}S_4)_3Cp^*{}_6]$	221
$[FeW(\mu_3\text{-}S)(\eta^5\text{-}C_9H_7)(CO)_8]$	247
$[FeWCu(\mu\text{-}S)_4(PPh_3)_2Br_2][NEt_4]$	254
$[FeWCu(\mu\text{-}S)_4(PPh_3)_2Cl_2][NEt_4]$	190
$[FeWAg(\mu\text{-}S)_4(PPh_3)_2Br_2][NEt_4]$	256
$[FeWAg(\mu\text{-}S)_4(PPh_3)_2Cl_2][NEt_4]_4$	190
$[Fe_2W(\mu_3\text{-}\eta^2,\eta^2,\eta^1\text{-}C\equiv CPh)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5Cp]$	172
$[Fe_2W(\mu_3\text{-}\eta^2,\eta^2\text{-}C\equiv CPh)(CO)_8Cp]$	239
$[Fe_2W(\mu_3\text{-}O)(\mu\text{-}SEt)(CO)_8(\eta^5\text{-}C_5H_4COOEt)]$	205
$[Fe_2W(\mu_3\text{-}S)(H)(CO)_8(\eta^5\text{-}C_5H_4COMe)]$	179
$[Fe_2W(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_{10}]$	257
$[Fe_2W(\mu_3\text{-}Se)(H)(CO)_8(\eta^5\text{-}C_5H_4COMe)]$	179
$[Fe_2W(\mu_3\text{-}Se)(\mu_3\text{-}Te)(CO)_{10}]$	208
$[Fe_2W(\mu_3\text{-}Se)(\mu\text{-}H)(CO)_8Cp]$	258
$[Fe_2W(\mu_3\text{-}Se)_2(CO)_{10}]$	208
$[Fe_2W(\mu_3\text{-}Te)(\mu\text{-}H)(CO)_8Cp]$	259
$[FeW_2(\mu_3\text{-}S)(CO)_7(\eta^5\text{-}C_5H_4Me)Cp]$	263
$[FeW_2(\mu_3\text{-}S)(CO)_7(\mu_2\text{-}\eta^5,\eta^5\text{-}1,8\text{-}C_5H_4(CH_2)_2O(CH_2)_2O(CH_2)_2C_5H_4)]$	264
$[FeW_2(\mu_3\text{-}S)(CO)_7(\mu_2\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2C_5H_4)]$	264

(*Continued*)

Table 2 (Continued)

	References
$[Fe_2W(\mu_3\text{-}S)(\mu\text{-}H)(CO)_8\{\eta^5\text{-}C_5H_4C{=}NMeNH\text{-}2,4\text{-}(NO_2)_2C_6H_4\}]$	265
$[FeW_2(\mu_3\text{-}\sigma^1,\eta^2,\eta^3\text{-}C_4H_4)(CO)_8Cp_2]$	266
$[FeW_2(\mu_3\text{-}Se)(CO)_7Cp_2]$	170
$[Fe_2W_2(\mu_3\text{-}S)_2(\mu\text{-}S)_3(\mu\text{-}Me_2P(CH_2)_2S)_2(S)Cl]$	37
$[Fe_2W_2(\mu_3\text{-}S)_2\{\mu\text{-}\eta^4\text{-}C{=}CPhCOPhC{=}C\}(CO)_4Cp_2]$	267
$[Fe_2W_2(\mu_3\text{-}S)_4(NO)Cp^*{}_2]$	219
$[Fe_2W_2(\mu_3\text{-}Se)_2(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_5Cp_2]$	268
$[Fe_2W_2\{(\mu_3\text{-}S)(\mu\text{-}S)\}_2(CO)_6Cp^*{}_2]$	269
$[Fe_2W_3(\mu_3\text{-}S)_2(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)_2(CO)_{12}Cp_2]$	270
$[Fe_2W_4\{(\mu_3\text{-}S)\{(\mu\text{-}\eta^5,\ \eta^5\text{-}C_5H_4CO(CH_2)_2COC_5H_4)(CO)_7\}_2]$	193
$[Fe_3W(\mu_3\text{-}S)(\mu_4\text{-}\ \eta^2\text{-}C{\equiv}CPh)\{\mu_3\text{-}\eta^2\text{-}2\text{-}SCH{=}C(fc)\}(CO)_7Cp^*]$	229
$[Fe_3W_2(\mu_3\text{-}\eta^2,\eta^2\text{-}C{\equiv}CPh)(\mu_3\text{-}CCH_2Ph)(\mu_3\text{-}S)_2(CO)_7Cp_2]$	239
$[Fe_3W_2(\mu_3\text{-}\eta^2,\eta^2\text{-}C{\equiv}CPh)\{\mu_3\text{-}C(CH_2Ph)\}(\mu_3\text{-}Se)_2(CO)_7Cp_2]$	239
$[Fe_3W_2(\mu_4\text{-}\eta^4\text{-}2,3\text{-}C_4Ph_2)(\mu_3\text{-}S)_2(\mu\text{-}CO)(CO)_5Cp^*{}_2]$	271
$[Fe_2W_2(\mu_4\text{-}\eta^4\text{-}2,4\text{-}C_4Ph_2)(\mu_3\text{-}S)_2(\mu\text{-}CO)_2(CO)_4Cp_2]$	267
$[Fe_4W_4(\mu_3\text{-}S)_4(\mu\text{-}S)_8(\mu\text{-}Me_2P(CH_2)_2S)_4]$	37
$[Fe_5W(\mu_6\text{-}N)(\mu\text{-}CO)_3(CO)_{11}Cp][PPh_4]_2$	240
Fe—Group 7	
$[Fe_2Mn(\mu_3\text{-}CPh)(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6Cp]$	46
$[Fe_2Mn(\mu_3\text{-}\eta^2\text{-}CH{=}CPh)(\mu\text{-}CO)_2(CO)_6Cp]$	276
$[Fe_2Mn(\mu_3\text{-}NH)(\mu\text{-}NO)(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)Cp_2][FeBr_4]$	277
$[Fe_2Mn(\mu_3\text{-}NH)(\mu\text{-}NO)(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)_3]$	277
$[Fe_2Mn(\mu_3\text{-}NH)(\mu\text{-}NO)(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)Cp_2][BPh_4]$	277
$[Fe_2Mn(\mu_3\text{-}NO)(\mu\text{-}NO)(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)_2Cp]$	277
$[Fe_2Mn(\mu_3\text{-}NOH)(\mu\text{-}NO)(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)_2Cp][CF_3SO_3]$	277
$[Fe_2Mn(\mu_3\text{-}NOMe)(\mu\text{-}NO)(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)_2Cp][CF_3SO_3]$	277
$[Fe_2Mn(\mu_3\text{-}NOMe)(\mu\text{-}NO)(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)Cp_2][CF_3SO_3]$	277
$[Fe_2Mn(\mu_3\text{-}PO\text{-}2,4,6\text{-}C_6H_2Bu^t{}_3)(\mu\text{-}CO)(CO)_8Cp^*]$	278
$[Fe_2Mn_2(THF)_4(CO)_8]$	279
$[Fe_3Mn(\mu_4\text{-}O)(CO)_{12}][PPN]$	280
$[Fe_3Mn(\mu_4\text{-}O)(\mu\text{-}dmpm)(\mu\text{-}H)(CO)_{10}]$	281
$[Fe_3Mn(\mu_4\text{-}S)(CO)_{12}][PPN]$	280
$[Fe_5Mn(\mu_6\text{-}N)(\mu\text{-}CO)_2(CO)_{14}][NMe_3CH_2Ph]$	340
$[Fe_2Re(\mu_3\text{-}CPh)(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6Cp]$	312
$[Fe_2Re(\mu_3\text{-}CPh)(\mu\text{-}H)(PPh_3)(\mu\text{-}CO)_2(CO)_5Cp]$	312
$[Fe_2Re(\mu_3\text{-}S)_2(\mu\text{-}CO)(CO)_6Cp]$	313
$[Fe_2Re_2(\mu_3\text{-}\eta^2\text{-}HC{=}CPh)(CO)_{15}]$	314
$[Fe_2Re_2(\mu_4\text{-}\eta^2\text{-}\eta^2\text{-}HC{=}CPh)(CO)_{13}]$	314
Fe—Group 8	
$[Fe_2Ru(\mu_3\text{-}\eta^2{:}\eta^2,\sigma^1\text{-}3\text{-}CH{=}C{=}CHPh)(CO)_7Cp]$	69
$[FeRu_2(CO)_{12}]$	318
$[FeRu_2(CNBu^t)(CO)_{11}]$	325
$[FeRu_2(CNBu^t)_2(\mu\text{-}CO)_2(CO)_8]$	325
$[FeRu_2(\mu_3\text{-}\eta^2\text{-}HC{=}CH)(\mu_3\text{-}CO)(\mu\text{-}H)(\mu\text{-}dppm)(CO)_4Cp^*]$	321
$[FeRu_2(\mu_3\text{-}\eta^2,\sigma^2\text{-}PhC{=}CPh)(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_3Cp_2]$	319
$[FeRu_2(\mu_3\text{-}P_5)(\eta^5\text{-}1,3\text{-}C_5H_3Bu^t{}_2)_2Cp^*]$	320
$[FeRu_2(\mu_3\text{-}\eta^2,\eta^2\text{-}C{\equiv}CH)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_4Cp^*]$	321
$[FeRu_3(\mu_4\text{-}\sigma^5\text{-}COMe)(\mu\text{-}H)(CO)_{12}]$	322
$[FeRu_3\{\mu\text{-}\sigma^2\text{-}\eta^4\text{-}Pr^iNCHCHC(CH_3)\}\{\mu\text{-}\sigma^2\text{-}\eta^4\text{-}Pr^iNCHCHC(Ph)\}(\mu\text{-}CO)(CO)_9]$	72
$[FeRu_5(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{14}]$	323
$[FeRu_6(\mu_5\text{-}\eta^2,\eta^2\text{-}C_2)(\mu_5\text{-}\eta^2,\eta^2\text{-}CCH)(\mu\text{-}CO)(CO)_{15}Cp]$	324
$[Fe_2Ru(\mu_3\text{-}S_2)_2\{\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}_2Cp^*][PF_6]$	269
$[Fe_2Ru(CNBu^t)(\mu\text{-}CO)_2(CO)_9]$	325
$[Fe_2Ru(CNBu^t)_2(\mu\text{-}CO)_2(CO)_8]$	325
$[Fe_2Ru(\mu_3\text{-}P_5)(\eta^5\text{-}1,3\text{-}C_5H_3Bu^t{}_2)Cp^*{}_2]$	320
$[Fe_2Ru(\mu\text{-}CO)_2(CO)_{10}]$	318,343
$[Fe_2Ru(\mu_3\text{-}CCH{=}CH_2)(\mu\text{-}CO)_2(CO)_6Cp]$	326
$[Fe_2Ru(\mu_3\text{-}\eta^2,\eta^2,\sigma^1\text{-}1\text{-}CH{=}C{=}CHPh)(CO)_7Cp]$	69

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Table 2 (Continued)

	References
$[Fe_2Ru(\mu_3-\eta^2-2-CCH=CHPh)(PPh_3)(\mu-CO)_2(CO)_4Cp]$	326
$[Fe_2Ru(\sigma^2-py-2-CHNPr^i)(\mu-CO)_2(CO)_8]$	71
$[Fe_2Ru_2(\mu_3-CO)_4Cp_2Cp^{*}_{2}]$	327
$[Fe_2Ru_2(\mu_4-\eta^2,\eta^2-C\equiv C)(\mu-H)(CO)_{11}Cp^{*}]$	328
$[Fe_2Ru_2(\mu_4-C=C)(\mu-CO)_2(CO)_8Cp^{*}_{2}]$	328
$[Fe_2Ru_2(\mu_4-C=C)(\mu-dppm)(\mu-CO)_2(CO)_6Cp^{*}_{2}]$	321
$[Fe_2Ru_2(\mu_4-C=C)(\mu-O_2CCHMeCl)(\mu-H)(\mu-CO)_2(CO)_6Cp^{*}_{2}]$	321
$[Fe_2Ru_2(\mu_4-C_2)(\mu-\eta^2-PhC\equiv CPh)(\mu-CO)_2(CO)_4Cp^{*}_{2}]$	329
$[Fe_2Ru_2(\mu_4-\eta^2,\eta^3-C_6H_4)(\mu-CO)(CO)_8Cp_2]$	330
$[Fe_2Ru_2(\mu_4-\eta^2-C\equiv CH)(\mu-dppm)(\mu-CO)_2(CO)_5Cp^{*}_{2}][BF_4]$	321
$[Fe_2Ru_2\{\mu_3-\eta^2,\eta^2-C_3(Ph)C(Ph)C(O)C(Ph)C(Ph)\}(\mu-CO)_2(CO)_6Cp^{*}_{2}]$	329
$[FeRu_2(\mu_3-B_4H_4)(\mu_3-CO)(CO)_3Cp^{*}_{2}]$	332
$[Fe_2Ru_3(\mu_4-S)(\mu-CO)_2(CO)_{12}][NEt_4]_2$	333
$[Fe_2Ru_3(\mu_4-SMe)(\mu-CO)(CO)_{13}][NEt_4]$	333
$[Fe_2Ru_3(\mu_4-Se)(\mu-CO)_2(CO)_{12}][NEt_4]_2$	334
$[Fe_2Ru_5(\mu_6-C_2)(\mu_3-SMe)_2(\mu-PPh_2)_2(\mu-CO)(CO)_{15}]$	335
$[Fe_2Ru_6(\mu_6-\eta^2,\eta^2-C_2)_2(\mu-CO)_3(CO)_{14}Cp^{*}_{2}]$	328
$[Fe_3Ru(\mu_4-Se)_2(\mu-CO)(CO)_{10}]$	336
$[Fe_3Ru(\mu_4-\eta^2-PhC\equiv N)(CO)_{12}]$	337
$[Fe_3Ru_3\{\mu_6-\eta^2,\eta^3-6-(CO)-C_8\}(\mu-CO)(CO)_{12}Cp^{*}_{4}]$	338
$[FeRu_3\{\mu_3-\eta^3-\eta^5-C_5H_3P(Fc)Ph\}(\mu-H)(\mu-CO)(CO)_8Cp]$	341
$[FeOs(\mu-PPh_2)(\mu-CO)(CO)_{11}Cp]$	307
$[FeOs_2(\mu-OH)_2(CO)_{10}]$	309
$[FeOs_2(CO)_{12}]$	309
$[FeOs_3(\mu_3-\eta^5,\sigma^2-PEt_2C_5H_4)(\mu-\eta^5,\sigma^1-C_5H_4)(\mu-H)_2(CO)_8]$	310
$[Fe_2Os_3\{\mu_3-P(\eta^5-C_5H_4)_2\}(\mu-CO)_2(CO)_7(\mu-\eta^5,\sigma^1-C_5H_4)Cp]$	387
$[Fe_2Os(\mu-CO)_2(CO)_{10}]$	311
$[FeOs_3\{\mu_3-PhP(\eta^5-C_5H_4)\}(\mu-CO)_2(CO)_7(\mu-\eta^5,\sigma^1-C_5H_4)]$	310
Fe—Group 9	
$[FeCo_2\{\mu_3-C=NC(O)Ph\}(\mu_3-S)(PPh_3)(CO)_2Cp_2]$	284
$[FeCo_2(\mu_3-S)(CNTol^p)(PPh_3)(\mu_3-CO)(CO)Cp_2]$	285
$[FeCo_2(\mu_3-S)(\mu_3-SMe)(PPh_3)(CO)_2Cp_2]I$	286
$[FeCo_2(\mu_3-S)(\mu_3-C=S)(PPh_3)(CO)_2Cp_2]$	286
$[FeCo_2(\mu_3-S)\{\mu-NHC(S)Me\}(CO)_7]$	287
$[FeCo_2(\mu_3-S)(\mu-PhSCH_2PPh_2)(CO)_7]$	288
$[FeCo_2(\mu_3-S)\{\mu-SC(PPh_2)SCH_3\}(CO)_7]$	289
$[FeCo_2(\mu_3-S)\{P(OCH_2Ph)_3\}(CO)_8]$	290
$[FeCo_2(\mu_3-S)\{\eta^2-4,5-(Ph_2P)_2-1-3-C_5H_2O_2\}(CO)_7]$	291
$[FeCo_2(\mu_3-S)\{\mu-(AsPh)_6\}(CO)_7]$	292
$[FeCo_2(\mu_3-S)\{\mu-(PPh)_6\}(CO)_7]$	292
$[FeCo_2(\mu_3-S)\{\mu-(SCH_2CH_2SP)_2O\}(CO)_7]$	293
$[FeCo_2(\mu_3-S)_2(CO)_9]$	162
$[FeCo_2\{\mu_3-CSC(S)S\}(\mu_3-S)(PPh_3)(CO)Cp_2]$	294,295
$[FeCo_2\{\mu_3-CSC(SMe)S\}(\mu_3-S)(PPh_3)(CO)Cp_2]$	295
$[FeCo_2(\mu_3-Se)(\mu-PPh_2C_5H_4N)(CO)_7]$	296
$[FeCo_2(\mu_3-SPPh)\{\mu_3-(PPh)_5\}(CO)_5]$	292
$[FeCo_2(\mu_3-\eta^2,\eta^2-2-C=CHPh)(AsPh_3)(CO)_8]$	297
$[FeCo_2(\mu_3-\eta^2,\eta^2-C\equiv CPh)(\mu-PPh_2)(PPh_3)\{P(OMe)_3\}(CO)_5]$	298
$[FeCo_2(\mu_3-\eta^2-2-C=CHPh)(PPh_3)(CO)_8]$	297
$[FeCo_2(\mu_3-\eta^2-2-C=CHPh)(\mu-dppm)(CO)_7]$	297
$[FeCo_2(\mu-PPh_2)_2\{PPh(CH_3)_2\}(CO)_5]$	289
$[FeCo_2\{C_6H_{12}N_3(CH_2C_6H_3Bu^tO)_3\}_2]$	299
$[FeCo_2\{\mu-(\eta^5-C_5H_4)_2-B=N(Bu^t)(SiMe_3)\}(CO)_8]$	300
$[FeCo_2\{\mu_3-\eta^2-(COOCH_3)_2C=C\}(CO)_9]$	301
$[FeCo_2\{\mu_3-\eta^2-CCH(Fc)\}(CO)_9]$	302,303
$[FeCo_2(\mu_3-\eta^7-C_{16}H_{22})(\mu-CO)(CO)_6]$	304
$[FeCo_3(\mu_4-P_2O)(\mu_3-P_2)(\mu_3-PO)(\eta^5-1,3-C_5H_3Bu^t{}_2)_3]$	305

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Table 2 (Continued)

	References
$[FeCo_3(\mu-CO)_3(CO)_9][PPN]$	306
$[Fe_2Co(\mu_3-P_4)(\eta^5-C_5H_4Bu^t)Cp^*_2]$	342
$[Fe_2Co(\mu_3-S)(PPh_3)(CO)_8][NEt_4]$	56,423
$[Fe_2Co(\mu_3-S)(\mu_3-Se)(CO)_6Cp]$	346
$[Fe_2Co(\mu_3-Se)(CO)_9][NEt_4]$	344
$[Fe_2Co(\mu_3-Se)(\mu_3-Te)(CO)_6Cp]$	345
$[Fe_2Co(\mu_3-Se)_2(CO)_6Cp]$	346
$[Fe_2Co_2(\mu_4-\eta^4-C{\equiv}CH)(\mu-CO)(CO)_9Cp]$	352
$[Fe_2Co_2(\mu_3-S)\{\mu-PPh_2(\eta^5-C_5H_4)\}_2(CO)_7]$	183
$[Fe_2Co_3(\mu_5-CCH)(\mu-CO)_3(CO)_7Cp_2]$	80
$[Fe_2Co_4\{\mu_6-\eta^2-C{=}C{=}C(H)C\}(\mu-CO)_2(CO)_{14}Cp^*]$	56
$[Fe_2Co_4(\mu_5-\eta^2,\eta^2,\eta^2,\eta^2-C{\equiv}CC{\equiv}C)(\mu-CO)_2(CO)_{14}Cp^*]$	56
$[Fe_2Co_5(\mu_3-\eta^3-C_3HC)(\mu-CO)_5(CO)_9Cp^*_2]$	56
$[Fe_3Co(\mu_3-S)(CO)_{11}Cp]$	347
$[Fe_3Co(\mu_4-S)(CO)_{11}(\eta^5-C_5H_4Me)]$	348
$[Fe_3Co(\mu_4-\eta^2,\eta^2-C{\equiv}CC{\equiv}C)(CO)_{11}Cp^*]$	56
$[Fe_3Co(\mu_4-\eta^2,\eta^2-C{\equiv}C)(\eta^5-C_5Me_4Et)(CO)_{11}]$	393
$[Fe_3Co(\mu-CO)_4(CO)_9][NEt_4]$	354
$[Fe_3Co_2(\mu_5-\eta^2-C{\equiv}CC{\equiv}C)(\mu-CO)(CO)_{11}Cp^*_2]$	56
$[Fe_3Co_3(\mu_6-C)(\mu-CO)(CO)_{14}][PhNMe_3]$	355
$[FeCo_5(\mu_6-C_2)(\mu-CO)_2(CO)_{15}][PPh_4]$	356
$[FeRh_2(\mu_3-S)_2Cl_2Cp^*_2]$	357
$[FeRh_2(\mu-\eta^5,\eta^5-1,1'-C_5H_4SiMe_2C_5Me_4)(\mu-CO)_2(CO)_4]$	86
$[Fe_2Rh(PPh_3)(\mu-CO)_2(CO)_7][PPh_4]$	358
$[Fe_3Rh(\mu_4-Se)(CO)_9Cp^*]$	359
$[Fe_3Rh_3(\mu_3-O)(\mu_3-CO)_3(CO)_{12}][PPN]$	360
$[Fe_4Rh_2(\mu_6-N)(\mu-CO)_3(CO)_{12}][PPh_4]_2$	361
$[Fe_5Rh(\mu_6-N)(\mu-CO)_3(CO)_{12}][PPh_4]$	361
$[FeIr_2(\mu_3-S)_2Cl_2Cp^*_2]$	357
$[FeIr_2(\mu_3-Se)(\mu_3-S)Cl_2Cp^*_2]$	96
$[FeIr_4(\mu_3-S)_4Cp^*_4][BPh_4]_2$	357
$[FeIr_4(\mu_3-S)_4Cp^*_4][BPh_4]$	357
$[FeIr_4(\mu_3-Se)_4Cp^*_4][BPh_4]_2$	91
$[FeIr_4(\mu-CO)_3(CO)_{10}][PPh_4]_2$	363
$[Fe_2Ir(\mu_3-Te)(CO)_7Cp^*]$	359
$[Fe_2Ir_4(\mu-CO)_4(CO)_{12}][Me_3NCH_2Ph][NEt_4]$	363
$[Fe_3Ir(\mu_3-Te)(CO)_9Cp^*]$	359
$[Fe_5Ir(\mu_6-N)(\mu-CO)_4(CO)_{11}][PPh_4]_2$	361
Fe—Group 10	
$[FeNi\{C_6H_{12}N_3(CH_2C_6H_3(Bu^t)S)_3\}_2][ClO_4]_2$	364
$[FeNi\{C_6H_{12}N_3(CH_2C_6H_3(Bu^t)S)_3\}_2][ClO_4]_3$	364
$[FeNi_2(\mu_3-C_2H_2)(CO)_3Cp_2]$	365
$[FeNi_2(\mu_4-\eta^2,\eta^2-C_2H_2)(CO)_6Cp_2]$	365
$[Fe_3Ni(\mu-CO)_4(CO)_8][Me_3NCH_2Ph]_2$	366
$[FeNi_5(\mu-CO)_6(CO)_7][NEt_4]_2$	366
$[Fe_2Ni(\mu_3-S)_2(\mu-dppfc)(CO)_6]$	367
$[Fe_2Ni(\mu-SePh)_6(CO)_6]$	368
$[Fe_2Ni_4(\mu_6-Cl)\{(PhSiO_2)_6\}_2(OMe)_2(MeOH)_4]$	369
$[Fe_4Ni_2(\mu_3-S)_4\{\mu-S(CH_2)_2N(Et)(CH_2)_3N(Et)(CH_2)_2S\}_2I_2]$	370
$[Fe_4Ni_2(\mu_3-S)_4\{\mu-S(CH_2)_2S(CH_2)_3S(CH_2)_2S\}_2(2,4,6-SC_6H_2Pr^i_3)_2]$	370
$[Fe_4Ni_2(\mu_3-S)_4\{\mu-S(CH_2)_2NEt(CH_2)_3NEt(CH_2)_2S\}_2(2,4,6-SC_6H_2Pr^i_3)_2]$	370
$[Fe_4Ni_4(\mu_4-S)_6(PPh_2CH_3)_4I_4]$	371
$[Fe_6Ni_2(\mu_4-S)_6(PPh_2Me)_2I_6][Et_3NCH_2Ph]_2$	371
$[Fe_2Pd(\eta^5-Et_4)_4[\{Fe(\eta^5-C_4Et_4P)_2\}_2Pd]$	372
$[Fe_2Pd_2\{\mu-2,6-(C_5H_4SCH_2)_2-C_5H_3N\}_2(NCMe)_2][BF_4]_4$	377
$[Fe_2Pd_2\{\mu_3-\eta^2,\eta^2-(PPh_2C{\equiv}CPh)\}(\mu-PPh_2)(\mu-I)(PPh_2C{\equiv}CPh)(CO)_7]$	378
$[Fe_2Pd_2(\mu-\eta^5-PC_4Et_4)_2Cl_2Cp_2]$	107
$[Fe_2Pd_2(\mu-\eta^5-PC_4PhMe_2H)_2Cl_2Cp_2]$	107

(*Continued*)

Table 2 (Continued)

	References
[Fe$_3$Pd(μ_4-η^2-C=CHPh)(μ-dppp)(CO)$_9$]	350
[FePt$_2$(μ_3-Se)(PPh$_2$Py)$_2$(CO)$_5$]	380
[FePt$_2$(μ-NHC(O)Bu^t)$_4$(NH$_3$)$_4$][ClO$_4$]$_3$	381
[FePt$_2${μ_3-σ^2,η^2-1,2-(C$\equiv$C)Ph$_2$}(PPh$_3$)$_2$(CO)$_5$]	382
[FePt$_2${μ_3-η^2-PhC=CC=CPh}(PPh$_3$)$_2$(CO)$_5$]	383
[FePt$_2$(μ_3-Se)(PPh$_3$)$_2$(CO)$_5$]	384
[Fe$_2$Pt(μ_3-CP-1,3,5-C$_6$H$_2$Me$_3$)(PPh$_3$)(μ-CO)$_2$(CO)Cp$_2$]	385
[Fe$_2$Pt(μ-H)$_2$(η^5-C$_4$H$_4$BPh)$_2$(NC$_5$H$_4$CH$_3$)$_2$(CO)$_4$]	386
[Fe$_2$Pt$_5$(PBu$^t_3$)$_2$(μ-CO)(CO)$_{11}$]	374
[Fe$_3$Pt$_4$(PBu$^t_3$)(μ-CO)(CO)$_{14}$]	374
[Fe$_4$Pt(μ_5-C)(PPhMe$_2$)$_2$(CO)$_{12}$]	379
[Fe$_4$Pt(μ_5-C)(η^2,η^2-1,5-COD)(CO)$_{12}$]	102
Fe—Group 11	
[Fe$_3$Cu(μ_3-Te)(μ-CO)$_3$(CO)$_6$Cl][PPN]$_2$	389
[Fe$_4$Cu$_2$(μ-PPh$_2$)$_2$(dppp)(μ-CO)$_2$(CO)$_6$]	391
[Fe$_6$Cu$_5$(μ_4-S)$_6$(PPh$_3$)$_2$(μ-CO)$_6$(CO)$_{12}$][NEt$_4$]	392
[Fe$_2$Ag{μ_3-2,6-(PPh$_2$)$_2$C$_5$H$_3$N}$_2$(CO)$_8$][ClO$_4$]	150
[FeAg$_2${μ_3-2,6-(PPh$_2$)$_2$C$_5$H$_3$N}$_2$(OEt$_2$)(μ-CO)(CO)$_2$]	394
[FeAg$_3$(μ-dppm)$_3$(CO)$_4$][NO$_3$]	395
[Fe$_4$Ag$_4$(CO)$_{16}$][PhCH$_2$NMe$_3$]	396
[Fe$_4$Ag$_5$(CO)$_{16}$][NEt$_4$]$_3$	396
[Fe$_4$Ag$_8$(μ-dppm)$_2$(CO)$_{16}$]	397
[Fe$_8$Ag$_{13}$(CO)$_{32}$][PPN]$_2$	398
[FeAu$_2$(PPh$_3$)$_2$(CO)$_4$]	399
[FeAu$_2$(PPh$_3$)$_2$(CO)$_2$(η^5-C$_4$H$_4$BPh)]	138
[FeAu$_3$(μ-dppm)$_2$(CO)$_4$]	395
[Fe$_2$Au(μ-SPr^i)(PPh$_3$)(μ-CO)(CO)$_6$]	401
[Fe$_2$Au$_3$(μ-dppm)(CO)$_8$][NEt$_4$]	402
[Fe$_2$Au$_5$(μ-dppm)$_2$(CO)$_8$][BF$_4$]	402
[Fe$_3$Au(PPh$_3$)(μ-CO)(CO)$_{10}$][PPh$_4$]	403
[Fe$_3$Au(μ_3-O)(PPh$_3$)(μ-CO)$_3$(CO)$_6$][NEt$_4$]	400
[Fe$_3$Au(μ_3-OBu^t)(PPh$_3$)(CO)$_9$]	404
[Fe$_3$Au(μ_3-S)(PPh$_3$)(CO)$_9$]$_2$[Au$_6$(μ_3-S)$_2$(PPh$_3$)$_6$]	400
[Fe$_3$Au(μ_3-SPr^i)(PPh$_3$)(CO)$_9$]	405
[Fe$_3$Au(μ_3-Te)(PPh$_3$)(CO)$_9$][PPh$_4$]	406
[Fe$_3$Au(μ_4-σ^2,η^4-C$\equiv$CBu^t)(PPh$_3$)(CO)$_9$]	407
[Fe$_3$Au$_2$(μ_3-O)(PPh$_3$)$_2$(CO)$_9$]	360
[Fe$_3$Au$_2$(μ_5-P)(μ-H)(PPh$_3$)$_2$(CO)$_9$]	408
[Fe$_3$Au$_3$(μ_3-CCOOEt)(PPh$_3$)$_3$(CO)$_9$]	356
[Fe$_3$Au$_3$(μ_6-P)(PPh$_3$)$_3$(CO)$_9$]	408
[Fe$_3$Au$_4$(μ_7-P)(PPh$_3$)$_4$(CO)$_9$][B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]	409
[Fe$_4$Au(CO)$_{16}$][PhCH$_2$NMe$_3$]$_2$[Cl]	410
[Fe$_4$Au(μ_5-C)(NO)(PPh$_3$)(CO)$_{11}$]	411
[Fe$_4$Au$_2$(μ_5-C)(μ-dppm)(μ-CO)(CO)$_{11}$]	412
[Fe$_4$Au$_4$(CO)$_{16}$][NEt$_4$]	413
[Fe$_4$Au$_8$(μ-dppe)$_2$(CO)$_{16}$]	390
[Fe$_5$Au$_2$(μ_5-C)(μ-dppm)(μ-CO)$_4$(CO)$_{10}$]	414
[Fe$_6$Au(μ_6-C)(PPh$_3$)(μ-CO)$_3$(CO)$_{13}$][NEt$_4$]	411
[Fe$_6$Au$_3${μ_3-1,1,1-C(CH$_2$(PPh$_2$))$_3$CH$_3$}(μ-η^2-2-CH=CHPh)$_3$(μ-CO)$_3$(CO)$_{18}$]	415
Fe—Group 12	
[FeZn$_2$(η^2-NMe$_2$CH$_2$CH$_2$NMe$_2$)$_2$(CO)$_4$Cl$_2$]	420
[Fe$_2$Zn$_4$(THF)$_4$(μ-Cl)$_4$(CO)$_8$]$_n$	420
[Fe$_2$Zn$_4$(μ-Cl)$_6$(CO)$_8$]$_n$[Na(H$_3$CO(CH$_2$)$_2$OCH$_3$)$_3$]$_{2n}$	420
[FeCd$_4$(μ_3-Cl)$_2$(μ-Cl)$_4$(CO)$_4$(μ-THF)(THF)$_4$]$_n$	420
[Fe$_2$Cd(μ-PPh$_2$C$_5$H$_4$N)$_2${Si(OMe)$_3$}$_2$(CO)$_6$]	421
[Fe$_2$Cd$_2$(μ-Br)$_2$(SiPh$_3$)$_2$(PHPh$_2$)$_2$(CO)$_6$]	421
[Fe$_4$Cd(μ-CO)$_4$(CO)$_{12}$][PPh$_4$]$_2$	422

(*Continued*)

Table 2 (Continued)

	References
$\mathrm{[Fe_4Cd_8(\mu\text{-}Cl)_9(THF)_6(CO)_{16}]_2[Fe(THF)_4(H_2O)_2]}$	420
$\mathrm{[Fe_6Cd_6(\mu\text{-}Cl)_2(CH_3OCH_2CH_2OCH_3)_2(CO)_{24}][Na(H_3COCH_2CH_2OCH_3)_3]_2}$	420
$\mathrm{[FeHg_2(\mu\text{-}2\text{-}PPh_2C_5H_4N)(\mu\text{-}Cl)_2Cl_2(CO)_4]}$	149
$\mathrm{[FeHg_2(\mu\text{-}2\text{-}PPhMeC_5H_4N)_2(\mu\text{-}Cl)_2Cl_2(CO)_3]}$	149
$\mathrm{[FeHg_2(\mu\text{-}2\text{-}PPhMeC_5H_4N)_2(\mu\text{-}I)_2I_2(CO)_3]}$	149
$\mathrm{[Fe_2Hg(CO)_4Cp_2]}$	424
$\mathrm{[Fe_2Hg(CO)_8][Yb(NCMe)_2(py)_5]}$	425
$\mathrm{[Fe_2Hg(CO)_8][Yb(egde)_2(NCMe)_2]}$	425
$\mathrm{[Fe_2Hg(COOEt)_2(CO)_8]}$	426
$\mathrm{[Fe_2Hg(COOMe)_2(CO)_8]}$	426
$\mathrm{[Fe_2Hg\{2,6\text{-}(Me)_2C_6H_3CO\}_2(PPh_3)(\mu\text{-}CO)_2(CO)_4]}$	427
$\mathrm{[Fe_2Hg\{Si(OMe)_3\}_2\{PPh_2CH_2P(O)Ph_2\}_2(CO)_6]}$	428
$\mathrm{[Fe_2Hg\{Si(OMe)_3\}_2\{PPh_2CH_2P(S)Ph_2\}_2(CO)_6]}$	428
$\mathrm{[Fe_2Hg\{Si(OMe)_3\}_2(\mu\text{-}dppm)_2(\mu\text{-}CO)(CO)_5]}$	428
$\mathrm{[Fe_2Hg\{\eta^5,\eta^5\text{-}C_5H_4(CH_3)_2CC(CH_3)_2C_5H_4\}_2][BF_4]_2}$	376
$\mathrm{[Fe_2Hg_3Br_2(CO)_8]}$	137
$\mathrm{[Fe_2Hg_3Cl_2(CO)_8]}$	137
$\mathrm{[Fe_2Hg_4(\mu_4\text{-}Cl)_2(\mu\text{-}PPh_2)_2(CO)_8]}$	154
$\mathrm{[Fe_3Hg(\mu_3\text{-}Se)(I)(CO)_9]}$	334
$\mathrm{[Fe_3Hg_4\{\mu_3\text{-}2,6\text{-}(PPh_2)_2C_5H_3N\}_2(CH_3COO)_2(CO)_8]}$	150
$\mathrm{[Fe_3Hg_5\{\mu\text{-}P(Bu^t)_2\}_2(\mu\text{-}Br)_2(CO)_{12}]}$	137
$\mathrm{[Fe_3Hg_{15}(\mu_6\text{-}Br)(\mu_3\text{-}Br)_2(\mu_3\text{-}PBu^t)_8(\mu\text{-}Br)_5(CO)_{12}]}_n$	154
$\mathrm{[Fe_4Hg(\mu\text{-}C{=}CHCH_2OCH_3)_2(\mu\text{-}SBu^t)_2(CO)_{12}]}$	215
$\mathrm{[Fe_4Hg_4\{\mu_3\text{-}2,6\text{-}(PPh_2)_2C_5H_3N\}_2(CO)_{12}]}$	150
$\mathrm{[Fe_4Hg_8(\mu_4\text{-}dpp)_2(\mu_3\text{-}Cl)_4\{P(Pr)_3\}_2(CO)_{16}]}$	137
$\mathrm{[Fe_4Hg_8(\mu_4\text{-}dpp)_2(\mu_3\text{-}Cl)_4(PPh_2Et)_2(CO)_{16}]}$	137
$\mathrm{[Fe_4Hg_{10}(\mu_3\text{-}PBu^t)_4(\mu_3\text{-}Cl)_4(CO)_{16}]}$	137
$\mathrm{[Fe_4Hg_{10}(\mu_4\text{-}dpp)_2(\mu_3\text{-}Br)_4\{P(Pr)_3\}_2(CO)_{24}]}$	137
$\mathrm{[Fe_5Hg_7(\mu\text{-}SBu^t)(CO)_{20}]Cl}$	216
$\mathrm{[Fe_5Hg_{14}(\mu_6\text{-}Cl)_2(\mu_3\text{-}PBu^t)_4(\mu\text{-}PBu^t)_4(CO)_{20}]}$	137
$\mathrm{[Fe_6Hg(\mu_3\text{-}Se)_2(CO)_{18}][NEt_4]_2}$	272
$\mathrm{[Fe_6Hg_{10}(\mu_4\text{-}1,2\text{-}dpp)_2(\mu_3\text{-}Br)_2(\mu\text{-}Br)_2Br_2(CO)_{24}][Li(THF)_4]_2}$	154
$\mathrm{[Fe_7Hg_{12}(\mu_5\text{-}Br)_2(\mu_3\text{-}PBu^t)_4(\mu\text{-}Me_3SiPBu^t)(CO)_{28}][Me_3SiOP(Pr^i)_3]}$	137
$\mathrm{[Fe_8Hg_{12}(\mu_5\text{-}Br)_2(\mu_3\text{-}PBu^t)_4(CO)_{32}][PPh_4]_2}$	154
$\mathrm{[Fe_8Hg_{12}(\mu_5\text{-}Cl)_2(\mu_3\text{-}PBu^t)_4(CO)_{32}][PPh_4]_2}$	154
$\mathrm{[Fe_8Hg_{20}(\mu_5\text{-}Br)_2(\mu\text{-}Br)_2(\mu_3\text{-}PBu^t)_{10}(CO)_{32}]}$	154
$\mathrm{[Fe_8Hg_{20}(\mu_5\text{-}Cl)_2(\mu\text{-}Cl)_2(\mu_3\text{-}PBu^t)_{10}(CO)_{32}]}$	154
$\mathrm{[Fe_{10}Hg(\mu_5\text{-}C)_2(\mu\text{-}CO)_6(CO)_{22}][NEt_4]_2}$	273
$\mathrm{[Fe_{18}Hg_{14}(\mu_4\text{-}S)_2(\mu_3\text{-}S)_4(\mu_3\text{-}SBu^t)_2(\mu\text{-}SBu^t)_6(\mu\text{-}Br)_6Br_{12}(CO)_{24}]}$	216
$\mathrm{[Fe_{26}Hg_{39}(\mu\text{-}SBu^t)_{14}S_8Br_{28}(CO)_{72}]}$	216

Table 3 Heterometallic iron cluster compounds containing three or more different metals with known structure

	References
Fe—Group 5	
$\mathrm{[FeTa_2Mo(\mu_4\text{-}P)_5(CO)_5(\eta^5\text{-}1\text{-}3\text{-}C_5H_3Bu^t{}_2)_2Cp^*]}$	161
Fe—Group 6	
$\mathrm{[FeCrCo(\mu_3\text{-}S)(CO)_8Cp]}$	162
$\mathrm{[FeCrCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4COOEt)]}$	162
$\mathrm{[FeMoW(\mu_3\text{-}S)(CO)_7(\eta^5\text{-}C_5H_4COOMe)]}$	168
$\mathrm{[FeMoW(\mu_3\text{-}S)(CO)_7(\eta^5\text{-}C_5H_4COOMe)_2]}$	168

(Continued)

Table 3 (Continued)

	References
$[\mathrm{FeMoW(\mu_3\text{-}S)(CO)_7(\eta^5\text{-}C_5H_4Me)Cp}]$	169
$[\mathrm{FeMoW(\mu_3\text{-}Se)(CO)_7Cp_2}]$	170
$[\mathrm{FeMoMn(\mu_3\text{-}S)_2(CO)_8Cp}]$	171
$[\mathrm{FeMoCo(\mu_3\text{-}\eta^2,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_6Cp}]$	172
$[\mathrm{FeMoCo(\mu_3\text{-}CPh)(H)(CO)_8(\eta^5\text{-}C_5H_4COOEt)}]$	173
$[\mathrm{FeMoCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4COOEt)}]$	174
$[\mathrm{FeMoCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4COCH_2CH_2COOMe)}]$	175
$[\mathrm{FeMoCo(\mu_3\text{-}S)(C{\equiv}NC_6H_{11})(CO)_7(\eta^5\text{-}C_5H_4COMe)}]$	176
$[\mathrm{FeMoCo(\mu_3\text{-}S)(C{\equiv}NC_6H_{11})_2(CO)_6(\eta^5\text{-}C_5H_4COOMe)}]$	176
$[\mathrm{FeMoCo(\mu_3\text{-}S)(PPh_3)(CO)_7(\eta^5\text{-}C_5H_4COCH_2CH_2COOEt)}]$	178
$[\mathrm{FeMoCo(\mu_3\text{-}S)(PPh_3)(CO)_7(\eta^5\text{-}C_5H_4COMe)}]$	179,180
$[\mathrm{FeMoCo(\mu_3\text{-}Se)(PPh_3)(CO)_7(\eta^5\text{-}C_5H_4COMe)}]$	180
$[\mathrm{FeMoCo(\mu_3\text{-}CPh)(H)(CO)_8(\eta^5\text{-}C_5H_4COOEt)}]$	173
$[\mathrm{FeMoCo(\mu_3\text{-}S)(CO)_8\{\eta^5\text{-}C_5H_4C(O)C_6H_4COOMe\}}]$	181
$[\mathrm{FeMoCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4COOEt)}]$	174
$[\mathrm{FeMoCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4Me)}]$	184
$[\mathrm{FeMoCo(\mu_3\text{-}S)(CO)_8Cp}]$	185
$[\mathrm{FeMoCo(\mu_3\text{-}S)(PPh_3)(CO)_7\{\eta^5\text{-}C_5H_4C(O)EtCOOEt\}}]$	178
$[\mathrm{FeMoCo(\mu_3\text{-}S)(PPh_3)(CO)_7(\eta^5\text{-}C_5H_4COMe)}]$	179
$[\mathrm{FeMoCo(\mu_3\text{-}S)(PPh_3)(CO)_7(\eta^5\text{-}C_5H_4COMe)}]$	180
$[\mathrm{FeMoCo(\mu_3\text{-}S)(\mu\text{-}dppe)(CO)_6(\eta^5\text{-}C_5H_4Me)}]$	177
$[\mathrm{FeMoCo(\mu_3\text{-}Se)(CO)_8(\eta^5\text{-}C_5H_4COMe)}]$	182
$[\mathrm{FeMoNi(\mu_3\text{-}S)(CO)_5(\eta^5\text{-}C_5H_4CHO)Cp}]$	186
$[\mathrm{FeMoNi(\mu_3\text{-}S)(CO)_5(\eta^5\text{-}C_5H_4COMe)Cp}]$	187
$[\mathrm{FeMoNi(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_5CpCp^{*}}]$	27,188
$[\mathrm{FeMoNi(\mu_3\text{-}S)(CO)_5(\eta^5\text{-}C_5H_4CHO)Cp}]$	186
$[\mathrm{FeMoNi(\mu_3\text{-}S)(CO)_5(\eta^5\text{-}C_5H_4COMe)Cp}]$	187
$[\mathrm{FeMoCu(\mu\text{-}S)_4(Br)_2(PPh_3)_2}]$	189
$[\mathrm{FeMoAg(\mu\text{-}S)_4(PPh_3)_2Cl_2}][\mathrm{NEt_4}]$	190
$[\mathrm{Fe_2MoCo(\mu_4\text{-}As_6)(CO)_3Cp^{*}{}_3}]$	211
$[\mathrm{Fe_2MoW(\mu_4\text{-}Se)(\mu_3\text{-}Se)(O)(CO)_8(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)Cp^{*}}]$	212
$[\mathrm{Fe_2MoCo(\mu_3\text{-}S)(CO)_8Cp}]$	185
$[\mathrm{Fe_2MoNi(\mu_4\text{-}S)(CO)_{10}(\eta^5\text{-}C_5H_4COMe)Cp}]$	282
$[\mathrm{Fe_2MoCo_2(\mu_4\text{-}\eta^2\text{-}C{=}CPh)(\mu_3\text{-}Te)_3(CO)_9Cp}]$	210
$[\mathrm{Fe_2MoCo_2(\mu_4\text{-}\eta^2\text{-}C{=}CPh)(\mu_3\text{-}Te)_2(CO)_9Cp}]$	210
$[\mathrm{Fe_2Mo_2Ru(\mu_4\text{-}\eta^2,\eta^2\text{-}C{=}CPhCPh{=}C)(\mu_3\text{-}S)_2(\mu\text{-}CO)(CO)_5Cp_2}]$	227
$[\mathrm{Fe_2Mo_2Rh\{\mu_4\text{-}\eta^2\text{-}2,3\text{-}C{=}CPhC{=}CPh\}(\mu_3\text{-}S)_2(\mu\text{-}CO)(CO)_5Cp}]$	227
$[\mathrm{Fe_2Mo_2W(\mu_3\text{-}S)_2(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)_2(\mu\text{-}O)(O)(CO)_9Cp_2}]$	228
$[\mathrm{Fe_2Mo_2Co_2(\mu_3\text{-}S)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4COCH_2CH_2C(O)C_5H_4\}(CO)_{16}}]$	225
$[\mathrm{Fe_2Mo_2Ni_2(\mu_3\text{-}S)_2(CO)_{10}\{\mu\text{-}\eta^5,\eta^5\text{-}1,4\text{-}C_5H_4(COEtCO)C_5H_4\}Cp_2}]$	282
$[\mathrm{Fe_2Mo_2Ni_2\{(\mu_3\text{-}S)(CO)_5Cp\}_2\{\mu\text{-}1,4\text{-}(C_5H_4)_2COOCH_2CH_2CO\}}]$	282
$[\mathrm{Fe_4MoW(\mu_4\text{-}S)(\mu_3\text{-}S)_3(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(CO)_{14}Cp^{*}}]$	212
$[\mathrm{Fe_4MoAuHg(\mu_5\text{-}C)(PPh_3)(CO)_{15}Cp}]$	241
$[\mathrm{Fe_4MoHg(\mu_4\text{-}C)(CO)_{15}Cp}][\mathrm{PPN}]$	242
$[\mathrm{Fe_4Mo_2W(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu_3\text{-}S)_4(\mu\text{-}O)_2(\mu\text{-}S)(CO)_{12}Cp^{*}}]$	212
$[\mathrm{Fe_5MoAu(\mu_6\text{-}C)(PMe_3)(\mu\text{-}CO)_2(CO)_{15}}][\mathrm{NEt_4}]$	243
$[\mathrm{Fe_5MoAu_2(\mu_6\text{-}C)(\mu\text{-}dppm)(\mu\text{-}CO)_3(CO)_{14}}]$	243
$[\mathrm{Fe_{12}Mo_4K_3(\mu_6\text{-}S)_4(\mu_5\text{-}S)_4(\mu_3\text{-}S)_{12}(\mu\text{-}S)_2(PEt_3)_4(C_6Cl_4O_2)_4}][\mathrm{PPh_3Me}]_5$	246
$[\mathrm{FeWRu_4(\mu_6\text{-}\eta^2,\eta^2,\eta^2,\eta^2\text{-}C{\equiv}CC{\equiv}C)(\mu\text{-}H)(CO)_{17}Cp}]$	248
$[\mathrm{FeWCo(\mu_3\text{-}Se)(CO)_8(\eta^5\text{-}C_5H_4COOMe)}]$	249
$[\mathrm{FeWCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4CHO)}]$	250
$[\mathrm{FeWCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4COC_6H_4COOMe)}]$	181
$[\mathrm{FeWCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4COMe)}]$	251
$[\mathrm{FeWCo(\mu_3\text{-}S)(CO)_8(\eta^5\text{-}C_5H_4COOEt)}]$	252
$[\mathrm{FeWCo(\mu_3\text{-}S)(CO)_8Cp}]$	253
$[\mathrm{FeWCo(\mu_3\text{-}S)(C{\equiv}NC_6H_{11})(CO)_7(\eta^5\text{-}C_5H_4COMe)}]$	176
$[\mathrm{FeWCo(\mu_3\text{-}S)(C{\equiv}NC_6H_{11})_2(CO)_6(\eta^5\text{-}C_5H_4COOMe)}]$	176

(*Continued*)

Table 3 (Continued)

	References
[FeWCo(μ_3-S)(PPh$_3$)(CO)$_7$(η^5-C$_5$H$_4$COMe)]	179
[FeWCo(μ_3-Se)(CO)$_8$(η^5-C$_5$H$_4$COOMe)]	249
[FeWCo(μ_3-S)(C$\equiv$NC$_6$H$_{11}$)(CO)$_7$(η^5-C$_5$H$_4$COMe)]	176
[FeWCo(μ_3-S)(C$\equiv$NC$_6$H$_{11}$)$_2$(CO)$_6$(η^5-C$_5$H$_4$COMe)]	176
[FeWCo(μ_3-S)(C$_9$H$_7$)(CO)$_8$]	247
[FeWCo(μ_3-S)(CO)$_8${η^5-C$_5$H$_4$)$_2$C(O)C$_6$H$_4$COOMe}]	181
[FeWCo(μ_3-S)(CO)$_8$(η^5-C$_5$H$_4$CHO)]	250
[FeWCo(μ_3-S)(CO)$_8$(η^5-C$_5$H$_4$COMe)]	251
[FeWCo(μ_3-S)(CO)$_8$(η^5-C$_5$H$_4$COOEt)]	252
[FeWCo(μ_3-S)(CO)$_8$Cp]	253
[FeWCo(μ_3-S)(PPh$_3$)(CO)$_7$(η^5-C$_5$H$_4$COMe)]	179
[FeWCo(μ_3-S)$_2${μ-1,4-(C$_5$H$_4$)$_2$COEt(O)}(CO)$_{16}$]	225
[FeWCu(μ-S)$_4$(PPh$_3$)$_2$Br$_2$][NEt$_4$]	254
[FeWCu(μ-S)$_4$(PPh$_3$)$_2$Cl$_2$][NEt$_4$]	190
[FeWAg(μ-S)$_4$(PPh$_3$)$_2$Br$_2$][NEt$_4$]	256
[FeWAg(μ-S)$_4$(PPh$_3$)$_2$Cl$_2$][NEt$_4$]$_4$	190
[Fe$_2$WCo(μ_4-C)(μ-dmpe)(CO)$_{11}$][PPN]	260
[Fe$_2$WRu(μ_4-C$_2$C$\equiv$C)(PPh$_3$)$_2$(CO)$_8$Cp$_2$]	261
[Fe$_2$WRh(μ_4-η^2,η^2-C$\equiv$CC$\equiv$C)(PPh$_3$)(CO)$_{11}$Cp]	262
[Fe$_2$WRu$_3$(μ_6-η^2,η^2,η^2, η^2-C$\equiv$CC$\equiv$C)(μ-H)(CO)$_{17}$Cp]	248
[Fe$_2$WRu$_4$(μ_6-η^2,η^2,η^2, η^2-C$\equiv$CC$\equiv$C)(μ-H)(CO)$_{17}$Cp]	248
[FeW$_2$Ru$_2$(μ_3-η^4-C$\equiv$CPh)$_2$(μ_3-S)$_2$(CO)$_9$Cp$_2$]	227
[Fe$_2$W$_2$Co$_2${(μ_3-S)(CO)$_8$}$_2${μ-η^5,η^5-C$_5$H$_4$CO(CH$_2$)$_2$C(O)C$_5$H$_4$}]	225
[Fe$_2$WCo(μ_4-C)(μ-dmpm)(CO)$_{11}$][PPN]	260
[Fe$_3$W$_2$Ru$_2$(μ_3-η^2,η^2-C$\equiv$CPh)$_2$(μ_3-S)$_2$(CO)$_9$Cp$_2$]	227
[Fe$_4$WIr(μ_6-η^2,η^2,η^2, η^2-C$\equiv$CC$\equiv$C)(PPh$_3$)(CO)$_{16}$Cp]	262
[Fe$_5$WHg(μ_5-C)(μ-CO)$_3$(CO)$_{14}$Cp][NEt$_4$]	273
Fe—Group 7	
[FeMnCo(μ_3-CPh)(μ-CO)$_2$(CO)$_6$Cp]	274
[FeMnPt(μ_3-η^2-C=CPh)(PPh$_2$CH$_2$PPh$_2$O)(μ-CO)(CO)$_5$Cp]	275
[FeReCo(μ_3-CPh)(μ-CO)$_2$(CO)$_6$Cp]	274
[FeReCo$_2$(μ_3-η^2,η^2-C$\equiv$CPh)(μ-CO)(CO)$_{12}$]	283
Fe—Group 8	
[FeRuPt(μ_3-η^2,η^2-C$_3$HPh)(PPh$_3$)(CO)$_5$Cp]	316
[FeRuPt(μ_3-η^3-C$_3$HPh)(PPh$_3$)$_2$(μ-CO)(CO)$_3$Cp]	316
[FeRuPt(μ_3-η^2,η^2-CH$_2$=C=CPh)(PPh$_3$)(CO)$_5$Cp]	316
[FeRuPt(μ_3-η^3-1-CH$_2$=C=CPh)(PPh$_3$)$_2$(μ-CO)(CO)$_3$Cp]	316
[FeRuCo$_2$(μ_4-η^2-C$\equiv$C)(μ-CO)$_2$(CO)$_8$Cp*]	352
[Fe$_2$Ru$_2$Pd(μ_5-C)(μ-H){η^3-β-Me$_2$(C$_8$H$_9$)}(CO)$_{12}$]	331
[Fe$_3$RuPd$_2$(μ_6-C)(η^3-C$_{10}$H$_{15}$)$_2$(CO)$_{12}$]	339
Fe—Group 9	
[Fe$_3$CoRh(μ_5-C)(PPh$_3$)(μ-CO)(CO)$_{12}$]	349
[Fe$_3$CoPd(μ_5-C)(η^3-CH$_2$=CH=CH$_2$)(CO)$_{12}$]	351
[Fe$_3$CoPd(μ_5-C)(η^3-CH$_2$=CH=CH$_2$)(CO)$_{12}$]	351
[Fe$_3$CoAu(μ_5-C)(PPh$_3$)(CO)$_{12}$]	317
[Fe$_3$CoAu(μ_5-C)(PPh$_3$)(CO)$_{12}$]	353
[Fe$_4$CoNi(μ_6-C)(μ-CO)(CO)$_{14}$][NEt$_4$]	355
[Fe$_4$CoNi(μ_6-C)(μ-CO)(CO)$_{14}$][NEt$_4$]	355
[Fe$_2$Rh$_2$Au(PPh$_3$)(μ-CO)$_3$(CO)$_9$][PPh$_4$]	358
[Fe$_3$Rh$_2$Au(PPh$_3$)(μ-CO)$_3$(CO)$_9$][PPh$_4$]	358
[Fe$_3$Rh$_3$(μ_3-O)(μ_3-CO)$_3$(CO)$_{12}$][PPN]	360
[Fe$_4$Rh$_2$(μ_6-N)(μ-CO)$_3$(CO)$_{12}$][PPh$_4$]$_2$	361
[Fe$_4$Rh$_2$Au$_2$(μ_6-C)(PPh$_3$)$_2$(μ-CO)$_5$(CO)$_{10}$]	362
Fe—Group 10	
[Fe$_2$PdHg(μ-dppm)$_2$(Si(OMe)$_3$)$_2$(μ-CO)(CO)$_5$]	373
[Fe$_3$PdPt$_3$(PBu$^{t}_{3}$)(μ-CO)(CO)$_{14}$]	374

(Continued)

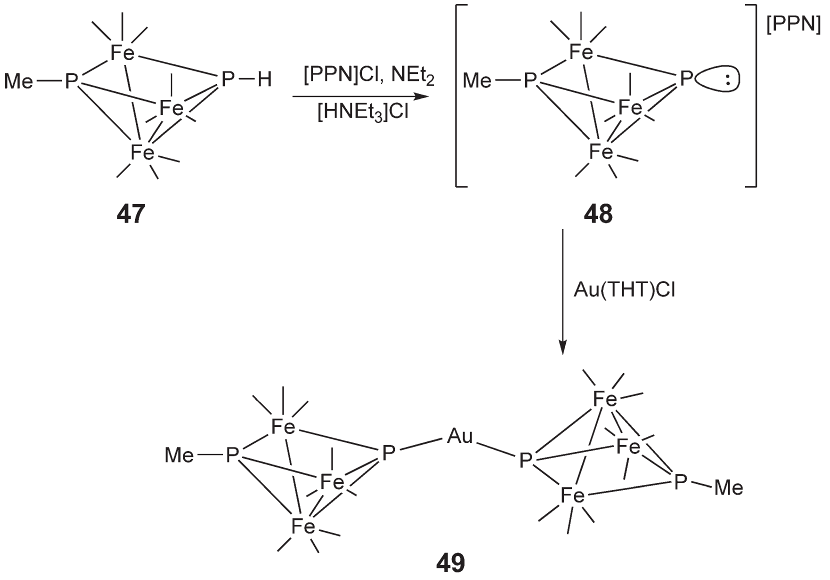
Table 3 (Continued)

	References
$[Fe_2PdSn(\mu\text{-dppm})_2(Bu)_2(CO)_6]$	375
$[FePdGe(\mu\text{-dppm})(NBu^t{}_2SiMe_2)\{\mu\text{-}Si(OMe)_3\}(CH_3)(\mu\text{-}CO)(CO)_2]$	116
$[Fe_3Pd_2Ru(\mu_6\text{-}C)\{\eta^3\text{-}Me_2(C_8H_9)\}_2(CO)_{12}]$	339
$[FePtAu_2\{\mu\text{-}P(C_6H_{11})_2\}(\eta^4\text{-COD})(PPh_3)_2(CO)_3][PF_6]$	102
$[FePtHg(dppm)(NCBu^t)\{Si(OMe)_3\}(C_6Cl_5)(PPh_3)(CO)_3]$	144
$[Fe_2Pt_3Pd_2(PBu^t{}_3)_2(\mu\text{-}CO)(CO)_{11}]$	374
$[Fe_3Pt_3Pd(PBu^t{}_3)(\mu\text{-}CO)(CO)_{14}]$	374
Fe—Group 11	
$[Fe_2CuHg(\mu\text{-dppm})_2(Si(OMe)_3)_2(CO)_6][PF_6]$	388
$[Fe_4Cu_2Au_6(\mu\text{-dppe})_2(CO)_{16}]$	390
$[Fe_4Cu_2Au_6(\mu\text{-1,2-dppe})_2(CO)_{16}]$	390
$[Fe_4Ag_4Au_4(\mu\text{-dppe})_2(CO)_{16}]$	397
$[Fe_4AuHgMo(\mu_5\text{-}C)(PPh_3)(CO)_{15}Cp]$	241
$[Fe_5AuMo(\mu_6\text{-}C)(PMe_3)(\mu\text{-}CO)_2(CO)_{15}][NEt_4]$	243
$[Fe_5Au_2Mo(\mu_6\text{-}C)(\mu\text{-dppm})(\mu\text{-}CO)_3(CO)_{14}]$	243

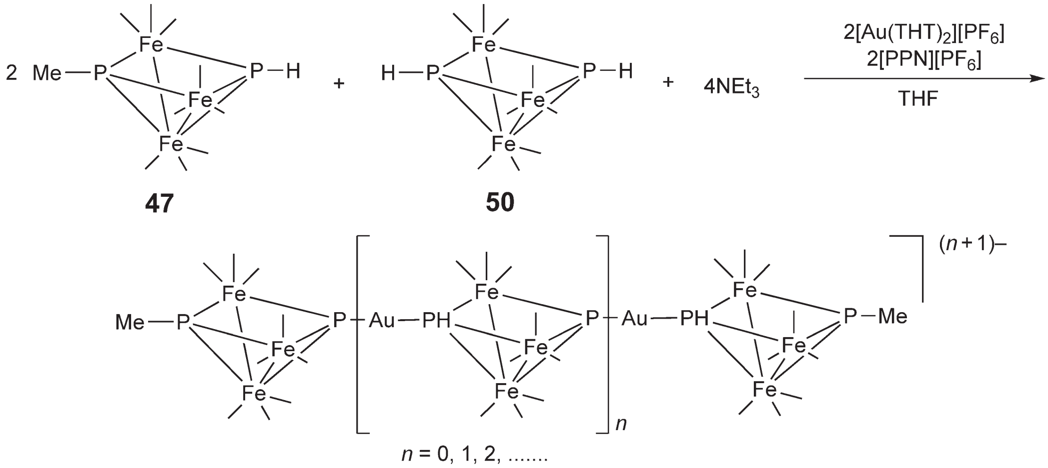
this class of compounds. Several aspects of study on iron mixed-metal clusters should be highlighted, as they either mark significant differences in these important elements compared with the heavier congeners, or illustrate important chemical principles that are of great interest to the chemistry community.

One of the fascinating properties of transition metal cluster compounds is their conformational non-rigidity in both solution and solid state. Studies on the dynamic behavior of metal clusters in the solid state shed light on the important problem of adsorbate mobility on metal surfaces. $[Fe_3(CO)_{12}]$ is a well-known example that shows solid-state fluxionality, with a number of mechanisms having been suggested.[151–153] In this connection, a series of mixed-metal clusters with the formula $[Fe_nM_{3-n}(CO)_{12}]$ ($M = Ru$, $n = 1, 2$; $M = Os$, $n = 2$) have been investigated by ^{13}C magic angle spinning (MAS) NMR spectroscopy, extended X-ray absorption fine structure (EXAFS), and VT X-ray diffraction techniques. Dynamic disorders that arise from a reorientational jumping motion of the metal triangle in $[Fe_2Os(CO)_{12}]$ were established by crystallography.[308,311] This observation gave new insight into the "old" problem that is associated with $[Fe_3(CO)_{12}]$ fluxional processes. In addition, $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ also showed a dynamic disorder that is associated with metal atoms in the crystalline solid. Both of these compounds undergo a phase transition from a non-centrosymmetric space group at low temperatures to a centrosymmetric space group at higher temperatures due to an increase in the metal atom disorder.[318,437]

Methods of rational cluster buildup are a central area of intense research for organometallic chemists. The ionic coupling reaction between cluster anions and metal electrophiles is successful for many metal combinations. In particular, the coinage metals were incorporated with a larger number of transition metal carbonyl cluster anions to generate mixed-metal clusters. Gold(I) complexes show a pronounced tendency to self-adhere, and give rise to many stable homo- and heterometallic clusters with diverse structures. Schauer *et al.* showed that Au(I) acted as a link in the preparation of extended cluster chains. The deprotonation of **47** with triethylamine gave anionic **48**, which contains a lone pair on the phosphorus center. Subsequent reaction with a 0.5 equiv. of [Au(THT)Cl] (THT = tetrahydrothiophene) afforded the dicluster **49** in quantitative yield. Extended cluster chains were prepared by the utilization of a mixture of **47** and bifunctional **50** as the cluster source. ^{31}P NMR spectroscopy was used to characterize these oligomeric species.[416]

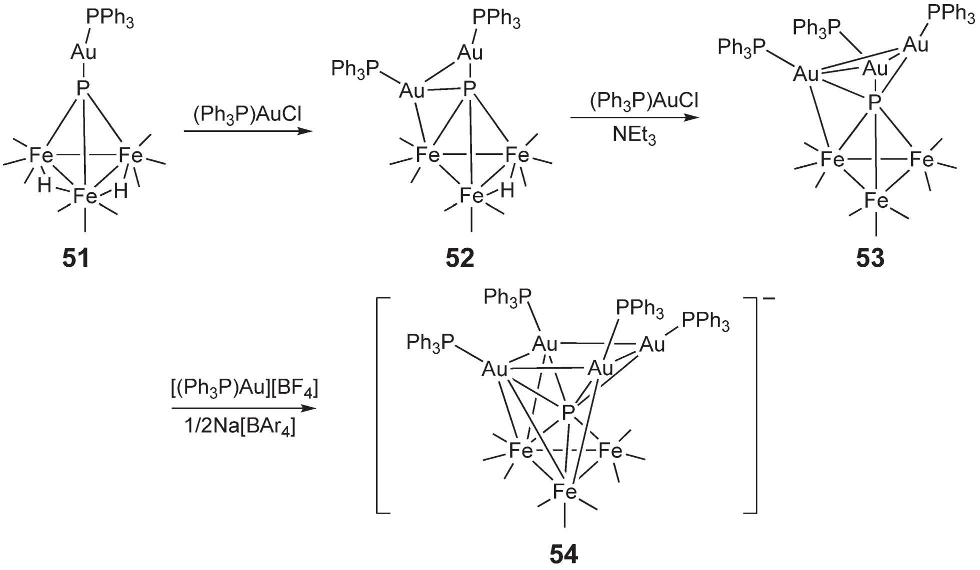


47 **48** **49**



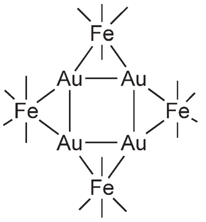
47 **50**

AuPR$_3$ units were also employed through a systematic addition to build up Fe–Au mixed-metal clusters **51–54** that contain encapsulated phosphorus atoms. Cluster **54** challenged the classical bonding theory, as one would regard the cluster as an $Fe_3(CO)_9$ derivative of $[P\{Au(PPh_3)\}_4]^+$, in which bonding to the Fe_3 core requires six electrons from the P^{3-} ion.[409]

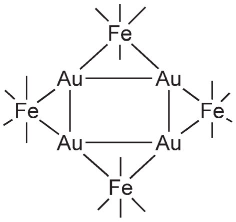


51 **52** **53** **54**

A series of high-nuclearity Fe–M (M = Cu, Ag, and Au) clusters that are stabilized with $Fe(CO)_4$ fragments were prepared and studied by Longoni *et al.* They display extensive metal–metal connectivity with coinage metals that contain non-coordinating ligands. The reaction of $[Fe(CO)_4]^{2-}$ with $[AuBr_2]^-$ in THF gave the $[Fe_4Au_4(CO)_{16}]^{4-}$ **55** cluster anion, which exists in two structural modifications that consist of a square gold core **55a** and a rectangular gold core **55b** that are bridged by $Fe(CO)_4$ groups at the edges.[413]

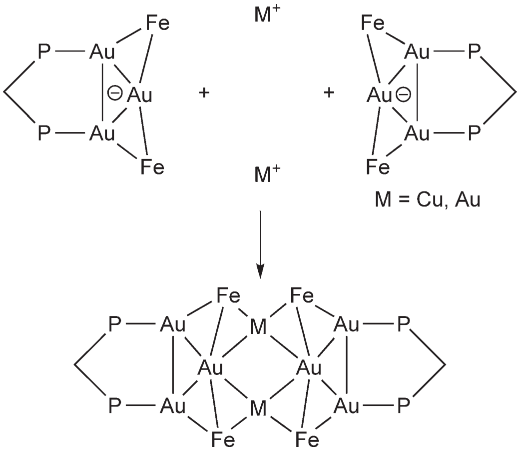

Square isomer

55a

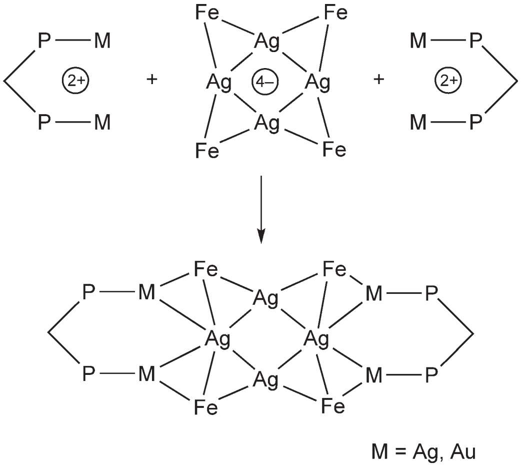

Rectangular isomer

55b

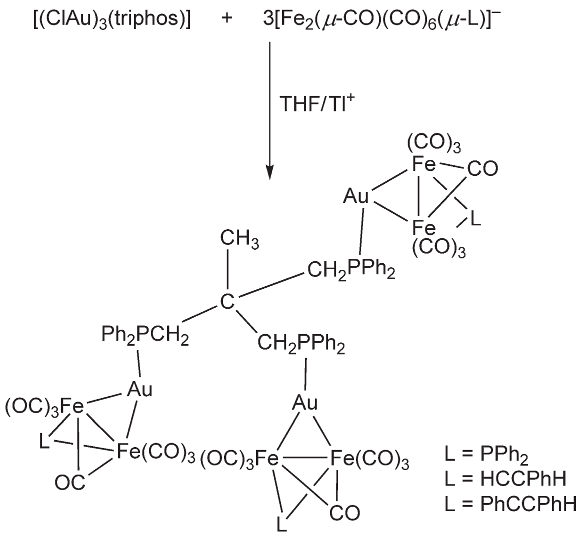
Trimetallic systems that contain Fe and two different coinage metals are accessible through two synthetic routes, as shown in Schemes 1 and 2.[390,397] Electronic structures of $[Fe_4M_4(CO)_{16}]^{4-}$ (M = Cu, Ag, Au) have been studied using density functional calculations. A charge transfer from the coinage metal to the $Fe(CO)_4$ groups was observed,



Scheme 1



Scheme 2

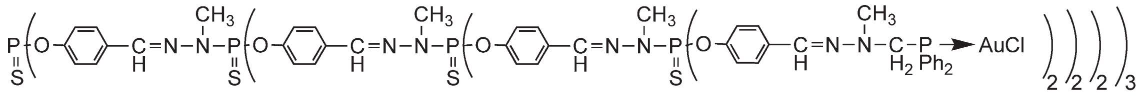


Scheme 3

and thus the coinage metal can be regarded as being in a formal +1 oxidation state. The electron-deficient nature of these compounds is also apparent.[417]

Multidentate phosphine–gold(I) fragments can be used to build up high-nuclearity mixed-metal clusters. The interaction of [(triphos)(AuCl)$_3$] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) with the iron anions [Fe$_2$(μ-L)(CO)$_7$]$^-$ (L = PPh$_2$, HC=CHPh, PhC=CHPh, CO) gave the corresponding mixed-metal clusters [{Fe$_2$(μ-L)(CO)$_7$Au}$_3$(triphos)], as shown in Scheme 3.[415]

Based on a similar principle, a series of ClAu-terminated dendrimers, such as the third-generation dendrimer, (ClAu)$_{24}$[G$_3$] **56**, when treated with the iron anions [Fe$_2$(PPh$_2$)(CO)$_7$]$^-$ and [Fe$_3$(CO)$_{11}$]$^{2-}$, led to the new dendrimer species that is decorated on the surface by Fe$_2$Au or Fe$_3$Au units, including one example that has up to 192 Fe$_2$Au clusters.[418,419]

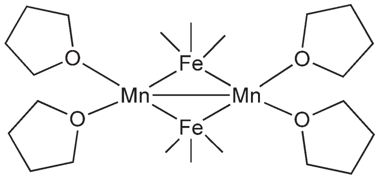


$$\underset{\|}{\overset{}{P}}(=S)\left(O-C_6H_4-CH=N-N(CH_3)-P(=S)\left(O-C_6H_4-CH=N-N(CH_3)-P(=S)\left(O-C_6H_4-CH=N-N(CH_3)-P(=S)\left(O-C_6H_4-CH=N-N(CH_3)-CH_2-PPh_2\rightarrow AuCl\right)_2\right)_2\right)_2\right)_3$$

56

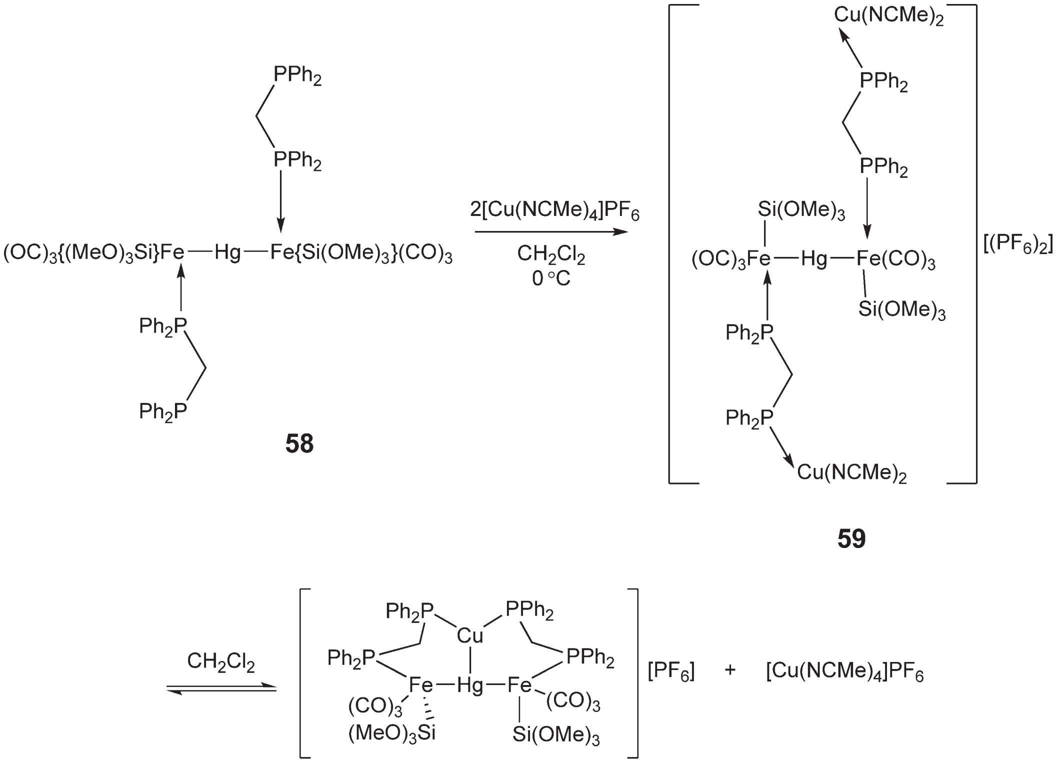
Fenske *et al.* reported the syntheses and structures of several giant mixed-metal Fe–Hg clusters. The reactions of [Fe(CO)$_4$(HgX)$_2$] (X = Cl, Br) with Bu^{t}SSiMe$_3$ led to the orange compound [Fe$_5$Hg$_7$(CO)$_{20}$(SBu^t)$_3$Cl] for X = Cl, and [Fe$_{18}$Hg$_{14}$(CO)$_{24}$S$_6$(SBu^t)$_8$Br$_{18}$] and [Fe$_{26}$Hg$_{39}$(CO)$_{72}$S$_8$(SBu^t)$_{14}$Br$_{28}$] for X = Br, respectively.[433]

A new type of xenophilic metal cluster that was termed by Whittlesey was synthesized and studied. These clusters are compounds that contain two very different types of metal centers that are bonded together through substantial covalent interaction. The neutral cluster **57** was obtained readily from the reaction of the metal-bridged complex Mn[Mn$_7$(THF)$_6$(CO)$_{12}$]$_2$ with Fe(CO)$_5$ in THF, and is an important example of this class of novel clusters.[279]



57

Braunstein *et al.* demonstrated, for the first time, the existence of d^{10} closed-shell interactions between Cu(I) and Hg(II) in a system that contained a linear Fe–Hg–Fe chain. The heterotrinuclear Fe–Hg complex **58** with free rotation about the metal–metal bonds reacted with [Cu(NCMe)$_4$]PF$_6$ in CH$_2$Cl$_2$ at 0 °C to give the yellow trimetallic cluster **59** in quantitative yield. At RT, cyclic species **60** was formed, together with 1 equiv. of [Cu(NCMe)$_4$]PF$_6$ regenerated. X-ray analysis revealed that the Cu–Hg distance of 2.689(2) Å is comparable to the sum of the covalent radii of the two elements. In addition, extended Hückel calculations on a model system of **60** showed that the effective interaction between Cu and Hg involves the 6*s* orbital of Hg and the $d_x{}^2$ orbital of the copper fragment.[388] More recently, the cluster **58** was also employed to incorporate a Pd(0) atom that is stabilized by d^{10}–d^{10} interaction.[373]

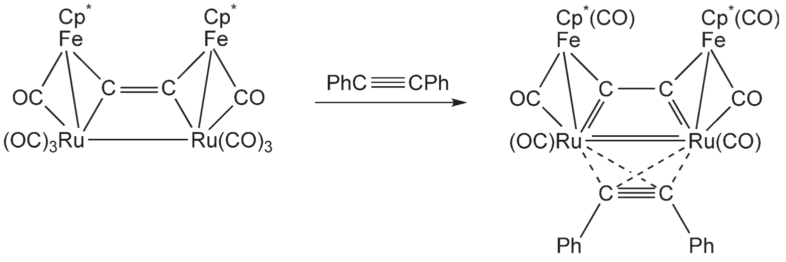


58

59

60

The ability of metal clusters to support organic ligands in unusual coordination modes or valence states is a well-recognized research area. The cooperative interaction that is offered by different metals in a heterometallic system gives another dimension to this capacity. A recent report by Akita *et al.* neatly illustrates this statement through the isolation of a μ_4-dicarbyne-containing cluster with unprecedented coordination mode. The reaction of the permetallated ethene [Fe$_2$Ru$_2$(μ_4-C=C)(CO)$_{10}$Cp$^*{}_2$] with diphenylacetylene yielded the adduct **61** with a novel C_2-binding mode that contains a dimetallacyclobutatriene core.[329]



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6.11

Mononuclear Ru/Os Compounds without Hydrocarbon Ligands

M K Whittlesey, University of Bath, Bath, UK

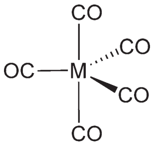
6.11.1 Introduction

Ruthenium and osmium porphyrin carbonyl complexes have been excluded from this review; readers are referred to the following leading references for further details.[1–4]

6.11.2 Simple Carbonyls, Anions and Cations

6.11.2.1 Homoleptic Carbonyl Complexes

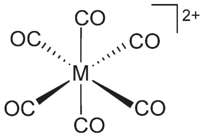
The main developments in the chemistry of the parent pentacarbonyl complexes $[M(CO)_5]$ ($M = Ru$ **1a**, Os **1b**) and their derivatives have been largely computational in nature. A range of approaches has been applied to determining Ru and Os carbonyl bond-dissociation energies and bond lengths in these species. While exact values show some differences, all cases reveal the Os–CO bond to be stronger than the Ru–CO bond. The first ligand-dissociation energies of **1a** and **1b** were calculated to be 127 and 174 kJ mol^{-1}, respectively, using the coupled-cluster theory approach. Good correlation is seen between the calculated M–C bond lengths ($r(Ru–CO_{ax}) = 1.943$, $r(Ru–CO_{eq}) = 1.952$, $r(Os–CO_{ax}) = 1.963$, $r(Os–CO_{eq}) = 1.945$ Å) and those measured by gas-phase electron diffraction for $M(CO)_5$. The computed $M–CO_{ax}$ bond lengths for singlet $[M(CO)_4]$ are significantly longer than the equatorial distances.[5] A non-local, quasi-relativistic, density functional method ($NL-SCF+QR$) has determined a shortening of the M–C distance and strengthening of the M–CO dissociation energies upon moving from **1a** to **1b**. Relativistic effects are proposed to explain the shortening of M–CO by ca. 0.07 Å on going from Ru to Os as well as the bond strengthening (calculated first bond-dissociation energy of 136 (Ru) to 143 (Os) kJ mol^{-1}).[6]



1a: M = Ru
1b: M = Os

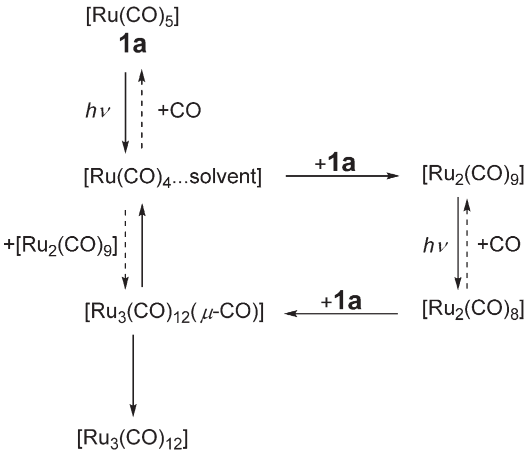
Experimentally, high-resolution variable-energy photoelectron spectra of [Os(CO)$_4$(L)] (L = CO, PMe$_3$) have allowed assignment of the Os 5*d*-based bands and established that the electronic structure of [Os(CO)$_5$] **1b** is similar to that of the iron analog, both of which are known to be trigonal bipyramidal.[7] Laser ablation of Ru and Os atoms in CO-doped low-temperature Ne matrices provides a route to [Ru(CO)$_x$] and [Os(CO)$_x$] (x = 1–5) during sample deposition or upon annealing. Subsequent electron capture affords [Ru(CO)$_x$]$^-$ and [Os(CO)$_x$]$^-$ (x = 1–4), while [RuCO]$^+$ and [OsCO]$^+$ cations are produced by metal cation reactions and identified from ^{13}CO and C^{18}O isotopic substitution, density functional calculations, and behavior on doping with the electron trap CCl$_4$.[8] Treatment of [M(CO)$_4$]$^{2-}$ with HgCl$_2$ (ratio 2 : 1) in THF yields [Hg{M(CO)$_4$}$_2$]$^{2-}$ (M = Ru*, Os*), which display high thermal stability, not decomposing until 170 and 220 °C, respectively. (Throughout the chapter, complexes which have been structurally characterized are denoted with an asterisk (*).) When a 1 : 1 ratio was employed, the polymeric complexes [Hg{M(CO)$_4$}]$_x$ were formed.[9]

In closely related work, [Ru(CO)$_6$]$^{2+}$ **2a** and [Os(CO)$_6$]$^{2+}$ **2b** have been spectroscopically characterized (FT Raman, FTIR, ^{13}C MAS-NMR) as the [Sb$_2$F$_{11}$]$^-$ salts following the reductive carbonylation of [M(SO$_3$F)$_3$] (M = Ru, Os) under 1 atm CO in liquid SbF$_5$ at 60–90 °C.[10] This methodology, along with a route employing the reductive carbonylation of [OsF$_6$] in HF/SbF$_5$ to give **2b**, has allowed the very recent structural characterization of both the Ru and Os dications as their [SbF$_6$]$_2$ and [Sb$_2$F$_{11}$]$_2$ salts. The structural properties prove to be independent of the anion.[11,12]



2a: M = Ru
2b: M = Os

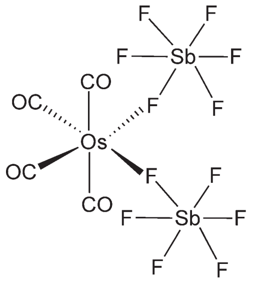
Time-resolved infrared spectroscopy (TRIR) has been used to study the photochemistry of [Ru$_3$(CO)$_{12}$], [Ru(CO)$_5$] **1a**, and [Ru$_2$(CO)$_9$] in solution (Scheme 1).[13,14]



Scheme 1

6.11.2.2 Carbonyl Halide Complexes

The structurally characterized octahedral tetracarbonyl complex *cis*-$[Os(CO)_4(FSbF_5)_2]$ 3 is formed upon fluorination of $[Os_3CO_{12}]$ with HF/SbF_5.[15] The oxidative fluorination of $[M_3(CO)_{12}]$ with XeF_2 in anhydrous HF provides a route to *cis*-$[M(CO)_4F_2]$ (M = Ru 4a, Os 4b). Both the ruthenium and osmium complexes were characterized by multinuclear NMR spectroscopy, along with $[M(CO)_5F]^+$ (M = Ru 5a, Os 5b), *mer*- and *fac*-$[Ru(CO)_3F_3]^-$ 6 and 7, and a range of dinuclear complexes, which were formed as minor products. Removal of the HF solvent *in vacuo* results in conversion of $[M(CO)_4F_2]$ to the tetrameric species $[\{Os(CO)_3F_2\}_4]$.[16,17]



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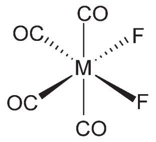
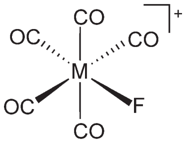
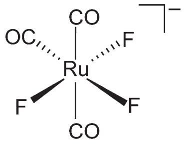


4a: M = Ru
4b: M = Os



5a: M = Ru
5b: M = Os



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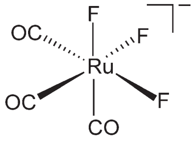
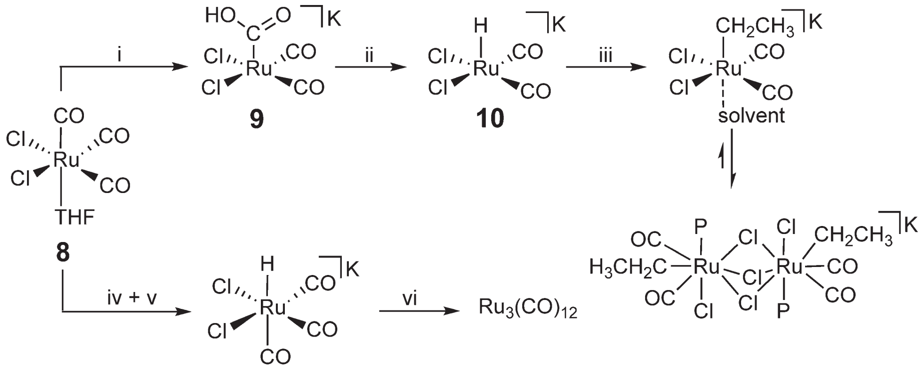


7

The synthesis and reactivity of simple ruthenium carbonyl halides has received some renewed attention. Addition of [PPN]Cl to $[Ru(CO)_3Cl_2]_2$ at room temperature generates $[PPN][Ru(CO)_3Cl_3]$, which upon heating to 160 °C in DMF is converted into $[PPN][Ru(CO)_2Cl_3(\kappa\text{-}(O)\text{-}OCHNMe_2)]^*$.[18] Addition of NaCN to $[Ru(CO)_3Cl_2]_2$ in the presence of CO, followed by addition of $[PPh_4]Cl$, produces $[PPh_4][Ru(CO)_3(CN)_3]^*$.[19] Treatment of $[Ru(CO)_2Cl_2(THF)]$ 8 with 1 equiv. of KOH in 2-methoxyethanol at room temperature results in the ready formation of the hydroxycarbonyl species $K[Ru(CO)_2\{C(O)OH\}Cl_2]$ 9, which can dimerize[20] or (as shown by trapping experiments with ethene) undergo decarboxylation to yield $K[Ru(CO)_2HCl_2]$ 10. In the presence of CO, this is converted to the unseen carbonyl hydride intermediate $K[Ru(CO)_3HCl_2]$, which affords $[Ru_3(CO)_{12}]$ via reductive elimination of HCl.[21] On the basis of these steps, a one-pot route has been developed that gives a 90% yield of $[Ru_3(CO)_{12}]$ from $RuCl_3{\cdot}3H_2O/KOH/CO$ in less than 4 h (Scheme 2).[22]

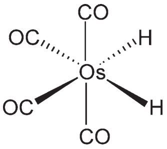


i, KOH; ii, Δ; iii, C_2H_4; iv, KOH; v, CO, Δ; vi, CO

Scheme 2

6.11.3 Ruthenium and Osmium Carbonyl Hydrides

Room temperature solutions of $[M_3(CO)_{12}]$ in anhydrous HF show ^{1}H and ^{13}C{^{1}H} NMR spectra consistent with the formation of the pentacarbonyl species $[M(CO)_5H]^+$ (M = Ru, Os).[23] Microwave rotational spectroscopy has been used to establish the gas-phase structure for six isotopomers of *cis*-$[Os(CO)_4H_2]$ **11**. The H···H distance of 2.40(2) Å is consistent with the complex being viewed as a dihydride rather than a dihydrogen complex.[24]

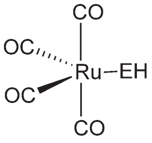


11

Transition energies to the low-lying singlet electronic excited states of **11** have been calculated at the CASSCF/MS-CASPT2 level of theory using relativistic effective core potentials in the *ab initio* model potential (AIMP) approach, and found to contrast markedly with those for *cis*-$[Fe(CO)_4H_2]$. The iron complex reductively eliminates H_2 upon photolysis at 254 nm, while the dominance of a high density of metal–ligand charge-transfer (MLCT) states (5*d* Os to πCO^*) in the lowest part of the absorption spectrum for the Os complex results in the transitions required for photodissociation (5*d* Os to σu^* and 5*d* Os to σg^*) occurring beyond 166 nm.[25]

6.11.4 Ruthenium and Osmium Complexes with Group 13 Ligands

DFT calculations on the trigonal-bipyramidal species $[Ru(CO)_4(EH)]$ **12** (E = B, Al, Ga, In, Tl) show that the configuration with the group 13 element in the equatorial plane is between 4.5 and 18.1 kJ mol^{-1} more stable than the isomer with it situated axially. The extent of σ-donation (M←E) and π-back-donation (M→E) decreases on going from B to Tl.[26]

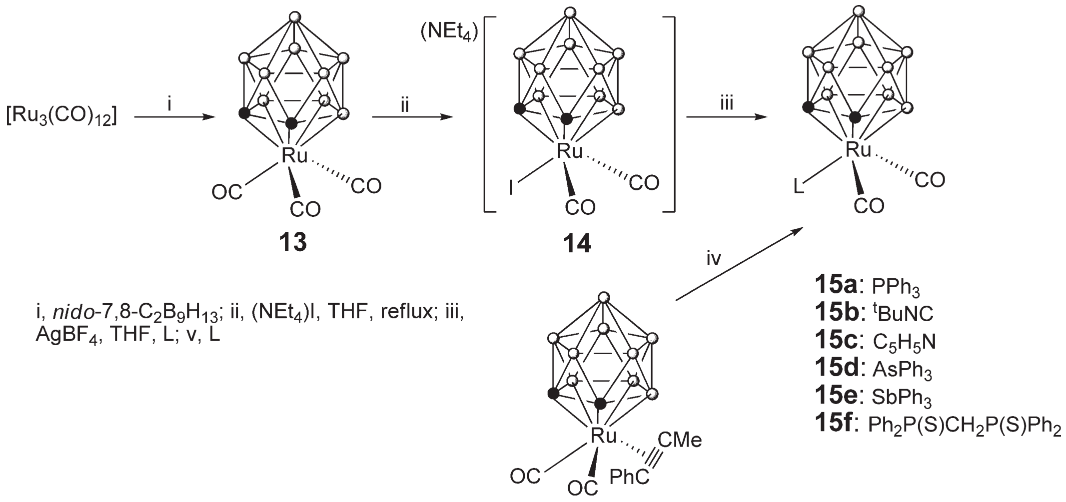


12

E = B, Al, Ga, In, Tl

The carborane ruthenium tricarbonyl complexes $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_3]$ **13** and $[Ru(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)(CO)_3]$ both react with $[NEt_4]I$ to afford the anionic dicarbonyl species $[NEt_4][Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2I]$ **14** and $[NEt_4][Ru(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)(CO)_2I]$, respectively.[27,28] Halide abstraction by $AgBF_4$ yields THF adducts of the two complexes,[29] which provide access to $RuL(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$ complexes (L = PPh_3 **15a**, CN^{t}Bu **15b**, C_5H_5N **15c**). The $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(L)]$ complexes with L = $AsPh_3$ **15d**, $SbPh_3$ **15e**, or $Ph_2P(S)CH_2P(S)Ph_2$ **15f** result from displacement of alkyne from $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(\eta^2\text{-}MeC{\equiv}CPh)]$, whereas PEt_3 affords the ylidic complex $[Ru(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})\{C(Me){=}C(Ph)PEt_3\}]^*$ (Scheme 3).[30]

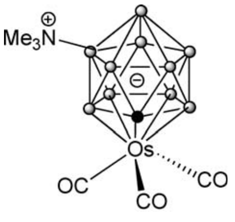
The monocarbonyl complex $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(PPh_3)_2(CO)]^*$ results from addition of CO to $K[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(PPh_3)_2H]$, although, in contrast, the [K(18-crown-6)] salt affords the salt [K(18-crown-6)] $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(PPh_3)(CO)H]$.[31] The anionic species $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(PPh_3)(CO)X]^-$ (X = Cl, I*) have been later synthesized.[32] The anionic $[Os(\eta^5\text{-}7\text{-}C_2B_{10}H_{11})(CO)_3]^-$ and zwitterionic $[Os(\eta^5\text{-}5\text{-}NMe_3\text{-}7\text{-}C_2B_{10}H_{10})(CO)_3]^*$ **16** tricarbonyl compounds of osmium result from refluxing $[Os_3(CO)_{12}]$ in bromobenzene with [PPN][*nido*-7-$CB_{10}H_{13}$] and $[HNMe_3]$[*nido*-7-$CB_{10}H_{13}$], respectively.[33] Treatment of $[Ru(\eta^2{:}\eta^5\text{-}9\text{-}C(H){=}C(H)R\text{-}10,11\text{-}\{C(H){=}C(H)R\}_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_2]$ (R = ^{t}Bu, $SiMe_3$) with PMe_3 affords $[Ru(\eta^5\text{-}9,10,11\text{-}\{C(H){=}C(H)^tBu\}_3\text{-}7,$



i, *nido*-7,8-$C_2B_9H_{13}$; ii, $(NEt_4)I$, THF, reflux; iii, $AgBF_4$, THF, L; v, L

Scheme 3

8-$C_2B_9H_8$)(PMe_3)$(CO)_2$] and [Ru(σ,η^5-9-C(H)(PMe_3)C(H)$SiMe_3$-10,11-{C(H)=C(H)$SiMe_3$}$_2$-7,8-$C_2B_9H_8$)$(CO)_2$], respectively.[27]



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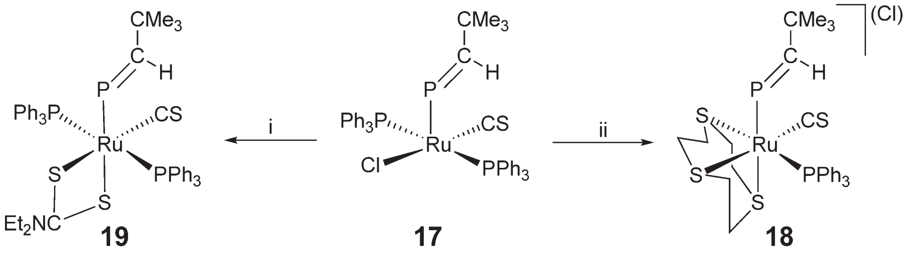
6.11.5 Ruthenium and Osmium Compounds with Group 14 Ligands (Including CS and CS_2)

The most common group 14 ligand excluding CO is CS; as most complexes employing this as a spectator ligand do so usually in direct comparison with CO, CS (and CS_2) have been included in the sections on metal carbonyl chemistry. Similarly, CS/CS_2 complexes, in which there is also an η^1- or η^2-η^4- ligand present, are described in the relevant chapters, although interested readers are referred to the following references.[34–38]

The following brief section considers examples of ruthenium and osmium group 14 ligands where the ligand is dominant. For example, the pentamethylated [60]fullerene dicarbonyl complex [(η^5-$C_{60}Me_5$)$Ru(CO)_2Cl$]* has been prepared by treatment of [$Ru(CO)_3Cl_2$] with $KC_{60}Me_5$ at room temperature. One of the carbonyl groups can be readily substituted to give the phosphine derivative [(η^5-$C_{60}Me_5$)Ru(PR_3)(CO)Cl] (R = Et*, Ph).[39]

The macrocycle 1,4,7-trithiacyclononane ([9]aneS_3) can be used to support a range of thiocarbonyl complexes, including [Ru(PPh_3)([9]aneS_3)(CS)X](ClO_4) (X = H, Cl), [Ru(PPh_3)([9]aneS_3)(CS)(SCN)](ClO_4), and [Ru(PPh_3)([9]aneS_3)(CS)(SR)](ClO_4).[40] Addition of HC≡CMe to a solution of [Os$(PPh_3)_3$(CO)(CS)] affords [Os$(PPh_3)_2$(CO)(CS)(C≡CMe)H] and [Os$(PPh_3)_2$(CO){η^2-C(S)CMeCHCHCMe}]. Treatment of the former with HCl leads to isolation of the propenylthioacyl complex [Os$(PPh_3)_2$(CO){η^2-C(S)CH=CHMe}Cl]*.[41]

The phosphaalkenyl thiocarbonyl complex [Ru$(PPh_3)_2$(CS)(η^1-P=CH^{t}Bu)Cl] **17** readily adds [9]aneS_3 or [Et_2NH_2](S_2CNEt_2) to give [Ru(PPh_3)(CS)(η^1-P=CH^{t}Bu)([9]aneS_3)](Cl) **18** and [Ru$(PPh_3)_2$(CS)(η^1-P=CH^{t}Bu)(κ^2-S_2CNEt_2)] **19**, respectively (Scheme 4).[42]



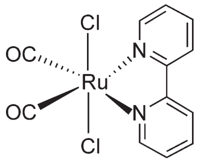
i, [Et$_2$NH$_2$](S$_2$CNEt$_2$); ii, [9]aneS$_3$

Scheme 4

6.11.6 Ruthenium and Osmium Compounds with Group 15 Ligands

6.11.6.1 Compounds with Nitrogen Ligands

The synthesis and characterization of a wide range of ruthenium bipyridyl carbonyl complexes, including [Ru(N–N)(CO)$_2$Cl$_2$]* (N–N = 2,2′-bipyridine **20**, 4,4′-Me$_2$-2,2′-bipyridine **21**, 4,4′5,5′-Me$_4$-2,2′-bipyridine, *n*,*n*′-L$_2$-2,2′-bipyridine (L = CO$_2$R; R = Me, Et; *n* = 3,4,5,6), [Ru(N–N)(CO)$_2$X$_2$]* (N–N = 2,2′-bipyridine **22**, 6,6′-Me$_2$-2,2′-bipyridine; X = Cl, I, Br, SCN), and [Ru(2,4′-bipyridine)(CO)$_3$Cl$_2$]* **23**, have been reported by Pakkanen and co-workers.[43–50] Subsequent interest has concentrated largely on their substitution and isomerization chemistry, particularly that which is photo-induced.[51–56] The chelating nitrogen donor carbonyl complexes [Ru(N–N) (CO)Cl$_3$] (N–N = 1,10-phenanthroline* **24**, 2,2′-bipyridine*) can be formed by reaction of ruthenium trichloride with N–N in the presence of non-aqueous HCO$_2$H,[57] while the related [Ru(CO)$_2$(N–N)Cl$_2$] species (N–N = 4,4′-^{t}Bu$_2$-2,2′-bipy, 6,6′-Me$_2$-4,4′-^{t}Bu$_2$-2,2′-bipy, 6,6′-Ph$_2$-4,4′-^{t}Bu$_2$-2,2′-bipy, 2,9-Ph$_2$-1,10-phen, 3,3′-CO$_2$R-bipy (R = Me, Et, ^{i}Pr, ^{t}Bu)) incorporating bulky bidentate nitrogen donors have been prepared from either RuCl$_3$·3H$_2$O or [Ru(CO)$_2$Cl$_2$]$_x$ at elevated temperatures.[58,59]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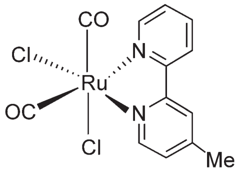
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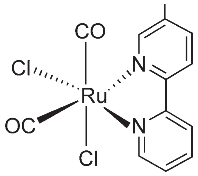
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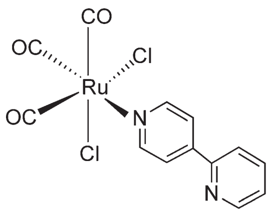
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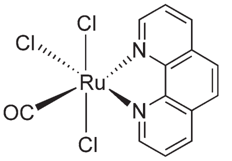
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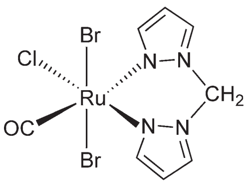
The formation of either mononuclear or binuclear ruthenium and osmium carbonyl complexes bearing bis(2-pyridyl)amine (Hdpa) or the deprotonated ligand (dpa) can be driven by choice of solvent and reaction temperature. For example, [Ru$_3$(CO)$_{12}$] reacts with Hdpa in HCl solution at 200 °C to give mainly *cis*,*cis*-[Ru(hdpa) (CO)$_2$Cl$_2$]*, whereas in toluene solution in the absence of HCl at 200 °C, {Ru(dpa)(CO)$_2$}$_2^*$ predominates.[60] In related chemistry, [Ru(CO)$_2$Cl$_2$]$_n$ reacts with bis(pyrazol-1-yl)methane (BPM), bis(3,5-dimethylpyrazol-1-yl) methane (dmBPM), or bis(*N*-methylimidazol-2-yl)methane (BIM) to yield [Ru(N–N)$(CO)_2X_2$] (N–N = BPM, X = Cl, Br **25**; N–N = dmBPM*, BIM, X = Cl). Decarbonylation of [Ru(BPM)$(CO)_2Cl_2$] in the presence of BPM and $NaBPh_4$ yields [Ru$(BPM)_2$(CO)Cl]$(BPh_4)^*$ **26**.[61] The expected Ru–Si bond-cleavage reaction is not seen upon addition of the strong nucleophile $PhCH_2NH_2$ to [Ru$(CO)_4(SiPhMe_2)_2$I]; instead, the amine coordinates to yield [Ru$(CO)_2(NH_2CH_2Ph)_2(SiPhMe_2)$I]*.[62]



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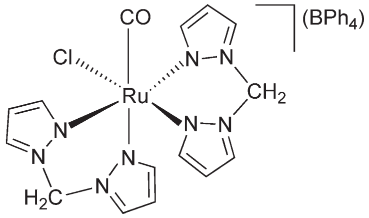

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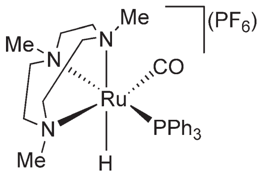
A series of carbonyl complexes bearing the 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) ligand have been described. Thus, reaction of HCO_2H and [Ru(Me_3tacn)Cl_3] leads to [Ru$(CO)_2$(Me_3tacn)Cl]$(PF_6)^*$, while either [Ru$(PPh_3)_3$(CO)HCl] or [Ru$(PPh_3)_2(CO)_2Cl_2$] are precursors for [Ru(PPh_3)(CO)(Me_3tacn)H]$(PF_6)^*$ **27**, one of the few piano-stool ruthenium complexes with three different L ligands.[63] Reductive carbonylation of ethylene glycol by Ru(III) has been used as a source of CO for the formation of [Ru$(biq)_2$(CO)Cl]$(PF_6)^*$ (biq = 2,2′-biquinoline) and [Ru$(bpy)_2$(CO)Cl](PF_6).[64] Treatment of [Ru(trpy)(CO)Cl_2] (trpy = 2,2′:6′,2″-terpyridine) with KO^{t}Bu and either 3,6-di-*tert*-butylcatechol or *o*-monothiocatechol gives [Ru(trpy)(CO)(3,6-Bu_2seq)Cl] (3,6-Bu_2seq = 3,6-di-*tert*-butylsemiquinone) and [Ru(trpy)(CO)(*o*-monothiocat)] **28**, respectively.[65]



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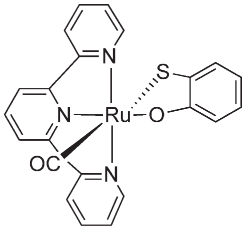
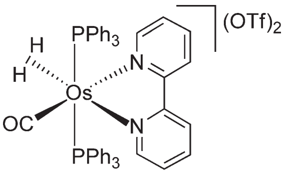


28

A series of *N*-heterocycle-based phosphine carbonyl complexes [Ru$(PPh_3)_2$(CO)(L)Cl_2] (L = C_5H_5N, 2-CNC_5H_4N, 4-$MeC_5H_4N^*$) have been used to establish correlations of $E_{1\backslash 2}$ and pK_a.[66] In the presence of tropylium tetrafluoroborate, [Ru$(PPh_3)_3(CO)H_2$] reacts with a range of nitrogen-donor ligands L to give [Ru$(PPh_3)_2$(CO)$(L)_2$H](BF_4) (L = pyridyl, 4-Me-pyridyl*, 2,2-bipyridyl).[67] Treatment of [Os$(PR_3)_2$(CO)(bpy)H] (OTf) with HOTf affords the dicationic η^2-H_2 complexes [Os$(PR_3)_2$(CO)(bpy)(η^2-H_2)]$(OTf)_2$ (PR_3 = PPh_3 **29**, $PMePh_2$). Similar protonations yield [Ru$(PPh_3)_2$(CO)(bpy)(η^2-H_2)]$(OTf)_2$ and [Os$(PPh_3)_2$(CO)(phen)(η^2-H_2)]$(OTf)_2$.[68,69]



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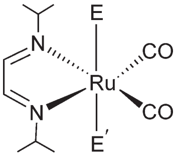
Probably the most interest in nitrogen-supported carbonyl complexes relates to extensive synthetic, structural, and spectroscopic studies that have been carried out on the α-diimine complexes [M(L–L)$(CO)_2$(R)X] (M = Ru, Os; L–L = 2,2-bipy, pyridine-2-carbaldehyde-*N*-isopropylimine, ^{i}Pr-DAB; R = SnR$_3$, alkyl; X = halide, Mn(CO)$_5$),[70–78] with major emphasis placed on the *N,N′*-diisopropyl-1,4-diaza-1,3-butadiene (^{i}Pr-DAB) systems [Ru(^{i}Pr-DAB)(CO)$_2$E(E′)] **30** (E = halide, Me, SnR$_3$, Mn(CO)$_5$, Co(CO)$_4$; E′ = alkyl, SnR$_3$, PbR$_3$, Mn(CO)$_5$, Re(CO)$_5$, Co(CO)$_4$).[79–84] The photochemical properties of these systems are discussed in Chapter 6.10.1.



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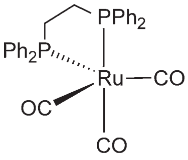
6.11.6.2 Compounds Bearing Phosphorus Ligands

6.11.6.2.1 Zerovalent phosphine carbonyl complexes

6.11.6.2.1.1 M(CO)$_3$ species

The photolysis of [Ru$_3$(CO)$_{12}$] under a flow of ethene at room temperature yields [Ru(CO)$_4$(η^2-C$_2$H$_4$)], which upon reaction with an excess of PPh$_3$ in the absence of both ethene and light gives [Ru(PPh$_3$)(CO)$_4$] and [Ru(PPh$_3$)$_2$(CO)$_3$].[85] Addition of a wide range of bidentate phosphine ligands P–P to the *in situ* generated [Ru(CO)$_4$(η^2-C$_2$H$_4$)] affords [Ru(η^1-P–P)(CO)$_4$], which undergoes facile chelation to yield [Ru(η^2-P–P)(CO)$_3$] {P–P = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1,2*,3,4), Ph$_2$P(NMe)PPh$_2$, Ph$_2$P(*o*-C$_6$H$_4$)PPh$_2$*, R$_2$P(CH$_2$)$_2$PR$_2$ (R = Me, Cy)}. Kinetic studies employing IR spectroscopy reveal that the chelation reaction ranges from being purely dissociative to appreciably associative, depending on the nature of the P–P ligand.[86]

Reaction of [Ru$_3$(CO)$_{12}$] with the chelating phosphite BBMB (2,2′-bis{(1,1′-biphenyl-2,2′-diyl)phosphite}-3,3-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl) yields [Ru(BBMB)(CO)$_3$]*.[87] In the presence of sodium diphenylketyl, [Ru$_3$(CO)$_{12}$] reacts with P(C$_4$H$_3$S)$_3$ to give in very low yields [Ru$_3${P(C$_4$H$_3$S)$_3$}$_2$(CO)$_{10}$] and [Ru{P(C$_4$H$_3$S)$_3$}$_2$(CO)$_3$]*, the latter displaying the expected trigonal-bipyramidal structure with *trans*-axial phosphines.[88] In contrast, the structure of [Ru(dppe)(CO)$_3$]* **31** is found to be intermediate between trigonal bipyramid (apical P/CO) and square-based pyramid (apical CO). Addition of 1 equiv. of ferrocenium ion leads to the dimeric species [Ru$_2$(dppe)$_2$(CO)$_6$]$^{2+*}$, which disproportionates in MeCN solution to give a 1 : 1 mixture of [Ru(dppe)(CO)$_2$(MeCN)$_2$]$^{2+}$ and **31**.[89] The photochemical reaction of **31** with parahydrogen[90] has been studied by *in situ* photochemistry resulting in NMR spectra of *all-cis*-[Ru(dppe)(CO)$_2$H$_2$] **32** that show significant enhancement of the hydride resonances. This effect is associated with a singlet electronic state for the intermediate [Ru(dppe)(CO)$_2$], consistent with DFT calculations.[91] More unusual M(0) species have been reported. Donor–acceptor heterometallic complexes result from treating *trans*-[Ru(PPh$_2$-*o*-C$_5$H$_4$N)$_2$(CO)$_3$] with ZnCl$_2$, CdCl$_2$, and HgCl$_2$. All form simple Ru → M* adducts, except in the Hg case where there is an unsupported Ru–Hg* bond **33**.[92]



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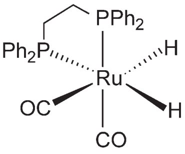

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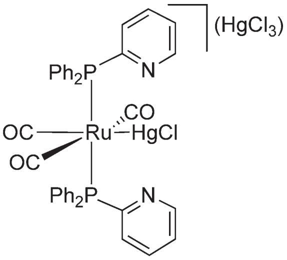

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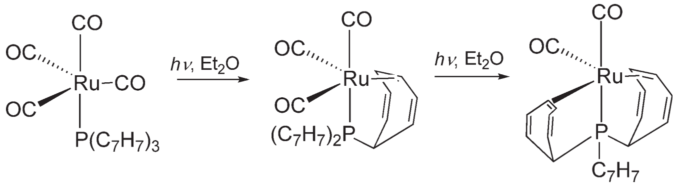
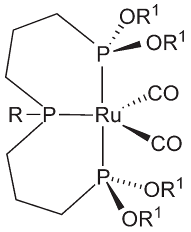
6.11.6.2.1.2 M(CO)$_2$ species

Photolysis of $[Ru_3(CO)_{12}]$ in the presence of tri(1-cyclohepta-2,4,6-trienyl)phosphine, $P(C_7H_7)_3$, affords $[Ru\{P(C_7H_7)_3\}(CO)_4]$ **34**, which can undergo further photolysis to afford ultimately the bis-alkene coordinated complex $[Ru\{P(C_7H_7)(\eta^2\text{-}C_7H_7)_2\}(CO)_2]$ **35**. This species isomerizes slowly in solution to yield $[Ru\{P(C_7H_7)_2(\eta^4\text{-}C_7H_7)\}(CO)_2]$, in which only one of the three seven-membered rings is coordinated to the metal center.[93]



34 **35**

The tridentate phosphine complexes $[Ru(RP\{(CH_2)_3P(OR^1{}_2)_2\})(CO)_2]$ **36** ($R = Ph$, $R^1 = {}^iPr^*$; $R = Cy$, $R^1 = {}^iPr$; $R = Ph$, $R^1 = Me^*$; $R = Cy$, $R^1 = Me$) can be generated by refluxing $[Ru_3(CO)_{12}]$ in toluene in the presence of the appropriate phosphine ligand. Thermolysis of $[Ru(PPh_3)_3(CO)H_2]$ in the presence of methyl benzoate and $CH_2{=}CHSi(OEt)_3$ generates $[Ru(PPh_3)_2(CO)_3]^*$ and, upon exposure of the reaction mixture to air, the peroxo complex $[Ru(PPh_3)_2(CO)_2(\eta^2\text{-}O_2)]^*$.[94] The isopropoxy complexes $[Ru(RP\{(CH_2)_3P(O^iPr_2)_2\})(CO)_2]$ react slowly with an excess of EtI, ^nPrI, ^iPrI, or I_2 to yield $[Ru(RP\{(CH_2)_3P(O^iPr_2)_2\})(CO)_2I](I)$ ($R = Ph^*$, Cy^*).[95] Photolysis of $[Ru(dmpe)(CO)_3]$ or $[Ru(PMe_3)_2(CO)_2H_2]$ and $[Ru(PMe_3)_2(CO)_3]$ in low-temperature matrices yields $[Ru(dmpe)(CO)_2\cdots S]$ and $[Ru(PMe_3)_2(CO)_2\cdots S]$ ($S =$ matrix host, Ar, CH_4, etc.), respectively.[96,97]



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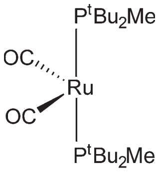
The stoichiometric reduction of *trans,cis,cis*-$[Ru(P^tBu_2Me)_2(CO)_2Cl_2]$ with Mg turnings in THF affords the deep red, 16-electron complex $[Ru(P^tBu_2Me)_2(CO)_2]^*$ **37**.[98] The same complex can be made by low-temperature (−78 °C) addition of MeLi to $[Ru(P^tBu_2Me)_2(CO)_2HCl]$ followed by slow warming to room temperature in the presence of CO. The analogous four-coordinate complex can be made if the phosphine is P^iPr_3, but not with PPh_3.[98] The molecular structure of **37** is free of any stabilizing agostic interactions and is non-planar ($\angle C\text{–}Ru\text{–}C = 133°$, ($\angle P\text{–}Ru\text{–}P = 166°$); DFT calculations with an $[Ru(PH_3)_2(CO)_2]$ model show similar angles indicating that the steric bulk of the P^tBu_2Me ligand is not responsible for the structure, which in fact results from the high energy of the *d*-orbitals and powerful back-donation into CO π^*-orbitals.[98] Addition of two-electron donors L affords $[Ru(P^tBu_2Me)_2(CO)_2(L)]$ ($L = CO$, $O_2{}^*$, CS_2, $PhC{\equiv}CPh$, MeCN, C_2H_4), while facile oxidative addition is found with H_2, HCl, and $HC{\equiv}CPh$.[99]



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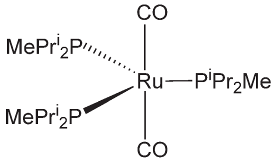
Facile oxidative addition of H_2, O_2, Cl_2, HCl, and HC≡CH to $[Ru(P^tBu_2Me)_2(CO)_2]$ **37** occurs at room temperature in the solid state. With Me_3SiH, the dihydride complex $[Ru(P^tBu_2Me)_2(CO)_2H_2]$ and Si_2Me_6 are formed. The solid-state reactions of either **37** or $[Ru(P^tBu_2Me)_2(CO)HCl]$ with CO to give either $[Ru(P^tBu_2Me)_2(CO)_3]$ or $[Ru(P^tBu_2Me)_2(CO)_2HCl]$ are found to be slow, on account of the lack of change in molecular volume, which results in passivation of the solid surface by the product. In contrast, a fast reaction occurs between CO and solid $[Ru(P^iPr_3)_2H_2Cl_2]$ to give $[Ru(P^iPr_3)_2(CO)_2Cl_2]$ and $[Ru(P^iPr_3)_2(CO)_2HCl]$ due to a change in geometry (*cis*-L_2 to *trans*-L_2).[100] Studies of d^8-ML_5 species have shown that other isomers beside the expected trigonal-bipyramidal (TBP) structure with equatorial π-acids can exist both in solution and in the solid state. Solution-phase IR spectroscopy shows that $[RuL_3(CO)_2]$ (L = PEt_3, P^iPr_2Me, PPh_3) exist in two different structural forms. In the P^iPr_2Me case, these two isomeric structures, *trans*-CO TBP **38** and square-pyramidal **39**, can be co-crystallized (1 : 1 ratio), revealing by X-ray diffraction very different C–Ru–C angles (174° and 147°). *Ab initio* calculations at the MP2 level on $[Ru(PH_3)_3(CO)_2]$ indicate very little electronic preference for the binding site of CO with the three isomeric forms of a TBP lying within 13 kJ mol^{-1} of each other.[101] Further extension of this work to additional five-coordinate complexes $[Ru(PEt_3)_2\{P(2\text{-furyl})_3\}(CO)_2]$, $[Ru(PEt_3)_2(AsPh_3)(CO)_2]$, and $[Ru(PEt_3)_2(CO)_2(\eta^2\text{-PhC}{\equiv}\text{CPh})]$ indicates that the bulkiness of the substituents on the phosphine ligands is the major influence on the preferred isomer.[102] Further evidence for the subtleties of the sustituents on PR_3 are revealed by calorimetric measurements of the binding of CO, PhC≡CPh, and CNMe to $[Ru(PR_3)_2(CO)_2]$ ($PR_3 = P^tBuMe_2$, P^iPr_3, PCy_3).[103,104] PCy_3 and P^iPr_3 show opposing steric and electronic effects that have different influences depending on the substrate involved – thus, the binding of the alkyne is more exothermic for PCy_3, but less exothermic for the isonitrile and CO.



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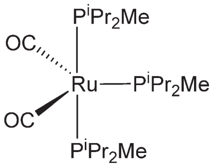

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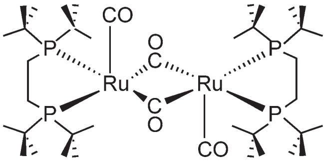
In subsequent work, the dark green 16-electron species $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2]$ is formed upon exposure of the corresponding ethene complex $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2(C_2H_4)]$ to vacuum.[105] In contrast to the P^tBu_2Me analog, however, the dtbpe complex exists as the carbonyl-bridged dimer **40** in the solid state.[105,106] In solution, the monomer does exist and oxidatively adds C–H bonds in HC≡CR (R = H, Ph) and C_6F_5H to yield $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2(C{\equiv}CR)H]$ and $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2(C_6F_5)H]$, respectively. DFT calculations on $[Ru(H_2PCH_2CH_2PH_2)(CO)_2]$ indicate a structure close to square planar.[107] Osmium(0) complexes containing the powerful π-acceptor ligand $P(NC_4H_4)_3$ can be prepared by photochemical phosphine exchange with $[Os(PPh_3)_3(CE)_2]$ to give $[Os(PPh_3)_2\{P(NC_4H_4)_3\}(CE)_2]$ (E = O*, S).[108]



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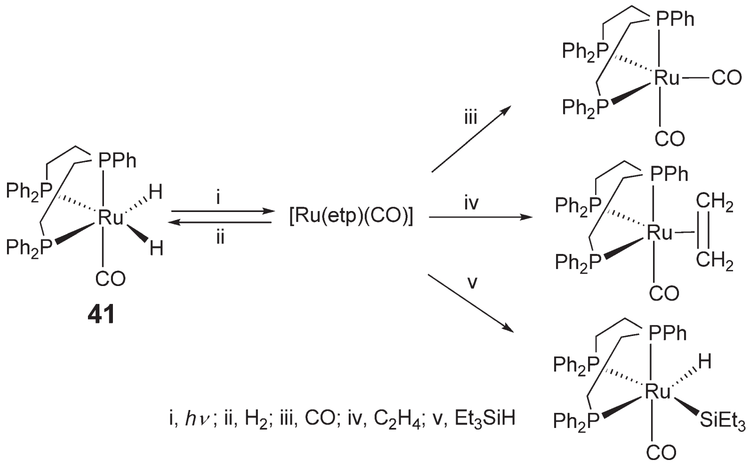
6.11.6.2.1.3 M(CO) species

Photolysis of $[M(PP_3)H_2]$ (M = Ru, Os; $PP_3 = P(CH_2CH_2PPh_2)_3$) in the presence of CO affords $[M(PP_3)(CO)]$, the ruthenium complex also being accessible by reduction of the dichloride complex with sodium naphthalenide under an atmosphere of CO.[109] Nanosecond laser flash photolysis studies on $[Ru(etp)(CO)H_2]$ **41** (etp = $PhP(CH_2CH_2PPh_2)_2$) generate the expected 16-electron Ru(0) species [Ru(etp)(CO)], which back reacts



Scheme 5

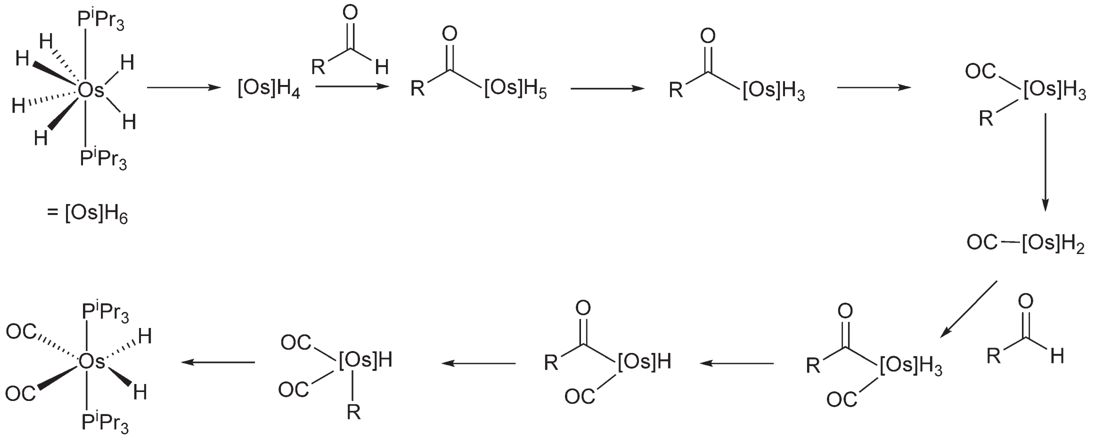
with H_2 or reacts with CO, Et_3SiH, and C_2H_4 with rate constants of ca. $10^8\,dm^3\,mol^{-1}\,s^{-1}$ (Scheme 5).[110] The solution IR spectrum of the five-coordinate species $[Ru(dmpm)_2(CO)]$ shows ν_{CO} at $1864\,cm^{-1}$;[111] in contrast, $[Os(dmpe)_2(CO)]$ displays a band at $1851\,cm^{-1}$ in a low-temperature matrix, but in solution this cannot be detected due to facile secondary photolysis to afford $[Os(dmpe)(CO)_3]$.[112]

6.11.6.2.2 Divalent phosphine carbonyl complexes

6.11.6.2.2.1 Divalent monodentate phosphine carbonyl complexes

Over the last decade, the major emphasis has been in the use of bulky phosphines to stabilize coordinatively unsaturated species and/or impart high/unusual reactivity patterns, and the following section is subdivided into the main phosphine types (P^iPr_3, P^tBu_2Me, PCy_3, etc.) which have received the major research focus.

Two reviews cover the overall reactivity of the $[M(P^iPr_3)_2(CO)]$' fragment in terms of both fundamental chemistry and also homogeneous catalysis.[113,114] The absence of stabilizing agostic interactions in the five-coordinate complexes $[Ru(P^iPr_3)_2(CO)HCl]^*$ **42** and $[Ru(P^iPr_3)_2(CO)Cl_2]^*$ **43**[115] is attributed to the mix of ligands with a strong *trans*-influence (H, CO) and good π-donor ability (Cl).[116] The dicarbonyl complex $[Os(P^iPr_3)_2(CO)_2H_2]$ **44** is formed by reaction of $[Os(P^iPr_3)_2H_6]$ with RCHO (R = Cy, ^{i}Pr) in refluxing toluene via two C–H_α activation–decarbonylation steps (Scheme 6).[117]



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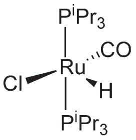
Scheme 6



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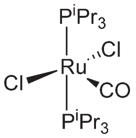

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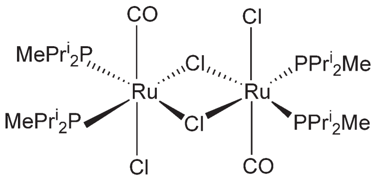
Treatment of $[Os(P^iPr_3)_2(CO)HCl]$ with HCl yields the dihydrogen complex $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}H_2)Cl_2]$, which reacts with CO to form $[Os(P^iPr_3)_2(CO)_2HCl]$.[118] The addition of the lithium salts $Li[(C_5H_4(CH_2)_2X)]$ to $[Os(P^iPr_3)_2H_2Cl_2]$ in THF affords $[Os(\eta^5\text{-}C_5H_4(CH_2)_2X)(P^iPr_3)_2H_2][Os(P^iPr_3)_2(CO)HCl_2]$ ($X = NMe_2{}^*$, OMe), the source of the carbonyl ligand being the solvent.[119]

The coordinatively unsaturated complex $[Ru(P^iPr_2\{3,5\text{-}(CF_3)_2C_6H_3\})_2(CO)HCl]$ cannot be prepared in an analogous way to other $[Ru\{P(alkyl)_3\}_2(CO)HCl]$ complexes from $RuCl_3{\cdot}xH_2O$ and PR_3 in alcoholic solvent with NEt_3 present. Instead, Na_2CO_3 is needed as the base. With a smaller phosphine, the related complex $[Ru(P^iPr_2Me)_3(CO)HCl]$ is formed, although this readily loses phosphine in solution. Indeed, this phosphine is small enough to allow $[Ru(P^iPr_2Me)_2(CO)Cl_2]^*$ **45** to dimerize in both the solid and solution states.[120,121]



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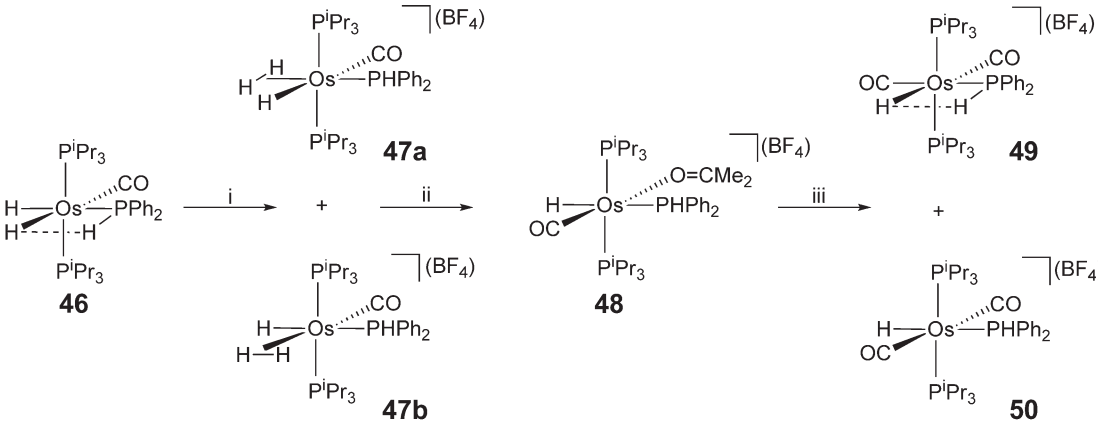
The five-coordinate precursors $[M(P^iPr_3)_2(CO)HCl]$ react with $P^iPr_2(CHMePh)$ to give $[M\{P^iPr_2(CHMePh)\}_3(CO)HCl]$ (M = Ru, Os). The phosphine trans to the M–H bond proves to be quite labile affording the substitution products $[M\{P^iPr_2(CH(Me)Ph)\}_2(CO)(L)HCl]$ (L = CO, $P(OMe)_3$). The reaction of the chiral bidentate phosphines (*S*,*S*)-DIOP or (*S*,*S*)-Chiraphos ($P^*\text{–}P^*$) with $[M(P^iPr_3)_2(CO)HCl]$ or $[M(P^iPr_3)_2(CO)(\eta^2\text{-}H_2BH_2)H]$ leads to diastereoisomers of the compounds $[M(P^*\text{–}P^*)(P^iPr_3)(CO)HCl]$ and $[M(P^*\text{–}P^*)(P^iPr_3)(CO)H_2]$.[122] The bis(silyl)chelating ligand xantsil ({9,9-dimethylxanthene-4,5-diyl}bis(dimethylsilyl)) allows access to the orange presumed 14-electron species $[Ru(PCy_3)(CO)(xantsil)]$, which can be trapped by CO as the isolable tricarbonyl complex $[Ru(PCy_3)(CO)_3(xantsil)]^*$.[123]

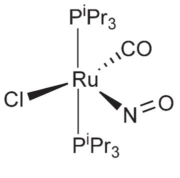
The addition of 1 equiv. of diphenylphosphine $PHPh_2$ to either $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}CH_2{=}CHEt)H_2]$ or $[M(P^iPr_3)_2(CO)(\eta^2\text{-}H_2BH_2)H]$ yields $[M(P^iPr_3)_2(PHPh_2)(CO)H_2]$ ($M = Ru^*$, Os **46**). Protonation (HBF_4/CH_2Cl_2) of the osmium complex affords two isomers of $[Os(P^iPr_3)_2(PHPh_2)(CO)(\eta^2\text{-}H_2)H](BF_4)$ **47a** and **47b**, which differ in the positions of the dihydrogen and hydride ligands. Both of these isomeric species lose H_2 in the presence of added acetone to give the solvent complex $[Os(P^iPr_3)_2(PHPh_2)(CO)(\eta^1\text{-}OCMe_2)H](BF_4)$ **48**. The acetone ligand is readily displaced by CO to give a 2 : 1 mixture of the *cis*,*trans*-complex **49*** and **50** (Scheme 7).[124] The bidentate pyrazolylborate complexes $[M(P^iPr_3)_2(CO)(\eta^2\text{-}HB(pz)_3)H]$ (M = Ru, Os) dissociate a phosphine ligand in refluxing toluene to yield $[M(P^iPr_3)(CO)(\eta^3\text{-}HB(pz)_3)H]$; subsequent protonation by HBF_4 affords the cationic dihydrogen complexes $[M(P^iPr_3)(CO)(\eta^3\text{-}HB(pz)_3)(\eta^2\text{-}H_2)](BF_4)$.[125]

Addition of equimolar NO to $[M(P^iPr_3)_2(CO)HCl]$ (M = Ru, Os) affords a 1 : 1 mixture of $[Ru(P^iPr_3)_2(CO)(NO)Cl]^*$ **51** and $[Ru(P^iPr_3)_2(CO)(HNO)HCl]$ **52**, while in the osmium case, only $[Os(P^iPr_3)_2(CO)(NO)HCl]$ is observed with 0.5 equiv. NO and a 4 : 1 mixture of $[Os(P^iPr_3)_2(CO)(NO)Cl] : [Os(P^iPr_3)_2(CO)(HNO)HCl]$ is formed with an excess of reagent.[126] The dimeric species $\{Ru(P^iPr_3)_2HCl\}_2$ decarbonylates aldehydes RC(O)H (R = Et, ^{t}Bu, $CH_2{}^tBu$, Ph), formates ROC(O)H (R = CH_2Me, ^{t}Bu, Ph), and formamides $NR_2C(O)H$ (R = Me) to afford $[Ru(P^iPr_3)_2(CO)HCl]$ **42** with release of RH or R_2NH.[127] The reaction of **42** with $AgBF_4$ in acetone affords the solvent complex $[Ru(P^iPr_3)_2(CO)_2(\eta^1\text{-}OCMe_2)H](BF_4)$, which reacts with H_2O, MeCN, and CO with loss of acetone. With the potentially chelating ligands CS_2 and SCNR (R = Me, Ph), insertion into the Ru–H bond occurs.[128]



i, HBF_4, CH_2Cl_2; ii, Me_2CO; iii, CO

Scheme 7



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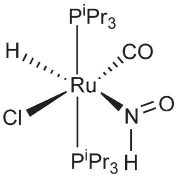

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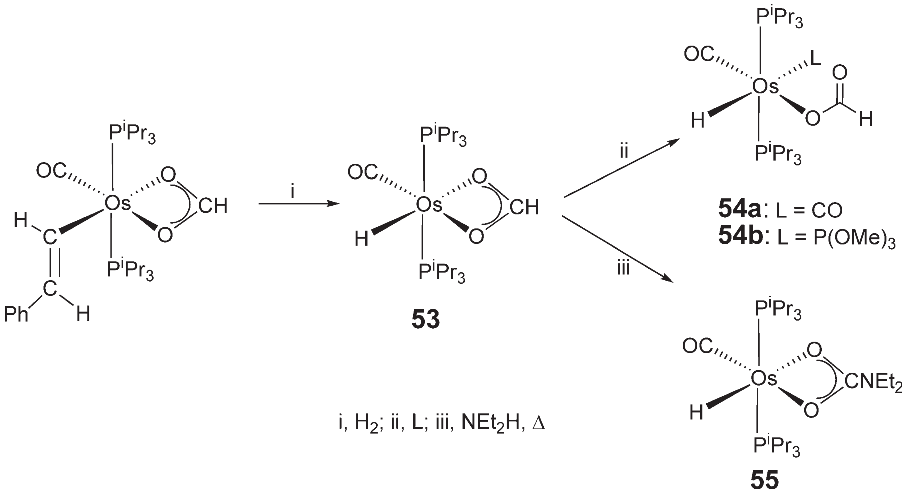
Treatment of $[Os(P^iPr_3)_2(CO)HCl]$ with Ph_2CN_2 or $Cl_4C_5N_2$ affords the diazoalkane complexes $[Os(P^iPr_3)_2(CO)(N_2CR_2)HCl]$. A similar species, $[Os(P^iPr_3)_2(CO)(N_2C(H)SiMe_3)HCl]$, can be observed upon reaction with Me_3SiCHN_2 at low temperature; this is an intermediate on the way to the ultimate product, $[Os(P^iPr_3)_2(CO)({=}C(H)SiMe_3)HCl]$.[129] Addition of CH_2N_2 to $[Ru(P^iPr_2Ph)_2(CO)HCl]$ at room temperature generates the ionic compound $(PMe^iPr_2Ph)[Ru(P^iPr_2Ph)_2(CO)HCl_2]^*$.[130] Hydrogenation of the styryl complex $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHPh\}(\kappa^2\text{-}O_2CH)]$ affords styrene and $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}O_2CH)H]$ **53**, which reacts (Scheme 8) with two-electron donors L (CO, $P(OMe)_3$) to give $[Os(P^iPr_3)_2(CO)(L)(\eta^1\text{-}O_2CH)H]$ **54a** and **54b**, and with NEt_2H forming $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}O_2CNEt_2)H]$ **55**.[131] Treatment of $[Ru(P^iPr_3)_2(CO)Cl_2]$ **43** with CS_2 results

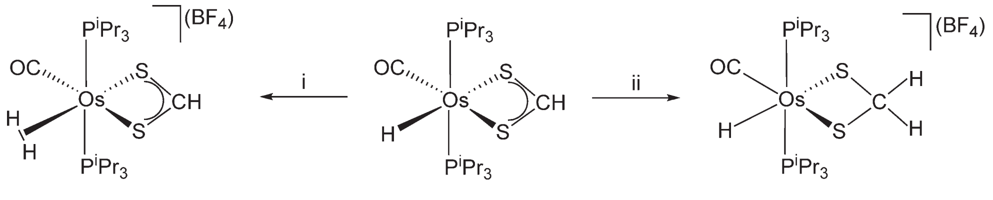


Scheme 8

in insertion into an Ru–P bond to afford $[Ru(P^iPr_3)(CO)(\eta^2\text{-}S_2CP^iPr_3)Cl]^*$.[115] The cationic five-coordinate carbene complexes $[Ru(P^iPr_3)_2(CO)({=}CHCH_2R)Cl](BF_4)$ ($R = H$, ^tBu) react with MeCN by cleavage of the ruthenium–carbene bond resulting in formation of the six-coordinate complexes $[Ru(P^iPr_3)_2(CO)(MeCN)_2Cl](BF_4)$ and $[Ru(P^iPr_3)_2(CO)(MeCN)_2H]X$ ($X = Cl$, BF_4, PF_6).[132]

Addition of CS_2 to $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}CH_2{=}CHEt)H_2]$ affords $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}S_2CH)H]$ **56**. Subsequent protonation with $HBF_4{\cdot}OEt_2$ gives the dihydrogen complex $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}S_2CH)(\eta^2\text{-}H_2)](BF_4)$ **57** in CD_2Cl_2, but the methanedithiolate species $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}S_2CH_2)H](BF_4)$ **58** in diethyl ether (Scheme 9).[133] Addition of NaSH at room temperature to $[M(P^iPr_3)_2(CO)HCl]$ yields $[M(P^iPr_3)_2(CO)(SH)H]$ (M = Ru, Os **59**). Addition of Lewis bases affords the coordinatively saturated complexes $[M(P^iPr_3)_2(CO)(L)(SH)H]$ ($L = CO$, $P(OMe)_3$), while addition of $MeO_2CC{\equiv}CCO_2Me$ to $[Os(P^iPr_3)_2(CO)(SH)H]$ results in insertion into the S–H bond to form the monothio-β-diketonato complex $[Os(P^iPr_3)_2(CO)\{SC(CO_2Me)CHC(OMe)O\}H]^*$ **60**, in which there is a *trans*-OC–Os–S stereochemistry. Insertion into the SH bond of $[Ru(P^iPr_3)_2(CO)(SH)H]$ also occurs, initially to yield the *trans*-OC–Ru–O isomer, which rapidly rearranges in solution to the *trans*-OC–Ru–S species* **61**.[134] Treatment of $[Os(P^iPr_3)_2(CO)HCl]$ with KOH in MeOH affords $[Os(P^iPr_3)_2(CO)(OH)H]$ **62**. This undergoes reaction at the Os–OH bond with $MeO_2CC{\equiv}CCO_2Me$, CO_2, and PhNCO generating $[Os(P^iPr_3)_2(CO)\{OC(OMe)CHC(CO_2Me)O\}H]^*$, $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}O_2COH)H]$, and $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}O_2CNHPh)H]$ **63**, respectively (Scheme 10).[135]

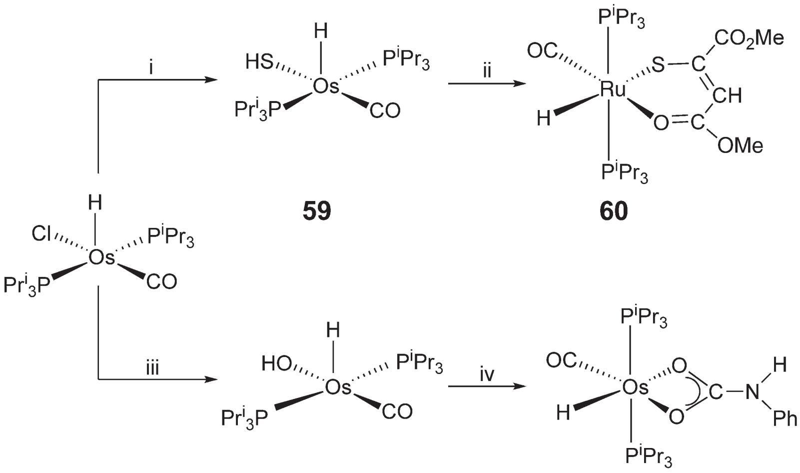
The first trihydrido-silyl, -germyl, and -stannyl derivatives of osmium(IV) $[Os(P^iPr_3)_2(CO)(ER_3)H_3]$ (**64**, $ER_3 = SiHPh_2^*$, $SiPh_3$, $Si(OMe)_2Ph$, $GeHPh_2$, $GePh_3$, $GeEt_3$, $SnPh_3$, Sn^nBu_3) have been prepared by reactions of $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}CH_2{=}CHEt)H_2]$ or $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}H_2BH_2)H]$ with $R_3E–H$.[136] Addition of COS to the



57 **56** **58**

i, $HBF_4{\cdot}OEt_2$, CH_2Cl_2; ii, $HBF_4{\cdot}OEt_2$, Et_2O

Scheme 9



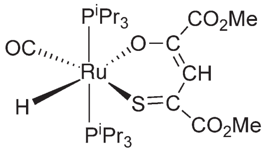
59 **60**

62 **63**

i, NaSH, THF/MeOH; ii, DMA; iii, KOH, MeOH; iv, PhN=C=O

Scheme 10

16-electron fragments [Os(P^{i}Pr$_2$R)$_2$(NO)Cl] (R = ^{i}Pr, Ph) affords [Os(P^{i}Pr$_2$R)$_2$(NO){κ^2-(*C*,*S*)-S=C=O}(NO)Cl], which undergo sulfur abstraction upon addition of PMe$_3$ to form [Os(P^{i}Pr$_2$R)$_2$(CO)(NO)Cl].[36] The square-planar Os(0) complexes [Os(PR$_3$)$_2$(NO)Cl] (PR$_3$ = P^{i}Pr$_3$, P^{i}Pr$_2$Ph) react spontaneously with CO to form [Os(PR$_3$)$_2$(NO)(CO)Cl].[137] Hydrogenation of the Δ^3-1,2-azaosmetine derivatives [Os(P^{i}Pr$_3$)$_2$(CO)(=CH=CPhN=CR$_2$)Cl] (CR$_2$ = CMe$_2$, C(CH$_2$)$_4$CH$_2$) leads to elimination of the 2-aza-1,3-butadienes CH$_2$=C(Ph)N=CR$_2$ and formation of [Os(P^{i}Pr$_3$)$_2$(CO)(η^2-H$_2$)H$_2$].[138]



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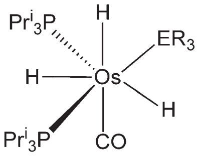

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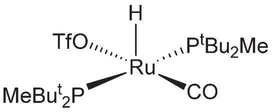
The reaction of [Ru(P^{t}Bu$_2$Me)$_2$(CO)HCl] with ^{n}BuLi at low temperature was initially reported to generate the 14-electron species [Ru(P^{t}Bu$_2$Me)$_2$(CO)] via dehydrohalogenation.[139] Subsequently, it was shown that the product was actually [Ru(P^{t}Bu$_2$Me)$_2$(CO)H$_2$]; this complex shows only two distinct hydride resonances in the ^{1}H NMR spectrum below −70 °C (in fact, extreme signal broadening results in no hydride signals being observable above −30 °C) and also proves to be in equilibrium with [Ru(P^{t}Bu$_2$Me)$_2$(CO)(η^2-H$_2$)H$_2$], giving a mixture of products unless great care is taken to remove H$_2$ from the system. This 16-electron system, which is unusual in having no stabilization from π-donor ligands, is calculated to have a square-based pyramidal structure with an apical hydride. In terms of reactivity, H$_2$ is eliminated upon oxidative addition of C–H, O–H, or Si–H bonds, or upon addition of CO.[140] Halide- and/or hydride-bridged dimers are invoked to explain the exchange reactions seen, for example, between [Ru(P^{t}Bu$_2$Me)$_2$(CO)HCl] and [Ru(P^{t}Bu$_2$Me)$_2$(CO)DI], and between [Ru(P^{t}Bu$_2$Me)$_2$(CO)HX] and [Ru(P^{i}Pr$_3$)$_2$(CO)HCl] 42.[141]

A comparison of experimentally determined and calculated CO stretching frequencies across a range of five-coordinate complexes [Ru(P^{t}Bu$_2$Me)$_2$(CO)HX] (X = I, Br, Cl, F, OPh, OH, OCH$_2$CF$_3$, OEt, OCPh$_3$, OB(Mes)$_2$, OSiR$_3$, NHPh, SPh, C$_2$Ph) has been used to try to rationalize the order of ν_{CO} in terms of the electron-donating abilities of X. The shift to lower frequency on going from I → Br → Cl → F → OR is too great to be explained by π-donor effects alone and necessitates the involvement of σ-effects.[142] The nature of the X ligand has also been shown to impact on the reactivity of these complexes toward H$_2$/D$_2$. Thus, formation of Ru–D occurs faster for [Ru(P^{t}Bu$_2$Me)$_2$(CO)HI] than [Ru(P^{t}Bu$_2$Me)$_2$(CO)HF], while DBU/H$_2$ will convert [Ru(P^{t}Bu$_2$Me)$_2$(CO)HI] but not [Ru(P^{t}Bu$_2$Me)$_2$(CO)HCl] into [Ru(P^{t}Bu$_2$Me)$_2$(CO)(η^2-H$_2$)H$_2$].[143] The formation of [Ru(P^{t}Bu$_2$Me)$_2$(CO)HCl] upon reaction of [Ru(P^{t}Bu$_2$Me)$_2$(CO)Cl$_2$] with H$_2$ releases HCl, which reacts with the precursor complex to give [HP^{t}Bu$_2$Me][Ru$_2$(P^{t}Bu$_2$Me)$_2$(CO)$_2$Cl$_5$].[144] Addition of Me$_3$SiOTf to [Ru(P^{t}BuMe$_2$)$_2$(CO)HF] affords [Ru(P^{t}BuMe$_2$)$_2$(CO)H(OTf)]* 65, which undergoes metathesis with NaBAr$^F{}_4$ in CH$_2$Cl$_2$ to yield [Ru(P^{t}BuMe$_2$)$_2$(CO)H(η^2-CH$_2$Cl$_2$)]*. If the metathesis is performed in fluorobenzene as the solvent, the “naked” 14-electron species [Ru(P^{t}BuMe$_2$)$_2$(CO)H](BAr$^F{}_4$)* 66 is formed, which, in the solid state, displays two agostic interactions.[145] [Os(P^{t}Bu$_2$Me)$_2$(CO)HCl] forms the nitrosyl complex [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)Cl] upon reaction with *p*-tolyl-SO$_2$N(NO)Me. Chloride abstraction with NaBAr$^F{}_4$ yields the non-planar osmium(0) species [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)](BAr$^F{}_4$). This species coordinates CO and oxidatively adds H$_2$ to afford [Os(P^{t}Bu$_2$Me)$_2$(CO)$_2$(NO)](BAr$^F{}_4$) and [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)H$_2$](BAr$^F{}_4$), respectively. Deprotonation of the latter with NEt$_3$ gives trigonal-bipyramidal [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)H].[146] The interaction between [Os(P^{t}Bu$_2$Me)$_2$(CO)HCl] and (CF$_3$)$_2$CHOH results in hydrogen bonding to the chloride ligand according to low-temperature IR spectroscopy. Calculations indicate that the steric bulk of the phosphine prevents interaction of the alcohol with the metal center.[147]



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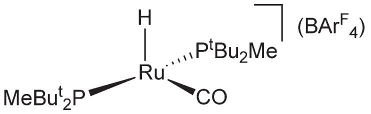

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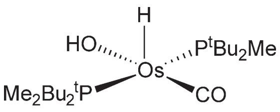
The aryl hydride complex [Os(P^{t}Bu$_2$Me)$_2$(CO)(Ph)H] reacts with HSiR$_3$ by elimination of benzene to form [Os(P^{t}Bu$_2$Me)$_2$(CO)(SiR$_3$)H$_3$] (SiR$_3$ = SiMe$_3$, SiPh$_3$, SiH$_2$Ph).[148] Hydrolysis of [Os(P^{t}Bu$_2$Me)$_2$(CO)(Ph)H] affords the 16-electron hydroxyl–hydride complex $[Os(P^tBu_2Me)_2(CO)(OH)H]^*$ **67**. Cleavage of the Os–OH bond occurs rapidly upon addition of H_2 to give $[Os(P^tBu_2Me)_2(CO)(\eta^2\text{-}H_2)H_2]$.[149] Halide abstraction from $[Ru(P^tBu_2Me)_2(CO)(NO)Cl]$ with $AgBF_4$ affords the thermally stable five-coordinate complex $[Ru(P^tBu_2Me)_2(CO)(NO)(F\text{-}BF_3)]^*$ **68**; upon reaction of this or the chloride precursor with $NaBAr^F{}_4$, however, the four-coordinate cationic species $[Ru(P^tBu_2Me)_2(CO)(NO)](BAr^F{}_4)$ **69** is produced. The non-planar structure of the cation (∠P–Ru–P = 157.33(8)°, ∠N–Ru–C = 120.4(3)°) is indicative of greater backbonding than present in the isoelectronic species $[Ru(P^tBu_2Me)_2(CO)_2]$ **37**. The potent back-donation to the NO ligand makes the metal center less π-basic and reduces its reactivity toward π-acids and oxidants. Thus, in contrast to **37**, $[Ru(P^tBu_2Me)_2(CO)(NO)](BAr^F{}_4)$ shows no reaction with either CO or H_2.[150] The bulky functionalized phosphine $P^tBu_2(CH_2CH_2OPh)$ reacts with ruthenium trichloride in $MeOH/NEt_3$ under H_2 at 80 °C to afford $[Ru\{P^tBu_2(CH_2CH_2OPh)\}_2(\eta^2\text{-}H_2)HCl]$ and $[Ru\{P^tBu_2(CH_2CH_2OPh)\}_2(CO)HCl]^*$ **70**, the latter being the only product if the mixture is stirred at 80 °C in the absence of H_2. Treatment of this complex with CsF affords the fluoride analog, while addition of CO gives $[Ru\{P^tBu_2(CH_2OCH_2Ph)\}_2(CO)_2HCl]$.[151]



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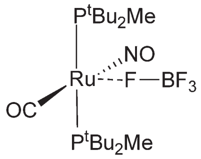

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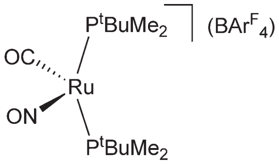

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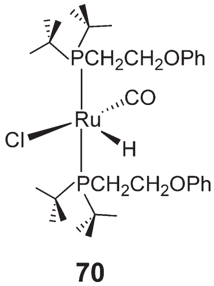

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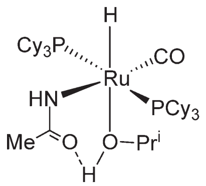
In the presence of $KOH/^iPrOH$, the cationic hydride complex $[Ru(PCy_3)_2(CO)(MeCN)_2H](BF_4)$ is converted to the acetamido species $[Ru(PCy_3)_2(CO)\{NHC(O)Me\}(^iPrOH)H]^*$ **71**, which received subsequent attention as a precursor for the catalytic transfer hydrogenation of ketones and imines[152] and conjugate addition of alcohols to acrylic compounds.[153] The reaction of $[Ru(PCy_3)_2(CO)HCl]$ with pyrrolidine and ethene yields, after workup, the anionic amido complex $Na[Ru(PCy_3)_2(CO)(C_4H_8N)HCl]^*$ **72** – this is an active precursor for the intermolecular coupling of alkenes and amines.[154]



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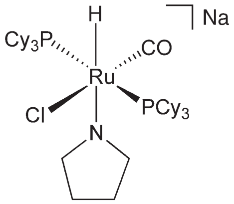
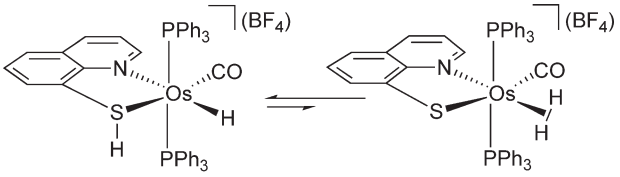


72

The bis-silane complexes $[Ru(PCy_3)_2\{(\eta^2\text{-}HSiMe_2)_2X\}H_2]$ (X = O, $–(CH_2)_2–$, $–(CH_2)_3–$, Me_2SiO_2) react with CO to give $[Ru(PCy_3)_2(CO)_2H_2]$.[155] Prolonged heating of $[Ru(PCy_3)_2\{{=}C(H)OEt\}Cl_2]$ results in the clean formation of $[Ru(PCy_3)_2(CO)HCl]^*$.[156,157] This compound can also be prepared by treatment of $[Ru(PCy_3)_2(CO)\{(E)\text{-}CH{=}CHPh\}Cl]$ with C_2H_4 at elevated temperature.[158] The one-pot reaction of $RuCl_3{\cdot}3H_2O$, PCy_3, Et_2NH, and CO_2 gave the carbamato complex $[Ru(PCy_3)_2(CO)(O_2CNEt_2)H]^*$.[159]

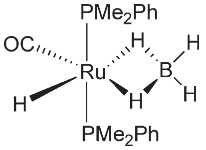
The five- and six-coordinate *cis*-carbonyl complexes $[Ru(PPh_3X)(CO)_2Cl_2]$ (X = O, S, Se) and $[Ru(PPh_3X)_2(CO)_2Cl_2]$ (X = O, S*, Se) are formed upon reaction of $[Ru(CO)_2Cl_2]_x$ with 1 or 2 equiv. of PPh_3X, respectively. Irrespective of the coordination number, the values of ν_{CO} decrease in the order $Ph_3PO > Ph_3PS > Ph_3PSe$.[160] The X-ray crystal structure of $[Ru(PPh_3)_3(CO)H_2]^*$ shows hydrogen bonding between Ru–H and an *ortho*-C–H of a phenyl group of one of the phosphine ligands.[161] Ultrafast laser flash photolysis studies of this compound revealed rapid dissociation of H_2 within 6 ps to afford the 16-electron fragment $[Ru(PPh_3)_3(CO)]$, which has been characterized by IR and UV–VIS spectroscopies.[162] Protonation of $[M(PPh_3)_2(CO)(L)H]$ (M = Ru, Os; L = quinoline-8-thiolate (quS), pyridine-8-thiolate (pyS)) with $HBF_4{\cdot}OEt_2$ at −80 °C gives a mixture of the tautomeric complexes $[M(PPh_3)_2(CO)(LH)H](BF_4)$ and $[M(PPh_3)_2(CO)(L)(\eta^2\text{-}H_2)](BF_4)$, although these tend to be thermally unstable, usually with respect to loss of H_2 gas.[163] In the case of $[Os(PPh_3)_2(CO)(quSH)H](BF_4)$ **73** and $[Os(PPh_3)_2(CO)(quS)(\eta^2\text{-}H_2)](BF_4)$ **74**, these exist in a temperature-dependent equilibrium.[164]



73 **74**

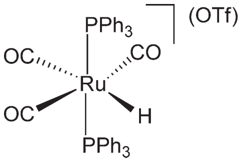
The carboxylate complex $[Ru(PPh_3)_2(CO)_2(MeCO_2)_2]$ reacts with H_2 at 100 °C to give $[Ru(PPh_3)_2(CO)_2H_2]$, which can be converted to $[Ru(PPh_3)_2(CO)_2(MeCO_2)H]$ at room temperature with acetic acid. Excess acid reforms the initial bis-carboxylate complex.[165]

Addition of $NaBH_4$ to the *trans*-PMe_2Ph isomer of $[Ru(PMe_2Ph)_2(CO)_2(\eta^3\text{-}C_3H_5)](BF_4)$ affords two products, the metallocyclobutane $[Ru(CH_2CH_2CH_2)(PMe_2Ph)_2(CO)_2]$ and the borohydride complex $[Ru(PMe_2Ph)_2(CO)(\eta^2\text{-}H_2BH_2)H]$. Treatment of the latter with C_2H_4 at low temperature leads to a rapid equilibrium between $[Ru(PMe_2Ph)_2(CO)(\eta^2\text{-}H_2BH_2)H]$ **75**, C_2H_4, and $[Ru(PMe_2Ph)_2(CO)(\eta^2\text{-}C_2H_4)(\eta^1\text{-}HBH_3)H]$, with slower conversion to $[Ru(PMe_2Ph)_2(CO)(Et)(\eta^2\text{-}H_2BH_2)]$.[166]



75

Under reflux conditions, $[Ru(PPh_3)_3(CO)HCl]$ reacts with $CH_2{=}CMeCH_2OH$ to give two isomers of $[Ru(PPh_3)_2(CO)\{\eta^2\text{-}(Me)CHCO_2\}Cl]$.[167] Ethyl carbamate ($H_2NCO_2Et$) or urea ($H_2NCONH_2$) react with $[Ru(PPh_3)_3(CO)H_2]$ under refluxing conditions to form $[Ru(PPh_3)_3(CO)(NCO)H]$. With $[Ru(PPh_3)_4H_2]$ as the precursor, $[Ru(PPh_3)_2(CO)_2(NCO)H]^*$ is produced; in all cases, these reactions occur by loss of alcohol or ammonia from *N*-bonded carbamato or ureido intermediates.[168] The substitutionally labile dialkylcarbamate complex $[Ru(PPh_3)_2(CO)_2(O_2CN^iPr_2)_2]$[169] reacts with TfOH to yield $[Ru(PPh_3)_2(CO)_2(O_2CN^iPr_2)](OTf)$ and $[Ru(PPh_3)_2(CO)_2(OTf)_2]$. A reinvestigation of a literature route to the latter complex via reaction of $[Ru(PPh_3)_2(CO)_3]$ with HOTf gave *mer*-$[Ru(PPh_3)_2(CO)_3H](OTf)$ **76** as an intermediate species. This can be trapped as the methanol adduct, $[Ru(PPh_3)_2(CO)_2(MeOH)H](OTf)^*$ **77**.[170]



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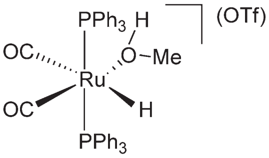

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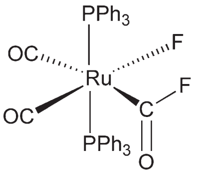
The fluoroacyl complex $[Ru(PPh_3)_2(CO)_2\{C(O)F\}F]$ 78 proves to be unstable at room temperature and decomposes by elimination of CO to yield $[Ru(PPh_3)_2(CO)_2F_2]^*$ 79. The osmium analog may be formed by thermolysis of the fluoroacyl complex $[Os(PPh_3)_2(CO)_2\{C(O)F\}F]$ in solution.[171]. An alternative route to both the Ru and Os species involves treatment of $[M(PPh_3)_2(CO)_2H_2]$ with anhydrous HF.[172] The dark green solids produced on removal of excess $HOTeF_5$ from solutions of $[M(PPh_3)_2(CO)_3]$ showed ^1H NMR spectra consistent with the formation of $[M(PPh_3)_2(CO)_3H]^+$.[173] Addition of $P(C_6H_4\text{-}p\text{-}OH)_3$ to the tetrameric species $[\{Os(CO)_3F(\mu\text{-}F)\}_4]$[16,17] affords $[Os\{\kappa^3\text{-}(P,O,O)\text{-}P(C_6H_4\text{-}2\text{-}OH)(2\text{-}OC_6H_4)_2\}(CO)_3]^*$.[174] Refluxing $[Ru(PPh_3)_3Cl_2]$ in DMF affords $[Ru(PPh_3)_2(CO)(DMF)Cl_2]^*$.[175]



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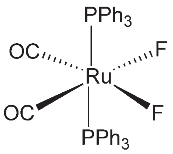
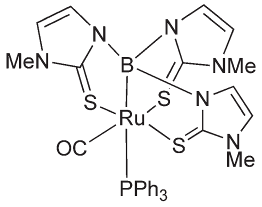


79

Treatment of $[Ru(PPh_3)_3(CO)RCl]$ (R = $CH{=}CHCPh_2OH$, $CH{=}CH_2$, $CH{=}CH(p\text{-tolyl})$, Ph) with $Na[HB(mt)_3]$ (mt = 2-sulfanyl-1-methylimidazole) affords the novel ruthenaboratrane complex $[Ru(PPh_3)(CO)\{B(mt)_3\}]^*$ 80.[176] This same species results from the hydrogenation of $PhC{\equiv}CH$ by $[Ru(PPh_3)(CO)\{\kappa^3\text{-}(H,S,S)\text{-}HB(mt)_3\}H]^*$, which is formed upon addition of $Na[HB(mt)_3]$ to either $[Ru(PPh_3)_3(CO)HCl]$ or $[Ru(PPh_3)_2(CO)(MeCN)_2H](ClO_4)$.[177] Addition of LiNHPh to $[Ru(PPh_3)(CO)\{HB(pz)_3\}(OTf)]$[178] gives the amido complex $[Ru(PPh_3)(CO)\{HB(pz)_3\}(NHPh)]^*$, while reaction with an excess of NH_2Ph affords the cationic amine complex $[Ru(PPh_3)(CO)\{HB(pz)_3\}(NH_2Ph)](OTf)$.[179] The '$[M(PPh_3)_2(CO)]$' fragment (M = Ru, Os) has been used to support phosphaalkenyl and mixed phosphaalkenyl/phosphaalkene complexes, including 81, 82 and 83.[38,42,180,181] The coordinatively unsaturated phosphaalkenyl complex $[Ru(PPh_3)_2(CO)(\eta^1\text{-}P{=}CHCMe_3)Cl]$ reacts with CO and $[9]aneS_3$ to afford $[Ru(PPh_3)_2(CO)_2(\eta^1\text{-}P{=}CHCMe_3)Cl]$ and $[Ru(PPh_3)(CO)(\eta^1\text{-}P{=}CHCMe_3)([9]aneS_3)]Cl$, analogous to the reaction shown for the CS analog in Scheme 4. Reaction with CN^tBu affords the mono- and bis-isocyanide complexes $[Ru(PPh_3)_2(CO)(\eta^1\text{-}P{=}CHCMe_3)(CN^tBu)Cl]$ and $[Ru(PPh_3)_2(CO)(\eta^1\text{-}P{=}CHCMe_3)(CN^tBu)_2]Cl$ depending on the amount of CN^tBu added,[42] while $[Au(PPh_3)X]$, $HgCl_2$, or Hg_2Cl_2 result in addition of the M–X group across the Ru–P bond to give $[Ru(PPh_3)_2(CO)\{P(AuPPh_3){=}CHCMe_3\}ClX]$ (X = Cl^*, $C{\equiv}C\text{-}p\text{-tolyl}$) and $[Ru(PPh_3)_2(CO)\{P(HgCl){=}CHCMe_3\}Cl_2]$.[182] The reaction of $[Ru(PPh_3)_2(CO)(CN\text{-}2,6\text{-}Me_2C_6H_3)(P{=}CH^tBu)Cl]$ with HBF_4 provides, rapidly and reversibly, the phosphaalkene complex $[Ru(PPh_3)_2(CO)(CN\text{-}2,6\text{-}Me_2C_6H_3)(HP{=}CH^tBu)Cl](BF_4)$, which is converted by KHF_2 or NBu_4F to the fluorophosphine complex $[Ru(PPh_3)_2\{PHF(CH_2{}^tBu)\}(CN\text{-}2,6\text{-}Me_2C_6H_3)(CO)Cl](BF_4)^*$.[183] The reaction of $[Ru(PPh_3)_3(CO)_2]$ with phosphaalkyne $P{\equiv}C(2,4,6\text{-}{}^tBu_3C_6H_2)$ yields the phosphorus-bound σ-phosphaalkyne complex $[Ru(PPh_3)_2(CO)_2\{P{\equiv}C(2,4,6\text{-}{}^tBu_3C_6H_2)\}]$.[184]



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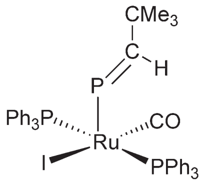

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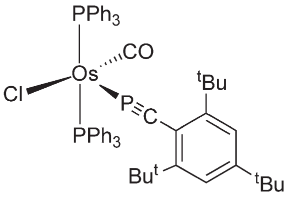

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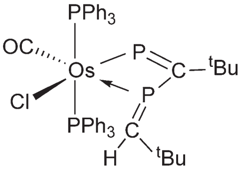
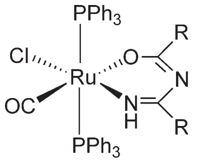


83

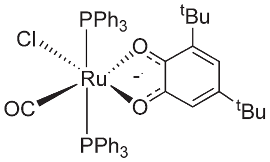
The reactions of $[Ru(PPh_3)_3(CO)HCl]$, $[Ru(PPh_3)_2(CO)(SnPh_3)Cl]$, or $[Ru(PPh_3)_2(CO)(NCMe)_2H](BF_4)$ with tris-pyrazolylborate yields $[Ru(PPh_3)_2(CO)\{\eta^2\text{-}HB(pz)_3\}H]$, which converts into $[Ru(PPh_3)(CO)\{\eta^3\text{-}HB(pz)_3\}H]$ upon thermolysis. Analogous reactivity is seen with $[Ru(PPh_3)_3(CS)HCl]$ or $[Os(PPh_3)_2(CO)(Ph)Cl]$ as precursors.[185]

The carbonyl complexes $[M(PPh_3)_2(CO)\{NHC(CF_3)NC(CF_3)NH\}H]^*$(M = Ru^*, Os), $[M(PPh_3)_2(CO)\{NHC(CF_3)NC(CF_3)\ NH\}Cl]$, and $[Ru(PPh_3)_2(CO)\{NHC(CF_3)NC(CF_3)NH\}(O_2CCF_3)]$ bearing the *N*,*N'*-chelating 1,1,1,5,5,5-hexafluoro-3-azapentane-2,4-diiminate ligand have been described.[186] In the presence of water, aromatic nitriles react with $[Ru(PPh_3)_3(CO)HCl]$ at 120 °C to afford the *N*-imidoylimidato complexes $[Ru(PPh_3)_2(CO)\text{-}\{NH{=}CRN{=}CRO\}Cl]$ 84 (R = *p*-tolyl*, *m*-tolyl, Ph). The hydride–chloride precursor reacts at the same high temperature with a 1 : 1 mixture of $RCONH_2/R^1CN$ to give the cross-linked species $[Ru(PPh_3)_2(CO)(NH{=}CRN{=}CR^1O)Cl]$ ($R = Ph$, $R^1 = p$-tolyl; $R = p$-tolyl, $R^1 = Ph^*$).[187] With benzoylacetonitrile in refluxing benzene, $[Ru(PPh_3)_2(CO)\{O{=}CPhC(CN){=}C(CH_2COPh)NH\}Cl]^*$ is generated.[188]



84

The $[Ru(PPh_3)_2(CO)]$ and $[Ru(CO)_2]$ fragments have been used to stabilize a range of odd-electron ligands in the form of the semiquinone complexes $[Ru(PPh_3)_2(CO)(dbsq)Cl]^*$ **85**, $[Ru(PPh_3)_2(CO)(tcsq)Cl]$, $[Ru(PPh_3)_2(CO)(tcsq)H]$, and $[Ru(CO)_2(phenoxsq)_2]^*$ (dbsq = 3,5-$^tBu_2$-*o*-benzoquinone; tcsq = 3,4,5,6-Cl_4-*o*-benzoquinone; phenoxsq = 2,4,6,8-$^tBu_4$-phenoxazin-1-one)[189,190] and azo radical anion species $[Ru(PPh_3)_2(CO)(L^{\cdot -})X]$, $[Ru(PPh_3)_2(CO)(L^{\cdot -})H]$, and $[Ru(PPh_3)(CO)(L^{\cdot -})_2]$ (L = 1-methyl-2-(*p*-chlorophenylazo)imidazole, $X = Cl^*$; L = 2-(phenylazo)pyridine, $X = Cl^*$, Br^* **86**).[191–193]



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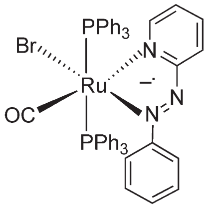
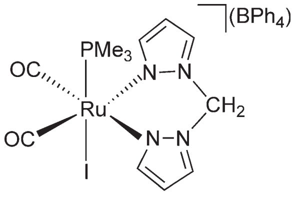


86

Related osmium derivates of the radical anions have also been prepared.[194] The trisimidazole ligands tris(*N*-methylimidazol-2-yl)methanol $\{(mim)_3COH\}$ and tris(*N*-ethoxymethylimidazol-2-yl)methanol $\{(emim)_3COH\}$ react with $[M(PPh_3)_3(CO)HCl]$ to afford $[M(PPh_3)(CO)\{(mim)_3COH\}H](Cl)$ and $[M(PPh_3)(CO)\{(emim)_3COH\}H](Cl)$ ($M = Ru^*$, Os).[195] Complexes bearing an additional PPh_3 ligand, for example, $[Ru(PPh_3)_2(CO)\{(MeN_2H_2C_3)_2CO\}H](BF_4)^*$, are formed if related bidentate imidazole-based ligands are used.[196] Exposure of the water-soluble dimer $Na_4[\{Ru(TPPMS)_2Cl\}_2(\mu\text{-}Cl)_2]$ to an atmosphere of CO in MeOH affords $Na_2[Ru(TPPMS)_2(CO)Cl_2]$; the same compound also results from hydrolysis or carbonylation of the vinylidene complex $Na_2[Ru(TPPMS)_2({=}C{=}CHPh)Cl_2]$.[197]

Parahydrogen-induced polarization (PHIP) studies have been utilized extensively to probe the formation and isomerization of ruthenium phosphine/arsine carbonyl hydride complexes $[RuL_2(CO)_2H_2]$ ($L = AsMe_2Ph$, PMe_2Ph, Pcy_3, PMe_3), and $[Ru(PPh_3)_3(CO)H_2]$.[198–200] The bis-phosphine dicarbonyl complexes $[RuL_2(CO)_2H_2]$ exist as three isomers (*all-cis; cis,cis,trans*-L; *cis,cis,trans*-CO) with equilibrium ratios that are highly dependent on the electronic properties of L.[90] NOE and PGSE NMR measurements have been used to establish cation–anion interactions and distances in a range of ruthenium and osmium carbonyl complexes such as *trans*-$[M(PMe_3)_2(CO)(COMe)(CH_2pz_2)]^+$ ($M = Ru$[201,202]), $[Ru(PMe_3)(CO)(COMe)(\eta^3\text{-}pz_3CH)]^+$,[203] $[Ru(PMe_3)(CO)_2(Me(CH_2pz_2)]^+$,[203] $[Ru(PMe_3)(CO)_2I(CH_2pz_2)]^+$, **87**[203] and *trans*-$[Ru(PMe_3)_2(CO)(COMe)(N\text{–}O)]^+$ (N–O = 2-acetylpyridine, 2-benzoylpyridine, 2,2′-dipyridylketone).[204]



87

Upon refluxing in MeOH and then recrystallization from wet hexane, *all-trans*-[Ru(PEt_3)$_2$(CO)$_2$Cl$_2$] converts to *trans*-[Ru(PEt_3)$_2$(CO)(H_2O)Cl$_2$]*; the coordinated water is readily substituted by CO to reform the precursor.[205] Cleavage of {Os(CO)$_3$(μ-Cl)Cl}$_2$ with a variety of phosphines PR_3 affords *trans,cis,cis*-[Os(PR_3)$_2$(CO)$_2$Cl$_2$] (PR_3 = PEt_3^{*}, PCy_3, PPh_3, $PEtPh_2$, $PMePh_2$).[206]

6.11.6.2.2.2 [M(PPh_3)$_2$(CO)] based complexes in "Roper chemistry"

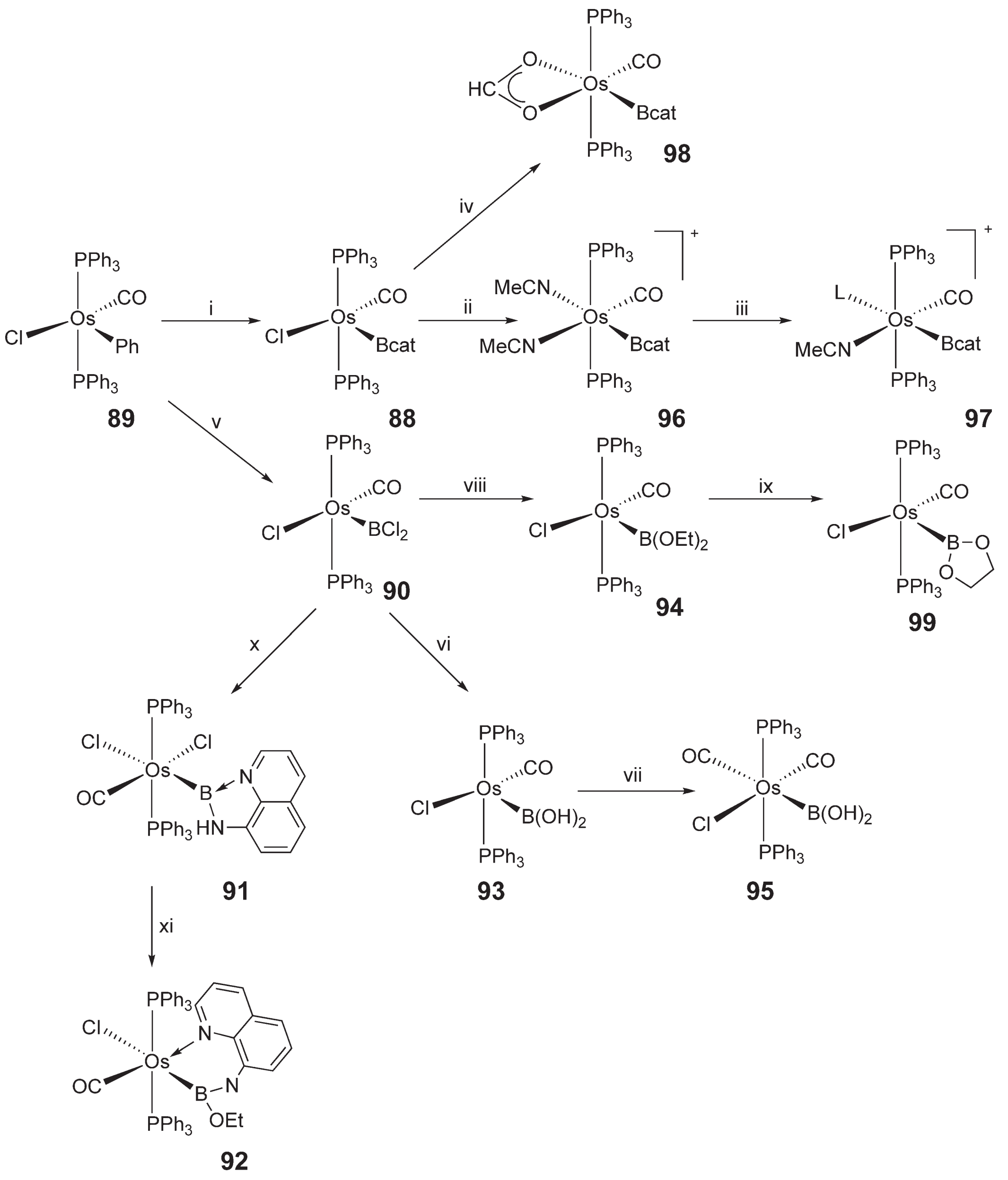
Extensive studies with the [M(PPh_3)$_2$(CO)] (M = Ru, Os) fragments have originated from the Roper group and will be dealt with in this separate section due to the overlap of a wide range of studies. These are discussed in sections relating to boryl, silyl, and stannyl ligands in turn.

The five-coordinate boryl complexes [Ru(PPh_3)$_2$(CX)(BR_2)Cl] (X = O, BR_2 = $BO_2C_6H_4$, $BO_2C_{10}H_6$, B(NH)$_2C_6H_4$, B(NH)SC_6H_4; X = S, BR_2 = $BO_2C_6H_4$, B(NH)SC_6H_4; X = N-4-MeC_6H_4, BR_2 = $BO_2C_6H_4$) result from addition of the appropriate borane to [Ru(PPh_3)$_2$(CX)HCl]. Related osmium boryl complexes **88** cannot be formed from the Os hydride precursors, but rather from [Os(PPh_3)$_2$(CX)(Ph)Cl] (X = O **89**, S) and borane.[207] Using the same methodology, [Os(PPh_3)$_2$(CO)(BCl_2)Cl] **90** can be formed. Addition of 8-aminoquinoline yields the base-stabilized terminal borylene complex* **91**, which is transformed into the ethoxyaminoboryl complex* **92** upon addition of EtOH.[208] Related pyridyl boryl complexes and amino boryl/borylene systems can also be formed.[209,210] Addition of water or alcohols to **90** affords [Os(PPh_3)$_2$(CO){B(OR)$_2$}Cl] (R = H* **93**, Me, Et* **94**), which can be trapped by CO to give the dicarbonyl adduct **95** (Scheme 11).[211]

Reductive elimination of RBcat (R = *o*-tolyl; Bcat = B-1,2-$O_2C_6H_4$) from the osmium aryl–boryl complex *trans,cis,cis*-[Os(PPh_3)$_2$(CO)$_2$(R)(Bcat)] in the presence of HBcat or $CHCl_3$ generates *trans,cis,cis*-[Os(PPh_3)$_2$(CO)$_2$(Bcat)H] and *trans,cis,cis*-[Os(PPh_3)$_2$(CO)$_2$Cl$_2$], respectively. Both *trans,cis,cis*-[Os(PPh_3)$_2$(CO)$_2$(R)(Bcat)] and *trans,cis,cis*-[Os(PPh_3)$_2$(CO)(CN-*p*-tolyl)(R)(Bcat)] lose RBcat in the presence of B_2cat_2 to afford *cis,trans,cis*-[Os(PPh_3)$_2$(CO)(L)(Bcat)$_2$] (L = CO, CN-*p*-tolyl*).[212,213] The related Ru bis-Bcat complexes *cis,trans,cis*-[Ru(PPh_3)$_2$(CO)(L)(Bcat)$_2$] (L = CO*, CN-*p*-tolyl*) are generated upon addition of B_2cat_2 to [Ru(PPh_3)$_3$(CO)L].[213] Treatment of [Os(PPh_3)$_2$(CO)(Bcat)Cl] with $AgSbF_6$ in THF affords the solvent-stabilized cationic boryl complex [Os(PPh_3)$_2$(CO)(Bcat)(THF)$_2$][SbF_6]. Loss of THF occurs readily in MeCN to yield [Os(PPh_3)$_2$(CO)(Bcat)(NCMe)$_2$][SbF_6] **96**. This complex in turn loses the nitrile ligand *trans* to the boryl group upon addition of π-acceptor ligands (CO, *p*-tolyl-NC) to give [Os(PPh_3)$_2$(CO)(Bcat)(MeCN)L][SbF_6] **97**. The neutral six-coordinate boryl complexes [Os(PPh_3)$_2$(CO)(Bcat)(η^2-O_2CH)] **98**, [Os(PPh_3)$_2$(CO)(Bcat)(η^2-O_2N)], and [Os(PPh_3)$_2$(CO)(Bcat)(η^2-S_2CNEt_2)] can be isolated upon reaction of **88** with formate, nitrite, and diethyldithiocarbamate, respectively.[214] Boryl exchange can be brought about by diols. Thus, addition of HO(CH_2)$_n$OH (*n* = 2, 3) and 2 equiv. of Me_3SiCl to [Os(PPh_3)$_2$(CO){B(OEt)$_2$}Cl] **94** generates [Os(PPh_3)$_2$(CO){BOC_2H_4O}Cl]* **99** and [Os(PPh_3)$_2$(CO){BOC_3H_6O}Cl]*. If only 1 equiv. of chlorosilane is used in the 1,2-ethanediol reaction, a mixture of **99** and [Os(PPh_3)$_2$(CO){B(OEt)(OC_2H_4OH)}Cl]* is formed.[215]

The six-coordinate silyl complex [Ru(PPh_3)$_2$(CO)($SiPh_2Cl$)(κ^2-S_2CNMe_2)]*, prepared by addition of $HSiPh_2Cl$ to [Ru(PPh_3)$_2$(CO)(κ^2-S_2CNMe_2)H]*, undergoes Si–Cl bond cleavage with 2-hydroxypyridine, 2-aminopyridine, and thallium acetate producing the monophosphine complexes, [Ru(PPh_3)(CO){κ^2-(*Si,N*)-$SiPh_2OC_5H_4N$}(κ^2-S_2CNMe_2)]*, [Ru(PPh_3)(CO){κ^2-(*Si,N*)-$SiPh_2NHC_5H_4N$}(κ^2-S_2CNMe_2)]*, and [Ru(PPh_3)(CO){κ^2-(*Si,O*)-$SiPh_2OCMeO$}(κ^2-S_2CNMe_2)]*.[216] Treatment of [Ru(PPh_3)$_3$(CO)HCl] or [M(PPh_3)$_3$(CO)PhCl] (M = Ru, Os **89**) with $HSiMeCl_2$ produces the five-coordinate dichloro(methyl)silyl complexes, [M(PPh_3)$_2$(CO)($SiMeCl_2$)Cl] (M = Ru, Os), which both react with OH^- and with EtOH to give [M(PPh_3)$_2$(CO){SiMe(OH)$_2$}Cl] (M = Ru, Os) and [M(PPh_3)$_2$(CO){SiMe(OEt)$_2$}Cl] (M = Ru, Os*). Very different Os–Si distances are found in [Os(PPh_3)$_2$(CO){SiMe(OEt)$_2$}Cl] (2.3196(11) Å) and the CO addition product [Os(PPh_3)$_2$(CO)$_2${SiMe(OEt)$_2$}Cl]* (2.4901(8) Å). Addition of 8-aminoquinoline to [M(PPh_3)$_2$(CO)($SiMeCl_2$)Cl] results in loss of one PPh_3 ligand to yield [M(PPh_3)(CO)($SiMeCl_2$){κ^2-(*N,N*)-$NC_9H_6NH_2$-8}Cl] (M = Ru*, Os); both species react readily with EtOH to afford the ethanolysis products [M(PPh_3)(CO){SiMe(OEt)$_2$}{κ^2-(*N,N*)-$NC_9H_6NH_2$-8}Cl]. In the ruthenium case, an intermediate species, [Ru(PPh_3)(CO){SiMeCl(OEt)}{κ^2-(*N,N*)-$NC_9H_6NH_2$-8}Cl]*, is isolable.[217]

Oxidative addition of tri-*N*-pyrrolylsilane to [M(PPh_3)$_3$(CO)$_2$] affords [M(PPh_3)$_2$(CO)$_2$($SiPyr_3$)H] (M = Ru, Os*; Pyr = 1-NC_4H_4), whereas use of [M(PPh_3)$_2$(CO)(Ph)Cl] as the precursor leads to loss of benzene and formation of [M(PPh_3)$_2$(CO)($SiPyr_3$)Cl], which affords the six-coordinate dicarbonyl complex for Os upon addition of CO.[218] The Os phenyl-chloro precursor **89** also reacts with HSi(OEt)$_3$ to yield [Os(PPh_3)$_2$(CO){Si(OEt)$_3$}Cl]* **100**, which reversibly binds CO **101**.[219] Other five-coordinate osmium silyl complexes [Os(PPh_3)$_2$(CO)(SiR_3)Cl] (R = F*, Cl*, OH*, Me* **103**) can be prepared from [Os(PPh_3)$_2$(CO)($SiCl_3$)Cl] **102** (Scheme 12).[220]

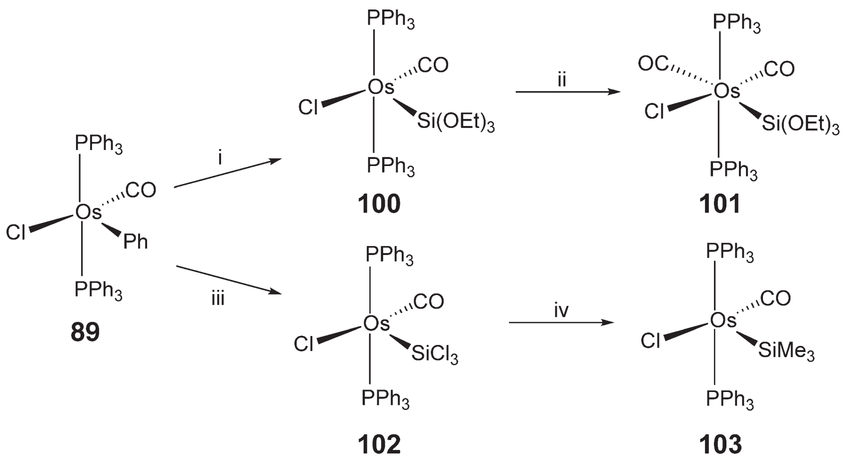


i, HBcat, Δ; ii, AgSbF$_6$, MeCN; iii, L; iv, NaO$_2$CH; v, HBCl$_2$·OEt$_2$, Δ; vi, H$_2$O; vii, CO; viii, EtOH; ix, HOC$_2$H$_4$OH, 2Me$_3$SiCl; x, 8-aminoquinoline; xi, EtOH

Scheme 11

A range of functionalized silicon-based ligands can be supported on the [Os(PPh$_3$)$_2$(CO)] fragment including the silatranes [Os(PPh$_3$)$_2$(CO)$_2${Si(OCH$_2$CH$_2$)$_3$N}H]*[221] and [Os(PPh$_3$)$_2$(CO){Si(OCH$_2$CH$_2$)$_3$N}(κ^2-S$_2$CNMe$_2$)]*,[222] silanolate [Os(PPh$_3$)$_2$(CO)(SiMe$_2$OLi)Cl], osmadisiloxanes [Os(PPh$_3$)$_2$(CO)(SiMe$_2$OSiMe$_3$)Cl]* and [Os(PPh$_3$)$_2$(CO)(SiMe$_2$OSiMe$_3$)(κ^2-S$_2$CNMe$_2$)]*, and the osmastannasiloxane [Os(PPh$_3$)$_2$(CO)(SiMe$_2$OSnMe$_3$)Cl]*.[223]

Addition of an excess of HSiMe$_2$NMe$_2$ to [M(PPh$_3$)$_2$(CO)(SiMe$_2$Cl)Cl] affords a mixture of [M(PPh$_3$)$_2$(CO)(SiMe$_2$NMe$_2$SiMe$_2$)Cl] (M = Ru, Os*) and [M(PPh$_3$)$_2$(CO)(SiMe$_2$NMe$_2$SiMe$_2$)H] (M = Ru, Os*); for M = Ru, the diruthenium species [Ru(SiMe$_2$NMe$_2$SiMe$_2$)(CO)(μ-{SiMe$_2$})$_2$(μ-Cl)Ru(PPh$_3$)(CO)H$_2$]* is also formed.[224]



i, $HSi(OEt)_3$, Δ; ii, CO; iii, $HSiCl_3$, Δ; iv, MeLi

Scheme 12

Oxidative addition of the group 14 hydrides $H–ER_2R^1$ to $[M(PPh_3)_3(CO)_2]$ yields $[M(PPh_3)_2(CO)_2(ER_2R^1)H]$ (M = Os, E = Si*, R = R^1 = Me, Et*, Ph, R = Ph, R^1 = H; E = Ge*, Sn, R = R^1 = *p*-tolyl*; M = Ru, E = Ge, Sn, R = R^1 = *p*-tolyl). NMR and IR spectroscopy show that all of these compounds have *cis*-phosphines and *trans*-carbonyl groups, with the exception of $[Os(PPh_3)_2(CO)_2(SiPh_2H)H]$.[225] A range of simple stannyl complexes is available from 18-electron hydride–chloride complexes.[226,227,228] Photolysis of $[M(PPh_3)_3(CO)HCl]$ (M = Ru, Os) in the presence of $(CH_2{=}CH)SnR_3$ affords the transient species $[Ru(PPh_3)_2(CO)(CH_2CH_2SnR_3)Cl]$, which eliminates C_2H_4 to give the stannyl complexes $[Ru(PPh_3)_2(CO)(SnR_3)Cl]$ (R = Me*, ^{n}Bu, *p*-tolyl).[226,229] Trapping of these 16-electron complexes by two-electron donors such as CO and CN-*p*-tolyl gives the coordinatively saturated complexes; chloride abstraction takes place upon addition of carboxylate or dialkyldithiocarbamates.[227] Addition of CO to $[Os(PPh_3)_2(NO)\{Sn(p\text{-tolyl})_3\}HCl]$ affords the formally Os(0) stannyl complex $[Os(PPh_3)(CO)_2(NO)\{Sn(p\text{-tolyl})_3\}]^*$.[229] Trimethylstannane reacts with $[Os(PPh_3)_3(CO)HCl]$, $[Os(PPh_3)_2(CO)Ph(X)]$ (X = Cl, I), or $[Os(PPh_3)_2(CO)(SiMe_2Cl)Cl]$ to give the same product in all cases, namely $[Os(PPh_3)_2(CO)(SnMe_3)H_2]$.[225] Treatment of $[Os(PPh_3)_2(CO)(SnMe_3)Cl]$ with pyridine or NaOAc leads to migration of one of the tin methyl groups to the osmium center.[230,231]

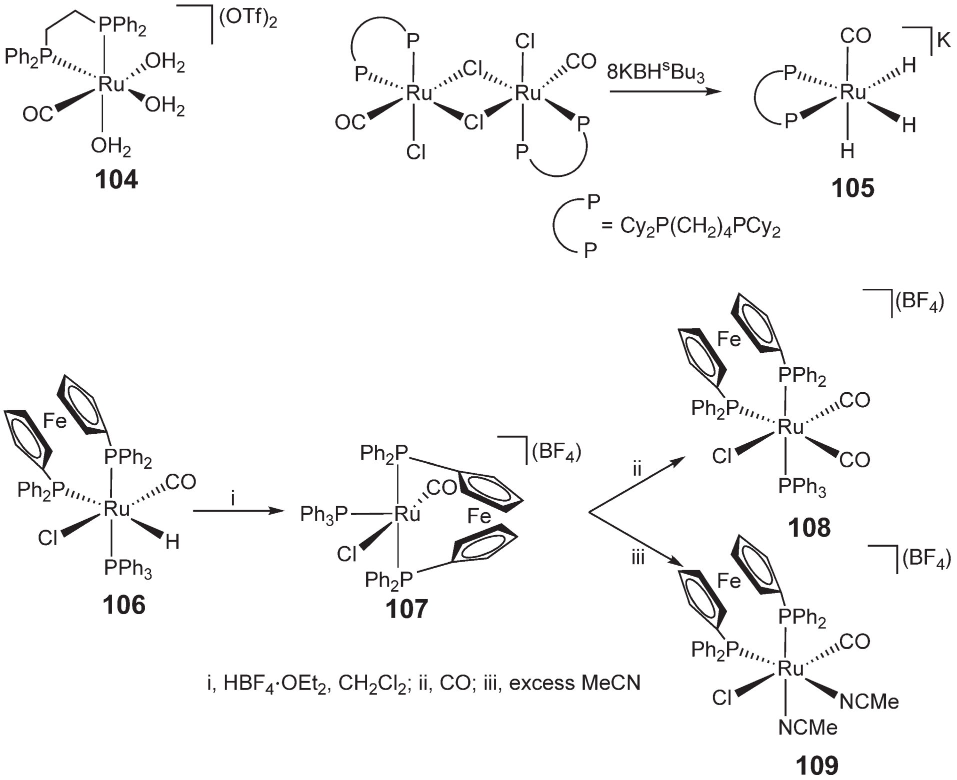
Photolysis of $[Os(PPh_3)_3(CO)_2]$ in the presence of Me_3SnH affords four isomers of the oxidative addition product, the major product being *cis,trans,cis*-$[Os(PPh_3)_2(CO)_2(SnMe_3)H]$. Treatment with Me_2SnCl_2 leads to a redistribution reaction at the stannyl ligand to generate four isomers of $[Os(PPh_3)_2(CO)_2(SnMe_2Cl)H]$, the major species now being the *trans,cis,cis*-isomer. A related redistribution reaction with SnI_4 gives just the *trans,trans,cis*-$[Os(PPh_3)_2(CO)_2(SnMeI_2)H]$ product; *trans,trans,cis*-$[Os(PPh_3)_2(CO)_2(SnMeI_2)I]^*$ is formed upon subsequent reaction with I_2.[232] The $[Os(PPh_3)_2(CO)]$ fragment has been used as a framework to support a range of ligand sets, such as in the stannatrane $[Os(PPh_3)_2(CO)\{Sn(OEt)_3N\}(\kappa^2\text{-}S_2CNMe_2)]^*$[222] and osmastannasiloxane $[Os(PPh_3)_2(CO)(SiMe_2OSnMe_3)Cl]^*$.[223]

6.11.6.2.3 Divalent bidentate phosphine carbonyl complexes

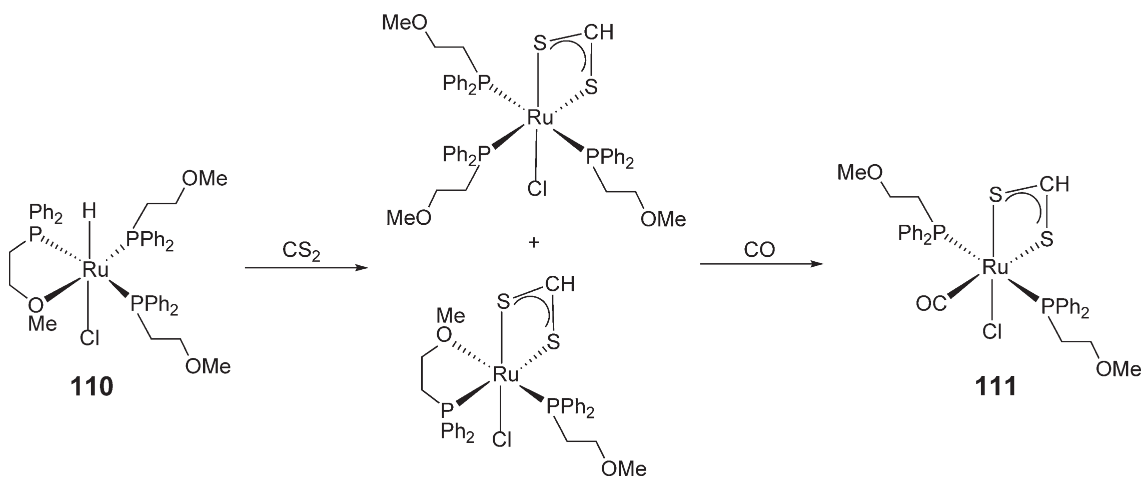
At elevated temperatures, $[Ru(PPh_3)_3(CO)H_2]$ loses two phosphine ligands in the presence of bidentate phosphines P–P to give $[Ru(PPh_3)(P–P)(CO)H_2]$ (P–P = dppe, dppp*, dppb, dppf).[233] These undergo cyclometallation of the chelating phosphine upon heating in the presence of styrene. Treatment of $[Ru(PPh_3)_3(CO)HCl]$ with 1 equiv. of chelating phosphines P–P affords three different products. At short times and room temperature, $[Ru(PPh_3)_2\{\kappa\text{-}P\text{-}(P–P)\}(CO)HCl]$ (P–P = dppm, dppe, dppp) are formed, while prolonged reaction times and more vigorous conditions afford $[Ru(PPh_3)(P–P)(CO)HCl]$ (P–P = dppm, dppe, dppp, dppb), two isomers being found in the cases of P–P = dppm and dppe. When 2 equiv. of P–P is reacted with either $[Ru(PPh_3)_3(CO)HCl]$ or $[Ru(PPh_3)_2(CO)(MeCN)_2H]^+$, *trans*-$[Ru(P–P)_2(CO)H](X)$ (P–P = dppm, dppe, dppp; X = Cl, PF_6) can be isolated.[234] Addition of AgOTf to *all-cis*-$[Ru(dppe)(CO)_2Cl_2]$ affords *all-cis*-$[Ru(dppe)(CO)_2(OTf)_2]^*$, which reacts with water in solution to give $[Ru(dppe)(CO)(H_2O)_3](OTf)_2^*$ **104**; facile substitution occurs with a range of two-electron donors L (MeCN, DMSO) to give $[Ru(dppe)(CO)(L)_3](OTf)_2$.[235–237] The analogous tris-aqua complex is made with the chelating alkyl phosphine dtbpe in place of dppe. Both the dppe and dtbpe complexes show water gas shift chemistry with CO_2, forming the tricarbonyl hydride complexes $[Ru(P–P)(CO)_3H](OTf)^*$.[238] In the bidentate phosphine complex *all-cis*-$[Ru(dppe)(CO)_2H_2]$ **32**, interchange of the hydride positions in the *cis,cis,cis*-isomer occurs along with synchronized CO exchange and interchange of the two phosphorus atoms via a postulated η^2-H_2 complex.[90]

The dicarbonyl complexes $[Ru\{MeP(CH_2CH_2PMe_2)_2\}(CO)_2]^*$ and $[Ru\{MeP(CH_2CH_2CH_2PMe_2)_2\}(CO)_2]^*$ react instantaneously with MeI at room temperature to give *fac,cis*- and *mer,cis*-$[RuMe\{MeP(CH_2CH_2PMe_2)_2\}(CO)_2]I$ and *mer,trans*- and *mer,cis*-$[RuMe\{MeP(CH_2CH_2CH_2PMe_2)_2\}(CO)_2]I$. CO insertion with *mer,cis*-$[RuMe\{MeP(CH_2CH_2CH_2PMe_2)_2\}(CO)_2]I$ affords the acetyl complex, *mer,trans*-$[Ru(COMe)\{MeP(CH_2CH_2CH_2PMe_2)_2\}(CO)_2]I$.[239] Complete transformation of $[Ru(dcypb)(CO)Cl_2]_2$ to $K[Ru(dcypb)(CO)H_3]^*$ **105** (dcypb = $Cy_2PCH_2CH_2CH_2CH_2PCy_2$) occurs upon addition of 8 equiv. of KBH^sBu_3; the trihydride anion reduces benzophenone to benzhydrol under mild conditions.[240] Reactions of *cis*-$Cy_2PCH_2CH{=}CHCH_2PCy_2$ with $[M(PPh_3)_3(CO)HCl]$ (M = Ru, Os) yield $[M(PPh_3)(Cy_2PCH_2CH{=}CHCH_2PCy_2)(CO)HCl]$; if the ruthenium complex is refluxed in $MeOH/CH_2Cl_2$, the tridentate pincer complex $[Ru(PPh_3)\{Cy_2PCH_2CH(CH_2)_2PCy_2\}(CO)Cl]^*$ forms. Subsequent reaction of this species with H_2 in the presence of $NaBPh_4$ produces $[Ru(PPh_3)\{Cy_2P(CH_2)_4PCy_2\}(CO)HCl]$.[241]

The chelating alkylphosphine complex, $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2Cl_2]$, which is synthesized as an inseparable mixture of isomers, has been used as a starting point for the formation of a range of hydride complexes, including $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2HCl]$, $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2H_2]$, and $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2H]^+$. The dihydride $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2H_2]$ yields the H_2-loss products $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_3]$ and $[Ru(^tBu_2PCH_2CH_2P^tBu_2)(CO)_2(\eta^2\text{-}C_2H_4)]$ with CO and ethene, respectively, under mild conditions.[107] Refluxing dppf with $[Ru(PPh_3)_3(CO)HCl]$ affords $[Ru(dppf)(PPh_3)(CO)HCl]^*$**106**,[234] which upon protonation with $HBF_4{\cdot}OEt_2$ loses H_2 to give the five-coordinate *trans*-phosphine complex, $[Ru(dppf)(PPh_3)(CO)Cl](BF_4)^*$ **107**; reactions with a range of Lewis bases L (CO, MeCN, CN^tBu) fill the vacant coordination site, yielding **108 and 109** (Scheme 13).[242] Addition of HX to the allyl precursor $[Ru(dppf)(CO)(\eta^3\text{-}2\text{-}C_3H_4Me)Cl]$ (X = Cl, Br) in CH_2Cl_2 gives the



Scheme 13



Scheme 14

halide-bridged dimers $[\{Ru(dppf)(CO)Cl\}_2(\mu\text{-}X)_2]$, which can be cleaved by CO under reflux and at room temperature by other two-electron donor ligands L to yield to give *all-cis*-$[Ru(dppf)(CO)(L)Cl_2]$ (L = CO, $PhCH_2NC$, $C_5H_5N^*$, $PhNH_2$).[243]

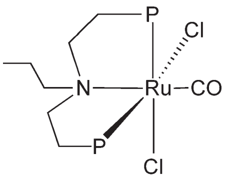
Addition of CO to the phosphino-ester dichloride complex $[Ru\{\kappa^2\text{-}(P,O)\text{-}{}^iPr_2PCH_2CO_2Me\}_2Cl_2]$ affords $[Ru\{\kappa^2\text{-}(P,O)\text{-}{}^iPr_2PCH_2CO_2Me\}(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)(CO)Cl_2]$. In contrast, the bromo analog gives the dicarbonyl $[Ru(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)(CO)_2Br_2]$ and the monocarbonyl only upon reaction in the solid state.[244] The five-coordinate cationic complex $[Ru(Ph_2PNMeNMePPh_2)_2Cl](BF_4)$ adds CO at room temperature to give *trans*-$[Ru(Ph_2PNMeNMePPh_2)_2(CO)Cl](BF_4)^*$ with a measured reaction enthalpy of $-142\,kJ\,mol^{-1}$.[245] The 1 : 1 reaction of $[Ru(CO)_2Cl_2]_x$ with $Ph_2P(CH_2)_nP(S)Ph_2$ affords *cis*-$[Ru\{\kappa^2\text{-}(P,S)\text{-}Ph_2PCH_2P(S)Ph_2\}(CO)_2Cl_2]$ and *cis*-$[Ru\{\kappa\text{-}(P)\text{-}Ph_2P(CH_2)_nP(S)Ph_2\}(CO)_2Cl_2]$ ($n = 2$, 3, 4). With 2 equiv. of phosphine, *cis*-$[Ru\{\kappa\text{-}(P)\text{-}Ph_2P(CH_2)_nP(S)Ph_2\}_2(CO)_2Cl_2]$ ($n = 1$, 2, 3, 4) are formed, although for the complex with $n = 1$, partial decarbonylation takes place in CH_2Cl_2/hexane to yield $[Ru\{\kappa^2\text{-}(P,S)\text{-}Ph_2P(CH_2)_nP(S)Ph_2\}_2(CO)Cl](Cl)^*$.[246] Treatment of the hemilabile complex **110** with CS_2 produces isomers of the $\eta^2\text{-}S_2CH$ complex, which can be trapped by CO forming **111*** (Scheme 14).[247]

The chelated ruthenium(II) dicarbonyl species $[Ru(biPSi)(CO)_2H]$ $\{biPSi = SiMe(CH_2CH_2CH_2PPh_2)_2\}$ undergoes hydrolysis with water/piperidine to give the siloxy complex $[Ru\{OSiMe(CH_2CH_2CH_2PPh_2)_2\}(CO)_2H]$, which can be isolated as the trimethyl phosphite derivative*. Oxidation of $[Ru(biPSi)(CO)_2H]$ with O_2 yields $[Ru\{OSi(OMe)(CH_2CH_2CH_2PPh_2)_2\}(CO)(L)H]$ (L = CO, $P(OMe)_3{}^*$).[248] At elevated temperature, the phosphinohydrazones (*Z*)-$PPh_2CH_2C^tBu{=}NNR_2$ react with $[Ru(CO)_2Cl_2]_x$ to yield $[Ru\{PPh_2CH_2C^tBu{=}NNR_2\}(CO)_2Cl_2]$ (R = Me) and $[Ru\{PPh_2CH_2C^tBu{=}NNR_2\}_2(CO)Cl](Cl)$ (R = H*), respectively. A mixture of *fac,cis*-* and *mer,cis*-$[Ru\{PPh_2CH_2C^tBu{=}NN{=}C^tBuCH_2PPh_2\}(CO)Cl_2]$ is formed upon using the diphosphine azine (*Z,Z*)-$PPh_2CH_2C^tBu{=}NN{=}C^tBuCH_2PPh_2$. UV photolysis of the *mer,cis*-isomer converts it cleanly to the *fac,cis*-species, while standing in daylight at room temperature reverses the isomerization.[249]

6.11.6.2.4 Divalent multidentate phosphine carbonyl complexes

Photoinduced loss of H_2 from $[Ru(etp)(CO)H_2]$ (etp = $PhP(CH_2CH_2PPh_2)_2$) generates the expected 16-electron Ru(0) species [Ru(etp)(CO)], which undergoes facile back reaction with H_2 (rate constant $\approx 10^8\,dm^3\,mol^{-1}\,s^{-1}$).[110] Addition of the tetradentate phosphine $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ to $[Ru(CO)_2Cl_2]_n$ yields the η^3-(*O,P,P*) coordinated *trans*-dichloride complex $[Ru\{Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2\}(CO)Cl_2]^*$.[250] The neutral phosphinoester complex $[Ru\{\kappa^3\text{-}(P,O,O)\text{-}P^tBu(CH{=}C(OMe)O)(CH_2C(OMe){=}O)\}\{\kappa^2\text{-}(P,O)\text{-}P^tBu(CH_2C(OMe){=}O)(CH_2CO_2Me)\}Cl]^*$ reacts with CO to give $[Ru\{\kappa^2\text{-}(P,O)\text{-}P^tBu(CH{=}C(OMe)O)(CH_2CO_2Me)\}\{\kappa^2\text{-}(P,O)\text{-}P^tBu(CH_2C(OMe){=}O)(CH_2CO_2Me)\}(CO)Cl]$.[251] Octahedral ruthenium(II) complexes of the type *mer*-$[Ru(Cyttp)(CO)(\kappa^2\text{-}O_2CX)]_n$ (Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$; $n = 0$, X = O; $n = 1$, X = Me, Ph, OMe, OEt) and *cis,mer*-$[Ru(Cyttp)(CO)X_2]$ (X = Cl, I) show high stability toward *syn*-to-*anti* and/or *anti*-to-*syn* isomerization, where *syn*/*anti* refer to Ph group orientation at P.[252]

The reaction of *mer,trans*-$[(PNP)Ru(PPh_3)Cl_2]$ ($PNP = CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$) with $PhC{\equiv}CH/H_2O$ in THF solution at 60 °C in a closed system produces *fac,cis*-$[(PNP)Ru(CO)Cl_2]$ **112** in quantitative yield.[253,254] A mechanism consistent with the experimental findings is shown in Scheme 14 in Chapter 6.05.



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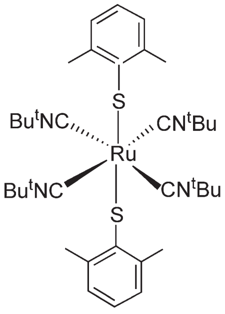
6.11.6.3 Compounds with Other Group 15 Ligands

Addition of Sb^iPr_3 to $RuCl_3{\cdot}xH_2O$ in ethanol in the presence of sodium carbonate forms *mer*-$[Ru(Sb^iPr_3)_3(CO)HCl]$, whereas addition of the stibine to a carbonylated hot ethanolic solution of $RuCl_3{\cdot}xH_2O$ forms *mer*-$[Ru(Sb^iPr_3)_3(CO)Cl_2]^*$, which reacts with CO to give *trans,cis,cis*-$[Ru(Sb^iPr_3)_3(CO)_2Cl_2]$. Analogously, using $OsCl_3{\cdot}xH_2O$ as the starting material yields *mer*-$[Os(Sb^iPr_3)_3(CO)HCl]$, which upon reduction with $NaBH_4$ or $LiAlH_4$ affords $[Os(Sb^iPr_3)_2(CO)H_4]$.[255] The use of SbR_3 ligands to support complexes with η^1-η^4 ligands is described in Chapter 6.05.

6.11.7 Isocyanide Complexes

Both cyclooctene ligands are readily displaced from *cis*-$[Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2]$ by CN^tBu to give *trans*-$[Ru(acac)_2(CN^tBu)_2]^*$; upon heating, isomerization to the more stable *cis*-compound* takes place.[256] The six-coordinate bis-isocyanide complexes *trans,trans,cis*-$[Ru(PPh_3)_2(CNR)_2Cl_2]$ (R = 2,6-xylyl, ^{t}Bu, ^{i}Pr, $PhCH_2$, *o*-OMe, *p*-ClC_6H_4) isomerize with first-order kinetics to *trans,cis,cis*-$[Ru(PPh_3)_2(CNR)_2Cl_2]$ upon heating at ≥100 °C in the solid state. Powder X-ray diffraction analysis on the conversion of complexes *trans,trans,trans*-$[Ru(PPh_3)_2(CN^tBu)_2Cl_2]$ shows that the *trans,cis,cis*-isomer produced is a polymorph of that produced by recrystallization of pure *trans,cis,cis*-$[Ru(PPh_3)_2(CN^tBu)_2Cl_2]$.[257] The ruthenium(IV) thiolate complex $[Et_3NH][Ru\{S(2,6\text{-}Me_2C_6H_3)\}_3(C{\equiv}CPh)Cl]$ reacts with an excess of CN^tBu to afford *trans*-$[Ru\{S(2,6\text{-}Me_2C_6H_3)\}_2(CN^tBu)_4]^*$ **113**.[258] The reactivity of $[Ru(PPh_3)_2\{HB(pz)_3\}Cl]$ with CN^tBu proves to be highly solvent dependent. In THF or CH_2Cl_2, the neutral mono-isonitrile complex $[Ru(PPh_3)(CN^tBu)\{HB(pz)_3\}Cl]^*$ is produced, while in a more polar solvent (CH_2Cl_2/MeOH) in the presence of NH_4PF_6, ionization of the Ru–Cl bond occurs to afford $[Ru(PPh_3)_2(CN^tBu)\{HB(pz)_3\}](PF_6)$. Treatment of $[Ru(PPh_3)_2\{HB(pz)_3\}Cl]$ with an excess of CN^tBu in MeOH/THF or reaction of $[Ru(PPh_3)(CN^tBu)\{HB(pz)_3\}Cl]$ with an excess of CN^tBu in CH_2Cl_2/MeOH yields the bis-isocyanide complex $[Ru(PPh_3)(CN^tBu)_2\{HB(pz)_3\}](PF_6)$ **114**.[259]



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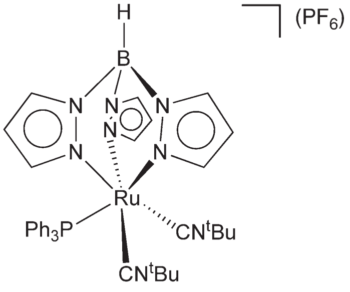


114

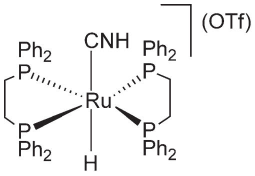
Addition of a stoichiometric amount of CN^tBu to $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}H_2)Cl_2]$ forms $[Os(P^iPr_3)_2(CO)(CN^tBu)HCl]$.[118] The bis-silane complexes $[Ru(PCy_3)_2\{(\eta^2\text{-}HSiMe_2)_2X\}H_2]$ (X = O, $-(CH_2)_2-$, $-(CH_2)_3-$, Me_2SiO_2) react with CN^tBu to give $[Ru(PCy_3)_2(CN^tBu)_2H_2]$.[155]

Addition of an excess of HOTf to *trans*-[Ru(P–P)$_2$(CN)H] under 1 atm of H_2 yields *trans*-[Ru(P–P)$_2$(CNH)(η^2-H$_2$)](OTf)$_2$; the same species can also be made by addition of HOTf to *trans*-[Ru(P–P)$_2$(CNH)H](OTf). However, [Ru(P–P)$_2$(CNH)(η^2-H$_2$)](OTf)$_2$ slowly, but reversibly, loses H_2 in solution to give [Ru(P–P)$_2$(CNH)(OTf)](OTf) (P–P = dppe*, dppp).[260] The isonitrile complexes *fac,cis*-[Ru(PNP)(CNR)Cl$_2$] are formed upon heating the secondary aminocarbene species *fac,cis*-[Ru(PNP){=C(NHR)(CH$_2$Ph)}Cl$_2$] (R = CH$_2$CH$_2$CH$_3$, Ph, Cy, *(R)*-(+)-CHMePh, *(R)*-(+)-CHMeEt, *(R)*-(+)-CHMe(1-naphthyl)*, H) in THF/water – the presence of water is vital as use of anhydrous organic solvents prevents any reaction taking place.[261]

The reaction of CN^{t}Bu with [Ru(L$_{OEt}$)(PPh$_3$)$_2$Cl] (L$_{OEt}$ = (η^5-C$_5$H$_5$)Co{P(O)(OEt)$_2$}$_3$) at 60 °C generates a low yield of [Ru(L$_{OEt}$)(PPh$_3$)(CN^{t}Bu)Cl],[262] while the dialkylthiophosphorylamide complex [Ru{N(SP^{i}Pr$_2$)$_2$}$_2$(PPh$_3$)] reacts with CN^{t}Bu to generate the bis-isocyanide complex [Ru{N(SP^{i}Pr$_2$)$_2$}$_2$(CN^{t}Bu)$_2$].[263] The bis-isocyanide complex [Ru(dppf)(CO)(CN^{t}Bu)$_2$Cl](BF$_4$) is formed at room temperature upon reaction of the isocyanide with [Ru(dppf)(PPh$_3$)(CO)Cl](BF$_4$).[242] Mixed phosphine–isocyanide complexes are formed upon reaction of *trans*-[Ru(dppm)$_2$Cl$_2$] with CNR, the product(s) depending upon the concentration of CNR used, whether R is alkyl or aryl, the solvent, and finally whether a halogen-abstracting agent is present.[264]

The phosphino-ester complex [Ru{κ^2-(*P,O*)-^{i}Pr$_2$PCH$_2$CO$_2$Me}$_2$Cl$_2$] reacts with 1 equiv. of CN^{t}Bu to afford [Ru{κ^2-(*P,O*)-^{i}Pr$_2$PCH$_2$CO$_2$Me}(κ-*P*-^{i}Pr$_2$PCH$_2$CO$_2$Me)(CN^{t}Bu)Cl$_2$], which reacts further at room temperature with more isocyanide to give [Ru(κ-*P*-^{i}Pr$_2$PCH$_2$CO$_2$Me)$_2$(CN^{t}Bu)$_2$Cl$_2$]. This same bis-CN^{t}Bu product can be formed directly upon addition of 2 equiv. of CN^{t}Bu to [Ru{κ^2-(*P,O*)-^{i}Pr$_2$PCH$_2$CO$_2$Me}(κ-*P*-^{i}Pr$_2$PCH$_2$CO$_2$Me)(=C=CHPh)Cl$_2$].[244]

The related bis-isocyanide species [Ru{κ^2-(*P,O*)-P^{t}Bu(CH=C(OMe)O)(CH$_2$CO$_2$Me)}{κ-*P*-P^{t}Bu(CH$_2$CO$_2$Me)$_2$}(CNMe)$_2$Cl] **116** is formed upon reaction of [Ru{κ^3-(*P,O,O*)-P^{t}Bu(CH=C(OMe)O)(CH$_2$C(OMe)=O)}{κ^2-(*P,O*)-P^{t}Bu(CH$_2$C(OMe)=O)(CH$_2$CO$_2$Me)}Cl] with CNMe,[251] while [Ru(κ^2-^{i}Pr$_2$PCH$_2$PPh$_2$)(η^2-OC$_6$Cl$_5$)$_2$] undergoes ring opening of the both the phenoxide and phosphine ligands in the presence of CN^{t}Bu, leading to [Ru(κ-Ph$_2$PCH$_2$P^{i}Pr$_2$)(CN^{t}Bu)$_3$(OC$_6$Cl$_5$)$_2$].[265] The pentamethyl [60]fullerene-supported mono- and bis-isocyanide complexes [(η^5-C$_{60}$Me$_5$)Ru(CNR)(CO)Cl] (R = ^{t}Bu, Me, 2,6-Me$_2$C$_6$H$_3$) and [(η^5-C$_{60}$Me$_5$)Ru(CNR)$_2$Cl] (R = ^{t}Bu, 2,6-Me$_2$C$_6$H$_3$) are formed from [(η^5-C$_{60}$Me$_5$)Ru(CO)$_2$Cl].[39]



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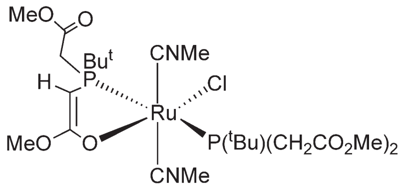


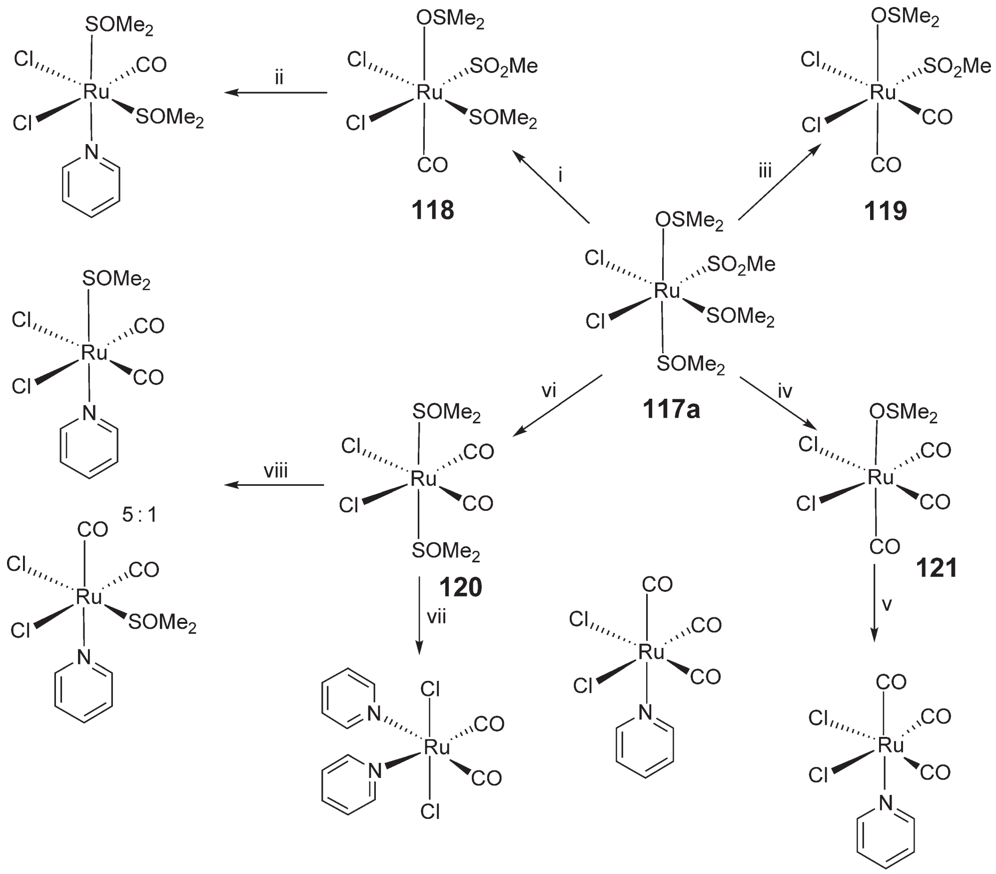
116

An excess of dppm reacts with *trans*-[Ru(CNR)$_4$Cl$_2$] (R = Ph, ^{t}Bu) in refluxing toluene to give *trans,cis,cis*-[Ru{κ-(*P*)-Ph$_2$PCH$_2$PPh$_2$}$_2$(CNPh)$_2$Cl$_2$] and *mer*-[Ru(dppm)(CNR)$_3$Cl](Cl) (R = Ph, ^{t}Bu).[266] Reactions of [M(PPh$_3$)$_3$(CNR)HCl] with HgPh$_2$ give the five-coordinate aryl complexes [M(PPh$_3$)$_2$(CNR)(Ph)Cl] (M = Ru, Os, R = *p*-tolyl; M = Os, R = *p*-ClC$_6$H$_4$). These react with dioxygen to give seven-coordinate [M(PPh$_3$)$_2$(η^2-CPh=NR)(η^2-O$_2$)Cl]*, in which the phenyl group has migrated onto the isocyanide ligand to form an η^2-iminoacyl ligand. The related complex [Ru(PPh$_3$)$_2$(η^2-CPh=N-*p*-tolyl)(CO)Cl] is also isolable.[267] A kinetic study of the reaction of *trans,cis*-[Os(PMe$_3$)$_2$(CO)$_2$(Me)I] with CO and CNCy, to afford *trans,cis*-[Os(PMe$_3$)$_2$(CO)$_2$(COMe)I] and *trans*-[Os(PMe$_3$)$_2$(CO)(CNCy)(COMe)I], indicates that the mechanism involves methyl group migration.[268]

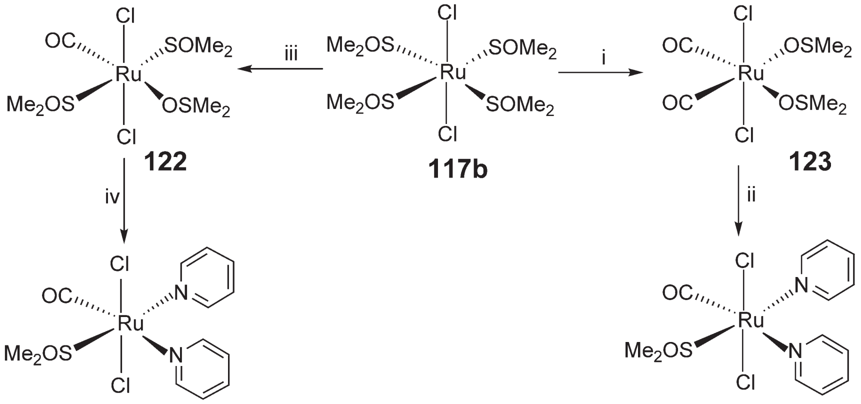
6.11.8 Ruthenium and Osmium Complexes with Group 16 Ligands

The remarkable cationic species, [Os(CO)$_4$O$_2$]$^{2+}$, is made by by reaction of [OsO$_4$] with a slight excess of CO in SbF$_5$ at room temperature. The complex has been characterized through vibrational spectroscopy (indicating a *trans*-arrangement of oxygen atoms), ^{13}C MAS-NMR, and UV–VIS spectroscopy. The complex represents the first cationic metal carbonyl species with an oxidation state > 4.[269]

At ambient pressure, carbon monoxide reacts with *cis*- and *trans*-[Ru(DMSO)$_4$Cl$_2$] **117a and 117b** to afford *cis,trans,cis*-[Ru(DM*S*O)$_2$(DM*S*O)(CO)Cl$_2$]* **118**, *cis,cis,cis*-[Ru(DM*S*O)(DM*S*O)(CO)$_2$Cl$_2$] **119**, *trans,cis,cis*-[Ru(DM*S*O)$_2$(CO)$_2$Cl$_2$]* **120**, *fac*-[Ru(DMS*O*)(CO)$_3$Cl$_2$]* **121**, *trans,trans,trans*-[Ru(DMS*O*)$_2$(DMS*O*)(CO)Cl$_2$]* **122**, and *cis,cis,trans*-[Ru(DMS*O*)$_2$(CO)$_2$Cl$_2$] **123**. Some of these complexes show subsequent reactivity with pyridine, as



i, CO, MeOH; ii C_5H_5N, MeOH, Δ; iii, excess CO, MeOH; iv, excess CO, EtOH, Δ; v, excess C_5H_5N, MeOH; vi, excess CO, toluene, Δ; vii, C_5H_5N, MeOH, Δ; viii, C_5H_5N, MeOH



i, excess CO; ii C_5H_5N, MeOH, Δ; iii, CO, MeOH; iv, C_5H_5N, MeOH

Scheme 15

outlined in Scheme 15.[270] The related systems $[(\mathrm{DMSO})_2\mathrm{H}][\mathit{trans}\text{-}\mathrm{Ru}(\mathrm{DMS}\mathit{O})(\mathrm{CO})\mathrm{Cl}_4]$ and $\mathit{cis,mer}\text{-}[\mathrm{Ru}(\mathrm{DMS}\mathit{O})_2(\mathrm{CO})\mathrm{Cl}_3]$ also readily substitute the DMSO *trans* to CO for *N*-based donors.[271] The reaction of $\mathit{cis}\text{-}[\mathrm{Ru}(\mathrm{TMSO})_4\mathrm{Cl}_2]$ (TMSO = tetramethylenesulfoxide) with CO has allowed isolation of $\mathit{cis}\text{-}[\mathrm{Ru}(\mathrm{TMSO})_3(\mathrm{CO})\mathrm{Cl}_2]^*$, $\mathit{cis}\text{-}[\mathrm{Ru}(\mathrm{TMSO})_2(\mathrm{CO})_2\mathrm{Cl}_2]^*$, and $\mathit{fac}\text{-}[\mathrm{Ru}(\mathrm{TMSO})(\mathrm{CO})_3\mathrm{Cl}_2]^*$. Addition of pyridine to the monocarbonyl complex affords $\mathit{trans}\text{-}[\mathrm{Ru}(\mathrm{TMSO})(\mathrm{CO})(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_2\mathrm{Cl}_2]^*$ as the major product.[272]

Substitution of the trifluoroacetate ligand in *fac*-$[Ru(CO)_3\{OC(O)CF_3\}(H_2O)]^*$ by water affords *fac*-$[Ru(CO)_3(H_2O)_3](BF_4)_2{}^*$, which was the first structurally characterized complex bearing only carbonyl and water ligands. This species is in fast equilibrium with *fac*-$[Ru(CO)_2(CO_2H)(H_2O)_3](BF_4)$, which slowly extrudes CO_2 to give the hydride complex *fac*-$[Ru(CO)_2(H_2O)_3H](X)$ (X = BF_4, OTf). In the presence of C_2H_4 in H_2O, the hydride complex undergoes an insertion reaction to generate *fac*-$[Ru(CO)_2(H_2O)_3Et](OTf)^*$, which exists as a dimer in the solid state; remarkably, this complex is unaffected by the addition of strong acids and is stable for hours in boiling water! However, it does undergo facile reaction with CO to form the migratory insertion product, *fac*-$[Ru(CO)_2(H_2O)_3\{C(O)Et\}](OTf)$.[273]

Dehydration of this complex with propionic anhydride leads as well to acylation of the acyl ligand to afford $[Ru(CO)_2\{CEt(OC(O)Et)_2\}(OTf)]^*$. The tridentate ligand proves to be fragile; thus, dissolution of the complex in THF/H_2O reforms the starting acyl, while addition of CO affords *mer*-$[Ru(CO)_3\{CEt(OC(O)Et)_2\}(OTf)]$.[274] This species is a key intermediate in both ethene hydrocarboxylation and ethene hydrocarbonylation.[275] The application of high pressures of CO to solutions of $[Ru(H_2O)_6]^{2+}$ allows formation of $[Ru(CO)_3(H_2O)_3]^{2+}$, $[Ru(CO)_2(H_2O)_4]^{2+*}$, and $[Ru(CO)(H_2O)_5]^{2+*}$. The use of ^{17}O NMR spectroscopy reveals that the rate of water exchange in the tricarbonyl complex is too slow to measure, while both the mono- and dicarbonyl exhibit rate constants for exchange of the *cis*-H_2O groups that are slower than in the parent hexa-aqua compound.[276–278]

A mechanistic investigation into the $[Ru_3(CO)_{12}]$-catalyzed water gas shift reaction in acidic media has revealed that the ruthenium trimer reacts with CF_3CO_2H to afford $[Ru_2(CO)_6\{\mu\text{-}\eta^2\text{-}OC(CF_3)O\}_2]$, which disproportionates to $[Ru_3(CO)_{12}]$ and *fac*-$[Ru(CO)_3(OCOCF_3)_3]^-$. This latter species undergoes nucleophilic attack by H_2O in THF to generate an equilibrium mixture of $[Ru(CO)_2(L)(OCOCF_3)_2H]^-$, $[Ru(CO)_2(L)_2(OCOCF_3)H]$, and $[Ru(CO)_2(L)_3H]^+$ (L = THF, H_2O). Addition of C_5H_5N converts the mixture to the isolable pyridine–hydride compound *fac*-$[Ru(CO)_2(C_5H_5N)_3H]^{+*}$.[279]

A few more diverse examples of group 16 complexes are known. The reaction of a 1 : 1 molar ratio of $[Ru(CO)_3Cl_2]$ with aqueous NaOH in CH_2Cl_2 affords the polymeric hydroxyl–carbonyl complexes $[Ru(CO)_2(OH)Cl]_n$ and $[Ru(CO)_2(OH)_2]_n$, as characterized by elemental analysis and IR spectroscopy. Addition of 1 or 2 equiv. of NaOH(aq) to $[Os(CO)_3Cl_2]$ results in slower reactions that yield $[Os(CO)_3(OH)Cl]_2$, $[Os(CO)_3(OH)_2]_2$, and the polymeric material $[Os(CO)_3(OH)_2]_n$.[280] The dioxolene ligand in $[Ru(PPh_3)_2(CO)_2(L)]^*$ (H_2L = 7,8-dihydroxy-6-methoxycoumarin) undergoes reversible redox chemistry associated with formation of a semiquinone radical.[281] Gamma-ray irradiation of $[Ru(acac)_3]$ in alcohol solvents under an atmosphere of CO affords $[Ru(acac)_2(CO)(ROH)]$ (ROH = MeOH*, EtOH, ^{i}PrOH).[282] Treatment of $\{Ru(CO)_3Cl_2\}_2$ with Ph_2S in air affords $[Ru(CO)_2(SPh_2)_2Cl_2]^*$ if the solvent is THF and $[Ru(CO)_3(H_2O)Cl_2]^*$ if CH_2Cl_2 is used.[283] The reaction of $[Ru(PPh_3)_2(CX)(CH{=}CH_2)Cl]$ (X = O, S) with $TeCl_4$ yields the novel trichlorotelluronium complex $[Ru(PPh_3)_2(CX)(TeCl_3)Cl]$.[284]

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6.12
Mononuclear Ru/Os Compounds with Hydrocarbon Ligands: Compounds with η^1-Ligands

M K Whittlesey, University of Bath, Bath, UK

6.12.1 Introduction

Some general reviews relating to the chemistry of Ru/Os-η^1 hydrocarbon complexes appear in the literature: the reactivity of Ru–H bonds with alkenes and alkynes,[1] aspects of ruthenium/osmium vinylidene/allenylidene/cumulenylidene complexes,[2–7] equilibria of M–R/M$=$CR$_2$/M$\equiv$CR complexes,[8] the organometallic chemistry of metal porphyrin complexes,[9] and the reactions of [Os(P^{i}Pr$_3$)$_2$(CO)HCl],[10] ruthenium pyrazolylborate complexes,[11] and metallabenzynes.[12] Other reviews relate more to applications of some of the complexes outlined in this chapter. See, for example, metal vinylidenes in catalysis,[13,14] the development of Grubbs-type alkene metathesis catalysts,[15] applications of ruthenium/osmium carbene complexes in metathesis polymerization,[16] and the role of Ru *N*-heterocyclic carbene complexes in metathesis polymerization.[17]

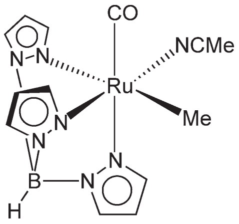
Not considered within this review are the wide range of porphyrin and other nitrogen macrocycle-stabilized ruthenium and osmium hydrocarbyl complexes. Readers should see the following as a starting point for information on this type of alkyl/aryl,[18] alkynyl,[19,20] vinylidene,[21,22] allenylidene,[22] and carbene complexes.[23–31]

6.12.2 Alkyl and Aryl Complexes

6.12.2.1 General Synthesis

Addition of equimolar MeLi to [RuL$_2$(NO)Cl] yields the four-coordinate methyl complexes [RuL$_2$(NO)Me] (L = P^{t}Bu$_2$Me, P^{i}Pr$_3$*). (Throughout the chapter, complexes which have been structurally characterized are denoted with an asterisk (*).)[32] The alkyl complexes [(η^5-C$_{60}$Me$_5$)Ru(CO)$_2$R] (R = Me*, CH$_2$SiMe$_3$) containing the pentamethyl [60]fullerene ligand result from treating [(η^5-C$_{60}$Me$_5$)Ru(CO)$_2$Cl] with the respective Grignard reagents.[33] At room temperature (RT), reactions of [Ru{HB(pz)$_3$}(COD)Cl] with AlR$_3$ (R = Me, Et) afford [Ru{HB(pz)$_3$}(COD)R] in high yields, although Et$_2$Mg, EtMgBr, or EtLi also result in significant quantities of the hydride complex, [Ru{HB(pz)$_3$}(COD)H].[34] The oxidative addition of MeI to the tridentate phosphine complexes [Ru(RP{(CH$_2$)$_3$-P(OR^1)$_2$}$_2$)(CO)$_2$] affords *mer, trans*-[Ru(RP{(CH$_2$)$_3$P(OR^1)$_2$}$_2$)(CO)$_2$(Me)](I) (R = Ph, R^1 = ^{i}Pr*; R = Cy, R^1 = ^{i}Pr; R = Ph, R^1 = Me; R = Cy, R^1 = Me).[35]

The low-temperature addition of MeLi to the cationic solvento complex [Ru{HB(pz)$_3$}(CO)$_2$(THF)](PF$_6$) generates [Ru{HB(pz)$_3$}(CO)$_2$Me], which can be converted into [Ru{HB(pz)$_3$}(CO)(MeCN)Me]* **1** upon refluxing with Me$_3$NO in the presence of acetonitrile.[36] Subsequent thermolysis of this complex in a 1.4 : 1 mixture of C$_6$H$_6$/MeCN yields [Ru{HB(pz)$_3$}(CO)(MeCN)Ph] **2**, which is a precursor for the catalytic insertion of alkenes into the C–H bond of benzene.[37] A combination of experimental studies involving kinetic studies with different alkene/arene combinations, along with density functional theory (DFT) calculations, point to a pathway involving displacement of MeCN by alkene, followed by concerted insertion of the alkene into the Ru–Ph bond.[38]



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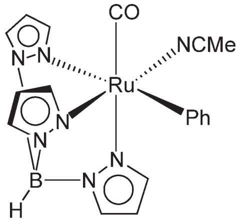

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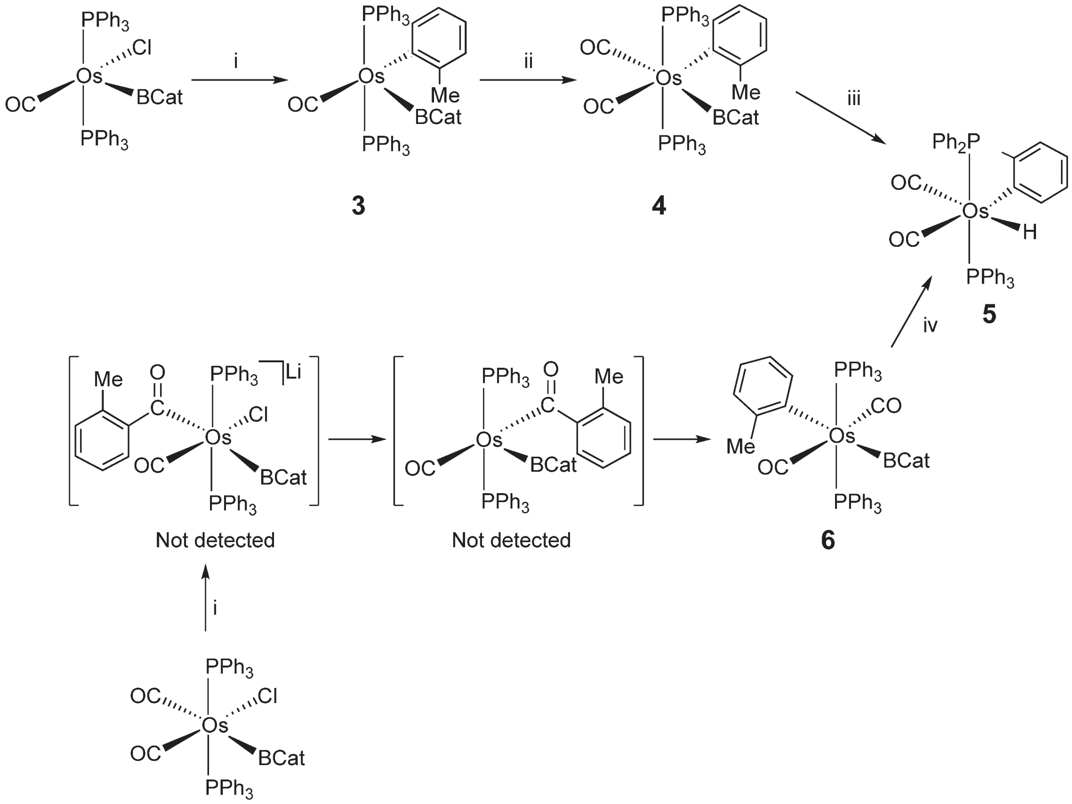
The reduction of [Ru(PPh$_3$){HB(pz)$_3$}(MeCN)Cl] by NaBH$_4$/EtOH is thought to produce the intermediate hydride complex [Ru(PPh$_3$){HB(pz)$_3$}(MeCN)H], which decarbonylates the alcohol solvent to give the observed methyl product, [Ru(PPh$_3$)(CO){HB(pz)$_3$}Me]. The corresponding σ-organyl complexes [Ru(PPh$_3$)(CO){HB(pz)$_3$}R] can be produced by appropriate choice of alcohol RCH$_2$OH (R = H, Et, Pr, Ph, *p*-tolyl, *p*-ClC$_6$H$_4$). Support for the role of Ru-η^2-RCHO and Ru-η^2-H$_2$ complexes in the decarbonylation pathway is provided by detection of [Ru(PPh$_3$){HB(pz)$_3$}(η^2-H$_2$)H].[39] A similar decarbonylation pathway, although this time coupled to a C–H activation process, explains the formation of the aryl hydride complex [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(Ph)H] from reaction of [Os(P^{i}Pr$_3$)$_2$H$_6$] with benzaldehyde in refluxing toluene.[40] The related ethyl hydride complex, [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(Et)H], is formed upon reaction of [Os(P^{i}Pr$_3$)$_2$(CO)(OH)H] with allyl alcohol.[41] Addition of Li(2,2,6,6-tetramethylpiperidide) to [Os(P^{i}Pr$_3$)$_2$(NO)(OTf)H$_2$] results in a surprizing methyl-transfer reaction to generate [Os(P^{i}Pr$_3$)$_2$(NO)(Me)H$_2$] in

50% yield. The formation this methyl dihydride complex leaves a cyclic imine co-product, which itself is readily deprotonated by LiTMP before reacting with the Os precursor to give $[Os(P^iPr_3)_2(\eta^1\text{-}C_8H_{14}N)(NO)H_2]^*$.[42]

Treatment of $[Os(PPh_3)_2(CO)\{Si(OEt)_3\}Cl]$ with aryllithium agents affords the five-coordinate complexes $[Os(PPh_3)_2(CO)\{Si(OEt)_3\}R]$ ($R = Ph^*$, *o*-tolyl*), which are readily trapped by CO to give the corresponding coordinatively saturated species $[Os(PPh_3)_2(CO)_2\{Si(OEt)_3\}R]$ ($R = Ph^*$, *o*-tolyl*).[43] The reactions between $[Ru(PPh_3)_3(CX)HCl]$ and $Hg(aryl)_2$ give the five-coordinate complexes $[Ru(PPh_3)_2(CX)(aryl)Cl]$ (X = S, aryl = Ph; X = O, aryl = *p*-tolyl),[44,45] while subsequent addition affords the six-coordinate derivatives $[Ru(PPh_3)_2(CS)\{H_2B(pz)_2\}(Ph)]$ and $[Ru(PPh_3)(CO)([9]aneS_3)(p\text{-tolyl})](PF_6)$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane).[45,46] Treatment of $[M(PPh_3)_3(CX)HCl]$ with the *o*-halophenyl-Hg compounds $Hg(o\text{-}C_6H_4Y)_2$ (Y = Cl, Br, I) gives $[M(PPh_3)_2(CX)(o\text{-}YC_6H_4)Cl]$ (M = Ru, X = O, Y = Cl, Br; M = Os, X = O*, Y = Cl*, Br*, I*; M = Os, Y = S, X = Cl, Br). The structurally characterized osmium carbonyl systems show significant bonding interactions between the metal center and the *ortho*-halo-substituent of the coordinated phenyl ligand. Addition of CO forms $[M(PPh_3)_2(CX)(CO)(o\text{-}YC_6H_4)Cl]$; the X-ray structure for M = Os, X = O, Y = Cl reveals no $M\cdots X\text{-}C_6H_4$ interaction.[47]

The aryl boryl complexes $[Os(PPh_3)_2(CO)(R)(Bcat)]$ **3** and *trans,cis,cis*-$[Os(PPh_3)_2(CO)(L)(R)(Bcat)]$ (L = CO* **4**, CN^{t}Bu; R = *o*-tolyl; Bcat = B-1,2-$O_2C_6H_4$) are isolated from the reaction of $[Os(PPh_3)_2(CO)(Cl)(Bcat)]$ with *o*-tolyllithium in Et_2O/C_6H_6, followed by addition of L. At RT, **4** undergoes slow reductive elimination of RBcat to give the orthometallated complexes $[Os(PPh_3)(PPh_2C_6H_4)(CO)(L)H]$ (L = CO* **5**), which is also formed from *trans,trans,trans*-$[Os(PPh_3)_2(CO)_2(R)(Bcat)]^*$ **6**. However, in this case, UV irradiation of a hot sample of **6** is required to bring about the initial reductive elimination of RBcat prior to metallation (Scheme 1).[48,49]

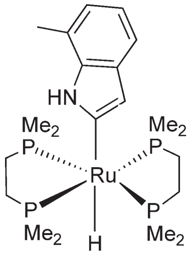
Bond activation by coordinatively unsaturated metal fragments provides a convenient route to aryl complexes in a number of cases. Thermolysis of $[Ru(dmpe)_2(C_{10}H_8)H]$ with 1 equiv. of 2,6-xylyl isocyanide at 60 °C generates *trans*-$[Ru(dmpe)_2(7\text{-methylindole-}C^2)H]^*$ **7**, which undergoes isomerization to the *cis*-isomer **8** upon heating at 100 °C. The



i, (*o*-tolyl)Li; ii, CO; iii, RT, benzene; iv, Δ/*hν*

Scheme 1

mechanism involves thermal reductive elimination of naphthalene to afford the reactive metal intermediate [Ru(dmpe)$_2$] (which can also be formed by photochemical loss of H$_2$ from *cis*-[Ru(dmpe)$_2$H$_2$]) followed by arene C–H bond oxidative addition. The reaction proves applicable to a range of substituted isocyanides including ethylphenyl isocyanide and *para*-R-*o*-tolyl isocyanides (R = OMe, Me, F), which all yield isolable aryl hydride complexes.[50] C–F bond activation of C_6F_6 by *cis*-[Ru(dmpe)$_2$H$_2$] occurs at low temperature to afford *trans*-[Ru(dmpe)$_2$(C$_6$F$_5$)H]* 9; partially fluorinated aromatics (C$_6$F$_5$H, 1,2,3-C$_6$F$_3$H$_3$) also prove susceptible to C–F bond cleavage, with no evidence for C–H activation.[51] In a somewhat related set of data, DFT calculations show a thermodynamic preference for C–F bond activation to yield model complexes of the form [Os(PH$_3$)$_2$(CO)(C$_6$H$_4$F)F] over the alternative C–H activation pathway that would yield [Os(PH$_3$)$_2$(CO)(C$_6$H$_3$F$_2$)H].[52]



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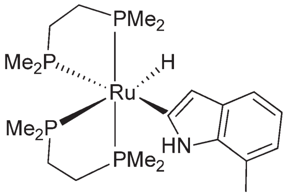

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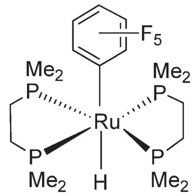

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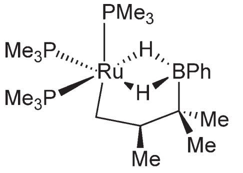
The alkene complex, [Ru(dmpe)$_2$(η^2-C$_2$H$_4$)] reacts with 4-HSC$_6$H$_4$Me and H$_2$PPh at RT to form *cis*-[Ru(dmpe)$_2$(C$_2$H$_5$)(4-SC$_6$H$_4$Me)]* and *cis*-[Ru(dmpe)$_2$(C$_2$H$_5$)(PHPh)]*, respectively.[53] In contrast to these thermal routes, photolysis of [M(PP$_3$)H$_2$] (M = Ru, Os; PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$) in the presence of benzene produces the corresponding phenyl hydride complexes.[54] C–H bond cleavage of some thiophenes also takes place with [M(PP$_3$)H$_2$].[55] Addition of [BH$_2$(CMe$_2$CHMe$_2$)]$_2$ to the benzyne complex [Ru(PMe$_3$)$_4$(η^2-C$_6$H$_4$)] gives the novel RuC$_3$B(μ-H)$_2$-metallaheterocycle [Ru(PMe$_3$)$_3${η^1,η^2-CH$_2$CHMeCMe$_2$BPh(μ-H)$_2$}]* 10 formed via B–C bond formation and C–H activation of the thexyl arm.[56] The fluoromethyl triflate complex [Ru(P^{t}Bu$_2$Me)(CO)(CF$_2$H)OTf] results from the addition of Me$_3$SiOTf to [Ru(P^{t}Bu$_2$Me)$_2$(CO)(=CF$_2$)HF]. Simple dissolution of the carbene complex in THF generates the fluoro analog, [Ru(P^{t}Bu$_2$Me)$_2$(CO)(CF$_2$H)F] 11.[57,58] Moreover, treatment of the carbene complex with Et$_3$N·3HF gives the trifluoromethyl fluoro complex, [Ru(P^{t}Bu$_2$Me)$_2$(CO)(CF$_3$)F], which rapidly binds CO to give [Ru(P^{t}Bu$_2$Me)$_2$(CO)$_2$(CF$_3$)F].[58]



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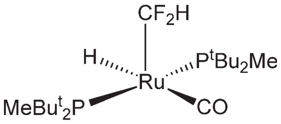
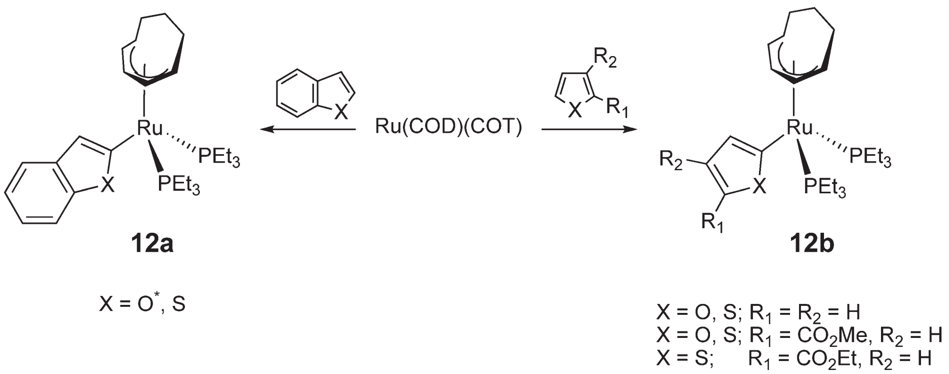
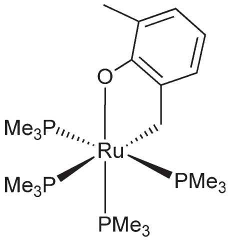


11

C–H bond activation of a range of heterocycles including benzo[*b*]thiophene, benzo[*b*]furan, and substituted thiophenes and furans by [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] in the presence of PEt$_3$ affords [Ru(PEt$_3$)$_2$(1-5-η^5-C$_8$H$_{11}$)(aryl)] 12, via the zero-valent intermediate [Ru(PEt$_3$)$_3$(1-4-η^4-1,3,5-COT)] (Scheme 2).[59] Protonation of [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] by HOAr in the presence of PMe$_3$ affords [Ru(PMe$_3$)$_3$(η^5-C$_8$H$_{11}$)](OAr)·(HOAr)$_n$ (Ar = 2,6-Me$_2$C$_6$H$_3$), which forms the oxaruthenacycle *cis*-[Ru(PMe$_3$)$_4${OC$_6$H$_3$(2-CH$_2$)(6-Me)}] 13 upon heating at 70 °C with an excess of PMe$_3$.[60] Upon heating a dichloroethane solution of [Ru(Ph$_2$P-arene)(Ph$_2$POH)(OTf)](OTf) (arene = 1,1′-binaphthylyl) with RCN (R = Me, *p*-tolyl) at 100 °C, the η^1-arene/aryl complexes [Ru(Ph$_2$P-η^1-arene)(Ph$_2$POH)(NCR)$_3$](OTf)$_2$ are formed; in the case of R = Me, trapping allows the aqua derivative [Ru(Ph$_2$P-η^1-arene)(Ph$_2$POH)(NCR)(H$_2$O)](OTf)$_2$* to be structurally characterized.[61]



Scheme 2



13

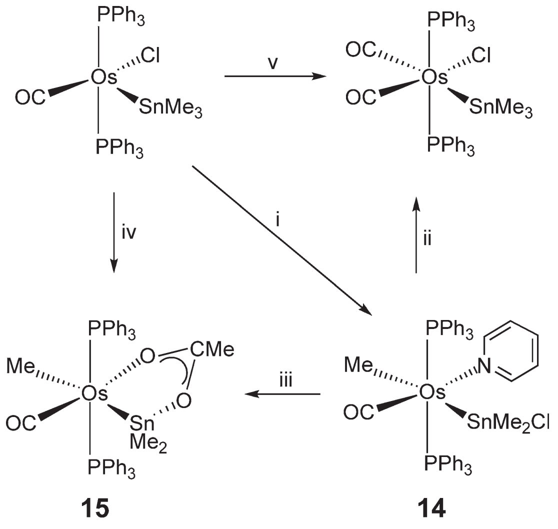
Alkyl allyl sulfides insert into the Ru–H bond of $[Ru(PPh_3)_3(CO)HCl]$ at or below RT yielding rapidly interconverting isomers of $[Ru(PPh_3)_2(CO)(CH_2CH_2CH_2SR)Cl]$ ($R = CH_3$, $CH_2C_6H_5$, $CH_2CH{=}CH_2$). Subsequent thermolysis in the case of the methyl derivative yields the dinuclear complex $[Ru_2(PPh_3)_3(CO)_2(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}SMe)Cl]$ through loss of propene.[62] In contrast to the reactivity found for $[Ru(P^iPr_3)_2HCl]$ (see Section 6.5.2.1.8.3),[63] the 14-electron species $[Ru(P^tBu_2Me)_2(CO)H](BAr^F{}_4)$ reacts with vinyl ethers $CH_2{=}CH(OR)$ at −60 °C to give $[Ru(P^tBu_2Me)_2(CO)(CH_2CH_2OR)](BAr^F{}_4)$ ($R = Me^*$, Et),[64] which contain a Ru-β-OR interaction. DFT calculations on the model insertion product $[Ru(PH_3)_2(L)(CH_2CH_2OMe)]$ (L = CO or Cl) indicates that CO significantly stabilizes such species relative to chloride.[65] NMR studies on the five-coordinate ruthenium aryl compounds $[Ru(P^tBu_2Me)_2(CO)PhCl]$ and $[Ru(P^tBu_2Me)_2(CO)PhH]$ reveal only slow Ru–aryl C bond rotation at RT.[66]

There are a number of cases of alkyl/aryl complex formation from unsaturated hydrocarbyl ligands. Thus, addition of Cl_2 or I_2 to $[M(PPh_3)_2(CO)_2(\eta^2\text{-}C_2F_4)]$ yields the fluoroalkyl complexes $[M(PPh_3)_2(CO)_2(C_2F_4X)X]$ (M = Ru, Os*; X = Cl, I*). Contrasting chemistry is seen upon iodine addition to the Ru and Os isocyanide derivatives $[M(PPh_3)_2(CO)(CN\text{-}p\text{-tolyl})(\eta^2\text{-}C_2F_4)]$; for osmium $[Os(PPh_3)_2(CO)(CN\text{-}p\text{-tolyl})(C_2F_4I)I]$ forms, whereas in the case of ruthenium only $[Ru(PPh_3)_2(CO)(CN\text{-}p\text{-tolyl})I_2]$ is produced.[67] Hydrolysis and rearrangement of the chloro-(2-pyrrolyl)carbene complex $[Ru(PPh_3)_2(CO)\{{=}C(2\text{-}C_4H_3NH)Cl\}Cl_2]$ affords $[Ru(PPh_3)_2(CO)_2(2\text{-}C_4H_3NH)Cl]$, which may also be generated by the addition of (2-pyrrolyl)mercuric chloride to $[Ru(PPh_3)_3(CO)_2]$; the Os analog can be similarly prepared.[68] Treatment of $[Os(PPh_3)_2(CO)({\equiv}CR)Cl]$ with $PhICl_2$ leads to the corresponding monochlorocarbene complexes $[Os(PPh_3)_2({=}CClR)(CO)Cl_2]$, which upon hydrolysis lose HCl and subsequently rearrange to the aryl complexes $[Os(PPh_3)_2(CO)_2(R)Cl]$ (R = 1-naphthyl, 2-naphthyl*).[69]

6.12.2.2 Reactivity

The aryl hydride complex $[Os(P^tBu_2Me)_2(CO)PhH]$ reacts with silanes ($HSiMe_3$, H_2SiPh_2, H_3SiPh) by elimination of benzene to form $[Os(P^tBu_2Me)_2(CO)(SiR_3)H_3]$.[70] Thermolysis of $[Os(PPh_3)_2(CO)(p\text{-tolyl})(\kappa^2\text{-}O_2CH)]$ in the presence of the pyrrolyl phosphine $P(NC_4H_4)_3$ gives $[Os(PPh_3)_2\{P(NC_4H_4)_3\}(CO)(p\text{-tolyl})H]$, which in contrast to the above P^tBuMe_2 system proves to be totally resistant to reductive elimination of toluene, even in refluxing benzene.[71] Addition of C_2H_4 to the borohydride complex $[Ru(PMe_2Ph)_2(CO)(\eta^2\text{-}H_2BH_2)H]$ at low temperature leads to a rapid equilibrium between $[Ru(PMe_2Ph)_2(CO)(\eta^2\text{-}H_2BH_2)(CO)H]$, C_2H_4, and $[Ru(PMe_2Ph)_2(CO)(\eta^2\text{-}C_2H_4)(\eta^1\text{-}HBH_3)H]$, with slower conversion to the ethyl complex $[Ru(PMe_2Ph)_2(CO)(Et)(\eta^2\text{-}H_2BH_2)]$.[72] Reaction of this ethyl complex with PMe_2Ph at low temperature produces $[Ru(PMe_2Ph)_3(CO)(Et)(\eta^1\text{-}HBH_3)]$, which upon warming to ca. −20 °C converts into a mixture of the migratory insertion product, $[Ru(PMe_2Ph)_3(\eta^2\text{-}H_2BH_2)(COEt)H]$, and the ethyl hydride complex $[Ru(PMe_2Ph)_3(CO)(Et)H]$ (H *trans* to CO). An alternative isomer with the ethyl ligand *trans* to CO can be made by reaction of $[Ru(PMe_2Ph)_2(CO)(Et)(\eta^2\text{-}H_2BH_2)]$ with 4-methylpyridine/PMe_2Ph. Both isomers rapidly eliminate ethane above −20 °C. Deuterium-labeling studies, kinetic isotope effect (KIE) measurements, and a determination of entropies of activation exclude any participation of a σ-alkane complex intermediate in the reductive elimination reaction.[73]

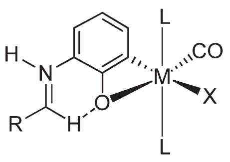
Isomerization of *trans,cis*-$[Os(PMe_3)_2(CO)_2(Me)I]$ to the *trans,trans*-isomer takes place upon photolysis in the solid state.[74] Methyl group abstraction from the ruthenium analog, *trans,cis*-$[Ru(PMe_3)_2(CO)_2MeI]$, by $B(C_6F_5)_3$ affords a range of uncharacterizable products in the absence of any trapping agent; however, in the presence of water, hydrolysis leads initially to *trans,cis*-$[Ru(PMe_3)_2(CO)_2\{HOB(C_6F_5)_3\}I]$, although this slowly transforms into *trans,cis*-$[Ru(PMe_3)_2(CO)_2(H_2O)I](HOB(C_6F_5)_3)$.[75] The reaction of *trans,cis*-$[M(PMe_3)_2(CO)_2(Me)I]$ and *fac*-$[Ru(PMe_3)(CO)_3(Me)I]$ with bis- and tris(pyrazolyl)methane ligands (following silver-induced halide abstraction) has been found to be much faster for ruthenium than with the osmium analog due to the difficulty of initially ionizing the Os–I bond.[76] Treatment of $[Os(PPh_3)_2(CO)(SnMe_3)Cl]$ with pyridine results in reversible methyl migration from Sn to Os to afford $[Os(PPh_3)_2(CO)(Me)(C_5H_5N)(SnMe_2Cl)]^*$ **14**; addition of CO leads to loss of pyridine along with methyl migration to give the trimethylstannyl compound $[Os(PPh_3)_2(CO)_2(SnMe_3)Cl]$. The reaction of the Os methyl complex with sodium acetate yields $[Os(PPh_3)_2(CO)(Me)\{SnMe_2OC(Me)O\}]^*$ **15**, which can also be formed directly by addition of NaOAc to $[Os(PPh_3)_2(CO)(SnMe_3)Cl]$ (Scheme 3).[77] In the presence of primary amines, $[M(PPh_3)_3X_2]$ reacts with 4-methyl-2,6-diformylphenol via decarbonylative metallation to afford **16** (M = Ru, X = Cl, M = Os, X = Br).[78] The M–X bond is readily cleaved to afford carboxylate[79] and nitrate/nitrite[80,81] derivatives. Under conditions of reflux, **16** reacts with HC≡CR through insertion into the Ru–aryl bond to afford **17** (X = H, R = Me, Et*, *p*-tolyl, 4-ClC$_6$H$_4$; R = Ph, R = Me, Et, Ph*, *p*-tolyl).[82] Similar reactivity has been found for the nitrite derivative.[83] Kinetic studies point to the need for replacing the phenolate linkage by a labile solvent molecule to give an intermediate capable of undergoing insertion.[84] Isocyanides[85] and CO[86] can both be inserted into the Ru–aryl bond.



15 **14**

i, C_5H_5N; ii, CO; iii, NaOAc; iv, NaOAc; v, CO

Scheme 3



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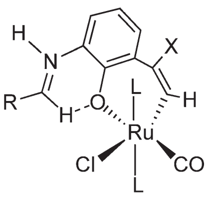
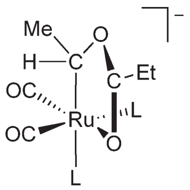


17

L = PPh_3
X = H, R = Me, Et, $4\text{-}MeC_6H_4$, $4\text{-}Cl\text{–}C_6H_4$
X = Ph, X = H, R = Me, Et, Ph, $4\text{-}MeC_6H_4$

At elevated temperature, $[Ru(CO)\{HB(pz)_3\}(MeCN)Me]$ reacts with both furan and thiophene resulting in C–H bond activation of the heterocycle at the 2-position (with elimination of CH_4) to yield $[Ru(CO)\{HB(pz)_3\}(MeCN)(aryl)]$ (aryl = $CH(CH)_3O$, $CH(CH)_3S^*$). While the thiophenyl complex crystallizes successfully from CH_2Cl_2/hexane, the use of CH_2Cl_2/cyclohexane affords the dimer $[Ru(CO)\{HB(pz)_3\}(\mu\text{-}C,S\text{-thienyl})]_2{}^*$, resulting from loss of acetonitrile. DFT calculations suggest that electrophilic attack of the metal center on the aromatic substrate is involved in the C–H activation; oxidative addition involving an Ru(IV) species is not implicated.[87] Addition of AgOTf to the alkyl complexes, $[Ru(CO)\{HB(pz)_3\}(MeCN)(R)]$ (R = Me, $CH_2CH_2C_6H_5$) in CD_2Cl_2 results in alkyl elimination reactions (verified through the production of CH_3D plus C_2H_6, or $Ph(CH_2)_2Ph$, $PhCH{=}CH_2$, and $PhCH_2CH_2(H/D)$, respectively) and formation of $[Ru(CO)\{HB(pz)_3\}(MeCN)OTf]$. The proposed mechanism involves oxidation to the Ru(III) species $[Ru(CO)\{HB(pz)_3\}(MeCN)(R)](OTf)$, which have been shown by DFT calculations to have $Ru\text{–}C_{alkyl}$ bond dissocation energies >100 kJ mol^{-1} lower than the Ru(II) complexes.[88]

The ethyl complexes, $[Ru(CO)_2(L)(H_2O)_2(Et)]$ (L = $C_2H_5CO_2{}^-$, $CF_3SO_3{}^-$) undergo dehydration by propionic acid in the presence of ethene to yield the dimeric species $[\{Ru(CF_3SO_3)(CHCH_3\{O(C(O)C_2H_5\})(CO)_2\}_2]$ via the intermediacy of the ethylidene carboxylate complex $[RuL_2(CHCH_3\{O(C(O)C_2H_5\})(CO)_2]^-$ 18.[89]



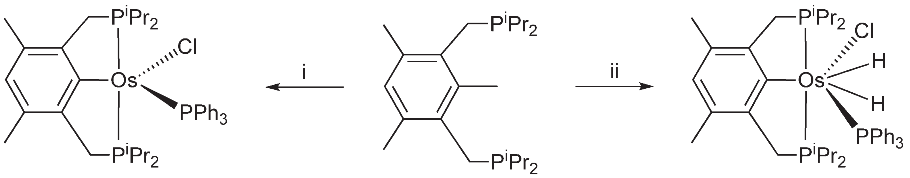
18

a: L = $EtCO_2{}^-$
b: L = OTf^-

6.12.2.3 Pincer Phosphine/Amine Complexes

A wide range of ruthenium and osmium complexes incorporating metallated pincer phosphines or pincer amines have been prepared and characterized and used in applications ranging from materials to catalysis. These will not be reviewed in great detail here—for information, readers are referred to the following citations.[90–110]

A number of the pincer systems show novel formation or reactivity patterns (particularly with respect to bond activation chemistry) worthy of extended discussion. The reaction of $[Ru\{2,6\text{-}(CH_2PPh_2)_2C_6H_3\}(PPh_3)OTf]$ with additional free phosphine yields the rare aryl agostic η^2-C-H stabilized tetrakis-phosphine complex 19.[111] Even more unusual is the formation of 20 and 21 involving C–C bond activation of $\{1,3,5\text{-}Me_3\text{-}2,6\text{-}({}^iPr_2PCH_2)_2C_6H\}$ upon heating with either $[Os(PPh_3)_3HCl]$ or $[Os(PPh_3)_3Cl_2]$ in the presence of H_2 (Scheme 4).[112] Treatment of $[Ru\{2,6\text{-}(CH_2P^tBu_2)_2C_6H_3\}(CO)_2Cl]$ with $AgPF_6$ gives $[Ru\{2,6\text{-}(CH_2P^tBu_2)_2C_6H_3\}(CO)_2](PF_6)^*$ 22, which contains an agostic interaction between Ru and one of the *tert*-butyl groups of the phosphine. This species reacts with H_2 to yield $[Ru\{2,6\text{-}(CH_2P^tBu_2)_2C_6H_3\}(CO)_2H](PF_6)$ 23, which displays an $\eta^2\text{-}C_{ipso}\text{–}H$ interaction between the metal and the aromatic ring.[113] Treatment of the pincer phosphine carbonyl complex $[Ru\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}(CO)Cl]$ with TMSOTf, LiNHPh, and finally PMe_3, or with PMe_3 and then LiNHPh, gives the same product, namely the anilido complex $[Ru\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}(PMe_3)(CO)(NHPh)]$. This reacts with acetonitrile to give the amidinate complex $[Ru\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}(CO)\{N(H)C(Me)N(Ph)\}]^*$.[102] Analogous compounds are formed in



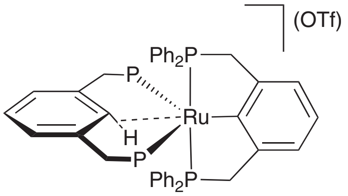
20

21

i, $[Os(PPh_3)_3HCl]$, Δ; ii, $[Os(PPh_3)_3Cl_2]$, H_2, Δ

Scheme 4

reactions with the aryl-substituted nitriles PhCN, $4\text{-}FC_6H_4CN$, and $4\text{-}MeC_6H_4CN$. Addition of C_6F_5CN to $[Ru\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}(CO)\{N(H)C(Me)N(Ph)\}]$ results in loss of MeCN and formation of $[Ru\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}(CO)\{N(H)C(C_6F_5)N(Ph)\}]$. With an excess of nitrile, this is converted into $[Ru\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}(CO)\{N(H)C(Me)NH(Ph)\}F]^*$, which shows an intramolecular Ru–F···H hydrogen bonding interaction with the terminal amidinate proton.[114]



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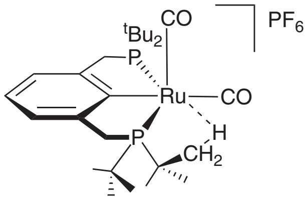

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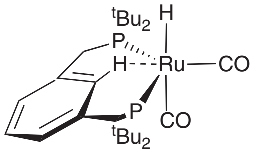
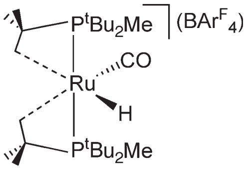


23

The pincer-supported parent amido complex $[Ru\{2,6\text{-}(CH_2P^tBu_2)_2C_6H_3\}(CO)(NH_2)]$ undergoes intramolecular C–H bond activation of a methyl group in a *tert*-butyl arm at RT to yield $[Ru\{C_6H_3\text{-}2\text{-}(CH_2P^tBu_2)\text{-}6\text{-}(CH_2P(^tBu)CMe_2CH_2)\}(CO)]$; the same product results from decomposition of the methyl complex $[Ru\{2,6\text{-}(CH_2P^tBu_2)_2C_6H_3\}(CO)Me]$.[115]

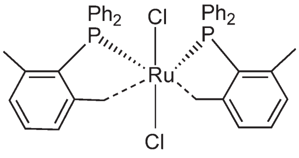
6.12.2.4 Complexes with Agostic Interactions

A number of examples of agostic complexes have been reported. Treatment of the coordinatively unsaturated complex $[Ru(P^tBu_2Me)_2(CO)H(OTf)]$ with $NaBAr^F_4$ in fluorobenzene yields the highly unsaturated, 14-electron cation, $[Ru(P^tBu_2Me)_2(CO)H]^+$ **24**, which is stabilized by agostic interactions with a ^{t}Bu methyl group on each phosphine ligand.[116] The complex binds CH_2Cl_2 in an η^2-fashion to yield the first example* of dichloromethane as a bidentate ligand in a platinum group metal complex.[65,117] The importance of having a combination of ligands with a high *trans*-influence and strong π-donor properties in influencing agostic interactions is illustrated by comparing the structures of $[Ru(P^iPr_3)_2(CO)(Ph)Cl]^*$ (no agostic interactions) and $[Ru(P^iPr_3)_2(CO)(Ph)](BAr^F_4)^*$ (two agostic interactions).



24

Loss of chloride creates two low-lying orbitals suitable for forming the agostic bonds, which as NMR spectroscopy reveals, remain even in solution.[118] Stabilization of the 14-electron compound $[Ru\{(2,6\text{-}Me_2C_6H_3)PPh_2\}_2Cl_2]^*$ **25** is shown to be aided by the presence of two δ-C–H agostic interactions between the Ru and the *ortho*-methyl groups as revealed by X-ray and neutron diffraction studies. However, the reliable location of the hydrogen atoms through the neutron structure shows that the interaction is non-classical in the sense that a whole CH_2 group acts as the donor rather than a single C–H bond.[119,120] The reaction of **25** with HCHO/Et_3N gives the thermally stable *ortho*-metallated complex **26**, which proves to be a highly active precursor for the catalytic transfer hydrogenation of ketones.[119] Addition of $HSiMe_2CH_2Cl$ to *cis*-[Ru(PMe_3)$_4$($SiMe_3$)H] affords *cis*-[Ru(PMe_3)$_4$(CH_2SiMe_2Cl)H], which upon either mild heating or photolysis dissociates phosphine to give *fac*-[Ru(PMe_3)$_3$(CH_2SiMe_2)HCl]*as the major product (the *mer*-isomer* is the minor product). Both compounds contain β-Si–H agostic interactions as judged by NMR spectroscopy ($J_{HSi} = 77.5$ Hz (*fac*)) and X-ray diffraction (Ru···H/Si···H = 1.550,1.664 Å (*fac*); 1.732/1.557 Å (*mer*)).[121] NMR spectra of the δ-agostic *tert*-butyl complex *mer,trans*-[Ru(PPh_3){$PPh_2CH_2C(^tBu)$═N-N═C(Me)^{t}Bu}Cl_2] indicate that all nine hydrogen atoms of the *tert*-butyl group interact with the Ru center on the NMR timescale.[122]



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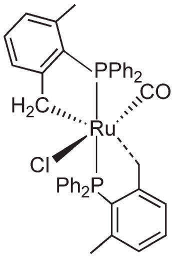
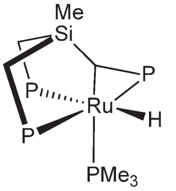


26

6.12.2.5 Metallated Complexes

Addition of a strong base (KO^{t}Bu or KN($SiMe_3$)$_2$) to the tetrakis-phosphine complexes [Ru(PMe_3)-{MeSi(CH_2PMe_2)$_3$}Cl_2] or [Ru(PMe_3){MeSi(CH_2PMe_2)$_3$}(NH_3)H](BPh_4) generates the "internally" cyclometallated species [Ru(PMe_3){MeSi(CH_2PMe_2)$_2$CHPMe$_2$}H]* **27**. In contrast, thermolysis of the methyl hydride [Ru(PMe_3)-{MeSi(CH_2PMe_2)$_3$}(Me)H] affords the "externally" metallated complex [Ru(CH_2PMe_2){MeSi(CH_2PMe_2)$_3$}H] **28**; these two complexes show no evidence of interconversion in the presence of any initiator such as acid, base, or dihydrogen.[123] The cyclometallated complex [Ru(PMe_3)$_3${P(Me)$_2CH_2$}Me] **29** transforms to the methyl hydroxyl complex **30** upon addition of a slight excess of water.[124] The solvated benzoyloxoruthenium complex [Ru(PMe_3)$_4$(*o*-$OCH_2C_6H_4$)]·$C_6H_5CH_2OH^*$ is formed upon the low temperature reaction of benzaldehyde with [Ru(PMe_3)$_4H_2$]; when the reaction is performed at RT, the ruthenacycloketone complex [Ru(PMe_3)$_4${*o*-C(O)C_6H_4}] is the main product instead.[125]



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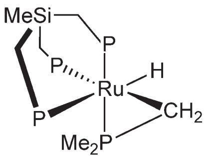

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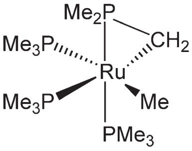

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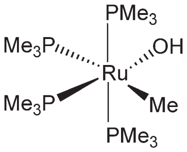
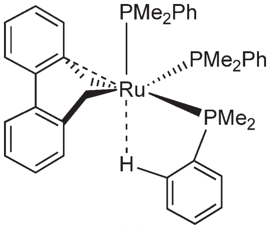


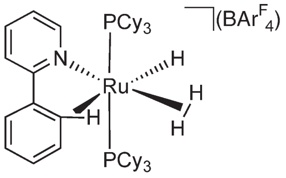
30

Heating $[OsCl_6]^{2-}$ with 1,5-bis(di-*tert*-butylphosphino)pentane in the presence of NEt_3 at 140 °C under an atmosphere of H_2 affords the cyclometallated complex [Os{CH($C_2H_4P^tBu_2$)$_2$}H_2Cl]*; this undergoes reversible dehydrogenation at high temperature to give the carbene complex [Os{═C($C_2H_4P^tBu_2$)$_2$}HCl]*.[126] The same hexachloro precursor reacts with PPh_2(2,6-$Me_2C_6H_3$) in ^{i}PrOH/H_2O to afford [Os(bdps){(2-CH_2-6-MeC_6H_3)PPh_2}Cl]* (Section 6.5.2.2, p. 32).[127] The thermally unstable ruthenacycloheptadiene [Ru(PMe_2Ph)$_3${(2-$CH_2C_6H_4$)$_2$}]* **31** forms upon the low temperature addition of [Li(TMEDA)$_2$]$_2$[(2-$CH_2C_6H_4$)$_2$] to *cis*-[Ru(PMe_2Ph)$_4Cl_2$]. In refluxing THF, the same ruthenium precursor reacts with 2-{(THF)$_n$ClMgCH_2}$C_6H_4C_6H_4$Me-2′ to give the metallated product [Ru{$PC_6H_4Me_2$}(PMe_2Ph)$_3$Cl].[128] The cyclometallated complexes [Ru(PCy_3)$_2$(*o*-C_6H_4X)(L)H] (X = C(O)R (R = Me, Ph), L = η^2-H_2, CO) can be formed from reactions of ketones with the bis-dihydrogen dihydride complex [Ru(PCy_3)$_2$(η^2-H_2)$_2H_2$]. The same methodology can be used to synthesize [Ru(PCy_3)$_2$(*o*-$C_6H_4C_5H_4N$)(η^2-H_2)H],[129] although a simpler route is available for the triisopropylphosphine analog, which can be prepared via a one-pot route employing [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)], P^{i}Pr$_3$, and 2-phenylpyridine under 3 bar H$_2$.[130] Treatment of the dimer {Ru(P^{i}Pr$_3$)$_2$HCl}$_2$ with PhCH=NMe affords the metallated dihydrogen complex [Ru(P^{i}Pr$_3$)$_2$(C$_6$H$_4$CH=NMe)(η^2-H$_2$)Cl]*, which loses H$_2$ at elevated temperature to form the unsaturated complex [Ru(P^{i}Pr$_3$)$_2$(C$_6$H$_4$-CH=NMe)Cl].[131]



31

Protonation of [Ru(PCy$_3$)$_2$(*o*-C$_6$H$_4$C$_5$H$_4$N)(η^2-H$_2$)H] with HBAr$^F{}_4$ yields [Ru(PCy$_3$)$_2$(*o*-C$_6$H$_4$C$_5$H$_4$N)(η^2-H$_2$)H](BAr$^F{}_4$)* **32**, which displays another rare agostic aromatic C–H bond interaction. This species reversibly converts into the cyclometallated species [Ru(PCy$_3$)$_2$(*o*-C$_6$H$_4$C$_5$H$_4$N)(η^2-H$_2$)(THF)](BAr$^F{}_4$) **33**.[132] The cyclometallated species [Ru(dcypb)(CO){*o*-C(O)(Ph)C$_6$H$_4$}H]* (dcypb = Cy$_2$PCH$_2$CH$_2$CH$_2$CH$_2$PCy$_2$) has been shown to be a catalytic sink in the Murai coupling of aromatic ketones with alkenes.[133] The reactivity of [Ru(PPh$_3$)$_3$(*o*-C$_6$H$_4$C(O)Me)H]* for the same process has been described, along with complexes in which the equatorial PPh$_3$ group *trans* to the activated aryl ring has been substituted for CO* or DMSO*.[134] Continuing the theme of metallated complexes in catalysis, a possible intermediate* (see Section 6.5.2.2, scheme 3, figure 18) in the Ru(BINAP)-catalyzed enantioselective hydrogenation of alkenes/ketones can be isolated from the reaction of (*Z*)-methyl α-acetamidocinnamate with the solvento complex [Ru{(*R*)-BINAP}(MeCN)(S)$_2$H](BF$_4$) (S = THF, MeOH) (BINAP = 2,2-bis(diphenylphosphanyl)-1,1-binaphthyl).[135]



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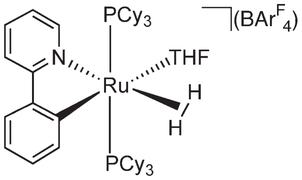
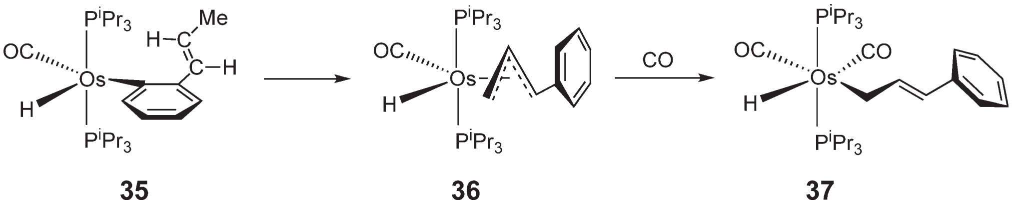
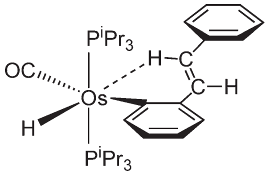


33

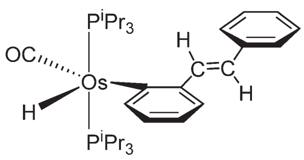
Upon reaction with MeLi or BuLi in hexane solution, the alkenyl complex [Os(P^{i}Pr$_3$)$_2$(CO){(*E*)-CH=CHPh}Cl] forms the hydrido–aryl complexes [Os(P^{i}Pr$_3$)$_2$(CO)(C$_6$H$_4$-2-{(*E*)-CH=CHPh})H]* **34**[136] and [Os(P^{i}Pr$_3$)$_2$(CO)(C$_6$H$_4$-2-{(*E*)-CH=CHMe})H] **35**, respectively. The proposed mechanism of formation involves reductive coupling to give the zero-valent intermediates [Os(P^{i}Pr$_3$)$_2$(CO)(η^2-CHR=CHPh)], followed by insertion into a C$_{\mathrm{aryl}}$–H bond. NMR spectroscopy indicates that both **34** and **35** contain agostic Ru···C–H interactions, although NMR spectroscopy convincingly shows that **34** exists in solution as a mixture of both agostic **34a** and non-agostic isomers **34b**. Addition of CO to **34** yields the six-coordinate compounds [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(C$_6$H$_4$-2-{(*E*)-CH=CHPh})H]; this contrasts with the reactivity of [Os(P^{i}Pr$_3$)$_2$(CO)(C$_6$H$_4$-2-CH$_2$=CHPh)H],[137] which upon addition of L (CO, P(OMe)$_3$) is converted into [Os(P^{i}Pr$_3$)$_2$(CO)(L){(*E*)-CH$_2$=CHPh}H], indicating that alkenic C–H activation is kinetically preferred to arene C–H cleavage in this case. Isomerization of **35** takes place in solution at RT to yield [Os(P^{i}Pr$_3$)$_2$(CO)(η^3-CH$_2$CHCHPh)H] **36**, which reacts with CO to form [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(η^1-CH$_2$CH=CHPh)H] **37** (Scheme 5).[136]



Scheme 5

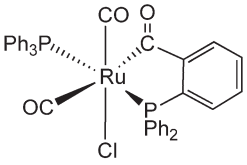


34a



34b

Upon reaction with $CH_2{=}C(Me)CH_2OH$ at RT, $[Ru(PPh_3)_3(CO)HCl]$ is converted into the insertion product $[Ru(PPh_3)_3(CO)(CH_2CHMeCH_2OH)Cl]$,[138] although elevated temperature and the presence of water are required for generating the cyclometallated complex $[Ru(PPh_3)_3(CO)(C_6H_3MeCH{=}NCH_2C_6H_4\text{-}o\text{-}Me)Cl]^*$ from *o*-toluonitrile.[139] Treatment of $[Ru(PPh_3)_3(CX)HCl]$ with $[Hg(o\text{-}C_6H_4NNC_6H_5)_2]$ yields the cyclometallated azobenzene complexes $[Ru(PPh_3)_2(CS)(\eta^2\text{-}C,N\text{-}o\text{-}C_6H_4NNC_6H_5)Cl]$ ($X = O^*$, S^*), which reveal different *cis*-push–pull influences of the CX ligands; the chloride is readily exchanged for Br, I, acetate, or S_2CNEt_2.[140,141] Similarly, the reactions of $[M(PPh_3)_3(CO)HCl]$ with $[Hg(o\text{-}C_6H_4PPh_2)_2]$ yield the cyclometallated complexes $[M(PPh_3)_2(CO)(o\text{-}C_6H_4PPh_2)Cl]$ ($M = Ru$, Os^*). Loss of PPh_3 occurs upon treatment with CO to afford the analogous dicarbonyl complexes, although in the case of Ru, there is an accompanying insertion of coordinated CO into the Ru–C bond to yield the cyclic acyl complex $[Ru(PPh_3)(CO)_2\{o\text{-}C(O)C_6H_4PPh_2\}Cl]$ 38.[142] Addition of $Hg\{2\text{-}C_4H_3NC(O)Me\}_2$ or $Hg\{2\text{-}C_4H_3NSO(O)Ph\}_2$ to $[M(PPh_3)_3(CO)HCl]$ ($M = Ru$, Os) gives the bidentate 2-pyrrolyl complexes $[M(PPh_3)_2(CO)\{2\text{-}C_4H_3NC(O)Me\}Cl]$ or $[M(PPh_3)_2(CO)\{2\text{-}C_4H_3NSO(O)Ph\}Cl]$, 39a and 39b respectively. The chloride ion in 39a is readily removed with $AgSbF_6$ in the presence of CO to give $[Ru(PPh_3)_2(CO)_2(2\text{-}C_4H_3NSO(O)Ph)](SbF_6)$, or $AgSbF_6/Me_2NCS_2$ forming $[M(PPh_3)_2(CO)\{2\text{-}C_4H_3NSO(O)Ph\}(\eta^2\text{-}S_2CNMe_2)](SbF_6)^*$.[143] Treatment of $[M(PPh_3)_3(CO)HCl]$ with Hg(8-quinolyl)$_2$ or Hg(PyPh$_2$) (PyPh = 2-(2′-pyridyl)phenyl) yields the metallated species $[Os(PPh_3)_2(CO)(\eta^2\text{-}C,N\text{-}8\text{-quinolyl})Cl]$ and $[M(PPh_3)_2(CO)(\eta^2\text{-}C,N\text{-}PyPh)Cl]$ ($M = Ru$, Os^*). Both sets of compounds undergo silver-induced metathesis to afford $[Os(PPh_3)_2(CO)(\eta^2\text{-}C,N\text{-}8\text{-quinolyl})I]^*$, $[Os(PPh_3)_2(CO)(\eta^1\text{-}8\text{-quinolyl})(\eta^2\text{-}S_2CNMe_2)]^*$ 40, $[M(PPh_3)_2(CO)(\eta^2\text{-}C,N\text{-}PyPh)I]$, $[M(PPh_3)_2(CO)_2(\eta^2\text{-}C,N\text{-}PyPh)](SbF_6)$, and $[M(PPh_3)(CO)(\eta^2\text{-}C,N\text{-}PyPh)(\eta^2\text{-}S_2CNMe_2)]$ ($M = Ru$, Os^*).[144,145] Alkylation, stannylation, and acetylation of the quinolyl ligand in $[Os(PPh_3)_2(CO)(\eta^2\text{-}C,N\text{-}8\text{-quinolyl})Cl]$ can be readily undertaken[146] as can electrophilic substitution of the phenyl ring in $[M(PPh_3)_2(CO)(\eta^2\text{-}C,N\text{-}PyPh)Cl]$.[145]



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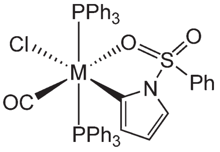
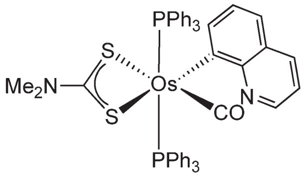


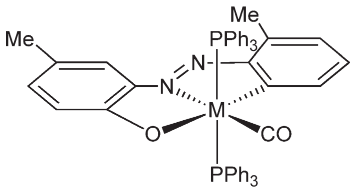
39

a: M = Ru
b: M = Os



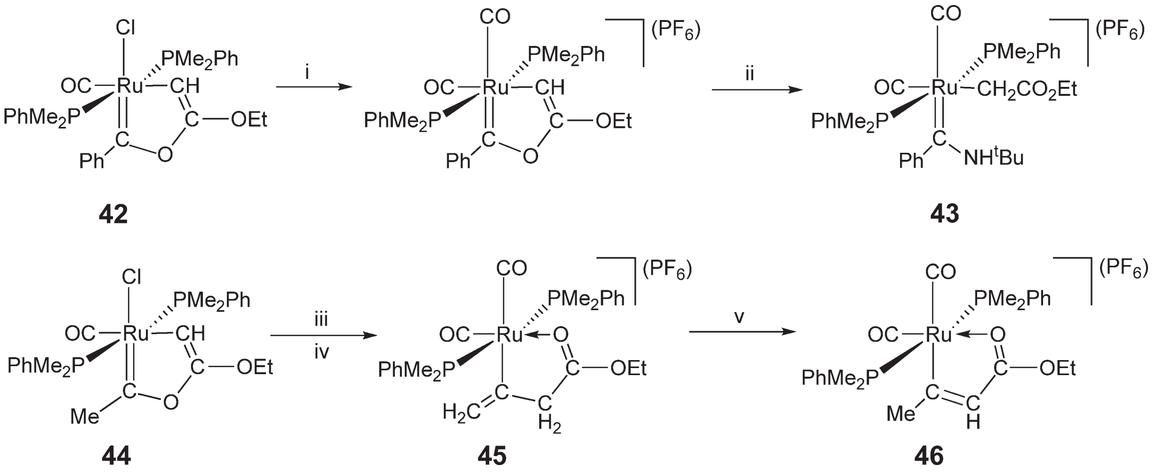
40

A range of nitrogen-based ligand sets have been employed to prepare cyclometallated Ru/Os complexes.[147–152] Refluxing 2-(2′,6′-dimethylphenylazo)-4-methylphenol with either $[Ru(PPh_3)_3Cl_2]$ or $[Os(PPh_3)_3Br_2]$ results in methyl migration and oxidation to afford the metallated carbonyl complexes 41a and 41b.[153] Reaction of $[Ru(tpy)Cl_3]$ with Htbp (Htbp = 6-(2-thienyl)-2,2′-bipy; tpy = 2,2′ : 6′,2′-terpyridyl) in MeOH/H_2O allows isolation of the metallated salt $[Ru(tbp)(tpy)](PF_6)$, which reversibly forms the non-metallated species upon addition of acid or base.[154]



41

a: M = Ru
b: M = Os

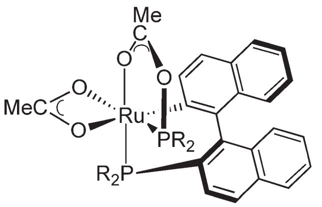


i, $AgPF_6$, CO; ii, $^tBuNH_2$; iii, $AgPF_6$, CO; iv, ethyl propiolate, –20 °C; v, RT

Scheme 6

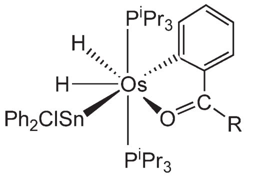
The reaction of $[Os(P^iPr_3)_2(CO)(OH)H]$ with methyl vinyl ketone ($CH_2{=}CHC(O)Me$) gives the metallacycle $[Os(P^iPr_3)_2(CO)\{CHCHC(O)Me\}H]$.[41] Ruthenafuran complexes are formed reversibly from $[RuL_2(CO)_2RCl]$ ($L = PMe_2Ph^*$, $R = CH{=}CHOEt$, $CH{=}CHCMe_3$, Me or Ph^*; $L = PMe_3$, $R = CH{=}CHOEt$ or $CH{=}CHPh$) and $EtOC{\equiv}CH$ via the intermediate acyl complexes $[RuL_2(CO)(COR)Cl]$, which can be trapped when the reverse reaction is performed in the presence of ^tBuNC.[155] The structurally characterized species **42*** shows no tendency to undergo nucleophilic attack at the $Ru{=}C$ group until the metal center is charged; thus, treatment of **42** with $AgPF_6$ in the presence of CO, followed by addition of $^tBuNH_2$, gives the non-cyclic aminocarbene species **43***. Treatment of the methyl analog **44** with $AgPF_6$/CO, followed by low temperature addition of $EtOC{\equiv}CH$ affords **45**, which slowly converts into the metallacycle **46*** (Scheme 6).[156]

Addition of PMe_2Ph to $[Ru(\eta^2:\eta^5\text{-}10\text{-}CH{=}CH_2\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2]$ produces the ylide $[Ru\{\sigma,\eta^5\text{-}10\text{-}CH(PMe_2Ph)\text{-}CH_2\text{-}7,8\text{-}C_2B_9H_{10}\}(CO)_2]^*$.[157] A combination of P–C bond cleavage and cyclometallation affords complexes **47a** and **47b** after reaction of $[Ru(p\text{-cymene})(OAc)_2]$ and the appropriate aliphatic BINAP ligands at elevated temperature.[158]



47

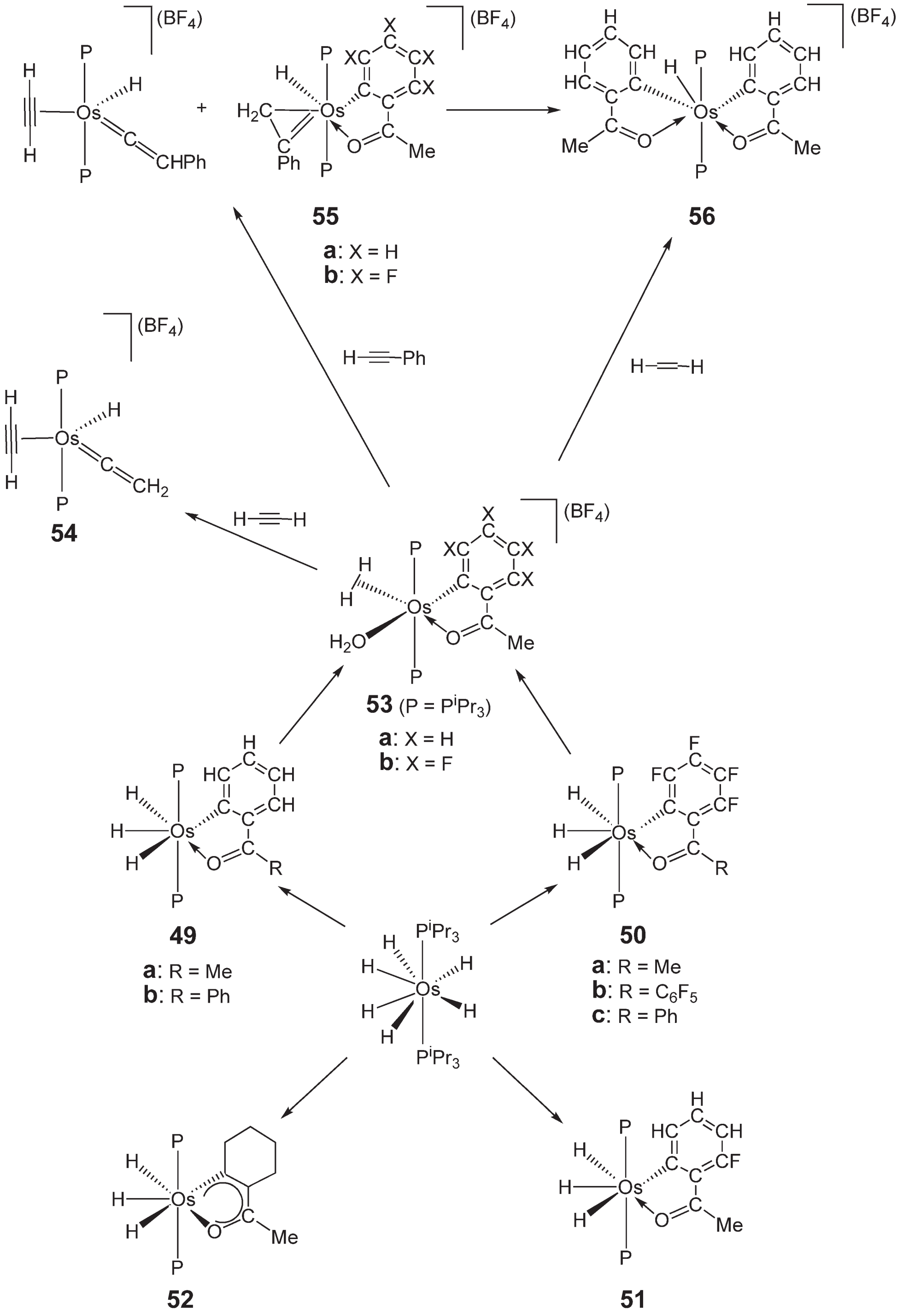
a: R = ^{i}Pr
b: R = Cy



48

a: R = Me
b: R = Ph
c: R = C_6F_5

Addition of benzophenone imine to $[Ru(P^iPr_3)_2(CO)(C{\equiv}CPh)_2]$ gives the orthometallated complex $[Ru(P^iPr_3)_2(CO)\{NH{=}C(Ph)C_6H_4\}(C{\equiv}CPh)]$, which, upon treatment with HBF_4, eliminates $HC{\equiv}CPh$ to afford $[Ru(P^iPr_3)_2(CO)\{NH{=}C(Ph)C_6H_4\}(FBF_3)]$. The weakly coordinated tetrafluoroborate ligand can be displaced by a range of Lewis bases (CO, MeCN); substitution of one phosphine ligand takes place on addition of $P(OMe)_3$, while reaction with MeLi gives the methyl complex $[Ru(P^iPr_3)_2(CO)\{NH{=}C(Ph)C_6H_4\}Me]$, which converts into the hydride species $[Ru(P^iPr_3)_2(CO)\{NH{=}C(Ph)C_6H_4\}H]$ upon dissolution in MeOH (cf. the Os analog which is stable in MeOH).[159,160] The orthometallated ketone aryl stannyl complexes $[Os(P^iPr_3)_2\{C_6H_4C(O)R\}(SnPh_2Cl)H_2]$ (**48**, $R = Me^*$, Ph, C_6F_5), $[Os(P^iPr_3)_2\{C_6H_3FC(O)Me\}(SnPh_2Cl)H_2]$, and $[Os(P^iPr_3)_2\{C_6H_4C(NH)Ph\}(SnPh_2Cl)H_2]^*$ result from C–H bond activation reactions of $[Os(P^iPr_3)\{\eta^2\text{-}H_2C{=}C(Me)P^iPr_2\}(SnPh_2Cl)H_3]$ with acetophenone, benzophenone, 2,3,4,5,6-pentafluorobenzophenone, 2-fluoroacetophenone, and benzophenone imine, respectively, at RT.[161] *Ortho*-C–H bond activation of acetophenone and benzophenone and *ortho*-C–F bond activation of pentafluoroacetophenone, decafluorobenzophenone, and 2,6-difluoroacetophenone also occur with the hexahydride precursor $[\mathrm{Os(P^iPr_3)_2H_6}]$ in refluxing toluene solution to give $[\mathrm{Os(P^iPr_3)_2\{C_6H_4C(O)R\}H_3}]$ (R = Me* **49a**, Ph **49b**), $[\mathrm{Os(P^iPr_3)_2\{C_6F_4C(O)R\}H_3}]$ (R = Me **50a**, C_6F_5 **50b**), and $[\mathrm{Os(P^iPr_3)_2\{C_6H_3FC(O)Me\}H_3}]$ **51**. An alternative route to 49 and 50 involves reaction of the starting hexahydride with 2,3,4,5-tetrafluoroacetophenone and 2-fluoroacetophenone, respectively; this selectivity for C–H cleavage contrasts with selectivity for the C–F bond seen in the formation of $[\mathrm{Os(P^iPr_3)_2\{C_6F_4C(O)Ph\}H_3}]^*$ **50c** from 2,3,4,5,6-pentafluorobenzophenone (Scheme 7). DFT calculations indicate

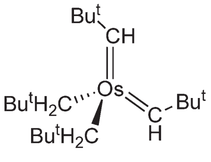


Scheme 7

that: (i) *ortho*-C–F activation is thermodynamically preferred over *ortho*-C–H activation, while (ii) the C–H bond activation of 2,3,4,5-tetrafluoroacetophenone and 2-fluoroacetophenone is a kinetic effect arising partly from a favorable F–C–C–C=O *anti*-arrangement in the reacting ketone.[162] Activation of cycloalkyl ketones is also possible; $[Os(P^iPr_3)_2H_6]$ reacts with cyclohexylmethyl ketone to afford $[Os(P^iPr_3)_2\{C_6H_8C(O)Me\}H_3]^*$ **52** via activation of three C–H bonds.[163] Protonation of **49a** or **50a** with $HBF_4{\cdot}H_2O$ gives the elongated dihydrogen complexes $[Os(P^iPr_3)_2\{C_6X_4C(O)R\}(\eta^2\text{-}H_2)(H_2O)](BF_4)$ (X = H **53a**, F **53b**) ($r_{HH} \sim 1.3$ Å), which react with either $HC{\equiv}CH$ or $HC{\equiv}CCy$ to form the four-electron donor alkyne vinylidene species $[Os(P^iPr_3)_2({=}C{=}CH_2)(\eta^2\text{-}HC{\equiv}CR)H](BF_4)^*$ (R = Cy, H **54**). In contrast, $HC{\equiv}CPh$ yields a mixture of products, although mainly $[Os(P^iPr_3)_2({=}C{=}CHPh)(\eta^2\text{-}HC{\equiv}CPh)H](BF_4)$ and $[Os(P^iPr_3)_2\{C_6X_4C(O)R\}\{C(Ph)CH_2\}H](BF_4)$ (X = H **55a**, F **55b**.) Further reaction of **55a** with acetophenone forms the unusual bis-metallated compound $[Os(P^iPr_3)_2\{C_6H_4C(O)Me\}_2H](BF_4)^*$ **56**.[164] In the presence of terminal alkynes $RC{\equiv}CH$, $[Os(P^iPr_3)_2\{C_6H_4C(O)Me\}\{N(OH){=}CMe_2\}(\eta^2\text{-}H_2)](BF_4)$ eliminates acetophenone to yield the amphoteric carbyne complexes $[Os(P^iPr_3)_2\{\kappa^2\text{-}N,O\text{-}ON{=}CMe_2\}({\equiv}CCH_2R)H](BF_4)$ (R = Ph*, Cy, ^{t}Bu).[165] Protonation of $[Os(P^iPr_3)_2\{C_6H_4C(O)Me\}\,H_3]$ by $HBF_4{\cdot}OEt_2$ in Et_2O/acetone yields the orthometallated dihydrogen complex $[Os(P^iPr_3)_2(C_6H_4C(O)Me)(\kappa^1\text{-}Me_2CO)(\eta^2\text{-}H_2)](BF_4)^*$, which substitutes acetone for halide in the presence of either NaCl or CsF.[166]

6.12.2.6 High Valent Complexes

Addition of an excess of R_2Zn (R = $CH_2{}^tBu$, CH_2CMe_2Ph, CH_2SiMe_3) to $[PPh_4][OsO_2Cl_4]$ affords the air-stable alkyl complexes $[OsO_2R_2]$. For R = CH_2SiMe_3, the product appears not to be monomeric, although trapping by pyridine generates the monomeric species *trans*-$[OsO_2(CH_2SiMe_3)_2(C_5H_5N)_2]$. Treatment of $[OsO_2(CH_2{}^tBu)_2]$ with 2 equiv. of $[Ta({=}CH^tBu)(CH_2{}^tBu)_3]$ at low temperature affords *syn*,*anti*-$[Os({=}CH^tBu)_2(CH_2{}^tBu)_2]$ **57**, which can be converted into *anti*,*anti*-$[Os({=}CH^tBu)_2(CH_2{}^tBu)_2]$ **58** upon photolysis at low temperature in toluene solution. Similar reactions afford *syn*,*anti*- and *anti*,*anti*-$[Os({=}CH^tBu)_2(CH_2SiMe_3)_2]^*$.[167,168] Protonation of $[Os({=}CH^tBu)_2(CH_2{}^tBu)_2]$ at one of the α-carbene centers and hydrogen abstraction by pyridinium triflate/pyridine affords the dialkyl carbyne complex $[Os({\equiv}C^tBu)(CH_2{}^tBu)_2(C_5H_5N)_2(OTf)]$ **59**.[167] High-valent ruthenium and osmium alkyl complexes have been ued as “scaffolds” for stabilizing heteroatom (nitride, sulfide, etc.) complexes.[169,170,171] Treatment of OsO_4 with RMgBr affords a mixture of products, among which are the homoleptic aryl species OsR_4 (R = *o*-tolyl, 2,5-$Me_2C_6H_3$), along with Os(VI) oxo-aryl and Os(V) dioxo-aryl compounds.[172] The aryl rings in $[Os(2,5\text{-}Me_2C_6H_3)_4]$ can be functionalized (acylated, brominated) by electrophilic attack, and, in the case of the bromo derivatives, subjected to subsequent Suzuki cross-coupling reactions.[173]



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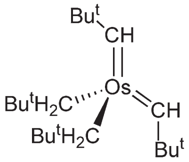

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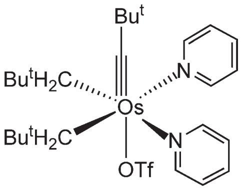

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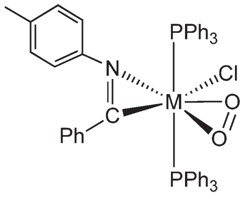
6.12.3 Acyl Complexes

The alkenyl aryl complexes $[RuL_2(CO)_2(CH{=}CHR)(p\text{-}C_6H_4X)]$ (L = PMe_3, PMe_2Ph, $P(OMe)_2Ph$; R = ^{t}Bu, Ph, OEt; X = H, Cl, OMe) bearing *cis*-phosphine groups are found to undergo migration of one of the organic groups onto a CO ligand upon treatment with Lewis bases (CO, ^{t}BuNC, $P(OMe)_3$). Products resulting from alkenyl group migration retain their mutually *cis*-arrangement of L ligands, but are unstable. Aryl migration yields stable products with mutually *trans*-L groups. Alkenyl migration is preferrred to aryl migration by electron-donating R groups, electron-withdrawing X groups, good σ-donor L ligands, and use of ^{t}BuNC as the incoming ligand (kinetic studies reveal a zero-order dependence on isocyanide concentration). In all cases, the incoming ligand enters *trans* to the newly formed acyl functionality.[174] Extension to the mixed ligand systems $[RuLL^1(CO)_2(CH{=}CHR)(p\text{-}C_6H_4X)]$ (L = L^1 = PMe_3, PMe_2Ph, $P(OMe)_2Ph$, PPh_3; L = PMe_3, L^1 = PPh_3; R = ^{t}Bu, Ph, OEt, H, Me; X = H, Cl, OMe) reveals that the ratio of products formed by these two pathways is determined by kinetic rather than thermodynamic factors.[175]

Upon contact with oxygen, the phenyl group in [M(PPh$_3$)$_2$(CNR)(Ph)Cl] migrates to the isocyanide group to yield the η^2-iminoacyl complexes [M(PPh$_3$)$_2$(η^2-CPh═NR)(η^2-O$_2$)Cl] (M = Ru 60a, Os 60b, R = *p*-tolyl; M = Os, R = *p*-ClC$_6$H$_4$*); the adduct [Os(PPh$_3$)$_2${η^2-CPh═N(*p*-ClC$_6$H$_4$)}(η^2-SO$_4$)Cl]* results from addition of SO$_2$, while [Ru(PPh$_3$)$_2${η^2-CPh═N(*p*-tolyl)}(CO)Cl], resulting from phenyl group migration, can be isolated upon reaction of [Ru(PPh$_3$)$_2$(CN-*p*-tolyl)(Ph)Cl] with CO.[176] Addition of CS$_2$ to the ruthenium carbyne complex [Ru(PPh$_3$)$_2$(CO)(≡CPh)Cl] gives the insertion product [Ru(PPh$_3$)$_2$(CS)(η^2-SCPh)Cl]*.[44] Treatment of an isomeric mixture of [Ru(dppe)(CO)$_2${C(O)OMe}$_2$][177] with isopropyl- or benzylamine affords the bis-carbamoyl complexes [Ru(dppe)(CO)$_2${C(O)NHCHMe$_2$}$_2$]* and [Ru(dppe)(CO)(NH$_2$CH$_2$Ph){C(O)NHCH$_2$Ph}$_2$]*, respectively.[178] The nitrosoarene complex [Ru(dppe)(CO)$_2${η^2-ON(C$_6$H$_3$ClCF$_3$)C(O)}] 61 is the final product from the reaction of the tricarbonyl [Ru(dppe)(CO)$_3$] and the nitroarene in the presence of CO.[179] The η^2-carbamoyl intermediate [Ru(P^{i}Pr$_3$)$_2${η^2-C(O)NMe$_2$}H$_2$Cl]* lies on the pathway for decarbonylation of dimethylformamide (DMF) by {Ru(P^{i}Pr$_3$)$_2$HCl}$_2$ to give [Ru(P^{i}Pr$_3$)$_2$(CO)HCl].[131]



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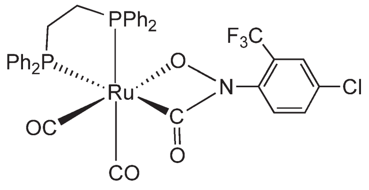
a: M = Ru
b: M = Os



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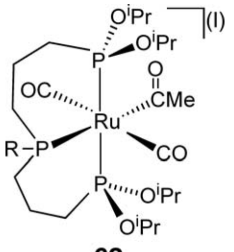
CO-induced migratory insertion occurs with the tripodal phosphine complexes *mer,cis*-[Ru(MeP{(CH$_2$)$_3$PMe$_2$}$_2$)(CO)$_2$(Me)](I) and *mer,trans*-[Ru(RP{(CH$_2$)$_3$P(OR^1$_2$)$_2$})(CO)$_2$(Me)]I (R = Ph, R^1 = ^{i}Pr; R = Cy, R^1 = ^{i}Pr; R = Ph, R^1 = Me; R = Cy, R^1 = Me) to afford the acetyl complexes *mer,trans*-[Ru{MeP{(CH$_2$)$_3$-PMe$_2$}$_2$}(CO)$_2$(COMe)](I)[180] and *mer,trans*-[Ru(RP{(CH$_2$)$_3$P(O^{i}Pr)$_2$}$_2$)(CO)$_2$(COMe)]I 62.[35] Equlibrium constants for the reaction of *trans,cis*-[M(PMe$_3$)$_2$(CO)$_2$MeI] (Ru, Os) with CO to give *trans,cis*-[M(PMe$_3$)$_2$(CO)$_2$(COMe)I] (M = Ru, Os) and *trans,trans*-[Ru(PMe$_3$)$_2$(CO)$_2$(COMe)I] have been measured over a 50 °C temperature range above ambient. Kinetic measurements on the carbonylation of *trans,cis*-[M(PMe$_3$)$_2$(CO)$_2$MeI] (M = Ru, Os) and *trans, trans*-[Ru(PMe$_3$)$_2$(CO)$_2$MeI] (and reaction of *trans,cis*-[Os(PMe$_3$)$_2$(CO)$_2$MeI] with CNCy) point to a pathway involving methyl migration.[74,181] Slow migratory insertion occurs in [Os(PPh$_3$)$_2$(CS)(CO)(*o*-YC$_6$H$_4$)Cl] upon heating to yield the η^2-thioacyl complexes [Os(PPh$_3$)$_2$(CO)(η^2-C(S)-*o*-YC$_6$H$_4$)Cl] (Y = Cl*, Br*).[47] NMR spectroscopy shows that [Ru(P^{t}Bu$_2$Me)$_2$(CO){C(O)Me}I] exists as two conformers in solution, which differ in their rotational conformations about the Ru–P bonds.[66] Heating the formally 14-electron species [Ru(P^{t}Bu$_2$Me)$_2$(CO){CH═C(SiMe$_3$)Ph}](BAr^F$_4$) with CO results in coordination of three CO molecules to give [Ru(P^{t}Bu$_2$Me)$_2$(CO)$_3${C(O)CH═C(SiMe$_3$)Ph}](BAr^F$_4$).[182]



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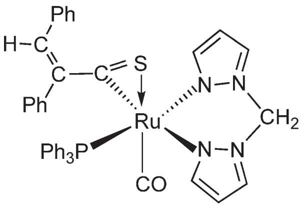
R = Ph, Cy



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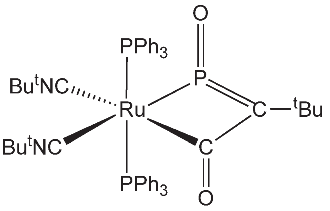

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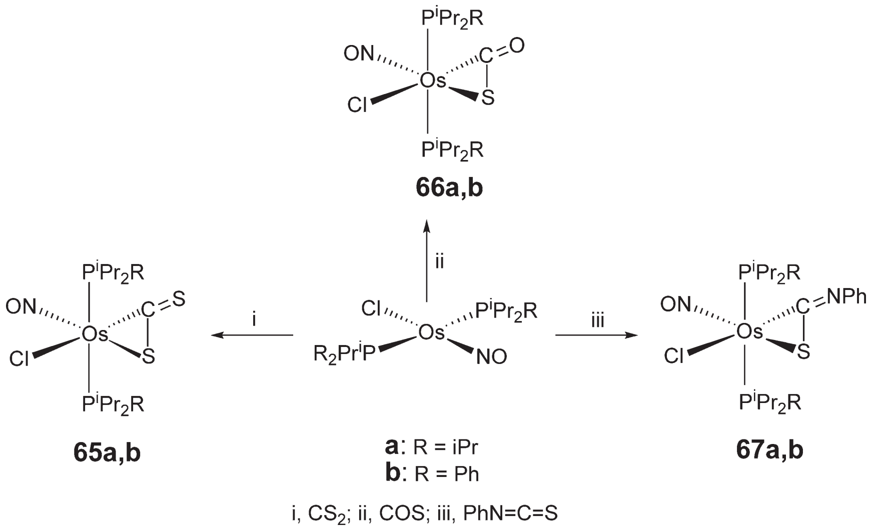


Scheme 8

The fluoroacyl complex $[Ru(PPh_3)_2(CO)_2\{C(O)F\}F]$ is unstable at RT, undergoing elimination of CO to yield the difluoride *trans,cis,cis*-$[Ru(PPh_3)_2(CO)_2F_2]$.[183] A rapid reaction occurs upon addition of CO to $[Ru(PPh_3)_2(CS)\{H_2B(pz)_2\}\{(Z)\text{-}CPh{=}CHPh\}]$ to form $[Ru(PPh_3)(CO)\{H_2B(pz)_2\}\{\eta^2\text{-}SCCPh{=}CHPh\}]$ **63**,[46] while the phospha-alkenyl complex $[Ru(PPh_3)_2(CO)(\eta^1\text{-}P{=}CHCMe_3)(CN^tBu)_2]Cl$ undergoes slow aerial decomposition to afford the phospha-alkenyl metallacycle $[Ru(PPh_3)_2\{\eta^2\text{-}P({=}O)C^tBuC(O)\}(CN^tBu)_2]^*$ **64**.[184,185] The 16-electron compounds $[Os(P^iPr_2R)_2(NO)Cl]$ react with CS_2, COS, and SCNPh to afford the 1 : 1 adducts $[Os(P^iPr_2R)_2\{\kappa^2\text{-}(C,S)\text{-}CS_2\}(NO)Cl]$ **65a** and **65b**, $[Os(P^iPr_2R)_2\{\kappa^2\text{-}(C,S)\text{-}S{=}C{=}O\}(NO)Cl]$ **66a** and **66b** and $[Os(P^iPr_2R)_2\{\kappa^2\text{-}(C,S)\text{-}S{=}C{=}NPh\}(NO)Cl]^*$ ($R = {}^iPr^*$ **67a**, Ph **67b**), respectively (Scheme 8). Treatment of $[Os(P^iPr_3)_2(NO)Cl]$ with $Ph_2C{=}C{=}O$ gives $[Os(P^iPr_3)_2(\kappa^2\text{-}(C,O)\text{-}O{=}C{=}CPh_2)(NO)Cl]^*$.[186]

Macchioni's group have employed nuclear overhauser effect (NOE) and pulsed gradient spin echo (PGSE) NMR techniques to establish the nature of cation–anion interactions and their separation for a range of cationic ruthenium and osmium acetyl complexes, including *trans*-$[M(PMe_3)_2(CO)(COMe)(CH_2pz_2)]^+$ (M = Ru,[187–189] Os[76]), *trans*-$[Ru(PMe_3)_2(CO)(COMe)(\eta^3\text{-}pz_3CH)]^+$,[190] $[Ru(PMe_3)(CO)_2(COMe)(CH_2pz_2)]^+$,[190] and *trans*-$[Ru(PMe_3)_2(CO)\text{-}(COMe)(N\text{-}O)]^+$ (N-O = 2-acetylpyridine, 2-benzoylpyridine, 2,2′-dipyridylketone).[191]

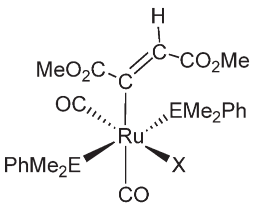
6.12.4 Alkenyl Complexes

6.12.4.1 Formation via Insertion of Alkyne

The established route to alkenyl complexes via alkyne insertion into an M–H bond has continued to afford new complexes. Thus, the five-coordinate alkenyl thiolate complexes $[M(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHR\}SH]$ (M = Ru, R = Ph; M = Os, R = Ph, CO_2Me) result from insertion of $HC{\equiv}CR$ into the M–H bond of $[M(P^iPr_3)_2(CO)(SH)H]$.[192] Insertion into the Ru–H bond in $[Ru(PPh_3)_2(CX)(BTD)HCl]$ (X = O, S; BTD = 2,1,3-benzothiadiazole) generates $[Ru(PPh_3)_2(CX)(CR{=}CHR^1)(BTD)Cl]$ (X = O; R = H, R^1 = *p*-tolyl, $CPh_2(OH)$; $R = R^1$ = H, *p*-tolyl; X = S, $R = R^1$ = Ph), which undergo facile substitution to yield pyrazolylborate derivatives, including $[Ru(PPh_3)_2(CO)\{H_2B(pz)_2\}(CH{=}CH_2)]^*$ and [9]aneS_3 adducts.[46,193] Chiral salts of $[Ru(PPh_3)(CO)([9]aneS_3)(CR{=}CHR^1)](PF_6)$ ($R = R^1 = H$,* $R = R^1$ = Ph, R = H, R^1 = *p*-tolyl) are formed by treatment of the coordinatively unsaturated alkenyl complexes $[Ru(PPh_3)_2(CO)(CR{=}CHR^1)Cl]$ with $[9]aneS_3/KPF_6$.[45]

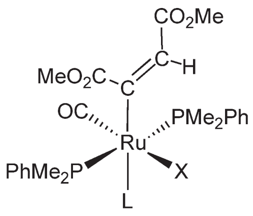
The reactions of $[RuL_2(L^1)HCl]$ ($L = P^iPr_3$, L^1 = CO; $L = PCy_3$, L^1 = CO, MeCN) with $HC{\equiv}CR$ (R = H, Ph, ^{t}Bu) produce the alkenyl complexes $[RuL_2(CO)(CH{=}CHR)Cl]$ and $[Ru(PCy_3)_2(MeCN)(CH{=}CHPh)Cl]$. In contrast, reactions of the stibine-substituted derivative $[Ru(PCy_3)_2\{Sb(CH_2Ph)_3\}HCl]$ with $HC{\equiv}CR$ (R = H, Ph) produce the vinylidene hydride complexes $[Ru(PCy_3)_2({=}C{=}CHR)HCl]$.[194] Addition of $HC{\equiv}CCMe{=}CH_2$ to $[Os(P^iPr_3)_2(CO)HCl]$ gives $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}C(H)C(Me){=}CH_2\}Cl]$,[195] while reactions of the propargylic alcohol $HC{\equiv}CCPh_2(OH)$ with $[M(PPh_3)_3(CO)HCl]$ (M = Ru, Os) afford the γ-hydroxyalkenyl complexes $[M(PPh_3)_2(CO)\{CH{=}CHCPh_2(OH)\}Cl]$ and $[Ru(PPh_3)_2\{CH{=}CHCPh_2(OH)\}(MeCN)_2Cl]$.[196]

The insertion of $MeO_2CC{\equiv}CCO_2Me$ into the Ru–H bond of $[Ru(EMe_2Ph)_2(CO)_2HX]$ (E = P, As; X = H, Cl) affords the alkenyl complexes **68** by *trans*-addition, whereas reaction with the trisphosphine monocarbonyl analog $[Ru(PMe_2Ph)_3(CO)HCl]$ generates the *cis*-addition product **69**. The replacement of CO by PMe_2Ph in $[Ru(PMe_2Ph)_2(CO)_2\{C(CO_2Me){=}CH(CO_2Me)\}Cl]$ has no effect on the geometry of the alkenyl ligand (generating **70**), thereby allowing the two (non-interconverting) isomers to be detected.[197] The ancillary ligand is found to have a dramatic effect on the reactivity of $[Ru(P^tBu_2Me)_2(CO)HX]$ (X = halide, alkoxide etc.) with alkynes. Thus, no reaction of butyne is found with X = F or Cl at RT, although the iodo complex $[Ru(P^tBu_2Me)_2(CO)HI]$ rapidly gives the insertion product $[Ru(P^tBu_2Me)_2(CO)\{(Z)\text{-}CMe{=}CHMe\}I]$ even at −80 °C. With oxygen-donor ligands X = OPh, $OSiPh_3$, OCH_2CF_3, addition of $PhC{\equiv}CH$ affords $[Ru(P^tBu_2Me)_2(CO)(C{\equiv}CPh)H]$, whereas the iodo complex $[Ru(P^tBu_2Me)_2(CO)HI]$ initially forms $[Ru(P^tBu_2Me)_2(CO)\{(E)\text{-}CH{=}C(H)Ph)\}I]$, which subsequently eliminates styrene to give a product resulting from metallation of the phosphine.[198] The reactivity of these five-coordinate systems is not confined to solution chemistry; ethyne reacts with $[Ru(P^tBu_2Me)_2(CO)HCl]$ in the solid state to give $[Ru(P^tBu_2Me)_2(CO)(CH{=}CH_2)Cl]$.[199]



E = P, As; L = CO; X = H, Cl

68



L = PMe_2Ph; X = Cl

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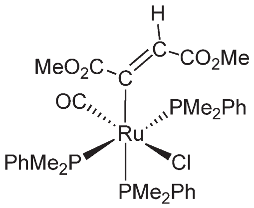

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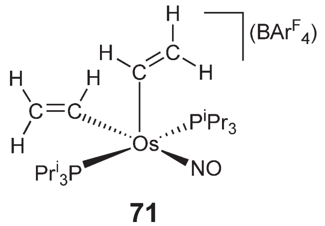
Protonation of $[RuL_2(CO)(CH{=}CHR)Cl]$ with HBF_4 yields the cationic five-coordinate carbene complexes $[RuL_2(CO)({=}CHCH_2R)Cl](BF_4)$ (L = $P^iPr_3{}^*$, PCy_3; R = H, Ph, $^tBu^*$). Subsequent reactions of these with PMe_3 or P^iPr_3 and MeCN result in either deprotonation and regeneration of the alkenyl compounds or cleavage of the ruthenium–carbene bond giving the six-coordinate acetonitrile complexes $[Ru(P^iPr_3)_2(CO)(MeCN)_2Cl](BF_4)$ and $[Ru(P^iPr_3)_2(CO)(MeCN)_2H]X$. $[Ru(PCy_3)_2(CO)(\kappa^2\text{-}O_2CMe)H]$ reacts with $HC{\equiv}CR$ (R = H, Ph) to yield $[Ru(PCy_3)_2(CO)(CH{=}CHR)(\kappa^2\text{-}O_2CMe)]$, which generates the corresponding cationic carbene complex $[Ru(PCy_3)_2(CO)({=}CHMe)(\kappa^2\text{-}O_2CMe)](BF_4)$ upon protonation.[194]

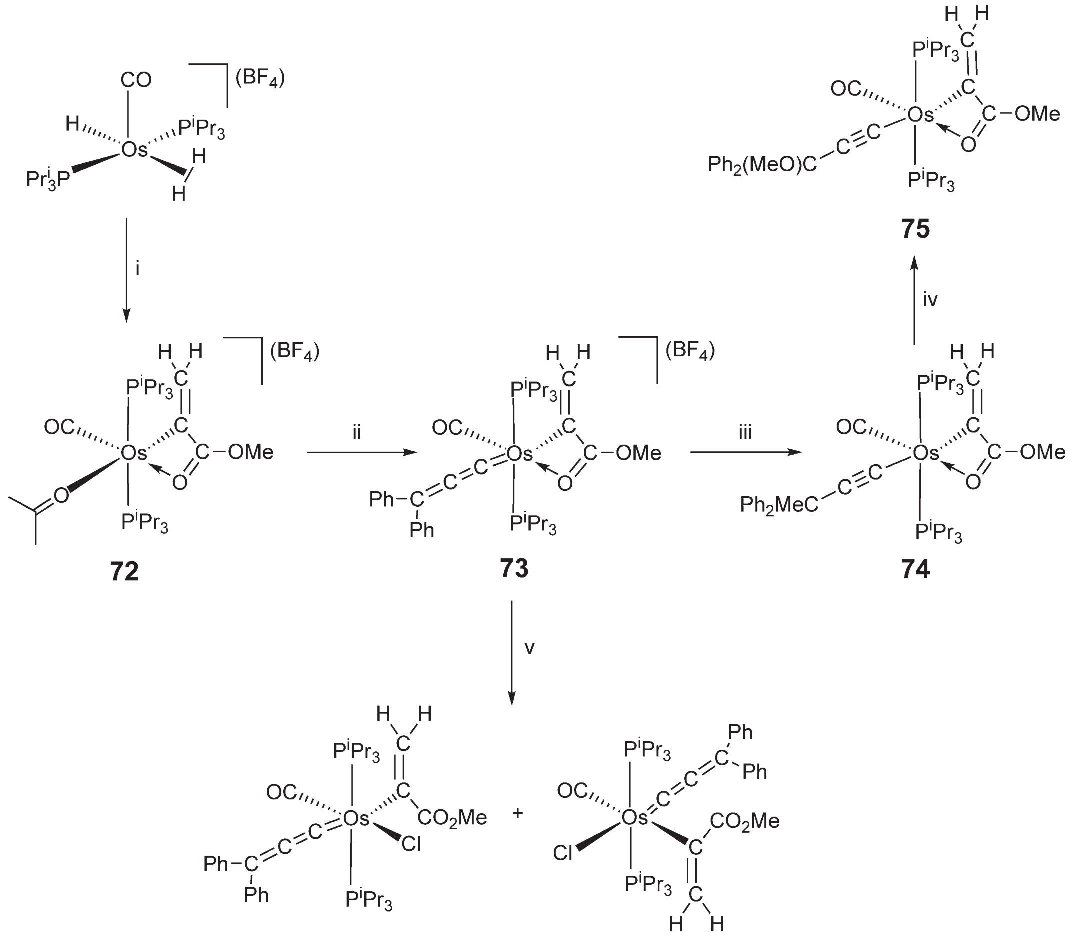
Slightly more complex insertion reactions have been documented. Addition of 3 equiv. of $MeC{\equiv}CPh$ to $[Os(PPh_3)_3H_3Cl]$ at RT gives the coordinated phenylallene complex $[Os(PPh_3)_2(CMe{=}CHPh)(CH_2{=}C{=}CHPh)Cl]^*$ (also formed by reaction of $[Os(PPh_3)_3HCl]$ and an excess of $MeC{\equiv}CPh$) and the hydrogenation product $CHMe{=}CHPh$. The solid-state structure shows an agostic interaction with a β-H of the alkenyl ligand.[200] The zwitterionic resonance form $[\{Ru^+\}(P^iPr_3)_2(CO)\{{=}CHCH{=}CMeCH_2{}^-\}Cl]$ makes a major contribution to the structure of the α,β-coordinatively unsaturated alkenyl complex $[Ru(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHCMe{=}CH_2\}Cl]^*$ on the basis of the short Ru–C_α bond length (1.989(3) Å). This can be trapped by CO to afford $[Ru(P^iPr_3)_2(CO)_2\{(E)\text{-}CH{=}CHCMe{=}CH_2\}Cl]$, which then undergoes alkylation by MeLi or reaction with $H_2C{=}CHMgBr$ to yield $[Ru(P^iPr_3)_2(CO)_2\{(E)\text{-}CH{=}CHCMe{=}CH_2\}(L)]$ (L = Me, $CH{=}CH_2$).[201] Addition of prop-2-ynyltriphenylphosphonium bromide $[Ph_3PCH_2C{\equiv}CH]Br$ to $[Ru(PPh_3)_3(CO)HCl]$, followed by treatment with NH_4PF_6, affords $[Ru(PPh_3)_2(CO)(CH{=}CHCH_2PPh_3)Br](PF_6)^*$. This coordinatively unsaturated species reacts with a range of two-electron donors (CO, CN-2,6-$Me_2C_6H_3$, NaS_2CNMe_2) to yield six-coordinate analogs.[202]

The bis-alkenyl complex $[Os(P^iPr_3)_2(CH{=}CH_2)_2(NO)](BAr^F{}_4)^*$ **71**, containing inequivalent and rapidly exchanging σ-organyl ligands, results from the double insertion of $HC{\equiv}CH$ into both Os–H bonds of $[Os(P^iPr_3)_2(NO)H_2](BAr^F{}_4)$.[203] Less stable ruthenium and osmium bis-alkenyl complexes can be formed by alternative methodologies.[204] The silylalkyne $Me_3SiC{\equiv}CPh$ undergoes silyl migration with the coordinatively unsaturated hydride complex $[Ru(P^tBu_2Me)_2(CO)H](BAr^F{}_4)$ to afford the formally 14-electron species, $[Ru(P^tBu_2Me)_2(CO)\{CH{=}C(SiMe_3)Ph\}](BAr^F{}_4)^*$, which is stabilized both in the solid state and in solution by two agostic interactions.[181] The reaction of $[Os(P^iPr_3)_2(CO)H_4]$ with $MeO_2CC{\equiv}CH$ generates $[Os(P^iPr_3)_2(CO)(C{\equiv}CCO_2Me)\{CH{=}CHC(OMe){=}O\}]^*$,[205] while the five-coordinate dihydrogen hydride complex $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}H_2)H](BF_4)$ reacts with the same alkyne in acetone to give $[Os(P^iPr_3)_2(CO)\{\eta^2\text{-}C(CO_2Me){=}CH_2\}(\kappa^1\text{-}OCMe_2)](BF_4)$ **72**

(Scheme 9). Treatment with additional methyl propiolate or $HC{\equiv}CCPh_2(OH)$ results in acetone dissociation and formation of $[Os(P^iPr_3)_2(CO)\{\eta^2\text{-}C(CO_2Me){=}CH_2\}({=}C{=}CHCO_2Me)](BF_4)$ and the allenylidene complex $[Os(P^iPr_3)_2(CO)\{\eta^2\text{-}C(CO_2Me){=}CH_2\}({=}C{=}C{=}CPh_2)](BF_4)^*$ 73, respectively. The latter reacts with MeLi to give the alkenyl alkynyl complex $[Os(P^iPr_3)_2(CO)\{\eta^2\text{-}C(CO_2Me){=}CH_2\}(C{\equiv}CCPh_2Me)]$ 74, which is unstable in MeOH, eliminating CH_4 to form $[Os(P^iPr_3)_2(CO)\{\eta^2\text{-}C(CO_2Me){=}CH_2\}(C{\equiv}CCPh_2OMe)]$ 75–this product is formed directly upon reaction of 73 and NaOMe. In the presence of NaCl, 73 produces *trans*- and *cis*-(*Cl*, *CO*)$[Os(P^iPr_3)_2(CO)\{C(CO_2Me){=}CH_2\}({=}C{=}C{=}CPh_2)Cl]$ 76a and 76b. Upon heating to 60 °C, both these species convert into the allenyl derivative $[Os(P^iPr_3)_2(CO)\{\kappa^2\text{-}(C,O)\text{-}C(C\{C(O)OMe\}{=}CH_2){=}C{=}CPh_2\}Cl]^*$, resulting from migratory insertion of the allenylidene ligand into the Os–C(alkenyl) bonds.[206]



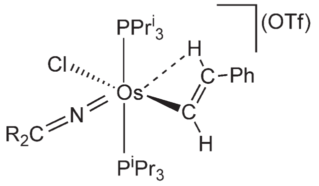
71



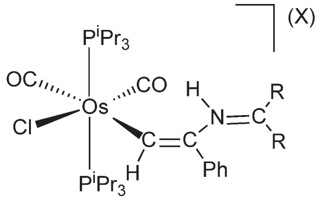
i, methyl propiolate; ii, 1,1-diphenyl-2-propyn-1-ol; iii, MeLi; iv, MeOH; v, NaCl

Scheme 9

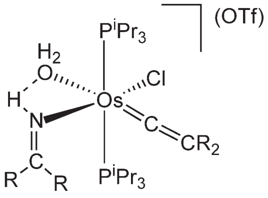
The reactions of RC≡CH with a mixture of $[Os(P^iPr_3)_2({=}N{=}CR^1_2)HCl_2]$ ($CR^1_2 = CMe_2$, $C(CH_2)_4CH_2$) and AgOTf at low temperature produce the alkenyl azavinylidene species $[Os(P^iPr_3)_2({=}N{=}CR^1_2)\{(E)\text{-}HC{=}CHR\}Cl](OTf)$ (R = Cy, R = Ph **77a** and **77b**). The coordinatively unsaturated osmium center is stabilized by agostic interactions with H_β on the alkenyl ligands.[207,208] Under an atmosphere of CO, **77a** and **77b** undergo C–N coupling of the styryl and azavinylidene ligands to give Δ^2-1,2-aza-osmetine derivatives $[Os(P^iPr_3)_2(CO)({=}CHCHPhN{=}CR^1_2)Cl](OTf)$ ($CR_2 = CMe_2$, $C(CH_2)_4CH_2$), which react upon prolonged treatment with CO by 1,2-hydrogen migration from the CHPh carbon atoms to the nitrogen atoms and carbonylation to generate $[Os(P^iPr_3)_2(CO)_2\{(Z)\text{-}HC{=}CPhNH{=}CR_2\}Cl](X)$ ($CR_2 = CMe_2$ **78a**, $C(CH_2)_4CH_2^*$ **78b**; X = OTf, BF_4^*).[209] Addition of NaCl at low temperature cleaves the agostic interaction in **77a** and **77b** to give the neutral compounds $[Os(P^iPr_3)_2({=}N{=}CR_2)\{(E)\text{-}CH{=}CHPh\}Cl_2]$. Both these complexes are unstable at RT and transform via hydrogen transfer to the imine–vinylidene species $[Os(P^iPr_3)_2(NH{=}CR_2)({=}C{=}CHPh)Cl_2]$. **77a** and **77b** convert with water at low temperature into $[Os(P^iPr_3)_2({=}N{=}CR_2)\{(E)\text{-}CH{=}CHPh\}(H_2O)Cl](OTf)$ **79a** and **79b**, via the spectroscopically characterized intermediate aqua complexes $[Os(P^iPr_3)_2({=}N{=}CR_2)\{(E)\text{-}CH{=}CHPh\}(H_2O)Cl](OTf)$.[207]



77
a: R = CMe$_2$
b: R = C(CH$_2$)$_4$CH$_2$



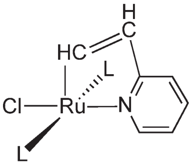
78
a: R = CMe$_2$
b: R = C(CH$_2$)$_4$CH$_2$



79
a: R = CMe$_2$
b: R = C(CH$_2$)$_4$CH$_2$

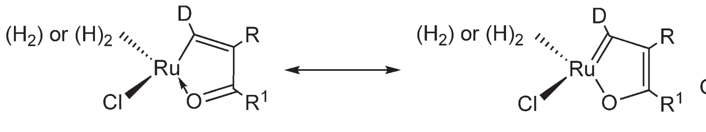
Insertion into other M–X bonds, where X ≠ H, has also been developed. Ethyne insertion into the Ru–silyl bond of $[Ru(PPh_3)_2(CO)(SiR_3)Cl]$ affords $[Ru(PPh_3)_2(CO)\{(E)\text{-}CH{=}CHSiR_3\}Cl]$, which adds two-electron donor ligands such as CO and CN-*p*-tolyl to give $[Ru(PPh_3)_2(CO)(L)\{(E)\text{-}CH{=}CHSiR_3\}Cl]$ (L = CO, $SiR_3 = SiMe_3$, $SiEt_3$, $SiMe_2OEt^*$; L = CN-*p*-tolyl, $SiR_3 = SiMe_3$).[210] In the case of the structurally characterized dimethylethoxysilyl system, the alkenyl ligand and CO are shown to be coplanar. Subsequent calculations have shown that such an arrangement helps to maximize the amount of overlap between metal t_{2g} and π^* orbitals of these ligands.[211] The metallacycle $[Ru(PPh_3)_2(CO)\{CH{=}CHSiMe_2(OH)\}Cl]$ results from reaction of $[Ru(PPh_3)_2(CO)\{SiMe_2(OH)\}Cl]$ with HC≡CH. Subsequent reactions with $AgClO_4$/MeCN followed by addition of L^1 gave $[Ru(PPh_3)_2(L^1)(CO)\{CH{=}CHSiMe_2(OH)\}](ClO_4)$ (L = MeCN, CO, CN-*p*-tolyl*), which can undergo deprotonation of the Si–OH group by KOH for L = CO or CN-*p*-tolyl.[210] Addition of the sodium salt of the tripodal oxygen donor ligand NaL_{OEt} ($L_{OEt} = (\eta^5\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$) to $[Ru(PPh_3)_2(CO)\{(E)\text{-}CH{=}CHPh\}Cl]$ generates $[Ru(L_{OEt})(PPh_3)(CO)\{(E)\text{-}CH{=}CHPh\}]$.[212]

A tethered alkenyl complex results from C–H bond activation of vinylpyridine by $[Os(P^iPr_3)_2H_6]$, which gives the trihydride complex $[Os(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH{=}CH)H_3]^*$; protonation by HBF_4 in the presence of H_2 reforms $[Os(P^iPr_3)_2H_6]$, but if HBF_4 is added under an argon atmosphere, the cationic dihydrogen hydride adduct $[Os(P^iPr_3)_2(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(\eta^2\text{-}H_2)H](BF_4)^*$ is formed. Dissolution in CH_2Cl_2 converts this into the neutral species $[Os(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH{=}CH)(\eta^2\text{-}H_2)Cl]$.[213] Coordination of 2-vinylpyridine to the ruthenium precursor $[Ru(P^iPr_3)_2HCl]$ occurs at RT to give the pyridyl-coordinated alkenyl complex $[Ru(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH{=}CH)Cl]^*$ **80**. With generic alkenes of the form D(H)C=CR(EWG)-containing push (D) and pull (EWG) substituents, such as MeO(H)C=C(H)C(O)Me and $Me_2N(H)C{=}C(Me)C(O)H$, related heteroatom-coordinated complexes are also formed, which lie between the two extremes of being viewed as alkenyl **81a** or carbene complexes **81b**.[214] Addition of HC≡CR to $[Ru(P^iPr_3)_2(CO)(\eta^2\text{-}PhC{\equiv}CPh)]$ gives the alkenyl alkynyl complexes $[Ru(P^iPr_3)_2(CO)(C{\equiv}CR)\{(E)\text{-}CH{=}CHR\}]$ (R = Cy, CO_2Me, $SiMe_3$).[215] The propanoato complex $[Ru(PPh_3)_2(CO)(\eta^2\text{-}O_2CEt)Cl]$ reacts with HC≡CR to produce $[Ru(PPh_3)_2(CO)\{C({=}CHR)OC(O)Et\}Cl]$ (R = Ph* **82**, $(CH_2)_4CH_3$, CH_2OH).[216]



L = P^iPr_3

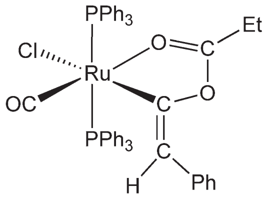
80



81a

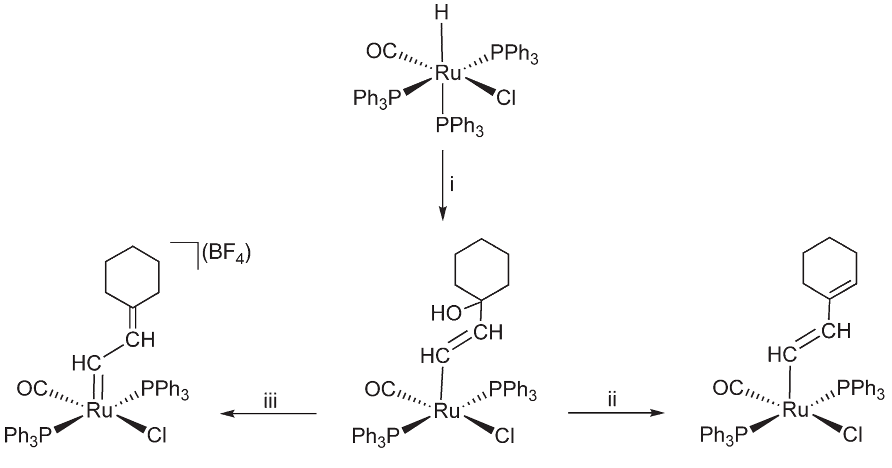
81b

D = OMe, R = H, R^1 = Me
D = NMe_2, R = Me, R^1 = H
D = Ph, R = H, R^1 = Me



82

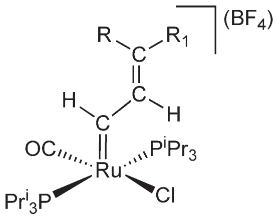
The hydroxyalkenyl complexes $[Ru(PPh_3)_2(CO)\{CH{=}CHCRR^1(OH)\}Cl]$ ($R = Ph$, $R^1 = Me$; $R = R^1 = H$; $R = R^1 = Me$; $R = Me$, $R^1 = Et$; $RR^1 = \textit{cyclo}\text{-}C_6H_{10}$) are formed upon addition of $HC{\equiv}CCRR^1(OH)$ to $[Ru(PPh_3)_3(CO)HCl]$. Dehydration of $[Ru(PPh_3)_2(CO)\{CH{=}CHCPhMe(OH)\}Cl]$ and $[Ru(PPh_3)_2(CO)\{CH{=}CH(\textit{cyclo}\text{-}C_6H_{10})(OH)\}Cl]$ 83 by alumina yields the dienyl complexes $[Ru(PPh_3)_2(CO)(CH{=}CH\text{-}CPh{=}CH_2)Cl]$ and $[Ru(PPh_3)_2(CO)(CH{=}CH\text{-}\textit{cyclo}\text{-}C_6H_9)Cl]$ 84, respectively, while addition of HBF_4 or $[Ph_3C]BF_4$ to the same two hydroxyalkenyl species yields the alkenylcarbene complexes $[Ru(PPh_3)_2(CO)({=}CH\text{–}CH{=}CPhMe)Cl](BF_4)$ and $[Ru(PPh_3)_2(CO)\{{=}CHCH{=}C(CH_2)_5\}Cl](BF_4)$ 85 (Scheme 10).[217] Treatment of a toluene solution of $[Ru(P^iPr_3)_2(CO)HCl]$ with $HC{\equiv}CCRR^1(OH)$ affords $[Ru(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHCRR^1(OH)\}Cl]$ ($R = R^1 = H$; $R = H$, $R^1 = Ph$; $R = R^1 = Ph$), which upon protonation with $HBF_4{\cdot}OEt_2$ gives the alkenylcarbene complexes $[Ru(P^iPr_3)_2(CO)({=}CHCH{=}CRR^1)Cl](BF_4)$ (86, $R = H$, $R^1 = Ph$; $R = R^1 = Ph^*$). Similar reactivity occurs with $HC{\equiv}CC(OH)H(CH_2)_4CH_2$.[218] An analogous tricyclohexylphosphine derivative, $[Ru(PCy_3)_2(CO)({=}CHCH{=}CPh_2)\text{-}Cl](BAr^F{}_4)$, is known.[219] Addition of $HC{\equiv}CCMe{=}CH_2$ to $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}H_2)Cl_2]$ affords $[Os(P^iPr_3)_2(CO)({=}CHCH{=}CMe_2)Cl_2]$, which can also be formed by addition of HCl to $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}C(H)CMe{=}CH_2\}Cl]$.[195] The alkenylcarbene salt $[Ru(PPh_3)_2(CO)(S_2CNMe_2)({=}CHCH{=}CPh_2)](PF_6)$ 87, obtained from $[Ru(PPh_3)_3(CO)HCl]$, $HC{\equiv}CCPh_2(OH)$, $Na(S_2CNMe_2)$, and HPF_6, reacts with F^-, RO^-, $BH_4{}^-$, or OH^- at the γ-carbon atom to give γ-functionalized alkenyl complexes 88.[220]



85 **83** **84**

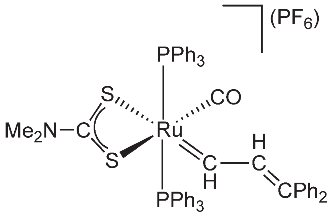
i, 1-ethynylcyclohexanol; ii, Al_2O_3; iii, HBF_4

Scheme 10

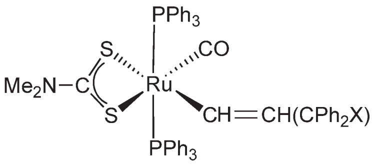


86

a: R = H, R^1 = Ph
b: R = R^1 = Ph



87

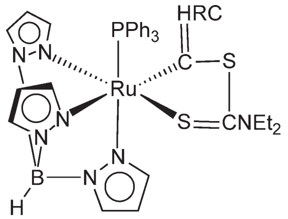


88

X = F, OEt, H, OH

6.12.4.2 Formation via Decomposition Pathways

Addition of CO to the carbyne complex $[Os(P^iPr_3)_2(\equiv CCH_2Ph)HCl_2]$ generates the carbene $[Os(P^iPr_3)_2(CO)(=CHCH_2Ph)Cl_2]$, which reacts with excess CO by HCl elimination to form $[Os(P^iPr_3)_2(CO)_2\{(E)\text{-}CH=CHPh\}Cl]$.[221] The reaction of $[Ru(PPh_3)_2\{HB(pz)_3\}Cl]$ with HC≡C-*p*-tolyl yields $[Ru(PPh_3)\{HB(pz)_3\}(=C=CH\text{-}p\text{-tolyl})Cl]$, which reacts with $[Et_2NH_2][S_2CNEt_2]$ to give the metallacyclic alkenyl complex $[Ru(PPh_3)\{HB(pz)_3\}\{C(=CH\text{-}p\text{-tolyl})(SC(NEt_2)S)\}]$ **89**.[222] In the presence of O_2, $[Os(P^iPr_3)_2(=C=CHPh)HCl]$ cleaves the O–O bond to give the dioxo-styryl complex $[Os(P^iPr_3)_2\{(E)\text{-}CH=CHPh\}(O)_2Cl]^*$.[223] Addition of PEt_3 to $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(\eta^2\text{-}MeC\equiv CPh)]$ gives the ylide $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2\{C(Me)=C(Ph)PEt_3\}]^*$.[224] Similarly, reaction of $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(\eta^2\text{-}MeC\equiv CPh)]$ with PPh_3 affords the analogous ylide, while reaction with $K[BH(CHMeEt)_3]$ and then 18-crown-6 yields $[K(18\text{-crown-}6)][Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2\{C(Me)=C(H)Me\}]$.[157]



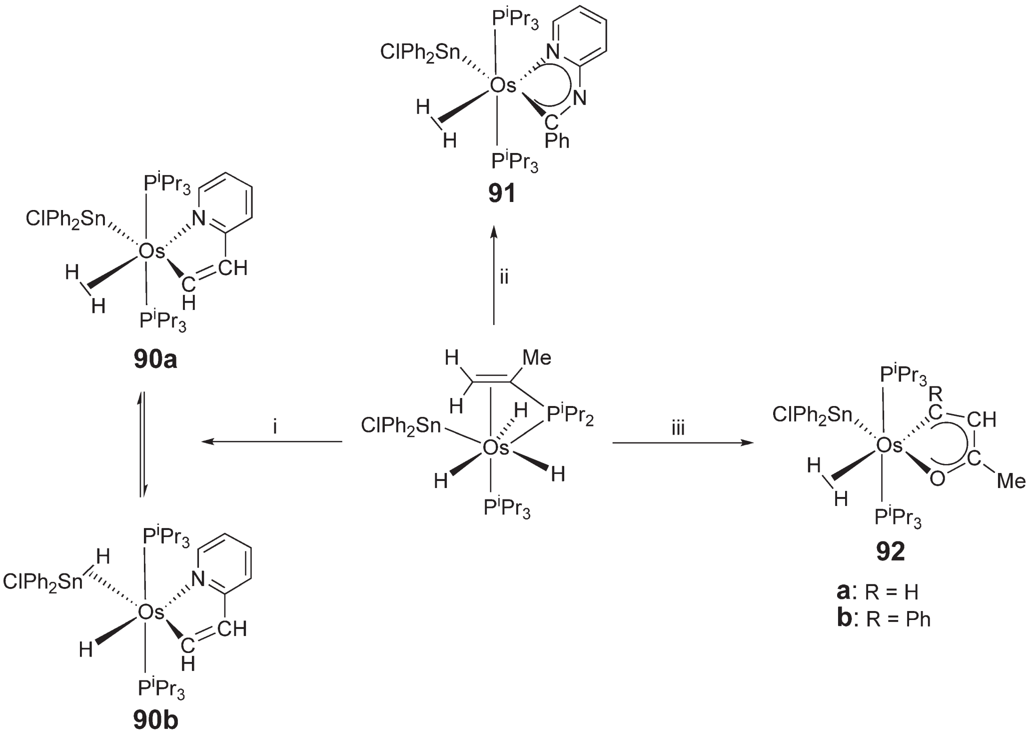
89

R = *p*-tolyl

The aryl boryl complex *trans,cis,cis*-$[Os(PPh_3)_2(CO)_2(R)(Bcat)]^*$ (Bcat = B-1,2-$O_2C_6H_4$; R = 2-MeC_6H_4) undergoes slow reductive elimination of RBcat in the presence of $Cl_2C=CCl_2$ to yield the alkenyl complex $[Os(PPh_3)_2(CO)_2(CCl=CCl_2)Cl]^*$.[48,49]

Treatment of $[Os(P^iPr_3)\{\eta^2\text{-}H_2C=C(Me)P^iPr_2\}(SnPh_2Cl)H_3]$ with vinylpyridine affords $[Os(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH=CH)(SnPh_2Cl)(\eta^2\text{-}H_2)]^*$ **90a**, which exists in solution in equilibrium with the tautomer $[Os(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH=CH)(HSnPh_2Cl)H]$ **90b**. If the vinylpyridine is "bulked up" to (*E*)-*N*-(phenylmethylene)-2-pyridylamine, C–H activation also occurs to give $[Os(P^iPr_3)_2(NC_5H_4\text{-}2\text{-}NCPh)(SnPh_2Cl)(\eta^2\text{-}H_2)]$ **91**; in solution, this shows no evidence for tautomerization. C–H activation of the $C_\beta(sp^2)$–H bond of α,β-unsaturated ketones is also possible. Thus, RCH=C(H)C(O)Me reacts to give $[Os(P^iPr_3)_2\{C(R)CHC(O)\}Me)(SnPh_2Cl)(\eta^2\text{-}H_2)]$ (R = H* **92a**, Ph **92b**), which display blocked rotation of the dihydrogen ligand in solution (Scheme 11). To establish the preference for *ortho*-C–H versus $C_\beta(sp^2)$–H activation, $[Os(P^iPr_3)\{\eta^2\text{-}H_2C=C(Me)P^iPr_2\}(SnPh_2Cl)H_3]$ was treated with benzylideneacetophenone resulting in a kinetic preference for $C_\beta(sp^2)$–H bond cleavage but ultimately giving the product from *ortho*-C–H activation as the thermodynamic product.[225]

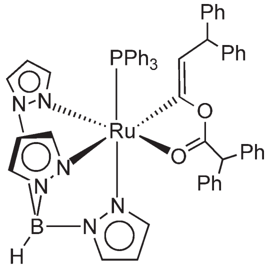
Addition of an excess of LiC≡CPh to $[Os\{2,6\text{-}(Ph_2PCH_2)_2C_5H_3N\}(PPh_3)Cl]$ results in an unsual insertion reaction of the alkynyl group into the PNP backbone to yield $[Os\{2\text{-}Ph_2PCH(CPh=CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N\}(PPh_3)Cl]^*$. Addition of $NaBF_4$ in the presence of H_2 and base, followed by HBF_4, affords the cationic dihydrogen complex $[Os\{2\text{-}Ph_2PCH(CPh=CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N\}(PPh_3)(\eta^2\text{-}H_2)](BF_4)$, in which this alkenyl ligand is maintained. However, addition of H_2 leads to Os–C_α cleavage to give two isomers of the dihydrogen hydride complex $[Os\{2\text{-}Ph_2PCH(CPh=CH_2)\text{-}6\text{-}Ph_2PCH_2C_5H_3N\}(PPh_3)(\eta^2\text{-}H_2)H](BF_4)$.[226] The chelate complex



i, $H_2C{=}CHC_5H_4N$; ii, (*E*)-PhCH=N-C_5H_4N; iii, RCH=CHC(O)Me

Scheme 11

[Ru(PPh$_3$){HB(pz)$_3$}{κ^2-(*C,O*)-C(=CHCHPh$_2$)OC(CHPh$_2$)=O}]* **93** results from a slow RT reaction of [Ru(PPh$_3$){HB(pz)$_3$}(η^2-O$_2$CCHPh$_2$)] with diphenylcyclopropene. The same precursor reacts with HC≡CPh to give [Ru(PPh$_3$){HB(pz)$_3$}{κ^2-(*C,O*)-C(=CHPh)OC(CHPh$_2$)=O}]*.[227]



93

Deprotonation of the the cationic vinylidene [Ru(PPh$_3$)$_2${HB(pz)$_3$}(=C=CPhCH$_2$CN)]I affords the cyclopropenyl complex [Ru(PPh$_3$)$_2${HB(pz)$_3$}(C=CPhCHCN)], which upon reaction with pyrazole at RT affords the metallacyclic alkenyl complex, [Ru(PPh$_3$)$_2${HB(pz)$_3$}{(C$_3$H$_3$NN)C=CPhCH$_2$CN}]*.[228]

6.12.5 Alkynyl Complexes

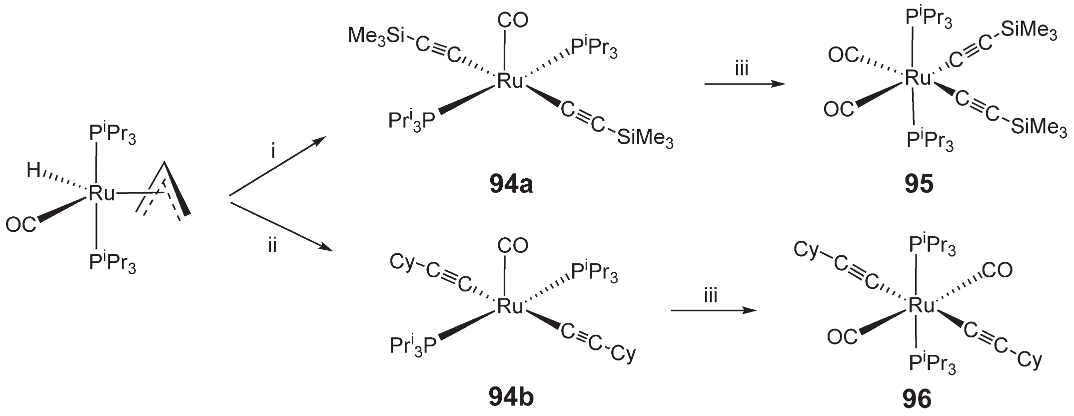
6.12.5.1 Formation via Oxidative Addition

The structural characterization of [Ru(P^{t}Bu$_2$Me)$_2$(CO)(C≡CSiMe$_3$)(SiMe$_3$)]* (formed by oxidative addition of Me$_3$SiC≡CSiMe$_3$ to [Ru(P^{t}Bu$_2$Me)$_2$(CO)H$_2$]) reveals a square-pyramidal geometry with SiMe$_3$ in the apical site and CO *trans* to the alkynyl ligand in two of the basal sites.[229] Facile formation of the parent alkynyl complex [Ru(P^{t}Bu$_2$Me)$_2$(CO)$_2$(C≡CH)H] occurs at RT upon exposure of solid, microcrystalline [Ru(P^{t}Bu$_2$Me)$_2$(CO)$_2$] to ethyne.[199] The coordinatively unsaturated osmium(0) nitrosyl species $[Os(P^tBu_2Me)_2(CO)(NO)](BAr^F{}_4)$ reacts with $PhC{\equiv}CH$ forming $[Os(P^tBu_2Me)_2(CO)(NO)(\eta^2\text{-}PhC{\equiv}CH)](BAr^F{}_4)$, which undergoes intramolecular rearrangement to the oxidative addition product $[Os(P^tBu_2Me)_2(CO)(NO)(C{\equiv}CPh)H](BAr^F{}_4)$, and then onto the vinylidene complex $[Os(P^tBu_2Me)_2(CO)(NO)({=}C{=}CHPh)](BAr^F{}_4)$; a mixture of these cations is deprotonated by NEt_3 to give $[Os(P^tBu_2Me)_2(CO)(NO)(C{\equiv}CPh)]$.[230]

Addition of $HC{\equiv}CMe$ to a solution of $[Os(PPh_3)_3(CO)(CS)]$ generates the alkynyl hydride complex $[Os(PPh_3)_2(CO)(CS)(C{\equiv}CMe)H]^*$ as the major product, although this is converted into the propenylthioacyl complex $[Os(PPh_3)_2(CO)\{\eta^2\text{-}C(S)CH{=}CHMe\}Cl]^*$ in the presence of HCl.[231] The square-planar Os(0) complexes $[Os(PR_3)_2(NO)Cl]$ react with $HC{\equiv}CPh$ to form $[Os(PR_3)_2(NO)(C{\equiv}CPh)HCl]$ ($PR_3 = P^iPr_3$, P^iPr_2Ph), which cannot be converted into the corresponding vinylidene complexes either thermally or photochemically. In contrast, $[Os(PR_3)_2(NO)\{C{\equiv}CPh_2(OH)\}HCl]$, resulting from reaction with $HC{\equiv}CCPh_2(OH)$, can be converted into the allenyl complexes $[Os(PR_3)_2(NO)(CH{=}C{=}CPh_2)Cl_2]$ ($PR_3 = P^iPr_3{}^*$, P^iPr_2Ph) upon treatment with chloride-containing alumina under acidic conditions.[232]

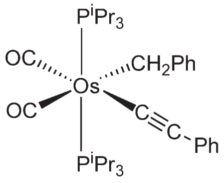
Reaction of $[Ru(Sb^iPr_3)_3(CO)HCl]$ with $HC{\equiv}CPh$ or $HC{\equiv}CCPh_2(OH)$ affords the alkynyl and allenylidene species $[Ru(Sb^iPr_3)_3(CO)(C{\equiv}CPh)Cl]$ and $[Ru(Sb^iPr_3)_2(CO)({=}C{=}C{=}CPh_2)Cl_2]^*$, respectively; the additional chloride ligand in the latter arises from workup involving chloride-containing Al_2O_3.[233] Terminal alkynes react with $[Ru(P^iPr_3)_2(CO)(\eta^3\text{-}C_3H_5)H]$ to give *trans*-bis-alkynyl species $[Ru(P^iPr_3)_2(CO)(C{\equiv}CR)_2]$ ($R = SiMe_3$ **94a**, Cy **94b**) and the alkynyl alkenyl complex $[Ru(P^iPr_3)_2(CO)(C{\equiv}CR)\{(E)\text{-}CH{=}CHSiMe_3)]$. These are converted into the six-coordinate dicarbonyl complexes with different geometries **95** and **96** upon addition of CO (Scheme 12).[215]

Addition of $PhC{\equiv}CH$ to the carbamato complex $[Ru(PCy_3)_2(CO)(O_2CNEt_2)H]$ results in evolution of CO_2 gas and concomitant formation of the bis-alkynyl complex $[Ru(PCy_3)_2(CO)(C{\equiv}CPh)_2]^*$.[234] The alkynyl η^2-dihydrogen complexes $[Os(P^iPr_3)_2(CO)(C{\equiv}CR)(\eta^2\text{-}H_2)H]$ ($R = Ph$, $SiMe_3$) form upon addition of $RC{\equiv}CH$ to $[Os(P^iPr_3)_2(CO)H_4]$. If for $R = Ph$, the complex is left under an atmosphere of H_2, conversion into $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}CH_2{=}CHPh)H_2]$ takes place in solution over a number of hours. The double insertion product, $[Os(P^iPr_3)_2(CO)(C{\equiv}CCO_2Me)\text{-}\{CH{=}C(H)C(OMe){=}O\}]^*$, results if $R = CO_2Me$.[205] Treatment of $[Os(P^iPr_3)_2(CO)(C{\equiv}CPh)(\eta^2\text{-}H_2)H]$ with an extra equivalent of phenylethyne affords the bis-alkynyl compound $[Os(P^iPr_3)_2(CO)(C{\equiv}CPh)_2]$. Addition of water to this species in refluxing ^{i}PrOH cleaves one of the $C{\equiv}C$ bonds to give $[Os(P^iPr_3)_2(CO)_2(CH_2Ph)(C{\equiv}CPh)]$ **97**. Labeling experiments with $H_2{}^{18}O$ give $[Os(P^iPr_3)_2(C^{18}O)(CO)(CH_2Ph)(C{\equiv}CPh)]$ and with H_2O/d_8-isopropanol affords $[Os(P^iPr_3)_2(CO)_2(CD_2Ph)(C{\equiv}CPh)]$, implying a pathway involving Os-promoted, solvent-catalyzed hydration–disproportionation of the transformed alkynyl ligand. $[Os(P^iPr_3)_2(CO)_2(CH_2Ph)(C{\equiv}CPh)]$ isomerizes in MeOH in the presence of CF_3CO_2H to yield the osma-indene complex, $[Os(P^iPr_3)_2(CO)_2\{C(CH_2Ph){=}CHC_6H_4\}]^*$ **98**. When the reaction is repeated using CF_3CO_2D in CD_3OD, $[Os(P^iPr_3)_2(CO)_2\{C(CH_2Ph){=}CHC_6H_4\}]$ and $[Os(P^iPr_3)_2(CO)_2\{C(CH_2Ph){=}CDC_6H_4\}]$ are formed (ratio 2.5 : 1). The position of the deuterium on the alkenyl C_β atom is consistent with electrophilic attack of H^+ at alkynyl C_β and migratory insertion of the resultant vinylidene ligand in the Os–benzyl linkage.[235]



i, 1-cycylohexylethyne; ii, trimethylsilylethyne; iii, CO

Scheme 12



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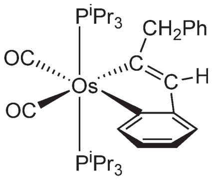

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Reaction of $[Ru(L–L)_2Cl_2]$ or $[Ru(L–L)_2H_2]$ with terminal alkynes in MeOH solution affords the bis-alkynyl compounds *trans*-$[Ru(L–L)_2(C{\equiv}CR)_2]$ (L–L = dmpe*, depe; R = ^{t}Bu, Ph*, *p*-$HC{\equiv}CC_6H_4$, *p*-$MeOC_6H_4$, 3,5-$(F_3C)_2C_6H_3$).[236] Upon addition of 2 equiv. of $PhC{\equiv}CH$ to $[Ru(PMe_3)_4(NH_3)H](PF_6)$ at RT, styrene is liberated and $[Ru(PMe_3)_4(NH_3)(C{\equiv}CPh)](PF_6)$ is formed. In contrast, reactions of the neutral dihydride *cis*-$[Ru(PMe_3)_4H_2]$ with $RC{\equiv}CH$ (R = Ph, $SiMe_3$, CO_2Me) require heating to yield *trans*-$[Ru(PMe_3)_4(C{\equiv}CR)_2]$.[237]

The alkyl amido complex $[Ru(PMe_3)_2\{HB(pz)_3\}(NH^tBu)]$ reacts immediately with $PhC{\equiv}CH$ at RT to give the ion pair $[Ru(PMe_3)_2\{HB(pz)_3\}(NH_2^tBu)](C{\equiv}CPh)$, which converts into $[Ru(PMe_3)_2\{HB(pz)_3\}(C{\equiv}CPh)]$ upon heating. No evidence for analogous acid/base chemistry is observed for $[RuL_2\{HB(pz)_3\}(NHPh)]$ (L = PMe_3, $P(OMe)_3$), which react directly with excess $PhC{\equiv}CH$ at elevated temperature to yield $[RuL_2\{HB(pz)_3\}(C{\equiv}CPh)]$. These and the related compound $[Ru(PPh_3)(CO)\{HB(pz)_3\}(C{\equiv}CPh)]$ may also be formed by reaction of $[RuL_2\{HB(pz)_3\}X]$ (X = OTf, Cl) with $LiC{\equiv}CPh$.[238]

6.12.5.2 Formation by Metathesis or Base Abstraction

A mixture of *cis*-$[Ru(dppe)_2Cl_2]/3NaPF_6/6Et_3N$ reacts with $RC{\equiv}CH$ to form the bis-alkynyl species *trans*-$[Ru(dppe)_2(C{\equiv}CR)_2]$; addition of 2 equiv. of NH_4PF_6 gives the cationic ammonia species, *trans*-$[Ru(dppe)_2(C{\equiv}CR)(NH_3)](PF_6)$ (R = Ph*, ^{t}Bu, $SiMe_3$),[239,240] which act as useful precursors for a range of alkynyl complexes such as *trans*-$[Ru(dppe)_2(C{\equiv}CR)H]$, *trans*-$[Ru(dppe)_2(C{\equiv}CR)(L)](PF_6)$ (L = CO, $CNCH_2Ph$, CNCy, CN^{t}Bu), *trans*-$[Ru(dppe)_2(C{\equiv}CR)(C{\equiv}CR^1)]$ (R^1 = ^{n}Bu, Ph, *p*-$NO_2C_6H_4$), and *trans*-$[Ru(dppe)_2(C{\equiv}CCH_2OMe)_2]$.[241] Treatment of *cis*-$[Ru(dppe)_2Cl_2]$ with $HC{\equiv}CC_6H_4C{\equiv}CSi^iPr_3$ in the presence of $NaPF_6/NEt_3$ produces *trans*-$[Ru(dppe)_2(C{\equiv}CC_6H_4C{\equiv}CSi^iPr_3)Cl]$. Subsequent reaction with $[Bu_4N]F$ results in desilylation to yield *trans*-$[Ru(dppe)_2(C{\equiv}CC_6H_4C{\equiv}CH)Cl]$, whereas reaction with $HC{\equiv}CC_6H_4C{\equiv}CH/NaPF_6$ followed by treatment with NEt_3 generated the homobimetallic system $[ClRu(dppe)_2(C{\equiv}CC_6H_4C{\equiv}C)Ru(dppe)_2Cl]$.[242] A system containing 12 carbon atoms between two $[Ru(dppe)_2]$ units can similarly be prepared.[243]

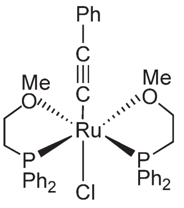
Addition of $RC{\equiv}CH$ to $[M\{S(2,6\text{-}Me_2C_6H_3)\}_3(MeCN)Cl]$ in the presence of Et_3N yields $[Et_3NH][M\{S(2,6\text{-}Me_2C_6H_3)\}_3(C{\equiv}CR)Cl]$ (M = Ru, R = Ph, 4-$MeC_6H_4^*$; M = Os, R = Ph).[244] Treatment of $[Ru(tpy)(bpy)(OH_2)]^{2+}$ with $RC{\equiv}CH$ in the presence of Et_3N gives $[Ru(tpy)(bpy)(C{\equiv}CR)]^+$ (R = *p*-FC_6H_4, *p*-ClC_6H_4, Ph, *p*-tolyl*, *p*-$MeOC_6H_4^*$, ^{t}Bu, $Ph(p\text{-}C_6H_4C{\equiv}C)_n$ (n = 1, 2)). For a small number of these complexes, protonation in MeOH gives the methoxycarbene complexes $[Ru(tpy)(bpy)\{{=}C(OMe)CH_2R\}]^{2+}$ (R = *p*-$MeOC_6H_4^*$, ^{t}Bu).[245]

Addition of 1 equiv. of the alkynyldithiocarboxylates $[RC{\equiv}CCS_2]^-$ to $[Ru(PPh_3)_3(CO)(CPh{=}CHPh)Cl]$ produces $[Ru(PPh_3)_2(CO)(CPh{=}CHPh)(S_2CC{\equiv}CR)]$ (R = Mes, Ph*, ^{t}Bu) as the major products along with smaller amounts of the alkynyl complexes $[Ru(PPh_3)_2(CO)(C{\equiv}CPh)(S_2CC{\equiv}CR)]$ (R = Mes*, Ph).[246]

The unsymmetrical bis-alkynyl species $[M(dppm)_2(C{\equiv}CR)(C{\equiv}CR^1)]$ (M = Ru, R = 4-$NO_2C_6H_4$, R^1 = Ph, *p*-tolyl, 4-$NO_2C_6H_4$; M = Ru, R = Ph, R^1 = *p*-tolyl; M = Os, R = 4-$NO_2C_6H_4$, R^1 = Ph, *p*-tolyl*; M = Os, R = Ph, R^1 = *p*-tolyl) form upon addition of $Me_3SnC{\equiv}CR^1$ to *trans*-$[M(dppm)_2(C{\equiv}CR)Cl]$.[247] Addition of methyl triflate and then $LiC{\equiv}CR$ (R = Ph, 4-MeC_6H_4) to $[Ru\{PPh(OEt)_2\}_4H_2]$ yields *trans*-$[Ru\{PPh(OEt)_2\}_4(C{\equiv}CR)H]$.[248] Similarly, $[RuL_4(C{\equiv}CR)Cl]$ complexes (L = $P(OEt)_3$, $P(OMe)_3$; R = Ph, 4-MeC_6H_4, 1,4-$C_6H_4C{\equiv}CH$, $SiMe_3$, ^{t}Bu, CO_2Me) can be prepared by the reaction of $[RuL_4Cl_2]$ with $RC{\equiv}CH$ in the presence of an excess of NEt_3. Treatment of the dichloride precursors with $LiC{\equiv}CR$ afforded the bis(alkynyl) complexes, *trans*-$[RuL_4(C{\equiv}CR)_2]$ (L = $P(OEt)_3^*$, $P(OMe)_3$, $PPh(OEt)_2$; R = 1,4-$HC{\equiv}CC_6H_4$, *p*-tolyl, Ph*, ^{t}Bu).[249,250] Alkynylation of the pentamethyl [60]fullerene complex $[(\eta^5\text{-}C_{60}Me_5)Ru(CO)_2Cl]$ with $MC{\equiv}CR$ (M = Li, MgX) generates $[(\eta^5\text{-}C_{60}Me_5)Ru(CO)_2(C{\equiv}CR)]$ (R = H, Ph*, ^{n}Bu, $SiMe_3$).[33]

The hemilabile P,O complex $[Ru\{\kappa^2\text{-}(P,O)\text{-}Ph_2PCH_2CHOMe\}\{\kappa^1\text{-}(P)\text{-}Ph_2PCH_2CHOMe\}_2HCl]$ reacts with $PhC{\equiv}CH$ to give the alkynyl complex **99**, which readily incorporates CO to afford **100**. The related complex $[Ru\{\kappa^1\text{-}(P)\text{-}Ph_2PCH_2CHOMe\}_2(CO)(C{\equiv}CPh)(\kappa^2\text{-}S_2CH)]$ is formed upon reaction of $[Ru\{\kappa^1\text{-}(P)\text{-}Ph_2PCH_2CHOMe\}_2(CO)(\kappa^2\text{-}S_2CH)Cl]$ with $PhC{\equiv}CH$ in the presence of $AgBF_4$.[251] The bis-alkynyl species

$[Ru(PPh_3)_2(X_2bipy)(C{\equiv}C\text{-}p\text{-}NO_2C_6H_4)_2]$ ($X_2bipy = 4,4'\text{-}X_2\text{-}2,2'$-bipyridyl; X = Me, Br*, I*) can be prepared by reacting an excess of alkyne with $[Ru(PPh_3)_2(X_2bipy)(C{\equiv}C\text{-}p\text{-}NO_2C_6H_4)Cl]$ in the presence of $TlPF_6$. Attempts to incorporate two bulkier alkynyl groups through preparation of $[Ru(PPh_3)_2(Me_2bipy)(C{\equiv}C^tBu)_2]$ proved unsuccessful, yielding instead the cationic monoalkynyl dinitrogen complex $[Ru(PPh_3)_2(Me_2bipy)(C{\equiv}C^tBu)N_2](PF_6)$.[252]



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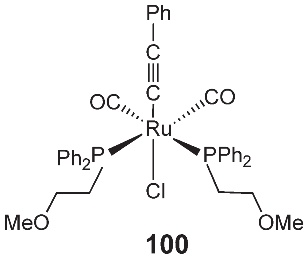

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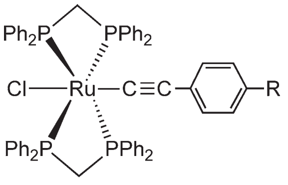
6.12.5.3 Via Vinylidene Precursors

Upon refluxing *trans*-$[M(P\text{–}P)_2Cl_2]$ with $Me_3SnC{\equiv}CPh$ or $Me_3SnC{\equiv}CRC{\equiv}CSnMe_3$ ($R = p\text{-}C_6H_2Me_2$) in the presence of CuI, *trans*-$[M(P\text{–}P)_2(C{\equiv}CPh)_2]$ (M = Ru, P–P = depe, dppm, dppe*; M = Os, P–P = dppm) and polymeric *trans*-$[Ru(P\text{–}P)_2(C{\equiv}CRC{\equiv}C)]_n$ (P–P = dppm, dppe) are formed.[253,254] The cationic vinylidene complexes *trans*-$[M(P\text{-}P)_2({=}C{=}CHR)Cl](PF_6)$ are readily deprotonated by alumina or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give *trans*-$[M(P\text{–}P)_2(C{\equiv}CR)Cl]$ (M = Ru, Os; P–P = dppm, dppe; R = Ph, $p\text{-}PhC_6H_4$, $p\text{-}NO_2C_6H_4$, $2\text{-}Me\text{-}4\text{-}NO_2C_6H_3$, *p*-tolyl). This same methodology can be applied to a wide range of alkyl-substituted vinylidene complexes *trans*-$[M(dppm)_2({=}C{=}CHR)Cl](PF_6)$ (M = Ru, Os; R = H*, Me, ^{n}Bu, ^{t}Bu, CH_2OH, CH_2OMe, CO_2Me, CH_2Cl) to generate the corresponding neutral alkynyl compounds.[247,253,255] The cationic vinylidene complexes $[Ru\{\kappa^2\text{-}(P,O)\text{-}{}^iPr_2PCH_2CH_2OMe\}_2({=}C{=}CHR)Cl](OTf)$ (R = Ph, *p*-tolyl, $m\text{-}HC{\equiv}CC_6H_4$) react with basic alumina to yield different isomers (*cis*-Cl, alkynyl and *trans*-Cl, alkynyl) of the alkynyl complex $[Ru\{\kappa^2\text{-}(P,O)\text{-}{}^iPr_2PCH_2CH_2OMe\}_2(C{\equiv}CR)Cl]$ (R = Ph), which undergo Ru–OMe cleavage in the presence of CO to yield *cis*- and *trans*-$(CO)_2$ isomers of $[Ru(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CH_2OMe)_2(CO)_2(C{\equiv}CPh)Cl]$.[256]

The unsymmetrical bis-alkynyl complexes *trans*-$[M(dppm)_2(C{\equiv}CR)\{C{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2\}]$ (R = Ph, ^{t}Bu) can be prepared by the reaction of *cis*-$[M(dppm)_2Cl_2]$ with the diyne $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ in the presence of base.[257] Similarly, treatment of the same dichloride precursor with $HC{\equiv}CSiPh_2C{\equiv}CH$ or $HC{\equiv}CSiMe_2OSiMe_2C{\equiv}CH$ in the presence of $NaPF_6$, followed by deprotonation, yields *trans*-$[M(dppm)_2(C{\equiv}CSiPh_2C{\equiv}CH)Cl]$ (M = Ru*, Os*) and *trans*-$[M(dppm)_2(C{\equiv}CSiMe_2OSiMe_2C{\equiv}CH)Cl]$ (M = Ru, Os).[258] The reaction of the five-coordinate monochloride $[Ru(dppe)_2Cl](OTf)$ with $HC{\equiv}C\text{–}X\text{–}CHO$ (X = thienyl-based spacer) initially affords the cationic complexes, *trans*-$[Ru(dppe)_2\{{=}C{=}C(\text{–}X\text{–}CHO)H\}Cl](OTf)$, which can be converted into the neutral alkynyl species *trans*-$[Ru(dppe)_2\{C{\equiv}C(\text{–}X\text{–}CHO)\}Cl]$ upon treatment with NEt_3.[259] The cationic vinylidene complexes *trans*-$[Ru(dppe)_2({=}C{=}CHR)Cl](PF_6)$ (R = Ph, ^{t}Bu, H)[239,240] provide useful precursors in giving: (i) the corresponding neutral alkynyl complexes *trans*-$[Ru(dppe)_2(C{\equiv}CR)Cl]$ in good yield upon stirring with K_2CO_3 and (ii) allowing access to the unsymmetrical bis-alkynyl complexes *trans*-$[Ru(dppe)_2(C{\equiv}CR)(C{\equiv}CR^1)]$ (R = Ph, $R^1 = {}^tBu$, $p\text{-}NO_2C_6H_4$; R = ^{n}Bu, $R^1 = p\text{-}NO_2C_6H_4$; $R = p\text{-}MeOC_6H_4$, $R^1 = p\text{-}NO_2C_6H_4$) upon treatment with an additional 1.5 equiv. of a second alkyne in the presence of $NaPF_6$ and NEt_3.[240] Addition of $HC{\equiv}CCPh_2(OH)$ to *trans*-$[Ru(dppe)_2({=}C{=}CHPh)Cl](PF_6)$ in the presence of NH_4PF_6/Et_3N produces the mixed alkynyl allenylidene complex *trans*-$[Ru(dppe)_2(C{\equiv}CPh)({=}C{=}C{=}CPh_2)](PF_6)$.[239] Reaction of $[Ru(PPh_3)_2(Me_2bipy)Cl_2]$ with terminal alkynes $HC{\equiv}CR$ in the presence of $TlPF_6$ affords $[Ru(PPh_3)_2(Me_2bipy)({=}C{=}CHR)Cl][PF_6]$, which afford the alkynyl species $[Ru(PPh_3)_2(Me_2bipy)(C{\equiv}CR)Cl]$ (R = ^{t}Bu*, $p\text{-}MeC_6H_4$, Ph) through chemical deprotonation by K_2CO_3 or electrochemical reductive dehydrogenation.[260]

6.12.5.4 Alkynyl Complexes for Non-Linear Optics (NLO) Applications

The use of metal alkynyl complexes, particularly with respect to the work by Humphreys and co-workers in non-linear optical (NLO) applications, will be covered elsewhere (see Chapter 6.09) and thus will be only briefly mentioned here with respect to the synthesis and types of alkynyl complexes reported.[261] Emphasis has been placed on incorporating variable donor/acceptor properties into complexes such as in *trans*-[Ru(dppm)$_2$(C$\equiv$C-*p*-RC$_6$H$_4$)Cl] (**101**, R = H, NO$_2$*, *p*-NO$_2$C$_6$H$_4$, (*E*)-CH$=$CH-*p*-NO$_2$C$_6$H$_4$), *trans*-[Ru(dppm)$_2$(C$\equiv$C-*p*-RC$_6$H$_4$)$_2$] (**102**, R = NO$_2$* *p*-NO$_2$C$_6$H$_4$*, (*E*)-CH$=$CH-*p*-NO$_2$C$_6$H$_4$), and *trans*-[Ru(dppm)$_2$(C$\equiv$C-*p*-NO$_2$C$_6$H$_4$)(C$\equiv$CPh)]*.[262–265] Elucidation of optical properties shows that the presence of strong acceptor substituents (e.g., R = NO$_2$) and lengthening of the unsaturated chain results in higher values of the quadratic hyperpolarizibility (β). Related diruthenium systems have been described.[266] Variations in the alkynyl substituents have been probed with synthesis of *trans*-[Ru(dppm)$_2$ (2-C$\equiv$C-5-RC$_5$H$_3$N)Cl] (R = H, NO$_2$*),[267] *trans*-[Ru(dppm)$_2${(*E*)-4,4′-C$\equiv$CC$_6$H$_4$N$=$NC$_6$H$_4$NO$_2$}Cl],[268] [Ru(dppm)$_2${C$\equiv$C-*p*-C$_6$H$_4$N$=$CCH$=$C^{t}BuC(O)C^{t}Bu$=$CH}Cl],[269] and *trans*-[Ru(dppm)$_2$(C$\equiv$CC$_6$H$_4$-*m*-CHO)Cl].[270] Similarly, variations of metal and phosphine have been probed with preparation of *trans*-[M{(*R*,*R*)-diph}$_2$(C$\equiv$C-*p*-RC$_6$H$_4$)Cl] (**103**, M = Ru, R = H, NO$_2$, (*E*)-CH$=$CH-*p*-NO$_2$C$_6$H$_4$; M = Os, R = NO$_2$; diph = MePhPC$_6$H$_4$PMePh),[271] *trans*-[Ru(L–L)$_2${(*E*)-*p*-C$\equiv$CC$_6$H$_4$CH$=$CHPh}Cl] (L–L = dppm, dppe)[272] and *trans*-[Ru(dppe)$_2$(X)(Y)] (X = Cl, Y = 4-C$\equiv$CC$_6$H$_4$I, 4-C$\equiv$CC$_6$H$_4$C$\equiv$CSiMe$_3$; X = C$\equiv$CPh, Y = 4-C$\equiv$CC$_6$H$_4$C$\equiv$CH).[273]



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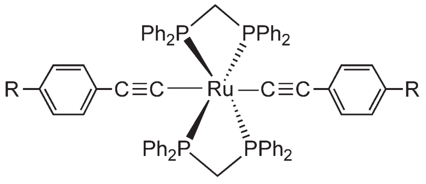

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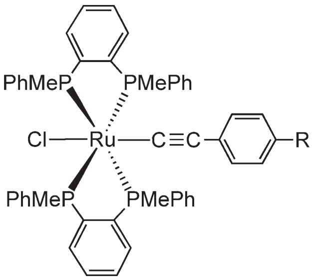
R = H
R = *p*-NO$_2$
R = *p*-NO$_2$C$_6$H$_4$
R = (*E*)-CH=CH-*p*-NO$_2$C$_6$H$_4$



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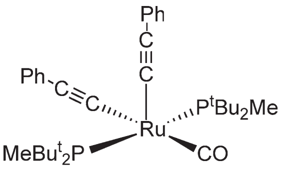
6.12.5.5 Reactions of Alkynyl Complexes

Protonation of the monoalkynyl complexes [RuL$_4$(C$\equiv$CR)Cl] with triflic acid yields the vinylidene derivatives [RuL$_4${$=$C$=$C(H)R}Cl](OTf) (L = P(OEt)$_3$, P(OMe)$_3$; R = Ph, *p*-tolyl, *p*-C$_6$H$_4$C$\equiv$CH).[249,250] The bis-alkynyl species *trans*-[RuL$_4$(C$\equiv$CR)$_2$] react with HBF$_4$·OEt$_2$ or MeOTf to produce the vinylidene alkynyl complexes [RuL$_4$($=$C$=$CRR^1)(C$\equiv$CR)](X) (L = P(OEt)$_3$*, P(OMe)$_3$; R = *p*-tolyl, Ph*, ^{t}Bu; R^1 = Me*, H; X = BF$_4$, OTf*), which in the case of R^1 = H, rearrange readily is solution to the known enynyl species [RuL$_4$(η^3-RC$_3$CHR)]$^+$ via a five-coordinate intermediate formed upon loss of vinylidene. The electrophiles [ArN$_2$]$^+$ (Ar = Ph, *p*-tolyl), I$_2$, and R^{1}SCl also react with *trans*-[RuL$_4$(C$\equiv$CR)$_2$] to afford [RuL$_4$($=$C$=$CRR^1)(C$\equiv$CR)](X) (L = P(OMe)$_3$, P(OEt)$_3$; R = Ph; R^1 = N$_2$Ar, I, S{2,4-(NO$_2$)$_2$C$_6$H$_4$}).[250] Knoevenagel condensation of *trans*-[Ru(dppe)$_2$(C$\equiv$C-4-CHOC$_6$H$_4$)Cl] with barbituric acid gave the blue complex **104**. Successive protonation–deprotonation allow facile switching between **104**, **105** and the vinylidene derivatives **106** and **107** (Scheme 13).[274]

Two-electron oxidation of [Ru(P^{t}Bu$_2$Me)$_2$(CO)(C$\equiv$CPh)$_2$] **108** and [Ru(P^{t}Bu$_2$Me)$_2$(CO)(CH$=$CHPh)(C$\equiv$CPh)] **109** (E°(V) (vs. [Cp$_2$Fe]/[Cp$_2$Fe]$^+$) = 0.28 (MeCN), 0.20 (CH$_2$Cl$_2$); 0.10 (MeCN), 0.15 (CH$_2$Cl$_2$)) results in the reductive elimination of PhC$\equiv$CC$\equiv$CPh and PhC$\equiv$CCH$=$CHPh, respectively, to give [Ru(P^{t}Bu$_2$Me)$_2$-(CO)(NCMe)$_3$](BF$_4$)$_2$ as the main ruthenium product in MeCN and a solvent-/anion-stabilized [Ru(P^{t}Bu$_2$Me)$_2$(CO)]$^{n+}$ (n = 1, 2) fragment in CH$_2$Cl$_2$. Kinetic and thermodynamic data in both solvents have been determined.[275]



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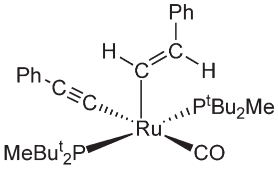

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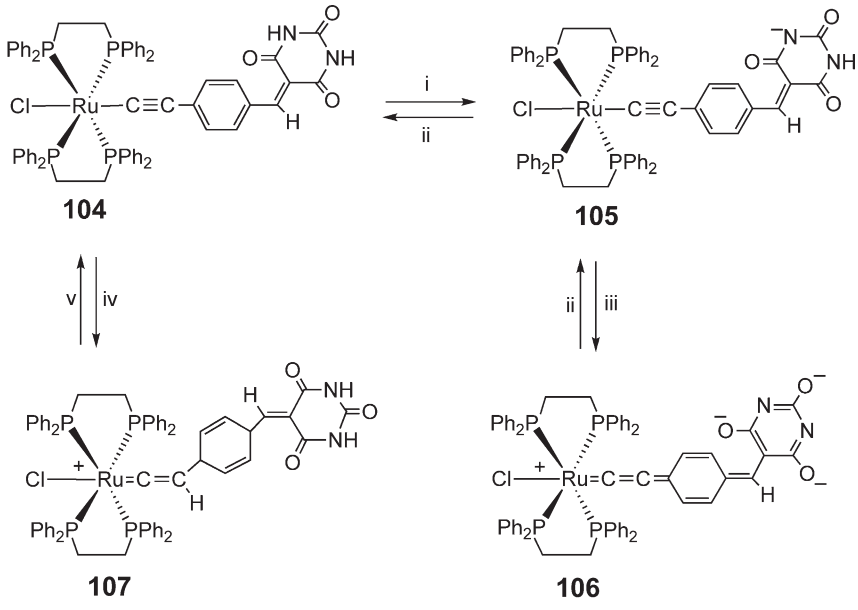


i, $N(^iPr)_2Et$; ii, $MeCO_2H$; iii, DBU; iv, CF_3CO_2H; v, K_2CO_3

Scheme 13

6.12.6 Vinylidene Complexes

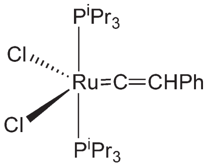
A series of general headings can be applied to the synthetic routes used for generating vinylidene complexes: (i) reactions of alkynes with labile and/or coordinatively unsaturated species, (ii) reactions with alkynes in the presence of a halide abstracting agent, (iii) formation from alkynyl complexes, and (iv) formation from carbyne complexes.

6.12.6.1 From Coordinatively Unsaturated or Labile Precursors

Vinylidene complexes of varying stability result from the reactions of HC≡CR with $[RuL_2(acac)_2]$ ($L = Sb^iPr_3$, P^iPr_3). Thus, $[Ru(Sb^iPr_3)_2(acac)_2({=}C{=}CPh_2)]$ decomposes upon attempted fractional crystallization or column chromatography, whereas $[Ru(P^iPr_3)_2(acac)_2({=}C{=}CRPh)]$ (R = Ph, $SiMe_3$) are almost air stable. The related precursor $[Ru(PCy_3)_2(O_2CMe)_2]$ reacts with HC≡CR to afford $[Ru(PCy_3)_2(\eta^2\text{-}O_2CMe)(\eta^1\text{-}O_2CMe)({=}C{=}CHR)]$ (R = Ph, CO_2Me).[276] In contrast to the oxidative addition seen with $[Ru(P^tBu_2Me)_2(CO)H_2]$,[229] the nitrosyl species $[RuL_2(NO)(OTf)]$ react with $Me_3SiC{\equiv}CSiMe_3$ in the presence of $NaBAr^F{}_4$ in C_6H_5F to afford the four-coordinate vinylidene complexes $[RuL_2\{{=}C{=}C(SiMe_3)_2\}(NO)](BAr^F{}_4)$ ($L = P^tBu_2Me$, P^iPr_3). DFT calculations suggest that this change in reactivity results from the three-coordinate nitrosyl intermediate $[RuL_2(NO)]^+$ being more π-basic, and thus reducing, than electron deficient.[32] The vinylidene complexes $[Ru(P^tBu_2Me)_2({=}C{=}CHR)HX]$ (X = Cl, I), along with free alkene $RCH{=}CH_2$, are rapidly formed upon mixing the terminal alkynes RC≡CH (R = Ph, $SiMe_3$) with $[Ru(P^tBu_2Me)_2H_3X]$ in a 2 : 1 stoichiometry. The use of PhC≡CD gives $[Ru(P^tBu_2Me)_2({=}C{=}CHPh)DI]$ and PhCH=CHD suggesting that addition of Ru–H across the C≡C alkyne bond occurs en route to the final product. This pathway is also supported by DFT calculations.[277,278] No H/D exchange into the vinylidene ligand of $[Ru(P^tBu_2Me)_2({=}C{=}CHPh)DX]$ (X = Cl, I) occurs over 24 h at RT, indicating that the (unobserved) isomeric carbyne complexes $[Ru(P^tBu_2Me)_2({\equiv}CCHDPh)X]$ are not readily accessible under these conditions. DFT calculations with model complexes support this, showing that while the isomers $[M(PH_3)_2({=}C{=}CH_2)HCl]$ (M = Ru, Os) and $[M(PH_3)_2({\equiv}CMe)Cl]$ are close in energy (−4.5 (Ru), 10.3 (Os) kJ mol^{-1}), the energies needed to reach the transition states for the 1,3-migration needed to interconvert them are inaccessible at RT (187.5 (Ru), 223.3 (Os) kJ mol^{-1}). Rotation of 180° about the C–C axis in $[M(PH_3)_2({=}C{=}CH_2)HCl]$ is calculated to have a low barrier (33.4 (Os), 17.7 (Ru) kJ mol^{-1}) accounting for the isomers observed for $[Os(P^iPr_3)_2({=}C{=}CHPh)HCl]$.[223,279]

Treatment of $[Os(P^tBu_2Me)_2(CO)(NO)](BAr^F{}_4)$ with $Me_3SiC{\equiv}CSiMe_3$ gives $[Os(P^tBu_2Me)_2(CO)(NO)\text{-}\{{=}C{=}C(SiMe_3)_2\}](BAr^F{}_4)$, which can be doubly hydrolyzed to give $[Os(P^tBu_2Me)_2(CO)(NO)({=}C{=}CH_2)](BAr^F{}_4)$.

Addition of $HC\equiv CH$ to $[Os(P^tBu_2Me)_2(CO)(NO)](BAr^F{}_4)$ gives the stable alkyne complex $[Os(P^tBu_2Me)_2(CO)(NO)(\eta^2\text{-}HC\equiv CH)](BAr^F{}_4)$, which does not isomerize to $[Os(P^tBu_2Me)_2(CO)(NO)(=C=CH_2)](BAr^F{}_4)$ even upon heating to 60 °C.[230] The low temperature reaction of $[Ru\{N(^tBu_2PCH_2SiMe_2)_2\}Cl_2]$ with $RC\equiv CH$ affords $[Ru\{NCCHR(^tBu_2PCH_2SiMe_2)_2\}Cl]$ ($R = H, Ph^*$) as a result of alkyne insertion into the Ru–N bond.[280] Treatment of $[Ru(PPh_3)_3X_2]$ with an excess of $^tBuC\equiv CH$ at RT affords vinylidene products. Initially, two kinetic products are seen with inequivalent *cis*-phosphines, the thermodynamic products $[Ru(PPh_3)_2(=C=CH^tBu)X_2]$ ($X = Cl, Br^*$) displaying a *trans*-arrangement of phosphine ligands.[281] The ruthenium(IV) dihydride complex $[Ru(P^iPr_3)_2H_2Cl_2]$ reacts with $PhC\equiv CH$ at RT to give a mixture of the five-coordinate species $[Ru(P^iPr_3)_2(=C=CHPh)Cl_2]$ 110 and $[Ru(P^iPr_3)_2(=CHCH_2Ph)Cl_2]$ in a ratio of ca. 10 : 1. Reaction with $HC\equiv CH$ yields just the methylcarbene complex $[Ru(P^iPr_3)_2(=CHMe)Cl_2]$.[282] Phosphine substitution in $[RuL_2(=C=CHR)Cl_2]$ ($L = PCy_3$, $R = {}^tBu$; $L = P^iPr_3$, $R = Ph$) by $Cy_2P(CH_2)_4PCy_2$ (dcypb) yields $[Ru(dcypb)(=C=CHR)Cl_2]$.[283]



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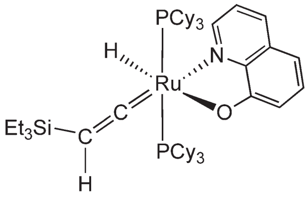
Addition of $HC\equiv CCy$ to $[Os(P^iPr_3)_2(CO)HCl]$ affords $[Os(P^iPr_3)_2(CO)(=C=CHCy)HCl]$, which converts over days in solution at RT into the alkenyl complex $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH=CHCy\}Cl]$. Subsequent treatment with HCl gives the vinylidene dichloride complex $[Os(P^iPr_3)_2(CO)(=C=CHCy)Cl_2]$.[284] In the presence of $HC\equiv CPh$, $[Os(P^iPr_3)_2(\eta^2\text{-}O_2CMe)H_3]$ is converted into $[Os(P^iPr_3)_2(=C=CHPh)(\eta^2\text{-}O_2CMe)H]$, which is a precursor for the catalytic dimerization of $HC\equiv CPh$.[285] Irradiation of $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)_2Cl_2]$ in the presence of $HC\equiv CR$ affords the vinylidene complexes $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}{}^iPr_2PCH_2\text{-}CO_2Me)(=C=CHR)Cl_2]$ ($R = H$, Me, ^tBu, Ph). Related products can be formed upon photolysis of $HC\equiv CPh$ in the presence of the bromo or iodo precursors, or with $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Et)_2Cl_2]$. Interestingly, the mixed phosphine complex $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)(PPh_3)Cl_2]$ reacts with $HC\equiv CPh$ at RT to give $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)(PPh_3)(=C=CHPh)Cl_2]$. Access to vinylidenes under thermal conditions also occurs upon treatment of $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)_2Cl_2]$ with $HC\equiv C(CH_2)_2OH$ or $HC\equiv CC_6H_4C\equiv CH$ to give $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)(=C=C(CH_2)_3O)Cl_2]$ and $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)(=C=CH\{C_6H_4\text{-}4\text{-}C\equiv CH\})Cl_2]$, respectively.[286] The cationic vinylidene complexes $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CH_2OMe)_2(=C=CHR)Cl](OTf)$ ($R = Ph$, *p*-tolyl, *m*-$HC\equiv CC_6H_4$) are prepared in yields of 70–80% by reaction of the dichloride precursor with alkyne and silver triflate.[256]

A range of precursors such as $[Ru(P^iPr_3)_2(\eta^2\text{-}H_2)HCl]$, $\{Ru(P^iPr_3)_2Cl_2\}_n$ or $[Ru(p\text{-}cymene)Cl_2]_2/P^iPr_3$ react with $RC\equiv CH$ to afford $[Ru(P^iPr_3)_2(=C=CHR)Cl_2]$ ($R{=}H$, Ph^*, ^tBu, $4\text{-}MeO_2CC_6H_4$, $4\text{-}MeOC_6H_4$, ferrocenyl).[287–289] Analogous tricyclohexylphosphine complexes $[Ru(PCy_3)_2(=C=CHR)Cl_2]$ ($R = Ph^*$, ^tBu, ferrocenyl, H, $CH=CH_2$) result from reaction of the appropriate alkyne with either $[Ru(PCy_3)_2H_2Cl_2]$ or $[Ru(p\text{-}cymene)Cl_2]_2/PCy_3$[287,288] or reaction of 1,3-butadiene or 1,2-propadiene with $[Ru(PCy_3)_2(=CHPh)Cl_2]$.[290] Addition of $HC\equiv CR$ ($R = H$, Ph) to $[Ru(PCy_3)_2\{Sb(CH_2Ph)_3\}HCl]$ affords the hydrido(vinylidene) complexes $[Ru(PCy_3)_2(=C=CHR)HCl]$.[194] Addition of 2 equiv. of either $HC\equiv C^tBu$ or $HC\equiv CPr$ to $[Os\{1,3\text{-}(CH_2P^tBu_2)_2C_6H_3\}H_2Cl]$ yields the vinylidene complexes $[Ru\{1,3\text{-}(CH_2P^tBu_2)_2C_6H_3\}(=C=CHR)Cl]$ ($R = {}^tBu^*$, Pr^*).[291]

A number of complexes bearing labile η^2-dihydrogen ligands have been used as precursors. The reaction of the trioctylphosphine $[P(Coc)_3]$ complex $[Ru(PCoc_3)_2(\eta^2\text{-}H_2)HCl]$ with $HC\equiv CH$ at low temperature gives $[Ru(PCoc_3)_2(=C=CH_2)HCl]$.[292] The bulky monodentate phosphine system $[Ru(^tBu_2PCH_2CH_2Ph)_2(\eta^2\text{-}H_2)HCl]$ reacts with ethyne at low temperature to give $[Ru(^tBu_2PCH_2CH_2Ph)_2(=C=CH_2)HCl]$; low temperature addition of $HBF_4{\cdot}OEt_2$ converts this into the carbyne complex $[Ru(^tBu_2PCH_2CH_2Ph)_2(\equiv CMe)(OEt_2)HCl](BF_4)$.[293] The dihydrogen hydride complexes $[Ru(PCy_3)_2(NC_5H_4X)(\eta^2\text{-}H_2)H]$ ($X = O$, NH) and $[Ru(PCy_3)_2(NC_9H_6O)(\eta^2\text{-}H_2)H]$ react with an excess of $CH_2=CHSiEt_3$ to give the vinylidene complexes $[Ru(PCy_3)_2(NC_5H_4\text{-}X)(=C=C(H)SiEt_3)H]$ and $[Ru(PCy_3)_2(NC_9H_6O)(=C=CHSiEt_3)H]$ 111, respectively.[294]



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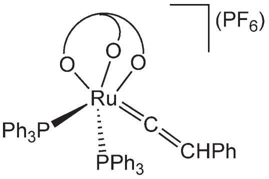
The reaction of $[Ru(PPh_3)_3Cl_2]$ with $PhC{\equiv}CSe^iPr$ provides the selenolatovinylidene complex $[Ru(PPh_3)_2\{{=}C{=}C(Se^iPr)Ph\}Cl_2]^*$, which eliminates the free alkyne upon addition of CO or CN(2,6-$Me_2C_6H_3$).[295] The hetero-allenylidene species *trans*-$[Ru(dppm)_2\{{=}C{=}C{=}C(SeFc)C_2H_4CH{=}CH_2\}Cl](SbF_6)$ may be formed by trapping *trans*-$[Ru(dppm)_2({=}C{=}C{=}C{=}CH_2)Cl]$ (SbF_6) with allylferrocenyl selenide.[296]

Both $HC{\equiv}CPh$ and $HC{\equiv}C$-*p*-tolyl react with $[Ru(Me_3tacn)(PMe_3)_2(\kappa^1\text{-}O_2CCF_3)](PF_6)$ in refluxing 1,2-dichloroethane to give the vinylidene complexes $[Ru(Me_3tacn)(PMe_3)({=}C{=}CHR)(\eta^1\text{-}O_2CCF_3)](PF_6)$. The role of phosphine dissociation in these reactions is indicated by the inertness of $[Ru(Me_3tacn)(dmpe)(\kappa^1\text{-}O_2CCF_3)](PF_6)$ to the same two alkynes. Addition of methanolic KOH to the vinylidene species in the presence of PMe_3 or $P(OMe)_3$ yields $[Ru(Me_3tacn)(PMe_3)(L)(C{\equiv}CR)](PF_6)$ ($L = PMe_3$, $P(OMe)_3{}^*$, $R = Ph^*$; $L = PMe_3$, $R = 4\text{-}MeC_6H_4$).[297] The dinuclear bridging dinitrogen complex $[\{Ru(\eta^3\text{-}NN^1N)Cl_2\}_2(\mu\text{-}N_2)]$ (NN^1N = 2,6-bis-{(dimethyamino)methyl}pyridine) reacts with $HC{\equiv}CPh$ to afford *mer,cis*-$[Ru(\eta^3\text{-}NN^1N)({=}C{=}CHPh)Cl_2]^*$; the cationic analogs $[Ru(\eta^3\text{-}NN^1N)(PPh_3)({=}C{=}CHPh)X](Y)$ ($X = Cl$, $Y = BF_4$; $X = OTf$, $Y = OTf^*$) result from addition of the alkyne to $[Ru(\eta^3\text{-}NN^1N)(PPh_3)Cl_2]$ in the presence of the appropriate silver salt.[298]

Chloride abstraction from $[Ru\{HB(pz)_3\}(tmen)Cl]$ ($tmen = Me_2NCH_2CH_2NMe_2$) with $NaBPh_4$ affords the cationic solvento species $[Ru\{HB(pz)_3\}(tmen)(solvent)](BPh_4)$ (solvent = acetone, dmf), which react with $PhC{\equiv}CH$ to form $[Ru\{HB(pz)_3\}(tmen)({=}C{=}CHPh)](BPh_4)^*$.[299] Interestingly, $[Ru\{HB(pz)_3\}(PCy_3)(OCH_2R)Cl]$ (R = H, Me) react with $HC{\equiv}CR^1$ ($R^1 = {}^nBu$, Ph, $SiMe_3$, CO_2Et) to yield the vinylidene complexes $[Ru\{HB(pz)_3\}(PCy_3)({=}C{=}CHR^1)Cl]$.[300]

In the case of $[Ru\{HB(pz)_3\}(PPh_3)_2Cl]$, rapid reaction with $RC{\equiv}CH$ gives $[Ru\{HB(pz)_3\}(PPh_3)({=}C{=}CHR)Cl]$ ($R = p\text{-}MeC_6H_4$, Ph^*).[301,302] The latter species is proposed to be the catalytic precursor for alkyne dimerization to enynes, which is found when $[Ru\{HB(pz)_3\}(PPh_3)_2Cl]$ reacts with an excess of alkyne in refluxing toluene.[302] Treatment of $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)Cl]$ with $HC{\equiv}CR$ in refluxing MeOH affords the cationic vinylidene complexes $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHR)]Cl$ ($R = Ph^*$, CH_2Ph, CO_2Et);[303] if the solvent is changed to toluene, phosphine/hydrocarbyl ligand coupling takes place to give $[Ru\{HB(pz)_3\}\{\kappa^3\text{-}(P,C,C)\text{-}Ph_2PCH{=}CHCR{=}CH_2\}]Cl$ ($R = Ph$, CH_2Ph, CO_2Et^*).[304] Neutral κ^1-*P,O* based vinylidene complexes result from reaction of $HC{\equiv}CR$ ($R = Ph$, ${}^nBu$, cyclohexenyl) with $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2OMe)Cl]$ and these can be used to afford κ^2-*P,O*-stabilized cationic vinylidene, neutral alkynyl and 1,4-enynyl complexes.[305] Terminal alkynes react with $[Ru(dippe)\{HB(pz)_3\}Cl]$ in the presence of $NaBPh_4$ to give the vinylidene complexes $[Ru(dippe)\{HB(pz)_3\}({=}C{=}CHR)](BPh_4)$ ($R = Ph$, CO_2Me). In the presence of MeOH, the carboxylate ester derivative reacts further to yield the methoxycarbene $[Ru(dippe)\{HB(pz)_3\}\{{=}C(OMe)CH_2CO_2Me\}](BPh_4)^*$. Both this and the vinylidene compounds are deprotonated by KO^tBu to afford $[Ru(dippe)\{HB(pz)_3\}(C{\equiv}CR)]$.[306]

Addition of $PhC{\equiv}CH/NH_4PF_6$ to $[Ru(L_{OEt})(PPh_3)_2Cl]$ ($L_{OEt} = (\eta^5\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$) produced $[Ru(L_{OEt})(PPh_3)_2({=}C{=}CHPh)](PF_6)^*$ **112**.[212] Addition of an excess of $HC{\equiv}CR$ to *cis*-$[M(dppm)_2Cl_2]$ (M = Ru, Os) in the presence of $NaPF_6$ affords *trans*-$[M(dppm)_2({=}C{=}CHR)Cl](PF_6)$, ($R = Ph$, $p\text{-}PhC_6H_4$, $4\text{-}NO_2C_6H_4$, $2\text{-}Me\text{-}4\text{-}NO_2C_6H_3$, *p*-tolyl).[255] The reaction of $[Ru(dcypb)Cl(\mu\text{-}Cl)_3Ru(dcpb)(N_2)]$ with $TlOC_6F_5$ and excess $HC{\equiv}C^tBu$ at RT affords the vinylidene complex $[Ru(dcypb)(OC_6F_5)_2({=}C{=}CH^tBu)]^*$ **113**.[307] The ferrocenylphosphine-based precursor $[Ru(dppf)\{HB(pz)_3\}Cl]$ reacts with $HC{\equiv}C$-*p*-tolyl/$AgPF_6$ to generate $[Ru(dppf)\{HB(pz)_3\}\text{-}\{{=}C{=}C(p\text{-}tolyl)H\}](PF_6)$.[301]



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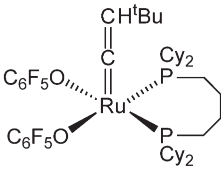

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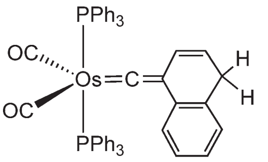
6.12.6.2 Interconversion of Vinylidenes and Carbynes

Addition of 1 equiv. of NaOMe to [Os(P^{i}Pr$_3$)$_2$(≡CCH$_2$Ph)HCl$_2$] yields [Os(P^{i}Pr$_3$)$_2$(=C=CHPh)HCl] (which exists as two conformers in solution); this acts as a precursor for the six-coordinate vinylidene hydride complexes [Os(P^{i}Pr$_3$)$_2$(=C=CHPh){P(OMe)$_3$}HCl], [Os(P^{i}Pr$_3$)$_2$(=C=CHPh)(acac)HCl], and [Os(P^{i}Pr$_3$)$_2$(=C=CHPh)(η^2-O$_2$CMe)H].[223] Similarly, the vinylidene hydride complex [Os(PCy$_3$)$_2$(=C=CHPh)HCl] is formed upon addition of NaOMe to [Os(PCy$_3$)$_2$(≡CCH$_2$Ph)HCl$_2$].[308] Treatment of the cationic species [Os(PPh$_3$)$_2$(CO)$_2$(≡CR)](ClO$_4$) with LiEt$_3$BH affords the neutral vinylidene species [Os(PPh$_3$)$_2$(CO)$_2$(=C=CR)] (R = 1-naphthyl **114**, 2-naphthyl **115***). Multinuclear NMR studies reveal that **114 and 115** are formed by attack at the *p*- and *o*-positions of the naphthyl ring, respectively, while addition of HCl to either species affords the naphthylmethyl complexes [Os(PPh$_3$)$_2$(CO)$_2$(CH$_2$R)Cl].[309]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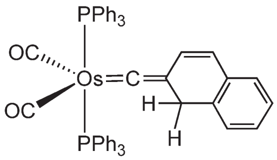
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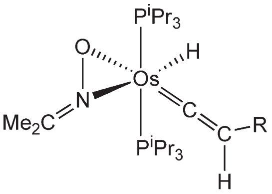
Deprotonation of [Os(P^{i}Pr$_3$)$_2$(≡CCH$_2^t$Bu)(κ^2-O$_2$CMe)H](BF$_4$) and [Os(P^{i}Pr$_3$)$_2$(≡CMe)(κ^2-O$_2$CMe)H](BF$_4$) by KOH affords [Os(P^{i}Pr$_3$)$_2$(=C=CH^{t}Bu)(κ^2-O$_2$CMe)H] and [Os(P^{i}Pr$_3$)$_2$(=C=CH$_2$)(κ^2-O$_2$CMe)H], respectively,[310] and the amphoteric carbyne complexes [Os(P^{i}Pr$_3$)$_2$(≡CCH$_2$R)(κ^2-*N,O*-ON=CMe$_2$)H](BF$_4$) (R = Ph*, Cy, ^{t}Bu) react with KOH to give [Os(P^{i}Pr$_3$)$_2$(=C=CHR)(κ^2-*N,O*-ON=CMe$_2$)H] (**116**, R = Ph*, Cy, ^{t}Bu).[165]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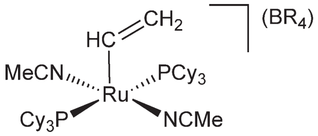
R = Ph, Cy, ^{t}Bu

6.12.6.3 Reactions of Vinylidenes

Direct protonation of the vinylidene complex [Os(PCy$_3$)$_2$(=C=CHPh)HCl] with HBF$_4$·OEt$_2$ produces [Os(PCy$_3$)$_2$(≡CCH$_2$Ph)HCl](BF$_4$).[308] The close analog [Os(P^{i}Pr$_3$)$_2$(=C=CHSiMe$_3$)HCl] reacts with Me$_3$Si-C≡CH to yield the alkenyl vinylidene complex [Os(P^{i}Pr$_3$)$_2$(=C=CHSiMe$_3$){(*E*)-CH=CHSiMe$_3$}Cl]*, which upon reaction with CO, undergoes migration of the alkenyl ligand onto the vinylidene α-carbon to yield Os(P^{i}Pr$_3$)$_2${C(CH=CHSiMe$_3$)=CHSiMe$_3$}(CO)$_2$Cl].[311] Addition of ^{n}BuLi to [Os(P^{i}Pr$_3$)$_2$(NH=CR$_2$)(=C=CH-Ph)Cl$_2$] affords the azavinylidene complexes [Os(P^{i}Pr$_3$)$_2$(=N=CR$_2$)(=C=CHPh)Cl$_2$] (CR$_2$ = CMe$_2^*$, C(CH$_2$)$_4$CH$_2$), which are also produced in equilibrium with the starting materials upon reaction of the imine vinylidenes with triethylamine and diallylamine. If these amines are replaced by allylamine or aniline, long reaction times afford [Os(P^{i}Pr$_3$)(NH=CR$_2$)(=C=CHPh)(NH$_2$R^1)Cl$_2$] (R^1 = allyl; CR$_2$ = CMe$_2^*$, C(CH$_2$)$_4$CH$_2$; R^1 = Ph; CR$_2$ = CMe$_2$, C(CH$_2$)$_4$CH$_2$).[312] Low temperature addition of NaCl to [Os(P^{i}Pr$_3$)$_2$(NH=CMe$_2$){(*E*)-CH=CHCy}Cl](OTf) results in hydrogen transfer to give [Os(P^{i}Pr$_3$)$_2$(NH=CMe$_2$)(=C=CHCy)Cl$_2$].[208]

In contrast to the simple substitution chemistry seen between dcypb and [RuL$_2$(=C=CHR)Cl$_2$] (L = PCy$_3$, R = ^{t}Bu; L = P^{i}Pr$_3$, R = Ph), [Ru(PCy$_3$)$_2$(=C=CH$_2$)HCl] reacts with an excess of dcypb by hydride to C$_\alpha$ migration giving the six-coordinate alkenyl complex *trans*-[Ru(dcypb)$_2$(CH=CH$_2$)Cl]. Protonation and addition of NH$_4$PF$_6$ yields the carbene complex *trans*-[Ru(dcypb)$_2$(=CHMe)Cl]PF$_6$. The carbene complex [Ru(PCy$_3$)$_2$(=CHPh)Cl$_2$]

undergoes phosphine substitution by P–P to give $[Ru(P{-}P)({=}CHPh)Cl_2]$ (P–P = dcypb, dppf*).[283] Deprotonation of $[Ru(PPh_3)_2\{HB(pz)_3\}({=}C{=}CPhCH_2CN)](I)$, resulting from addition of ICH_2CN to $[Ru(PPh_3)_2\{HB(pz)_3\}(C{\equiv}CPh)]$, affords the cyclopropenyl complex $[Ru(PPh_3)_2\{HB(pz)_3\}(C{=}CPhCHCN)]$, which can be ring opened by electrophiles to give $[Ru(PPh_3)_2\{HB(pz)_3\}\{{=}C{=}CPhCH(CN)HgCl\}](Cl)$ and $[Ru(PPh_3)_2\{HB(pz)_3\}\{{=}C{=}CPhCH(CN)\text{-}(CPh_3)\}](Cl)$.[228,313] Addition of an excess of KPF_6 to $[Ru(PCy_3)_2({=}C{=}CH_2)HCl]$ or $[Ru(PCy_3)_2({=}C{=}CHPh)HCl]$ in CH_2Cl_2/MeCN gives the alkenyl complexes $[Ru(PCy_3)_2(CH{=}CH_2)(MeCN)_2]X$ ($X = PF_6$) and $[Ru(PCy_3)_2(CH{=}CH_2)(MeCN)_3]X$ (X = Cl, PF_6), respectively. Anion exchange of the bis-acetonitrile species affords more reactive borate salts ($X = BPh_4$*, $BAr^F{}_4$ **117a**, BF_4 **117b**); in the case of **117a** and **117b**, protonation with $[H(OEt)_2](BAr^F{}_4)$ or HBF_4, respectively, affords the novel dicationic carbene complexes $[Ru(PCy_3)_2({=}CHMe)\text{-}(MeCN)_2]X_2$ **118a** and **118b**.[314] The diacetato complex $[Os(P^iPr_3)_2(\kappa^2\text{-}O_2CMe)\{\kappa^1\text{-}OC(O)Me\}H_2]$ reacts with $HC{\equiv}CCMe{=}CH_2$ to give the α,β-unsaturated vinylidene $[Os(P^iPr_3)_2({=}C{=}CHCMe{=}CH_2)(\kappa^2\text{-}O_2CMe)H]$, which, in the presence of CO, converts into the dienyl derivative $[Os(P^iPr_3)_2(CO)_2\{(Z)\text{-}CH{=}CHCMe{=}CH_2\}(\kappa^1\text{-}OC(O)Me)]$ via migratory insertion of the vinylidene group to the Os–H bond (the (*E*)-isomer can be prepared in two steps from $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHCMe{=}CH_2\}Cl])$.[315] The vinylidene complex $Na_2[Ru(TPPMS)_2({=}C{=}CHPh)Cl_2]$, which forms from treatment of the water-soluble dimer $Na_4[\{Ru(TPPMS)_2Cl\}_2(\mu\text{-}Cl)_2]$ with $HC{\equiv}CPh$ upon warming, reacts with CO to give $Na_2[Ru(TPPMS)_2(CO)Cl_2]$ via retro-tautomerization of vinylidene to free alkyne.[316]



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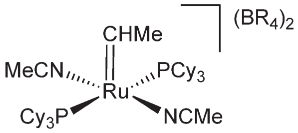
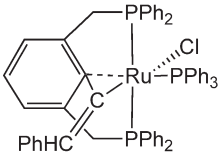
a: R = 3,5-$(CF_3)_2C_6H_3$
b: R = F



118

a: R = 3,5-$(CF_3)_2C_6H_3$
b: R = F

A number of examples of coupling reactions have been reported that involve either isolable or postulated vinylidene complexes. Addition of $PhC{\equiv}CH$ to the the pincer complex $[Ru(PCP)(PPh_3)Cl]$ generates the coupling product $[Ru(PPh_3)\{\eta^4\text{-}CHPh{=}C\text{-}2,6\text{-}(CH_2PPh_2)_2C_6H_3\}Cl]$* **119**,[109] presumably via the intermediate vinylidene $[Ru(PCP)(PPh_3)({=}C{=}CHPh)Cl]$. If alcohol-substituted alkynes are employed, dehydration of the resulting insertion products occurs; thus, for example, $HC{\equiv}CCPhMe(OH)$ affords $[Ru(PPh_3)\{\eta^4\text{-}CH_2{=}CPhCH{=}C\text{-}2,6\text{-}(CH_2PPh_2)_2C_6H_3\}Cl]$.[110] More complex reactivity occurs with the osmium analog; thus, a mixture of $[Os(PCP)(PPh_3)H]$ and $[Os(PCP)(PPh_3)H_3]$, reacts with $PhC{\equiv}CH$ to give $[Os(1\text{-}(CHPh{=}C)\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)(PPh_3)(C{\equiv}CPh)({=}C{=}CHPh)]$.[317] Addition of $Me_3SiC{\equiv}CH$ to $[Os(P^iPr_3)_2({=}C{=}CHSiMe_3)HCl]$ yields the alkenyl vinylidene complex $[Os(P^iPr_3)_2({=}C{=}CHSiMe_3)\ \{(E)\text{-}CH{=}CHSiMe_3\}Cl]$*, which upon reaction with CO, undergoes migration of the alkenyl ligand onto the vinylidene α-carbon to yield $[Os(P^iPr_3)_2(CO)_2\{C(CH{=}CHSiMe_3){=}CHSiMe_3\}Cl]$ **120**. In contrast, $[Ru(P^tBu_2Me)_2(CO)H](BAr^F{}_4)$ reacts with two molecules of alkyne affording the C–C coupled product $[Ru(P^tBu_2Me)_2(CO)_2\{\eta^3\text{-}(Me_3Si)CH{=}CCH{=}CH(SiMe_3)\}]\text{-}(BAr^F{}_4)$*.[311]



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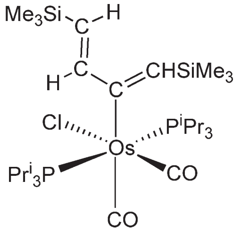

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Treatment of *mer,trans*-$[(PNP)Ru(PPh_3)Cl_2]$ with $HC{\equiv}CR$ (R = Ph, *p*-tolyl) affords the vinylidene complexes *fac,cis*-$[(PNP)Ru\{{=}C{=}CH(R)\}Cl_2]$ in refluxing THF, but the alternative *cis,mer*-isomer in refluxing THF/EtOH. Subsequent addition of $LiC{\equiv}CPh$ converts the *fac,cis*-species into the alkynyl enynyl complex *anti,mer*-$[(PNP)Ru(C{\equiv}CPh)(\eta^3\text{-}PhC_3{=}CHR)]$ ($R = Ph^*$, *p*-tolyl) and the *cis,mer*-species to the alkynyl dienynyl *mer*-$[(PNP)Ru(C{\equiv}CPh)\{\eta\text{-}PhC{=}C(C{\equiv}CPh)CH{=}CH(R)\}]$ ($R = Ph$, *p*-tolyl*).[318] The reaction of *mer,trans*-$[(PNP)Ru(PPh_3)Cl_2]$ with $PhC{\equiv}CH/H_2O$ in THF solution at 60 °C in a closed system yields *fac,cis*-$[(PNP)Ru(CO)Cl_2]$ in quantitative yield.[319] Model experiments, along with studies under different reaction conditions (e.g., open and closed reaction vessels) and isotope labeling work revealed that the pathway shown in Scheme 14 is operational. Species **121–125** can be detected directly, while the role of intermediates **B** and **C** is inferred by trapping to give **126 and 127**.

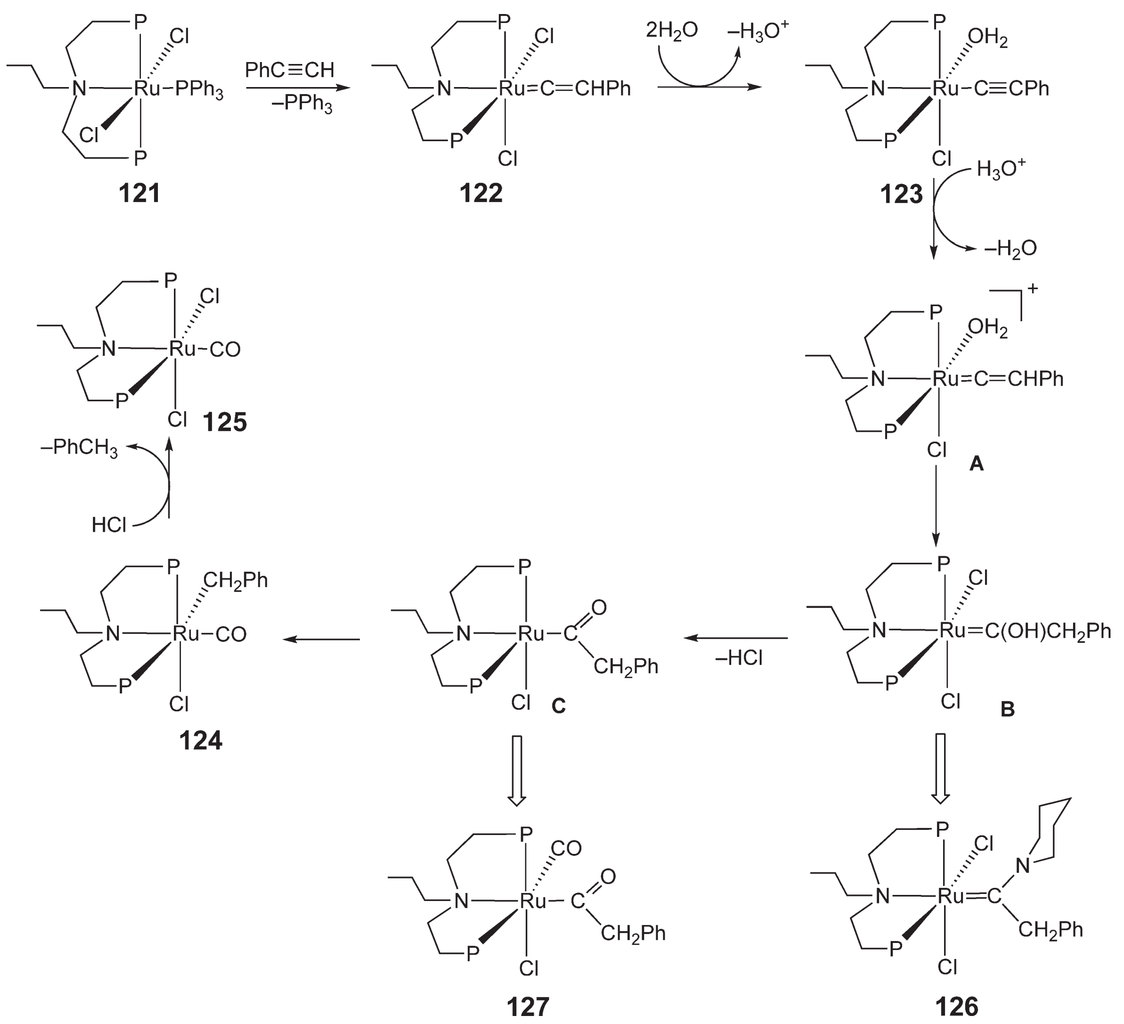
Addition of $HC{\equiv}CCMe_3$ to $[Os(PPh_3)_3Cl_2]$ generates two products, $[Os(PPh_3)_2({=}C{=}CHCMe_3)\{C(C{\equiv}CCMe_3){=}CHCMe_3\}Cl]^*$ and $[Os(PPh_3)_2({\equiv}CCH_2CMe_3)Cl_3]$. The expected simple vinylidene species $[Os(PPh_3)_2({=}C{=}CHCMe_3)Cl_2]$, although not isolated, was postulated to be an intermediate on the way to the carbyne product.[320]

Similarly, the reaction of an excess of $HC{\equiv}CSiMe_3$ with $[Os(PPh_3)_3Cl_2]$ in the presence of moisture gave a mixture of $[Os(PPh_3)_2({\equiv}CMe)Cl_3]$ (14%), $[Os(PPh_3)_2({=}C{=}C(H)SiMe_3)\{C(C{\equiv}CSiMe_3){=}CHSiMe_3\}Cl]$ (22%), $[Os(PPh_3)_2({=}C{=}C(H)SiMe_3)(C{\equiv}CSiMe_3)\{C(C{\equiv}CSiMe_3){=}CHSiMe_3\}]^*$ (4%), and the metallabenzyne $[Os(PPh_3)_2\{{\equiv}CC(SiMe_3)C(Me)C(SiMe_3)C\}Cl_2]$ (30% yield).[321]

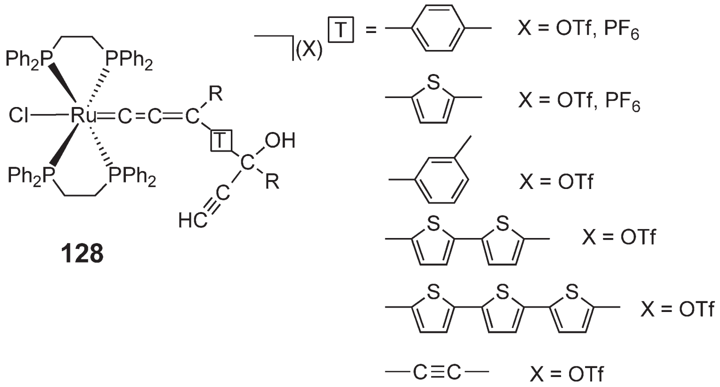
6.12.7 Cumulenylidenes

Upon heating, $HC{\equiv}CCPh_2(OH)$ reacts with $[M(PPh_3)_3Cl_2]$ ($M = Ru, Os$) to afford $[M(PPh_3)_2({=}C{=}C{=}CPh_2)Cl_2]$. Substitution reactions of the ruthenium complex take place under relatively mild conditions; thus, $[Ru(PCy_3)_2({=}C{=}C{=}CPh_2)Cl_2]$, $[Ru(PPh_3)_2(CO)({=}C{=}C{=}CPh_2)Cl_2]$ $[Ru(PPh_3)({=}C{=}C{=}CPh_2)([9]aneS_3)Cl]Cl$, and $[Ru(dppe)_2({=}C{=}C{=}CPh_2)Cl]Cl$ are formed by reaction with PCy_3, CO, $[9]aneS_3$, and dppe, respectively.[322] Reaction of $[Ru(Sb^iPr_3)_2(CO)HCl]$ with $HC{\equiv}CCPh_2(OH)$ affords the allenylidene species $[Ru(Sb^iPr_3)_2(CO)({=}C{=}C{=}CPh_2)Cl_2]^*$; the additional chloride ligand in the latter arises from workup involving chloride-containing Al_2O_3.[233] The hemilabile phosphine complex $[Ru(\kappa^2\text{-}P,O\text{-}^iPr_2PCH_2CO_2Me)_2Cl_2]$ reacts with $HC{\equiv}CCRR^1(OH)$ to form $[Ru(\kappa^2\text{-}P,O\text{-}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}^iPr_2PCH_2CO_2Me)\{{=}C{=}CHCRR^1(OH)\}Cl_2]$ ($R = Ph$, $R^1 = Ph$, *o*-tolyl); these undergo dehydration at 80 °C to give the allenylidene species $[Ru(\kappa^2\text{-}P,O\text{-}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}^iPr_2PCH_2CO_2Me)({=}C{=}C{=}CRR^1)Cl_2]$ ($R = Ph^*$, $R^1 = Ph^*$, *o*-tolyl).[286] Activation of $HC{\equiv}CCRPh(OH)$ ($R = Me, Ph$) by $[RuL_2Cl_2]$ ($L = $ 1-(2-diphenylphosphinoethyl)-3,5-dimethylpyrazole) in the presence of $NaBPh_4$ yields $[RuL_2(C{=}C{=}CPhMe)Cl](BPh_4)$ and $[RuL_2(C{=}C{=}CPh_2)Cl](BPh_4)^*$, while addition of $HC{\equiv}CPh/KPF_6$ affords the vinylidene complex $[RuL_2({=}C{=}CHPh)Cl](PF_6)$.[323] Treatment of $[Ru(PPh_3)_4Cl_2]$ or $[Ru(p\text{-cymene})Cl_2]_2$ with $HC{\equiv}CCPh_2(OH)$ in the presence of 2 equiv. of PCy_3 affords $[Ru(PCy_3)_2({=}C{=}C{=}CPh_2)Cl_2]^*$; this reacts with the *N*-heterocyclic carbene, IMes, at 40 °C to form $[Ru(PCy_3)(IMes)({=}C{=}C{=}CPh_2)Cl_2]^*$.[324] Addition of $LiC{\equiv}CC{\equiv}CSiMe_3$ to *cis*-$[Ru(dppm)_2Cl_2]$ yields *cis*-$[Ru(dppm)_2(C{\equiv}CC{\equiv}CSiMe_3)_2]$, *trans*-$[Ru(dppm)_2(C{\equiv}CC{\equiv}CSiMe_3)_2]$, and *trans*-$[Ru(dppm)_2(C{\equiv}CC{\equiv}CSiMe_3)Cl]$ depending on the molar ratio of reactants and whether the solvent used is Et_2O or THF.[325]

The 16-electron salts $[Ru(dppe)_2Cl](X)$ ($X = PF_6$, OTf) react with 2 equiv. of $(HC{\equiv}C(OH)R)_2\text{–}T$ ($R = Ph$, H; $T = m$, $p\text{-}C_6H_3$, 2,5-(thiophene), 5,5′-(2,2′-bithiophene), 5,5″-(2,2′:5′,2″-terthiophene), $\text{–}C{\equiv}C\text{–}$) to yield the allenylidene complexes *trans*-$[Ru(dppe)_2({=}C{=}C{=}C(R)\text{–}T\text{–}C(OH)(R)C{\equiv}CH)Cl](X)$ **128**.[326] The formation of *trans*-$[Ru(dppe)_2({=}C{=}C{=}CAr_2)Cl](PF_6)$ ($Ar = Ph$, $4\text{-}ClC_6H_4$, $4\text{-}FC_6H_4$) can be accomplished via direct reaction of *cis*-$[Ru(dppe)_2Cl_2]$ with $HC{\equiv}CCAr_2(OH)/NaPF_6$ or by treatment of $[\{Ru(PPh_3)_2({=}C{=}C{=}CAr_2)\}_2(\mu\text{-}Cl)_3](PF_6)$ with dppe.[327] A range of cationic mixed alkynyl allenylidene complexes *trans*-$[Ru(dppe)_2(C{\equiv}CR)({=}C{=}C{=}CR^1R^2)](PF_6)$ ($R^1 = R^2 = Ph$, $R = H$, ^nBu, Ph^*, $p\text{-}XC_6H_4$ ($X = OMe$, NO_2); $R^1 = R^2 = p\text{-}MeOC_6H_4$, $R = Ph$; $R^1 = H$, $R^2 = p\text{-}NMe_2C_6H_4$, $R = p\text{-}NO_2C_6H_4$) result from the reactions of *trans*-$[Ru(dppe)_2(C{\equiv}CR)Cl](PF_6)$ with $HC{\equiv}CCR^1R^2(OH)$ in the presence of $NaPF_6/Et_3N$.[239] Treatment of *cis*-$[Ru(dppm)_2Cl_2]$ with $HC{\equiv}CCR_2(OH)/NaPF_6$ yields *trans*-$[Ru(dppm)_2({=}C{=}C{=}CR_2)Cl](PF_6)$ ($R = Ph$, $4\text{-}ClC_6H_4$, $4\text{-}FC_6H_4$, Me). These show subsequent reactivity. Thus, *trans*-$[Ru(dppm)_2({=}C{=}C{=}CPh_2)Cl](PF_6)$ undergoes nucleophilic attack at C(3) to give the alkynyl complexes *trans*-$[Ru(dppm)_2(C{\equiv}CCPh_2X)Cl](PF_6)$ ($X = OMe$, H), while *trans*-$[Ru(dppm)_2({=}C{=}C{=}CMe_2)Cl](PF_6)$ undergoes facile deprotonation by DBU at C(4) to form *trans*-$[Ru(dppm)_2(C{\equiv}CCMe{=}CH_2)Cl]$. Monosubstituted propargyl alcohols $HC{\equiv}CCHR(OH)$ react with *cis*-$[Ru(dppm)_2Cl_2]/NaPF_6$ to give *trans*-$[Ru(dppm)_2({=}C{=}C{=}CHR)Cl](PF_6)$ ($R = Ph$, $4\text{-}ClC_6H_4$, $4\text{-}FC_6H_4$, $4\text{-}MeOC_6H_4$), *trans*-$[Ru(dppm)_2({=}C{=}C{=}CHCH{=}CHPh)Cl](PF_6)$, and *trans*-$[Ru(dppm)_2({=}C{=}CHCH{=}CH_2)Cl](PF_6)$.[328]



Scheme 14



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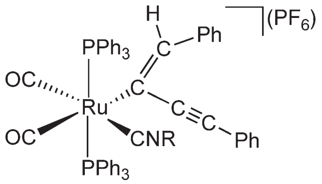
The reaction of *mer,trans*-[(PNP)Ru(PPh$_3$)Cl$_2$] with HC≡CCRR^1(OH) (R = R^1 = Me, Ph; R = Me, R^1 = Ph) in refluxing THF affords either the alkenylvinylidene species *fac,cis*-[(PNP)Ru{=C=C(H)C(R)=CH$_2$}Cl$_2$] (R = Me, Ph) or the allenylidene complex *fac,cis*-[(PNP)Ru{=C=C=CPh$_2$}Cl$_2$]*. Regioselective C$_\alpha$–C$_\beta$ bond cleavage occurs in all of these complexes on addition of water, yielding of *fac,cis*-$[(PNP)Ru(CO)Cl_2]$ and the free alkenes $H_2C{=}CRR^1$.[329]

The propargylic alcohol $HC{\equiv}CCMePh(OH)$ reacts with $[Ru(dippe)\{HB(pz)_3\}Cl]$ to generate the allenylidene complex $[Ru(dippe)\{HB(pz)_3\}({=}C{=}C{=}CMePh)](BPh_4)$, which can be deprotonated by KO^tBu to give $[Ru(dippe)\{HB(pz)_3\}(C{\equiv}CCPh{=}CH_2)]^*$.[306] Treatment of $[Ru(PPh_3)_2\{HB(pz)_3\}Cl]$ with $HC{\equiv}CCPh_2(OH)$ produces the neutral complex $[Ru(PPh_3)\{HB(pz)_3\}({=}C{=}C{=}CPh_2)Cl]$; if the reaction is performed in the presence of $AgPF_6$, the cationic complex $[Ru(PPh_3)_2\{HB(pz)_3\}({=}C{=}C{=}CPh_2)](PF_6)^*$ is produced. This undergoes reversible deprotonation with NaOMe to generate $[Ru(PPh_3)_2\{HB(pz)_3\}(C{\equiv}CC(OMe)Ph_2)]$.[301] Both the neutral and cationic allenylidene species react with $Na(S_2CNMe_2)$ to give the metallacyclic allenyl complex $[Ru(PPh_3)\{HB(pz)_3\}\{C({=}C{=}CPh_2)SC(NMe_2)S\}]$. The close analog, $[Ru(PPh_3)(CO)\{C({=}C{=}CPh_2)SC(NMe_2)S\}(\kappa^2\text{-}S_2CNMe_2)]^*$, can be isolated via a more roundabout procedure.[222]

The thioallenylidene complexes $[Ru(dppm)_2\{{=}C{=}C{=}C(SEt)Me\}](SbF_6)$, $[Ru(dppm)_2\{{=}C{=}C{=}C(SMe)CH_2CH_2CH{=}CH_2\}](SbF_6)$, and $[Ru(dppe)_2\{{=}C{=}C{=}C(SCH_2CH{=}CH_2)CH_2CH_2CH{=}CH_2\}](OTf)$ can be formed upon trapping Ru butatrienylidenes with thiols or allylic thioethers. *In situ* spectroelectrochemical studies reveal that oxidation takes place at the Ru center whereas reduction occurs at the C-heteroatom terminus.[330] The hemilabile species $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)({=}C{=}C{=}CRR^1)Cl_2]$ ($R = Ph$, $R^1 = Ph$, *o*-tolyl) react with a range of ligands L (CO, CN^tBu, C_5H_5N) to form $[Ru(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)_2(L)({=}C{=}C{=}CRR^1)Cl_2]$. Protonation of $[Ru(\kappa^2\text{-}P,O\text{-}{}^iPr_2PCH_2CO_2Me)(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)({=}C{=}C{=}CPh_2)Cl_2]$ with HCl results in attack on the central carbon atom to yield the alkenyl carbene complex $[Ru\{\kappa^2\text{-}(P,O)\text{-}{}^iPr_2PCH_2CO_2Me\}(\kappa\text{-}P\text{-}{}^iPr_2PCH_2CO_2Me)({=}CClCH{=}CPh_2)]$.[286] The cationic system $[Ru\{\kappa^2\text{-}(P,O)\text{-}PCy_2CH_2CH_2OMe\}_2({=}C{=}C{=}CPh_2)Cl](PF_6)^*$ can be protonated by $HBF_4{\cdot}OEt_2$ to give the cationic carbyne complex $[Ru\{\kappa^2\text{-}(P,O)\text{-}PCy_2CH_2CH_2OMe\}(\kappa\text{-}P\text{-}PCy_2CH_2CH_2OMe)({\equiv}CCH{=}CPh_2)Cl](PF_6)_2$.[331]

The allenylidene complex *trans*-$[Ru(dppm)_2({=}C{=}C{=}C(NMe_2)CH_2CH_2Fc)Cl](SbF_6)$ was prepared by addition of $FcCH_2NMe_2$ to $[Ru(dppm)_2({=}C{=}C{=}C{=}CH_2)]^+$, generated *in situ* in PhCl. Electrochemical and spectrochemical studies have been used to probe the species resulting from oxidation at both the ferrocenyl and ruthenium centers.[332] Spectroscopic and electrochemical studies of $[RuL_2\{HB(pz)_3\}\{{=}C{=}C{=}C(Ph)R\}](SbF_6)$ ($L_2 = (PPh_3)_2$, dppf*; $R = Ph^*$, Fc) reveal how variations of the electron donating power of L_2 or R on the oxidation of ferrocenyl sites can be used to raise or lower the energies of the IR and electronic absorption bands.[333] Ferricinium-induced oxidation of *trans*-$[Ru(dppe)_2(C{\equiv}CHPh)Cl]$ yields a 1 : 1 mixture of *trans*-$[Ru(dppe)_2({=}C{=}C{=}CPh_2)Cl](PF_6)$ and *trans*-$[Ru(dppe)_2\{{=}C{=}CH(CHPh_2)\}Cl](PF_6)$ via the intermediacy of the stabilized γ-C radical species $[Ru(dppe)_2(C{\equiv}CCPh_2)]^{\cdot}$ (detectable by low temperature EPR spectroscopy). In contrast, different reactivity is seen if the substituents on the alkynyl group are changed from Ph to Me or H resulting from inability to delocalize the free radical onto an aryl ring.[334] Radical stabilization also explains similar reactivity seen in other ruthenium allenylidene complexes.[335]

Treatment of $[Ru(dppe)_2Cl](PF_6)$ with a range of alkynes $HC{\equiv}CR$ ($R = C{\equiv}CPh$, $COCHPh_2$, $CH(OH)CHPh_2$) affords the buta-1,2,3-trienylidene $[Ru(dppe)_2({=}C{=}C{=}C{=}CHPh)Cl](PF_6)$, acylvinylidenes $[Ru(dppe)_2({=}C{=}CHCOR)Cl](PF_6)$ ($R = CH_2Ph$, $CHPh_2$), and alkenylvinylidene $[Ru(dppe)_2({=}C{=}CH\text{–}CH{=}CPh_2)Cl](PF_6)$. Deprotonation of the latter two classes of products affords the acyl alkynyl complexes $[Ru(dppe)_2(C{\equiv}CCOR)Cl]$ ($R = CH_2Ph$, $CHPh_2$) and $[Ru(dppe)_2(C{\equiv}C\text{–}CH{=}CPh_2)Cl](PF_6)$.[336] Protonation of $[Ru(PPh_3)_2(CO)_2(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)]$ with HPF_6 affords $[Ru(PPh_3)_2(CO)_2(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)](PF_6)$, which upon reaction with CN^tBu or $CN(2,6\text{-}Me_2C_6H_3)$ generates the stable 1,4-diphenylbut-1-en-3-yn-2-yl derivatives $[Ru(PPh_3)_2(CO)_2\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}L](PF_6)\})$ **129**.[337]



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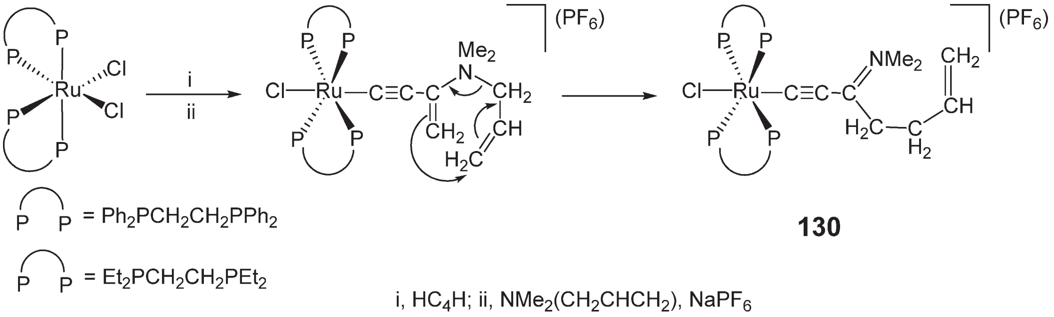
R = ^tBu
R = 2,6-$Me_2C_6H_3$



Scheme 15

The pentadiynes $XC{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2$ ($X = H$, $SnBu_3$) react with *cis*-$[Ru(dppm)_2Cl_2]$ in the presence of $NaPF_6$ in THF/Et_3N ($X = H$) or CH_2Cl_2 ($X = SnBu_3$) to yield *trans*-$[Ru(dppm)_2\{C{\equiv}CC{\equiv}CPh_2(OSiMe_3)\}Cl]$. The allenylidenes *trans*-$[Ru(dppm)_2\{{=}C{=}C{=}C(OMe)CH{=}CPh_2\}Cl](X)$ ($X = BF_4$, PF_6) and *trans*-$[Ru(dppm)_2\{{=}C{=}C{=}CCH{=}CPh_2(o\text{-}C_6H_4)\}Cl](X)$ ($X = BF_4$, PF_6^*) can be formed by subsequent protonation in MeOH or CH_2Cl_2, respectively, or directly from *cis*-$[Ru(dppm)_2Cl_2]$ upon reaction with the diynes and $NaPF_6$ in these same solvents. The bis-allenylidene $[Ru(dppm)_2\{{=}C{=}C{=}C(OMe)CH{=}CPh_2\}_2](BF_4)_2^*$ results from treatment of *cis*-$[Ru(dppm)_2Cl_2]$ with $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ and NH^iPr_2, followed by protonation (HBF_4 in MeOH).[338]

In the presence of $NaPF_6$, *cis*-$[Ru(dppm)_2Cl_2]$ reacts with $HC{\equiv}CC{\equiv}CH$ to give a proposed butatrienylidene intermediate, which in the presence of a tertiary amine, can be trapped as the ammoniobutenynyl species *trans*-$[Ru(dppm)_2\{C{\equiv}CC(NR_3){=}CH_2\}Cl](PF_6)$ ($NR_3 = NEt_3^*$, NPr_3, Me_2NCH_2Ph, Me_3tacn, $EtN(C_2H_4)_2O$, $Me_2NCH_2\text{-}3\text{-}MeOC_6H_5$, $4\text{-}NMe_2C_5H_4N$).[339,340] Attempts to prepare *N*-allyl analogs resulted in a rearrangement via an aza-Cope pathway to generate the amino-substituted allenylidene derivatives *trans*-$[Ru(P\text{–}P)_2\{{=}C{=}C{=}C(NMe_2)CH_2CH_2CH{=}CH_2\}Cl](PF_6)$ (**130**, P–P = dppe*, depe) at RT (Scheme 15).[339] Electrophilic attack of the butatrienylidene complex *trans*-$[Ru(dppm)_2({=}C{=}C{=}C{=}CH_2)Cl]^+$ on pyrroles or *N*-methylindole followed by proton migration yields pyrrolyl- or indolyl-substituted allenylidene complexes. Resonance Raman studies show that the π-system of the heterocycle is incorporated into the conjugated carbon chain of the allenylidene.[341]

6.12.8 Carbene Complexes

6.12.8.1 Formation via Carbene Transfer

Diazoalkanes react with $[Os(P^iPr_3)_2(CO)HCl]$ to afford the carbene complexes $[Os(P^iPr_3)_2(CO)({=}CHR)HCl]$ ($R = H$, Ph, CO_2Et^*, $SiMe_3^*$).[342,343] For R = Ph, addition of HCl or HBF_4/H_2O results in Os–H bond cleavage to give $[Os(P^iPr_3)_2(CO)({=}CHPh)Cl_2]^*$ and $[Os(P^iPr_3)_2(CO)({=}CHPh)(H_2O)Cl](BF_4)$, respectively. Similarly to the hydride chloride precursor, $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHPh\}Cl]$ reacts with $PhCHN_2$ to afford $[Os(P^iPr_3)_2(CO)({=}CHPr)\{(E)\text{-}CH{=}CHPh\}Cl].[Os(P^iPr_3)_2(CO)({=}CHPh)HCl]$ and can also be formed by reaction of $[Os(P^iPr_3)_2(CO)HCl]$ with $Ph_2S{=}CHPh$ at low temperature.[344] Synthesis of an analogous ruthenium complex necessitates the use of the bulkier P^iPr_2Ph ligand and addition of the appropriate diazomethane at low temperature.[345] The η^2-carboxylate complex $[Ru(PPh_3)\{HB(pz)_3\}(\eta^2\text{-}O_2CCHPh_2)]$ reacts with phenyldiazomethane to generate $[Ru(PPh_3)\{HB(pz)_3\}({=}CHPh)(\eta^1\text{-}O_2CCHPh_2)]$. The closely related complex $[Ru(PCy_3)\text{-}\{HB(pz)_3\}\text{-}({=}CHCH{=}CMe_2)(\eta^1\text{-}O_2CCHPh_2)]$ is formed by treating $[Ru(PCy_3)\{HB(pz)_3\}({=}CHCH{=}CMe_2)Cl]$ with AgO_2CCHPh_2. Subsequent addition of HCl to $[Ru(PPh_3)\{HB(pz)_3\}({=}CHPh)(\eta^1\text{-}O_2CCHPh_2)]$ or $[Ru(PCy_3)\{HB(pz)_3\}({=}CHCH{=}CMe_2)(\eta^1\text{-}O_2CCHPh_2)]$ affords $[Ru(PR_3)\{HB(pz)_3\}({=}CHR^1)Cl]$ ($R = R^1 = Ph$; $R = Cy$, $R^1 = CHCMe_2$), respectively.[227]

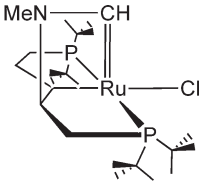
Treatment of $[OsO_2(CH_2{}^tBu)_2]$ or $[OsO_2(CH_2SiMe_3)_2]$ with 2 equiv. of $[Ta({=}CH^tBu)(CH_2^tBu)_3]$ at low temperature affords *syn,anti*-$[Os({=}CH^tBu)_2(CH_2{}^tBu)_2]$ and a 1 : 1 ratio of *syn,anti*- and *anti,anti*-$[Os({=}CH^tBu)_2(CH_2SiMe_3)_2]^*$, respectively. Photolysis at low temperature in toluene solution can be used to form other rotamers.[168] The reaction of $[Os({=}CH^tBu)_2(CH_2{}^tBu)_2]$ with pyridinium triflate in the presence of an excess of pyridine affords the dialkyl carbyne complex $[Os({\equiv}C^tBu)(CH_2{}^tBu)_2(C_5H_5N)_2(OTf)]$.[167]

6.12.8.2 Formation from Alkenyl, Vinylidene or Carbyne Complexes

The alkenyl complexes $[RuL_2(CO)(CH{=}CHR)Cl]$ are protonated by HBF_4 to give the cationic five-coordinate carbene complexes $[RuL_2(CO)({=}CHCH_2R)Cl](BF_4)$ ($L = P^iPr_3{}^*$, PCy_3; $R = H$, Ph, $^tBu^*$). Subsequent reactions of the carbene complexes with PMe_3 or P^iPr_3 and MeCN result in either deprotonation and regeneration of the alkenyl compounds or cleavage of the ruthenium–carbene bond resulting in formation of the six-coordinate complexes $[Ru(P^iPr_3)_2(CO)(MeCN)_2Cl](BF_4)$ and $[Ru(P^iPr_3)_2(CO)(MeCN)_2H]X$. Addition of HBF_4 to $[Ru(PCy_3)_2(CO)(CH{=}CH_2)(\kappa^2\text{-}O_2CMe)]$ affords the corresponding cationic carbene complex $[Ru(PCy_3)_2(CO)({=}CHMe)(\kappa^2\text{-}O_2CMe)](BF_4)$.[194] Protonation of five-coordinate $[Ru(P^iPr_3)_2({=}C{=}CHPh)(\kappa^2\text{-}O_2CR)Cl]$ or six-coordinate $[Ru(P^iPr_3)_2({=}C{=}CHPh)(\kappa^1\text{-}O_2CR^1)(\kappa^2\text{-}O_2CR^2)Cl]$ with $[H(OEt_2)_2](BAr^F{}_4)$ affords the unsaturated cyclic carbene complexes $[Ru(P^iPr_3)_2\{{=}C(CH_2Ph)OC(O)R\}](BAr^F{}_4)$ ($R = H^*$, Me, Ph) or saturated analogs $[Ru(P^iPr_3)_2\{{=}C(CH_2Ph)OC(O)R^2\}(\kappa^2\text{-}O_2CR^1)](BAr^F{}_4)$ ($R^1 = R^2 = CH_2F$; $R^1 = CF_3$, $R^2 = H$). When the R group in $[Ru(P^iPr_3)_2(\kappa^2\text{-}O_2CR)({=}C{=}CHPh)Cl]$ is changed to CH_2F, CHF_2, CF_3, 4-$NO_2C_6H_4$, 2-$NO_2C_6H_4$, C_6F_5, or 2,4-$(NO_2)_2C_6H_3$, protonation yields an equilibrium mixture of $[Ru(P^iPr_3)_2\{{=}C(CH_2Ph)OC(O)R\}](BAr^F{}_4)$ **131** and $[Ru(P^iPr_3)_2({\equiv}CCH_2Ph)(\kappa^2\text{-}O_2CR)Cl](BAr^F{}_4)$ **132**, the position of the equilibrium depending on the basicity of the carboxylate group (Scheme 16).[289,346]

6.12.8.3 Formation via Bond Activation

Triple C–H bond activation of 1,5-bis(di-*tert*-butylphosphino)-2-(*S*)-dimethylaminopentane by $\{Ru(p\text{-cymene})Cl_2\}_2$ yields the chiral carbene complex **133***.[347] The cyclometallated complex $[Os\{CH(C_2H_4P^tBu_2)_2\}H_2Cl]$ undergoes reversible dehydrogenation at high temperature to give the pincer carbene complex $[Os\{{=}C(C_2H_4P^tBu_2)_2\}HCl]^*$.



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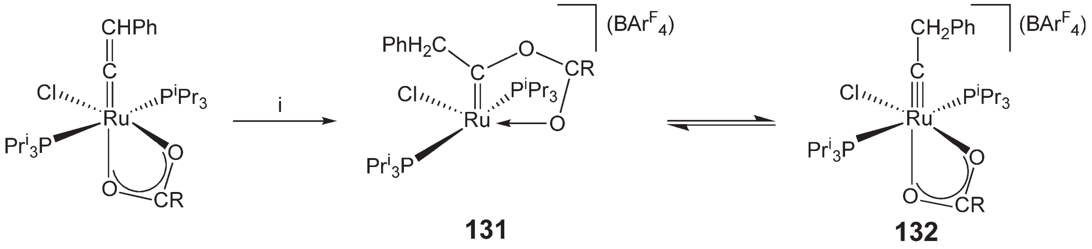
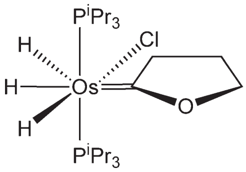
The analogous ruthenium species is formed directly as one of two products upon thermolysis of $\{Ru(p\text{-cymene})Cl_2\}_2$ with 1,5-bis(di-*tert*-butylphosphino)ethane (dtbpe) and lutidine at 90 °C.[126] The 14-electron fragment $[Ru(P^iPr_3)_2HCl]$ effects a 1,2-hydrogen migration in vinyl ethers to afford the carbene complexes $[Ru(P^iPr_3)_2\{{=}CMe(OR)\}HCl]$ ($R = Et$, Cy, $SiMe_3$, $CH_2CH_2O^nBu$, CH_2CH_2OH, $(CH_2CH_2O)_2H$, CH_2CH_2F, $CH_2CH_2NEt_2$, CH_2CHOCH_2); in some cases, the reactions are immediate even at low temperature (e.g., with $CH_2{=}C(OEt)H$, reaction takes place at −65 °C).[63] NMR studies at this temperature indicate formation of a coordinated alkene complex—employing the labeled alkene $CH_2{=}C(OEt)D$ indicates H/D exchange at −20 °C consistent with: (i) reversible binding in the η^2-fashion of the vinyl ether and (ii) reversible migration of H (or D) from Ru to both alkenic carbons. DFT calculations on the model $[Ru(PH_3)_2(\eta^2\text{-}CH_2{=}CHX)HCl]/[Ru(PH_3)_2({=}CMeX)HCl]$ ($X = H$, OMe) systems show that the OMe group favors the carbene structure by ca. 57 kJ mol^{-1}.[63] Vinyl amides are also transformed into carbene complexes, in which amide oxygen coordination completes the metal coordination sphere, as shown by the crystal structure of $[Ru(P^iPr_3)_2\{{=}C(Me)NC(O)CH_2CH_2CH_2\}HCl]^*$.[348,349]



i, $[H(OEt_2)_2](BAr^F{}_4)$

Scheme 16

Double dehydrogenation of the carbon α to the oxygen in cyclic ethers in the presence of the hydrogen acceptor $CH_2{=}CH^tBu$ using either $\{Ru(P^iPr_3)_2HCl\}_2$ or $[Os(P^iPr_3)_2H_3Cl]$ yields the coordinated cyclic carbene compounds $[M(P^iPr_3)_2\{{=}CO(CH_2)_2E\}HCl]$ ($M = Ru$, $E = CH_2$, O; $M = Os$, $E = CH_2$). The osmium complex reacts with H_2 to give two isomeric carbene products **134, 135**. Geminal dehydrogenation of cyclic amines $RN(CH_2)_4$ ($R = H$, Me) also occurs readily with the ruthenium dimer to give analogous *N*-substituted carbene complexes, such as $[Ru(P^iPr_3)_2\{{=}C(NH)(CH_2)_3\}HCl]^*$. In contrast, the reaction of $[Os(P^iPr_3)_2H_3Cl]$ with pyrrolidine is slow and ultimately affords the trihydride carbene complex $[Os(P^iPr_3)_2\{{=}C(NH)(CH_2)_3\}H_3Cl]$.[350]



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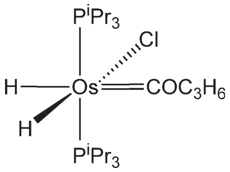

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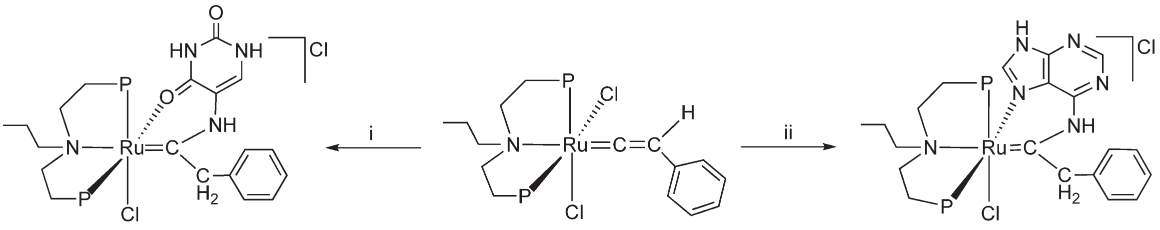
The carbene complexes $[Os(P^tBu_2Me)_2\{{=}C(OR)Me\}HCl]$ form rapidly at low temperatures upon addition of vinyl ethers to $[Os(P^tBu_2Me)_2H_3Cl]$, via the intermediacy of η^2-alkene complexes. While the carbene complexes generally decompose upon warming to form a mixture of products, changing the phosphine to P^iPr_3 allows the clean formation of the carbyne complex $[Os(P^iPr_3)_2({\equiv}CMe)HCl]$ ($R = Ph$) from $H_2C{=}CH(OPh)$, but the vinylidene $[Os(P^iPr_3)_2({=}C{=}CH_2)HCl]$ with $H_2C{=}CH(OEt)$. This difference in reactivity arises from the better stability of PhO^- compared to EtO^- as a free nucleophile, and the Bronsted basicity of the ethoxide anion that allows it to deprotonate a $Os{\equiv}CMe$ to afford the vinylidene product.[351]

Fluoride abstraction from $[Ru(P^tBu_2Me)(CO)HF]$ by Me_3SiCF_3 affords the difluorocarbene $[Ru(P^tBu_2Me)(CO)({=}CF_2)HF]^*$. The CF_2 ligand undergoes facile hydrolysis to CO and is also subject to fluoride abstraction by Me_3SiOTf to form $[Ru(P^tBu_2Me)(CO)(CF_2H)OTf]$. The related species $[Ru(P^tBu_2Me)_2(CO)(CF_2H)F]$ slowly forms upon dissolution of $[Ru(P^tBu_2Me)_2(CO)({=}CF_2)HF]$ in THF via a phosphine dissociation pathway.[57,58] In contrast, the osmium analog $[Os(P^tBu_2Me)_2(CO)({=}CF_2)HF]$ is stable in THF, although isomerization does occur at elevated temperatures, but to give $[Os(P^tBu_2Me)_2(CO)({=}CFH)F_2]$. The rationale for this difference in reactivity is the tendency for third-row metals to prefer higher oxidation states.[58]

Addition of a three-fold excess of RNH_2 to the vinylidene complex *fac,cis*-$[Ru(PNP)({=}C{=}CHPh)Cl_2]$[352] affords the secondary aminocarbene species *fac,cis*-$[Ru(PNP)\{{=}C(NHR)(CH_2Ph)\}Cl_2]$ ($R = {}^nPr$, Ph, *cyclo*-C_6H_{11}, *(R)*-(+)-CHMePh, *(R)*-(+)-CHMeEt, *(R)*-(+)-CHMe(1-naphthyl)*, H). Formation of these compounds involves deprotonation of the vinylidene C_β atom to give phenylalkynyl complexes, coordination of a second molecule of amine to the ruthenium and subsequent intramolecular nucleophilic attack at C_β of the phenylalkynyl ligand. The aminocarbene complexes are transformed into the isonitrile derivatives *fac,cis*-$[Ru(PNP)(CNR)Cl_2]$ upon heating in wet solvents,[353] while in the specific case of *fac,cis*-$[Ru(PNP)\{{=}C(NHPh)(CH_2Ph)\}Cl_2]$, reaction with $TlPF_6/PhC{\equiv}CH$ gives *mer*-$[Ru(PNP)\{{=}C(NHPh)(CH_2Ph)\}({=}C{=}CHPh)Cl](PF_6)$, a rare example of a complex bearing both carbene and vinylidene ligands.[354] The reactivity of the vinylidene complex *fac,cis*-$[Ru(PNP)({=}C{=}CHPh)Cl_2]$ has been extended from simple amines to biologically important molecules such as adenine. Thus, reaction with either 5-aminouracil or adenine in dimethylformamide (DMF) at 110 °C gives the carbene nucleobase compounds *fac,cis*-$[Ru(PNP)\{{=}C(NHC_4H_3N_2O_2)(CH_2Ph)\}Cl]Cl^*$ **136** and *fac,cis*-$[Ru(PNP)\{{=}C(NHC_5H_3N_4)(CH_2Ph)\}Cl]Cl$ **137**, respectively (Scheme 17).[355] The aminocarbenes $[Ru\{HB(pz)_3\}\{{=}C(R)NH\text{-}2\text{-}C_5H_4N\}]$ ($R = Ph^*$, *p*-$MeOC_6H_4$, Np) are formed upon reaction of the imines $(2\text{-}C_5H_4N)N{=}CHR$ with $[Ru\{HB(pz)_3\}(COD)Cl]$ at elevated temperature.[356]

The hydroxyosmacyclopropene complexes $[Os(P^iPr_3)_2\{C\{CRR^1(OH)\}CH_2\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ undergo a 1,2-migration of the Os–H group to the osmacyclopropene CH_2 followed by coordination of the hydroxyl group on the resulting carbene ligand to generate the cyclic hydroxycarbene species $[Os(P^iPr_3)_2\{{=}CMeCRR^1(OH)\}\text{-}.(\kappa^2\text{-}O_2CMe)](BF_4)$ ($R = R^1 = Ph$, Me; $R = Ph^*$, $R^1 = Me^*$). Addition of NaOMe to $[Os(P^iPr_3)_2\{{=}CMeCMePh(OH)\}(\kappa^2\text{-}O_2CMe)](BF_4)$ at 0 °C results in deprotonation of the hydroxycarbene ligand to give the neutral osmaoxacyclobutene derivative $[Os(P^iPr_3)_2\{{=}CMeC(O)MePh\}(\kappa^2\text{-}O_2CMe)]$.[357] The osmium carbene complexes $[Os(P^iPr_3)_2({=}CHCH_2R)(CO)Cl_2]$ are formed upon by addition of CO to the carbyne species $[Os(P^iPr_3)_2({\equiv}CCH_2R)HCl_2]$ ($R = Ph$, Me), followed by 1,2-hydride migration from Os to carbyne C_α;[221] $[Os(P^iPr_3)_2(CO)({=}CHCH_2Ph)Cl_2]^*$ also results from the reaction of $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}H_2)Cl_2]$ with $PhC{\equiv}CH$ at RT or addition of HCl to $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHPh\}Cl]$.[195] Chloride abstraction from the carbene complexes by $NaBAr^F_4$



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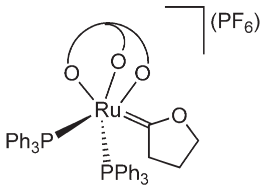
i, 5-aminouracil, DMF, Δ; ii, adenine, DMF, Δ

Scheme 17

yields $[Os(P^iPr_3)_2(CO)({=}CHCH_2R)Cl](BAr^F{}_4)$.[221] Protonation of the related ruthenium alkenyl complex $[Ru(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHC(Me){=}CH_2\}Cl]$ with HBF_4 yields $[Ru(P^iPr_3)_2(CO)\{{=}CHCH{=}CMe_2\}\text{-}Cl](BF_4)$.[201]

Addition of HX to the neutral carbyne complexes $[M(PPh_3)_2(CO)({\equiv}CR)Cl]$ generates the carbene complexes $[M(PPh_3)_2({=}CHR)(CO)XCl]$ (M = Os, R = 1-naphthyl, X = Cl; M = Os, R = 2-naphthyl, X = Cl*; M = Ru, R = Ph, X = Cl; M = Ru, R = 1-naphthyl, X = Cl; M = Os, R = 1-naphthyl, X = ClO_4; M = Os, R = 1-naphthyl, X = F). Alternatively, treatment of $[Os(PPh_3)_2(CO)({\equiv}CR)Cl]$ with $PhICl_2$ leads to the corresponding monochlorocarbene complexes $[Os(PPh_3)_2({=}CClR)(CO)Cl_2]$ (R = 1-naphthyl, 2-naphthyl).[69]

The reaction of 3-butyn-1-ol with $[Ru(L_{OEt})(PPh_3)_2Cl]$ ($L_{OEt} = (\eta^5\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$), followed by addition of NH_4PF_6, gave the cyclic carbene complex $[Ru(L_{OEt})(PPh_3)_2({=}C(CH_2)_3O)](PF_6)$* 138.[212] Substitution of COD in $[Ru\{HB(pz)_3\}(COD)Cl]$ by the N–O donor ligand 2-acetamidopyridine (Haapy), and subsequent reaction with $HC{\equiv}CR$ at elevated temperature affords the amidocarbene complexes $[Ru\{HB(pz)_3\}({=}C{=}CH_2R\text{–}aapy)Cl]$ (R = Ph*, ^{n}Bu) in good yields. If $HC{\equiv}CCMePh(OH)$ or $HC{\equiv}CCy$ are used, the alkenyl carbene complexes $[Ru\{HB(pz)_3\}({=}CCH{=}CMePh\text{–}aapy)Cl]$ and $[Ru\{HB(pz)_3\}({=}CCH{=}CC_6H_{10}\text{–}aapy)Cl]$ are formed instead, presumably via amidocarbene species that then undergo a facile H_2O loss or 1,3-hydrogen shift, respectively.[358]



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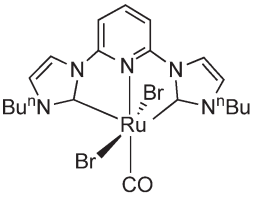
Under an atmosphere of CO, the alkenyl azavinylidene species $[Os(P^iPr_3)_2({=}N{=}CR_2)\{(E)\text{-}HC{=}CHPh\}Cl](OTf)$ undergo C–N coupling of the styryl and azavinylidene ligands to give Δ^2-1,2-aza-osmetine derivatives $[Os(P^iPr_3)_2(CO)({=}CHCHPhN{=}CR_2)Cl](OTf)$ ($CR_2 = CMe_2$*, $C(CH_2)_4CH_2$).[209] A range of cationic cyclic oxycarbene complexes of the form $[Ru\{L\text{–}L\}_2\{{=}C(CH_2)_2CH(CH)_3O\}Cl](PF_6)$ (L–L = dppm*, (dppene)(bpy)*), $[Ru\{L\text{–}L\}_2\text{-}({=}C(CH_2)_2CH(CH)_3O)_2]^{2+}$ (L–L = bpy), and $[Ru\{L\text{–}L\}_2({=}C(CH_2)_3O]^+$ (L–L = dppm*) have been prepared.[359]

6.12.9 *N*-Heterocyclic Carbene Complexes

While the major emphasis of *N*-heterocyclic carbene (NHC) ligands (e.g., IMes, SIMes) has been directed at the preparation of new complexes with catalytic properties, there have been a number of reports dealing with the fundamental chemistry of this class of ligands.

Substitution of one phosphine in $[Ru(PCy_3)_2(CO)HCl]$ by IMes occurs upon heating at 80 °C to give $[Ru(IMes)(PCy_3)(CO)HCl]$* which is an active alkene hydrogenation catalyst.[360] The analogous systems $[Ru(NHC)(PPh_3)(CO)HCl]$ (NHC = IMes, SIMes) show hydrogenation activity higher than that of the PCy_3 complex.[361] Reaction of $\{Ru(P^iPr_3)_2HCl\}_2$ with the unsaturated cyclic carbene $:C(NMeCH)_2$ yields the 16-electron square-pyramidal species $[Ru(P^iPr_3)_2(CNMeCHCHNMe)HCl]$* by a chloride bridge-splitting reaction. Double dehydrogenation of the heterocycle $H_2C(NMeCH_2)_2$ by $\{Ru(P^iPr_3)_2HCl\}_2$ in the presence of

^{t}BuCH$=$CH$_2$ produces the saturated carbene analog.[362] Chelating pyridyl–NHC ligands allow the straightforward synthesis of [Ru(CNC)(CO)Br$_2$] **139** and [Ru(CNC)$_2$](PF$_6$)$_2$ (CNC = 2,6-bis(butylimidazol-2-ylidene)pyridine). The neutral complex acts as a precursor for catalytic hydrogen transfer from alcohols to ketones and oxidation of alkenes.[363]



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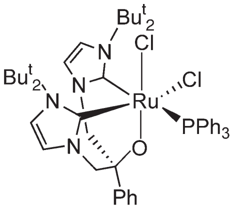
The potentially tridentate anionic carbenes Ag/Tl[OCPh(CH$_2${1-C(NCHCHN^{t}Bu)})$_2$] react with [Ru(PPh$_3$)$_3$Cl$_2$] to give the trivalent complex [Ru(PPh$_3$){OCPh(CH$_2${1-C(NCHCHN^{t}Bu)}$_2$)}Cl$_2$] **140**.[364] The photoluminescence of **141**, an NHC analog of [Ru(bpy)$_3$]$^{2+}$, along with that of a [Ru(terpy)$_3$]$^{2+}$ analog has been studied in aqueous solution.[365]



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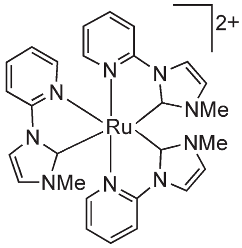

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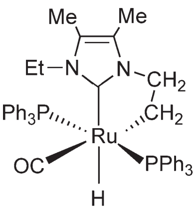
The bis-dihydrogen dihydride complex [Ru(PCy$_3$)$_2$(η^2-H$_2$)$_2$H$_2$] reacts with bis-cationic 1,2,3,4-tetramethyl-1,2,4-triazolium to yield two isomers of the cationic NHC complex [Ru(PCy$_3$)$_2$(C$_6$H$_{12}$N$_3$)H(OTf)](OTf)*.[366] Addition of {2,6-(*o*-dialkyl)phenylimidazolylidene}pyridine (L) to [Ru(PPh$_3$)$_3$Cl$_2$] yields the bis-carbene complex [Ru(PPh$_3$)(L)Cl$_2$].[367] Attempts to isolate [Ru(IMes)$_2$(AsPh$_3$)(CO)H$_2$] resulted instead in the formation of the *trans*-dihydride solvento complexes [Ru(IMes)$_2$(CO)(S)H$_2$] (S = EtOH*, H$_2$O*, H$_2$S*). These undergo reactions with a range of substrates including CO, CO$_2$, and MeCN to generate [Ru(IMes)$_2$(CO)$_2$(XH)H] (X = O*, S*), [Ru(IMes)$_2$(CO){κ^2-O$_2$COH}H], [Ru(IMes)$_2$(CO)$_2$(κ-OC(O)OH)H]*, and [Ru(IMes)$_2$(CO){κ^2-(*O*,*N*)-OCMeNCMeNH}H]*.[368,369]

A number of reports concern degradation of the NHC ligand through bond activation reactions. Thermolysis of the bis-NHC complex [Ru(PPh$_3$)(IMes)$_2$(CO)H$_2$] results in C–C bond activation of an *ortho*-*sp*^{2}-*sp*^{3} bond, with elimination of methane; in contrast, the mono-NHC complex [Ru(PPh$_3$)$_2$(IMes)(CO)H$_2$] undergoes intramolecular C–H activation of an *ortho*-methyl C–H bond of one of the mesityl substituents upon addition of trimethylvinylsilane at RT. The reaction is reversed by addition of H$_2$ at RT.[370] Intermolecular C–H and C–C activation by [Ru(NHC)$_{3-x}$(PH$_3$)$_x$(CO)$_2$] has been probed computationally.[371] Facile intramolecular C–H bond activation of *N*-aryl-substituted NHC ligands has been described in [Ru(IMes)(L–L)(CO)H$_2$] (L–L = dppp*, arphos)[372] and upon reaction of [Ru(PPh$_3$)$_3$HCl] with either IMes or SIMes.[373] Some differences are seen with *N*-alkyl-substituted carbenes; C–H bond activation of the ethyl group in [Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)H$_2$] affords [Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)H]* **142** upon initiation with HC$=$CHSiMe$_3$,[374] whereas treatment of the more electron rich system, [Ru(PPh$_3$)$_3$HCl], with I^{t}Bu produces a red solution that, upon reaction with H$_2$, produces the dihydride [Ru(I^{t}Bu)(PPh$_3$)$_2$H$_2$]* as a mixture of two isomers, containing an I^{t}Bu agostic C–H bond. However, no C–H activation is detected.[373] If the synthesis of [Ru(SIMes)(PCy$_3$)($=$CHPh)Cl$_2$] is carried out without the rigorous exclusion of air, intramolecular C–H activation is seen affording **143***.[375] The first complexes containing NHC and dihydrogen ligands are formed upon treating [Ru(PCy$_3$)$_2$(η^2-H$_2$)$_2$H$_2$] with IMes under an atmosphere of hydrogen. Both [Ru(PCy$_3$)(IMes)(η^2-H$_2$)$_2$H$_2$]* and [Ru(IMes)$_2$(η^2-H$_2$)$_2$H$_2$] **144** are formed; the former undergoes intra- and intermolecular C–H bond activation reactions as evidenced by H/D exchange.[376]



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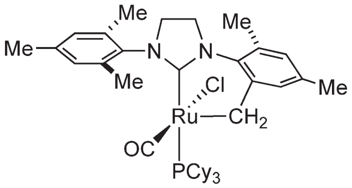

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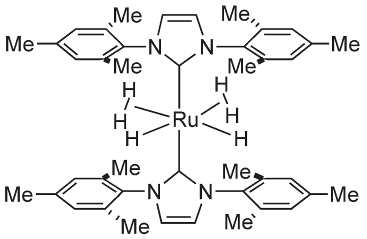

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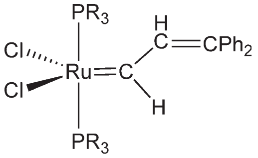
6.12.10 Grubbs-Type Carbene Complexes

The following three sections focus on the development of carbene complexes of the general form $[\text{RuL}_2(=\text{CRR}^1)\text{Cl}_2]$, developed initially by the Grubbs group for alkene metathesis polymerization chemistry. A significant number of papers have resulted from work aimed at modifying L = phosphine for L = *N*-heterocyclic carbene, functionalizing the $=\text{CRR}^1$ unit (e.g., the synthesis of Hoveyda-type complexes bearing coordinated aryl ether substituents) and incorporating other labile ligands in the ruthenium coordination sphere. While the catalytic activity of the these complexes is covered elsewhere, brief mention is made below of their activity for ring-opening metathesis polymerisation (ROMP) and ring-closing metathesis polymerization (RCM) in order to put the context for synthesis of complexes into perspective.

6.12.10.1 Monodentate Phosphine-based Systems

Following on from reports of $[\text{Ru}(\text{PPh}_3)_2(=\text{CHCH}=\text{CPh}_2)\text{Cl}_2]$ **145** in 1992,[377] as well as related PPh_3 derivatives,[378,379] ruthenium carbene complexes bearing PCy_3 **146**, P^iPr_3 and other tertiary phosphine ligands have been prepared by simple substitution of **145**.[380–382] Alternatively, treatment of $[\text{Ru}(\text{PCy}_3)_2(\eta^2\text{-H}_2)\text{HCl}]$ with the propargylic chlorides $\text{HC}\equiv\text{CCRR}^1\text{Cl}$ provides a route to $[\text{Ru}(\text{PCy}_3)_2(=\text{CHCH}=\text{CRR}^1)\text{Cl}_2]$ ($\text{R} = \text{H}$, $\text{R}^1 = \text{H}$, Me, Ph; $\text{R} = \text{R}^1 = \text{Me}$, $-(\text{CH}_2)_5-$). If $\text{CHCl}=\text{CRR}^1$ are employed, the alkylcarbene species $[\text{Ru}(\text{PCy}_3)_2(=\text{CHCHRR}^1)\text{Cl}_2]$ ($\text{R} = \text{R}^1 = \text{H}$; $\text{R} = \text{H}$, $\text{R}^1 = \text{Me}$) are produced.[383]



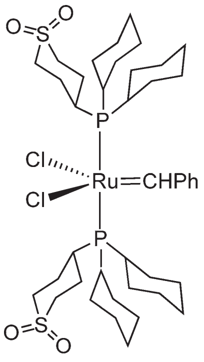
145: R = Ph
146: R = Cy

A mixture of $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]/\text{PCy}_3$ reacts with PhCHCl_2 at RT to afford $[\text{Ru}(\text{PCy}_3)_2(=\text{CHPh})\text{Cl}_2]$, which is also formed by phosphine exchange with $[\text{Ru}(\text{PPh}_3)_2(=\text{CHPh})\text{Cl}_2]$[384,385] or by reaction of the sulfur ylide $\text{PhS}=\text{CHPh}$ with $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]/2\text{PCy}_3$ at low temperature.[344] The reaction of the Chaudret complex $[\text{Ru}(\text{PCy}_3)_2(\eta^2\text{-H}_2)_2\text{H}_2]$ with either C_2H_4 and then CHXCl_2 ($\text{X} = \text{Ph}$, CO_2Me) or directly with CH_2Cl_2 provides an alternative route to the parent carbene complex $[\text{Ru}(\text{PCy}_3)_2(=\text{CH}_2)\text{Cl}_2]$.[384,386] Treatment of the same precursor with CHRCl_2 ($\text{R} = \text{H}$, Ph) or $\text{Cl}_2\text{C}=\text{CH}_2$ yields $[\text{Ru}(\text{PCy}_3)_2(=\text{CHR})\text{Cl}_2]$ ($\text{R} = \text{H}$, Ph) and $[\text{Ru}(\text{PCy}_3)_2(=\text{CHMe})\text{Cl}_2]$, respectively. The latter product arises through hydrogenation of the C=C bond of the presumed vinylidene primary product by released H_2; the same pathway accounts for the formation of CH_3R, HCl, and $[\text{Ru}(\text{PCy}_3)_2(\eta^2\text{-H}_2)\text{HCl}]$ from $[\text{Ru}(\text{PCy}_3)_2(=\text{CHR})\text{Cl}_2]$ ($\text{R} = \text{H}$, Ph). Changing the precursor to the dinitrogen adduct, $[\text{Ru}(\text{PCy}_3)_2(\text{H})_2(\text{N}_2)_2]$, to avoid generation of H_2 leads to clean formation of $[\text{Ru}(\text{PCy}_3)_2(=\text{CHR})\text{Cl}_2]$. The bis-dinitrogen complex reacts with Cl_2CHEt to afford $[\text{Ru}(\text{PCy}_3)_2(=\text{CHEt})\text{Cl}_2]$ and with PhCH_2Cl to yield initially $[\text{Ru}(\text{PCy}_3)_2(\text{CH}_2\text{Ph})\text{H}_2\text{Cl}]$, which slowly eliminates toluene over hours.[387]

More straightforward routes to these types of complexes have been developed by a number of groups. A simple, one-pot synthesis of $[\text{Ru}(\text{PR}^1{}_3)_2(=\text{CHR})\text{Cl}_2]$ can be carried out by reduction of RuCl_3 in THF with $\text{Mg/ClCH}_2\text{CH}_2\text{Cl}$ in the presence of phosphine under an atmosphere of H_2 at elevated temperature (60–85 °C), followed by cooling to −40 °C and reaction with 2 equiv. of $HC{\equiv}CH$ in the presence of an excess of water. High yields of product are formed, for example, with $R = Me$ and $R^1 = Cy$, 75% yield.[388] The ruthenium(IV) dihydride complex $[Ru(P^iPr_3)_2H_2Cl_2]$, formed as a component of a "red solution" produced by boiling $[Ru(COD)Cl_2]_n$ with P^iPr_3/H_2 in ^tBuOH, reacts with $HC{\equiv}CH$ at RT to give the methylcarbene complex $[Ru(P^iPr_3)_2({=}CHMe)Cl_2]$.[283] Similarly, a red solution afforded by refluxing $[Ru(COD)Cl_2]_n$ with P^iPr_3/NEt_3 in ^iPrOH but without H_2 (which was mistakenly reported to give $[Ru(P^iPr_3)_2HCl]$[389]) reacts with $PhC{\equiv}CH$, followed by $HCl/PhCH{=}CH_2$ to afford $[Ru(P^iPr_3)_2({=}CHPh)Cl_2]$ in ca. 75% yield.[390] Addition of $PhC{\equiv}CH$ to $[Ru(P^iPr_3)_2H_2Cl_2]$ at RT affords $[Ru(P^iPr_3)_2({=}CHCH_2Ph)Cl_2]^*$ as the minor component in a mixture with $[Ru(P^iPr_3)_2({=}C{=}CHPh)Cl_2]$. By way of contrast, reaction with $HC{\equiv}CC^iPr_2(OH)$ or $HC{\equiv}CCPh_2(OAc)$ gives only $[Ru(P^iPr_3)_2({=}CHCH{=}CR_2)Cl_2]$ ($R = {}^iPr$, Ph).[287]

Treatment of $[Ru(PPh_3)_3HCl]$ with $HC{\equiv}CCMe_2Cl$ or $Ph_2C{=}C{=}CHCl$ in CH_2Cl_2 affords the carbene compounds $[Ru(PPh_3)_2({=}CHR)Cl_2]$ ($R = CH{=}CMe_2{}^*$, $CH{=}CPh_2$), although a simple change of solvent to the more coordinating MeCN results in the formation of $[Ru(PPh_3)_2({=}CHCH{=}CMe_2)(MeCN)Cl_2]$ instead. NMR studies in CD_2Cl_2 show this species to be in equilibrium with MeCN and $[Ru(PPh_3)_2({=}CHCH{=}CMe_2)Cl_2]$. Treatment of the acetonitrile complex with Me_3SiOTf in the presence of an excess of MeCN produces $[Ru(PPh_3)_2({=}CHCH{=}CMe_2)(MeCN)_2](OTf)_2$, an unusual dicationic and halide-free derivative of a Grubbs-type complex.[391] Upon refluxing a mixture of $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ with $Tl\{RB(pz)_2\}$ (R = 1,5-cyclooctanediyl), the agostic-stabilized complex $[Ru(PCy_3)\{RB(pz)_2\}({=}CHPh)Cl_2]^*$ can be generated.[392]

The synthesis of complexes containing different types of phosphine ligands, particularly water-soluble phosphines (e.g., 147 and 148), has been described.[393–396] Substitution of the two phosphine ligands in $[Ru(PR_3)_2({=}CHX)Cl_2]$ ($R = Ph$, $X = CH{=}CMe_2{}^*$; $R = Cy$, $X = Ph$) for the rigid bicyclic phosphine 9-cyclohexyl-9-phosphabicyclo[3.3.1]nonane (PhobCy) gives a new air-stable species.[397] The reaction of the trioctylphosphine complex $[Ru(PCoc_3)_2(\eta^2\text{-}H_2)HCl]$ with $HC{\equiv}CH$ in the presence of $MgCl_2/H_2O$ generates $[Ru(PCoc_3)_2({=}CHMe)Cl_2]$, which shows only poor activity as a metathesis catalyst; in the absence of $MgCl_2$ and H_2O, the hydrido(vinylidene) complex $[Ru(PCoc_3)_2({=}C{=}CH_2)HCl]$ is formed.[292] 1-Pyrroline reacts with $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ through phosphine substitution to give $[Ru(PCy_3)(1\text{-pyrroline})({=}CHPh)Cl_2]$; acyclic imines $RN{=}CHR^1$ ($R = Pr$, $R^1 = {}^iPr$; $R = {}^tBu$, $R = Pr$; $R = Ph$, $R^1 = Et$) react at the carbene functionality to generate the new Fischer carbenes $[Ru(PCy_3)_2({=}C(H)NHR)Cl_2]$.[398] The carbene group can also be modified to allow incorporation of $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ onto polymer surfaces.[399]



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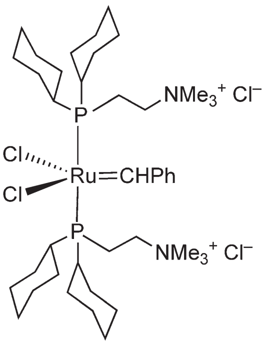

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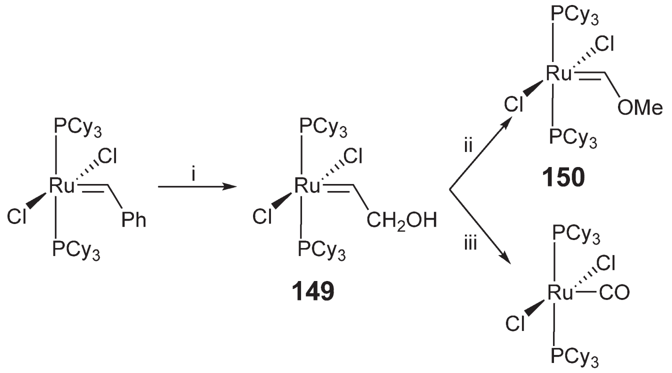
The active alkene metathesis catalyst $[Ru(PCy_3)_2(3\text{-phenylinden-1-ylidene})Cl_2]$ was obtained in high yield using a simple one-pot procedure via reaction of $[Ru(PPh_3)_3Cl_2]$ with $HC{\equiv}CCPh_2(OH)$ to afford $[Ru(PPh_3)_2(3\text{-phenylinden-1-ylidene})Cl_2]$, followed by exchange of PPh_3 for PCy_3.[400] Under rigorous air- and moisture-free conditions, $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ reacts with KO^tBu to form the four-coordinate species $[Ru(PCy_3)({=}CHPh)(O^tBu)_2]^*$. The complex is separated from the released PCy_3 by addition of CuCl to precipitate a copper chloride–PCy_3 polymer. The analogous fluorinated alkoxide complexes $[Ru(PCy_3)({=}CHPh)(OR)_2]$ ($R = C(CF_3)_2CH_3$, $C(CF_3)_3$) are produced by addition of the corresponding alcohols to the bis-*tert*-butoxide complex. All three precursors are active RCM catalysts, but only upon addition of HCl.[401] The cationic pyrazolylborate systems $[Ru(PCy_3)\{HB(pz)_3\}(L)({=}CHPh)](BF_4)$ ($L = H_2O^*$, MeCN, C_5H_5N) are unreactive for RCM of diethyl diallymalonate; however, their immediate precursor $[Ru(PCy_3)\{HB(pz)_3\}({=}CHPh)Cl]$ is active in the presence of HCl, CuCl, or $AlCl_3$.[402] The potent reducing agent and π-basic 14-electron complex $[Ru(P^iPr_3)_2HCl]$, available via the dimeric precursor $\{Ru(P^iPr_3)_2HCl\}_2$, reacts with THF



i, $H_2C{=}CHCH_2OH$; ii, solid; iii, solution

Scheme 18

under refluxing conditions by a double C–H activation reaction to yield the carbene complex $[Ru(P^iPr_3)_2\{{=}C(CH_2)_3O\}HCl]$ and an equimolar amount of the dihydrogen hydride species $[Ru(P^iPr_3)_2(\eta^2\text{-}H_2)HCl]$. The same chemistry occurs with $[Os(P^iPr_3)_2H_3Cl]$ and THF in the presence of the sacrificial hydrogen acceptor $^tBuCH{=}CH_2$.[403] The heteroatom derivatives $[Ru(P^iPr_3)_2({=}CHCH_2CH_2\text{-}C,N\text{-}C_5H_4N)Cl_2]^*$ and $[Ru(P^iPr_3)_2({=}CHS\text{-}p\text{-}RC_6H_4)Cl_2]$ ($R = H^*$, Me) are both air stable and active in metathesis reactions.[404]

Relatively recently, a number of reports have described decomposition pathways for Grubbs-type species. Thus, while the metathesis reaction of $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ ($L = PCy_3$) and allyl alcohol does indeed afford the expected (hydroxymethyl)carbene complex $[Ru(PCy_3)_2({=}CHCH_2OH)Cl_2]$ **149**, this proves to be unstable in solution decomposing to give the five-coordinate carbonyl species $[Ru(PCy_3)_2(CO)Cl_2]$. When a solid sample of **149** under argon is maintained at 60 °C for 6 h in the absence of solvent, the methoxycarbene isomer $[Ru(PCy_3)_2\{{=}C(OMe)H\}Cl_2]$ **150** is formed quantitatively (Scheme 18).[405] Reaction of $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ with primary alcohols at 70 °C results in alcohol dehydrogenation; in the case of $PhCH_2OH$, $[Ru(PCy_3)_2(CO)(Ph)Cl]$ is formed.[406] Facile hydrogenolysis of $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ to afford a range of interconvertible hydrido chloride complexes has been described.[407]

6.12.10.2 Bidentate Phosphine-based Systems

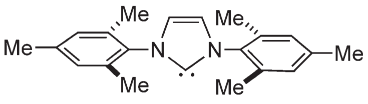
Treatment of $[Ru(COD)Cl_2]_x/Et_3N$ with dtbpm under a pressure of H_2 at elevated temperature affords the dimeric species $[\{Ru(dtbpm)H\}_2(\mu\text{-}Cl)_2]^*$, which upon subsequent reaction with $HC{\equiv}CCMe_2Cl$ generates $[Ru(dtbpm)\{{=}CHCH{=}CMe_2\}Cl_2]^*$, an interesting species in that it displays the stereoelectronic features of Grubbs-type systems, but has a novel *cis*-phosphine stereochemistry.[408] The dimeric precursor reacts with other terminal alkynes, chloroallene, or vinyl chlorides to yield a range of complexes $[Ru(dtbpm)\{{=}CHR\}Cl_2]$ ($R = CH{=}C(CH_2)_4CH_2$, $CH{=}CPh_2$, $CHMe_2^*$).[409] Two related complexes containing a *cis*-chelating phosphine ligand have been synthesized in the form of $[Ru(dtbpe)({=}CHPh)Cl_2]^{*}$[410] and the solvent-stabilised cationic complex $[Ru(^tBu_2PCH_2P^tBu_2)({=}CHCH{=}CMe_2)(MeCN)Cl](OTf)$.[411] Phosphine exchange in $[Ru(PPh_3)_2({=}CHPh)Cl_2]$ with the ferrocenylphosphine dppf also yields a *cis*-bidentate phosphine complex*; the more flexible phosphine xantphos is able to coordinate in a *trans*-arrangement*.[412]

The reaction of $[Ru(PPh_3)_3HCl]$ with $HC{\equiv}CCMe_2Cl$ affords $[Ru(PPh_3)_2({=}CHCH{=}CMe_2)Cl_2]$; although highly stable in the solid state, it slowly dimerizes in solution. Rapid phosphine exchange takes place with either PCy_3 or 1,3-$Cy_2PCH_2C_6H_4CH_2PCy_2$ (dcpx) at RT to afford $[Ru(PCy_3)_2({=}CHCH{=}CMe_2)Cl_2]$ and $[Ru(dcpx)({=}CHCH{=}CMe_2)Cl_2]$, respectively.[413] Rapid reaction takes place upon addition of $HC{\equiv}CPr$ to $[Ru\{1,3\text{-}(CH_2P^tBu_2)_2C_6H_4\}HCl]$ at RT to give two isomers of the carbene complexes $[Ru\{1,3\text{-}(CH_2P^tBu_2)_2C_6H_3\}({=}CMePr)Cl]^*$.[291]

6.12.10.3 NHC-based Systems

Facile substitution of PCy_3 in $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ by a range of aryl- and alkyl-substituted NHCs to give active air- and moisture-stable mixed phosphine–NHC alkene metathesis catalysts was first described in 1999.[414,415]

Subsequent reports have shown that replacement of one PCy_3 in $[Ru(PCy_3)_2({=}CHR)Cl_2]$ (R = Ph, $CH{=}CMe_2$) with an NHC ligand can be carried out by treatment with preformed NHC (IMes **151**, SIMes **152**, IPr **153**) or in a one-pot procedure involving use of imidazolium salt and potassium *tert*-butoxide or -amylate.[416–420] Related methodology has allowed derivitization of the NHC backbone with phenyl and alkyl groups to be undertaken.[421]



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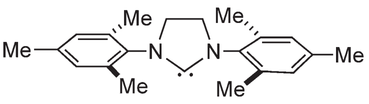

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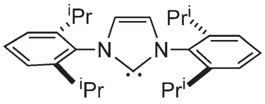
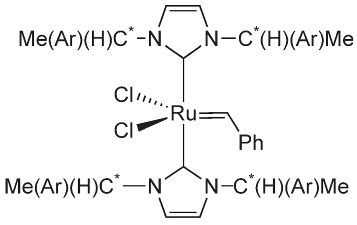


153

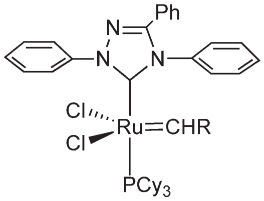
The NHC-susbstituted systems offer advantages in both stability and reactivity for ROMP and ring-closing metathesis polymerization.[422,423] The labile triphenylphosphine ligands in $[Ru(PPh_3)_2({=}CHCH{=}CMe_2)Cl_2]$ are readily replaced by PCy_3, IMes, or $2,6\text{-}(Cy_2PCH_2)_2C_6H_3$ to yield new metathesis catalysts. The reaction with IMes can be controlled to give either $[Ru(PPh_3)(IMes)({=}CHCH{=}CMe_2)Cl_2]$ or $[Ru(IMes)_2({=}CHCH{=}CMe_2)Cl_2]$. This contrasts with reaction of $[Ru(PPh_3)_2({=}CHPh)Cl_2]$, which does not yield the bis-carbene complex even upon reaction with a significant excess of carbene;[424,425] $[Ru(IMes)_2({=}CHPh)Cl_2]^*$ is formed upon addition of 1 equiv. of IMes to the bis-pyridine adduct $[Ru(IMes)({=}CHPh)(C_5H_5N)_2Cl_2]$.[426] Similarly, bis-NHC compounds can be prepared; thus, $[Ru(I^iPr_2)_2({=}CHPh)Cl_2]$ is highly active for ROMP of cyclooctene at RT, although the influence of substituent effects is apparent by the lack of reactivity of **154a** and **154b** in the same reaction until 60 °C.[427] Overall, reactivity follows the general order $[Ru(NHC)(PR_3)({=}CHR^1)Cl_2] > [Ru(NHC)_2({=}CHR^1)Cl_2] > [Ru(PR_3)_2({=}CHR^1)Cl_2]$.[428] The influence on $[Ru(L)(PR_3)({=}CHR^1)Cl_2]$ of L, R, R^1, and X on the use of these carbene complexes in catalytic alkene metathesis has been studied; in all cases, dissociative phosphine loss initiates catalytic activity. The higher activity seen with L = NHC compared to phosphine arises from increased selectivity for alkene binding over ligand recoordination (Scheme 19).[429,430]

A combined experimental and computational study of substrate-induced decomposition pathways for alkene metathesis catalysts reveals the importance of β-hydride transfer from ruthenacyclobutane intermediates. Subsequent steps afford allyl hydride species, which then eliminate H_2 to give catalytically inactive unsaturated complexes of the form $[RuL(\eta^2\text{-alkene})Cl_2]$.[431]



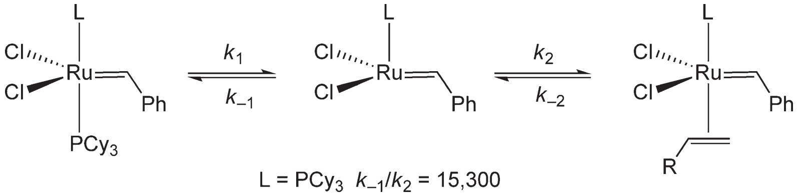
154

a: Ar = Ph
b: Ar = naphthyl



155

R = Ph
R = CH=CMe$_2$

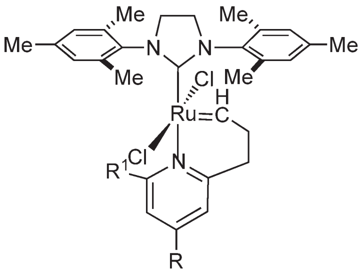


L = PCy_3 $k_{-1}/k_2 = 15{,}300$
L = SIMes $k_{-1}/k_2 = 1.25$

Scheme 19

Protected NHC alcohol or chloroform adducts provide a facile new methodology for the preparation of Grubbs-type metathesis complexes. While the triazole systems **155** can be made but prove to be unstable in solution, SIMes(H)(O^{t}Bu) readily loses ^{t}BuOH allowing formation of $[Ru(SIMes)(PCy)_3({=}CHPh)Cl_2]$. This complex shows unwanted side reactions with primary alcohols affording the known hydride chloride complex $[Ru(SIMes)(PCy_3)(CO)HCl]$,[432] and if not prepared with the rigorous exclusion of air, undergoes intramolecular NHC C–H activation to give **143***. Displacement of the remaining phosphine ligand by NHC in $[Ru(SIMes)(PCy_3)({=}CHPh)Cl_2]$ is not possible; synthesis of the bis-NHC complexes $[Ru(SIMes)_2({=}CHPh)Cl_2]$ and $[Ru(SIMes)(IMes)({=}CHPh)Cl_2]^*$ requires reaction of the bis-pyridine precursor $[Ru(SIMes)(C_5H_5N)_2({=}CHPh)Cl_2]$ with $SIMes(H)(CCl_3)$ or IMes, respectively.[375] The pyridine complex $[Ru(SIMes)(C_5H_4N)_2({=}CHPh)Cl_2]$[433] will react with various PR_3 ($R = p\text{-}XC_6H_4$ ($X = CF_3$, F, Cl, H, Me, OMe)) ligands at RT to afford a series of complexes of general structure $[Ru(SIMes)(PR_3)({=}CHPh)Cl_2]$. Rate constants for phosphine dissociation and relative rates for phosphine reassociation have been determined; the rate of phosphine loss increases with decreasing phosphine donor strength.[434] $[Ru(SIMes)(3\text{-}BrC_5H_3N)_2({=}CHPh)Cl_2]$ is easily prepared by the reaction of $[Ru(SIMes)(PCy_3)({=}CHPh)Cl_2]$ and 3-bromopyridine at RT.[435,436]

Addition of 2-(3-butenyl)pyridine to $[Ru(SIMes)(C_5H_4N)_2({=}CHPh)Cl_2]$ in CH_2Cl_2 gave $[Ru(SIMes)\{CH(CH_2)_2\text{-}C,N\text{-}2\text{-}C_5H_4N\}Cl_2]^*$ **156a** (with *trans*-NHC and pyridyl groups), which slowly isomerizes in solution to the *cis*-NHC/pyridyl species* **157**. The former species is more active than its isomer in RCM of diethyl diallylmalonate and ROMP of dicyclopentadiene.[437] The *in situ* combination of $\{Ru(p\text{-cymene})Cl_2\}_2$, IMesHCl, NaO^{t}Bu, and ^{t}BuC≡CH affords a coordinatively unsaturated carbene species of the form "$[Ru(IMes)({=}CH_2)Cl_2]$", which proves to be highly active for metathesis reactions and is also robust enough to be made up on the benchtop using reagent grade solvents and substrates.[438]



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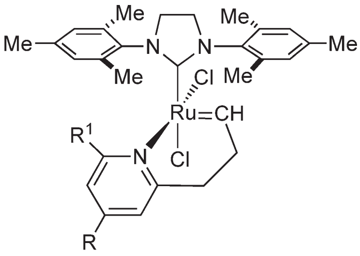
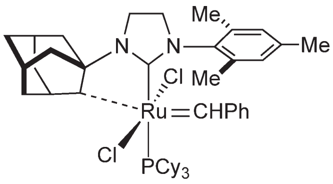


157

a: R = R^1 = H
b: R = Me, R^1 = H
c: R = H, R^1 = Me

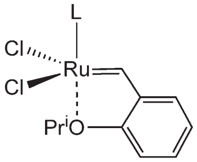
A range of new carbene complexes $[Ru(PCy_3)(L)\{{=}C(H)ER\}Cl_2]$ {$L = PCy_3$, ER = OEt*, SEt, SPh*, N(carbazole)*, N(pyrrolidinone)*; L = IMes, ER = OEt*, SEt, N(carbazole), N(pyrrolidinone) have been produced by addition of excess $H_2C{=}C(H)ER$ to $[Ru(PCy_3)_2({=}CHR)Cl_2]$ (R = Ph, $CHCMe_2$), and, where appropriate, subsequent reaction with the NHC. The thermal stability of the bis-phosphine systems decreases in the order ER = NR > CR > SR > OR, while the mixed PCy_3–IMes complexes all prove to be particularly thermally robust.[439] The molecular structure of the unsymmetrical NHC complex $[Ru(PCy_3)(SIAdMes)({=}CHPh)Cl_2]^*$ **158** shows that it is stabilized by an agostic interaction with the adamantyl group.[440]



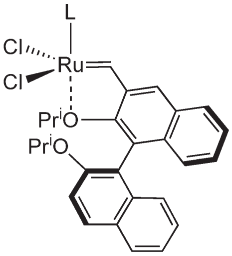
158

The substituted pyridine precursor [Ru(SIMes)(3-BrC$_5$H$_3$N)$_2$(═CPhH)Cl$_2$] reacts with (*Z*)-MeCH═CHMe, (*E*)-EtCH═CHEt and (*E*)-^{n}PrCH═CH^{n}Pr to give [Ru(SIMes)(3-BrC$_5$H$_3$N)$_2${═C(R)H}Cl$_2$] (R = Me*, Et, ^{n}Pr), respectively.[441,442] Addition of CH$_2$═CHOEt to these compounds affords [Ru(SIMes)(3-BrC$_5$H$_3$N)$_2$-{═C(OEt)H}Cl$_2$]; [Ru(SIMes)(3-BrC$_5$H$_3$N)$_2${═C(R)H}Cl$_2$] (R = Me, Et, ^{n}Pr) react with PCy$_3$ at RT to give [Ru-(SIMes)-(PCy$_3$){═C(R)H}Cl$_2$] (R = Me*, Et, ^{n}Pr).[441,442] Replacement of the halide ligands in [Ru(IMes)(C$_5$H$_5$N)(═CHPh)Cl$_2$] to give [Ru(IMes)(═CHPh)(C$_5$H$_5$N)(OC$_6$F$_5$)$_2$]* affords a highly active RCM catalyst.[443] [Ru(SIMes)(PCy$_3$)(═CHPh)Cl$_2$] reacts with α,β-unsaturated carbonyl compounds to form the enoyl carbene species [Ru(SIMes)(PCy$_3$)(═CHCOX)Cl$_2$] (X = H, R, OR, OH).[444] Alkene metathesis between [Ru(SIMes)(PCy$_3$)-(═CHPh)Cl$_2$] and H$_2$C═CF$_2$ affords the first example of a structurally characterized ruthenium methylidene complex, [Ru(SIMes)(PCy$_3$)(═CH$_2$)Cl$_2$]*, as well as the difluorocarbene species, [Ru(SIMes)-(PCy$_3$)(═CF$_2$)Cl$_2$]*.[445]

Considerable effort has been directed at the preparation of more active metathesis catalysts through transformations of the Ru═CRR^1 functionality.[446] Thus, the monophosphine system bearing a coordinated alkoxy functionality **159*** is formed in good yield upon reaction of [Ru(PPh$_3$)$_3$Cl$_2$] with the isopropoxy-functionalized aryldiazomethane at low temperature, followed by addition of PCy$_3$. Related methylether and naphthyl[447] complexes can likewise be synthesized. Other efforts have focused on the NHC derivatives with isolation of the green complex **160***,[448] biphenyl,[449] and functionalized aryl derivatives (e.g., **161**).[450,451] Both phosphine and NHC complexes can be incorporated onto dendritic[448] and polymer supports[452–454] and in sol-gels.[455,456] Most recently, variants incorporating chiral substituents into the NHC ligand[457–459] have started to be developed.

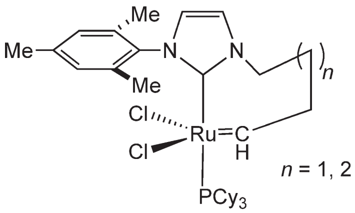


159: L = PCy$_3$
160: L = SIMes



161: L = SIMes

Other methodologies have employed chelating carbene ligands derived from 2-vinylbenzaldehyde or 2-vinylbenzoic acid ester,[460,461] backbone and *N*-alkyl-functionalized *N*-heterocyclic carbene ligands, including the novel chelate complexes **162**[462] and other types types of *N*-heterocyclic carbene ligands.[463] The carbene complex **163*** bearing a four-membered *N*-heterocyclic carbene is readily prepared by treatment of [Ru(PPh$_3$)(═CH-*o*-^{i}PrOC$_6$H$_5$)Cl$_2$] with the iminium salt and base at 60 °C.[464]



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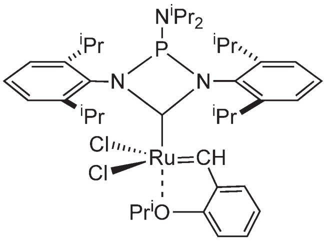
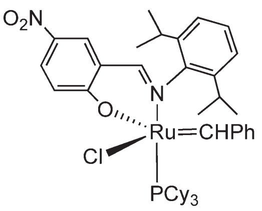
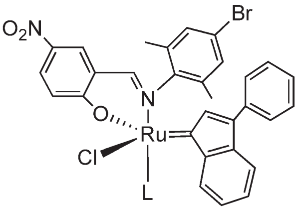


163

The Schiff base-stabilized complexes **164***, **165**, and especially **166** are readily prepared and prove to be air and moisture stable. They show good activity for ROMP of cyclopentene and cyclooctene.[465,466] Polymer-supported variants of both [Ru(PCy$_3$)$_2$(═CHR)Cl$_2$] and [Ru(PCy$_3$)(NHC)(═CHR)Cl$_2$] have been prepared.[417] Air- and moisture-stable Grubbs–Hoveyda-type complexes of the form [Ru(SIMes)(═CH-*o*-^{i}Pr-O-C$_6$H$_4$)(OTf)$_2$], [Ru(SIMes)(═CH-*o*-^{i}Pr-O-C$_6$H$_4$)(CF$_3$CO$_2$)$_2$]*, and [Ru(SIMes)(═CH-*o*-^{i}Pr-O-C$_6$H$_4$)(OTf)Cl]* show high activity for RCM at elevated temperature both in solution and upon being heterogenized onto polymer surfaces.[467] Additional complexes incorporating one NHC and either a chelating pyridinyl alcohol[468] or imine functionality[469] can be synthesized.



164

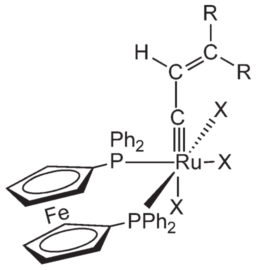


165: L = PCy$_3$
166: L = SIMes

6.12.11 Carbyne and Carbide Complexes

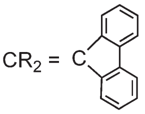
Simple hydride chloride complexes act as precursors for carbyne complexes upon reaction with alkynes. Treatment of [Os(PCy$_3$)$_2$H$_2$Cl$_2$] with 3 equiv. of HC≡CR (R = Ph, SiMe$_3$) at 60 °C yields [Os(PCy$_3$)$_2$(≡CCH$_2$R)HCl$_2$]; for R = SiMe$_3$, addition of traces of water results in complete conversion into [Os(PCy$_3$)$_2$(≡CMe)HCl$_2$]. With NaOMe, [Os(PCy$_3$)$_2$(≡CCH$_2$Ph)HCl$_2$] is converted into the vinylidene hydride complex [Os(PCy$_3$)$_2$(=C= CHPh)HCl], which is subject to protonation by HBF$_4$·OEt$_2$ yielding [Os(PCy$_3$)$_2$(≡CCH$_2$Ph)HCl](BF$_4$).[308] Thermolysis of terminal alkynes with the tri-isopropylphosphine analog, [Os(P^{i}Pr$_3$)$_2$H$_2$Cl$_2$], similarly generates [Os(P^{i}Pr$_3$)$_2$(≡CCH$_2$R)HCl$_2$] (R = Ph*, Cy, CPh$_2$(OH), CH$_2$C≡CSiMe$_3$), although with HC≡CSiMe$_3$, [Os(P^{i}Pr$_3$)$_2$-(≡CMe)HCl$_2$] is formed. Upon changing to the functionalized alkynes HC≡CCRR^1(OH) (R = Me, R^1 = Et; R = H, R^1 = cyclic-(CH$_2$)$_5$) or HC≡CCMe=CH$_2$, the hydrido alkenylcarbyne complexes **167–169** can be isolated (Scheme 20).[470]

The hemilabile phosphine complexes [Os{κ^2-(*P*,*O*)-^{i}Pr$_2$*P*CH$_2$C(*O*)OMe}{κ^1-(*P*)-^{i}Pr$_2$PCH$_2$C(O)OMe}H$_2$Cl$_2$] and [Os{κ^2-(*P*,*O*)^{i}Pr$_2$*P*CH$_2$C(*O*)OMe}$_2$Cl$_2$] react with HC≡CCPhR(OH) to give [Os{κ^2-(*P*,*O*)-^{i}Pr$_2$*P*CH$_2$C(*O*)OMe}-{κ^1-(*P*)-^{i}Pr$_2$PCH$_2$C(O)OMe}(≡CCH=CPhR)Cl$_2$] (R = Ph*, Me). The reaction of the related precursor [Os(P^{i}Pr$_3$){κ^1-(*P*)-^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$}H$_2$Cl$_2$] with HC≡CCPh$_2$(OH) affords the analogous carbyne product [Os(P^{i}Pr$_3$){κ^1-(*P*)-^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$}(≡CCH=CPh$_2$)HCl$_2$], while with HC≡CPh, the vinylidene complex [Os(P^{i}Pr$_3$){κ^2-(*P*,*N*)-^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$}(=C=CPh$_2$)Cl$_2$]* forms.[471] The reaction of [Ru(dppf)(η^3-2-C$_3$H$_4$Me)$_2$] with HC≡CCR$_2$(OH) in the presence of 3.5 equiv. of HX at RT provides a straightforward synthetic route to the alkenyl carbyne complexes *fac*-[Ru(dppf)(≡CCH=CR$_2$)X$_3$] (**170**, R = Ph*, ^{i}Pr*; R$_2$ = C$_{13}$H$_8$; X = Cl*, Br).[472] The intermediacy of dinuclear allenylidene species [{Ru(dppf)$_2$(=C=C=CR$_2$)X(μ-X)}$_2$] in the reaction pathway can be established through their preparation and isolation from **170**.



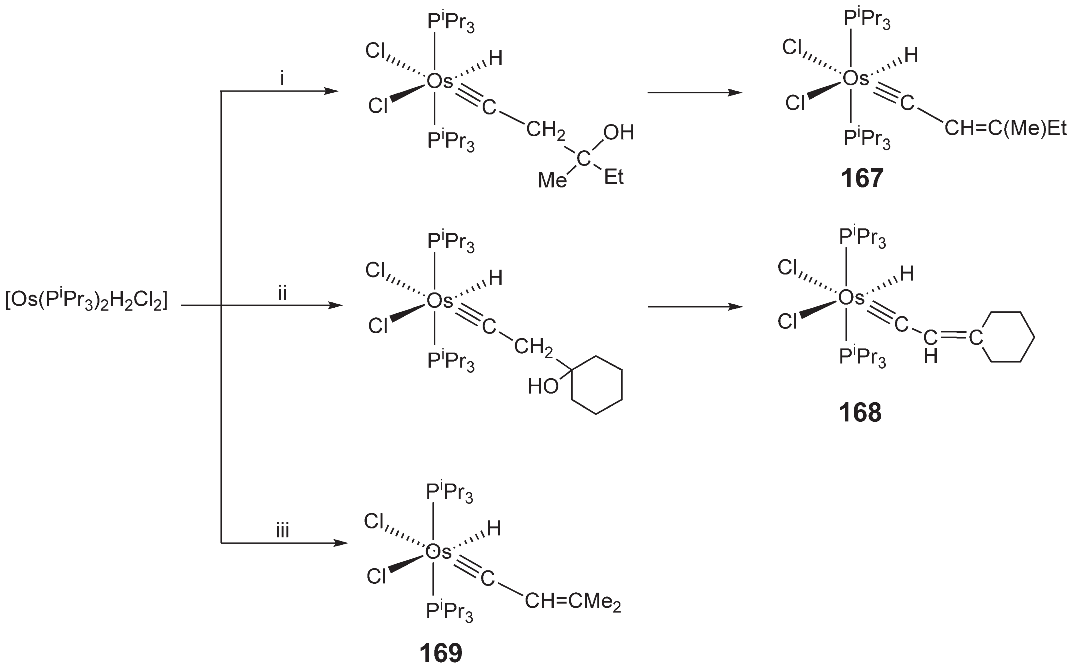
170

R = Ph, ^{i}Pr



X = Cl, Br

Propargylic chlorides also provide a route to osmium carbyne complexes.The reaction of [Os(PCy$_3$)$_2$H$_3$Cl] with HC≡CMe$_2$Cl at −40 °C affords a mixture of [Os(PCy$_3$)$_2$(≡CCH=CMe$_2$)HCl$_2$]* and [Os(PCy$_3$)$_2$(=CHCH= CMe$_2$)-(η^2-H$_2$)Cl$_2$]; the former is the sole product isolated upon warming to RT.[308] Related species have also been reported by Caulton and co-workers[473] as being formed upon heating [Os(P^{i}Pr$_3$)$_2$H$_2$Cl$_2$] with either CH$_2$=CHMe or



i, 3-methyl-1-pentyn-3-ol; ii, 1-ethynyl-1-cyclohexanol; iii, 2-methyl-1-buten-3-yne

Scheme 20

$CH_2{=}CHPh$ at 60 °C. Treatment of $[Ru(PPh_3)_3HCl]$ with a fourfold excess of $HC{\equiv}CCMe_2Cl$ produces the Ru(IV) carbyne complex $[Ru(PPh_3)_2({\equiv}CCH{=}CMe_2)Cl_3]$.*[413]

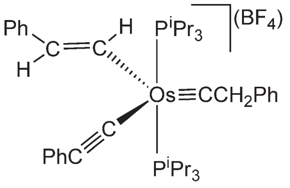
Addition of $HC{\equiv}CR$ to $[Os(PPh_3)_3Cl_2]$ affords $[Os(PPh_3)_2({\equiv}CCH_2CMe_3)Cl_3]^*$ along with $[Os(PPh_3)_2({=}C{=}CHMe)\{C(C{\equiv}CCMe){=}CHCMe_3\}Cl]$,[320] (although it is formed as the only product if the reaction is performed in the presence of HCl), whereas $[Os(PPh_3)_2({\equiv}CCR)Cl_3]$ (R = Ph*, *p*-tolyl, ^{t}Bu) can be generated more cleanly.[474] The reaction with R = $CPh_2(OH)$ at RT produces both *fac*- and *mer*-$[Os(PPh_3)_2({\equiv}CCH{=}CPh_2)Cl_3]^*$ in conjunction with the allenylidene $[Os(PPh_3)_2(CO)({=}C{=}C{=}CPh_2)Cl_2]^*$. Only the latter two complexes form if the reaction is performed in refluxing toluene.[475] Addition of 1 equiv. of $HC{\equiv}CH$, $HC{\equiv}C^tBu$, or $HC{\equiv}CSiMe_3$ to $[Os(P^iPr_3)_2(\kappa^2\text{-}O_2CMe)(H_2O)H_2](BF_4)$ affords the carbyne complexes $[Os(P^iPr_3)_2({\equiv}CCMe)(\kappa^2\text{-}O_2CMe)H](BF_4)$, $[Os(P^iPr_3)_2({\equiv}CH_2CMe_3)(\kappa^2\text{-}O_2CMe)H](BF_4)$, and $[Os(P^iPr_3)_2({\equiv}CMe)(\kappa^2\text{-}O_2CMe)H](BF_4)$, respectively, along with elimination of water.[310,476] With the propargylic alkynes, $HC{\equiv}CCMe_2(OH)$ and $HC{\equiv}CCPhMe(OH)$, $[Os(P^iPr_3)_2\{{\equiv}CCH_2CMe_2(OH)\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ and $[Os(P^iPr_3)_2\{{\equiv}CCH_2CMePh(OH)\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ are formed.[357] The low-temperature addition of $H_2C{=}CH(OPh)$ to $[Os(P^iPr_3)_2H_3Cl]$ allows the clean formation of $[Os(P^iPr_3)_2({\equiv}CMe)(OPh)HCl]$ upon warming the mixture above RT.[351] The related species $[Os(P^iPr_3)_2({\equiv}CMe)(O_2CCF_3)HCl]$ can be prepared from $H_2C{=}C(H)O_2CCF_3$; in contrast, $\{Ru(P^iPr_3)_2HCl\}_2$, which affords the same "$[M(P^iPr_3)_2HCl]$" intermediate produces the carbene complex $[Ru(P^iPr_3)_2({=}CHMe)(O_2CCF_3)Cl]$. This difference is again attributable to Os preferring a higher coordination number and oxidation state, as described earlier.[58,477] Similarly, the trihydride precursor reacts with either $CH_2{=}CHF$ or $CH_2{=}CF_2$ to yield $[Os(P^iPr_3)_2({\equiv}CMe)HFCl]$.[478]

A number of vinylidene complexes have been converted into carbyne complexes upon protonation. Thus, the low temperature (−80 °C) addition of $HBF_4{\cdot}OEt_2$, $[HNMe_2Ph]\{B(C_6F_5)_4\}$, or $[H(OEt_2)_2](BAr^F{}_4)$ to $[Ru(PCy_3)_2({=}C{=}CH_2)Cl_2]$ gives the cationic carbyne complexes $[Ru(PCy_3)_2({\equiv}CMe)Cl_2](X)$ (X = BF_4, $B(C_6F_5)_4$, $BAr^F{}_4$). These compounds are quite unstable, decomposing over ca. 30 min in solution at RT.[479] In an effort to prepare more stable complexes, $[Ru(P^iPr_3)_2(\kappa^2\text{-}O_2CR)({=}C{=}CHPh)Cl]$ (R = CH_2F, CHF_2, CF_3, 4-$NO_2C_6H_4$, 2-$NO_2C_6H_4$, C_6F_5, 2,4-$(NO_2)_2C_6H_3$) have been used, the aim of the electron-withdrawing substituents on the carboxylate group being to reduce intramolecular chemistry that leads to carbene formation instead. In fact, as exemplified by the trifluoromethyl derivative, $[Ru(P^iPr_3)_2({\equiv}CCH_2Ph)(\kappa^2\text{-}O_2CCF_3)Cl](BAr^F{}_4)^*$ exists in solution in equilibrium with the corresponding carbene complex, $[Ru(P^iPr_3)_2\{{=}C(CH_2Ph)OC(O)CF_3\}Cl]$ $(BAr^F{}_4)$ (Scheme 16; R=CF_3).[289,346]

Similarly, addition of $HBF_4{\cdot}OEt_2$ to $[Ru({}^tBu_2PCH_2CH_2Ph)_2({=}C{=}CH_2)HCl]$ at −78 °C produces $[Ru({}^tBu_2PCH_2CH_2Ph)_2\ ({\equiv}CMe)(OEt_2)HCl](BF_4)$;[293] and $[Ru(PR_3)_2({=}C{=}CHR)Cl_2]$ reacts with $[H(OEt_2)_2]$-$(BAr^F{}_4)$ to give $[Ru(PR_3)_2\ ({\equiv}CCH_2R)Cl_2](BAr^F{}_4)$ ($PR_3 = P^iPr_3{}^*$, PCy_3; $R = Ph^*$, ${}^tBu$).[346]

Treatment of the vinylidene complex $[Os(P^iPr_3)_2(\kappa^2\text{-}O_2CMe)({=}C{=}CHCMe{=}CH_2)H]$ with $HBF_4{\cdot}OEt_2$ affords the cationic carbyne complex $[Os(P^iPr_3)_2(\kappa^2\text{-}O_2CMe)({\equiv}CCH{=}CMe_2)H](BF_4)^*$[315] while reaction of $[Os(P^iPr_3)_2(NH{=}CMe_2)HCl_2]$ with AgOTf and then $HC{\equiv}CR$, $HC{\equiv}CCMe{=}CH_2$, or $HC{\equiv}CCPhR^1(OH)$ forms $[Os(P^iPr_3)_2(NH{=}CMe_2)({\equiv}CCH_2R)Cl](OTf)$ ($R = H^*, Cy, (CH_2)_2CH_3$), $[Os(P^iPr_3)_2(NH{=}CMe_2)$-$({\equiv}CCH{=}CMe_2)Cl](OTf)$, and $[Os(P^iPr_3)_2(NH{=}CMe_2)\{{\equiv}CCH{=}C(R^1)Ph\}Cl](OTf)$ ($R^1 = H$, Me, Ph), respectively.[208] Protonation of $[Ru\{\kappa^2\text{-}(P,O)\text{-}PCy_2CH_2CH_2OMe\}_2\}({=}C{=}C{=}CPh_2)Cl](PF_6)$ by $HBF_4{\cdot}OEt_2$ yields the cationic carbyne complex $[Ru\{\kappa^2\text{-}(P,O)\text{-}PCy_2CH_2CH_2OMe)\}(\kappa\text{-}P\text{-}PCy_2CH_2CH_2OMe)({\equiv}CCH{=}CPh_2)$-$Cl](PF_6)_2$.[331] The vinylidene alkyne complex $[Os(P^iPr_3)_2({=}C{=}CH_2)(\eta^2\text{-}HC{\equiv}CR)H](BF_4)$ reacts with $Me_2C{=}NOH$ affording $[Os(P^iPr_3)_2({\equiv}CMe)\{\kappa\text{-}(N,O)\text{-}ON{=}CMe_2\}H](BF_4)$.[164] The cyclometallated complex $[Os(P^iPr_3)_2\{C_6H_4C(O)Me\}\ \{N(OH){=}CMe_2\}(\eta^2\text{-}H_2)](BF_4)$ eliminates acetophenone in the presence of $RC{\equiv}CH$ to afford $[Os(P^iPr_3)_2\{\kappa\text{-}N,\kappa\text{-}O\text{-}(ON{=}CMe_2)\}({\equiv}CCH_2R)H](BF_4)$ ($R = Ph^*, Cy, {}^tBu$). Treatment with $HBF_4{\cdot}Et_2O$ generates the fluoro–oxime $[Os(P^iPr_3)_2(F{\cdot\cdot}HON{=}CMe_2)({\equiv}CCH_2R)H](BF_4)$ ($R = Ph$, Cy^*, ${}^tBu$) complexes.[165] The remarkable, but thermally unstable, complex $[Os(P^iPr_3)_2({\equiv}CCH_2Ph)(C{\equiv}CPh)\{(E)\text{-}CH{=}CHPh\}](BF_4)^*$**171**, a species containing three different types of metal–carbon bonds, results from addition of $PhC{\equiv}CH/HBF_4{\cdot}OEt$ to $[Os(P^iPr_3)_2\{C_6H_4C(O)\text{-}Me\}(H_2O)(\eta^2\text{-}H_2)](BF_4)$ at low temperature.[480]

Addition of of an excess of NaCl to **171** yields the isometallabenzene complex* **172** which has the structure of a 1,2,4-cyclohexatriene.[480] In somewhat related chemistry, the neutral and cationic metallabenzyne complexes $[Os$-$(PPh_3)_2\{{\equiv}CC(SiMe_3)CMeC(SiMe_3)C\}Cl_2]^*$,[321] $[Os(PPh_3)_2\{{\equiv}CC(R)CMeC(R)C\}Br_2]$ ($R = Br^*, H^*$), and $[Os(PPh_3)_2$-$\{{\equiv}CC(R)CMeC(R)C\}(H_2O)Cl](BF_4)$ ($R = SiMe_3{}^*$, H) have been produced by reaction of $[Os(PPh_3)_3Cl_2]$ with an excess of $HC{\equiv}CSiMe_3$, and subsequent protonation or electrophilic substitution.[481]



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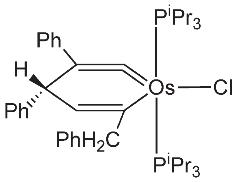

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Addition of 2 equiv. of LiR (R = 1-naphthyl, Ph) to THF solutions of $[M(PPh_3)_2(CO)({=}CCl_2)Cl_2]$ (M = Ru, Os) at low temperature affords the carbyne complexes $[M(PPh_3)_2(CO)({\equiv}CR)Cl]$; the synthesis of the osmium 2-naphthyl analog requires the presence of tmeda. Upon addition of CO in the presence of $AgClO_4$, the cationic dicarbonyl carbyne complexes $[M(PPh_3)_2(CO)_2({\equiv}CR)](ClO_4)$ proved isolable (M = Os, R = 1-naphthyl*, 2-naphthyl; M = Ru, R = Ph, 1-naphthyl).[69] Chloride abstraction from $[Ru(PCy_3)_2({=}CHPh)Cl_2]$ using 2 equiv. of $TlOC_6F_5$ at RT produces the highly coordinatively unsaturated species $[Ru(PCy_3)_2({\equiv}CPh)(OC_6F_5)]^*$, which remarkably proves to be air stable.[443]

Halide abstraction from $[RuL_2({=}C{=}CHR)HCl]$ ($L = P^tBu_2Me$, P^iPr_3; $R = H, Ph$) by NaOPh affords $[RuL_2({=}C{=}CHR)H(OPh)]$; the parent complex (R = H) spontaneously isomerizes at RT in benzene or toluene over the course of an hour to give the the four-coordinate carbyne complexes $[RuL_2({\equiv}CMe)(OPh)]$. The rate of this isomerization may be slowed dramatically if the solvent is changed to THF. Direct addition of NaOPh (2 equiv.) to the benzylidene complexes $[RuL_2({=}CHPh)Cl_2]$ rapidly affords the analogous $[RuL_2({\equiv}CPh)(OPh)]$ complex ($L = P^iPr_3{}^*$, PCy_3).[482]

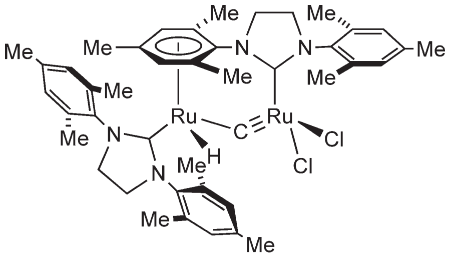
There are cases of carbyne derivitization. Addition of 1 equiv. of NaOMe to $[Os(P^iPr_3)_2({\equiv}CCH_2Ph)HCl_2]$ yields $[Os(P^iPr_3)_2({=}C{=}CHPh)HCl]$; this complex converts into the cationic carbyne species $[Os(P^iPr_3)_2$ $({\equiv}CCH_2Ph)(H_2O)HCl](BF_4)$ upon reaction with $HBF_4{\cdot}H_2O$.[223] Under 1 atm of CO, $[Os(P^iPr_3)_2({\equiv}CCH_2R)HCl_2]$ (R = Ph, Me) affords the osmium carbene complexes $[Os(P^iPr_3)_2({=}CHCH_2R)(CO)Cl_2]$. Chloride abstraction from the carbyne complexes by $NaBAr^F{}_4$ yields $[Os(P^iPr_3)_2({\equiv}CCH_2R)HCl](BAr^F{}_4)$, which, for R = Ph, reacts with L^1 (CO, $HC{\equiv}CR^1$ ($R^1 = {}^tBu$, Me)), initially to produce the carbene species $[Os(P^iPr_3)_2(L^1)({=}CHCH_2Ph)Cl](BAr^F{}_4)$, but ultimately (through release of HCl and then reprotonation) either $[Os(P^iPr_3)_2(CO)_3Cl](BAr^F{}_4)$ and $CH_2{=}CHPh$ or $[Os(P^iPr_3)_2({\equiv}CCH_2R^1)\{(E)\text{-}CH{=}CHPh\}Cl](BAr^F{}_4)$.[221]

The six-coordinate carbyne complex $[Os(P^iPr_3)_2(\equiv CCH_2Ph)HCl_2]$ reacts with pyrazole (Hpz) in the presence of KOH to yield the vinylidene species $[Os(P^iPr_3)_2(=C=CHPh)(Hpz)(pz)H]^*$. Addition of $HBF_4 \cdot OEt_2$ affords the fluoro carbyne complex $[Os(P^iPr_3)_2(\equiv CCH_2Ph)(Hpz)HF](BF_4)^*$, the structure of which displays intra- and intermolecular F$\cdots$H–pz hydrogen bonding interactions. Facile displacement of H_2O in $[Os(P^iPr_3)_2(\equiv C\text{-}CH_2Ph)(H_2O)HCl](BF_4)$ by pyrazole or MeCN yields $[Os(P^iPr_3)_2(\equiv CCH_2R)(L)HCl](BF_4)$ (L = Hpz, MeCN).[483]

Treatment of $[Os(=CH^tBu)_2(CH_2^tBu)_2]$ with pyridinium triflate in the presence of an excess of pyridine yields $[Os(\equiv C^tBu)(CH_2^tBu)_2(C_5H_5N)_2(OTf)]$, which reacts with a range of nucleophiles to give $[Os(\equiv C^tBu)(CH_2^tBu)_2(L)]$ (L = $N(SiMe_3)_2$, η^5-C_5H_5, $HB(pz)_3{}^*$).[167]

The low-temperature reaction of $[Os(P^iPr_3)_2\{\equiv CCH_2CMePh(OH)\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ with NaOMe results in deprotonation and dehydration to give the alkenyl vinylidene complex $[Os(P^iPr_3)_2(=C=CHCPh=CH_2)(\kappa^2\text{-}O_2CMe)H]$. In the absence of NaOMe, both $[Os(P^iPr_3)_2\{\equiv CCH_2CMePh(OH)\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ and $[Os(P^iPr_3)_2\{\equiv CCH_2CMe_2(OH)\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ undergo slow dehydration (accelerated by addition of Al_2O_3) forming $[Os(P^iPr_3)_2\{\equiv CCH=C(Me)R\}(\kappa^2\text{-}O_2CMe)H](BF_4)$.[357]

The stoichiometric reaction between $[Ru(PCy_3)(L)(=CHPh)Cl_2]$ and *trans*-2,3-dicarbomethoxymethylenecyclopropane remarkably affords the ruthenium carbide complexes $[Ru(PCy_3)(L)(\equiv C)Cl_2]$ (L = PCy_3, IMes*).[484] The bis-PCy_3 complex* can also be made through addition of an excess of PCy_3 to $[Ru(PPh_3)_2\{=C(CHCO_2Me)_2\}Cl_2]$ and shows good donor properties yielding heterobimetallic complexes with Mo and Pd.[485] Protonation of the carbide complex $[RuLL^1(\equiv C)Cl_2]$ by $[H(OEt_2)_2](BX_4)$ (X = C_6F_5, F) produces the 14-electron phosphonium carbene complexes $[RuL(=CHL^1)Cl_2](BX_4)$ (L = L^1 = P^iPr_3, PCy_3; L = SIMes*, L^1 = $PCy_3{}^*$).[486,487] The bridging carbide complex **173*** is formed via a decomposition pathway of the carbene complex $[Ru(SIMes)(PCy_3)(=CH_2)Cl_2]$.[488]



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6.13
Mononuclear Ru/Os Compounds with Hydrocarbon Ligands: Compounds with η^2–η^4 Ligands

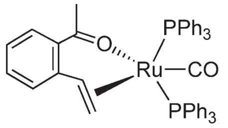
M K Whittlesey, University of Bath, Bath, UK

6.13.1 Ruthenium and Osmium η^2-Alkene Complexes

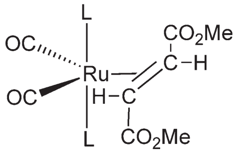
Room temperature (RT) photolysis of $[Ru_3(CO)_{12}]$ under a flow of ethene yields $[Ru(CO)_4(\eta^2\text{-}C_2H_4)]$[1,2] in quantitative yield; this complex can be trapped as $[Ru(CO)_3(\eta^2\text{-}C_2H_4)(MeCN)]$ if acetonitrile is added to the photolysis mixture (ethene flow being maintained). Photolysis of the cluster in the presence of an excess of acrylonitrile instead of ethene gives $[Ru(CO)_4(\eta^2\text{-}CH_2{=}CHCN)]$, which reacts under the photolytic conditions with MeCN (but in the absence of acrylonitrile) to form $[Ru(CO)_3(\eta^2\text{-}CH_2{=}CHCN)(MeCN)]$; additional acrylonitrile leads to $[Ru(CO)_3(\eta^2\text{-}CH_2{=}CHCN)_2]$.[3] Facile ethene loss from $[Ru(CO)_4(\eta^2\text{-}C_2H_4)]$ occurs in the presence of bidentate phosphine to afford $[Ru(\eta^1\text{-P–P})(CO)_4]$ (P–P = dppe, dppp, dppa, dppm, dpph).[4] Photolysis of $[Ru_3(CO)_{12}]$ in the presence of the alkene-functionalized polymer supports butenyl polystyrene or acryloyl polystyrene yields the air-stable, supported species $[Ru(CO)_4(\eta^2\text{-alkene})]$. These release about 30% of the $[Ru(CO)_4]$ fragment in the presence of ligands such as PPh_3.[5] Reversible dissociation of ethene and methyl acrylate from $[Ru(CO)_4(\eta^2\text{-alkene})]$ affords $[Ru(CO)_4]$; the kinetics of competition between alkene and 12 PR_3 ligands indicates a negligible dependence of rate on the electron-donating ability of the phosphine, although there is a small dependence on size.[6] While previous low-temperature X-ray[7] and vibrational spectroscopy[8] studies indicated the metallocyclopropane nature of $[Os(CO)_4(\eta^2\text{-}C_2H_4)]$, the use NMR spectroscopy in liquid crystal solvents has allowed measurement of $^{13}C–^1H$ and $^1H–^1H$ dipolar couplings in solution, thereby providing values for bond angles and bond lengths within the ethene fragment—these show that the osmacyclopropane structure is still retained in solution.[9] The kinetics of alkene loss from $[Os(CO)_4(\eta^2\text{-alkene})]$ in the presence of $P(OEt)_3$ or PPh_3 suggest a dissociative pathway with entropies of activation ($\Delta S^{\ddagger} = 60–80\,J\,K^{-1}\,mol^{-1}$) which are far more positive than reported for the dissociative loss of CO from $[Os(CO)_5]$ ($\Delta S^{\ddagger} = -2 \pm 10\,J\,K^{-1}\,mol^{-1}$). Carbonyl dissociation occurs in addition to alkene loss as shown by the formation of substantial amounts of $[Os(PR_3)_2(CO)_3]$.[10] The first mononuclear η^2-C_{60} complex of osmium, $[Os(PPh_3)_2(CO)(\eta^2\text{-}C_{60})(CN^tBu)]^*$ (throughout the chapter, complexes which have been structurally characterized are denoted with an asterisk), results from refluxing $[Os(PPh_3)_3(CO)H_2]$ with C_{60} in the presence of the isocyanide.[11]

Thermolysis of $[Ru(PPh_3)_3(CO)H_2]$ first with a stoichiometric amount of $CH_2{=}CHPh$, and then with a stoichiometric amount of *o*-acetylstyrene, yields the alkene complex **1**.[12] The fluxional, five-coordinate Ru(0) ethene complex $[Ru(PPh_3)_3(CO)(\eta^2\text{-}C_2H_4)]^*$ was readily prepared by refluxing the same ruthenium dihydride precursor under a flow of ethene.[13] A range of alkene complexes $[RuLL^1(CO)_2(\eta^2\text{-alkene})]$ $\{L = L^1 = PMe_2Ph, AsMe_2Ph,$

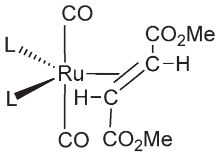
$L = PMe_2Ph$, $L^1 = P(OMe)_3$, alkene = (*E*/*Z*)-$MeO_2CCH{=}CHCO_2Me$; $L = L^1 = PMe_2Ph$, alkene = $H_2C{=}CH_2$, $H_2C{=}CHCO_2Me$, (*E*)-$NCCH{=}CHCN$, (*Z*)-$MeO_2CCH{=}CClCO_2Me$, (*E*/*Z*)-$MeO_2CCH{=}CPhCO_2Me$} have been found by NMR, IR, and X-ray crystallography to exist in three stereochemical arrangements **2a–2c**.[14] The 14-electron agostic-stabilized species $[Ru(P^tBu_2Me)_2(CO)H](BAr^F{}_4)$ coordinates ethene, propene, and C_2H_3F *trans* to hydride. Vinyl ethers $CH_2{=}CH(OR)$ bind to the ruthenium center initially via an η^1-ether oxygen interaction (*trans* to CO), although facile isomerization takes place at −60 °C to give $[Ru(P^tBu_2Me)_2(CO)(\eta^2\text{-}CH_2CH_2OR)]$ (R = Me*, Et).[15]



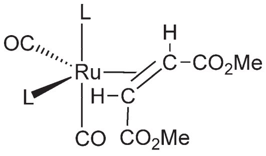
1



2a



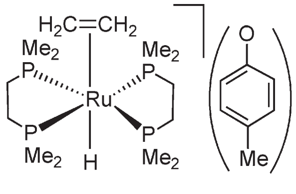
2b



2c

The ruthenium(0) ethene complex, $[Ru(dmpe)_2(\eta^2\text{-}C_2H_4)]$, can be prepared by dehydration of *trans*-$[Ru(dmpe)_2(OH)H]$ in the presence of ethene at high temperature[16] or, more conveniently, by reaction of *trans*-$[Ru(dmpe)_2Cl_2]$ with an excess of ethene in the presence of sodium metal. Subsequent reactions of the ethene complex with a range of electrophiles HX lead, in most cases, to products $[Ru(dmpe)_2(X)H]$; in the case of 4-HOC_6H_4Me, however, the intermediate alkene hydride complex, *trans*-$[Ru(dmpe)_2(\eta^2\text{-}C_2H_4)H](4\text{-}OC_6H_4Me)$ **3** can be isolated at low temperature en route to the final cresolate hydride, *trans*-$[Ru(dmpe)_2(4\text{-}OC_6H_4Me)H]$*.

The PMe_3 variant, $[Ru(PMe_3)_4(\eta^2\text{-}C_2H_4)]$, shows similar chemistry, although interestingly, it does react with C_2D_4 to yield $[Ru(PMe_3)_3(\eta^2\text{-}C_2H_4)(\eta^2\text{-}C_2D_4)]$, pointing to the lability of the coordinated phosphines.[17] Treatment of $[Ru(PMe_3)_4(\eta^2\text{-}C_2H_4)]$ with $[B(C_8H_{14})(\mu\text{-}H)]_2$ at −80 °C affords $[Ru(PMe_3)_3\{\eta^2,\eta^1\text{-}CH_2{=}CHB(C_8H_{14})(\mu\text{-}H)\}H]$, as a 2 : 1 mixture of *fac*-* and *mer*-isomers **4a and 4b**.[18] The dihydride $[Ru(PPh_3)_4H_2]$ reacts with $H_2C{=}CHCO_2Me$ to form two isomers of $[Ru(PPh_3)_2(H_2C{=}CHCO_2Me)_2]$ in solution; in the major isomer, one of the ligands is η^2-coordinated and the other η^4-coordinated as a 1-oxabutadiene ligand **5**. In the presence of water, a five-coordinate aqua adduct* is trapped out.[19] Addition of C_2H_4 to $[Ru(PCy_3)_2(\eta^2\text{-}H_2)_2H_2]$ yields $[Ru(PCy_3)\{(\eta^3\text{-}C_6H_8)PCy_2\}(\eta^2\text{-}C_2H_4)]$, which contains an η^3-cyclohexenyl ring. When the alkene is changed to dimethyl maleate, the ruthenium(II) alkene dihydride complex $[Ru(PCy_3)_2(\eta^2\text{-}MeO_2CCH{=}CHCO_2Me)H_2]$ is formed.[20] Phenyl vinyl ether and vinyl sulfides react with $[Ru(\eta^4\text{-}1,5\text{-}COD)(\eta^6\text{-}1,3,5\text{-}COT)]$ in the presence of depe to yield $[Ru(depe)(\eta^4\text{-}1,5\text{-}COD)\{\eta^2\text{-}H_2C{=}CH(EX)\}]$ (EX = OPh*, SPh*, SCH_2Ph, SEt, $SCHMe_2$). Addition of PMe_3 to $[Ru(depe)(\eta^4\text{-}1,5\text{-}COD)\{\eta^2\text{-}H_2C{=}CHSPh\}]$ yields a 2 : 1 mixture of $[Ru(depe)(PMe_3)_2\{\eta^2\text{-}H_2C{=}CHSPh\}]$ and $[Ru(depe)(PMe_3)(\eta^4\text{-}1,5\text{-}COD)]$, but upon phosphine addition to $[Ru(depe)(\eta^4\text{-}1,5\text{-}COD)\{\eta^2\text{-}H_2C{=}CHCH_2Ph\}]$, a 30 : 70 mixture of $[Ru(depe)(PMe_3)_2\{\eta^2\text{-}H_2C{=}CHCH_2Ph\}]$ and $[Ru(depe)(PMe_3)(\eta^4\text{-}1,5\text{-}COD)]$ is formed.[21]



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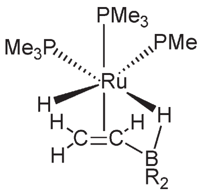
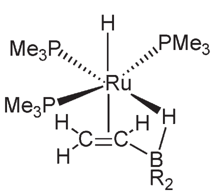
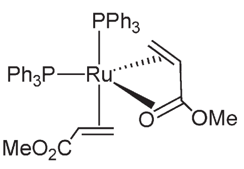


4a



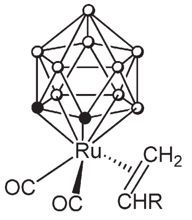
4b



5

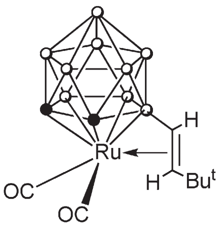
The coordinated THF ligand in the carborane-stabilized dicarbonyl solvent complex $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(THF)]$[22] is easily displaced by alkenes to give $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(\eta^2\text{-alkene})]$ (alkene = C_2H_4 **6a**, $MeCH{=}CH_2$ **6b**, $Me_3SiCH{=}CH_2$ **6c**).[23] A range of non-simple coordinated alkene complexes are formed by reactions of $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(L)(CO)(THF)]$ (L = CO, PPh_3)[22,24] with $RC{\equiv}CH$. Thus, reaction of 1 mol equivalent of $^tBuC{\equiv}CH$ with the dicarbonyl species gives the isomeric species $[Ru(\eta^2{:}\eta^5\text{-}9\text{-}CH{=}CH^tBu\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2]$*

7 and [Ru(η^2:η^5-10-CH═CH^{t}Bu-7,8-$C_2B_9H_{10}$)$(CO)_2$]. In the case of the phosphine carbonyl, reaction with PhC≡CH generates [Ru(η^2:η^5-(*E*)-9-CH═CHPh-7,8-$C_2B_9H_{10}$)(PPh_3)(CO)]* while ^{t}BuC≡CH produces [Ru(η^2:η^5-9-(*E*)-CH═CH^{t}Bu-10-(*E*)-C(H)═C(H)^{t}Bu-7,8-$C_2B_9H_9$)(PPh_3)(CO)], in which only one of the alkenyl groups is coordinated to the metal, the other being pendant. The coordinated alkene is displaced upon addition of a Lewis base, CO, PMe_3, or ^{t}BuNC. The reaction of the dicarbonyl complex with Me_3SiC≡CH leads to coordination as well as competitive C–Si bond cleavage (such cleavage also occurs with the phosphine carbonyl precursor), resulting in [Ru(η^2:η^5-9-CH═CHR-7,8-$C_2B_9H_{10}$)$(CO)_2$] and [Ru(η^2:η^5-10-CH═CHR-7,8-$C_2B_9H_{10}$)$(CO)_2$] (R = $SiMe_3$, H).[23]



6

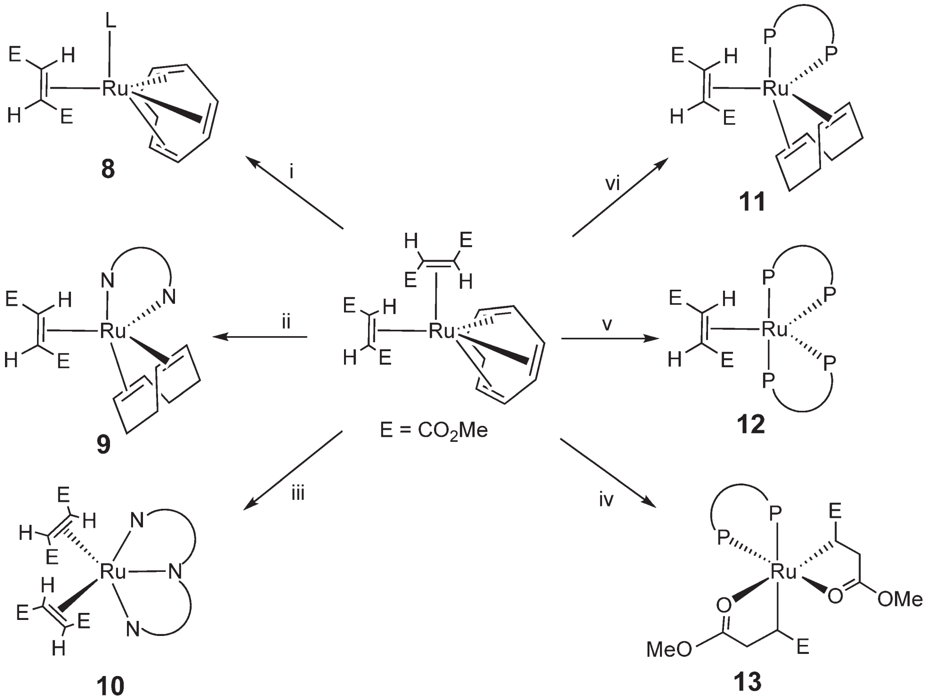
a R = H
b R = Me
c R = $SiMe_3$



7

The zero-oxidation-state complexes [M(PP_3)(η^2-C_2H_4)] can be formed upon photolysis of the corresponding dihydride complexes at RT under an atmosphere of ethene.[25]

Substitution of one dimethyl fumarate ligand in [Ru(η^6-COT)(η^2-(*E*)-MeO_2CCH═CHCO_2Me$)_2$] occurs with a range of monodentate ligands L (L = PR_3, R_3 = Ph_3, $MePh_2$*, Me_2Ph, Et_3; RNH_2, R = Pr, $PhCH_2$; Me_2NH, C_5H_5N) to afford [Ru(η^6-COT)(η^2-(*E*)-MeO_2CCH═CHCO_2Me)(L)] 8. Bi- and tridenate nitrogen donors afford [Ru(η^4-COT)(η^2-(*E*)-MeO_2CCH═CHCO_2Me)(N–N)] 9 and [Ru(N–N–N)(η^2-(*E*)-MeO_2CCH═CHCO_2Me$)_2$] 10, respectively (Scheme 1).



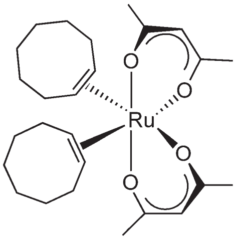
i, PR_3/RNH_2/R_2NH, CH_2Cl_2, or THF; ii, 2,2′-bpy/1,10-phen, Et_2O; iii, terpy, acetone, Δ; iv, dppe (0.8 equiv.), toluene, Δ; v, dppe (2 equiv.), toluene, Δ; vi, dppm

Scheme 1

Contrasting reactivity is seen with bidentate phosphines; dppm yields [Ru(η^4-COT)(η^2-(E)-MeO$_2$CCH=CH-CO$_2$Me)(dppm)] **11**, while dppe affords [Ru(dppe)$_2$(η^2-(E)-MeO$_2$CCH=CHCO$_2$Me)] **12** or the C–H activated product **13***, depending on the conditions employed.[26] Photolysis of [Ru(CO)$_4${P(C$_7$H$_7$)$_3$}] affords the bis-alkene coordinated complex [Ru(CO)$_2${P(C$_7$H$_7$)(η^2-C$_7$H$_7$)$_2$}], which slowly isomerizes in solution to [Ru(CO)$_2${P(C$_7$H$_7$)$_2$(η^4-C$_7$H$_7$)}], in which only one of the three seven-membered rings is coordinated to the metal centre.[27]

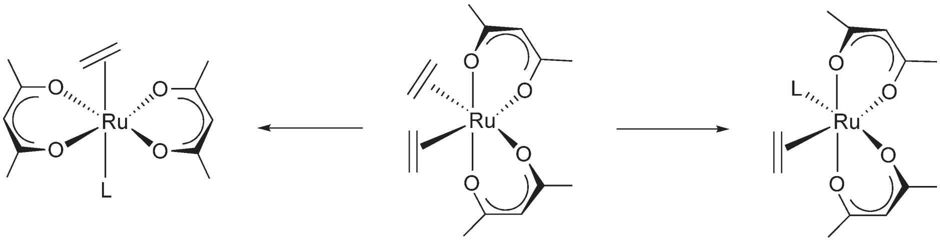
6.13.2 Di- and Trivalent Ruthenium and Osmium η^2-Alkene Complexes

The hexaaqua complex [Ru(H$_2$O)$_6$]$^{2+}$ catalyzes the dimerization of ethene in aqueous solution via the intermediacy of [Ru(η^2-C$_2$H$_4$)(H$_2$O)$_5$]$^{2+}$ and [Ru(η^2-C$_2$H$_4$)$_2$(H$_2$O)$_4$]$^{2+}$.[28] Subsequent kinetic measurements employing ^{17}O NMR spectroscopy reveal that both complexes form via a dissociative interchange (I$_d$) mechanism but that the rate constant for formation of the monoalkene complex is faster than that of the bis-species.[29,30] The Ru(II) alkene complexes [Ru(acac)$_2$(LL^1)] (LL^1 = o-CH$_2$=CHC$_6$N$_4$NMe$_2$*, o-CH$_2$=CMeC$_6$H$_4$NMe$_2$, CH$_2$=CHCH$_2$CH$_2$NMe$_2$, 2-CH$_2$=CHCH$_2$C$_5$H$_4$N, CH$_2$=CMeCH$_2$COMe, o-CH$_2$=CHC$_6$H$_4$OMe, CH$_2$=CHCH$_2$CH$_2$OMe), which exist as pairs of diastereoisomers in solution, benefit from the stabilization of having the alkene incorporated into part of an N/O chelate ligand. Reversible oxidation by Ag$^+$ or ferrocinium generates the first stable ruthenium(III) alkene complexes.[31,32] Reduction of [Ru(acac)$_3$] by Zn dust in hot aqueous THF in the presence of alkene provides a route to bis-alkene complexes cis-[Ru(acac)$_2$(η^2-C$_2$H$_4$)$_2$]* **14** and cis-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] **15**.[33–35] One of the ethene ligands in **14** can be displaced at RT to yield [Ru(acac)$_2$(η^2-C$_2$H$_4$)(L)] (L = SbPh$_3$, MeCN, NH$_3$*, C$_5$H$_5$N*, P^{i}Pr$_3$*, PCy$_3$*), in some cases as mixtures of cis- and $trans$-isomers **16a** and **16b** (Scheme 2).[33,34] Addition of C$_2$H$_4$ to [Ru(Sb^{i}Pr$_3$)$_2$(acac)$_2$] yields [Ru(Sb^{i}Pr$_3$)(acac)$_2$(η^2-C$_2$H$_4$)], which is only stable in an ethene atmosphere.[36]



15

Low-temperature 1- and 2-D NMR spectroscopy following reaction of (Z)-methyl α-acetamidocinnamate with the solvent complex [Ru{(R)-BINAP}(MeCN)(S)$_2$H](BF$_4$) (S = THF, MeOH) has allowed determination of the

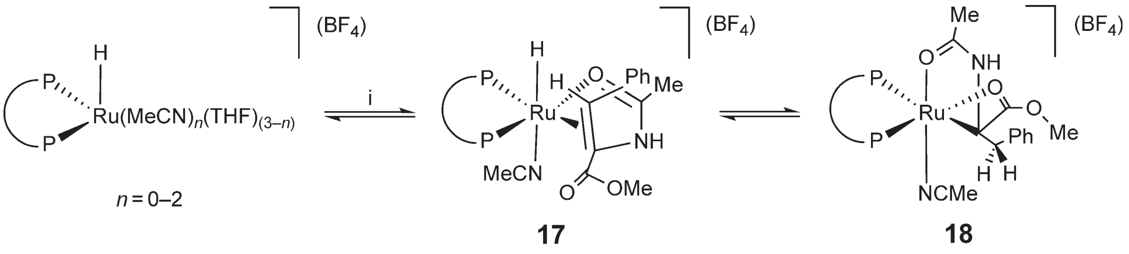


16b
L = NH$_3$
L = C$_5$H$_5$N

14

16a
L = SbPh$_3$
L = MeCN
L = NH$_3$
L = C$_5$H$_5$N

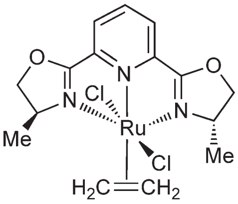
Scheme 2



i, (*Z*)-methyl-α-acetamidocinnamate, THF, 233 K

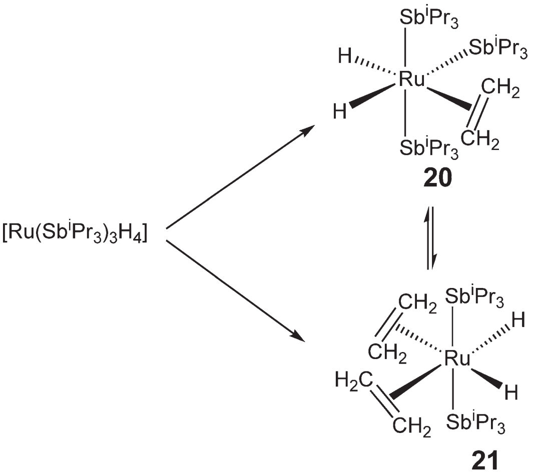
Scheme 3

diastereomeric alkene hydride adduct **17** that forms prior to the possible catalytically important intermediate **18** (BINAP = 2,2-bis(diphenyl-phosphanyl)-1,1-binaphthyl) (Scheme 3).[37,38] The ruthenium(II) ethene complex *trans*-[Ru(^{i}Pr-pybox)(η^2-C_2H_4)Cl_2] **19**[39,40] and related pybox[41,42] and 2,6-bis(imino)pyridyl alkene complexes[43] have attracted attention as catalytic precursors for the asymmetric cyclopropanation of alkenes.



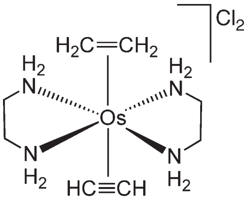
19

Treatment of *cis*-[Ru(dmpe)$_2$Me$_2$] with [H(OEt)$_2$](BAr$^F{}_4$) forms the cationic species [Ru(dmpe)$_2$Me](BAr$^F{}_4$), which reacts with ethene at RT to yield *cis*-[Ru(dmpe)$_2$(η^2-C_2H_4)Me](BAr$^F{}_4$).[44] RT reaction of C_2H_4 with [Ru(Sb^{i}Pr$_3$)$_3$(η^2-H_2)H_2] leads to formation of the mono- and bis-ethene species [Ru(Sb^{i}Pr$_3$)$_3$(η^2-C_2H_4)H_2] **20** and [Ru(Sb^{i}Pr$_3$)$_2$(η^2-C_2H_4)$_2$$H_2$] **21** (Scheme 4); the former can be isolated, whereas the latter is only stable and characterizable in solution.[45] Ethene displaces one of the coordinated Sb^{i}Pr$_3$ ligands in [Ru(Sb^{i}Pr$_3$)$_3$(CO)HCl] to give [Ru(Sb^{i}Pr$_3$)$_2$(CO)(η^2-$H_2C{=}CH_2$)HCl].[46] Addition of $H_2C{=}CH_2$ and then $HC{\equiv}CH$ to [Os(en)$_2$(η^2-H_2)(H_2O)]$^{2+}$ yields the first stable ethene–ethyne complex [Os(en)$_2$(η^2-$H_2C{=}CH_2$)(η^2-$HC{\equiv}CH$)]Cl_2* **22**. The X-ray crystal



Scheme 4

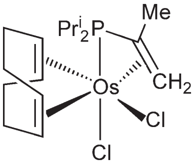
structure shows that the two organometallic ligands are almost orthogonal to each other, at an angle ca. 78 °.[47] The expected η^2-coordination of C_{60} is observed in $[Ru(PPh_3)_2(\eta^2\text{-}C_{60})(NO)Cl]^*$.[48]



22

While $[Ru(P^iPr_3)_2(CO)HCl]$ forms no adduct at RT when placed under an atmosphere of C_2H_4, the osmium analog affords $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}C_2H_4)DCl]$, which shows only slow H/D exchange at RT. Density functional theory (DFT) calculations indicate that 18-electron $Os(\eta^2\text{-}C_2H_4)$ is more stable than either the 16-electron $Os–CH_2CH_3$ or 18-electron $Os({=}C(H)CH_3)$ forms. The poorer backbonding ability of Ru compared to Os explains the failure to detect a Ru–ethene complex. However, the subtlety of ligand effects is seen in that $[Ru(P^iPr\{3,5\text{-}(CF_3)_2C_6H_3\})_2(CO)HCl]$ does form a detectable ethene adduct, which is in equilibrium with the corresponding ethyl complex.[49]

Under reflux in toluene, $[Os(P^iPr_3)_2H_2Cl_2]$ reacts with 1,5-COD to give the isopropenylphosphine species $[Os\{(\eta^2\text{-}CH_2{=}CMe)P^iPr_2\}(\eta^4\text{-}COD)Cl_2]^*$ **23**, but if the reaction is performed at lower temperature, $[Os(P^iPr_3)\{\eta^4\text{-}C_8H_{11}P^iPr_3\}HCl_2]^*$ **24** forms instead. Subsequent reaction of this with 1,5-COD and 2,5-NBD affords **23** and $[Os\{(\eta^2\text{-}CH_2{=}CMe)P^iPr_2\}(\eta^4\text{-}NBD)Cl_2]$, respectively. Refluxing tetrafluorobenzobarralene (TFB) with $[Os(P^iPr_3)_2H_2Cl_2]$ produces a mixture of $[Os\{(\eta^2\text{-}CH_2{=}CMe)P^iPr_2\}(\eta^4\text{-}TFB)Cl_2]$ and $[Os\{(\eta^2\text{-}CH_2{=}CHCH_2)P^iPr_2\}(\eta^4\text{-}TFB)Cl_2]$ **25***.[50] Addition of $CH_2{=}CHCO_2Me$ to $[Os(P^iPr_3)_2(CO)(OH)H]$ generates the six-coordinate complex $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}CH_2{=}CHCO_2Me)(OH)H]^*$.[51] The stannyl polyhydride complex $[Os(P^iPr_3)_2(SnPh_3)H_4Cl]$ reacts with $PhC{\equiv}CPh$ at RT to give $[Os(P^iPr_3)\{\eta^2\text{-}CH_2{=}CMeP^iPr_2\}(SnClPh_2)H_3]$ **26** via P–^{i}Pr dehydrogenation, alkyne to alkene reduction, hydrogenolysis of an $SnPh_3$ ligand, and Os to Sn chloride migration![52] Protonation of $[Os(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH{=}CH)H_3]$ affords the cationic alkene–dihydrogen complex $[Os(P^iPr_3)_2(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(\eta^2\text{-}H_2)H](BF_4)^*$ **27**, which is a catalytic precursor for the hydrogenation of 2-vinylpyridine to 2-ethylpyridine. Dissolution of **27** in dichloromethane produces $[Os(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH{=}CH)(\eta^2\text{-}H_2)Cl]$.[53]



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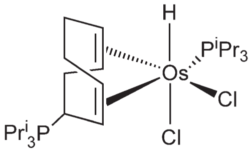

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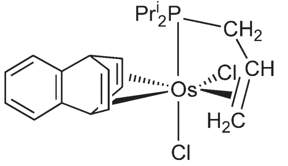
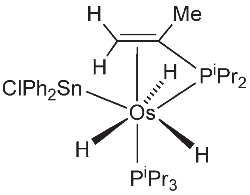


25

Both alkynes ($HC{\equiv}CCO_2R$, R = Me, Et) and alkenes ($H_2C{=}CHCO_2R$, R = Me, Et) react with $[Ru(PP_3)H_2]$ ($PP_3 = P(CH_2CH_2PPh_2)_3$) to give $[Ru(PP_3)(\eta^2\text{-}H_2C{=}CHCO_2R)]$, which appear to have structures halfway between Ru(0)–alkene and ruthenacyclopropanes.[54] If ethene reacts with the dihydride in the presence of MeOTf, the air-stable cation $[Ru(PP_3)(\eta^2\text{-}C_2H_4)H]^+$ is formed.[55] The ethene dihydride complex $[Os(P^iPr_3)_2(\eta^2\text{-}C_2H_4)(NO)H_2](X)$ ($X = BAr^F{}_4$, $PF_6{}^*$) forms readily upon addition of C_2H_4 to *trans,cis*-$[Os(P^iPr_3)_2(NO)H_2](X)$[56] and has been structurally characterized as the $PF_6{}^-$ salt. In solution, one hydride ligand and all four ethene hydrogen atoms reversibly exchange above −20 °C ($\Delta G^\ddagger = 62\,kJ\ mol^{-1}$) in a mechanism involving reversible insertion of the alkene into a *cis*-OsH bond, exchange of agostic β-hydrogens of the ethyl ligand and β-hydrogen elimination. DFT calculations reveal that motion of the NO ligand does not play a part in the reaction.[57]

Addition of the allylsilane $(H_2C{=}CHCH_2)Me_2SiH$ to $[Ru(PCy_3)_2(\eta^2\text{-}H_2)_2H_2]$ yields the η^2-alkene η^2-silane complex $[Ru(PCy_3)_2\{\eta^4\text{-}HSiMe_2(CH{=}CHMe)\}H_2]^*$ **28**.[58] The diphosphine 1,5-bis(di-*tert*-butylphosphino)ethane (dtbpp) reacts with $[Ru(p\text{-}cymene)Cl_2]_2$ in the presence of lutidine at 90 °C to afford the alkene hydride complex $[Ru(^tBu_2PCH_2CH_2\{(E)\text{-}CH{=}CH\}CH_2P^tBu_2)HCl]^*$ **29** as one of two products. In the solid state, the complex exists as two isomers differing in the configuration of the *trans*-pent-2-ene chair.[59] The alkene dihydride complex

$[Os(P^iPr_3)_2(CO)(\eta^2\text{-}CH_2{=}CHEt)H_2]$ reacts with $R_3E–H$ to give the corresponding $[Os(P^iPr_3)_2(CO)(ER_3)H_3]$ ($E = Si, Ge, Sn$) complexes.[60]



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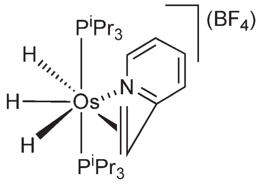

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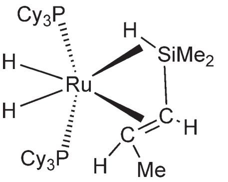

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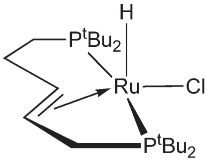
The ruthenium ethene complex $[Ru(L)(\eta^2\text{-}C_2H_4)Cl_2]$ (L = 2,6-bis{1-(2,6-dimethylphenylimino)ethyl}pyridine) is prepared by refluxing the free ligand L with the arene dimer $[Ru(p\text{-cymene})Cl_2]_2$ in ethanol under an ethene atmosphere. Treatment with $NaBAr^F{}_4$ under an ethene atmosphere affords the structurally distorted bis(ethene) complex $[Ru(L)(\eta^2\text{-}C_2H_4)_2Cl][BAr^F{}_4]^*$. Alkylation of this with $(tmeda)MgMe_2$ in the presence of additional $NaBAr^F{}_4$ generates the cationic methyl ethene species $[Ru(L)(\eta^2\text{-}C_2H_4)Me][BAr^F{}_4]$ **30**, which proves stable to methyl migration to the coordinated alkene even at elevated temperatures.[61] Protonation of $[Ru(L_{OEt})(PPh_3)(CO)\{(E)\text{-}CH{=}CHPh\}]$ ($L_{OEt} = (\eta^5\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$) with $HBF_4{\cdot}OEt_2$ produced $[Ru(L_{OEt})(PPh_3)(CO)\{\eta^2\text{-}CH_2{=}CHPh\}](BF_4)$, which eliminates styrene in wet CH_2Cl_2 over days at RT forming $[Ru(L_{OEt})(PPh_3)(CO)(H_2O)](BF_4)$.[62]

The osmium(II) alkene complexes $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}CH_2{=}CHR)H_2]$ result from addition of ^nBuLi to $[Os(P^iPr_3)_2(CO)HCl]$ ($R = Et$)[63] or upon subjecting $[Os(P^iPr_3)_2(CO)(C{\equiv}CR)(\eta^2\text{-}H_2)H]$ ($R = Ph$) to H_2 in solution.[64] The butene ligand is readily displaced by cyclopentadiene to give $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}C_5H_6)H_2]$, while reaction with $EtC{\equiv}CC(Me){=}CH_2$ and $PhC{\equiv}CH$ gives the methylhexadiene species $[Os(P^iPr_3)_2(CO)(\eta^4\text{-}CH_2{=}C(Me)C{=}CHEt)]$ and diphenylbutenynyl complex $[Os(P^iPr_3)_2(CO)(C{\equiv}CPh)(\eta^3\text{-}C(C{\equiv}CPh){=}CHPh)]$, respectively.[65] A range of stable alkene complexes *mer*, *trans*-$[Ru(\eta^3\text{-}NN'N)(\eta^2\text{-}CH{=}CHR)Cl_2]$ ($NN'N$ = 2,6-bis-{(dimethylamino)methyl}pyridine; $R = H, CH{=}CH_2, CH_2Ph, CH_2Br, CH_2OH, CHO, CN, C(O)OMe, Ph$; $CH = CHR$ = maleic anhydride) can be formed by the addition of the appropriate alkene to the dinuclear dinitrogen complex $[\{Ru(\eta^3\text{-}NN'N)Cl_2\}_2(\mu\text{-}N_2)]$.[66] A range of functionalized alkene ligands (e.g., 3-cyclohexene-1-one, 3-cyclohexene-1-methanol, 1,3-dimethyluracil) have been coordinated to the $[Ru(hedta)]^-$ moiety (hedta = *N*-hydroxyethylethylenediaminetriacetate) as evidenced by upfield shifts in both the ^1H and ^{13}C NMR resonances of the alkene.[67] Studies aimed at elucidating in detail the mechanism of Ru-catalysed ring-opening metathesis allow detection and isolation of the novel intramolecularly coordinated alkene complex **31***.[68]



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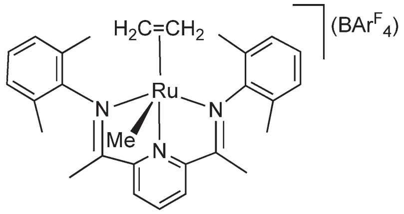

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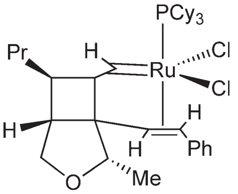
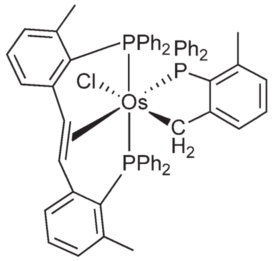


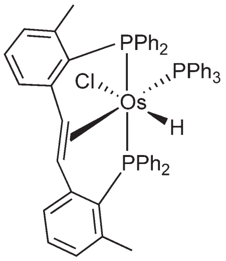
31

Treatment of the half-sandwich dicarbonyl complexes $[(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CRR^1)Ru(CO)_2Cl]$ with $AgBF_4$ results in chloride abstraction and formation of $[(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CRR^1)Ru(CO)_2]^+$ ($n = 1$, $R = Me$, $R^1 = H$; $n = 1$, $R = H$, $R^1 = Me$; $n = 1^*$, 2^*, $R = R^1 = H$), in which the double bond is coordinated to the ruthenium.[69] Addition of $NaBH_4$ breaks this η^2-interaction to give the hydride complex $[(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CRR^1)Ru(CO)_2H]$, while alkoxide attacks one of the Ru–CO bonds to give the chelated alkoxycarbonyl alkene complex $[(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CRR^1)Ru(C(O)OR^2)(CO)]$ ($R^2 = Me^*$, Et).[70] Refluxing $[OsCl_6]^{2-}$ (in $^iPrOH/H_2O$) or $[Os(PPh_3)_3Cl_2]$ (in toluene) with $PPh_2(2,6\text{-}Me_2C_6H_3)$ yields $[Os(bdps)\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}Cl]^*$ **32** and $[Os(bdps)(PPh_3)HCl]$ **33**, respectively, as a result of dehydrogenative C–C coupling of two phosphine *o*-methyl groups.[71] The related Os–alkene complex $[Os(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}HCl]$ **34** is formed upon reaction of $[Os(PPh_3)_3H_3Cl]$ with (*E*)-$Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$ at RT. Addition of HOTf yields the dihydrogen chloride complex

$[Os(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}(\eta^2\text{-}H_2)Cl](OTf)$, which surprisingly does not undergo C=C reduction upon addition of H_2, but rather eliminates HCl to give $[Os(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}(\eta^2\text{-}H_2)H](OTf)$ **35**.[72]



32



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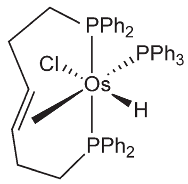

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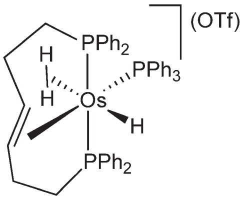
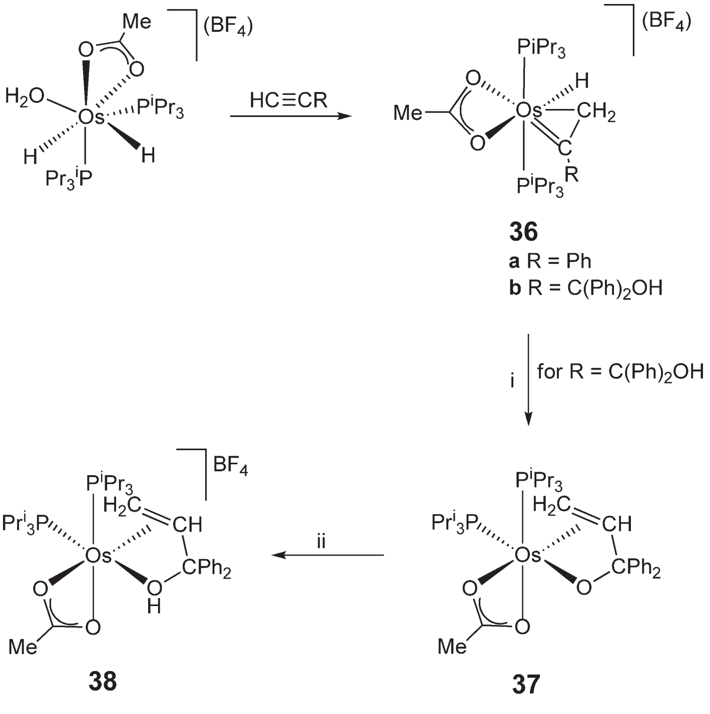


35

Addition of 3 equiv. of MeC≡CPh to $[Os(PPh_3)_3H_3Cl]$ at RT gives the alkenyl allene complex $[Os(PPh_3)_2\{CMe{=}CHPh\}(CH_2{=}C{=}CHPh)Cl]^*$, which contains an agostic interaction with a β-H of the alkenyl ligand.[73] Protonation of the trihydride complex $[Os(P^iPr_3)_2(NC_5H_4\text{-}o\text{-}CH{=}CH)H_3]$ by HBF_4 yields the cationic dihydrogen hydride alkene species $[Os(P^iPr_3)_2(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(\eta^2\text{-}H_2)H](BF_4)^*$.[53] Addition of 1 equiv. of HC≡CPh or $HC{\equiv}CCPh_2OH$ to $[Os(P^iPr_3)_2(\kappa^2\text{-}O_2CMe)(H_2O)H_2](BF_4)$ yields rare examples of metallacyclopropene complexes, $[Os(P^iPr_3)_2\{C(Ph)CH_2\}(\kappa^2\text{-}O_2CMe)H](BF_4)^*$ **36a** and $[Os(P^iPr_3)_2\{C\{C(OH)Ph_2\}CH_2\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ **36b**, respectively (Scheme 5).[74] The analogous compounds $[Os(P^iPr_3)_2\{C\{C(OH)Me_2\}CH_2\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ and $[Os(P^iPr_3)_2\{C\{C(OH)(Me)Ph\}CH_2\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ are formed as minor components alongside the carbyne complexes $[Os(P^iPr_3)_2\{{\equiv}CCH_2C(OH)Me_2\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ and $[Os(P^iPr_3)_2\{{\equiv}CCH_2C(OH)(Me)Ph\}(\kappa^2\text{-}O_2CMe)H](BF_4)$ from $HC{\equiv}CCMe_2OH$ and $HC{\equiv}CC(Me)PhOH$, respectively. All three hydroxyosmacyclopropene



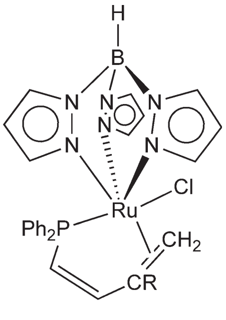
i, NaOMe (1.4 equiv.); ii, $HBF_4{\cdot}OEt_2$

Scheme 5

complexes readily isomerize in dichloromethane solution to the corresponding hydroxycarbene species $[Os(P^iPr_3)_2\{CMeC(OH)RR^1\}(\kappa^2\text{-}O_2CMe)](BF_4)$ ($R = R^1 = Ph$, Me; $R = Ph$, $R^1 = Me$).[75] In the case of **36b**, addition of 1.4 equiv. of NaOMe at RT yields $[Os(P^iPr_3)_2\{\eta^2\text{-}CH_2{=}C(Ph)_2O\}(\kappa^2\text{-}O_2CMe)]^*$ **37**, which upon addition of HBF_4 undergoes protonation at the oxygen atom of the η^2-alkenyl alkoxide ligand to form the η^2-1,1-diphenyl-2-propenol complex, $[Os(P^iPr_3)_2\{\eta^2\text{-}CH_2{=}CHC(OH)Ph_2\}(\kappa^2\text{-}O_2CMe)](BF_4)$ **38** (Scheme 5).[75]

The Os(II) vinyl ether complexes $[Os(\eta^2\text{-}RCH{=}CR(OR^1)(NH_3)_5](OTf)_2$ can be prepared by three routes: (i) Zn/Hg reduction in the presence of $RCH{=}CR(OR^1)$ ($R = H$, $R^1 = Et$; $R = Me$, $R^1 = Me$, Et), (ii) treatment of $[Os(\eta^2\text{-}RCH{=}CHX)(NH_3)_5](OTf)_2$ with R^1OH/H^+ ($R = H$, $X = Et$, $R^1 = Me$), or (iii) addition of R^1OH to $[Os(\eta^2\text{-}RC{\equiv}CR)(NH_3)_5](OTf)_2$ ($R = Me$, $R^1 = Me$). Protonation of $[Os\{\eta^2\text{-}CHMe{=}CMe(OMe)\}(NH_3)_5](OTf)_2$ with HOTf affords the osmacyclopropene complex $[Os\{\eta^2\text{-}CMeCH_2\}(NH_3)_5](OTf)_3$, whereas addition of HOTf to $[Os\{\eta^2\text{-}CH_2{=}CH(OEt)\}(NH_3)_5](OTf)_2$ generates $[Os({\equiv}CMe)(NH_3)_5](OTf)_3$.[76]

While the reaction of $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)Cl]$ with $HC{\equiv}CR$ in refluxing MeOH generated the expected cationic vinylidene complexes $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHR)](Cl)$, changing to toluene gave, unexpectedly, $[Ru\{HB(pz)_3\}(\kappa^3\text{-}(P, C, C)\text{-}Ph_2PCH{=}CHC(R){=}CH_2)Cl]$ (R = Ph **39a**, CH_2Ph **39b**, CO_2Et^* **39c**.) Mechanistic studies with $DC{\equiv}CPh$ show that no deuterium incorporation into the $Ph_2PCH{=}CHCPh{=}CH_2$ chain occurs, indicating that the terminal CH_2 must originate from the backbone of the original aminophosphine ligand.[77] Extension of this reactivity involving coupling of alkynes to (the more reactive) Ru-coordinated $Ph_2PCH_2CH_2NEt_2$ and $Ph_2PCH_2CH_2N^iPr_2$ groups affords $[Ru\{HB(pz)_3\}(\kappa^3\text{-}(P, C, C)\text{-}Ph_2PCH_2CH(NR_2)C(R^1){=}CH_2)Cl]$ and $[Ru\{HB(pz)_3\}(\kappa^3\text{-}(P, C, C)\text{-}Ph_2PCH_2CH(NR_2)CH{=}C(R)H)]$ ($R = Et$, ^iPr; R^1 = ferrocenyl, Ph, ^nBu).[78] The lower reaction temperatures employed with the ethyl and isopropyl systems removes C–N bond cleavage and amine elimination from the reaction cycle.



39

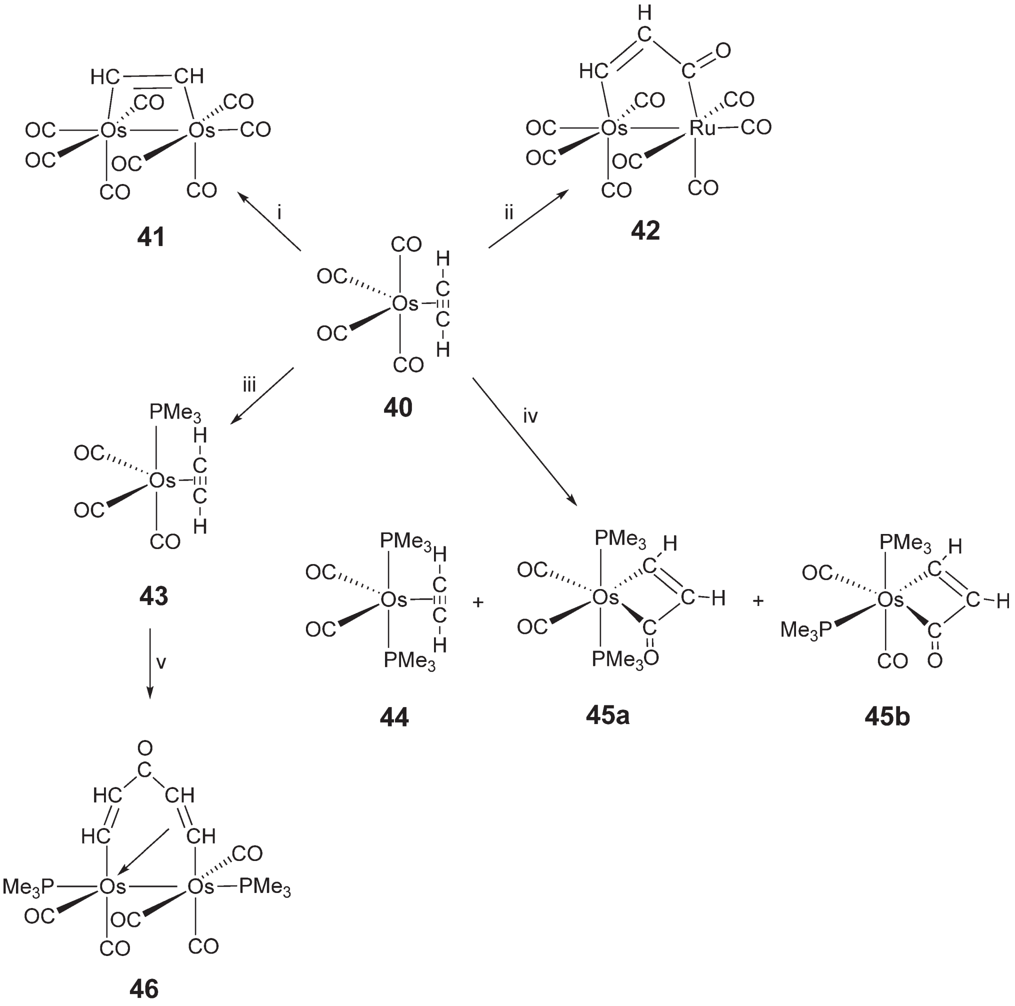
a R = Ph
b R = CH_2Ph
c R = CO_2Et

Loss of chloride in solution from $[Ru(\eta^4\text{-}1,2,3,4\text{-}Me_4\text{-}NUPHOS)(en)Cl_2]$ ($1,2,3,4\text{-}Me_4\text{-}NUPHOS$ = 1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene) generates $[Ru(1,2,3,4\text{-}Me_4\text{-}NUPHOS)(en)Cl](X)$ (X = Cl, ClO_4^*), in which the coordination mode of the chelating phosphine changes to η^6 through both phosphorus atoms and one of the double bonds of the butadiene backbone.[79]

6.13.3 Ruthenium and Osmium η^2-Alkyne Complexes

Kinetic studies have shown that the tetracarbonyl ethyne complex $[Os(CO)_4(\eta^2\text{-}C_2H_2)]$ **40** initially loses CO before reacting with the parent pentacarbonyls $[M(CO)_5]$ (M = Ru, Os) to give the osmacyclobutene $[Os_2(CO)_8(\mu\text{-}\eta^2\text{-}HC{=}CH)]$ **41** or the dimetallacyclopentenone $[OsRu(CO)_8\{\mu\text{-}\eta^2\text{-}HC{=}CHC(O)\}]$ **42** (Scheme 6).[80] The rate of production of $[M(CO)_3(PR_3)(\eta^2\text{-}F_3CC{\equiv}CCF_3)]$ (M = Ru, Os) from reaction of $[M(CO)_4(\eta^2\text{-}F_3CC{\equiv}CCF_3)]$ with PR_3 is found to be independent of the nature and concentration of the phosphine, indicating that CO dissociation is rate determining (k (s^{-1}), 1.25×10^{-2} (Ru), 3.5×10^{-3} (Os); $\Delta H^{\neq}$ ($kJ\,mol^{-1}$), 103.6 ± 2.4 (Ru), 99.5 ± 0.8 (Os); $\Delta S^{\neq}$ ($cal\,mol^{-1}\,K^{-1}$), 66 ± 8.6 (Ru), 21 ± 2.7 (Os)). In comparison to the rates of CO loss from $[M(CO)_5]$ (M = Ru, Os), CO loss from the alkyne complexes is between 10^2 (Ru) and 10^7 (Os) times faster, the increased lability attributed mainly to stabilization of the transition state by four-electron donation from the alkyne ligand.[81] The low-temperature addition of PR$_3$ to the ethyne complex **40** results in range of products. With 1 equiv. of PMe$_3$, [Os(PMe$_3$)(CO)$_3$(η^2-HC≡CH)] **43** is formed; in the presence of an excess of phosphine (10 equiv.), [Os(PMe$_3$)$_2$(CO)$_2$(η^2-HC≡CH)] **44** and two isomers of the the osmacyclobutenone [Os(PMe$_3$)$_2$(CO)$_2${η^1:η^1-C(O)C$_2$H$_2$}] **45a** and **45b** are formed. At RT, **44** converts into [Os(PMe$_3$)$_2$(CO)$_2$(C≡CH)H], whereas the monophosphine complex **43** gives the bimetallic flyover-bridged compound [Os$_2$(PMe$_3$)$_2$CO)$_5${μ-η^1:η^1:η^2-H$_2$C$_2$C(O)C$_2$H$_2$}] **46** (Scheme 6). In the reaction of **40** with P^{t}Bu$_3$, the only isolated product is the doubly CO inserted osmacyclopentene-2,4-dione [Os(P^{t}Bu)(CO)$_3$(η^1:η^1-C(O)C$_2$H$_2$(O)C)]*. As with the hexafluorobutyne species, kinetic studies point to a dissociative reaction pathway; the η^2-HC≡CH system is more reactive than the η^2-F$_3$CC≡CCF$_3$ analog due to enhanced four-electron stabilization of the coordinatively unsaturated intermediate.[82,83]

The coordinatively unsaturated osmium(0) species [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)](BAr$^F{}_4$) reacts with PhC≡CH forming [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)(η^2-PhC≡CH)](BAr$^F{}_4$), which rearranges first to [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)(C≡CPh)H](BAr$^F{}_4$) and then to [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)(=C=CHPh)](BAr$^F{}_4$). Addition of HC≡CH to [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)](BAr$^F{}_4$) gives the alkyne complex [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)(η^2-HC≡CH)](BAr$^F{}_4$), which is stable up to 60 °C. In contrast, addition of Me$_3$SiC≡CSiMe$_3$ to [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO)](BAr$^F{}_4$) gives [Os(P^{t}Bu$_2$Me)$_2$(CO)(NO){=C=C(SiMe$_3$)$_2$}](BAr$^F{}_4$).[84]



i, [Os(CO)$_5$]; ii, [Ru(CO)$_5$]; iii, PMe$_3$ (1 equiv.), –78 °C;
iv, PMe$_3$ (10 equiv.), 0 °C; v, 0 °C

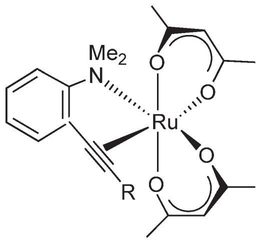
Scheme 6

Addition of 3 equiv. of $PhC{\equiv}CPh$ to $[Os(P^iPr_3)_2(CO)H_4]$ at RT yields $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}PhC{\equiv}CPh)]^*$, which reacts with CO to afford $[Os(P^iPr_3)_2(CO)_2(\eta^2\text{-}PhC{\equiv}CPh)]$. In contrast, while the four-coordinate ruthenium analog $[Ru(P^iPr_3)_2(CO)(\eta^2\text{-}PhC{\equiv}CPh)]$ can be isolated via reaction of $PhC{\equiv}CPh$ with $[Ru(P^iPr_3)_2(CO)(\eta^2\text{-}H_2BH_2)H]$; addition of CO leads to elimination of $PhC{\equiv}CPh$ and formation of $[Ru(P^iPr_3)_2(CO)_3]$.[85] Hydrogenation of the styryl complex $[Os(P^iPr_3)_2(CO)\{(E)\text{-}CH{=}CHPh\}(\eta^2\text{-}O_2CH)]$ affords styrene and $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}O_2CH)H]$, which reacts with $MeO_2CC{\equiv}CCO_2Me$ to give the alkyne complex $[Os(P^iPr_3)_2(CO)(\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)(\eta^1\text{-}O_2CH)H]$.[86] Dissolution of $[Os({=}CH^tBu)_2(CH_2{}^tBu)_2]$ in neat PMe_3 yields $[Os(PMe_3)_3(\eta^2\text{-}{}^tBuC{\equiv}C^tBu)]^*$. Two potential mechanisms seem plausible, both starting from phosphine-induced α-H abstraction to afford $[Os(PMe_3)_2({\equiv}C^tBu)({=}CH^tBu)(CH_2{}^tBu)]$. A second phosphine abstraction can then occur to give a bis-carbyne species followed by reaction with phosphine; alternatively, coupling of the carbyne and carbene groups yields an η^2-alkenyl species, which then eliminates neopentane and coordinates phosphine. The orange-red air-sensitive butyne complex can be protonated by $[H(OEt_2)_2](BAr^F{}_4)$ to generate $[Os(PMe_3)_3(\eta^2\text{-}{}^tBuC{\equiv}C^tBu)H](BAr^F{}_4)$ and also undergoes loss of a PMe_3 ligand in the presence of CO, forming $[Os(PMe_3)_2(CO)_2(\eta^2\text{-}{}^tBuC{\equiv}C^tBu)]$.[87]

The alkyne complexes $[Ru(acac)_2(o\text{-}RC{\equiv}CC_6H_4NMe_2)]$ (R = Ph **47a**, $SiMe_3$ **47b**, H **47c**) can be reversibly oxidized chemically or electrochemically to the corresponding ruthenium(III) cations. A comparison of the $Ru(\eta^2\text{-}C{\equiv}C)$ distances in the X-ray crystal structures for **47a** and **47a**$^+$ reveals that the alkyne binds more strongly in the oxidized complex.[88]

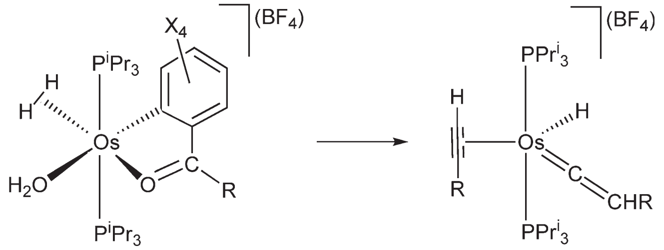
Dimethyl acetylendicarboxylate displaces one of the coordinated Sb^iPr_3 ligands in $[Ru(Sb^iPr_3)_3(CO)HCl]$ to give $[Ru(Sb^iPr_3)_2(CO)(\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)HCl]$,[46] while reaction of $[Ru(PPh_3)_3(CO)_2]$ with diphenylbutadiyne yields $[Ru(PPh_3)(CO)_2(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)]$.[89] Addition of $PhC{\equiv}CPh$ to $[Ru(P^iPr_3)_2(CO)(\eta^3\text{-}C_3H_5)H]$ gives $[Ru(P^iPr_3)_2(CO)(\eta^2\text{-}PhC{\equiv}CPh)]$, which reacts with terminal alkynes $HC{\equiv}CR$ ($R = C_6H_{11}$, CO_2Me) to give the alkynyl alkenyl complexes $[Ru(P^iPr_3)_2(CO)(C{\equiv}CR)\{(E)\text{-}CH{=}CHR\}]$.[90]

Protonation of $[Os(P^iPr_3)_2\{C_6X_4C(O)Me\}H_3]$ (X = (F, H)) with $HBF_4{\cdot}H_2O$ gives the elongated dihydrogen complexes $[Os(P^iPr_3)_2\{C_6X_4C(O)Me\}(\eta^2\text{-}H_2)(H_2O)](BF_4)$, which react with $HC{\equiv}CR$ ($R = H$, C_6H_{11}) to form the four-electron donor alkyne vinylidene species $[Os(P^iPr_3)_2({=}C{=}CHR)(\eta^2\text{-}HC{\equiv}CR)H](BF_4)^*$ **48a** and **48b**. In contrast, with $HC{\equiv}CPh$, a mixture of products is produced, containing mainly $[Os(P^iPr_3)_2({=}C{=}CHPh)(\eta^2\text{-}HC{\equiv}CPh)H](BF_4)$ **48c** and $[Os(P^iPr_3)_2\{C_6X_4C(O)Me\}\{C(Ph)CH_2\}H](BF_4)$.[91]



47

a R = Ph
b R = SiMe$_3$
c R = H



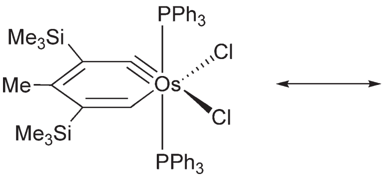
48

a R = H
b R = C$_6$H$_{11}$
c R = Ph

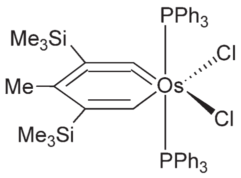
The coordinated THF ligand in the carborane-stabilized dicarbonyl solvent complex $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(THF)]$[22] is easily displaced by $RC{\equiv}CR^1$ to give $[Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(\eta^2\text{-}RC{\equiv}CR)]$ ($R = R^1 = Me$, Ph).[23] The low-temperature addition of $MeC{\equiv}CPh$ to the 16-electron species $[Ru(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ in CH_2Cl_2 yields $[Ru(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta^2\text{-}MeC{\equiv}CPh)]^*$, which forms the ylide $[Ru(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})\{C(Me) = C(Ph)PEt_3\}]^*$ upon treatment with PEt_3.[92]

The reaction of an excess of $HC{\equiv}CSiMe_3$ with $[Os(PPh_3)_3Cl_2]$ in the presence of moisture provides a route to $[Os(PPh_3)_2\{{\equiv}CC(SiMe_3)C(Me)C(SiMe_3)CH\}Cl_2]^*$, the first example of a metallabenzyne complex.[93] The key features of the X-ray structure are the planar six-membered metallacycle along with the $Os{\equiv}C$ bond length of 1.815(4) Å, slightly longer than those observed in Os carbyne systems. These data are suggestive of contributions from both resonance structures **49a** and **49b**. The additional neutral species $[Os(PPh_3)_2\{{\equiv}CC(R)C(Me)C(R)CH\}X_2]$ ($R = Br$, $X = Br^*$; $R = H$, $X = Cl$) are known, while the cationic derivatives $[Os(PPh_3)_2\{{\equiv}CC(R)C(Me)C(R)CH\}$

(H$_2$O)Cl](BF$_4$) (R = SiMe$_3$*, H **50**) have been produced by subsequent protonation or electrophilic substitution.[94,95] Although not strictly related, mention is also made at this point of metallabenzene systems. Addition of HC≡CMe to a solution of [Os(PPh$_3$)$_3$(CO)(CS)] affords mainly [Os(PPh$_3$)$_2$(CO)(CS)(C≡CMe)H] but, in a smaller amount, the osmabenzene complex {OsC(S)CMeCHCHCMe}(CO)(PPh$_3$)$_2$ is also formed.[96,97] Electrophilic substitution reactions on the osmabenzene complex {OsC(SMe)CHCHCHCH}I(CO)(PPh$_3$)$_2$ can be performed. Thus, reaction with Cu(NO$_3$)$_2$/acetic anhydride and Fe/Br$_2$ results in nitration* **51** and bromination* *para* to the SMe substituent.[98] Addition of excess NaCl to the thermally unstable [Os(P^{i}Pr$_3$)$_2$(≡CCH$_2$Ph)(C≡CPh){(*E*)-CH═CHPh}](BF$_4$) yields the iso-metallabenzene complex* **52**, which has the structure of a 1,2,4-cyclohexatriene.[99]



49a



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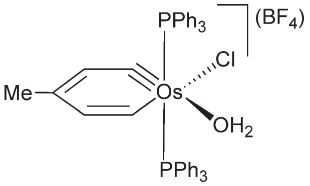

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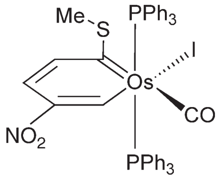

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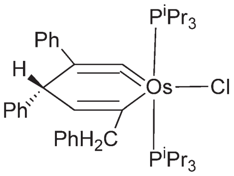


52

6.13.4 Ruthenium and Osmium η^3-Complexes

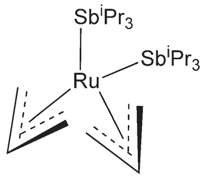
6.13.4.1 Parent Allyl Complexes

Treatment of [Ru(COD)Cl$_2$]$_2$ with ^{i}Pr$_2$P(CH$_2$)$_n$P^{i}Pr$_2$ in refluxing ethanol followed by addition of CH$_2$═CHCH$_2$MgCl affords [Ru(^{i}Pr$_2$P(CH$_2$)$_n$P^{i}Pr$_2$)(η^3-C$_3$H$_5$)$_2$] (n = 2, 3),[100] which act as precursors for mono- and dinuclear hydride complexes.[101]

The bis-allyl complex [Ru(Sb^{i}Pr$_3$)$_2$(η^3-C$_3$H$_5$)$_2$] **53** has been structurally characterized following reaction of [Ru(Sb^{i}Pr$_3$)$_3$(η^2-H$_2$)H$_2$] with propene.[45] Allylmagnesium bromide reacts with [M(P^{i}Pr$_3$)$_2$(CO)HCl] (M = Ru, Os) to afford the stereochemically rigid complexes [M(P^{i}Pr$_3$)$_2$(CO)(η^3-C$_3$H$_5$)H].[90,102] Addition of C$_3$H$_5$MgBr to [Ru(P^{i}Pr$_3$)$_2$(CO)HCl] affords [Ru(P^{i}Pr$_3$)$_2$(CO)(η^3-C$_3$H$_5$)H], which shows reactivity with terminal alkynes to yield bis-alkynyl and alkenyl alkynyl complexes.[103]

Thermolysis of allyl phenyl ether with [Ru(COD)(COT)] in the presence of PMe$_3$ affords [Ru(PMe$_3$)$_2$(η^3-C$_3$H$_5$)(OPh)]* **54** via ether C–O bond oxidative addition. In contrast, a combination of the Ru(0) precursor and PEt$_3$ reacts with allylphenol to yield the oxaruthenacycle [Ru(PEt$_3$)$_3${OC$_6$H$_4$(η^3-C$_3$H$_4$)}]* **55**.[103] Reaction of [Ru(PMe$_2$Ph)$_2$(CO)(η^3-C$_3$H$_5$)Cl] with CO and AgBF$_4$ yields two isomers of [Ru(PMe$_2$Ph)$_2$(CO)$_2$(η^3-C$_3$H$_5$)](BF$_4$) **56a** and **56b**, with *cis*- and *trans*-phosphine ligands. Complex **56b** is attacked by Cl$^-$ to first form [Ru(PMe$_2$Ph)$_2$(CO)$_2$(η^1-C$_3$H$_5$)Cl] **57**, which subsequently loses CO to yield [Ru(PMe$_2$Ph)$_2$(CO)(η^3-C$_3$H$_5$)Cl] **58**. Addition of NaBH$_4$ to **56b** affords two products, the metallacyclobutane [Ru(PMe$_2$Ph)$_2$(CO)$_2$(CH$_2$CH$_2$CH$_2$)] **59** and the borohydride complex, [Ru(PMe$_2$Ph)$_2$(CO)(η^2-H$_2$BH$_2$)H] (Scheme 7). Treatment of the borohydride complex with ethene at low temperature leads to a rapid equilibrium between [Ru(PMe$_2$Ph)$_2$(CO)(η^2-H$_2$BH$_2$)H], C$_2$H$_4$, and [Ru(PMe$_2$Ph)$_2$(CO)(η^2-C$_2$H$_4$)(η^1-HBH$_3$)H], with slower conversion to [Ru(PMe$_2$Ph)$_2$(CO)(η^2-H$_2$BH$_2$)Et].[104] The RT reaction of [Ru(PPh$_3$)$_2$(CO)(CH═CH$_2$)Cl] with CH$_2$N$_2$ generated [Ru(PPh$_3$)$_2$(CO)(η^3-C$_3$H$_5$)Cl], which can also be formed by heating [Ru(PPh$_3$)$_3$(CO)HCl] with MeC≡CH or CH$_2$═C═CH$_2$.[105] The allyl vinylidene complex

$[Os(P^iPr_3)_2({=}C{=}CH_2)(\eta^3\text{-}C_3H_5)H]$ results from addition of MeMgCl to $[Os(P^iPr_3)_2({=}C{=}CH_2)(\eta^2\text{-}HC{\equiv}CH)\text{-}H](BF_4)$.[91]



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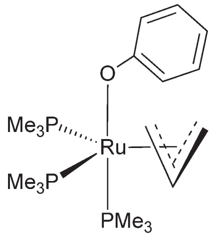

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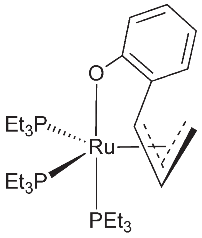
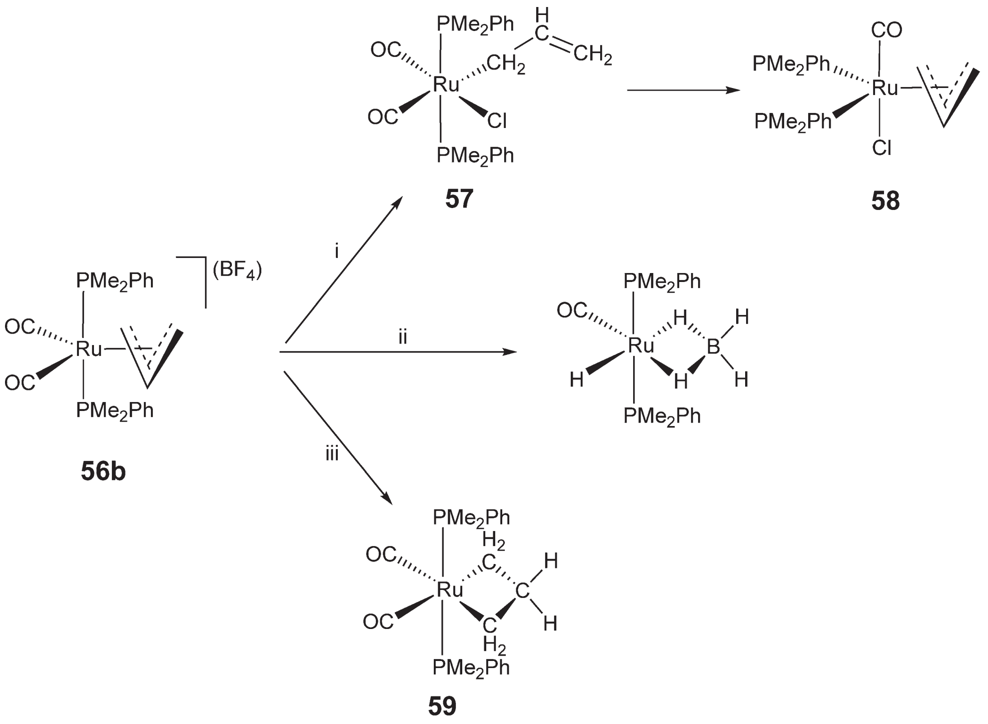


55

6.13.4.2 Substituted Allyl Complexes

The bis-allyl complexes $[Ru(P\text{–}P)(\eta^3\text{-}H_2CCMeCH_2)_2]$ (P–P = dppb, (*R*)-BINAP*) form upon refluxing $[Ru(COD)(\eta^3\text{-}H_2CCMeCH_2)_2]$ with the corresponding bisphosphine ligand.[106] Subsequent solution-calorimetric measurements on this system with a variation of the chelating phosphines (P–P = dppm, dppf*, dppe, dppb, dppp, depe*, dmpe) show that the most σ-donating phosphines afford the most thermodynamically stable complexes.[107] Similarly, reaction of $[Ru(\eta^4\text{-}C_8H_{12})(\eta^3\text{-}H_2CC(Me)CH_2)_2]$ with the C_2 chiral ligands *trans*-1,2-$C_5H_8(PR_2)_2$ yields $[Ru\{1,2\text{-}C_5H_8(PR_2)_2\}(\eta^3\text{-}H_2CCMeCH_2)_2]$ (R = Me, Ph*, NC_5H_{10}*, OPh),[108] while treatment of $[Ru(COD)Cl_2]_2$ with P–P in refluxing ethanol followed by addition of an allyl Grignard provides a route to $[Ru\{^iPr_2P(CH_2)_nP^iPr_2\}(\eta^3\text{-}C_3H_5)_2]$ ($n = 2, 3$)[100] and complexes with unsymmetrical P–P and P–As ligands, $[Ru\{Ph_2P(CH_2)_nPR_2\}(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$ ($n = 1$, 2; R = ^{i}Pr*, Cy) and $[Ru(Ph_2PCH_2CH_2As^tBu_2)(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$.[109,110] The carbonyl derivatives $[Ru(P\text{–}P)(CO)(\eta^3\text{-}2\text{-}C_3H_4R)X]$ (R = H, Me; X = Cl, Br) are easily made by reaction of $[Ru(CO)_3(\eta^3\text{-}2\text{-}C_3H_4R)X]$[111] with dppf or dippf at elevated temperature.[112] These



i, Cl$^-$; ii, BH$_4^-$; iii, BH$_4^-$

Scheme 7

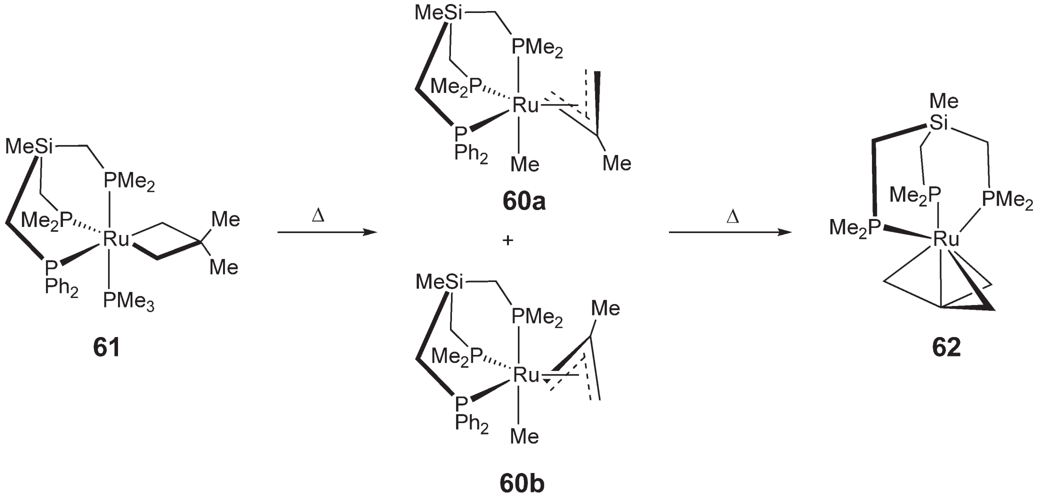
types of allyl complexes have been employed as labile precursors in later transformations. Thus, reaction of [Ru(dppf)(η^3-2-C$_3$H$_4$Me)$_2$] with HC≡CC(OH)R$_2$ in the presence of excess HX is a route to the alkenyl carbyne complexes *fac*-[Ru(dppf){≡CC(H)=CR$_2$}X$_3$] (R = Ph, ^{i}Pr; R$_2$ = C$_{13}$H$_8$; X = Cl, Br).[113] Halide abstraction from [Ru(dppf)(CO)(η^3-2-C$_3$H$_4$Me)Cl]* with AgSbF$_6$ yields the 16-electron complex [Ru(dppf)(CO)(η^3-2-C$_3$H$_4$Me)](SbF$_6$), which is readily trapped by a range of ligands L to give [Ru(dppf)(CO)(η^3-2-C$_3$H$_4$Me)(L)](SbF$_6$) (L = MeCN, CO, CNCH$_2$C$_6$H$_5$*).[114]

A 6 : 1 mixture of *endo*/*exo* isomers of the allyl complex [Ru(SiP$_3$)(Me)(η^3-CH$_2$CMeCH$_2$)Me] **60a** and **60b** forms upon thermolysis of the ruthenacyclobutane [Ru(SiP$_3$)(PMe$_3$)(η^2-CH$_2$CMe$_2$CH$_2$)]* (SiP$_3$ = MeSi(CH$_2$PMe$_2$)$_3$) **61**.[115] Subsequent heating of the allyl complex leads to loss of CH$_4$ and formation of the trimethylenemethane complex [Ru(SiP$_3$){η^4-C(CH$_2$)$_3$}]* **62** (Scheme 8).[116]

The five-coordinate alkenyl complex [Os(P^{i}Pr$_3$)$_2$(CO)(=CHPh){(*E*)-CH=CHPh}Cl] reacts with PhCHN$_2$ to afford [Os(P^{i}Pr$_3$)$_2$(CO)(=CHPh){(*E*)-CH=CHPh}Cl], which slowly rearranges in solution to [Os(P^{i}Pr$_3$)$_2$(CO)(η^3-PhCHCHCHPh)Cl].[117] A cationic variant of this, [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(η^3-PhCHCHCHPh)](BF$_4$), forms as the major product upon protonation of [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(C≡CPh)(CH$_2$Ph)] with HBF$_4$.[118] Slow isomerization of [Ru(PPh$_3$)$_2$(CO)(η^3-CH$_2$CHCMe$_2$)Cl] to [Ru(PPh$_3$)$_2$(CO)(η^3-CH$_2$CMeCHMe)Cl]* occurs both is solution and in the solid state.[119] The addition of aryl-substituted allenes H$_2$C=C=CHR to [Ru(PPh$_3$)$_2$(CO)(L–L^1)H] (L–L^1 = unsymmetrical bidentate N–N, N–O, O–O) gives one pair of enantiomers of [Ru(PPh$_3$)(CO)(L–L^1)(η^3-CH$_2$CHCHR)] (R = Ph, tolyl).[120]

Isomerization of [Os(P^{i}Pr$_3$)$_2$(CO){C$_6$H$_4$-2-(*E*)-CH=CHMe}H] takes place in solution at RT to yield [Os(P^{i}Pr$_3$)$_2$(CO)(η^3-CH$_2$CHCHPh}H], which upon addition of CO gives [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(η^1-CH$_2$CH=CHPh}H].[121] A mechanistic study on formation of the η^3-allyl species shows that it involves an intramolecular process involving reductive elimination of phenylpropene followed by C–H activation of the methyl group on the alkene. The benzyl alkynyl complex [Os(P^{i}Pr$_3$)$_2$(CO)$_2$(CH$_2$Ph)(C≡CPh)] reacts with HBF$_4$ to give a mixture of [Os(P^{i}Pr$_3$)(CO)$_2${C(CH$_2$Ph)=CHC$_6$H$_4$}] and the η^3-allyl complex [Os(P^{i}Pr$_3$)(CO)$_2${η^3-CH(Ph)CHCHPh}](BF$_4$). Deuterium-labeling experiments employing [Os(P^{i}Pr$_3$)(CO)$_2$(CD$_2$Ph)(C≡CPh)] give a mixture of [Os(P^{i}Pr$_3$)(CO)$_2${C(CD$_2$Ph)=CHC$_6$H$_4$}] and [Os(P^{i}Pr$_3$)CO)$_2${η^3-CD(Ph)CDCHPh}](BF$_4$) suggesting the intermediacy of [Os(P^{i}Pr$_3$)(CO)$_2${C(CH$_2$Ph)=CHPh}](BF$_4$), which undergoes a 1,2-hydrogen shift to yield the final allyl product.[118] The alkoxycarbonylallyl complexes [Ru(PPh$_3$)$_2$(η^3-CH$_2$CHCHCO$_2$R)H] are produced upon reaction of MeCH=CHCO$_2$R (R = Me, Et, Bu, Cy) and either [Ru(PPh$_3$)$_4$H$_2$] or [Ru(PPh$_3$)$_2$(PPh$_2$C$_6$H$_4$)(η^2-C$_2$H$_4$)H].[122]

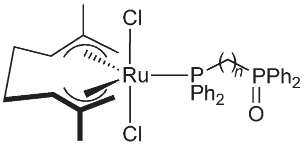
The allyl dimer [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(μ-Cl)}$_2$] reacts with arylamines in MeOH to give the adducts [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(NH$_2$R)] (R = Ph, 4-NH$_2$C$_6$H$_4$, 2-NH$_2$C$_6$H$_4$).[123] Upon addition of SbPh$_3$, P(OPh)$_3$, or 4-NCC$_5$H$_4$N to [Ru(η^3:η^3-C$_{10}$H$_{16}$)(μ-Cl)Cl]$_2$, the neutral complexes [Ru(η^3:η^3-C$_{10}$H$_{16}$)(L)Cl$_2$] (L = SbPh$_3$*, P(OPh)$_3$)[124] and [Ru(η^3:η^3-C$_{10}$H$_{16}$)(4-NCC$_5$H$_4$N)Cl$_2$]* are formed.[125] Treatment of [{Ru(η^3:η^3-C$_{10}$H$_{16}$)(μ-Cl)Cl}$_2$] with the diphosphine monoxides Ph$_2$P(CH$_2$)$_n$P(O)Ph$_2$ (n = 1, 3, 4) generates [Ru(κ^1-*P*-Ph$_2$P(CH$_2$)$_n$P(O)Ph$_2$)(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$] **63**, which upon reaction with AgBF$_4$ undergo partial chloride metathesis to afford the chelated complexes [Ru(κ^2-(*P, O*)-Ph$_2$P(CH$_2$)$_n$P(O)Ph$_2$)(η^3:η^3-C$_{10}$H$_{16}$)Cl](BF$_4$) **64**. The analogous dppm adduct can similarly be prepared.[126] Electrophilic attack by either H$^+$ or CH$_2$OMe$^+$ on [M(η^2-C$_5$H$_6$)(NH$_3$)$_5$](OTf)$_2$ (M = Ru, Os) provides a route to the corresponding cationic allyl complexes, which upon treatment with mild nucleophiles yield substituted η^2-cyclopentene complexes.[127]



Scheme 8

6.13.4.3 Pendant η^3-Ligands

Quite a common occurrence has been the conversion of a ligand cyclohexyl group into an η^3-cyclohexenyl moiety. Addition of C_2H_4 to $[Ru(PCy_3)_2(\eta^2\text{-}H_2)_2H_2]$ yields $[Ru(PCy_3)\{(\eta^3\text{-}C_6H_8)PCy_2\}(\eta^2\text{-}C_2H_4)]$ 65, which contains an η^3-cyclohexenyl ring; the same structural motif occurs in the related ruthenium(IV) trihydride complex $[Ru(PCy_3)\{(\eta^3\text{-}C_6H_8)PCy_2\}H_3]$ 66, which is formed upon addition of 3 equiv. of $CH_2{=}CHSiEt_3$ or $CH_2{=}CH^tBu$ to the bis-dihydrogen dihydride complex. With 5 equiv. of alkene, C–H activation of both PCy_3 ligands occurs to afford $[Ru\{(\eta^2\text{-}C_6H_9)PCy_2\}\{(\eta^3\text{-}C_6H_8)PCy_2\}H]$ 67 (Scheme 9). All three of these reactions can be reversed by addition of H_2.[20] The arrested Si–H oxidative-addition product $[Ru(PCy_3)\{(\eta^3\text{-}C_6H_8)PCy_2\}(\eta^2\text{-}H\text{-}SiMe_2Cl)H]^*$ is formed upon addition of 2 equiv. of $HSiMe_2Cl$ to the ethene complex $[Ru(PCy_3)\{(\eta^3\text{-}C_6H_8)PCy_2\}(\eta^2\text{-}C_2H_4)H]$.[128] At elevated temperature, $[Ru(Cy_2P(CH_2)_3PCy_2)(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$ undergoes C–H bond activation to generate the η^3-cyclooctenyl complex $[Ru\{\kappa^2\text{-}(P,P)\text{-}(\eta^3\text{-}C_6H_8)CyPCH_2CH_2CH_2PCy_2\}(\eta^3\text{-}C_8H_{13})]$ 68.[129] The allylamide complex *fac*-$[Ru(PMe_3)_3\{NHC_6H_3{}^iPr(\eta^3\text{-}CH_2CCH_2)\}]^*$ is formed in the reaction of *trans*-$[Ru(PMe_3)_4Cl_2]$ with $Li\{NH\ (2,6\text{-}{}^iPr_2C_6H_3)\}$.[130]



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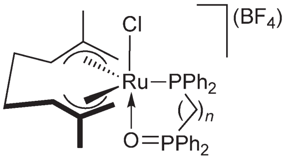

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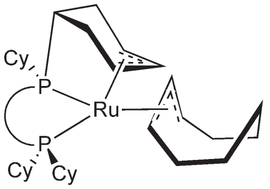
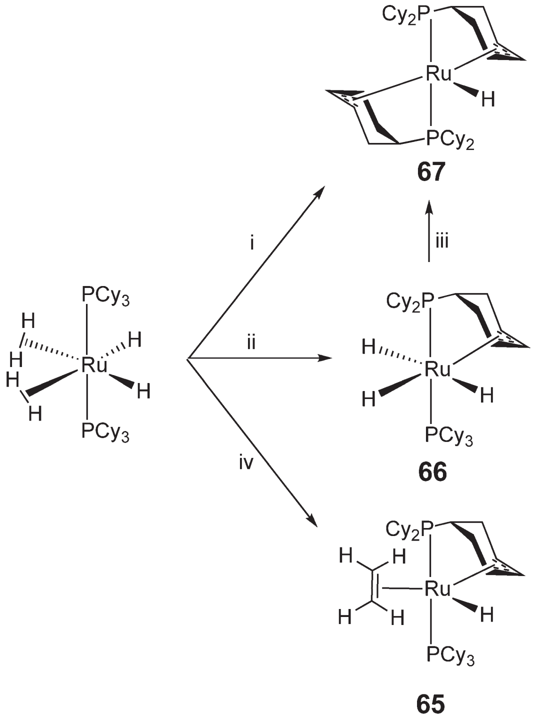


68

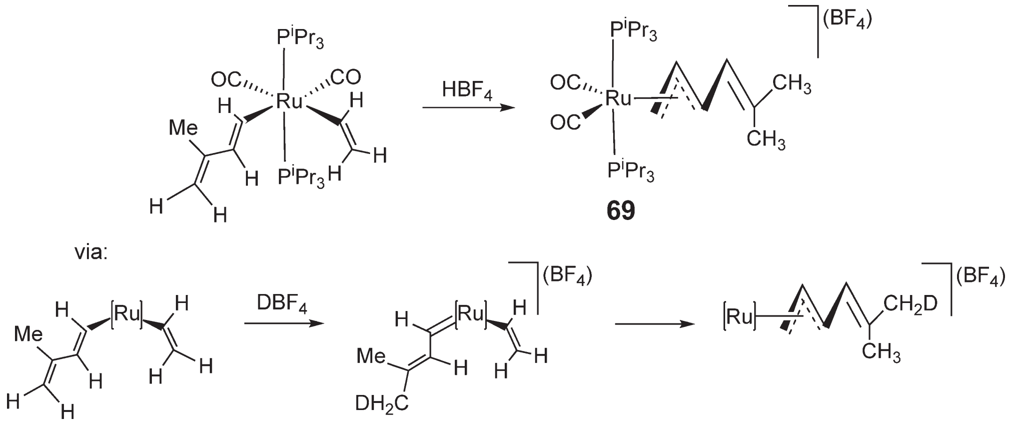
6.13.4.4 Unsaturated η^3-Ligands

Reaction of the coordinatively saturated bis-alkenyl complex $[Ru(P^iPr_3)_2(CO)_2\{(E)\text{-}CH{=}CHC(Me){=}CH_2\}(CH{=}CH_2)]$ with 1 equiv. of HBF_4 affords a mixture of products, the major one (50%) being the α,β-unsaturated allyl complex $[Ru(P^iPr_3)_2(CO)_2\{\eta^3\text{-}CH_2CHCHCH{=}CMe_2\}](BF_4)$ 69. The mechansism of formation is proposed to involve



i, $H_2C{=}CH^tBu$ (5 equiv.); ii, $H_2C{=}CHSiEt_3$ (3 equiv.); iii, $H_2C{=}CH^tBu$ (2 equiv.); iv, C_2H_4

Scheme 9



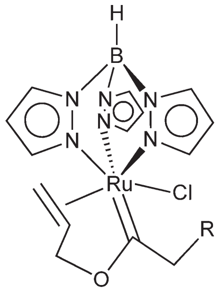
Scheme 10

electrophilic attack by H$^+$ on the β-C of the α,β-unsaturated ligand, followed by alkenyl migration from Ru to the α-C of the resulting α,β-unsaturated carbene ligand—studies with DBF$_4$ provide some support for this pathway (Scheme 10). Treatment of the mixture of products including 69 with an excess of either NaCl or KO$_2$CCH$_3$ affords [Ru(P^{i}Pr$_3$)$_2$(CO)$_2$ {η^3-CH$_2$CHCHCH=CMe$_2$}Cl]* and [Ru(P^{i}Pr$_3$)$_2$(CO){η^3-CH$_2$CHCHCH=CMe$_2$}(η^1-OC(O)Me)], respectively.[131]

The reaction of [Ru{HB(pz)$_3$}(DMSO)$_2$Cl] with an excess of RC≡CH and allyl alcohol under refluxing conditions produces the (allyloxy)carbene complexes [Ru{HB(pz)$_3$}(=C(CH$_2$R)OCH$_2$CH=CH$_2$)Cl] (70, R = Ph, C$_6$H$_9$, CO$_2$Me, C$_7$H$_{15}$*). With the latter alkyne, [Ru{HB(pz)$_3$}{η^3-(*O, C, C*)-H$_2$C=CHCH$_2$COC$_7$H$_{15}$}Cl] is also produced in a small amount. Treatment of [Ru{HB(pz)$_3$}(COD)Cl] with excess trimethylsilylacetylene and allyl alcohol affords [Ru{HB(pz)$_3$}{=C(CH$_2$SiMe$_3$)OCH$_2$CH=CH$_2$}Cl]*.[132] Protonation of [Ru(PPh$_3$)$_2$(CO)$_2$(η^2-PhC≡CC≡CPh)] with HPF$_6$ or HCl affords [Ru(PPh$_3$)$_2$(CO)$_2$(η^3-PhC≡CC=CHPh)](PF$_6$)* and [Ru(PPh$_3$)$_2$(CO)$_2$(η^1-PhC≡CC=CHPh)Cl], respectively.[89] The cationic hydride complex [Ru(P^{t}Bu$_2$Me)$_2$(CO)H](BAr$^F{}_4$) reacts with two molecules of alkyne affording the C–C coupled product [Os(P^{t}Bu$_2$Me)$_2${η^3-(Me$_3$Si)CH=CCH=CH(SiMe$_3$)}(CO)$_2$] (BAr$^F{}_4$)* 71.[133]

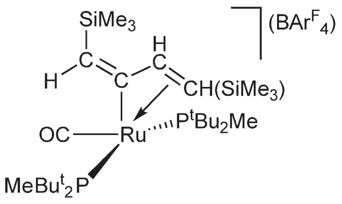
Upon refluxing with excess HC≡CPh in KOH/methanol, [Ru(Me$_3$tacn)(PMe$_3$)$_2$Cl](PF$_6$) is converted into [Ru(Me$_3$tacn)(PMe$_3$)(η^3-PhC$_3$=CHPh)](PF$_6$)*. Two isomeric η^3-butenynyl species [Ru(Me$_3$tacn)(PMe$_3$){η^3-PhC$_3$=CH(4-MeC$_6$H$_4$)}](PF$_6$) 72a and [Ru(Me$_3$tacn)(PMe$_3$){η^3-(4-MeC$_6$H$_4$)C$_3$=CHPh}](PF$_6$) 72b result from the reaction of [Ru(Me$_3$tacn)(PMe$_3$)(=C=CHPh)(η^1-O$_2$CCF$_3$)](PF$_6$) with HC≡C-*p*-tolyl in methanolic KOH.[134] The reaction of [Ru(SIMes)(PCy$_3$)(=CHPh)Cl$_2$] with RC≡CPh results in loss of phosphine and formation of [Ru(SIMes){η^3-(CHPh)(CR)(CPh)}Cl$_2$] (R = Ph*, Me). In the case of PhC≡CC≡CPh, a mixture of products [Ru(SIMes){η^3-(CHPh)(CC≡CPh)(CPh)}Cl$_2$] and [Ru(SIMes){η^3-(CHPh)(CPh)(CC≡CPh)}Cl$_2$] is formed.[135]

Treatment of [Ru(η^3:η^3-C$_{10}$H$_{16}$)(μ-Cl)Cl]$_2$ with PF$_3$ followed by reaction with PCy$_3$ results in nucleophilic attack of the second phosphine at the C3 carbon of the dienediyl ligand to generate the zwitterionic η^2:η^3-alkene(allyl) complex [Ru(PF$_3$){η^2:η^3-CH$_2$=C(Me)CH(PCy$_3$)(CH$_2$)$_2$CHC(Me)CH$_2$}Cl$_2$]* 73.[136]

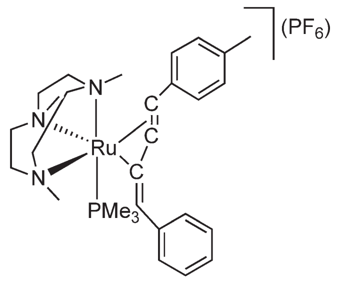


70

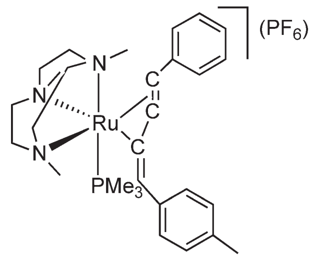
R = Ph
R = cyclohexenyl
R = CO$_2$Me
R = hexyl
R = SiMe$_3$



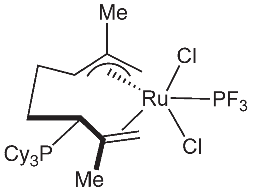
71



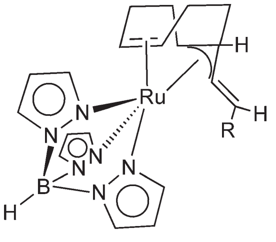
72a



72b



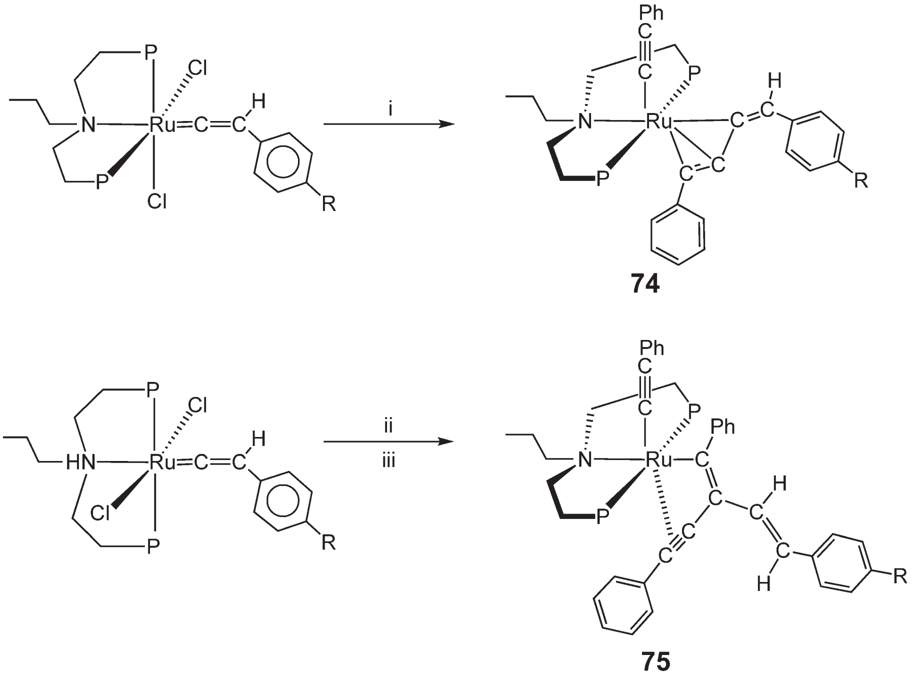
73



76

R = Ph
R = cyclohexenyl
R = ferrocenyl
R = benzyl
R = ^{n}Bu

Addition of LiC≡CPh converts *fac,cis*-[(PNP)Ru{=C=CH(R)}Cl$_2$] into the alkynyl η^3-benynyl complexes *anti, mer*-[(PNP)Ru(C≡CPh){η^3-PhC$_3$=CHR}] (R = Ph*, *p*-tolyl) **74**. By comparison, the alternative isomer *mer,trans*-[(PNP)Ru{=C=CH(R)}Cl$_2$] reacts under the same conditions to afford the alkynyl η-dienynyl complexes *mer*-[(PNP)Ru(C≡CPh){η-PhC=C(C≡CPh)CH=CH(R)}] (R = Ph, *p*-tolyl*) **75** (Scheme 11).[137] Treatment of [Ru{HB(pz)$_3$}(COD)Cl] or [Ru{HB(pz)$_3$}(κ^3-(*P*, *C*, *C*)-Ph$_2$PCH=CHC(Ph)=CH$_2$)Cl] **39a** with NaOEt/HC≡CR (R = Ph, C$_6$H$_9$, ferrocenyl, CH$_2$Ph, ^{n}Bu) in MeOH resulted in coupling of the alkene and alkyne to give (*Z*) and (*E*)-isomers of the η^3-butadienyl complex **76**. The mechanism for formation involves initial formation of the expected cationic vinylidene complex, a [2 + 2]-cycloaddition reaction of the Ru=C and alkene bonds to give a cationic metallacyclobutane and finally deprotonation of one of the C$_\beta$ hydrogen atoms.[138,139]



i, LiC≡CPh (2 equiv.); ii, LiC≡CPh (3 equiv.); iii, EtOH

Scheme 11

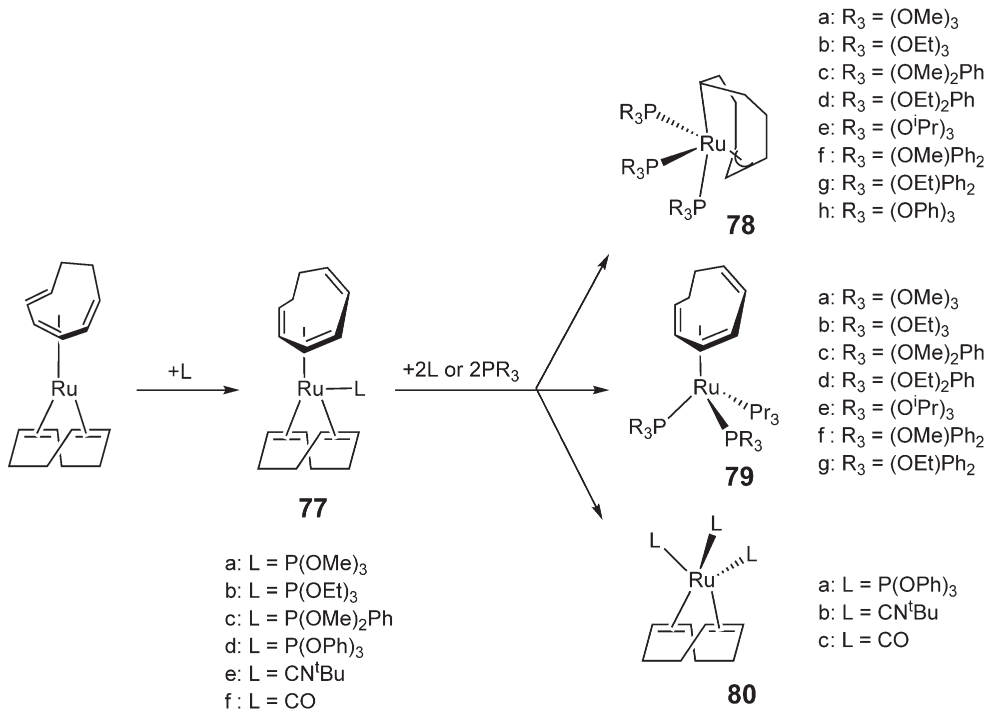
6.13.5 Ruthenium and Osmium Compounds with η^4-Ligands

The reactivity of [Ru(depe)(η^4-1,5-COD){η^2-H$_2$C=CHEX}] (EX = SPh, CH$_2$Ph) with PMe$_3$ has been described above. In contrast, for EX = OPh, addition of phosphine at RT generates [Ru(depe)(PR$_3$)(η^4-1,5-COD)] (PR$_3$ = PMe$_3$*, PMe$_2$Ph) and [Ru(depe) (κ^1-(*P*)-Et$_2$PCH$_2$CH$_2$PEt$_2$)(η^4-1,5-COD)].[21] Under 1 atm of H$_2$ in CH$_2$Cl$_2$, [Ru{(−)-Me-DuPHOS}(η^6-COT)H](BF$_4$) affords [Ru{(−)-Me-DuPHOS}(η^4-COD)H](BF$_4$) as the major species.[140]

A number of pyrazolyl-derived ligands have been used to support COD complexes of ruthenium to afford [Ru{HB(pz)$_3$}(η^4-1,5-COD)Cl], [Ru{HB(pz)$_3$}(η^4-1,5-COD)H], and [Ru(Hpz)$_2$(η^4-1,5-COD)Cl$_2$].[141] Addition of AgOTf to [Ru(η^4-1,5-COD)(bpzm)HCl] (bpzm = bis(pyrazol-1-yl)methane)[142] followed by PR$_3$ (PR$_3$ = PMe$_2$Ph, P(OMe)$_3$) affords *trans*-[Ru(η^4-1,5-COD)(bpzm)(PR$_3$)H](OTf), which readily isomerizes to *cis*-[Ru(η^4-1,5-COD)(bpzm)(PR$_3$)H](OTf).[143] Addition of MeMgCl to [Ru(η^4-1,5-COD)(bpzm)Cl$_2$] produces [Ru(η^4-1,5-COD)(bpzm)(Me)Cl], which upon addition of AgOTf and then either K{HB(pz)$_3$} or K{HB(pz*)$_3$} (pz* = 3,5-dimethylpyrazolyl) gives [Ru(η^4-1,5-COD){HB(pz)$_3$}Me] and [Ru(η^4-1,5-COD){HB(pz*)$_3$}Me]*. This latter compound shows an unsual binding mode involving two of the three nitrogen rings binding to the ruthenium, the third "sting" of the scopionate coming from the B–H group.[144] Condensation of pyrrole-2-aldehyde and 2-picolylamine yields the monoanionic tridentate ligand Pyr-Pic-H, which upon addition of BuLi and then [{Ru(η^4-1,5-COD)Cl}$_2$(μ-Cl)$_2$] generates [Ru(η^4-1,5-COD)(Pyr-Pic-H$_2$)Cl]; reaction with AgOTf affords [Ru(η^4-1,5-COD)(Pyr-Pic-H$_2$)OTf]. The reaction of the ruthenium COD dimer with potassium salt of the tetradentate ligand pyren (*N*,*N*′-ethylenebis(2-pyrrolyliminato)dianion) gave [Ru(η^4-1,5-COD)(pyren)]*.[145]

Addition of Ag$_2${μ_2,η-PhNC(H)=NPh}$_2$ to [Ru(η^4-1,5-COD)(MeCN)$_2$Cl$_2$] or [Ru(η^4-NBD)(C$_5$H$_5$N)$_2$Cl$_2$] forms [Ru(η^4-1,5-COD){η^2-PhNC(H)=NPh}$_2$]* and [Ru(η^4-NBD){η^2-PhNC(H)=NPh}$_2$]*, respectively. Alternatively, the reaction of Li{^{i}PrNC(Me)=N^{i}Pr} with [Ru(η^4-1,5-COD)Cl$_2$]$_n$ or [Ru(η^4-NBD)(C$_5$H$_5$N)$_2$Cl$_2$] gives [Ru(η^4-1,5-COD){η^2-^{i}PrNC(Me)=N^{i}Pr}$_2$]* and [Ru(η^4-NBD){η^2-^{i}PrNC(Me)=N^{i}Pr}$_2$]. Upon careful addition of just 1 equiv. of Li{^{i}PrNC(Me)=N^{i}Pr} to [Ru(η^4-NBD)(C$_5$H$_5$N)$_2$Cl$_2$], the monoamidinate complex [Ru(η^4-NBD){η^2-^{i}PrNC(Me)=N^{i}Pr}(C$_5$H$_5$N)Br]* can be isolated.[146]

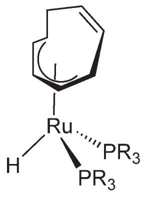
Addition of P(OMe)$_3$, P(OEt)$_3$, P(OMe)$_2$Ph, P(OEt)$_2$Ph, P(O^{i}Pr)$_3$, P(OMe)Ph$_2$ or P(OEt)$_2$Ph to [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] yields initially [Ru(η^4-1,5-COD)(η^4-1,3,5-COT){P(OR)$_3$}] 77, which subsequently loses COD to give [Ru(6-η^1:1-3-η^3-COT){P(OR)$_3$}$_3$] 79 and [Ru(η^4-1,3,5-COT){P(OR)$_3$}$_3$] 78 (Scheme 11). With the strong



Scheme 12

π-acceptor $P(OPh)_3$, $[Ru(\eta^4\text{-1,5-COD})(\eta^4\text{-1,3,5-COT})\{P(OPh)_3\}]$ converts into a mixture of $[Ru(6\text{-}\eta^1\text{:1-3-}\eta^3\text{-COT})\{P(OPh)_3\}_3]$ and $[Ru(\eta^4\text{-1,5-COD})\{P(OPh)_3\}_3]$ **80**, before finally forming the metallated species $[Ru\{P(OC_6H_4)(OPh)_2\}_2\{P(OPh)_3\}_2]$. When the Lewis base is changed from phosphite to isocyanide, 1,3,5-COT is liberated to afford $[Ru(\eta^4\text{-1,5-COD})(CN^tBu)_3]^*$, which subsequently reacts with the free triene to eventually give $[Ru(6\text{-}\eta^1\text{:1-3-}\eta^3\text{-COT})(CN^tBu)_3]$.[147]

Addition of tertiary phosphines to $[Ru(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ gives $[Ru(\eta^4\text{-1,3,5-COT})(PR_3)_3]$ ($PR_3 = PMe_3$, PEt_3^*, PMe_2Ph, PEt_2Ph, P^nBu_3). For the PEt_3, PEt_2Ph, and P^nBu_3 complexes, phosphine dissociation occurs in solution leading to the hydride complexes $[Ru(\eta^5\text{-}C_8H_9)(PR_3)_2H]$ **81**. Upon heating, both $[Ru(\eta^4\text{-1,3,5-COT})(PMe_3)_3]$ and $[Ru(\eta^4\text{-1,3,5-COT})(PMe_2Ph)_3]$ undergo oxidative addition of the cyclooctatriene group to yield $[Ru(6\text{-}\eta^1\text{:1-3-}\eta^3\text{-COT})\{PMe_3\}_3]$ and $[Ru(6\text{-}\eta^1\text{:1-3-}\eta^3\text{-COT})\{PMe_2Ph\}_3]$, respectively, whereas prolonged heating of $[Ru(\eta^4\text{-1,3,5-COT})(PEt_3)_3]$ leads to disproportionation of the hydrocarbon ligand to give $[Ru(\eta^4\text{-}C_8H_8)(PEt_3)_3]^*$ and $[Ru(\eta^5\text{-}C_8H_{11})(PEt_3)_2H]$. Isomerization chemistry is observed upon heating $[Ru(\eta^4\text{-1,3,5-COT})(PEt_2Ph_3)_3]$ or upon prolonged heating of $[Ru(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ with PEt_3, to give $[Ru(\eta^4\text{-bicyclo[4.2.0]octa-2,4-diene})L_3]$ (**82**, $L = PEt_2Ph$, PEt_3).[148] Treatment of $[Ru(\eta^4\text{-1,3,5-COT})(PEt_3)_3]$ with a stoichiometric amount of allyl alcohol at RT affords the η^4-acrolein complex $[Ru(PEt_3)_3\{\eta^4\text{-}H_2C{=}CHCH(O)\}]^*$ (the same product is formed in the *in situ* reaction from $[Ru(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]/PEt_3$).[149] The chemistry of $[Ru(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ for a range of bond activation reactions has been summarized.[150] An improved synthesis of $[Ru(\eta^4\text{-1,5-COD})(MeCN)_4]^+$ leading to the BF_4 salt results in a 75% higher yield than the previous three-step route to the PF_6^- salt.[151]



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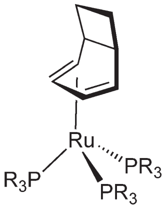


82

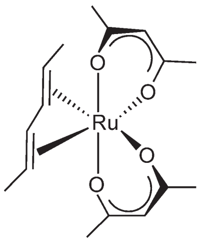
Silver salt abstraction of chloride from $[Ru\{HB(pz)_3\}(\eta^4\text{-1,5-COD})Cl]$ has allowed the isolation of $[Ru\{HB(pz)_3\}(\eta^4\text{-1,5-COD})L](OTf)$ ($L = H_2O^*$, MeCN, DMSO, C_5H_5N).[152]

A range of new $[Ru(\eta^6\text{-arene})(\eta^4\text{-1,5-COD})]$ (arene = phenanthrene*, anthracene, 9,10-dihydroanthracene) have been prepared. Treatment with HPF_6 yields a number of products; $[Ru(\eta^6\text{-phenanthrene})(\eta^4\text{-1,5-COD})H](PF_6)$ is isolated in 53% yield, whereas protonation of the dihydroanthracene species gives an equilibrium mixture of $[Ru(\eta^6\text{-9,10-dihydroanthracene})(\eta^4\text{-1,5-COD})H](PF_6)$ and the agostic cyclooctenyl complex $[Ru(\eta^6\text{-9,10-dihydroanthracene})(\eta^1,\eta^3\text{-}C_8H_{13})](PF_6)$. The latter can be trapped as the CO adduct $[Ru(\eta^6\text{-9,10-dihydroanthracene})(1\text{-}3\text{-}\eta^3\text{-}C_8H_{13})(CO)](PF_6)$.[154] At elevated temperature, $[Ru\{HB(pz)_3\}(\eta^4\text{-1,5-COD})Cl]$ reacts with K[quin] (quin = quinolin-8-olate) to afford $[Ru(\eta^4\text{-1,5-COD})(quin)_2]^*$, which can also be formed upon reaction of $[Ru(\eta^4\text{-1,5-COD})Cl_2]_2$ with quinolinol in the presence of base.[154,155]

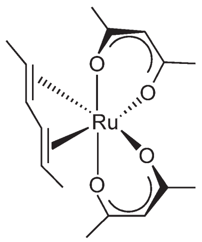
Co-condensation of ruthenium or osmium atoms with mixtures of arene/hexafluorobenzene at −196 °C affords the mixed compounds $[M(\eta^6\text{-arene})(\eta^4\text{-}C_6F_6)]$ ($M = Ru^*$, Os; arene = 1,3,5-$Me_3C_6H_3^*$, 1,3-$Me_2C_6H_4$, C_6H_6).[156] The addition of a slight excess of PR_3 or ^tBuNC to $[Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-1,5-COD})]$ at or below RT leads to the η^4-naphthalene complexes $[Ru(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-1,5-COD})(L)]$ ($L = PMe_3^*$, PEt_3^*, $P(OMe)_3^*$, $P(OEt)_3$, CN^tBu). Structural characterization reveals a hinge angle of ca. 40° in the bent naphthalene ligand.[157]

The osmium(IV) dihydride complex $[Os(P^iPr_3)_2H_2Cl_2]$ reacts with 1,5-COD in refluxing toluene to give the isopropenylphosphine species **23**. At lower temperature, $[Os(P^iPr_3)\{\eta^4\text{-}C_8H_{11}P^iPr_3\}HCl_2]$ is formed, although this converts into **23** and $[Os\{(\eta^2\text{-}CH_2{=}CMe)P^iPr_2\}(\eta^4\text{-NBD})Cl_2]$ upon reaction with 1,5-COD and 2,5-NBD, respectively. Refluxing tetrafluorobenzobarralene with $[Os(P^iPr_3)_2H_2Cl_2]$ produces a mixture of $[Os\{(\eta^2\text{-}CH_2{=}CMe)P^iPr_2\}(\eta^4\text{-TFB})Cl_2]$ and $[Os\{(\eta^2\text{-}CH_2{=}CHCH_2)P^iPr_2\}(\eta^4\text{-TFB})Cl_2]$ **25**.*[50]

The ruthenium(II) diene complexes $[Ru(acac)_2(diene)]$ (diene = 2,5-dimethyl-2,4-hexadiene*, 1,2,4,5-tetramethyl-1,4-cyclohexadiene*), formed upon addition of free diene and zinc to $[Ru(acac)_3]$ in EtOH, exist in solution as a pair of diastereoisomers **83a and 83b**.[158] Thermolysis of $[Ru(PPh_3)_3(CO)HCl]$ with neat $CH_2{=}C(Me)CH_2OH$ at 80 °C affords the ruthenium(0) complex $[Ru(PPh_3)_2(CO)\{\eta^4\text{-}CH_2{=}C(Me)CH{=}O\}]^*$.[159]



83a

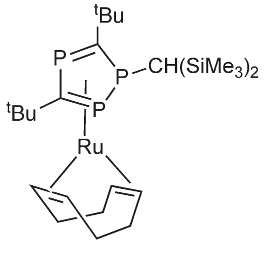


83b

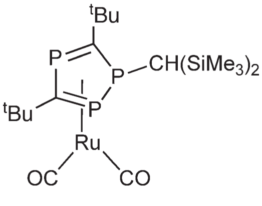
The trimethylenemethane complex **62*** forms upon thermolysis of the allyl complex [Ru(SiP$_3$)(PMe$_3$)(η^3-CH$_2$CMeCH$_2$)Me] **61** (SiP$_3$ = MeSi(CH$_2$PMe$_2$)$_3$).[116] Trimethylenemethane complexes also result from addition of CH$_2$=C(CH$_2$SnMe$_3$)$_2$ to [M(CO)$_3$Cl$_2$]$_2$ to give [M{η^4-C(CH$_2$)$_3$}(CO)$_3$] (M = Ru*, Os).[160] The ring opening of alkylidenesiliiranes provides a route to η^4-silatrimethylenemethane Ru complexes.[161]

The bis(cyclooctatetraene) complex [Ru{(1-6-η)-C$_8$H$_8$}{(1-4-η)-C$_8$H$_8$}]* is highly fluxional in solution displaying an equilibration of all carbon and hydrogem atoms in the (1-4-η)-ring, a 1,5-shift in the (1-6-η)-ring and an exchange of hapticity between the two rings. Upon addition of L to afford [Ru{(1-4-η)-C$_8$H$_8$}{(1,2,5,6-η)-C$_8$H$_8$}(L)] (L = PMe$_3$*, PEt$_3$, P(OMe)$_3$, CO*, ^{t}BuNC*), neither fluxionality is observed in the (1,2,5,6-η)-ring nor there is interchange of the ring hapticities.[162] Treatment of suspensions of [M(PMe$_2$Ph)$_3$(η^6-*o*-C$_6$H$_4$Me$_2$)](PF$_6$)$_2$ with KO^{t}Bu generated the *endo*-*o*-xylylene complexes [M(PMe$_2$Ph)$_3${η^4-*o*-(CH$_2$)$_2$C$_6$H$_4$}] (M = Ru*, Os*). Both complexes are fluxional due to restricted rotation of the M(PMe$_2$Ph)$_3$ unit.[163] DFT studies on [Ru(PH$_3$)$_3${η^4-*o*-(CH$_2$)$_2$C$_6$H$_4$}] suggest that the *exo* isomer is more stable than the *endo* isomer due to the enhanced aromatic character of the six-membered ring upon coordination at the *exo* site.[164]

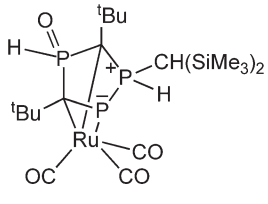
A range of [Ru(NH$_3$)$_4$(η^4-diene)]$^{2+}$ complexes (diene = 1,3-butadiene*, 1,4-pentadiene, 1,5-hexadiene) results from the addition of the diene to [Ru(NH$_3$)$_4$(Me$_2$CO)$_2$]$^{2+}$ at RT.[165] Thermolysis of [Ru$_3$(CO)$_{12}$] with 1,4-di-*tert*-butylbuta-1,3-diene at 140 °C affords [Ru(CO)$_3$(η^4C$_4$H$_4$^{t}Bu$_2$)], which is fluxional in solution.[166] Related ruthenium phosphine isoprene and pentadiene complexes have been spectroscopically characterized.[167] The yellow ruthenium(0) phosphole complex [Ru(η^4-1,5-COD)(η^5-P$_3$C$_2$^{t}Bu$_2${CH(SiMe$_3$)$_2$})]* **84** undergoes an unusual hydrogen migration reaction upon heating to yield [Ru(η^5-C$_8$H$_{11}$)(η-P$_3$C$_2$^{t}Bu$_2$H{CH(SiMe$_3$)$_2$})]*; the bonding of the phosphorus ligand in the latter can be viewed as consisting of a three-electron η^3-1,3diphosphaallyl component, along with two-electron donation from a σ^3-P center.[168] The reaction of **84** with CO affords the dicarbonyl complex [Ru(CO)$_2$(η^5-P$_3$C$_2$^{t}Bu$_2${CH(SiMe$_3$)$_2$})] **85**, which upon treatment with CO/H$_2$O converts into **86**.[169] The reaction of [Ru(PPh$_3$)$_3$(CO)$_2$] with 4,7,10-trithiatrideca-2,11-diyne (TTDD) at RT affords the cyclopentadienone complex [Ru(PPh$_3$)(CO){η^4-κ-*S*-S(C$_2$H$_4$SCCMe)$_2$CO}]* **87**, which upon refluxing in toluene in the presence of dppe gives [Ru(dppe)(CO){η^4-S(C$_2$H$_4$SCCMe)$_2$CO}].[170]



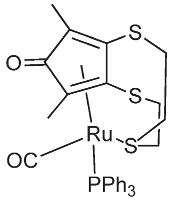
84



85



86



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Reductive coupling of two alkenyl fragments occurs upon reaction of [Os(P^{i}Pr$_3$)$_2$(CO){(*E*)-CH=CHR}Cl] (R = Ph, H) with H$_2$C=CHMgBr to afford [Os(P^{i}Pr$_3$)$_2$(CO)(η^4-C$_4$H$_5$R)], which shows a distorted square pyramidal structure with an apical P^{i}Pr$_3$ ligand and *cis*-oriented phosphine and CO groups in the base. Addition of the same Grignard reagent to [Ru(P^{i}Pr$_3$)$_2$(CO){(*E*)-CH=CHPh}Cl] gives [Ru(P^{i}Pr$_3$)$_2$(CO){(*E*)-CH=CHPh}(CH = CH$_2$)], which forms [Ru(P^{i}Pr$_3$)$_2$(CO)(η^4-C$_4$H$_5$Ph)] in solution at 50 °C. Addition of CO to this π-(phenyl)butadiene complex forms [Ru(P^{i}Pr$_3$)$_2$(CO)$_2${(*E*)-CH=CHPh}(CH=CH$_2$)].[171] Addition of butadiene to [Ru(Sb^{i}Pr$_3$)$_3$(η^2-H$_2$)H$_2$] affords the five-coordinate butadiene complex [Ru(Sb^{i}Pr$_3$)(η^4-C$_4$H$_6$)$_2$].[45] In solution at RT, the alkyne vinylidene complex [Os(P^{i}Pr$_3$)$_2$(=C=CHPh)(η^2-HC≡CPh)H](BF$_4$) converts into the diphenylbutadiene species [Os(P^{i}Pr$_2$^{n}Pr)(η^4-C$_4$H$_4$Ph$_2$){(η^2-H$_2$C=CMe$_2$)P^{i}Pr$_2$}H](BF$_4$)*, which contains a monoisopropenylphosphine ligand.[91]

The reaction of $PhC{\equiv}CPh$ with $[Ru(PPh_3)_3(CO)_2]$ or $[Ru(PPh_3)_2(CO)_3]$ in refluxing toluene gives the 2-phenylindenone complex $[Ru(PPh_3)_2(CO)(\eta^4\text{-}O{=}CCPh{=}CHC_6H_4)]^*$ and tetraphenylcyclopentadienone species $[Ru(PPh_3)(CO)_2(\eta^4\text{-}O{=}CC_4Ph_4)]^*$, respectively.[172] Treatment of the pincer phosphine complex [Ru(PCP)(PPh$_3$)Cl] (PCP = 2,6-$(Ph_2PCH_2)_2C_6H_3$) with norbornadiene in the presence of CuCl yields the η^4-diene complex $[Ru(PCP)(NBD)Cl]^*$; reactions with TlOTf, $NaBH_4$, or TlO_2CH afford [Ru(PCP)(NBD)X] (X = OTf, H, OC(O)H), respectively.[173]

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6.14
Mononuclear Ru/Os Compounds with Cyclic C_5–C_6 Ligands (Except Compounds Containing Monohapto Ligands)

J Gimeno, V Cadierno, and P Crochet, Universidad de Oviedo, Oviedo, Spain

6.14.1 Introduction

Since the publication of COMC (1995), the number of reports devoted to the chemistry of arene– and cyclopentadienyl–ruthenium and –osmium complexes has exponentially increased. This particular interest has been essentially motivated by the numerous applications of this type of derivatives both in stoichiometric and catalytic organic synthetic processes. Moreover, some of them have attracted interest due to their biological activity. New developments are mainly focused on the preparation of asymmetric complexes including planar chirality, chiral arene or cyclopentadienyl ligands, chiral ancillary ligands, and/or chirality at the metal. On the other hand, important efforts have been devoted to the synthesis of tethered-type derivatives which are known to present increased thermal and configurational stability. The synthetic approaches developed for half-sandwich arene–ruthenium and arene–osmium complexes are almost exclusively based on the dinuclear species $[\{MCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ (M = Ru, Os). In the cyclopentadienyl series, along with the classical precursors $[RuCl(\eta^5\text{-}C_5R_5)(PPh_3)_2]$ and $[RuCl(\eta^5\text{-}C_5R_5)(CO)_2]$, the tris-solvato derivatives $[Ru(\eta^5\text{-}C_5R_5)(NCMe)_3][PF_6]$ have gained in popularity due to the substitutional lability of the acetonitrile ligands.

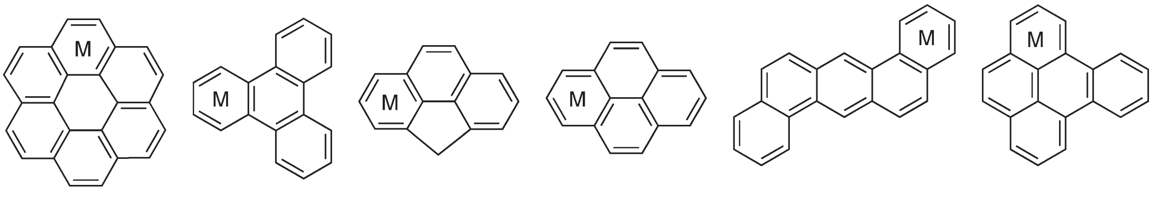
This chapter covers the literature published from January 1994 to December 2004. Due to the large number of articles published during the period considered only a selection of representative results is reviewed here. Throughout this chapter, a compound formula or number, or alternatively a reference, bearing an asterisk indicates that an X-ray structural determination has been carried out.

6.14.2 Sandwich-Type Compounds

6.14.2.1 Bis(Arene) Complexes

6.14.2.1.1 Monocyclic and polycyclic arenes (except cyclophanes)

As previously reported,[1] the most reliable synthetic approach for dicationic bis(arene) complexes $[M(\eta^6\text{-arene})(\eta^6\text{-arene}')]^{2+}$ (M = Os, Ru) consists in heating the tris-solvato derivatives $[M(\text{acetone})_3(\eta^6\text{-arene})]^{2+}$ (isolated or generated *in situ*) with an excess of the incoming arene′ in trifluoroacetic acid for a short time, usually a few minutes. Following this approach, the novel ruthenium complexes $[Ru(\eta^6\text{-cym})(\eta^6\text{-arene})][BF_4]_2$ (arene = naphthalene, phenanthrene, anthracene, 9,10-dihydroanthracene, *trans*-stilbene, fluorene,* coronene (**1**; Figure 1)) have been obtained in moderate to good yields using $[Ru(\text{acetone})_3(\eta^6\text{-cym})][BF_4]_2$ **2** as starting material.[2] Phenanthrene and anthracene bind the metal selectively through the outer ring, as assessed by ^{13}C NMR spectroscopy.



1 **3** **4** **5*** **6** **7**

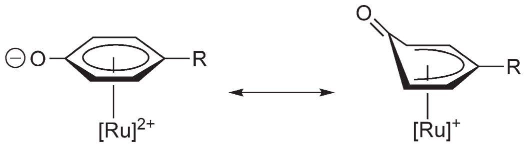
M indicates the ring linked to the metal

Figure 1 Structure of the polycyclic arenes **1–7**.

Symmetrical bis(arene) derivatives $[Ru(\eta^6\text{-arene})_2][BF_4]_2$ (arene = biphenyl,* bibenzyl, *trans*-stilbene) are similarly prepared from $[Ru(acetone)_3(\eta^6\text{-arene})][BF_4]_2$.[3] The fluorene analog $[Ru(\eta^6\text{-fluorene})_2][BF_4]_2$* has been isolated as a 1 : 1 mixture of diastereomers, arising from the two planar chiralities present in the molecule.[3] Like ruthenium, the analogous osmium tris-solvato derivative $[Os(acetone)_3(\eta^6\text{-}C_6H_6)][PF_6]_2$, generated from $[OsCl_2(NCMe)(\eta^6\text{-}C_6H_6)]$ and $Ag[PF_6]$ in acetone, reacts with hexamethylbenzene, 1,3,5-triethylbenzene, 1,2,3,5-tetramethylbenzene, or naphthalene in trifluoroacetic acid to give the corresponding $[Os(\eta^6\text{-}C_6H_6)(\eta^6\text{-arene})][PF_6]_2$ complexes.[4] A modified procedure, replacing CF_3CO_2H by CH_2Cl_2, is used to obtain selectively $[Ru(\eta^6\text{-cym})(\eta^6\text{-arene})][BF_4]_2$ (arene = **3–7**; Figure 1).[5] Under these conditions, longer reaction times (2 days) are required; however, problems associated with the formation of Ru(II) trifluoroacetate complexes are avoided. Similarly, treatment of the triflate salt of **2** with the fully protected amino acid *N*-acetyl-L-phenylalanine methylester (Ac-Phe-OMe), in refluxing dichloromethane, leads to $[Ru(\eta^6\text{-cym})(\eta^6\text{-Ac-Phe-OMe})][OTf]_2$.*[6] In contrast, when unprotected or half-protected amino acids are used $\kappa^2(N,O)$- or $\kappa^1(N)$-coordinations, respectively, are achieved. However, performing these reactions in trifluoroacetic acid results in the protonation of both amino and carboxylic groups promoting the η^6-coordination of the amino acid. In this way, the amino acid-based products Phe, Ac-Phe,[6] L-dopa (L-dopa = L-3,4-dihydroxyphenylalanine),[7] Ac-Tyr, Trp, Ac-Trp, and Ac-Trp-OMe*[8] have been coordinated to the $[Ru(\eta^6\text{-cym})][OTf]_2$ unit. As a general trend, coordination of the aromatic side chain of the tyrosine derivatives is associated with a marked enhancement in acidity of the *p*-hydroxy function. The structures of the deprotonated species present a significant contribution of the η^5-oxohexadienyl resonance form (Figure 2), as confirmed by X-ray analysis in the case of $[Ru(\eta^6\text{-cym})\{OC_6H_4CH_2CH(CO_2H)(NH_3)\}][OTf]_2$.*[8] The reactivity of $[Ru(acetone)_3(\eta^6\text{-cym})][OTf]_2$ with dipeptides has also been investigated.[8,9] The studies, performed with Tyr-Trp, Trp-Tyr, Trp-Phe, Phe-Tyr, Tyr-Phe, and Phe-Trp, reveal that their η^6-coordination to the fragment "$[Ru(\eta^6\text{-cym})]^{2+}$" is chemospecific in the order Trp > Tyr > Phe.

Ruthenium cymene bis(triflate) derivative **8**, formulated either as $[Ru(OTf)_2(\eta^6\text{-cym})]$ or $[\{Ru(OTf)_2(\eta^6\text{-cym})\}_x]$, has also proved to be a suitable precursor for dicationic bis(arene) complexes. For instance, its reaction with indole-type ligands in diethyl ether at room temperature affords the compounds $[Ru(\eta^6\text{-cym})(\eta^6\text{-arene})][OTf]_2$ **9** (arene = indole **9a**, 2,3-dimethylindole **9b**, 2-methylindole **9c**, *N*-methylindole **9d**).[10] It is noteworthy that the acidity of the pyrrolic ring dramatically increases upon coordination. Thus, deprotonation of the NH group in **9a–c** is readily achieved with neutral alumina or NaOH affording the monocationic complexes **10** (Figure 3) in which the benzene fragment, and not the five-membered heterocycle, is still coordinated to the metal. Following the same methodology used for **9**, indoline-containing complexes $[Ru(\eta^6\text{-arene})(\eta^6\text{-}N\text{-Me-indoline})][OTf]_2$ (arene = cym **11a**,* C_6H_6 **11b**) have been prepared starting from **8** or its benzene analog.[11] Alternatively, the synthesis of **11a** can be easily achieved through hydrogenation of the carbon–carbon double bond in **9d** promoted by an Rh/C catalyst.[11] Remarkably, under identical reaction conditions the free indole is hardly reduced to indoline.

Functionalized alkynyl and alkenyl derivatives $[Ru(\eta^6\text{-cym})(\eta^6\text{-}C_6H_5R)][OTf]_2$ ($R = C{\equiv}CPh$ **12a**, $C{\equiv}CEt$ **12b**, $CH{=}CH_2$ **13**) have also been synthesized.[12] Treatment of **12a** and **12b** and **13** with K_2CO_3 in methanol and subsequent addition of triflic acid induces formal intramolecular hydroalkylations affording the tethered complexes **14 and 15**, respectively (Figure 3). Monitoring the reaction of **12b** with base in CD_3OD by NMR spectroscopy reveals the successive formation of intermediates **16 and 17** during the process.[12] This transformation can be therefore explained by initial nucleophilic attack of the methoxide anion at the *ortho*-position of the C_6H_5R ring, followed by base-catalyzed carbon–carbon coupling, and final removal of the *exo*-OMe group promoted by triflic acid. Metallation of benzaldehyde and acetophenone with **8** proceeds in nitromethane at 60 °C to give $[Ru(\eta^6\text{-cym})\{\eta^6\text{-}C_6H_5C({=}O)R^1\}][OTf]_2$ ($R^1 = H$ **18**,* Me **19**).[13] Their coordination dramatically enhances the reactivity of the carbonyl group with nucleophiles. As an example, complex **18** is over 1 million times more reactive toward water than is free benzaldehyde. Attack on **18** and **19** by water or methanol generates the derivatives $[Ru(\eta^6\text{-cym})\{\eta^6\text{-}C_6H_5C(R^1)(OH)(OR^2)\}][OTf]_2$ ($R^1 = H$, Me; $R^2 = H$, Me). Hydroxy-functionalized compounds $[Ru(\eta^6\text{-cym})(\eta^6\text{-arene})][OTf]_2$ (arene = *p*- or *o*-$ClC_6H_4O(CH_2)_2OH$, $C_6H_5(CH_2)_mOH$, $m = 3$, 4) have also been prepared starting



[Ru] = $[Ru(\eta^6\text{-cym})]$; 1,4-HOC_6H_4R = Tyrosine-based derivatives

Figure 2 Resonance forms of the deprotonated tyrosine-based derivatives.

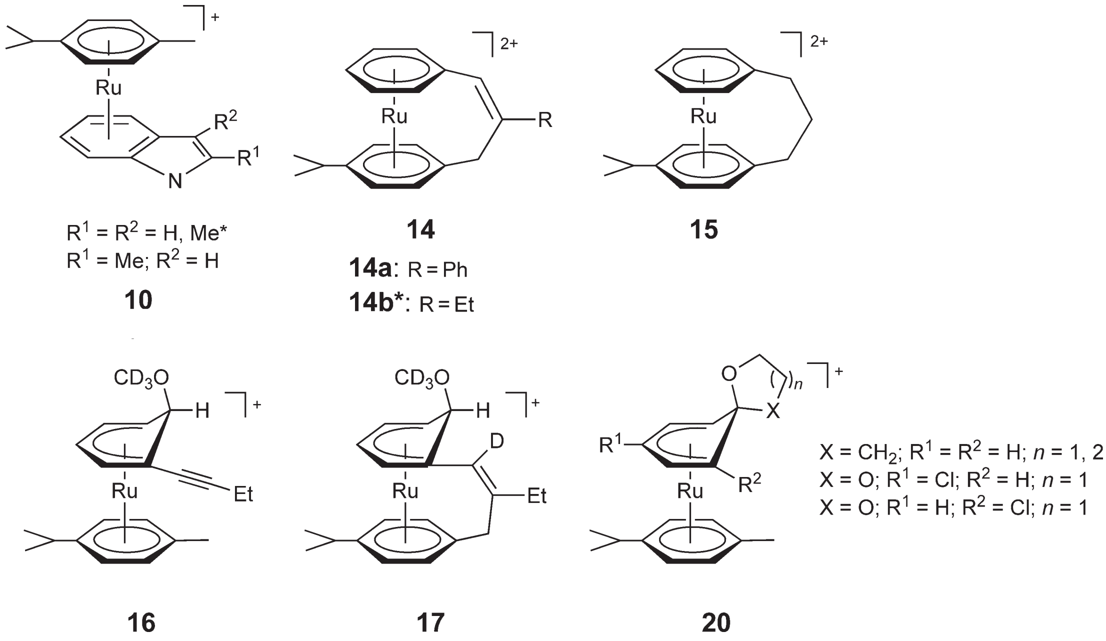


Figure 3 Structure of compounds **10**, **14–17**, and **20**.

from 8.[14] Under basic conditions, they selectively evolve into the corresponding spirocyclic η^5-cyclohexadienyls **20** (Figure 3), via intramolecular alkoxide addition at the *ipso*-carbon of the arene.

Aromatization of 2-cyclohexen-1-one is achieved in the presence of $[Ru(H_2O)_6][OTs]_2$ generating the bis-phenol derivative $[Ru(\eta^6\text{-}C_6H_5OH)_2][OTs]_2$.[15] Complex $[Ru(H_2O)_6][OTs]_2$ also reacts with tetramethylparaquinone to form the zwitterionic species $[Ru(\eta^6\text{-}MeC_6H_4SO_3)(\eta^6\text{-}HOC_6Me_4O)]$,* containing one η^6-hydrotetramethylquinone ligand and an η^6-coordinated tosylate.[15]

6.14.2.1.2 Cyclophanes

Substitution of labile acetone ligands in the tris-solvato precursors $[M(acetone)_3(\eta^6\text{-}C_6H_6)][BF_4]_2$ (M = Ru, Os) by cyclophanes **21–24** is readily achieved in trifluoroacetic acid yielding complexes $[M(\eta^6\text{-}C_6H_6)(\eta^6\text{-arene})][BF_4]_2$ (M = Ru, Os; arene = **21–24**; Figure 4).[16] The bis-cyclophane derivative $[Ru(\eta^6\text{-}\mathbf{21})_2][BF_4]_2$ has been similarly made.[16] All these compounds undergo two-electron electrochemical reduction to Ru(0) and Os(0) species in which the cyclophane ligand adopts a boat-shaped geometry η^4-bound to the metal. Cyclic voltammetry studies at different scan rates evidence that the generated Os(0) derivatives have higher stability than their ruthenium counterparts.

The capping reaction of vinyl-functionalized cyclophanes requires the elimination of CF_3CO_2H in the preparation method in order to avoid the acid-catalyzed polymerization of the ligand. This is illustrated in the synthesis of monocapped complexes $[Ru(\eta^6\text{-hmb})(\eta^6\text{-arene})][BF_4]_2$ (hmb = hexamethylbenzene, arene = **25a–c**, **26a–c**; Figure 5),[17,18] which are obtained from the tris-solvato $[Ru(acetone)_3(\eta^6\text{-hmb})][BF_4]_2$ by treatment with 1 equiv. of cyclophanes **25a–c** and **26a–c** in boiling acetone. Complexation of monosubstituted cyclophanes **25a–c** leads to two

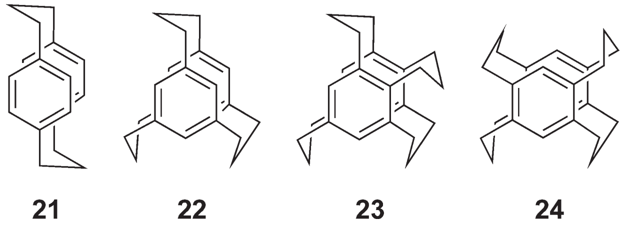


Figure 4 The cyclophane ligands **21–24**.

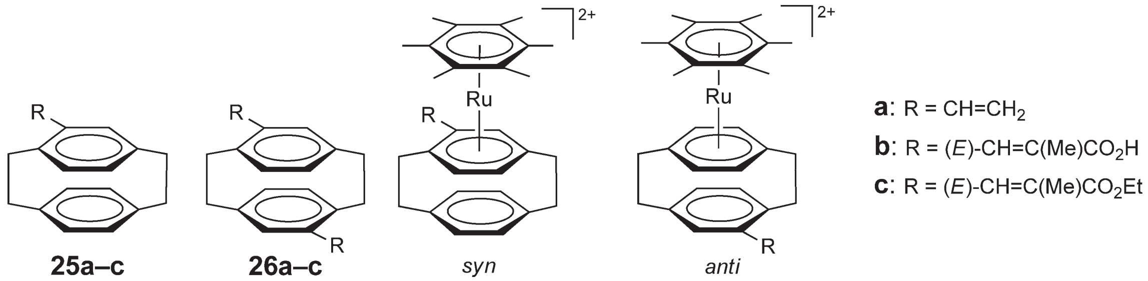


Figure 5 Cyclophanes 25 and 26.

different regioisomers, *syn* and *anti*, depending on the face linked to the metal (Figure 5). In all the cases, a mixture of *syn*- and *anti*-isomers is observed, the latter being the more abundant. Bis-capped compounds $[\{Ru(\eta^6\text{-hmb})\}_2(\eta^6{:}\eta^6\text{-arene})][BF_4]_4$ (arene = **25a**, **26a**) are obtained employing a 10-fold excess of the hexamethylbenzene–ruthenium solvate. Cyclic voltammetry of all these vinyl-functionalized complexes reveals chemically reversible two-electron reduction. On the other hand, they can be electrochemically oxidized in an irreversible process forming a polymeric film on the electrode surface.

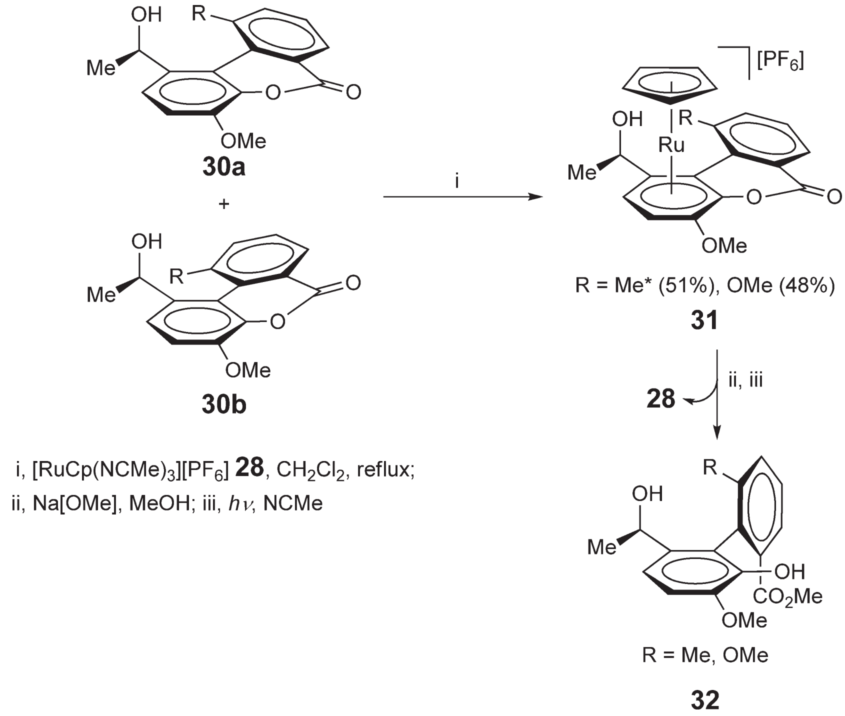
6.14.2.2 Mixed (η^5-C_5R_5)M(η^6-C_6R_6) Complexes

A review covering the literature published up to 2001 on the synthesis and reactivity of ruthenium cyclopentadienyl–arene complexes is available.[19]

6.14.2.2.1 Complexes containing a CpM fragment (M = Os, Ru)

The earlier synthesis of $[RuCp(\eta^6\text{-}C_6H_6)][PF_6]$ **27**, based on the reaction of the dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)\}_2]$ with a stoichiometric amount of thallium cyclopentadienyl and subsequent Cl/PF_6 exchange,[1] has been recently modified in order to achieve a high-scale and environmentally friendly process. Thus, thallium-free preparation of **27** has been performed by heating $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)\}_2]$ with an excess of cyclopentadiene and potassium carbonate in anhydrous ethanol at 60 °C, followed by the addition of an aqueous solution of $[NH_4][PF_6]$.[20] Complexes $[RuCp(\eta^6\text{-arene})][Y]$ (arene = hmb, Y = Cl;[21] arene = cym, Y = PF_6)[20] have been similarly synthesized. Photoirradiation of an acetonitrile solution of **27** results in its quantitative conversion into $[RuCp(NCMe)_3][PF_6]$ **28** within 12 h.[1,20] Complex **28** can be alternatively obtained by displacement of the naphthalene ligand in $[RuCp(\eta^6\text{-naphthalene})][PF_6]$ **29** by acetonitrile at room temperature, irradiation not being required in this case.[22] The precursor **29** is accessible in high yield from the reaction of ruthenocene with naphthalene, $AlCl_3$, aluminum powder, and $TiCl_4$ in decalin at 140 °C for 3 days after anion exchange with $K[PF_6]$.[22] The constant efforts to improve the synthesis of **28** arise from its synthetic utility. Indeed, the acetonitrile ligands in **28** are thermally labile and when this complex is heated in the presence of arene ligands, in a non-coordinating solvent, the corresponding η^6-arene derivatives $[RuCp(\eta^6\text{-arene})][PF_6]$ are obtained in good yields.[1,19] This procedure represents actually the most common entry to ruthenium cyclopentadienyl–arene complexes and it is compatible with a wide range of functionalities on the arene ring. For example, *N*,*N*-dimethylaniline,[23] phenyl allyl ether, acetophenone,[24] *trans*-stilbene,[25] chlorobenzene, 1,2-dichlorobenzene, and 1,2-benzenediamine[26] have been η^6-coordinated on the $[CpRu]^+$ fragment using this methodology. Similarly, the osmium complexes $[OsCp(\eta^6\text{-arene})][PF_6]$ (arene = anthracene, 5,6,11,12-tetraphenylnaphthacene (rubrene)) have been prepared by treating an acetone solution of $[OsCp(NCMe)_3][PF_6]$ with the appropriate arene.[27] In these compounds, the metal selectively binds through the outermost ring of the fused polycyclic moiety.

When the arene ring is substituted with different groups at the 1,2- or 1,3-positions, the resulting complexes [RuCp(arene)][X] exist in two enantiomeric forms with R_p and S_p planar chirality, respectively. Therefore, complexation of *rac*-1,2-$RC_6H_4CH(Me)(OH)$ (R = OMe, Me, $SiMe_3$) to the $[CpRu]^+$ unit gives rise to a mixture of two diastereomers, (S_pS_C/R_pR_C) and (S_pR_C/R_pS_C), with a diastereoselectivity ranging from 92% to 95%.[28] The reaction of $[RuCp(NCMe)_3][PF_6]$ **28** with an atropoisomeric mixture of the δ-lactones **30a** and **30b** leads to the optically pure derivatives **31** (Scheme 1).[28] During this process, the atropoisomerization of **30b** into **30a** takes place, although it is not clear whether the isomerization occurs before or after coordination to the metal. Further ring opening of the



i, $[RuCp(NCMe)_3][PF_6]$ **28**, CH_2Cl_2, reflux;
ii, Na[OMe], MeOH; iii, *hν*, NCMe

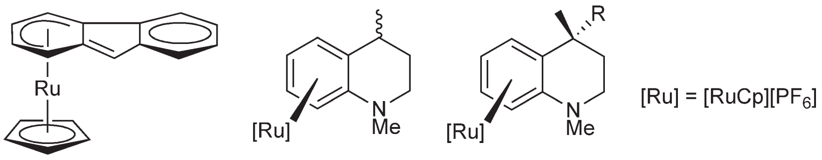
Scheme 1

lactone, performed with NaOMe in methanol, and subsequent demetallation by photoirradiation in the presence of acetonitrile regenerates 28, and liberates the biaryls 32 as single atropoisomers.[28]

The η^6-coordination strongly affects the reactivity of the arene moiety, and in particular the acidity of benzylic protons. Thus, complexes $[RuCp(\eta^6\text{-fluorene})][PF_6]$ **33** and $[RuCp(\eta^6\text{-hmb})][PF_6]$ **34** exhibit p*K*a values of 14.7 and 29.3, respectively, while p*K*a values for free fluorene and hexamethylbenzene are 22.6 and 43, respectively.[29] Deprotonation of **33** and **34** with KH or $KOBu^t$ in THF leads to the η^5-cyclohexadienyl derivatives 35 (Figure 6) and $[RuCp(\eta^5\text{-}C_5Me_5C{=}CH_2)]$,* respectively.[29]

The diastereomeric mixture of 36 (Figure 6) can also be deprotonated at the benzylic position with NaH in THF. Subsequent addition of bromoalkanes, methyl chloroformate, or acetic anhydride gives complexes 37 (R = Et, Bz, $CH_2CH{=}CH_2$, $CH_2CH{=}CMe_2$, $CH_2CMe{=}CH_2$, $CH_2C{\equiv}CMe$, CO_2Me, $C({=}O)Me^*$) isolated in all cases as a single diastereomer.[30] The selectivity of the process arises from the sterically favored approach of the electrophile to the face opposite to the metal. Using a similar reaction sequence, the stereoselective benzylic alkylation of η^6-coordinated 1,3-dimethylindoline has also been achieved.[30]

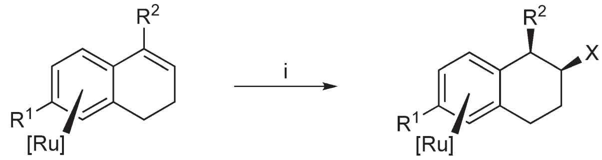
Unexpectedly, nucleophilic attack on the α,β-unsaturated arene rings in compounds 38 takes place preferentially on the *endo*-face, affording complexes *endo*-39 as the predominant isomer (Equation (1)). This stereochemical outcome can be compared to classical S_N2' reactions, which are known to occur with *syn*-stereochemistry between the nucleophile (i.e., CN^- or PhS^-) and the leaving group (in this case the metal).[31] Addition of LiMe or BrMgMe to the carbonyl group of the aldehyde ligand in *rac*-$[RuCp(\eta^6\text{-}o\text{-methoxybenzaldehyde})][PF_6]$ proceeds with high diastereoselectivity to give (S_pS_C/R_pR_C)-$[RuCp\{\eta^6\text{-}o\text{-}MeOC_6H_4CH(Me)(OH)\}][PF_6]$ as the major product.[28] On



35 **36** **37**

Figure 6 Structure of sandwich complexes 35–37.

the other hand, the other diastereomer (R_pS_C/S_pR_C) is obtained predominantly by reduction of *rac*-[RuCp(η^6-*o*-methoxyacetophenone)][PF_6] with Na[BH_4].[28]



[Ru] = [RuCp][PF_6]

38

i, DMF/H_2O, KCN or HSPh/$NEtPr^i_2$

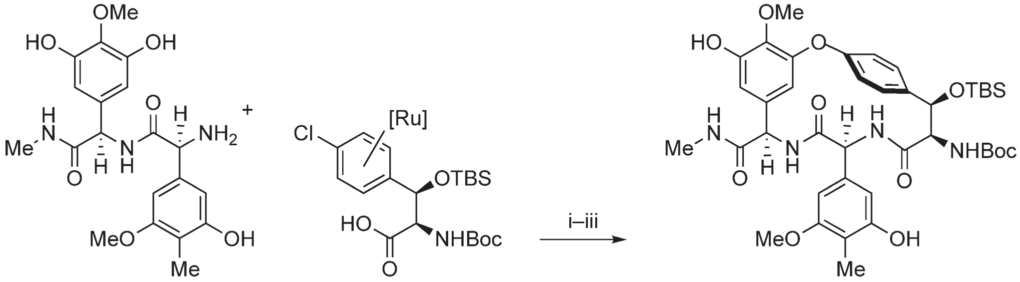
endo-**39**

R^1 = R^2 = H; X = CN *endo* : *exo* = 1 : 1
R^1 = OMe; R^2 = H; X = CN *endo* : *exo* = 2 : 1
R^1 = OMe; R^2 = Me; X = CN *endo** : *exo* = 3 : 1
R^1 = R^2 = H; X = SPh *endo* : *exo* = 3 : 1
R^1 = OMe; R^2 = H; X = SPh *endo* : *exo* = 5 : 4
R^1 = OMe; R^2 = Me; X = SPh *endo only*

(1)

Derivatives containing η^6-coordinated haloarenes can be readily functionalized, through nucleophilic aromatic substitution processes, with various oxygen- and nitrogen-based nucleophiles.[26,32,33,34] For example, sequential chloride replacements in [RuCp(η^6-1,4-$C_6H_4Cl_2$)][PF_6], first by 1-aza-18-crown-6 or 1-aza-15-crown and then by piperidine, are achieved in THF and in the presence of pyridine leading to complexes [RuCp(η^6-arene)][PF_6] (arene = p-$C_5H_{10}NC_6H_4\overline{N(CH_2CH_2O)_nCH_2CH_2}$, $n = 4$, 5).[34] Subsequent exposure to UV light results in the decomplexation of the aza-crown ethers. Double nucleophilic aromatic substitutions are sometimes problematic since the replacement of the first halide of the arene generally increases the electron density of the ligand, therefore impeding subsequent nucleophilic additions. For example, only one chloride substituent of the CpRu-coordinated 1,2-dichlorobenzene ligand is exchanged by *tert*-butylamine or sodium benzimidazolate, even in the presence of a large excess of reagent or after prolonged refluxing periods.[26]

The syntheses of a wide range of macrocyclic peptides incorporating a biaryl–ether linkage have been successfully performed employing arene–cyclopentadienyl–ruthenium derivatives.[19,35,36] For example, condensation between the dipeptide **40** and the arylserine–ruthenium complex **41** can be achieved in smooth conditions, with little or no epimerization during the process (Equation (2)). In a second step, the intramolecular S_NAr reaction provides exclusively the corresponding η^6-coordinated 16-membered macrocycle, which finally can be demetallated by photoirradiation in acetonitrile. The organometallic moiety is recovered as [RuCp($NCMe)_3$][PF_6] **28** and can be reused.[37]



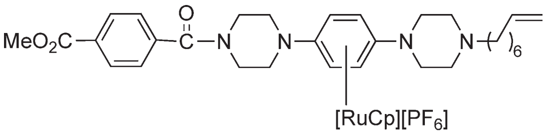
40 **41** **42**

[Ru] = [RuCp][PF_6]; i, HATU, TMP, DMF, 0 °C; ii, Cs_2CO_3, DMF, RT; iii, $h\nu$, NCMe, RT

(2)

As commented before, decomplexations of the arene ligands are usually performed by simple exposure of acetonitrile solutions of the complexes to UV light. Nevertheless, in the case of electron-rich ruthenium derivatives, the process is not really efficient under these conditions and requires the addition of 1,10-phenanthroline, which acts as a competing ligand for the organometallic moiety. This methodology has been employed, for example, for the demetallation of **43** (Figure 7).[32]

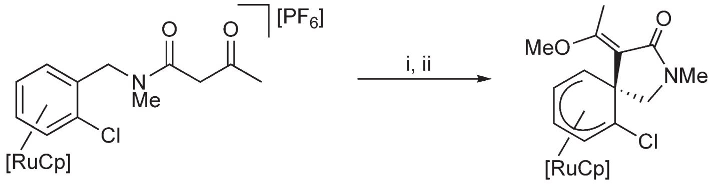
Notably, attempted intramolecular S_NAr reactions of complex **44** under basic conditions to accomplish the formation of tetrahydroisoquinoline derivatives lead only to decomposition products. Nevertheless, when methyl tosylate is added to the reaction medium, the stable η^5-cyclohexadienyl spirocyclic lactam **45** can be isolated (Equation (3)).[38,39] It results from the intramolecular attack of the *in situ* generated enolate at the *ipso*-position of



43

Figure 7 The mixed Cp-arene ruthenium(II) complex **43**.

the arene ligand, followed by a second deprotonation and a further *O*-methylation. Related derivatives are obtained when the chloride substituent of the arene is replaced by hydrogen or a methoxy group.



44 **45**

i, KOBu^t, 18-crown-6, THF reflux; ii, Me[OTs]

(3)

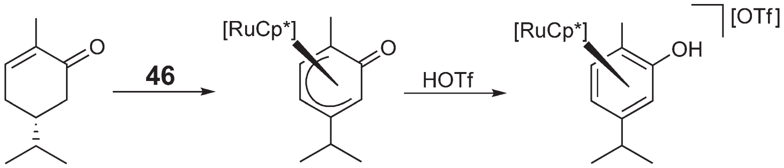
6.14.2.2.2 Complexes containing a Cp*Ru fragment

Complexes of general formula [RuCp*(η^6-arene)][X] can be prepared through several routes. The most common precursor is the dinuclear species [{Ru(μ-OMe)Cp*}$_2$] **46** which can be easily protonated with triflic acid to generate *in situ* the "[RuCp*][OTf]" fragment. When a free arene is present, the desired [RuCp*(η^6-arene)][OTf] complex is directly formed. The following examples have been prepared using this synthetic approach:

(i) Complexes [RuCp*(η^6-arene)][OTf] (arene = C_6F_5OH, C_6F_6,[40] *p*-MeOC$_6$H$_4$(CH$_2$)$_2$CO$_2$-*N*-succinimidyl*).[41] The oxocyclohexadienyl derivative [RuCp*(η^5-C$_5$F$_5$C=O)] is formed by reacting **46** with C_6F_5OH in the absence of acid). Surprisingly, the hexafluoro compound [RuCp*(η^6-C$_6$F$_6$)][OTf] undergoes spontaneous nucleophilic substitution of one fluoride by OMe by simply keeping the complex in methanol solution at room temperature for a short period of time. A second substitution can be achieved in refluxing methanol giving [RuCp*{η^6-1,4-C$_6$F$_4$(OMe)$_2$}][OTf].[40]

(ii) Compounds [RuCp*(η^6-arene)][OTf] (arene = MeOC$_6$H$_4$CH=CHC$_5$H$_4$N, [MeOC$_6$H$_4$CH=CHC$_5$H$_4$NMe]-[OTf]) obtained by the selective coordination of *trans*-4-methoxystilbazole or *trans*-4-methoxy-*N*-methylstilbazolium triflate through the more electron-rich aromatic ring, that is, the methoxy-substituted one.[42]

On the other hand, the *in situ* generated fragment "[RuCp*][OTf]" is able to aromatize different six-membered cyclic molecules. Thus, complex [RuCp*(η^6-C$_6$H$_6$)][OTf] **47** is formed from the reaction with cyclohexene sulfide, which proceeds with concomitant release of dihydrogen and hydrogen sulfide.[43] Complex **47** can also be obtained by dehydrochlorination of chlorocyclohexane or 1,2-dichlorocyclohexane. The reaction with lindane (1,2,3,4,5,6-hexachlorocyclohexane) gives a 9:1 mixture of **47** and [RuCp*(η^6-C$_6$H$_5$Cl)][OTf] **48**, whereas the activation of 2,2,6,6-tetrachlorocyclohexanol leads to a mixture of **47**, **48**, and [RuCp*(η^6-C$_6$H$_5$OH)][OTf].[43] Similarly, complex [RuCp*(η^6-cym)][OTf] is formed after dehydration of (*R*)-7,8-dihydrocarvone. In contrast to these results, dehydrogenation of (*R*)-7,8-dihydrocarvone by **46** occurs in the absence of acid (Scheme 2).[44] Although the stereogenicity of



49 **50**

Scheme 2

the carbon atom is lost during this transformation, the resulting η^5-oxocyclohexadienyl derivative **49** is obtained as a single planar chiral enantiomer. Its aromatization is easily accomplished by protonation, providing the enantiopure complex **50**. The same derivative **50** is generated in racemic form from the reaction of **46** with carvacrol (2-methyl-5-isopropyl-phenol) in the presence of HOTf.[44]

Other synthetic routes for [RuCp*(η^6-arene)][X] complexes include the following:

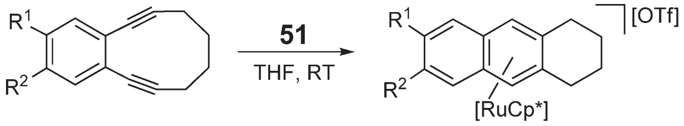
(i) The dehydrohalogenation/dehydrogenation of *trans*-5-methoxycarbonyl-2-cyclohexenyl chloride through its reaction with [RuClCp*(COD)] (COD = 1,5-cyclooctadiene) which gives [RuCp*(η^6-C$_6$H$_5$CO$_2$Me)]Cl.[45]

(ii) The one-pot procedure used to prepare compounds [RuCp*(η^6-arene)][PF$_6$] (arene = toluene, 1,3,5-C$_6$H$_3$Me$_3$, 1-chloro-2-methoxybenzene, benzophenone, acetophenone, 4-methylbenzenesulfonic acid, 1,4-ClC$_6$H$_4$CH$_2$CH$_2$-NHBoc (Boc = *tert*-butoxycarbonyl), etc.,) based on the reaction of RuCl$_3$·nH$_2$O with zinc dust in ethanol, followed by addition of 2 equiv. of the appropriate arene, and then pentamethylcyclopentadiene and Na[PF$_6$].[46]

(iii) The reaction of [{RuCl$_2$Cp*}$_2$] with the amino acids L-phenylalanine, L-chlorophenylalanine, L-tyrosine, L-dopa, DL-phenylserine, L-tryptophan, and 5-hydroxy-L-tryptophan in refluxing methanol which affords the corresponding [RuCp*(η^6-arene)]Cl complexes (in this case the solvent is acting as reducing agent).[47]

(iv) The acetonitrile derivative [RuCp*(NCMe)$_3$][OTf] **51** has also proved to be an efficient precursor for the synthesis of complexes bearing η^6-coordinated arenes by displacement of the acetonitrile ligands. For instance, the following arenes have been coordinated: phenylalanine and tryptophan derivatives,[48] bifluorenylidene,[49] fluoradene,*[50] corannulene,*[51,52] functionalized naphthalenes,[53] di-, tri-, tetra-, penta-, and hexachlorobenzene,[54,55] and tetrahydroanthracene.*[56] Remarkably, under the same reaction conditions, the use of tryptamine does not lead to the related η^6-arene derivative giving instead [RuCp*(NCMe)$_2${κ^1(N)-tryptamine}][OTf] by selective coordination of the ligand through the primary amine function.[57] Nevertheless, the desired η^6-tryptamine complex can be prepared in good yield through a two-step process involving the initial coordination of the N-Boc protected ligand and subsequent deprotection by treatment with Me$_3$SiCl and NaI in acetonitrile.

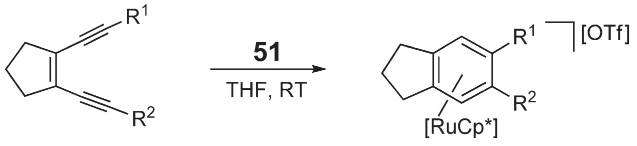
Complex **51** has also been used to promote, under mild conditions (RT), the cycloaromatization 0of the strained-ring benzo–enediynes **52** leading to the formation of tetrahydroanthracenes **53** (Equation (4)).[56] In contrast, *tert*-butyl-1,2-diprop-1-ynylbenzene, a strain-free acyclic enediyne, fails to cyclize even after prolonged refluxing periods giving instead the corresponding (η^6-arene)-ruthenium adduct.[58] Cyclopenten-1,2-diynes **54** also undergo cycloaromatization affording complexes **55** (Equation (5)). On the basis of isotopic labeling, formation of a p-benzyne intermediate has been proposed.[58] Compound [RuCp*{S-2,6-C$_6$H$_3$(Mes)$_2$}] (**148** in Equation (15)) promotes the cyclotrimerization of phenylacetylene or 1-pentyne to form selectively the η^6-coordinated 1,2,4-trisubstituted benzene derivatives [RuCp*(η^6-1,2,4-C$_6$H$_3$R$_3$)][S-2,6-C$_6$H$_3$(Mes)$_2$] (R = Ph,* Pr^n), obtained as sulfide salts.[59]



52 **53**

R^1 = Bu^t; R^2 = H
R^1 = R^2 = Me

(4)



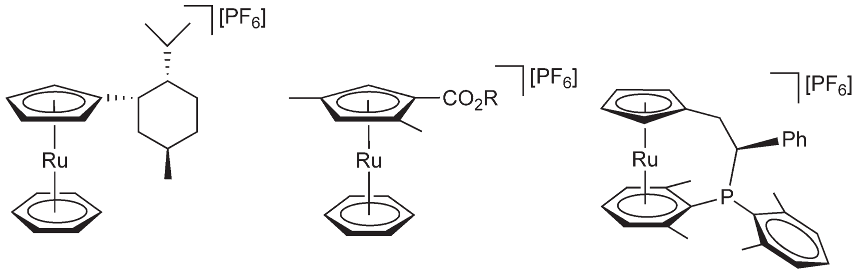
54 **55**

R^1 = Me; R^2 = H
R^1 = R^2 = Me
R^1 = R^2 = Pr^n
R^1 = R^2 = Bu^{i*}
R^1 = Me; R^2 = SiMe$_3$

(5)

6.14.2.2.3 Complexes containing other functionalized cyclopentadienyl ligands

Cations [Ru(η^5-C$_5$Me$_4$CF$_3$)(η^6-arene)]$^+$ (arene = C$_6$H$_6$, hmb) are formed by heating the dimer [{RuCl(μ-Cl)(η^5-C$_5$Me$_4$CF$_3$)}$_2$] with an excess of the appropriate arene ligand in methanol or ethanol, and subsequent precipitation as PF$_6$ salts upon addition of [NH$_4$][PF$_6$].[60] Treatment of the dimer [{RuCl(μ-Cl)(η^6-C$_6$H$_6$)}$_2$] with the thallium salt of (+)-neomenthylcyclopentadiene and [NH$_4$][PF$_6$] affords **56** (Figure 8).[61] Similarly, the use of the optically active salt Tl[2,4-Me$_2$C$_5$H$_2$CO$_2$R] (R = (−)-menthyl) gives the related derivative **57** as a 1 : 1 mixture of the two possible



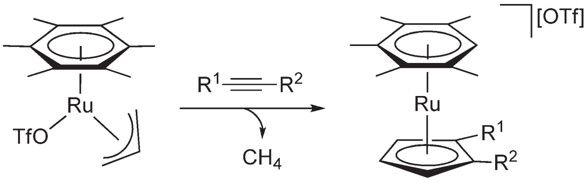
56 **57** **58**

R = (–)-menthyl

Figure 8 The chiral sandwich-type complexes 56–58.

diastereomers. Fractional crystallization allows the isolation of the enantiopure complexes albeit in very low yields.[62] The reaction of bis(allyl)–ruthenium(IV) dimer [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-dien-1,8-diyl) with the phosphine ligand (*S*)-CpHCH$_2$CHPhP(2,6-xylyl)$_2$, Li_2CO_3, and K[PF$_6$], in a mixture of acetonitrile–ethanol, leads to the tethered derivative **58**. The expected coordination of the phosphorus atom to ruthenium is prevented by the steric hindrance of the xylyl substituents.[63]

Surprisingly, coupling reactions between the hexamethylbenzene-ruthenium-allyl compound **59** and various alkynes generate complexes **60**, in which one methyl substituent of the hmb ligand has been replaced by hydrogen (Equation (6)).[21,64] Presumably, this dealkylation process involves an *endo*-hexamethyl-η^5-cyclohexadienyl intermediate.[21]



59 **60**

$R^1 = R^2 = Me$
$R^1 = R^2 = Ph$
$R^1, R^2 = -(CH_2)_6-$
$R^1 = Me, R^2 = Bu^t$

(6)

6.14.2.3 Other Sandwich Complexes

Reaction of [RuCp(NCMe)$_3$][PF$_6$] **28** with 2-*N*,*N*-dimethylaminopyridine selectively gives the π-bonded complex [RuCp(η^6-$Me_2NC_5H_4N$)][PF$_6$].[*23] The presence of a bulky substituent at the 2-position is crucial to avoid the coordination through the nitrogen atom of the pyridine ring. Similarly, sterically demanding phosphinines react with [RuClCp*(η^4-C_6H_{10})] (C_6H_{10} = 2,3-dimethyl-1,3-butadiene) and Ag[BF$_4$], leading exclusively to the η^6-coordinated derivatives **61** (Figure 9).[65] The silabenzene anion [$C_5H_5Si(Bu^t)H$]$^-$, generated *in situ* from silacyclohexadiene and LiBu^n, reacts either with [{RuClCp*}$_4$] or [{Ru(μ-OMe)Cp*}$_2$] **46** to give the silacyclohexadienyl derivative [RuCp*{η^5-$C_5H_5Si(Bu^t)H$}] as a single isomer, presumably with an *exo*-disposition of the *tert*-butyl group, which in presence of BPh_3 is converted into the corresponding silabenzene [RuCp*(η^6-$C_5H_5SiBu^t$)][HBPh$_3$].[66] Nevertheless, its spectroscopic data suggest that the bonding of the silabenzene may best be described as an η^5:κ^1(*Si*)-interaction, with limited delocalization within the ligand.[66] The 1,2-azaboratabenzene compound **62** (Figure 9) has been prepared from the reaction of the potassium salt of the ligand and [{RuClCp*}$_4$]. This complex undergoes reversible protonation on the nitrogen atom. Notably, π-complexation markedly increases the acidity of the protonated form (p*Ka* = 9.21 vs. 26 in the free dihydroazaborine).[67]

Complexes [{M(OTf)$_2$(η^6-cym)}$_x$] (M = Ru **8**, Os), generated *in situ* in the case of osmium, react with tetramethylpyrrole affording [M(η^5-NC_4Me_4)(η^6-cym)][OTf]* **63**, in which the pyrrole ligand is deprotonated.[68] *N*-Methylation with [Me][OTf] generates the related dicationic complexes [M(η^5-$MeNC_4Me_4$)(η^6-cym)][OTf]$_2$ **64** (M = Os, Ru). Compounds **63** also undergo hydride addition to the *p*-cymene ligand furnishing the η^5-cyclohexadienyl derivatives [M(η^5-NC_4Me_4)(η^5-$MePr^iC_5H_3CH_2$)] (M = Os, Ru). The attack takes place predominantly at the *ortho*-position with respect to the methyl group. Unlike **63**, the dicationic compounds **64** add hydride to the

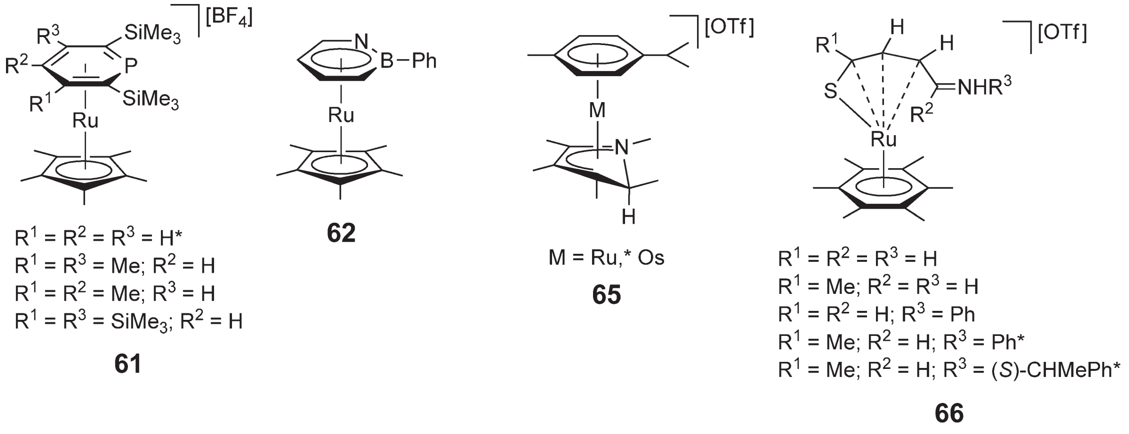


Figure 9 Structure of compounds **61, 62, 65,** and **66**.

pyrrole ring rather than to the arene, affording complexes **65** (Figure 9).[68] Syntheses of mixed arene–thiophene derivatives are readily achieved by treatment of the appropriate triflate precursor [{M(OTf)$_2$(η^6-arene)}$_x$] with an excess of the thiophene ligand. Following this synthetic approach, the osmium and ruthenium derivatives [M(η^5-L)(η^6-arene)][OTf]$_2$ (M = Os, arene = cym, L = SC$_4$H$_4$, 2,5-SC$_4$H$_2$Me$_2$, SC$_4$Me$_4$;[*69] M = Ru, arene = hmb, L = 2-SC$_4$H$_3$-(*E*)-CH═CH-4-C$_6$H$_4$X, X = OMe, Me, H, Br, NO$_2$; M = Ru, arene = cym, L = 2-SC$_4$H$_3$-(*E*)-CH═CH-4-C$_6$H$_4$NO$_2$)[70] have been obtained in good yields. Remarkably, π-thiophene complexes undergo aminolysis in the presence of ammonia or primary amines to give acyclic allylthiolate compounds **66** (Figure 9). In the case of the monosubstituted thiophene ligands (R^1 = Me, R^2 = H), the C–S bond cleavage occurs regiospecifically at the CH–S, and not at C(Me)–S linkage.[71,71a]

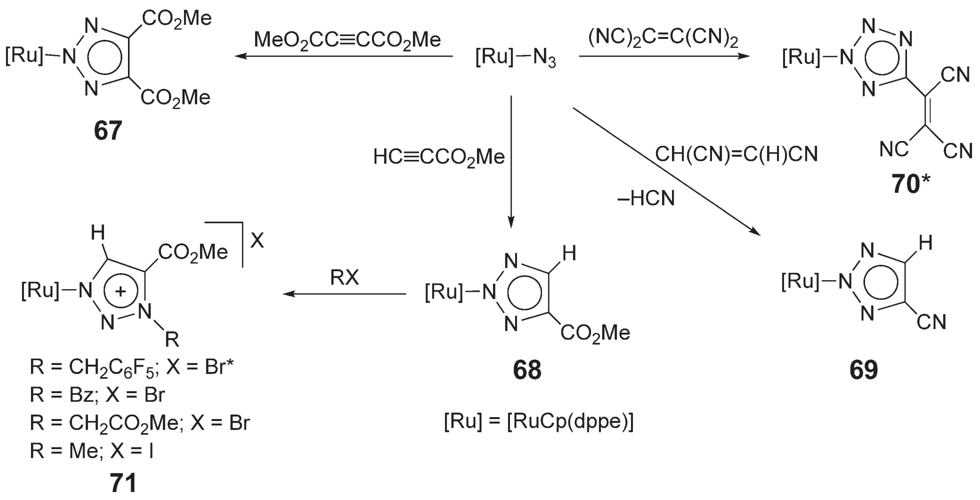
6.14.3 Half-Sandwich η^5-Cyclopentadienyl and η^5-Indenyl Compounds

6.14.3.1 Complexes Containing N- and O-Donor Ligands

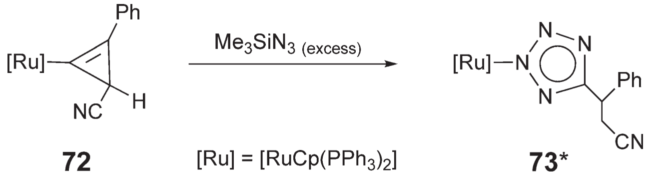
6.14.3.1.1 Monodentate N-donor ligands

Stable dinitrogen–Ru(II) adducts [Ru(N$_2$)(η^5-C$_5$R$_5$)(L^1)(L^2)][Y] (L^{1}L^2 = dippe (dippe = 1,2-bis(diisopropylphosphino)ethane),* Et$_2$PCH$_2$CH$_2$PEt$_2$, R = H, Y = BAr$^F{}_4$; L^{1}L^2 = dippe, R = Me, Y = BPh$_4$; L^{1}L^2 = dppm (dppm = bis(diphenylphosphino)methane),* dppe (dppe = 1,2-bis(diphenylphosphino)ethane), R = Me, Y = BAr$^F{}_4$; L^1 = PMePr$^i{}_2$, L^2 = PMePr$^i{}_2$, PPh$_3$, R = H, Y = BAr$^F{}_4$ (BAr$^F{}_4$ = tetrakis{3,5-bis(trifluromethyl)phenyl}-borate); L^1 = L^2 = PEt$_3$, R = Me, Y = BPh$_4$) have been synthesized by reacting the corresponding chloride precursor [RuCl(η^5-C$_5$R$_5$)(L^1)(L^2)] with Na[BPh$_4$] or Na[BAr$^F{}_4$] under an N$_2$ atmosphere.[72–76] The reversible coordination of N$_2$ to the 16-electron complex [RuCp(tmeda)][BAr$^F{}_4$] (tmeda = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) has been reported, the corresponding adduct [Ru(N$_2$)Cp(tmeda)][BAr$^F{}_4$] being favored at low temperature (−90 °C).[77] The 16-electron osmium derivative [OsBrCp*(PPr$^i{}_3$)] also binds N$_2$ reversibly at low temperature to give a mixture of the terminal and bridging dinitrogen complexes [Os(N$_2$)BrCp*(PPr$^i{}_3$)] and [{OsBrCp*(PPr$^i{}_3$)}$_2$(μ-N$_2$)].[78]

The azido–ruthenium compounds [Ru(N$_3$)(η^5-C$_5$R$_5$)(L^1)(L^2)] (R = H, L^1 = L^2 = PPh$_3$;* R = H, L^{1}L^2 = dppe, dppf (dppf = 1,1′-bis(diphenylphosphino)ferrocene); R = Me, L^{1}L^2 = dppp (dppp = 1,3-bis(diphenylphosphino)-propane))[79–84] and [Ru(N$_3$)(η^5-C$_9$H$_7$)(COD)][85] have been synthesized by salt metathesis reactions between the corresponding chloride precursor and NaN$_3$. Taking advantage of the hemilabile properties of the allyl–phosphine ligands Ph$_2$PCH$_2$C(R)═CH$_2$, complexes [Ru(N$_3$)(η^5-C$_9$H$_7$){κ^1(*P*)-Ph$_2$PCH$_2$CR═CH$_2$}(PPh$_3$)] (R = H, Me) have been obtained by reacting [Ru(η^5-C$_9$H$_7$){κ^3(*P*,*C*,*C*)-Ph$_2$PCH$_2$CR═CH$_2$}(PPh$_3$)][PF$_6$] with NaN$_3$.[86] Complex [Ru(N$_3$)Cp(dppe)] undergoes [3 + 2]-cycloaddition reactions with alkynes, alkenes, and nitriles affording heterocyclic triazolato **67–69** or tetrazolato **70*** derivatives (Scheme 3). Regiospecific alkylations of triazolate complex **68**, which generate the cationic species **71**, have also been described.[82] According to Equation (7), the related tetrazolato–ruthenium complex **73*** is formed when the cyclopropenyl derivative **72** is treated with a large excess of Me$_3$SiN$_3$.[87,87a]



Scheme 3



(7)

Although decomposition of diazo compounds by η^5-C$_5$ ruthenium and osmium complexes represents a well-known route to generate carbene-type derivatives (see Chapter 6.15), the stable diazo–Ru(II) complex [RuCp*{κ^1(*N*)-N$_2$CPh$_2$}{κ^1(*P*)-P∼O}$_2$][BPh$_4$] (P∼O = (1,3-dioxan-2-ylmethyl)diphenylphosphine) has been isolated from the reaction of the hemilabile derivative [RuCp*{κ^2(*P*,*O*)-P∼O}{κ^1(*P*)-P∼O}][BPh$_4$] with diphenyldiazomethane N$_2$CPh$_2$.[88] A number of dicationic aryldiazenido complexes [Ru{κ^1(*N*)-N$_2$-4-C$_6$H$_4$OMe}(η^5-C$_5$R$_5$)(L^1)(L^2)][BF$_4$]$_2$ (R = H, L^1 = L^2 = PPh$_3$,* PMe$_3$; R = H, L^{1}L^2 = dppe; R = Me, L^1 = L^2 = PMe$_3$) have been synthesized by reacting the appropriate chloride precursor [RuCl(η^5-C$_5$R$_5$)(L^1)(L^2)] with an excess of [N$_2$-4-C$_6$H$_4$OMe][BF$_4$] in refluxing acetone. In contrast, treatment of [RuCl(η^5-C$_5$R$_5$)(PPh$_3$)$_2$] with [N$_2$-4-C$_6$H$_4$OMe][BF$_4$] in toluene at 40 °C generates the monocationic derivatives [RuCl{κ^1(*N*)-N$_2$-4-C$_6$H$_4$OMe}(η^5-C$_5$R$_5$)(PPh$_3$)][BF$_4$] (R = H, Me) via release of PPh$_3$.[89]

A large variety of ruthenium complexes containing coordinated amines has been described. Representative examples include the following:

(i) Complexes [RuCp(NH$_2$R)(PPh$_3$)$_2$][X] (R = Bz, X = BF$_4$;* R = Cy, X = ClO$_4$)[90,91] and **75** (Figure 10),[92] obtained by reacting the appropriate chloride precursor with the free amine in the presence of a silver(I) salt.

(ii) Tethered Cp–amine complexes [Ru{η^5:κ^1(*N*)-C$_5$H$_4$(CH$_2$)$_2$NEt$_2$}(PTA)$_2$][PF$_6$][93] (PTA = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane) and [Ru{η^5:κ^1(*N*)-C$_5$H$_4$(CH$_2$)$_n$NMe$_2$}(dppm)][BF$_4$] (n = 2, 3*),[94] obtained by chloride abstraction from [RuCl{η^5-C$_5$H$_4$(CH$_2$)$_2$NEt$_2$}(PTA)$_2$] and [RuCl{η^5-C$_5$H$_4$(CH$_2$)$_n$NMe$_2$}(dppm)], respectively. The related complex [Ru{η^5:κ^1(*N*)-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}(PPh$_3$)$_2$][BF$_4$], generated by treatment of [RuH{η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}(PPh$_3$)$_2$] with HBF$_4$, is also known.[95]

(iii) Complexes **75**, containing a κ^3(*N*,*C*,*C*)-coordinated 7-azabicyclo[2.2.1]hepta-2,5-diene (Figure 10), obtained by displacement of the COD ligand in [RuCl(η^5-C$_5$R$_5$)(COD)] (R = H, Me).[96]

(iv) Pyridine complexes [RuClCp(py)(PPh$_3$)],[97] [Ru(η^5-C$_9$H$_7$)(py)(COD)][BF$_4$],*[85] **76** (diastereomerically pure),[98] and [RuCp(py)(η^4-C$_5$H$_4$O)][OTf]* (C$_5$H$_4$O = cyclopenta-2,4-dienone) obtained by classical ligand substitution reactions. The latter, upon treatment with an excess of PMe$_3$, dmpm (dmpm = bis(dimethylphosphino)methane), or dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane), can be transformed into [Ru(η^5-C$_5$H$_4$OH)(py)(L^1)(L^2)][BAr$^F_4$] (L^1 = L^2 = PMe$_3$; L^{1}L^2 = dmpm, dmpe).[99,100,101]

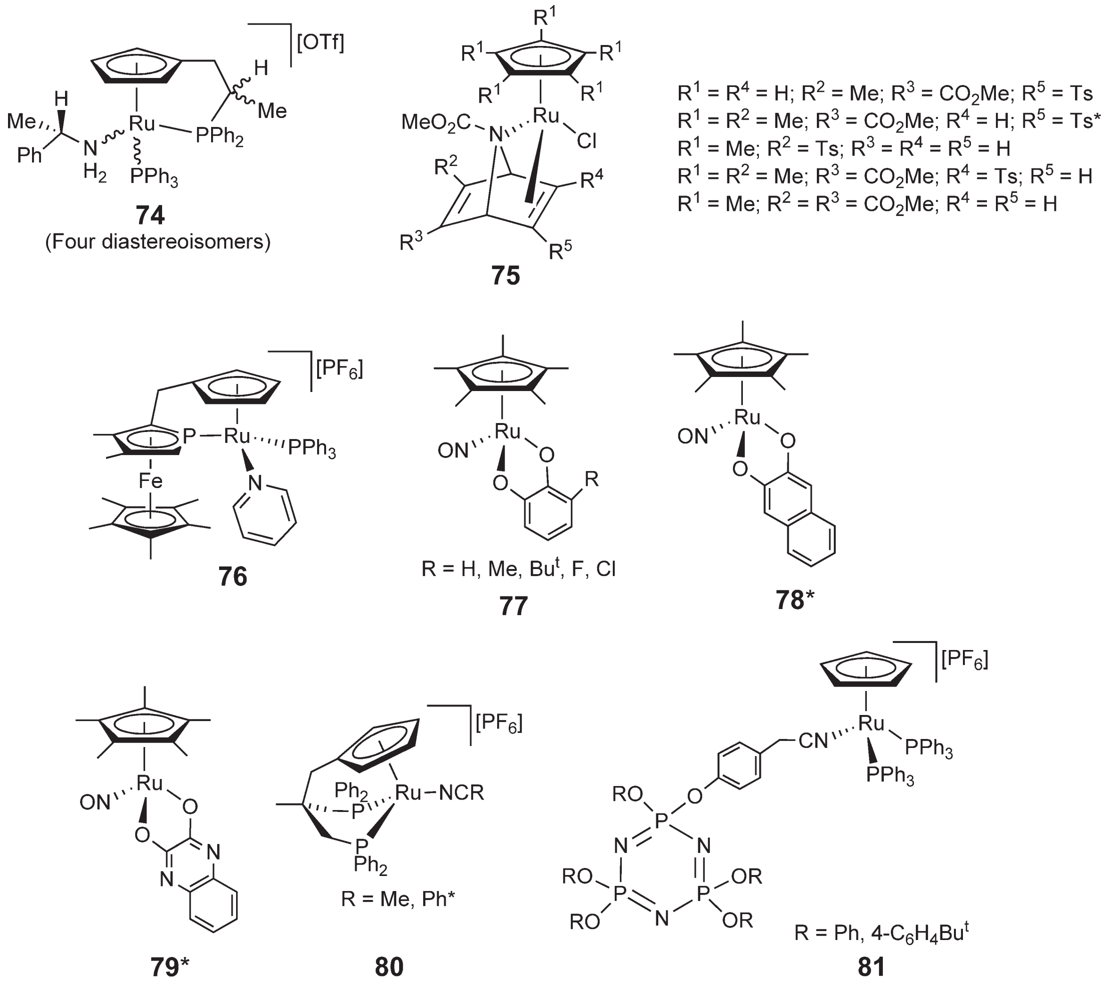


Figure 10 The half-sandwich ruthenium complexes 74–81.

The 16-electron derivative $[\mathrm{RuClCp^*(PPr^i_2Ph)}]$ readily reacts with $\mathrm{Li[NHPh]}$ to generate the unsaturated amido complex $[\mathrm{Ru(NHPh)Cp^*(PPr^i_2Ph)}]$ which in the presence of CO can be converted into the saturated species $[\mathrm{Ru(NHPh)Cp^*(CO)(PPr^i_2Ph)}]$.[102]

Treatment of [RuClCp(dppf)] and $[\mathrm{OsBrCp(PPh_3)_2}]$ with Na[NCS] results in the formation of complexes $[\mathrm{Ru}\{\kappa^1(N)\text{-NCS}\}\mathrm{Cp(dppf)}]^*$ and $[\mathrm{Os}\{\kappa^1(N)\text{-NCS}\}\mathrm{Cp(PPh_3)_2}]$, respectively.[103,104] Reaction of the chloro-substituted permethylcyclopentadienyl derivative $[\mathrm{RuCl(\eta^5\text{-}C_5Me_4CH_2Cl)(CO)_2}]$ with an excess of K[NCS] in MeOH generates a separable mixture of $[\mathrm{Ru(NCS)(\eta^5\text{-}C_5Me_4CH_2NCS)(CO)_2}]$, $[\mathrm{Ru(NCS)(\eta^5\text{-}C_5Me_5)(CO)_2}]$, and $[\mathrm{Ru(NCS)(\eta^5\text{-}C_5Me_4CH_2OMe)(CO)_2}]$, the latter being also accessible by direct treatment of $[\mathrm{RuCl(\eta^5\text{-}C_5Me_4CH_2OMe)(CO)_2}]$ with K[NCS].[105] The hemilabile derivatives $[\mathrm{RuCp^*}\{\kappa^3(P,C,C)\text{-}\mathrm{Ph_2P(CH_2)}_n\mathrm{CH{=}CH_2}\}\{\kappa^1(P)\text{-}\mathrm{Ph_2P(CH_2)}_n\mathrm{CH{=}CH_2}\}][\mathrm{PF_6}]$ ($n = 0, 1$) also react with Na[NCS] to afford $[\mathrm{Ru(NCS)Cp^*}\{\kappa^1(P)\text{-}\mathrm{Ph_2P(CH_2)}_n\mathrm{CH{=}CH_2}\}_2]$ ($n = 0$, 1).[106,107]

The reactions between $[\mathrm{Os(\equiv N)Ph_2(py)_2}][\mathrm{BF_4}]$ and sodium cyclopentadienide or potassium indenide result in the formation of the half-sandwich nitrido–Os(VI) complexes $[\mathrm{Os(\equiv N)CpPh_2}]^*$ and $[\mathrm{Os(\equiv N)(\eta^5\text{-}C_9H_7)Ph_2}]$,* respectively.[108]

Nitrosylation of chloride complexes $[\mathrm{RuClCp^*L_2}]$ ($\mathrm{L = PMe_3, PMe_2Ph, PPh_3}$) with $[\mathrm{NO}][\mathrm{BF_4}]$ gives a mixture of $[\mathrm{Ru(NO)ClCp^*L}][\mathrm{BF_4}]$ and $[\mathrm{Ru(NO)Cp^*L_2}][\mathrm{BF_4}]_2$.[109] In contrast, treatment of $[\mathrm{RuClCp^*(dppe)}]$ with $[\mathrm{NO}][\mathrm{PF_6}]$ generates exclusively the dicationic derivative $[\mathrm{Ru(NO)Cp^*(dppe)}][\mathrm{PF_6}]_2^*$.[110] The reduction of complexes $[\mathrm{Ru(NO)Cp^*L_2}][\mathrm{BF_4}]_2$ ($\mathrm{L = PMe_3, PMe_2Ph}$) and $[\mathrm{Ru(NO)Cp(PPh_3)_2}][\mathrm{BF_4}]_2$ has been studied by means of electrochemical and spectroscopic (IR, NMR, EPR) techniques. They exhibit two successive one-electron cathodic processes due to the sequential reduction of coordinated NO^+ to $NO^{\cdot}$ and NO^-, respectively.[111] Chemical reduction using cobaltocene allows the spectroscopic characterization of the neutral ruthenium(II) derivatives [Ru(NO)Cp*L] (L = PMe_3, PMe_2Ph) and [Ru(NO)Cp(PPh_3)].[111]

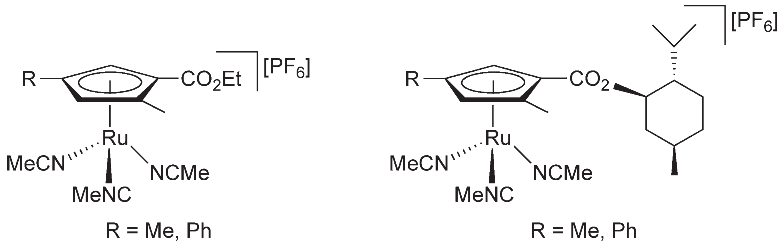
Treatment of [Ru(NO)(OTf)MeCp*] with Li[$HBEt_3$] in toluene generates the highly unstable (η^2-toluene)–Ru(0) complex [Ru(NO)Cp*(η^2-C_6H_5Me)], via reductive elimination of CH_4, which readily reacts with PPh_3 yielding [Ru(NO)Cp*(PPh_3)].[112] This (η^2-toluene)–Ru(0) complex is also able to undergo oxidative addition of silanes and disulfides generating a variety of novel nitrosyl derivatives (see Sections 6.14.3.3 and 6.14.3.4). Protonation of [Ru(NO)Me_2(η^5-C_5R_5)] with 2 equiv. of HOTf generates the labile ditriflato complexes [Ru(NO)$(OTf)_2$(η^5-C_5R_5)] ($C_5R_5 = C_5Me_5$, $C_5Me_4Et^*$). The aqueous chemistry of these complexes, along with that of the parent dichlorides [Ru(NO)Cl_2(η^5-C_5R_5)] ($C_5R_5 = C_5Me_5$, C_5Me_4Et), has been explored allowing the isolation of the mononuclear aqua complex salts [Ru(NO)(OTf)(η^5-C_5Me_4Et)(H_2O)][OTf]* and [Ru(NO)(η^5-C_5Me_4Et)$(H_2O)_2$]$[OTf]_2^*$, and the dinuclear μ-hydroxy species [{Ru(NO)(η^5-C_5R_5)}$_2$(μ-OH)$_2$]$[OTf]_2$ ($C_5R_5 = C_5Me_5$, $C_5Me_4Et^*$).[113] Displacement of the triflate ligands in [Ru(NO)$(OTf)_2$Cp*] by the bidentate *N*-donor ligands 2,2′-bipyridine (bipy) or dipyrido[3,2-*a*:2′,3′-*c*]-phenazine (dppz) leads to the dicationic derivatives [Ru(NO)Cp*(bipy)]$[OTf]_2^*$ and [Ru(NO)Cp*(dppz)]$[OTf]_2^*$, respectively. Remarkably, fluorescence-monitored titration of a DNA solution containing [Ru(NO)Cp*(dppz)]$[OTf]_2$ with ethidium bromide provides evidence that this complex intercalates into DNA, allowing its cleavage when photolyzed or treated with H_2O_2 or $K_2S_2O_8$.[114]

Using the dichloride derivative [Ru(NO)Cl_2Cp*] as starting material, novel nitrosyl complexes containing catecholate **77**, naphthalenediolate **78***, and quinoxalinediolate **79*** chelating ligands have been synthesized (Figure 10).[115,115a] Related compounds containing dichalcogenido-type ligands have also been described (see Section 6.14.3.3). Treatment of the dinuclear osmium(III) compound [{OsBr(μ-Br)Cp*}$_2$] with either $NO_{(g)}$ or "diazald" (TsN(NO)Me) generates the mononuclear nitrosyl–Os(II) derivative [Os(NO)Br_2Cp*].[116,117] This complex reacts with Na[BH_4] to yield the dihydride derivative [Os(NO)H_2Cp*] which loses H_2 over several days in solution to form [{OsCp*}$_2$(μ-NO)$_2$]*.[118] Its reactivity toward dichalcogenide ligands has also been studied (see Section 6.14.3.3).

Reaction of ruthenocene with thiazyltrichloride results in the formation of the air- and moisture-sensitive thionitrosyl complex [Ru(NS)Cl_2Cp] which, in its IR spectrum, shows a characteristic sharp absorption band at 1270 cm^{-1} assignable to the NS stretching vibration.[119]

Nitriles are classical auxiliary ligands in η^5-C_5 ruthenium and osmium chemistry (see COMC (1995)). In accord, a large number of novel nitrile complexes have been described in the last years, most of them obtained through halide/nitrile substitution reactions. Representative examples are the following: [Ru(NCR)Cp(L^1)(L^2)][X] (R = Me, L^1L^2 = dppr (dppr = 1,1′-bis(diphenylphosphino)ruthenocene), X = PF_6; R = Me, L^1L^2 = dppf, X = BPh_4;* R = Me, $L^1 = L^2$ = PTA, X = PF_6; $L^1 = L^2 = PPh_3$, R = CH_2Fc, C$\equiv$CPh,* X = PF_6),[93,103,120,121,122] [Ru(NCR)Cp*(L^1)(L^2)][X] (R = Me, $L^1 = L^2$ = PTA, X = PF_6; R = Me, $L^1 = L^2 = PHPh_2$, X = OTf; R = Me, L^1L^2 = dppe, dppf, (*S*,*S*)-chiraphos (chiraphos = 2,3-bis(diphenylphosphino)butane), (*R*)-prophos (prophos = 1,2-bis-(diphenylphosphino)propane), X = PF_6),[93,123,124] [M(NCR)(η^5-C_9H_7)$(PPh_3)_2$][X] (M = Ru, R = Me, Et, Ph, X = PF_6; M = Os, R = Me, X = BF_4),[125,126] [Ru(NCMe)(η^5-C_5H_4Me)(CO){κ^1(*P*)-$PPh_2CH{=}CH_2$}][PF_6],[127] [Ru(NCMe){η^5-$C_5H_4(CH_2)_2NEt_2$}$(PTA)_2$][PF_6],*[93] the tethered complexes **80**,[128] and the cyclotriphosphazenes **81** (Figure 10).[129,129a] Remarkably, some CpRu(II) derivatives containing coordinated *p*-substituted benzonitriles [Ru{NC-(*E*)-$(CH{=}CH)_n$-4-C_6H_4R}Cp(L^1)(L^2)][X] (L^1L^2 = dppe, (+)-DIOP (DIOP = *O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane); n = 0, 1; R = Me, Ph, F, Br, OMe, NH_2, NMe_2, NO_2, 4-$C_6H_4NO_2$; X = PF_6, BF_4, OTf, NO_3, ClO_4, BPh_4 (not all combinations)) have found to exhibit second- and third-order nonlinear optical properties.[130,130a,130b]* In addition, compounds [Ru{NC-4-C_6H_4R}Cp(L^1)(L^2)][PF_6] ($L^1 = L^2 = PPh_3$, R = OEt,* $OC_{16}H_{33}$; $L^1 = L^2 = PPh_2$(4-Tol), PPh_2(4-C_6H_4Ph), R = $OC_{16}H_{33}$) have been used for the fabrication of Langmuir–Blodgett films.[131]

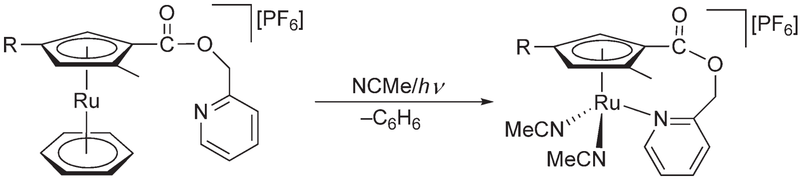
The cationic complex [RuCp$(NCMe)_3$][PF_6] **28** has gained in popularity during the last years as an alternative to the classical precursors [RuClCp$(PPh_3)_2$] and [RuClCp$(CO)_2$] due to the substitutional lability of the acetonitrile ligands. Thus, using this complex as starting material, the preparation of a large variety of ruthenium(II) compounds of stoichiometries [RuCp(L^1)$(NCMe)_2$][PF_6], [RuCp(L^1)(L^2)(NCMe)][PF_6], and [RuCp(L^1)(L^2)(L^3)][PF_6] has been described. This chemistry, which has been recently reviewed,[132] will not be summarized here, being described in different sections of this chapter and Chapter 6.15 depending on the nature of the incoming L ligands. As commented in Section 6.14.2.2.1, the most common synthetic approach to [RuCp$(NCMe)_3$][PF_6] consists in the release of the benzene ligand from [RuCp(η^6-C_6H_6)][PF_6] by photoirradiation of an acetonitrile solution. Following an analogous synthetic approach, the following η^5-C_5 tris(acetonitrile) compounds have been described: Ru(η^5-C_5H_4Me)$(NCMe)_3$][PF_6],[127] [Ru{η^5-C_5H_4-(+)-neomenthyl}$(NCMe)_3$][PF_6],[61] [Ru(η^5-$C_5Me_4CF_3$)$(NCMe)_3$][PF_6],[133]



82 **83**

Figure 11 The planar-chiral tris(acetonitrile) solvates 82 and 83.

and the planar chiral derivatives 82 and 83 (Figure 11).[62,134] In contrast, irradiation of sandwich complexes 84 with UV light in acetonitrile generates the bis(acetonitrile) derivatives 85 in which the pyridine unit of the functionalized Cp ring is coordinated to ruthenium (Equation (8)).[135]



84 R = Me, Ph **85** (8)

An optimized synthetic procedure for the known complex $[\mathrm{RuCp^*(NCMe)_3}][\mathrm{PF_6}]$, based on the treatment of an acetonitrile solution of $[\{\mathrm{RuCl_2Cp^*}\}_n]$ with $\mathrm{Na[PF_6]}$ and zinc dust, has appeared.[136] In addition, formation of $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_4PPh_3})(\mathrm{NCMe})_3][\mathrm{PF_6}]_2$ from the reaction of $[\mathrm{RuBr}(\eta^5\text{-}\mathrm{C_5H_4PPh_3})(\eta^4\text{-}\mathrm{C_5H_4O})][\mathrm{PF_6}]$ ($\mathrm{C_5H_4O}$ = cyclopenta-2,4-dienone) with $\mathrm{Ag[PF_6]}$ in acetonitrile has been reported.[137]

6.14.3.1.2 Bidentate and tridentate N-donor ligands

Treatment of dimer $[\{\mathrm{RuCp^*}(\mu\text{-OMe})\}_2]$ with 2 equiv. of lithium amidinates $\mathrm{Li[CR^1(NR^2)_2]}$ affords the mononuclear 16-electron derivatives $[\mathrm{Ru}\{\kappa^2(N,N)\text{-}\mathrm{CR^1(NR^2)_2}\}\mathrm{Cp^*}]$ ($\mathrm{R^1 = Me, R^2 = Pr^i; R^1 = Ph, R^2 = Cy,^* Bu^{t*}}$). These species are highly reactive toward two-electron donor ligands leading to the 18-electron derivatives $[\mathrm{Ru}\{\kappa^2(N,N)\text{-}\mathrm{CR^1(NR^2)_2}\}\mathrm{Cp^*(L)}]$ ($\mathrm{R^1 = Me}$, $\mathrm{R^2 = Pr^i}$, L = py, $\mathrm{PPh_3}$, CN-2,4,6-$\mathrm{C_6H_2Me_3}$, CO,* ethylene, tetracyanoethylene; $\mathrm{R^1 = Ph}$, $\mathrm{R^2 = Bu^t}$, L = CO*).[138] Oxidative addition of allylic halides, acetates, and carbonates to $[\mathrm{Ru}\{\kappa^2(N,N)\text{-}\mathrm{CR^1(NR^2)_2}\}\mathrm{Cp^*}]$ results in the formation of the coordinatively saturated cationic Ru(IV) complexes $[\mathrm{Ru}\{\kappa^2(N,N)\text{-}\mathrm{CR^1(NR^2)_2}\}(\eta^3\text{-2,3-}\mathrm{C_3H_3R^3R^4})\mathrm{Cp^*}][\mathrm{X}]$ ($\mathrm{R^1 = Me}$, $\mathrm{R^2 = Pr^i}$, $\mathrm{R^3 = H}$, $\mathrm{R^4 = H, Ph^*}$; $\mathrm{R^1 = Me}$, $\mathrm{R^2 = Pr^i}$, $\mathrm{R^3 = Me, CH_2SiMe_3}$, $\mathrm{R^4 = H}$; $\mathrm{R^1 = Ph}$, $\mathrm{R^2 = Bu^t}$, $\mathrm{R^3 = H,^*}$ Me, $\mathrm{R^4 = H}$) in which the allyl ligand adopts an *endo*-orientation.[139,139a] In contrast, one-electron oxidation of $[\mathrm{Ru}\{\kappa^2(N,N)\text{-}\mathrm{CMe(NPr^i)_2}\}\mathrm{Cp^*}]$ was observed upon treatment with $\mathrm{CCl_4}$, $\mathrm{CH_2Cl_2}$, or $\mathrm{CHCl_3}$ leading to the paramagnetic ruthenium(III) derivative $[\mathrm{Ru}\{\kappa^2(N,N)\text{-}\mathrm{CMe(NPr^i)_2}\}\mathrm{ClCp^*}]$.*[140]

The tris(acetonitrile) solvate $[\mathrm{RuCp(NCMe)_3}][\mathrm{PF_6}]$ reacts with tmeda to afford $[\mathrm{RuCp}\{\kappa^2(N,N)\text{-tmeda}\}(\mathrm{NCMe})][\mathrm{PF_6}]$ which can be transformed into $[\mathrm{RuClCp}\{\kappa^2(N,N)\text{-tmeda}\}]$ upon treatment with $[\mathrm{Et_4N}]\mathrm{Cl}$.[77,141] This chloro complex, as well as its Cp* counterpart, can be alternatively obtained from $[\mathrm{RuCl}(\eta^5\text{-}\mathrm{C_5R_5})(\mathrm{COD})]$ (R = H, Me) by substitution of the 1,5-cyclooctadiene ligand.[142*] Chloride abstraction using $\mathrm{Na[BAr^F_4]}$ generates the stable 16-electron derivatives $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5R_5})\{\kappa^2(N,N)\text{-tmeda}\}][\mathrm{BAr^F}_4]$ (R = H,* Me*) which are able to coordinate a large variety of two-electron donor ligands (L), such as CO, olefins, alkynes, $\mathrm{N_2}$, $\mathrm{O_2}$, to generate the corresponding saturated species $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5R_5})(\mathrm{L})\{\kappa^2(N,N)\text{-tmeda}\}][\mathrm{BAr^F}_4]$.[77,143] Substitution of COD in $[\mathrm{RuClCp^*(COD)}]$ by the chelating ligands 1-ethyl-2-pyrrolidinyl-methylamine and bis(mesityl)ethylenediimine has also been reported.[144*,145] Treatment of the previously known complex $[\mathrm{RuClCp}\{\kappa^2(N,N)\text{-}\mathrm{Pr^i}\text{-DAB}\}]$ ($\mathrm{Pr^i}$-DAB = 1,4-diisopropyl-1,4-diazabutadiene) with Ag[OTf] leads to the stable 16-electron derivative $[\mathrm{RuCp}\{\kappa^2(N,N)\text{-}\mathrm{Pr^i}\text{-DAB}\}][\mathrm{OTf}]$ which reacts with a variety of neutral ligands affording $[\mathrm{RuCp(L)}\{\kappa^2(N,N)\text{-}\mathrm{Pr^i}\text{-DAB}\}][\mathrm{OTf}]$ (L = CO, py, $\mathrm{PPh_3}$, ethylene, propene,* 2-methylpropene, 2-butene, dimethyl maleate, dimethyl fumarate, fumaronitrile, acetylene, dimethyl acetylenedicarboxylate).[146] Related chemistry starting from [RuClCp{κ^2(*N*,*N*)-*p*-Tol-DAB}] has also been described.[147*]

The complex [RuCl(η^5-C_5Me_4Et)$(CO)_2$] reacts thermally with 1,10-phenanthroline (phen) or diethylenetriamine in the presence of [NH_4][PF_6] to afford [Ru(η^5-C_5Me_4Et){κ^2(*N*,*N*)-phen}(CO)][PF_6] and [Ru(η^5-C_5Me_4Et){κ^2(*N*,*N*)-NH$(CH_2CH_2NH_2)_2$}(CO)][PF_6], respectively, via chloride and CO displacement.[148] Under similar reaction conditions, a large variety of cationic ruthenium(II) complexes of general composition [RuCp(PPh_3){κ^2(*N*,*N*)-L}][PF_6] have been prepared from [RuClCp$(PPh_3)_2$] using the Schiff bases **86**[149,149a] and the polypyridyl derivatives **87–91** (Figure 12) as ligands.[150,150a] The related Os(II) complexes [OsCp(PPh_3){κ^2(*N*,*N*)-bipy}][BF_4] and [OsCp(PPh_3){κ^2(*N*,*N*)-phen}][BF_4] have been analogously prepared.[104] The reactivity of [RuClCp$(PPh_3)_2$] toward the enantiomerically pure pyrrolecarbaldimine anions (*S*)-**92** and (*R*)-**93** has also been explored.[151] The resulting neutral complexes [RuCp(PPh_3){κ^2(*N*,*N*)-L}] (L = **92** or **93**) are obtained in both cases as equilibrium mixtures of the $S_{Ru}S_C{}^*/R_{Ru}S_C$ and $S_{Ru}R_C/R_{Ru}R_C$ diastereoisomers, respectively.

Displacement of the labile acetonitrile ligands by bipy in complex **85** (Equation (8)) generates **94** (Figure 13).[135] Similarly, complexes [RuCp*{κ^2(*N*,*N*)-L}(NCMe)][PF_6] (L = bipy, phen, 4,4′-dimethyl-bipy, 4,4′-di-*tert*-butyl-bipy) have been obtained by reacting [RuCp*$(NCMe)_3$][PF_6] with the appropriate bidentate ligand. These compounds undergo oxidative addition of allyl or cinnamyl chloride to yield, in the presence of K[PF_6], the dicationic Ru(IV) derivatives [Ru(η^3-1-C_3H_4R)Cp*{κ^2(*N*,*N*)-L}][PF_6]$_2$ (R = H, L = phen; R = Ph, L = bipy, phen,* 4,4′-dimethyl-bipy, 4,4′-di-*tert*-butyl-bipy), which are active species in catalytic allylic substitution processes.[152] The acetonitrile solvates [RuCp(L)$(NCMe)_2$][PF_6] (L = NCMe, CO, PPh_3, PPr^i_3, PMe_3) have also been used as suitable starting materials for the preparation of complexes **95**,[23] **96**,[153,153a] and **97***[153,153a] (Figure 13). In addition, diastereomeric mixtures of ($S_{Ru}S_C$)- and ($R_{Ru}S_C$)-[Ru(η^5-C_5R_5)(L){κ^2(*N*,*N*)-**98**}][PF_6] (R = H, L = CO; R = Me, L = CO,* PPh_3*) and

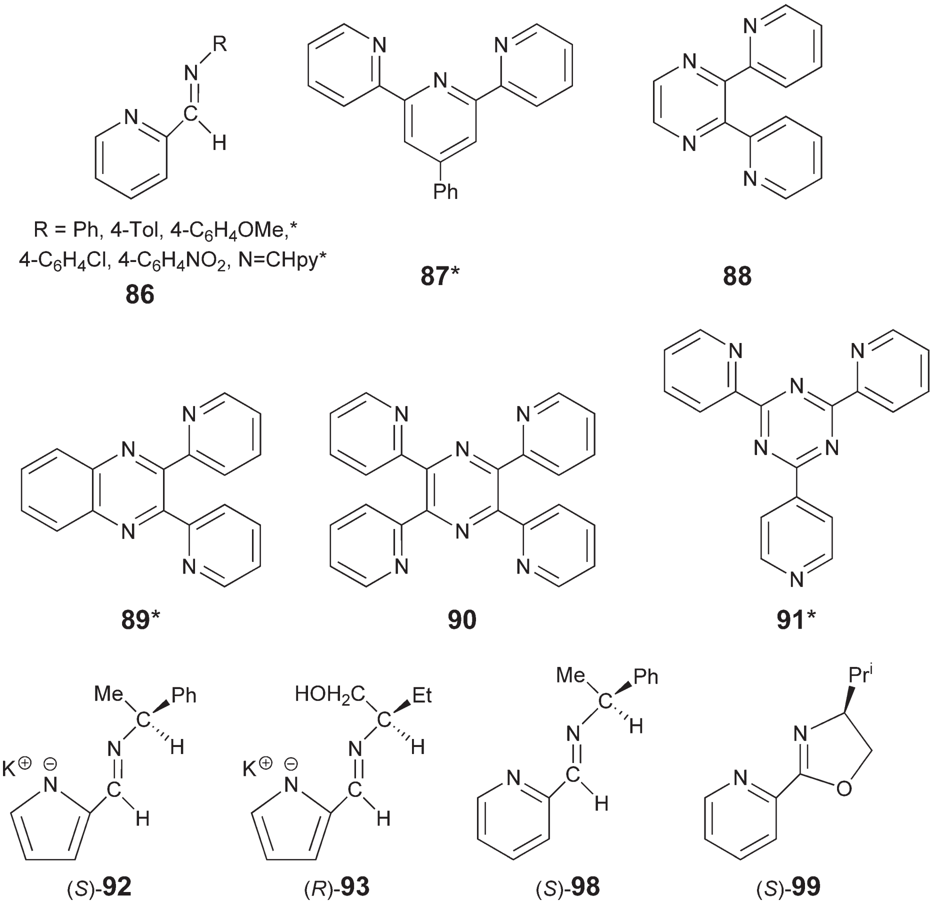


Figure 12 Structure of the polydentate N-donor ligands **86–93** and **98–99**.

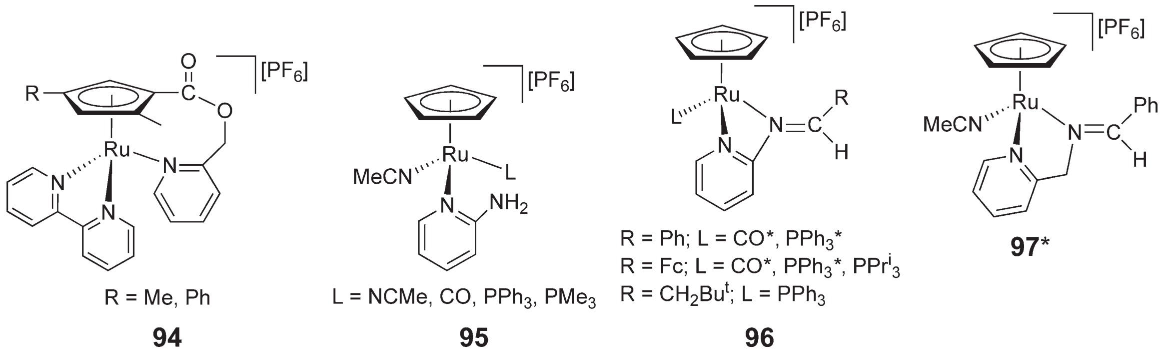


Figure 13 CpRu(II) complexes **94–97**.

($S_{\mathrm{Ru}}S_{\mathrm{C}}$)- and ($R_{\mathrm{Ru}}S_{\mathrm{C}}$)-[RuCp*(CO){$\kappa^2$($N$,$N$)-99}][PF$_6$] have been obtained by reacting [Ru(η^5-C$_5$R$_5$)(NCMe)$_3$][PF$_6$] (R = H, Me) with the enantiomerically pure ligands 98 and 99 (Figure 12) in the presence of CO or PPh$_3$.[154]

The reaction between [RuCl$_3${κ^3(N,N,N)-tmtacn}] (tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) and 3 equiv. of Ag[OTf] generates an uncharacterized green species which upon treatment with 1-(trimethylsilyl)cyclopentadiene and 1-(trimethylsilyl)indene, in the presence of zinc dust and [NH$_4$][PF$_6$], yields [RuCp{κ^3(N,N,N)-tmtacn}][PF$_6$] and [Ru(η^5-C$_9$H$_7$){κ^3(N,N,N)-tmtacn}][PF$_6$],* respectively.[155]

6.14.3.1.3 O-donor ligands

Ruthenium(II) fragments [Ru(η^5-C$_5$R$_5$)(L^1)(L^2)]$^+$ are not only prone to coordinate dinitrogen but also dioxygen. Thus, when acetone or methanolic solutions of complexes [RuClCp*(L^1)(L^2)] are exposed to air, in the presence of a chloride abstractor, irreversible O$_2$ coordination takes place leading to [Ru(κ^2-O$_2$)Cp*(L^1)(L^2)][X] (L^{1}L^2 = dppe, X = PF$_6$;* L^{1}L^2 = dippe, X = BPh$_4$;* L^{1}L^2 = dppf, X = BF$_4$;* L^{1}L^2 = dppm, X = BPh$_4$;* L^1 = L^2 = PEt$_3$, X = BPh$_4$).[73,110,156,157,158] Complexes [Ru(κ^2-O$_2$)Cp*(dppm)][BF$_4$] and [Ru(κ^2-O$_2$)Cp*(dppe)][BF$_4$], along with minor amounts of the corresponding (bisphosphine)monoxides [Ru(κ^2-O$_2$)Cp*{κ^2(P,O)-Ph$_2$P(CH$_2$)$_n$P(=O)Ph$_2$}]-[BF$_4$] (n = 1, 2), are also formed by exposure of [RuH$_2$Cp*(dppm)][BF$_4$] and [RuH$_2$Cp*(dppe)][BF$_4$] to air.[158] Dioxygen complexes [Ru(κ^2-O$_2$)Cp*{κ^1(P)-P ∼ O}$_2$][BPh$_4$]* (P ∼ O = (1,3-dioxan-2-ylmethyl)diphenylphosphine),[88] [Ru(OTs)(κ^2-O$_2$)Cp(PPh$_3$)],[159] **100*** (Figure 14),[160] and [Ru(κ^2-O$_2$)(η^5-C$_5$R$_5$){κ^2(N,N)-tmeda}][BAr$^F{}_4$] (R = H, Me)[77,143] have also been described although the latter are only stable at low temperature (ca. −60 °C).

Despite water, alcohols, and ketones being extremely labile ligands, some stable solvates have been described, including the following:

(i) Acetone complexes [Ru{κ^1(O)-OCMe$_2$}Cp*(CO)(PMePr$^i_2$)][BAr$^F{}_4$],[161] [Ru{κ^1(O)-OCMe$_2$}Cp*(dippe)][BPh$_4$],[72] and [Ru{κ^1(O)-OCMe$_2$}(η^5-C$_5$Me$_4$Et)(CO)$_2$][BF$_4$],[148] obtained from acetone solutions of the appropriate halide precursor after halide abstraction, and [Ru{κ^1(O)-OCMe$_2$}Cp(CO)(PPr$^i_3$)][BF$_4$] which is generated by protonation of the hydride derivative [RuHCp(CO)(PPr$^i_3$)] with HBF$_4$ in acetone, via displacement of the initially formed dihydrogen ligand.[162] Optically active complexes **101–103** containing coordinated acetone, methacrolein, and water ligands have also been synthesized, via classical halide substitution processes, in the context of studies directed to design efficient catalysts for asymmetric Diels–Alder reactions (Figure 14).[163–167]

(ii) The aquo–ruthenium complexes [Ru(H$_2$O)Cp*(NBD)][BF$_4$]*[168] and **104*** (Figure 14),[169] the latter being an active catalyst for the *anti*-Markovnikov hydration of alkynes.

(iii) Ruthenium–aminocyclopentadienyl **105** and –hydroxycyclopentadienyl complexes (**106** and **107**) containing alcohol ligands (Figure 14), synthesized by reacting the corresponding chloride precursor with Ag[BF$_4$] in the presence of 2-propanol or benzyl alcohol. They undergo rapid exchange of the coordinated alcohol ligand with free alcohol even at −47 °C.[170]

A large number of half-sandwich Ru and Os complexes containing coordinated oxyanions are actually known. Among them, those featuring weakly coordinating ability have received special attention in the last years due to their

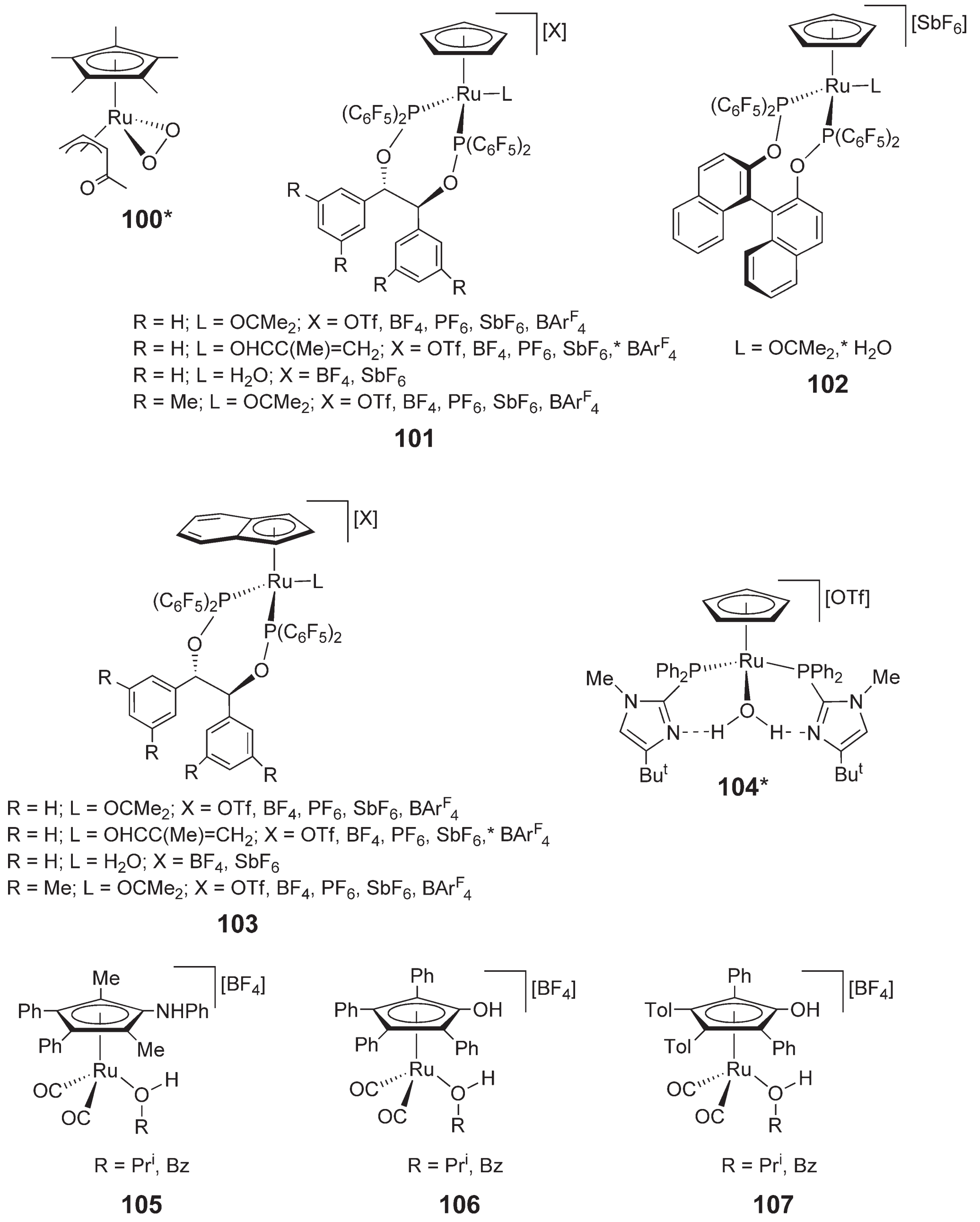


Figure 14 Half-sandwich ruthenium complexes containing O-donor ligands.

potential as versatile starting materials via substitution reactions. The following η^5-C_5 derivatives belong to this class of precursors:

(i) Triflate complexes [M(OTf)(η^5-C_5R_5)(L^1)(L^2)] (M = Ru, R = Me, L^1L^2 = butadiene,* κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$;* M = Os, R = H, $L^1 = L^2 = PPh_3$*)[171–173] and [Ru(OTf){η^5-2,5-Me_2-3,4-Ph_2-C_5NHPh}$(CO)_2$],*[174] obtained by reactions of the appropriate halide precursor with Ag[OTf] or Tl[OTf]. The related species [Os(OTf)Cp*(dppm)] and [Ru(OTf)Cp(dfepe)]* (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) have been synthesized by treatment of hydride complexes [OsHCp*(dppm)] and [RuHCp(dfepe)] with Me[OTf] or HOTf, respectively, via methane or dihydrogen elimination.[175,176]

(ii) Tosylate complexes $[Ru(OTs)Cp(L)(PPh_3)]$ (L = CO, PPh_3, NCMe, NH_2Ph), obtained by reacting the polymeric material $[\{Ru(OTs)Cp(PPh_3)\}_n]$ with the appropriate two-electron donor ligand. This polymer is generated by protonation of $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)Cp(PPh_3)]$ with HOTs.[159] If this protonation reaction is performed in the presence of ethylene, the monomeric compound $[Ru(OTs)Cp(\eta^2\text{-}C_2H_4)(PPh_3)]$ is formed.[97]

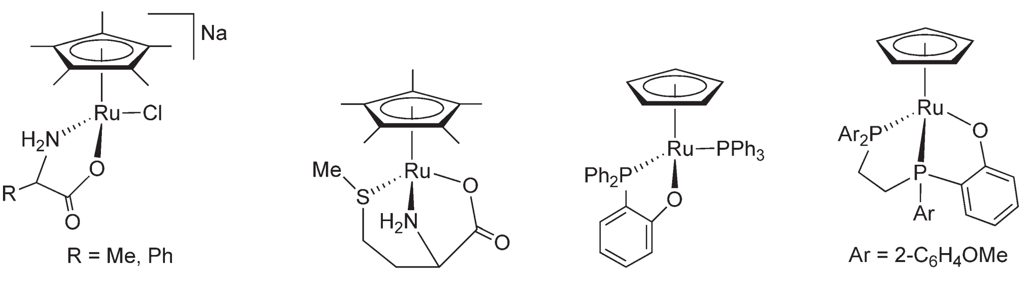
(iii) Nitrate complexes $[Ru\{\kappa^1(O)\text{-}NO_3\}Cp(L)(CO)]$ ($L = AsPh_3$,* PPh_3, $P(OPh)_3$, $P(4\text{-}C_6H_4OMe)_3$, $PPh_2(2\text{-}C_6H_4OMe)$), obtained by reacting $[RuClCp(L)(CO)]$ with $Ag[NO_3]$. Kinetics of substitution of the weakly coordinating nitrate by chloride have been measured.[177]

A large number of carboxylate complexes featuring both $\kappa^1(O)$- and $\kappa^2(O,O)$-coordination modes have been described. Thus, bidentate complexes $[Ru\{\kappa^2(O,O)\text{-}O_2CR^2\}(\eta^5\text{-}C_5R^1{}_5)(PPh_3)]$ ($R^1 = H$, $R^2 = Me$, Bu^t, CF_3; $R^1 = Me$, $R^2 = Me$, Bu^{t*}) have been prepared by ligand displacement from the allyl precursors $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(\eta^5\text{-}C_5R^1{}_5)(PPh_3)]$ and R^2CO_2H.[159] When these reactions were performed in the presence of ethylene, compounds $[Ru\{\kappa^1(O)\text{-}O_2CR^2\}(\eta^5\text{-}C_5R^1{}_5)(\eta^2\text{-}C_2H_4)(PPh_3)]$ ($R^1 = R^2 = Me$; $R^1 = H$, $R^2 = CF_3$) could be isolated.[97,159] A series of analogous monodentate carboxylate complexes are known. Representative examples are: $[Ru\{\kappa^1(O)\text{-}O_2CR^2\}(\eta^5\text{-}C_5R^1{}_5)(L)(PPh_3)]$ ($L = PPh_3$, $R^1 = H$, $R^2 = Me$, CF_3; L = CO, $R^1 = H$, $R^2 = Bu^t$, CF_3; L = CO, $R^1 = Me$, $R^2 = Me$, Bu^t; L = CNMe, $R^1 = H$, $R^2 = Me$),[159] $[Ru\{\kappa^1(O)\text{-}OAc\}(\eta^5\text{-}C_5Me_4Et)(CO)_2]$,[148] $[Ru\{\kappa^1(O)\text{-}O_2CCF_3\}Cp^*(\eta^4\text{-butadiene})]$,*[171] $[Os\{\kappa^1(O)\text{-}OAc\}Cp(PPr^i{}_3)_2]$,[178] and $[Ru\{\kappa^1(O)\text{-}O_2CCF_3\}\{\eta^5\text{-}2,5\text{-}Ph_2\text{-}3,4\text{-}Tol_2\text{-}C_5OH\}(CO)_2]$.[179] The $\kappa^2(N,O)$-aminoacidate complexes **108** and **109** (Figure 15) have been obtained from the reactions of $[\{RuCp^*Cl_2\}_2]$ with L-alanine, L-phenylalanine, and L-methionine in methanol and in the presence of Na[OMe].[47]

Formate complexes can be formed by CO_2 insertion into Ru–H bonds. Thus, $[Ru\{\kappa^1(O)\text{-}O_2CH\}\{\eta^5\text{-}C_5H_4(CH_2)_nNHMe_2\}(dppm)][BF_4]$ have been obtained by reacting the hydride derivatives $[RuH\{\eta^5\text{-}C_5H_4(CH_2)_nNHMe_2\}(dppm)][BF_4]$ ($n = 2$, 3) with CO_2. Nevertheless, they are readily converted into $[Ru\{\eta^5{:}\kappa^1(N)\text{-}C_5H_4(CH_2)_nNMe_2\}(dppm)][BF_4]$ by extrusion of formic acid.[94] The complex $[Ru\{\kappa^2(O,O)\text{-}O_2CH\}Cp^*(PCy_3)]$ has been synthesized starting from the 16-electron derivative $[RuClCp^*(PCy_3)]$ by reaction with carbon dioxide in the presence of $Na[BH_4]$, via hydride attack on the intermediate species $[RuClCp^*(CO_2)(PCy_3)]$.[180] The insertion of CO_2 into the Ru–alkynyl bond of the 16-electron species $[Ru(C{\equiv}CPh)Cp^*(PPh_3)]$, leading to complex $[Ru\{\kappa^2(O,O)\text{-}O_2CC{\equiv}CPh\}Cp^*(PPh_3)]$, has also been reported.[181]

Mononuclear 2,4-pentanedionate complexes of general composition $[Ru\{\kappa^2(O,O)\text{-}OC(R^1)CR^3C(R^2)O\}Cp^*(L)]$ ($L = PPh_3$, PMe_3, $P(OMe)_3$, CO) have been readily prepared by reacting the dimeric complexes $[(Ru\{\kappa^2(O,O)\text{-}OC(R^1)CR^3C(R^2)O\}Cp^*)_2]$ ($R^1 = R^2 = OEt$, $R^3 = H$; $R^1 = R^2 = Me$, $R^3 = Bz$; $R^1 = Me$, $R^2 = OEt$, $R^3 = H$; $R^1 = Me$, $R^2 = Ph$, $R^3 = H$;* $R^1 = Me$, $R^2 = CF_3$, $R^3 = H$) with two-electron donor ligands L. In addition, labile adducts of the same composition with σ-*S* and *N*-donor ligands (L = methyl *p*-tolyl sulfoxide, ethyl methyl sulfide, tetrahydrothiophene, 3-cyanopyridine, diaza[2.2.2]bicyclooctane) were detected in solution.[182] The complex [Ru(acac)Cp(CO)], obtained from the reaction of **28** with acetylacetone/NEt_3 under a CO atmosphere, has also been described.[141]

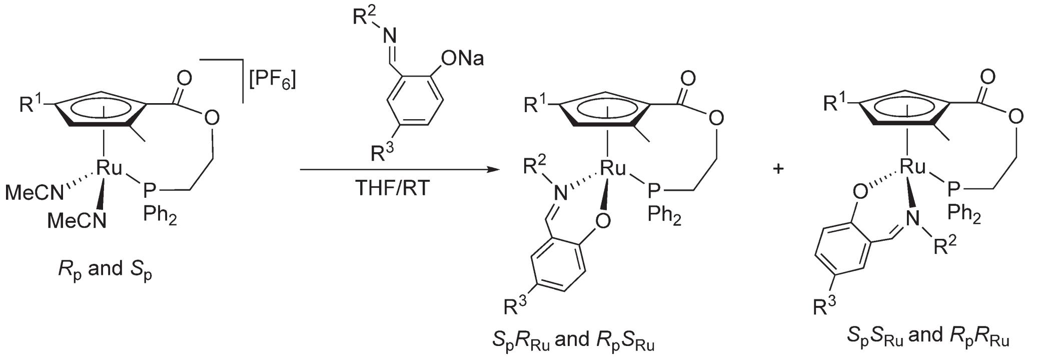
The $(\eta^5\text{-}C_5)$-ruthenium fragments have also proved to be able to bind alkoxy groups. Thus, starting from the 16-electron complexes $[RuClCp^*(PR_3)]$ ($PR_3 = PCy_3$, $PPr^i{}_2Ph$), compounds $[Ru(OR)Cp^*(PR_3)]$ ($PR_3 = PCy_3$, $R = CH_2CF_3$,* $SiPh_3$;* $PR_3 = PPr^i{}_2Ph$, $R = CH_2CF_3$, $SiPh_3$, $SiMe_2Ph$) are readily obtained by reactions with $Tl[OCH_2CF_3]$, $K[OSiPh_3]$ and $K[OSiMe_2Ph]$. These unsaturated species further react with CO yielding the 18-electron derivatives $[Ru(OR)Cp^*(CO)(PR_3)]$.[102*] The related complexes $[Ru(OC_6Cl_5)Cp(CO)(PPh_3)]$ and $[Ru(OMe)Cl(\eta^3\text{-}C_3H_5)Cp^*]$ are also known.[159,183] As illustrated in Equations (9) and (10), reactions of



108 **109** **113** **114***

Figure 15 Cp- and Cp*-Ru(II) complexes containing mixed donor ligands.

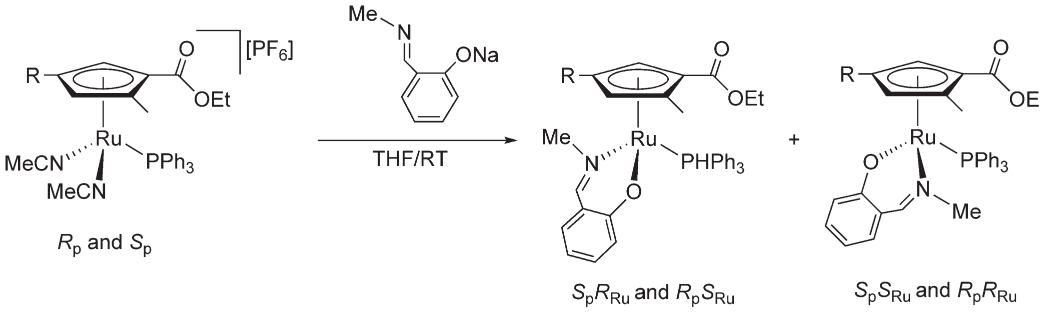
planar-chiral bis(acetonitrile) ruthenium complexes with sodium salicylideneaminates lead to compounds of type **110** and **111** in which the salicylideneaminate ligands adopt a $\kappa^2(N,O)$-coordination mode. Remarkably, while the reactions leading to complexes **110**, containing a tethered Cp–phosphine, are highly diastereoselective (up to 99% de; configuration of the major isomers S_pR_{Ru} and R_pS_{Ru}), formation of **111**, having no anchor phosphine ligands, proceeds with a low selectivity (5-22% de).[184] Formation of the salicylideneaminate complex **112**, which has been isolated as an 88 : 12 mixture of the $R_{Ru}S_C/S_{Ru}S_C$ diastereomers, has also been reported (Equation (11)).[151] Reactions of $[RuCp(NCMe)_3][PF_6]$ with potassium oxinate or potassium 5-Cl-oxinate (oxinate = quinolin-8-olate) under CO atmosphere lead to $[Ru\{\kappa^2(N,O)\text{-oxinate}\}Cp(CO)]$ and $[Ru\{\kappa^2(N,O)\text{-5-Cl-oxinate}\}Cp(CO)]$, respectively.[141] Other examples of alcoholate complexes are **113** and **114*** (see Figure 15) obtained by treatment of $[RuClCp(PPh_3)_2]$ with the phosphine–ether ligands $Ph_2P\text{-}2\text{-}C_6H_4OCH_2OMe$ and $(2\text{-}C_6H_4OMe)_2PCH_2CH_2P(2\text{-}C_6H_4OMe)_2$, respectively, the coordination of the ligands being accompanied with the elimination of $MeOCH_2Cl$ or MeCl.[185,186]



(9)

R^1 = Me; R^2 = Me; R^3 = H, OMe, NO_2
R^1 = Me; R^2 = Ph*, Pr^i; R^3 = H
R^1 = Ph; R^2 = Me*, Ph; R^3 = H

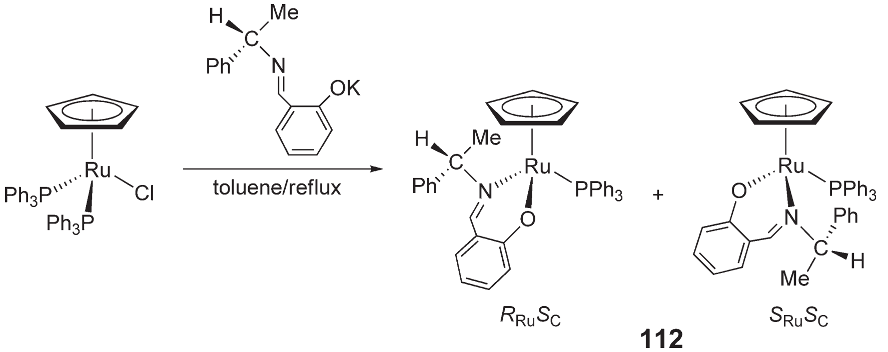
110



(10)

R = Me, Ph

111



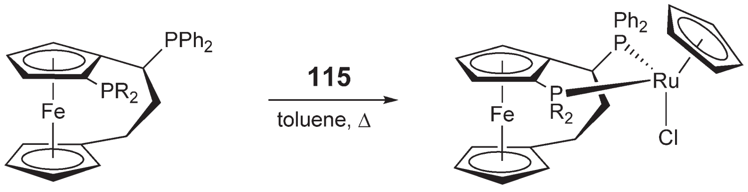
(11)

112

6.14.3.2 Complexes Containing P-, As-, and Sb-donor Ligands

The well-known bis(triphenylphosphine) compounds [RuCl(η^5-C$_5$R$_5$)(PPh$_3$)$_2$] (R = H **115**, Me **116**) and [RuCl(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] **117** have proved to be useful precursors for other half-sandwich complexes containing *P*-donor ligands. Indeed, thermal disubstitution of the PPh$_3$ ligands readily takes place in the presence of a wide range of mono- or bidentate phosphines in non-polar solvents. Numerous novel derivatives such as [RuClCp*(PTA)$_2$],*[187] [RuClCp{κ^1(*P*)-Ph$_2$P(CH$_2$)$_6$C≡CMe}$_2$],[188] and [RuCl(η^5-C$_9$H$_7$){κ^2(*P*,*P*)-(*S*,*S*)-(C$_6$F$_5$)$_2$POCH(Ph)CH(Ph)OP(C$_6$F$_5$)$_2$}][165] have been synthesized following this conventional methodology. On the other hand, products of monosubstitution can be selectively prepared modulating the quantity of the ligand added, and/or carrying out the reaction at lower temperatures. In this way, derivatives [RuClCp(L)(PPh$_3$)] (L = PHPh$_2$;*[189] Ph$_2$PNHR, R = Ph,* Cy),[190] [RuClCp*(PHPh$_2$)(PPh$_3$)],*[191] and [RuCl(η^5-C$_9$H$_7$)(L)(PPh$_3$)] (L = PMePh$_2$, PMe$_2$Ph, PMe$_3$),[192] among others, have been made. Arsolenes are also able to displace one triphenylphosphine ligand in **115** to give complexes [RuClCp(PPh$_3$){κ^1(*As*)-R$\overline{\text{AsCH}_2\text{C(Me)}{=}\text{C(Me)C}}H_2$}] (R = Ph, Me).[193] Kinetic studies evidence that such mono- and disubstitution processes occur through a dissociative mechanism.[192] The higher rates observed starting from the electron-rich indenyl precursor **117** in comparison with its Cp analog **115** are ascribed to its greater ability to stabilize transient 16-electron intermediates.[192]

Bidentate unsymmetrical diphosphines, such as (*R*)-prophos, (*R*)-phenphos (phenphos = 1-phenyl-1,2-bis(diphenylphosphino)ethane), and (*rac*)-renorphos (renorphos = *trans*-2,3-bis(diphenylphosphino)bicyclo[2.2.1]heptane), react with **116** to give two diastereomers of [RuClCp*(P ~ P)], with a ratio varying from 50 : 50 to 95 : 5 depending on the nature of the ligand employed and the reaction temperature.[124] In contrast, coordination of non-racemic diphosphines **118** to the CpRuCl fragment occurs with complete control of the chirality at the metal affording enantiopure derivatives **119** (Equation (12)).[194]



(12)

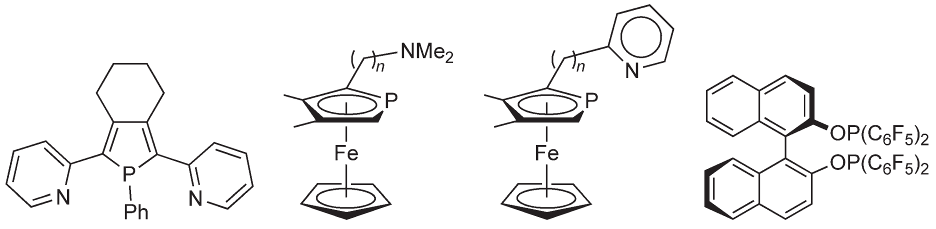
R = Ph, Cy, Pr^i **118**

R = Ph, Cy, Pr^i **119**

The Os(II) complex [OsClCp(PPr$^i_3$)$_2$] has been synthesized in 52% yield from the reaction of [OsH$_2$Cl$_2$(PPr$^i_3$)$_2$] and cyclopentadienylthallium in toluene at room temperature.[195] [OsClCp(PPr$^i_3$)$_2$] is prone to dissociate one triisopropylphosphine in the presence of different two-electron donor ligands and, therefore, readily affords [OsClCp(PPr$^i_3$)(L)] (L = P(OMe)$_3$,[195] PPh$_3$,[196] PHPh$_2$[197]) by addition of the corresponding monodentate phosphite or phosphine. The indenyl–osmium derivatives [OsX(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (X = Cl **120**, Br **121**) have been synthesized by reacting [OsX$_2$(PPh$_3$)$_3$] with indenyllithium, while their iodo analog is obtained via halide metathesis from **120**.[126,198] The substitution of one PPh$_3$ ligand by PMe$_2$R in **121**, to give [OsBr(η^5-C$_9$H$_7$)(PPh$_3$)(PMe$_2$R)] (R = Me, Ph), only proceeds in very low yield. In addition, such a substitution process fails starting from **120**.[126]

Displacement of the labile 1,5-cyclooctadiene ligand in [RuCl(η^5-C$_5$R$_5$)(COD)] (C$_5$R$_5$ = Cp **122**, Cp* **123**, indenyl **124**) by mono- or bidentate P-, Sb-, As-donors provides also a general synthetic approach to complexes of the type [RuCl(η^5-C$_5$R$_5$)(L)$_2$].[85,199–202] As an example, Ph$_2$PNPhPPh$_2$ and its monochalcogenides Ph$_2$PNPhP(=E)Ph$_2$ (E = S, Se) have been chelated on a Cp*RuCl unit following this methodology.[199] The high lability of COD also enables the coordination of mixed *P*,*N*-donor ligands, less coordinating than diphosphines, the resulting products not being accessible starting from the classical bis(triphenylphosphine) precursors. Thus, reactions of the imino-phosphine 2-Ph$_2$PC$_6$H$_4$CH=NBu^t or the pyridylphosphole **125** (Figure 16) with [RuCl(η^5-C$_9$H$_7$)(COD)] **124** and [RuCl(η^5-C$_5$R$_5$)(COD)] (R = H **122**, Me **123**), respectively, afford the corresponding complexes [RuCl(η^5-C$_9$H$_7$){κ^2(*P*,*N*)-2-Ph$_2$PC$_6$H$_4$CH=NBu^t}][85] and [RuCl(η^5-C$_5$R$_5$){κ^2(*P*,*N*)-**125**}] (R = H, Me).[200] In addition to the stereogenic center formed at the metal, chelation of **125** also induces chirality on the phosphorus atom giving rise to a mixture of diastereomers for the Cp derivative. In contrast, the more crowded Cp* analog is obtained in a diastereoselective manner.[200] Enthalpies of substitution reactions of **122** and **123** with a wide range of phosphines and arsines have been measured. This extended study points out the overwhelming importance of the steric factors versus the electronic ones and evidences the higher exothermicity displayed by the Cp system over its Cp* parent.[203,203a–203d]

Although the COD-containing precursors are the most common, other derivatives with a labile diene ligand can be successfully employed for the introduction of *P*-donor ligands. As an example, the reaction of [RuClCp*(η^4-C$_6$H$_{10}$)]



125 **129a**: *n* = 1 **129b**: *n* = 2 **130a**: *n* = 1 **130b**: *n* = 2 **133**

Figure 16 Structure of ligands **125, 129, 130,** and **133**.

($C_6H_{10} = 2$,3-dimethyl-1,3-butadiene) with 2 equiv. of 2-bromo-4,5-dimethylphosphinine (L) in refluxing THF quantitatively affords the bis-phosphinine complex [RuClCp*{κ^1(*P*)-L}$_2$].[65] The related diene precursor [RuClCp*(η^4-isoprene)] reacts with 2-diphenylphosphinoethylamine to give [RuClCp*{κ^2(*P,N*)-$Ph_2P(CH_2)_2NH_2$}] in high yield.[204]

The osmium(II) 1,5-cyclooctadiene complex [OsBrCp*(COD)] **126** has been prepared by refluxing the Os(III) dimer [{OsBr(μ-Br)Cp*}$_2$] with an excess of COD in ethanol. Ethanol probably serves as reductant in this reaction.[117] Compound **126** also undergoes diene substitution processes with mono- and bidentate phosphines in boiling heptane, leading to [OsBrCp*(L^1)(L^2)] ($L^1 = L^2 = PEt_3$; L^1L^2 = dmpm, dmpe, dppm) in moderate yields.[117]

The labile tetrameric ruthenium(II) cluster [{RuCp*(μ_3-Cl)}$_4$] **127** instantaneously reacts with the phosphino–ester ligand $Pr^i{}_2PCH_2CO_2Me$ **128** at room temperature to afford the chelate complex [RuClCp*{κ^2(*P,O*)-**128**}].[205] Treatment of tetramer **127** with the racemic amino-phosphaferrocene **129a** (Figure 16) generates [RuClCp*{κ^1(*P*)-**129a**}$_2$], isolated as a mixture of two isomers arising from the incorporation of two ligands with identical or opposite configuration.[206] In contrast, κ^2(*P,N*)-complexation of the related amino- and pyridyl-phosphaferrocenes **129b** and **130a** and **130b** (Figure 16) is readily achieved starting from **127**.[206,207] The resulting six-membered metallacycles [RuClCp*{κ^2(*P,N*)-L}] (L = **129b**,* **130a**) are generated with total diastereoselectivity, while the more flexible seven-membered chelate complex [RuClCp*{κ^2(*P,N*)-**130b**}] is obtained as a 95 : 5 mixture of diastereomers. The bulky phosphine $PMePr^i{}_2$ reacts with **127** to provide the 16-electron complex [RuClCp*($PMePr^i{}_2$)], isolated as an extremely air sensitive deep blue solid. In solution at low temperature (180 K), the momomeric form of this 16-electron complex is in equilibrium with the related chloro-bridged dimer [{Ru(μ-Cl)Cp*($PMePr^i{}_2$)}$_2$].[73] Similarly, **127** and its iodide and bromide analogs coordinate only one bulky $PPhPr^i{}_2$ ligand affording the purple derivatives [RuXCp*($PPhPr^i{}_2$)] (X = Cl, I,* Br). Notably, these tetrameric precursors remain unchanged after treatment with more sterically demanding phosphines such as $PPhBu^t{}_2$ or P(*o*-Tolyl)$_3$.[102]

Like **127**, the ruthenium(III) chloro-bridged complex [{$RuCl_2Cp^*$}$_n$] **131**, formulated both as a polymer or a dimer (*n* = 2), has proved to be a suitable precursor for a wide range of bis-phosphine Ru(II) derivatives [RuClCp*(L)$_2$]. Nevertheless, in this case a prior reduction step, usually promoted by zinc dust, is required. Alternatively, the solvent (ethanol) or an excess of the phosphine ligands can act as reducing agent. For instance, treatment of **131** with zinc and at least 2 equiv. of the appropriate *P*-donor ligand affords complexes [RuClCp*(L_2)] (L_2 = 2 $Ph_2PC{\equiv}CPh$,*[208] BINAP (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), DIOP,[157] 2 $Ph_2PCH_2CH_2OMe$, 2 Ph_2PCH_2R (R = $\overline{\text{CHO(CH}_2)_n\text{O}}$, *n* = 2, 3, or 4; R = $\overline{\text{CH(CH}_2)_3\text{O}}$)).[209] Under the same reaction conditions, the bis-stibine ruthenium(II) derivative [RuClCp*($SbPh_3$)$_2$] is also selectively formed starting from **131**. In contrast, the ruthenium(III) species [$RuCl_2Cp^*$($SbPh_3$)] has been isolated performing this reaction with only 1 equiv. of $SbPh_3$ and in the absence of zinc.[210]

The synthesis of the bromo-bridged osmium(III) dimer [{OsBr(μ-Br)Cp*}$_2$] **132***, closely related to **131**, has been achieved in 75% yield by refluxing hexabromo-osmic acid $H_2[OsBr_6]$ and C_5Me_5H in ethanol or *tert*-butyl alcohol.[211] Reaction of **132** with triphenylphosphine in boiling ethanol gives either the osmium(III) species [$OsBr_2Cp^*$(PPh_3)][211] or the bis-phosphine osmium(II) derivative [OsBrCp*(PPh_3)$_2$].[117] The preparation of [OsBrCp*(PMe_3)$_2$] starting from **132** has also been described.[117]

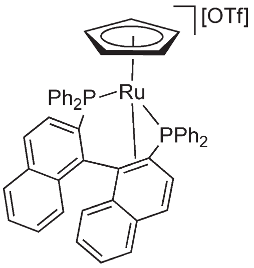
Sequential displacement of one, two, or three labile acetonitrile ligands from [RuCp(NCMe)$_3$][PF_6] **28** by two-electron donor ligands, including phosphines, stibines, and arsines, allows the access to derivatives of the type [RuCp(NCMe)$_2$(L)][PF_6], [RuCp(NCMe)(L^1)(L^2)][PF_6], and [RuCp(L^1)(L^2)(L^3)][PF_6], the selectivity of this process depending mainly on the incoming ligands.[132] In particular, chelation of heteroditopic phosphines, bearing an amino group or an olefinic function, has been readily achieved by this procedure providing, for example, derivatives

$[RuCp(NCMe)\{\kappa^2(P,N)\text{-}Ph_2P(CH_2)_2NMe_2\}][PF_6]$[141] and $[RuCp(NCMe)\{\kappa^3(P,C,C)\text{-}Ph_2P(CH_2)_2CH{=}CH_2\}][PF_6]$.*[212] The coordination chemistry of **28** and its catalytic applications have been reviewed.[132] As its Cp counterpart, the pentamethylcyclopentadienyl complex $[RuCp^*(NCMe)_3][PF_6]$ is also a valuable precursor for bis-phosphine derivatives such as $[RuCp^*(NCMe)(L^1)(L^2)][PF_6]$ ($L^1=L^2=PMe_3$, $L^1L^2=$ dmpm, (*S*,*S*)-chiraphos, (*S*,*S*)-$Ph_2PCHMeCH_2CHMePPh_2$).[136]

The dicarbonyl complex $[RuI(\eta^5\text{-}C_5Me_4CF_3)(CO)_2]^*$ reacts with triphenylphosphine in boiling ethanol to afford the monosubstituted product $[RuI(\eta^5\text{-}C_5Me_4CF_3)(CO)(PPh_3)]$.[213] Using a similar synthetic approach, complexes $[RuX(\eta^5\text{-}C_5Me_4Et)(CO)(L)]$ ($X=Cl$, Br, I; $L=PPh_3$, $PPhMe_2$, $AsPh_3$, $P(OPh)_3$, $P(OMe)_3$; not all combinations) have been prepared starting from the appropriate halide–dicarbonyl compounds, in refluxing benzene or toluene.[148] Addition of Me_3NO, able to oxidize CO into CO_2, usually favors the CO extraction process and offers the possibility to perform these substitution reactions at room temperature. Thus, treatment of THF solutions of $[OsBr(\eta^5\text{-}C_5Ph_5)(CO)_2]$ with Me_3NO and L readily gives $[OsBr(\eta^5\text{-}C_5Ph_5)(CO)(L)]$ ($L=PMe_2Ph$, $P(OEt)_3$, $P(OCH_2)_3CMe$).[214] Remarkably, starting from all the dicarbonyl precursors described above only monosubstitution is possible. For instance, attempts to synthesize the chelate complex $[RuBr(\eta^5\text{-}C_5Me_4Et)(dppm)]$ by replacement of both CO ligands in $[RuBr(\eta^5\text{-}C_5Me_4Et)(CO)_2]$ failed, giving instead the binuclear species $[\{RuBr(CO)(\eta^5\text{-}C_5Me_4Et)\}_2(\mu\text{-}dppm)]$.[148] Nevertheless, carbonyl disubstitution is possible starting from the hydride–dicarbonyl precursor $[RuHCp(CO)_2]$, generated *in situ* from $[Ru_3(CO)_{12}]$ and CpH, which reacts with bidentate phosphines in refluxing heptane to generate $[RuHCp(L{\sim}L)]$ ($L{\sim}L=(S,S)\text{-}(C_6F_5)_2POCH(Ph)CH(Ph)OP(C_6F_5)_2$,[163] BINAP,[215] **133**[166] (Figure 16)). These hydrides can be readily converted into the related iodide complexes by treatment with iodoform.[163,166,215]

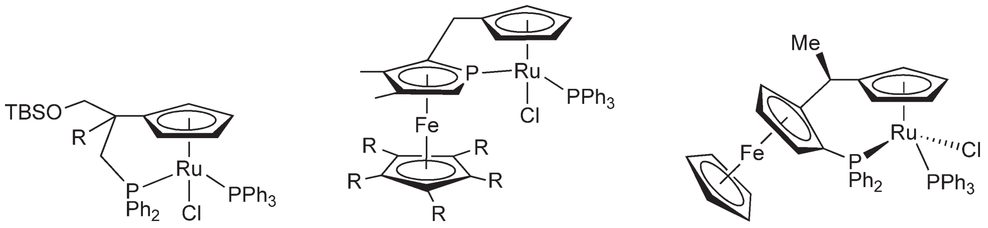
Chloride abstraction from $[RuClCp^*(L^1)(L^2)]$ ($L^1=L^2=PMePr^i_2$; $L^1L^2=$ dippe), performed in fluorobenzene with 1 equiv. of $Na[BAr^F_4]$ under argon atmosphere, gives the rare examples of cationic 16-electron complexes $[RuCp^*(L^1)(L^2)][BAr^F_4]$ ($L^1=L^2=PMePr^i_2$ **134**;* $L^1L^2=$ dippe **135***).[216] Their deep blue color is a characteristic feature exhibited by other unsaturated half-sandwich ruthenium derivatives. In solid state, compound **135** is stabilized by an agostic interaction with one of the hydrogen atoms of an isopropyl group, whereas such an interaction is absent in the case of **134**. The Cp analogs $[RuCp(L^1)(L^2)][BAr^F_4]$ ($L^1=L^2=PMePr^i_2$; $L^1L^2=$ dippe) can be generated under the same conditions but are too reactive to be isolated.[74] Iodide removal from $[RuICp\{\kappa^2(P,P)\text{-}BINAP\}]$ affords the saturated derivative $[RuCp\{\kappa^4(P,P,C,C)\text{-}BINAP\}][OTf]^*$ **136**, in which the BINAP ligand is coordinated through both phosphorus atoms and one adjacent carbon–carbon double bond (Figure 17).[215] Similar derivatives $[RuCp\{\kappa^4(P,P,C,C)\text{-}L_2\}][BF_4]^*$ and $[Ru(\eta^5\text{-}C_4H_4N)\{\kappa^4(P,P,C,C)\text{-}L_2\}][BF_4]$ ($L_2=$ MeO-Biphep; Biphep = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl) have been made by protonation of $[Ru(OAc)_2\{\kappa^2(P,P)\text{-}MeO\text{-}Biphep\}]$ with HBF_4 in the presence of CpH or pyrrole, respectively.[217]

During the last decade, the preparation of tethered cyclopentadienyl complexes has received particular attention with the aim of generating more robust and configurationally stable species. This chemistry has been recently reviewed.[218,218a] A general synthetic approach to ruthenium derivatives of this type consists of the reaction of $[RuCl_2(PPh_3)_3]$ with the appropriate functionalized cyclopentadienyl anions, usually generated *in situ*. In this way, compounds **137**,[219] **138a**,[98] and $[RuCl\{\eta^5{:}\kappa^1(P)\text{-}1,3\text{-}BzC_5H_3(CH_2)_4PPh_2\}(PPh_3)]$[220] have been obtained as a mixture of diastereomers, while **138b***[98] and **139***[221] are formed diastereoselectively (Figure 18). The complex $[RuCl\{\eta^5{:}\kappa^2(P,P)\text{-}C_5H_4CH_2CMe(CH_2PPh_2)_2\}]$ bearing a tripodal ligand has been similarly made.[128] The bis(allyl)–ruthenium(IV) derivative $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ ($C_{10}H_{16}=$ 2,7-dimethylocta-2,6-diene-1,8-diyl) is converted



136*

Figure 17 The BINAP-Ru(II) derivative **136**.



R = H,* Bz*

137

138a: R = H

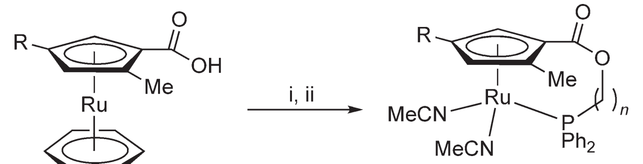
138b: R = Me*

138

139*

Figure 18 The tethered ruthenium(II) complexes **137**–**139**.

into the tethered ruthenium(II) species $[Ru\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4CH_2CH(R)PPh_2\}(NCMe)_2][PF_6]$ (R = H, Ph **140**) by reaction with the appropriate cyclopentadiene–phosphine ligand, $Li_2[CO_3]$ and $K[PF_6]$ in a mixture of ethanol and acetonitrile.[63] Alternatively, the tetrafluoroborate salt of **140** is accessible by refluxing an acetonitrile solution of the ruthenium(IV) bis-dienyl derivative $[RuH\{\eta^5\text{-}CH_2CMeCHCMeCH_2\}_2][BF_4]$ in the presence of $CpHCH_2CHPh\text{-}PPh_2$.[222] Esterification of the sandwich derivatives **141** with $HO(CH_2)_nPPh_2$ ($n = 2$, 3), and subsequent replacement of the benzene ligand by photoirradiation in acetonitrile gives complexes **142** (Equation (13)).[135] In the case of $R = Bu^t$, substitution of one acetonitrile ligand by PPh_3, $PBu^n{}_3$, or $P(OPh)_3$ has found to proceed with total diastereoselectivity.[223]



141

i, $(COCl)_2$, $HO(CH_2)_nPPh_2$; ii, $h\nu$ NCMe

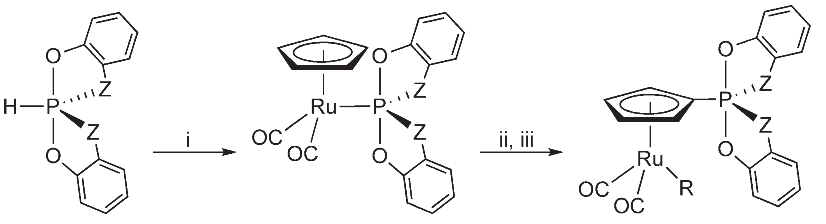
$n = 2$, R = Me, Ph, Bu^t
$n = 3$, R = Me

142

(13)

The osmium-tethered complex $[OsCl\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4CH_2CH_2PPh_2\}(PPr^i{}_3)]$ has been obtained in three steps from $[OsCl_2H_2(PPr^i{}_3)_2]$ in 59% overall yield.[224] Firstly, the reaction of $[OsCl_2H_2(PPr^i{}_3)_2]$ with $Li[C_5H_4(CH_2)_2PPh_2]$ gives the dihydride derivative $[OsH_2\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4CH_2CH_2PPh_2\}(PPr^i{}_3)]Cl$,* which is readily deprotonated upon treatment with K[OH] in MeOH affording $[OsH\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4CH_2CH_2PPh_2\}(PPr^i{}_3)]$. A final hydride/chloride exchange with chloroform leads to $[OsCl\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4CH_2CH_2PPh_2\}(PPr^i{}_3)]$.

Chloride abstraction with $AlCl_3$ from the phosphido complexes $[M\{\kappa^1(P)\text{-}PClNPr^i{}_2\}Cp^*(CO)_2]$ (M = Ru,* Os), formed by reacting the appropriate anion $[MCp^*(CO)_2]^-$ with $Cl_2PNPr^i{}_2$, generates the terminal phosphinidene species $[MCp^*({=}PNPr^i{}_2)(CO)_2][AlCl_4]$ (M = Ru,* Os*).[225] The first *P*-metallated-iminophosphorane of ruthenium, namely $[RuCp^*\{\kappa^1(P)\text{-}P({=}NPh)(OR)_2\}(CO)_2]$, has been prepared by deprotonation of $[RuCp^*\{\kappa^1(P)\text{-}P(NHPh)(OR)_2\}(CO)_2][BF_4]$ with sodium amide.[226] Complexes $[RuCp^*\{\kappa^1(E)\text{-}E(SiMe_3)_2\}(CO)_2]$ (E = As, P), generated by reacting $[RuBrCp^*(CO)_2]$ with the appropriate lithium salt $Li[E(SiMe_3)_2]$, insert carbon disulfide into the E–Si bond to afford the corresponding metalla-, arsa- and phospha-alkenes $[RuCp^*\{\kappa^1(E)\text{-}E{=}C(SSiMe_3)_2\}(CO)_2]$.[227] The reactions of ruthenadisilylphosphanes $[Ru\{\kappa^1(P)\text{-}P(SiMe_3)_2\}(\eta^5\text{-}C_5R_5)(CO)_2]$ ($C_5R_5 = 1,2,4\text{-}C_5H_2Pr^i{}_3$, $1,3\text{-}C_5H_3Bu^t{}_2$, $1,3\text{-}C_5H_3(SiMe_3)_2$) with $ArPCl_2$ ($Ar = 2,4,6\text{-}C_6H_2Bu^t{}_3$) give rise to the metalladiphosphene species $[Ru\{\kappa^1(P)\text{-}P{=}PAr\}(\eta^5\text{-}C_5R_5)(CO)_2]$.[228] Treatment of these complexes with hexafluoroacetone generates the cycloadducts **143**, which can further isomerize into the oxa–diphosphetane derivatives **144** (Equation (14)).[228] Ruthenium metallaphosphorane derivatives **146** have been prepared by reacting $[RuClCp(CO)_2]$ with the appropriate phosphoranide anion, generated by deprotonation of **145** (Scheme 4). Upon treatment with LDA and RX, the phosphorane fragment in **146** migrates from the metal to the cyclopentadienyl ligand generating complexes **147**.[229,230]



145 **146**

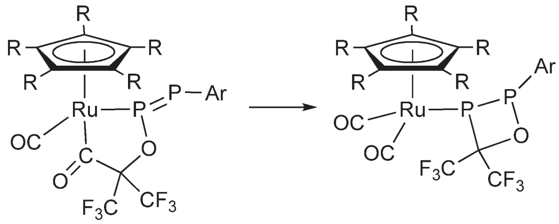
Z = NMe; R = Me, Bz,* $SnPh_3$, H
Z = O; R = Me
147

i, $LiBu^n$, $[RuClCp(CO)_2]$; ii, LDA; iii, RX

Scheme 4

C_5R_5 = 1,2,4-$C_5H_2Pr^i_3$,
1,3-$C_5H_3Bu^t_2$,
1,3-$C_5H_3(SiMe_3)_2$

Ar = 2,4,6-$C_6H_2Bu^t_3$



C_5R_5 = 1,3-$C_5H_3Bu^t_2$,
1,3-$C_5H_3(SiMe_3)_2$

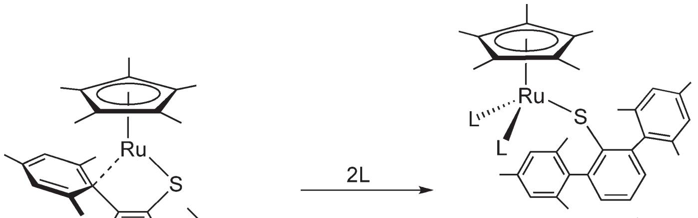
Ar = 2,4,6-$C_6H_2Bu^t_3$ (14)

143 **144**

6.14.3.3 Complexes Containing S-, Se- and Te-donor Ligands

6.14.3.3.1 Thiolates, thiols, thioethers, and related ligands

The most direct route to CpRu–thiolato complexes involves the reaction between a metal–chloride precursor and the sodium or lithium salt of the ligand (isolated or generated *in situ*; see COMC (1995)). Following this synthetic approach, a large variety of novel thiolato complexes of general formula $[Ru(SR)Cp(L^1)(L^2)]$ (R = Me, Et, Ph, Bz, CH_2Bz, CH_2CO_2Et, CH_2-2-furyl, $CH_2CH(NHAc)CO_2H$, $SiPr^i_3$, $CH_2CH{=}CH_2$, 2-benzimidazolyl, 2-benzothiazolyl, 2-benzoxazolyl; L^1L^2 = dppm, dppe, (*S*,*S*)-chiraphos or $L^1 = PPh_3$, $L^2 = CO$, PPh_3 (not all combinations)) have been synthesized.[231–238] In addition, readily available bis-triphenylphosphine thiolato derivatives $[Ru(SR)Cp(PPh_3)_2]$ have been used as suitable starting materials for the preparation of complexes $[Ru(SR)Cp(L^1)(L^2)]$ ($L^1 = L^2 = P(OPh)_3$, R = Ph, Bz, Me; L^1L^2 = bbpe (bbpe = bis(binaphthylphosphonito)ethane), R = Ph, Bz; L^1L^2 = dppe, R = $SiPr^i_3$; $L^1 = PPh_3$, $L^2 = CO$, R = $CH_2CH{=}CH_2$, 2-benzimidazolyl, 2-benzothiazolyl, 2-benzoxazolyl; $L^1 = PPh_3$, $L^2 = PMe_3$, $P(OMe)_3$, R = $SiPr^i_3$; $L^1 = PPh_3$, L^2 = NO, R = Bu^t,* Pr^i, *p*-Tol) via PPh_3 substitution processes.[232,236–239*] The reaction of [RuClCp(dppf)] with thiophenol has been reported to yield [Ru(SPh)Cp(dppf)]*, the initial formation of Na[SPh] or Li[SPh] being in this case not required.[240] Indenyl–ruthenium(II) complexes $[Ru(SR)(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (R = Et, Bz, Pr^i, *p*-Tol), obtained from $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and the appropriate Na[SR] salt, are also known.[241] The reaction of $[\{Cp^*RuCl\}_4]$ with an excess of the bulky 2,6-dimesitylphenyl thiolate ligand affords the mononuclear Ru(II) complex **148**.*[59] In accord with its coordinative unsaturation and the lability of the coordinated *ipso*-carbon, complex **148** readily reacts with CO, $CNBu^t$, 2,2′-bipyridine, and 1,10-phenanthroline to yield the 18-electron thiolato complexes **149** (Equation (15)).[59]



L = CO,* $CNBu^t$*
L–L = bipy,* phen*

(15)

148* **149**

A large variety of thiolato–CpRu(II) complexes have been prepared through the addition of nucleophiles at the electrophilic carbon atom of highly reactive thiobenzaldehyde derivatives $[Ru\{\kappa^1(S)\text{-}S{=}CHR\}Cp(L^1)(L^2)][PF_6]$, including the cationic species $[Ru\{SCHPh(PMe_3)\}Cp(L^1)(L^2)][PF_6]$ ($L^1L^2 = $ dppm, dppe; $L^1 = PPh_3$, $L^2 = P(OMe)_3$), obtained by the addition of PMe_3, and the neutral complexes $[Ru(SCH_2R)Cp(L^1)(L^2)]$ ($L^1L^2 = $ dppm, dppe, R = Ph, 4-C_6H_4OMe), $[Ru\{SCHPh(O\text{-}p\text{-}Tol)\}Cp(dppe)]$, $[Ru\{SCHR^1(SR^2)\}Cp(L^1)(L^2)]$ ($L^1L^2 = $ dpme (dpme = [2-(dimethylphosphino)ethyl]diphenylphosphine), $R^1 = Ph$, $R^2 = Me$; $L^1L^2 = $ dppm, $R^1 = 4\text{-}C_6H_4Cl$, $R^2 = Me$, $CH_2\text{-}4\text{-}C_6H_4OMe$; $L^1L^2 = $ dppm, $R^1 = 4\text{-}C_6H_4OMe$, $R^2 = Bz$), $[Ru\{SCHPh(R)\}Cp(L^1)(L^2)]$ ($L^1L^2 = $ dppm, dppe, R = Bu^n, $CH{=}CH_2$), and $[Ru\{SCHPh(CH(CO_2R)_2)\}Cp(L^1)(L^2)]$ ($L^1L^2 = $ dppm, dppe, R = Me, OMe; $L^1L^2 = $ dpme, R = Me), obtained by the addition of H^-, OR^-, SR^-, and carbanions.[242]

Treatment of the η^2-toluene derivative $[RuCp^*(NO)(\eta^2\text{-}C_6H_5Me)]$ with disulfides RSSR has been reported to yield the dithiolato complexes $[Ru(SR)_2Cp^*(NO)]$ (R = Me, Ph, *p*-Tol, Bu^{t*}) via substitution of the toluene ligand and oxidative addition of the disulfide.[112] S–S bond activation also occurs when $[RuCp(NCMe)_3][PF_6]$ **28** is treated with bis(2-pyridyl)disulfide, the reaction leading to complex $[Ru\{\kappa^2(N,S)\text{-}Spy\}_2Cp][PF_6]^*$ which contains two chelating (2-pyridyl)thiolate (Spy) ligands.[243] The dichloride precursor $[RuCl_2Cp^*(NO)]$ reacts with the sodium salts of 2,3,5,6-tetrafluorobenzenethiol and 4-methylbenzene-1,2-dithiol to afford the dithiolato complexes $[Ru(SC_6F_4H)_2\text{-}Cp^*(NO)]^*$ and $[Ru\{\kappa^2(S,S)\text{-}S_2C_7H_6\}Cp^*(NO)]$, respectively.[244] The analogous dichalcogenolate derivatives $[Ru(EPh)_2Cp^*(NO)]$ (E = Se, Te) have been prepared following a similar approach.[244]

The electron-rich complexes $[RuClCp^*(L^1)(L^2)]$ ($L^1 = L^2 = PEt_3$; $L^1L^2 = $ dippe) undergo oxidative addition of H_2S, in the presence of $Na[BPh_4]$, to afford the ruthenium(IV) hydrido-metallothiols $[RuH(SH)Cp^*(L^1)(L^2)][BPh_4]$ ($L^1 = L^2 = PEt_3$;* $L^1L^2 = $ dippe).[245,246] Treatment of $[RuH(SH)Cp^*(dippe)][BPh_4]$ with LDA results in the formation of the neutral hydrosulfido-Ru(II) complex $[Ru(SH)Cp^*(dippe)]$.[246]

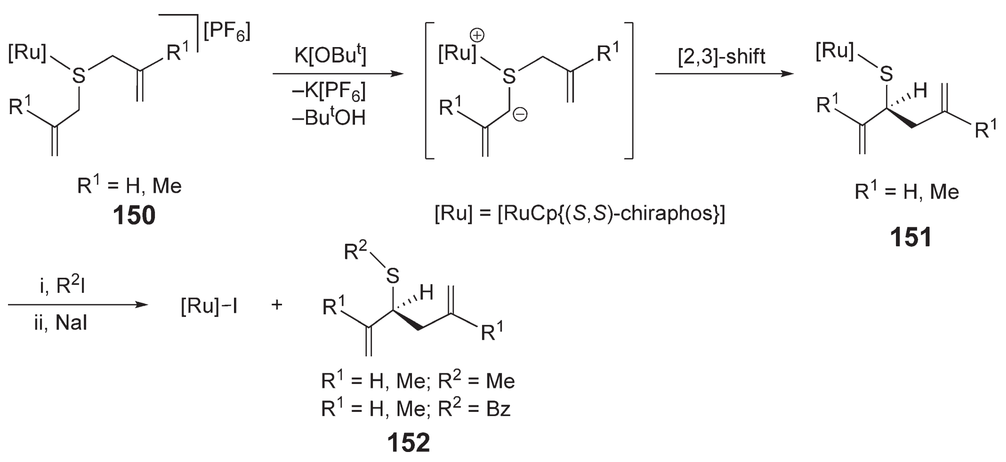
Chloride precursors $[RuClCp(EPh_3)_2]$ react with disodium maleonitriledithiolate (Na_2mnt) to give chelate complexes $[Ru\{\kappa^2(S,S)\text{-}mnt\}Cp(EPh_3)]^-$ (E = P, As, Sb) by displacement of both the chloride and one EPh_3 ligand.[247,248] Similarly, treatment of $[RuCl_2Cp^*(NO)]$ with the appropriate disodium salt generates $[Ru\{\kappa^2(S,S)\text{-}L\}Cp^*(NO)]$ (L = mnt,* i-mnt (2,2-dicyano-1,1-ethylenedithiolate), tdas* (1,2,5-thiadiazole-3,4-dithiolate), dmit* (1,3-dithiol-2-thione-4,5-dithiolate)).[249–252] Complexes $[M\{\kappa^2(E,E)\text{-}E_2Fc\}Cp^*(NO)]$ (M = Ru, E = S, Se; M = Os, E = S,* Se, Te), containing a chelate 1,1′-ferrocenedichalcogenato ligand ($FcE_2{}^{2-}$), are also known.[253]

Alkynethiolato and alkyneselenolato complexes $[Ru(EC{\equiv}CR^2)(\eta^5\text{-}C_5R^1{}_5)L_2]$ (E = S, $R^1 = H$, L = PPh_3, $R^2 = Ph$,* $SiMe_3$, Bu^t,* Cy; E = S, $R^1 = Me$, L = PEt_3, $R^2 = Ph$;* E = Se, $R^1 = H$, L = PPh_3, $R^2 = Ph$,* $SiMe_3{}^*$) have been synthesized by reacting $[RuCl(\eta^5\text{-}C_5R^1{}_5)L_2]$ with the corresponding lithium alkynechalcogenolates $Li[EC{\equiv}CR^2]$.[254,255]

CpRu–thioether complexes are usually obtained by reacting metallic chloride precursors $[RuClCp(L^1)(L^2)]$ with the appropriate thioether ligand in the presence of a chloride abstractor (see COMC (1995)). Following this classical synthetic approach, novel thioether–ruthenium(II) complexes $[Ru(SR^1R^2)Cp(L^1)(L^2)][Y]$ ($SR^1R^2 = SEt_2$, SPh_2, SEtPh, $S(p\text{-}Tol)_2$, SMePh, SMeCy, $SMePr^i$, SMeBz, $SBzPr^i$, SBzEt; $L^1L^2 = $ dppm, dppe, dpme, dtpe (dtpe = 1,2-bis(di-*p*-tolylphosphino)ethane), (*S*,*S*)-chiraphos or $L^1 = CO$, $L^2 = PPh_3$; Y = PF_6 or BF_4 (not all combinations)) have been readily prepared in high yields.[256,256a*,257,258]

The coordinated sulfur atom of thiolato–ruthenium complexes $[Ru(SR^1)Cp(L^1)(L^2)]$ is highly nucleophilic reacting easily with allyl bromides to give cationic allyl thioether complexes $[Ru\{S(R^1)CHR^2CH{=}CR^3R^4\}Cp(L^1)(L^2)]Br$ ($R^1 = $ Me, Et, Ph, Bz; $CHR^2CH{=}CR^3R^4 = $ 2-propenyl, 2-cyclohexenyl, 2-methyl-2-buten-4-yl; $L^1L^2 = $ dppm, dppe, (*S*,*S*)-chiraphos, (*S*,*S*)-bbpe or $L^1 = L^2 = P(OPh)_3$ (not all combinations)), isolated as the corresponding hexafluorophosphate salts after $Br^-/PF_6{}^-$ exchange.[231,232] The related allyl thioether complex $[Ru\{S(Me)CH_2CH{=}CH_2\}\text{-}Cp(PPh_3)(CO)][PF_6]$ was prepared by treatment of $[Ru(SCH_2CH{=}CH_2)Cp(PPh_3)(CO)]$ with MeI in the presence of $[NH_4][PF_6]$.[238] The enantiomerically pure diallyl thioether complexes **150**, obtained from $[RuClCp\{(S,S)\text{-}chiraphos\}]$, $S(CH_2CR^1{=}CH_2)_2$, and $[NH_4][PF_6]$, react with $K[OBu^t]$ to yield complexes **151** as 78 : 22 ($R^1 = H$) and 87 : 13 ($R^1 = Me$) mixtures of chromatographically separable *SSS*/*SSR* diastereomers (Scheme 5). The process involves the initial deprotonation of one SCH_2 unit to generate a sulfur ylide which undergoes a subsequent [2,3]-sigmatropic rearrangement. Treatment of **151** with MeI or BzI and then NaI affords enantiomerically enriched thioethers **152** and $[RuICp\{(S,S)\text{-}chiraphos\}]$.[259]

The sulfur atom in complexes $[Ru(SR)Cp(L^1)(L^2)]$ can be also readily protonated by HBF_4 to give the corresponding thiol complex salts $[Ru(RSH)Cp(L^1)(L^2)][BF_4]$ ($L^1 = L^2 = PPh_3$, R = Bu^t, *p*-Tol, Pr^i; $L^1 = PPh_3$, $L^2 = CO$, R = $CH_2CH{=}CH_2$).[238,260] The related species $[Ru(CySH)Cp(PPh_3)_2][BF_4]^*$ and $[Ru(PhSH)Cp(dippe)][BPh_4]$ **153** have been prepared by treating the parent chloride with the free thiol in the presence of $Ag[BF_4]$ or $Na[BPh_4]$.[246,261] Complex **153** is extremely air sensitive being readily oxidized to the Ru(III) thiolate $[Ru(SPh)Cp(dippe)][BPh_4]$ **154**.*[246] All efforts to isolate the Cp^* analog of **153** from the reaction of $[RuClCp^*(dippe)]$ with $Na[BPh_4]$ and PhSH failed, leading instead to the paramagnetic Ru(III) thiolate



Scheme 5

$[Ru(SPh)Cp^*(dippe)][BPh_4]$ **155**.[246] Reduction of the Ru(III) complexes **154** and **155** upon treatment with $K[OBu^t]$ yields the neutral diamagnetic Ru(II) derivatives $[Ru(SPh)(\eta^5\text{-}C_5R_5)(dippe)]$ (R = H,* Me).[246]

Chloride precursors $[RuClCp(L^1)(L^2)]$ react with the cyclic thioethers tetrahydrothiophene (tht), trimethylenesulfide (tms) and 1,4-thioxane (SC_4H_8O), in the presence of Ag[OTf], $[NH_4][PF_6]$, or $Ag[BF_4]$, to afford the cationic species $[Ru\{\kappa^1(S)\text{-tht}\}Cp(L^1)(L^2)][Y]$ ($L^1 = L^2 = PPh_3$, Y = OTf;* L^1L^2 = dppm, dppe, $Y = PF_6$), $[Ru\{\kappa^1(S)\text{-tms}\}Cp(PPh_3)_2][OTf]$*, and $[Ru\{\kappa^1(S)\text{-}SC_4H_8O\}Cp(PPh_3)_2][BF_4]$, respectively.[256,256a,262–264] The thioaldehyde function in complexes $[Ru\{\kappa^1(S)\text{-}S{=}C(H)\text{-}4\text{-}C_6H_4X\}Cp(L^1)(L^2)][PF_6]$ easily undergo [4 + 2]-cycloadditions with 2,3-dimethylbutadiene and cyclopentadiene to afford the 3,6-dihydro-2*H*-thiopyrane derivatives **156** and **157**, respectively (Figure 19).[242] Related cycloaddition reactions using thiocinnamaldehyde–Ru(II) complexes, as well as enantiomerically pure thioaldehyde–Ru(II) complexes, have been briefly presented within a review article.[265]

Cationic complexes $[Ru(SC_4H_4)Cp(L^1)(L^2)][BF_4]$ (L^1L^2 = dppe, dppm, (*S*,*S*)-chiraphos, (2*S*,3*S*)-bis(dibenzophospholyl)butane), containing a labile *S*-bonded thiophene ligand, have been made from $[RuClCp(L^1)(L^2)]$ via chloride abstraction with $Ag[BF_4]$.[266–268] In a similar way, the reaction of $[RuClCp(CO)(PPh_3)]$ with Ag^+ and selenophenes (Seln) produces the stable selenium-bound selenophene derivatives $[Ru(Seln)Cp(CO)(PPh_3)][BF_4]$ (Seln = selenophene, 2-methylselenophene,* 2,5-dimethylselenophene).[258] Synthetic, structural, and binding studies of a series of Ru(II) complexes **158** containing dibenzothiophene ligands have been described and related to the processes involved in the hydrodesulfurization of petroleum feedstocks (Figure 20).[258,269,270]

The synthesis of a series of ruthenium complexes containing cyclic di- and trithioether ligands has also been reported. Thus, treatment of dimer $[\{RuCp^*(\mu\text{-OMe})\}_2]$ with trifluoromethanesulfonic acid and 1,4-dithiane ($S_2C_4H_8$) gives the mononuclear neutral complex $[Ru\{\kappa^2(S,S)\text{-}S_2C_4H_8\}Cp^*(OTf)]$.[43] The related cationic complex $[Ru\{\kappa^2(S,S)\text{-}S_2C_4H_8\}Cp(PPh_3)][BF_4]$* has been prepared by reacting $[RuClCp(PPh_3)_2]$ with 1,4-dithiane in the presence of $Ag[BF_4]$, via AgCl elimination and concomitant loss of one PPh_3 ligand.[271] In contrast, treatment of $[RuClCp(PPh_3)_2]$ with 1,3-dithiane and 1,3,5-trithiane, in the presence of Ag[OTf], affords the mononuclear complexes $[Ru\{\kappa^1(S)\text{-}S_2C_4H_8\}Cp(PPh_3)_2][OTf]$* and $[Ru\{\kappa^1(S)\text{-}S_3C_3H_6\}Cp(PPh_3)_2][OTf]$,* respectively, in which the thioethers

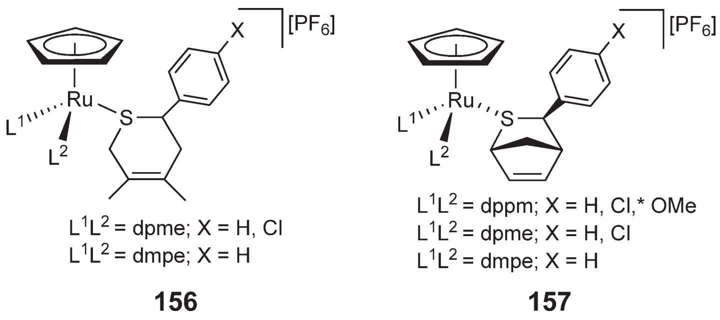
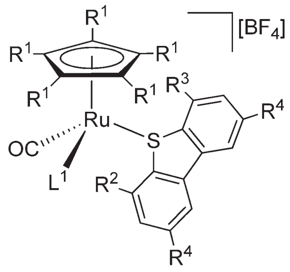


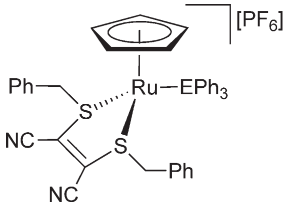
Figure 19 Structure of the 3,6-dihydro-2H-thiopyrane derivatives **156** and **157**.



L^1 = CO; R^1 = Me; R^2 = H; R^3 = H,* Me,* R^4 = H
L^1 = CO; R^1 = Me; R^2 = R^3 = Me; R^4 = H*
L^1 = CO; R^1 = H; R^2 = R^3 = R^4 = H*
L^1 = PPh_3; R^1 = H; R^2 = R^3 = H; R^4 = Me

158

Figure 20 The dibenzothiophene-ruthenium(II) complexes **158**.



E = P, As, Sb

159

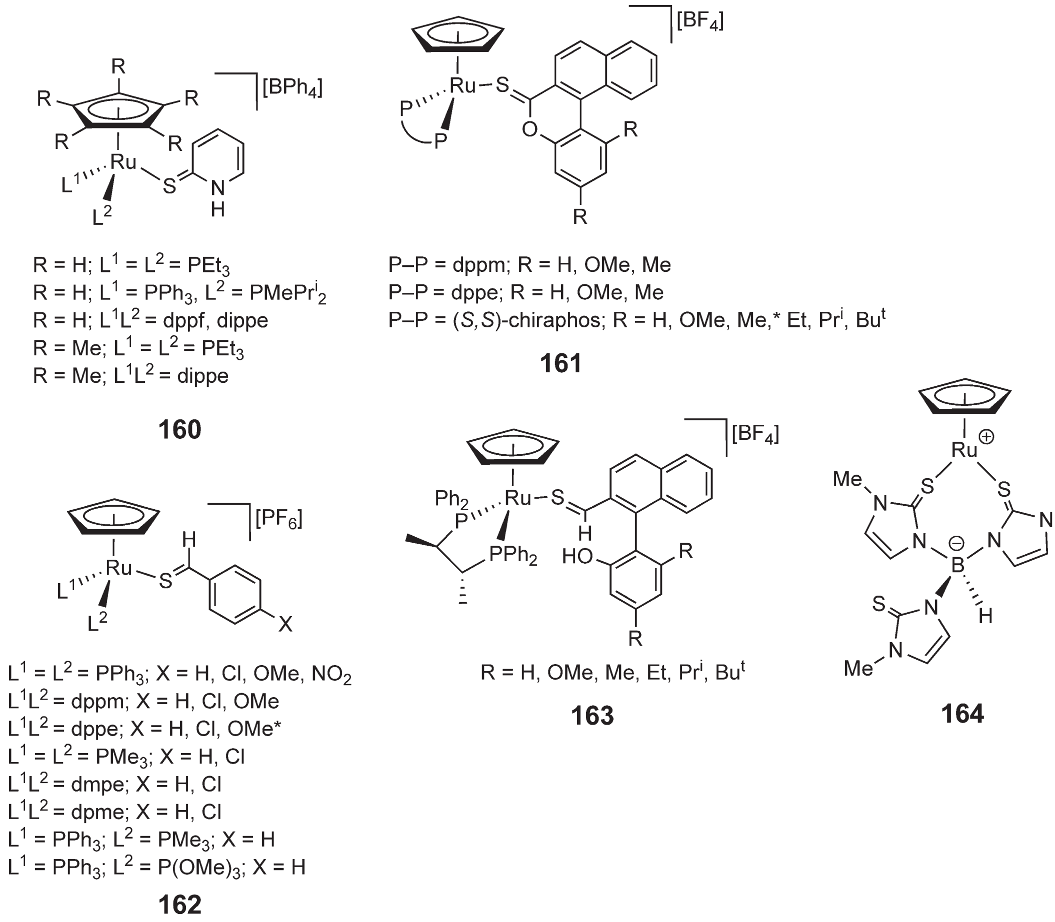
Figure 21 CpRu(II) derivatives **159** containing a dithiomaleonitrile ligand.

act as monodentate ligands.[271] These results seem to indicate that chelation occurs only when the sulfur atoms are separated by at least two C atoms. In accord with this, chelation of dibenzyldithiomaleonitrile takes place upon reaction with $[RuClCp(EPh_3)_2]/NH_4PF_6$ (E = P, As, Sb) affording complexes **159** (Figure 21).[247,248] Mixed sandwich complexes involving κ^3-coordinated trithioether ligands $[Ru\{\kappa^3(S,S,S)\text{-L}\}Cp][PF_6]$ (L = 1,4,7-trithiacyclononane,* 1,4,7-trithiacyclodecane*)[272,273] and $[Ru\{\kappa^3(S,S,S)\text{-1,4,7-trithiacyclononane}\}Cp^*][PF_6]$,*[274] are also known.

6.14.3.3.2 Ligands containing C═S groups

The stable adduct $[Ru\{\kappa^2(C,S)\text{-}CS_2\}Cp^*\{\kappa^1(P)\text{-P}{\sim}O\}_2][BPh_4]$ (P∼O = (1,3-dioxan-2-ylmethyl)diphenylphosphine), in which a CS_2 molecule is *C,S*-bonded to ruthenium, has been obtained by reacting $[RuCp^*\{\kappa^2(P,O)\text{-P}{\sim}O\}\{\kappa^1(P)\text{-P}{\sim}O\}][BPh_4]$ with carbon disulfide.[88] Treatment of complexes [RuClCp(P–P)] (P–P = dppf, dppm, dppe) with thiourea and thiobutyrolactone, in the presence of $[NH_4][PF_6]$, generates $[Ru\{\kappa^1(S)\text{-S═C}(NH_2)_2\}Cp(dppf)][PF_6]$*[240] and $[Ru\{\kappa^1(S)\text{-S═CC}_3H_6O\}Cp(P\text{–}P)][PF_6]$ (P–P = dppe, dppm),[275] respectively. The related complexes $[Ru\{\kappa^1(S)\text{-S═CC}_2H_4S_2\}Cp(dppf)]Cl^*$ and $[Ru\{\kappa^1(S)\text{-S═CC}_2H_2S_2\}Cp(dppf)]Cl^*$ have been prepared directly from [RuClCp(dppf)] and ethylene or vinylene trithiocarbonate, respectively, the presence of a chloride abstractor not being required in this case.[240]

The reaction of chloride precursors $[RuCl(\eta^5\text{-}C_5R_5)(L^1)(L^2)]$ with pyridine-2-thiol (HSPy) and $Na[BPh_4]$ yields cationic complexes **160** in which the HSPy ligand is tautomerized into its 1*H*-pyridine-2-thione form as inferred from spectral data (Figure 22).[240,245,246] A related isomerization of pyrimidine-2-thiol (HSPym) into 1*H*-pyrimidine-2-thione has also been observed in the reaction of [RuClCp(dippe)] with HSPym and $Na[BPh_4]$.[246] Compounds **161**, containing an *S*-coordinated biaryl–thionolactone ligand (Figure 22), have been prepared by substitution of the labile thiophene ligand in cationic complexes $[Ru(SC_4H_4)Cp(P\text{–}P)][BF_4]$ (P–P = dppm, dppe, (*S*,*S*)-chiraphos).[266,268,275] The chemical reduction of the C═S bond in thionolactone complexes **161** has been extensively explored allowing the preparation of a large variety of novel thiolato– and thioether–ruthenium complexes. Since this chemistry has been recently reviewed,[276] no details will be given here. Hydride abstraction from benzyl thiolate derivatives of general formula $[Ru(SCH_2\text{-4-}C_6H_4X)Cp(L^1)(L^2)]$ using triphenylcarbenium hexafluorophosphate yields cationic thiobenzaldehyde complexes **162** (Figure 22).[242] The synthesis of the optically active thioaldehyde derivatives **163** from the corresponding biaryl–thionolactone complexes **161** has also been reported.[268] The 16-electron complex **164**, in which the tripod *S*-donor ligand tris(methimazolyl)hydroborate adopts an unusual bidentate coordination, is also known.[277]



R = H; $L^1 = L^2 = PEt_3$
R = H; $L^1 = PPh_3$, $L^2 = PMePr^i_2$
R = H; L^1L^2 = dppf, dippe
R = Me; $L^1 = L^2 = PEt_3$
R = Me; L^1L^2 = dippe

160

P–P = dppm; R = H, OMe, Me
P–P = dppe; R = H, OMe, Me
P–P = (*S,S*)-chiraphos; R = H, OMe, Me,* Et, Pr^i, Bu^t

161

$L^1 = L^2 = PPh_3$; X = H, Cl, OMe, NO_2
L^1L^2 = dppm; X = H, Cl, OMe
L^1L^2 = dppe; X = H, Cl, OMe*
$L^1 = L^2 = PMe_3$; X = H, Cl
L^1L^2 = dmpe; X = H, Cl
L^1L^2 = dpme; X = H, Cl
$L^1 = PPh_3$; $L^2 = PMe_3$; X = H
$L^1 = PPh_3$; $L^2 = P(OMe)_3$; X = H

162

R = H, OMe, Me, Et, Pr^i, Bu^t

163

164

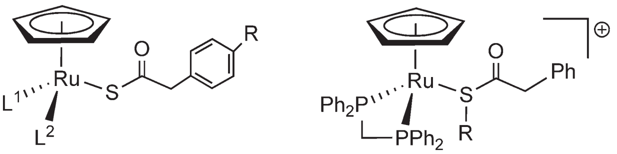
Figure 22 Structure of the ruthenium complexes 160–164.

6.14.3.3.3 Dithiocarbamates and related anionic ligands

Complexes of this type are usually obtained by reacting metallic halide or nitrile precursors with the appropriate sodium or potassium salt of the ligand (see COMC (1995)). Following this synthetic approach, the novel dithiocarbamato derivatives $[Ru\{\kappa^2(S,S)\text{-}S_2CNR^2{}_2\}(\eta^5\text{-}C_5R^1{}_5)(L)]$ ($R^1 = H$, $L = PMePr^i{}_2$, $R^2 = Et$; $R^1 = H$, $L = PPh_3$, $R^2 = Me$;* $R^1 = Me$, $L = PEt_3$, $R^2 = Et$)[245,278] and $[Ru\{\kappa^1(S)\text{-}SC({=}S)CNEt_2\}Cp(PEt_3)_2]$,[245] and xanthato complexes $[Ru\{\kappa^2(S,S)\text{-}S_2COR^2\}(\eta^5\text{-}C_5R^1{}_5)(L)]$ ($R^1 = H$, $L = PMePr^i{}_2$, R^2 = Me, Et, Pr^i; R^1 = Me, $L = PEt_3$, R^2 = Me, Et, Pr^{i*})[245] and $[Ru\{\kappa^1(S)\text{-}SC({=}S)OR\}Cp(PEt_3)_2]$ (R = Me, Et, Pr^i),[245] have been readily prepared. Similarly, the reaction of sodium cyanodithioformate with $[RuClCp(PPh_3)_2]$, in methanol at room temperature, results in the formation of the complex $[Ru\{\kappa^1(S)\text{-}SC({=}S)CN\}Cp(PPh_3)_2]$ which releases PPh_3 on heating in benzene to give $[Ru\{\kappa^2(S,S)\text{-}S_2CCN\}Cp(PPh_3)]$.[279] Insertion of isothiocyanates into the S–H bond of thiolato complexes $[Ru(SH)Cp(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$; L^1L^2 = dppe) also generates dithiocarbamate species $[Ru\{\kappa^2(S,S)\text{-}S_2CNHR\}Cp(PPh_3)]$ (R = Ph, napht) (napht = 1-naphthyl) and $[Ru\{\kappa^1(S)\text{-}SC({=}S)N(H)R\}Cp(dppe)]$ (R = Ph, napht).[280]

The $\kappa^1(S)$-coordinated thiocarboxylates **165** have been obtained by reacting thiolato complexes $[Ru(SH)Cp(L^1)(L^2)]$ with acyl chlorides $ClC({=}O)CH_2\text{-}4\text{-}C_6H_4R$ (Figure 23).[281] Alkylation of these species with methyl tosylate or triethyloxonium hexafluorophosphate takes place selectively on the sulfur atom leading to thioester complexes **166** (Figure 23). They also react with trifluoromethanesulfonic anhydride generating the $\kappa^2(C,S)$-thioketene complexes **167** via initial thioacylation at oxygen followed by intramolecular 1,2-elimination of CF_3SO_3H (Scheme 6).[281]

Insertion of carbon disulfide into M–H, M–C and M–S bonds is a well-known process (see COMC (1995)). In accord, thiolato complex $[Ru(SCH_2CH{=}CH_2)Cp(PPh_3)_2]$ readily reacts with CS_2 to give the thioxanthate complex



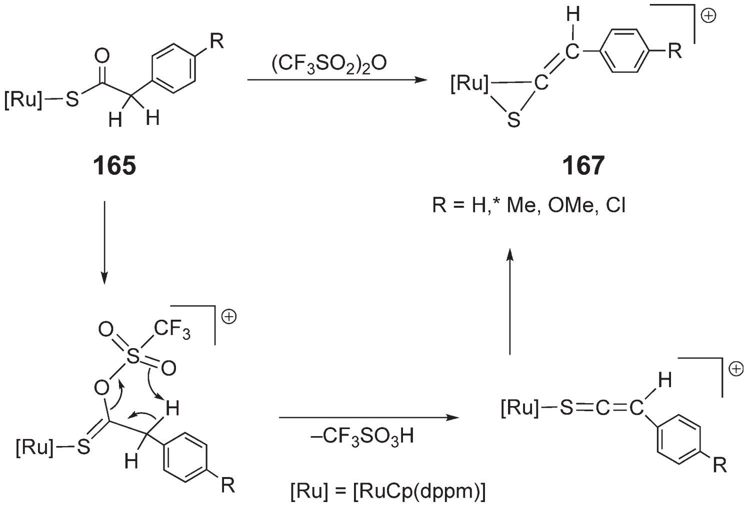
L^1 = L^2 = PPh$_3$; R = H, Me, OMe, Cl
L^{1}L^2 = dppm; R = H,* Me, OMe, Cl
L^{1}L^2 = dppe; R = H, Me, OMe, Cl
L^1 = PPh$_3$; L^2 = CO; R = H

165

R = Me, Et

166

Figure 23 Thiocarboxylate and thioester Ru(II) complexes 165 and 166.



165

167

R = H,* Me, OMe, Cl

[Ru] = [RuCp(dppm)]

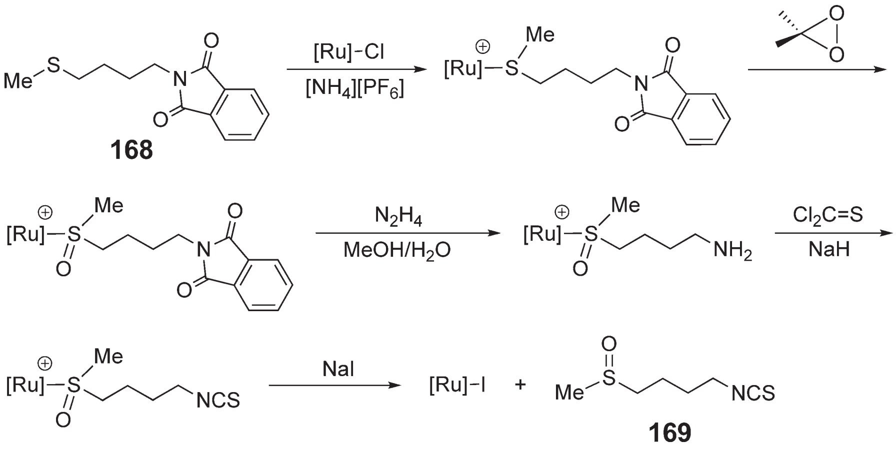
Scheme 6

[Ru{$\kappa^2(S,S)$-S$_2$CSCH$_2$CH=CH$_2$}Cp(PPh$_3$)].[238] Similarly, the dithioformate derivative [Ru{$\kappa^1(S)$-SC(=S)H}{η^5-C$_5$H$_4$(CH$_2$)$_3$NHMe$_2$}(dppm)][BF$_4$] has been prepared by reacting hydride complex [RuH{η^5-C$_5$H$_4$(CH$_2$)$_3$-NHMe$_2$}(dppm)][BF$_4$] with CS$_2$.[94] Treatment of vinylidene complex [RuCl{=C=C(H)Bu^t}Cp*(PPh$_3$)] with CS$_2$, in the presence of NaOMe, generates the alkynyl–dithiocarboxylate derivative [Ru{$\kappa^2(S,S)$-S$_2$CC≡CBu^t}Cp*(PPh$_3$)]* via insertion of CS$_2$ into the Ru–C bond of the 16-electron σ-alkynyl intermediate [Ru(C≡CBu^t)Cp*(PPh$_3$)].[282,282a]

6.14.3.3.4 Ligands containing S=O and S–S=O groups

The S-bonded sulfoxide complexes [Ru{$\kappa^1(S)$-S(=O)R^{1}R^2}Cp(L^1)(L^2)][PF$_6$] (R^{1}R^2 = MePh, MeBz, MePr^i, MeCy, EtBz, BzPr^i, C$_4$H$_8$; L^{1}L^2 = dppm, dppe, dpme, (S,S)-chiraphos or L^1 = CO, L^2 = PPh$_3$ (not all combinations)) have been obtained by reaction of the corresponding chloride precursor [RuClCp(L^1)(L^2)] with the free sulfoxide in the presence of [NH$_4$][PF$_6$], or by oxidation of the coordinated thioether ligand in complexes [Ru(SR^{1}R^2)Cp(L^1)(L^2)][PF$_6$] with dimethyldioxirane (DMD).[256,256a*] Moderate diastereoselectivities have been observed for the oxygen transfer to the chiral, racemic thioether compounds [Ru(SR^{1}R^2)Cp(CO)(PPh$_3$)][PF$_6$] (de = 8–28%) and [Ru(SR^{1}R^2)Cp(dpme)][PF$_6$] (de = 34–60%). In contrast, oxidation of complexes [Ru(SR^{1}R^2)Cp{(S,S)-chiraphos}][PF$_6$] is highly stereoselective (de = 46–98%). Such oxidation reactions have been applied to the preparation of the natural product sulforaphane 169 starting from phthalimidobutyl methyl sulfide 168 and the chloride complexes [RuClCp(P–P)] (P–P = dppe, (S,S)- or (R,R)-chiraphos) (Scheme 7).[283] The use of those precursors containing the optically pure chiraphos ligands allowed the enantioselective synthesis of the R- and S- enantiomers of sulforaphane (80% ee).

Sulfine complexes [Ru{$\kappa^2(C,S)$-O=S=CHR}Cp(L^1)(L^2)][PF$_6$] (L^1 = L^2 = PMe$_3$, R = Ph, 4-C$_6$H$_4$Cl, 4-C$_6$H$_4$OMe; L^{1}L^2 = dppm, R = Ph, 4-C$_6$H$_4$Cl, 3-C$_6$H$_4$F) are accessible by oxidation of thioaldehyde derivatives

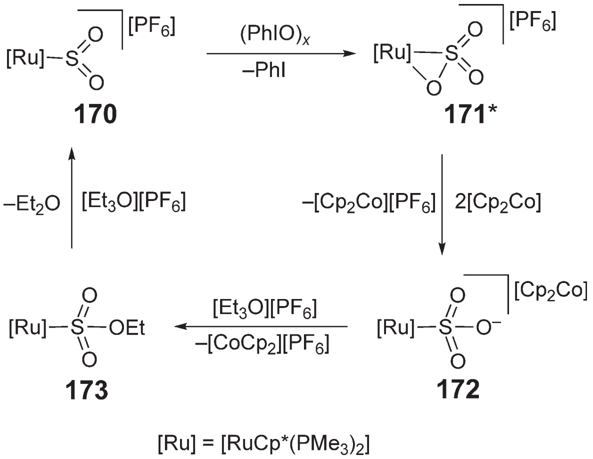


Scheme 7

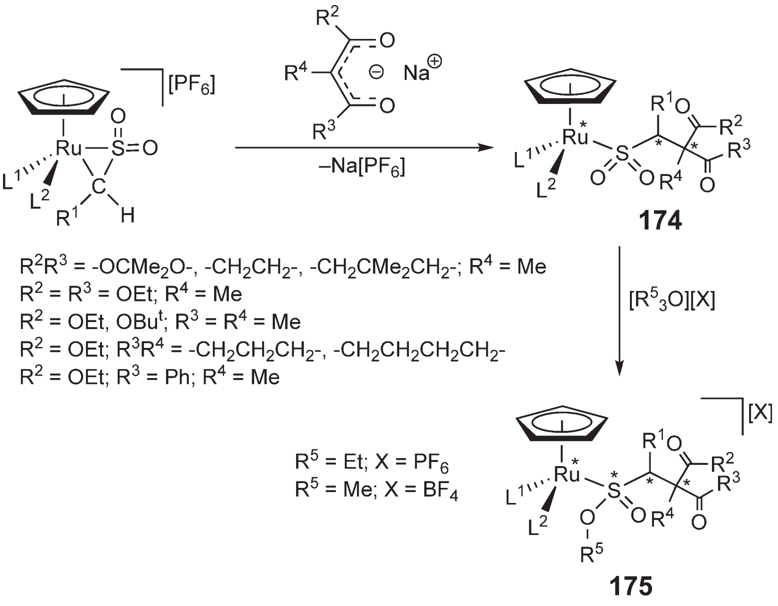
$[\mathrm{Ru}\{\kappa^1(S)\text{-S}{=}\mathrm{CHR}\}\mathrm{Cp}(\mathrm{L}^1)(\mathrm{L}^2)][\mathrm{PF}_6]$ with 2-tosyl-3-phenyloxaziridine or magnesium monoperoxyphthalate.[234] Treatment of the silylated sulfinato complex $[\mathrm{Ru}\{\kappa^1(S)\text{-S}({=}\mathrm{O})_2\mathrm{CH}_2\mathrm{SiMe}_3\}\mathrm{Cp}(\mathrm{PMe}_3)_2]$ with $[\mathrm{Et}_3\mathrm{O}][\mathrm{PF}_6]$ leads to the parent sulfine complex $[\mathrm{Ru}\{\kappa^2(C,S)\text{-O}{=}\mathrm{S}{=}\mathrm{CH}_2\}\mathrm{Cp}(\mathrm{PMe}_3)_2][\mathrm{PF}_6]$, via initial *O*-alkylation and subsequent elimination of $\mathrm{EtOSiMe}_3$.[234] The synthesis of sulfine derivatives by methylene addition to a sulfur monoxide complex is also possible. Thus, $[\mathrm{Ru}\{\kappa^2(C,S)\text{-O}{=}\mathrm{S}{=}\mathrm{CH}_2\}\mathrm{Cp}^*(\mathrm{PMe}_3)_2][\mathrm{PF}_6]$ was obtained by the addition of diazomethane to $[\mathrm{Ru}\{\kappa^1(S)\text{-SO}\}\mathrm{Cp}^*(\mathrm{PMe}_3)_2][\mathrm{PF}_6]$.[234]

The *S*-bonded SO_2 complexes $[\mathrm{Ru}\{\kappa^1(S)\text{-SO}_2\}(\eta^5\text{-C}_5\mathrm{R}_5)(\mathrm{L}^1)(\mathrm{L}^2)][\mathrm{PF}_6]$ ($\mathrm{R}=\mathrm{Me}$, $\mathrm{L}^1=\mathrm{L}^2=\mathrm{PMe}_3$; $\mathrm{R}=\mathrm{Me}$, $\mathrm{L}^1\mathrm{L}^2=$ dmpm, (*S*,*S*)-chiraphos; $\mathrm{R}=\mathrm{H}$, $\mathrm{L}^1\mathrm{L}^2=$ dppm) have been obtained by exchange of the labile acetonitrile ligand in complexes $[\mathrm{Ru}(\eta^5\text{-C}_5\mathrm{R}_5)(\mathrm{NCMe})(\mathrm{L}^1)(\mathrm{L}^2)][\mathrm{PF}_6]$ for SO_2.[136,284] The closely related chiral salts $[\mathrm{Ru}\{\kappa^1(S)\text{-SO}_2\}\mathrm{Cp}\{(S,S)\text{-chiraphos}\}][\mathrm{PF}_6]^*$ and $[\mathrm{Ru}\{\kappa^1(S)\text{-SO}_2\}\{\eta^5\text{-C}_5\mathrm{H}_4(\mathrm{C}_{10}\mathrm{H}_{19})\}(\mathrm{dpme})][\mathrm{PF}_6]$ ($\mathrm{C}_{10}\mathrm{H}_{19}=(+)$-neomenthyl) were prepared by reacting the corresponding chloride precursor with SO_2 in the presence of $[\mathrm{NH}_4][\mathrm{PF}_6]$.[285] Treatment of $[\mathrm{RuCp}^*\{\kappa^2(P,O)\text{-P}{\sim}\mathrm{O}\}\{\kappa^1(P)\text{-P}{\sim}\mathrm{O}\}][\mathrm{BPh}_4]$, containing the hemilabile *P*,*O*-donor ligand (1,3-dioxan-2-ylmethyl)diphenylphosphine, with SO_2 generates $[\mathrm{Ru}\{\kappa^1(S)\text{-SO}_2\}\mathrm{Cp}^*\{\kappa^1(P)\text{-P}{\sim}\mathrm{O}\}_2][\mathrm{BPh}_4]$ via Ru–P–O chelate ring opening.[88] Remarkably, treatment of complex $[\mathrm{Ru}\{\kappa^1(S)\text{-SO}_2\}\mathrm{Cp}^*(\mathrm{PMe}_3)_2][\mathrm{PF}_6]$ **170** with iodosobenzene generates **171**,* the first sulfur trioxide complex reported in the literature (Scheme 8).[286] Cobaltocene reduces **171** to the sulfito complex **172** which can be converted back into the starting material **170** by double alkylation via the ethylsulfito derivative **173**.

Insertion of SO_2 into the Ru–$\mathrm{C}_{\mathrm{alkyl}}$ bond of compounds $[\mathrm{Ru}(\mathrm{R})\mathrm{Cp}^*(\mathrm{PMe}_3)_2]$ ($\mathrm{R}=\mathrm{Me}$, Bz, $\mathrm{CH}_2\text{-4-C}_6\mathrm{H}_4\mathrm{Cl}$, $\mathrm{CH}_2\mathrm{SiMe}_3$) generates the sulfinato complexes $[\mathrm{Ru}\{\kappa^1(S)\text{-S}({=}\mathrm{O})_2\mathrm{R}\}\mathrm{Cp}(\mathrm{PMe}_3)_2]$.[233,234] The related aryl–sulfinato derivative $[\mathrm{Ru}\{\kappa^1(S)\text{-S}({=}\mathrm{O})_2\text{-}p\text{-Tol}\}\mathrm{Cp}(\mathrm{PMe}_3)_2]$ has been obtained by reacting $[\mathrm{RuClCp}(\mathrm{PMe}_3)_2]$ with



Scheme 8



Scheme 9

$Na[S(=O)_2$-*p*-Tol].[233] The less electron-rich complexes $[Ru\{\kappa^1(S)\text{-}S(=O)_2R\}Cp(L^1)(L^2)]$ ($L^1L^2 = $ dppm, R = Me, Bz, Ph, CH_2-4-C_6H_4Cl, CH_2Bz, CH_2CO_2Et; $L^1 = CO$, $L^2 = PPh_3$, R = Me, Ph, Bz) have been prepared by double oxidation of the corresponding thiolato derivatives $[Ru(SR)Cp(L^1)(L^2)]$ with *m*-CPBA (*m*-CPBA = *meta*-chloroperbenzoic acid) or magnesium monoperoxyphthalate.[233,234] Alkylation of these sulfinato complexes with oxonium salts ($[Et_3O][PF_6]$ or $[Me_3O][BF_4]$) leads to cationic sulfinic acid ester complexes of general composition $[Ru\{\kappa^1(S)\text{-}S(=O)(OR^1)R^2\}Cp(L^1)(L^2)][X]$.[233]

The reaction of sulfur dioxide complexes $[Ru\{\kappa^1(S)\text{-}SO_2\}Cp(L^1)(L^2)][PF_6]$ with diazomethane or diazoethane gives sulfene derivatives $[Ru\{\kappa^2(C,S)\text{-}S(=O)_2=CHR\}Cp(L^1)(L^2)][PF_6]$ ($L^1L^2 = $ dppm, R = H, Me; $L^1L^2 = $ dpme, R = H, Me; $L^1L^2 = $ dppe, R = H; $L^1L^2 = (S,S)$-chiraphos, R = H; $L^1 = L^2 = PMe_3$, R = H).[284,285] Sulfene complex $[Ru\{\kappa^2(C,S)\text{-}S(=O)_2=CH_2\}Cp^*(PMe_3)_2][PF_6]$ is also known, being obtained by oxidation of $[Ru\{\kappa^2(C,S)\text{-}O=S=CH_2\}Cp^*(PMe_3)_2][PF_6]$ with DMD (dimethyl-dioxirane).[234] The reactivity of sulfene complexes $[Ru\{\kappa^2(C,S)\text{-}S(=O)_2=CHR\}Cp(L^1)(L^2)][PF_6]$ ($L^1L^2 = $ dppm, dppe, dpme, (S,S)-chiraphos; R = H, Me, Ph (not all combinations)) has been explored. Thus, addition reactions of various enolates derived from 1,3-diketones, *β*-oxo-esters, and 1,3-diesters lead to the neutral C–C coupling products **174** in high yields and 20–90% de (Scheme 9).[284,285]* The S=O function of the sulfinate ligands thus formed can be alkylated with $[Et_3O][PF_6]$ or $[Me_3O][BF_4]$ yielding cationic complexes **175** from which the organic fragment can be easily removed by exchange with acetonitrile.[284,285]

Complexes [Ru(SH)Cp(P–P)] react with sulfonyl chlorides RSO_2Cl to give the air sensitive thiosulfonato derivatives $[Ru\{S(SO_2R)\}Cp(P\text{–}P)]$ (P–P = dppm, R = Me, Ph, 4-C_6H_4Cl, 4-$C_6H_4NO_2$; P–P = dppe, R = Me, Ph, 4-C_6H_4Cl,* 4-$C_6H_4NO_2$) via HCl elimination.[287] The silanethiolato complexes $[Ru(SSiPr^i{}_3)Cp(L^1)(L^2)]$ readily react with SO_2 affording the highly unstable *O*-silylthiosulfito complexes $[Ru\{SS(=O)OSiPr^i{}_3\}Cp(L^1)(L^2)]$ ($L^1 = PPh_3$, $L^2 = CO$, PMe_3, $P(OMe)_3$; $L^1L^2 = $ dppe), the formal 1,2-insertion of SO_2 into the S–Si bond being unprecedented.[237] The related compounds $[Ru\{SS(=O)NHPh\}Cp(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$; $L^1L^2 = $ dppe) have been prepared by reaction of $[Ru(SH)Cp(L^1)(L^2)]$ with *N*-thionylaniline via addition of the S–H bond to the N=S double bond of PhNSO.[237]

6.14.3.3.5 Polysulfide and polysulfanide ligands

The reaction of unsaturated half-sandwich Ru(II) fragments with elemental sulfur usually generates dinuclear Ru(III) species containing a disulfide μ-$S_2{}^{2-}$ bridge (see COMC (1995)). Following this synthetic approach, the novel disulfido derivatives $[\{(\eta^5\text{-}C_5R_5)(L^1)(L^2)Ru\}_2(\mu\text{-}S_2)][BPh_4]_2$ ($L^1L^2 = $ dippe, R = H, Me; $L^1L^2 = $ dppf, R = H;* $L^1 = L^2 = PEt_3$, R = H, Me; $L^1 = PPh_3$, $L^2 = PPr^i{}_2Me$, R = H) have been readily prepared by reacting the corresponding chloride precursor $[RuCl(\eta^5\text{-}C_5R_5)(L^1)(L^2)]$ with S_8 in the presence of $Na[BPh_4]$.[103,245,246] In contrast, treatment of $[\{RuCp(CO)_2\}_2]$ with elemental selenium leads to an orange crystalline product of composition $[Ru_2Cp_2(CO)_2Se_3]$ for which two formulas have been suggested, that is, the diselenido- and monoselenido-bridged structures $[\{Cp(CO)_2Ru\}(\mu\text{-}Se)_2\{RuCpSe\}]$ and $[\{Cp(CO)_2Ru\}(\mu\text{-}Se)\{RuCpSe_2\}]$, respectively. Reaction of this dinuclear complex with acyl chlorides generates the mononuclear selenocarboxylate derivatives $[Ru\{\kappa^1(Se)\text{-}SeCOR\}Cp(CO)_2]$ (R = Ph, 3-$C_6H_4NO_2$, 4-$C_6H_4NO_2$, 4-C_6H_4COCl).[288]

The reactions of $[OsBr_2Cp^*(NO)]$ with Na_2S_4 and $[Et_4N]_2Se_6$ lead to mononuclear tetrachalcogenido complexes $[Os(E_4)Cp^*(NO)]$ (E = S, Se), whereas dinuclear products $[\{OsCp^*(NO)\}_2(\mu\text{-}E)_2]$ (E = S, Se, Te) are obtained from the reactions of $[OsBr_2Cp^*(NO)]$ with the lithium salts Li_2E. The molecular geometry of $[Os(Se_4)Cp^*(NO)]$ has been determined by an X-ray crystal structure analysis which confirms the presence of a non-planar cyclotetraselenido chelate ligand.[116]

Oxidation of the thiolate complex $[Ru(S\text{-}p\text{-}Tol)Cp(PPh_3)(CO)]$ with $[NO][BF_4]$ results in the formation of the disulfide-bridged dicationic dimer $[\{RuCp(PPh_3)(CO)\}_2\{\mu\text{-}\eta^1,\eta^1\text{-}S_2(p\text{-}Tol)_2\}][BF_4]_2$.[239] In contrast, the bulkier derivative $[Ru(SBu^t)Cp(PPh_3)(CO)]$ reacts with $[NO][BF_4]$ to yield the mononuclear disulfide complex $[Ru\{\kappa^1(S)\text{-}S_2Bu^t{}_2\}Cp(PPh_3)(CO)][BF_4]$ via cleavage of the corresponding dimeric dication $[\{RuCp(PPh_3)(CO)\}_2(\mu\text{-}\eta^1,\eta^1\text{-}S_2Bu^t{}_2)][BF_4]_2$.[239] Treatment of $[Ru(SH)Cp(PPh_3)(CO)]^*$ with the sulfur-transfer reagents RSphth (phth = phthalimido) gives mixtures containing the air-stable disulfanido and trisulfanido complexes $[Ru(SSR)Cp(PPh_3)(CO)]$ (R = p-Tol, Pr^n, Pr^{i*}) and $[Ru(SSSR)Cp(PPh_3)(CO)]$ (R = p-Tol, Pr^n,* Pr^i), respectively, which can be easily separated by column chromatography.[289]

6.14.3.4 Complexes Containing B-, Al-, Ga-, Si-, Ge-, and Sn-donor Ligands

Boryl–ruthenium(II) complexes $[Ru(BR_2)Cp^*(CO)_2]$ (BR_2 = B-1,2-$O_2C_2Me_4$, B-1,2-$O_2C_6H_2$-3,5-Me_2, B-1,2-$S_2C_6H_2$-3,5-Me_2, BCy_2, BMe_2, 9-borabicyclo[3.3.1]nonyl) have been synthesized by reacting the potassium salt $K[RuCp^*(CO)_2]$ with the appropriate chloroborane $ClBR_2$.[290,290a] DFT analysis of the bonding in the model complex $[Ru(B\text{-}1,2\text{-}O_2C_2H_2)Cp(CO)_2]$ concludes that covalent terms are roughly twice as important to the overall metal–boryl interaction than are ionic terms, with σ-donation from the boryl unit predominating over π-backdonation.[291]

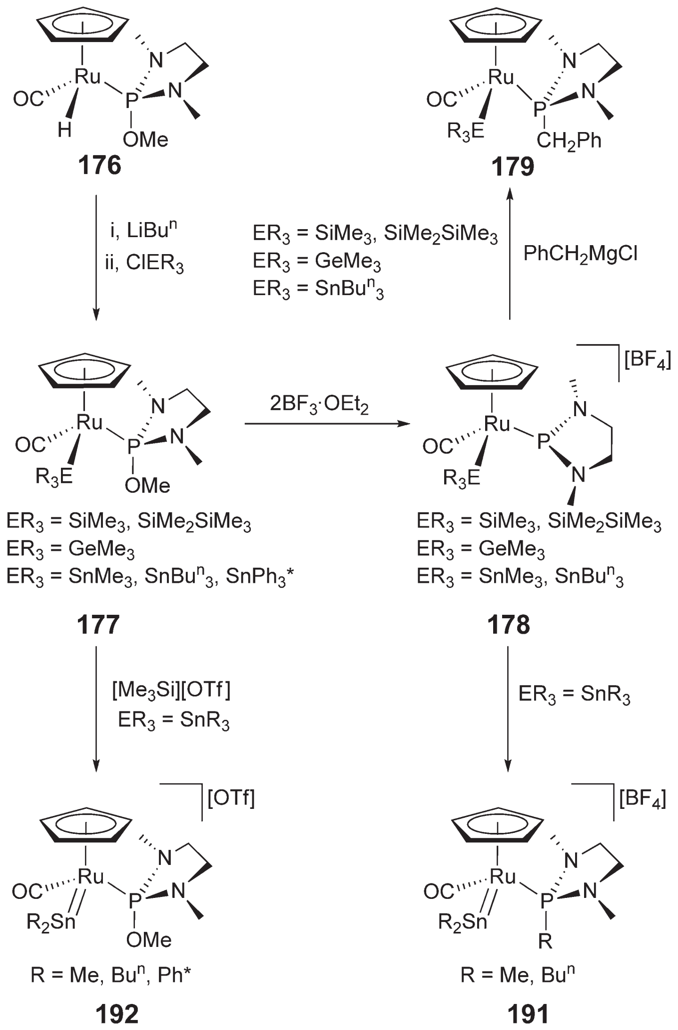
Aminodihaloboranes $X_2B{=}NMe_2$ react with $Na[RuCp(CO)_2]$ to afford the boryl derivatives $[Ru\{BX({=}NMe_2)\}Cp(CO)_2]$ (X = Cl, Br).[292] In contrast, treatment of $Na[RuCp(CO)_2]$ with 2 equiv. of $Cl_2B{=}N(SiMe_3)_2$ generates $[Ru\{BCl({=}N(SiMe_3)BCl\{{=}N(SiMe_3)_2\})\}Cp(CO)_2]^*$ as a result of the coupling of two $Cl_2B{=}N(SiMe_3)_2$ units.[292] The sodium salt $Na[RuCp(CO)_2]$ also reacts with $BrB({=}NMe_2)BBr({=}NMe_2)$ to afford the structurally characterized diboranyl ruthenium(II) complex $[Ru\{B({=}NMe_2)BBr({=}NMe_2)\}Cp(CO)_2]$.*[293] The trimethylphosphine-complexed primary boryl derivative $[Ru(BH_2\cdot PMe_3)Cp^*(CO)_2]^*$ is also known.[294]

The mononuclear alane–ruthenium(II) complex $[Ru(AlCl\{\kappa^2(C,N)\text{-}(CH_2)_3NMe_2\})Cp(CO)_2]$ has been synthesized by the reaction of $K[RuCp(CO)_2]$ with $[AlCl_2\{\kappa^2(C,N)\text{-}(CH_2)_3NMe_2\}]$.[295] In a similar way, treatment of the anionic complex $K[RuCp^*(bipy)]$, obtained by reduction of $[RuClCp^*(bipy)]$ with potassium graphite (KC_8), with $[GaCl_2(Trip)(THF)]$ (Trip = 2,4,6-triisopropylphenyl) generates the neutral gallyl derivative $[Ru\{GaCl(Trip)\}Cp^*(bipy)]$.[296]

Silyl–Ru(II) and Os(II) complexes $[M(SiX_3)(\eta^5\text{-}C_5R_5)(CO)_2]$ (M = Ru, R = H, SiX_3 = $SiHCl_2$, SiHCl(p-Tol), $SiCl_2SiCl_3$; M = Ru, R = Me, SiX_3 = $SiMe_3$, $SiH(p\text{-}Tol)_2$, $SiH(o\text{-}Tol)_2$, $SiHMe_2$, $SiHCl_2$, $SiClMe_2$, $SiCl_2Me$, $SiCl_3$, $SiCl_2SiCl_3$, $SiMe_2SiMe_3$; M = Os, R = H, SiX_3 = SiH_2Bu^t, $SiHClBu^t$; M = Os, R = Me, SiX_3 = $SiMe_3$, SiH_2Bu^t, $SiMe_2SiMe_3$, $SiClMe_2$) have been synthesized by reacting the appropriate chlorosilane $ClSiX_3$ with the metallating reagents $A[M(\eta^5\text{-}C_5R_5)(CO)_2]$ (M = Ru, R = H, A = Na; M = Ru, R = Me, A = Li, Na or K; M = Os, R = H, Me, A = Na).[297–301] The chlorosilyl derivatives $[Ru(SiHCl_2)(\eta^5\text{-}C_5R_5)(CO)_2]$ (R = H, Me) and $[Ru\{SiHCl(p\text{-}Tol)\}Cp(CO)_2]$ undergo Cl/H exchange upon treatment with $Li[AlH_4]$ to give $[Ru(SiH_3)(\eta^5\text{-}C_5R_5)(CO)_2]$ (R = H, Me) and $[Ru\{SiH_2(p\text{-}Tol)\}Cp(CO)_2]$, respectively.[299–300] Using the same synthetic procedure, the ruthenapentachlorodisilane complex $[Ru(SiCl_2SiCl_3)Cp(CO)_2]$ has been converted into its pentahydrido analog $[Ru(SiH_2SiH_3)Cp(CO)_2]$ which undergoes selective chlorination with CCl_4 or $CHCl_3$ at the α-silicon to generate $[Ru(SiCl_2SiH_3)Cp(CO)_2]$.[301] Oxofunctionalization of $[Ru(SiHR_2)Cp^*(CO)_2]$ (R = Me, o-Tol) and $[Ru\{SiH_2(p\text{-}Tol)\}Cp(CO)_2]$ with DMD affords the ruthena-silanols $[Ru\{SiR_2(OH)\}Cp^*(CO)_2]$ (R = Me, o-Tol*) and $[Ru\{Si(p\text{-}Tol)(OH)_2\}Cp(CO)_2]$, respectively.[300] The related disilanetriol complex $[Ru\{SiCl_2Si(OH)_3\}Cp^*(CO)_2]$ has been obtained by treatment of $[Ru(SiCl_2SiCl_3)Cp^*(CO)_2]$ with water.[302] Base-assisted condensation of $[Ru\{Si(o\text{-}Tol)_2(OH)\}Cp^*(CO)_2]$ and $[Ru\{SiCl_2Si(OH)_3\}Cp^*(CO)_2]$ with chlorodimethylsilane leads to the siloxane derivatives $[Ru\{Si(o\text{-}Tol)_2(OSiHMe_2)\}Cp^*(CO)_2]$ and $[Ru\{SiCl_2Si(OSiHMe_2)_3\}Cp^*(CO)_2]$, respectively.[300,302] The reactivity of the sodium salt $Na[RuCp(CO)_2]$ toward $ClSiMe_2SiMe_2Cl$ and $ClSiMe_2SiR_2SiMe_2Cl$ (R = Me, Pr^i) has also been reported leading, in the presence of py/MeOH, to the formation of complexes [Ru{SiMe$_2$SiMe$_2$(OMe)}Cp(CO)$_2$] and [Ru{SiMe$_2$SiR$_2$SiMe$_2$(OMe)}Cp(CO)$_2$] (R = Me, Pr^i), respectively.[303,304]

Hydride complexes [RuHCp(L)$_2$] readily react with a variety of chlorosilanes to produce equimolar mixtures of the ruthenium(II)–silyl derivatives [Ru(SiR$_3$)CpL$_2$] (L = PMe$_3$, SiR$_3$ = SiCl$_3$,* SiHCl$_2$, SiH$_2$Cl, SiCl$_2$Me,* SiHClMe, SiClMe$_2$, SiCl$_2$Ph;* L = PMe$_2$Ph, SiR$_3$ = SiCl$_3$,* SiHCl$_2$, SiH$_2$Cl, SiHClMe; L = PMePh$_2$, SiR$_3$ = SiHCl$_2$, SiH$_2$Cl) and the ruthenium(IV) dihydrides [RuH$_2$CpL$_2$]Cl (L = PMe$_3$, PMe$_2$Ph, PMePh$_2$).[305–307] Formation of the dihydride side-products, which result from the concomitant protonation of the starting materials [RuHCpL$_2$] by the HCl eliminated in the formation of [Ru(SiR$_3$)CpL$_2$], can be in some cases avoided by performing these reactions in the presence of base (Et$_3$N or DBU) (DBU = 1,8-diazabicyclo [5.4.0]undec-7-ene).[305,305a,307] Remarkably, protonation of [Ru(SiCl$_3$)Cp(PMe$_3$)$_2$] with [H(OEt$_2$)$_2$][BAr$^F{}_4$] generates the cationic complex [Ru{κ^2(*Si*,*H*)-SiHCl$_3$}Cp(PMe$_3$)$_2$][BAr$^F{}_4$]* which shows an agostic interaction between the Si–H bond and the ruthenium center.[305,305a,308] The hydrido complex **176** has been used as starting material for the preparation of silyl–ruthenium(II) derivatives of the type **177–179** (Scheme 10).[309] The synthesis and structural characterization of [Ru(SiMe$_2$Ph)H$_2$Cp*(Ppyl$_3$)]* (Ppyl$_3$ = tripyrrolylphosphine), obtained by reacting [RuH$_3$Cp*(Ppyl$_3$)] with HSiMe$_2$Ph, has also been reported.[310]

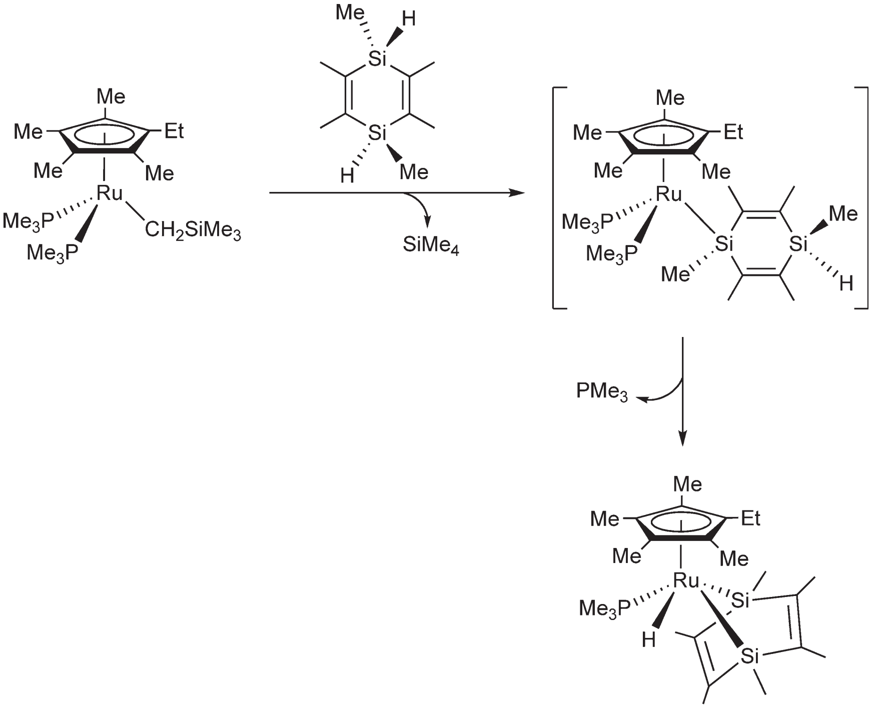
The reaction of ruthenium(II)–alkyl complexes of general formula [Ru(Me)(η^5-C$_5$R$_5$)(PR$_3$)$_2$] or [Ru(CH$_2$SiMe$_3$)(η^5-C$_5$R$_5$)(PR$_3$)$_2$] with silanes HSiR$_3$ is a well-known route for the preparation of silyl derivatives [Ru(SiR$_3$)(η^5-C$_5$R$_5$)(PR$_3$)$_2$] (see COMC (1995)). This process can be viewed as proceeding through the following four steps: (i) thermal dissociation of PR$_3$, (ii) oxidative addition of HSiR$_3$ to generate an 18-electron Ru(IV) intermediate,



Scheme 10

(iii) reductive elimination of CH_4 or $SiMe_4$, and (iv) recoordination of PR_3. Following this synthetic approach, the novel silyl complexes $[Ru(SiR_3)Cp(PPh_3)_2]$ ($SiR_3 = SiMe_2$(*p*-Tol), $SiEt_3$) and $[Ru(SiR_3)Cp(PMePh_2)_2]$ ($SiR_3 = SiCl_3$, $SiCl_2Me$) have been obtained starting from $[Ru(Me)Cp(PR_3)_2]$ ($L = PMe_3$, $PMePh_2$) and the appropriate silane.[307,311,312] The related derivatives $[Ru(SiR_3)Cp(PMe_3)_2]$ ($SiR_3 = SiCl_3$, $SiCl_2Me$, $SiCl_2Cp^*$,* $SiClMe_2$, $SiEt_3$) and $[Ru(SiR_3)Cp^*(PMe_3)_2]$ ($SiR_3 = SiCl_3$, $SiClPr^i{}_2$, $SiCl(SCy)_2$, $SiCl(SMes)_2$, $SiMe_2$(S-*p*-Tol), $Si(SPh)_3$, $Si(SEt)_3$, Si(S-2-Naphthyl)$_3$, Si(S-*p*-Tol)$_3$,* $Si(NMe_2)_3$, Si(O-*o*-Tol)$_3$) have been synthesized using $[Ru(CH_2SiMe_3)(\eta^5\text{-}C_5R_5)(PMe_3)_2]$ (R = H, Me) as precursors.[312–316] Complexes $[Ru\{Si(SR)_3\}Cp^*(PMe_3)_2]$ (R = Ph, Et, *p*-Tol), [Ru{Si(O-*p*-Tol)$_3$}Cp*(PMe$_3$)$_2$], and [Ru{SiMe$_2$(S-*p*-Tol)}Cp*(PMe$_3$)$_2$] react with 1 equiv. of $[Me_3Si][OTf]$ to generate the triflatosilyl derivatives $[Ru\{Si(SR)_2(OTf)\}Cp^*(PMe_3)_2]$ (R = Ph, Et, *p*-Tol*), [Ru{Si(O-*p*-Tol)$_2$(OTf)}Cp*(PMe$_3$)$_2$], and $[Ru\{SiMe_2(OTf)\}Cp^*(PMe_3)_2]$, respectively.[314–316] Extended reaction of [Ru{Si(S-*p*-Tol)$_3$}Cp*(PMe$_3$)$_2$] with an excess of $[Me_3Si][OTf]$ results in the exchange of two thiolate groups affording the bis(triflato) complex [Ru{Si(S-*p*-Tol)(OTf)$_2$}Cp*(PMe$_3$)$_2$]*.[314] Treatment of this bis(triflato) derivative with the chelating dithiolate reagents $LiSCH_2CH_2SLi$ and $Li_2[1,2,4\text{-}S_2C_6H_3Me]$ generates [Ru{Si(S-*p*-Tol)(*cyclo*-SCH$_2$CH$_2$S)}Cp*(PMe$_3$)$_2$] and [Ru{Si(S-*p*-Tol)(*cyclo*-1,2,4-S$_2$C$_6$H$_3$Me)}Cp*(PMe$_3$)$_2$], respectively.[315,315a] The synthesis and structural characterization of the metallodisilanorbornadiene complex **180*** has also been described (Scheme 11).[317]

In contrast to the case of ruthenium, treatment of the alkyl–Os(II) complex $[Os(CH_2SiMe_3)Cp^*(PMe_3)_2]$ with an excess of $HSiClR_2$ (R = Me, Ph) leads to a mixture of $[Os(SiClR_2)Cp^*(PMe_3)_2]$ and the corresponding bis(silyl)hydride derivatives $[Os(SiClR_2)_2HCp^*(PMe_3)]$.[173] Remarkably, when the more electronegative silanes $HSiCl_2Me$ and $HSiCl_3$, or the bulkier $HSiClPr^i{}_2$, are used, the second Si–H oxidative addition is disfavored allowing the selective formation of $[Os(SiCl_2Me)Cp^*(PMe_3)_2]$, $[Os(SiCl_3)Cp^*(PMe_3)_2]$, and $[Os(SiClPr^i{}_2)Cp^*(PMe_3)_2]^*$.[173,318,318a] Complexes $[Os(SiClR_2)Cp^*(PMe_3)_2]$ can be easily transformed into the triflatosilyl derivatives $[Os\{SiR_2(OTf)\}Cp^*(PMe_3)_2]$ (R = Me,* Pr^{i*}) by reaction with $[Me_3Si][OTf]$.[173,318,318a] The reactivity of the CpOs(II) complexes $[Os(CH_2SiMe_3)Cp(PR_3)_2]$ ($PR_3 = PMe_3$, PPh_3) toward $HSiClR_2$ (R = Me, Ph) has also been explored leading to the selective formation of $[Os(SiClPh_2)Cp(PMe_3)_2]$ and $[Os(SiClR_2)_2HCp(PPh_3)]$ (R = Me, Ph).[173] The different behavior observed has been explained on the basis of the higher strength of the Os–PMe_3 versus Os–PPh_3 bond.



180*

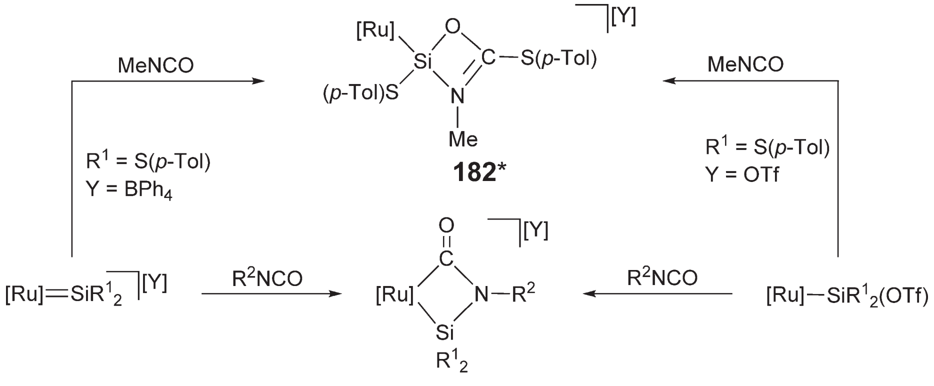
Scheme 11

The 16-electron half-sandwich Os(II) complex $[\mathrm{OsBrCp^*(PPr^i_3)}]$ readily undergoes oxidative addition of silanes $\mathrm{HSiR_3}$ to generate the 18-electron (silyl)hydride–Os(IV) derivatives $[\mathrm{Os(SiR_3)HBrCp^*(PPr^i_3)}]$ ($\mathrm{SiR_3 = SiHMe_2}$,* $\mathrm{SiHPh_2}$,* $\mathrm{SiH_2Ph}$,* $\mathrm{SiH_2(C_6F_5)}$,* $\mathrm{SiH_2Mes}$, $\mathrm{SiH_2(2,4,6\text{-}C_6H_2Pr^i_3)}$, $\mathrm{SiH_2(2,6\text{-}C_6H_3Pr^i_2)}$, $\mathrm{SiH_2(Hex^n)}$, $\mathrm{SiH_2Si(SiMe_3)_3}$, $\mathrm{SiH_2SiPh_3}$,* $\mathrm{SiH_3}$).[78,319,320] The complex $[\mathrm{Os(SiHPh_2)HBrCp^*(PPr^i_3)}]$ can be transformed into $[\mathrm{Os\{SiPh_2(OTf)\}H_2Cp^*(PPr^i_3)}]^*$ upon treatment with Ag[OTf] via intermediate formation of the silylene species $[\mathrm{Os\{{=}SiPh_2\}H_2Cp^*(PPr^i_3)}][\mathrm{OTf}]$.[319] The complex $[\mathrm{OsClCp(PPr^i_3)_2}]$ also undergoes the oxidative addition of silanes $\mathrm{HSiR_3}$ to yield the related (silyl)hydride derivatives $[\mathrm{Os(SiR_3)HClCp(PPr^i_3)}]$ ($\mathrm{SiR_3 = SiEt_3}$, $\mathrm{SiPh_3}$, $\mathrm{SiMe_2CH_2CH{=}CH_2}$, $\mathrm{SiHPh_2}$,* $\mathrm{SiH_2Ph}$), via initial release of one $\mathrm{PPr^i_3}$ ligand.[321] Treatment of $[\mathrm{Os(SiPh_3)HClCp(PPr^i_3)}]$ with LiR reagents results in the formation of the Cp-functionalized dihydride derivatives $[\mathrm{Os(SiPh_3)H_2(\eta^5\text{-}C_5H_4R)(PPr^i_3)}]$ ($\mathrm{R = Bu^s}$, $\mathrm{NEt_2}$, $\mathrm{N(CH_2CH{=}CH_2)_2}$, $\mathrm{PPh_2}$) along with minor amounts of aryl orthometallated side-products (see Chapter 6.15).[322] This reaction involves the initial formation of unstable intermediates $[\mathrm{Os(SiPh_3)HRCp(PPr^i_3)}]$ which undergo Cp–H/R exchange.[322] The hydrido–silyl–ruthenium(II) derivative $[\mathrm{Ru(SiPh_3)HCp^*(NO)}]$ is also known, being obtained by reacting the (η^2-toluene)–Ru(0) complex $[\mathrm{RuCp^*(\eta^2\text{-}C_6H_5Me)(NO)}]$ with triphenylsilane.[112]

Triflatosilyl–Ru(II) and Os(II) complexes of general composition $[\mathrm{M\{SiR_2(OTf)\}Cp^*(PMe_3)_2}]$ extensively dissociate in acetonitrile solution existing as the base-stabilized silylene adducts $[\mathrm{M\{SiR_2(NCMe)\}Cp^*(PMe_3)_2}][\mathrm{OTf}]$.[173,314,323] In accord with this behavior, the ruthenium complexes $[\mathrm{Ru\{SiR_2(NCMe)\}Cp^*(PMe_3)_2}][\mathrm{BPh_4}]$ (R = Me,* Ph, S(p-Tol),* O(p-Tol)) have been isolated upon treatment of these acetonitrile solutions with $\mathrm{Na[BPh_4]}$.[314] In addition, base-free silylene complexes $[\mathrm{M({=}SiR_2)Cp^*(PMe_3)_2}][\mathrm{Y}]$ (M = Ru, R = Me,* Ph, $\mathrm{Pr^i}$, SPh, $\mathrm{Y = B(C_6F_5)_4}$; M = Ru, R = SEt, SCy, S(p-Tol), $\mathrm{Y = BPh_4}$; M = Os, R = Me,* $\mathrm{Pr^i}$,* $\mathrm{Y = B(C_6F_5)_4}$) could be prepared by treatment of the appropriate silyl derivative $[\mathrm{M(SiR_2X)Cp^*(PMe_3)_2}]$ (X = OTf, Cl) with $\mathrm{Li[B(C_6F_5)_4]}$ or $\mathrm{Na[BPh_4]}$ in a non-coordinating solvent.[315–316,318,318a] In contrast to the case of ruthenium, the silylene–Os(II) derivatives $[\mathrm{Os({=}SiR_2)Cp^*(PMe_3)_2}][\mathrm{B(C_6F_5)_4}]$ (R = Me, $\mathrm{Pr^i}$) are readily oxidized by chlorocarbons, via a radical pathway, to form highly unstable Os(III) chlorosilyl species $[\mathrm{Os(SiClR_2)Cp^*(PMe_3)_2}][\mathrm{B(C_6F_5)_4}]$.[318,318a]

The reactivity of complexes $[\mathrm{Ru({=}SiR_2)Cp^*(PMe_3)_2}]^+$ has been explored. Thus, $[\mathrm{Ru({=}SiMe_2)Cp^*(PMe_3)_2}][\mathrm{B(C_6F_5)_4}]$ readily reacts with Lewis bases such as phosphines and ylides to afford the base-stabilized silylene derivatives $[\mathrm{Ru\{SiMe_2(PR_3)\}Cp^*(PMe_3)_2}][\mathrm{B(C_6F_5)_4}]$ (R = Me, Ph) and $[\mathrm{Ru\{SiMe_2(CH_2PPh_3)\}Cp^*(PMe_3)_2}][\mathrm{B(C_6F_5)_4}]^*$, respectively.[315,315a] This compound also reacts with methyl or phenyl isocyanate to generate the [2 + 2]-cycloaddition products **181** (Scheme 12). Analogous triflate salts have been prepared starting directly from the silyl derivative $[\mathrm{Ru\{SiPh_2(OTf)\}Cp^*(PMe_3)_2}]$ and the appropriate isocyanate.[324] In contrast to these results, treatment of $[\mathrm{Ru\{{=}Si(S\text{-}\mathit{p}\text{-}Tol)_2\}Cp^*(PMe_3)_2}][\mathrm{BPh_4}]$ or $[\mathrm{Ru\{Si(S\text{-}\mathit{p}\text{-}Tol)_2(OTf)\}Cp^*(PMe_3)_2}]$ with methyl isocyanate generates the 1,2-dipolar addition product **182** as a result of the insertion of the isocyanate into an Si–S bond.[324]

Treatment of compounds $[\mathrm{Os(SiH_2R)HBrCp^*(PPr^i_3)}]$ with $\mathrm{Li[B(C_6F_5)_4]}$ generates the stable dihydride–osmium(IV) silylenes $[\mathrm{Os({=}SiHR)H_2Cp^*(PPr^i_3)}][\mathrm{B(C_6F_5)_4}]$ (R = H, $\mathrm{C_6F_5}$, $\mathrm{2,4\text{-}C_6H_3Pr^i_2}$, $\mathrm{2,4,6\text{-}C_6H_2Pr^i_3}$, $\mathrm{Si(SiMe_3)_3}$)



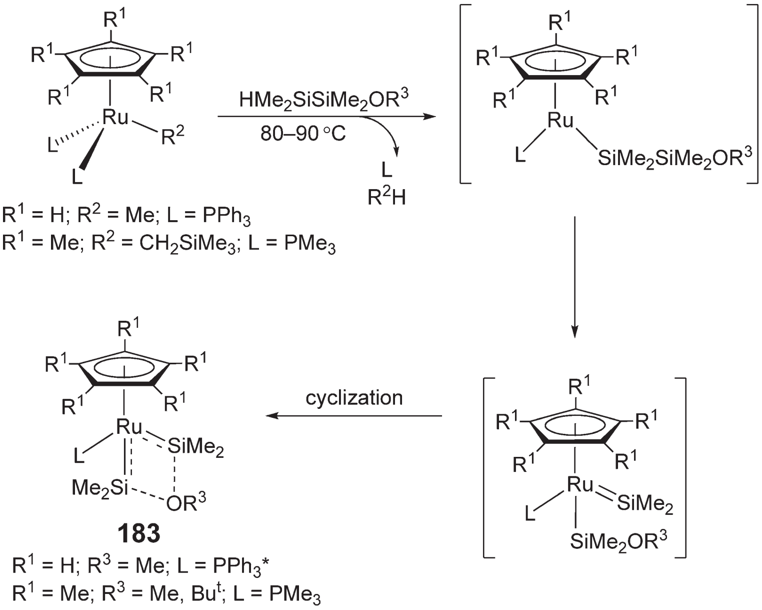
$\mathrm{R^1 = Me}$; $\mathrm{R^2 = Me, Ph}$; $\mathrm{Y = B(C_6F_5)_4}$
$\mathrm{R^1 = Ph}$; $\mathrm{R^2 = Me,^*\ 4\text{-}C_6H_4Cl,\ 4\text{-}C_6H_4OMe}$; Y = OTf
$[\mathrm{Ru}] = [\mathrm{RuCp^*(PMe_3)_2}]$

Scheme 12

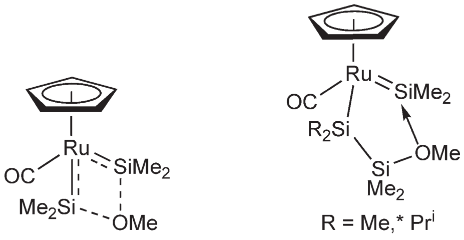
via abstraction of the bromide ligand followed by 1,2-H migration from silicon to the metal center. The reaction of $[Os\{SiH_2(SiPh_3)\}HBrCp^*(PPr^i_3)]$ with $Li[B(C_6F_5)_4]$ also generates the corresponding silylene $[Os\{{=}SiH(SiPh_3)\}H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$ which readily rearranges into $[Os\{{=}SiPh(SiPh_2H)\}H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$ via H/Ph exchange. The complex $[Os\{{=}SiH(SiPh_3)\}H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$ can be trapped as the base-stabilized silylene adduct $[Os\{SiH(SiPh_3)(DMAP)\}H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$ by performing the reaction in the presence of 4-(dimethylamino)pyridine (DMAP).[319] Treatment of $[Os\{{=}SiH(2,4,6\text{-}C_6H_2Pr^i_3)\}H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$ and its ruthenium counterpart $[Ru({=}SiHPh)H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$, obtained from $[Ru(SiH_2Ph)HClCp^*(PPr^i_3)]$ and $Li[B(C_6F_5)_4]$, with 1-hexene results in the formation of $[Os\{{=}Si(Hex^n)(2,4,6\text{-}C_6H_2Pr^i_3)\}H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$ and $[Ru\{{=}Si(Hex^n)Ph\}H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$, respectively.[320] On the basis of this observation, a catalytic hydrosilylation of alkenes using $[Ru({=}SiHPh)H_2Cp^*(PPr^i_3)][B(C_6F_5)_4]$ has been developed.[320,325]

Alkoxy-bridged bis(silylene)–ruthenium complexes **183** have been synthesized by treatment of $[RuMeCp(PPh_3)_2]$ or $[Ru(CH_2SiMe_3)Cp^*(PMe_3)_2]$ with the appropriate disilane $HMe_2SiSiMe_2OR^3$ under thermal conditions (Scheme 13).[311,326] The related carbonyl complex **184*** (Figure 24) is also known, being obtained by photolytic decarbonylation of $[Ru(SiMe_2SiMe_2OMe)Cp(CO)_2]$.[303] In a similar way, photolysis of the 3-methoxytrisilanyl derivatives $[Ru(SiMe_2SiR_2SiMe_2OMe)Cp(CO)_2]$ ($R = Me, Pr^i$) generates the methoxy-stabilized disilanyl–silylene complexes **185** (Figure 24).[304]

The reaction of the bis(silylene)–ruthenium complex $[Ru\{\kappa^2(Si,Si)\text{-}(SiMe_2)_2OMe\}Cp(PPh_3)]$ **183** with methanol affords the hydrido–bis(silyl)–Ru(IV) derivative **186** which, in the presence of a large excess of methanol, is slowly

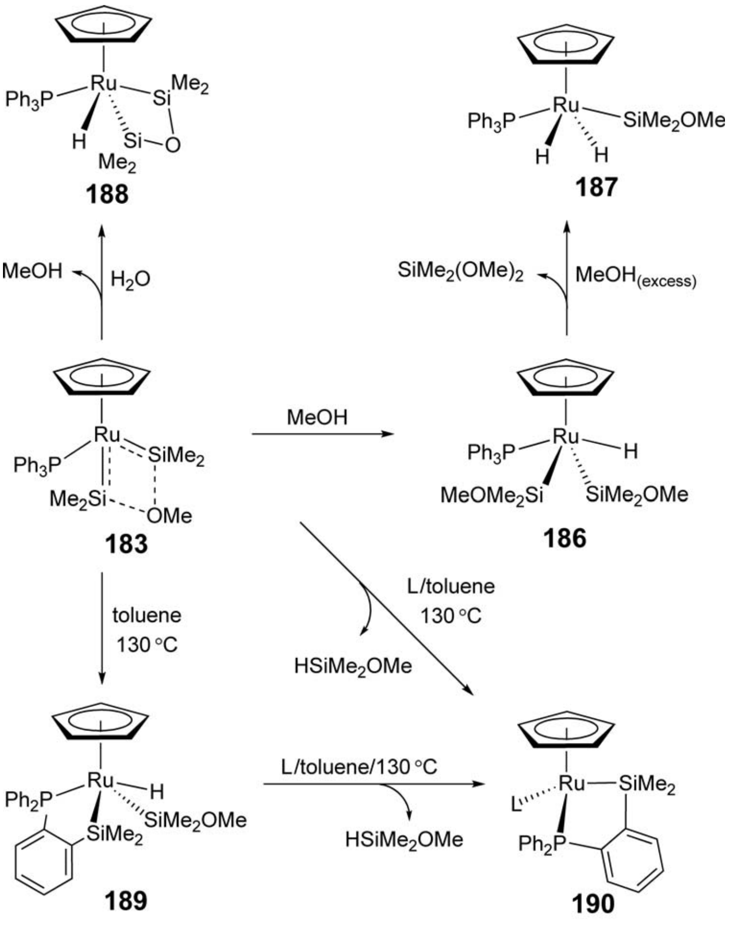


Scheme 13



184* **185**

Figure 24 Structure of the CpRu complexes **184** and **185**.



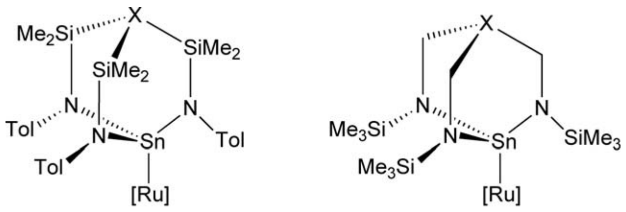
L = PPh_3, PMe_3,* PEt_3, $P(OMe)_3$, $CNBu^t$

Scheme 14

converted into the dihydride species **187** (Scheme 14).[327] In contrast, the reaction of **183** with water yields the hydrido–bis(silyl)–Ru(IV) metallacycle **188**.[327] Intramolecular aromatic C–H activations, to generate complexes **189** and **190**, have also been reported starting from **183** (Scheme 14).[328]

Germyl–Ru(II) and Os(II) complexes $[M(GeR_3)Cp^*(CO)_2]$ (M = Ru, $GeR_3 = GePh_2Cl$; M = Os, $GeR_3 = GeMe_3$) have been obtained by reaction of the lithium salts $Li[MCp^*(CO)_2]$ with the appropriate chloride derivatives $ClGeR_3$.[297,298] Oxidative addition of germanes $HGeR_3$ to $[OsClCp(PPr^i_3)_2]$ generates the hydride–germyl–Os(IV) complexes $[Os(GeR_3)HClCp(PPr^i_3)]$ ($GeR_3 = GeEt_3$, $GePh_3$, $GeHPh_2$).[321] Treatment of $[Os(GePh_3)HClCp(PPr^i_3)]$ with LiR reagents leads to the Cp-substituted dihydride derivatives $[Os(GePh_3)H_2(\eta^5\text{-}C_5H_4R)(PPr^i_3)]$ (R = Me, Bu^n, Bu^s, NEt_2, $N(CH_2CH{=}CH_2)_2$,* PPh_2).[322] The synthesis of germyl–Ru complexes **177–179** (see Scheme 10) has also been reported.[309]

Heterobimetallic Ru–Sn complexes $[Ru(SnX_3)(\eta^5\text{-}C_5R_5)(L^1)(L^2)]$ (X = F, R = H, $L^1 = L^2 = PPh_3$,* $PMePh_2$; X = F, R = H, L^1L^2 = dppe; X = Br, R = H, $L^1 = L^2 = PPh_3$,* $PMePh_2$; X = Br, R = H, L^1L^2 = dppe;* X = Cl, R = H, $L^1 = L^2 = PPh_3$,* $PMePh_2$; X = Cl, R = H, L^1L^2 = dppe, dippe, dppf; X = Cl, R = Me, L^1 = CO, $L^2 = PEt_3$, $PMePr^i_2$; X = Cl, R = Me, L^1L^2 = dippe, COD*) have been synthesized by insertion of SnX_2 into the Ru–X bond of the appropriate halide precursor $[RuX(\eta^5\text{-}C_5R_5)(L^1)(L^2)]$.[81,156,161,240,329,330] The complex $[Ru(SnF_3)Cp(PPh_3)_2]$ can be alternatively prepared from $[RuClCp(PPh_3)_2]$ by treatment with SnF_2 in the presence of a large excess of $[NH_4]F$.[331,331a] The reaction of $[\{RuClCp^*\}_4]$ with 1-hexene in the presence of $SnCl_2$ has been reported to yield the mononuclear derivative $[Ru(SnCl_3)Cp^*(\eta^4\text{-}1,3\text{-hexadiene})]$ via dehydrogenation of 1-hexene by the trichlorostannyl unit $[Ru(SnCl_3)Cp^*]$.[329] Complexes $[Ru(SnX_2Cl)Cp(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$, X = Br, F;* L^1L^2 = dppe, X = Br,* F), containing asymmetric SnX_2Cl^- anions, have been obtained by insertion of $SnBr_2$ or SnF_2 into the



X = SiMe, CH X = CMe, CPh

193 [Ru] = [RuCp(CO)$_2$] **194**

Figure 25 The stannyl-ruthenium derivatives **193** and **194**.

Ru–Cl bond of chloride complexes [RuClCp(L^1)(L^2)].[332] These compounds exist as formulated only in the solid state, disproportionating in solution to a mixture of species of composition [Ru(SnX$_n$Cl$_{3-n}$)Cp(L^1)(L^2)] (n = 0, 1, 2, 3) as revealed by variable-temperature ^{119}Sn NMR experiments. The related compounds [Ru(SnX$_2$Br)Cp(L^1)(L^2)] (L^1 = L^2 = PPh$_3$, X = F, Cl; L^{1}L^2 = dppe, X = Cl) are also known, being prepared from [RuBrCp(L^1)(L^2)] and the appropriate tin(II) halide.[333]

The anionic derivatives K[RuCp*(bipy)] and Na[RuCp*(tmbp)] (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) react with ClSnR$_3$ (R = Me, Ph) to produce the stannyl complexes [Ru(SnMe$_3$)Cp*(bipy)] and [Ru(SnR$_3$)Cp*(tmbp)] (R = Me, Ph), respectively.[296,334] Stannyl complexes of type **177–179** have been synthesized starting from the hydride **176** (see Scheme 10). Remarkably, complexes **178** undergo a spontaneous migration of one of the alkyl groups from Sn to the phosphenium phosphorus atom to give the stannylene derivatives **191** (Scheme 10).[309] Treatment of stannyl complexes of type **177** with [Me$_3$Si][OTf] generates the related stannylene complexes **192** via RSiMe$_3$ elimination (Scheme 10).[309] The synthesis of complexes **193** and **194** has also been reported (Figure 25).[335,336]

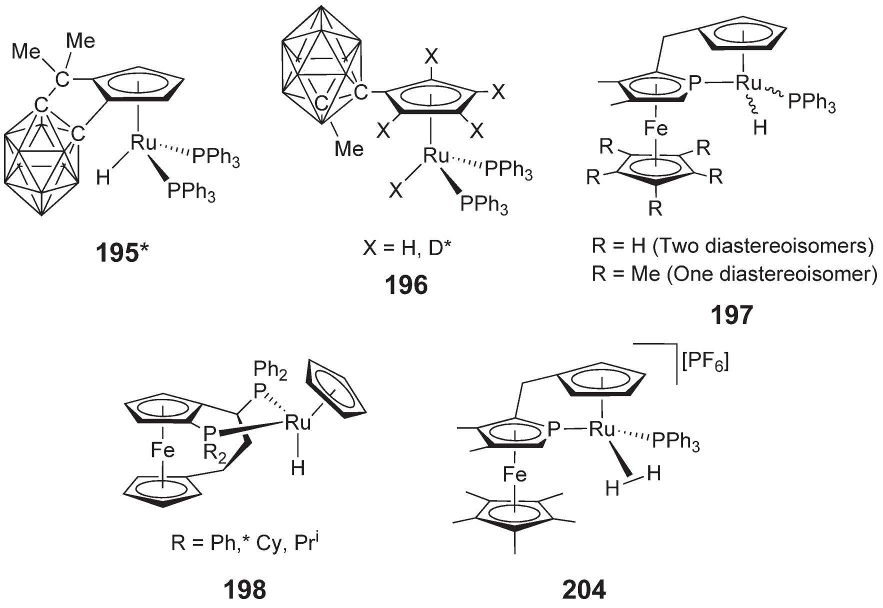
Oxidative addition of stannanes HSnR$_3$ to [OsClCp(PPr$^i_3$)$_2$] generates the hydrido–stannyl–Os(IV) derivatives [Os(SnR$_3$)HClCp(PPr$^i_3$)] (R = Bu^n, Ph). In the presence of an excess of HSnBu$^n_3$, the complex [Os(SnBu$^n_3$)HClCp(PPr$^i_3$)] is converted to the dihydride derivative [Os(SnBu$^n_3$)H$_2$Cp(PPr$^i_3$)].[321] The half-open ruthenocenes [Ru(η^5-CH$_2$CMeCHCMeX)Cp*] (X = CH$_2$, O) also undergo oxidative addition of SnCl$_4$ to afford the allyl–stannyl–Ru(IV) complexes [Ru(SnCl$_3$)(η^3-CH$_2$CMeCHCMe=X)ClCp*] (X = CH$_2$, O*).[160]

6.14.3.5 Complexes Containing Hydride and Dihydrogen Ligands

The chemistry of half-sandwich η^5-C$_5$ ruthenium and osmium complexes containing hydride ligands has been considerably developed over the last decade, which resulted in the discovery of novel features of these compounds. The main results are probably associated with those complexes of general formula [MH$_2$(η^5-C$_5$R$_5$)(L^1)(L^2)] since they show interesting structural variations depending on the electronic properties of the metal fragment. Thus, these species can exist in the dihydrogen [M(H$_2$)(η^5-C$_5$R$_5$)(L^1)(L^2)] or dihydride [MH$_2$(η^5-C$_5$R$_5$)(L^1)(L^2)] form, or as a mixture of both. Moreover, interconversions between both forms, as well as *cis/trans* isomerism in the dihydride derivatives, are also well known processes. A summary of recent advances in this field, as well as related chemistry of mono- and polyhydrides, is given in this section. Two reviews covering aspects related to this chemistry have appeared.[337,337a]

The classical synthetic methods to generate transition metal hydrides are based on: (i) the β-hydrogen elimination from a methoxide complex, usually generated *in situ* by treatment of a chloride precursor with Na[OMe] or K[OMe], and (ii) halide/hydride metathesis using Na[BH$_4$] or Li[AlH$_4$]. Following these approaches, the novel monohydride derivatives have been synthesized:

(i) Cyclopentadienyl–ruthenium complexes [RuHCp(L^1)(L^2)] (L^{1}L^2 = dpbz (dpbz = 1,2-bis(diphenylphosphino)-benzene);* L^1 = L^2 = PMePh$_2$, PMe$_2$Ph, PMe$_3$,* PTA;* L^1 = PPh$_3$, L^2 = (R)-Ph$_2$POCHMeCH$_2$C(=O)-NHPh),[187,338–342] [RuHCp*(L^1)(L^2)] (L^{1}L^2 = dppf,* κ^2(P,N)-Ph$_2$PCH$_2$CH$_2$NH$_2$),[204,343] [RuH(η^5-C$_5$H$_4$R)(PPh$_3$)$_2$] (R = Bu^t, Bz),[344] [RuH{η^5-C$_5$H$_4$(CH$_2$)$_n$NMe$_2$}(dppm)] (n = 2, 3),[94] [RuH-{η^5-C$_5$Me$_4$CH$_2$O(CH$_2$)$_n$CH=CHR}(CO)$_2$] (R = H, n = 1, 2; R = Me, n = 1),[345] the 1,2-dicarba-*closo*-dodecarboranyl-substituted derivatives **195*** and **196**,[346,347] the Cp-tethered phosphaferrocenes **197**,[98] and the diastereomerically pure complexes



195*

X = H, D*

196

R = H (Two diastereoisomers)
R = Me (One diastereoisomer)

197

R = Ph,* Cy, Pr^i

198

204

Figure 26 Some hydride and dihydrogen ruthenium complexes.

198 containing chiral ferrocenyl diphosphines (Figure 26).[194] A single crystal neutron diffraction study of $[RuHCp(PMe_3)_2]$ has been reported.[348]

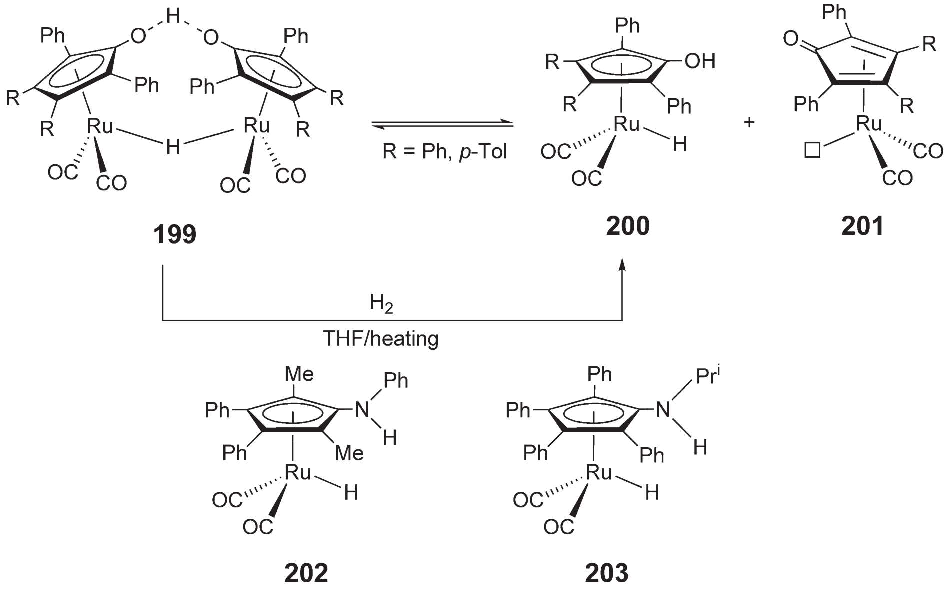
(ii) Cyclopentadienyl–osmium complexes $[OsHCp(L^1)(L^2)]$ ($L^1L^2 = $ dppm, dppe, dppp; $L^1 = PPr^i_3$, $L^2 = PPh_3$, PPr^i_3)[195,196,349] and $[OsHCp^*(L^1)(L^2)]$ ($L^1L^2 = $ dppm, dmpm, dmpe, COD; $L^1 = L^2 = PPh_3$, PEt_3, PMe_3).[117]

(iii) Indenyl derivatives $[RuH(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$,* PMe_2Ph; $L^1L^2 = $ dppm,* dppe, dppp, (*S*)-$(Ph_2P)_2NCHMePh$;* $L^1 = PPh_3$, $L^2 = PMe_3$, PMe_2Ph, $PMePh_2$, $PPh_2CH_2CH{=}CH_2$; $L^1 = CO$, $L^2 = PPr^i_3$),[86,350–352] $[RuH(\eta^5\text{-}1,2,3\text{-}C_9H_4Me_3)(L^1)(L^2)]$ ($L^1L^2 = $ dppm; $L^1 = CO$, $L^2 = PPh_3$, PPr^i_3),[352] $[RuH(\eta^5\text{-}C_9Me_7)(CO)(PPr^i_3)]$,[352] and $[OsH(\eta^5\text{-}C_9H_7)(PPh_3)_2]$.[126]

Oxidative addition of H–X bonds to electron-rich metal fragments is an alternative procedure to generate monohydride complexes. Thus, the treatment of chloride complexes $[RuClCp^*(L^1)(L^2)]$ ($L^1 = L^2 = PEt_3$, $PMePr^i_2$; $L^1L^2 = $ dippe) with HCl in the presence of $Na[BAr^F{}_4]$ has been reported to yield the chloro–hydrido derivatives $[RuHClCp^*(L^1)(L^2)][BAr^F{}_4]$ ($L^1 = L^2 = PEt_3$, $PMePr^i_2$; $L^1L^2 = $ dippe), via addition of HCl to the corresponding 16-electron intermediate $[RuCp^*(L^1)(L^2)]^+$.[353] In a similar way, the complex $[RuCp\{\kappa^2(N,N)\text{-tmeda}\}][BAr^F{}_4]$ reacts with HCl to generate $[RuHClCp\{\kappa^2(N,N)\text{-tmeda}\}][BAr^F{}_4]$.[77] Related oxidative additions of silanes, germanes, and stannanes, as well as the C–H bond of terminal alkynes, leading to the formation of monohydride species, are also well-known processes (see Section 6.14.3.4 and Chapter 6.15).

Dihydrogen has been found to react photochemically with $[\{RuCp(CO)_2\}_2]$ to give the previously known hydride $[RuHCp(CO)_2]$.[354] The optically active compounds $[RuHCp\{(S,S)\text{-BIPHOP-F}\}]$ (BIPHOP-F = 1,2-bis[bis(pentafluorophenyl)phosphanyloxy]-1,2-diphenylethane) and $[RuHCp\{(R)\text{-BINOP-F}\}]$ (BINOP-F = 2,2′-bis[bis(pentafluorophenyl)phosphanyloxy]-1,1′-binaphthalene) have been obtained by substitution of the two carbonyls in $[RuHCp(CO)_2]$ by the corresponding bidentate ligand.[163,166] The monocarbonyl complex 176 (see Scheme 10) has also been obtained from $[RuHCp(CO)_2]$ via substitution of one of the CO ligands by the diamino phosphite.[309] The optimized synthesis of the previously known monohydride derivative $[OsHCp^*(CO)_2]$ by photolysis of $[OsBu^nCp^*(CO)_2]$ has been described. The reaction involves release of 1-butene through a β-elimination process.[355]

Dinuclear ruthenium(II) complexes 199, which have been used as catalysts in a large number of hydrogen-transfer reactions, are known to dissociate in solution into the mononuclear hydride complexes 200 and the coordinatively unsaturated dienone derivatives 201 (Scheme 15). Remarkably, hydrides 200 are selectively formed when THF solutions of 199 are heated under hydrogen atmosphere. This process involves the conversion of 201 into 200 via heterolytic addition of H_2.[179,356] The related amino–cyclopentadienyl complexes 202 and 203 are also known, being obtained by treatment of the appropriate chloride precursor with NaOMe/MeOH or Na_2CO_3/Pr^iOH.[174,357]



Scheme 15

Monohydride complexes [$MHCp(CO)(PPr^i_3)$] (M = Ru, Os) have been obtained by reacting the corresponding five-coordinate derivatives [$MHCl(CO)(PPr^i_3)_2$] with an excess of cyclopentadiene in boiling methanol.[162,358] Other hydrido–Os compounds containing PPr^i_3 ancillary ligands are [$OsHClCp(PPr^i_3)_2$][BF_4] and *cis*-[$OsHCl_2Cp(PPr^i_3)$].[321]

One-electron oxidation of [$RuHCp^*(dppf)$]* with ferrocinium hexafluorophosphate generates the metastable Ru(III) hydride [$RuHCp^*(dppf)$][PF_6]. This complex undergoes atom-transfer reactions with CCl_4, [$MnBr(CO)_5$], and I_2 to afford the corresponding Ru(IV) species [$RuHXCp^*(dppf)$][PF_6] (X = Cl, Br, I). In a similar way, treatment of [$RuHCp^*(dppf)$][PF_6] with $HSnBu^n_3$ leads to the *trans*-dihydride [$RuH_2Cp^*(dppf)$][PF_6].[343] The electrochemical behavior of [$RuH(\eta^5\text{-}C_5H_4R)(PPh_3)_2$] (R = H, Bu^t, Bz, $C(p\text{-Tol})_3$,* $CPh_2(p\text{-}C_6H_4OMe)$) has been investigated by cyclic voltammetry. Thus, while for R = H, Bu^t, Bz, uncomplicated reversible one-electron oxidation processes are observed, for the trityl-substituted species (R = $C(p\text{-Tol})_3$, $CPh_2(p\text{-}C_6H_4OMe)$), the cyclic voltammograms indicate the presence of two isomeric cation radicals that exist in a dynamic equilibrium. It has been suggested that this may be the result of an interaction between the 17-electron Ru center in the cation radical and the π-system of one of the aromatic rings of the trityl groups which yields a weakly bonded 19-electron adduct of the cation radical.[344] In accord with these observations, chemical oxidation of [$RuHCp(PPh_3)_2$] with ferrocinium hexafluorophosphate in acetonitrile generates the highly unstable species [$RuHCp(PPh_3)_2$][PF_6] (half-life of seconds) which readily disproportionates into a 1 : 1 mixture of [$Ru(NCMe)Cp(PPh_3)_2$][PF_6] and [$RuH_2Cp(PPh_3)_2$][PF_6]. When this oxidation process is performed in the presence of bases (pyrrolidine, piperidine, or quinuclidine), [$Ru(NCMe)Cp(PPh_3)_2$][PF_6] is exclusively formed via H-transfer from [$RuHCp(PPh_3)_2$][PF_6] to the base. Such a transfer process has been kinetically studied.[359] The optically active compounds [RuHCp{(*S*,*S*)-chiraphos}] and [RuHCp{(*R*,*R*)-norphos}] (norphos = *trans*-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene) have shown to be efficient catalysts for the enantioselective hydrogenation of iminium cations. An ionic mechanism, involving initial hydride transfer from ruthenium to the iminium cation, has been proposed for this transformation.[360] In this context, a kinetic study on such a H^- transfer process from hydride complexes [RuHCp(P–P)] (P–P = dppm,* dppe,* dppp, dppb (dppb = 1,4-bis(diphenylphosphino)butane),* dpbz*) to 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate has been performed.[338] The measured rate constants indicate that hydride transfer is faster when the bite angle of the diphosphine is smaller.

Concerning the chemistry of dihydride/dihydrogen complexes, two general methods are usually applied for the preparation of these compounds: (i) oxidative addition of H_2 to an unsaturated metal fragment, and (ii) protonation of monohydride precursors [$MH(\eta^5\text{-}C_5R_5)(L^1)(L^2)$]. The stability of dihydride complexes relative to the corresponding dihydrogen tautomers is strongly dependent on the metal and auxiliary ligands. Thus, as suggested by theoretical calculations (DFT) on several model systems, the use of monodentate phosphines seems to favor the formation of dihydrides while the dihydrogen complexes are favored by bidentate phosphines of small chelating ring sizes.[353,361]

In this context, a range of novel Ru(IV) dihydride complexes $[\mathrm{RuH_2(\eta^5\text{-}C_5R_5)(L^1)(L^2)}][\mathrm{X}]$ ($\mathrm{R=H}$, $\mathrm{L^1=L^2=PEt_3}$, $\mathrm{PMePr^i{}_2}$, $\mathrm{X=BPh_4}$; $\mathrm{R=H}$, $\mathrm{L^1=PPh_3}$, $\mathrm{L^2=PMePr^i{}_2}$, $\mathrm{X=BPh_4}$; $\mathrm{R=H}$, $\mathrm{L^1L^2}$ = dippe, $\mathrm{X=BPh_4}$; $\mathrm{R=Me}$, $\mathrm{L^1=L^2=PEt_3}$, $\mathrm{PMePr^i{}_2}$, $\mathrm{X=BPh_4}$; $\mathrm{R=Me}$, $\mathrm{L^1L^2}$ = dippe, $\mathrm{X=BPh_4}$;* $\mathrm{R=Me}$, $\mathrm{L^1L^2}$ = dppe, X = OTf; $\mathrm{R=Me}$, $\mathrm{L^1=L^2=PPh_3}$, $\mathrm{PPhPr^i{}_2}$,* $\mathrm{SbPh_3}$, $\mathrm{X=BAr^F{}_4}$), in which the hydride ligands adopt a mutually *trans*-disposition, have been prepared by reacting the appropriate chloride precursor $[\mathrm{RuCl(\eta^5\text{-}C_5R_5)(L^1)(L^2)}]$ with $\mathrm{H_2}$ in the presence of $\mathrm{Na[BPh_4]}$, $\mathrm{Na[BAr^F{}_4]}$, or Ag[OTf].[72,73,110,210,353] These reactions proceed through the initial formation of 16-electron intermediates $[\mathrm{Ru(\eta^5\text{-}C_5R_5)(L^1)(L^2)}]^+$ which undergo oxidative addition of one $\mathrm{H_2}$ molecule. Deprotonation of these cationic dihydrides with $\mathrm{KOBu^t}$ leads to the corresponding neutral monohydrides $[\mathrm{RuH(\eta^5\text{-}C_5R_5)(L^1)(L^2)}]$, which can be protonated back by $\mathrm{HBF_4}$ to give the starting dihydrides. Remarkably, formation of metastable dihydrogen intermediates $[\mathrm{Ru(H_2)Cp^*(L^1)(L^2)}][\mathrm{BF_4}]$ ($\mathrm{L^1=L^2=PEt_3}$, $\mathrm{SbPh_3}$; $\mathrm{L^1L^2}$ = dippe) has been observed when these protonations were performed at low temperature. These dihydrogen complexes readily rearrange to their dihydride tautomers when the temperature is raised.[72,73,210]

The Os(II) complexes $[\mathrm{OsBrCp^*(PPr^i{}_3)}]$ and $[\mathrm{OsClCp(PPr^i{}_3)_2}]$ react with $\mathrm{H_2}$ to yield the Os(IV) dihydrides *trans*-$[\mathrm{OsH_2BrCp^*(PPr^i{}_3)}]$[78] and $[\mathrm{OsH_2ClCp(PPr^i{}_3)}]$,[321] respectively. The latter has been obtained as a mixture of the *cis*- and *trans*-isomers. It has also been reported that, under an atmosphere of $\mathrm{H_2}$, the chloride complex $[\mathrm{OsClCp\{\kappa^3(\mathit{P,C,C})\text{-}Pr^i{}_2PCMe{=}CH_2\}}]$ is in equilibrium with the *trans*-dihydride $[\mathrm{OsH_2ClCp\{\kappa^1(\mathit{P})\text{-}Pr^i{}_2PCMe{=}CH_2\}}]$ pointing out the hemilabile character of the $\mathrm{Pr^i{}_2PCMe{=}CH_2}$ ligand.[362] This property is also shown in the reaction of $[\mathrm{OsCp\{\eta^2\text{-}(\mathit{Z})\text{-}PhCH{=}CHPh\}\{\kappa^3(\mathit{P,C,C})\text{-}Pr^i{}_2PCMe{=}CH_2\}}][\mathrm{PF_6}]$ with LiMe which affords $[\mathrm{OsH(\eta^5\text{-}C_5H_4Me)\{\eta^2\text{-}(\mathit{Z})\text{-}PhCH{=}CHPh\}\{\kappa^1(\mathit{P})\text{-}Pr^i{}_2PCMe{=}CH_2\}}]$ as a result of the initial formation of $[\mathrm{OsMeCp\{\eta^2\text{-}(\mathit{Z})\text{-}PhCH{=}CHPh\}\{\kappa^1(\mathit{P})\text{-}Pr^i{}_2PCMe{=}CH_2\}}]$ and subsequent Me/CpH exchange. The *Z*-stilbene ligand in this hydride complex isomerizes, in solution and in the solid state, to give $[\mathrm{OsH(\eta^5\text{-}C_5H_4Me)\{\eta^2\text{-}(\mathit{E})\text{-}PhCH{=}CHPh\}\{\kappa^1(\mathit{P})\text{-}Pr^i{}_2PCMe{=}CH_2\}}]$.*[362]

Treatment of $[\mathrm{RuClCp^*(dfepe)}]$ (dfepe = $\mathrm{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2}$) with $\mathrm{Ag[BF_4]}$ or Ag[OTf] under $\mathrm{H_2}$ atmosphere generates the cationic *trans*-dihydride $[\mathrm{RuH_2Cp^*(dfepe)}]^+$, which can be deprotonated with $\mathrm{PPh_3}$ to yield $[\mathrm{RuHCp^*(dfepe)}]$.* In contrast, the reaction of [Ru(OTf)Cp(dfepe)] with $\mathrm{H_2}$ generates the unstable dihydrogen compound $[\mathrm{Ru(H_2)Cp(dfepe)}]$[OTf] which is spontaneously converted into [RuHCp(dfepe)] via HOTf elimination.[176] As suggested by T_1 relaxation time measurements, the dihydrogen-type complexes **204** (see Figure 26) and $[\mathrm{Ru(H_2)Cp\{\kappa^2(\mathit{N,N})\text{-}tmeda\}}][\mathrm{BAr^F_4}]$ are also formed in the reaction of the appropriate chloride precursor and $[\mathrm{RuCp\{\kappa^2(\mathit{N,N})\text{-}tmeda\}}][\mathrm{BAr^F_4}]$, respectively, with $\mathrm{H_2}$.[77,98]

Protonation of $[\mathrm{RuHCp(PMe_3)_2}]$ with $\mathrm{HBF_4}$ produces the cationic dihydride complex *trans*-$[\mathrm{RuH_2Cp(PMe_3)_2}][\mathrm{BF_4}]$ whose structure has been studied by both single crystal X-ray and neutron diffraction analysis.[340,348] A neutron diffraction study of the previously known complex $[\mathrm{Ru(H_2)Cp(dppm)}][\mathrm{BF_4}]$, which contains an elongated dihydrogen ligand, has also been reported.[363] Protonation reactions of monohydrides **198** (Figure 26) with $\mathrm{HBF_4}$ and HOTf have been explored. Thus, when 1 equiv. of $\mathrm{HBF_4}$ is used, a mixture of dihydrogen and *trans*-dihydride complexes is formed, while with 3 equiv. of HOTf the *trans*-dihydride derivatives are the only products detected. The use of 1 equiv. of HOTf results in the formation of reaction mixtures containing the *trans*-dihydrides along with adducts showing extremely short [Ru]–H···HOTf interactions.[194] Protonation of $[\mathrm{RuHCp(CO)(PPr^i{}_3)}]$ with $\mathrm{HBF_4}$ leads also to an equilibrium mixture containing the dihydrogen $[\mathrm{Ru(H_2)Cp(CO)(PPr^i{}_3)}][\mathrm{BF_4}]$ and *trans*-dihydride $[\mathrm{RuH_2Cp(CO)(PPr^i{}_3)}][\mathrm{BF_4}]$ complexes.[162] Kinetics of formation of dihydrogen complexes by protonation of $[\mathrm{RuHCp(L^1)(L^2)}]$ ($\mathrm{L^1=L^2=PPh_3}$; $\mathrm{L^1L^2}$ = dppm, dppe) with $\mathrm{HBF_4}$ in THF have been measured.[364]

Addition of 1 equiv. of $\mathrm{HBF_4}$ to $[\mathrm{RuH\{\eta^5\text{-}C_5H_4(CH_2)_\mathit{n}NMe_2\}(dppm)}]$ ($n = 2$, 3) leads to $[\mathrm{RuH\{\eta^5\text{-}C_5H_4(CH_2)_\mathit{n}NHMe_2\}(dppm)}][\mathrm{BF_4}]$ in which the amine function has been protonated. Relaxation time T_1 measurements indicate the existence of an intramolecular N–H···H–Ru hydrogen bond interaction in these compounds. Moreover, spin saturation transfer studies and H/D exchange experiments reveal fast Ru–H/N–H exchange probably involving a dihydrogen complex intermediate.[94] Remarkably, replacement of the dppm ligand by two less donating $\mathrm{P(OPh)_3}$ ligands ($n = 2$) dramatically reduces the strength of the intramolecular N–H···H–Ru hydrogen bond which is now hardly evidenced by NMR measurements.[365] Complexes $[\mathrm{RuH\{\eta^5\text{-}C_5H_4(CH_2)_\mathit{n}NHMe_2\}(dppm)}][\mathrm{BF_4}]$ are thermally unstable and in solution are converted into $[\mathrm{Ru\{\eta^5{:}\kappa^1(\mathit{N})\text{-}C_5H_4(CH_2)_\mathit{n}NMe_2\}(dppm)}][\mathrm{BF_4}]$ ($n = 2$, 3^*) via $\mathrm{H_2}$ elimination. This process is reversible. Addition of 1 equiv. of $\mathrm{HBF_4}$ to $[\mathrm{RuH\{\eta^5\text{-}C_5H_4(CH_2)_\mathit{n}NHMe_2\}(dppm)}][\mathrm{BF_4}]$ or 2 equiv. of $\mathrm{HBF_4}$ to $[\mathrm{RuH\{\eta^5\text{-}C_5H_4(CH_2)_\mathit{n}NMe_2\}(dppm)}]$ generates the dicationic dihydrogen derivatives $[\mathrm{Ru(H_2)\{\eta^5\text{-}C_5H_4(CH_2)_\mathit{n}NHMe_2\}(dppm)}][\mathrm{BF_4}]_2$ ($n = 2$, 3).[94] The related hydride complex $[\mathrm{RuH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(PPh_3)_2}]^*$ is also known, being obtained by reacting $[\mathrm{RuH(OAc)(PPh_3)_3}]$ with the sodium salt $\mathrm{Na[C_5H_4(CH_2)_2NMe_2]}$.[95] Treatment of this complex with 1 equiv. of $\mathrm{HBF_4}$ leads to the direct formation of $[\mathrm{Ru\{\eta^5{:}\kappa^1(\mathit{N})\text{-}C_5H_4(CH_2)_2NMe_2\}(PPh_3)_2}][\mathrm{BF_4}]$ after elimination of $\mathrm{H_2}$. However, using $[\mathrm{HNEt_3}][\mathrm{BPh_4}]$ or

$[HPBu^n_3][BPh_4]$ as protonating agent, it is possible to isolate the intermediate $[RuH\{\eta^5\text{-}C_5H_4(CH_2)_2NHMe_2\}\text{-}(PPh_3)_2][BPh_4]^*$. Although an intramolecular N–H···H–Ru hydrogen bond interaction was not observed in the X-ray crystal structure of this complex, T_1 measurements are consistent with the existence of such interactions in solution. Moreover, in contrast to its dppm counterpart, the addition of an excess of acid to $[RuH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(PPh_3)_2]$ results in the selective formation of the dicationic dihydride $[RuH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NHMe_2\}(PPh_3)_2][PF_6]_2$.[95] The synthesis and X-ray crystal structures of $[RuH(\eta^5C_5H_4C_5H_9NMe)(PPh_3)_2]$ ($C_5H_9NMe = 4$-*N*-methylpiperidyl) and its protonated form $[RuH(\eta^5\text{-}C_5H_4C_5H_9NHMe)(PPh_3)_2][BF_4]$ have also been reported.[366]

Reaction of $[RuHCp^*(COD)]$ with HBF_4 at −76 °C generates the dihydrogen derivative $[Ru(H_2)Cp^*(COD)][BF_4]$ which readily changes into $[RuCp^*(\eta^6\text{-}1,3,5\text{-}COT)][BF_4]$ (COT = 1,3,5-cyclooctatriene) at room temperature, via release of H_2 and concomitant dehydrogenation of the COD ligand. In contrast, the treatment of $[RuHCp^*(NBD)]$ with HBF_4 generates a mixture of nortricyclene and the bimetallic complex $[(RuCp^*)_2(\mu\text{-}H)(\mu\text{-}C_5H_5\text{–}CH{=}CH_2)][BF_4]$, which are likely formed via the dihydrogen intermediate $[Ru(H_2)Cp^*(NBD)][BF_4]$.[367] Such an intermediate has also been proposed in the reaction of $[Ru(H_2O)Cp^*(NBD)][BF_4]$ with H_2 which, in benzene solution, leads to a mixture of nortricyclene and $[RuCp^*(\eta^6\text{-}C_6H_6)][BF_4]$. The formation of nortricyclene in these reactions has been theoretically explained as the result of a metal-mediated formal homo-Diels–Alder cycloaddition of H_2 to NBD.[368]

The protonation of the dicarbonyl–Os(II) derivative $[OsHCp^*(CO)_2]$ with triflic acid gives an equilibrium mixture (87 : 31) of the dihydride $[OsH_2Cp^*(CO)_2][OTf]$ and the dihydrogen complex $[Os(H_2)Cp^*(CO)_2][OTf]$.[369] In contrast, protonation of $[OsHCp(L^1)(L^2)]$ ($L^1 = PPr^i_3$, $L^2 = CO$, PPh_3, PPr^i_3; L^1L^2 = dppm, dppe, dppp) with HBF_4 leads exclusively to the cationic dihydrido–osmium(IV) derivatives *trans*-$[OsH_2Cp(L^1)(L^2)][BF_4]$ ($L^1 = PPr^i_3$, $L^2 = CO$, PPh_3, PPr^i_3; L^1L^2 = dppm, dppe, dppp; only when the auxiliary ligands are dppm and dppe are minor amounts of the *cis*-isomer formed).[195,196,349,358] The related *trans*-dihydrides $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2E\}(PPr^i_3)_2]Cl$ ($E = NMe_2$,* OMe) have been obtained by reacting $[OsH_2Cl_2(PPr^i_3)_2]$ with the functionalized cyclopentadienyllithium salts $Li[C_5H_4(CH_2)_2E]$.[370] These complexes can be easily deprotonated to afford the neutral Os(II) monohydrides $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2E\}(PPr^i_3)_2]$. Similar reactions using $[OsH_2Cl_2(PPr^i_3)_2]$ and $Li[C_5H_4(CH_2)_2PPh_2]$ as starting materials allow the preparation of *trans*-$[OsH_2\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4(CH_2)_2PPh_2\}(PPr^i_3)]Cl^*$ and $[OsH\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4(CH_2)_2PPh_2\}(PPr^i_3)]$.[224] Treatment of $[OsBrCp^*(PPr^i_3)]$ with $K[B(C_6F_5)_4]$ produces the related dihydride species $[OsH_2Cp^*\{\kappa^3(P,C,C)\text{-}Pr^i_2PC(Me){=}CH_2\}][B(C_6F_5)_4]^*$, via initial formation of the 14-electron intermediate $[OsCp^*(PPr^i_3)][B(C_6F_5)_4]$, which then activates two of the C–H bonds in the PPr^i_3 ligand. Deprotonation of this complex with $K[N(SiMe_3)_2]$ leads to the neutral monohydride $[OsHCp^*\{\kappa^3(P,C,C)\text{-}Pr^i_2PCMe{=}CH_2\}]$.[319]

Treatment of $[OsClCp(PHPh_2)(PPr^i_3)]$ with $Tl[PF_6]$ in wet acetone or methanol affords the cationic *trans*-dihydrides $[OsH_2Cp\{P(OR)Ph_2\}(PPr^i_3)][PF_6]$ (R = H, Me). Experimental evidence, using deuterium-labeled substrates, suggests that the formation of these complexes takes place via the hydrido–phosphido intermediate $[OsHCp(PPh_2)(PPr^i_3)][PF_6]$ generated by intramolecular P–H oxidative addition of diphenylphosphine in the unsaturated metallic fragment $[OsCp(PHPh_2)(PPr^i_3)][PF_6]$. Once the hydrido–phosphido species is formed, RO–H (R = H, Me) addition to the Os–phosphido bond affords the final dihydrides. Deprotonation of $[OsH_2Cp\{P(OH)Ph_2\}(PPr^i_3)][PF_6]$ with NaOMe leads to the formation of the dihydrido–phosphinito derivative *trans*-$[OsH_2Cp\{P({=}O)Ph_2\}(PPr^i_3)]$. In contrast, deprotonation of $[OsH_2Cp\{P(OMe)Ph_2\}(PPr^i_3)][PF_6]$ yields $[OsHCp\{P(OMe)Ph_2\}(PPr^i_3)]$ as the result of the abstraction of one of the two hydride ligands.[197]

Protonation reactions of indenyl–ruthenium(II) monohydrides $[RuH(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ with triflic or tetrafluoroboric acid have been explored at −60 °C, the nature of the resulting products being also strongly dependent on the auxiliary ligands.[350,352] Thus, while dihydride complexes *trans*-$[RuH_2(\eta^5\text{-}C_9H_7)(L^1)(L^2)][Y]$ ($L^1 = L^2 = PPh_3$, Y = OTf, BF_4;* $L^1 = L^2 = PMe_3$, $Y = BF_4$) are selectively formed when monodentate phosphines are present, the dihydrogen derivative $[Ru(H_2)(\eta^5\text{-}C_9H_7)(dppm)][OTf]$ is exclusively obtained by protonation of $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$. The use of diphosphines with bigger chelating ring sizes (dppe, dppp) leads to mixtures of the corresponding dihydrogen and dihydride tautomers. Protonation of $[OsH(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with HBF_4 generates the stable dihydride *trans*-$[OsH_2(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ selectively.[126]

η^5-C_5 Ru and Os complexes containing polyhydride ligands are also known. Thus, the novel trihydrido–Ru(IV) complexes $[RuH_3Cp^*(Ppyl_3)]^*$ ($Ppyl_3$ = tripyrrolylphosphine) and $[RuH_3Cp^*(EPh_3)]$ (E = Sb, As) have been obtained by reacting the dichloride precursors $[RuCl_2Cp^*(Ppyl_3)]$ and $[RuCl_2Cp^*(EPh_3)]$, respectively, with an excess of $Na[BH_4]$ in ethanol.[210,371] Formation of thermally unstable bis(dihydrogen) complexes $[Ru(H_2)_2Cp^*(EPh_3)][BF_4]$ (E = Sb, As), by protonation of $[RuH_3Cp^*(EPh_3)]$ with HBF_4 at −80 °C, has been reported.[210] The reactivity of the trihydride complex $[RuH_3Cp^*(Ppyl_3)]$ has also been explored. Thus, it reacts, under thermal conditions, with an excess of $Ppyl_3$ and CO to generate the monohydride derivatives $[RuHCp^*(Ppyl_3)_2]$ and $[RuHCp^*(CO)(Ppyl_3)]$, respectively.[310] In a similar way, its treatment with $CNBu^t$ leads first to $[RuHCp^*(CNBu^t)(Ppyl_3)]$, but the reaction proceeds further to yield, through an unprecedented decyanation reaction, the cyano complex $[Ru(CN)Cp^*(CNBu^t)(Ppyl_3)]$.*[310] Protonation of $[RuHCp^*(CO)(Ppyl_3)]$ with HBF_4 at −78 °C generates the dihydrogen derivative $[Ru(H_2)Cp^*(CO)(Ppyl_3)][BF_4]$ which readily decomposes at room temperature by loss of H_2.[310]

The related trihydrido Os(IV) complexes $[OsH_3Cp^*(EPh_3)]$ (E = P, As) have been obtained by treatment of $[OsBr_2Cp^*(EPh_3)]$ with $Na[BH_4]$.[211,372] Protonation of these complexes with HBF_4 affords the dihydrogen–dihydrido derivatives $[Os(H_2)H_2Cp^*(EPh_3)][BF_4]$ (E = P, As) whose formulation has been confirmed by a single crystal neutron diffraction study on $[Os(H_2)H_2Cp^*(PPh_3)][BF_4]$.[372] The trihydrido complex $[OsH_3Cp(PPr^i_3)]$, obtained by reacting $[OsH_2ClCp(PPr^i_3)]$ with $Na[BH_4]$, is also known.[321] Treatment of the dimeric Os(III) complex $[\{OsBr(\mu\text{-}Br)Cp^*\}_2]$ **132** with $Li[AlH_4]$ leads to the formation of the mononuclear pentahydrido–Os(VI) derivative $[OsH_5Cp^*]$ whose ^1H NMR spectrum shows a single hydride resonance.[211] Since vibrational studies were inconclusive as to whether the molecule adopted a C_{5v} (pseudo-pentagonal-pyramid with the Cp* ring occupying the axial position) or a pseudo-C_{4v} (pseudo-octahedral with the Cp* ring considered as occupying one site) orientation in the ground state, theoretical calculations were performed on the model complex $[OsH_5Cp]$.[373,373a] Geometry optimizations, as well as frequency calculations, support the notion of a highly fluxional pseudo-C_{4v} structure which exchanges the hydride ligands through a Bailar or trigonal-twist mechanism without passing through the C_{5v} geometry.

6.14.3.6 Complexes Containing Carbonyl and Isocyanide Ligands

Dicarbonyl complexes $[MClCp(CO)_2]$ (M = Ru, Os) are classical precursors in organometallic chemistry that allow the easy preparation of wide range of half-sandwich ruthenium(II) and osmium(II) derivatives through (i) substitution reactions of the carbonyl ligands or (ii) chloride metathesis processes (see COMC (1995)). Several synthetic procedures for the preparation of these compounds are known, all of them involving polynuclear carbonyl intermediates, that is, $[M_3(CO)_{12}]$ and $[\{MCp(CO)_2\}_2]$, as starting materials.[374] Improved preparations of $[MClCp(CO)_2]$ (M = Ru, Os) starting from the readily available precursors $RuCl_3{\cdot}nH_2O$ and OsO_4 have been reported by Selegue's group in 1994.[374] Thus, $[\{RuCl_2(CO)_3\}_2]$, produced by refluxing $RuCl_3{\cdot}nH_2O$ in hydrochloric and formic acids, reacts with $C_5H_5SiMe_3$ to give $[RuClCp(CO)_2]$ in 74% overall yield from $RuCl_3{\cdot}nH_2O$. Known conversion of OsO_4 to $[NH_4]_2[OsCl_6]$, reduction to $OsCl_3$, and carbonylation to $[\{OsCl_2(CO)_3\}_2]$ in a tube furnace, and finally reaction with $C_5H_5SiMe_3$ gives $[OsClCp(CO)_2]$ in 26% overall yield from OsO_4.

During the period covered by this account, novel halide–dicarbonyl Ru(II) and Os(II) complexes have been reported, including the following:

(i) The pentamethylated [60]fullerene derivative $[RuCl(\eta^5\text{-}C_{60}Me_5)(CO)_2]^*$ (**205**; Figure 27), prepared by reacting $[\{RuCl_2(CO)_3\}_2]$ with the potassium salt of the fullerene ligand ($K[C_{60}Me_5]$).[375]

(ii) The optically active derivative $[RuBr(\eta^5\text{-}C_5Ph_4R)(CO)_2]^*$ (R = menthyl), synthesized by treatment of $[Ru_3(CO)_{12}]$ with (−)-bromomenthyltetraphenylcyclopentadiene.[376]

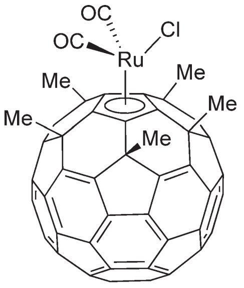
(iii) Aminocyclopentadienyl–ruthenium(II) complexes **206** (Figure 27), obtained by reacting $[Ru_3(CO)_{12}]$ with the appropriate cyclopenta-2,4-dienimine in a mixture of $CHCl_3/Pr^iOH$.[174,357,377,378]

(iv) Hydroxycyclopentadienyl–ruthenium(II) derivatives $[RuX(\eta^5\text{-}C_5Ph_4OH)(CO)_2]$ (X = Cl,* I*), obtained by treatment of the dinuclear Shvo complex **199** ((R = Ph); see Scheme 15) with $CHCl_3$ or I_2.[379,380]

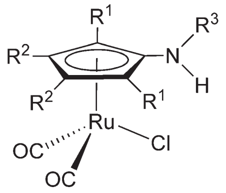
(v) Complexes $[RuI(\eta^5\text{-}C_5Me_4CF_3)(CO)_2]^*$ and $[RuX(\eta^5\text{-}C_5H_4Me)(CO)_2]$ (X = Br,* I) synthesized in two steps from $[Ru_3(CO)_{12}]$ and the appropriate cyclopentadiene. This classical procedure involves the initial formation of dimers $[\{Ru(\eta^5\text{-}C_5Me_4CF_3)(CO)_2\}_2]^*$ and $[\{Ru(\eta^5\text{-}C_5H_4Me)(CO)_2\}_2]^*$, respectively, and subsequent treatment with I_2 or Br_2.[127,213]

(vi) The Os(II) derivatives $[OsBr(\eta^5\text{-}C_5R_5)(CO)_2]$ (R = Ph,* *p*-Tol) and $[OsBr(\eta^5\text{-}C_5Ph_4\text{-}4\text{-}C_6H_4Bu^t)(CO)_2]$, prepared by refluxing a mixture of $[Os_3(CO)_{12}]$ and the appropriate bromide C_5R_5Br in chlorobenzene.[214]

Carbonylation of the dimeric tetramethylfulvene derivative $[\{RuCl_2(\eta^6\text{-}C_5Me_4CH_2)\}_2]$, which is in turn made by oxygenation of $[\{RuCl_2Cp^*\}_2]$, generates the dicarbonyl–chloro complex $[RuCl(\eta^5\text{-}C_5Me_4CH_2Cl)(CO)_2]^*$ **207**.[105] The overall process represents a nice example of C–H activation of one methyl group of the Cp* ring in $[\{RuCl_2Cp^*\}_2]$. The related trifluoromethyl derivative **208** (Figure 27) has also been prepared by carbonylation of a dimeric fulvene-type ruthenium complex.[381] Remarkably, two methyls in each Cp* ligand can be readily activated if the oxidation/carbonylation processes of $[\{RuCl_2Cp^*\}_2]$ are performed in the presence of *N*-chlorosuccinimide. In this

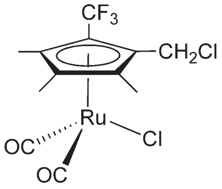


205*

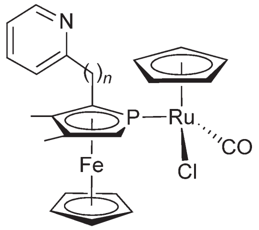


$R^1 = R^2 = Ph$; $R^3 = Ph, Pr^i,^* Pr^n, Bu^t$, 4-$C_6H_4OMe$,
4-$C_6H_4NO_2$, 4-C_6H_4Cl, 4-$C_6H_4NMe_2$
$R^1 = Me$; $R^2 = Ph$; $R^3 = Ph,^* Pr^i$
$R^1 = R^2 = Bu^n$; $R^3 = Pr^i$

206



208



$n = 1, 2$

210

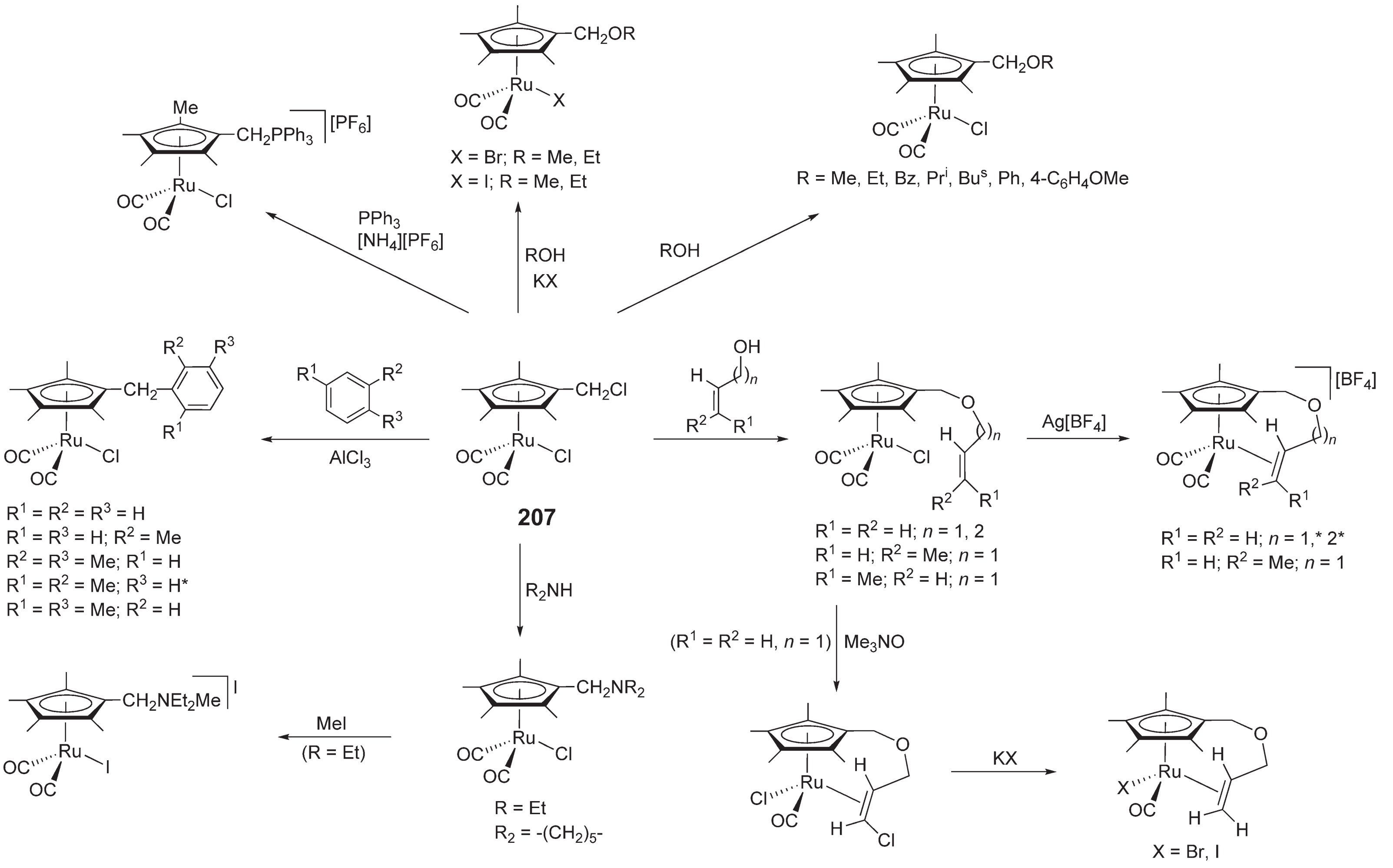
Figure 27 Some examples of mono- and dicarbonyl Ru(II) complexes.

way, the 1,2- and 1,3-isomers of $[RuCl\{\eta^5\text{-}C_5Me_3(CH_2Cl)_2\}(CO)_2]^*$ are formed in 1 : 1 ratio.[382] The presence of a C–Cl bond in **207** has been exploited for the preparation of a large variety of functionalized ruthenium complexes through nucleophilic substitution reactions with alcohols, amines, and phosphines, as well as Friedel–Crafts reactions with arenes (this chemistry is summarized in Scheme 16).[105,383,384] Hydrolysis of **207** in the presence of collidine leads to the alcohol complex $[RuCl(\eta^5\text{-}C_5Me_4CH_2OH)(CO)_2]$ which easily forms esters $[RuCl(\eta^5\text{-}C_5Me_4CH_2O_2CR)(CO)_2]$ (R = Me, CH=CH$_2$, 2-furyl, 2-thienyl) on reaction with $RC(=O)Cl/Et_3N$.[385] In addition, oxidation of the alcohol group in $[RuCl(\eta^5\text{-}C_5Me_4CH_2OH)(CO)_2]$ by DMSO/oxalyl chloride generates the aldehyde $[RuCl\{\eta^5\text{-}C_5Me_4C(=O)H\}(CO)_2]$ **209** which has been used as a versatile starting material for the preparation of a variety of dicarbonyl–ruthenium(II) complexes through classical organic transformations (see Scheme 17).[385]

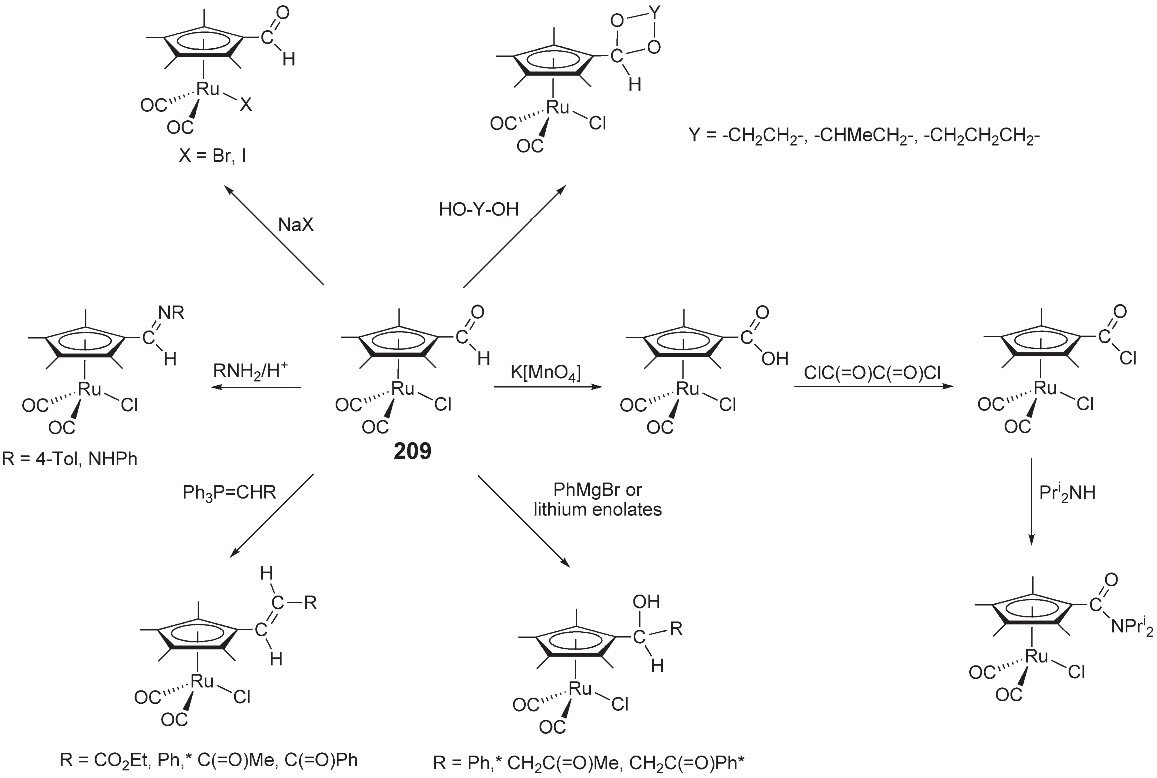
The anionic species $[Ru(\eta^5\text{-}C_5R_5)(CO)_2]^-$ (R = H, Me) have been recognized as versatile synthons for the synthesis of wide range of half-sandwich Ru(II) complexes by treatment with electrophiles (see COMC (1995) and Section 6.14.3.4). Reduction of $[\{Ru(\eta^5\text{-}C_5R_5)(CO)_2\}_2]$ with Na–K alloy or sodium amalgam is the most conventional route to these anions. Nevertheless, in the case of $[RuCp^*(CO)_2]^-$, the reaction requires very long time (3 days) and the anion decomposes easily during filtration for removal of Na–K alloy. An alternative and more convenient procedure for the preparation of $Li[RuCp^*(CO)_2]$ based on the deprotonation of $[RuHCp^*(CO)_2]$ with $LiBu^n$ has been recently reported, the reaction proceeding immediately at −45 °C.[298] Following a similar synthetic approach, the anionic osmium(II) complexes $Li[Os(\eta^5\text{-}C_5R_5)(CO)_2]$ can be easily generated from hydrides $[OsH(\eta^5\text{-}C_5R_5)(CO)_2]$ (R = H, Me).[297] Preparation of the sodium salt $Na[OsCp(CO)_2]$ by treatment of $[OsICp(CO)_2]$ with sodium naphthalenide has also been described.[297]

Cationic dicarbonyls are also known. Thus, substitution of the labile acetone ligand in $[Ru\{\kappa^1(O)\text{-}OCMe_2\}Cp(CO)(PPr^i_3)][BF_4]$ by CO leads to the quantitative formation of $[RuCp(CO)_2(PPr^i_3)][BF_4]$.[162] The related complex $[RuCp^*(CO)_2(PMePr^i_2)][BAr^F_4]^*$ has been synthesized by reacting $[RuClCp^*(CO)(PMePr^i_2)]$ with $Na[BAr^F_4]$ under a CO atmosphere.[386]

Treatment of $[Ru\{\kappa^1(O)\text{-}OCMe_2\}Cp(CO)(PPr^i_3)][BF_4]$ with NaCl results in the formation of the neutral monocarbonyl derivative $[RuClCp(CO)(PPr^i_3)]$.[162] Its osmium counterpart $[OsClCp(CO)(PPr^i_3)]$ has been obtained by displacement of the hydride ligand in $[OsHCp(CO)(PPr^i_3)]$ by chloride after addition of CCl_4.[358] The related species $[RuXCp^*(CO)(PPhPr^i_2)]$ (X = Cl, Br, I) have been synthesized by bubbling CO into solutions containing the 16-electron derivatives $[RuXCp^*(PPhPr^i_2)]$ (X = Cl, Br, I).[102] Following classical synthetic routes, a number of other neutral halide–monocarbonyl complexes have been reported. Representative examples are: $[RuClCp(CO)\{PPh_2(2\text{-}Tol)\}]$,[387] $[RuClCp^*(CO)(L)]$ (L = $PMePr^i_2$,[161] PEt_3,[161] $\kappa^1(P)\text{-}Pr^i_2PCH_2CO_2Me$,[205] $\kappa^1(P)\text{-}Ph_2PCH_2CH_2NMe_2$[172]),


Me
CH2PPh3
[PF6]
OC
Ru
Cl
OC
CH2OR
Ru
X
X = Br; R = Me, Et
X = I; R = Me, Et
CH2OR
Ru
Cl
R = Me, Et, Bz, Pri, Bus, Ph, 4-C6H4OMe
PPh3
[NH4][PF6]
ROH
KX
ROH
R2
R3
CH2
R1
R1 = R2 = R3 = H
R1 = R3 = H; R2 = Me
R2 = R3 = Me; R1 = H
R1 = R2 = Me; R3 = H*
R1 = R3 = Me; R2 = H
AlCl3
CH2Cl
207
OH
H
n
R2
R1
O
R1 = R2 = H; n = 1, 2
R1 = H; R2 = Me; n = 1
R1 = Me; R2 = H; n = 1
Ag[BF4]
[BF4]
R1 = R2 = H; n = 1,* 2*
R1 = H; R2 = Me; n = 1
R2NH
CH2NR2
R = Et
R2 = -(CH2)5-
MeI
(R = Et)
CH2NEt2Me
I
(R1 = R2 = H, n = 1)
Me3NO
Cl
KX
X
X = Br, I

Scheme 16



Scheme 17

$[RuCl(\eta^5\text{-}C_9H_7)(CO)(L)]$ ($L = PPh_3$,[388] PCy_3,[85] PPr^i_3[85]), $[RuBr(\eta^5\text{-}1,2,3\text{-}C_9H_4Me_3)(CO)(L)]$ ($L = PPh_3$, PPr^i_3),[352] $[RuBr(\eta^5\text{-}C_9Me_7)(CO)(PPr^i_3)]$,[352] and phosphaferrocenes **210** (see Figure 27).[207]

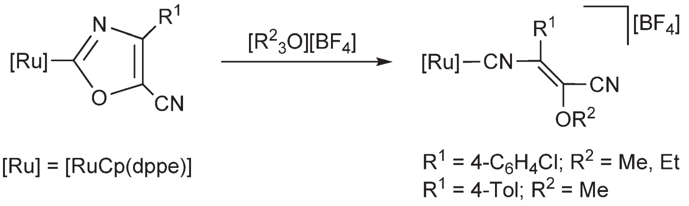
In accord with the hemilabile properties of vinyl– and allyl–phosphine ligands, the cationic monocarbonyl derivatives $[RuCp^*(CO)\{\kappa^1(P)\text{-}Ph_2P(CH_2)_nCH{=}CH_2\}_2][PF_6]$ ($n = 0$, 1) are formed when complexes $[RuCp^*\{\kappa^3(P,C,C)\text{-}Ph_2P(CH_2)_nCH{=}CH_2\}\{\kappa^1(P)\text{-}Ph_2P(CH_2)_nCH{=}CH_2\}][PF_6]$ are treated with CO.[106,107] Chelate ring opening also occurs in the reactions of $[RuCp\{\kappa^2(P,O)\text{-}Ph_2PCH_2C({=}O)Bu^t\}(PPh_3)][PF_6]$ and $[Ru(\eta^5\text{-}C_5R_5)\{\kappa^2(P,O)\text{-}P{\sim}O\}\{\kappa^1(P)\text{-}P{\sim}O\}][SbF_6]$ ($R = H$, Me; $P{\sim}O$ = (1,3-dioxan-2-ylmethyl)diphenylphosphine) with CO, leading to complexes $[RuCp\{\kappa^1(P)\text{-}Ph_2PCH_2C({=}O)Bu^t\}(CO)(PPh_3)][PF_6]$ and $[Ru(\eta^5\text{-}C_5R_5)(CO)\{\kappa^1(P)\text{-}P{\sim}O\}_2][SbF_6]$ ($R = H$, Me), respectively.[209,389] Displacement of coordinated acetonitrile ligands in complexes $[RuCp(NCMe)(dppr)][PF_6]$ and $[Ru(\eta^5\text{-}C_5Me_4CF_3)(NCMe)_3][PF_6]$ by CO, to generate $[RuCp(CO)(dppr)][PF_6]^*$ and $[Ru(\eta^5\text{-}C_5Me_4CF_3)(CO)(NCMe)_2][PF_6]$, has also been reported.[120,133]

Formation of carbonyl complexes by hydrolysis of transition metal vinylidenes $[M]{=}C{=}CR^1R^2$ is a well-known process (see Chapter 6.15). In accord with this, carbonyl compounds $[RuCp^*(CO)(PMe_2Ph)_2][PF_6]$,*[390] $[RuCp^*(CO)(dippe)][PF_6]$,*[391] and $[Ru(\eta^5\text{-}C_5H_4Me)(CO)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}_2][PF_6]$*[127] have been obtained by addition of water to $[Ru\{{=}C{=}C(H)Ph\}Cp^*(PMe_2Ph)_2][PF_6]$, $[Ru\{{=}C{=}C(H)CH_2OH\}Cp^*(dippe)][PF_6]$, and $[Ru\{{=}C{=}C(H)Ph\}(\eta^5\text{-}C_5H_4Me)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}_2][PF_6]$, respectively.

The carbonyl ligands in the pentamethylated [60]fullerene complex **205** (Figure 27) can be replaced by isocyanides. Thus, treatment of **205** with a slight excess of CNR ($R = Me$, Bu^t, Xyl) in toluene at 70 °C results in the high yield formation of the monosubstituted complexes $[RuCl(\eta^5\text{-}C_{60}Me_5)(CNR)(CO)]$ ($R = Me$, Bu^t,* 2,6-xylyl). In addition, when a large excess of the isocyanide ligand is used, and the reactions are performed at 100 °C, the bis(isocyanide) derivatives $[RuCl(\eta^5\text{-}C_{60}Me_5)(CNR)_2]$ ($R = Bu^t$, 2,6-xylyl) could be isolated.[375] Carbonyl substitution in $[OsBr(\eta^5\text{-}C_5Ph_5)(CO)_2]$ by $CNBu^t$, to generate $[OsBr(\eta^5\text{-}C_5Ph_5)(CNBu^t)(CO)]$, has also been reported requiring the presence of Me_3NO.[214]

Chloride substitution in $[RuCl(\eta^5\text{-}C_5R_5)(dippe)]$ ($R = H$, Me) by CO and $CNBu^t$ takes place in the presence of $Na[BPh_4]$ to yield the cationic species $[Ru(\eta^5\text{-}C_5R_5)(L)(dippe)][BPh_4]$ ($R = H$, $L = CO$, $CNBu^t$;* $R = Me$, $L = CO$, $CNBu^t$).[72] Similarly, treatment of $[RuCl\{\eta^5{:}\kappa^2(P,P)\text{-}C_5H_4CH_2CMe(CH_2PPh_2)_2\}]$ with CO and CNCy, in the presence of Tl[PF$_6$], generates [Ru{η^5:κ^2(*P*,*P*)-C$_5$H$_4$CH$_2$CMe(CH$_2$PPh$_2$)$_2$}(L)][PF$_6$] (L = CO, CNCy). The related complex [Ru{η^5:κ^2(*P*,*P*)-C$_5$H$_4$CH$_2$CMe(CH$_2$PPh$_2$)$_2$}(CNMe)][OTf] has been prepared by methylation of the neutral cyanide derivative [Ru(CN){η^5:κ^2(*P*,*P*)-C$_5$H$_4$CH$_2$CMe(CH$_2$PPh$_2$)$_2$}] with MeOTf.[128]

An unusual deoxygenation of one carbonyl ligand has been reported to occur in the reaction of [RuICp(CO)$_2$] with the iminophosphorane-phosphine Ph$_2$P(CH$_2$)$_3$N=PPh$_3$ which yields the isocyanide complex [RuICp{η^1-CN(CH$_3$)$_3$PPh$_2$}(CO)] via Ph$_3$P=O elimination.[392] As illustrated in Equation (16), a series of cationic vinyl isocyanide Ru(II) complexes **212** have been synthesized by ring-opening of the neutral 2-oxazolyl derivatives **211** through their selective *O*-alkylation with alkyloxonium salts.[393]



211 **212** (16)

6.14.3.7 Complexes Containing η^2-, η^3-, η^4-, and η^5-Ligands

Treatment of [RuClCp(dippe)] with alkynes RC≡CR (R = CO$_2$Me, H), in the presence of Na[BPh$_4$] as chloride abstractor, gives the cationic π-alkyne complexes [RuCp(η^2-RC≡CR)(dippe)][BPh$_4$] (R = CO$_2$Me, H).[394] Following a similar synthetic approach, the sugar-based derivatives **213** and **214**, and the tethered compound **215**[*] have been readily synthesized starting from the appropriate chloride precursor (Figure 28).[128,395] Displacement of one triisopropylphosphine ligand in [OsClCp(PPr$^i_3$)$_2$] by PhC≡CPh affords the neutral compound [OsClCp(η^2-PhC≡CPh)(PPr$^i_3$)] which, in the presence of K[PF$_6$], undergoes an intramolecular hydrogen-transfer process from the phosphine PPr$^i_3$ to the π-coordinated alkyne leading to the stilbene derivative [OsCp{κ^3(*P*,*C*,*C*)-Pr$^i_2$PCMe=CH$_2$}(η^2-(*Z*)-PhCH=CHPh)][PF$_6$].[*362] When propargylic alcohols are used, the metastable compounds [OsClCp(η^2-HC≡CCR$_2$OH)(PPr$^i_3$)] (R = Ph, Me; R$_2$ = -(CH$_2$)$_5$-) are formed, isomerizing thermally into the more stable allenylidene or alkenylvinylidene isomers (see Chapter 6.15).[195,396] Remarkably, treatment of [OsClCp(η^2-HC≡CCR$_2$OH)(PPr$^i_3$)] (R = Ph, Me) with Tl[PF$_6$] leads to [OsCp(η^2-HC≡CCR$_2$OH)(PPr$^i_3$)][PF$_6$] (R = Ph,[*] Me), in which the propargylic alcohol acts as a four-electron donor ligand.[397] Reduction of allyl–Ru(IV) complexes [RuX$_2$(η^3-1-C$_3$H$_4$R^1)Cp*] (R^1 = H, Me; X = Cl, Br) with Rieke zinc in the presence of alkynes has been reported to yield the Ru(II) derivatives [Ru(η^3-1-C$_3$H$_4$R^1)Cp*(η^2-R^{2}C≡CR^3)] (R^1 = H, R^2 = R^3 = Ph,[*] Me, SiMe$_3$; R^1 = H, R^2 = Me, R^3 = SiMe$_3$; R^1 = Me, R^2 = R^3 = Ph, Me) which, under thermal conditions, undergo an allyl–alkyne coupling to give acyclic η^5-dienyls [RuCp*{η^5-CH(R^1)CHCHC(R^2)CH(R^3)}].[398] The reversible coordination of acetylene, as well as ethylene, to the 16-electron species [RuCp{κ^2(*N*,*N*)-tmeda}][BAr$^F_4$] has also been described.[77]

Cationic π-olefinic derivatives [RuCp(η^2-CH$_2$=CHR){κ^2(*P*,*P*)-(*p*-Tol)$_2$PCH$_2$CH$_2$P(*p*-Tol)$_2$}][BF$_4$] (R = Ph, 2-C$_6$H$_4$NO$_2$)[399] and [Ru(η^5-C$_5$R$_5$)(η^2-CH$_2$=CH$_2$)(dippe)][BPh$_4$] (R = H,[*] Me)[72] are readily obtained from the reactions of [RuClCp{κ^2(*P*,*P*)-(*p*-Tol)$_2$PCH$_2$CH$_2$P(*p*-Tol)$_2$}] and [RuCl(η^5-C$_5$R$_5$)(dippe)], respectively, with the appropriate olefin in the presence of Ag[BF$_4$] or Na[BPh$_4$]. In contrast, the closely related cationic compounds [RuCp(η^2-CH$_2$=CHR)(CO)$_2$][PF$_6$] (R = Me, Pr^n, *n*-C$_{14}$H$_{29}$) have been prepared by reacting the alkyl complexes [Ru(CH$_2$CH$_2$R)Cp(CO)$_2$] with [Ph$_3$C][PF$_6$], via hydride abstraction from the β-carbon atom.[400] Treatment of the hemilabile complex [RuCp*{κ^2(*P*,*O*)-P ~ O}{κ^1(*P*)-P ~ O}][BPh$_4$] (P ~ O = (1,3-dioxan-2-ylmethyl)diphenylphosphine) with ethylene leads to the ready cleavage of the Ru–O bond resulting in the quantitative and reversible formation of [RuCp*(η^2-CH$_2$=CH$_2$){κ^1(*P*)-P ~ O}$_2$][BPh$_4$].[88] The cationic bis-alkene complex [OsCp(η^2-HN=CH$_2$)(η^2-CH$_2$=CH$_2$)$_2$][OTf] is also known, being obtained by bubbling ethylene through a dichloromethane solution of the methylimido species [OsCp(≡NMe)(CH$_2$SiMe$_3$)$_2$][OTf].[401]

The neutral olefinic compound [OsClCp{η^2-CH$_2$=CHC(Me)=O}(PPr$^i_3$)] is accessible by the substitution of one PPr$^i_3$ ligand in [OsClCp(PPr$^i_3$)$_2$] by methyl vinyl ketone.[195] Remarkably, coordination of the enone takes place selectively through the carbon–carbon double bond instead of the C=O group. Complex [OsClCp(PPr$^i_3$)$_2$] is also able to promote the decomposition of ethyl diazoacetate to generate [OsClCp(η^2-EtO$_2$CCH=CHCO$_2$Et)(PPr$^i_3$)] which contains a molecule of π-coordinated diethyl maleate.[195] The related ruthenium complexes [RuClCp(η^2-EtO$_2$CCH=CHCO$_2$Et)(PPh$_3$)] and [RuClCp*(η^2-EtO$_2$CCH=CHCO$_2$Et)(PPh$_3$)] have been similarly

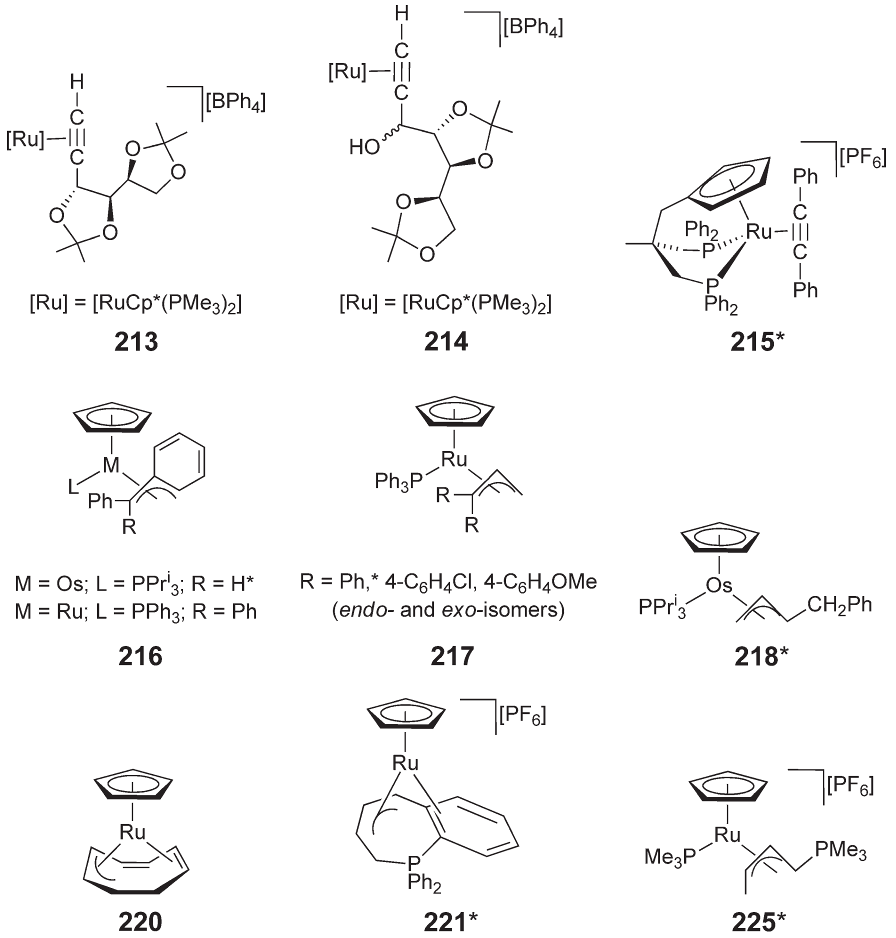
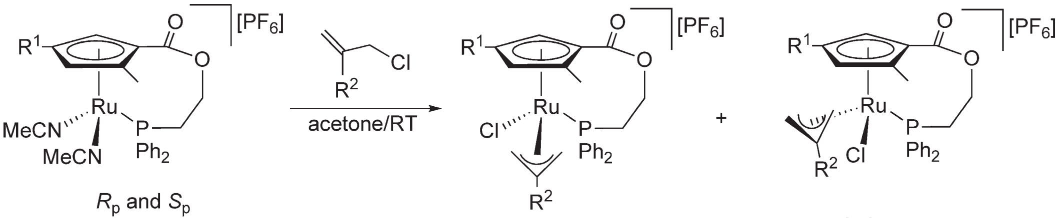


Figure 28 Some examples of η^2-alkyne and η^3-allyl complexes.

synthesized.[97,402] Treatment of [Ru(η^3-2-C_3H_4Me)Cp*(PPh_3)] with HCl under an ethylene atmosphere generates [RuClCp*(η^2-$CH_2{=}CH_2$)(PPh_3)] which readily reacts with HC$\equiv$CMe yielding the π-allene complex [RuClCp*(η^2-$CH_2{=}C{=}CH_2$)(PPh_3)], via ethylene substitution and concomitant metal-assisted alkyne–allene tautomerization. If the internal alkyne $Me_3SiC{\equiv}CCO_2Et$ is used instead of propyne, the stable π-alkyne complex [RuClCp*(η^2-$Me_3SiC{\equiv}CCO_2Et$)(PPh_3)] is formed.[97] π-Olefin ligands can also result from the coupling between carbene and alkyl moieties. Thus, alkylation of osmium and ruthenium carbenic species [OsClCp(=CHPh)($PRPr^i_2$)] (R = Pr^i, CMe=CH_2) and [RuClCp(=CR^1R^2)(PPh_3)] ($R^1 = R^2$ = Ph, 4-C_6H_4Cl, 4-C_6H_4OMe; R^1 = H, R^2 = Ph, $SiMe_3$) with LiMe leads to the corresponding alkene–hydride derivatives [OsHCp(η^2-$CH_2{=}CHPh$)($PRPr^i_2$)] (R = Pr^i, CMe=CH_2)[403,404] and [RuHCp(η^2-$CH_2{=}CR^1R^2$)(PPh_3)] ($R^1 = R^2$ = Ph, 4-C_6H_4Cl, 4-C_6H_4OMe; R^1 = H, R^2 = Ph, $SiMe_3$),[97] respectively. These reactions can be rationalized in terms of the addition of the nucleophilic Me^- unit to the carbenic carbon, followed by the dissociation of the chloride and final β-elimination. In contrast to these results, treatment of [OsClCp(=CHPh)(PPr^i_3)] and [RuClCp(=CR_2)(PPh_3)] (R = Ph, 4-C_6H_4Cl, 4-C_6H_4OMe) with LiPh, BrMgCH=CH_2, or ClMgCH_2CH=CH_2 selectively affords the allyl species 216–218 (Figure 28).[97,403] Addition of bromide to carbyne [OsHCp($\equiv$CCH_2Ph)(PPr^i_3)] promotes its rearrangement into the styrene derivative [OsBrCp(η^2-$CH_2{=}CHPh$)(PPr^i_3)].[*405]

Oxidative addition of a variety of allyl chlorides or bromides to the tris(acetonitrile) complex [RuCp*($NCMe)_3$][PF_6] results in the formation of the stable (η^3-allyl)–Ru(IV) derivatives [RuX(η^3-1,2-$C_3H_3R^1R^2$)Cp*(NCMe)][PF_6] ($R^1 = R^2$ = H, X = Cl; R^1 = H, R^2 = Me, X = Cl; R^1 = Me, R^2 = H, X = Cl, Br;* R^1 = Ph, Pr^n, R^2 = H, X = Cl).[406] In a similar way, treatment of [RuCp(L)($NCMe)_2$][PF_6] with allyl bromide generates [RuBr(η^3-C_3H_5)Cp(L)][PF_6] (L = NCMe, PPh_3, PCy_3, PMe_3, $AsPh_3$, $SbPh_3$).[24,141] The complex

$[RuBr(\eta^3\text{-}C_3H_5)Cp(PPh_3)][PF_6]$ undergoes nucleophilic addition of Et_3N yielding the π-olefinic derivative $[RuBr(\eta^2\text{-}CH_2{=}CHCH_2NEt_3)Cp(PPh_3)][PF_6]$.*[141] The reactivity of planar-chiral cyclopentadienyl ruthenium complexes **142** toward allyl chlorides has also been explored (Equation (17)). The chirality at the ruthenium center in the resulting products **219**, which are obtained with de of 60–98%, depends mainly on the substituent at the 4-position of the cyclopentadienyl group. Nucleophilic additions of Et_3N to allyl complexes **219** have also been reported.[407]



(17)

R_p and S_p

142

S_pR_{Ru} and R_pS_{Ru}

S_pS_{Ru} and R_pR_{Ru}

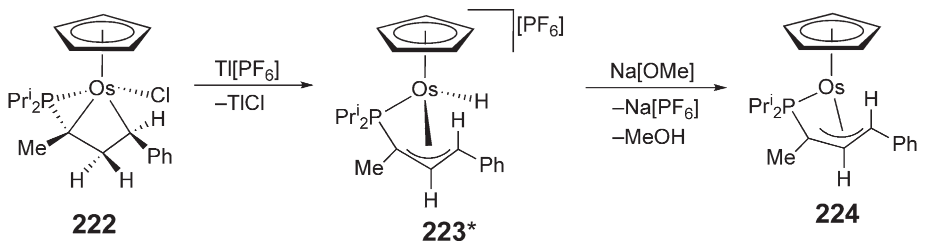
R^1 = Me; R^2 = H, Me*
R^1 = Ph; R^2 = H, Me
R^1 = Bu^t; R^2 = H, Me

219

The previously known allyl–Ru(IV) complexes $[RuCl_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5R^1{}_5)]$ ($R^1 = H$, Me) are suitable starting materials for the preparation of the novel neutral derivatives $[RuCl_2(\eta^3\text{-}1,1,2\text{-}C_3H_2R^2R^3R^4)(\eta^5\text{-}C_5R^1{}_5)]$ ($R^1 = R^3 = R^4 = H$, $R^2 = Me$ (two isomers); $R^1 = R^4 = H$, $R^2 = R^3 = Me$; $R^1 = R^2 = Me$, $R^3 = R^4 = H$; $R^1 = R^4 = Me$, $R^2 = CH_2Cl$, $R^3 = H^*$) via allyl group exchange. This metathetical process involves the initial reduction of $[RuCl_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5R^1{}_5)]$ with Et_3Al at low temperature, followed by the *in situ* oxidative addition of the appropriate allylic chloride.[408] The related complex $[RuCl_2(\eta^3\text{-}1\text{-}C_3H_4Ph)Cp^*]^*$ has been synthesized by direct oxidative addition of cinnamyl chloride to $[RuClCp^*(COD)]$.[409] Oxidative addition of I_2 or Cl_2 to half-open ruthenocenes $[Ru\{\eta^5\text{-}CH_2C(R)CHC(R)Y\}Cp^*]$ ($Y = CH_2$, $R = Me$; $Y = O$, $R = Me$, Bu^t) generates the neutral allyl–Ru(IV) complexes $[RuX_2\{\eta^3\text{-}CH_2C(R)CHC({=}Y)R\}Cp^*]$ ($X = Cl$, I; $Y = CH_2$, $R = Me$; $X = Cl$, I, $Y = O$, $R = Me$, Bu^t) which are in all cases formed as mixtures of *endo,anti*/*exo,syn* isomers. The oxodienyl derivative $[Ru\{\eta^5\text{-}CH_2C(Me)CHC(Me)O\}Cp^*]$ also reacts with two-electron donor ligands affording the allyl–Ru(II) species $[Ru\{\eta^3\text{-}CH_2CMeCHC({=}O)Me\}Cp^*(L)]$ ($L = CO$, PPh_3, $PHPh_2$, PMe_3).[160] Treatment of the dimeric tetramethylfulvene–Ru(II) complex $[\{RuCl_2(\eta^6\text{-}C_5Me_4CH_2)\}_2]$ with an excess of $ClMgCH_2CH{=}CH_2$ gives the tethered compound $[Ru(\eta^3\text{-}C_3H_5)(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)]^*$ in which allyl moieties have added both to the fulvene methylene carbon and to the ruthenium center.[410] Oxidative addition of allyl chloride to fulvene $[(RuCl_2\{\eta^6\text{-}1,2\text{-}C_5Me_3(CF_3)CH_2\})_2]$, leading to $[RuCl_2(\eta^3\text{-}C_3H_5)\{\eta^5\text{-}1,2\text{-}C_5Me_3(CF_3)CH_2Cl\}]$, has also been reported.[381]

Nucleophilic addition of a hydride ion to the cationic species $[RuCp(\eta^6\text{-cyclooctatetraene})][PF_6]$ results in the formation of the neutral complex **220** in which the *cyclo*-C_8 ligand is η^5-coordinated to ruthenium through one allyl and one olefinic unit (Figure 28).[411] The related cationic complex **221**,* featuring also an η^5-allyl–olefin coordination of the organic fragment, is also known (Figure 28). It has been obtained in the reaction of $[RuCp(PPh_3)(NCMe)_2][PF_6]$ with acetylene as the result of the coupling of two acetylene molecules with the coordinated PPh_3 ligand.[412]

Treatment of the dimeric precursor $[\{OsBr(\mu\text{-}Br)Cp^*\}_2]$ **132** with 3-bromo-2-methylpropene or 1,3-cyclooctadiene affords the 2-methylpropenyl and cyclooctenyl products $[OsBr_2(\eta^3\text{-}2\text{-}C_3H_4Me)Cp^*]$ and $[OsBr_2(\eta^3\text{-}C_8H_{13})Cp^*]$,* respectively. The former reacts with an excess of LiEt to yield the ethylene–Os(II) complex $[Os(\eta^3\text{-}2\text{-}C_3H_4Me)Cp^*(\eta^2\text{-}CH_2{=}CH_2)]$ via initial formation of the diethyl species $[OsEt_2(\eta^3\text{-}2\text{-}C_3H_4Me)Cp^*]$ which undergoes a β-elimination process followed by reductive elimination of ethane. A variety of alkyl–allyl Os(IV) derivatives have also been prepared using complex $[OsBr_2(\eta^3\text{-}2\text{-}C_3H_4Me)Cp^*]$ as starting material (see Chapter 6.15).[211,413] The cationic allyl–Os(IV) derivative $[OsH(\eta^3\text{-}2\text{-}C_3H_4Ph)(\eta^5\text{-}C_5H_4SiPh_3)(PPr^i{}_3)][BF_4]^*$ has been synthesized by thermal isomerization of the carbyne complex $[OsH({\equiv}CCHMePh)(\eta^5\text{-}C_5H_4SiPh_3)(PPr^i{}_3)][BF_4]$.[414] According to Equation (18), the abstraction of the chloride ligand in the osmaphosphabicyclopentane **222** provokes the destruction of the bicycle affording the cationic α-allylphosphine complex **223*** which can be readily deprotonated with NaOMe to give the neutral derivative **224**.[404]



(18)

Vinylidene and allenylidene ligands can be also used as precursors of allyl-type units. Thus, the reaction of the neutral vinylidene $[\mathrm{RuCl({=}C{=}CHCO_2Me)Cp(PPh_3)}]$ with $\mathrm{Sn(CH{=}CH_2)_4}$, in the presence of CuCl, gives the (2-4η)-butadienyl compound $[\mathrm{Ru}(\eta^3\text{-}\mathrm{CH_2CHC{=}CHCO_2Me)Cp(PPh_3)}]$.[415] A similar C–C coupling process leading to the formation of the (3-5η)-pentatrienyl derivatives $[\mathrm{Ru}(\eta^3\text{-}\mathrm{CH_2CHC{=}C{=}CPh_2)Cp^*}\{\kappa^1(P)\text{-}\mathrm{Pr^i_2PCH_2CO_2Me}\}]$ and $[\mathrm{Os}(\eta^3\text{-}\mathrm{CH_2CHC{=}C{=}CPh_2)Cp(PPr^i_3)}]$ occurs on treatment of the allenylidene compounds $[\mathrm{RuCl({=}C{=}C{=}CPh_2)}$-$\mathrm{Cp^*}\{\kappa^1(P)\text{-}\mathrm{Pr^i_2PCH_2CO_2Me}\}]$ and $[\mathrm{OsCl({=}C{=}C{=}CPh_2)Cp(PPr^i_3)}]$, respectively, with $\mathrm{BrMgCH{=}CH_2}$.[396,415]

Displacement of the acetonitrile ligands by dienes in $[\mathrm{RuCp(L)(NCMe)_2}][\mathrm{PF_6}]$ readily takes place affording complexes $[\mathrm{RuCp(L)}(\eta^4\text{-diene})][\mathrm{PF_6}]$ (diene = COD, L = $\mathrm{PPh_3}$, $\mathrm{PMe_3}$, NCMe; diene = butadiene, L = $\mathrm{PMe_3}$, NCMe; diene = isoprene, L = $\mathrm{PMe_3}$).[141] Remarkably, reaction of $[\mathrm{RuCp(NCMe)}(\eta^4\text{-butadiene})][\mathrm{PF_6}]$ with an excess of $\mathrm{PMe_3}$ yields the allyl–phosphonio derivative **225*** (Figure 28), via nucleophilic attack of the phosphine on the coordinated diene, subsequent 1,4-hydrogen shift, and concomitant $\mathrm{MeCN/PMe_3}$ exchange.[101] Treatment of planar-chiral complexes **142** (see Equation (17)) with a variety of prochiral dienes also leads to the expected ligand exchange reaction that generates the corresponding (η^4-diene)–ruthenium derivatives with high enantiofacial selectivity (up to 99% de).[416,416a*] The reaction of 2-(*tert*-butyldimethylsiloxy)-4-methyl-1,3-pentadiene with the tetramer $[\{\mathrm{RuCp^*Cl}\}_4]$ generates the corresponding diene complex $[\mathrm{RuClCp^*}(\eta^4\text{-diene})]^*$ which is spontaneously converted into the sandwich species $[\mathrm{RuCp^*}(\eta^5\text{-dienyl})]^*$ via release of HCl.[417]

Treatment of $[\mathrm{RuXCp^*}(\eta^4\text{-butadiene})]$ (X = Cl, Br) with an excess of butadiene in the presence of Ag[OTf] followed by CO results in the formation of $[\mathrm{RuCp^*}(\eta^4\text{-COD})(\mathrm{CO})][\mathrm{OTf}]$. A similar [4 + 4]-cycloaddition also occurs in the reaction of $[\mathrm{RuClCp^*}(\eta^4\text{-isoprene})]$ with isoprene, Ag[OTf], and CO to give $[\mathrm{RuCp^*}(\eta^4\text{-3,7-dimethyl-1,5-cyclooctadiene})(\mathrm{CO})][\mathrm{OTf}]$. Remarkably, when the reactions of $[\mathrm{RuXCp^*}(\eta^4\text{-butadiene})]$ (X = Cl, Br) with butadiene and Ag[OTf] are performed in the absence of CO, linear dimerization of butadiene takes place affording $[\mathrm{RuCp^*}(\eta^6\text{-1,3,7-octatriene})][\mathrm{OTf}]$.* Regioselective dimerization of 1,3-pentadiene also occurs in the reaction of $[\mathrm{RuClCp^*}(\eta^4\text{-1,3-pentadiene})]$ with Ag[OTf] and an excess of 1,3-pentadiene, which gives the bis(allyl) derivative $[\mathrm{Ru}\{\text{4-methyl-(1-3-}\eta^3\text{:6-8-}\eta^3\text{)-nonadienediyl}\}\mathrm{Cp^*}][\mathrm{OTf}]$.*[418]

The reactions of $[\mathrm{RuCp}\{\kappa^1(P)\text{-}\mathrm{Ph_2PNHPh}\}(\mathrm{NCMe})_2][\mathrm{PF_6}]$ with terminal alkynes $\mathrm{HC{\equiv}CR}$ (R = Ph, Bu^n, Bz) lead to the formation of the η^4-butadiene–amido complexes **226** as the result of the coupling of two molecules of the alkyne with the coordinated phosphine (Figure 29). When 1,6-heptadiyne and 1,7-octadiyne are used, a related intramolecular C–C coupling takes place leading to complexes **227**.[419] Reactions of the tethered derivative $[\mathrm{RuCl}(\eta^5\text{:}\eta^2\text{-}\mathrm{C_5Me_4CH_2OCH_2CH{=}CH_2})(\mathrm{CO})]$ with alkynes $\mathrm{R^1C{\equiv}CR^2}$ in the presence of Ag[BF$_4$] give the cationic

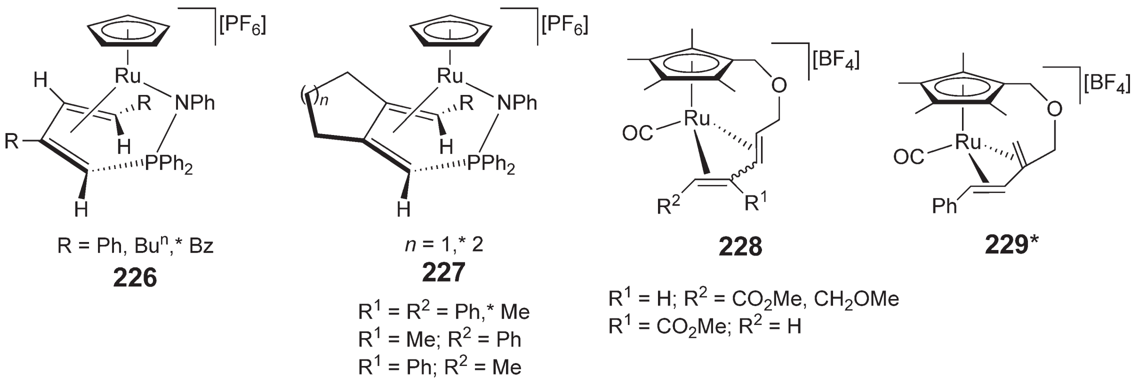
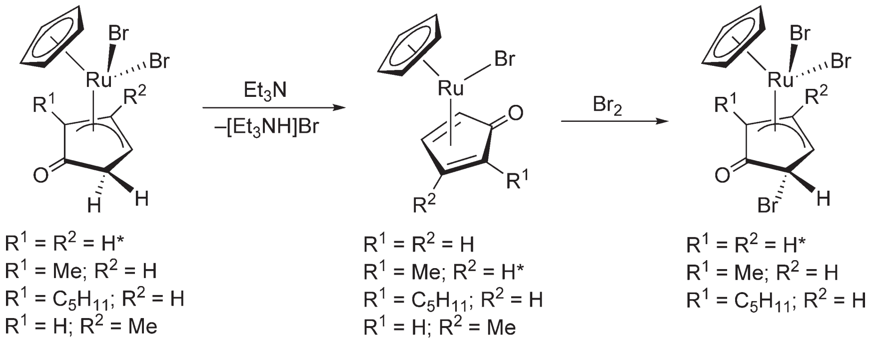


Figure 29 The η^4-diene Ru(II) derivatives 226–229.



230 **231** **232**

Scheme 18

diene chelates 228 (*E*- and *Z*-isomers) and 229* (Figure 29). Formation of 228 is the result of the regiospecific addition of the acetylenes to the terminal carbon of the allylic ether. In contrast, 229* results from the addition of phenylacetylene to the internal carbon of the olefin.[420]

A variety of (η^3-cyclopentenoyl)ruthenium(IV) complexes 230 (Scheme 18) has been synthesized by reacting [RuBrCp(COD)] with 4-bromo-2-cyclopenten-1-ones. Addition of Et_3N to solutions of these compounds gives rise to facile dehydrobromination, giving the corresponding (η^4-cyclopentadienone)ruthenium(II) complexes 231 which undergo oxidative addition of Br_2 to yield the novel (η^3-cyclopentenoyl)–Ru(IV) derivatives 232. Remarkably, bromine addition occurs in all cases *anti* to the coordinated ruthenium and exclusively α to the C=O moiety.[421,421a] Related (η^3-cyclopentenoyl)–Ru(II) complexes [RuCp(η^3-C_5H_4O-2-PR_3)(L)][OTf] (L = py, $PR_3 = PBu^n_3$, PCy_3, PMe_2Ph, PMe_3; L = thiourea, $PR_3 = PBu^n_3$,* PCy_3, PMe_2Ph, PMe_3) are also known. They have been obtained by regioselective *anti*-nucleophilic addition of monodentate phosphines PR_3 to the cyclopentadienone (C_5H_4O) ligand in complexes [RuCp(η^4-C_5H_4O)(L)][OTf]. In solution, compounds [RuCp(η^3-C_5H_4O-2-PR_3)(L)][OTf] spontaneously convert into the corresponding 1,2-disubstituted ruthenocenes [RuCp(η^5-C_5H_3OH-2-PR_3)][OTf].[99]

Bromine addition reactions to diene complexes of general formula [RuBr(η^5-C_5R_5)(η^4-diene)] have been extensively studied by Kirchner and co-workers, the nature of the resulting products being strongly dependent on the substitution pattern of the diene moiety. Thus, starting from 1,3-butadiene and mono- and 1,2-disubstituted-1,3-butadiene complexes, bromo-substituted Ru(IV) *anti*-η^3-allyl complexes 233 are formed in high yields (Figure 30). This process involves addition of bromine on the *exo*-face of the diene ligand which takes place regioselectively at the terminal carbon bearing no substituent.[422,423] 1,4-Disubstituted 1,3-butadiene complexes also react with Br_2 to give the bromo-substituted (η^3-allyl)–Ru(IV) derivatives 234, adopting in this case the *syn*-configuration exclusively. These compounds are not stable in solution and decompose, by release of the free diene, into the dimeric species [{$RuBr_3Cp^*$}$_2$] and [{$RuBr_3$(η^5-C_5Me_4Et)}$_2$].*[423] In contrast to these results, bromination of 2,3-disubstituted-1,3-butadiene complexes affords the novel cationic (η^4-diene)–Ru(IV) derivatives 235 isolated as the corresponding triflate salts after Br^-/OTf^- exchange with Ag[OTf].[422,423] Treatment of complex [$RuBr_2Cp^*$(η^4-butadiene)][OTf] (235; R = H) with [Et_4N]X and Na[O_2CCF_3] leads to the (η^3-allyl)–Ru(IV) derivatives 236 as the result of the *anti*-nucleophilic addition of the anions at a terminal carbon atom of the coordinated diene.[171] A related nucleophilic addition also occurs in the reaction of [$RuBr_2Cp^*$(η^4-butadiene)][OTf] with SEt_2. Thus, the cationic allyl complex 237 is initially formed, isomerizing slowly into the thermodynamically favoured *syn*-product 238.*[424]

6.14.4 Half-Sandwich η^6-Arene Compounds

6.14.4.1 Precursor Complexes [{MCl(μ-Cl)(η^6-arene)}$_2$] (M = Ru, Os)

The chloro-bridged dimers [{RuCl(μ-Cl)(η^6-arene)}$_2$] are the most common precursors used to prepare mononuclear half-sandwich arene ruthenium(II) derivatives. They are usually made by heating the appropriate cyclohexa-1,3-diene or cyclohexa-1,4-diene with $RuCl_3 \cdot nH_2O$ in ethanol, or eventually in methanol or acetone.[1] Recent synthetic efforts have been essentially focused on the preparation of chiral compounds. By the procedure described above, ruthenium dimers [{RuCl(μ-Cl)(η^6-arene)}$_2$] with the following functionalized arene ligands have been made: 9,10-dihydroanthracene,[425] $C_6H_5CHMeEt$,[426] 1,2,4-$C_6H_3Me_3$,[427] indane,*[428] $C_6H_5CO_2R$ (R = Me, Et*),[429,430] $C_6H_5(CH_2)_nCO_2R$ (n = 1, R = H, Et; n = 3, R = H),[431] $C_6H_5CO_2CH_2CH_2OC(=O)CMe=CH_2$,[432]

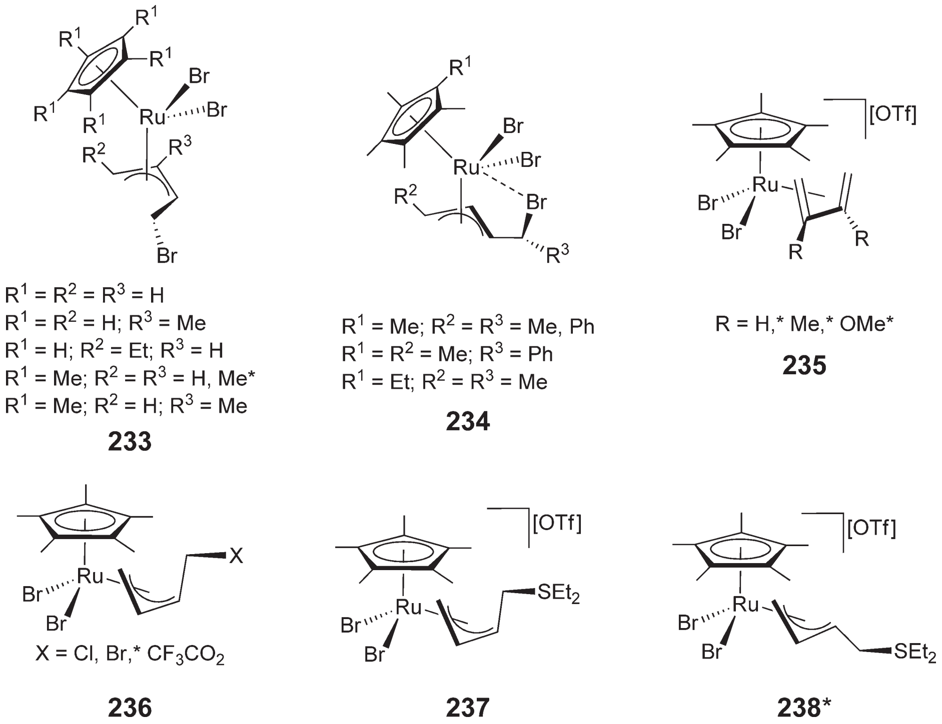


Figure 30 Structure of the Ru(IV) complexes 233–238.

$C_6H_5CH_2CH_2OC({=}O)R$ (R = Fc, Ph, $(CH_2)_3Ph$),[433,434] C_9H_9OH (239; Figure 31),[435] $C_9H_9OC({=}O)Fc$ (240; Figure 31),[436] (*S*)-$C_6H_5CHMeCH_2OH$,[437] $C_6H_5(CH_2)_nR$ (R = OH, $n = 3$; R = NH_3Cl, $n = 2$, 3; R = (*R*,*S*)-NHCHMeCHPhOH, $n = 3$),[438–440] (*R*)-$C_6H_5CHMeCH_2CH_2OH$,[441] (*R*)-$C_6H_5CH(CO_2Et)NHC({=}O)R$ (R = Me, CF_3),[442] and $[C_6H_5CH_2CH_2C_5H_8N_2][BF_4]$ (241; Figure 31).[443] A related synthetic method starting from $OsCl_3{\cdot}nH_2O$ has been employed to prepare the novel osmium dimers $[\{OsCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ (arene = toluene, C_6H_5Et, $C_6H_5Pr^i$, $C_6H_5Bu^t$) in high yields.[444] Complex 242* (Figure 31) has been obtained by an alternative procedure through an arene exchange process by heating $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$ in molten trindane at 175 °C during 4 days.[445] Treatment of zerovalent complexes $[M(\eta^4\text{-diene})(\eta^6\text{-arene})]$ (M = Ru, diene = COD, arene = C_6Et_6,*[446] $C_6H_5CHMeBu^t$;[426] M = Os, diene = cyclohexa-1,4-diene, arene = $[2_2]$-1,4-cyclophane)[447] with HCl affords the related dimeric compounds $[\{MCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ (see also Section 6.14.4.7). Reactions of the polymeric material $[\{RuCl_2(COD)\}_n]$ with the appropriate arene and zinc dust in refluxing THF, and subsequent

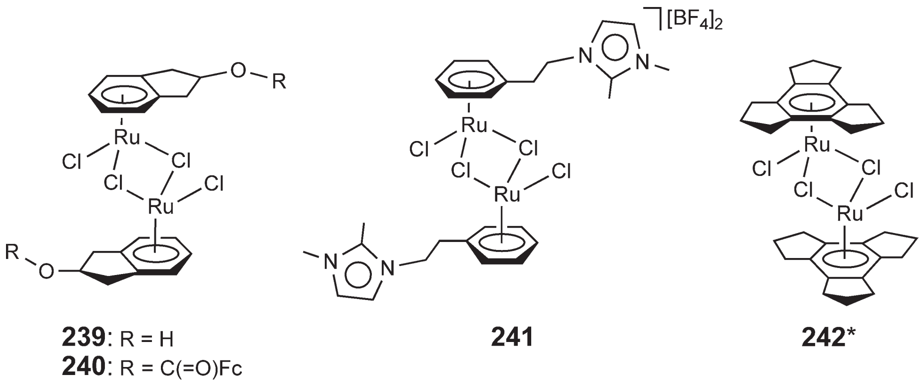


Figure 31 The dimeric Ru(II) derivatives 239–242.

addition of HCl to the resulting intermediate, provide the chloro-bridged dimers of biphenyl, bibenzyl, fluorene, and *trans*-stilbene in ca. 10–20 % yield.[3] The previously known complexes $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$,*[448] $[\{RuBr(\mu\text{-}Br)(\eta^6\text{-cym})\}_2]$,*[449] and $[\{RuI(\mu\text{-}I)(\eta^6\text{-cym})\}_2]$*[449] have been structurally characterized by X-ray diffraction methods.

The richness of the chemistry presented by half-sandwich ruthenium and osmium complexes arises from the following:

(i) The easy cleavage of the halide bridges in dimers $[\{MX(\mu\text{-}X)(\eta^6\text{-arene})\}_2]$ (M = Ru, Os; X = halide) by a two-electron donor ligand, L, which gives rise to mononuclear complexes $[MX_2(L)(\eta^6\text{-arene})]$.
(ii) The possibility of substituting one or two chloride ligands in order to prepare cationic and dicationic derivatives of the type $[MX(L^1)(L^2)(\eta^6\text{-arene})]^+$ and $[M(L^1)(L^2)(L^3)(\eta^6\text{-arene})]^{2+}$. These reactions are favored in polar solvents and/or in the presence of an halide abstractor.
(iii) The easy metathesis of the chloride atoms by other anionic ligands.

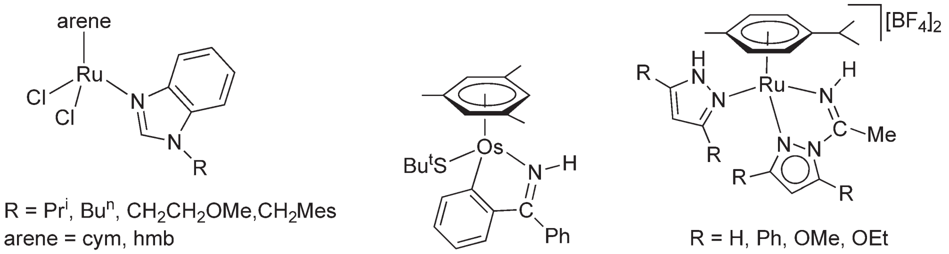
6.14.4.2 Complexes Containing N- and O-donor Ligands

6.14.4.2.1 Monodentate N-donor ligands

A wide range of complexes $[RuCl_2\{\kappa^1(N)\text{-}L\}(\eta^6\text{-arene})]$ which contain monodentate *N*-donor ligands has been synthesized through conventional methodology.[1] They include derivatives with: primary and secondary amines (L = 1,2-$H_2NC_6H_4OH$,[450] H_2NBz,*[451] $NHMe_2$),[452] hydrazines (L = $H_2N\overline{N(CH_2)_3C}HCH_2OMe$),[453] pyridines (L = 3-NC_5H_4-$NHCH_2Fc$,*[454] 4-NC_5H_4CN*),[455] pyrazoles (L = Me_2HPz*) (Me_2HPz = 3,5-dimethyl-1*H*-pyrazole),[456] imidazolines (L = $\overline{N{=}CHNRCH_2C}H_2$ (R = Et, Ph, CH_2CH_2OMe, CH_2Mes)),[457,458] imidazoles (complexes **243** in Figure 32; L = $\overline{N{=}CHN(4\text{-}C_6H_4CN)CH{=}C}H$),[459,460] tetrahydropyrimidines (L = $\overline{N{=}CHNR(CH_2)_2C}H_2$, R = Me, Bz, Ph, *p*-Tol),[457] and nitriles.[441] The reaction of $[\{OsCl(\mu\text{-}Cl)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2]$ with $HN{=}CPh_2$ leads to the monomer adduct $[OsCl_2\{\kappa^1(N)\text{-}HN{=}CPh_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ **244** in which the imine is coordinated via the nitrogen atom rather than through the C=N double bond.[461] Treatment of **244** with an equimolar amount of $NaSBu^t$ affords the cyclometallated complex **245** (Figure 32). Cationic complexes $[RuCl_2(NO)(\eta^6\text{-}C_6H_6)]Cl$ and $[RuCl_2(NS)(\eta^6\text{-}C_6H_6)]Cl$, containing a nitrosyl and thionitrosyl ligand, respectively, have also been described.[119]

Cationic derivatives of the type $[MCl\{\kappa^1(N)\text{-}L\}_2(\eta^6\text{-arene})]^+$ are formed by performing the reactions in polar solvents and/or in the presence of a halide scavenger. For example, bis(pyrazolyl) and bis(pyridyl) complexes $[RuCl\{\kappa^1(N)\text{-}HPz\}_2(\eta^6\text{-}C_6H_6)]Cl$*[456] (HPz = 1*H*-pyrazole) and $[RuCl\{\kappa^1(N)\text{-}3\text{-}NC_5H_4\text{-}NHCH_2Fc\}_2(\eta^6\text{-cym})][PF_6]$,[454] respectively, have been obtained by this procedure. In contrast, heating $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$ with pyrazoles and $[NH_4][BF_4]$ in acetonitrile affords the dicationic amidine complexes **246** (see Figure 32) as the result of a nitrogen–carbon coupling process between the acetonitrile and one pyrazole ligand.[462*] Mixed cationic complexes $[MCl(L^1)\{\kappa^1(N)\text{-}L^2\}(\eta^6\text{-arene})]^+$ are also known. They have been prepared from mononuclear compounds $[MCl_2(L^1)(\eta^6\text{-arene})]$ by reaction with the appropriate *N*-donor ligand in the presence of a chloride scavenger. Representative examples are the following: $[RuCl(L)\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CHMeCH_2CH_2PPh_2\}][BF_4]$ (L = H_2NPh,* HNC_5H_{10},* H_2NBz, H_2NBu^t, imidazole),[430] $[RuCl(PR_3)(L)(\eta^6\text{-arene})][PF_6]$ (PR_3 = PPh_3, PEt_3, $PMePr^i_2$; L = 4-NC_5H_4CN, 1,4-$C_6H_4(CN)_2$; arene = benzene, cym, hmb),[463*] and $[RuCl(L)\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5(CH_2)_3PPh_2\}][PF_6]$ (L = NCMe, py).[464]

Dicationic compounds $[Ru(L)\{\kappa^2(P,O)\text{-}Ph_2PCH(Me)P({=}O)Ph_2\}(\eta^6\text{-cym})][SbF_6]_2$ (L = py,* 3,5-lutidine, isoquinoline)[465] have been synthesized from the reaction of ($R_{Ru}S_C$/$S_{Ru}R_C$)-$[RuCl\{\kappa^2(P,O)\text{-}Ph_2PCH(Me)\text{-}P({=}O)Ph_2\}(\eta^6\text{-cym})][SbF_6]$ with $Ag[SbF_6]$ and the corresponding pyridine ligand. Epimerization at the metal center



R = Pr^i, Bu^n, CH_2CH_2OMe,CH_2Mes
arene = cym, hmb

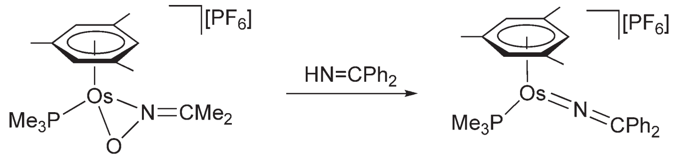
R = H, Ph, OMe, OEt

243 **245** **246**

Figure 32 Some (η^6-arene)-Ru(II) and Os(II) complexes with N-donor ligands.

occurs during the process giving rise in all cases to a mixture of diastereomers. The reaction of $[\{Ru(OTf)_2(\eta^6\text{-cym})\}_x]$ with indoline in acetonitrile, and in the presence of acetic acid, leads to $[Ru(NCMe)_2\{\kappa^1(N)\text{-indoline}\}(\eta^6\text{-cym})][OTf]_2$* (see also Section 6.14.2.1.1).[466]

Azavinylidene osmium derivatives $[Os(PPr^i_3)({=}N{=}CPh_2)(\eta^6\text{-arene})][PF_6]$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$) are readily available by treatment of $[Os\{\kappa^2(O,O)\text{-OAc}\}(PPr^i_3)(\eta^6\text{-arene})][PF_6]$ with an excess of diphenylketimine in dichloromethane.[461] The formation of these azavinylidenes is accompanied by the release of acetic acid. The analogous complex $[Os(PMe_3)({=}N{=}CPh_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]$ **248** has been prepared by an alternative route from diphenylketimine and the oximato osmium complex **247** (Equation (19)).[461]



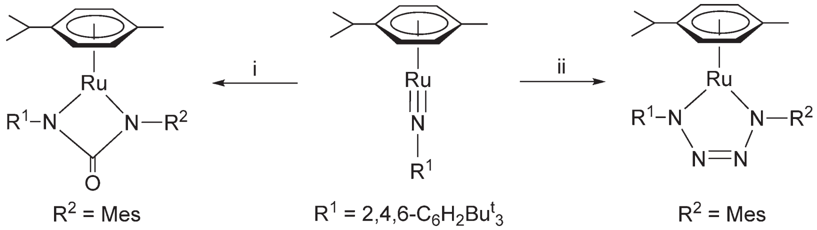
247 **248** (19)

A series of anionic monodentate *N*-donor ligands such as azido, isocyanato, isothiocyanato, and nitro groups have been used to form neutral pseudohalide complexes. They are usually obtained by exchange reactions between a chloride precursor and the appropriate sodium or silver salt of the ligand. Representative examples include the following:

(i) Compounds (R_C,S_{Ru})-$[RuX(C_{10}H_6CHMeNMe_2)(\eta^6\text{-}C_6H_6)]$ (X = N_3,* NCO,* NCS,* NO_2;* $C_{10}H_6$ = 2,3-naphthalenediyl)[467] obtained diastereoselectively from the treatment of a diastereomeric mixture of (R_C,S_{Ru})- and (R_C,R_{Ru})-$[RuCl(C_{10}H_6CH(Me)NMe_2)(\eta^6\text{-}C_6H_6)]$ **249** with NaN_3, AgNCO, NaNCS, or $NaNO_2$. For the ambidentate ligands NCO^-, NCS^- and NO_2^-, coordination through the nitrogen atom has been confirmed by X-ray diffraction analyses. When $[RuCl(C_6H_4CHMeNMe_2)(\eta^6\text{-}C_6H_6)]$ is used as starting material, instead of **249**, a small amount of the *O*-bonded NO_2^- and *S*-bonded NCS^- complexes is also formed.[468]

(ii) The bis(azido) and bis(isocyanato) complexes $[RuX_2\{\kappa^1(P)\text{-L}\}(\eta^6\text{-cym})]$ (L = $Ph_2PCH_2P\{{=}NP({=}O)(OR_2)\}Ph_2$ (R = Et, Ph), X = N_3, NCO*;[469] L = $Ph_2PCH_2P({=}NR)Ph_2$ (R = p-C_6F_4CN, p-C_5F_4N), X = N_3, NCO)[470] made from the cationic $[RuCl\{\kappa^2(P,O)\text{-L}\}(\eta^6\text{-cym})]^+$ or $[RuCl\{\kappa^2(P,N)\text{-L}\}(\eta^6\text{-cym})]^+$ precursors and an excess of NaN_3 or NaNCO, via chelate ring opening.

The unusual terminal imido complex $[Ru({\equiv}NAr)(\eta^6\text{-cym})]$* (Ar = 2,4,6-tri-*tert*-butylphenyl) **250**[471,472] has been prepared from the reaction of $[\{RuCl(\mu\text{-Cl})(\eta^6\text{-cym})\}_2]$ with 4 equiv. of Li[NHAr] in THF. The steric requirements of the imido substituent play a crucial role in the stabilization of such a species. In fact, dinuclear imido compounds, such as $[(\eta^6\text{-cym})Ru(\mu\text{-NAr})_2Ru(\eta^6\text{-cym})]$ (Ar = 2,6-diisopropylphenyl;* 2,6-xylyl), are isolated when less sterically demanding ligands are used.[471,472] Moreover, the analogous imido–osmium complex $[(\eta^6\text{-cym})Os(\mu\text{-NAr})_2Os(\eta^6\text{-cym})]$* (Ar = 2,6-diisopropylphenyl) previously described as a mononuclear species has been shown to be dinuclear, at least in the solid state.[471,472] Coupling between the imido ligand in **250** and mesityl isocyanate or mesityl azide leads to the corresponding non-symmetrical ureato **251*** and tetrazene **252*** derivatives (Scheme 19).[473] Treatment of $[Os({\equiv}NBu^t)(\eta^6\text{-cym})]$ with $HOCMe(CF_3)_2$ and dimethyl malonate gives rise to the formation of the amido



251* **250*** **252***

i, Mes-NCO, THF, RT; ii, Mes-N_3, light petroleum, –78 °C

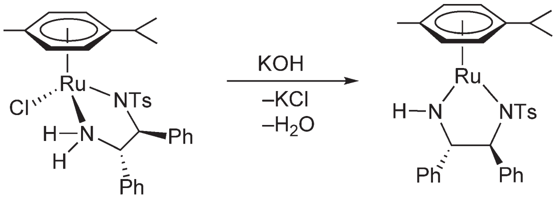
Scheme 19

complexes $[\mathrm{Os(NHBu^t)}\{\kappa^1(O)\text{-}\mathrm{OCMe(CF_3)_2}\}(\eta^6\text{-cym})]$ and $[\mathrm{Os(NHBu^t)}\{\eta^1\text{-}\mathrm{CH(CO_2Me)_2}\}(\eta^6\text{-cym})]$, respectively.[474] The derivatives $[\mathrm{RuI(R^1)(PMe_3)}(\eta^6\text{-hmb})]$ ($\mathrm{R^1 = Me, Ph}$) react with a slight excess of $\mathrm{K[NHR^2]}$ to give the corresponding anilide complexes $[\mathrm{Ru(NR^2H)(R^1)(PMe_3)}(\eta^6\text{-hmb})]$ ($\mathrm{R^1 = Ph, R^2 = Ph,}^*$ *p*-Tol; $\mathrm{R^1 = Me, R^2 = Ph}$)[475] **253**. Carbon dioxide inserts into the N–Ru bond of **253** to form the carbamate species $[\mathrm{Ru}\{\kappa^1(O)\text{-}\mathrm{OC({=}O)NHR^2}\}\mathrm{(R^1)(PMe_3)}(\eta^6\text{-hmb})]$ (see also Chapter 6.15).

6.14.4.2.2 Bidentate N-donor ligands

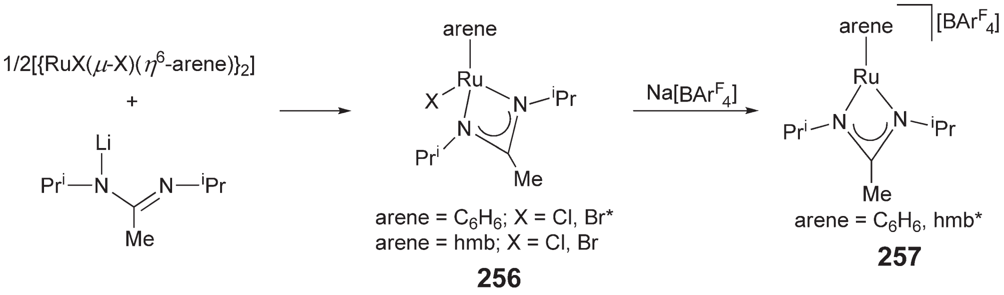
The synthesis of arene–ruthenium complexes containing diamino ligands has received considerable attention recently due to their anticancer properties as well as their applications in homogeneous catalysis. Thus, a wide range of complexes $[\mathrm{RuX}\{\kappa^2(N,N)\text{-}\mathrm{H_2NCH_2CH_2NHR}\}(\eta^6\text{-arene})][\mathrm{PF_6}]$ (X = Cl, I; R = H, Et, arene = C_6H_6, cym, biphenyl, 1,4,9,10-tetrahydroanthracene, 9,10-dihydroanthracene, $C_6H_5CO_2Et$; not all combinations),*[425,476,477] showing DNA recognition ability, have been prepared from the reactions of dimers $[\{\mathrm{RuX}(\mu\text{-X})(\eta^6\text{-arene})\}_2]$ with the appropriate diamine ligand in methanol or water, and subsequent counteranion exchange ($\mathrm{Cl^-/PF_6^-}$). Compounds $[\mathrm{RuCl}\{\kappa^2(N,N)\text{-L}\}(\eta^6\text{-arene})]\mathrm{Cl}$ (L = bis[(1*R*,2*S*)-2-hydroxy-1-methyl-2-phenylethyl]-1,2-diamino-ethane, arene = cym;*[478] L = (*S*)-2-aminomethyl-1-ethylpyrrolidine, (*S*)-2-(pyrrolidinylmethyl)pyrrolidine, (1*R*,2*R*)-1,2-diphenylethylenediamine, arene = C_6H_6, cym*[479]), containing chiral diamines, have been similarly synthesized. The osmium analog $[\mathrm{OsCl}\{\kappa^2(N,N)\text{-dabp}\}(\eta^6\text{-}C_6H_6)][\mathrm{PF_6}]$ (dabp = 1,1′-biphenyl-2,2′-diamine) has been obtained starting from the acetonitrile precursor $[\mathrm{OsCl_2(NCMe)}(\eta^6\text{-}C_6H_6)]$.[480]

Chiral amino–amide complexes $[\mathrm{RuCl}\{\kappa^2(N,N)\text{-L}\}(\eta^6\text{-arene})]$ (L = (1*S*,2*S*)- or (1*R*,2*R*)-$\mathrm{TsNCHPhCHPhNH_2}$, arene = C_6H_6,*[481] cym,*[482] 1,3,5-$C_6H_3Me_3$,*[483] $C_6H_5OCH_2CH_2OH$;*[484] L = (1*R*,2*R*)- or (1*S*,2*S*)-$\mathrm{ArSO_2NCHPhCHPhNH_2}$ (Ar = Mes, Napht), arene = C_6H_6, cym)[485] have been obtained in enantiomerically pure form from the reactions of $[\{\mathrm{RuCl}(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$ with chiral *N*-sulfonylated diamines in the presence of triethylamine. Treatment of $[\mathrm{RuCl}\{(1S,2S)\text{-}\mathrm{TsNCHPhCHPhNH_2}\}(\eta^6\text{-cym})]^*$ **254** with 1 equiv. of KOH in dichloromethane gives the formally 16-electron diamido derivative $[\mathrm{Ru}\{(1S,2S)\text{-}\mathrm{TsNCHPhCHPhNH}\}(\eta^6\text{-cym})]^*$ **255** (Equation (20); see also Section 6.14.4.6).[482] The X-ray structure analysis of **255** reveals a square-planar geometry around the ruthenium atom. The HN–Ru distance (1.897 Å), shorter than the N–Ru bond in an amide complex but longer than that shown by ruthenium–imido derivatives, evidences the significant double bond character for this nitrogen–ruthenium bond. Species **255** has proved to be a highly selective catalyst for asymmetric transfer hydrogenation of ketones.



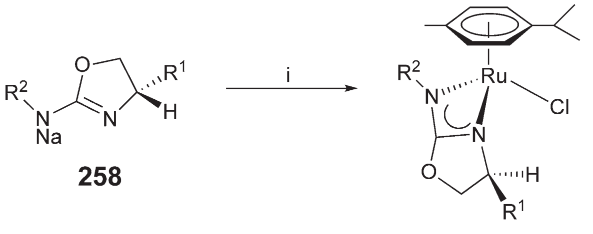
254* **255*** (20)

Neutral amidinate complexes $[\mathrm{RuX}\{\kappa^2(N,N)\text{-}\mathrm{CMe(NPr^i)_2}\}(\eta^6\text{-arene})]$ **256** have been synthesized by reacting the dimers $[\{\mathrm{RuX}(\mu\text{-X})(\eta^6\text{-arene})\}_2]$ with the lithium salts of the appropriate ligands (Scheme 20).[486] The related cationic compounds **257** are obtained by exchange of the halogen atom with the weakly coordinating $\mathrm{BAr^F{}_4}$ counteranion.



Scheme 20

DFT calculations on the model $[Ru\{\kappa^2(N,N)\text{-}CH(NH)_2\}(\eta^6\text{-}C_6H_6)]^+$ suggest that the coordination of π-electrons of the amidinate ligand stabilizes these 16-electron ruthenium species. As expected, the unsaturated compounds **257** readily react with two-electron donor ligands affording the corresponding 18-electron adducts $[Ru(L)\{\kappa^2(N,N)\text{-}CMe(NPr^i)_2\}(\eta^6\text{-arene})][BAr^F_4]$ (L = CO, py, $H_2C{=}CH_2$, PPh_3, $CNBu^t$). Photoirradiation of the related amidinate compound $[RuCl\{\kappa^2(N,N)\text{-}CPh(NBu^t)_2\}(\eta^6\text{-}C_6H_6)]$ in toluene, anisole, or fluorobenzene leads to the formation of $[RuCl\{\kappa^2(N,N)\text{-}CPh(NBu^t)_2\}(\eta^6\text{-}C_6H_5R)]$ (R = Me, OMe,* F) as the result of the arene ligand substitution.[487] The diazaallyl derivative $[RuCl\{\kappa^2(N,N)\text{-}(NPh)_2CNHPh\}(\eta^6\text{-cym})]$* was made by reacting an excess of 1,2,3-triphenylguanidine with $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$.[488] Coordination of the chiral amino-oxazolinates **258** to an arene–ruthenium(II) fragment has also been reported leading to complexes **259**, isolated as single diastereomers (Equation (21)).[489]



258

259

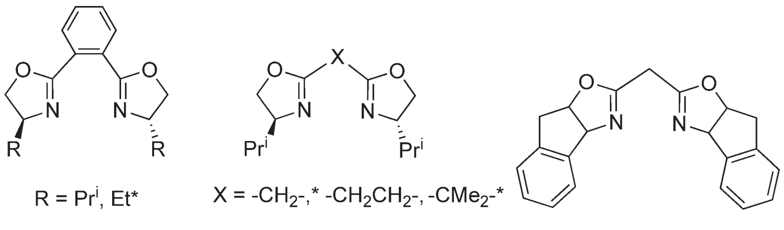
$R^1 = Bu^t$; R^2 = Ph,* 3,5-$C_6H_3Me_2$, adamantyl
$R^1 = R^2$ = Ph
i, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$ in THF

(21)

In the context of studies directed to the application of arene–ruthenium(II) complexes to asymmetric catalysis, a wide range of cationic $[RuCl\{\kappa^2(N,N)\text{-}L_2\}(\eta^6\text{-arene})]^+$ complexes containing optically active bis-oxazoline ligands (e.g., arene = cym, 1,3,5-$C_6H_3Me_3$; L_2 = **260**, **261**, **262**) have been prepared following classical synthetic routes (Figure 33).[490–493] Related ruthenium(II) and osmium(II) derivatives bearing $\kappa^2(N,N)$-coordinated bipyridine-type ligands (L_2 = 1,1′-biisoquinoline,*[494] dipyrido[3,2-*a*:2′,3′-*c*]phenazine,*[495] bipy[496]) have also been synthesized. Reduction of $[MCl(bipy)(\eta^6\text{-arene})][PF_6]$ (M = Ru, Os; arene = benzene, cym, hmb) with potassium affords the highly sensitive zerovalent derivatives $[M(bipy)(\eta^6\text{-arene})]$.[496]

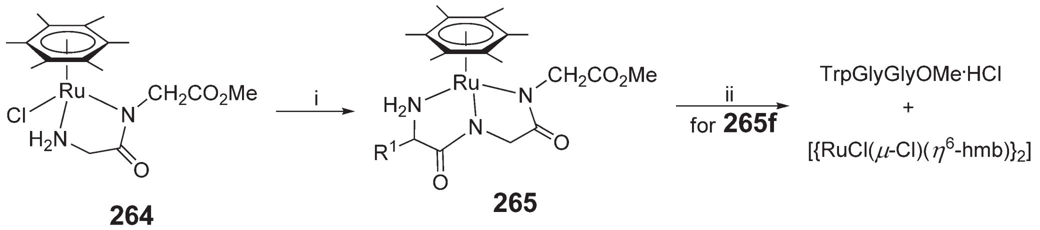
6.14.4.2.3 Tridentate N-donor ligands

Dicationic complexes $[Os\{\kappa^3(N,N,N)\text{-}L\}(\eta^6\text{-arene})][PF_6]_2$ (arene = cym, C_6H_6; L = 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn),* 1,4,7-triazacyclononane (tacn)*) have been obtained by heating the dimeric precursors $[\{OsCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ with the appropriate triamino ligand in methanol and further treatment with $Na[PF_6]$ or $[NH_4][PF_6]$.[497] This synthetic approach fails in the preparation of the ruthenium analog $[Ru\{\kappa^3(N,N,N)\text{-}tmtacn\}(\eta^6\text{-}C_6H_6)]^{2+}$ which can be alternatively synthesized from the reaction of $[RuCl_3\{\kappa^3(N,N,N)\text{-}tmtacn\}]$, Ag[OTf], and 1,3-cyclohexadiene.[155] The (*p*-cymene)-ruthenium(II) fragment can act as a template in the self-condensation of 2-aminobenzaldehyde giving rise to the selective formation of the triimino derivative **263*** (Equation (22)).[498] Arene–ruthenium(II) units have also been used as mediators in the synthesis of linear tripeptides. As an example, the diglycine methyl ester compound $[RuCl\{\kappa^2(N,N)\text{-}GlyGlyOMe\}(\eta^6\text{-hmb})]$ **264** reacts with amino acid esters affording complexes **265a–f** (Scheme 21). Demetallation of the tripeptide formed in **265f** can be readily achieved upon treatment with a methanolic HCl solution.[499] Tricoordinated tris(pyrazolyl)borate and tris(pyrazolyl)methane derivatives $[Ru\{\kappa^3(N,N,N)\text{-}RX(Pz)_3\}(\eta^6\text{-arene})]^{n+}$ (X = B, *n* = 1, R = H,* isopinocampheyl,* arene = benzene, cym, 1,2,4,5-$C_6H_2Me_4$; X = C, *n* = 2, R = H, arene = benzene, cym,* 1,2,4,5-$C_6H_2Me_4$; not all combinations)[500–503]



260 **261** **262**

Figure 33 The bis-oxazoline ligands **260–262**.

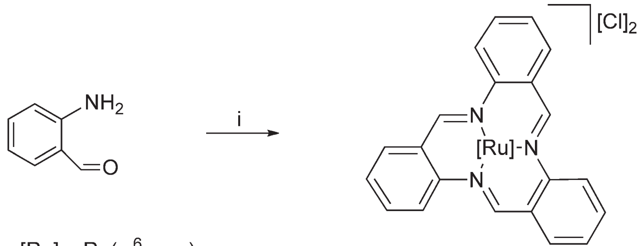


i, 1 equiv. $[NH_3CHR^1CO_2R^2]Cl$ (R^2 = Me, Et), 2 equiv. NaOMe, MeOH; ii, HCl in MeOH

265a: R^1 = H*	**265d**: R^1 = Bu^i
265b: R^1 = Me	**265e**: R^1 = Bz
265c: R^1 = Pr^i	**265f**: R^1 = CH_2-indole-3-yl

Scheme 21

were prepared using the acetonitrile solvates $[RuCl_2(NCMe)(\eta^6\text{-arene})]$ as precursors. In the presence of $Na[BH_4]$, NaOH, and KCN, complex $[Ru\{\kappa^3(N,N,N)\text{-}HB(Pz)_3\}(\eta^6\text{-}C_6H_6)][PF_6]$ undergoes nucleophilic attack on the arene ring generating the η^5-cyclohexadienyl derivatives **266** (Equation (23)).[502,503] Encapsulation of the Ru^{2+} cation by the ligand 1,3,5-tris(1-methylimidazol-2-ylmethyl)-2,4,6-trimethylbenzene **267**, leading to the arene derivative **268** (Equation (24)), has also been reported.[504]

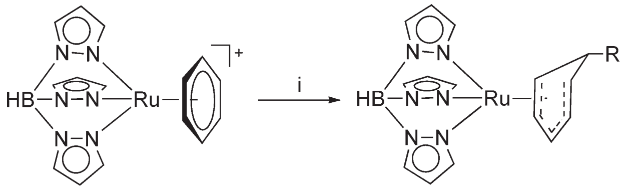


[Ru] = Ru(η^6-cym)

i, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$/EtOH/reflux

263*

(22)

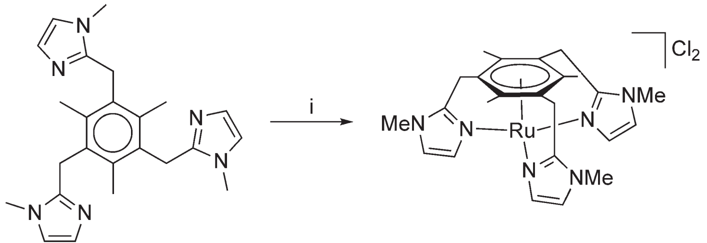


R = OH, H, CN*

266

i, NaOH in MeOH, $Na[BH_4]$ in THF or KCN in THF

(23)



267 **268**

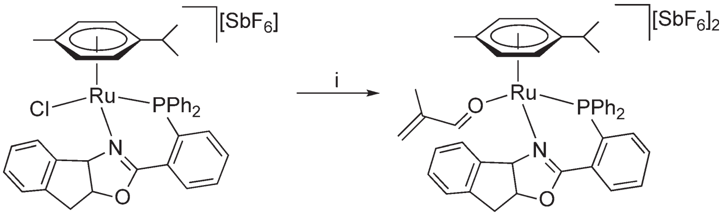
i, $[RuCl_2(DMSO)_4]$, EtOH/H_2O, Δ, 10 h

(24)

6.14.4.2.4 O-donor ligands

In aqueous solution, the carbenic derivative [RuCl$_2$(η^1-L)(η^6-cym)] (L = $\overline{\text{CNMeCH=CHN}}$Bu^n) readily transforms into the mono- and diaqua species [RuCl(H$_2$O)(η^1-L)(η^6-cym)]Cl and [Ru(H$_2$O)$_2$(η^1-L)(η^6-cym)]Cl$_2$. The reversibility of this process was confirmed after addition of KCl.[505] Similarly, complex [RuCl{κ^2(*O,O*)-acac}(η^6-cym)] spontaneously undergoes chloride dissociation in water to form [Ru(H$_2$O){κ^2(*O,O*)-acac}(η^6-cym)]Cl **269**, as assessed by conductivity and spectroscopic measurements. A ^{1}H NMR pH titration of **269** gave a pK_a value of 9.41 for the aqua ligand.[506] This value, considerably higher than that observed for [Ru(H$_2$O){κ^2(*N,N*)-H$_2$NCH$_2$CH$_2$NH$_2$}(η^6-cym)]$^{2+}$ (pK_a = 8.25),[477] has been attributed to the high electron density on the ruthenium atom conferred by the acac ligand. Addition of ammonia, methylamine or *n*-butylamine to a solution of [Ru(H$_2$O){κ^2(*N,N*)-bpop}(η^6-C$_6$H$_6$)][BF$_4$]$_2$* (bpop = 2,2-bis[4(*R*)-phenyl-1,3-oxazolon-2-yl]propane) in CH$_2$Cl$_2$ leads to [Ru(NH$_2$R){κ^2(*N,N*)-bpop}(η^6-C$_6$H$_6$)][BF$_4$]$_2$ (R = H, Me,* Bu^n) by substitution of the coordinated water molecule.[507] In contrast, reactions with secondary or tertiary amines such as NHEt$_2$ and NEt$_3$ generate, as inferred by NMR spectroscopy, the hydroxo complex [Ru(OH){κ^2(*N,N*)-bpop}(η^6-C$_6$H$_6$)][BF$_4$]. Nevertheless, all attempts to isolate this highly unstable species failed.

The dicationic arene–ruthenium(II) units have a great Lewis acid character which makes them able to coordinate aldehydes. Thus, treatment of **270** with Ag[SbF$_6$] and a large excess of methacrolein affords the corresponding dicationic adduct **271*** (Equation (25)).[508] An X-ray diffraction study showed a κ^1(O)-coordination mode of the methacrolein ligand which adopts an *s-trans*-configuration. Complexes [Ru{κ^1(*O*)-O=CHPh}{κ^2(*P,O*)-Ph$_2$PCH$_2$P(=O)Ph$_2$}(η^6-cym)][SbF$_6$]$_2$*[509] and [Os{κ^1(*O*)-aldehyde}{κ^2(*P,O*)-Ph$_2$PCH(Me)P(=O)Ph$_2$}(η^6-cym)]-[SbF$_6$]$_2$ (aldehyde = *trans*-cinnamaldehyde,* methacrolein, crotonaldehyde)[510] have been similarly prepared.



(25)

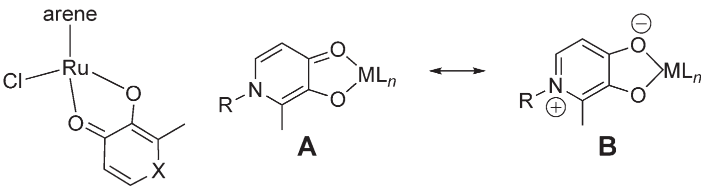
270 **271***

i, Ag[SbF$_6$], CH$_2$Cl$_2$/acetone, methacrolein

Although alcohols are known to be extremely labile ligands, some stable arene–ruthenium(II) complexes containing intramolecularly coordinated alcohol functions have been synthesized. Thus, thermal treatment of a methanolic solution of [{RuCl(μ-Cl)(η^6-(*R*)-C$_6$H$_5$CHMeCH$_2$CH$_2$OH)}$_2$] **272** leads to the formation of the tethered-type derivative [RuCl$_2${η^6:κ^1(*O*)-(*R*)-C$_6$H$_5$CHMeCH$_2$CH$_2$OH}].*[441] Related cationic complexes [RuCl(L){η^6:κ^1(*O*)-(*R*)-C$_6$H$_5$CHMeCH$_2$CH$_2$OH}][BF$_4$] (L = phosphine, phosphite, pyridine) have been obtained through a two-step process using **272** as precursor. This involves the initial treatment of **272** with the appropriate L ligand and subsequent reaction of the resulting adducts with Ag[BF$_4$]. The dicationic tethered compounds [Ru{κ^2(*N,N*)-L}{η^6:κ^1(*O*)-C$_6$H$_5$(CH$_2$)$_3$OH}][BF$_4$]$_2$ (L = bipy, phen,* (*R*)-bpop*) have also been described.[438] Remarkably, these species can be easily deprotonated affording the corresponding alkoxides [Ru{κ^2(*N,N*)-L}{η^6:κ^1(*O*)-C$_6$H$_5$(CH$_2$)$_3$O}][BF$_4$]. The unsaturated bis(alkoxide)–Os(II) complex [Os(OBu^t)$_2$(η^6-cym)] has been synthesized by reacting [{OsCl(μ-Cl)(η^6-cym)}$_2$] with 3 equiv. of KOBu^t in THF.[474] Treatment of this complex with H$_2$NBu^t generates the imido derivative [Os(≡NBu^t)(η^6-cym)]. Related reactions with pinacol or catechol provide the corresponding pinacolate or catecholate derivatives [Os{κ^2(*O,O*)-L$_2$}(η^6-cym)] (L$_2$ = -OCMe$_2$CMe$_2$O-, 1,2-C$_6$H$_4$O$_2$).

Mono(acetylacetonate) complexes [MCl{κ^2(*O,O*)-L}(η^6-arene)] (M = Ru, Os; arene = benzene, *o*-xylene, 1,3,5-C$_6$H$_3$Me$_3$, hmb; L = acac, hexafluoroacetylacetonate; not all combinations) are readily obtained by reacting [{MCl(μ-Cl)(η^6-arene)}$_2$] with a two-fold excess of the appropriate thallium or sodium salt of the ligand.[511] Addition of a supplementary equivalent of acac to the benzene or xylene derivatives generates the bis(acetylacetonate) complexes [M(η^1-acac){κ^2(*O,O*)-acac}(η^6-arene)] (M = Ru, arene = benzene; M = Os, arene = benzene, *o*-xylene*), in which the incoming ligand is η^1-coordinated to the metal through the central carbon atom. In contrast, when more sterically demanding arenes, such as mesitylene or hexamethylbenzene, are present, the second acac ligand bonds to the metal through the oxygen atom, giving rise to the selective formation of [M{κ^1(*O*)-acac}{κ^2(*O,O*)-acac}(η^6-arene)] (M = Ru, arene = 1,3,5-C$_6$H$_3$Me$_3$, hmb; M = Os, arene = 1,3,5-C$_6$H$_3$Me$_3$,* hmb).

Treatment of [{OsCl(μ-Cl)(η^6-arene)}$_2$] (arene = cym, 1,3,5-C$_6$H$_3$Me$_3$) with an excess of silver tosylate leads to the bis(tosylato) derivatives [Os{κ^1(*O*)-OTs}{κ^2(*O,O*)-OTs}(η^6-arene)].[512] The ^{1}H NMR spectra of these compounds display, both at 295 and 243 K, only one set of signals for the C$_6$H$_4$ and Me protons of the tosylate units, indicating



arene = cym
273a–d: X = NMe, NPr^n,* NPh, N-2-C$_6$H$_4$CO$_2$Me
arene = 1,3,5-C$_6$H$_3$Me$_3$
274*: X = O

Figure 34 The resonance forms of complexes **273**.

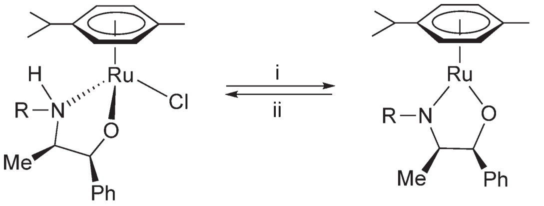
that a rapid interconversion between the κ^1- and the κ^2-bonding modes occurs. The bis(dialkylcarbamato) species [Ru{κ^1(*O*)-O$_2$CNEt$_2$}{κ^2(*O,O*)-O$_2$CNEt$_2$}(η^6-cym)] has been similarly prepared.[452]

Sodium salts of *N*-substituted hydroxypyridones (generated *in situ*) readily react with [{RuCl(μ-Cl)(η^6-cym)}$_2$] to form the mononuclear complexes **273** (Figure 34).[513] X-ray diffraction analysis of **273b** reveals that the zwitterionic form “B” contributes significantly to the electronic structure of these compounds. The electron-donating character of the pyridone ligands facilitates the substitution of the chloride ligand by amines, phosphines, or water under smooth conditions. The pyranone derivative **274***, showing similar properties, is also known.[514]

6.14.4.2.5 Mixed N,O-donor ligands

In the context of studies devoted to elucidate the stereochemical stability of chiral-at-metal complexes, Brunner and coworkers have synthesized a wide range of arene–ruthenium and –osmium derivatives containing coordinated chiral Schiff bases derived from salicylaldehyde. In particular, complexes [MCl{κ^2(*N,O*)-2-OC$_6$H$_4$CH═N-(*S*)-CR^{1}R^{2}R^3}(η^6-arene)] (M = Ru, Os; arene = benzene, cym, 1,3,5-C$_6$H$_3$Me$_3$, hmb; R^1/R^2/R^3 = napht/H/Me, Cy/H/Me, CH$_2$OH/H/Pr^i, CO$_2$Me/H/Pr^i, CO$_2$Bz/H/Pr^i, CO$_2$Me/H/Ph, CO$_2$Me/H/Bz, Ph/H/Me; not all combinations)[515] have been prepared and shown to be configurationally labile at the metal center in solution. As an example, when the diastereomerically pure compound (R_{Os},S_{C})-[OsCl{κ^2(*N,O*)-2-OC$_6$H$_4$CH═NCHPr^i(CO$_2$Me)}(η^6-cym)]* (($R_{\mathrm{Os}}S_{\mathrm{C}}$)-**275**) is dissolved in CD$_2$Cl$_2$ at −60 °C, it experiences a rapid epimerization process upon warming up the sample, the 65 : 35 ratio observed between ($R_{\mathrm{Os}}S_{\mathrm{C}}$)-**275** and ($S_{\mathrm{Os}}S_{\mathrm{C}}$)-**275** at room temperature corresponding to the thermodynamic equilibrium.[515] Erroneous conclusions concerning the stereochemical behavior of similar complexes previously reported have been revisited by Brunner (see also Chapter 6.15).[516] Remarkably, the compound [RuCl{κ^2(*N,O*)-2-OC$_6$H$_4$CH═N-(*S*)-CHPr^i(CO$_2$Me)}(η^6-cym)] **276** has found to crystallize as a 1 : 1 mixture of the two diastereoisomers ($R_{\mathrm{Ru}}S_{\mathrm{C}}$)-**276** and ($S_{\mathrm{Ru}}S_{\mathrm{C}}$)-**276** in the same lattice.[517,518] This surprising fact is attributed to the molecular recognition between both diastereomers through hydrogen bonds of the type C–H···Cl and C–H···O. Related behavior has also been observed for several similar complexes. In contrast, crystals obtained from the analogous osmium derivative ($R_{\mathrm{Os}}S_{\mathrm{C}}$/$S_{\mathrm{Os}}S_{\mathrm{C}}$)-**275** contain the $R_{\mathrm{Os}}S_{\mathrm{C}}$ diastereoisomer exclusively.[517,518]

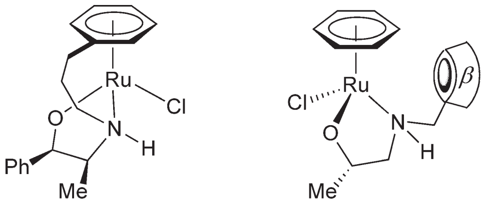
A large number of *in situ* generated chiral alkoxo–amino complexes of the type [RuCl{κ^2(*N,O*)-L}(η^6-arene)] (HL = β-amino alcohol) have been used as pre-catalysts for the transfer hydrogenation of ketones. However, only a few derivatives have been isolated and fully characterized. Thus, compound **277*** is readily obtained by reacting [{RuCl(μ-Cl)(η^6-cym)}$_2$] with (1*S*,2*R*)-*N*-(4-biphenylmethyl)norephedrine in the presence of NEt$_3$.[519] Treatment of **277** with 1 equiv. of KOH in CH$_2$Cl$_2$ generates the 16-electron alkoxo–amido complex **278** which rapidly reverts into **277** when dissolved in CHCl$_3$, via HCl capture (Equation (26)).[519] Other ruthenium derivatives [RuCl{κ^2(*N,O*)-L}(η^6-arene)] (arene = cym, L = (1*S*,2*R*)-OCHPhCHPhNH$_2$;*[520] arene = C$_6$H$_6$, L = (1*R*,2*R*)-OCHPhCHPh-NH$_2$),[521], analogous to **277**, have also been described. In addition, related complexes containing a tethered ligand **279**[440] or a β-cyclodextrin moiety **280**[522] are known (Figure 35).



277* R = CH$_2$-4-C$_6$H$_4$Ph **278**

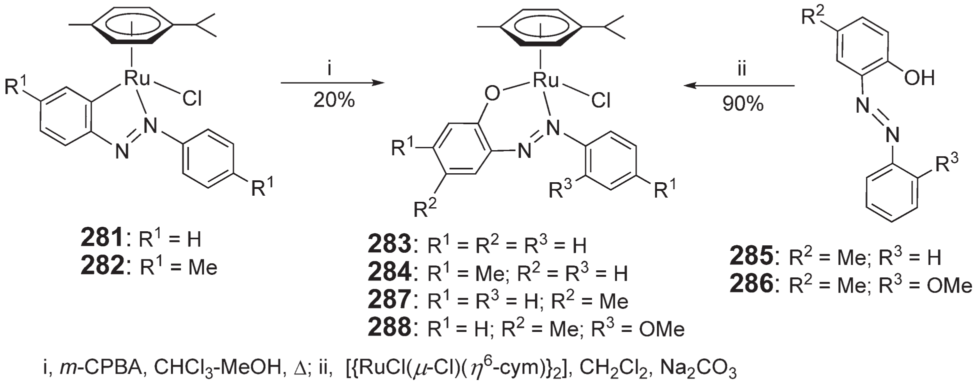
i, 1 equiv. KOH, CH$_2$Cl$_2$, 40 °C, 20 min; ii, CHCl$_3$, 20 °C, 30 min

(26)



279 **280**

Figure 35 Structure of the Ru(II) complexes 279 and 280.



281: $R^1 = H$
282: $R^1 = Me$

283: $R^1 = R^2 = R^3 = H$
284: $R^1 = Me; R^2 = R^3 = H$
287: $R^1 = R^3 = H; R^2 = Me$
288: $R^1 = H; R^2 = Me; R^3 = OMe$

285: $R^2 = Me; R^3 = H$
286: $R^2 = Me; R^3 = OMe$

i, *m*-CPBA, $CHCl_3$-MeOH, Δ; ii, [{RuCl(μ-Cl)(η^6-cym)}$_2$], CH_2Cl_2, Na_2CO_3

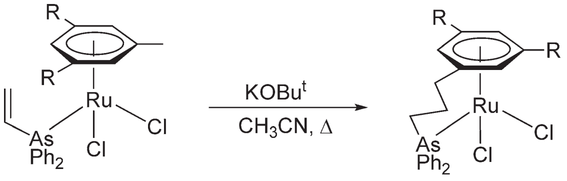
Scheme 22

It has been described that treatment of azophenyl complexes 281 and 282 with *m*-chloroperbenzoic acid affords the azophenolate derivatives 283 and 284 in low yields (≈20%), as the result of oxygen insertion into the ruthenium–carbon bond (Scheme 22).[523] An alternative synthetic approach starting from [{RuCl(μ-Cl)(η^6-cym)}$_2$] and azophenol ligands 285 and 286 allows the preparation of analogous species 287 and 288 (Scheme 22).

6.14.4.3 Complexes Containing P-, As-, and Sb-donor Ligands

6.14.4.3.1 As- and Sb-donor ligands

Neutral and cationic derivatives have been prepared through conventional methodologies using both monodentate and bidentate arsine and stibine ligands. Thus, monodentate arsines and stibines readily cleave the chloride bridges of [{MCl(μ-Cl)(η^6-arene)}$_2$] to generate mononuclear complexes [MCl_2(L)(η^6-arene)] (M = Ru, arene = cym, L = $SbPr^i_3$,[524] $SbCy_3$, $AsCy_3$;[525] M = Ru, arene = toluene,* cym,* *o*-xylene,* *p*-xylene,* 1,3,5-$C_6H_3Me_3$,* 1,2,4,5-$C_6H_2Me_4$,* hmb, L = $Ph_2AsCH{=}CH_2$, $Cy_2AsCH{=}CH_2$ (not all combinations);[526] M = Os, arene = 1,3,5-$C_6H_3Me_3$, L = $AsPr^i_3$, $SbPr^i_3$).[527] Further treatment of [$RuCl_2${κ^1(*As*)-$AsPh_2(CH{=}CH_2)$}(η^6-arene)] (arene = toluene, 1,3,5-$C_6H_3Me_3$) 289 with $KOBu^t$ in refluxing acetonitrile affords the tethered-type complexes 290 as the result of a C–C coupling process between the vinylic function and a methyl substituent of the arene ligand (Equation (27)).[526] The cleavage of the azido bridges in [{RuX(μ-N_3)(η^6-hmb)}$_2$] (X = Cl, N_3) by triphenylarsine, which yields [RuX(N_3)($AsPh_3$)(η^6-hmb)] (X = Cl, N_3), has also been described.[528] Coordination of arsines and stibines can be also achieved through exchange reactions as clearly exemplified in the substitution of the carbene ligand in [$OsCl_2$(=CPh_2)(η^6-1,3,5-$C_6H_3Me_3$)] by EPr^i_3 (E = Sb, As) or the pyridine ligand in [$RuCl_2$(4-NC_5H_4CN)(η^6-cym)] by EPh_3 (E = Sb, As), which provides [$OsCl_2(EPr^i_3)$(η^6-1,3,5-$C_6H_3Me_3$)][512] and [$RuCl_2(EPh_3)$(η^6-cym)],[455] respectively.



R = H, Me* **289** R = H, Me **290** (27)

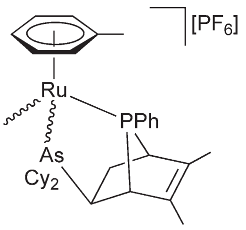
Cationic complexes are also accessible. As examples, the bis(arsine) and bis(stibine) derivatives $[RuCl(ER_3)_2(\eta^6\text{-cym})][Y]$ ($R = Pr^i$, $E = Sb$, $Y = PF_6$;[524] $R = Ph$, $E = As, Sb$, $Y = BF_4$)[529] have been conventionally synthesized starting from dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$, $[NH_4][PF_6]$ or $[NH_4][BF_4]$, and an excess of the appropriate ER_3 ligand in methanol. In contrast, under similar reaction conditions, if $Ag[PF_6]$ is used as chloride abstractor, the hydrido–Ru(II) complexes $[RuH(EPh_3)_2(\eta^6\text{-arene})][PF_6]$ ($E = As$, Sb; arene $= C_6H_6$, cym, hmb) are formed selectively.[530] The chloride ligand in $[RuCl\{\kappa^2(S,S)\text{-}S_2P(OEt)_2\}(\eta^6\text{-cym})]$ is easily replaced by $AsPh_3$ affording $[Ru(AsPh_3)\{\kappa^2(S,S)\text{-}S_2P(OEt)_2\}(\eta^6\text{-cym})]^+$ which has been isolated as the corresponding BPh_4 salt.[531] Compounds $[RuCl(EPh_3)\{\overline{N{=}CHN(4\text{-}C_6H_4CN)CH{=}CH}\}(\eta^6\text{-arene})]^+$ ($E = As$, Sb; arene $= C_6H_6$, cym, hmb) have been similarly prepared starting from $[RuCl_2\{\overline{N{=}CHN(4\text{-}C_6H_4CN)CH{=}CH}\}(\eta^6\text{-arene})]$.[459]

Complexes containing bidentate *As,P*- and *As,O*-donor ligands are also known. Representative examples include: $[RuCl(\kappa^2\text{-}L)(\eta^6\text{-cym})]^+$ ($L = (S_C)$-1-[(R_P)-2-(diphenylarsino)ferrocenyl]ethyldicyclohexylphosphine.[532] $Bu^t_2AsCH_2CH_2PPh_2$, $Bu^t_2AsCH_2PPr^i_2$, $Bu^t_2AsCH_2CH_2P({=}O)Ph_2$)[533] and complex **291*** isolated as a mixture of two diastereomers (Figure 36).[534]

No examples of arene–ruthenium or osmium complexes containing bismuthine ligands has been reported up to now.

6.14.4.3.2 P-donor ligands

Due to the continuous interest in the use of half-sandwich $[M(\eta^6\text{-arene})]$ fragments as classical organometallic moieties to coordinate mono- and polydentate phosphines, a large number of novel derivatives have appeared since COMC (1995). Most of them have been designed for further reactivity studies including their use as pre-catalysts. Only a few reports deal with the study of the physicochemical properties of this type of complexes. In this regard, the enthalpies of the reactions between $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$ and 19 different monodentate phosphine or phosphite ligands have been measured, the values ranging from -55.3 to $-33.4\,\text{kcal mol}^{-1}$.[535] The enthalpy trend can be explained in terms of electronic and steric contributions, both of them playing an important role. On the other hand, ^{187}Os NMR spectra of a large series of osmium complexes $[OsCl_2\{P(OR)_3\}(\eta^6\text{-cym})]$ **292** ($R = Me$,* Et, Bu^n, Ph, Pr^i), $[OsCl_2(PR_3)(\eta^6\text{-cym})]$ **293** ($PR_3 = PMe_3$,* PMe_2Ph, PPh_2Me, PBz_3,* PBu^n_3, PPh_3,* $P(m\text{-}Tol)_3$, PPr^i_3, PCy_3), $[OsI_2(PR_3)(\eta^6\text{-cym})]$ **294** ($PR_3 = PMe_2Ph$, PPh_2Me, PBu^n_3, PPh_3, PPr^i_3, PCy_3) have been recorded showing chemical shift values in the range -3201 to -1697 ppm.[444] The observed ^{187}Os chemical shifts within the series **293** and **294** are linearly dependent on Tolman's steric parameter θ of the phosphine ligand, with the osmium nucleus becoming progressively more deshielded as larger phosphine ligands are introduced. In contrast, the chemical shifts in the series **292** vary with the electronic properties of the phosphite ligands.



291*

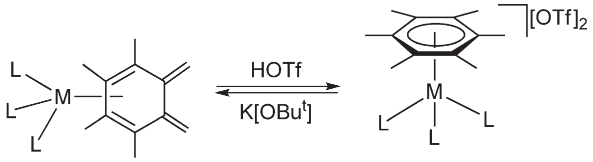
Figure 36 Structure of the arene-ruthenium complex **291**.

The following series of phosphino complexes have been reported:

(i) A large number of mononuclear adducts of the type $[MX_2(L)(\eta^6\text{-arene})]$ (L = phosphine) made conventionally from $[\{MX(\mu\text{-}X)(\eta^6\text{-arene})\}_2]$ (M = Ru, Os; X = Cl, I, Br).[1] In particular, the coordination of the appropriate ligand L gives rise to water-soluble (L = $P(CH_2OH)_3$,[536] TPPTS; TPPTS = tris-3-sulfonatophenylphosphine trisodium salt)[537] or enantioselective (L = chiral phosphoramidites)*[538] pre-catalysts, biologically active complexes (L = PTA)*[539,448] or spin-labeled derivatives (L = $p\text{-}Ph_2PC_6H_4N(Bu^t)O^{\cdot}$).[540] In some cases, due to the low solubility of dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)\}_2]$, the corresponding monomeric adducts are generated in low yields. In these cases, improved yields are generally obtained using the acetonitrile solvate $[RuCl_2(NCMe)(\eta^6\text{-}C_6H_6)]$ as starting material.[541]

(ii) Cationic bis(phosphine) complexes $[MX(L^1)(L^2)(\eta^6\text{-arene})]^+$ are readily obtained from the reaction of mononuclear derivatives $[MX_2(L^1)(\eta^6\text{-arene})]$ (M = Ru, Os; X = halide; L^1 = phosphine) with a halide abstractor and the appropriate ligand. As an example, treatment of $[OsCl_2(L)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (L = PMe_3, PPh_3, PCy_3) with stoichiometric amounts of $[NH_4][PF_6]$ and PMe_3 in methanol leads to the formation of $[OsCl(PMe_3)(L)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]$ (L = PMe_3, PPh_3, PCy_3).[527]

(iii) The tris(phosphine) derivative $[Os(PMe_2Ph)_3(\eta^6\text{-}1,2\text{-}C_6H_4Me_2)][PF_6]_2$ is formed by heating $[Os\{\kappa^2(O,O)\text{-}O_2CCF_3\}\{\kappa^1(O)\text{-}O_2CCF_3\}(\eta^6\text{-}1,2\text{-}C_6H_4Me_2)]$ with an excess of PMe_2Ph and $[NH_4][PF_6]$ in methanol.[542] Related hexamethylbenzene complexes **296** have been prepared by protonation of the *endo*-tetramethyl-*o*-xylylene species **295*** with HOTf. This process is reversible, the zerovalent derivatives **295** being readily regenerated upon treatment of **296** with base (Equation (28)).[543]

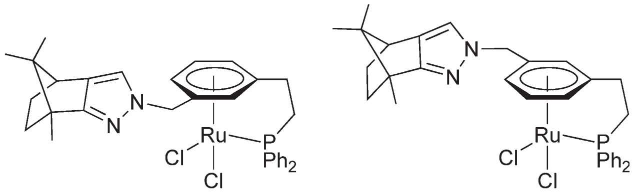


295 **296**

M = Ru, L = PMe_3; M = Os, L = PMe_3; M = Os, L = PMe_2Ph

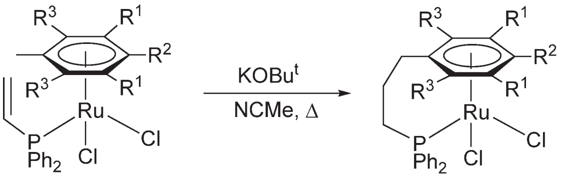
(28)

(iv) Arene–phosphine-tethered derivatives $[RuCl_2\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5YCH_2PR_2\}]$ (R = Bu^t, Y = CH_2, OCH_2;[544] R = Cy,* Ph,* Et, Y = CH_2;[545] R = Cy, Y = $(CH_2)_2$*)[546] are conveniently prepared in two steps, by reaction of $C_6H_5YCH_2PR_2$ with $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$ and subsequent substitution of the *p*-cymene ligand by heating the resulting adduct $[RuCl_2\{\kappa^1(P)\text{-}C_6H_5YCH_2PR_2\}(\eta^6\text{-cym})]$ in chlorobenzene at 130–140 °C. The analogous complexes $[RuCl_2\{\eta^6{:}\kappa^1(P)\text{-}RC_6H_4CH_2CH_2PPh_2\}]$ (R = 2-CH_2OH,* 3-CH_2OH*)[429] and $[RuCl_2\{\eta^6{:}\kappa^1(P)\text{-}(R)\text{-}C_6H_5CHMeCH_2CH_2PPh_2\}]$[430] are better synthesized starting from dimers $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5CO_2R)\}_2]$ (R = Et,[429] Me*),[430] which contain a more labile arene. This methodology allows also the synthesis of the planar chiral complex **297** which has been isolated as a 1 : 1 mixture of the corresponding (R,R_p)- and (R,S_p)-diastereoisomers, evidencing the lack of facial recognition during the arene substitution process despite the presence of a bulky chiral auxiliary (Figure 37).[547] Nevertheless, (R,R_p)-**297** and (R,S_p)-**297** can be easily separated by column chromatography on silica gel. Displacement of the cymene ligand in $[RuCl_2\{\kappa^1(P)\text{-}Ph_2P(CH_2)_3Ph\}(\eta^6\text{-cym})]$ can be also achieved electrochemically affording $[RuCl_2\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5(CH_2)_3PPh_2\}]$ in good yield.[548] Tethered complexes **298**, prepared as previously described for their arsine analogs **290**, are also known (Equation (29)).[549]



(R,R_p)-**297** (R,S_p)-**297**

Figure 37 The two diastereoisomers of the planar chiral complex **297**.



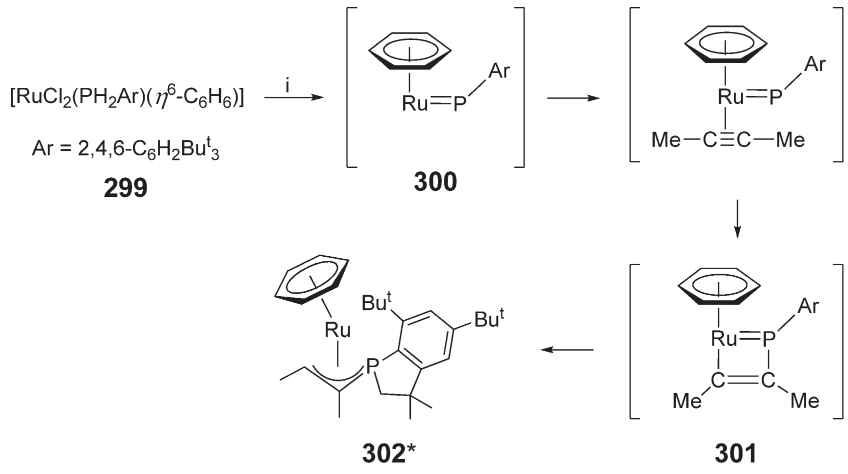
298

R^1 = Me; R^2 = R^3 = H
R^2 = Pr^i; R^1 = R^3 = H
R^1 = R^2 = R^3 = Me
R^2 = Me; R^1 = R^3 = H
R^1 = R^2 = R^3 = H

(29)

(v) Osmium and ruthenium derivatives [MX$_2$(PH$_2$Ar)(η^6-arene)] (Ar = 2,4,6-C$_6$H$_2$Bu$^t{}_3$; M = Os, arene = C$_6$H$_6$, X = I; arene = cym, X = Cl; M = Ru, X = Cl, arene = C$_6$H$_6$, cym)[550] **299**, containing a coordinated primary phosphine, which have found to be suitable precursors of the highly reactive unsaturated phosphinidene species [M(=PAr)(η^6-arene)] **300**. Formation of **300** involves a dehydrohalogenation process promoted by the addition of DBU to complexes **299**. Compounds **300** can be stabilized by coordination of one monodentate L ligand giving the 18-electron derivatives [M(=PAr)(L)(η^6-arene)]* (M = Ru, Os; arene = C$_6$H$_6$, cym; L = PPh$_3$, PMe$_3$, CO or NCBu^t; not all combinations). These saturated species have a characteristic low field resonance (δ 674–896 ppm) in their ^{31}P NMR spectra, typical for a terminal phosphinidene group.[550] The transient ruthenium phosphinidene [Ru(=PAr)(η^6-C$_6$H$_6$)] **300** reacts with 2-butyne to give the phospha-allyl complex **302**.*[550] It is postulated that this reaction occurs via initial π-coordination of the alkyne to **300**, followed by a cyclization process leading the four-membered metallacycle **301** which finally undergoes an intramolecular insertion of the P-center into a C–H bond of one Bu^t group, with concomitant hydrogen transfer to an olefinic carbon (Scheme 23). Phosphinidene complexes [Ru(=PAr)(PR$_3$)(η^6-cym)] (Ar = 2,4,6-C$_6$H$_2$Bu$^t{}_3$, R = Cy,* Ph) have been alternatively prepared from the reaction of [RuCl$_2$(PR$_3$)(η^6-cym)] with PH$_2$Ar in the presence of DBU.[551] Their oxidation with O$_2$ gives rise to the first fully characterized monomeric metaphosphonate derivatives [Ru{κ^2(*P*,*O*)-ArP(=O)$_2$}(PR$_3$)(η^6-cym)] (Ar = 2,4,6-C$_6$H$_2$Bu$^t{}_3$, R = Cy,* Ph), in which the dioxophosphorane ligand is π-coordinated through one P=O double bond.[551]

The ability of half-sandwich [M(η^6-arene)] fragments to coordinate chelating diphosphines has also been shown. Thus, osmium and ruthenium derivatives [OsCl(L$_2$)(η^6-cym)][Y] (L$_2$ = (*S*)-BINAP, Y = SbF$_6$;[552] L$_2$ = dppf, Y = PF$_6$*)[553] and [RuX(L$_2$)(η^6-arene)][Y] (L$_2$ = (*S*)-BINAP, arene = C$_6$H$_6$, X = Y = Cl, Br, I or X = Cl, Y = BF$_4$,* BPh$_4$; arene = cym, X = Y = Cl, Br, I;[554] L$_2$ = 1,2-(Ph$_2$P)$_2$C$_6$H$_4$, arene = C$_6$H$_6$, X = Y = Cl),[555] containing a rigid diphosphine ligand, can be easily obtained from the corresponding dimeric precursors. A general characteristic of these complexes is the lability of the coordinated arene ligand, especially in the case of electron-poor arenes.[554–556] As a consequence, complex [RuCl{κ^2(*P*,*P*)-(*S*)-BINAP}(η^6-C$_6$H$_5$CO$_2$Et)]Cl slowly decomposes in solution at room temperature.[554] Treatment of [RuCl{κ^2(*P*,*P*)-(*S*)-BINAP}(η^6-C$_6$H$_6$)]Cl with an excess of sodium acetate at 50 °C in THF also results in the release of the arene ligand, leading to the formation of the bis-acetato derivative



i, DBU, 2-butyne, toluene/CH$_2$Cl$_2$, 0 °C

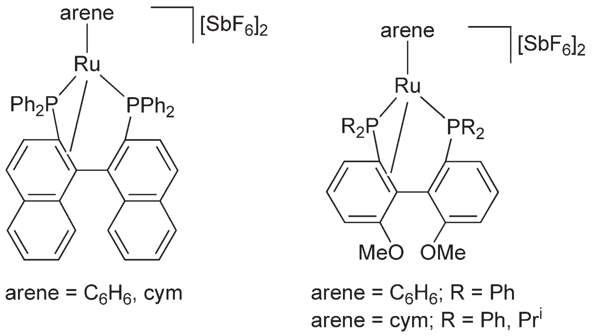
Scheme 23

[Ru{κ^2(*O*,*O*)-OAc)$_2${κ^2(*P*,*P*)-(*S*)-BINAP}],[554] a well-known hydrogenation catalyst. Elimination of *p*-cymene has also been observed in the reactions of [RuCl{κ^2(*P*,*P*)-L$_2$}(η^6-cym)][Cl] (L$_2$ = (*S*)-BINAP, 1,2-($Ph_2P)_2C_6H_4$) with a slight excess of dialkylammonium chlorides [NR_2H_2]Cl which generate the anionic dinuclear species [{κ^2(*P*,*P*)-L$_2$}RuCl(μ-Cl)$_3$ RuCl{κ^2(*P*,*P*)-L$_2$}][NR_2H_2] (L$_2$ = (*S*)-BINAP, R = Me, Et, Bz, Pr^i, Cy or R$_2$ = -($CH_2)_5$-; L$_2$ = 1,2-($Ph_2P)_2C_6H_4$, R = Et*).[556]

The dicationic derivatives **303** and **304** (Figure 38) have been generated by abstraction of the chloride ligand in [RuCl{κ^2(*P*,*P*)-L$_2$}(η^6-arene)]Cl (L$_2$ = *rac*-BINAP, (*S*)-(6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine), (*R*)-(6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diisopropylphosphine); arene = C_6H_6, cym; not all combinations).[557] In these compounds, the diphosphine acts as a six-electron donor ligand by coordination of the two phosphorus atoms and one carbon–carbon double bond adjacent to phosphorus. Proof of this coordination mode stems from the high field ^{13}C NMR resonances observed for the complexed carbon nuclei. In contrast, chloride abstraction in the osmium derivative [OsCl{κ^2(*P*,*P*)-(*S*)-BINAP}(η^6-cym)][SbF_6] generates a dicationic compound, formulated as the 16-electron species [Os{κ^2(*P*,*P*)-(*S*)-BINAP}(η^6-cym)][SbF_6]$_2$, in which BINAP ligand only acts as κ^2(*P*,*P*)-donor. Nevertheless, the formation of a saturated solvento complex [Os(solvent){κ^2(*P*,*P*)-(*S*)-BINAP}(η^6-cym)][SbF_6]$_2$ could not be totally discounted.[552]

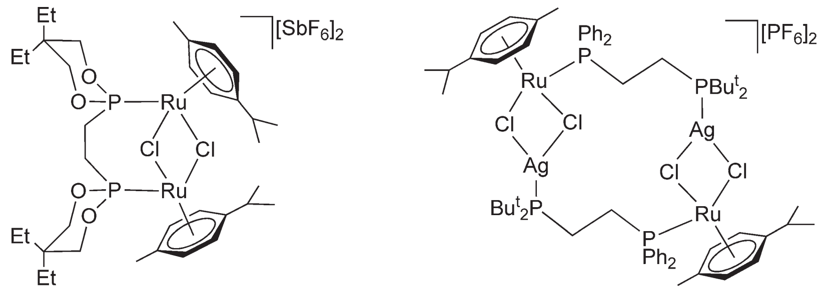
The high yield syntheses of [RuCl{κ^2(*P*,*P*)-$Ph_2P(CH_2)_nPPh_2$}(η^6-cym)][Y] ($n = 1,^* 2,^*$ or 3; Y = Cl, BF_4) containing chelated flexible diphosphines have also been described.[558,559] However, it should be noted that the selective κ^2(*P*,*P*)-coordination of this type of diphosphines is usually complicated and requires specific reaction conditions (large excess of the diphosphine, moderate temperature) in order to avoid the formation of by-products, including phosphine-bridged bimetallic complexes and bis-diphosphine species resulting from arene displacement. In this context, all attempts to synthesize [RuCl{κ^2(*P*,*P*)-1,2-di(2′,2′-diethyl-1′,3′-propanedioxy)phosphinoethane}(η^6-cym)][SbF_6] failed, affording instead the dicationic diphosphinite-bridged dimer **305*** (Figure 39).[560] Surprisingly, the unusual tetranuclear complex **306*** is formed in the reaction of [{RuCl(μ-Cl)(η^6-cym)}$_2$] with $Ph_2PCH_2CH_2PBu^t_2$ and Ag[PF_6], while the expected product [RuCl{κ^2(*P*,*P*)-$Ph_2PCH_2CH_2PBu^t_2$}(η^6-cym)][PF_6] is selectively obtained when [NH_4][PF_6] is employed as chloride scavenger.[533]

A rather unusual route has been described for the synthesis of compounds **308** (Equation (30)), which are obtained as mixtures of diastereomers from the phosphole derivatives **307** via intramolecular [4 + 2]-cycloadditions with diphenylvinylphosphine in the presence of a chloride abstractor.[561,562]



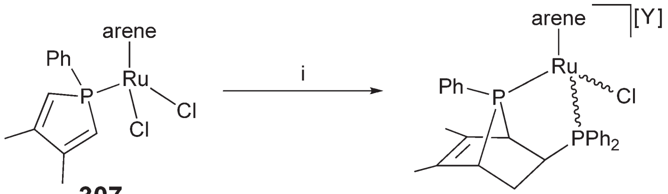
303 **304**

Figure 38 The structure of compounds **303** and **304**.



305* **306***

Figure 39 The polynuclear cymene derivatives **305** and **306**.



307

Y = PF_6; arene = C_6H_6,* C_6H_5Me,* cym,* hmb*
Y = OTf; arene = C_6H_6, cym,* 1,3,5-$C_6H_3Me_3$,* hmb*

308

i, $Ph_2PCH{=}CH_2$, Na[PF_6] or Ag[OTf], CH_2Cl_2, RT

(30)

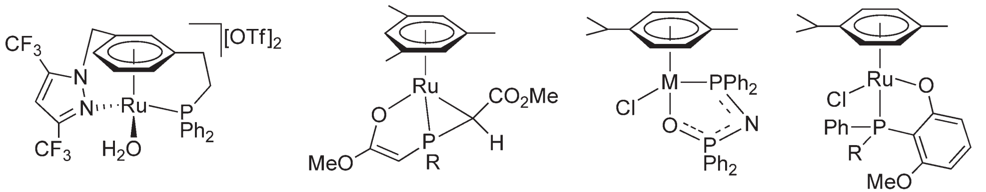
6.14.4.3.3 Mixed P,O- and P,N-donor ligands

The coordination of heteroditopic *P*,*X*-donor ligands on (η^6-arene)–ruthenium and osmium entities has been extensively investigated in the last few years, especially when X = O, N. Less extensive studies involving *P*,*As*-, *P*,*S*-, and *P*,*Se*-donor ligands have also been performed and the corresponding results are summarized in Sections 6.14.4.3.1 and 6.14.4.4.3, respectively.

Chelation of *P*,*O*- or *P*,*N*-donor ligands to $[MCl(\eta^6\text{-arene})]^+$ fragments implies the creation of a stereogenic center on the metal and therefore diastereomeric mixtures can be formed when a chiral ligand is employed. Thus, the synthesis of $[OsCl\{\kappa^2(P,O)\text{-}Ph_2PCHMeP({=}O)Ph_2\}(\eta^6\text{-cym})][SbF_6]^{*}$[510] gives rise to two diastereoisomers (in racemic form) in a 3.8 : 1 ratio, while the ruthenium analogs $[RuCl\{\kappa^2(P,O)\text{-}Ph_2PCHRP({=}O)Ph_2\}(\eta^6\text{-cym})][SbF_6]$ (R = Me, Pr^n,* Ph)[509] are isolated as a single diastereomer. High diastereoselectivity is also observed in the formation of complexes (R_M)-$[MCl\{\kappa^2(P,O)\text{-}(S)\text{-BINAP(O)}\}(\eta^6\text{-cym})][SbF_6]$ (**309**; (*S*)-BINAP(O) = (*S*)-BINAP monoxide; M = Ru,*[563] Os*).[552] Abstraction of the remaining chloride ligand in **309**, using Ag[SbF_6], provides the Lewis acids $[M\{\kappa^2(P,O)\text{-}(S)\text{-BINAP(O)}\}(\eta^6\text{-cym})][SbF_6]_2$ (**310**; M = Ru, Os*) which have proved to be efficient catalysts in asymmetric Diels–Alder cycloadditions.[552,563] Replacement of the chloride ligand in $(R_{Ru}R_C/S_{Ru}S_C)$-$[RuCl\{\kappa^2(P,O)\text{-}Ph_2PCHMeP({=}O)Ph_2\}(\eta^6\text{-cym})][SbF_6]$ by pyridine, 3,5-lutidine, or isoquinoline generates the dicationic complexes $[Ru(L)\{\kappa^2(P,O)\text{-}Ph_2PCHMeP({=}O)Ph_2\}(\eta^6\text{-cym})][SbF_6]_2$ (L = py,* $Me_2C_5H_3N$, C_9H_7N), the process involving epimerization at the metal center.[465] Formation of the unsaturated intermediate species $[Ru\{\kappa^2(P,O)\text{-}Ph_2PCHMeP({=}O)Ph_2\}(\eta^6\text{-cym})][SbF_6]_2$ is responsible for the inversion of stereochemistry associated with these reactions. The particular geometry of the tethered $\eta^6{:}\kappa^2(P,N)$ ligand in compound **311** ensures the configurational stability at the metal center, and even in the event of phosphorus, pyrazole, or water decomplexation the chirality can be totally recovered (Figure 40). Both enantiopure complexes $(R_{Ru}S_P)$-**311** and $(S_{Ru}R_P)$-**311** have been prepared and the stability of their stereochemistry has been checked under several conditions.[564]

The presence of both soft (phosphorus) and hard (oxygen or nitrogen) donor atoms in these heteroditopic ligands confers hemilabile properties on the resulting arene complexes, as shown in cationic derivatives $[RuCl(\kappa^2\text{-}L^1)(\eta^6\text{-arene})]^+$ containing phosphino–ether ($L^1 = Pr^i{}_2PCH_2CH_2OMe$),[565] keto–phosphines ($L^1 = Ph_2PC(R^1)(R^2)CH_2C({=}O)R^3$; R^1 = H, Me; R^2 = Me, Ph; R^3 = Bu^t, Me, Ph; not all combinations),[566] phosphino–ester ($L^1 = Ph_2PCH_2CO_2Me$),[567] and iminophosphorane–phosphine ligands ($L^1 = Ph_2PCH_2P({=}NR)Ph_2$; R = 4-$C_6F_4CN$, 4-$C_5F_4N$).[470] These compounds are prone to undergo chelate ring-opening processes in the presence of two-electron ligands (L^2) affording complexes of the type $[RuCl\{\kappa^1(P)\text{-}L^1\}(L^2)(\eta^6\text{-arene})]^+$ (L^2 = nitrile, sulfide, pyridine, phosphine, isocyanide, or CO).

An additional feature of *P*,*O*- or *P*,*N*- chelate keto–phosphine, phosphino–ester, or phosphino–oxazoline ligands is the acidity of the PCH proton which can be easily deprotonated in the presence of a base. This reactivity is nicely shown by



(R_{Ru},S_p)-**311**

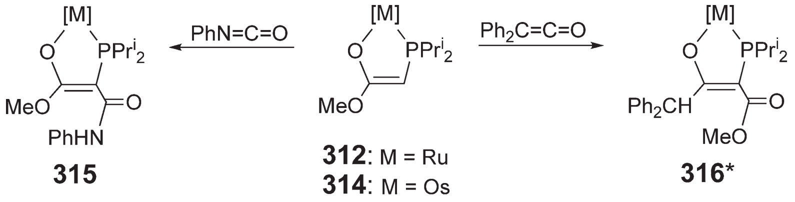
R = Pr^i,* Bu^t

M = Ru,* Os*

R = 2,6-$C_6H_3(OMe)_2$

313 **317** **318***

Figure 40 Structure of compounds 311, 313, 317, and 318.

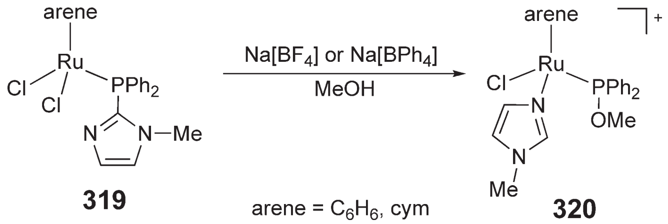


[M] = [MCl(η^6-1,3,5-$C_6H_3Me_3$)]

Scheme 24

$[RuCl\{\kappa^2(P,O)\text{-}Ph_2PCHR^1C(=O)R^2\}(\eta^6\text{-arene})]^+$ ($R^1 = H$, Me; $R^2 = Bu^t$, Ph; arene = C_6H_6, cym, 1,3,5-$C_6H_3Me_3$, hmb; not all combinations), $[MCl\{\kappa^2(P,O)\text{-}Pr^i_2PCH_2C(=O)OMe\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]^+$ (M = Os, Ru), and $[RuCl\{\kappa^2(P,N)\text{-}Ph_2PCH_2\overline{C=NCH_2CH_2O}\}(\eta^6\text{-cym})]^+$ which are readily deprotonated into $[RuCl\{\kappa^2(P,O)\text{-}Ph_2PC(R^1)=C(R^2)O\}(\eta^6\text{-arene})]$,[568] $[MCl\{\kappa^2(P,O)\text{-}Pr^i_2PCH=C(OMe)O\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (M = Ru **312**, Os),[565,569] and $[RuCl\{\kappa^2(P,N)\text{-}Ph_2PCH=\overline{CNCH_2CH_2O}\}(\eta^6\text{-cym})]$,[570] respectively. The formation of the anionic phosphino–enolate-type ligands implies the loss of the hemilabile behavior. Phosphinoester–enolate complex **312** slowly rearranges, in benzene at room temperature, into the thermodynamically favored phosphinomethanide isomer $[\overline{RuCl\{\kappa^2(P,C)\text{-}Pr^i_2PC}HCO_2Me\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$.*[565] Remarkably, the two coordination modes, $\kappa^2(P,O)$- and $\kappa^2(P,C)$-, can co-exist in the same molecule. Thus, treatment of the dicationic phosphino–diester species $[Ru\{\kappa^3(P,O,O)\text{-}RP(CH_2CO_2Me)_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]_2$ (R = Pr^i,* Bu^t) with base affords **313** (Figure 40), resulting from *O*-metallation of one $PCHCO_2Me$ unit and *C*-metallation of the second one.[571] The phosphinoester–enolate derivative **312** and its osmium counterpart **314** readily insert heterocumulenes such as phenyl isocyanate or diphenyl ketene into the enolate C–H bond affording complexes **315** and **316***, respectively (Scheme 24).[565,569] N–H deprotonation of $[MCl\{\kappa^2(P,O)\text{-}Ph_2PNHP(=O)Ph_2\}(\eta^6\text{-cym})]^+$ (M = Os,*[572] Ru)[573] has also been performed allowing the preparation of the neutral species **317*** (Figure 40).

The κ^2-coordinated heteroditopic *P,O*- and *P,N*-donor ligands become more reactive allowing their subsequent transformation. As an example, the bis(2,6-dimethoxyphenyl)phenylphosphine ligand undergoes a spontaneous C–O bond cleavage of an ether function during the coordination process to provide, under mild conditions (RT), the phenoxide derivative **318*** (Figure 40).[574] The reactions of complexes **319** (Equation (31)) with an equivalent of $Tl[BF_4]$ in dichloromethane lead to the expected abstraction of one chloride ligand allowing the conventional $\kappa^2(P,N)$-coordination of the phosphine. In contrast, when methanolic solutions of **319** are treated with $Na[BF_4]$ or $Na[BPh_4]$, the phosphinite complex **320** is selectively formed (Equation (31)).[541] This transformation implies a P–C bond cleavage and concomitant phosphine functionalization with methanol.



(31)

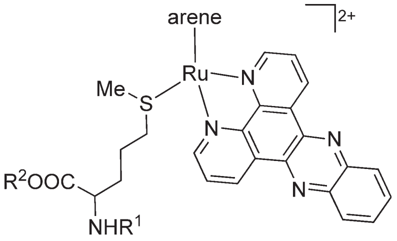
6.14.4.4 Complexes Containing S-, Se-, and Te-donor Ligands

6.14.4.4.1 Thioethers, thiolates, and related ligands

Telluro–ether complexes $[RuCl_2\{\kappa^1(Te)\text{-}TeR^1R^2\}(\eta^6\text{-cym})]$ ($R^1 = R^2 =$ 2-(2-thienyl)ethyl;* $R^1 = 4\text{-}C_6H_4OMe$, $R^2 =$ 2-(2-thienyl)ethyl,[575] $CH_2CH_2\overline{N(CH_2)_2OCH_2CH_2}$,[576] CH_2CH_2-*N*-phthalamide;*[577] $R^1 = 4\text{-}C_6H_4OEt$, $R^2 = CH_2\overline{CH(CH_2)_4O}$,* $CH_2CH_2\overline{CHO(CH_2)_3O}$;*[578] $R^1 = R^2 = CH_2CH_2\overline{CHO(CH_2)_3O}$*)[579] are readily prepared starting from $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-cym})\}_2]$ via chloride bridge cleavage. Attempts to coordinate the tellurated Schiff base

4-MeOC_6H_4TeCH_2CH_2N=CMe-2-C_6H_4OH result in the hydrolysis of the imine function giving the derivative [RuCl{κ^2(*Te,N*)-4-MeOC_6H_4TeCH_2CH_2NH_2}(η^6-cym)]Cl.*[580] Treatment of a dichloromethane solution of [{RuCl(μ-Cl)(η^6-cym)}$_2$] with 1,3-dithiane affords the neutral thioether complex [RuCl_2{κ^1(*S*)-1,3-dithiane}(η^6-cym)].*[581] In contrast, under the same conditions, 1,4-dithiane leads to the cationic species [RuCl{κ^2(*S,S*)-1,4-dithiane}(η^6-cym)]$^+$,* isolated both as chloride and PF_6^- salt.[581] The syntheses of the bis(thioether) derivatives [RuCl{κ^1(*S*)-1,3-dithiane}$_2$(η^6-cym)][PF_6],[581] [RuCl{κ^2(*S,S*)-L_2}(η^6-arene)][Y] (L_2 = [15]aneS_2O_3 (1,4,7-trioxa-10,13-dithiacyclopentadecane), [18]aneS_2O_4 (1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane); arene = C_6H_6, cym, hmb; Y = BPh_4, PF_6; not all combinations),*[582] and the zwitterionic compound [RuCl{κ^2(*S,S*)-7,8-(SPh)$_2$-7,8-*nido*-$C_2B_9H_{10}$}(η^6-cym)]*[583] have also been described. Dimethyl sulfide reacts with [RuCl_2{κ^1(*P*)-L}(η^6-arene)] (L = Ph_2PCH(Ph)CH_2C(=O)Me, arene = cym; L = Ph_2PCH_2CO_2Me, arene = C_6H_6, cym, 1,3,5-$C_6H_3Me_3$), in the presence of a chloride abstractor, to generate [RuCl{κ^1(*P*)-L}(SMe_2)(η^6-arene)]$^+$.[566,567] In these compounds, the strengh of the Ru–SMe_2 bond decreases with increasing arene functionalization and electron richness. Similar arene influence has also been observed in complexes **321** (Figure 41), in which the lability of thioether ligand follows the order $C_6Me_6 > C_6H_3Me_3 > C_6H_6$.[495]

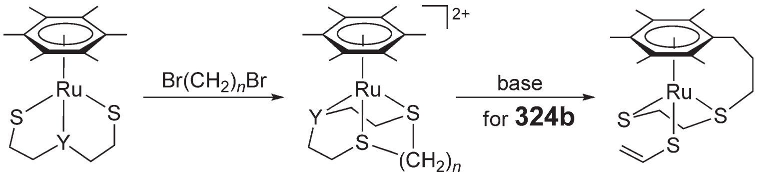
The (bis)thiolate derivatives [Ru{κ^3(*S,Y,S*)-S(CH_2)$_2$Y(CH_2)$_2$S}(η^6-hmb)] (Y = S **322**,*[584] NH **323***)[585] have been prepared starting from the corresponding dianionic ligand (generated *in situ*) and [{RuCl(μ-Cl)(η^6-hmb)}$_2$]. Treatment of **322** and **323** with 1 equiv. of HCl or alkyl halides (RX) leads to the cationic thioether–thiolate complexes [Ru{κ^3(*S,Y,S*)-RS(CH_2)$_2$Y(CH_2)$_2$S}(η^6-hmb)]$^+$ (Y = S, R = H, Me; Y = NH, CH_2CH=CH_2,* CH_2CH_2CH=CH_2*), isolated as their chloride, iodide, bromide, or PF_6^- salts. Diprotonated or dialkylated products [Ru{κ^3(*S,Y,S*)-Y(CH_2CH_2SR)$_2$}(η^6-hmb)]$^{2+}$ (Y = S, R = H, Me; Y = NH, Me,* CH_2CH=CH_2*) are obtained when an excess of HCl or RX is used.[584,585] Similar alkylation reactions with dibromoalkanes lead to the dicationic macrocyclic thioether complexes **324** and **325** (Scheme 25).[584,585] Alternatively, complex **324b** can be prepared starting directly from dimer [{RuCl(μ-Cl)(η^6-hmb)}$_2$] by reaction with 1,4,7-trithiacyclononane and Ag[PF_6] in acetone.[586] Treatment of **324b** with an excess of base leads to the tethered derivative **326**.*[586] Intermediate species [Ru{κ^3(*S,S,S*)-S(CH_2)$_2$S(CH_2)$_2$SCH=CH_2}(η^6-hmb)]$^{+*}$ and [Ru{κ^1(*S*)-SCH=CH_2}{κ^2(*S,S*)-S(CH_2)$_2$SCH=CH_2}(η^6-hmb)],* which result from one and two deprotonation/C–S bond cleavage sequences, respectively, have also been isolated.



arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, hmb
R^1 = Ac; R^2 = H
R^1 = GlyGly; R^2 = H
R^1 = H; R^2 = Me

321

Figure 41 The thioether ruthenium(II) complexes **321**.



322*: Y = S
323*: Y = NH

324: Y = S
324a*: *n* = 1
324b: *n* = 2
324c*: *n* = 3
324d*: *n* = 4

326*

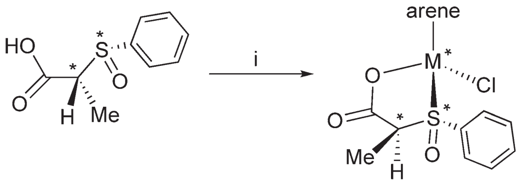
324e: *n* = 5
325: Y = NH
325a*: *n* = 2
325b: *n* = 3
325c*: *n* = 4

Scheme 25

Bulky chalcogenolate anions react with $[\{\mathrm{RuCl}(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$ in methanol to generate the 16-electron complexes $[\mathrm{Ru}\{\kappa^1(E)\text{-ER}\}_2(\eta^6\text{-arene})]$ (ER = S-2,6-xylyl, arene = C_6H_6,* cym,* hmb; ER = S-2,4,6-$C_6H_2Pr^i_3$, arene = C_6H_6, cym, hmb;*[587] ER = Se-Mes, arene = cym, hmb).[588] Attempts to prepare tellurolate analogs have failed.[588] The less sterically demanding chalcogenates PhE$^-$ generate, in low to moderate yields, the dinuclear species $[(\eta^6\text{-arene})\mathrm{Ru}(\mu\text{-EPh})_3\mathrm{Ru}(\eta^6\text{-arene})]^+$ (arene = cym, E = Se, Te; arene = hmb, E = Se) in which three bridging chalcogenate units have been incorporated.[588] Exchange reactions of the imido complex $[\mathrm{Os}(\equiv\mathrm{NBu^t})(\eta^6\text{-cym})]$ with bulky thiols give rise to bis(thiolates) $[\mathrm{Os}\{\kappa^1(S)\text{-SR}\}_2(\eta^6\text{-cym})]$ (R = Bu^t, 2,6-xylyl, Mes) with concomitant elimination of *tert*-butylamine.[474] In contrast, thiol HS-*p*-Tol, containing a smaller substituent, generates the dimeric compound $[(\mathrm{Os}\{\kappa^1(S)\text{-S-}p\text{-Tol}\}(\mu\text{-S-}p\text{-Tol})(\eta^6\text{-cym}))_2]$. Complexes $[\mathrm{M}\{\kappa^2(S,S)\text{-1,2-}S_2C_2B_{10}H_{10}\}(\eta^6\text{-arene})]$ **327** (arene = cym, M = Ru, Os;*[589] arene = hmb; M = Ru; 1,2-$S_2C_2B_{10}H_{10}$ = carboranyl dithiolate)[590] and $[\mathrm{Ru}\{\kappa^2(S,S)\text{-1,2-}S_2C_6H_4\}(\eta^6\text{-hmb})]$, containing a bidentate dichalcogenolate ligand, have been prepared starting from the appropriate dianion and dimers $[\{\mathrm{MCl}(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$. Nevertheless, the latter compound is more conveniently formed by substitution of the thiolate ligands in $[\mathrm{Ru}\{\kappa^1(S)\text{-S-2,6-xylyl}\}_2(\eta^6\text{-hmb})]$ with the disodium salt of 1,2-benzenedithiolate.[587] As a general trend, all these dichalcogenate 16-electron complexes react with two-electron donor ligands such as phosphines, phosphites, amines, hydrazine, sulfides, CO, isocyanides, and DMSO to afford the corresponding saturated adducts in good yields.[587–590] As an example, $[\mathrm{Ru}\{\kappa^2(S,S)\text{-1,2-}S_2C_2B_{10}H_{10}\}(\eta^6\text{-cym})]$ reacts with diethyl sulfide or tetrahydrothiophene to form $[\mathrm{Ru}\{\kappa^1(S)\text{-L}\}\{\kappa^2(S,S)\text{-1,2-}S_2C_2B_{10}H_{10}\}(\eta^6\text{-cym})]$ (L = SEt_2, SC_4H_8).[589] Moreover, the reactivity of complexes **327** with alkynes has also been investigated (see Chapter 6.15).

6.14.4.4.2 Ligands containing S=O and C=S groups

The following sulfoxide derivatives have been described: (i) The chelate complex $[\mathrm{RuCl}\{\kappa^2(S,S)\text{-EtS}(=\mathrm{O})\mathrm{CH_2CH_2S}(=\mathrm{O})\mathrm{Et}\}(\eta^6\text{-cym})][\mathrm{PF_6}]$* in which the *meso*-form of the disulfoxide EtS(=O)CH_2CH_2S(=O)Et is acting as a bidentate ligand.[591] (ii) The optically pure derivatives **328*** obtained from the deprotonated salt of (*R*)-2-[(*R*)-phenylsulfinyl]propionic acid (Equation (32)). Notably, during the coordination process, the chirality at carbon C2 is completely inverted.[592] Moreover, X-ray diffraction analyses of the previously known complex $[\mathrm{RuCl_2}\{\kappa^1(S)\text{-DMSO}\}(\eta^6\text{-cym})]$[593] and $[\mathrm{Ru}\{\kappa^1(S)\text{-DMSO}\}\{\kappa^1(S)\text{-S-2,6-xylyl}\}_2(\eta^6\text{-}C_6H_6)]$ **329** have been reported.[588] Nevertheless, in solution, **329** completely dissociates into $[\mathrm{Ru}\{\kappa^1(S)\text{-S-2,6-xylyl}\}_2(\eta^6\text{-}C_6H_6)]$ and free DMSO as assessed by NMR spectroscopy.



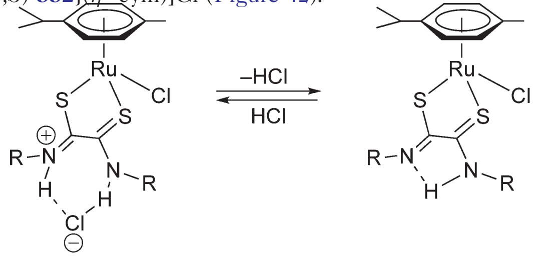
M = Ru; arene = cym,* hmb*
M = Os; arene = cym*

328

(32)

i, 1/2[{MCl(μ-Cl)(η^6-arene)}$_2$], K[OBu^t], THF

Chelate coordination of dithio-oxamides provides complexes formulated as the hydrogen chloride salts **330** (Equation (33)).[594] Compounds **330** easily lose HCl after chromatographic workup or upon addition of alkylamines to generate the neutral rubeanate complexes **331**. Protonation of **331** reversibly restores the ion pairs **330**. Reaction of 2 equiv. of the sodium salt of **332** with $[\{\mathrm{RuCl}(\mu\text{-Cl})(\eta^6\text{-cym})\}_2]$ results in the formation of the tridentate complex $[\mathrm{Ru}\{\kappa^3(S,S,S)\text{-}\mathbf{332}\}(\eta^6\text{-cym})]\mathrm{Cl}$ (Figure 42).*[277]

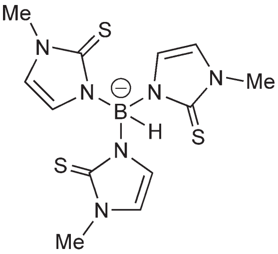


R = Pr^i, Cy, (*R*)-CHMePh, *rac*-CHMePh

(33)

330 **331**

Other complexes containing ligands featuring a C=S bond include: (i) dithioformates $[\mathrm{Ru}\{\kappa^2(S,S)\text{-}S_2\mathrm{CH}\}\{\kappa^1(P)\text{-}\mathrm{Ph_2PCH_2R}\}(\eta^6\text{-hmb})][\mathrm{BF_4}]$ (R = CH_2OMe,* $\overline{\mathrm{CHO(CH_2)_3O}}$, $\overline{\mathrm{CHO(CH_2)_2O}}$),[595] (ii) compounds



332

Figure 42 The tridentate S-donor ligand **332**.

[RuCl{κ^2(S,S)-S_2CPR_3}(η^6-arene)][PF_6] (R = Cy, Pr^i; arene = C_6H_6, cym, hmb) bearing trialkylphosphine–carbon disulfide adducts,[596] and (iii) the diethyldithiocarbamate complex [RuCl{κ^2(S,S)-S_2CNEt_2}(η^6-cym)].*[597]

6.14.4.4.3 S- and Se-donor ligands containing phosphorus

In addition to the phosphino–thioether derivatives [RuCl{κ^2(P,S)-L_2}(η^6-cym)]$^+$ (L_2 = $Me_2PCH_2CH_2SR$ (R = Me, Et,* Ph),[598] Ph_2PCH_2SPh),[599] complexes of this type are mostly derived from the coordination of phosphine–chalcogenide ligands usually obtained by oxidation of the free phosphine with elemental sulfur or selenium. Examples include the following:

(i) Diphosphine–monochalcogenide chelate compounds [RuCl{κ^2(P,E)-L_2}(η^6-arene)]$^+$ (arene = cym, L_2 = 2-$Ph_2PNHC_6H_4P$(=S)Ph_2,[600] Ph_2P(1,2-ferrocendiyl)CH(Me)P(=Se)$Bu^t{}_2$;*[601] arene = hmb, L_2 = Ph_2PCH_2-P(=Se)Ph_2).[602]

(ii) Diphosphine–dichalcogenide complexes [RuCl{κ^2(E,E)-L_2}(η^6-arene)]$^+$ (L_2 = (E=PPh_2)$_2CH_2$ (E = S, Se), arene = hmb,[602] cym;[603] L_2 = (S=PPh_2)$_2$CHMe, arene = cym).[603] Deprotonation of the methylene function in these compounds generates bicyclic methanide species containing Ru–C bonds (see Chapter 6.15).

(iii) Neutral derivatives [RuCl{κ^2(E,E)-(E=PPh_2)$_2$N}(η^6-arene)] (E = S, arene = C_6H_6, cym; E = Se, arene = hmb, cym)[604] which result from the spontaneous deprotonation of the dichalcogenide ligands (E=PPh_2)$_2$NH during the coordination process. The synthesis of this type of compound can be also achieved starting from the preformed anion (E=PPh_2)$_2N^-$ and the appropriate dimeric precursors.[572,605]

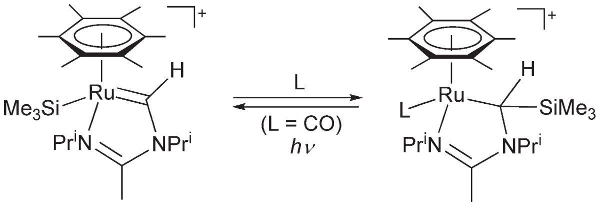
(iv) The triphosphine–trichalcogenide zwitterionic complex [Ru{κ^3(S,S,S)-(S=PPh_2)$_3$C}(η^6-cym)]$^+$,* which contains a tridentate anionic ligand.[606]

(v) Derivatives containing bi- and tridentate N-thiophosphorylated iminophosphorane–phosphine ligands [RuCl(κ^2(P,S)-Ph_2PCH_2P{=NP(=S)(OR)$_2$}Ph_2)(η^6-cym)][SbF_6] (R = Et, Ph) and [Ru(κ^3(P,N,S)-Ph_2PCH_2-P{=NP(=S)(OR)$_2$}Ph_2)(η^6-cym)][SbF_6]$_2$ (R = Et, Ph), respectively.[607] Their deprotonation leading to novel arene–ruthenium complexes containing Ru–C bonds has also been investigated (see Chapter 6.15).

6.14.4.5 Complexes Containing Si- and Sn-donor Ligands

Bis-silyl ruthenium(IV) complexes [$RuH_2(SiMe_3)_2$(η^6-arene)] (arene = cym, hmb*) have been obtained by heating the appropriate dimeric precursor [{RuCl(μ-Cl)(η^6-arene)}$_2$] with an excess of trimethylsilane.[608] Remarkably, thermolysis of [$RuH_2(SiMe_3)_2$(η^6-hmb)] in C_6D_6 at 150 °C leads to the formation of [RuD_2{Si(CD_3)$_3$}$_2$(η^6-C_6D_6)] as the result of (i) the H/D exchange in all positions of the molecule and (ii) the substitution of the arene ligand. Similar H/D scrambling is also observed when C_6D_6 is replaced by cyclohexane-d_{12} although in this case displacement of hmb does not occur.[608] The complex [Ru(CO){κ^2(Si,Si)-xantsil}(η^6-toluene)]* **333** (xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)) has been prepared by heating a toluene solution of [Ru(CO)$_4${κ^2(Si,Si)-xantsil}].[609] Extremely facile exchange of the η^6-toluene ligand for benzene takes place at room temperature, affording [Ru(CO){κ^2(Si,Si)-xantsil}(η^6-C_6H_6)] in quantitative yield in only 1 h.[609] The toluene ligand in **333** is also displaced by PMe_3 to give fac-[Ru(PMe_3)$_3$(CO){κ^2(Si,Si)-xantsil}].*[610]

Reactions of [$RuCl_2(PPh_3)_3$] with arenes and hydrosilanes in the presence of 1-octene provide compounds [Ru(SiX_3)$_2$(PPh_3)(η^6-arene)] (SiX_3 = $SiCl_3$, arene = C_6H_6;* SiX_3 = $SiCl_2Me$, arene = C_6H_6,* toluene, o-xylene, m-xylene, p-xylene, 1,3,5-$C_6H_3Me_3$, anisole).[611] In this transformation, 1-octene, which acts as a hydrogen acceptor, is converted into octane as assessed by GC analysis. Methylation of the Si–Cl bonds in complexes $[Ru(SiX_3)_2(PPh_3)(\eta^6\text{-}C_6H_6)]$ ($SiX_3 = SiCl_3$, $SiCl_2Me$) using $AlMe_3$ generates $[Ru(SiMe_3)_2(PPh_3)(\eta^6\text{-}C_6H_6)]$.*[611] The zwitterionic species $[Ru(SiMe_3)(PMe_3)_2(\eta^6\text{-}C_6H_5BHPh_2)]$* has been made from $[RuH(SiMe_3)(PMe_3)_4]$ and BPh_3. In this reaction, triphenylborane assists the dissociation of the phosphine ligands, which are eliminated as $Me_3P\text{–}BPh_3$, and abstracts the hydride to furnish the η^6-coordinated borate unit.[612] The unsaturated amidinate complex $[Ru\{\kappa^2(N,N)\text{-}CMe(NPr^i)_2\}(\eta^6\text{-hmb})][Y]$ ($Y = PF_6$ or BAr^F_4) readily reacts with trimethylsilyldiazomethane to afford the carbene species **334*** (Equation (34)).[613] This compound arises from the initial formation of an $Ru{=}CHSiMe_3$ carbene intermediate which undergoes intramolecular attack of one nitrogen atom of the amidinate ligand at the carbenic carbon and a final 1,2-shift of the $SiMe_3$ function. Addition of CO or $CNBu^t$ to **334** promotes $SiMe_3$ group migration from the metal to the carbenic carbon providing **335*** and **336**, respectively (Equation (34)). The reverse process is performed by photochemical dissociation of the CO ligand in **335**.[613]



(34)

334*

335*: L = CO
336: L = $CNBu^t$

Tin(II) chloride readily inserts into the Ru–Cl bond of complexes $[RuCl\{\kappa^2(S,S)\text{-}S_2CPR_3\}(\eta^6\text{-arene})][PF_6]$ (arene = C_6H_6, cym, hmb; R = Cy, Pr^i) to generate $[Ru(SnCl_3)(\kappa^2(S,S)\text{-}S_2CPR_3)(\eta^6\text{-arene})][PF_6]$.[596] Similarly, treatment of $[RuCl_2(PPh_3)(\eta^6\text{-cym})]$ and $[RuCl_2\{P(OMe)_3\}(\eta^6\text{-cym})]$ with $SnCl_2$ gives $[RuCl(SnCl_3)(PPh_3)(\eta^6\text{-cym})]$ and $[Ru(SnCl_3)_2\{P(OMe)_3\}(\eta^6\text{-cym})]$ as the result of mono- and di-insertion processes, respectively.[614]

6.14.4.6 Complexes Containing Hydride, Carbonyl, and Isocyanide Ligands

6.14.4.6.1 Hydride ligands

Neutral monohydride ruthenium complexes are easily prepared from suitable chloride precursors and primary or secondary alcohols in the presence of a base. For example, the complexes $[RuH\{\kappa^2(P,O)\text{-}Ph_2PCR{=}C(Bu^t)O\}(\eta^6\text{-hmb})]$ (R = H, Me) are easily made by heating $[RuCl\{\kappa^2(P,O)\text{-}Ph_2PCR{=}C(Bu^t)O\}(\eta^6\text{-hmb})]$ with K_2CO_3 in methanol.[568] Similarly, $[RuClH(PCy_3)(\eta^6\text{-}C_6H_6)]$ has been prepared stirring a methanolic solution of $[RuCl_2(PCy_3)(\eta^6\text{-}C_6H_6)]$ in the presence of 1 equiv. of sodium formate.[615]

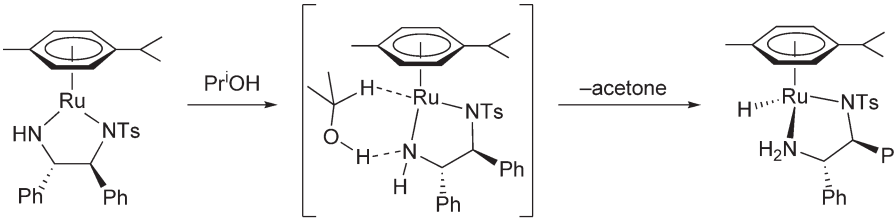
Cationic monohydride derivatives are commonly obtained by treating the appropriate chloride precursor with a silver salt in alcoholic media. Thus, the reaction of $[RuCl(PCy_3)\{\eta^6{:}\kappa^1(O)\text{-}C_6H_5(CH_2)_3OH\}][BF_4]$ with $Ag[BF_4]$ in MeOH leads to $[RuH(PCy_3)\{\eta^6{:}\kappa^1(O)\text{-}C_6H_5(CH_2)_3OH\}][BF_4]$.[615] The same process, performed sequentially, has been used to prepare $[RuH\{\kappa^2(P,P)\text{-}L_2\}(\eta^6\text{-cym})][SbF_6]$ **337** (L_2 = BINAP, (6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenyl phosphine)).[557] Thus, in a first step, treatment of $[RuCl\{\kappa^2(P,P)\text{-}L_2\}(\eta^6\text{-cym})][SbF_6]$ with $Ag[SbF_6]$ in dichloromethane gives the dicationic complexes **303 and 304** (see Figure 38) which, in a second step, are readily converted into the hydride derivatives **337** when dissolved in methanol. The synthesis of $[RuH(EPh_3)_2(\eta^6\text{-arene})][Y]$ (E = P, Sb, As; arene = C_6H_6, cym, hmb; Y = BF_4, PF_6) has been performed in a one-pot procedure starting from $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$, the appropriate ligand EPh_3, and $Ag[BF_4]$ or $Ag[PF_6]$ in methanol.[530]* Alternatively, cationic monohydrides $[RuH\{\kappa^2(P,P)\text{-}L_2\}(\eta^6\text{-arene})][Y]$ (L_2 = BINAP, (6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine), (6,6′-dimethoxybiphenyl-2,2′-diyl)bis(di-(3,5-di-*tert*-butylphenyl)phosphine)*; arene = cym, C_6H_6, toluene, ClC_6H_5, $C_6H_5C({=}O)NH_2$, $C_6H_5CH(OH)Me$, $C_6H_5C({=}O)Me$, 1,4-MeC_6H_4NHAc, 1,4-$C_6H_4(NHAc)_2$, $C_6H_5NHC({=}O)Ph$; Y = OTf, BF_4; not all combinations) have been made by protonation of $[Ru\{\kappa^2(O,O)\text{-}OAc\}_2(\kappa^2\text{-}L_2)]$ with 2 equiv. of HOTf or HBF_4 in presence of the arene ligand and 2-propanol.[616,617] The formation of the solvato–hydride intermediates $[RuH(Pr^iOH)_x(L_2)][Y]$ ($x = 2$ or 3) is proposed in this reaction.

The water-soluble hydride $Na_3[RuH(\kappa^2(P,P)\text{-}1,2\text{-}\{(4\text{-}O_3SC_6H_4)_2P\}_2C_6H_4)(\eta^6\text{-cym})]$ has been obtained under hydrogen pressure (45 bar) and basic conditions (pH = 8) from the related chloride precursor.[559] In contrast, the preparation of complexes $Na_5[RuH\{P(3\text{-}C_6H_4SO_3)_3\}_2(\eta^6\text{-arene})]$ (arene = C_6H_6, toluene, *p*-xylene, ethylbenzene, cumene, tetralin, dihydrocinnamic alcohol, *cis*-cinnamic alcohol), also water soluble, is carried out starting from the dimeric complex $[(RuCl(\mu\text{-}Cl)\{P(3\text{-}C_6H_4SO_3Na)_3\}_2)_2]$ and the appropriate arene under 35 bar of hydrogen at 60 °C.[618]

Reduction of [RuCl(dippe)(η^6-arene)][BPh_4], [$RuCl_2$(=CNMeC_6H_4NMe)(η^6-hmb)], or [$RuCl_2${κ^1(*P*)-Ph_2PCH_2R}(η^6-hmb)] with Na[BH_4] in ethanol or 2-propanol leads to the monohydrides [RuH(dippe)(η^6-arene)][BPh_4] (arene = C_6H_6,* cym)[619] and the dihydrides [RuH_2(=CNMeC_6H_4NMe)(η^6-hmb)][620] and [RuH_2{κ^1(*P*)-Ph_2PCH_2R}(η^6-hmb)] **338** (R = CH_2OMe, CHO$(CH_2)_3$O, CHO$(CH_2)_2$O),[595] respectively. Hydride abstraction in **338** can be easily achieved using [Ph_3C][BF_4] which gives rise to [RuH{κ^2(*P,O*)-Ph_2PCH_2R}(η^6-hmb)][BF_4] **339** (R = CH_2OMe, CHO$(CH_2)_3$O, CHO$(CH_2)_2$O).[595]

Hydride derivatives can also be generated by direct hydrogen transfer from alcohols. This elegant procedure has been discovered in the context of Noyori's mechanistic studies on the catalytic transfer hydrogenation of ketones. It consists of the reaction of the unsaturated diamide complex **255*** (see Equation (20)) with 2-propanol which gives in a diastereoselective manner the related amino–amide hydride species (R_{Ru})-[RuH{κ^2(*N,N*)-(*S,S*)-H_2NCHPh-CHPhNTs}(η^6-cym)]* **340** with concomitant release of acetone.[482] The transfer of two hydrogen atoms from the alcohol to the diamide complex takes place in a concerted way through a six-membered transition state, as illustrated in Scheme 26.[621] Both **255** and **340** are active species in catalytic asymmetric transfer hydrogenations of a wide range of prochiral ketones.[621] Following the same procedure, the enantiopure complex [RuH{κ^2(*N,O*)-(1*S*,2*R*)-OCHPhCHMeNH(CH_2R)}(η^6-cym)] **341** (R = 4-biphenyl) could be synthesized starting from the 16-electron derivative [Ru{κ^2(*N,O*)-(1*S*,2*R*)-OCHPhCHMeN(CH_2R)}(η^6-cym)] **278**.[519] This hydrido complex **341**, spectroscopically characterized at temperatures below 0 °C, rapidly decomposes at room temperature.

Due to the well-known inertness of osmium vs. ruthenium compounds, different synthetic strategies for access to osmium hydride complexes are usually required. The most reliable synthetic method consists in treatment of the appropriate chloride precursor with magnesium amalgam (10% of Mg) in THF and in the presence of a small amount of ethanol which acts as hydride source. Following this reaction pathway, dihydrido compounds [OsH_2(CNR)(η^6-1,3,5-$C_6H_3Me_3$)] (R = Me, Bu^t, Ph, Cy, 2,6-xylyl)[622] and [OsH_2{κ^1(*P*)-$Pr^i{}_2PCH_2CO_2Me$}(η^6-1,3,5-$C_6H_3Me_3$)][623] have been synthesized from the corresponding dichloro precursors. Alternatively, [OsH_2(CNMe)(η^6-1,3,5-$C_6H_3Me_3$)] can be obtained by reacting [$OsCl_2$(CNMe)(η^6-1,3,5-$C_6H_3Me_3$)] **342** with an excess of zinc dust in methanol and in the presence of glacial acetic acid.[622] Selective syntheses of monohydride complexes are also known. Thus, when the reaction of **342** with magnesium amalgam is carried out in the absence of ethanol, the monohydrido complex [OsHCl(CNMe)(η^6-1,3,5-$C_6H_3Me_3$)] is selectively formed.[622] In this case, THF is assumed to be the hydride source. Monohydrides [OsHCl(CNR)(η^6-1,3,5-$C_6H_3Me_3$)][622] (R = Me, Bu^t, Ph) and [OsHCl(CO)(η^6-1,3,5-$C_6H_3Me_3$)][624] are also accessible by the treatment of [OsPhI(CNR)(η^6-1,3,5-$C_6H_3Me_3$)] and [OsCl(CH_2Cy)(CO)(η^6-1,3,5-$C_6H_3Me_3$)] with Mg/Hg/THF/EtOH followed by protonation with HCl of the intermediate species [OsPhH(CNR)(η^6-1,3,5-$C_6H_3Me_3$)] and [OsH(CH_2Cy)(CO)(η^6-1,3,5-$C_6H_3Me_3$)], respectively. Complexes [OsHCl{κ^1(*P*)-$Pr^i{}_2PCH_2CH_2$-OMe}(η^6-1,3,5-$C_6H_3Me_3$)]* **343** and [OsH_2{κ^1(*P*)-$Pr^i{}_2PCH_2CH_2OMe$}(η^6-1,3,5-$C_6H_3Me_3$)] can be isolated in pure form when the reaction of [$OsCl_2${κ^1(*P*)-$Pr^i{}_2PCH_2CH_2OMe$}(η^6-1,3,5-$C_6H_3Me_3$)] with magnesium amalgam and ethanol is performed sequentially, according to the quantity of magnesium amalgam used.[569] Chloride abstraction from **343** with a silver salt generates [OsH{κ^2(*P,O*)-$Pr^i{}_2PCH_2CH_2OMe$}(η^6-1,3,5-$C_6H_3Me_3$)][PF_6] as the result of the intramolecular coordination of the ether moiety. Attempts to deprotonate this complex with $KOBu^t$ result in the unexpected formation of [OsH(OMe)(κ^1(*P*)-$Pr^i{}_2PCH{=}CH_2$)(η^6-1,3,5-$C_6H_3Me_3$)], the process involving the cleavage of the C–OMe bond of the chelating unit.[569] Monohydrido complexes [OsHCl(PR_3)(η^6-cym)] **344** (PR_3 = PMe_3, PMe_2Ph, PPh_2Me, $PBu^n{}_3$, $PPr^i{}_3$, PCy_3) have been synthesized by heating the parent dichlorides with an excess of triethylamine in ethanol.[444] Their ^{187}Os chemical shifts and $^1J(^{187}Os\text{-}^1H)$ coupling constants have been reported. Protonation of the zerovalent species [Os{κ^2(*N,N*)-bipy}(η^6-arene)] (arene = cym, hmb) with [NH_4][PF_6] and further counteranion exchange furnish the osmium(II) derivatives [OsH{κ^2(*N,N*)-bipy}(η^6-arene)][BPh_4]. Complex



255*

340

Scheme 26

$[OsH\{\kappa^2(N,N)\text{-bipy}\}(\eta^6\text{-hmb})][BPh_4]$ can be reversibly reduced into the neutral radical species $[OsH\{\kappa^2(N,N)\text{-bipy}\}(\eta^6\text{-hmb})]$ which has been characterized by EPR.[496]

6.14.4.6.2 Carbonyl and isocyanide ligands

Both isocyanide and carbon monoxide derivatives have proved to be valuable precursors of a wide range of compounds including hydrido (*vide supra*) and aryl or alkyl complexes (see Chapter 6.15). Compounds $[MCl_2(CNR)(\eta^6\text{-arene})]$ (M = Os, arene = 1,3,5-$C_6H_3Me_3$, R = Cy, 2,6-xylyl;[625] M = Ru, arene = 1,2,4,5-$C_6H_2Me_4$, R = NEt_2, NPr^i_2,* (*S*,*R*)-$\overline{NCHMe(CH_2)_3C}HMe$;[626] M = Ru, R = (*E*)-4-C_6H_4-N=NPh, arene = cym,* 1,3,5-$C_6H_3Me_3$, 1,2,3-$C_6H_3Me_3$, 1,2,3,5-$C_6H_2Me_4$, 1,2,3,4-$C_6H_2Me_4$, hmb)[627] are readily prepared by the cleavage of the chloride bridges in $[\{MCl(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$ (M = Os, Ru) with the appropriate isocyanide ligand. In spite of carbon monoxide being known to react easily with dimers $[\{MCl(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$, no novel complexes $[MCl_2(CO)(\eta^6\text{-arene})]$ have been reported since the publication of COMC (1995).

Cationic isocyanide and carbonyl derivatives can be prepared by coordination of isocyanide or CO in the vacant sites generated after halide abstraction in the appropriate precursors. For instance, the following compounds have been isolated: $[RuCl(CO)\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5(CH_2)_3OPPr^i_2\}][PF_6]$,[438] $[RuPh(CO)(PPh_3)(\eta^6\text{-cym})][SbF_6]$,[628] $[OsI(CO)(PR_3)(\eta^6\text{-cym})][PF_6]$ **345** (PR_3 = PCy_3, $PMePh_2$, PPh_3, PMe_3, PBu^n_3, PPr^i_3),[629] $[Ru(L)\{\kappa^2(P,O)\text{-}Ph_2P(2\text{-O-6-}MeOC_6H_3)\}(\eta^6\text{-hmb})][PF_6]$ (L = CO, CN-2,6-xylyl*),[630] $[RuCl(CNPh)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}(\eta^6\text{-arene})][PF_6]$ (arene = cym, 1,3,5-$C_6H_3Me_3$, 1,2,4,5-$C_6H_2Me_4$, hmb*),[631] $[RuCl(CNPh)\{\eta^6{:}\kappa^1(P)\text{-arene}\}][PF_6]$ (arene = 1,4-$Pr^iC_6H_4(CH_2)_3PPh_2$, 1,3,5-$Me_2C_6H_3(CH_2)_3PPh_2$*).[631] Osmium-187 and oxygen-17 NMR spectra of carbonyl complexes **345** have been recorded.[629] The ^{17}O chemical shift of the carbonyl ligand is linearly correlated with the Tolman's steric parameter θ of the ancillary phosphine ligand. In contrast, their ^{13}CO chemical shifts, as well as $\nu(C{\equiv}O)$ frequencies, do not show any regular trend.[629]

Isocyanides or CO can be also coordinated via partial displacement of chelate hemilabile trifluoroacetate, phosphino–ether or iminophosphorane–phosphine ligands. Examples prepared through this route include: $[Os\{\kappa^1(O)\text{-}O_2CCF_3\}_2(CNR)(\eta^6\text{-1,3,5-}C_6H_3Me_3)]$ (R = Me, Bu^t),[512] $[RuX(L)(\kappa^1(P)\text{-}Ph_2PCH_2CH_2OMe)(\eta^6\text{-hmb})][Y]$ (X = Cl, L = $CNBu^t$, CO,* Y = BPh_4; X = Me, L = CO, Y = BF_4),[632] $[RuH(L)\{\kappa^1(P)\text{-}Ph_2PCH_2R\}(\eta^6\text{-hmb})][BF_4]$ (L = $CNBu^t$,* CO, R = CH_2OMe,* $\overline{CHO(CH_2)_3O}$, $\overline{CHO(CH_2)_2O}$),[595] $[RuCl(L)\{\kappa^1(P)\text{-}Pr^i_2PCH_2CH_2OMe\}(\eta^6\text{-arene})][PF_6]$ (L = CO, $CNBu^t$, arene = 1,3,5-$C_6H_3Me_3$, hmb),[565] $[RuCl(CNR^1)\{\kappa^1(P)\text{-}Ph_2PCH_2P({=}NR^2)Ph_2\}(\eta^6\text{-cym})][PF_6]$ (R^1 = Cy, 2,6-xylyl, R^2 = 4-C_6F_4CN, 4-C_5F_4N).[470] As a general trend, isocyanide derivatives are more stable than their CO counterparts, due to the stronger donor ability of the former.[550,565]

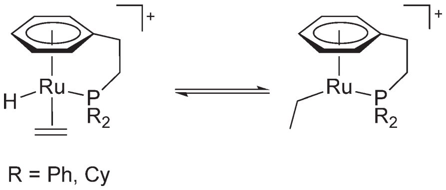
Electrophilic carbenic species can undergo the addition of water to the M=C bonds yielding carbonyl complexes. Thus, the transformation of the vinylidene derivative $[RuCl\{{=}C{=}C(H)Ph\}(PPh_3)(\eta^6\text{-hmb})][PF_6]$ (generated *in situ* by treatment of $[RuCl_2(PPh_3)(\eta^6\text{-hmb})]$ with phenylacetylene and $K[PF_6]$) into $[RuCl(CO)(PPh_3)(\eta^6\text{-hmb})][PF_6]$ has been reported to take place in the presence of water.[633] Similarly, dichloromethane solutions of $[RuCl(NCMe)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}(\eta^6\text{-hmb})][PF_6]$ and $HC{\equiv}CPh$ slowly transform into the carbonyl complex $[RuCl(CO)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}(\eta^6\text{-hmb})][PF_6]$, probably due to presence of traces of water.[634] The hydrolysis of carbenes $[Os\{\kappa^1(O)\text{-}CF_3CO_2\}_2({=}CR_2)(\eta^6\text{-1,3,5-}C_6H_3Me_3)]$ (R = Ph, 4-Tol, 4-C_6H_4OMe) into the unexpected carbonyl derivatives $[OsR_2(CO)(\eta^6\text{-1,3,5-}C_6H_3Me_3)]$ has also been reported (see Chapter 6.15).[512]

6.14.4.7 Complexes Containing η^2-, η^3-, η^4-, and η^5-Ligands

The most direct way to prepare η^2-alkene or η^2-alkyne (arene)–ruthenium(II) and osmium(II) complexes consists of the coordination of the unsaturated hydrocarbon in a vacant metal site. Thus, chloride abstraction from $[OsCl\{\kappa^2(P,O)\text{-}Pr^i_2PC(CO_2Me){=}C(CHPh_2)O\}(\eta^6\text{-1,3,5-}C_6H_3Me_3)]$ allows the π-coordination of dimethyl acetylenedicarboxylate (DMAD) affording $[Os(\eta^2\text{-DMAD})\{\kappa^2(P,O)\text{-}Pr^i_2PC(CO_2Me){=}C(CHPh_2)O\}(\eta^6\text{-1,3,5-}C_6H_3Me_3)][PF_6]$,* representing the only example of an arene–osmium–alkyne species characterized by X-ray diffraction methods.[569] The DMAD backbone C–C≡C–C deviates from linearity, showing C–C–C angles of 146.2(7)° and 147.7(8)°.

Coordination of alkenes has been readily achieved using compounds $[RuX\{\kappa^2(P,O)\text{-}Ph_2PCH_2R\}(\eta^6\text{-hmb})][BF_4]$ (X = Me, R = CH_2OMe; X = H, R = CH_2OMe, $\overline{CHO(CH_2)_3O}$, $\overline{CHO(CH_2)_2O}$), containing hemilabile phosphino–ether ligands, as precursors. These compounds readily react with ethylene to give $[RuX(\eta^2\text{-}CH_2{=}CH_2)\{\kappa^1(P)\text{-}Ph_2PCH_2R\}(\eta^6\text{-hmb})][BF_4]$.[595,632] Notably, no insertion of the olefin into the Ru–X (X = H, Me) bond has been observed. In contrast, the reactions of $[RuX(Ph)(PR_3)(\eta^6\text{-cym})]$ (X = Br, R = Ph; X = Cl, R = OMe) with $Ag[SbF_6]$ and C_2H_4 do not yield the expected η^2-ethylene complexes leading instead to $[RuH(\eta^2\text{-}CH_2{=}CHPh)(PR_3)(\eta^6\text{-cym})][SbF_6]^*$ **346** as the result of the olefin insertion into the Ru–Ph bond and further β-elimination.[628] Complexes **346** are formed as mixtures of diastereomers due to the chirality at the metal and the *Re*- or *Si*-face coordination of the prochiral styrene.

An alternative approach for the generation of vacant metal sites is the electrophilic abstraction of one methyl group from $[RuMe_2\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PPh_2\}]$ **347** upon treatment with $[H(Et_2O)_2][BAr^F{}_4]$. Thus, in the presence of ethylene, complex $[RuMe(\eta^2\text{-}CH_2{=}CH_2)\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PPh_2\}][BAr^F{}_4]$ is readily formed.[635] Nevertheless, in dichloromethane solution, this complex slowly decomposes giving the dimeric derivative $[\{Ru(\mu\text{-}Cl)(\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PPh_2)\}_2][BAr^F{}_4]_2$.* Treatment of **347** and the related species $[RuMe_2\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PCy_2\}]$ with $[Ph_3C][PF_6]$ leads to the hydride complexes $[RuH(\eta^2\text{-}CH_2{=}CH_2)\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PR_2\}][PF_6]$ (R = Ph, Cy*).[636] In this case, the η^2-olefin ligand arises from the hydride abstraction of one methyl substituent, subsequent carbon–carbon coupling, and final β-elimination of the corresponding ruthenium–ethyl intermediate. It has been proposed, on the basis of spectroscopic data and 2D EXSY experiments, that these complexes undergo a fast reversible olefin–hydride insertion at room temperature (Equation (35)). Similarly, $[OsH(\eta^2\text{-}CH_2{=}CH_2)(CNMe)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]^+$ has been generated *in situ* from $[OsMe_2(CNMe)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$.[622] Deprotonation of this hydride complex, which has been not isolated, with NaH gives rise to the zerovalent complex $[Os(\eta^2\text{-}CH_2{=}CH_2)(CNMe)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ **348**. Photoirriadiation of **348** in benzene at 5 °C leads to the release of ethylene and subsequent oxidative addition of benzene giving $[OsHPh(CNMe)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$. In contrast, photolysis of **348** in toluene-d_8 at −80 °C results in the C–H activation of the ethylene ligand yielding $[OsH(\eta^1\text{-}CH{=}CH_2)(CNMe)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ **349**. Compound **349** is stable in solution at room temperature and does not isomerize back to **348** under ambient conditions. The related zero-valent species $[Os(\eta^2\text{-}CH_2{=}CMe_2)(CO)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ is formed through a β-elimination process induced by the halide abstraction in $[OsX(\eta^1\text{-}CH_2CHMe_2)(CO)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (X = Cl, I), followed by the deprotonation of the hydride intermediate with Al_2O_3.[624]



(35)

The bis-alkene complex $[Os(\eta^2\text{-}CH_2{=}CHBu^t)_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ has been synthesized by heating an alcoholic solution of $[\{OsCl(\mu\text{-}Cl)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2]$ in the presence of base and the appropriate olefin.[624] Similar zero-valent ruthenium compounds $[Ru\{\eta^2\text{-}(E)\text{-}MeCO_2CH{=}CHCO_2Me\}_2(\eta^6\text{-arene})]$ (arene = C_6H_6, toluene, *p*-xylene, 1,3,5-$C_6H_3Me_3$, $C_6H_5Bu^t$, anisole,* *N*,*N*-dimethylaniline,* biphenyl, methylbenzoate, naphthalene) have been made at 110 °C from the precursor $[Ru\{\eta^2\text{-}(E)\text{-}MeCO_2CH{=}CHCO_2Me\}_2(\eta^6\text{-COT})]$ and an excess of arene, which acts both as reagent and as solvent.[637]

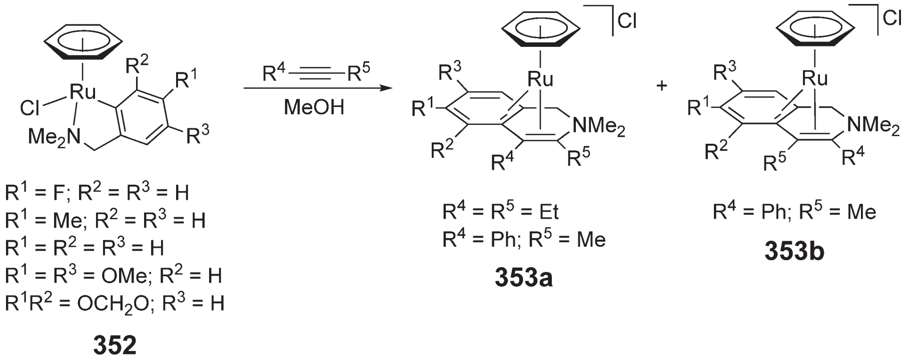
The discovery of a systematic synthetic route to ruthenium(0) derivatives of the type $[Ru(\eta^4\text{-COD})(\eta^6\text{-arene})]$, starting from the easily available complex $[Ru(\eta^4\text{-COD})(\eta^6\text{-naphthalene})]$ **350** (accessible in high yield from $[Ru(acac)_2(COD)]$ and sodium naphthalene), allowed the isolation of a wide range of compounds. The substitution of the naphthalene ligand by other arenes generally proceeds smoothly at room temperature in THF and in the presence of a small amount of acetonitrile. Following this synthetic approach, the complexes with the following functionalized arenes have been prepared: *rac*-$C_6H_5CHMeBu^t$,[426] bromobenzene, 1,4-dibromobenzene, 2-bromotoluene,[638] fluorobenzene, 1,3-difluorobenzene, 3-fluorotoluene, 3-chlorotoluene, 1,4-dichlorobenzene, 2-bromo-1,4-xylene, 1,3-dibromobenzene, 1-bromo-4-fluorobenzene,* 1-bromo-4-iodobenzene,* 4,4′-difluoro-1,1′-biphenyl,[639] 3-bromoacetophenone, 2-methylbenzaldehyde, 1,2-$RC_6H_4C({=}O)Me$ (R = Me, OMe), C_6H_5R (R = CH_2CO_2Et, (*R*)-$CHMeCH_2CO_2Me$,* $CH_2C({=}O)NEt_2$, (*S*)-$CHMeNHC({=}O)Pr^i$).[640] The yields of these reactions strongly depend on the substituents of the incoming ligand. Alternatively, this type of complex can be made by reacting $[Ru(\eta^4\text{-COD})(\eta^6\text{-COT})]$ with the appropriate arene at room temperature under hydrogen pressure.[1] As an example, $[Ru(\eta^4\text{-COD})(\eta^6\text{-}C_6H_5\text{-bornyl})]^*$ has been isolated in moderate yield by this methodology.[638] Nevertheless, this procedure has only a limited compatibility with functionalized substituents on the arene. The synthesis of novel $[Ru(\eta^4\text{-COD})(\eta^6\text{-arene})]$ complexes has also been achieved starting from **350** and an excess of alkyne, which after a cyclotrimerization process affords the arene ligand. Thus, **350** reacts with 3-hexyne in THF at room temperature to generate $[Ru(\eta^4\text{-COD})(\eta^6\text{-}C_6Et_6)]$.*[446] Other internal alkynes such as 2-butyne, 4-octyne, diphenylacetylene, and

2-hexyne have also been used.[641] The reactions with terminal alkynes $HC{\equiv}CR$ ($R = Bu^n$, $CH_2CH(Me)Et$, Ph, $(CH_2)_5C{\equiv}CH$, Pr^i, Bu^t, $SiMe_3$, (*S*)-CH(Me)R ($R = Et$, Pr^i, Bu^t)) lead to a mixture of the regioisomers $[Ru(\eta^4\text{-COD})(\eta^6\text{-}1,3,5\text{-}C_6H_3R_3)]$ and $[Ru(\eta^4\text{-COD})(\eta^6\text{-}1,2,4\text{-}C_6H_3R_3)]$, the former being largely prevalent when bulky alkynes are used.[641,642] Notably, all attempts to use the closely related complexes $[Ru(\eta^4\text{-COD})(\eta^6\text{-cym})]$ and $[Ru(\eta^4\text{-COD})(\eta^6\text{-}C_6H_6)]$ as precursors have failed.[446]

It is worth mentioning that the addition of hydrochloric acid to complexes $[Ru(\eta^4\text{-COD})(\eta^6\text{-arene})]$ constitutes the usual synthetic route to produce the dinuclear complexes $[\{RuCl(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$[426,446] whose 1,3- or 1,4-dihydroarenes are not readily available (see Section 6.14.4.1). In contrast, treatment of $[Ru(\eta^4\text{-COD})(\eta^6\text{-phenanthrene})]$ **351** with an acid containing a non-coordinating counteranion, that is, HPF_6, furnishes the hydrido derivative $[RuH(\eta^4\text{-COD})(\eta^6\text{-phenanthrene})][PF_6]$, the reaction being reversible upon addition of base.[643]

This ready access to η^6-arene ruthenium(0) complexes has allowed the entry to other functionalized derivatives. Thus, electrophilic substitution reactions have been performed starting from $[Ru(\eta^4\text{-COD})(\eta^6\text{-haloarene})]$ via sequential addition of $LiBu^n$ and a suitable electrophile at low temperature. A wide range of electrophiles such as acyl chlorides, chloroformates, chlorophosphines, epoxides, ketones, γ-lactones, etc., have been involved in this transformation.[638*,639*,644*] As an example, lithiation of $[Ru(\eta^4\text{-COD})(\eta^6\text{-}1,2\text{-}MeC_6H_4Br)]$ and further reaction with (−)-menthyl chloroformate leads to the formation of $[Ru(\eta^4\text{-COD})(\eta^6\text{-}1,2\text{-}MeC_6H_4CO_2\text{-menthyl})]$, isolated as a 1 : 1 mixture of diastereomers.[638] Isolation of one of these chiral planar isomers was accomplished by fractional crystallization. On the other hand, complexes $[Ru(\eta^4\text{-COD})(\eta^6\text{-arene})]$ bearing ketone, aldehyde, ester, or amide groups on the arene are valuable precursors to obtain more functionalized species through standard organic synthetic procedures.[640,644] In particular, aldol reactions, reductions of ester and amide, and Wittig-type olefinations have been performed.

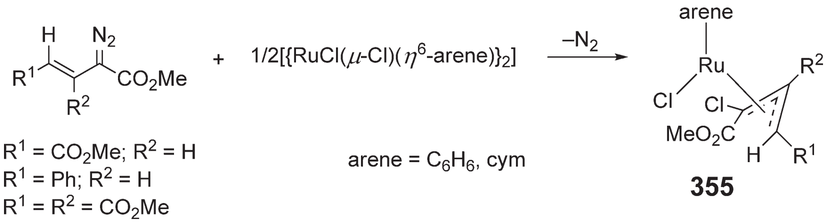
The syntheses of other diene derivatives have also been reported, including: (i) the reduction of the bis(arene) $[Os(\eta^6\text{-}C_6H_6)(\eta^6\text{-}[2_2]\text{-}1,4\text{-cyclophane})][BF_4]_2$ with Red-Al (Red-Al = sodium bis(2-methoxyethoxy)dihydroaluminate) which produces $[Os(\eta^4\text{-}C_6H_8)(\eta^6\text{-}[2_2]\text{-}1,4\text{-cyclophane})]$ in good yield,[447] and (ii) the formation of η^4-coordinated isoquinoline heterocycles by reaction of the *C,N*-cycloruthenated compounds **352** with 3-hexyne and 3-phenyl-2-propyne in methanol (Equation (36)).[645] Two regioisomers, **353a** and **353b**, are obtained in the case of the unsymmetrical alkyne $PhC{\equiv}CMe$.



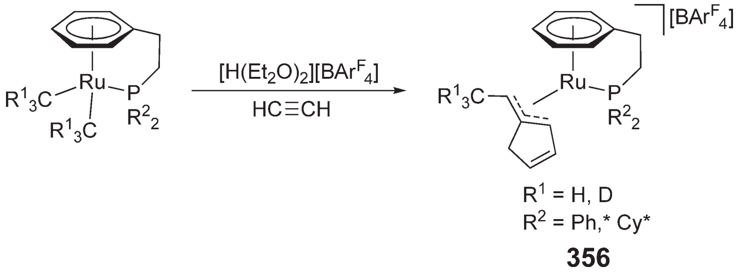
(36)

Only a few η^3-allyl derivatives have been reported. Hydride complexes $[OsH(\eta^3\text{-}2\text{-}C_3H_4R)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (**354**; R = H, Me) are isolated from the reactions of $[\{OsCl(\mu\text{-Cl})(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2]$ with the appropriate alkene $CH_2{=}CRMe$ and NaOH in 2-propanol.[624] The addition of CCl_4 to **354** leads to a hydride–chloride exchange providing the chloride derivatives $[OsCl(\eta^3\text{-}2\text{-}C_3H_4R)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (R = H, Me*). The reaction of $[\{RuCl(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$ with vinyl diazoacetate gives unexpectedly the chloride-functionalized allyl derivatives **355** (Equation (37)).[646*] The formation of **355** could be explained through the initial chloro bridge cleavage and subsequent dissociation of one chloride to give an η^3-vinylcarbene intermediate. Final attack of the dissociated Cl^- to the carbenic carbon atom affords complexes **355**. The ability of carbenic species to generate allyl derivatives has been used to form $[OsBr(\eta^3\text{-}1,1\text{-}C_3H_3Ph_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$, which is obtained by reacting $[Os\{\kappa^1(O)\text{-}O_2CCF_3\}_2({=}CPh_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ with the vinyl Grignard reagent $BrMgCH{=}CH_2$.[647] Its protonation with CF_3CO_2H liberates 1,1-diphenylpropene with concomitant formation of $[OsBr\{\kappa^2(O,O)\text{-}O_2CCF_3\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$.[512] Treatment of $[Ru(CR^1{}_3)_2\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PR^2{}_2\}]$ (R^1 = H, D; R^2 = Ph, Cy) with $[H(Et_2O)_2][BAr^F{}_4]$ under acetylene atmosphere affords the allyl derivatives **356** along with polyacetylene (Equation (38)).

Complexes **356** arise from the coupling of one methyl ligand and 3 equiv. of acetylene.[635] The allyl derivative $[RuCl\{\eta^3\text{-}(CN)_2CCPhC{=}C(CN)_2\}(\eta^6\text{-hmb})]$ is also known, being obtained by reacting the alkynyl complex $[RuCl(C{\equiv}CPh)(PPh_3)(\eta^6\text{-hmb})]$ with tetracyanoethylene.[648] A possible path for this reaction consists of the $[2\pi + 2\pi]$-cycloaddition between the triple bond of the alkynyl species and the C=C of tetracyanoethylene, followed by the rearrangement of the resulting cyclobutene through a ring-opening process.



(37)



(38)

The synthesis of the acyclic η^5-dienyl species $[Ru(\eta^5\text{-}CH_2CMeCHCMeCH_2)(\eta^6\text{-arene})][BF_4]$ (arene $= C_6H_6$, toluene) has been performed using the bis(allyl) ruthenium(IV) precursor $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ ($C_{10}H_{16} =$ 2,7-dimethylocta-2,6-diene-1,8-diyl). This dimer reacts with 2,4-dimethylpenta-1,3-diene and the appropriate arene, in ethanol and in the presence of $Ag[BF_4]$, to afford the final η^5-dienyl species.[649] Several η^5-cyclohexadienyl derivatives have been obtained by nucleophilic addition to bis(arene) or cyclopentadienyl arene–ruthenium compounds (see Sections 6.14.2.1 and 6.14.2.2).

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6.15
Mononuclear Ru/Os Compounds with η^1 and C_5–C_6 Ligands

J Gimeno and V Cadierno, Universidad de Oviedo, Oviedo, Spain

6.15.1 Introduction

Ruthenium and osmium moieties bearing η^5-cyclopentadienyl and η^6-arene rings are classical metal fragments capable of stabilizing a large range of η^1-M–C bonds. Since the publication of COMC (1995), they have been used extensively in novel synthetic and reactivity studies continuing the interest to provide both electron-deficient and electron-rich fragments. New developments are mainly focused on osmium chemistry, which has attracted a particular interest due to the accessibility of novel precursors. This contribution covers the literature published from January 1994 to December 2004. Several reviews recounting particular aspects of this chemistry have appeared and will be referred to for further additional details in the following sections. General reviews have been also reported (including a special issue of *Coord. Chem. Rev.* devoted to the chemistry of vinylidene, allenylidene, and metallacumulene complexes).[1,1a–1c] Throughout this chapter, a compound formula or number, or alternatively a reference, bearing an asterisk indicates that an X-ray structural determination has been carried out).

6.15.2 Half-Sandwich η^5-Cyclopentadienyl and η^5-Indenyl Complexes

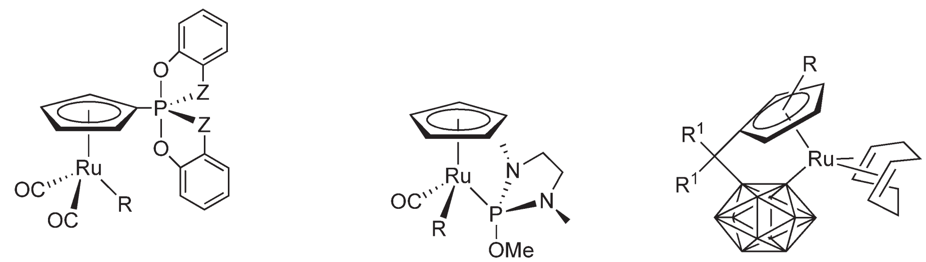
6.15.2.1 Alkyl, Aryl, and Acyl Complexes

A relatively large series of η^1-alkyl and aryl derivatives has been described, the latter mostly arising from cyclometallation reactions (see Section 6.15.2.2). Two classical synthetic methodologies are used to prepare a number of η^1-alkyl derivatives:

(i) Method A: This is based on the electrophilic addition of an alkyl halide to organometallic anions $[Ru(\eta^5\text{-}C_5R_5)L_2]^-$. It has been used to prepare complexes of the type: (a) $[RuMeCp^*(tmbp)]$ (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine,[2] (b) $[RuMeCp^*(bipy)]$,[3] (c) complexes **1** containing a phosphorane-substituted cyclopentadienyl ligand (Figure 1),[4] and (d) the diamino-substituted phosphite derivatives **2**.[5]

(ii) Method B: This is based on the transmetallation reaction of halide complexes with lithium or sodium alkyls MR or Grignard reagents XMgR. This methodology has been used to prepare: (a) pentamethylated [60]fullerene derivatives $[RuR(\eta^5\text{-}C_{60}Me_5)(CO)_2]$ (R = Me*, CH_2SiMe_3),[6] (b) ruthenium complexes **3** (Figure 1) incorporating cyclopentadienyl–carboranyl ligands (cyclopentadienyl ring = $\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)C_2B_{10}H_{10}{}^*$, $\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)\text{-}C_2B_{10}H_{10}{}^*$, $\eta^5{:}\sigma\text{-}H_2C(C_{13}H_8)C_2B_{10}H_{10}{}^*$) as well as analogous compounds containing a bidentate phosphine or 2,2′-bipyridine ligand instead of 1,5-cyclooctadiene (COD),[7] and (c) the osmium(II) complexes $[Os(CH_2SiMe_3)Cp(L^1)(L^2)]$ ($L^1 = L^2 = PMe_3$, PPh_3) and $[OsRCp^*(PMe_3)_2]$ (R = CH_2SiMe_3, Ph).[8]

Attempts to prepare dialkyl complexes from the dibromide precursor $[OsBr_2Cp^*(NO)]$ by reactions with MgR_2 failed due to the slow kinetics affording instead the monoalkyl derivatives $[OsBr(R)Cp^*(NO)]$ (R = Ph, Me, CH_2SiMe_3, 2-C_6H_4Me). Nevertheless, the dimethyl complex $[OsMe_2Cp^*(NO)]$ could be obtained by the treatment of $[OsBr(Me)Cp^*(NO)]$ with Ag[OTf] followed by addition of $MgMe_2$.[9] This contrasts (see COMC (1995)) with the analogous reactions of $[RuCl_2Cp^*(NO)]$ with alkylating agents, which readily afford the corresponding dialkylated derivatives. This observation is a clear example of the well-known slower ligand-substitution reactions in osmium with respect to ruthenium.[10] Transmetallation of $[RuClCp(PPh_3)_2]$ with the sodium salt of (phenylsulphonyl)acetonitrile gives rise to a 59:41 mixture of $[Ru\{\eta^1\text{-}CH(CN)SO_2Ph\}Cp(PPh_3)_2]$ and its zwitterionic isomer $[Ru^+\{\kappa^1(N)\text{-}NC(CH^-)SO_2Ph\}Cp(PPh_3)_2]^*$, representing the first examples of *C*- and *N*-bound isomers of a coordinated α-cyanocarbanion. The *C*-bound complex is less stable and readily converts into the *N*-bound isomer in solution. A series of related derivatives including monodentate PPr^i_3, PMe_2Ph, $PMePh_2$, or bidentate bis(diphenylphosphino)methane* (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino) butane (dppb), 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,2-bis(dicyclohexylphosphino)ethane (dcpe) phosphines have also been prepared through PPh_3 ligand exchange and used to study the influence of the ancillary ligands in the thermal stability of both isomers.[11] Mechanistic studies of this interconversion process have been later



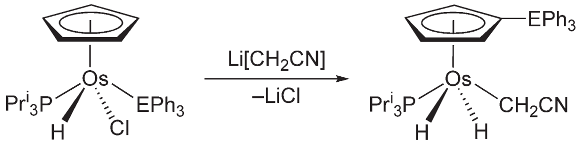
Z = NMe; R = Me, CH_2Ph,* CD_3
Z = O; R = Me
1

R = Me, CH_2SiMe_3
2

R^1 = H, Me
3*

Figure 1 Structure of the alkyl-ruthenium(II) complexes **1**–**3**.

reported.[12] In the context of studies devoted to the synthesis of substituted cyclopentadienyl–osmium(IV) complexes, new derivatives containing [Os]–CH_2CN bonds have been synthesized according to Equation (1).[13]



E = Si, Ge

(1)

The discovery of a synthetic route [$Os_2Br_4Cp^*_2$] provided a useful precursor of novel organoosmium(IV) derivatives. In particular, its ready conversion to the allyl compound [$OsBr_2(\eta^3$-2-$C_3H_4Me)Cp^*$], upon treatment with 3-bromo-2-methylpropene, has allowed the entrance to the new alkyl–osmium(IV) derivatives [$OsMe_2(\eta^3$-2-$C_3H_4Me)Cp^*$] and [$OsBr(R)(\eta^3$-2-$C_3H_4Me)Cp^*$] (R = Me, CH_2SiMe_3). They have been obtained in moderate yields by reaction of the allyl–dibromide complex with LiMe and either $MgMe_2$ or Li[CH_2SiMe_3], respectively. The cationic aquo complex [$OsMe(\eta^3$-2-$C_3H_4Me)Cp^*(H_2O)$][BF_4]* has also been prepared through the treatment of [$OsMe_2(\eta^3$-2-$C_3H_4Me)Cp^*$] with HBF_4 in the presence of H_2O.[14] The related aquo–ruthenium complex [$RuMeCp^*(NO)(H_2O)$][$BAr^F{}_4$] has also been obtained by protonation of the dimethyl derivative [$RuMe_2Cp^*(NO)$] with [$H(OEt_2)_2$][$BAr^F{}_4$] ($BAr^F{}_4$ = tetrakis{3,5-bis(trifluoromethyl)phenyl}borate) in the presence of water. Substitution of the coordinated water molecule by PMe_3 affords [$RuMeCp^*(NO)(PMe_3)$][$BAr^F{}_4$].[15] When triflic acid HOTf is used for the protonation of [$RuR_2Cp^*(NO)$], the corresponding triflate complexes [$RuR(OTf)Cp^*(NO)$] (R = Me, Ph*, 4-C_6H_4Me) are isolated.[16] Monoalkylated ruthenium(II) nitrosyls [$RuMeCp^*(NO)(PR_3)$][BF_4] (PR_3 = PMe_3, PMe_2Ph) are accessible through the reactions of [$RuMeCp^*(PR_3)_2$] with [NO][BF_4].[17]

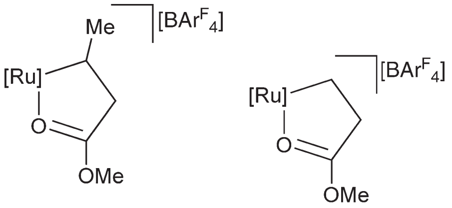
Optimized syntheses of the previously known methyl derivatives [$OsMeCp^*(CO)_2$] and [$RuMeCp(PPh_2Me)_2$] have been described using methods A and B, respectively.[18,18a] In addition, the preparation of the osmium(IV) methyl–hydride complex [$OsH(Me)Cp^*(dmpm)$][$HC(SO_2CF_3)_2$] through the protonation of [$OsMeCp^*(dmpm)$] with the carbon acid $H_2C(SO_2CF_3)_2$ has also been reported (dmpm = bis(dimethylphosphino)methane). This complex undergoes a rapid exchange of hydrogen atoms between the hydride and methyl ligands.[19]

While studying the mechanism of catalytic dimerization of methyl acrylate, the stoichiometric reactivity of the aquo complex [$RuMeCp^*(NO)(H_2O)$][$BAr^F{}_4$] toward methyl acrylate was investigated. Following the initial η^2-coordination of the olefin to the metal, a migratory insertion gives the chelate complex **4*** (Figure 2). When an excess of methyl acrylate is used, the unsubstituted chelate complex **5**, along with free methyl crotonate MeHC=CHCO$_2$Me, is obtained after 36 h of reaction.[15]

A further route to generate alkyl derivatives based on the insertion of the methylene group of CH_2N_2 into the Ru^{IV}–Cl bond in the allyl complex [$RuCl_2(\eta^3$-$C_3H_5)Cp^*$] to give the chloromethyl–ruthenium complex [$RuCl(CH_2Cl)(\eta^3$-$C_3H_5)Cp^*$] has been described. However, due to the relatively strong Ru^{IV}–Cl bond, the reaction is rather slow and a large excess of CH_2N_2 is required.[20]

The availability of stable osmium(IV) alkyl complexes bearing imido ligands has allowed the entrance to series of cyclopentadienyl–alkyl complexes, which are generated through the reactivity of the imido group (see COMC (1995)). Following these previous results, the novel methylene–amido derivative [$Os(=N=CH_2)(CH_2SiMe_3)_2Cp$] has been obtained from deprotonation of the cationic methylimido complex [$Os(\equiv NMe)(CH_2SiMe_3)_2Cp$][OTf] with NaH.[21]

Studies on the reactivity of the alkylidene complex [$OsCl(=CHPh)Cp\{\kappa^1(P)$-$Pr^i{}_2PCMe=CH_2\}$] show that the carbene carbon atom presents an amphiphilic character reacting with both nucleophiles and electrophiles. In accordance with the



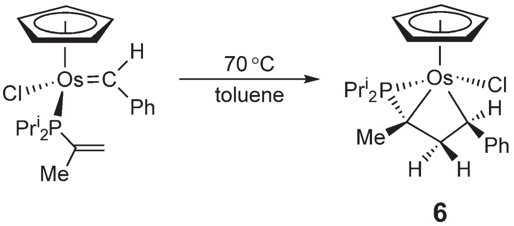
4*

5

[Ru] = [RuCp*(NO)]

Figure 2 The chelate ruthenium complexes **4** and **5**.

nucleophilic character, the reaction with HBF_4 leads to the formation of the benzyl–osmium(IV) complex $[OsCl(CH_2Ph)Cp\{\kappa^3(P,C,C)\text{-}Pr^i{}_2PCMe{=}CH_2\}][BF_4]$ arising from the regioselective protonation of the C_α-atom of the alkylidene group. On the other hand, under heating, the alkylidene $[OsCl({=}CHPh)Cp\{\kappa^1(P)\text{-}Pr^i{}_2PCMe{=}CH_2\}]$ undergoes an intramolecular and diasteroselective [2 + 2]-cycloaddition process between the C=C double bond of the phosphine and the Os=C bond affording the unprecedented osmaphosphabicyclopentane derivative **6** (Equation (2)).[22]



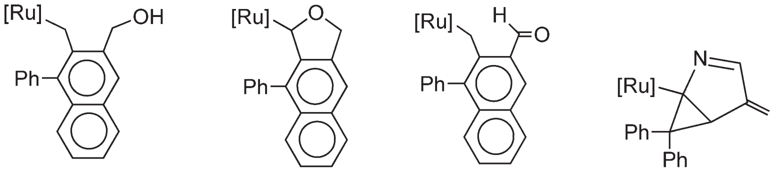
6

(2)

Studies devoted to the condensation of propargyl alcohol and propargyl amines with the allenylidene ligand of the $CpRu^{II}$ complex $[Ru({=}C{=}C{=}CPh_2)Cp(CO)(PPr^i{}_3)][BF_4]$ have disclosed a variety of carbene and alkenyl derivatives formed through C–O, C–C, and C–N coupling reactions (see Sections 6.15.2.3 and 6.15.2.5). Such compounds have been used as starting materials for the preparation of the novel derivatives **7–10** containing η^1-carbon polycyclic ligands (Figure 3).[23,24] The η^1-diphenylmethyl osmium complex $[Os(CHPh_2)Cp(CO)(PPr^i{}_3)]$ containing the related fragment $[OsCp(CO)(PPr^i{}_3)]$ has also been described.[25]

Acyl-type complexes are usually generated through alkyl-migration reactions in carbonyl compounds. The rates of alkyl migration in the series $[MRCp(CO)_2]$ (M = Ru, Os; $R = n\text{-}C_mH_{2m-1}$ with $m = 1$–3, 6, 8, 10, 12, 18) have been measured showing dependence on both the alkyl group and the metal.[26] The formation of unstable cationic Fischer-type hydroxy–carbenes $[M]^+{=}C(OH)R$ is an alternative synthetic route of acyl derivatives [M]–COR via deprotonation reactions. In this regard, deprotonation with Al_2O_3 of hydroxy–carbenes $[Ru\{{=}C(OH)R\}Cp(CO)(PPr^i{}_3)_2]$-$[BF_4]$, either isolated or generated *in situ* (see Section 6.15.2.5), affords the neutral acyl derivatives $[Ru(COR)Cp(CO)(PPr^i{}_3)_2](R = CH{=}CH_2,\ CH{=}CPh_2{}^*,\ CH{=}CC_5H_{10})$.[27]

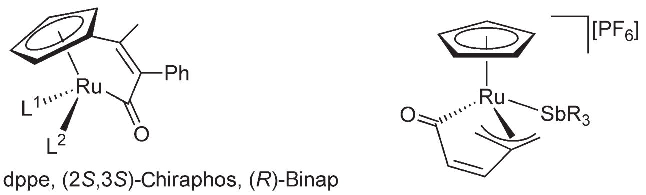
The unexpected formation of the acyl derivatives **11** (Figure 4) from the treatment of $[RuCl(\eta^5\text{-}C_5H_4COCH_3)(L^1)(L^2)]$ with $HC{\equiv}CPh$ has been reported. In this reaction, the oxygen atom of the pendant acetyl group of the cyclopentadienyl ligand is transferred to the C_α-atom of the vinylidene group in the intermediate complex $[Ru\{{=}C{=}C(H)Ph\}(\eta^5\text{-}C_5H_4COCH_3)]Cl$, with concomitant formation of the C=C bond.[28] It has been also described how the cationic vinylidene $[Ru\{{=}C{=}C(Ph)CH_2CN\}Cp(PPh_3)\{P(OMe)_3\}][PF_6]$ undergoes, in the presence of acid,



7 **8*** **9** **10***

[Ru] = $[RuCp(CO)(PPr^i{}_3)]$

Figure 3 Structure of the polycyclic CpRu(II) derivatives **7–10**.



L^1L^2 = dppe, (2*S*,3*S*)-Chiraphos, (*R*)-Binap
$L^1 = L^2 = PPh_3{}^*$

11

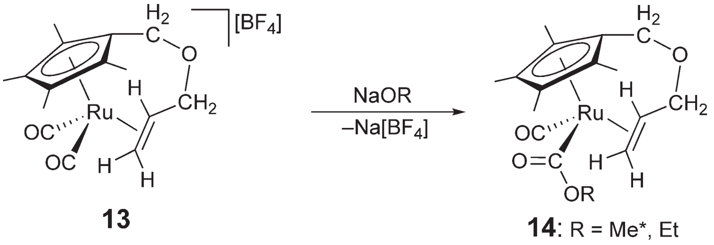
12: R = Ph, Bu^n

Chiraphos = 2,3-bis(diphenylphosphino)butane
Binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl

Figure 4 Structure of the ruthenium complexes **11** and **12**.

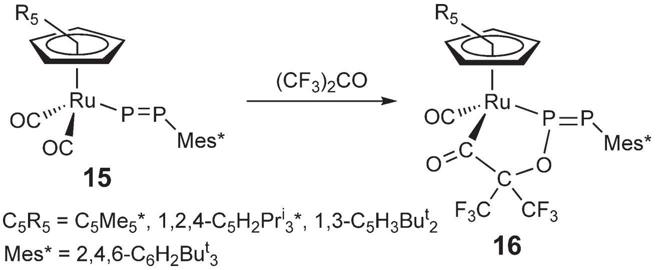
a carbon–carbon bond cleavage to give the neutral acyl derivative [Ru(COCH$_2$Ph)Cp(PPh$_3$){P(OMe)$_3$}]*.[29] While studying the synthesis of alkylidene complexes (see Section 6.15.2.6.3) from [RuCp(NCMe)$_2$(SbR$_3$)][PF$_6$] (R = Ph, Bu^n), the η^3-allyl–acyl complexes **12** were isolated from the reaction with HC≡CCH$_2$(OH).[30]

Alkoxy–carbonyl complexes **14** are unexpectedly formed in the reactions of the bis-carbonyl ruthenium(II) derivative **13**, containing a tethered olefinic side chain, with sodium alkoxides (Equation (3)), the process involving the addition of the alkoxide anions to one coordinated carbonyl ligand.[31]



(3)

According to Equation (4), the addition of anhydrous hexafluoroacetone to the phosphorus atom of the diphosphene ligand in **15** gives complexes **16** featuring a five-membered metallaheterocycle containing an acyl group. It is claimed that complexes **16** result from an intramolecular attack to a carbonyl ligand after the addition of hexafluoroacetone to the phosphorus atom.[32]



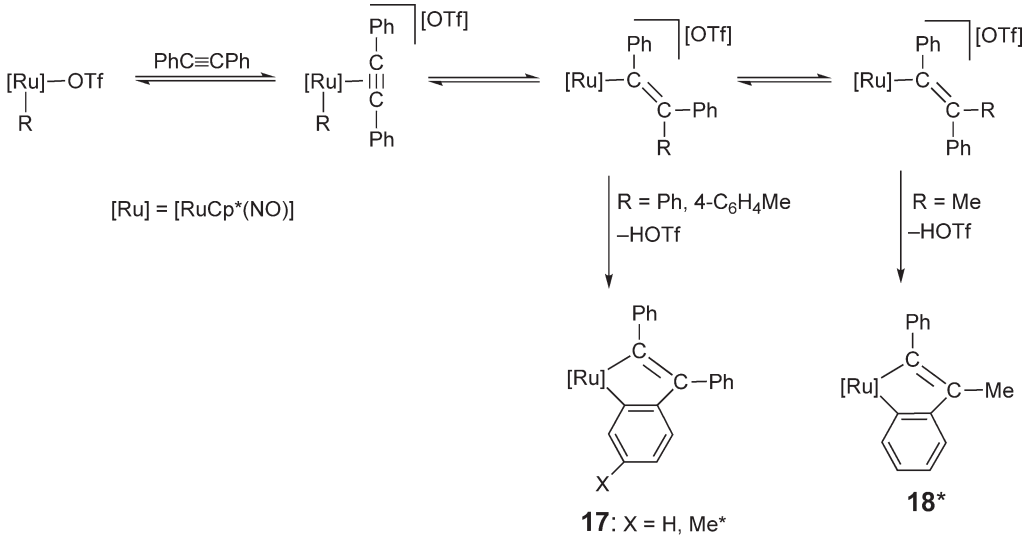
(4)

6.15.2.2 Cyclometallated Complexes

The activation of aryl C–H bonds through orthometallation reactions constitutes one of the most classical routes to generate metal–aryl bonds. Activation of alkyl C–H bonds is also known, albeit to a lesser extent, since the former is kinetically and thermodynamically favored. η^5-Cp ruthenium and osmium fragments, as well as η^6-arene derivatives (see Section 6.15.3.3), have been largely employed for promoting such transformations. The presence of a relatively electron-poor ligand or the generation of a free coordination site on the metal favors the intramolecular activation of C–H bonds. This is nicely illustrated by the reaction of the triflate complexes [RuR(OTf)Cp*(NO)] (R = Me, Ph, 4-C$_6$H$_4$Me) with PhC≡CPh, which leads to the formation of the orthometallated alkenyl derivatives **17** and **18** (Scheme 1). The phenyl C–H activation process, which proceeds through an unsaturated alkenyl intermediate, is relatively rapid for R = Ph and 4-C$_6$H$_4$Me versus the observed *cis–trans* isomerization for R = Me.[16]

Similarly, the triflato-osmium(II) complex [Os(OTf)Cp(PPh$_3$)$_2$] spontaneously evolves into the hydrido–osmium(IV) derivative **19** both in solution and in the solid state as the result of the orthometallation of one of the phenyl groups of the PPh$_3$ ligand (Figure 5).[8] Phenyl C–H activation of coordinated PPh$_3$ also occurs through the abstraction of the chloride ligand, upon treatment with Tl[PF$_6$], in the osmium(II)–chloride precursor [OsClCp(PPh$_3$)(PPr$^i_3$)], which leads to the corresponding orthometallated complex **20***.[33] The abstraction of the hydride ligand in **20** yields the neutral cyclometallated osmium(II) complex **21**. A related C–H activation process involving one phenyl ring of coordinated P(OPh)$_3$ also occurs when [RuCl(η^5-C$_5$H$_4$CH$_2$CH$_2$NMe$_2$){P(OPh)$_3$}$_2$] is treated with Ag[OTf] leading to complex **22**.[34]

The dissociation of the chloride ligand in the complex [OsClCp(PPr$^i_3$)$_2$] takes place in polar solvents. The resulting unsaturated metal fragment [OsCp(PPr$^i_3$)$_2$]$^+$ is able to activate a methyl C–H bond of one of the coordinated PPr$^i_3$ ligands to give the cyclometallated complex **23** (Figure 5). This compound, isolated as the corresponding hexafluorophosphate salt after treatment of the solution with Na[PF$_6$] or Tl[PF$_6$], is generated as a 1 : 1 mixture of two diastereoisomers.[35] Following a similar approach, the cyclometallated complex **24**, containing a tethered cyclopentadienyl–phosphine ligand, has been synthesized.[36] This is a rare example in which a selective alkyl C–H activation in the presence of phenyl groups has occurred in spite of the preference of the C–H aryl versus alkyl activation.



Scheme 1

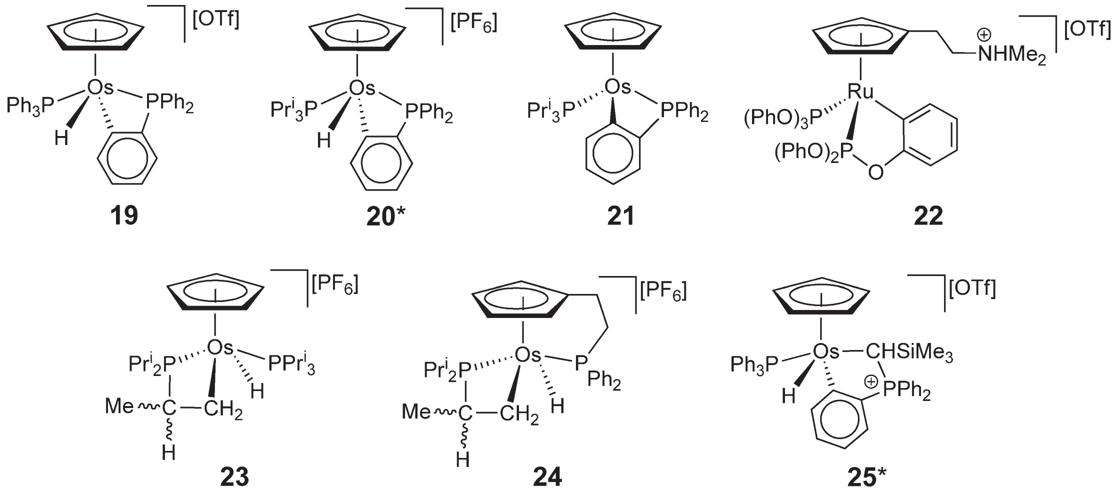
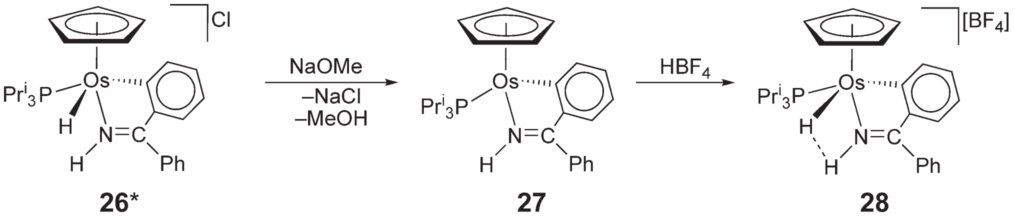


Figure 5 The cyclometallated complexes **19**–**25**.

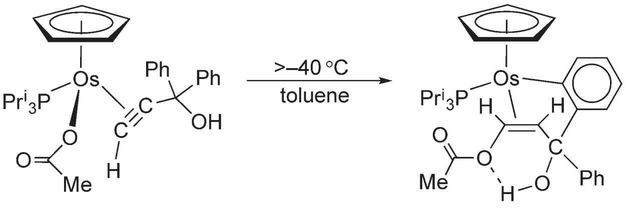
Remarkably, both alkyl and aryl C–H activations have been described in the formation of the metallacyclic osmium(IV)–hydride complex **25***, generated as the minor component (12%) of a mixture with the deprotonated methylene–amido complex [Os(=N=CH$_2$)Cp(CH$_2$SiMe$_3$)$_2$], from the reaction of the imido complex [Os(≡NMe)Cp(CH$_2$SiMe$_3$)$_2$][OTf] with PPh$_3$.[37]

Intramolecular activation of aryl C–H bonds after the coordination of ligands containing phenyl groups is relatively common. Thus, the reaction of [OsClCp(PPr$^i_3$)$_2$] with benzophenone imine HN=CPh$_2$ in pentane at RT leads after the dissociation of one PPr$^i_3$ ligand to a selective phenyl C–H bond activation to give complex **26*** (Equation (5)). In this case, the C–H activation of one of the phenyl groups of the imine is preferred versus the methyl C–H activation of the isopropyl group. The neutral complex **27** has been obtained by reaction of **26** with NaOMe. Protonation of **27** with HBF$_4$ gives the cationic complex **28** (Equation (5)).[33]



(5)

According to Equation (6), the coordination of 1,1-diphenyl-2-propyn-1-ol via dissociation of PPr^i_3 in $[Os(OAc)Cp(PPr^i_3)_2]$ also promotes the selective C–H activation of one of the phenyl groups instead of an isopropyl group. The formation of the resulting cyclometallated complex **29*** also involves the *O*-addition of the carboxylate group to the carbon–carbon triple bond of the coordinated alkyne.[38]

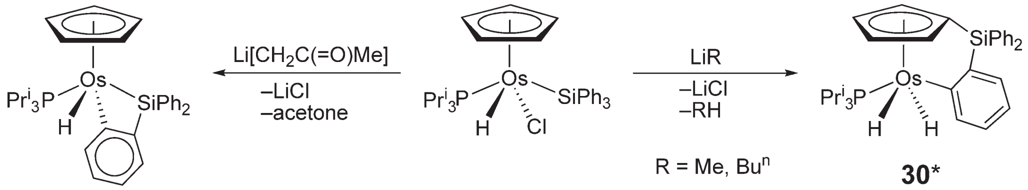


29*

(6)

Selective C–H activation of one of the phenyl rings instead of an isopropyl group also occurs in the reaction of $[OsHClCp(PPr^i_3)(SiPh_3)]$ with LiR (R = Me, Bu^n) to afford complex **30*** (Scheme 2). An $SiPh_3(Os)/H(Cp)$ exchange in which a migration of a triphenylsilyl group takes place from osmium to the cyclopentadienyl group is initially involved in this reaction. In contrast, the treatment of $[OsHClCp(PPr^i_3)(SiPh_3)]$ with the lithium enolate $Li[CH_2C({=}O)Me]$ does not afford the corresponding substituted cyclopentadienyl derivative giving rise instead to the orthometallated complex **31**. The formation of **31** probably involves the initial replacement of the chloride ligand by the enolate followed by the reductive elimination of acetone to give the 16-electron species $[OsCp(P^iPr_3)(SiPh_3)]$, which induces the C–H activation.[13]

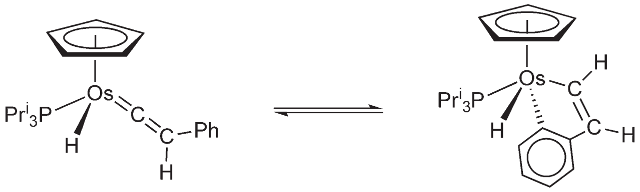
The activation of a C–H bond of a phenyl group is also observed in the reaction of the cationic carbyne complex $[OsH({\equiv}CCH_2Ph)Cp(PPr^i_3)][BF_4]$ with KOH, which yields the cyclometallated hydride–osmium(IV) derivative **33**. This complex is obtained in equilibrium with its vinylidene isomer **32** (Figure 6).[39] The related cyclometallated alkenyl complex **34*** is also known.[40] It is proposed that these C–H activations take place via the unsaturated alkenyl complexes $[Os\{C(H){=}C(R)Ph\}(\eta^5\text{-}C_5H_4X)(PPr^i_3)]$ (R = H, X = H; R = Me, X = $SiPh_3$), which are formed by migration of the hydride ligand to the C_α-atom of the vinylidene group ${=}C{=}C(R)Ph$ (R = H, Me). The reaction of the



31

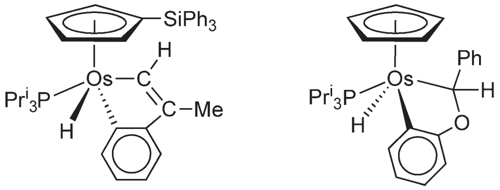
30*

Scheme 2



32

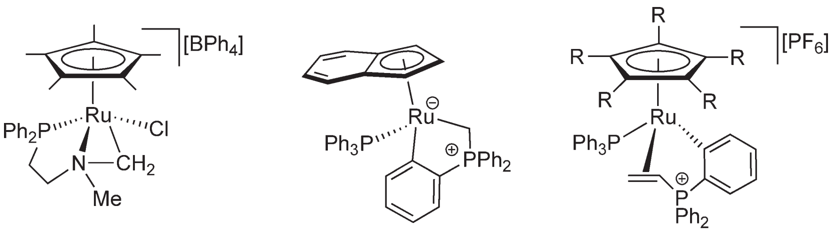
33



34*

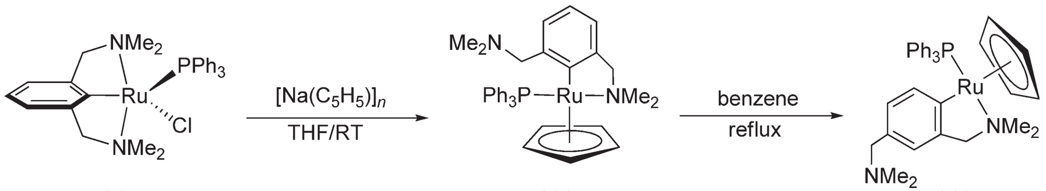
35*

Figure 6 Structure of the CpOs derivatives **32**–**35**.



36* **37*** **38**: R = H, Me*

Figure 7 The cyclometallated–ruthenium complexes **36**–**38**.



39 **40*** **41***

Scheme 3

carbyne complex [Os(≡CPh)Cp(PPr$^i_3$)] with phenol also gives rise to a cyclometallation process affording complex **35***. Formation of this cyclometallated product involves the initial addition of phenol to the carbyne Os≡C unit to generate the hydride–alkoxycarbene intermediate [OsH{=C(OPh)Ph}Cp(PPr$^i_3$)], which evolves into the unsaturated species [Os{CH(OPh)Ph}Cp(PPr$^i_3$)] by hydride migration from the metal to the C$_\alpha$-atom of the carbene group. Final C–H activation of one of the *ortho*-C–H bonds of the OPh group leads to the osmium(IV) cyclometallated complex **35**.[25]

Reports on C–H activation promoted by ruthenium fragments are much scarcer. The following examples have been described.

(i) The cyclometallated complex **36*** obtained from [RuClCp*{κ^2(*P*,*N*)-$Ph_2P(CH_2)_2NMe_2$}] after chloride abstraction with Na[BPh$_4$] in CH_2Cl_2 (Figure 7). Activations of C–H bonds adjacent to nitrogen are rare compared to those adjacent to phosphorus.[41]

(ii) The phosphorus–ylide complex **37*** results from the reaction of the indenyl complex [RuCl(η^5-C_9H_7)(PPh$_3$)$_2$] with KOH/Pr^{i}OH in CH_2Cl_2. In this compound one of the phenyl C–H bonds of the phosphine is activated and the methylene group of the dichloromethane is incorporated to the molecule (Figure 7).[42]

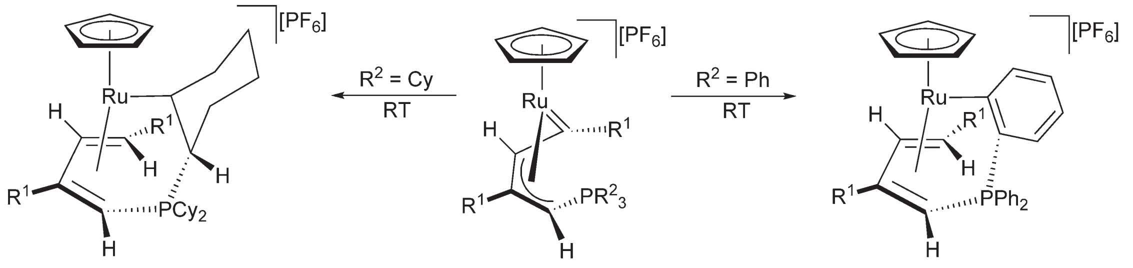
(iii) Complexes **38** are formed in low yield after heating acetonitrile solutions of the vinylidene derivatives [Ru(=C=CH$_2$)(η^5-C_5R_5)(PPh$_3$)$_2$][PF$_6$] in the presence of PPh$_3$ for 5 days (Figure 7). A mechanism involving addition of the phosphine at the C$_\alpha$-atom of the vinylidene group followed by orthometallation of the resulting phosphonio–alkenyl species is proposed. The spectroscopic characterization of the phosphonio–alkenyl complex [Ru{C(PMePh$_2$)=CH$_2$}Cp(PMePh$_2$)$_2$][PF$_6$] supports this plausible pathway.[43]

(iv) The cyclopentadienyl complex **40*** is obtained by reaction of [Na(C$_5$H$_5$)]$_n$ with the five-coordinate derivative **39** (Scheme 3). Similar to its η^6-*p*-cymene counterpart (see Section 6.15.3.3), complex **40** undergoes an intramolecular rearrangement in refluxing benzene to give the isomer **41***, which results from a formal shift of the metal–C$_{aryl}$ bond from position 1 to position 3 on the aromatic ring of the metallated ligand.[44]

(v) Complexes **43** and **44** are generated from allyl carbenes **42**, which, at RT, are able to dehydrogenate aryl or alkyl groups of the coordinated PPh$_3$ and PCy$_3$ ligands, respectively, through a C–H bond activation (Scheme 4).[45]

6.15.2.3 Alkenyl, Allenyl, and Related Complexes Containing η^1-M–C Bonds

The classical synthetic methodologies for alkenyl complexes based on the nucleophilic additions to π-alkyne complexes and the insertion reactions of alkynes into [M]–H and [M]–R bonds have been employed to prepare a number of alkenyl, butadienyl, and analogous derivatives. Nevertheless, the chemistry of vinylidene and allenylidene complexes has disclosed new routes to alkenyl derivatives, most of them incorporating heterocyclic systems.



44: R^1 = C_6H_9,* *p*-C_6H_4OMe

42

R^1 = C_6H_9,* Bu^n, 4-$C_6H_4NO_2$, $[Cc]^+$
$[Cc]^+$ = Cobaltocenium
43

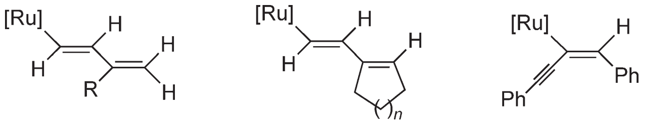
Scheme 4

Although the nucleophilic attack on π-alkyne complexes is hampered by nucleophile–alkyne ligand exchange, alkenyl complexes $[Ru\{C(CO_2Me){=}C(OMe)CO_2Me\}Cp(N{-}N)]$ (N–N = 1,4-diisopropyl-1,3-diazabutadiene) have been obtained from the reaction of sodium methoxide with the π-alkyne derivatives $[Ru\{\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me\}Cp(N{-}N)][OTf]$. A mixture of both (*E*)- and (*Z*)-stereoisomers together with minor amounts of the methoxide complex $[Ru(OMe)Cp(N{-}N)]$ is obtained.[46]

Hydride indenyl–ruthenium(II) complexes $[RuH(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ have proved to be suitable starting materials for the synthesis of a variety of alkenyl complexes. Thus, the treatment with activated alkynes $RC{\equiv}CCO_2Me$ (R = H, CO_2Me) leads to the regio- and stereoselective 1,2-insertion products (*syn*-addition) $[Ru\{(E)\text{-}C(CO_2Me){=}CHR\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (R = H, L^1L^2 = dppe, dppm, (*S*)-$(Ph_2P)_2NCHMePh$; R = H, $L^1 = L^2 = PMe_2Ph$; R = H, $L^1 = PPh_3$, $L^2 = PMe_3$; R = CO_2Me, L^1L^2 = dppe, dppm, (*S*)-$(Ph_2P)_2NC(H)MePh^*$; R = CO_2Me, $L^1 = L^2 = PMe_2Ph$; R = CO_2Me, $L^1 = PPh_3$, $L^2 = PMe_2Ph$, PMe_3).[47,48] The reaction of these hydride complexes with phenylacetylene has peculiar structural requirements since only those complexes containing the less sterically demanding diphosphine ligands dppm and (*S*)-$(Ph_2P)_2NCHMePh$ are reactive, leading to $[Ru\{(E)\text{-}CPh{=}CH_2\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (L^1L^2 = dppm, (*S*)-$(Ph_2P)_2NCHMePh$). In contrast, the cyclopentadienyl complex $[RuH(\eta^5\text{-}C_5H_5)(dppm)]$ and the related indenyl derivatives $[RuH(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (L^1L^2 = dppe or monodentate phosphines) do not react even under forcing conditions. A kinetic study of the reaction between $[RuX(\eta^5\text{-}C_9H_7)(dppm)]$ (X = H, D) and phenylacetylene, disclosing an associative mechanism, has also been carried out.[47] Analogous indenyl-substituted complexes $[Ru\{(E)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\eta^5\text{-}1,2,3\text{-}C_9H_4Me_3)(CO)L]$ (L = PPh_3, PPr^i_3) have been synthesized starting from the corresponding hydride precursors.[47]

The hydride derivative $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ also reacts with the propargylic alcohols $HC{\equiv}CCRMe(OH)$ (R = H, Me) and 1-ethynyl-1-cycloalkanols to give, in a regio- and stereoselective manner, the α,β-unsaturated alkenyl complexes 45 and 46, respectively (Figure 8). The insertion of these propargylic alcohols into the Ru–H bond leads to the transient formation of hydroxyalkenyl complexes $[Ru\{(E)\text{-}CH{=}CHCR_2(OH)\}(\eta^5\text{-}C_9H_7)(dppm)]$, which undergo a rapid dehydration process to give the final products. The hydroxyalkenyl derivative $[Ru\{(E)\text{-}CH{=}CHCH_2(OH)\}(\eta^5\text{-}C_9H_7)(dppm)]$ is sufficiently stable toward dehydration and can be isolated.[49] In a similar way, complex 47* is selectively obtained from the reaction of $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ with 1,4-diphenyl-1,3-butadiyne, $PhC{\equiv}CC{\equiv}CPh$.[50]

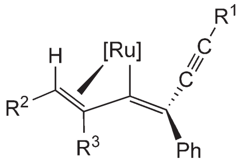
An insertion reaction also occurs when the 16-electron alkynyl complex $[Ru(C{\equiv}CPh)Cp^*(PPh_3)]$, generated *in situ* by deprotonation of the vinylidene $[RuCl\{{=}C{=}C(H)Ph\}Cp^*(PPh_3)]$, is treated with the 1,3-enyne *trans*-$PhCH{=}CHC{\equiv}CPh$. The reaction affords the $\eta^1{:}\eta^2$-alkynylbutadienyl derivative 48* ($R^1 = R^2$ = Ph, R^3 = H), which is formed through the insertion of the alkyne group of the enyne in the Ru–alkynyl bond (Figure 9).[51]



45: R = H, Me **46**: *n* = 1, 2, 3 **47***

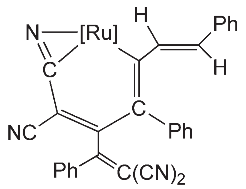
[Ru] = $[Ru(\eta^5\text{-}C_9H_7)(dppm)]$

Figure 8 The alkenyl-ruthenium(II) derivatives **45**–**47**.



$R^1 = R^2 = Ph; R^3 = H^*$
$R^1 = SiMe_3; R^2 = CO_2Me; R^3 = H$
$R^1 = SiMe_3; R^2 = CO_2Me; R^3 = CH{=}CHSiMe_3^*$

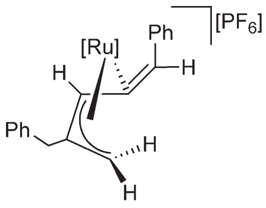
48



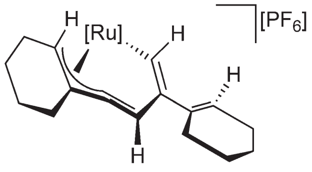
49*

$[Ru] = [RuCp^*(PPh_3)]$

Figure 9 $Cp^*Ru(II)$ complexes **48** and **49**.

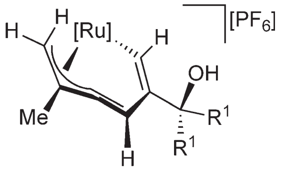


50: R = Ph,* Bu^n



51: R = Ph, Bu^n

$[Ru] = [RuCp(SbR_3)]$



$R^1 = Me; CR^1_2 = C_6H_{10}$
$R = Bu^n$

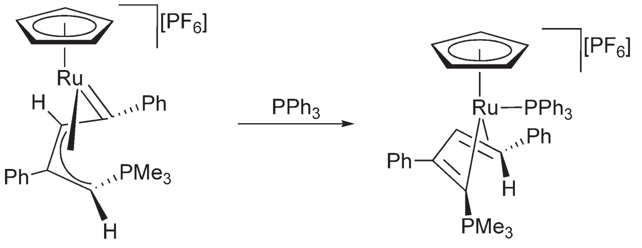
52

Figure 10 The alkenyl-ruthenium complexes **50**–**52**.

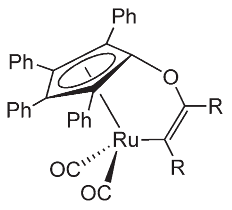
Related complexes have been obtained from the reaction of the vinylidene $[RuCl\{{=}C{=}C(H)CO_2Me\}Cp^*(PPh_3)]$ with $HC{\equiv}CPh/NaOMe$ ($R^1 = R^2 = CO_2Me$, $R^3 = H^*$) or by the treatment of $[Ru\{\kappa^2(C,O)C(C{\equiv}CPh){=}CH\text{-}(CO_2Me)\}Cp^*(PPh_3)]$ with $HC{\equiv}CSiMe_3$ ($R^1 = SiMe_3$, $R^2 = CO_2Me$, $R^3 = H$, $CH{=}CHSiMe_3^*$).[52] The unusual formation of an η^2-bonded polycyanocarbon ligand has been established in complex **49*** formed by the reaction of **48** ($R^1 = R^2 = Ph$, $R^3 = H$) with tetracyanoethene, $C_2(CN)_4$.[53] The synthesis of the 16-electron derivative $[Ru(CMe{=}CMeC{\equiv}CBu^t)Cp^*(PPh_3)]$, by insertion of $MeC{\equiv}CMe$ into the Ru–C bond of the *in situ*-formed alkynyl species $[Ru(C{\equiv}CBu^t)Cp^*(PPh_3)]$ (see Section 6.15.2.4), has also been reported. Exposure of a benzene solution of this complex to CO leads to the saturated complex $[Ru(CMe{=}CMeC{\equiv}CBu^t)Cp^*(PPh_3)(CO)]$.[54]

A formal insertion of the coordinated alkyne into the Ru–allyl bond has been found in the reaction of complexes $[Ru(\eta^3\text{-}C_3H_5)Cp^*(\eta^2\text{-}RC{\equiv}CR)]$ with CO, which leads to the $\eta^1{:}\eta^2$-alkenyl–olefin coupling products $[Ru(\eta^1{:}\eta^2\text{-}CR{=}CRCH_2CH{=}CH_2)Cp^*(CO)]$ (R = Ph, Me). An excess of 2-butyne is required to avoid the alkyne substitution by CO.[55] During studies directed to the synthesis of $\eta^1{:}\eta^2$-butadienyl carbenes (see Section 6.15.2.6.3), competitive processes leading to the η^3-allyl–acyl complexes **12** (Figure 4) or the $\eta^1{:}\eta^3$-alkenyl–allyl derivatives **50** (Figure 10) have been observed. The latter are generated from the reactions of $[RuCp(NCMe)_2(SbR_3)][PF_6]$ with $HC{\equiv}CCH_2Ph$.[30] When the alkynes used do not contain α-C–H bonds, such as the enyne $HC{\equiv}CC_6H_9$ (C_6H_9 = 1-cyclohexenyl) or the propargylic alcohols $HC{\equiv}CCR^1_2(OH)$ ($R^1 = Me$, $CR^1_2 = C_6H_{10}$), the $\eta^1{:}\eta^3$-alkenyl–butadienyl species **51** and **52**, respectively, are formed.[30,56]

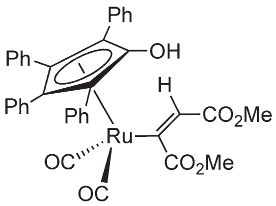
The related $\eta^1{:}\eta^2$-butadienyl complex **54** is obtained by the reaction of the allyl carbene **53** with PPh_3 (Equation (7)), revealing that this carbene is acting as pseudo-16-electron species (see Section 6.15.2.6.3).[57]



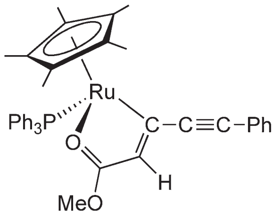
53 **54** (7)



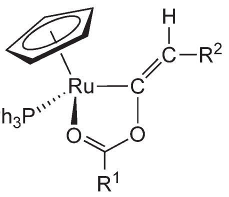
55*: R = 4-C_6H_4Cl



56*



57*



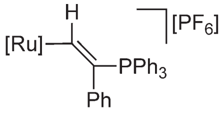
$R^1 = Bu^t$; $R^2 = CO_2Me$
$R^1 = Me$; $R^2 = Ph$

58

Figure 11 Structure of the ruthenium complexes **55**–**58**.

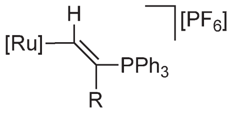
The osmium–styryl complex [Os{(*E*)-CH═CHPh}Cp{P(OMe)$_3$}(PPr$^i_3$)] resulting from the treatment of the vinylidene–hydride complex [OsH{═C═C(H)Ph}Cp(PPr$^i_3$)] with P(OMe)$_3$ has also been described. It is proposed that the reaction proceeds through a migration of the hydride to the C_α-atom of the vinylidene group to give the unsaturated styryl intermediate [Os{(*E*)-CH═CHPh}Cp(PPr$^i_3$)] followed by the coordination of the phosphite.[39] The reactions of the bridging-hydride diruthenium complex [Ru$_2$(η^5-Ph$_4$C$_4$COHOCC$_4$Ph$_4$-η^5)(μ-H)(CO)$_4$] (Shvo's complex) with (4-C$_6$H$_4$Cl)C≡C(4-C$_6$H$_4$Cl) and MeO$_2$CC≡CCO$_2$Me yield the alkenyl derivatives **55*** and **56***, respectively (Figure 11). Related reactions with the alkynes PhC≡CR (R = Ph, H) have also been studied.[58] A κ^2(*O*,*C*)-alkoxycarbonyl–vinyl moiety is generated in complex **57*** from the reaction of the neutral vinylidene complex [RuCl{═C═C(H)Ph}Cp*(PPh$_3$)] with AgC≡CCO$_2$Me. This C–C coupling process proceeds through the initial replacement of the chloride ligand by the alkynyl unit C≡CCO$_2$Me followed by a proton shift from the phenyl vinylidene to the alkynyl group. Then, the insertion of the resulting vinylidene group ═C═CHCO$_2$Me into the Ru–C≡CPh bond takes place with concomitant chelation of the ester carbonyl group in the vacant coordination site.[52] Alkenyl ester compounds **58** are readily accessible by treatment of acetato complexes [Ru{κ^2(*O*,*O*)-O$_2$CR^1}Cp(PPh$_3$)] with the terminal alkynes HC≡CR^2 (R^2 = CO$_2$Me, Ph).[59]

Although the exchange of η^2-coordinated alkynes by more basic ligands is a well-documented reaction, the nucleophilic attack of phosphines on the coordinated C≡C bond, leading to (*E*)-phosphonio–alkenyl complexes, has arisen as a competitive process. This has been assessed in a series of nucleophilic additions of PPh$_3$ to indenyl–ruthenium(II) vinylidene complexes of general composition [Ru(═C═CHR)(η^5-1,2,3-C$_9$H$_4$R$_3$)(L^1)(L^2)]$^+$, in refluxing methanol, which result in the formation of the phosphonio–alkenyl derivatives **59**–**62** (Figure 12). The reactions proceed through an initial η^1-vinylidene to π-alkyne tautomerization giving rise to the intermediate species [Ru(η^5-1,2,3-C$_9$H$_4$R$_3$)(η^2-HC≡CR)(L^1)(L^2)]$^+$, which readily undergo the regioselective nucleophilic attack of PPh$_3$.[60,61]



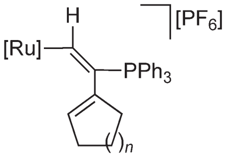
[Ru] = [Ru(η^5-1,2,3-C$_9$H$_4$R$_3$)(CO)(PR$_3$)]
R = Me; PR$_3$ = PPh$_3$*
R = H; PR$_3$ = PPr$^i_3$

59



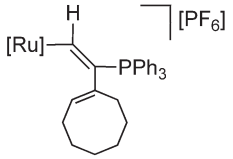
[Ru] = [Ru(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]
R = CH=CPh$_2$, (*E*)-CH=CHFc*, (*E*)-CH=CH(4-C$_6$H$_4$OMe)

60



[Ru] = [Ru(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]
n = 2*, 3

61



[Ru] = [Ru(η^5-1,2,3-C$_9$H$_4$R$_3$)(CO)(PR$_3$)]
R = Me; PR$_3$ = PPh$_3$
R = H; PR$_3$ = PPr$^i_3$

62

Figure 12 The phosphonio-alkenyl derivatives **59**–**62**.

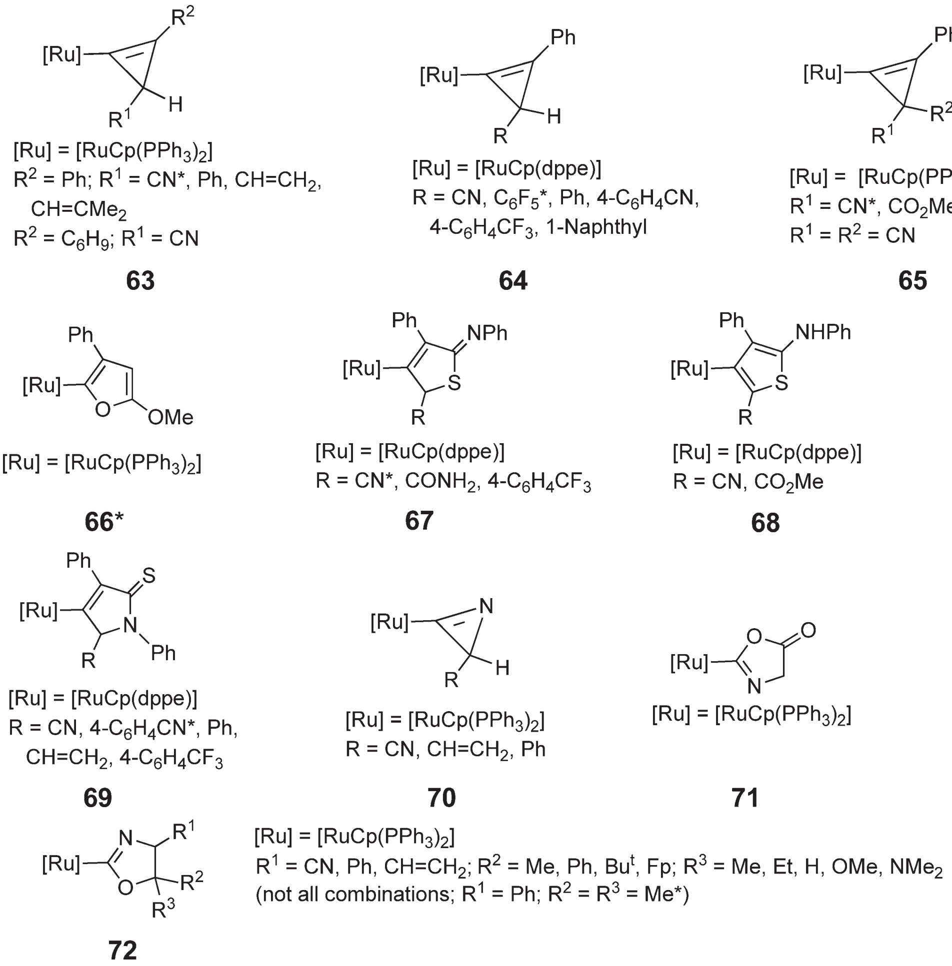
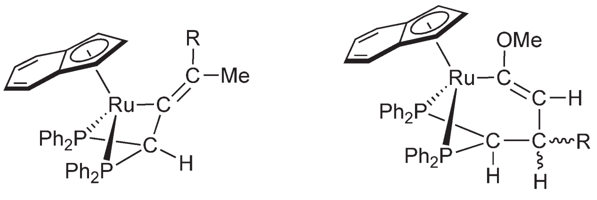


Figure 13 Structure of the cyclic compounds **63**–**72**.

Both theoretical and experimental studies have shown the electrophilicity of the C_α-atom of the vinylidene chain (see Section 6.15.2.8). On this basis, the intramolecular cycloaddition of carbanions in vinylidene complexes $[Ru\{{=}C{=}C(CH_2R)Ph\}Cp(L^1)(L^2)]^+$ ($L^1 = L^2 = PPh_3$; L^1L^2 = dppe) and $[Ru\{{=}C{=}C(CH_2CN)C_6H_9\}Cp(PPh_3)_2]^+$ bearing acidic methylenic CH_2 groups at the C_γ-atom has been investigated. The deprotonation of these complexes with $[Bu^n{}_4N][OH]$ induces a novel cyclization reaction yielding neutral cyclopropenyl complexes **63** and **64** (Figure 13).[62,63] The related species **65** are also known to be obtained from the appropriate vinylidene precursors.[62] In contrast, deprotonation of the methylenic unit in $[Ru\{{=}C{=}C(CH_2CO_2Me)Ph\}Cp(PPh_3)_2]^+$ induces a different type of cyclization, affording instead the neutral furan complex **66***.[62]

Five-membered heterocyclic derivatives **67**–**69** (Figure 13) have also been obtained from deprotonation of vinylidene complexes $[Ru\{{=}C{=}CPhC({=}NPh)SCH_2R\}Cp(dppe)]^+$ or $[Ru\{{=}C{=}CPhC({=}S)NPhCH_2R\}Cp(dppe)]^+$.[64,65] Moreover, using this strategy, novel three-membered ring azirinyl complexes **70** are isolated as thermally unstable solids from cationic isocyanide complexes $[Ru(CNCH_2R)Cp(PPh_3)_2]^+$ after deprotonation with $[Bu^n{}_4N][OH]$ or $[Bu^n{}_4N]F$. However, under the same reaction conditions, deprotonation of isocyanide complex $[Ru(CNCH_2CO_2Me)Cp(PPh_3)_2]^+$ gives the oxazolone complex **71**. Azirinyl complexes **70** react regioselectively with ketones, aldehydes, esters, and amides, yielding a variety of five-membered oxazolinyl derivatives **72**, which are formed through the formal insertion of the carbonyl group into the C–C bond of the azirinyl ring (Figure 13). These insertion processes proceed in a diastereoselective manner, being controlled by the steric effects arising from the carbonyl substituents.[66]

The electrophilicity of the C_α-atom of the vinylidenes $[Ru\{{=}C{=}C(Me)R\}(\eta^5\text{-}C_9H_7)(dppm)][OTf]$ ($R = Ph, Bu^t$) also allows the intramolecular nucleophilic attack of a methanide group generated *in situ* by deprotonation of the methylene unit of the $\kappa^2(P,P)$-coordinated dppm ligand. The reaction affords the alkenyl metallacycles **73**



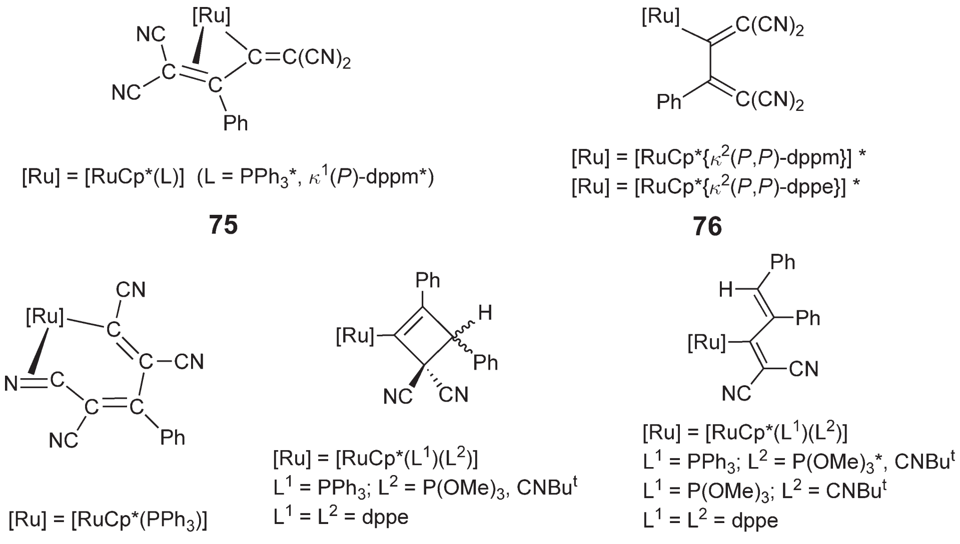
73: R = Bu^t, Ph

74: R = H, Ph

Figure 14 The indenyl–ruthenium(II) metallacycles **73** and **74**.

(Figure 14). The related metallacycles **74** have been also obtained by deprotonation of the α,β-unsaturated methoxy carbenes [Ru{=C(OMe)CH=CHR}(η^5-C_9H_7)(dppm)][PF_6] (R = H, Ph) with LiBu^t.[67]

[2 + 2]-Cycloadditions of acetylide metal complexes with unsaturated organic substrates such as electron-deficient alkenes, heterocumulenes, and related species are well documented. The outcome of the cycloaddition is dependent both on the organic substrate as well as the ancillary ligands on the metal. Many studies of this type have been developed using [RuCp(L^1)(L^2)] (L^1 and L^2 = mono- or bidentate phosphines) fragments (see COMC (1995)), giving rise, through C–C coupling reactions, to a variety of complexes containing σ-Ru–C bonds bearing long unsaturated hydrocarbon chains. As a continuation of earlier studies with the [RuCp(PPh_3)$_2$] fragment, Bruce and co-workers have studied extensively the reactivity of [Ru(C≡CPh)Cp*(L^1)(L^2)] with tetracyanoethene $C_2(CN)_4$. Thus, η^1:η^2-allylic complexes **75** are generated from the reactions in benzene (Figure 15). However, when the reactions are performed in THF, the presence of chelate diphosphines precludes the coordination of the C=C double bond to ruthenium and η^1-tetracyanobuta-1,3-dien-2-yl complexes **76** are isolated.[68,69] Thermolysis of **75** (L = PPh_3) in refluxing benzene overnight gives a mixture from which complex **77*** can be isolated along with two additional dinuclear derivatives.[68] Spontaneous rearrangement of **76** (P–P = dppm) into [Ru(CN){κ^2(*C*,*P*)-C(CN)=C[CPh=C(CN)$_2$]PPh$_2$CH$_2$PPh$_2$}Cp]* takes place in CH_2Cl_2 at RT, the process involving an unusual migration of CN from the polycyanocarbon chain to ruthenium, in addition to a more classical P–C coupling.[53] Analogous reactions of [Ru(C≡CPh)Cp(L^1)(L^2)] with H(Ph)C=C(CN)$_2$ have been reported to yield cyclobutenyl complexes **78** which readily transform into the butadienyl derivatives **79** (Figure 15).[29]



[Ru] = [RuCp*(L)] (L = PPh$_3$*, κ^1(*P*)-dppm*)

75

[Ru] = [RuCp*{κ^2(*P*,*P*)-dppm}] *
[Ru] = [RuCp*{κ^2(*P*,*P*)-dppe}] *

76

[Ru] = [RuCp*(PPh$_3$)]

77*

[Ru] = [RuCp*(L^1)(L^2)]
L^1 = PPh$_3$; L^2 = P(OMe)$_3$, CNBu^t
L^1 = L^2 = dppe

78

[Ru] = [RuCp*(L^1)(L^2)]
L^1 = PPh$_3$; L^2 = P(OMe)$_3$*, CNBu^t
L^1 = P(OMe)$_3$; L^2 = CNBu^t
L^1 = L^2 = dppe

79

Figure 15 Structure of the ruthenium complexes **75**–**79**.

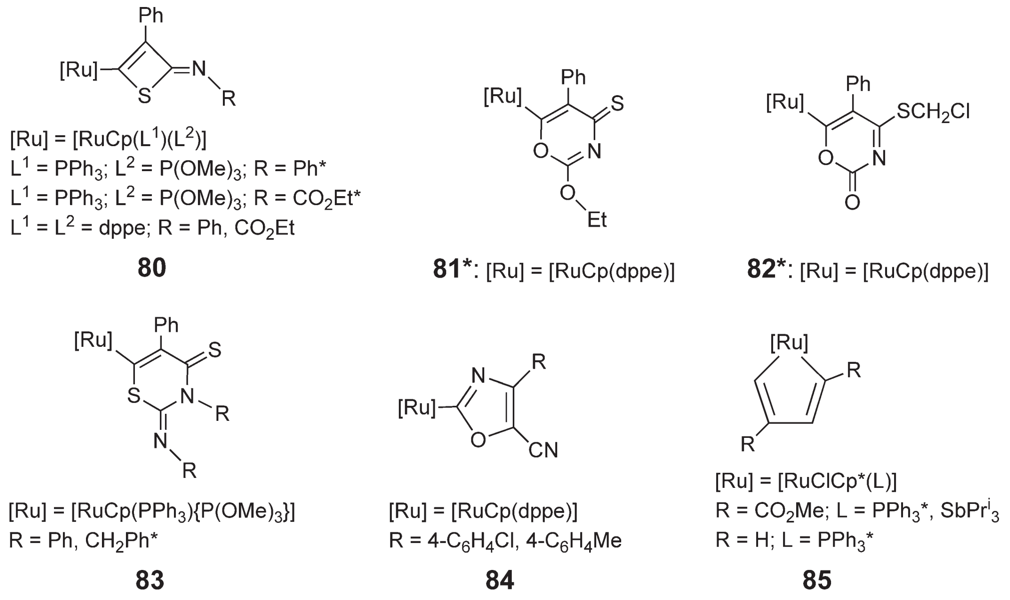


Figure 16 The ruthenium(II) complexes **80–85**.

Using ruthenium acetylide precursors and isothiocyanates as organic substrates, the following cycloaddition products have also been described (see Figure 16).

(i) Complexes containing four-membered ring 2-iminothiete groups 80 and six-membered ring 1,3-oxazin-2-one 81*, and oxazinethione 82* ligands.
(ii) Complex 83 (R = Ph), containing the six-membered ring 2-imino-1,3-thiazine-4-thione ligand, generated by the expansion of the 2-iminothiete ring in 80 through a coupling with a second molecule of isothiocyanate. Its benzyl counterpart ($R = CH_2Ph$) is also known, being directly obtained from $[Ru(C{\equiv}CPh)Cp(PPh_3)\{P(OMe_3)\}]$ and $PhCH_2NCS$.[70,71]

The $C{\equiv}N$ triple bond of cyanide complexes is also capable of undergoing cycloaddition reactions. Thus, the treatment of $[Ru(CN)Cp(dppe)]$ with *gem*-dicyanoepoxides gives the oxazol-2-yl derivatives 84 (Figure 16).[72] In the course of the synthesis of the vinylidene complex $[RuCl\{{=}C{=}C(H)CO_2Me\}Cp^*(PPh_3)]$ from the reaction of $[RuClCp^*(PPh_3)_2]$ with $HC{\equiv}CCO_2Me$, a minor amount (21%) of the ruthenacyclopentadiene 85 ($R = CO_2Me$, $L = PPh_3$) was isolated.[73] Selective formation of an analogous stibine complex is also known.[74] Similarly, $[RuClCp^*(PPh_3)_2]$ reacts with $HC{\equiv}CH$ in the presence of $CuCl_2$ to give selectively the analogous unsubstituted metallacycle ($R = H$, $L = PPh_3$).[75] Structural parameters from X-ray diffraction analysis are in accordance with the presence of a hydrocarbon metallacyclopentadiene backbone in contrast to the analogous examples formulated as ruthenacyclopentatriene derivatives (see Section 6.15.2.6.2).

The reactivity of allenylidene ligands in ruthenium and osmium complexes (see Section 6.15.2.9) has been widely exploited in recent years due to the presence of a highly polarized unsaturated chain involving both electrophilic and nucleophilic sites. Among the synthetic utilities of this feature, the reactions with nucleophiles Nu–H (Nu = primary and secondary amines, as well as heterocyclic, propargyl, and diallyl amines) and unsaturated dipolar organic substrates (heterocumulenes and related species) disclose a wide series of addition processes affording complexes containing metal–alkenyl and allenyl bonds. Most of them are heterocyclic systems, arising from intramolecular cycloaddition processes. The following examples, mainly from Esteruelas and co-workers, illustrate the potential of this synthetic approach using as precursors the allenylidenes $[M({=}C{=}C{=}CPh_2)Cp(CO)(PPr^i_3)][X]$ ($X = BF_4$, $M = Ru$; $X = PF_6$, $M = Os$).

(i) Ruthenium complexes 86–89 (Figure 17) obtained by the reaction with pyrazole derivatives, 2-aminopyridine, pyridine-2-thiol, and thioisonicotinamide, respectively (neutral heterocyclic derivatives obtained by deprotonation of these complexes are also known).[76,77]
(ii) Alkenyl complexes 90 ((*E*)- and (*Z*)-isomers), containing azetidine skeletons, obtained from the reactions with carbodiimides $RN{=}C{=}NR$ ($R = Cy$, Pr^i). The ruthenium derivative has been used as suitable precursor for the

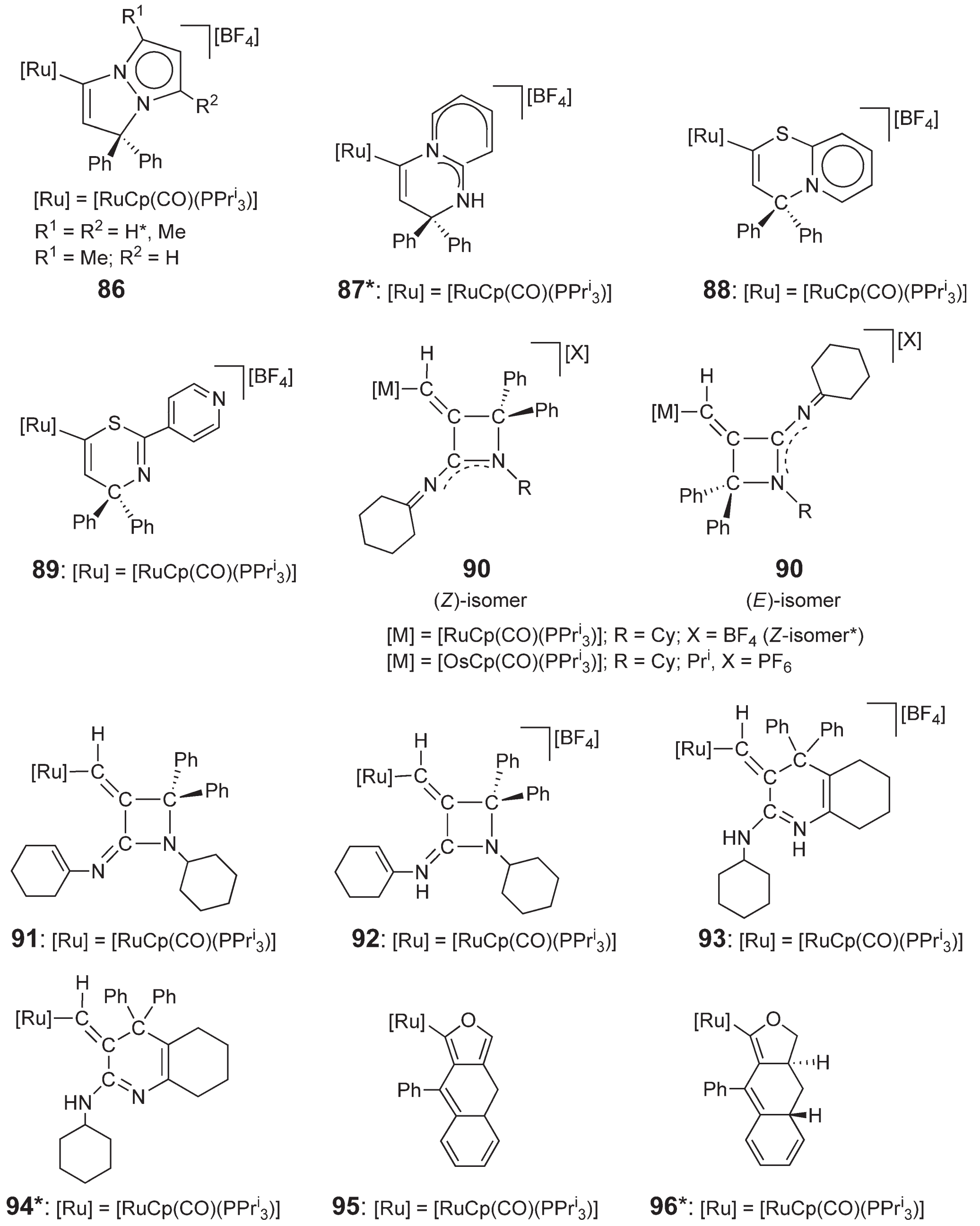


Figure 17 The heterocyclic Ru(II) and Os(II) derivatives **86**–**96**.

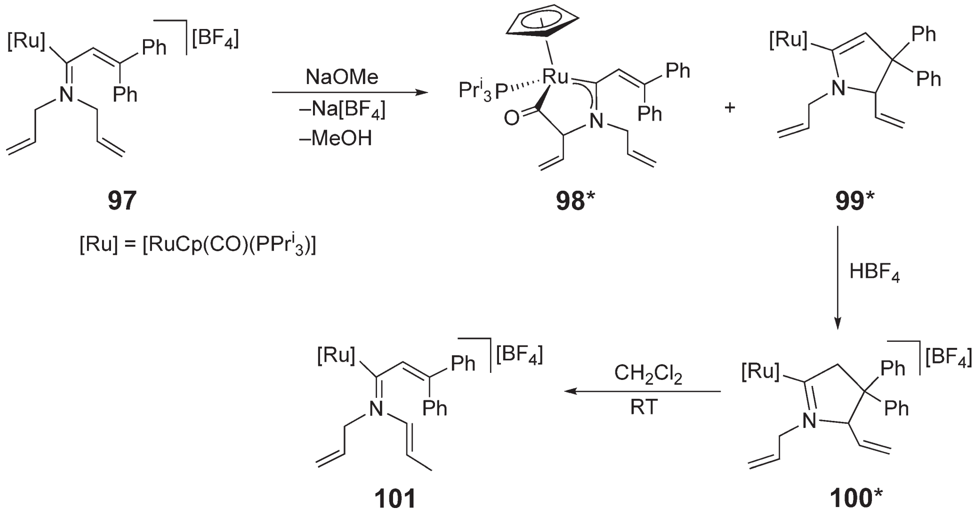
preparation of the iminoazetidinylidenemethyl complex 91 and its protonated form 92 (Figure 17). Complex 92 evolves in solution into the hexahydroquinolinylidenemethyl complex 93, which reacts with sodium methoxide to give 94*.[78,79]

(iii) Tricyclic alkenyl complexes 95 and 96* isolated after deprotonation of the α,β-unsaturated (propargyloxy)carbene complex $[Ru\{{=}C(OCH_2C{\equiv}CH)CH{=}CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$, obtained from the nucleophilic attack of propargyl alcohol $HC{\equiv}CCH_2OH$ on the allenylidene–ruthenium complex (see Section 6.15.2.5), and the analogous allyloxycarbene $[Ru\{{=}C(OCH_2CH{=}CH_2)CH{=}CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$, respectively. The latter affords firstly the alkoxyallenyl derivative $[Ru\{C(OCH_2CH{=}CH_2){=}C{=}CPh_2\}Cp(CO)(PPr^i_3)]$, which at RT undergoes an intramolecular Diels–Alder reaction to form the tricyclic tetraenyl complex 96*.[23,80]

(iv) Azoniabutadienyl ruthenium and osmium complexes $[\mathrm{M\{C({=}NR^1R^2)CH{=}CPh_2\}Cp(CO)(PPr^i_3)}][\mathrm{X}]$ ($\mathrm{M = Os}$, $\mathrm{X = PF_6}$, $\mathrm{R^1 = H}$, $\mathrm{R^2 = Ph}$; $\mathrm{M = Ru}$, $\mathrm{X = BF_4}$, $\mathrm{R^1 = H}$, $\mathrm{R^2 = Ph}$, $\mathrm{Pr^n}$, $\mathrm{CH_2CH{=}CH_2}$, $\mathrm{CH_2C{\equiv}CH}$, 2-$\mathrm{C_5H_4N}$; $\mathrm{M = Ru}$, $\mathrm{X = BF_4}$, $\mathrm{R^1 = Me}$, $\mathrm{R^2 = CH_2C{\equiv}CH}$; $\mathrm{M = Ru}$, $\mathrm{X = BF_4}$, $\mathrm{R^1 = R^2 = Et^*}$; $\mathrm{M = Ru}$, $\mathrm{X = BF_4}$, $\mathrm{R^1R^2 = C_5H_{10}}$), which are generated from the N–H addition of primary or secondary amines to the $\mathrm{C_\alpha{=}C_\beta}$ double bond of the allenylidene chain. Structural data indicate that the contribution of the expected amino carbene resonance form $[\mathrm{M\{{=}C(NR^1R^2)CH{=}CPh_2\}Cp(CO)(PPr^i_3)}][\mathrm{X}]$ is negligible.[24,77,79,81] The preparation of the related azoniabutadienyl $[\mathrm{Ru\{C({=}NR^1R^2)CH{=}CPh_2\}Cp^*(CO)(PMePr^i_2)}][\mathrm{BAr^F_4}]$ ($\mathrm{R^1 = H}$, $\mathrm{R^2 = Me}$, $\mathrm{CH_2C{\equiv}CH^*}$ $\mathrm{R^1 = R^2 = Pr^i}$) and thiabutadienyl $[\mathrm{Ru\{C({=}SPr^n)CH{=}CPh_2\}Cp^*(CO)(PMePr^i_2)}][\mathrm{BAr^F_4}]^*$ species has also been reported.[82] Deprotonation reactions of the azoniabutadienyl derivatives afford neutral azabutadienyl species $[\mathrm{M\{C({=}NR^2)CH{=}CPh_2\}Cp(CO)(PPr^i_3)}]$ if $\mathrm{R^1 = H}$, or aminoallenyl complexes $[\mathrm{M\{C(NR^1R^2){=}C{=}CPh_2\}\text{-}Cp(CO)(PPr^i_3)}]$ if $\mathrm{R^1}$ and $\mathrm{R^2 \neq H}$. The closely related α,β-unsaturated-2-aza-allenyl complexes $[\mathrm{Ru\{C({=}N{=}CPh_2)\text{-}CH{=}CPh_2\}Cp(CO)(PPr^i_3)}][\mathrm{BF_4}]^*$ and $[\mathrm{Ru\{C({=}N{=}CPh_2)C(H){=}CPh_2\}Cp(CO)(PMePr^i_2)}][\mathrm{BAr^F_4}]^*$ are also known, being obtained by reacting the appropriate allenylidene precursor with benzophenoneimine.[27,82]

(v) The *N*-allyl-4-azonia-1,3,6-heptatrienyl derivative **97**, formed by the addition of diallylamine $\mathrm{HN(CH_2CH{=}CH_2)_2}$ to $[\mathrm{Ru({=}C{=}C{=}CPh_2)Cp(CO)(PPr^i_3)}][\mathrm{BF_4}]$. Complex **97** undergoes the deprotonation of one of the $\mathrm{NCH_2}$ groups by treatment with sodium methoxide to give a 1 : 1 mixture of the ($R_{\mathrm{Ru}}R_{\mathrm{C}}$/$S_{\mathrm{Ru}}S_{\mathrm{C}}$)-ruthenapyrrolinone **98*** and ($R_{\mathrm{Ru}}S_{\mathrm{C}}$/$S_{\mathrm{Ru}}R_{\mathrm{C}}$)-pyrrolinyl **99*** complexes (Scheme 5). Protonation of the pyrrolinyl derivative yields complex **100***, which evolves in dichloromethane solution into the *N*-allyl-4-azonia-1,3,5-heptatrienyl derivative **101**.[83]

(vi) The *N*-heterocyclic ruthenium derivatives **102*** and **103*** (Figure 18) formed through intramolecular C–C and C–N coupling reactions. The dihydronaphthopyrrolyl complex **102** is obtained as a 1 : 1 mixture of two diastereoisomers from the deprotonation of $[\mathrm{Ru\{C({=}NMeCH_2C{\equiv}CH)CH{=}CPh_2\}Cp(CO)(PPr^i_3)}][\mathrm{BF_4}]$, while the dihydropyridiniumyl derivative **103** is generated by reaction of $[\mathrm{Ru({=}C{=}C{=}CPh_2)\text{-}Cp(CO)(PPr^i_3)}][\mathrm{BF_4}]$ with 1,1-diethylpropargylamine $\mathrm{H_2NCEt_2C{\equiv}CH}$.[24]



Scheme 5

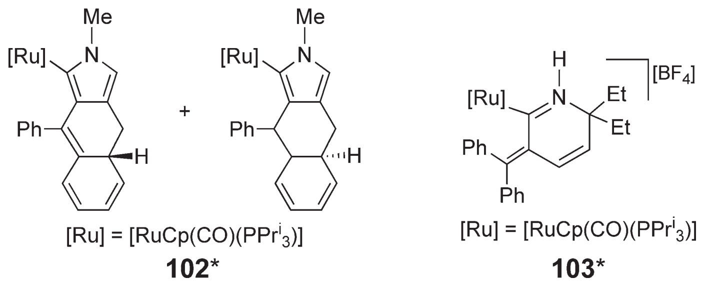
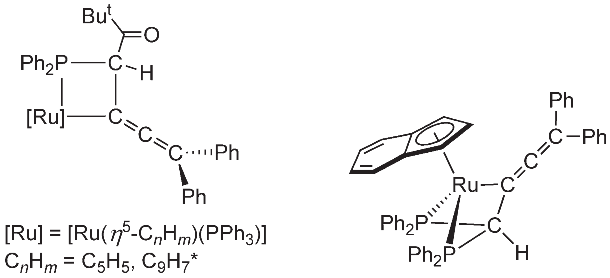


Figure 18 The *N*-heterocyclic ruthenium(II) derivatives **102** and **103**.



104 **105**

Figure 19 Structure of the allenyl–Ru(ii) derivatives **104** and **105**.

Besides the aza-allenyl complexes discussed above, a variety of allenyl derivatives are known. Phosphonio–allenyl complexes, which are the most common derivatives, are prepared through the regioselective nucleophilic additions of phosphines to the C_α-atom of an allenylidene chain. The control of the regioselective addition at C_α versus C_γ is the basis of the selective formation of the allenyl group; otherwise, phosphonio–alkynyl derivatives are obtained (see Section 6.15.2.4). This regioselectivity seems to be controlled not only by the metallic fragment but also by the cone angle of the phosphine. Thus, complexes $[Ru\{C(PR_3)=C=CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$ ($PR_3 = PPh_3$, $PMePh_2$, $PHPh_2$) and $[Ru\{C(PMe_2Ph)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ have been obtained from the treatment of the allenylidenes $[Ru(=C=C=CPh_2)Cp(CO)(PPr^i_3)][BF_4]$ and $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$, respectively, with the appropriate phosphine.[84,85,85a] In contrast, complex $[Ru\{C(PMe_3)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ arises from the slow isomerization of the phosphonio–alkynyl derivative $[Ru\{C\equiv CCPh_2(PMe_3)\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ through the thermodynamically favorable phosphine migration.[85,85a] The related species $[Ru\{C(PR_3)=C=CPh_2\}Cp^*(CO)(PMePr^i_2)][BAr^F_4]$ ($PR_3 = PMe_3$, $PMePr^i_2{}^*$) are also known.[82] Deprotonation of $[Ru\{C(PHPh_2)=C=CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$ with Et_3N has been reported to yield $[Ru\{C(PPh_2)=C=CPh_2\}Cp(CO)(PPr^i_3)]^*$.[84]

The following are the other neutral allenyl derivatives described:

(i) The thio–allenyl complexes $[Ru(\eta^5\text{-}C_9H_7)\{C(S\text{-}2\text{-}C_6H_4Me)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(dppm)]$[85,85a] and $[Ru\{C(S\text{-}2\text{-}C_5H_4N)=C=CPh_2\}Cp(CO)(PPr^i_3)]$,[76] and the osmium methoxy–allenyl derivative $[Os\{C(OMe)=C=CPh_2\}Cp(CO)(PPr^i_3)]$.[79]

(ii) Compounds $[Ru\{C(R)=C=CPh_2\}Cp(CO)(PPr^i_3)]$ ($R = Me$, $C\equiv CPh$) obtained by addition of LiMe and $LiC\equiv CPh$ to the cationic allenylidene $[Ru(=C=C=CPh_2)Cp(CO)(PPr^i_3)][BF_4]$. They have been isolated from a mixture with the corresponding alkynyl derivatives $[Ru\{C\equiv CC(R)Ph_2\}Cp(CO)(PPr^i_3)]$, which arise from the addition to both the C_α- and C_γ-atoms of the allenylidene chain.[86]

(iii) The complexes $[Ru\{C(X)=C=CPh_2\}Cp(CO)(PPr^i_3)]$ ($X = OMe$, OEt, SPr^n) and $[Ru\{C(N=CPh_2)=C=CPh_2\}Cp(CO)(PPr^i_3)]$, obtained by deprotonation of cationic α,β-unsaturated carbenes $[Ru\{=C(X)CH=CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$ and the 2-aza-allenyl complex $[Ru\{C(=N=CPh_2)CH=CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$, respectively.[27]

Intramolecular nucleophilic addition of carbanions to the C_α-atom of allenylidene chains also give rise to allenyl derivatives. They include complexes 104 and 105 obtained from the deprotonation of the methylene group of the phosphine ligands in $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_nH_m)\{\kappa^1(P)\text{-}Ph_2PCH_2COBu^t\}(PPh_3)][PF_6]$ and $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)\{\kappa^2(P,P)\text{-}Ph_2PCH_2PPh_2\}][PF_6]$, respectively (Figure 19).[85,85a,87]

6.15.2.4 Alkynyl, Enynyl, and Related Complexes

The chemistry of alkynyl–metal complexes has been reviewed recently.[88] Classical synthetic routes to half-sandwich alkynyl–ruthenium and alkynyl–osmium complexes of general composition $[M(C\equiv CR)(\eta^5\text{-}C_nH_m)(L^1)(L^2)]$ are based on the reactions of appropriate halide precursors $[MX(\eta^5\text{-}C_nH_m)(L^1)(L^2)]$ with lithium/sodium alkynyl reagents or with terminal alkynes in the presence of a base (see COMC (1995)). The latter method involves the *in situ* formation of a cationic vinylidene intermediate $[M\{=C=C(H)R\}(\eta^5\text{-}C_nH_m)(L^1)(L^2)]^+$, which is readily deprotonated by the base. Following these classical synthetic approaches, novel alkynyl derivatives have been prepared, including the following:

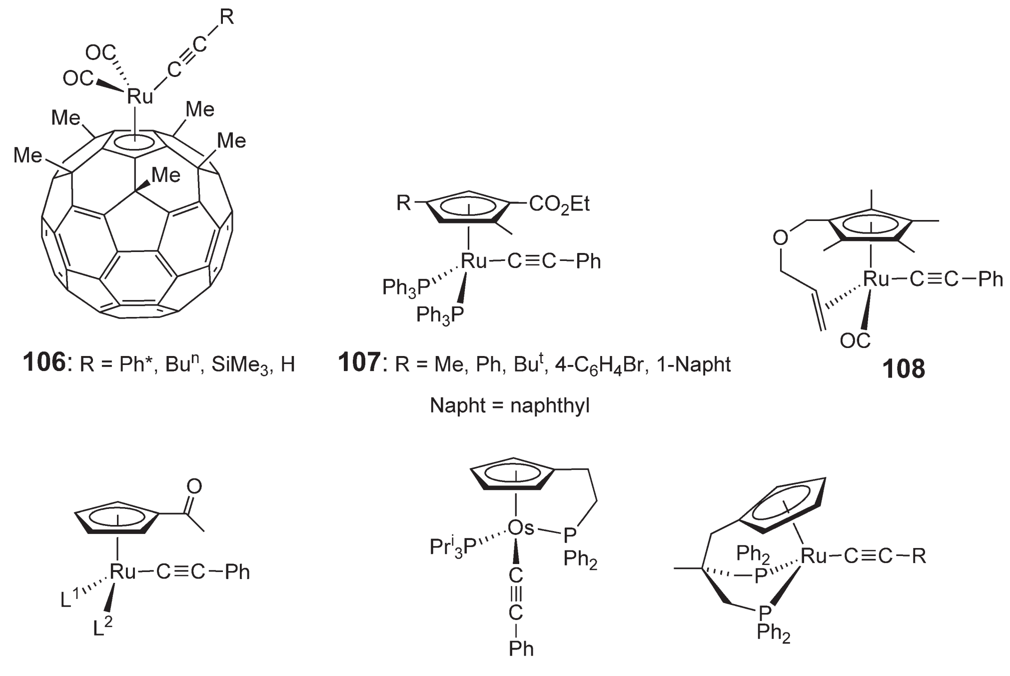
(i) Cyclopentadienyl complexes [Ru(C$\equiv$CR)Cp(L^1)(L^2)] (L^1 = L^2 = PPh$_3$, R = Fc, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$H$_5$), (η^5-C$_5$H$_4$)Ru(η^5-C$_5$Me$_5$)*, 2,4,6-cycloheptatrien-1-yl*, 4-C$_6$H$_4$PPh$_2$, 3,5-C$_6$H$_3$(C$\equiv$CH)$_2$, 3,5-C$_6$H$_3$(C$\equiv$CFc)$_2$; L^{1}L^2 = dppe, R = Fc, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$H$_5$), (η^5-C$_5$H$_4$)Ru(η^5-C$_5$Me$_5$); L^{1}L^2 = dppm, R = C$\equiv$CFc*; L^{1}L^2 = dppf, R = Fc)[89–95] and [OsH(C$\equiv$CPh)Cp(PPr$^i_3$)(EPh$_3$)] (E = Si, Ge*).[40]

(ii) Pentamethylcyclopentadienyl derivatives [Ru(C$\equiv$CR)Cp*(L^1)(L^2)] (L^1 = L^2 = PPh$_3$, R = Ph*, Bu^t, CO$_2$Me, Fc, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$H$_5$), (η^5-C$_5$H$_4$)Ru(η^5-C$_5$Me$_5$); L^{1}L^2 = dppm*, (+)-Binap, (−)-Binap, (+)-Diop, (−)-Diop, R = Ph; L^{1}L^2 = dppe, R = Fc, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$Me$_5$); Binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; Diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane).[69,73,89,91,96,97,97a]

(iii) Indenyl complexes [Ru(C$\equiv$CR)(η^5-C$_9$H$_7$)(L^1)(L^2)] (L^1 = L^2 = PPh$_3$, R = 4-C$_6$H$_4$Me, Cy, Bu^n, Bu^t, Pr^n, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$H$_5$), (η^5-C$_5$Me$_4$)Ru(η^5-C$_5$H$_5$)*, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$Me$_5$); L^{1}L^2 = dppe, R = Ph*, Bu^t, Pr^n, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$H$_5$)*, (η^5-C$_5$Me$_4$)Ru(η^5-C$_5$H$_5$), (η^5-C$_5$H$_4$)Ru(η^5-C$_5$Me$_5$); L^{1}L^2 = dppm, 1,3-bis(diphenylphosphino)propane (dppp), dppb, R = Ph; L^1 = PPh$_3$, L^2 = Ph$_2$PCH$_2$CH=CH$_2$, R = Ph, 4-C$_6$H$_4$Me, 4-C$_6$H$_4$Cl) and [Ru(C$\equiv$CPh)(η^5-1,2,3-C$_9$H$_4$Me$_3$)(CO)(PPh$_3$)].[61,98–101]

(iv) The pentamethylated [60]fullerene complexes **106**,[6] the planar-chiral derivatives **107**,[102] the tethered compound **108**,[103] and the acetyl-substituted CpRu^{II} species **109** (Figure 20).[28] Remarkably, the formation of alkynyl complexes **109**, from the reactions of chloride precursors [RuCl{η^5-C$_5$H$_4$C(=O)Me}(L^1)(L^2)] with LiC$\equiv$CPh, involves the initial attack of the phenylacetylide anion on the carbonyl unit to generate the intermediate species [RuCl{η^5-C$_5$H$_4$C(C$\equiv$CPh)(OH)Me}(L^1)(L^2)], which evolves into **109** through an unprecedented migration of the acetylide unit from the Cp ring to Ru.

In addition to lithium/sodium alkynyls, tributyltin acetylides Bu$^n_3$SnC$\equiv$CR have also proved to be suitable transmetallating reagents for the preparation of alkynyl derivatives. Thus, the dicarbonyl complexes [Ru(C$\equiv$CR)Cp(CO)$_2$] (R = H, Ph, Pr^n) could be obtained in good yields from the reactions of [RuICp(CO)$_2$] with Bu$^n_3$SnC$\equiv$CR in the presence of catalytic amounts of [PdCl$_2$(NCMe)$_2$].[104] KF-induced desilylation of trimethylsilyl-substituted alkynes Me$_3$SiC$\equiv$CR and related polyynes and subsequent reactions with [RuClCp(L^1)(L^2)] have also



106: R = Ph*, Bu^n, SiMe$_3$, H

107: R = Me, Ph, Bu^t, 4-C$_6$H$_4$Br, 1-Napht

Napht = naphthyl

108

109: L^1 = L^2 = PPh$_3$; L^{1}L^2 = (*R*)-Binap

110

111: R = Ph*, Bu^t

Figure 20 Some examples of alkynyl–Ru(II) and Os(II) complexes.

been used to synthesize the alkynyl–ruthenium(II) complexes $[Ru(C{\equiv}CR)Cp(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$, R = 4-$C_6H_4C{\equiv}CSiMe_3^*$, $C{\equiv}CPh^*$, $C{\equiv}CC{\equiv}CPh$; L^1L^2 = dppe, R = $C{\equiv}CFc^*$).[93,105] Desilylation of $[Ru(C{\equiv}C\text{-}4\text{-}C_6H_4\text{-}C{\equiv}CSiMe_3)Cp(PPh_3)_2]$ by reaction with methanolic $[Bu^n{}_4N]F$ affords $[Ru(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CH)Cp(PPh_3)_2]$, which can be transformed into $[Ru(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CPh)Cp(PPh_3)_2]$ upon treatment with PhI/CuI/Et_2NH.[106]

Deprotonation of isolated cationic monosubstituted vinylidenes $[M]^+{=}C{=}C(H)R$ (see Section 6.15.2.8) has also been widely used for the preparation of neutral alkynyl complexes. Examples include the following:

(i) The indenyl–Ru(II) and indenyl–Os(II) derivatives $[M(C{\equiv}CR)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (M = Ru, $L^1 = L^2 = PPh_3$, R = H, CHPhOMe; M = Ru, L^1L^2 = dppe, R = H; M = Ru, L^1L^2 = dppm, R = Bu^t; M = Ru, $L^1 = PPh_3$, $L^2 = PMe_3$, R = H; M = Os, $L^1 = L^2 = PPh_3$, R = H, Bu^t).[67,98,107–109]

(ii) The CpRu and Cp*Ru complexes $[Ru(C{\equiv}CR^2)(\eta^5\text{-}C_5R^1{}_5)(L^1)(L^2)]$ (R^1 = H, L^1L^2 = 1,2-bis(diisopropylphosphino)ethane (dippe), R^2 = H, Ph, Bu^t, CO_2Me; R^1 = Me, L^1L^2 = dippe, R^2 = H, Ph, Bu^t, $SiMe_3$, CO_2Me; R^1 = Me, L^1L^2 = dppe, $R^2 = H^*$; R^1 = Me, L^1L^2 = dppm, $R^2 = H^*$; R^1 = Me, $L^1 = L^2 = PMe_2Ph$, R^2 = Ph, CH_2OMe, CHMeOMe; R^1 = Me, L^1 = CO, $L^2 = PMePr^i{}_2$, R^2 = H, Bu^t).[110–113]

(iii) The tethered Cp–phosphine derivatives **110 and 111** (Figure 20).[36,114]

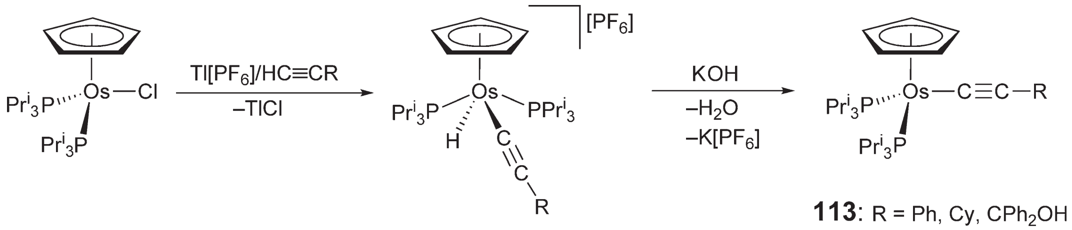
Deprotonation reactions of neutral vinylidene complexes $[RuCl\{{=}C{=}C(H)R\}Cp^*(PPh_3)]$ (R = Ph, Bu^t) have been explored. Thus, treatment of these compounds with NaOMe or Et_3N generates the highly unstable 16-electron alkynyls $[Ru(C{\equiv}CR)Cp^*(PPh_3)]$ via release of HCl. These species cannot be isolated but are trapped *in situ* with a variety of two-electron donor ligands yielding $[Ru(C{\equiv}CR)Cp^*(PPh_3)(L)]$ (R = Ph, L = CO^*, O_2^*, $\kappa^1(P)$-dppm, $PhC{\equiv}CPh$; R = Bu^t, L = CO^*, $P(OMe)_3$, $AsPh_3$, $\kappa^1(P)$-dppe*, $\kappa^1(P)$-$Ph_2PC{\equiv}CPPh_2$, S_2^*, $C_2H_4^*$) and $[Ru(C{\equiv}CBu^t)Cp^*\{\kappa^2(P,P)\text{-}L^2\}]$ (L_2 = dppm*, *cis*-$Ph_2PCH{=}CHPPh_2^*$).[97,97a,115]

Deprotonation of ethynyl complexes $[Ru(C{\equiv}CH)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = PPh_3$, $L^2 = PPh_3$, PMe_3; L^1L^2 = dppe) with $LiBu^t$ at −78 °C gives the lithiated species $[Ru(C{\equiv}CLi)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ which have been used *in situ* as precursors of the novel alkynyl compounds $[Ru(C{\equiv}CI)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$; L^1L^2 = dppe), $[Ru(C{\equiv}CSnPh_3)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = PPh_3$, $L^2 = PPh_3$, PMe_3; L^1L^2 = dppe), and $[Ru\{C{\equiv}CAu(PPh_3)\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = PPh_3$, $L^2 = PPh_3$, PMe_3; L^1L^2 = dppe) by reaction with $[I(py)_2][BF_4]$, Ph_3SnCl, and $[AuCl(PPh_3)]$, respectively.[107] In a similar way, sequential treatment of $[Ru(C{\equiv}CH)Cp(PPh_3)_2]$ with $LiBu^n$, to generate the intermediate species $[Ru(C{\equiv}CLi)Cp(PPh_3)_2]$, and phenyl cyanate (PhOCN) affords $[Ru(C{\equiv}CC{\equiv}N)Cp(PPh_3)_2]$ in good yield.[116] The related lithioacetylide complex $[Ru(C{\equiv}CLi)Cp^*(PPh_3)_2]$ has been generated by double deprotonation of the cationic unsubstituted vinylidene $[Ru({=}C{=}CH_2)Cp^*(PPh_3)_2][PF_6]$ with $LiBu^t$ and trapped with Me_3SiCl and MeI to give $[Ru(C{\equiv}CR)Cp^*(PPh_3)_2]$ (R = $SiMe_3^*$, Me).[117]

The previously known complex $[Ru(C{\equiv}CPh)Cp(PPh_3)_2]$ has been used as starting material for the preparation of novel alkynyl derivatives via PPh_3 ligand substitution. Thus, treatment of this complex with $P(OMe)_3$ under thermal conditions, or with dmpm under photochemical conditions, leads to the novel phenylacetylide species $[Ru(C{\equiv}CPh)Cp(PPh_3)\{P(OMe)_3\}]$ and $[Ru(C{\equiv}CPh)Cp(dmpm)]$, respectively.[70,118]

Oxidative addition of terminal alkynes and alkynols to the electron-rich ruthenium(II) fragments $[RuCp^*(dippe)]^+$, $[RuCp^*(PEt_3)_2]^+$, and $[RuCp^*(PMePr^i{}_2)_2]^+$ has been reported to yield hydrido–alkynyl ruthenium(IV) complexes $[RuH(C{\equiv}CR)Cp^*(dippe)][BPh_4]$ (R = H, Ph, CO_2Me^*, CO_2Et, $SiMe_3$, CPh_2OH, CHPhOH, CHMeOH),[111,111a,119,120] $[RuH(C{\equiv}CR)Cp^*(PEt_3)_2][BPh_4]$ (R = H^*, Ph, CO_2Me, $SiMe_3$, Bu^t, CH_2OH, CPh_2OH, CMe_2OH, CHPhOH, CHMeOH, CMePhOH, $C_6H_{10}OH$),[121,121a,122] and $[RuH(C{\equiv}CR)Cp^*(PMePr^i{}_2)_2][BAr^F{}_4]$ (R = Ph, CO_2Me^*, $SiMe_3$, CH_2OH, CPh_2OH^*, CMe_2OH, CHPhOH, CHMeOH, CMePhOH, $C_6H_{10}OH$),[123] respectively. The reactions are usually performed by adding the appropriate chloride precursor $[RuClCp^*(L^1)(L^2)]$ to a methanolic solution of the corresponding alkyne and $Na[BPh_4]$ or $Na[BAr^F{}_4]$ at low temperature. In this way, the metastable hydrido–alkynyl ruthenium(IV) complexes readily precipitate from the reaction media avoiding their irreversible isomerization into the corresponding vinylidene isomers (see Section 6.15.2.8). Related oxidative additions to the osmium(II) fragment $[OsCp(PPr^i{}_3)_2]^+$, leading to the cationic Os(IV) derivatives **112**, have also been reported (Scheme 6). Complexes **112** can be converted into the neutral alkynyl–Os(II) derivatives **113** upon treatment with KOH.[124,125] Analogous hydrido–alkynyl osmium(IV) complexes are $[OsH\{C{\equiv}CCPh_2(OH)\}Cp(PPr^i{}_3)(PHPh_2)][PF_6]$[79] and $[OsH(C{\equiv}CR)\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4CH_2CH_2PPh_2\}(PPr^i{}_3)][PF_6]$ (R = Ph, CPh_2OH).[36]

Due to the extensive contribution of the metal–alkynyl resonance form $[M]{-}C{\equiv}C{-}C^+R^1R^2$, cationic transition metal–allenylidene complexes $[M]^+{=}C{=}C{=}CR^1R^2$ have been found to be excellent building blocks for the preparation of functionalized alkynyl derivatives through the addition of nucleophiles. Although the reactivity of cationic allenylidenes is governed by the electron deficiency of both the C_α- and C_γ-atoms of the unsaturated chain, it is now well established that nucleophilic additions at C_γ regioselectively occur when electron-rich and/or bulky



112: R = Ph*, Cy, CPh_2OH, CMePhOH

113: R = Ph, Cy, CPh_2OH

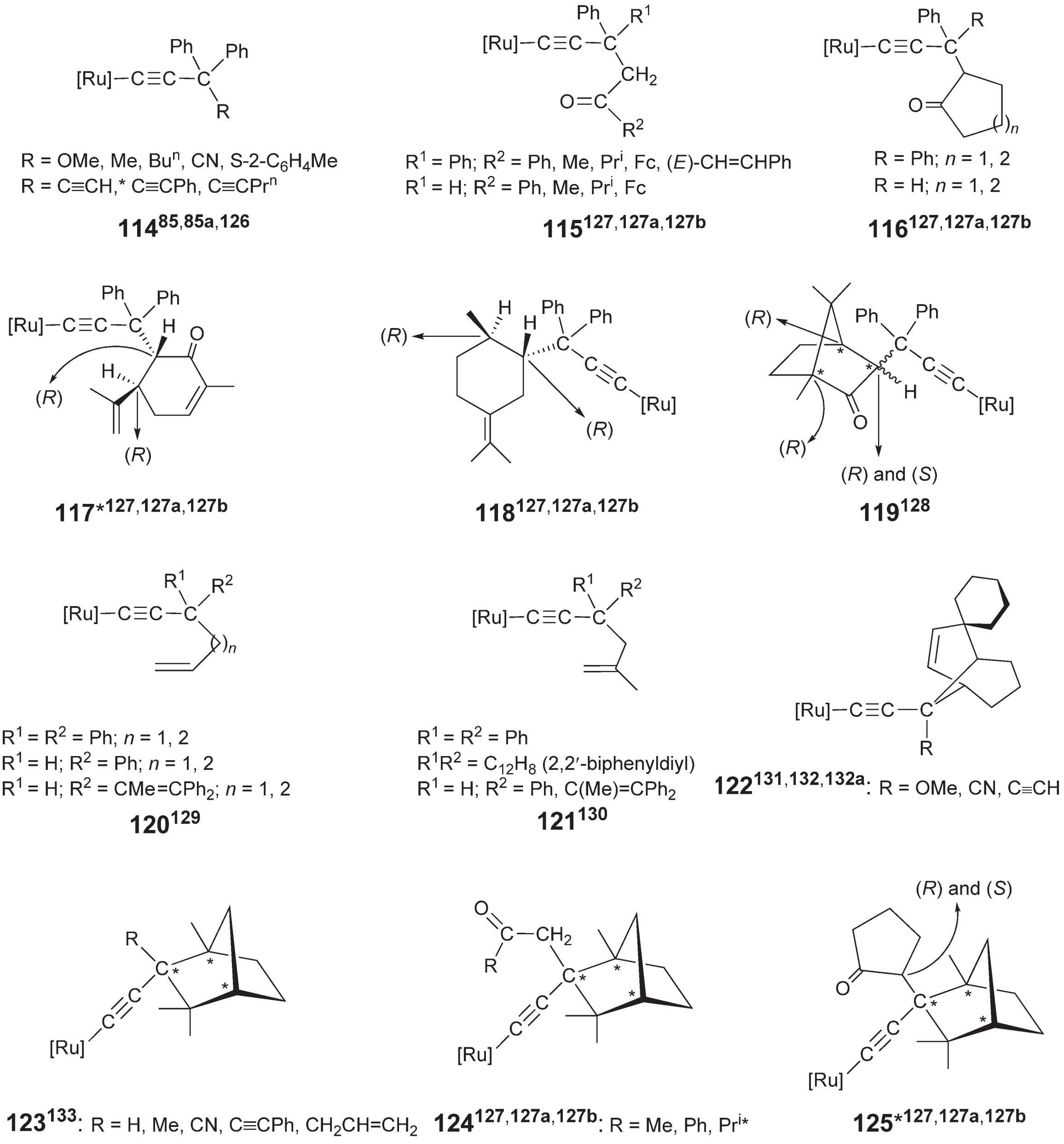
Scheme 6

metallic fragments are used, leading to a large variety of alkynyl complexes $[M]{-}C{\equiv}C{-}C(Nu)R^1R^2$.[1,1a–c] This behavior is nicely illustrated in the chemistry of the indenyl–ruthenium(II) allenylidene complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ which undergo the regioselective C_γ-addition of a wide range of anionic nucleophiles leading to alkynyl derivatives **114–125**[85,85a,126–133] (Figure 21). These nucleophilic additions are, in some cases, not only regioselective but also diastereoselective, as in the formation of compounds **117 and 118**, resulting from the addition of lithium enolates derived from (−)-carvone and (+)-pulegone, respectively, to $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$, or in the formation of **123–125** starting from the optically pure allenylidene $[Ru\{=C=C=C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($C(C_9H_{16})$ = (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene).

Other neutral alkynyl complexes generated from nucleophilic additions to cationic allenylidenes are $[Ru\{C{\equiv}CCPh_2(Nu)\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (L^1L^2 = dppe, Nu = OMe, Me, Bu^n; L^1L^2 = dppm, Nu = OMe),[85,85a] $[Ru\{C{\equiv}CCPh_2(Nu)\}Cp(PPh_3)_2]$ (Nu = Me, OMe,* CN,* Cp*),[134] $[Ru\{C{\equiv}CCPh_2(Nu)\}(\eta^5\text{-}1,2,3\text{-}C_9H_4Me_3)(CO)(PPh_3)]$ (Nu = OMe, $C{\equiv}CH$),[135] $[Ru\{C{\equiv}CCPh_2(Nu)\}(\eta^5\text{-}C_nH_m)\{\kappa^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}(PPh_3)]$ (C_nH_m = Cp, Nu = OMe, OEt; $C_nH_m = C_9H_7$, Nu = OMe),[87] $[Ru\{C{\equiv}CCPh_2(Nu)\}Cp(CO)(PPr^i_3)]$ (Nu = Me, OH, OMe, $C{\equiv}CPh$, $CH_2C(=O)Me$, $CH\{C(=O)Me\}_2$),[84,86] $[Ru\{C{\equiv}CCRPh(Nu)\}Cp^*(dippe)]$ (R = H, Nu = $CH_2C(=O)Me$, pyrazolyl; R = Ph, Nu = $CH_2C(=O)Me^*$, pyrazolyl*),[136] $[Ru\{C{\equiv}CCH(NEt_2)C(Me)=CR^1R^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ ($R^1 = R^2$ = Ph; R^1 = H, $R^2 = C(Me) = CPh_2$),[137,137a] and $[Os\{C{\equiv}CCPh_2(Nu)\}Cp(PPr^i_3)_2]$ (Nu = Me, OMe, $CH_2C(=O)Me$).[124] The closely related alkynyl derivatives $[Ru\{C{\equiv}CCPh_2(Nu)\}Cp(CO)(PPr^i_3)]$ (Nu = pyrazolyl, 3-methylpyrazolyl) have been obtained by deprotonation of alkenyl-type complexes **86** (see Figure 17) with NaOMe.[76]

Phosphines are also added regioselectively to the allenylidene group of indenyl–Ru(II) complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$, the final position of the addition (at C_α or C_γ) being controlled by the ancillary ligands on the ruthenium atom. Thus, complexes $[Ru\{=C=C=C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = H, Ph), containing bulky PPh_3 ligands, react with monodentate phosphines to generate the stable phosphonio–alkynyl derivatives $[Ru\{C{\equiv}CC(PR_3)RPh\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = H, $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3; R = Ph, $PR_3 = PMe_3$, PMe_2Ph).[85,85a] Compounds $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(dppe)][PF_6]$ and $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ also react with PMe_3 to yield $[Ru\{C{\equiv}CC(PMe_3)Ph_2\}(\eta^5\text{-}C_9H_7)(dppe)][PF_6]$ and $[Ru\{C{\equiv}CC(PMe_3)Ph_2\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$, respectively. The latter slowly rearranges in solution to give the thermodynamically more stable allenyl–phosphonio complex $[Ru\{C(PMe_3)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (other allenyl–phosphonio complexes can be obtained through this approach; see Section 6.15.2.3).[85,85a] Phosphonio–alkynyl complexes **126 and 127** have been prepared by direct activation of the corresponding propargylic alcohol by $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ in the presence of a large excess of PPh_3, the process involving the regioselective C_γ-addition of PPh_3 to unstable allenylidene intermediates (Scheme 7).[60,138,138a] The related phosphonio–alkynyl complexes $[Ru\{C{\equiv}CC(PEt_3)R_2\}Cp^*(PEt_3)_2][BPh_4]$ (R = Me*; $CR_2 = C_6H_{10}$) and $[Ru\{C{\equiv}CC(PMe_3)Ph_2\}Cp^*(CO)(PMePr^i_2)][BAr^F_4]$ are also known.[82,121,121a]

Deprotonation of phosphonio–alkynyl complexes $[Ru\{C{\equiv}CC(PR_3)HR^1\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = H, $PR_3 = PPh_3$; R^1 = Ph, $PR_3 = PMe_3$), containing an acidic hydrogen atom at C_γ, generates the highly unstable ylide–alkynyl derivatives $[Ru\{C{\equiv}CC(R^1)=PR_3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **128**, which are suitable precursors for the preparation of a wide series of neutral enynyl **129**[131,139,139a] and polyenynyl **130–132**[139,139a,140] complexes by means of Wittig-type processes with carbonyl compounds (Scheme 8). When aldehydes are used, inseparable mixtures of the corresponding (*E*)- and (*Z*)-stereoisomers are generally obtained. Phenyl isocyanate and $PhC{\equiv}CCHO$ can also be used in these Wittig-type reactions, leading to the alkynyl–keteniminyl and ynenynyl complexes **133 and 134**, respectively, the latter being able to undergo Pauson–Khand cyclizations with norbornadiene and norbornene to afford tricyclic



R = OMe, Me, Bu^n, CN, S-2-C_6H_4Me
R = C≡CH,* C≡CPh, C≡CPr^n
114[85,85a,126]

R^1 = Ph; R^2 = Ph, Me, Pr^i, Fc, (*E*)-CH=CHPh
R^1 = H; R^2 = Ph, Me, Pr^i, Fc
115[127,127a,127b]

R = Ph; *n* = 1, 2
R = H; *n* = 1, 2
116[127,127a,127b]

117*[127,127a,127b]

118[127,127a,127b]

119[128]

R^1 = R^2 = Ph; *n* = 1, 2
R^1 = H; R^2 = Ph; *n* = 1, 2
R^1 = H; R^2 = CMe=CPh_2; *n* = 1, 2
120[129]

R^1 = R^2 = Ph
R^1R^2 = $C_{12}H_8$ (2,2′-biphenyldiyl)
R^1 = H; R^2 = Ph, C(Me)=CPh_2
121[130]

122[131,132,132a]: R = OMe, CN, C≡CH

123[133]: R = H, Me, CN, C≡CPh, $CH_2CH=CH_2$

124[127,127a,127b]: R = Me, Ph, Pr^i*

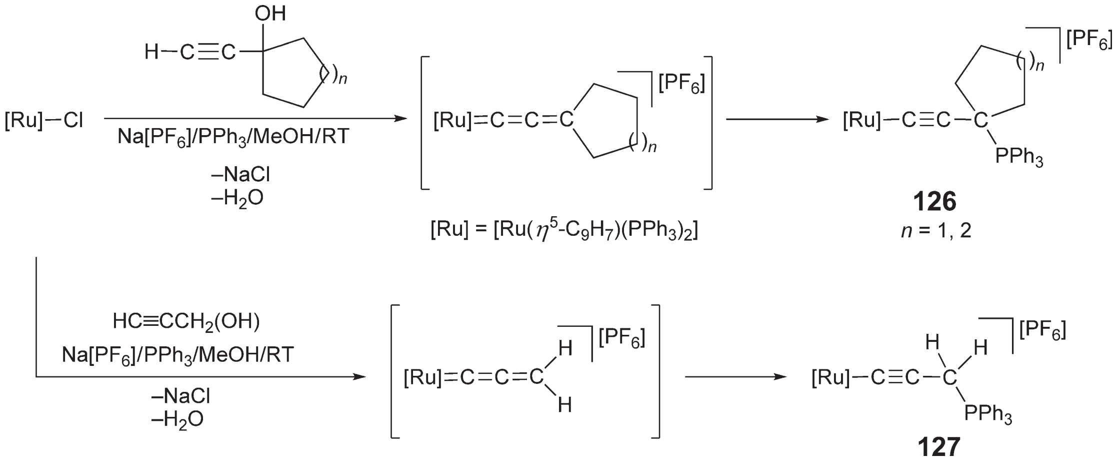
125*[127,127a,127b]

[Ru] = [Ru(η^5-C_9H_7)(PPh_3)$_2$]

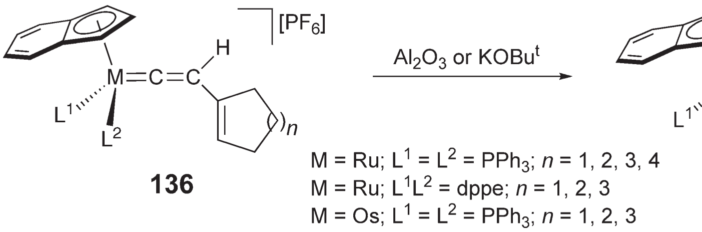
Figure 21 Indenyl–Ru(II) derivatives containing functionalized alkynyl chains.

cyclopentenone derivatives **135**.[139,139a,141] Related Pauson–Khand reactions starting from the complex [Ru{C≡CCPh$_2$(C≡CH)}(η^5-C_9H_7)(PPh_3)$_2$] have also been reported.[141]

Half-sandwich σ-enynyl complexes have also been synthesized by deprotonation of isolated monosubstituted alkenyl–vinylidene complexes. In this way, indenyl–Ru(II) and indenyl–Os(II) σ-enynyl derivatives **137** have been prepared in high yields by treatment of vinylidene precursors **136** with Al_2O_3 or $KOBu^t$ under mild conditions (RT) (Equation (8)).[60,109,132,132a] The related CpRu(II) complex [Ru(C≡CC$_6H_9$)Cp(CO)(PPr$^i_3$)] (C_6H_9 = 1-cyclohexenyl) has also been obtained by deprotonation of the corresponding alkenyl–vinylidene precursor.[27]

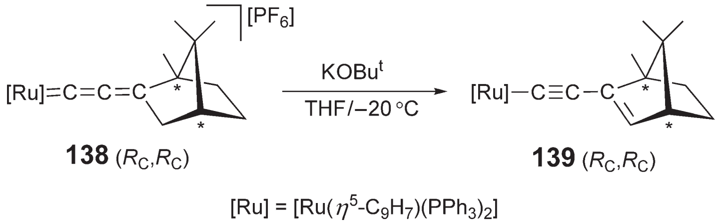


Scheme 7



(8)

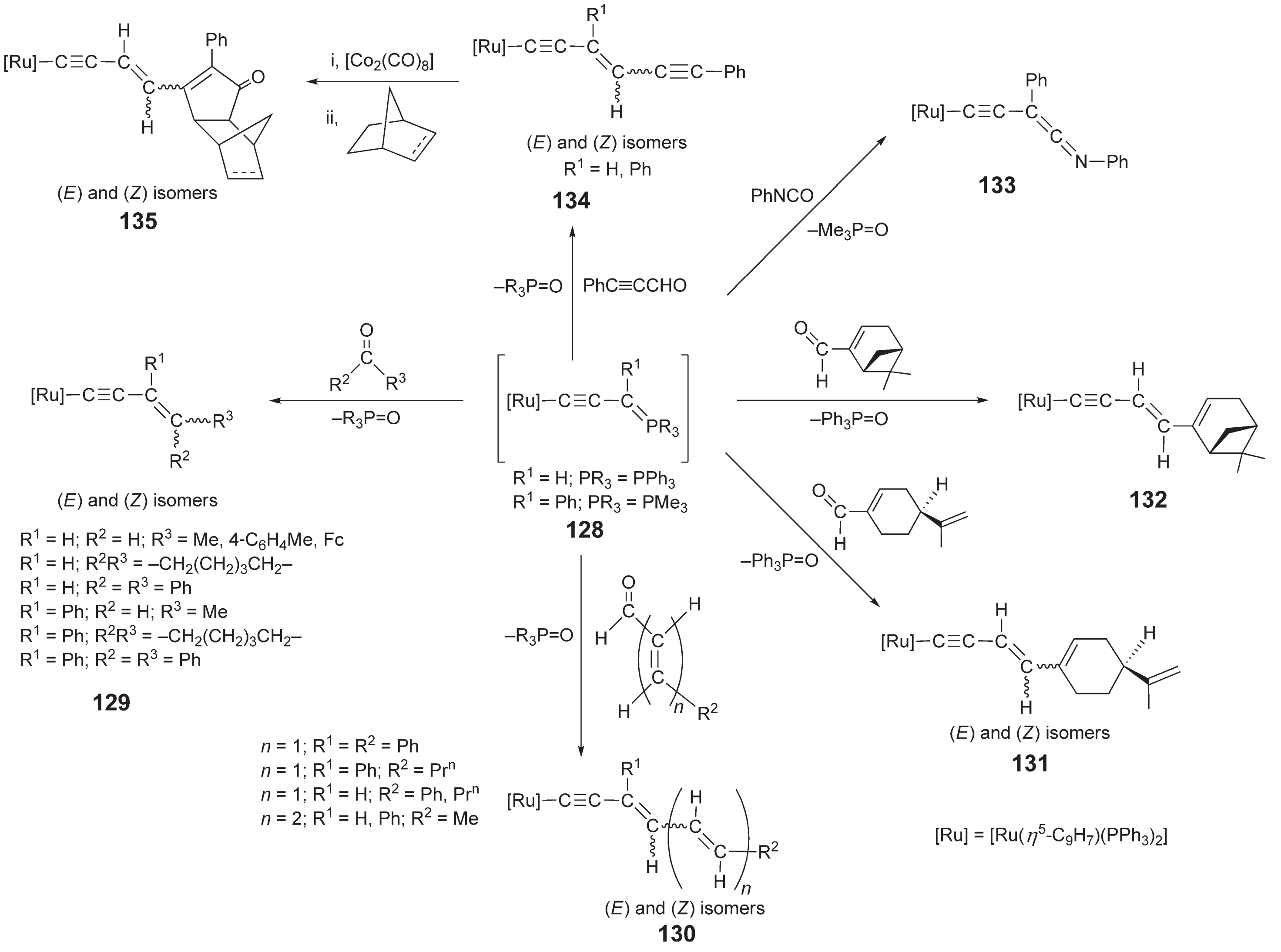
Deprotonation of cationic allenylidene complexes containing a C–H bond in δ-position is also known to generate enynyl-type derivatives. In this way, treatment of allenylidene–ruthenium(II) complexes $[Ru\{=C=C=CMe(2\text{-}C_4H_3NMe)\}Cp(PPh_3)_2][PF_6]$ ($2\text{-}C_4H_3NMe = N$-methyl-2-pyrrolyl) and $[Ru\{=C=C=C(Me)Ph\}Cp^*(dippe)][BPh_4]$ with LiBu^n or KOBu^t affords compounds $[Ru\{C\equiv CC(2\text{-}C_4H_3NMe)=CH_2\}Cp(PPh_3)_2]$ and $[Ru(C\equiv CCPh=CH_2)Cp^*(dippe)]^*$, respectively, via selective deprotonation of the methyl substituent.[142,142a,143] The related hydride–enynyl–Ru(IV) and hydride–enynyl–Os(IV) derivatives $[RuH(C\equiv CCPh=CH_2)Cp^*(PEt_3)_2][BPh_4]$ and $[OsH(C\equiv CCPh=CH_2)Cp(PPr^i_3)_2][PF_6]$ are also known. They have been obtained by dehydration of the methyl-substituted 3-hydroxyalkynyl ligand in complexes $[RuH\{C\equiv CC(OH)MePh\}Cp^*(PEt_3)_2][BPh_4]$ and $[OsH\{C\equiv CC(OH)MePh\}Cp(PPr^i_3)_2][PF_6]$, respectively.[121,121a,124] Deprotonation of the optically active indenyl–ruthenium(II) allenylidene **138** with KOBu^t to yield **139** has also been reported (see Equation (9)).[133]



(9)

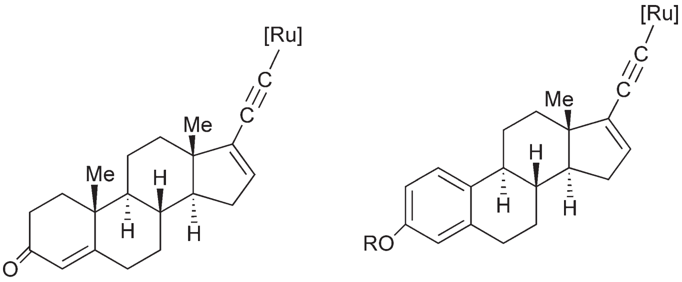
Enynyl derivatives $[Ru(C\equiv CCPh=CH_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$; $L^1L^2 =$ dppm, dppe) have been obtained by treatment of mixtures containing allenylidenes $[Ru\{=C=C=C(Me)Ph\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ and their alkenyl–vinylidene tautomers $[Ru(=C=CHCPh=CH_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ with K_2CO_3.[108] Compounds **140 and 141**, containing steroidal skeletons, have also been synthesized from related tautomeric mixtures (Figure 22).[144]

The reactions of the alkenyl–aminoallenylidene complex $[Ru\{=C=C=C(NEt_2)CMe=CPh_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ with alkyl carbanions such as $Li[CH_2R]$ or allylmagnesium bromide lead to the unusual



[Ru]–C≡C–C(H)=C(H)
(E) and (Z) isomers
135
i, [Co2(CO)8]
ii,
[Ru]–C≡C–C(R1)=C–C≡C–Ph
(E) and (Z) isomers
R1 = H, Ph
134
–R3P=O
PhC≡CCHO
PhNCO
–Me3P=O
[Ru]–C≡C–C(Ph)=C=N–Ph
133
[Ru]–C≡C–C(R1)=C(R2)R3
R2C(O)R3
(E) and (Z) isomers
R1 = H; R2 = H; R3 = Me, 4-C6H4Me, Fc
R1 = H; R2R3 = –CH2(CH2)3CH2–
R1 = H; R2 = R3 = Ph
R1 = Ph; R2 = H; R3 = Me
R1 = Ph; R2R3 = –CH2(CH2)3CH2–
R1 = Ph; R2 = R3 = Ph
129
[[Ru]–C≡C–C(R1)=PR3]
R1 = H; PR3 = PPh3
R1 = Ph; PR3 = PMe3
128
–Ph3P=O
[Ru]–C≡C–C(H)=C(H)
132
–Ph3P=O
[Ru]–C≡C–C(H)=C(H)
(E) and (Z) isomers
131
–R3P=O
n = 1; R1 = R2 = Ph
n = 1; R1 = Ph; R2 = Prn
n = 1; R1 = H; R2 = Ph, Prn
n = 2; R1 = H, Ph; R2 = Me
[Ru]–C≡C–C(R1)=C(H)–(C(H)=C(H))n–R2
(E) and (Z) isomers
130
[Ru] = [Ru(η5-C9H7)(PPh3)2]

Scheme 8

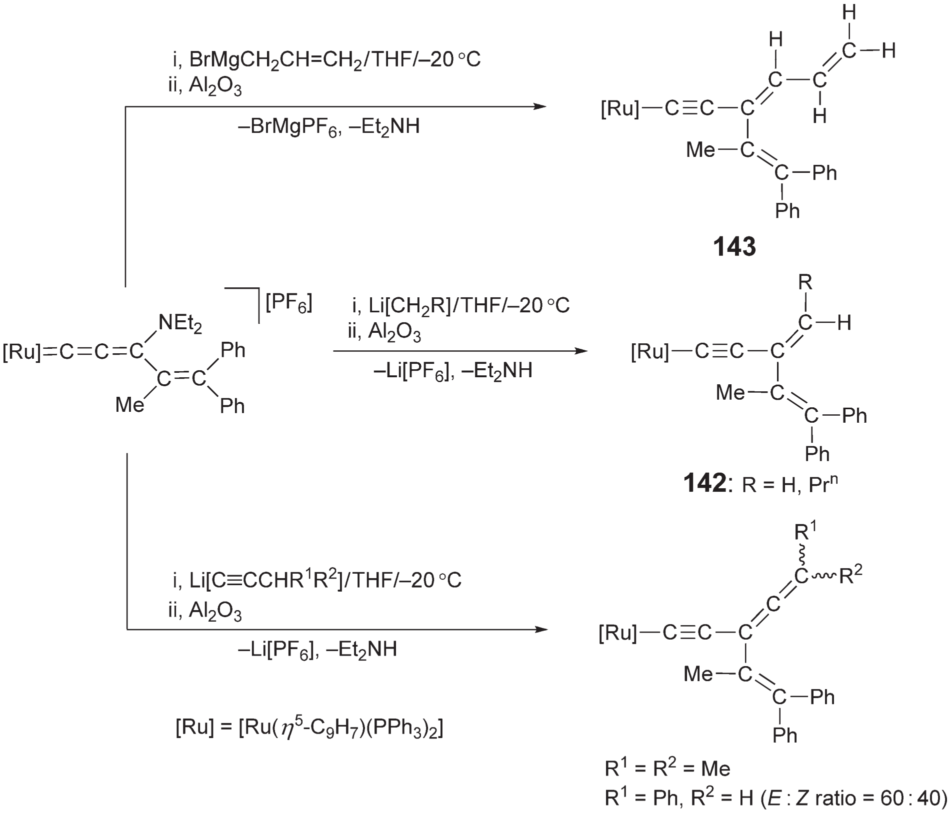


140

141: R = H, Me

[Ru] = [Ru(η^5-C_9H_7)(PPh_3)$_2$]

Figure 22 Enynyl–Ru(II) complexes containing steroidal skeletons.



143

142: R = H, Pr^n

$R^1 = R^2 = Me$
R^1 = Ph, R^2 = H (E : Z ratio = 60 : 40)

144

Scheme 9

enynyl and dienynyl derivatives **142** and **143**, respectively (Scheme 9). The process involves the initial nucleophilic addition of the carbanion to the electrophilic γ-carbon of the allenylidene chain to generate an intermediate amino-substituted alkynyl complex, which in the presence of Al_2O_3 eliminates Et_2NH. Related reactions with lithium acetylides Li[C≡CCHR^{1}R^2] ($R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = H$) afford the 3-alkenyl-3,4,5-hexatrien-1-ynyl species **144**.[137,137a]

The highly unstable butatrienylidene derivative [Ru(=C=C=C=CH_2)Cp(PPh_3)$_2$][PF_6], generated *in situ* by activation of HC≡CC≡CH with [RuCp(THF)(PPh_3)$_2$][PF_6], readily reacts with PPh_3 to afford the cationic enynyl species $[Ru\{C{\equiv}CC(PPh_3){=}CH_2\}Cp(PPh_3)_2][PF_6]$ via selective nucleophilic addition of the phosphine at the electrophilic γ-carbon of the unsaturated chain.[142,142a] When water is used as nucleophile, the acetyl–ethynyl complex $[Ru\{C{\equiv}CC({=}O)Me\}Cp(PPh_3)_2]$ is formed. Similarly, activation of the diyne $HC{\equiv}CC{\equiv}CFc$ by $[RuClCp(dppe)]$, in the presence of $Na[BPh_4]/NEt_3$, gives (Z)-$[Ru\{C{\equiv}CC(NEt_3){=}CHFc\}Cp(dppe)][BPh_4]^*$. Treatment of this enynyl derivative with I_2 leads to the formation of (Z)-$[RuI\{\eta^5\text{-}C_5H_4C{\equiv}C\text{-}C(NEt_3){=}CHFc\}(dppe)][I_3]^*$ as the result of the migration of the alkynyl group from Ru to the Cp ring.[93] The *in situ*-generated butatrienylidenes $[Ru({=}C{=}C{=}C{=}CH_2)Cp(PR_3)_2][PF_6]$ ($PR_3 = PPh_3$, $P(OMe)_3$) also react with arylimines to afford either substituted quinolines **145**, by attack of the terminal carbon of the butatrienylidene ligand at the imine carbon followed by C–C coupling, or 1-azabuta-1,3-dienyl complexes **146**, formed by cycloaddition of $N{=}CH$ group to $C_\gamma{=}C_\delta$ of the carbene, followed by opening of the resulting four-membered ring (Scheme 10). Formation of **145** or **146** depends mainly on the nature of the substituents in the N– and C–aryl groups of the imine. The nitrogen atoms in these functionalized alkynyl complexes are strongly basic, being readily protonated, methylated, or aurated.[145,145a] It is also worth noting that the amino–allenylidene complex $[Ru\{{=}C{=}C{=}C(NPh_2)Me\}Cp(PPh_3)_2][PF_6]$ slowly decomposes in dichloromethane solution yielding the chloro-enynyl derivative $[Ru\{C{\equiv}CCH{=}C(H)Cl\}Cp(PPh_3)_2]^*$, via chloride addition at the C_γ-carbon of the butatrienylidene intermediate $[Ru({=}C{=}C{=}C{=}CH_2)Cp(PPh_3)_2][PF_6]$, presumably formed by deamination of the allenylidene precursor by traces of HCl.[142,142a]

The addition of tetracyanoethene to the $C_\gamma{\equiv}C_\delta$ triple bond of polyynyl complexes $[Ru(C{\equiv}CC{\equiv}CR)Cp(PPh_3)_2]$ ($R = Ph$, $C{\equiv}CPh$) and $[Ru(C{\equiv}CC{\equiv}CFc)Cp(dppe)]$ has been reported to yield the functionalized enynyl derivatives $[Ru\{C{\equiv}CC\{{=}C(CN)_2\}CR{=}C(CN)_2\}Cp(PPh_3)_2]$ ($R = Ph,^*$ $C{\equiv}CPh^*$) and $[Ru\{C{\equiv}CC[{=}C(CN)_2]\text{-}CFc{=}C(CN)_2\}Cp(dppe)]^*$, respectively.[93,105]

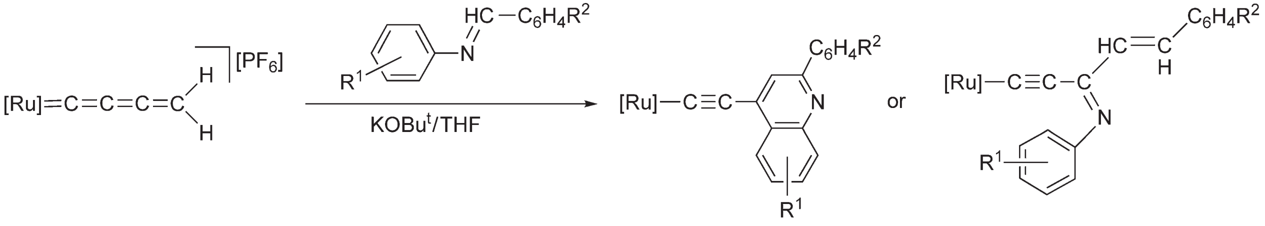
The non-linear optical (NLO) properties of organometallic complexes have attracted significant attention over the past decade.[146,146a,146b] In this context, a series of half-sandwich alkynyl and enynyl ruthenium(II) and osmiun(II) complexes with a conjugated donor-bridge-acceptor composition have been prepared by standard procedures (see Table 1), and their second-order NLO properties have been evaluated. The synthesis of organoruthenium complexes **147 and 148**, analogs of Crystal Violet, has also been reported (Scheme 11). These carbocationic species exhibit intense electronic absorption in the near-infrared region.[160]

6.15.2.5 Fischer-type Carbene Complexes

Only a few examples have been obtained through the classical methodologies followed in group 6 metal chemistry. Most η^5-C_5 Fischer-type ruthenium and osmium carbenes arise from the nucleophilic additions of alcohol and amino groups at the electrophilic carbenic C_α-atom of both allenylidene and vinylidene complexes. The fate of the reaction depends on the electrophilicity as well as the steric hindrance around the C_α-atom, which can control its accessibility, especially for bulky nucleophiles. These features have been thoroughly discussed in a recent review.[1b]

With regard to the η^5-indenyl metal fragments $[Ru(\eta^5\text{-}C_9H_7)(L^1)(L^2)]^+$, the protection arising from the phenyl groups of the ancillary phosphines (L^1/L^2) and the benzo group of the indenyl ring has to be considered as well. Thus, cationic allenylidene complexes $[Ru\{{=}C{=}C{=}C(H)R\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ ($L^1L^2 = dppm$, $R = H$, Ph; $L^1L^2 = dppe$, $R = Ph$) and $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}1,2,3\text{-}C_9H_4Me_3)(CO)(PPh_3)][BF_4]$ (either isolated or generated *in situ*) react with alcohols to form the α,β-unsaturated alkoxy–carbene derivatives $[Ru\{{=}C(OMe)CH{=}CHR\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ ($L^1L^2 = dppm$, $R = H$, Ph; $L^1L^2 = dppe$, $R = Ph$) and $[Ru\{{=}C(OR)CH{=}CPh_2)(\eta^5\text{-}1,2,3\text{-}C_9H_4Me_3)(CO)(PPh_3)][BF_4]$ ($R = Me$, Ph), respectively.[108,135] In contrast, the disubstituted allenylidene derivatives $[M({=}C{=}C{=}CPh_2)(\eta^5\text{-}1,2,3\text{-}C_9H_4R_3)(L^1)(L^2)]^+$ ($M = Ru$, $R = H$, $L^1 = L^2 = PPh_3$, $L^1L^2 = dppe$, dppm; $M = Os$, $R = H$, $L^1 = L^2 = PPh_3$; $M = Ru$, $R = Me$, $L^1L^2 = dppm$) are unreactive toward alcohols.

The higher electrophilicity and accessibility of the C_α-atom of the allenylidene complex $[Ru({=}C{=}C{=}CPh_2)Cp(CO)(PPr^i_3)][BF_4]$ has allowed not only the synthesis of the methoxy and ethoxy carbenes $[Ru\{{=}C(OR)C(H){=}CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$ ($R = Me$, Et) by the reactions with methanol and ethanol, respectively,[27] but also has proved to be a good precursor of the functionalized allyloxy $[Ru\{{=}C(OCH_2CH{=}CH_2)\text{-}CH{=}CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$[80] and propargyloxy carbene $[Ru\{{=}C(OCH_2C{\equiv}CH)CH{=}CPh_2\}Cp(CO)\text{-}(PPr^i_3)][BF_4]^*$ complexes, obtained by reactions with functionalized alcohols such as allyl alcohol and propargyl alcohol, respectively.[23] Analogous hydroxy $[Ru\{{=}C(OH)CH{=}CR_2\}Cp(CO)(PPr^i_3)][BF_4]$ ($R = H$, Ph)[27] and methoxy carbenes $[Ru\{{=}C(OMe)\text{-}(E)\text{-}CH{=}CH\text{-}4(C_6H_4R)\}Cp(CO)(PPh_3)][BF_4]$ ($R = CH(OH)C{\equiv}CH$, $CH{=}CH_2$) have also been isolated.[161]



145 **146**

[Ru] = $[RuCp(PR_3)_2]$

R^1	*R*^{2}	*PR*$_3$
H*	H*	PPh$_3$*
6-Me*	H*	PPh$_3$*
H*	4-NO$_2$*	PPh$_3$*
H	4-NO$_2$	P(OMe)$_3$
H	3-NO$_2$	PPh$_3$
H*	4-CO$_2$Me*	P(OMe)$_3$*
6-OMe	4-NO$_2$	PPh$_3$
6-OMe*	4-NO$_2$*	PPh$_3$*
5-Cl	H	PPh$_3$
7-Cl	H	PPh$_3$
benzo*	H*	PPh$_3$*

R^1	*R*^{2}	*PR*$_3$
H	H	P(OMe)$_3$
4-Me	4-Me	PPh$_3$
4-Me	4-Me	P(OMe)$_3$
4-OMe	4-OMe	PPh$_3$
4-OMe*	4-OMe*	P(OMe)$_3$*
4-NO$_2$	H	PPh$_3$
3-NO$_2$*	H*	PPh$_3$*
H	4-CO$_2$Me	PPh$_3$
4-NO$_2$	4-CO$_2$Me	PPh$_3$
4-NO$_2$	4-CO$_2$Me	PPh$_3$
4-CO$_2$Et	H	PPh$_3$
H	benzo	PPh$_3$

Scheme 10

Table 1 Half-sandwich alkynyl and enynyl ruthenium(II) and osmium(II) complexes of the donor–acceptor type

Complex	*References*
$[Ru(C\equiv C-4-C_6H_4NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$*	147,148,149,150
$[Ru(C\equiv C-4-C_6H_4NO_2)(\eta^5-C_5H_5)(PMe_3)_2]$*	147,148,149
$[Ru(C\equiv C-4-C_6H_4NO_2)(\eta^5-C_5H_5)(dppe)]$*	150
$[Ru(C\equiv C-4-C_6H_4NO_2)(\eta^5-C_5H_5)(CO)_2]$*	150
$[Ru(C\equiv C-4-C_6H_4CHO)(\eta^5-C_5H_5)(PPh_3)_2]$	151
$[Ru(C\equiv C-4-C_6H_4CH\{OC(=O)Me\}_2)(\eta^5-C_5H_5)(PPh_3)_2]$	151
$[Ru(C\equiv C-4-C_6H_4-4-C_6H_4NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$	152
$[Ru(C\equiv C-4-C_6H_4C\equiv C-4-C_6H_4NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$*	149,152
$[Ru(C\equiv C-4-C_6H_4C\equiv C-Th-NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru(C\equiv C-4-C_6H_4C\equiv C-4-C_5H_4N)(\eta^5-C_5H_5)(PPh_3)_2]$	154
$[Ru(C\equiv C-4-C_6H_4C\equiv C-4-C_5H_4NH)(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$	154
$[Ru(C\equiv C-4-C_6H_4C\equiv C-4-C_5H_4NMe)(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$	154
$[Ru\{C\equiv C-4-C_6H_4-(E)-CH=CH-4-C_6H_4NO_2\}(\eta^5-C_5H_5)(PPh_3)_2]$*	148,149,153,155
$[Ru\{C\equiv C-4-C_6H_4-(E)-CH=CH-4-C_6H_4NO_2\}(\eta^5-C_5H_5)(PMe_3)_2]$	148
$[Ru\{C\equiv C-4-C_6H_4-(E)-CH=CH-Th-NO_2\}(\eta^5-C_5H_5)(PPh_3)_2]$*[a]	153
$[Ru\{C\equiv C-4-C_6H_4-(E)-CH=CH-4-C_5H_4N\}(\eta^5-C_5H_5)(PPh_3)_2]$	154
$[Ru\{C\equiv C-4-C_6H_4-(E)-CH=CH-4-C_5H_4NH\}(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$	154
$[Ru\{C\equiv C-4-C_6H_4-(E)-CH=CH-4-C_5H_4NMe\}(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$	154
$[Ru(C\equiv C-4-C_6H_4N=CH-4-C_6H_4NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$	147,149
$[Ru(C\equiv C-4-C_6H_4N=CH-4-C_6H_4NO_2)(\eta^5-C_5H_5)(PMe_3)_2]$	148
$[Ru(C\equiv C-4-C_6H_4N=CH-Th-NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru\{C\equiv C-4-C_6H_4N=C(C_{13}H_{20}O)\}(\eta^5-C_5H_5)(PPh_3)_2]$*[b]	156
$[Ru\{C\equiv C-4-C_6H_4-(E)-N=N-4-C_6H_4NO_2\}(\eta^5-C_5H_5)(PPh_3)_2]$	157
$[Ru(C\equiv C-4-C_5H_4N)(\eta^5-C_5H_5)(PPh_3)_2]$	154
$[Ru(C\equiv C-4-C_5H_4NH)(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$	154
$[Ru(C\equiv C-4-C_5H_4NMe)(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$	154
$[Ru(C\equiv C-2-C_5H_4N)(\eta^5-C_5H_5)(PPh_3)_2]$	158
$[Ru(C\equiv C-2-C_5H_3N-5-NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$	158
$[Ru(C\equiv C-Th-NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$[a]	159
$[Ru(C\equiv C-Th-NO_2)(\eta^5-C_5H_5)(CO)(PPh_3)]$[a]	159
$[Ru(C\equiv C-Th-NO_2)(\eta^5-C_5H_5)(CO)_2]$[a]	159
$[Ru(C\equiv C-Th-NO_2)(\eta^5-C_5Me_5)(PMe_2Ph)_2]$[a]	159
$[Ru(C\equiv C-Th-CHO)(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru(C\equiv C-Th-C\equiv C-4-C_5H_4N)(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru(C\equiv C-Th-C\equiv C-4-C_5H_4NMe)(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$[a]	153
$[Ru(C\equiv C-Th-C\equiv C-Th-NO_2)(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru\{C\equiv C-Th-CH=C(CN)_2\}(\eta^5-C_5H_5)(PPh_3)_2]$*[a]	153
$[Ru\{C\equiv C-Th-(E)-CH=CH-4-C_6H_4NO_2\}(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru\{C\equiv C-Th-(E)-CH=CH-4-C_5H_4N\}(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru\{C\equiv C-Th-(E)-CH=CH-4-C_5H_4NMe\}(\eta^5-C_5H_5)(PPh_3)_2][PF_6]$[a]	153
$[Ru\{C\equiv C-Th-(E)-CH=CH-Th-NO_2\}(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru\{C\equiv C-Th-(E)-CH=CH-Th-CHO\}(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru\{C\equiv C-Th-(E)-CH=CH-Th-CH=C(CN)_2\}(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru\{C\equiv C-Th-(E)-CH=CH-Th-(E)-CH=CH-4-C_6H_4NO_2\}(\eta^5-C_5H_5)(PPh_3)_2]$[a]	153
$[Ru(C\equiv C-4-C_6H_4NO_2)(\eta^5-C_9H_7)(PPh_3)_2]$	138,149
$[Ru(C\equiv C-4-C_6H_4NO_2)(\eta^5-C_9H_7)(dppm)]$	138
$[Ru(C\equiv C-4-C_6H_4NO_2)(\eta^5-C_9H_7)(dppe)]$	138
$[Ru(C\equiv C-4-C_6H_4C\equiv C-4-C_6H_4NO_2)(\eta^5-C_9H_7)(PPh_3)_2]$	138
$[Ru(C\equiv C-4-C_6H_4N=CH-4-C_6H_4NO_2)(\eta^5-C_9H_7)(PPh_3)_2]$	138
$[Ru\{C\equiv CCH=C(3-C_6H_4NO_2)_2\}(\eta^5-C_9H_7)(PPh_3)_2]$*	138,149
$[Ru\{C\equiv C-(E,Z)-CH=CH-4-C_6H_4NO_2\}(\eta^5-C_9H_7)(PPh_3)_2]$	138,149
$[Ru\{C\equiv C-(E,Z)-CH=CH-4-C_6H_4CN\}(\eta^5-C_9H_7)(PPh_3)_2]$	138,149
$[Ru\{C\equiv C-(E,Z)-CH=CH-Fu-NO_2\}(\eta^5-C_9H_7)(PPh_3)_2]$[c]	138
$[Ru\{C\equiv C-(E)-CH=CH-Th-NO_2\}(\eta^5-C_9H_7)(PPh_3)_2]$[a]	138
$[Ru\{C\equiv C-(E)-CH=CH-4-C_5H_4N\}(\eta^5-C_9H_7)(PPh_3)_2]$	138,149
$[Ru\{C\equiv C-(E,Z)-CH=CH-(E)-CH=CH-4-C_6H_4NO_2\}(\eta^5-C_9H_7)(PPh_3)_2]$*	138,149

(Continued)

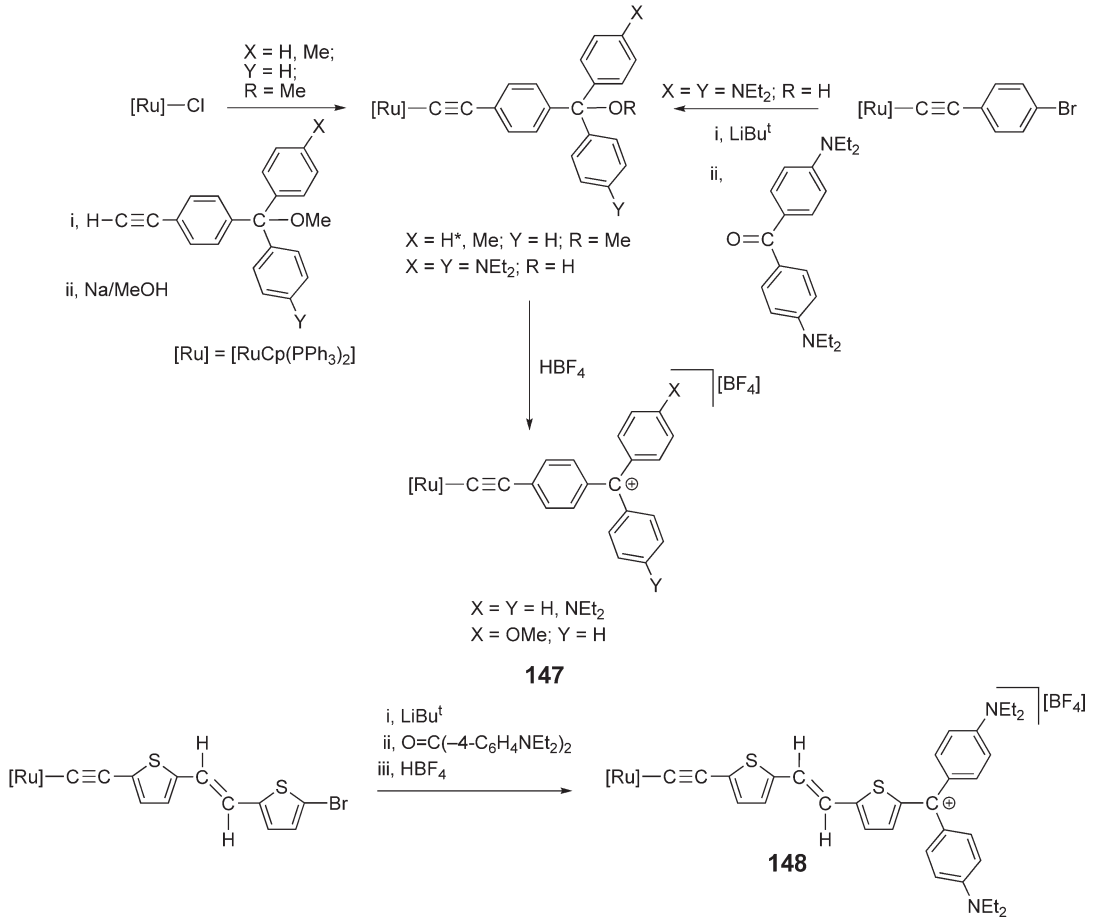
Table 1 (Continued)

Complex	*References*
$[Os(C{\equiv}C\text{-}4\text{-}C_6H_4NO_2)(\eta^5\text{-}C_5H_5)(PPh_3)_2]$	150
$[Os(C{\equiv}C\text{-}4\text{-}C_6H_4NO_2)(\eta^5\text{-}C_5H_5)(dppe)]$	150

[a] Th = 2,5-disubstituted thiophene.

[b] $C(C_{13}H_{20}O)$ = 2,6-di-*tert*-butyl–2,5-cyclohexadienone–4-ylidene.

[c] Fu = 2,5-disubstituted furan.



Scheme 11

Vinylidene complexes can be alternatively used as sources of Fischer-type carbenes. Examples are the following:

(i) Indenyl complexes $[Ru\{{=}C(OR)Me\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ ($L^1 = L^2 = PPh_3$, $R^2 = Me$, Et; $L^1L^2 = dppe$, $R^2 = Me$, Et; $L^1L^2 = dppm$, $R^2 = Me$, Et), which are obtained by addition of MeOH or EtOH to the unsubstituted vinylidenes $[Ru({=}C{=}CH_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$, generated *in situ* by reacting the chloride precursors $[RuCl(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ with $HC{\equiv}CSiMe_3$ in MeOH or EtOH in the presence of $[NH_4][PF_6]$. Complex $[Ru\{{=}C(OMe)CH_2Ph\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ has been analogously synthesized. Remarkably, in the absence of alcohols, the amino–carbene complex $[Ru\{{=}C(NH_2)Me\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ could be isolated from dichloromethane solutions.[98] Vinylidene intermediates could be isolated in some cases (see Section 6.15.2.8).

(ii) Complex $[Ru\{{=}C(OMe)Me\}(\eta^5\text{-}C_5H_4Me)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}_2][PF_6]^*$ formed by the reaction of $[Ru(\eta^5\text{-}C_5H_4Me)(NCMe)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}_2][PF_6]$ with $HC{\equiv}CSiMe_3$ in a mixture CH_2Cl_2/MeOH. The corresponding vinylidene intermediate could not be isolated or detected in this case.[162] The related complex $[Ru\{{=}C(OMe)Me\}\{\eta^5{:}\kappa^2(P,P)\text{-}C_5H_4CH_2CMe(CH_2PPh_2)_2\}][PF_6]$ has been obtained through a similar route.[114]

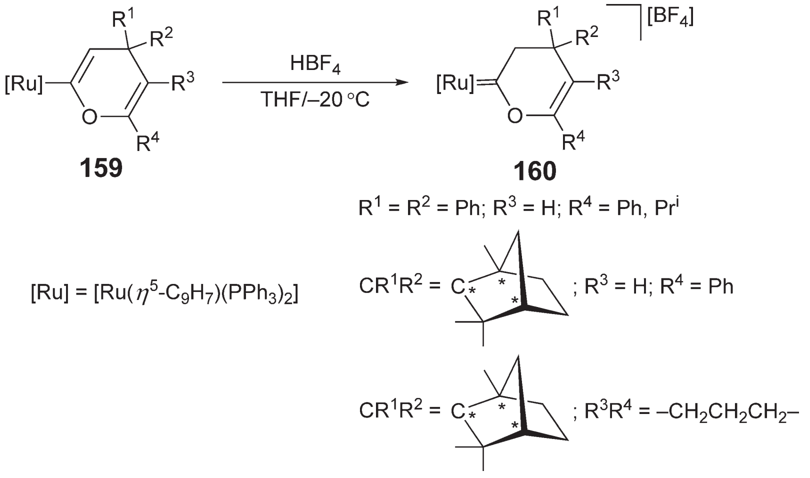
(iii) The methoxycarbene **149*** bearing a uracil-type substituent (Ur) which has been prepared by activation of the corresponding terminal alkyne $HC{\equiv}CUr$ with $[RuClCp(PPh_3)_2]$ in MeOH in the presence of $[NH_4][PF_6]$ (Figure 23).[163]

(iv) The neutral amino carbene $[RuCl\{{=}C(NHBz)Bz\}Cp\{PPh_2(2\text{-}C_6H_4Me)\}]$ generated by the reaction of the isolated vinylidene complex $[RuCl\{{=}C{=}C(H)Ph\}Cp\{PPh_2(2\text{-}C_6H_4Me)\}]$ with benzylamine.[164]

The intramolecular nucleophilic addition of a pendant –OH group at the C_α-atom of a hydroxy–vinylidene ligand is a well-known process which gives rise to cyclic oxa–cyclocarbene units.[165] The starting vinylidene complexes can be either isolated or formed *in situ* by the reaction of the appropriate ruthenium precursor with hydroxy-1-alkynes. This process provides an efficient entrance to the synthesis of a wide variety of cyclic oxa–carbene complexes containing indenyl and cyclopentadienyl ruthenium fragments such as **150**,[166] **151**,[167] **152**,[168] and **153–156**[169] (Figure 23). Similarly, the formation of complexes **157** has been proposed to proceed through an intramolecular OH attack to the C_α-atom in transient allenylidenes generated by activation of enynols $HC{\equiv}CCMe{=}CCHR(OH)$ with $[RuClCp^*(PMe_3)_2]$.[170]

An intramolecular cycloaddition reaction is also observed in the formation of the very unusual 1-furanylidene derivative **158** (Figure 23), which is isolated by deprotonation of the propargyloxy–carbene complex $[Ru\{{=}C(OCH_2C{\equiv}CH)CH{=}CPh_2\}Cp(CO)(PPr^i_3)][BF_4]$ with Na_2CO_3. This reaction is strongly dependent on the nature of the base used, since by using $Na[BH_4]$ or NaOMe, mixtures of rare cycloaddition products, including compounds **7–9** (see Figure 3), are formed.[23]

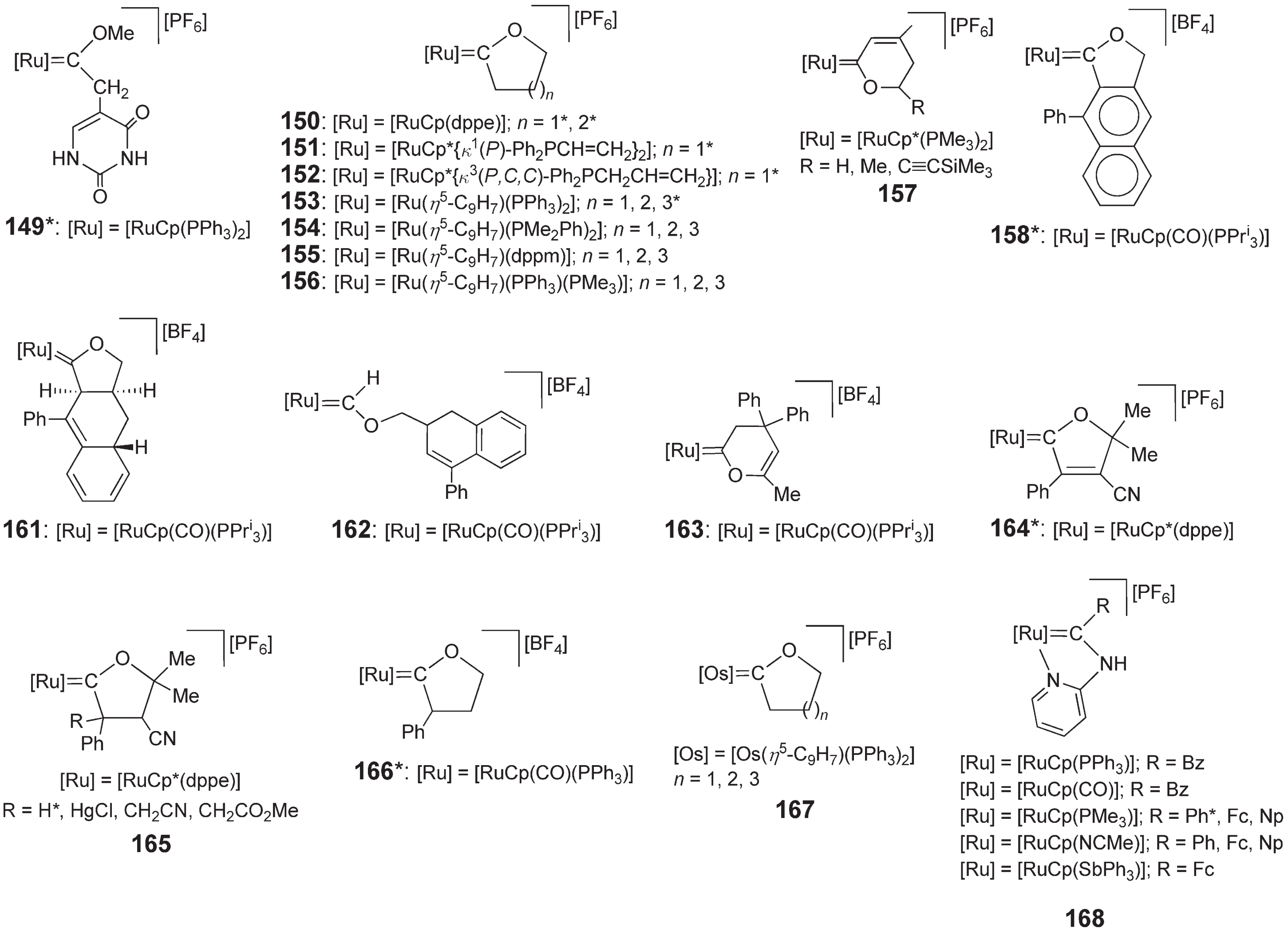
Indenyl–ruthenium(II) oxa-cyclocarbene derivatives **160** have been prepared by selective protonation of the alkenyl unit in complexes **159** (Equation (10)).[127,127a,127b] Following a similar synthetic approach, the cyclopentadienyl derivative **161** (Figure 23) has been prepared by protonation of **96** (see Figure 17). Complex **161** slowly isomerizes in THF solution at 50 °C to generate the acyclic alkoxycarbene **162** (Figure 23). In methanol solution, the alkoxy group of **162** is exchanged by the methoxy group affording the carbene $[Ru\{{=}C(OMe)H\}Cp(CO)(PPr^i_3)][BF_4]$.[80] Other oxa-cyclic carbenes **163**,[86] **164***,[171] **165**,[171] and **166***[172] are also known (see Figure 23).



(10)

Nucleophilic attack of carbanions on carbonyl ligands followed by an electrophilic addition to the resulting acylate is the most common route for group 6 Fischer-type oxacarbenes. Although this synthetic methodology is scarcely employed in ruthenium and osmium chemistry, it has been applied to the synthesis of the acyloxycarbenes $[Ru\{{=}C(OCOR)Ph\}Cp(SnPh_3)(CO)]$ (R = Me, Ph, Bu^t), which are obtained from the reaction of $[RuCp(SnPh_3)(CO)_2]$ with LiPh followed by the treatment with RCOCl.[173] Related reactions starting from $Li[CH_2R]$ generate the corresponding acyloxycarbenes, which are not stable and evolve into the vinylidenes $[Ru\{{=}C{=}C(H)R\}Cp(SnPh_3)(CO)]$ (R = H, Me, Pr^n, Ph) (see Section 6.15.2.8).[174] The synthesis and crystallographic characterization of the ethoxy–carbene complex $[RuCl\{{=}C(OEt)Pr^n\}Cp(CO)]$ has also been reported.[175]

Fischer-type osmium alkoxycarbenes are scarce when compared to those of ruthenium. The addition of alcohols to the electrophilic C_α-atom of vinylidene or allenylidene groups has also proved to be, as for the ruthenium complexes,



149*: [Ru] = [RuCp(PPh_3)$_2$]

150: [Ru] = [RuCp(dppe)]; *n* = 1*, 2*

151: [Ru] = [RuCp*{κ^1(*P*)-$Ph_2PCH{=}CH_2$}$_2$]; *n* = 1*

152: [Ru] = [RuCp*{κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}]; *n* = 1*

153: [Ru] = [Ru(η^5-C_9H_7)(PPh_3)$_2$]; *n* = 1, 2, 3*

154: [Ru] = [Ru(η^5-C_9H_7)(PMe_2Ph)$_2$]; *n* = 1, 2, 3

155: [Ru] = [Ru(η^5-C_9H_7)(dppm)]; *n* = 1, 2, 3

156: [Ru] = [Ru(η^5-C_9H_7)(PPh_3)(PMe_3)]; *n* = 1, 2, 3

[Ru] = [RuCp*(PMe_3)$_2$]
R = H, Me, C≡C$SiMe_3$
157

158*: [Ru] = [RuCp(CO)(PPr^i_3)]

161: [Ru] = [RuCp(CO)(PPr^i_3)]

162: [Ru] = [RuCp(CO)(PPr^i_3)]

163: [Ru] = [RuCp(CO)(PPr^i_3)]

164*: [Ru] = [RuCp*(dppe)]

[Ru] = [RuCp*(dppe)]
R = H*, HgCl, CH_2CN, CH_2CO_2Me
165

166*: [Ru] = [RuCp(CO)(PPh_3)]

[Os] = [Os(η^5-C_9H_7)(PPh_3)$_2$]
n = 1, 2, 3
167

[Ru] = [RuCp(PPh_3)]; R = Bz
[Ru] = [RuCp(CO)]; R = Bz
[Ru] = [RuCp(PMe_3)]; R = Ph*, Fc, Np
[Ru] = [RuCp(NCMe)]; R = Ph, Fc, Np
[Ru] = [RuCp($SbPh_3$)]; R = Fc

168

Figure 23 Some examples of half-sandwich Ru and Os Fischer-type carbenes.

an efficient synthetic route. Thus, indenyl–osmium cyclic oxacarbenes of type **167** have been obtained by intramolecular nucleophilic additions of pendant –OH groups to the C_α-atom of hydroxy–vinylidene chains (Figure 23).[109,176] It has also been reported that the treatment of the osmium allenylidene $[Os({=}C{=}C{=}CPh_2)Cp(CO)(PPr^i_3)][PF_6]$ with MeOH affords the α,β-unsaturated methoxy–carbene derivative $[Os\{{=}C(OMe)CH{=}CPh_2\}Cp(CO)(PPr^i_3)][PF_6]$.[79] The C_α-atom of the carbynes $[Os({\equiv}CPh)CpL]$ ($L = PPr^i_3$, $Pr^i_2P(CMe{=}CH_2)$) also undergoes the addition of MeOH leading to the hydride methoxy–carbenes $[OsH\{{=}C(OMe)Ph\}CpL]$ ($L = PPr^i_3$, $Pr^i_2P(CMe{=}CH_2)$).[22,25]

Complexes **168** are a particular class of Fischer-type carbenes featuring a chelate $\kappa^2(C,N)$-coordination of the amino–carbene group (Figure 23). They have been obtained using aldimines and aminals as sources of the carbene ligand by reaction with the bis-acetonitrile complexes $[RuCp(NCMe)_2L][PF_6]$ ($L = CO$, PPh_3, PMe_3, NCMe, $SbPh_3$). The additional coordination of the carbene group relies on the presence of a pyridinyl substituent in the amino group.[177,178,178a]

6.15.2.6 Alkylidene Complexes

The high catalytic activity of Grubbs-type alkylidene complexes $[Ru({=}CR^1R^2)Cl_2L_2]$ in alkene metathesis and the tolerance toward many polar functional groups has triggered the search for analogous species. At the time of COMC (1995), only the methylidene complex $[Ru({=}CH_2)Cp(dppe)]^+$ was known. It was prepared *in situ* and observed by ^1H NMR. In addition, the bis-carbene complex $[RuBr(1{,}4\text{-}C_4H_2Ph_2)Cp]^*$ and the allyl–carbene $[RuCp(\eta^1{:}\eta^3\text{-}CPh\text{-}CPhCPhCHPh)]^*$ had been isolated and crystallographically characterized.[179,180,180a]

The discovery of new synthetic methodologies has allowed the availability of half-sandwich-type alkylidenes. This fact has motivated not only the generalization of stoichiometric studies but also their potential utility in other catalytic transformations. The following years have witnessed the extent of this type of carbenes in such a way that they deserved specialized reviews.[181,181a–181c]

6.15.2.6.1 Monohapto alkylidenes

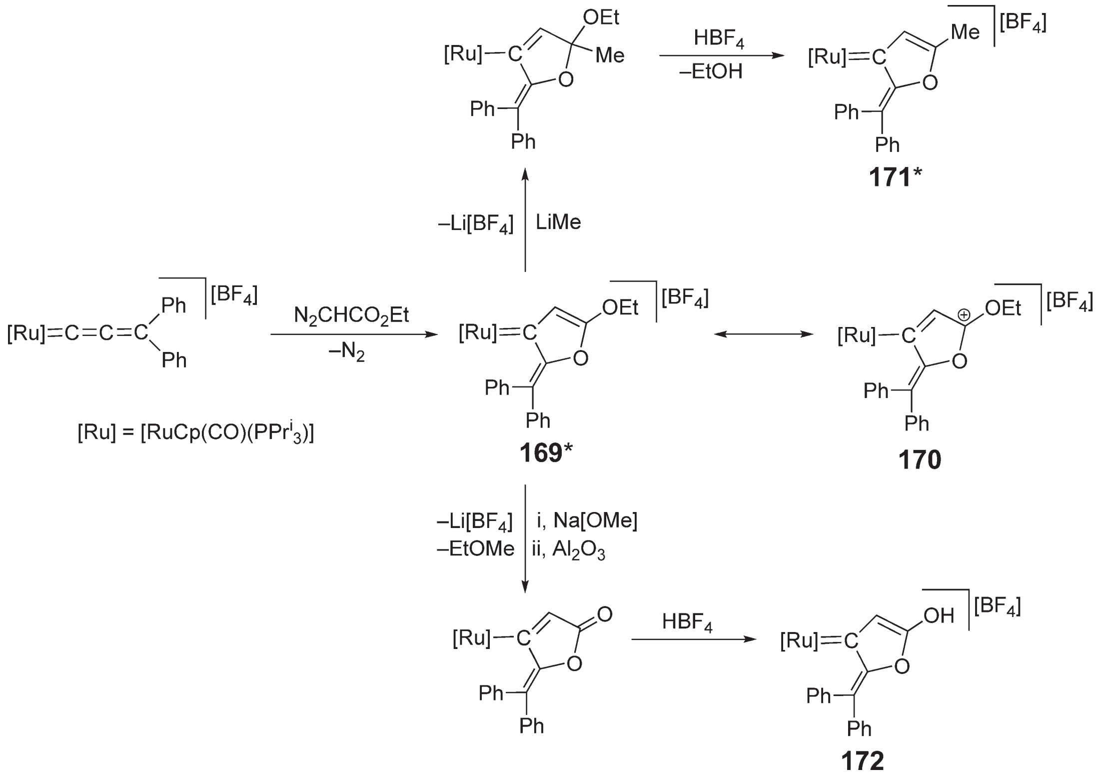
The "diazoalkane route" has been applied for the preparation of alkylidene complexes including both ruthenium and osmium derivatives. The synthetic approach consists in the treatment of the starting metal complex, containing a labile ligand, with a diazoalkane $R^1R^2CN_2$, which acts as source of the carbene group R^1R^2C via N_2 elimination. The reaction generally proceeds through an exchange of the labile ligand with the carbene group. The following complexes have been isolated and characterized through this synthetic methodology: $[RuCl({=}CR^1R^2)Cp(PPh_3)]$ ($R^1 = R^2 = Ph^*$, $4\text{-}C_6H_4Cl$, $4\text{-}C_6H_4OMe$; $R^1 = Ph$, $R^2 = 4\text{-}C_6H_4Me$),[59,182,183] $[Ru\{\kappa^1(O)\text{-}O_2CMe\}({=}CPh_2)Cp(PPh_3)]$,[59] $[RuCl({=}CPh_2)Cp\{PPh_2(2\text{-}C_6H_4Me)\}]$,[164] $[OsCl({=}CHPh)Cp\{\kappa^1(P)\text{-}Pr^i_2P(CMe{=}CH_2)\}]^*$,[22] $[OsCl({=}CHPh)Cp(PPr^i_3)]$,[25] $[Ru\{\kappa^1(O)\text{-}O_2CCF_3\}({=}CHPh)(\eta^5\text{-}C_5R_5)(PPh_3)]$ ($R = H$, Me),[184] $[Ru\{\kappa^1(O)\text{-}O_2CCF_3\}({=}CR_2)Cp(PPh_3)]$ ($R = Ph$, $4\text{-}C_6H_4Cl$, $4\text{-}C_6H_4OMe$),[184] $[RuCl({=}CHPh)(\eta^5\text{-}C_5R_5)(PPh_3)]$ ($R = H$, Me),[184] $[RuCl({=}CHSiMe_3)Cp(PPh_3)]$,[184] $[Ru({=}CPh_2)Cp(CO)(PPh_3)][X]$ ($X = AlCl_4$, $PF_6{}^*$),[184] and $[RuCl\{{=}C(COPh)Ph\}Cp(PPh_3)]^*$.[184] Furthermore, $[RuCl\{{=}CH(CO_2Et)\}Cp(PPh_3)]$ has been generated *in situ* by reacting $[Ru\{\kappa^2(O,O)\text{-}O_2CMe\}Cp(PPh_3)]$ with ethyl diazoacetate in the presence of Me_2SiCl_2 and characterized by NMR spectroscopy.[185] Some of these alkylidenes have been tested as catalysts for olefin-cyclopropanation reactions.

Ethyl diazoacetate is also the source of the doubly α,β-unsaturated oxygen-containing alkylidene **169***, which is generated from the 1,3-addition of the organic reagent at the C_α–C_β double bond of the allenylidene chain of $[Ru({=}C{=}C{=}CPh_2)Cp(CO)(PPr^i_3)][BF_4]$ (Scheme 12). Structural parameters arising from the X-ray data indicate however that the contribution of the alkenyl resonance form **170** is dominant. Related methyl- and hydroxo-substituted alkylidenes **171*** and **172**, respectively, could be obtained using **169** as precursor.[186]

A number of α,β-unsaturated ruthenium and osmium alkylidenes have also been proposed as intermediate species in a series of catalytic processes involving diazo derivatives as substrates.[187,187a–187e]

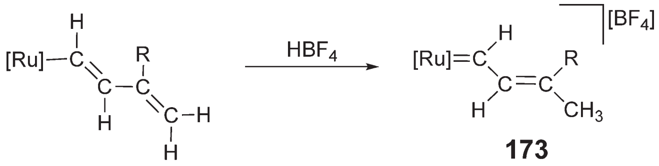
The complex $[Os({=}CH_2)Cp^*(dppm)][OTf]^*$ containing the simplest alkylidene, a terminal methylidene $={CH_2}$, is also known. It has been obtained by the treatment of $[OsHCp^*(dppm)]$ with 2 equiv. of MeOTf in pentane at RT. The ^1H NMR spectrum at −30 °C shows that the two hydrogen atoms of the methylidene group are inequivalent, which is in accord with a preferred orientation of the methylidene ligand locating one of the hydrogen atoms closer to, and the other distal from, the Cp^* ring.[188]

Another direct route to prepare alkylidene complexes relies on the marked nucleophilic character of the C_β-atom of an alkenyl group, which therefore is prone to undergo electrophilic additions: $[M]\text{–}CH{=}CR_2 + E^+ \rightarrow [M]^+{=}CH\text{–}C(E)R_2$. This synthetic methodology provides an alternative procedure to the diazo route which is especially useful



Scheme 12

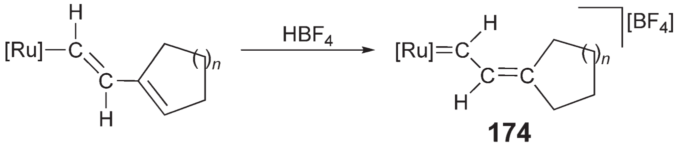
when this reagent is not readily available. This is the case for complex $[Os\{=CH(CH_2Ph)\}Cp\{P(OMe)_3\}(PPr^i{}_3)][BF_4]$ obtained by treatment of the alkenyl derivative $[Os(CH=CHPh)CpP(OMe)_3(PPr^i{}_3)]$ with HBF_4.[39] Starting from precursors containing unsaturated alkenyl groups, a series of cationic α,β-unsaturated ruthenium alkylidenes has also been synthesized, including the alkenyl alkylidenes **173** and **174**,[48,49] and the alkynyl alkylidenes **175**[50,86] (Equations (11)–(13)). Although the presence of unsaturated alkylidene groups in these complexes resembles some of the Grubbs-type catalysts, that is, $[Ru(=CH–CH=CPh_2)Cl_2(PPh_3)_2]$, their catalytic properties have not been studied. It has only been reported that indenyl–ruthenium(II) complexes **174** are not active in ring-closing metathesis (RCM) of diethyl diallylmalonate.[48]



173

[Ru] = [Ru(η^5-C_9H_7)(dppm)]; R = H, Me

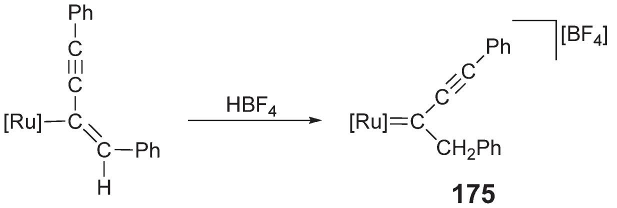
(11)



174

(12)

[Ru] = [Ru(η^5-C_9H_7)(dppm)]; *n* = 1, 2, 3
[Ru] = [Ru(η^5-C_9H_7){(*S*)-$(Ph_2P)_2$NCHMePh}]; *n* = 1, 3, 4

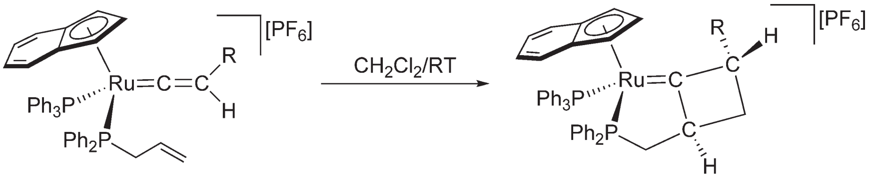


175

[Ru] = [Ru(η^5-C$_9$H$_7$)(dppm)]*
[Ru] = [RuCp(CO)(PPr$^i_3$)]*

(13)

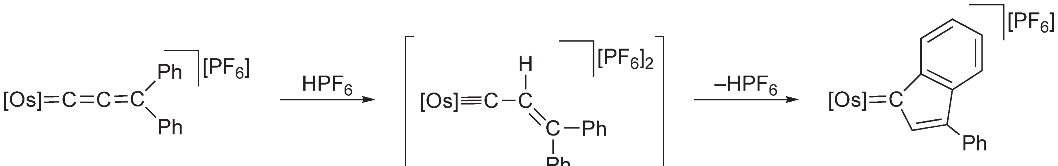
The isolation and characterization of the unusual bicyclic cyclobutylidene–ruthenium(II) complexes **176** have been described (Equation (14)). These alkylidenes have been generated via an intramolecular and diastereoselective [2 + 2]-cycloaddition of the vinylidene $C_\alpha{=}C_\beta$ bond with the allyl group of the coordinated allyl phosphine $\kappa^1(P)$-$Ph_2PCH_2CH{=}CH_2$. It is remarkable that the [2 + 2]-cycloaddition process proceeds under mild thermal conditions (RT).[189,189a]



176: R = Ph*, 4-C$_6$H$_4$Me

(14)

Seeking to prepare the carbyne–osmium complex **177** by protonation of the allenylidene derivative [Os(=C=C=CPh$_2$)Cp(CO)(PPr$^i_3$)][PF$_6$], two rotamers of the osmium α,β-unsaturated alkylidene **178**, bearing the 3-phenyl-1-indenylidene unit, are formed (Equation (15)).[79] The reaction proceeds through carbyne **177**, which readily isomerizes into **178** through a formal electrophilic substitution of an *ortho*-proton of one of the phenyl groups by the C_α-atom of the alkenylcarbyne moiety with concomitant elimination of HPF$_6$. An analogous (η^6-*p*-cymene)–ruthenium derivative is known, but in contrast to the osmium derivatives **178**, which are isolated as air-stable solids, it decomposes at RT (see Section 6.15.3.5). It is worth mentioning that a wide series of five-coordinate 16-electron ruthenium(II) 3-phenyl-1-indenylidene complexes has also been reported (see Chapter 6.12).



[Os] = [OsCp(CO)(PPr$^i_3$)]

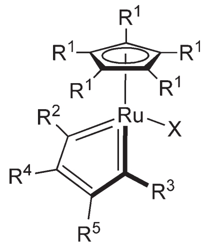
177

178*
Two rotamers

(15)

6.15.2.6.2 Bis-alkylidenes (Metallacyclopentatrienes)

Only the bis-alkylidene ruthenium complexes **179**,*[190,190a,190b] **180**,*[191] **181**,*[192] and **182***[193] are known to date (Figure 24). They are prepared by reaction of [RuClCp*(COD)] or [RuBrCp(COD)] with the corresponding terminal alkyne via a head-to-head oxidative coupling of two molecules of the alkyne. In general, the formation of these derivatives proceeds in THF, benzene, or CH$_2$Cl$_2$ at 0–20 °C in a few hours. A longer time (4 days) is used to form the bis-carbene **182** from the appropriate 1,6-diyne bearing phenyl terminal groups. These bis-alkylidenes have been fully characterized, including NMR spectroscopy and X-ray crystallography. The main structural features are: (i) the typical low-field carbon resonance in the $^{13}C\{^1H\}$ NMR spectra of the carbenic carbon atoms (ca. 245–270 ppm), (ii) the relatively short Ru–C distances (ca. 1.94–1.99 Å) indicative of partial double-bond character, and (iii) the almost identical C–C bond lengths within the ruthenacycle. These facts indicate that the metallacyclopentatriene unit has a highly delocalized structure which can be described as the contribution of two resonance forms. The electronic structure and the geometrical features of the model [RuClCp(C$_4$H$_4$)] have been theoretically studied.[194,194a] Note that related species formulated as metallacyclopentadienes (**85** in Figure 16), instead of metallacyclopentatrienes, are known (see



179*: $R^1 = Me$; $R^2 = R^3 = Ph$; $R^4 = R^5 = H$; X = Cl
180*: $R^1 = Me$; $R^2 = R^3 = 4\text{-}C_6H_4Br$; $R^4 = R^5 = H$; X = Cl
181*: $R^1 = H$; $R^2 = R^3 = Fc$; $R^4 = R^5 = H$; X = Br
182*: $R^1 = Me$; $R^2 = R^3 = Ph$; $R^4R^5 = -CH_2OCH_2-$; X = Cl

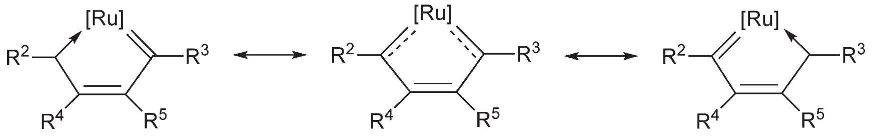


Figure 24 The bis-alkylidene ruthenium complexes **179–182**.

Section 6.15.2.3). A number of unsaturated bis-alkylidene complexes have been also proposed as intermediates either in stoichiometric processes or catalytic cyclotrimerization of alkynes to give substituted arenes.[193,194a]

6.15.2.6.3 Polyhapto alkylidenes

The presence of both an unsaturated chain as substituent of the alkylidene moiety and potential free coordination sites in the metal fragment enables the formation of a series of complexes in which the unsaturated chain is attached to the metal center. The following types of these polyhapto coordination modes are known (Figure 25): η^1:η^3-allyl carbenes **I**, η^1:η^2-butadienyl carbenes **II**, and η^1:η^2-allenyl carbenes **III**.

In a series of elegant reports, Kirchner and co-workers have developed a systematic synthetic route to allyl, butadienyl, and allenyl carbenes from the reactions of the readily accessible labile complexes $[RuCp(PR_3)(NCMe)_2][PF_6]$ with a wide range of alkynes, including terminal $HC\equiv CR^1$ and internal $R^1C\equiv CR^2$ alkynes and diynes $R^1C\equiv CCH_2(CH_2)_nCH_2C\equiv CR^1$ ($n = 1, 2$). This chemistry has been reviewed recently.[195] The reactions generally proceed rapidly at RT and the carbenes are obtained in good yields. Scheme 13 collects the synthesis of allyl carbenes **185 and 186**.[57,196–199]

Structural parameters obtained from X-ray diffraction studies of several of these complexes confirm both the alkylidene carbon double bond to the ruthenium atom and the presence of an η^3-allyl system. The four carbon atoms of the allyl carbene chain are nearly in a plane. Although no intermediates have been isolated, it is proposed on the basis of NMR data that the formation of these carbene complexes most probably proceeds via the ruthenacyclopentatriene transient species **183 and 184** generated from the oxidative head-to-tail coupling of the alkynes (see Section 6.15.2.6.2), which undergo a subsequent intramolecular migration of the phosphine to one of the electrophilic carbene carbon atoms. The remarkable electrophilicity of the C_α-atom promotes the ready rearrangement. Analogous Cp^*Ru allyl carbenes **187 and 188** have also been synthesized (Figure 26).[45,191] These allyl carbenes show a versatile reactivity including the addition of PPh_3 at the metal center, protonation at the carbenic carbon atom, as well as dehydrogenation of aryl or alkyl groups and of a Cp^* ring through C–H bond activation.

Competitive processes leading to the formation of η^1:η^2-butadienyl–carbene complexes instead of the expected η^1:η^3-allyl carbenes can be operative. These processes are the result of a preferred 1,2-hydrogen shift pathway versus ligand migration (Figure 27), which is favored due to the presence of either: (i) a too bulky and/or nucleophilic, poor co-ligand ($AsPh_3$; $SbR_3 = SbPh_3$, $SbBu^n{}_3$; $PR_3 = PCy_3$, PPh_3) or (ii) an alkyne with an α-alkyl substituent.[30,56,197,198,200]

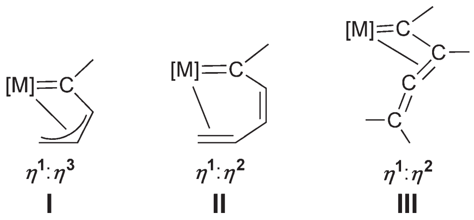
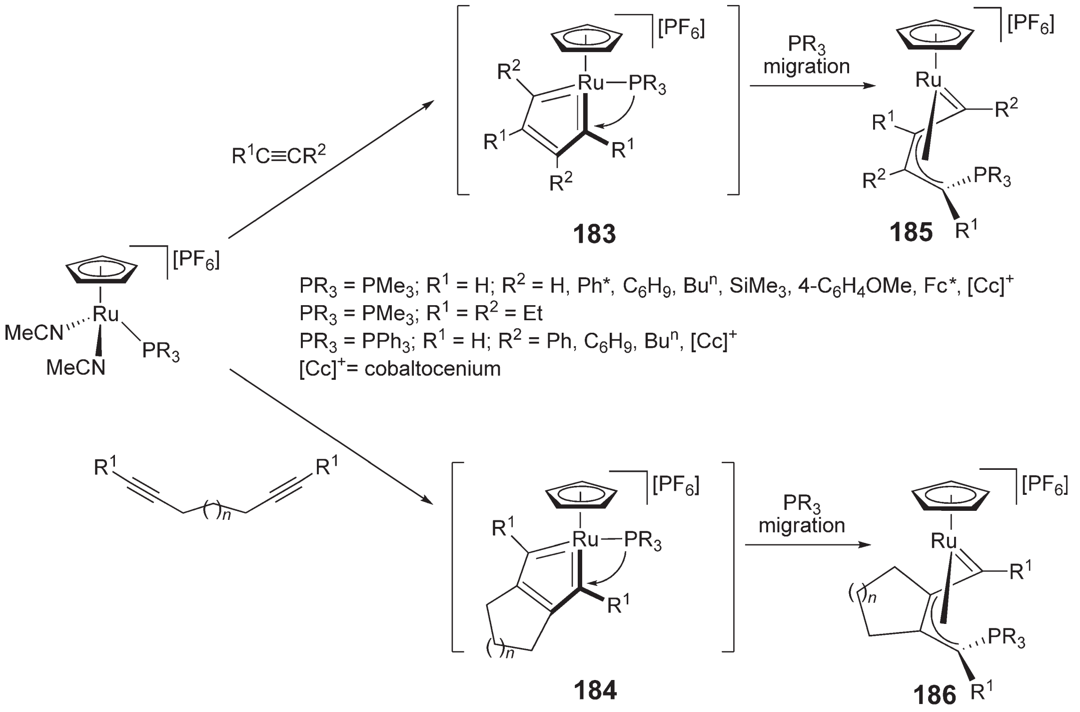


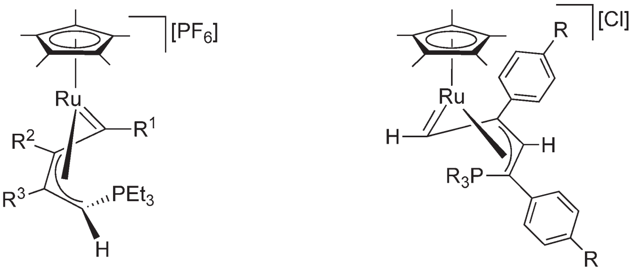
Figure 25 Coordination modes of polyhapto alkylidenes.



$PR_3 = PMe_3$; $R^1 = H$; $R^2 = H, Ph^*, C_6H_9, Bu^n, SiMe_3, 4\text{-}C_6H_4OMe, Fc^*, [Cc]^+$
$PR_3 = PMe_3$; $R^1 = R^2 = Et$
$PR_3 = PPh_3$; $R^1 = H$; $R^2 = Ph, C_6H_9, Bu^n, [Cc]^+$
$[Cc]^+$= cobaltocenium

$PR_3 = PMe_3$; $R^1 = H$; $n = 1^*, 2$
$PR_3 = PMe_3$; $R^1 = Me$; $n = 1, 2$
$PR_3 = PPh_3$; $R^1 = H, Me^*$; $n = 1$
$PR_3 = PCy_3$; $R^1 = H, Me^*$; $n = 1$

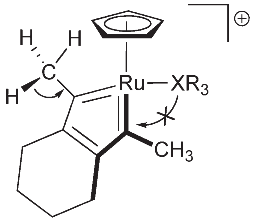
Scheme 13



$R^1 = R^3 = CO_2Me, {}^nBu$; $R^2 = H$
$R^1 = H$; $R^2R^3 = –CH_2CH_2CH_2–$
187

$PR_3 = PMe_3$; $R = H^*, Br$
$PR_3 = PO(OMe)_2$; $R = Br^*$
188

Figure 26 The allyl-carbene ruthenium complexes **187** and **188**.

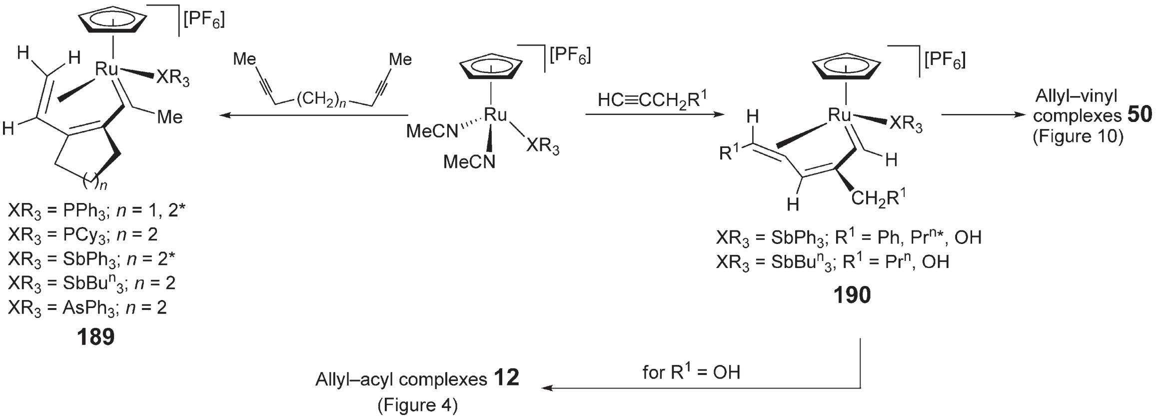


X = P, As, Sb
[1,2]-H shift

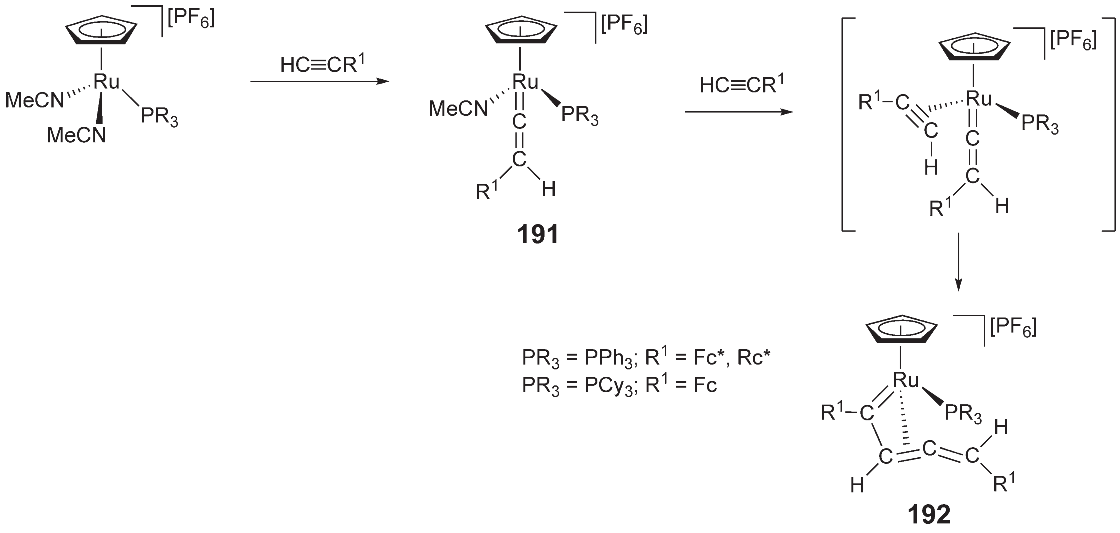
Figure 27 The competitive [1,2]-H shift.

The reactions of $[RuCp(XR_3)(NCMe)_2][PF_6]$ with 2,7-nonadiyne, 2,8-decadiyne, and $HC{\equiv}CCH_2R^1$ ($R^1 = Pr^n$, Ph, OH) illustrate the formation of η^1:η^2-butadienyl carbenes **189** and **190** (Scheme 14).[30,56,197,198] For $HC{\equiv}CCH_2R^1$ ($R^1 = Pr^n$, Ph, OH), the butadienyl–carbene group in **190** rearranges to give η^3-allyl–acyl (**12**; Figure 14) and η^3-allyl–vinyl (**50**; Figure 10) complexes.[30,56] A series of theoretical studies rationalizing the mechanisms of the competitive processes has also been performed.[30,198,200]

In contrast, the reactions of $[RuCp(PR_3)(NCMe)_2][PF_6]$ with the terminal alkynes ethynylferrocene (HC≡CFc) and ethynylruthenocene (HC≡CRc) proceed in a completely different way, affording η^1:η^2-allenyl–alkylidene complexes **192** (Scheme 15).[196,198] The proposed mechanism involves the intermediate formation of a vinylidene complex **191** followed by the coordination of a second alkyne molecule to give an η^2-alkyne–vinylidene species $[Ru\{{=}C{=}C(H)R^1\}Cp(\eta^2\text{-}HC{\equiv}CR^1)(PR_3)][PF_6]$. The subsequent alkyne insertion into the Ru═C bond gives the final product **192**. The observed π-conjugation of the allenyl–carbene unit with one of the Cp π-systems in the ferrocenyl and ruthenocenyl moieties likely favors the C–C coupling through the efficient stabilization of the positive charge. When $HC{\equiv}CSiMe_3$ is used, only the formation of vinylidene complexes $[Ru\{{=}C{=}C(H)SiMe_3\}Cp(NCMe)(PR_3)][PF_6]$ ($PR_3 = PPh_3$, PCy_3) is observed.[198]



Scheme 14



Scheme 15

6.15.2.7 Complexes Containing *N*-heterocyclic Carbenes (NHCs)

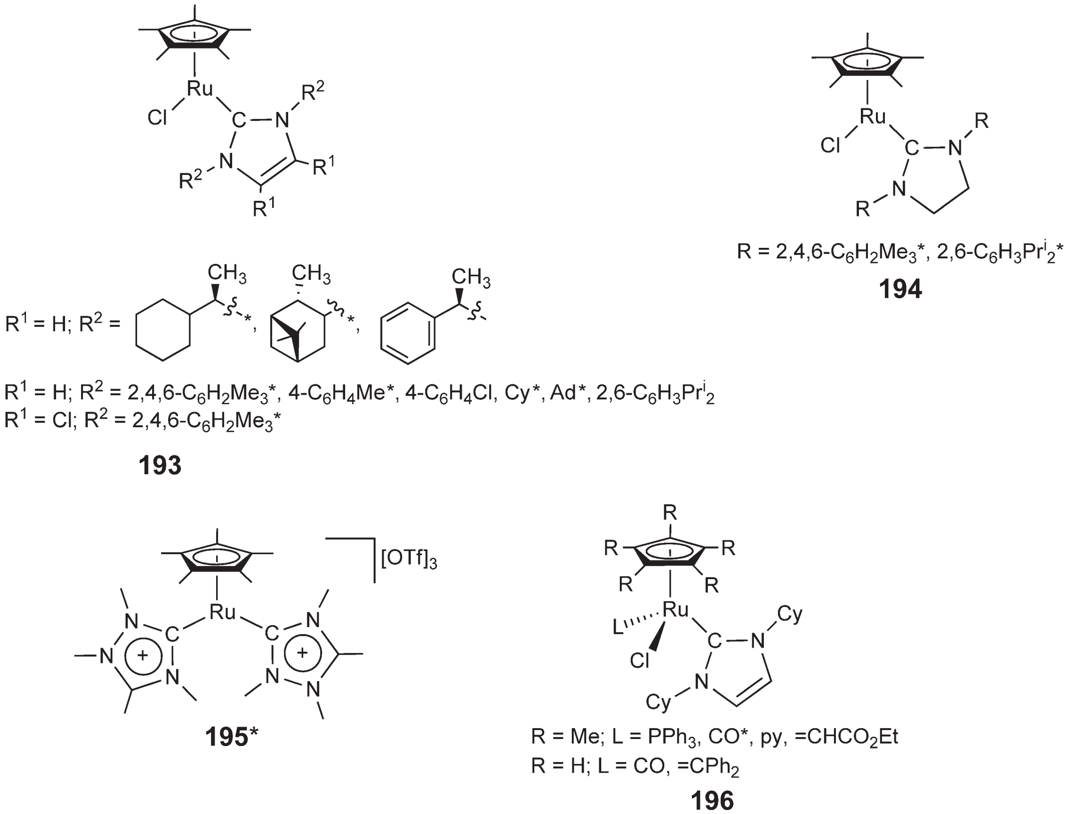
Nucleophilic *N*-heterocyclic carbenes (NHCs) are very attractive alternatives to basic phosphine ligands. The use of these carbenes in organometallic catalytic systems has continuously increased mainly due to their greater thermal stability, which usually leads to an improved catalytic performance. The catalytic activity in olefin-metathesis reactions of 16-electron ruthenium five-coordinate complexes containing NHCs $[RuCl_2\{{=}C(H)R\}(PCy_3)(NHC)]$ (Grubbs' second-generation catalysts) has triggered the popularity of these ligands in organometallic chemistry. In contrast to the large number of five-coordinate ruthenium complexes known to date, only a few half-sandwich derivatives have been reported (no osmium representatives are known). They belong to two types (see Figure 28).

(i) 16-Electron derivatives $[RuCp^*Cl(NHC)]$ (NHC = imidazol-2-ylidenes **193** or 4,5-dihydroimidazol-2-ylidenes **194**) prepared by treatment of $\{RuCp^*Cl\}_4$ with 4 equiv. of the appropriate NHC ligand (all of them containing bulky and/or chiral substituents). Single crystal X-ray structural determinations and thermochemical studies have been performed which shed light on the electron donor properties as well as the steric parameters associated with these ligands.[201–204] The tricationic bis-carbene complex **195*** is also known.[205]

(ii) 18-Electron cyclopentadienyl neutral complexes of formula $[RuCl(\eta^5\text{-}C_5R_5)L(NHC)]$ **196** obtained from $[RuCl(\eta^5\text{-}C_5R_5)L(PR_3)]$ through exchange reactions of PR_3 with the free carbene ligand.[206]

6.15.2.8 Vinylidene Complexes

The most general route to generate vinylidene complexes $[M]{=}C{=}C(H)R$ is the direct activation of terminal alkynes $HC{\equiv}CR$ by a coordinatively unsaturated transition metal complex, via the generation of unstable η^2-alkyne or hydride–alkynyl intermediates which tautomerize into the thermodynamically more stable vinylidene isomers (Scheme 16).[1a,1c,207] Several theoretical and kinetic studies on the metal-mediated alkyne–vinylidene isomerization have been published, all of them being summarized in a recent review.[208]



R^1 = H; R^2 =

R^1 = H; R^2 = 2,4,6-$C_6H_2Me_3$*, 4-C_6H_4Me*, 4-C_6H_4Cl, Cy*, Ad*, 2,6-$C_6H_3Pr^i_2$
R^1 = Cl; R^2 = 2,4,6-$C_6H_2Me_3$*

193

R = 2,4,6-$C_6H_2Me_3$*, 2,6-$C_6H_3Pr^i_2$*

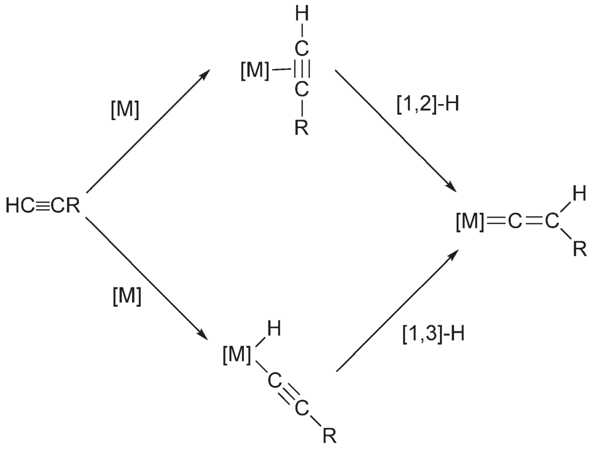
194

195*

R = Me; L = PPh_3, CO*, py, =$CHCO_2Et$
R = H; L = CO, =CPh_2

196

Figure 28 Cp– and Cp*–ruthenium complexes containing NHC ligands.



Scheme 16

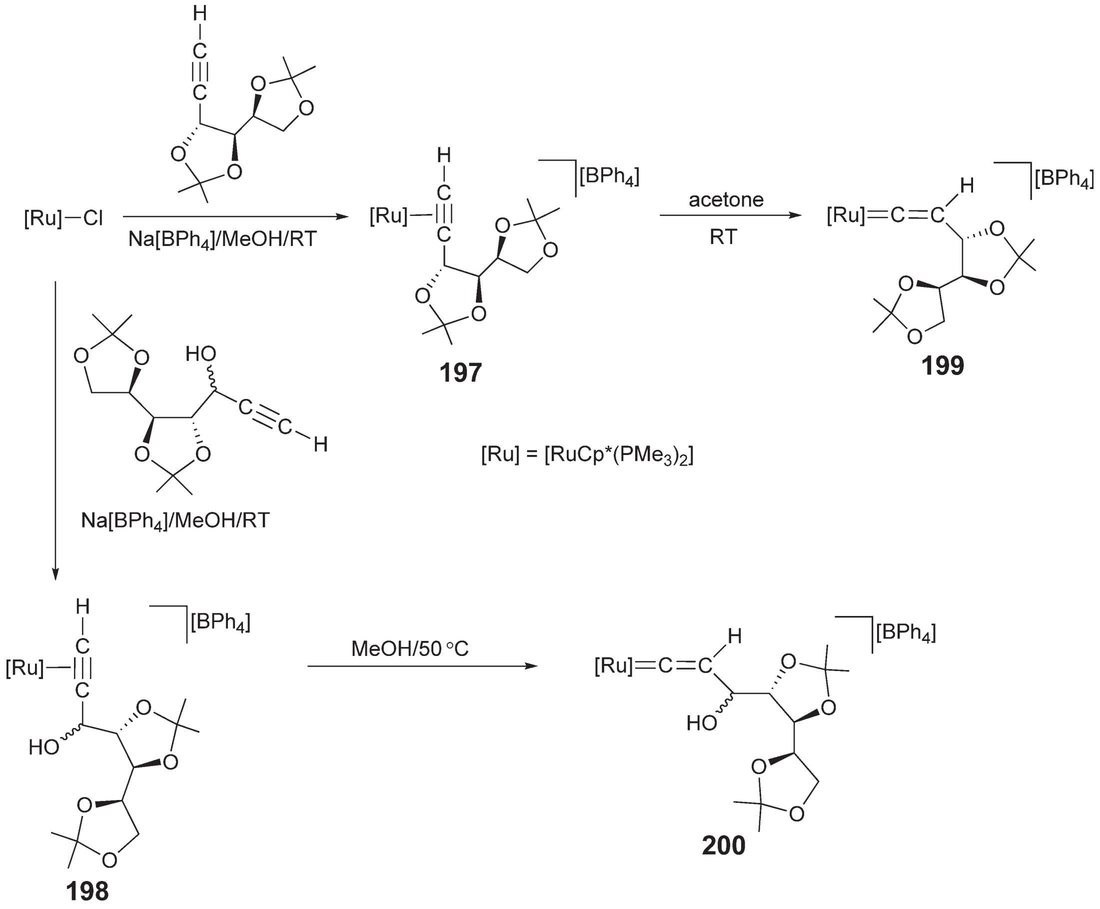
6.15.2.8.1 Simple vinylidenes

Following former synthetic approaches, halide complexes have continued to be used as suitable precursors for the activation of terminal alkynes.[1a,1c,207] The generation of a free coordination site on the metal can be easily achieved upon treatment with a halide abstractor (sodium or silver salts). Following this synthetic approach, the following novel monosubstituted cationic vinylidenes have been synthesized:

(i) Cyclopentadienyl–ruthenium(II) complexes [Ru{=C=C(H)R^2}(η^5-C$_5$R$^1_5$)(L^1)(L^2)][X] (R^1 = Me, L^1 = L^2 = PPh$_3$, R^2 = CO$_2$Me, X = PF$_6$*; R^1 = Me, L^1 = L^2 = PEt$_3$, R^2 = Ph, CO$_2$Me*, Bu^t, X = BPh$_4$; R^1 = Me, L^1 = L^2 = PMePr$^i_2$, R^2 = Ph, SiMe$_3$*, X = BAr$^F_4$; R^1 = Me, L^1 = L^2 = PMe$_2$Ph, R^2 = Ph, X = PF$_6$; R^1 = Me, L^{1}L^2 = dippe, R^2 = Ph, SiMe$_3$, CO$_2$Me*, Bu^t, X = BPh$_4$; R^1 = Me, L^1 = CO, L^2 = PMePr$^i_2$, R^2 = Ph, Bu^{t*}, X = BAr$^F_4$; R^1 = H, L^1 = L^2 = PPh$_3$, R^2 = 4-C$_6$H$_4$F, 4-C$_6$H$_4$Me, 4-C$_6$H$_4$OMe, Pent^n, Hex^n, Bu^t, X = PF$_6$; R^1 = H, L^1 = L^2 = PPh$_3$, R^2 = 4-C$_6$H$_4$CH$_2$CHNHCO$_2$Bu^t, X = BF$_4$; R^1 = H, L^{1}L^2 = dippe, R^2 = Ph, CO$_2$Me, Bu^t, X = BPh$_4$),[73,110,111,111a,113,122,123,209,210] [Ru{=C=C(H)R}{η^5:κ^2(P,P)-C$_5$H$_4$CH$_2$CMe(CH$_2$PPh$_2$)$_2$}][PF$_6$] (R = Bu^{t*}, Ph),[114] and [Ru{=C=C(H)Ph}{η^5:κ^1(P)-(S,S)-C$_5$H$_4$CHMe-2-FcPPh$_2$}(PPh$_3$)][PF$_6$]*.[211] Vinylidenes **199 and 200**, containing protected polyhydroxylated substituents derived from D-xylose, have been also obtained by activation of the appropriate terminal alkyne with [RuClCp*(PMe$_3$)$_2$] (Scheme 17). These species represent a new class of precursors for water-soluble unsaturated carbenes via deprotection of the diacetonide groups. The π-alkyne intermediate complexes **197 and 198** could be isolated and characterized.[212] In contrast, the reactions of pyridyl-functionalized alkynes HC≡C–X–C$_5$H$_4$N (X = –4-C$_6$H$_4$C≡C–, –4-C$_6$H$_4$-(E)-CH=CH–) with [RuClCp(PPh$_3$)$_2$], in the presence of [NH$_4$][PF$_6$], are not selective, affording mixtures of the expected vinylidenes [Ru{=C=C(H)–X–C$_5$H$_4$N}Cp(PPh$_3$)$_2$][PF$_6$] and the acetylide–pyridinium derivatives [Ru(C≡C–X–C$_5$H$_4$NH)Cp(PPh$_3$)$_2$][PF$_6$] (when 4-ethynylpyridine is used, the corresponding acetylide–pyridinium salt is exclusively formed). Selective vinylidene formation can be induced if the pyridyl nitrogen atom is protonated or methylated. In this way, the dicationic vinylidenes [Ru{=C=C(H)C$_5$H$_4$NR}Cp(PPh$_3$)$_2$][PF$_6$]$_2$ (R = H, Me) and [Ru{=C=C(H)-4-C$_6$H$_4$-(E)-CH=CH–C$_5$H$_4$NR}Cp(PPh$_3$)$_2$][PF$_6$]$_2$ (R = H, Me) have been synthesized and fully characterized.[154]

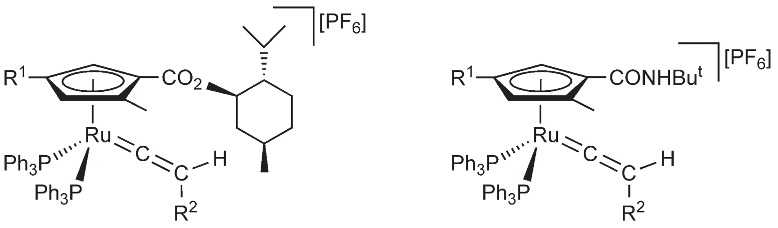
(ii) Indenyl–ruthenium(II) complexes [Ru{=C=C(H)R}(η^5-C$_9$H$_7$)(L^1)(L^2)][PF$_6$] (L^1 = L^2 = PPh$_3$, R = Ph, Bu^t, Pr^n, 4-C$_6$H$_4$NO$_2$, CH$_2$OH, (CH$_2$)$_4$OH, Fc; L^{1}L^2 = dppe, R = Ph, Bu^t, Pr^n, 4-C$_6$H$_4$NO$_2$; L^{1}L^2 = dppm, R = Ph, Bu^t, 4-C$_6$H$_4$NO$_2$; L^1 = L^2 = PMe$_2$Ph, R = (CH$_2$)$_4$OH; L^1 = PPh$_3$, L^2 = PMe$_3$, R = (CH$_2$)$_4$OH).[67,98,108,131,138,138a,169] In contrast to these results, the more electrophilic indenyl–Ru(II) precursors [RuX(η^5-1,2,3-C$_9$H$_4$R$_3$)(CO)(PR$_3$)][BF$_4$] (X = Br, R = Me, PR$_3$ = PPh$_3$, PPr$^i_3$; X = I, R = H, PR$_3$ = PPr$^i_3$) react with Ag[BF$_4$] and phenylacetylene, in dichloromethane at RT, to yield equilibrium mixtures containing the corresponding vinylidene and π-bonded alkyne complexes.[61] This behavior is in accord with theoretical calculations performed on the model complexes [Ru(=C=CH$_2$)(η^5-C$_9$H$_7$)(PH$_3$)(L)]$^+$ (L = CO, PH$_3$), which indicate that the lesser the electron density at the ruthenium atom, the more the tendency of η^1-vinylidene ligands to rearrange to η^2-alkyne ligands.[61]

(iii) Osmium(II) derivatives [Os{=C=C(H)Ph}(η^5-C$_5$H$_5$)(CO)(PPr$^i_3$)][BF$_4$],[213] [Os{=C=C(H)Ph}{η^5:κ^1(P)-C$_5$H$_4$-(CH$_2$)$_2$PPh$_2$}(PPr$^i_3$)][PF$_6$],[36] and [Os{=C=C(H)R}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Bu^{t*}, CH$_2$(CH$_2$)$_2$CH$_2$OH).[109,176]



Scheme 17

Complexes containing labile ligands have also been used as precursors of vinylidene derivatives. Thus, treatment of complexes $[RuCp(dppr)(NCMe)][PF_6]$ (dppr = 1,1′-bis(diphenylphosphino)ruthenocene) and $[Ru(OTf)Cp^*\{\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2\}]$ with phenylacetylene results in the immediate formation of $[Ru\{{=}C{=}C(H)Ph\}Cp(dppr)][PF_6]$ and $[Ru\{{=}C{=}C(H)Ph\}Cp^*\{\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2\}][OTf]^*$, respectively, via displacement of the acetonitrile and triflate ligands by the alkyne.[41,214] Following this synthetic approach, the enantiopure planar-chiral vinylidene complexes 201 and 202 have been synthesized from the appropriate acetonitrile precursors (Figure 29).[102] Taking advantage of the hemilabile properties of the $\kappa^3(P,C,C)$-coordinated diphenylvinylphosphine ligand, vinylidene complexes $[Ru\{{=}C{=}C(H)R\}Cp^*\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}_2][PF_6]$ ($R = H^*$, Ph, CH_2OH) have been prepared by reaction of $[RuCp^*\{\kappa^3(P,C,C)\text{-}Ph_2PCH{=}CH_2\}\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}][PF_6]$ with $HC{\equiv}CR$



R^1 = Me; R^2 = H, Ph
R^1 = Ph; R^2 = H, Ph
201

202: R^1 = Me; R^2 = H, Ph

Figure 29 Planar-chiral vinylidene Ru(II) and complexes **201** and **202**.

($R = SiMe_3$, Ph, CH_2OH).[167,215] In a similar way, the allyl derivative $[RuCp^*\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}][PF_6]$ reacts with phenylacetylene to afford $[Ru\{{=}C{=}C(H)Ph\}Cp^*\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}_2][PF_6]$.[168] Cleavage of the Ru–O bond by $HC{\equiv}CPh$ in complex $[RuCp^*\{\kappa^2(P,O)\text{-}P{\sim}O\}\{\kappa^1(P)\text{-}P{\sim}O\}][BPh_4]$, which contains the hemilabile ether–phosphine ligand (1,3-dioxan-2-ylmethyl)diphenylphosphine ($P{\sim}O$), leads to the cationic vinylidene $[Ru\{{=}C{=}C(H)Ph\}Cp^*\{\kappa^1(P)\text{-}P{\sim}O\}_2][BPh_4]$.[216]

Activation of $HC{\equiv}CSiMe_3$ by transition metal complexes represents the simplest route to generate unsubstituted vinylidene derivatives since the cleavage of the C–Si bond can be readily achieved in protic media.[207] Following this synthetic approach, the novel primary vinylidenes $[Ru({=}C{=}CH_2)(\eta^5\text{-}C_5R_5)(L^1)(L^2)][Y]$ ($R = Me$, $L^1 = L^2 = PMe_2Ph$, PPh_3^*, $Y = PF_6$; $R = Me$, $L^1L^2 = dppm^*$, $dppe^*$, $Y = PF_6$; $R = Me$, $L^1 = CO$, $L^2 = PMePr^i_2$, PPh_3^*, $Y = BAr^F_4$; $R = H$, $L^1L^2 = dippe$, $Y = BPh_4$),[110–113,117] $[Ru({=}C{=}CH_2)\{\eta^5{:}\kappa^2(P,P)\text{-}C_5H_4CH_2CMe(CH_2PPh_2)_2\}][PF_6]^*$,[114] and $[M({=}C{=}CH_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ ($M = Ru$, Os, $L^1 = L^2 = PPh_3$; $M = Ru$, $L^1L^2 = dppe$)[98,109] have been prepared starting from the appropriate chloride precursors. The 16-electron complex $[RuCp\{\kappa^2(N,N)\text{-}TMEDA\}][BAr^F_4]$ also reacts with $HC{\equiv}CSiMe_3$ in fluorobenzene to afford the stable silylated vinylidene $[Ru\{{=}C{=}CH(SiMe_3)\}Cp\{\kappa^2(N,N)\text{-}TMEDA\}][BAr^F_4]$, which can be converted into $[Ru({=}C{=}CH_2)Cp\{\kappa^2(N,N)\text{-}TMEDA\}][BAr^F_4]$ upon treatment with gaseous HCl at −100 °C (the formation of $[Ru\{{=}C{=}C(H)Ph\}Cp\{\kappa^2(N,N)\text{-}TMEDA\}][BAr^F_4]$ starting from $[RuCp\{\kappa^2(N,N)\text{-}TMEDA\}][BAr^F_4]$ and $HC{\equiv}CPh$ has also been reported).[217] In contrast, complexes $[Ru({=}C{=}CH_2)Cp^*(L^1)(L^2)][BPh_4]$ ($L^1 = L^2 = PEt_3^*$; $L^1L^2 = dippe$) have been obtained by direct reaction of the electron-rich precursors $[RuClCp^*(L^1)(L^2)]$ ($L^1 = L^2 = PEt_3$; $L^1L^2 = dippe$) with acetylene gas in the presence of $Na[BPh_4]$.[111,111a,122]

The regioselective addition of electrophiles to the nucleophilic β-carbon of neutral σ-alkynyl derivatives $[M]–C{\equiv}C–R$ is also a well-known route to produce cationic vinylidene complexes $[M]^+{=}C{=}C(H)R$.[207] In accord with this, complexes $[Ru\{{=}C{=}CH(4\text{-}C_6H_4C{\equiv}CH)\}Cp(PPh_3)_2][PF_6]$,[106] $[Ru\{{=}C{=}C(H)CMePh_2\}Cp(CO)(PPr^i_3)][BF_4]$,[86] $[Ru\{{=}C{=}C(H)CRPhCH_2C({=}O)Me\}Cp^*(dippe)][BF_4]$ ($R = H$, Ph),[136] $[Ru\{{=}C{=}C(H)R\}(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}][BF_4]$ ($R = Ph$, $4\text{-}C_6H_4Me$),[101] and $[Os\{{=}C{=}C(H)R\}Cp(PPr^i_3)_2][PF_6]$ ($R = Ph^*$, Cy)[125] have been readily synthesized by protonation of the corresponding alkynyls with HPF_6 or HBF_4. In a similar way, a large series of functionalized vinylidene derivatives containing the indenyl–ruthenium(II) fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ has been prepared through protonation (using HBF_4) of compounds **114–125** (see Figure 21 and associated references). Treatment of the amino allenylidene $[Ru\{{=}C{=}C{=}C(NEt_2)CMe{=}CPh_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ with HBF_4 leads to the dicationic vinylidene complex $[Ru\{{=}C{=}CHC({=}NEt_2)\text{-}CMe{=}CPh_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6,BF_4]$, corroborating the important contribution of the alkynyl resonance form $[Ru\{C{\equiv}CC({=}NEt_2)CMe{=}CPh_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ to the structure of the amino allenylidene.[137,137a]

Disubstituted vinylidene complexes $[Ru\{{=}C{=}C(Me)R\}(\eta^5\text{-}C_9H_7)(L^1)(L^2)][OTf]$ ($L^1 = L^2 = PPh_3$, $R = Ph$, Bu^t, Pr^n; $L^1L^2 = dppe$, $R = Ph$, Bu^t, Pr^n; $L^1L^2 = dppm$, $R = Ph$, Bu^t; $L^1 = PPh_3$, $L^2 = Ph_2PCH_2CH{=}CH_2$, $R = Ph$, $4\text{-}C_6H_4Me$) and $[Os\{{=}C{=}C(Me)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][OTf]$ have been prepared by methylation of the corresponding σ-alkynyl derivatives $[M(C{\equiv}CR)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ with methyl triflate in dichloromethane at RT.[67,98,101,109] In contrast, treatment of ethynyl complexes $[Ru(C{\equiv}CH)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$; $L^1L^2 = dppe$) with MeOTf leads to mixtures containing the dimethylvinylidenes $[Ru({=}C{=}CMe_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][OTf]$ ($L^1 = L^2 = PPh_3^*$; $L^1L^2 = dppe$) and the unsubstituted derivatives $[Ru({=}C{=}CH_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][OTf]$ ($L^1 = L^2 = PPh_3$; $L^1L^2 = dppe$).[98] Nevertheless, complexes $[Ru({=}C{=}CMe_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][OTf]$ ($L^1 = PPh_3$, $L^2 = PPh_3$, PMe_3; $L^1L^2 = dppe$) can be regioselectively obtained by reaction of the lithioalkynyl species $[Ru(C{\equiv}CLi)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (generated *in situ* from $[Ru(C{\equiv}CH)(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (see Section 6.15.2.4) with an excess of MeOTf.[107] The related methyl-substituted vinylidenes $[Ru\{{=}C{=}CMe(4\text{-}C_6H_4C{\equiv}CH)\}Cp(PPh_3)_2][OTf]$ and $[Ru\{{=}C{=}C(Me)R\}\{\eta^5{:}\kappa^2(P,P)\text{-}C_5H_4CH_2CMe(CH_2PPh_2)_2\}][OTf]$ ($R = Ph^*$, Bu^t) are also known.[106,114]

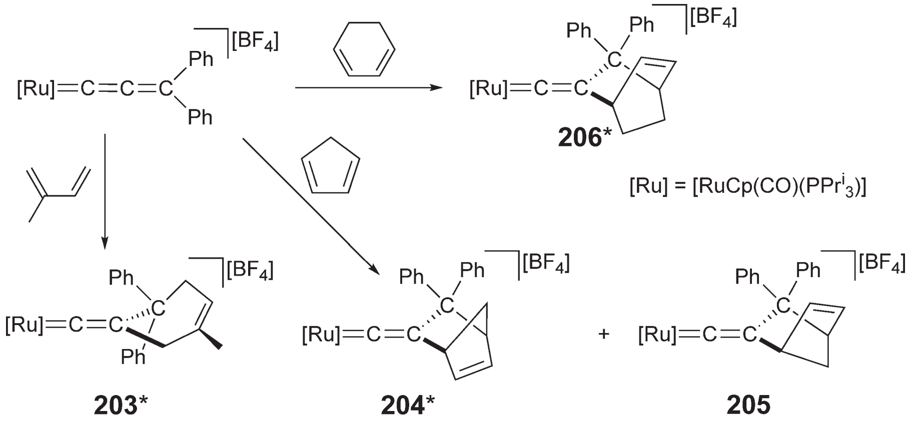
A number of cationic disubstituted vinylidenes of composition $[Ru\{{=}C{=}C(R)Ph\}Cp(L^1)(L^2)]^+$ ($L^1 = L^2 = PPh_3$, $R = CH_2CN$, CH_2Ph, CH_2CO_2Me, CH_2CO_2Et, CH_2OMe, $CH_2CH{=}CH_2$, $CH_2CH{=}CMe_2$; $L^1L^2 = dppe$, $R = CH_2CN$, CH_2CO_2Me, CH_2Ph, $CH_2C_6F_5$, $CH_2\text{-}4\text{-}C_6H_4CN$, $CH_2\text{-}4\text{-}C_6H_4CF_3$, CH_2-1-Napht; $L^1 = PPh_3$, $L^2 = P(OMe)_3$, $R = CH_2CN$) have been prepared from the electrophilic addition of organic halides RX to the phenylacetylide complexes $[Ru(C{\equiv}CPh)Cp(L^1)(L^2)]$ ($L^1 = L^2 = dppe$).[29,62,63] Most of these compounds have been isolated as the corresponding hexafluorophosphate salts after X^-/PF_6^- exchange using $[NH_4][PF_6]$. In a similar way, the alkynyl complexes $[Ru(C{\equiv}CHex^n)Cp(PPh_3)_2]$ and $[Ru(C{\equiv}CCO_2Me)Cp^*(PPh_3)_2]$ react with MeI or $PhCH_2Br$ to afford $[Ru\{{=}C{=}C(Me)Hex^n\}Cp(PPh_3)_2][PF_6]$ and $[Ru\{{=}C{=}C(CH_2Ph)CO_2Me\}Cp^*(PPh_3)_2]Br$, respectively.[73,209]

Reaction of $[RuClCp(PPh_3)_2]$ with $PhC{\equiv}CSePr^i$ and $Na[BPh_4]$ provides the selenatovinylidene complex $[Ru\{{=}C{=}C(SePr^i)Ph\}Cp(PPh_3)_2][BPh_4]$ through an unprecedented [1,2]-shift of the selenolate $SePr^i$ unit.[218] The related salt $[Ru\{{=}C{=}C(SePh)Ph\}Cp(PPh_3)_2][PF_6]$ is also known, being obtained by electrophilic addition of PhSeCl to $[Ru(C{\equiv}CPh)Cp(PPh_3)_2]$ and subsequent Cl^-/PF_6^- counteranion metathesis with $[NH_4][PF_6]$.[218] Treatment of this alkynyl complex with the appropriate aryldiazonium salt $[N{\equiv}NR][BF_4]$ generates the novel aryldiazovinylidene complexes $[Ru\{{=}C{=}C(N{=}NR)Ph\}Cp(PPh_3)_2][BF_4]$ (R = 3,5-$C_6H_3(NO_2)_2$, 2-$C_6H_4OMe^*$) whose second- and third-order NLO properties have been evaluated both in solution and in solid state.[219,219a]

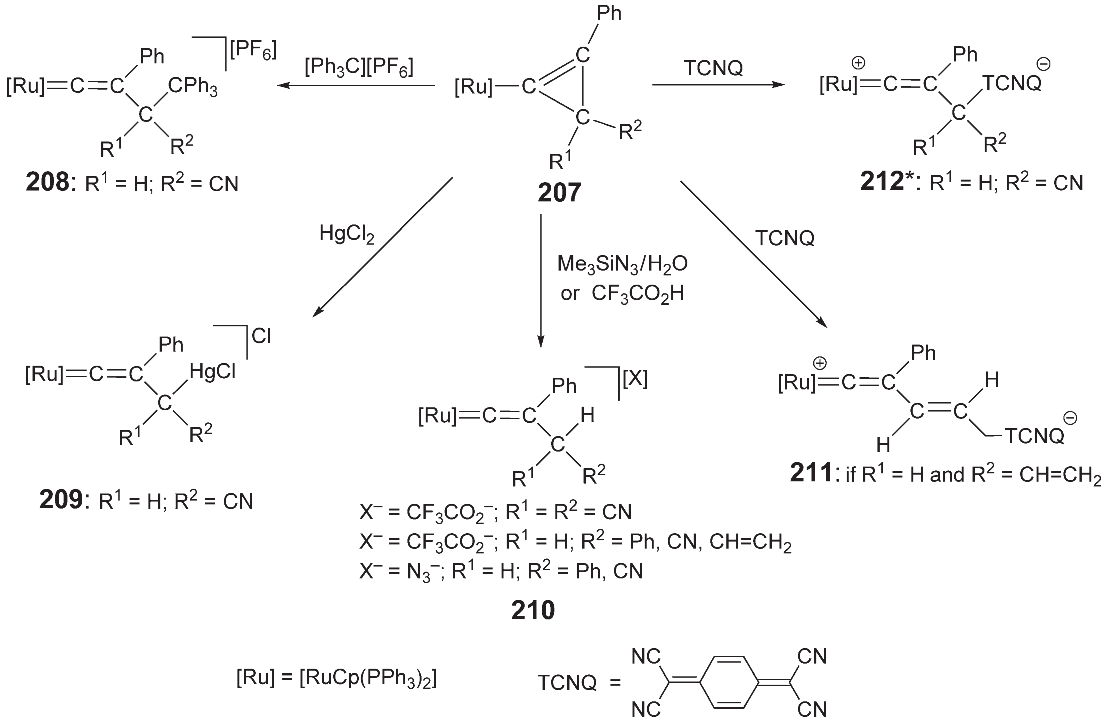
Activation of propargylic alcohols $HC{\equiv}CC(OH)HR$ (R = H, Me) by $[RuClCp^*(PMe_2Ph)_2]$, in methanol in the presence of $[NH_4][PF_6]$, has been reported to yield the vinylidene derivatives $[Ru\{{=}C{=}C(H)$-$CHR(OMe)\}Cp^*(PMe_2Ph)_2][PF_6]$ (R = H, Me^*), the reaction involving the addition of the O–H bond of methanol across the $C_\beta{=}C_\gamma$ double bond of highly unstable allenylidene intermediates $[Ru\{{=}C{=}C{=}C(H)R\}$-$Cp^*(PMe_2Ph)_2][PF_6]$.[110] The related methoxyvinylidene $[Ru\{{=}C{=}C(H)CHPh(OMe)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ is also readily formed when $[Ru\{{=}C{=}C{=}C(H)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ is dissolved in methanol.[108] The stable allenylidene complex $[Ru({=}C{=}C{=}CPh_2)Cp(CO)(PPr^i_3)][BF_4]$ reacts with isoprene, cyclopentadiene, and 1,3-cyclohexadiene to afford the disubstituted cationic vinylidenes **203–206**, as the result of the regioselective Diels–Alder addition of the dienes to the $C_\beta{=}C_\gamma$ bond of the cumulenic chain (Scheme 18). The reaction with isoprene is also regioselective with regard to the diene, affording complex **203*** exclusively. In addition, while the reaction with cyclopentadiene affords an equimolar mixture of diastereoisomers **204*** and **205**, the addition of 1,3-cyclohexadiene occurs with specific substrate orientation giving complex **206*** as a single diastereoisomer.[220] The addition of weakly nucleophilic reagents such as pyrazole, 3,5-dimethylpyrazole, or thiophenol to the $C_\beta{=}C_\gamma$ double bond of the secondary allenylidene $[Ru\{{=}C{=}C{=}C(H)Ph\}Cp^*(dippe)][BPh_4]$ has been reported to yield vinylidene complexes $[Ru({=}C{=}CHCHRPh)Cp^*(dippe)][BPh_4]$ (R = pyrazolyl, 3,5-dimethylpyrazolyl, phenylsulfanyl).[136] Related additions of pyrrole and 2-methylfuran takes place only in the presence of acid, suggesting the involvement of the dicationic alkenyl carbyne $[Ru({\equiv}CCH{=}CHPh)Cp^*(dippe)]^{2+}$ in these addition processes.

In the context of reactivity studies of cyclopropenyl–ruthenium(II) complexes **63–65** in (Figure 13), compounds **207** have also been used as starting materials for the preparation of vinylidenes **208–212** via electrophilic additions to the three-membered ring (Scheme 19; related reactions have also been reported for their dppe counterparts).[62,63,221,221a] In addition, the treatment of the four-membered cycloalkenyl–ruthenium complex **213** with organic halides has been reported to yield mixtures containing the disubstituted cationic vinylidenes **216 and 217** (Scheme 20). Formation of these complexes involves the initial transformation of **213** into the zwitterionic species **214 and 215**, via cleavage of the C–S bond of the four-membered ring, which undergo an alkylation process at the sulfur or nitrogen atom, respectively.[64,65]

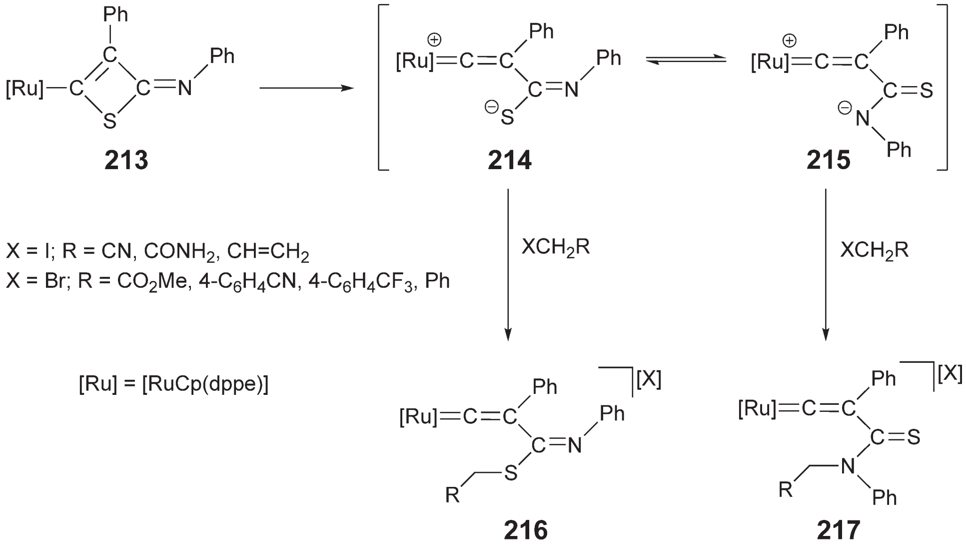
Although less numerous than their cationic counterparts, neutral (η^5-C_5)–Ru and –Os vinylidenes are also known. Thus, complexes $[RuCl\{{=}C{=}C(H)R\}Cp^*(PPh_3)]$ (R = Ph^*, Me, Bu^n, Bu^t, CO_2Me^*, $SiMe_3{}^*$) have been prepared by reacting $[RuClCp^*(PPh_3)_2]$ with the appropriate terminal alkyne under thermal conditions.[73,97,97a,115,222] In order to avoid the dissociation of the chloride ligand and therefore the formation of cationic species $[Ru\{{=}C{=}C(H)R\}Cp^*(PPh_3)_2]^+$, these reactions have been performed in non-polar solvents (benzene or THF). The substitution of the PPh_3 ligand by the incoming alkyne seems to be favored by the steric bulk of the Cp^* unit, since, under the same conditions, the formation of neutral vinylidenes from $[RuClCp(PPh_3)_2]$ has not been observed. Only when the bulkier phosphine $PPh_2(2\text{-}C_6H_4Me)$ was used as auxiliary ligand, that is, starting from complex $[RuClCp\{PPh_2(2\text{-}C_6H_4Me)\}_2]$, could the neutral vinylidene $[RuCl\{{=}C{=}C(H)Ph\}Cp\{PPh_2(2\text{-}C_6H_4Me)\}]$ be prepared.[164] The related complex $[Ru(OTf)\{{=}C{=}C(H)Ph\}Cp^*(PPh_3)]$ is also known, being obtained from $[RuCl\{{=}C{=}C(H)Ph\}Cp^*(PPh_3)]$ by metathesis of the chloride ligand with MeOTf.[222] Taking advantage of the



Scheme 18



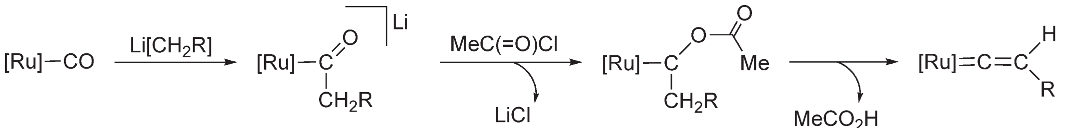
Scheme 19



Scheme 20

well-known ability of the allyl ligand to act as a leaving group in acidic media, the stepwise treatment of [Ru(η^3-2-C_3H_4Me)Cp(PPh_3)] and [Ru(η^3-2-C_3H_4Me)Cp*(PPh_3)] with HC≡CCO$_2$R and HCl leads to the formation of the neutral vinylidenes [RuCl{═C═C(H)CO$_2$Me}Cp(PPh_3)] and [RuCl{═C═C(H)CO$_2$R}Cp*(PPh_3)] (R = Me, Et), respectively.[184,223] Treatment of the hemilabile chelate complex [RuClCp*{κ^2(*P*,*O*)-Pr$^i_2$PCH$_2$C(═O)OMe}] with methyl propiolate or 1,1-diphenyl-2-propyn-1-ol results also in the formation of the neutral vinylidene derivatives [RuCl{═C═C(H)R}Cp*{κ^1(*P*)-Pr$^i_2$PCH$_2$C(═O)OMe}] (R = CO$_2$Me*, CPh$_2$OH).[224]

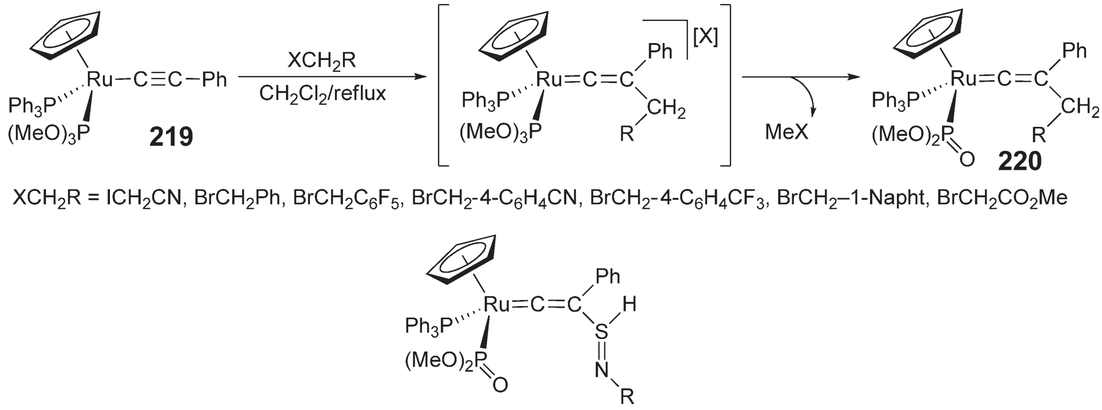
A one-pot but two-step method for the preparation of neutral monosubstituted vinylidenes [Ru{═C═C(H)R}(SnPh$_3$)Cp(CO)] 218 starting from the dicarbonyl compound [Ru(SnPh$_3$)Cp(CO)$_2$] is known



$[Ru] = [Ru(SnPh_3)Cp(CO)]$

218: R = H, Me, Ph, Pr^n

Scheme 21



XCH$_2$R = ICH$_2$CN, BrCH$_2$Ph, BrCH$_2$C$_6$F$_5$, BrCH$_2$-4-C$_6$H$_4$CN, BrCH$_2$-4-C$_6$H$_4$CF$_3$, BrCH$_2$–1-Napht, BrCH$_2$CO$_2$Me

221: R = Ph*, Bz

Scheme 22

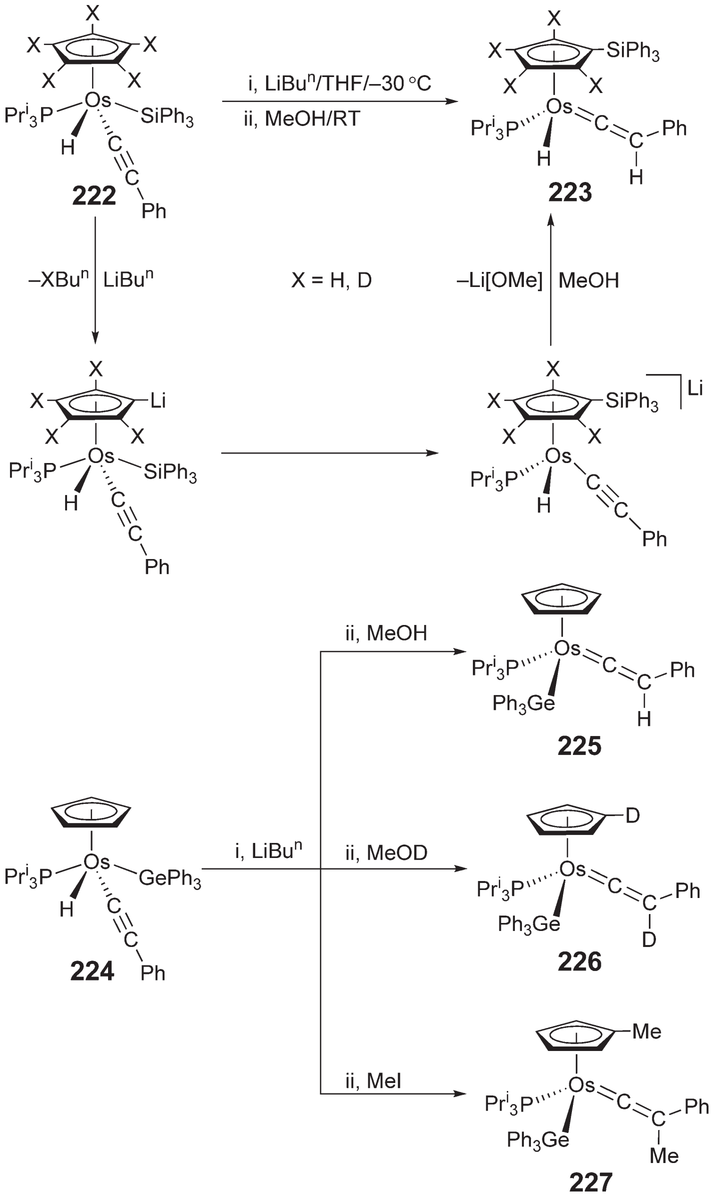
(Scheme 21). It involves the initial formation of anionic acyl complexes by addition of Li[CH$_2$R] reagents to the carbonyl ligand, which, by reaction with acetyl chloride, generate the vinylidenes via spontaneous loss of MeCO$_2$H from intermediate acyl(oxy) carbenes.[174]

Disubstituted neutral vinylidenes 220 have been prepared by reaction of the σ-alkynyl complex [Ru(C≡CPh)Cp(PPh$_3$){P(OMe)$_3$}] 219 with organic halides XCH$_2$R via electrophilic addition of the methylenic CH$_2$R unit to the C$_\beta$-atom of the phenylacetylide chain and subsequent Arbuzov-like dealkylation of the phosphite ligand (Scheme 22).[29] The formation of minor amounts of vinylidenes 221 in the reactions of 219 with isothiocyanates has also been reported.[70]

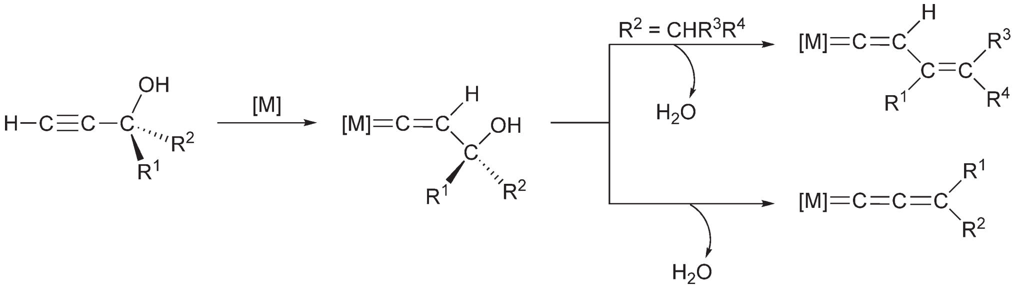
Taking advantage of the tendency shown by [OsClCp(PPr$^i_3$)$_2$] to release one of the phosphines, the neutral vinylidene–Os(II) complex [OsCl{=C=C(H)Ph}Cp(PPr$^i_3$)] has been prepared by treatment of [OsClCp(PPr$^i_3$)$_2$] with HC≡CPh in pentane at RT.[35] Treatment of tetrahydrofuran solutions of the hydride–alkynyl Os(IV) complexes 222 with 3 equiv. of LiBu^n leads to solutions that react with methanol to give the neutral vinylidene–osmium(II) derivatives 223 (Scheme 23).[40] Formation of these compounds involves: (i) initial single deprotonation of the cyclopentadienyl ring, (ii) subsequent migration of the silyl group from the Os atom to the cyclopentadienyl ligand, and (iii) final attack of the acidic proton of methanol at the C$_\beta$-atom of the alkynyl group. In agreement with this mechanism, the addition of methanol-d_4 to the solutions resulting from the treatment of 222 (X = H) with LiBu^n leads to the deuterated vinylidene [OsH{=C=C(D)Ph}(η^5-C$_5$H$_4$SiPh$_3$)(PPr$^i_3$)]. In contrast to these results, the treatment of THF solutions of the related germyl derivative 224 with 3 equiv. of LiBu^n leads to solutions that react with methanol, methanol-d_4, and methyl iodide to give Os(II)–vinylidenes 225, 226, and 227, respectively. Formation of 226 and 227 indicates that a double deprotonation of 224, at the metallic center and at the Cp ligand, takes place upon addition of LiBu^n. Furthermore, in contrast to 222, the deprotonation of the Cp ring of 224 does not give way to the migration of the germyl group from the osmium atom to the Cp ligand, in agreement with the higher thermodynamic stability of the Os–Ge bond in comparison with the Os–Si one.[40]

6.15.2.8.2 Alkenyl vinylidenes and related α,β-unsaturated vinylidenes

Activation of propargylic alcohols containing a C–H bond in β-position with respect to the OH group by a coordinatively unsaturated complex is probably the most general route for the preparation of alkenyl–vinylidene derivatives [M]=C=CHCR^1=CR^{3}R^4 (Scheme 24).[181] This process proceeds through the initial formation of an unstable hydroxy–vinylidene intermediate, which undergoes a spontaneous dehydration. In some cases, stable



Scheme 23

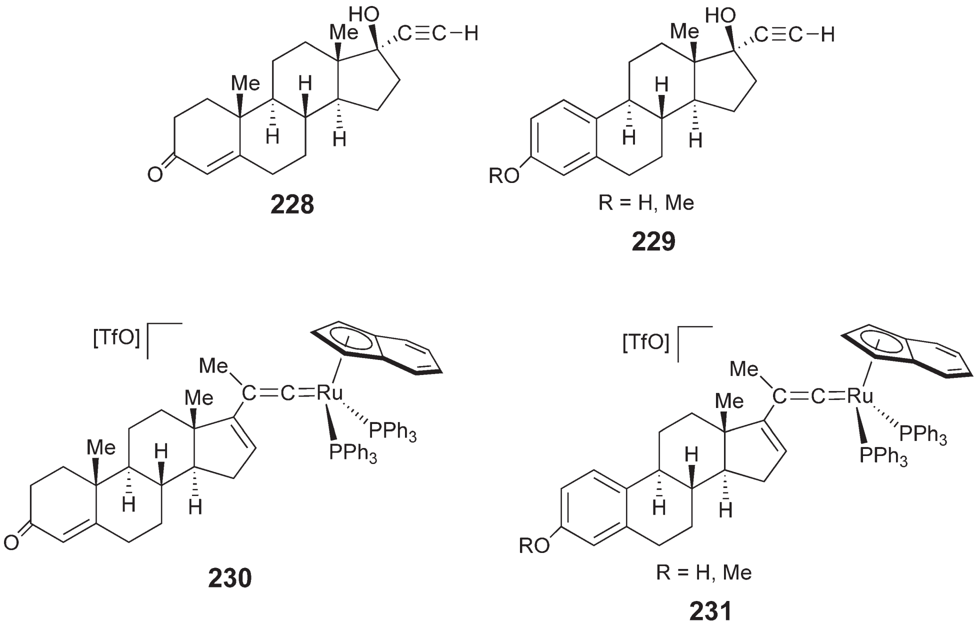


Scheme 24

hydroxy–vinylidene complexes could be isolated and fully characterized, that is, $[Ru\{=C=CHCR^1R^2(OH)\}Cp^*(L^1)(L^2)][X]$ ($L^1 = L^2 = PMe_2Ph$, $CR^1R^2 = CH_2$, $X = PF_6$; $L^1 = L^2 = PMePr^i_2$, $CR^1R^2 = CH_2$, CMe_2, CPh_2, CHMe, CHPh, CMePh, C_6H_{10}, $X = BAr^F_4$; $L^1 = L^2 = PEt_3$, $CR^1R^2 = CH_2$, CMe_2, CPh_2, CHMe, CHPh, CMePh, C_6H_{10}, $X = BPh_4$; L^1L^2 = dippe, $CR^1R^2 = CH_2$, CMe_2, CPh_2, CHMe, CHPh, $X = BPh_4$).[110,119,121,121a,123,143] It is interesting to note that although dehydration of the hydroxy–vinylidene intermediates can take two different reaction pathways, leading either to alkenyl–vinylidene or tautomeric allenylidene $[M]=C=C=CR^1R^2$ derivatives, in most cases, it affords vinylidenes regioselectively (the chemistry of allenylidene complexes will be discussed in Section 6.15.2.9).[181] A rationalization of this general behavior has been provided on the basis of theoretical calculations using the models $[Ru(=C=CHCH=CH_2)(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$ and $[Ru\{=C=C=C(H)CH_3\}(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$, which disclose that the alkenyl–vinylidene tautomer is ca. 2.1 kcal mol^{-1} more stable than the allenylidene.[144] Nevertheless, it should be noted that the fate of dehydration reaction strongly depends on the nature of the metal auxiliary as well as the propargylic alcohol substituents pointing out the limitations of this synthetic methodology.

Following this synthetic approach, the cationic alkenyl–vinylidene derivatives **136** (see Equation (8)) have been selectively synthesized through the activation of 1-ethynyl–1-cycloalkanols by the indenyl–chloride precursors $[MCl(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ (M = Ru, Os, $L^1 = L^2 = PPh_3$; M = Ru, L^1L^2 = dppe).[60,109,132,132a] The related species $[Ru(=C=CHC_6H_9)Cp^*(L^1)(L^2)][X]$ (C_6H_9 = 1-cyclohexenyl; $L^1 = L^2 = PPh_3$, $X = PF_6$; $L^1 = L^2 = PEt_3$, $X = BPh_4$; $L^1 = L^2 = PMePr^i_2$, $X = BAr^F_4$) and $[Ru(=C=CHCR=CH_2)Cp^*(L^1)(L^2)][X]$ ($L^1 = L^2 = PEt_3$, R = H, Ph^*, Me, $X = BPh_4$; $L^1 = L^2 = PMePr^i_2$, R = H, Me, $X = BAr^F_4$) have been similarly obtained.[121,121a,123,225] In contrast, mixtures of alkenyl–vinylidene $[Ru(=C=CHCPh=CH_2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ and allenylidene $[Ru(=C=C=CMePh)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ tautomers have been obtained by reacting complexes $[RuCl(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$ ($L^1 = L^2 = PPh_3$; L^1L^2 = dppe, dppm) with $HC\equiv CC(OH)MePh$.[108] Similar results have been observed in the activation of the biologically active propargylic alcohols ethisterone **228**, 17α-ethynylestradiol **229** (R = H), and mestranol **229** (R = Me) by $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (Figure 30).[144]

A large series of monosubstituted alkenyl– and polyalkenyl–vinylidene derivatives containing the $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ unit have been synthesized by protonation of the corresponding neutral enynyl or polyenynyl precursors **129–134** with HBF_4 (see Scheme 8 and associated references). Similarly, the cationic phosphonio–enynyl derivative $[Ru\{C\equiv CC(PPh_3)=CH_2\}Cp(PPh_3)_2][PF_6]$ undergoes C_β-protonation with HPF_6 to afford the dicationic species $[Ru\{=C=CHC(PPh_3)=CH_2\}Cp(PPh_3)_2][PF_6]_2$.[142,142a] Disubstituted alkenyl vinylidenes $[Ru\{=C=C(Me)C_6H_9\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][OTf]^*$ (C_6H_9 = 1-cyclohexenyl), **230**, and **231**, obtained by reacting the corresponding σ-enynyls with Me[OTf], have been described.[60,144] The reactions of $[Ru(C\equiv CPh)Cp(L^1)(L^2)]$



228

R = H, Me

229

230

R = H, Me

231

Figure 30 The structure of compounds **228**–**231**.

(L^1L^2 = dppe; $L^1 = PPh_3$, $L^2 = CNBu^t$) with Cl(Ph)C=C(CN)$_2$ to generate complexes [Ru{=C=CPh-CPh=C(CN)$_2$}Cp(L^1)(L^2)][PF$_6$] have also been reported.[29]

Treatment of the Os(II) precursor [OsClCp(PPr$^i_3$)$_2$] with 2-methyl-3-butyn-2-ol and 1-ethynylcyclohexanol in toluene at 85 °C results in the formation of the neutral alkenyl vinylidenes [OsCl{=C=C(H)R}Cp(PPr$^i_3$)] (R = CMe=CH$_2$, 1-cyclohexenyl) via release of PPr$^i_3$. Intermediate species containing these propargylic alcohols π-coordinated to osmium could be isolated working at RT.[35] The related allenyl vinylidene [OsCl{=C=C(CO$_2$Me)C-(CO$_2$Me)=C=CPh$_2$}Cp(PPr$^i_3$)] has been synthesized by reacting the neutral allenylidene derivative [OsCl(=C=C=CPh$_2$)Cp(PPr$^i_3$)] with dimethyl acetylenedicarboxylate. Formation of this compound involves the insertion of the alkyne into the C_α=C_β double bond of the cumulenic chain. Reduction of the C_β=C_γ double bond of this allenylidene, using Na[BH$_4$]/MeOH, has also been reported to yield [OsCl(=C=CHCHPh$_2$)Cp(PPr$^i_3$)].[226]

6.15.2.9 Allenylidene and Related Cumulenylidene Complexes

The simplest and most general synthetic approach to half-sandwich ruthenium complexes with an allenylidene ligand C=C=CR^{1}R^2, originally introduced by Selegue for the preparation of [Ru(=C=C=CPh$_2$)Cp(PMe$_3$)$_2$][PF$_6$],[227] consists of the formal dehydration of propargylic alcohols HC≡CCR^{1}R^2(OH) by treatment with an unsaturated metallic fragment (Scheme 24).[1] Following this route, several allenylidenes **232** have been prepared by reacting ethanolic solutions of [RuClCp(PMe$_3$)$_2$] with [NH$_4$][PF$_6$] and the appropriate propargylic alcohol (Figure 31).[228] Allenylidenes **232** have found to be active catalysts for the dehydrogenative dimerization of tin hydrides. In a similar way, the cationic species [Ru(=C=C=CPh$_2$)Cp(PPh$_3$)$_2$][PF$_6$],[134] [Ru{=C=C=C(R)Me}Cp(dippe)][BPh$_4$] (R = Me, Ph*),[143] and [Ru(=C=C=CPh$_2$){η^5:κ^2(*P*,*P*)-C$_5$H$_4$CH$_2$CMe(CH$_2$PPh$_2$)$_2$}][PF$_6$]*[114] have been generated by treatment of solutions containing the corresponding chloride precursor and propargylic alcohol with a halide abstractor. Strongly polarized allenylidene derivatives **233**, which show second-order NLO properties, have also been obtained, starting from [RuClCp(PPh$_3$)$_2$].[90] Treatment of [RuCp(acetone)(CO)(PPr$^i_3$)][BF$_4$] with 1,1-diphenyl-2-propyn-1-ol in dichloromethane generates the cationic diphenylallenylidene [Ru(=C=C=CPh$_2$)Cp(CO)(PPr$^i_3$)][BF$_4$] via displacement of the labile acetone ligand.[27] In accord with the hemilabile properties of the β-keto-phosphine ligand Ph$_2$PCH$_2$C(=O)Bu^t, the cyclopentadienyl complex [RuCp{κ^2(*P*,*O*)-Ph$_2$PCH$_2$C(=O)Bu^t}(PPh$_3$)][PF$_6$] easily reacts with HC≡CCPh$_2$(OH) to yield [Ru(=C=C=CPh$_2$)Cp{κ^1(*P*)-Ph$_2$PCH$_2$C(=O)Bu^t}(PPh$_3$)][PF$_6$].[87]

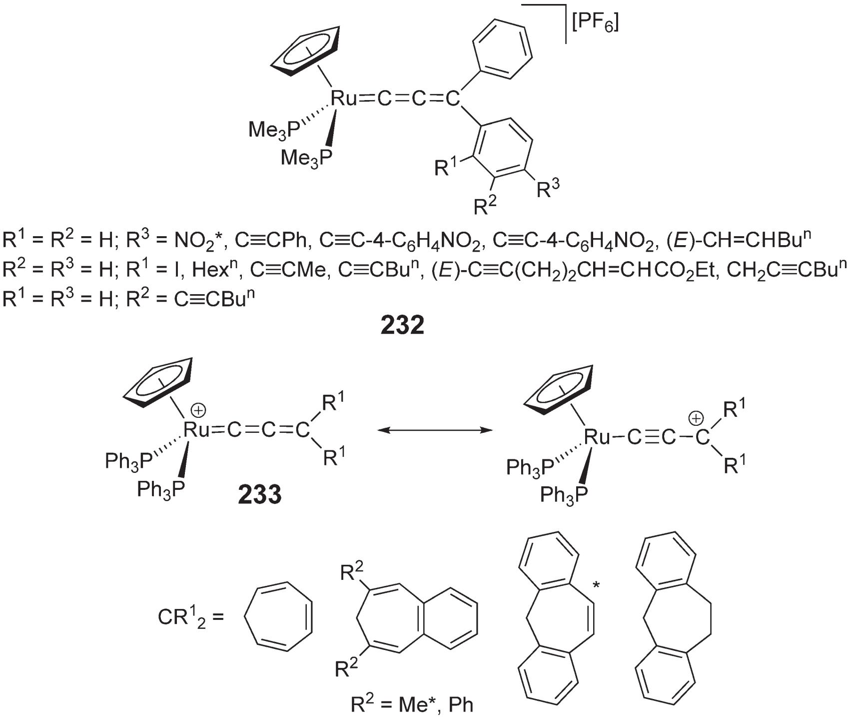


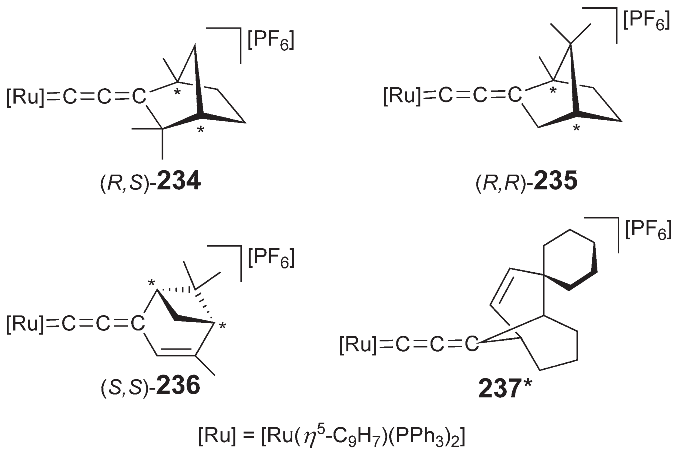
Figure 31 CpRu(II) allenylidene derivatives **232** and **233**.

A large series of Cp^*Ru(II) allenylidenes of the type $[Ru\{=C=C=C(R^1)(R^2)\}Cp^*(L^1)(L^2)][X]$ (L^1L^2 = dippe, $R^1 = R^2$ = Me, Ph, $X = BPh_4$;[119,143] L^1L^2 = dippe, R^1 = Ph, R^2 = H*, Me, $X = BPh_4$;[119,143] $L^1 = L^2 = PEt_3$, R^1 = Ph, R^2 = H, Me, Ph*, $X = BPh_4$;[121,121a] $L^1 = L^2 = PMePr^i_2$, R^1 = Ph, R^2 = H, Me, Ph, $X = BAr^F{}_4$;[123] L^1 = CO, $L^2 = PMePr^i_2$, $R^1 = R^2$ = Ph, $X = BAr^F{}_4$[113]) is also known. They have been obtained by reacting the corresponding chloride precursor with the appropriate propargylic alcohol in the presence of $Na[BPh_4]$ or $Na[BAr^F{}_4]$. In some cases, 3-hydroxy–vinylidene intermediates $[Ru]=C=C(H)C(OH)(R^1)(R^2)$ are stable, and do not dehydrate spontaneously into the allenylidenes, the treatment with acidic Al_2O_3 being required.[121,121a,123]

Another large family of allenylidenes is formed by η^5-indenyl derivatives. They are formed via activation of 1,1-diphenyl-2-propyn-1-ol, 1-phenyl-2-propyn-1-ol, or 9-ethynyl-9-fluorenol by indenyl–ruthenium(II) chloride complexes $[RuCl(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$, in methanol and in the presence of $Na[PF_6]$, affording the cationic complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(L^1)(L^2)][PF_6]$ ($R^1 = R^2$ = Ph, $L^1 = PPh_3$, $L^2 = PPh_3{}^*$, $PMePh_2$, PMe_2Ph; $R^1 = R^2$ = Ph, L^1L^2 = dppm, dppe; R^1 = H, R^2 = Ph, $L^1 = PPh_3$, $L^2 = PPh_3$, $PMePh_2$; $R^1R^2 = C_{12}H_8$ (2,2′-biphenyldiyl), $L^1 = PPh_3$, $L^2 = PPh_3$; $R^1R^2 = C_{12}H_8$ (2,2′-biphenyldiyl), L^1L^2 = dppm, dppe).[108,126] In a similar way, the chiral allenylidene–ruthenium(II) complexes (*R*,*S*)-**234**, (*R*,*R*)-**235**, and (*S*,*S*)-**236** have been prepared by reacting $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with $Na[PF_6]$ and propargylic alcohols derived from the optically active ketones (−)-fenchone, (+)-camphor, and (−)-verbenone (Figure 32).[127,127a,127b,133] A series of diphenylallenylidene complexes containing the substituted 1,2,3-trimethylindenyl ligand $[Ru(=C=C=CPh_2)(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(L^1)(L^2)][BF_4]$ (L^1 = CO, $L^2 = PPh_3{}^*$, PPr^i_3; L^1L^2 = dppm) have been obtained by treatment of $[RuBr(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(L^1)(L^2)]$ with $HC\equiv CC(OH)Ph_2$ in the presence of $Ag[BF_4]$.[135] As observed for its Cp counterpart, complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^2(P,O)\text{-}Ph_2PCH_2C(=O)Bu^t\}(PPh_3)][PF_6]$ easily reacts with 1,1-diphenyl-2-propyn-1-ol to yield the cationic diphenylallenylidene derivative $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}(PPh_3)][PF_6]$.[87] The reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with an excess of 1-ethynyl-1-cyclohexanol and $Na[PF_6]$ in refluxing methanol gives the unusual allenylidene complex **237***, containing a spirobicyclic organic skeleton, via an unprecedented coupling of two dehydrated molecules of the propargylic alcohol.[132,132a] The initial product in this reaction is the alkenyl–vinylidene complex $[Ru(=C=CHC_6H_9)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (C_6H_9 = 1-cyclohexenyl), which undergoes the addition of a second molecule of 1-ethynyl-1-cyclohexanol.

The nucleophilic addition of $NHPh_2$ to the butatrienylidene complex $[Ru(=C=C=C=CH_2)Cp(PPh_3)_2][PF_6]$, prepared *in situ* by reacting a THF solution of $[RuClCp(PPh_3)_2]$ with buta-1,3-diyne and $Ag[PF_6]$, affords the cationic amino–allenylidene derivative $[Ru\{=C=C=C(NPh_2)Me\}Cp(PPh_3)_2][PF_6]^*$. A related C–H addition of *N*-methylpyrrole across the $C_\gamma=C_\delta$ bond of the butatrienylidene chain generates the allenylidene complex $[Ru\{=C=C=C(\text{–}2\text{-}C_4H_3NMe)Me\}Cp(PPh_3)_2][PF_6]^*$.[142,142a]

Chemical oxidation of acetylide complexes constitutes a particular synthetic approach of allenylidenes. Thus, one-electron oxidation of ferrocenylacetylide complexes $[Ru(C\equiv CFc)(\eta^5\text{-}C_5R_5)L_2]$ (L = PPh_3, R = H, Me; L_2 = dppf, R = H) with ferrocenium hexafluorophosphate has been reported to yield the cationic allenylidene radicals **238** (Figure 33).[89] Related dicationic allenylidenes **239** have been prepared by two-electron oxidation of $[Ru(C\equiv CRc)(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (Rc = ruthenocenyl) and $[Ru(C\equiv CRc')(\eta^5\text{-}C_5R_5)L_2]$ (L = PPh_3, R = H; L_2 = dppe, R = H, Me; Rc′ = 2,3,4,5-tetramethylruthenocenyl), using 2 equiv. of a mixture *p*-benzoquinone/$BF_3{\cdot}OEt_2$.[91,100]



(*R*,*S*)-**234**

(*R*,*R*)-**235**

(*S*,*S*)-**236**

237*

$[Ru] = [Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$

Figure 32 Indenyl–Ru(II) allenylidene complexes **234**–**237**.

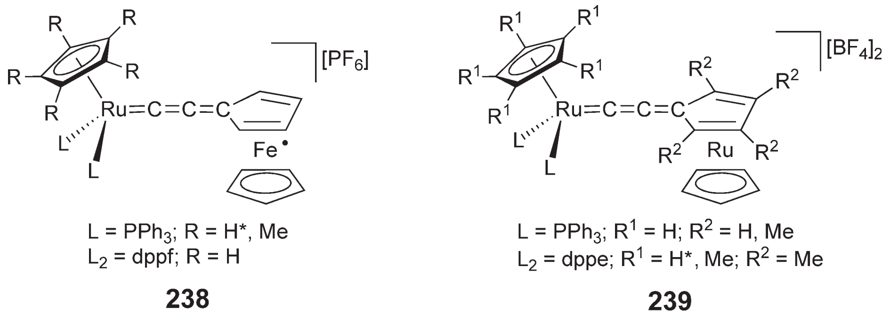
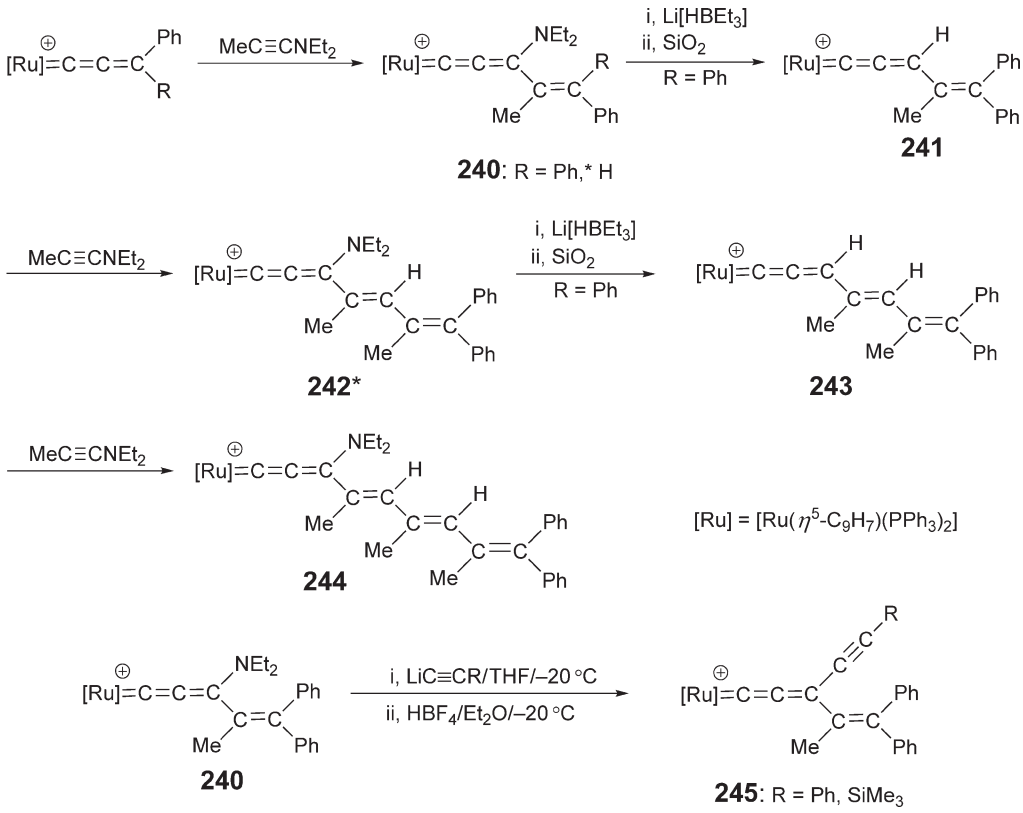


Figure 33 Structure of the allenylidene derivatives **238** and **239**.

A systematic route to prepare polyalkenyl–allenylidene complexes sequentially has been reported (Scheme 25). The first step consists of the insertion of the ynamine $MeC{\equiv}CNEt_2$ into the $C_\beta{=}C_\gamma$ bond of complexes $[Ru\{{=}C{=}C{=}C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R = H$, Ph), which leads to the stereoselective formation of cationic amino-allenylidenes 240. When $R = Ph$, complex 240 can be transformed into the secondary derivative 241 via treatment with $Li[BHEt_3]$ and subsequent purification on silica column. Sequential insertions of $MeC{\equiv}CNEt_2$ into 241 allow the preparation of allenylidenes 242–244, disclosing an unprecedented synthetic approach of polyunsaturated cumulene chains. The silylated ynamine $Me_3SiC{\equiv}CNEt_2$ also inserts into complex $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$, affording the amino-allenylidene $[Ru\{{=}C{=}C{=}C(NEt_2)C(SiMe_3){=}CPh_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$, which, by treatment with KF in MeOH, can be converted into $[Ru\{{=}C{=}C{=}C(NEt_2)CH{=}CPh_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$. The reactivity of amino-allenylidene 240 ($R = Ph$) toward lithium acetylides has also been explored allowing the preparation of the unusual alkynyl–alkenyl allenylidenes 245.[137,137a]

The preparation of the neutral diphenylallenylidene derivative $[RuCl({=}C{=}C{=}Ph_2)Cp^*\{\kappa^1(P)\text{-}Pr^i{}_2PCH_2C({=}O)OMe\}]$, by treatment of the hemilabile complex $[RuClCp^*\{\kappa^2(P,O)\text{-}Pr^i{}_2PCH_2C({=}O)OMe\}]$ with



Scheme 25

$HC{\equiv}CCPh_2(OH)$, has also been reported.[224] This reaction requires the use of acidic Al_2O_3 to dehydrate the stable hydroxy–vinylidene intermediate $[RuCl\{{=}C{=}CHCPh_2(OH)\}Cp^*\{\kappa^1(P)\text{-}Pr^i{}_2PCH_2C({=}O)OMe\}]$. Formation of $[RuCl({=}C{=}C{=}Ph_2)Cp(PPh_3)]$ from the allyl complex $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)Cp(PPh_3)]$ and $HC{\equiv}CCPh_2(OH)/HCl$ also requires the use of acidic Al_2O_3 as dehydrating agent.[184]

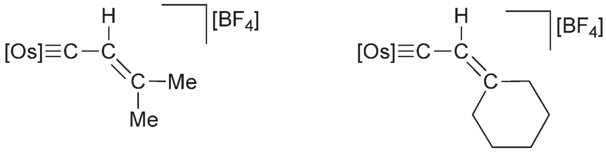
Allenylidene–osmium complexes have also been described. Thus, complex $[OsClCp(PPr^i{}_3)_2]$ reacts with 1,1-diphenyl-2-propyn-1-ol in the presence of $Tl[PF_6]$ to give the stable hydride–hydroxyalkynyl–osmium(IV) derivative $[OsH\{C{\equiv}CCPh_2(OH)\}Cp(PPr^i{}_3)_2][PF_6]$ as the result of the extraction of the chloride ligand and oxidative addition of the alkynol $C(sp)$–H bond to the metal. Dehydration of this complex to generate the cationic allenylidene $[Os({=}C{=}C{=}CPh_2)Cp(PPr^i{}_3)_2][PF_6]$, catalyzed by HCl, can be achieved in refluxing chloroform.[124] In a similar way, the treatment of an acetone solution of $[OsCl\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4(CH_2)_2PPh_2\}(PPr^i{}_3)]$ with $HC{\equiv}CC(OH)Ph_2$ and $Tl[PF_6]$ at 10 °C leads to $[OsH\{C{\equiv}CCPh_2(OH)\}\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4(CH_2)_2PPh_2\}(PPr^i{}_3)][PF_6]$, which slowly evolves at RT into the allenylidene derivative $[Os({=}C{=}C{=}CPh_2)\{\eta^5{:}\kappa^1(P)\text{-}C_5H_4(CH_2)_2PPh_2\}(PPr^i{}_3)][PF_6]$.[36] The unsaturated π-alkyne complex $[Os\{\eta^2\text{-}HC{\equiv}CCPh_2(OH)\}Cp(PPr^i{}_3)][PF_6]$ reacts with CO and $PHPh_2$ in refluxing dichloromethane to afford the saturated cationic allenylidenes $[Os({=}C{=}C{=}CPh_2)Cp(PPr^i{}_3)(L)][PF_6]$ ($L = CO^*$, $PHPh_2{}^*$) via the corresponding hydride–hydroxyalkynyl–osmium(IV) intermediates, which in the case of $L = PHPh_2$, could be isolated and characterized.[79] Apparently, the replacement of $PPr^i{}_3$ by PPh_3 in the coordination sphere of the metal destabilizes these hydride intermediates and facilitates the formation of the allenylidene derivatives. Thus, the reaction of $[OsBrCp(PPh_3)_2]$ with $HC{\equiv}CC(OH)Ph_2$ and $[NH_4][PF_6]$ leads directly to the allenylidene complex $[Os({=}C{=}C{=}CPh_2)Cp(PPh_3)_2][PF_6]^*$.[229] Cationic indenyl–osmium(II) allenylidenes $[Os({=}C{=}C{=}CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R^1 = R^2 = Ph^*$; $R^1R^2 = C_{12}H_8$) have also been directly prepared by reaction of $[OsCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with the corresponding propargylic alcohol and $Na[PF_6]$ in refluxing methanol.[108] Neutral allenylidene–Os(II) derivatives $[OsX({=}C{=}C{=}CPh_2)Cp(PPr^i{}_3)]$ ($X = Cl,^*$ I) are also known.[226]

6.15.2.10 Alkylidyne Complexes

Despite five- and six-coordinate alkylidyne–ruthenium and alkylidyne–osmium complexes having been extensively studied (see Chapter 6.12), the chemistry of η^5-Cp derivatives is yet to be developed. It is interesting to note that no η^5-Cp–ruthenium derivative appears in the information contained in COMC (1995), and only one example of osmium, namely, $[Os({\equiv}CBu^t)(CH_2Bu^t)_2Cp]$, is reported.[230] Since then, only two types of alkylidyne–ruthenium complexes have been described, namely, $[RuCl({\equiv}CCH_2R)Cp(PPh_3)][X]$ ($X = BAr^F{}_4$, $R = Bu^{t*}$, Bu^n; $X = BF_4$, $R = Ph$)[222] and the dicationic α,β-unsaturated derivatives $[Ru\{{\equiv}CC(H){=}C(R)Ph\}Cp^*(dippe)][BAr^F{}_4]_2$ ($R = H$, Ph^*).[136] They are prepared by protonation of the vinylidene $[RuCl\{{=}C{=}C(H)R\}Cp^*(PPh_3)]$ and allenylidene $[Ru\{{=}C{=}C{=}C(R)Ph\}Cp^*(dippe)][BAr^F{}_4]$ ruthenium(II) complexes, respectively.

The ready accessibility of the η^5-Cp osmium precursor $[OsClCp(PPr^i{}_3)_2]$ has allowed general access to a wide range of derivatives containing η^1-Os–C bonds, some of them used as precursors of alkylidyne complexes. This chemistry was exclusively developed by Esteruelas and co-workers, and has been recently reviewed.[231] The seminal work stems from the reaction of the vinylidene complex $[OsCl\{{=}C{=}C(H)Ph\}Cp(PPr^i{}_3)]$ with HBF_4 which leads to the formation of the cationic carbyne $[OsCl({\equiv}CCH_2Ph)Cp(PPr^i{}_3)][BF_4]$ in good yield. Analogous α,β-unsaturated carbynes 246 and 247* have been similarly prepared from the C_δ-protonation of alkenyl vinylidenes $[OsCl({=}C{=}CHCMe{=}CH_2)Cp(PPr^i{}_3)]$ and $[OsCl\{{=}C{=}C(H)C_6H_9\}Cp(PPr^i{}_3)]$, respectively (Figure 34).[35]

Vinylidene complexes are also suitable precursors via protonation of carbynes $[Os\{{\equiv}CCH(R)Ph\}(\eta^5\text{-}C_5H_4SiPh_3)(GePh_3)(PPr^i{}_3)][BF_4]$ ($R = H$, Me) and the first isolated hydride–carbyne derivative $[OsH({\equiv}CCH_2Ph)(\eta^5\text{-}C_5H_4SiPh_3)(PPr^i{}_3)][BF_4]$.[40] The ability of vinylidene complexes to undergo protonation at the C_β-atom is also invoked in the formation of the carbyne 248, which is obtained by addition of HBF_4 to solutions

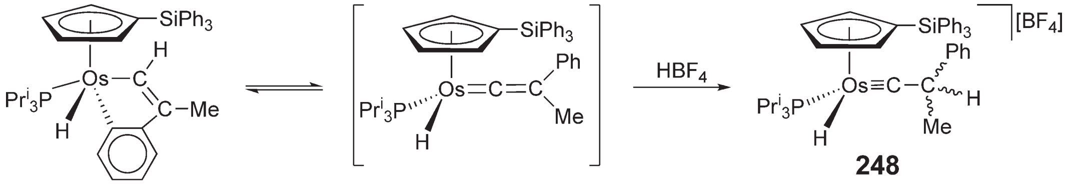


246 **247***

$[Os] = [OsClCp(PPr^i{}_3)]$

Figure 34 The alkenyl–carbyne osmium complexes **246**–**247**.

of the orthometallated complex **34** (Equation (16)). Its formation is rationalized on the basis of the presence in solution of an equilibrium of the metallated complex **34** with no detectable concentrations of the hydride–vinylidene [$OsH(=C=CMePh)(\eta^5$-$C_5H_4SiPh_3)(PPr^i_3)$], which undergoes the electrophilic addition.[40]



34*

248
Two diastereoisomers

(16)

The protonation of osmium allenylidenes has also proved to be an efficient synthetic approach to carbynes. In agreement with the nucleophilic nature of the C_β-atom of the allenylidene chain, the neutral complex [$OsCl(=C=C=CPh_2)Cp(PPr^i_3)$] reacts with HBF_4 to afford the cationic α,β-unsaturated carbyne [$OsCl(\equiv CCH=CPh_2)Cp(PPr^i_3)$][$BF_4$].[226] Likewise, the analogous cationic allenylidenes [$Os(=C=C=CPh_2)$-$Cp(L)(PPr^i_3)$][PF_6] are also able to undergo protonation by the addition of HPF_6 in acetone to afford the dicationic carbyne complexes [$Os(\equiv CCH=CPh_2)Cp(L)(PPr^i_3)$][$PF_6$]$_2$ ($L = PHPh_2$, $PPr^i_3{}^*$).[79,124] The suitability of this synthetic route starting from allenylidene complexes has been assessed by the synthesis of the η^5-Cp–phosphine-tethered alkenyl–carbyne complex [$Os(\equiv CCH=CPh_2)\{\eta^5{:}\kappa^1(P)$-$C_5H_4(CH_2)_2PPh_2\}(PPr^i_3)$][$PF_6$]$_2$.[36]

All these η^5-Cp osmium carbynes have been obtained in almost quantitative yields and isolated as air-stable solids. These efficient synthetic routes prove the utility of vinylidene and allenylidene complexes as valuable starting materials, which are prone to undergo protonations even in cationic allenylidene precursors.

It has been also proposed that the addition of HPF_6 to dichloromethane solutions of [$Os(=C=C=CPh_2)$-$Cp(CO)(PPr^i_3)$][PF_6] leads to a transient carbyne derivative [$Os(\equiv CCH=CPh_2)Cp(CO)(PPr^i_3)$][$PF_6$]$_2$ **177**, which, in contrast to the above-mentioned alkylidynes, rapidly undergoes an intramolecular electrophilic substitution and concomitant elimination of HPF_6 to give the indenylidene complex **178** (see Equation (15)).[79] Deuteration proves the formation of the alkylidyne intermediate. Analogous indenylidene five-coordinated ruthenium complexes (see Chapter 6.12) as well as one η^6-*p*-cymene derivative (see Section 6.15.3.5) have also been reported. This behavior shows the influence on the carbyne group stability of the relatively electron-poor fragment [$OsCp(CO)(PPr^i_3)$]$^+$, which favors the rearrangement of the resulting carbyne species. In contrast, the electron-rich ruthenium or osmium metallic fragments [$MClCp(PR_3)$] inhibit the isomerization, and, therefore, carbyne complexes are stabilized.

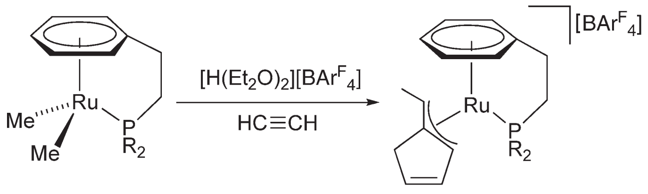
Two unusual routes have been described for the synthesis of the very reactive osmium hydride–alkylidynes [$OsH(\equiv CR^1)Cp(PPr^i_2R^2)$][$PF_6$] ($R^2 = CMe=CH_2$, Pr^i). Phenylcarbyne complexes [$OsH(\equiv CPh)Cp(PPr^i_2R^2)$][$PF_6$] ($R^2 = CMe=CH_2$, Pr^{i*}) are prepared by treatment of the alkylidenes [$OsCl(=CHPh)Cp(PPr^i_2R^2)$] with Tl[$PF_6$].[22,25] These hydride–carbyne derivatives result from the extraction of the chloride ligand and migration of the hydrogen atom of the alkylidene group from the carbon atom to the metallic center. However, complex [$OsH(\equiv CPh)Cp\{\kappa^1(P)$-$Pr^i_2PCMe=CH_2\}$][$PF_6$] is not stable in acetone evolving selectively into the phosphinoallyl–hydride complex [$OsH\{\kappa^4(P,C,C,C)$-$Pr^i_2PCMeCHCHPh\}Cp$][PF_6]* as the result of an intramolecular [2 + 2]-cycloaddition between the isopropenyl substituent of the phosphine and the carbyne ligand.[22] On the other hand, the analogous benzyl carbyne [$OsH(\equiv CCH_2Ph)Cp(PPr^i_3)$][$BF_4$] is obtained in nearly quantitative yield by addition of 2 equiv. of HBF_4 to diethyl ether solutions of the hydride–alkynyl species [$OsH(C\equiv CPh)Cp(EPh_3)(PPr^i_3)$] (E = Si, Ge). The formation of $FEPh_3$ was also detected.[39]

The acidity of the hydride ligand in carbyne complex [$OsH(\equiv CPh)Cp(P^iPr_3)$][$PF_6$] and the hydrogen atom of the alkylidene group in [$OsCl(=CHPh)Cp(PPr^i_3)$] allow the deprotonation by treatment with sodium methoxide yielding the neutral carbyne [$Os(\equiv CPh)Cp(PPr^i_3)$]*.[25] Through a similar deprotonation, the carbyne derivative [$Os(\equiv CPh)Cp\{\kappa^1(P)$-$Pr^i_2PCMe=CH_2\}$] has been obtained and isolated as a dark brown oil only stable under argon at −20 °C.[22]

6.15.3 Half-Sandwich η^6-Arene Complexes

6.15.3.1 Alkyl and Aryl Complexes

In the context of the interest in using alkyl derivatives as precursors of active catalysts, a series of methyl–ruthenium complexes have been isolated. In particular, the search for new types of Ziegler–Natta catalysts with tolerance toward polar functional groups has stimulated the synthesis of new complexes. This is illustrated by the isolation of tethered dimethyl–ruthenium(II) complexes $[RuMe_2\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PR_2\}]$ (R = Et, Cy*, Ph*) prepared in ca. 35% yield from the dichloride derivatives $[RuCl_2\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PR_2\}]$ by alkylation with an excess of LiMe. In contrast to the previously reported non-tethered analogs $[RuMe_2(\eta^6\text{-}C_6H_6)(PPh_3)]$ and $[RuMe_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PMe_2Ph)]$, which readily decompose at RT, they show a remarkable thermal stability.[232] In order to promote insertion reactions into the Ru–Me bond, the electrophilic abstraction of one methyl group with $[H(Et_2O)_2][BAr^F{}_4]$ has been performed in the presence of CO, ethylene, acetylene, and norbornene. While the reaction with CO afforded the stable complexes $[RuMe\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PR_2\}(CO)][BAr^F{}_4]$ (R = Cy*, Ph), in the presence of ethylene (R = Ph), the cationic olefin–methyl derivative $[RuMe\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PR_2\}(\eta^2\text{-}CH_2{=}CH_2)][BAr^F{}_4]$ is initially formed although it readily decomposes in CH_2Cl_2 solution to give the dimeric species $[\{Ru\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PPh_2\}(\mu\text{-}Cl)\}_2][BAr^F{}_4]_2$. In contrast, the reaction with acetylene gives polyacetylene along with the allyl complexes **249**, the latter resulting from the insertion of acetylene into the Ru–methyl bond (Equation (17)). The dimethyl derivatives in the presence of $[H(Et_2O)_2][BAr^F{}_4]$ are active catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene at RT.[233]



(17)

249: R = Cy*, Ph*

Non-tethered η^6-arene–monomethyl derivatives $[RuMe(\eta^6\text{-}C_6H_5X)(PPh_3)_2][AlCl_2Me_2]$ (X = H*, F) and $[RuMe(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPh_3)_2][AlCl_2Me_2]$ have been synthesized in high yields by reaction of $[RuCl_2(PPh_3)_3]$ with an excess of $AlMe_3$ in the presence of benzene, fluorobenzene, or mesitylene.[234] The ruthenium(II) dimethyl complexes $[RuMe_2(\eta^6\text{-}C_6Me_6)(PR_3)]$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3), obtained by reacting the corresponding dichloride precursors with LiMe, are able to activate benzene or toluene C–H bonds at 85–105 °C. Thus, prolonged thermolysis in a sealed tube (50–300 h) affords the methyl–aryl complexes $[RuMe(Ar)(\eta^6\text{-}C_6Me_6)(PR_3)]$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PEt_3; Ar = Ph, *m*- and *p*-C_6H_4Me; not all combinations) along with some decomposition products derived from the dissociation of the hexamethylbenzene ligand. When toluene is used, the resulting mixed methyl–aryl complexes are in all cases 2 : 1 mixtures of the *m*- and *p*-tolyl isomers. Remarkably, the reactions of $[RuMe_2(\eta^6\text{-}C_6Me_6)(PMe_3)]$ with benzene and toluene in the presence of $[FeCp_2][PF_6]$ proceed rapidly at RT giving rise to the methyl–aryl derivatives $[RuMe(Ar)(\eta^6\text{-}C_6Me_6)(PMe_3)]$ (Ar = Ph, *m*- and *p*-C_6H_4Me) selectively. However, under the same reaction conditions, starting from dimethyl complexes $[RuMe_2(\eta^6\text{-}C_6Me_6)(PR_3)]$ containing bulkier phosphines, such as PMe_2Ph or $PMePh_2$, mixtures of the expected methyl–aryl derivatives together with intramolecular orthometallated complexes are obtained.[235] Mixed methyl–phenyl complexes $[RuMe(Ph)(\eta^6\text{-}C_6Me_6)(PR_3)]$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3) can be alternatively prepared starting from the appropriate dichloride $[RuCl_2(\eta^6\text{-}C_6Me_6)(PR_3)]$ by sequential treatment with PhMgBr and LiMe.[235]

Transmetallation reactions of $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ (PR_3 = PPh_3, $P(OMe)_3$) with PhMgBr give the phenyl derivatives $[RuBr(Ph)(\eta^6\text{-}p\text{-cymene})(PPh_3)]$ and $[RuCl(Ph)(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$, respectively, isolated as air stable complexes after chromatographic workup.[236] In a similar way, complexes $[RuCl_2(\eta^6\text{-}C_6Me_6)(PR_3)]$ (PR_3 = $PMePh_2$, PEt_3) react with PhMgBr to generate $[RuCl(Ph)(\eta^6\text{-}C_6Me_6)(PR_3)]$ (PR_3 = $PMePh_2$, PEt_3).[235] Remarkably, the treatment of $[RuBr(Ph)(\eta^6\text{-}p\text{-cymene})(PPh_3)]$ with $Ag[SbF_6]$ under a CO atmosphere does not give the expected benzoyl insertion product, leading instead to the formation of the stable cationic carbonyl compound $[Ru(Ph)(\eta^6\text{-}p\text{-cymene})(CO)(PPh_3)][SbF_6]$.[236] Iodide–phenyl or –methyl derivatives $[RuI(R)(\eta^6\text{-}C_6Me_6)(PMe_3)]$ (R = Ph, Me) are obtained in good yields by reaction of $[RuI_2(\eta^6\text{-}C_6Me_6)(PMe_3)]$ with LiPh or LiMe, respectively. Exchange reactions of the iodide ligand with potassium amides afford complexes $[Ru(R)(NR^1R^2)(\eta^6\text{-}C_6Me_6)(PMe_3)]$ (R = Ph, R^1 = H, R^2 = Ph*, 4-C_6H_4Me; R = Me, R^1 = H, Me, R^2 = Ph), which are able to undergo net insertion of CO_2 into the Ru–N bond to generate $[Ru(R)\{\kappa^1(O)\text{-}O_2CNR^1R^2\}(\eta^6\text{-}C_6Me_6)(PMe_3)]$ (R = Ph, R^1 = H, R^2 = Ph, 4-C_6H_4Me; R = Me, R^1 = H, R^2 = Ph).[237]

Reaction of $[\{OsCl(\mu\text{-}Cl)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2]$ with RCH_2OH/NaOH in the presence of propene leads to complete fragmentation of the primary alcohol and formation of the alkyl–carbonyl–hydride complexes $[OsH(R)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i). These complexes undergo H/Cl exchange upon treatment with CCl_4 to afford the corresponding chlorides $[OsCl(R)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$, which can be alternatively prepared by protonation of the known dialkyl derivatives $[OsR_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ with HCl. The bromide complex $[OsBr(Me)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ could be also obtained by H/Br exchange with $CHBr_3$.[238] The carbonyl precursor $[OsCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ reacts with an excess of Bu^iMgI to give a mixture of $[OsBu^i{}_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$, $[OsIBu^i(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$, and $[OsI_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$. In contrast, treatment with $CyCH_2MgBr$ yields $[Os(CH_2Cy)_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ along with the π-olefin complex $[Os(\eta^2\text{-}CH_2{=}C_6H_{10})(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ and $[OsHBr(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$. Protonation of $[Os(CH_2Cy)_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ with HCl generates $[OsCl(CH_2Cy)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$, which can be transformed into $[OsH(CH_2Cy)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ upon treatment with Mg/Hg in the presence of EtOH.[238] Transmetallation reactions of isocyanide–osmium derivatives $[OsCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CNR)]$ ($R = Me$, Bu^t, Cy, Xyl, Ph) have also been studied. In general, the reactions with either Grignard or lithium reagents are not selective, giving rise to mixtures of complexes including mono- and disubstituted derivatives along with chloride–halide exchange products.[239,240] Related alkyl–osmium(II) compounds $[OsIEt(\eta^6\text{-}p\text{-cymene})(PEt_3)]$ and $[OsIMe(\eta^6\text{-}p\text{-cymene})(PCy_3)]$ are also known, being obtained from complexes $[OsI_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ and $AlEt_3$ or Al_2Me_6.[241]

The diaryl–carbonyl species $[OsAr_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)]$ ($Ar = Ph$, $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4OMe$) have been selectively synthesized by hydrolysis of the appropriate carbene derivative $[Os(OTf)_2({=}CAr_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$. On the basis of labeling experiments, a mechanism for this unusual C–C bond cleavage, which involves the nucleophilic attack of water on the key carbyne intermediate $[OsAr(OTf)({\equiv}CAr)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$, has been proposed.[242]

Very unusual phenyl–ruthenium(II) derivatives **251**, which also represent the first transition metal complexes of the ligands P(OH)(OR)Ph, are formed by stereospecific P–C bond-cleavage and P–O bond-forming reactions of the coordinated $Ph_2P(OH)$ ligand with alcohols in chiral Binap-based arene–ruthenium complexes **250** (Scheme 26). The formation of the new Ru–phenyl bond involves the migration of a P–phenyl group to the metal center.[243,243a,244] Treatment of the triflate precursor **250** with ethylene glycol and potassium carbonate leads to the neutral oxo–phosphine derivative **252** via deprotonation of the $[Ru]\text{–}P(OH)(OCH_2CH_2OH)Ph$ intermediate complex ($[Ru] = [Ru(Ph)\{\eta^6{:}\kappa^1(P)\text{-}Ph_2P\text{-binaphthyl}\}][OTf]$; type **251**).[243,243a] The spectroscopic characterization of the highly unstable phenyl derivative **253** has also been reported.[244] Related chemistry in 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (Biphep) and *p*-Tol-Binap-based arene–Ru complexes is known and has been recently reviewed.[245] Easy migration of a phenyl group from a phosphino–enolato ligand to ruthenium also occurs in the reaction of complexes $[RuCl\{\kappa^2(P,O)\text{-}Ph_2PCR{=}CBu^tO\}(\eta^6\text{-arene})]$ with K[OAc]/MeOH, which leads to the selective formation of compounds $[RuPh\{\kappa^2(P,O)\text{-}Ph(MeO)PCR{=}CBu^tO\}(\eta^6\text{-arene})]$ ($\text{arene} = C_6Me_6$, $R = H$, Me; $\text{arene} = 1,3,5\text{-}C_6H_3Me_3$, $R = H$, Me).[246] Dialkyl complexes **254**, in which an arene moiety and only one P atom of the chiral bis(3,5-di-*tert*-butylphenyl)phosphino MeO–Biphep ligand are coordinated to ruthenium, are formed in the reaction of complex $[Ru(OAc)_2\{\kappa^2(P,P)\text{-MeO-Biphep}\}]$ with methyl- or (trimethylsilyl)methyl-lithium. The methyl derivative reacts smoothly with HBF_4 in the presence of an excess of benzene to yield the somewhat more conventional monomethyl complex **255**.[247]

Although β-diketonates are prone to coordinate metal fragments as $\kappa^2(O,O)$ chelate ligands, several late transition metal complexes show ability to bind to the γ-carbon atom. In this respect, complexes $[MCl\{\kappa^2(O,O)\text{-acac}\}(\eta^6\text{-arene})]$ react with thallium acetylacetonate to give bis(acetylacetonate) derivatives $[M\{\kappa^2(O,O)\text{-acac}\}(\eta^1\text{-acac})(\eta^6\text{-arene})]$ ($M = Ru$, $\text{arene} = C_6H_6$; $M = Os$, $\text{arene} = C_6H_6$, $1,2\text{-}C_6H_4Me_2{}^*$, $1,2,3\text{-}C_6H_3Me_3$), in which one of the acac ligands is bound through the C_γ-atom.[248]

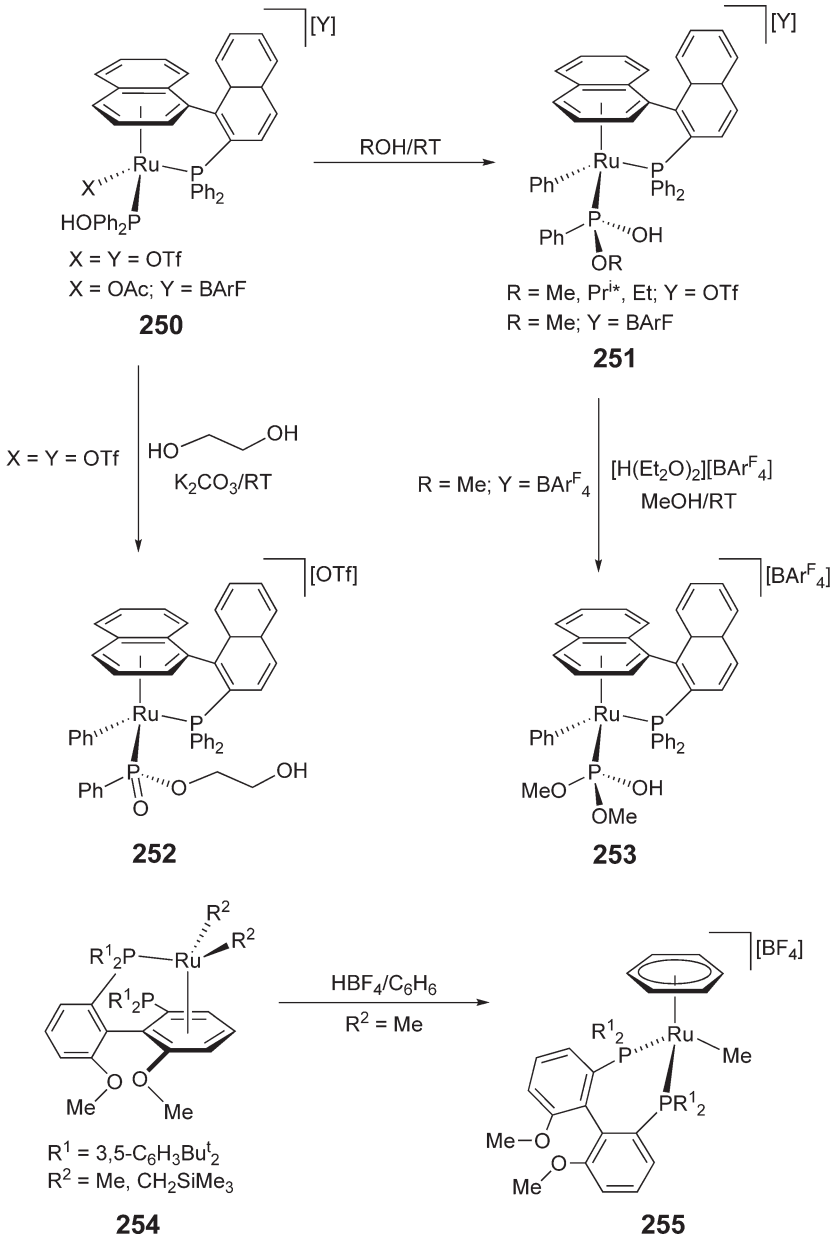
6.15.3.2 Alkynyl, Alkenyl, Allenyl, and Related Complexes Containing η^1-M–C Bonds

A series of alkynyl complexes $[Ru(C{\equiv}CR)(\eta^6\text{-arene})L_2]$ has been prepared through classical methodologies consisting in the reactions of appropriate η^6-arene chloride ruthenium precursors with (i) terminal alkynes in the presence of a base or (ii) lithium/sodium alkynyl reagents. Examples containing κ^2-bidentate chelating ligands include the following:

(i) $[Ru(C{\equiv}CR)(\eta^6\text{-}p\text{-cymene})(N\text{–}N)][BAr^F{}_4]$ (N–N = 1,10-phenanthroline; $R = H^*$, Ph, $SiMe_3$). It is interesting to note that protonation of $[Ru(C{\equiv}CH)(\eta^6\text{-}p\text{-cymene})(N\text{–}N)][BAr^F{}_4]$ with HOTf yields the acyl derivative $[Ru\{C({=}O)CH_3\}(\eta^6\text{-}p\text{-cymene})(N\text{–}N)][BAr^F{}_4]$,* resulting from the addition of adventitious water on the highly unstable dicationic vinylidene intermediate $[Ru({=}C{=}CH_2)(\eta^6\text{-}p\text{-cymene})(N\text{–}N)]^{2+}$.[249]

(ii) $[Ru(C{\equiv}CR)(\eta^6\text{-}p\text{-cymene})(N\text{–}O)]$ (N–O = optically pure L-alaninate or L-prolinate; $R = Ph$, CO_2Me).[250]

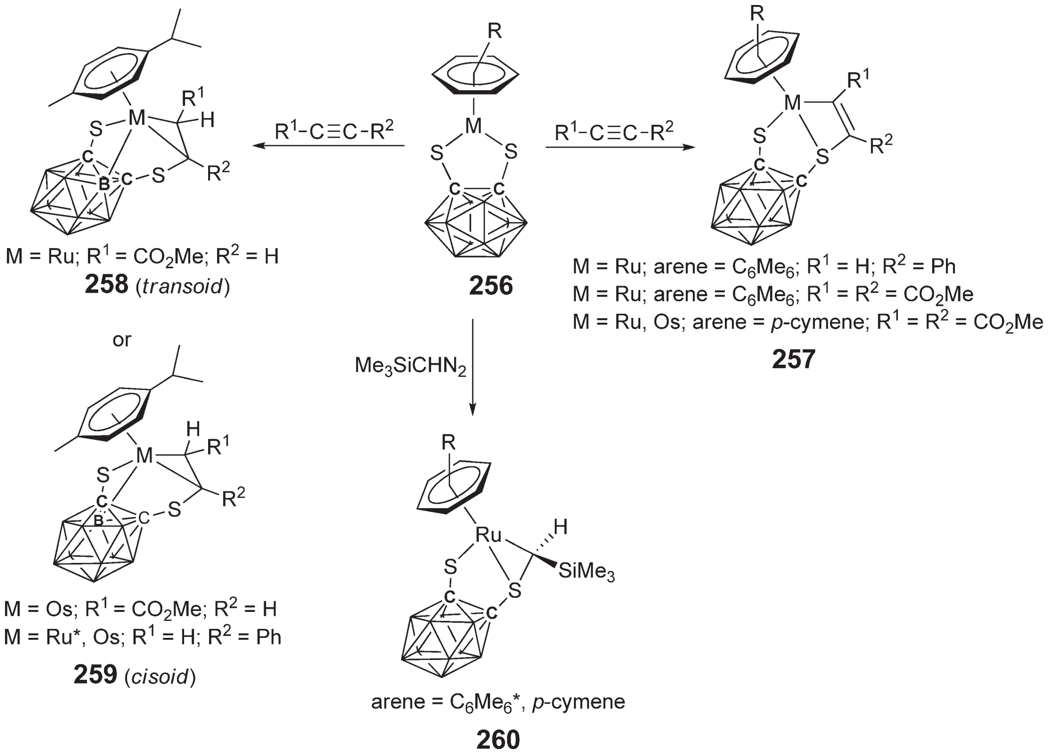
(iii) $[Ru(C{\equiv}CR)(\eta^6\text{-}C_6Me_6)(P\text{–}O)]$ ($P\text{–}O = Ph_2P(2\text{-}O\text{-}6\text{-}C_6H_3OMe)$; $R = Ph^*$, CO_2Me, CH_2OH^*, CMe_2OH, CHMeOH).[251]



Scheme 26

Other atypical alkynyls are: the diynyl derivatives $[\mathrm{RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{PR_3})]$ ($\mathrm{PR_3} = \mathrm{PMe_3}^*$, $\mathrm{PMe_2Ph}$, $\mathrm{PMePh_2}$) obtained from the reaction of $[\mathrm{RuCl_2}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{PR_3})]$ with the terminal diyne $\mathrm{HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)}$ in the presence of $\mathrm{Na[PF_6]}$ and $\mathrm{HNPr^i{}_2}$,[252] and the bis-alkynyl complex $[\mathrm{Ru(C{\equiv}CPh)_2}(\eta^6\text{-}p\text{-cymene})(\mathrm{PMe_3})]^*$, which results from the treatment of $[\mathrm{RuCl_2}(\eta^6\text{-}p\text{-cymene})(\mathrm{PMe_3})]$ with an excess of $\mathrm{LiC{\equiv}CPh}$.[249] The preparation of the neutral Os(II) derivatives $[\mathrm{OsI(C{\equiv}CPh)}(\eta^6\text{-}p\text{-cymene})(\mathrm{PR_3})]$ ($\mathrm{PR_3} = \mathrm{PMe_3}^*$, $\mathrm{PPr^i{}_3}^*$, $\mathrm{PPh_3}$) has also been reported.[241]

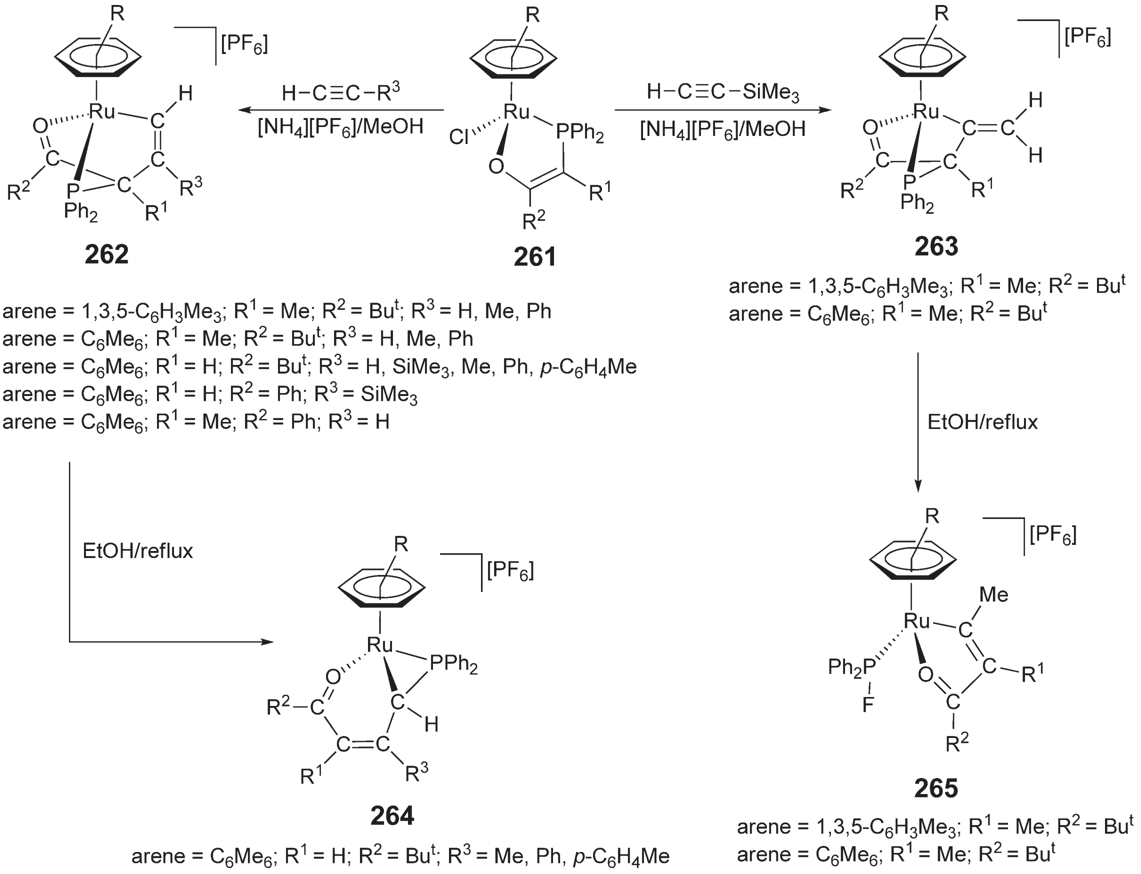
The alkenyl–osmium(II) derivative $[\mathrm{OsH(CH{=}CH_2)}(\eta^6\text{-}1,3,5\text{-}\mathrm{C_6H_3Me_3})(\mathrm{CNMe})]$ has been obtained by photolysis of the ethene–Os(II) complex $[\mathrm{Os}(\eta^2\text{-}\mathrm{CH_2{=}CH_2})(\eta^6\text{-}1,3,5\text{-}\mathrm{C_6H_3Me_3})(\mathrm{CNMe})]$ via intramolecular oxidative C–H addition.[240] A new activation of propargylic alcohols, leading to the formation of alkenyl oxametallacycles $[\mathrm{Ru}\{\kappa^2(C,O)\text{-}\mathrm{CH{=}C(4\text{-}C_6H_4NMe_2)C({=}O)H}\}(\eta^6\text{-arene})(\mathrm{PR_3})][\mathrm{PF_6}]$ (arene = 1,2,4,5-$\mathrm{C_6H_2Me_4}$, $\mathrm{PR_3} = \mathrm{PPh_3}^*$, $\mathrm{PMe_3}$;



Scheme 27

arene = C_6Me_6, PR_3 = PMe_3), has been discovered in the reaction of [$RuCl_2(\eta^6$-arene)(PR_3)] with HC≡CCH(OH)(4-$C_6H_4NMe_2$). In contrast to the well-known dehydration process observed for a wide range of propargylic alcohols giving rise to unsaturated carbene derivatives (see Sections 6.15.3.4 and 6.15.3.7), an unprecedented 1,2-migration of the dimethylaminophenyl substituent occurs in this case.[253] The 16-electron (η^6-arene)–ruthenium and –osmium complexes **256**, containing the κ^2(*S*,*S*)-coordinated 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato ligand (1,2-$S_2C_2(B_{10}H_{10})$), have been shown to be excellent substrates to undergo addition of terminal or internal alkynes affording complexes bearing novel M–C bonds (Scheme 27). Thus, two types of derivatives have been obtained: (i) alkenyl species **257** resulting from the formal insertion of the alkyne into one of the Ru–S bonds,[254,255] and (ii) the *p*-cymene isomers **258** and **259**, in which the alkyne is regioselectively inserted into one of the M–S bonds, and a metal–boron bond is generated after transferring one of the hydrogen atom of the carborane cage to the former alkyne. In this latest case, a formal η^2-olefin complex is formed.[254,256] Analogously, a methylene group can be also inserted into the Ru–S bond, by reaction with Me_3SiCHN_2, to afford complex **260** which contains a bicyclocarbometallacyclic ring.[255]

The phosphino–enolate complexes **261** react with terminal alkynes in MeOH in the presence of [NH_4][PF_6] to afford the isomeric alkenyl ruthenacycles **262** and **263** (Scheme 28). The five-membered Ru–C–C–C–P cycle in **262** formally arises from the π-coordination of the alkyne to ruthenium, and a subsequent C–C coupling of the C_β-atom of the alkyne with the nucleophilic enolate-carbon atom. In contrast, complexes **263**, exhibiting a four-membered ruthenacycle, result from the nucleophilic attack of enolate-carbon atom on the electrophilic α-carbon of a vinylidene intermediate.[246,257] Both **262** and **263** are thermally unstable, evolving into the three-membered ruthenacycles **264** and the alkenyl derivatives **265**, respectively. Formation of **265** involves the formal addition of HF (formed *in situ* by decomposition of the PF_6^- anion in the presence of traces of water) to **263**, resulting in the cleavage of the bridging phosphorus–carbon bond.[246,257] A related intramolecular nucleophilic attack of the κ^1(*P*)-phosphine $Ph_2PCH{=}CH_2$ on a π-coordinated alkyne also takes place in the reaction of complex [$RuCl_2\{\kappa^1(P)$-$PPh_2CH{=}CH_2\}(\eta^6$-C_6Me_6)] with HC≡CCMe$_2$NH$_2$, which, in the presence of Na[PF_6], leads to the phosphonio–alkenyl derivative [RuCl{κ^2(*C*,*N*)-CH=C(PPh$_2$CH=CH$_2$)CMe$_2$NH$_2$}(η^6-C_6Me_6)][PF_6]*.[258]



262

arene = 1,3,5-$C_6H_3Me_3$; R^1 = Me; R^2 = Bu^t; R^3 = H, Me, Ph
arene = C_6Me_6; R^1 = Me; R^2 = Bu^t; R^3 = H, Me, Ph
arene = C_6Me_6; R^1 = H; R^2 = Bu^t; R^3 = H, $SiMe_3$, Me, Ph, *p*-C_6H_4Me
arene = C_6Me_6; R^1 = H; R^2 = Ph; R^3 = $SiMe_3$
arene = C_6Me_6; R^1 = Me; R^2 = Ph; R^3 = H

261

263

arene = 1,3,5-$C_6H_3Me_3$; R^1 = Me; R^2 = Bu^t
arene = C_6Me_6; R^1 = Me; R^2 = Bu^t

264

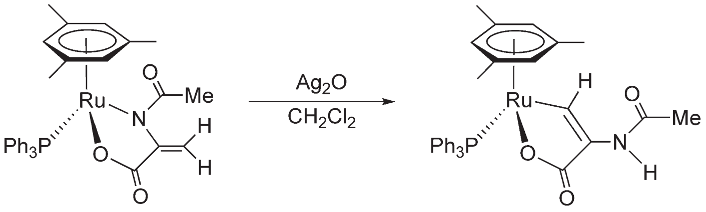
arene = C_6Me_6; R^1 = H; R^2 = Bu^t; R^3 = Me, Ph, *p*-C_6H_4Me

265

arene = 1,3,5-$C_6H_3Me_3$; R^1 = Me; R^2 = Bu^t
arene = C_6Me_6; R^1 = Me; R^2 = Bu^t

Scheme 28

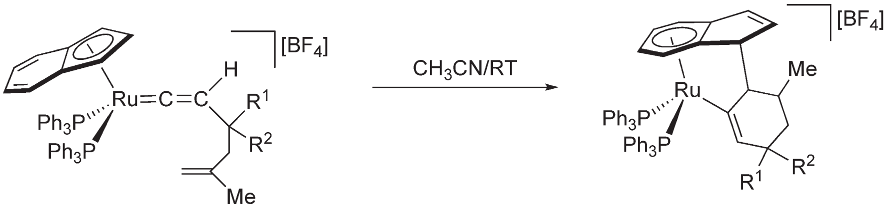
An unusual Ag_2O-mediated isomerization of mesitylene complex **266**, containing a dianionic chelating ligand derived from 2-acetamidocinnamic acid, has been reported to yield the cyclometallated alkenyl derivative **267** (Equation (18)).[259] Other alkenyl-cyclometallated derivatives **285** are also known (see Section 6.15.3.3).



266 **267**

(18)

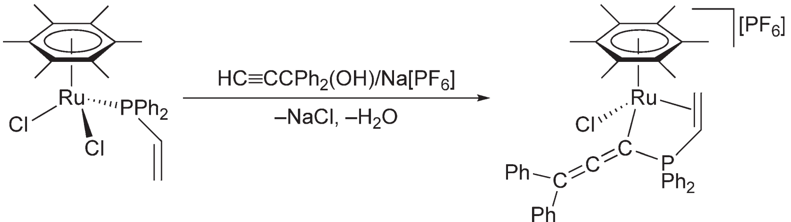
In the context of reactivity studies of half-sandwich ruthenium complexes with vinylidene and allenylidene groups, an unexpected C–C coupling leading to unprecedented cyclometallated alkenyl derivatives has been discovered (Equation (19)). Thus, although η^5-indenyl vinylidene–ruthenium complexes are known to undergo demetallation reactions in acetonitrile to give the corresponding terminal alkynes, through an initial vinylidene–π-alkyne tautomerization, the alkenyl–vinylidene complexes **268** rearrange in CH_3CN at RT to afford a very unusual class of cyclometallated η^6-indene complexes **269** in good yields.[130]



268 **269** (19)

R^1 = H; R^2 = Ph; R^1R^2 = 2,2′-biphenyldiyl*

Although nucleophilic attack at C_α-atom of allenylidene chains is mainly hampered by the steric protection of the electrophilic sites, a number of (η^6-arene)–allenylidene derivatives are prone to undergo addition of methanol or phosphines to afford allenyl derivatives. The following examples have been reported: (i) $[OsCl\{C(OMe){=}C{=}CPh_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PMe_3)]$,[260] (ii) $[OsCl\{C(PR^2_3){=}C{=}CPh_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PR^1_3)][PF_6]$ ($R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Ph$; $R^1 = Cy$, $R^2 = Me$),[260] and (iii) complex **270*** (Equation (20)), which results from the intramolecular attack of the coordinated $Ph_2PCH{=}CH_2$ ligand in the allenylidene intermediate $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}C_6Me_6)\{\kappa^1(P)\text{-}Ph_2PCH{=}CH_2\}][PF_6]$, facilitated by the ability of the vinyl group to coordinate to the metal in an η^2-mode.[258]

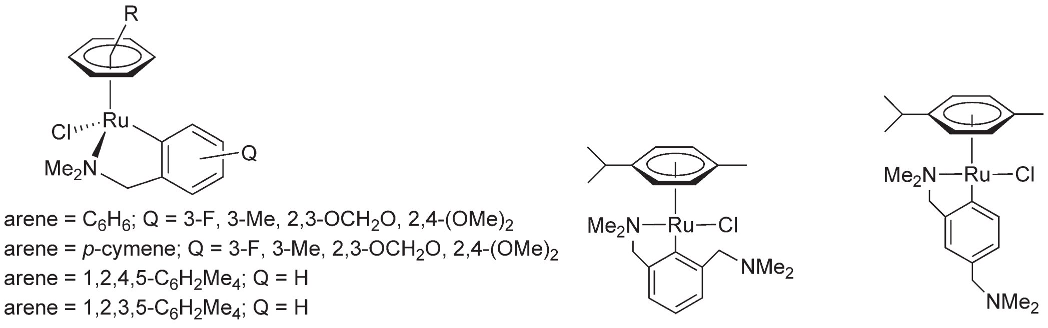


270* (20)

6.15.3.3 Cyclometallated Complexes

The ability of η^6-arene ruthenium and osmium complexes to promote cyclometallation processes is well documented (see COMC (1995)). This feature has continued to be of primary interest in the last few years. In particular, the dimeric precursors $[\{MCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ are more prone to form cyclometallated derivatives. Although they are able to promote intramolecular C–H activation in aryl or alkyl moieties of coordinated ligands, most frequently, transmetallation reactions using mercurated or zincated reagents turn out to be the more suitable synthetic approach. Cyclometallated *N*-donor complexes resulting from the activation of the aryl C–H bond in aryl amino, imino, and azo ligands, among others, are typical examples.

Cycloruthenated complexes **271** (Figure 35) bearing a rigid five-membered *C,N*-chelate ring can be obtained by transmetallation of dimers $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ with mercurated derivatives of a variety of



arene = C_6H_6; Q = 3-F, 3-Me, 2,3-OCH_2O, 2,4-$(OMe)_2$
arene = *p*-cymene; Q = 3-F, 3-Me, 2,3-OCH_2O, 2,4-$(OMe)_2$
arene = 1,2,4,5-$C_6H_2Me_4$; Q = H
arene = 1,2,3,5-$C_6H_2Me_4$; Q = H

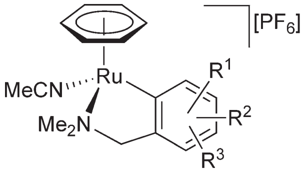
271 **272*** **273***

Figure 35 Structure of the cyclometallated Ru(II) complexes **271**–**273**.

N,*N*-dimethylbenzylamines. These reactions are governed by steric rather than electronic factors since an increase in the number of alkyl substituents in the η^6-arene ligand, or the presence of bulky groups *ortho* to Hg in the starting material, leads to a significant decrease of the yields of the cycloruthenated products.[261] Remarkably, attempts to prepare complexes **271** by using either lithium derivatives of the ligands or an intramolecular C–H activation, via direct reaction of the dimer with the free *N*,*N*-dimethylbenzylamines, have been unsuccessful or lead to very low yields.[261] In contrast, the lithium salt of 1,3-bis[(dimethylamino)methyl]benzene $[\text{Li}\{2,6\text{-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\}]_2$ is found to be a suitable reagent for transmetallation in the reaction with $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-cymene})\}_2]$ affording the cyclometallated derivative **272***. This complex undergoes an intramolecular rearrangement in refluxing benzene to give the isomer **273*** which results from a shift of the metal–C_{aryl} bond from position 1 to position 3 on the aromatic ring of the metallated NCN ligand. Complex **273** can also be obtained, in low yield but in a one-pot manner, by reaction at RT of 1,3-bis[(dimethylamino)methyl]benzene with $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-cymene})\}_2]$ in the presence of $\text{Na}[\text{PF}_6]$.[44]

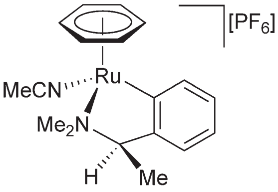
A synthetic strategy avoiding the use of transmetallation reagents has been applied, starting from benzylamines. It has been found that using acetonitrile as solvent, cycloruthenation of a large variety of *N*,*N*-dimethylbenzylamines takes place by reaction with $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{H}_6)\}_2]$ in the presence of a mixture of NaOH and $\text{K}[\text{PF}_6]$, affording cationic complexes **274** in good yields (Figure 36).[262,263] Reaction with the enantiomerically pure (*R*)-(+)-*N*,*N*-dimethyl-1-phenylethylamine leads to a mixture of diastereomeric ruthenacycles **275** in $R_\text{C}S_\text{Ru}/R_\text{C}R_\text{Ru}$ ratio ca. 3 : 1.[262]

The enantiomerically pure mercurated (*R*)-(+)- or (*S*)-(−)-*N*,*N*-dimethyl-1-phenylethylamine react with $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$ (arene = C_6H_6, toluene, *p*-cymene) in CH_3CN at RT to form in each case a mixture of two diastereomeric ruthenacycles **276** (($R_\text{C}S_\text{Ru}$) major and ($R_\text{C}R_\text{Ru}$) minor or ($S_\text{C}R_\text{Ru}$) major and ($S_\text{C}S_\text{Ru}$) minor) in good yield (Figure 37).[264] The 20 : 1 diastereoisomeric ($R_\text{C}S_\text{Ru}$) and ($R_\text{C}R_\text{Ru}$) mixture of the η^6-benzene complexes readily undergoes clean metathesis reactions with an excess of NaBr or NaI in CH_2Cl_2/EtOH solution to form in a stereospecific manner the corresponding bromo* and iodo* analogs (ca. 93–94% de in each mixture).[265] Pseudohalide azide, nitrite, thiocyanate, and cyanate derivatives have also been prepared in a diastereoselective manner from **276** through the corresponding halide substitution.[266*] Substitution reactions of acetonitrile by PMe_2Ph in cationic complexes **275** lead to the corresponding ruthenacycles **277** as a diastereomeric ($R_\text{C}S_\text{Ru}$) and ($R_\text{C}R_\text{Ru}$) mixture in 60/40 ratio.[267]



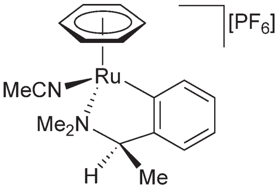
274

R^1	R^2	R^3
H	H	H
4-Me	H	H
3-Me	4-Me	H
4-OMe	H	H
3-OMe	H	H
2-OMe	3-OMe	H
3-OMe	4-OMe	H
3-OMe	5-OMe	H
2-OMe	3-OMe	4-OMe
3-OMe	4-OMe	5-OMe
4-F	H	H
3-CF_3	H	H
3-NO_2	H	H
4-CF_3	H	H
4-Bu^t	H	H
4-NMe_2	H	H
4-NO_2	H	H
4-CN	H	H



$R_\text{C}S_\text{Ru}$

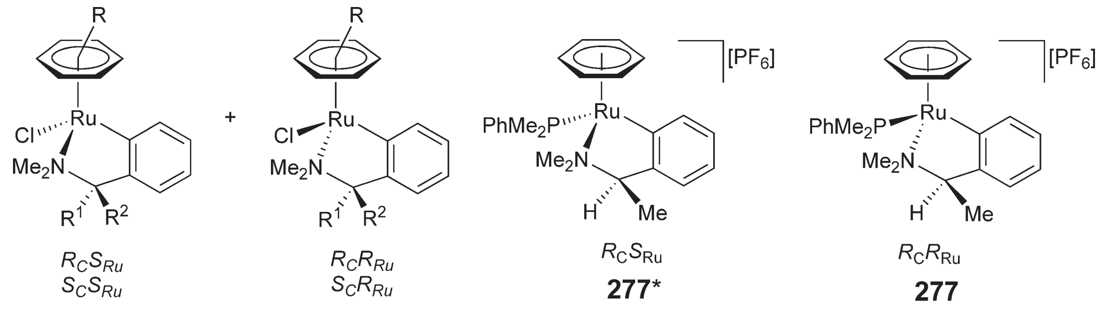
275



$R_\text{C}R_\text{Ru}$

275

Figure 36 The cyclometallated Ru(II) complexes **274** and **275**.



R_CS_{Ru}
S_CS_{Ru}

R_CR_{Ru}
S_CR_{Ru}

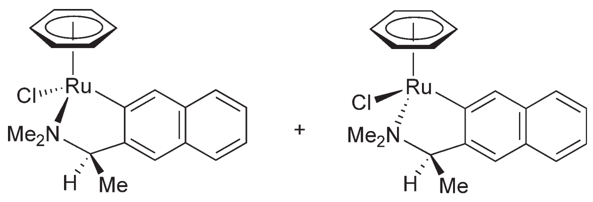
R_CS_{Ru}
277*

R_CR_{Ru}
277

arene = C_6H_6, *p*-cymene, toluene
(R_C) R^1 = H, R^2 = Me
(S_C) R^1 = Me, R^2 = H
(R_CS_{Ru})* (arene = *p*-cymene)
(S_CR_{Ru})* (arene = C_6H_6, toluene)

276

Figure 37 Structure of the chiral complexes **276** and **277**.



R_CS_{Ru}
278*

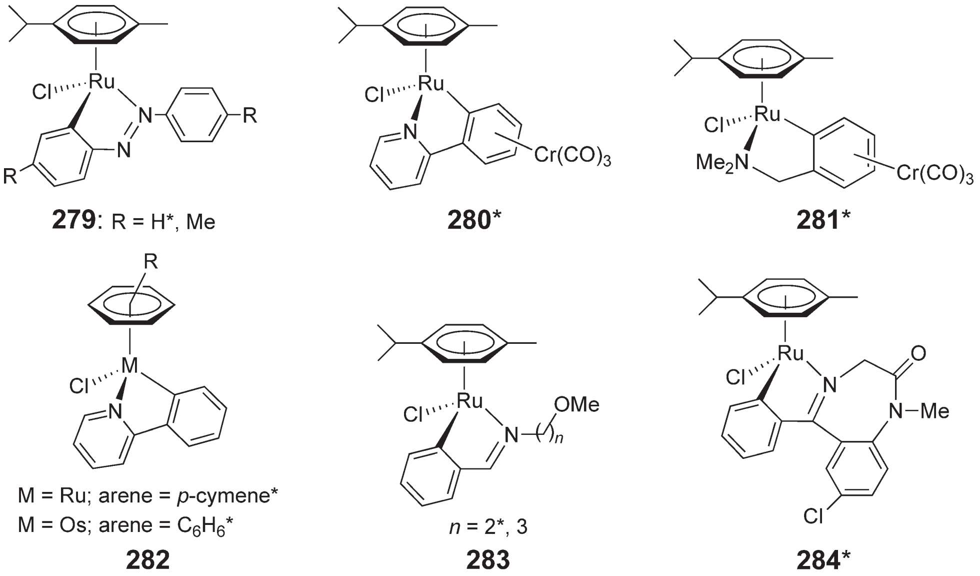
R_CR_{Ru}
278

Figure 38 The naphthyl-ruthenium complexes **278**.

Analogous cyclometallated ruthenium complexes 278 (Figure 38) have been synthesized from [{RuCl(μ-Cl)(η^6-C_6H_6)}$_2$] through transmetallation reactions with enantiomerically pure mercurated (*R*)-(+)-*N*,*N*-dimethyl-α-(2-naphthyl)ethylamine. Subsequent chloride substitutions of the resulting mixture of the two diastereomers ((R_CS_{Ru}) major and (R_CR_{Ru}) minor) by bromide, iodide, azide, cyanate, thiocyanate, and nitrite gives rise to the isolation of large series of neutral cyclometallated derivatives. Substitutions of chloride by two-electron-donor nitrogen and phosphorus ligands lead to cationic complexes. Diastereoselective ligand substitutions are generally observed and confirmed by extensive X-ray crystal structure determinations.[268*] Related cyclometallated derivatives containing the (η^6-toluene)–ruthenium fragment have also been prepared.[269*]

Although the cyclometallated ruthenium complexes were formerly claimed to be configurationally stable at the stereogenic metal, Brunner and co-workers have shown that they are indeed configurationally labile. Revisiting previous NMR spectroscopic data, variable-temperature NMR studies (−80 to 21 °C) were carried out, and showed that epimerization processes take place.[270,270a,271] This has also been assessed by the isolation of cyclometallated ruthenium and osmium derivatives which have been synthesized through transmetallation reactions of [{MCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (M = Ru, Os) with the enantiomerically pure mercurated (*S*)-(+)-*N*,*N*-dimethyl(1-phenyl)ethylamine. In both cases, two diastereoisomers (R_M,S_C) and (S_M,S_C) were obtained, which undergo epimerization in solution showing that they are labile. On crystallization, the (R_M,S_C)-isomers were obtained in a diastereomerically pure manner and their structures determined by X-ray structure analysis.[272] It is apparent that previous misinterpretation of the configurational stability at the metal atom must be corrected.

A range of azo and imine derivatives has also been shown to be suitable for cyclometallation reactions. Thus, cycloruthenated (phenylazo)phenyl and 4,4′-dimethyl(phenylazo)phenyl derivatives 279 (Figure 39) have been obtained by reactions of the corresponding mercurated azo derivatives with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] in refluxing $CHCl_3$ or MeOH.[273] Transmetallation methodology has also proved to be efficient for the cycloruthenation of



279: R = H*, Me

280*

281*

M = Ru; arene = *p*-cymene*
M = Os; arene = C_6H_6*

282

n = 2*, 3

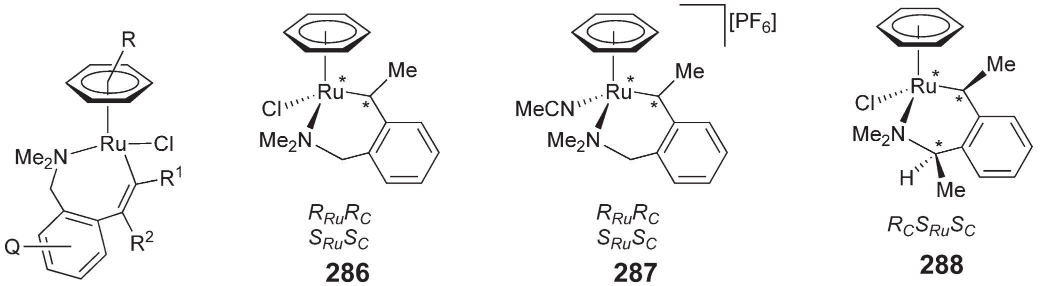
283

284*

Figure 39 The cyclometallated derivatives **279**–**284**.

substituted pyridines, as exemplified by the reaction of racemic *ortho*-mercurated 2-[tricarbonyl(η^6-phenyl)chromium]pyridine with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$], which affords the corresponding dinuclear product 280* in moderate yield.[274] An analogous dinuclear complex 281*, obtained by reaction with *ortho*-mercurated tricarbonyl(η^6-*N*,*N*-dimethylbenzylamine)chromium, has also been isolated.[274] In both cases, the direct ruthenation methodology, using basic conditions and in the presence of K[PF_6], was found to give only decomposition products. The dinuclear derivative 280 spontaneously evolves in solution by loss of the $Cr(CO)_3$ moiety to afford complex 282* (M = Ru, arene = *p*-cymene), which can alternatively be obtained by reaction of [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with mercurated 2-phenylpyridine.[274] The synthesis of a related cyclometallated (η^6-benzene)–osmium complex from [{OsCl(μ-Cl)(η^6-C_6H_6)}$_2$] and mercurated 2-phenylpyridine has been reported.[275] Despite all these examples that seem to disfavor the synthetic approach using basic reagents, cyclometallation of both alkylimines derived from benzaldehyde (complexes 283) and benzodiazepine (complex 284*) by [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] has been achieved in the presence of Na[OAc] and Et_3N/Na[BPh_4], respectively, at RT.[276,277] Other orthometallated *N*-phenyltriazolinylidene complexes are also known (see Section 6.15.3.6).

Insertion reactions of unsaturated organic substrates into the Ru–C bond of aryl-cycloruthenated complexes have been reported. Thus, alkenyl-type derivatives 285 (Figure 40) have been synthesized by reacting ruthenacycles



R$_{Ru}$*R*$_C$
S$_{Ru}$*S*$_C$
286

R$_{Ru}$*R*$_C$
S$_{Ru}$*S*$_C$
287

R$_C$*S*$_{Ru}$*S*$_C$
288

$R^1 = CO_2Et$; R^2 = Ph; arene = C_6H_6; Q = H, 5-Me, 4,5-OCH_2O, 4,5-$(OMe)_2$
$R^1 = R^2 = CO_2Me$; arene = C_6H_6; Q = H, 5-F, 5-Me, 4,5-OCH_2O, 4,5-$(OMe)_2$
$R^1 = R^2 = CO_2Me$; arene = *p*-cymene; Q = H, 5-F, 4,5-OCH_2O, 4,5-$(OMe)_2$

285

Figure 40 Arene-Ru(II) complexes **285**–**288**.

271 with the activated alkynes $PhC{\equiv}CCO_2Et$ and $MeO_2CC{\equiv}CCO_2Me$.[278] The cycloruthenated *N*,*N*-dimethylbenzylamine complexes $[RuCl\{\kappa^2\text{-}(C,N)\text{-}2\text{-}C_6H_4CH_2NMe_2\}(\eta^6\text{-}C_6H_6)]$ and $[Ru\{\kappa^2\text{-}(C,N)\text{-}2\text{-}C_6H_4CH_2\text{-}NMe_2\}(\eta^6\text{-}C_6H_6)(NCMe)][PF_6]$ also react with ethylene under mild conditions (MeOH/RT) to afford, besides free 2-vinyl-*N*,*N*-dimethylbenzylamine, the new organoruthenium derivatives 286 and 287, respectively. Interestingly, both complexes, which result from the overall insertion of only one carbon atom in the Ru–C bond of the starting materials, are obtained in a diastereoselective manner (a racemic mixture of the (R_{Ru},R_C) and (S_{Ru},S_C) enantiomers is formed). The chiral control of this insertion process was assessed by reacting the optically active complex (R_C,S_{Ru})-$[RuCl\{\kappa^2\text{-}(C,N)\text{-}2\text{-}C_6H_4CH(Me)NMe_2\}(\eta^6\text{-}C_6H_6)]$ (type 276) with ethylene which leads to complex 288 as a single enantiomer.[279]

Cyclometallated complexes obtained via activation of aliphatic C–H bonds are also known. Their formation generally arises from the enhanced acidity of the C–H bond in α-position to the phosphorus atom of a ligand. In this respect, methanide anions formed by deprotonation with strong bases of methylenic groups of bidentate bis(iminophosphorano)methane or (iminophosphorano–phosphine)methane ligands have been used as transmetallation reagents to give cycloruthenated complexes. Typical examples are complexes 289–293 (Figure 41), which have been obtained as air-stable solids in good yield by reactions of the lithium or sodium methanide salts with the appropriate (η^6-arene)–ruthenium precursor.[280–282] Analogous deprotonations in the methylenic group of the

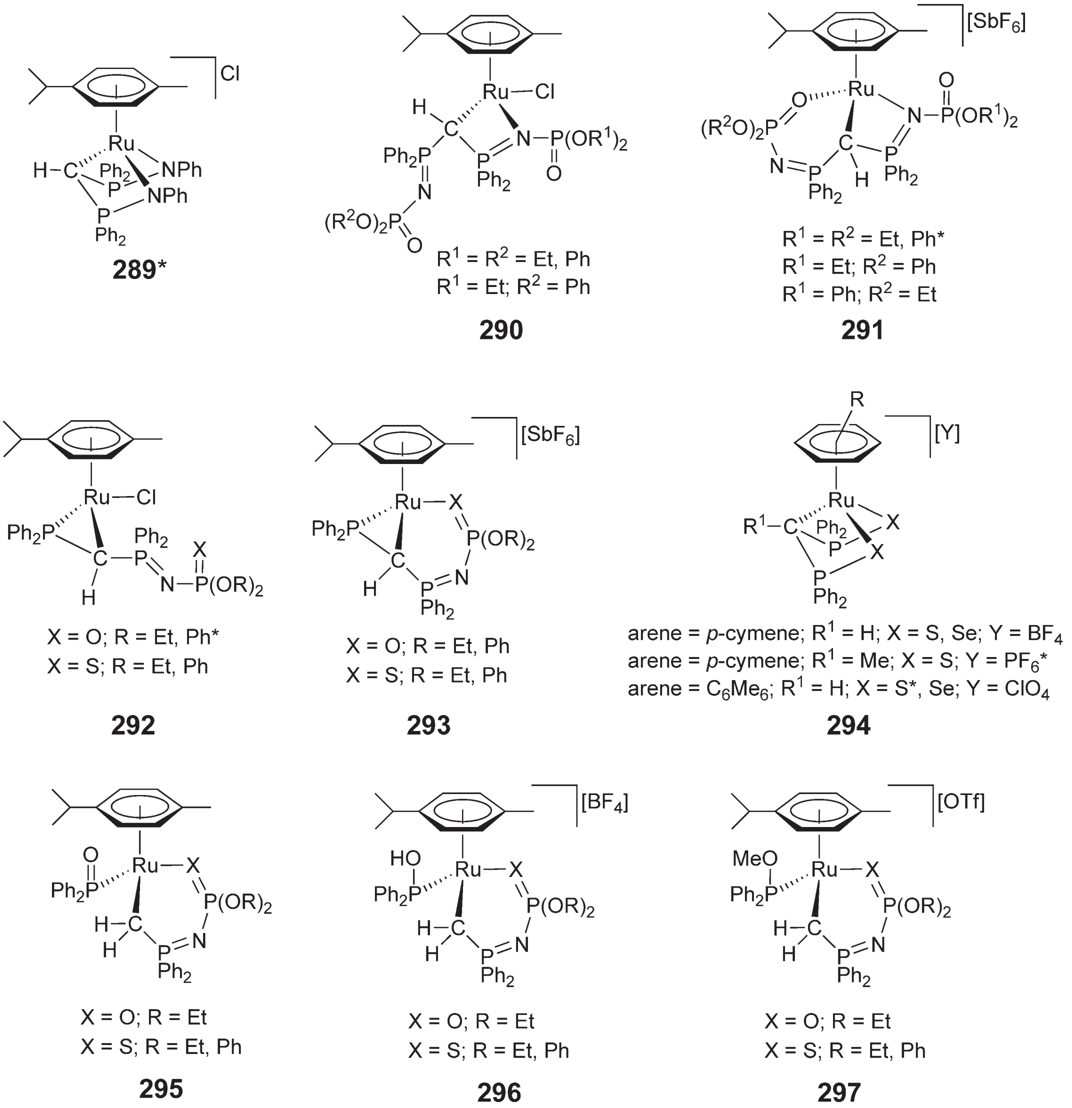
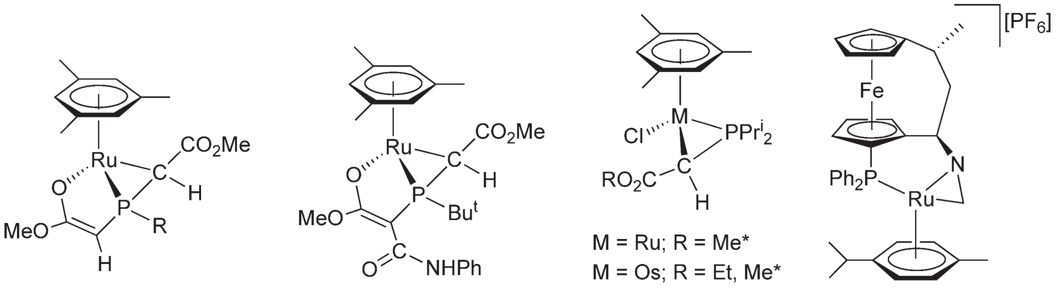


Figure 41 Ru(II) complexes obtained by aliphatic C–H bond activation.



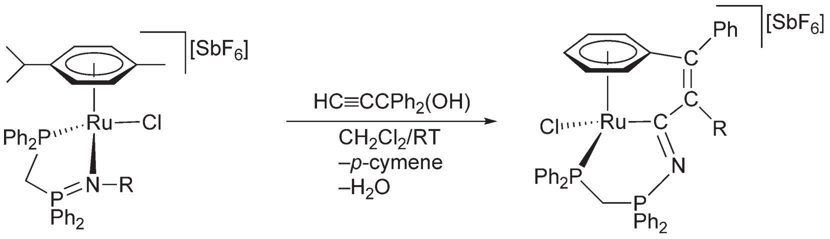
298: R = Bu^t, Pr^{i*} **299** **300** **301***

Figure 42 The structure of compounds **298**–**301**.

coordinated dichalcogenides $CH_2\{P({=}X)Ph_2\}_2$ (X = S, Se) and $CHMe\{P({=}S)Ph_2\}_2$ in cationic complexes $[RuCl(\kappa^2(X,X)\text{-}CHR\{P({=}X)Ph_2\}_2)(\eta^6\text{-arene})][Y]$ afford the cyclometallated derivatives 294.[283–285] Despite the stability of these metallacycles, the corresponding P–C bonds become reactive and are prone to cleavage, generating novel ruthenacycles. As an example, treatment of complexes 292 or 293 with an excess of NaH in THF/H_2O generates the phosphinito derivatives 295, which formally arise from an OH^--promoted P–C bond splitting with concomitant formation of P=O and C–H bonds. Protonation and methylation of these complexes take place selectively at the oxygen atom of the phosphinito group, affording the cationic species 296 and 297, respectively.[282]

In a similar way, the dicationic complexes $[Ru\{\kappa^3(P,O,O)\text{-}RP(CH_2CO_2Me)_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]_2$ (R = Pr^i, Bu^t) react with an excess of KOBu^t in Bu^{t}OH to give the bicyclic $\kappa^3(P,C,O)$-derivatives 298, containing both a five-membered phosphino-enolate and a three-membered phosphinomethanide ring, as the result of the deprotonation of the two methylenic units of the coordinated tridentate ligand (Figure 42). The insertion of PhCNO into the olefinic =C–H bond of one of these complexes (R = Bu^t) results in the formation of the ruthenabicycle 299.[286,286a] The bidentate β-phosphino-ester ligand in complex $[RuCl\{\kappa^2(P,O)\text{-}Pr^i{}_2PCH_2CO_2Me\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]$ is also easily deprotonated. However, the resulting phosphino-enolate complex $[RuCl\{\kappa^2(P,O)\text{-}Pr^i{}_2PCH{=}C(OMe)O\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ is thermally labile and slowly rearranges in benzene at RT to give the thermodynamically more stable $\kappa^2(P,C)$-metallated isomer 300.[287,287a] Related osmium derivatives are also known, being obtained by reacting $[OsCl_2\{\kappa^1(P)\text{-}Pr^i{}_2PCH_2CO_2R\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (R = Me, Et) with Al_2O_3/NaH.[288] Deprotonation of aliphatic C–H bonds in the α-position to a nitrogen atom is rare. Nevertheless, a selective C–H abstraction at an N–CH_3 moiety has been reported to occur in the reaction of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ with a bidentate [3]ferrocenophane $\kappa^2(P,N)$-chelate ligand and K[PF_6], which leads to a mixture containing the cyclometallated complex 301*.[289]

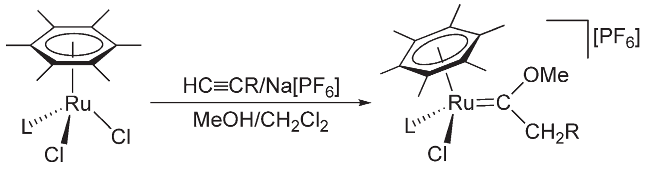
During the course of studies on the chemistry of allenylidene (η^6-*p*-cymene)–ruthenium complexes containing chelate iminophosphorane groups –PPh_2=NR, an unusual C–C coupling with concomitant elimination of the *p*-cymene ring was discovered (Equation (21)). The reaction, which proceeds at RT, generates a new class of tethered arene ruthenium(II) complexes with pendant *P*- and *C*-donor atoms exhibiting two stable ruthenacarbocycles 302.[290]



R = 4-C_5F_4N, 4-C_6F_4CN, 4-C_6F_4CHO, 3,4-$C_6F_3(CN)_2$* **302** (21)

6.15.3.4 Fischer-type Carbene Complexes

Similar to the analogous η^5-C_5 complexes (see Section 6.15.2.5), half-sandwich η^6-C_6 Fischer-type carbenes have also been prepared from vinylidene and allenylidene derivatives (either isolated or formed *in situ*). Most of them are related to those described in COMC (1995), adding new members to this series of complexes. Thus, following previous studies, Dixneuf and co-workers have prepared new methoxycarbene ruthenium(II) derivatives $[RuCl\{=C(OMe)CH_2R\}(\eta^6\text{-}C_6Me_6)L][PF_6]$ **303** by the reaction of terminal alkynes with $[RuCl_2(\eta^6\text{-}C_6Me_6)L]$ in methanol and in the presence of $Na[PF_6]$ (Equation (22)).[291] Under the same reaction conditions, $HC\equiv CSiMe_3$ undergoes C–Si bond cleavage to afford $[RuCl\{=C(OMe)Me\}(\eta^6\text{-}C_6Me_6)L][PF_6]$ ($L = PPh_2Fc$, $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4COOH)$ (Hdpf)). It is now well known that the intermediate complexes in all these processes are vinylidene derivatives.



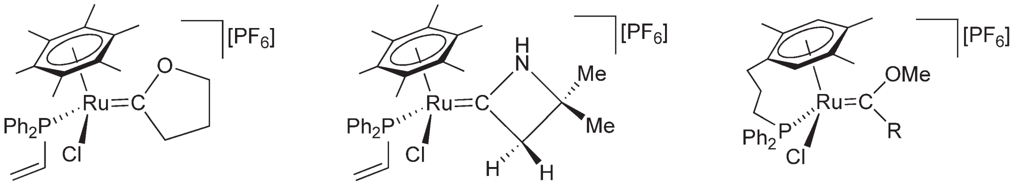
303

R = Fc; L = PMe_3, PPh_3, PPh_2Fc, Hdpf*
R = Ph; L = PPh_2Fc, Hdpf
Hdpf = $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4COOH)$ (22)

Analogous methoxy-carbenes $[RuCl\{=C(OMe)Me\}(\eta^6\text{-}C_6Me_6)(PR_3)][PF_6]$ ($PR_3 = PMe_3{}^*$, $PPh_3{}^*$, $Ph_2PCH=CH_2{}^*$) and $[RuCl\{=C(OMe)CH_2Ph\}(\eta^6\text{-}C_6Me_6)(PR_3)][PF_6]$ ($PR_3 = PMe_3{}^*$, $PPh_3{}^*$, $Ph_2PCH=CH_2{}^*$) have also been synthesized by reacting $[RuCl(\eta^6\text{-}C_6Me_6)(NCMe)(PR_3)][PF_6]$ with the corresponding terminal alkyne in methanol. When 3-butyn-1-ol is used as alkyne, the cyclic oxycarbene **304*** is formed through an intramolecular nucleophilic addition of the OH group at the C_α-atom of the intermediate hydroxo–vinylidene complex. The cyclic amino–carbene complex **305** is also formed, albeit in a very low yield, from the reaction with dimethylpropargyl amine (Figure 43).[258]

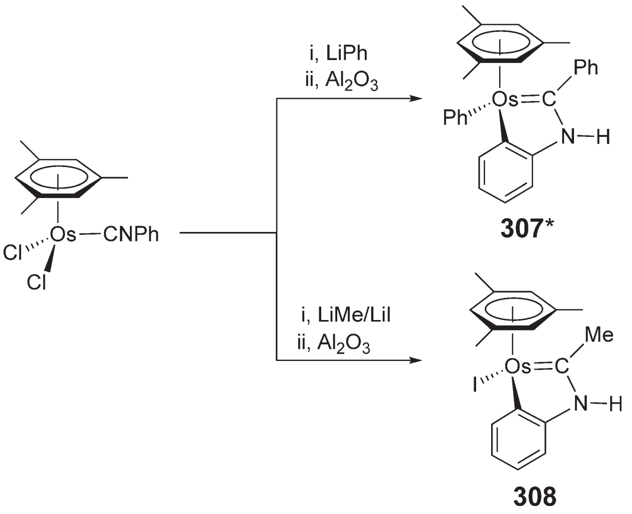
The following (η^6-arene)–ruthenium complexes, prepared through this straightforward manner from terminal alkynes, have also been isolated: (i) $[RuCl\{=C(OMe)R\}(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)\{\kappa^1(P)\text{-}Ph_2PCH=CH_2\}][PF_6]$ ($R = CH_2Ph$, Me^*),[292] (ii) $[RuCl\{=C(OMe)CH_2R\}(\eta^6\text{-}C_6Me_6)\{\kappa^1(P)\text{-}Ph_2PCH=CH_2\}][PF_6]$ (R = 1-cyclehexenyl),[293] (iii) tethered derivatives **306** ($R = CH_2Ph^*$, Me^*; Figure 43),[292] and (iv) $[Ru\{=C(OMe)CH_2Ph\}(\eta^6\text{-}C_6Me_6)\{\kappa^2(P,O)\text{-}Ph_2P(2\text{-}O\text{-}6\text{-}C_6H_3OMe)\}][PF_6]$.[251]

In addition, α,β-unsaturated methoxy-carbenes are isolated from similar reactions with alkynols $HC\equiv CCR_2(OH)$ in methanol or ethanol. Examples include the ruthenium complexes $[RuCl\{=C(OMe)CH=CC_4H_8\}(\eta^6\text{-}C_6Me_6)\{\kappa^1(P)\text{-}Ph_2PCH=CH_2\}][PF_6]$ (CC_4H_8 = cyclopentylidene),[293] **306** ($R = CH=CPh_2{}^*$; Figure 43),[292] $[Ru\{=C(OMe)CH=CMe_2\}(\eta^6\text{-}C_6Me_6)\{\kappa^2(P,O)\text{-}Ph_2P(2\text{-}O\text{-}6\text{-}C_6H_3OMe)\}][PF_6]$,[251] and $[RuCl\{=C(OMe)\text{-}(E)\text{-}CH=CH\text{-}2\text{-}C_6H_4OMe\}(\eta^6\text{-}C_6Me_6)(PMe_3)][PF_6]$,[294] and the osmium derivatives $[OsCl\{=C(OR)CH=CPh_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PMe_3)][PF_6]$ ($R = Me$, Et^*).[260] These complexes are probably generated via the allenylidene intermediates $M^+=C=C=CR_2$, which undergo nucleophilic addition of the alcohol (methanol or ethanol) at the electrophilic C_α-atom of the cumulenic chain. More elaborate Fischer-type alkenyl carbenes containing functional or highly conjugated substituents, such as $[RuCl\{=C(OMe)\text{-}(E)\text{-}CH=CH\text{-}4\text{-}C_6H_4R\}(\eta^6\text{-}C_6Me_6)(PMe_3)][PF_6]$ ($R = CH(OH)C\equiv CH$, CHO, $CH=CH_2$, $CH=CHCH=CH_2$),[161] $[RuCl\{=C(OMe)\text{-}(E)\text{-}CH=CH\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH=CHCO_2Me\}(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PMe_3)][PF_6]^*$,[295] and $[RuCl\{=C(OMe)CH=C=C=CPh_2\}(\eta^6\text{-}C_6Me_6)(PMe_3)][PF_6]$,[252] have also been synthesized, although the intermediate cumulenylidene complexes $[RuCl\{=C=C=CH(4\text{-}C_6H_4R)\}(\eta^6\text{-}arene)(PMe_3)][PF_6]$ and $[RuCl(=C=C=C=C=CPh_2)(\eta^6\text{-}C_6Me_6)(PMe_3)][PF_6]$, respectively, have neither been isolated nor detected. Probably because of their high electrophilicity, these complexes are prone to undergo methanol addition to give the Fischer-type carbenes. In fact, the latter not only is able to add methanol at the C_α- but also at the C_γ-atom to give simultaneously the alkoxy allenylidene



304* **305** **306**: R = Me*, CH_2Ph^*, $CH=CPh_2{}^*$

Figure 43 Fischer-type ruthenium carbenes **304**–**306**.



Scheme 29

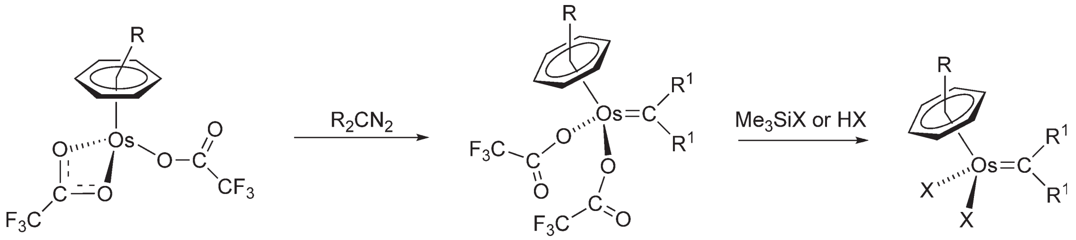
$[RuCl({=}C{=}C{=}C(OMe)CH{=}CPh_2)(\eta^6\text{-}C_6Me_6)(PMe_3)][PF_6]$.[252] Despite the ability of these cumulenylidene η^6-arene complexes to undergo nucleophilic additions, it should be noted that the related allenylidenes $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}p\text{-cymene})(PR_3)][PF_6]$ ($PR_3 = PCy_3$, PPr^i_3, PPh_3) are unreactive toward alcohols, reflecting, as shown for η^5-C_5 complexes (see Section 6.15.2.5), the influence of the electronic and/or steric properties of the metal fragments to enable the nucleophilic additions.[296,296a,296b]

The synthesis of the orthometallated Os(II) amino-carbenes **307*** and **308**, obtained by reacting the isocyanide precursor $[OsCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CNPh)]$ with an excess of PhLi or MeLi/LiI, respectively, has also been reported (Scheme 29).[239,240]

6.15.3.5 Alkylidene and Alkylidyne Complexes

η^6-Arene (C_6) –alkylidene and –alkylidyne complexes are much more scarce than those of η^5-C_5 derivatives. As for the Cp–Ru and –Os alkylidenes (see Sections 6.15.2.6 and 6.15.2.10), the diazoalkane route, via elimination of N_2, has also been used as a synthetic procedure. However, only osmium derivatives were isolated as stable species. Although initial attempts to prepare $[OsX_2({=}CR_2)(\eta^6\text{-arene})]$ from the reactions of $[\{OsX(\mu\text{-}X)(\eta^6\text{-arene})\}_2]$ ($X = Cl$, Br, I) with diazo compounds failed, an efficient synthetic approach has been found, starting from the bis-trifluoroacetate complexes $[Os\{\kappa^1(O)\text{-}O_2CCF_3\}\{\kappa^2(O,O)\text{-}O_2CCF_3\}(\eta^6\text{-arene})]$. Thus, the treatment of these precursors with a solution of the corresponding diaryldiazomethane in benzene gives alkylidene complexes **309**, isolated as moderately air sensitive solids in good yields (Scheme 30). Using the bis-trifluoroacetate carbene complexes **309** as starting materials, the corresponding halide derivatives $[OsX_2({=}CR_2)(\eta^6\text{-arene})]$ ($X = Cl$, Br, I) **310** become accessible either by reaction with Me_3SiX or through the treatment with HCl or HBr in benzene. Complexes **310** have also been obtained as air-stable solids in good yields. In addition, the treatment of $[OsCl_2({=}CR_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ with $Ag[PF_6]$ and PPh_3 in THF gives the cationic alkylidenes $[OsCl({=}CR_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPh_3)][PF_6]$ ($R = C_6H_5$, $p\text{-}C_6H_4Me^*$).[242,297]

In contrast to osmium, alkylidene–ruthenium derivatives prepared by the diazoalkane route are very reactive compounds generally proposed as transient species either in stoichiometric processes or catalytic metathesis of olefins. Nevertheless, it should be noted that coordinatively unsaturated species, generated by displacement of the η^6-arene ring, have been usually proposed as the real active species in these catalytic processes. Illustrative examples are: (i) transient vinyl–alkylidene species $[RuCl_2\{{=}C(CO_2Me)C(R^1){=}CH(R^2)\}(\eta^6\text{-arene})]$ formed in the reactions of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ with vinyldiazoacetates, which afford the η^3-allyl complexes $[RuCl\{\eta^3\text{-}CCl(CO_2Me)C(R^1)CH(R^2)\}(\eta^6\text{-arene})]$;[298] (ii) alkylidene–ruthenium complexes formed when dichloride precursors $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ are activated by addition of trimethylsilyldiazomethane, and proposed as active catalytic species in ROMP of functionalized norbornenes and cyclooctenes;[299] and (iii) the methylidene-tethered phosphine complexes $[RuMe({=}CH_2)\{\eta^6{:}\kappa^1(P)\text{-}C_6H_5CH_2CH_2PR_2\}][PF_6]$ ($R = Ph$, Cy) proposed as key intermediates in the

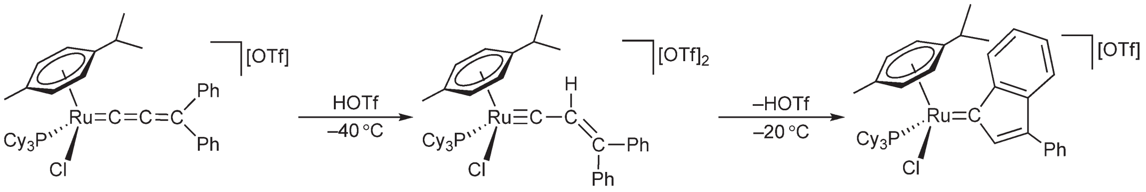


309 **310**

Arene	R^1
C_6H_5Me	p-C_6H_4Me
p-cymene	C_6H_5
p-cymene	p-C_6H_4Me
1,3,5-$C_6H_3Me_3$	C_6H_5
1,3,5-$C_6H_3Me_3$*	p-C_6H_4Me*
1,3,5-$C_6H_3Me_3$	p-C_6H_4Cl
1,3,5-$C_6H_3Me_3$	p-C_6H_4OMe

X	Arene	R^1
Cl, Br, I	p-cymene	C_6H_5
Cl, Br, I	p-cymene	p-C_6H_4Me
Cl*, Br, I	1,3,5-$C_6H_3Me_3$*	C_6H_5*
Cl	1,3,5-$C_6H_3Me_3$	p-C_6H_4Me
Cl	1,3,5-$C_6H_3Me_3$	p-C_6H_4OMe

Scheme 30



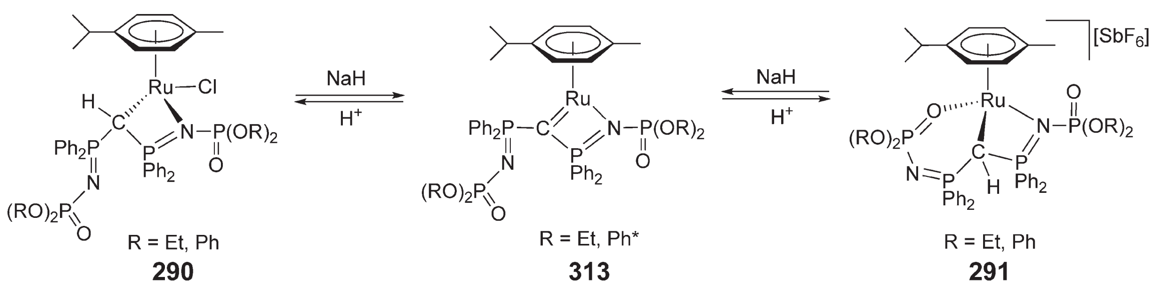
311 **312**

Scheme 31

formation of the hydride–olefin derivatives [RuH(η^2-$CH_2{=}CH_2$){η^6:κ^1(P)-$C_6H_5CH_2CH_2PR_2$}][PF_6] from the reactions of [$RuMe_2${η^6:κ^1(P)-$C_6H_5CH_2CH_2PR_2$}] with [Ph_3C][PF_6].[300]

The ability of allenylidene complexes [RuCl(=C=C=CPh$_2$)(η^6-p-cymene)(PR$_3$)][X] to promote catalytic RCM of dienes and enynes, as well as ROMP reactions,[301] has led to the discovery that the protonation of [RuCl(=C=C=CPh$_2$)(η^6-p-cymene)(PCy$_3$)][OTf] with HOTf largely increases the rate of these catalytic processes. Monitoring the protonation by NMR spectroscopy, the formation of a transient carbyne at −40 °C, that is, [RuCl(≡CCH=CPh$_2$)(η^6-p-cymene)(PCy$_3$)][OTf]$_2$ **311**, and subsequent conversion into the 3-phenyl-1-indenylidene complex **312** at −20 °C, is observed (Scheme 31).[302] Complex **311**, which is only stable at low temperature, is the only C_6-carbyne that has been described till now in the literature. The indenylidene derivative **312** results from the formal substitution of an *ortho*-H of the phenyl groups by the electrophilic C_α-carbon atom of the carbyne moiety in **311**, with concomitant elimination of HOTf. An analogous transformation is also observed in the protonation of the Cp–Os(II) allenylidene [Os(=C=C=CPh$_2$)Cp(CO)(PPr$^i_3$)][PF$_6$] to give the analogous 3-phenyl-1-indenylidene complex **178** (see Equation (15)). In contrast to the Cp–osmium derivative **178**, which has been isolated as an air-stable solid, the C_6-indenylidene–ruthenium complex **312** decomposes at RT, but it has proved to be highly active for ROMP of cyclooctene and cyclopentene and RCM of dienes.[302]

Finally, it is interesting to note that treatment of metallated bis(iminophosphorano)methanide–ruthenium complexes **290** or **291** with an excess of NaH leads to unprecedented ruthenium carbenes [Ru(κ^2(C,N)-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)(η^6-p-cymene)] **313** via deprotonation of the acidic σ-Ru–CH proton (see Scheme 32). DFT calculations on the model [Ru(κ^2(C,N)-C[P{=NP(=O)(OMe)$_2$}Me$_2$]$_2$)(η^6-C_6H_6)] suggest a nucleophilic character for the carbon atom in the Ru=C unit. In agreement with this theoretical prediction, protonation of complexes **313** with HCl or HBF$_4$ takes place selectively on the carbenic carbon regenerating the σ-Ru–CH moiety of the starting complexes.[281] These unusual carbenes belong to a scarce series of transition metal complexes in which the carbene moiety is part of a four-membered chelate ligand in a κ^2(C,N)-coordination mode. This type of compound has been recently reviewed.[303]



Scheme 32

6.15.3.6 Complexes Containing NHCs

Similar to the η^5-C_5 analogs, the last decade has witnessed the development of the chemistry of η^6-arene derivatives containing NHCs. It is interesting to note that no examples were described in COMC (1995). These complexes are accessible through three synthetic routes depending on the precursor of the NHC ligand:

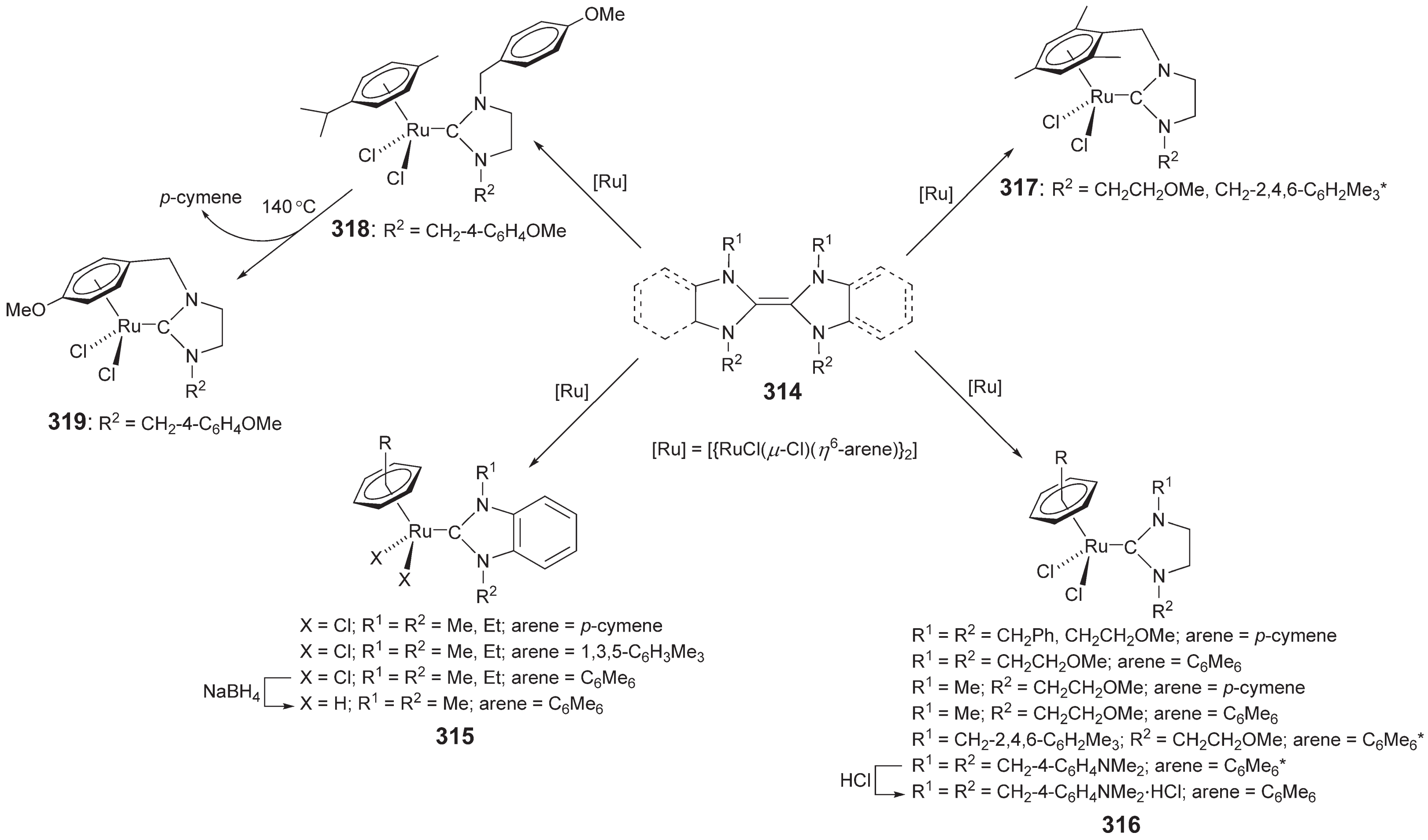
(i) From electron-rich enetetra-amines **314**, which undergo the cleavage of the C=C bond by reaction with $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ in toluene or xylene at 100 °C to give neutral complexes of general composition $[RuCl_2(NHC)(\eta^6\text{-arene})]$ (see Scheme 33). Benzimidazolidin-2-ylidene **315** and imidazolidin-2-ylidene complexes **316–319** have been prepared through this methodology in good yields and isolated as air-stable solids.[304–307a] In addition, a series of ruthenium complexes $[RuCl_2(NHC)(\eta^6\text{-arene})]$ (arene = *p*-cymene, C_6Me_6) have been immobilized by sol–gel methodology to give morphologically different silicas which can act as recyclable catalysts for furan formation.[308]

(ii) From NHC ligands, either isolated or generated *in situ* (from the appropriate imidazolium salt), in the presence of dimeric precursors $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$. Typical examples are complexes **320** (Figure 44) formed in high yields by the reaction of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ with 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) in THF at RT.[309] A large number of this type of complex (**320**; R^1 = aryl or alkyl group; R^2 = H, Cl, or alkyl group) have been generated *in situ* and proved to be efficient catalysts in ROMP of cyclooctene,[310] and in atom-transfer radical polymerization of methyl methacrylate and styrene.[311] However, it is claimed that the active species does not contain the arene group. The tethered derivative **321** has also been synthesized using this methodology.[307,307a] Related cationic complexes **322**, containing a bidentate NHC ligand, have been isolated by the reaction of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ with the double deprotonated NHC precursors methylenebis(*N*-methylimidazolium) iodide and ethylenebis(*N*-methylimidazolium) chloride. Complexes **323** resulting from the monodeprotonation of this type of NHC precursors could be prepared also.[312] *N*-Phenyltriazolium perchlorate salts have also been used as precursors of triazolinylidene ligands, which react *in situ* with $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ to afford the orthometallated *N*-phenyltriazolinylidene complexes **324** (X = Cl) via NEt_3-promoted HCl elimination. Treatment of these species with NaI/MeOH or $Ag[BF_4]$/NCMe leads to **324** (X = I) and **325**, respectively.[313]

(iii) Through a carbene-transfer methodology from $[Ag(NHC)_2][AgCl_2]$ (NHC = 1-butyl-3-methylimidazol-2-ylidene). The treatment of this silver salt with $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ in CH_2Cl_2 gives complex **320** (R^1 = Me/Bu^n, R^2 = H; see Figure 44).[314] The same methodology has been applied for the synthesis of the chelate alkoxy imidazol-2-ylidene complex **326** starting from the silver or thallium salt of the corresponding alkoxy di-NHC.[315] It is interesting to note that no η^6-arene–osmium derivatives containing NHC ligands have been described to date.

6.15.3.7 Vinylidene, Allenylidene, and Related Cumulenylidene Complexes

Although arene–ruthenium(II) complexes $[RuCl_2(\eta^6\text{-arene})(PR_3)]$ have been extensively used as precursors for promoting the catalytic activation of terminal alkynes, only a few stable vinylidene derivatives of this type have been isolated. This chemistry has been reviewed.[316,316a] Moreover, the higher electrophilicity of $[RuCl(\eta^6\text{-arene})(PR_3)]^+$ versus $[Ru(\eta^5\text{-}C_5R_5)(PR_3)_2]^+$ makes the resulting vinylidenes much more reactive, being usually trapped *in situ* by addition of nucleophiles, such as alcohols (see Section 6.15.3.4). The cationic complex



314

[Ru] = [{RuCl(μ-Cl)(η^6-arene)}$_2$]

317: $R^2 = CH_2CH_2OMe$, CH_2-2,4,6-$C_6H_2Me_3$*

318: $R^2 = CH_2$-4-C_6H_4OMe

319: $R^2 = CH_2$-4-C_6H_4OMe

X = Cl; $R^1 = R^2$ = Me, Et; arene = *p*-cymene
X = Cl; $R^1 = R^2$ = Me, Et; arene = 1,3,5-$C_6H_3Me_3$
X = Cl; $R^1 = R^2$ = Me, Et; arene = C_6Me_6
X = H; $R^1 = R^2$ = Me; arene = C_6Me_6

315

$R^1 = R^2 = CH_2Ph$, CH_2CH_2OMe; arene = *p*-cymene
$R^1 = R^2 = CH_2CH_2OMe$; arene = C_6Me_6
R^1 = Me; $R^2 = CH_2CH_2OMe$; arene = *p*-cymene
R^1 = Me; $R^2 = CH_2CH_2OMe$; arene = C_6Me_6
$R^1 = CH_2$-2,4,6-$C_6H_2Me_3$; $R^2 = CH_2CH_2OMe$; arene = C_6Me_6*
$R^1 = R^2 = CH_2$-4-$C_6H_4NMe_2$; arene = C_6Me_6*
$R^1 = R^2 = CH_2$-4-$C_6H_4NMe_2 \cdot HCl$; arene = C_6Me_6

316

Scheme 33

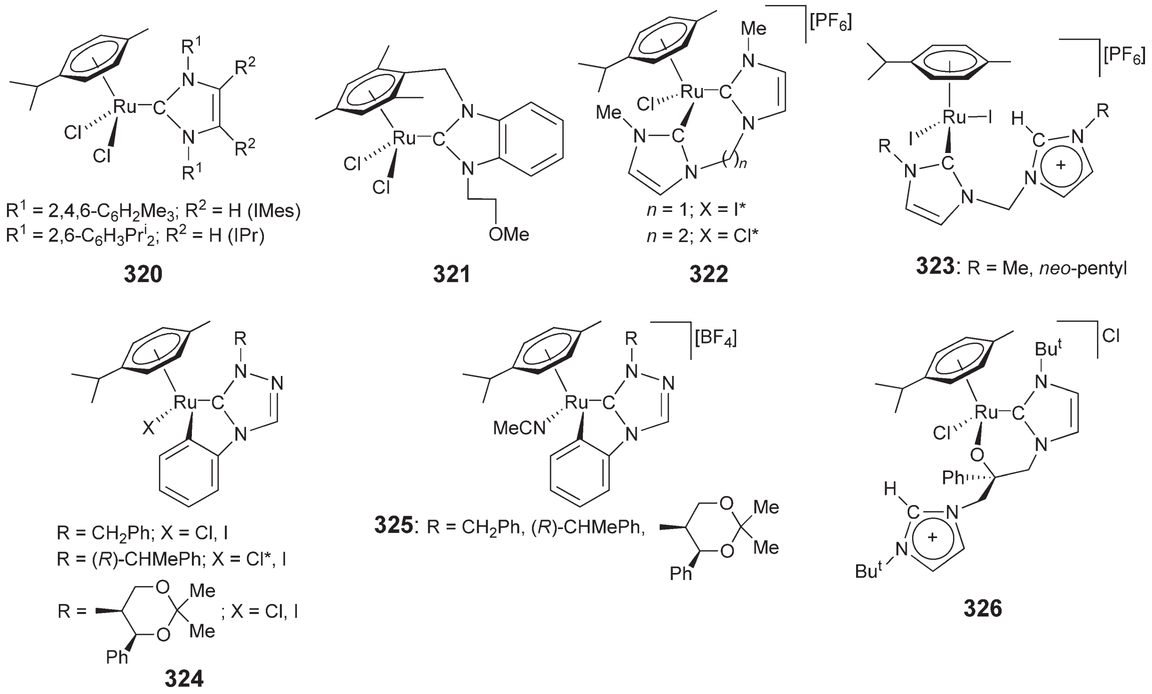
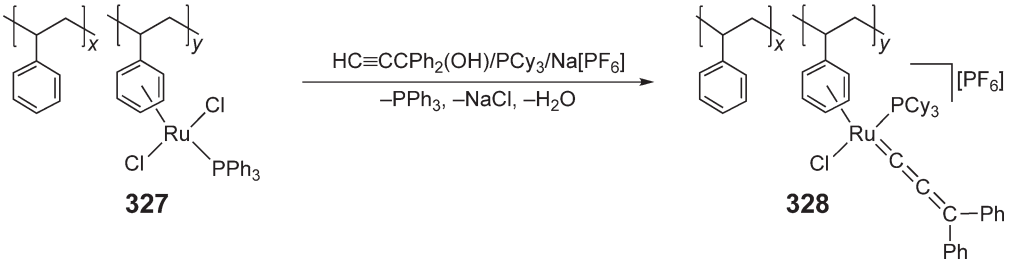


Figure 44 Arene–ruthenium complexes containing NHC ligands.

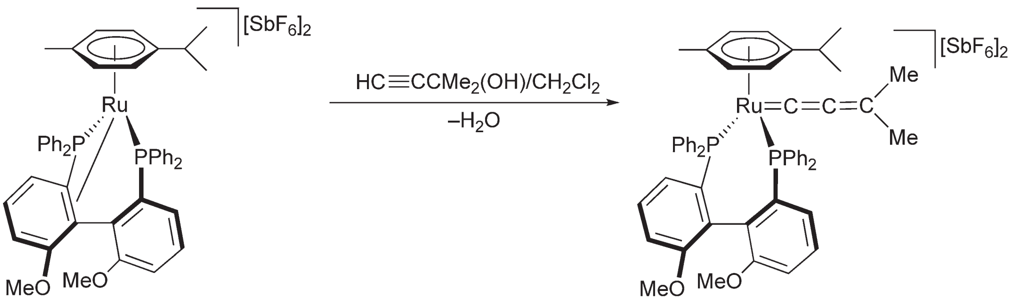
$[Ru\{{=}C{=}C(H)Ph\}\{\kappa^2(P,O)\text{-}Ph_2P(2\text{-}O\text{-}6\text{-}C_6H_3OMe)\}(\eta^6\text{-}C_6Me_6)][PF_6]$, obtained by reacting $[RuCl\{\kappa^2(P,O)\text{-}Ph_2P(2\text{-}O\text{-}6\text{-}C_6H_3OMe)\}(\eta^6\text{-}C_6Me_6)]$ with $HC{\equiv}CPh$ in CH_2Cl_2 and in the presence of $Na[PF_6]$, is the only stable (η^6-arene)–Ru(II) vinylidene complex reported during the period covered by this account.[251]

In contrast, the search for stable allenylidene–ruthenium(II) complexes of general formula $[RuCl({=}C{=}C{=}CR_2)(\eta^6\text{-arene})(PR_3)][X]$ has received special attention in the last few years, since it has been recently demonstrated that they can act as efficient pre-catalysts for olefin metathesis. In addition, to show comparable performances when compared to the classical Grubbs-type carbenes $[Ru({=}CHR)Cl_2(PCy_3)_2]$ ($R = Ph$, $CH{=}CPh_2$), they are in general readily accessible.[301] The most general synthetic route for the preparation of complexes $[RuCl({=}C{=}C{=}CR_2)(\eta^6\text{-arene})(PR_3)][X]$ is the direct treatment of the appropriate dichloride precursor $[RuCl_2(\eta^6\text{-arene})(PR_3)]$ in MeOH with a propargylic alcohol $HC{\equiv}CCR_2(OH)$ in the presence of $Na[PF_6]$ or $Na[BPh_4]$. Nevertheless, in some cases, the replacement of the sodium salt by $Ag[X]$ ($X = PF_6$, OTf, BF_4) results in a more practical and flexible synthetic method allowing work under aprotic conditions. Thus, treatment of $[RuCl_2(\eta^6\text{-arene})(PR_3)]$ with $Ag[X]$ in CH_2Cl_2 initially generates the isolable 16-electron species $[RuCl(\eta^6\text{-arene})(PR_3)][X]$, which readily reacts with suitable propargylic alcohol derivatives in CH_2Cl_2 to afford the desired allenylidenes. This later route prevents side-reactions such as the well-known nucleophilic attack of MeOH at the α-carbon of the allenylidene chain to yield catalytically inert Fischer-type carbene complexes of the type $[RuCl\{{=}C(OMe)CH{=}CR_2\}(\eta^6\text{-arene})(PR_3)][X]$ (see Section 6.15.3.4). The following allenylidene derivatives have been obtained following these approaches: $[RuCl({=}C{=}C{=}CR^1R^2)(\eta^6\text{-}p\text{-cymene})(PR_3)][X]$ ($R^1 = R^2 = Ph$, $PR_3 = PCy_3$, $X = PF_6$, BF_4, BPh_4, OTf, SbF_6; $R^1 = R^2 = Ph$, $PR_3 = PPh_3$, $X = PF_6$, OTf; $R^1 = R^2 = Ph$, $PR_3 = PPr^i{}_3$, $X = PF_6{}^*$, OTf; $R^1 = R^2 = Ph$, $PR_3 = Cy_2PCH_2CH_2\{(\eta^5\text{-}C_5H_4)TiCpCl_2\}$, $X = OTf$; $R^1 = R^2 = p\text{-}C_6H_4Cl$, $PR_3 = PCy_3$, $X = BF_4$, OTf; $R^1 = R^2 = p\text{-}C_6H_4OMe$, $PR_3 = PCy_3$, $X = OTf$; $R^1 = R^2 = p\text{-}C_6H_4F$, $PR_3 = PCy_3$, $X = OTf$; $R^1 = H$, $R^2 = (E)\text{-}CH{=}CH\text{-}p\text{-}C_6H_4NMe_2$, $PR_3 = PCy_3$, $X = BF_4$; $R^1R^2 = 2,2'$-biphenyldiyl, $PR_3 = PCy_3$, $X = BF_4$),[296,296a,296b,302,317,318] $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PCy_3)][OTf]$,[302] $[RuCl({=}C{=}C{=}CPh_2)\{\eta^6{:}\kappa^1\text{-}C_6H_5(CH_2)_nPR_2\}][X]$ ($R = Cy$, $n = 3$, $X = OTf^*$, PF_6; $R = Bu^t$, $n = 2$, $X = PF_6$),[296b,319] and $[RuCl({=}C{=}C{=}CPh_2)\{\eta^6{:}\kappa^1\text{-}C_6H_5O(CH_2)_2PBu^t{}_2\}][PF_6]$.[319] The synthesis of the polystyrene-supported allenylidene **328**, which can be recovered quantitatively and reused in catalytic RCM reactions, has also been successfully achieved starting from the immobilized dichloride precursor **327** (Equation (23)).[320]



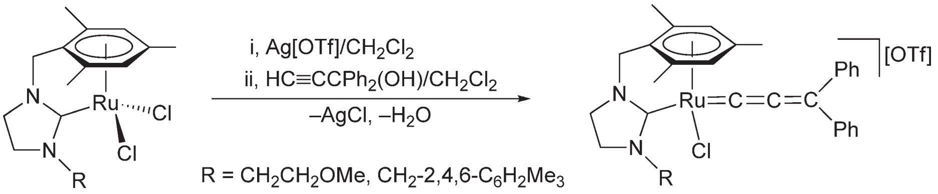
327 **328** (23)

Taking advantage of the hemilabile properties of the $\kappa^2(P,N)$-coordinated iminophosphorane–phosphine ligand $Ph_2PCH_2P({=}NR)Ph_2$ ($R = 4\text{-}C_5F_4N$), the stable diphenylallenylidene complexes $[RuCl({=}C{=}C{=}CPh_2)\{\kappa^1(P)\text{-}Ph_2PCH_2P({=}NR)Ph_2\}(\eta^6\text{-arene})][SbF_6]$ (arene = 1,3,5-$C_6H_3Me_3$*, C_6Me_6) have been prepared by reacting a dichloromethane solution of $[RuCl\{\kappa^2(P,N)\text{-}Ph_2PCH_2P({=}NR)Ph_2\}(\eta^6\text{-arene})][SbF_6]$ with 1,1-diphenyl-2-propyn-1-ol.[290] In a similar way, treatment of complex 329 with HC≡CCMe$_2$(OH) results in the formation of the dicationic allenylidene 330 via displacement of the labile olefinic unit of the diphosphine ligand (Equation (24)).[321] The related dicationic complex $[Ru({=}C{=}C{=}CPh_2)\{\kappa^2(P,N)\text{-}PPh_2Py\}(\eta^6\text{-}C_6Me_6)][BF_4]_2$ (PPh_2Py = diphenyl-2-pyridylphosphine) is also known.[322]



329 **330** (24)

Allenylidene–ruthenium(II) complexes containing NHCs, instead of the classical phosphines, as ancillary ligands are known. Thus, complex $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}p\text{-cymene})(IMes)][PF_6]^*$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) has been obtained by reacting $[RuCl_2(\eta^6\text{-}p\text{-cymene})(IMes)]$ 320 with HC≡CCPh$_2$(OH) in the presence of Na[PF$_6$].[309] In contrast, the related complex $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}p\text{-cymene})(IMesH_2)][PF_6]$ ($IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)dihydroimidazol-2-ylidene), which is an active catalyst for the atom-transfer radical polymerization of vinyl monomers, was synthesized starting from $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][PF_6]$ via substitution of the PCy$_3$ ligand by the NHC.[323] Allenylidenes 331 have also been prepared from the appropriate dichlorides 317 (Equation (25)).[307,307a] It has also been reported that the treatment of a series of imidazoline- and benzimidazole–ruthenium(II) complexes of general formula $[RuCl_2(\eta^6\text{-arene})(N\text{-donor})]$ (arene = *p*-cymene, C_6Me_6) with Ag[OTf] and HC≡CCPh$_2$(OH) generates *in situ* the corresponding allenylidenes $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-arene})(N\text{-donor})][OTf]$, which are able to catalyze the cycloisomerization of diallylamines into pyrrolidines. Nevertheless, these species are not stable enough to be isolated and properly characterized.[324,325]



317 **331** (25)

The cationic allenylidene–osmium(II) complexes $[OsX({=}C{=}C{=}CR_2)(\eta^6\text{-arene})(L)][PF_6]$ (arene = 1,3,5-$C_6H_3Me_3$, X = Cl, R = Ph, L = PMe$_3$*, PPh$_3$, PCy$_3$, AsPr$^i_3$, SbPr$^i_3$; arene = 1,3,5-$C_6H_3Me_3$, X = Cl, R = *p*-Tol, L = PCy$_3$; arene = C_6H_6, X = I, R = Ph, L = PCy$_3$; arene = *p*-cymene, X = Cl, R = Ph, L = PCy$_3$) are also known.[260] They have been obtained by reaction of the corresponding dihalide precursor $[OsX_2(\eta^6\text{-arene})(L)]$ with the appropriate propargylic alcohol in the presence of Ag[PF$_6$]. Treatment of $[OsCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PCy_3)][PF_6]$

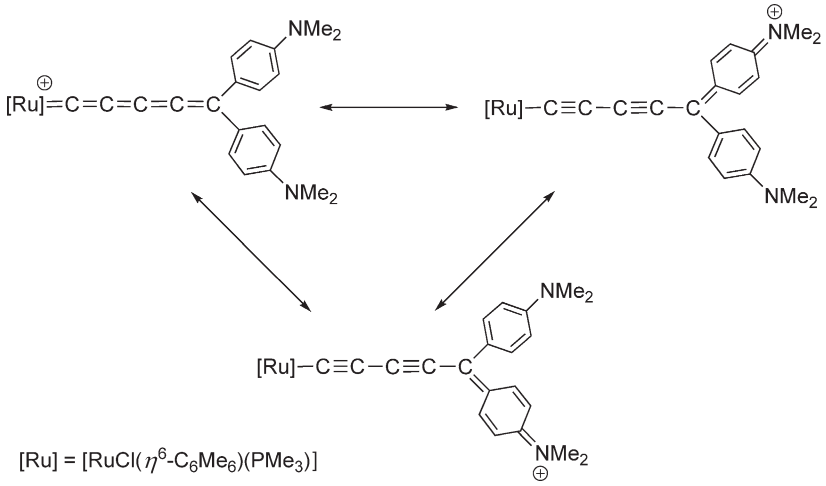


Figure 45 Resonance forms of the penta-1,2,3,4-tetraenylidene Ru complex.

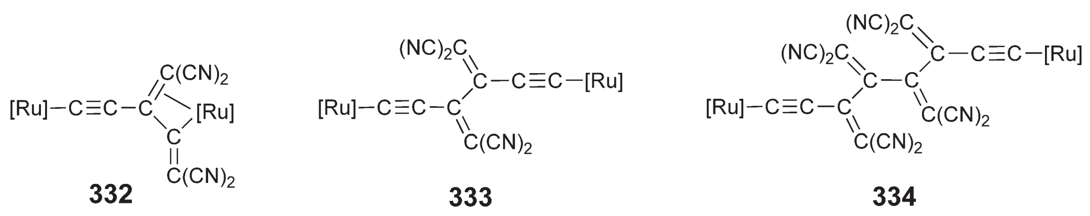
with KBr, NaI, and Ag$[O_2CCF_3]$ leads to the formation of the corresponding bromo, iodo, and trifluoroacetato complexes $[OsX({=}C{=}C{=}CPh_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PCy_3)][PF_6]$ ($X = Br, I, CF_3CO_2$).[260]

Reactions between $[RuCl_2(\eta^6\text{-}C_6Me_6)(PR_3)]$ ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$), Na$[PF_6]$, and $HC{\equiv}CC{\equiv}CPh_2(OSiMe_3)$ in ethanol or 2-propanol lead selectively to alkenyl(alkoxy)–allenylidenes $[RuCl\{{=}C{=}C{=}C(OR)CH{=}CPh_2\}(\eta^6\text{-}C_6Me_6)(PR_3)][PF_6]$ (R = Et, $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$; $R = Pr^i$, $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$). In (±)-butan-2-ol, the PEt_3 complex $[RuCl\{{=}C{=}C{=}C(OCHMeEt)CH{=}CPh_2\}(\eta^6\text{-}C_6Me_6)(PEt_3)][PF_6]$ has been obtained as an almost equimolar mixture of two diastereoisomers (the ruthenium center is a stereogenic center; two diastereoisomers of the PMe_2Ph complex are also formed (3 : 2 ratio) when pure (+)-butan-2-ol was used as solvent). The closely related alkenyl(amino)allenylidenes $[RuCl\{{=}C{=}C{=}C(NPh_2)CH{=}CPh_2\}(\eta^6\text{-}C_6Me_6)(PR_3)][PF_6]$ ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$) have been synthesized by performing these reactions in CH_2Cl_2 and in the presence of diphenylamine. All these results can be rationalized in terms of the initial formation of a highly unstable penta-1,2,3,4-tetraenylidene intermediate $[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(\eta^6\text{-}C_6Me_6)(PR_3)][PF_6]$, via elimination of $SiMe_3(OH)$, which readily undergoes the nucleophilic addition of the alcohol or amine to the electrophilic γ-carbon of the unsaturated chain.[252,326] Such an intermediate, that is, $[RuCl\{{=}C{=}C{=}C{=}C{=}C(p\text{-}C_6H_4NMe_2)_2\}(\eta^6\text{-}C_6Me_6)(PMe_3)][PF_6]$, could be stabilized by activation of the silylated diyne $Me_3SiC{\equiv}CC{\equiv}C(p\text{-}C_6H_4NMe_2)_2(OSiMe_3)$. This penta-1,2,3,4-tetraenylidene derivative is inert toward the addition of alcohols, its stability arising from mesomeric diynyl contributions (Figure 45).[326]

6.15.4 Binuclear Complexes Containing Hydrocarbon Bridges with no M–M Bonds

The chemistry of bimetallic compounds containing hydrocarbon bridges linking the metal fragments is of particular interest due to their unique chemical and physical properties. This section covers some recent developments in this field involving species featuring half-sandwich ruthenium and osmium fragments without metal–metal bonds. General reviews covering particular aspects related to this chemistry are available.[327,327a]

Alkynyl moieties are the dominant hydrocarbon bridges among the most common functionalities linking the metal fragments. These bridging systems not only provide stability to the resulting binuclear entity, but also are able to promote an electronic communication between the terminal metallic fragments. These features have triggered the interest to develop the chemistry of previously known series of bridging acetylide–diruthenium(II) derivatives (see COMC (1995)). To this regard, Bruce and co-workers continuing previous work have developed this chemistry, providing new synthetic routes along with the extension of reactivity and electrochemical studies. Thus, an improved synthetic procedure of the known diacetylide-bridged diruthenium derivative $[\{Cp(PPh_3)_2Ru\}_2\{\mu\text{-}C{\equiv}C\}_2]^*$, based on the reaction of a methanol solution of $[RuClCp(PPh_3)_2]$ with 0.5 equiv. of $Me_3Si(C{\equiv}C)_2SiMe_3$ in the presence of KF, has been reported.[105] The related complexes $[\{Cp(PPh_3)_2Ru\}_2\{\mu\text{-}C{\equiv}C\}_n]$ ($n = 3^*$, 4) can be synthesized in a similar fashion starting from $[RuClCp(PPh_3)_2]$ and $Me_3Si(C{\equiv}C)_nSiMe_3$ ($n = 3$, 4).[105,328] All these compounds ($n = 2$, 3, 4)



332 **333** **334**

$[Ru] = [RuCp(PPh_3)_2]$

Figure 46 Structure of the dinuclear ruthenium complexes **332**–**334**.

readily react with tetracyanoethylene (tcne) to afford the mono-**332** and -**333**, and bis-tcne adducts **334**, respectively (Figure 46).[105,328,329] Formation of these species involves cycloaddition of tcne with the C$\equiv$C triple bonds followed by ring-opening to give a 1,1,4,4-tetracyanobuta-1,3-diene framework. In a similar way, the previously known ethynediyl derivative $[\{Cp(CO)_2Ru\}_2\{\mu\text{-}C{\equiv}C\}]$ reacts with tcne to afford the bimetallic tetracyanobutadienyl species $[\{Cp(CO)_2Ru\}_2\{\mu\text{-}C[{=}C(CN)_2]C[{=}C(CN)_2]\}]^*$.[330]

The series of bridging diacetylide–ruthenium complexes has been extended with the synthesis of analogous derivatives $[\{Cp^*(L^1)(L^2)Ru\}_2\{\mu\text{-}C{\equiv}C\}_2]$ ($L^1L^2 = dppe^*$, $dppm^*$). They have been obtained by oxidative coupling of ethynyls $[Ru(C{\equiv}CH)Cp^*(L^1)(L^2)]$ ($L^1L^2 = dppe^*$, $dppm^*$) and subsequent deprotonation of the resulting bis(vinylidenes) $[Cp^*(L^1)(L^2)Ru{=}C{=}CHCH{=}C{=}Ru(L^1)(L^2)Cp^*][PF_6]_2$ ($L^1L^2 = dppe^*$, $dppm^*$).[112] In addition, the one- and two-electron oxidized species $[\{Cp(PPh_3)_2Ru\}_2(\mu\text{-}C_4)][PF_6]_n$ ($n = 1$, 2) and $[\{Cp^*(dppe)Ru\}_2\{\mu\text{-}C_4\}][PF_6]_n$ ($n = 1$, 2) could be isolated by chemical oxidation of the appropriate diacetylide derivative with 1 or 2.5 equiv. of $Ag[PF_6]$, respectively.[112,331,331a] Remarkably, the X-ray crystal structure of the oxidized products $[\{Cp^*(dppe)Ru\}_2\{\mu\text{-}C_4\}][PF_6]_n$ ($n = 1$, 2) could be determined, confirming a dicarbene–cumulene structure for the $Ru{=}C{=}C{=}C{=}C{=}Ru$ bridge in the dicationic derivative $[\{Cp^*(dppe)Ru\}_2\{\mu\text{-}C_4\}][PF_6]_2$.[112]

In a series of electrochemical studies, the stability of these bridging systems has been nicely shown. For instance, cyclic voltammetry studies show that complex $[\{Cp(PPh_3)_2Ru\}_2\{\mu\text{-}C{\equiv}C\}_2]$ and its PMe_3- and dppe-substitution products, that is, $[\{Cp(PMe_3)_2Ru\}_2\{\mu\text{-}C{\equiv}C\}_2]$ and $[\{Cp(dppe)Ru\}_2\{\mu\text{-}C{\equiv}C\}_2]^*$, undergo a series of four stepwise one-electron oxidation processes, the first three reversible and the fourth irreversible.[331,331a,332] Electrochemistry of the more electron-rich derivatives $[\{Cp^*(L^1)(L^2)Ru\}_2\{\mu\text{-}C{\equiv}C\}_2]$ ($L^1L^2 = dppe^*$, $dppm^*$) also reveals a sequence of four one-electron redox steps.[112] The synthesis and electrochemistry of the asymmetrically end-capped diynyl complexes $[\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{Ru(dppe)(\eta^5\text{-}C_5R_5)\}]$ (R = H, Me), generated from $[Ru(C{\equiv}CC{\equiv}CSiMe_3)Cp(PPh_3)_2]$ and the appropriate chloride $[RuCl(\eta^5\text{-}C_5R_5)(dppe)]$ in the presence of KF, has also been reported.[332]

Heterodinuclear diacetylide-bridging complexes are also accessible. An efficient synthetic approach is based on the replacement of H in complexes $[Ru(C{\equiv}CC{\equiv}CH)Cp(PPh_3)_2]$ or $[Ru(C{\equiv}CC{\equiv}CH)Cp^*(dppe)]$ by different metallic fragments. Following this synthetic route, $[Ru\{C{\equiv}CC{\equiv}CAu(PPh_3)\}Cp(PPh_3)_2]^*$ and $[Ru\{C{\equiv}CC{\equiv}CAu(PR_3)\}Cp^*(dppe)]$ ($R = Ph^*$, $p\text{-}Tol^*$) have been obtained by reacting these compounds with $AuCl(PR_3)$ in the presence of $K[N(SiMe_3)_2]$.[332] Remarkably, the Pd(0)/Cu(I)-catalyzed coupling of the heterobimetallic derivative $[Ru\{C{\equiv}CC{\equiv}CAu(PPh_3)\}Cp^*(dppe)]$ with $I(C{\equiv}C)_3I$ affords $[\{Cp^*(dppe)Ru\}_2\{\mu\text{-}C{\equiv}C\}_7]^*$, the first C_{14}-complex to be structurally characterized, via $[ClAu(PPh_3)]$ elimination.[333] Complexes $[\{Cp(CO)_2Ru\}C{\equiv}CC{\equiv}C\{W(CO)_3Cp\}]$ and $[\{(\eta^5\text{-}C_5R_5)(CO)_2Ru\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp^*\}]$ (R = H, Me) are also known, being obtained by Cu-catalyzed coupling between $[W(C{\equiv}CC{\equiv}CH)Cp(CO)_3]$ or $[Fe(C{\equiv}CC{\equiv}CH)Cp^*(CO)_2]$ with the appropriate ruthenium chloride precursor $[RuCl(\eta^5\text{-}C_5R_5)(CO)_2]$.[334,335] Treatment of the silylated derivative $[W(C{\equiv}CC{\equiv}CSiMe_3)Cp(CO)_3]$ with $[RuClCp(PPh_3)_2]$ in the presence of KF generates the closely related species $[\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{W(CO)_3Cp\}]$, which readily reacts at the W–C$\equiv$C– triple bond with tcne to give $[\{Cp(PPh_3)_2Ru\}C{\equiv}CC\{{=}C(CN)_2\}C\{{=}C(CN)_2\}\{W(CO)_3Cp\}]^*$.[336] The preparation of complexes $Hg[C{\equiv}CC{\equiv}C\{Ru(L^1)(L^2)(\eta^5\text{-}C_5R_5)\}]_2$ (R = Me, $L^1L^2 = dppe^*$; R = H, $L^1 = L^2 = PPh_3$), by treatment of $[Ru(C{\equiv}CC{\equiv}CH)(\eta^5\text{-}C_5R_5)(L^1)(L^2)]$ with $[Hg(OAc)_2]$, has been also reported.[337]

Other bimetallic complexes containing bridging alkynyl groups are the following:

(i) $[1,4\text{-}C_6H_4\{C{\equiv}CRuCp(PPh_3)_2\}_2]$ prepared by fluoride-induced desilylation of $[Ru(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CSiMe_3)Cp(PPh_3)_2]$ and subsequent reaction with $[RuClCp(PPh_3)_2]$.[105]

(ii) $[\{Cp(PPh_3)_2RuC{\equiv}C\text{-}4\text{-}C_6H_4\text{-}\}_2C{=}O]$ generated by direct activation of 4,4′-diethynylbenzophenone with $[RuClCp(PPh_3)_2]$ in the presence of $[NH_4][PF_6]$ and Et_3N. Treatment of this complex with

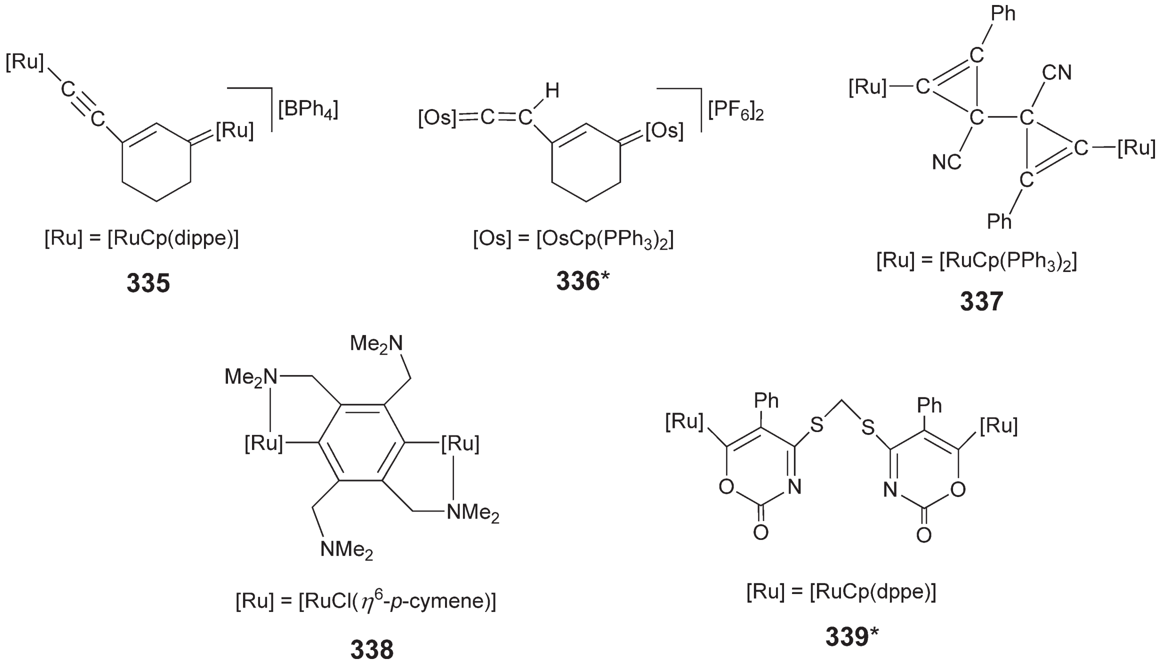
4-bromo-*N*,*N*-dimethylaniline/LiBu^t leads, after hydrolysis, to [{Cp(PPh$_3$)$_2$RuC≡C-4-C$_6$H$_4$–}$_2$C(OH)(4-C$_6$H$_4$NMe$_2$)], which can be readily transformed into the stable triaryl carbocation [{Cp(PPh$_3$)$_2$RuC≡C-4-C$_6$H$_4$–}$_2$C(4-C$_6$H$_4$NMe$_2$)]$^+$ by protonation with HBF$_4$.[160]

(iii) [1,3,5-C$_6$H$_4$(C≡CR){C≡CRuCp(PPh$_3$)$_2$}$_2$] (R = H, Fc) obtained by reacting a methanol solution of 1,3,5-triethynylbenzene or 1,3-diethynyl-5-(ferrocenylethynyl)benzene with 2 equiv. of [RuClCp(PPh$_3$)$_2$] in the presence of Na.[92,95]

(iv) [{Cp(PPh$_3$)$_2$Ru}$_2$(μ-C≡C-4-C$_6$H$_4$C≡CC≡C-4-C$_6$H$_4$C≡C)] generated by oxidative coupling of [Ru(C≡C-4-C$_6$H$_4$C≡CH)Cp(PPh$_3$)$_2$] using a Cu(I)/TMEDA catalyst. Complex [Ru(C≡C-4-C$_6$H$_4$C≡CH)Cp(PPh$_3$)$_2$] has been also used as suitable starting material for the preparation of a large variety of bimetallic derivatives of general composition [Ru]C≡CC$_6$H$_4$C≡C[M] (M = W, Rh, Ir, Pt, Au, Hg).[106,338]

(v) [Th{C≡CRuCp(CO)$_2$}$_2$] (Th = 2,5-disubstituted thiophene) obtained by reacting [RuICp(CO)$_2$] with 2,5-bis-[(tributyltin)ethynyl]thiophene in the presence of catalytic amounts of [PdCl$_2$(NCMe)$_2$].[339]

Closely related bridging systems are the cumulenic allenylidene–vinylidene chains, which have also been used to bridge Ru(II) and Os(II) fragments, that is, [{M}=C=C=CHCH=C={M}][BF$_4$]$_2$ ({M} = {RuCp*(dppe)}, {RuCp(PPh$_3$)$_2$}, {OsCp(PPh$_3$)$_2$}). These compounds have been obtained by treatment of the corresponding chloride precursor with Ag[BF$_4$] and 0.5 equiv. of HC≡CCH(OH)C≡CH. Deprotonation of these dicationic compounds with Al$_2$O$_3$ generates the bimetallic derivatives [{M}=C=C=CHC≡C{M}][BF$_4$] ({M} = {RuCp*(dppe)}, {RuCp(PPh$_3$)$_2$}*, {OsCp(PPh$_3$)$_2$}*) which show an important electronic delocalization within the bridging allenylidene–alkynyl chain.[340,340a,341] Heterobimetallic alkynyl–carbene-bridged complexes [(η^5-C$_9$H$_7$)(PPh$_3$)(L)Ru{C≡CC(R)PhCH$_2$C(OMe)=M(CO)$_5$}] (L = PPh$_3$, R = Ph, M = Cr, Mo, W; L = PPh$_3$, R = H, M = Cr, W; L = PMePh$_2$, R = Ph, M = Cr, W; L = PMePh$_2$, R = H, M = Cr, W; L = PMe$_2$Ph, R = Ph, M = Cr, W) are also known. They have been prepared by regioselective nucleophilic addition of anionic Fischer-type carbene derivatives Li[(CO)$_5$M{=C(OMe)CH$_2$}] at the allenylidene C$_\gamma$-atom of cationic indenyl–ruthenium complexes [Ru{=C=C=C(R)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)(L)][PF$_6$].[126,139] Treatment of these species with HBF$_4$ yields the corresponding bimetallic derivatives [(η^5-C$_9$H$_7$)(PPh$_3$)(L)Ru{=C=CHCRPhCH$_2$C(OMe)=M(CO)$_5$}][BF$_4$], which contain a vinylidene–carbene bridge, as the result of the selective protonation of the Ru–alkynyl unit.[126,139*] The related heterobimetallic Ru–W bis-carbene [(η^6-1,2,4,5-C$_6$H$_2$Me$_4$)Cl(PPh$_3$)Ru{=C(OMe)CH=CH-4-C$_6$H$_4$CH=CHC(NMe$_2$)=W(CO)$_5$}][PF$_6$] is also known.[295]



[Ru] = [RuCp(dippe)]

335

[Os] = [OsCp(PPh$_3$)$_2$]

336*

[Ru] = [RuCp(PPh$_3$)$_2$]

337

[Ru] = [RuCl(η^6-*p*-cymene)]

338

[Ru] = [RuCp(dppe)]

339*

Figure 47 Structure of the bimetallic derivatives **335**–**339**.

Other bimetallic complexes containing hydrocarbon bridges recently reported are (see Figure 47) the following:

(i) Compounds **335** and **336*** obtained by activation of the propargylic alcohol $HC{\equiv}CCMe_2(OH)$ with $[RuClCp(dippe)]$ or $[OsBrCp(PPh_3)_2]$, respectively.[143,229]

(ii) The bis-cyclopropenyl derivative **337** generated by deprotonation/cyclopropanation of the corresponding dinuclear bis-vinylidene $[Ru]^+{=}C{=}CPhCH(CN)CH(CN)CPh{=}C{=}{}^+[Ru]^*$.[62] Related chemistry starting from bis-vinylidenes $[Ru]^+{=}C{=}C(CH_2R)\text{-}4\text{-}C_6H_4C(CH_2R){=}C{=}{}^+[Ru]$ ($[Ru]=[RuCp(PPh_3)_2]$; $R=Ph$, $CH{=}CH_2{}^*$, CN, CO_2Me, CO_2Et) has been also reported.[342]

(iii) The orthometallated species **338** prepared starting from dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ and the polymeric dilithium salt $[1,4\text{-}Li_2\{2,3,5,6\text{-}C_6(CH_2NMe_2)_4\}]_n$.[44]

(iv) Complex **339*** containing two organometallic oxazin-2-one fragments linked by a methylene group, which has been obtained by dimerization of the appropriate [1,3]-oxazin-2-one–ruthenium precursor.[71]

(v) The diruthenium ethylene-bridged complex $[Cp(CO)_2RuCH_2CH_2Ru(CO)_2Cp]^*$, a model for Fischer–Tropsch surface intermediates, prepared by reacting $Na[RuCp(CO)_2]$ with 0.5 equiv. of 1,2-dichloroethane. This compound is also formed in the reaction of $Na[RuCp(CO)_2]$ with the cationic ruthenium–ethylene derivative $[Ru(\eta^2\text{-}CH_2{=}CH_2)Cp(CO)_2][PF_6]$.[343]

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6.16
Mononuclear Ru/Os Compounds: Ruthenocenes and Osmocenes

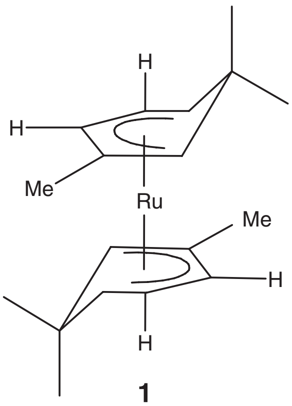
I R Butler and D Thomas, University of Wales – Bangor, Bangor, UK

6.16.1 Introduction

Although it may be argued that the general chemistry of ruthenocenes and osmocenes has progressed more slowly than the corresponding chemistry of ferrocene, which is a reflection of the number of researchers in these respective fields, nevertheless there has been significant progress in the development of the chemistry of these metallocenes. For pertinent reviews in the area, the reader is directed to the Royal Society of Chemistry's *Annual Reports on Organometallic Chemistry*.[1]

6.16.2 General Synthetic Methods

The traditional synthesis of ruthenocene from ruthenium trichloride and cyclopentadiene under reducing conditions (usually zinc) has been complemented by a further synthesis: desilylation has been used as an effective route to ruthenocene; treatment of silylated cyclopentadienes with ruthenium trichloride in EtOH or Pr^iOH resulted in the preparation of ruthenocenes with yields in excess of 90%.[2] The bis(ruthenocenium) dication has also been obtained electrochemically in the presence of $[B(C_6F_5)_4]^-$ in a simple and effective manner.[3] A review article on optically active organometallic compounds considers optically active ruthenocenes in addition to ferrocenes and cymantrenes.[4] Palladium-catalyzed cross-coupling of zincated ruthenocenes has been used to afford 1,1′-bis(quinolyl)ruthenocenes. While this is only one example, clearly this methodology is generally applicable.[5] A specific example of such optically active ruthenocenes would be the preparation of enantiomerically pure haloruthenocenium salts.[6] The reaction of $[RuCp(\eta^4\text{-butadiene})Cl]$ with $[Te(OC_6F_5)]$ in refluxing THF gives $[RuCp(2\text{-}6\text{-}\eta^5)\text{-}C_6F_5O)]$ (70%), which on vacuum pyrolysis at 640 °C affords the pentafluoro–ruthenocene $[RuCp(\eta^5\text{-}C_5F_5)]$ in high yield, which has been structurally characterized.[7] The open ruthenocenes $[Ru(2\text{-}CH_3\text{-}4\text{-}C_6H_5C_5H_5)_2]$ have been prepared directly from $RuCl_3$ with the appropriate diene and zinc metal in ethanol.[8] Related to these metallocenes is the edge-bridged open ruthenocene **1**, which is prepared in an analogous manner from 2,4,6,6-tetramethylcyclohexadiene, $RuCl_3$, and zinc. A related series of these edge-bridged open ruthenocenes has also been obtained from di-μ-chlorodichlorobis-[(1-3η:6-8η)-2,7-dimethyloctadienyl]diruthenium and dienes.[9]



1

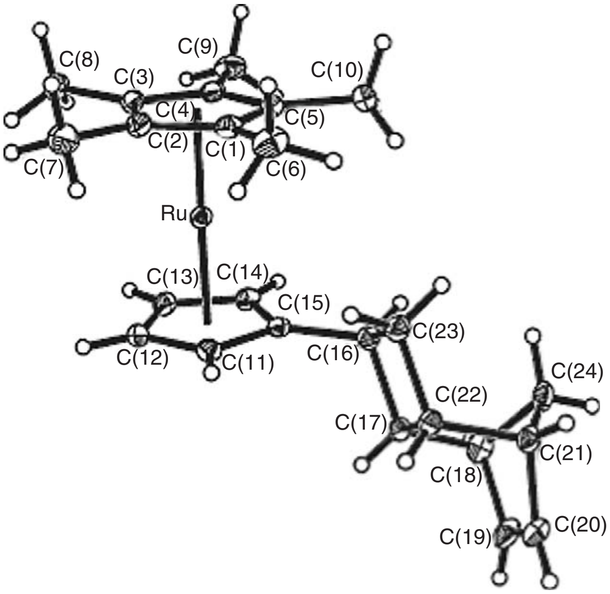
A range of half-open ruthenocenes which contain alkylated or arylated pentadienyl ligands has been prepared from $[RuCp^*Cl]_4$.[10] Using the same starting compound, half-open ruthenocenes containing heteroatoms have also been obtained.[11]

6.16.2.1 Metallation Reactions

The lithiation procedure for the preparation of monolithio- and 1,1′-dilithioruthenocene, originally described in 1993, has been reviewed and updated.[12] The new methodology yields ~81% monolithioruthenocene, which on a dimethylformamide (DMF) quench gives ruthenocenaldehyde. The permercuration of ruthenocene has also been reported under similar reaction conditions to those used in the mercuration of ferrocene: refluxing ruthenocene with $Hg(OAc)_2$ in dichloroethane gives decakis(acetoxymercurio)ruthenocene in 88% yield, which in turn may be used to obtain decachloro-, decabromo-, and decaiodoruthenocene, respectively, by treatment with cupric chloride dihydrate, potassium tribromide in water, or potassium iodide in water. The reactions of pentamethylruthenocene with mercuric acetate in an ether:alcohol mixture gives pentakis(acetoxymercurio)pentamethylruthenocene in 88% yield also. Similarly, halogenation is possible to give the pentamethylpentahaloruthenocenes.[13] The reactions of pentakis(chloromercurio)pentamethylruthenocene or decakis(chloromercurio)ruthenocene with dimethylzinc result in the formation of the perzincated cyclopentadienyl compounds, which may subsequently be further derivatized.[14] Permagnesiated ruthenocenes,[15] in addition to decalithioruthenocene, may also be prepared using similar strategies.[16] It can be noted that osmocene may be similarly permercurated and halogenated, which was initially somewhat of a surprise because of the known formation of its adducts when treated with mercuric chloride.[17]

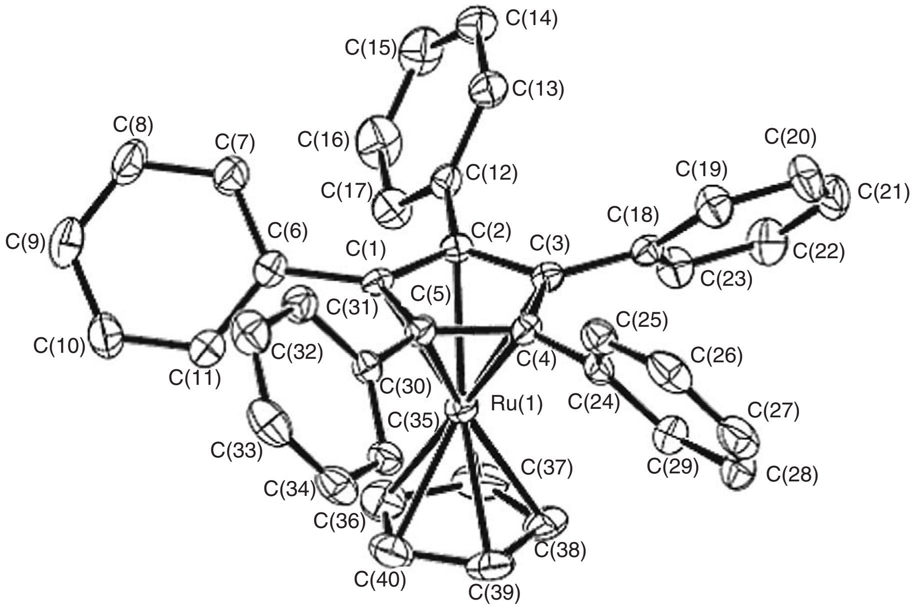
6.16.2.2 General Synthesis

A number of formylruthenocenes have been obtained by Vilsmeier formylation, cyclopentadienyl–methyl oxidation, or in the case of pentamethylruthenocene, via the two-electron oxidation in the presence of HBF_4, to obtain the fulvene complex $[RuCp(\eta^6\text{-}C_5H_4CH_2)^+]BF_4^-$. This was treated with KOH to give the hydroxymethyl compound, which was subsequently oxidized with activated MnO_2. The formylruthenocenes were also treated with $TiCl_4$/Zn to give the corresponding dinuclear ethylene compounds such as *trans*-1,2-bis(1′,2′,3′,4′,5′-pentamethylruthenocenyl)ethylene, *trans*-1,2-bis(ruthenocenyl)ethylene, and *trans*-1,2-bis(2,3,4,5-tetramethylruthenocenyl)ethylene.[18] Hydroxyruthenocene has been obtained from the reaction of $[RuCp(\eta^4\text{-}C_5H_4O)Br]$ with zinc in 22% yield. The work follows the earlier success obtained on the reactions of $[RuCp(\eta^4\text{-}C_5H_4O)CH_3CN]PF_6$ with nucleophiles.[19] A simple metathesis route to bridged metallocenes has been applied to ruthenocenes as well as ferrocenes and zirconocene dihalides. The 1,1′-diallylruthenocene is transformed into the C_4-bridged compound under high dilution conditions using Grubbs catalyst.[20]



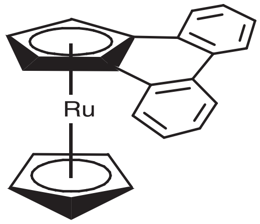
2

The substituted ruthenocene complex [Cp*Ru(η^5-C$_5$H$_4$C$_9$H$_{10}$)], shown as 2, is obtained on reaction of [Cp$^*_2$Ru$_2$Cl$_2$] with an excess of 1,5-norbornadiene in ethanol. In this reaction the substituted cyclopentadienyl ligand is obtained from the coupling of two norbornadiene units, followed by C–C bond cleavage and hydrogen migration and finally HCl loss.[21]



3

The crystal structures of three bulky mixed ligand ruthenocenes [Ru(η^5-C$_5$Ph$_5$)Cp], [Ru(η^5-C$_5$(p-MeC$_6$H$_4$)$_5$)Cp], and [Ru(η^5-C$_5$Ph$_5$)Cp*], 3, have been reported. These compounds which are pale yellow solids were obtained either by pyrolysis of a carbonyl precursor or by the reaction of Li(C$_5$Ph$_5$) with [RuCp*(COD)Cl] in the case of the complex 3.[22] The salts of the monocations [Cp*M(η^5-C$_5$Me$_4$CH$_2$)]$^+$BF$_4^-$ (M = Ru, Os) on reaction with oxygen in CF$_3$SO$_3$H give the trications [{1,2-(CH$_2$)$_2$C$_5$Me$_3$}M(C$_5$Me$_4$CH$_2$)]$^{3+}$, which are hydrolytically sensitive. The NMR characteristics of these trications have been discussed and density functional (DFT) calculations of their geometry have been made.[23] 2-Ruthenocenyl-4,4,5,5-tetramethyl-1,3-dioxa-2-boralane has been used as a precursor in coupling reactions with a series of dihaloaromatic compounds. Interestingly, ruthenoceno[1]phenanthrene, **4**, and ruthenocenyl[*a*]acenapahthylene, **5**, were obtained as by-products when 2,2′-diiodobiphenyl and 1,8-di-iodonaphthane, respectively, were the precursors.[24]



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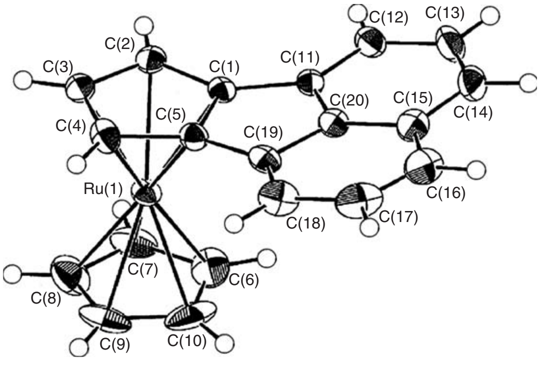
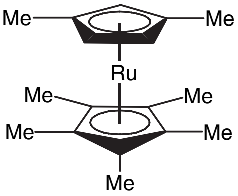


5

Unsymmetrically substituted ruthenocenes may also be prepared using gas-phase electrocyclic reactions of pentadienylruthenium complexes. The precursor compounds are obtained by zinc reduction of either ruthenium trichloride in the presence of 5,5-dimethylcyclohexadiene to give bis(6,6-dimethylcyclohexadienyl)ruthenium or $\{Cp^*RuCl_2\}_2$ in the presence of 2,4-di-*tert*-butyl-1,3-pentadiene to give (pentamethylcyclopentadienyl)(2,4-di-*tert*-butylpentadienyl)ruthenium or dimethylcyclohexadiene to give (pentamethylcyclopentadienyl)(6,6-dimethylcyclohexadienyl)ruthenium. Sublimation of these compounds at 400–450 °C afforded the ruthenocenes **6–8**.[25]



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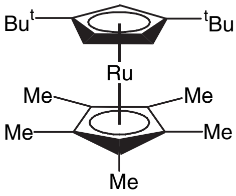

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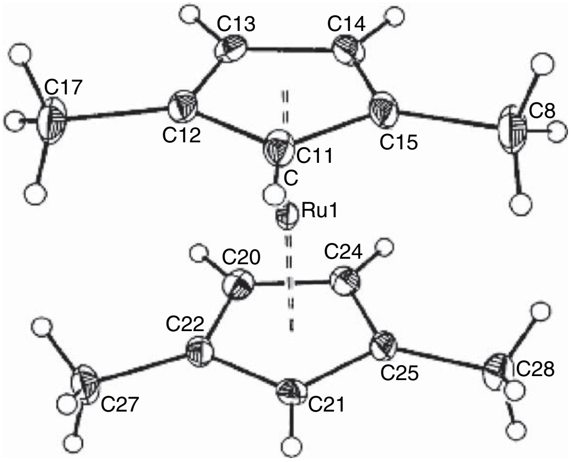
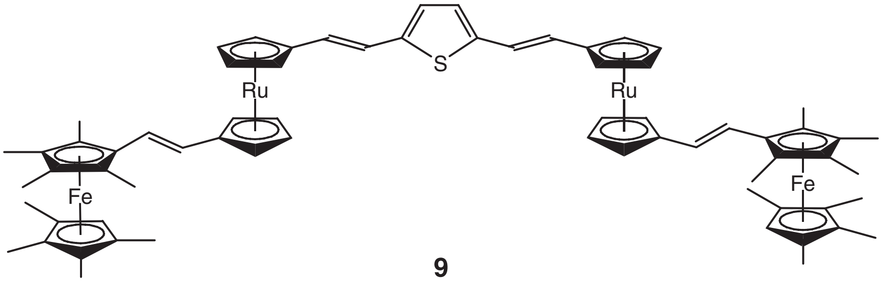


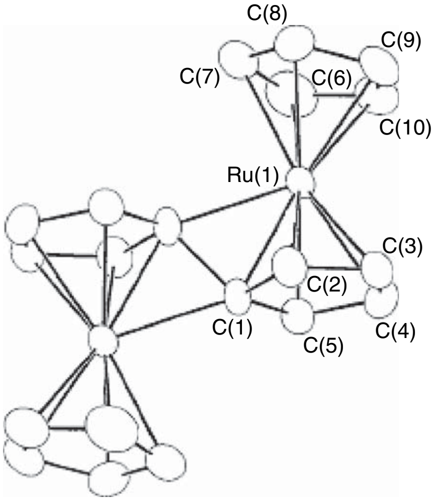
8

The reaction of $[RuCp^*(\eta^3\text{-}C_5H_5O)Br_2]$ with triflic acid results in the preparation of $[RuCp^*(\eta^5\text{-}C_5H_4OH)Br]CF_3SO_3$ which in water gives $[RuCp^*(\eta^4\text{-}C_5H_4O)Br]$ which crystallizes as a dihydrate.[26] The reaction of $\{Ru(\mu_3\text{-}Cl)Cp^*\}_4$ with $[Tl\{1,2\text{-}C_5H_3(C(O)Ph)_2\}]$ results in the formation of the 1,2-dibenzoylruthenocene $[Ru\{\eta^5\text{-}1,2\text{-}C_5H_3(C(O)Ph)_2\}Cp^*]$. Further reaction of this compound with hydrazine hydrate results in the formation of the pyridazine $[Ru\{\eta^5\text{-}1,2\text{-}C_5H_3(CPh)_2N_2\}Cp^*]$.[27] Acyclic η^5-pentadienylruthenium complexes are obtained on the thermolysis of precursors of the type $[(\eta^5\text{-}C_5Me_5)Ru(R^1C{\equiv}CR^2)(\eta^3\text{-}C_3H_7)]$. These may be considered as half-open ruthenocenes.[28] The synthon $[Cp^{\#}Ru(NCCH_3)_3]PF_6$ ($Cp^{\#}$ = 1-trifluoromethyl-2,3,4,5-tetramethylcyclopentadienyl), which is photochemically generated from $[Cp^{\#}RuBz](PF_6)$ in acetonitrile, has been used in the synthesis of a number of mixed sandwich compounds.[29] In a general article on the synthesis of metallocene alcohols, the synthesis of 1-ruthenocenylprop-2-en-1-one, ruthenocene-1-1′-bis(3-chloropropan-1-one), and the structurally characterized *rac*-1,1′-diphenyl-1,1′-(1,1′-ruthenocenediyl)dimethanol have been reported in a synthetic scheme, which begins with traditional Friedel–Crafts reactions of ruthenocene.[30] Novel quatermetallocenes in which two ferrocenes are connected to two ruthenocenes with ethane or thiophene bridges, such as **9**, have been prepared by a Wittig olefination strategy.[31]



9

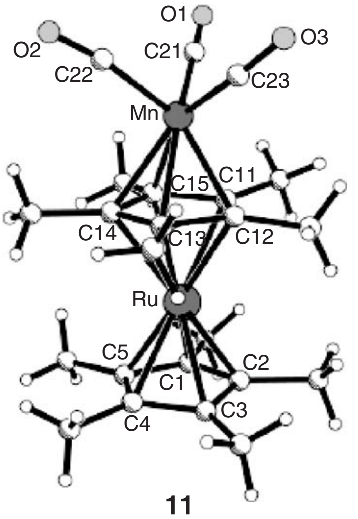
It has been shown that the reaction of biruthenocene in benzene with *para*-benzoquinone in the presence of boron trifluoride diethyl etherate results in the formation of the salt [CpRu(μ_2-η^6:η^6-$C_{10}H_8$)RuCp](BF_4)$_2$, **10**, which, on treatment with bromine and triphenylphosphine, respectively, gives cationic compounds [BrCpRu^{IV}FvRu^{IV}CpBr]$^{2+}$ (green) and [CpRu^{IV}FvRu^{IV}($C_5H_4P^+Ph_3$)] (yellow), where Fv = fulvalene.[32]



10

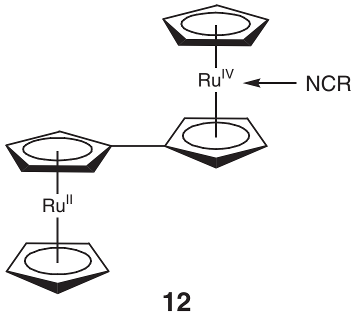
The same research group has prepared mixed valence biruthenocene salts [Ru^{II}Cp($C_5H_4C_5H_4$)-CpRu^{IV}L]$^{2+}$(BF_4^-)$_2$ (L = NCCH$_3$, N(CH)$_4$N) in the similar oxidation reaction where small quantities of acetonitrile or pyrazine were present.[33] Nickelocene has been doped into single crystals of ruthenocene, and near-infrared luminescence properties have been examined.[34] The low-energy electronic excited states of benzoyl-substituted ruthenocenes have also been examined, and the results obtained have been discussed in terms of the similarities and differences observed between these compounds and the corresponding ferrocenes.[35] Theoretical investigations have also been carried out on the molecular organization in crystals of ruthenocene and nickelocene.[36] Stable bimetallic "capped" ruthenocene cations may also be prepared by reaction of the manganese tricarbonyl-transfer reagent [(η^6-naphthalene)Mn(CO)$_3$]$^+$ with [Cp$^*_2$Ru]. An example of such a structure is shown as **11**.[37]

A heterobimetallic Ru, Rh complex [Cp*Ru(μ-η^5,η^3-C_8H_6)Rh(η^4-COD)] has been prepared starting from the pentalene complex [Cp*Ru(η^5-C_8H_7)]. The product is obtained in a two-step synthesis. It may be used as a catalyst in the dehydrogenative silylation of styrene.[38] Vapor-phase UV studies of half-open metallocenes have also been carried out.[39] A simple ruthenocenyl surfactant prepared by the reaction of dimethylaminomethylruthenocene with 1-bromodecane has been examined, and its critical micelle concentration in aqueous 0.1 M HCl has been established as well as its electrochemistry.[40] The electrochemical synthesis of a polyruthenocenyl film has been described. Essentially, the electroreduction of [RuCp(η^5-C_5H_4CCl=CHCHO)] in acetonitrile has been carried out to give the film, which has been observed to be moderately reversibly oxidizable.[41]



11

The absolute configurations of (−)-1-[(4-nitrophenylthio)ethyl]ruthenocene and (+)-1-[(4-nitrophenylthio)ethyl]-osmocene, which were prepared from (*R*)-(−)-1-(hydroxyethyl)–ruthenocene and –osmocene by simple substitution respectively, have been established, which indicates that the substitution reaction goes with retention of configuration.[42] An improved synthesis of biruthenocene by oxidation of ruthenocene with an excess of *p*-benzoquinone and BF_3 has been developed; this reaction affords the biruthenocenium dication as the BF_4 salt which on crystallization gives the mixed valence salt **12**, which is shown as **13**.[43]



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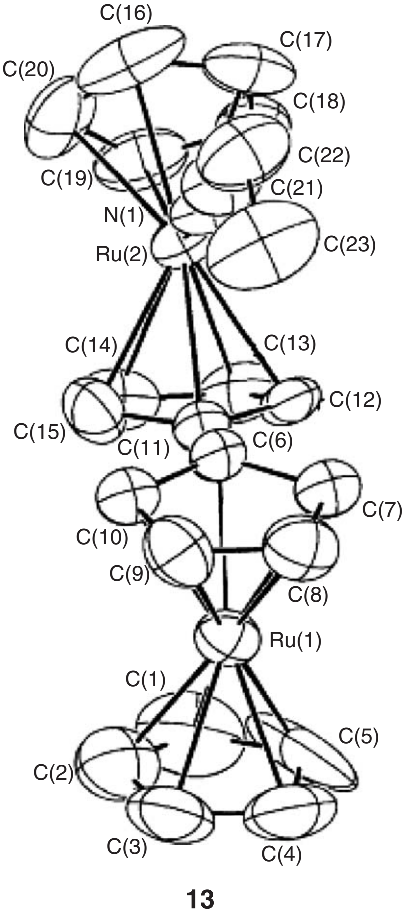
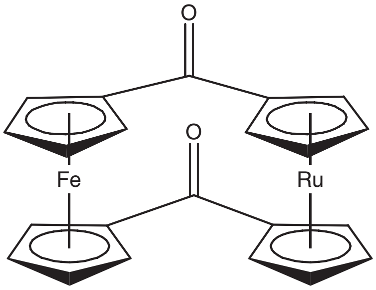


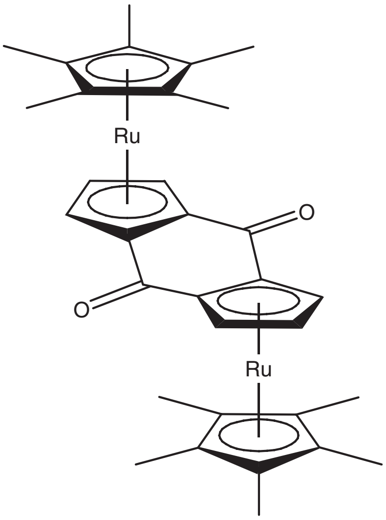
13

The structures of the mixed ferrocene ruthenocene compounds α-carbonium {[1]-(1,1′)ferroceno[1](1,1′)ruthenocenophane}-1-ylium hexafluorophosphate,[44] the mercury-bridged ferrocenophane $[\{C_5H_4(CH_3)_2\}_2Fe–Hg–Fe\{C_5H_4(CH_3)_2\}_2](BF_4^-)_2$,[45] and *anti*-ferrocenium[1,1]ruthenocenophanes such as **14** have also been reported.[46]



14

Three interesting ruthenocenyl diones have been obtained: **15** by treatment of the compound $[RuCp^*(\eta^5\text{-}C_5H_4CO_2H)]$ with $(CF_3CO)_2O$ and **16** and **17** from reaction of ruthenocene carbonyl chloride with $AlCl_3$.[47]



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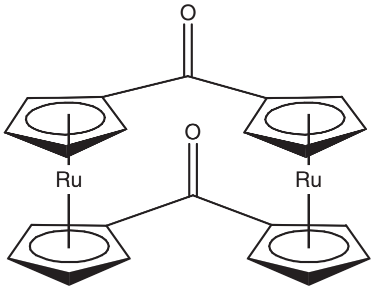

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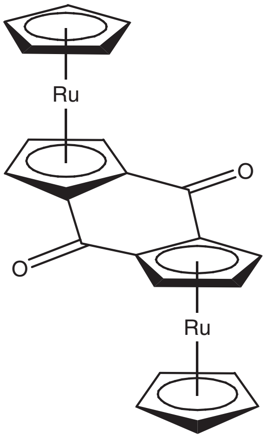
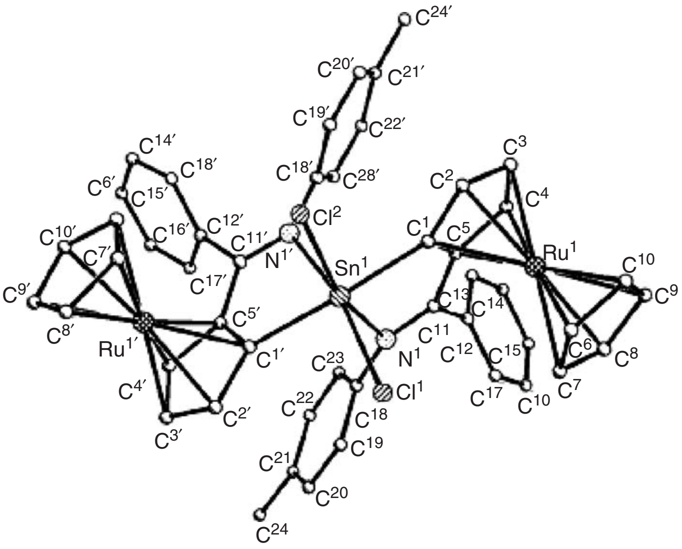


17

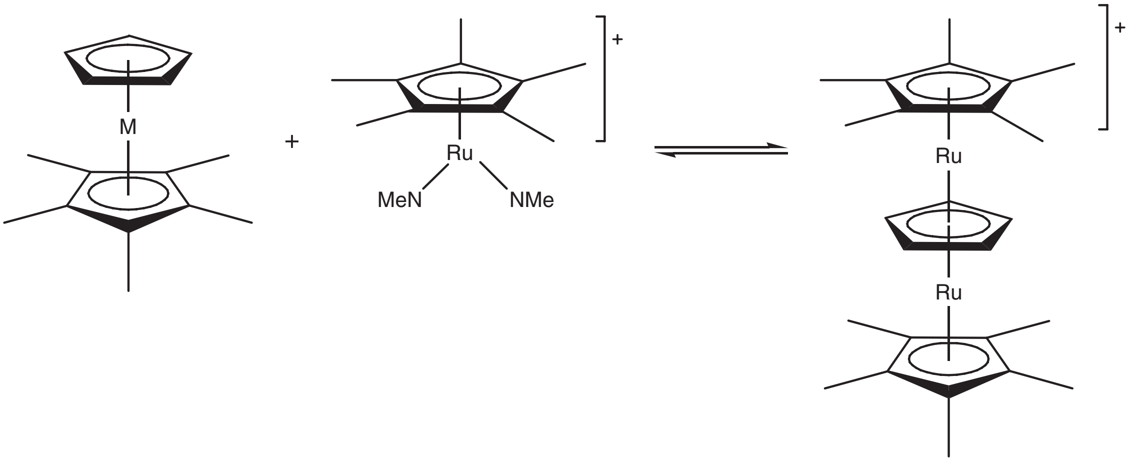
In related work 1-ethynyl-2,3,4,5-tetramethylruthenocene has been obtained from the 1-formyl precursor compound by treatment either with Me_3SiCHN_2/*n*-BuLi or via the 1-(2′,2′-dichlorovinyl)-2,3,4,5-tetramethylruthenocene, which was obtained under standard conditions ($Cl_3CP(O)(OEt)_2$/*n*-BuLi), followed by reaction with *tert*-butyllithium.[48] Aza-crown-substituted ruthenocenes have been prepared with either a carbonyl spacer or a methylene spacer starting with either dimethylaminomethylferrocene or ferrocenecarboxylic acid.[49] The β,β'-fused metallocenoporphyrins including the ruthenocene derivatives have been obtained in an elegant synthetic strategy which uses cyclopentene-fused porphyrin precursors.[50] Synthetic methods for the preparation of singly-, doubly- and triply-charged cations based on decamethylruthenocenes have been reported using a formyl protonation strategy.[51,52] It is also observed that cyclopalladated α-(*p*-tolylimino)benzylruthenocene reacts with metallic tin to produce bis-chelate complexes such as **18**.[53]



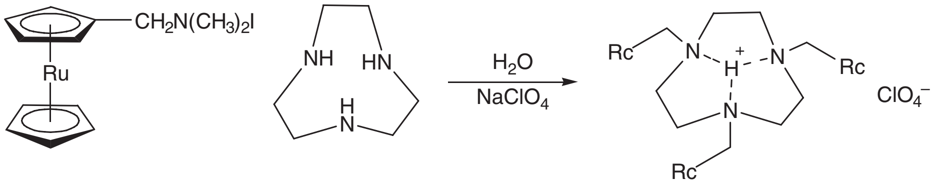
18

A supramolecular host *N*,*N*′,*N*″-tri(ruthenocenylmethyl)-1,4,7-triazacyclononane perchlorate has been prepared and structurally characterized. The preparation includes the straightforward reaction of 1,4,7-triazacyclononane with *N*,*N*′,*N*″-trimethylruthenocenylammonium iodide (Scheme 1).[54]

Triple-decker salts of the type $[\mathrm{Cp^*M}(\mu\text{-Cp})\mathrm{RuCp^*}][\mathrm{CF_3SO_3}]$ have been obtained (M = Fe, Ru) from pentamethylmetallocenes. In addition, a range of metalloelectrophiles of the general type $[\mathrm{LM(solv)_3}]^{2+}$ has been reacted with pentamethylruthenocene to give product cations of the type $[\mathrm{Cp^*RuCpML}]^+$. A typical such structure is shown as **19**.[55]



19

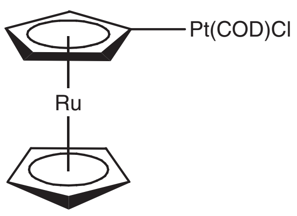


Scheme 1

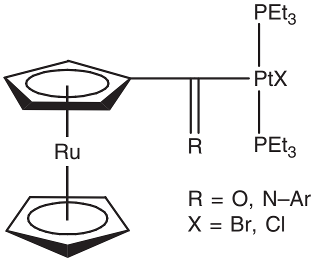
6.16.3 Ruthenocenophanes

The octamethyl[3]ruthenocenophane $[\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_3C_5Me_3\}Ru]$ has been obtained simply by refluxing $RuCl_3{\cdot}xH_2O$ with $HC_5Me_4(CH_2)_3C_5Me_4H$ at 200 °C. The method is suitable for the preparation of a number of sterically congested ruthenocenes, and it has been applied to the preparation of $[Cp_2^*Ru]$ and $[(\eta^5\text{-}C_5Me_4H)_2Ru]$.[56] The disilane-bridged [2]ruthenocenophane $[Ru(\eta\text{-}C_5H_4SiMe_2)_2]$ was simply obtained on treatment of [*cis*-$RuCl_2(DMSO)_4$] with the dilithium salt of the $[(C_5H_4SiMe_2)_2]$ dianion. This compound is a sublimable pale yellow crystalline solid. The bis(silane)-bridged [2][2]ruthenocenophane $[Ru\{\eta\text{-}C_5H_3(SiMe_2)_2\}_2]$ was also prepared in the same study, and was found to be considerably ring-strained (tilt angle 129°); however, it is resistant to thermal ring-opening polymerization.[57] The reaction of the bis(triflates) $[\{\eta^5\text{-}C_5H_4(CH_2)_nOTf\}_2Ru]^{2+}$ ($n = 3, 4, 6$), which derive from the bis(alcohols) $\{\eta^5\text{-}C_5H_4(CH_2)_nOH\}_2Ru$, on treatment with triflic anhydride, with $Na_2[Os(CO)_4]$ results in the formation of the osmametallocenophanes $\{\eta^5\text{-}C_5H_4(CH_2)_nOs(CO)_4(CH_2)_nC_5H_4\text{-}\eta^5\}Ru$.[58]

The σ-ruthenocenylplatinum complexes of the type **20** have been obtained in the transmetallation reactions of trimethyltin-substituted ruthenocenes with $[Pt(1,5\text{-}COD)Cl_2]$. These complexes may then be derivatized to the corresponding phosphine complexes by ligand exchange, and in turn these may be reacted with carbon monoxide and aryl isocyanides to give the insertion products **21**.[59]

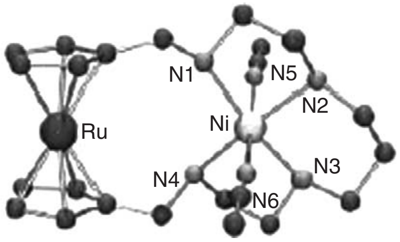


20



21

The structure and electrochemistry of a number of diruthenium(II, III) tetrametallocene carboxylates have been studied in a general paper, which examines the coordination chemistry of ferrocene and ruthenocene bis-carboxylates.[60] Ruthenocene (and ferrocene)-functionalized tetraazamacrocyclic ligands have been obtained from 1,1′-diformylruthenocene on treatment with *N*,*N*′-bis(2-aminoethyl)-1,3-propanediamine. These ligands may be used to obtain a range of metal complexes such as the nickel complex shown in **22**.[61]



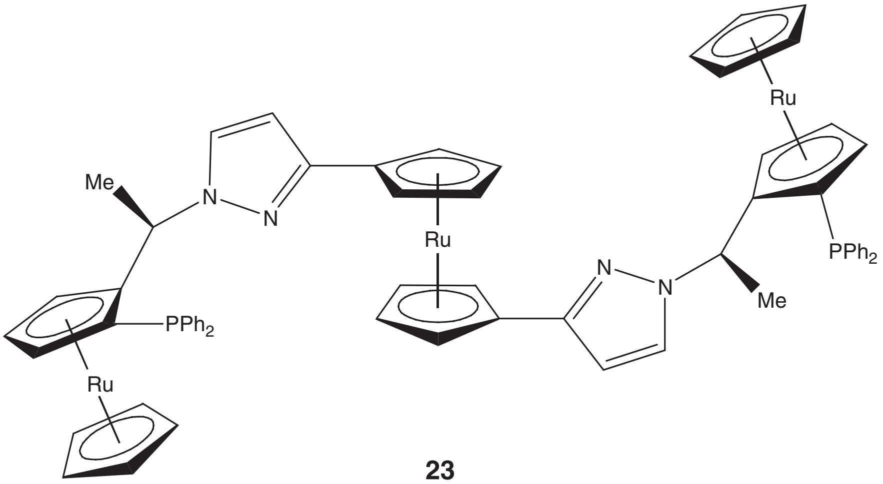
22

6.16.4 Physical Chemistry and Catalysis

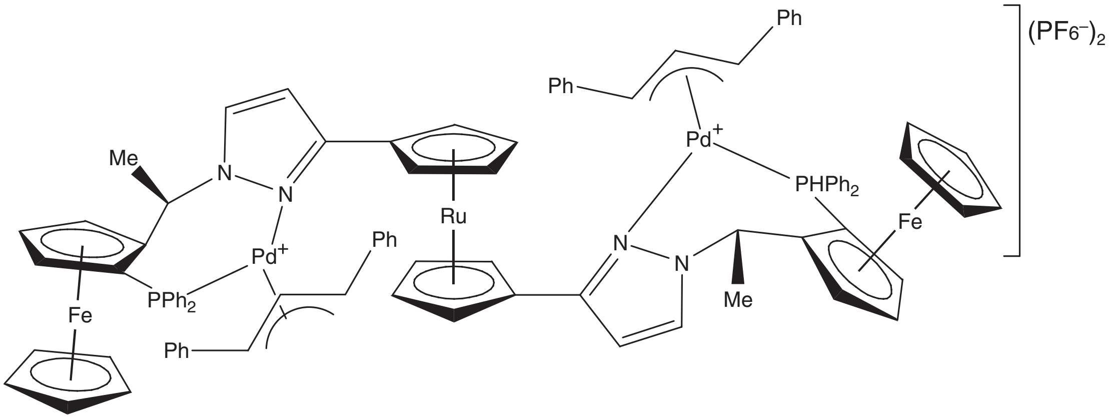
The density functional approach has been used in an investigation of the protonation of ferrocene, ruthenocene, and osmocene in the gas phase, and the general conclusion is that the addition of a proton to the carbon atoms in the cyclopentadienyl ring is favored in ferrocene, whereas metal protonation is favored with ruthenocene and osmocene. The results obtained from these calculations were used in the interpretation of electrophilic substitution reactions of metallocenes.[62] The basicity of the ligand group 1,1′-bis(diphenylphosphino)metallocene has also been examined. This is an important aspect for catalysis because it has proved difficult to obtain results which correlate with catalytic expectations in the past. In this work, the heat of protonation of dppf and dppr has been determined by titration calorimetry using CF_3SO_3H in 1,2-dichloroethane, and it is concluded that the basicity of these phosphines is lower than that of triphenylphosphine, and that the heats of protonation of the ferrocenyl- and ruthenocenyl-based phosphines are actually very similar.[63] It has been concluded that the nature of the metal in ferrocene and ruthenocene has little effect on the C–H bond length in metallocenes – this appears to be a general conclusion.[64] An application where basicity of ruthenocenes is clearly important is where they are used as ligands: for example, methoxycarbonylation of styrene, in which the dppf, dppr, and dppo together with their methylated analogs are used as ligands in the palladium-catalyzed reaction in the presence of a strong acid.[65] The electronic structure perturbations in substituted ruthenocenes have also been examined using photoelectron spectroscopy, where the substituents are methyl groups and halogens. Interestingly, it is concluded that in the case of an η^5-C_5F_5 ligand in comparison with an η^5-C_5Cl_5 ligand, the ring is only slightly more electron withdrawing in the perfluoro example despite the higher electronegativity of the fluorine.[66] The anodic electrochemistry of ferrocenylphosphine and ruthenocenylphosphine chalcogenide complexes and their Lewis acid adducts (BH_3) have also been examined.[67] More interesting is the electrochemical preparation of the bis-(ruthenocenium)dication which arises from the electrochemical oxidation of ruthenocene in dichloromethane containing either $[NBu_4]^+[B(C_6F_5)_4]^-$ or $[NBu_4]^+[B(C_6H_3(CF_3)_2)_4]^-$, where the product $[RuCp_2][B(C_6F_5)_4]$ precipitates allowing a simple isolation.[68] Oxidation of biruthenocene with iodine results in the formation of the monocationic iodoruthenocenyl salt $[Ru^{II}Cp(C_5H_5C_5H_4)CpRu^{II}I]^+I_3^-$.[69]

A general paper describes the synthesis of 1,1′-bis(diphenylphosphino)osmocene and its use as a ligand in the palladium-catalyzed methoxycarbonylation of olefins.[70,65] A number of related papers also describe the use of dppr and related ligands. For example, the reaction of $[RuClCp(PPh_3)_2]$ with dppr in benzene affords [RuClCp(dppr)], which forms the salt $[RuCp(CH_3CN)(dppr)]PF_6$ in the presence of NH_4PF_6 in boiling acetonitrile, which in turn reacts with ethynylbenzene to give the vinylidene complex $[Ru(C{=}CHPh)Cp(dppr)]PF_6$.[71] The nickel, palladium, and platinum dichloride complexes are also described in the context of a comparison of their structures with the ferrocenylphosphine analog complexes,[72] and their electrochemical behavior has also been investigated.[73] Simple phosphine exchange in $RuCl_2(PPh_3)_3$ with dppr also affords $[RuCl_2(dppr)(PPh_3)]$, which in turn gives the carbonyl complex $[RuCl_2(CO)(dppr)]$ and two isomeric forms of $[RuCl_2(NCCH_3)_2(dppr)]$ on treatment with CO or acetonitrile, respectively.[74] Not surprisingly, chiral ruthenocenylphosphines which mimic their ferrocene analogs, which were prepared in the early 1980s, have been obtained. Their chemistry is essentially comparable with the ferrocene-based analogs.[75,76]

Also, pincer ligands have been prepared from 1,3-bis(diisopropyl or *t*-butyl)(phosphinomethyl)ruthenocene. Notably, the iridium and rhodium complexes of these have been discussed. The iridium hydride complex $[Ir(H)(Cl)[\{2,5\text{-}(Bu^tPCH_2)_2C_5H_2\}Ru(Cp)]]$ exists in the form of a mixture of *endo*- and *exo*-isomers, the *exo* being the more thermodynamically favorable.[77] Trimetallic ruthenocene/ferrocene ligands **23** have been prepared in three steps from 1,1′-diacetylruthenocene, and further derivatized to the pentametallic bis-palladium allyl complex **24**.



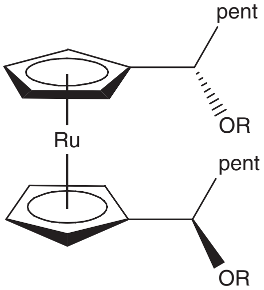
23



24

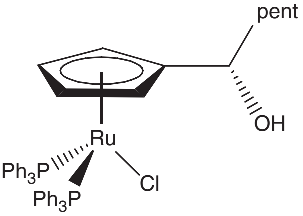
The former complex has subsequently been used as a catalyst in the palladium-catalyzed substitution reactions of ethyl(1,3-diphenylallyl)carbonate with benzylamine.[78]

Planar chiral benzyl and ethyl(phenyl) ferrocenylphosphines on reaction with $[(CH_3CN)Ru(\eta^4\text{-}C_5H_4O)Cp][CF_3SO_3^-]$ give planar chiral 2-phosphonioruthenocenols as mixed diastereomers.[79] A new enantioselective synthesis of chiral α-oxygen-substituted cyclopentadienyl ruthenocenes has been reported by Knochel. Examples are the complexes **25** and **26**.[80]



R = H, TBDMS
pent = pentyl

25

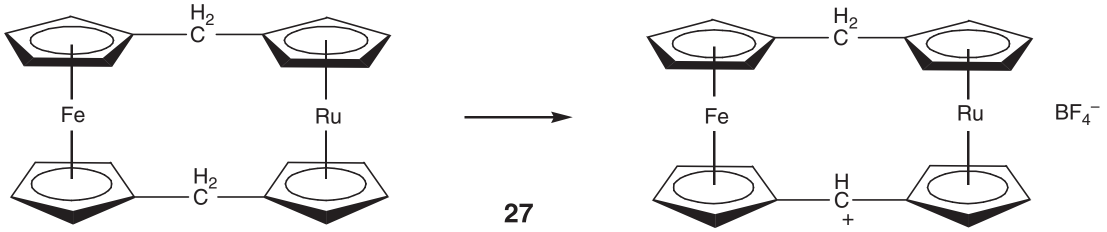


26

6.16.4.1 Protonation

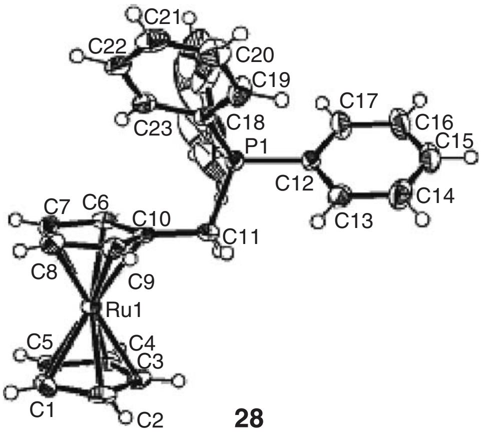
Following the early work on the IR spectroscopic study on the interaction of metallocenes with a range of phenols to form hydrogen-bonded adducts, the protonation of ruthenocene and osmocene has been examined.[81] The protonated metallocene $[Cp^*{}_2OsH]^+$ is observed to form hydrogen bonds with the counteranions.[82] The mechanism of the protonation of the metallocenes and their permethylated analogs with trifluoroacetic acid has also been examined, and it has been concluded that the formation of the hydrogen-bonded complex is the first stage of the protonation reaction.[83] The protonation and deuteration of [1.1]metallocenophanes have further elucidated the protonation mechanism. The work confirms that the protonation of ruthenocene occurs at the metal center only, in contrast with the protonation of ferrocene which occurs on the ring.[84] Extended Hückel and density functional theory (DFT) methods have been used to examine the intramolecular M–HO bond in α-metallocenylcarbinols; the approximate intramolecular M···H bond energies calculated are 4.1 and 5.0 kcal mol^{-1} for the ruthenocenyl– and osmocenyl–carbinols.[85]

The oxidation of [1.1]ferrocenylruthenocenophane with bromo- or chlororuthenocenium tetrafluoroborate gave the diamagnetic salt **27**, which was crystallographically characterized.[86] The molecular structures of $[RcHCl]^+BF_4^-$ and $[RcRcCl]^+BF_4^-$ were also determined.[87]



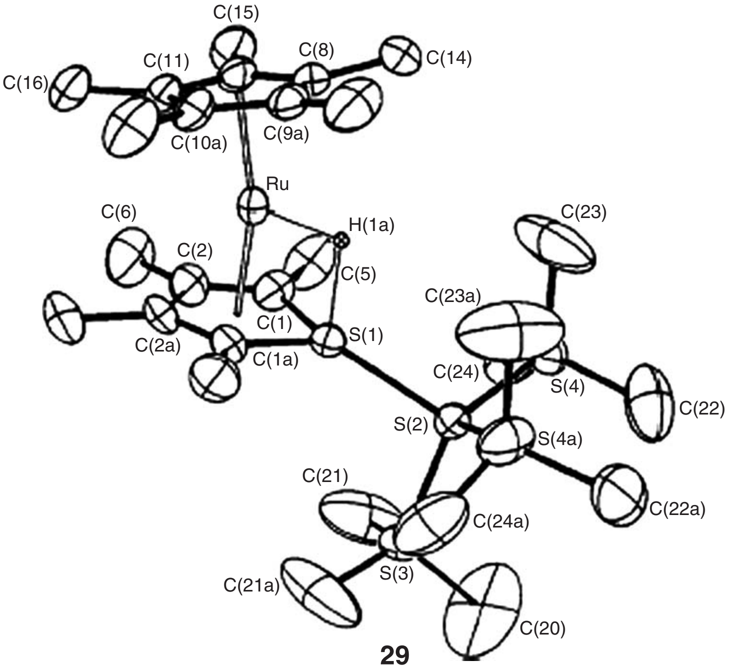
27

The dications which are obtained from decamethylruthenocene and -osmocene exhibit significant interactions between the carbocations and the metal centers; a *gauche*-conformation is preferred as indicated by both NMR and extended Hückel calculations.[88] The isolation and structures of η^5-cyclopentadienyl-η^6-fulvene ruthenium(II) salts, which are the products of the interaction of ruthenocenylmethanol with either Brønsted or Lewis acids, have been structurally characterized. These salts undergo reactions with triphenylphosphine to give complexes such as $[\mathrm{Rc{-}CH_2PPh_3}]^+\mathrm{BF_4}^-$ 28, where HBF_4 has been used as the acid in the synthesis.[89]



28

Stable silacyclopentadienyl complexes of $[\mathrm{Cp^*Ru\{\eta^5\text{-}Me_4C_4SiSi(SiMe_3)_3\}}]$ have also been prepared and the protonated form has been structurally characterized. In the crystal structure, shown as 29, the proton–metal interaction is clearly visible with the Ru–H bond distance of 1.48(7) Å, representative of a normal single bond length.[90]

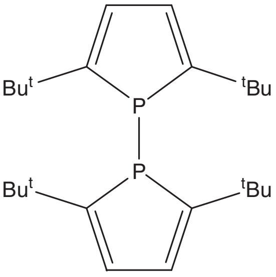


29

Decamethylruthenocene reacts with bromine in toluene in the presence of either HF or acetic acid to give a mixture of $[Cp^*{}_2RuBr]Br_3$ and $[Cp^*(C_5(CH_3)_4CH_2OH)RuBr]Br_3$.[91] The related complex $[Cp_2RuCl]PF_6$ reacts with electron-rich methylene C–H bond in benzylruthenocene in acetonitrile to give phenylruthenocenylmethylium cation and ruthenocene. It has been further observed that $[Cp_2MX]^+$ (M = Ru, Os; X = Cl, Br, I) react with leuco malachite green and leuco crystal violet to form carbenium ions.[92]

6.16.5 Phospharuthenocenes

While there are clearly fewer examples of phospharuthenocenes than those of the corresponding ferrocenes, there are several interesting examples. The air stable complex $[RuCp^*(Bu^t{}_2C_4H_2P)]$ has been prepared by two methods: the first is a redox reaction between $\{RuCp^*Cl_2\}_2$ and the 2,5-bis(*t*-butyl)phospholide anion $[2,5\text{-}{}^tBu_2C_4PH_2]^-$ and the second is the direct reaction of lithium metal with a bisphosphole **30**, and the same ruthenium precursor.[93] Other related phospholes which have been obtained are $[Ru({}^tBu_2C_2P_3)({}^tBu_3C_5P_2)]$ and $[RuCp(P_5)]$.[94,95] The crystal structure of the new phospharuthenocene is shown as **31**.



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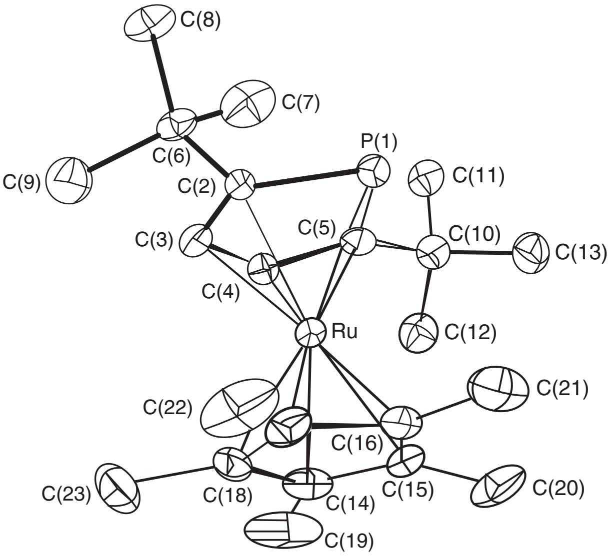
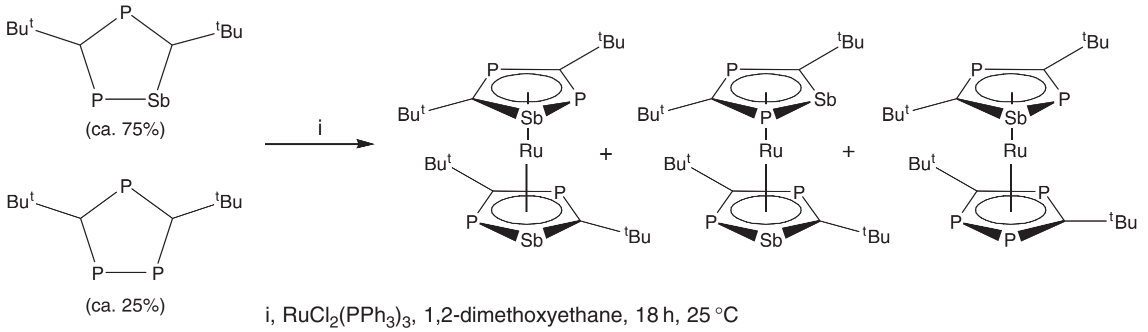


31

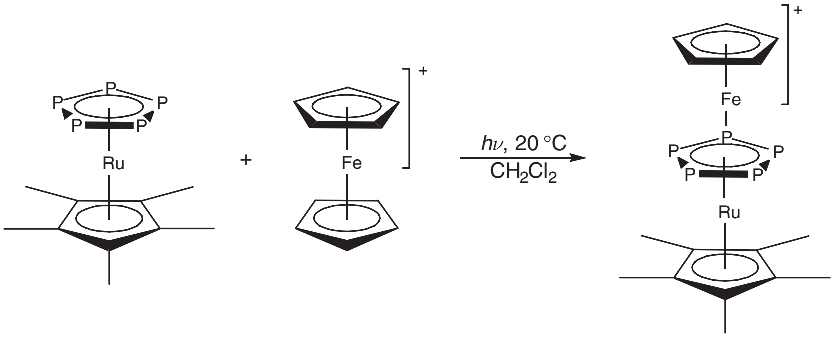
A range of related tri-, penta-, and hexaphospharuthenocenes has been obtained using $[RuCl_2(PPh_3)_3]$ as a precursor on reaction with the metal salts of the phosphole anions.[96] A range of 2-silyl-sybstituted phospharuthenocenes have been used as precursors to acyl(trifluoroacetyl), (2-phospharuthenocenyl)methanol, and (2-phospharuthenocenyl)methylphosphine.[97] Variable-temperature NMR spectroscopy has been used to examine the solution behavior of mono- and diphospha-metallocenes with chiral menthyl substituents. The restricted rotation caused by the bulky ligands meant that a mixture of two slowly interconverting diastereoisomers could be observed.[98] A series of polyheteroferrocenes and ruthenocenes which derive from the 1,4,2-diphosphastiboyl ring anion $[P_2SbC_2{}^tBu_2]^-$ have been obtained, again using $[RuCl_2(PPh_3)_3]$ as the key precursor. Variable-temperature NMR spectroscopy has again been used to examine the solution behavior of the ring rotation. It is observed that there is an antimony–antimony interaction which restricts fluxionality. A synthetic scheme for the preparation of these compounds is shown in Scheme 2.[99]

Triple-decker compounds with central pentaphospholyl ligands have been obtained and structurally characterized. These are obtained by reaction of pentaphosphametallocenes $[Cp^*M(\eta\text{-}P_5)]$ with half-sandwich fragments $[(\eta\text{-}C_5R_5)M']^+$ (M = Fe, Ru). Such complexes are prepared as represented in Scheme 3.[100] A simple and effective synthesis has been developed for the production of pentamethylated and pentaphenylated aza ruthenocenes.[101]



i, $RuCl_2(PPh_3)_3$, 1,2-dimethoxyethane, 18 h, 25 °C

Scheme 2



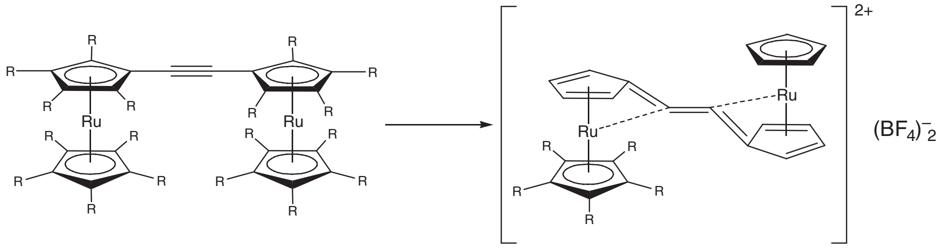
Scheme 3

6.16.6 Mixed Valence Biruthenocenes

A series of papers on mixed valence biruthenocenes have appeared essentially following the success in the case of the mixed valence biferrocenes. The oxidation of ethylbiruthenocene with $[RCHX]^+[Y]^-$ ($X = Cl$, Br, I; $Y = PF_6^-$, I_3^-) results in the formation of the mixed valence halo-1′-ethylbiruthenocenium salts in which the electron exchange is accompanied by a halide migration.[102] The iodine oxidation of ferrocenylruthenocene to give the iodo-ferrocenylruthenocenium$^+I_3^-$ salt has been examined by ^1H and ^{13}C NMR spectroscopy. While most ferrocenium and biferrocenium salts are paramagnetic, the mixed ferrocene ruthenocene tetraiodide is diamagnetic.[103] A subsequent report followed up this work with an examination of the oxidation of 1,1″-biruthenocene with iodoruthenocenium(IV)$^+Y^-$ salts to give the iodo-1,1″-biruthenocenium(II, IV)$^+Y^-$ salts ($Y = PF_6$, BF_4, etc.),[104] some of which were crystallographically characterized.[105] Similar work was subsequently carried out on the [1.1]ferrocenylruthenocenophanium salts.[106,107]

6.16.7 Ruthenocenyl Alkynes

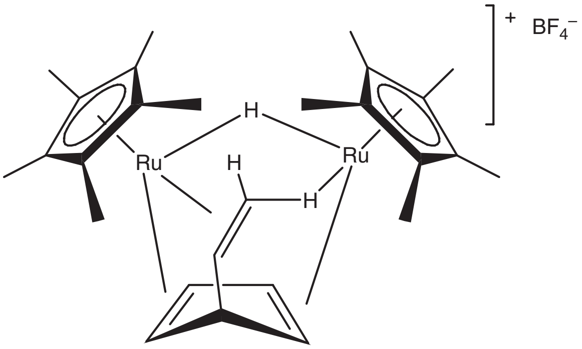
Ethynylruthenocene reacts with platinum halides under standard coupling conditions (CuI, diethylamine) to give the corresponding acetylide complexes. For example *trans*-$[Pt(C{\equiv}CRc)(C_6H_4X\text{-}p)(PPh_3)_2]$ ($X = H$, Me, OMe, Cl, CO_2Me) are obtained from the corresponding iodide complex; similarly *cis*-$[Pt(C{\equiv}CRc)(C_6H_4OMe\text{-}p)(dppe)]$ has been reported in the same preparative report.[108] The titanocene bis-acetylide complexes $[(\eta\text{-}C_5H_4SiMe_3)_2Ti\{(C{\equiv}C)Rc\}_2]$ react with silver hexafluorophosphate to give heptanuclear complexes of the form $[(C_5H_4SiMe_3)_2Ti_2\{(C{\equiv}C)Rc\}_4Ag](PF_6)$, which is a complex which has a "molecular tweezer" -like structure.[109] The reaction of ethynylruthenocene with $[RuClL_2(\eta^5\text{-}C_5R_5)]$ ($R = H$, Me; $L_2 = (PPh_3)_2$ or dppe) in the presence of NH_4PF_6 followed by chromatography on basic alumina gives the yellow crystalline complexes $[RcC{\equiv}CRu(PPh_3)_2Cp^+]$ ($Cp^+ = Cp$, Cp^*). A range of pentamethylruthenocene-containing analog complexes were also prepared.[110] A series of μ_2-η^6:η^6-bis(cyclopentadienylidene)ethene complexes have been obtained by the two-electron oxidation of 1,2-bis(ruthenocenyl)ethynes and bis(1′,2′,3′,4′,5′-pentamethylruthenocenyl)ethynes. An example is shown below (Scheme 4).[111]



Scheme 4

6.16.7.1 Structural Chemistry

The treatment of [Cp*Ru(H$_2$O)(nbd)]BF$_4$ with HCO$_2$Na in THF gave a bimetallic complex, which on further treatment with HBF$_4$ gave the known bimetallic complex 32, which may also be obtained directly by treatment of [Cp*RuH(nbd)] with HBF$_4$. On standing, this disproportionated to a mixture of three compounds including the triple-decker complex 33 and [Cp*Ru(η^5-C$_5$H$_4$Et)].[112]



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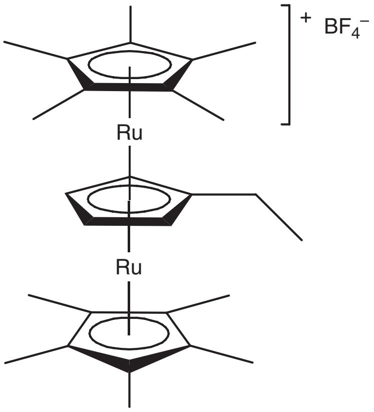
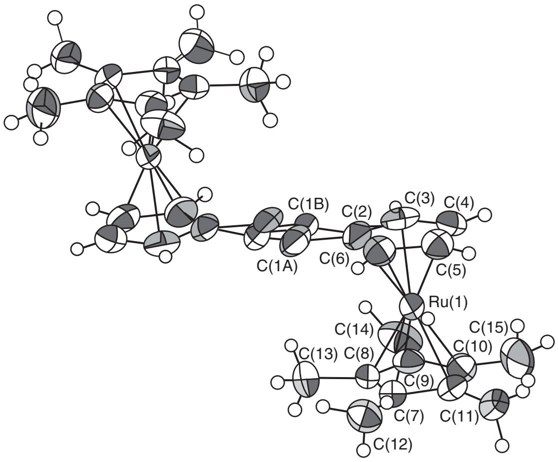


33

The reaction of 1,2,3,4,5-pentamethylruthenocene with dimethylformamide and POCl$_3$ gives 1′,2′,3′,4′,5′-pentamethyl-1-formylruthenocene, which can be oxidized to 2,3,4,5-tetramethyl-1-formylruthenocene by MnO$_2$ in low yield. Treatment of these aldehydes with TiCl$_4$/Zn results in the production of the dinuclear ethylenes, one of which was structurally characterized and is shown as 34. Following oxidation with *p*-benzoquinone–BF$_3$·OEt$_2$, this results in the formation of the air stable [(μ-η^6:η^6-pentafulvadiene)diruthenium] complexes, one of which was structurally characterized, and is shown as 35.[113] It has been observed that [(η^5-pentamethylcyclopentadienyl)(η^5-5,6,7-trihydro-4,8-dimethyl-5-indacenyl)ruthenium(II)] is isostructural with its ferrocene analog.[114]



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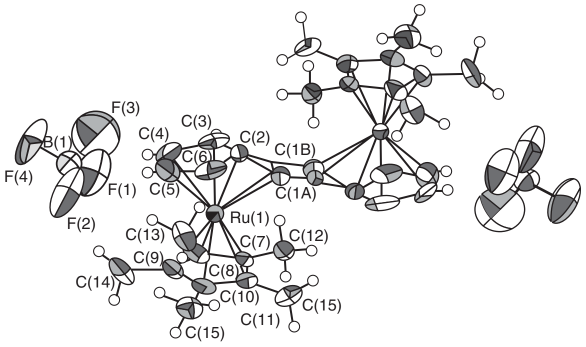
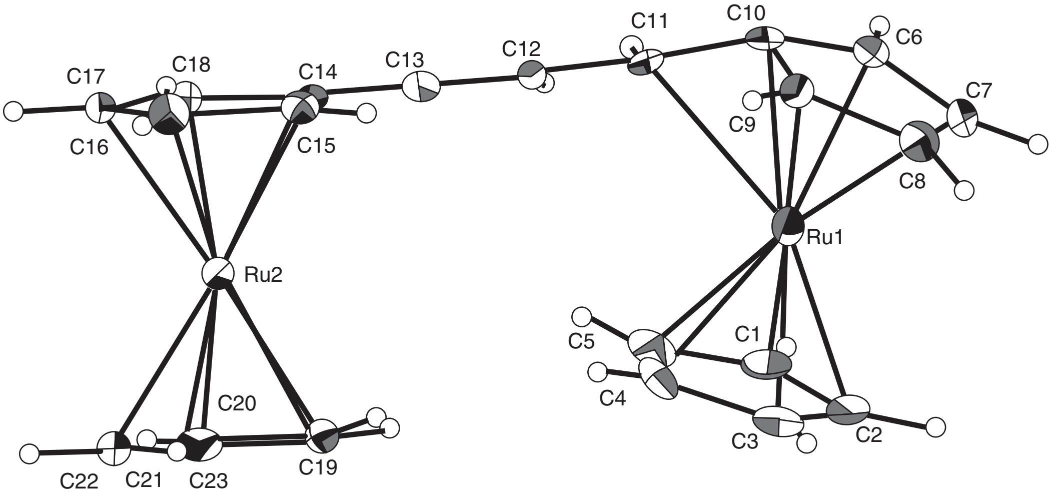


35

Finally, the 1,3-bis(ruthenocenyl)allylium cation has been crystallographically characterized, 36.[115] Several other key synthetic references are listed as follows: silabenzene complexes of [Cp*Ru],[116] conjugated ruthenocenes for non-linear optics,[117] self-exchange reactions of substituted ruthenocenes,[118] and a rational approach to polymetallocenes for their optical properties.[119]



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6.17
Dinuclear Ru/Os Compounds with Metal–Metal Bonds

J D Wilton-Ely, University of Oxford, Oxford, UK

6.17.1 Introduction

Due to the nature of the complexes involved, a review of dinuclear ruthenium and osmium compounds will always encounter problems of classification. This review of the literature since 1993 will use the nature of the principal bridging ligand as the basis for classification. However, the prevalence of complexes with a mixture of bridging ligands, encompassing different modes, will inevitably lead to compounds having equal right to be discussed in more than one section.

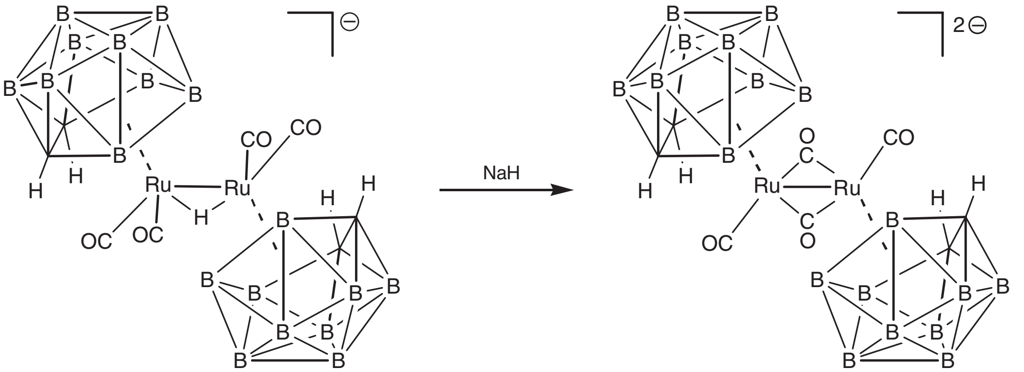
6.17.2 Complexes with Non-Hydrocarbon Bridging Ligands

6.17.2.1 Complexes with Ligands Containing Donors of Groups 13 or 14

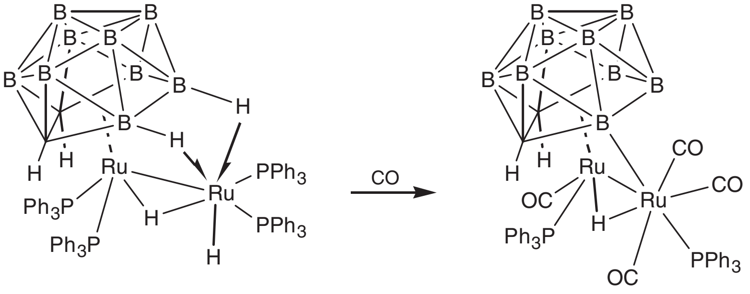
6.17.2.1.1 Complexes with boron and gallium ligands

A small number of carborane complexes containing ruthenium–ruthenium bonds has been reported, drawing on the formal relationship between the pentahapto bonding modes of cyclopentadienyl ligands and certain carboranes.

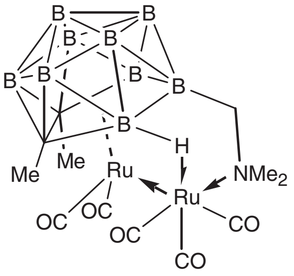
The bridging between the metal centers in complex **1** (NEt_4^+ or K(18-crown-6)$^+$ salts; non-coordinating BH hydrogens omitted in complexes **1–7**) is assisted by a hydride ligand with the carborane moieties acting as supporting ligands.[1] Treatment of **1** (K(18-crown-6)$^+$ salt) with sodium hydride in tetrahydrofuran leads to deprotonation and formation of the dianion **2** (K(18-crown-6)$^+$ double salt).[1] The complex [K(18-crown-6)][$RuH(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$] reacts with $RuCl_2(PPh_3)_3$ to yield **3**, in which the carborane bridges two metal centers through interactions of the BH bonds. On treatment with CO, these interactions are broken and a direct Ru–B bond results **4**.[2] Reaction of a triruthenium carborane, $Ru_3(CO)_8(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$, with $Me_2NCH_2NMe_2$ results in the formation of two dinuclear compounds **5** and **6a**. Reaction of the same precursor with pyridine gives two further diruthenium species **6b** and **6c**. A related product, **7**, was obtained from the reaction of the same precursor with trimethylphosphine.[3]



1 **2**



3 **4**



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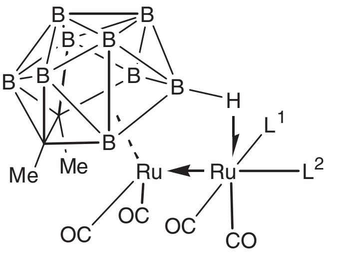
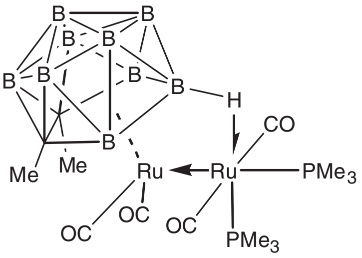


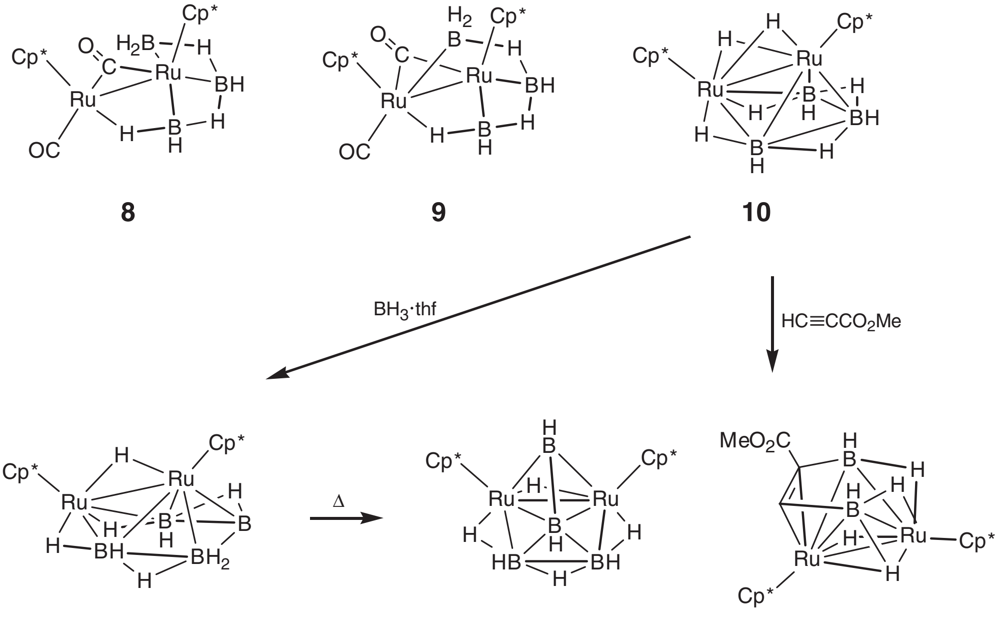
6a: L^1 = $NHMe_2$ L^2 = CO
6b: L^1 = py L_2 = CO
6c: L^1 = py L_2 = py



7

A number of ruthenaborane products results from the reaction of $Co_2(CO)_8$ with 1,2-$(Cp^*RuH)_2B_3H_7$. The only dinuclear species is isolated in low yield and exists in two forms, one involving a single B–H–Ru bridge **8** and the other exhibiting a supplementary Ru–B interaction **9**.[4] The yields of these isomers were found to be dependent on solvent effects and a mechanism involving radical pathways was postulated.

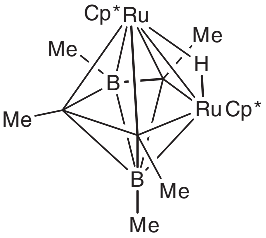
The reactions of $\{Cp^*RuCl_2\}_2$ and $Li[BH_4]$[5] or $\{Cp^*RuCl\}_4$ and $BH_3{\cdot}thf$[6] result in the formation of *nido*-1,2-$(Cp^*Ru)_2$-$(\mu\text{-}H)_2B_3H_7$ **10**, which reacts further with $BH_3{\cdot}thf$ to yield *nido*-1,2-$(Cp^*Ru)_2(\mu\text{-}H)B_4H_9$ **11**. Thermolysis of complex **11** leads to loss of hydrogen to give *pileo*-2,3-$(Cp^*Ru)_2B_4H_8$ **12**.[5] Complex **10** reacts with $HC\equiv CCO_2Me$ to yield **13**, in which the alkyne is incorporated into the borane framework rather than solely coordinated to a metal site.[7] In addition to the reactions above, compound **10** is the starting point for a wealth of alkyne insertion[8–11] and other chemistry.[6,12,13]



8 **9** **10**

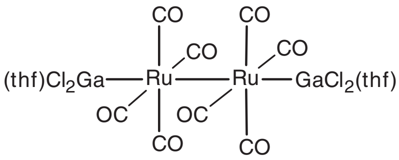
11 **12** **13**

The diruthenium *isocloso*-cluster [1,5-(*p*-cymene)$_2$-1,5-$Ru_2B_8H_8$] **14** was characterized as the only isolable product from the reaction between [6,9-(*p*-cymene)$_2$-*nido*-6,9-$Ru_2B_8H_{12}$] and KH followed by treatment with $[PtCl_2(PMe_2Ph)_2]$.[14] Another unexpected ruthenaborane is the *closo*-cluster **15**, which is formed by the ejection of sulfur from $[Cp^*Ru\{\eta^5\text{-}(CMe)_3(BMe)_2\}Ru{=}S]$.[15] The crystal structure shows a hydride bridging apical and basal ruthenium centers. This material is discussed in greater depth in Chapters 3.04 and 3.05.



15

A rare example of a diruthenium complex with gallium ligands is provided by compound **16**, which is formed from the reaction of $Ru_3(CO)_{12}$ with Ga_2Cl_4 in the presence of gallium metal in refluxing toluene. Crystallization from tetrahydrofuran provides the solvated species shown below.[16]



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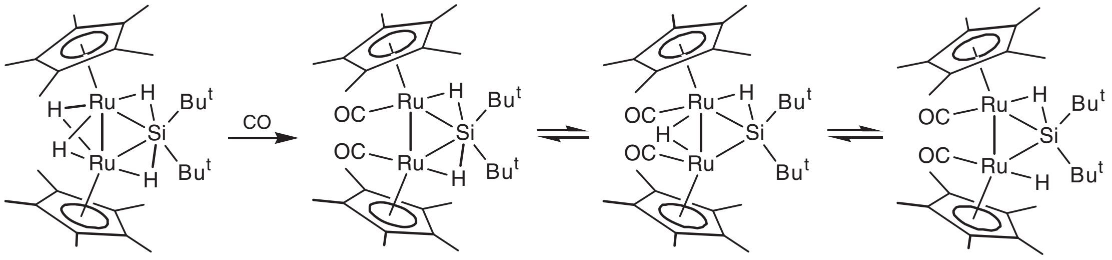
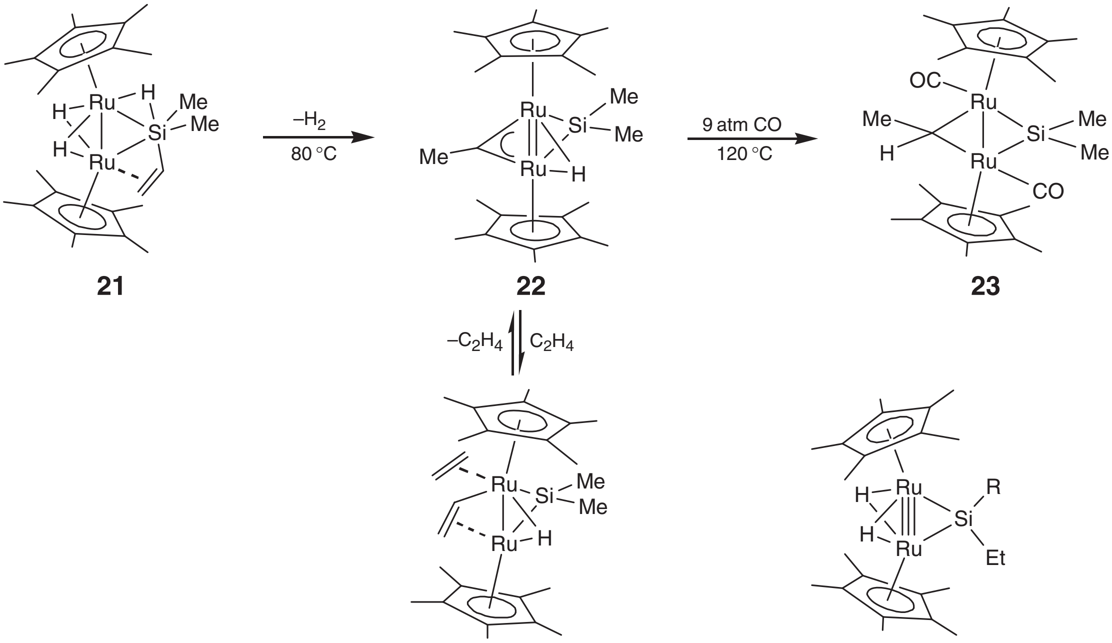
6.17.2.1.2 Complexes with silicon ligands

There has been significant growth in the number of diruthenium complexes bridged by silicon-based ligands over the last decade. The tetrahydride complex $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ is often used as an entry point for chemistry exploring the bridging of ruthenium centers with silane ligands. Treatment of this complex with $Bu^t{}_2SiH_2$ leads to complex **17**, which displays an unusual coordination mode for the silane ligand. The bridging hydrides are displaced on reaction with carbon monoxide at room temperature (RT) to provide **18**, which is in equilibrium with two isomers, **19** and **20**, with differing bridging hydride arrangements.[17]



17 **18** **19** **20**

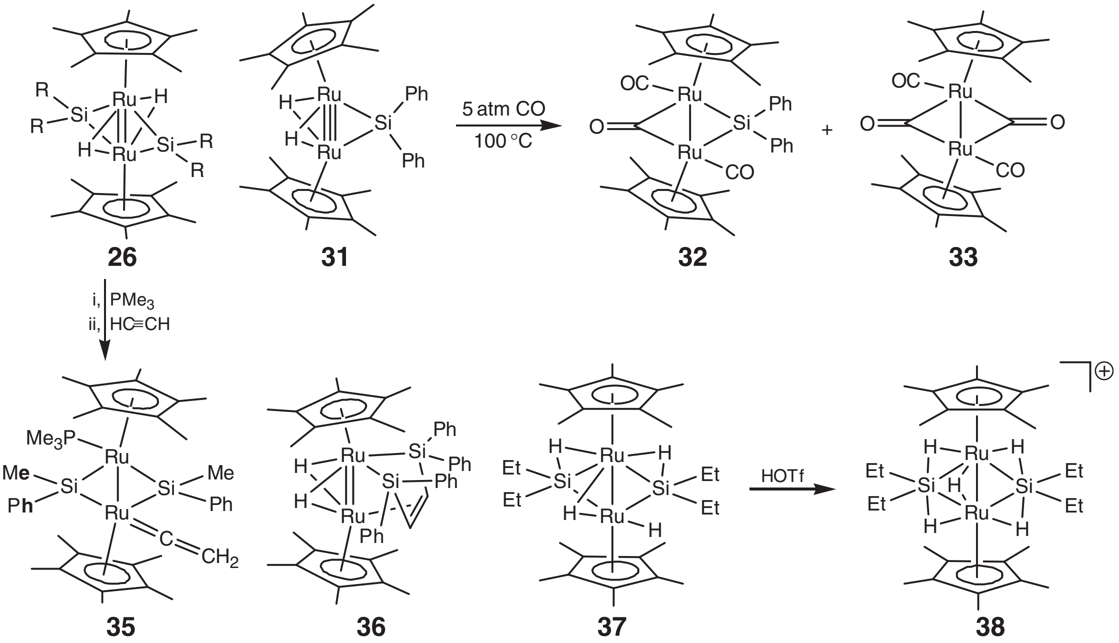
Reaction of $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ with dimethylvinylsilane provides **21** in quantitative yield.[18] The reaction mechanism was investigated using $DSi(Me)_2CH{=}CH_2$, suggesting that elimination of hydrogen occurs followed by coordination of the Si–H bond. Compound **21** was also structurally characterized. Further elimination of hydrogen occurs when **21** is heated to afford a μ-silylene μ-ethylidyne complex, **22** (70% yield), via Si–C(sp^2) bond cleavage and subsequent insertion of the C=C bond into an Ru–H bond. Exposure of **22** to CO at elevated temperatures leads to transformation to a μ-ethylidene complex **23**, while treatment with ethene provides an ethenyl complex, **24**, with coordinated alkene ligand.[18] In contrast to the synthesis of **21**, reactions of $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ with $RSi(H)_2CH{=}CH_2$ (R = Me, Ph) result in $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}SiREt)$ **25**.[19]



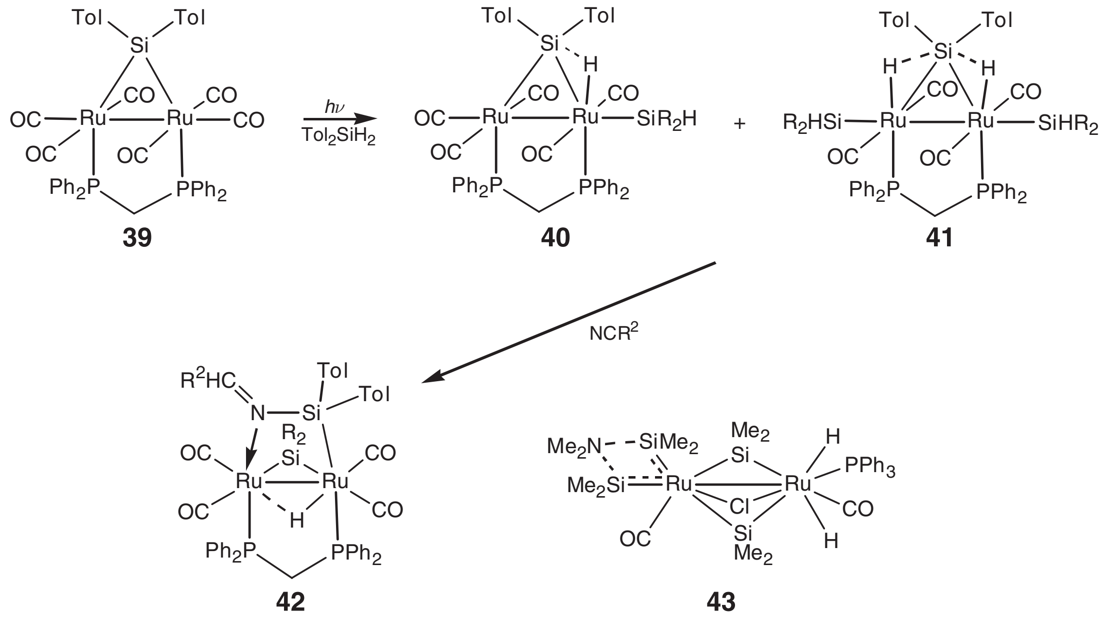
21 **22** **23** **24** **25**

Reaction of Ph_2MeSiH with $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ provides a mixture of *syn*- and *anti*-diastereomers of **26** (R = Me, Ph), whereas treatment with $PhMe_2SiH$ leads to isolation of both $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}SiPhMe)(\mu\text{-}SiMe_2)$ **27** and $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}SiMe_2)_2$ **28**.[19] While $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}SiPh_2)_2$ **29** reacts quantitatively with CO (5 atm) to yield $\{Cp^*Ru(CO)\}_2(\mu\text{-}SiPh_2)_2$ **30**, the mono μ-silylene compound **31** gives two products **32** and **33** when treated with 8 atm of CO at 100 °C.[19] A phosphine complex $\{Cp^*Ru(\mu\text{-}SiPhMe)\}_2(PMe_3)(H)_2$ **34** is obtained from reaction of **26**

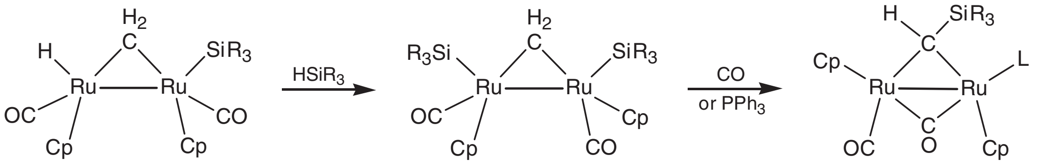
(R = Me, Ph) with PMe_3 in good yield. This product undergoes slow reaction with ethyne to yield the vinylidene complex **35**.[19] This contrasts with the reaction of **29** with ethyne, which yields complex **36** as a result of insertion of the alkyne into the Ru–Si bond.[20] The bis-μ-diethylsilyl compound **37** reacts with triflic acid to give the cationic bis-μ-diethylsilane complex **38** ($CF_3SO_3^-$, BPh_4^- salts).[21]



$Ru_3(CO)_{10}(\mu\text{-dppm})$ reacts with Tol_2SiH_2 in toluene to give complexes **39** and **40** (R = Tol). Complex **40** (R = Tol) can be obtained from **39** by irradiation with an excess of Tol_2SiH_2, allowing the reaction to be followed by ^1H NMR spectroscopy. A further product, **41** (R = Tol), with two agostic Si–H interactions is also formed and its yield enhanced by removal of CO from the reaction vessel.[22] An unusual μ-iminosilyl complex, **42** (R^1 = Tol; R^2 = Me, Ph, Bu^t, CH═CH_2), is obtained on reaction of **41** with nitriles, NCR^2. Furthermore, **41** (R = Tol) is an effective catalyst for the hydrosilylation of imines and ketones.[23] An unexpected product (20% yield) from the reaction of the coordinatively unsaturated silyl complex $RuCl(SiMe_2Cl)(CO)(PPh_3)_2$ with an excess of $HSi(Me)_2NMe_2$ is the unique chloro and bis(silylene)-bridged complex **43**.[24]

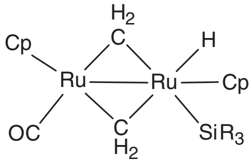


The preparation of silyl compounds from methylene-bridged diruthenium complexes is achieved by treatment of the complex $[Ru_2Cp_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)]$ with hydrosilanes to yield **44** ($SiR_3 = SiMe_3$, $SiPh_3$, $SiMe_2Ph$), and **45** ($SiR_3 = SiMe_3$, $SiEt_3$, $SiPh_3$, $SiMe_2Ph$) on further reaction with $HSiR_3$.[25] Heating **45** with $HSiMe_3$ produces a mixture of products including methane, leading the authors to discuss the system as a model for the Fischer–Tropsch mechanism.[25] Reaction of **45** (R = Me, Ph) with CO or PPh_3 leads to C–H/Si–C activation of the neighboring silyl groups to give **46** (L = CO, PPh_3; R = Me, Ph).[26]



44 **45** **46**

Bis(methylene) species have also been employed as precursors to silyl (**47**; $SiR_3 = SiMe_3$, $SiHEt_2$) and silylene **48** complexes.[27] Diruthenium bridging vinylidene species react with hydrosilanes to yield bridging alkenyl complexes (**49**; $SiR_3 = SiMe_2Ph$, $SiPh_3$).[28] Complex **50** ($R = SiMe_2Ph$)[29] was isolated from oxidative addition of $HSiMe_2Ph$ to (μ^2-η^3:η^5-4,6,8-trimethylazulene)$Ru_2(CO)_5$ in benzene at 60 °C for 18 h.



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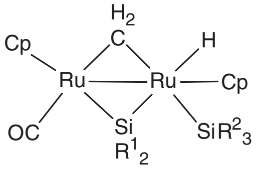
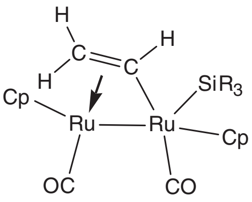


48

R^1 = Me $SiR^2_3 = SiMe_2Ph$
R^1 = Et $SiR^2_3 = SiHEt_2$
R^1 = Ph $SiR^2_3 = SiPh_3$, $SiHPh_2$



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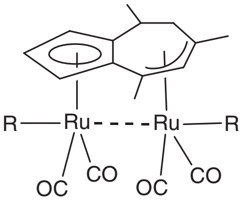
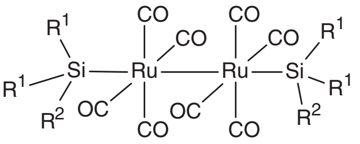
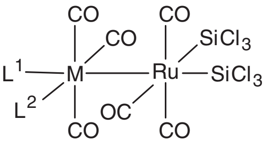


50

Dinuclear complexes containing unbridged dative metal–metal linkages are still relatively rare. One example is the structurally characterized, solvatochromic species **51** (R^1 = Me, R^2 = Ph), which was prepared in an investigation of the polymers $[\text{–}SiR^1R^2\text{–}Ru(CO)_4\text{–}Ru(CO)_4\text{–}SiR^1R^2\text{–}C_6H_4\text{–}]_n$.[30] Irradiation of the siloxyl-substituted ruthenium cluster, $[Ru_3(\mu\text{-}H)\{\eta^2\text{-}Si(OSiMe_3)_3\}(CO)_{10}]$, results in high yields of **51** ($R^1 = R^2 = OSiMe_3$).[31] The $Ru(CO)_3(SiCl_3)_2$ fragment proves an exceptionally good acceptor for $M(CO)_3(L^1)(L^2)$ units, allowing homo- and heterobimetallic complexes **52** to be formed.[32]



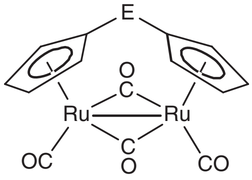
51



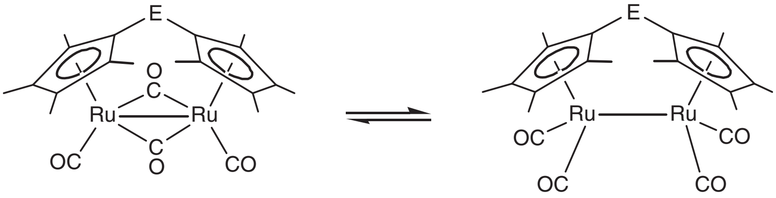
52

M	L^1	L^2
Ru	$P(OCH_2)_3CMe$	CO
Ru	$CNBu^t$	$CNBu^t$
Ru	PMe_3	CO
Os	PMe_3	CO

The preparation of complexes bearing silicon-bridged cyclopentadienyl ligands has been reported from the reaction between $(C_5H_5)E(C_5H_5)$ and $Ru_3(CO)_{12}$ (**53**; E = $SiMe_2$,[33] $Me_2SiSiMe_2$,[34] $Me_2SiOSiMe_2$,[35] $Me_2SiOSiMe_2OSiMe_2$[35]). In some cases (e.g., **53**, E = $Me_2SiSiMe_2$), heating in heptane results in Si–Si bond cleavage and formation of a product without an Ru–Ru bond, $\{(\mu,\eta^1:\eta^5\text{-}C_5H_4SiMe_2)Ru(CO)_2\}_2$.[34] Similar tetramethylcyclopentadienyl complexes are also known (**54**; E = $SiMe_2$,[36] $Me_2SiSiMe_2$[37]). The study involving **54** (E = $SiMe_2$)[36] shows that C–Si cleavage can be achieved photochemically. A solvent-dependent equilibrium between **54** (E = $SiMe_2$) and a species without CO bridges **55** was also proposed and studied using density functional theory (DFT) calculations.[36] Cyclopentadienyl complexes with a double silicon bridge are discussed in Section 6.17.3.4.



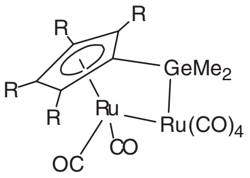
53



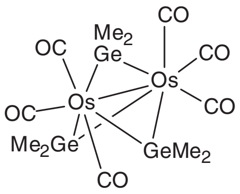
54 **55**

6.17.2.1.3 Complexes with germanium and tin ligands

Compared to silicon, diruthenium complexes bearing germanium or tin ligands are relatively rare. The germanium analog of **53** (E = $GeMe_2$)[35] is known as well as complex **56** (R = H or Me), which is isolated from the reaction of germanium-cyclopentadiene compounds with $Ru_3(CO)_{12}$ as the only product with Ru–Ru and Ge–Ru bonds.[38] The compound $[Os(GeMe_2)(CO)_4]_2$ is prepared from $Na_2[Os(CO)_4]$ and Me_2GeCl_2 in hexane in moderate yield. Pyrolysis of this species in hexane at 100 °C leads to formation of a rare example of a diosmium complex bridged by germanium ligands **57**, along with clusters of higher nuclearity.[39]

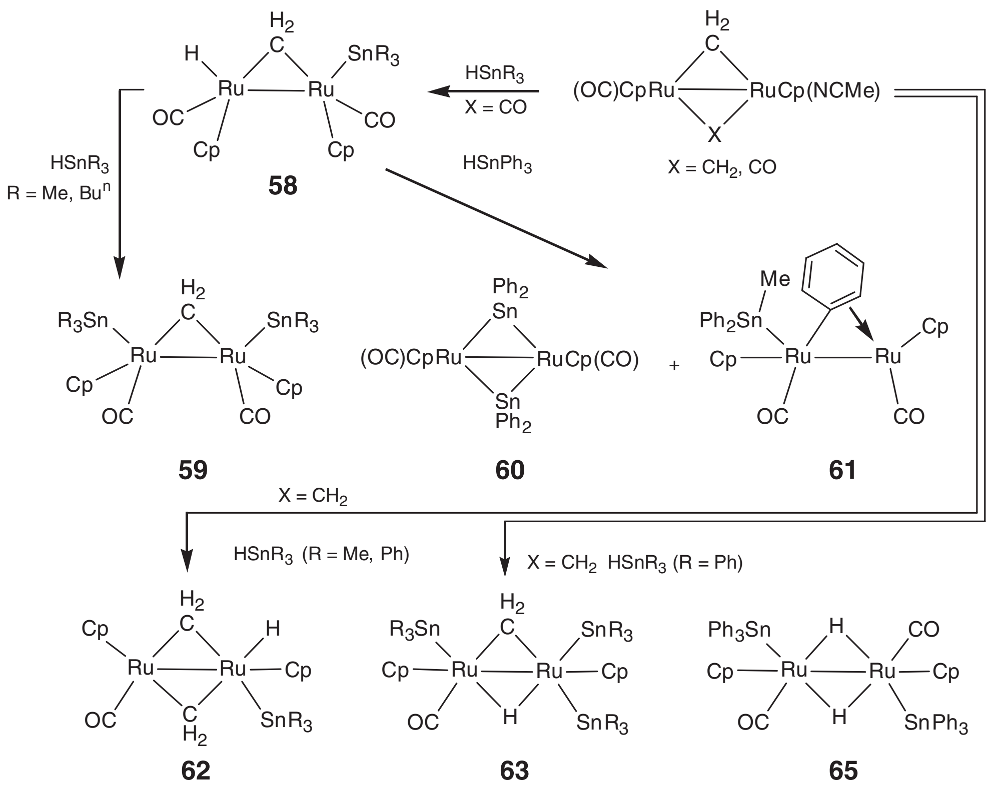


56



57

The versatile starting material $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(MeCN)$ reacts with $HSnR_3$ quantitatively to provide **58** (R = Me, Bu^n, Ph) in under a minute at RT.[40] Reaction of **58** (R = Me, Bu^n) with further $HSnR_3$ over 3 h leads to **59** (R = Me, Bu^n), also quantitatively. However, complex **58** (R = Ph) does not follow this route and provides a mixture of products including a bridging stannylene complex **60** and a μ-phenyl complex **61** on reaction with $HSnPh_3$.[40] This work was extended to include the reaction of the bis(μ-methylene) complex $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ with hydrostannanes.[27] With $HSnMe_3$, complex **62** (R = Me) is the exclusive product by simple oxidative addition. However, when $HSnPh_3$ is employed, a hydrido tristannyl complex is formed (**63**; R = Ph) in addition to **62** (R = Ph). The compound $[Ru_2(CO)_6(\mu\text{-}SnR_2)(\mu\text{-dppm})]$ (**64**; R = 2,4,6-triisopropylphenyl) is prepared by addition of SnR_2 to $[Ru_3(CO)_{10}(\mu\text{-dppm})]$.[41] Treatment of $[Ru_2Cp_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)(NCMe)]$ with $HSnPh_3$ in benzene at RT leads to elimination of ethene and formation of the doubly hydride-bridged complex **65** in low yield.[28]



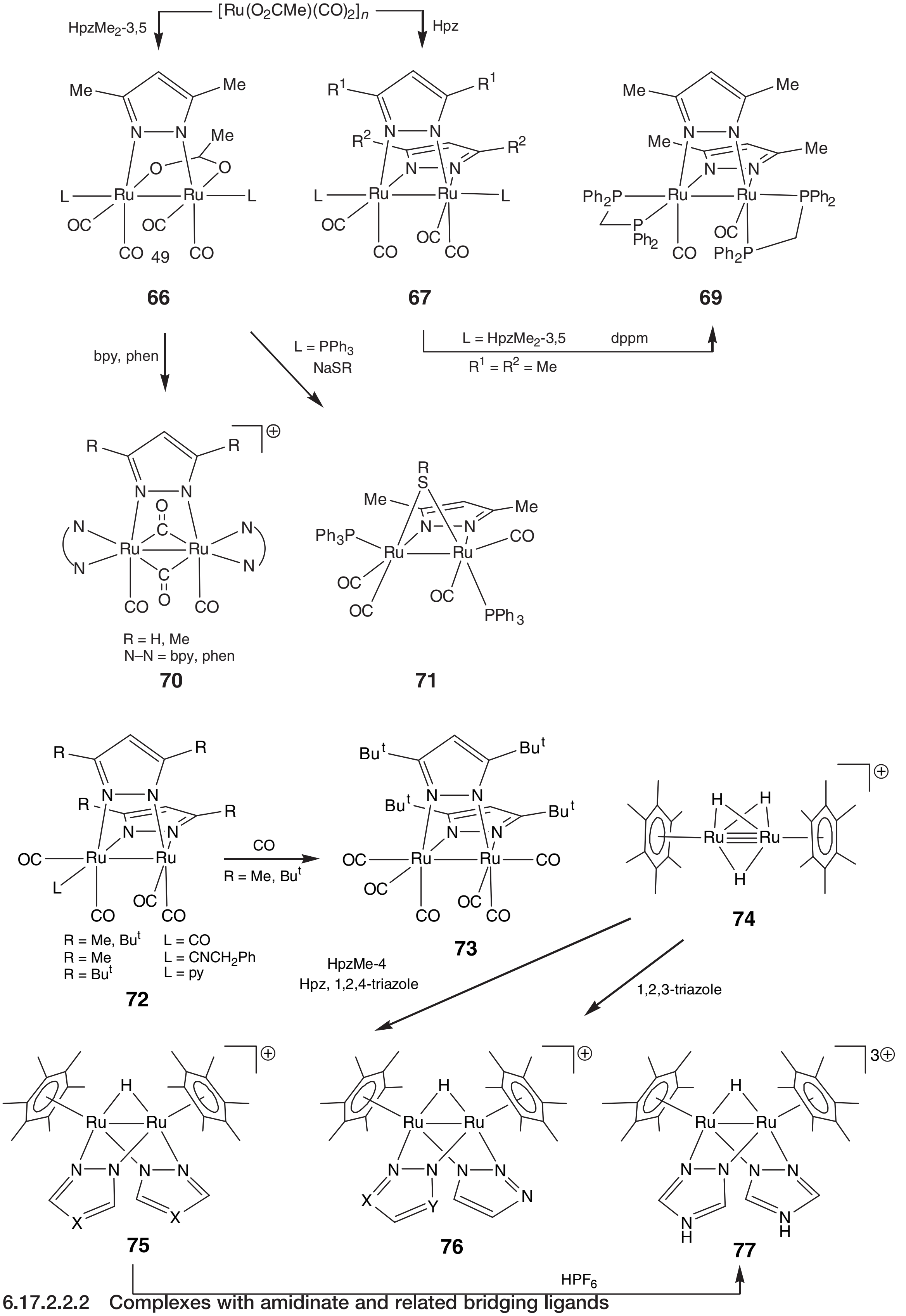
6.17.2.2 Complexes with Nitrogen Bridging Ligands

6.17.2.2.1 Complexes with bridging pyrazole ligands

Nitrogen-based ligands have been a very popular choice for stabilizing dinuclear complexes of many metals and particularly ruthenium. Perhaps the simplest example of this class of bridging ligand is pyrazole. In the presence of triethylamine, *catena*-$[Ru(O_2CMe)(CO)_2]_n$ reacts with 3,5-dimethylpyrazole or pyrazole to yield 66 (L = $HpzMe_2$-3,5) and 67 ($R^1 = R^2 = H$, L = Hpz), respectively.[42] A route to 67 ($R^1 = R^2 = Me$, L = $HpzMe_2$-3,5) is provided by reaction of pyrazoles with the acetonitrile complex $[Ru_2(CO)_4(MeCN)_6](BF_4)_2$ 68.[43] Displacement of the non-bridging pyrazole ligands in 66 and 67 by triphenylphosphine can be readily achieved to yield 66 (L = PPh_3) and 67 (L = PPh_3; $R^1 = R^2 = H$, Me; $R^1 = Me$, $R^2 = H$). Reaction of 67 (L = Hpz; $R^1 = R^2 = H$) with dppm leads to 67 (L = η^1-dppm; $R^1 = R^2 = H$), while reaction of 67 (L = $HpzMe_2$-3,5, $R^1 = R^2 = Me$) with dppm leads to additional displacement of two carbonyl ligands to give 69. Addition of bidentate nitrogen ligands (bpy, phen) to 66 (L = $HpzMe_2$-3,5) or 67 ($R^1 = R^2 = H$, Me; L = Hpz, $HpzMe_2$-3,5) leads to loss of an acetate/pyrazolyl ligand and formation of cationic complexes with bridging carbonyl ligands (70; R = H, Me; N–N = bpy, phen; BPh_4^- or PF_6^- salts). The μ-acetato bridge in 66 (L = PPh_3) can be replaced by a stronger anionic σ-donor such as pz^- (67; $R^1 = H$, $R^2 = Me$, L = PPh_3) or SR^- (71; R = Ph, Bu^t).[42]

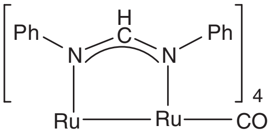
Coordinatively unsaturated pyrazole complexes have also received some attention. Forcing autoclave conditions are required to prepare the pentacarbonyl complex 72 (R = Me, Bu^t; L = CO) from $Ru_3(CO)_{12}$ and the corresponding pyrazoles.[44] Addition of carbon monoxide yields $[Ru_2(CO)_6(pzBu^t{}_2\text{-}3,5)_2]$ 73. Interestingly, addition of benzyl isonitrile or pyridine to 72 (L = CO; R = Me) and 72 (L = CO; R = Bu^t) leads to 72 (R = Me, L = $CNCH_2Ph$; R = Bu^t, L = py), with the new ligand taking up an equatorial rather than axial position without resulting in coordinative saturation.[44] The authors propose that the steric bulk of the $pzBu^t{}_2$-3,5 ligand leads to the observed difference in chemical and physical behavior in the complexes compared to analogs bearing pyrazole ligands with less bulky substituents. The ruthenium and osmium complexes $[M_2(CO)_6\{pz(CF_3)_2\text{-}3,5\}_2]$ (M = Ru,[45] Os[46]) have found use as precursors for the deposition of thin metallic films.

The cation 74 (SO_4^{2-} salt) reacts in aqueous solution with pyrazole, HpzMe-4 and 1,2,4-triazole to give 75 (X = CH, CMe, N; SO_4^{2-} salts) and with 1,2,3-triazole to yield 76, which exists as two isomers (X = CH, Y = N or X = N, Y = CH; SO_4^{2-} salts). Treatment of 75 (X = N; SO_4^- salt) with HPF_6 leads to the protonated form 77 (PF_6^- triple salt) via a mixture of monoprotonated products.[47]



6.17.2.2.2 Complexes with amidinate and related bridging ligands

The diphenylformamidinate anion (dpf) has been found to be a simple and effective supporting ligand for the exploration of the (electro)chemistry of dinuclear complexes. An example of this is the stable monocarbonyl compound 78,[48] which can be prepared by electrolysis of $(dpf)_4Ru_2Cl$ to generate $(dpf)_4Ru_2$ under an atmosphere of carbon monoxide. A recent investigation of high- and low-spin diruthenium compounds makes use of the same ligand to provide complexes with a single anionic axial ligand, such as $(dpf)_4Ru_2CN$ **79** and 80 (X = NCS, N_3).[49] The effect of the axial ligands on structural, redox, and magnetic properties was investigated in the related complexes 81, which contain the axial ligands, X = CN, N_3, $N(CN)_2$, I.[50] When X = CN, the compound is diamagnetic, while the complexes with the other ligands are paramagnetic. An unusual coordination mode for this type of bridging ligand is found in the naphthyridine complex 82, in which all three nitrogen donors coordinate.[51] A related compound, 83, is formed from reactions of $Ru_3(CO)_{12}$ or $[RuCl_2(CO)_3]$ with bis(2-pyridyl)amine.[52] Complex 84 is obtained either by heating $Ru_3(CO)_{12}$ with the free amidine, PhNC(Me)NHPh, under a carbon monoxide atmosphere, or through reaction of $[Ru_2(O_2CMe)_2(CO)_4]_n$ with the amidine under CO in the presence of base.[53]



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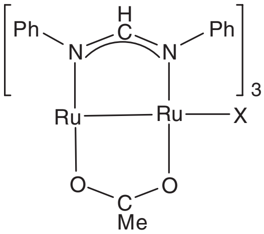

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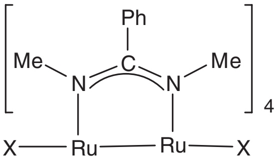

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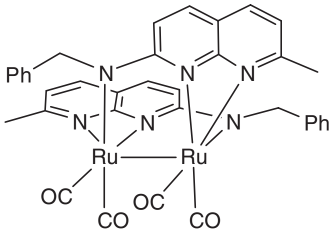

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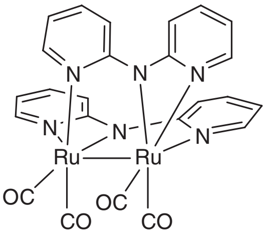

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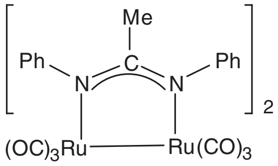
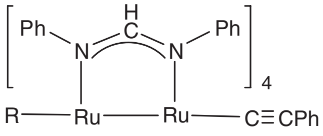


84

Due to the great interest in organometallic wires and their redox and charge-transfer properties, alkynyl diruthenium complexes have enjoyed much attention. The supporting nitrogen-based ligands are often versions of the formamidinate or anilinopyridinate anions.

The complexes, $Ru_2(dpf)_4(C{\equiv}CPh)(R)$ 85 (R = none, C≡CPh; dpf = diphenylformamidinate), were prepared from $Ru_2(dpf)_4Cl$ and LiC≡CPh and their electrochemistry explored.[54] The effect of axial ligands on the oxidation state, structure, and electronic configuration of the same compounds was later addressed. It is found that when R = none (containing a Ru_2^{5+} core), the complex is paramagnetic and when R = C≡CPh (Ru_2^{6+} core), diamagnetic behavior results.[55] The effect of the substituents on the aromatic groups of the diarylformamidinate ligand in 86 (R^1 = Ph; $R^2 = C_2Ph$, none; X = *p*-OMe, H, *p*-Cl, *m*-Cl, *m*-CF_3, 3,4-Cl_2, 3,5-Cl_2) has been studied and a good correlation between the electrode potential and the Hammett constant of the substituent established.[56,57] The formamidinato complexes 86 ($R^1 = C_2SiMe_3$; R^2 = none, C_4SiMe_3; X = *m*-OMe) were the first examples of M–M bonded compounds bearing σ-poly-ynyl ligands.[58] The application of formamidinato diruthenium units as redox-active linkages has been explored for organometallic chains at the nanometer scale 87 and 88.[59]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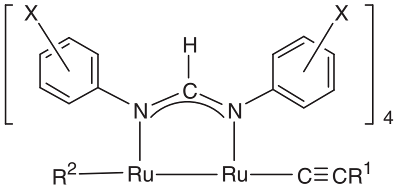
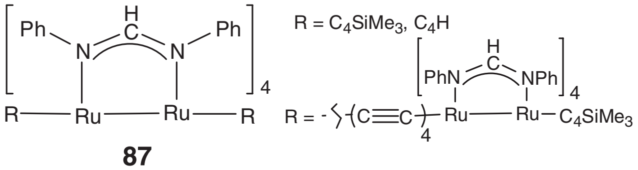
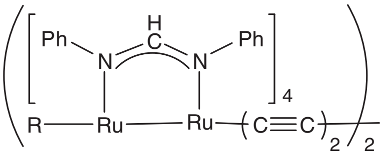
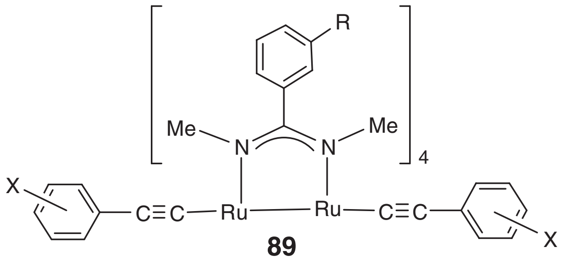

86

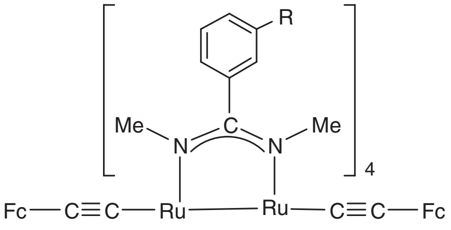


87


88

A variation of the dpf ligand is dimethylbenzamidinate (dmba), in which the electronic properties of the ligand can be "tuned" through modification of the substituents on the aromatic group.[60,61] In the series represented by complexes **89** (R = H, OMe; X = H, *p*-NO_2, *p*-CN, *m*-CN, *p*-NMe_2), the substituents on the alkynyl ligand were varied to examine the associated Hammett constants.[62] Many of the complexes are prepared from reaction of $[Ru_2(dmba)_4](NO_3)_2$ with unactivated alkynes in the presence of NEt_3. This approach is significant as it overcomes the inherent limitations of lithiated alkynes for the introduction of a wide range of functionalized alkynyl ligands into such complexes.[62] Further functionalization of the alkynyl substituents with ferrocenyl groups in **90** (R = H, OMe, OC_4H_9) allowed the electron transfer between the iron centers through the alkynyl and diruthenium units to be measured using spectroscopic and other techniques. The results indicated that facile electron transfer was indeed achieved over the 10 Å distance in the complex.[63]

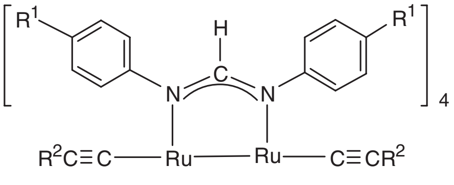

89


90

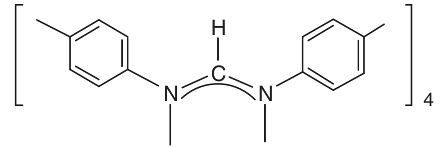
The introduction of further metals into these systems can be achieved by placing pyridyl-functionalized alkynyl groups in the axial positions **91** and then coordinating rhenium bipyridine complexes **92**.[64] Again, electron delocalization was observed along the heterobimetallic axis. The inclusion of such donors in both axial positions allows a wide range of metal subunits to be introduced into these systems.

Another area of recent interest is the use of a mixture of bidentate nitrogen donors to broaden the structural possibilities of these "paddlewheel" diruthenium complexes. This is achieved using a combination of dpf- and dmba-derived ligands.

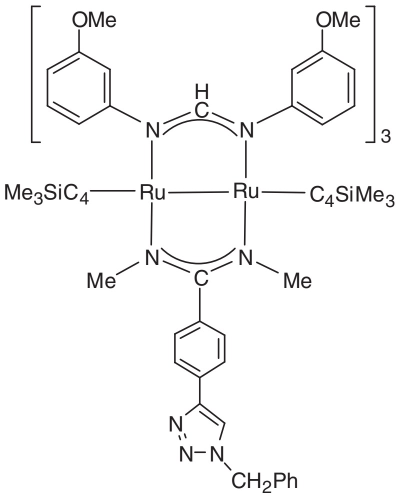
An ethynylferrocene unit was introduced into the dmba ligand and the resulting electrochemistry examined for the complexes **92** (R = C_4SiMe_3, C_2Ph; X = I, $C_2SiPr^i_3$, C_2Fc).[65] Variants **93** can be prepared by incorporating 1,2,3-triazole units into the dmba ligand at either the carbon or nitrogen (**94**; X = none, C_4SiMe_3; R = Ph, $C_6H_4C_2HN_3CH_2Ph$). These peripheral modifications, achieved through copper-catalyzed coupling of azide with an alkyne unit, however, induce minimal changes in the molecular structure and electronic properties of the complexes.[65]


R^1 = H, CH_3 R^2 = 4-Pyridyl

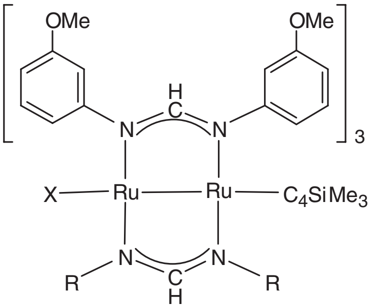
91


[Re] = $[Re(CO)_3(Bu^t{}_2bipy)]OTf$

92

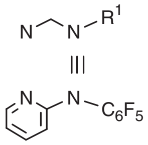


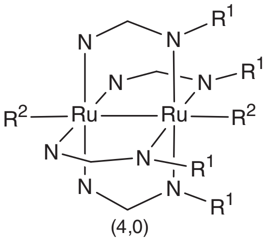
93



94

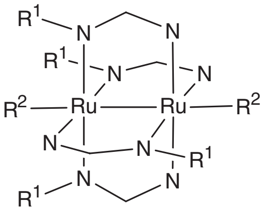
The other main class of bridging nitrogen ligand commonly employed in paddlewheel complexes is the 2-anilinopyridinate (ap) anion. Complexes such as $Ru_2(ap)_4(C{\equiv}CR)_n$ (**95**; $n=1$, $R=SiMe_3$,[66] H,[66] CH_2OMe,[66] $n=1$ or 2, C_2SiMe_3[67]) are accessible directly from the reaction of $Ru_2(ap)_4Cl$ and lithiated alkynes. Tailoring of the ligand by modification of the phenyl substituent is demonstrated by the pentafluoro variant, $Ru_2(F_5ap)_4(C{\equiv}CPh)_2$ **96**.[68] Later, three isomers of the same compound (**97–99**; $R^1=C_6F_5$, $R^2=C_2Ph$) were isolated and structurally characterized.[69] As these complexes illustrate, the unsymmetrical nature of the ap ligand leads in many cases to isomerism, in contrast to symmetrical ligands such as dpf or dmba. Four geometric isomers are possible for dimetal complexes with four unsymmetrical bridging ligands: (4,0), (3,1), (2,2) *trans*, and (2,2) *cis*.





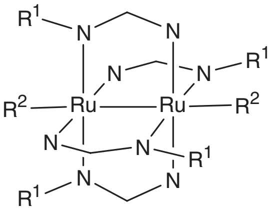
(4,0)

97



(3,1)

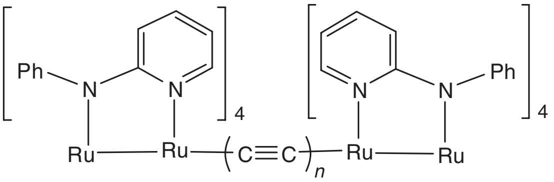
98



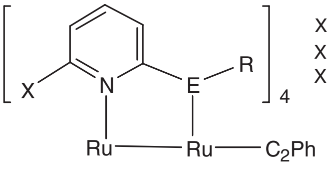
(2,2) *trans*

99

Dilithiated butadiyne reacts with $Ru_2(ap)_4Cl$ to introduce a C_4 conjugated carbon chain between the metal centers (**100**; $n=2$).[70] The potential for using the diruthenium units as redox-active terminal electron reservoirs was taken further with synthesis of a C_8 carbon chain (**100**; $n=4$) as part of the same project. A correlation between the coupling between the metal centers and the organic bridge was determined by electrochemical (cyclic voltammetry, differential pulse voltammetry) and spectrochemical studies.[71] With a greater range of functionalized alkynyl complexes being explored, new synthetic routes[62] have been required in order for the synthesis of the desired target molecules to be achieved. Another recent advance in this area is the use of alkynyl(trimethyl)stannanes with Pd(II)/CuI in reactions with Ru_2(bridging ligand)$_4$Cl to yield the desired alkynyl compounds under very mild conditions. This is illustrated in the preparation of the complexes **101**, which bear three types of *N*,*N*- and *N*,*O*-bridging ligands.[72]



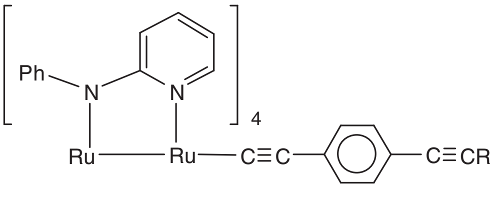
100



X = Cl, E = O, R = H
X = Br, E = O, R = H
X = H, E = N, R = Ph

101

The majority of dialkynyl complexes prepared with two axial ligands have the same axial functionality, but there has been interest in creating mixed variants such as $[Ru_2(ap)_4(C{\equiv}CR^1)(R^2)]$ (**102**; $R^1 = H$, Ph, $SiMe_3$, C_2SiMe_3; $R^2 = C_2Ph$, C_2SiMe_3).[73,74] Rich redox chemistry and intense charge-transfer characteristics were observed for these species.[74] An alternative route to C_n poly-ynyl spacers is the use of alkynylbenzene units, as demonstrated by **103** ($R = H$, $SiMe_3$, $Ru_2(ap)_4$) and **104**.[75] These can be used to connect two dimetal units through a more structurally diverse conjugated organic framework. However, the evidence collected implied a disappointing level of electronic communication between the diruthenium units.



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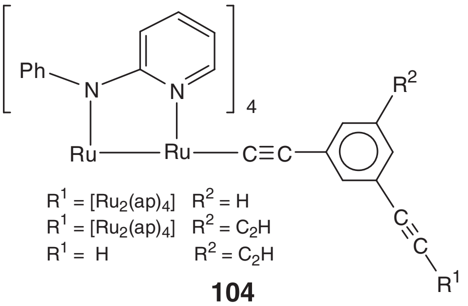
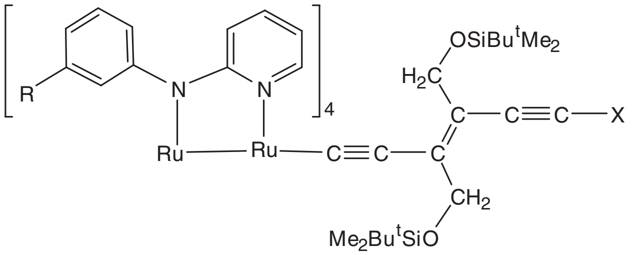


104

The use of the unusual spacer, *E*-hex-3-ene-1,5-diyn-diyl, has been reported recently for the construction of polymetallic assemblies (**105**; $R = H$, OMe; $X = H$, $Ru_2(X\text{-}ap)_4$).[76] Voltammetry experiments were used to confirm the conjugation through the unsaturated spacer and the materials were found to show promising magnetic and (molecular wire) charge-transfer properties.

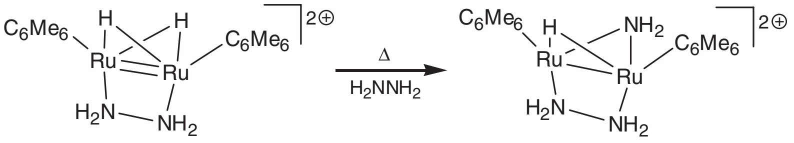


105

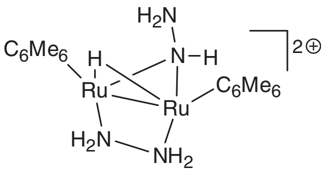
Recent reviews cover homo-dinuclear σ-alkynyl complexes of the type described here[77,78] and another discusses substituent effects in dinuclear "paddlewheel" compounds.[79]

6.17.2.2.3 Complexes with other nitrogen-based bridging ligands

The coordination of hydrazine to diruthenium complexes has been explored in complexes **106–108** (p-$MeC_6H_4SO_3$ salts).[80] The starting material, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3][p\text{-}MeC_6H_4SO_3]$, undergoes loss of a hydride bridge on reaction with NH_2NH_2 in aqueous solution to form a species with an intact hydrazine ligand and an Ru=Ru bond **106**. Heating **106** in water with further hydrazine leads to a complex with a bridging amido ligand **107**. Insight into the mechanism is provided by the isolation and characterization of a hydrazido intermediate **108** from the reaction.

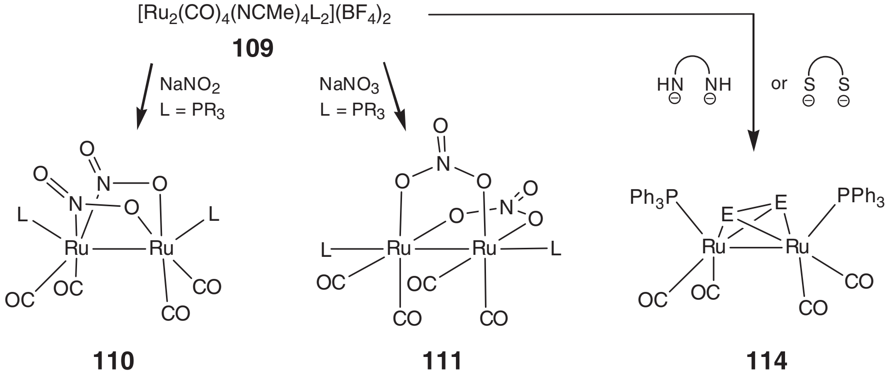


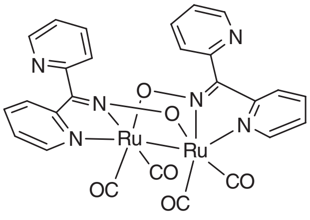
106 **107**



108

In an attempt to prepare nitrosyl complexes, the compounds [Ru$_2$(CO)$_4$(MeCN)$_4$L$_2$](BF$_4$)$_2$ (**109**; L = PPh$_3$, PPh$_2$(allyl), PPh$_2$Me, PMe$_3$)[43] were allowed to react with NaNO$_2$. Instead, bis(μ-nitro) diruthenium complexes (**110**; L = PPh$_3$, PPh$_2$(allyl), PPh$_2$Me, PMe$_3$) were isolated. Analogous treatment of **109** (L = PPh$_3$, PPh$_2$(allyl), PPh$_2$Me, PPhMe$_2$, PMe$_3$) with NaNO$_3$ leads to compounds with two nitrato bridges, **111**. Reaction of **111** (L = PPh$_3$) with NaN$_3$ or NaI results in the complexes [Ru$_2$(CO)$_4$(μ-N$_3$)$_2$(PPh$_3$)$_2$] **112** and [Ru$_2$(CO)$_4$(μ-I)$_2$(PPh$_3$)$_2$] **113**, respectively.[81] Further evidence of the significant reactivity of **109** (L = PPh$_3$) is provided by the reaction with doubly deprotonated diamines and dithiols to yield **114** (E–E = 1,2-(NH)$_2$C$_6$H$_4$, 1,2-(NH)$_2$C$_{10}$H$_6$, 1,2-(NH)$_2$-4,5-Cl$_2$C$_6$H$_2$, 1,2-(NH)$_2$-4,5-Me$_2$C$_6$H$_2$, 9,10-(NH)$_2$C$_{14}$H$_8$, 1,2-S$_2$C$_6$H$_4$).[43] A related complex stabilized by a μ-dppm unit, [Ru$_2${μ-C$_6$H$_4$(NH)$_2$-*o*}(μ-dppm)(CO)$_2$(PPh$_3$)$_2$](PF$_6$)$_2$ **115**, has been investigated in structural and theoretical studies.[82] Treatment of Ru$_3$(CO)$_{12}$ with bis(2-pyridyl) ketone oxime (Hdpko) in refluxing tetrahydrofuran leads to **116** and Ru$_3$(μ,η^3-dpko-*N*,*N*,*O*)$_2$(CO)$_8$. The oximate species produced display modest activity as DNA cleavage agents.[83] Aerial oxidation of [RuCp(apy)(NCMe)$_2$]PF$_6$ (apy = 2-aminopyridine) leads to the dinuclear complex **117**, in which the deprotonated apy ligands span the metal centers via an amido bridge.[84] The mononuclear nitrosyl complex Cp*OsBr$_2$(NO) reacts with NaBH$_4$ to yield Cp*OsH$_2$(NO), which loses hydrogen over a period of days to form the dinuclear complex **118**. This nitrosyl-bridged species can also be prepared directly by reduction of Cp*OsBr$_2$(NO) with zinc powder.[85]





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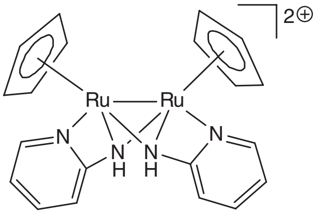

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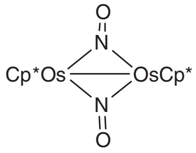

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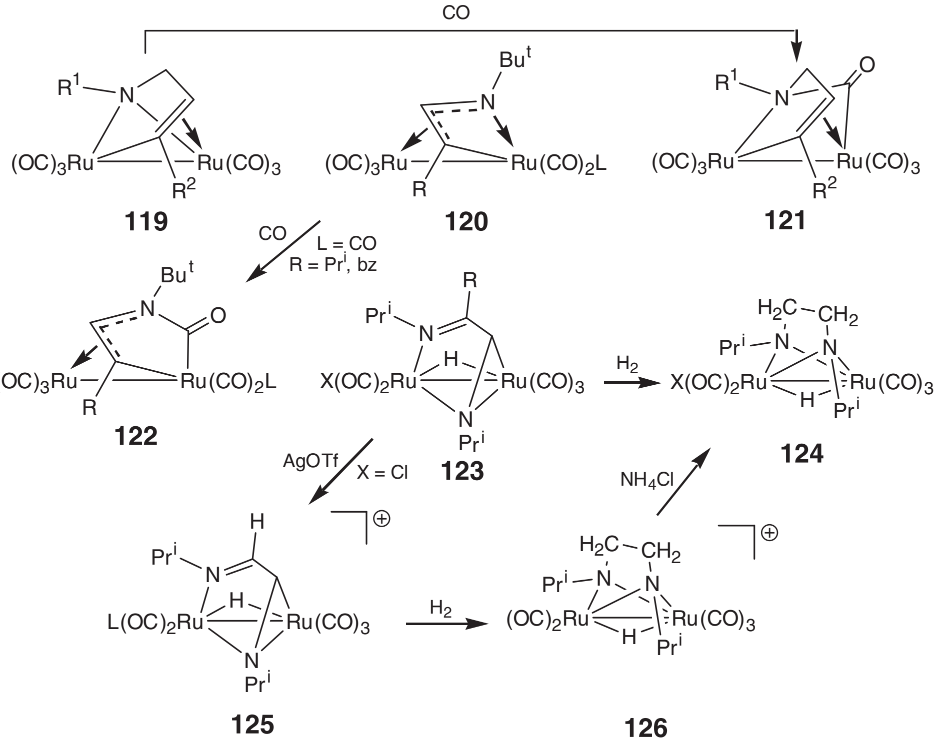
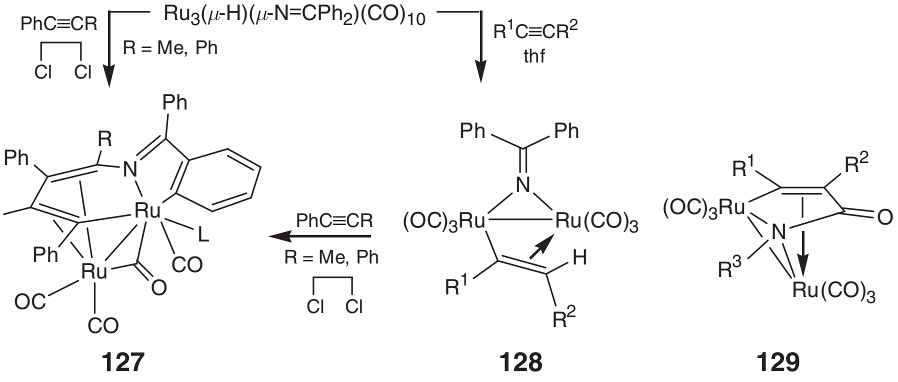
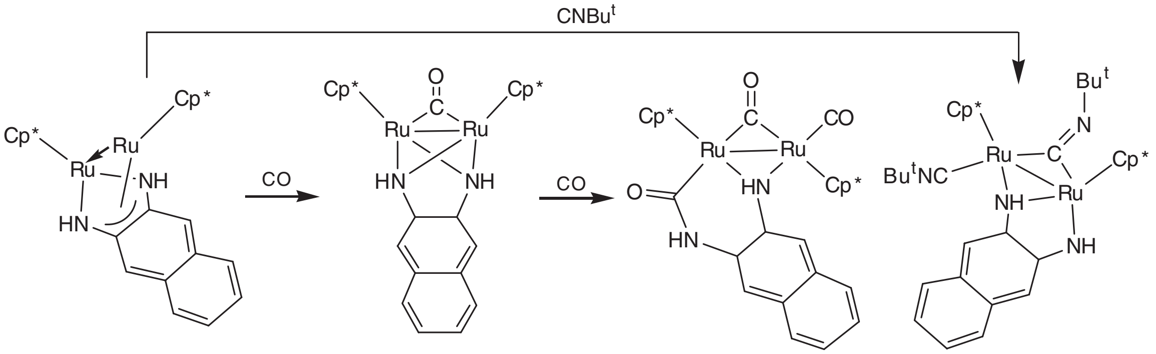
The amido-bridged compounds **119** (R^1 = Pr^i, R^2 = Me) and **120** (R = Pr^i, CH$_2$Ph, L = CO) react with carbon monoxide via insertion into the metal–amido bond to yield **121** (R^1 = Pr^i, R^2 = Me) and **122** (R = Pr^i, CH$_2$Ph, L = CO), respectively.[86] On irradiation, the reaction between **120** (R = Pr^i, L = CO) and triphenylphosphine also leads to insertion of a coordinated CO ligand into the Ru–N bond to form **122** (R = Pr^i, L = PPh$_3$).[86] Compound **123** (R = H, Me; X = H) reacts with CX$_4$ (X = Cl, I) to replace the terminal hydride and generate **123** (R = H, X = Cl, I; R = Me, X = Cl), which undergo reaction with H$_2$ at 90 °C (when R = H, X = Cl, I) to form **124** (X = Cl, I). The chloride ligand in **123** (R = H, X = Cl) can be abstracted using silver triflate to prepare the cationic complex **125** (L = none; triflate salt), in which one ruthenium center is coordinatively unsaturated. The vacant site can be used to coordinate carbon monoxide or CNBu^t to generate **125** (L = CO, CNBu^t; triflate salts), while cyanide or anionic metal fragments react to form **123** (X = CN, Co(CO)$_4$, Mn(CO)$_5$; triflate salts). Treatment of **125** (L = none; triflate salt) with H$_2$ results in coordinatively unsaturated **126** (triflate salt), which reacts with NH$_4$Cl to generate **124** (X = Cl).[87]



The azavinylidene-bridged cluster $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}$ reacts with $PhC{\equiv}CR$ (R = Me, Ph) in refluxing 1,2-dichloroethane to yield **127** (R = Me, Ph) through insertion into the Ru–N bond. No insertion of this kind is observed when the reaction is conducted with $R^1C{\equiv}CR^2$ ($R^1 = R^2 = H$, Et, Ph; $R^1 = Ph$, $R^2 = H$, Me; $R^1 = Bu^t$, Tol, $R^2 = H$; $R^1 = H$, $R^2 = Bu^t$) at lower temperatures in refluxing tetrahydrofuran, when the bridging alkenyl complexes **128** are formed with the $\mu\text{-}N{=}CPh_2$ moiety retained. Compounds **128** ($R^1 = Ph$, $R^2 = Me$, Ph) are converted into **127** (R = Me) or **127** (R = Ph) in refluxing 1,2-dichloroethane with $PhC{\equiv}CMe$ or $PhC{\equiv}CPh$, respectively.[88,89] An isonitrile derivative, **127** ($L = CNBu^t$; $R^1 = R^2 = Ph$), has also been structurally characterized.[90] The starting complex $Ru_3(\mu_3\text{-}NR)(\mu_3\text{-}CO)(CO)_9$ (R = Ph) undergoes reaction with activated alkynes $R^1C{\equiv}CR^2$ ($R^1 = CO_2Me$, $R^2 = H$, Ph; $R^1 = C{\equiv}CMe$, $R^2 = Me$; $R^1 = C{\equiv}CPh$, $R^2 = Ph$; $R^1 = CH_2C{\equiv}CSiMe_3$, $R^2 = H$) to give **129** ($R^3 = Ph$) along with tetranuclear derivatives.[91] The dinuclear metallapyrrolidone complex **129** ($R^1 = H$, $R^2 = Ph$, $R^3 = OMe$) is isolated in low yield from the reaction of $Ru_3(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)(CO)_9$ and phenylacetylene in refluxing *n*-octane.[92]

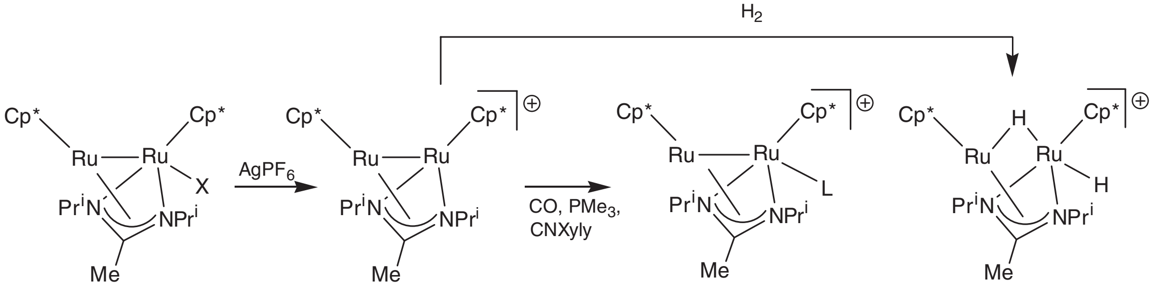


Another route to bridging amido complexes is provided by the reaction of dilithium 2,3-naphthalenediamide and $\{Cp^*RuCl\}_4$ to yield **130**. This complex reacts readily with carbon monoxide to create a bridging carbonyl unit in the symmetrical complex **131**. Prolonged reaction with CO induces C–N bond formation between amido and carbon monoxide ligands, resulting in three CO ligands being incorporated in the final product **132**. In contrast, two molecules of $CNBu^t$ are introduced into the bonding system when **130** reacts with isonitrile to give **133**.[93]



130 **131** **132** **133**

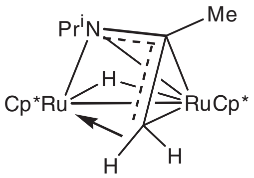
Amidinate ligands can adopt bridging modes other than those observed for the dpf ligand (Section 6.17.2.2.2), as demonstrated by the synthesis of the μ_2-amidinate species **134** (X = Cl, Br) from $RuCp^*\{Pr^iN{=}C(Me)NPr^i\}$ and $\{Cp^*RuX\}_4$.[94] Silver salts can be used to remove the halide ligand from these complexes to provide rare examples of coordinatively unsaturated diruthenium complexes (**135**; PF_6^-, BF_4^-, SbF_6^-, $B(C_6F_5)_4^-$ salts).[95] The vacant site can be used to coordinate a range of two-electron donors (**136**; L = CO, $CNC_6H_2Me_3$-2,4,6, PMe_3; $B(C_6F_5)_4^-$ salts).[94,95] Compound **135** ($B(C_6F_5)_4^-$ salt) also undergoes reaction with hydrogen (1 atm) to give the hydrido complex **137** ($B(C_6F_5)_4^-$ salt) in almost quantitative yield.[95]



134 **135** **136** **137**

This research was extended to include non-symmetrical amidinate complexes of the same type with mixed Cp and Cp^* ligands, such as the cationic species $[Cp^*Ru\{\mu_2\text{-}Pr^iN{=}C(Me)NPr^i\}RuCp(L)]$ (**138**; L = none, NCMe, $CNBu^t$, PMe_3; BF_4^- salts). For **138** (L = $CNBu^t$), there is NMR evidence that the isonitrile ligand switches between the ruthenium centers.[96] Coordinatively unsaturated intermediates play a key role in catalytic processes, and thus complexes **138** (L = none; PF_6^- salt)[96] and **135** (PF_6^- salt)[97] were found to catalyze the atom-transfer radical cyclization of *N*-allyl trichloroacetamides. It was discovered that the greater protection offered by the steric bulk of the Cp^* ligand led to the superior performance of **135** (PF_6^- salt).[96]

The reaction of $\{Cp^*RuCl\}_4$ with $LiNPr^i_2$ leads to formation of **139** via dehydrogenation of one isopropyl group.[98,99] The agostic interaction observed in the crystal structure is also detected in solution from the chemical shifts in the ^1H and ^{13}C NMR spectra. This interaction is displaced by a carbonyl ligand on treatment with carbon monoxide.[99] Compound **140** was prepared as part of an investigation into regioselective C–C bond formation between ethyne and α-naphthylcarbaldimines catalyzed by $Ru_3(CO)_{12}$.[100] A similarly unexpected product, compound **141**, which contains both amido and thiolate bridges, was obtained from the reaction of $\{RuCp^*Cl_2\}_2$ with $Li(Bu^tNSPh)$.[101]



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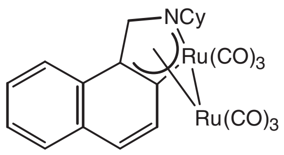

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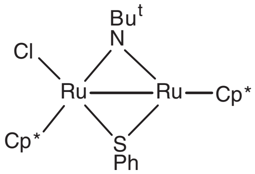
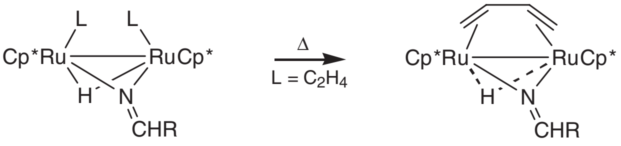


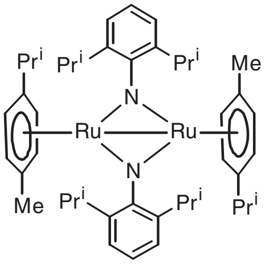
141

Diruthenium μ-alkylideneamido complexes (**142**; R = Me, Et; L = NCMe, L–L = toluene, naphthalene) have been reported to result from treatment of $\{Cp^{*}Ru(\mu\text{-}H)_2\}_2$ with nitriles (RCN) in the presence of an arene solvent such as toluene or naphthalene. The arene bridges the dinuclear unit unless the reaction is conducted only in acetonitrile, in which case molecules of solvent coordinate to each metal center.[102] The reaction of **142** (R = Me, Et; L = NCMe) with ethene results in replacement of the nitrile ligands and formation of **142** (R = Me, Et; L = C_2H_4). Heating this product in toluene leads to dehydrogenative coupling of the coordinated ethene molecules to yield **143** (R = Me, Et).[102]



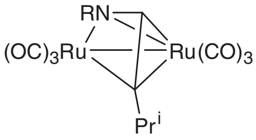
142 **143**

A compound bearing two bridging imido ligands **144** results from reaction of 4 equiv. of $LiNHC_6H_3Pr^i{}_2$-2,6 with $\{RuCl_2(p\text{-cymene})\}_2$. The increased steric bulk of $LiNHC_6H_3Bu^t{}_2$-2,4,6 with the same starting complex leads to a monomeric complex containing a terminal imido ligand.[103]



144

Three diruthenium products **145–147** are isolated from the reaction of $[Ru_3(CO)_{12}]$ with senecialdimine, $Me_2C{=}CHCH{=}NR$ (R = Pr^i, Bu^t). The species obtained depend on the reaction conditions and R substituent. When R = Pr^i, reaction in heptane at 80–100 °C results mainly in **145** (R = Pr^i), whereas both **145** (R = Pr^i) and **146** (R = Pr^i) are obtained in refluxing heptane along with the cluster $[HRu_6(CO)_{18}]^-$. When R = Bu^t, all three dinuclear products are formed.[104]



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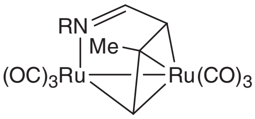

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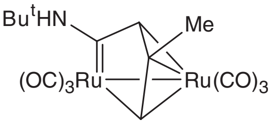
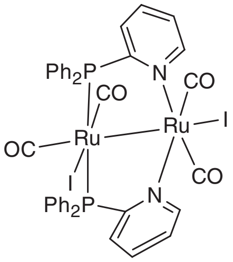


147

Pyridyl groups have been used to span the dinuclear unit in a number of diruthenium complexes. One example, formed from $[Ru_3(CO)_9(Ph_2Ppy)_3]$ and CdI_2, is **148**, in which 2-(diphenylphosphino)pyridine forms a bridge between the ruthenium centers.[105] A series of similar pyridylphosphine-bridged complexes **149–151** are obtained by reactions of the corresponding ligand with the polymers $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4]_n$ (R = H, Me, Et) or its acetonitrile adducts, $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4(NCMe)_2]$ (R = H, Me, Et).[106]



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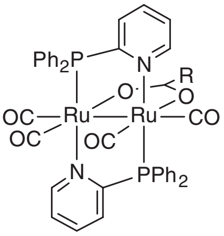

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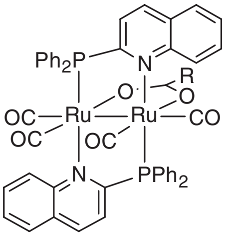

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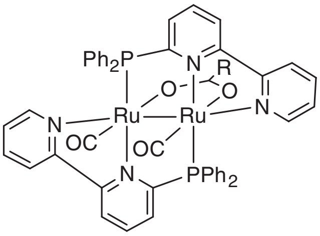
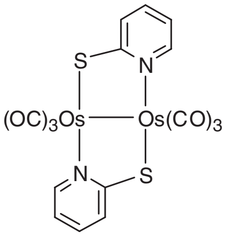


151

In a similar fashion, pyridinethiolate ligands can also be used to stabilize dinuclear assemblies as seen in the diosmium compound **152**, which is isolated as one of the products from the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 2-2′-dipyridyl disulfide.[107] Complex **153** was isolated and characterized from the conversion of diphenylacetylene into α-phenylcinnamaldehyde mediated by a hydrido triruthenium cluster, $Ru_3(\mu\text{-}H)(\mu\text{-}MeNpy)(CO)_9$, bearing the 2-(methylamino)pyridyl (MeNpy) ligand.[108] Bipyridinyl (bpy) ligands have been used in many diruthenium species, although they are rarely found in bridging mode. Both staggered and *anti*-eclipsed (shown) conformations of **154** (R = H) have been structurally characterized in attempts to model intermediates in water-gas shift reactions.[109] The analogous methyl substituted 2,2′-bipyridinyl complexes **154** (R = Me) were also prepared.[110] In studies of electrochemical routes to metallic polymers, $\{Ru\{C(O)OMe\}(CO)_2(bpy)\}_2$ was prepared by reaction of **154** (R = H) with methanol and K_2CO_3.[111,112] The acetonitrile adduct, $[Ru(CO)_2(bpy)(NCMe)]_2(PF_6)_2$ **155**, has also been characterized.[113] An unusual complex containing dirhenium and diruthenium units **156** has been prepared in which the Ru–Ru bond is supported by a pyridyl bridge.[114] Thermolysis of $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$ in refluxing chlorobenzene leads to formation of $[Ru_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)_2(CO)_4(NC_5H_5)_2][Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24}]$ (**157**, cluster anion not shown), in which two pyridyl units support the diruthenium bond.[115–117] *Catena*-$[Ru(O_2CMe)(CO)_2]_n$ and $K[HB(tz)_3]$ (potassium hydrotris(1,2,4-triazolyl)borate) were used to prepare $[Ru\{\kappa^3\text{-}HB(tz)_3\}(CO)_2]_2$ **158**, an example of a diruthenium compound stabilized by two facially coordinated tridentate nitrogen donors.[118]



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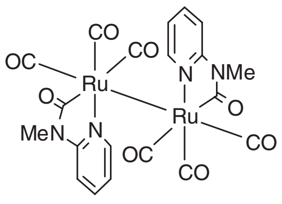

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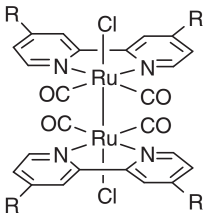

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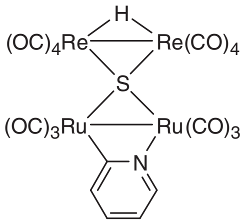

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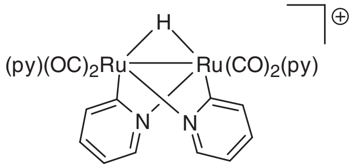

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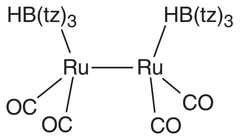


158

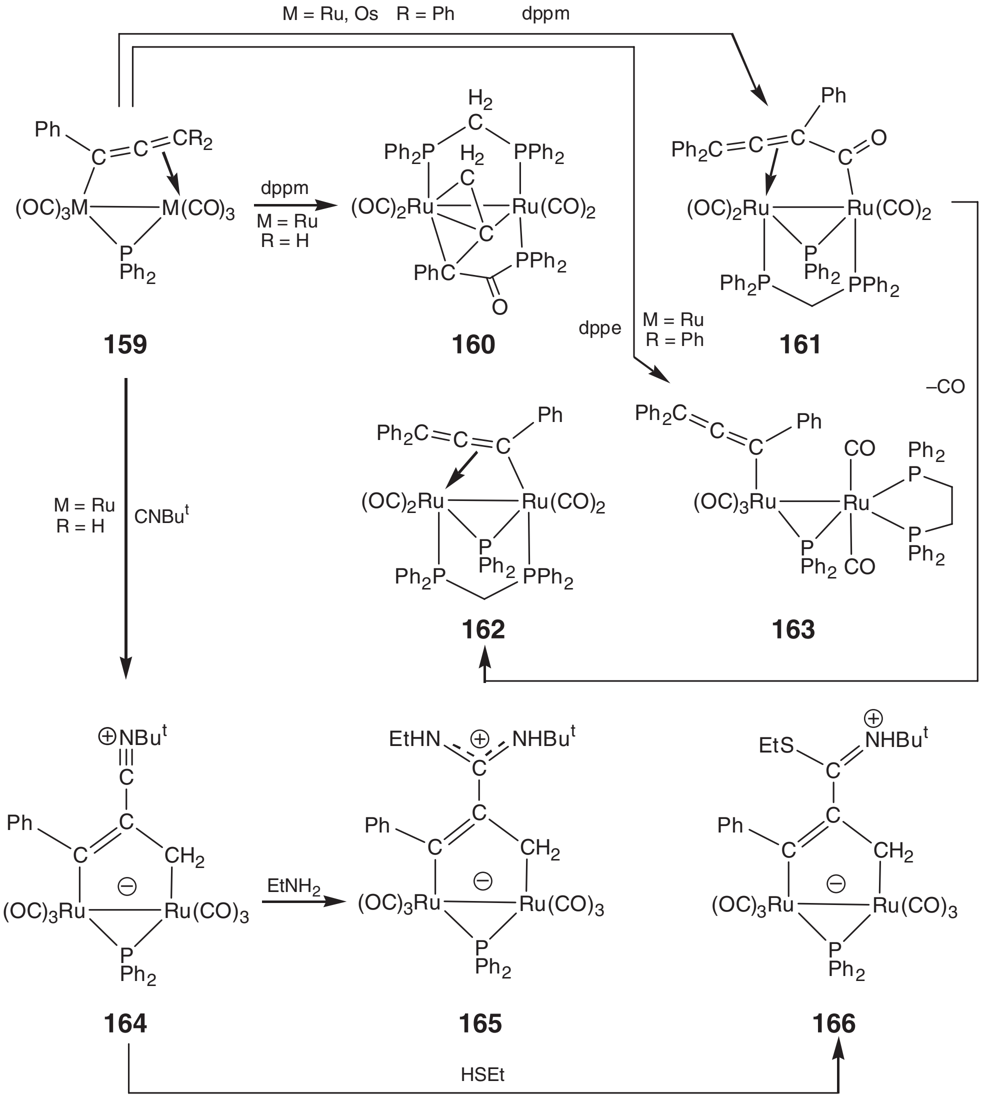
6.17.2.3 Complexes with Phosphorus Bridging Ligands

Phosphorus-bridging units constitute a major class of ligands for diruthenium compounds. Phosphido ligands span the metal centers with a single phosphorus donor atom, while two phosphorus donors are employed in diphosphine and diphosphazane complexes to bridge the dinuclear unit.

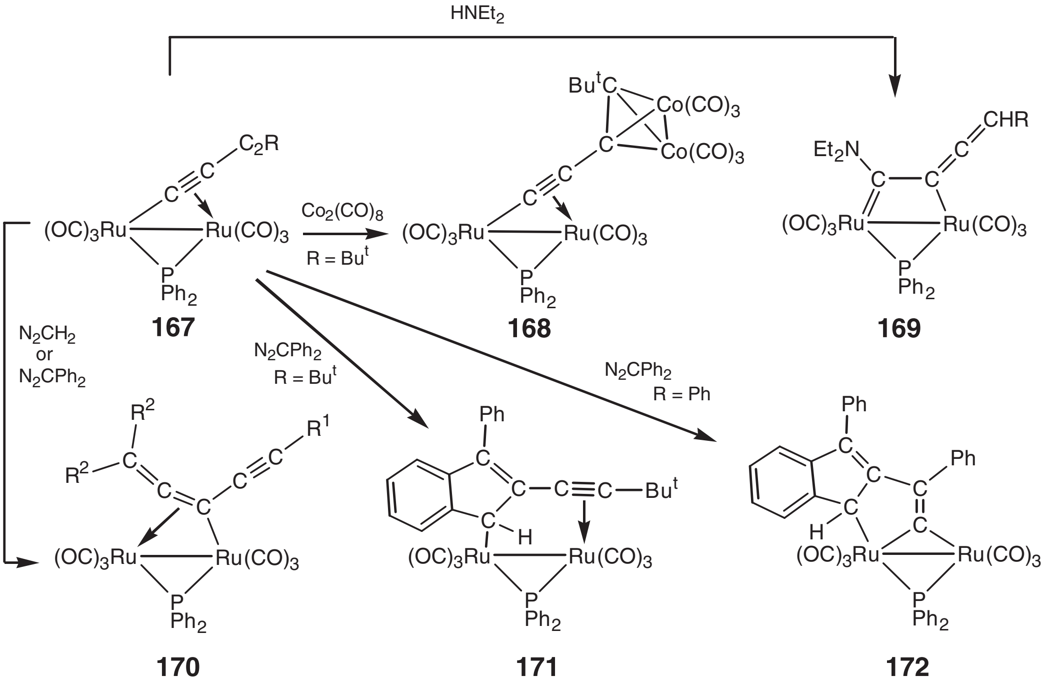
6.17.2.3.1 Complexes with phosphido ligands

Phosphido-bridged dinuclear chemistry is well established (see COMC (1982) and COMC (1995)) and the stability of these species provides a platform for a range of transformations involving the attached organic groups. The bridging alkynyl complexes $M_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_6$ (M = Ru, Os) react with diazomethane to yield the allenyl complexes **159** (M = Ru, Os; R = H).[119,120] An unusual rearrangement ensues to yield **160** when **159** (M = Ru, R = H) is treated with dppm in toluene at 60 °C.[120] The diphenylallenyl complex **159**

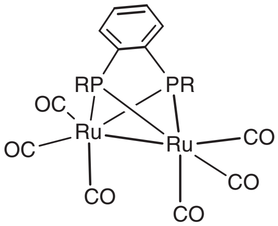
(M = Ru, R = Ph), which bridges through the α- and β-carbons, reacts with dppm in *n*-heptane via insertion of a carbonyl into the Ru–C bond to give **161**. This complex goes on to lose CO at RT to provide **162**. In contrast, reaction of **159** (M = Ru, R = Ph) with dppe leads to a product, **163**, in which the allenyl ligand does not span the Ru–Ru unit.[121] Reaction of **159** (M = Ru, R = H) with CNBu^t leads to attack at the β-C of the bridging allenyl ligand to give the zwitterion **164** in quantitative yield. The delocalization of the negative charge onto the Ru(CO)$_3$ units is suggested by infrared spectroscopic data. This species reacts with the nucleophiles EtNH$_2$ and HSEt to yield **165** and **166**, respectively.[122]



Complex **167** (R = SiMe$_3$, Ph, Bu^t) is obtained in low yield (20–31%) from the thermolytic P–C cleavage of the phosphino–diyne ligand in Ru$_3$(CO)$_{11}$(PPh$_2$C≡CC≡CR). The C$_4$R ligand undergoes rapid exchange between the metal sites, as evidenced by NMR spectroscopy. A crystal structure reveals that the interaction between the Cα═Cβ bond and the neighboring ruthenium center causes deviation from linearity in the C$_4$ unit. The non-coordinated triple bond retains its alkyne character, as demonstrated by reaction of **167** (R = Bu^t) with Co$_2$(CO)$_8$ to give **168**.[123] Treatment of **167** (R = Ph, Bu^t) with HNEt$_2$ leads to the diethylaminobutatriene complex **169** (R = Ph, Bu^t).[124] Attempts to extend the carbon chain of the diynyl ligand in **167** (R = Ph, Bu^t) with diazomethane or diphenyldiazomethane led to the formation of **170** (R^1 = Ph, R^2 = H) and **170** (R^1 = Ph, R^2 = Ph; R^1 = Bu^t, R^2 = Ph), respectively, through attack at Cα. In the case of diphenyldiazomethane, carbene addition also occurs at Cβ to give indenyl complexes **171** and **172** from **167** (R = Bu^t) and **167** (R = Ph), respectively.[125]



Complex **173** (R = Ph, Bu^t) displays a linked bis(μ-phosphido) ligand bridge and was investigated, along with some triruthenium derivatives, as a catalyst precursor for the homogeneous and heterogeneous (silica support) hydrogenation of 1-octene.[126,127] A rare example of a phosphido-bridged diosmium species with two phosphorus environments, **174**, has been characterized crystallographically.[128] The reaction of [Ru$_2$(CO)$_4$(μ-O$_2$CMe)(μ-dppm)$_2$]BF$_4$ with PPh$_3$ provides **175**, in which both products of a P–C cleavage reaction (i.e., the μ-PPh$_2$ and μ_1,η^2-CH$_2$PPh$_2$ ligands) are still coordinated.[129] Tri-(2-furyl)phosphine reacts with Ru$_3$(CO)$_{12}$ by the established route to give **176**.[130] A crystal structure[131] revealed that the Ru–Ru bond is bridged by a metal-bound 2-furyl group in addition to a phosphido ligand. Reaction of **176** with Ph$_2$P(X)PPh$_2$ yields **177** (X = CH$_2$, NH, NMe). However, when dppf or Ph$_2$P(X)PPh$_2$ (X = (CH$_2$)$_4$, (CH$_2$)$_5$) are used, a mixture of complexes with two diruthenium units linked by a diphosphine is formed alongside the corresponding polymeric products. Reactions with dppe and dppp provided a still different product **178** (X = CH$_2$, CH$_2$CH$_2$) through orthometallation.[130]



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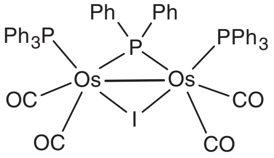

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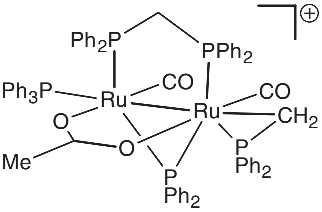

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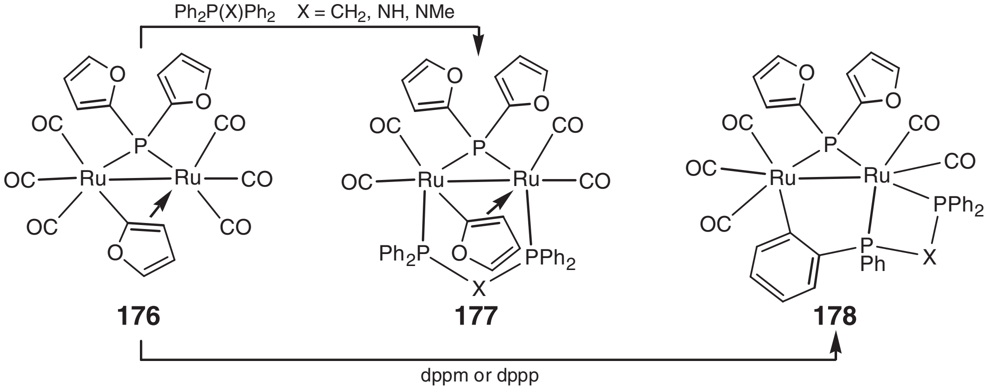
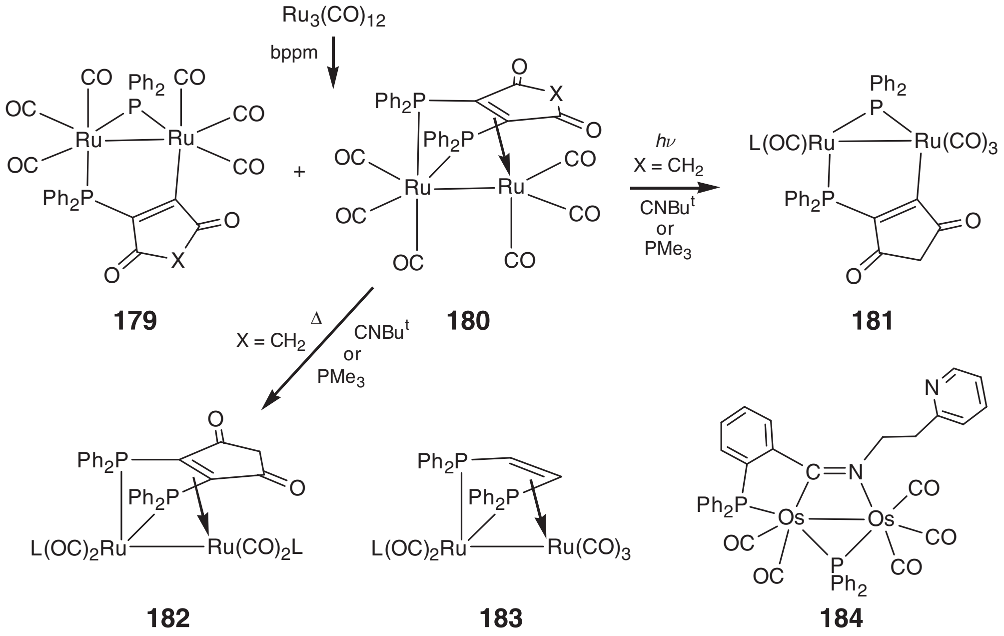
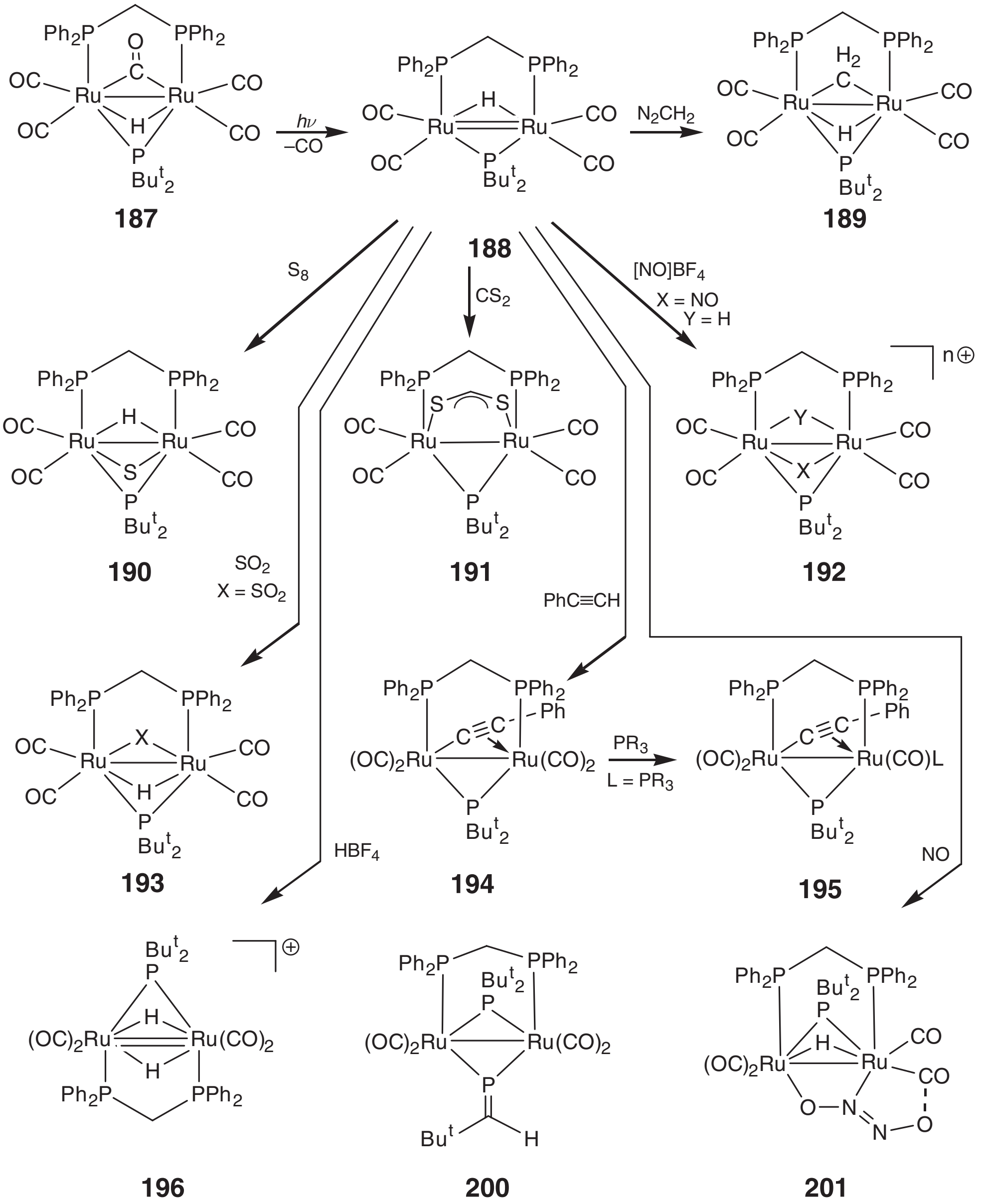


In a similar manner, 2,3-bis(diphenylphosphino)-*N*-phenylmaleimide (bppm) reacts with $Ru_3(CO)_{12}$ to give the phosphido complex **179** ($X = CH_2$) and the donor–acceptor complex **180** ($X = CH_2$).[132,133] Two further analogs ($X = O$, NPh) of the bppm ligand react with $Ru_3(CO)_{12}$ to yield the corresponding compounds **179** ($X = O$,[134] NPh[132]) and **180** ($X = O$,[134] NPh[132]). Under photochemical conditions, **180** ($X = CH_2$) reacts with PMe_3 or $CNBu^t$ to provide mixtures of **179** ($X = CH_2$) and **181** ($L = PMe_3$, $CNBu^t$). The same reaction under thermal conditions yields only **182** ($L = PMe_3$, $CNBu^t$).[135] The related donor–acceptor complex, **183** ($L = PMe_3$), is obtained from $Ru_2(CO)_6$(*Z*-$Ph_2PCH{=}CHPPh_2$) and PMe_3 upon irradiation in the near-UV or in the presence of Me_3NO.[136] Pyrolysis of $Os_3(CO)_{12}$ with Ph_2P(*o*-C_5H_4N)$CH{=}N(CH_2)_2$(*o*-C_5H_4N) in a sealed system leads to activation of the imino carbon of the ligand and affords the phosphido complex **184** in low yield.[137]

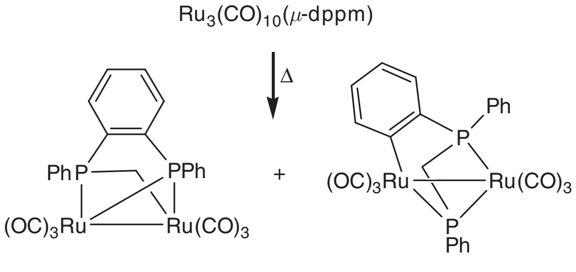


The reaction of $Ru_3(CO)_{12}$ with $HPBu^t_2$ leads to the formation of the coordinatively unsaturated compound $Ru_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PBu^t_2)(CO)_3(PHBu^t_2)_2$ **185** as well as $Ru_3(CO)_9(PHBu^t_2)_3$ and $Ru(CO)_3(PHBu^t_2)_2$. The reversible addition of carbon monoxide to this species leads to $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PBu^t_2)(CO)_5(PHBu^t_2)]$ **186**.[138] Displacement of a carbonyl and a phosphine ligand from **186** with dppm leads to complex **187**, which itself loses CO under thermal or photolytic conditions to yield **188**. Compound **188** is a versatile starting point for a range of μ-phosphido complexes. Diazomethane can be added across the Ru═Ru bond in **188** to provide the μ-methylene complex **189**,[139] while reaction with elemental sulfur yields **190** and treatment with CS_2 affords **191**. Chlorinated solvents such as CCl_4 and $CHCl_3$ react with **188** to give **192** ($X = Cl$, $Y =$ none, $n = 0$), whereas treatment with $[NO]BF_4$ yields **192** ($X = NO$, $Y = H$, $n = 1$).[140] Oxidation of **190** with 3-phenyl-2-(phenylsulfonyl)oxaziridine yields the complex **193** ($X = SO$). The corresponding bridging sulfur dioxide complex **193** ($X = SO_2$) is formed reversibly from the reaction of **188** with SO_2.[141] Treating **188** with phenylacetylene for 8 h in refluxing toluene yields **194** with loss of hydrogen and the bridging mode of the alkynyl ligand is confirmed by a structural study. Complex **194** undergoes CO substitution reactions with phosphines at one ruthenium center to give **195** ($L = PBu^n_3$, PCy_2H, η^1-dppm).[142] Protonation of **188** with HCl, however, leads to three products: **192** ($X = Cl$, $Y =$ none, $n = 0$), **196** (chloride salt), and $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)]Cl$ **197**. The tetrafluoroborate salt of **196** can be obtained more conveniently using HBF_4. This reaction is reversible on treatment with a non-nucleophilic base such as 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) to generate **188**. In a similar manner, **192** ($X = NO$, $Y =$ none, $n = 0$) can be formed from $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}NO)(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)]BF_4$ **198**.[143]

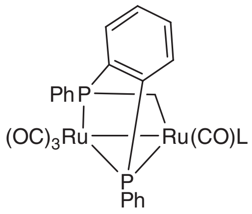
The sluggish reaction of **188** with alkynes[142] is paralleled with phospha-alkynes and so the more reactive species $[Ru_2(CO)_3(PBu^n_3)(\mu\text{-}H)(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)]$ **199** is used for the reaction and yields **200** after 3 h reflux with $P{\equiv}CBu^t$ in 1,2-dimethoxyethane (DME). It is noteworthy that the product gains a CO ligand which presumably is generated from other side-reactions. A crystal structure of **200** confirmed the bridging mode of the phospha-ethenyl ligand and the multiple nature of the P═C bond.[144] Despite the failure of the analogous diiron complex to react (see Chapter 6.02), treatment of **188** with nitric oxide leads to the clean formation of **201**, in which two molecules of NO are dimerized into a μ-η^2-ONNO (hyponitrite) bridging ligand.[145] Structural and computational studies reveal an interaction with the metal-bonded carbonyl closest to the hyponitrite ligand.



The phosphido complexes 202 and 203 are formed by the pyrolysis of $Ru_3(CO)_{10}(\mu\text{-dppm})$ as well as from the reaction of the same material with the benzyl halides $C_6X_5CH_2Br$ (X = H, Me, or F).[146] Complexes 202 and 203 were also later obtained unexpectedly from the reaction between $Ru_3(CO)_{10}(\mu\text{-dppm})$ and $Te_2(C_6H_4OEt\text{-}4)_2$.[147] Pyrolysis of $Ru_3(CO)_9(\mu\text{-dppm})(PPh_3)$, however, leads to compounds 204 (L = CO, PPh_3), in which only one phosphorus donor spans the metal centers directly.[148] The reaction of $Os_3(CO)_{12}$ with 1,8-bis(diphenylphosphino)naphthalene in refluxing toluene results in cleavage of a P–C bond and formation of 205, which contains a stabilizing interaction between the naphthalene moiety and one osmium center.[149] The compound $Ru(CO)_3\{\eta^2\text{-}Ph_2PN(Me)PPh_2\}$ undergoes cleavage of an N–P bond in *n*-heptane followed by attack of the cleaved nitrogen on a carbonyl ligand to form 206.[150] Heating $\{Re_3(\mu\text{-H})_3(CO)_{11}\}(\mu\text{-}C_2(PPh_2)_2)\{Ru_3(CO)_{11}\}$ results in the formation of 207 [$ML_n = Re_3(\mu\text{-H})_3(CO)_{11}$], in which the diruthenium unit is bridged both by phosphido and alkynyl ligands.[151]



202 **203**



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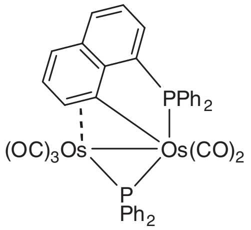

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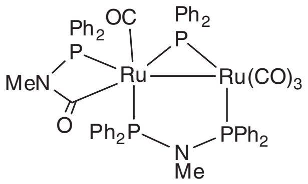

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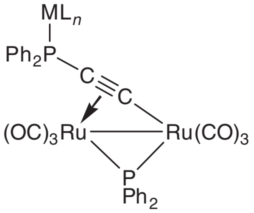

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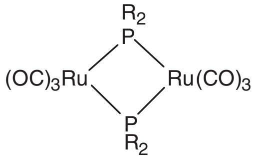
Treatment of $[Ru_2(CO)_4(\mu\text{-}O_2CEt)_2(PR_2H)_2]$ (R = Ph, Cy) with carbon monoxide leads to formation of a mixture of the bis(μ-phosphido) complexes **208** (R = Ph, Cy) and the phosphido–phosphinito compounds **209** (R = Ph, Cy).[152] It was later revealed by variable-temperature NMR studies that **208** (R = Cy) exists as two interconverting isomers in solution.[153] Complex **210**, which is bridged by linked Cp rings and a bridging carbonyl, contains a μ-phosphido ligand originating from cleavage of the P–C bond in triphenylphosphine.[154] An unusual example of a diruthenium μ-arsenido complex, **211**, is obtained on heating $[Ru_3(CO)_{11}(AsMe_2Ph)Cr(CO)_3]$ in refluxing *n*-octane along with $[Ru_3(CO)_8(H)(AsMe_2)\{C_6H_4Cr(CO)_3\}]$.[155]



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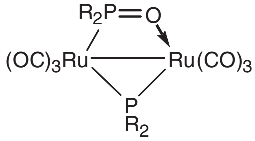

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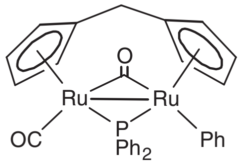

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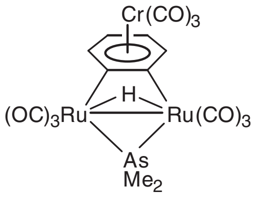
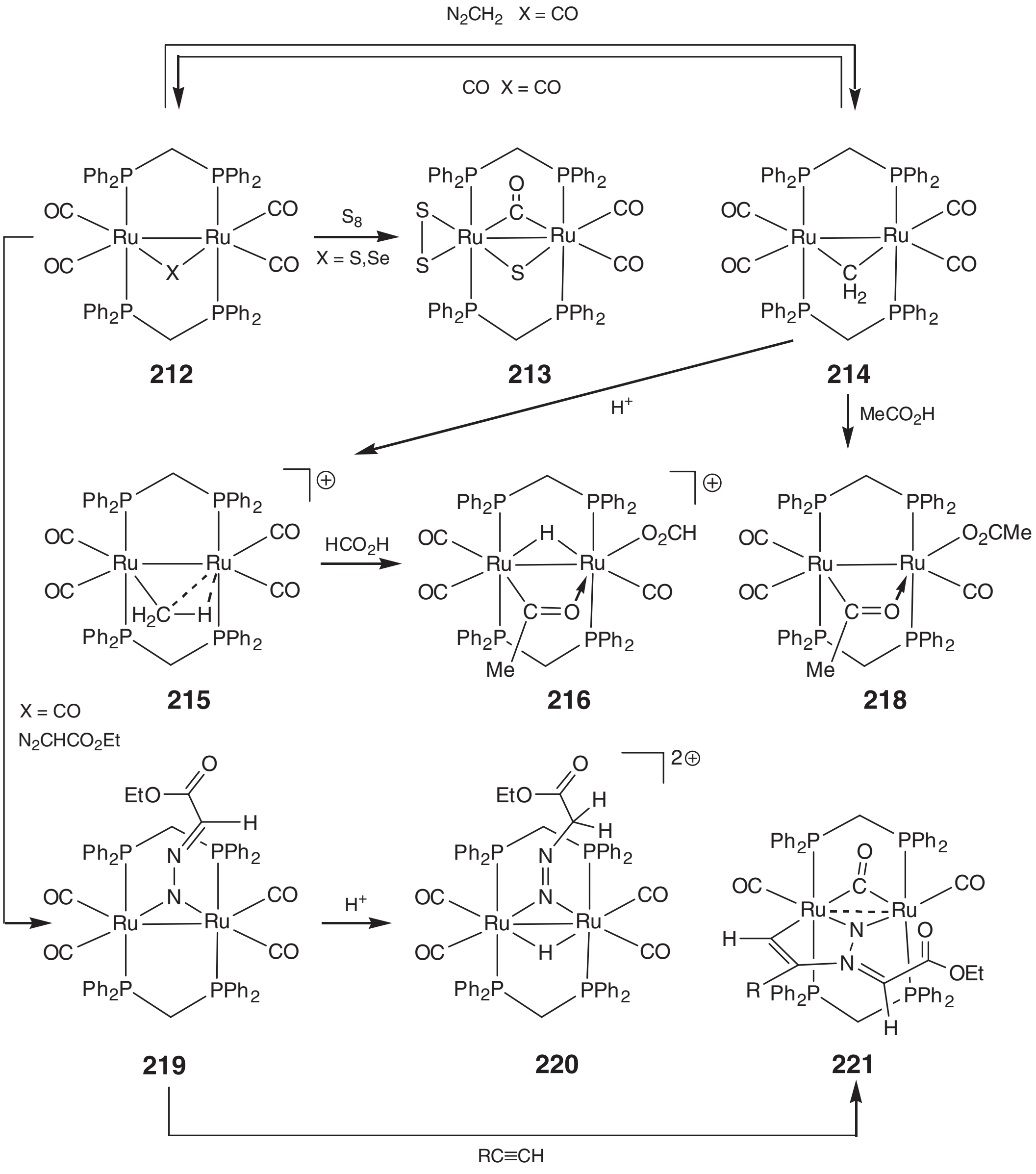


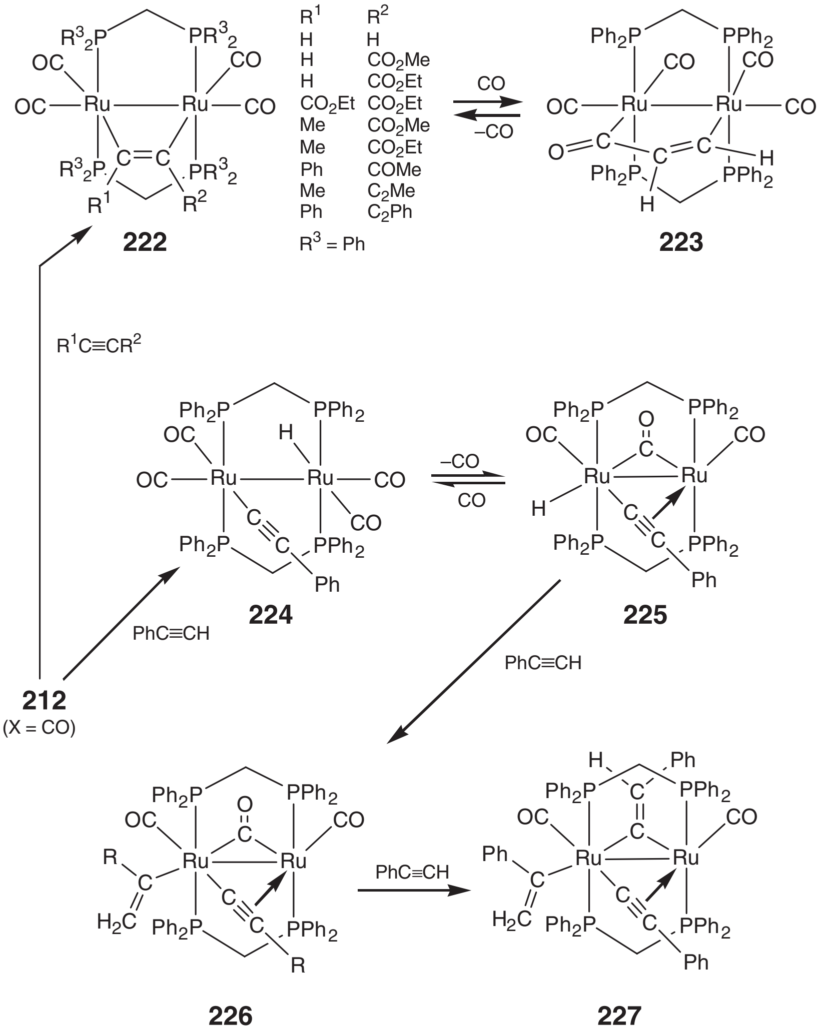
211

6.17.2.3.2 Complexes with two diphosphine ligands

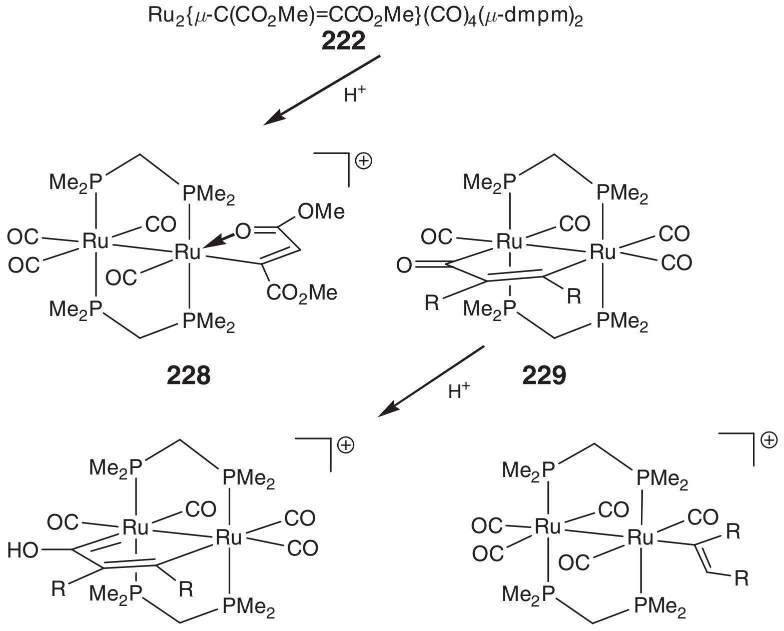
Diruthenium complexes with two diphosphine ligands, most commonly dppm, have been used to explore a wide range of reactivity toward heteroatom and organic reagents. A versatile entry point for this chemistry is the carbonyl complex **212** (X = CO), prepared by the reduction of ruthenium acetate in the presence of carbon monoxide.[156] A later high-pressure method was also used to synthesize this compound and its dmpm (bis(dimethylphosphino)methane) analog.[157] Compound **212** (X = CO) undergoes reactions with elemental sulfur (or H_2S, propylene sulfide) and selenium to give **212** (X = S, Se), respectively, through displacement of the bridging CO ligand.[158] Treatment of **212** (X = CO) with SO_2 leads to **212** (X = SO_2), however attempts to oxidize **212** (X = S) to yield the same product failed. Reaction of **212** (X = S or Se) with an excess of sulfur leads to the isolation of **213**, the structure of which contains a bridging CO ligand and an S_2 ligand.[158] Reaction of **212** (X = CO) with an excess of diazomethane results in the bridging methylene complex **214**. This reaction is carried out at 50 °C in toluene and proceeds with substantial parallel decomposition of CH_2N_2 to polymethylene. Complex **212** (X = CO) is regenerated on treatment of **214** with carbon monoxide. Protonation of **214** with HBF_4 or HOTf yields **215** (BF_4^-, TfO^- salts), in which an agostic bridging interaction between the methyl group and the other ruthenium center is detected by NMR techniques.[159] Complex **214** is also a catalyst precursor for the decomposition of formic acid to CO_2 and H_2, as is **212** (X = CO) in acetone solution.[160,161] Formic acid reacts with **215** at low temperature to give the μ-acetyl species **216** (HCO_2^- salt) which is stable only in the temperature range −10 °C to 0 °C, above which liberation of CO_2 and CH_4 occurs. The organometallic products of this process are **212** (X = CO) and $[Ru_2H(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ **217**. With acetic acid, **214** reacts to give an acyl species **218** directly. On treatment with HBF_4 or HOTf, a solution of complex **214** was found to catalyze the ring-opening polymerization of norbornene at RT. The polymerization was slow (at RT) but the active species was shown to have a long lifetime (1 week).[159] Compound **214** also catalyzes the head-to-tail dimerization of phenylacetylene.[162] The exploration of the reactivity of **212** (X = CO) with diazoalkane reagents was extended to include the reaction of N_2CHCO_2Et, which yielded the diazoalkane complex **219** rather than a bridging carbene.[163] Treatment of the product with CO regenerates **212** (X = CO). Protonation of **219** leads to the isolation of the dication **220** (BF_4^- double salt), although a singly protonated intermediate can be identified at −20 °C. Phenyl- and tolylacetylene react with **219** over 3 h to give **221** (R = Ph, Tol); however, other alkynes (e.g., internal alkynes) fail to react or give mixtures of products.[163]



Complex 212 (X = CO) itself reacts with alkynes. Treatment with ethyne yields 222 ($R^1 = R^2 = H$, $R^3 = Ph$), which loses CO in the initial reaction. If the reaction is carried out in a sealed flask, the liberated CO inserts into the Ru–C bond to give 223 in a reversible process.[164] The reaction to form 222 ($R^1 = R^2 = H$, $R^3 = Ph$) can be extended to a wide range of alkynes to yield products of the same structure 222.[165–167] However, the reaction of 212 (X = CO) with phenylacetylene proceeds by oxidative addition of the alkyne to yield the alkynyl complexes 224 and 225, which can interconvert through reversible μ-CO and μ-η^2-alkynyl interactions. Dissolution of 225 in CH_2Cl_2 provides a chlorinated version through replacement of the hydride. With an excess of PhC≡CH, 225 reacts further by insertion of the alkyne into the Ru–H bond to form an alkenyl complex, 226 (R = Ph). However, this product is difficult to isolate in pure form as the reaction continues to yield ultimately a compound with alkynyl, alkenyl, and vinylidene groups 227. The NMR spectra of 227 are temperature dependent due to the stereochemically non-rigid nature of the species. The complex was also structurally characterized. The use of RC≡CH (R = Bu^n, $CH_2CH_2C{\equiv}CH$) allows isolation of pure 226 (R = Bu^n, $CH_2CH_2C{\equiv}CH$) as further reactions do not occur with these alkynes.[166]



Although less research has been done on complexes with the more electron-rich $Ru_2(\mu\text{-dmpm})_2$ framework, the dmpm complex 222 ($R^1 = R^2 = CO_2Me$, $R^3 = Me$) has been shown to protonate at carbon to give the (*Z*)-alkenyl complex 228 (BF$_4^-$ salt) with HBF$_4$·OEt$_2$, while the diruthenacyclopentenone 229 (R = CO$_2$Me) reacts with the same reagent to yield 230 (R = CO$_2$Me, BF$_4^-$ salt) by protonation at oxygen. The authors discuss the importance of carbenoid forms in the reactivity of dmpm metallacycles in the context of these results. Insertion of dimethyl acetylenedicarboxylate into the Ru–H bond of [Ru$_2$(μ-H)(CO)$_5$(μ-dmpm)$_2$]BF$_4$ leads to the (*E*)-alkenyl complex 231 (R = CO$_2$Me; BF$_4^-$ salt).[168]

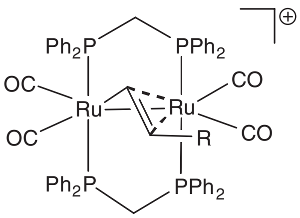

$Ru_2\{\mu\text{-}C(CO_2Me)=CCO_2Me\}(CO)_4(\mu\text{-dmpm})_2$

222

228 **229**

230 **231**

Complex 212 (X = CO) also catalyzes hydrogen transfer from formic acid to alkynes. Generating alkenes in this manner from alkynes provides an alternative to the traditional method of using hydrogen gas for such transformations. In the course of this work,[169] it was found that the protonation product of 212 (X = CO) with formic acid, [Ru$_2$(CO)$_4$(μ-H)(μ-CO)(μ-dmpm)$_2$]CO$_2$H 232, reacts with phenylacetylene to yield the bridging alkenyl compound 233 (R = Ph; CO$_2$H$^-$ salt). An analogous product 233 (R = H; TfO$^-$ salt)[170] is formed from the reaction between HC≡CH and [Ru$_2$(CO)$_3$(μ-H)(μ-CO)(μ-dppm)$_2$]$^+$ (234, TfO$^-$ salt),[159] which is generated by protonation of 214 by HOTf. However, the reaction of 234 (TfO$^-$ salt) with diphenylacetylene yields the triflate salt of 235 (in equilibrium with the starting complex, 234), in which two CO ligands bridge the diruthenium unit rather than the alkenyl ligand.[170]



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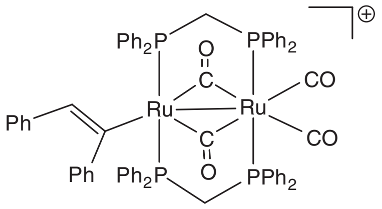
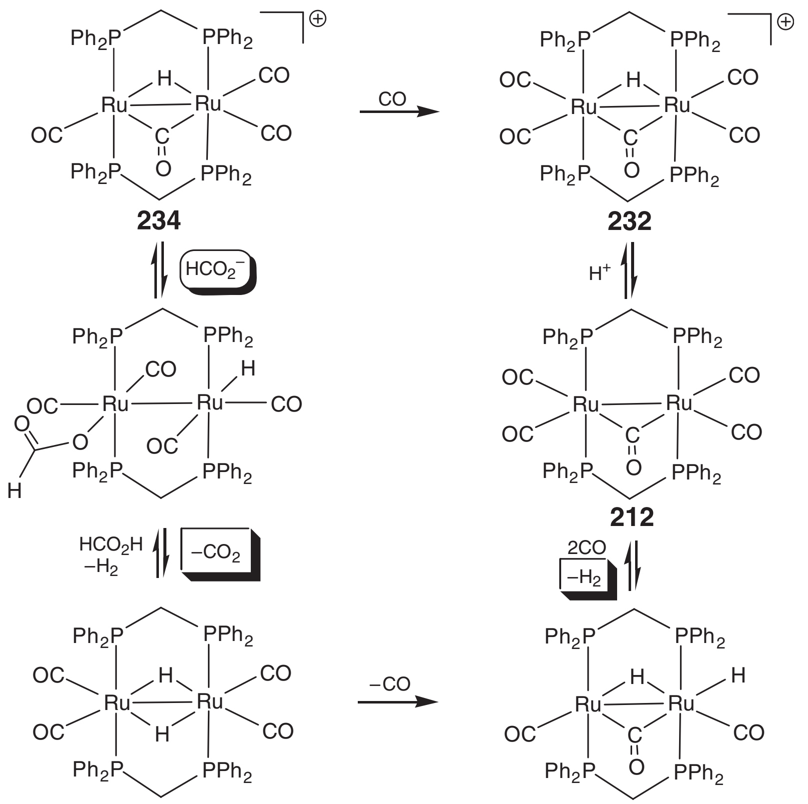
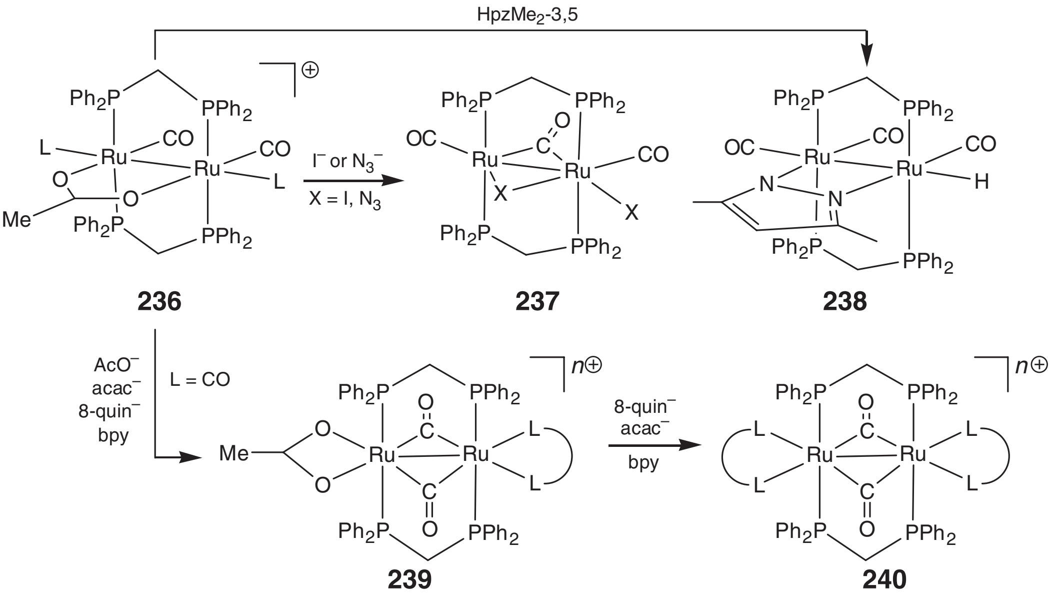


235

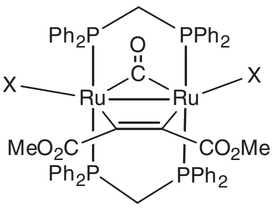
In the presence of triethylamine, the coordinatively unsaturated hydride salt, 234, is an efficient catalyst for the decomposition of formic acid to CO$_2$ and H$_2$.[170]



Another versatile starting point for dppm-bridged diruthenium chemistry is the acetate complex 236 (L = CO, BF_4^- salts),[171] which reacts with iodide and azide through displacement of the acetate ligand to give 237 (X = I, N_3). The same ligand is also lost on treatment with bridging nitrogen donors such as 3,5-dimethylpyrazole to give the hydride compound 238.[171] Reaction of 236 (L = CO, BF_4^- salt) with two-electron donors such as phosphites and nitriles leads to replacement of the axial CO ligands to yield 236 (L = $P(OMe)_3$, NCMe; BF_4^- salts).[129] The reactivity of 236 (L = CO; PF_6^- salt) was also investigated with neutral and anionic bidentate donors to yield the bis(μ-CO) compounds 239 ($n = 0$, $L_2 = O_2CMe$, acac, 8-quinolate; $n = 1$, L_2 = bpy, PF_6^- salt) and, on treatment with an excess of L_2, 240 ($n = 0$, L_2 = acac, 8-quinolate; $n = 2$, L_2 = bpy; PF_6^- double salts).[172]



As observed in the preparation of $[Ru_2(CO)_4(MeCN)_4(PPh_3)_2](BF_4)_2$ **109**,[43] removal of the bridging acetate in **236** (L = CO; BF_4^- salt) can be achieved by treatment with an excess of $[Et_3O]BF_4$ in acetonitrile to give $[Ru_2(CO)_4(MeCN)_2(\mu\text{-dppm})_2](BF_4)_2$ **241**, which converts rapidly to $[Ru_2(MeCN)_4(\mu\text{-CO})_2(\mu\text{-dppm})_2](BF_4)_2$ **242** as the final product.[173,174] This species reacts readily with an excess of halide, thiolate, or azide to provide $[Ru_2X_2(\mu\text{-CO})_2(\mu\text{-dppm})_2]$ (**243**; X = Cl, Br, I, SH, STol, SPr^i, N_3), which were initially reported to contain an Ru–Ru triple bond based on effective atomic number (EAN) considerations.[173] Later crystallographic studies showed, however, that the Ru–Ru bond lengths (2.74–2.81 Å) fall in the range common for Ru–Ru single bonds and that the halide (or pseudohalide) ligands enter into multiple bonding with the metal centers, lengthening the metal–metal bond. The Ru–X distances were also found to be shorter than typical values.[174] These species (**243**; X = Br, I) also show reactivity toward activated alkynes, as illustrated by the bridging dimethyl acetylenedicarboxylate complexes **244** (X = Br, I). Compound **243** (X = Cl) reacts with trimethylamine *N*-oxide dihydrate to provide a mixture of two isomers **245a** and **245b** (X = Cl), containing bridging hydride and hydroxide ligands.[173,174]



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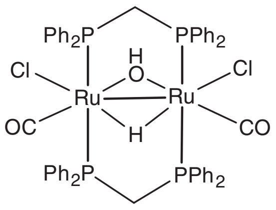
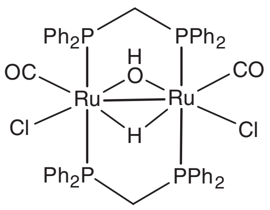
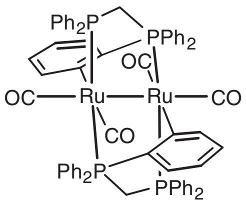


245a



245b

When the zerovalent complex **212** (X = CO) is heated in benzene, orthometallation occurs at both diphosphine ligands to give the unusual complex **246**, which constitutes the first example of simple orthometallation of dppm at a dinuclear center.[175] Although a large body of work exists in which two diphosphines are employed to bridge the dinuclear unit, relatively few compounds are known in which a single diphosphine is used, such as in complex **247** (TfO^- double salt).[176] A number of examples also exist of complexes in which diphosphine ligands are employed but not in a bridging role. The complex **248** (PF_6^- salt), which contains an unsupported Ru–Ru bond, is obtained by one-electron oxidation of $[Ru(CO)_3(dppe)]$ with $[Cp_2Fe]PF_6$. This species was found to be fluxional in solution and variable-temperature NMR experiments were used to investigate the exchange mechanism and the associated rate constants.[177] The coordinatively unsaturated compound $[Ru(CO)_2(Bu^t{}_2PCH_2CH_2PBu^t{}_2)]$ is a monomer in solution but crystallizes as the dimeric complex **249** (R = Bu^t) in the solid state, which is in contrast to the analogs bearing monodentate phosphines, $[Ru(CO)_2(PR_3)_2]$.[178,179]



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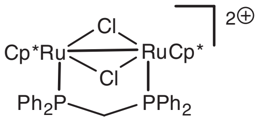

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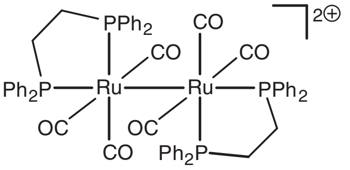

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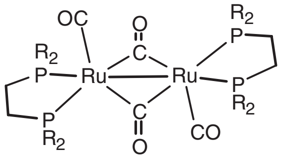


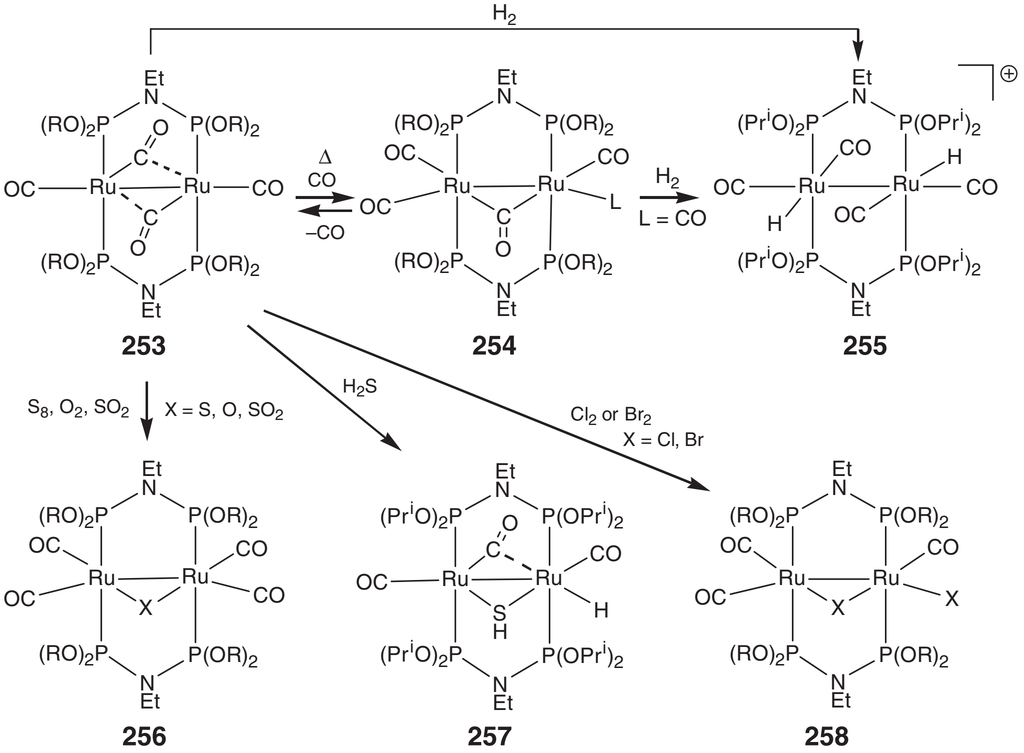
249

A few dinuclear complexes have been reported with monodentate phosphine or stibine ligands, such as the halide-bridged compounds $Os_2(\mu\text{-I})_2(CO)_5(PPh_3)$ **250**,[180] $Os_2(\mu\text{-I})_2(CO)_4(PPh_3)_2$ **251**,[180] and $Ru_2Br_2(\mu\text{-Br})_3(SbMe_2Ph)_4$ **252**.[181]

6.17.2.3.3 Complexes with diphosphazane ligands

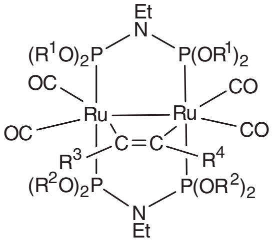
Diphosphazane ligands bridge the diruthenium unit in a similar manner to diphosphines (e.g., dppm); however, it has been shown that modification of the OR substituents on the phosphazane ligands can have a significant effect on the reactivity of the complexes.

The diphosphazane carbonyl complexes **253** (R = Me, Pr^i)[182] and **254** (R = Me, Pr^i; L = CO)[183] are convenient starting points for much of the chemistry supported by these ligands. The former displays semi-bridging carbonyl ligands, as determined by a structural study.[182] The two complexes can be interconverted by heating under argon in toluene at 80 °C (to form **253**; R = Me, Pr^i) or exposure to carbon monoxide (to generate **254**; L = CO). Both complexes (when R = Pr^i) react with hydrogen (reversibly) to yield $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **255**.[182] Compounds **253** (R = Me, Pr^i) undergo reaction with isonitrile to form **254** (R = Me, Pr^i; L = $CNC_6H_3Me_2$-2,6) as well as reactions in which the μ-CO ligand is replaced by a wide range of bridging species. Reaction with [NO][SbF_6] yields the μ-NO variant **256** (SbF_6^- salt), while reaction with elemental sulfur or oxygen (air) in toluene solution leads to the formation of **256** (R = Pr^i; X = S, O; $n = 0$). Further complexes bearing bridging sulfur donors are accessible, such as the μ-SO_2 (**256**; R = Pr^i; X = SO_2; $n = 0$) or μ-SH complexes **257**, both obtained from passing SO_2 or H_2S, respectively, through toluene solutions of **253** (R = Pr^i).[182] In the same manner, treatment of **253** (R = Me, Pr^i) with Cl_2 or Br_2 leads to the μ-halide complexes **258** (R = Me, X = Cl; R = Pr^i, X = Cl, Br) by oxidative addition. In contrast, reaction of **253** (R = Pr^i) with iodine leads to a cationic species with only one iodide ligand, $[Ru_2(CO)_4(\mu\text{-}I)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ **259**, as the principal product after treatment with $[NH_4]PF_6$.[182] Protonation of **253** (R = Pr^i) with HPF_6 or $HBF_4{\cdot}OEt_2$ leads to the hydride complex $[Ru_2(\mu\text{-}H)(CO)_3(\mu\text{-}CO)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (**260**; PF_6^- or BF_4^- salts).[182,184] It was discovered that reaction of **253** (R = Me, Pr^i) with tin(II) chloride also results in displacement of the bridging carbonyl and the isolation of a bridging tin unit in **256** (R = Me, Pr^i; X = $SnCl_2$; $n = 0$).[182]



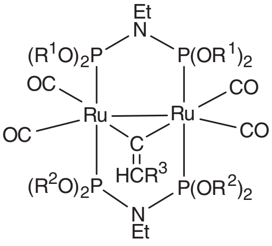
Compound **253** (R = Me, Pr^i) also reacts with alkynes; however, the nature of the phosphorus substituents plays an important role in the products formed.[185] When **253** (R = Me) is used, bubbling ethyne through a toluene solution at 80 °C leads to the ethenediyl-bridged species **261** ($R^1 = R^2$ = Me, R^3 = H) as the major product with small amounts of the vinylidene-bridged complex **262** ($R^1 = R^2$ = Me, R^3 = H). When **253** (R = Pr^i) is employed, reaction with ethyne leads to compound **261** ($R^1 = R^2 = Pr^i$, $R^3 = R^4$ = H) as the minor product and **262** ($R^1 = R^2 = Pr^i$, $R^3 = R^4$ = H) as the major product. A number of terminal and internal alkynes were investigated and only in two cases were exclusive products isolated; reaction of **253** (R = Me, Pr^i) with $PhC{\equiv}CH$ gives only the μ-vinylidene species **262** ($R^1 = R^2$ = Me, Pr^i; R^3 = Ph) and treatment of **253** (R = Me, Pr^i) with $MeO_2CC{\equiv}CCO_2Me$ yielded just the bridging alkenediyl compounds **261** ($R^1 = R^2$ = Me, Pr^i;

$R^3 = R^4 = CO_2Me$).[185] The authors established that the two types of complex form via different mechanisms and that alkynes with larger substituents tend to adopt the μ-vinylidene form with the bulkier tetraisopropoxydiphosphazane complexes. As part of these investigations, versions of **253** with one tetraisopropoxydiphosphazane and one tetramethoxydiphosphazane ligand were also employed.[185]



261

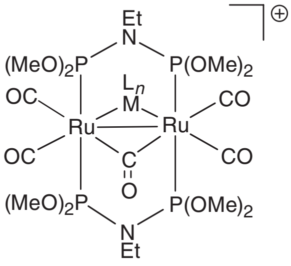
R^1	R^2	R^3	R^4
Me	Me	H	H
Me	Me	H	Me
Me	Me	H	CO_2Me
Me	Me	CO_2Me	CO_2Me
Et	Et	H	H
Pr^i	Pr^i	H	H
Pr^i	Pr^i	H	CO_2Me
Pr^i	Pr^i	CO_2Me	CO_2Me
Me	Pr^i	H	H



262

R^1	R^2	R^3
Me	Me	H, Me, Ph
Et	Et	H
Pr^i	Pr^i	H, Me, Ph, CO_2Me
Me	Pr^i	H

Treatment of **253** (R = Me) with equimolar quantities of metal-containing electrophiles such as $AuCl(PPh_3)$, silver(I) salts, $[Cu(NCMe)_4]PF_6$, $HgCl_2$, and $SbCl_3$ affords cationic products in which the metal units are coordinated in a bridging mode (**263**; $ML_n = AuPPh_3$, $Ag(NCMe)_x$, $Ag(py)_x$, $Cu(NCMe)_2$; PF_6^- or SbF_6^- salts) or terminally (**264**; X = HgCl, $SbCl_2$; SbF_6^- or $Sb_2Cl_7^-$ salts). The silver adducts form the solvato species **265** (R = Me, Pr^i; L = NCMe, NCPh, $OCMe_2$; SbF_6^- double salts) in the presence of coordinating solvent. These species react with a range of nucleophiles to give **265** (R = Me, L = $CNC_6H_3Me_2$-2,6; R = Pr^i, L = py, η^1-4,4′-bpy, SMe_2, tetrahydrothiophene; SbF_6^- double salts).[186]



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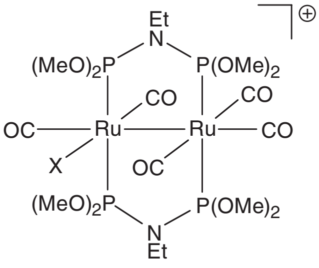

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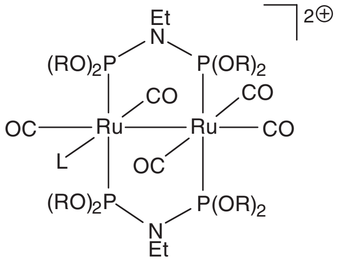
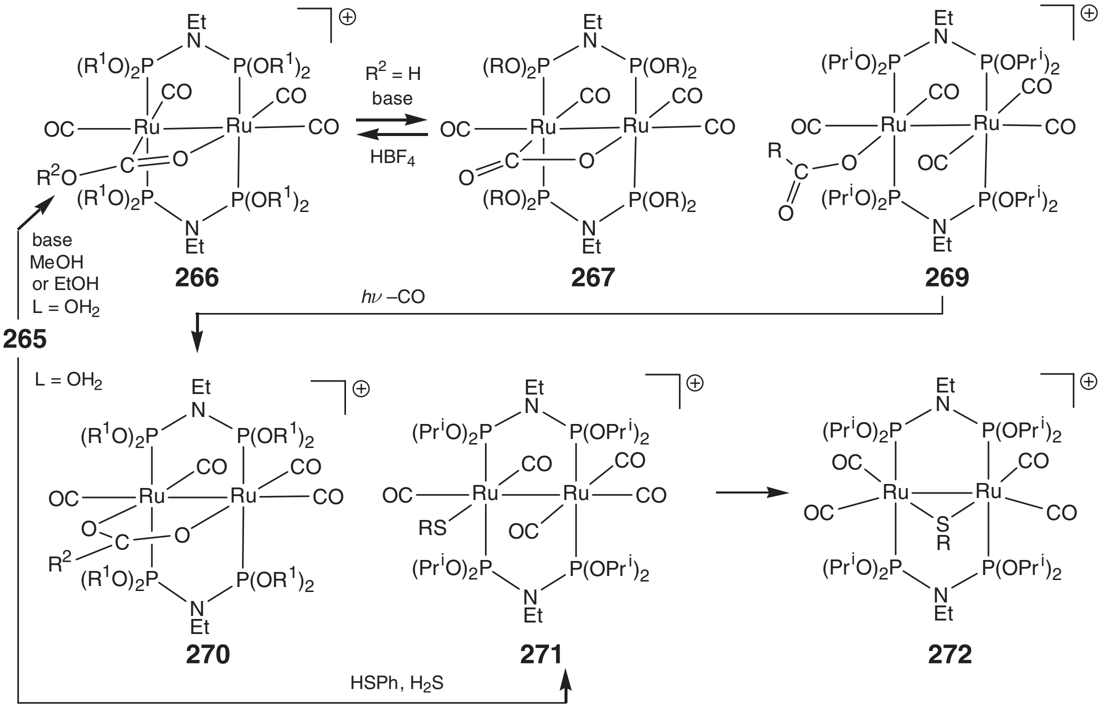


265

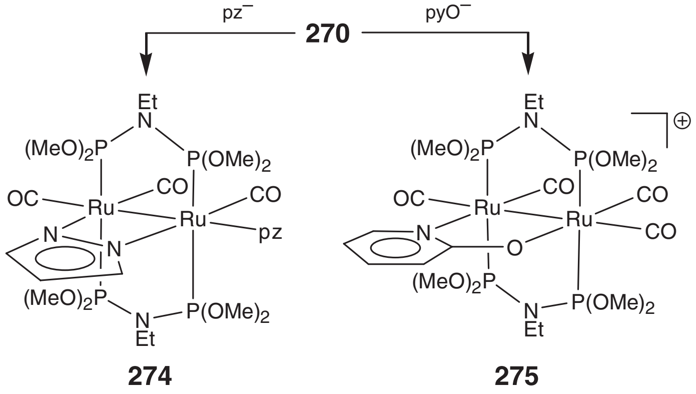
R	L
Me, Pr^i	NCMe, NCPh, $OCMe_2$ HOEt, HOMe, OH_2
Me	$CNC_6H_3Me_2$-2,6
Pr^i	py, 4,4′-bipy, $OCEt_2$, O_2NMe, SMe_2, SC_4H_8

In the presence of base, the aqua complexes **265** (R = Me, Pr^i; L = OH_2; SbF_6^- double salts) react with ethanol or methanol to yield the alkoxycarbonyl species **266** (R^1 = Me, Pr^i; R^2 = Me, Et; SbF_6^- salts), which are also accessible by oxidation of **254** (L = CO) with $AgSbF_6$ in methanol or ethanol.[187] The corresponding hydroxycarbonyl derivatives **266** (R^1 = Me, Pr^i; R^2 = H; SbF_6^- salts) are also formed on reaction of **265** (R = Me, Pr^i; L = OH_2; SbF_6^- salts) with base (py or NEt_3). If an excess of triethylamine or a stronger base (e.g., KOH) is used, deprotonation of **266** (R^1 = Me, Pr^i; R^2 = H; SbF_6^- salts) occurs to yield the unusual bridging carbon dioxide complexes **267** (R = Me, Pr^i), the second of which was structurally characterized.[187] Stepwise protonation ($HBF_4 \cdot OEt_2$) reverses the reaction sequence to give **266** (R^1 = Me, Pr^i; R^2 = H; BF_4^- salts) and then **265** (R = Me, Pr^i; L = OH_2; BF_4^- double salts). The aqua complex **265** (R = Pr^i; L = OH_2; SbF_6^- double salt) also reacts with carboxylic acids (RCO_2H; R = H, Me, Ph, CF_3) to provide $[Ru_2(CO)_5(RCO_2H)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2](SbF_6)_2$ (**268**; R = H, Me, Ph, CF_3), a reaction that is reversed with water. Compounds **268** (R = H, Me, Ph, CF_3) can be deprotonated (reversibly) to give **269**

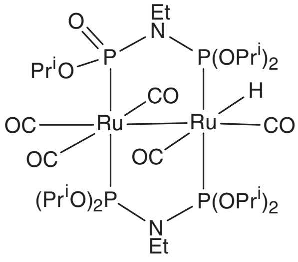
(R = H, Me, Ph, CF_3; SbF_6^- salts), which lose CO on irradiation to yield ultimately **270** ($R^1 = Pr^i$; $R^2 = H$, Me, Ph, CF_3; SbF_6^- salts). The corresponding carboxylates react with **265** ($R = Pr^i$; $L = OH_2$; SbF_6^- double salt) to give **270** ($R^1 = Pr^i$; $R^2 = H$, Me, Ph; SbF_6^- salts) directly, apart from $R = CF_3$, for which the intermediate **269** ($R = CF_3$; SbF_6^- salt)[187] can be isolated before conversion to **270** ($R^1 = Pr^i$, $R^2 = CF_3$; SbF_6^- salt). Complex **265** ($R = Pr^i$; $L = OH_2$; SbF_6^- double salt) also reacts with the sulfur donors thiophenol and hydrogen sulfide in acetone to give **271** (R = H, Ph; SbF_6^- salts) through loss of a proton. Over extended periods in acetone solution, compounds **271** (R = H, Ph; SbF_6^- salts) are converted into the products **272** (R = H, Ph; SbF_6^- salts).



Compound **270** ($R^1 = Me$, Pr^i; R = Me, Ph; PF_6^- salts) can also be formed from **254** (R = Me, Pr^i; L = CO) in a two-electron oxidation using silver(I) carboxylates in acetone or tetrahydrofuran (followed by metathesis with NH_4PF_6). The exception to this is the reaction of **254** (R = Me, Pr^i; L = CO) with AgO_2CCF_3, which yields $[Ru_2(CO)_5(O_2CCF_3)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ (**273**; R = Me, Pr^i) after metathesis with NH_4PF_6. The acetate ligand in **270** ($R^1 = Me$; $R^2 = Me$; PF_6^- salts) can be displaced by other anionic ligands such as pyrazolate and oxy-2-pyridinate to provide **274** and **275** (PF_6^- salt), respectively.[188]

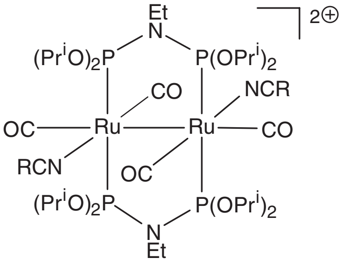


Exposure of 253 (R = Pr^i) to ultraviolet radiation leads to an unusual Arbuzov-type rearrangement to yield 276. This photochemical dealkylation reaction results in a bridging phosphonate and a new hydride ligand located on the other ruthenium center (as demonstrated by a structural study).[189]



276

A study to investigate the redox behavior of 253 (R = Pr^i) and its conversion to the nitrile species 277 (R = Me, Ph; SbF_6^- salts) using silver(I) salts led to the preparation of an electron-transfer salt 278 (R = Pr^i; tcnq = 7,7,8,8-tetracyano-*p*-quinodimethane; thf = tetrahydrofuran; $tcnq^-$ salt) from 253 (R = Pr^i) and tcnq in tetrahydrofuran. Cyclic voltammetry was used to examine the redox processes occurring in acetonitrile and benzonitrile solution.[190]



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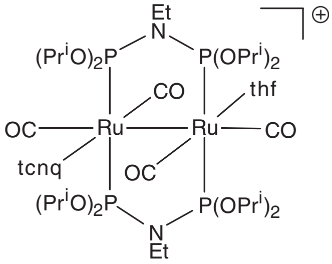

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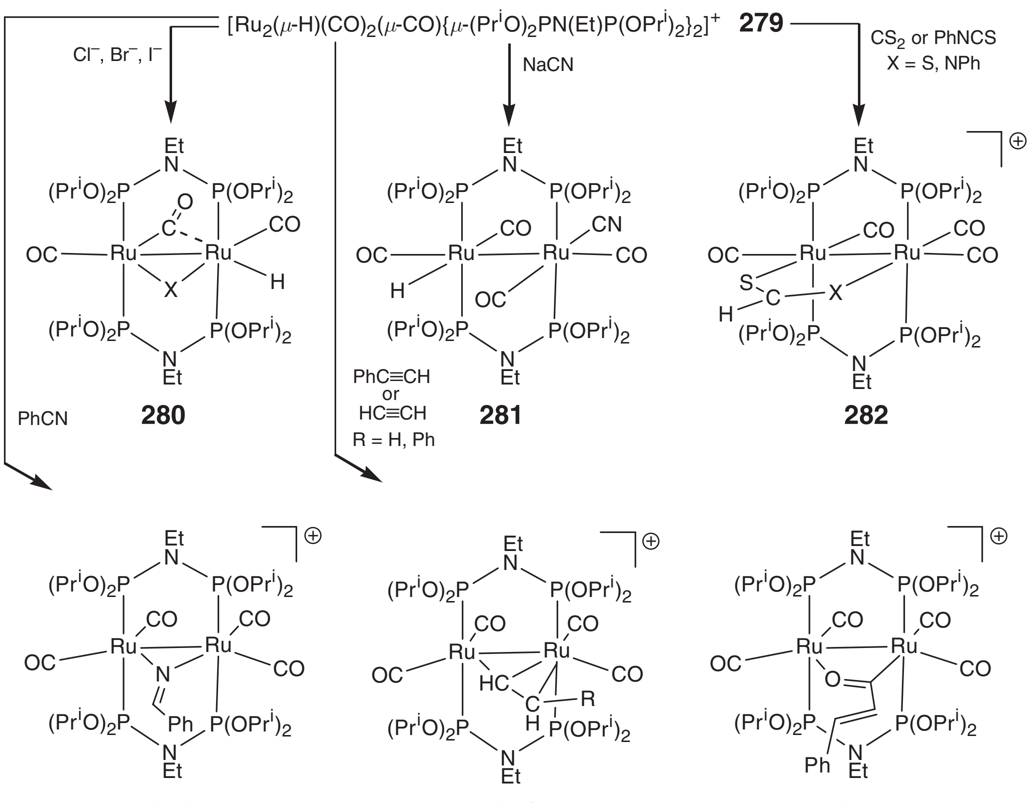
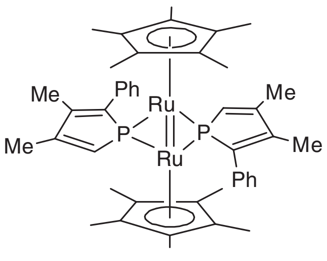
The diruthenium hydride complex $[Ru_2(\mu\text{-}H)(CO)_3(\mu\text{-}CO)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ 279; PF_6^- or BF_4^- salts) was originally formulated with a terminal hydride but a later crystal structure determination revealed a bridging mode for the hydride ligand.[184] Unsurprisingly, the coordinatively unsaturated nature of this species leads to reactions with nucleophiles. Treatment with $NaBH_4$ in acetone leads to $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$, while reactions with halides result in the complexes 280 (X = Cl, Br, I) with a semi-bridging CO ligand (crystal structure of iodide). Sodium cyanide reacts with 279 (PF_6^- salt) to give the cyanohydride complex 281, while CS_2 inserts into the Ru–H bond to yield 282 (X = S; PF_6^- salt). Another heterocumulene, PhNCS, reacts in an analogous fashion to afford 282 (X = NPh; PF_6^- salt).[184] The reaction between 279 (PF_6^- salt) and benzonitrile also proceeds through Ru–H insertion to give the azavinylidene complex 283 (PF_6^- salt). Ethyne and phenylethyne (isoelectronic with PhCN) both react readily with 279 (PF_6^- salt) in acetone at RT to provide complexes with a bridging alkenyl group, 284 (R = H, Ph; PF_6^- salt). The ethenyl product was characterized crystallographically.[184] The pentacarbonyl hydride $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (285; PF_6^- salt) reacts in the same way as 279 with the majority of anionic nucleophiles; however, treatment of 285 (PF_6^- salt) with phenylacetylene does not yield 284, but instead provides the bridging acyl complex 286 (PF_6^- salt) through insertion into the Ru–H bond, followed by migratory insertion of a terminal carbonyl ligand.[184]



6.17.2.3.4 Complexes with other phosphorus and arsenic ligands

Complex **287** was obtained from the reaction of a phospholide with $[RuCp^*Cl]_4$ in an investigation of routes to phospharuthenocenes. The complex was characterized crystallographically and found to contain two phosphacycles bridging the diruthenium double bond.[191] A complex with a $Cp^*{}_2Ru_2$ unit bridged by 2,2′-biphosphinine ligands **288** is formed by the reduction of $RuCp^*Cl(tmbp)$ (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) with 1 equiv. of sodium naphthalenide.[192]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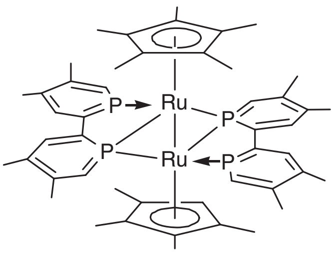
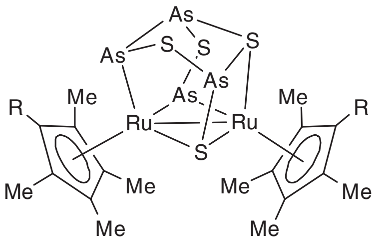

288

The reactions of $Cp'_2Ru_2(CO)_4$ ($Cp' = \eta^5\text{-}C_5Me_5$, $\eta^5\text{-}C_5Me_4Et$) with β-realgar in boiling *n*-decane provide **289** (R = Me, Et) in good yields along with some **290** (R = Me, Et). Structural determinations show that both complexes feature arsenic bridges between the ruthenium centers and, in the case of **290** (R = Me, Et), the diruthenium unit is spanned solely by arsenic bridges.[193]



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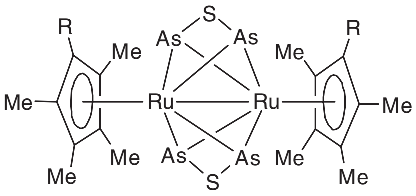

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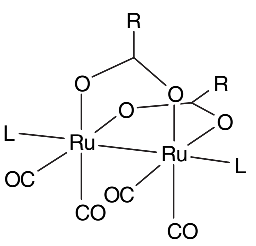
6.17.2.4 Complexes with Chalcogen Bridging Ligands

6.17.2.4.1 Complexes with oxygen bridging ligands

The most common oxygen donor ligand class is that of carboxylate compounds, and many examples were discussed in COMC (1995). Recent contributions to this field center on carboxylate species with nitrogen donors in the axial positions. Treatment of $Ru_3(CO)_{12}$ with benzoic acid in the presence of pyridine yields **291** (R = Me, L = py) via a polymeric dicarboxylate intermediate.[194] Pyrazole (**291**; R = Me, L = pyrazole, 3,5-dimethylpyrazole)[195] and acetonitrile (**291**; R = CF_3, L = NCMe)[196] analogs of this complex have also been prepared and characterized crystallographically. A convenient alternative synthetic route to such complexes is the generation of polymeric $[RuCl_2(CO)_2]_n$, which is then reduced by addition of carboxylate salts. Addition of monodentate ligands to these materials, such as pyridine or 3-methylpyridine, provides the complexes **291** (R = Me, Et, Bu^t, Ph, CF_3, L = py; R = Me, L = 3-methylpyridine) in satisfactory yield.[197,198] This route is based on $RuCl_3 \cdot xH_2O$ and avoids the use of expensive $Ru_3(CO)_{12}$. A structural study of the phosphine adducts, **291** (R = Me, CF_3, Ph; L = PPh_3), and similar literature compounds, revealed that the axial ligand is the most influential factor in determining the Ru–Ru bond length in such complexes.[199] With di(2-pyridyl)amine (dpa) this method produces **291** (R = Me, L = dpa), in which the dpa ligand is coordinated in an unusual monodentate fashion. Heating this compound in ethanol results in the closure of the nitrogen chelates, expulsion of acetate, and bridging of the diruthenium unit by two carbonyl ligands to give the acetate salt **292** (R = Me). The benzoate analog **292** (R = Ph; chloride salt) was also prepared.[200] A further example containing a monodentate nitrogen donor ligand, **291** (R = Me, L = 2-aminopyridine), was prepared by a different route based on $Ru_3(CO)_{12}$.[201] The coordination of a wide range of bidentate nitrogen donors to diruthenium acetate complexes was explored in the preparation of **293** (N–N = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline; BPh_4^- salts).[202]



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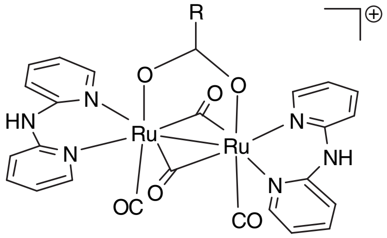

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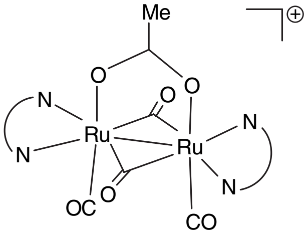
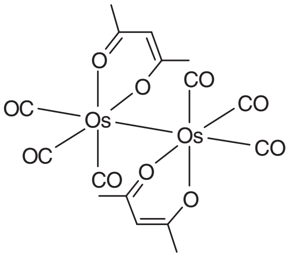


293

Reaction of $Os_3(CO)_{12}$ with a hexane solution of 2,2-dimethyl-3,5-heptanedionate (thdH) in a sealed autoclave at 190 °C leads to the tetraosmium chain complex $\{Os_2(CO)_5(thd)_2\}_2$ **294**. Treatment of this compound with carbon monoxide yields the diosmium complex **295**.[203] In an investigation of the catalytic activity of diruthenium carboxylate complexes in the water-gas shift[204] and Reppe olefin carbonylation rections,[205] the trifluoroacetate compounds **296**

($X = O_2CCF_3$, $Y = CO$; $X = CO$, $Y = O_2CCF_3$) were prepared from the reversible reaction of $Ru_2(O_2CCF_3)_2(CO)_6$ with carbon monoxide.[206]



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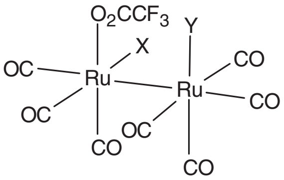
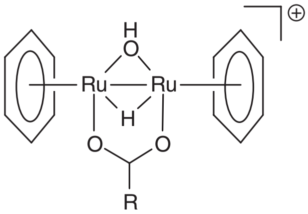


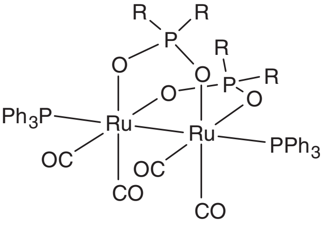
296

Treatment of an aqueous solution of $[Ru_2(\eta^6\text{-}C_6H_6)_2Cl_4]$ with silver carboxylates, followed by low-pressure hydrogenation, results in the formation of **297** ($R = Me$, $CH_2C_6H_4OH$, Ph, CH(OH)Me, CH(OH)Et), in which the metal centers are bridged by two different oxygen-containing ligands and a hydride.[207]



297

Although carboxylates dominate the chemistry of oxygen-containing ligands in dinuclear ruthenium and osmium chemistry, other ligand types are also known. Examples of phosphinate-bridged species are **298** ($R = Me$, Ph), formed from the reactions of $Ru_3(CO)_{12}$ with dimethyl- or diphenylphosphinic acid in tetrahydrofuran, to give a dimeric species, followed by addition of triphenylphosphine.[208] Polyoxoanion ligands have also been used to stabilize diruthenium compounds, such as in **299** ($NBu_4{}^{n+}$ quadruple salt), which is obtained from $[Ru_2(CO)_4(NCMe)_6](PF_6)_2$ **300** and $P_3O_9{}^{3-}$. Compound **300** is also a versatile precursor for a range of tetracarbonyl diruthenium adducts, $[Ru_2(CO)_4(py)_6]^{2+}$ **301**, $[Ru_2(CO)_4(NCMe)_4(PPh_3)_2]^{2+}$ **302**, and $[Ru_2(O_2CMe)_2(CO)_4(NCMe)_2]$ **303**.[209]



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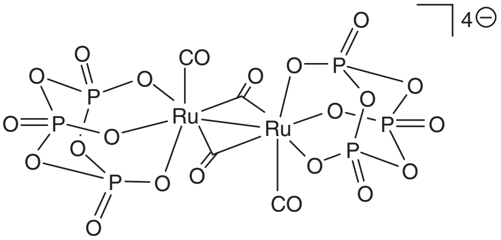
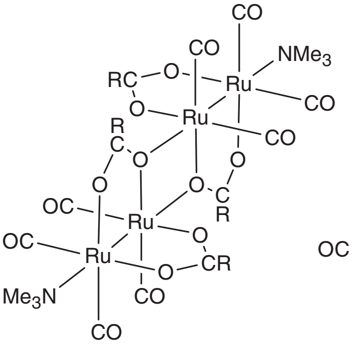


299

Compound **304** ($R = CH_2CH{=}CH_2$), formed from $Ru_3(CO)_{12}$ and 1-butenoic acid in the presence of trimethylamine N-oxide, displays bridging of two diruthenium units through the carboxylate ligand.[210] The linking of diruthenium units can also be achieved through the use of dicarboxylic acids. Reaction of $Ru_3(CO)_{12}$ with 1.5 equiv. of malonic acid and 3 equiv. of trimethylphosphine leads to complex **305** ($L = PMe_3$), in which the dicarboxylate ligand joins two diruthenium units in a "molecular loop". However, under the same conditions, oxalic acid reacts to form an unusual "molecular square", **306** ($L = PMe_3$), containing four diruthenium units. Thus, the flexibility and orientation of the methylene bridge in malonic acid causes entirely different structures to result from the same stoichiometry of reagents.[211]



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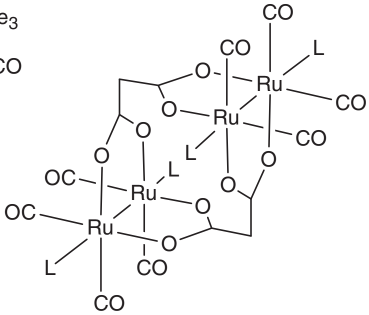

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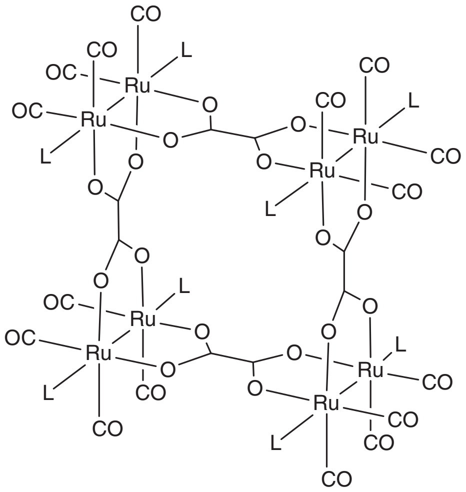


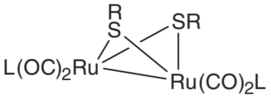
306

Diruthenium phosphine compounds with acetate ligands [$Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(PBu^n{}_3)_2$] **307**; [$Ru_2(CO)_4\text{-}(\mu\text{-}O_2CMe)_2(PR_3)_2$] (**308**; R = Pr^i, Bu^t),[212] and [$Ru_2(CO)_4(\mu\text{-}O_2CH)_2(PCy_2H)_2$] **309**[213] have also been reported.

6.17.2.4.2 Complexes with sulfur, selenium, and tellurium bridging ligands

Thiolate ligands have dominated the complexes of the heavier chalcogen donors and continue to be employed in stabilizing the diruthenium unit. Many of the catalytic applications found for diruthenium compounds over the last decade have involved thiolate-bridged species.

The carbonyl compounds **310** (R = Bu^t,[214,215] Pr^i,[214] Ph,[214,216] Bz,[215] Tol;[215] L = PPh$_3$), **310** (R = Ph; L = PMe$_3$),[214] and **310** (R = Et; L = CO)[217] are all bridged by two bidentate thiolate ligands. Dithiolate molecules have been used to prepare the corresponding μ-dithiolate species **311** (n = 2, 3; L^1 = L^2 = CO,[217,218] PPh$_3$;[215] L^1 = PPh$_3$, L^2 = CO[218]). Due to the different possible orientations of the thiolate substituents, isomers (*anti*, *syn–endo*, *syn–exo*) are often observed.[214,215] Protonation of **311** with HBF$_4$·OEt$_2$ yields the μ-hydrido complexes **312** (n = 2, 3; BF_4^- salt).[219] Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-(phenylthio)cyclobutene at RT in dichloromethane provides $Os_3(\mu\text{-}\eta^2\text{-}$cyclobutenyl)($\mu$-SPh)(CO)$_{10}$ in 34% yield and **313** in 44% yield.[220,221] Treatment of the same starting material with 1,4-dithiacyclohexane leads initially to coordination to the triosmium cluster through displacement of the acetonitrile ligands but on heating continues to give fragmentation into carbon- and sulfur-bridged Os$_3$ clusters. One of these, $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)_2$, yields a dinuclear product, **314** (R = H), on heating at 125 °C in n-octane.[222] A chiral version, **314** (R = Me), is obtained as a racemic mixture by heating $Os_3(CO)_{10}(NCMe)_2$ with the chiral cyclic trisulfide, S$_3$C(H)CH$_3$C(H)CH$_3$S.[223] Complex **315** was prepared by a similar method using 3,6-dihydro-1,2-dithiin.[224]



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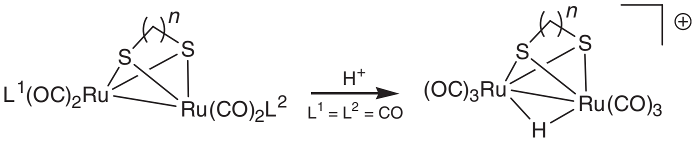
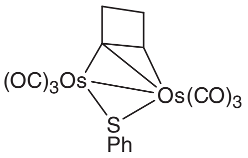


311 **312**



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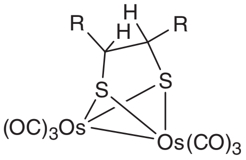

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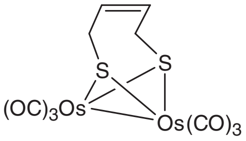
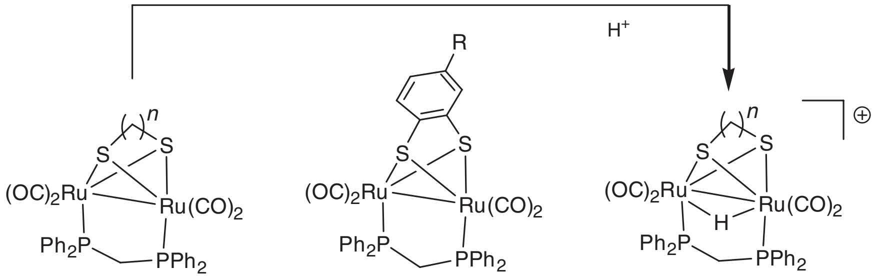
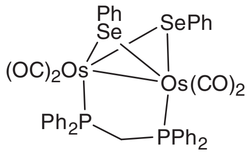


315

Heating $Ru_3(CO)_{10}(\mu\text{-dppm})$ with HS(CH$_2$)$_n$SH or 3,4-toluenedithiol in tetrahydrofuran results in the diruthenium complexes **316** (n = 2, 3) and **317** (R = H, Me), respectively. The hydride complexes **318** (n = 2, 3; BF_4^- salts) are prepared by protonation of **316**.[219] Treatment of $Os_3(CO)_{10}(\mu\text{-dppm})$ with $(PhSe)_2$ at 110 °C in toluene leads to the displacement of an $Os(CO)_4$ unit by two μ-SePh ligands in **319**,[225] while the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Ph_2PCH_2P(Se)Ph_2$ under very mild conditions (RT, CH_2Cl_2) results in complex **320**.[226] The ruthenium and osmium compounds **321** ($M = Ru$, Os; $L^1 = L^2 = CO$) bearing a bridging benzene-1,2-dithiolate ligand are obtained by heating the corresponding dithiol with $M_3(CO)_{12}$ in toluene at reflux. Protonation with HBF_4 introduces a hydride bridge between the metal centers to yield **322** ($M = Ru$, Os; $X = H$; $L^1 = L^2 = CO$; BF_4^- salts).[227] Treatment of **321** ($M = Ru$; $L^1 = L^2 = CO$) with phosphines leads to **321** ($M = Ru$; $L^1 = CO$, $L^2 = PPr^i_3$, PCy_3, PPh_3) and, on reaction with further phosphine, **321** ($M = Ru$; $L^1 = L^2 = PPr^i_3$, PCy_3, PPh_3). The compounds **321** ($M = Ru$; $L^1 = L^2 = CO$, PPr^i_3) can be protonated to give **322** ($M = Ru$; $X = H$; $L^1 = L^2 = CO$, PPr^i_3; BF_4^- salts) and also react with $[Au(PPh_3)]BF_4$ or $HgCl_2$ to yield **322** ($M = Ru$; $X = AuPPh_3$, $HgCl_2$; $L^1 = L^2 = CO$, PPr^i_3).[228]



316 **317** **318**



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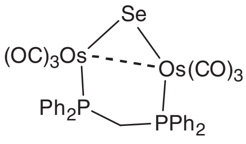

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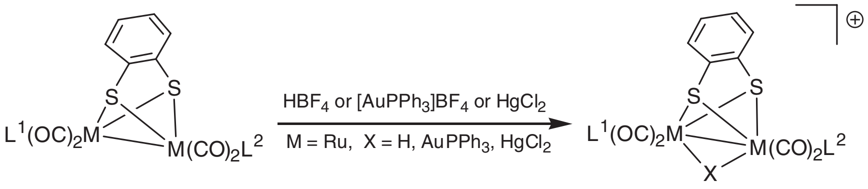
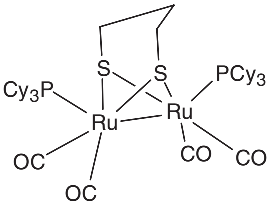


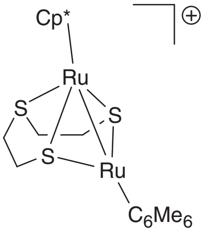
321 **322**

Recently, a thiolate-bridged diruthenium complex **323** was used as a model for the Fe-only hydrogenase site (see Chapter 6.02). The phosphine ligands were chosen to simulate the electronic role of the cyanide donor ligands found in the enzyme. The complex undergoes reaction with hydrogen under UV-photolytic conditions to yield $[Ru_2(S_2C_3H_6)(\mu\text{-H})(H)(CO)_3(PCy_3)_2]$ **324**.[229]



323

Thioether ligands have also been used to bridge diruthenium centers such as those in the hexafluorophosphate salts **325** and **326**, which are obtained from the reaction of ruthenium arene or Cp* chloro-bridged dimers and monomeric 3-thiapentane-1,5-dithiolate (tpdt) complexes. The hexamethylbenzene and pentamethylcyclopentadienyl ligands provide the additional support and protection for the ruthenium centers.[230] The acetonitrile compound **327** reacts with the mononuclear species [Ru(η^6-C_6Me_6)(tpdt)] and NH_4PF_6 to yield the trinuclear complex **328** (PF_6^- salt), which retains the diruthenium unit. The electrochemistry of selected complexes was also studied.[231] The 1,1′-ferrocenedithiolate complex **329** ($C_{10}H_{14}$ = *p*-cymene) is prepared by reaction of {(*p*-cymene)$RuCl_2$}$_2$ with the ferrocenedithiolate ligand followed by reduction with Na/Hg to form an Ru–Ru bond. This complex reacts with electrophiles such as H^+ (to give **330**; TfO^- salt) and Me^+ to yield **331** (TfO^- salt). However, the reactions occur at different sites, with protonation generating a bridging hydride and alkylation occurring at the sulfur donor.[232]



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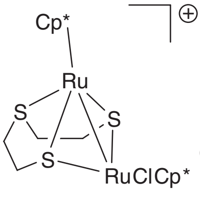

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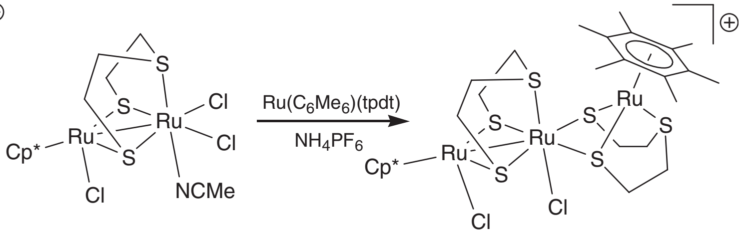
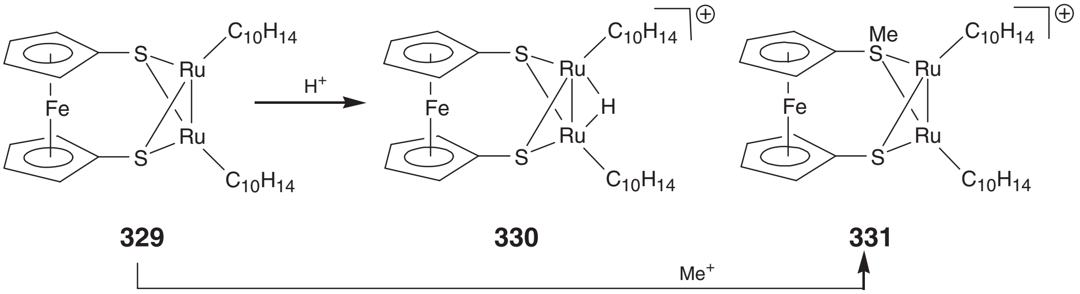
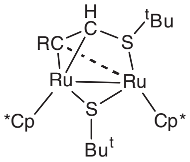


327 **328**



329 **330** **331**

The compounds {Cp*Ru(μ-SR)}$_2$ (R = Et, Pr^i, Bu^t, Bz)[233] are active catalysts for the formation of vinyl thioethers from thiols and alkynes.[234] Although these species do not contain an Ru–Ru bond, they are starting points for much diruthenium chemistry. Reactions of {Cp*Ru(SBu^t)}$_2$ with HC≡CR (R = Ph, CO_2Me) lead to insertion of the alkyne into one of the Ru–S bonds, leaving the other intact (**332**; R = Ph, CO_2Me). In the same reaction with 3 equiv. of HC≡CCO_2Me, the complex [RuCp$^*{}_2$(μ-SBu^t)$_2${=C=C(CO_2Me)CH=CHCO_2Me}{=C=C(H)CO_2Me}] is formed. This species contains a vinylidene ligand at one metal center and a vinylvinylidene (through coupling of two alkyne units) at the other, but has no Ru–Ru bond. However, elimination of 1 equiv. of HC≡CCO_2Me leads to a new product with a ruthenium–ruthenium bond (**333**; R = CO_2Me). In contrast, reaction of the μ-SC_6F_5 complex **334**[235] with HC≡CCO_2Me results in isolation of just the alkyne complex **335** (R = CO_2Me) as the only product.[234] The trimetallic compound [(Cp*Ru)$_3$(μ_3-S)(μ_3-Cl)] undergoes reaction with the same alkyne to give the sulfur-bridged allyl complex **336**.[236]



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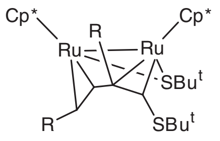

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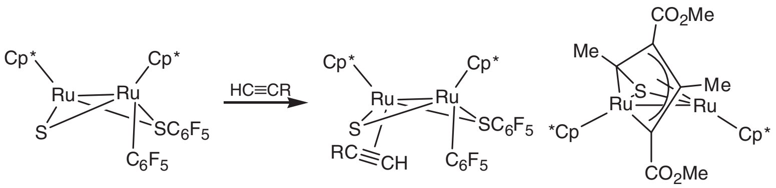
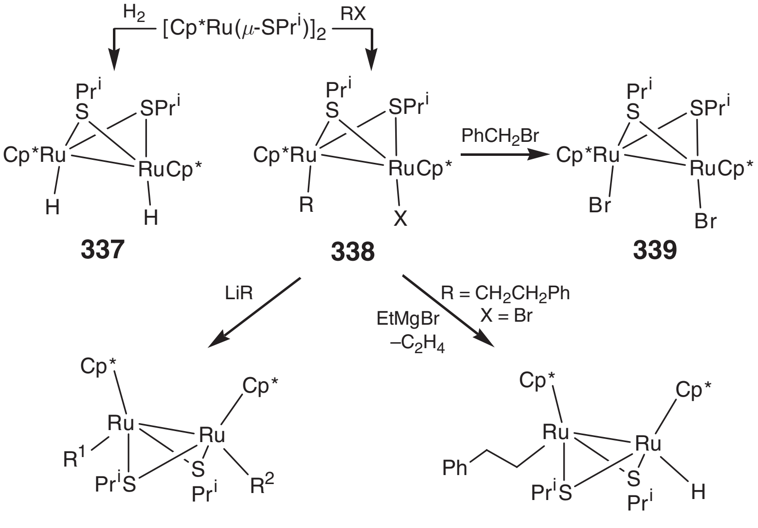


334 **335** **336**

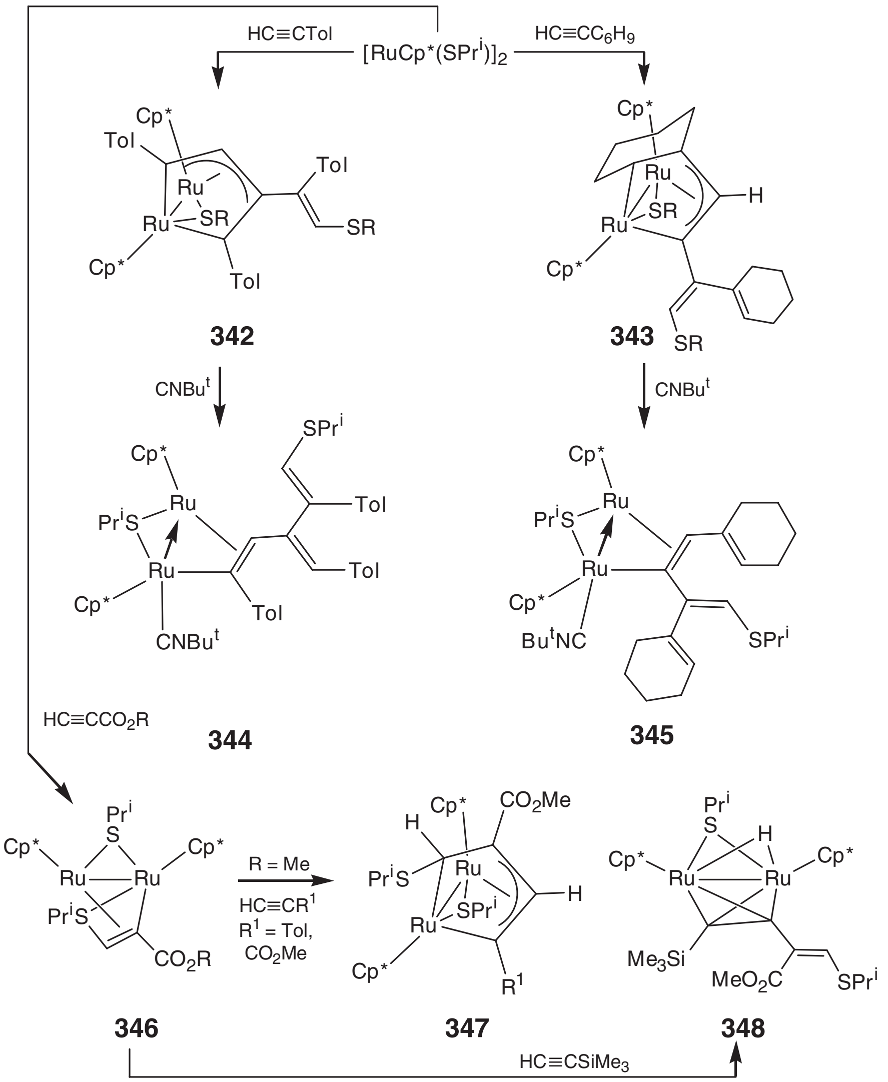
The compounds $\{Cp^*Ru(\mu\text{-}SR)\}_2$ ($R = Pr^i$, Bu^t)[233,237,238] can also be prepared from $\{Cp^*RuCl\}_4$ and NaSR.[239] Reaction of the dithiolate complex $\{Cp^*Ru(\mu\text{-}SPr^i)\}_2$ with hydrogen (1 atm) results in oxidative addition to yield **337**, while haloalkanes also add across the Ru–Ru bond to provide **338** ($R = CH_2CH_2Ph$, CH_2Ph, $X = Br$; $R = Me$, Et, $X = I$). With an excess of $PhCH_2Br$, **338** ($R = CH_2Ph$, $X = Br$) is converted into the dibromide **339** and $PhCH_2CH_2Ph$ is liberated.[239] Treatment of **338** ($R = CH_2CH_2Ph$, CH_2Ph, $X = Br$; $R = Me$, $X = I$) with Grignard or lithium reagents results in isolation of the dialkyl complexes **340** ($R^1 = R^2 = CH_2CH_2Ph$; $R^1 = R^2 = Me$; $R^1 = Me$; $R^2 = CH_2Ph$; $R^1 = CH_2CH_2Ph$, $R^2 = C{\equiv}CPh$).[238] Somewhat surprisingly, reaction of **338** ($R = CH_2CH_2Ph$, $X = Br$) with EtMgBr at −50 °C results in **341** by β-elimination from the ethyl intermediate. The organyl ligands can be cleaved with iodine, as shown by the elimination of $(C{\equiv}CPh)_2$ from **340** ($R^1 = R^2 = C{\equiv}CPh$).[238]



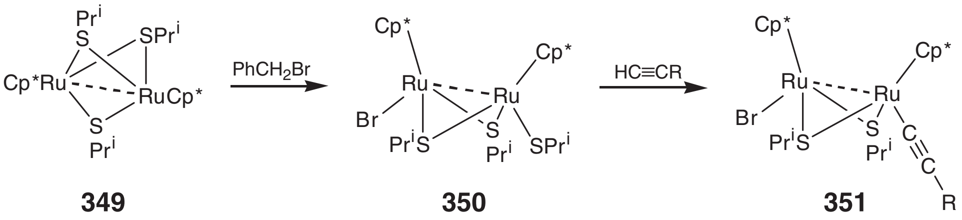
337 **338** **339**

340 **341**

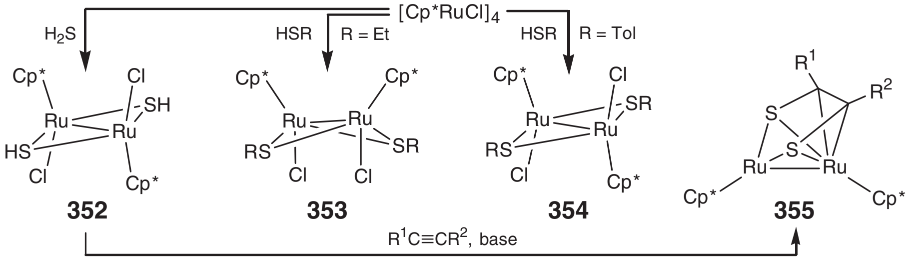
The thiolate-bridged diruthenium species $\{Cp^*Ru(\mu\text{-}SPr^i)\}_2$ reacts with ethynyltoluene at RT in tetrahydrofuran to yield **342** ($R = Pr^i$) in which oligomerization occurs to provide an η^3-bonded product. A similar reaction ensues with ethynylcyclohexene to provide **343** ($R = Pr^i$).[240] Initially, the products of the reactions of these compounds with $CNBu^t$ were formulated as simple isonitrile adducts formed by rupture of the thiolate bridge. However, the structures of the products formed from **342** ($R = Pr^i$) and **343** ($R = Pr^i$) with $CNBu^t$ were later revealed to be the bridging alkenyl species **344** and **345**, respectively.[241] With $HC{\equiv}CCO_2R$ ($R = Me$, Et, Bu^t), $\{Cp^*Ru(\mu\text{-}SPr^i)\}_2$ reacts to give the alkenyl complexes **346** ($R = Me$, Et, Bu^t), which contain a four-membered RuC_2S ring. This can be treated with $HC{\equiv}CCO_2Me$ or $HC{\equiv}CTol$ to provide the η^3-enyl complex **347** ($R^1 = CO_2Me$, Tol). However, reaction of $HC{\equiv}CSiMe_3$ with **346** yields the bridging alkyne species **348**. This reacts with iodine to liberate the free enyne.[237]



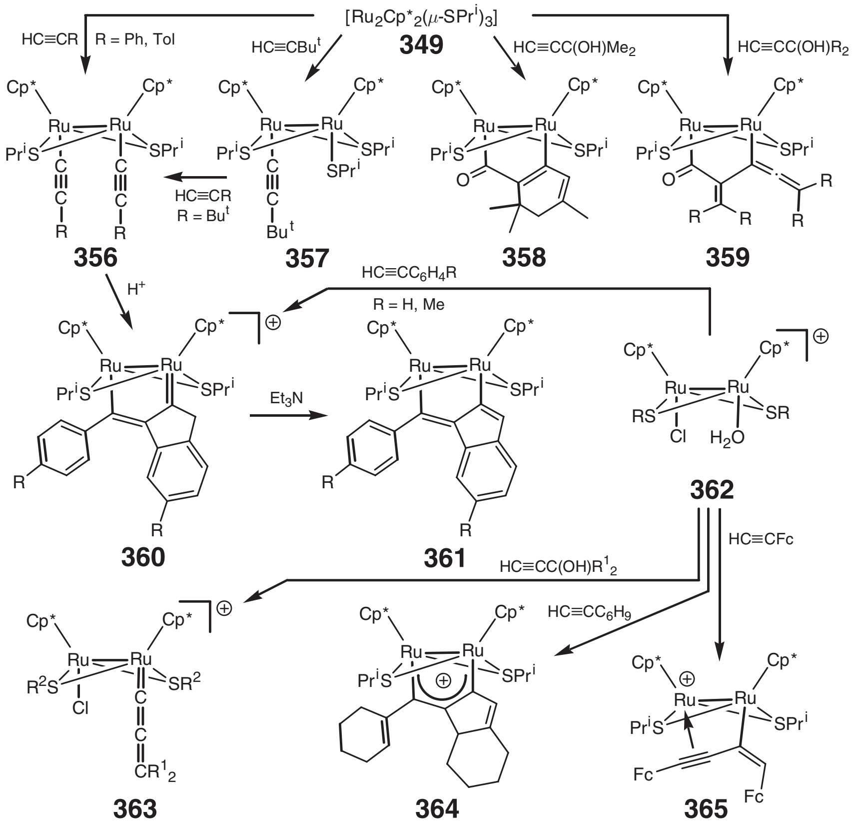
The Ru(II)/Ru(III) triple thiolate-bridged complex **349**[242,243] reacts with PhCH$_2$Br in hexane via rupture of one μ-SPr^i bridge and elimination of (PhCH$_2$)$_2$ to yield **350**. On heating with HC≡CR (R = Tol, Bu^t) in toluene, **350** loses the pendant thiolate ligand to provide the alkynyl species **351** (R = Tol, Bu^t).[244]



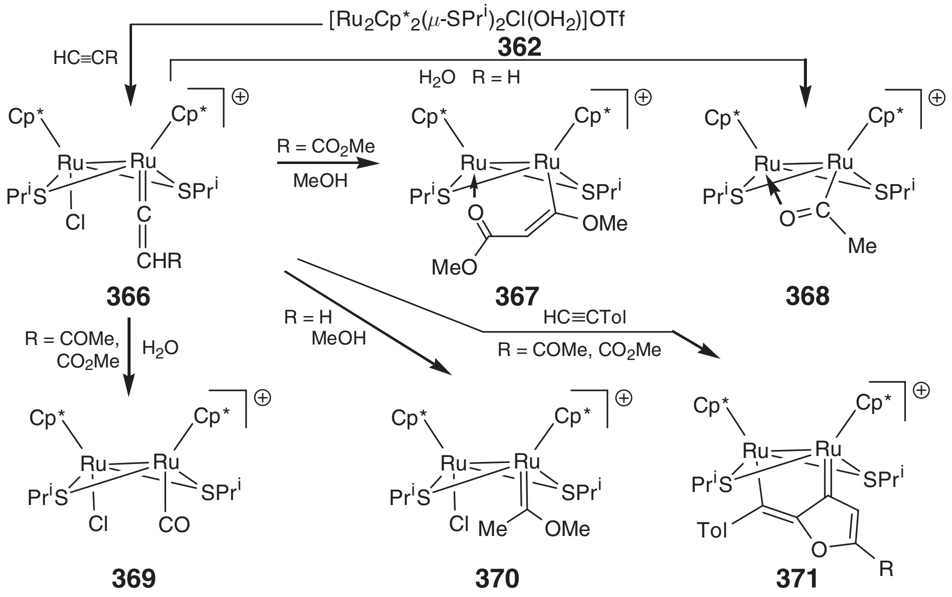
Tetrameric {Cp*RuCl}$_4$ reacts with an excess of H$_2$S in tetrahydrofuran at RT to yield the diruthenium hydrosulfido complex **352** and a sulfur-capped triruthenium species, (Cp*Ru)$_3$(μ_3-S)$_2$(μ-H). NMR data indicate that **352** undergoes *syn–anti* isomerization in solution, which is a common observation for compounds with bridging thiolates. The corresponding reactions with HSR (R = Et, Tol) result in formation of structural isomers **353** (R = Et) and **354** (R = Tol).[245] Complex **354** (R = Ph) has also been prepared in a study of the catalytic addition of organic disulfides to alkenes to give vicinal dithioethers.[246] Reactions of **352** with R^{1}C≡CR^2 in the presence of NEt$_3$ lead to the dithiolene-bridged compounds **355** (R^1 = H, R^2 = H, Bu^t, Tol; R^1 = R^2 = Ph, CO$_2$Me) through dehydrohalogenation.[247]



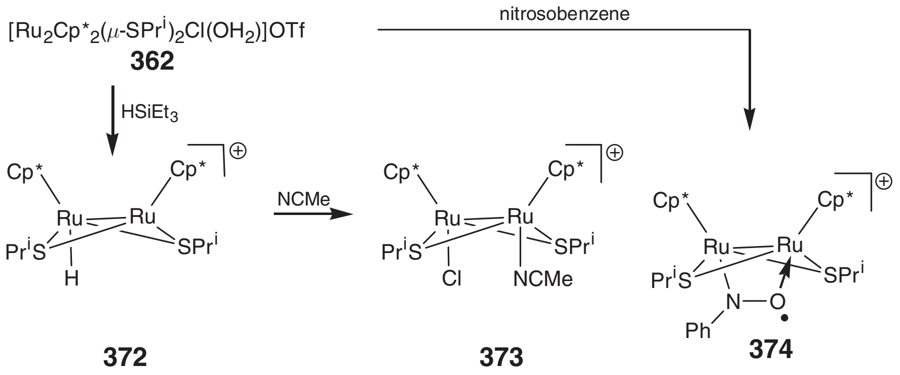
The reactivity of complex **349** has been explored widely. This species reacts with terminal alkynes (5–10 equiv.) to form the dialkynyl complexes **356** (R = Ph, Tol, cyclohexenyl, Bu^t). In the reaction with HC≡CBu^t, a trithiolate intermediate **357** can be isolated, which is converted into **356** (R = Bu^t) by heating with HC≡CBu^t in tetrahydrofuran.[242] The propargylic alcohols, HC≡CC(OH)Me_2 and HC≡CC(OH)R_2 (R = Ph, Tol), react with **349** to give unusual diruthenacyclopentenone **358** and diruthenacyclopentanone complexes (**359**; R = Ph, Tol), respectively.[243] The authors suggest that coupling of the organic ligands may proceed via a γ-hydroxyalkynyl ligand on one metal center and an allenylidene/vinylvinylidene on the other. Both complexes were structurally characterized. Protonation of **356** (R = Ph, Tol) with HBF_4 leads to aromatic C–H activation and coupling between the alkynyl ligands to give the diruthenacyclopentadienoindane complexes **360** (R = H, Me; BF_4^- salts) in excellent yield. These compounds can be deprotonated using triethylamine to give the corresponding indene **361** (R = H, Me).[242] A chloride can be abstracted from the dichloride complex **353** (R = Pr^i) using AgOTf in tetrahydrofuran to give the reactive species $[Ru_2(Cp^*)_2(\mu\text{-}SR)_2Cl(OH_2)]OTf$ (**362**; R = Pr^i).[248–251] The formulation was initially solvent free but was later revised to contain a molecule of water.[252] In contrast to **349**, compound **362** reacts with HC≡CC(OH)R^1_2 to give the allenylidene complexes **363** (R^1 = Ph, Tol, R^2 = Pr^i; TfO^- salts) in excellent yields. With HC≡CC_6H_4R, the compounds **360** (R = H, Me; BF_4^- salts) are obtained while treatment with ethynylcyclohexene leads to **364** (TfO^- salt) in 89% yield.[248] The reaction between **362** (TfO^- salt) and HC≡CFc yields the butenynyl complex **365** (TfO^- salt) formed by head-to-head coupling of the alkynes at the ruthenium centers. The complex was characterized structurally and was found to be an efficient catalyst for the di- and trimerization of ferrocenylethyne.[249]



With other alkynes, such as HC≡CR (R = H, COMe, CO_2Me), **362** (TfO^- salt) reacts to yield the vinylidene complexes **366** (R = H, COMe, CO_2Me; TfO^- salts).[252] On exposure to methanol, **366** (R = CO_2Me; TfO^- salt) forms the alkenyl complex **367** (TfO^- salt), in which the ester group donates to the adjacent ruthenium site. With water **366** (R = H; TfO^- salt) undergoes attack at the α-carbon of the vinylidene and subsequent loss of chloride to give the acyl complex **368** (TfO^- salt). However, reaction of **366** (R = COMe, CO_2Me; TfO^- salts) under the same conditions ultimately yields the carbonyl-containing species **369**. A postulated mechanism for this transformation involves initial formation of an acyl complex (as for R = H), followed by interaction with the neighboring metal center, rearrangement and then acidolysis to expel a molecule of acetone (if R = COMe) or methyl acetate (if R = CO_2Me).[252] Complex **366** (R = H; TfO^- salt) reacts with methanol through attack at the vinylidene C_α to give the methoxycarbene **370** (TfO^- salt). Reactions of **366** (R = COMe, CO_2Me; TfO^- salts) with ethynyltoluene proceed via formation of an alkynyl ligand at the metal site adjacent to the vinylidene, followed by coupling to provide **371** (R = Me, OMe; TfO^- salts).[252]

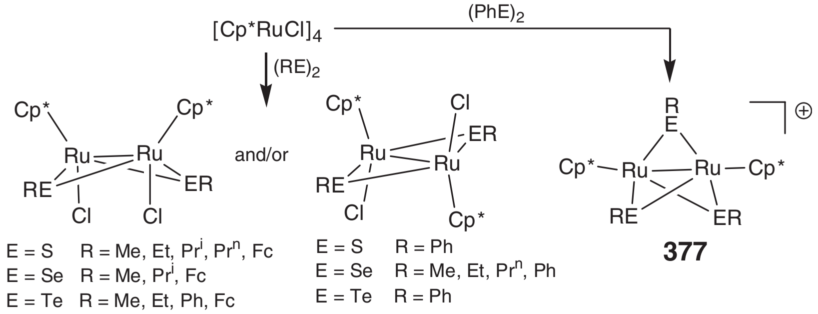


Conversion of **362** (TfO^- salt) to the coordinatively unsaturated hydride complex **372** (TfO^- salt) is achieved by treatment with $HSiEt_3$ at RT.[253] This product forms an adduct with acetonitrile at its vacant site (**373**; TfO^- salt) while the hydride remains intact. Complex **362** (TfO^- salt) also reacts with nitrosobenzene to give **374** (TfO^- salt), which was investigated crystallographically and by electron spin resonance (ESR) techniques.[253]

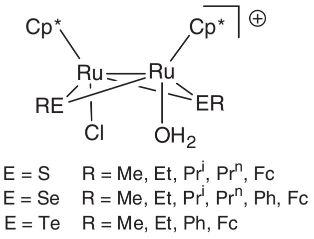


A number of processes catalyzed by the dithiolate-bridged species have been mentioned already; however, the extensive reactivity of alkynes within these systems has led to a number of more recent reports on their use in catalysis. The allenylidene complex **363** (R^1 = Tol, R^2 = Me; BF_4^- salt) has been identified as an intermediate in the catalysis of propargylic alcohol substitution reactions with alcohols in high yields and with complete regioselectivities by 353 (R = Me).[254] The catalytic nature of this system is a clear improvement on earlier stoichiometric processes for this transformation (e.g., Nicholas reaction). This was extended to the development of a general route to propargylic sulfides from propargylic alcohols and thiols using 362 (R = Me; TfO$^-$ salt).[255] Recently, chiral versions of 353 and 362 have been prepared with substituents such as R = CH(Ph)Me for enantioselective propargylic alkylation of propargylic alcohols with acetone.[256] Other processes catalyzed by 353 and 362 include silylative dimerization of aromatic aldehydes,[250] allylation of arenes,[251] cyclization[257] and *Z*-dimerization[258] of terminal alkynes, synthesis of γ-keto acetylenes,[259] cycloaddition of propargylic alcohols with phenol derivatives,[260] propargylation of aromatic compounds with propargylic alcohols,[261] C–C bond formation between propargylic alcohols and alkenes,[262] allylation of aromatic compounds,[263] cycloaddition between propargylic alcohols and 1,3-dicarbonyl compounds,[264] and double phosphinylation of propargylic alcohols.[265] Catalytic processes have also been reported using these compounds in conjunction with co-catalysts ($PtCl_2$, $PdCl_2$, $AuCl_3$), such as in the synthesis of tri- and tetrasubstituted furans and pyrroles[266] and the selective synthesis of fused polycyclic compounds.[267] The early developments in the use of dinuclear ruthenium thiolate compounds in organic synthesis have been covered in a review.[268]

The synthesis of complexes with bridging ligands containing the heavier chalcogens has also been achieved. Reactions of $\{Cp^*RuCl\}_4$ with $(RE)_2$ (R = alkyl, aryl, E = S, Se, Te) results in the formation of complexes 375 (*syn*-form) or 376 (*anti*-form) or, in the case of the selenium compounds, a mixture of both.[269,270] *Ab initio* molecular orbital calculations have also been performed to investigate the formation of these isomers.[270] When R = Ph, in addition to the *anti*-complexes 376 (E = S, Se, Te), compound 377 (ER = TePh; chloride salt) is also formed in 24% yield.[270] Treatment of 375 (ER = SR, SeR,[271] TeR) with AgOTf in tetrahydrofuran gives the aqua species 378 (TfO$^-$ salts) in the same way as for 362 (TfO$^-$ salt).[270] The use of these chalcogenate-bridged species in the catalysis of propargylic substitution reactions was also explored, and the allenylidene species 379 (E = S, Se, Te; TfO$^-$ salts) were identified as key intermediates.[272]



375 **376** **377**



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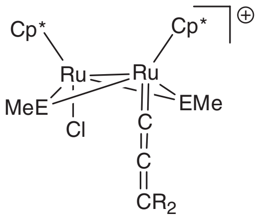
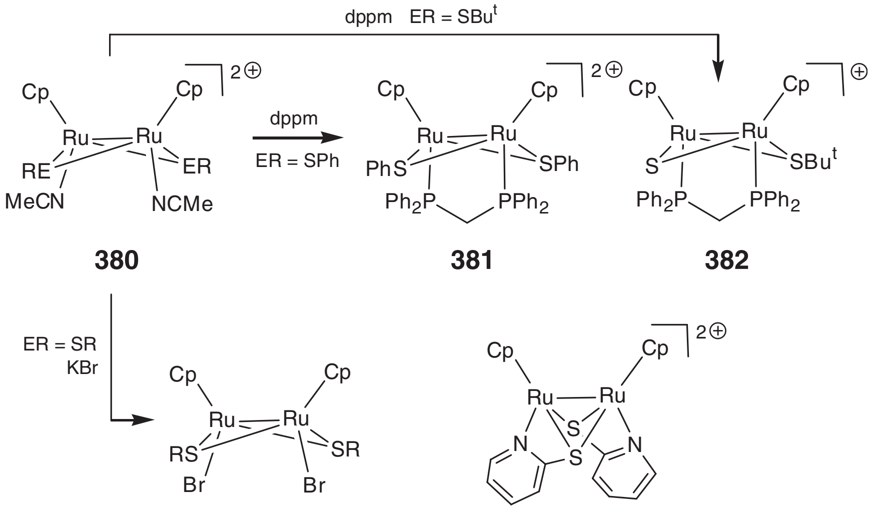


379

Although Cp* is usually favored as a capping ligand, the less bulky Cp ligand has also been used in dithiolate-bridged complexes. The highly reactive mononuclear complex $[RuCp(NCMe)_3]PF_6$ reacts with alkyl and aryl disulfides (and aryl diselenides) to provide the dicationic diruthenium complexes 380 (ER = SBu^t, SPh, STol, SePh; PF_6^- double salts) in essentially quantitative yield.[273] The acetonitrile ligands can be displaced by diphosphine donors, as shown by reaction of 380 (ER = SPh, PF_6^- double salt) with dppm to yield 381 (PF_6^- double salt) However, treatment of 380 (ER = SBu^t, PF_6^- double salt) with dppm leads to loss of a Bu^t substituent and generation of a sulfido ligand (382, PF_6^- salt). The neutral species 383 (ER = SBu^t, SPh) are obtained on reaction of 380 (ER = SBu^t, SPh; PF_6^- double salts) with KBr. Functionalized substituents can also be introduced as demonstrated by the reaction (under argon) of $[RuCp(NCMe)_3](PF_6)_2$ with 0.5 equiv. of bis(2-pyridyl) disulfide to provide 384

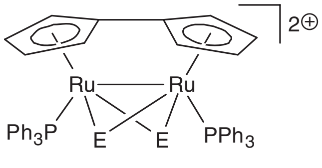
(PF_6^- double salt). If this process is carried out in air with 1 equiv. of bis(2-pyridyl) disulfide, the mononuclear complex [RuCp(*N*,*S*-pyS)$_2$]PF_6 results.[273]



380 **381** **382**

383 **384**

The thiolate-bridged diruthenafulvalene compounds **385** (E = SPh, STol, SC_6H_4Cl-4) and **385** (E–E = 1,2-benzenedithiolate, 3,4-toluenedithiolate) are obtained from the reactions of [$(MeCN)_2(PPh_3)Ru(\mu^2$-η^5:η^5-$C_{10}H_8)Ru(PPh_3)(NCMe)_2](BF_4)_2$ with the thiols EH and NaE–ENa, respectively. In contrast, treatment of the same starting material with the thiolates NaSR (R = Ph, Tol, C_6H_4Cl-4) leads to formation of the neutral tetrathiolate complexes **386**. With NaSBu^t, a complex with a coordinatively unsaturated Ru atom **387** (BF_4^- or PF_6^- salts) is obtained due to the steric bulk of the thiolate substituents.[274] The mononuclear thiolate complexes RuCp(SR)$(PPh_3)_2$ (R = Bu^t, $CHMe_2$, Tol) react with the electrophile methylthiophthalimide (MeSphth) to give **388** (X = phth, R = Bu^t, $CHMe_2$; X = STol, R = Tol) as well as mononuclear phthalimide complexes.[275] The 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligands, $(B_{10}H_{10})C_2(ELi)_2$ (E = S, Se), were found to react with mononuclear ruthenium precursors to give chalcogenide-bridged species. CpRuCl$(PPh_3)_2$ and $(B_{10}H_{10})C_2(SLi)_2$ react to yield **389**, while $(B_{10}H_{10})C_2(SeLi)_2$ provides **390** with {Cp*RuCl(μ-Cl)}$_2$.[276]



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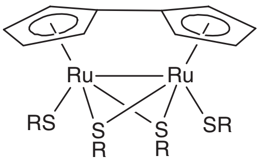

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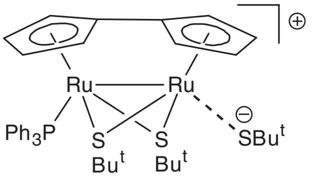

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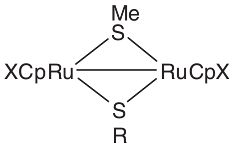

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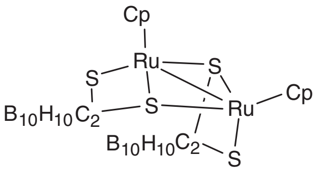

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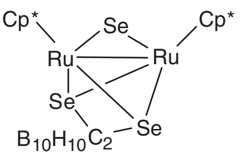
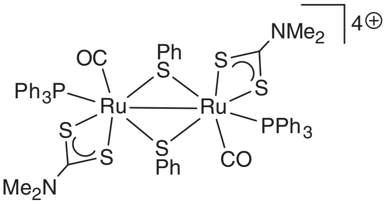


390

The oxidation of {Ru(μ-SPh)$(S_2CNMe_2)(CO)(PPh_3)$}$_2$ to **391** (nitrate quadruple salt) leads to formation of an Ru–Ru bond in the cationic product, illustrating the unusual four-electron redox behavior of this pair of complexes.[277] A new pathway to the ring-opening of coordinated thiophene is demonstrated by the reaction of the complex Cp*Ru(η^4-$C_4MeR^2R^2R^1S$) with [Ru(η^5-$C_5R^3_5$)$(NCMe)_3$]PF_6 to yield **392** ($R^1 = R^2 = Me$, $R^3 = H$; $R^1 = Me$, $R^2 = R^3 = H$; $R^1 = R^3 = H$, $R^2 = Me$; $R^1 = R^2 = R^3 = Me$; PF_6^- salts).[278] The triosmium cluster, $Os_3(CO)_{10}${μ-$(SCH_2CMe_2CH_2)_3$}, forms **393** on partial oxidation with [Cp_2Fe]PF_6 and subsequent treatment with carbon monoxide. The diosmium unit in the product is bridged by both acyl and thiolate ligands.[279] Another example of a complex containing both oxygen and sulfur bridging donors is the unusual compound **394**, prepared in a study of the ring-opening of 1,3-dithietane-1,1-dioxide by $Os_3(CO)_{10}(NCMe)_2$.[280] Relatively few examples of bridging tellurium ligands in dinuclear ruthenium (and particularly) osmium complexes are known. Benzo[*b*]tellurophene undergoes reaction with $Os_3(CO)_{10}(NCMe)_2$ to give $Os_3(\mu\text{-}C_8H_6Te)(CO)_{10}$ through opening of the tellurocycle. Loss of $Os(CO)_4$ from this species results in **395** (M = Os), which, on heating, loses elemental tellurium to yield an osmametallaindene, **396**. The ruthenium analogs, **395** (M = Ru) and **396** (M = Ru), were also prepared and the former characterized crystallographically.[281] 2-Vinyltetrahydrothiophene ring-opens at the alkenyl-substituted carbon on reaction with $Os_3(CO)_{10}(NCMe)_2$ at RT to yield $Os_3(CO)_{10}\{\mu\text{-}SCH_2CH_2C(H){=}C(H)C(H){=}CH_2\}(\mu\text{-}H)$ and a diosmium complex **397** in 27% yield.[282]



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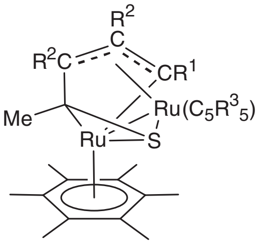

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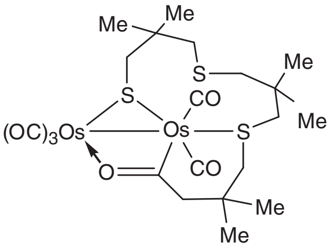

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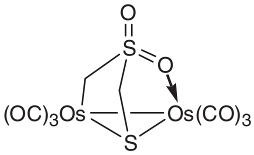

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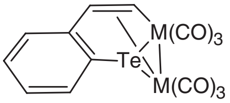

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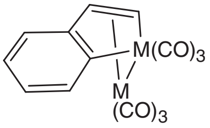

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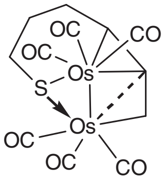

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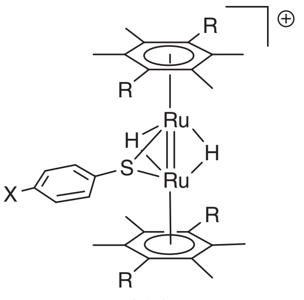
An alternative entry point into μ-SR complex chemistry is provided by the arene compounds $[Ru_2L_2(\mu\text{-}H)_3]BF_4$ ($L = \eta^6\text{-}C_6Me_6$, $\eta^6\text{-}C_6H_2Me_4$-1,2,4,5). They react with 1 equiv. of HSC_6H_4X-4 (X = Me, Br) to yield mixtures of the dihydride **398** (R = H, Me; X = Me, Br; BF_4^- salts) and the monohydride **399** (R = H, Me; X = Me, Br; BF_4^- salts). Treatment with 2 equiv. of HSC_6H_4X-4 (X = Me, Br) provides the monohydride complexes exclusively. Complex **399** (R = Me; X = Br; BF_4^- salt) is sufficiently robust that Suzuki cross-coupling with 3-thiopheneboronic acid could be performed using $Pd(PPh_3)_4$ as catalyst to yield **400** (BF_4^- salt).[283] Reactions of $\{Cp^*Ru(\mu\text{-}OMe)\}_2$ with thiols have been shown to yield the corresponding bridging thiolate complexes $\{Cp^*Ru(\mu\text{-}SR)\}_2$.[233] The corresponding reaction occurs with dithiocatechol, $C_6H_4(SH)_2$-1,2, to yield $[Cp^*Ru(\mu_2\text{-}\eta^4\text{-}o\text{-}C_6H_4S_2)RuCp^*]$, with no Ru–Ru bond, but containing an interaction between the arene ring and a ruthenium center. The reaction with $[Cp^*RuCl(\mu\text{-}Cl)]_2$ and two equivalents of the same ligand results in **401**, in which one sulfur donor bridges the diruthenium unit while the other donates to one metal center only.[284] This is similar to the situation found in **384**, the charged nature of this complex apart. An unusual example of C–S and C–P bond cleavage followed by C–C bond formation has been reported in the synthetic route to the phosphido complex **402**. This compound is prepared from reaction of $RuH_2(CO)(PPh_3)_3$ and thiophene in the presence of styrene (as a hydrogen acceptor). The authors propose that the thiolate ligand derives from the coupling of a ruthenacyclohexadiene intermediate with a metal-bonded phenyl group cleaved from PPh_3 during phosphido formation.[285]

Some of the work based on $\{Cp^*Ru(\mu\text{-}OMe)\}_2$ as a precursor for diruthenium complexes bridged by nitrogen and sulfur donors has been reviewed.[286]

6.17.2.5 Complexes with Bridging Metal Fragments

Metal fragments have also been employed as bridging ligands for diruthenium species. Treatment of the mixed Ru–Ti complex $[Cp_2Ti(\mu\text{-}SH)_2RuClCp^*]$ with an excess of triethylamine leads to the formation of the cubane-type sulfido cluster $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$. Formation of an Ru–Ru bond occurs on double oxidation of this species with $[Cp_2Fe]PF_6$ to yield **403** (PF_6^- double salt), which also has long Ti–Ru interactions. A two-electron oxidation of $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ also takes place with HCl gas to give the neutral cluster **404** with a different structure. The two products are interconvertible by reaction with Et_4NCl (to give **404**) or NH_4PF_6 (to yield **403**).[287] The hydrosulfido-bridged compound **352** reacts with $SbCl_3$ and $BiCl_3$ to provide clusters **405** (M = Sb, Bi), although no direct M–Ru contacts are observed in the crystal structure.[288] Reactions of $[Cp^*M(NCMe)_3](PF_6)_2$ (M = Rh, Ir) and $Cp^*_2Ru_2S_4$ yield the persulfide-bridged clusters **406** (M = Rh, Ir). These complexes are stereochemically non-rigid as indicated by coalescence of the Cp^* methyl resonances at higher temperatures. The intermediate, **407**, was proposed to explain these dynamics and the reaction of **406** (M = Rh) with acetone to form the *S*-acetonyl complex **408**.[289]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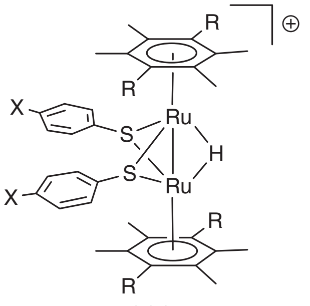
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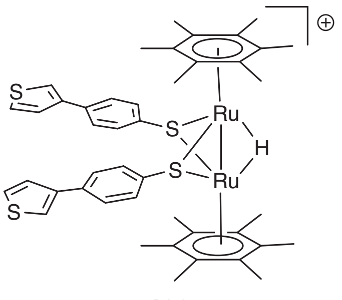
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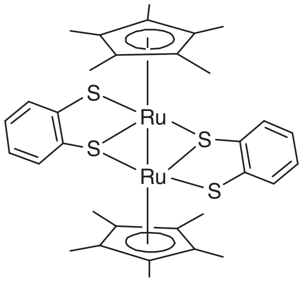
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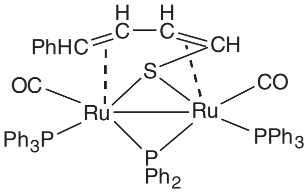
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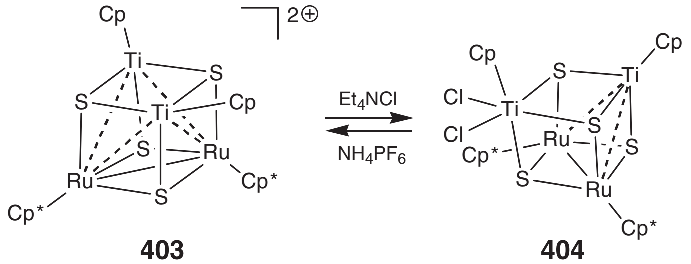
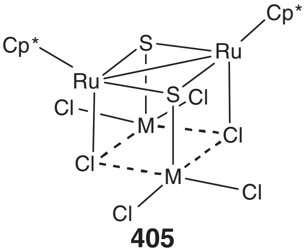


403 **404**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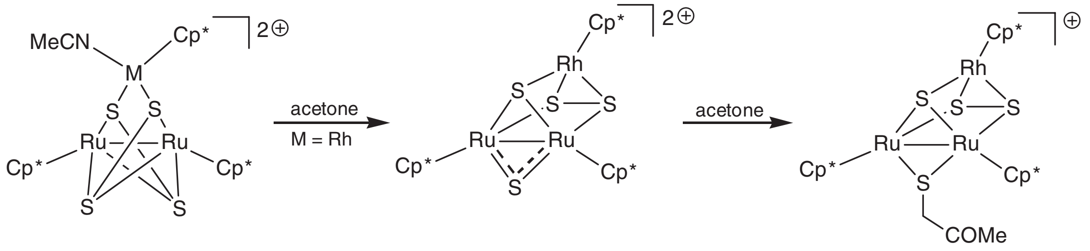
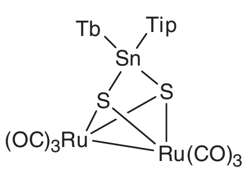


406 **407** **408**

The use of hydrosulfide metal fragments for bridging diruthenium species has also been explored. The dimercaptostannane complex $Tb(Tip)Sn(SH)_2$, with bulky groups 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl (Tb) and 2,4,6-triisopropylphenyl (Tip) reacts with $Ru_3(CO)_{12}$ in toluene at 70 °C to give **409** in 67% yield.[290] Two cobalt-bridged diruthenium species, **410 and 411**, have been isolated from the reactions of $[Cp^*Co(CO)_2]$ with $[Ru_3(\mu\text{-}H)_2(CO)_9\text{-}(\mu_3\text{-}NOMe)]$ and $[Ru_3Co(CO)_{12}(\mu_4\text{-}N)]$, respectively. The products were structurally characterized and found to contain nitrene **410** and nitrido **411** capping units.[291]



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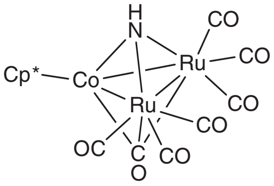

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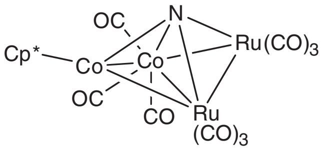
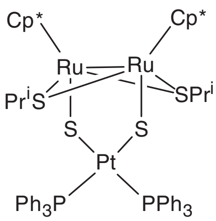


411

Platinum fragments are also found to bridge diosmium units, as occurs in the complex $[Os_2Pt(CO)_8(PPh_3)_2]$ **412**, isolated from the reaction of $[Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)]$ with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$. Due to redistribution of the phosphine ligands, the product exists in three isomeric forms, one of which was the subject of a structural study.[292] The compounds $[M(PPh_3)_4]$ (M = Pt, Pd) react with the disulfide complex $[Ru_2Cp^*_2(\mu\text{-}S_2)(\mu\text{-}SPr^i)_2]$ to give **413** and **414**, respectively. A dramatic difference in structure is observed with the $(Ph_3P)_2PtS_2$ moiety forming a five-membered metallacycle with the diruthenium unit in **413**, while two palladium units are built into the cluster in **414**.[293] Treatment of **414** with 1 equiv. of $PhCH_2Br$ leads to **415** (X = SPr^i), while an excess results in **415** (X = Br). Compound **352** undergoes reaction with $Pd(PPh_3)_4$ to yield the structurally similar product **416** (chloride salt).[294] Compound **417** is derived from the reaction between the cluster $Pt_2Ru_4(CO)_{18}$, diphenylacetylene and dppe.[295] A more straightforward route involving reaction of $Ru(CO)_5$ with $Pd(PBu^t_3)_2$ yields **418** (L = PBu^t_3), in which one ruthenium center bears four terminal carbonyl groups and the other four bridging CO ligands. With $Pt(PBu^t_3)_2$, $Ru(CO)_5$ reacts initially to give $PtRu_2(CO)_9(PBu^t_3)$, but reacts further with $Pt(PBu^t_3)_2$ to yield **419** (L = PBu^t_3). This product undergoes reaction with H_2 at 1 atm in hexane at 68 °C to provide **420** (L = PBu^t_3), in which two of the bridging carbonyls are substituted by bridging hydrides.[296]



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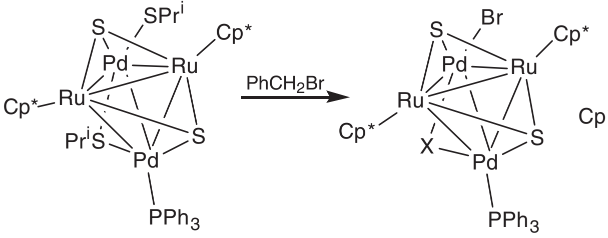
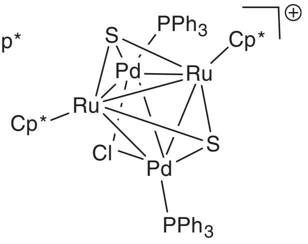


414 **415**



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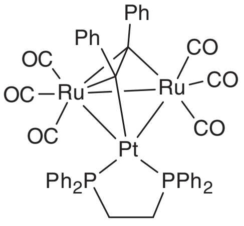

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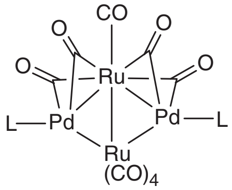

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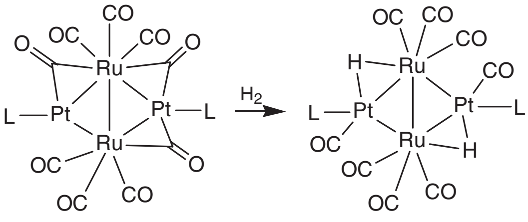


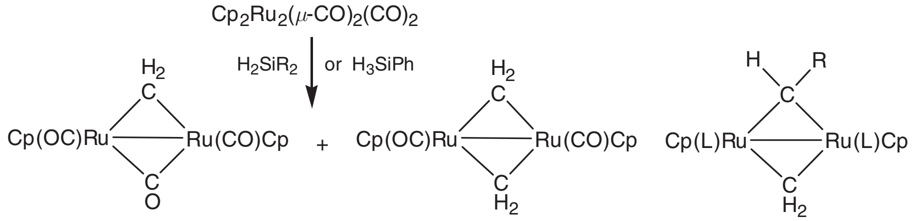
419 **420**

Heterometallic clusters are treated in greater depth in Chapter 6.10.

6.17.3 Complexes with Hydrocarbon Bridging Ligands

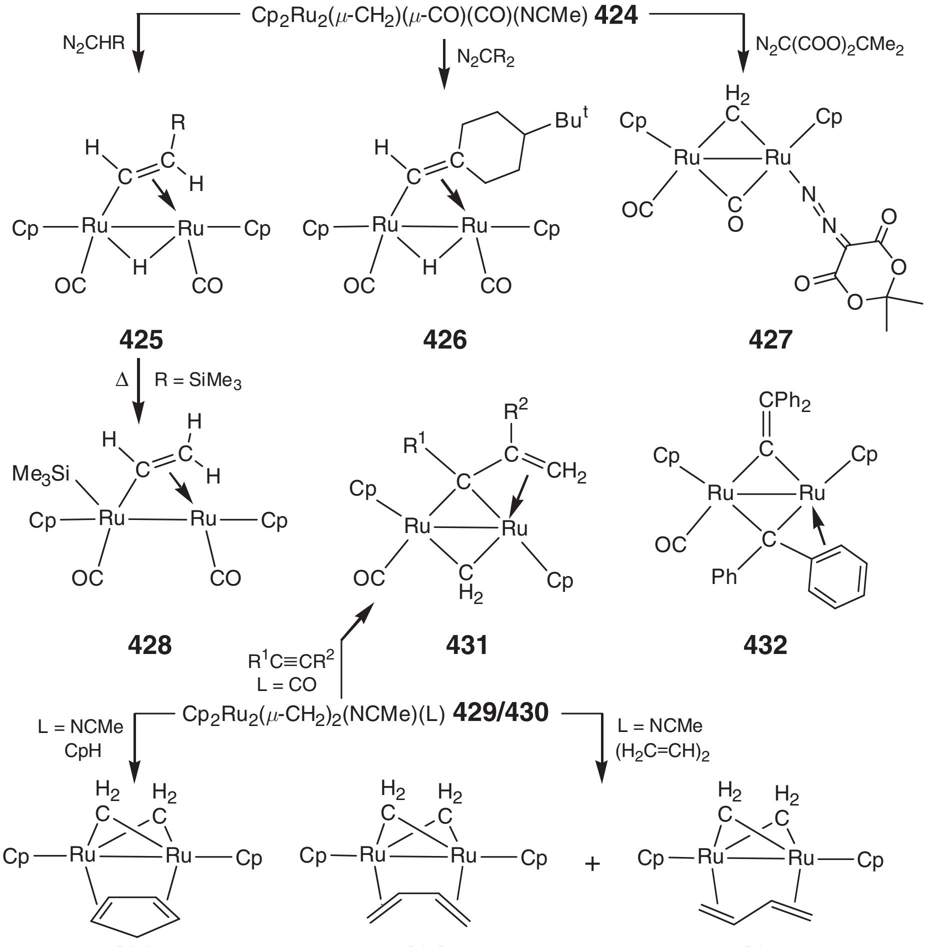
6.17.3.1 Complexes with σ-bonded Ligands

Bridging methylene complexes can be generated from $[Cp_2Ru_2(\mu\text{-}CO)_2(CO)_2]$ with H_2SiR_2 (R = Et, Ph) or H_3SiPh. A mixture of products containing one **421** or two **422** methylene bridges is formed. Complete conversion to **422** can be achieved by treatment of **421** in isolation with H_2SiR_2 (R = Et, Ph) or H_3SiPh. The μ-ethylidene compound $[Cp_2Ru_2(\mu\text{-}CHMe)(\mu\text{-}CO)(CO)_2]$ also undergoes reaction with H_2SiEt_2 to yield **423** (R = Me, L = CO).[297]



421 **422** **423**

The complex $[Ru_2Cp_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)]$ 424[298] couples with monosubstituted diazoalkanes to yield products with both bridging alkenyl and hydride ligands (425; $R = H$, Me, Ph, $SiMe_3$, CO_2Et).[299] Under the same conditions, most disubstituted diazoalkanes lead to alkenes and a complicated mixture of organometallic products. Exceptions to this are revealed when diazo-4-*t*-butylcyclohexylidene is used, providing 426, and the reaction with $N_2C(COO)_2CMe_2$ which gives the adduct 427.[300] Thermolysis of 425 ($R = SiMe_3$) at 100 °C affords 428.[299,300] Irradiation of 422 in the presence of acetonitrile yields the adduct $[Ru_2Cp_2(\mu\text{-}CH_2)_2(CO)(NCMe)]$ 429 and, over longer periods, $[Ru_2Cp_2(\mu\text{-}CH_2)_2(NCMe)_2]$ **430** as well.[27] With alkynes, $R^1C{\equiv}CR^2$ ($R^1 = Ph$, $R^2 = H$, Ph; $R^1 = SiMe_3$, $R^2 = H$), 429 reacts to give 431, in which the vinylalkylidene ligand coordinates in an η^3-fashion to one of the metal centers.[27] Treatment of 429 with diphenyldiazomethane in benzene gives 432, in which the diruthenium unit is bridged by both diphenylvinylidene and diphenylmethylene ligands. The bis(acetonitrile) adduct **430** reacts with cyclopentadiene to yield 433 and with butadiene to give both the *cis*- and *trans*-isomers 434 and 435.[27]

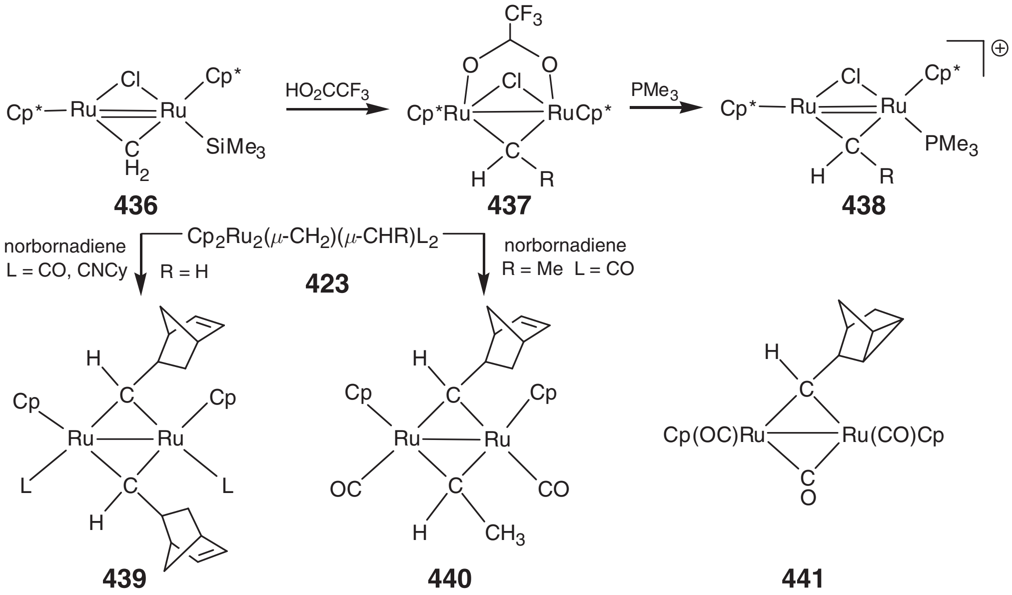


425 **426** **427**

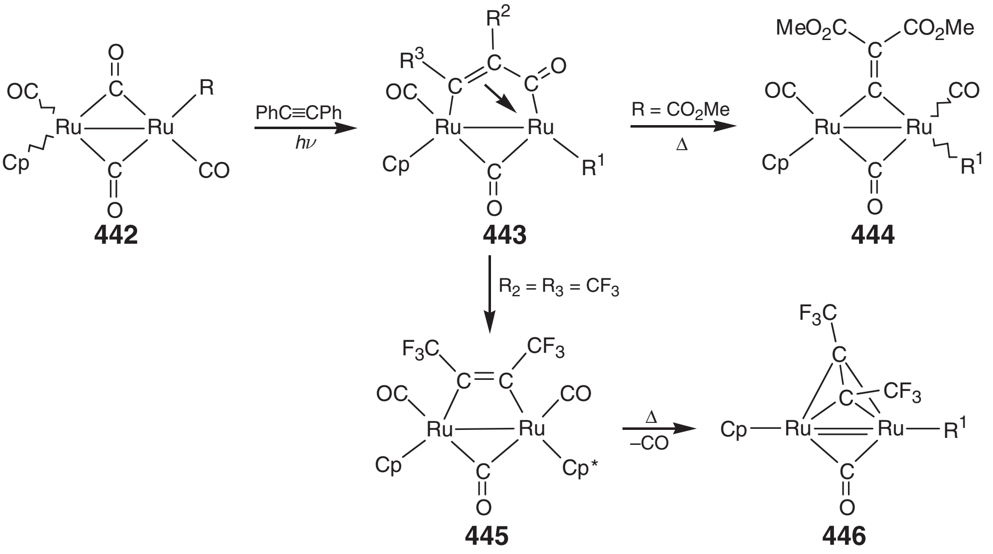
428 **431** **432**

433 **434** **435**

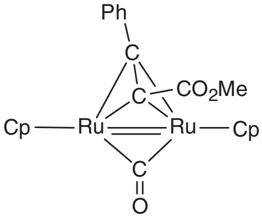
Treatment of $\{Cp^*RuCl\}_4$ with $Mg(CH_2SiMe_3)_2$ leads to the formation of 436, which contains a μ-CH_2 group originating from the scission of the α-C–Si bond of a CH_2SiMe_3 ligand. An X-ray structure established that the Ru–Ru distance of 2.527(1) Å is double in nature.[301,302] Protonation of 436 with HO_2CCF_3 at −78 °C results in elimination of $HSiMe_3$ and formation of 437 (R = H); however, if the reaction is carried out at RT, elimination of hydrogen also occurs to yield a second product, 437 ($R = SiMe_3$). Treatment of 437 (R = H) and 437 ($R = SiMe_3$) with PMe_3 leads to displacement of the trifluoroacetate ligand and formation of the complexes 438 ($R = H, SiMe_3$; $F_3CCO_2^-$ salts).[302] On irradiation, insertion of a C=C bond of norbornadiene into the C–H bonds of the bridging methylene ligands in complexes 423 (R = H, L = CO; R = H, L = CNCy) occurs to yield 439. When 423 (R = Me, L = CO) is used, 440 is formed. Deuteration studies show that intramolecular H–D exchange occurs between the two methylene units.[303,304] Complex 421 reacts with norbornadiene to give the nortricyclyl compound 441 via C–C coupling.[304]



The mixed Cp/Cp* carbonyl-bridged species 442 (R = Cp*) can be prepared from $[RuCp^*(I)(CO)_2]$ and $Na[RuCp(CO)_2]$ in 82% yield as a mixture of *cis*- and *trans*-products. Reaction of 442 (R = Cp*) with PhC≡CPh in UV light for 10 h leads to 443 ($R^1 = Cp^*$; $R^2 = R^3 = Ph$) which, on heating with RC≡CR ($R = CO_2Me, CF_3$), forms the dimetallacyclopentenone complexes 443 ($R^1 = Cp^*$; $R^2 = R^3 = CO_2Me, CF_3$). When $R = CO_2Me$, refluxing of this compound in toluene leads to two isomeric μ-vinylidene species 444 ($R^1 = Cp^*$). Heating 443 ($R^1 = Cp^*$; $R^2 = R^3 = CF_3$) in toluene provides the dimetallacyclobutene compound 445. Decarbonylation occurs on further heating to yield the dimetallatetrahedrane 446 ($R^1 = Cp^*$).[305]



Investigation of the reactivity of the Cp analog, 443 ($R^1 = Cp$, $R^2 = R^3 = Ph$), revealed that heating at reflux in toluene with $PhC{\equiv}CCO_2Me$ results in inseparable mixtures of the isomers 443 ($R^1 = Cp$, $R^2 = Ph$, $R^3 = CO_2Me$) and 443 ($R^1 = Cp$, $R^2 = CO_2Me$, $R^3 = Ph$).[306] Similar mixtures of 443 ($R^1 = Cp$, $R^2 = Me$, $R^3 = CO_2Me$) and 443 ($R^1 = Cp$, $R^2 = CO_2Me$, $R^3 = Me$) are obtained with $MeC{\equiv}CCO_2Me$. Photolysis of a mixture of 443 ($R^1 = Cp$, $R^2 = CO_2Me$, $R^3 = Ph$) and 443 ($R^1 = Cp$, $R^2 = Ph$, $R^3 = CO_2Me$) leads to formation of the products 447, 448, and $[Ru_3Cp_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(CO)(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^2\text{-}C(Ph)C(CO_2Me)\}]$. However, the methyl analogs 443 ($R^1 = Cp$, $R^2 = CO_2Me$, $R^3 = Me$) and 443 ($R^1 = Cp$, $R^2 = Me$, $R^3 = CO_2Me$) react under the same conditions to yield 449 as the sole isolable product.[306]



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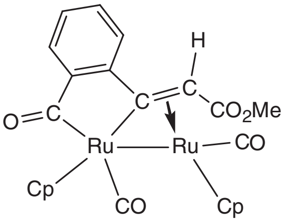

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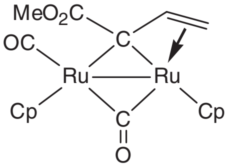
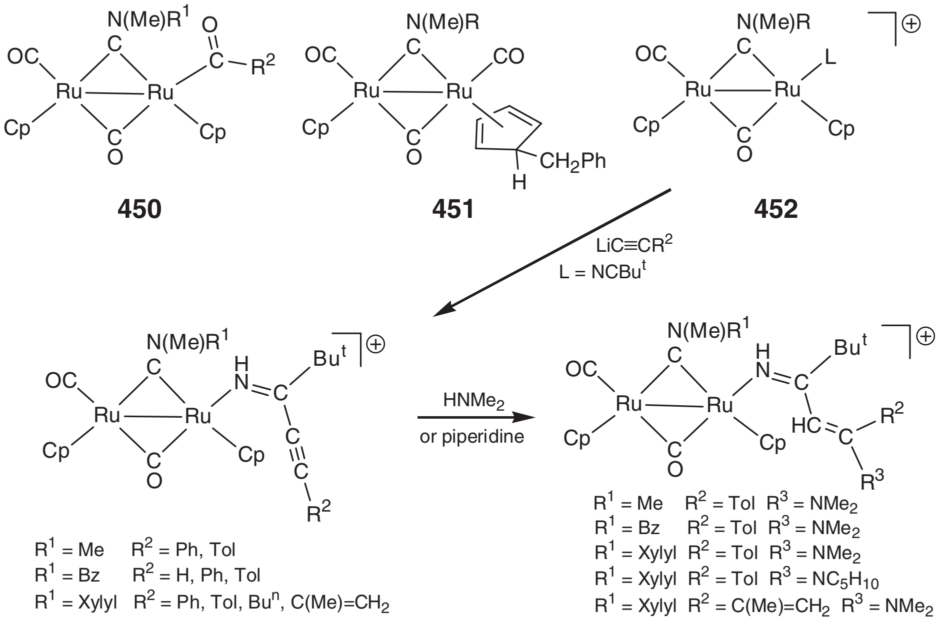


449

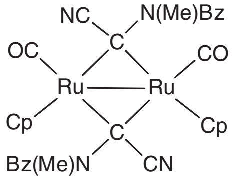
Reaction of $[Ru_2Cp_2\{\mu\text{-}CN(Me)R^1\}(\mu\text{-}CO)(CO)_2]OTf$ ($R^1 = Me$, CH_2Ph) with $Li_2Cu(CN)R^2{}_2$($R^2 = Me$, Ph, Bu^n) in tetrahydrofuran at 40 °C result in the formation of acyl complexes 450 ($R^1 = Me$, $R^2 = Me$, Ph, Bu^n; $R^1 = CH_2Ph$, $R^2 = Me$). The corresponding reaction with $ClMgCH_2Ph$ results in a mixture of the acyl species 450 ($R^1 = Me$, $R^2 = CH_2Ph$; $R^1 = R^2 = CH_2Ph$) and the cyclopentadiene complexes 451 ($R = Me$, CH_2Ph).[307] The compounds $[Ru_2Cp_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2]OTf$ (R = Me, Bz, Xylyl) react with Bu^tCN and Me_3NO in tetrahydrofuran to yield 452 ($L = NCBu^t$; R = Me, Bz, Xylyl; OTf^- salts). The carbon of the coordinated nitrile in 452 ($L = NCBu^t$; R = Me, Bz, Xylyl; OTf^- salts) is the site of nucleophilic attack by $LiC{\equiv}CR^2$ ($R^2 = H$, Bu, Ph, Tol, $CMe{=}CH_2$) to provide 453 (OTf^- salts).[308] Amination of 453 ($R^1 = Me$, Bz, Xylyl; $R^2 = Tol$; OTf^- salts) with dimethylamine leads to 454 ($R^1 = Me$, Bz, Xylyl; $R^2 = Tol$; $R^3 = NMe_2$; OTf^- salts), whereas reaction of 453 ($R^1 = xylyl$, $R^2 = Tol$; OTf^- salt) with piperidine yields 454 ($R^1 = Xylyl$, $R^2 = Tol$, $R^3 = NC_5H_{10}$; OTf^- salt).[308]



450 **451** **452**

453 **454**

Repeated stepwise addition of MeOTf and $[NBu_4]CN$ to the bis(isocyanide) complex $[Ru_2Cp_2(\mu\text{-}CNBz)_2(CO)_2]$ **455** yields the μ-aminoalkylidene compound 456 as a racemic mixture.[309] Nucleophilic attack of hydride ($NaBH_4$) or cyanide ($[NBu_4]CN$) occurs at the μ-C alkylidyne carbon of **452** (L = CO; R = Bz; triflate salt) to provide compounds **457** (X = H, CN),[310] while the μ-aminocarbyne complex $[Ru_2Cp_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(NCMe)]OTf$ reacts with $NaBH_4$ in acetonitrile to form the μ-hydride compound **458**.[311]



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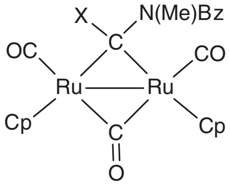

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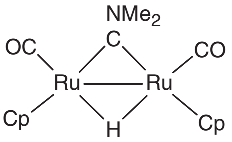
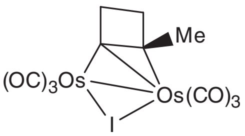


458

The iodide-bridged compound **459** was obtained in 5% yield from the reaction of 1-iodo-2-methylcyclobutene with $Os_3(CO)_{10}(NCMe)_2$ along with three trinuclear species.[312] Complex **460** has a similar structure and was the subject of extensive NMR studies to investigate its fluxional behavior in solution.[313] A bridging alkenyl unit is also found in complex **461**, prepared from the reaction of $Ru_3(CO)_{12}$ with $[NiCp\{\eta^1{:}\eta^2\text{-}C_5H_5C_2(CO_2Me)_2\}]$, in which a Cp and an alkenyl group (from the bicyclo[2.2.1]hepta-2,5-dienyl ligand) are transferred from nickel to ruthenium.[314] Triruthenium dodecacarbonyl also reacts with the cinnamic acid amides, $PhCH{=}CHCO(NR^1R^2)$, to give $[Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}\eta^3\text{-}PhC{=}CHC(O)NR^1R^2\}(CO)_{10}]$ and **462** ($R^1 = R^2 =$ Me, Et; $R^1 =$ H, $R^2 =$ Me; R^1–$R^2 = (CH_2)_4$), in which a (*Z*)-alkenyl ligand bridges the diruthenium unit as well as forming an oxaruthenacycle.[315] The complexes **463** (M = Os; $R^1 = R^2 =$ Et, Ph; $R^1 =$ H, $R^2 = Bu^t$; $R^1 =$ Me, $R^2 = Bu^t$) are formed from the reaction of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\gamma\text{-}C_5H_3O_2)$ with $R^1C{\equiv}CR^2$ under thermal or photochemical conditions.[316] The reaction of $[Ru_3\{\mu\text{-}HCC(Ph)C(O)(Ph)CCPh\}(dppm)(CO)_6]$ with 10 atm of CO in a reactor at 80 °C leads to the diruthenium complex **464**.[317]



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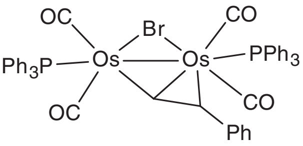

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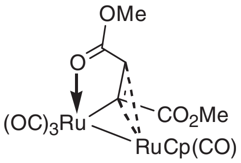

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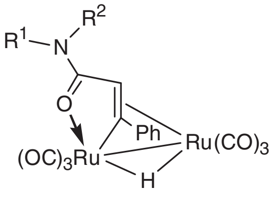

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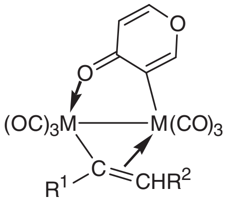

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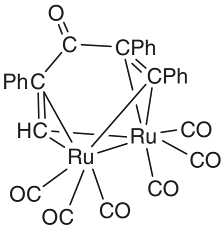
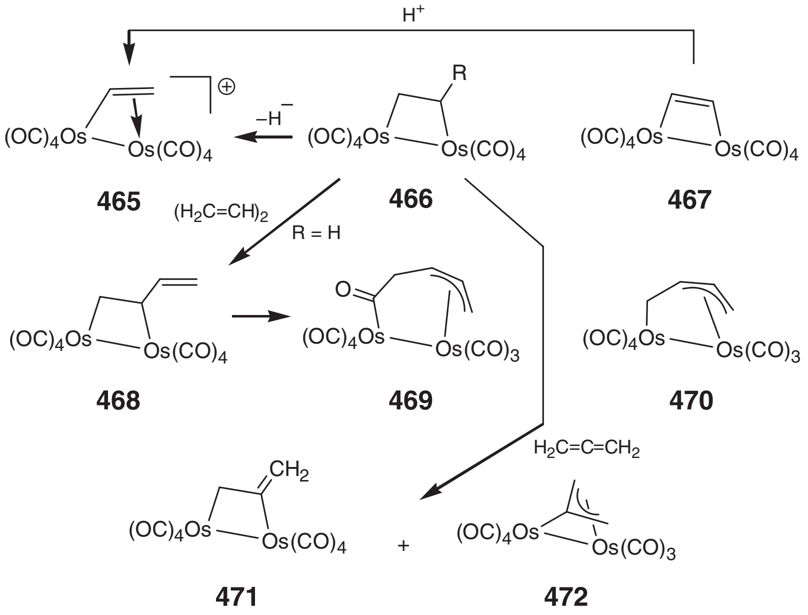


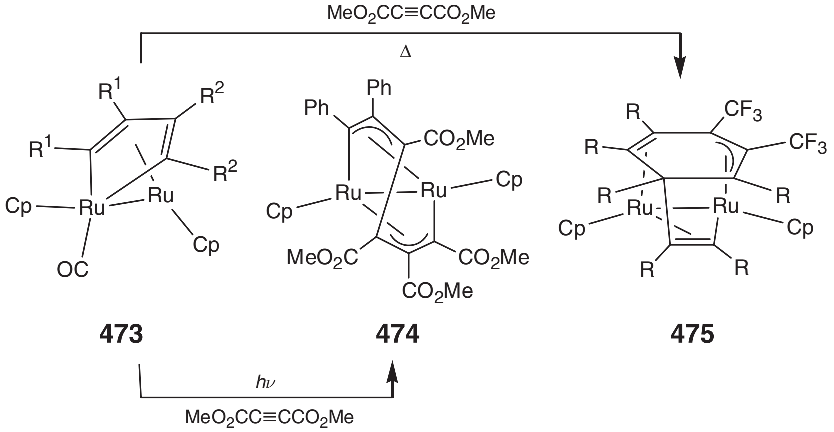
464

The alkenyl-bridged cationic species **465** (BF_4^- salt) is obtained by hydride abstraction from the diosmacyclobutane compound **466** (R = H) or via protonation of the diosmacyclobutene **467**.[318] With butadiene, compound **466** (R = Me) gives the 1,2-adduct **468** as kinetic product and the allyl–acyl complex **469** (derived from **468** through CO insertion) as the thermodynamic product.[319] The same product is obtained by photolysis of $Os_3(CO)_{12}$ in the presence of butadiene in dichloromethane, along with $Os(H_2C{=}CHCH{=}CH_2)(CO)_3$ and compound **470** in 30% yield. Stirring a pentane solution of **466** (R = Me) under allene leads to the formation of the alkenyl compound **471** as the major product and allyl species **472** as the minor product.[319]



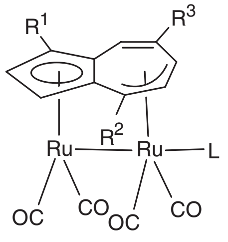
6.17.3.2 Complexes with η^3-enyl Ligands

The Ru═Ru double-bonded μ-alkyne complexes $[Ru_2Cp_2(\mu\text{-}CO)(\mu\text{-}RC_2R)]$ ($R = Ph, CF_3$) react with $R^2C{\equiv}CR^2$ ($R^2 = CF_3, CO_2Me$) in xylene at reflux to yield 473 ($R^1 = Ph$, $R^2 = CF_3$; $R^1 = R^2 = CF_3$; $R^1 = CF_3$, $R^2 = CO_2Me$), in which the metallacyclopentadiene coordinates in an η^4-fashion to the adjacent ruthenium center. Further reaction with $MeO_2CC{\equiv}CCO_2Me$ occurs on irradiation of 473 ($R^1 = Ph$, $R^2 = CO_2Me$) to provide 474. Heating 473 ($R^1 = CF_3$; $R^2 = CO_2Me$) under reflux in xylene with an excess of $MeO_2CC{\equiv}CCO_2Me$ for 5 days leads to 475 ($R = CO_2Me$), presumably through an intermediate similar to 474, although this was not detected.[320]



A mixture of isomers of $(\mu_2\text{-}\eta^3{:}\eta^5\text{-guaiazulene})Ru_2(CO)_5$ reacts photochemically or thermally with phosphines and phosphites to yield the single haptotropic isomers 476 ($R^1 = R^2 = Me$, $R^3 = Pr^i$; $L = PMe_3$, $P(OPh)_3$, $P\{(OCH_2)_3CMe\}$) through displacement of a CO ligand. When the reaction is carried out at RT (without irradiation), an intermediate in the process (477; $R^1 = R^2 = Me$, $R^3 = Pr^i$; $L = PMe_3$, $P(OPh)_3$, $P\{(OCH_2)_3CMe\}$) is isolated, which the authors suggest is the key to explaining why only one isomer, 476 ($R^1 = R^2 = Me$, $R^3 = Pr^i$; $L = PMe_3$, $P(OPh)_3$, $P\{(OCH_2)_3CMe\}$), is formed from the reaction.[321] With CNR ($R = Bu^t$, $C_6H_2Me_3$-2,4,6 $C_6H_3Pr^i_2$-2,6), the isomeric mixture of $[(\mu_2\text{-}\eta^3{:}\eta^5\text{-guaiazulene})Ru_2(CO)_5]$ initially forms 478 ($R = Bu^t$, $C_6H_2Me_3$-2,4,6, $C_6H_3Pr^i_2$-2,6), which on heating gives the η^3-bonded isomers 479 ($R = Bu^t$, $C_6H_2Me_3$-2,4,6, $C_6H_3Pr^i_2$-2,6) and 480 ($R = Bu^t$, $C_6H_2Me_3$-2,4,6, $C_6H_3Pr^i_2$-2,6).[322]

Studies on the interconversion of 476 ($R^1 = R^2 = R^3 = H$; L = CO) and 477 ($R^1 = R^2 = R^3 = H$; L = CO) have also been carried out.[323] Treatment of the related complex, $[(\mu_2\text{-},\eta^3\text{:}\eta^5\text{-4,6,8-trimethylazulene})Ru_2(CO)_5]$, with $HSiMe_2Ph$ in benzene at 60 °C results in loss of CO and formation of the silyl complex 481 ($R = SiMe_2Ph$). The oxidative addition of two molecules of $HSiMe_2Ph$ to the diruthenium species is followed by transfer of the metal-bonded hydrides to the double bond of the azulene ligand, creating an unsaturated linkage.[29]



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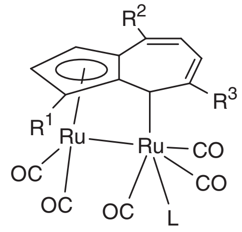

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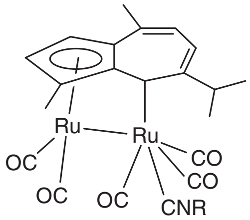

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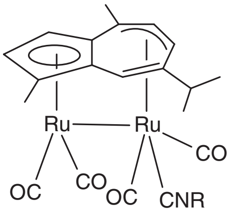

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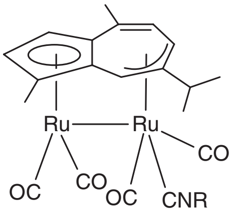

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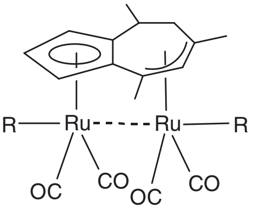
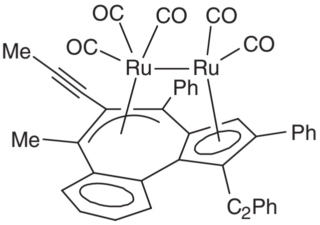


481

An η^3-azulene–diruthenium complex 482 has been reported to result from reaction of 2,4-hexadiyne with the trinuclear cluster $[Ru_3(\mu\text{-}\eta^2\text{-apyr})\{\mu_3\text{-}\eta^6\text{-}C_5(CPh)(C{\equiv}CPh)(C{\equiv}CPh)HPh_2\}(CO)_7]$ (Hapyr = 2-aminopyrimidine) in refluxing tetrahydrofuran.[324] The di(2-furyl)phosphido complex 176 reacts with $HC{\equiv}CR$ (R = Ph, Tol, $C_6H_4NO_2$-4, $(C_4H_2S)C_2H$, $(C_4H_2S)_2C_2H$) in refluxing toluene to yield 483.[131]



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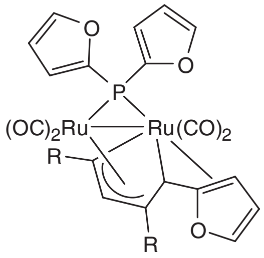
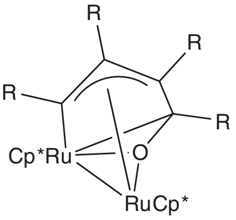


483

The tetranuclear hydroxoruthenium complex $\{Cp^*Ru(\mu\text{-}OH)\}_4$ reacts with dimethyl acetylenedicarboxylate to yield the ruthenacycle 484 ($R = CO_2Me$) via an intramolecular attack of the hydroxide ligand on the coordinated organic ligand.[325] A [2.2]paracyclophane ligand bridges the diruthenium unit in 485 with an η^3-coordination mode at each metal center, causing the coordinated ring to adopt a boat conformation. This species is obtained by degradation of the complex $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$, in which the paracyclophane bridges all three ruthenium centers.[326,327] The complex $\{Cp^*Ru(\mu\text{-}H)_2\}_2$ (486; discussed in Section 6.17.3.4.) reacts with an excess of thiophene or 2-methylthiophene to provide the complexes 487 (R = H, Me) in near quantitative yield through C–S bond cleavage.[328]



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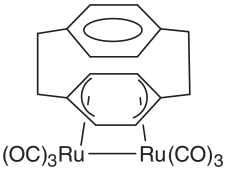

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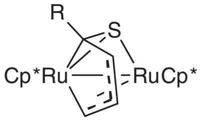
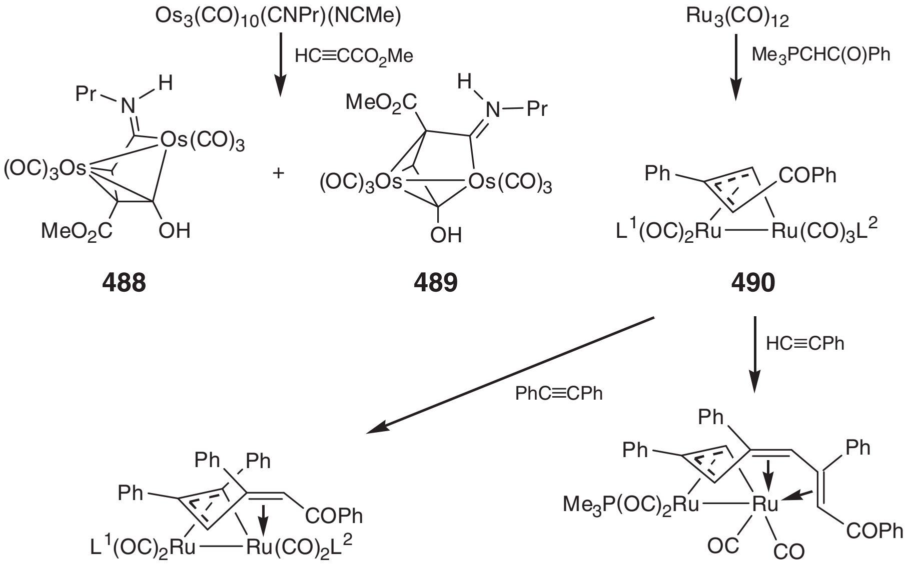


487

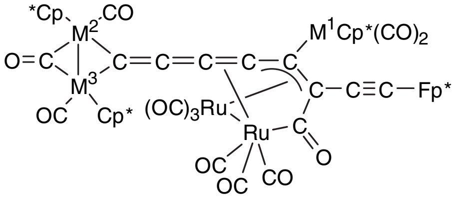
Under very mild conditions, the reaction between methyl propiolate and [$Os_3(CO)_{10}(CNPr)(NCMe)$] yields complexes **488** (37%) and **489** (7%). Both contain the organic ligand bound in an η^3-fashion to one osmium center. Crystal structures of the products show that regioselective coupling of the alkyne with both CO and CNR ligands occurs during the reaction.[329] The ylide $Me_3PCHC(O)Ph$ induces fragmentation of $Ru_3(CO)_{12}$ to form the σ,π-bonded allyl compounds **490** ($L^1 = L^2 = CO$; $L^1 = PMe_3$, $L^2 = CO$).[330] Diphenylacetylene inserts into the Ru–C σ-bonds in **490** ($L^1 = PMe_3$, $L^2 = CO$) to form two isomers of **491** ($L^1 = PMe_3$, $L^2 = CO$; $L^1 = CO$, $L^2 = PMe_3$). The allyl bonding mode is maintained in these products and a new interaction is formed between the extended unsaturated chain and the other ruthenium center. On reaction of **490** ($L^1 = PMe_3$, $L^2 = CO$) with phenylacetylene, double insertion of the alkyne occurs to yield **492**.[330]



488 **489** **490**

491 **492**

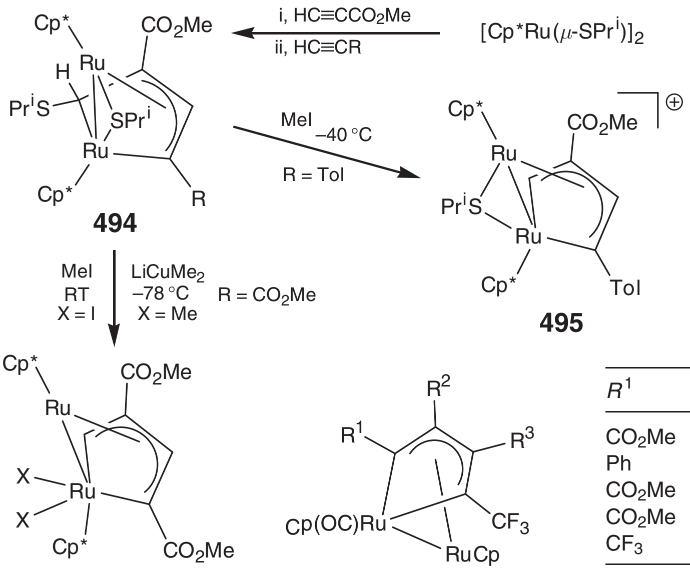
The butadiynediyldiiron complex $Fp^*C{\equiv}CC{\equiv}CFCp^*$ ($Fp^* = Fe(CO)_2Cp^*_2$) reacts with $Ru_3(CO)_{12}$ in refluxing dichloromethane to yield a mixture of $Ru_3(CO)_{10}(\mu_3\text{-}CC{\equiv}C\mu\text{-}C)Fe_2Cp^*_2(CO)_3$ and the unusual dimerized diruthenium product **493** ($M^1 = M^2 = M^3 = Fe$). The dinuclear unit is stabilized by an η^3-allyl interaction with one metal center as well as coordination of the other to a double bond of the cumulene moiety. Two isomers of an isostructural C_8 complex, **493** ($M^1 = M^3 = Ru$, $M^2 = Fe$) and **493** ($M^1 = M^2 = Ru$, $M^3 = Fe$) are formed in the reaction between $Fp^*C{\equiv}CC{\equiv}CRuCp^*(CO)_2$ and $Ru_3(CO)_{12}$ under the same conditions.[331]



493

6.17.3.3 Complexes with η^4-diene Ligands

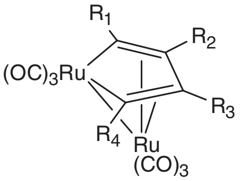
Compound **494** (R = Tol, CO_2Me) reacts with an excess of methyl iodide at −40 °C followed by warming to RT to yield the iodide salt **495** by removal of an SPr^i group. At RT, the reaction of **494** (R = CO_2Me) with an excess of MeI provides the diiodo compound **496** (X = I) through cleavage of both SPr^i units. A methylated complex (**496**; X = Me) is obtained only on reaction of **494** (R = CO_2Me) with $LiCuMe_2$ at −78 °C.[237] A series of complexes **497** is formed from the reactions of $R^1C{\equiv}CR^2$ with the cluster [$Ru_3Cp_2(MeCN)(CO)_2(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}$].[332]



494 **495** **496** **497**

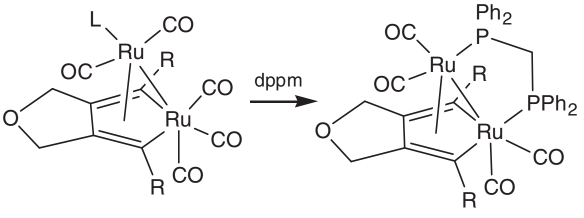
R^1	R^2	R^3
CO_2Me	Me	CF_3
Ph	Ph	CF_3
CO_2Me	Me	CF_3
CO_2Me	CO_2Me	CF_3
CF_3	Ph	Ph

Infrared spectroscopy has been used to investigate rotational isomerism in the “ruthenole” complexes 498 bearing ferrocenylalkynyl substituents.[333] Triruthenium dodecacarbonyl reacts with diynes to provide 499 (L = CO; R = Ph, CO_2Me) along with a mononuclear side-product. Compound 499 (L = CO, R = CO_2Me) reacts with Me_3NO to give 499 (L = NMe_3, R = CO_2Me), which undergoes substitution reactions with phosphines to provide 499 (L = PPh_3, PPh_2py, η^1-dppe; R = CO_2Me) and 500 (R = CO_2Me) with dppm. Using Me_3NO, complexes with bidentate phosphine and pyridylphosphine chelates, 501 (R = CO_2Me) and 502 (R = CO_2Me), respectively, are formed from 499 (L = η^1-dppe, PPh_2py). Treatment of 499 (L = NMe_3, R = CO_2Me) with 5 equiv. of $MeO_2CC{\equiv}CCO_2Me$ results in the bridging alkyne complex 503 (R = CO_2Me).[334]

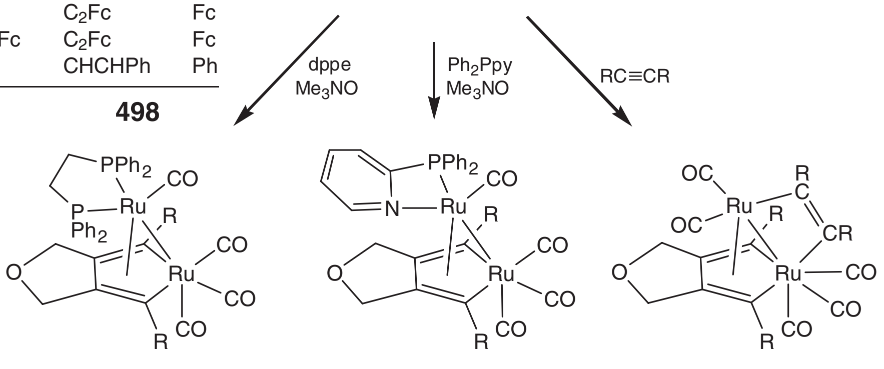


R^1	R^2	R^3	R^4
C_2Fc	Fc	C_2Fc	Fc
Fc	C_2Fc	C_2Fc	Fc
CHCHPh	Ph	CHCHPh	Ph

498

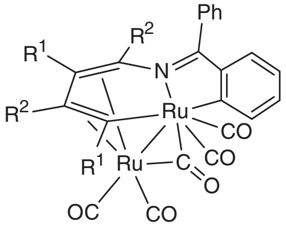


499 **500**



501 **502** **503**

Complexes 504 (R^1 = Ph, R^2 = Me; R^1 = R^2 = Et) are accessible from reactions of the μ-1-azavinylidene-μ-alkenyl diruthenium complex $[Ru_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N{=}CHPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}PhC{=}CHPh)(CO)_6]$ with $PhC{\equiv}CMe$ or $EtC{\equiv}CEt$. The same precursor reacts with $PhC{\equiv}CH$ to give 505 (which does not contain an Ru–Ru interaction) and a mononuclear side-product, $[Ru\{\eta^5\text{-}PhC{=}C(H)C(Ph){=}C(H)C(Ph){=}C(H)N{=}C(C_6H_4)Ph\}(CO)_2]$. Heating $[Ru_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N{=}CHPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}PhC{=}CHPh)(CO)_6]$ in the absence of alkyne results in a tetraruthenium cluster, $C_{48}H_{30}N_2O_8Ru_4$, and 506.[335]



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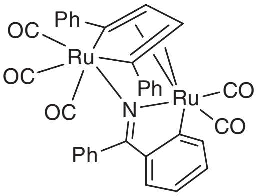

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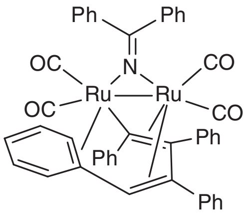
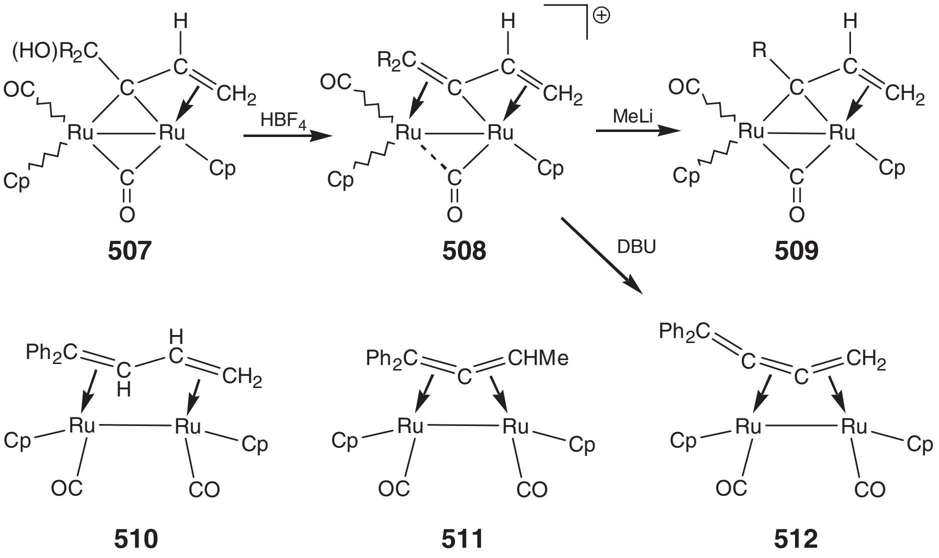
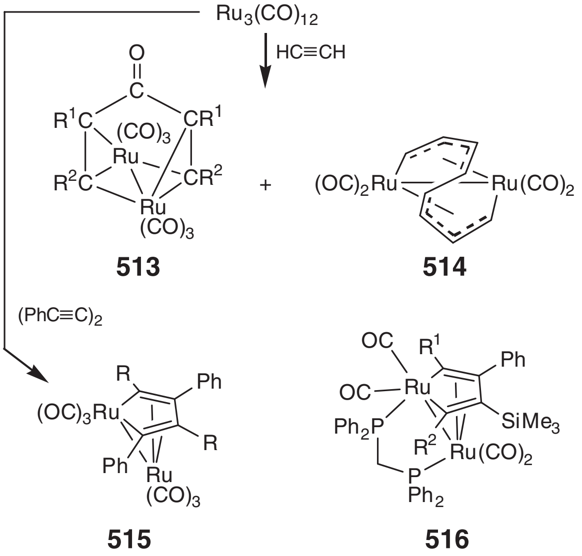


506

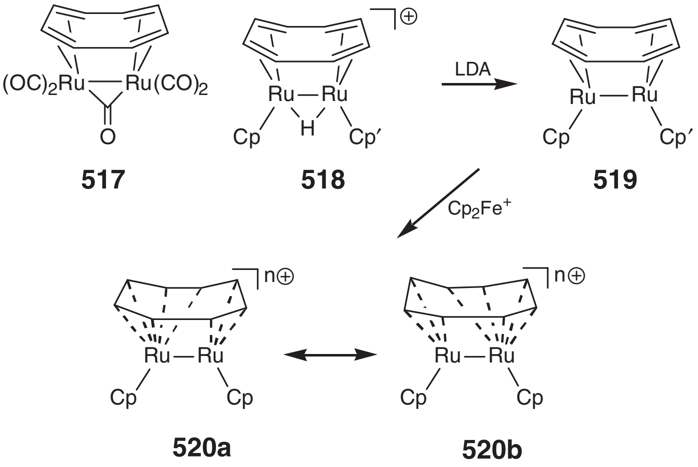
Compound 424 reacts with the propargyl alcohols $HC{\equiv}CCR_2OH$ (R = H, Me, Ph) to give the μ-allylidenes 507 (R = H, Me, Ph), which go on to react with HBF_4 to yield the butadienyl complexes 508 (R = H, Me, Ph; BF_4^- salts). Reaction of 508 (R = Me) with $LiBHEt_3$ provides 509 (R = Pr^i), while treatment of 508 (R = H) with $LiBHEt_3$ or MeLi yields 509 (R = Me) and 509 (R = Et), respectively. Compound 508 (R = Ph) yields a mixture of 509 (R = $CHPh_2$), 510, and 511 on reaction with $LiBHEt_3$, depending on the site of attack of the hydride. With the non-nucleophilic base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 508 (R = Ph) provides 512. However, a proton at the other end of the butadienyl ligand is lost when 508 (R = Me) reacts with DBU to give 509 (R = $CMe{=}CH_2$).[336]



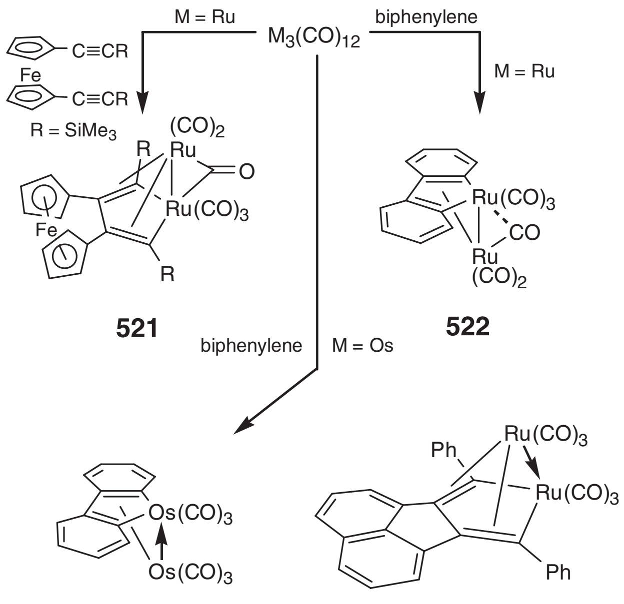
The triruthenium paracyclophane-bridged complex $[Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})]$ reacts with diphenylacetylene to give a mixture of products including a dinuclear dienyl derivative, 513 ($R^1 = R^2 = Ph$) with the best yields of the diruthenium complex being obtained over longer reaction times.[327] A similar product 513 ($R^1 = R^2 = H$) is believed to be produced in the reaction of $Ru_3(CO)_{12}$ with ethyne in tetrahydrofuran at reflux or in the presence of Me_3NO. The other isolated compound from this reaction, complex 514, was characterized structurally. The open-chain ethyne tetramer that bridges the metal centers in this compound shows η^4-coordination to each ruthenium center.[337] The same reaction with 1,4-diphenylbuta-1,3-diyne in the presence of Me_3NO provides the metallacyclopentadiene 515 ($R = C_2Ph$) in 43% yield, along with 513 ($R^1 = Ph$, $R^2 = C_2Ph$) in 10% yield.[338] The cluster $Ru_3(CO)_8(\mu_3\text{-}PhC_2C{\equiv}CPh)(\mu\text{-dppm})$ undergoes reaction with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ to give another example of a ruthenacyclopentadiene complex, 516 ($R^1 = C{\equiv}CPh$, $R^2 = C{\equiv}CSiMe_3$), along with tri- and tetraruthenium products.[339]



The reaction of $Ru_3(CO)_{12}$ with cyclooctatetraene in refluxing octane results in the formation of **517**, in which the C_8H_8 ligand adopts a boat configuration spanning the two metal centers in an η^4:η^4 manner.[340] Treating CpRu(1,2,3-η:6,7-η-C_8H_9) with $[Ru(Cp')(NCMe)_3]PF_6$ (Cp′ = Cp, Cp*) leads to formation of the bridging hydrido complexes **518** (Cp′ = Cp, Cp*; PF_6^- salts). Deprotonation with lithium diisopropylamide (LDA) yields the neutral compounds **519** (Cp′ = Cp, Cp*). One example (Cp′ = Cp) was analyzed crystallographically and found to possess an Ru–Ru bond of 2.956(1) Å. Oxidation with $[Cp_2Fe]PF_6$ causes a contraction of this distance to 2.8215(9) Å in **520** ($n = 1$; PF_6^- salt) along with a marked change in hapticity to an $\eta^5:\eta^5$ bonding mode through the interconversion between η^5- and η^3-resonance forms **520a and 520b** ($n = 1$; PF_6^- salts). Further oxidation to **520** ($n = 2$; PF_6^- double salts) does not alter the coordination mode but leads to a decrease in Ru–Ru distance to 2.6608(6) Å.[341]

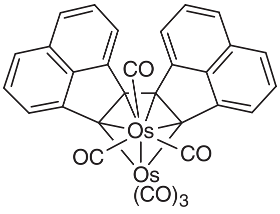


One of the products from treatment of 1,1′-bis(trimethylsilylethynyl)ferrocene with $Ru_3(CO)_{12}$ is a dinuclear product (**521**, R = $SiMe_3$) based around a ferrocenophane skeleton with a bridging carbonyl.[342] A similar structural motif is found in complex **522**, produced in the reaction between $Ru_3(CO)_{12}$ and biphenylene, along with the carbide cluster $Ru_6(\mu_6\text{-}C)(CO)_{17}$.[343] The corresponding reaction with $Os_3(CO)_{12}$ requires much harsher conditions (decane, 200 °C, 15 h) and results in only low conversion to **523** and $Os_4\{\mu_4\text{-}\eta^2\text{-}(C_6H_3)Ph\}(CO)_{12}$.[343] Complex **522** is also produced in the desulfurization of dibenzothiophene with $Ru_3(CO)_{12}$.[344] The reaction of $Pt_2Ru_4(CO)_{18}$ with 1,8-bis(phenylethynyl)naphthalene also proceeds by intramolecular alkyne coupling to provide **524** in good yield along with a heterobimetallic cluster in low yield. This product features a dative bond between the metal centers, giving a structure resembling that of osmium complex **523**.[345]



523 **524**

The triosmium complex $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_{12}H_6)$ is accessible from the reaction between acenaphthylene and $Os_3(CO)_{10}(NCMe)_2$. Further treatment with acenaphthylene at 160 °C leads to identification of four products, including two dinuclear species, 525 and 526, both of which share structural similarities with 523.[346] A further analogous example is 527 (R = C≡CFc), obtained from the reaction between $(FcC{\equiv}C)_2$ and $Os_3(CO)_{10}(NCMe)_2$.[347]



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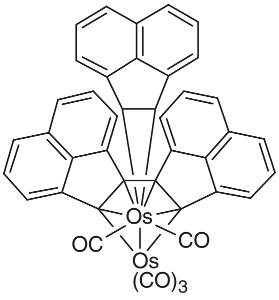

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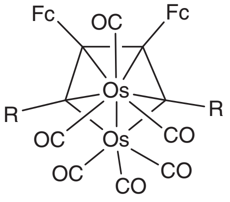
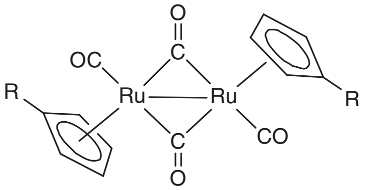


527

6.17.3.4 Complexes with η^5-dienyl Ligands

Apart from the many Cp and Cp* compounds, classified by bridging ligand, detailed above, a further collection of complexes containing Cp, Cp*, other η^5-dienyl ligands and linked variants will be discussed here.

In addition to a more accurate determination of its crystal structure,[348] the compound $Cp'_2Ru_2(\mu\text{-}CO)_2(CO_2)$ (**528**; Cp′ = Cp) has found use in the preparation of Pt/Ru bimetallic fine particles through precipitation from polyamic acid solutions containing the dinuclear species and a range of platinum complexes.[349] A large number of variants of **528** have been reported including the complexes **528** (Cp′ = Cp*, $C_5H_4Bu^t$, $C_5H_4SiMe_3$, $C_5Me_4Bu^t$, C_5HPh_4, $C_5H_3Bu^t{}_2$-1,3, $C_5H_3Ph_2$-1,3, $C_5H_3MeBu^t$-1,3) as part of an investigation into the *cis–trans* isomerism in these complexes.[350] Compounds **528** (Cp′ = $C_5Me_4CF_3$)[351] and 529 (R = Me)[352] have also been prepared from $Ru_3(CO)_{12}$ in the same way. The more unusual aminocyclopentadienyl complexes 530 (*cis,trans* isomers) were prepared from $Ru_3(CO)_{12}$ and *N*-phenyl-2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienimine in a study of the use of ruthenium hydride complexes in the reduction of benzaldehyde to benzyl alcohol.[353] Treatment of the μ-alkylidene complex 436 with ethyne results in loss of HCl and formation of the first example of an unsubstituted metallabenzene complex 531.[354] Other products formed in the reaction are the known metallacyclopentadiene complex 532 and mononuclear $[Cp^*Ru(\eta^6\text{-}C_6H_6)]Cl$.[355] A substituted ruthenabenzene compound, 533 (R = H, Me), is formed from the C–C bond cleavage of norbornadiene by $Cp^*{}_2Ru_2(\mu\text{-}H)_4$. The origin of this reactivity was ascribed to the cooperative action of the two adjacent ruthenium centers.[356]



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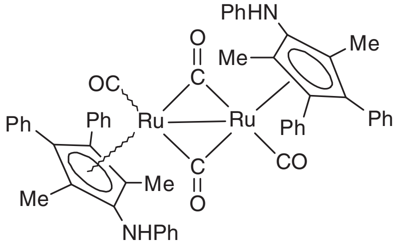

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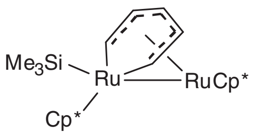

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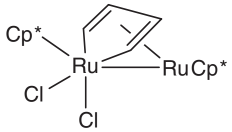

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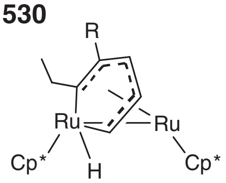
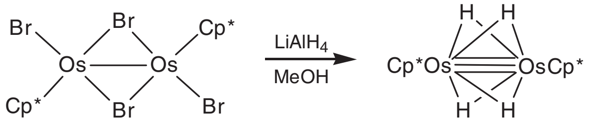
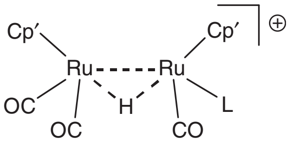


533

Refluxing a mixture of hexabromo-osmic acid and 1.5 equiv. of C_5Me_5H in ethanol results in good yields of **534**. The structure of this complex is similar to that of the ruthenium analog and, unusually, shows shorter bond distances for the bridging bromides than those bonded in terminal positions.[357] Treatment of **534** with $LiAlH_4$ in diethyl ether followed by methanol at −78 °C yields the mononuclear pentahydride Cp^*OsH_5. On photolysis in benzene, this species forms the hydride-bridged complex **535**, which is formulated with an osmium–osmium triple bond.[357] The effect of the cyclopentadienyl (and related) ligands on the enthalpy of protonation of the Ru–Ru bond was investigated using the conversion of the complexes **528** ($Cp' = Cp$, Cp^*, η^5-$C_5Me_4CF_3$, η^5-indenyl, η^5-$HBpz_3$) and the linked Cp derivatives, **528** ($Cp'_2 = Cp_2CH_2$, $CpCH_2CH_2Cp$, $\eta^5{:}\eta^5$-$C_{10}H_8$) to the bridging hydride species **536** (L = CO; TfO^- salts).[358] This study was later extended to include phosphine variants, which allowed the effect of varying the basicity of the diruthenium unit on conversion to the corresponding protonation products **536** ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3) to be examined. Protonation was still found to occur across the metal–metal bond rather than at the ruthenium center rendered more basic by bonding of the phosphine.[359] The electrochemistry and $Ru_2(\mu$-H) bond dissociation enthalpies of the complexes were also investigated in a later study.[360] A series of complexes, **537** (R = Me, Et, Pr^i, Cy, Bz, OMe, OPh), was prepared from $Cp^*_2Ru_2(\mu$-$H)_4$ and 1 equiv. of the appropriate phosphine. These compounds were used to examine the way in which migration of the phosphine ligand between the metal centers occurs to allow sharing of electron density from the PR_3 ligand. Crystal structures were obtained for all compounds and DFT calculations were performed on the complexes. These data were used to propose a through-space backbonding interaction between the ruthenium and phosphorus atoms.[361] The reaction of $\{Cp^*RuCl\}_4$ with enones and enals leads to the formation of half-open mononuclear ruthenocenes incorporating oxo-dienyl ligands. Along with these products, dinuclear species (**538**; $R^1 = H$, $R^2 = Me$, Et; $R^1 = R^2 = Me$), formed by abstraction of CO from the oxo-dienyl ligand, are also obtained.[362] Treatment of C_{60} with combined stoichiometric amounts of $\{Cp^*Ru(\mu$-$H)_2\}_2$ and $\{Cp^*Ru(\mu$-$Cl)_2\}_2$ produces **539**, in which the dinuclear unit is bonded to two conjugated C–C π-bonds of C_{60}. If the reaction is carried out with 2 equiv. of $\{Cp^*Ru(\mu$-$Cl)_2\}_2$, a compound without an Ru–Ru bond, $[Cp^*_2Ru_2(\mu$-$Cl)_2(C_{60})]$, is formed.[363]



534 **535**



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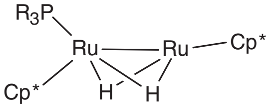

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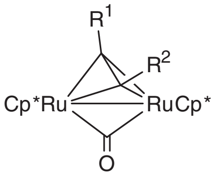

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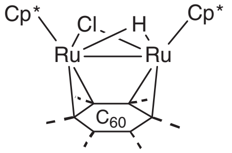
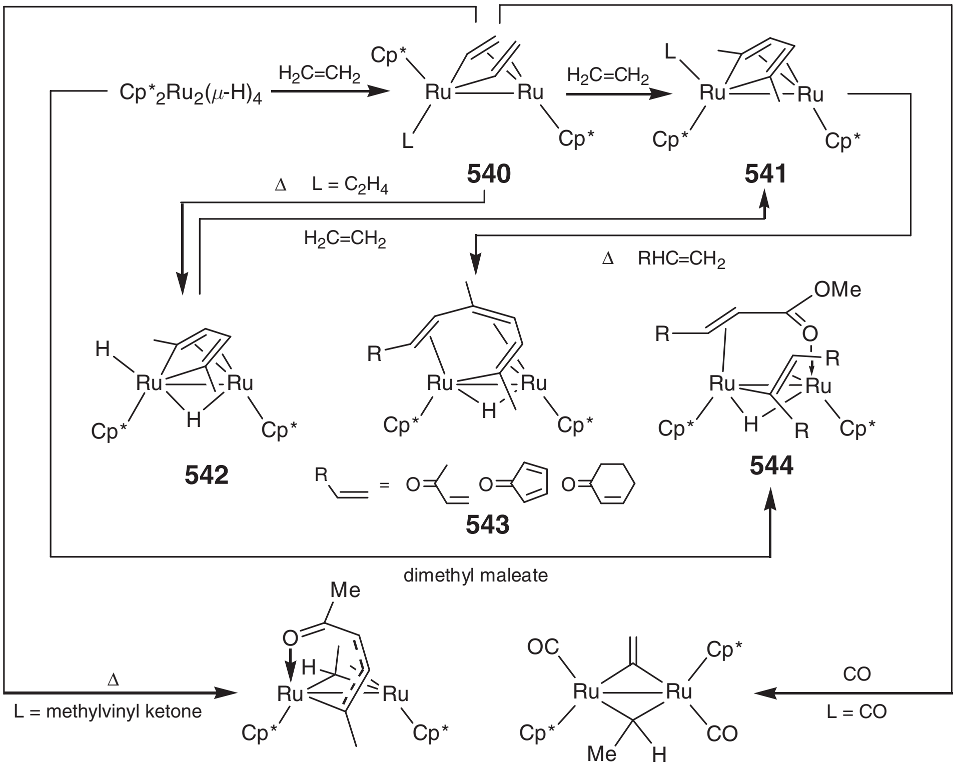


539

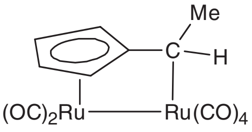
Although the complex $Cp^*_2Ru_2(\mu$-$H)_4$ is normally formulated with a triple bond between the ruthenium centers, *ab initio* calculations have suggested that the short Ru–Ru distance could be due to four three-center two-electron

M–H–M bonds.[364,365] The tetrahydride complex reacts with ethene at RT in toluene to give divinyl compound **540** (L = C_2H_4) in 73% yield.[365] Further reaction with ethene in toluene at 60 °C results in the formation of the 2,5-dimethylruthenacyclopentadiene **541** (L = C_2H_4); however, if the reaction is carried out in the absence of ethene, a dihydride complex **542** is formed. Compound **542** is converted quantitatively to **541** (L = C_2H_4) on exposure to ethene, suggesting its role as an intermediate in the formation of **541** (L = C_2H_4) from **540** (L = C_2H_4). Extension of the carbon chain can be achieved by heating **541** (L = C_2H_4) at 110 °C in toluene to provide **543** (R = H). Electron-deficient alkenes (methyl vinyl ketone, cyclopentenone, cyclohexenone) can also be introduced into the carbon skeleton in the same manner to give **543**. With maleic anhydride, the reaction yields **541** (L = maleic anhydride) together with **543** (R = H). With the activated alkene, dimethyl maleate, $Cp^*{}_2Ru_2(\mu\text{-}H)_4$, reacts to provide the alkenyl complex **544** (R = CO_2Me), which is stabilized by two interactions with a dimethyl fumarate molecule. Treatment of **540** (L = C_2H_4) with methyl vinyl ketone (mvk) results in displacement of ethene to yield **540** (L = mvk), which forms the unusual η^3-allyl μ-alkylidene compound **545** on heating at 110 °C in toluene. A μ-alkylidene product **546** also results from the reaction of the carbonyl divinyl complex **540** (L = CO) with 1 atm carbon monoxide at RT. The authors propose that this transformation proceeds through C_α–H bond activation followed by insertion of a vinylic C═C moiety into the resulting Ru–H bond.[365]



545 **546**

In addition to a new structural study of the diruthenium–fulvene compound **547**,[366] 1,2,3,4-tetramethylfulvene analogs **548** (L = CO, PMe_3) have been prepared and the fluxionality of the compounds investigated.[367] Complex **549** is a dinuclear complex bridged both through carbon and nitrogen donors by a quinolyl–fulvene ligand, formed from $Ru_3(CO)_{12}$ and a quinolylcyclopentadienyl molecule.[368] Complexes supported by linked indenyl ligands are rare; however, a dinuclear example, compound **550**, is obtained on heating $Ru_3(CO)_{12}$ with 1,2-bis(3-indenyl)ethane in xylene. The other product from this reaction is $\{Ru(CO)_2(\eta^5\text{-}C_9H_6C_2H_4C_9H_7)\}_2$ **551**, in which each metal center is bonded to a separate bis(indenyl) ligand.[369]



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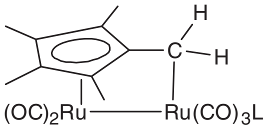

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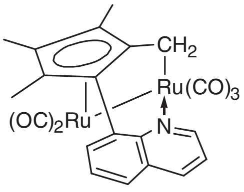

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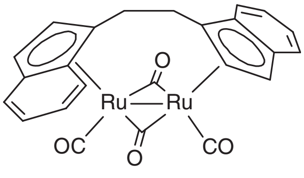
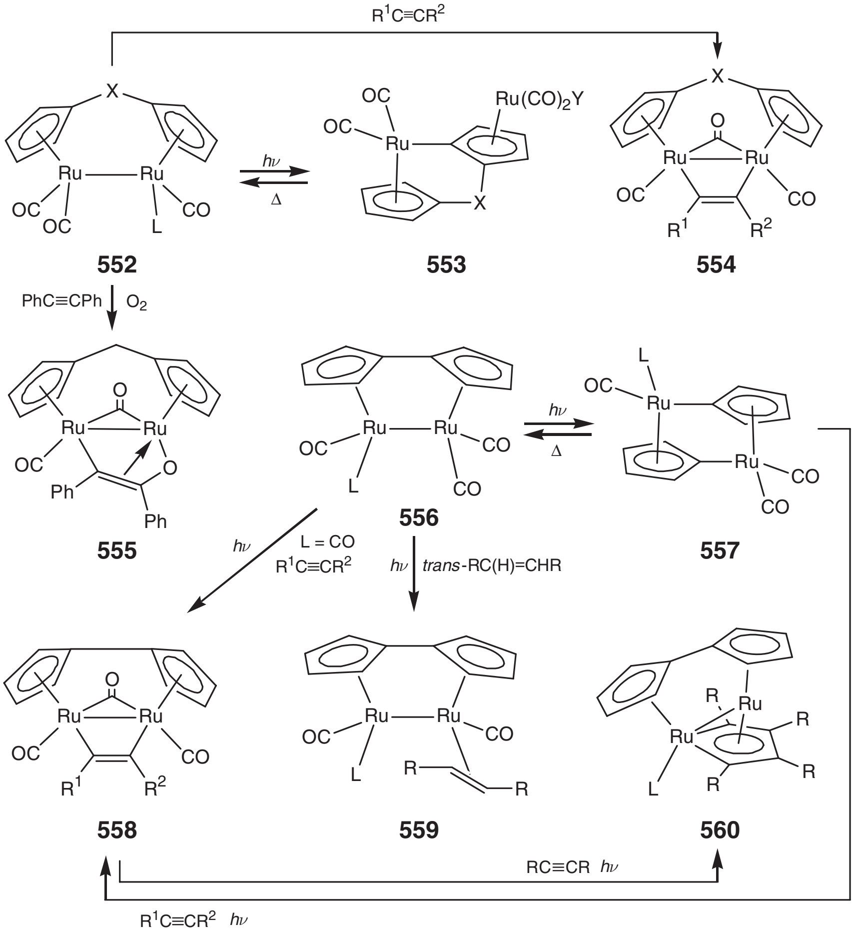
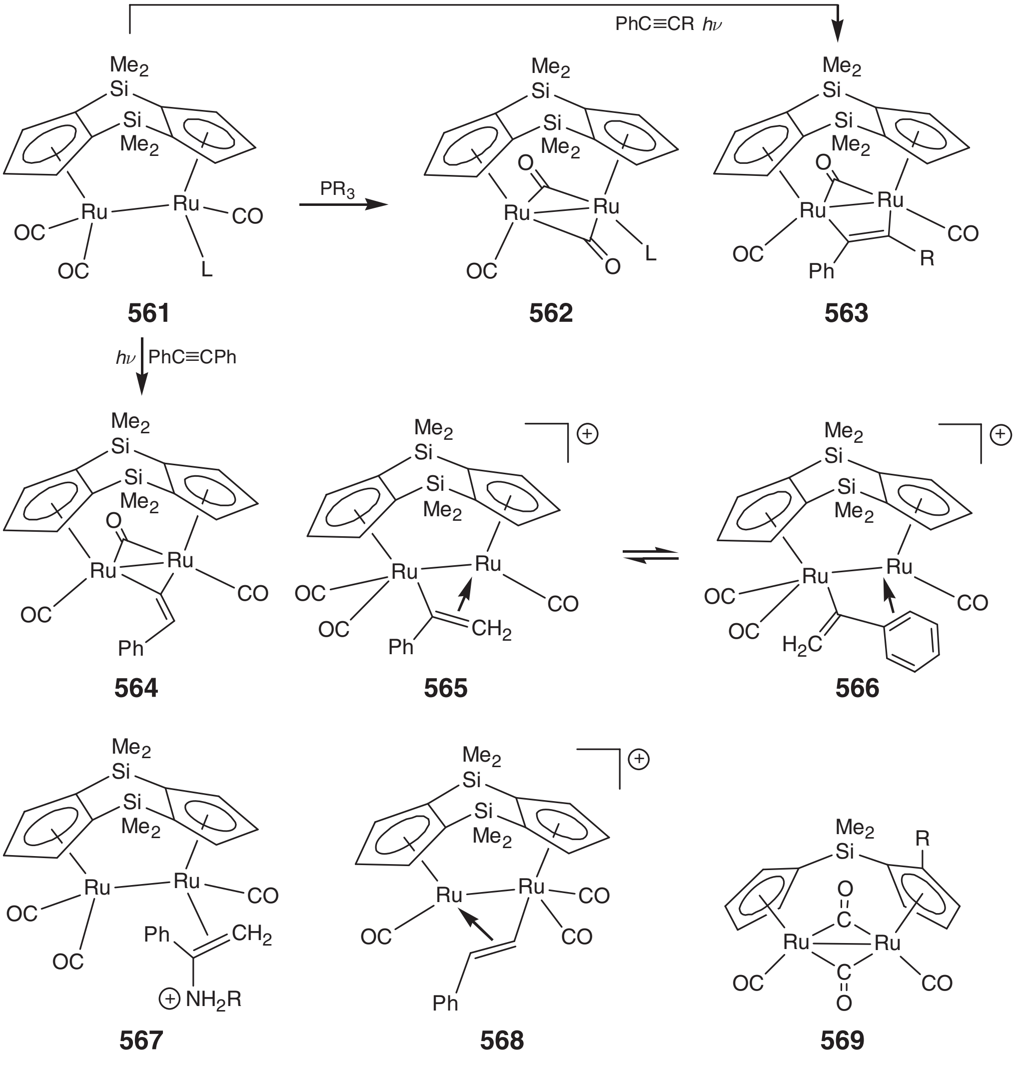


550

A number of ligands consisting of singly- or doubly-linked cyclopentadienyl rings have been employed to bridge the diruthenium unit. In addition to those with silicon linkages described in Section 6.17.2.1.2, the complexes **552** (L = CO; X = CH_2, CH_2CH_2, CMe_2, $SiMe_2$) have been prepared from $\{RuCl_2(CO)_3\}_2$ and bis(cyclopentadienyl)thallium compounds. Small quantities of **553** (X = CMe_2, Y = Cl), which does not contain a diruthenium unit, were also formed in these reactions.[370] The quantitative and efficient conversion of **552** (L = CO, X = CMe_2) to **553** (X = CMe_2, Y = H) on irradiation and the reverse reaction on heating have been investigated using DFT calculations and the results confirmed experimentally by differential scanning calorimetry.[371] Complex **552** (L = CO, X = CH_2) reacts with $R^1C{\equiv}CR^2$ ($R^1 = R^2 = Ph$), under photolytic conditions to yield **554** (X = CH_2).[154] When traces of oxygen are present in the reaction, insertion of oxygen into the Ru–C bond occurs to yield **555** ($R^1 = R^2 = Ph$). Complex **554** ($R^1 = R^2 = Ph$) can be converted to **554** ($R^1 = R^2 = CO_2Me$; $R^1 = H$, $R^2 = Ph$) by acetylene exchange.[154] The ligand-exchange reactions of the related fulvalene complex **556** (L = CO) with PMe_3, PEt_3, and $P(OMe)_3$ lead to formation of **556** (L = PMe_3, PEt_3, and $P(OMe)_3$) under thermal conditions.[372] Under photochemical conditions, in the absence of added ligands, **556** (L = CO) undergoes a rearrangement to compound **557** (L = CO), which is surprising considering the robust nature of fulvalene ligands. This reaction is reversed on heating. The phosphite analog **557** (L = $P(OMe)_3$) is also obtained on irradiation of **556** (L = $P(OMe)_3$). The photochemically induced loss of carbon monoxide from **557** (L = CO) in the presence of $RC{\equiv}CR$ (R = H, Ph, COMe) leads to formation of **558**, the analog of **554**.[372] These studies were later extended to examine the photosubstitution reactions of **556** (L = CO) with alkenes.[373] Irradiation of **556** (L = CO) with *trans*-RCH=CHR (R = CO_2Me) in tetrahydrofuran leads to a mixture of mainly **559** (L = CO) with some **559** (L = *trans*-RCH=CHR) and **559** (L = *cis*-RC(H)=CHR). It was also found that **556** (L = CO) reacts photochemically with $RC{\equiv}CR$ (R = CO_2Me) to first yield **558** ($R^1 = R^2 = CO_2Me$) and then, over extended periods, to form the dimetallacyclopentadiene **560** (R = CO_2Me, L = CO) in good yield. Remarkably, this complex loses the CO ligand under exposure to light in tetrahydrofuran solution to form the highly air sensitive complex **560** (R = CO_2Me, L = thf). Substitution of the solvent in this species with alkenes, thiophene, dimethyl sulfoxide, and triphenylphosphine results in **560** (R = CO_2Me; L = *cis*-RCH=CHR, thiophene, dmso, PPh_3).[373]

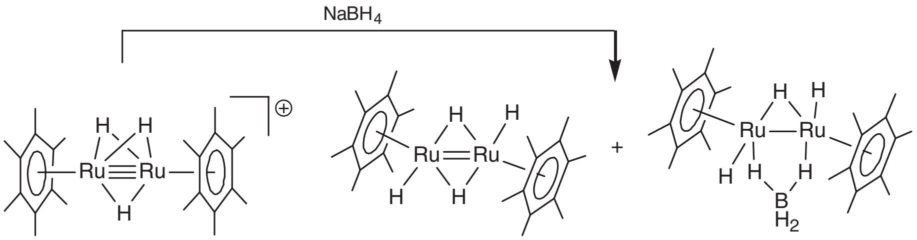


A substantial body of work exists on double silicon-bridged derivatives, such as **561** (L = CO), formed from the reaction of $Ru_3(CO)_{12}$ with $(C_5H_4)_2(SiMe_2)_2$.[374,375] Treatment of **561** (L = CO) with phosphines leads to bridging of the diruthenium unit by the carbonyl ligands in the product **562** (L = PMe_3, PCy_3, PPh_3).[376] With alkynes (PhC≡CR; R = H, Ph), reactions of **561** (L = CO) under photochemical conditions lead to **563** (R = Ph) when R = Ph, whereas **564** is formed when R = H. In both cases other dinuclear compounds without Ru–Ru bonds are also formed.[376] Protonation of **561** (L = CO) leads to $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(\mu\text{-}H)(CO)_4]^+$ (no Ru–Ru bond), which undergoes attack by secondary amines at a carbonyl to give **561** (L = NH_3, NH_2Me, $NHMe_2$, $NH(CH_2(CH_2CH_2)_2O$, $NH(CH_2CH_2)_2CH_2$, $NH(CH_2CH_2)_2$) and the corresponding formamide.[374,375] The same cationic precursor also reacts with alkenes in the presence of Me_3NO to yield **561** (L = $H_2C{=}CH_2$, $H_2C{=}CHMe$). Protonation of these species, to give $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(\text{alkene})(\mu\text{-}H)]^+$, followed by treatment with the desired nucleophile (secondary amine, PMe_3, NaOMe, NaSMe) yields a dinuclear compound and a hydrofunctionalized alkene product.[377] A later report showed how $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(\mu\text{-}H)(CO)_3(C_2H_4)]BF_4$ catalyzes the intermolecular hydroamination of arylalkynes with arylamines to give imines, albeit with a limited catalyst lifetime.[378] The complexes **561** (L = NH_2R), **563** (R = H), **565** and **566** (in equilibrium with each other), and **567** are characterized intermediates in the reaction. Complex **564** is catalytically inactive and is the only ruthenium-containing product at the end of the reaction. Compound **568** was also isolated and characterized structurally.[378] Although relatively robust in the functional group transformations described above, the Si bridges can be removed partially or completely. In $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(\mu\text{-}H)(CO)_4]BF_4$, this can be achieved with $Bu^n{}_4NF$ in tetrahydrofuran with traces of water to give **528** (Cp′ = Cp).[379] Reaction of the same precursor with sodium methoxide in tetrahydrofuran results in removal of only one Si bridge to give **569** (R = H). When this reaction is carried out in methanol, the silicon bridge is broken but the silicon unit retained to yield **569** (R = $SiMe_2OMe$).[379]

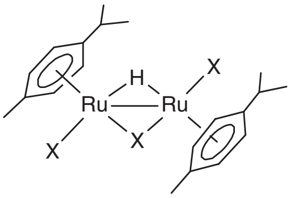


6.17.3.5 Complexes with η^6-arene Ligands

A new route to compound **74** (PF_6^- salt) from the reaction of $[Ru(C_6Me_6)(OH_2)_3]^{2+}$ and $NaBH_4$ has been reported. Under biphasic conditions (water/diethyl ether), further reaction with sodium borohydride results in the dinuclear hydrido species **570** and **571**. In the latter, the borohydride anion bonds to the complex and bridges the dinuclear unit. Two separate fluxional processes can be distinguished in variable-temperature NMR studies of the complex, one centered on the bridging and terminal hydrido ligands and the other involving the coordinated and non-coordinated hydrogen substituents of the BH_4 bridge.[380] The μ-hydrido *para*-cymene complex **572** (X = Cl) reacts with NaF, NaBr, and NaI to yield the corresponding compounds **572** (X = F, Br, I), while treatment with HX leads to the complexes $\{(p\text{-cymene})RuX(\mu\text{-}X)\}_2$ (X = F, Br, I), which contain no Ru–Ru bond.[381] With catechol and 3,5-di-*tert*-butyl-1,2-benzoquinone, $Ru_3(CO)_{12}$ reacts to yield the complexes **573** (R = H) and **573** (R = Bu^t), respectively, along with tetranuclear side-products. Although **573** (R = Bu^t) fragments into mononuclear species on reaction with most Lewis bases, treatment with pyridine leads to the formation of the unusual pyridine adduct **574**, in which two diruthenium units form a cyclic motif with benzoquinone linkages.[382]



74 **570** **571**



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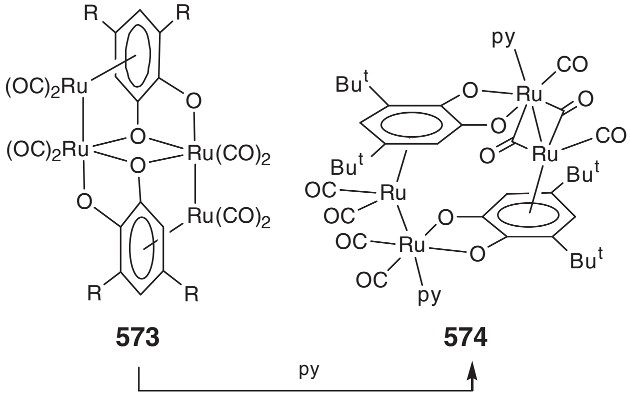

573 **574**

Abbreviations

Tol	4-tolyl (C_6H_4Me-4)
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Bz	benzyl
Cy	cyclohexyl
pz	pyrazolyl
py	pyridine
phen	1,10-phenanthroline
bpy	2,2′-bipyridinyl
dmso	dimethyl sulfoxide
thf	tetrahydrofuran
dcm	dichloromethane

dme	1,2-dimethoxyethane
p-cymene	*p*-isopropyltoluene
DBU	1,8-diazabicylo[5.4.0]undec-7-ene
dppm	bis(diphenylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
acac	acetylacetone, 2,4-pentanedione
LDA	lithium diisopropylamide
TfO$^-$	triflate, trifluoromethanesulfonate
8-quin$^-$	8-quinolate
AcO$^-$	acetate
RT	room temperature
EAN	Effective Atomic Number (rule)

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6.18
Trinuclear Clusters of Ru/Os without Hydrocarbon Ligands

P R Raithby and A L Johnson, University of Bath, Bath, UK

6.18.1 Introduction

This section is dedicated to a description of the chemistries of triruthenium and triosmium clusters that do not contain hydrocarbon ligands. This section should be viewed as an addition to the chemistry described in sections 32.5 and 33 of COMC (1982)[1,2] and section 12 of COMC (1995)[3], as most of the main themes have been developed in the previous two decades. Overall, the interest in the cluster chemistry of ruthenium and osmium during the period 1994–2004 has tended to focus mainly on higher nuclearity and mixed metal clusters in order to enhance the developments in catalysis and bridge the gap between molecular clusters and nanoparticles. However, triruthenium and triosmium clusters continue to play a pivotal role in the chemistry of ruthenium and osmium. Both classes of clusters can be, and are, used extensively as precursors for the synthesis of higher nuclearity clusters as well as the formation of mono- and bimetallic complexes. No up-to-date review of the chemistry of either $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ and their compounds is available, but several annual reviews of the chemistry of ruthenium and osmium, which include the chemistry of the trinuclear clusters, are available.[4–23]

As noted above, $\{Ru_3\}$ and $\{Os_3\}$ systems are used as precursors to a wide range of systems of both higher and lower nuclearity. As such this review has, to a large extent, focused only on the chemistry of trinuclear species as the products of reactions rather than the extensive number of reactions in which they are used as starting materials.

Comprehensive reviews in several areas have appeared; annual reviews for the chemistry of ruthenium and osmium, annual surveys of organometallic cluster chemistry for 1993–2002 have also appeared.[6–14] A review of the of photo-activation of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ for use in the synthesis of both novel target compounds and high nuclearity clusters has been published.[24] A review of low-valent transition metal clusters containing nitrene/imido ligands has appeared.[25] A perspective on the fluxional and dynamic behavior of metal carbonyl clusters has been published.[26] A review describing the chemistry of triruthenium hydride species and their utility and activity in catalytic hydrogenation processes has appeared.[27] The chemistry of triruthenium clusters that carry face-capping amino-pyridine systems[28] and face-capping hererocycles containing pyridinyl nitrogens[29] has been extensively reviewed.

6.18.2 Simple Carbonyls and Carbonyl Hydrides

The synthesis of common starting materials has been reviewed previously,[3] but several new methods for the production of well-known materials have appeared in the literature.

$Ru_3(CO)_{12}$ has been synthesized in reproducibly high yields and under mild conditions (1 atm) by a two-step methodology involving: (i) first carbonylation of $RuCl_3{\cdot}nH_2O$ dissolved in ethylene glycol to give a mixture of tri- and dicarbonyl ruthenium(II) species, probably of the form $Ru(CO)_3Cl_2$(ethylene glycol) and $Ru(CO)_2Cl_2$(ethylene glycol)$_x$ ($x = 1, 2$) and (ii) addition of specific amounts of alkali carbonates and further reductive carbonylation to give the desired ruthenium carbonyl cluster. The selectivity of the second step is controlled by: (i) the nature and quantity of the alkali carbonate (Na_2CO_3 or K_2CO_3); (ii) the gas-phase composition (CO or CO + H_2); and (iii) temperature.[30,31]

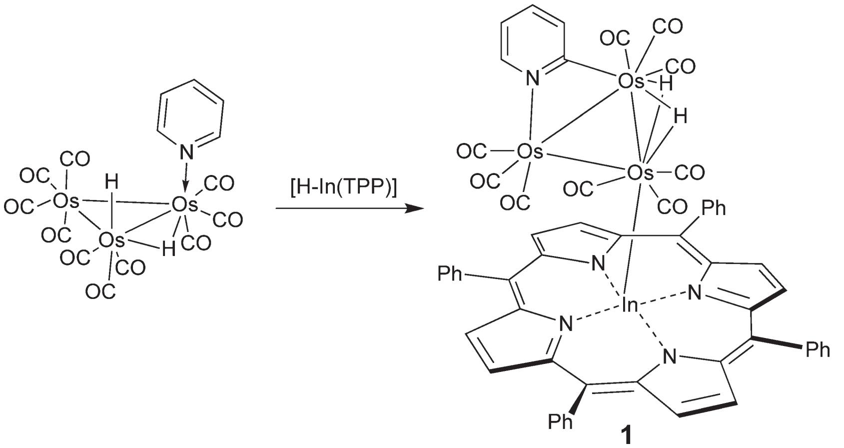
Photolysis has also been used to produce $Ru_3(\mu\text{-}H)_2(CO)_{10}$ from $Ru_3(CO)_{12}$ in the presence of H_2.[32] The reaction of the labile complex $Ru_3(CO)_{11}(NCMe)$ with H_2 under an inert atmosphere also provides an effective route to this highly reactive system.[33]

The anionic hydride species, $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$, has been synthesized in a new one-step reaction of $Ru_3(CO)_{12}$ with 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me_3-TAC). The osmium complex can be synthesized in a comparable fashion by reaction of Me_3-TAC with the more labile $Os_3(CO)_{10}(NCMe)_2$.[34]

It has been well established since the early 1970s that carbonyl fluxionality in metal carbonyl clusters is a ubiquitous phenomenon. $Ru_3(CO)_{12}$ has been examined by high resolution MAS ^{13}C NMR spectroscopy, the results of which, in combination with ^{13}C spin-lattice (T_1) and spin-spin (T_2) relaxation times, have been used to evaluate the activation energy for intramolecular CO exchange of carbonyl groups measured as a function of temperature in CD_2Cl_2 solution.[35]

Although electron counting and bonding within trinuclear clusters is well established, and has been thoroughly covered in COMC (1982)[1,2] and COMC (1995),[3] density functional theory (DFT) and comparative calculations have been used extensively to explore and rationalize behavior and bonding of ligands in trimetallic clusters. The number of such calculations has increased to such an extent that they are somewhat commonplace; as a result, it is difficult to review all the uses of computational experiments in trimetallic cluster chemistry. However, some do warrant mention: SCF, MP2, and DFT levels of theory show that only DFT is able to properly describe the energies of trimetallic clusters with C_{2v} and D_{3h} symmetry from the whole triad of metals. The quantitative computational results, associated with a qualitative MO analysis, allow one to conclude that the structural preferences are determined by a critical balance of metal–bridge bonding, metal–metal bonding, and intermetallic repulsion. Although the M–M bond order is expected to be 1 in all cases, the bridge-supported bond is experimentally and computationally shorter than the unsupported one.[36]

The family of $M_3(CO)_{12}$ (M = Fe, Ru, Os) clusters, where $\{M_3\}$ is any possible combination of Fe, Ru, and Os, has been studied using DFT methods (ADF program). The optimized geometries were compared with those of the clusters, for which structures are available.[37]



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6.18.3 Trinuclear Clusters with Group 13 (Al, Ga, In, and Tl) Donor Ligands

Although reactions between $M_3(CO)_{12}$ (M = Ru and Os) and various group 13 compounds have been known previously, in more recent times such reactions are rare. One of these rare examples is the reaction of $Ru_3(CO)_{12}$ with the gallium(II) species Ga_2Cl_4 in the presence of gallium metal in refluxing toluene, which produces Ru{GaCl(THF)$_2$}{GaCl$_2$(THF)}$_2$(CO)$_3$ and Ru$_2${GaCl$_2$(THF)}$_2$(CO)$_8$ (THF = tetrahydrofuran).[38]

Reaction of the porphyrin indium hydride species In(TPP)H (TPP = 5,10,15,20-tetraphenylporphirinato) with $H(\mu\text{-}H)Os_3(CO)_{10}(C_5H_5N)$ under anaerobic conditions affords the In–Os bonded cluster-porphyrin compound (TPP)In-$Os_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}\eta^2\text{-}C_5H_4N)$ 1. The indium porphyrin moiety occupies an equatorial position on the $\{Os_3\}$ ring, and is bound to the single Os atom that is not bridged by an *N*-heterocyclic ring. The indium porphyrin moiety is looked upon as a one-electron donor.[39]

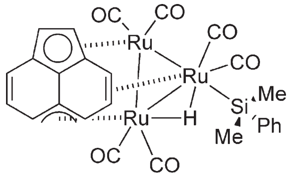
6.18.4 Trinuclear Clusters with Si, Ge, Sn, and Pb Donor Ligands

The reactions of $[Ru_3(CO)_7(\mu\text{-}CO)_3(\mu\text{-}3,5\text{-}Me_2\text{-pyrazole})]^-$ with R_3SiH and R_3SnH have been explored.[40] In a related study, activation of the edge-bridged cluster $Ru_3(CO)_7(\mu\text{-}CO)_3(\mu\text{-pyridazine})$ by 2 equiv. of silane (R_3SiH) or stannane (R_3SnH) affords the clusters $Ru_3(\mu\text{-}H)_2(ER_3)_2(CO)_8(\mu\text{-pyridazine})$ (where $ER_3 = SiEt_3$, $SiPh_3$, $Si(OMe)_3$, $SnBu_3$, or $SnPh_3$). The molecular structure of $Ru_3(\mu\text{-}H)_2(SiEt_3)_2(CO)_8(\mu\text{-pyridazine})$ has been determined by X-ray crystallography.[41]

A study on the reactivity of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)$ with H_2, R_3SiH, and R_3SnH has shown that H_2 reacts with the 1-azavinylidene cluster to give $H_4Ru_4(CO)_{12}$ and H_2NCHPh_2 as the end products, with the imido and amido intermediates $Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}NCHPh_2)$ and $Ru_3(CO)_{10}(\mu\text{-}H)(\mu_3\text{-}HCHPh_2)$, respectively, being observed during the reaction. While no reaction was observed between the starting cluster and tertiary organosilanes, R_3SnH (where $R = Ph$, Bu) readily reacts to afford $Ru_3(CO)_9(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(SnR_3)$, of which in the case of the triphenylstannyl complex the molecular structure has been determined by single crystal X-ray diffraction.[42]

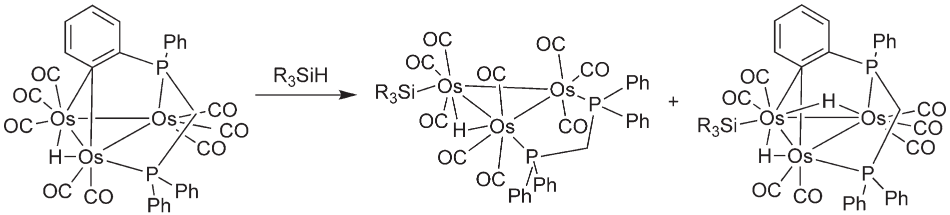
Treatment of the Ru cluster $Ru_3(CO)_7(\mu_3,\eta^2:\eta^3:\eta^5\text{-acenaphthylene})$ with stoichiometric amounts of trialkylsilanes results in liberation of a CO ligand followed by oxidative addition of an Si–H bond and the trinuclear silyl complex $Ru_3(\mu\text{-}H)(SiMe_2Ph)(CO)_6(\mu_3\text{-}\eta^2:\eta^3:\eta^5\text{-acenaphthylene})$ was isolated in good yield. $Ru_3(CO)_7(\mu_3\text{-}\eta^2:\eta^3:\eta^5\text{-acenaphthylene})$ has been shown to be an effective catalyst for the hydrosilylation of olefins, acetylenes, ketones, and aldehydes. In particular, the reactions of aldehydes and ketones proceed at room temperature to form the corresponding silyl ethers in good yield. The reactions with cyclic ethers result in ring-opening polymerization and take place under similar conditions. Polymerization of THF was studied as a representative example. Treatment of trialkylsilanes with an excess of THF (10–102 equiv. with respect to silanes) in the presence of a catalytic amount of triruthenium catalyst gives poly-tetrahydrofuran with $M_n = 1{,}000\text{–}200{,}000$ Da and $M_w/M_n = 1.3\text{–}2.0$. Changes in the ratio of THF to $HSiR_3$ can be used to control the molecular weight distribution of the resulting polymer.[43]

The oxidative addition of $PhMe_2SiH$ to the triruthenium carbonyl cluster $Ru_3(CO)_7(\mu_3\text{-}\eta^5:\eta^5\text{-}4,6,8\text{-trimethylazulene})$, bearing 4,6,8-trimethylazulene, has been studied in relation to mechanisms of hydrosilylation of ketones[44] and vinyl ethers[45] catalyzed by such clusters. Reaction results in the liberation of a CO ligand, oxidative addition of the Si–H bond, and hydrogenation of one carbon–carbon double bond in the azulene ligand to form a novel 46-electron cluster, $Ru_3(\mu\text{-}H)(SiMe_2Ph)(CO)_6(\mu_2\text{-}\eta^3:\eta^5\text{-}4,5\text{-dihydro-}4,6,8\text{-trimethylazulene})$ **2**. Comparison with the diruthenium trimethylazulene complex, which shows no catalytic activity, suggests the existence of a reaction pathway without cluster fragmentation, in which the triruthenium cluster is involved in the catalytic cycle.



2

Oxidative addition of the silanes R_3SiH ($R_3 = Ph_3$, Et_3, $EtMe_2$) to the unsaturated cluster $Os_3(\mu\text{-}H)\{\mu_3\text{-}Ph_2PCH_2PPh(C_6H_4)\}(CO)_8$ **3** results in the formation of clusters of the general form $Os_3(\mu\text{-}H)(SiR_3)(CO)_9(\mu\text{-dppm})$ **4–6** and $Os_3(\mu\text{-}H)_2(SiR_3)\{\mu_3\text{-}Ph_2PCH_2PPh(C_6H_4)\}(CO)_7$ **7–9**. Single crystal X-ray diffraction analysis reveals the structure of $Os_3(\mu\text{-}H)(SiPh_3)(CO)_9(\mu\text{-dppm})$ to be one in which all non-CO ligands are coordinated equatorially and the hydride and the silyl groups are mutually *cis*. Variable-temperature NMR spectra show highly fluxional systems with rapid exchange of H and SiR_3 groups. The synchronous motion of H and SiR_3 only occurs when these ligands are mutually *cis*, and this process probably requires the formation of a transient silane complex $Os_3(\eta^2\text{-}HSiR_3)(CO)_9(\mu\text{-dppm})$. Protonation of $Os_3(\mu\text{-}H)(SiR_3)(CO)_9(\mu\text{-dppm})$ systems to give $[Os_3(\mu\text{-}H)_2(SiR_3)(CO)_9(\mu\text{-dppm})]^+$ totally suppresses the dynamic behavior because there are no edge vacancies.[46]



3

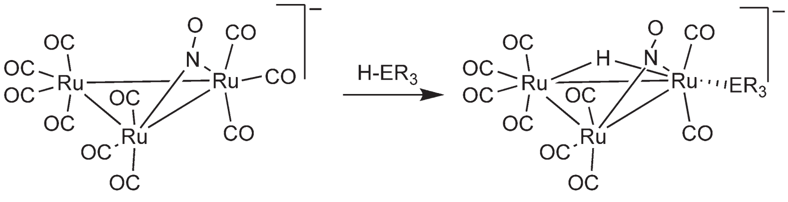
4: $SiR_3 = SiPh_3$
5: $SiR_3 = SiEt_3$
6: $SiR_3 = SiEtMe_2$

7: $SiR_3 = SiPh_3$
8: $SiR_3 = SiEt_3$
9: $SiR_3 = SiEtMe_2$

Thermal reactions of the bulky siloxysilanes $HSi(OSiMe_3)_3$ and $HSiMe(OSiMe_3)_2$ with $Ru_3(CO)_{12}$ led to the formation of siloxyl-substituted triruthenium clusters, in which oxidative addition and replacement of one, or more, CO ligands from $Ru_3(CO)_{12}$ generates the triruthenium clusters $Ru_3H(CO)_{11}\{Si(OSiMe_3)_3\}$, $Ru_3H_2(CO)_{10}\{Si(OSiMe_3)_3\}_2$, $Ru_3H(CO)_{11}\{SiMe(OSiMe_3)_2\}$, and $Ru_3H_2(CO)_{10}\{SiMe(OSiMe_3)_2\}_2$. Further loss of CO from $Ru_3H(CO)_{11}\{Si(OSiMe_3)_3\}$ and $Ru_3H(CO)_{11}\{SiMe(OSiMe_3)_2\}$ and formation of a dative SiO→Ru interaction results in the formation of $Ru_3H(CO)_{10}\{\mu\text{-}Si(OSiMe_3)_3\}$ and $Ru_3H(CO)_{10}\{\mu\text{-}SiMe(OSiMe_3)_2\}$, respectively. The siloxyl-substituted compounds are thermodynamically unstable and decompose within several hours.[47]

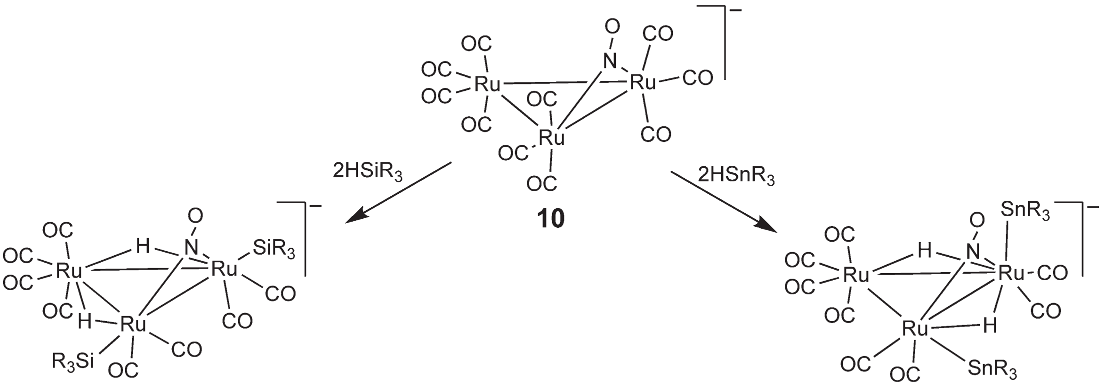
The tin(II) complexes, SnR_2 (R = 2,4.6-triisopropylphenyl) and the trimer $(SnR_2)_3$, react with $Ru_3(CO)_{12}$ to produce $Ru_3(CO)_{10}(\mu\text{-}SnR_2)_2$ and $Ru_3(CO)_9(\mu\text{-}SnR_2)_3$. Use of $Ru_3(CO)_{10}(\mu\text{-dppm})$ in place of $Ru_3(CO)_{12}$ and $(SnR_2)_3$ leads to $Ru_3(CO)_8(\mu\text{-dppm})(\mu\text{-}SnR_2)_2$. Comparatively, $Ru_3(CO)_{10}(\mu\text{-dppm})$ and the monomeric tin reagent SnR_2 yields the diruthenium complex $Ru_2(CO)_6(\mu\text{-dppm})(\mu\text{-}SnR_2)$. The molecular structures of all four clusters have been determined.[48]

The PPN salt of the edge-bridged cluster anion $[Ru_3(\mu\text{-}NO)(CO)_{10}]^-$ **10** reacts with 1 or 2 equiv. of tertiary silanes and stannanes to give trinuclear $[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)(ER_3)(CO)_9]$ **11–14** or $[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)_2(ER_3)_2(CO)_8]$ **15–18**, respectively ($ER_3 = SiEt_3$, $SiPh_3$, $SnBu_3$, $SnPh_3$).[49]



10

11: $ER_3 = SiEt_3$
12: $ER_3 = SiPh_3$
13: $ER_3 = SnBu_3$
14: $ER_3 = SnPh_3$



10

15: R = Et
16: R = Ph

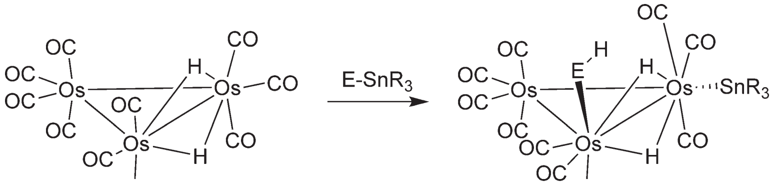
17: R = Bu
18: R = Ph

The kinetics and mechanism of HER_3 (where E = Si, R = Et; E = Ge, Sn, R = Bu; E = Sn, R = Ph) addition to $H_2Os_3(CO)_{10}$ have been investigated. Products of the general formula $H_3Os_3(CO)_{10}(ER_3)$ are formed initially in these reactions. In the case of $HSiEt_3$ the reaction is reversible, with a K_{eq} of $100\,M^{-1}$ at 303 K. The rate law is found to be first order in HER_3 and the cluster.[50]

The triruthenium cluster complex $Ru_3(\mu_3\text{-}\eta^3(C,N,N)\text{-Habq})(CO)_9$ (H_2abqH = 2-amino-7,8-benzoquinoline) reacts with tertiary stannanes at room temperature (but not with tertiary silanes) to give $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-Habq-}C,N,N)(SnR_3)(CO)_8$ (R = Ph, Bu). These compounds slowly release HR at room temperature to afford $Ru_3(\mu_3\text{-}\eta^3(C,N,N)\text{-Habq})(\mu\text{-}SnR_2)(\mu\text{-}CO)(CO)_7$, which contain bridging stannylene ligands.[51]

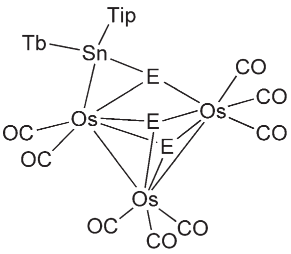
Mechanistic studies of the hydrosilylation of diphenylacetylene using the cluster complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy})(CO)_9$ and $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy})(CO)_8(PPh_3)$ (Hampy = 2-amino-6-methylpyridine) as catalysts, show that initial reaction between the cluster and $HSiR_3$ results in oxidative addition of Si–H across an Ru–Ru bond and the formation of the compounds $Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})\{Si(OMe)_3\}(CO)_8$, $Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(SiR_3)_2(CO)_8$ (R = Et, OMe), $Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1:\eta^2\text{-PhC:CHPh}\}(SiR_3)(CO)_7$ (R = Et, OMe), and $Ru_3(\mu_3\text{-}\eta^2\text{-ampy})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-PhC=CHPh}\}(SiEt_3)(CO)_6(PPh_3)$. In these compounds the $-SiR_3$ and diphenylalkenyl groups coexist in the ligand shell of triruthenium clusters, but are attached to different ruthenium atoms. It is thought to be for this reason that these clusters are unsuccessful as catalysts for hydrosilylation.[52] In a related investigation into the hydrostannation of diphenylacetylene catalyzed by triruthenium clusters, an identical reaction pathway and need for –$SnPh_3$ and diphenylalkenyl groups to be attached to the same ruthenium atom has been revealed. Sequential reactions of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy})(CO)_9$ with diphenylacetylene and R_3SnH (R = Bu, Ph) and of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy})(CO)_9$ with R_3SnH and diphenylacetylene result in the isolation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy})(SnR_3)_2(CO)_8$ and one of two isomers of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy})(SnR_3)(\mu\text{-}\eta_1:\eta_2\text{-PhC{=}CHPh})(CO)_7$.[53]

The reactions of aminotributylstannanes (E-$SnBu_3$) or aminotrimethylstannanes (E-$SnMe_3$) with $Os_3(\mu\text{-}H)_2(CO)_{10}$ afford the heterometallic clusters $Os_3(\mu\text{-}H)(CO)_{10}(HE)(SnR_3)$ (HE = H-dimethylamine, H-pyrrolidine, H-piperidine, and H-morpholine) **19–26**. In the case of pyrrolidine tributylstannane derivative, C–H bond activation of the secondary amine moiety occurs to produce $Os_3(\mu\text{-}H)(CO)_{10}(N{=}CHCH_2CH_2CH_2)(SnBu_3)$. In all these heterometallic clusters the secondary amine ligand occupies a weak axial coordination site on the Os triangle, the stannyl ligand ($SnBu_3$ or $SnMe_3$) occupying an equatorial position on the Os triangle, as expected for a bulky substituent.[54]

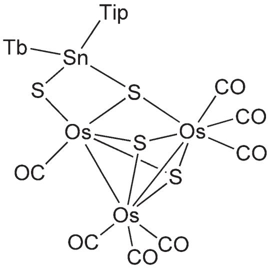


19: EH = Me_2NH; R = Me
20: EH = Me_2NH; R = *n*-Bu
21: EH = $(CH_2)_4NH$; R = Me
22: EH = $(CH_2)_4NH$; R = *n*-Bu
23: EH = $(CH_2)_5NH$; R = Me
24: EH = $(CH_2)_5NH$; R = *n*-Bu
25: EH = $O(CH_2)_4NH$; R = Me
26: EH = $O(CH_2)_4NH$; R = *n*-Bu

Reactions of the 1,2,3,4,5-tetrachalcogenastannolanes $Tb(Tip)SnE_4$ (E = S or Se; Tip = 2,4,6-triisopropylphenyl; Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) with $Os_3(CO)_{12}$ afforded the triosmium complexes $(\mu_3\text{-}E)_3\text{-}Os_3(CO)_8\{Tb(Tip)Sn\}$ (E = S, Se) **27, 28** together with triosmium complexes $(\mu_2\text{-}S)_3(\mu_2\text{-}S)Os_3(CO)_7\{Tb(Tip)Sn\}$ **29** and the diosmium complexes $(\mu_3\text{-}E)_2Os_2(CO)_6\{Tb(Tip)Sn\}$ (E = S and Se). In the case of $Ru_3(CO)_{12}$, these reactions result in the formation of triruthenium complexes $(\mu_3\text{-}E)_3(\mu_2\text{-}E)Ru_3(CO)_7\{Tb(Tip)Sn\}$ (E = S, Se) **30, 31** and diruthenium complexes $(\mu_3\text{-}E)_2Ru_2(CO)_6\{Tb(Tip)Sn\}$ (E = S, Se).[55]



27: E = S
28: E = Se



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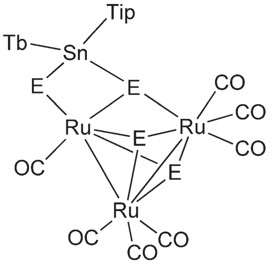
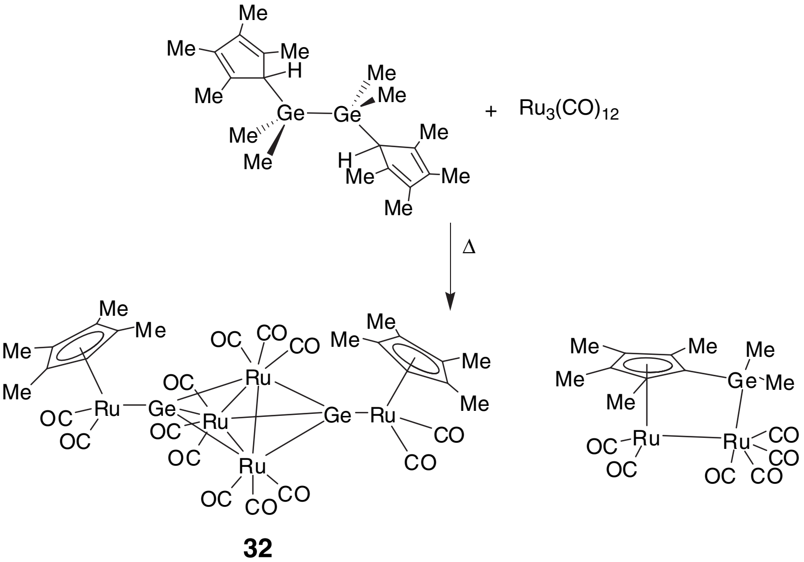


30: E = S
31: E = Se

Photolysis of $\{Os(CO)_4(GeMe_2)\}_2$ in hexane affords the known $\{Os(CO)_3(GeMe_2)\}_3$ as the major product, along with the new clusters $Os_3(GeMe_2)_2(CO)_{11}$ and $Os_4(GeMe_2)_4(CO)_{12}$. The skeleton of $Os_3(GeMe_2)_2(CO)_{11}$ consists of two $\{Os_2Ge\}$ triangles that share a common osmium atom, in a "bow-tie" arrangement.[56]

Reaction of $\{(tBuC_5H_4)Ge\}_2$ with $Ru_3(CO)_{12}$ in refluxing nonane results in extensive thermal rearrangement and the formation of the triruthenium cluster $Ru_3(CO)_9\{\mu_3\text{-}Ge\text{-}Ru(CO)_2(\mu_5\text{-}t\text{BuC}_5H_4)\}_2$ **32** which has been isolated and structurally characterized.[57]



32

Treatment of $Pb(CH_2SiMe_3)_2$ with $Ru_3(CO)_{12}$ affords $Ru_3(CO)_9(\mu\text{-}CO)_2\{Pb(CH_2SiMe_3)_2\}$ and $Ru_3(CO)_9(\mu\text{-}CO)\{Pb(CH_2SiMe_3)_2\}_2$. Single crystal X-ray analysis of the latter of these two clusters reveals the presence of a planar pentametallic core where the two PbR_2 groups bridge two sides of the $\{Ru_3\}$ triangle.[58]

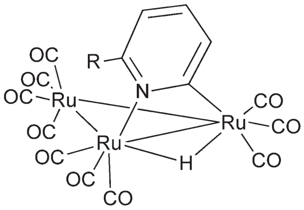
6.18.5 Trinuclear Clusters with N-Donor Ligands

Nitrogen-donor ligands make up a considerable proportion of the systems that this survey covers. As such, a large number of systems such as pyridine and heteroatom-containing benzocycles have been included, but focus is given toward the heteroatom and its binding to the $\{Ru_3\}$ and $\{Os_3\}$ cluster units.

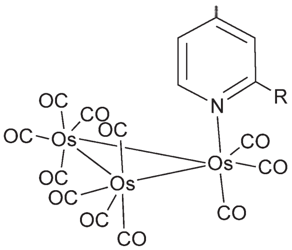
The reaction of $Ru_3(CO)_{12}$ with [PPN][N_3] yields the isocyanato complex $[Ru_3(NCO)(\mu\text{-}CO)_2(CO)_9]^-$. Kinetic measurement of this rapid reaction reveals a first-order rate law in both cluster and azide (rate $= k[Ru][N_3^-]$) with the activation parameters $\Delta H^{\ddagger} = 61.6 \pm 3.4\,\text{kJ mol}^{-1}$ and $\Delta S^{\ddagger} = 3.5 \pm 11.8\,\text{J K}^{-1}\,\text{mol}^{-1}$.[59]

The solution structures and the dynamic behavior of the acetonitrile-substituted cluster compounds $M_3(CO)_{12-x}(NCMe)_x$ ($M = Os$, $x = 1$ or 2; $M = Ru$, $x = 1$, 2, or 3) have been investigated by ^{13}C NMR spectroscopy. The acetonitrile ligands in the above complexes adopt axial positions. In the bisubstituted derivatives the nitriles are bound to different metal atoms on opposite sides of the metal plane and in the trisubstituted compound two of the three nitrile ligands lie on the same side of the metal plane. Like the parent metal carbonyls $M_3(CO)_{12}$ ($M = Ru$, Os), the osmium derivatives and the mono-substituted ruthenium derivative have ground-state structures in which all CO ligands are terminally bound. The bi- and trisubstituted ruthenium complexes also contain bridging CO ligands. All the complexes are fluxional in solution and the fluxionality is dependent upon the degree of nitrile substitution.[60]

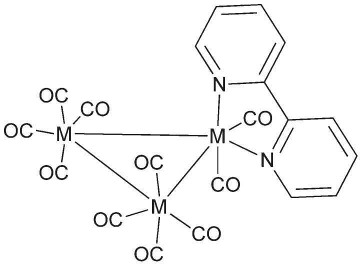
Photochemical activation of triruthenium and triosmium dodecacarbonyls in the presence of nitrogen-containing heterocycles results in the isolation of photosubstitution products. Reaction of $Ru_3(CO)_{12}$ with pyridine results in *ortho*-metalation and formation of the C–H activated complex $Ru_3(\mu\text{-}H)(CO)_{10}(C_5H_4N)$ **33**, whereas in the case of osmium the simple substitution product $Os_3(CO)_{11}(py)$ **34** is isolated. With 2-methylpyridine the products $Ru_3(\mu\text{-}H)(CO)_{10}(2\text{-}MeC_5H_3N)$ **35** and $Os_3(CO)_{11}(2\text{-}MeC_5H_4N)$ **36** are formed from the respective dodecacarbonyls. Photolysis of the $\{Ru_3\}$ and $\{Os_3\}$ staring materials in the presence of 2,2′-bipyridine (bpy) leads to the formation of $M_3(CO)_{10}(bpy)$ **37, 38** complexes. Similarly reactions with the dinitrogen heterocycle pyridazine (pydz) lead to the formation of $M_3(CO)_{10}(pydz)$ **39, 40**.[61] In a related study into the reaction of triruthenium systems with ethylpyridine, the complex, $Ru_3(\mu\text{-}H)(CO)_{10}(2\text{-}EtC_5H_3N)$, has been isolated and its molecular structure elucidated.[62] The molecular structure of the bis(*ortho*-metallated) complex $Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}NC_5H_4)_2$ has also been reported.[63]



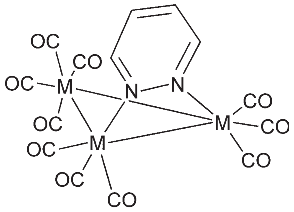
33: R = H
35: R = Me



34: R = H
36: R = Me



37: M = Ru
38: M = Os



39: M = Ru
40: M = Os

The reaction between $Ru_3(\mu\text{-AuPPh}_3)(\mu\text{-Cl})(CO)_{10}$ and pyridine afforded a mixture of products including $Ru_3(\mu\text{-H})(\mu\text{-NC}_5H_4)(CO)_9(PPh_3)$, $Ru_3(\mu\text{-Cl})_2(CO)_8(NC_5H_5)(PPh_3)$, and $Ru_3(\mu\text{-Cl})_2(CO)_8(NC_5H_5)_2$.[64]

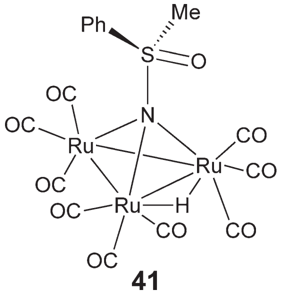
The complexes $Os_3(CO)_{10}(L)$ (L = 2,2′-bipyridine, 2,2′-bipyrimidine (bpym), 2,3-dipyrid-2-ylpyrazine (dpp), and 2,3-dipyrid-2-ylbenzoquinoxaline (dpb)) have been synthesized by photochemical activation of $Os_3(CO)_{12}$. Their low energy Os to ligand charge transfer (MLCT) transitions have been characterized by Raman spectroscopy.[65] In a related study, irradiation of the clusters $Os_3(CO)_{10}(L)$ (L = pyridine-2-carbaldehyde-*N*-R-imine (R-PyCa) R = $Me_2N(CH_2)_2$, $Me_2N(CH_2)_3$, (2-pyridyl)$(CH_2)_2$; L = 2-acetylpyridine-N-R-imine (R-AcPy), R = $Me_2N(CH_2)_2$, (2-pyridyl)$(CH_2)_2$) with visible light results in CO insertion into Os–N bonds to form novel CO–bridged photoproducts.[66]

Reaction of the activated complex $Os_3(CO)_{10}(NCMe)_2$ with *trans*-1, 2-bis(2-pyridyl)ethene results in addition of the ethene group to the cluster and the formation of a series of triosmium clusters with pyridyl coordination.[67]

The solid–gas reactions between $Os_3(CO)_{11}(NCMe)$ or $Os_3(CO)_{11}(CH_2CH_2)$ with gaseous NH_3 result in substitution of the axial acetonitrile and the equatorial ethene ligand to afford $Os_3(CO)_{11}(NH_3)$. The single crystal X-ray diffraction analysis shows the NH_3 to be coordinated in an axial position.[68]

The reactions of ammonia with either $Ru_3H(\mu\text{-H})(\eta\text{-CO})(CO)_{10}$ or $Os_3H(\mu\text{-H})(CO)_{11}$ in CD_2Cl_2 solutions yield $[NH_4][M_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]$ (M = Ru, Os). When the reactions are followed at low temperature (183 K) by means of ^1H, ^{13}C, and ^{15}N NMR spectroscopy, it is possible to detect the formation of kinetic products which are derived from the addition of an ammonia molecule to a carbonyl carbon atom. In the Ru case, ammonia is bonded to the bridging carbonyl carbon atom and maintains its wholeness. In the Os system a carbamoyl moiety is formed by transfer of one hydrogen atom from NH_3 to the oxygen atom of the carbonyl group to form an O–H bond.[69]

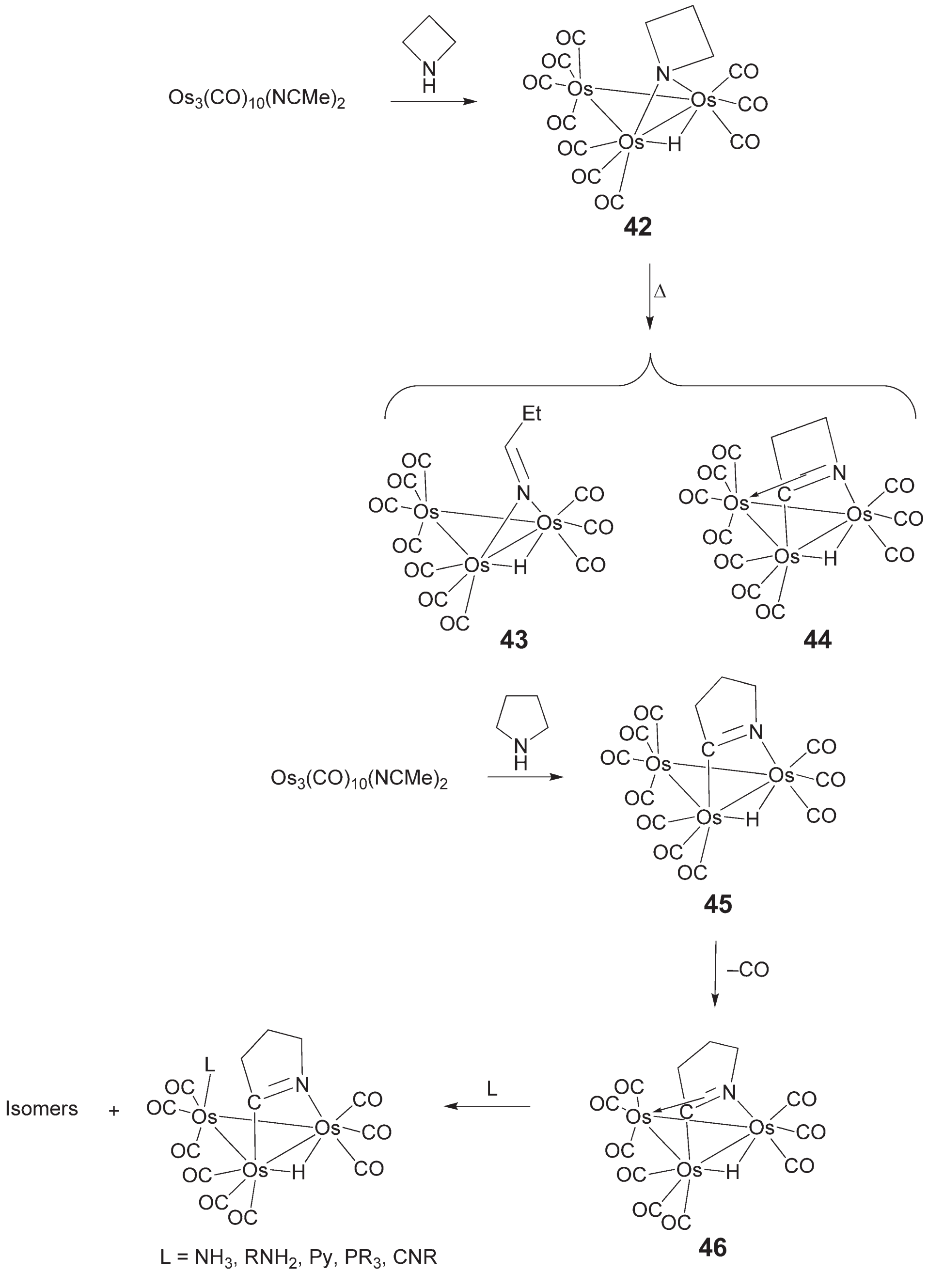
The triosmium cluster $Os_3(\mu\text{-H})_2(CO)_8(\mu_3\text{-S})(L)$ (L = the enatiomerically pure amine (*S*)-$H_2NCHPhMe$) has been synthesized and the "turn-stile" rotational fluxionality of the $\{Os(CO)_2L\}$ unit studied.[70]



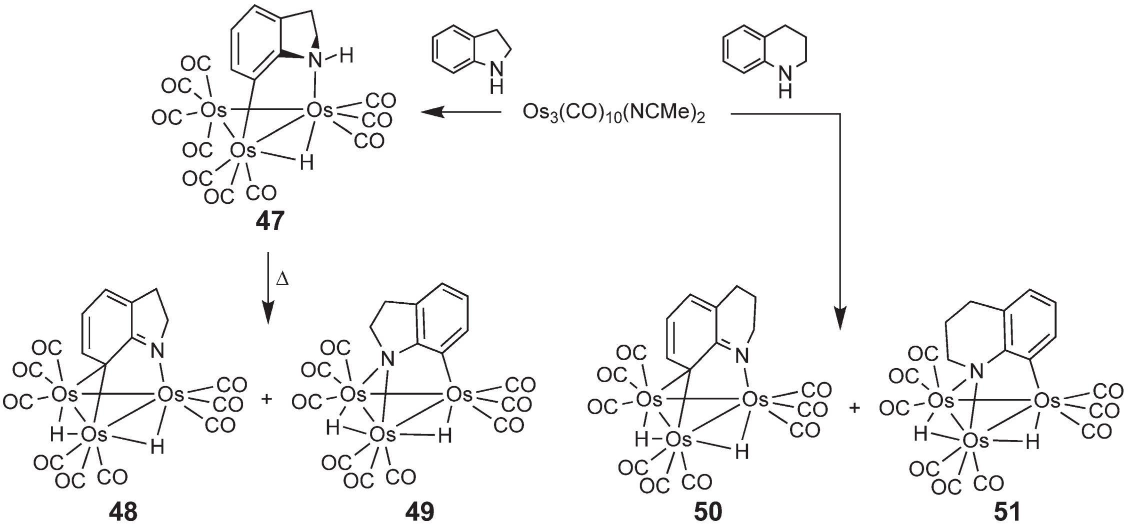
41

Reaction of $Ru_3(CO)_{12}$ with the chiral acid (*R*)-MePhS(O)NH results in the formation of the cluster $Ru_3(CO)_9$-$(\mu\text{-H})\{\mu_3\text{-NS(O)MePh}\}$**41**.[71] Triruthenium clusters containing other methylsulfoximido capping or bridging groups have been examined by DFT and extended Hückel theory (EHT) in order to analyze the bonding between the cluster and the sulfoximido ligand.[72] The reaction of **41** with 4-$NO_2C_6H_4C{\equiv}C$-Ph has also been investigated.[73]

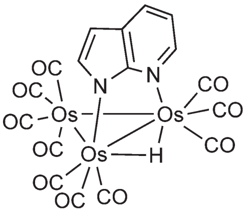
Reaction of azetidine with $Os_3(CO)_{10}(NCMe)_2$ yields the N–H activated complex $Os_3(CO)_{10}(\mu\text{-H})\{\mu\text{-N}(CH_2)_3\}$ **42** in which the azetidine bridges two of the osmium atoms via the nitrogen atom. Thermal activation of this complex results in both C–H activation and ring opening to form $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-N}{=}CHEt)$ **43** and $Os_3(CO)_{10}(\mu\text{-H})(\mu_3\text{-}NCH_2CH_2C)$ **44**, as well as a small amount of a penta-osmium cluster.[74] The related complex $Os_3(CO)_9(\mu\text{-H})\{\mu_3\text{-}\eta^2\text{-}C{=}N(CH_2)_3\}$ **46**, formed from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $HN(CH_2)_4$, reacts with a range of nitrogen donors (L = NH_3, RNH_2 (R = *n*-Bu, *i*-Bu, *s*-Bu, *t*-Bu), $BzNH_2$, pyridine, RCN (R = Me, Ph)), and phosphines (L = PR_3, R = Ph, Me, OMe). Attack of the donor ligand on the cluster results in displacement of the C=N π-bond and coordination of the donor ligand to the osmium atom that is not connected to the imidoyl ligand. The kinetics of the reactions and the distribution of the *syn*- and *anti*-product isomers and factors affecting them have also been investigated.[75]



Indoline reacts with $Os_3(CO)_{10}(NCMe)_2$ at room temperature to form $Os_3(CO)_{10}(\mu\text{-H})(\mu_3\text{-}\eta^2C_8H_7N)$ **47**, which thermally decarbonylates to give a mixture of tautomeric complexes $Os_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}C_8H_7N)$ **48, 49** whose structures differ by having a μ-alkylidene-imido bonding mode versus a μ–amido–aryl bonding mode. In the case of the reaction of tetrahydroquinoline with $Os_3(CO)_{10}(NCMe)_2$, no analog of **47** is isolated, but a pair of tautomers analogous to **48** and **49**, $(Os_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}C_9H_9N))$ **50, 51**, is formed.[76]



The reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1 equiv. of 7-azaindole (HL) at room temperature leads to two structural isomers of formula $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-L})$ **52, 53**. The coordinating 7-azaindole bridges along an edge of the triosmium triangle with both nitrogen atoms bound to two osmium atoms in complex **52**. However, the ligand was found to be *ortho*-metallated in complex **53**. A minor product, $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-L})$, in which the pyridinic and pyrrolic nitrogen atoms coordinate to the osmium triangle, was also isolated **54**.[77]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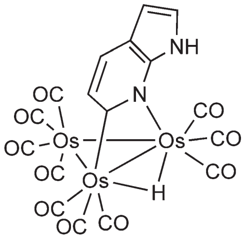
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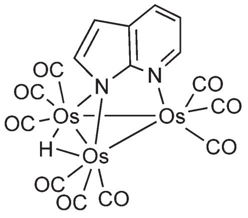
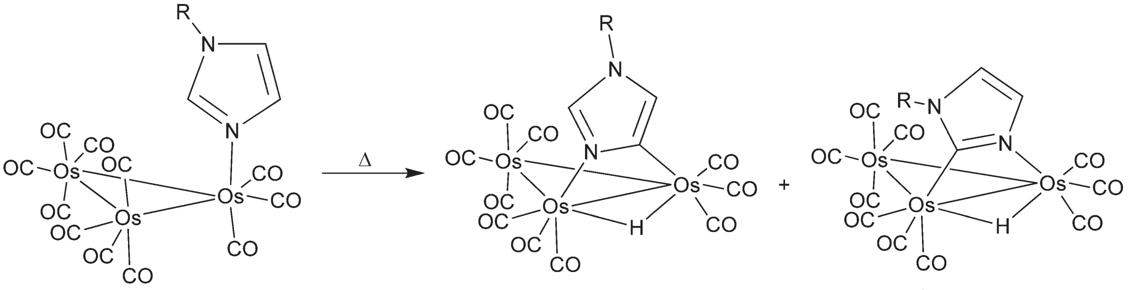

54

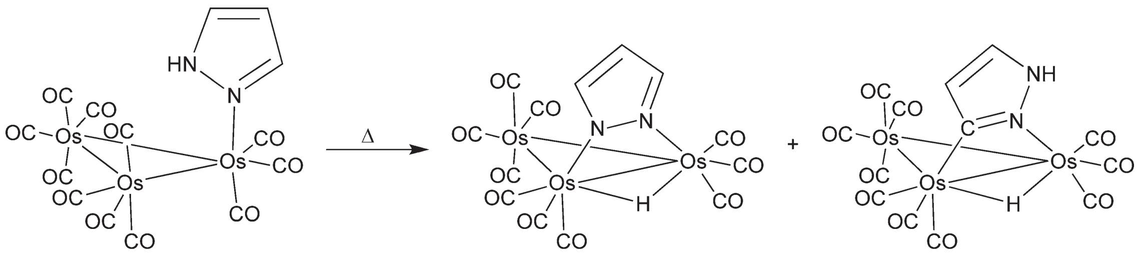
Reactions of $Os_3(CO)_{11}(NCMe)$ with imidazole, 1-vinylimidazole, or pyrazole result in the formation of the complexes $Os_3(CO)_{11}(L)$ **55, 56, 61**, respectively. Thermolysis of these complexes results in loss of CO and the formation of complexes with the general formula $Os_3(H)(CO)_{10}(\mu\text{-L})$ **57, 58, 59, 60, 62, 63**. In the case of vinylimidazole and imidazole, the isomers are formed by the activation of the two C–H bonds adjacent to the nitrogen atom. In the case of pyrazole, the two isomers are formed by either C–H or N–H activation. The corresponding reactions of 1-vinylimidazole and imidazole with $Ru_3(CO)_{12}$ in the presence of sodium diphenylketyl yields ruthenium compounds that are analogous to the osmium clusters.[78]



55: R = H
56: R = $CHCH_2$

57: R = H
58: R = $CHCH_2$

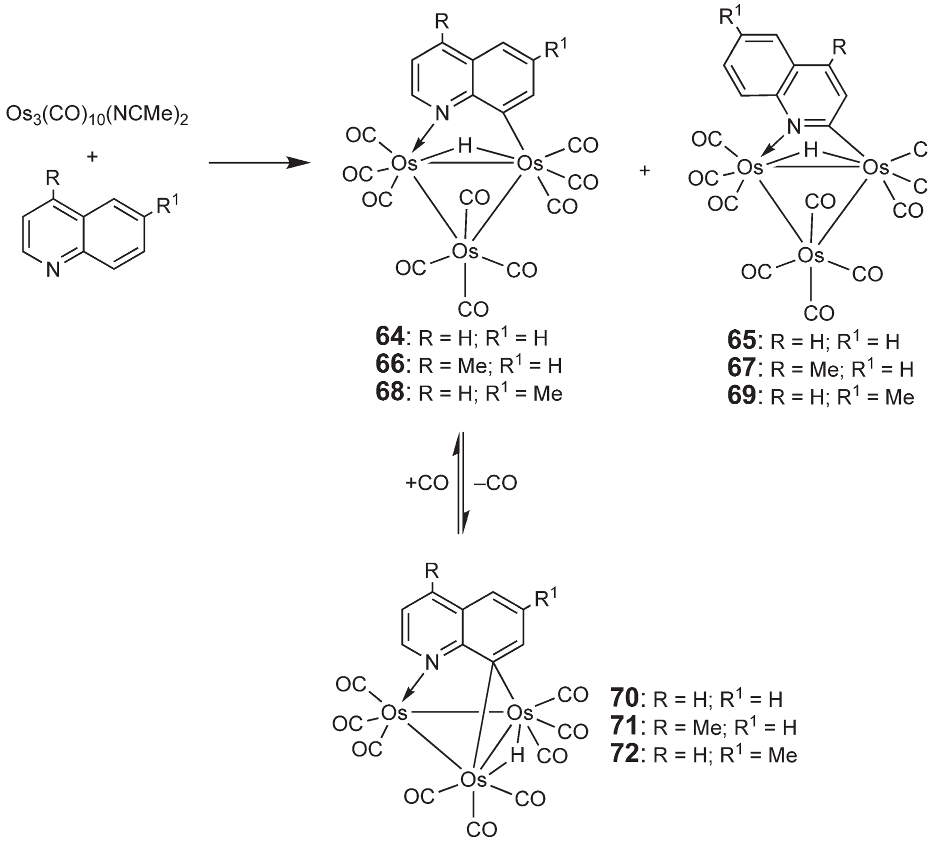
59: R = H
60: R = $CHCH_2$



61 **62** **63**

The reactions of $Os_3(CO)_{10}(NCMe)_2$ with quinolines at room temperature yield a series of complexes of the general form $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^2\text{-}C_9H_4RR'N)$ **64–69**. Of these two structural isomers, only the 1,8-*N*,*C*-bridging isomer loses CO reversibly to form the formally electron-deficient 46-electron quinoline complexes $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_4RR'N)$ **70–72**.[79] Reduction of the coordinated quinoline ring by H_2/D_2[80] and *para*-dihydrogen[81] and the sequential reactions with hydride donors, for example $Li[Et_3BH]$, and protonation have also been investigated.[80] Extensive chemistry concerning the reaction and functionalization of these species by reactions with a wide range of carbanions has been published.[82] NMR studies of **70** and other derivatives show that the quinoline ligand undergoes dynamic σ–π interchange processes, which are thought to have an effect on the stereochemistry of nucleophilic attack on the quinoline ring.[83]

Coordination of ammonia and aliphatic amines RNH_2 (R = Et, *n*-Bu, *s*-Bu, *t*-Bu, cyclohexyl) and Et_2NH to the osmium clusters $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)$ and $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}\eta^2\text{-}XC_9H_5N)$ (X = 5-NH_2, 3-NH_2, 6-NH_2, 5-Br, 5-CH_3) has been extensively studied. Initial formation of the adducts and the ratio of isomers formed, and their variation with change in temperature and solvent polarity have also been studied.[84]

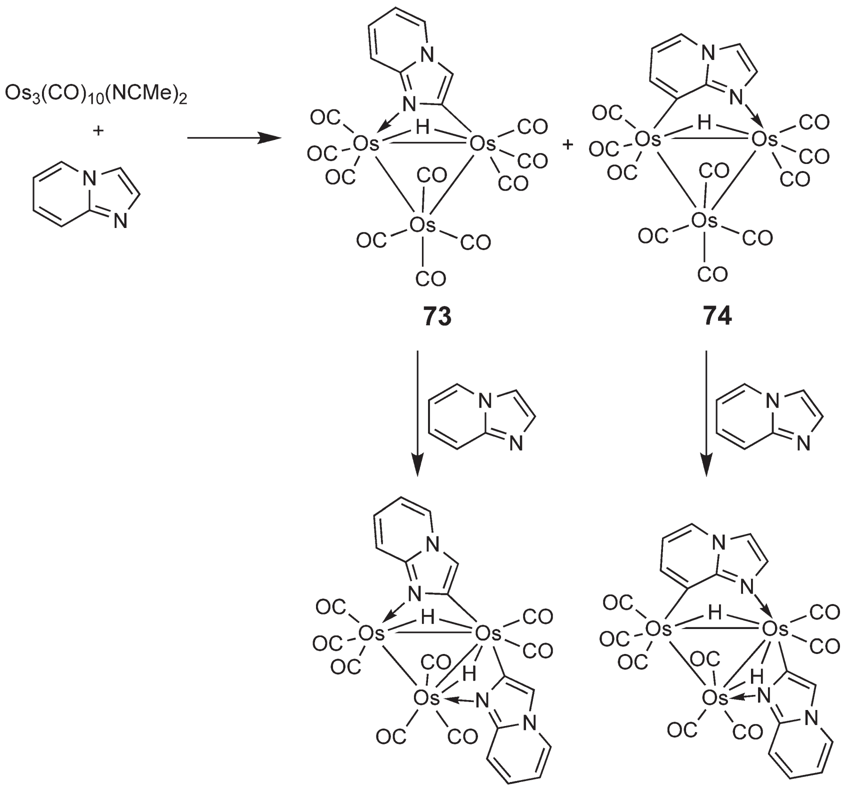


64: R = H; R^1 = H
66: R = Me; R^1 = H
68: R = H; R^1 = Me

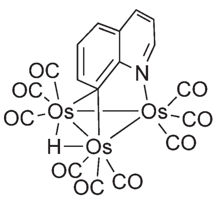
65: R = H; R^1 = H
67: R = Me; R^1 = H
69: R = H; R^1 = Me

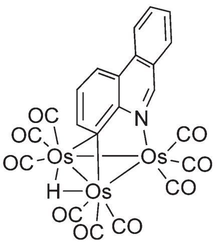
70: R = H; R^1 = H
71: R = Me; R^1 = H
72: R = H; R^1 = Me

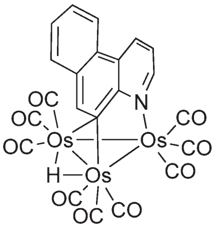
Similarly, treatment of $Os_3(CO)_{10}(NCMe)_2$ with an excess of imidazopyridine yields the C–H activated complexes $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}1,2\text{-}\eta^2\text{-}C_7H_5N_2)$ and $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}1,7\text{-}\eta^2\text{-}C_7H_5N_2)$, the structures of which differ with respect to the C–H group that is activated and binds to the cluster. The reaction between the monoacetonitrile complex $Os_3(CO)_{11}(NCMe)$ and imidazo[1,2-*a*]pyridine forms the substitution complex $Os_3(CO)_{11}(\mu\text{-}C_7H_6N)$, which reacts further upon heating to form **73** and **74**. Complexes **72** and **73** react with a second equivalent of imidazopyridine to afford $Os_3(\mu\text{-H})_2(CO)_8(\mu\text{-}1,2\text{-}\eta^2\text{-}C_7H_5N_2)_2$ **75** and $Os_3(\mu\text{-H})_2(CO)_8(\mu\text{-}1,7\text{-}\eta^2\text{-}C_7H_5N_2)(\mu\text{-}1,2\text{-}\eta^2\text{-}C_7H_5N_2)$ **76**, respectively.[85]

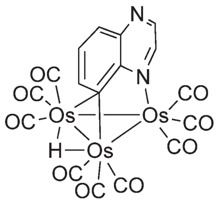


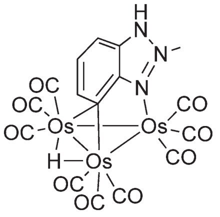
In addition to substituted quinolines, a number of other heterocycles containing pyridinyl nitrogens – such as 5,6-benzoquinoline, phenanthridine, quinoxaline, 2-methylbenzotriazole, 2-R-benzothiazole, 2-benzothiazole, and 2-methylbenzimidazole when reacted with the labile complex $Os_3(CO)_{10}(NCMe)_2$ – undergo C–H activation and loss of CO to form a family of electron-deficient clusters containing face-capping μ_3-heterocyclic groups.[29,86] The structures of this family of benzoheterocyclic triosmium clusters are shown below. As with the quinoline complexes, the reactivity of these systems with donor ligands, such as phosphines[87] and carbanions,[88] has been extensively explored. The formation of stable radical anions,[89] their electrochemistry,[90,91] the reactions between these complexes with acids (HBF_4 or CF_3CO_2H) and bases (*n*-butylamine),[92] and rates of hydrogen atom abstraction[93] have also been investigated but beyond the scope of this compendium to be fully outlined here.


quinoline

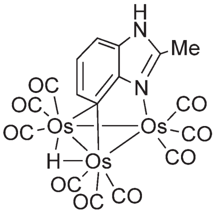

phenanthridine


5,6-benzoquinoline

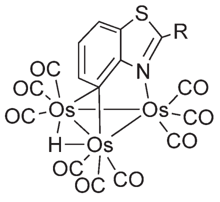

quinoxaline



2-Me-benzotriazole

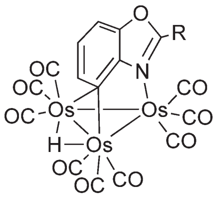


2-Me-benzimidazole



R = H, Me

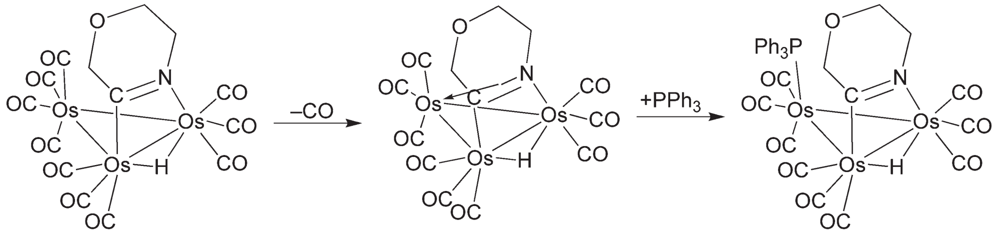
2-R-benzothiazole



R = H, Me

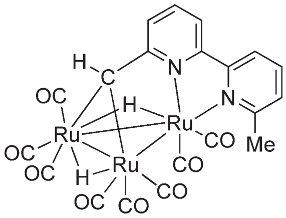
2-R-benzoxazole

Reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with morpholine in benzene at 60 °C afforded $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}NC_4H_6O)(\mu\text{-}H)$ 77. Decarbonylation of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}NC_4H_6O)(\mu\text{-}H)$ at high temperatures yields $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}NC_4H_6O)(\mu\text{-}H)$ 78, which readily reacts with PPh_3 at ambient temperature to give an addition product $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}NC_4H_6O)(PPh_3)(\mu\text{-}H)$ 79. The reaction of $Ru_3(CO)_{12}$ with morpholine in the presence of Me_3NO in refluxing benzene afforded $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}NC_4H_6O)(\mu\text{-}H)$.[94]



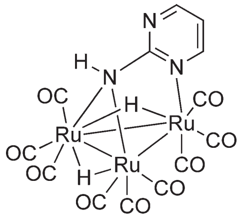
77 78 79

Reaction of 6,6′-dimethyl-2,2′-bipyridine with $Ru_3(CO)_{12}$ results in the loss of CO from one of the three Ru atoms and chelating coordination of the bipy nitrogens to the ruthenium; concomitant with this is the C–H activation of one of the two methyl groups to form the complex $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}HCbipyMe)(CO)_8$ 80.[95]



80

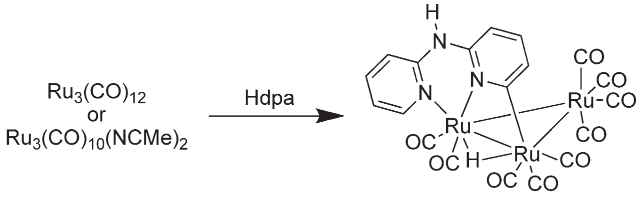
The 2-aminopyrimidine (Hapyr)-containing cluster $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}apyr)(CO)_9$ 81 has been synthesized by the reaction of Hapyr with $Ru_3(CO)_{12}$,[96] and its reactivity toward conjugated dienes, MeC_4Me, PhC_4Ph, and $PhOCH_2C_4CH_2OPh$ has been assessed.[97]



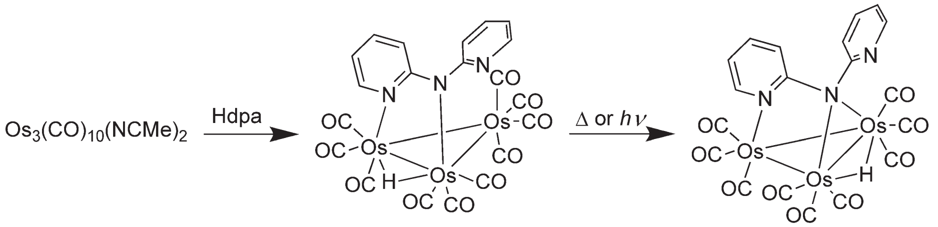
81

Treatment of $Ru_3(CO)_{12}$ or $Ru_3(CO)_{10}(NCMe)_2$ with di(2-pyridyl)amine (Hdpa) gives the cluster complex $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^3\text{-dpa-}C,N,N)(CO)_9$ 82. The dpa ligand in this compound chelates an Ru atom through both pyridinic nitrogens while attached to another Ru atom through the C atom of a metallated pyridine ring, keeping the amino

NH fragment uncoordinated. The related osmium compounds $Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-dpa-}N,N)(CO)_{10}$ 83 and $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-dpa-}N,N)(CO)_9$ 84, which have been prepared stepwise from $Os_3(CO)_{10}(NCMe)_2$ and Hdpa, contain edge-bridging and face-capping *N*-deprotonated dpa ligands coordinated through the N atom of a pyridine ring and the N atom of the original amino fragment.[98]

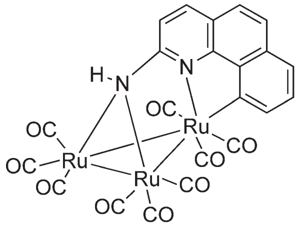


82



83 **84**

$Ru_3(CO)_{10}(NCMe)_2$ reacts with H_2abq (2-amino-7,8-benzoquinoline) to form the complexes $Ru_3(\mu_3\text{-}\eta^2\text{-abq-}C,N,N)(CO)_9$ 85 and $Ru_3(\mu\text{-}H)_2(\mu^3\text{-}\eta^3\text{-abq-}C,N,N)_2(CO)_6$ 86 sequentially. Reaction of the osmium cluster $Os_3(CO)_{10}(NCMe)_2$ with H_2abqH gives the amino-bridged complex $Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-Habq-}N)(CO)_{10}$ 87.[99]



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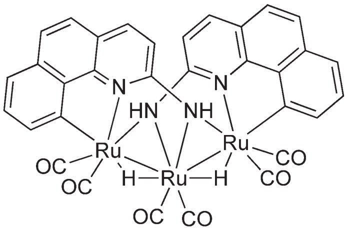

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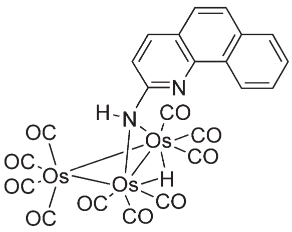
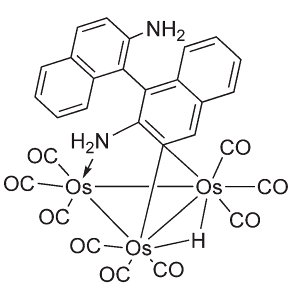


87

Reaction of 2,2′diamino-1,1′-binaphthalene (H_2binam) with $Os_3(CO)_{10}(NCMe)_2$ affords the coordinatively unsaturated complex $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-Hbinam-}N,C)(CO)_9$ 88. The analogous reaction with $Ru_3(CO)_{10}(NCMe)_2$ does not form similar compounds. Instead, an alternative stepwise treatment of $Ru_3(CO)_{12}$ with monolithiated LiHbinam and $[HOEt_2][BF_4]$ leads to $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-binam-}N)(CO)_{10}$ 89 in which the Hbinam ligand acts as an edge-bridging amido ligand.[100]



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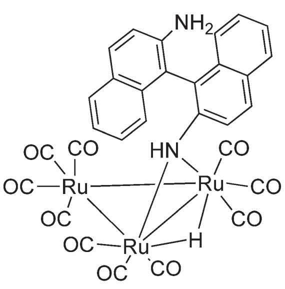
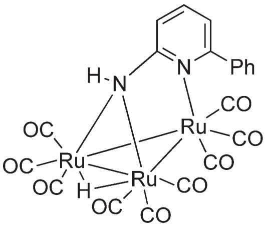


89

The reaction chemistry of the triruthenium hydrazine complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HNNMe_2)(CO)_9$ along with the chemistry of the protonated complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}H_2NNMe_2)(CO)_9][BF_4]$ and the influence of the hydrazine group on substitution chemistry with PPh_3 has been investigated.[101] The reactivity and insertion chemistry of $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HNNMe}_2)(CO)_9$ with alkynes (PhCCPh, HCCH, MeO_2CCCO_2Me, PhCCH, MeO_2CCH, $HOMe_2CCCH$, and 2-PyCCH) has been investigated and results in addition and formation of a range of trinuclear clusters containing edge-bridging or face-capping alkynyl ligands.[102]

Treatment of $Ru_3(CO)_{12}$ with 2-amino-6-phenylpyridine (H_2apyPh) results in the formation of the triruthenium complexes $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HapyPh-}N,N)(CO)_9$ **90** and $Ru_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-HapyPh-}N,N,C)_2(CO)_6$ **91** as well as hexanuclear co-products. The reaction of the osmium cluster $Os_3(\mu\text{-H})_2(CO)_{10}$ with H_2apyPh gives a 1 : 5 mixture of the edge-bridging decacarbonyl compounds $Os_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HapyPh-}N)(CO)_{10}$ **92** and $Os_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HapyPh-}N,N)(CO)_{10}$ **93**.[103] The reactivity of the cluster $[Ru_3(\mu_3\text{-}\eta^3\text{-}C,N_2\text{-Habq})(CO)_9]$ (H_2abqH = 2-amino-7,8-benzoquinoline) toward alkynes, $H[BF_4]$, H_2, silanes, and stananes has been investigated.[51]



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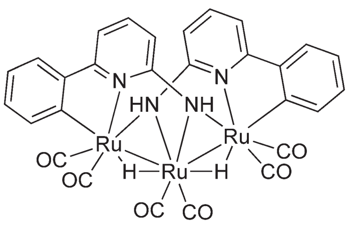

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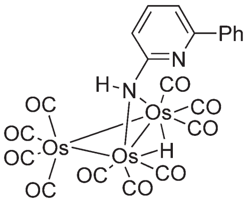

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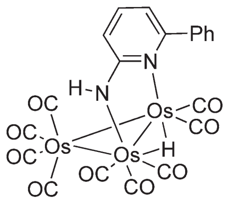
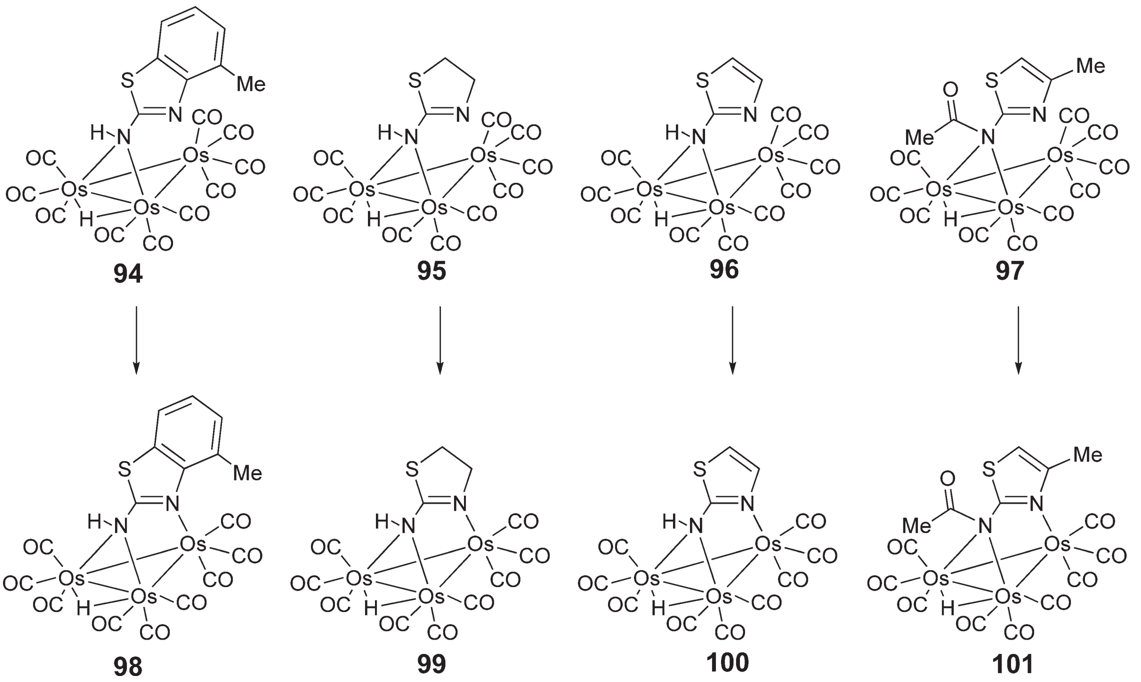


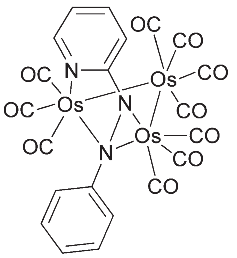
93

The aminothiazole ligands HL (2-amino-4-methylbenzothiazole, 2-amino-2-thiazoline, 2-amino-thiazole, and 2-acetamido-4-methylthiazole) react with $Os_3(CO)_{10}(NCMe)_2$ to form a series of triosmium hydride clusters with the general formula $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-L-}N)$ **94–97** in which the imine group of the ligand bridges one of the three edges of the $\{Os_3\}$ ring. Thermolysis of these complexes results in loss of CO from the $\{Os(CO)_4\}$ group and secondary coordination of the heterocyclic ring via the nitrogen atom to form complexes of the form $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}\eta^2\text{-L-}N,N)$ **98–101**.[104]



Variable-temperature ^{13}C NMR studies on $Ru_3(CO)_9(\mu\text{-CO})(\mu_3\text{-NPh})$ reveal the presence of two distinct CO exchange processes that involve localized equatorial/axial carbonyl scrambling at each ruthenium vertex and exchange of the equatorial and triply-bridging CO groups. The kinetics and activation parameters for these exchange processes have been determined by both band shape analysis and 2D-EXSY experiments.[105] The NMR ^{13}C spin-lattice relaxation times of the phenyl group and equatorial carbonyl carbons in $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NPh)$ have also been measured as a function of temperature and resonance frequency.[106]

2-Phenylazopyridine (2-PAP) reacts with $Os_3(CO)_{10}(NCMe)_2$ to form $Os_3(CO)_{10}(NC_5H_4N{=}NPh)$ **102** and the *ortho*-metallated species $Os_3(CO)_9(\mu\text{-}H)\{NC_5H_3N{=}N(O)Ph\}$ **103** without cleavage of the N=N bond.[107] Similar reaction with (2-(5-bromo-2-pyridiazo)-5-diethylamino)phenol affords $Os_3(CO)_{10}(\mu\text{-}NHC_5NH_3Br)\{\mu\text{-}N(C_{10}H_{13}NO)\}$ **104**, in which the two types of N-ligand bridge across the same Os–Os edge.[108]



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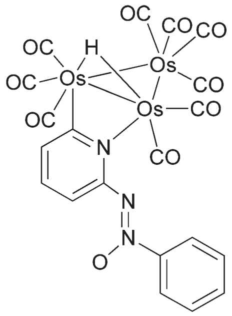

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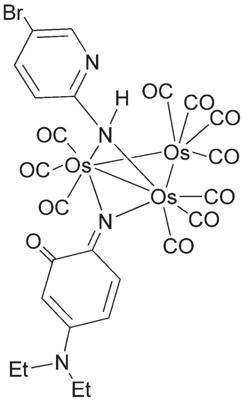

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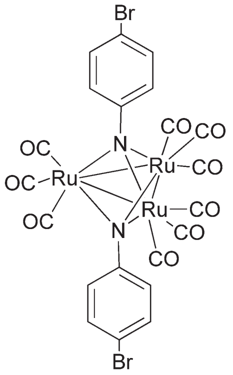
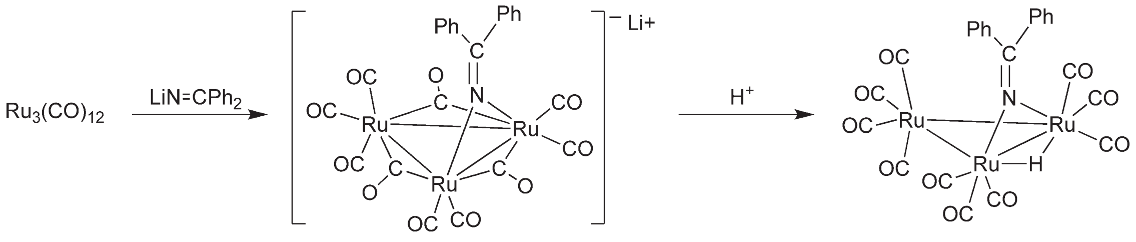


105

4,4′-Dibromoazobenzene undergoes N=N bond cleavage on reaction with $Ru_3(CO)_{12}$ to form the bis(bromophenylimide) complex $Ru_3(\mu_3\text{-}NC_6H_4Br)_2(CO)_9$ **105**, the molecular structure of which has been reported.[109] Reactions of $Ru_3(CO)_{12}$ or $Ru_3(CO)_{10}(NCMe)_2$ with 2 equiv. of PhNSO result in the formation of the known bis-imido complex $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$.[110]

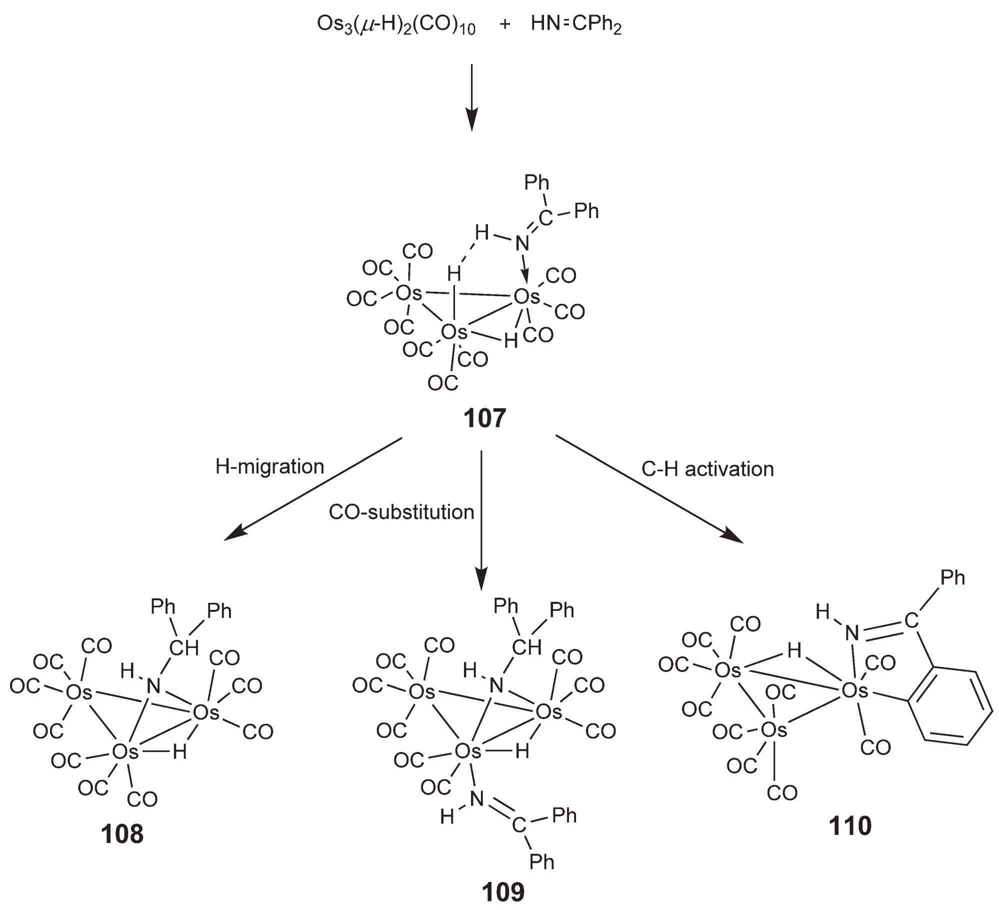
The reaction of $Ru_3(CO)_{12}$ with the lithium salt of benzophenone imine ($LiN{=}CPh_2$) followed by protonation with trifluoroacetic acid leads to the η^1-1-azavinylidene cluster complex $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}$ **106**. The reactions of this complex with dppm and PPh_3, and the reversible loss of CO due to thermolysis of the resultant complexes have also been investigated.[111]



106

Reactions of the phosphine-substituted derivatives $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}dppm)(CO)_8$, $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_3)(CO)_9$, and $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_3)_2(CO)_8$ with $H[BF_4]$ result in protonation at the metal atoms to give the cationic dihydrido derivatives $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}dppm)(CO)_8][BF_4]$, $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(PPh_3)(CO)_9][BF_4]$, and $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(PPh_3)_2(CO)_8][BF_4]$, respectively. Extended Hückel molecular orbital (EHMO) calculations on the phosphine-substituted complexes have been performed in order to rationalize the observed reactivity.[112] The reactivity of **106** toward dienes has also been studied and results in the formation of a series of triruthenium complexes which undergo Ru–H, Ru–C, and Ru–N insertion of dienes.[113]

Reaction of benzophenone imine with the activated osmium precursor $Os_3(\mu\text{-}H)_2(CO)_{10}$ results in formation of the imine adduct, $Os_3(H)(\mu\text{-}H)(HN{=}CPh_2)(CO)_{10}$ **107**, which undergoes thermally induced reaction to form the complexes $Os_3(\mu\text{-}H)(\mu\text{-}HNCHPh_2)(CO)_{10}$ **108**, $Os_3(\mu\text{-}H)(\mu\text{-}HNCPh_2)(HN{=}CPh_2)(CO)_9$ **109**, and $Os_3(\mu\text{-}H)\{\eta^2\text{-}HN{=}CPh(C_6H_4)\}(CO)_{10}$ **110**.[114]

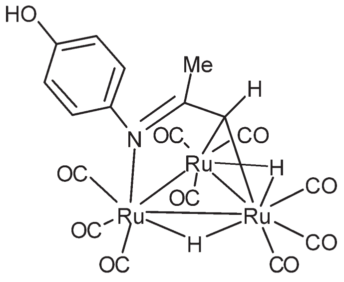


Reaction of ammonia with the carbene triosmium cluster $Os_3(CO)_9(\mu^3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Ph)$ gives the intermediate amino-substituted cyclohexadienyl cluster, which is transformed to $Os_3(CO)_9(\mu^3\text{-}\eta^2:\eta^2:\eta^2\text{-}HN{=}C_6H_5Ph)$ by reaction with $[Ph_3C][BF_4]$.[115]

Reaction of $Os_3(CO)_{12}$ with Me_3-TAC results in the formation of the amidino complex $Os_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^2\text{-}CH(NMe_2)\}$.[34]

The Schiff-base 4-hydroxyphenyl-*N*,*N*-dimethylimide reacts with $Ru_3(CO)_{12}$ to form the structurally characterized double C–H activated product $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}N,C\text{-}4\text{-}HOC_6H_4N{=}CMeCH)(CO)_9$ **111**.[116]

Nitrous oxide gas reacts with the anionic cluster $[Ru_3(CO)_9(C_2R)]^-$ (R = *t*-Bu or $SiMe_3$) to give the neutral nitrosyl complex $Ru_3(CO)_9(C_2R)(\mu\text{-}NO)$ **112**, the molecular structure of which has been determined.[117]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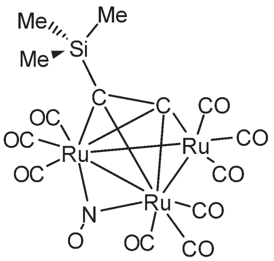
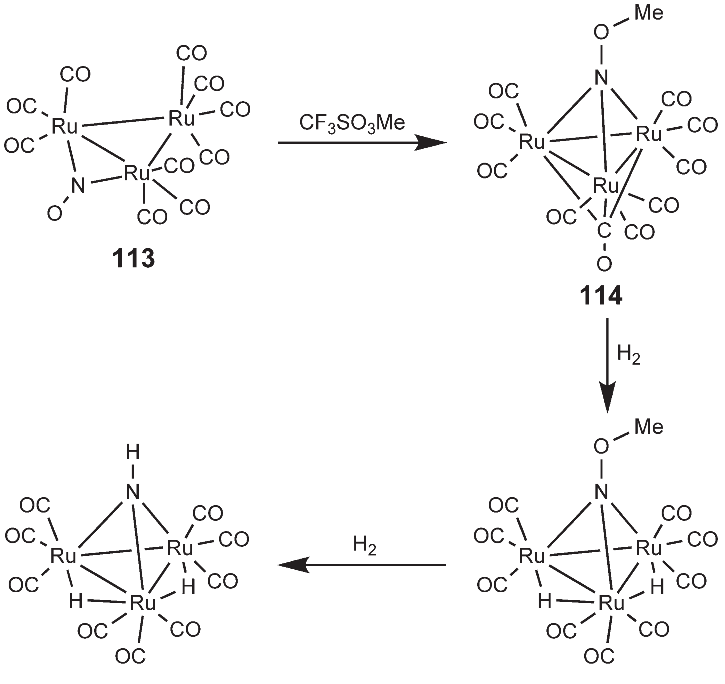
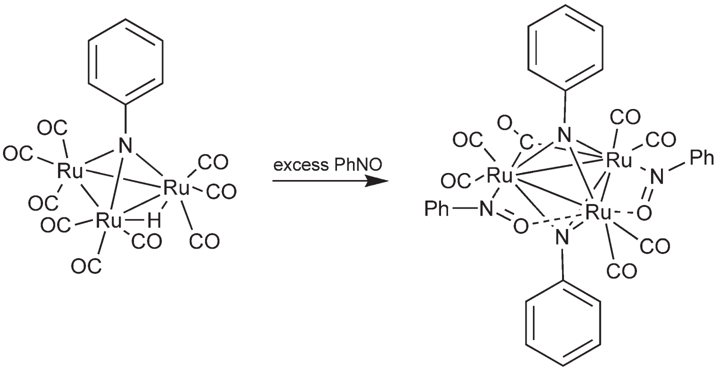

112

Methylation of the ruthenium cluster $[Ru_3(CO)_{10}(NO)]^-$ **113** with $MeOSO_2CF_3$ results in the formation of $Ru_3(CO)_{10}(\mu\text{-}NOMe)$ **114**, the molecular structure of which reveals a face-capping coordination of the {NOMe} fragment. Hydrogenation of **114** results in the formation of the hydride clusters $Ru_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}NOMe)$ **115** and $Ru_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}NH)$ **116**.[118] Protonation of $[Ru_3(CO)_{10}(NO)]^-$ with $HOSO_2CF_3$ (or DO_2CCF_3) yields the compound $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOH)$. Using NMR techniques, the rate of proton/deuterium transfer from the nitrosyl group to the metal has been assessed.[119]



113 **114** **115** **116**

The μ_3-imido cluster $Ru_3(\mu\text{-}H)(\mu\text{-}NPh)(CO)_{10}$ reacts with an excess of nitrosobenzene to give the bis-imido complex $Ru_3(\mu\text{-}NPh)_2(\mu\text{-}CO)(CO)_6(\mu\text{-}\eta^2\text{-}ONPh)_2$ **117**.[120]

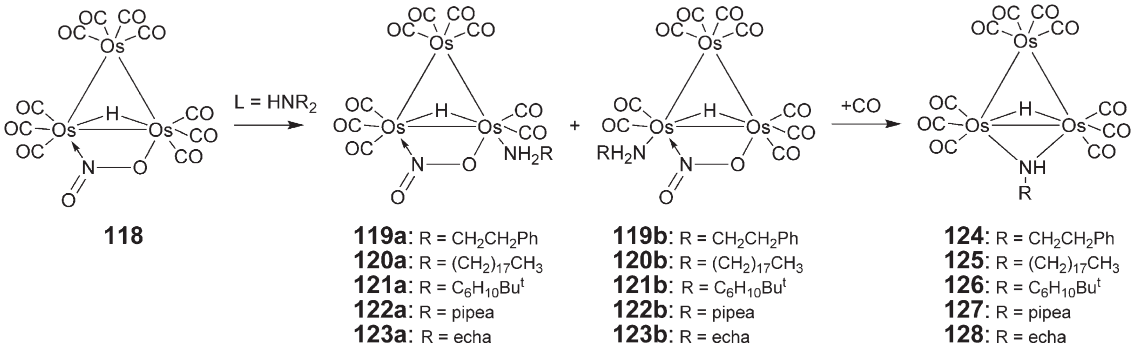


117

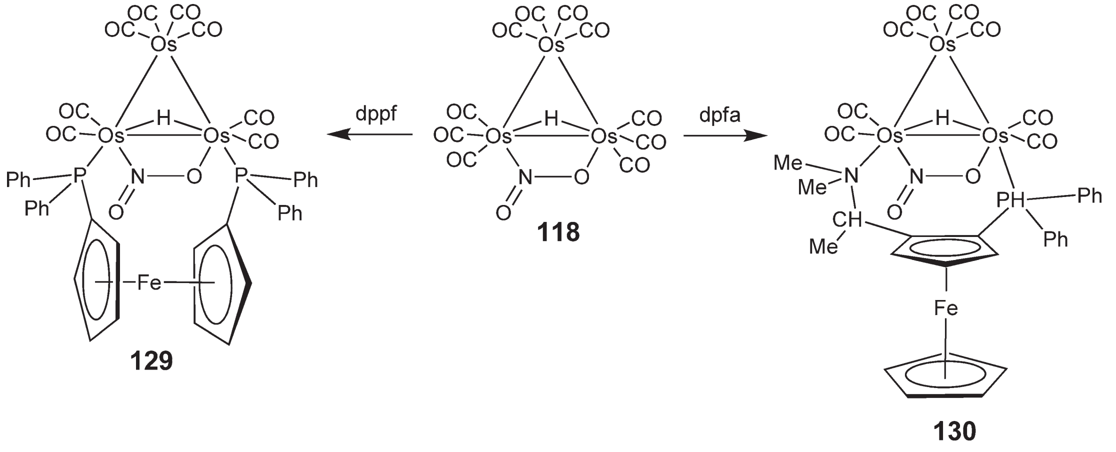
The nitrite cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)$ **118** reacts with trimethylamine *N*-oxide in CH_2Cl_2 to give a pair of isomers (**a** and **b**) with formula $Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}\eta^2\text{-}NO_2)(NMe_3)$. Reaction of **118** with PPh_3 and Me_3NO in CH_2Cl_2 yields a pair of isomers $Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}\eta^2\text{-}NO_2)(PPh_3)$ and $Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}\eta_2\text{-}NO_2)(PPh_3)_2$. Analogous reaction with *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) yields a pair of isomers of $Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}NO_2)$(dppen) and $Os_3(\mu\text{-}H)(CO)_6(\mu\text{-}\eta^2\text{-}NO_2)$(dppen)$_2$. Reaction with bis(diphenylphosphino)acetylene (dppa) gives $Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}NO_2)$(dppa).[121]

Reactions of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)$ **118** with ammonia and some amines (2-phenylethylamine, octadecylamine, 4-*tert*-butylcyclohexylamine, piperidine-1-ethanamine (pipea), and 1-ethynylcyclohexylamine (echa)) afford isomers with the general formula $Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}\eta^2\text{-}NO_2)(NH_2R)$ **119a–123a** and **119b–123b** (R = H,

CH_2CH_2Ph, $(CH_2)_{17}CH_3$, $C_6H_{10}Bu^t$-4, pipea, or echa). Subsequent reactions of these nitrite clusters with CO result in the formation of the complexes **124–128**.[122]



The triosmium nitrite carbonyl cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)$ **118** reacts with 1,1′-bis(diphenylphosphino) ferrocene (dppf) and *N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine (ppfa) in the presence of Me_3NO to afford the clusters $Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}NO_2)(\mu\text{-}dppf)$ **129** and $Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}NO_2)(\mu\text{-}ppfa)$ in moderate yields **130**.[123]

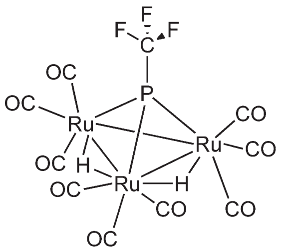


6.18.6 Trinuclear Clusters with P-Donor Ligands

As with previous publications (COMC (1982) and COMC (1995)), phosphorus ligands feature heavily in the chemistry of ruthenium and osmium. In many instances the focus of the publications is such that the phosphorus-containing species are peripheral to the specific reactivity that a publication might be dealing with. For this reason, phosphorus ligands are somewhat ubiquitous within cluster chemistry. Here, an attempt has been made to focus on the phosphorus and its interaction with the cluster.

The compound CF_3PH_2 reacts with $Ru_3(CO)_{12}$ to form $Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PCF_3)$ **131** in which the three ruthenium atoms are coordinated by a face-capping μ_3-PCF_3 group.[124] Ph_2PH reacts with $Ru_3(CO)_{10}(\mu\text{-}dppm)$ to give $Ru_3(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)_2(\mu_3\text{-}CH_2PPh)$ which consists of a triruthenium cluster with an unusual example of a triply-bridging CH_2PPh ligand and two doubly bridging PPh_2 ligands.[125]

The reactions of $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ with secondary phosphines R_2PH ($R = {}^tBu$, 1-Ad) lead to the formation of the electron-deficient metal cluster complexes $Ru_3(\mu\text{-}CO)(CO)_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}PR_2)_2(\mu\text{-}dppm)$ (**132** $R = {}^tBu$; **133** R = 1-Ad) in good yields. The related reaction of the starting dppm complex with the less bulky phosphine Cy_2PH gives the electronically saturated complex $Ru_3(CO)_6(\mu\text{-}H)_2(\mu\text{-}PCy_2)_2(\mu\text{-}dppm)$ **134**. All reactions proceed via the isolated intermediates, $Ru_3(CO)_9(R_2PH)(\mu\text{-}dppm)$.[126]



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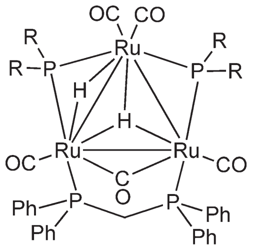
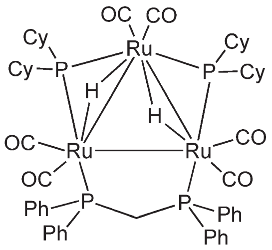


132: R = tBu
133: R = Ad



134

Upon reaction with $Os_3(CO)_{11}(MeCN)$, $(CF_3)_2C(OH)PH(CF_3)$ undergoes P–C bond cleavage to afford the phosphido-bridged cluster $Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-PH}(CF_3)\}$ and the linked cluster $\{Os_3(\mu\text{-H})(CO)_{11}\}\{\mu\text{-PH}(CF_3)\}\{Os_3(CO)_{11}\}$. Reaction with $Os_3(CO)_{10}(NCMe)_2$ affords the complex $Os_3(\mu\text{-H})(CO)_9\{\mu\text{-HN{=}CMeP}(CF_3)\}$.[127]

Reaction of $^tBu_2PF$ with $Os_3(CO)_{11}(NCMe)$ yields the complex $Os_3(CO)_{11}(PF^tBu_2)$. Reaction with the bis-acetonitrile complex $Os_3(CO)_{10}(NCMe)_2$ forms $Os_3(CO)_{10}(PF^tBu_2)_2$ and $Os_3(CO)_{10}(PF_2{}^tBu)(PF^tBu_2)$.[128]

The kinetics of the substitution reactions of $Ru_3(CO)_{11}L$ and $Ru_3(CO)_{10}L_2$ ($L = PCy_3$, PBu_3, $P(p\text{-}MeOC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, and etpb ($P(OCH_2)_3CEt$)) with $AsPh_3$ or various P-donor nucleophiles, L, in hexane have been studied. The reactions proceed through both [L]-independent (CO dissociative) and [L]-dependent (associative) paths. The values of the rate constant k_1 for the dissociative path for $Ru_3(CO)_{11}L$ can be combined with other published data and are found to fit well to the equation: $\log k_1 = \alpha + \beta_L\delta_L + \gamma_L\theta_L$ (where β_L and γ_L are constants that define how sensitive the values of $\log k_1$ are to Bodner's electronic parameter, δ_L, and to Tolman's steric parameter, θ_L, respectively). The second-order reactions of $M_3(CO)_{11}L$ with Me_3NO (M = Ru or Os) also fit an equation analogous to that given, and the values of β_L and γ_L obtained for these assisted CO displacement reactions are compared with those for the unimolecular unassisted CO dissociation.[129]

Application of standard "quantitative analysis of ligand effects" (QALE) methodology enabled the rate constants for the reactions of $Ru_3(CO)_{12}$ with 32 phosphine ligands to be analyzed according to the electronic and steric properties of the nucleophiles. It was unexpectedly found necessary to include what has become known as the aryl effect in this analysis, together with a positive contribution to the rates due to the π-acidity of phosphite nucleophiles.[130]

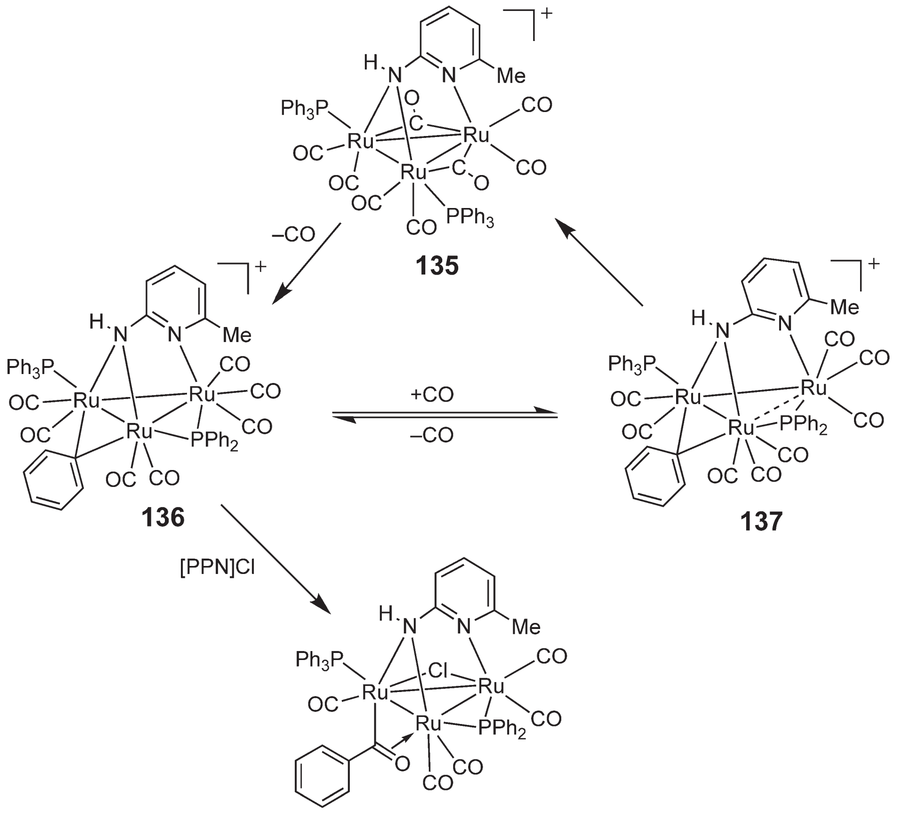
The kinetics for the addition of *P*-donor ligands to the unsaturated cluster $Os_3(\mu\text{-H})_2(CO)_{10}$ show that the reactions proceed by simple bimolecular concerted attack to form $Os_3(\mu\text{-H})(H)(CO)_{10}L$. The second-order rate constants, at 30 °C, for 16 nucleophiles fit very well to the equation $\log k_2 = \alpha + \beta(pK_{a'} + 4) + \gamma(\theta - \theta_{th})\lambda$, where $pK_{a'}$ measures the σ-donicity and θ the Tolman cone angle of each nucleophile.[131]

Carbonyl substitution of the dimethylhydrazine complexes $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HNNMe}_2)(CO)_9$ and $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-H}_2NNMe_2)(CO)_9][BF_4]$ with PPh_3 yields $Ru_3(\mu\text{-H})(\mu_3\text{-H}_2NNMe_2)(C_6H_4PPh_2)(PPh_3)(CO)_6$ and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-HNNMe}_2)(PPh_3)_n(CO)_{9-n}][BF_4]$ ($n = 1$–3), respectively. Analogous reactions of $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HNNMe}_2)(CO)_9$ with dppm yield $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HNNMe}_2)(CO)_7(dppm)$.[132]

The triallylphosphine-substituted clusters $Ru_3(CO)_{11}\{P(CH_2CH{=}CH_2)_3\}$, $Ru_3(CO)_{10}\{P(CH_2CH{=}CH_2)_3\}_2$, and $Ru_3(CO)_{10}\{\sigma,\pi\text{-}CH_2{=}CHCH_2P(CH_2CH{=}CH_2)_2\}$ undergo reversible loss of CO and coordination of allyl groups of the phosphine.[133]

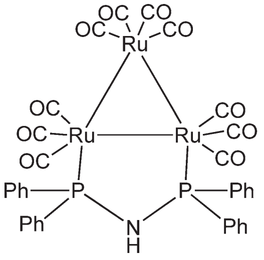
The cluster complexes $[PPN][Ru_3(\mu_3\text{-}\eta^2\text{-PhNpy})(CO)_9]$, react with $P(n\text{-}Bu)_3$ or PPh_3 at room temperature to yield product $[PPN][Ru_3(\mu\text{-}\eta^2\text{-PhNpy})(CO)_9L]$ ($L = P(n\text{-}Bu)_3$, PPh_3), which slowly lose either the phosphine or a CO ligand to give a mixture of products. $[PPN][Ru_3(\mu_3\text{-}\eta^2\text{-MeNpy})(CO)_9]$ and $[PPN][Ru_3(\mu_3\text{-}\eta^2\text{-Spy})(CO)_9]$ react with $P(n\text{-}Bu)_3$ to yield the monosubstituted complex $[PPN][Ru_3(\mu_3\text{-}\eta^2\text{-MeNpy})(CO)_8\{P(n\text{-}Bu)_3\}]$ and the disubstituted complex $[PPN][Ru_3(\mu_3\text{-}\eta^2\text{-Spy})(CO)_7\{P(n\text{-}Bu)_3\}_2]$. The rates of reaction increase in the order 2-MeNpy < 2-Spy < 2-PhNpy. The reactivity order of these complexes toward nucleophiles is rationalized in terms of the electronic effects of their ancillary ligands.[134]

Heating of the 48-electron cationic cluster complex $[Ru_3(\mu_3\text{-ampy})(PPh_3)_2(\mu\text{-CO})_2(CO)_6][BF_4]$ **135** (Hampy = 2-amino-6-methylpyridine) leads to the loss of CO and activation of the P–Ph bond of the coordinated PPh_3 to form the complex $[Ru_3(\mu\text{-Ph})(\mu_3\text{-ampy})(\mu\text{-PPh}_2)(PPh_3)(CO)_7][BF_4]$ **136**. Treatment with CO regenerates the starting material, proceeding via the 50-electron intermediate $[Ru_3(\mu\text{-Ph})(\mu_3\text{-ampy})(\mu\text{-PPh}_2)(PPh_3)(CO)_8][BF_4]$ **137**. Treatment of **136** with [PPN]Cl results in addition of Cl^- to the cluster and insertion of the bridging phenyl group into an Ru–CO bond to form the neutral acyl derivative $Ru_3(\mu\text{-PhCO})(\mu\text{-Cl})(\mu_3\text{-ampy})(\mu\text{-PPh}_2)(PPh_3)(CO)_5$ **138**.[135]



The hydride complex $Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}OCNMe_2)(NMe_3)$ readily reacts with the allyl phosphine ligand $Ph_2P(CH_2CH{=}CH_2)$ to form the phosphine complex $Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}OCNMe_2)\{P(CH_2CH{=}CH_2)Ph_2\}$. Co-polymerization of the complex with styrene forms a phosphine-substituted polystyrene system with triosmium clusters attached to the phosphine sites.[136]

$Ru_3(CO)_{12}$ reacts with bis(diphenylphosphino)amine (dppa) under varying conditions in the presence of sodium diphenylketyl to form $Ru_3(CO)_{10}$(dppa) **139** or the disubstituted product $Ru_3(CO)_8(dppa)_2$ **140**.[137]



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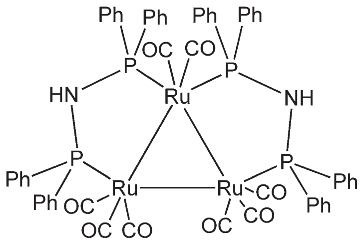

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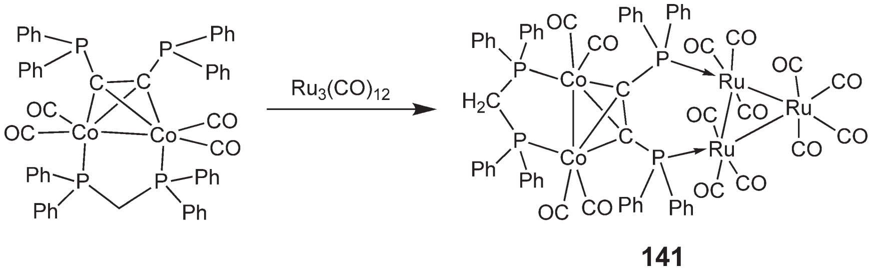
The reactions between dppm or dppe and $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CH_2(OH)\}(CO)_9$ in the presence of $HBF_4{\cdot}OMe_2$ afford complexes containing novel diphosphacycloalkyne ligands, that is, $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCPPh_2CH_2PPh_2CH_2)(CO)_9][BF_4]$ (from dppm) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}CCPPh_2CH_2PPh_2CH_2CH_2)(CO)_9]$ (from dppe), formed by double nucleophilic attack of the ditertiary phosphine on an intermediate allenylidene complex.[138]

Treatment of $Os_3(CO)_7(PhC_2Ph)(dppm)$ (dppm = $Ph_2PCH_2PPh_2$) with *P*-donors gives the monoadducts $Os_3(CO)_7(PhC_2Ph)(dppm)L$ (L = PBu_3, PPh_3, PMe_2Ph, or $P(OMe)_3$). Spectroscopic studies have established that these adducts exist in three isomeric forms, the ratio of which depends on the polarity of the solvent used in the reaction.[139]

The bis-acetonitrile compound $Os_3(CO)_{10}(NCMe)_2$ and the butadiene compound $Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)$ react with $Ph_2P(CH_2)_5PPh_2$ (dppp) to give exclusively $Os_3(CO)_{10}(\mu\text{-dppp})$. Protonation of $Os_3(CO)_{10}(\mu\text{-dppp})$ with trifluoroacetic acid leads to the formation of $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-dppp})]^+$, in which the hydride ligand bridges the same osmium atoms as the dppp. $Os_3(CO)_{10}(\mu\text{-dppp})$ reacts with dppp high temperatures to give $Os_3(CO)_9(\eta^1\text{-dppp})(\mu\text{-dppp})$, whereas $Os_3(CO)_{10}(\mu\text{-dppm})$ under the same conditions reacts with dppm to give $Os_3(CO)_8(\mu\text{-dppm})_2$. Protonation with trifluoroacetic acid gives $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-dppm})_2]^+$ with the hydride bridging the unsubstituted Os–Os edge. The monoacetonitrile compound $Os_3(CO)_{11}(NCMe)$ reacts with dppp to give two complexes: $Os_3(CO)_{11}(\eta^1\text{-dppp})$, which contains one coordinated and one free phosphorus atom, and $\{Os_3(CO)_{11}\}_2(\mu\text{-dppp})$ in which one dppp ligand bridges two $\{Os_3(CO)_{11}\}$ moieties.[140]

Reaction between $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4\text{-}o)\}(CO)_9$ and HC_2Ph results in insertion of a diene, formed by coupling of the alkyne into an Ru–P(phosphido) bond to give a $PPh(C_6H_4)CH_2PPh(C_4H_2Ph_2)$ ligand. Thermolysis regenerates the original phosphido-phosphine ligand and the alkyne dimer, which coordinates in the usual $\mu\text{-}\eta^4$-mode.[141] Thermolysis of $Ru_3(\mu_3\text{-C{=}C{=}CPh}_2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7$ affords $Ru_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-}C_9H_5Ph_2)(CO)_n$ ($n = 6$, 5) by trapping of the Ph group (from P–C bond cleavage in the dppm ligand) by the allenylidene and cyclization to a 1,3-diarylindenyl ligand, which is attached to the cluster via one of the Ar groups.[142]

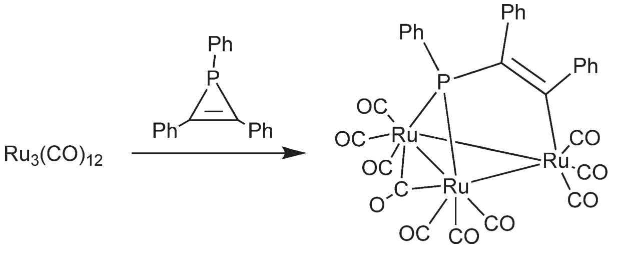
The cobalt-containing diphosphine complex $Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-PPh}_2\text{CCPPh}_2)$ reacts with $Ru_3(CO)_{12}$ to form the chelating complex $Ru_3(CO)_{10}\{\mu\text{-}P,P\text{-PPhCCPPh}\}Co_2(CO)_4(\mu\text{-dppm})$ **141**, where the cobalt diphosphine complex bonds across one of the Ru–Ru edges of the $\{Ru_3\}$ cluster.[143]



141

$Os_3(CO)_{10}(NCMe)_2$ undergoes acetonitrile substitution upon reaction with the diphosphine ligand (Z)-$Ph_2PCH{=}CHPPh_2$, forming the bridging complex $Os_3(CO)_{10}(\mu\text{-PPh}_2\text{CH{=}CHPPh}_2)$ which transforms to the chelating isomer upon heating.[144]

Reaction of $Ru_3(CO)_{12}$ with 1,2,3-triphenylphosphirene, $PhP(CPh)_2$, results in ring opening of the phophirene ring and formation of the triruthenium clusters $Ru_3(CO)_{10}(\mu\text{-}\eta^3\text{-PhPCPhCPh})$ **142**, and $Ru_3(CO)_8(\mu^3,\eta^4\text{-PhPCPhCPhPPhCPhCPh})$.[145]



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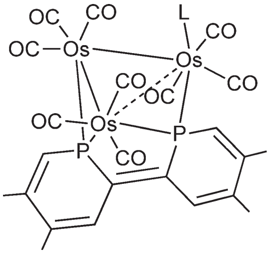
The triruthenium cluster $HRu_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^1\text{-C}{\equiv}\text{CPh})$ reacts with the diphosphine ligand bpcd in the presence of Me_3NO to afford the new clusters $HRu_3(CO)_7(\mu_3\text{-}\eta^2,\eta^2,\eta^1\text{-C}{\equiv}\text{CPh})$ and $HRu_3(CO)_7\{\mu_3\text{-}\eta^2,\eta^2,\eta^1,\eta^1,\eta^1\text{-1-Ph}_2\text{PC{=}CC(O)CH}_2\text{C(O)PPh}_2\text{C{=}CPh}\}$.[146]

Reactions between $Ru_3(CO)_{12}$ and 1,8-bis(diphenylphosphino)naphthalene (dppn) produce the triruthenium cluster complex $Ru_3(\mu\text{-H})\{\mu_3\text{-PPh}_2(\text{nap})\text{PPh}(C_6H_4)\}(CO)_8$ as well as several tetraruthenium clusters.[147] 1,8-Bis(diphenylphosphino)naphthalene also reacts with $Os_3(CO)_{12}$ to produce $Os_3(\mu\text{-H})_2\{\mu\text{-PPh}_2(\text{nap})\text{PPh}(C_6H_4)\}_2(CO)_6$ and $Os_3(\mu\text{-H})\{\mu_3\text{-PPh}_2(\text{nap})\text{PPh}(C_6H_4)\}(CO)_8$.[148]

The structure and electrochemistry of the 1,1′-bis(diphenylphosphino)ferrocene (dppf) derivartives of ruthenium $Ru_3(CO)_{10}(dppf)$, $Ru_3(CO)_8(dppf)_2$ and the bridged system $\{Ru_3(CO)_{11}\}_2(\mu\text{-dppf})$ have been investigated.[149]

The bonding properties and electrochemical behavior of triosmium carbonyl clusters containing the redox-active ligand 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp) have been investigated. The clusters studied were $Os_3(CO)_{10}$(tmbp) **143** and its derivative $Os_3(CO)_9(PPh_3)$(tmbp) **144**.[150]

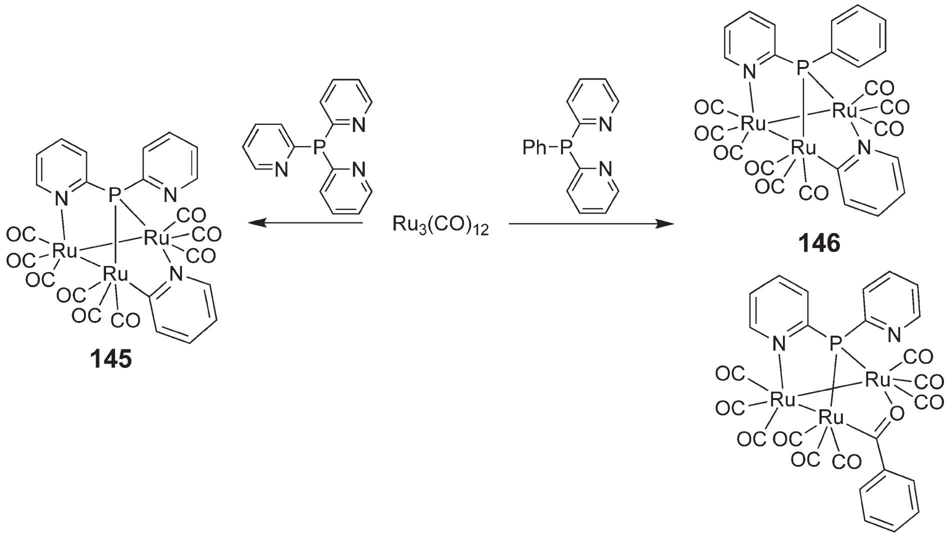


143: L = CO
144: L = PPh_3

Reactions of the 1-naphthyl derivatives $E(1\text{-}C_{10}H_7)_3$ (E = P, As) with $M_3(CO)_{12}$ (M = Ru, Os) afford the series of naphthyne complexes $M_3(CO)_8(\mu\text{-}H)\{\mu_3\text{-}\eta^4\text{-}(C_{10}H_5)E(C_{10}H_7)_2\}$ in moderate to good yield, via double metalation of the unsubstituted aromatic ring.[151]

The complexes $Ru_3(CO)_{10}\{P(2\text{-}C_4H_3S)_3\}_2$ and $Ru_3(CO)_{10}\{P(NEt_2)_3\}_2$ have been synthesized and structurally characterized.[152]

The compound tri(2-pyridyl)phosphine, $P(2\text{-}C_5H_4N)_3$, reacts with $Ru_3(CO)_{12}$ when catalyzed by [PPN]Cl, to give $Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9$ **145**, which has undergone cleavage of one of the pyridyl–P bonds. A similar reaction using phenyldi(2-pyridyl)phosphine, $PPh(2\text{-}C_5H_4N)_2$, leads to the competitive transfer of 2-pyridyl and Ph groups to give almost equal quantities of two products, $Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9$ **146** and $Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9$ **147**.[153] In contrast, reaction of $Os_3(CO)_{10}(NCMe)_2$ with the tertiary phosphines diphenyl(2-pyridyl)phosphine, phenyldi(2-pyridyl)phosphine, and tri(2-pyridyl)phosphine lead to the generation of clusters of the type $Os_3(CO)_{10}(\mu\text{-}L)$ as the major product, where the P and N atoms of the PN ligand are both coordinated to the cluster. Small amount of the mono- and bis-phosphine complexes $Os_3(CO)_{11}L$ and $Os_3(CO)_{10}L_2$, in which the ligand coordinates to the metal through the phosphorus atom alone, can also be obtained from the reaction mixture. Thermal treatment of the complex $Os_3(CO)_{10}\{\mu\text{-}PPh_2(C_5H_3N)\}$ **148** results in competitive fission of the P–Py and P–Ph bonds to form the complexes $Os_3(\mu\text{-}PPh_2)(\mu\text{-}C_5H_3N)(CO)_{10}$ **149**, $Os_3(Ph)\{\mu\text{-}\eta^3\text{-}(NC_5H_3)PPh\}(CO)_8$ **150**, and $Os_3(\mu\text{-}PhCO)\{\mu_3\text{-}P(2\text{-}C_5H_4N)Ph\}(CO)_9$ **151**.[154]



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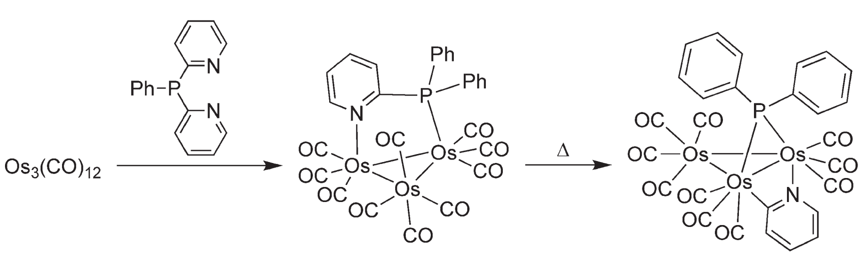

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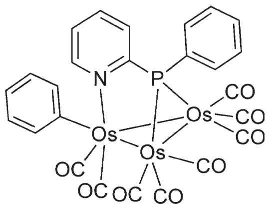

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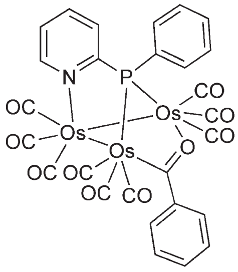

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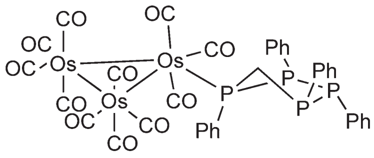
The reaction between the redox-active diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopentene-1,3-dione (bpcd) and $Ru_3(CO)_{12}$ at high temperatures affords the binuclear compounds $Ru_2(CO)_6$(bpcd) and $Ru_2(CO)_6\{\mu$-C=C(PPh_2)C(O)CH_2C(O)}(μ_2-PPh_2) as the major and minor products, respectively. The disubstituted cluster $Ru_3(CO)_{10}$(bpcd) can be synthesized under milder conditions and has been shown to contain a chelating bpcd ligand. This trimetallic cluster undergoes cluster fragmentation at ambient temperature in the dark to give the binuclear compound $Ru_2(CO)_6$(bpcd) and $Ru_3(CO)_{12}$.[155]

The imido-capped cluster $Ru_3(CO)_9(\mu_3$-CO)(μ_3-NPh) reacts with bpcd to furnish $Ru_3(CO)_7(\mu_3$-CO)(μ_3-NPh)(bpcd) and $Ru_3(CO)_5(\mu_3$-CO)(μ_3-NPh)(bpcd)$_2$ as the major and minor products, respectively. Thermolysis of the monosubstituted complex affords the new triruthenium compounds $Ru_3(CO)_5(\mu_2$-CO)$_2$(μ_3-NPh)(μ_2-PPh_2){μ,η^1,η^1-C=C(PPh_2)C(O)CH_2C(O)}, $Ru_3(CO)_6(\mu_2$-CO)(μ_3-NPh)(μ-PhCO){μ_2,η^2,η^1-PPhC=C(PPh_2)C(O)-CH_2C(O)}, and $Ru_3(CO)_9(\mu_3$-NPh)(μ_3-PPh).[156] The reaction between $Ru_3(\mu$-H)(CO)$_{10}$(μ-PPh_2) and bpcd proceeds rapidly in the presence of Me_3NO to furnish $Ru_3(\mu$-H)$_2$(CO)$_7$(μ-CO)(bpcd)(μ_3-$PPhC_6H_4$-κ^3(*P*,*P*,*C*)). Treatment of the nonacarbonyl cluster $Ru_3(\mu$-H)(CO)$_9$(μ-PPh_2) with bpcd affords cluster $Ru_3(\mu$-H)$_2$(CO)$_7$(μ-CO)(bpcd) (μ_3-$PPhC_6H_4$-*P*,*P*,*C*) as the major product.[157] The related complex $Ru_3(CO)_{10}$(bpcbd) (bpcbd = 1,2-bis(diphenylphosphino)cyclobutenedione) undergoes decomposition to form the ruthenium complex $Ru_3(CO)_{10}$(bma) (bma = 2,3-bis(-diphenylphosphino)maleic anhydride), which further decomposes to $Ru_2(CO)_6(\mu$-bma) and $Ru_2(CO)_{10}(\mu$-2,3-bis(diphenylphosphino)-succinic anhydride).[158]

The cyclophosphanes $(EtP)_5$ and $(PhP)_5$ react with the unsaturated triosmium cluster $Os_3(\mu$-H)$_2$(CO)$_{10}$ to give $Os_3(\mu$-H)(CO)$_8$(μ-η^3-P_5R_5H) (R = Et or Ph) and $Os_3(CO)_{10}$\{1,3-(PEt)$_5$\}. Treatment of $(EtP)_5$ with $Os_3(CO)_{10}$ $(NCMe)_2$ affords $Os_3(CO)_{10}$\{1,2-(PEt)$_5$\}. The analogous reaction at higher temperatures results in formation of the thermodynamically preferred 1,3-isomer.[159] Similar reaction of $(PhP)_5$ with $Os_3(CO)_{10}(NCMe)_2$ yields the 1,2- and 1,3-coordination isomers with the formula $Os_3(CO)_{10}$\{PPh\}$_5$.[160]

Reactions of 1,2,3,4-tetraphenyl-1,2,3,4-tetraphospholane, $(PhP)_4CH_2$, with $Os_3(CO)_{11}$(NCMe) or $Os_3(CO)_{10}(NCMe)_2$ afford the substituted cluster $Os_3(CO)_{11}\{(PPh)_4CH_2\}$ **152** and the isomeric linked bis(trinuclear) clusters $\{Os_3(CO)_{11}\}_2\{\mu$-1,4-η^2-$(PPh)_4CH_2\}$ **153** and $\{Os_3(CO)_{11}\}_2\{\mu$-1,3-η^2-$(PPh)_4CH_2\}$ **154**. Reaction at higher temperatures affords the disubstituted 1,4-bridged trinuclear cluster $Os_3(CO)_{10}\{\mu$-1,4-η^2-$(PPh)_4CH_2\}$ **155**. When $(PhP)_4CH_2$ reacts with a twofold molar amount of $\{Os_3(CO)_{10}(\mu$-H$)_2\}$, the 1,2,3,4-linked bis(trinuclear) hydride cluster $\{Os_3(CO)_8(\mu$-H$)_2\}_2\{\mu_4$-1,2,3,4-η^4-$(PPh)_4CH_2\}$ **156** is obtained.[161]



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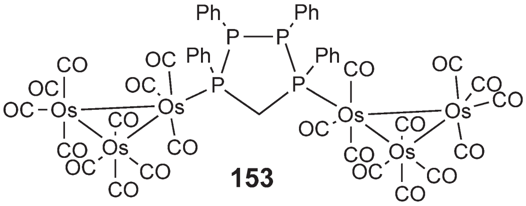

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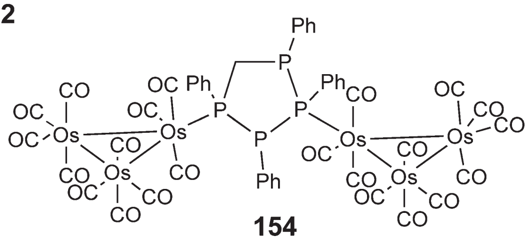

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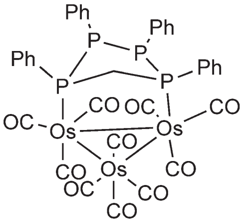

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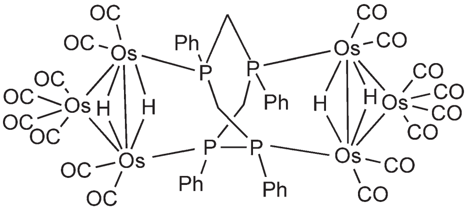

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The five-membered ring triphospholene $(CPh)_2(PPh)_3$ (L) undergoes mono- and disubstitution reactions with $Os_3(CO)_{11}(NCMe)$ to afford the monosubstituted cluster $Os_3(CO)_{11}$(2-PhPPhPPhPCPh=CPh), and the disubstituted bridged cluster $Os_3(CO)_{10}(\mu$-1,3-PhPPhPPhPCPh=CPh), as well as the linked cluster $\{Os_3(CO)_{11}\}_2$(1,3-PhPPhPPhP-CPh=CPh). Reactions with $Os_3(CO)_{10}(NCMe)_2$ gives two isomers of $Os_3(CO)_{10}$(1,3-PhPPhPPhPCPh=CPh), differing in the orientation of the Ph group attached to the central uncoordinated phosphorus atom. Reactions at elevated temperatures result in cleavage of one P–P bond of the ligand yielding the open cluster $Os_3(CO)_9(\mu_3$-η^3-PhPPhPCPh=CPhPPh), and cleavage of two P–P bonds giving $Os_3(CO)_9(\mu_3$-PPh)(μ_3-η^2-PhPCPh=CPhPPh), which arises from the formation of phosphinidene species.[162]

Phosphorus ylides undergo oxidative addition to $Ru_3(CO)_{12}$ to yield a wide range of Ru_3 clusters with triply-bridging organic ligands derived from the ylides. $Ph_3P{=}CH_2$ forms $HRu_3(CO)_9(\mu_3$-$Ph_3PCHCO)$ containing the phosphonio enolate ligand $Ph_3P{=}CHO$. The ylide $Ph_3P{=}CHCHO$ yields a product mixture containing the phosphonio enolate-bridged cluster and its PPh_3 derivative, the phosphoniomethylidyne-bridged compound $H_2Ru_3(CO)_9(\mu_3$-$CPPh_3)$ and the ketenylidene-bridged compound $H_2Ru_3(CO)_8(PPh_3)(\mu_3$-CCO).[163] The reactivity of $Ru_3(CO)_{12}$ with the phosphorus ylide $Ph_3P{=}C(CH)_4$, has been investigated, as well as the resulting triruthenium clusters, which contain μ_2-$\eta^5:\eta^1$-C_5H_4 units.[164]

The ligand bis(diphenyphosphino)acetylene reacts with $Ru_3(CO)_8(\mu$-dppm$)_2$ to form $Ru_3(CO)_6\{\mu_3$-$OPPh_2C_2H(C_6H_4)PPhCH_2PPh\}(\mu_3$-$OPPh_2)Ph$ and $Ru_3(CO)_6\{\mu$-$OPPh_2C_2H(C_6H_4)PPhO\}(\mu$-$PPh_2)(\mu$-$PPh_2O)$.[165]

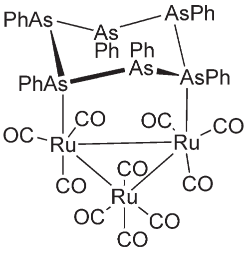
The reaction of 2,2-dimethylpropylidynephosphine ($^tBuC{\equiv}P$) with the cluster $Os_3(CO)_{10}(\mu_3$-$\eta^1:\eta^2:\eta^1$-$C_2Me_2)$ results in P–C bond cleavage and insertion of the precoordinated but-2-yne ligand into the P≡C triple bond of the incoming phospha-alkyne, resulting in the formation of a novel bridging $\{C_3P\}$-moiety in the structurally characterized complex $Os_3(CO)_8(\mu_2$-$PCBu^t)(\mu_3$-$PCMeCMeCBu^t)$.[166]

Reaction of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene with $Ru_3(CO)_{12}$ results in P=P bond cleavage with concomitant C–H activation to form the triruthenium complex $Ru_3(\mu$-$H)_2(CO)_8(\mu$-PC_6H_2-2,4-$^tBu_2$-6-$CMe_2CH_2)_2$.[167]

6.18.7 Trinuclear Clusters with As and Sb donor Ligands

$(CF_3)_2As$-$N{=}PPh_3$ has been examined for its CO substitution reactivity with $Os_3(CO)_{11}(NCMe)$ and $Os_3H_2(CO)_{10}$. The clusters isolated from these reactions are $Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh\}$ and $Os_3(\mu$-$H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}$ respectively. Both clusters possess highly delocalized As=N=P linkages.[168]

Reaction of $Ru_3(CO)_{10}(NCMe)_2$ with *cyclo*-$(PhAs)_6$ in toluene at ambient temperature gives $Ru_3\{\mu$-*cyclo*-$(PhAs)_6\}(CO)_{10}$ **157**, in which the intact six-membered rings adopt chair conformations and bridge metal–metal edges via two As atoms in the 1,5-positions of the ring. Conversely, treatment of $Ru_3(CO)_{12}$ with *cyclo*-$(PhAs)_6$ in toluene at elevated temperature results in fragmentation of the six-membered ring to afford $Ru_4(\mu_3\text{-}AsPh)_2(CO)_{13}$.[169]



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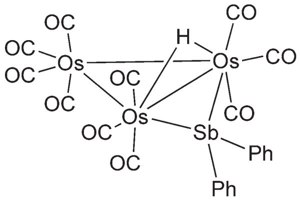
Reaction between $Ru_3(CO)_9(\mu\text{-}H)(C_{12}H_{17})$ and $AsPh_3$ results in insertion into the cluster-bound hydrocarbon moiety. The product of the reaction, $Ru_3(CO)_6(\mu\text{-}CO)(\mu\text{-}AsPh_2)(\mu\text{-}O{=}CC_{12}H_{17})$, was characterized in solution and the solid-state structure was determined by X-ray crystallography.[170]

The clusters $Os_3(\mu\text{-}H)(CO)_{10}L\{ON(CF_3)_2\}$ (where $L = PPh_3$, $AsPh_3$, or $SbPh_3$) have been synthesized from $Os_3H_2(CO)_{10}L$ and the bis(trifluoromethyl)nitroxyl radical $(CF_3)_2NO$ and characterized by ^{19}F NMR measurements and X-ray crystallography. The temperature-dependent ^{19}F NMR spectra originate from a restricted rotation about the N–O bond.[171]

Reactions of $Ru_3(CO)_{12}$ or the diphosphine complex $Ru_3(CO)_{10}(dppm)$ with $SbPh_3$ in the presence of diphenyl ketyl radical anion result in the formation and isolation of $Ru_3(\mu\text{-}SbPh_2)(\mu_2\text{-}\eta^2\text{-}OCPh)(CO)_{10}$ and $Ru_3(SbPh_3)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_9$, respectively.[172]

The reaction of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CO)]^-$ with Ph_2SbCl leads to $Os_3(\mu\text{-}H)(\mu\text{-}SbPh_2)(CO)_{10}$ **158**, $Os_3(\mu\text{-}SbPh_2)_2(CO)_{10}$ **159**, and $[Os_3(H)(\mu\text{-}SbPh_2)(CO)_{10}]_2$ **160**. All three structures have been determined by single crystal X-ray diffraction.[173]



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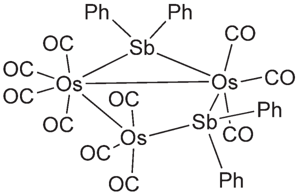

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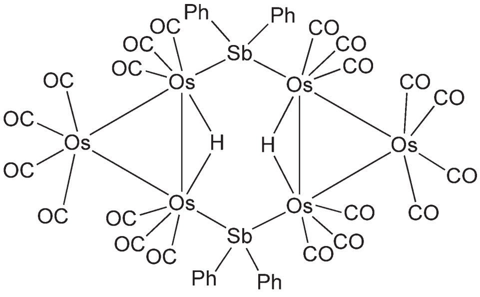

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The osmium–antimony cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SbPh_2)$ has been shown to react with donor ligands by cleavage of the antimony-bridged and hydrido-bridged Os–Os bond to give the adducts $Os_3(CO)_{10}(H)(\mu\text{-}SbPh_2)L$ (where $L =$ various ligands). The incoming ligand occupies an equatorial site on the $\{Os_3Sb\}$ framework, as verified by X-ray analysis on the $AsPh_3$ and $SbPh_3$ complexes. Solution NMR studies confirm the presence of an isomeric mixture in each case, which reflects different ligand arrangements relative to the antimony vertex.[174]

The thermolysis of $Os_3(CO)_{11}(EPh_3)$ ($E = As$[175],Sb[176]) results in the formation of $Os_3(\mu_3\text{-}AsPh)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$, $Os_3(\mu\text{-}H)(\mu\text{-}AsPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$, $Os_3(\mu\text{-}AsPh_2)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_7$, $Os_3(\mu_3\text{-}AsPh)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_8(AsPh_3)$ and $Os_3(\mu\text{-}H)(\mu\text{-}SbPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ and $Os_6(\mu_3\text{-}SbPh)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_{20}$, respectively. Prolonged heating of the antimony systems results in the formation of hexanuclear Os–Sb species.

Treatment of $Os_3(\mu\text{-}H)(\mu\text{-}SbPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ with either $PhC{\equiv}CH$ or *t*$BuC{\equiv}CH$ results in C–C bond coupling of the phenylene ligand with the terminal alkynes. The triosmium antimony cluster also serves as an effective catalyst for the cyclotrimerization of diphenylacetylene.[177] In contrast, cluster condensation has been found to occur when $Os_3(\mu\text{-}H)(\mu\text{-}SbPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ reacts with alkenes and dienes to form $Os_5(CO)_{14}(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)(\mu\text{-}\eta^2\text{-}C_6H_4)$ and $Os_5(CO)_{14}(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3\text{-}\eta^6\text{-}C_6H_4)(Ph)$.[178] Addition of PPh_3

to $Os_3(CO)_9(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_6H_4)$ furnishes $Os_3(CO)_9(PPh_3)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_2\text{-}\eta^2\text{-}C_6H_4)$, which can lose CO, coupled with phenylene recoordination to give $Os_3(CO)_8(PPh_3)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_6H_4)$, or isomerize and de-*ortho*-metalate to give $Os_3(CO)_9(PPh_3)(\mu\text{-}SbPh_2)(Ph)$. Reaction with an excess of PPh_3 leads to the new cluster $Os_3(CO)_8(PPh_3)_2(\mu\text{-}SbPh_2)(Ph_2PC_6H_4)$. A crossover study using the *p*-tolyl derivative $Os_3(CO)_9\{P(p\text{-tol})_3\}(\mu\text{-}H)(\mu\text{-}SbPh_2)(\mu_2\text{-}\eta^2\text{-}C_6H_4)$ with an excess of PPh_3 reveals that the *ortho*-metallation reaction involves the activation of the coordinated $P(p\text{-tol})_3$ ligand and not the incoming PPh_3 ligand.[179]

6.18.8 Trinuclear Clusters with Chalcogen (O, S, Se, Te) Donor Ligands

There is much chemistry of osmium and ruthenium with sulfur and selenium-containing ligands which generally lead to the production of higher nuclearity clusters. Comparatively, the chemistry of triruthenium and triosmium clusters with oxygen-containing ligands is still limited. Again, here we have focused on products of reactions which are trimetallic.

Reaction of $[PPN][Os_3(\mu\text{-}H)(CO)_{11}]$ with $Cu(PPh_3)_2BH_4$ in CH_2Cl_2 at room temperature affords $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}]$ and two isomers with the molecular formula $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_8(PPh_3)_2]$. In all three clusters the OH and hydride ligands bridge a single Os–Os edge. The two diphosphine complexes differ only in the relative positions of the phosphine ligands.[180,181]

Reaction of $Ru_3(CO)_{12}$ with (*R*)-BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] in the presence of "wet" Me_3NO does not give $Ru_3(CO)_{10}(BINAP)$ as expected, but instead an 80% yield of the dihydroxy complex $Ru_3(\mu\text{-}OH)_2(CO)_8\{\mu\text{-}(R)\text{-BINAP}\}$.[182]

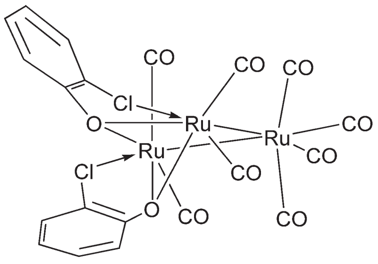
Reaction of $Os_3(CO)_{12}$ with MeOH in the presence of 2 equiv. of Me_3NO results in the formation and isolation of the methoxy-bridged osmium species $Os_3(\mu\text{-}OMe)(\mu\text{-}H)(CO)_{10}$. The analogous reaction with an increased amount of Me_3NO results in the formation of the related bis-methoxy complex $Os_3(\mu\text{-}OMe)_2(CO)_{10}$.[183]

Attempts to react $CpOs(PPh_3)_2Br$ with $Os_3(\mu_3\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_9$ in methanol afford the bis-methoxy cluster $Os_3(\mu_3\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(\mu\text{-}OMe)_2(CO)_9$, which exhibits an opened core, where the two non-bonded Os–Os vectors are each bridged by one OMe group.[184]

The hydroxy osmium cluster $Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}$ reacts with diol systems in a condensation reaction to form complexes having the general formula $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}O{\sim}OH)$. The reactivity of the glycol-coordinated clusters has also been examined. $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2OH)$ undergoes esterification with benzoyl chloride to give $Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}OCH_2CH_2OC(O)Ph\}$, along with $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CHO)$. The allylation chemistry of this latter cluster and its reactivity toward PhMgBr have also been investigated.[185]

The hydroxy-diyne ligand $HOCH_2C_4CH_2OH$ reacts with $Os_3(\mu\text{-}H)_2(CO)_{12}$ to form the triosmium cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}\eta^3\text{-}OCH{=}CHC{=}CCMe)$. Reactions of the hydroxy-containing cobalt cluster $Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}HOCH_2C_4CH_2OH)$ and $\{Co_2(CO)_6\}_2(\mu_2\text{-}\eta^2:\mu_2\text{-}\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ with $Os_3(\mu\text{-}H)_2(CO)_{12}$ have also been investigated.[186]

Ortho-substituted halo-phenols HOC_6H_4X (X = F, Cl, Br) react with $Ru_3(CO)_{12}$ in the presence of Me_3NO to form the phenoxy-bridged clusters $Ru_3(\mu\text{-}\eta^2\text{-}OC_6H_4X)_2(CO)_8$ **161**. Single crystal X-ray analysis of the chloro derivative shows additional bonding between the osmium atoms of the bridging edge and the halogen atoms such that the phenoxy ligand can be considered to be a five-electon donor ligand. Reversible addition and loss of CO from these clusters is thought to be at the expense of Ru–X bonding. Similar reaction between $Ru_3(CO)_{12}$ and hydroxymethyl-pyridine results in the formation of the analogous compound $Ru_3(\mu\text{-}\eta^2\text{-}OCH_2C_6H_4N)_2(CO)_8$ which shows secondary Ru–N bonding.[187]



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Treatment of $Ru_3(CO)_{12}$ with bis(2-pyridyl)ketone oxime (Hdpko) results in the formation of the triruthenium bis-oxime cluster $Ru_3(\mu\text{-}\eta^3\text{-dpko-}N,N,O)_2(CO)_8$ and other products. Elucidation of the molecular structure reveals that two ruthenium atoms in the cluster are doubly bridged by two dpko ligands which are attached to one ruthenium through the oxime O atom and through the nitrogen atoms of the pyridyl group and the N atom of the oxime group. Similar reactions with the activated clusters $M_3(CO)_{10}(NCMe)_2$ (M = Ru, Os) result in formation of the complexes $M_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^3\text{-dpko-}N,N,O)$. Thermal treatment of the osmium mono-dpko hydride cluster yields $Os_3(\mu\text{-}\eta^3\text{-dpko-}N,N,O)_2(CO)_8$.[188]

The hydroxylamine 7-chloro-4-(hydroxyamino)quinoline reacts with $Os_3(CO)_{10}(MeCN)_2$ yielding the cluster $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^1\text{-}OC_9H_6N_2Cl)$, which is shown by X-ray diffraction analysis to contain the oximate ligand that bridges adjacent osmium centers by an oxygen atom. This product undergoes molecular transformation to $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}ONC_9H_6NCl)$. Hydrogen bond formation is thought to be the driving force behind the molecular rearrangement.[189]

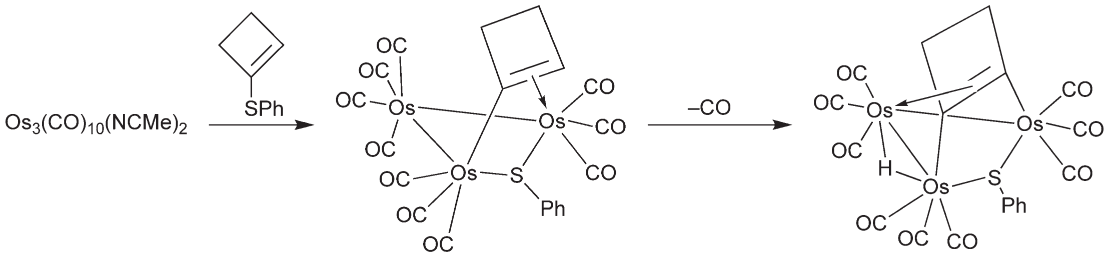
Facile replacement of the hydroxy ligand in $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})$ by siloxy ligands furnishes $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiR}_2R')$ (R = Et, Ph; R′ = Et, Ph, OH, $SiPh_2OH$). These clusters have been examined as models to better understand the reactivity of osmium carbonyls on silica surfaces. The X-ray crystal structures of $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2OH)$ and $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2OSiPh_2OH)$ have been determined.[190] The thermal and chemical stabilities of these clusters have also been examined.[191]

18β-Glycyrrhetinic acid (18β-GA) reacts with $Os_3(CO)_{10}(MeCN)_2$ and $Ru_3(CO)_{12}$ to give $Os_3(\mu\text{-H})(\mu\text{-}O_2C\text{-}C_{29}H_{45}O_2)(CO)_{10}$ and $Ru_2(\mu\text{-}O_2CC_{29}H_{45}O_2)_2(CO)_4(THF)_2$, respectively. The molecular structure of the trisomium cluster clearly shows that the 18β-GA residue is coordinated to the $\{Os_3\}$ frame by the carboxylate moiety.[192]

Reaction of phthalic acid and $Os_3(CO)_{10}(NCMe)_2$ gives two products $\{Os_3(CO)_{10}(\mu\text{-H})\}_2\{O_2CC_6H_4CO_2\}$ and $Os_3H(CO)_{10}\{O_2CC_6H_4C(O)O\}Os_3H(CO)_{11}$. The latter of these two complexes can undergo photolytic-induced loss of CO to form the former cluster.[193]

The solid-state reaction of $Os_3(\mu\text{-H})_2(CO)_{10}$ with H_2S results in formation of the intermediate hydrogen sulfide complex $Os_3(H)_2(CO)_{10}(H_2S)$, which rapidly transforms into the known complex $Os_3(H)_2(CO)_9(\mu_3\text{-S})$.[194]

1-(Phenylthio)cyclobutene reacts with $Os_3(CO)_{10}(NCMe)_2$ to give the cyclobutene complexes $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-C}{=}CHCH_2CH_2)(\mu\text{-SPh})$ **162** and $Os_2(CO)_6(\mu\text{-}\eta^2\text{-C}{=}CHCH_2CH_2)(\mu\text{-SPh})$ by addition to the cyclobutenyl group and cleavage of the carbon–sulfur bond. When treated with Me_3NO in a refluxing CH_2Cl_2 solution, compound **162** is converted to the complex $Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-SPh})$ **163**.[195] In a related study, 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene reacts with $Os_3(CO)_{10}(MeCN)_2$ by MeCN displacement and C–H bond activation of the alkene moiety to give $Os_3(CO)_{10}\{\mu\text{-PhSC}_2CH_2C(Me)^tBu\}(\mu\text{-H})$. Loss of CO from this cluster yields $Os_3(CO)_9\{\mu_3\text{-SPhC}_2CH_2C(Me)^tBu\}(\mu\text{-H})$, which contains a metallated cyclobutenyl ligand. Heating this nonacarbonyl cluster leads to Ph–S bond cleavage and production of the new cluster $Os_3(CO)_9\{\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu\}(\mu_3\text{-S})$.[196]

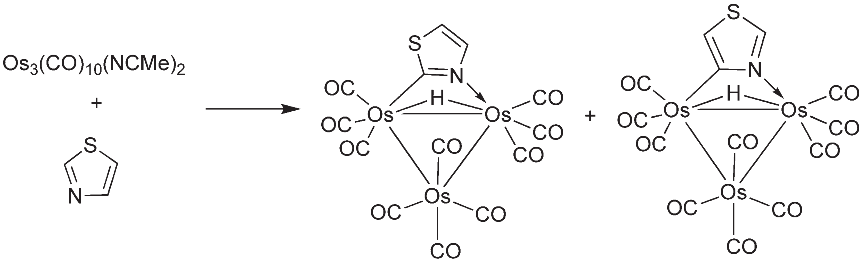


162 **163**

The kinetics and mechanism for the isomerization of $HRu_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$ to $Ru_3(\mu\text{-SEt})(\mu_3\text{-}\eta^3\text{-CCMeCHMe})(CO)_9$ have been investigated and the overall process shown to involve C–H elimination, C–S and Ru–Ru bond cleavage, and $Ru_2(\mu\text{-S})$ bond formation. Activation parameters for the isomerization were determined from the temperature dependence ($\Delta H^\ddagger = 127(3)\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^\ddagger = 56(11)\,\mathrm{J\,mol^{-1}\,K^{-1}}$) and from the pressure dependence of the rate constant.[197]

Reactions of thiacyclohexane (TCH) with $Os_3(CO)_{10}(NCMe)_2$, $Os(CO)_{11}(NCMe)$, and $Os_3(CO)_{12}$ have been investigated, and yielded the products $Os_3(CO)_{10}(TCH)_2$, $Os_3(CO)_{10}(TCH)$, and the hydrides $Os_3(CO)_9(\mu\text{-SCH}_2CH_2CH_2C)(\mu\text{-H})_2$ and $Os_3(CO)_8(\mu\text{-SCH}_2CH_2CH_2C)(THT)$, respectively.[198] In a similar reaction, $Os_3(CO)_{10}(SCH_2CH_2CH_2CH_2)_2$ is readily prepared by the reaction of $Os_3(CO)_{10}(NCMe)_2$ and tetrahydrothiophene (THT). Heating induces loss of one molecule of THT and C–H activation of one of the methylene groups adjacent to the sulfur atom of the remaining coordinated THT to form $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}SCH_2CH_2CH_2CH)(\mu\text{-}H)$. Further heating results in loss of CO and cleavage of one of the C–S bonds to form the complex $Os_3(CO)_9\{\mu\text{-}\eta^3\text{-}S(CH_2)_2CH{=}CH_2\}(\mu\text{-}H)$ which contains a 3-butenethiolate ligand in which the sulfur atom bridges one of the metal–metal bonds and the double bond is π-coordinated to one of the sulfur-bridged metal atoms.[199]

The reaction of thiomorpholine ($HN(CH_2CH_2)_2S$) with $Ru_3(CO)_{12}$ affords $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9$ which has been shown to consist of a closed triruthenium cluster with a $\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2$ ligand formed by the ring-opening cleavage of thiomorpholine with elimination of a $\{C_2\}$ fragment. Reaction of thiazolidine with $Os_3(CO)_{10}(NCMe)_2$ results in the formation of the complexes **164** and **165** by C–H abstraction.[200]

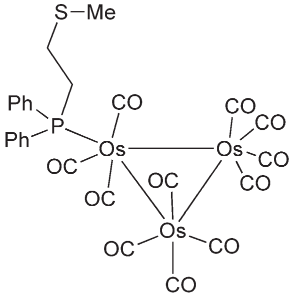


164 **165**

2-(Methylthio)thiophene ($2\text{-}MeSC_4H_3S$) oxidatively adds to $Os_3(CO)_{10}(NCMe)_2$ with cleavage of the C–H bond at the 3-position to give $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}MeS\text{-}3\text{-}C_4H_2S)(CO)_{10}$, the molecular structure of which possesses an MeS group which is coordinated to Os through the S atom, while the thiophene ring is coordinated to Os through the 3-C atom. Thermal treatment of the cluster in the dark gives only one product, $Os_3(\mu\text{-}H)(\mu_3\text{-}2\text{-}MeS\text{-}3\text{-}C_4H_2S)(CO)_9$, which is derived by loss of a CO from the $\{Os(CO)_4\}$ unit with concomitant η^2-coordination of the thiophene ring of bridging $MeSC_4H_2S$ at the third metal atom. Visible irradiation of the sample at room temperature leads to the formation of various products derived by migration of the MeS group.[201]

3,6-Dihydro-1,2-dithiin reacts with $Os_3(CO)_{10}(NCMe)_2$ at 0 °C to give the isomeric clusters $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CH{=}CHCH_2S)$ and $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$. Both compounds contain open triosmium clusters with bridging 2-butenedithiolato ligands formed by cleavage of the S–S bond.[202]

1-Diphenylphosphino-2-methylthioethane, $Ph_2PCH_2CH_2SMe$, reacts with $Os_3(CO)_{11}(NCMe)$ yielding $Os_3(CO)_{11}(Ph_2PCH_2CH_2SMe)$ **166**. Treatment of $Os_3(CO)_{10}(NCMe)_2$ with 1 equiv. of the P, S ligand initially yields the cluster $1,2\text{-}Os_3(CO)_{10}(\mu\text{-}Ph_2PCH_2CH_2SMe)$ **167**, in which the phosphine and the thioether moieties coordinate to different metal atoms of the metal triangle. Addition of two or more equivalents of the ligand yields $1,2\text{-}Os_3(CO)_{10}(\mu\text{-}Ph_2PCH_2CH_2SMe)$ **167** and $Os_3(CO)_{10}(Ph_2PCH_2CH_2SMe)_2$. The cluster $1,2\text{-}Os_3(CO)_{10}(\mu\text{-}Ph_2PCH_2CH_2SMe)$ is metastable and undergoes a slow isomerization reaction at room temperature to form $1,1\text{-}Os_3(CO)_{10}(Ph_2PCH_2CH_2SMe)$ **168**, in which the ligand chelates one Os atom.[203]



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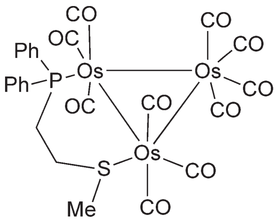

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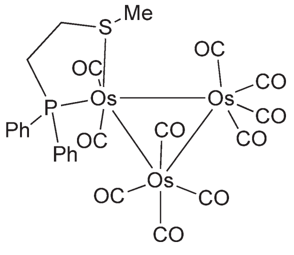

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Treatment of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$ with Me_3NO in a refluxing CH_2Cl_2 results in formation of $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$, the molecular structure of which shows the complex to contain a triply-bridging cyclobutyne ligand formed by the cleavage of the alkenyl C–H bond in the cyclobutenyl ligand and the transfer of the hydrogen atom to the metal atoms. Heating results in further transformations.[195]

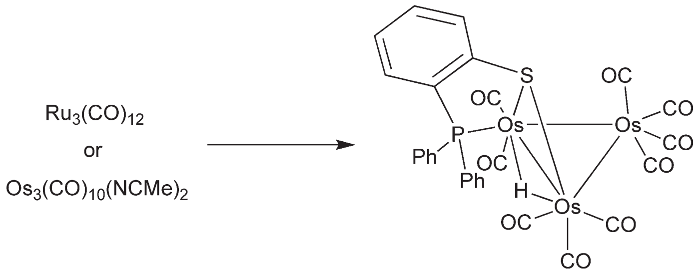
The complexes $Ru_3(CO)_9(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CR)$ (R = Me, Ph) are formed by the reactions of the corresponding ethylthio-alkynes with $Ru_3(CO)_{12}$.[204] The compounds $Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CR)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR^1)$ (R = $SiMe_3$,

$R^1 = Si^iPr_3$; $R = Si^iPr_3$, $R^1 = SiMe_3$; $R = Si^iPr_3$, $R^1 = H$; $R = H$, $R^1 = Si^iPr_3$) have been obtained by cleavage of one S–C bond of the thioethers $^iPr_3SiC{\equiv}CSC{\equiv}CR$ (R = H, $SiMe_3$) in the presence of $Ru_3(CO)_{12}$. Thermal treatment of $Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSi^iPr_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CH)$ yields higher nuclearity clusters.[205]

The reaction of $Ru_3(CO)_{12}$ with 1,2-ethanedithiol affords $Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)$, whereas the reaction with 1,3-propanedithiol yields $\{(\mu\text{-}H)Ru_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)$ and $Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)$. Treatment of $Os_3(CO)_{10}(MeCN)_2$ with 1,2-ethanedithiol and 1,3-propanedithiol gives $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SCH_2CH_2SH)$ and $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)$, respectively.[206]

Reaction of 1,2-dimercaptobenzene with the cluster $Os_3(CO)_{10}(NCMe)_2$ results in the formation of the bis-substituted complex $\{Os_3(CO)_{10}(\mu\text{-}H)\}_2(\mu:\mu\text{-}S_2C_6H_4)$.[193]

2-(Diphenylphosphino)thiophenol ($HSC_6H_4PPh_2$) reacts with the carbonyl clusters $Ru_3(CO)_{12}$ and $Os_3(CO)_{10}(NCMe)_2$ to give mixtures of products, the composition of which depends upon the reaction conditions and the ratio of the reactants. The $SC_6H_4PPh_2$ ligand of $M_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SC_6H_4PPh_2)(CO)_9$ (M = Ru **169**, Os **170** has the sulfur atom spanning the same M–M edge as the hydride ligand and the phosphorus atom attached to one of the bridged metal atoms. $Ru_3(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}Ph)(\mu\text{-}PPh_2)(PPh_3)(CO)_6$ which is also isolated contains sulfide, Ph, diphenylphosphanyl, and triphenylphosphine ligands that arise from decomposition of $HSC_6H_4PPh_2$. The $\{Ru_3\}$ triangle is capped by the sulfide and two Ru–Ru edges are spanned by bridging Ph and diphenylphosphanyl ligands.[207]



169: M = Ru
170: M = Os

The 2-mercaptopyridine-substituted triosmium cluster complexes, $\{Os_3H(CO)_{10}\}_2(\mu\text{-}SC_5H_3NCO_2)$, $Os_3H(CO)_{10}\{SC_5H_3N(OH)\}$, and $Os_3H(CO)_{10}(SC_5H_4N)$, undergo photochemical decarbonylation reactions in which the nitrogen of the mercaptopyridine ligand displaces a carbonyl on the third osmium of the thiolate-bridged triangle to yield $\{Os_3H(CO)_9\}(\mu\text{-}SC_5H_3NCO_2)\{Os_3H(CO)_{10}\}$, $Os_3H(CO)_9\{SC_5H_3N(OH)\}$, and $Os_3H(CO)_9(SC_5H_4N)$.[208]

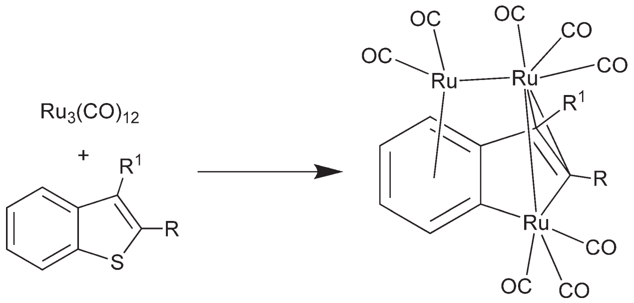
Reaction of $Os_3(CO)_{10}(NCMe)_2$ with thiosalicylic acid affords two products $\{Os_3(CO)_{10}(\mu\text{-}H)\}_2SC_6H_4CO_2$ and $Os_3H(CO)_{10}\{SC_6H_4C(O)O\}Os_3H(CO)_{11}$. The later complex undergoes CO dissociation to give $\{Os_3(CO)_{10}(\mu\text{-}H)\}_2SC_6H_4CO_2$ or fragmentation to give $Os_3H(CO)_{10}\{SC_6H_4COOH\}$. Unlike thiosalicylic acid, treatment of $Os_3(CO)_{10}(NCMe)_2$ with 1 equiv. of 2,2′-dithiosalicylaldehyde yields $Os_3(CO)_{10}(SC_6H_4CHO)_2$ and $Os_3(CO)_{10}(\mu\text{-}H)(SC_6H_4CHO)$.[193]

The reaction of $Os_3(CO)_{11}(NCMe)$ with 2-vinylthietane yields two products: $Os_2(CO)_6(\mu\text{-}\eta^4\text{-}SCH_2CH_2\text{-}CH{=}CHCH_2)$ and $Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}O{=}C(CH_2CH{=}CHCH_2CH_2S)\}$ The triosmium cluster contains an $\{Os_3\}$ core with ten terminal carbonyl ligands and a 3-hexenoylthiolate ligand that bridges an open edge of the cluster through both the sulfur atom and the ketonyl group termini.[209]

Treatment of $Os_3(CO)_{10}(MeCN)_2$ with 2-vinyltetrahydrothiophene at room temperature produces $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SCH_2CH_2CH{=}CHCH{=}CH_2)$ and $Os_2(\mu\text{-}H)(CO)_6(\mu\text{-}\eta^4\text{-}S(CH_2)_3CH{=}CHCH_2)$. X-ray analysis of the $\{Os_3\}$ product verifies the coordination of the hexadienethiolate ligand to a triangular triosmium frame. Ring-opening of the 2-vinyltetrahydrothiophene substrate by the $\{Os_3\}$ cluster occurs exclusively at the vinyl-substituted carbon atom.[210]

The 2-vinylthiacyclohexane cluster complex $Os_3(CO)_{10}\{\mu\text{-}\eta^3\text{-}S(CH_2)_4CH{=}CHCH_2\}$ is transformed into the complex $Os_3(CO)_{10}\{\mu\text{-}\eta^4\text{-}S(CH_2)_4CH{=}CHCH_2\}$ by a ring-opening cleavage of one C–S bond, a CO ligand shift, and opening of the cluster.[211]

$Ru_3(CO)_{12}$ reacts with benzothiophene,[212] 2-methylbenzothiophene, and 3-methylbenzothiophene[213] resulting in the formation of the ring-opened and desulfurized trinuclear complexes $Ru_3(CO)_8(\mu_3\text{-}C_8H_5R)$ (R = H, Me) **171–173**. In comparison the reactions with triosmium clusters yield the products $Os_3(CO)_{10}(\mu\text{-}SCCHC_6H_5)(\mu\text{-}H)$ and $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}SCCC_6H_5)$.[214,215]



171: R = H; R^1 = H
172: R = H; R^1 = Me
173: R = Me; R^1 = H

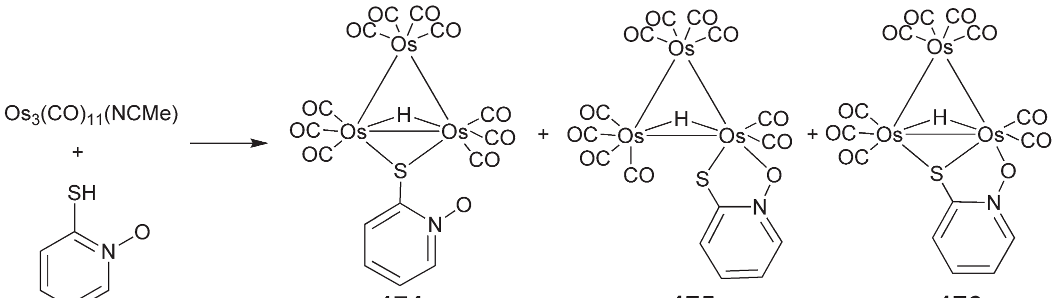
Similarly, $Os_3(CO)_{10}(NCMe)_2$ reacts with 1-bromobenzothiophene to form two products $Os_3(CO)_{10}(\mu\text{-}SCCHC_6H_5)(\mu\text{-}Br)$ and $Os_3(CO)_9(\mu\text{-}SCCHC_6H_5)(\mu\text{-}Br)$, both of which have been characterized by single crystal X-ray diffraction analyses. The two products contain benzothienyl ligands formed by the oxidative addition of the C–Br bond of the bromobenzothiophene to the cluster. In $Os_3(CO)_{10}(\mu\text{-}SCCHC_6H_5)(\mu\text{-}Br)$ the benzothienyl ligand is coordinated across the open edge of an open triosmium cluster through the sulfur and adjacent carbon atom. Similar coordination is observed in $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}SCCHC_6H_5)(\mu\text{-}Br)$ except that the benzothienyl ligand is a triply-bridging ligand using the sulfur atom and the C=C double bond of the five-membered heterocycle to bind to the $\{Os_3\}$ cluster.[214]

The reaction of SPh_2 with $Ru_3(CO)_{12}$ affords $Ru_3(CO)_8(\mu\text{-}SPh)(\mu\text{-}\eta^1:\eta^6\text{-}C_6H_5)$, as a result of S–Ph cleavage. Similarly, the ferrocenyl derivative FcSPh and $Ru_3(CO)_{12}$ affords $Ru_3(CO)_8(\mu\text{-}SFc)(\mu\text{-}\eta^1,\eta^6\text{-}C_6H_5)$ in good yield in addition to smaller amounts of $Ru_3(CO)_7(\mu\text{-}SFc)_4$.[216]

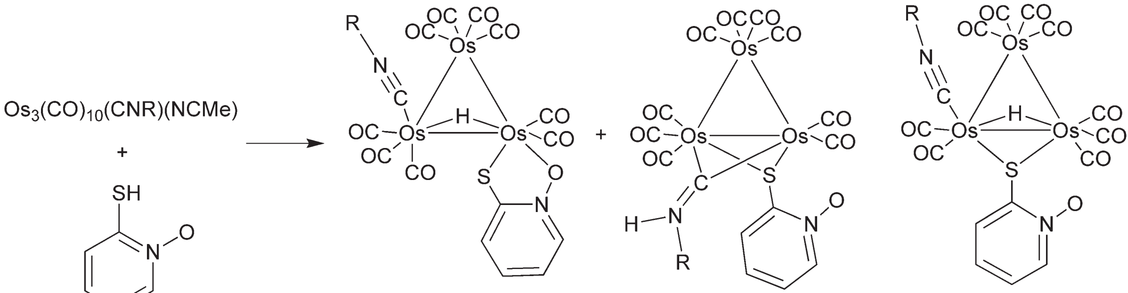
2,2′-Dipyridyl disulfide (pySSpy) undergoes oxidative addition with $Os_3(CO)_{10}(NCMe)_2$ to yield the triosmium clusters $Os_3(\mu\text{-}Spy)_2(CO)_{10}$, $Os_3(\mu\text{-}Spy)(\mu\text{-}\eta^2\text{-}Spy)(CO)_9$ together with diosmium complexes, and the hydride species $Os_3(\mu\text{-}H)(\mu\text{-}Spy)(CO)_9$.[217]

The 2-mercaptopyridine triosmium cluster complexes $\{Os_3H(CO)_{10}\}_2(\mu\text{-}SC_5H_3NCO_2)$, $Os_3H(CO)_{10}\{\mu\text{-}SC_5H_3N(OH)\}$, and $Os_3H(CO)_{10}(SC_5H_4N)$ upon exposure to irradiation at 366 nm undergo photochemical decarbonylation reactions in which the nitrogen of the mercaptopyridine ligand displaces a carbonyl on the third osmium of the thiolate-bridged triangle to yield $\{Os_3H(CO)_9\}(m\text{-}SC_5H_3NCO_2)\{Os_3H(CO)_{10}\}$, $Os_3H(CO)_9\{\mu_3\text{-}SC_5H_3N(OH)\}$, and $Os_3H(CO)_9(\mu_3\text{-}SC_5H_4N)$.[218]

The reaction of 1-hydroxypyridine-2-thione with $Os_3(CO)_{11}(NCMe)$ yields three complexes: $Os_3(CO)_{10}(\mu\text{-}H)\{\mu\text{-}\eta^1\text{-}SC_5H_4N(O)\}$ **174**, $Os_3(CO)_{10}(\mu\text{-}H)\{\eta^2\text{-}SC_5H_4N(O)\}$ **175**, and $Os_3(CO)_9(\mu\text{-}H)\{\mu\text{-}\eta^2\text{-}\eta^1SC_5H_4N(O)\}$ **176**. Treatment of 1-hydroxypyridine-2-thione with triosmium isocyanide complexes $Os_3(CO)_{10}(CNR)(NCMe)$ (R = CH_2Ph; R = Pr) has led to the formation of $Os_3(CO)_9(\mu\text{-}H)(CNR)\{\eta^2\text{-}SC_5H_4N(O)\}$ **177–178**, $Os_3(CO)_9(\mu\text{-}\eta^1\text{-}C{=}NHCH_2Ph)\{\mu\text{-}\eta^1\text{-}SC_5H_4N(O)\}$ **179–180**, and $Os_3(CO)_9(\mu\text{-}H)(CNR)\{\mu\text{-}\eta^1\text{-}SC_5H_4N(O)\}$ **181–182**.[219]



174 **175** **176**

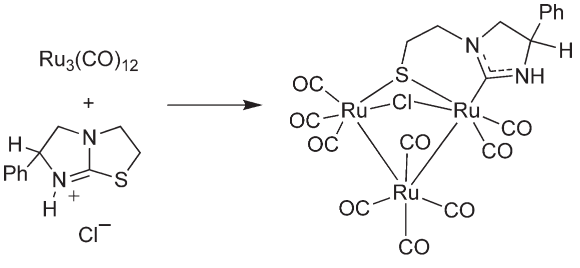


177: R = CH$_2$Ph
178: R = Pr
179: R = CH$_2$Ph
180: R = Pr
181: R = CH$_2$Ph
182: R = Pr

Reaction of elemental sulfur or cyclohexene sulfide with the carbene triosmium cluster $Os_3(CO)_9(\mu^3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Ph)$ gives the corresponding thioketone cluster $Os_3(CO)_9(\mu^3\text{-}\eta^2:\eta^2:\eta^2\text{-}SC_6H_5Ph)$.[220]

$Os_3(CO)_{10}(NCMe)_2$ reacts with phenylthiourea and *N*,*N*′-diphenylthiourea to yield the thioureato–triosmium cluster complexes $Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}SC{=}NH(NH_2)\}$ and $Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}SC{=}NPh(NPhH)\}$ in which the thioureate moiety bridges two osmium atoms via the sulfur atom. Photolysis of the complexes results in loss of CO and secondary coordination of a nitrogen atom of the thioureate ligand.[221]

The reaction of $Ru_3(CO)_{12}$ with levamisole hydrochloride ([Hlvms]Cl) leads to formation of $Ru_3(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}C_{11}H_{13}N_2S\text{-}C,S)(CO)_9$ **183**. This complex contains a new ligand that arises from an unprecedented oxidative addition of an S–C bond of protonated levamisole to a metal atom.[222]



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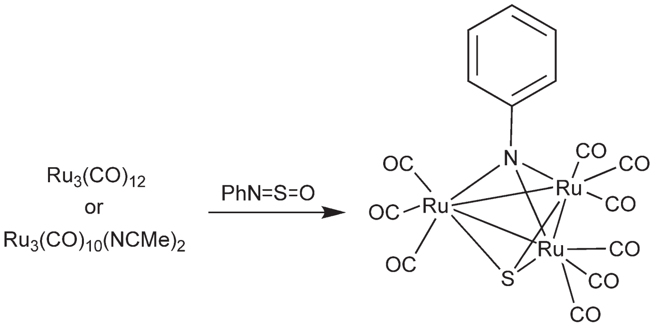
The difunctional carboxylate ligands 2-mercaptobenzoic acid, 3-mercaptopropanoic acid, and 2,6-dicarboxypyridine react with the triosmium cluster $Os_3(CO)_{10}(NCMe)_2$ to form the linked clusters, $[\{Os_3H(CO)_{10}\}_2(\mu\text{-}L)]$ (where L represents the carboxylate ligand).[223]

The cluster $[PPN]_2[Ru_3(CO)_{11}]$ reacts with SO_2 to give $[PPN]_2[Ru_3(CO)_9SO_2]$ and $[PPN]_2[Ru_3(CO)_7(SO_2)_3]$. In both clusters, SO_2 exhibits the μ_3,η^2-bonding mode, and in the latter cluster μ-SO_2 bridging two metals through S is also observed.[224] The reaction of SO_2 with $Ru_3(CO)_{12}$, $[Ru_3(CO)_{11}Cl]^-$, or $Ru_3(CO)_{10}(MeCN)$ produces polymeric materials $[Ru_3(CO)_3(SO)_2]_n$.[225]

Reaction of $Ru_3(CO)_{12}$ with the SO_2 analog *N*-sulfinylaniline (PhN=S=O) produces the sulfido triruthenium clusters $Ru_3(\mu_3\text{-}S)(\mu_3\text{-}NPh)(CO)_9$ **184**. Reaction of the labile cluster $Ru_3(CO)_{10}(NCMe)_2$ with PhNSO affords **184** as the major product and is accompanied by CO_2 evolution.[110]



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Elemental selenium reacts with the unsaturated cluster $Os_3(\mu\text{-}H)(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}$ at 110 °C to give the two triosmium clusters $Os_3(CO)_7(\mu_3\text{-}Se)_2(\mu\text{-}dppm)$ and $Os_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}Se)(\mu\text{-}dppm)$.[226]

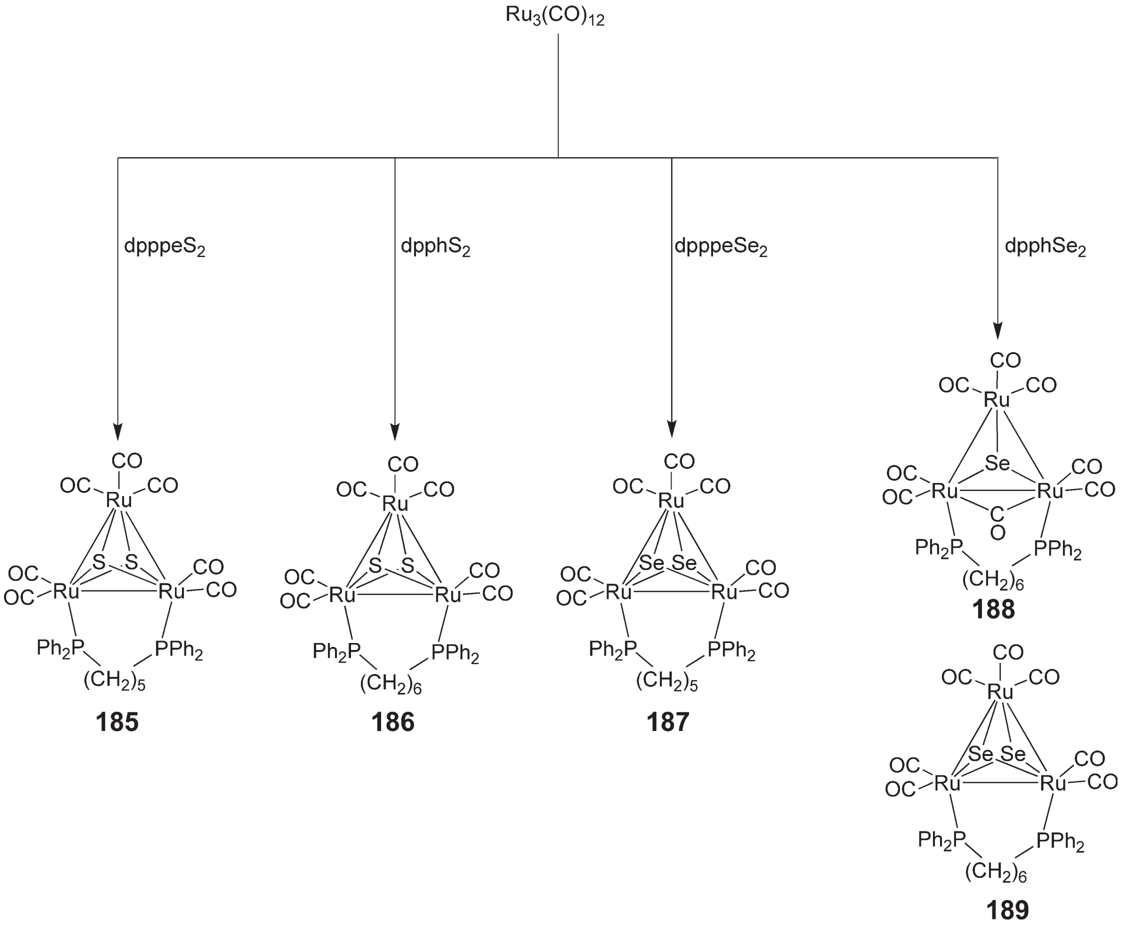
Phosphine selenide (P=Se) compounds have been used extensively to produce a wide range of metal selenide clusters.[227] The simple phosphine selenide $Ph_3P{=}Se$ readily reacts with $Ru_3(CO)_{12}$ in a highly selective reaction to yield the disubstituted trinuclear $Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2$ in very high yield (>90%). Minor products are the mono- and trisubstituted analogs, $Ru_3(\mu_3\text{-}Se)_2(CO)_8(PPh_3)$ and $Ru_3(\mu_3\text{-}Se)_2(CO)_6(PPh_3)_3$.[228,229] The monoselenido clusters $Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_8(PR^1R_2)$ and $Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7(PR^1R_2)_2$ ($R = Ph$, $R^1 = Ph$ or CH_2Ph; $R = R^1 =$ *p*-C_6H_4OMe) are similarly obtained by the reaction of the phosphine selenides R_2R^1 P=Se with $Ru_3(CO)_{12}$. The monoselenide derivatives undergo a second attack by $R_2R^1P{=}Se$ affording the corresponding diselenide derivative $Ru_3(\mu_3\text{-}Se)_2(CO)_7(PR^1R_2)$.[230] The reactions between $Ph_3P{=}Se$ and the triosmium clusters $Os_3(CO)_{11}(NCMe)$, $Os_3(CO)_{10}(NCMe)_2$, and $Os_3(\mu\text{-}H)_2(CO)_{10}$ have also been investigated. The reaction with an equimolar amount of

$Os_3(CO)_{11}(NCMe)$ afforded known clusters $Os_3(\mu_3\text{-}Se)_2(CO)_9$, and $Os_3(CO)_{11}(PPh_3)$, as well as $Os_3(\mu_3\text{-}Se)(CO)_9(PPh_3)$. The reaction with $Os_3(\mu\text{-}H)_2(CO)_{10}$ gave two new clusters, $Os_3(\mu_3\text{-}Se)(\mu\text{-}H)_2(CO)_8(PPh_3)$ and $Os_6(\mu_3\text{-}Se)(H)(\mu\text{-}H)_3(CO)_{18}(PPh_3)_2$, both of which have been structurally characterized.[231]

Similarly, the thiophene-substituted phosphine selenide $Ph_2(C_4H_3S)P{=}Se$ reacts with $Ru_3(CO)_{12}$ to afford the expected open triangular 50-electron cluster $Ru_3(\mu_3\text{-}Se)_2(CO)_7\{P(C_4H_3S)Ph_2\}_2$. A secondary product, $Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(\mu\text{-}C_4H_3S)(CO)_6\{P(C_4H_3S)Ph_2\}$, derived from cleavage of a phosphorus–thiophene P–C bond, is also isolated from the reaction mixture. Single crystal X-ray diffraction analysis shows the cluster to possess two ligands (a phosphide and a thienyl) bridging two sides of the metal triangle, which is capped by the selenium atom ligand.[232] The reaction of the bis(phosphine selenide) $CH_2(Ph_2PSe)_2$ and $Ru_3(CO)_{12}$ (1 : 1) in refluxing toluene in the presence of Me_3NO affords the expected bicapped cluster $Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppm)$. The harsh reaction conditions used result in cluster fragmentation and formation of $\{Ru_4(\mu_4\text{-}Se)_2\}$ clusters as co-products.[233]

The monosubstituted selenido–carbonyl open-triangular *nido*-cluster $Ru_3(\mu_3\text{-}Se)_2(CO)_8(L)$ (L = tripyrrolidinophosphine, tpnp), formed from the reaction of $Ru_3(CO)_{12}$ with tpnpSe, reacts with tris(*p*-methoxyphenyl)phosphine and 1,2-bis(diphenylphosphinomethyl)benzene (dpmb), giving respectively, the di- and trisubstituted $Ru_3(\mu_3\text{-}Se)_2(CO)_6(tpnp)(dpmb)$ and $Ru_3(\mu_3\text{-}Se)_2(CO)_7(tpnp)\{P(C_6H_4OMe)_3\}$ clusters.[234]

The phosphine sulfides and selenides $Ph_2P(E)(CH_2)_5P(E)Ph_2$ ($dpppeE_2$) and $Ph_2P(E)(CH_2)_6P(E)Ph_2$ ($dpphE_2$) (E = S, Se) react with $Ru_3(CO)_{12}$ to yield the bicapped chalcogenide clusters $Ru_3(\mu\text{-}E)_2(CO)_7(\mu\text{-}dpppe)$ (E = S, **185**; E = Se, **187** and $Ru_3(\mu\text{-}E)_2(CO)_7(\mu\text{-}dpph)$ (E = S, **186**; E = Se, **189**. Reaction of $dpphSe_2$ with $Ru_3(CO)_{12}$ also yields the monoselenide cluster $Ru_3(\mu\text{-}Se)(CO)_8(\mu\text{-}dppph)$ **188**.[235]



Reactions of $Ru_3(CO)_{12}$ with the chiral diphosphazane monoselenide $Ph_2PN(R)P(Se)Ph_2$ (R = (*S*)-C^*HMePh) yield the selenium monocapped triruthenium cluster $Ru_3(\mu_3\text{-}Se)(\mu\text{-}CO)(CO)_7\{\mu\text{-}PPh_2N((S)\text{-}C^*HMePh)PPh_2\}$. An analogous reaction of the diphosphazane monosulfide $(PhO)_2PN(Me)P(S)(OPh)_2$ that bears a strong π-acceptor phosphorus shows a different reactivity pattern yielding the triruthenium clusters

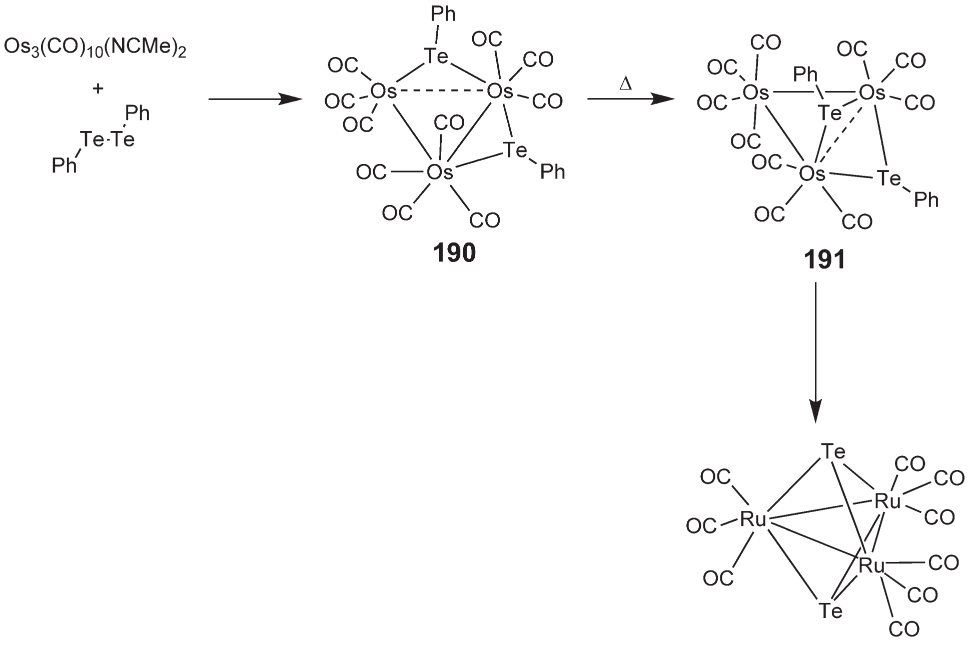
$Ru_3(\mu\text{-}S)(\mu\text{-}CO)(CO)_7\{\mu\text{-}P(OPh)_2N(Me)P(OPh)_2\}$ and $Ru_3(\mu\text{-}S)_2(CO)_5\{\mu\text{-}P(OPh)_2N(Me)P(OPh)_2\}\{\mu\text{-}P(OPh)_2\text{-}N(Me)P(OPh)_2\}$, when reacted with $Ru_3(CO)_{12}$.[236]

The diselenide ligand $Se{=}PPh_2NPPh_2PPh_2NPh_2P{=}Se$ reacts with $Ru_3(CO)_{12}$ in a reaction that includes P–P bond breakage and formation of complex $Ru_3(CO)_6(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(Ph_2PNPPh_2NPPh_2)$.[237]

The redox-active diselenide, 1,1-bis(diphenylphosphino)ferrocene diselenide (dppfSe$_2$), reacts with $Ru_3(CO)_{12}$ to afford the two isomeric *nido*-clusters $Ru_3(\mu_3\text{-}Se)_2(dppf)(CO)_7$ and $Ru_3(\mu_3\text{-}Se)_2(CO)_7(\mu\text{-}dppf)$, which contain dppf as chelating and bridging ligand, respectively. Thermal treatment of $Ru_3(\mu_3\text{-}Se)_2(dppf)(CO)_7$, in which the two phosphorus atoms of dppf ligand are coordinated to one Ru atom, results in a molecular rearrangement and formation of the thermodynamically more stable isomer $Ru_3(\mu_3\text{-}Se)_2(\mu\text{-}dppf)(CO)_7$ in which the dppf ligand bridges the open $\{Ru_2Se_2\}$ face.[238]

The trinuclear carbonyl clusters $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(MeCN)_2$ have been shown to react with benzo[*b*]tellurophene under mild conditions in refluxing THF, to give compounds containing the open-chain ligands $C_6H_4CHCHTe$ or the fragments Te and C_8H_6 as bridging ligands. Of the complexes isolated and characterized, only $Os_3(\mu\text{-}C_8H_6Te)(CO)_{10}$ is a trimetallic telluride.[239]

$Os_3(CO)_{10}(MeCN)_2$ reacts with Ph_2Te_2 at room temperature to give $Os_3(CO)_{10}(\mu\text{-}TePh)_2$ **190**, which possesses an open Os–Os edge that is bridged by one of the TePh units. Thermolysis of this product results in isomerization and formation of the bis-TePh bridged cluster $Os_3(CO)_{10}(\mu\text{-}TePh)_2$ **191**, which undergoes further reaction to form the cluster $Os_3(CO)_9(\mu_3\text{-}Te)_2$ **192**. Treatment of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with Ph_2Te_2 led to a complex mixture of several osmium compounds.[240]



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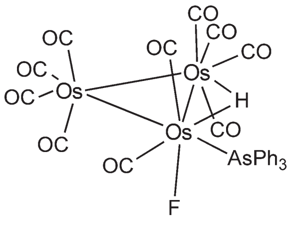
The reaction of the niobium hydrotelluride $[Cp^*{}_2Nb(Te_2H)]$ with $Ru_3(CO)_{12}$ in boiling toluene gave $Ru_3(\mu_2\text{-}H)_2(CO)_9(\mu_3\text{-}Te)$, $[Ru_6(\mu_3\text{-}H)(CO)_{15}(\mu_3\text{-}Te)_3][Cp^*{}_2Nb(CO)_2]$ and $[Ru_5(\mu_2\text{-}H)(CO)_{14}(\mu_4\text{-}Te)][Cp^*{}_2Nb(CO)_2]$ along with $Ru_4(CO)_{11}(\mu_4\text{-}Te)_2$. The reaction of $Ru_3(\mu_2\text{-}H)_2(CO)_9(\mu_3\text{-}Te)$ with bis(diphenylphosphino)methane (dppm) gave $Ru_3(\mu_2\text{-}H)_2(CO)_7(dppm)(\mu_3\text{-}Te)$. Reaction between $Ru_4(CO)_{11}(\mu_4\text{-}Te)_2$ and dppm results in cluster oxidation with reduction in nuclearity to give $Ru_3(CO)_7(dppm)(\mu_3\text{-}Te)_2$ and $Ru_4(CO)_9(dppm)(\mu_4\text{-}Te)_2$.[241]

6.18.9 Trinuclear Clusters with Halogen Ligands

Kinetic data for CO substitution in $[Os_3(CO)_{10}LX]^-$ (where L = PPh or CO; X = NCO^-, Cl^-, Br^-, or I^-) by PPh_3 have been reported. The activation parameters are indicative of a mechanism involving CO loss that is assisted by the X ligand. Mechanistic details and the effect of the bridging X ligand on the transition state of the substitution reaction have been discussed.[242]

The isolation and X-ray crystallographic characterization of $Ru_3(\mu\text{-}Cl)_2(THF)_2(CO)_8$ has been published.[243]

Reaction of hydrogen halides HX (X = F, Cl, Br, I) with the osmium hydride clusters $[Os_3(\mu\text{-}H)(CO)_{11}][ON(CF_3)_2]$ and $[Os_3(\mu\text{-}H)(CO)_{10}(EPPh_3)][ON(CF_3)_2]$ (E = P, As, Sb) results in the synthesis and isolation of a series of halogenated triosmium clusters of the general formula $Os_3(\mu\text{-}H)(CO)_{11}(X)$ and $Os_3(\mu\text{-}H)(CO)_{10}(EPPh_3)(X)$. The reaction of $[Os_3(\mu\text{-}H)(CO)_{10}(EPPh_3)][ON(CF_3)_2]$ with HF gives two isomers, one of which was established from X-ray crystallography to be $Os_3(\mu\text{-}H)(CO)_{10}(AsPh_3)(F)$ **193** with $AsPh_3$ and F bonded to the same Os centre.[244]



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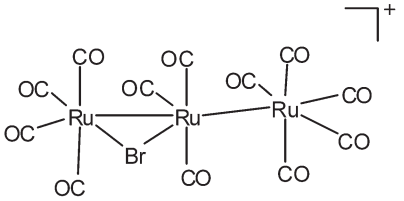
The reaction of $Os_3(CO)_{10}(CNR)(MeCN)$ with HCl has been studied as a model for the fine-tuning of site-selective protonation in metal clusters. Protonation, which takes place at either the osmium center or the nitrogen atom of the isocyanide ligand, can be tuned by changing factors such as the nature of the isocyanide ligand, solvent polarity and acid strength. The molecular structures of $Os_3(CO)_{10}(\mu\text{-}Cl)(\mu\text{-}C{=}NHCH_2Ph)$ and $Os_3(\mu\text{-}H)Cl(CO)_{10}(CNPr)$ have been established by single crystal X-ray diffraction experiments.[245]

The oxidative addition of HX (X = Cl, Br, I) to $H_2Os_3(CO)_{10}$ affords four new clusters with the general formula $Os_3H(\mu\text{-}H)_2(CO)_{10}(X)$, which differ only in the positions occupied by the terminal hydride ligand. The base-catalyzed oxidative addition in the presence of NH_3 is also discussed.[246]

Reaction of triruthenium dodecacarbonyl with a source of Br^+ results in the formation of the linear $[Ru_3(CO)_{12}(\mu\text{-}Br)]^+$ cation **194**, which may be considered to be a derivative of $[Ru_2(CO)_8(\mu\text{-}Br)]^+$ in which one of the carbonyl ligands has been replaced by an $\{Ru(CO)_5\}$ unit. Comparatively, reaction of $Os_3(CO)_{12}$ with Br^+ results in the formation of $[Os_3(CO)_{12}(\mu\text{-}Br)]^+$ cation **195**, which contains a planar four-membered $\{Os_3Br\}$ ring.[247]

Direct bromination of $Os_3(CO)_{11}(EPh_3)$ (where E=P, Sb) with Br_2 affords the trimetallic chain clusters $Br_2Os(CO)_3Os(CO)_4Os(CO)_4(EPh_3)$ and $Br(CO)_4OsOs(CO)_4Os(CO)_3Br(EPh_3)$. The clusters have been shown to contain two donor–acceptor Os–Os bonds in tandem, and VT ^{31}P-NMR studies provide evidence for the presence of an intermediate bromonium adduct that collapses in the presence of bromide ion to give both of the observed products.[248]



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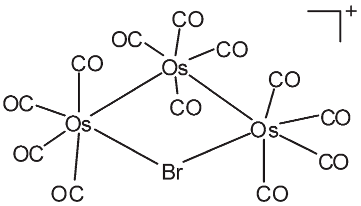

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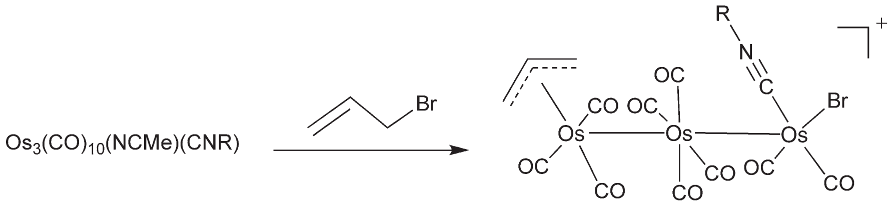
Bromination of the disubstituted triosmium clusters $Os_3(CO)_{10}(EPh_3)_2$ (E = P, As) with Br_2 results in the formation of the cluster cations $[Os_3(CO)_{10}(EPh_3)_2(\mu\text{-}Br)]^+$, which crystallized as the $[Os(CO)_3Br_3]^-$ salts.[249]

The ruthenium–chloro cluster $[PPN][Ru_3(CO)_{12}(\mu\text{-}Cl)]$ reacts with the propargyl alcohol derivatives $CH_3CC{\equiv}CH_2OH$ and $CH_3CC{\equiv}CH_2OTs$ in a series of reactions analogous to cobalt-specific $Co_2(CO)_8$ addition of alkynes, resulting in the formation of neutral allenyl species $Ru_3(\mu\text{-}Cl)(\mu\text{-}\eta^3\text{-}CH_3CCCH_2)(CO)_9$.[250]

The cationic cluster complex $[Ru_3(\mu_3\text{-}ampy)(CO)_{10}][BF_4]$ (Hampy = 2-amino-6-methylpyridine) reacts with chloride, iodide, and acetate anions (as $[PPN]^+$ or $[Bu_4N]^+$ salts) to give the 50-electron neutral compounds. $[Ru_3(\mu\text{-}X)(\mu_3\text{-}ampy)(CO)_9]$ (X = Cl, I, $MeCO_2$).[251]

The reaction between $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ and pyridine afforded a mixture of products including the bridged chloro-species $Ru_3(\mu\text{-}Cl)_2(CO)_8(NC_5H_5)(PPh_3)$ and $Ru_3(\mu\text{-}Cl)_2(CO)_8(NC_5H_5)_2$.[64]

The linear triosmium clusters $(\eta^3\text{-}C_3H_5)Os(CO)_3Os(CO)_4OsBr(CO)_3(CNR)$ **196** (R = Pr, CH_2Ph) and $(\eta^3\text{-}C_3H_5)Os(CO)_3Os(CO)_4OsBr(CO)_4$ **197** have been prepared from the reduction of $Os_3(CO)_{10}(CNR)(MeCN)$ and $Os_3(CO)_{11}(MeCN)$ with allyl bromide, respectively. The molecular structure of the propyl isonitrile derivative has been determined by single crystal X-ray diffraction analysis.[252]



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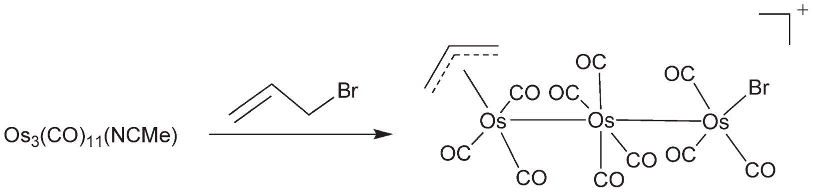

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Adams and coworkers have investigated the C–X (X = Br, I) activation of halocyclobutene derivatives 1-bromocyclobutene[253] and 1-iodo-2-methyl-cyclobutene,[254] by $Os_3(CO)_{10}(NCMe)_2$. Initial reactions in both systems produce triosmium complexes of the general formula $Os_3(CO)(\mu\text{-}X)(\mu\text{-}CCRCHCH_2)$ (X = Br, R = H; X = I, R = Me) which contain a bridging σ, π-coordinated cyclobutenyl ligand and bridging halide across the open face of the triosmium cluster. Thermal rearrangement of these systems results in ring-opening of the cyclobutenyl ligand and formation of a series of isomeric triosmium alkenylidene systems.

$Os_3(CO)_{10}(NCMe)_2$ reacts with 1-bromobenzothiophene in a C–Br activated oxidative addition reaction to form two products: $Os_3(CO)_{10}(\mu\text{-}SCCHC_6H_5)(\mu\text{-}Br)$ and $Os_3(CO)_9(\mu\text{-}SCCHC_6H_5)(\mu\text{-}Br)$.[214]

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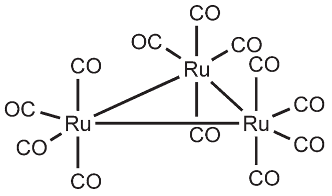
6.19
Trinuclear Clusters of Ru/Os with Hydrocarbon Ligands

P R Raithby and A L Johnson, University of Bath, Bath, UK

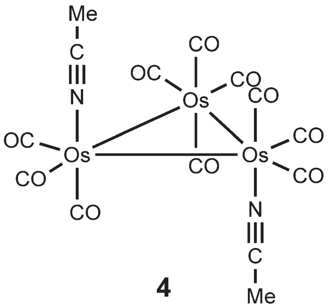
6.19.1 Introduction

This chapter is generally devoted to triruthenium and triosmium clusters that have hydrocarbon ligands except for those clusters that contain cyclopentadienyl or arene ligands. In some cases ligands that contain non-coordinating heteroatoms as part of the hydrocarbon ligands are also included. This section should be read in conjunction with COMC (1982), volume 4, chapters 32.5 and 33.3,[1] and COMC (1995), volume 7, chapter 13,[2] where much of the basic hydrocarbon ligand chemistry is laid out, and this contribution should be treated as an updating of this area containing material published during the period 1994–2005. In the period covered by this review the majority of the work has involved systems where the hydrocarbon ligands interact with the metal centers through π-orbitals, and η^1-alkyl, acyl, alkylidene, vinylidene, or alkylidyne ligand interactions are rare, and will only be mentioned briefly. Where they coordinate to a cluster that also bears another hydrocarbon ligand, they will, in general, be discussed at the same time as the other ligand grouping. Generally, the emphasis of the research in this area has changed over the last decade, and fewer new vinylidene, alkyne and allyl clusters have been reported, but there has been a growth in studies using diynes and larger conjugated molecules, and the discussions laid out below will tend to focus more on these new areas.

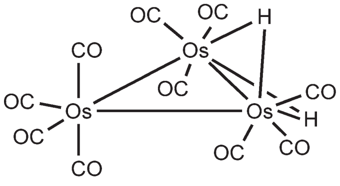
As in COMC (1982)[1] and COMC (1995)[2] the starting materials leading to the formation of trinuclear clusters of ruthenium or osmium that contain hydrocarbon ligands are the triruthenium or triosmium cluster carbonyls themselves. The simplest of these are the binary carbonyls $[M_3(CO)_{12}]$ (M = Ru **1**, Os **2**),[3,3a] but for these clusters to react with hydrocarbons forcing conditions involving pyrolysis or thermolysis are required, and these conditions generally lead to the formation of several products, each in low yield. For hydrocarbon-containing cluster products to be obtained under milder conditions the lightly ligated acetonitrile-substituted clusters $[M_3(CO)_{10}(NCMe)_2]$ (M = Ru **3**, Os **4**),[4,5] or, for osmium, the unsaturated dihydride cluster, $[Os_3(\mu\text{-H})_2(CO)_{10}]$ **5**, are used.[6] When using the acetonitrile complexes in reactions with unsaturated hydrocarbon ligands the labile acetonitriles are usually replaced by the hydrocarbon ligand, but ligand and metal framework rearrangements are common. With **5**, the hydrocarbon ligand adds to the cluster and this process is frequently accompanied by transfer of hydrogen from the metal framework to the organic group; this may also cause rearrangement of the cluster. The formation of hydrocarbon-substituted clusters may also be achieved by the reaction of a hydrocarbon ligand with a cluster that can create a vacant coordination site by a ligand rearrangement such as the hemilabile deprotonated 2-aminopyridine ligands (apy ligands) as found in the complex $[Ru_3(\mu\text{-H})(\mu_3\text{-apy})(CO)_9]$ **6**.[7]



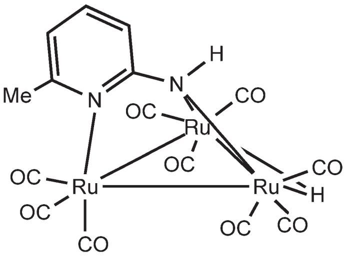
1



4

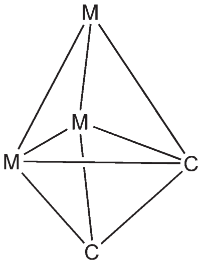


5



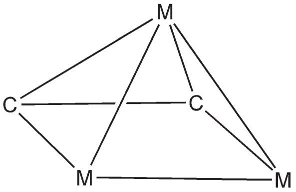
6

The nature of the bonding between ruthenium and osmium cluster frameworks and hydrocarbon ligands has long been the subject of discussion. It is often helpful in rationalizing the framework geometry particularly of alkene- and alkyne-substituted triosmium and triruthenium clusters, and indeed, of diyne or allyl-substituted clusters, to consider the carbon atoms of the unsaturated units as part of the core framework.[8,8a–8d] In such cases PSEP theory[9] can be used to good effect such that, for example, an M_3C_2 core can be considered as either a *closo*-trigonal bipyramid **7**, with six electron pairs for cluster bonding, or as a square-based pyramid (a *nido*-octahedron) **8** with seven electron pairs for cluster bonding. Another significant development in the understanding of the bonding in hydrocarbon-substituted ruthenium and osmium carbonyl clusters that has occurred within the last 10 years has been the use of density functional theory (DFT) methods backed up by experimental measurements.[10,11]



P = 6
closo-Trigonal bipyramid

7



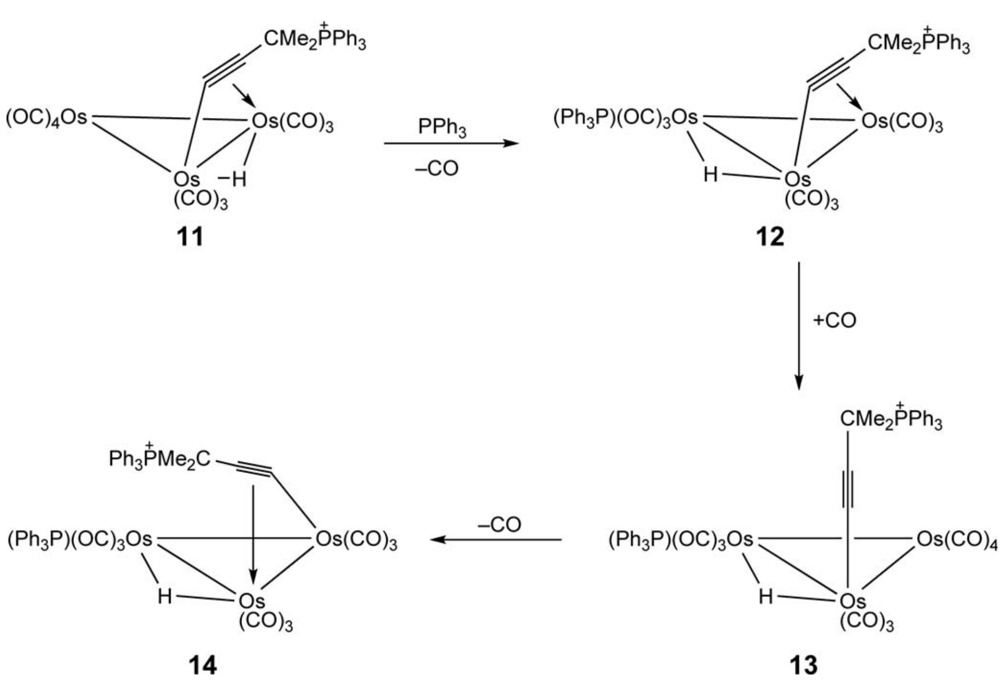
P = 7
nido-Octahedron

8

6.19.2 Clusters with Alkyl, Alkylidene, and Alkylidyne Ligands

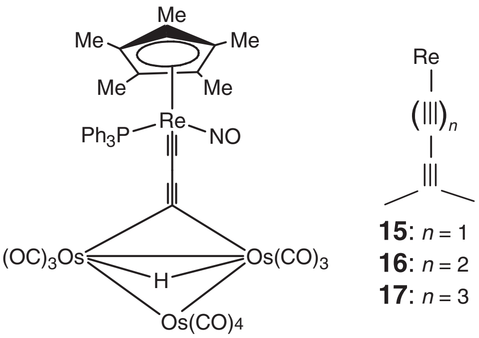
During the period 1994–2005 the number of new clusters that have been prepared that contain hydrocarbon ligands with η^1-alkyl, η^1-acyl, η^1-alkylidene, or η^1-alkylidyne ligands is relatively small, and they will be treated in one section.

The cluster cation $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1{:}\eta^2\text{-}{=}C{=}C{=}CMe_2)]^+$ **9**, as its $[BF_4]^-$ salt, reacts with PPh_3 at −78 °C to give isomeric phosphonium derivatives of the formula $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCMe_2PPh_3)]^+$ **10** and **11**. A second PPh_3 molecule attacks **11** at the $Os(CO)_4$ metal center, substituting a CO group for the phosphine to give $[Os_3(\mu\text{-H})(CO)_9(PPh_3)(\mu\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCMe_2PPh_3)]^+$ **12**, which further transforms to the η^1-acetylide complex to give $[Os_3(\mu\text{-H})(CO)_{10}(PPh_3)(\sigma\text{-}C{\equiv}CCMe_2PPh_3)]^+$ **13** (Scheme 1), which has been characterized crystallographically. This cation can then go on to decarbonylate to form $[Os_3(\mu\text{-H})(CO)_9(PPh_3)(\mu\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCMe_2PPh_3)]^+$ **14** which is an isomer of **12**. Cluster **13** may be considered as an intermediate in the isomerization of **12** and **14**.[12]



Scheme 1

As part of a research program to prepare metal centers linked by poly-ynes in order to make molecular wires, the activated cluster $[Os_3(CO)_{10}(NCMe)_2]$ has been treated with $[Cp^*Re(NO)(PPh_3)(C{\equiv}C)_{n-1}(C{\equiv}C)H]$ ($n = 1, 2, 3$) to form the linked complexes $[Os_3(\mu\text{-}H)(CO)_{10}(C{\equiv}C)(C{\equiv}C)_{n-1}Re(NO)(PPh_3)Cp^*]$ ($n = 1$ **15**, 2 **16**, 3 **17**) in which one carbon atom of the acetylenic unit bridges an edge of the Os_3 cluster core.[13] The stability of the complexes decreased with chain length. The reaction of **15** with $HBF_4 \cdot Et_2O$ gives $[Os_3(\mu\text{-}H)_2(CO)_{10}(C{\equiv}C)Re(NO)(PPh_3)Cp^*][BF_4]$. A crystal structure of the $[SbF_6]^-$ salt of **18** shows an ReC_2Os_3 unit similar to that in **15** except that the hydrides are bridging different edges of the metal triangle.[14] The related $[Os_3(CO)_{11}({=}C(OMe)C{\equiv}C)Re(NO)(PPh_3)Cp^*]$ **19** decarbonylates to give $[Os_3(CO)_9(OMe)(CCC)Re(NO)(PPh_3)Cp^*]$ **20** in which the ReCCC terminal unit binds to three osmium atoms, and the central carbon binds to the osmium that is not methoxide-bridged (Scheme 2).



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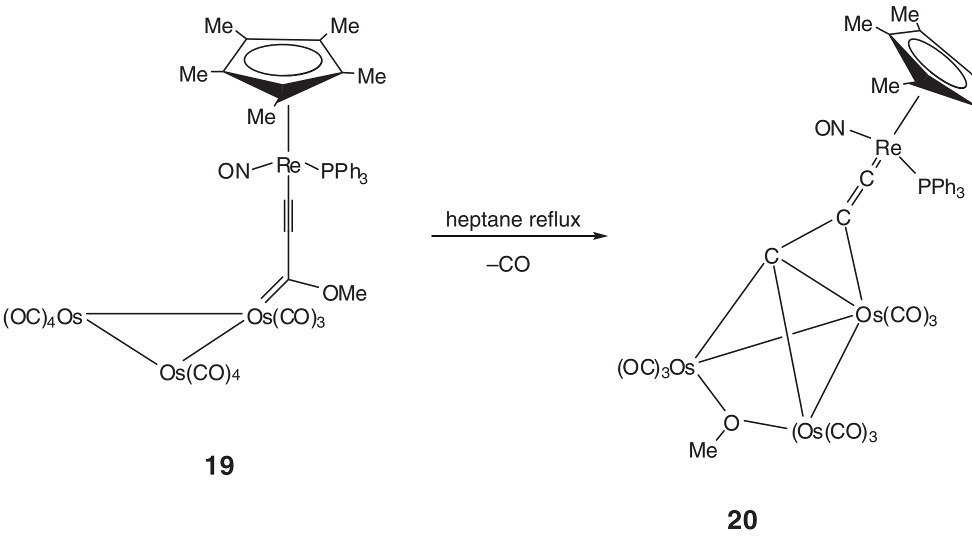
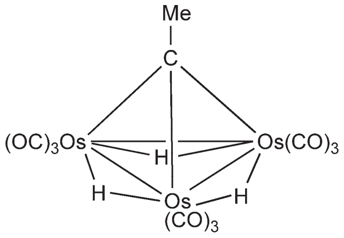
Variable-temperature ^1H and ^{13}C NMR studies on $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CH_3)]$ **21** have been carried out. The proton and carbon NOE and T_1 spin-lattice relaxation data on the methyl and methylene tautomers have allowed the interproton distances to be calculated. Parallel NMR studies on $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CH)]$ **22** have also been reported.[15] A ^{13}C-2D EXSY study on $[Os_3(\mu\text{-}H)(H)(CO)_{11}]$ **23** reveals the existence of a low-energy process that involves the



Scheme 2

intramolecular exchange between the two enantiomeric forms of this cluster.[16] The reduction of the ketenylidene ligand in $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CCO)]$ using borane gives the methylidyne-capped cluster $[Os_3\text{-}(\mu\text{-}H_3)(CO)_9(\mu_3\text{-}CMe)]$ **24** in moderate yield. Depending upon the nature of the reducing agent employed, the intermediate vinylidene cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ **25** could be observed on the NMR timescale. Use of the isotopically labeled $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}^{13}CCO)]$ gave $[Os_3(\mu\text{-}H_3)(CO)_9(\mu_3\text{-}^{13}CMe)]$ without any sign of isotopic scrambling.[17]



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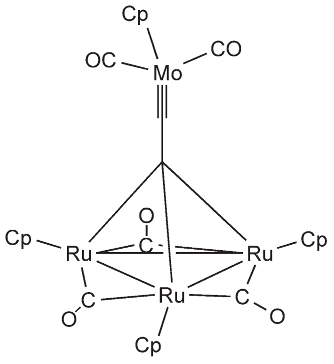
In general, the addition of a $\mu_3\text{-}\eta^1\text{-}CR_3$ group as a cap to a triruthenium or triosmium cluster adds stability to the metal framework, and the capping carbon can be considered as part of the cluster core. The cluster may then be considered as a tetrahedral cluster with five electron pairs for cluster bonding. In this context, capping $\mu_3\text{-}\eta^1\text{-}CC(O)OH$ and $\mu_3\text{-}\eta^1\text{-}CC{\equiv}O$ groups support the trinuclear cluster cores in $[Os_3(\mu\text{-}H)_3(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}\eta^1\text{-}CC(O)OH)]$ **25**[18] and $[Os_3(\mu\text{-}H)_2(CO)_8(SC_4H_8S)(\mu_3\text{-}\eta^1\text{-}CC{\equiv}O)]$ **26**,[19] respectively.

Also, in the context of the stability of the cluster core, the series of clusters $[Ru_3(\mu\text{-}H)_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}CR)]$ ($R = CH_2CHCH_2$, $n = 0$ **27**; $R = CH_2CHCH_2$, $n = 3$ **28**; $R = C_6H_4Me$, $n = 0$ **29**; $R = C_6H_4Me$, $n = 3$ **30**) have been synthesized in good yield and their electrochemical properties investigated.[20] The electrochemical data indicate that the π-system of the apical substituent does not interact significantly with the cluster and, therefore, it should be available for further reaction chemistry.

The reaction of the dinuclear metallo–alkyne complex $[\{Ru(CO)_2Cp\}_2(\mu\text{-}C{\equiv}C)]$ with $[Mo_2(CO)_4Cp_2]$ has been shown by crystallography to give the electron-precise $\mu_3\text{-}\eta^1$-capped cluster $[Ru_3(\mu\text{-}CO)_3Cp_3\{\mu_3\text{-}\eta^1\text{-}C\text{-}C{\equiv}Mo(CO)_2Cp\}]$ **31** and indicates that there is delocalization over the linear C–C–Mo unit imparting some Mo–C carbenoid character.[21,21a] The reactions of the butadiynediyldimetal complexes $[Ru(CO)_2(\eta^5\text{-}C_5R_5)C{\equiv}CC{\equiv}CFp^*]$ ($R = Me$, H; $Fp^* = FeCp^*(CO)_2$) with $[Ru_3(CO)_{12}]$ result in the migration of a σ-bonded metal fragment along the C_4 chain to form, among other products, the zwitterionic μ-but-2-yn-1-ylidene-4-ylidyne complex $[Ru_3(CO)_{10}(\mu_3\text{-}\eta^1\text{-}CC{\equiv}C\text{-}\mu\text{-}C)Fe_2Cp^*_2(CO)_3]$ **32**.[22]



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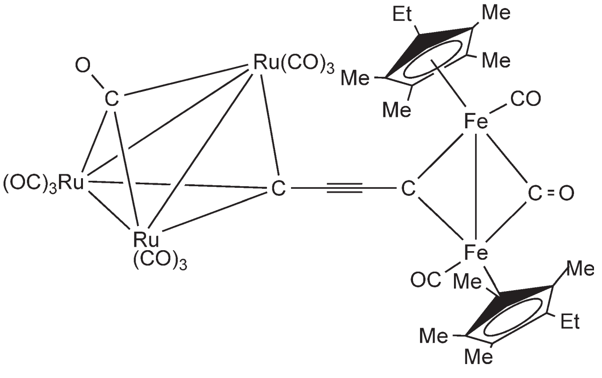

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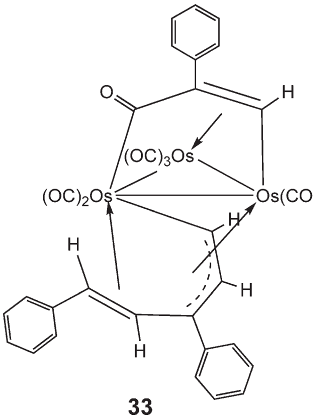
6.19.3 Clusters with η^2-Vinyl, η^2-Vinylidene, and η^2-Acetylide Ligands

When assessing the reaction products of triruthenium and triosmium clusters with alkenes and alkynes, it is often difficult to determine whether the product was derived from an alkene or an alkyne because the nature of the bonding of the fragment to the cluster is often similar. In this section we will analyze the reactions in terms of the bonding mode of the hydrocarbon fragment to the cluster. η^2-Alkene and η^2-alkyne bonding modes are rare because of the facile oxidative addition reactions that result in the transfer of one of the ligand hydrogens to the cluster framework, and no triruthenium or triosmium clusters that contain an η^2-alkene or η^2-alkyne coordinated only to a single metal center have been crystallographically characterized during the period of this review. There are, however, a small number of examples of an η^2-alkene coordinated to a single metal center where the alkene forms part of a larger ligand system but the alkene is bound to the rest of the ligand by an interaction approximating to a C–C single bond. Examples of this include $[Os_3(CO)_7(\mu\text{-}\eta^2{:}\eta^3\text{-}PhCH{=}CHCPhCHCH)\{\mu_3\text{-}\eta^2\text{-}C(O)CPh{=}CH\}]$ 33 and $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}CHNC_5H_4(\eta^2\text{-}CH{=}CH_2)\}]$ 34, that are both obtained in low yield from the reaction of the alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}CH_2)]$ with the asymmetric alkyne under thermal conditions.[23] A related bonding mode to that observed in 33 is also found in the structure of $[Ru_3(CO)_8(\eta^2\text{-}PhC{=}CH\text{-}\mu_3\text{-}\eta^4\text{-}C_4Ph_2CH{=}CHPh)]$ 35.[24]



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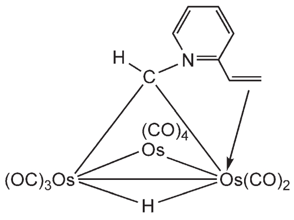

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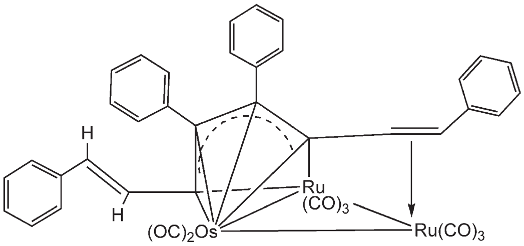

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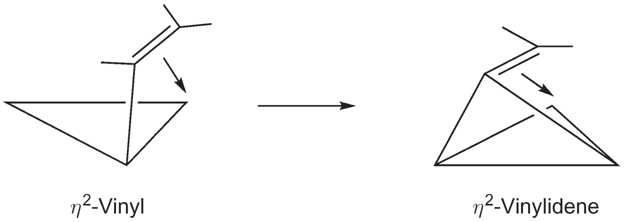
The simplest bonding mode found in trinuclear hydrocarbon-substituted clusters of osmium and ruthenium is the η^2-vinyl coordination in which one carbon center is formally σ-bound to one metal atom in the triangular core and the alkene/alkyne unit is formally π-bound to an adjacent metal, so that the ligand donates three electrons to the cluster. Vinyl complexes are generally prepared by alkyne insertion into $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ or by the oxidative addition of an alkene to $[Os_3(CO)_{10}(NCMe)_2]$ or $[Os_3(CO)_{12}]$, and may be considered to be intermediates in reactions to other hydrocarbon-containing cluster products.[2] A list of reported η^2-vinyl- and the related η^2-acetylide-substituted complexes is presented in Table 1. The related η^2-vinylidene-substituted clusters, in which one carbon atom of the ligand is σ-bonded to two metal centers and the alkene unit is formally π-bound to the third metal center, can be prepared by the thermal conversion of an η^2-vinyl cluster (Scheme 3). The η^2-vinylidene formally donates four electrons to the cluster core.

Table 1 η^2-Vinyl and η^2-acetylide clusters

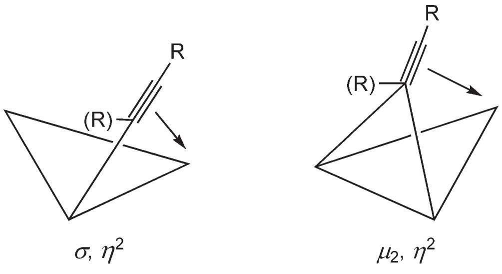
Complex	*Structure*	*References*
$[Ru_3(CO)_{11}(\eta^2\text{-}HC{\equiv}CH)]$	**36**	25
$Ru_3(CO)_7(\mu\text{-}\eta^1{:}\eta^2\text{-}PhC{=}CHPh)\{\mu\text{-}\eta^2{:}\eta^1\text{-}PPh(C_5H_2O_2)PPh_2\}$	**37**	26
$[Os_3(\mu\text{-}H)(CO)_{10}(\eta^2\text{-}HCCC_6H_{10})]$	**38**	27
$Os_3(\mu\text{-}H)(CO)_8\{\mu\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4PPh(C_{12}H_6)_2PPh_2\}$ (from (*R*)-binap)	**39**	28
$[Ru_3(CO)_6(\mu_3\text{-}Se)(\eta^2\text{-}C_4H_2S)(\mu\text{-}PPh_2)(PPh_2(C_4H_3S))]$	**40**	29
$Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^1{:}\eta^2\text{-}CHC[SiMe_3]C{\equiv}CSiMe_3\}$	**41**	30
$[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCMe_2PPh_3)]^+$	**10**	12
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_4H_3NMe)]$	**42**	31
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_4HMe_2NMe)]$	**43**	31
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_4HMe_2NH)]$	**44**	31
$[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}HC_2C_3NH_2Me)]$	**45**	31
$[Ru_3(\mu\text{-}H)(\mu_3\text{-}BH)Cp^*{}_3\{\mu_3\text{-}\eta^2\text{-}HC_2(C_6H_4)S\}]$	**46**	32
$Ru_3(CO)_6(\mu_3\text{-}Se)(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C_4H_2S(C_5H_4N)\}\{PPh_2C_4H_2S(C_5H_4N)\}$	**47**	33
$[Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_4NH_6)(\mu\text{-}\sigma{:}\eta^2\text{-}PhC_2HPh)]$	**48**	34
$[Os_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^2\text{-}(C_4H_2S)SMe\}]$	**49**	35
$[Os_3(\mu\text{-}H)(CO)_8(PPh_3)(\mu_3\text{-}\eta^2\text{-}5,6\text{-benzoquinolinyl-}C,N)]$	**50**	36
$[Os_3(CO)_7(\mu\text{-}SbPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(\eta^2\text{-}PhC_2HPh)]$	**51**	37
$[Ru_3(CO)_6(\mu\text{-}PPh_2)_2(\eta^2\text{-}C_2{}^tBu)_2]$	**52**	38
$[Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\eta^2\text{-}C_2{}^tBu)_2]$	**53**	38
$[Ru_3(CO)_6(PPh_3)(\mu\text{-}PPh_2)_2(\eta^2\text{-}C_2{}^tBu)_2]$	**54**	38
$[Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\eta^2\text{-}C_2Ph)_2]$	**55**	38
$Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}\eta^1{:}\eta^2\text{-}CHCHC_5H_4N\text{-}\mu_3\text{-}C[Os_3(\mu\text{-}H)_2(CO)_9]\}$	**56**	39
$[Os_3(\mu\text{-}H)(CO)_{10}(\eta^2\text{-}2\text{-benzothienyl})]$	**57**	40
$Ru_3(CO)_8(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}CPhCPhPPhCPh{=}CPhPPh)$	**58**	41
$[Ru_3(CO)_6(PPh_3)(\mu_3\text{-}S)(\mu\text{-}PPh_2)(\eta^2\text{-}C_6H_4)]$	**59**	42
$[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$	**60**	43
$[Ru_3(\mu\text{-}H)(CO)_9(\mu\text{-}Ph_2PCH{=}CH)]$	**61**	43
$[Os_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}\eta^2\text{-}C_{12}H_7)]$	**62**	44



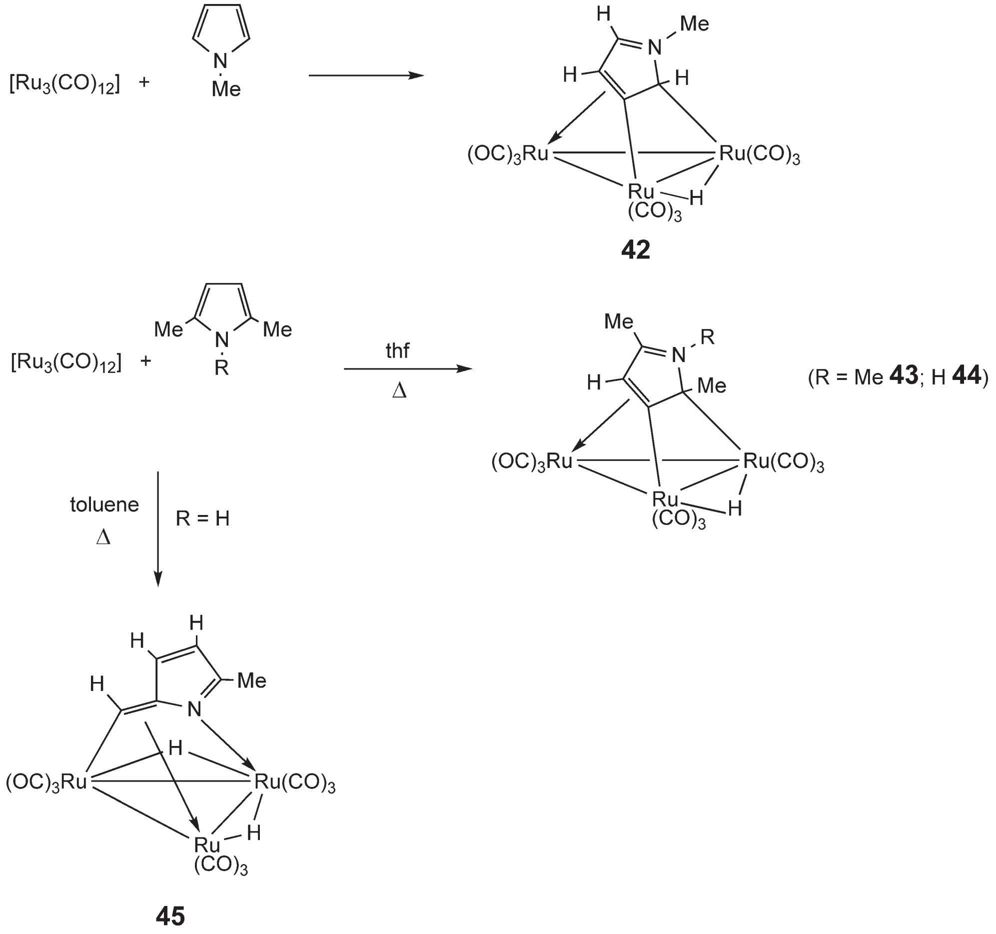
Scheme 3

In the related η^2-acetylide-substituted clusters the acetylene or η^2-ethynyl unit can also adopt the two bonding modes as illustrated in Scheme 4.

An important subset of the η^2-vinyl-substituted clusters that has developed are the systems in which the vinyl substituent is part of or attached to a ring system which also coordinates to the third metal of the trinuclear cluster, usually through an orthometallation reaction, as illustrated for the series of clusters obtained by the direct thermal reaction of $[Ru_3(CO)_{12}]$ with 1-methylpyrrole, 1,2,5-trimethylpyrrole, or 2,5-dimethylpyrrole, in thf, which leads to the formation of the clusters $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_4H_3NMe)]$ **42**, $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_4HMe_2NMe)]$ **43**, and $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_4HMe_2NH)]$ **44**, respectively (Scheme 5).[31] In solution, **42** exists in a dynamic equilibrium between two isomers, as detected by ^1H NMR spectroscopy. The structure of **42** is best described as a zwitterion with the positive charge localized on the NMe group and the negative charge delocalized on the metal triangle. Only a single isomer is found in solution, at low temperature, for **43** and **44**. When the reaction between $[Ru_3(CO)_{12}]$ and 2,5-dimethylpyrrole is repeated in toluene, under reflux, different products are obtained. The products are the vinyl complex $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}HC_2C_3NH_2Me)]$ **45** and



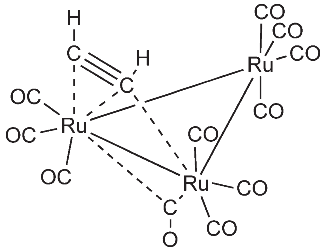
Scheme 4



Scheme 5

[Ru$_3$(μ-H)(CO)$_9$(μ-CO){μ_3-η^2-CHC$_4$H$_2$(Me)N}]. Changing the solvent for the reaction has resulted in cleavage of the N–H bond to give *N*-bonded ligands together with activation of a methyl group and loss of H$_2$.[31]

The reactions of the hydrido cluster, [Ru$_3$H(μ-H)(CO)$_{11}$], with alkynes at low temperatures afford [Ru$_3$(CO)$_{11}$(η^2-alkyne)],[25] which for [Ru$_3$(CO)$_{11}$(η^2-HC≡CH)] 36 has been characterized by multinuclear NMR spectroscopy. At 183 K the ^{1}H NMR shows two doublets at δ 8.45 and 5.97 ($^3J_{HH}$ 8.6 Hz) and the ^{13}C NMR, at the same temperature, run on a ^{13}CO-enriched sample displays 11 carbonyl resonances. The η^2-alkyne complex is only stable at low temperatures, and at ambient temperature conversion to the previously reported cluster [Ru$_3$(CO)$_9$(μ-CO)(μ_3-η^2-HC≡CH)][45,45a] occurs. An estimation of the distance between the two hydrogens in the alkyne ligand has been obtained by measuring the ^{1}H NMR relaxation time at 213 K. Both hydrogens show the same T_1 value of 1.6 s, and the H–H distance obtained from the calculation is 2.48 Å. Assuming a C≡C distance of 1.27 Å and a C–H distance of 1.1 Å, the average H–C–C angle in the alkyne was calculated as 123.5°. In an analogous reaction with HC≡CPh, only one possible isomer of the product [$Ru_3(CO)_{11}(\eta^2$-HC≡CPh)] **36a** was observed in the ^1H NMR spectrum at low temperature.



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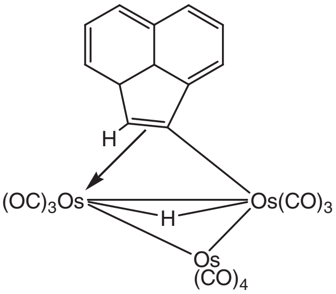
The reaction of [$Os_3(CO)_{10}(NCMe)_2$] with an excess of acenaphthylene at room temperature affords the η^2-vinyl type complex [$Os_3(\mu$-H)$(CO)_{10}(\mu_2$-η^2-$C_{12}H_7)$] **62** in which the σ,π-coordinated acenaphthyl ligand bridges an edge of the cluster.[44] On heating to reflux in cyclohexane solution **62** readily decarbonylates and a hydrogen shifts from the ligand to the cage to give [$Os_3(\mu$-H$)_2(CO)_9(\mu_3$-η^2-$C_{12}H_6)$] **63** which contains a triply-bridging acenaphthyne ligand.



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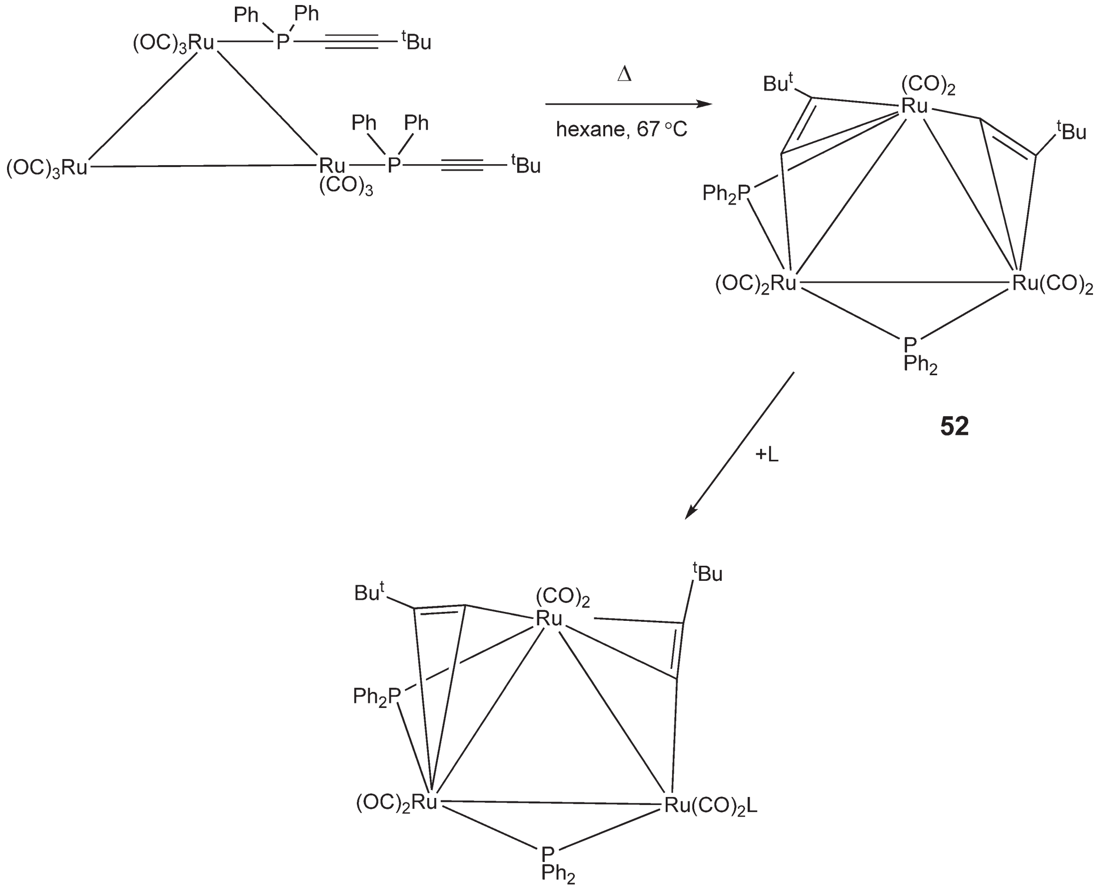
A fascinating series of reactions involving the coordination of μ-η^1,η^2-C≡CR acetylides to electron-rich triruthenium clusters has developed from the thermolysis of [$Ru_3(CO)_{10}(Ph_2PC{\equiv}C^tBu)_2$] which gives the 48-electron cluster [$Ru_3(CO)_6(\mu$-$PPh_2)_2(\eta^2$-$C_2{}^tBu)_2$] **52** together with a series of di- and tetraruthenium clusters.[38] Cluster **52** readily adds CO or PPh_3 to give the novel 50-electron clusters [$Ru_3(CO)_7(\mu$-$PPh_2)_2(\eta^2$-$C_2{}^tBu)_2$] **53** and [$Ru_3(CO)_6(PPh_3)$-$(\mu$-$PPh_2)_2(\eta^2$-$C_2{}^tBu)_2$] **54**, respectively (Scheme 6). Interestingly, thermolysis of [$Ru_3(CO)_{10}(Ph_2PC{\equiv}CPh)_2$] gives [$Ru_3(CO)_7(\mu$-$PPh_2)_2(\eta^2$-$C_2Ph)_2$] **55** directly. Cluster **55** converts smoothly to the 48-electron diyne complex [$Ru_3(CO)_7$ $(\mu$-$PPh_2)_2(\mu$-η^2-$PhC_2C{\equiv}CPh)$] **64**.[38]

A rich chemistry of clusters of the type [$Ru_3(\mu$-H$)(\mu_3$-apy$)(CO)_9$] **6** (apy = 2-aminopyridine) has developed in the last decade.[7] In reactions with alkynes edge-bridged σ,π-alkenyl derivatives are obtained. The position and orientation of the alkenyl group within the ligand framework in these clusters depends on the presence or absence of subsituents on the amidic nitrogen atom.[46] The phosphane-substituted clusters **65** and **66** also afford σ,π-alkenyl derivatives on reaction with diphenylacetylene as shown in Scheme 7.[47,48] Under these reaction conditions, cluster **66** undergoes a P–C bond cleavage to give a phenyl derivative **67**.[48] The monosubstituted alkenyl derivative [$Ru_3(\mu_3$-apyMe$)(\mu_2$-PhCH=CPh$)(PPh_3)(CO)_7$] **68** promotes the catalytic hydrogenation of diphenylacetylene under relatively mild reaction conditions (1 atm, 80 °C). A kinetic analysis of this reaction suggests that an intermediate trinuclear cluster acts as the catalytic species.[49]

In the period of the review only a small number of new η^2-vinylidene-substituted triruthenium clusters have been reported. The archetypical η^2-vinylidene [$Ru_3(\mu$-H$)_2(CO)_9(\mu_2$-η^2-$C_2Ph)$] **69** has been obtained as one of the products of a thermolysis reaction of [$Ru_3(CO)_{12}$] with alkenes and has been structurally characterized.[50,50a]



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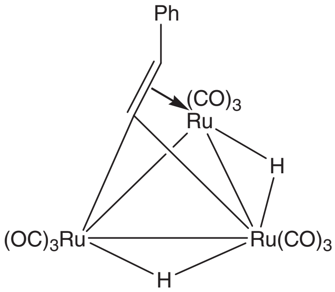
53: L = CO
54: L = PPh$_3$

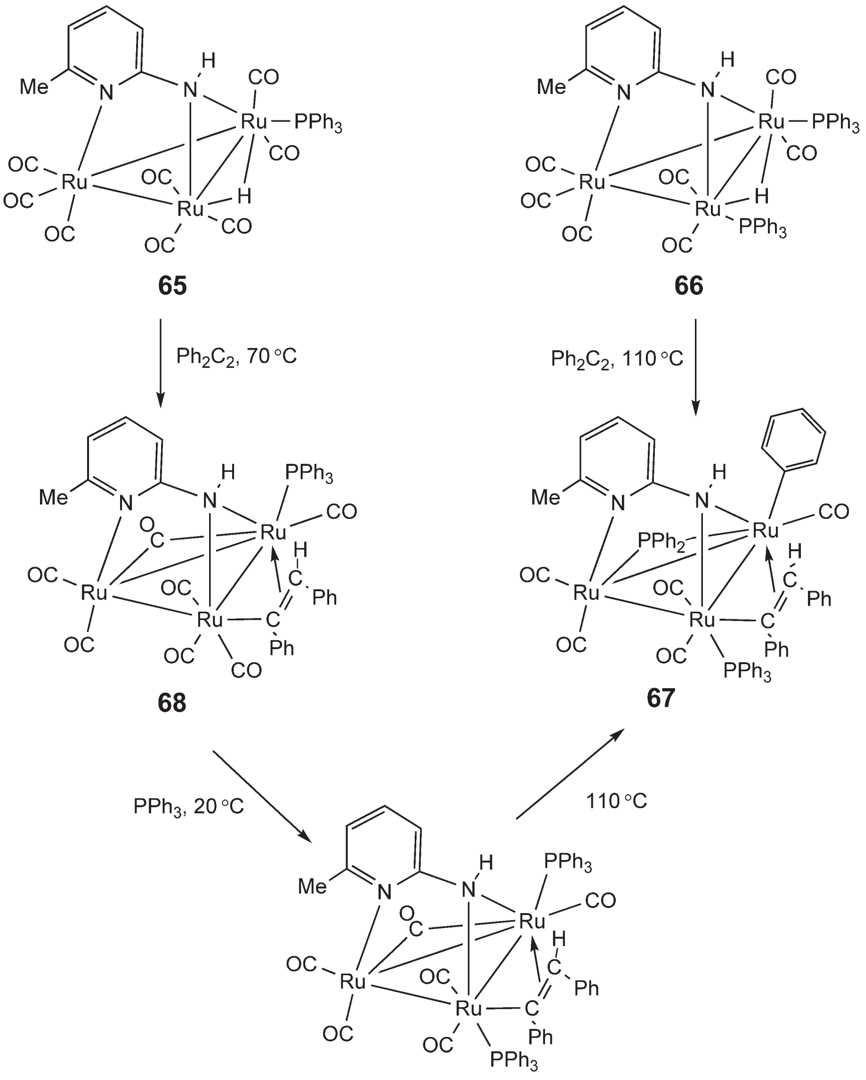
Scheme 6



69

An η^2-vinylidene interaction is observed in the cluster $[Ru_3(CO)_8\{\mu_2\text{-}\eta^2\text{-}C_2CPh_2OC(O)\}\{\mu_3\text{-}Au_3(PPh)_3\}]$ **70**,[51] which is prepared by the sequential attack of $K[BHBu''_3]$ and $AuCl(PPh_3)$ on the hydrido-alkynyl cluster $[Ru_3(\mu\text{-}H)(CO)_9\{\mu\text{-}C_2CPh_2(OH)\}]$. The reaction proceeds by the intramolecular attack of alkoxide on an adjacent CO ligand.

A third example of an η^2-vinylidene interaction has been observed in the developing chemistry of the cyclopentadienyl-substituted triruthenium cluster $[Ru_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3Cp^*{}_3]$. Reaction of this cluster with methyl methacrylate under mild conditions gives the vinylidene cluster $[Ru_3(\mu_3\text{-}H)_3Cp^*{}_3\{\mu_2\text{-}\eta^2\text{-}C_2CH_2CH_2OC(O)\}]$ **71**,[52] which is shown to be an intermediate in the formation of $\mu_3\text{-}\eta^2\text{-}\|$-alkyne clusters.



Scheme 7

6.19.4 Clusters with μ_3-η^2-$\|$ and μ_3-η^2-$\perp$-Alkyne Ligands

Within the area of alkyne-substituted cluster chemistry by far the most common structural arrangements found are clusters in which the alkyne caps a triangular cluster either in a parallel or perpendicular mode, as described in the introduction to this section. This area of chemistry has been reviewed and particular attention has been paid to the chemical transformations that could occur during catalytic reactions.[53] Table 2 lists the μ_3-η^2-$\|$-alkyne triruthenium and triosmium clusters reported, whereas Table 3 lists the μ_3-η^2-$\perp$-alkyne clusters.

The known cluster $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2H)]$ **72**[102] has been prepared from the reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ and acetylene and has been characterized along with a series of Ru_4, Ru_5, and Ru_6 hydrocarbon-substituted clusters.[54] The structure of **72** has now been confirmed by an X-ray analysis. Thermolysis of this cluster in hexane solution at 50 °C afforded the μ_3-η^2-$\perp$ alkyne $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2H)]$ **121** as the major product in 50% yield. The crystal structure of **121** is also reported.

The methanol-catalyzed elimination of the Cl^- anion from the 50-electron anionic cluster $[Ru_3(CO)_9(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]^-$ **73** in the presence of $Ph_2PCH_2PPh_2$ (dppm) affords a high yield route to either the "unsaturated" 46-electron cluster $[Ru_3(CO)_7(dppm)(\mu_3\text{-}\eta^2\text{-}\perp\text{-}PhC_2Ph)]$ **132** or its 48-electron carbonyl adduct $[Ru_3(CO)_8(dppm)(\mu_3\text{-}\eta^2\text{-}\|\text{-}PhC_2Ph)]$ **74** (Scheme 8).[55] The carbonyl-induced conversion of **132** to **74** is completed within a few seconds at

Table 2 μ_3-η^2-||-Alkyne clusters

Complex	*Structure*	*References*
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2H)]$	**72**	54
$[Ru_3(CO)_9(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]^-$	**73**	55
$[Ru_3(CO)_8(dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**74**	55
$[Ru_3(CO)_6(dppm)_2(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**75**	55
$[Ru_3(\mu\text{-}H)_2(CO)_7(dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**76**	55
$[Ru_3(\mu\text{-}H)_2(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2\text{-}EtC_2Et)]$	**77**	56
$[Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}EtC_2Et)]$	**78**	56
$[Ru_3(\mu\text{-}H)_3(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}EtC_2Et)]^+$	**79**	56
$[Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}EtC_2Et)(\mu_2\text{-}Cl)]^+$	**80**	56
$[Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}EtC_2Et)(\mu_2\text{-}I)]^+$	**81**	56
$[Ru_3(\mu\text{-}H)(CO)_5(\mu_3\text{-}\eta^2\text{-}HC_2PPh_2C_2PPh_2)]$	**82**	57
$[Ru_3(\mu\text{-}H)(\mu\text{-}AuPPh_3)(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2H)]$	**83**	58
$[Ru_3(\mu\text{-}H)_2Cp^*{}_3(\mu_3\text{-}CMe)(\mu_3\text{-}\eta^2\text{-}HC_2H)]$	**85**	59
$[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu\text{-}CMeH)(\mu_3\text{-}\eta^2\text{-}HC_2H)]$	**85**	59
$[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}C{=}CH_2)(\mu_3\text{-}\eta^2\text{-}C_2H_2)]$	**86**	59
$[Ru_3H_3Cp_3(\mu_3\text{-}\eta^2\text{-}HC_2H)]$ calculation	**87**	60
$[Ru_3H_2Cp^*{}_3(\mu_3\text{-}CMe)(\mu_3\text{-}\eta^2\text{-}HC_2CO_2Me)]$	**88**	61
$[Ru_3H_2Cp^*{}_3(\mu_3\text{-}CMe)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)]$	**89**	61
$[Ru_3H_2Cp^*{}_3(\mu_3\text{-}CMe)\{\mu_3\text{-}\eta^2\text{-}HC_2(CH_2)_3\}]$	**90**	61
$[Ru_3H_2Cp^*{}_3(\mu_3\text{-}CMe)\{\mu_3\text{-}\eta^2\text{-}HC_2(CH_2)_4\}]$	**91**	61
$[Ru_3H_2Cp^*{}_3(\mu_3\text{-}CMe)\{\mu_3\text{-}\eta^2\text{-}HC_2CO(CH_2)_2\}]$	**92**	61
$[Ru_3Cp_2(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**93**	62
$[Ru_3Cp_2(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}\eta^2\text{-}F_3CC_2CF_3)]$	**250**	62
$[Ru_3Cp_2(CO)_2(\mu\text{-}CO)(\mu_3\text{-}CO)(NCMe)(\mu_3\text{-}\eta^2\text{-}F_3CC_2CF_3)]$	**94**	63
$[Os_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}3,5\text{-}Me_2\text{-}pyrazolyl)]^-$	**95**	64
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2CH_2OH)]$	**96**	65
$[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}Me_3SiC_2(C_5H_4)Fe(C_5H_4C{\equiv}CSiMe_3)\}]$	**97**	66
$Ru_3(\mu\text{-}H)(CO)_7\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2{:}\eta^1\text{-}CPhC(PPh_2)(C_5H_2O_2)PPh_2\}$	**98**	26
$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_{10})]$	**99**	27
$[Os_3(CO)_9(\mu\text{-}CO)\ (\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})]$	**100**	67
$[Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})_2]$	**101**	67
$[\{Os_3(CO)_9(\mu\text{-}CO)\}_2\{\mu_3\text{-}\eta^2{:}\ \mu_3\text{-}\eta^2\text{-}C_2(CH_2)_5C_2(CH_2)_5\}]$	**102**	68
$[Ru_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}\eta^2\text{-}C_2(CH_2)_3\}]$	**103**	69
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2PPh_2CHPPh_2)]$	**104**	70
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2PPh_2CH_2PPh_2)]^+$	**105**	70
$[Ru_3(CO)_9(P^iPr_3)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**106**	71
$[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_{10})]$	**107**	72
$[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_{12})]$	**108**	73
$[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_8)]$	**109**	74
$[Ru_3(CO)_6(AuPPh_3)_2(PPh_2)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)]$	**110**	75
$[Ru_3(\mu\text{-}H)_2Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}C_5H_6))]$	**111**	52
$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_{12}H_6)]$	**63**	44
$[Os_3(CO)_7(\mu\text{-}AsPPh_2)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)]$	**112**	76
$[Ru_3(CO)_7\{\mu_3\text{-}\eta^6\text{-}{}^tBuCCHCPhC(CPh_2OH)\}\{\mu_3\text{-}\eta^2\text{-}PhC_2(CPh_2OH)\}]$	**113**	77
$[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}C_2(C_6H_3Bu^tC{\equiv}C)_5C_6H_3Bu^t\}]$	**114**	78
$[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}C_{14}H_{20}Me_2(CO)_4Cp_2\}]$	**115**	79
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2\text{-}CH_2\text{-}9\text{-}acridone)]$	**64**	80
$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}dibenzothiophene\text{-}C,C)]$	**116**	81
$[Ru_3(CO)_6(\mu\text{-}CO)(\eta^6\text{-}[2.2]\text{-}paracyclophane)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**117**	82
$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}2\text{-}benzothienyl)]$	**118**	40
$[Ru_3(\mu\text{-}H)_2(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}C_2C_5H_5Me)]$	**119**	83
$[Os_3(CO)_7(P^nBu_3)(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**120**	84

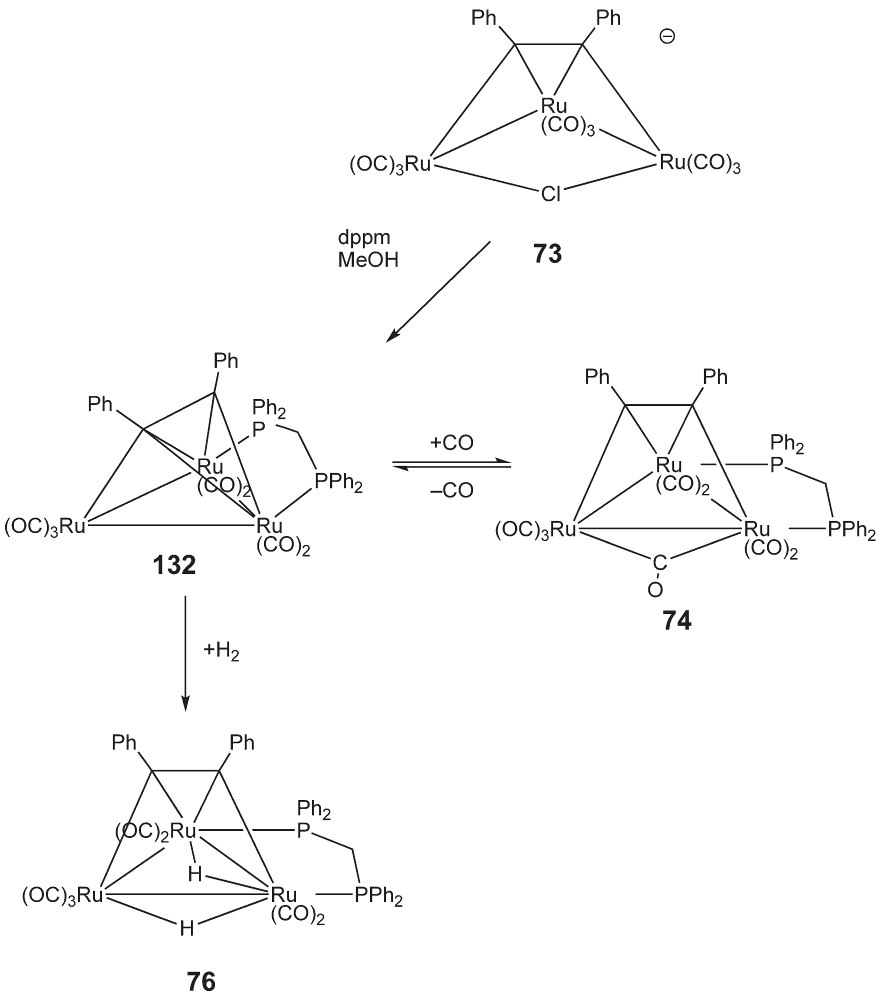
room temperature under an atmosphere of CO; the reverse transformation takes an hour at 80 °C. The high reactivity of **132** with nucleophiles is illustrated by its reaction with an equivalent of dppm which leads to the facile formation of the substitution product $[Ru_3(CO)_6(\mu\text{-}dppm)_2(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$ **75**. The hydrogenation of **132** gives the dihydrido species $[Ru_3(\mu\text{-}H)_2(CO)_7(dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$ **76** which exists as a mixture of two isomers that differ in the orientation of the alkyne relative to the edge-bridging dppm ligand.

Table 3 $\mu_3\text{-}\eta^2\text{-}\perp$-Alkyne clusters

Complex	*Structure*	*References*
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2H)]$	**121**	54
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2Ph)]$	**122**	85,53
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2SiMe_3)]$	**123**	85,86
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2SiPh_3)]$	**124**	86
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2C_6H_4Me\text{-}4)]$	**125**	53
$[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2OH)]$	**126**	87
$[Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^2\text{-}C_2(C_5H_4)FeCp\}]$	**127**	88
$[Ru_3(\mu\text{-}H)(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)]_2(dppa)$	**128**	89
$[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2Fc)(\mu_2\text{-}C{\equiv}C\text{-}Fc)]$	**129**	90
$[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)]$	**130**	86
$[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2SiPh_3)]$	**131**	86
$[Ru_3(CO)_7(dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$ $(46\ e^-)$	**132**	55
$[Ru_3(\mu\text{-}H)(CO)_6(PPh_3)(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}C_2H)]$	**133**	91
$[Ru_3(\mu\text{-}H)(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(bpcd)]$	**134**	92
$[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2C_4Me_4Et)]$	**135**	93
$[Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{-}C_2CH_2O\text{-}\mu_3\text{-}C(O)(CO_3(CO)_9)\}]$	**136**	94
$[Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^2\text{-}C_2(C(C_6H_4)_2)\}]$	**137**	95
$[Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^2\text{-}C_2(C_6H_4)NH_2\}]$	**138**	96
$[Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}dppm)\{\mu_3\text{-}\eta^2\text{-}C_2CMePh(OH)\}]$	**139**	97
$[Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}C_2C{=}CH_2Ph)]$	**140**	97
$[Ru_3(CO)_8(AuPPh_3)_3(\mu_3\text{-}\eta^2\text{-}C_2Ph)]$	**141**	98
$[Ru_3(CO)_9(\mu\text{-}AuPPh_3)\{\mu_3\text{-}\eta^2\text{-}C_2\text{-}(C_5H_4)FeCp\}]$	**142**	99, 99a
$[Os_3(CO)_9(\mu\text{-}AuPPh_3)\{\mu_3\text{-}\eta^2\text{-}C_2\text{-}(C_5H_4)FeCp\}]$	**143**	99, 99a
$[Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}C_2C_5H_5Me)]$	**144**	83
$[Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}C_2C_5H_6)]$	**145**	83
$[Os_3(CO)_6(P(OMe)_3)(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$	**146**	84
$[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}C_5H_6)]$	**147**	100
$[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}C_6H_8)]$	**148**	100
$[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}PhC_2H)]$	**149**	101
$[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}{}^tBuC_2H)]$	**150**	101
$[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}PhC_2Me)]$	**151**	101

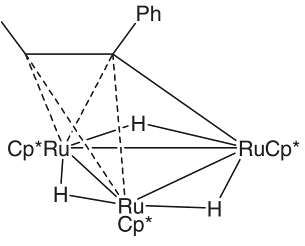
The reaction of $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2Cp^*{}_3]$ with an excess of methyl methacrylate, in toluene at 80 °C for 48 h, gives the new cluster $[Ru_3(\mu\text{-}H)_2Cp^*{}_3(\mu_3\text{-}CMe)(\mu_3\text{-}\eta^2\text{-}HC_2CO_2Me)]$ **88** which was characterized as a $\mu_3\text{-}\eta^2\text{-}\|$-alkyne-$\mu_3$-methylidene complex on the basis of spectroscopic evidence.[61] Similarly, $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2Cp^*{}_3]$ reacts with α-methylstyrene, methylenecyclopentane, methylcyclohexane, and α-methylene-γ-butyrolactone to afford the analogous $\mu_3\text{-}\eta^2\text{-}\|$-alkyne-$\mu_3$-methylidene clusters **89–92**. The ligand conformation has been confirmed by an X-ray analysis of $[Ru_3(\mu\text{-}H)_2Cp^*{}_3(\mu_3\text{-}CMe)\{\mu_3\text{-}\eta^2\text{-}HC_2(CH_2)_3\}]$ **90**.[61] The reaction of $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2Cp^*{}_3]$ with acetylene has also been investigated. In this case the $\mu_3\text{-}\eta^2\text{-}\|$-ethyne-$\mu_3$-ethylidene cluster $[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu\text{-}CMeH)(\mu_3\text{-}\eta^2\text{-}\|\text{-}C_2H_2)]$ **85** is formed via a bis(μ-vinyl) intermediate $[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH{=}CH_2)_2]$ **149**.[59] An α–C–H bond in the ethylidene ligand of **85** undergoes oxidative addition upon thermolysis to give the $\mu_3\text{-}\eta^2\text{-}\|$-alkyne-$\mu_3$-ethylidene complex $[Ru_3(\mu\text{-}H)_2Cp^*{}_3(\mu_3\text{-}CMe)(\mu_3\text{-}\eta^2\text{-}HC_2H)]$ **84** (Scheme 9), which shows fluxional behavior of both the alkyne ligand and the hydrides.[59] Further C–H bond cleavage of the ethylidyne ligand gives the μ-vinylidene-$\mu\text{-}\eta^2\text{-}\|$-ethyne complex $[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}C{=}CH_2)(\mu_3\text{-}\eta^2\text{-}\|\text{-}C_2H_2)]$ **86**.[59] Treatment of **84** with an excess of acetylene results in C–C bond formation at the triruthenium core and the formation of the μ_3-ethylidyne-$\mu_3\text{-}\eta^3$-diruthena-allyl cluster $[Ru_3(\mu\text{-}H)Cp^*{}_3(\mu_3\text{-}CMe)(\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-}CHCHCCH_3)]$ **150** (Scheme 9) (see Section 6.7.2.2).[59]

Treatment of $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2Cp^*{}_3]$ with cycloalkenes, however, results in the formation of the $\mu_3\text{-}\eta^2\text{-}\perp$-cycloalkyne clusters $[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_nH_{2n-4})]$ ($n = 5$, 6) as a result of vinylic C–H bond cleavage. Variable-temperature NMR studies indicate that the perpendicularly coordinated cycloalkyne undergoes a fluxional process. Reaction of $[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_6H_8)]$ **151** with carbon monoxide affords the 48-electron cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}\|\text{-}C_6H_8)]$ **152** which has a parallel coordinated alkyne ligand.[100] In a related series of studies with substituted alkynes, $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2Cp^*{}_3]$ affords as the only products, the trinuclear clusters $[Ru_3(\mu\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R^1)]$ ($R = Ph$, $R^1 = H$ **153**; $R = {}^tBu$, $R^1 = H$ **154**; $R = Ph$, $R^1 = Me$ **155**) in which the alkyne



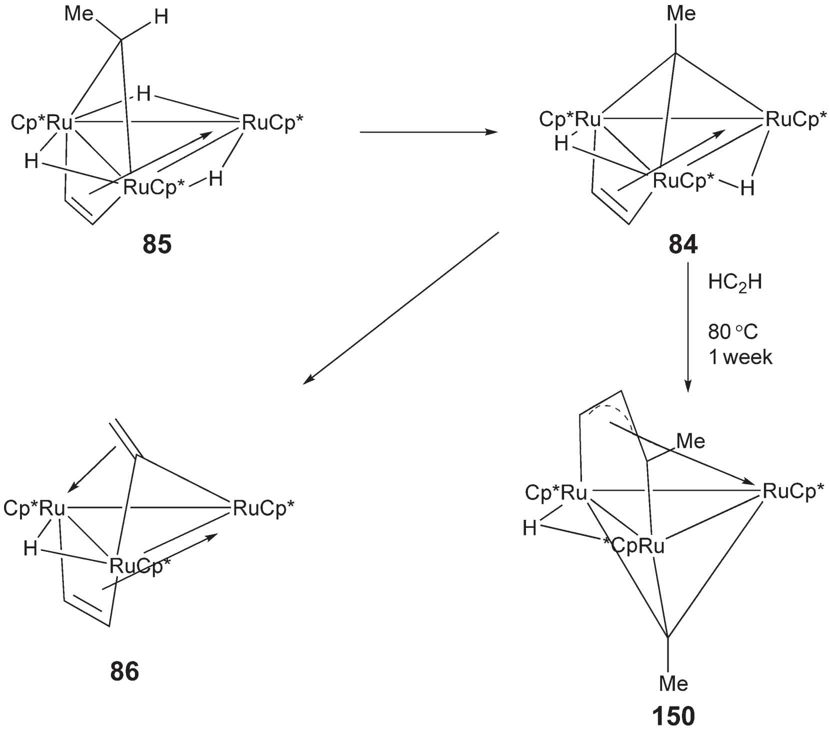
Scheme 8

adopts a perpendicular coordination mode.[101] An X-ray crystal structure for $[Ru_3(\mu\text{-}H)_3Cp^*_3(\mu_3\text{-}\eta^2\text{-}\perp\text{-}PhC_2H)]$ **153** is reported, and in the ^{13}C NMR spectrum the α-acetylenic carbon located above the Ru_3 triangle appears at particularly high field.[101]



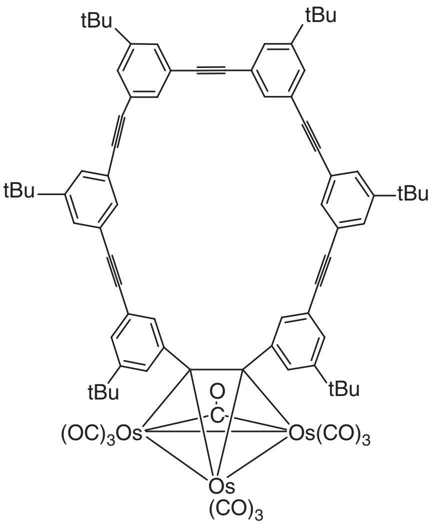
153

In a fascinating reaction, $[Os_3(CO)_{10}(NCMe)_2]$ was treated with 1 equiv. of a member of new class of hexameric *meta*-cyclophenylene-ethynylenes, obtained from dipropynylated benzenes by alkyne metathesis. The alkyne groups within the *meta*-cyclophenylene-ethynylene are susceptible to attack by the metal centers and the $[Os_3(CO)_{10}(NCMe)_2]$ cluster coordinates to the ligand, with loss of the acetonitrile groups, to form a μ_3-η^2-$\|$-alkyne complex $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}C_2(C_6H_3Bu^tC{\equiv}C)_5C_6H_3Bu^t\}]$ **114** which has been characterized by single crystal X-ray analysis. The attachment of the cluster to the *meta*-cyclophenylene-ethynylene leads to a significant disruption



Scheme 9

of the planarity of the ring. This can be attributed to the induced nonlinearity of the coordinated alkyne group and the unfavorable steric interactions between the carbonyl ligands and the bulky *tert*-butyl groups.[78]



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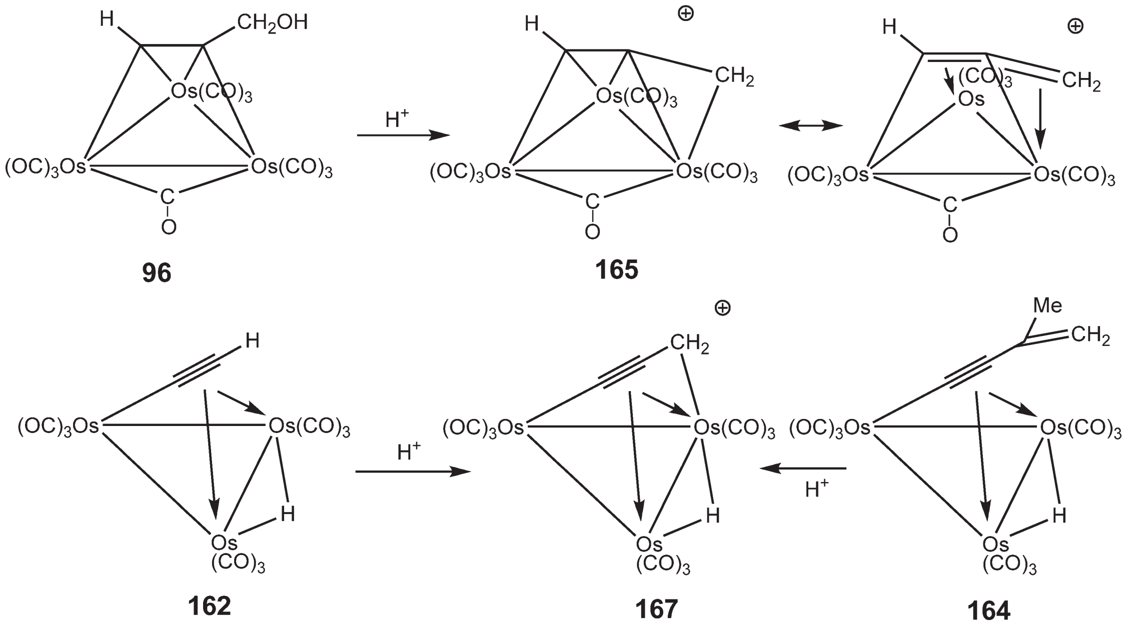
6.19.5 Reactions of Alkene- and Alkyne-Substituted Clusters

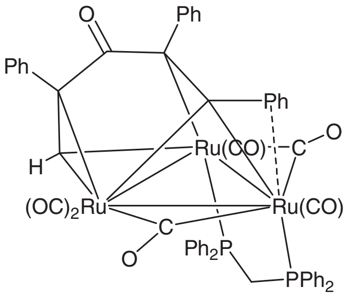
As has been indicated above, the reactions of alkynes with either the ruthenium and osmium binary carbonyls, or their activated or unsaturated derivatives, lead to the formation of a range of products with different nuclearities and with organic ligands that may result from rearrangements, C–C bond formation, C–C bond cleavage, and hydrogen migration. Attempts are now being made to better understand the nature of the reactions and, to this end, mechanistic studies on the hydrogenation of alkynes with $[Os_3(\mu\text{-}H)(CO)_{10}]$ have been made using *para*-hydrogen as a probe.[103] Four reaction products have been obtained from the reaction of 1-pentyne and acetylene with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ in the presence of *para*-H_2 at 3–4 atm and 50–60 °C. Of these, only the σ,π-vinyl complex $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHR)]$ (R = H **156**, ^{n}Pr **157**) goes on to yield alkene and the starting cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. The μ-η^2-acetylido cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}CCR)]$ **157**, a product that results from the loss of hydrogen, is not formed under these conditions, in the presence of excess dihydrogen. The μ_3-η^2-alkyne complex $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2R)]$ **158** is formed when $[Os_3(CO)_{10}(NCMe)_2]$ reacts with alkynes in the presence of *para*-H_2, but does not react with *para*-H_2. An unstable α,β-unsaturated aldehyde complex $[Os_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^4\text{-}RC{=}CC(O)H\}]$ **159** is observed, and is thought to go on to form the μ_3-η^4-metallacyclohexadienone cluster $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}(RC{=}CH)_2C(O)\}]$ **160** after loss of hydrogen and addition of a second mole of alkyne. Cluster **159** is also detected when $[Os_3(CO)_{10}(NCMe)_2]$ is reacted with 1-pentyne or acetylene in the presence of *para*-H_2. The observation of this complex represents an example of direct detection of C–CO coupling in a transient intermediate on a trimetallic site. Labeling experiments with ^{13}CO and deuterio-1-pentyne help to provide evidence for the origin of **159**, and the observation of hyperpolarized intermediates using *para*-H_2 confirms that it is a valuable tool for elucidating the whole system of reactions.

In principle, one of the simplest reactions is protonation. Protonation of the μ_3-η^2-$\|$-alkyne clusters $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CR)]$ (R = CH_2OH **96**, CMe_2OH **161**) and the μ_3-η^2-$\perp$-alkyne clusters $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)]$ (R = CH_2OH **162**, CMe_2OH **163**, and $CMe{=}CH_2$ **164**) gives cationic complexes with the five-electron and six-electron propargyl ligands $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CCR^1{}_2)]^+$ (R^1 = H **165**, Me **166**) and $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}CCCR^1{}_2)]^+$ (R^1 = H **167**, Me **168**), respectively (Scheme 10).[65] Treatment of solutions of the cationic complexes with PPh_3 leads to the formation of phosphonium derivatives with the formula $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CCR^1{}_2PPh_3)]$ (R^1 = H **169**, Me **170**) and $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}Ph_3PC{=}C{=}CR^1{}_2)]$ (R^1 = H **171**, Me **172**).

It is well established that unsaturated 46-electron clusters such as $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ readily add nucleophiles. It is, therefore, not surprising that the unsaturated 46-electron cluster $[Ru_3(CO)_7(dppm)(\mu_3\text{-}\eta^2\text{-}\perp\text{-}PhC_2Ph)]$ **132** reacts with phenylacetylene under mild conditions to give a mixture of the “fly-over” type cluster $[Ru_3(CO)_6(dppm)\{\mu\text{-}CHCPhC(O)CPhCPh\}]$ **173** and the diruthena-cyclopentadiene complex $[Ru_2(CO)_4(\mu\text{-}dppm)(\mu\text{-}CHCPhCPhCPh)]$.[55] The formation of the disymmetric edge-bridging dialkenyl ketone ligand in **173** results from the regioselective coupling between the two alkynes and a carbonyl group. Under mild thermolysis conditions **173** converts into the vinylidene alkenyl ketone derivative $[Ru_3(\mu\text{-}H)(CO)_6(dppm)\{\mu\text{-}CCPhC(O)CPhCPh\}]$ **174**.



Scheme 10



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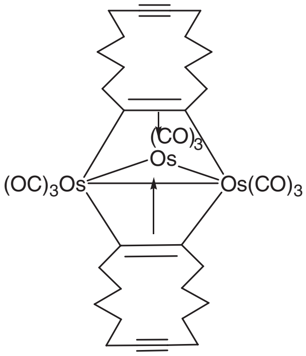
The electrochemical and chemical oxidations of the 48-electron clusters $[Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}RC_2R^1)]$ ($RCCR^1 = EtCCEt$ **78**, HCCOEt, PhCCPh) give unstable radical cations.[56] The radical cation derived from $[Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}EtC_2Et)]$ **78** decomposes in the presence of halide by disproportionation to $[Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}EtC_2Et)(\mu_2\text{-}Cl)]^+$ **80**. Electrophilic addition using Cl_2, I_2, and CF_3CO_2H gives the analogous clusters $[Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)_3(\mu_3\text{-}\eta^2\text{-}EtC_2Et)(\mu_2\text{-}X)]^+$ (X = Cl **80**, I **81**, H).[56]

The bis(cyclodiyne) cluster $[Os_3(CO)_8\{\mu_3\text{-}\eta^2\text{-}C_2(CH_2)_5C{\equiv}C(CH_2)_5\}_2]$ **101** has been prepared by the reaction of $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})]$ **100** with cyclotetradeca-1,8-diyne ($C_{14}H_{20}$) in the presence of Me_3NO.[67] Thermolysis of **101** leads to the osmacyclopentadiene complex $[Os_3(CO)_9\{\mu\text{-}\eta^4\text{-}(C_{14}H_{20})_2\}]$ **175**. The tris(cyclodiyne) complex $[\{Os_3(CO)_8\}_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})_2]$ **176** is obtained from the reaction of $[\{Os_3(CO)_{10}\}_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]$ **177** with Me_3NO and $C_{14}H_{20}$, while photoirradiation of **177** and $C_{14}H_{20}$ affords the bis(osmacyclopentadiene) cluster $[\{Os_3(CO)_9\}_2\{\mu,\mu\text{-}\eta^4,\eta^4\text{-}(C_{14}H_{20})_3\}]$ **178** which has been characterized crystallographically. Co-irradiation of **100** and **175** also produces **178**. The clusters **101**, **175**, **176**, and **178** may be considered as cluster-intercalated, belt-like polycyclodiynes.



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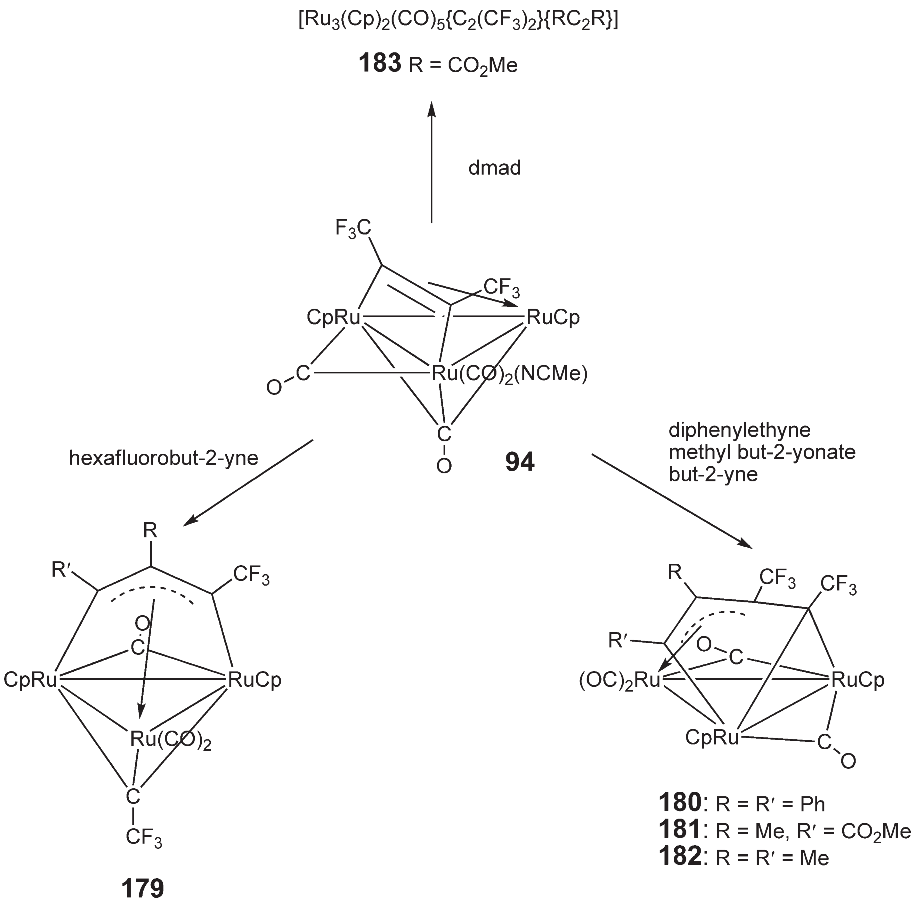
The reaction of hexafluorobut-2-yne with $[Ru_3Cp_2(CO)_2(\mu\text{-}CO)(\mu_3\text{-}CO)(NCMe)(\mu_3\text{-}\eta^2\text{-}F_3CC_2CF_3)]$ **94**, at or below room temperature, gives $[Ru_3Cp_2(CO)_2(\mu\text{-}CO)\{\mu_3\text{-}\eta^3\text{-}C_3(CF_3)_3\}(\mu_3\text{-}CCF_3)]$ **179** which contains a ruthenium triangle with a μ_3-perfluoroethylidyne and a $\mu_3\text{-}\eta^3\text{-}C_3(CF_3)_3$ ligand arising from the cleavage of one of the hexafluorobut-2-yne molecules (Scheme 11). In contrast, **94** reacts at room temperature with diphenylethyne, methyl but-2-ynoate and but-2-yne to give the species $[Ru_3Cp_2(CO)_2(\mu\text{-}CO)_2\{\mu_3\text{-}C_4(CF_3)_2R(R^1)\}]$ ($R = R^1 = Ph$ **180**; $R = Me$, $R^1 = CO_2Me$ **181**; $R = R^1 = Me$ **182**), respectively.[63] X-ray analyses have shown that in all these clusters the alkynes have linked to form a $\mu_3\text{-}C_4(CF_3)_2R(R^1)$ ligand bound to the Ru_3 triangle via a doubly bridging interaction with one pair of metal atoms and in an η^3-allyl mode with the other. Dimethyl acetylenedicarboxylate (dmad) reacts with **94** at room temperature differently again to give $[Ru_3Cp_2(CO)_5\{C_2(CF_3)_2\}\{C_2(CO_2Me)_2\}]$ **183** which on heating affords $[Ru_3Cp_2(CO)_3\{\mu_3\text{-}C_4(CF_3)_2(CO_2Me)_2\}]$ **184** which contains a *closo*-pentagonal-bipyramidal Ru_3C_4 cluster core in which the $\mu_3\text{-}C_4(CF_3)_2(CO_2Me)_2$ ligand bridges an open Ru_3 triangle. This cluster is formed directly when **94** is heated with dmad in refluxing toluene. Analogous clusters $[Ru_3Cp_2(CO)_3\{\mu_3\text{-}C_4(CF_3)_2R(R^1)\}]$ ($R = Me$, $R^1 = CO_2Me$ **185**; $R = R^1 = Ph$ **186**; $R = R^1 = Me$ **187**) were obtained on heating **94** with methyl but-2-ynoate, diphenylethyne and but-2-yne, respectively. The last two reactions also gave isomers $[Ru_3Cp_2(CO)_3\{\mu_3\text{-}C_4(CF_3)R_2(CF_3)\}]$ (R = Ph **188**, Me **189**) in which formal insertion of the incoming alkyne into the coordinating $CF_3C{\equiv}CCF_3$ bond had occurred. In addition, the reaction of **94** with but-2-yne produced $[Ru_3Cp_2(CO)_2(\mu\text{-}CO)\{\mu_3\text{-}\eta^3\text{-}C_3(CF_3)Me_2\}\{\mu_3\text{-}CCF_3\}]$ that is analogous to **179**.



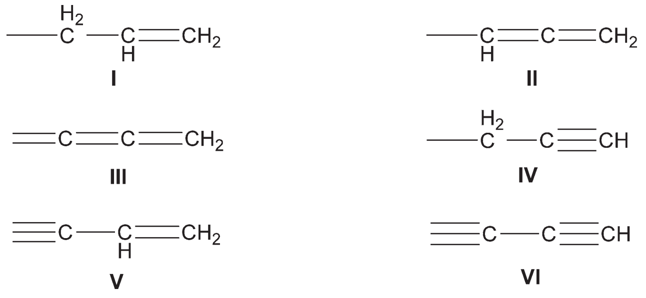
Scheme 11

6.19.6 Clusters with Allyl and Related Ligands

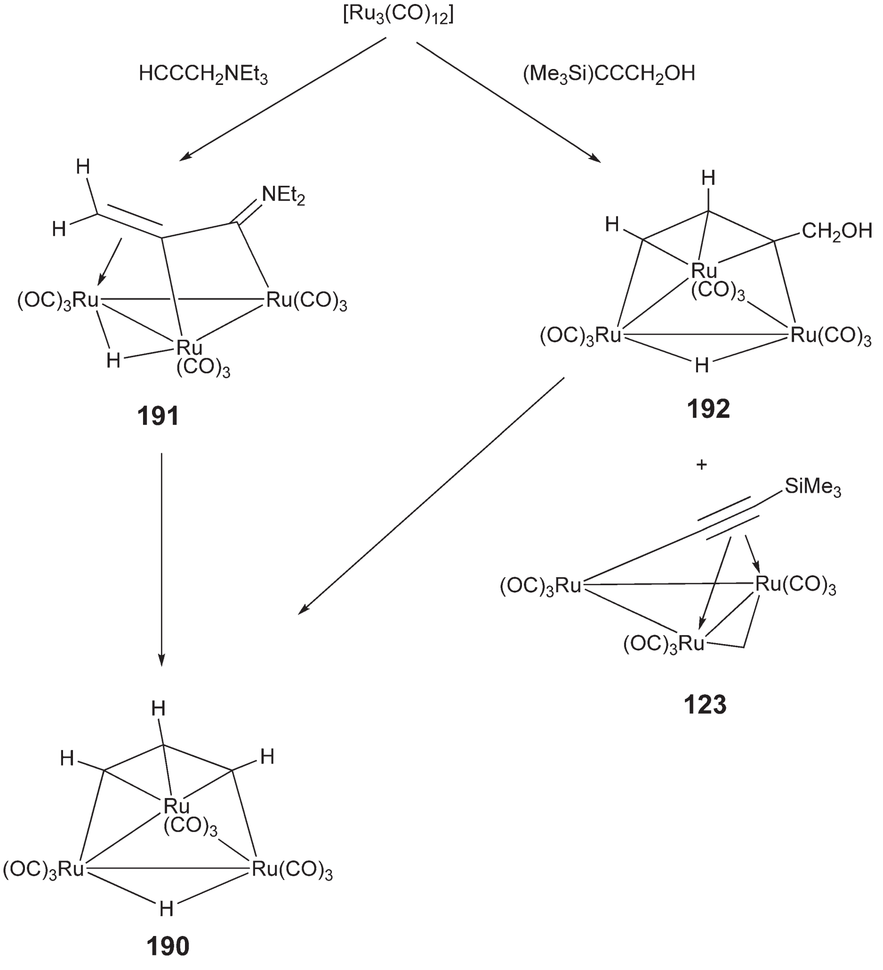
This section contains an overview of trinuclear clusters of osmium and ruthenium that contain C_3 hydrocarbyl ligands. The potential ligand types include those shown in Scheme 12.[104] The most common complexes are those that contain the allyl group **I**, and there has been some work on complexes containing the propargyl ligand **IV** because of its synthetic utility, but the remaining C_3 hydrocarbyl ligands, allenyl **II**, allenylidene **III**, propenylidyne **V**, and propynylidyne **VI** have not been extensively used in complex formation. Some C_3 systems have already been mentioned as they occur as reaction products in the reactions of alkyne and vinyl clusters, and others are formed at the same time as alkyne clusters, so a few key products are described in this section.

The allylic cluster $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^3\text{-}C_3H_3)]$ **190** can be obtained by two different methods as illustrated in Scheme 13.[105] One is the deamination of diethylaminopropyne, $HC{\equiv}CCH_2NEt_2$, in the presence of $[Ru_3(CO)_{12}]$ under thermal conditions. The second method involves the reaction of trimethylsilylpropargyl alcohol, $(HO)H_2CC{\equiv}C(SiMe_3)$, with $[Ru_3(CO)_{12}]$. For the reaction with trimethylsilylpropargyl alcohol, other reaction products derived from the loss of $SiMe_3$ and HCHO fragments from the alcohol are also obtained. The structure of **190** has been established by X-ray crystallography.

Facile coupling and isomerization of allene ($CH_2{=}C{=}CH_2$) is observed to occur on its interaction, at low temperatures, with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to give the diallyl clusters $[Os_3(CO)_{10}(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^3\text{-}C_6H_8)]$ **193** and $[Os_3(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^3\text{-}C_6H_8)]$ **194** in which two allene molecules are bonded in an end-to-center array.[106] Cluster **194** converts either in solution or in the solid state into two different clusters, $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}C_6H_7)]$ **195** and the metallocyclopentadiene cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_8)]$ **196** which could be regarded as the result of 1,3-hydrogen shifts of the coupled allene at the triosmium centers. The reaction pathway is illustrated in Scheme 14.

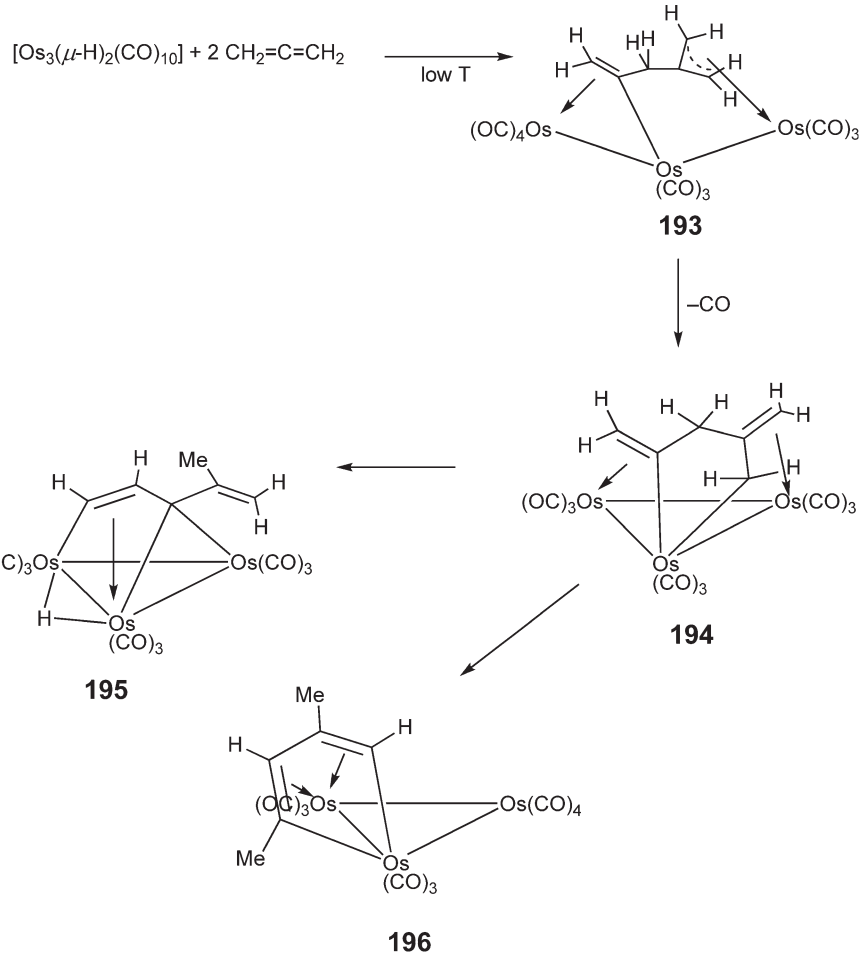


Scheme 12



Scheme 13

The reaction of $[\mathrm{Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}C_2CAr_2(OH)\}}]$ (Ar = Ph **197**, *p*-tolyl **198**) with dppm in the presence of $\mathrm{HBF_4{\cdot}OMe_2}$ gives $[\mathrm{Ru_3(CO)_8(\mu\text{-}dppm)(\mu_3\text{-}CCCAr_2)}]$ (Ar = Ph **199**, *p*-tolyl **200**),[87] which on heating undergo aryl group migration to form the indenylidene ligand.[51] The reaction of $[\mathrm{Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}C_2CH_2(OH)\}}]$ **201** and dppm with $\mathrm{HBF_4{\cdot}OMe_2}$ gives the salt $[\mathrm{Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2PPh_2CH_2PPh_2)}][\mathrm{BF_4}]$ **106** the cation of which contains a novel heterocyclic alkyne.[70] Cluster **197** goes on to react with $\mathrm{HC{\equiv}CSiMe_3}$ to give $[\mathrm{Ru_3(CO)_9(\mu\text{-}OH)\{\mu\text{-}CH(SiMe_3)CHCC{=}CPh_2\}}]$ **201** and $[\mathrm{Ru_3(CO)_8\{\mu_3\text{-}Me_3SiCCHCHC(SiMe_3)CC{=}CPh_2\}}]$ **202**, whereas with $\mathrm{HC{\equiv}CPh}$, the two isomeric complexes $[\mathrm{Ru_3(CO)_8(\mu_3\text{-}CRCR^1CR^1CRCC{=}CPh_2)}]$ (R = Ph, H **203**, $\mathrm{R^1}$ = H, Ph **204**) were obtained.[107] These are formed by insertion of the alkyne into an Ru–C bond, with migration of the cluster hydride

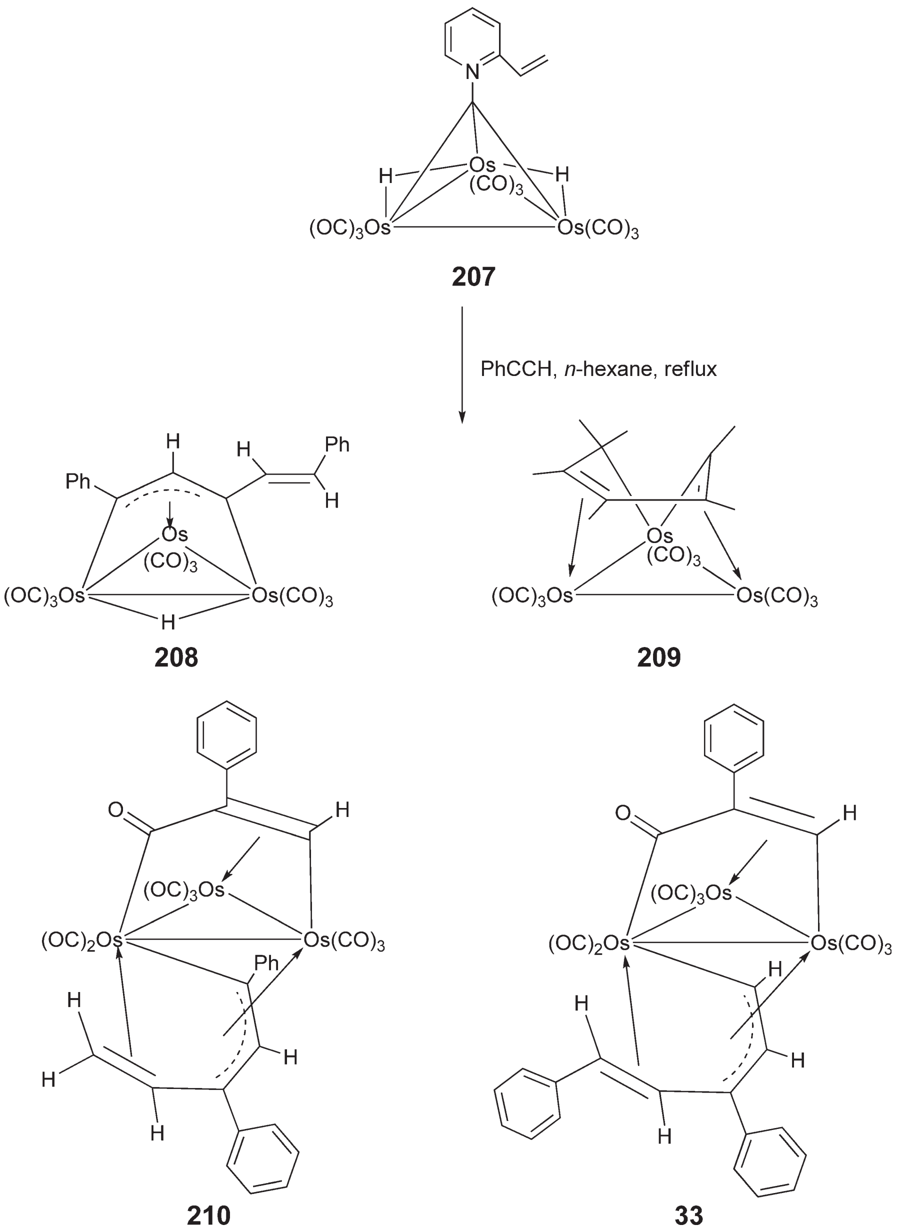


Scheme 14

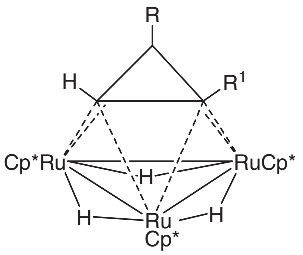
atom to the organic ligand. For **203** and **204**, elimination of the OH group with one alkyne hydrogen atom gives water. The reaction of **197** with HC≡CFc gives the metallabenzene complex $[Ru_3(CO)_9\{\mu_3\text{-}(FcCCCH)_2(CC{=}CPh_2)\}]$ **205** while the allenyl cluster $[Ru_3(CO)_9(\mu\text{-}OH)(\mu_3\text{-}Ph_2CCCCPh{=}CHPh)]$ **206** is formed from **197** and PhC≡CPh.

The reaction of the alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}CH_2)]$ 207 with the unsymmetrical alkyne PhC≡CH, under thermal conditions, affords two pairs of geometric isomers $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^3\text{-}PhCCH\text{-}CCH{=}CHPh)]$ 208, $[Os_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}PhCHCH{=}CHCH{=}CPh\}]$ 209, $[Os_3(CO)_7\{\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2{=}CH\text{-}CPhCHCPh)\{\mu_3\text{-}\eta^2\text{-}C(O)CPh{=}CH\}]$ 210 and $[Os_3(CO)_7(\mu\text{-}\eta^2{:}\eta^3\text{-}PhCH{=}CHCPhCHCH)\{\mu_3\text{-}\eta^2\text{-}C(O)CPh{=}CH\}]$ 211 as illustrated in Scheme 15.[23] The four compounds have been characterized crystallographically. In the structure of 208 the methylidyne carbon in the "Os_3C" core couples with two phenylacetylene molecules to form a novel C_5 hydrocarbyl ligand coordinated in an allyl fashion on the metal triangle. Cluster 209 contains a *cis,cis*-1,5-diphenyl-penta-1,3-diene ligand on a triangular array of Os atoms which, together with one of the Os atoms, forms an osmacyclohexa-2,4-diene ring with two localized double bonds. The structures of 209 and 211 both show the coupling of three alkyne molecules with 207, resulting in the formation of two discrete organic fragments. An interesting feature of both compounds is the formation of a keto ligand with a $\mu_3\text{-}\eta^2$-coordination mode which is derived from the coupling of one carbonyl ligand and a phenylacetylene molecule. The other fragment adopts a $\mu\text{-}\eta^2{:}\eta^3$-coordination mode with a π-bond and an η^3-allyl bond to give a metallacyclic ring system.

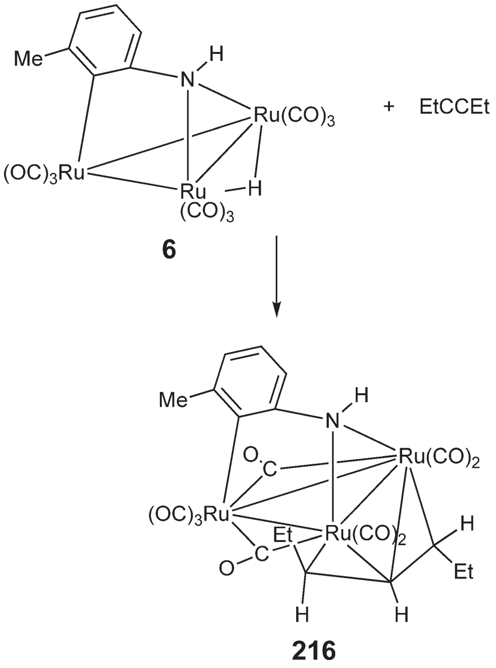
Oxidation of the $\mu_3\text{-}\eta^3$-diruthena-allyl cluster $[Ru_3(\mu\text{-}H)_4(Cp^*)_3(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHCRCR^1)]$ ($R = H$, $R^1 = Me$ **212**; $R = R^1 = Me$ **213**) with $[Cp_2Fe][PF_6]$ results in the formation of a cationic cluster $[Ru_3(\mu_3\text{-}H)_3Cp^*{}_3(\mu_3\text{-}\eta^3\text{-}CHCRCR^1)][PF_6]$ ($R = H$, $R^1 = Me$ 214; $R = R^1 = Me$ 215) in which $\mu_3\text{-}C_3$ ring lies parallel to and caps the Ru_3 plane, the cluster being formed as a result of bimetallic reductive C–C coupling.[108]



Scheme 15



R = H, R^1 = Me **214**
R = R^1 = Me **215**



Scheme 16

The reactions of $[Ru_3(\mu\text{-}H)(\mu_3\text{-apy})(CO)_9]$ **6** with alkynes that have α-hydrogen atoms give trinuclear derivatives that contain edge-bridging allyl or face-capping alkenyl ligands. The reaction of **6** with 3-hexyne gives two isomeric allyl derivatives that differ in the orientation of the allyl substituents, $[Ru_3(CO)_8(\mu_3\text{-apy})(\mu_3EtCHCHCHMe)]$ **216** (Scheme 16), while with 1-phenyl-1-propyne and 1-hexyne mixtures of three products only one of which was the allyl derivative were obtained; the other products were face-capped alkenyl derivatives.[109]

6.19.7 Clusters with Diyne and Polyyne Ligands

Generally the synthesis of diyne- and polyyne-subsituted triruthenium and triosmium clusters follows the same methodologies as those adopted for the simple alkyne systems described above. Three general synthetic routes have been reported: (i) the direct reaction of saturated or unsaturated metal cluster carbonyls with diynes and polyynes, (ii) the coupling of σ-alkynyl groups with concomitant aggregation of metal fragments, and (iii) the reaction of σ-diynyl-substituted metal complexes with other metal-containing units.[110] With $[Ru_3(CO)_{12}]$, $[Ru_3(CO)_{10}(NCMe)_2]$, $[Ru_3(CO)_{10}(\mu\text{-dppm})]$, $[Os_3(CO)_{12}]$, $[Os_3(CO)_{10}(NCMe)_2]$, and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ as starting materials for the reactions with diynes, it is generally found that cluster fragmentation and build-up reactions occur in addition to the addition of the diyne to the trinuclear cluster core, even under relatively mild reaction conditions. In the initial reaction products it appears that most commonly one of the triple $C{\equiv}C$ bonds of the diyne coordinates to the triangular metal framework in either a parallel or perpendicular $\mu_3\text{-}\eta^2$-bonding mode, as has been found for the analogous alkyne clusters (Section 6.7.2.4), but that subsequent reactions occur with the diynes that lead to a range of products. A selection of the triruthenium and triosmium diyne and polyyne clusters reported in the period 1994–2004 in which one of the alkyne units coordinates to the trinuclear cluster core in the $\mu_3\text{-}\eta^2\text{-}\|$ mode is presented in Table 4 while the smaller number in which the coordinated alkyne adopts the $\mu_3\text{-}\eta^2\text{-}\perp$ bonding mode is presented in Table 5.

While the reaction of $[Ru_3(CO)_{12}]$ with $PhC{\equiv}CC{\equiv}CPh$ in hexane under reflux leads to the formation of dinuclear ruthenium complexes,[114] the reactions of $[Ru_3(CO)_{10}(NCMe)_2]$ with $RC{\equiv}CC{\equiv}CR$ (R = Ph,[112,111] $SiMe_3$,[113] $C_5H_8(OH)$,[115] $CH_2(OH)$[114]) afford $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}\|\text{-}RC_2\text{-}C{\equiv}CR)]$ (R = Ph **217**, $SiMe_3$ **218**, $C_5H_8(OH)$ **220**, $CH_2(OH)$ **219**) in low to moderate yields. The cluster $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_5H_8(OH)C_2C{\equiv}CC_5H_8(OH))]$ **220** can also be obtained from the reaction of $[Ru_3(CO)_{12}]$ and 1,4-bis(1-hydroxycyclopentyl)buta-1,3-diyne in

Table 4 $\mu_3\text{-}\eta^2\text{-}\|$ Diynes

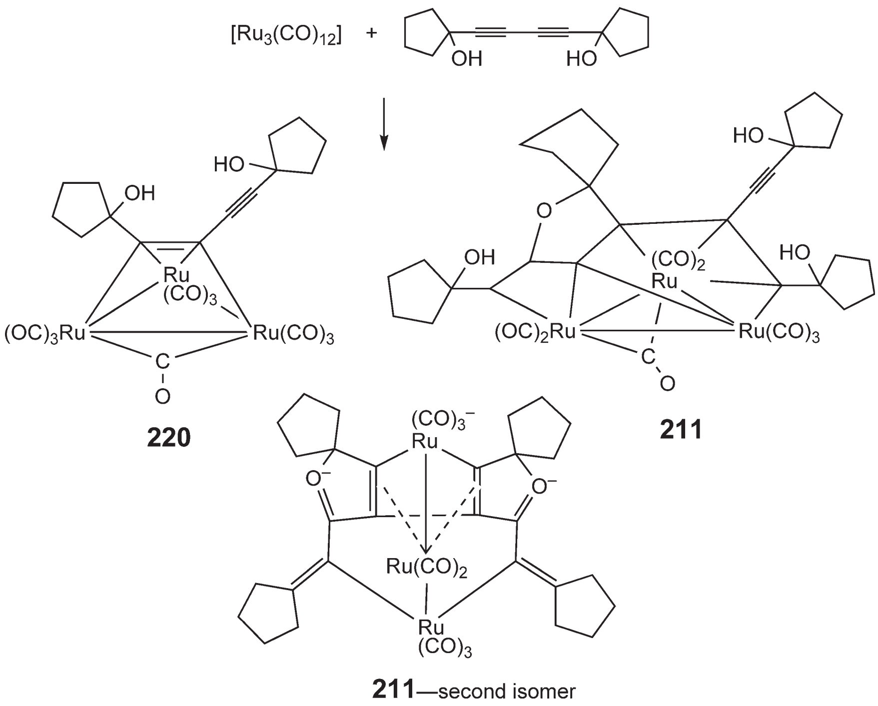
Complex	*Structure*	*References*
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$	**217**	111,112
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$	**218**	113
$[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}CH_2(OH)C_2C{\equiv}CCH_2(OH)\}]$	**219**	114
$[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}C_5H_8(OH)C_2C{\equiv}CC_5H_8(OH)\}]$	**220**	115
$[Ru_3(CO)_7(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$	**221**	116
$[Ru_3(CO)_7(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CFc)]$	**222**	117
$[Ru_3(CO)_7(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CFc)]$	**223**	117
$[Ru_3(CO)_9(\mu\text{-}OH)(\mu_3\text{-}\eta^2\text{-}PhC_2C{=}CHPh)]$	**224**	118
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CFc)]$	**225**	117
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CFc)]$	**226**	117
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2(C{\equiv}CSiMe_3)_2]$	**227**	119
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)]$	**228**	120,121
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$	**229**	111
$[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}(HO)CH_2C_2C{\equiv}CCH_2(OH)\}]$	**230**	114
$[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}Me_2(OH)CC_2C{\equiv}CC(OH)Me_2\}]$	**231**	122
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$	**232**	30
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)]$	**233**	113,30
$[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{:}\mu_3\text{-}\eta^2\text{-}HC_2C_2SiMe_3[Co_2(CO)_6]\}]$	**234**	30
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CC{\equiv}CC{\equiv}CFc)]$	**235**	123
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC{\equiv}CC_2C{\equiv}CC{\equiv}CFc)]$	**236**	123
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CFc)]$	**237**	124
$[\{Os_3(CO)_9(\mu\text{-}CO)\}_2(\mu_3\text{-}\eta^2\text{:}\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CC_2C{\equiv}CFc)]$	**238**	123
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}E\text{-}FcCHCHC_2C{\equiv}CC{\equiv}CFc)]$	**239**	125
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{: }\mu_3\text{-}\eta^2\text{-}HC_2C_2SiMe_3)\{Co_2(CO)_6\}]$	**240**	113
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{: }\mu_3\text{-}\eta^2\text{-}MeC_2C_2H\{Fe_2(CO)_6Se_2\})]$	**241**	126
$[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{: }\mu_3\text{-}\eta^2\text{-}{}^nBuC_2C_2H\{Fe_2(CO)_6Se_2\})]$	**242**	126
$[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{: }\mu_3\text{-}\eta^2\text{-}{}^nBuC_2C_2H\{Fe_2(CO)_6Se_2\})]$	**243**	126
$[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}Me_2(HO)CCH{=}CHC{\equiv}CC(OH)Me_2\}]$	**244**	127
$[Os_3(CO)_8(\mu\text{-}CO)(NCMe)(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)]$	**245**	121
$[Os_3(CO)_8(\mu\text{-}CO)(NCMe)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$	**246**	121
$[Ru_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}\eta^2\text{-}H_2C{=}CHC{\equiv}CC({=}O)OCH_3\}]$	**247**	128
$[Ru_3(CO)_7(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}C{}^tBu)]$	**248**	38
$[Ru_3(CO)_7(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$	**249**	38

Table 5 $\mu_3\text{-}\eta^2\text{-}\perp$ Diynes

Complex	*Structure*	*References*
$[Os_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^2\text{-}C_2C{\equiv}CRe(NO)(PPh_3)Cp^*\}]$	**264**	13,14
$[Ru_3(\mu\text{-}H)(CO)_5(\mu\text{-}dppm)_2(\mu_3\text{-}\eta^2\text{-}C_2C{\equiv}CSiMe_3)]$	**263**	113
$[Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{;}\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)\{Co_2(\mu\text{-}dppm)(CO)_4\}]$	**265**	113
$[Os_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{;}\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C)\{Co_2(CO)_6\}]$	**266**	30
$[Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}\eta^2\text{-}C_2C{\equiv}CFc)]$	**256**	117
$[Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^2\text{-}C_2C{\equiv}CW(CO)_3Cp\}]$	**267**	132
$[Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}dppm)\{\mu_3\text{-}\eta^2\text{-}C_2C{\equiv}CW(CO)_3Cp\}]$	**268**	132

chloroform at 68 °C together with two isomers of another trinuclear product in which C–C bond formation has occurred (Scheme 17).

The analogous reactions of $[Os_3(CO)_{10}(NCMe)_2]$ with a range of symmetrically substituted 1,3-diynes also give $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}\|\text{-}RC_2C{\equiv}CR)]$ (R = Me,[120,121] Et, ^{t}Bu, Ph,[111] $SiMe_3$,[30] Fc[124]). However, even when the reaction is carried out at room temperature, the trinuclear complex with the diyne in the $\mu_3\text{-}\eta^2\text{-}\|$-bonding mode is seldom the only product. A reinvestigation of the reaction between $[Os_3(CO)_{10}(NCMe)_2]$ and $MeC{\equiv}CC{\equiv}CMe$ confirms that in addition to $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)]$, three previously uncharacterized triosmium clusters are obtained.[121] These are $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{:}\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-}MeC_2C_2MeOC_5Me_2\}Os_3(\mu\text{-}CO)(CO)_9]$ **251**,



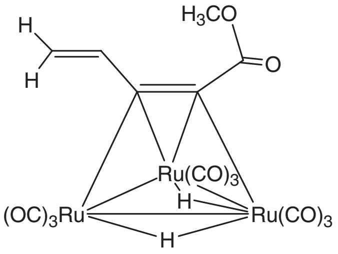
Scheme 17

$[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}[(MeC_2)C_2Me]CO[MeC_2(C_2Me)]\}]$ **252** and $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}[(MeC_2)C_2Me]CO[(MeC_2)C_2C_2Me]\}]$ **253** (Scheme 18). Cluster **251** incorporates two triosmium clusters joined by an unsaturated five-membered metallacycloether ring while **252** contains an alkyne-functionalized metallacyclohexadieneone ring.

The asymmetric diyne-substituted cluster $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)]$ **233** may be generated from $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}\|\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ **232** by desilylation in methanol as illustrated in Scheme 19. Only one isomer of **233** is obtained.

The room temperature reaction of $[Ru(CO)_5]$ with 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne leads to the formation of $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}(Me_3SiC{\equiv}C)C_2(C{\equiv}CSiMe_3)]$ **227** and $[Ru_4(CO)_{12}\{\mu_4\text{-}\eta^2\text{-}C_2(C{\equiv}CSiMe_3)_2\}]$ **254** in relatively low yields (Scheme 20). Cluster **227** is obtained in better yield when $[Ru_3(CO)_{10}(NCMe)_2]$ is used as the metal-containing precursor, and subsequent reaction of **227** with $[Ru(CO)_5]$ affords **254** which suggests that the mononuclear carbonyl is probably the precursor to **254** in the original reaction.[119]

The reaction of $[Ru_3(CO)_{12}]$ with 1,4-dichlorobut-2-yne, in methanolic KOH, followed by acidification with HCl, gives $[Ru_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}\eta^2\text{-}H_2C{=}CHC{\equiv}CC({=}O)OCH_3\}]$ **247** which has been shown by X-ray crystallography to contain a "parallel" ene-yne acetyl substituent.[128] The reaction pathway for the synthesis involves the activation of CO and methanol.



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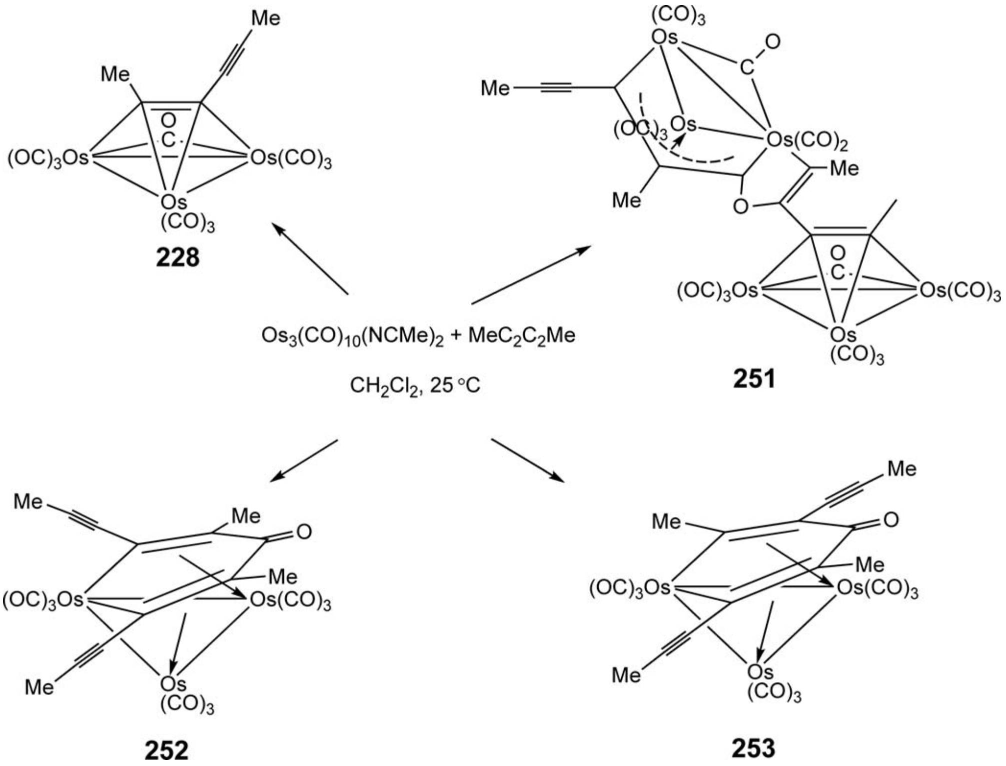
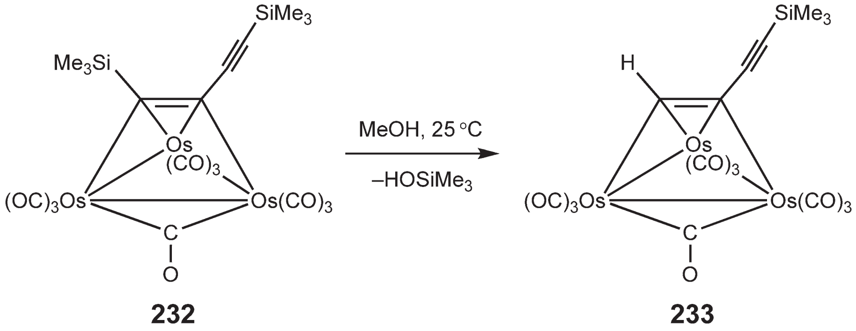
The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 1,8-bis(ferrocenyl)-1,3-butadiyne, $FcC{\equiv}CC{\equiv}CFc$, gives $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CFc)]$ **237** and the linear triosmium complex $[Os_3(CO)_{11}(\mu_3\text{-}FcC_2C_2Fc)]$ (Scheme 21),[124]

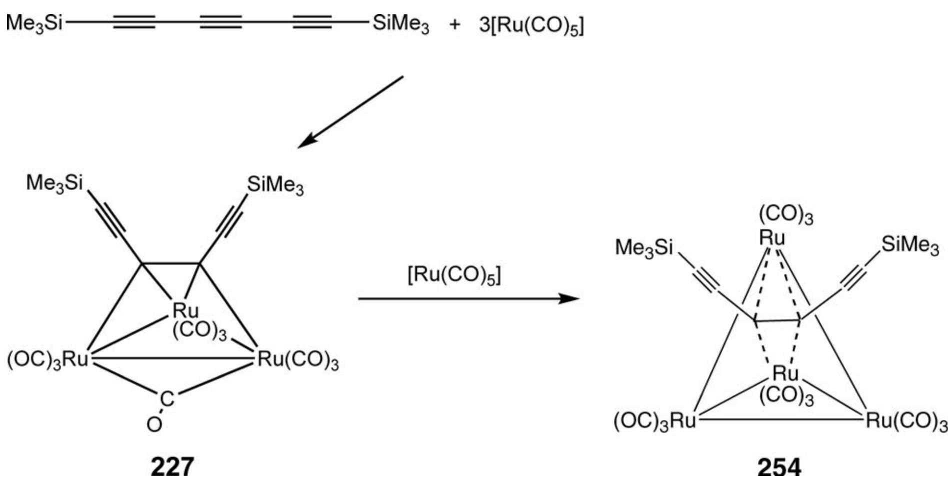


Scheme 18

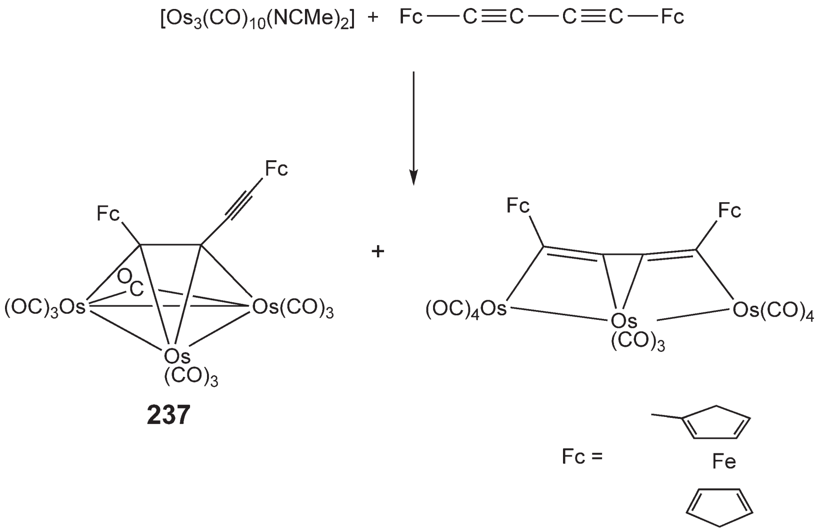


Scheme 19

whereas the same diyne with $[Ru_3(CO)_{12}]$, under reflux, gives all three isomers of the metallacyclopentadiene $[Ru_2(CO)_6\{\mu\text{-}2\eta^1{:}\eta^4\text{-}C_4Fc_2(C{\equiv}CFc)_2\}]$ and two isomers of the dimetallacycloheptadienone $[Ru_2(CO)_6\{\mu\text{-}\eta^1,\eta^2{:}\eta^1,\eta^2\text{-}C_4Fc_2(C{\equiv}CFc)_2CO\}]$.[24] With 1,8-bis(ferrocenyl)-1,3-butadiyne, the reaction with either $[O_3(CO)_{11}(NCMe)]$ or $[Os_3(CO)_{10}(NCMe)_2]$ affords both $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CFc)]$ **237** and $[Os_3(CO)_{11}(\mu_3\text{-}FcC_2C_2Fc)]$, although the yield of the former cluster is higher when the bis-acetonitrile osmium cluster is used.[124] $[Os_3(CO)_{11}(\mu_3\text{-}FcC_2C_2Fc)]$ contains an open triosmium unit with two C–C triple bonds coordinated in a parallel fashion to the three metal atoms. Similarly, using 1,8-bis(ferrocenyl)octatetrayne in a reaction with $[Os_3(CO)_{11}(NCMe)]$, four new products are obtained: $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CC{\equiv}CC{\equiv}CFc)]$ **235**, and its isomer $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC{\equiv}CC_2C{\equiv}CC{\equiv}CFc)]$ **236**, $[Os_3(CO)_{11}(\mu_3\text{-}\eta^4\text{-}C_4C{\equiv}CC{\equiv}CFc)]$, and $[Os_6(CO)_{21}(FcC_2C_3COCC{\equiv}CFc)]$.[129] Again, higher yields of $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CC{\equiv}CC{\equiv}CFc)]$ **235** and $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcC{\equiv}CC_2C{\equiv}CC{\equiv}CFc)]$ **236** are obtained if $[Os_3(CO)_{10}(NCMe)_2]$ is used, and a new hexaosmium cluster $[Os_6(CO)_{20}(\mu_6\text{-}\eta^4\text{-}FcC{\equiv}CC_2C{\equiv}CC_2Fc)]$ is also obtained.[123] These ferrocenyl derivatives have attracted interest



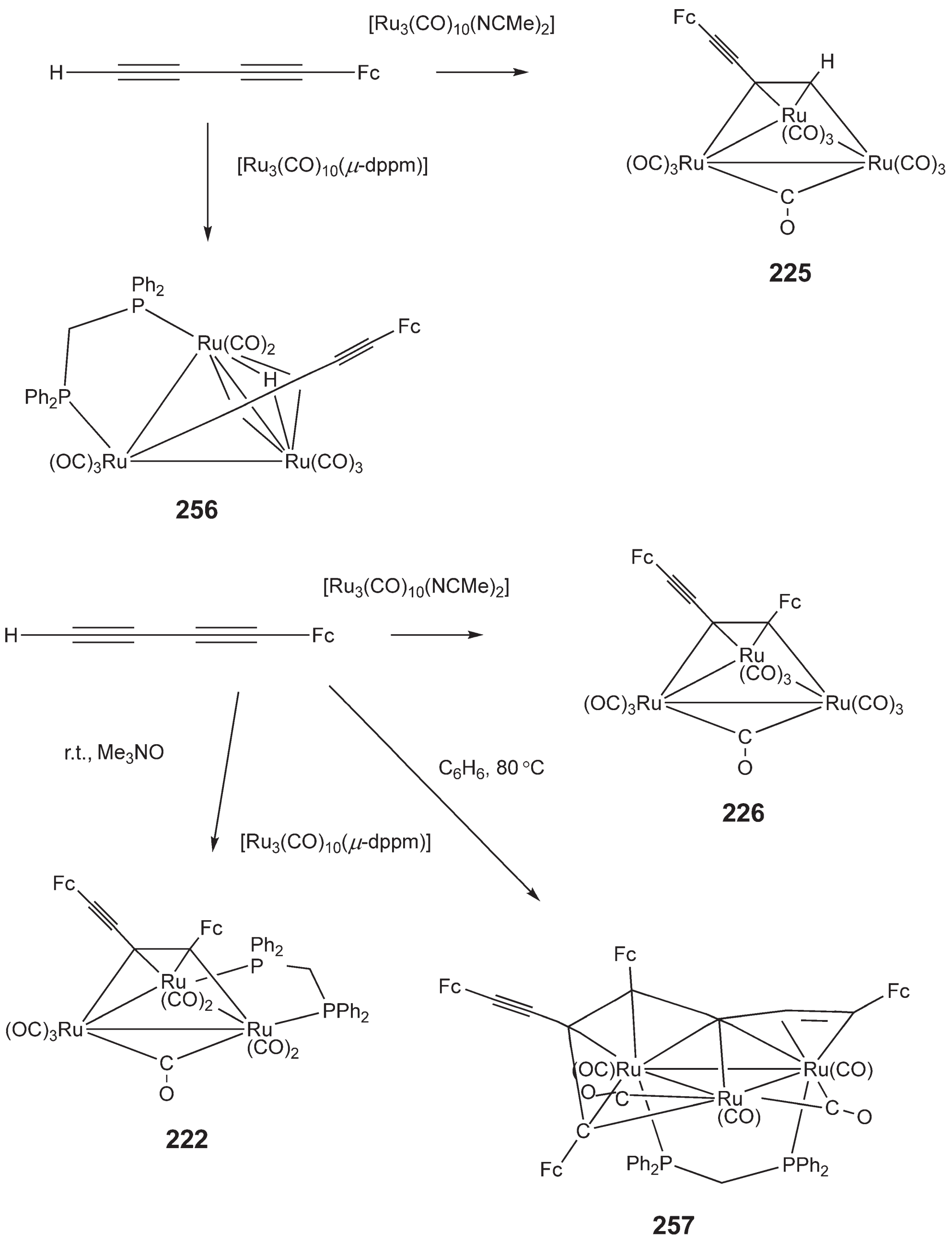
Scheme 20



Scheme 21

because they have the potential to act as models for molecular wires. The electronic communication between the two ferrocenyl centers has been measured by cyclic voltammetry; however, the redox potentials are closely spaced in both the diyne and octatetrayne systems suggesting that there is little communication between the iron centers. However, in $[Os_3(CO)_{11}(\mu_3\text{-}FcC_2C_2Fc)]$ and $[Os_3(CO)_{11}(\mu_3\text{-}\eta^4\text{-}C_4C{\equiv}CC{\equiv}CFc)]$ there is a significant increase in the separation of the redox potentials, $\Delta E_p =$ ca. 0.14 V, that may indicate that there is significant electrocommunication. This increase can be attributed to greater interactions in the π-orbital network induced by the coordination to the chain of metal atoms. Another two-strand chain cluster, $[Os_3(CO)_{11}\{\mu_3\text{-}\eta^4\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$ **255**, has been obtained by the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with $(C_4H_3S)C{\equiv}CC{\equiv}C(C_4H_3S)$ under mild conditions, but attempts to measure the electrocommunication along this chain have not been made.[130]

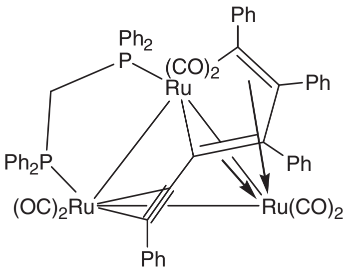
Related reactions have been carried out between $FcC{\equiv}CC{\equiv}CFc$ or $HC{\equiv}CC{\equiv}CFc$ and $[Ru_3(CO)_{10}(NCMe)_2]$ or $[Ru_3(CO)_{10}(\mu\text{-dppm})]$. With $[Ru_3(CO)_{10}(NCMe)_2]$ and diynes $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}RC_2C{\equiv}CFc)]$ ($R = Fc$ 226, H 225) are obtained as the major products, while with $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ the symmetric diyne gives $[Ru_3(CO)_7(\mu\text{-}CO)(\mu\text{-dppm})(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CFc)]$ 222. With the asymmetric diyne and $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ both the parallel-bound $\mu_3\text{-}\eta^2$-product, $[Ru_3(CO)_7(\mu\text{-}CO)(\mu\text{-dppm})(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CFc)]$ **223** and the perpendicular-bound $\mu_3\text{-}\eta^2$-product, $[Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-dppm})(\mu_3\text{-}\eta^2\text{-}C_2C{\equiv}CFc)]$ 256 are obtained (Scheme 22).[117] When the reaction



Scheme 22

between FcC≡CC≡CFc and $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ is carried out in benzene at 80 °C, $[Ru_3(CO)_5(\mu\text{-CO})(\mu\text{-dppm})\{\mu_3\text{-}C_4Fc_2(C{\equiv}CFc)_2\}]$ 257 is obtained in which head-to-tail dimerization of the diyne has occurred on the cluster, with one of the free C≡CFc groups coordinating in a η^2-fashion to the third Ru atom. This product can also be obtained when dppm is added to a solution of $[Ru_3(CO)_{12}]$ and the 1,3-diyne and the mixture heated to reflux.[61]

The bridging phosphine-substituted cluster $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ has also been used in reactions with 1,3-diynes. When $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ is treated with PhC≡CC≡CPh, in the presence of Me_3NO that activates the carbonyls, the expected product $[Ru_3(CO)_7(\mu\text{-CO})(\mu\text{-dppm})(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ is obtained as the major component together with $[Ru_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ **217** and $[Ru_3(CO)_6(\mu\text{-dppm})\{\mu\text{-}C_4Ph_2\text{-}(C{\equiv}CPh)_2\}]$ 258, in which two molecules of the diyne have combined to give a ruthenole, which is attached to the other two Ru atoms by an η^4-interaction from the ring and by the η^2-coordination of one $C{\equiv}C$ triple bond, respectively.[116]



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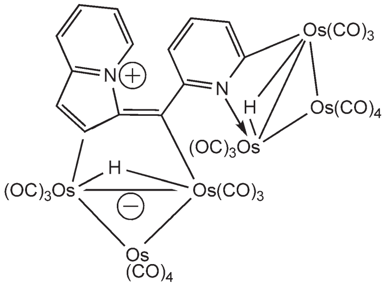
Interestingly, the room-temperature reaction between $[Os_3(CO)_{10}(NCMe)_2]$ and the symmetric pyridine-substituted diyne, 1,4-dipyridylbuta-1,3-diyne, in CH_2Cl_2, does not give the expected μ_3-η^2-||-bound product but coordination occurs through an orthometallated pyridine ring with a proton being transferred from the pyridine ring to the metal framework.[131] The reaction is illustrated in Scheme 23. Three products are generated: the yellow cluster $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^2\text{-}(NC_5H_3)C_2C_2(C_5H_4N)\}]$ **259** in 50% yield, a second yellow product $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2\{\mu\text{-}\eta^2\text{-}(NC_5H_3)C_2\}_2]$ **260** in 20% yield, and a navy blue minor product $[\{Os_3(CO)_{10}\}_2\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{-}C_2(NC_5H_4)\}_2]$ **261**, in 10% yield, in which the ligand is coordinated through a μ-carbene and a σ-*N*-interaction. The cluster **259** goes on to react with $[Os_3(\mu_2\text{-}H)_2(CO)_{10}]$ to form the linked cluster $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2\{\mu\text{-}\eta^1\text{:}\eta^1,\mu\text{-}\eta^1\text{:}\eta^1\text{-}(C_8H_5N)C(C_5H_3N)\}$ **262** with the formation of an indolizine ring system. This example illustrates that when good donor atoms are present within the substituent groups of the diyne, competitive reactions can occur and the formation of the M_3-alkyne interaction is not necessarily favored.



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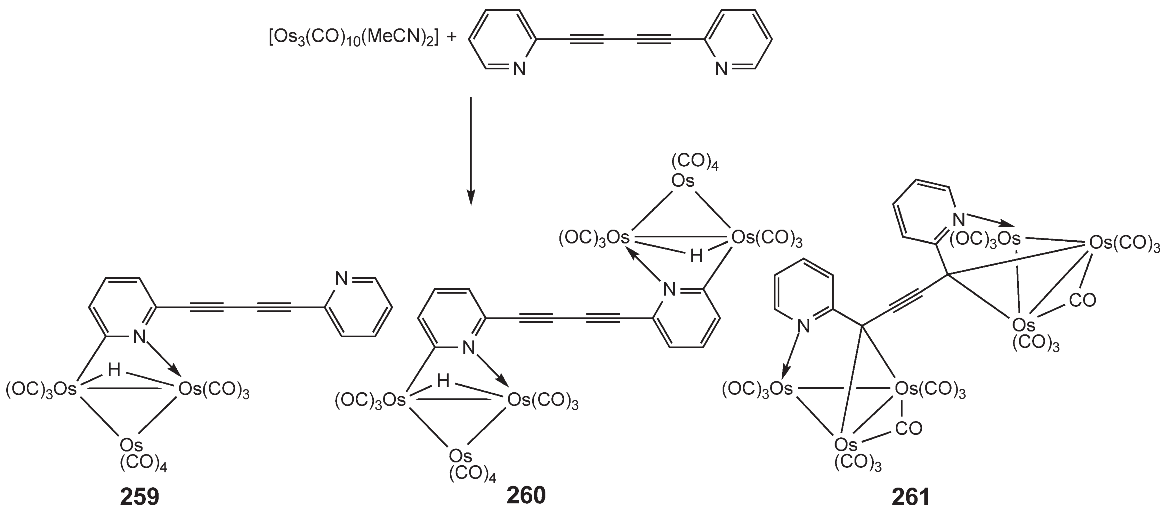
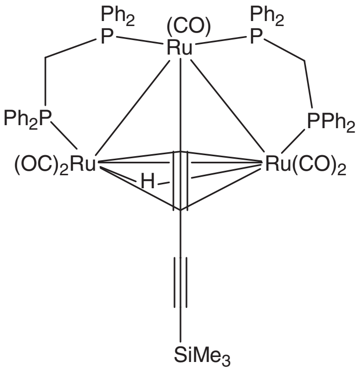


Scheme 23

So far the discussion has concentrated on the reactions of symmetric 1,3-diynes with trinuclear ruthenium and osmium clusters. Related reactions occur with asymmetric diynes. For example, the reaction of $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ with $HC{\equiv}CC{\equiv}CSiMe_3$ in thf gives $[Ru_3(\mu\text{-H})(CO)_5(\mu\text{-dppm})_2(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2C{\equiv}CSiMe_3)]$ **263** via the oxidative addition of the terminal $C{\equiv}CH$ component of the diynyl ligand across one of the dppm-bridged Ru–Ru bonds.[113]



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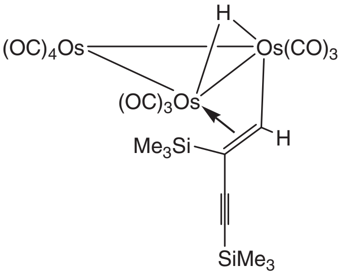
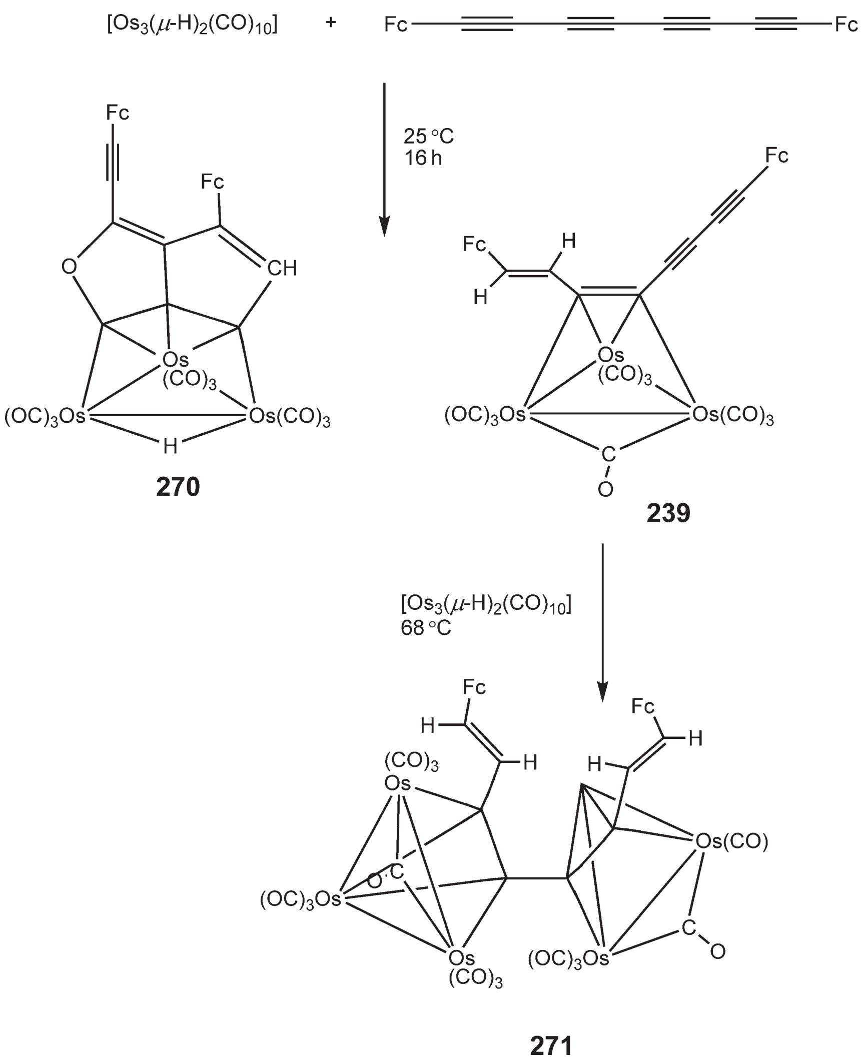
There is an additional possible reaction pathway in reactions between the 46-electron unsaturated cluster $[Os_3(\mu_2\text{-}H)_2(CO)_{10}]$ and diynes and polyynes in that one of the cluster hydrides can transfer to the ligand which may initiate rearrangement processes. The room temperature reaction between $[Os_3(\mu\text{-H})_2(CO)_{10}]$ and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ does give $[Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}\|\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ **232**[30] as the major product, particularly when an excess of diyne is used, which is the same product as is obtained with $[Os_3(CO)_{10}(NCMe)_2]$;[30] however, $[Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-}\eta^1,\eta^2\text{-}HC_2(SiMe_3)C{\equiv}C(SiMe_3)\}]$ **269** is also obtained in significant yield.



269

The reaction of $[Os_3(\mu\text{-H})_2(CO)_{10}]$ with 1,8-bis(ferrocenyl)octatetrayne affords three products, $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^3\text{-}FcCCHC_4COC{\equiv}CFc)]$ **270**, $[Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}E\text{-}FcCHCHC_2C{\equiv}CC{\equiv}CFc)]$ **239** and $[Os_6(CO)_{20}(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}E,E\text{-}FcCHCHC_2C_2CHCHFc)]$ **271** (Scheme 24).[125] This contrasts with the products obtained from the reaction with $[Os_3(CO)_{10}(NCMe)_2]$ where $[Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CC{\equiv}CC{\equiv}CFc)]$, $[Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}FcC{\equiv}CC_2C{\equiv}CC{\equiv}CFc)]$, and $[Os_6(CO)_{20}(\mu_6\text{-}\eta^4\text{-}FcC{\equiv}CC_2C{\equiv}CC_2Fc)]$ are obtained.[123] In the products **239** and **271** obtained from $[Os_3(\mu\text{-H})_2(CO)_{10}]$, both protons have transferred from the Os_3 framework to the octatetrayne ligand to convert an alkyne group to an alkene group with (*E*)-stereochemistry. Cyclic and differential pulse voltammetry measurements show two reversible one-electron oxidation peaks for **270** and **239** for their inequivalent ferrocenyl groups, while **271** shows only one two-electron oxidation of the two ferrocenyl groups, indicating no significant electrocommunication between them.

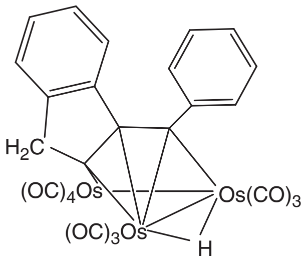
In this reaction it is assumed that **270** is obtained by an intramolecular cyclization involving three of the C–C triple bonds of the tetrayne chain, a coupling of one of the CO ligands, and the transfer of one of the hydride ligands to a carbon atom. There are three possibilities for the formation of **239** (and **271**). The first could involve *trans*-insertion, one allyne is inserted into a metal–hydrogen bond to give a σ-π alkenyl intermediate with the *trans*-stereochemistry. The second could be a two-step process involving first *cis*-addition of both hydrogen atoms followed by an independent *Z*- to *E*-isomerization, and the third could involve the formation of an *E*-olefinic group via a *cis*-insertion followed by a *trans*-addition of the second hydrogen atom.



270 **239** **271**

Scheme 24

When the terminal SiMe$_3$ groups (*vide supra*)[30] in the 1,3-butadiyne are replaced by phenyl groups a completely different reaction sequence occurs. The reaction of [Os$_3$(μ-H)$_2$(CO)$_{10}$] with 1,4-diphenylbuta-1,3-diyne does not produce a product that contains a μ_3-η^2-bonded alkyne fragment, but gives two isomers of a 50-electron "open" triangular cluster [Os$_3$(μ-H)(CO)$_{10}${μ_3-η^1:η^3:η^1-PhCC$_9$H$_6$}] 272 in which the PhCC$_9$H$_6$ ligand consists of a fused six- and five-membered ring system, obtained from the ring closure of the diyne, and which coordinates to the cluster framework through an allylic interaction.[133] The presence of the phenyl groups must facilitate the ring closure reaction through C–H activation of the hydrogen on the β-carbon atom.



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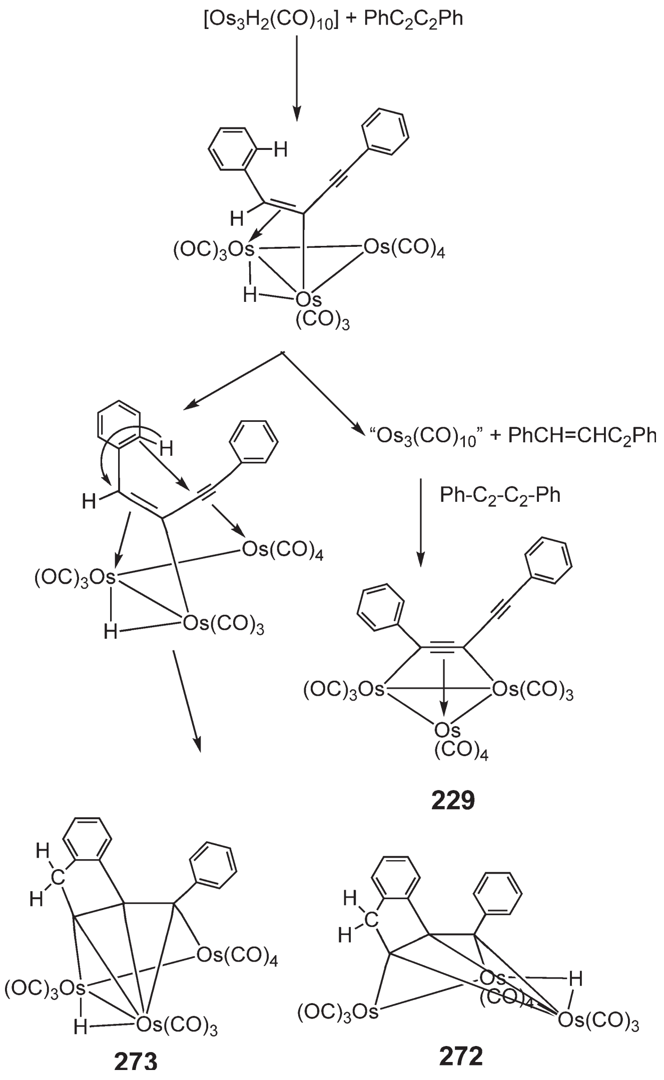
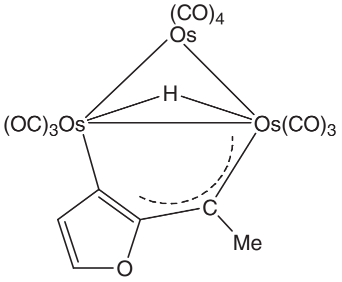


Scheme 25

A possible mechanism for the formation of **272**, its structural isomer **273**, and small quantities of $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ **229** is illustrated in Scheme 25. The first step involves the formation of an alkenyl intermediate, followed by an intramolecular cyclization process that leads to the formation of **272** and **273**. An alternative pathway involves the coordination of the second hydride onto the coordinated ligand which results in the expulsion of an enyne and the further reaction of an unsaturated "$Os_3(CO)_{10}$" fragment with another diyne molecule to give **229**.

The reactivity of symmetric and asymmetric 1,3-butadiynes that contain a potentially reactive, electrophilic center in the β-position of the substituent have then been explored in reactions with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. Generally, facile rearrangements occur to form coordinated, five-membered rings. The cyclization has been shown to proceed via nucleophilic attack of the β-atom of the substituent on the coordinated diyne chain to give five-membered nitrogen or oxygen heterocycles. The diynes used include $RC{\equiv}CC{\equiv}CR^1$ ($R = R^1 = CH_2OH$; $R = Ph$, $R^1 = CH_2OH$; $R = Ph$, $R^1 = C(O)Ph$; $R = R^1 = CMe_2(OH)$; $R = Ph$, $R^1 = CH_2NHPh$; $R = Ph$, $R^1 = CH_2NHCH_2Ph$; $R = R^1 = CH_2NHPh$; $R = R^1 = C_5H_4N$). The reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $HOCH_2C{\equiv}CC{\equiv}CCH_2OH$ affords $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu_2\text{-}\eta^3\text{-}\overline{O\text{–}CH{=}CH\text{–}C{=}C}\text{–}CMe\}]$ **274** in which the rearranged ligand forms a pseudo-furan ring with the C-Me substitutent in the α-position.[134]

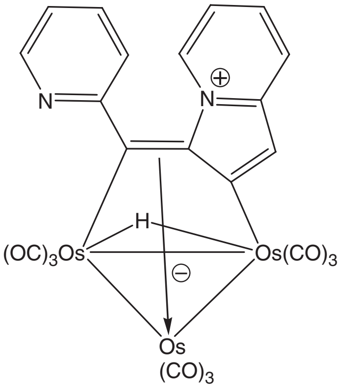


274

With the asymmetric diynes $PhC{\equiv}CC{\equiv}CCH_2OH$ and $PhC{\equiv}CC{\equiv}CC(O)Ph$, $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^1{:}\eta^2\text{-}CCHOC(CH_2Ph){=}CH\}]$ **275** and $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^1{:}\eta^1\text{-}CC(CPh)OCPhCH\}]$ **276** are formed, respectively.[122] Both ligands contain a furan ring coordinated to the 48-electron cluster core. On heating **276**, the furan ring remains intact, but a carbonyl dissociates to form $[Os_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}C(CH{=}CPhO)CCPh\}]$ **277** which has a closed Os_3C_3 core. With $Me_2C(OH)C{\equiv}CC{\equiv}CC(OH)Me_2$, the reaction with $[Os_3(\mu_2\text{-}H)_2(CO)_{10}]$ does not result in cyclization but the clusters $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}Me_2(OH)CCH{=}CHC{\equiv}CC(OH)Me_2)]$ **278** and $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}Me_2(OH)CC_2C{\equiv}CC(OH)Me_2)]$ **231** are obtained. The mechanisms for the formation of the products **275, 276, 277**, and **278** have been investigated using deuterium labeling, and it is likely that the reaction involves the initial formation of a vinyl intermediate followed by nucleophilic attack of the oxygen onto the third atom of the diyne chain, and hydrogen shifts along the coordinated organic ligand giving either $\mu_2\text{-}\eta^1{:}\eta^2$- or $\mu_2\text{-}\eta^1{:}\eta^1$-coordinated furan rings, depending on the nature of the substituents. For with $Me_2C(OH)C{\equiv}CC{\equiv}CC(OH)Me_2$ it appears that the β-methyl groups prevent cyclization because of their inability to participate in 1,3-shifts along the hydrocarbon chain. Instead, products that contain the coordinated diyne or the partially reduced enyne ligand are formed.

The next group of 1,3-butadynes investigated for their ability to undergo cyclization reactions with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ were those with β-amino moieties as the substituents. The reaction of the dihydride with $PhC{\equiv}CC{\equiv}CCH_2NHPh$, $PhC{\equiv}CC{\equiv}CCH_2NHCH_2Ph$, and $PhCH_2NHCH_2C{\equiv}CC{\equiv}CCH_2NHCH_2Ph$ afforded the products $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^1{:}\eta^2\text{-}PhCH_2CH{=}CCH{=}CNPh)]$ 279, $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^1{:}\eta^2\text{-}PhCH_2CH{=}CCH{=}CNCH_2Ph)]$ 280, and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_3CC{=}CCH{=}CHNPh)]$ 281, respectively.[135] The three products all contain substituted pyrrolyl rings and adopt coordination modes dependent on the nature of the substituents in the original diynes. The reaction pathway is thought to involve an initial transfer of a hydride onto a coordinated diyne followed by a series of 1,3-shifts and subsequent nucleophilic attack of the nitrogen on the third carbon atom of the diyne system. The possible mechanism is illustrated in Scheme 26.

Finally, in contrast to the products 259, 260 and 261 obtained with $[Os_3(CO)_{10}(NiMe)_2]$, the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with 1,4-dipyridylbuta-1,3-diyne yields two clusters, $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^1{:}\eta^1\text{-}(C_8H_5N)C(C_5H_4N)\}]$ 281 and $[Os_3(\mu\text{-}H)(CO)_{10}\text{-}\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-}(C_5H_4N)CC(C_8H_6N)\}]$ 282, in which the diyne has rearranged to form a substituted indolizine-ring system (Scheme 27). Complex 281 converts slowly to 282 at room temperature and may be decarbonylated to yield $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}(C_8H_5N)\text{-}C\text{-}(C_5H_4N)\}]$ 283.[131]



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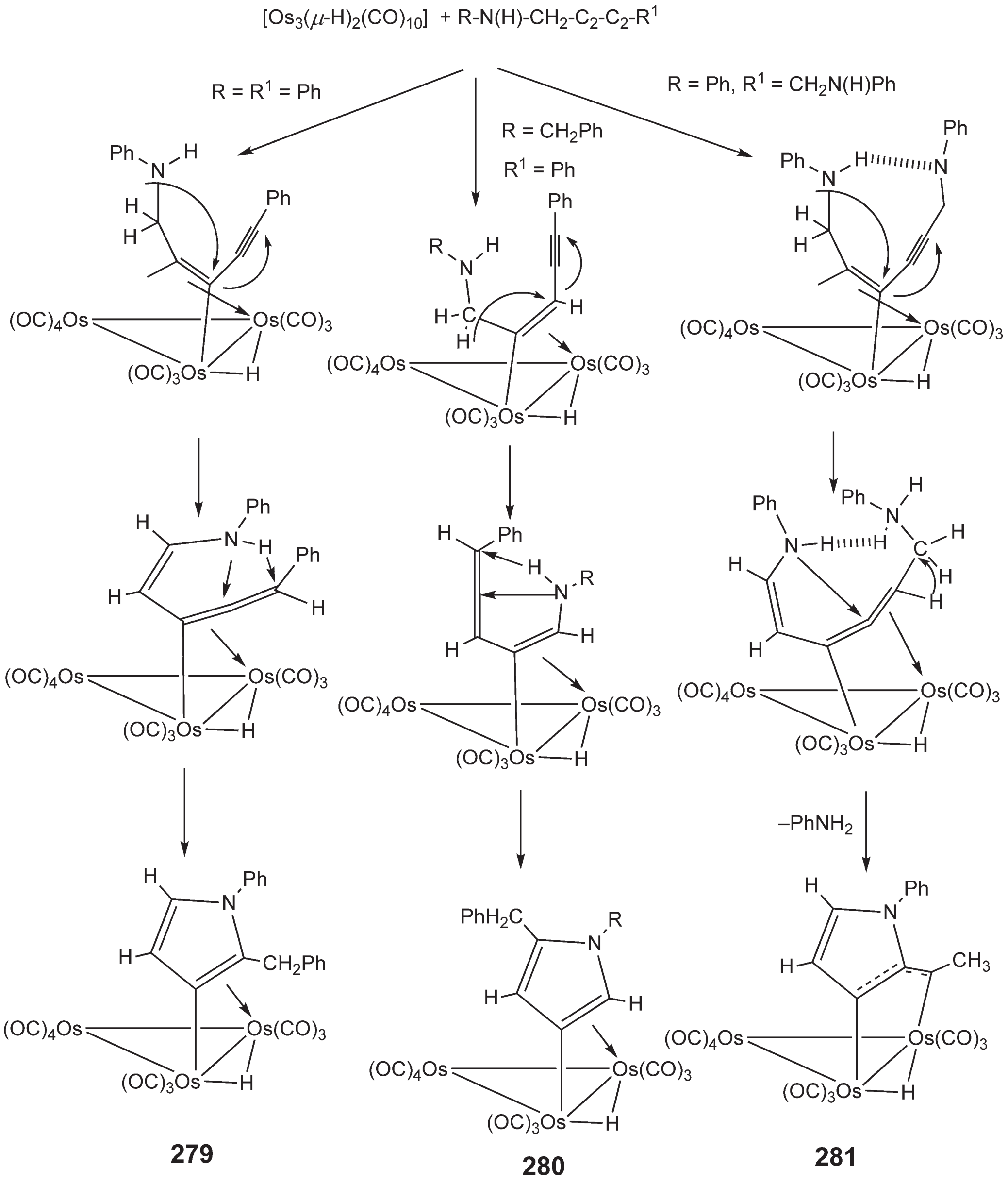
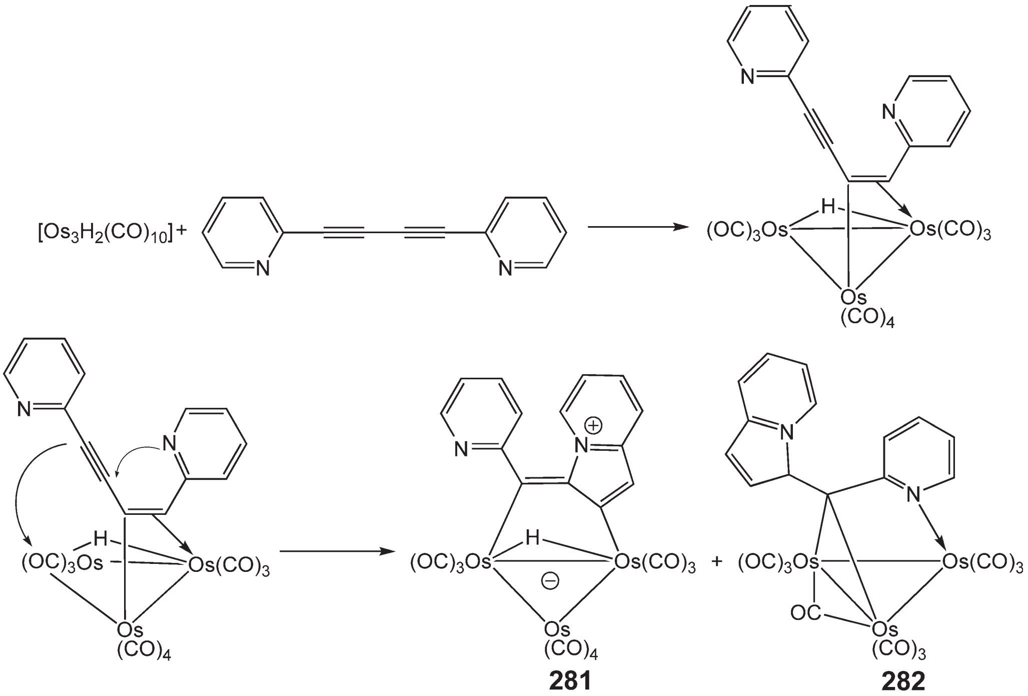


Scheme 26

The 2-aminopyridine-containing cluster [Ru_3(μ-H)(μ_3-apy)$(CO)_9$] 6 reacts with diphenylbutadiyne and 1.6-diphenoxyhexa-2,4-diyne in thf under reflux to give the ynenyl derivatives [$Ru_3(CO)_8$(μ_3-apyMe)-(μ-RCCC=CHR)] (R = Ph 284, CH_2OPh 285) (Scheme 28). These products contain a 1,4-disubstituted butynen-3-yl ligand η^3-coordinated to two Ru atoms. The unusual cluster [$Ru_3(CO)_7$(μ_3-apyMe)(μ_3-η^6-$PhCC_5$(C≡CPh)HPh_2)] 286 which contains an η^5-cyclopentadienyl ring and a bridging carbene fragment, has also been observed from the reaction of 6 with diphenylbutadiyne.[136,136a] As the diynes contain asymmetric alkyne fragments for each complex, there are two possible products resulting from the insertion of one of the alkyne fragments into a metal–hydride bond. While the structures of 284 and 285 show that they contain butynen-3-yl ligands that result from one of the two possible insertion regioisomers, cluster 286 arises from an unprecedented [3 + 2]-cycloaddition reaction of an unobserved 1,4-diphenylbutynen-4-yl ligand with a triple bond of a second diphenylbutadiyne molecule. The reaction of 6 with an excess of hexa-2,4-diyne gives the trinuclear cluster



Scheme 27

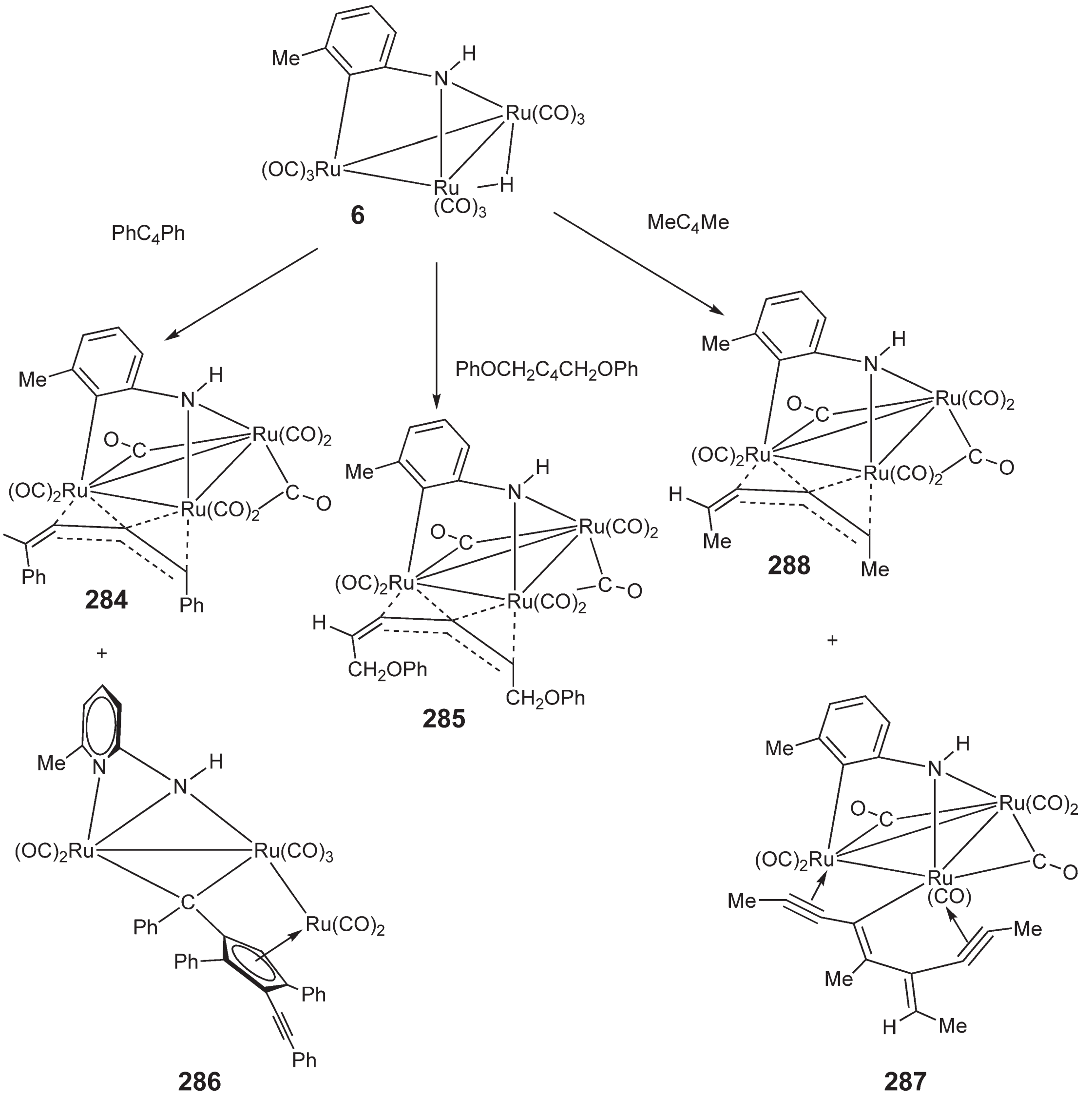
$[\mathrm{Ru_3(CO)_7}(\mu_3\text{-apyMe})\{\mu\text{-}\eta^5\text{-MeC{\equiv}CC({=}CHMe)(CMe{=}CC{=}CMe)}\}]$ 287 as the final product. This complex contains a diyndienyl ligand that arises from the coupling of hexa-2,4-diyne with the hex-2-yn-4-en-4-yl ligand of the intermediate $[\mathrm{Ru_3(CO)_8}(\mu_3\text{-apyMe})(\mu\text{-MeCH{=}CC{\equiv}CMe})]$ 288. This intermediate is the first compound observed in the reaction of 6 with hexa-2,4-diyne.[137] From the results described here, it is apparent that alkynes can easily be activated in the form of alkenyl (vinyl) ligands by 6 and its derivatives. The presence of the face-capping apy ligand is thought to be essential in maintaining the cluster nuclearity.

The structures of these ynyl and related clusters have been analyzed using DFT calculations and it has been shown that the face-capping products are slightly more stable than the edge-bridging ones.[138]

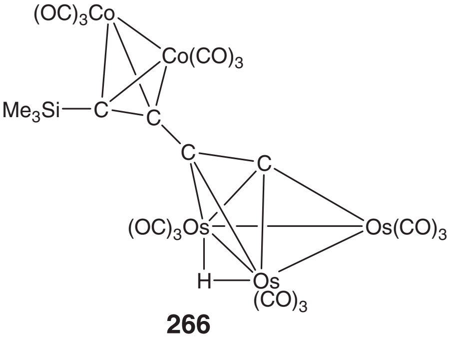
6.19.8 Reactions of 1,3-Diyne- and Polyyne-Substituted Clusters

In addition to the ligand rearrangement and decarbonylation reactions that are observed for triruthenium and triosmium clusters, with diyne- and polyyne-substituted clusters there is also the possibility of carrying out reaction chemistry on the free alkyne unit when this has not been involved in cyclization reactions during the initial synthesis.

For example, $[\mathrm{Os_3(CO)_9}(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-HC_2C{\equiv}CSiMe_3})]$ 233 reacts readily with $[\mathrm{Co_2(CO)_8}]$ to give the dark green adduct $[\mathrm{Os_3(CO)_9}(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-HC_2C_2SiMe_3})\{\mathrm{Co_2(CO)_6}\}]$ **234** in which the $\mathrm{Co_2(CO)_6}$ fragment has been added to the uncoordinated C≡C triple bond adjacent to the $\mathrm{SiMe_3}$ group in 233.[113] There is no evidence for the formation of the other isomer where the free C≡C triple bond is associated with the terminal hydrogen. It is worthy of note that this reaction contrasts that of the addition of $[\mathrm{Co_2(CO)_8}]$ to $[\mathrm{Ru_3(CO)_9}(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-PhC_2C{\equiv}CPh})]$ **217** where the bow-tie cluster $[\mathrm{Ru_3Co_2}(\mu\text{-CO})_3\mathrm{(CO)_{10}}(\mu_4\text{-PhC_2C_2Ph})]$ **289** is formed by the insertion of the cobalt species into an Ru–Ru bond,[139] and that with $[\mathrm{Ru_3(CO)_7}(\mu\text{-CO})(\mu\text{-dppm})(\mu_3\text{-}\eta^2\text{-PhC_2C{\equiv}CPh})]$ **221** where a cluster in which the diyne has been cleaved to form two $\mathrm{C_2Ph}$ units has been obtained.[116] In an independent investigation of the reaction between $[\mathrm{Os_3(CO)_9}(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-HC_2C{\equiv}CSiMe_3})]$ 233 and $[\mathrm{Co_2(CO)_8}]$, in addition to $[\mathrm{Os_3(CO)_9}(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-HC_2C_2SiMe_3})(\mathrm{Co_2(CO)_6})]$ **234**, a second product $[\mathrm{Os_3}(\mu\text{-H})\mathrm{(CO)_9}(\mu_3\text{-}\eta^1{:}\eta^2;\mu\text{-}\eta^2\text{-Me_3SiC_2C_2})\{\mathrm{Co_2(CO)_6}\}]$ 266 was isolated.[3] It was found that **234** converts to 266 in the presence of sunlight.



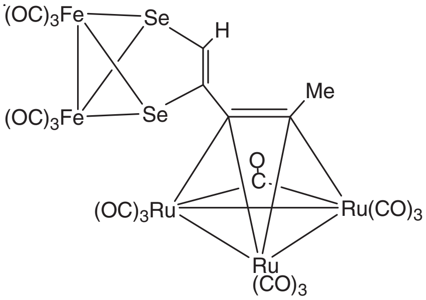
Scheme 28



266

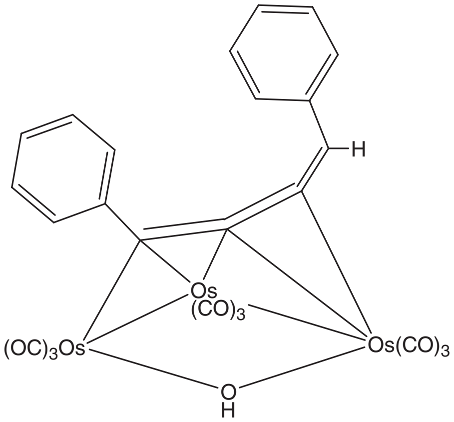
The clusters $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)]$ 228, $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2{:}\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}MeC_2C_2MeOC_5Me_2)\text{-}Os_3(\mu\text{-}CO)(CO)_9]$ 251, $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}[(MeC_2C_2Me)]CO[MeC_2(C_2Me)]\}]$ 252 and $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}[(MeC_2)\text{-}C_2MeCO[(MeC_2)C_2C_2Me]\}]$ 253, prepared from the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with $MeC{\equiv}CC{\equiv}CMe$, and $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ 229 all react with $[Co_2(CO)_8]$ at room temperature in dichloromethane solution to produce products in which one free alkyne functionality coordinates to a $Co_2(CO)_6$ unit in each case.[121] The reaction scheme and the products $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}MeC_2C_2Me)(Co_2(CO)_6)]$ **290**, $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2{:}\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\mu\text{-}\eta^2\text{-}MeC_2C_2MeOC_5Me_2)_3Os_3(\mu\text{-}CO)(CO)_8(Co_2(CO)_6)]$ **291**, $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}[(MeC_2)C_2Me)]CO[MeC_2(C_2Me)]\}(Co_2(CO)_6)]$ **292**, two isomers of $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}[(MeC_2)C_2MeCO[(MeC_2)\text{-}C_2C_2(Me)]]\}(Co(CO)_6)]$ **293, 294** and $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(Co_2(CO)_6)]$ **295** are shown in Scheme 29.

Alternatively, mixed metal species can be obtained by the reaction of a pre-formed dinuclear metal complex with an osmium or ruthenium cluster. $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2{:}\mu_3\text{-}\eta^2\text{-}RC_2C_2H\{Fe_2(CO)_6Se_2\}]$ ($R = Me$ **241**; ^nBu **242**) and $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2{:}\mu_3\text{-}\eta^2\text{-}{}^nBuC_2C_2H\{Fe_2(CO)_6Se_2\}]$ **243** can be prepared by the reaction of $[Fe_2(CO)_6\{\mu\text{-}SeCH{=}C(C{\equiv}CR)Se)\}]$ ($R = Me$, ^nBu) with $[M_3(CO)_{10}(NCMe)_2]$ ($M = Ru$, Os), respectively.[126]



241

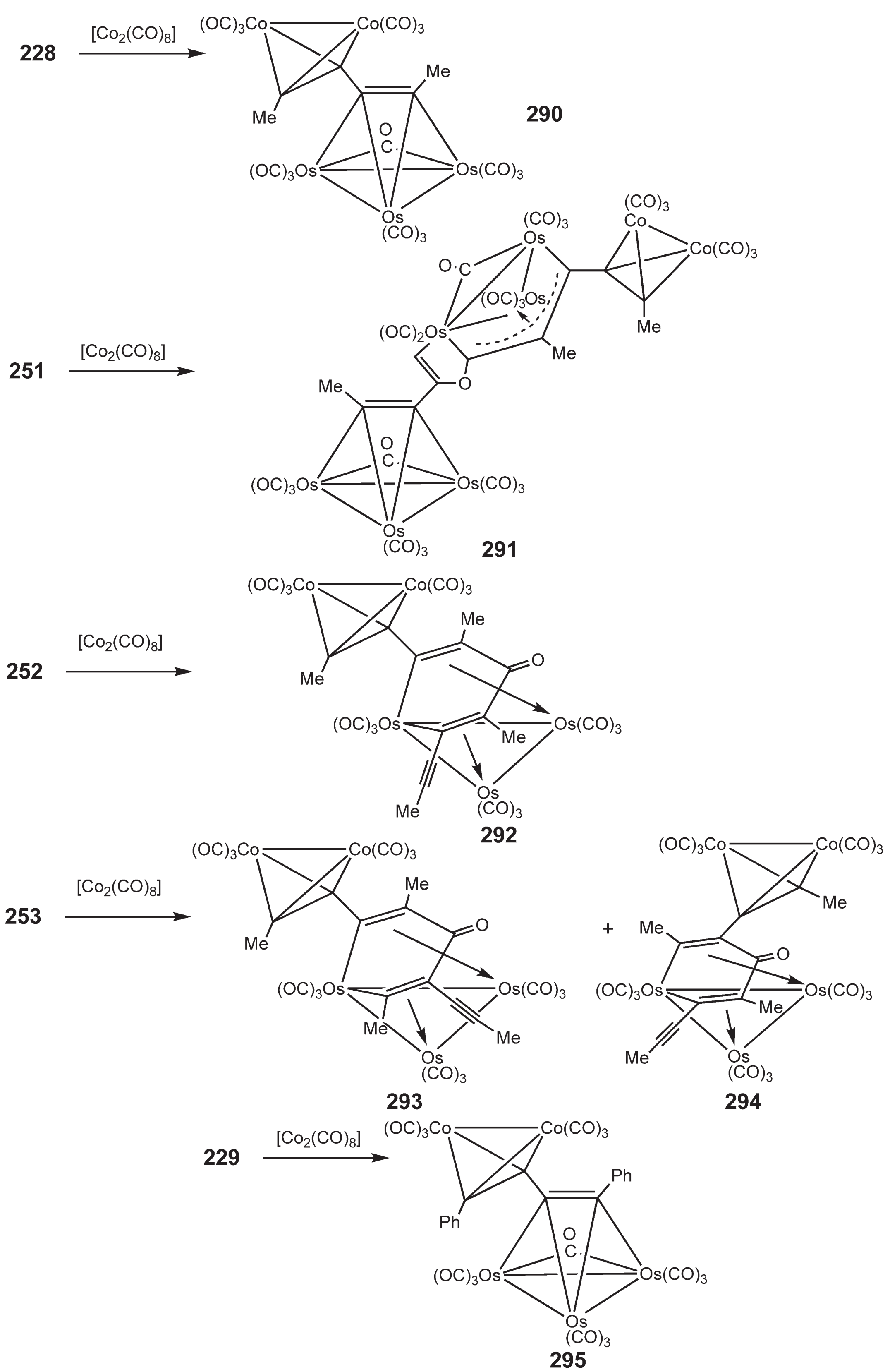
Attempts have been made to activate the metal cluster core of diyne-substituted clusters to facilitate further reactions. For example, $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)]$ **228** and $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ **229** both react with Me_3NO in acetonitrile which results in the replacement of one carbonyl ligand with a MeCN group to give $[Os_3(CO)_8(\mu\text{-}CO)(NCMe)(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)]$ **245** and $[Os_3(CO)_8(\mu\text{-}CO)(NCMe)(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)]$ **246**.[121] These two clusters then go on to react with water to form the "open" 50-electron clusters $[Os_3(CO)_9(\mu\text{-}OH)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}RC_3CHR)]$ ($R = Me$ (two isomers, **296**, **297**); $R = Ph$ **298**).[121] The reaction of $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}[(MeC_2C_2Me)]CO[MeC_2(C_2Me)]\}]$ **252** with Me_3NO in acetonitrile results in the substitution of a CO ligand with either Me_3N or NCMe at the metallocyclic Os atom to afford the clusters $[Os_3(CO)_8(L)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}\{(MeC_2)C_2Me\}_2CO)]$ ($L = NCMe$ **299**, NMe_3 **300**).[121]



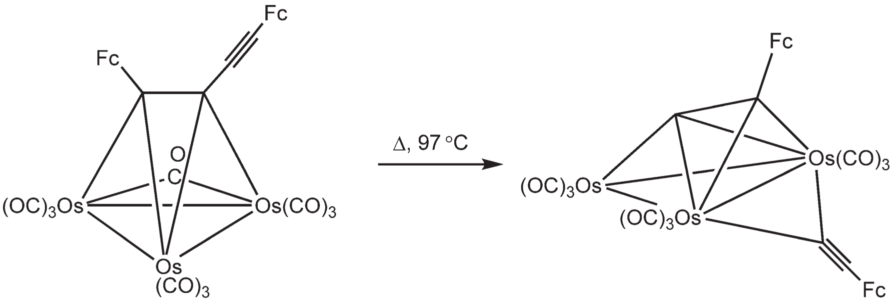
298

The 50-electron cluster $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}Ph(C)C_9H_6\}]$ **272** also reacts with Me_3NO in the presence of MeCN to give the acetonitrile substituted cluster $[Os_3(\mu\text{-}H)(CO)_9(NCMe)\{\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}Ph(C)C_9H_6\}]$ **301**.[131]

Rather than replacing a carbonyl group with an acetonitrile ligand, heating of the diyne-substituted cluster, or even its being left to stand in solution, can result in decarbonylation. For example, on standing for two days in the light the cluster $[Os_3(CO)_{11}\{\mu_3\text{-}\eta^4\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$ **302** decarbonylates to give


228
[Co$_2$(CO)$_8$]
290
251
[Co$_2$(CO)$_8$]
291
252
[Co$_2$(CO)$_8$]
292
253
[Co$_2$(CO)$_8$]
293
+
294
229
[Co$_2$(CO)$_8$]
295
(OC)$_3$Co
Co(CO)$_3$
(OC)$_3$Os
Os(CO)$_3$
Os
(CO)$_3$
(OC)$_2$Os
Me
Ph
O
C

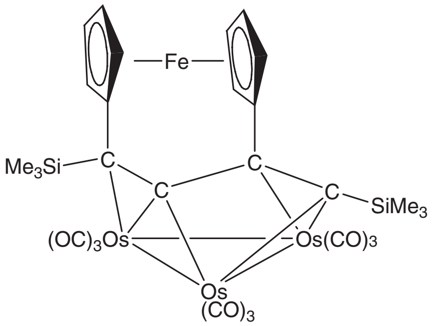
Scheme 29



237 **305**

Scheme 30

$[\mathrm{Os_3(CO)_{10}}\{\mu_3\text{-}\eta^2\text{-}(\mathrm{C_4H_3S})\mathrm{C_2C_2}(\mathrm{C_4H_3S})\}]$ **303** in which the metal framework is a closed triangle and one of the diyne C≡C triple bond coordinates in an μ_3-η^2-mode to the Os$_3$ triangle.[130] The reaction between $[\mathrm{Os_3(CO)_{10}(NCMe)_2}]$ and $[\mathrm{Fe}\{\mathrm{C_5H_4(C_2SiMe_3)}\}_2]$ yields $[\mathrm{Os_3(CO)_{10}}\{\mu_3\text{-}\eta^2\text{-}\mathrm{Fe[C_5H_4(C_2SiMe_3)]_2}\}]$ which decarbonylates $[\mathrm{Os_3(CO)_9}(\mu\text{-CO})\{\mu_3\text{-}\eta^2\text{-}(\mathrm{C_4H_3S})\mathrm{C_2C{\equiv}C}(\mathrm{C_4H_3S})\}]$ **304** in which the osmium triangle is capped by a dienediyl fragment derived from both the alkyne functionalities of the substituted ferrocene. The cyclic voltammogram of **304** showed a reversible one-electron oxidation of the ferrocene unit and an irreversible two-electron reduction of the triosmium cluster core.[66]



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When $[\mathrm{Os_3(CO)_9}(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}\mathrm{FcC_2C{\equiv}CFc})]$ **237** is thermolyzed in heptane (97 °C), it is transformed into $[\mathrm{Os_3(CO)_9}(\mu_3\text{-}\eta^2\text{-}\mathrm{C{\equiv}CFc})(\mu\text{-}\eta^2\text{-}\mathrm{C{\equiv}CFc})]$ **305** which contains two bridging ferrocenylacetylide ligands formed by cleaving the C–C bond between the two alkynyl groups (Scheme 30).[90]

References

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6.20
Trinuclear Ruthenium Clusters with Cyclopentadienyl Ligands

H Suzuki and T Takao, Tokyo Institute of Technology, Tokyo, Japan

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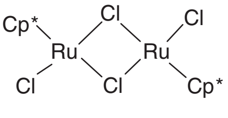
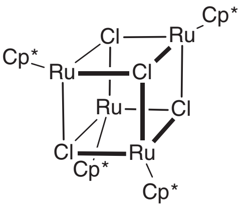
Although a large number of studies on the synthesis and reaction chemistry of trinuclear ruthenium carbonyl clusters, $\mathrm{Ru_3L_m(CO)_n}$, have been reported, only a small number of clusters have been reported having cyclopentadienyl group as an auxiliary ligand. The cyclopentadienyl group is perhaps one of the most common and important ligands in organotransition metal chemistry because it is firmly bound to the metal center and almost inert toward substitution. The cyclopentadienyl groups, especially $\mathrm{C_5Me_5}$ group, are strongly electron releasing and their π-accepting ability is much weaker than that of carbon monoxide. Introduction of the cyclopentadienyl groups into the cluster framework, therefore, increases the electron density at the metal center, and makes an important change in the reactivity of the cluster.

For the synthesis of the trinuclear ruthenium cluster bearing the cyclopentadienyl ligand, chlororuthenium and methoxoruthenium complexes, such as $[\mathrm{Cp^*RuCl_2}]_2$ (**1**, $\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$),[1–5] $[\mathrm{Cp^*RuCl}]_4$ **2**,[3,4,6–9] $\{\mathrm{Cp^*Ru(OMe)}\}_2$ **3**,[3,10,11] and $\mathrm{CpRu(PPh_3)_2Cl}$ **4a**,[12–16] are often used as the precursors.



1



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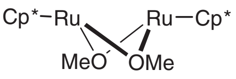

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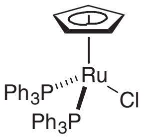


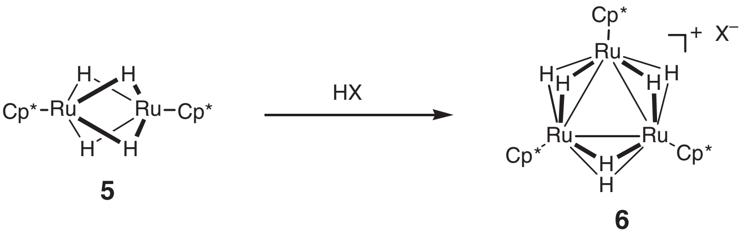
4a

This account makes a few references to the related clusters that have fused-ring cyclopentadienyl derivatives, such as indenyl, azulene, and acenaphthylene, in addition to the cyclopentadienyl clusters with common C_5R_5 groups. Some interesting trinuclear ruthenium complexes are also referred to even though they have no metal–metal bonds in the molecule.

6.20.1 Triruthenium Cyclopentadienyl Hydrido and Carbonyl Clusters

Polyhydrido clusters are a very interesting class of compounds from the viewpoint of reaction chemistry because they easily generate vacant coordination sites upon heating or treatment with a hydrogen acceptor such as an alkene. Electron density at the metal centers of the cyclopentadienyl polyhydrido cluster is higher than that of the carbonyl cluster and the reactivities of these clusters are different from each other.

Only a few examples of triruthenium polyhydrido clusters, which have no supporting ligands other than cyclopentadienyl groups, have been reported during the past two decades. Cationic triruthenium hexahydride complexes **6** ($X = BF_4$, CF_3SO_3, $1/2\ SO_4$, $C_6H_5CO_2$, and CH_3CO_2) were synthesized by the reaction of diruthenium tetrahydride **5**[17] with the corresponding acid, HX (Equation (1)).[18] Cationic hexahydride **6** was alternatively obtained by the hydrogenation (50 atm, 25 °C) of **1** in aqueous solution.[19]

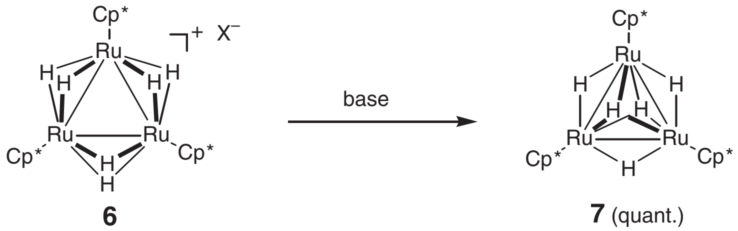


5

6

(1)

The treatment of **6** with CH_3ONa in methanol selectively affords a neutral pentahydrido cluster **7** (Equation (2)), which undergoes an intermolecular H/D exchange with C_6D_6 as the result of arene C–H bond activation via an η^2-arene intermediate.[18] The two kinds of hydrido ligands, μ-H and μ_3-H, mutually exchange coordination sites in solution. Pentahydrido cluster **7** displays remarkable activity in reactions with non-activated hydrocarbons such as alkanes.[20,21]

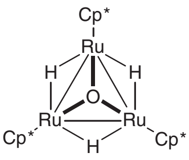


6

7 (quant.)

(2)

Electron density at the metal centers is tunable by introducing a heteroatom or an electropositive metal into the Ru_3 core of **7** as a bridging ligand. The μ_3-oxo and μ_3-sulfido ligands are introduced by the reaction of **7** with O_2 (1 equiv.) and thiophenol or diphenyl sulfide, respectively.[18] A μ_3-iodo complex **10** is also prepared by the treatment of **7** with CH_3I. The pentahydride **7** reacts with metal alkyls, such as Et_2Zn, $^iPr_2Mg$, MeLi, Et_3Al, and Me_3Ga, to yield complexes **11–15** that contain a triply-bridging metal ligand.[22] The treatment of **7** with carbon monoxide generates a paramagnetic trinuclear tetracarbonyl complex $(Cp^*Ru)_3(\mu\text{-CO})_3(\mu_3\text{-CO})$ **16**.[18]



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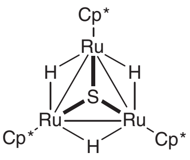

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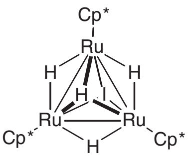

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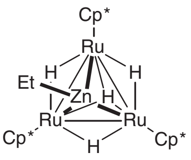

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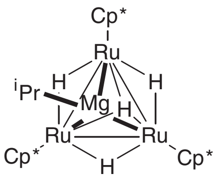
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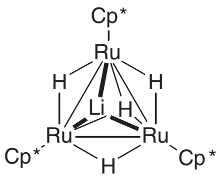
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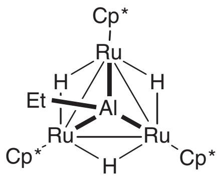
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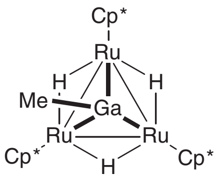
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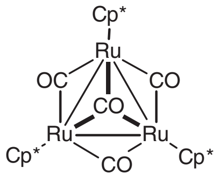
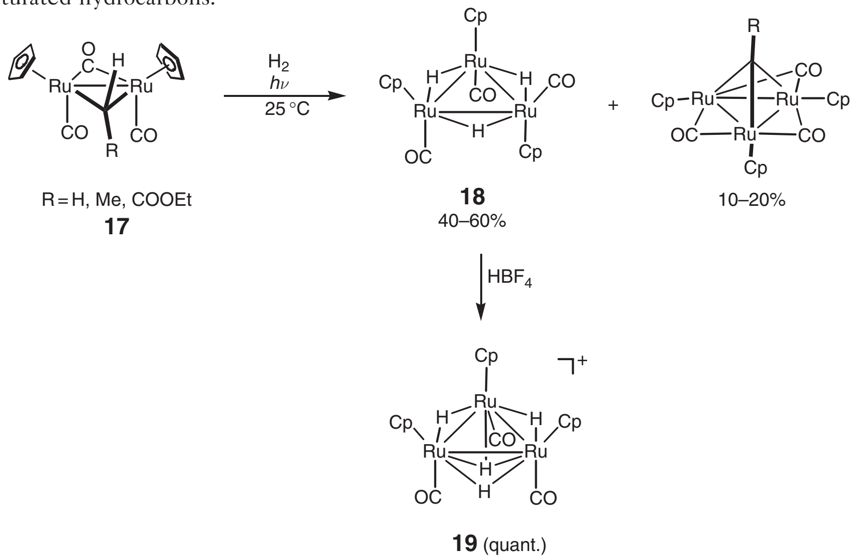

16

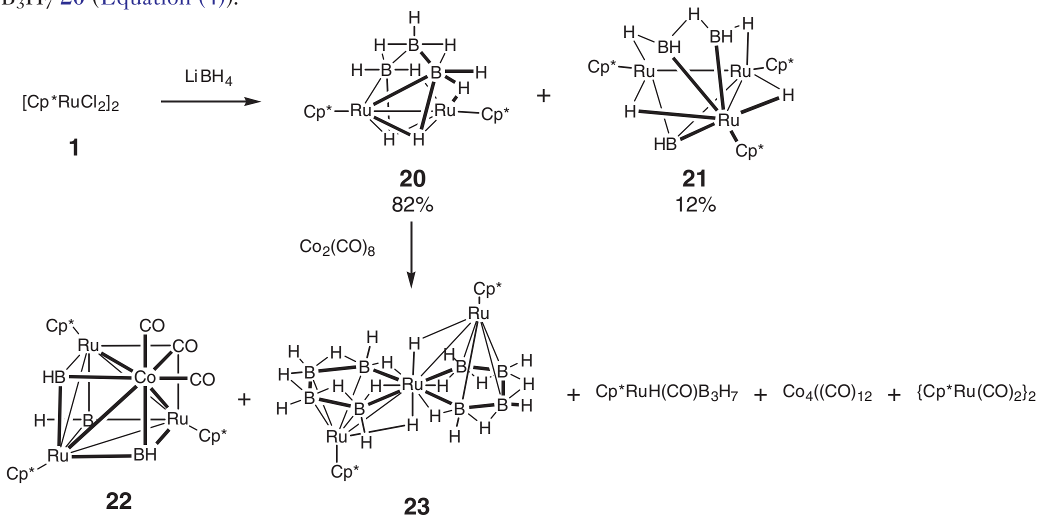
The synthesis of a trinuclear cyclopentadienyl trihydrido complex having carbonyl ligands had been reported prior to the synthesis of **6** and **7**. Treatment of (CpRu)$_2$(CO)$_2$(μ-CO)(μ-CHR) **17** with H$_2$ (1 atm) under UV irradiation provides fluxional complex **18**.[23] The fluxionality involves the passage of η-C$_5$H$_5$ and CO ligands from one side of the Ru$_3$ plane to the other. Protonation of **18** yields a non-fluxional cation **19** in which all three cyclopentadienyl ligands are on the same side of the Ru$_3$ plane (Equation (3)). Compound **18** has been shown to react readily with a wide variety of unsaturated hydrocarbons.[24,25]



(3)

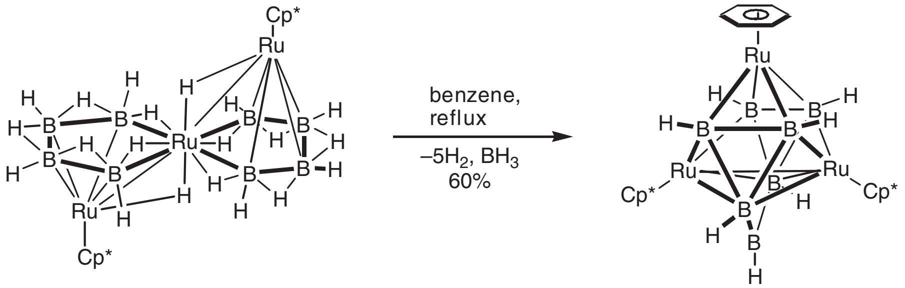
6.20.2 Triruthenium Cyclopentadienyl Clusters Containing Group 13 Elements

Several metallaboranes containing the Cp*Ru moiety have been synthesized. The reaction of dimeric dichloride **1** with LiBH$_4$ affords trinuclear ruthenaborane (Cp*Ru)$_3$(μ-H)$_2$B$_3$H$_6$ **21** as a byproduct of the synthesis of (Cp*Ru)$_2$(μ-H)$_2$B$_3$H$_7$ **20** (Equation (4)).[26,27]



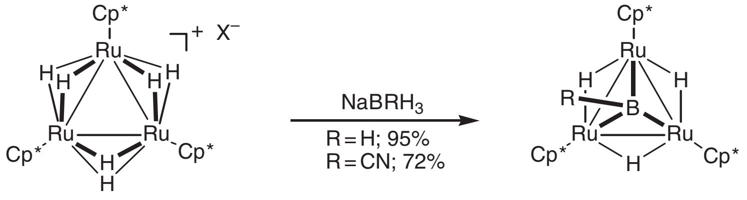
(4)

The structure of **21** consists of a 1,2,3-$(Cp^*Ru)_3B_2H_2$ square pyramid with the triruthenium face capped by the third BH fragment. Treatment of **20** with $Co_2(CO)_8$ leads to hydrogen loss and formation of the more highly condensed cluster, $(Cp^*Ru)_3Co(CO)_2(\mu_3\text{-}CO)B_3H_3$ **22**, and small amount of linear trinuclear ruthenaborane, *commo*-$\{1\text{-}(Cp^*Ru)(\mu\text{-}H)B_4H_9\}_2Ru$ **23**.[28,29] The linear cluster **23** is converted into $(Cp^*Ru)_2(\eta^6\text{-}C_6H_6)RuB_7H_7$ **24** upon heating at 95 °C in benzene (Equation (5)).[30] From the viewpoint of reaction chemistry of the triruthenium polyhydrido cluster **7**, the reactivity has been modified by introducing μ_3-BH group into the Ru_3 core. The reaction of cationic polyhydrido cluster **6** with $NaBH_4$ resulted in the exclusive formation of a single-faced μ_3-borylene cluster $(Cp^*Ru)_3(\mu_3\text{-}BH)$ $(\mu\text{-}H)_3$ **25a** (Equation (6)).[31] A cluster **25b** having a μ_3-BCN ligand has been prepared by using $NaBH_3(CN)$. The borylene cluster **25a** readily cleaves a C–S bond of benzothiophene to form a thiaruthenacycle similar to the reaction of the starting pentahydrido complex **7** with benzothiophene.



23 **24**

(5)

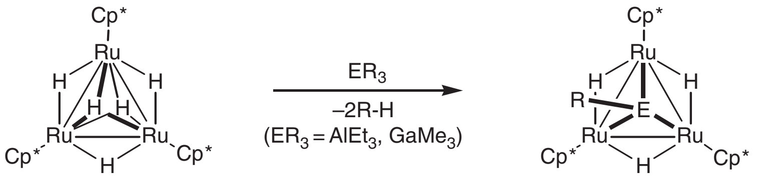


6

25a: R = H
25b: R = CN

(6)

As mentioned previously, trinuclear clusters containing μ_3-AlEt and μ_3-GaMe ligands have been prepared by the reaction of **7** with Et_3Al and Me_3Ga, respectively (Equation (7)).[22]



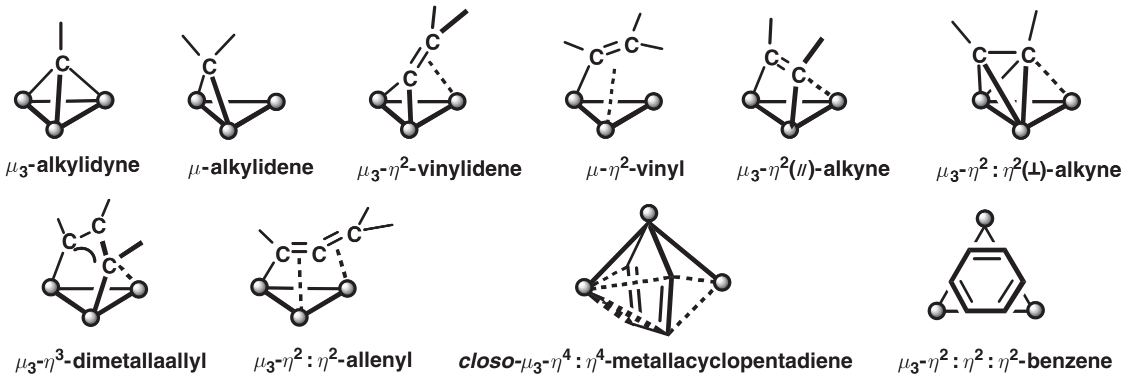
7

14: E = Al, R = Et (70%)
15: E = Ga, R = Me (99%)

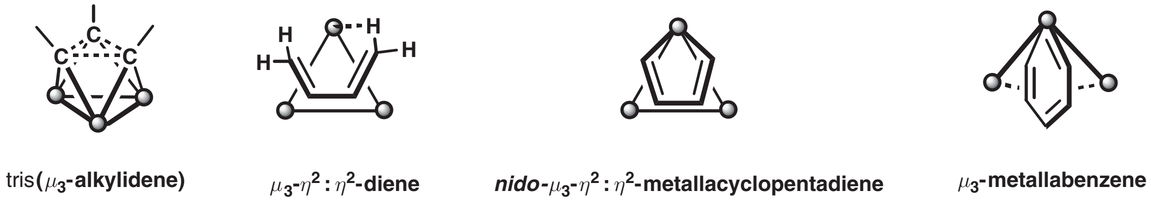
(7)

6.20.3 Triruthenium Cyclopentadienyl Clusters Containing Hydrocarbyl Groups

Many types of hydrocarbyl ligands are known for the triruthenium clusters containing a cyclopentadienyl ligand: μ_3-alkylidyne,[23,32–41] μ-alkylidene,[36] μ_3-η^2-vinylidene,[36,37,42] μ_3-η^2-vinyl,[23,36] μ_3-η^2(‖)-alkyne,[36,37,43–45] μ_3-$\eta^2:\eta^2$ (⊥)-alkyne,[45,46] μ_3-η^3-diruthenaallyl,[36,38,41,47] μ_3-$\eta^2:\eta^2$-allenyl,[48] *closo*-μ_3-$\eta^4:\eta^4$-ruthenacyclopentadiene,[38,41,49] and μ_3-$\eta^2:\eta^2:\eta^2$-benzene complexes,[50] which are also reported for carbonyl clusters. Some of these complexes, for example, a μ_3-η^2(‖)-alkyne–μ_3-alkylidyne complex,[36] contain a different type of hydrocarbyl ligand on each face of the Ru_3 plane.



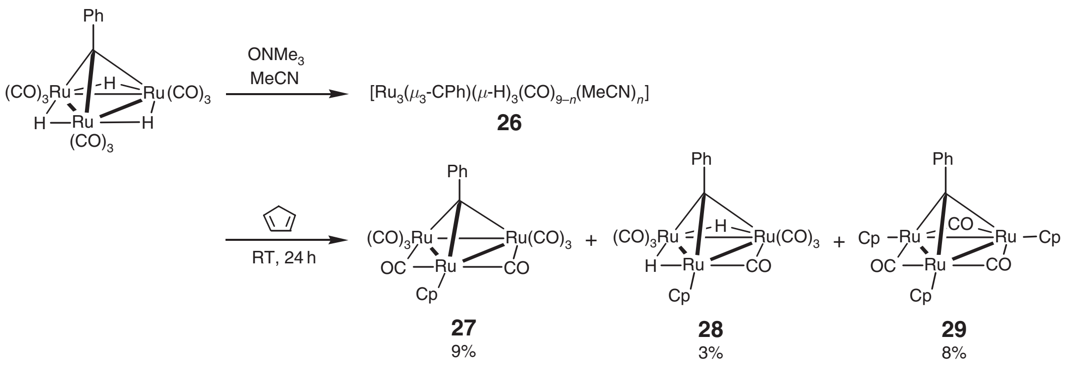
As for the complexes which have never been observed for the triruthenium carbonyl clusters, several types of the hydrocarbyl ligands have been originally reported for the triruthenium complexes bearing cyclopentadienyl ligands: tris(μ-alkylidene),[51,52] *s-cis*-μ_3-$\eta^2:\eta^2$-diene,[47] *nido*-μ_3-$\eta^2:\eta^2$-ruthenacyclopentadiene,[53] and μ_3-$\eta^5:\eta^6$-ruthenabenzene[54] complexes are known.



Synthetic methods for these complexes were roughly classified into three types as described below: (i) substitution of one of the supporting ligands L of a carbonyl cluster by cyclopentadiene, (ii) construction of the triruthenium skeleton by the reaction of mono- or bimetallic hydrocarbyl complexes bearing a cyclopentadienyl ligand with a coordinatively unsaturated monometallic species generated *in situ*, and (iii) reaction of the trimetallic complex bearing a cyclopentadienyl ligand with hydrocarbons. These synthetic methods will be described in the order as well as the skeletal rearrangement of these complexes (see below).

6.20.3.1 Reaction of a Triruthenium Carbonyl Cluster with Cyclopentadiene

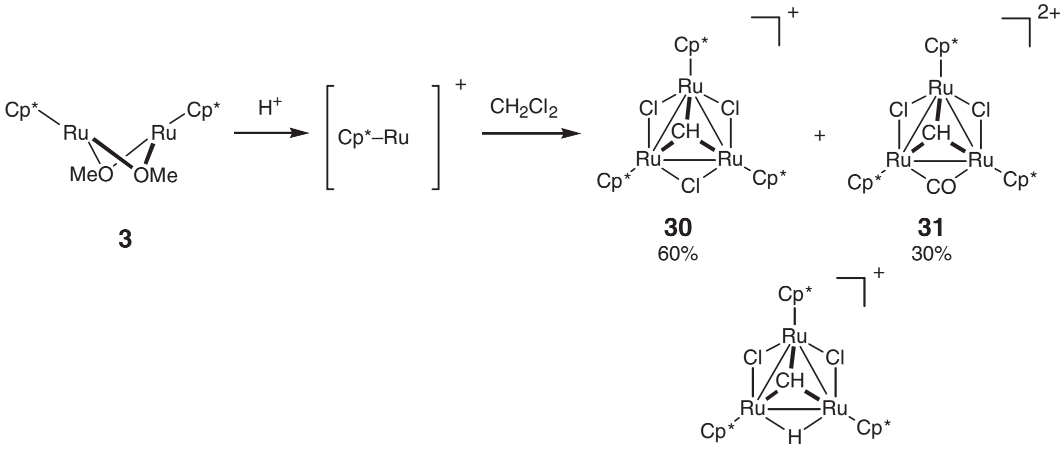
A mixture of acetonitrile complexes **26**, which were prepared by the treatment of the carbonyl cluster having a μ_3-alkylidyne ligand with an excess of acetonitrile in the presence of amine oxide, was shown to react with cyclopentadiene (Equation (8)).[33] A mixture of μ_3-alkylidyne complexes **27–29** containing one or three cyclopentadienyl ligands was obtained in low yields. In this reaction, one of the carbonyl groups was substituted by a cyclopentadiene. The cyclopentadienyl ligand would be formed by the C–H bond cleavage followed by the elimination of dihydrogen. A similar substitution reaction was also reported for the carbonyl cluster containing a μ_3-acetylide ligand, which was obtained by the reaction of $Ru_3(CO)_{12}$ with terminal alkyne.[32]



(8)

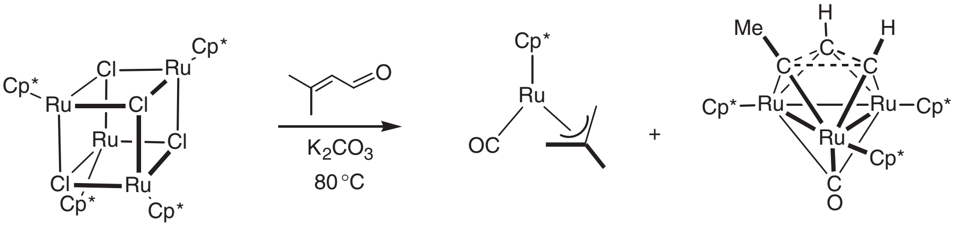
6.20.3.2 Formation of an Ru_3 Framework by the Reaction of a Coordinatively Unsaturated Monometallic Species

The bimetallic μ-methoxo complex, $\{Cp^*Ru(\mu\text{-}OMe)\}_2$ **3**, is a suitable precursor for the generation of the cationic monometallic species, $[Cp^*Ru]^+$. The reaction of **3** with dichloromethane in the presence of acid afforded a mixture of μ_3-methylydiyne complexes **30** and **31** as a result of carbon–chlorine bond cleavage (Equation (9)).[34,34a] In this reaction, the C–Cl bond is cleaved by the monometallic species $[Cp^*Ru]^+$ generated by the protonation of **3**. Then, the mononuclear species aggregates to form the triruthenium skeleton. Complex **30** was synthesized alternatively by the reaction of $(Cp^*RuCl_2)_2$ **1** with acetaldehyde in the presence of $AgBF_4$.[35] When ethanol was used instead of acetaldehyde, a hydrido complex **32** was obtained in 40% yield.

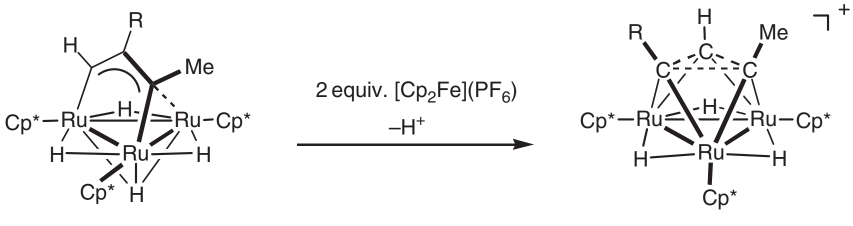


3 **30** 60% **31** 30% **32** (9)

The reaction of the cubane complex, $[Cp^*RuCl]_4$ **2**, with *trans*-3-methyl-2-butanal yielded a considerable amount of the trimetallic complex **34** together with a monometallic η^3-allyl complex **33** (Equation (10)).[51] Complex **34** contains a μ_3-η^3-C_3 ring on the Ru_3 plane, which was confirmed by X-ray studies. A similar complex **36**, which also possessed a μ_3-η^3-C_3 ring, was synthesized by the oxidation of μ_3-diruthena-allyl complex **35** (Equation (11)).[52]



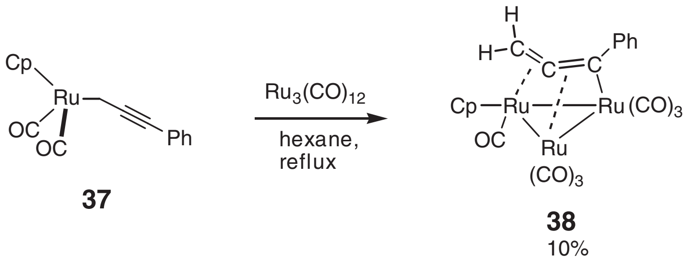
2 **33** 30% **34** 42% (10)



R = H, Me **35** **36** (quant.) (11)

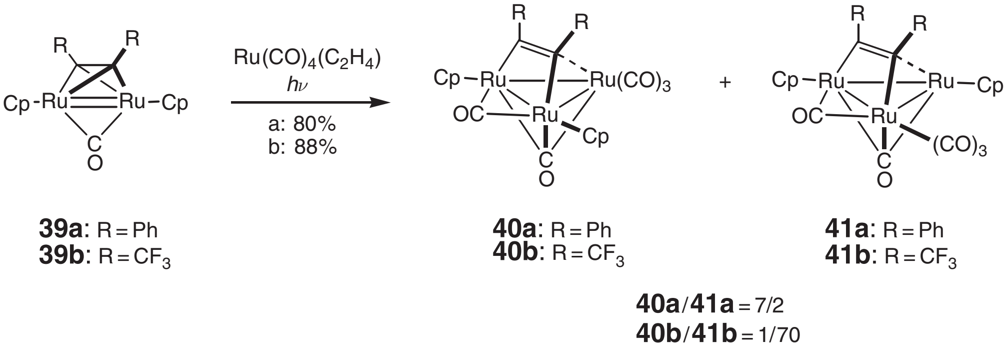
The C–C bond distances in the μ_3-η^3-C_3 ring were revealed to be 1.56–1.60 Å by the X-ray diffraction studies, which are considerably longer than that of a C–C single bond (1.54 Å). The large J_{C-H} value of 180 Hz was also reported for the ring carbon. These facts indicated that the ring carbon possessed carbenic character, and DFT calculations proved that the μ_3-η^3-C_3 ring adopts a resonance form between the μ_3-η^3-cyclopropenyl and the tris(μ-alkylidene) structure.[52]

A triruthenium μ_3-allenyl complex **38** was synthesized by the reaction of a monometallic propagyl complex **37** with $Ru_3(CO)_{12}$ in 10% yield (Equation (12)).[48] In contrast, the reaction of **37** with $Fe_3(CO)_{12}$ afforded a mixture of several complexes including the μ_3-allenyl complex.



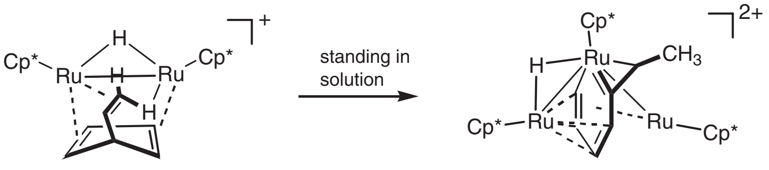
(12)

Knox and co-workers synthesized a triruthenium cluster by the reaction of the coordinatively unsaturated diruthenium alkyne complex $(CpRu)_2(\mu$-CO)(μ-RCCR) **39** with a monometallic carbonyl complex $M(CO)_4(L)$ (M = Fe, Ru).[43] Two isomers, **40** and **41**, were formed in the reaction of **39** with $Ru(CO)_4(CH_2=CH_2)$ (Equation (13)). The ratio between **40** and **41** was shown to be dependent on the nature of the substituents of the alkyne. In the case of diphenylacetylene complex, coalescence of the ^{1}H signals of these isomers, **40a** and **41a**, was observed. This shows that isomerization between the two isomers took place at considerable rate. In contrast, the reaction of **39** with $Fe(CO)_4$(thf) exclusively afforded a μ_3-η^2(‖)-alkyne complex, in which the alkyne moiety was π-coordinated to an iron center. Knox and co-workers also reported the syntheses of triruthenium μ_3-alkylidyne complexes by the photolysis of a bimetallic μ-alkylidene complex[23] and a bimetallic diruthenacyclopentenone complex.[44] In these reactions, formation of the triruthenium frameworks was rationalized by the coupling reaction of the monometallic coordinatively unsaturated species generated by the photolysis with the starting bimetallic complexes.



(13)

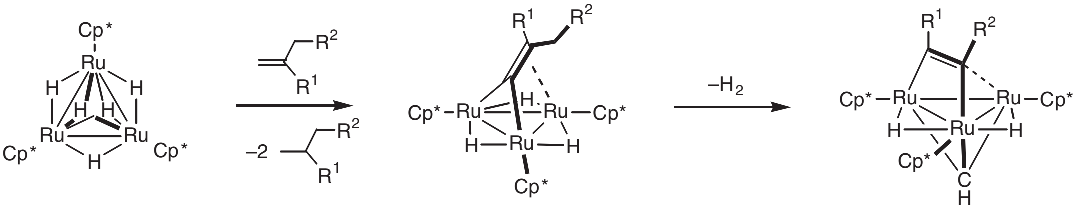
Although mechanistic details are still unclear, an open-form triruthenium complex **43**, which adopted a ruthenabenzene structure, was derived from the bimetallic 1,4-cyclohexadiene complex **42** (Equation (14)).[54] On the basis of the fact that complex **43** was dicationic, the trimetallic skeleton is most likely formed by the reaction of **42** with a cationic monometallic species, $[Cp^*Ru]^+$, generated by the partial decomposition of **42**. The X-ray diffraction study of **43** showed that the central ruthenabenzene moiety was coordinated to one of the peripheral ruthenium atoms in an η^6-fashion and to the other in an η^5-fashion. This nonsymmetrical structure arises from the hydrido ligand bridging on one of the Ru–Ru bonds.



42 **43** (14)

6.20.3.3 Reaction of a Trimetallic Complex Bearing a Cyclopentadienyl Ligand with Hydrocarbons

The triruthenium pentahydrido complex $\{Cp^{*}Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ 7[18] shows remarkable reactivity toward hydrocarbons, such as diene, alkyne, alkene, and even alkane, and various hydrocarbyl complexes have been synthesized in good yields.[20] From the reaction of 7 with 1,1-disubstituted alkene, a μ_3-methylidyne–μ_3-η^2(||)-alkyne complex 45 was obtained as a result of the C═C bond cleavage of a μ_3-η^2-vinylidene intermediate 44 (Equation (15)).[37] The μ_3-methylidyne–μ_3-η^2(||)-alkyne complexes were alternatively synthesized by the thermolysis of μ_3-diruthena-allyl complexes 35a and 35b, which were obtained by the reaction of 7 with butadiene and isoprene, respectively (Equation (16)).

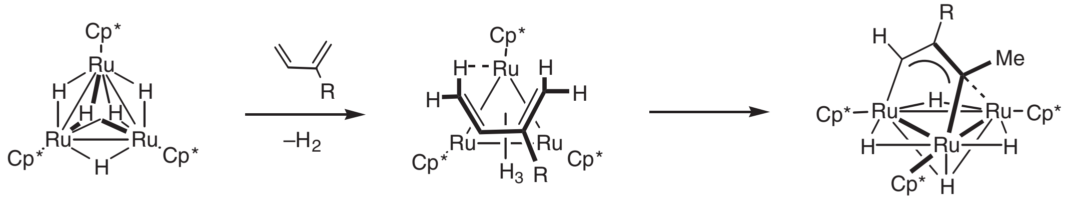


7

44a: $R^1 = CO_2Me$, $R^2 = H$
44b: $R^1 = Ph$, $R^2 = H$
44c: $R^1 = R^2 = \text{-}(CH_2)_3\text{–}$
44d: $R^1 = R^2 = \text{-}(CH_2)_4\text{–}$
44e: $R^1 = R^2 = \text{-}CO_2CH_2\text{–}$

45a (87%)
45b (97%)
45c (62%)
45d (78%)

(15)



7

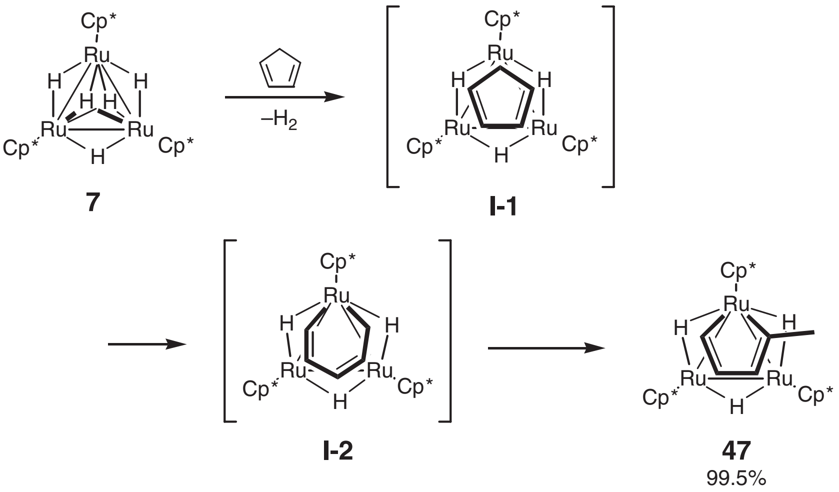
46a: R = H
46b: R = Me

35a: R = H (70%)
35b: R = Me (73%)

(16)

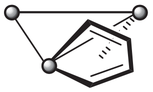
The reaction of 7 with diene has been shown to proceed via the formation of a μ_3-$\eta^2:\eta^2$-diene intermediate 46, in which the C═C double bonds were coordinated to two of the three ruthenium centers as shown in Equation (16).[37] The NMR studies of the μ_3-$\eta^2:\eta^2$-diene intermediate 46 showed that an agostic Ru–H–C interaction is present between one of the terminal C–H moieties of the diene and the ruthenium center. The diruthena-allyl skeleton in 35 would be formed via cleavage of the bond. The reactivity of 7 toward diene heavily depends on the shape and size of the diene due to the shape selectivity arising from the Ru_3 field surrounded by the three Cp^{*} groups.

In the reaction of 7 with cyclopentadiene, cleavage of the $C(sp^3)$–$C(sp^2)$ bond of cyclopentadiene under mild conditions was observed, and *nido*-μ_3-$\eta^2:\eta^2$-ruthenacyclopentadiene complex 47 was quantitatively formed (Scheme 1). The reaction proceeds via an intermediate diene complex I-1 and a ruthenacyclohexadiene I-2. These processes were supported by DFT calculations.[55]

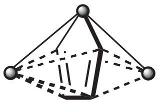


Scheme 1

There have been several examples of the trimetallic clusters containing a metallacyclopentadiene moiety, and they mainly belong to two distinct types, **A** and **B**.[56,56a] A metallacyclopentadiene moiety is formed on one edge of the metal triangle and is coordinated to one of the metal centers in a μ-$\eta^1:\eta^1:\eta^4$ fashion in type **A**. Type **B** has a *closo*-type structure (pentagonal-bipyramidal structure), in which a metallacyclopentadiene moiety bisects one of the metal–metal vectors and the metallacycle moiety is coordinated to the two peripheral metal nuclei in an η^4-fashion. The face-capping metallacyclopentadiene ligand as found in **47** is still rare, and a few examples are known for trimetallic complexes.[57,57a,57b]

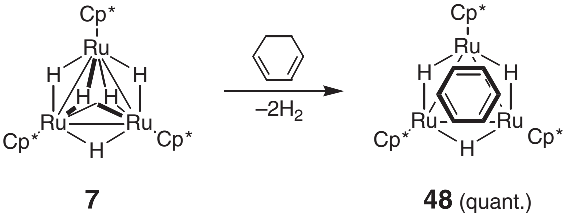


type A: μ-η^4-



type B: μ_3-$\eta^4:\eta^4$-

By the reaction of **7** with 1,3-cyclohexadiene, the face-capping benzene complex **48** was quantitatively obtained as a result of C–H bond cleavage (Equation (17)).[50] The face-capping benzene complexes are well known for Ru and Os clusters,[58,58a–58e] and they are regarded as good models for benzene absorbed on a metal surface.



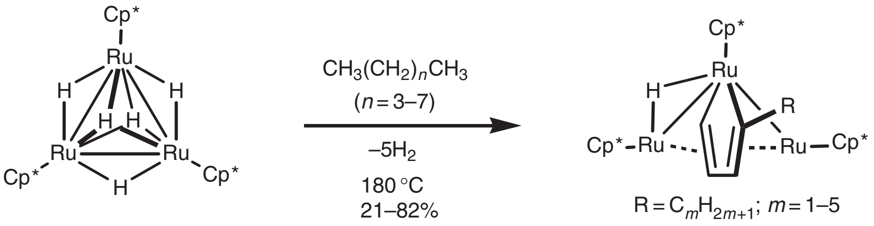
(17)

Complex **7** also reacted with acetylene at ambient temperature to afford μ-ethylidene–μ_3-η^2(||)-ethyne complex **50** via the formation of μ-divinyl complex **49** (Scheme 2).[36] Further skeletal rearrangement of the C_2 moiety took place upon thermolysis, which led to the formation of the μ_3-ethylidyne–μ_3-η^2(||)-ethyne complex **51** and μ_3-η^2-vinylidene–μ_3-η^2(||)-ethyne complex **52**. The tricarbonyl complex, $\{CpRu(CO)(\mu\text{-}H)\}_3$ **18**, reacts with acetylene, and insertion of acetylene into an Ru–H bond resulting in formation of a μ-vinyl complex was observed.[23]

The reaction of **7** with terminal alkynes quantitatively afforded coordinatively unsaturated (⊥)-alkyne complexes **53** (Scheme 3).[46] This contrasts with the reactions of $Ru_3(CO)_{12}$ with terminal alkynes resulting in the formation of a μ_3-acetylide complex as a result of C–H bond cleavage.[59,59a,59b] The (⊥)-nitrile complexes **54**, whose structure is very similar to that of **53**, were prepared by the reaction of **7** with benzonitrile and pivalonitrile.[60]

The (⊥)-alkyne complexes were also synthesized by the reaction of **7** with internal alkynes[46] and cyclic olefins.[45] Such perpendicular coordination of the alkyne ligand to one of the M–M bonds of the trimetallic cluster is characteristic of the complex adopting a 46-electron configuration, while the alkyne ligand is coordinated parallel to the M–M bond for the 48-electron complexes.[61,61a,61b] The (⊥)-cyclohexyne complex **53e** rearranged to a coordinatively saturated μ_3-η^2(||)-cyclohexyne complex upon treatment with 1 atm of CO.[45]

A *closo*-ruthenacyclopentadiene complex **55** was obtained by the reaction of **7** with linear alkanes (Equation (18)).[49] During this reaction, six C–H bonds of alkane were successively cleaved. Such multiple C–H bond cleavage was rationalized by the cooperative action of the neighboring ruthenium centers of the trimetallic framework, which promotes the incorporation of alkane into the reaction field of the cluster. Such *closo*-type metallacyclopentadiene complexes have been intensively studied using carbonyl clusters, and often prepared by the coupling reaction between the two alkyne ligands of the bis(μ_3-η^2(||)-alkyne) complex, so-called "violet isomer."[62,62a,62b] The μ_3-sulfido complex **9** obtained by the reaction of **7** with thiophenol also reacts with alkane to yield a μ_3-alkylidyne complex.[39]

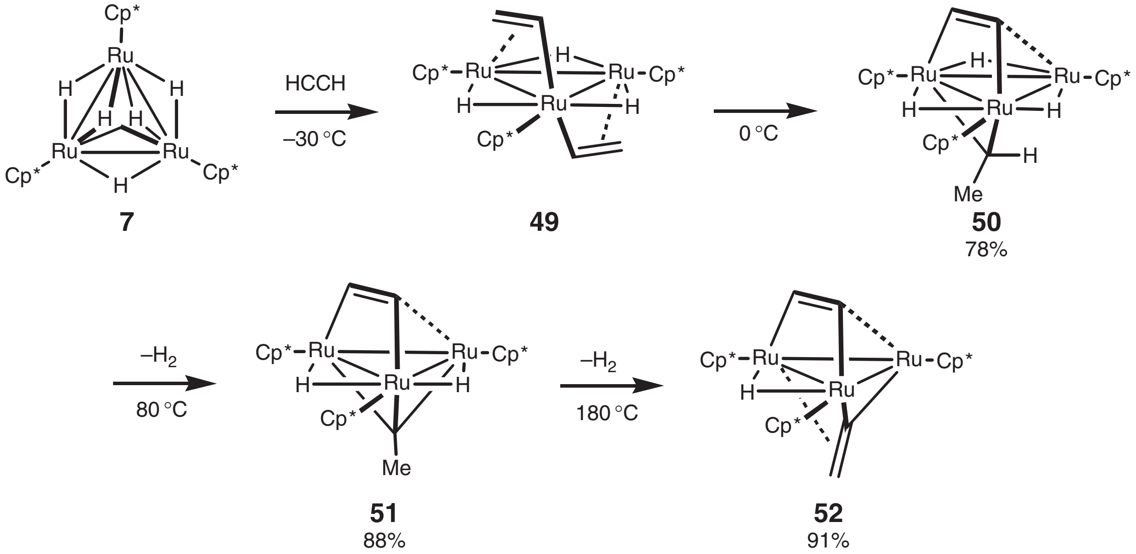


7 **55** (18)

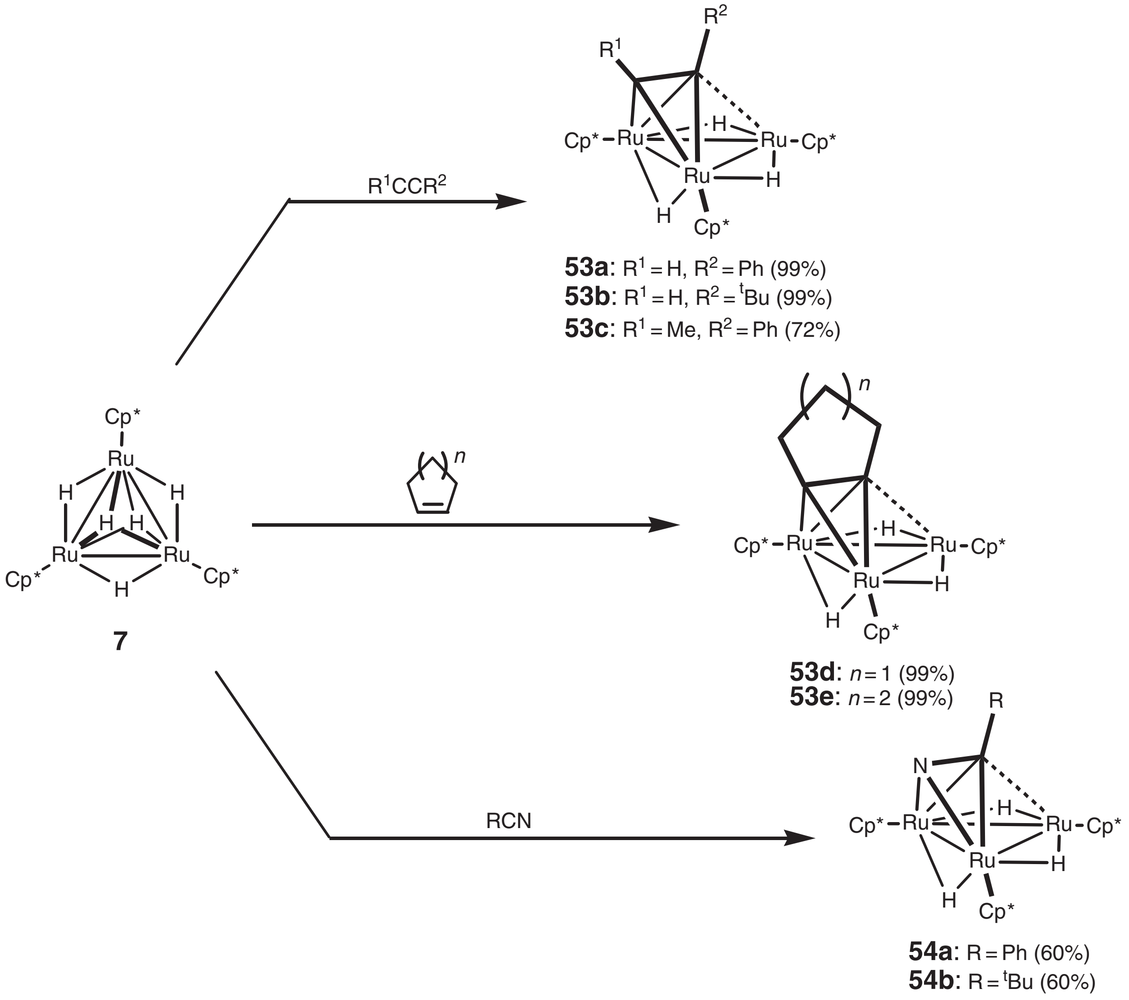
6.20.3.4 Skeletal Rearrangement of the Hydrocarbyl Ligands on the Triruthenium Clusters

Some of hydrocarbyl complexes mentioned above undergo skeletal rearrangement of the ligand upon thermolysis or oxidation.[36] As shown in Scheme 2, such sequential skeletal rearrangement on the triruthenium cluster provides mechanistic insight into the reaction performed on a metal surface. In this regard, many studies have been performed using carbonyl clusters.

Thermolysis of the *nido*-ruthenacyclopentadiene complex **47** at 130 °C afforded a *closo*-type complex **57** (Scheme 4).[38] Complex **57** has a structure similar to **55**, but the position of the methyl group is different from that of **55**. When the



Scheme 2

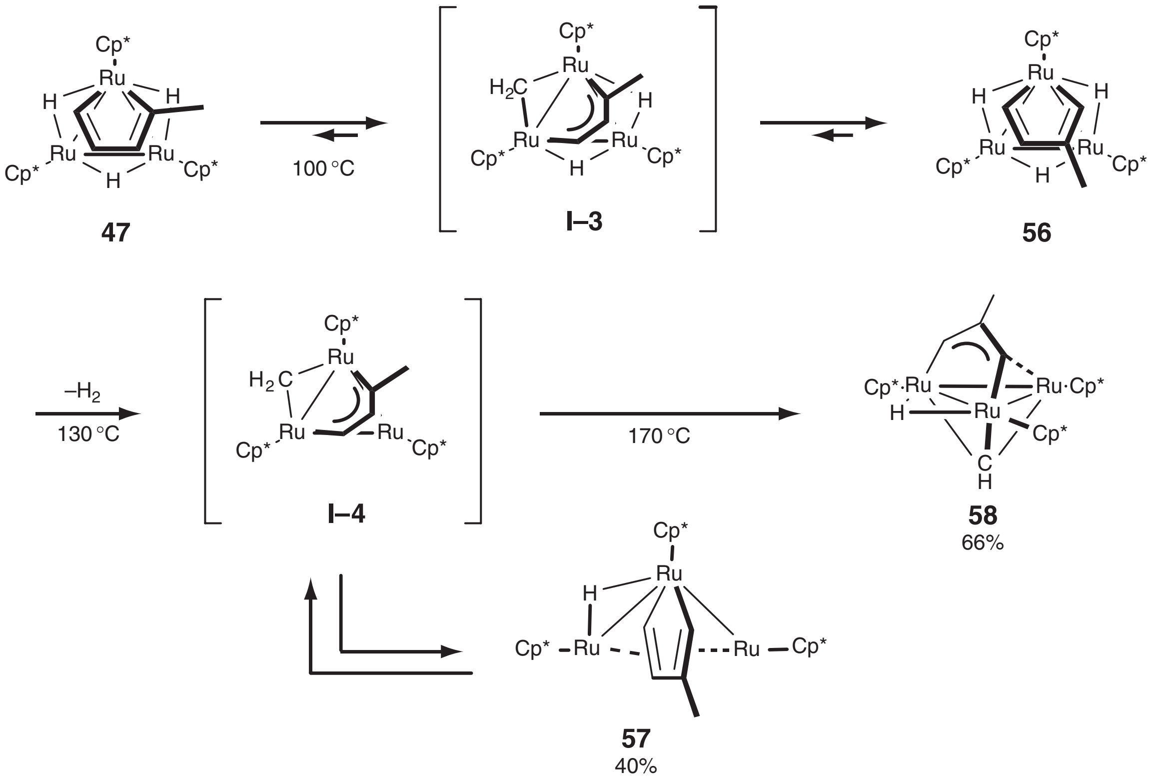


Scheme 3

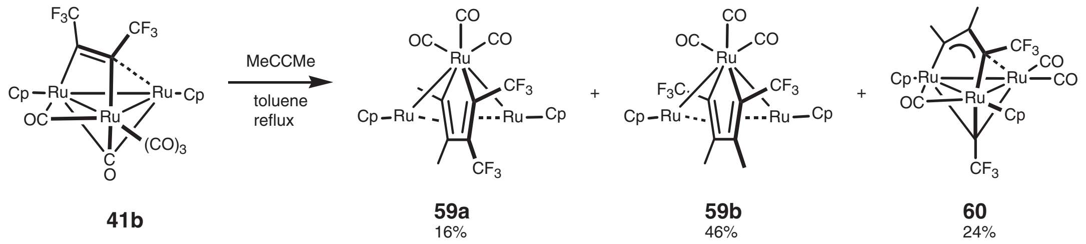
thermolysis was carried out at slightly lower temperature (100 °C), isomerization of *nido*-**47** to *nido*-**56** took place prior to the formation of the *closo*-**57**. During this isomerization, the methyl group at the 2-position of the ruthenacyclopentadiene moiety in **47** seemingly migrated to the 3-position. The DFT calculation suggested that this isomerization proceeded via the formation of a μ_3-allyl–μ-carbene intermediate **I-3**.[63]

The *closo*-**57** complex is formed via the same intermediate **I-3**. Elimination of dihydrogen from **I-3** would generate intermediate **I-4**, which would undergo flipping of the μ-carbene ligand to the opposite face of the triruthenium plane. Subsequent reductive C–C bond formation across the Ru_3 plane resulted in the formation of the *closo*-**57**. The μ_3-methylidyne–μ_3-η^3-diruthena-allyl complex **58** was formed upon thermolysis of **47** at 170 °C probably via intermediate **I-4**.

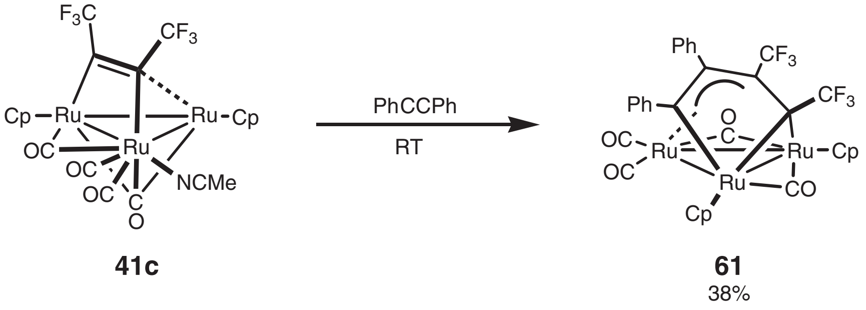
A similar skeletal rearrangement was observed during the reaction of the μ_3-$\eta^2(\|)$-alkyne complex **41** with internal alkynes.[41] A mixture of the *closo*-ruthenacyclopentadiene complexes, **59a** and **59b**, and the μ_3-alkylidyne–μ_3-η^3-diruthena-allyl complex **60** was obtained by the reaction of **41b** with 2-butyne (Equation (19)). Among these products, complex **59b**, which was seemingly formed as a result of C–C bond cleavage of the hexafluoro-2-butyne moiety in **41b**, was a major product. Complex **41c** reacted with diphenylacetylene at ambient temperature to generate complex **61** via the coupling reaction of two alkyne molecules on the triruthenium plane (Equation (20)). In complex **61**, considerable elongation of the $C(CF_3)$–$C(CF_3)$ bond was observed. The electron-withdrawing nature of the CF_3 groups promotes the back-donation from the metal centers.



Scheme 4

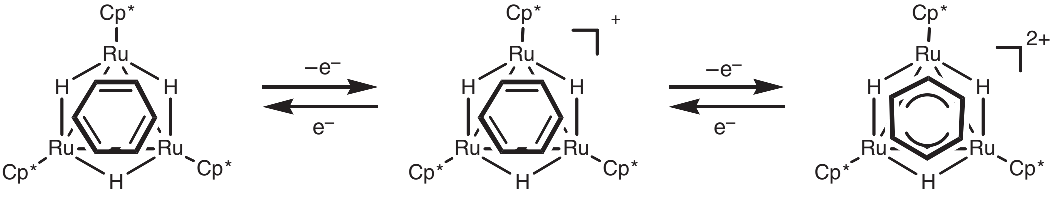


(19)



(20)

Some interesting rearrangements of the hydrocarbyl ligands have been reported in the oxidation of μ_3-$\eta^2:\eta^2:\eta^2$-benzene complex 48. Treatment of 48 with 2 equiv. of ferrocenium salt resulted in rotation of the face-capping benzene ligand, and the dicationic complex 63, in which the C_6 cycle was shown to be coordinated in a bis(η^3-allyl) fashion, was obtained (Equation (21)).[50]



48 **62** (quant.) **63** (quant.) (21)

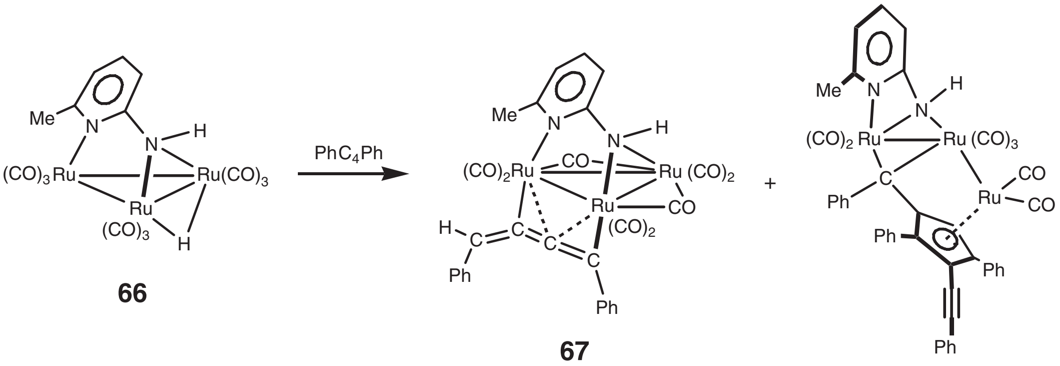
As shown in Equation (11), the tris(μ-alkylidene) complex **36** is formed by the two-electron oxidation of the μ_3-diruthena-allyl complex **35**.[52] Although two-electron oxidation is required to complete the reaction, the product **36** is monocationic. It was proposed that liberation of H^+ from a dicationic intermediate took place during the reaction. Two-electron oxidation accompanied by H^+ liberation was also reported for the oxidation of the μ_3-ethylidyne complex to yield a μ_3-η^2-vinylidene complex.[64]

There are a few examples of the intermolecular coupling between the coordinated alkyne ligand and added alkyne molecules.[36,41] Formation of alkane by the hydrogenation of the μ_3-alkylidyne ligand is an important step in regard to the catalytic hydrogenation of alkyne and alkene. Thus, these reactions have been intensively studied mainly on the carbonyl clusters.[65–66a] Although the fate of the eliminated hydrocarbons is unknown, hydrogenation of the μ_3-ethylidyne–μ_3-η^2(‖)-ethyne complex **51** was shown to regenerate the starting pentahydrido complex **7**.[36] Hydrogenation of the (⊥)-alkyne complex **53a** under atmospheric pressure afforded **7** together with styrene and ethylbenzene.[46] This reaction presumably proceeded via the formation of a (‖)-alkyne intermediate having a 48-electron configuration. Although the nuclearity of the active species is unclear at present, hydrogenation of alkynes using **41** as a precursor of the catalyst has been reported.[67,68]

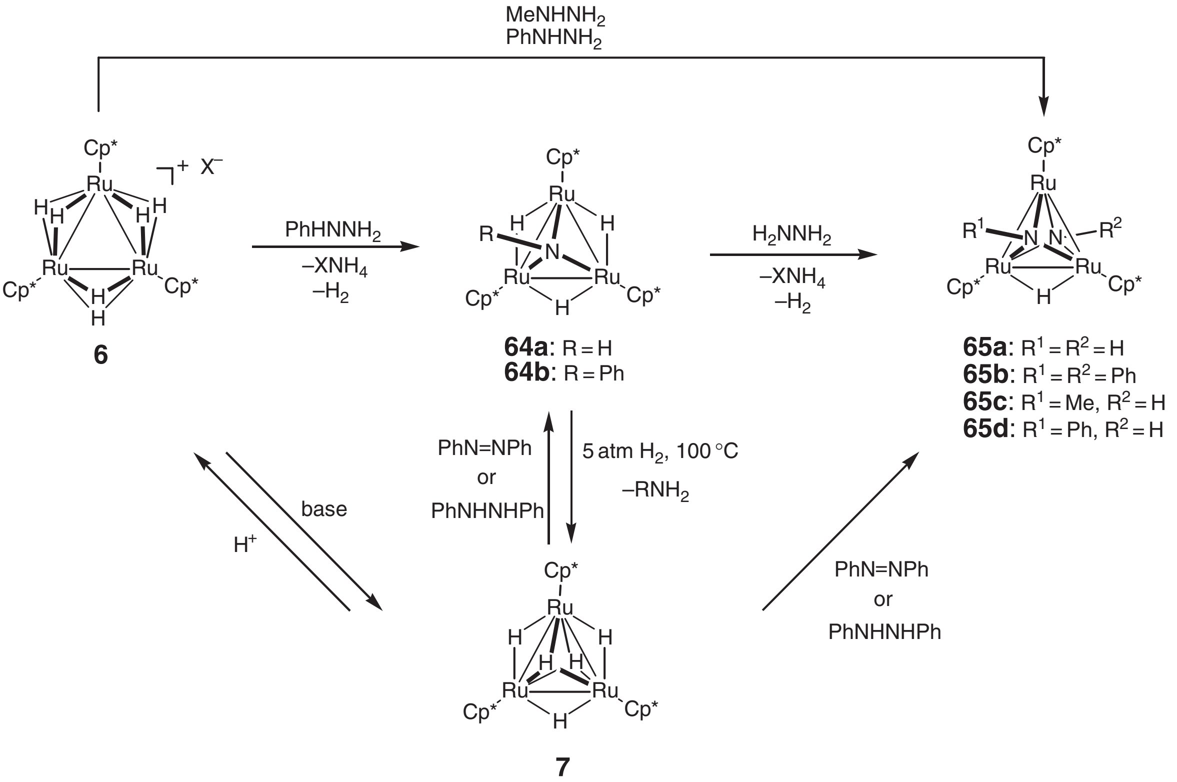
6.20.4 Triruthenium Cyclopentadienyl Clusters Containing Group 15 Elements

A series of mono(μ_3-imido) and bis(μ_3-imido) complexes were derived from triruthenium polyhydrido complexes, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ **7** and $[\{Cp^*Ru(\mu\text{-}H)_2\}_3]X$ **6** (X = 1/2 SO_4, BF_4, PF_6, and BPh_4), by reactions with hydrazine and azobenzene (Scheme 5). The reaction of **6** with hydrazine leads to the formation of mono(μ_3-imido) complex **64a** as a result of an N–N bond cleavage of the hydrazine.[69] Complex **64a** further reacted with hydrazine (in the presence of a proton from **6**) to yield bis(μ_3-imido) complex **65a**. Mono(μ_3-phenylimido) complex **64b** and bis(μ_3-phenylimido) complex **65b** are formed via independent routes in the reactions of **7** with 1,2-diphenylhydrazine or azobenzene.[70] The reaction of **7** with a monosubstituted hydrazine such as methylhydrazine and phenylhydrazine results in the exclusive formation of the nonsymmetrically capped bis(μ_3-imido) complex $(Cp^*Ru)_3(\mu_3\text{-}NR)(\mu_3\text{-}NH)$ (**65c**, R = Me; **65d**, R = Ph).[71] Mono(μ_3-NR) complexes **64** undergo hydrogenolysis to generate **7** and the corresponding amines NRH_2, while bis(μ_3-phenylimido) complex **65b** offers resistance to the reaction with hydrogen.[69,70]

Trinuclear complex, $Ru_3(\mu\text{-}\eta^2\text{-ampy})\{\mu_3\text{-}\eta^6\text{-}PhCC_5(C{\equiv}CPh)HPh_2\}(CO)_7$ (**68**, Hampy = 2-amino-6-methylpyridine), containing an η^5-cyclpentadienyl ring and a bridging carbene fragment, has been obtained from the reaction of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy})(CO)_9$ **66** with diphenylbutadiyne (Equation (22)).[72] This compound arises from a remarkable [3 + 2]-cycloaddition of a first-formed 1,4-diphenylbutyn-4-yl ligand with a triple bond of a second diphenylbutadiyne molecule.

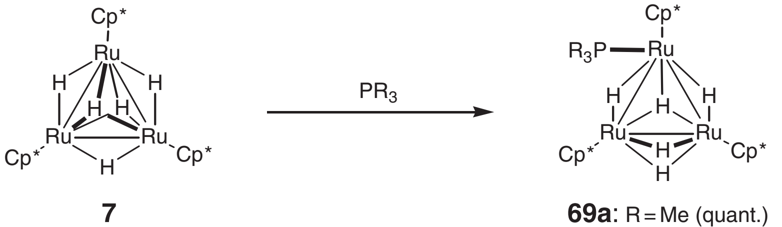


66 **67** 24% **68** 9% (22)



Scheme 5

Compound **7** reacts with trimethylphosphine via an associative path to give a pentahydrido(trimethylphosphine) complex **69a** (Equation (23)).[18] The triphenylphosphite analog **69b** is prepared in a similar manner.

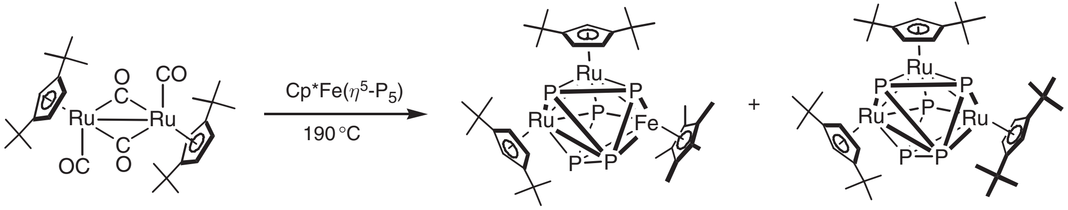


7

69a: R = Me (quant.)
69b: R = OPh (quant.)

(23)

Triangulated dodecahedral triruthenium cluster, $[(Cp''Ru)_3P_5]$ (**72**, $Cp'' = 1,3\text{-}Bu_2C_5H_3$), with cyclopentadienyl and P_5 ligands, has been obtained as a side-product (17%) in the co-thermolysis of $[Cp^*Fe(\eta^5\text{-}P_5)]$ and $\{Cp''Ru(CO)_2\}_2$ **70** (Equation (24)).[73] The reaction is less selective and several other products including hetero-trimetallic and tetrametallic iron–ruthenium clusters are formed.



70

71
7%

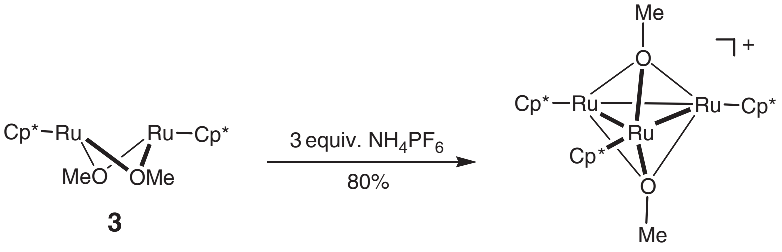
72
17%

(24)

6.20.5 Triruthenium Cyclopentadienyl Clusters Containing Group 16 Elements

6.20.5.1 Triruthenium Cyclopentadienyl Complexes Containing μ_3-O Ligands

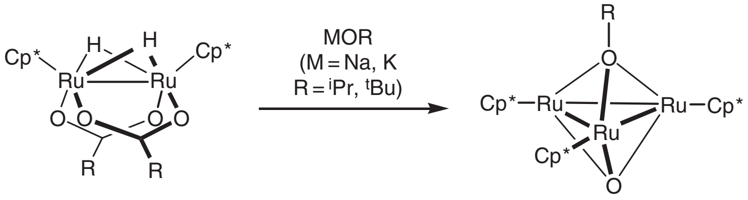
Treatment of **3** with NH_4PF_6 (3 equiv.) in methanol affords a trinuclear di(μ_3-methoxo) complex **73** in high yield (Equation (25)).[10] Analogous μ_3-oxo–μ_3-alkoxo clusters **75a** and **75b** are prepared by the reactions of $(Cp^*Ru)_2(\mu\text{-}H)_2(\mu\text{-}OCOCF_3)_2$ **74** with alkalis metal alkoxide MOR (R = ^{i}Pr and ^{t}Bu, M = Na and K) in the corresponding alcohol or THF (Equation (26)).[74] Complexes **75a** and **75b** are also prepared by the treatment of **1** with NaO^{i}Pr and KO^{t}Bu, respectively. These complexes have been characterized by X-ray diffraction studies.



3

73

(25)

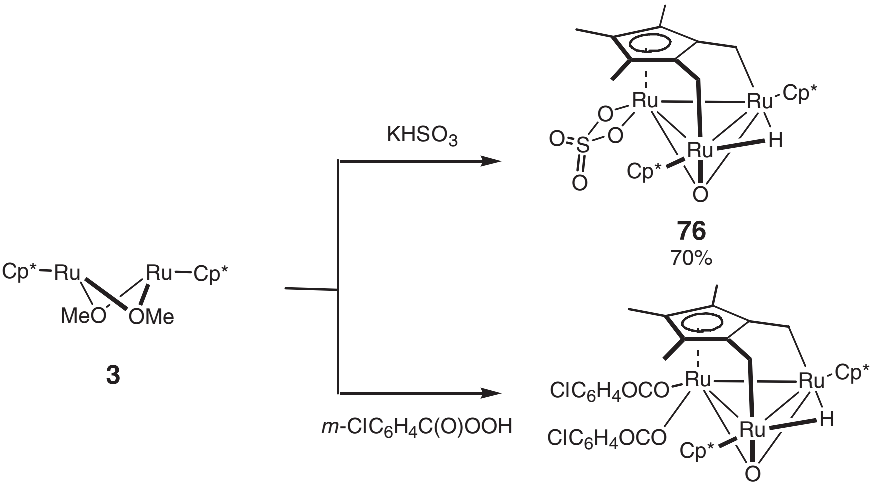


74

75a: R = ^{i}Pr (76%)
75b: R = ^{t}Bu

(26)

The reaction of **3** with $KHSO_3$ in a two-phase medium such as CH_2Cl_2–H_2O or in methanol produces **76** in which two adjacent methyl groups of a Cp* ligand have been activated and are coordinated to two ruthenium atoms giving rise to a novel μ_3-η^7-dimethylene–trimethylcyclopentadiene ligand (Equation (27)).[75] A similar cluster **77** is formed in the reaction of **3** with *m*-chloroperbenzoic acid. Hydrolysis of **1** with H_2O/K_2CO_3 affords **78**, which is a hydroxo analog of **76** and **77** (Equation (28)).[76]

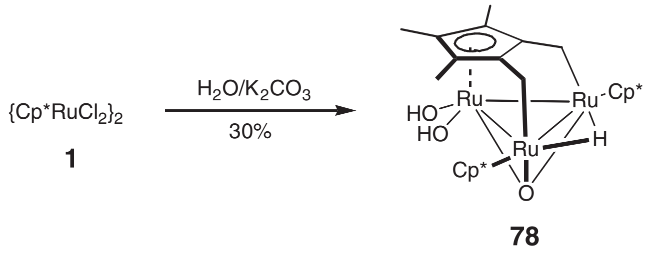


76
70%

3

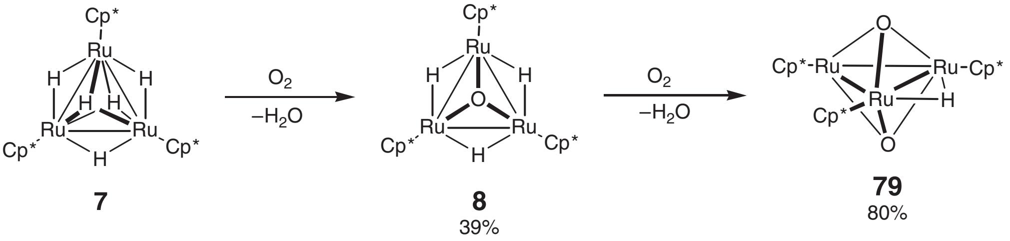
77

(27)



(28)

Trihydrido complex **8** having a μ_3-oxo ligand is synthesized by the reaction of the triruthenium pentahydrido complex **7** with an equimolar amount of dioxygen (Equation (29)).[18] In this reaction, one oxygen atom of the dioxygen was incorporated into the cluster, while the second was reduced by the hydrido ligands to form water. Complex **8** is still reactive toward another molecule of dioxygen, and affords bis(μ_3-oxo) complex **79**, which is the main product of the reaction of **7** with a large excess of dioxygen.



(29)

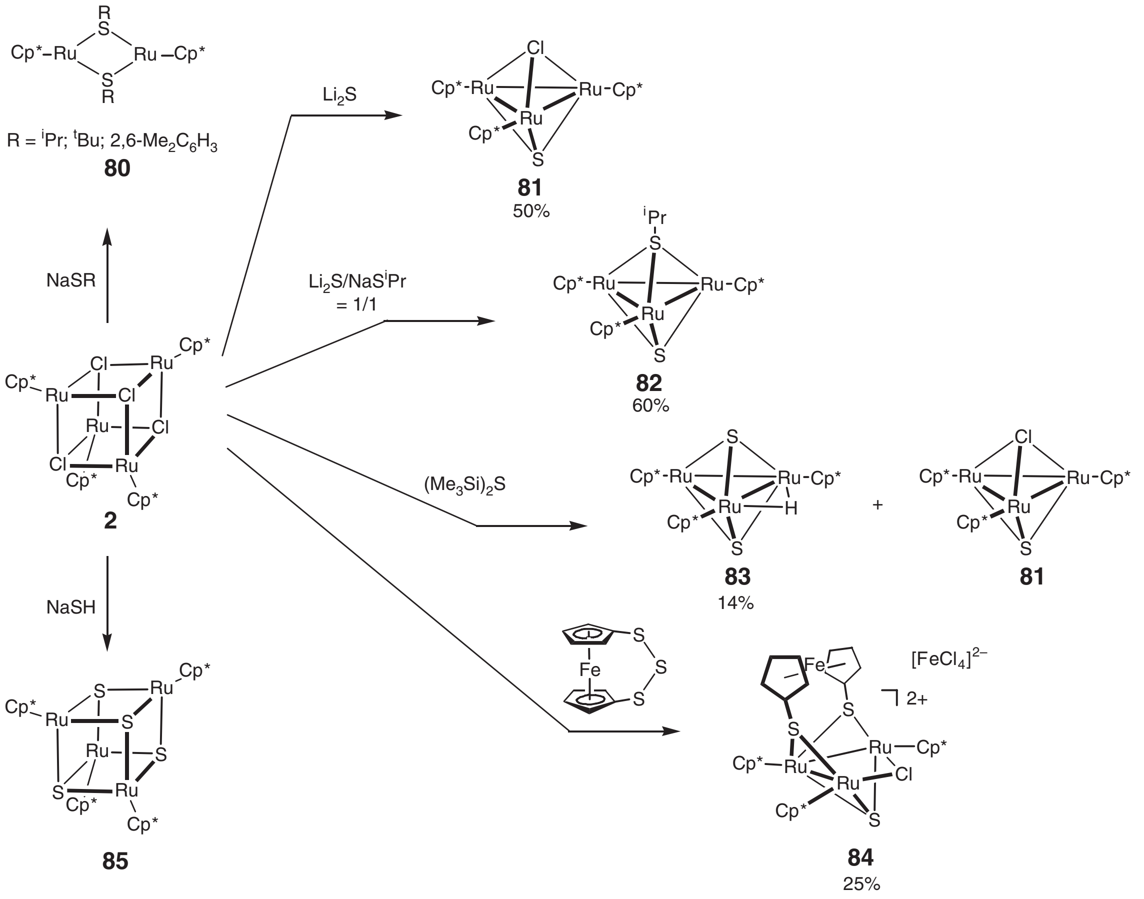
6.20.5.2 Triruthenium Cyclopentadienyl Complexes Containing μ-S And μ_3-S Ligands

Transition metal complexes with sulfido or thiolato ligands are of continuing interest as models for biological systems and for industrial applications, such as the hydrodesulfurization process. In this point of view, several triruthenium complexes having a cyclopentadienyl ligand have been synthesized and structurally characterized. It is interesting that a trimetallic framework can be constructed from a mono- and bimetallic species using a sulfido or a thiolato ligand as a clamp, and it has been shown that the framework of the produced cluster is highly affected by the nature of substituents of thiolate or sulfide.

In the reactions of a triruthenium cluster with compounds containing a sulfur atom, formation of a μ_3-sulfido ligand as a result of C–S bond cleavage is observed, which would provide an important mechanistic insight into the hydrodesulfurization process. Synthetic methods for complexes containing a bridging sulfur atom are roughly classified into three types as follows: (i) construction of the trimetallic framework from monometallic species having a cyclopentadienyl ligand; (ii) construction of the triruthenium framework by the reaction of monometallic species with a bimetallic complex; and (iii) introduction of a sulfido ligand into a triruthenium complex. These synthetic methods will be described in the order as well as reactivity of some of these complexes (see below).

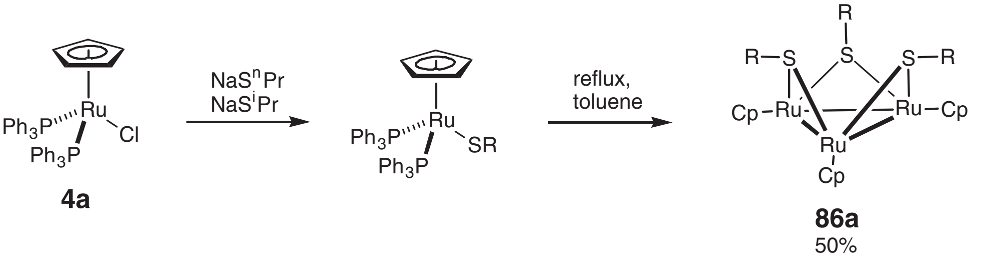
6.20.5.2.1 Construction of the trimetallic framework from monometallic species

It is well known that the coordinatively unsaturated species, [Cp*RuCl], is readily generated from the tetrametallic cubane complex {Cp*Ru(μ_3-Cl)}$_4$ **2**. The reactions of **2** with sulfides exclusively afforded triruthenium complexes containing μ_3-sulfido ligands. While the reactions of **2** with NaSR (R = ^{i}Pr, ^{t}Bu, 2,6-$Me_2C_6H_3$) resulted in the formation of bimetallic bis(μ-thiolate) complexes **80**,[77] μ_3-sulfido–μ_3-chloro complex **81** was exclusively formed by the use of Li_2S, and was isolated in 50% yield (Scheme 6).[78,79] In the presence of NaS^{i}Pr, triruthenium complex **82** having a μ_3-thiolato ligand was selectively obtained. Bis(μ_3-sulfido) complex **83** was obtained together with **81** in the reaction of **2** with $(Me_3Si)_2S$. The hydride of **83** was presumably derived from adventitious water in the solvent. The μ_3-sulfido complex containing a ferrocenyl group **84** was prepared by the reaction of **2** with 1,2,3-trithia[3]ferrocenophane.[80] It has been also reported that the tetrametallic cubane-type complex **85** was formed by the reaction of **2** with NaSH.[81]

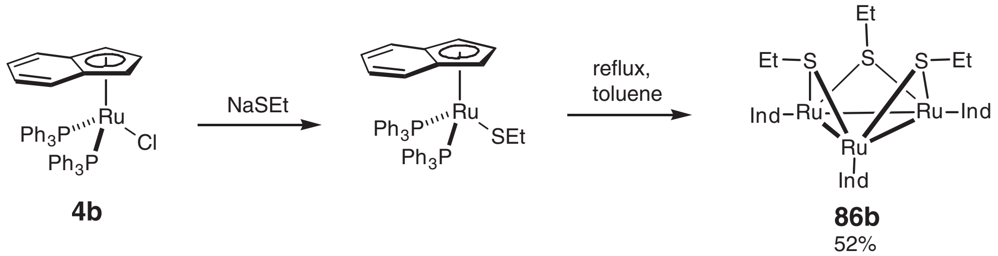


Scheme 6

Triruthenium complexes containing a doubly-bridging thiolato ligand were prepared by the reactions of monometallic complex $CpRu(PPh_3)_2Cl$ **4a**. Tris(μ-thiolato) complexes **86a** were obtained from the reactions of **4a** with NaSR ($R = {}^nPr$, ${}^iPr$) (Equation (30)).[82] By the X-ray diffraction studies for **86a**, it was proved that two of the three alkyl groups on the μ-thiolato ligands occupying the equatorial-like positions with respect to the Ru_3S_3 core while the third group occupies the axial. This structure is maintained in solution, and is shown to be rigid by the VT-NMR studies; no axial–equatorial exchange takes place. The observed orientation of the alkyl group was most likely achieved due to minimizing the repulsion among the lone pairs on the thiolato ligands. A similar reaction was reported for the η^5-indenyl analog **4b**.[83] In this reaction, however, only ethyl isomer **86b** was isolated (Equation (31)). When allyl thiolate was employed, bis(μ_3-sulfido)–μ-thiolato complex **87** was formed as a result of C–S bond cleavage (Equation (32)).[84] The μ-allylthiolato group bridged the two ruthenium atoms, between which no direct Ru–Ru interaction is present.



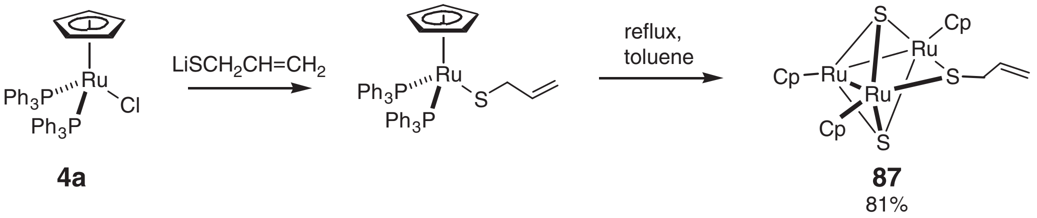
(30)



4b

86b
52%

(31)



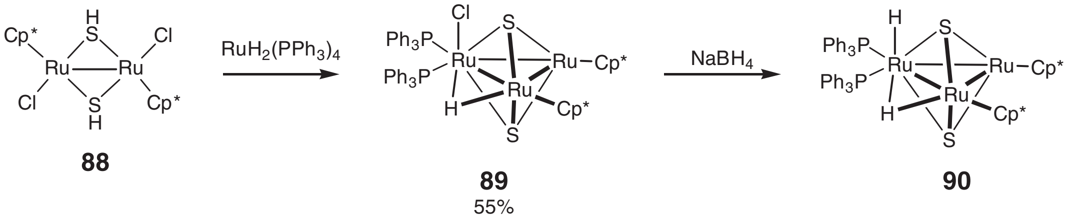
4a

87
81%

(32)

6.20.5.2.2 Construction of the triruthenium framework by the reaction of monometallic species with a bimetallic complex

The diruthenium μ-hydrosulfido complex **88** reacted with a monometallic hydrido complex to yield bis(μ_3-sulfido) complex **89** having a terminally bonded chloro ligand (Equation (33)).[85] The hydrido derivative **90** was obtained by the treatment of **89** with NaBH$_4$.



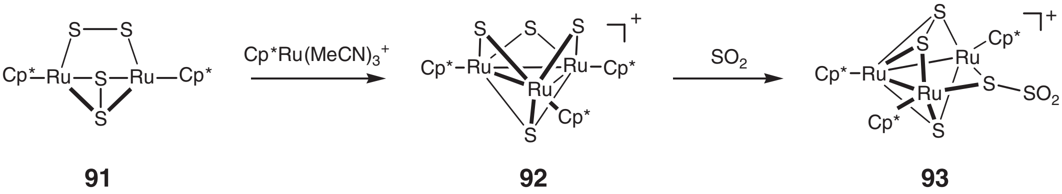
88

89
55%

90

(33)

The diruthenium disulfido complex **91** reacted with the cationic complex [Cp*Ru(NCMe)$_3$](PF$_6$) to yield the cationic complex **92** (Equation (34)).[86] The C_3 symmetry observed in the NMR spectra implied that complex **91** possesses three μ- and one μ_3-sulfido ligands in its structure. The diffraction studies for the SO$_2$-adduct **93**, which adopted an open-form structure, also supported the proposed structure for **92**. By the reaction of the divalent ruthenium complex having a tridentate sulfido ligand **94** with the trivalent chloride complex **1**, trimetallic complexes, **96** and **97**, were formed (Scheme 7).[87] A coordinatively unsaturated species would be generated by the liberation of the η^6-hexamethylbenzene ligand of **94** as a result of a redox reaction between the Ru(II) center of **94** and the Ru(III) center of **1**. The diruthenium complex **95** was formed by the reaction of **1** with the generated coordinatively unsaturated species, and subsequent substitution of the chloro ligand of **95** by the thiolato of **94** resulted in the formation of **96**. The trivalent ruthenium complex **98**, which was Cp* analog of the hexamethylbenzene complex **94**, afforded triruthenium complex **99** in the reactions with divalent chloro-ruthenium complexes.

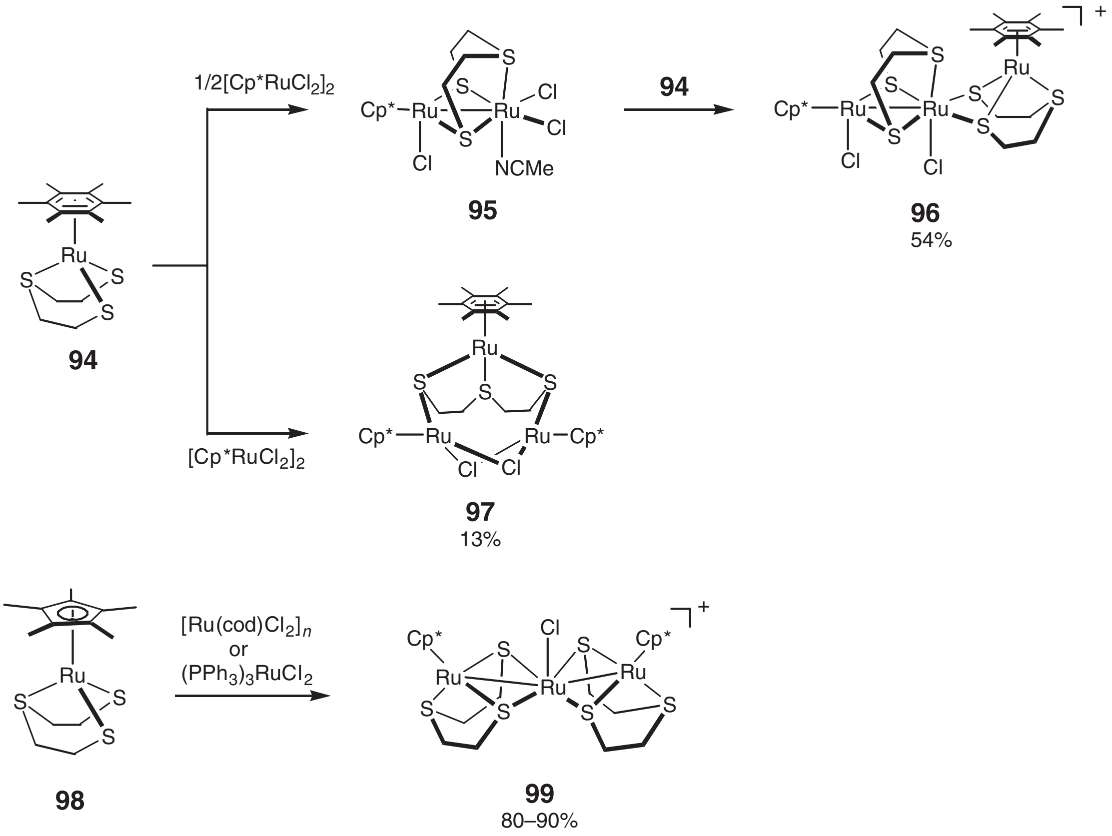


91

92

93

(34)



Scheme 7

6.20.5.2.3 Introduction of a sulfido ligand into a triruthenium complex

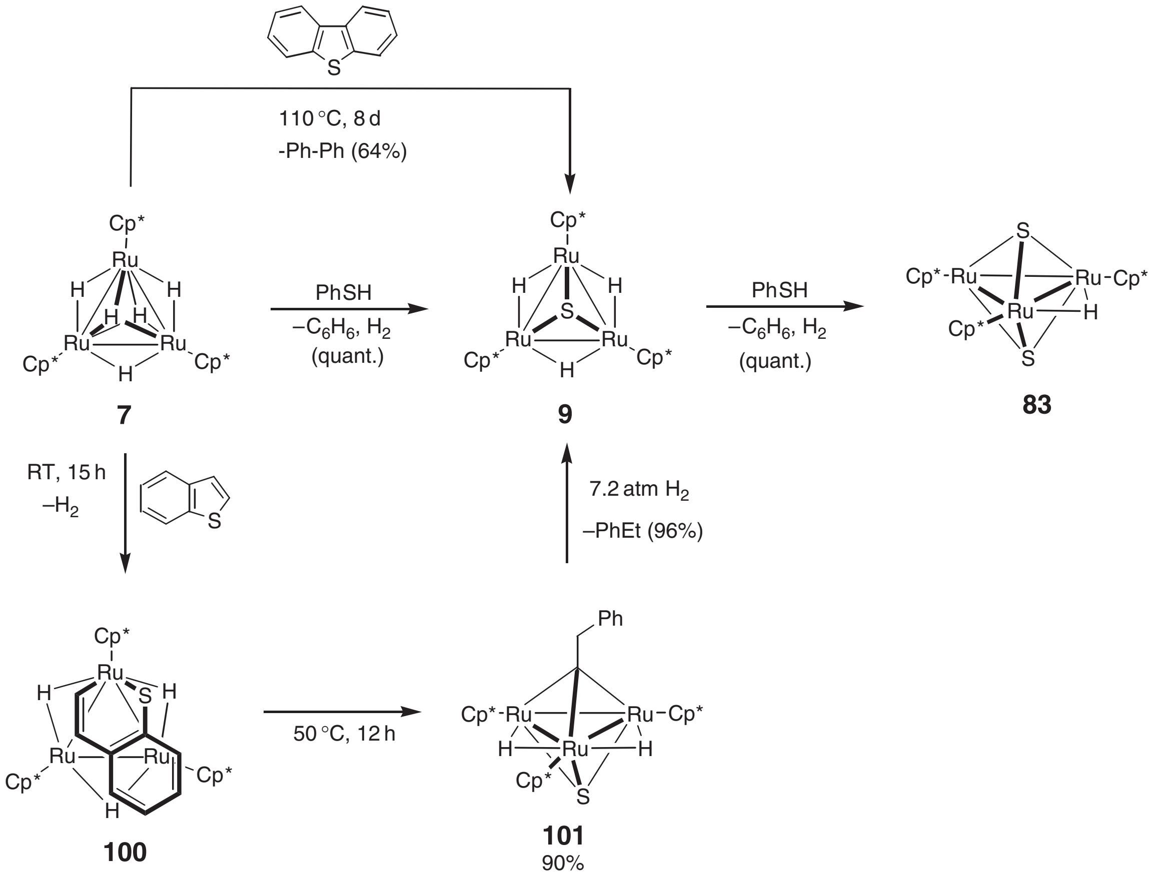
The trihydrido complex **9** having a μ_3-sulfido ligand was prepared by the reaction of the pentahydrido complex **7** with thiophenol (Scheme 8).[40] In this reaction, C–S bond cleavage followed by the liberation of benzene took place. Complex **9** further reacted with additional thiophenol with formation of bis(μ-sulfido) complex **83**, which was alternatively synthesized by the reaction of **2** with $(Me_3Si)_2S$ as shown in Scheme 6.[79]

The μ_3-sulfido complex **9** was also obtained by the reaction of **7** with dibenzothiophene. In this reaction, biphenyl was produced as a result of two C–S bond cleavages. The reaction of **7** with benzothiophene afforded μ_3-phenethylidyne–μ_3-sulfido complex **101** via the formation of a thiaruthenacycle intermediate **100**. Hydrogenation of **101** resulted in the liberation of the μ_3-phenethylidyne ligand as ethylbenzene, which also afforded trihydrido complex **9**.

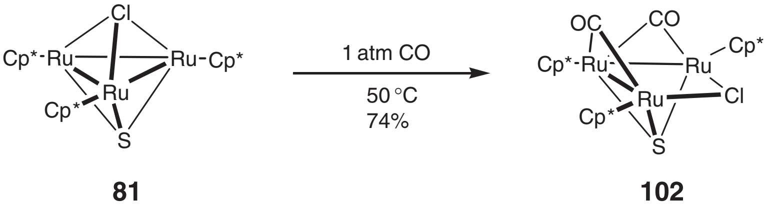
6.20.5.2.4 Reactivity of the thiolate and sulfido complexes

While addition of an electrophile, such as H^+ and Me^+, to the μ-sulfido and μ-thiolato ligands is commonly observed,[83,86] there have been no reports of electrophilic addition to the μ_3-sulfido ligand.

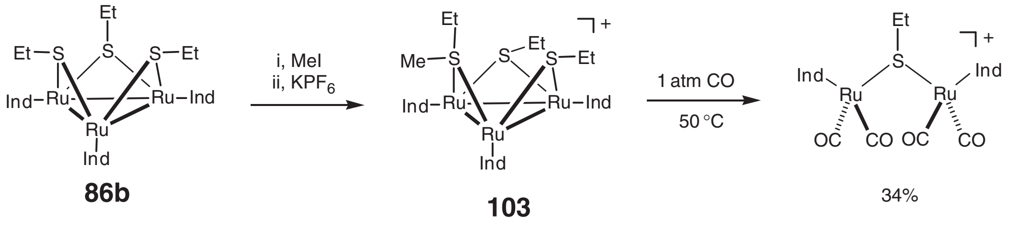
The μ_3-sulfido complex **81** containing a μ_3-Cl ligand readily reacted with carbon monoxide.[79] One of the Ru–Ru bonds was cleaved and the 50-electron complex **102** having two bridging carbonyl groups was formed (Equation (35)). The cationic complex **103**, which was prepared by the treatment of **86b** with MeI, was also reacted with CO although it is coordinatively saturated (Equation (36)).[83] Since similar reactions did not take place using **86a**, which bears Cp groups instead, reactivity toward CO arises from the η^5-indenyl group of **86b**, the coordination site for the CO molecule being generated by the ring slippage of the η^5-indenyl group.



Scheme 8



(35)

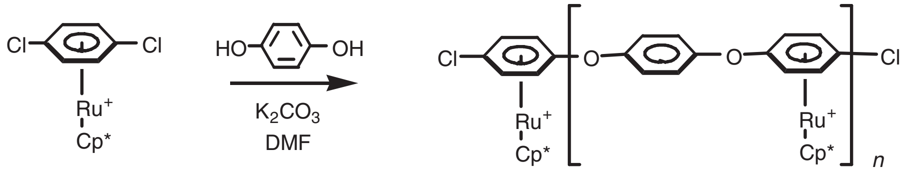


(36)

As mentioned in the previous section, the trihydrido complex **9** reacts with various alkanes to yield a μ_3-alkylidyne–μ_3-sulfido complex **101** via a selective C–H bond cleavage of alkane at the terminal position.[39]

6.20.6 Triruthenium Cyclopentadienyl Clusters without any M–M Bonds

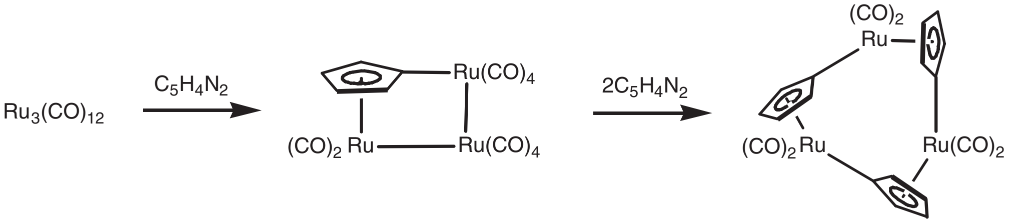
A few triruthenium cyclopentadienyl clusters having no Ru–Ru bonds are known. It is well known that a cationic coordinatively unsaturated species, $[Cp^*Ru]^+$, is stabilized by the formation of a coordinatively saturated η^6-arene complex, $[Cp^*Ru(\eta^6\text{-arene})]^+$.[88] Thus, triruthenium compounds are readily available by the reaction of $[CpRu^+]$ with organic compounds in which at least three C_6-aromatic rings were included. Triruthenium compounds **104a** and **104b** were obtained by the coupling reaction at the aromatic ring of the $[Cp^*Ru(\eta^6\text{-}1,4\text{-}Cl_2C_6H_4)]^+$ moiety, which possesses two functional groups in the arene ligand (Equation (37)).[89]



(37)

104a: $n = 1$
104b: $n = 2$

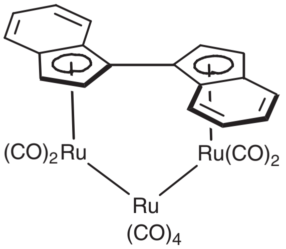
The unique triruthenium cluster **106** having no direct Ru–Ru bonds in which cyclopentadienyl groups adopted an η^1:η^5-coordination mode was synthesized by the reaction of $Ru_3(CO)_{12}$ with diazocyclopentadiene (Equation (38)).[90]



(38)

105 **106**

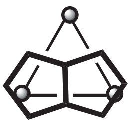
The interatomic distance between the ruthenium atoms was lengthened to ca. 4 Å by the insertion of diazocyclopentadiene into an Ru–Ru bond. When the reaction was carried out using an equimolar amount of diazocyclopentadiene, formation of an intermediate **105**, in which only one of the Ru–Ru bonds was cleaved, was observed. A similar triruthenium complex was prepared by using diazoindene.[91] In this case, coupling between the two η^5-indenyl moieties also took place, and trimetallic cluster **107** adopting an open-form structure was obtained as a byproduct.



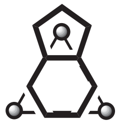
107

6.20.7 Triruthenium Clusters Having a Face-Capping C$_5$ Cycle

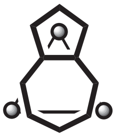
In addition to the η^5-cyclopentadienyl ligand, face-capping coordination of a fused-ring compound through its five-membered ring in an η^5-fashion is known. These compounds have been extensively investigated in relation to the metal-surface chemistry. Although pentalene is too unstable to be isolated under normal conditions, it has been effectively stabilized by complexation to transition metal centers. Several di- and triruthenium complexes having a μ-pentalene ligand have thus far been synthesized and structurally determined,[92–95] which provided important information about the metal-to-ring bonding interaction. Trimetallic μ-pentalene complexes have been already reviewed[96] in COMC(1995)[97].



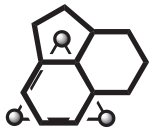
Pentalene



Indene

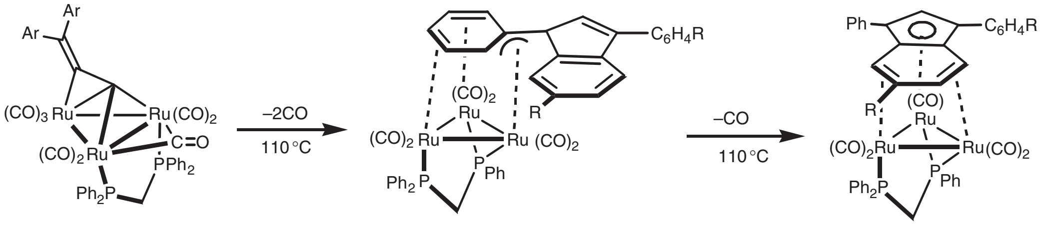


Azulene



Acenaphthylene

Only tetrametallic clusters having a face-capping indene ligand were isolated by the reaction of $M_3(CO)_{12}$ (M = Fe, Ru) with indene.[98–100] Trimetallic indene complex **110** was obtained by the thermolysis of the μ_3-allenylidene complex **108** which contains a dppm ligand (Equation (39)).[101,102] In this reaction, P–C bond cleavage of the dppm ligand and the formation of the μ_3-arene complex **109** took place. The μ_3-indene complex **110** was formed by subsequent ring slippage. It was proved that the indene framework was derived from the μ_3-allenylidene moiety.



(39)

Ar = Ph or 4-MePh

108

R = H or Ph

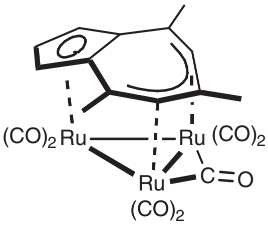
109

R = H or Ph

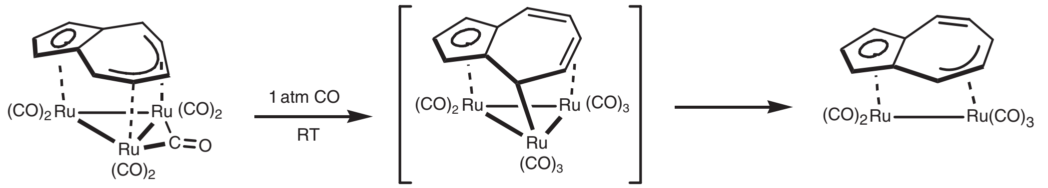
110

In contrast to the reaction with indene, a triruthenium complex having a face-capping azulene ligand was isolated from the reaction of $Ru_3(CO)_{12}$ with azulene,[103–106] while formation of a tetrametallic azulene complex was also observed.[103,107] It has been shown by means of X-ray diffraction studies that the azulene is coordinated to one of the ruthenium centers through its C_5 ring in an η^5-fashion similar to the μ_3-indene complex, and the seven-membered ring also bridges the other two ruthenium atoms.

It has been shown that 4,6,8-trimethylazulene complex **111** catalyzees hydrosilylation of acetophenone.[108] While it was reported that the reactions of $Ru_3(CO)_{12}$ with hydrosilanes often resulted in degradation of the trimetallic framework, the trimetallic framework containing a face-capping azulene or acenaphthylene ligand was maintained during the reactions with hydrosilanes. However, treatment of a face-capping azulene complex **112** with CO at atmospheric pressures at room temperature led to the formation of diruthenium complex having a μ-azulene ligand (Equation (40)).[109] A trinuclear intermediate **113** was observed by means of NMR spectroscopy during this degradation.



111

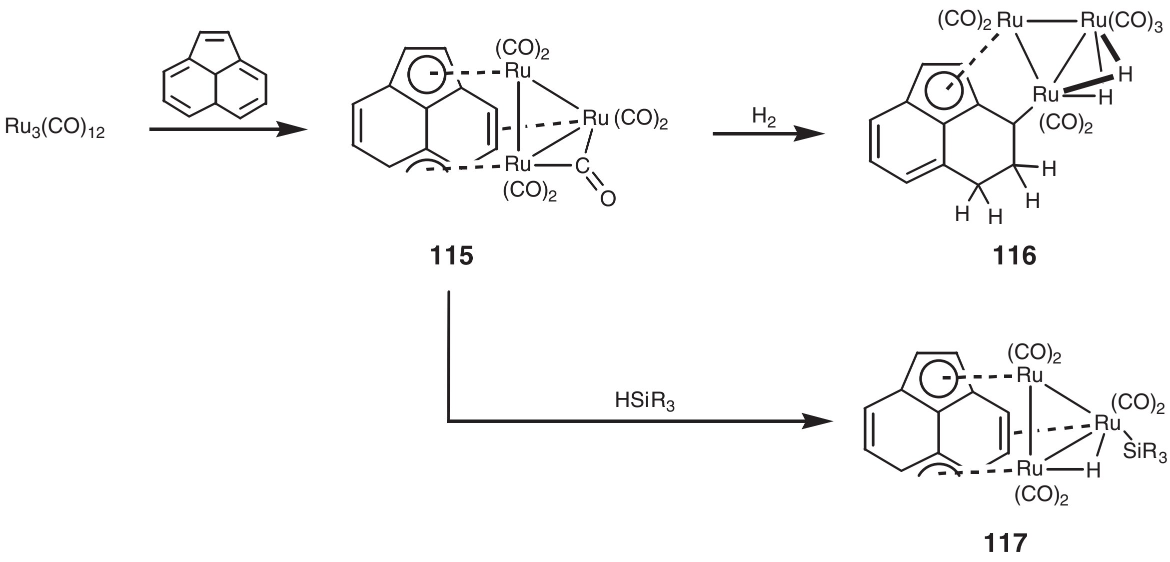


(40)

112

113

114



Scheme 9

Acenaphthylene has been shown to be coordinated to the triruthenium center in a face-capping mode. Treatment of $Ru_3(CO)_{12}$ with acenaphthylene afforded μ_3-$\eta^5:\eta^3:\eta^2$-acenaphthylene complex **115** in high yield (Scheme 9).[110] An η^5-coordination of the five-membered ring was clearly shown by the diffraction studies. Complex **115** readily reacted with dihydrogen. In this reaction, partial hydrogenation of the six-membered ring and ring slippage of the acenaphthylene moiety resulting in formation of the μ-fulvene type complex **116** took place.[111]

Similar to the μ_3-azulene complex **111**, complex **115** also catalyzes hydrosilylation of acetophenone.[112] In addition, complex **115** has been shown to catalyze ring-opening polymerization of THF[113] and cyclic siloxanes[114] using hydrosilanes as initiators, while $Ru_3(CO)_{12}$ did not promote the polymerization under the same conditions. This fact implied that coordination of an acenaphthylene was important for the reactivity of **115**, with especially facile generation of the vacant site on the triruthenium plane by the ring slippage of the face-capping ligand.

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6.21
Trinuclear Ru/Os Clusters Containing Arene Ligands

P J Dyson, Institut des sciences et ingénierie chimiques, Lausanne, Switzerland
J S McIndoe, University of Victoria, Victoria, BC, Canada

6.21.1 Introduction

The bonding modes adopted by arene ligands with transition metal complexes and clusters have been reviewed previously.[1,1a] While a large range of different bonding modes has been observed, with trinuclear ruthenium and osmium clusters two types dominate, these being the terminal η^6 and the face-capping μ_3-η^2:η^2:η^2 bonding modes. A few examples of other bonding modes that can essentially be viewed as derivations from idealized μ_3-η^2:η^2:η^2 bonding have also been characterized in the solid state, although in solution, rapid rotation of the arene in either bonding mode generally takes place. The ruthenium and osmium clusters containing arene ligands that have been characterized in the solid state are listed in Table 1.

6.21.2 Terminal η^6 Arene Compounds

Coordination of arenes to metal centers in an η^6 fashion is textbook material with notable examples being the arene chromium(0) tricarbonyl compounds used in stoichiometric organic synthesis and arene ruthenium(II) compounds which have a wide range of applications, in particular, as catalysts/pre-catalysts (see COMC III). Several triruthenium and triosmium clusters with η^6 arene ligands have been reported in the last decade. In these compounds the arene does not exhibit any special structural features that are different to those typical of mononuclear compounds. In some cases the η^6 arene is derived from the reaction of a face-capping (μ_3-η^2:η^2:η^2) arene via migration, but as far as we are aware the reverse process has not been reported (at least in the trinuclear systems). For example, $Ru_3(CO)_9(\mu_3$-η^2:η^2:η^2-$C_{16}H_{16})(C_{16}H_{16}=[2.2]$paracyclophane) reacts with diphenylacetylene to afford $Ru_3(CO)_7(\mu_3$-η^1:η^2:η^1-PhCCPh)(η^6-$C_{16}H_{16}$) (see Section 6.21.3.3).[13] Several clusters have two or three terminal arene ligands (see Table 1). The mixed-arene clusters $[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-Cl})(\mu_3\text{-O})(\mu\text{-H})_2]^+$, $[Ru_3(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)(\mu_3\text{-O})(\mu\text{-H})_3]^+$, and $[Ru_3(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)(\mu_3\text{-O})(\mu\text{-H})_2(\mu\text{-OH})]^+$ are efficient precursors of highly active heterogeneous (nanocluster) arene hydrogenation catalysts.[37] It cannot be ruled out that a type of supramolecular catalysis process also takes place as arenes can associate with the cluster face without covalently binding as shown in the solid-state structures of triruthenium clusters each with three η^6 arene ligands in Figure 1.[38,38a] Furthermore, electrospray ionization mass spectrometry (ESI-MS) shows that the weak supramolecular interaction established in the solid state persists in solution. Cold-spray ionization mass spectrometry also reveals H-bonding interactions between substrates and the oxide ligand in $[Ru_3(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)(\mu_3\text{-O})(\mu_2\text{-H})_3]^+$.[39] Other related compounds have been reported.[40] The reactivity of η^6-arenes coordinated to trinuclear clusters has not been developed.

Table 1 Triruthenium and osmium compounds with arene ligands characterized by single crystal X-ray diffraction

Compound	*References*
Terminal arene ligands	
$Ru_3(CO)_6(\mu_3\text{-}NPh)(\eta^6\text{-}C_6H_6)$	2
$Os_3(CO)_7(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}MeCCMe)(\eta^6\text{-}C_6H_6)$	3
$Ru_3(CO)_7\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}CO(Ph)CCPh\}(\eta^6\text{-}C_6H_6)$	4
$Fe_3(CO)_7(\mu_3\text{-}CCl)(\mu_3\text{-}CCOOEt)(\eta^6\text{-}C_6H_6)$	5
$Fe_3(CO)_7(\mu_3\text{-}P^tBu)(\eta^6\text{-}C_6H_5Me)$	6
$Ru_3(NCMe)_2PPh_3(\mu_3\text{-}S)_2(\eta^6\text{-}{}^iPrC_6H_4Me)_2$	7
$[Ru_3(NCMe)(PPh_3)_2(\mu_3\text{-}S)_2(\eta^6\text{-}{}^iPrC_6H_4Me)_2]^+$	
$[Ru_3(\mu_3\text{-}\eta^3\text{-}C_6H_{12}S_3)(\mu_3\text{-}S)_2(\eta^6\text{-}{}^iPrC_6H_4Me)_2]^+$	
$[Ru_3(\mu\text{-}H)_2(\mu\text{-}OH)(\mu_3\text{-}O)(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)]^+$	8
$[Ru_3(\mu_3\text{-}S)_2(\eta^6\text{-}{}^iPrC_6H_4Me)_3]^+$	9
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}C_6Me_6)_2\{\eta^6\text{-}C_6H_5(CH_2)_2OOCPh\}]^+$	10
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}C_6Me_6)_2\{\eta^6\text{-}C_6H_5(CH_2)_2OOC(CH_2)_3Ph\}]^+$	
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}C_6Me_6)_2\{\eta^6\text{-}MeC_6H_4COO(CH_2)_2OOC(Me){=}CH_2\}]^+$	11
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}C_6H_2Me_4)_3]^+$	12
$Ru_3(CO)_7(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}PhCCPh)(\eta^6\text{-}C_{16}H_{16})$	13
$(S)\text{-}[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)\{\eta^6\text{-}C_6H_5[CH(CH_3)CH_2OH]\}(\eta^6\text{-}C_6Me_6)_2][BF_4]$	14
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_2Me_4)_2][BF_4]$	15
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)\{\eta^6\text{-}C_6H_5(CH_2)_2OH\}(\eta^6\text{-}C_6H_2Me_4)_2][BF_4]$	
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)][BF_4]$	16
$[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}{}^iPrC_6H_4Me)_2(\eta^6\text{-}C_6H_6)][BF_4]$	17
$[C_6H_6 \subset Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)\{\eta^6\text{-}C_6H_5(CH_2)_2OH\}(\eta^6\text{-}C_6Me_6)_2][PF_6]$	18
$[C_6H_6 \subset Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}(\eta^6\text{-}C_6Me_6)_2][BF_4]$	
Face-capping arenes	
$Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$	19
$Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$	20
$Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$	13
$Ru_3(CO)_8(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5\{C(Me){=}CH_2\})$	21
$Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_4\{C(Me){=}CH_2\}_2)$	
$Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^4\text{-acenaphthalene})$	22
$HRu_3(CO)_6(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^4\text{-acenaphthalene})(SiMe_2CH_2Ph)$	23
$H_3Ru_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$	24
Terminal and face-capping arenes	
$Os_3(CO)_6(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$	25
Edge-bridging arenes	
$H_2Ru_3(CO)_7(\mu\text{-}\eta^1{:}\eta^5\text{-4,5-dihydroacenaphthalene})$	22
$H_2Ru_3(CO)_7(\mu\text{-}\eta^1{:}\eta^5\text{-dihydroacenthrylene})$	26
Fullerenes	
$Os_3(CO)_7(CNBz)(\mu_3\text{-}CNBz)(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}C_{60})$	27
$Os_3(CO)_7(CNBz)(\mu_3\text{-}CNBz)(PMe_3)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$	
$Os_3(CO)_7(CNBz)(\mu_3\text{-}CNBz)(\mu\text{-}H)_2(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$	28
$Os_3(CO)_7(CNBz)_2(\mu_3\text{-}CNBz)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$	
$Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$	29
$Os_3(CO)_7(PMe_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$	30
$Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$	
$Os_3(CO)_9(\mu_3\text{-}CNBz)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$	31
$Os_3(CO)_8(CNBz)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$	32
$Os_3(CO)_8(CNBz)(\mu_3\text{-}CNBz)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (two isomers)	
$Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$	33
$Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})$	34
Benzynes	
$Os_3(CO)_7\{\mu\text{-}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}SbPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)$	35
$Ru_3(CO)_6(\mu_2\text{-}PPh_2)_2(AuPPh_3)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)$	36

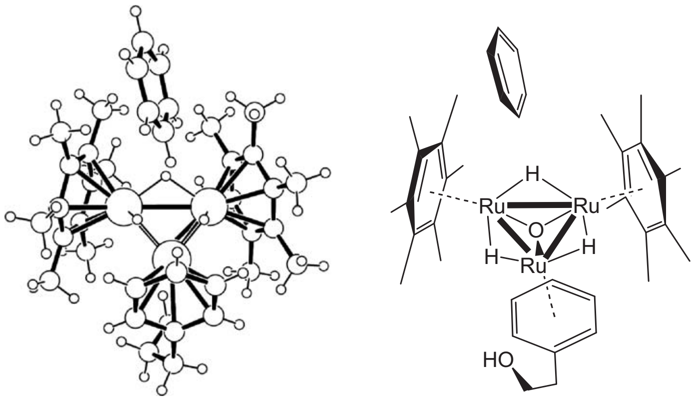


Figure 1 Host–guest interactions between benzene solvate in the hydrophobic cavity of the cluster clathrate complex [$C_6H_6 \subset Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)\{\eta^6\text{-}C_6H_5(CH_2)_2OH\}(\eta^6\text{-}C_6Me_6)_2$][$PF_6$].

6.21.3 Face-Capping Arene Compounds

The coordination of arenes over trimetal faces provides the opportunity to study them in a strikingly new environment. In the μ_3-η^2:η^2:η^2 bonding mode for benzene the bond lengths alternate short and long around the C_6 ring. The short (double) bonds lie directly above the metal atoms while the longer (single) bonds straddle the metal atoms as illustrated in Figure 2 for $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$. In addition, the hydrogen atoms bend out of the plane of the ring away from the metal surface. Combined, these distortions from the structure of free benzene have been ascribed to a rehybridization of the sp^2 carbon atoms toward sp^3 leading to a better overlap between the C_6-ring and the trimetal face.[41] The spectroscopic properties of the μ_3-η^2:η^2:η^2 benzene ligand are also in agreement with such a hypothesis. Typically, the ^{1}H signal in the NMR spectrum is at lower frequency than either that observed for free benzene or for η^6 benzene with δ values in the range 3–4 ppm. For arene ligands other than benzene, the distortions that occur on coordination in the μ_3-η^2:η^2:η^2 mode are less clear.

There are two main synthetic routes used to prepare triruthenium and triosmium clusters with face-capping arene ligands. The simplest method involves direct reaction between the cluster and the arene, although this does not work for benzene and simple arenes, in the case of $Ru_3(CO)_{12}$ providing mostly hexaruthenium-carbido clusters containing η^6 arene ligands,[42] and $Os_3(CO)_{12}$ being essentially unreactive. However, arenes with unsaturated side-arms, polyaromatics, and fullerenes (see below) react directly under thermal conditions to afford the desired products, and homoleptic cluster precursors are not necessarily required. Face-capping benzene compounds must be prepared via cyclohexadiene. The original route, from 1985, commenced with the reaction between $H_2Os_3(CO)_{10}$ and cyclohexa-1,3-diene in octane under reflux to afford the cyclohexadienyl complex $HOs_3(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_7)$ in the first instance (see Scheme 1).[19] Subsequent abstraction of a hydride from the cyclohexadienyl ring with [Ph_3C][BF_4]

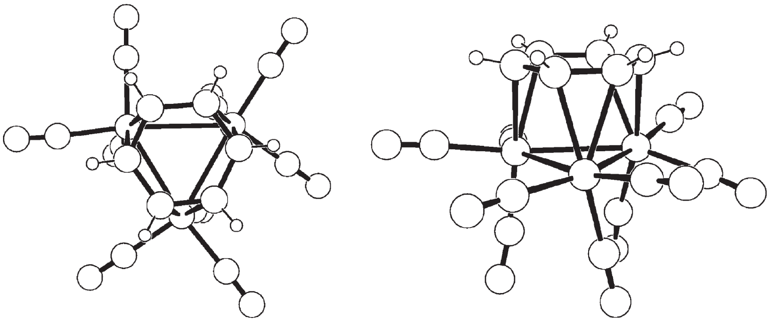
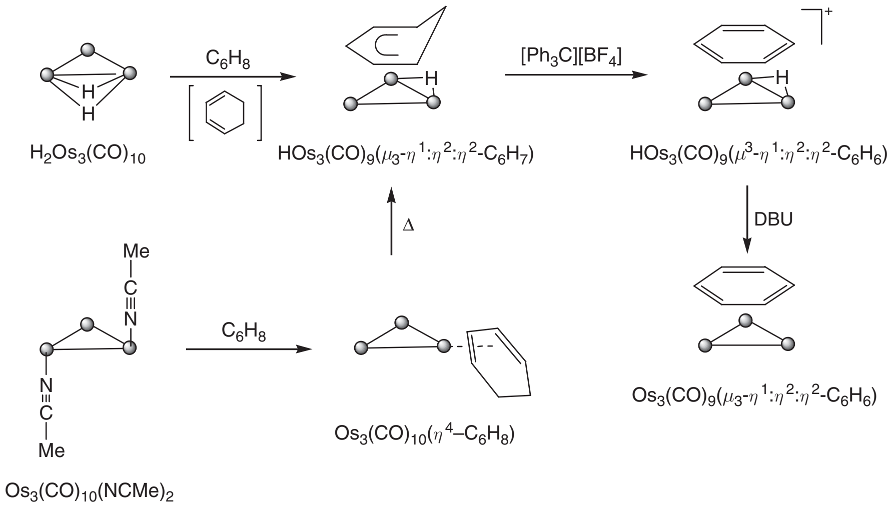


Figure 2 Top (left) and side-on (right) views of the structure of $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ showing the distortions to benzene on coordination to a trimetal face.

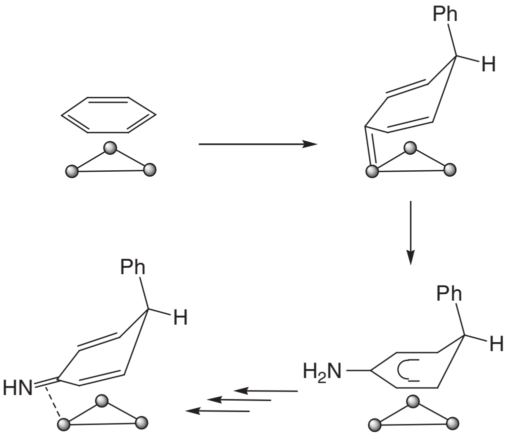


Scheme 1

affords $[HOs_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_6H_6)]^+$, containing a face-capping benzene ring, which then reacts with the poorly nucleophilic base 1,8-diazabicyclo[5.4.0]undeca-7-ene (DBU) to give the neutral species $Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$. In a more recent alternative synthesis, $Os_3(CO)_{10}(NCMe)_2$ reacts with cyclohexa-1,3-diene to form $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$, which gives the same cyclohexadienyl species that is converted to $Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ using the above approach.[43]

The reactivity of the face-capping benzene ring in $Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ has been explored. For example, under photolytic conditions it undergoes transformation to the benzyne derivative $H_2Os_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_6H_4)$.[44] It also reacts to form an unusual carbene system that can be converted in a stepwise manner, via reaction with NH_3, then DBU and $[N(PPh_3)_2]Cl$ and lastly $[Ph_3C][BF_4]$, to give a side-on coordinated imine ligand as shown in Scheme 2.[45,45a]

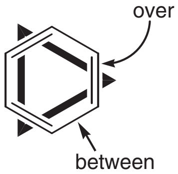
The analogous ruthenium-benzene compound may be prepared by the original route used to prepare the osmium compound,[20] although it was subsequently found that the route could be streamlined such that $Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ is formed in a single step from the reaction of $Ru_3(CO)_{12}$ with cyclohexa-1,3-diene in the presence of trimethylamine-*N*-oxide.[43] Some clusters with face-capping arene ligands have been analyzed by mass spectrometry, including laser desorption ionization-time of flight (LDI-TOF) analysis leading to cluster aggregation reactions,[46] and electrospray ionization which provides a reliable method for the determination of their molecular weights.[47]



Scheme 2

6.21.3.1 Bonding in Face-Capping Arenes

As mentioned in Figure 2, facial coordination of arenes to a triangular array of metal atoms results in a Kekulé distortion of the ring toward a “cyclohexatriene” arrangement, with the shorter bonds positioned over the metal atoms and the longer ones between.



Wadepohl has surveyed this effect for 12 members of a class of tricobalt clusters $Co_3(\eta\text{-}C_5H_4R'')_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_4RR')$ and concluded that the prototypical facial arene ligand is expanded with respect to free benzene and exhibits a small, but significant, Kekulé distortion.[48] Conducting a similar analysis of all group 8 trinuclear clusters with a face-capping arene ligand, we come to essentially the same conclusion despite a more disparate collection of clusters (see Table 2).

The mean length of C–C bonds positioned over a metal atom for the 12 structures is 1.415 Å (standard deviation = 0.027 Å), and for those between metal atoms 1.459 Å (standard deviation = 0.032 Å). Application of Student’s *t*-test gives 99% confidence intervals of 1.403–1.427 Å and 1.444–1.473 Å for each mean, respectively, indicating that the 0.044 Å bond length difference is highly significant. These data are summarized in histogram format in Figure 3, which shows the two populations separately and combined. Despite the overlap at around 1.43 Å, the presence of two discrete populations is obvious.

The similarity of this statistical survey with that of Wadepohl is noteworthy, especially considering quite different metals and ancillary ligand sets were included. The appearance of a Kekulé distortion in face-capping arenes, including fullerenes, appears to be quite general.

6.21.3.2 Face-Capping Arenes with Unsaturated Appendages

Isopropenylbenzene and 1,3-diisopropenylbenzene react directly with $Ru_3(CO)_{12}$ to form an assortment of clusters with nuclearities up to seven, including two triruthenium clusters with face-capping ligands (see Figure 4).[21] Not only does the C_6-ring form a $(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2)$ interaction with the underlying cluster unit, but the exocyclic double bonds also coordinate; thus, isopropenylbenzene and diisopropenylbenzene are formally eight- and 10-electron donors, respectively. The low yield of the isolated products has precluded the possibility of reactivity studies of the multiply coordinated ligands.

6.21.3.3 Face-Capping Polyaromatic and Related Ligand Systems

Although not strictly a polyaromatic ligand, [2.2]-paracyclophane has proved to be a versatile ligand in cluster chemistry, forming face-capping interactions, such as in $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ and derivatives such as $Ru_3(CO)_8(PR_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ (R = Ph or Cy) as shown in Figure 5.

Table 2 Face-capping arenes used for bond length analysis

M_3	*Arene*	*Ancillary ligands*	*CCDC ref. code*
Os_3	Benzene	$(CO)_9$	DEMGEH10
Os_3	C_{60}	$(CO)_8(PPh_3)$	HISVAG
Os_3	Benzene	$(CO)_8(\eta^2\text{-}C_2H_4)$	JEDDOL10
Os_3	C_{60}	$(CO)_7(PMe_3)_2$	MAZLUU
Os_3	C_{60}	$(CO)_8(CNCH_2Ph)$	OBINUW
Ru_3	Benzene	$(\eta^5\text{-}C_5Me_5)_3$	REKPOM
Ru_3	Benzene	$(CO)_9$	SELCER
Ru_3	C_{60}	$(CO)_9$	TOPNER
Os_3	Benzene	$(CO)_8(PPh_3)$	VUDFAB
Os_3	Benzene	$(CO)_6(\eta^6\text{-}C_6H_6)$	YIJKUX
Ru_3	[2.2]-Paracyclophane	$(CO)_8(PPh_3)$	YOJTEW
Ru_3	Isopropenylbenzene	$(CO)_8$	ZITDEL

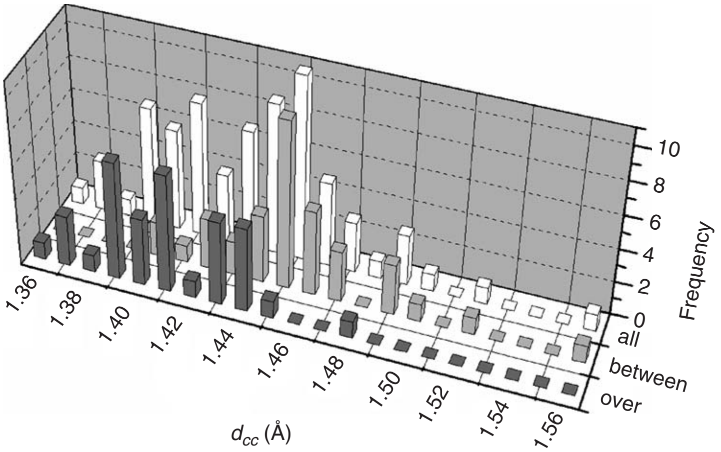


Figure 3 Bond length distributions for the C–C bond lengths in the face-capping arene ligands listed in Table 2. Sampling interval is 0.01 Å.

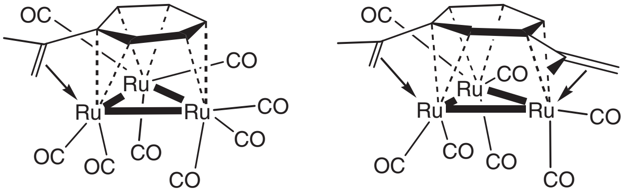


Figure 4 The coordination of isopropenylbenzene and diisopropenylbenzene to a triruthenium cluster.

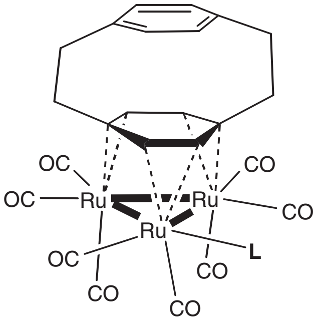
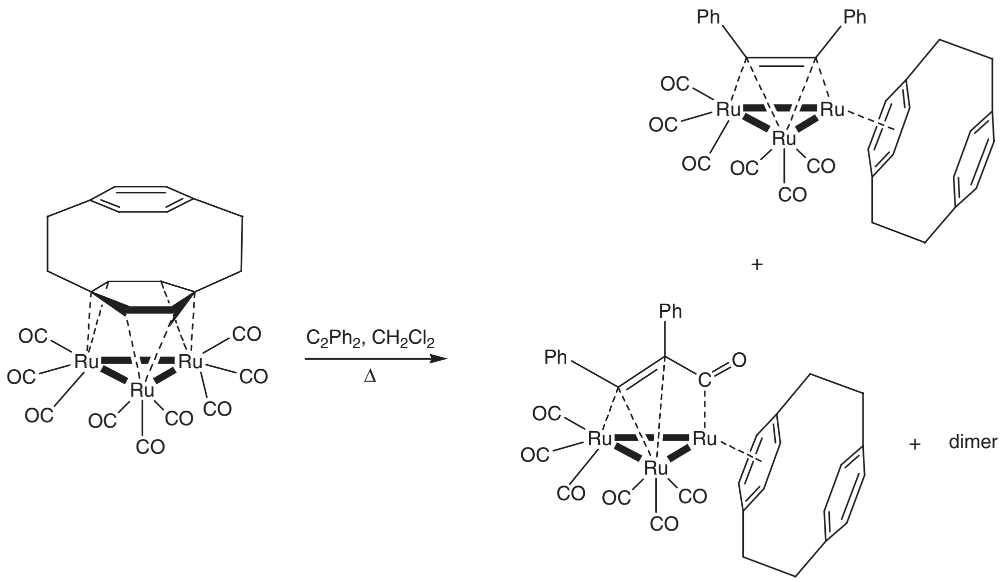


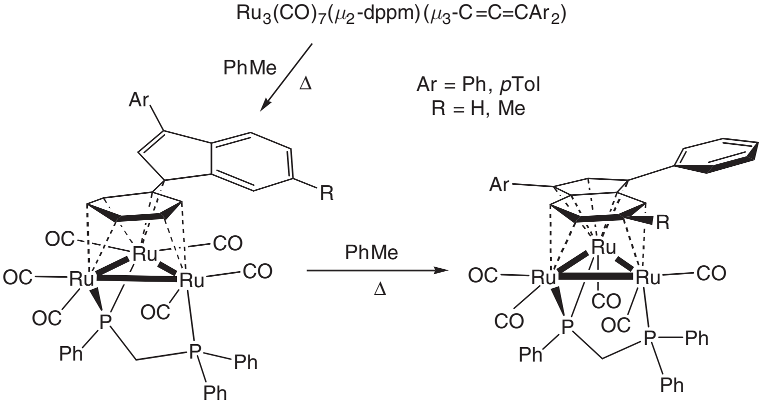
Figure 5 Structure of $Ru_3(CO)_8(L)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$; L = CO, PPh_3 or PCy_3.

As has been observed previously for $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, the coordination mode of the [2.2]-paracyclophane ligand in $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ can be adjusted to a terminal mode by reaction with diphenylacetylene in the presence of trimethylamine-*N*-oxide; the alkyne caps the triruthenium face in the place of the arene. When the reaction is conducted thermally in the absence of trimethylamine-*N*-oxide, additional products are also observed, including a related compound formed by insertion of a CO ligand into the alkyne–metal bond as shown in Scheme 3.

The triruthenium cluster, $Ru_3(CO)_6(\mu_3\text{-}PhPCH_2PPh_2)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^3\text{-}C_6H_5C_9H_5Ph)$, with a highly unusual *pseudo*-arene ligand is formed in a remarkable reaction in which $Ru_3(CO)_7(\mu\text{-dppm})(\mu_3\text{-}C{=}C{=}CPh_2)$ is merely heated in toluene (see Scheme 4); a phenyl ring from the dppm ligand cyclizes with the coordinated allenylidene.[49] Further thermolysis results in a considerable rearrangement of the coordinated arene such that it is displaced by the indenyl unit. Further examples of closely related clusters with face-capping indenyl ligands have also been reported.[50]



Scheme 3 Products isolated from the reaction of $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ with diphenylacetylene in dichloromethane at reflux.



Scheme 4

A triruthenium cluster with a face-capping acenaphthalene ligand has been isolated and its reactivity toward H_2 is explored in some detail. The cluster $Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^4\text{-acenaphthalene})$ was first reported in 1993 and at that time it was also shown that the bonding mode and nature of the polyaromatic ring system could be modified by reaction with H_2 resulting in the selective hydrogenation of the acenaphthalene system with a simultaneous change in bonding mode.[22] The structures of $Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^4\text{-acenaphthalene})$ and the hydrogenated product $H_2Ru_3(CO)_7(\mu\text{-}\eta^1{:}\eta^5\text{-4,5-dihydroacenaphthalene})$ are shown in Figure 6.

More recently, the cluster-mediated selective hydrogenation of acenaphthalene has been shown to be synthetically useful since the ring can easily be removed from the cluster by reaction with carbon monoxide.[26] Furthermore, the product obtained is different to that obtained using other (non-cluster mediated) routes as shown in Scheme 5.

Related chemistry has also been demonstrated with the polyaromatic acenthrylene system and the structure of $H_2Ru_3(CO)_7(\mu\text{-}\eta^1{:}\eta^5\text{-dihydroacenthrylene})$ has been established in the solid state (see Figure 7).

$Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^4\text{-acenaphthalene})$ reacts with stoichiometric amounts of trialkylsilanes with loss of CO and concomitant oxidative addition of the Si–H bond.[23] Under appropriate conditions, the same cluster catalyzes the

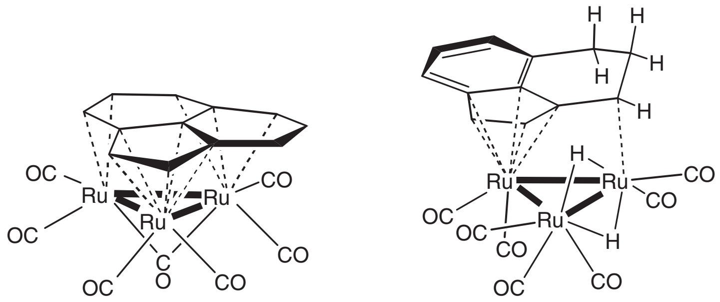
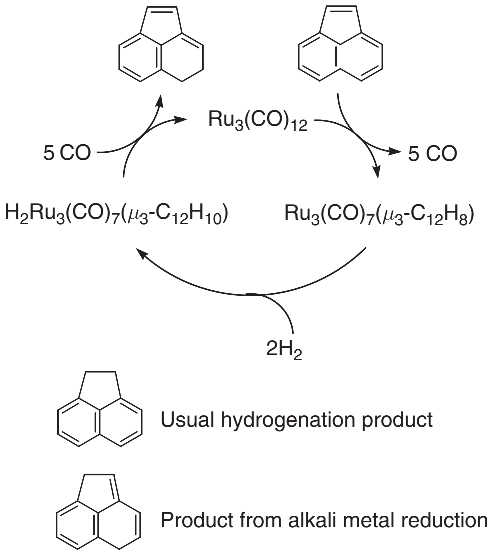


Figure 6 The structures of $Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^4\text{-acenaphthalene})$ and $Ru_3(\mu\text{-}H)_2(CO)_7(\mu\text{-}\eta^1{:}\eta^5\text{-4,5-dihydroacenaphthalene})$.



Scheme 5 Selective hydrogenation of acenaphthalene to 4,5-dihydroacenaphthalene using a cluster template.

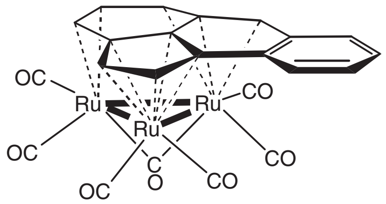


Figure 7 The structure of $H_2Ru_3(CO)_7(\mu\text{-}\eta^1{:}\eta^5\text{-dihydroacenthrylene})$.

hydrosilylation of olefins, acetylenes, ketones, and aldehydes, in some cases giving different regio- and stereoselectivities, as well as superior activities, to $RhCl(PPh_3)_3$. Catalytic amounts of $Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^4\text{-acenaphthalene})$ have also been shown to facilitate ring-opening polymerization reactions.

6.21.3.4 Fullerene Compounds

The first *hexahapto*-fullerene complex was formed in low yield via direct reaction of $Ru_3(CO)_{12}$ with C_{60} in refluxing hexane,[51] a synthesis later improved by using chlorobenzene as the solvent.[52] The product, $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$, features a Ru_3 triangular face bonded to a six-membered ring of the fullerene (Figure 8). C_{70} was found to react similarly to form $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})$ and $\{Ru_3(CO)_9\}_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})$ (see Figure 8).[53]

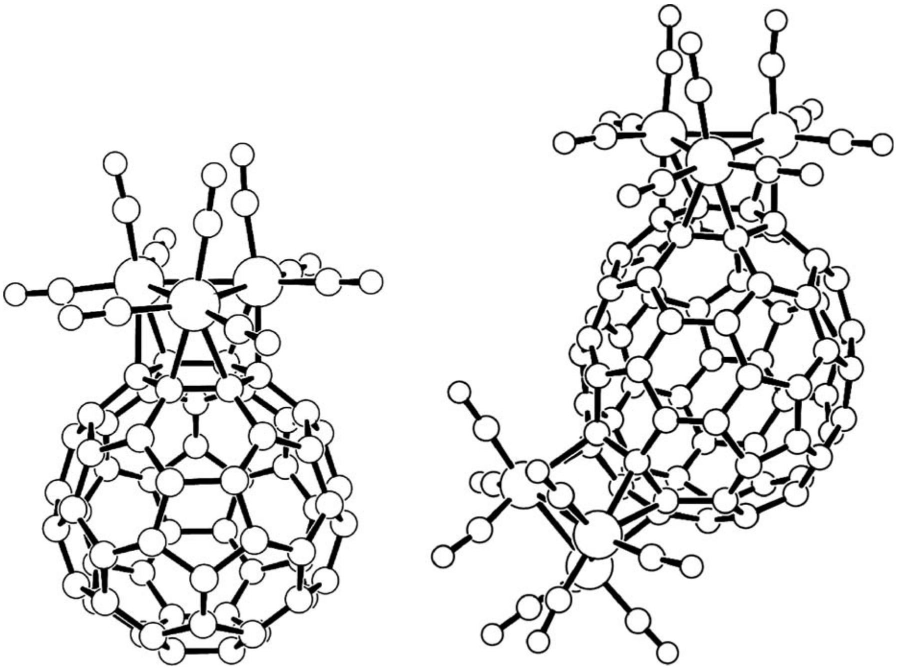


Figure 8 The molecular structures of $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ and $\{Ru_3(CO)_9\}_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}\mu_{3'}\text{-}\eta^{2'}{:}\eta^{2'}{:}\eta^{2'}\text{-}C_{70})$.

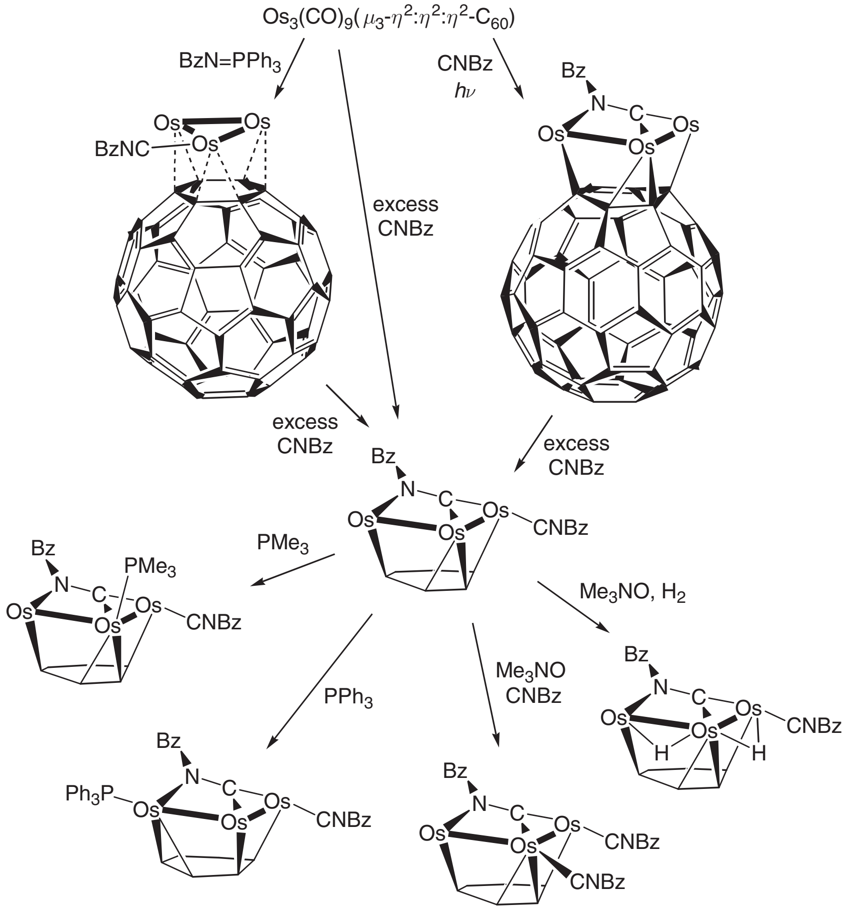
In all three structures, the Ru_3 triangle is located centrally over a six-membered carbon ring of the fullerene. The Ru_3 and C_6 planes are parallel and the C–C bond lengths alternate around the ring, with the Ru atoms positioned over the short C–C bonds. The alternation is not particularly marked for the C_{60} compound (1.43 Å vs. 1.47 Å) but is greater for the C_{70} compound (1.39/1.40 Å vs. 1.49/1.48 Å, two independent molecules in the unit cell).

$Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ may be prepared from $Os_3(CO)_{10}(NCMe)_2$ and C_{60} in refluxing chlorobenzene.[54] The phosphine-substituted clusters $Os_3(CO)_8(PPh_3)$ $(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{60})$[55] and $Os_3(CO)_{9-n}(PMe_3)_n(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$[56] ($n=1$–3) are readily accessible following decarbonylation of the parent carbonyl cluster with Me_3NO/MeCN. $Os_3(CO)_9$ $(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ is also reactive toward isocyanides and a relatively extensive chemistry of these derivatives has been developed (see Scheme 6).[57] Interestingly, the bonding mode of the C_{60} ligand is considerably changed in these derivatives, mostly due to the fact that one of the Os–Os bonds is cleaved during the reaction and the triangle of metal atoms opens out into a bent Os_3 configuration. The bonding changes to a $(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ mode, in which the C_6 ring assumes a boat shape, with sp^3-hybridized carbon atoms at bow and stern positions, which σ-bond to the two outside osmium atoms. The ring is 1,4-cyclohexadiene-like, with two of the C–C bonds having multiple bond character (1.44, 1.36 Å) and the other four exhibiting single bond character (average 1.52 Å). The longer of the C=C bonds is π-coordinated to the central Os atom, and the remaining C=C bond is uncoordinated. In one derivative, $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{60})$, the steric demands of the bulky phosphine induce a change in coordination of the six-membered ring to one that resembles a 1,3-cyclohexadiene, with the uncoordinated C=C bond next to a C=C bond coordinated to one of the terminal Os atoms.

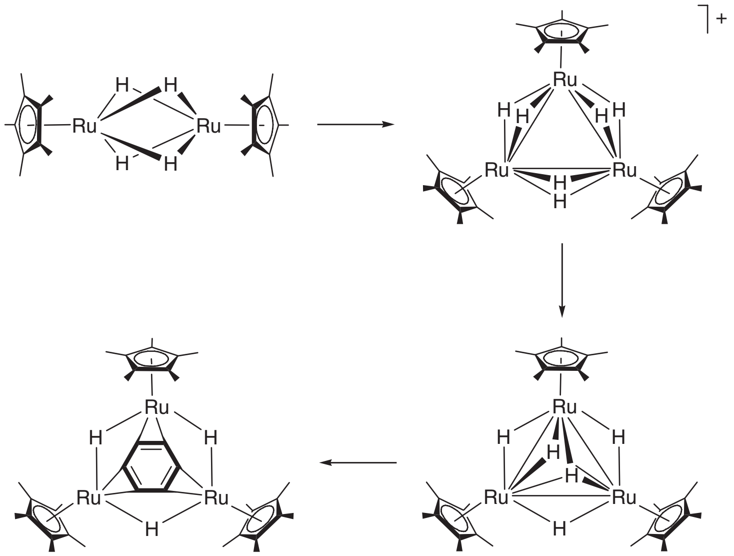
Self-assembled monolayers of an $Os_3(CO)_8\{CN(CH_2)_3Si(OEt)_3\}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ cluster on indium–tin oxide or gold surfaces have been shown to be electrochemically stable, being reducible to tetra-anionic species in their cyclic voltammograms.[58] Further derivatization through tethering a zinc porphyrin complex to the cluster generated a high-performance photovoltaic cell with potential applications in artificial photosynthesis.[59]

6.21.3.5 Other Systems

Suzuki has developed an elegant synthesis of a triruthenium cluster with a face-capping benzene ligand, viz. $H_3Ru_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, shown in Scheme 7.[24] The chemistry of this and related compounds has been explored in some detail and is described in COMC III, Section 6.7.2.2.



Scheme 6 Isocyanide derivatives of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (Bz = CH_2Ph).



Scheme 7

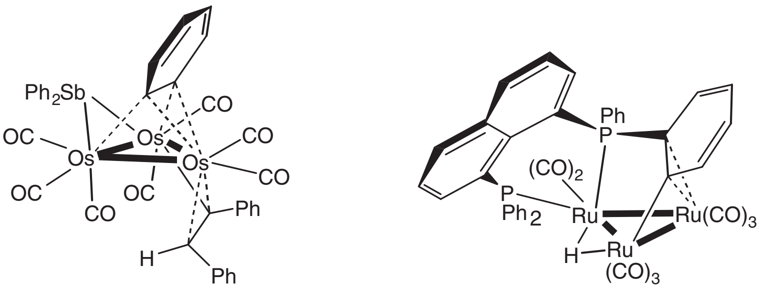


Figure 9 (left) $Os_3(CO)_7\{\mu\text{-}\eta^2\text{-}C(Ph)=CHPh\}(\mu\text{-}SbPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)$; (right) $Ru_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}2\text{-}(PPh_2)\text{-}1\text{-}((\eta^2\text{-}2\text{-}C_6H_4)PPh)\text{-naphthalene}\}$.

A number of benzyne cluster complexes have been prepared in the last dozen years. The bonding mode of the benzyne is "edge-on" with respect to the ligand, and the benzyne is usually positioned over an M_3 face (Figure 9 left).[60,60a] Benzyne ligands are typically derived by orthometallation of an EPh_3 ligand (E = P, As, Sb) and cleavage of one E–Ph bond. There are a number of examples of intermediate species in which the phenyl ring has been orthometallated but E–Ph cleavage has not yet occurred (Figure 9 right).[61,61a,61b]

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6.22
Trinuclear Clusters of Ru/Os: Compounds Containing M–C Bonds to Heteroatom Ligands

E Sappa, Universita del Piemonte Orientale, Alessandria, Italy

6.22.1 Introduction

During the last 10 years, a large number of triruthenium and triosmium clusters containing heteroatoms bonded through carbons to the metal frame have been synthesized. This makes it difficult to discuss all the compounds and give an exhaustive reference list in a limited number of pages. An effort has been made, however, to mention all the research groups working in the field, their scope, and the most significant literature reports. In some instances it was necessary to mention complexes containing heteroelements but not characterized by M–C–E bonds; in this case, only one reference (usually, the more recent) is given for each research group.

An ordering based in part on structural schemes and in part on synthetic approaches has been adopted. For example, common structural schemes are observed: (i) for complexes containing apical ligands; (ii) for complexes obtained from functionalized alkynes or acetylides (disposed in parallel or perpendicular fashion); and (iii) for pentagonal-bipyramidal structures. Common synthetic methods are, among others: (i) use of lightly ligated clusters as precursors; (ii) nucleophilic or electrophilic attack on coordinated ligands (in particular, activation of CO and methanol); and (iii) reactions of functionalized alkynes (in particular, alkynols and aminoalkynes). When more than one heteroelement is present in the complexes, the choice has been made considering the structure type or the synthetic methods. The literature of the period 1993–2004 and some articles that appeared in 2005 have been considered.

6.22.2 Group 16 Ligands

6.22.2.1 Ligands Bonded through Carbon and Oxygen

6.22.2.1.1 Triruthenium and triosmium complexes obtained from functionalized alkynes

The allylic cluster $(\mu\text{-H})Ru_3(CO)_8(PPh_3)\{\mu_3\text{-CHCHC(OH)}\}$ **1a** has been obtained from $(\mu\text{-H})Ru_3(CO)_9(\mu\text{-C}{\equiv}CH)$ upon treatment with $K[BHBu^t{}_3]$ and $[AuCl(PPh_3)]$.[1] The reactivity of the open allylic clusters $(\mu\text{-H})Ru_3(CO)_{9-n}(PPh_3)_n\{\mu_3\text{-}\eta^2\text{-XCCRCR}^1\}$ (X = OMe, Et_2N; R^1 = H, Me, EtO) has been studied; reactions with electrophiles and one-electron oxidation were described.[2]

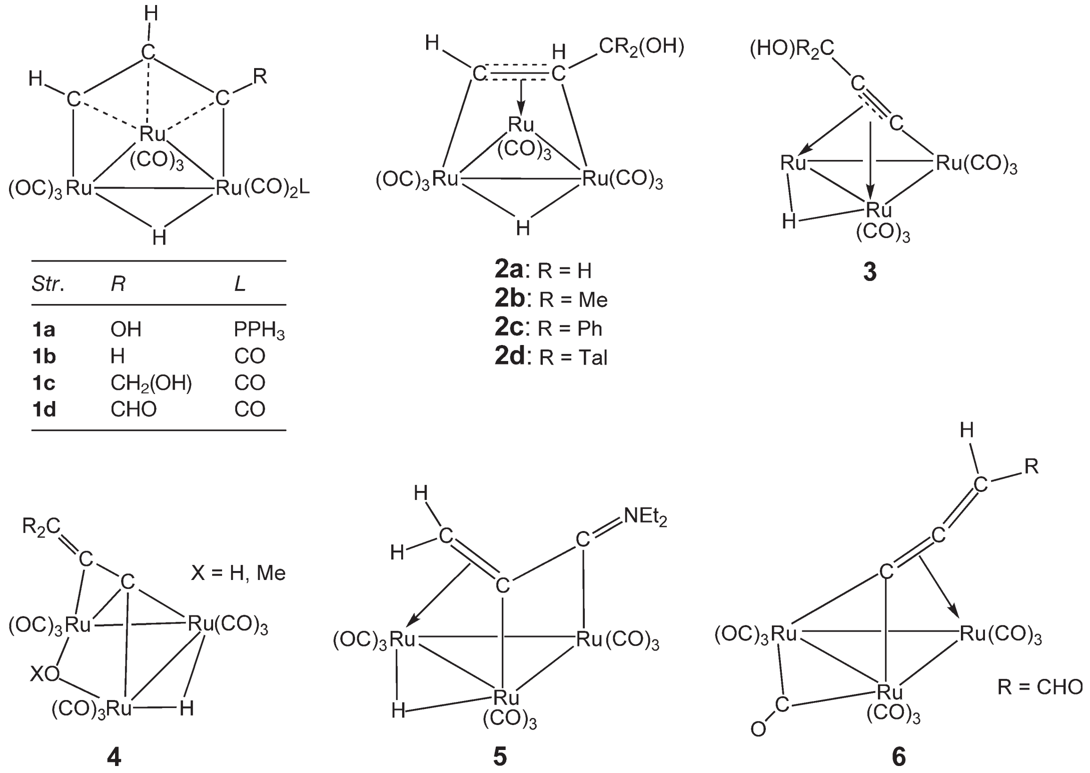
The reaction of the lightly ligated $Ru_3(CO)_{10}(NCMe)_2$ with alkynols leads to the clusters $Ru_3(CO)_9(\mu\text{-CO})\{HC{\equiv}CCR_2(OH)\}$ (**2**: R = H, Me, Ph, Tol), with an alkyne coordinated in parallel fashion;[3] under thermal conditions these undergo loss of CO and shift of hydrogen forming the hydrides $(\mu\text{-H})Ru_3(CO)_9\{C{\equiv}CCR_2(OH)\}$ **3**, with an acetylide bound in perpendicular fashion.[4] These are further protonated (with $HBF_4{\cdot}OMe_2$); the open allenylidene derivatives $(\mu\text{-H})(\mu\text{-OX})Ru_3(CO)_9(C{=}C{=}CPh_2)$ (**4**: X = H, Me) are obtained, together with the closed $(\mu\text{-H})_2Ru_3(CO)_9(C{=}C{=}CPh_2)$, which has lost the OH, presumably as water.

Simple thermal substitution of CO in the reaction of $Ru_3(CO)_{12}$ with hexa-2,4-diyne-1,6-diol leads to $Ru_3(CO)_9(\mu\text{-CO})\{(HO)CH_2C{\equiv}CC{\equiv}CCH_2(OH)\}$ with a parallel alkyne.[5] The acetylide complexes $(\mu\text{-H})Ru_3(CO)_9\{C{\equiv}CCR(OH)R^1\}$ (R = Me, R^1 = Me, Ph) and their dppm (dppm = bis(diphenylphosphino)-methane) derivatives are also obtained (in four optical isomers) via thermal substitution; ^1H and ^{13}C NMR fluxionality and hydration–dehydration reactions have been studied.[6] Dehydration leads to the vinylacetylene derivatives $(\mu\text{-H})Ru_3(CO)_7(dppm)(C{\equiv}CC{=}CH_2Ph)$, formed by loss of the OH group and of one hydrogen of the methyl substituent on the same carbon atom.[7]

In some instances, indeed, the functionalized alkynes react, losing (in part or totally) their functionalities both under thermal and under basic methanolic conditions. This happens, for example, when $Ru_3(CO)_{12}$ is reacted with diethylaminopropyne or with trimethylsilyl propargyl alcohol; the final product is the allylic derivative $(\mu\text{-H})Ru_3(CO)_9(HCCHCH)$ **1b**. Intermediate products are the hydride allylic clusters $(\mu\text{-H})Ru_3(CO)_9(H_2C{=}CC{=}NEt_2)$ **5** or $(\mu\text{-H})Ru_3(CO)_9\{HCCHCCH_2(OH)\}$ **1c**.[8] Similar behavior is observed when but-2-yn-1,4-diol is reacted with $Ru_3(CO)_{12}$;[9] the allylic $(\mu\text{-H})Ru_3(CO)_9\{HCCHC(CHO)\}$ **1d** is formed, whereas under basic conditions, the allenylidene $Ru_3(CO)_9(\mu\text{-CO})\{C{=}C{=}CH(CHO)\}$ **6** is obtained, along with the open $(\mu\text{-Cl})Ru_3(CO)_9(H_2CCHCH_2)$ isomeric with $(\mu\text{-Cl})Ru_3(CO)_9(H_3CCCH_2)$, described by Lavigne and co-workers (Figure 1).[10]

Contrasting with these results, the thermal reaction of but-3-yn-2-ol $[HC{\equiv}CCH(OH)CH_3]$ with $Ru_3(CO)_{12}$ leads to clusters containing four to seven ruthenium atoms where partial dehydrogenation of the coordinated ligands has occurred; interestingly, loss of hydrogen (presumably from the OH) results in the formation of acetyl groups (CH_3CO) bound only to the carbon atom chains, or in the formation of oxygen-containing metallacyclic structures.[11]

The reactions of $Ru_3(CO)_{12}$ with 1-ethynylcyclopentanol, 1-ethynylcycloheptanol, and 1-ethynylcyclooctanol lead mostly to substituted hexa-ruthenium clusters; only for 1-ethynylcyclopentanol (ligand **a**), the trinuclear cluster $Ru_3(CO)_9(\mu\text{-CO})\{HC_2(C_5H_6)(OH)\}$ **7** with a parallel alkyne, was obtained.[12] In contrast, from the reaction of $Ru_3(CO)_{12}$ with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne (ligand **b**), four heavily substituted trinuclear derivatives were obtained, namely the two isomers $Ru_3(CO)_7(C_{28}H_{34}O_3)$ **8a and 8b**, which react with an excess of the ligand to form $Ru_3(CO)_5(C_{43}H_{49}O_5)$ **9** and the open cluster $Ru_3(CO)_8(C_{28}H_{32}O_2)$ **10**. The same ligand reacts with $Ru_3(CO)_{10}(NCMe)_2$ forming the cluster $Ru_3(CO)_9(\mu\text{-CO})(C_{14}H_{18}O_2)$ **11**, containing only one molecule of the ligand, coordinated in parallel fashion, and using only one of the C≡C bonds.[13] Finally, the thermal reaction of $Ru_3(CO)_{12}$ with 9-ethynylfluoren-9-ol (ligand **c**) leads to tetra- and hexa-ruthenium clusters and to two trinuclear complexes



Str.	R	L
1a	OH	PPH_3
1b	H	CO
1c	$CH_2(OH)$	CO
1d	CHO	CO

Figure 1

(μ-H)$Ru_3(CO)_9\{C{\equiv}C(C_{13}H_{19})\}$ **12** with a perpendicular acetylide and the closed, disubstituted $Ru_3(CO)_7$(μ-C)$\{(HOC_{13}H_8)CCHC(C_{13}H_8OH)CH\}$ **13** (Figure 2).[14]

The lightly ligated $Os_3(CO)_{10}(NCMe)_2$ reacts with but-3-yn-1-ol ($HC{\equiv}CCH_2CH_2OH$) under thermal conditions, yielding the complex $Os_3(CO)_9$(μ-CO)($HC{\equiv}CCH_2CH_2OH$) (parallel alkyne); it loses CO and gives the perpendicular acetylide complex (μ-H)$Os_3(CO)_9(C{\equiv}CCH_2CH_2OH)$, which under thermal conditions isomerizes to the dihydrofuran derivative (μ-H)$_2Os_3(CO)_9(C{=}CCH_2CH_2O)$ **14**.[15] Similar behavior has been observed for functionalized diynes; thus, 2,4-hexadiyne-1,6-diol reacts with $H_2Os_3(CO)_{10}$ forming the complex (μ-H)$Os_3(CO)_{10}(OCH{=}CHC{=}CCH_2OH)$ **15**, with the heterocyclic ligand bridging the same cluster edge as the hydride.[16] Other diynes behave in the same way, giving, for example, the complex (μ-H)$Os_3(CO)_{10}\{PhC{=}CHC{=}C(O)CPh\}$ **16a**.[17] Finally, the reaction of $H_2Os_3(CO)_9(PR_3)$ with 2,4-hexadiyne-1,6-diol results in the formation of (μ-H)$Os_3(CO)_8(PR_3)(H_3CCC{=}CHCH{=}CO)$ **16b** and $Os_3(CO)_8(PR_3)(H_3CCC{=}CHCH{=}CO)$ **17** and of complex **18**.[18] The structures of complexes **14–18** are given in Figure 3.

Among the functionalized alkynes which have been reacted with triruthenium and triosmium clusters, there is 11-β-ethynylestradiol. The aim of the studies on these complexes was to obtain high-affinity markers and receptors for this estrogen, which plays an important role in breast cancer.[19,19a,19b] Complexes with the alkyne bound in parallel way or the acetylide bound perpendicularly were obtained.

6.22.2.1.2 Complexes containing ligands with methoxycarbonyl (or acetato) groups

Several ruthenium clusters have been obtained, starting from alkynes bearing COOMe substituents. Examples are: (μ-H)$_2Ru_3(CO)_7$(μ-dppm)$\{C_2(COOMe)_2\}$ with a parallel alkyne,[20] and the spiked triangular, $Cp^*{}_2Ru_4(CO)_5$(μ-CO)$\{C_4(COOMe)_2\}$ (Cp^* = pentamethylcyclopentadienyl).[21] The COOMe groups may interact with the cluster metals using the oxygen atom as in $Ru_3(CO)_6$(μ-dppm)$\{O{=}C(OMe)CC(CO_2Me)C(Ph)C(Ph)\}$ **19** and in the isomers $Ru_3(CO)_7$(μ-dppm)$\{O{=}C(OMe)CC(H)C(Ph)C(Ph)\}$ **20a** and **20b** (Figure 4).[22] A structure comparable

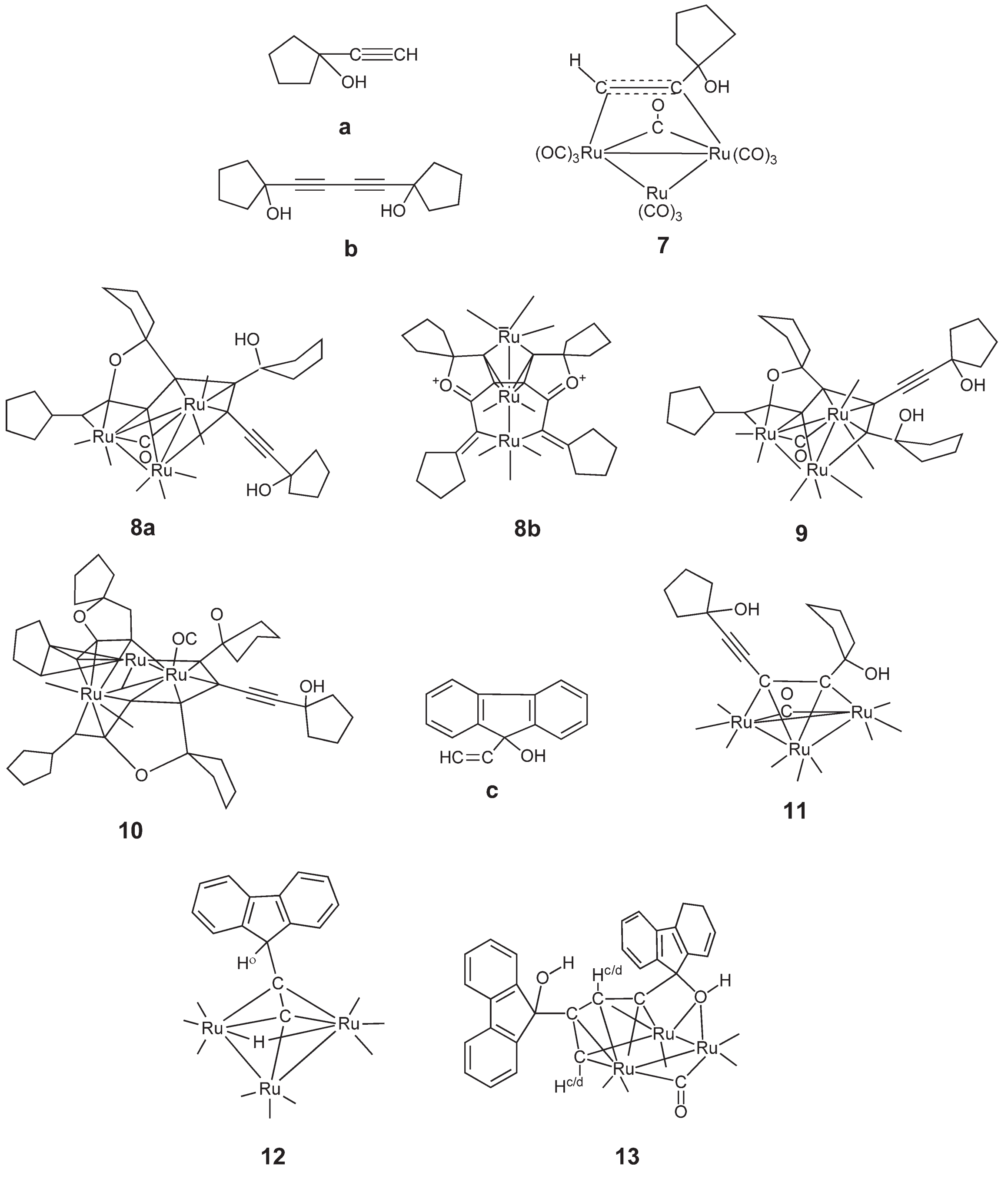
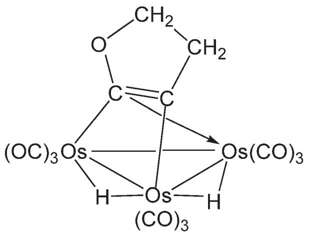


Figure 2

with those of **20** had been found earlier for $Ru_3(CO)_6(\mu\text{-dppm})\{O{=}C(OMe)C_4(COOMe)_3\}$.[23] Di-ruthenium[24] and penta-ruthenium[25] complexes containing alkynes bearing COOMe substituents have also been obtained.

Insertion of CO into Ru–C bonds has been reported by Vahrenkamp and co-workers in the reactions of $Ru_3(CO)_{12}$ with phosphorus ylides [$Ph_3P{=}CH_2$, $Ph_3P{=}CH{-}C({=}O)Me$]: the hydrides $(\mu\text{-H})Ru_3(CO)_8L\{(PPh_3)(H)C{=}CO\}$ **21a–c**: L=CO, PPh_3), $(\mu\text{-H})Ru_3(CO)_9\{(PMe_3CC(OBu^t){=}O\}$, and $(\mu\text{-H})Ru_3(CO)_9\{(PPh_3)C_2C(OMe)\}$ with a parallel alkyne were obtained. Other reaction products are the dihydrides $(\mu\text{-H})_2Ru_3(CO)_8\{(C_6H_4)PPh_2CCR{=}O\}$ (**22**: R = H, Me, OEt), characterized by a *ortho*-metallated phenyl group (Figure 5).[26]



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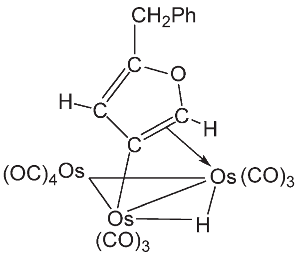
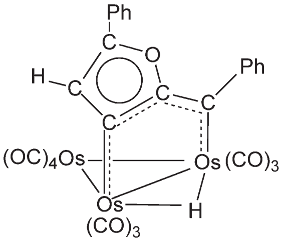
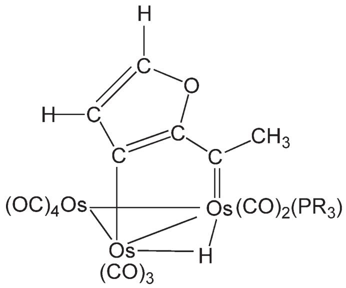


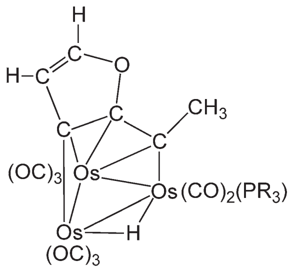
15



16a



16b



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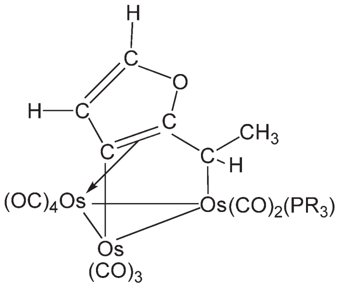
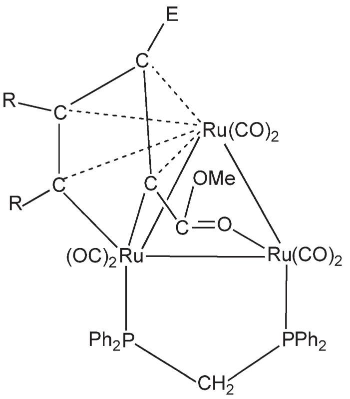


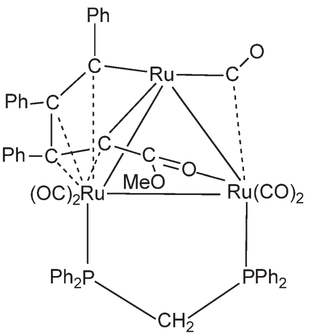
18

Figure 3

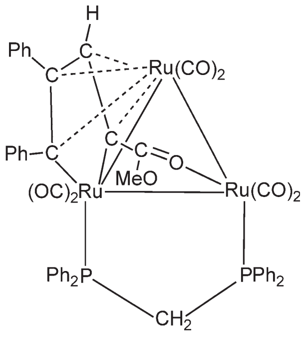


E = COOMe, H
R = Ph, COOMe

19

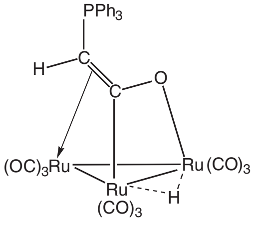


20a

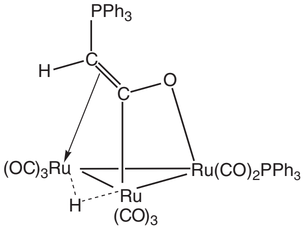


20b

Figure 4



21a



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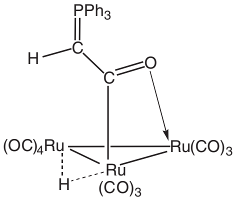
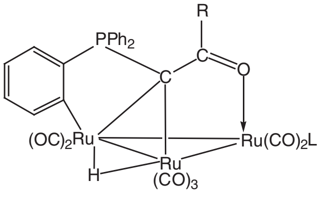


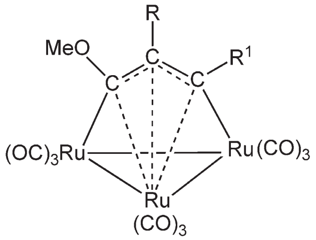
21c



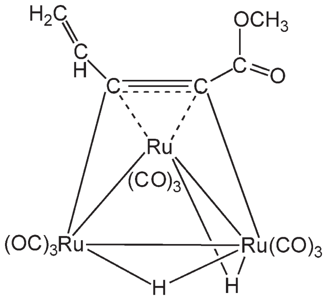
L = CO, PPh_3
R = H, CH_3, OEt, OBu^t

22

Figure 5



23



24

R	*R*^{1}
Me, Ph, CH$_2$OPh	C$\equiv$CR
C$\equiv$CR	Me, Ph, CH$_2$OPh
Ph	CH=CHPh
CH=CHPh	Ph

Figure 6

The reaction of the methoxymethylidyne-bridged clusters (μ-H)Ru$_3$(CO)$_{10}$(μ-COMe) and H$_3$Ru$_3$(CO)$_9$(μ_3-COMe) with the diynes RC$\equiv$CC$\equiv$CR (R = Me, Ph, CH$_2$OPh) leads to the allylic hydrides (μ-H)Ru$_3$(CO)$_9${(MeO)CCRC(C$\equiv$ CR^1)}, (μ-H)Ru$_3$(CO)$_9${(MeO)CCPhC(CH=CHPh)}, and (μ-H)Ru$_3$(CO)$_9${(MeO)CC(CH=CHPh)CPh} (complexes 23).[27]

The reaction of Ru$_3$(CO)$_{12}$ with 1,4-dichloro-but-2-yne in CH$_3$OH/KOH solution leads to the loss of chlorine and formation of the allylic (μ-H)Ru$_3$(CO)$_9$(MeCCHCH) and of (μ-H)$_2$Ru$_3$(CO)$_9${H$_2$C=C(H)C$\equiv$CC(=O)OCH$_3$} 24, containing an acetate substituent.[28] The formation of this ligand requires the activation of CO and methanol, a process frequently observed under basic methanolic conditions (Figure 6).

The addition of OMe$^-$ to cluster-coordinated CO has been used in the electrospray spectrometry of metal carbonyl complexes.[29] Heterometallic clusters such as Cp*Fe(CO)(μ-CO)$_2$Ru$_2$(CO)$_4$(μ-H){μ-MeC(COO)Cl} have been obtained upon carbonyl substitution with MeC(Cl)HCOOH on the tetra-heterometallic precursor.[30] An efficient synthetic method for Ru$_3$(CO)$_{12}$ starting from ruthenium dioxide hydrate has been reported;[31] in the presence of formic or acetic acid, carboxylate complexes are obtained. These favor the reductive carbonylation of nitrobenzene to aniline and *N*,*N*′-diphenylurea.

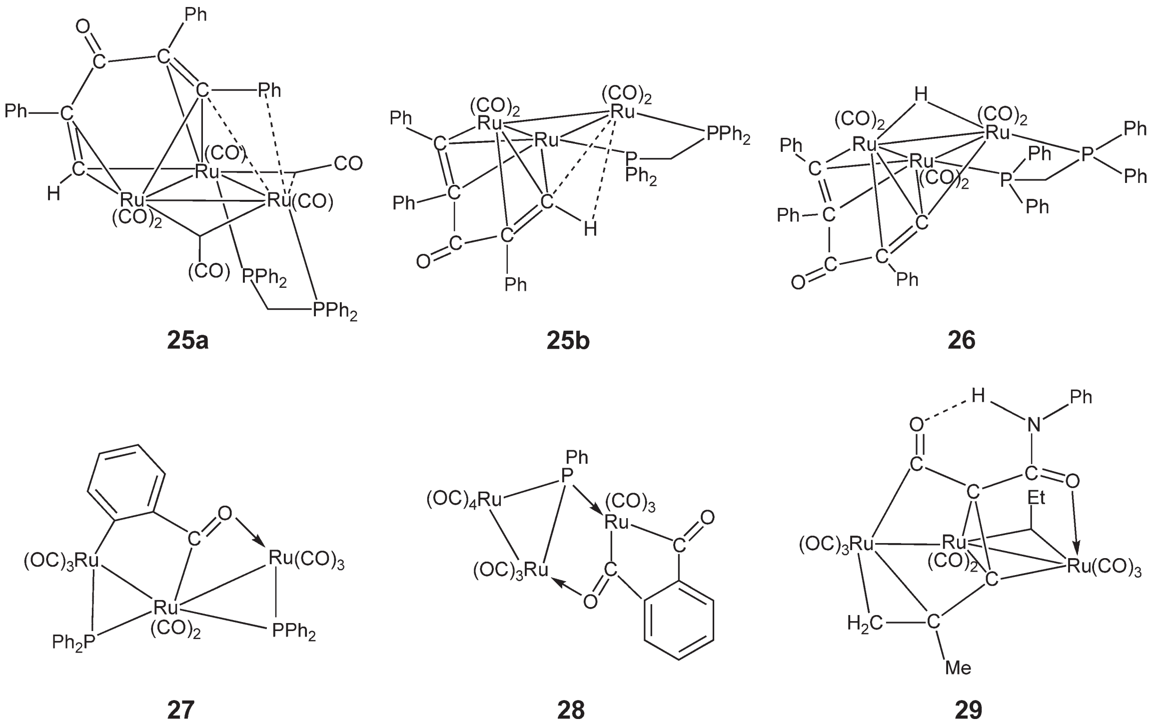
Triosmium derivatives have been synthesized in smaller numbers with respect to ruthenium. An early example is the ethoxy-containing triosmium cluster (μ-OH)Os$_3$(CO)$_9$(μ-Et=O)(PPh$_2$C$\equiv$CPr^i).[32] Other examples are the heterometallic clusters Cp*WOs$_3$(CO)$_{11}$(C$\equiv$CCH$_2$OMe)[33] and Rh$_2$Os$_2$(CO)$_7$(μ-CO)$_2${H$_2$C=CHCH$_2$(COO)}$_2$.[34]

6.22.2.1.3 Complexes obtained upon CO insertion into M–C bonds

Insertion of CO into M–C bonds is a common process in the chemistry of the cluster carbonyls of the iron triad. Examples are: (i) the spiked triangular Ru$_4$(CO)$_9$(μ-CO)$_2$(tmeda)(HCCHCO) (tmeda = tetramethylethylenediamine);[35] (ii) the open Ru$_3$(CO)$_6$(μ-CO)(μ-dppm){C(SiMe$_3$)=C(C$\equiv$CSiMe$_3$)C(=CPh)C(=CPh)C(O)};[36] (iii) the open, pentanuclear {CpW(CO)$_2$}Ru$_3$(CO)$_8$[O=CHCCC(=O)CHCC$\equiv$C{CpW(CO)$_3$}C];[37] and the electronically unsaturated Ru$_3$(CO)$_7$(μ-PPh$_2$){Ru(CO)$_4$}{O=CC(PPh$_2$)CPhCCPh} obtained starting from Ru$_2$(CO)$_4$(μ-PPh$_2$)(C$\equiv$CPh).[38]

CO insertion was also observed during homogeneous catalytic reactions: this is the case of Ru$_3$(CO)$_8$(μ-CO)(μ-dppm)(C$_2$Ph$_2$) (parallel alkyne) which loses CO to form Ru$_3$(CO)$_7$(μ-dppm)(C$_2$Ph$_2$) (perpendicular alkyne).[39,39a] The latter reacts with phenylacetylene forming two “flyover” compounds,[40] the isomeric Ru$_3$(CO)$_6$(dppm){HCCPhC(O)PhCCPh}, 25a and 25b, which undergo C–H activation forming the flyover (μ-H)Ru$_3$(CO)$_6$(dppm){CCPhC(O)PhCCPh} 26 or, under CO pressure, decompose into the binuclear flyover Ru$_2$(CO)$_6${HCCPhC(O)CPhCPh}.[41]

Finally, the open clusters Ru$_3$(CO)$_8$(μ-PPh$_2$)$_2$(C$_6$H$_4$CO) 27 and Ru$_3$(CO)$_{10}$(μ_3-PPh){C$_6$H$_4$(CO)$_2$} 28 have been obtained, respectively, from the benzyne derivatives Ru$_3$(CO)$_7$(μ-PPh$_2$)$_2$(C$_6$H$_4$) or Ru$_4$(CO)$_{10}$(μ-CO)(μ_4-PPh)(C$_6$H$_4$) under CO.[42,42a,42b] These complexes were also formed during homogeneous[43] or solid-gas catalytic hydrogenation reactions.[44,44a]



25a **25b** **26**

27 **28** **29**

Figure 7

The heterometallic complex $\{Cp^*W(O)_2\}\{CCCMeCH_2\}Ru_3(CO)_8(\mu_3\text{-}NPh)$ inserts CO and forms the open cluster $Ru_3(CO)_8(\mu\text{-}CO)\{H_2CCMeCCC(O)N(Ph)(H)\cdots(O)C\}$ **29** with a heteroatomic ring closed by an H···O hydrogen bond (Figure 7).[45]

During mechanistic studies on the hydrogenation of terminal alkynes with $H_2Os_3(CO)_{10}$ (using para-hydrogen as a probe), three metallacyclohexadienone products **30** were isolated together with the hydridic $(\mu\text{-}H)Os_3(CO)_8\text{-}\{Me(CH_2)_2C{=}CHC({=}O)H\}$ **31**.[46]

The reaction of $Os_3(CO)_{11}(NCMe)$ with 1,8-bis(ferrocenyl)octatetrayne yields, among other products, the hexanuclear cluster $Os_6(CO)_{21}\{FcCC{=}COCC({=}C)CC{\equiv}CFc\}$ **32** (Fc = ferrocenyl), containing an oxygenated cycle.[47] The thermal reaction of the same ligand with $H_2Os_3(CO)_{10}$ gives the trinuclear $(\mu\text{-}H)Os_3(CO)_9\text{-}(FcCCHC_4COC{\equiv}CFc)$ **33** where hydrogenation of an alkyne group has also occurred. This cluster contains two cyclic ligands sharing a C–C bond and coordinated to the metals in the allylic fashion.[48]

Finally, the reaction of $Os_3(CO)_{10}(NCMe)_2$ with the diyne MeC_2C_2Me yields the trinuclear complexes $Os_3(CO)_9\{(MeC_2)CC(Me)C({=}O)C(Me)C(C_2Me)\}$ **34**, the metallacyclohexadienonic isomers **35a** and **35b** $Os_3(CO)_8(\mu\text{-}CO)\{(MeC_2)CCMeCOC(C_2Me){=}CMe\}$, and the dimeric $\{Os_3(CO)_9(\mu\text{-}CO)\}_2\{(MeC_2)\text{-}CCMeCOC({=}CMe)CC{=}CMe\}$ **36** (Figure 8).[49]

6.22.2.1.4 Hydration–dehydration reactions of alkynols promoted by silica or alumina

Hydration–dehydration reactions are quite common for alkynol-substituted clusters.[7,50,50a] The reactions are usually favored or promoted by chromatographic supports such as alumina or silica. For example, the thermal reactions of $Ru_3(CO)_{10}(NCMe)_2$ with alkynols lead first to complexes $Ru_3(CO)_9(\mu\text{-}CO)\{HC{\equiv}CCRR^1(OH)\}$ ($R = R^1 = H$, Me, Ph; R = Ph, R^1 = H, Me) with a parallel alkyne, which isomerizes thermally or in the presence of Al_2O_3 into the hydridic $(\mu\text{-}H)Ru_3(CO)_9\{C{\equiv}CCRR^1(OH)\}$. The latter, upon protonation, loses water forming complexes containing ene-yne or allenylidene ligands.[51] Similar reactions (in particular dehydration) may also be promoted by silica.[52]

The reactions of $(\mu\text{-}H)Ru_3(CO)_8(CNMe)(C{\equiv}CBu^t)$ with $HC{\equiv}CCPh_2(OH)$ or $PhC{\equiv}CCPh_2OH$ lead to the isomeric $Ru_3(CO)_6\{Bu^tCCC(CPh_2OH)CH_2\}\{HCCHC(O)CHCH\}$ and $Ru_3(CO)_6\{Bu^tCCCHCH(CPh_2OH)\}\{HCCHC(O)\text{-}CHCH\}$ **37a**, **37b**, containing a metallacyclic oxygenated ring.[53] Previous work had shown that the ring is formed upon

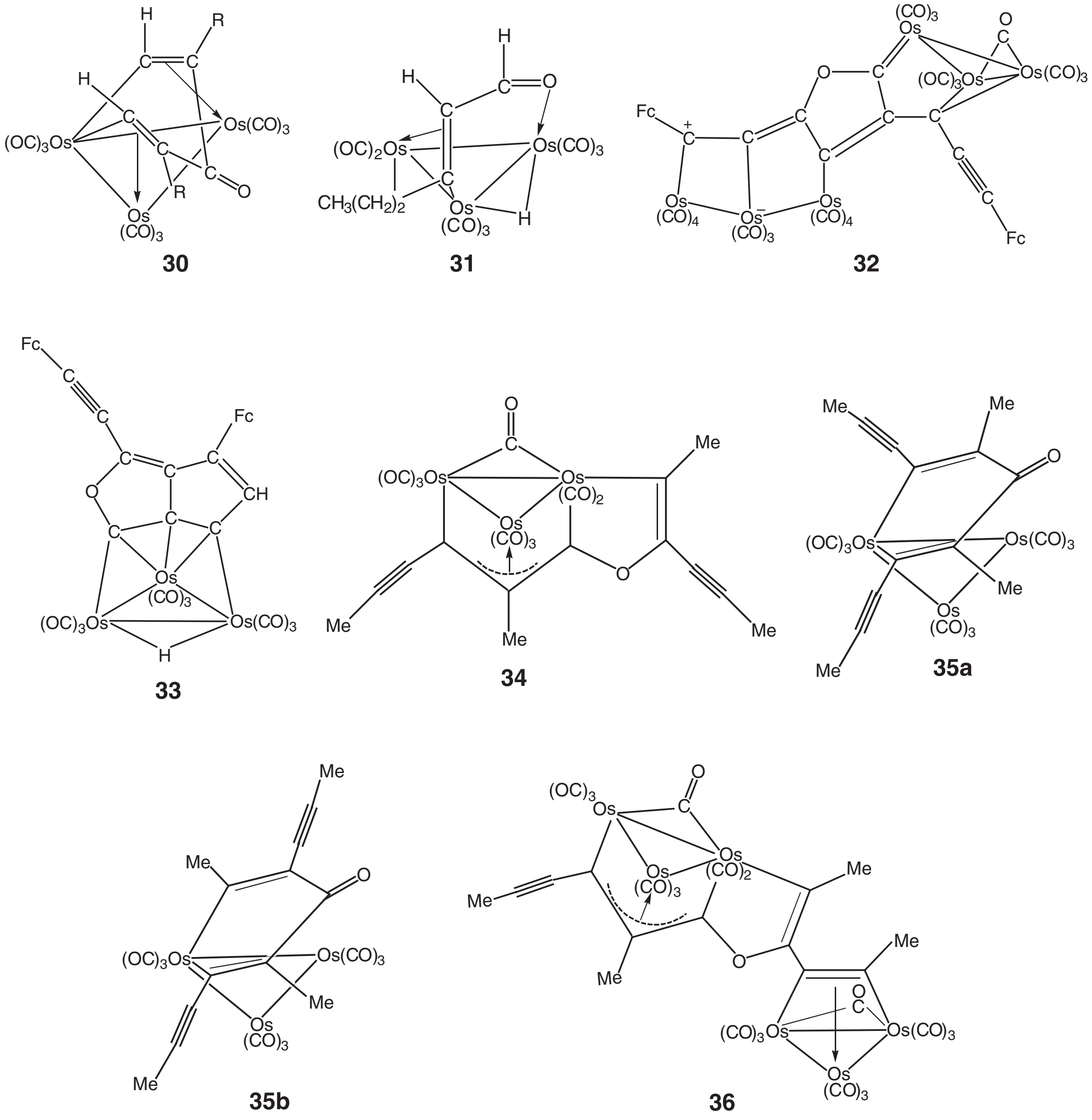


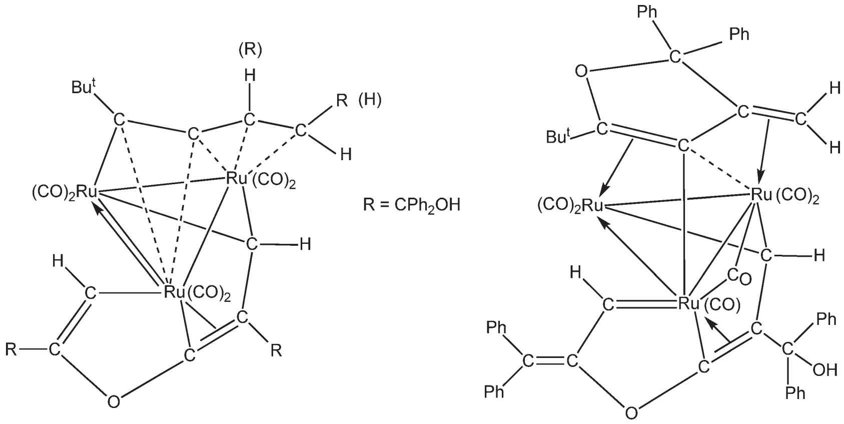
Figure 8

insertion of a cluster-bound CO into Ru–C bonds.[54] Dehydration of the isomers occurs on silica gel to form the new complex $Ru_3(CO)_5(\mu\text{-}CO)(CCBu^tOCPh_2CCH)\{CHC(CPh_2OH)COC(CPh_2)CH\}$ 38 (Figure 9).

To our knowledge, there are no recent examples for hydration–dehydration processes involving osmium. However, the reactions of $Os_3(CO)_{10}(NCMe)_2$ with $HSi(OR)_3$ (R = Me, Et) lead to the trinuclear clusters $(\mu\text{-}H)Os_3(CO)_9\{\mu\text{-}(RO)_2SiOR\}$ and $(\mu\text{-}H)Os_3(CO)_9\{\mu\text{-}(RO)_2Si(OR)_2\}$, which could represent models for the interaction of metal clusters with silica.[55] Similar reactions were performed by Ugo and co-workers during their work on "surface organometallic chemistry".[56]

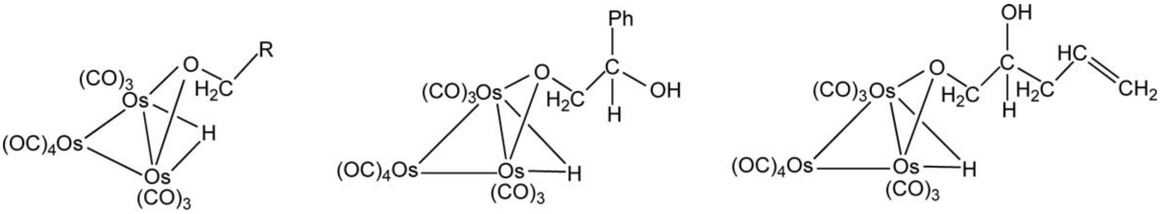
6.22.2.1.5 Osmium derivatives obtained from oxygenated ligands

The reactions of $(\mu\text{-}H)(\mu\text{-}OH)Os_3(CO)_{10}$ with glycols lead to $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OCH_2CH_2OH)$ 39a, which undergoes reactions with benzoyl chloride, PhMgBr, partial oxidation, or allylation giving, respectively,



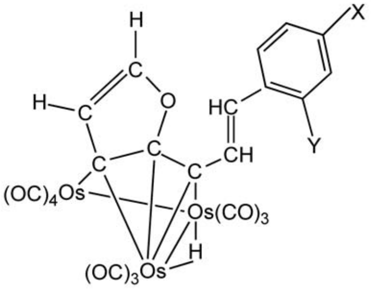
37a,b **38**

Figure 9



39 **40** **41**

39a: R = CH$_2$OH
39b: R = CH$_2$OCOPh
39c: R = CHO



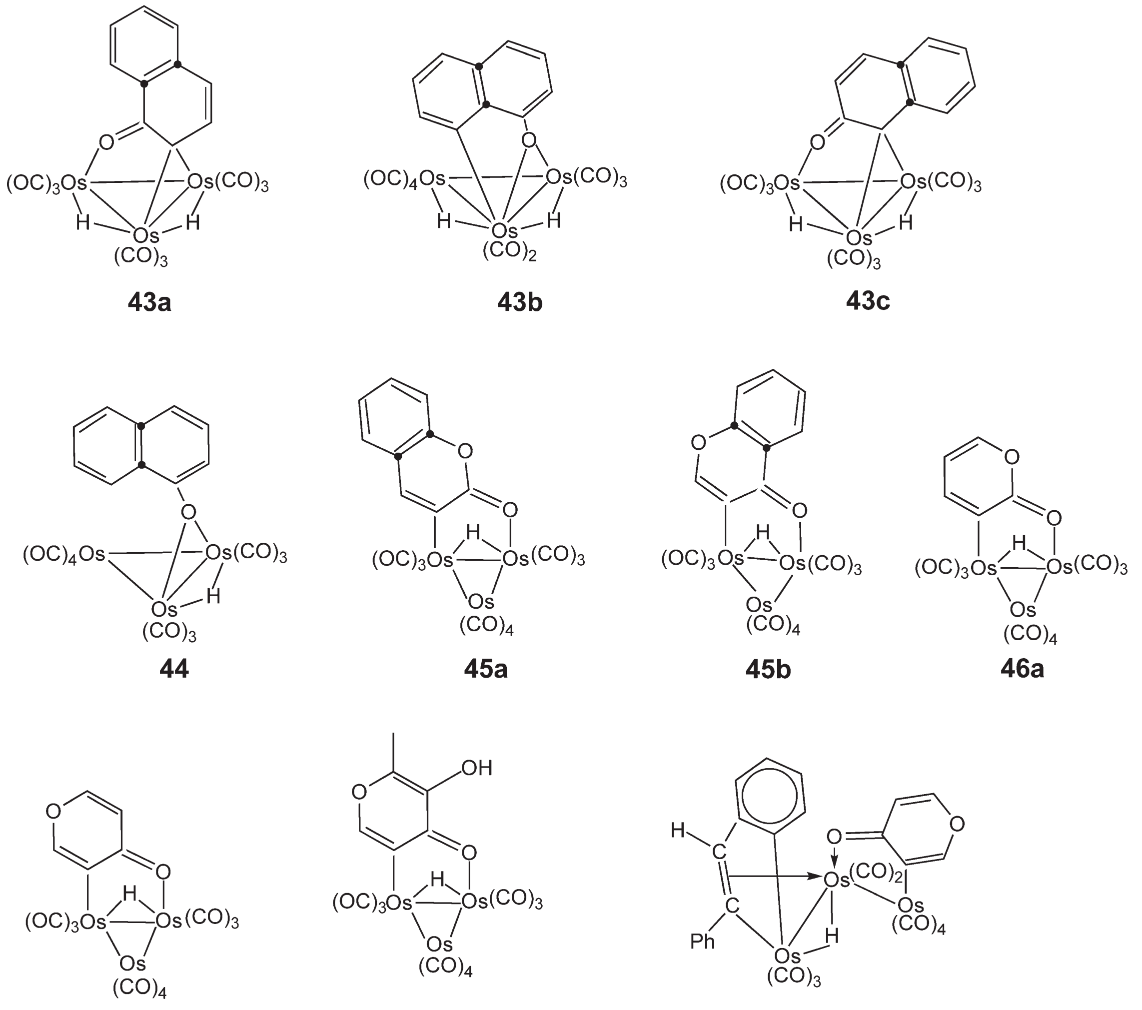
42

Figure 10

(μ-H)Os$_3$(CO)$_{10}${μ-OCH$_2$CH$_2$OC(O)Ph} **39b**, (μ-H)Os$_3$(CO)$_{10}${μ-OCH$_2$CH(OH)Ph} **40**, (μ-H)Os$_3$(CO)$_{10}$(μ-OCH$_2$CHO) **39c** and (μ-H)Os$_3$(CO)$_{10}${μ-OCH$_2$CH(OH)CH$_2$CH=CH$_2$} **41**.[57]

In the reaction of (μ-H)Os$_3$(CO)$_{10}$(OC$_4$H$_2$CCH$_3$) **16b** with aromatic aldehydes, an unusual C–H bond activation occurs along with aldol condensation to form the new carbenic complexes (μ-H)Os$_3$(CO)$_{10}${OC$_4$H$_2$CCH=CHC$_6$H$_4$XY} (X or Y, alternatively = H, NO$_2$, OH) **42** (Figure 10).[58]

The oxidative addition of furan to a triosmium cluster had already been reported;[59] more recently, the reaction of (μ-H)(μ-OH)Os$_3$(CO)$_{10}$ with naphthols has given hydride clusters **43a–c**, and **44** with the naphthol ligand acting as a



43a **43b** **43c**

44 **45a** **45b** **46a**

46b **47** **48**

Figure 11

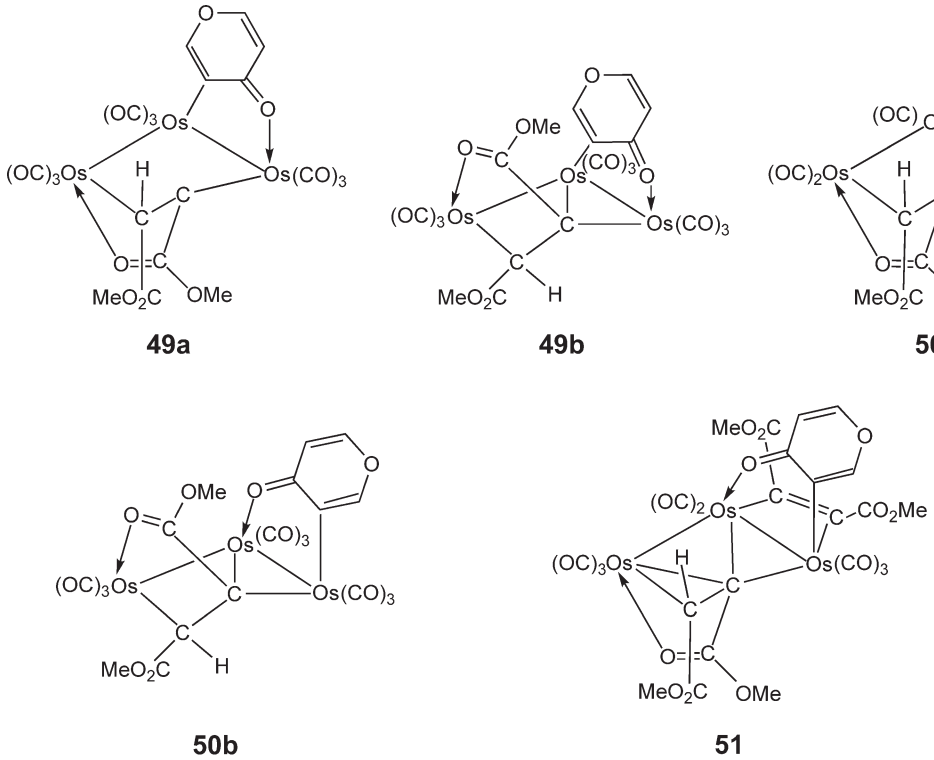
bridge through the oxygen atom, or bonded through a C═O and the aromatic ring.[60] Pyrones also react with $Os_3(CO)_{10}(NCMe)_2$ affording complexes **45a**, **45b**, **46**, and **47**.[61] One of these, (μ-H)$Os_3(CO)_{10}(C_5H_3O_2)$ **46**, reacted with alkynes; Os–Os bond cleavage occurs to form open trinuclear (such as **48**) (Figure 11) and binuclear clusters bearing the alkyne on the opposite side of the coordinated pyrone. In addition, the alkynes may displace the pyrone ligands forming open or closed trinuclear disubstituted clusters.[62] (μ-H)$Os_3(CO)_{10}(C_5H_3O_2)$ **46** reacts photochemically with dimethyl acetylenedicarboxylate forming the open isomeric clusters **49a**, **49b**, **50a**, and **50b** and the disubstituted complex **51** (Figure 12).[63]

Last, but not least, catalytic isomerization of *N*-allylic substrates occurs on the chiral triosmium clusters (μ-H)(μ-O═CNRR^1)$Os_3(CO)_{10}$.[64] The full catalytic cycle shown in Scheme 1 below and involving structures (**A–D**), in which only one osmium atom acts as the reactive site, has been proposed.

6.22.2.2 Ligands Bonded through Carbon and Sulfur

6.22.2.2.1 Triruthenium complexes containing capping chalcogens

Triruthenium clusters with sulfur-containing organic ligands are relatively in small number, when compared with the many derivatives containing only sulfur. The open bicapped clusters (μ_3-E)$_2$$Ru_3(CO)_7$($\mu$-dppm) (E = S, Se) and



49a **49b** **50a**

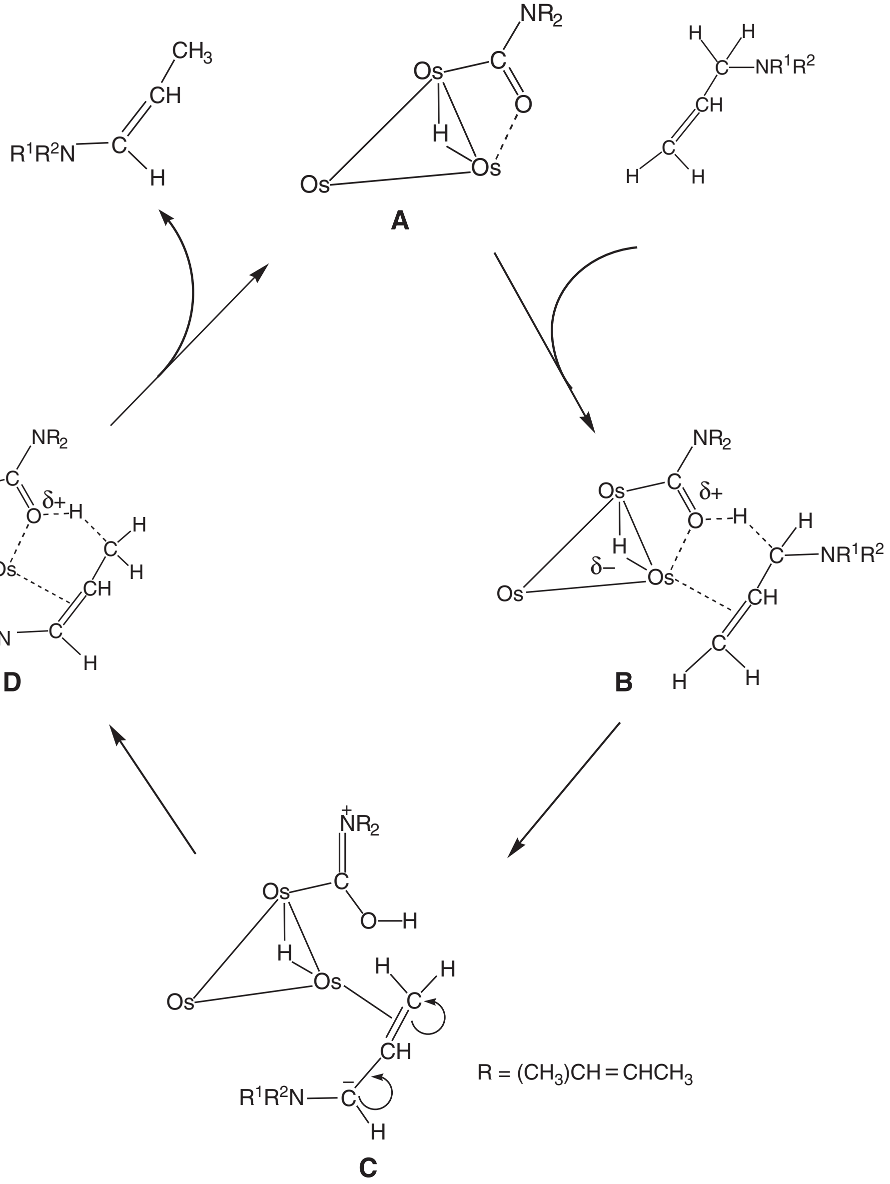
50b **51**

Figure 12

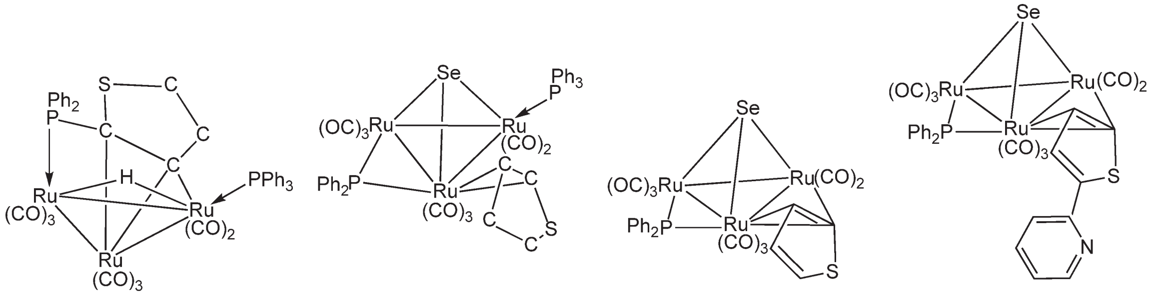
related compounds have been described,[65] and their chemistry has been extensively studied.[66] In two cases, the reactivity of these clusters leads to complexes with Ru–C–S bonds: these are the isomeric diphenyl-2-thienylphosphine derivatives $Ru_3(\mu\text{-Se})(\mu\text{-PPh}_2)(C_4H_3S)(CO)_6\{P(C_4H_3S)Ph_2\}$, **52a** and **52b**,[67,68] and $Ru_3(\mu\text{-Se})(\mu\text{-PPh}_2)(\mu\text{-pyth})(CO)_6\{P(pyth)Ph_2\}$ [pyth = 5-(2-pyridyl)-2-thienyl)], **53a** and **53b** (Figure 13).[69] Some clusters capped with selenium have been used in the homogeneous catalytic hydrogenation of diphenylacetylene. Contrasting with the expected behavior, cluster fragmentation was observed.[70] The optical limiting properties of triruthenium clusters with capping sulfur and phosphine ligands have also been studied.[71]

Hidai and co-workers have developed the synthesis of binuclear complexes with SR bridges and organic substituents (including alkynols),[72,72a] and of trinuclear clusters such as $(Cp^*Ru)_3(\mu_3\text{-Cl})(\mu_3\text{-S})$,[73,73a] which are the precursors of $(Cp^*Ru)_3(\mu_3\text{-SPr}^i)(\mu_3\text{-S})$ **54**, and of the metallacyclic $(Cp^*Ru)_2\{(\mu_2\text{-S})CMeC(COOMe)CMe\text{-}C(COOMe)\}$.[74,74a] The trihydride borylene complexes $(Cp^*Ru)_3(\mu\text{-H})(\mu_3\text{-BX})$ (X = H, CN,OMe,OEt) react with benzothiophene, affording the complexes $(Cp^*Ru)_3(\mu\text{-H})(\mu_3\text{-BH})\{S(C_6H_4)CH{=}CH\}$ **55** and $(Cp^*Ru)_3(\mu\text{-H})_3\{S(C_6H_4)CH{=}CH\}$ **56**, which isomerizes into complex **57** (Figure 14).[75]

The trimer $(CpRu)_3(\mu_3\text{-S})_2(\mu\text{-SCH}_2CH{=}CH_2)$ **58** is obtained upon condensation of a cyclopentadienyl ruthenium monomer containing the same organic ligand.[76] The reaction of 2-(diphenylphosphanyl)thiophenol ($HSC_6H_4PPh_2$) with $Ru_3(CO)_{12}$ leads, among other complexes, to the hydridic $(\mu\text{-H})Ru_3(CO)_7(PPh_3)_2\{SC({=}NPh)({=}NHPh)\}$ **59**.[77] The asymmetric acetylenic thioethers $Pr^i{}_3SiC{\equiv}C\text{–}S\text{–}C{\equiv}CR$ (R = $SiMe_3$, H) react with $Ru_3(CO)_{12}$, initially forming the open clusters $Ru_3(CO)_9(C{\equiv}CR)(\mu_2\text{-SC}{\equiv}CR^1)$ and $Ru_3(CO)_9(\mu\text{-S})(RCCC{\equiv}CR^1)$, **60a** and **60b**.[78,78a] Upon heating, these undergo rearrangement to pentagonal-bipyramidal structures such as $Ru_3(CO)_6(\mu\text{-CO})_2(S)(CCC{\equiv}CSiPr^i{}_3)$ **61**. Thioethers containing ferrocenyl substituents behave in the same way and, in addition, give open triruthenium structures.[79] Other pentagonal-bipyramidal structures containing sulfur are also known.[80,80a,80b] A discussion of these structures and of their isolobal relationships is given in Ref. 40. Finally, alkylthio-alkynes $RC{\equiv}CSEt$ (R = Me, Ph) react with $Ru_3(CO)_{12}$, forming, among others, the open clusters $Ru_3(CO)_9(\mu\text{-SEt})(\mu_3\text{-C}{\equiv}CR)$ **62** and $Ru_3(CO)_7(\mu\text{-SEt})\{\mu_3\text{-EtSCC(CPh)CPhC(SEt)CPh}\}$ **63**.[81] The structures of complexes **58–63** are shown in Figure 15.

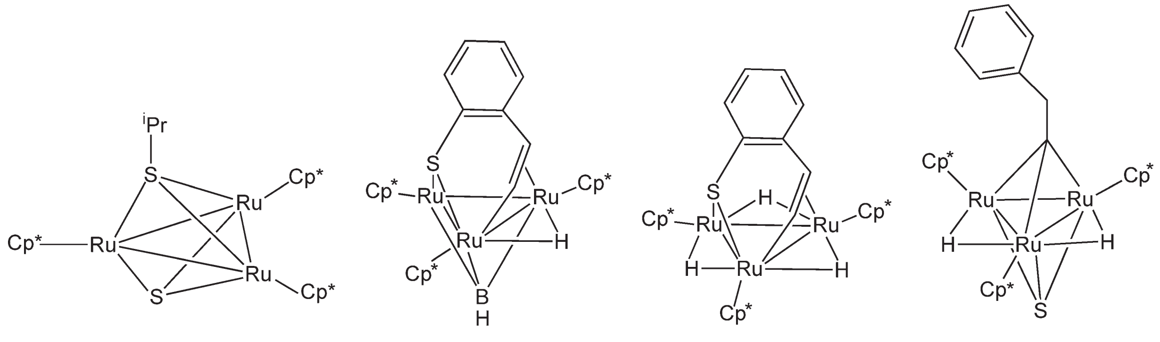


Scheme 1



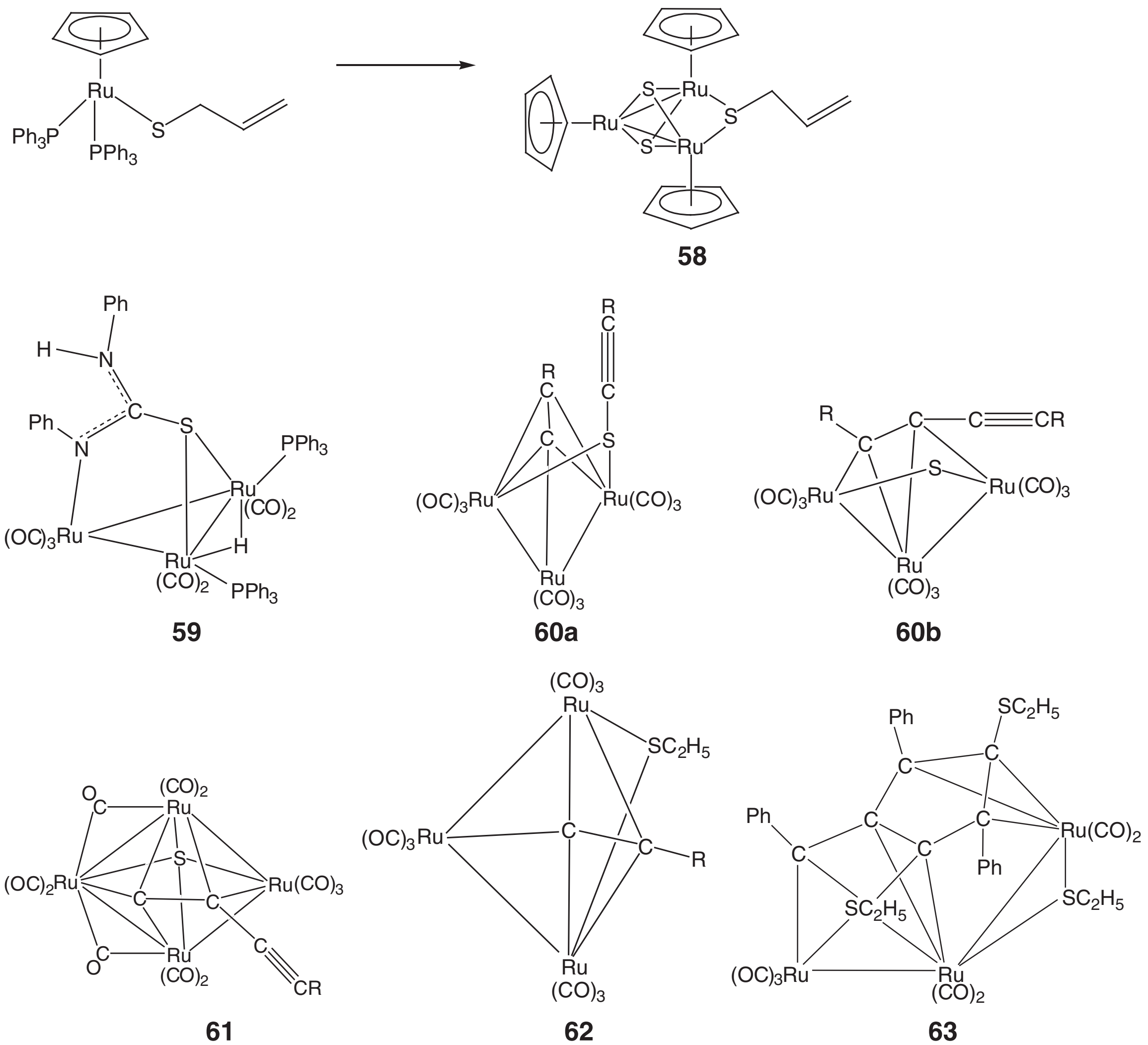
52a **52b** **53a** **53b**

Figure 13



54 **55** **56** **57**

Figure 14



58

59 **60a** **60b**

61 **62** **63**

Figure 15

6.22.2.2.2 Other ruthenium complexes

The reactions of sulfur-containing ferrocenyl ligands, e.g., $Cp_2(S)_3Fe$ with $\{Cp^*RuCl\}_4$ yield the complex $[Cp^*{}_3Ru_3(Cl)S_3\{Cp_2Fe\}]^+[FeCl_4]^-$.[82] Diruthenium complexes with sulfur-containing bridging ligands are homologs of the Fe-only hydrogenase active sites.[83]

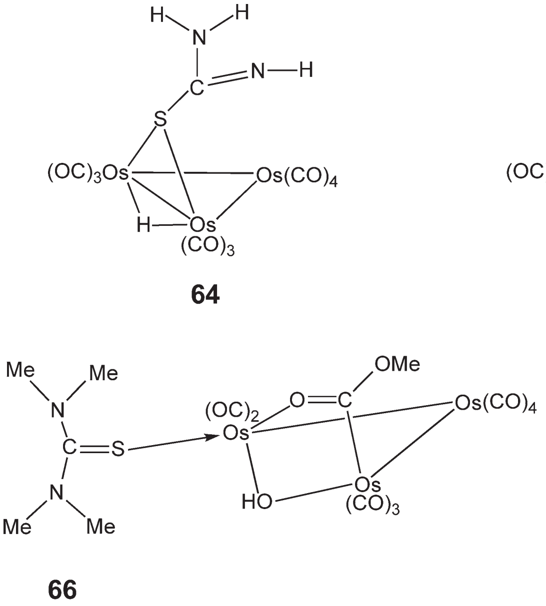
6.22.2.2.3 Triosmium complexes with thiols

$Os_3(CO)_{11}(NCMe)$ reacts with thiols, forming $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}SR)$ clusters through the intermediacy of $Os_3(CO)_{11}(HSR)$ complexes where the thiol is bound to one osmium atom through the S–H bond.[84] Thioureas also react with triosmium dodecacarbonyl;[85] closed (64, 65) and open (66, 67) clusters are formed (Figure 16).

$Os_3(CO)_{10}(NCMe)_2$ reacts with a thienyl-substituted diyne forming the closed $Os_3(CO)_9(\mu\text{-}CO)\{(C_4H_3S)C_2C_2(C_4H_3S)\}$ 68, where the diyne behaves as a parallel alkyne using only one triple bond, and the linear $Os_3(CO)_{11}\{(C_4H_3S)C{=}C{=}C{=}C(C_4H_3S)\}$ 69, where the diyne uses both the triple bonds forming a C_4 cumulene.[86] The complex $(\mu\text{-}H)Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}$ reacts with pyridine-2-thiol (pySH) to form the linear $H(\mu\text{-}H)Os_3(CO)_8(pyS)\{Ph_2PCH_2P(Ph)C_6H_4\}$ 70 and the closed $Os_3(CO)_8(pyS)\{Ph_2PCH_2P(Ph)C_6H_4\}$ 71 (Figure 17).[87,88]

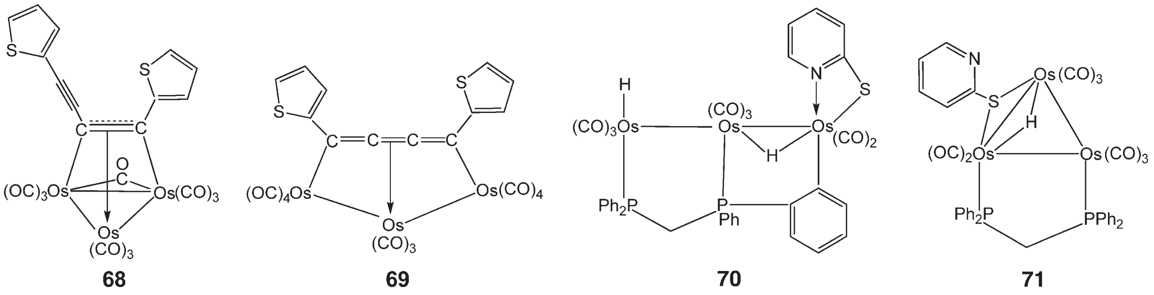
6.22.2.2.4 Triruthenium and triosmium complexes from sulfur-containing heterocycles

As a part of a study on the metal-catalyzed hydrodesulfurization reactions, $Os_3(CO)_{12}$ has been reacted with thiethanes,[89,89a] 2-vinylthiacyclohexane,[90] and tetrahydrothiophene;[91,91a] in these reactions, C–S bond cleavage



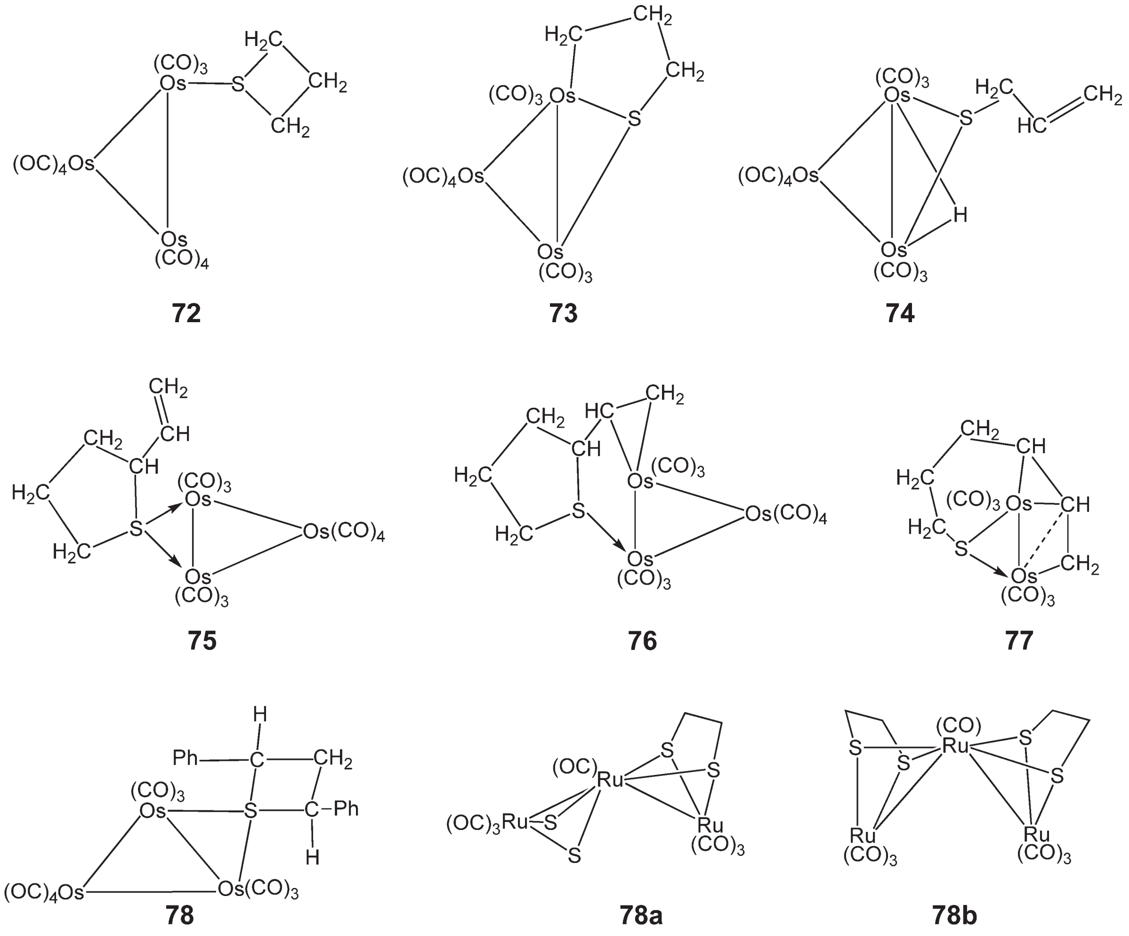
64
65
66
67

Figure 16



68
69
70
71

Figure 17



72 **73** **74**

75 **76** **77**

78 **78a** **78b**

Figure 18

and ring opening occurs as shown by complexes 72–77. The reaction of $\text{Ru}_3(\text{CO})_{12}$ with 1,2,5,6-tetrathiacycloctane leads to the open triruthenium clusters 78a and 78b.[92] Complexes 72–78 are shown in Figure 18.

6.22.2.2.5 Other triosmium complexes

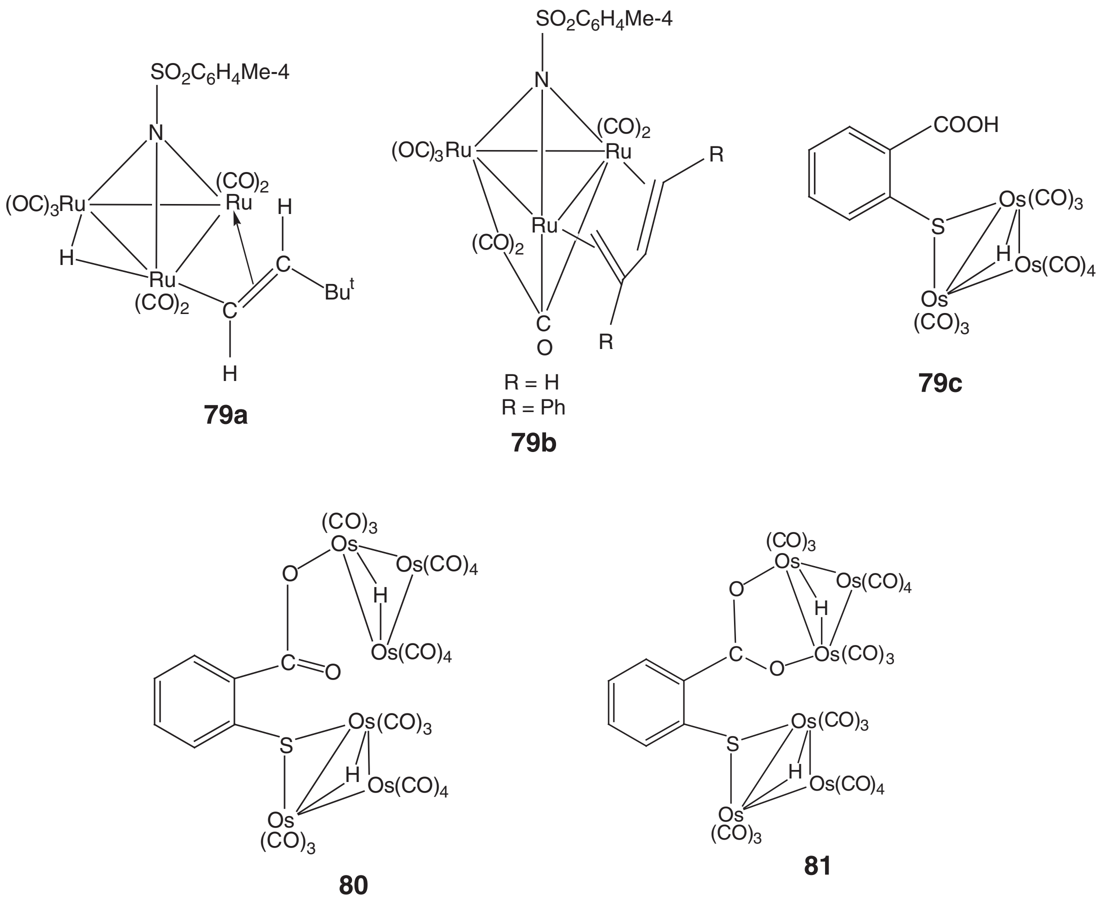
Dihydride triruthenium clusters capped by sulfur favor the reductive coupling of alkynes. This happens when $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu_3\text{-NSO}_2\text{C}_6\text{H}_4\text{Me-4})$ reacts with alkynes[93] to form the complexes 79a and 79b. Similar behavior is observed for $(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-SbPh}_2(\text{C}_6\text{H}_4)\}$, an open cluster.[94] Triosmium derivatives of diphenyl diselenide have been synthesized and their reactivity has been studied; however, no complexes with M–C–Se bonds were reported.[95] Finally, $\text{Os}_3(\text{CO})_{10}(\text{CNMe})_2$ reacts with sulfur and oxygen donors forming the trinuclear cluster 79c with sulfur bridges or dimeric complexes 80 and 81 with the ligand acting as a bridge (Figure 19).[96]

6.22.3 Group 15 Ligands

6.22.3.1 Ligands Bonded through Carbon and Nitrogen

6.22.3.1.1 Triruthenium and triosmium complexes with capping nitrogen ligands

The complex $\text{Ru}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-NPh})$ has been synthesized: its NMR behavior[97,97a,97b] and its reactivity toward alkynes and diynes have been studied.[98] No coupling between the apical nitrogen ligand and the alkyne carbons occurs. Similar behavior is also observed for the electron-deficient cluster $(\mu\text{-H})\text{Ru}_3(\text{CO})_9\{\mu_3\text{-NS(O)MePh}\}$, when



79a

R = H
R = Ph

79b

79c

80

81

Figure 19

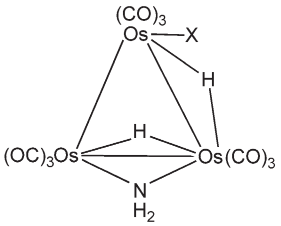
reacted with alkynes,[99] and for $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)$;[100,100a] this complex, however, may form polynuclear derivatives where the OMe group has been transferred on the cluster frame.[101]

The reaction of $Os_3(CO)_{12}$ with *O-t*-butylhydroxylamine hydrochloride leads to the hepta-osmium derivative $\{(\mu\text{-}H)_2Os_4(CO)_{11}(\mu\text{-}NH_2)\}\{(\mu\text{-}H)Os_3(CO)_{11}\}$ with a tetrahedron and a triangle of metals linked through an Os–Os bond.[102] Tetranuclear clusters are obtained by reacting the tetrahedral $(\mu\text{-}H)_4Os_4(CO)_{11}\{H_2NOCMe_3\}$. Upon protonation and addition of CO, however, the trinuclear $(\mu\text{-}H)(\mu\text{-}NH_2)Os_3(Cl)(CO)_9$ 82 is obtained.[103] The complex $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}CNC_5H_4C{=}CH_2)$ 83 reacts with alkynes giving trinuclear clusters, bearing two to four condensed molecules of alkynes (in some instances with CO insertion); it apparently loses the vinylpyridine capping ligand,[104] which leaves a capping carbon or a μ-CH ligand, which then undergoes reaction with alkynes.[105] Intermediate in this process is complex 84 (Figure 20).

The cluster 83 co-polymerizes with styrene in the presence of α,α'-azobis(isobutyronitrile) giving a polymer-immobilized alkylidyne triosmium cluster.[106]

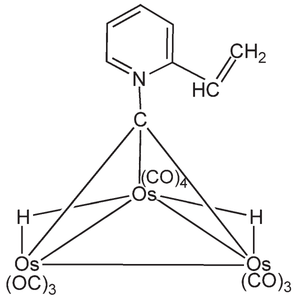
6.22.3.1.2 Ruthenium complexes with azavinylidene ligands

The 1-azavinylidene cluster $(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)Ru_3(CO)_{10}$ 85[107] reacts with alkynes undergoing fragmentation to binuclear products.[108,108a,108b] Sometimes, however, the reactions with diynes result in the coordination of these ligands on trinuclear frames and on the opposite side with respect to the orthometallated azavinylidene, or in the coupling of the diynes with one phenyl of the nitrogen-containing ligand (complexes 86–89).[109] The reactivity of complex 85 has been extensively studied; protonation occurs to form complexes 90 and the dihydride $[(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)Ru_3(CO)_9(PPh_3)]^+$ (isomers, depending on the position of the phosphine); EHMO calculations were performed.[110] The complex reacts with PPh_2H forming phosphido-bridged derivatives, which, in turn, undergo protonation.[111] Complexes 85–90 are shown in Figure 21.



X = Br, Cl

82



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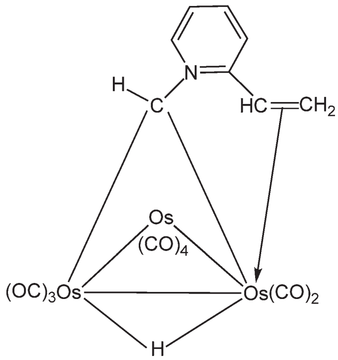
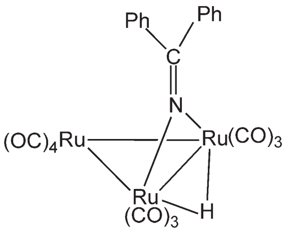


84

Figure 20



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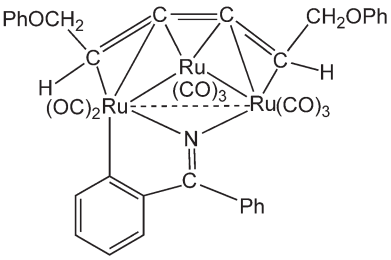

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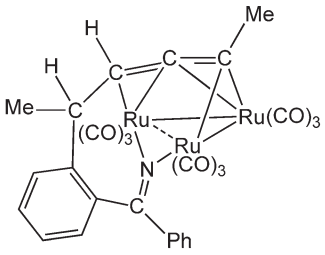

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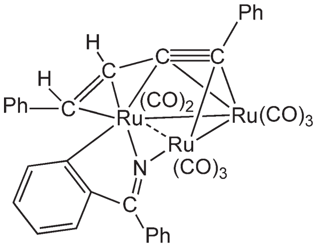

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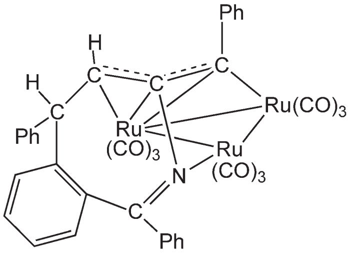

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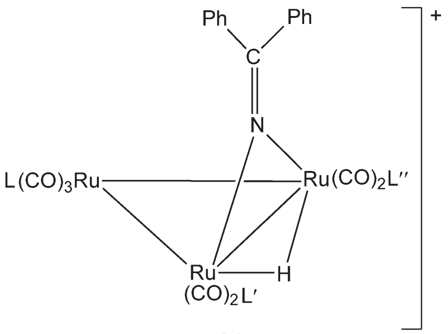


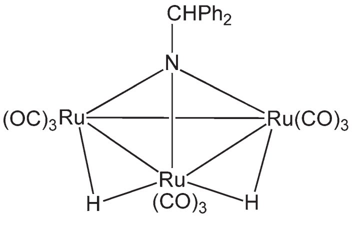
90

L′ = L″ = dppm
L = PPh$_3$
L′ = PPh$_3$
L = L′ = PPh$_3$

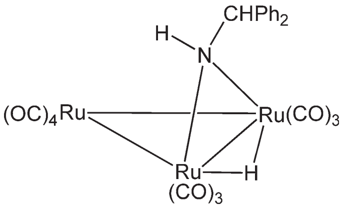
Figure 21

In a study of hydrosilylation and hydrostannation reactions, it has been found that cluster 85 reacts reversibly with CO and H_2, undergoing modifications. The dihydride $(\mu\text{-H})_2(\mu_3\text{-NCHPh}_2)Ru_3(CO)_9$ **91** is formed: this, upon heating, gives the mono-hydrides $(\mu\text{-H})(\mu\text{-HNCHPh}_2)Ru_3(CO)_n$ ($n = 9$, 10) **92**, which, under H_2, give $H_4Ru_4(CO)_{12}$ and H_2NCHPh_2 (Figure 22).[112]

When the cluster $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-}C,N\text{-}C_6H_4N)$ reacts with $Pt(PPr^i_3)(nb)_2$ [nb = bicyclo-(2,2,1)-hept-2-ene], the substitution of CO by phosphines occurs.[113]



91



92

Figure 22

6.22.3.1.3 Triruthenium complexes with aminopyridine and related ligands

The chemistry of these complexes has been studied in view of their use as homogeneous hydrogenation and hydroformylation catalysts. The first studies were performed by Lavigne and co-workers: they reacted labilized triruthenium complexes to form derivatives such as $[Ru_3(CO)_n\{X(C_5H_4N)\}]^-$ ($n = 9$, 10; X = O, S),[114] $Ru_3(CO)_8(\mu\text{-}PPh_2)\{(PhP)C_5H_4N\}$,[115] and $(\mu\text{-}H)Ru_3(CO)_9\{(PhN)(C_5H_4N)\}$;[116] the latter catalyze the polymerization of phenylacetylene and the hydroformylation of diphenylacetylene as shown in Figure 23.

An extensive study on the triruthenium chemistry of 2-amino-6-methylpyridine (Hampy) has been performed by Cabeza, Riera, and co-workers. The unsubstituted complex $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}Hampy)$ undergoes phosphine substitution, protonation, and methoxidation reactions.[117] The complex $Ru_3(CO)_8(\mu_3\text{-}Hampy)(PhC{=}CHPh)$ **93** catalyzes the hydrogenation of diphenylacetylene and, in the presence of hydrogen, also forms a dimer **94** linked through

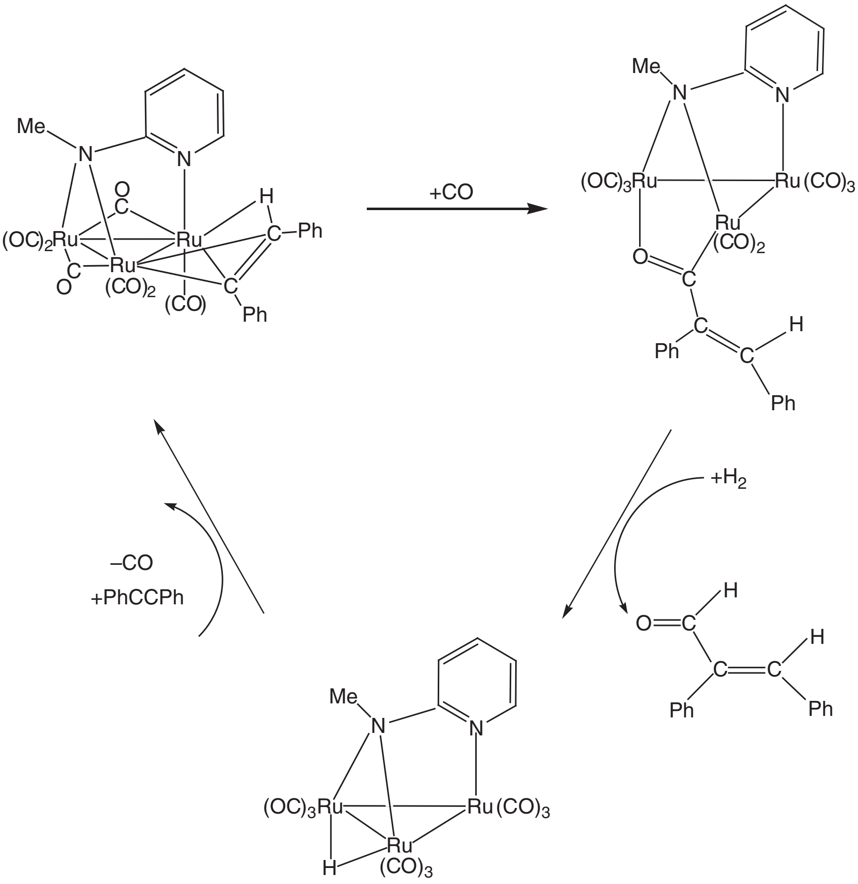
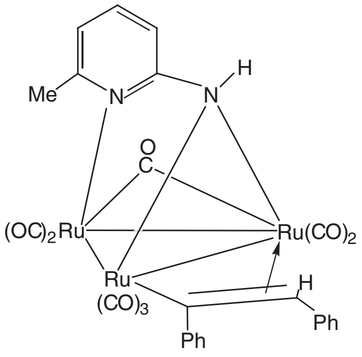


Figure 23



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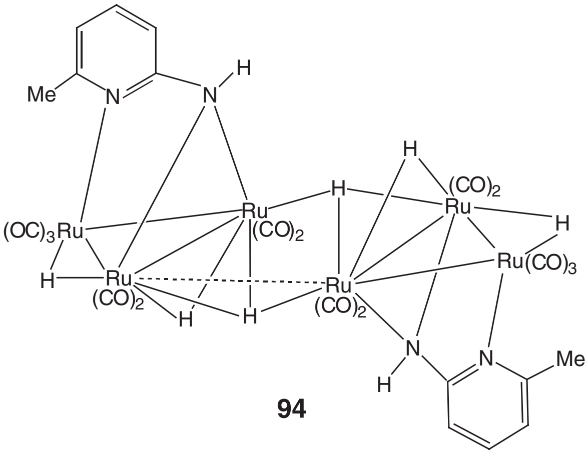
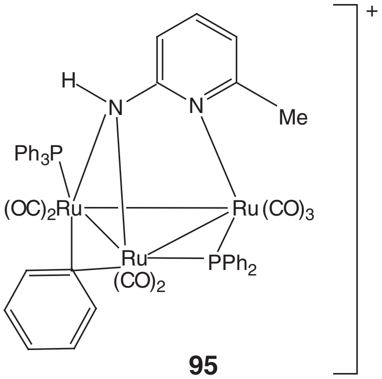
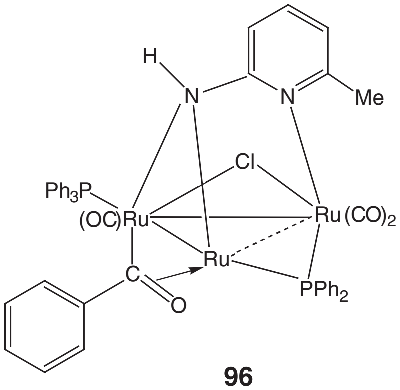


94



95



96

Figure 24

hydrogen bonds.[118,118a,118b] A full hydrogenation cycle for diphenylacetylene has been reported.[119] The complex also undergoes substitution with silanes: however, hydrosilylation of diphenylacetylene could not be carried out.[117] The unsubstituted Hampy derivative may also add μ-σ-benzyne **95** and forms the benzoyl derivative **96**.[120] Complexes **93–96** are shown in Figure 24.

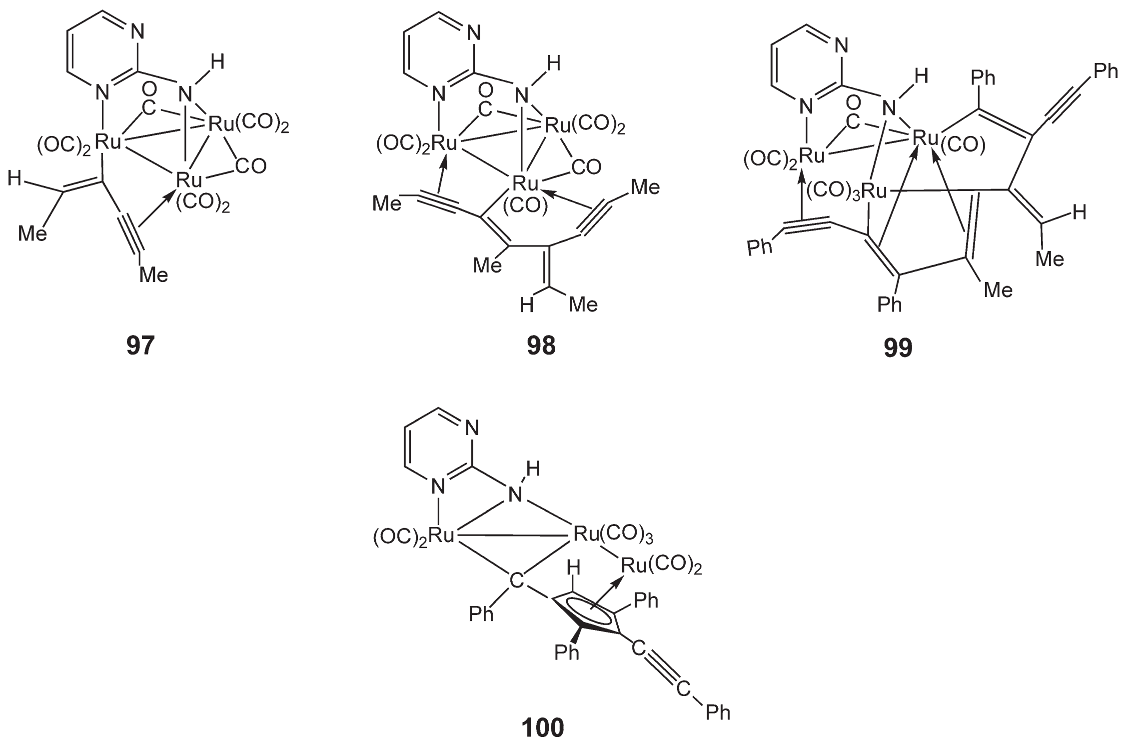
Finally, the synthesis of hexaruthenium derivatives of Hampy has been achieved.[121,121a] The triruthenium aminopyridine complexes have been the subject of a recent review.[122] This chemistry has been extended to other nitrogen ligands: triruthenium and triosmium complexes of deprotonated di(2-pyridyl)amine have been obtained.[123] In addition, a number of triruthenium derivatives of 2-amino-7,8-benzoquinoline have been synthesized.[124,124a]

Triruthenium aminopyridine clusters have also been reacted with diynes[125] and coupling of hexa-2,4-diyne and hex-2-yn-4-en-4-yl ligands has been observed (complexes **97**, **98**).[126] A carbon-rich hydrocarbyl ligand has been obtained; it is formed by the combination of three butadiyne molecules on an open triruthenium core **99**.[127] The coupling of three molecules of diynes may also lead to the formation of cyclopentadienyl **100**, bound via their ring to the metals (Figure 25).[128] The mechanism of formation of these ligands has been the object of an extensive study, showing that the substituted cyclopentadienyl ligands are formed upon cyclodimerization of a diene and of an alkyne ligand.[129]

The unusual reactivity of the cluster $(\mu\text{-H})Os_3(CO)_9\{\mu_3\text{-}\eta^2\text{-C=N(CH}_2)_4\}$ obtained from piperidine has been the object of a study.[130]

6.22.3.1.4 Triosmium clusters with quinoline and related ligands

The reactivity of the imidoyl complexes $(\mu\text{-H})Os_3(CO)_9\{C=N(CH_2)_3\}$ (e.g., complexes **101**, **102**) has been compared to that of the corresponding ruthenium complexes.[131] An extensive study has been performed on triosmium


97 **98** **99**

100

Figure 25

quinoline, dihydroquinoline, and benzoquinoline derivatives **103a–106** (Figure 26).[132,132a–132d] This work was aimed at obtaining electron-deficient, water-soluble molecules, capable of interacting with DNA and therefore useful for bioinorganic applications. The dependence of their reactivity on the nature of the organic ligand has been studied.[133] Parahydrogen exchange,[134] hydrogen abstraction,[135] electrochemical behavior,[136] and interaction with proteins[137] and with DNA[138,138a] have been considered; see clusters **107–110** in Figure 27. Quinoline-carboxaldehyde derivatives have also been reported.[139] Part of this research has been the subject of a review.[140]

When quinoline derivatives are reacted with thiols, electron-deficient, open clusters with μ-S or μ-SEt ligands are obtained.[141]

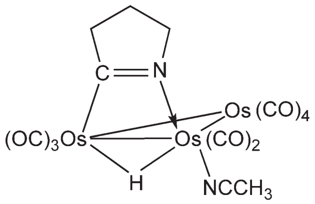
6.22.3.1.5 Miscellaneous triruthenium derivatives

Triruthenium clusters labilized by NCMe and containing alkynes do not undergo coupling of the ligands.[142] Clusters containing functionalized alkynes are also known,for example, $(\mu\text{-H})Ru_3(CO)_9\{C{\equiv}C(C_6H_4NH_2)\}$ and its protonation product,[143] and the isomers $(\mu\text{-dppm})Ru_3(CO)_7(\mu\text{-CO})(PPh_3)\{PhC{\equiv}C(C_6H_4X)\}$ ($X = NO_2$, CN, OMe, CHO).[144] The photo- and electrochemistry of the chelated $Ru_3(CO)_8(\mu\text{-CO})_2(\alpha\text{-diimine})$ (α-diimine = 2,2′-bipyridine; 4,4′-dimethyl-2,2′-bipyridine; 2,2′-bipyrimidine) has also been studied.[145] The open cluster $Ru_3(CO)_6(\mu\text{-Se})(\mu\text{-PPh}_2)(\mu\text{-C}_5H_4N)(\mu_3\text{-C}_5H_4N)$ contains two differently metallated 2-pyridyl fragments.[146]

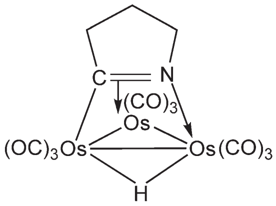
A reaction sequence leading to heterocyclic organic products starting from $RN(CMe_2C{\equiv}CH)_2$ (R = H, Me) and using the triruthenium clusters **111** and **112** as models of intermediates has been reported (Figure 28).[147]

6.22.3.1.6 Triosmium complexes substituted with amines and imines

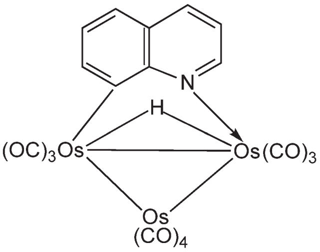
By reacting $H_2Os_3(CO)_{10}$ or $Os_3(CO)_{11}(NCMe)$ with ammonia, clusters containing an NH_3 group, for example, $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$,[148,148a,148b] are obtained. Similar reactions also lead to clusters containg sulfur-based ligands, such as $H(\mu\text{-H})Os_3(CO)_{10}(HSR)$,[149] and to imine derivatives, for example, $H(\mu\text{-H})Os_3(CO)_{10}(HN{=}CPh_2)$[150] and $H(\mu\text{-H})Os_3(CO)_{10}(HN{=}CRR^1)$ ($R = H$, $R^1 = Me$).[151] The reactivity of these complexes has been extensively studied. NMR studies showed that unconventional hydrogen bonds (e.g., Os–H- - -N–N) stabilize the clusters and that their bonding distances can be related to the nature of the amines.[152,152a] The activation of



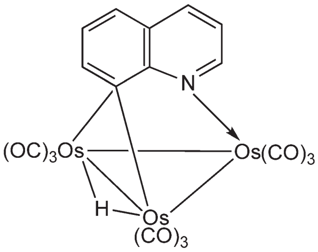
101



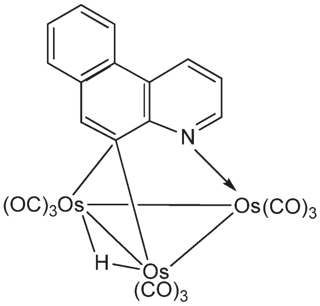
102



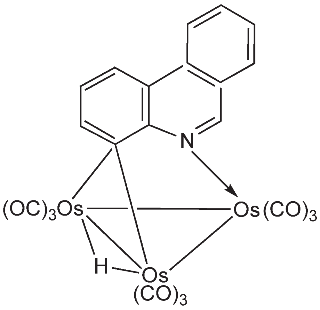
103a



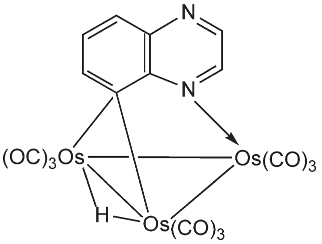
103b



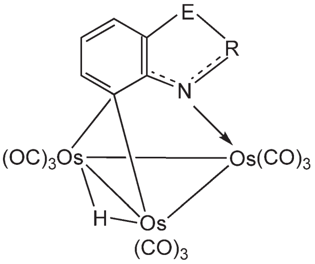
104a



104b



105



E = N, R = NCH_3
E = S, N, O
R = C–Me, C–H

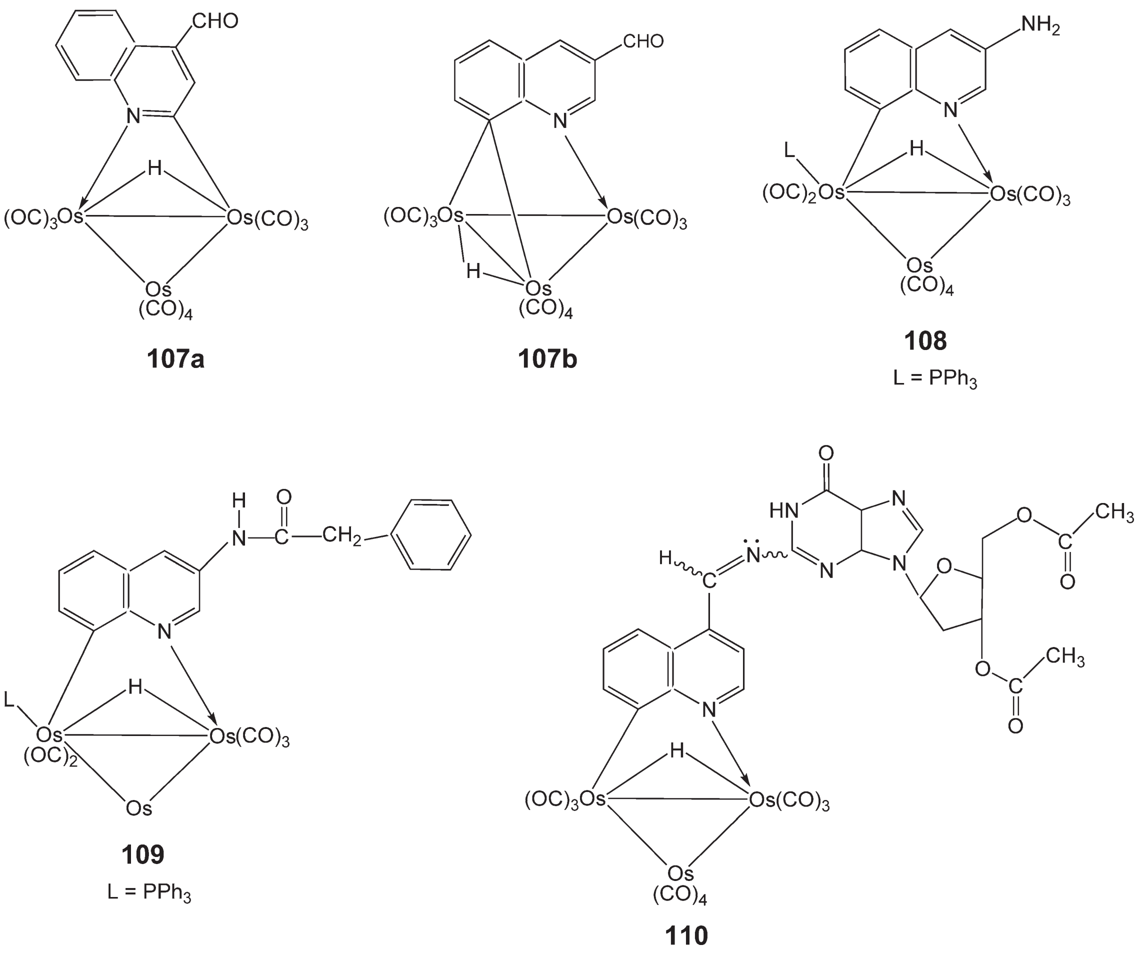
106

Figure 26

1,3,5-trimethyl-1,3,5-triazacyclohexane by $Os_3(CO)_{12}$ leads to the amidino $[(MeN)_2CH]$ complexes **113** and **114** and to the binuclear **115**.[153] Treatment of $Os_3(CO)_{10}(NCMe)_2$ with water or with HCl leads, respectively, to clusters with C(=O)NH(R) or C=NH(R) bridges.[154] Triosmium clusters with benzophenone imine (e.g., **116–118**) have been obtained.[155] Again, lightly ligated triosmium clusters react with aminothiazole derivatives, undergoing thermal CO substitution and forming a variety of nitrogen-bridged derivatives such as **119–121**.[156] The structures of complexes **113–121** are shown in Figure 29.

6.22.3.1.7 Triosmium clusters with pyridines and related ligands

The ligand fluxionality of clusters containing *N*-orthometallated 2-pyridylphosphines has been studied.[157] The new complexes **122**, **123a** and **123b** have been obtained starting from lightly ligated triosmium clusters.[158] The reaction of $(\mu\text{-H})(\mu\text{-py})Os_3(CO)_{10}$ (py = NC_5H_4) with bis(ferrocenyl)butadiyne leads to the open triosmium cluster **124** with a bridging pyridine ligand.[159] The reactions of lightly ligated triosmium clusters with 2,3-bis(2-pyridyl)pyrazine lead to the "dimeric sandwich" triosmium derivative **125**, where the trinuclear clusters are kept together by the nitrogen-containing ligand (Figure 30).[160] Finally, triosmium pyridine derivatives, when bound to indium porphyrins, show strong optical limiting capabilities.[161] The orthometallation of $Os_3(CO)_{10}(C_{14}H_{10}N_4)$ **126** leads to the isomeric hydride clusters **127a**,



107a **107b** **108**

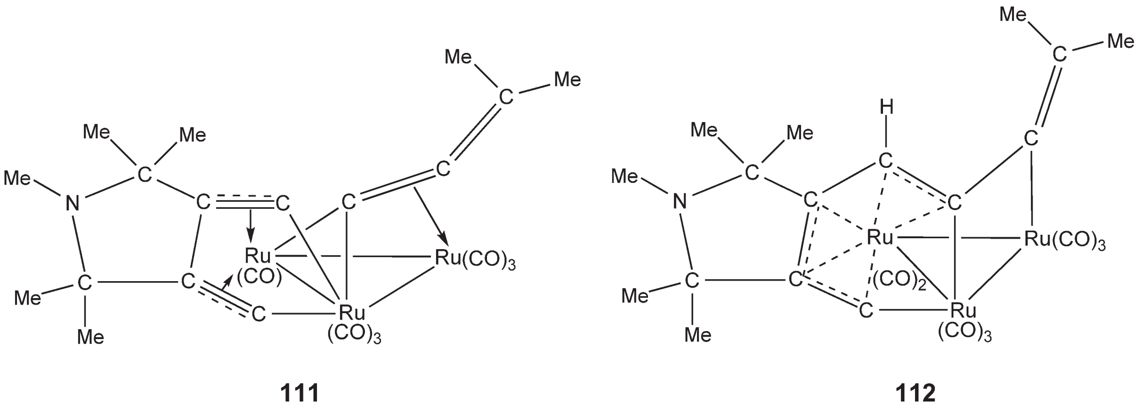
L = PPh3

109

L = PPh3

110

Figure 27

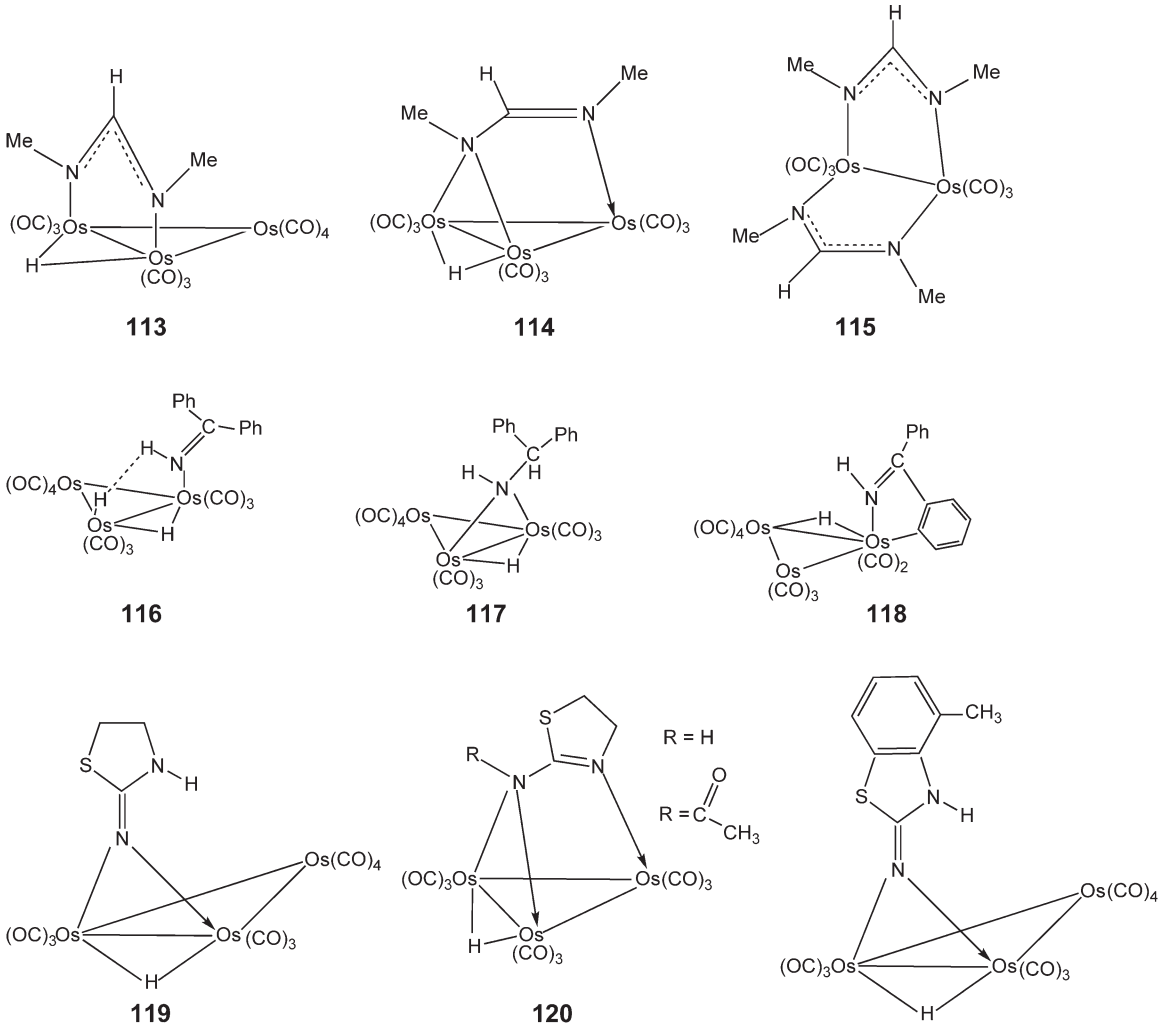


111 **112**

Figure 28

127b, 128a, and 128b.[162] Triosmium clusters with metallacyclic ligands are also obtained from $Os_3(CO)_{10}(NCMe)_2$ and 1,2-bis(2-pyridyl)ethene (complexes 129a, 129b, 129c, 130–132; Figure 31).[163]

The reactions of $H_2Os_3(CO)_{10}$ and $Os_3(CO)_{10}(MeCN)_2$ with 1,4-dipyridylbuta-1,3-diyne afford a variety of products, ranging from triosmium complexes with a parallel alkyne to clusters with the ligand rearranged to form a



113 **114** **115**

116 **117** **118**

119 **120** **121**

Figure 29

indolizine system coordinated in allylic way, and finally to "dimers" where two triosmium clusters are linked by the diyne using the pyridyne rings.[164]

6.22.3.1.8 Other osmium derivatives

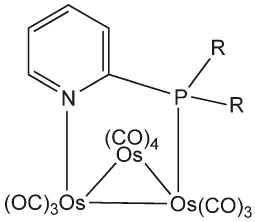
Small proteins may be labeled using triosmium carbonyl clusters, for example, **133**, acting as markers for C≡C bond containing estrogens (Figure 32).[165]

The oxidative addition of allyl bromide to $Os_3(CO)_{10}(NCMe)_2$ has also been studied. No carbon–nitrogen bonds are formed; cluster opening to linear trinuclear clusters is of some interest.[166] The reaction of lightly ligated triosmium clusters with fullerene C_{60} has been successfully attempted; in this case also, no C–N bonds are formed.[167]

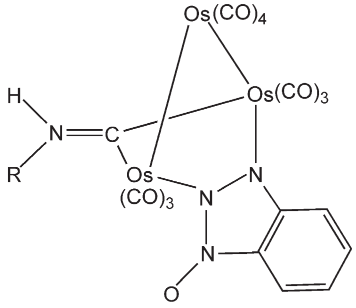
6.22.3.2 Ligands Bonded through Carbon and Phosphorus

6.22.3.2.1 Ruthenium clusters containing oxygenated diphosphine ligands

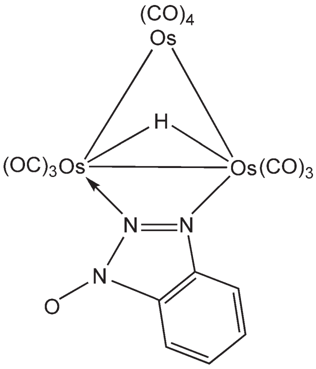
$Ru_3(CO)_{12}$ reacts thermally with 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) affording the trinuclear cluster $Ru_3(CO)_{10}$(dpcd) **134**, where the ligand is chelating using only the phosphorus atoms, and binuclear complexes such as $Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C{=}C(PPh_2)C(O)CH_2C(O)\}$, where the ligand also uses a C═C bond for



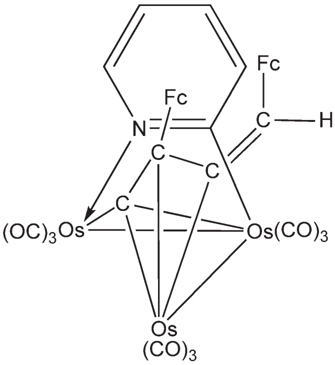
122



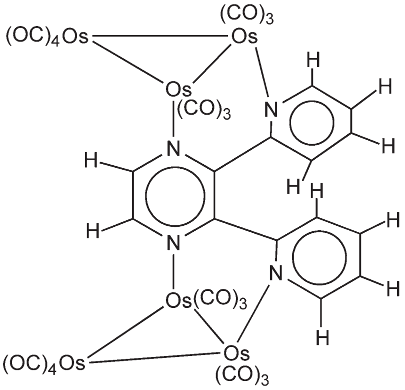
123a



123b



124



125

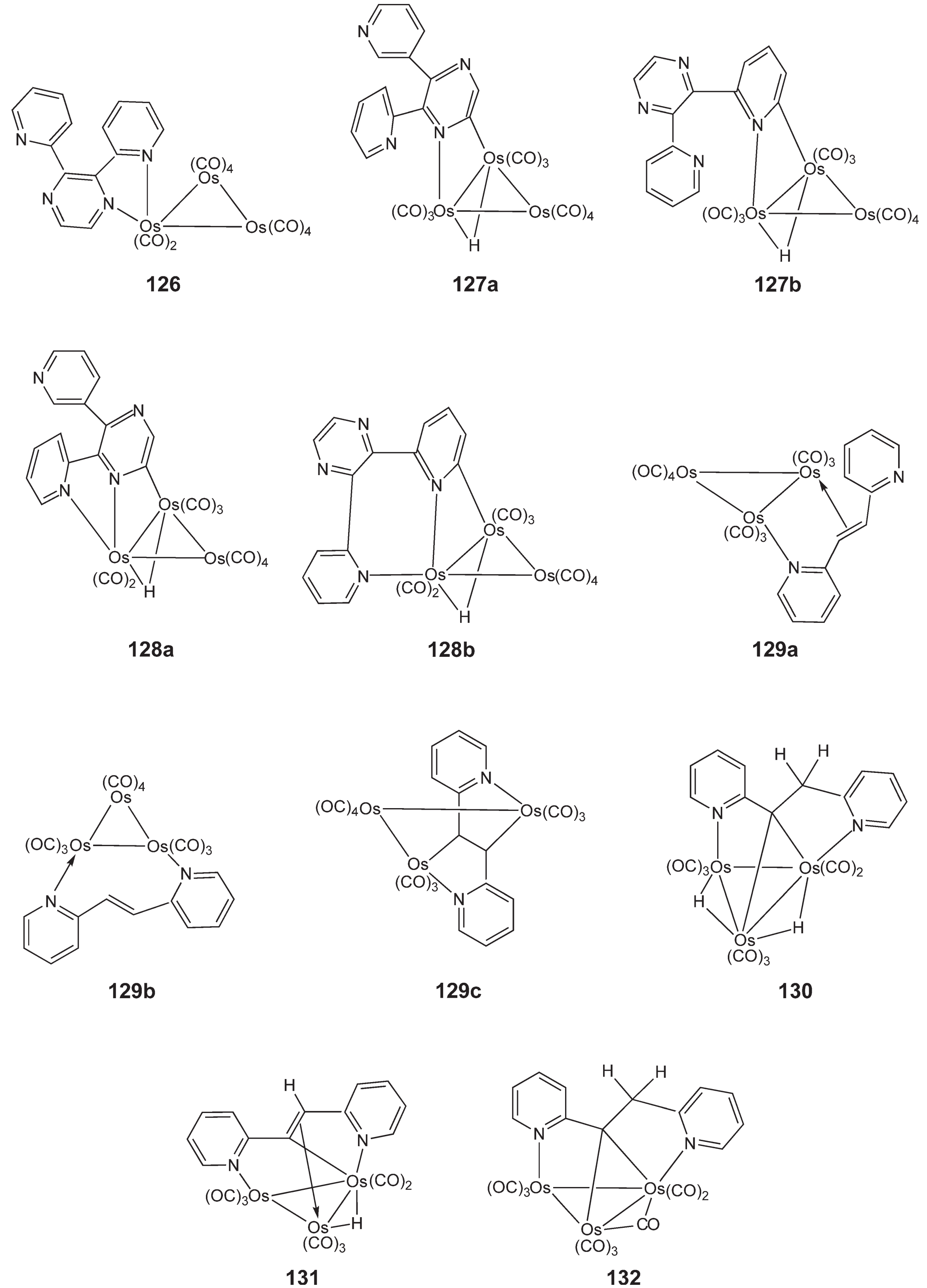
Figure 30

coordination to the metal.[168] Strictly comparable behavior is observed for the open cluster Ru$_3$(CO)$_9$(μ_3-S)$_2$[169] and for the closed Ru$_3$(CO)$_9$(μ_3-NPh)(μ_3-CO), which not only give the chelated and bridged-chelated trinuclear derivatives **135** and **136** but also the open cluster **137** containing a PhC=O ligand.[170] Finally, HRu$_3$(CO)$_7$(bpcd)(C≡CPh), with a perpendicular acetylide, reacts with an excess of the diphosphine ligand forming clusters in which P–C coupling or hydrogenation of the acetylide is observed.[171] Complexes **134–137** are shown in Figure 33.

Carty and co-workers have observed the coupling of the binuclear complexes Ru$_2$(CO)$_6$(μ-PPh$_2$)(μ-C≡CPh), obtaining, among others, the tetranuclear clusters **138–140**. Carbon–carbon bond formation and insertion of CO is also observed in these reactions.[172] The reactions of the diynyl derivatives Ru$_2$(CO)$_6$(μ-PPh$_2$)(μ-C≡C–C≡CR) result in the formation of tetra-, penta-, and hexanuclear complexes[173,173a] or of functionalized binuclear derivatives.[174,174a,174b] The reactions of Ru$_3$(CO)$_{12-n}${PPh$_2$C≡CC≡CR}$_n$ [$n = 1,2$] give polynuclear complexes[175] as well as the trinuclear derivative **141**.[176] The reactions of M$_3$(CO)$_{12}$ (M = Fe, Ru, Os) with P(C≡CBu^t)$_3$ give monosubstituted derivatives and open clusters such as M$_3$(CO)$_9$(C≡CBu^t){μ-P(C≡CBu^t)$_2$},[177] together with polynuclear complexes. Trinuclear clusters such as H$_2$Ru$_3$(CO)$_9$(μ_3-PNPr$^i_2$) **142** and Ru$_3$Pt(CO)$_{10}$(PPh$_3$)(μ_3-PNPr$^i_2$) **143** have been obtained in the reactions of Ru$_3$(CO)$_{12}$ with fragments containing other metals (Figure 34).[178,178a–178c]

6.22.3.2.2 Triruthenium and triosmium clusters obtained through orthometallation reactions

Bruce and co-workers have studied the reactions of Ru$_3$(CO)$_{10}$(μ-dppm) toward alkynes. Carbon–carbon bond formation is observed, together with cluster fragmentation or building up; trinuclear clusters containing orthometallated dppm ligands (e.g., **144**, **145**) have also been observed.[179,179a,179b] The reaction of Ru$_3$(CO)$_{10}$(μ-dppm) with benzyl halides also leads to trinuclear, orthometallated derivatives, along with more complex structures.[180]


N
N
N
N
(CO)$_4$
Os
Os
(CO)$_2$
Os(CO)$_4$
126
N
N
N
N
Os(CO)$_3$
(CO)$_3$Os
Os(CO)$_4$
H
127a
N
N
N
N
(CO)$_3$
Os
(OC)$_3$Os
Os(CO)$_4$
H
127b
N
N
N
N
Os(CO)$_3$
Os
Os(CO)$_4$
(CO)$_2$
H
128a
N
N
N
N
(CO)$_3$
Os
Os
Os(CO)$_4$
(CO)$_2$
H
128b
(OC)$_4$Os
(CO)$_3$
Os
N
Os
(CO)$_3$
N
129a
(CO)$_4$
Os
(OC)$_3$Os
Os(CO)$_3$
N
N
129b
N
(OC)$_4$Os
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Os
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N
129c
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N
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Os(CO)$_2$
H
H
Os
(CO)$_3$
130
H
N
N
(OC)$_3$Os
Os(CO)$_2$
Os
H
(CO)$_3$
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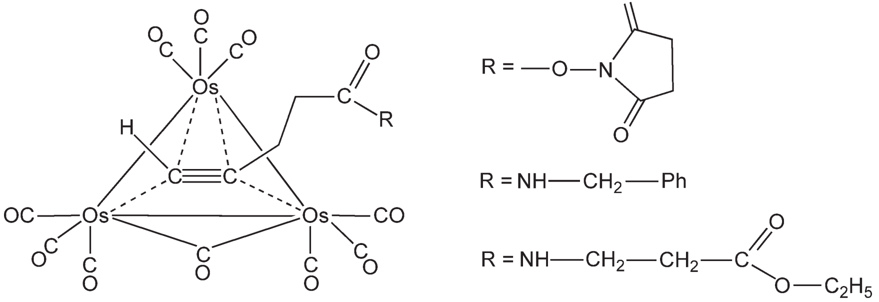
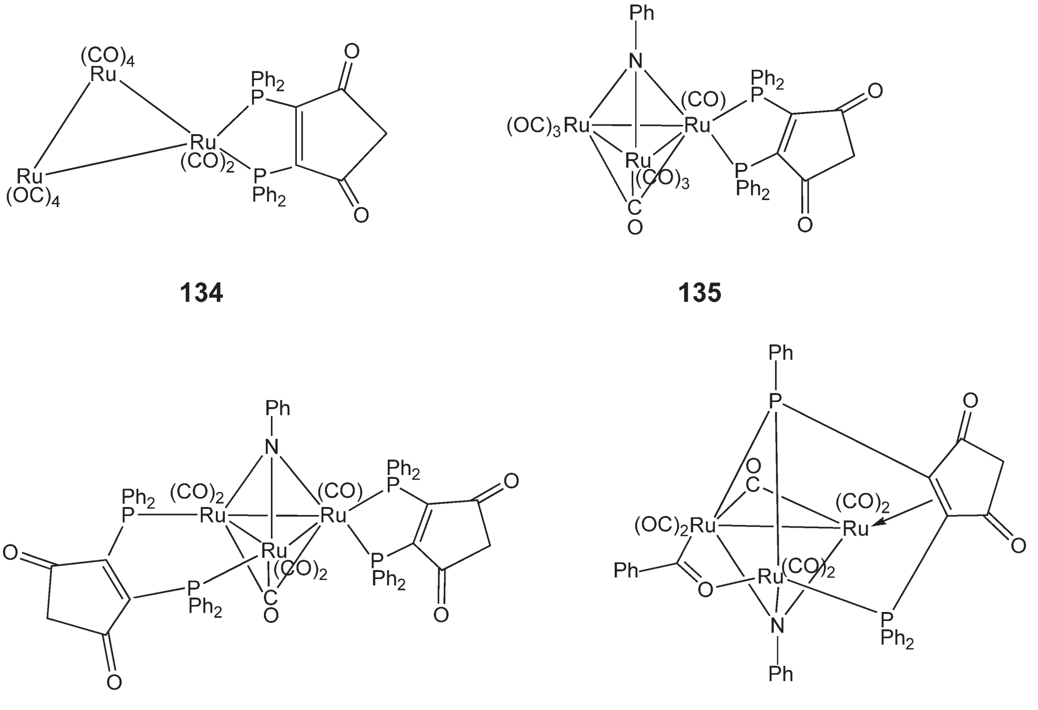
CO
(CO)$_3$
132

Figure 31



133

Figure 32



134

135

136

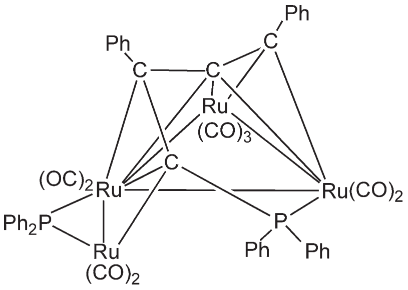
137

Figure 33

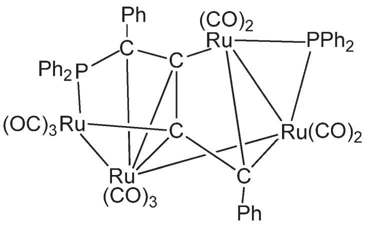
Orthometallation of phenyl groups on naphthyne ligands[181] and on 1,1′-bis(diphenylphosphino)ferrocene has also been observed by Cullen and co-workers.[182,182a] A number of complexes, including **146–150**, which represent significant examples, can be obtained.

Ferrocenylalkynes also react with $Ru_3(CO)_{10}(\mu\text{-dppm})$ forming trinuclear dppm clusters; however, no M–C–P bonds are formed.[183] The dimerization of (oxygen) functionalized alkynes occurs on dppm-substituted ruthenium clusters; in some instances, orthometallated derivatives also are observed.[22] Instead, in the presence of 1,4-diphenylbutadiyne, the dppm ligands may shift from bridging to chelating positions but do not undergo orthometallation.[184] Finally, orthometallation of bis(diphosphino)naphthyl ligands is observed for trinuclear clusters of both ruthenium and osmium complexes, **151–154** (Figure 35).[185,185a,185b]

Several triosmium complexes derived from phosphines or arsines, by loss or orthometallation of phenyl groups, have been isolated (this is a long-known process, see, e.g., ref. 186). Thermolysis of $Os_3(CO)_{11}(AsPh_3)$ leads to



138



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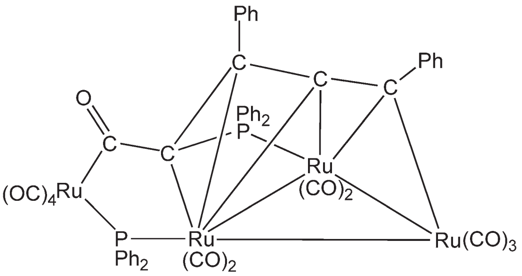

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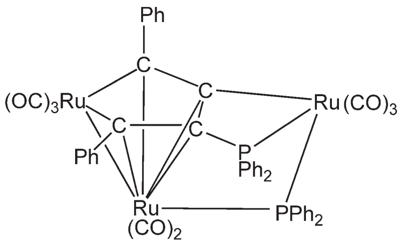

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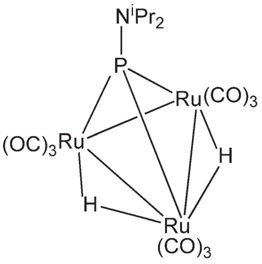

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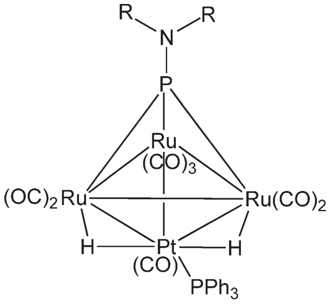


143

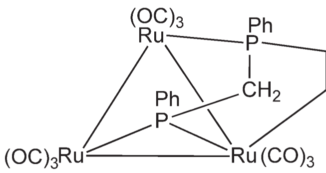
R = ^{i}Pr

Figure 34

trinuclear derivatives, with the triphenylarsine as a terminal ligand or with $AsPh_2$ or AsPh (Ph = phenyl) bridges, and a phenyl group coordinated (σ,σ,σ or σ,σ,π) to the metals;[187] no M–C–As bonds are formed. Thermolysis of the homologous complex containing triphenylstibine gives trinuclear and polynuclear products where no M–C–Sb bonds are formed.[188] The anion $[HOs_3(CO)_{10}(\mu_2\text{-}PPh_2)]^-$ reacts with MeI, and the product may undergo orthometallation of a Ph group forming the neutral $(\mu\text{-}H)_2Os_3(CO)_9\{PMe(C_6H_4)\}$ **155**; the anion reacts also with mercury and gold derivatives, forming, among others, $(\mu\text{-}H)\{\mu_2\text{-}Au(PMe_2Ph)\}Os_3(CO)_9(\mu_3\text{-}PPh)$ **156**.[189] Dppm derivatives of triosmium may also undergo oxidative addition of R_3SiH silanes; during the reactions, orthometallation of a dppm phenyl group occurs (complexes **157**, **158**).[190] Another example of orthometallation of a phenyl bound to a phosphine is given by $(\mu\text{-}H)_2Os_3(CO)_8\{Si(OMe)_3\}\{\mu\text{-}PMe_2(C_6H_4)\}$.[191]

Dppm-bridged triosmium clusters, lightly ligated by NCMe, undergo thermolysis and orthometallation of dppm; NCMe is involved in the formation of a ligand using both P and N in coordination (complex **159**).[192] Finally, in the reaction of 2,2-dimethylpropylidenephosphine with $Os_3(CO)_{10}(CNR)(NCMe)$ (R = Pr, CH_2Ph), cleavage of a P–C bond occurs and a phosphorus-containing metallacycle is formed (complex **160**). The structures **155–160** are given in Figure 36.[193]

Condensation of ethene or 1,3-butadiene with CO and C_2Ph_2[194] or of cluster-bound allenylidenes with dppm or dppe[195] on triruthenium clusters has also been observed. Complexes with Ru–C–P bonds have been characterized.



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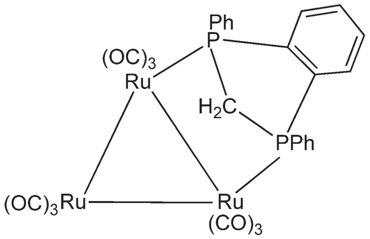

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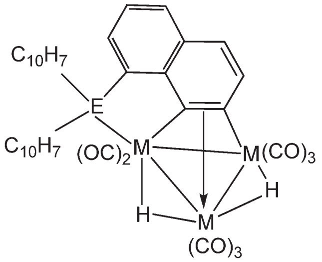

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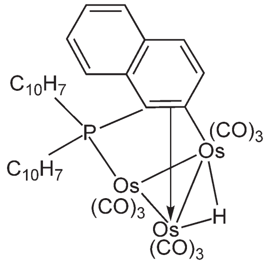
E = P, As



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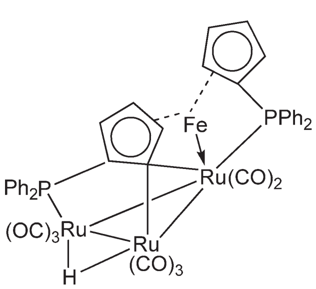

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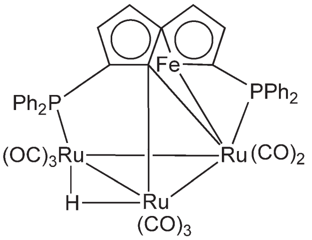

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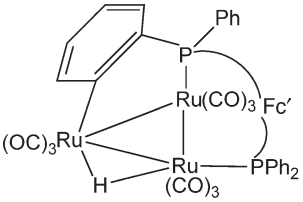

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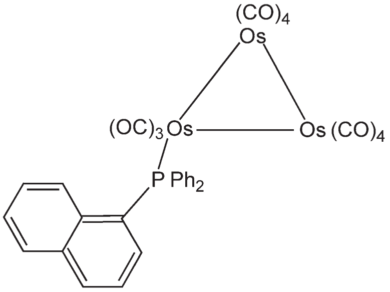
Fc′ = Fe(η-C_5H_4-$)_2$



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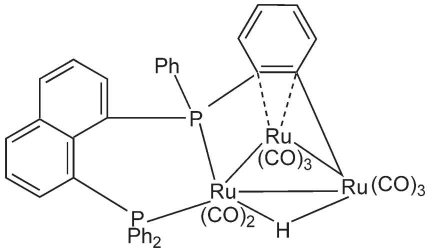

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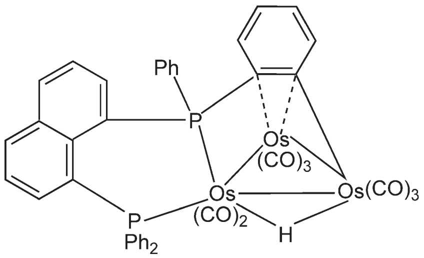

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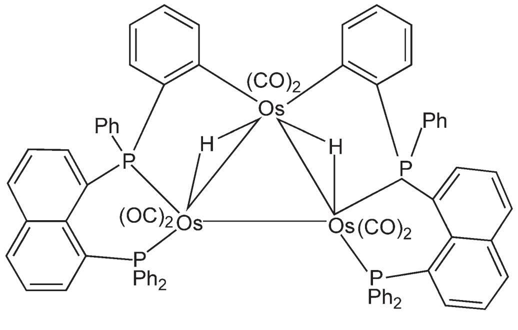

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Figure 35

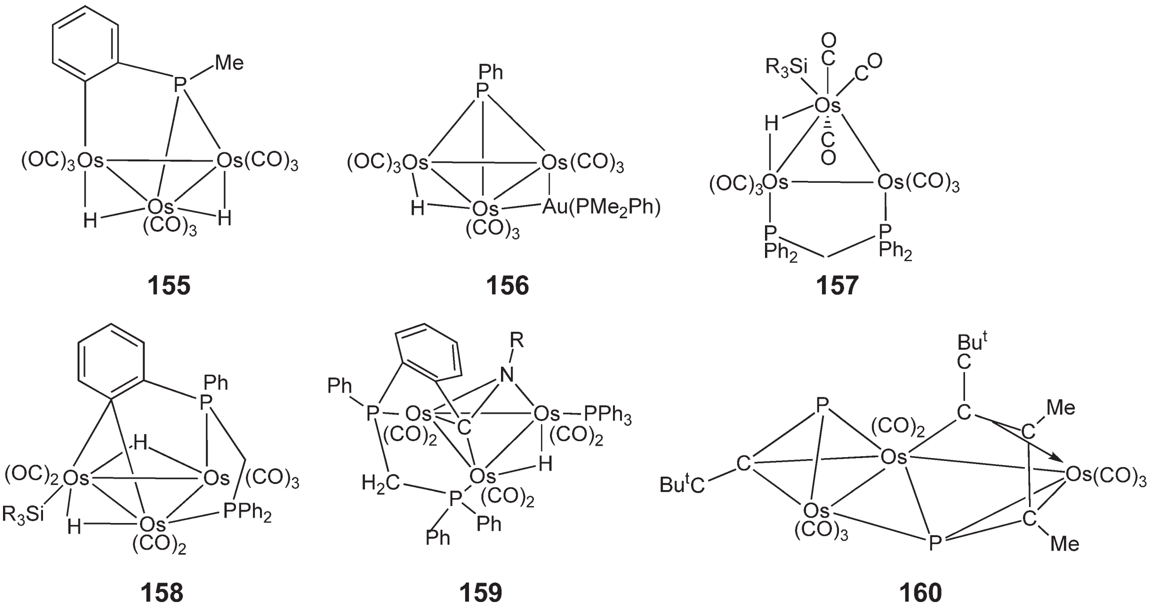


Figure 36

6.22.3.2.3 Triruthenium complexes isolated during catalytic experiments

Clusters with Ru–P–C bonds (e.g., **161**, **162**) have been isolated as byproducts during the homogeneous hydrogenation of *t*-butylacetylene catalyzed by phosphine-substituted or phosphido-bridged triruthenium clusters.[196] The same occurs for the open ruthenium clusters **163**, **164**, and for the already-mentioned clusters **27** and **28**, obtained as byproducts in the homogeneous[43] or solid–gas[44a] hydrogenation of alkynes and 1,4-cyclohexadiene. Diphosphane-substituted triruthenium clusters have also been used for the homogeneous hydrogenation of diphenylacetylene; however, parahydrogen studies did not show the presence of compounds with Ru–C–P bonds.[197,197a] The structures of complexes **161–164** are shown in Figure 37.

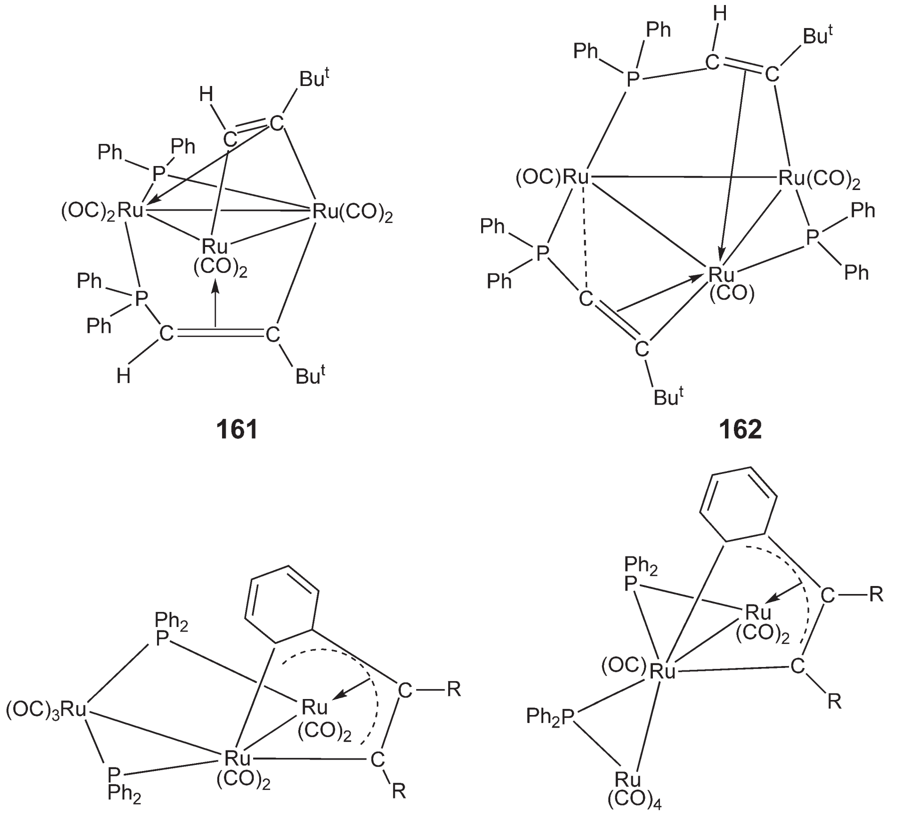
6.22.3.2.4 Addition of phosphorus ligands to cationic triosmium complexes

Protonation of (μ-H)$Os_3(CO)_9(C{\equiv}CR)$ (R = H, Me, CH_2OH, CMe_2OH) in the presence of PPh_3 leads to complexes **165** and **166**.[198] These undergo reversible CO uptake. The cationic allenylidene $[(\mu\text{-H})Os_3(CO)_{10}(C{=}C{=}CMe_2)]^+$ may also add triphenylphosphine, giving the acetylide complex **167**, which gives, as the final products, clusters **168** and **169**, characterized by a bridging or a terminal (phosphonio-substituted) alkyne.[199] The stepwise conversion of the allenylidene ligand to a terminal alkynic group is of interest. Complexes **165–169** are shown in Figure 38.

6.22.3.2.5 Miscellaneous complexes

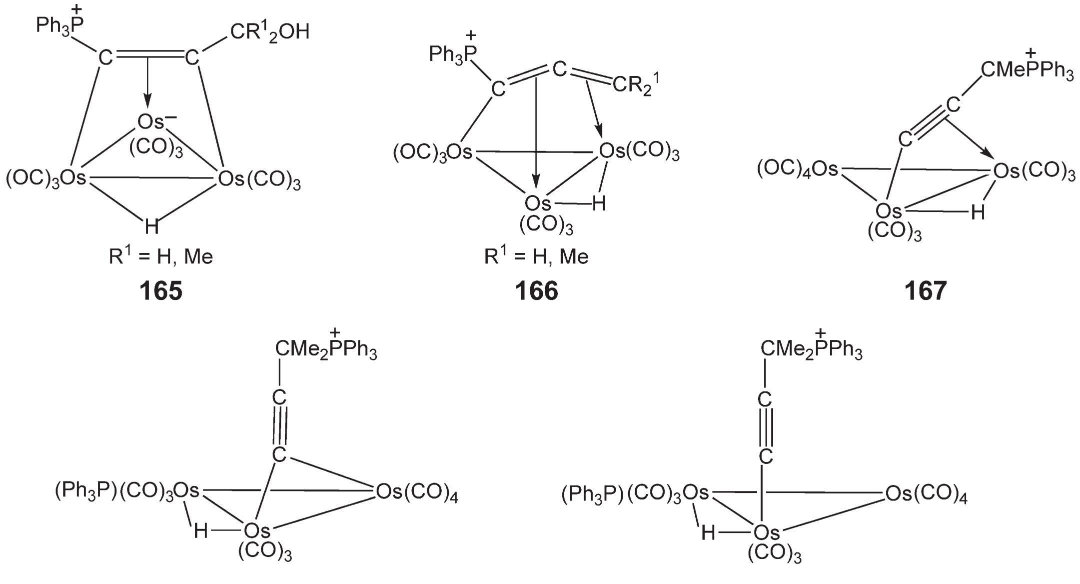
Bis(diphenylphosphino)alkynes (using phosphorus as the donor atom) may act as bridges between trinuclear clusters, for example, in $Os_3(CO)_{11}\{PPh_2{-}C{\equiv}C{-}PPh_2\}Ru_3(CO)_{11}$, which, upon thermal treatment, gives a phosphido-bridged Os_3Ru_2 dicarbide complex.[200,200a] Clusters with capping phosphinidene ligands have been obtained: one is $(\mu\text{-H})_2Ru_3(CO)_9\{\mu_3\text{-P}(2\text{-NH}_2C_6H_4)\}$, obtained by reacting $Ru_3(CO)_{12}$ with (2-aminophenyl)phosphine; the homologous osmium complex has also been reported.[201] Another example is given by the isomeric heterometallic $Cp^*W(\mu\text{-H})Ru_2(CO)_6(\mu_3\text{-PPh})$ obtained from $(\mu\text{-H})(\mu\text{-PPh}_2)Ru_3(CO)_{10}$.[202] The reactions of triruthenium carbonyls with polyfunctional phosphine ligands such as $P(C_4H_3S)_3$[203] or the alkynic $PPh_2C_6H_4\text{-4-C}{\equiv}CH$[204] lead to trinuclear clusters with terminal ligands (bonded through phosphorus).

In contrast, $Ru_3(CO)_{10}(\mu\text{-dppm})$ reacts with dppm(Se), giving, among others, the cluster $Ru_3(CO)_6(\mu_3\text{-CO})(\mu_3\text{-Se})(\mu\text{-dppm})\{\eta^1\text{-Ph}_2PCH_2P({=}O)Ph_2\}$ **170**.[205] The thermal reaction of $Ru_3(CO)_{12}$ with (9-anthracyl)diphenylphosphine affords, among other products the cluster $(\mu\text{-H})_2Ru_3(CO)_8\{Ph_2PC_{14}H_7\}$ **171** with a orthometallated, aromatic ring (Figure 39).[206] Finally, 2-indolylphosphines give trinuclear derivatives by bonding the ruthenium (and osmium) atoms both through P or through N (complexes **172–177**; see Figure 39).[207]



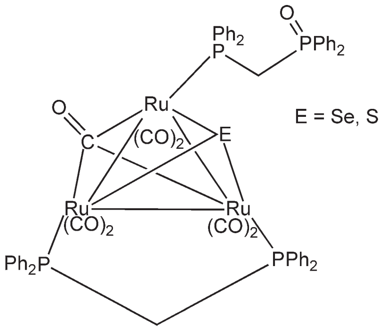
163 **164**

Figure 37



168 **169**

Figure 38



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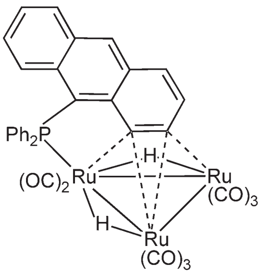

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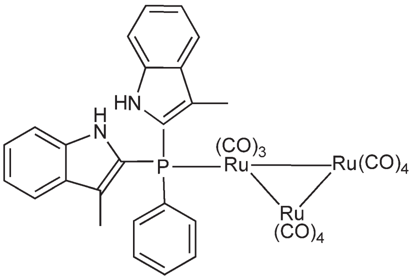

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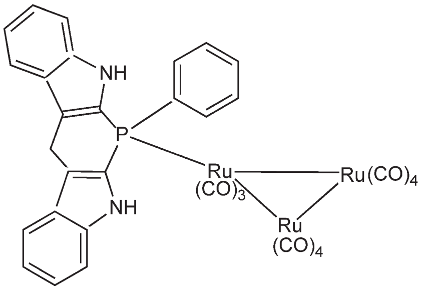

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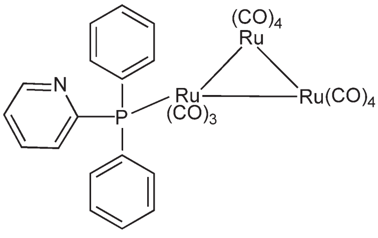

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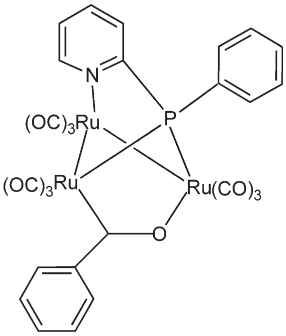

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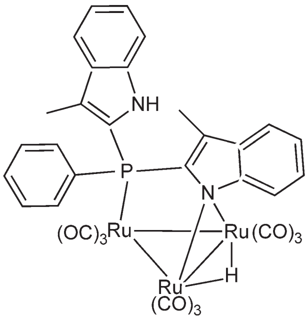

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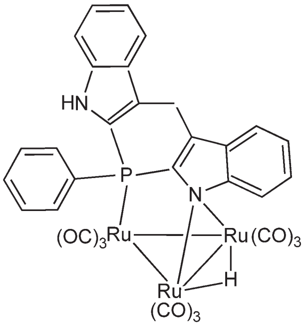

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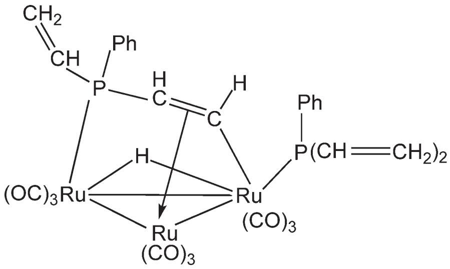
Figure 39

Oxidative addition of divinyl(phenyl)phosphine to $M_3(CO)_{12}$ (M = Ru, Os) leads to trinuclear complexes with M–P–C bonds (e.g., 178); these reactions are catalyzed by the silica of the TLC plates used for purification.[208] Ring opening of 1,2,3-triphenylphosphirene in the presence of $Ru_3(CO)_{12}$ leads to tri- and tetranuclear complexes 179–181 containing M–P–C bonds.[209] The reactions of $M_3(CO)_{12}$ (M = Ru, Os) with $Ph_2P(Se)CH_2C_6H_4CH_2P(Se)Ph_2$ lead, among other products, to $Ru_3(\mu_3\text{-Se})(\mu_3\text{-H})(\mu_2\text{-PPh}_2)(CO)_6(CHC_6H_4CH_2PPh_2)$ 182.[210] The *nido*-cluster $Ru_3(CO)_9\{\mu_3\text{-PC(CO)Bu}^t\}_2$ 183 reacts with mononuclear fragments, forming tetranuclear structures (Figure 40).[211]

The reaction of $Ru_3(CO)_{12}$ with bis(diphenylphosphino)amine leads to (bridged) mono- and disubstituted products.[212] Bis(diphenylphosphino)alkynes may also act as bridges between dicobalt and triruthenium fragments, using both the carbon (to cobalt) and the phosphorus (to ruthenium) atoms 184.[213] Linking of triosmium or triruthenium clusters to two or three $W(C_2Ph_2)_3$ fragments, through bis(diphenylphosphino)acetylene, has also been observed (complexes 185, 186).[214,214a] These compounds are at the border between organometallic and coordination chemistry (Figure 41). The same happens to the cation $[Ru_3(CO)_9\{\mu\text{-P(NPr}^i{}_2\}_2]_3{}^+$ in its compound with $[Ru_6(CO)_{15}(\mu_6\text{-C})\{\mu\text{-P(NPr}^i{}_2)_2\}]^-$.[215]



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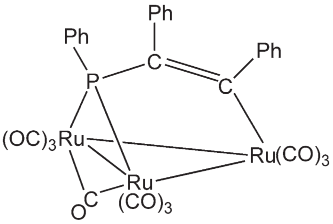

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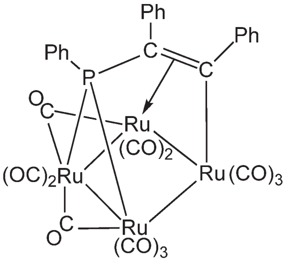

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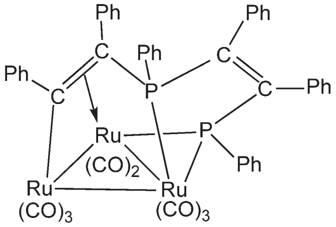

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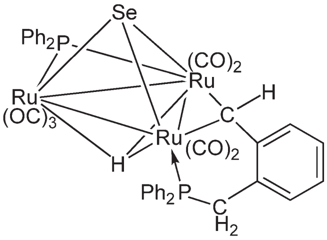

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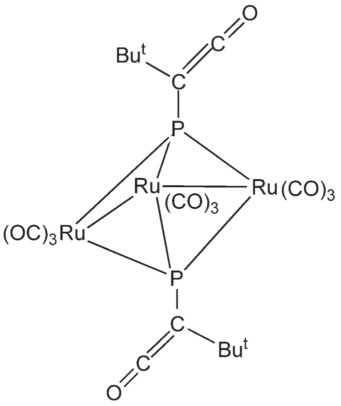

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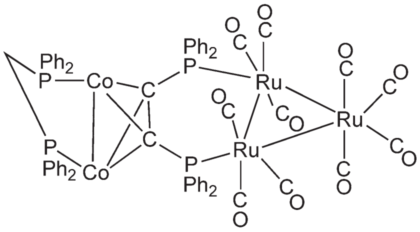
Figure 40



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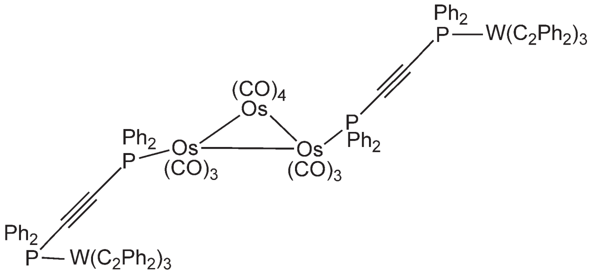

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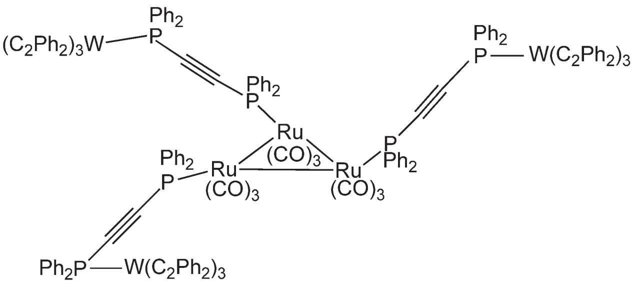

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Figure 41

Triruthenium complexes bridged by 1,1′-bis(diphenylphosphino)ferrocene, thus formally containing Ru–P–C bonds, have been reported.[216] Examples are complexes $Ru_3(CO)_{12-2n}L_n$ ($n=1$, 2). Phosphine-substituted complexes, such as $Ru_3(CO)_9(PTA)_3$ (PTA = 1,3,5-triaza-7-phospha-adamantane), are soluble in water.[217] Finally, triruthenium complexes, substituted with quinolines, react with dppm, forming clusters with Ru–C–P bonds due to the orthometallation of the dppm phenyls.[218]

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6.23
Tetranuclear Clusters of Ru/Os

R K Pomeroy and B K L Leong, Simon Fraser University, Burnaby, BC, Canada

6.23.1 Introduction

6.23.1.1 Perspective and Scope

This chapter covers the literature on tetraruthenium and tetraosmium organometallic compounds from 1995 until late 2005. The literature search was carried out with SciFinder Scholar. Compounds containing other transition metals have for the most part been omitted. Although not strictly cluster compounds, compounds containing a chain of four Ru or Os metal atoms are included. Also included for their intrinsic interest are tetranuclear cage compounds with two or less metal–metal bonds.

6.23.1.2 Overview of Structures

The carbonyl clusters of ruthenium (and osmium) form a bewildering diversity of structures not all of which can be rationalized by current theory. The tetranuclear clusters of ruthenium are no exception. Mononuclear ruthenium carbonyl complexes usually obey the 18-electron rule and therefore for a carbonyl compound with four Ru atoms requires a maximum of 72 valence electrons for Ru_4 bonding. Any more than 72 electrons should be considered as non-bonding electrons centered mainly on the ligands. For example, the cage compound $[Ru_4(\mu\text{-Se})_4(CO)_{12}]$ has 80 valence electrons, but it is best to consider eight of the electrons as forming lone pairs on the selenium atoms. In other words, each selenium atom donates four electrons to cage formation to give the molecule 72 cluster valence electrons (c.v.e.). This is consistent with the observation that there are no RuRu bonds present in the molecule.

For compounds with c.v.e. counts less than 72 to be electron precise requires sharing of electrons on the Ru atoms, that is, RuRu bond formation. For example, the anion $[Ru_4(CO)_{13}]^{2-}$ has 60 electrons and consistent with this count the Ru_4 nucleus is a tetrahedron with six RuRu bonds. For clusters with 62 (five RuRu bonds), 64 (four RuRu bonds) and 66 c.v.e. (three RuRu bonds), there a number of different configurations for the metal framework found for each count; these are shown in Figure 1 along with some possible structures for 68, 70, and 72 c.v.e. Ru_4 clusters.

Note that the 18-electron rule makes no prediction as to which of the various possibilities should be the most stable. The clusters often have bridging ligands and it is probably the requirements of these ligands, that in many cases, dictate which structure is most stable. Most of the clusters are prepared in thermolysis reactions at elevated temperatures and so it is reasonable to assume that in these cases the structure observed is the thermodynamically stable structure.

There are several classes of compounds that are exceptions to the predictions based on the 18-electron rule. Consider the acetylene derivative $[Ru_4(\mu_4\text{-}\eta^2\text{-CHCH})(CO)_{12}]$. The structure of this cluster may either be considered as a butterfly arrangement of Ru atoms with five RuRu bonds and the C_2H_2 ligand bridging all four Ru atoms across the wingtip atoms, or it may be considered as having a *closo*-Ru_4C_2 octahedron. If C_2H_2 is considered as a ligand, it brings four electrons for cluster bonding and hence the molecule has 60 c.v.e. The cluster is therefore two electrons short for a cluster with five RuRu bonds. If, however, each CH unit is considered as a vertex in the octahedron, then the unit brings five electrons for cluster bonding for a total of 66 c.v.e. Fifty-two electrons are removed to satisfy the external bonding requirements of C (two electrons each) and Ru (four electrons each) to leave 14 electrons (seven cluster bond pairs) for cluster bonding. According to

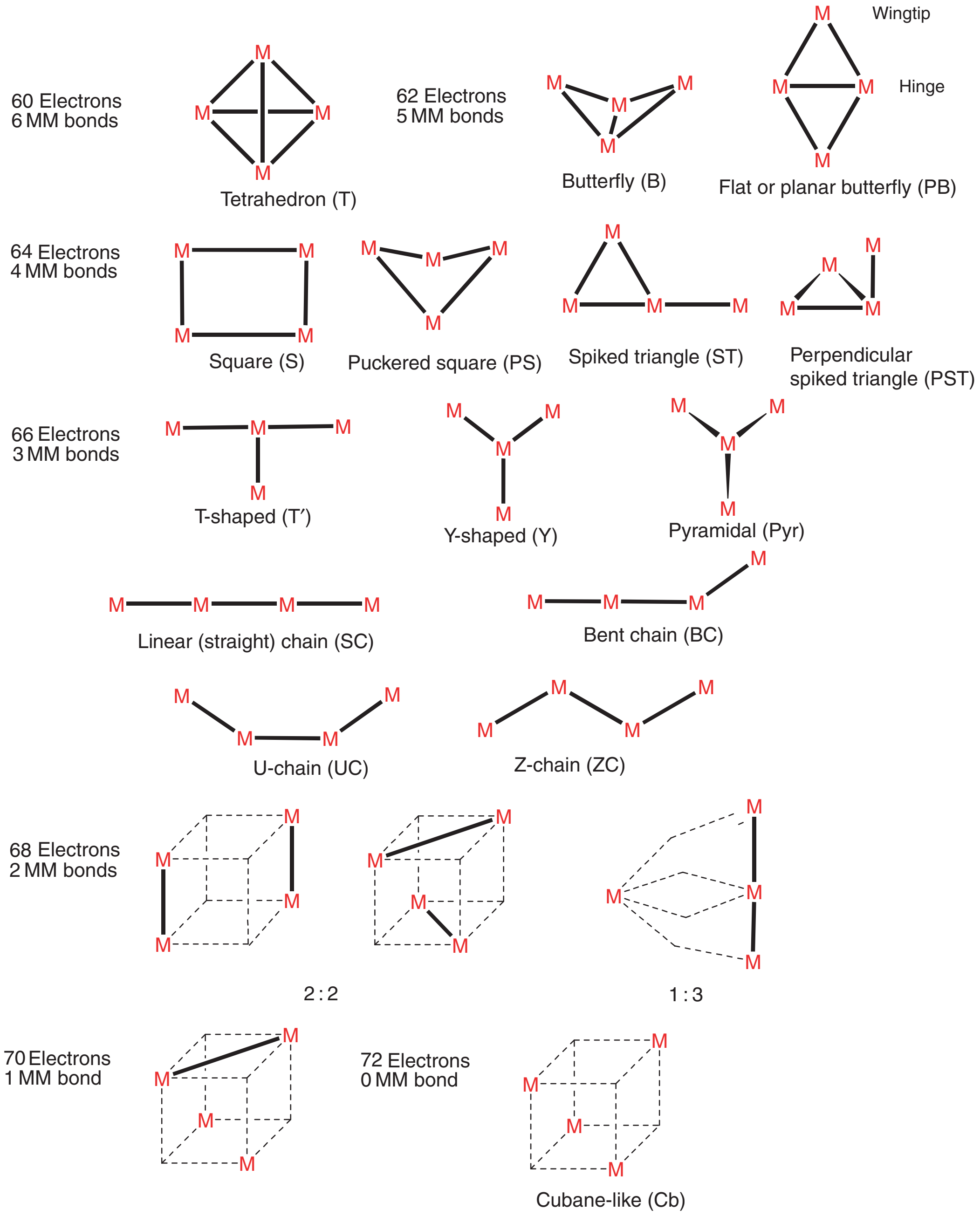


Figure 1 Possible metal arrangements based on the 18-electron rule for M_4 (M = Ru, Os) for a given c.v.e. count.

polyhedral skeletal electron pair theory (PSEPT), this count ($n+1$, where n is the number of vertices) corresponds to a *closo*-octahedron, which is observed.

A similar situation exists for $[Ru_4(\mu_4\text{-}\eta^2\text{-}CHCH)_2(\mu\text{-}CO)_2(CO)_9]$ and related clusters. If each alkyne ligand donates four electrons, then the molecule has a 62-electron count and again is two electrons short of the 66 c.v.e. required for the four RuRu bonds of the approximately square Ru_4 unit. By using the PSEPT formalism, however, the cluster has nine cluster bond pairs consistent with its *closo*-dodecahedral Ru_4C_4 core.

Yet another class of clusters where a problem exists are the $[Ru_4(\mu_4\text{-}PR)_2(\mu\text{-}CO)(CO)_{10}]$ clusters. It may appear that for highly condensed clusters the bonding is best rationalized with PSEPT. On the other hand, the $[Ru_4(\mu_4\text{-}PNR_2)_2(CO)_{12}]$ clusters are electron precise for the four RuRu bonds present in the molecules, but electron rich by

PSEPT for a *closo*-structure. The structures of the phosphorus derivatives have been rationalized using sophisticated MO arguments.

Another interesting class of Ru_4 clusters with unusual bonding are the $[Ru_4(\mu\text{-}PR_2)_2(CO)_{13}]$ clusters (see COMC (1995)). These clusters are formally 64 c.v.e. clusters and should have four RuRu bonds rather than the five observed. Three of the RuRu bonds are, however, extremely long. These clusters are regarded as electron rich with some of the cluster electrons occupying antibonding orbitals of the metal cluster.

6.23.1.3 Nomenclature

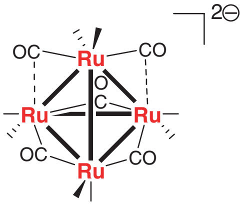
A cluster compound is best considered as a compound with a triangular or larger closed polyhedron of metal atoms. Compounds with 66 (chain compound), 68, 70, and 72 (cubane-like or cage compound) electrons are therefore not considered clusters, but as mentioned above are nevertheless included in this review because of their intrinsic interest.

In this review, for a cluster with an organic ligand multiply bound to the metal atoms through two or more carbon atoms, the general connectivity (hapticity) is denoted by one η-descriptor. Any non-carbon atoms of the ligand bound to a metal are included in the description. Four hapticity designators indicate the number of atoms of the ligand bound to each metal atom in the M_4 cluster starting at the vertex of the cluster and proceeding as far as possible in a clockwise manner around the cluster, for example, $[Ru_4(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(CO)_{12}]$ or $[Ru_4(\mu_4\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^2\text{-}C_2Ph_2)(CO)_{12}]$ ($[Ru_4(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}C_2Ph_2)(CO)_{12}]$).

6.23.2 Ruthenium Compounds without Hydrocarbon Ligands

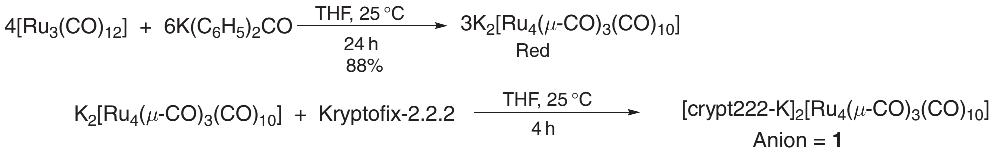
6.23.2.1 Carbonyl Anions

The red $[Ru_4(\mu\text{-}CO)_3(CO)_{10}]^{2-}$ anion **1** prepared by the stoichiometric reduction of $[Ru_3(CO)_{12}]$ with alkali metal diphenylketyl was first reported in 1980 (Scheme 1).[1] The structure of **1** as $[crypt222\text{-}K]_2[Ru_4(CO)_{13}]$ reveals a tetrahedral arrangement of metal atoms with three bridging carbonyls in a basal plane and two semibridging carbonyls to the apical Ru atom that also has two strictly terminal CO ligands.[2] This arrangement of carbonyls is different to that found in the Fe analog ($[Fe_4(\mu_3\text{-}CO)(CO)_{12}]^{2-}$). The three RuRu lengths of the Ru(μ-CO)Ru units in **1** are in the range 2.764(1)–2.797(1) Å whereas the unbridged RuRu distances are somewhat longer (2.859(1)–2.867(1) Å). The ^{13}C NMR spectrum of **1** from 20 to −138 °C displays a single resonance at δ 223.5, intermediate for bridging and terminal carbonyls.[2]



1

The anion $[Ru_4(\mu\text{-}H)_2(\mu\text{-}CO)_3(CO)_9]^{2-}$ **2** is conveniently prepared by the deprotonation of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ (Scheme 2).[3] The structure of **2** as the $[crypt221\text{-}Na]^+$ salt confirms the structure originally proposed based on spectroscopic evidence.[2] The RuRu lengths bridged by the carbonyl ligands have an average length of 2.770 Å; the RuRu vectors believed to be bridged by the hydride ligands have distances of 2.970(1) and 2.976(1) Å; the single unbridged RuRu bond has a length of 2.820(1) Å.



$$4[Ru_3(CO)_{12}] + 6K(C_6H_5)_2CO \xrightarrow[\substack{24\,h\\88\%}]{THF,\ 25\,°C} 3K_2[Ru_4(\mu\text{-}CO)_3(CO)_{10}]\ \text{Red}$$

$$K_2[Ru_4(\mu\text{-}CO)_3(CO)_{10}] + \text{Kryptofix-2.2.2} \xrightarrow[4\,h]{THF,\ 25\,°C} [crypt222\text{-}K]_2[Ru_4(\mu\text{-}CO)_3(CO)_{10}]\quad \text{Anion} = \mathbf{1}$$

Scheme 1

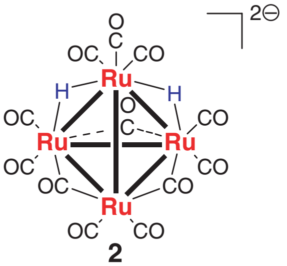
$$[Ru_4(\mu\text{-}H)_4(CO)_{12}] + 2KH \xrightarrow[24\,h]{THF,\ 50\,°C} K_2[Ru_4(\mu\text{-}H)_2(\mu\text{-}CO)_3(CO)_9] + 2H_2$$

Yellow, high yield

$$Na_2[Ru_4(\mu\text{-}H)_2(\mu\text{-}CO)_3(CO)_9] + \text{Kryptofix-2.2.1} \xrightarrow[4\,h]{THF,\ 25\,°C} [\text{crypt221-Na}]_2[Ru_4(\mu\text{-}H)_2(\mu\text{-}CO)_3(CO)_9]$$

Anion = **2**

Scheme 2



2

6.23.2.1.1 Carbonyl anions in synthesis and catalysis

The anion **1** is used in the preparation of $[Ru_4\{\mu_3\text{-}P(NPr^i{}_2)\}(CO)_{12}]$ **41b** (*vide infra*). Addition of $P(NPr^i{}_2)_2Cl$ to $K_2[Ru_4(CO)_{13}]$ gives $[Ru_3\{\mu\text{-}P(NPr^i{}_2)_2\}(CO)_9][Ru_6(\mu_6\text{-}C)\{\mu\text{-}P(NPr^i{}_2)_2\}(CO)_{15}]$.[4] The anion $[Ru_4(CO)_{12}]^{4-}$ is employed in the synthesis of $[Ru_4(\mu_4\text{-}PNR_2)_2(CO)_{12}]$ (*vide infra*). Like **1**, the precursor $[Ru_4(CO)_{12}]^{4-}$ is prepared by the action of potassium/benzophenone on $[Ru_3(CO)_{12}]$ in the correct molar ratio in THF.[1]

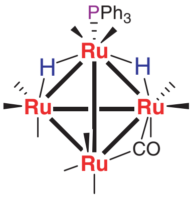
The compounds $K_2[Ru_4(CO)_{13}]$, $K_4[Ru_4(CO)_{12}]$, and $K_6[Ru_4(CO)_{11}]$ have received attention as catalysts in ammonia synthesis.[5–7] The compounds act as precursors for both the catalytically active ruthenium particles and the potassium promoter. The rate of the ammonia synthesis at 300 °C over these catalysts increases with the increase in the K:Ru ratio in the starting carbonyl metallate.[6]

6.23.2.2 Neutral Carbonyl Derivatives with Bridging Hydride Ligands

The cluster $[Ru_4(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{11}(PPh_3)]$ **3** is isolated (co-crystallized with $[Ru_3Ir(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}(PPh_3)]$) from the reaction of $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$ with $[Ir(CO)(PPh_3)_2(Cl)]$ (Equation (1)).[8] The H ligands are assumed to bridge the long MRu (M = Ru or Ir) bonds (average length 2.935 Å) that are *cis* to the P-donor ligand. The unbridged metal–metal bonds have an average length of 2.800 Å.

$$Na[Ru_3(\mu\text{-}H)(CO)_{11}] + [Ir(CO)(PPh_3)_2(Cl)] \xrightarrow[1\,h]{THF,\ 25\,°C}$$

<5%



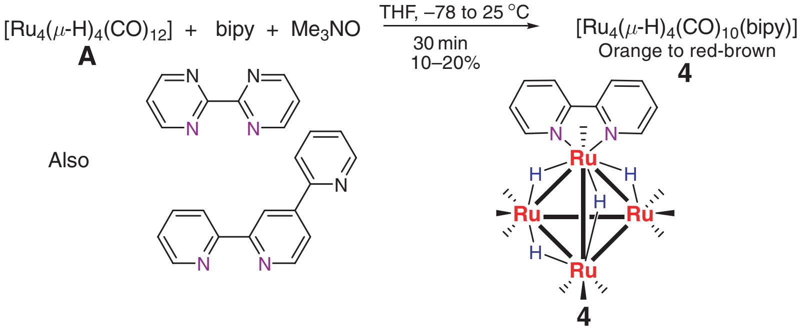
3

$$[Ru_4(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{11}(PPh_3)]/\,[Ru_3Ir(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}(PPh_3)] \quad (1)$$

Red brown

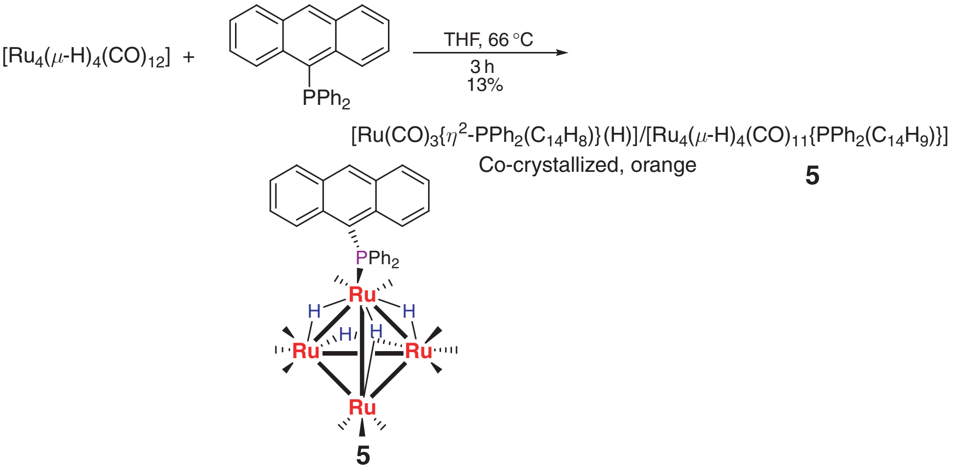
3

Previous studies have shown that $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(L)_x]$ ($x = 1–4$) derivatives may be prepared by: (i) heating the corresponding $[Ru_3(CO)_{12-x}(L)_x]$ clusters under hydrogen (20 atm), (ii) treatment of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ **A** and L with sodium diphenylketyl, and (iii) reaction of **A** and L in the presence of Me_3NO (see COMC (1995)). The red-brown derivatives $[Ru_4(\mu\text{-}H)_4(CO)_{10}(N–N)]$ (e.g., N–N = 2,2′-bipyridine, **4**) have been prepared by the amine oxide route (Equation (2)).[9] The structures of **4** and the 2,2′-bipyrimidine derivative indicate that three hydride ligands span the RuRu(N–N) bonds as shown.

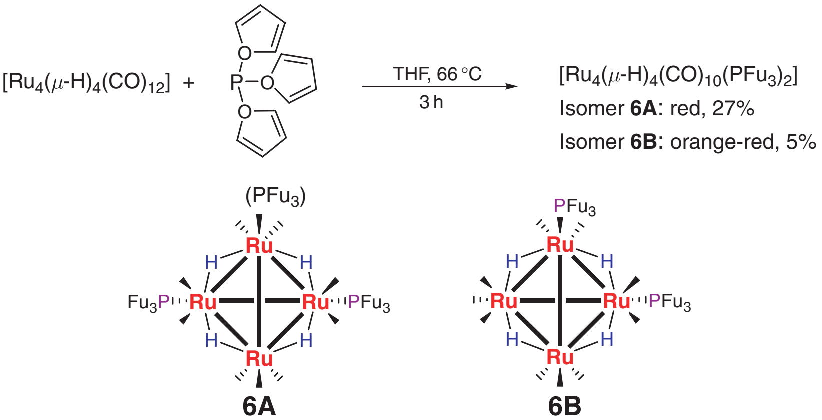


(2)

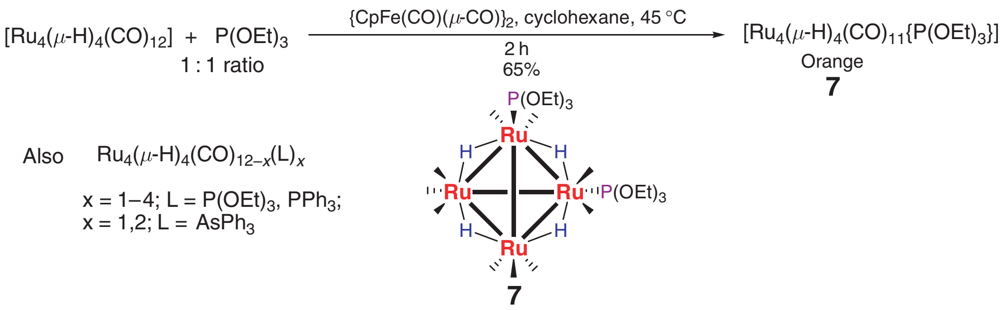
The co-crystallized molecules $[Ru(CO)_3\{\eta^2\text{-}PPh_2(C_{14}H_8)\}(H)]/[Ru_4(\mu\text{-}H)_4(CO)_{11}\{PPh_2(C_{14}H_9)\}]$ have been isolated from the reaction of **A** with $PPh_2(C_{14}H_9)$ (Equation (3)).[10] The structure reveals that in the tetranuclear moiety **5** the $Ru_4(\mu\text{-}H)_4$ unit has a less common isomeric form (for monosubstituted $[Ru_4(\mu\text{-}H)_4(CO)_{11}(L)]$ derivatives) with three hydrides attached to one Ru atom, which is also the Ru atom to which the P ligand is bound (see below). Heating **A** with tri(2-furyl)phosphine (PFu_3) in refluxing THF affords a number of products of which two are the isomers $[Ru_4(\mu\text{-}H)_4(CO)_{10}(PFu_3)_2]$ (**6A** and **6B**, Equation (4)). Both isomers were characterized by X-ray crystallography.[11] The clusters $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(L)_x]$ ($x = 1$–4, $L = P(OEt)_3$, PPh_3; $x = 1, 2$, $L = AsPh_3$) have been made from **A** and L in the correct molar ratio in the presence of a $\{CpFe(\mu\text{-}CO)(CO)\}_2$ catalyst (Equation (5)). The structure of $[Ru_4(\mu\text{-}H)_4(CO)_{10}\{P(OEt)_3\}_2]$ **7** is analogous to that of **6B**.[12]



(3)

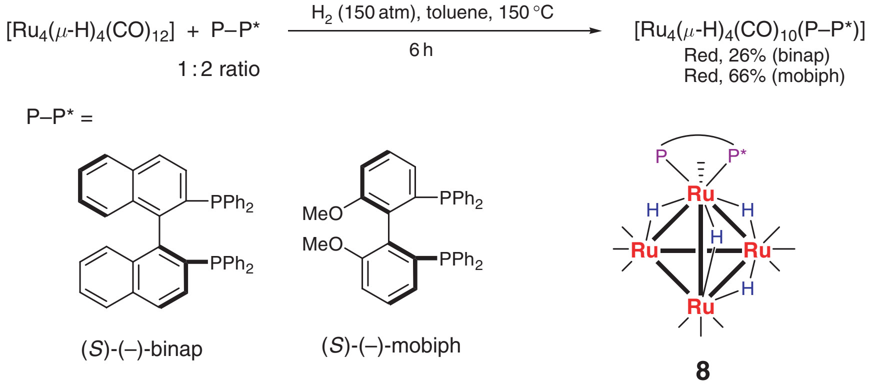


(4)



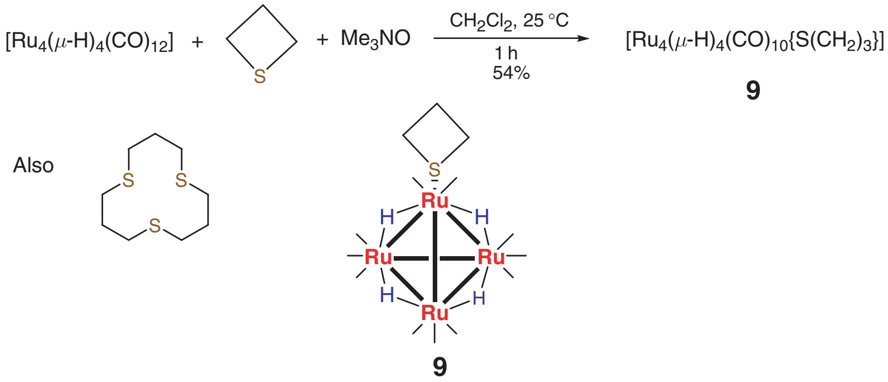
(5)

Direct reaction of **A** with the chiral diphosphine ligands (P–P*) (P–P* = (*S*)-(−)-binap or (*S*)-(−)-mobiph) at 150 °C under hydrogen pressure affords $[Ru_4(\mu\text{-}H)_4(CO)_{10}(P\text{–}P^*)]$ **8** as red crystals (Equation (6)). The structure shown is that determined crystallographically.[13]



(6)

The sulfur derivatives $[Ru_4(\mu\text{-}H)_4(CO)_{11}(SR_2)]$ ($SR_2 = S(CH_2)_3$, thietane **9**, and $SR_2 = \{S(CH_2)_3\}_3$, 1,5,9-trithiacyclododecacane) have been synthesized according to Equation (7).[14]



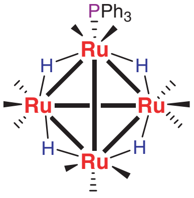
(7)

The structure of **9** is based on a comparison of its spectroscopic data with that of the $[Os_4(\mu\text{-}H)_4(CO)_{11}\{S(CH_2)_3\}_3]$ analog of known structure.[14]

One product isolated from the reaction of $Na[Ru_3(\mu\text{-}H)(CO)_{11}]$ and $[Ir(CO)(PPh_3)_2(Cl)]$ is $[Ru_4(\mu\text{-}H)_4(CO)_{11}(PPh_3)]$ **10** (Equation (8); see also Equation (1)).[8]

$$\mathrm{Na[Ru_3(\mu\text{-}H)(CO)_{11}]\ +\ [Ir(CO)(PPh_3)_2(Cl)]}\ \xrightarrow[\text{i, 1 h; ii, 2 h; <10\%}]{\text{i, THF, 25 °C, H}_3\text{PO}_4\text{; ii, hexane, H}_2}\ \mathrm{[Ru_4(\mu\text{-}H)_4(CO)_{11}(PPh_3)]}$$

Yellow
10



10

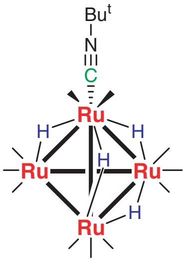
(8)

The yellow isocyanide complexes $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(CNBu^t)_x]$ ($x = 1$ **11**, and $x = 2$) result from the reaction of $[Ru_5(\mu_5\text{-}CNBu^t)_4(CO)_{14}(CNBu^t)]$ in toluene with hydrogen at 80 °C (Equation (9)).[15]

$$\mathrm{[Ru_5(\mu_5\text{-}CNBu^t)(CO)_{14}(CNBu^t)]}\ \xrightarrow[\text{30 min}]{\text{H}_2\text{, toluene, 80 °C}}\ \mathrm{[Ru_4(\mu\text{-}H)_4(CO)_{11}(CNBu^t)]\ +}$$

Yellow, 59%
11

$[Ru_4(\mu\text{-}H)_4(CO)_{10}(CNBu^t)_2]$
Yellow, 24%



11

(9)

Compound **11**, like **5**, is unusual for a monosubstituted derivative of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ in that it has three bridging hydride ligands to the same Ru atom (see next section).

Although the H atoms in $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(L)_x]$ are often not located by X-ray crystallography, their positions can readily be inferred from the RuRu bond lengths in the clusters. The RuRu lengths of Ru(μ-H)Ru linkages are typically in the range 2.92 to 3.02 Å, whereas the unbridged RuRu distances in $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(L)_x]$ clusters are in the range 2.75 to 2.80 Å. This is confirmed in the cases where the H ligands are located by X-ray crystallography and by a neutron diffraction study of $[Ru_4(\mu\text{-}H)_4(CO)_8\{P(OMe)_3\}_4]$ (COMC (1995)).

There are only two isomers of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$, the symmetric D_{2d} isomer in which the unbridged RuRu bonds are mutually *trans* (and do not share a common metal atom) and the more asymmetric C_s isomer where the unbridged RuRu bonds are *cis* and share a common Ru atom. These are shown in Figure 2. There are eight possible isomers for $[Ru_4(\mu\text{-}H)_4(CO)_{11}(L)]$ if the location of L at a given Ru atom (i.e., pseudo-*cis* or -*trans* to a bridged or unbridged RuRu bond) is taken into account (Figure 2). There are also eight isomers for $[Ru_4(\mu\text{-}H)_4(CO)_{10}(\eta^2\text{-}L\text{–}L)]$, where L–L is a bidentate ligand bound to a single Ru atom. The parent cluster **A** has the D_{2d} configuration (COMC (1995)). Most $[Ru_4(\mu\text{-}H)_4(CO)_{11}(L)]$ derivatives adopt the D1 structure in the solid state (e.g., **9** and **10**; for more examples, see COMC (1995)).[8,14] Exceptions are **5** and **11**. The former has a C2 configuration with the P and two H atoms in the mirror plane whereas **11** has a C1 configuration, where the CNBu^t substituent is not in the mirror plane.[15] Derivatives with a chelate ligand (e.g., **4** and **8**) similarly adopt a structure analogous to C1.[9,13] Compound **7** has the two $P(OEt)_3$ ligands transoid to different unbridged RuRu bonds whereas in $[Ru_4(\mu\text{-}H)_4(CO)_{10}(PPh_3)_2]$ the P ligands are in the pseudo-*trans*-positions to the same unbridged RuRu bond.[12] Both isomers have been isolated in the case of $[Ru_4(\mu\text{-}H)_4(CO)_{10}(PFu_3)_2]$ (i.e., **6A** and **6B**).[11] It is noted that these configurations avoid two strong σ-donor ligands (i.e., H and PR_3), being mutually *trans* to each other. It is also expected that RuRu bonds *cis* to PR_3 will be electron rich because of the poorer π-acceptor properties of the P ligand compared to CO, and for this reason might be preferred by hydride ligands.[16] From the NMR studies described below, it is apparent that more than one isomer is often present in solution for these derivatives indicating that some of the isomers have similar energies.

The ^{1}H NMR spectra of the $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(L)_x]$ ($x = 1$, 2) derivatives often show a singlet or broadened signals at room temperature indicative of rapid proton exchange (see also COMC (1995)).[8,11,12] Furthermore, for

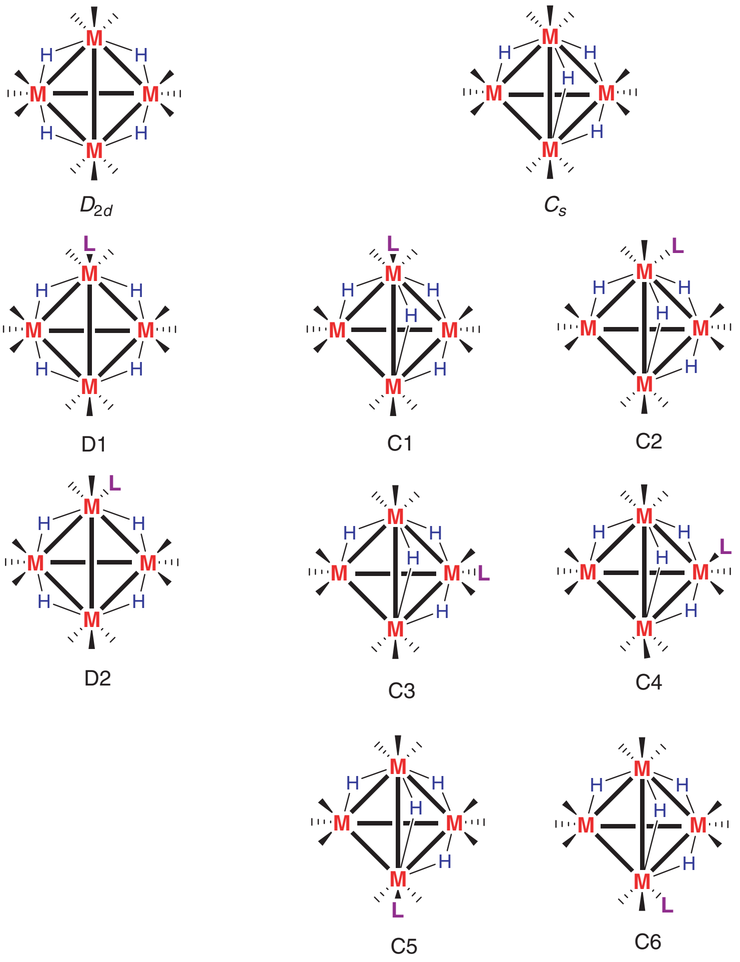


Figure 2 Possible isomers for $[M_4(\mu\text{-}H)_4(CO)_{12}]$ and $[M_4(\mu\text{-}H)_4(CO)_{11}(L)]$.

$[Ru_4(\mu\text{-}H)_4(CO)_{11}\{P(OEt)_3\}]$ in solution below −90 °C, the H exchange processes can be frozen where it is apparent that more than one isomer is present.[12] This is confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Because of the number of possible isomers it is difficult to interpret the low-temperature ^1H and ^{13}C NMR spectra of these derivatives. (The author's viewpoint is that the variable-temperature ^1H NMR spectra reported for $[Ru_4(\mu\text{-}H)_4(CO)_{11}\{P(OEt)_3\}]$ are better interpreted in terms of two isomers, namely D1 and C1, as being present rather than the three isomers suggested.[12]) Two isomers are found in solution for $[Ru_4(\mu\text{-}H)_4(CO)_{10}(L)_2]$ when L = PPh_3 or $AsPh_3$, but not for the $P(OEt)_3$ analog. Only one isomer is detected in solution for $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(L)_x]$ ($x = 3$, 4; L = PPh_3, $P(OEt)_3$). The ^1H NMR spectrum of $[Ru_4(\mu\text{-}H)_4(CO)_8(L)_4]$ consists of a quintet down to −100 °C indicative of rapid hydride exchange.[12] For 8, the hydride non-rigidity is stopped on the NMR timescale at about −20 °C (~0 °C for the mobiph analog) and the spectra also indicate the presence of two isomers.[13] From the P–H couplings in the spectra, it is apparent that one of the isomers is that found in the solid state (i.e., 8 analogous to C1) and the other with similar couplings probably indicates that the other isomer is the form analogous to C2. This in turn implies that the Ru(P–P*)(CO) unit does not rotate at this temperature. Simple migration of the basal H atom from one RuRu bond in the basal plane accomplishes the isomerization.

The $^{13}C\{^1H\}$ NMR spectra of $[Ru_4(\mu\text{-}H)_4(CO)_{11}(L)]$ (L = $P(OEt)_3$, PPh_3, $AsPh_3$) clusters at around −50 °C (where the hydride ligands are non-rigid) show that the CO ligands are rigid, but at higher temperatures some of the resonances broaden and collapse.[12] This is interpreted in terms of localized exchange of the $Ru(CO)_3$ groups.

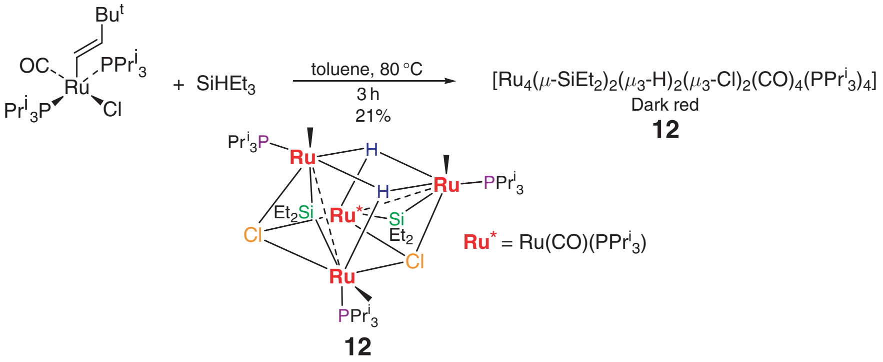
The variable-temperature ^1H NMR spectra of **A** in the solid state have been re-examined along with those of $[Ru_4(\mu\text{-}H)_4(CO)_{11}\{P(OMe)_3\}]$.[17,18] Line width and T_1 measurements of the hydride resonance are similar for both compounds and suggest that a common hydride movement occurs with $E_a = 17 \pm 2\,\mathrm{kJ\,mol^{-1}}$. A mechanism that involves a two-site H-flip about the H-bridged RuRu edges (i.e., each H atom remains bound to the same Ru atoms) and that preserves the site symmetry of the molecule is suggested to account for the changes.[17]

The electrochemical reduction of **A** generates a transient radical anion, $[Ru_4(\mu\text{-}H)_4(CO)_{12}]^{\cdot -}$ that produces the stable $[Ru_4(\mu\text{-}H)_3(CO)_{12}]^-$ with time. When the reduction is carried out in the presence of PPh_3, $[Ru_4(\mu\text{-}H)_4(CO)_{12-x}(PPh_3)_x]$ ($x = 1, 2$) are formed in yields depending on the concentration of the phosphine.[19] UV–VIS and resonance-Raman spectroscopy indicate significant $Ru(d_\pi) \rightarrow L(\pi^*)$ MLCT character of the lowest energy electronic transition in the $[Ru_4(\mu\text{-}H)_4(CO)_{10}(N\text{–}N)]$ complexes (e.g., **4**) mentioned above. Electrochemical reduction of $[Ru_4(\mu\text{-}H)_4(CO)_{10}(N\text{–}N)]$ gives the corresponding $[Ru_4(\mu\text{-}H)_4(CO)_{10}(N\text{–}N)]^{\cdot -}$ radical anions some of which are stable for minutes and can be characterized spectroscopically (IR, UV–VIS, ESR). The radical anions on uptake of a second electron or by thermal disproportionation yield $[Ru_4(\mu\text{-}H)_2(CO)_{10}(N\text{–}N)]^{2-}$ that contain bridging carbonyls.[9]

6.23.2.3 Carbonyl Derivatives with Bridging Ligands

6.23.2.3.1 Derivatives with bridging group 14 ligands other than C ligands

The compound $[Ru_4(\mu\text{-}SiEt_2)_2(\mu_3\text{-}H)_2(\mu_3\text{-}Cl)_2(CO)_4(PPr^i_3)_4]$ **12** is isolated from the reaction of $[Ru(CO)(PPr^i_3)_2(CHCHBu^t)(Cl)]$ and $SiHEt_3$ (Equation (10)).[20] There are two short RuRu interactions in the compound (2.822(1) and 2.828(1) Å) that normally would be indicative of RuRu bonds. The cluster has 64 valence electrons and does not require any RuRu bonds if each Ru atom has a 16 rather than an 18-electron configuration. The precursor complex, $[Ru(CO)(PPr^i_3)_2(CHCHBu^t)(Cl)]$, has a 16-electron configuration. The RuSi lengths in **12** are in the range 2.361(3) to 2.377(3) Å. The cluster is also a rare example of an Ru_4 carbonyl cluster with triply- bridging hydride ligands. The temperature-dependent ^{31}P NMR spectra of **12** have been interpreted in terms of dissociation of the tetranuclear structure into dinuclear fragments.[20]



(10)

6.23.2.3.2 Derivatives with bridging group 15 ligands

6.23.2.3.2.(i) Derivatives with bridging N ligands

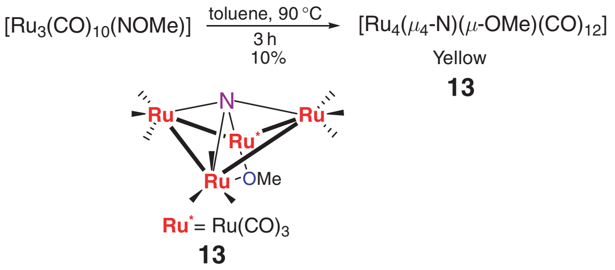
Compounds with bridging N ligands whose structures have been determined during the review period are given in Table 1. As can be seen, all but two compounds contain hydrocarbon ligands and hence are discussed later.

The cluster $[Ru_4(\mu_4\text{-}N)(\mu\text{-}OMe)(CO)_{12}]$ **13** is one product from the thermolysis of $[Ru_3(\mu_3\text{-}NOMe)(\mu_3\text{-}CO)(CO)_9]$ (Equation (11)).[21] The cluster has a butterfly (strictly speaking a puckered square) arrangement of metal atoms with the N atom bound to each Ru atom. In agreement with its 64 electron count, there are only four RuRu bonds in the cluster; the hinge RuRu vector (bridged by the methoxy group) is non-bonding at 3.22 Å. The RuN distances to the wingtip Ru atoms (1.903(5), 1.906(5) Å) are significantly shorter than the RuN bonds to the hinge atoms (2.131(4), 2.134(5) Å).[21]

Table 1 Crystallographic data for some clusters with bridging N ligands

Compound	*Structure*[a]	*RuRu* (Å)	*RuN* (Å)
μ_4-*N*			
$[Ru_4(\mu_4\text{-}N)(\mu\text{-}OMe)(CO)_{12}]$ **13**	**B (PS)**[b]	2.814(7), 2.8172(7), 2.8214(7), 2.8249(7), 2.8258(7)	1.903(5),[c] 1.906(5),[c] 2.131(4), 2.134(5)
μ_4-*NR*			
$[Ru_4(\mu_4\text{-}NOMe)(\mu_4\text{-}\eta^2\text{-}C_2HPh)(\mu\text{-}CO)_2(CO)_9]$ **157a**	**PS**	2.6731(7), 2.6945(7), 2.7287(7), 2.8021(7)	2.128(5), 2.151(5), 2.173(5), 2.230(5)
$[Ru_4(\mu_4\text{-}NOMe)(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}CO)_2(CO)_9]$ **157b**	**PS**	2.6830(4), 2.6910(4), 2.7278(4), 2.7920(4)	2.123(3), 2.127(3), 2.167(3), 2.235(3)
$[Ru_4(\mu_4\text{-}NC(O)OMe)(\mu_4\text{-}\eta^2\text{-}C_2HPh)(\mu\text{-}CO)_2(CO)_9]$ **158a**	**PS**	2.685(1), 2.699(1), 2.724(1), 2.807(1)	2.177(7), 2.178(6), 2.180(6), 2.221(7)
$[Ru_4(\mu_4\text{-}NC(O)OMe)(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}CO)_2(CO)_9]$ **158b**	**PS**	2.6988(8), 2.7076(9), 2.7398(9), 2.7445(8)	2.171(5), 2.176(5), 2.177(6), 2.190(6)
$[Ru_4(\mu_4\text{-}NOMe)(\mu_4\text{-}\eta^2\text{-}C_2HPh)(\mu\text{-}CO)_2(CO)_8(NCMe)]$ **160A**	**PS**	2.676(1), 2.700(2), 2.723(1), 2.786(1)	2.128(8), 2.161(8), 2.183(8), 2.214(9)
$[Ru_4(\mu_4\text{-}NOMe)(\mu_4\text{-}\eta^2\text{-}C_2HPh)(\mu\text{-}CO)_2(CO)_8(PPh_3)]$ **161**	**PS**	2.6703(6), 2.6967(6), 2.7933(6), 2.8161(6)	2.137(4), 2.148(4), 2.190(4), 2.221(4)
$[Ru_4(\mu_4\text{-}NOMe)(\mu_4\text{-}\eta^2\text{-}C_2HPh)(\mu\text{-}CO)_2(CO)_7(PPh_3)_2]$ **162**	**PS**	2.678(2), 2.686(2), 2.805(2), 2.808(2)	2.15(1), 2.16(1), 2.18(1), 2.25(1)
$[Ru_4(\mu_4\text{-}NPh)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu\text{-}CO)(CO)_{10}]$ **14**	**S**	2.727(2), 2.777(2), 2.806(2), 2.818(2)	2.19(1), 2.21(1), 2.22(1), 2.27(1)

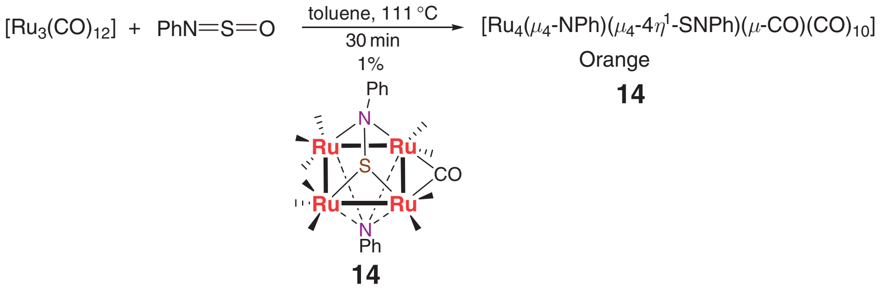
[a] See Figure 1.
[b] No hinge RuRu bond.
[c] To the wingtip Ru atoms.



$$[Ru_3(CO)_{10}(NOMe)] \xrightarrow[3\,h,\ 10\%]{\text{toluene, 90 °C}} [Ru_4(\mu_4\text{-}N)(\mu\text{-}OMe)(CO)_{12}] \qquad (11)$$

Yellow
13

The reaction of *N*-sulfinylaniline (PhN=S=O) and $[Ru_3(CO)_{12}]$ in refluxing toluene produces as many as nine products of which only four have been identified.[22] One minor product is $[Ru_4(\mu_4\text{-}NPh)(\mu_4\text{-}4\eta^1\text{-}SNPh)(\mu\text{-}CO)(CO)_{10}]$ **14** (Equation (12); see also Equation(40)). The μ_4-phenylamido (μ_4-NPh) ligand is considered a four-electron donor and the unusual μ_4-(phenylimido)thio ligand a six-electron donor to give **14** a 64 c.v.e. count which is therefore electron precise for a square cluster with four RuRu bonds.[22]



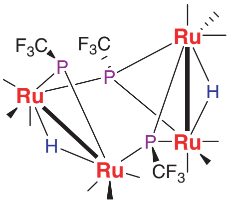
$$[Ru_3(CO)_{12}] + PhN{=}S{=}O \xrightarrow[30\,min,\ 1\%]{\text{toluene, 111 °C}} [Ru_4(\mu_4\text{-}NPh)(\mu_4\text{-}4\eta^1\text{-}SNPh)(\mu\text{-}CO)(CO)_{10}] \qquad (12)$$

Orange
14

6.23.2.3.2.(ii) Derivatives with bridging μ-P ligands

An unusual bridging Ru(μ-PR)Ru unit is found in $[Ru_4(\mu\text{-}H)_2\{\mu\text{-}P(CF_3)\}\{\mu_3\text{-}P(CF_3)\}_2(CO)_{12}]$ **15**, which is isolated in low yield from the reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with $\{P(CF_3)\}_n$ ($n=4$, 5) in CH_2Cl_2 at 70 °C in a sealed reaction vessel (Equation (13)).[23] The coordination about the P atom of this unit is pyramidal as expected; the RuPC(CF_3) angles are in the range 108.7(5)°–110.6(4)° in the two independent molecules. The RuP distances are long at 2.417(3), 2.403(3) (A) and 2.409(3), 2.424(3) Å (B) for molecules A and B. Compound **15** is also a rare example of a 68 c.v.e. Ru_4 compound and consistent with this view there are only two RuRu bonds (2.857(2), 2.967(2) (A) and 2.863(2), 2.980(2) Å (B)). The longer RuRu bond is that bridged by the unique P ligand plus a hydride ligand.

$$[Ru_4(\mu\text{-}H)_4(CO)_{12}] + \{P(CF_3)\}_4 \xrightarrow[\substack{16\,h\\ 8\%}]{CH_2Cl_2,\ 70\,°C} \underset{\substack{\text{Orange}\\ \mathbf{15}}}{[Ru_4\{\mu\text{-}P(CF_3)\}\{\mu_3\text{-}P(CF_3)\}_2(\mu\text{-}H)_2(CO)_{12}]} \qquad (13)$$

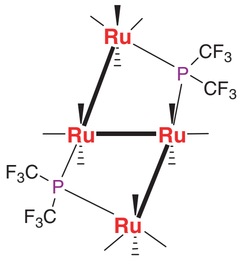


15

Reaction of $[Ru_3(CO)_{12}]$ with $(F_3C)_2PP(CF_3)_2$ in p-xylene at 140 °C yields $[Ru_4\{\mu\text{-}P(CF_3)_2\}_2(CO)_{14}]$ **16**, $[Ru_4\{\mu\text{-}P(CF_3)_2\}_2(CO)_{13}]$ **17**, and $[Ru_4\{\mu\text{-}P(CF_3)_2\}_4(CO)_{11}]$ **18** (Equation (14)).[24]

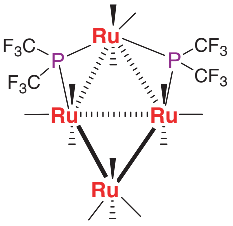
$$[Ru_3(CO)_{12}] + (CF_3)_2PP(CF_3)_2 \xrightarrow[18\,h]{p\text{-xylene, }140\,°C} \underset{\substack{\text{Orange, 6\%}\\ \mathbf{16}}}{[Ru_4\{\mu\text{-}P(CF_3)_2\}_2(CO)_{14}]} + \underset{\substack{\text{Red, 17\%}\\ \mathbf{17}}}{[Ru_4\{\mu\text{-}P(CF_3)_2\}_2(CO)_{13}]} + \underset{\substack{\text{Red, 2\%}\\ \mathbf{18}}}{[Ru_4\{\mu\text{-}P(CF_3)_2\}_4(CO)_{11}]} \qquad (14)$$

The Ru atoms of **16** have a planar Z chain arrangement with the 1,3 and 2,4 atoms bridged by the P ligands. The complex has three RuRu bonds consistent with its 66 c.v.e. counts. The outer RuRu bonds are crystallographically equivalent at 2.941(1) Å, with the inner RuRu length 2.935(1) Å. The RuP distances to the terminal Ru atoms are slightly longer than those to the inner metal atoms (2.384(2) vs. 2.312(2) Å).



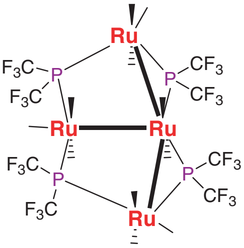
16

Cluster **17** has a flat butterfly structure previously found for $[Ru_4(\mu\text{-}PR_2)_2(CO)_{13}]$ (R = Ph, Pr^i, NPr^i, etc.; see Section 6.23.1 and COMC (1995)). As discussed previously, these are formally 64 c.v.e. clusters and should have four RuRu bonds rather than the five observed. These clusters are regarded as electron rich with some of the cluster electrons occupying antibonding orbitals of the metal cluster such that three of the RuRu bonds are long. In **17**, the RuRu vectors of the Ru(μ-PR_2)Ru units are, however, exceptionally long at 3.147(3) and 3.374(3) Å, with the hinge RuRu bond at 3.077(3) Å. In $[Ru_4(\mu\text{-}PPh_2)_2(CO)_{13}]$, these vectors are 3.185, 3.159, and 3.134 Å (COMC (1995)). The remaining RuRu lengths in **17** (2.869(3) and 2.913(3) Å) are in the range typical for RuRu bonds in open clusters. The Ru–P lengths in $[Ru_4(\mu\text{-}PR_2)_2(CO)_{13}]$ reflect the σ-donor/π-acceptor properties of the P ligands. The average RuP distance in **17** is 2.305(5) Å consistent with the view that $P(CF_3)_2$ is a strong π-acceptor ligand.



17

There are three RuRu bonds in **18** as expected for a 66 c.v.e. cluster; the bonds form a distorted T ("fan") arrangement. The central RuRu bond is long at 3.119(2) Å, whereas the bonds bridged by P ligands are 2.956(2) and 2.961(2) Å. The RuP lengths in **18** are significantly different: the average RuP length that spans non-bonded Ru atoms is 2.375(2) Å, whereas the average RuP length that bridges RuRu bonds is 2.287(2) Å.[24]

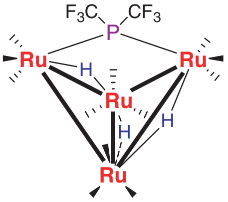


18

The cluster $[Ru\{\mu\text{-}P(CF_3)_2\}(\mu\text{-}H)_3(CO)_{12}]$ **19** is isolated from the reaction of $[Ru_3(CO)_{12}]$ and $PH(CF_3)_2$ at 80 °C and by the reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with $(F_3C)_2PP(CF_3)_2$ in *p*-xylene at 140 °C (Equations (15) and (16), respectively).[24,25] Compound **19** has 62 c.v.e.'s and consistent with this count has five RuRu bonds. The hydride ligands are assumed to bridge the long ((3.039(1) and 3.061(2) Å) peripheral bonds that are on opposite sides of the butterfly structure, and the hinge bond (2.946(1) Å). The unbridged RuRu bonds have lengths of 2.865(1) and 2.881(1); the RuP distances are 2.315(3) and 2.332(2) Å. The ^1H NMR spectrum of **19** at −85 °C is consistent with the solid-state structure. At 0 °C, only a singlet (coupled to phosphorus) is observed indicative of rapid exchange of the protons at this temperature.[24]

$$\underset{1:1\ \text{ratio}}{[Ru_3(CO)_{12}] + PH(CF_3)_2} \xrightarrow[18\,h]{CH_2Cl_2,\ 80\,°C} \underset{5\%}{\mathbf{18}} + \underset{\underset{\mathbf{19}}{\text{Orange, 20\%}}}{[Ru_4\{\mu\text{-}P(CF_3)_2\}(\mu\text{-}H)_3(CO)_{12}]} \qquad (15)$$

$$[Ru_4(\mu\text{-}H)_4(CO)_{12}] + (F_3C)_2PP(CF_3)_2 \xrightarrow[3\,h]{p\text{-xylene},\ 140\,°C} \underset{6\%}{\mathbf{17}} + \underset{10\%}{\mathbf{19}}$$



19

(16)

Some compounds with a bidentate P ligand bridging two Ru atoms are given in Table 2. The ligands are usually strictly spectator ligands taking the place of two carbonyl ligands.

Table 2 Some structural data for clusters with a simple μ_2-η^1:η^1-P–P or related ligand

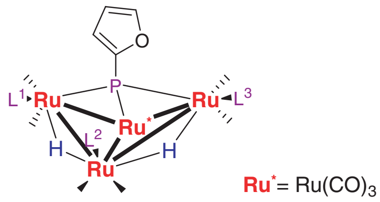
Compound	*RuP lengths* (Å)
$[Ru_4(\mu_4\text{-}S)_2\{\mu\text{-}(PPh_2CH_2)_2C_6H_4\}(\mu\text{-}CO)(CO)_8]$ **54**	2.305(2), 2.309(2)
$[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}PPr^i{}_2NHPPr^i{}_2)(\mu\text{-}CO)(CO)_8]$ **55**	2.304(2), 2.322(2)
$[Ru_4(\mu_3\text{-}Se)_4(\mu\text{-}PPh_2CH_2PPh_2)(CO)_{10}]$ **59**	2.348(3), 2.355(3)
$[Ru_4(\mu_4\text{-}Se)_2\{\mu\text{-}P,N\text{-}PPh_2(C_5H_4N)\}(\mu\text{-}CO)_2(CO)_7]$ **62**	2.303(3)
$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}PPh_2CH_2PPh_2)(\mu\text{-}CO)(CO)_8]$ **63**	2.304(1), 2.341(1)
$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}PPh_2NHPPh_2)(\mu\text{-}CO)(CO)_8]$ **64**	2.298(4), 2.287(4)
$[Ru_4\{\mu_4\text{-}\eta^2\text{-}C_2Ph(C_2Ph)\}(\mu\text{-}PPh_2CH_2PPh_2)(CO)_{10}]$[117]	2.280(4), 2.351(4)
$[Ru_4\{\mu_4\text{-}\eta^2\text{-}C_2Ph(C_2Ph)\}\{\mu_4\text{-}\eta^2\text{-}C_2(SiMe_3)(C_2SiMe_3)\}(\mu\text{-}PPh_2CH_2PPh_2)(\mu\text{-}CO)(CO)_8]$ **156**	2.27(2), 2.40(2)
$[Ru_3\{\mu_3\text{-}CC[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2]\}(\mu\text{-}PPh_2CH_2PPh_2)(CO)_7]$ **129**	2.288(1), 2.326(1)
$[Ru_4\{\mu_4\text{-}\eta^2\text{-}P(CH_2)_2PPh_2\}(\mu_4\text{-}\eta^4\text{-}C_6H_4)(\mu\text{-}CO)(CO)_9]$ **191**	2.310(3)
$[Ru_4(\mu_3\text{-}PPh_2(C_{10}H_6)PPhC_6H_4)(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_7]$ **222**	2.320(1), 2.341(1)
$[Ru_4(\mu_3\text{-}PPh_2(C_{10}H_6)PPh)(\mu\text{-}H)(\mu_3\text{-}C_6H_4)(CO)_{11}]$[101]	2.309(1)
$[Ru_4(\mu_2\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-}PPhCH_2PPh_2)(\mu\text{-}CO)(CO)_6]$ **195**	2.316(2)

6.23.2.3.2.(iii) Derivatives with bridging μ_3-P ligands

Structures with a P ligand bridging three Ru atoms are given in Table 3.

Three other compounds isolated from the reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with PFu_3 (see Equation (4)) are $[Ru_4(\mu_3\text{-}PFu)(\mu\text{-}H)_2(CO)_{12-x}(PFu_3)_x]$ ($x = 0$ **20**; $x = 2$ **21**; $x = 3$ **22**; Equation (17)).[11] All these clusters have similar butterfly metal skeletons with a PFu unit bridging the wingtip Ru atoms and just one of the hinge metal atoms. The peripheral RuRu bonds to the second hinge Ru atom are long and are assumed to be bridged by hydride ligands (see Table 3).

$$\underset{\textbf{A}}{[Ru_4(\mu\text{-}H)_4(CO)_{12}]} + PFu_3 \xrightarrow[3\,h]{THF,\ 66\,°C} \underset{\text{Orange, 12\%}\ \textbf{20}}{[Ru_4\{\mu_3\text{-}P(C_4H_3O)\}(\mu\text{-}H)_2(CO)_{12}]} + \underset{\text{Red, 10\%}\ \textbf{21}}{[Ru_4\{\mu_3\text{-}P(C_4H_3O)\}(\mu\text{-}H)_2(CO)_{10}(PFu_3)_2]} + \underset{\text{Red, 16\%}\ \textbf{22}}{[Ru_4\{\mu_3\text{-}P(C_4H_3O)\}(\mu\text{-}H)_2(CO)_9(PFu_3)_3]} \qquad (17)$$



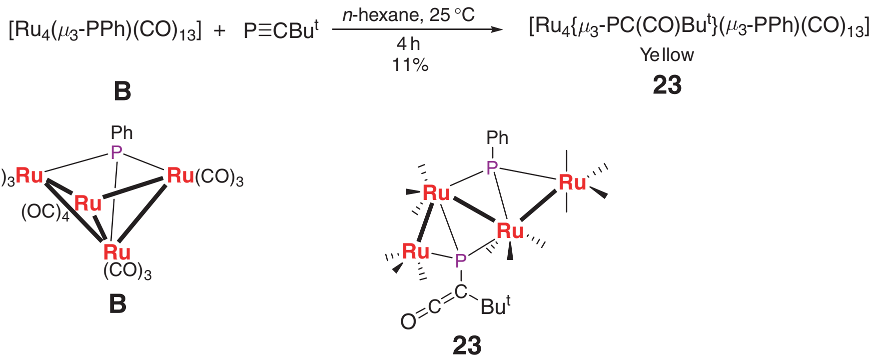
$L^1 = L^2 = L^3 = CO$ **20**
$L^1 = CO,\ L^2 = L^3 = PFu_3$ **21**
$L^1 = L^2 = L^3 = PFu_3$ **22**

Table 3 Structural data for some structures containing a μ_3-P-donor ligand

Compound	*Ru₄ Geometry*[a]	*RuRu lengths* (Å)
$[Ru_4(\mu_3\text{-}PFu)(\mu\text{-}H)_2(CO)_{12}]$ **20**	B	2.8225(4), 2.8534(4), 2.8626(4), 2.9946(4), 3.0110(4)
$[Ru_4(\mu_3\text{-}PFu)(\mu\text{-}H)_2(CO)_{10}(PFu_3)_2]$ **21**	B	2.8171(3), 2.8581(3), 2.8901(4), 3.0036(3), 3.0132(3)
$[Ru_4(\mu_3\text{-}PFu)(\mu\text{-}H)_2(CO)_9(PFu_3)_3]$ **22**	B	2.8159(8), 2.8581(9), 2.8675(9), 3.0099(8), 3.0207(9)
$[Ru_4(\mu_3\text{-}PPh)\{\mu_3\text{-}PC(CO)Bu^t\}(CO)_{12}]$ **23**	ZC	2.907(1), 2.930(1), 2.912(1)
$[Ru_4\{\mu_3\text{-}P(NPr^i{}_2)\}(CO)_{13}]$ **24**	B	2.775(1), 2.798(1), 2.856(1), 2.883(1), 2.960(1)
$[Ru_4\{\mu_3\text{-}P(OH)\}(CO)_{13}]$ **25**	B	2.802(1), 2.830(1), 2.859(1), 2.914(1), 2.924(1)
$[Ru_4(\mu_3\text{-}PPh)(CO)_{12}]^{2-}$ **26**	B	2.790(1), 2.852(1), 2.863(1), 2.897(1), 2.915(1)
$[Ru_4\{\mu_3\text{-}P(NPr^i{}_2)\}(CO)_{12}]$ **27**	T′	2.787(1), 2.810(1), 2.847(1), 2.848(1), 2.890(1)
$[Ru_4(\mu_3\text{-}PO)(CO)_{12}]^-$ **28**[b]	T′	2.788(1), 2.799(1), 2.818(1), 2.855(1), 2.856(1), 2.865(1)
$[Ru_4\{\mu_3\text{-}P(CF_3)\}_4(CO)_{12}]$ **30**	Cb	

[a] See Figure 1.
[b] $[H_2NPr^i{}_2]$ salt.

The 62 c.v.e. *nido*-$[Ru_4(\mu_3\text{-PPh})(CO)_{13}]$ cluster **B** has previously been shown to exhibit a rich and diverse chemistry in its reactions with alkynes and diynes (COMC (1995)). Reaction of the phospha-alkyne $PCBu^t$ with **B** at room temperature gives $[Ru_4(\mu_3\text{-PPh})\{\mu_3\text{-PC(CO)Bu}^t\}(CO)_{13}]$ **23** (Equation (18)).[26] The $PC(CO)Bu^t$ ligand contains a ketene unit resulting from attack by a CO molecule on the coordinatively unsaturated C atom of the methylidyne unit. The Ru_4 skeleton in **23** has a distorted Z chain that is consistent with its 66 c.v.e. count. The $PC(CO)Bu^t$ ligand bridges three consecutive metal atoms; the PPh unit bridges the two internal Ru atoms and the other terminal metal atom.[26]



(18)

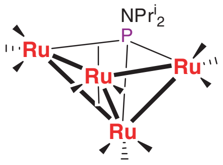
The synthetic route to $[Ru_4\{\mu_3\text{-P(NPr}^i{}_2)\}(CO)_{13}]$ **24** is shown in Equation (19).[27] The structure of **24** consists of a *nido*-square-pyramidal Ru_4P skeleton with the P atom occupying one of the basal sites. An alternative view of the structure is that it consists of butterfly arrangement of Ru atoms with the phosphinidene ligand bound to three of the Ru atoms. The hinge metal–metal bond is significantly longer than the peripheral RuRu bonds. The RuRu and RuP lengths in **24** are given in Tables 3 and 4, respectively. The PN distance is 1.671(4) Å. The cluster is a rare example of a butterfly structure where a hinge metal atom has four CO ligands.[27]

Table 4 RuP bond lengths and ^{31}P NMR chemical shifts for some compounds containing a μ_3-P ligand

Compound	*RuP lengths (Å)*	$\delta\ ^{31}P$ (ppm)
$[Ru_4(\mu_3\text{-PFu})(\mu\text{-H})_2(CO)_{12}]$ **20**	2.291(1), 2.294(1), 2.361(1)	352.7
$[Ru_4(\mu_3\text{-PFu})(\mu\text{-H})_2(CO)_{10}(PFu_3)_2]$ **21**	2.302(1), 2.303(1), 2.365(1), (2.287(1), 2.307(1))[a]	338.2 (−6.5, −18.0)[a]
$[Ru_4(\mu_3\text{-PFu})(\mu\text{-H})_2(CO)_9(PFu_3)_3]$ **22**	2.315(2), 2.318(2), 2.379(2), (2.292(2), 2.295(2), 2.320(2))[a]	322.1 (−10.1, −22.4)[a]
$[Ru_4(\mu_3\text{-PPh})\{\mu_3\text{-PC(CO)Bu}^t\}(CO)_{13}]$ **23**	2.330(2), 2.408(2), 2.352(2) (R)[b], 2.380(2), 2.383(2), 2.426(2) (Ph)	158 (R), 246 (Ph), ($J_{PP} = 179$)
$[Ru_4\{\mu_3\text{-P(NPr}^i{}_2)\}(CO)_{13}]$ **24**	2.310(1), 2.323(1), 2.413(1)	466.0
$[Ru_4\{\mu_3\text{-P(OH)}\}(CO)_{13}]$ **25**	2.266(1), 2.278(1), 2.367(1)	498.6
$[Ru_4(\mu_3\text{-PPh})(CO)_{12}]^{2-}$ **26**	2.289(1), 2.294(1), 2.344(1)	432
$[Ru_4\{\mu_3\text{-P(NPr}^i{}_2)\}(CO)_{12}]$ **27**	2.270(1), 2.298(1), 2.309(1)	467
$[Ru_4(\mu_3\text{-PO})(CO)_{12}]^-$ **28**	2.282(1), 2.293(1), 2.297(1)	476.2
$[Ru_4\{\mu_4\text{-}\eta^2{:}\eta^4{:}\eta^2{:}\eta^4\text{-C(C}_2\text{SiMe}_3\text{)C(C}_2\text{SiMe}_3\text{)-C(C}_2\text{SiMe}_3\text{)C}_3\text{(SiMe}_3\text{)C(C}_2\text{SiMe}_3\text{)-C(C}_2\text{SiMe}_3)\}(\mu_3\text{-PPh})(CO)_{10}]$	2.220(1), 2.339(1)[c]	427.3
$[Ru_4(\mu\text{-H})_2\{\mu\text{-P(CF}_3)\}\{\mu_3\text{-P(CF}_3)\}_2(CO)_{12}]$ **29**	2.388(3)–2.450(3)[d]	–
$[Ru_4\{\mu_3\text{-P(CF}_3)\}_4(CO)_{12}]$ **30**	2.384(2)–2.412(2)[d]	−77.2(m)[e]

[a] $Ru\text{-}PFu_3$.
[b] $R = C(CO)Bu^t$.
[c] Only two lengths quoted.
[d] Range.
[e] Attributed to virtual coupling.

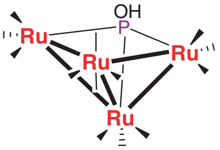
$$\underset{\mathbf{1}}{[Ru_4(CO)_{13}]^{2-}} + P(NPr^i_2)Cl_2 \xrightarrow[\text{2 h, 18–22\%}]{\text{THF, 25 °C}} \underset{\mathbf{24}}{\underset{\text{Dark red}}{[Ru_4\{\mu_3\text{-}P(NPr^i_2)\}(CO)_{13}]}} \quad (19)$$



24

Treatment of **24** in CH_2Cl_2 with $HBF_4{\cdot}OEt_2$ followed by removal of solvent, extraction, and repeated crystallization from undried hexane affords $[Ru_4\{\mu_3\text{-}P(OH)\}(CO)_{13}]$ **25** (Equation (20)).[28] The molecular structure of **25** consists of a distorted *nido*-square-pyramidal Ru_4P framework with the P atom of the POH ligand occupying a basal position. As in **24**, the hinge RuRu bond is the longest RuRu bond in the cluster (Table 3). The PO length of 1.627(2) Å is consistent with a PO single bond. In the solid pairs of molecules are linked by two O–H···· O hydrogen bonds. Deprotonation of the OH group in **25** with $NHPr^i_2$ gives $[NH_2Pr^i_2][Ru_4(\mu_3\text{-}PO)(CO)_{12}]$ described below.[28]

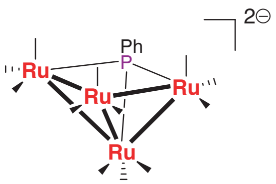
$$[Ru_4\{\mu_3\text{-}P(NPr^i_2)\}(CO)_{13}] + HBF_4{\cdot}OEt_2 \xrightarrow[\text{53\%}]{CH_2Cl_2\ (H_2O),\ 25\ °C} \underset{\mathbf{25}}{[Ru_4\{\mu_3\text{-}P(OH)\}(CO)_{13}]} \quad (20)$$



25

Addition of cobaltocene to **B** in CH_2Cl_2 results in the immediate precipitation of $[Cp_2Co]_2[Ru_4(\mu_3\text{-}PPh)(CO)_{12}]$(Anion = **26** Equation (21)).[29] The structure of the dianion is similar to that of the neutral parent cluster with its butterfly Ru_4 arrangement or, alternatively, a *nido*-square-pyramidal Ru_4P skeleton. The average RuRu distance in **26** (2.863 Å) is close to that in $[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]$ (2.867 Å). Unlike dianions such as $[Ru_4(\mu\text{-}CO)_3(CO)_{10}]^{2-}$ **1**, **26** has no bridging carbonyl ligands. The CO ligands do, however, undergo rapid exchange in solution as manifested by the singlet in the carbonyl ^{13}C NMR spectrum of the cluster at ambient temperature.[29]

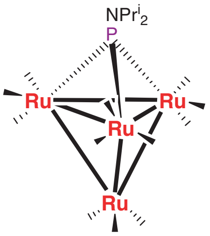
$$\underset{\mathbf{B}}{[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]} + [Cp_2Co] \xrightarrow[\text{5 min, 97\%}]{CH_2Cl_2,\ 25\ °C} \underset{\text{Anion} = \mathbf{26}}{\underset{\text{Dark red}}{[Cp_2Co]_2[Ru_4(\mu_3\text{-}PPh)(CO)_{12}]}} \quad (21)$$



26

Heating **24** in refluxing hexane causes loss of CO and formation of $[Ru_4\{\mu_3\text{-}P(NPr^i_2)\}(CO)_{12}]$ **27** with a *closo*-trigonal-bipyramidal or capped tetrahedral Ru_4P unit (Equation (22)).[27] The RuP distances in **27** are considerably shorter than those in **24** (Table 4); the PN bond is also shorter (1.636(3) Å). The $^{13}C\{^1H\}$ NMR spectrum of **27** consists of a single broad signal that indicates the carbonyls undergo exchange at room temperature.[27]

$$\underset{\textbf{24}}{[\mathrm{Ru_4\{\mu_3\text{-}P(NPr^i_2)\}(CO)_{13}}]} \xrightarrow[\text{3 h}\atop 64\%]{\text{hexane, 69 °C}} \underset{\text{Dark red}\atop \textbf{27}}{[\mathrm{Ru_4\{\mu_3\text{-}P(NPr^i_2)\}(CO)_{12}}]} \tag{22}$$



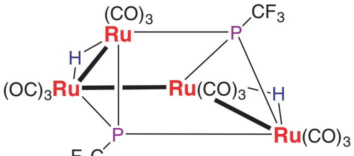
27

The phosphorus chemical shifts for μ_3-phosphinidine ligands (formally $[PR]^{2-}$) in ruthenium carbonyl clusters are in the range −77–497 ppm (see Table 4; see however compound **30** described below). The reasons for these extraordinary shifts are not understood.[30] A ^{31}P NMR study on a single crystal of $[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]$ **B** gave $\delta_{11} = 889$, $\delta_{22} = 294$, and $\delta_{33} = 60$ ppm. The deshielding is most pronounced when the applied magnetic field is approximately parallel to the PC bond of the PPh unit, while the greatest shielding occurs when the field is approximately perpendicular to the PC bond and the open face of the *nido*-Ru_4 cluster.[30]

Absorption of **27** on silica gel followed by solvent extraction yields $[NH_2Pr^i_2][Ru_4(\mu_3\text{-}PO)(CO)_{12}]$ (Anion = **28**); (Scheme 3).[27] Metathesis with $[NEt_4]Cl$ readily gives the corresponding tetraethylammonium salt. The **28** anion consists of a tetrahedron of Ru atoms capped symmetrically on one face by a PO ligand. The RuRu lengths are typical for tetrahedral Ru_4 clusters (Table 3). The PO length of 1.509(3) Å in **28** is consistent with significant multiple bond character resulting from the overlap of the O $2p\pi$ orbital with phosphorus $3p\pi$ or $3d\pi$ orbitals. There is hydrogen bonding between the O atom of the PO ligand and $NH_2Pr^i_2$ ion (O···H = 1.97, 2.09 Å). The ν(PO) frequency in the $NH_2Pr^i_2$ salt is at a lower energy than that in the NEt_4 counterpart (1079 vs. 1169 cm^{-1}).[27]

Density functional theory calculations have been carried out on various molecules and anions containing the phosphorus monoxide ligand including **28**. The calculations indicate that π-backbonding is more important than σ-bonding regardless of the coordination mode of the PO unit. Furthermore, it is found that σ-bonding does not affect the vibrational frequencies of PO significantly. A positive charge on the metal center however polarizes the PO orbitals, which increases the *d*-component in the π^*-orbital and increases the contribution of the phosphorus *p*-orbitals in the π-orbital. Both of these effects increase the PO bond strength and can give rise to PO stretching frequencies in complexes that are higher than in free PO ($\nu(PO) = 1220\ cm^{-1}$ in the gas phase; 1218 cm^{-1} in matrices).[31]

One product isolated from the reaction of $PH_2(CF_3)$ with $[Ru_3(CO)_{12}]$ in *p*-xylene at 120 °C or above is $[Ru_4(\mu\text{-}H)_2\text{-}[Ru\{(\mu_3\text{-}P(CF_3)_2\}(\mu\text{-}H)(CO)_{12}]$. It was assigned the structure **29** on the basis of spectroscopic evidence and by comparison with a partial crystal structure of the As analog. The ^1H NMR spectrum consists of a triplet attributed to virtual coupling.[32]



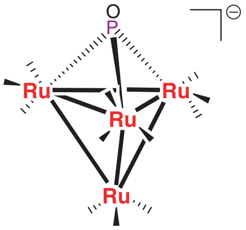
29

$$\underset{\textbf{27}}{[\mathrm{Ru_4\{\mu_3\text{-}P(NPr^i_2)\}(CO)_{12}}]} \xrightarrow[\text{“}H_2O\text{” (silica)}]{CH_2Cl_2,\ 25\ °C} [\mathrm{NH_2Pr^i_2}][\mathrm{Ru_4(\mu_3\text{-}PO)(CO)_{12}}]$$

Anion = **28**

$$\Big\downarrow{\scriptstyle CH_2Cl_2\ \ [NEt_4]Cl}$$

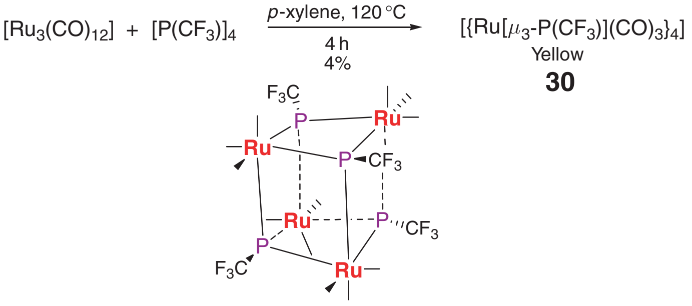
$[NEt_4][Ru_4(\mu_3\text{-}PO)(CO)_{12}]$
Red, 51%



28

Scheme 3

The interesting cubane compound $[Ru_4\{\mu_3\text{-}P(CF_3)\}(CO)_3\}_4]$ **30** results from the reaction of equimolar amounts of $[Ru_3(CO)_{12}]$ and $[P(CF_3)]_4$ in *p*-xylene at 120 °C (Equation (23)).[23] The molecule is best regarded as a 72 c.v.e. cage compound rather than the claimed 80 c.v.e. derivative; as such there are no RuRu bonds in **30**. The ^{31}P NMR resonance for **30** appears as a multiplet attributed to virtual coupling. As might be expected for this unusual complex, the chemical shift of the ^{31}P NMR resonance (δ −77) is outside the range found for other Ru(PR) derivatives (Table 4).



30

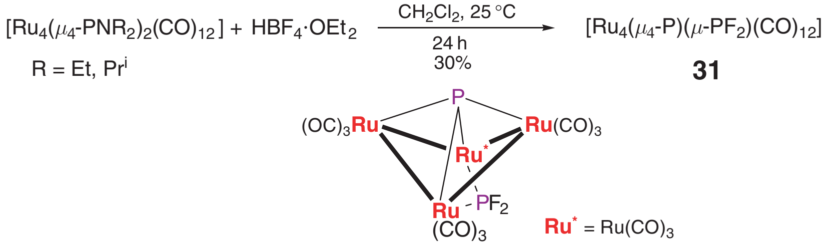
(23)

6.23.2.3.2.(iv) Derivatives with bridging μ_4-P ligands

Some structural data for clusters with a P ligand bound to four Ru atoms are given in Tables 5 and 6. The latter table also contains $^{31}P\{^1H\}$ NMR data for the clusters.

As indicated in Table 5, the Ru atoms of $Ru_4(\mu_4\text{-}PR)$ units have either a puckered square or spiked triangular arrangement of metal atoms. The RuRu bond lengths show considerable variation with the shortest bond usually bridged by a carbonyl or a bidentate P ligand. The compound $[Ru_4\{\mu_4\text{-}P(CF_3)\}\{\mu_4\text{-}\eta^2\text{-}C_2(CF_3)_2\}(CO)_{12}]$ **172** has no edge-bridging ligands.[33] The RuP lengths also show considerable variation especially in those clusters that have a spiked triangular skeleton.

Treatment of $[Ru_4(\mu_4\text{-}PNEt_2)_2(CO)_{12}]$ with $HBF_4{\cdot}OEt_2$ did not yield the expected $[Ru_4(\mu_4\text{-}PF)_2(CO)_{12}]$ but rather the isomeric $[Ru_4(\mu_4\text{-}P)(\mu\text{-}PF_2)(CO)_{12}]$ **31** (Equation (24)) with a bare phosphorus atom bridging a puckered square (butterfly) arrangement of metal atoms.[34] In this respect, **31** resembles $[Ru_4(\mu_4\text{-}N)(\mu\text{-}OMe)(CO)_{12}]$ **13**. The RuRu distances in **31** are considerably longer than in comparable compounds (Table 5). The RuP distances to the hinge Ru atoms are shorter than those to the wingtip Ru atoms (Table 6). The RuPRu angle to the hinge metal atoms is 95.4(1)° whereas the corresponding angle to the wingtip atoms is 148.7(2)°. The question arises as to whether the μ_4-P atom should be considered as a three-electron donor (i.e., as a vertex of a polyhedron) or a five-electron donor (i.e., a partially interstitial main group atom). DFT calculations on $[Ru_4(\mu_4\text{-}P)(\mu\text{-}PF_2)(CO)_{12}]^{2-/0/2+}$ support the latter view.[34]



31

(24)

Reaction of $[Ru_3(CO)_{12}]$ with $PH_2(CF_3)$ in xylene at elevated temperatures produces a number of products that include **29** and the spiked triangular cluster $[Ru_4(\mu_4\text{-}PCF_3)(\mu\text{-}H)_2(CO)_{13}]$ **32** (Equation (25)).[32] One of the hydride ligands in **32** is confidently placed along the spike RuRu bond on account of its length (3.013(1) Å). The second hydride ligand is placed along the RuRu bond furthest from the spike RuRu bond on the basis that no H–H coupling is observed between the hydride ligands in the ^1H NMR spectrum of the compound. This bond has a length of 2.900(1) Å although there is a second longer RuRu bond (2.920(1) Å) in the cluster. The ^1H NMR spectrum of **32** in $CDCl_3$ at −45 °C shows two doublets at δ −16.80 ($J_{PH} = 16.03$ Hz) and δ −20.20 ($J_{PH} = 15.05$ Hz) that indicate the hydride ligands are not equivalent at this temperature. On warming, the signals broadened and coalesce to a broad singlet at 25 °C indicative of rapid exchange of these protons.

Table 5 Structural data for clusters with μ_4-PR (μ_4-P) units

Compound	*Structure*[a]	*RuRu range* (Å)
μ_4-*P*		
$[Ru_4(\mu_4\text{-}P)(\mu\text{-}PF_2)(CO)_{12}]$ **31**	**PS (B)**	2.969(1)–2.988(1)
μ_4-*PPh*		
$[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}C_4H_3N)(\mu\text{-}CO)(CO)_{10}]$ (η^2-C,N) **169A**	**S**	2.804(1)–2.907(1)[b]
$[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}C_4H_3N)(\mu\text{-}CO)_2(CO)_9]$ (η^2-C,C) **169B**	**S**	2.753(1)–2.904(1)
$[Ru_4(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}PhC_4Bu^t)(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$ **166**	**S**	2.731(1)–2.889(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}\eta^2\text{-}(Me_3Si)C_6(SiMe_3\}(\mu\text{-}CO)(CO)_{10}]$ **167**	**S**	2.7293(2)–2.8973(2)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}\eta^2\text{-}(Me_3Si)C_6(SiMe_3\}(\eta^6\text{-}C_6H_5Me)(CO)_7]$ **168**	**S**	2.7330(3)–2.859(3)
$[Ru_4(\mu_4\text{-}PPh)(\mu\text{-}H)_4(\mu\text{-}PPh_2)_2(CO)_7(PPh_3)]$ **34**	**S**	2.825(1)–2.977(1)
$[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}PPh_2)_2(CO)_8]$ **35**	**S**	2.767(2)–2.866(2)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)Bu^t\}(\mu\text{-}CO)(CO)_{10}]$ **37**	**S**	2.7031(8)–2.909(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)C_6H_2Bu^t{}_3\}_2(\mu\text{-}CO)(CO)_{10}]$ **38**	**S**	2.712(1)–2.901(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}P(NPr^i{}_2)\}(\mu\text{-}CO)(CO)_{10}]$ **39**	**S**	2.724(1)–2.892(1)
$[Ru_4(\mu_4\text{-}PPh)(\mu\text{-}PHPh)_2\{\mu_4\text{-}P(Ph)P(Ph)\}(CO)_8]$ **43**	**S**	2.871(1)–3.055(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_3\text{-}\eta^2\text{-}C(Ph)C(W(Cp^*)(CO)\}(CO)_{10}]$[166]	**S**	2.699(1)–2.958(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}C(Ph)CW(Cp^*)(O)(\mu\text{-}O)\}(\mu\text{-}CO)_2(CO)_8]$ **233**	**S**	2.714(1)–2.962(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}C(Ph)CW(Cp^*)(O)(\mu\text{-}O)\}(\mu\text{-}CO)(CO)_6(\eta^6\text{-}C_6H_5Me)]$ **234**	**S**	2.672(1)–2.981(1)
μ_4-*P(CF$_3$)*		
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}CO)(CO)_{13}]$ **33**	**ST**	2.801(1)–2.959(1)[c]
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}CO)_2(CO)_{12}]$ **33**	**ST**	2.817(1)–2.971(1)[c]
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}H)_2(CO)_{13}]$ **32**	**ST**	2.838(1)–3.013(1)
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}CO)_2(CO)_9]$ **170b**	**S**	2.740(1)–2.920(2)
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu_4\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}CO)_2(CO)_9]$ **170a**	**S**	2.755(1)–2.900(1)
$[Ru_4\{\mu_4\text{-}P(CF_3)\}\{\mu_4\text{-}\eta^2\text{-}C_2(CF_3)_2\}(\mu\text{-}CO)_2(CO)_9]$ **172**	**S**	2.807(2)–2.917(2)
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\eta^4\text{-}C_4Me_4)(\mu\text{-}CO)_2(CO)_9]$[33]	**ST**	2.764(1)–2.843(1)
$[Ru_4\{\mu_4\text{-}P(CF_3)\}\{\mu_4\text{-}\eta^4\text{-}PhC(H)C(H)CCPh_4\}(CO)_{11}]$[33]	**S**	2.827(2)–2.922(2)
μ_4-*PC(CO)R*		
$[Ru_4\{\mu_4\text{-}PC(CO)Bu^t\}_2(\mu\text{-}CO)(CO)_{10}]$ **36**	**S**	2.708(1)–2.892(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)Bu^t\}(\mu\text{-}CO)(CO)_{10}]$ **37**	**S**	2.7031(8)–2.909(1)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)C_6H_2Bu^t{}_3\}(\mu\text{-}CO)(CO)_{10}]$ **38**	**S**	2.712(1)–2.901(1)
μ_4-*P(CH$_2$)$_2$PPh$_2$*		
$[Ru_4\{\mu_4\text{-}\eta^2\text{:}3\eta^1\text{-}P(CH_2)_2PPh_2\}(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}C_6H_4)(\mu\text{-}CO)(CO)_9]$ **191**	**S**	2.819(1)–2.935(1)
μ_4-*PNR$_2$*		
$[Ru_4\{\mu_4\text{-}(PNEt_2)\}_2(CO)_{12}]$ **41a**	**PS** (136.6°)	2.8711(5)–2.8808(5)
$[Ru_4\{\mu_4\text{-}(PNPr^i{}_2)\}_2(CO)_{12}]$ **41b**	**PS** (135.4°)	2.853(1)–2.873(1)

[a] See Figure 1.

[b] Monoclinic and triclinic forms.

[c] Two independent molecules.

$$[Ru_3(CO)_{12}] + PH_2(CF_3) \xrightarrow[18\ \text{h}]{p\text{-xylene, } 120\,^\circ\text{C}} \underset{\substack{\text{Yellow, 30\%} \\ \mathbf{32}}}{[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}H)(CO)_{13}]} + \underset{\text{Yellow, 15\%}}{\mathbf{29}} \qquad (25)$$

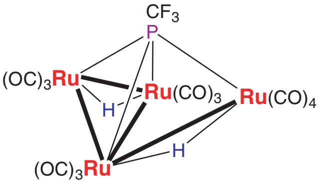


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Table 6 RuP distances and ^{31}P chemical shifts for derivatives with μ_4-PR (μ_4-P) units

Compound	*RuP distances (range)* (Å)	δ ^{31}P (ppm)
μ_4-P		
$[Ru_4(\mu_4\text{-}P)(\mu\text{-}PF_2)(CO)_{12}]$ **31**	2.274(3), 2.280(3) (h), 2.454(3), 2.458(3) (w)	671.9(249.5)
μ_4-PPh		
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}PhC_4Bu^t)(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$ **166**	2.362(2)–2.477(2)	251.5
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}\eta^2\text{-}(Me_3Si)C_6(SiMe_3\}\text{-}(\mu\text{-}CO)(CO)_{10}]$ **167**	2.3559(2)–2.4806(2)	228.2
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}\eta^2\text{-}(Me_3Si)C_6(SiMe_3)\}\text{-}(\eta^6\text{-}C_6H_5Me)(CO)_7]$ **168**	2.2656(7)–2.4632(7)	
$[Ru_4(\mu_4\text{-}PPh)(\mu\text{-}H)_4(\mu\text{-}PPh_2)_2(CO)_7(PPh_3)]$ **34**	2.429(2)–2.473(2)	68.2
$[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}PPh_2)_2(CO)_8]$ **35**	2.306(3)–2.424(3)	236.6
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}P(NPr^i{}_2)\}(\mu\text{-}CO)(CO)_{10}]$ **39**	2.380(2)–2.469(2)	189.7 (J_{PP}=66H$_Z$)
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)Bu^t\}(\mu\text{-}CO)(CO)_{10}]$ **37**	2.382(1)–2.473(2)	196
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)C_6H_2Bu^t{}_3\}_2(\mu\text{-}CO)(CO)_{10}]$ **38**	2.383(1)–2.477(1)	196
$[Ru_4(\mu_4\text{-}PPh)(\mu\text{-}PHPh)_2\{\mu_4\text{-}P(Ph)P(Ph)\}(CO)_8]$ **43**	2.383(2)–2.426(2)	508 (151.4, μ-P); 131.4, μ_4-P$_2$,)[a]
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}C(Ph)CW(Cp^*)(O)(\mu\text{-}O)\}\text{-}(\mu\text{-}CO)_2(CO)_8]$ **233**	2.312(2)–2.535(2)	172.6
$[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}C(Ph)CW(Cp^*)(O)(\mu\text{-}O)\}\text{-}(\mu\text{-}CO)(CO)_6(\eta^6\text{-}C_6H_5Me)]$ **234**	2.302(2)–2.505(2)	320.4
μ_4-P(CF$_3$)		
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}CO)(CO)_{13}]$ **33**	2.327(1)–2.877(1)[b]	73.07[c]
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}CO)_2(CO)_{12}]$ **33**	2.323(2)–2.864(2)[b]	
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}H)_2(CO)_{13}]$ **32**	2.331(3)–2.759(3)	108
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu_4\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}CO)_2(CO)_9]$ **170a**	2.358(2)–2.470(2)	212.7
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}CO)_2(CO)_9]$ **170b**	2.345(1)–2.413(1)	220.8
$[Ru_4\{\mu_4\text{-}P(CF_3)\}\{\mu_4\text{-}\eta^2\text{-}C_2(CF_3)_2\}(CO)_{12}]$ **172**	2.341(2)–2.367(2)	414.1
$[Ru_4\{\mu_4\text{-}P(CF_3)\}(\eta^4\text{-}C_4Me_4)(\mu\text{-}CO)_2(CO)_9]$[33]	2.330(1)–2.532(1)	194
$[Ru_4\{\mu_4\text{-}P(CF_3)\}\{\mu_4\text{-}\eta^4\text{-}PhC(H)C(H)CCPh_4\}(CO)_{11}]$[33]	2.363(3)–2.398(3)	139.1
μ_4-PC(CO)R		
$[Ru_4\{\mu_4\text{-}PC(CO)Bu^t\}_2(\mu\text{-}CO)(CO)_{10}]$ **36**	2.379(2)–2.556(2)	146.2
$[Ru_4\{\mu_4\text{-}PC(CO)Bu^t\}(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$ **37**	2.400(1)–2.528(1)	119
$[Ru_4\{\mu_4\text{-}PC(CO)C_6H_2Bu^t{}_3\}(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$ **38**	2.391(1)–2.477(1)	169
μ_4-P(CH$_2$)$_2$PPh$_2$		
$[Ru_4\{\mu_4\text{-}\eta^2{:}3\eta^1\text{-}P(CH_2)_2PPh_2\}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_4)(\mu\text{-}CO)(CO)_9]$ **191**	2.333(3)–2.428(3)	398.7
μ_4-PNR$_2$		
$[Ru_4\{\mu_4\text{-}P(NEt_2)\}_2(CO)_{12}]$ **41a**	2.256(1)–2.285 (1) (short), 2.612(1)–2.889(1) (long)	424.8
$[Ru_4\{\mu_4\text{-}P(NPr^i{}_2)\}_2(CO)_{12}]$ **41b**	2.273(2), 2.278(2) (short), 2.737(2), 2.812(2) (long)[d]	444.8
$[Ru_4\{\mu_4\text{-}P(NPr^i{}_2)\}(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$	2.412(2)–2.542(2)	249.6

[a] All J_{PP} = 60 Hz.
[b] Two independent molecules in unit cell.
[c] J_{PF} = 52.5 Hz.
[d] Molecule has a twofold axis.

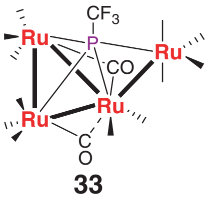
Heating $[Ru_3(CO)_{12}]$ and $\{P(CF_3)\}_4$ in solution gives $[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}CO)_x(CO)_{14-x}]$ ($x = 1, 2$ **33**) (Equation (26)).[23] There are two independent molecules in the unit cell, one with two bridging carbonyls and the other where one of these carbonyls is semibridging (as shown). Compound **33** has some of the longest RuP bonds determined (Table 6).

$$[Ru_3(CO)_{12}] + [P(CF_3)]_4 \xrightarrow[\text{16 h}\\ \text{4\%}]{CH_2Cl_2,\ 80\,^{\circ}C} [Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}CO)_2(CO)_{12}] \qquad (26)$$

1 : 1 ratio

Red

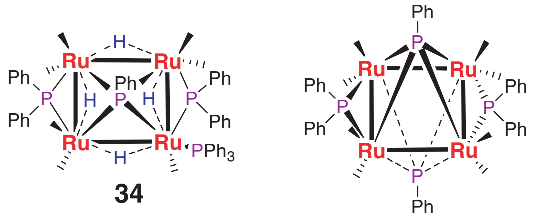
33



33

Treatment of either $[Ru_2(CO)_4(PPh_3)_2(MeCO_2)_2]$ or $[Ru(\mu\text{-}H)_4(CO)_8(PPh_3)_4]$ with hydrogen (100 atm) at 140 °C results in several products of which two are tetranuclear, namely, $[Ru_4(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)_2(\mu\text{-}H)_4(CO)_7(PPh_3)]$ **34** and $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}PPh_2)_2(CO)_8]$ (**35**; Equation (27)).[35] Each structure has a square arrangement of ruthenium atoms. In **34**, there is one capping μ_4-PPh unit to give a square-based pyramidal Ru_4P core. In **35**, the Ru_4 square is capped on both sides by a μ_4-PPh group to give an octahedral arrangement for the central Ru_4P_2 skeleton. If the μ_4-PPh unit is considered as a four-electron donor, then both **34** and **35** have a 62 c.v.e. count whereas a square arrangement of ruthenium atoms is normally associated with a 66 c.v.e. count. If however the PR unit is considered to donate six electrons to cluster bonding from PSEPT theory, then **34** and **35** have seven cluster bonding pairs. This is consistent with the skeletal arrangement of both **34** (a *nido*-octahedron) and **35** (*closo*-octahedron). Because of the asymmetry introduced into **34** by the presence of the PPh_3 ligand all the hydride ligands are inequivalent. As expected, there are four resonances in the hydride region of the ^1H NMR spectrum of **34** at room temperature. The resonances show couplings (1.6–2.0 Hz) to some of the P atoms and to the three other protons consistent with the view that the bonding in the cluster is delocalized.[35]

$$\begin{array}{l}[Ru_2(CO)_4(PPh_3)_2(MeCO_2)_2] + \underset{(100\ atm)}{H_2} \\ ([Ru_4(\mu\text{-}H)_4(CO)_8(PPh_3)_4])\end{array} \xrightarrow[\text{72 h}]{\text{cyclohexane, 140}\,^{\circ}C} \begin{array}{c}[Ru_4(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)_2(\mu\text{-}H)_4(CO)_7(PPh_3)] + \\ \sim 15\% \\ \mathbf{34} \\ [Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}PPh_2)_2(CO)_8] \\ \sim 10\% \\ \mathbf{35}\end{array} \qquad (27)$$



34

35

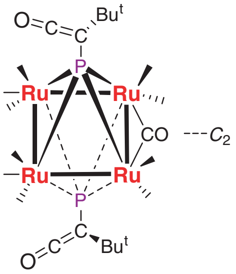
Reaction of $PCBu^t$ with $[Ru_3(CO)_{12}]$ affords $[Ru_3\{\mu_3\text{-}PC(CO)Bu^t\}_2(CO)_9]$ **C**. The ketene-substituted μ_3-phosphinidene ligands in **C** are believed to result from the attack of CO on a coordinated phospha-alkyne. Further reaction of **C** with a twofold excess of $[Ru_3(CO)_{12}]$ in refluxing THF results in $[Ru_4\{\mu_4\text{-}PC(CO)Bu^t\}_2(\mu\text{-}CO)(CO)_{10}]$ (**36**, Equation (28)).[36] The molecule has a crystallographic twofold axis passing through the C and O atoms of the bridging carbonyl. The three RuRu bonds not bridged by CO have similar lengths (2.856(1) Å, RuRu′, and 2.892(1)); the RuRu vector of the Ru(μ-CO)Ru unit is considerably shorter at 2.708(1) Å.

$$\underset{\mathbf{C}}{[Ru_3\{\mu_3\text{-}PC(CO)Bu^t\}_2(CO)_9]} + [Ru_3(CO)_{12}] \xrightarrow[\text{6 h}\\ \text{22\%}]{\text{THF, 66}\,^{\circ}C} [Ru_4\{\mu_4\text{-}PC(CO)Bu^t\}_2(\mu\text{-}CO)(CO)_{10}] \qquad (28)$$

1 : 2 ratio

Black

36

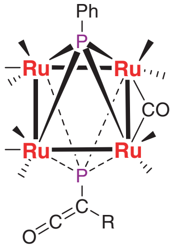


36

Ketene-substituted μ_4-phosphinidene ligands are also found in $[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)Bu^t\}(\mu\text{-}CO)(CO)_{10}]$ **37** and $[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)Ar'\}(\mu\text{-}CO)(CO)_{10}]$ (**38**, $Ar' = 2,4,6\text{-}C_6H_2Bu^t{}_3$) prepared by the routes shown in Equations (29) and (30), respectively.[26]

$$\underset{\mathbf{B}}{[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]} + P{\equiv}CBu^t \xrightarrow[\substack{\text{4 h} \\ 55\%}]{n\text{-hexane, 60 °C}} \underset{\mathbf{37}}{\underset{\text{Black}}{[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)Bu^t\}(\mu\text{-}CO)(CO)_{10}]}} \tag{29}$$

$$\underset{Ar' = 2,4,6\text{-}C_6H_2Bu^t{}_3}{[Ru_4(\mu_3\text{-}PPh)(CO)_{13}] + P{\equiv}CAr'} \xrightarrow[\substack{\text{2 h} \\ 35\%}]{n\text{-hexane, 45 °C}} \underset{\mathbf{38}}{\underset{\text{Red}}{[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}PC(CO)Ar'\}(\mu\text{-}CO)(CO)_{10}]}}$$



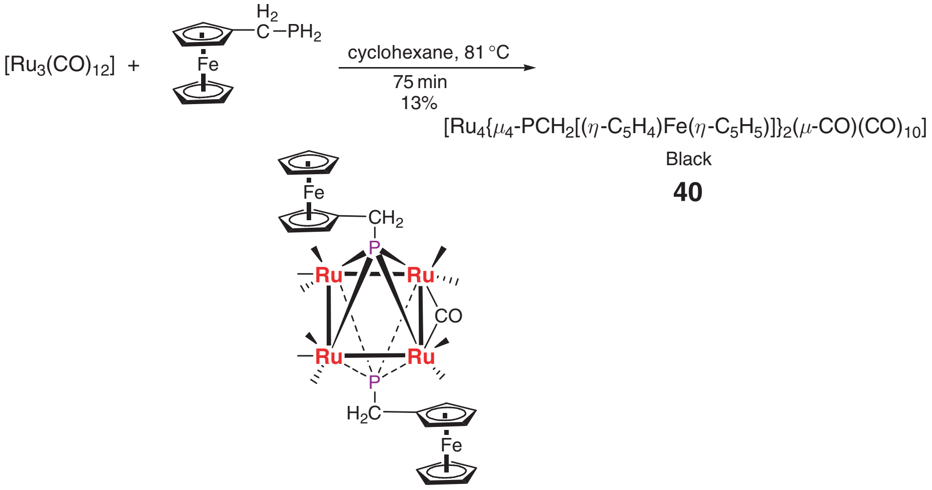
37: R = Bu^t
38: R = Ar′

(30)

Another derivative with mixed μ_4-PR units is $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}PNPr^i{}_2)(\mu\text{-}CO)(CO)_{10}]$ **39** prepared by the reaction of the anion **26** with $P(NPr^i{}_2)Cl_2$ in the presence of $AgBF_4$ (Equation (31)).[29]

$$\underset{\mathbf{26}}{[Ru_4(\mu_3\text{-}PPh)(CO)_{12}]^{2-}} + P(NPr^i{}_2)Cl_2 \xrightarrow[\substack{AgBF_4\text{, 5 min} \\ 17\%}]{CH_3CN\text{, 25 °C}} \underset{\mathbf{39}}{\underset{\text{Purple}}{[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}PNPr^i{}_2))(\mu\text{-}CO)(CO)_{10}]}} \tag{31}$$

Heating $[Ru_3(CO)_{12}]$ in refluxing hexane with $PH_2(CH_2R)$ (R = ferrocenyl: $Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)$) produces $[Ru_4\{\mu_4\text{-}P(CH_2R)\}_2(\mu\text{-}CO)(CO)_{10}]$ **40** as one of several products (Equation (32)).[37] The structure of **40** was assigned on the basis of spectroscopic evidence compared to that of the known $[Ru_4(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9]$ and $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ clusters.[37]



$$[Ru_3(CO)_{12}] + (\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CH_2PH_2) \xrightarrow[\substack{\text{75 min} \\ 13\%}]{\text{cyclohexane, 81 °C}} \underset{\mathbf{40}}{\underset{\text{Black}}{[Ru_4\{\mu_4\text{-}PCH_2[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]\}_2(\mu\text{-}CO)(CO)_{10}]}} \tag{32}$$

40
(characterized by
spectroscopic methods)

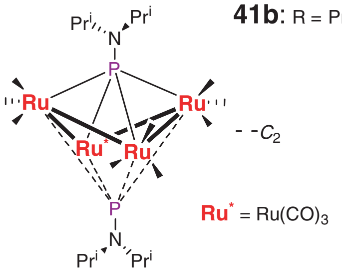
Two clusters in this category of special interest are the air stable $[Ru_4(\mu_4\text{-}PNR_2)_2(CO)_{12}]$ (R = Et **41a**, R = Pr^i **41b**) synthesized from $[Ru_4(CO)_{12}]^{4-}$ (prepared from $[Ru_3(CO)_{12}]$ and K/benzophenone) with $P(NR_2)Cl_2$ (Equation (33)).[29,38] The metal skeleton in these clusters consists of a severely puckered square (a D_{2d} butterfly without the hinge bond) with dihedral angles between the two Ru_3 planes of 136.6° **41a** and 135.4° **41b**. The RuRu lengths are approximately equal, but the distortion results in short and long RuP lengths that differ by almost 0.5 Å (Table 6).

$$[Ru_4(CO)_{12}]^{4-} + P(NR_2)Cl_2 \xrightarrow[2\,h]{THF,\ 25\,°C} [Ru_4(\mu_4\text{-}P(NR_2))_2(CO)_{12}] \qquad (33)$$

R = Et, Pr^i

41a: R = Et, dark orange, 21%

41b: R = Pr^i, dark red, 16%



41b

Unlike the $[Ru_4(\mu_4\text{-}PR)_2(\mu\text{-}CO)(CO)_{10}]$ clusters described above, clusters **41** have 66 c.v.e counts or eight skeletal electron pairs. In this case, the clusters are electron precise for the four RuRu bonds present in the molecules, but electron rich by PSEPT for a *closo*-structure. MO calculations indicate that for the $[Ru_4(\mu_4\text{-}PR)_2(\mu\text{-}CO)(CO)_{10}]$ clusters there is a molecular orbital located between the HOMOs and much higher energy LUMOs, but still too high in energy to be occupied. In **41** the asymmetric bonding ability of the PNR_2 ligand causes distortion of the $Ru_4(CO)_{12}$ moiety which in turn lowers the energy of the formally unoccupied LUMO so it becomes occupied.[38]

Addition of CO to $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ does not result in $[Ru_4(\mu_4\text{-}PPh)_2(CO)_{12}]$, but rather addition of two CO ligands occurs along with RuRu bond cleavage to give $[Ru_4(\mu_3\text{-}PPh)_2(CO)_{13}]$. Note also that the mixed derivative **39** has the more common regular square structure.[29] It is also interesting that $[Ru_4\{\mu_4\text{-}P(CF_3)\}_2\text{-}(\mu\text{-}CO)(CO)_{11}]$ (cf. Equation (26)) is unknown.

The ^{31}P chemical shifts for Ru_4 clusters with μ_4-PR ligands are given in Table 6; as can be seen, they span a large range, but not nearly as large as that for the μ_3-PR compounds (Table 4). This is probably a reflection of the smaller *p*-orbital imbalance in the more symmetric quadruply-bridged compounds. The clusters that show the largest paramagnetic (downfield) shift are **41a and 41b**; the shift is probably a consequence of a larger *p*-orbital imbalance due to the long and short RuP bonds in these clusters. The PP coupling in the derivatives with different μ_4-PR ligands are in the range 69–89 Hz. This is somewhat larger than typical *cis*-MPP′ couplings found in mononuclear complexes, but much smaller than the corresponding *trans*-MPP′ couplings.[39]

6.23.2.3.2.(v) Derivatives with bridging μ_4-PPhPPh ligands

The interesting PhPPPh ligand is found in $[Ru_4(\mu_4\text{-}PhPPPh)(\mu_3\text{-}PPh)_2(CO)_{10}]$ **42** and $[Ru_4\{\mu_4\text{-}P(Ph)P(Ph)\}(\mu_4\text{-}PPh)(\mu\text{-}PHPh)_2(CO)_8]$ **43** both isolated from the reaction of $[Ru_3(CO)_{12}]$ with $(PPh)_5$ (Equation (34)).[40] The RuP distances that involve this ligand are closely similar and are in the range 2.329(2)–2.358(2) Å; the PP distances are equal with in experimental error (2.163(2) and 2.169(3) Å in **42 and 43**, respectively). In the ^{31}P NMR spectrum of **43** has a triplet at δ 508.0 ($J_{PP} = 60$ Hz) is assigned to μ_4-P, a signal with coupling at δ 154.4 is assigned to the μ-P atoms and a singlet at δ 131.4 is assigned to the P atoms of the $\mu_4\text{-}P_2Ph_2$ unit.[40]

$$[Ru_3(CO)_{12}] + (PPh)_5 \xrightarrow[19\,h]{p\text{-xylene},\ 135\,°C} [Ru_4\{\mu_4\text{-}P(Ph)P(Ph)\}(\mu_3\text{-}PPh)_2(CO)_{10}] +$$

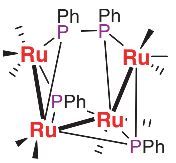
Red 2%

42

$$[Ru_4\{\mu_4\text{-}P(Ph)P(Ph)\}(\mu_4\text{-}PPh)(\mu\text{-}PHPh)_2(CO)_8] \qquad (34)$$

Dark red 4%

43



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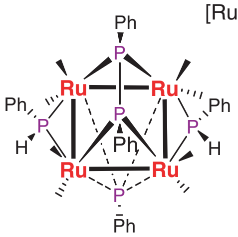


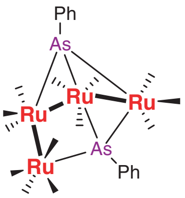
43

6.23.2.3.2.(vi) Derivatives with bridging As ligands

Structural data for some Ru_4 compounds with bridging As ligands are collected in Table 7; only **44** and **47** are discussed in this section.

Cluster **44** ($[Ru_4(\mu_3\text{-}AsPh)_2(CO)_{13}]$) is prepared by the reaction of *cyclo*-$(AsPh)_6$ with $[Ru_3(CO)_{12}]$ at 70 °C (Equation (35)).[41] The structure consists of a U-chain with three RuRu bonds in agreement with its 68 c.v.e. count. One arsenic ligand binds to the first three Ru atoms (1, 2, 3) of the chain; the second As ligand binds to the first, second, and fourth metal atoms (1, 2, 4).

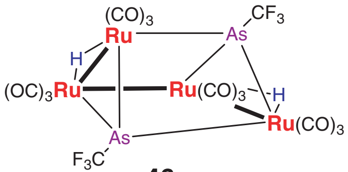
$$[Ru_3(CO)_{12}] + cyclo\text{-}(AsPh)_6 \xrightarrow[\substack{24\,h \\ 9\%}]{\text{toluene, }70\,^{\circ}C} \underset{\substack{\text{Dark yellow} \\ \mathbf{44}}}{[Ru_4(\mu_3\text{-}AsPh)_2(CO)_{13}]} \tag{35}$$



44

The CF_3 analog of **44**, $[Ru_4\{\mu_3\text{-}As(CF_3)\}_2(CO)_{13}]$ **45**, is one product isolated from the reaction of $[Ru_3(CO)_{12}]$ and $AsH_2(CF_3)$ at elevated temperatures. The other tetranuclear products are $[Ru_4(\mu_3\text{-}AsCF_3)_2(\mu\text{-}H)_2(CO)_{12}]$ **46** and $[Ru_4(\mu_4\text{-}AsCF_3)(\mu\text{-}H)_2(CO)_{13}]$ **47** (Equation (36)).[32] The structures of **46** and **47** were assigned by comparison with the P analogs (i.e., **29** and **32**) whose structures are known, a partial structure of **46** (heavy atoms only) and a complete structure of **47**. The fluxional behavior of the two hydride ligands in **47** mimics that of the P analog **32**.

$$\begin{aligned} [Ru_3(CO)_{12}] + AsH_2(CF_3) \xrightarrow[18\,h]{p\text{-xylene, }80\,^{\circ}C\ (120\,^{\circ}C)} & \underset{\substack{5\%\ (4\%) \\ \mathbf{45}}}{[Ru_4(\mu_3\text{-}AsCF_3)_2(CO)_{13}]} + \\ & \underset{\substack{8\%\ (11\%) \\ \mathbf{46}}}{[Ru_4(\mu_3\text{-}AsCF_3)_2(\mu\text{-}H)_2(CO)_{12}]} + \\ & \underset{\substack{23\%\ (16\%) \\ \mathbf{47}}}{[Ru_4(\mu_4\text{-}AsCF_3)(\mu\text{-}H)_2(CO)_{13}]} + \end{aligned} \tag{36}$$



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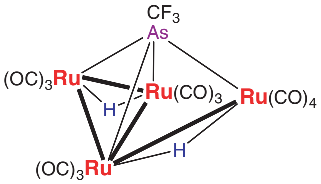


47

Table 7 Structures with bridging As atoms as ligands

Compound	*Structure*[a]	*RuRu range* (Å)	*RuAs range* (Å)
μ_3-AsPh			
$[Ru_4(\mu_3\text{-}AsPh)_2(CO)_{13}]$ **44**	U chain	2.921(1)–2.970(1)	2.434(1)–2.499(1)
μ_4-AsR			
$[Ru_4\{\mu_4\text{-}As(CF_3)\}(\mu\text{-}H)_2(CO)_{12}]$ **47**	ST	2.8684(4)–3.0310(3)	2.4245(4)–2.8568(4)
$[Ru_4\{\mu_4\text{-}As(CF_3)\}(\eta^4\text{-}C_4Me_4)(\mu\text{-}CO)_2(CO)_9]$[33]	ST	2.780(1)–2.870(1)	2.422(1)–2.595(1)
$[Ru_4\{\mu_4\text{-}As(C_{10}H_7)\}(\mu_4\text{-}\eta^2\text{-}C_{10}H_6)(\mu\text{-}CO)(CO)_{10}]$ **173**	S	2.789(7)–2.9062(7)	2.440(1)–2.515(1)

[a] See Figure 1.

6.23.2.3.3 Derivatives with bridging group 16 ligands

6.23.2.3.3.(i) Derivatives with bridging O ligands

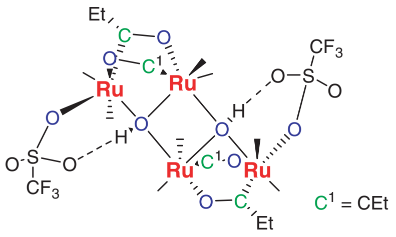
Derivatives that contain the hard donor oxygen atom as part of a bridging ligand are rare in Ru carbonyl cluster chemistry. Data from structures that have been determined in the 1995–2005 period are given in Table 8.

The cluster $[Ru_4(\mu\text{-OMe})(\mu_4\text{-N})(CO)_{12}]$ with a bridging methoxide unit has been previously discussed (compound **13**). The complex $[Ru_4(\mu\text{-MeCOO})_4(CO)_8(PBu_3)_2]$ is catalytically active in the hydrogenation of acetic acid and its role in this capacity has been further investigated.[42] The tetranuclear complex $[Ru_4(\mu_3\text{-OH})\text{-}\{\mu\text{-}\eta^2\text{-(O)CEt}\}(CF_3SO_3)_2(CO)_8]$ **48** was isolated (Equation (37)) in a study of the catalytic properties of the water-soluble *fac*-$[Ru(OCOCF_3)_2(CO)_3(H_2O)]$ and its derivatives.[43] There are no RuRu bonds in **48** consistent with its 72 c.v.e. count.

$$4\,fac[Ru\{C(O)Et\}(CO)_2(H_2O)_3][CF_3SO_3] \xrightarrow[\substack{-2CF_3SO_3H \\ 90\%}]{Et_2O,\ -20\,°C} [Ru_4(\mu_3\text{-OH})_2\{\mu\text{-}\eta^2\text{-C(O)Et}\}_4(CO)_8(CF_3SO_3)_2] \qquad (37)$$

Colorless

48



48

Another interesting and unique tetranuclear Ru species with a 72 c.v.e. count is the anion $[Ru_4(\mu_4\text{-O})(\mu\text{-Cl})_4(\mu\text{-CO})_2(CO)_8]^{2-}$ **49** that is produced cleanly by allowing a solution of $[Ru_4(\mu_3\text{-Cl})(CO)_{11}]^{2-}$ to stand in air (Scheme 4).[44] The anion has a central oxygen atom bound to the four Ru atoms in a distorted tetrahedral arrangement and represents a new member of the family of polymetallic oxo compounds. The Ru and Cl atoms define a slightly distorted quadratic antiprism with approximate D_2-symmetry. The anion is also formed by the treatment of $[Ru(CO)_3Cl_2(THF)]$ at 25 °C with aqueous KOH under reduced pressure (to remove CO_2 produced in the reaction).[45]

Table 8 Structural data for Ru_4 compounds that contain a bridging O atom

Compound	*Structure*[a]	*RuRu range* (Å)	*RuO* (Å)
μ-OMe			
$[Ru_4(\mu\text{-OMe})(\mu_4\text{-N})(CO)_{12}]$ **13**	B	2.8172(7)–2.8258(7)	2.093(4), 2.095(4)
μ_3-OH			
$[Ru_4(\mu_3\text{-OH})(\mu\text{-}\eta^2\text{-CHCC}_{13}H_8)(\mu\text{-CO})(CO)_{10}]$ **179**	B	2.808(5)[b]–2.975(5)	2.117(3), 2.121(3), 2.159(3)
$[Ru_4(\mu_3\text{-OH})_2\{\mu\text{-}\eta^2\text{-(O)CEt}\}(O_3SCF_3)(CO)_8]$ **48**			2.12(1), 2.14(1), 2.28(1)
μ_4-O			
$[Ru_4(\mu_4\text{-O})(\mu\text{-Cl})_4(\mu\text{-CO})_2(CO)_8]^{2-}$ **49**	[c]	3.057(1)–3.262(1)	2.078(4), 2.079(4), 2.080(5), 2.084(4)

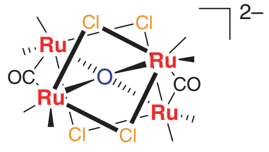
[a] See Figure 1.
[b] Ru(μ-CO)Ru.
[c] Tetrahedral μ_4-O; no RuRu bonds

$$[Ru_3(CO)_{12}] + [PPN]Cl \longrightarrow ([PPN][Ru_3(\mu_3\text{-Cl})(CO)_9]) \xrightarrow[\substack{\text{Ar purge, 1 h} \\ 70\%}]{\text{THF, 66 °C, [PPN]Cl}} \underset{\text{Red}}{[PPN]_2[Ru_4(\mu_3\text{-Cl})_2(CO)_{11}]}$$

$$[PPN]_2[Ru_4(\mu_3\text{-Cl})_2(CO)_{11}] \xrightarrow[\substack{\text{1 h} \\ 22\%}]{\text{air, CH}_2\text{Cl}_2} \underset{\text{Yellow}}{[PPN]_2[Ru_4(\mu_4\text{-O})(\mu\text{-Cl})_4(\mu\text{-CO})_2(CO)_8]}$$

Anion = **49**

Scheme 4



49

6.23.2.3.3.(ii) Derivatives with bridging S ligands

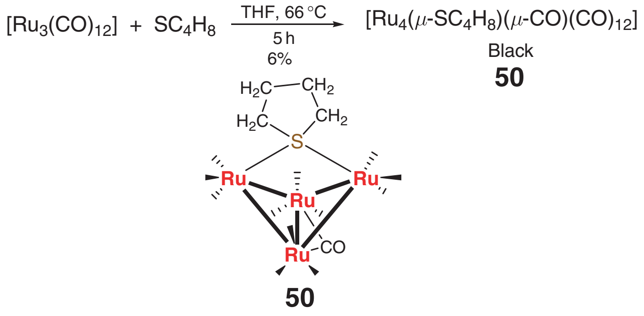
Recent structures of Ru_4 carbonyl clusters that contain a bridging S donor ligand are collected in Table 9. Of the clusters reported, there are eight that do not contain hydrocarbon ligands and are therefore discussed in this section.

The butterfly cluster $[Ru_4(\mu\text{-}SC_4H_8)(CO)_{13}]$ **50** is made by the reaction of tetrahydrothiophene and $[Ru_3(CO)_{12}]$ in refluxing THF (Equation (38)).[46] The S atom of the SC_4H_8 unit bridges just the wingtip Ru atoms of the butterfly; the hinge RuRu bond is bridged by CO and, as typically found, is the shortest RuRu bond in the cluster (2.795(1), 2.800(1) Å; two independent molecules). The corresponding reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with C_4H_8S affords $[Ru_4(\mu\text{-}SC_4H_8)(\mu\text{-}H)_2(CO)_{12}]$ **51** (Equation (39)).[46] The peripheral RuRu bond that is assumed to be hydrogen-bridged has a length of 3.028(1) Å whereas the other RuRu bonds have lengths of 2.839, 2.846, and 2.871(1) Å (molecule A). The hinge RuRu bond (2.893(1) Å) is considerably longer than that in **50**. The structure is similar to that of $[Ru_4(\mu\text{-}SMe_2)(\mu\text{-}H)_2(CO)_{12}]$. Cluster **50** exhibits two singlets in the ^1H NMR spectrum at δ −15.7 and −16.7 consistent with the assigned structure.

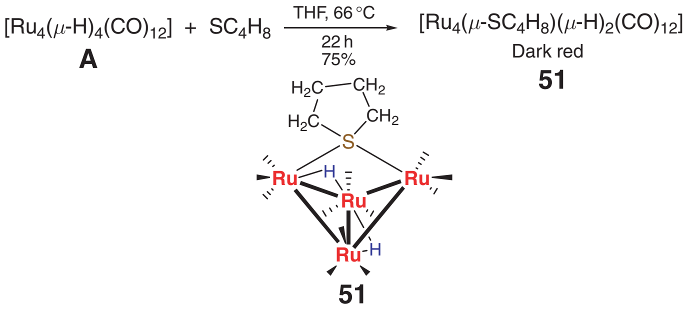
Table 9 Structures of Ru_4 carbonyl clusters that contain a bridging S donor ligand

Compound	*Structure*[a]	*RuRu range* (Å)	*RuS* (Å)
μ-SR			
$[Ru_4(\mu\text{-}SC_4H_8)(\mu\text{-}CO)(CO)_{12}]$ **50**	**B**	2.795(1)–2.870(1)	2.373(1), 2.384(4), 2.384(1), 2.400(1)[b]
$[Ru_4(\mu\text{-}SC_4H_8)(\mu\text{-}H)_2(CO)_{12}]$ **51**	**B**	2.839(1)–3.028(1)	2.382(2), 2.369(2), 2.368(2), 2.374(2)[b]
$[Ru_4(\mu\text{-}SMe)_2(\mu_4\text{-}C_2)(CO)_{12}]$	[c]	2.796(1), 3.130(1)[c]	2.420(2), 2.468(2) (S1); 2.425(2), 2.445(2) (S2)
$[Ru_4(\mu\text{-}SMe)_2(\mu_4\text{-}C_2Ph_2)(\mu\text{-}PPh)(CO)_{10}]$	**U** chain	2.816(1), 2.870(1), 2.890(1)	2.388(1), 2.397(1) (S1); 2.404(1), 2.443(1) (S2)
μ_4-S			
$[Ru_4(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu\text{-}CO)(CO)_{10}]$ **52**	**S**	2.813(2)–2.905(2)	2.424(2), 2.425(2), 2.428(2), 2.441(2)
$[Ru_4(\mu_4\text{-}S)\{\mu\text{-}\eta^2\text{-}CC(SiMe_3)\}_2(CO)_{12}]$	[c]	2.714(1), 2.719(1)	2.373(1), 2.374(1), 2.375(1), 2.382(1)
$[Ru_4(\mu_4\text{-}S)\{\mu\text{-}\eta^2\text{-}C(SiMe_3)C(C_2SiMe_3)\}(\mu\text{-}CO)_2(CO)_9]$	**S**	2.7410(3)–2.8541(4)	2.390(1), 2.417(1), 2.4752(1), 2.513(1)
$[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)_2(CO)_8\{P[2,4,6\text{-}C_6H_2(OMe)_3]_3\}]$ **53**	**S** (Ru_4S_2 oct.)	2.748(1), 2.749(1), 2.802(1), 2.819(1)	2.452(2)–2.520(2) (S1); 2.481(2)–2.527(2) (S2)
$[Ru_4(\mu_4\text{-}S)_2\{\mu\text{-}(PPh_2CH_2)_2C_6H_4\}\text{-}(\mu\text{-}CO)(CO)_8]$ **54**	**S** (Ru_4S_2 oct.)	2.741(1)–2.834(1)	2.459(2)–2.488(2) (S1); 2.483(2)–2.511(2) (S2)
$[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}PPr^i{}_2NHPPr^i{}_2)\text{-}(\mu\text{-}CO)(CO)_8]$ **55**	**S** (Ru_4S_2 oct.)	2.729(1), 2.730(1), 2.787(1), 2.797(1)	2.439(2)–2.516(2) (S1); 2.469(2)–2.525(2) (S2)
$[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}PPh_2NPr^iPPh_2)\text{-}(\mu\text{-}CO)(CO)_8]$ **56**	**S** (Ru_4S_2 oct.)	2.690(1), 2.771(1), 2.755(1), 2.824(1)	2.469 (Ave S1); 2.480 (Ave S2)
$[Ru_4(\mu_4\text{-}S)_2\{\mu\text{-}(PhO)_2PNMeP(OPh)_2\}\text{-}(\mu\text{-}CO)(CO)_8]$ **57**	**S** (Ru_4S_2 oct.)	2.696(1), 2.742(1), 2.791(1), 2.798(1)	2.468 (Ave S1); 2.486 (Ave S2)

[a] See Figure 1.
[b] Two independent molecules.
[c] Molecule has only two RuRu bonds.

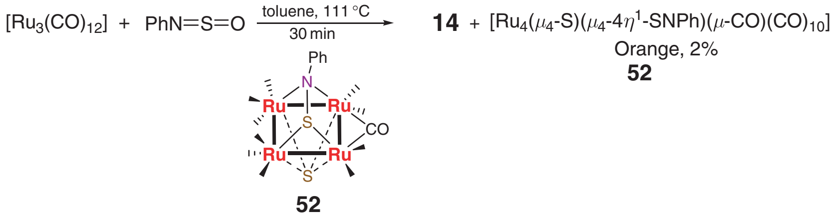


(38)



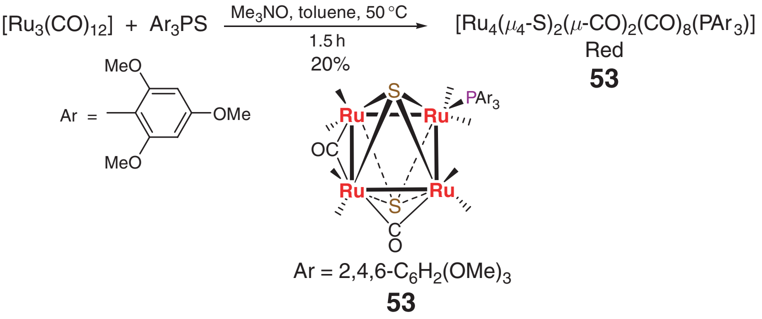
(39)

Another minor product isolated from the reaction of PhN=S=O and $[Ru_3(CO)_{12}]$ is $[Ru_4(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu\text{-}CO)(CO)_{10}]$ (**52**, Equation (40); see also Equation (12)).[22] Like **14**, **52** contains the unusual quadruply-bridging PhNS ligand.



(40)

An intriguing method of preparing clusters with Ru_4E_2 cores (E = naked S, Se) is the reaction of $[Ru_3(CO)_{12}]$ with phosphine or diphosphine sulfides and selenides (i.e., R_3PE) in the presence of Me_3NO. Three sulfur derivatives prepared in this fashion are $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)_2(CO)_8\{P[2,4,6\text{-}C_6H_2(OMe)_3]_3\}]$ (**53**, Equation (41)), $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}PPh_2CH_2C_6H_4CH_2PPh_2)(\mu\text{-}CO)(CO)_8]$ (**54**, Equation (42)),[47] and $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}PPr^i{}_2NHPPr^i{}_2)(\mu\text{-}CO)(CO)_8]$ (**55**, Equation (43)).[48] Analogs of **55** (e.g., $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}Ph_2PNRPPh_2)(\mu\text{-}CO)(CO)_8]$ (R = Pr^i **56**, R = (*S*)-CHMePh) and $[Ru_4(\mu_4\text{-}S)_2\{\mu\text{-}(PhO)_2PNMeP(OPh)_2\}(\mu\text{-}CO)(CO)_8]$ **57**) are prepared in a similar manner to the method shown in Equation (43).[49] As can be seen from the RuS lengths given in Table 9, the Ru_4S_2 octahedron is considerably distorted which is probably a reflection of the asymmetric distribution of ligands in the equatorial Ru_4 plane (see the discussion on the related Se clusters).

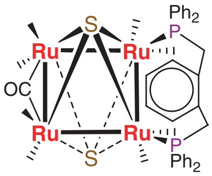


(41)

$$[\mathrm{Ru_3(CO)_{12}}] + \mathrm{SPPh_2CH_2C_6H_4CH_2PPh_2S} \xrightarrow[\substack{3\,\mathrm{h}\\ 15\%}]{\mathrm{Me_3NO,\ toluene,\ 70\,°C}} [\mathrm{Ru_4(\mu_4\text{-}S)_2(\mu\text{-}PPh_2CH_2C_6H_4CH_2PPh_2)(\mu\text{-}CO)(CO)_8}] \tag{42}$$

Red

54

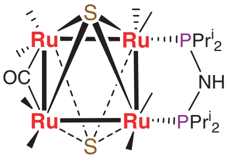


54

$$[\mathrm{Ru_3(CO)_{12}}] + \mathrm{NH[Pr^i{}_2P(S)]_2} \xrightarrow[\substack{1.5\,\mathrm{h}\\ 9\%}]{\mathrm{Me_3NO,\ toluene,\ 111\,°C}} [\mathrm{Ru_4(\mu_4\text{-}S)_2(\mu\text{-}PPr^i{}_2NHPPr^i{}_2)(\mu\text{-}CO)(CO)_8}] \tag{43}$$

Orange-red

55



55

The reaction of $PPh_2(SC_6F_5)$ with $[Ru_3(CO)_{12}]$ in refluxing heptane gives red $[Ru_4(\mu_3\text{-}SPPh_2)_2(\mu\text{-}SC_6F_5)_2(\mu\text{-}PPh_2)_2(SC_6F_5)_2(CO)_6]$ in 70% yield. The complex has a central Ru_2S_2 square; the compound does not have any RuRu bonds.[50]

6.23.2.3.3.(iii) Derivatives with bridging Se ligands

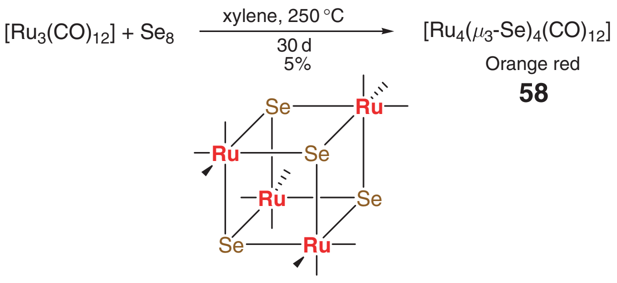
Recent structures of Ru_4 compounds with bridging Se ligands are given in Table 10.

Table 10 Structures of derivatives with bridging Se donor ligands

Compound	*Structure*[a]	*RuRu* (Å)	*RuSe (range)* (Å)
μ_3-Se			
$[Ru_4(\mu_3\text{-}Se)_4(CO)_{12}]$ **58**	C	(3.778(1))	2.561(1)
$[Ru_4(\mu_3\text{-}Se)_4(\mu\text{-}PPh_2CH_2PPh_2)(CO)_{10}]$ **59**	C		2.549(1)–2.577(1)
μ_4-Se			
$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_2(CO)_8(PPh_3)]$ **60**	S (Ru_4Se_2 oct.)	2.777(3), 2.784(3), 2.840(3), 2.875(1)[b]	2.554(2)–2.643(2) (Se1); 2.564(2)–2.615(2) (Se2)[b]
$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_2(CO)_7(PPh_3)_2]$ **61**	S (Ru_4Se_2 oct.)	2.700(1), 2.741(1), 2.823(1), 2.851(1)	2.500(2)–2.637(2) (Se1); 2.486(2)–2.600(2) (Se2)
$[Ru_4(\mu_4\text{-}Se)_2\{\mu\text{-}P,N\text{-}PPh_2(C_5H_4N)\}(\mu\text{-}CO)_2(CO)_7]$ **62**	S (Ru_4Se_2 oct.)	2.739(1), 2.771(1), 2.808(2), 2.816(1)	2.481(1)–2.659(2) (Se1); 2.565(1)–2.614(2) (Se2)
$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}PPh_2CH_2PPh_2)(\mu\text{-}CO)(CO)_8]$ **63**	S (Ru_4Se_2 oct.)	2.772(1), 2.793(1), 2.852(1), 2.855(1)	2.544(1)–2.626(1) (Se1); 2.561(1)–2.608(1) (Se2)
$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}PPh_2NHPPh_2)(\mu\text{-}CO)(CO)_8]$ **64**	S (Ru_4Se_2 oct.)	2.737(2), 2.758(2), 2.828(2), 2.851(2)	2.552(2)–2.578(2) (Se1); 2.555(2)–2.589(2) (Se2)
$[Ru_4(\mu_4\text{-}Se)_2\{\mu\text{-}PPh_2N[(S)\text{-}CHMePh]PPh_2\}(\mu\text{-}CO)(CO)_8]$ **65**	S (Ru_4Se_2 oct.)	2.733(1), 2.783(1), 2.835(1), 2.858(1)[b]	2.586(1)–2.599(1) (Se1); 2.558(2)–2.590(2) (Se2)[b]
$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}PPh_2NPr^iPPh_2)(\mu\text{-}CO)(CO)_8]$ **65**	S (Ru_4Se_2 oct.)	2.730(1), 2.790(1), 2.824(1), 2.900(1)	2.551(1)–2.607(1) (Se1); 2.564(1)–2.596(1) (Se2)

[a] See Figure 1.
[b] Molecule 1 of two independent molecules.
[c] Molecule has only two RuRu bonds.

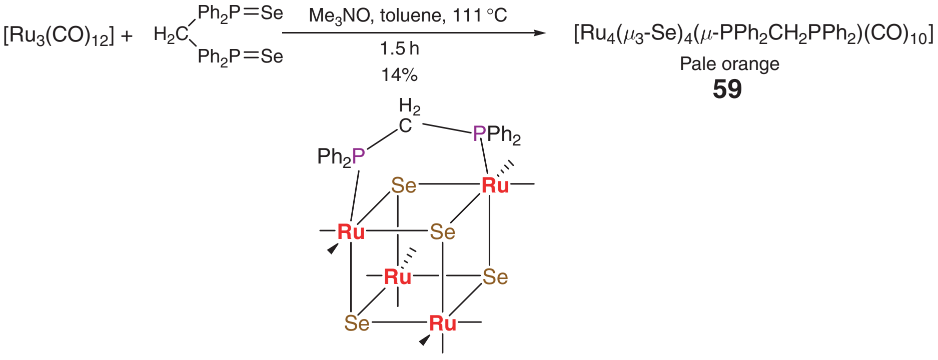
The highly symmetric cubane complex [$Ru_4(\mu_3\text{-}Se)_4(CO)_{12}$] **58** is isolated in low yield from the reaction of [$Ru_3(CO)_{12}$] and elemental selenium at 250 °C (Equation (44)).[51] The molecule has crystallographic cubic symmetry. Density functional calculations on the molecule were carried out. Its potential ability to act as a catalyst for the photo-oxidation of water was also investigated. It was found, however, that crystalline **58** has a high resistivity. In their theoretical discussions, the authors considered **58** to have 80 c.v.e. But as discussed in Section 6.23.1, a simpler view is to assign eight electrons to lone pairs on the Se atoms (i.e., Se is a four-electron donor to cage bonding) that leaves 72 c.v.e for bonding, consistent with no RuRu bonds in this cage compound.



58

(44)

The bisphosphine-substituted derivative of **58**, [$Ru_4(\mu_3\text{-}Se)_4(\mu\text{-}PPh_2CH_2PPh_2)(CO)_{10}$] **59**, is prepared from the reaction of [$Ru_3(CO)_{12}$] and $SePPh_2CH_2Ph_2PSe$ according to Equation (45).[52] Despite the presence of the diphosphine ligand, there is only a slight distortion of the Ru_4Se_2 unit from an ideal cubane structure. It is noted that the authors in this case considered **59** a 72 c.v.e. cage compound.



59

(45)

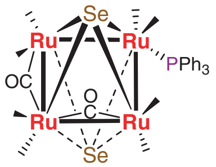
There have been four structures reported during the review period that contain the pseudo-octahedral Ru_4Se_2 unit, namely [$Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_2(CO)_7(L)(L')$] (L = CO, L′ = PPh_3, **60**; L = L′ = PPh_3, **61**)[53,54] and [$Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}L_2)(\mu\text{-}CO)(CO)_7$] ($L_2$ = *P*,*N*-$PPh_2(C_5H_4N)$ **62**; L_2 = $PPh_2CH_2PPh_2$ **63**; L_2 = PPh_2NHPPh_2 **64**, L_2 = $PPh_2N\{(S)\text{-}CHMePh\}PPh_2$ **65**).[55,56,48,49] The preparations of these clusters are given in Equations (46)–(51) along with appropriate line drawings for **61**, **62**, and **64**. The complexes with monodentate ligands (PPh_3) have two bridging carbonyl ligands that bridge adjacent RuRu bonds.[53,54] The parent carbonyl compound, [$Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_3(CO)_8$] has one bridging and two semibridging carbonyls (COMC (1995)). The clusters with bridging bidentate ligands have only one bridging carbonyl. The RuRu bonds bridged by carbonyls are usually the shorter metal–metal bonds in the clusters. An exception is **64** where the RuRu bond bridged by PPh_2NHPPh_2 is the shortest. This cluster also has the narrowest range of RuSe distances (Table 10).[56] The longer RuSe bonds in these clusters are usually adjacent to Ru atoms bound to bridging carbonyls.

$$[Ru_3(CO)_{12}] + Ph_3PSe \xrightarrow[\substack{1.5\,h\\ 21\%}]{Me_3NO,\ toluene,\ 111\,°C} [Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_2(CO)_8(PPh_3)]$$

1 : 1 ratio

Red-brown

60



60

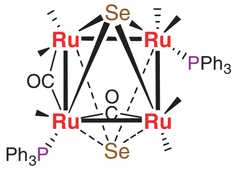
(46)

$$[Ru_3(CO)_{12}] + Ph_3PSe \xrightarrow[\substack{1.5\,h\\ 2.5\%}]{Me_3NO,\ toluene,\ 111\,°C} [Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_2(CO)_7(PPh_3)_2]$$

1 : 2 ratio

Yellow-brown

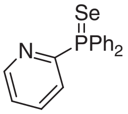
61



61

(47)

$[Ru_3(CO)_{12}]$ +

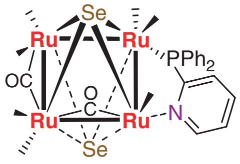


$$\xrightarrow[\substack{1\,h\\ 22\%}]{Me_3NO,\ toluene,\ 80\,°C}$$

$[Ru_4(\mu_4\text{-}Se)_2\{\mu\text{-}P,N\text{-}Ph_2(2\text{-}C_5H_4N)P\}(\mu\text{-}CO)_2(CO)_7]$

Pale orange

62



62

(48)

$$[Ru_3(CO)_{12}] + CH_2[Ph_2(Se)Ph]_2 \xrightarrow[1.5\,h]{Me_3NO,\ toluene,\ 111\,°C} \textbf{59} +$$

$[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}PPh_2CH_2PPh_2)(\mu\text{-}CO)(CO)_8]$ (49)

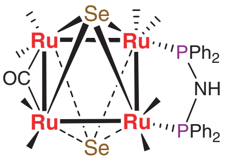
Light brown 5%

63

$$[Ru_3(CO)_{12}] + NH[Ph_2P(Se)]_2 \xrightarrow[\substack{1.5\,h\\ 39\%}]{Me_3NO,\ toluene,\ 111\,°C} [Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}PPh_2NHPPh_2)(\mu\text{-}CO)(CO)_8]$$

Orange

64



64

(50)

$$[Ru_3(CO)_{12}] + Ph_2PN(R)P(Se)Ph_2 \xrightarrow[1.5\,h]{Me_3NO,\ toluene,\ 111\,°C} [Ru_4(\mu_4\text{-}Se)_2\{\mu\text{-}PPh_2N(R)PPh_2\}(\mu\text{-}CO)(CO)_8] \qquad (51)$$

R = (*S*)-CHMePh, CHMe$_2$

R = (*S*)-CHMePh, 20%
R = CHMe$_2$, 30%

65

6.23.2.3.3.(iv) Derivatives with bridging Te ligands

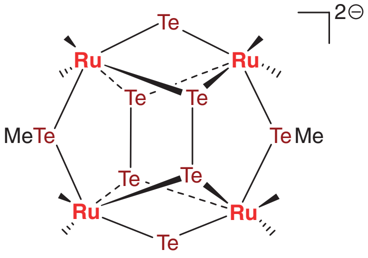
Table 11 reports recent Ru$_4$ structures with bridging Te ligands.

It had been previously shown that $[Ru_6Te_{14}(CO)_{12}]^{2-}$ results when Na$_2$Te$_2$ and [Ru$_3$(CO)$_{12}$] are heated together under hydrothermal conditions (110 °C). Carrying out the same reaction in methanol at 80 °C (a "methanothermal" synthesis) yields $[Ru_4(\mu_4\text{-}4\eta^1\text{-}Te_2)_2(\mu\text{-}Te)_2(\mu\text{-}TeMe)_2(CO)_8]^{2-}$ **66** isolated as its tetraphenylphosphonium salt (Equation (52)).[57] As shown in the equation, there has been partial methylation of Te in **66**. The structure contains a planar Ru$_4$ rectangle; the shorter sides of the rectangle are bridged by μ-Te^{2-} ligands, the longer sides by the μ-TeMe$^-$ ligands. The ditelluride ligands each bind, one above and one below the Ru$_4$ plane, to all the metal atoms in a $\mu_2,\mu_2\text{-}\eta^1,\eta^1$ ($\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1$) mode. The anion has a crystallographic inversion center; the bonding TeTe distance is 2.807(1) Å. This is another example of an interesting cage compound with 72 c.v.e. and no metal–metal bonds.

$$[Ru_3(CO)_{12}] + Na_2Te_2 + Ph_4PBr \xrightarrow[8\,h]{MeOH,\ 80\,°C} \qquad (52)$$

79%

$[Ph_4P]_2[Ru_4(\mu_4\text{-}4\eta^1\text{-}Te_2)_2(\mu\text{-}Te)_2(\mu\text{-}TeMe)_2(CO)_8]$
Dark brown
Anion = **66**



66

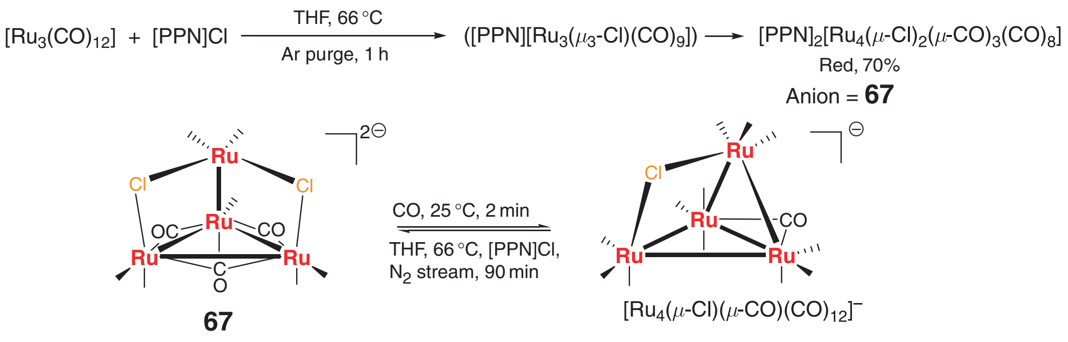
6.23.2.3.4 Derivatives with bridging group 17 ligands

Bridging chloride ligands are present in **12** and **49**. In **12**, the chloride ligands are triply-bridging; the RuCl bond lengths fall in the range 2.491(2)–2.686(2) Å.[20] In **49**, the chloride ligands bridge two ruthenium atoms. Each bridge is asymmetric with short (range 2.449(2)–2.463(2) Å) and long RuCl lengths (range 2.649(2)–2.836(2) Å).[44]

Table 11 Recent structures with bridging Te ligands

Compound	*Structure*[a]	*RuRu* (Å)	*RuTe* (Å)
μ_2-Te			
$[Ru_4(\mu_4\text{-}4\eta^1\text{-}Te_2)_2(\mu\text{-}Te)_2(\mu\text{-}TeMe)_2(CO)_8]^{2-}$ ([Ph$_4$P]$^+$ salt) **66**	**66**	(No RuRu bonds) Te–Te = 2.807(1), Te···Te = 3.394(1), 3.418(1)	2.710(1), 2.725(1) (Te); 2.676(1), 2.679(1) (TeMe); 2.722(1), 2.724(1), 2.727(1), 2.729(1) (Te$_2$)
μ_3-Te			
$[Ru_4(\mu_3\text{-}Te)(\mu\text{-}\eta^4\text{-}C_8H_6)(\mu\text{-}CO)_2(CO)_9]$[155]	ST[b]	2.765(1), 2.829(1), 2.836(1), 2.865(1)	2.624(1), 2.651(1), 2.772(1)
μ_4-Te			
$[Ru_4(\mu_4\text{-}Te)_2(\mu\text{-}CO)_2(CO)_8]$[2-c]	S(Ru$_4$Te$_2$oct.)	2.747(2), 2.972(2)[d]	2.720(1), 2.739(2) (Te1) 2.709(2), 2.724(2)(Te2)[d]

[a] See Figure 1.
[b] See 217.
[c] Das, B.K.; Kanatzidis, M.G. *Polyhedron* **1997**, *16*, 3061.
[d] Structure is centrosymmetric.



Scheme 5

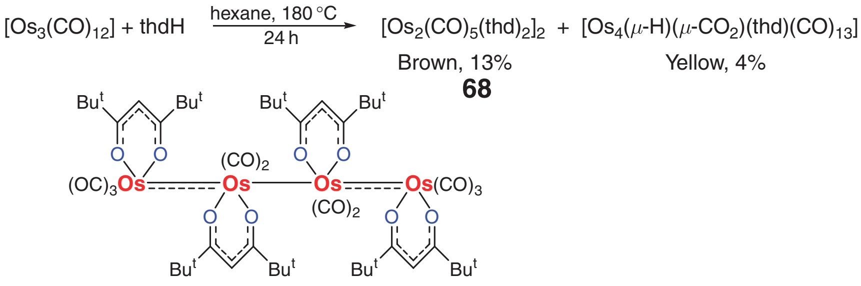
A curious tetranuclear Ru anion with bridging chloride ligands is $[Ru_4(\mu\text{-}Cl)_2(\mu\text{-}CO)_3(CO)_8]^{2-}$ **67**, made from the reaction of $[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]$ with [PPN]Cl in refluxing THF under a purge of argon (Scheme 5).[44] As indicated in the scheme, the trinuclear anion is readily prepared from $[Ru_3(CO)_{12}]$ and [PPN]Cl. Cluster **67** is the precursor to **49**, Scheme 4. Compound **67** has a rare spiked triangular structure where the spike Ru atom is orthogonal to the Ru_3 plane (see also **218**). The spike RuRu bond is somewhat shorter than the other RuRu bonds in the cluster (2.776(2) vs. 2.806(2), 2.812(2), and 2.870(2) Å). The RuCl lengths are in the range 2.416(4)-2.536(4)Å. Molecular orbital analysis supports the view that **67** is a saturated 48 c.v.e. triruthenium system with a mononuclear 16-electron square-pyramidal Ru fragment bound to one face. The cluster has 62 c.v.e. for which five RuRu bonds would normally be expected. Due to its unsaturation **67** is highly reactive. Reaction with carbon monoxide at room temperature results in rapid addition of CO and loss of a chloride ion to give the known butterfly anion $[Ru_4(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_{12}]^-$. The transformation is readily reversed as indicated in Scheme 5.[44]

6.23.3 Osmium Compounds without Hydrocarbon Ligands

6.23.3.1 Neutral Carbonyls and Simple Derivatives

6.23.3.1.1 Chain compounds

A hexane solution of $[Os_3(CO)_{12}]$ and thdH (thdH = 2,2,6,6-tetramethyl-3,5-heptandione) affords the chain complex $\{Os_2(CO)_5(thd)_2\}_2$ **68** and the CO_2 cluster complex $[Os_4(\mu\text{-}H)(\mu\text{-}CO_2)(thd)(CO)_{13}]$ in low yields (Equation (53)).[58] The latter complex **236** is discussed in Section 6.23.6.2. Complex **68** is best described as a metal chain complex with four osmium atoms aligned in a near linear fashion with short (2.7683(4) Å)–long (2.9778(6) Å)–short OsOs bonds (the molecule has a crystallographic C_2 axis).[59]



68

(53)

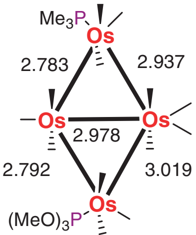
6.23.3.1.2 Cluster compounds

The neutral tetraosmium carbonyl cluster $[Os_4(CO)_{15}]$, mentioned in COMC (1995), has an unusual planar Os_4 skeleton with adjacent long and short peripheral metal–metal bonds (i.e., a “kite” structure). The stability of this planar metallic core configuration has been confirmed by extended Hückel calculations.[60]

The air-stable cluster $[Os_4(CO)_{13}(PMe_3)\{P(OMe)_3\}]$ **69** is obtained in high yield when $P(OMe)_3$ is added to a hexane solution of $[Os_4(CO)_{13}(PMe_3)]$ (Equation (54)). The structure of **69** consists of a planar Os_4 skeleton with long and short peripheral OsOs bonds similar to that of the parent $[Os_4(CO)_{15}]$ cluster. The bulky phosphorus ligands each occupy a sterically less hindered equatorial site at different wingtip osmium atoms *cis* to the $Os(CO)_3$ unit. It is found that **69** is rigid on the NMR time-scale in solution at −45 °C. Carbonyl exchange is observed at −6 °C in the ^{13}C NMR spectrum. The mechanism is believed to involve an axial–equatorial, merry-go-round carbonyl exchange in the two planes that contain the short OsOs bonds (2.783(3) and 2.792(2) Å). In other words, the hinge $Os(CO)_4$ group does not take part in the exchange since the exchange of these carbonyls would require the migration of the phosphorus ligands from one metal atom to another, which is a high-energy process in osmium cluster chemistry.[61,62] It is only at 70 °C that all the signals disappear into the base line. The exchange mechanism at the higher temperatures is unclear.[63]

$$[Os_4(CO)_{14}(PMe_3)] + P(OMe)_3 \xrightarrow[92\%]{\text{hexane, 25 °C}} [Os_4(CO)_{13}(PMe_3)\{P(OMe)_3\}] \qquad (54)$$

Red **69**

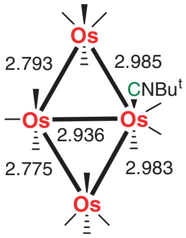


69

The cluster $[Os_4(CO)_{14}(CNBu^t)]$ **70** is prepared by the addition of Me_3NO to $[Os_4(CO)_{15}(CNBu^t)]$ in CH_2Cl_2 (Equation (55)).[63] It has the similar planar Os_4 structure as **69**. Indeed, the OsOs bond lengths in both **69** and **70** are all within 0.021 Å of their counterparts in $[Os_4(CO)_{15}]$. This suggests that the difference in the length of the long and short metal–metal bonds in these molecules cannot be attributed to the packing forces or the *trans*-influences of the peripheral ligands. It is noted that the isocyanide ligand in **70** occupies an axial site of a hinge osmium atom. Like $[Os_4(CO)_{15}]$ (see COMC (1995)), **70** is non-rigid in solution even at −120 °C; the mechanism is attributed to an all-equatorial, merry-go-round carbonyl exchange. The ^1H NMR spectrum at ambient temperature exhibits two signals, at δ 0.95 and 0.96, of almost equal intensity. This feature remains unchanged at −50 °C indicating the presence of two isomers in solution. One form is believed to have the structure found in the solid-state and the other with the isocyanide ligand at an axial position of a wingtip osmium atom.[63]

$$[Os_4(CO)_{15}(CNBu^t)] + Me_3NO \xrightarrow[62\%]{CH_2Cl_2,\text{ 25 °C}} [Os_4(CO)_{14}(CNBu^t)] \qquad (55)$$

Dark red **70**



70

6.23.3.2 Carbonyl Anions and Simple Derivatives

The synthesis of the tetraosmium anion $[Os_4(CO)_{13}]^{2-}$ **71** described by Shore and co-workers gives the anion in low yield.[64] A relatively simple route for the preparation of this dianion has been reported by Carty and co-workers which involves treating $Na_2[Os(CO)_4]$ with $[Os_3(CO)_{12}]$ in THF (Equation (56)).[27]

$$Na_2[Os(CO)_4] + [Os_3(CO)_{12}] \xrightarrow[\text{4 d, dark}]{\text{THF, 25 °C}} Na_2[Os_4(CO)_{13}] \qquad (56)$$

Anion = **71**

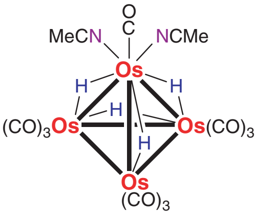
6.23.3.2.1 Carbonyl anions in synthesis

Lewis and co-workers have demonstrated the use of cluster anions $[Os_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$, $[Os_4(CO)_{13}]^{2-}$, and $[Os_4(CO)_{13}(X)]^-$ (X = Cl, Br, I) in the syntheses of mixed-metal species (Scheme 6).[65]

6.23.3.3 Neutral Carbonyl Derivatives with Bridging Hydride Ligands

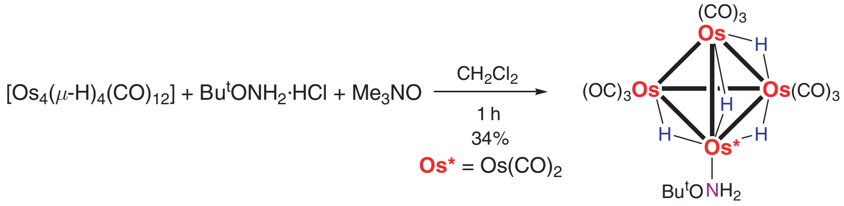
6.23.3.3.1 Derivatives with N ligands

The details for the synthesis of the activated tetraosmium hydrido cluster $[Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2]$ **72** have been previously reported; the X-ray structure has now been determined.[66] It consists of a tetrahedral metal core with each hydride ligand bridging the four OsOs bonds which are longer (2.915(3)–2.998(3) Å) compared to the remaining two (both 2.810(3) Å). The two acetonitrile ligands are coordinated to the same osmium atom (OsN = 2.02(4) and 2.07(5) Å). The molecule possesses approximate C_s symmetry.



72

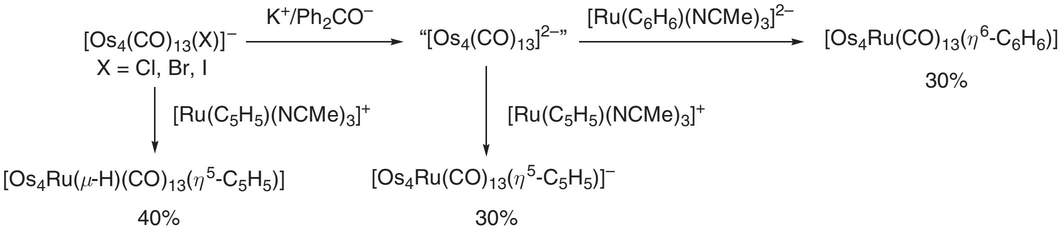
A dichloromethane solution of $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ and *O-tert*-butylhydroxylamine hydrochloride ($Bu^tONH_2{\cdot}HCl$) in the presence of Me_3NO yields $[Os_4(\mu\text{-}H)_4(CO)_{11}(\eta^1\text{-}NH_2OBu^t)]$ **73** (Equation (57)).[67] The OsOs distances of the tetrahedron span the range 2.803(2)–2.999(2) Å. The amine ligand is terminally coordinated to an osmium atom (OsN = 2.15(2) Å).[68]



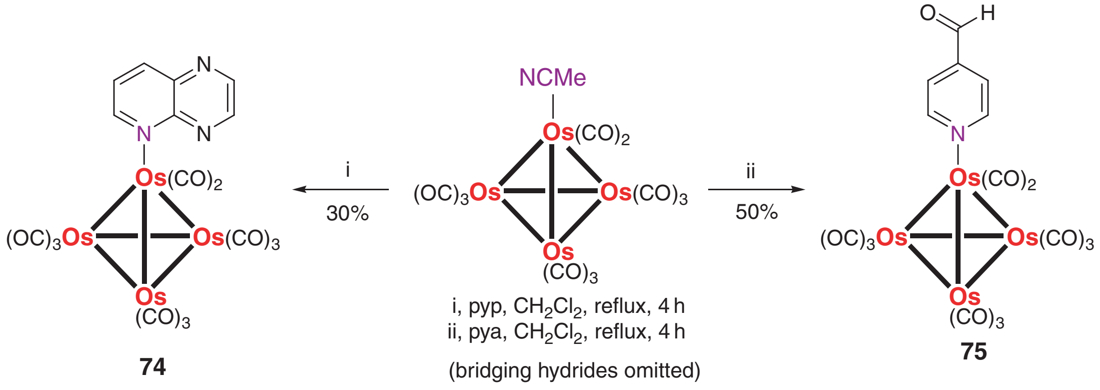
73

(57)

The reaction of the activated tetraosmium carbonyl cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(NCMe)]$ with the monopyridyl ligands pyrido[2,3-*b*]pyrazine (pyp) or 4-pyridinecarboxaldehyde (pya) in refluxing CH_2Cl_2 provides the monosubstituted clusters $[Os_4(\mu\text{-}H)_4(CO)_{11}(pyp)]$ **74** and $[Os_4(\mu\text{-}H)_4(CO)_{11}(pya)]$ **75**, respectively (Scheme 7).[69] In the former cluster, the pyp ligand is terminally bonded to an osmium atom through the pyridyl nitrogen atom with an OsN bond length



Scheme 6



Scheme 7

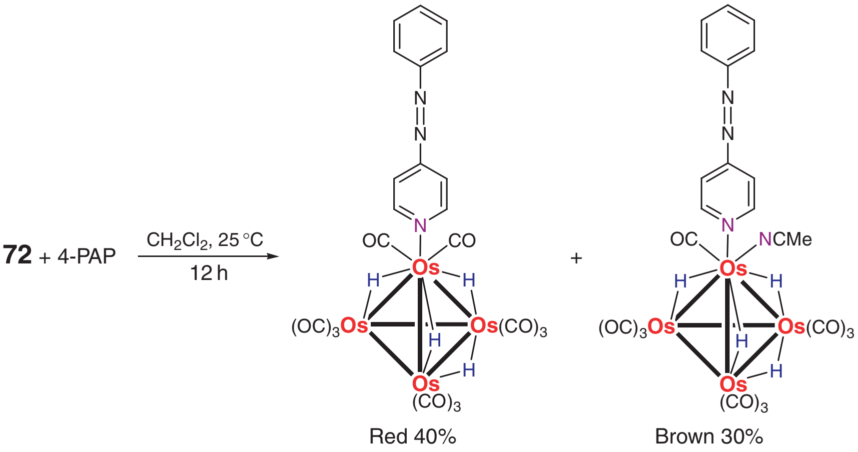
of 2.19(3) Å. The structure of **75** is similar to that of **74**.[69] See Table 12 for the selected bond lengths of these and other related compounds.

When the complex $[Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2]$ **72** is stirred in CH_2Cl_2 with 4-phenylazopyridine (4-PAP) at ambient conditions two clusters are formed, namely, $[Os_4(\mu\text{-}H)_4(CO)_{11}\{NC_5H_4(N{=}N)Ph\}]$ **76** and $[Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)\{NC_5H_4(N{=}N)Ph\}]$ **77** (Equation (58)).[70] In **76**, the four bridging hydrides are assigned to the four OsOs edges that are significantly longer (2.937(1)–2.997(1) Å) than the remaining two (2.812(1) and 2.808(1) Å). In both **76** and **77**, the azo ligand (4-PAP) is terminally bonded via the pyridyl nitrogen atom to an osmium atom of the Os_4 tetrahedron. The OsN distances are 2.17(2) Å in **76** and 2.14(2) Å in **77**. The pyridyl and phenyl rings of **76** are essentially coplanar (dihedral angle of 4.3°). Although the two clusters have the same molecular geometry, the tetrahedron of **77** is more distorted (OsOs = 2.797(2)–3.014(2) Å). The room temperature ^1H NMR spectrum of **76** (in CD_2Cl_2) gives evidence of fluxional hydride migrations along the different OsOs edges. At −55 °C, there is an indication of two isomers of **76** (with different bridging hydride dispositions). An attempt to add another 4-PAP ligand via displacement of the labile acetonitrile group in **77** was unsuccessful.[70] This is attributed to the severe steric hindrance imposed by the large 4-phenylazopyridine molecule that prevents the addition.

Table 12 Selected bond lengths for clusters **76–98** and **100–104**

Cluster	*OsOs bond length range* (Å)	*OsN length* (Å)
74	2.814(2)–2.988(2)	2.19(3)
75	2.801(1)–3.008(1)	2.14(2)
76	2.808(1)–2.997(1)	2.17(2)
77	2.797(2)–3.014(2)	2.14(2)
78	2.805(1)–3.013(1)	2.17(1)
79	2.816(1)–2.977(1)	2.03(2), 2.08(1)
80	2.809(1)–3.004(1)	2.18(1)
81	2.789(1)–3.095(1)	2.16(1),[a] 2.25(1)[b]
82	2.809(1)–3.022(1)	2.17(2)
83	2.786(1)–3.008(1)	2.08(1), 2.11(1)
84	2.800(2)–3.026(2)	2.12(3), 2.13(3)
85	2.790(2)–3.004(2)	2.07(3), 2.08(3)
86	2.789(1)–3.006(1)	2.08(2), 2.12(2)
88	2.777(1)–3.009(1)	2.09(2), 2.11(2)
89	2.793(2)–3.047(2)	2.11(2), 2.11(2)
90	2.799(2)–3.012(1)	2.11(2), 2.12(2)
91	2.777(1)–3.061(1)	2.11(1), 2.15(1)
92	2.793(1)–3.024(1)	2.07(2), 2.10(1)

[a] $Os{-}NC_5H_4(N{=}N)Ph$.
[b] $Os{-}NMe_3$.



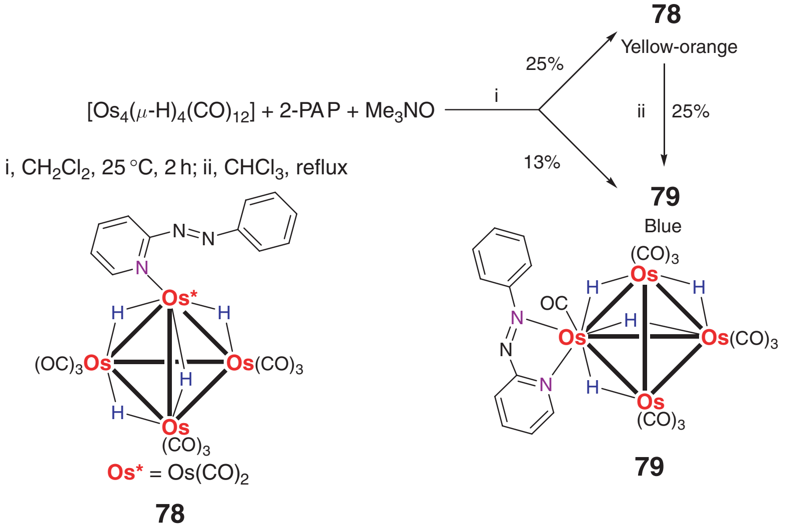
76 **77**

(58)

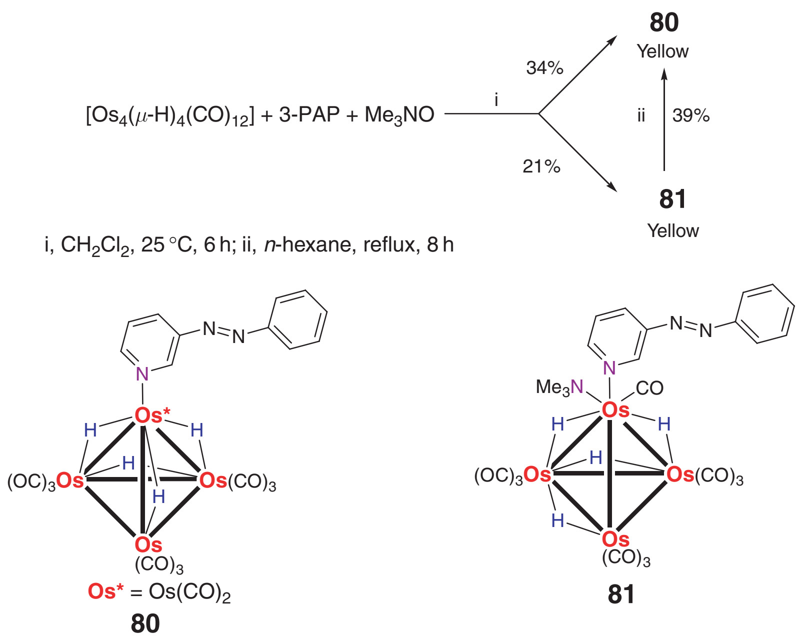
When a mixture of $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ and 2-phenylazopyridine (2-PAP) in CH_2Cl_2 is treated with Me_3NO, the cluster compounds $[Os_4(\mu\text{-}H)_4(CO)_{11}\{NC_5H_4(N{=}N)Ph\}]$ **78** and $[Os_4(\mu\text{-}H)_4(CO)_{10}\{\eta^2\text{-}NC_5H_4(N{=}N)Ph\}]$ **79** are formed. Cluster **78** can be converted into **79** in refluxing in chloroform (Scheme 8).[71]

In a similar reaction to the first reaction of Scheme 8, the addition of 3-phenylazopyridine (3-PAP) to $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ affords the clusters $[Os_4(\mu\text{-}H)_4(CO)_{11}\{NC_5H_4(N{=}N)Ph\}]$ **80** and $[Os_4(\mu\text{-}H)_4(CO)_{10}(NMe_3)\{NC_5H_4(N{=}N)Ph\}]$ **81**. In refluxing *n*-hexane over an 8 h period, less than half of **81** is converted to **80** (Scheme 9).[71]

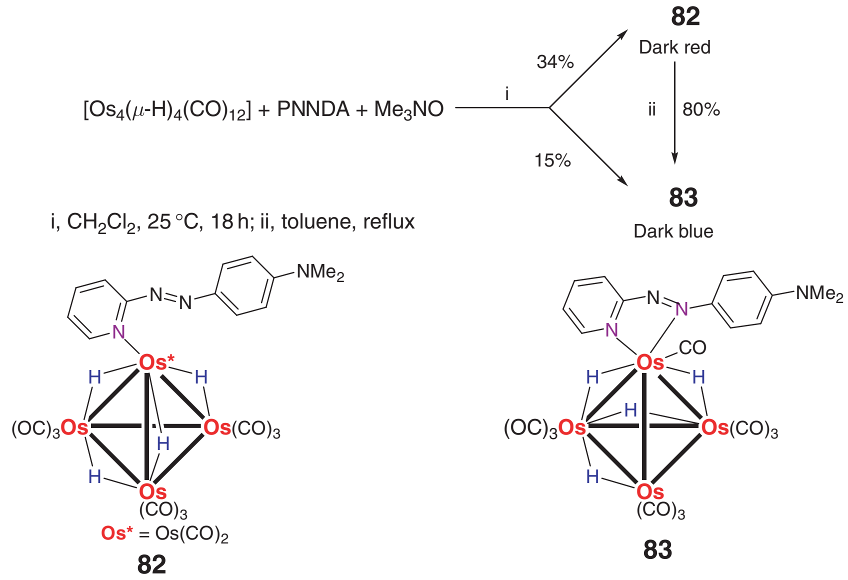
Clusters **78** and **80** have the same chemical formula, metal framework (distorted tetrahedron with OsOs bond lengths of 2.805(1)–3.013(1) Å), and ligand moieties, but differ in the position of the pyridine nitrogen atom in the azo ligand. The OsN bond lengths are 2.17(1) and 2.18(1) Å in **78** and **80**, respectively.[71] The molecular geometry of compound **81** is similar to that of **80**, except one terminal carbonyl ligand is replaced by a trimethylamine ligand, which also coordinates to the same osmium atom as the 3-PAP ligand in **81**. The length of the Os–NMe_3 bond (2.25(1) Å) is longer than the Os–$NC_5H_4(N{=}N)Ph$ bond (2.16(1) Å), consistent with the lability of the NMe_3 ligand. The chelating azo ligand (2-PAP) in cluster **79** binds to one osmium atom in the Os_4 tetrahedron with OsN bond distances of 2.03(2) and 2.08(1) Å. The dihedral angle between the pyridyl and phenyl rings in **79** is 33.2°.[71]



Scheme 8



Scheme 9



Scheme 10

The ^{1}H NMR data of 78 and 80 indicate fluxional behavior of hydride ligands at room temperature, but the presence of three isomers 78 and two isomers 80 at −40 °C.

In a reaction similar to those in Schemes 8 and 9, the addition of 4-(2-pyridylazo)-*N*,*N*-dimethylaniline (PNNDA) affords $[Os_4(\mu\text{-H})_4(CO)_{11}\{NC_5H_4(N{=}N)C_6H_4NMe_2\}]$ 82 and $[Os_4(\mu\text{-H})_4(CO)_{10}\{\eta^2\text{-}NC_5H_4(N{=}N)C_6H_4NMe_2\}]$ 83. Most of compound 82 is converted into 83 upon heating in toluene under reflux (Scheme 10).[72] The PNNDA ligand coordinates to one osmium atom via the pyridyl nitrogen atom in 82 (OsN = 2.17(2) Å), whereas two nitrogen atoms (one pyridyl and one azo) chelate an osmium atom in 83 (OsN = 2.078(6) and 2.111(7) Å). The pyridyl and phenyl rings are slightly twisted in both 82 and 83 with dihedral angles of 8.1° and 11.8°, respectively. The ^{1}H NMR spectra show the existence of two isomers of 82 and four isomers of 83 in solution.[72]

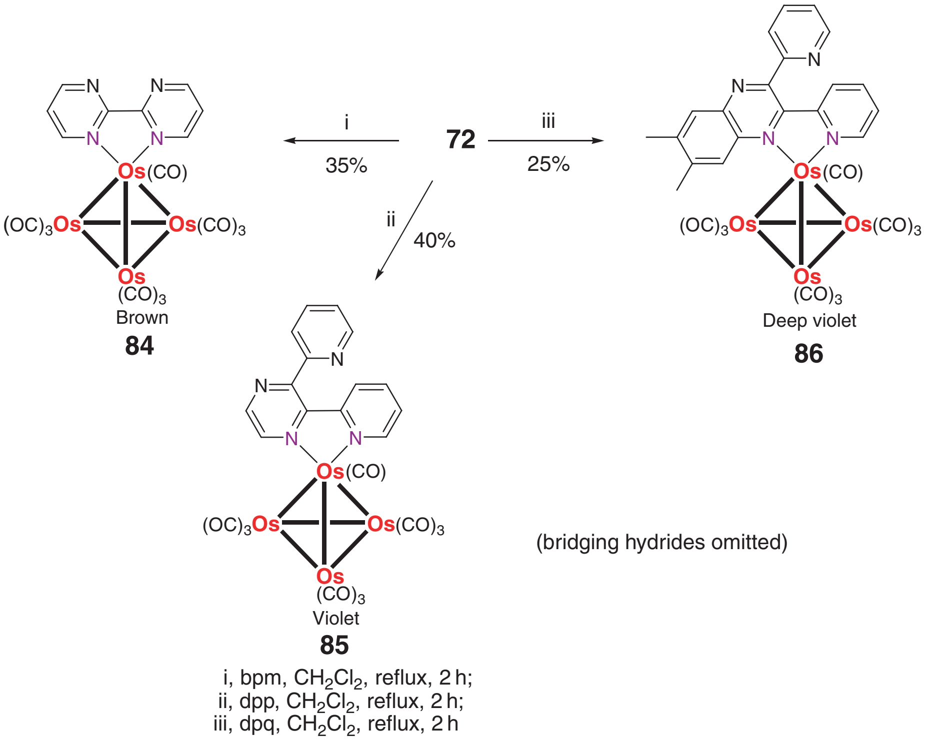
The reactions of $[Os_4(\mu\text{-H})_4(CO)_{10}(NCMe)_2]$ 72 with pyridyl-containing ligands 2,2′-bipyrimidine (bpm), 2,3-bis(2-pyridyl)pyrazine (dpp), and 2,3′-bis(2′-pyridyl)-5,6-dimethylquinoxaline (dpq) in refluxing CH_2Cl_2 forms new clusters $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-bpm})]$ 84, $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-dpp})]$ 85, and $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-dpq})]$ 86, respectively (Scheme 11).[73] All three have a tetrahedral metal core (see Table 12 for the selected bond lengths). The ^{1}H NMR spectrum of 84 suggests that some fluxionality of the bridging hydrides occurs at room temperature. It is noted that the pyridyl and pyrazine rings (those bonded to the osmium atom) in both 85 and 86 are not coplanar (dihedral angles of 16.7° and 27.4°, respectively). The two OsN bonds in 84 (and 85) do not differ by more than 0.01 Å (see Table 12). However, there is a slight variation (0.04 Å) in 86 which may be due to the bulky dpq group.[73]

Protonation of 85 by trifluoroacetic acid in CH_2Cl_2 yields the corresponding monocationic cluster $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-dpp})(H)]^+$ 87. Its presence is confirmed by positive ion electrospray mass spectrometric analysis and by a shift of approximately 50 cm^{-1} for the ν(CO) vibrations to the higher-energy region in the IR spectrum of 87 as compared to 85.[73]

When 72 reacts with bipyridyl-type ligands 2,2′-bipyridine (bpy) or 4,4′-diphenyl-2,2′-bipyridine (dpbpy) in refluxing CH_2Cl_2, the chelated disubstituted products $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-bpy})]$ 88 and $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-dpbpy})]$ 89 are formed, respectively (Scheme 12).[69] Cluster 89 (with a core structure similar to that of 72) contains two pyridine rings which are essentially coplanar with a dihedral angle of 1.5°. In the solid state, one phenyl ring is nearly coplanar with these two pyridine rings (dihedral angles of 2.0° and 2.9°) while the second phenyl is out of the ligand plane by 39.1°.[69]

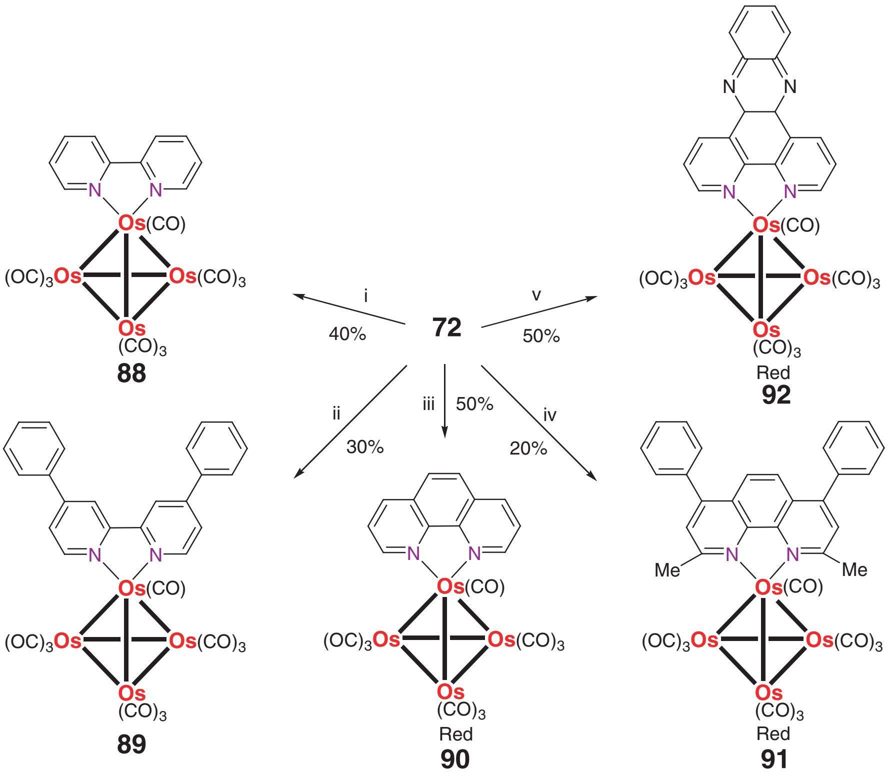
Three phenanthroline-type ligand substituted clusters $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-phen})]$ 90, $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-dmdpp})]$ 91, and $[Os_4(\mu\text{-H})_4(CO)_{10}(\eta^2\text{-dppz})]$ 92 are produced as a result of 72 reacting with phenanthroline (phen), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (dmdpp), or dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), respectively, in refluxing CH_2Cl_2 for 5 h (Scheme 12).[69]

Clusters 90–92 have similar molecular geometries (Table 12). The chelating phenanthroline ligand is symmetrically bonded to an osmium atom (OsN = 2.11(2) and 2.12(2) Å) in 90. In 91, the phenanthroline part of the ligand is essentially



i, bpm, CH_2Cl_2, reflux, 2 h;
ii, dpp, CH_2Cl_2, reflux, 2 h;
iii, dpq, CH_2Cl_2, reflux, 2 h

Scheme 11



(bridging hydrides omitted)

i, bpy, CH_2Cl_2, reflux, 4 h; ii, dpbpy, CH_2Cl_2, reflux, 4 h;
iii, phen, CH_2Cl_2, reflux, 5 h; iv, dmdpp, CH_2Cl_2, reflux, 5 h; v, dppz, CH_2Cl_2, reflux, 5 h

Scheme 12

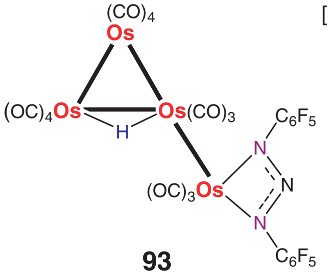
planar while the two phenyl rings are twisted with respect to the phenanthroline rings (dihedral angles of 62.0° and 70.1°). The interesting feature of **92** is the coplanar inverted Y-shaped ligand with OsN distances of 2.07(2) and 2.10(1) Å.[69]

Treatment of $[Os_3(H)(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ with $[Os_3(CO)_{11}(NCMe)]$ in hexane provides as the major product $[Os_4(\mu\text{-}H)(CO)_{14}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **93** (Equation (59)).[74]

$$[Os_3(H)(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)] + [Os_3(CO)_{11}(NCMe)] \xrightarrow[\substack{15\%\\16\,h}]{\text{hexane, 60 °C}} [Os_4(\mu\text{-}H)(CO)_{14}(\eta^2\text{-}C_6F_5NNNC_6F_5)] \quad (59)$$

orange

93

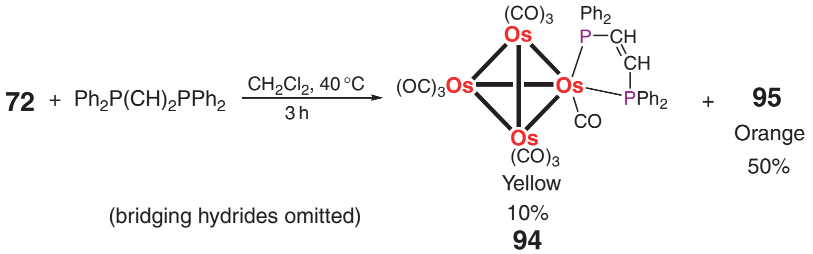


93

Compound **93** consists of a triangular $Os_3(\mu\text{-}H)(CO)_{11}$ unit spiked with an $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$ group. The lengths of the OsOs bonds in the Os_3 triangle are between 2.850(2)–3.042(2) Å (Os(μ-H)Os); the spike OsOs is 2.880(2) Å. The spike Os atom is 0.162 Å above the plane of the Os_3 triangle. The triazenide ligand occupies both an axial and an equatorial site of the spike osmium atom (OsN = 2.16(3) and 2.19(3) Å) to give an almost planar four-membered OsN_3 ring. The ^{19}F NMR spectrum, however, indicates a symmetrical arrangement of the triazenide ligand about this osmium atom.[74]

6.23.3.3.2 Derivatives with P ligands

When $[Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2]$ **72** reacts with *cis*-1,2-bis(diphenylphosphino)ethylene ($Ph_2PCH{=}CHPPh_2$, dppee) in refluxing CH_2Cl_2 the geometric isomers $[Os_4(\mu\text{-}H)_4(CO)_{10}(\eta^2\text{-dppee})]$ **94** and $[Os_4(\mu\text{-}H)_4(CO)_{10}(\mu\text{-dppee})]$ **95** are obtained in low and moderate yields, respectively (Equation (60)).[66]



94

(60)

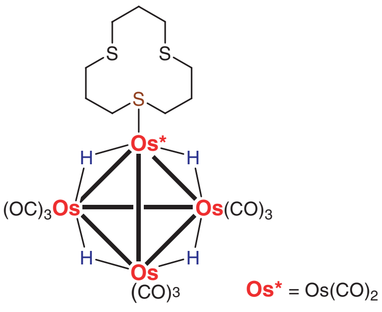
In **94**, dppee acts as a chelating ligand whereas it adopts a bridging mode in **95**. Molecular mechanical calculations using MM2 parameters indicate that **95** is probably kinetically favored whereas **94** is thermodynamically favored. This is reflected by the experimental yields (10% for **94** and 50% for **95**).[66] Table 13 contains OsOs bond length ranges and OsP bond lengths of these and related cluster compounds.

6.23.3.3.3 Derivatives with S ligands

The cluster compounds $[Os_4(\mu\text{-}H)_4(CO)_{11}(12S3)]$ **96** (12S3 = 1,5,9-trithiacyclododecane $\{S(CH_2)_3\}_3$) and $[Os_4(\mu\text{-}H)_4(CO)_{11}\text{-(thietane)}]$ (**97**; thietane = $\overline{SCH_2CH_2CH_2}$) are obtained in high yields from the reactions of $[Os_4(\mu\text{-}H)_4(CO)_{11}\text{-(NCMe)}]$ with 12S3 and thietane, respectively (Equations (61) and (62)).[14] The core of **96** is a distorted Os_4 tetrahedron with the four bridging hydrides assigned to the four longer OsOs bonds (2.948(1)–2.978(1) Å). The remaining two OsOs bonds are significantly shorter at 2.786(1) and 2.821(1) Å. The 12S3 ligand is coordinated to one osmium atom via one of its three sulfur atoms (OsS = 2.419(5) Å). The ^1H NMR spectrum of **96** at room temperature is consistent with the solid-state structure. However, when the temperature is lowered, the hydride resonances broaden and resolve into a new pattern indicating the existence of at least three isomers in solution (formed by the different hydride arrangements about the six metal–metal bonds). The IR and ^1H NMR spectra of **97** are similar to **96**, that is, compound **97** also exists as a mixture of isomers in solution.[14]

$$[Os_4(\mu\text{-}H)_4(CO)_{11}(NCMe)] + 12S3 \xrightarrow[\substack{2\,h\\91\%}]{CH_2Cl_2,\ 40\,°C} [Os_4(\mu\text{-}H)_4(CO)_{11}(12S3)]$$

96

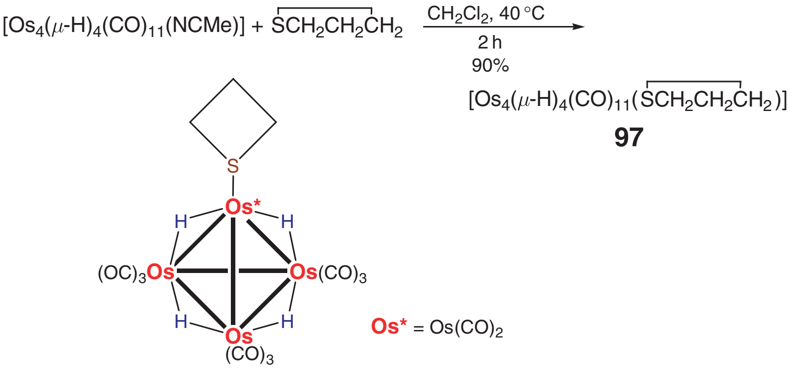


96

(61)

Table 13 OsOs OsP distances for some selected Os_4 clusters

Cluster	*OsOs* (Å) *range*	*OsP* (Å)
94	2.813(1)–3.026(1)	2.300(4), 2.313(4)
95	2.782(1)–2.985(1)	2.324(6), 2.358(6)
121	2.786(2)–2.980(1)	2.339(5), 2.354(5)
122	2.806(2)–2.996(2)	2.350(7), 2.353(7)
123	2.799(1)–2.998(1)	2.349(4), 2.356(2)



$$[Os_4(\mu\text{-}H)_4(CO)_{11}(NCMe)] + \overline{SCH_2CH_2CH_2} \xrightarrow[\substack{2\,h\\ 90\%}]{CH_2Cl_2,\ 40\,^{\circ}C} [Os_4(\mu\text{-}H)_4(CO)_{11}(\overline{SCH_2CH_2CH_2})] \quad \mathbf{97} \tag{62}$$

97

6.23.3.4 Hydrido Carbonyl Anions and Simple Derivatives

The syntheses in solution of high nuclearity osmium carbonyl clusters usually require $[Os_3(CO)_{12}]$ as a starting material. A relatively easy preparation of various anionic (and neutral) osmium carbonyl clusters has been reported[75,76] that gives high yields by the controlled reduction at atmospheric pressure of silica-supported α-$[\{Os(\mu\text{-}Cl)(CO)_3(Cl)\}_2]$ or silica-bound $[Os(CO)_3Cl_2(HOSi{\equiv})]$[77] in the presence of alkali metal carbonates. For example, the dianion $[Os_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$ **98** was first prepared in 39% yield from the reaction of $[Os_3(CO)_{12}]$ with sodium borohydride in refluxing dioxane for 4 h,[78] but now, heating α-$[\{Os(\mu\text{-}Cl)(CO)_3(Cl)\}_2]$ supported on silica doped with K_2CO_3 under 1 atm of CO at 200 °C gives **98** in 87–92% yield (Equation (63)).[79]

$$\alpha\text{-}[\{Os(CO)_3(\mu\text{-}Cl)(Cl)\}_2] + CO \xrightarrow[\substack{2\,d\\ 87\text{–}92\%}]{SiO_2,\ K_2CO_3,\ 200\,^{\circ}C} \underset{\text{Anion} = \mathbf{98}}{K_2[Os_4(\mu\text{-}H)_2(CO)_{12}]} \tag{63}$$

6.23.3.5 Carbonyl Derivatives with Bridging Ligands

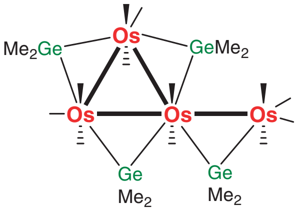
6.23.3.5.1 Derivatives with bridging group 14 ligands other than C ligands

Osmium forms numerous condensed carbonyl clusters because of its ability to readily form $Os(CO)_4$ and $Os(CO)_3$ units which can exhibit different geometries and bonding modes. However, higher-nuclearity osmium clusters with EMe_2 (E = Ge, Sn) units usually have an open, planar arrangements of metal atoms. This is because EMe_2 is isolobal with $Os(CO)_4$, which adopts an octahedral coordination.[80]

6.23.3.5.1.(i) Derivatives with bridging Ge ligands

UV photolysis of $[\{Os(\mu\text{-}GeMe_2)(CO)_4\}_2]$ in hexane affords the known compound $[\{Os(\mu\text{-}GeMe_2)(CO)_3\}_3]$ along with $[Os_3(\mu\text{-}GeMe_2)_2(CO)_{11}]$ and $[Os_4(\mu\text{-}GeMe_2)_4(CO)_{12}]$ **99** (Equation (64)).[80] Cluster **99** can also be obtained by pyrolysis of the same starting material in hexane at 100 °C. The structure of **99** contains an Os_3 triangle (OsOs = 2.860(1), 2.967(1), and 2.974(1) Å) spiked with a fourth osmium atom with a long OsOs bond length (3.069(1) Å). Each OsOs edge is bridged by a $GeMe_2$ ligand (OsGe = 2.475(2)–2.584(2) Å) resulting in a central triangulated (raft-like) Os_3Ge_3 unit with one osmium atom bound to an $Os(CO)_4(GeMe_2)$ fragment to give an Os_2Ge triangle that lies in the plane of the other metal atoms (dihedral angle of 3.3°). The central osmium atom has an extremely rare hexagonal-bipyramidal geometry. The ^1H NMR spectrum is consistent with the solid-state structure being retained in solution at 21 °C. However, there is evidence for the rotation of the $Os(CO)_4(GeMe_2)$ unit with respect to the rest of the molecule (i.e., the Os_3Ge_3 unit) above 60 °C.[80]

$$[\{Os(\mu\text{-}GeMe_2)(CO)_4\}_2] \xrightarrow[16.5\,h]{hexane,\ h\nu} \underset{\substack{Orange\\ 8\%}}{[\{Os(\mu\text{-}GeMe_2)(CO)_3\}_3]} + \underset{\substack{Pale\ yellow\\ 2\%}}{[Os_3(\mu\text{-}GeMe_2)_2(CO)_{11}]} + \underset{\substack{Orange\text{-}red\\ 4\%\\ \mathbf{99}}}{[Os(\mu\text{-}GeMe_2)_4(CO)_{12}]} \tag{64}$$

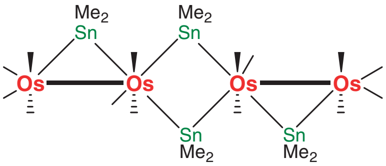


99

6.23.3.5.1.(ii) Derivatives with bridging Sn ligands

UV irradiation of $[\{Os(\mu\text{-}SnMe_2)(CO)_4\}_2]$ in hexane gives $[Os_4(\mu\text{-}SnMe_2)_4(CO)_{14}]$ **100**. The reaction is easily reversed by treating **100** with carbon monoxide (1 atm) in solution at 65 °C (Equation (65)).[81] Cluster **100** has a planar Os_4Sn_4 skeleton with a central rhomboidal Os_2Sn_2 unit such that each osmium atom is part of two outer Os_2Sn triangles. The OsSn bond lengths of the former unit are longer (2.760(1) and 2.780(1) Å) than in the latter (2.678(1) and 2.727(1) Å). The OsOs distance of 3.0414(5) Å is long for an OsOs bond not bridged by a hydride ligand (compare with the average OsOs length of 2.877 Å in $[Os_3(CO)_{12}]$).[81]

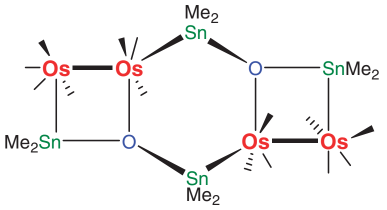
$$[\{Os(\mu\text{-}SnMe_2)(CO)_4\}_2] \xrightleftharpoons[65\,^\circ C,\ 1\ atm\ CO]{hexane,\ h\nu,\ 14\,h} \underset{\substack{Yellow\\ 30\%\\ \mathbf{100}}}{[Os_4(\mu\text{-}SnMe_2)_4(CO)_{14}]} \tag{65}$$



100

When $[\{Os(\mu\text{-}SnMe_2)(CO)_4\}_2]$ and Me_3NO are stirred in a solution of CH_2Cl_2 and MeCN, $[Os_4\{\mu_3\text{-}\eta^3\text{-}O(SnMe_2)_2\}_2(CO)_{14}]$ **101** is formed (Equation (66)).[81] Compound **101** may be considered as being derived from **100** by addition of two oxygen atoms such that the original three- and four-membered rings are expanded into four- and six-membered rings, respectively. Treatment of **100** with Me_3NO does not, however, yield **101** under the same conditions.[81] This cluster is further discussed in Section 6.23.3.5.3.(i).

$$[\{Os(\mu\text{-}SnMe_2)(CO)_4\}_2] + Me_3NO \xrightarrow[\substack{\sim 10\%\\ 1\,h}]{CH_2Cl_2/MeCN,\ 25\,^\circ C} \underset{\substack{Yellow\\ \mathbf{101}}}{[Os_4\{\mu_3\text{-}\eta^3\text{-}O(SnMe_2)_2\}_2(CO)_{14}]} \tag{66}$$

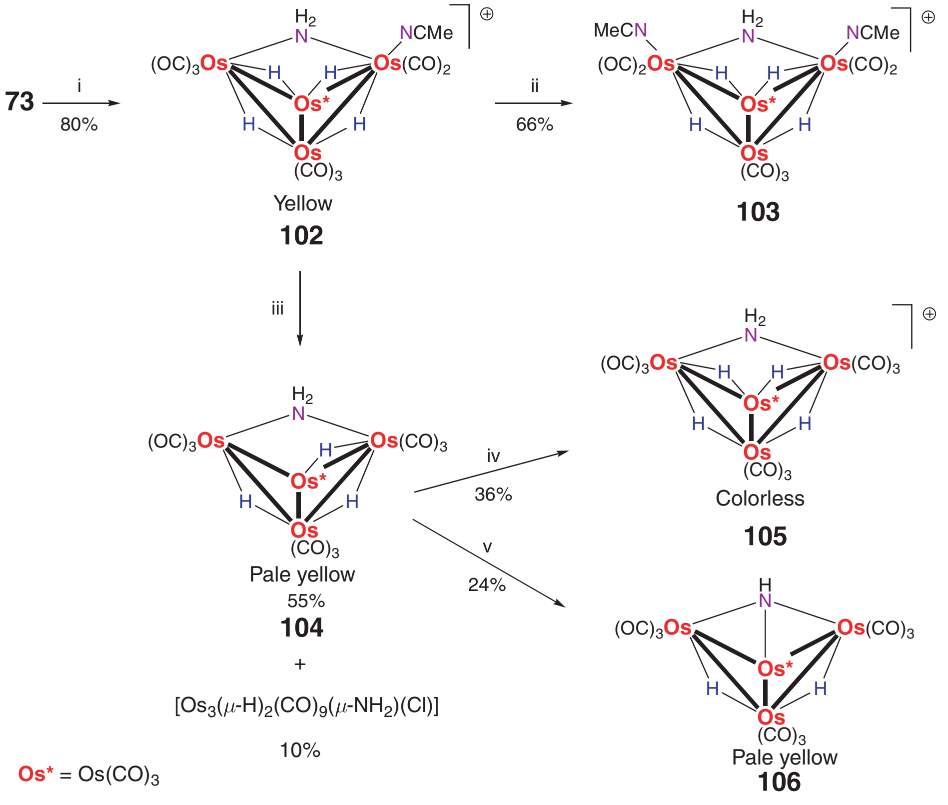


101

6.23.3.5.2 Derivatives with bridging group 15 ligands

6.23.3.5.2.(i) Derivatives with bridging N ligands

The cluster $[Os_4(\mu\text{-H})_4(CO)_{11}(\eta^1\text{-NH}_2OBu^t)]$ **73** has been used as a precursor for the synthesis of several tetra-osmium carbonyl clusters containing a bridging amido ligand.[67] The products include $[Os_4(\mu\text{-NH}_2)(\mu\text{-H})_4(CO)_{11}(NCMe)][BF_4]$ **102** (cation), $[Os_4(\mu\text{-NH}_2)(\mu\text{-H})_4(CO)_{10}(NCMe)_2][BF_4]$ **103**, (cation), $[Os_4(\mu\text{-NH}_2)(\mu\text{-H})_3(CO)_{12}]$ **104**, $[Os_4(\mu\text{-NH}_2)(\mu\text{-H})_4(CO)_{12}][CF_3SO_3]$ **105**, (cation), and $[Os_4(\mu_3\text{-NH})(\mu\text{-H})_2(CO)_{12}]$ **106**. Cluster **106** is the first example of an osmium nitrene (μ_3-NH) cluster. Scheme 13 gives details of each synthetic route to these clusters.[67] Compound **102** has a butterfly Os_4 framework with the amido ligand bridging the two wingtip osmium atoms. The hinge OsOs bond distance of 2.839(2) Å is the shortest in the Os_4 skeleton while the four hydrides bridge the remaining four hinge-to-wingtip OsOs bonds. The structure of cluster **103** is similar to that of **102** with a second carbonyl ligand replaced by the acetonitrile ligand (bound to the other wingtip osmium atom). The presence of the MeCN ligand helps stabilize the cationic metal cluster because of its good σ-donor and poor π-acceptor properties. Carbonylation of **102** replaces the labile acetonitrile group along with metal hydride elimination to give **104** (as the major product), which retains the amido-supported butterfly geometry. Deprotonation occurs preferentially at the metal hydride sites and not at the hydrogen atoms of the amido ligand. This is because the electron-rich amido ligand lowers the polarity of the NH bond such that the elimination of the NH proton becomes difficult. Protonation of **104** gives **105**, which is an analog of **102** and **103**, except it has a highly symmetric structure with a C_2 symmetry. It is noted that the metal–metal bond lengths of cationic clusters (such as **102**, **103**, and **105**) are longer than average due to the orbital contraction (from electron deficiency), which makes the orbital overlap less efficient. This lowers the metal–metal bond strength and hence gives longer bonds. The Os_4 butterfly arrangement of **106** contains a triply-bridging nitrene ligand (a four-electron donor) bridging one of the open triangular faces.[67] Selected bond lengths and dihedral angles of these clusters are listed in Table 14.



i, HBF_4, MeCN, 1 h; ii, Me_3NO, MeCN, 3 h; iii, CO purge $CHCl_3$, reflux, 10 h; iv, CF_3SO_3H, CH_2Cl_2, 3 h; v, toluene, reflux, 24 h

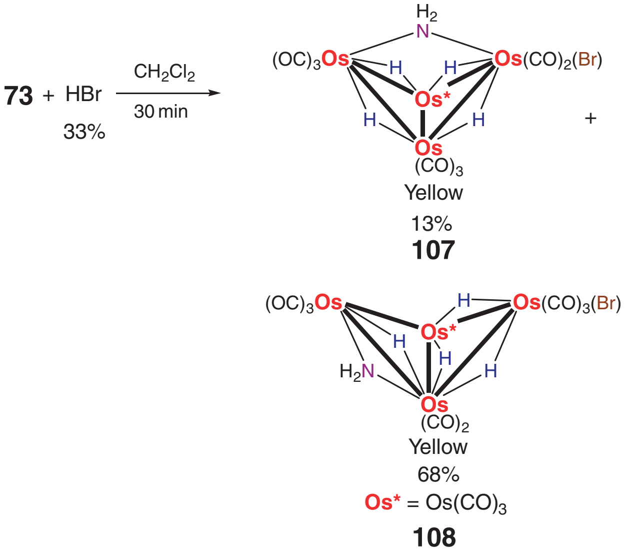
Scheme 13

Table 14 Selected bond lengths and butterfly dihedral angles for **102**–**109**

Cluster	*Peripheral OsOs* (Å)	*Hinge OsOs* (Å)	*OsN* (Å)	*Dihedral angle* (deg)
102	2.983(2)–3.041(2)	2.839(2)	2.08(3), 2.17(2)	95.5
103	3.000(1)–3.073(1)	2.818(1)	2.11(1), 2.13(1)	
104	2.837(1)–3.049(1)	2.812(1)	2.15(1), 2.15(2)	94.5
105	3.020(1)–3.036(1)	2.834(1)	2.11(2), 2.12(1)	83.7
106	2.762(1)–2.969(1)	2.856(2)	2.05(1),[a] 2.16(2)[b]	97.9
107	2.981(1)–3.070(1)	2.828(1)	2.13(2), 2.15(2)	83.2
108	2.811(1)–3.114(1)	2.941(1)	2.07(1), 2.14(1)	122.1
109	2.730(2)–2.982(2)		2.00(2), 2.21(2)	

[a] Hinge OsN bond.
[b] Wingtip OsN bond.

When hydrobromic acid (33%) is added to a solution of [$OS_4(\mu\text{-H})_4(CO)_{11}(\eta^1\text{-NH}_2OBu^t)$] **73**, geometric isomers of [$Os_4(\mu\text{-NH}_2)(\mu\text{-H})_4(CO)_{11}(Br)$] (**107** and **108**) are obtained (Equation (67)).[68]

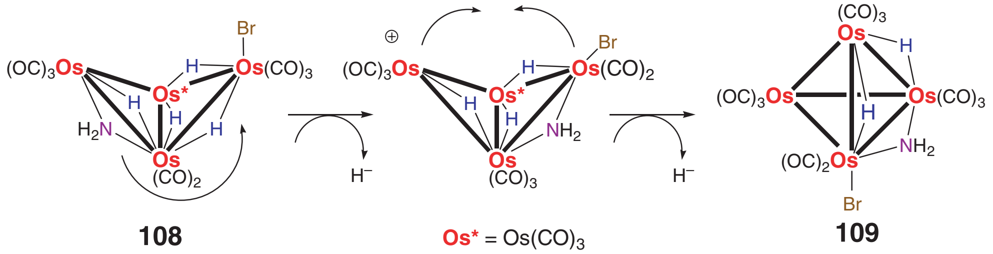


(67)

Compound **108** is one of the few examples of a 62 c.v.e. butterfly cluster with no supporting ligand between wingtip osmium atoms.[63,82,83,84,85] This is reflected by the exceptionally large dihedral angle of 122.1°. Also, the hinge OsOs bond is much longer (2.9407(7) Å) than the corresponding bond lengths in other related compounds (Table 14) due to the hydride ligand bridging along this vector. The OsOs bond doubly bridged by the hydride and amido ligands is the shortest (2.8109(8) Å) in length illustrating the shortening effect of the amido ligand. In the butterfly structure of **107**, the amido ligand bridges wingtip osmium atoms giving a relatively small dihedral angle (83.2°) comparable with those found in similar systems.[27,78,86,87,88] From ^1H NMR data, the two amido proton signals are at δ 3.06 and 2.59 in **108** while those of **107** are significantly shielded to δ 0.19 and −0.20, that is, due to an electron-rich environment.[68]

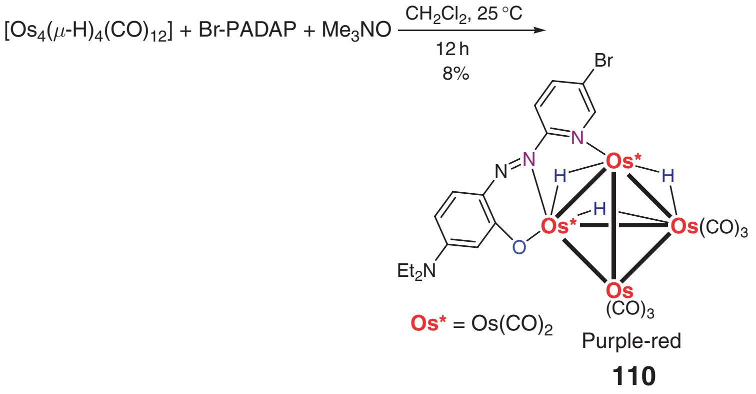
A dichloromethane solution of **108** and triphenylcarbenium tetrafluoroborate, [Ph_3C][BF_4], gives [$Os_4(\mu\text{-NH}_2)$-$(\mu\text{-H})_2(CO)_{11}(Br)$] **109** (Equation (68)) by elimination of two hydride ligands from the metal core.[68] This reaction was expected to yield a derivative with a μ_3- or μ_4-NH nitrene ligand, which acts as a four-electron donor in the electron-deficient tetraosmium metal core. The tetrahedral amido tetraosmium cluster **109**, however, resulted. In this case, the butterfly metal framework changes back to tetrahedral by forming a metal–metal bond instead of a nitrene cluster to eliminate the electron deficiency. The proposed mechanism is shown in Scheme 14.[68]

$$\mathbf{108} + [Ph_3C][BF_4] \xrightarrow[\text{5 h} \atop 30\%]{CH_2Cl_2} \underset{\text{green}}{\mathbf{109}} \qquad (68)$$



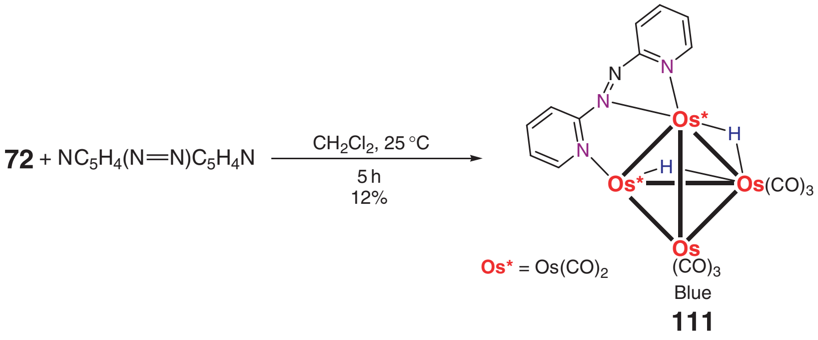
Scheme 14

The cluster $[Os_4\{\mu\text{-}\eta^3\text{-}Et_2NC_6H_3(O)(N{=}N)C_5NH_3Br\}(\mu\text{-}H)_3(CO)_{10}]$ **110** is obtained from the reaction between $[Os_4(\mu\text{-}H)_4(CO)_{12}]$, 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAP), and Me_3NO in CH_2Cl_2 (Equation (69)).[72] The azo ligand bridges one edge (OsOs = 2.7816(6) Å) of the Os_4 tetrahedron in **110** resulting in five- and six-membered metallacyclic rings (dihedral angle of 25.5° with respect to each other). The pyridyl and phenyl rings of the ligand are highly twisted with a dihedral angle of 60.3°. The ligand acts as a five-electron donor to give **110** a 60 c.v.e. count.



(69)

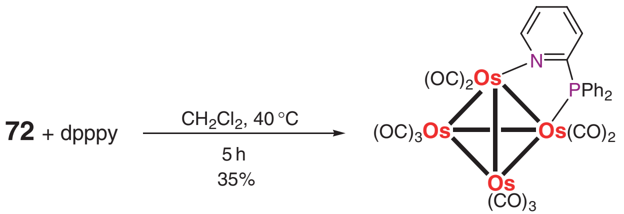
The reaction of $[Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2]$ **72** with 2,2′-azopyridine in CH_2Cl_2 gives $[Os_4\{\mu\text{-}\eta^3\text{-}NC_5H_4(N{=}N)C_5H_4N\}(\mu\text{-}H)_2(CO)_{10}]$ **111** (Equation (70)).[72] In this case, the azo ligand acts as a six-electron donor by bridging an OsOs edge (2.8145(8) Å) via three nitrogen atoms. The two pyridyl rings in this compound have a dihedral angle of 16.2°.[72]



(70)

6.23.3.5.2.(ii) Derivatives with bridging N ligands

Treatment of $[OS_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2]$ **72** with the nitrogen–phosphorus mixed donor ligand 2-(diphenylphosphino)pyridine (dpppy) in refluxing in CH_2Cl_2 under argon for 5 h gives $[Os_4(\mu\text{-}dpppy)(\mu\text{-}H)_4(CO)_{10})]$ **112** (Equation (71)).[69] A 2-(diphenylphosphino)pyridine-substituted triosmium cluster is known to undergo fluxional pyridine migrations between metal centers[89] but NMR spectroscopy does not give evidence of such behavior in **112**. This is likely due to stronger OsP and OsN bonds in **112** than in the triosmium case. Consistent with this view is that the OsP and OsN bonds are shorter (2.300(4) and 2.16(1) Å, respectively) than those in the triosmium case (2.380(4) and 2.22(1) Å, respectively).[69]



Orange

112

(bridging hydrides omitted)

(71)

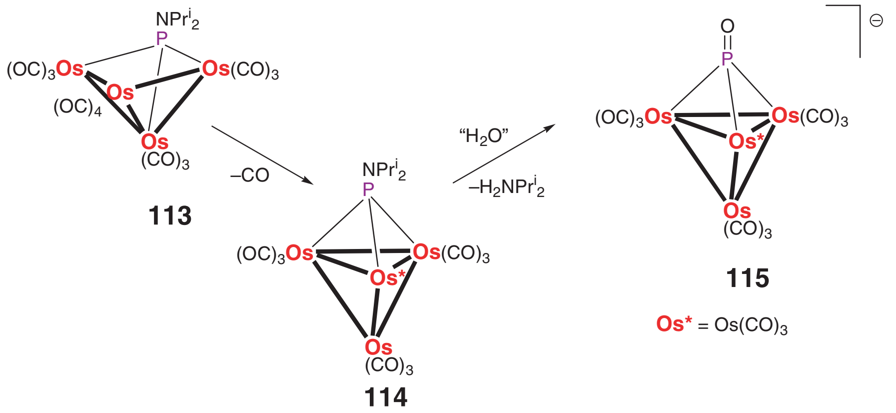
6.23.3.5.2.(iii) Derivatives with bridging N–P ligands

Addition of $Cl_2PNPr^i_2$ to a THF solution of $Na_2[Os_4(CO)_{13}]$ (Na_2 **71**; Equation (56)) affords $[Os_4(\mu_3\text{-}PNPr^i_2)(CO)_{13}]$ (**113**; Equation (72)).[27] Thermal decarbonylation of **113** generates $[Os_4(\mu_3\text{-}PNPr^i_2)(CO)_{12}]$ **114** (Equation (73)).[27]

$$\mathrm{Na_2}\,\mathbf{71} + \mathrm{Cl_2PNPr^i_2} \xrightarrow[\text{2 h, 33\%}]{\text{THF}} \underset{\mathbf{113}}{[\mathrm{Os_4(\mu_3\text{-}PNPr^i_2)(CO)_{13}}]} \tag{72}$$

$$\mathbf{113} \xrightarrow[\text{12 h, 65\%}]{\text{toluene, 111 °C}} \underset{\mathbf{114}}{[\mathrm{Os_4(\mu_3\text{-}PNPr^i_2)(CO)_{12}}]} \tag{73}$$

After the absorption of **114** onto silica gel, extraction with CH_2Cl_2 and MeCN leads to the recovery of the starting material **114** (55%) and $[H_2NPr^i_2][Os_4(\mu_3\text{-}PO)(CO)_{12}]$ ($[H_2NPr^i_2]$**115**) (34–38%) (Scheme 15). The source of the elements of H_2O required to cleave the PN bond in **114** is thought to be the basic and acidic sites on the surface of the silica gel. Possible mechanisms are reported in a later paper.[90] The metathesis of $[H_2NPr^i_2]$**115** in CH_2Cl_2 with $[Et_4N]Cl$ gives $[Et_4N]$**115** in quantitative yield.[27]



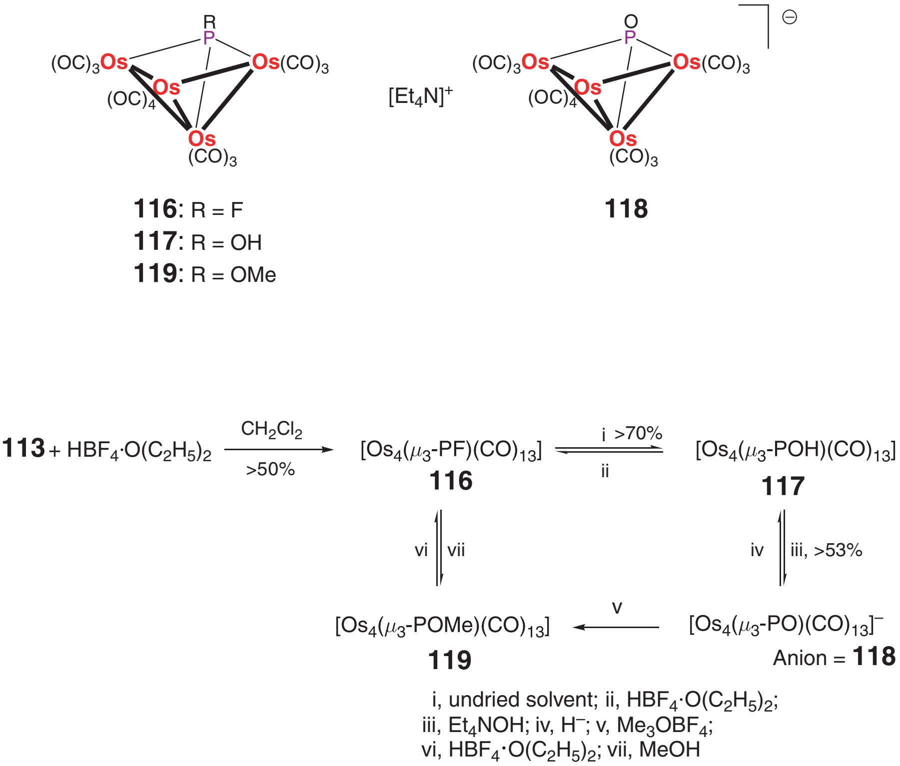
Scheme 15

Complex **113** contains a distorted *nido*-Os_4P square-based pyramid with the P atom occupying a basal position. It can also be viewed as an Os_4 butterfly skeleton with a triply-bridging $PNPr^i_2$ ligand (OsP = 2.337(3)–2.446(3) Å). The OsOs bond lengths are in the range of 2.793(1)–2.991(1) Å with the longest being the hinge OsOs bond. It is noted that one of the hinge osmium atoms has four terminal carbonyl ligands. This is uncommon for structures of this type, which usually have only three carbonyls bound to the metal atoms at the hinge positions.

Complex **114** has a *closo*-trigonal-bipyramidal structure with the phosphinidene ligand capping one face of the Os_4 tetrahedron. No X-ray crystallography data are available for **114**, but its structure is based on the similarity of the synthetic route and of its IR spectrum to that of the ruthenium analog, **27**.[27] Unlike the Ru analog, there is partial rigidity of the carbonyls in **114** as shown by ^{13}C NMR spectroscopy.

The phosphorus monoxide ligand symmetrically caps (OsP = 2.294(4)–2.321(3) Å) one face of the Os_4 tetrahedron in $[Et_4N]$**115** (with OsOs bond lengths between 2.811(1)–2.883(1) Å). The PO bond length of 1.48(1) Å is comparable with that in the free PO molecule (1.46–1.48 Å);[91,92] thus giving evidence of multiple bonding character of the PO ligand in the cluster. The $[Et_4N]$**115** compound was the first complex to be characterized with a PO unit.[27]

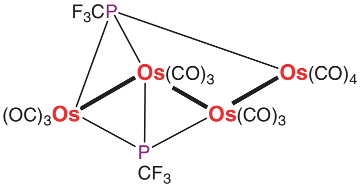
From the reaction of **113** with $HBF_4 \cdot O(C_2H_5)_2$ in CH_2Cl_2, the fluorophosphinidene complex $[Os_4(\mu_3\text{-PF})(CO)_{13}]$ **116** is obtained. On re-dissolution of **116** in undried solvents, the fluorine atom is replaced by an OH group giving the hydroxyphosphinidene complex $[Os_4(\mu_3\text{-POH})(CO)_{13}]$ **117**. Treatment of **117** with $[Et_4N][OH]$ produces the $[Et_4N]^+$ salt of $[Os_4(\mu_3\text{-PO})(CO)_{13}]^-$ **118**. The reaction of **118** with $[Me_3O]BF_4$ affords $[Os_4(\mu_3\text{-POMe})(CO)_{13}]$ **119**. Addition of MeOH to **116** also gives **119** (Scheme 16).[90] Note that three of the processes are reversible. Compounds **116** and **117** are the first examples of μ_3-PF and μ_3-POH clusters, respectively. The OH hydrogen atom of **117** was not found by X-ray analysis, but its presence is confirmed by the $[OsOH]^+$ ion in the mass spectrum. Compound **118** is a 62 c.v.e open *nido*-PO cluster where the μ_3-PO ligand occupies a basal vertex in the Os_4P square pyramid. Compound **117** has a similar structure to that of **118** with the PO bond being 0.11 Å longer than in the anion. The frameworks of **113** and **116–118** are believed to be similar based on the similarity of their IR spectra in the carbonyl stretching region. The infrared data also suggest substantial π-acceptor capability of the μ_3-PO ligands.[90]



Scheme 16

The cluster $[Os_4\{\mu_3\text{-}P(CF_3)\}_2(CO)_{13}]$ **120** is prepared by heating $[Os_3(CO)_{12}]$ with $\{P(CF_3)\}_4$ (Equation (74)).[23] It contains an open chain of four osmium atoms with each PCF_3 ligand bridging three Os atoms (see below). The OsOs bond lengths vary over a small range (2.917–2.985 Å) whereas the OsP bonds show a larger variation (2.336(8)–2.437(9) Å).[23]

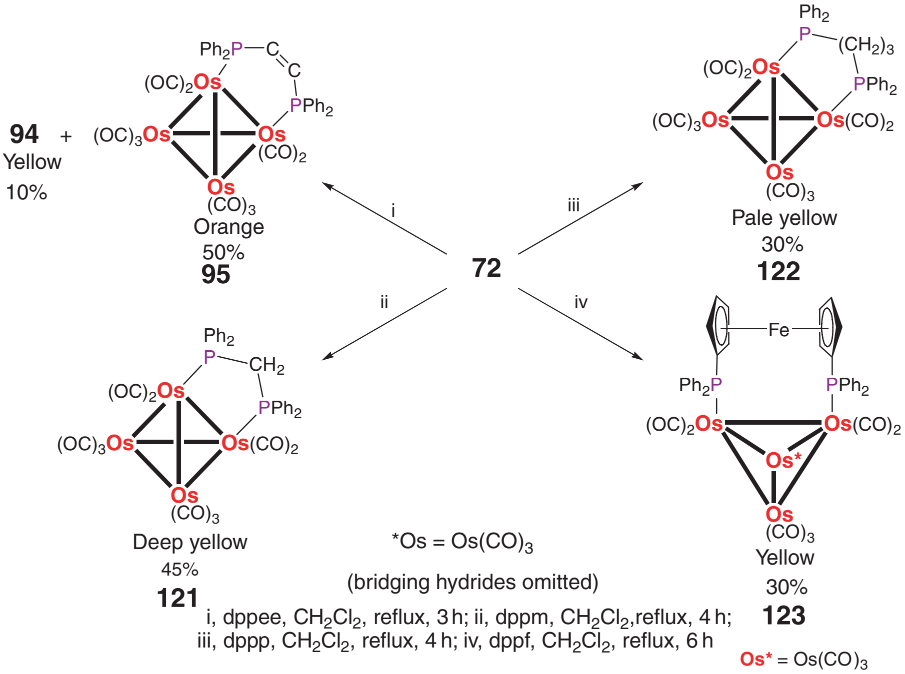
$$[Os_3(CO)_{12}] + (F_3CP)_4 \xrightarrow[\substack{16\,h \\ 10\%}]{209\,°C} \underset{\substack{\text{yellow} \\ \mathbf{120}}}{[Os_4(\mu_3\text{-}PCF_3)_2(CO)_{13}]} \qquad (74)$$



120

When $[Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2]$ **72** reacts with the bidentate phosphorus ligands, *cis*-1,2-bis(diphenylphosphino)ethylene ($Ph_2PCH{=}CHPPh_2$, dppee), bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$, dppm), 1,3-bis(diphenylphosphino)propane ($Ph_2P(CH_2)_3PPh_2$, dppp), and 1,1′-bis(diphenylphosphino)ferrocene ($(Ph_2PC_5H_4)_2Fe$, dppf), to form compounds **94** and **95** (see Equation (60)), $[Os_4(\mu\text{-dppm})(\mu\text{-}H)_4(CO)_{10}]$ **121**, $[Os_4(\mu\text{-dppp})(\mu\text{-}H)_4(CO)_{10}]$ **122**, and $[Os_4(\mu\text{-dppf})(\mu\text{-}H)_4(CO)_{10}]$ **123**, respectively (Scheme 17).[66]

Clusters **121–123** each have a distorted Os_4 tetrahedral skeleton. The range of lengths of the six OsOs bonds and two OsP bonds for each compound are listed in Table 13. The six-membered $Os_2P_2C_2$ ring in **95** has a twisted boat conformation. The five-membered Os_2P_2C ring in **121** and the seven-membered $Os_2P_2C_3$ ring in **122** are both twisted no doubt due to the large torsional strain in the ring. The ^1H NMR spectroscopic data of **121** and **122** indicate the hydrides are fluxional at ambient temperature. The positions of the bridging hydride ligands in **94,95,121–123** were not determined directly; they are assigned, as usual, to the four elongated OsOs bonds of the Os_4 tetrahedron.[66]



*Os = Os(CO)3

(bridging hydrides omitted)

i, dppee, CH_2Cl_2, reflux, 3 h; ii, dppm, CH_2Cl_2,reflux, 4 h; iii, dppp, CH_2Cl_2, reflux, 4 h; iv, dppf, CH_2Cl_2, reflux, 6 h

Os* = $Os(CO)_3$

Scheme 17

Heating $[\mathrm{Os_3}(\mu\text{-H})\{\mu\text{-}\mathrm{Ph_2PCH_2P(Ph)C_6H_4}\}(\mathrm{CO})_8]$ with elemental selenium in refluxing toluene provides two triosmium clusters as well as the tetraosmium cluster $[\mathrm{Os_4}(\mu_3\text{-Se})_4(\mu\text{-}\mathrm{Ph_2PCH_2PPh_2})(\mathrm{CO})_{10}]$ **124** (Equation (75)).[93] One of the triosmium products ($[\mathrm{Os_3}(\mu_3\text{-Se})_2(\mu\text{-}\mathrm{Ph_2PCH_2PPh_2})(\mathrm{CO})_7]$) and **124** are produced in slightly higher yields when $[\mathrm{Os_3(CO)_{10}(NCMe)_2}]$ and $\mathrm{Ph_2P(Se)CH_2P(Se)Ph_2}$ are heated in a refluxing solution of benzene (Equation (76)).[93] See also Section 6.23.3.5.3(iii)

$$[\mathrm{Os_3}(\mu\text{-H})(\mu\text{-}\mathrm{Ph_2PCH_2P(Ph)C_6H_4})(\mathrm{CO})_8] + \mathrm{Se_8} \xrightarrow[\text{1.5 h}]{\text{toluene, 111 °C}}$$

$$\underset{20\%}{[\mathrm{Os_3}(\mu_3\text{-Se})_2(\mu\text{-}\mathrm{Ph_2PCH_2PPh_2})(\mathrm{CO})_7]} +$$

$$\underset{47\%}{[\mathrm{Os_3}(\mu_3\text{-Se})(\mu\text{-}\mathrm{Ph_2PCH_2PPh_2})(\mu_3\text{-CO})(\mathrm{CO})_7]} + \tag{75}$$

$$[\mathrm{Os_4}(\mu_3\text{-Se})_4(\mu\text{-}\mathrm{Ph_2PCH_2PPh_2})(\mathrm{CO})_{10}]$$

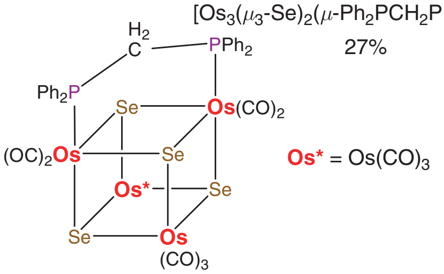
Orange yellow

5%

124

$$[\mathrm{Os_3(CO)_{10}(NCMe)_2}] + (\mathrm{Ph_2P(Se)CH_2P(Se)Ph_2} \xrightarrow[\text{2 h}]{\text{benzene, 80 °C}}$$

$$\underset{27\%}{[\mathrm{Os_3}(\mu_3\text{-Se})_2(\mu\text{-}\mathrm{Ph_2PCH_2PPh_2})(\mathrm{CO})_7]} + \underset{7\%}{\mathbf{124}} \tag{76}$$



124

6.23.3.5.3 Derivatives with bridging group 16 ligands

6.23.3.5.3.(i) Derivatives with bridging O ligands

The synthesis of $[\mathrm{Os_4}\{\mu_3\text{-}\eta^3\text{-O(SnMe_2)_2}\}_2(\mathrm{CO})_{14}]$ **101** was mentioned in Section 6.23.3.5.1.(ii) (Equation (66)). Cluster **101** has a crystallographic twofold axis that passes through the center of the $\mathrm{Os_2Sn_2O_2}$ ring. There are two non-carbonyl oxygen atoms having a planar μ_3-coordination mode. The central six-membered $\mathrm{Os_2Sn_2O_2}$ ring shares common OsO edges with two outer four-membered $\mathrm{Os_2SnO}$ rings. The oxygen atom binds to one osmium atom (OsO = 2.158(7) Å) and two tin atoms (SnO = 2.034(8) and 2.051(7) Å). The outer rings are planar while the central ring has a boat conformation. The OsOs bond distance (in the outer ring) of 2.9702(8) Å is shorter than in **100**.[81]

6.23.3.5.3.(ii) Derivatives with bridging S ligands

The original synthesis of $[\mathrm{OS_4}(\mu_3\text{-S})_2(\mathrm{CO})_{12}]$ **125** mentioned in COMC (1995) provides the cluster in less than 2% yield. A new method with slightly improved yields involves UV–VIS irradiation of $[\mathrm{Os_3}(\mu\text{-}\mathrm{SCH_2CH{=}CHCH_2S})(\mathrm{CO})_{10}]$ that results in the cleavage of two CS bonds and the elimination of butadiene (Equation (77)). The same products are produced thermally at 100 °C but with much lower yields.[94]

$$[\mathrm{Os_3}(\mu\text{-}\mathrm{SCH_2CH{=}CHCH_2S})(\mathrm{CO})_{10}] \xrightarrow{h\nu} \underset{56\%}{[\mathrm{Os_3}(\mu_3\text{-S})_2(\mathrm{CO})_9]} + \underset{\substack{5\% \\ \mathbf{125}}}{[\mathrm{Os_4}(\mu_3\text{-S})_2(\mathrm{CO})_{12}]} \tag{77}$$

6.23.3.5.3.(iii) Derivatives with bridging Se ligands

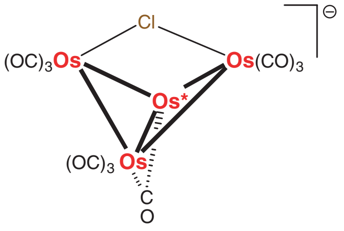
The structural assignment of $[Os_4(\mu_3\text{-}Se)_4(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{10}]$ **124** is based primarily on IR spectroscopic data due to the lack of X-ray quality crystals. The IR spectrum has ν(CO) frequencies similar to the ruthenium analog, **59**, of known structure.[52] A singlet at δ −7.4 in the $^{31}P\{^1H\}$ NMR spectrum indicates equivalent P nuclei. The proposed structure of **124** is a cubane-like cage of alternating Os and Se atoms with the $Ph_2PCH_2PPh_2$ ligand bridging two osmium atoms.[93]

6.23.3.5.5.(iv) Derivatives with bridging Te ligands

see compound **217** in Section 6.23.5.4.

6.23.3.5.4 Derivatives with bridging group 17 ligands

The anions $[Os_4(\mu\text{-}X)(\mu\text{-}CO)(CO)_{12}]^-$ (X = Cl **126**, Br, I), previously mentioned (Section 6.23.3.2.1), are obtained as the $[(Ph_3P)_2N]^+$, $[Et_4N]^+$, and $[Bu_4N]^+$ salts from reactions of $[Os_3(CO)_{12}]$ with the appropriate halide salts, in approximately 50% yield in each case.[65] Compound **126** has a butterfly arrangement of four osmium atoms with the Cl ligand bridging the two wingtip osmium atoms (OsClOs angle of 92.1°). The OsOs bond lengths are in the range of 2.811(2)–2.827(1) Å, while the two OsCl bonds have lengths of 2.481(6) and 2.490(4) Å. A carbonyl ligand bridges the two hinge osmium atoms.[65]



$[NR]^+$ (R = $(Ph_3P)_2$, Et_4, $Bu^t{}_4$)

Os* = $Os(CO)_3$

126

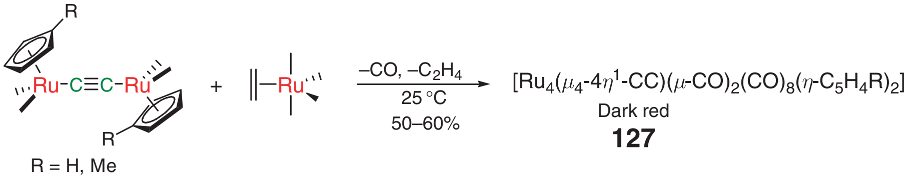
6.23.4 Ruthenium Compounds with Hydrocarbon Ligands

6.23.4.1 Derivatives with η^2-C_2 Ligands

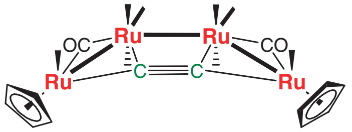
6.23.4.1.1 Derivatives with open Ru_4 clusters

Theoretical aspects of metal carbonyl clusters with exposed dicarbon entities including $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}]$ have been discussed.[95]

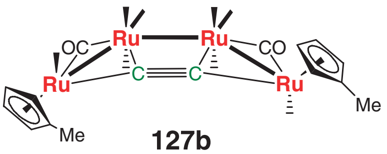
Reactions of $[\{Ru(\eta\text{-}C_5H_4R)(CO)_2\}_2(\mu_4\text{-}CC)]$ (R = H, Me) with $[Ru(CO)_4(C_2H_4)]$ at room temperature afford $[Ru_4(\mu_4\text{-}4\eta^1\text{-}CC)(\mu\text{-}CO)_2(CO)_8(\eta\text{-}C_5H_4R)_2]$ (**127a**, R = H; **127b**, R=Me, in good yield (Equation (78)).[96] Each product contains a U-shaped chain of Ru atoms with the naked dicarbon ligand bridging all four metal atoms to give an Ru_4C_2 unit that is approximately planar. The central RuRu bond is much longer than the corresponding outer bonds: 3.0190(5) versus 2.7873(5), 2.7988(4) Å in **127a**, and 3.0423(3), 3.0366(4) versus 2.8023(4), 2.8030(4) and 2.8060(4), 2.7992(4) Å in the two independent molecules of **127b**. The RuC bonds that involve the outer Ru atoms are significantly shorter (range 2.015(3)–2.030(3) Å) than those to the inner metal atoms (range 2.207(3)–2.241(3) Å). The CC lengths of the μ_4-C_2 unit (1.258(5) Å in **127a**; 1.258(4), 1.252(4) Å in **127b**) indicate a bond order midway between a triple and double CC bond. These lengths are significantly shorter than the corresponding lengths in the μ_4-C_2R_2 units described below. The major signals in the $^{13}C\{^1H\}$ NMR spectrum of ^{13}CO-enriched **127a** in C_6D_6 are consistent with the solid-state structure with non-exchanging carbonyl ligands [singlets at δ 191.2, 194.5, 198.3, 205.3 (CO), and 240.3 (μ-CO)]. Minor signals in the carbonyl region were attributed to the *anti*-isomer. A singlet at δ 154.9 was assigned to the C_2 ligand.[96]



$$[Ru_4(\mu_4\text{-}4\eta^1\text{-}CC)(\mu\text{-}CO)_2(CO)_8(\eta\text{-}C_5H_4R)_2] \qquad (78)$$



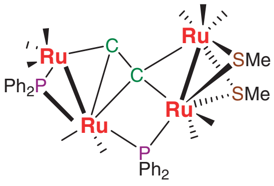
127a



127b

Treatment of $[Ru_5(\mu_5\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ with carbon monoxide (30 atm) at 120 °C gives $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **128** (Equation (79)) as one of the two isolated products.[97] There are only two RuRu bonds present and these have very different lengths: the outer RuRu bond bridged by a PPh_2 unit has a length of 2.796(1) Å whereas the other RuRu bond (bridged by SMe ligands) is of length 3.130(1) Å; the central RuRu vector is non-bonding at 3.571(1) Å. The dicarbon ligand bridges all four metal atoms (RuC = 2.027–2.499(6) Å); the CC bond is 1.239(9) Å. Extended Hückel calculations were used to rationalize the unusual bonding in **128**.[97]

$$[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}] + \underset{(30\ \text{atm})}{CO} \xrightarrow[\substack{2\ \text{h} \\ 19\%}]{\text{toluene, } 120\ ^\circ\text{C}}$$



128

$$[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$$

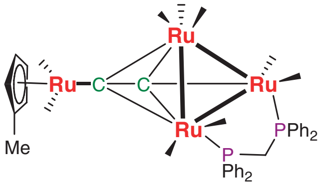
Yellow

128

(79)

Treatment of $[Ru_5(\mu_4\text{-}C_2)(\mu\text{-}PPh_2CH_2PPh_2)(\mu\text{-}CO)_2(CO)_7(\eta^5\text{-}C_5H_4Me)_2]$ with CO in toluene gives after chromatography $Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2)(\mu\text{-}PPh_2CH_2PPh_2)(CO)_9(\eta^5\text{-}C_5H_4Me)_2]$ **129**, (Equation (80)).[98] The RuRu bond lengths in the Ru_3 triangle are 2.7647(6), 2.7970(6) and 2.8158(6) Å. The C_2R ($R = Ru(\eta^5\text{-}C_5H_4Me)(CO)_2$) unit is bound to the Ru_3 triangle in the ubiquitous $\mu_3{:}\eta^1{:}\eta^2\eta^2{:}\eta^1{:}\eta^2{:}\eta^2$-mode (RuC = 2.194(5), 1.982(5), 2.217(5) Å (C1); 2.360(5), 2.382(5) Å (C2)). The RuC distance to the fourth Ru atom is 2.081(5) Å; the acetylide CC distance is 1.292(7) Å.[98]

$$[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}dppm)(\mu\text{-}CO)_2(CO)_7(\eta^5\text{-}C_5H_4Me)_2] \xrightarrow[\substack{14\ \text{h} \\ 9\%}]{\text{CO purge, toluene, } 25\ ^\circ\text{C}}$$



129

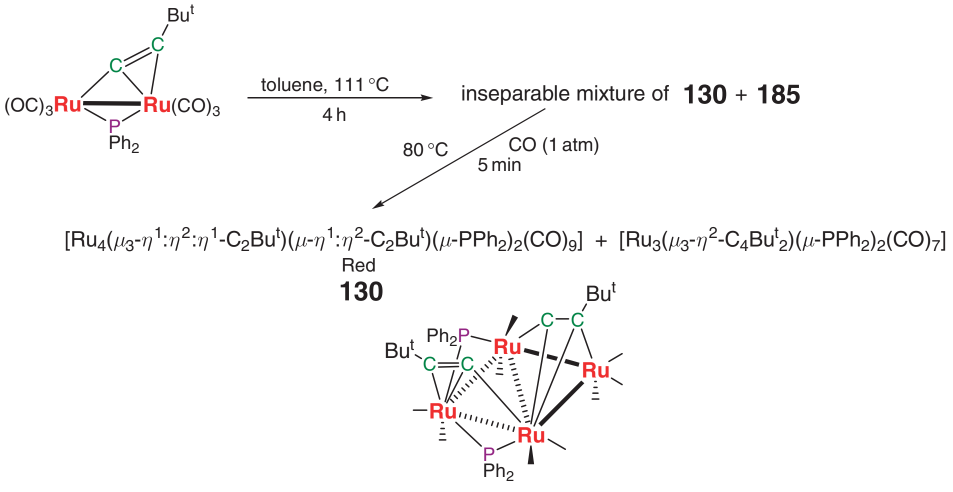
$$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_9(\eta^5\text{-}C_5H_4Me)]$$

Yellow

129

(80)

Thermolysis of $[Ru_2(\mu\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(CO)_6]$ in refluxing toluene affords a 1 : 1 mixture of $[Ru_4(\mu\text{-}C_2Bu^t)(\mu_3\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2(CO)_9]$ **130** and $[Ru_4(\mu\text{-}\eta^4\text{-}C_4Bu^t{}_2)(\mu\text{-}PPh_2)_2(CO)_8]$. (The later complex, **185**, is dicussed in section 6.23.4.5, Derivatives with η^4-C_4 ligands.) Treatment of the mixture with carbon monoxide in toluene at 80 °C caused conversion of the diyne complex to $[Ru_3(\mu_3\text{-}\eta^2\text{-}C_4Bu^t{}_2)\text{-}(\mu\text{-}PPh_2)_2(CO)_7]$ that could be separated from **130** by chromatography (Equation (81)).[99] The structure of **130** consists of a flattened butterfly with two RuRu bonds of normal length (2.782(1), 2.858(1) Å) and three elongated RuRu bonds (Ru(μ-PPh_2)Ru = 3.021(1), 3.097(1); hinge RuRu = 3.044(1) Å). This arrangement is similar to that found for the electron-rich 62 c.v.e. $[Ru_4(\mu\text{-}PPh_2)_2(CO)_{13}]$ clusters. Compound **130** contains a rare μ-η^2-C_2R grouping with an RuC σ-bond to the hinge metal atom (RuC = 2.052(4) Å) and a π-bond to the wingtip Ru atom (RuC = 2.293 (4), only one length quoted). The CC length in the acetylide ligand is remarkably short at 1.209(6) Å. The cluster also possesses the more common μ_3-η^2-C_2R unit with one RuC σ-bond (1.968(4) Å) and four RuC π-bonds (RuC = 2.222(4), 2.324(4) Å, hinge Ru; 2.205(4), 2.214(4) Å wingtip Ru). The CC length in the acetylide ligand is 1.296(6) Å.[99]



inseparable mixture of **130** + **185**

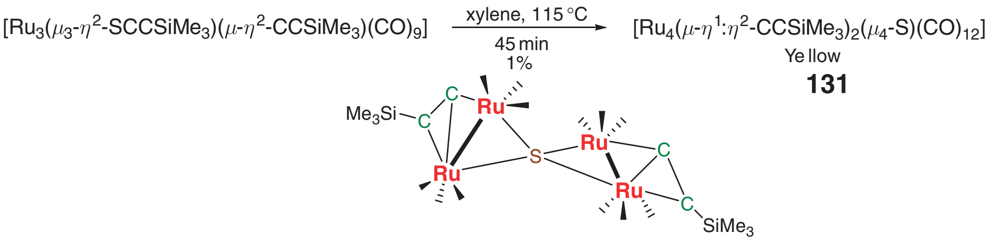
$[Ru_4(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_2Bu^t)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2(CO)_9]$ + $[Ru_3(\mu_3\text{-}\eta^2\text{-}C_4Bu^t{}_2)(\mu\text{-}PPh_2)_2(CO)_7]$ (81)

Red

130

130

Reaction of $[Ru_3(CO)_{12}]$ with $S(C{\equiv}CSiMe_3)_2$ yields $[Ru_3(\mu_3\text{-}\eta^2\text{-}SCCSiMe_3)(\mu_2\text{-}\eta^2\text{-}CCSiMe_3)(CO)_9]$. Thermolysis of this trinuclear derivative affords $[Ru_4(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}CCSiMe_3)_2(\mu_4\text{-}S)(CO)_{12}]$ **131** in low yield (Equation (82)).[100] The structure of **131** consists of two almost identical $Ru_2(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}CCSiMe_3)(CO)_6$ moieties linked by an S atom that has a flattened tetrahedral coordination to the four Ru atoms. If the S atom donates all six of its valence electrons to cluster bonding and the CCR units three electrons each, then the cluster has 68 c.v.e. which is consistent with **131** having two RuRu bonds. The lengths of these bonds are 2.714(1) and 2.719(1) Å. Heating **131** in xylene at 115 °C causes its ready conversion to $[Ru_4\{\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}C(SiMe_3)C(C_2SiMe_3)\}(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_9]$ **174**.



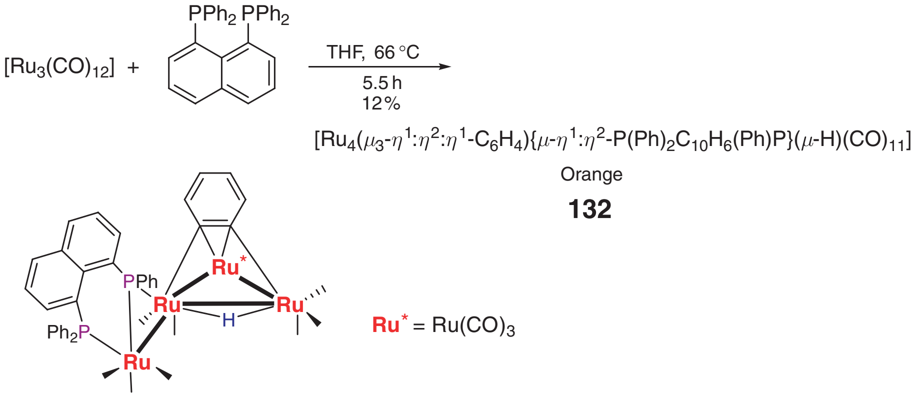
$[Ru_3(\mu_3\text{-}\eta^2\text{-}SCCSiMe_3)(\mu\text{-}\eta^2\text{-}CCSiMe_3)(CO)_9] \longrightarrow [Ru_4(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCSiMe_3)_2(\mu_4\text{-}S)(CO)_{12}]$ (82)

Yellow

131

131

The reaction between $[Ru_3(CO)_{12}]$ and 1,8-bis(diphenylphosphino)naphthalene in refluxing THF gives three products one of which is $[Ru_4(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_6H_4)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}PPh_2C_{10}H_6P(Ph)\}(\mu\text{-}H)(CO)_{11}]$ (**132**, Equation (83); see also Equation (165)).[101]



$[Ru_4(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_6H_4)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}P(Ph)_2C_{10}H_6(Ph)P\}(\mu\text{-}H)(CO)_{11}]$ (83)

Orange

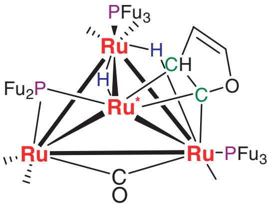
132

132

Compound **132** has a benzyne (C_6H_4) unit (μ-CC = 1.414(5) Å) bound in $\eta^1{:}\eta^2{:}\eta^1$ ($2\sigma/1\pi$) fashion to the triangular face of a spiked triangular Ru_4 framework. The spike RuRu bond is bridged by the phosphido–phosphine $PPhC_{10}H_6PPh_2$ ligand and has a length of 2.871(1) Å. The RuRu bond bridged by the hydride ligand has a length of 3.001(1) Å; the remaining RuRu distances are much shorter at 2.713(1) and 2.750(1) Å. As is typical, the RuC σ-bonds are shorter than the RuC π-bonds (2.088(3) and 2.108(3) vs. 2.245(3) and 2.297(3) Å).

Another compound isolated from the reaction of tri(2-furyl)phosphine (PFu_3) with $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ is $[Ru_4(\mu\text{-}\eta^1{:}\eta^2\text{-}C_4H_3O)(\mu\text{-}PFu_2)(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_7(PFu_3)_2]$ **133** (Equation (84); see also Equation (4)).[11] Although complexes where a furyl group is bound in a μ-η^2 vinyl-type bridge are known, this is the first case where it has been observed in a tetraruthenium cluster. The μ-CC length is 1.401(4) Å. Compound **133** has a tetrahedral Ru_4 skeleton with six RuRu bonds consistent with a 60 c.v.e. count. The lengths of these bonds show typical variation with the nature of the bridging groups and are in the range 2.726(1) (Ru(μ-CO)Ru)–3.011(1) Å (Ru(μ-H)Ru). The spectroscopic properties of **133** are consistent with the view that it has solution as in the solid state.

$$\underset{\mathbf{A}}{[Ru_4(\mu\text{-}H)_4(CO)_{12}]} + PFu_3 \xrightarrow[\substack{3\,h\\15\%}]{THF,\ 66\,^\circ C} \underset{\substack{\text{Deep red}\\ \mathbf{133}}}{[Ru_4(\mu\text{-}\eta^1{:}\eta^2\text{-}C_4H_3O)(\mu\text{-}PFu_2)(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_7(PFu_3)_2]} \qquad (84)$$

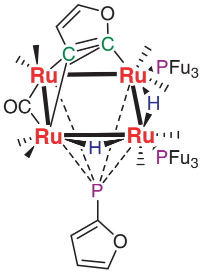


133

$Ru^* = Ru(CO)_2$

Also isolated from the reaction of PFu_3 with $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ is $[Ru_4(\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_4H_2O)(\mu_4\text{-}PFu)(\mu\text{-}H)_2\text{-}(\mu\text{-}CO)(CO)_8(PFu_3)_2]$ **134** (Equation (85); see also Equation (4)).[11]

$$\underset{\mathbf{A}}{[Ru_4(\mu\text{-}H)_4(CO)_{12}]} + PFu_3 \xrightarrow[\substack{3\,h\\8\%}]{THF,\ 66\,^\circ C} \underset{\substack{\text{Orange-red}\\ \mathbf{134}}}{[Ru_4(\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_4H_2O)(\mu_4\text{-}PFu)(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_8(PFu_3)_2]} \qquad (85)$$



134

The molecule contains a cyclic furyne ligand (μ-CC = 1.385(5) Å) bound to an Ru_4 base in an unprecedented μ-$\eta^1{:}\eta^1{:}\eta^2$-C(2)C(3) mode. The 64 c.v.e. count for **134** is consistent with the presence of four RuRu bonds. Once again, the RuRu bond lengths vary according to the bridging groups (range 2.740(1) (Ru(μ-CO)Ru)–3.073(1) Å (Ru-(μ-H)Ru)). The $^{31}P\{^1H\}$ NMR spectrum of **134** shows a poorly resolved resonance at δ 228.2 assigned to the μ_4-PFu ligand and two doublets at δ −15.0 ($^2J_{PP} = 116$ Hz) and δ −20.1 ($^2J_{PP} = 138$ Hz) assigned to the terminal PFu_3 ligands.[11]

6.23.4.1.2 Derivatives with closed Ru_4 clusters

6.23.4.1.2.(i) Derivatives with the *closo*-Ru_4C_2 unit

The *closo*-octahedral Ru_4C_2 unit found in $[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C_2RR^1)(CO)_{12}]$ (hereafter $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2RR^1)(CO)_{12}]$ compounds) is frequently encountered in tetraruthenium carbonyl cluster chemistry and several structures with this unit have been reported in the last 10 years (Table 15). An alternative view of the unit is that of an Ru_4 butterfly with the alkyne ligand capping the Ru atoms with the CC bond parallel to the hinge metal–metal bond (Figure 3). As discussed in Section 6.23.1, if these clusters are considered as butterfly structures, then the alkyne contributes only four electrons to the bonding for a total of 60 c.v.e. and is therefore two electrons short of the 62 c.v.e. required for a butterfly structure. On the other hand, if each CR unit is viewed as a vertex of an octahedron contributing five electrons to cluster bonding, then the cluster has the 66 c.v.e. and from PSEPT a *closo*-Ru_4C_2 octahedron is predicted as observed.

Structural parameters for various $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2RR^1)(CO)_{12}]$ and related clusters are collected in Tables 15 and 16. From Table 15, it can be seen that the peripheral RuRu bonds range from 2.671(3)–2.780(1) Å and are considerably shorter than those in more open Ru_4 clusters. The hinge bond is slightly longer (range 2.782(3)–2.880 Å). The RuC distances to the alkyne are displayed in Table 16. The RuC bonds to the hinge metal atoms may be viewed as σ-bonds and are in the range 2.073(5)–2.194(9) Å. The bonds of the alkyne to the wingtip metal atoms may be considered as π-bonds and are usually somewhat longer than the σ-bonds in a given cluster. The RuC bond lengths of the π-bonds are in the range 2.129(3)–2.26(1) Å. The CC bond lengths of the alkynes in this class of for clusters fall, with one exception, in the narrow range of 1.43–1.49 Å. The exception is the length of 1.55 Å reported

Table 15 RuRu bond lengths in $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2RR^1)(CO)_{12}]$ and related clusters

Compound	*Peripheral RuRu* (Å)	*Hinge RuRu* (Å)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)(CO)_{12}]$ **135**	2.725(3), 2.769(3)[a]	2.795(1)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Me_2)(CO)_{12}]$[b] **136**	2.710, 2.728[a]	2.880
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H(Ph)\}(CO)_{12}]$ **137** (A)	2.713(1), 2.724(1), 2.728(1), 2.762(1)	2.837(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H(Ph)\}(CO)_{12}]$ **137** (B)	2.710(1), 2.715(1), 2.715(1), 2.760(1), 2.724(1), 2.730(1), 2.746(1), 2.758(1)[c]	2.837(1), 2.826(1)[c]
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph_2)(CO)_{12}]$[d] **138**	2.71(1), 2.71(1), 2.74(1), 2.74(1)	2.85(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph(C_2Ph)\}(CO)_{12}]$ **139**	2.700(1), 2.704(1), 2.741(1), 2.765(1)	2.811(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph(C_2Ph)\}(\mu\text{-}PPh_2CH_2PPh_2)(CO)_{10}]$[117]	2.706(2), 2.712(2), 2.743(2), 2.747(2)	2.863(3)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}\ (CO)_{12}]$ **140** (A)	2.722(1), 2.723(1), 2.757(1), 2.764(1)	2.835(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}\ (CO)_{12}]$ **140** (B)	2.718(1), 2.720(1), 2.749(1), 2.758(1)	2.835(1)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_{12}]$ **141**	2.721(2), 2.725(2), 2.727(2), 2.743(2)	2.849(3)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_8H_{10})(CO)_{12}]$ **188**	2.698(1), 2.715(1), 2.737(1), 2.753(1)	2.808(1)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_{12}(\eta^6\text{-}C_{16}H_{16})]$ **142**	2.635(2), 2.636(2), 2.712(2), 2.729(2)	2.844(2)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_{14}H_8)(CO)_{12}]$ **144**	2.706(1), 2.719(1), 2.734(1), 2.751(1)	2.865(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2[CH(O)][\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\}(CO)_{12}]$ **145**	2.709(3), 2.717(3), 2.741(3), 2.766(3)	2.850(3)
$[\{Ru_4(CO)_{12}\}\{CO_2(CO)_6\}(\mu_4\text{-}2\eta^1{:}2\eta^2;\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC_6SiMe_3)]$ **146**	2.704(1), 2.732(1), 2.747(1), 2.780(1)	2.815(1)
$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^4\text{-}C_7H_6)](CO)_{11}]$ **147**	2.734(1), 2.755(1) (α-plane)	2.851(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CPhC_2(CH_2)_2(\eta\text{-}C_6H_5)\}(CO)_9]$ **148**	2.691(3), 2.718(3), 2.736(3), 2.739(3), 2.671(3), 2.726(3), 2.729(3), 2.746(3)[c]	2.782(3), 2.787(3)[c]
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CHCCH_2CH_2\text{-}(PMe_3)\}(CO)_{10}(PMe_3)]$ **178**	2.743(7), 2.757(7), 2.779(7), 2.798(7)	2.790(7)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)(CO)_9(\eta^6\text{-}C_6H_5Me)]$ **149**	2.7276(4), 2.7379(4), 2.7509(3), 2.7574(4);[e] 2.7221(7), 2.7480(5), 2.7617(6), 2.7558(5)[f]	2.7961(4)[e], 2.8082(7)[f]
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_9(\eta\text{-}C_6H_6)]$ (hinge isomer) **150a**	2.6476 (4), 2.6579(5), 2.6940(8), 2.7057(8)	2.8105(8)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_9(\eta\text{-}C_6H_6)]$ (wingtip isomer) **150b**	2.707(2), 2.722(2), 2.728(2), 2.733(2); 2.708(2), 2.729(2), 2.731(2), 2.739(2)[c]	2.812(2), 2.812(2)[c]

[a] Molecule has a crystallographic twofold axis.

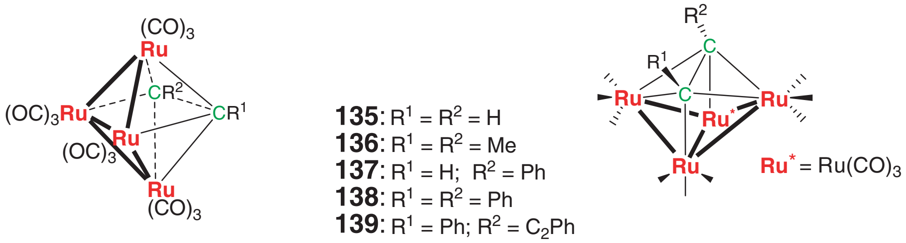
[b] Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Will, G. T.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 1190.

[c] Two independent molecules.

[d] Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1417.

[e] At −120 °C.

[f] At 27 °C.



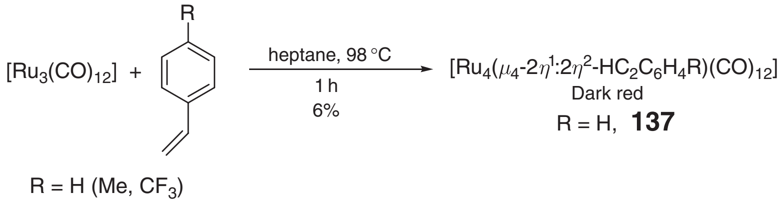
135: $R^1 = R^2 = H$
136: $R^1 = R^2 = Me$
137: $R^1 = H$; $R^2 = Ph$
138: $R^1 = R^2 = Ph$
139: $R^1 = Ph$; $R^2 = C_2Ph$

Figure 3

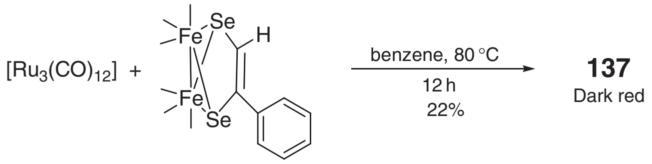
for one of the independent molecules of $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CPh(CH_2)_2(\eta\text{-}C_6H_5)\}(CO)_9]$. These lengths are between that of a typical CC double and single bond (1.34 and 1.54 Å, respectively).

The syntheses of $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)(CO)_{12}]$ **135**,[102] $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H(Ph)\}(CO)_{12}]$ **137**,[103,104] $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph(C_2Ph)\}(CO)_{12}]$ **139**,[105] $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}(CO)_{12}]$ **140**,[106,107] and $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8\}(CO)_{12}]$ **141**,[108] are given in Equations (86)–(93).

$$[Ru_3(CO)_{10}(NCMe)_2] + HCCH \xrightarrow[\substack{5\,\text{min}\\ 7\%}]{CH_2Cl_2,\ 25\,^\circ C} \underset{\substack{\text{Dark red}\\ \textbf{135}}}{[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)(CO)_{12}]} \tag{86}$$



(87)



(88)

$$[Ru_3(CO)_{10}(NCMe)_2] + Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph \xrightarrow[\substack{25\,^\circ C,1.5\,h\\ 2\%}]{CH_2Cl_2/MeCN} \underset{\substack{\text{Purple}\\ \textbf{139}}}{[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}PhC_2(C_2Ph)\}(CO)_{12}]} \tag{89}$$

$$[Ru(CO)_5] + Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3 \xrightarrow[\substack{20\,h\\ 36\%}]{\text{hexane, 0–25}\,^\circ C} \underset{\substack{\text{Red}\\ \textbf{140}}}{[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}(CO)_{12}]} \tag{90}$$

$$\underset{1:0.9\ \text{ratio}}{[Ru_3(CO)_{12}] + Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3} \xrightarrow[\substack{8\,h\\ 35\%}]{\text{hexane, 69}\,^\circ C} \underset{\substack{\text{Red}\\ \textbf{140}}}{[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}(CO)_{12}]} \tag{91}$$

Table 16 RuC and CC (alkyne) bond lengths $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2RR')(CO)_{12}]$ and related clusters

Compound	*Hinge RuC* (Å)	*Wingtip RuC* (Å)	*CC* (Å)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)(CO)_{12}]$ **135**	2.118(7)[a]	2.176(4), 2.188(7)	1.472(9)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Me_2)(CO)_{12}]$[b] **136**	2.16[a]	2.24, 2.27[a]	1.45
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H(Ph)\}(CO)_{12}]$ **137** (A)(molecule l)	2.125(8), 2.152(4)	2.188(4), 2.243(4), 2.178(4), 2.251(4)	1.451(6)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H(Ph)\}(CO)_{12}]$ **137** (B)[c]	2.126(8), 2.157(8); 2.113(7), 2.169(1)	2.156(8), 2.192(7); 2.236(7), 2.241(7); 2.169(7), 2.197(8), 2.225(7), 2.232(7)	1.46(1), 1.46(1)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph_2)(CO)_{12}]$ **138**[d]	2.16(1), 2.16(1)	2.24(1), 2.24(1), 2.25(1), 2.26(1)	1.46(2)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph(C_2Ph)]\}(CO)_{12}]$ **139**	2.139(7), 2.159(7)	2.208(8), 2.218(8), 2.231(8), 2.254(8)	1.46(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph(C_2Ph)\}(\mu\text{-}PPh_2CH_2PPh_2)(CO)_{10}]$[117]	2.15(1), 2.19(1)	2.23(1), 2.25(1), 2.29(1), 2.27(1)	1.46(2)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}(CO)_{12}]$ **140** (A)	2.133(5), 2.145(3)	2.215(3), 2.242(4), 2.206(3), 2.333(3)	1.47(5)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}(CO)_{12}]$ **140** (B)	2.12(1), 2.15(1)	2.21(1), 2.22(1), 2.23(1), 2.24(1)	1.45(1)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_{12}]$ **141**	2.123(5), 2.146(4)	2.234(5), 2.243(5), 2.244(5), 2.246(4)	1.455(7)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_8H_{10})\text{-}(CO)_{12}]$ **188**	2.17(1), 2.19(1)	2.24(1), 2.26(1), 2.23(1), 2.26(1)	1.45(2)
$[Ru_4(\mu_4\text{-}\eta^2\text{-}C_6H_8)(CO)_{12}(\eta^6\text{-}C_{16}H_{16})]$ **142**	2.07(2), 2.12(2)	2.22(1), 2.24(1), 2.25(2), 2.29(2)	1.44(2)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_{14}H_8)(CO)_{12}]$ **144**	2.151(5), 2.167(4)	2.244(4), 2.249(4), 2.238(4), 2.257(4)	1.464(6)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2[CH(O)][\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\}(CO)_{12}]$ **145**	2.09(2), 2.13(2)	2.20(2), 2.24(2), 2.19(2), 2.29(2)	1.45(3)
$[\{Ru_4(CO)_{12}\}\{CO_2(CO)_6\}(\mu\text{-}2\eta^1{:}2\eta^2;\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC_6SiMe)]$ **146**	2.139(8), 2.194(9)	2.215(8), 2.229(9), 2.228(8), 2.245(9)	1.47(1)
$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^4\text{-}C_7H_6)(CO)_{11}]$ **147**	2.096(5) (σ-plane)	2.181(8), 2.188(8)	1.49(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CPhC_2(CH_2)_2(\eta\text{-}C_6H_5)\}(CO)_9]$ **148**	2.13(3), 2.18(3)	2.20(2), 2.25(2), 2.09(2), 2.16(3)[e]	1.55(3), (1.49(4))[c]
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CHCCH_2(PMe_3)\}(CO)_{10}(PMe_3)]$ **178**	2.08(5), 2.14(4)	2.16(4), 2.17(5), 2.20(5) 2.23(4)[f]	1.48(7)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)(CO)_9(\eta^6\text{-}C_6H_5Me)]$ **149**	2.123(3), 2.129(3),[g] 2.126(4), 2.125(4)[h]	2.197(3), 2.208(3), 2.130(2), 2.135(3),[g] 2.194(3), 2.193(3), 2.129(3), 2.150(3),[h]	1.469(4),[h] 1.450(5)[i]
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_9(\eta\text{-}C_6H_6)]$ **150a**	2.073(5), 2.170(5)	2.223(5), 2.245(5), 2.251(5), 2.272(5)	1.43(1)
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_9(\eta\text{-}C_6H_6)]$ **150b**	2.11(2), 2.18(2), 2.15(2), 2.16(2)[c]	2.16(2), 2.18(2), 2.21(2), 2.26(2), 2.14(2), 2.20(2), 2.25(2), 2.29(2)[c]	1.45(3), 1.48(3)[c]

[a] Molecule has a crystallographic twofold axis.

[b] Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 1190.

[c] Two independent molecules.

[d] Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1417.

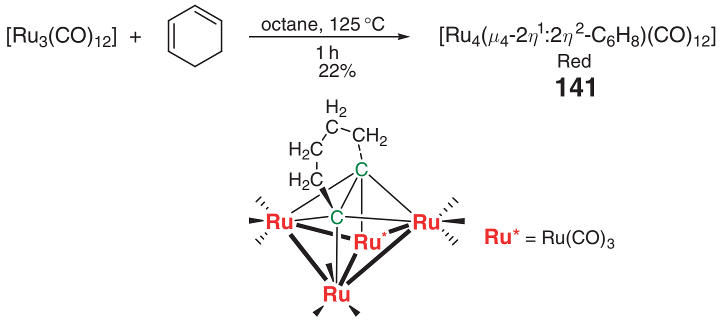
[e] Second molecule believed mislabeled.

[f] Has $Me_3P(\delta+)CHRu(\delta-)$ linkage, RuC = 2.07(5) Å.

[g] At −120 °C.

[h] At 27 °C.

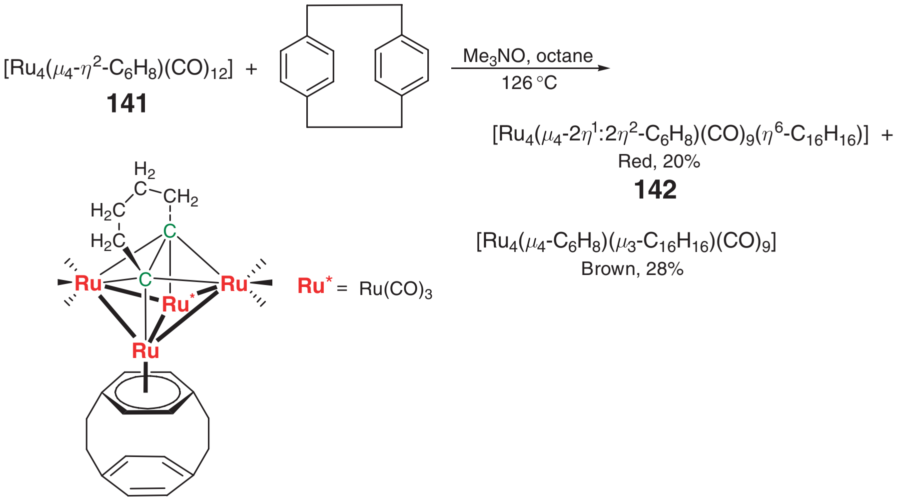
$$[Ru(CO)_5] + [Ru_3\{\mu_3\text{-}\eta^2\text{-}C_2(C_2SiMe_3)_2\}(CO)_{12}] \xrightarrow[\text{20 h}\atop 43\%]{\text{hexane, 0–25 °C}} \mathbf{140} \qquad (92)$$



141

(93)

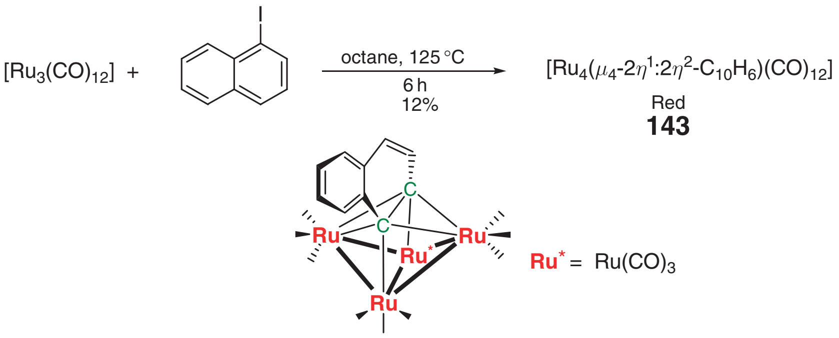
Heating **141** with [2.2]paracyclophane ($C_{16}H_{16}$) in octane gives two butterfly clusters, one of which is the simple substitution product $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_9(\eta^6\text{-}C_{16}H_{16})]$ **142** (Equation (94)).[109]



142

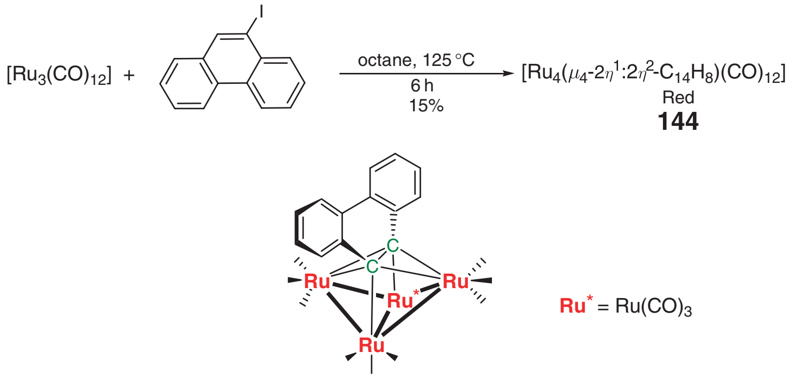
(94)

Reaction of $[Ru_3(CO)_{12}]$ with 1-iodonaphthalene in refluxing octane affords the 1,2-naphthyne derivative $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_{10}H_6)(CO)_{12}]$ **143** (Equation (95)).[110] The corresponding reaction with 9-iodophenanthrene affords the 9,10-phenanthryne analog **144** (Equation (96)). Structural details (Tables 15 and 16) were only reported for the latter cluster.[110]



143

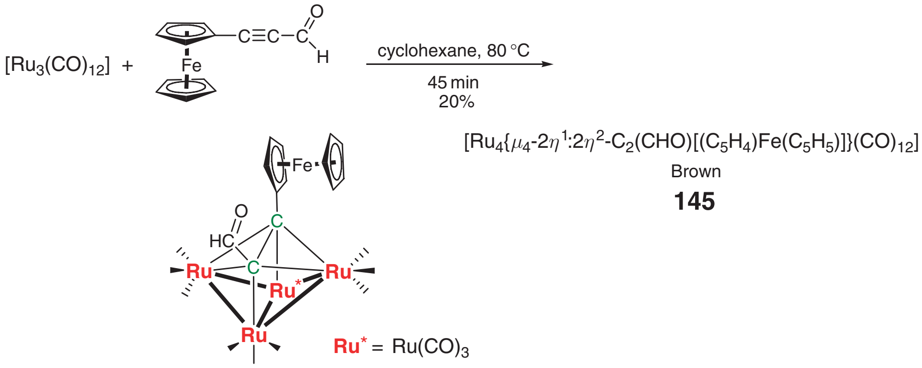
(95)



144

(96)

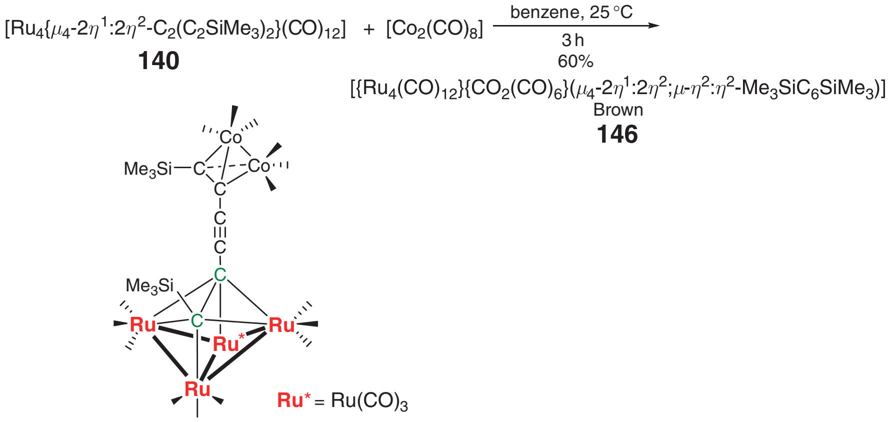
The novel ferrocenyl derivative $[Ru_4\{\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}C_2(CHO)Fc\}(CO)_{12}]$ **145** is prepared by heating $[Ru_3(CO)_{12}]$ with the ferrocenyl alkyne $FcC_2(CHO)$ (Equation (97)).[111] Pyrolysis of **145** in toluene yields $[Ru_3(CO)_{12}]$, dark violet $[Ru_5(\mu\text{-H})(\mu_5\text{-C})(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-CFc})(CO)_{13}]$, and the previously known $[Ru_6(\mu_6\text{-C})(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$.



145

(97)

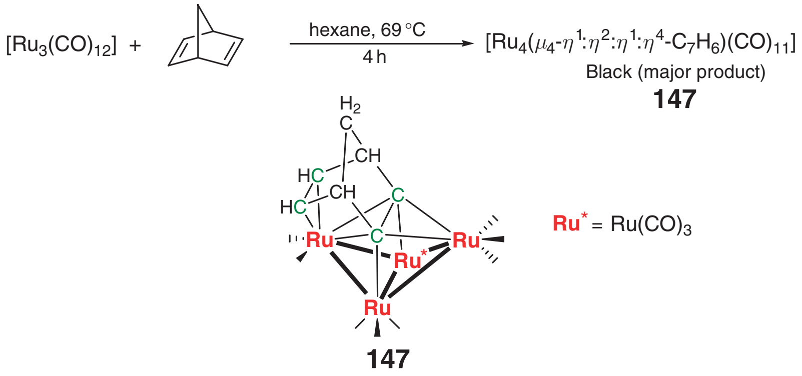
Compound **140** has two uncoordinated alkyne bonds. Stirring the compound with $[Co_2(CO)_8]$ readily affords $[\{Ru_4(CO)_{12}\}\{CO_2(CO)_6\}(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{;}\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_3SiC_6SiMe_3)]$ **146** (Equation (98)), where a $Co_2(CO)_6$ grouping is bound to a terminal alkyne unit in the typical fashion.[107] Note that in **146** the Ru_4 unit has slipped to an outer alkyne fragment from the inner alkyne unit in the starting material **140**. The uncoordinated CC triple bond in **146** has a length of 1.20(1) Å. From the ^{13}C NMR data of **146** it was concluded that there is a degree of conjugation between the metallocarbon moieties via the uncoordinated alkyne unit.[107]



146

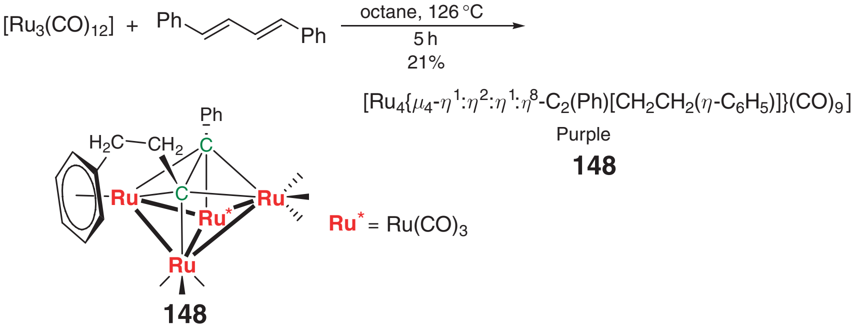
(98)

Heating $[Ru_3(CO)_{12}]$ with norbornadiene gives $[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^4\text{-}C_7H_6)(CO)_{11}]$ **147** (Equation (99)) as the major product.[112] In this complex, the alkyne unit of the bicyclic C_7H_6 ligand is bound to the Ru_4 butterfly in the usual fashion, with the double bond being coordinated to a wingtip Ru atom. The molecule may be viewed as a model for norbornadiene chemisorbed at a step site of a metal surface.



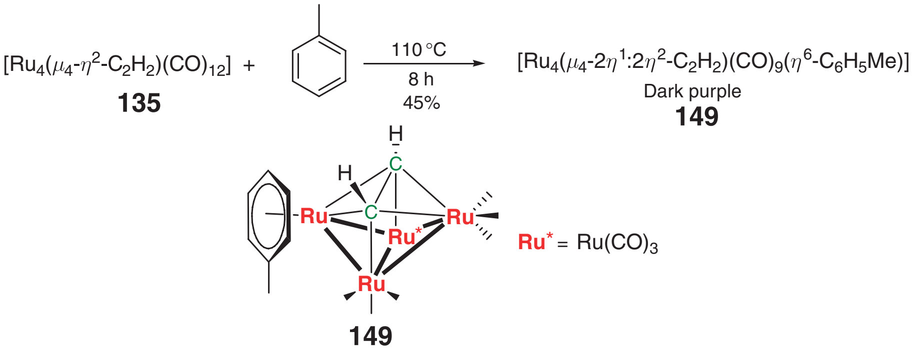
(99)

One product from the reaction of $[Ru_3(CO)_{12}]$ with 1,4-diphenylbutadiene is $[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^8\text{-}C_2Ph)(CH_2)_2(\eta\text{-}C_6H_5)\}(CO)_9]$ **148** (Equation (100)).[113] Note there has been isomerization of the diene to alkyne during the formation of the product and one of the phenyl rings is now bound in an η^6-mode to a wingtip Ru atom.



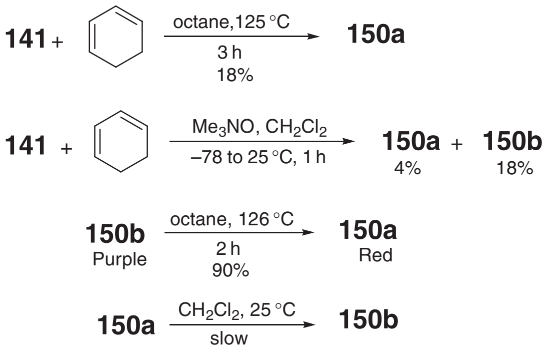
(100)

The thermal reaction between $[Ru_4(\mu_4\text{-}\eta^2\text{-}C_2H_2)(CO)_{12}]$ **135** and toluene produces $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)(CO)_9(\eta^6\text{-}C_6H_5Me)]$ **149** (Equation (101)).[114] The structure of **149** was determined at −120 and 27 °C. The structure at room temperature has a disordered component (9%). The nature of the disorder suggests the first stage of a putative migration of the arene from a wingtip to a hinge atom (see below).

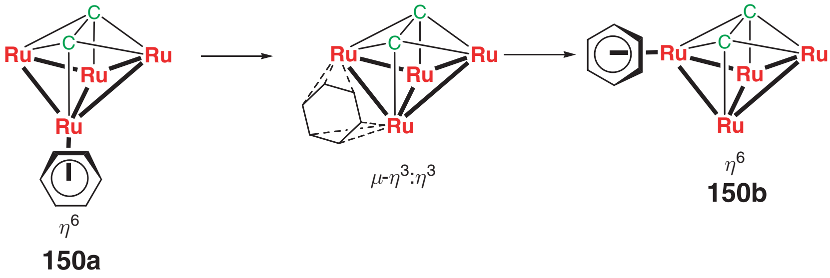


(101)

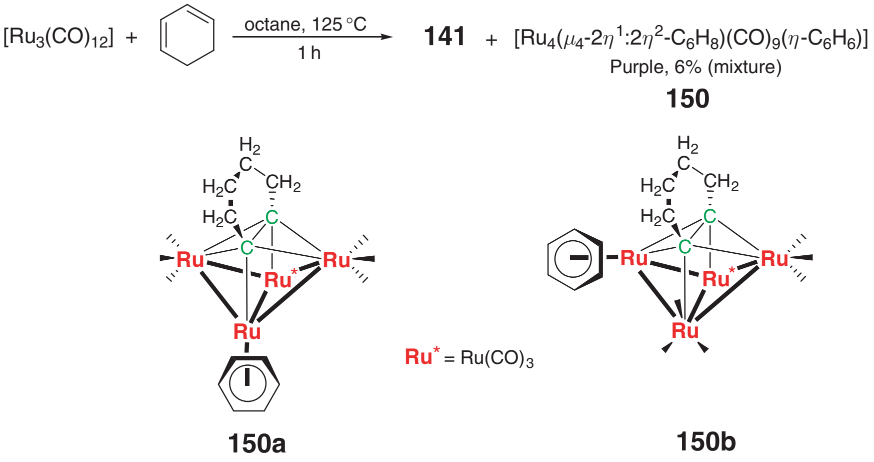
Besides **141**, $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_8)(CO)_9(\eta\text{-}C_6H_6)]$ (**150a** and **150b** as a mixture of wingtip and hinge isomers) is produced when $[Ru_3(CO)_{12}]$ is heated in refluxing cyclohexa-1,3-diene (Equation (102)).[108] The transformations depicted in Scheme 18 were established for the system and allowed pure samples of both isomers to be obtained and their structures determined (Tables 15 and 16). For the isomerization of **150a** to **150b** at room temperature, a ring slippage mechanism that involves a $\mu\text{-}\eta^3{:}\eta^3$ intermediate was suggested (Scheme 19).



Scheme 18



Scheme 19

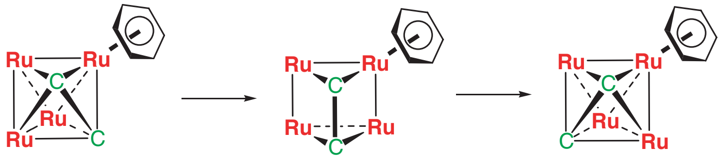


(102)

For the high-temperature isomerization in the reverse direction, a polyhedral rearrangement that involves a trigonal prismatic intermediate was put forward (Scheme 20).[108]

6.23.4.2 Derivatives with two η^2-C_2 Ligands

A second class of clusters with μ_4-alkyne units is $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2R_2)_2(\mu\text{-}CO)_x(CO)_{11-x}]$ ($x = 1$ or 2) compounds that have a μ_4-alkyne bound on either side of an Ru_4 unit that is best described as a tetrahedrally distorted square with four RuRu bonds. The Ru_4C_4 frame is a triangulated dodecahedron (Figure 4) that is consistent with nine skeletal electron



150b **150a**

Scheme 20

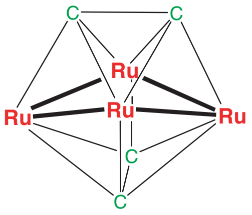
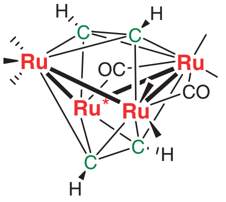


Figure 4

pairs (i.e., each CR unit donates five electrons to cluster bonding). As is typically found in Ru_4 carbonyl clusters, the RuRu bonds bridged by a CO ligand are usually (but not always) shorter than the corresponding unbridged bonds (Table 17). Each alkyne is bound to the Ru square via two σ- and two π-bonds as shown in Figure 4. As with the $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2R_2)(CO)_{12}]$ clusters, the RuC σ-bonds are usually slightly shorter than the π-bonds (Table 18).

The simplest member in this class, $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)_2(\mu\text{-}CO)_2(CO)_9]$ **151**, is isolated in very low yield from the reaction of $[Ru_3(CO)_{12}]$ with an excess of calcium carbide in refluxing THF (Equation (103)).[115] In the solid state, the molecule has a crystallographic plane of symmetry. Unlike other derivatives of this type, **151** has two, rather than one, bridging carbonyls.

$$\underset{1:10}{[Ru_3(CO)_{12}] + CaC_2} \xrightarrow[\substack{\text{overnight}\\ 1\%}]{\text{THF, 66 °C}} \underset{\substack{\text{Dark yellow}\\ \mathbf{151}}}{[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2H_2)_2(\mu\text{-}CO)_2(CO)_9]} \qquad (103)$$



151

Ru* = $Ru(CO)_2$

Table 17 RuRu bond lengths of $Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2RR^1)_2(\mu\text{-}CO)_x(CO)_{11-x}$ ($x = 1$ or 2) clusters

Compound	*Ru(μ-CO)Ru* (Å)	*Unbridged RuRu* (Å)
$[Ru_4(\mu_4\text{-}\eta^2\text{-}C_2H_2)_2(\mu\text{-}CO)_2(CO)_9]$ **151**	2.773(1)[a]	2.834(1)[a]
$[Ru_4(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)_2(\mu\text{-}CO)(CO)_{10}]$ **152**	2.7682(9)	2.7718(8), 2.8305(7), 2.837(7)
$[Ru_4\{\mu_4\text{-}\eta^2\text{-}C_2(Me)(CHCH_2)\}_2(\mu\text{-}CO)(CO)_{10}]$ **153**	2.7466(8)	2.8039(7), 2.8279(7), 2.8482(7)
$[Ru_4(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)\{\mu_4\text{-}\eta^2\text{-}C_2(C_2SiMe_3)_2\}(\mu\text{-}CO)(CO)_{10}]$ **155**	2.7567(6), 2.8339(6); 2.7448(5), 2.8123(7)[b]	2.8462(6), 2.8815(6); 2.7452(6), 2.8530(7)[b]
$[Ru_4\{\mu_4\text{-}\eta^2\text{-}C_2Ph(C_2Ph)\}\{\mu_4\text{-}\eta^2\text{-}C_2(SiMe_3)(C_2SiMe_3)\}\text{-}(\mu\text{-}PPh_2CH_2PPh_2)(\mu\text{-}CO)(CO)_8]$ **156**	2.717(8)	2.822(5), 2.873(7), 2.898(6)
$[Ru_4\{\mu_4\text{-}\eta^2\text{-}C_2(SiMe_3)(C_2SiMe_3)\}\{\mu_4\text{-}\eta^2\text{-}C_2(C_2SiMe_3)_2\}\text{-}(\mu\text{-}CO)(CO)_{10}]$	2.7583(2)	2.7948(2), 2.8386(2), 2.8521(3)

[a] Molecule has a crystallographic plane of symmetry.
[b] Two independent molecules.

Table 18 RuC and CC (alkyne) bond lengths in $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2RR^1)_2(\mu\text{-}CO)_x(CO)_{11-x}$ ($x = 1$ or 2)] clusters

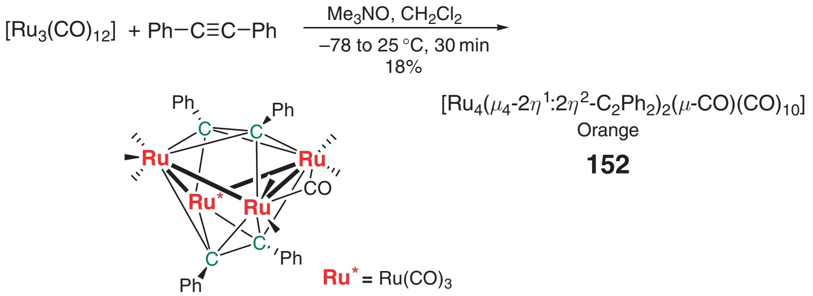
Compound	*σ RuC* (Å)	*π RuC* (Å)	*CC* (Å)
151	2.11(2), 2.14(1), 2.14(2)[a]	2.27(1), 2.28(1), 2.31(1), 2.31(1)[a]	1.37(2), 1.39(3)
152	2.181(4), 2.182(4), 2.185(4), 2.197(4)	2.303(4), 2.476(5) (Ru1); 2.285(4), 2.366(4) (Ru2); 2.311(4), 2.434(4) (Ru3); 2.371(4), 2.334(4) (Ru4)	1.404(6), 1.406(6)
153	2.150(6), 2.203(4), 2.198(6), 2.155(6)	2.274(6), 2.342(6) (Ru1); 2.303(6), 2.298(6) (Ru2); 2.314(6), 2.290(6) (Ru3); 2.361(6), 2.261(6) (Ru4)	1.409(9), 1.386(9)
155	2.161(5), 2.147(5), 2.150(5), 2.220(5); 2.122(6), 2.208(6), 2.170(6), 2.171(5)[b]	2.303(5), 2.419(5) (Ru1); 2.273(5), 2.290(5) (Ru2); 2.351(5), 2.397(5) (Ru3); 2.310(5), 2.328(5) (Ru4); 2.353(5), 2.350(6) (Ru1); 2.318(5), 2.267(5) (Ru2); 2.430(6), 2.344(6) (Ru3); 2.273(6), 2.358(6) (Ru4)	1.428(7), 1.422(7), 1.428(8), 1.509(8)[b]
156	2.23(5), 2.23(5), 2.16(5), 2.28(5)	2.23(5), 2.21(5) (Ru1); 2.36(5), 2.30(5) (Ru2); 2.34(5), 2.31(6) (Ru3); 2.27(5), 2.35(5) (Ru4)	[c]
154a	2.043(1), 2.188(2), 2.278(1), 2.223(2)	2.221(1), 2.263(1) (Ru1); 2.296(1), 2.296(1) (Ru2); 2.418(1), 2.329(1) (Ru3); 2.216(1), 2.412(1) (Ru4)	1.426(2), 1.416(2)

[a] Molecule has a crystallographic plane of symmetry.

[b] Two independent molecules.

[c] Not quoted: data poor.

The phenyl analog of **151**, that is, $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph_2)_2(\mu\text{-}CO)(CO)_{10}]$ **152**, has been prepared by the routes shown in Equations (104)–(106).[113,116]



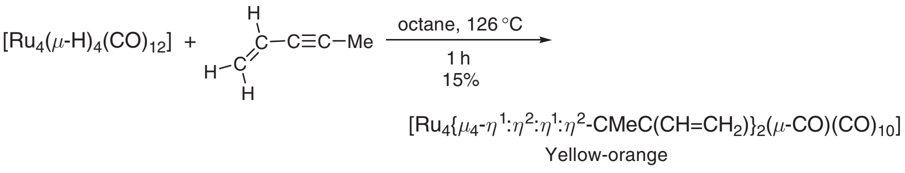
152

(104)

$$[Ru_3(CO)_{12}] + Ph{-}C{\equiv}C{-}Ph \xrightarrow[\substack{6\,h\\24\%}]{\text{hexane, }67\,^\circ C} \underset{\text{Brown}}{[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph_2)(CO)_{12}]} \qquad (105)$$

$$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Ph_2)(CO)_{12}] + Ph{-}C{\equiv}C{-}Ph \xrightarrow[\substack{6\,h\\51\%}]{\text{hexane, }67\,^\circ C} \underset{\text{Red}}{\mathbf{152}} \qquad (106)$$

One product isolated from the reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with pent-1-en-3-yne in refluxing octane is $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2Me(CH{=}CH_2)\}_2(\mu\text{-}CO)(CO)_{10}]$ **153** (Equation (107) see also Equation (131)).



153

(107)

Compounds with identical **154** or mixed alkynes **155** can be prepared from the Ru_4C_2 clusters with additional alkyne (Equations (108) and (109)).

A fourth compound in this class that has identical alkynes is $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2(C_2SiMe_3)_2\}_2(\mu\text{-}CO)(CO)_{10}]$ **154**, prepared in a similar manner to **152** (Equation (108)).

$$[\mathrm{Ru_4}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2R_2})(\mathrm{CO})_{12}] \;+\; \mathrm{R{-}C{\equiv}C{-}R} \xrightarrow[\text{8 h}\\ 23\%]{\text{hexane, 67 °C}} [\mathrm{Ru_4}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2R_2})_2(\mu\text{-CO})(\mathrm{CO})_{10}] \tag{108}$$

$\mathrm{R = C{\equiv}C{-}SiMe_3}$

Orange

154

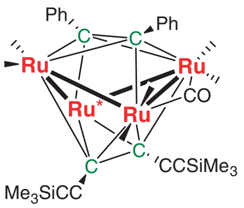
The mixed alkyne cluster $[\mathrm{Ru_4}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2Ph_2})\{\mu_4\text{-}\eta^2\text{-}\mathrm{C_2(C_2SiMe_3)_2}\}(\mu\text{-CO})_2(\mathrm{CO})_9]$ **155** (Equation (109)) is also prepared in a similar fashion.[116]

$$[\mathrm{Ru_4}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2Ph_2})(\mathrm{CO})_{12}] \;+\; \mathrm{R{-}C{\equiv}C{-}R} \xrightarrow[\text{8 h}\\ 49\%]{\text{hexane, 67 °C}} [\mathrm{Ru_4}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2Ph_2})(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2R_2})(\mu\text{-CO})(\mathrm{CO})_{10}] \tag{109}$$

$\mathrm{R = {-}C{\equiv}C{-}SiMe_3}$

Orange

155 (molecule 1)

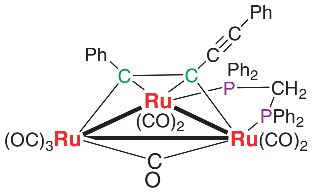


155 (molecule 1)

Ru* = Ru(CO)$_3$

molecule 2 has two semibridging CO's

One of five identified products formed by the reaction of $[\mathrm{Ru_3}\{\mu_3\text{-}2\eta^1{:}\eta^2\text{-}\mathrm{C_2Ph(C_2Ph)}\}(\mu\text{-}\mathrm{PPh_2CH_2PPh_2})(\mu\text{-CO})(\mathrm{CO})_7]$ with $\mathrm{Me_3SiCCCCSiMe_3}$ in THF is $[\mathrm{Ru_4}\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2Ph(C_2Ph)}\}\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2(SiMe_3)(C_2\text{-}SiMe_3)}\}(\mu\text{-}\mathrm{PPh_2CH_2PPh_2})(\mu\text{-CO})(\mathrm{CO})_8]$ **156** (Equation (110)).[117]

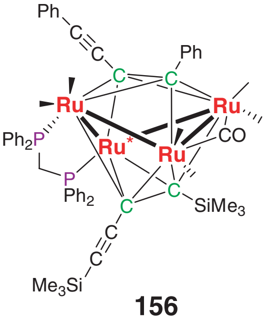


$$+ \;\mathrm{Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3} \xrightarrow[\text{2 h}\\ 3.6\%]{\text{THF, 66 °C}}$$

$$[\mathrm{Ru_4}\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{PhCC(C_2Ph)}\}\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{Me_3SiCC(C_2SiMe_3)}\}(\mu\text{-}\mathrm{PPh_2CH_2PPh_2})(\mu\text{-CO})(\mathrm{CO})_8] \tag{110}$$

Orange-red

156



Ru* = Ru(CO)$_2$

156

6.23.4.3 Derivatives with an η^2-$\mathrm{C_2}$ and μ_4-ER Ligands (E = Main Group Element)

A third class of clusters has the alkyne bridging one face of an $\mathrm{Ru_4}$ puckered square and a main group element fragment capping the opposite face. The alkyne may be bound in the familiar $\eta^1{:}\eta^2{:}\eta^1{:}\eta^2$ mode as found in $[\mathrm{Ru_4}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}\mathrm{C_2Ph_2})(\mu_4\text{-PPh})(\mu\text{-CO})(\mathrm{CO})_{10}]$ (Figure 5) or the rarer $\eta^1{:}\eta^1{:}\eta^1{:}\eta^1$ mode as in $[\mathrm{Ru_4}\{\mu_4\text{-}4\eta^1\text{-}\mathrm{C_2(CF_3)_2}\}(\mu_4\text{-}\mathrm{PCF_3})(\mathrm{CO})_{12}]$ (Figure 6).

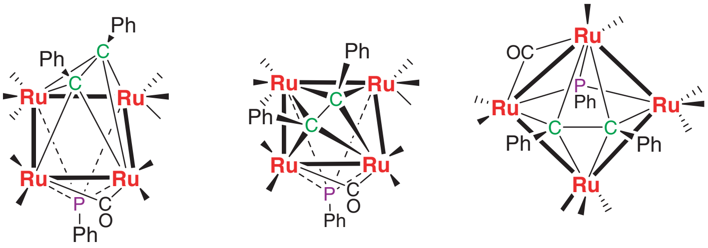
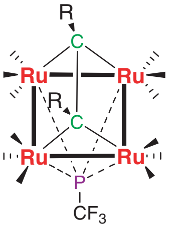


Figure 5



R = CF_3

Figure 6

The $4\eta^1$ cluster usually has 66 c.v.e. that are two more than that required for four RuRu bonds. As discussed previously however, if each CR unit donates five electrons to cluster bonding there are a total of eight cluster bonding pairs consistent with the observed capped trigonal bipyramidal Ru_4EC_2 skeleton (Figure 6).

The clusters $[Ru_4(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}RC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_9]$ (R = H **157a**; R = Ph **157b**) and $[Ru_4(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}RC_2Ph)\{\mu_4\text{-}NOC(O)OMe\}(\mu\text{-}CO)_2(CO)_9]$ **157a**, **157b** are prepared from the thermolysis of $[Ru_3(\mu_3\text{-}2\eta^2\text{-}PhC_2R)(\mu_3\text{-}NOMe)(CO)_9]$ in *n*-octane at 125 °C (Equation (111)).[118] One of the other products is the known $[Ru_4(\mu_4\text{-}NH)(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}PhC_2Ph)(\mu\text{-}CO)_2(CO)_9]$ **159**. Clusters **157a**, **157b**, **158a**, and **158b** all have similar $[Ru_4(\mu_4\text{-}NX)(\mu\text{-}CO)_2(CO)_9]$ units with the metal atoms in a slightly puckered square arrangement and bridging carbonyls across adjacent edges. The RuRu lengths associated with the Ru(μ-CO)Ru groups are somewhat shorter than the RuRu distances of the RuRu bonds not bridged by carbonyls (range 2.6731(7)–2.7076(9) vs. 2.724(1)–2.807(1) Å, respectively). The RuN distances in the four molecules are in the range 2.123(3) to 2.235(3) Å. Clusters **158a** and **158b** are rare examples of μ_4-NC(O)OMe carbamate ligands that result from the insertion of a carbon monoxide ligand into the NOMe bond present in the parent compound. However, treatment of **157a** with CO at 90 °C did not result in the formation of **158a**. The ^{15}N NMR resonances of the μ_4-NOMe units in **157a** and **157b** are at δ 308.0 and 301.6 whereas in the corresponding μ_4-N(CO)OMe derivatives the resonances appear at δ 52.8 and 79.9, respectively. The ^{15}N NMR signal for $[Ru_4(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}NH)(\mu\text{-}CO)_2(CO)_9]$ **159** appears at δ 47.6 ($J_{NH} = 70.5$ Hz), some 254.6 ppm upfield from the corresponding resonance of the μ_4-NOMe analog.[118]

$$[Ru_3(\mu_3\text{-}\eta^2\text{-}RC_2Ph)(\mu_3\text{-}NOMe)(CO)_9] \xrightarrow[3\,h]{n\text{-octane, }125\,^\circ C} [Ru_4(\mu_4\text{-}\eta^2\text{-}RC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_9] \tag{111}$$

R = H, Ph

Orange, 25% Orange, 18%

157a: R = H **157b**: R = Ph

+

$[Ru_4(\mu_4\text{-}\eta^2\text{-}RC_2Ph)\{\mu_4\text{-}NC(O)OMe\}(\mu\text{-}CO)_2(CO)_9]$

Orange, 15% Orange, 10%

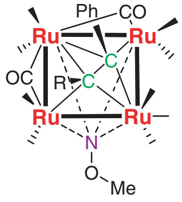
158a: R = H **158b**: R = Ph

+

$[Ru_4(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}NH)(\mu\text{-}CO)_2(CO)_9]$

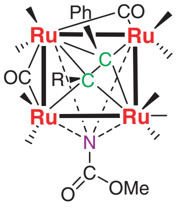
R = Ph 12%

159

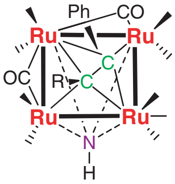


157

R = H, Ph



158



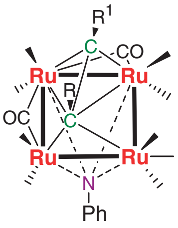
159

Aspects of the chemistry of compound **157a** are depicted in Scheme 21.[118] One isomer of [Ru(μ_4-$2\eta^1$:$2\eta^2$-HC_2Ph)(μ_4-NOMe)(μ-CO)$_2$(CO)$_8$(MeCN)] **160** the MeCN replaces the *pseudo*-axial CO of the Ru(CO)$_4$ of **157a** that is *syn* to the NOMe substituent. In the corresponding PPh$_3$ derivative [Ru$_4$(μ_4-$2\eta^1$:$2\eta^2$-HC_2Ph)(μ_4-NOMe)(μ-CO)$_2$(CO)$_8$(PPh$_3$)] **161**, the phosphine ligand occupies the *pseudo*-equatorial site, which is typical for carbonyl clusters of the group 8 elements.[118,119]

The reactions of asymmetric alkynes (RC≡CR^1) with [Ru$_3$(μ_3-NPh)(μ_3-CO)(CO)$_9$] give [Ru$_4$(μ_4-$2\eta^1$:$2\eta^2$-RC_2R^1)-(μ_4-NPh)(μ-CO)$_2$(CO)$_9$] (Equation (112)).[120] The structures of [Ru(μ_4-$2\eta^1$:$2\eta^2$-RC_2R^1)(μ_4-NPh)(μ-CO)$_2$(CO)$_9$] (R = CO$_2$Me, R^1 = Ph **163**; R = CCPh; R^1 = Ph **164**) are similar to those of [Ru$_4$(μ_4-$2\eta^1$:$2\eta^2$-PRC$_2$Ph)(μ_4-NRNOMe)(μ-CO)$_2$(CO)$_9$] (R = H, Ph; **157** and **158**). The Ru$_4$(μ_4-NPh) unit in **163** and **164** consists of a slightly distorted square with the RuRu bonds in the range 2.695(1)–2.7951(1) Å in **163** and 2.684(1)–2.812(1) Å in **164**. The RuN distances are in the range 2.145(3)–2.256(4) Å. The Ru atom bound to both bridging carbonyls is also attached to the C atom of the alkyne that has the most electron-withdrawing group.[120]

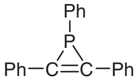
$$[Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)(CO)_9] + R{-}C{\equiv}C{-}R^1 \xrightarrow[\substack{35\text{ min–}2\text{ h}\\ 10\text{–}46\%}]{\text{hexanes, }69\,°\text{C}} [Ru_4(\mu_4\text{-}\eta^2\text{-}RC_2R^1)(\mu_4\text{-}NPh)(\mu\text{-}CO)_2(CO)_9] \tag{112}$$

Yellow-orange



R	*R*^{1}	
CO$_2$Me	H	
CO$_2$Me	Ph	**163**
C$_2$Me	H	
C$_2$Ph	Ph	**164**

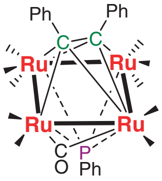
The compound [Ru(μ_4-$2\eta^1$:$2\eta^2$-PhC$_2$Ph)(μ_4-PPh)(μ-CO)$_2$(CO)$_9$] **165** is one product isolated from the reaction of [Ru$_3$(CO)$_{12}$] with 1,2,3-triphenylphosphirene (Equation (113)).[121]



$$[Ru_3(CO)_{12}] + \text{Ph–C=C–Ph (P–Ph)} \xrightarrow[\substack{24\text{ h}\\ 12\%}]{\text{THF, }66\,°\text{C}} [Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}CPhCPh)(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}] \tag{113}$$

Red

165



165

The structure of **165** has been previously determined.[122] The cluster shows moderate activity as a hydrogenation catalyst.[123]

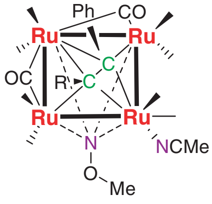
Pyrolysis of the monosubstituted cluster [Ru$_3$(CO)$_{11}${P(C≡CC≡CBu^t)Ph$_2$}] results in PC and RuRu cleavage to give a range of products. One of the products, isolated in low yield, is [Ru$_4$(μ_4-$2\eta^1$:$2\eta^2$-PhC$_4$Bu^t)(μ_4-PPh)(μ-CO)(CO)$_{10}$] **166** (Equation (114)).[124] See Tables 5 and 6 for RuRu and RuP lengths, respectively.

$$[Ru_4(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_9] \xrightarrow[\text{8 h, 50\%}]{[Cp_2Fe]^+,\ MeCN} [Ru_4(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_8(MeCN)]$$

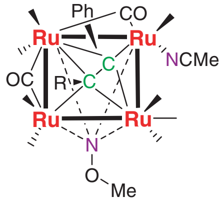
157a

Orange

160A and **160B**



160A



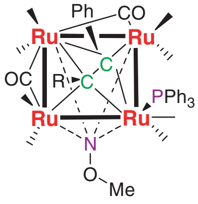
160B

$$[Ru_4(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_8(MeCN)] \xrightarrow[\text{1 h, 95\%}]{PPh_3/CH_2Cl_2} [Ru_4(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_8(PPh_3)]$$

160

Orange, 20%

161



161

$$[Ru_4(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_9] \xrightarrow[\text{15 min}]{PPh_3/Me_3NO} \mathbf{161} +$$

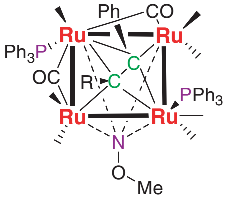
157a

30%

$[Ru_4(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}NOMe)(\mu\text{-}CO)_2(CO)_7(PPh_3)_2]$

Orange

162



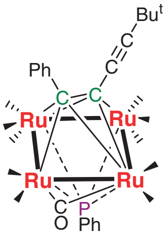
162

Scheme 21

$$[Ru_3(CO)_{11}\{P(CCCCBu^t)Ph_2\}] \xrightarrow[\text{4 h, 1\%}]{\text{THF, 66 °C}} [Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C(Ph)C(C_2Bu^t)\}(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}] \qquad (114)$$

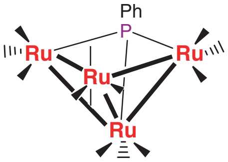
Red

166



166

The reaction of $[Ru_4(\mu_3\text{-PPh})(CO)_{13}]$ and the triyne $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ in refluxing pentane affords $[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-PPhC}(C{\equiv}C_2SiMe_3)C(C_2{\equiv}CSiMe_3)\}(\mu\text{-CO})_2(CO)_{10}]$ **D** and $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^1\text{-C}(C_3SiMe_3)C(C_3SiMe_3)\}(\mu_4\text{-PPh})(\mu\text{-CO})(CO)_{10}]$ **167** (Equation (115)).[125] Heating cluster **D** in refluxing hexane causes smooth conversion to **167** (Equation(116)). Heating **167** in refluxing toluene affords the toluene-substituted derivative $[Ru_4(\mu_4\text{-PPh})\{\mu_4\text{-}2\eta^1{:}2\eta^1\text{-C}(C_3SiMe_3)C(C_3SiMe_3)\}(\mu\text{-CO})_2(CO)_6(\eta^6\text{-}C_6H_5Me)]$ **168** as one product (Equation (117)). Bond length data for **167 and 168** are given in Tables 5 and 6.

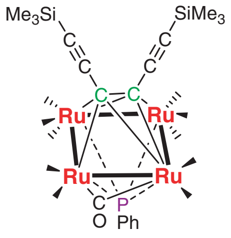


$[Ru_4(\mu_3\text{-PPh})(CO)_{13}]$
B

$$+\ Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3 \xrightarrow[\text{2 d} \atop 27\%]{\text{pentane, 35 °C}} \tag{115}$$

$[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-PPhC}(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)\}(\mu\text{-CO})_2(CO)_{10}]$ +
D
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}(Me_3SiC{\equiv}C)C_2(C{\equiv}CSiMe_3)\}(\mu_4\text{-PPh})(\mu\text{-CO})(CO)_{10}]$
Orange
167

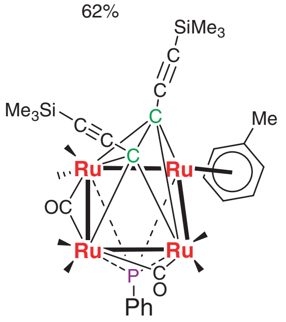
$$\mathbf{D} \xrightarrow[\text{1 h} \atop 70\%]{\text{hexane, 69 °C}} \mathbf{167} \tag{116}$$



167

$$\mathbf{167} \xrightarrow[\text{2 h} \atop 62\%]{\text{toluene,110 °C}} [Ru_4(\mu_4\text{-PPh})(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}(Me_3SiCCCCC{\equiv}CSiMe_3)] \tag{117}$$

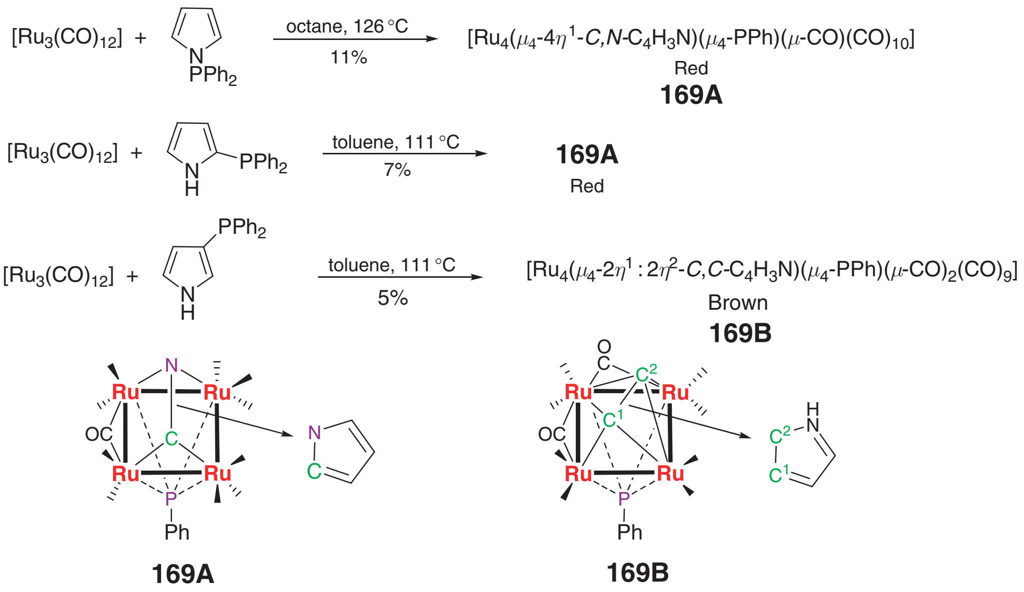
Dark red
168



168

Heating $[Ru_3(CO)_{12}]$ with diphenyl-*n*-pyrrolylphosphines ($PPh_2(n\text{-}C_4H_4N)$; $n = 1, 2, 3$) produces a number of products, two of which are the isomeric $[Ru_4(\mu_4\text{-}4\eta^1\text{-}C,N\text{-}C_4H_3N)(\mu_4\text{-PPh})(\mu\text{-CO})(CO)_{10}]$ **169A** and $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^1\text{-}C,C\text{-}C_4H_3N)(\mu_4\text{-PPh})(\mu\text{-CO})_2(CO)_9]$ **169B** (Scheme 22).[126] In the first isomer, the pyrrolyne ligand is bound to the Ru_4 unit via a nitrogen and a carbon atom in the 4σ ($4\eta^1$) arrangement with the CN axis parallel to two of the edges of the Ru square. In the second isomer, the pyrrolyne ligand is bound to the square-planar Ru_4 unit via two carbon atoms across an Ru···Ru diagonal in the more common $2\sigma/2\pi$ ($2\eta^1{:}2\eta^2$) mode. Ruthenium–carbon bond length data are given in Table 19; see also Table 5 for RuRu lengths.

Reactions of $[Ru_4(\mu_4\text{-ECF}_3)(\mu\text{-H})_2(CO)_{13}]$ (E = P **32** or As **47**) with the alkynes C_2R_2 (R = Ph or H) under relatively mild conditions yield $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2R_2)(\mu_4\text{-ECF}_3)(\mu\text{-CO})_2(CO)_9]$ (E = P, R = H **170a**; R = Ph **170b**; E = As, R = Ph **171**) (Equations (118) and (119)).[33]

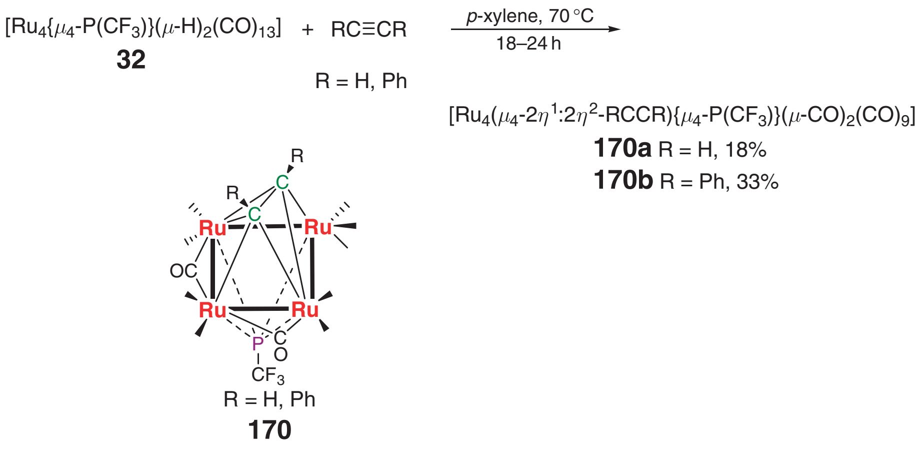


Scheme 22

Table 19 Selected RuC and CC bond lengths for clusters with an $Ru_4(\mu_4\text{-}\eta^2\text{-}C_2R_2)$ unit and a heteronuclear bridging atom

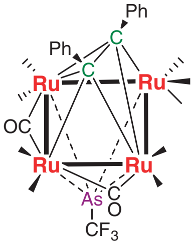
Compound	*RuC-σ lengths* (Å)	*RuC-π lengths* (Å)	*CC length* (Å)
$[Ru_4(\mu_4\text{-}4\eta^1\text{-}C,N\text{-}C_4H_3N)(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$[a] **169A**	2.217(4), 2.193(4), 2.211(4),[b] 2.194(4)[b]		1.462(6)[c]
$[Ru_4(\mu_4\text{-}4\eta^1\text{-}C,N\text{-}C_4H_3N)(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$[d] **169A**	2.188(5), 2.178(5), 2.177(5),[b] 2.170(5)[b]		1.441(7)[c]
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^1\text{-}C,C\text{-}C_4H_3N)(\mu_4\text{-}PPh)(\mu\text{-}CO)_2(CO)_9]$ **169B**	2.081(8), 2.187(7)	2.366(8)–2.468(8)	1.42(1)
$[Ru_4(\mu_4\text{-}\eta^2\text{-}C_2H_2)(\mu_4\text{-}PCF_3)(\mu\text{-}CO)_2(CO)_9]$ **170a**	2.111(7), 2.153(6)	2.305(6)–2.421(7)	
$[Ru_4(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu_4\text{-}PCF_3)(\mu\text{-}CO)_2(CO)_9]$ **170b**	2.147(3), 2.207(3)	2.383(4)–2.547(3)	1.400(4)
$[Ru_4\{\mu_4\text{-}4\eta^1\text{-}C_2(CF_3)_2\}(\mu_4\text{-}PCF_3)(CO)_{12}]$ **172**	2.164(6)–2.210(6)		1.510(8)
$[Ru_4(\mu_4\text{-}\eta^2\text{-}C_{10}H_6)\{\mu_4\text{-}As(C_{10}H_7)\}(\mu\text{-}CO)(CO)_{10}]$ **173**	2.187(5), 2.330(4) (C1); 2.195(5), 2.320(4) (C2)		

[a] Monoclinic form.
[b] RuN length.
[c] CN length.
[d] Triclinic form.



(118)

$$\underset{\mathbf{47}}{[\mathrm{Ru_4}\{\mu_4\text{-As(CF}_3)\}(\mu\text{-H})_2(\mathrm{CO})_{13}]} + \mathrm{PhC{\equiv}CPh} \xrightarrow[\substack{18\,\mathrm{h} \\ 21\%}]{p\text{-xylene, 70 °C}} \underset{\mathbf{171}}{[\mathrm{Ru_4}(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-PhCCPh})\{\mu_4\text{-As(CF}_3)\}(\mu\text{-CO})_2(\mathrm{CO})_9]} \quad (119)$$

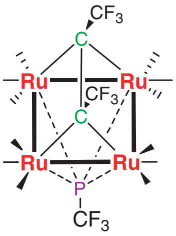


171

These clusters have the typical square-planar $\mathrm{Ru_4}$ array with the alkyne attached to the ruthenium atoms on one side of the plane via 2σ and 2π bonds, and a μ_4-$\mathrm{ECF_3}$ bound to the other side of the $\mathrm{Ru_4}$ plane. Bond length data for the heavy atoms of **170a** and **170** are given in Tables 5 and 6. (The structure of **171** was not determined.) The Ru-C bond lengths in the P derivatives are given in Table 19.

Under similar conditions, the reaction of **32** with $\mathrm{C_2(CF_3)_2}$ gives $[\mathrm{Ru_4}\{\mu_4\text{-}4\eta^1\text{-}\mathrm{C_2(CF_3)_2}\}(\mu_4\text{-}\mathrm{PCF_3})(\mathrm{CO})_{12}]$ **172** (Equation (120)) in which the perfluoroalkyne interacts with the $\mathrm{Ru_4}$ square face by 4σ bonds only. The alkyne sits above the $\mathrm{Ru_4}$ plane with the CC bond parallel to two opposite $\mathrm{Ru_2}$ bonds rather than along an Ru···Ru diagonal as in most other clusters mentioned in this section. The CC bond length in **172** (Table 19) is close to that expected for a CC single bond.

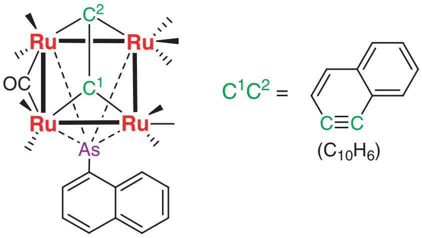
$$\underset{\mathbf{32}}{[\mathrm{Ru_4}\{\mu_4\text{-P(CF}_3)\}(\mu\text{-H})_2(\mathrm{CO})_{13}]} + \mathrm{F_3CC{\equiv}CCF_3} \xrightarrow[\substack{18\,\mathrm{h} \\ 16\%}]{\text{cyclohexane, 70 °C}} \underset{\substack{\text{Red} \\ \mathbf{172}}}{[\mathrm{Ru_4}\{\mu_4\text{-}4\eta^1\text{-C(CF}_3)\mathrm{C(CF}_3)\}\{\mu_4\text{-P(CF}_3)\}(\mathrm{CO})_{12}]} \quad (120)$$



172

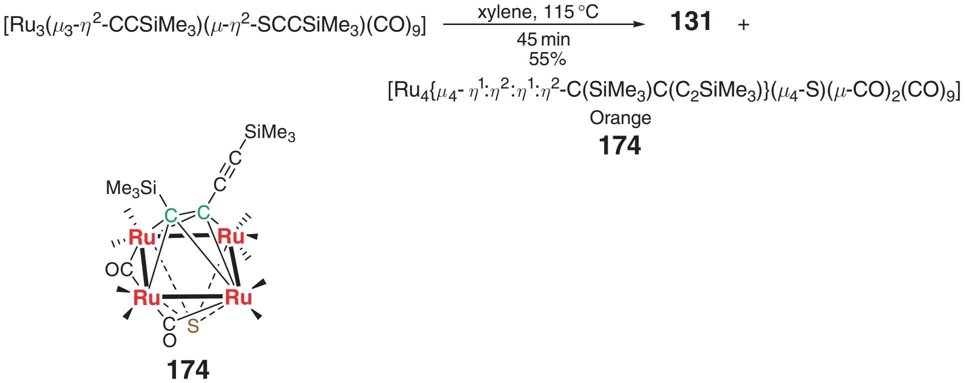
The naphthyne complex $[\mathrm{Ru_4}(\mu_4\text{-}\eta^1\text{-}\mathrm{C_{10}H_6})\{\mu_4\text{-As(C}_{10}\mathrm{H_7})\}(\mu\text{-CO})(\mathrm{CO})_{10}]$ **173** is isolated in trace amounts from the refluxing a solution of $[\mathrm{Ru_3(CO)_{12}}]$ and $\mathrm{As(1\text{-}C_{10}H_7)_3}$ in cyclohexane (Equation (121)).[127] The compound was characterized by X-ray crystallography alone. The μ_4-alkyne unit binds in the rare $4\eta^1$ mode as found for **172** (Table 19). The RuRu lengths in **173** are 2.7892(7) (Ru(μ-CO)Ru), 2.8704(7), 2.8934(7), 2.9062(7) Å. The authors considered **173** to be electron deficient (*cf.* compound **172** with 12 CO ligands), but it may be that the two longest RuRu bonds are bridged by hydride ligands.

$$[\mathrm{Ru_3(CO)_{12}}] + \mathrm{As(1\text{-}C_{10}H_7)_3} \xrightarrow[\text{10 h}]{\text{cyclohexane, 81 °C}} \underset{\substack{\text{Trace} \\ \mathbf{173}}}{[\mathrm{Ru_4}(\mu_4\text{-AsC}_{10}\mathrm{H_7})(\mu_4\text{-}4\eta^1\text{-}\mathrm{C_{10}H_6})(\mu\text{-CO})(\mathrm{CO})_{10}]} \quad (121)$$



173

Thermolysis of $[Ru_3(\mu\text{-}\eta^2\text{-}CCSiMe_3)(\mu\text{-}\eta^2\text{-}SCCSiMe_3)(CO)_9]$ in xylene yields **131** and $[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C(SiMe_3)\text{-}C(C_2SiMe_3)\}(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_9]$ **174** (Equation (122)).[100]



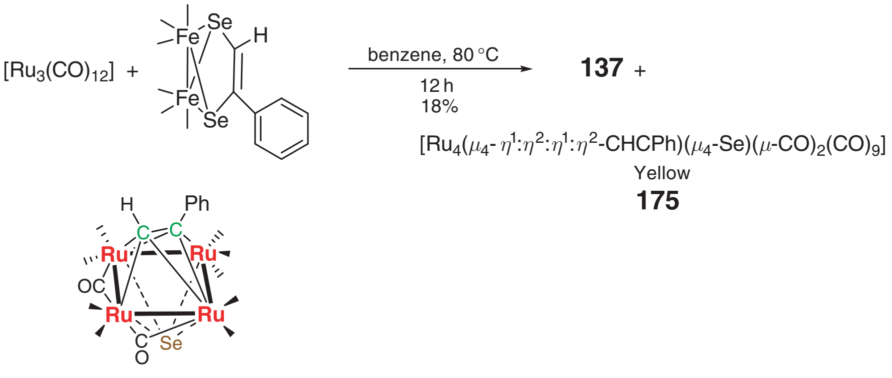
$$[Ru_3(\mu_3\text{-}\eta^2\text{-}CCSiMe_3)(\mu\text{-}\eta^2\text{-}SCCSiMe_3)(CO)_9] \xrightarrow[\text{45 min} \atop 55\%]{\text{xylene, 115 °C}} \mathbf{131} + [Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C(SiMe_3)C(C_2SiMe_3)\}(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_9]$$

174

(122)

The cluster $[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}CHC(C_2SiPr^i{}_3)\}(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_9]$ is the main product from the thermolysis of $[Ru_4\{\mu\text{-}SC_2(SiPr^i{}_3)\}(\mu_3\text{-}\eta^2\text{-}C_2H)(CO)_9]$ in xylene. It is believed to have a similar structure to that of **174**.[128]

Reaction of $[Fe_2(\mu\text{-}SeCHCPhSe)(CO)_6]$ with $[Ru_3(CO)_{12}]$ in refluxing benzene affords **137** and $[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}CHCPh)(\mu_4\text{-}Se)(\mu\text{-}CO)_2(CO)_9]$ **175** (Equation (123)).[104] The structure of **175** is based on a comparison of its spectroscopic data with that of similar compounds of known structure.



175

(123)

6.23.4.4 Derivatives with η^3-C$_3$ Ligands

Data for RuRu bond lengths for clusters with $\mu\text{-}\eta^3$-C ligands are given in Table 20.

Table 20 Skeletal structures and RuRu bond lengths for clusters with $\mu\text{-}\eta^3$-C ligands

Compound	*Structure*[a]	*Ru(μ-CO)Ru* (Å)	*Unbridged RuRu* (Å)
$[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C_3CBu^tC_4Bu^t)\}(\mu\text{-}PPh_2)_2(CO)_9]$ **176**	**PB**	2.778(2), 2.726(2)[b]	2.625(2), 2.830(2), 2.839(2)
$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}CMeCCH_2Me)(CO)_{12}]$ **177a**	**PB**	2.763(3), 2.768(3)[c]	2.717(3),[d] 2.898(2), 2.900(2)
$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}CPhCCH_2Ph)(CO)_{12}]$ **177b**	**PB**	2.763(4), 2.779(4);[c] 2.776(4), 2.763(4)[c,e]	2.753(4),[d] 2.902(3), 2.916(3); 2.752(4),[d] 2.905(3), 2.929(3)[e]
$[Ru_4(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CHCC_{13}H_8)_2(\mu_3\text{-}OH)(\mu\text{-}CO)(CO)_{10}]$ **179**	**B**	2.808(5)	2.835(5), 2.896(6), 2.916(5), 2.975(5)

[a] See Figure 1.
[b] Ru(μ-PPh$_2$)Ru
[c] Semibridging CO.
[d] Hinge RuRu bond.
[e] Two independent molecules.

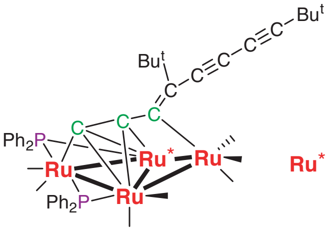
Themolysis of $[Ru_3(CO)_{11}\{P(CCCCBu^t)Ph_2\}]$ in refluxing THF produces a variety of products, one of which is $[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C_3CBu^tC_4Bu^t)(\mu\text{-}PPh_2)_2(CO)_9]$ **176** (Equation (124)).[124] The most striking feature of **176** is the C_8 hydrocarbon chain bound to a flat butterfly arrangement of four Ru atoms. The hydrocarbon ligand arises from the head-to-tail coupling of two diyne units. The bond lengths associated with the carbon chain suggest considerable delocalization over both the metal bound and pendant units. The hydrocarbon ligand is considered to donate six electrons to give the cluster the 62 c.v.e. count expected for a cluster with five metal–metal bonds.

$$[Ru_3(CO)_{11}\{P(C{\equiv}CC{\equiv}CBu^t)Ph_2\}] \xrightarrow[\substack{4\ h\\ 12\%}]{\text{THF, 66 °C}} \qquad (124)$$

$[Ru_4\{\mu_4\text{-}\ \eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C_3CBu^t(C_4Bu^t)\}(\mu\text{-}PPh_2)_2(CO)_9]$

Blue-green

176



176

$Ru^* = Ru(CO)_2$

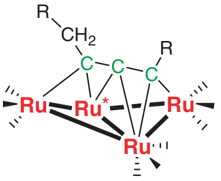
The reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with the 1,3-diynes RC_2C_2R (R = Me, Ph, $SiMe_3$) in refluxing heptane yields $[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}CRCCCH_2R)(CO)_{12}]$ (R = Me **177a**, Ph **177b**, $SiMe_3$) as one of two products isolated (Equation (125)).[129] The structures of **177a** and **177b** contain a flat Ru_4 butterfly with the hydrocarbon ligand bound to all four Ru atoms via three C atoms in a $\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2$ mode. The allene-1,3-diyl ligand is the result of a 1,1-dihydrogenation of the original diyne. Like the $[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_2RR^1)(CO)_{12}]$ clusters, the RuC σ-bonds are shorter (range 2.07–2.12 Å) than the RuC π-bonds (range 2.19–2.29 Å). The CC bond lengths for the CCC unit bound to the Ru cluster are in the range 1.27(3)–1.40(3) Å.

$$\underset{\text{A}}{[Ru_4(\mu\text{-}H)_4(CO)_{12}]} + R{-}C{\equiv}C{-}C{\equiv}C{-}R \xrightarrow[\text{3 h}]{\text{heptane, 98 °C}} [Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}CRC_2CH_2R)(CO)_{12}] \qquad (125)$$

R = Me, $SiMe_3$, Ph

R = $SiMe_3$: maroon, 30%
177a: R = Me: dark red, 45%
177b: R = Ph: maroon, 25%

177



$Ru^* = Ru(CO)_3$

R = Me, $SiMe_3$, Ph

177

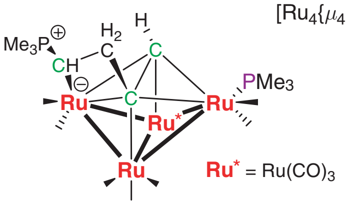
Treatment of $[Ru_3(\mu_3\text{-}C_2H_2)(\mu\text{-}CO)(CO)_9]$ with trimethylphosphine in the presence of trimethylamine oxide gives $[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^3\text{-}CHC[\mu\text{-}\eta^2\text{-}CH_2CH(PMe_3)]\}(CO)_{10}(PMe_3)]$ **178** in low yield (Equation (126); see also Tables 15 and 16). The compound has an ylidic $Me_3P(\delta+)CHRu(\delta-)$ linkage.[130]

$$[Ru_3(\mu_3\text{-}C_2H_2)(\mu\text{-}CO)(CO)_9] + PMe_3 \xrightarrow[\substack{25\ °C\\ 2\%}]{\text{THF, }Me_3NO} \qquad (126)$$

$[Ru_4\{\mu_4\text{-}\ \eta^1{:}\eta^2{:}\eta^1{:}\eta^3\text{-}CHC[\mu\text{-}\eta^2\text{-}CH_2CH(PMe_3)]\}(CO)_{10}(PMe_3)]$

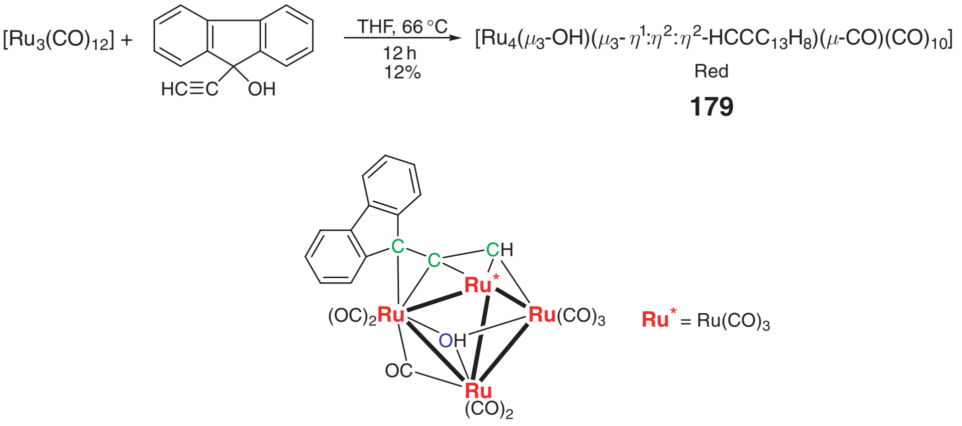
Red

178



178

Five compounds are isolated from the reaction of $[Ru_3(CO)_{12}]$ with 9-ethynylfluoren-9-ol in refluxing THF. One of the products is the tetranuclear $[Ru_4(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-CHCC}_{13}H_8)_2(\mu_3\text{-OH})(\mu\text{-CO})(CO)_{10}]$ **179** (Equation (127)).[131] The skeleton consists of a butterfly Ru_4 unit bridged by an OH group across the wingtip and one of the hinge Ru atoms to give an Ru_4O square pyramid. The hydrocarbon ligand bridges the wingtip Ru atoms and the other hinge Ru atom in a $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$ mode. The RuC σ-bond distance is 2.064(5) Å; the RuC π-bonds have lengths of 2.188(4), 2.236(5), and 2.421(4) Å (one length not quoted). The long RuC distance is that to the C atom attached to the $C_{13}H_8$ fragment. The CC length of the alkyne linkage is 1.379(7) Å.



179

(127)

6.23.4.5 Derivatives with η^4-C_4 Ligands

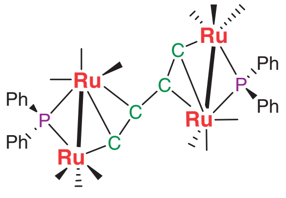
Structural data for Ru_4 derivatives that contain a bridging ligand with four bound carbon atoms are given in Tables 21 and 22. As discussed previously, RuC lengths of RuC σ-bonds (i.e., bound to a single metal atom) are somewhat shorter than the RuC distances of the π-bonds.

A *trans*-bent butadiynyl unit coordinated in a $\mu\text{-}\eta^1\text{:}\eta^2$ fashion to two $Ru_2(\mu\text{-PPh}_2)(CO)_6$ moieties is found in $[\{Ru_2(\mu\text{-PPh}_2)_2(CO)_2\}_2\{\mu\text{-}\eta^1,\eta^2\text{:}\mu\text{-}\eta^1,\eta^2\text{-CCCC}\}]$ **180**, a product formed by the pyrolysis of $[Ru_3(CO)_{11}\{P(CCCCSiMe_3)Ph_2\}]$ (Equation (128)).[124] The central Ru_4C_4 unit is nearly planar; the RuRu bonds of length 2.761(1) Å are identical by crystallographic symmetry. The RuC distances are significantly different: 2.049(8) (σ-bond), 2.296(8), 2.446(8) Å (π-bond); the inner CC bond has a length of 1.41(1)Å. The ^{13}C NMR spectrum of **180** has resonances at δ 103.3 ($J_{PC}=27$ Hz) and 129.0 ($J_{PC}=27$ Hz) attributed to C_α and C_β of the diyne unit, respectively.

$$[Ru_3(CO)_{11}\{P(C_4SiMe_3)Ph_2\}] \xrightarrow[\substack{2\,h\\14\%}]{\text{THF, 66 °C}} [\{Ru_2(\mu\text{-PPh}_2)(CO)_6\}_2\{\mu\text{-}\eta^1,\eta^2\text{:}\mu\text{-}\eta^1,\eta^2\text{-CCCC}\}]$$

Yellow-orange

180



180

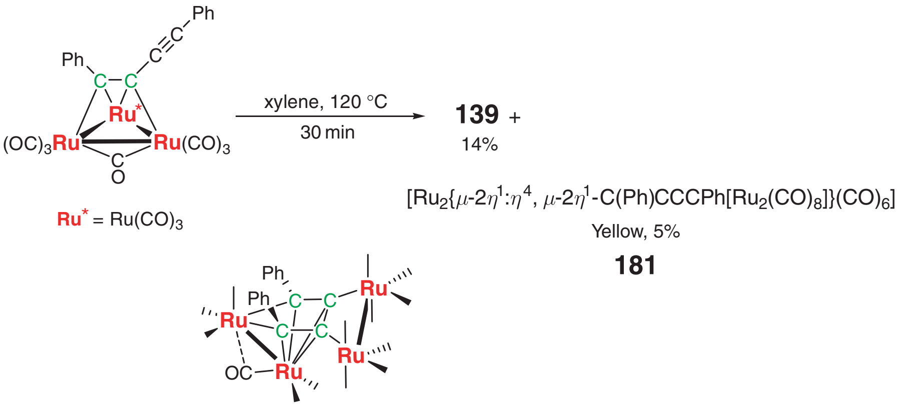
(128)

Table 21 Skeletal structures and RuRu bond lengths for clusters with μ-η^4 C_4 ligands

Compound	*Structure*[a]	*Ru(μ-CO)Ru* (Å)	*Other RuRu* (Å)
$[Ru_4(\mu_3\text{-}\eta^3{:}\eta^2{:}\eta^1\text{-}C_5H_6)(\mu_4\text{-}\eta^8\text{-}C_{10}H_{12})(CO)_8]$ **183**	**ST**		2.7299(4), 2.7942(5),[b] 2.8342(4), 2.9796(4)
μ_4-η^4			
$[Ru_4(\mu_4\text{-}2\eta^1{:}\eta^4{:}\mu\text{-}2\eta^1\text{-}CPhCCCPh)(CO)_{14}]$ **181**	[c]	2.693(4)[d]	2.874(3)
$[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^2\text{-}CHMeC_2CMe\}\{\mu\text{-}N_2CMeCHCMe\}(\mu\text{-}CO)(CO)_{10}]$ **190**	**ST**	2.781(1)	2.818(1), 2.846(1), 2.904(1)[b]
$[Ru_4(\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}C_6H_4)\{\mu_4\text{-}\eta^2{:}3\eta^1\text{-}P(CH_2)_2PPh_2\}(\mu\text{-}CO)(CO)_9]$ **191**	**S**	2.819(1)	2.892(2), 2.907(1), 2.935(1)
		Hinge RuRu	*Peripheral RuRu*
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CHMeCCCHMe\}(CO)_{12}]$ **184A**	**PB**	2.809(1)	2.779(1), 2.871(1)[e]
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CHPhCCCHPh\}(CO)_{12}]$ **184C**	**PB**	2.844(1)	2.766(1), 2.785(1), 2.887(1), 2.895(1)
$[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-}CHPhCCCHPh\}(CO)_{12}]$ **184C**	**PB**	2.838(3)	2.759(2), 2.779(2), 2.876(2), 2.890(2)
$[Ru_4\{\mu_4\text{-}4\eta^2\text{-}CHMeCCC(H)CH_2C(O)Me\}(CO)_{12}]$ **186**	**PB**	2.848(3)	2.770(3), 2.789(3), 2.878(3), 2.895(3)
$[Ru_4(\mu_4\text{-}\eta^2{:}\eta^3{:}\eta^1{:}\eta^2\text{-}CPhCPhCCCPh_2)(CO)_{12}]$ **187**	**PB**	2.797(1)	2.773(1), 2.788(1), 2.818(1), 3.031(1)

[a] See Figure 1.
[b] Spike RuRu bond.
[c] Compound has only two RuRu bonds.
[d] Semibridging CO.
[e] Molecule has a C_2 axis.
[f] Ru(μ-CO)Ru.

Another rare bridging μ_4-η^4-C_4 arrangement is found in $[Ru_2\{\mu\text{-}2\eta^1{:}\eta^4,\mu\text{-}2\eta^1\text{-}CPhCCCPh[Ru_2(CO)_8]\}(CO)_6]$ **181** prepared by the thermolysis of $[Ru_3\{\mu_3\text{-}2\eta^1{:}\eta^2\text{-}C_2Ph(C_2Ph)\}(\mu\text{-}CO)(CO)_9]$ (Equation (129)).[132]



181

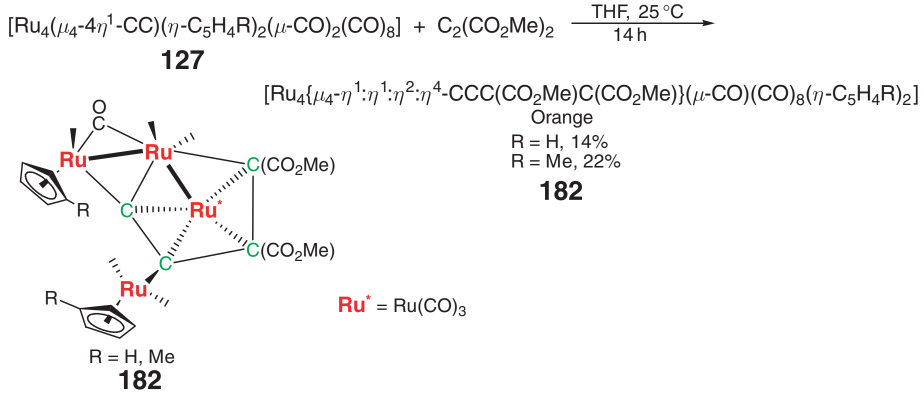
(129)

A similar bonding arrangement is found in $[Ru_4\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}CCC(CO_2Me)C(CO_2Me)\}(\mu\text{-}CO)_2(CO)_8(\eta\text{-}C_5H_4R)_2]$ (R = H, Me) **182** formed by the reactions of $[Ru_4(\mu\text{-}4\eta^1\text{-}CC)(\mu\text{-}CO)_2(CO)_8(\eta\text{-}C_5H_4R)_2]$ **127** with the activated alkyne $C_2(CO_2Me)_2$ (Equation (130)).[133]

Table 22 RuC and CC bond lengths for clusters with μ-η^4-C_4 ligands

Compound	*σ RuC* (Å)	*π RuC* (Å)	*CC of bridging unit* (Å)
183	2.084(4)	2.131(4), 2.148(4), 2.206(4), 2.273(4), 2.291(4)	1.351(5), 1.413(5), 1.378(6)
μ_4-η^4			
181	2.08(2), 2.10(2), 2.12(2), 2.13(2)	2.24(2), 2.25(2), 2.31(2), 2.35(2)	1.37(3), 1.39(3), 1.47(3)[b]
191	2.09(1), 2.12(1)	2.30(1), 2.32(1), 2.57(1), 2.63(1)	1.41(2), 1.41(1), 1.44(1)
184A		2.068(5), 2.266(5), 2.346(5)[c]	1.394(7), 1.43(1)[c]
184C		2.065(8), 2.083(9), 2.316(8), 2.337(8), 2.335(8), 2.343(8)	1.39(1), 1.41(1), 1.44(1)
184C		2.08(2), 2.73(1), 2.08(2), 2.70(2), 2.32(2), 2.33(1), 2.30(2), 2.31(2)	1.36(1), 1.48(2), 1.33(2)
186	2.04(3), 2.05(3)	2.29(3), 2.35(3), 2.29(3), 2.31(3)	1.40(3), 1.40(4), 1.41(4)
187	2.091(3), 2.12(3)	2.583(3), 2.323(3), 2.324(3), 2.414(3), 2.113(3), 2.516(3)	1.416(4), 1.443(4), 1.435(4)
190	2.118(9) (Ru1)[d]	2.195(8), 2.375(9) (Ru3); 2.225(9), 2.530(9) (Ru2); 2.375(9), 2.232(8), 2.223(8) (Ru4)	1.34(1), 1.40(1), 1.49(1)

[a] Not quoted in original paper.
[b] Only three of five CC bonds quoted.
[c] Molecule has a C_2 axis.
[d] Spike Ru atom (connected to Ru3).


$[Ru_4(\mu_4\text{-}4\eta^1\text{-CC})(\eta\text{-}C_5H_4R)_2(\mu\text{-CO})_2(CO)_8] + C_2(CO_2Me)_2 \xrightarrow[14\,h]{THF,\ 25\,°C}$

127

$[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-CCC(CO}_2\text{Me)C(CO}_2\text{Me)}\}(\mu\text{-CO})(CO)_8(\eta\text{-}C_5H_4R)_2]$

Orange

R = H, 14%

R = Me, 22%

182

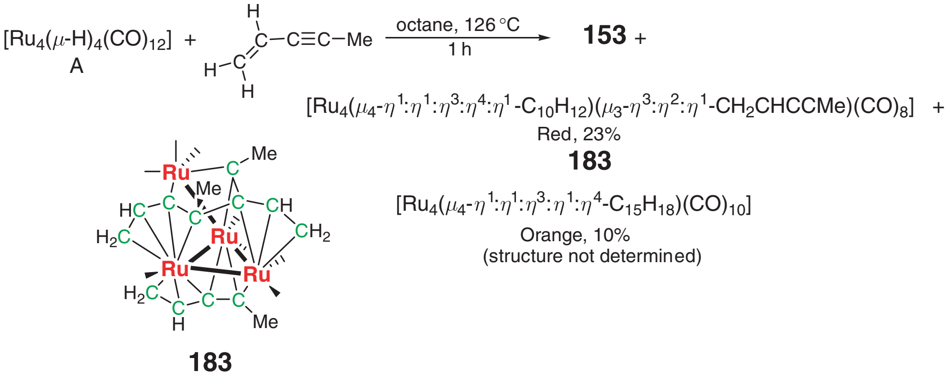
(130)

Ru* = Ru(CO)$_3$

R = H, Me

182

Besides **153** (Equation (107)), $[Ru_4\{\mu_4\text{-}(\eta^1{:}\eta^1){:}\eta^3{:}\eta^4{:}\eta^1\text{-}C_{10}H_{12}\}(\mu_3\text{-}\eta^3{:}\eta^2{:}\eta^1\text{-CH}_2\text{CHCCMe})(CO)_8]$ **183** is formed in the reaction of $[Ru_4(\mu\text{-H})_4(CO)_{12}]$ with pent-1-en-3-yne in refluxing octane (Equation (131)).[134] This complex is further discussed under the section dealing with μ_4-η^8-C ligands.


$[Ru_4(\mu\text{-H})_4(CO)_{12}]$ + $\xrightarrow[1\,h]{octane,\ 126\,°C}$ **153** +

A

$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^4{:}\eta^1\text{-}C_{10}H_{12})(\mu_3\text{-}\eta^3{:}\eta^2{:}\eta^1\text{-CH}_2\text{CHCCMe})(CO)_8]$ +

Red, 23%

183

$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^1{:}\eta^4\text{-}C_{15}H_{18})(CO)_{10}]$

Orange, 10%

(structure not determined)

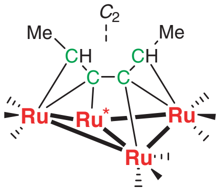
(131)

183

Besides compound **177** clusters of formula $[Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-RCHC}_2\text{CHR})(CO)_{12}]$ (R = Me, $SiMe_3$, Ph; **184**) are also formed in the reactions of $[Ru_4(\mu\text{-H})_4(CO)_{12}]$ with the 1,3-diynes RC_2C_2R (Equation (132)).[129] In this case, 1,4-hydrogenation of the diyne has taken place to give a 1,3-diene-2,3-diyl ligand bound to the Ru_4 butterfly in a $\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2$ arrangement.

$$\underset{\text{A}}{[Ru_4(\mu\text{-H})_4(CO)_{12}]} + R{-}C{\equiv}C{-}C{\equiv}C{-}R \xrightarrow[\text{3 h}]{\text{heptane, 98 °C}} \underset{25\text{–}40\%}{\mathbf{177}} +$$

R = Me, $SiMe_3$, Ph



184A

Ru* = Ru(CO)$_3$

$[Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-RCHC}_2\text{CHR})(CO)_{12}]$
184A R = Me: purple, 45%
184B R = $SiMe_3$: purple, 30%
184C R = Ph: purple, 30%
184

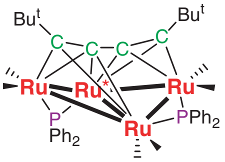
(132)

The phenyl derivative **184C** (R = Ph) is also one of the many products formed in the pyrolysis of $[Co_2Ru_3(\mu_5\text{-}PhC_2C_2Ph)(\mu\text{-}CO)_3(CO)_{11}]$ (Equation (133)).[130]

$$[Co_2Ru_3(\mu_5\text{-}PhC_2C_2Ph)(\mu\text{-}CO)_3(CO)_{11}] \xrightarrow[\substack{\text{overnight}\\ 6\%}]{\text{THF, 66 °C}} \underset{\text{Dark purple}}{\mathbf{184C}} \qquad (133)$$

Another derivative with a $\mu_4\text{-}\eta^4\text{-}C_4$ unit bound to an Ru_4 butterfly is $[Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^3\text{-C(Bu}^t)C_2C(Bu^t)(\mu\text{-}PPh_2)_2(CO)_8](CO)_{12}]$ formed by thermolysis of $[Ru_4(\mu\text{-}C_2Bu^t)(\mu_3\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2(CO)_9]$ **130** (Equation (134); see also Equation (81)).[99] The diyne is the result of end-to-end coupling of the acetylide ligands in the starting material. One of the contacts of a central C atom to a hinge Ru atom is non-bonding at 2.700(5) Å; the rest of the RuC distances are in the range 2.053(5)–2.430(5) Å. The observation of a singlet in both the $^1H(Bu^t)$ and $^{31}P\{^1H\}$ NMR spectra of **185** at −83 °C indicates the molecule has C_2 symmetry in solution.

$$\mathbf{130} \xrightarrow[\substack{\text{1 h}\\ \sim100\%}]{\text{toluene, 111 °C}} \underset{\mathbf{185}}{[Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^3\text{-CBu}^tC_2CBu^t)(\mu\text{-}PPh_2)_2(CO)_8]}$$



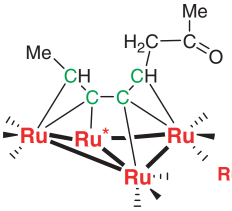
185

Ru* = Ru(CO)$_2$

(134)

Other clusters with $\mu_4\text{-}\eta^4\text{-}C_4$ units bound to an Ru_4 butterfly are $[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-CHMeCCC(H)CH}_2\text{C(O)Me}\}(CO)_{12}]$ **186** and $[Ru_4\{\mu_4\text{-}\eta^2{:}\eta^3{:}\eta^1{:}\eta^1\text{-CPhCPhCCCPh}_2\}(CO)_{12}]$ **187** prepared by the routes shown in Equations (135) and (136), respectively.[135,136]

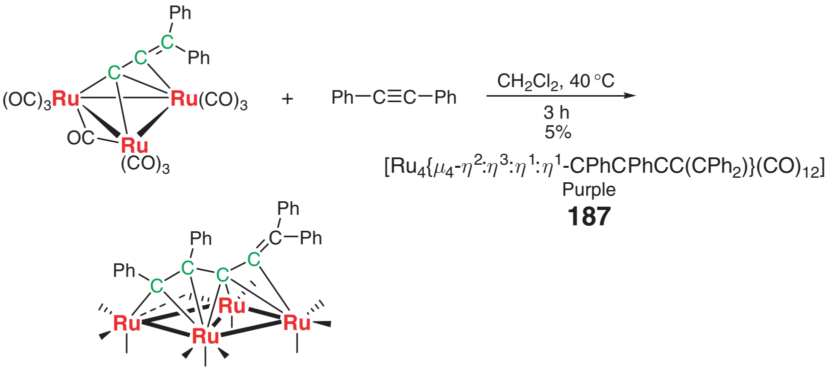
$$[Ru_3(CO)_{12}] + HC{\equiv}C\text{–}C(H)(Me)(OH) \xrightarrow[\substack{\text{8 h}\\ 10\%}]{\text{cyclohexane, 81 °C}} \underset{\substack{\text{Purple}\\ \mathbf{186}}}{[Ru_4\{\mu_4\text{-}2\eta^1{:}2\eta^2\text{-MeCHCCCHCH}_2\text{C(O)Me}\}(CO)_{12}}$$



Ru* = Ru(CO)$_3$

186

(135)



$[Ru_4\{\mu_4\text{-}\eta^2\text{:}\eta^3\text{:}\eta^1\text{:}\eta^1\text{-CPhCPhCC(CPh}_2)\}(CO)_{12}]$

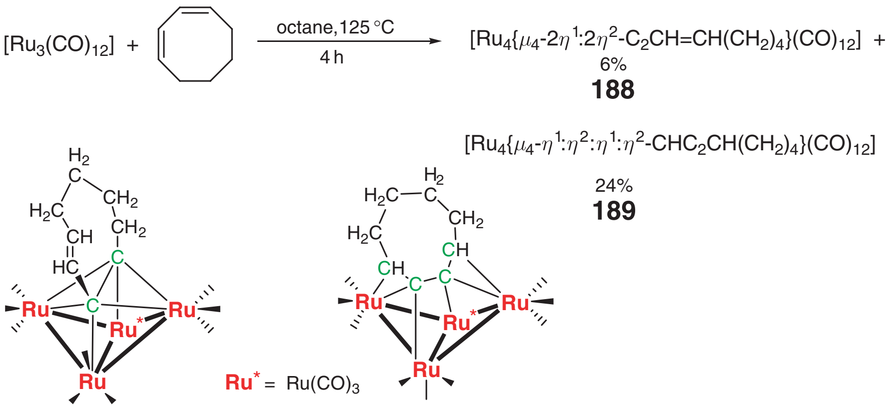
Purple

187

(136)

187

Two isomers are formed by heating $[Ru_3(CO)_{12}]$ in octane with cyclo-1,3-diene (Equation (137)).[137] One is $[Ru_4(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}C_8H_{10})(CO)_{12}]$ **188**, and has the common $\mu_4\text{-}2\eta^1\text{:}2\eta^2$ alkyne grouping (Table 15) and an uncoordinated C═C bond. In the second form of $[Ru_4(\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}C_8H_{10})(CO)_{12}]$ **189**, the hydrocarbon ligand is bound as a –CH═C═C═CH– unit. This unit formally donates six electrons (three double bonds) to the cluster give a 66 c.v.e. count rather than 64 c.v.e. as in **188**. Compound **189** is therefore electron precise for a cluster having four metal–metal bonds. Compound **188** readily converts to **189** on heating in hexane.



$[Ru_4\{\mu_4\text{-}2\eta^1\text{:}2\eta^2\text{-}C_2CH\text{=}CH(CH_2)_4\}(CO)_{12}]$ +

6%

188

$[Ru_4\{\mu_4\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^2\text{-CHC}_2CH(CH_2)_4\}(CO)_{12}]$

24%

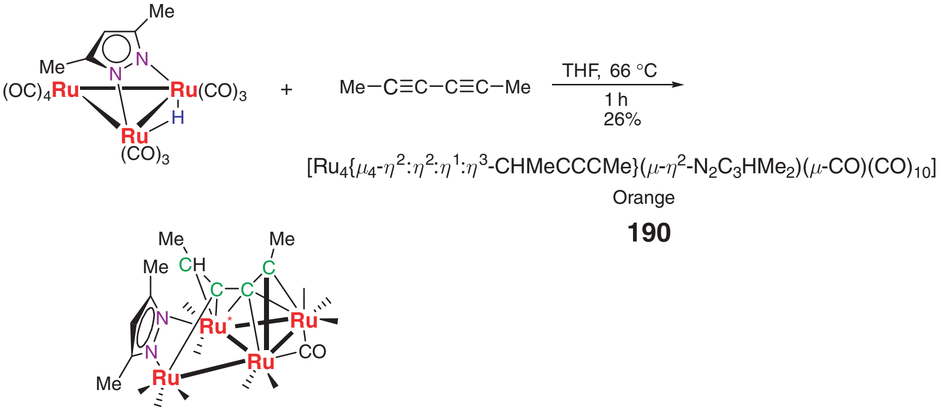
189

(137)

188

189

The cluster $[Ru_4\{\mu_4\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-CMeCCCHMe}\}(\mu\text{-}\eta^2\text{-}Me_2pz)(\mu\text{-CO})(CO)_{10}]$ **190** (Me$_2$pz = 3,5-dimethylpyrazolyl) is synthesized from the reaction of $[Ru_3(\mu\text{-}\eta^2\text{-}Me_2pz)(CO)_{10}]$ and 2,4-hexadiyne (Equation (138)).[138] In **190**, the Ru$_4$ skeleton adopts a rare planar spiked triangular geometry with the ynenyl ligand bound to all four Ru atoms in an $\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3$ mode.



$[Ru_4\{\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^3\text{-CHMeCCCMe}\}(\mu\text{-}\eta^2\text{-}N_2C_3HMe_2)(\mu\text{-CO})(CO)_{10}]$

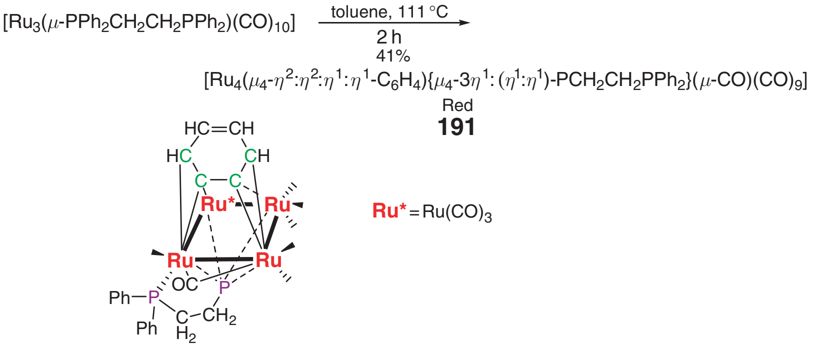
Orange

190

(138)

190

Pyrolysis of $[Ru_3(\mu\text{-}PPh_2CH_2CH_2PPh_2)(CO)_{10}]$ in refluxing toluene affords $[Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)\{\mu_4\text{-}3\eta^1{:}\eta^1{:}\eta^1\text{-}PCH_2CH_2PPh_2\}(\mu\text{-}CO)(CO)_9]$ **191** (Equation (139)) as the main product.[139,140] The structure of **191** reveals a benzyne ligand bound in an η^4-fashion to a square of Ru atoms. The other face of the Ru_4 square is capped by a $\mu_4\text{-}\eta^2\text{-}PCH_2CH_2PPh_2$ ligand. NMR studies found evidence for three independent dynamic processes: rotation of the benzyne ligand, CO migration, and a twisting motion of the $–CH_2CH_2–$ unit.[140]



$$[Ru_3(\mu\text{-}PPh_2CH_2CH_2PPh_2)(CO)_{10}] \xrightarrow[\substack{2\,h\\41\%}]{\text{toluene, 111 °C}} [Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)\{\mu_4\text{-}3\eta^1{:}(\eta^1{:}\eta^1)\text{-}PCH_2CH_2PPh_2\}(\mu\text{-}CO)(CO)_9] \qquad (139)$$

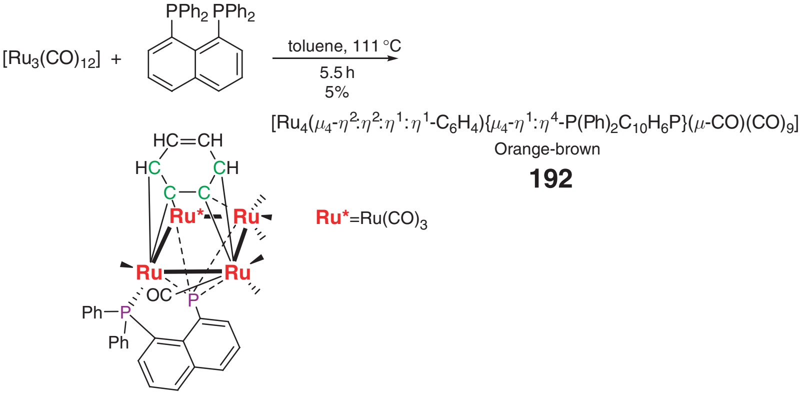
Red

191

Ru* = Ru(CO)$_3$

191

A cluster similar to **191** is $[Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\mu_4\text{-}3\eta^1{:}\eta^1{:}\eta^1\text{-}PC_{10}H_6PPh_2)(\mu\text{-}CO)(CO)_{10}]$ **192**, one of the products isolated from the reaction of $[Ru_3(CO)_{12}]$ with 1,8-bis(diphenylphosphino)naphthalene (Equation (140); see also Equation (83)).[101]



$$[Ru_3(CO)_{12}] + \text{1,8-}(PPh_2)_2C_{10}H_6 \xrightarrow[\substack{5.5\,h\\5\%}]{\text{toluene, 111 °C}} [Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)\{\mu_4\text{-}\eta^1{:}\eta^4\text{-}P(Ph)_2C_{10}H_6P\}(\mu\text{-}CO)(CO)_9] \qquad (140)$$

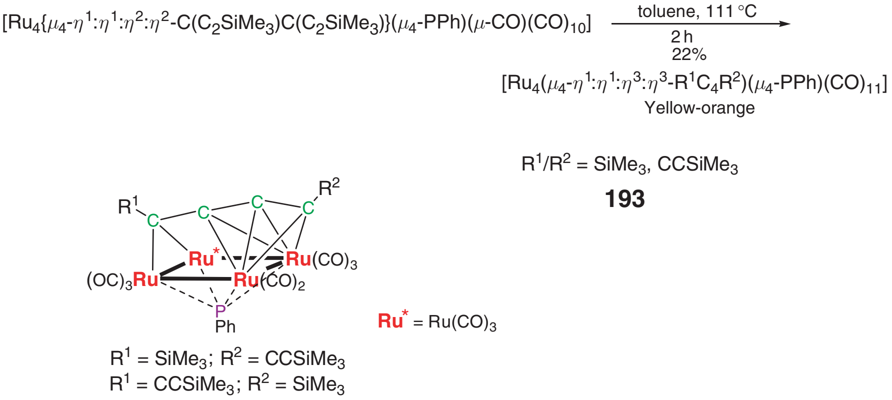
Orange-brown

192

Ru* = Ru(CO)$_3$

192

One product formed by the thermolysis of $[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}(Me_3SiC{\equiv}C)C_2(C{\equiv}CSiMe_3)\}(\mu\text{-}CO)(CO)_{10}]$ **167** in toluene is $[Ru_4(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}R^1CCCCR^2)(\mu_4\text{-}PPh)(CO)_{10}]$ ($R^1/R^2 = SiMe_3/CCSiMe_3$ **193** (Equation (141)).[125] The structure shown was assigned by spectroscopic methods.



$$[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(C_2SiMe_3)C(C_2SiMe_3)\}(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}] \xrightarrow[\substack{2\,h\\22\%}]{\text{toluene, 111 °C}} [Ru_4(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}R^1C_4R^2)(\mu_4\text{-}PPh)(CO)_{11}] \qquad (141)$$

Yellow-orange

$R^1/R^2 = SiMe_3, CCSiMe_3$

193

Ru* = Ru(CO)$_3$

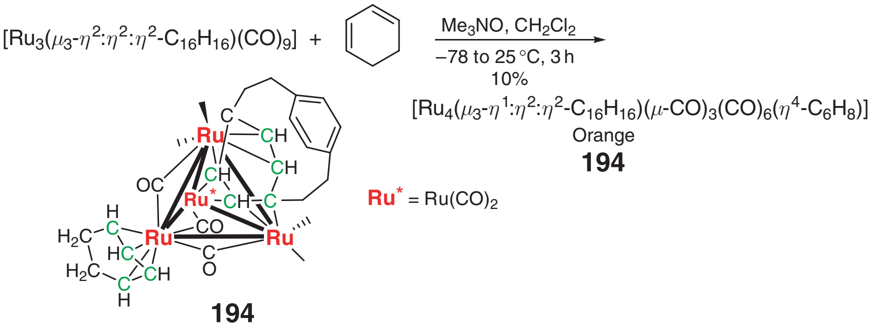
$R^1 = SiMe_3$; $R^2 = CCSiMe_3$
$R^1 = CCSiMe_3$; $R^2 = SiMe_3$

193

6.23.4.6 Derivatives with η^n-C_n ($n > 4$) Ligands

Table 23 contains some structural data for molecules in this class.

The reaction of the [2.2]paracylophane derivative $[Ru_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(CO)_9]$ with cyclohexa-1,3-diene in the presence of Me_3NO gives $[Ru_4(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}CO)_3(CO)_6(\eta^4\text{-}C_6H_8)]$ **194** (Equation (142)).[109] Cluster **194** contains an arene ring bound to an Ru_3 face of an Ru_4 tetrahedron in a previously unprecedented $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2$ configuration. The cluster contains an η^4-cyclohexadiene ligand bound to a single Ru atom that is also bound to three bridging carbonyls.



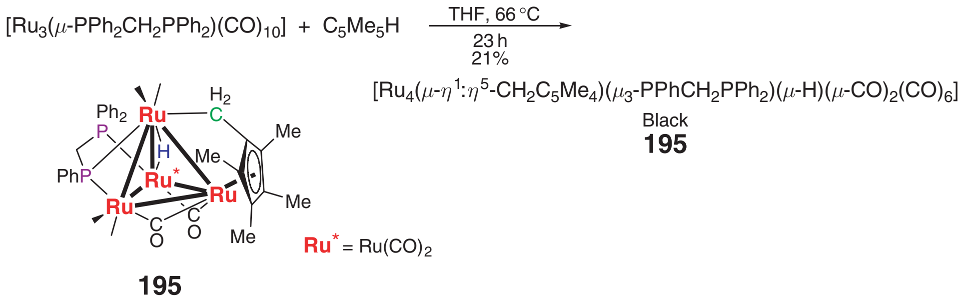
(142)

Table 23 Some structural data for derivatives with μ-η^n-C ligands ($n > 4$)

Compound	*Structure*[a]	*RuRu lengths*[b,c] (Å)
μ-η^6		
$[Ru_4(\mu_2\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}PPhCH_2PPh_2)(\mu\text{-}CO)_2(CO)_6]$ **195**	T	2.990(1),[b] 2.705(1),[c] 2.761(1),[c] 2.793(1), 2.813(1), 2.855(2)
$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^4\text{-}C_{15}H_{14})(CO)_{11}]$ **204**	ST	2.723(2),[e] 2.763(2), 2.827(2), 2.849(2)
μ-η^7		
$[Ru_4(\mu_2\text{-}\eta^3{:}\eta^4\text{-}C_7H_7)_2(\mu\text{-}CO)(CO)_6]$ **196**	T	2.745(1),[c] 2.728(2), 2.731(2), 2.810(2), 2.853(2), 2.868(2)
μ-η^8		
$[Ru_4(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^4\text{-}C_6H_5CCH_2Me)(\mu\text{-}CO)_2(CO)_8]$ **199**	T	2.693(1),[c] 2.693(1),[c] 2.852(1), 2.880(1), 2.908(1), 2.965(1)
$[Ru_4(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_6H_5CHCHMe)(\mu\text{-}CO)_2(CO)_8]$ Molecule A **197**	T	2.689,[c] 2.717,[c] 2.830, 2.832, 2.911, 2.945
$[Ru_4(\mu_3\text{-}\eta^8\text{-}C_6H_5CHCHMe)(\mu\text{-}CO)_2(CO)_8]$ Molecule B **197**	T	2.684,[c] 2.686,[c] 2.855, 2.859, 2.890, 2.932
$[Ru_4(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^4\text{-}C_6H_5CHCHMe)(\mu\text{-}CO)_2(CO)_8]$ Molecule C **197**	T	2.674,[c] 2.760,[c] 2.814, 2.888, 2.976
$[Ru_4(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^4\text{-}C_6H_5CHCHEt)(\mu\text{-}CO)_2(CO)_8]$ **198**	T	2.691, 2.693,[c] 2.846, 2.872, 2.920
$[Ru_4\{\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^4\text{-}1,4\text{-}C_6H_4(CMeCH_2)_2\}(\mu\text{-}CO)_2(CO)_8]$ **201**	T	2.6864(6),[c] 2.6924(5),[c] 2.8609(5), 2.8660(6), 2.8990(6), 2.9177(5)
$[Ru_4(\mu_4\text{-}\eta^4{:}\eta^2{:}\eta^1{:}\eta^3\text{-}C_{10}H_{12})(CO)_8]$ **183**	ST	2.7299(4), 2.7942(5),[d] 2.8342(4), 2.9769(4)
$[Ru_4(\mu_4\text{-}\eta^2{:}\eta^4{:}\eta^2{:}\eta^4\text{-}C_{28}H_{32}O_2)(CO)_{10}]$ **206**	LC	2.792(2), 2.986(2), 2.728(2)
μ-η^{10}		
$[Ru_4\{\mu_3\text{-}\eta^4{:}\eta^3{:}\eta^3\text{-}1,3,5\text{-}C_6H_4(CCH_2Me)_3\}(CO)_9]$ **202**	T	2.756(1), 2.859(2)[e]
μ-η^{11}		
$[Ru_4\{\mu_3\text{-}\eta^3{:}\eta^4{:}\eta^4\text{-}1,3,5\text{-}C_6H_4(CCH_2Me)_2Pr^i\}(\mu\text{-}CO)(CO)_8]$ **203**	T	2.6874(7),[c] 2.799(1), 2.8030(8), 2.8484(8), 2.8606(8), 2.8705(7)
$[Ru_4(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{15}H_{18})(CO)_9]$ **205**	T	2.711(1), 2.688(1), 2.841(1), 2.865(1), 2.873(1), 2.913(1)
μ-η^{12}		
$[Ru_4\{\mu_4\text{-}\eta^2{:}\eta^4{:}\eta^2{:}\eta^4\text{-}C(C_2SiMe_3)C(C_2SiMe_3)C(C_2SiMe_3)C_3(SiMe_3)C(C_2SiMe_3)C(C_2SiMe_3)\}(\mu_3\text{-}PPh)(CO)_{10}]$ **224**	UC	2.7912(4), 2.9964(4)[f]

[a] See Figure 1.
[b] Ru(μ-H)Ru.
[c] Ru(μ-CO)Ru.
[d] Spike RuRu.
[e] Only one outer RuRu length quoted.
[f] Molecule has C_3 axis.

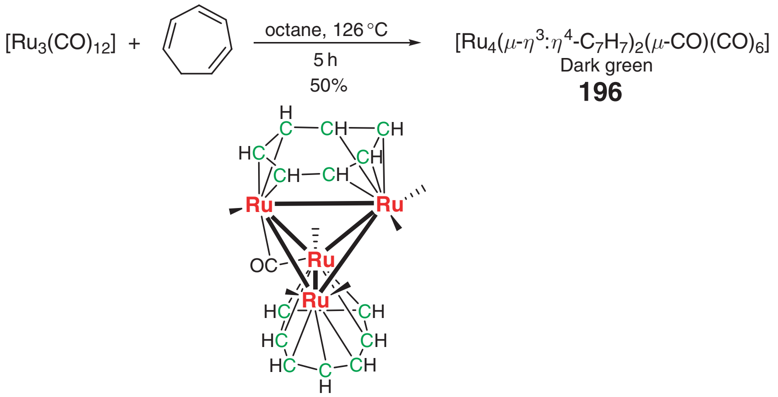
The reaction of $[Ru_3(\mu\text{-dppm})(CO)_{10}]$ with pentamethylcyclopentadiene in refluxing THF gives $[Ru_4(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)(\mu\text{-H})(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-CO})_2(CO)_6]$ **195** (Equation (143)).[141] Cluster **195** contains a tetrahedral Ru_4 nucleus with RuRu lengths in the range 2.705(1) (Ru(μ-CO)Ru)–2.990(1) Å (Ru(μ-H)Ru). One face of the tetrahedron is capped by the $\mu_3\text{-}PPhCH_2PPh_2$ ligand, with edges bridged by an H atom, two CO groups, and a $\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4$ ligand. The RuC σ-bond to the hydrocarbon ligand is somewhat long at 2.287(7) Å; the Ru–C(Cp) lengths are in the range 2.206(7)–2.276(7) Å.[141]



195

(143)

Reaction of $[Ru_3(CO)_{12}]$ with cycloheptatriene in refluxing octane affords $[Ru_4(\mu\text{-}\eta^3\text{:}\eta^4\text{-}C_7H_7)_2(\mu\text{-CO})(CO)_6]$ **196** with a tetrahedral Ru_4 skeleton encapsulated between two $\mu\text{-}\eta^3\text{:}\eta^4$ C_7H_7 ligands bridging opposite RuRu edges (Equation (144)).[142] The RuRu lengths in **196** are in the range 2.728(2)–2.868(2) Å. The RuC distances are in the range 1.90(1)–2.66(1) Å; the shortest bonds are to the pairs of C atoms that lie just above the two RuRu edges. The rings are approximately planar with the maximum elevation of a C atom above the plane of 0.14 Å. The ^1H NMR spectrum of **196** in $CDCl_3$ consists of a singlet (δ 4.18) consistent with rapid rotation of the cycloheptatrienyl rings on the NMR timescale.[142]

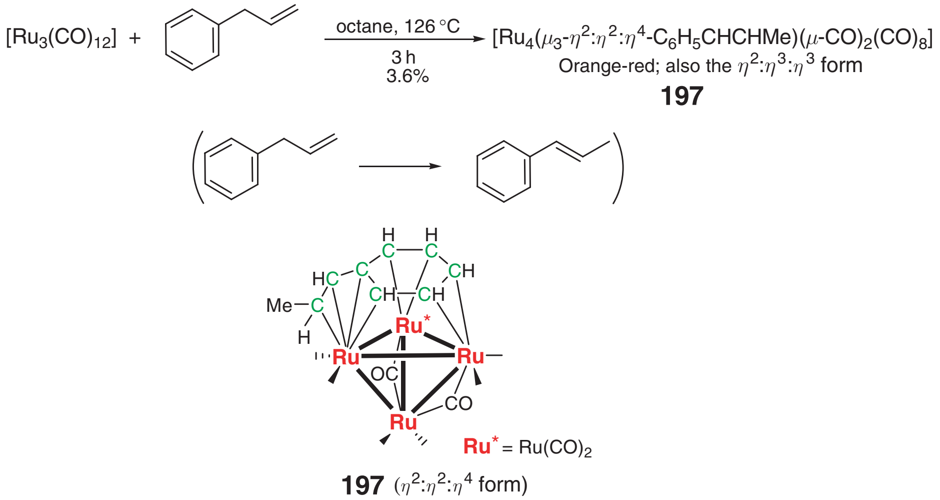


196

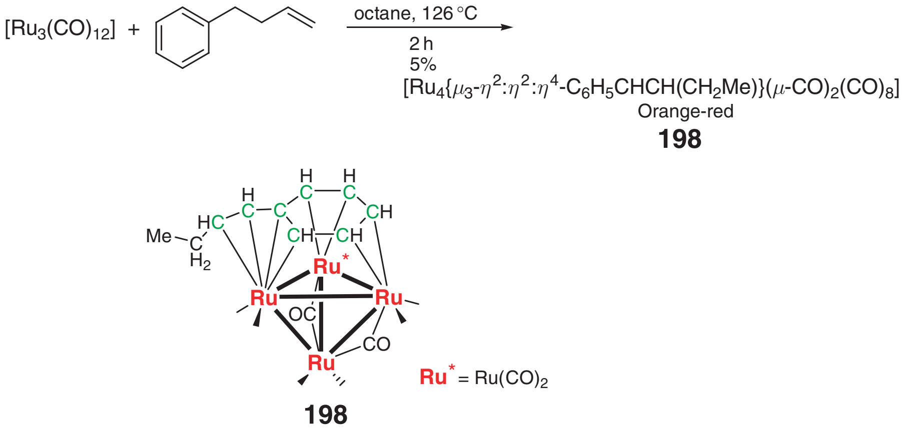
(144)

A series of tetrahedral Ru_4 clusters have been prepared in which an arene ring containing unsaturated side chains is bound to one face of the tetrahedron. These include $[Ru_4(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{-}C_6H_5CHCHMe)(\mu\text{-CO})_2(CO)_8]$ **197** and its $\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3$ form, $[Ru_4$ $(\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3\text{-}C_6H_5CHCHMe)(\mu\text{-CO})_2(CO)_8]$, $[Ru_4(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{-}C_6H_5CHCHEt)(\mu\text{-CO})_2(CO)_8]$ **198**,[143] $[Ru_4(\mu_3\text{-}\ \eta^2\text{:}\eta^2\text{:}\eta^4\text{-}\ C_6H_5CMeCH_2)(\mu\text{-CO})_2(CO)_8]$ **199**, $[Ru_4\{\mu_3\text{-}\eta^2\text{:}\eta^4\text{:}\eta^4\text{-}1,3\text{-}C_6H_4[C(Me)CH_2]_2\}(\mu\text{-CO})_2(CO)_7]$ **200**,[144] $[Ru_4\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{-}1,4\text{-}C_6H_4(CMeCH_2)_2\}(\mu\text{-CO})_2(CO)_8]$ **201**,[145] $[Ru_4\{\mu_3\text{-}\eta^4\text{:}\eta^4\text{:}\eta^3\text{-}1,3,5\text{-}C_6H_3(CMe_2)_2[C(Me)CH_2]\}(CO)_9]$

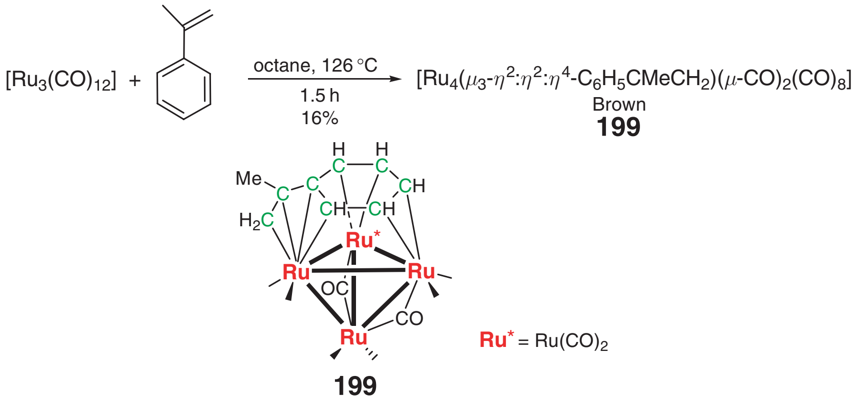
202, and $[Ru_4\{\mu_3\text{-}\eta^3\text{:}\eta^4\text{:}\eta^4\text{-}1,3,5\text{-}C_6H_3(CMeCH_2)_2(CHMe_2)\}(\mu\text{-}CO)(CO)_8]$ **203**.[146] The syntheses of the clusters are shown in Equations (145)–(150). Each cluster has a 60 c.v.e. count as expected for a tetrahedral Ru_4 core. The hydrocarbon ligand donates either eight electrons (**197**, **198**, **199**, and **201**) or 10 electrons (**200**, **202**, and **203**). Except for **202** (no μ-CO) and **203** (one μ-CO), each molecule has two bridging carbonyls. The RuRu bonds bridged by the CO ligands are, with one exception, shorter than the other RuRu bonds: Ru(μ-CO)Ru lengths range = 2.662(2) **200**–2.760(1) Å **197**; other RuRu lengths range = 2.756(1) (**202**)–2.976(1) Å (**197**). The one exception is a length of 2.837(2) quoted for an Ru(μ-CO)Ru distance in **200**. The $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination mode with alternating short and long CC lengths of a coordinated arene had been observed previously, but compounds **199** and **200** were the first examples where the arene is bound to a tetrahedron of metal atoms.[147] It is believed that coordination of the pendant arm helps favor the facial coordination of the aromatic ring. A consideration of the hydrocarbon precursor versus the coordinated form reveals that there is often migration of H atoms in the products (e.g., in **197** and **202**) presumably to allow the arene to bind more effectively to the Ru_3 face. The high yield of **200** is attributed to the strong $\mu_3\text{-}\eta^2\text{:}\eta^4\text{:}\eta^4$ coordination mode that is possible through the 1,3-disposition of the pendant isopropenyl sustituents. There are three crystallographically independent molecules in the unit cell of **197**. In one molecule, the arene ligand is bound to the Ru_3 face in a $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4$ arrangement, whereas in a second it is bound in a $\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3$ manner. The third molecule has the arene ligand bound in an intermediate fashion. Another feature of note in this class of clusters is that the ^{1}H NMR shifts of some of the protons of the arene CH groups are shifted upfield by as much as 7 ppm compared to those of the free ligand. This results in resonances close to 0 ppm.



(145)



(146)



$[Ru_3(CO)_{12}]$ + $\xrightarrow[\text{1.5 h, 16\%}]{\text{octane, 126 °C}}$ $[Ru_4(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^4\text{-}C_6H_5CMeCH_2)(\mu\text{-}CO)_2(CO)_8]$

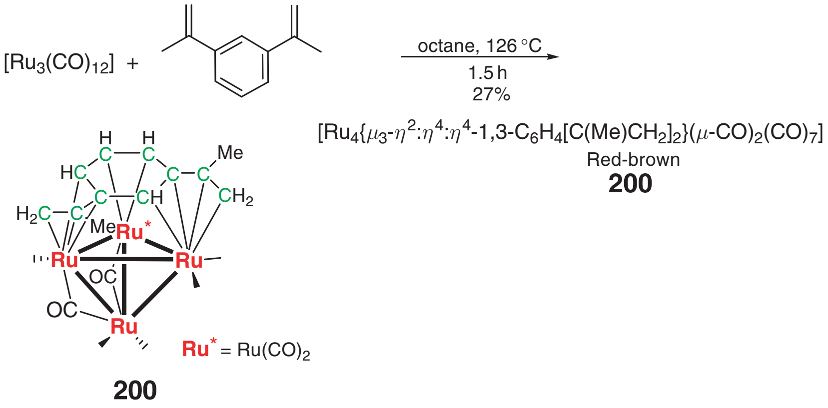
Brown

199

199

Ru* = $Ru(CO)_2$

(147)



$[Ru_3(CO)_{12}]$ + $\xrightarrow[\text{1.5 h, 27\%}]{\text{octane, 126 °C}}$

$[Ru_4\{\mu_3\text{-}\eta^2{:}\eta^4{:}\eta^4\text{-}1,3\text{-}C_6H_4[C(Me)CH_2]_2\}(\mu\text{-}CO)_2(CO)_7]$

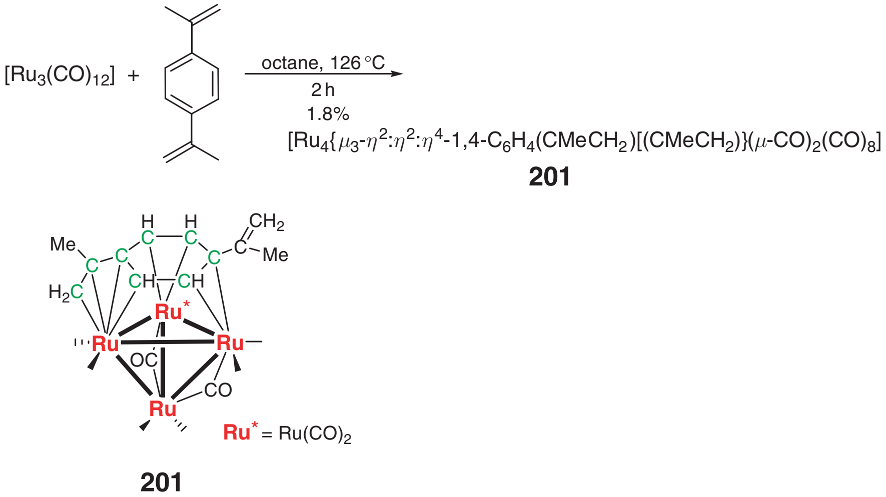
Red-brown

200

Ru* = $Ru(CO)_2$

200

(148)



$[Ru_3(CO)_{12}]$ + $\xrightarrow[\text{2 h, 1.8\%}]{\text{octane, 126 °C}}$

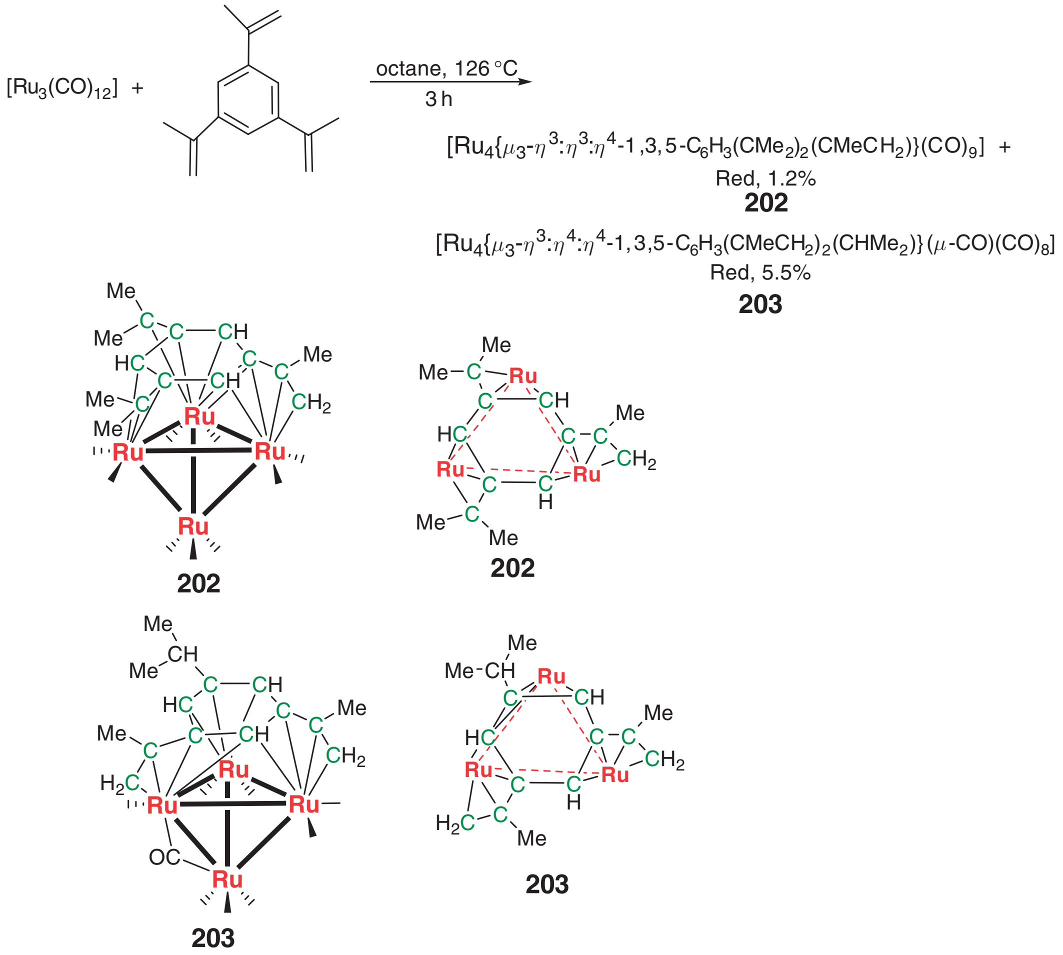
$[Ru_4\{\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^4\text{-}1,4\text{-}C_6H_4(CMeCH_2)[(CMeCH_2)\}(\mu\text{-}CO)_2(CO)_8]$

201

Ru* = $Ru(CO)_2$

201

(149)



$[Ru_4\{\mu_3\text{-}\eta^3{:}\eta^3{:}\eta^4\text{-}1,3,5\text{-}C_6H_3(CMe_2)_2(CMeCH_2)\}(CO)_9]$ +

Red, 1.2%

202

$[Ru_4\{\mu_3\text{-}\eta^3{:}\eta^4{:}\eta^4\text{-}1,3,5\text{-}C_6H_3(CMeCH_2)_2(CHMe_2)\}(\mu\text{-}CO)(CO)_8]$

Red, 5.5%

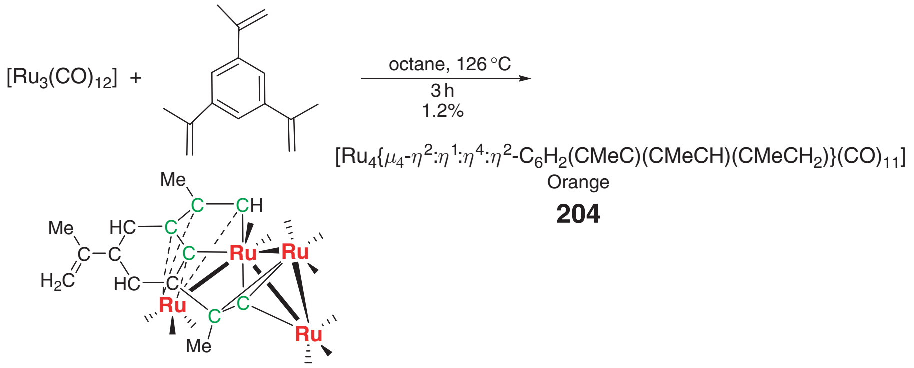
203

202 **202**

203 **203**

(150)

A third product isolated in low yield from the reaction of $[Ru_3(CO)_{12}]$ with 1,3,5-triisopropenylbenzene in refluxing octane is $[Ru_4\{\mu_4\text{-}\eta^2{:}\eta^1{:}\eta^4{:}\eta^2\text{-}C_6H_2(\eta^2\text{-}CMeC)(\eta^2\text{-}CMeCH)(CMeCH_2)\}(CO)_{11}]$ **204**, Equation (151), the first metallabicycle cluster.[148]



$[Ru_4\{\mu_4\text{-}\eta^2{:}\eta^1{:}\eta^4{:}\eta^2\text{-}C_6H_2(CMeC)(CMeCH)(CMeCH_2)\}(CO)_{11}]$

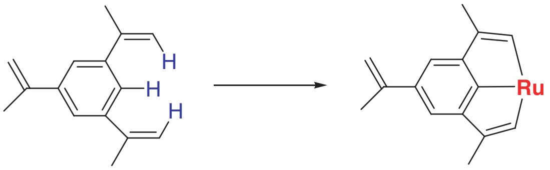
Orange

204

204

(151)

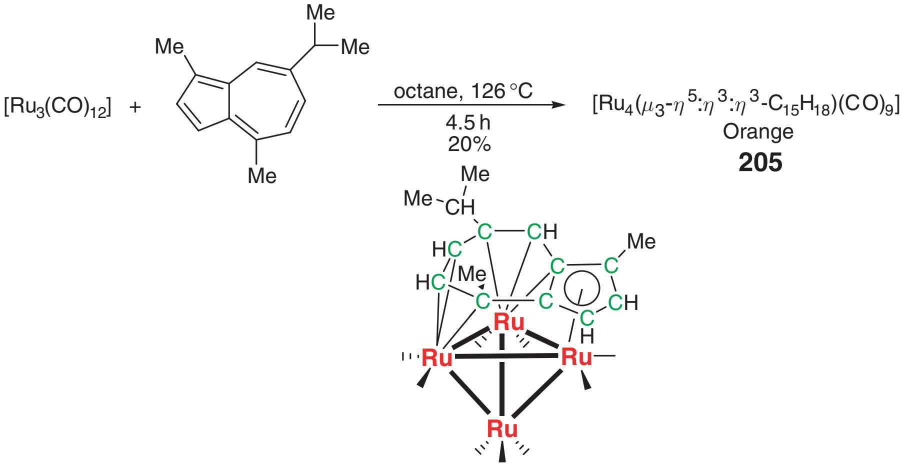
The hydrocarbon ligand is attached through 4σ and 3π bonds to an Ru_3 triangle and donates a total of 10 electrons. Four CH bonds of the original arene have been cleaved in the formation of **204** (e.g., Scheme 23). The metal core is



Scheme 23 Possible CH cleavage in 1,3,5-triisopropenylbenzene.

unusual in that it consists of a spiked triangular array of metal atoms; the spike RuRu bond at 2.723(2) Å is somewhat shorter than the other RuRu bonds (2.763(2), 2.827(2), 2.849(2) Å). One Ru atom forms a bridgehead in a nearly flat cyclopent[*c*,*d*]indenyl system ring system and is bound to the other three Ru atoms and two carbonyl ligands. Both five-membered metallacycles are π-bonded to other Ru atoms that are on opposite sides of the ligand plane.[148]

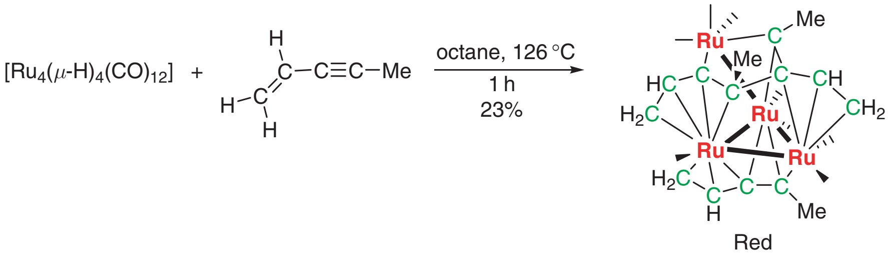
Heating guaiazulene (7-isopropyl-1,4-dimethylazulene) with $[Ru_3(CO)_{12}]$ in octane gives two products, one of which is the tetranuclear $[Ru_4(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{15}H_{18})(CO)_9]$ **205** (Equation (152)).[149] In cluster **205** both the five- and seven-membered organic rings are bound to the same face of the Ru_4 tetrahedron. The five-membered ring is bound in an η^5-mode to one Ru atom of the Ru_3 face; the seven-membered ring is bound to the other two metal atoms in an $\eta^3{:}\eta^3$ configuration. The azulene moiety donates 10 electrons to the cluster to give the molecule the usual 60 c.v.e. for an Ru_4 tetrahedron (the RuRu lengths are in the range 2.688(1)–2.913(1) Å); all the carbonyls are terminal.



205

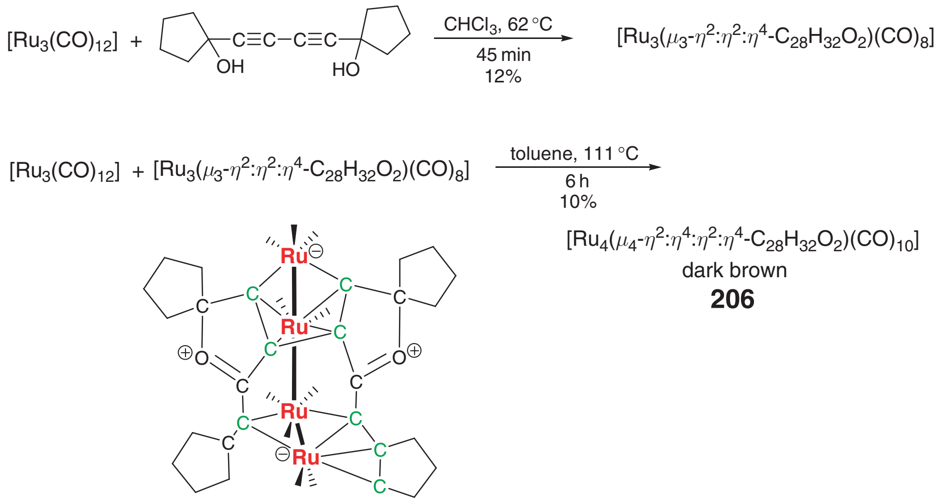
(152)

Coupling of alkynes on Ru_4 clusters is a feature of the chemistry of these compounds (see COMC (1995)). As mentioned previously (Equation (131)), $[Ru_4\{\mu_4\text{-}\eta^3{:}\eta^4{:}\eta^1{:}\eta^1{:}\eta^1\text{-}CH_2CHC(CMe)CMeCCHCH_2\}(\mu_3\text{-}\eta^3{:}\eta^2{:}\eta^1\text{-}C_5H_6)(CO)_8]$ **183** is formed in the reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with pent-1-en-3-yne in refluxing octane (Equation (153)).[134] The $C_{10}H_{12}$ ligand results from head-to-tail coupling of two alkyne units via the CC triple bonds. The Ru_4 skeleton consists of a spiked triangle with the spike Ru atom bent toward one of the edges of the triangle. The spike RuRu bond has a length of 2.794(1) Å; the RuRu lengths in the Ru_3 triangle are 2.730(1), 2.834(1), and 2.980(1) Å. The C_{10} chain in **183** donates 10 electrons to the cluster and the C_5 chain donates six. The $Ru_4(CO)_8$ unit has 48 electrons to yield a total of 64 c.v.e. for **182**. The four RuRu bonds in **183** are therefore in agreement with this count.



183

(153)



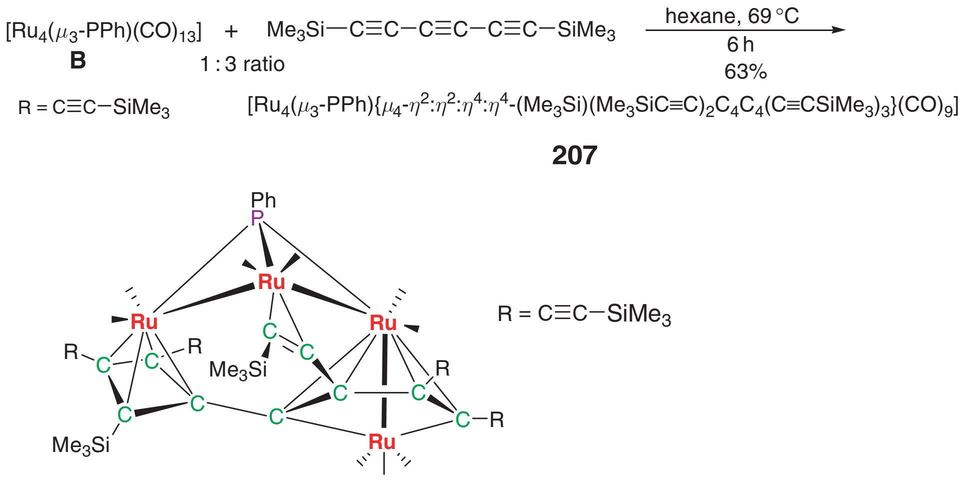
206

Scheme 24

Also isolated in the reaction of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with pent-1-en-3-yne is $[Ru_4(\mu_4\text{-}C_{15}H_{16})(CO)_{10}]$ (Equation (131)). The organic ligand is the result of coupling of three alkyne units. A structure based on spectroscopic data was proposed.[134]

Three triruthenium products are isolated from the reaction of $[Ru_3(CO)_{12}]$ with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne in refluxing chloroform. When one of the products ($[Ru_3(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^4\text{-}C_{28}H_{32}O_2)(CO)_8]$) is refluxed in toluene with more $[Ru_3(CO)_{12}]$, $[Ru_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^4{:}\eta^4\text{-}C_{28}H_{32}O_2)(CO)_{10}]$ **206** is isolated (Scheme 24).[150] The organic moiety in **206** is formed by coupling of two diyne ligands and is coordinated to an Ru_4 chain in a $\mu_4\text{-}\eta^2{:}\eta^4{:}\eta^2{:}\eta^4$ bonding mode. The RuRu lengths of the outer RuRu bonds (2.728(2) and 2.792(2) Å) are considerably shorter than the inner RuRu bond (2.986(2) Å).

The reaction of $[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]$ (compound **B**, see Equation (115)) with 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne ($Me_3SiC_6SiMe_3$) affords $Ru_4(\mu_3\text{-}PPh)\{\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^4{:}\eta^4\text{-}(Me_3Si)(Me_3SiC{\equiv}C)_2C_4C_4(C{\equiv}CSiMe_3)_3\}(CO)_9$ **207** in high yield (Equation (154)).[125,151] The organic ligand in **207** is a trimer of the starting alkyne and is an unusual example of a coordinated acyclic C_{18} fragment. The Ru_4 unit forms a U-shaped chain; the one outer RuRu bond given (2.791(1) Å) is significantly shorter than the inner RuRu bond (2.996(1) Å).



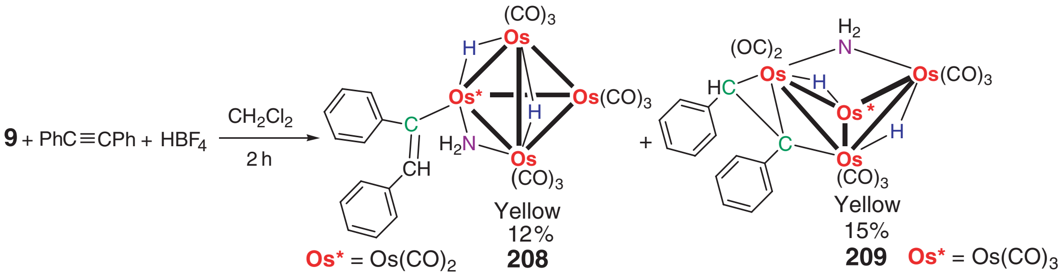
R = C≡C−SiMe3 (154)

207

6.23.5 Osmium Compounds with Hydrocarbon Ligands

6.23.5.1 Derivatives with η^1-C Ligands

The clusters $[Os_4\{\eta^1\text{-(Ph)CC(H)(Ph)}\}(\mu\text{-H})_2(\mu\text{-NH}_2)(CO)_{11}]$ **208** and $[Os_4\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CPh=CHPh}\}(\mu\text{-H})_2(\mu\text{-NH}_2)(CO)_{11}]$ **209** are obtained from the reaction of $[Os_4(\mu\text{-H})_4(CO)_{11}(\eta^1\text{-NH}_2OBu^t)]$ **73** and diphenylacetylene, C_2Ph_2 (Equation (155)).[67] The 1,2-diphenylethenyl ligand in **208** terminally binds to one osmium atom (OsC = 2.12(4) Å) of the distorted tetrahedron (OsOs lengths 2.752(2)–2.972(2) Å). It acts as a one-electron donor to give the characteristic 60 c.v.e. count. Also, an amido ligand bridges one OsOs edge (OsN = 2.03(2) and 2.12(3) Å).[67]



(155)

6.23.5.2 Derivatives with η^2-C_2 Ligands

The cluster $[Os_4\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CPh=CHPh}\}(\mu\text{-NH}_2)(CO)_{11}]$ **209** is a co-product and geometric isomer of **208** from the reaction shown in Equation (155). Unlike **208, 209** has an amido-supported Os_4 butterfly geometry (OsOs = 2.827(1)–3.028(1) Å) with a dihedral angle of 87.0°. The amido ligand bridges the two wingtip osmium atoms such that the OsN bond lengths are 2.09(1) and 2.13(1) Å. The 1,2-diphenylethenyl ligand acts as a three-electron donor with a $\mu\text{-}\eta^1\text{:}\eta^2$ coordination to one of the OsOs vectors.[67]

After stirring a solution of $[Os_4(\mu\text{-H})_4(CO)_{12}]$ and $Me_3NO{\cdot}2H_2O$ for 1.5 h, addition of 1,4-bis(ferrocenyl)butadiyne gives $[Os_4(\mu\text{-}\eta^2\text{:}\eta^1\text{-FcCCHC}_2\text{Fc})(\mu\text{-H})_3(CO)_{11}]$ **210**; Fc = $(\eta\text{-C}_5H_4)Fe(\eta\text{-C}_5H_5)$ (Equation (156)).[152] It contains an Os_4 tetrahedron with the bridging hydrides placed along the three longer OsOs bonds (2.9503(7)–2.9984(7) Å). The remaining (unbridged) OsOs bonds span the range of 2.7920(7)–2.7983(6) Å. The $FcCCHC_2Fc$ ligand bridges one OsOs edge where the two Os–C(Fc) bonds are equal (2.21(1) Å) while the Os–CHC_2Fc bond is longer (2.25(1) Å). The presence of the hydrogen atom in the $FcCCHC_2Fc$ unit is confirmed by the singlet at δ 3.88 in the ^{1}H NMR spectrum.[152]

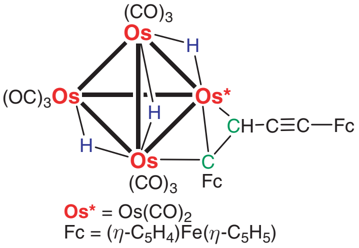
$$[Os_4(\mu\text{-H})_4(CO)_{12}] + Me_3NO{\cdot}2H_2O + \text{Fc–C≡C–C≡C–Fc} \xrightarrow[\text{2 h}]{\text{CH}_2\text{Cl}_2\text{/MeCN, reflux}}$$

9%

$[Os_4\{\mu\text{-}\eta^2\text{:}\eta^1\text{-FcCC(H)C}_2\text{Fc}\}(\mu\text{-H})_3(CO)_{11}]$

Red

210



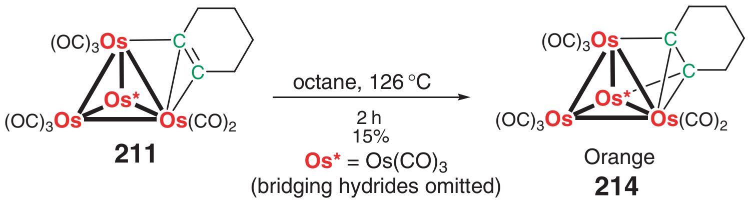
210

(156)

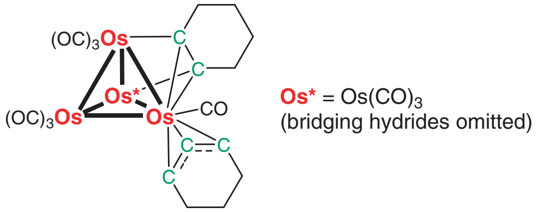
When $[Os_4(\mu\text{-H})_4(CO)_{10}(NCMe)_2]$ **72** reacts with cyclohexa-1,3-diene (C_6H_8) in refluxing CH_2Cl_2, a range of osmium clusters is produced (Equation (157)).[153] The first five products listed have been previously reported while the last three are new compounds, two of which contain an Os_4 core.

$$\mathbf{72} + \mathrm{C_6H_8} \xrightarrow[\text{18 h}]{\mathrm{CH_2Cl_2},\ 40\,^{\circ}\mathrm{C}} \underset{\mathbf{211}}{[\mathrm{Os_4}(\mu\text{-}\eta^2{:}\eta^1\text{-}\mathrm{C_6H_9})(\mu\text{-H})_3(\mathrm{CO})_{11}]} + [\mathrm{Os_4}(\mu\text{-H})_2(\mathrm{CO})_{12}(\eta^2\text{-}\mathrm{C_6H_8})] +$$
$$[\mathrm{Os_4}(\mu\text{-H})_2(\mathrm{CO})_{11}(\eta^4\text{-}\mathrm{C_6H_8})] + [\mathrm{Os_4}(\mu\text{-H})_2(\mathrm{CO})_{10}(\eta^6\text{-}\mathrm{C_6H_6})] +$$
$$[\mathrm{Os_4}(\mathrm{CO})_9(\eta^4\text{-}\mathrm{C_6H_8})(\eta^6\text{-}\mathrm{C_6H_6})] +$$
$$\underset{\substack{\text{Orange 5\%}\\ \mathbf{212}}}{[\mathrm{Os_4}(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}\mathrm{C_6H_8})(\mu\text{-H})(\mathrm{CO})_{10}(\eta^3\text{-}\mathrm{C_6H_9})]} + \tag{157}$$
$$\underset{\substack{\text{Orange 6\%}\\ \mathbf{213}}}{[\mathrm{Os_4}(\mu\text{-H})_2(\mathrm{CO})_{10}(\eta^6\text{-}\mathrm{C_6H_5C_6H_9})]} +$$
$$\underset{6\%}{[\mathrm{Os_5}(\mu\text{-H})_2(\mathrm{CO})_{13}(\eta^4\text{-}\mathrm{C_6H_8})]} +$$

Thermolysis of the known compound **211** in octane gives, by loss of two vinylic protons, the new cyclohexyne complex $[\mathrm{Os_4}(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}\mathrm{C_6H_8})(\mu\text{-H})_2(\mathrm{CO})_{11}]$ **214**; Equation (158).[153] Compound **214** similar in structure to **212**, which is discussed in Section 6.23.5.3. Structural information for **213** is present in Section 6.23.5.3.



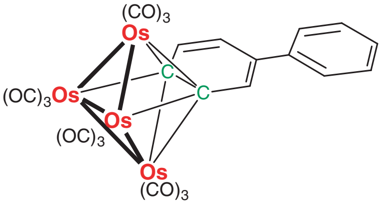
(158)



212

The reaction of biphenylene, $(\mathrm{C_6H_4})_2$, with $[\mathrm{Os_3(CO)_{12}}]$ yields $[\mathrm{Os_4}\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}(\mathrm{C_6H_3})\mathrm{Ph}\}(\mathrm{CO})_{12}]$ **215** (Equation (159)).[88] Complex **215** is the first butterfly cluster of the type $[\mathrm{Os_4(aryne)(CO)_{12}}]$. The hinge OsOs bond (2.883(2) Å) is significantly longer than the other four OsOs bonds (2.733(2)–2.778(1) Å) and is bridged by a phenylbenzyne moiety where the Os–C(benzyne) distances to the hinge osmium atoms (average 2.13(2) Å) are much shorter than those to the wingtip osmium atoms (average 2.29(2) Å). The dihedral angle between the benzene and phenyl plane is 33(1)°.[88]

$$[\mathrm{Os_3(CO)_{12}}] + (\mathrm{C_6H_4})_2 \xrightarrow[\text{15 h}]{n\text{-decane, } 200\,^{\circ}\mathrm{C}} \underset{23\%}{[\mathrm{Os_2}\{\mu\text{-}\eta^2{:}\eta^4\text{-}(\mathrm{C_6H_4})_2\}(\mathrm{CO})_6]} +$$
$$\underset{\substack{\text{Orange red}\\ 30\%\\ \mathbf{215}}}{[\mathrm{Os_4}\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}(\mathrm{C_6H_3})\mathrm{Ph}\}(\mathrm{CO})_{12}]} \tag{159}$$



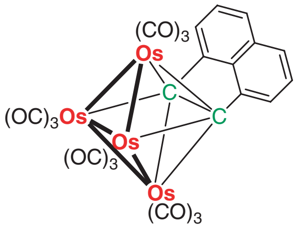
215

Refluxing an octane solution of $[\mathrm{Os_3}(\mu_3\text{-}\eta^2\text{-}\mathrm{C_{12}H_6})(\mu\text{-H})_2(\mathrm{CO})_9]$ and acenaphthylene ($\mathrm{C_{12}H_8}$) affords four new compounds, including the tetraosmium cluster $[\mathrm{Os_4}(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}\mathrm{C_{12}H_6})(\mathrm{CO})_{12}]$ **216** (Equation (160)).[154] As in **215**, the OsOs hinge bond of **216** is much longer (2.909(1) Å) than the other OsOs bonds (2.750(1)–2.773(1) Å). The four metal atoms are bridged by an acenaphthyne ligand where the σ bonds to the hinge osmium atoms are shorter (OsC = 2.123(7) and 2.128(7) Å) than the π bonds to the wingtip osmium atoms (OsC = 2.242(7)–2.261(7) Å).[154]

$$[\mathrm{Os_3}(\mu_3\text{-}\eta^2\text{-C_{12}H_6})(\mu\text{-H})_2(\mathrm{CO})_9] + \mathrm{C_{12}H_8} \xrightarrow[8\,\mathrm{h}]{\text{octane, }160\,^{\circ}\mathrm{C}}$$

$$\underset{\substack{\text{Orange }11\%\\ \mathbf{216}}}{[\mathrm{Os_4}(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-C_{12}H_6})(\mathrm{CO})_{12}]} + \underset{13\%}{[\mathrm{Os_2}(\mu\text{-}\eta^4\text{-C_{24}H_{12}})(\mathrm{CO})_6]}$$

$$+ \underset{4\%}{[\mathrm{Os_3}(\mu_3\text{-}\eta^4\text{-C_{24}H_{13}})(\mu\text{-H})(\mathrm{CO})_9]} + \underset{3\%}{[\mathrm{Os_2}(\mu\text{-}\eta^4\text{-C_{24}H_{12}})(\mathrm{CO})_5(\eta^2\text{-C_{12}H_8})]} \qquad (160)$$



216

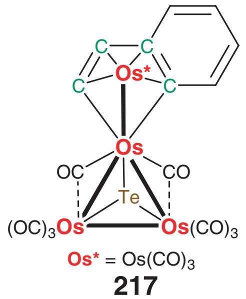
6.23.5.3 Derivatives with η^3-$\mathrm{C_3}$ Ligands

The complex $[\mathrm{Os_4}(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}\mathrm{C_6H_8})(\eta^3\text{-}\mathrm{C_6H_9})(\mu\text{-H})(\mathrm{CO})_{10}]$ **212** (see Equation (157)) has a distorted tetrahedron (OsOs 2.653(1)–2.891(1) Å) with two $\mathrm{C_6}$ rings, one of which coordinates to an osmium atom in an η^3-allylic manner (OsC = 2.12(4)–2.34(4) Å). The other $\mathrm{C_6}$ ring is a cyclohexyne-type ligand that bridges a triangular face by donating four electrons via two σ-bonds (OsC = 2.17(2) and 2.18(3) Å) and a π-interaction (OsC = 2.19(2) and 2.23(3) Å).[153]

6.23.5.4 Derivatives with η^4-$\mathrm{C_4}$ Ligands

Four major products are isolated from the reaction of $[\mathrm{Os_3(CO)_{12}}]$ and benzo[*b*]tellurophene ($\mathrm{C_8H_6Te}$) in *n*-heptane, one of which is $[\mathrm{Os_4}(\mu\text{-}2\eta^1{:}\eta^4\text{-}\mathrm{C_8H_6})(\mu_3\text{-Te})(\mathrm{CO})_{11}]$ **217** (Equation (161)).[155] The reaction involves the cleavage of the TeC bond rather than a CH bond in the benzo[*b*]tellurophene molecule. The structure of **217** contains a triangular $\mathrm{Os_3}$ skeleton (OsOs = 2.784(1)–2.886(1) Å) spiked by a fourth osmium atom (OsOs = 2.727(1) Å). The latter osmium atom supports the bridging $\mathrm{C_8H_6}$ unit. The tellurium atom (extruded from the heterocycle) bridges the $\mathrm{Os_3}$ triangle with OsTe distances between 2.636(1)–2.647(1) Å. The IR spectrum shows bands corresponding to two semibridging carbonyls (at 1926 and 1890 cm^{-1}). These two bridging carbonyls bind to one osmium atom with an average OsC bond length of 1.90 Å, and 2.57 Å to the second osmium atom.[155]

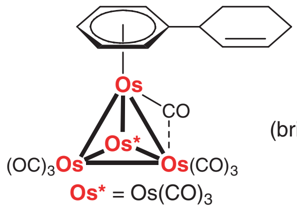
$$[Os_3(CO)_{12}] + C_8H_6Te \xrightarrow[14\ h]{n\text{-heptane, }98\ ^{\circ}C} \underset{18\%}{[Os_3(\mu\text{-}C_8H_6Te)(CO)_{10}]} + \underset{20\%}{[Os_2(\mu\text{-}C_8H_6Te)(CO)_6]} + \underset{10\%}{[Os_2(\mu\text{-}C_8H_6)(CO)_6]} + \underset{\substack{\text{Yellow}\\ 15\%\\ \mathbf{217}}}{[Os_4(\mu\text{-}\eta^4{:}\eta^2\text{-}C_8H_6)(\mu_3\text{-}Te)(CO)_{11}]} \qquad (161)$$



217

6.23.5.5 Derivatives with η^n-C_n ($n > 4$) Ligands

The synthesis of $[Os_4(\eta^6\text{-}C_6H_5C_6H_9)(\mu\text{-}H)_2(CO)_{10}]$ **213** is shown in Equation (155). Infrared data show the presence of both terminal and bridging carbonyl ligands. The OsOs bonds in the tetrahedron are in the range of 2.766(2)–2.951(2) Å. There is one semibridging carbonyl ligand which binds closer to one osmium atom (OsC = 1.95(2) Å) than to the other (OsC = 2.40(3) Å). The two-ring system of benzene and cyclohexene are connected via a single CC bond with the aromatic ring coordinating to an osmium atom in an η^6-manner.[153]



(bridging hydrides omitted)

213

6.23.6 Ru$_4$ and Os$_4$ Compounds with Carbon–Heteroatom Ligands

6.23.6.1 Ruthenium Derivatives

Some structural data for Ru_4 clusters with bridging carbon–heteroatom ligands are displayed in Table 24.

As indicated by electrospray mass spectroscopy, a number of products are formed when $[Ru_3(CO)_{12}]$ is heated in toluene with 4 equivalents of phenylisonitrile. Chromatography of the mixture produced a band containing two products from which crystals of $[Ru_4(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-CNPh})_2(CO)_{11}(CNPh)]$ **218** were isolated (Equation (162)).[156] The molecule has a rare spiked triangular Ru_4 framework where the spike Ru atom occupies an axial site of the Ru_3 cluster (i.e., essentially perpendicular to the Ru_3 plane). The η^1-CNPh ligand is bound in the axial site *trans* to the spike RuRu bond. The spike RuRu bond has a length of 2.826(1) Å, while the two other RuRu bonds bridged by the isonitrile ligands have lengths of 2.823(1) and 2.834(1) Å; the unbridged RuRu bond has a length of 2.890(1) Å.

Table 24 Skeletal structure and RuRu bond lengths for clusters with μ-E-η^n-C ligands

Compound	*Structure*[a]	*Ru(μ-CO)Ru* (Å)	*Other RuRu* (Å)
μ-N-η-C			
$[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}C_4H_3N)(\mu\text{-}CO)(CO)_{10}]$ **169A**[b]	**S**	2.804(1)	2.832(1), 2.852(1), 2.864(1)
$[Ru_4(\mu\text{-}\eta^2{:}\eta^4\text{-}NPhCHCHCPh)_2(\mu\text{-}CO)_2(CO)_8]$ **219**	**LC**	2.776(1)[c]	2.698(1)[c]
μ-P-η-C			
$[Ru_4\{\mu_4\text{-}\eta^3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}P(CF_3)CMeCMe\}_2(\mu\text{-}CO)_2(CO)_{10}]$ **220**	**B**	2.784(2), 2.833(1)	2.864(1),[d] 2.872(2), 2.906(2)
$[Ru_4(\mu_4\text{-}\eta^2{:}\eta^1{:}\eta^1{:}\eta^1\text{-}PPh_2CC)_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{10}]$ **221**	**U**		2.8699(7), 2.8902(6), 2.8159(6)
μ-O-η-C			
$[Ru_4\{\mu\text{-}\eta^1{:}\eta^2\text{-}OC(NC_4H_4)CHCPh\}_2(\mu_3\text{-}H)_2(CO)_{10}]$ **227**	**ZC**		3.011(1), 2.926(1)[c]
$[Ru_4(\mu_3\text{-}\eta^6{:}\eta^1{:}\eta^2\text{-}1,2\text{-}O_2C_6H_4)_2(CO)_8]1{:}3$ **229**	**Ru$_3$C**		2.846(1)[e]
$[Ru_4(\mu_3\text{-}\eta^6{:}\eta^1{:}\eta^2\text{-}1,2,3,5\text{-}O_2C_6H_2Bu^t{}_2)_2(CO)_8]$	**Ru$_3$C**		2.787(1), 2.791(1)
$[Ru_4(\mu_3\text{-}\eta^6{:}\eta^1{:}\eta^2\text{-}1,2,3,5\text{-}O_2C_6H_2Bu^t{}_2)_2(CO)_7\{CPhC(CO_2Et)\}]$ **232**	**Ru$_3$C**		2.802(2), 2.810(2)
$[Ru_4(\mu_3\text{-}\eta^6{:}\eta^1{:}\eta^2\text{-}1,2,3,5\text{-}O_2C_6H_2Bu^t{}_2)_2(CO)_6(py)_2]$ **231**	[f]		2.712(1), 2.846(1)
$[Ru_4(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-}OCCHCH)(\mu\text{-}CO)_2(CO)_9(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)]$ **228**	**ST**	2.8259(3),[g] 2.8910(2), 2.8111(2),[g] 2.8627(2)[f]	2.7699(3), 2.8613(3); 2.7656(3), 2.8702(3)[f]
μ-(O-W)-η-C			
$[Ru_4\{\mu_4\text{-}\eta^3{:}\eta^2{:}\eta^1{:}\eta^2\text{-}O[W(Cp^*)O]C_2Ph\}(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_9]$ **233**	**PS**	2.714(1), 2.780(1), 2.806(1) (RuW)	2.876(1), 2.962(1)
$[Ru_4\{\mu_4\text{-}\eta^3{:}\eta^2{:}\eta^1{:}\eta^2\text{-}O[W(Cp^*)O]C_2Ph\}(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_5(\eta^6\text{-}C_6H_5Me)]$ **234**	**PS**	2.672(1), 2.804(1) (RuW)	2.808(1), 2.827(1), 2.981(1)

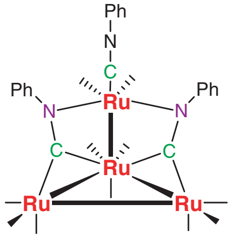
[a] See Figure 1. Ru$_3$C = Ru$_3$ chain.
[b] Triclinicform
[c] Molecule has an inversion center.
[d] Hinge RuRu bond.
[e] Molecule has a twofold axis.
[f] Two independent molecules. Molecule has two RuRu bonds.
[g] Spiked RuRu bond.

$$[Ru_3(CO)_{12}] + PhNC \xrightarrow[30\,\text{min}]{\text{toluene, }111\,°\text{C}} [Ru_4(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-}CNPh)_2(CO)_{11}(CNPh)] \tag{162}$$

1 : 4 ratio

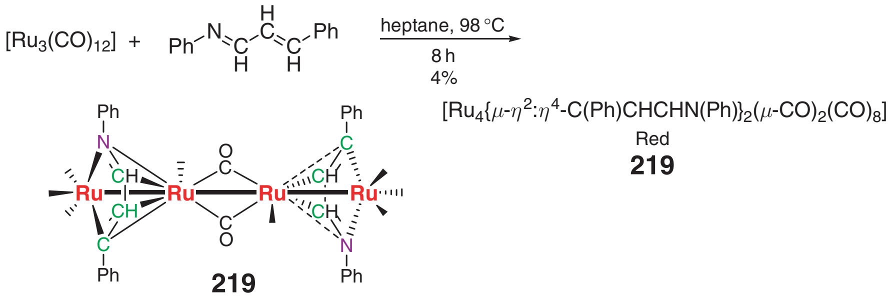
Red

218



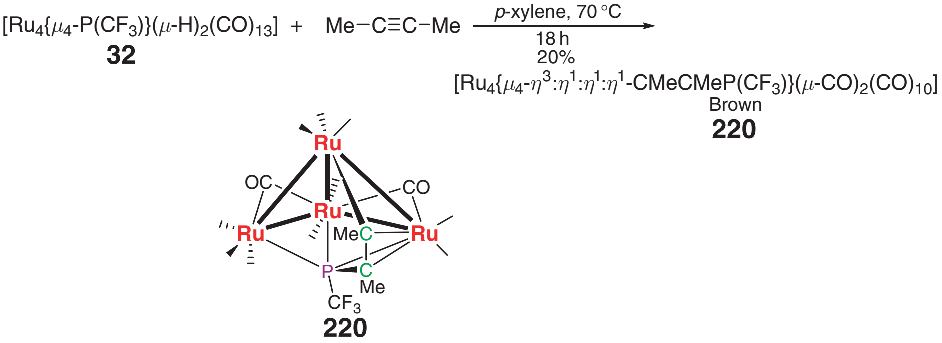
218

The reaction of $[Ru_3(CO)_{12}]$ with 3,*N*-diphenylprop-2-enimine gives a number of products, one of which is the tetranuclear $[Ru_4(\mu\text{-}\eta^2{:}\eta^4\text{-}CPhCHCHNPh_2)(\mu\text{-}CO)_2(CO)_8]$ **219** (Equation (163)).[157] The molecule has a crystallographic center of inversion with the outer RuRu length at 2.698(1) Å and the inner RuRu length at 2.776(1) Å. The molecule consists of two azaruthenacyclopentadienyl ligands that are connected by a central $Ru_2(\mu\text{-}CO)_2(CO)_2$ unit. If these ligands donate six electrons to the cluster, then **219** has 66 c.v.e. and the expected three RuRu bonds.



(163)

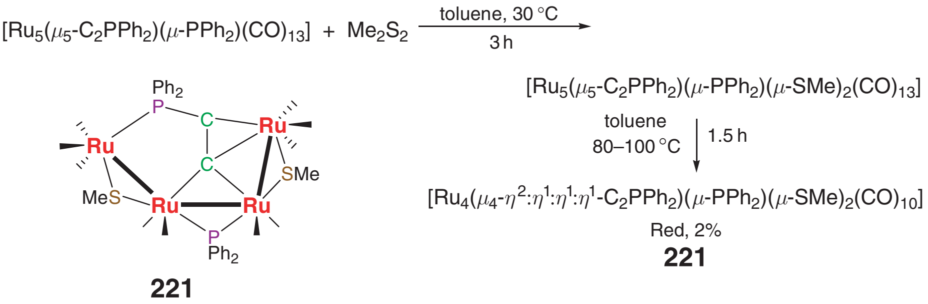
Addition of dimethylacetylene to $[Ru_4\{\mu_4\text{-}P(CF_3)\}(\mu\text{-}H)_2(CO)_{13}]$ **32** affords $[Ru_4\{\mu_4\text{-}\eta^3\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}CMeCMeP(CF_3)\}(\mu\text{-}CO)_2(CO)_{10}]$ **220** (Equation (164)).[33] The addition involves an Ru_4 skeletal transformation from a spiked triangle to butterfly geometry and formation of a PC(alkyne) bond. The RuRu bonds in **220** fall in the range 2.784(2) (Ru(μ-CO)Ru)–2.906(2) Å. As is typical, the RuC σ-bond (2.16(1) Å) is shorter than the RuC π-bonds (2.26(1) and 2.32(2) Å).



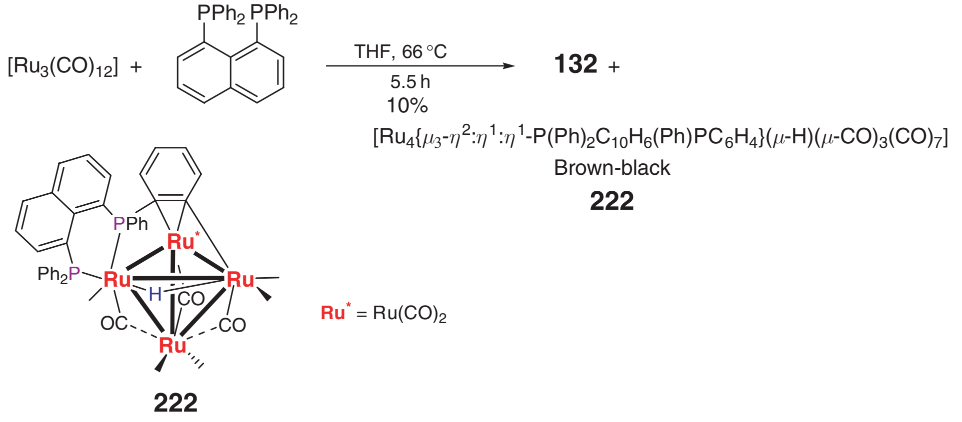
(164)

The compound $[Ru_4(\mu_4\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}SMe)_2(CO)_{10}]$ **221** is a minor product formed in the reaction of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ with dimethyl disulfide (Scheme 25).[158] The compound has a distorted U-shaped chain of four ruthenium atoms held together by the $\mu_4\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}C_2PPh_2$ group. The outer RuRu bonds bridged by the SMe ligands have lengths of 2.816(1) and 2.870(1) Å; the inner RuRu bond bridged by a PPh_2 ligand has a length of 2.890(1) Å.

A second product formed from the reaction between $[Ru_3(CO)_{12}]$ and 1,8-bis(diphenylphosphino)naphthalene in refluxing THF is $[Ru_4\{\mu_3\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-}PPh_2C_{10}H_6(Ph)P(C_6H_4)\}(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_7]$ **222** (Equation (165); see also Equation (83)).[101] Cluster **222** has one face of an Ru_4 tetrahedron spanned by a $PPh_2C_{10}H_6PPhC_6H_4$ ligand, previously found in an Ru_3 compound. The RuRu lengths of the tetrahedron are in the range 2.713(1) (Ru(μ-CO)Ru)–2.936(1) Å (Ru(μ-H)Ru). The C_6H_4 fragment bridges one RuRu bond (of length 2.824(1) Å) via a σ-bond (Ru–C = 2.120(5) Å) and a π-bond (Ru–C = 2.314(5), 2.302(5) Å).



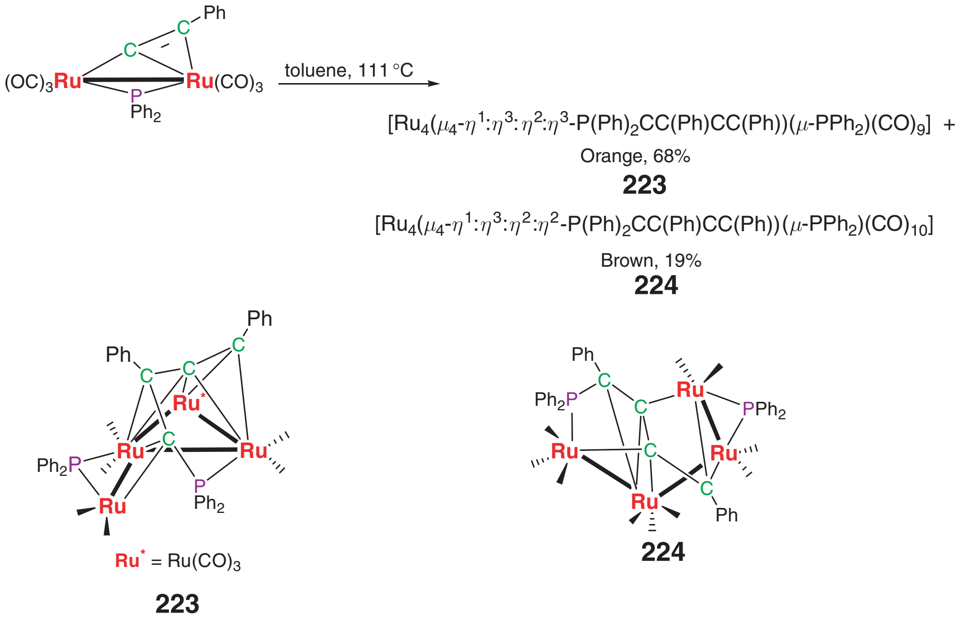
Scheme 25



(165)

The preparation of the naphthyne derivative $[Ru_4(\mu_4\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}PPh_2C_{10}H_5)(CO)_{11}]$ has been briefly mentioned.[159]

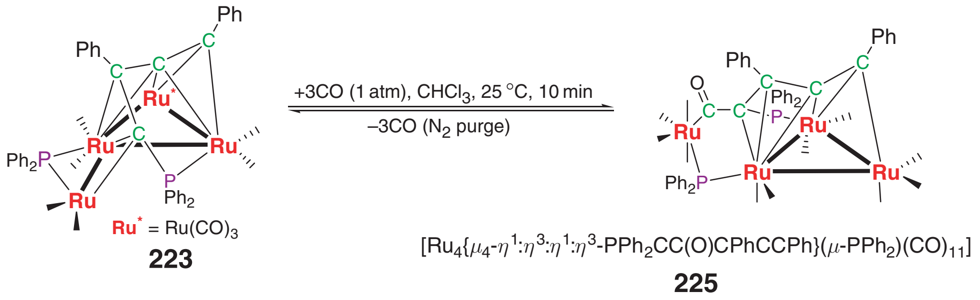
Refluxing a toluene solution of $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCPh)(\mu\text{-}PPh_2)(CO)_6]$ yields $[Ru_4(\mu_4\text{-}\eta^1\text{:}\eta^3\text{:}\eta^2\text{:}\eta^3\text{-}PPh_2CCPhCCPh)(\mu\text{-}PPh_2)(CO)_9]$ 223 and $[Ru_4(\mu_4\text{-}\eta^1\text{:}\eta^3\text{:}\eta^2\text{:}\eta^2\text{-}PPh_2CPhCCCPh)(\mu\text{-}PPh_2)(CO)_{10}]$ (224; Equation (166)).[160] Compound 223 has a spiked triangular cluster of Ru atoms. The spike RuRu bond has a length of 2.920(1) Å, while the other RuRu distances show a remarkable variation (2.677(2), 2.832(1), and 3.015(1) Å). A PC_4 chain is bound to all four Ru atoms and is the result of head-to-tail coupling of two ynyl ligands and formation of a PC bond between a phosphido bridge and the α-C of one acetylide. (Other ynyl–ynyl coupling is typically head-to-head.) The $Ph_2PCCPhCCPh$ ligand functions as a nine-electron donor to give 223 a 62 c.v.e. count which is two electrons short for four RuRu bonds. The spike Ru atom is considered to have a 16-electron count consistent with its unusual stereochemistry.



(166)

Cluster 224 has a twisted U-shaped Ru_4 chain with one short (2.746(1) Å, Ru(μ-PPh_2)Ru), and two normal (average 2.855 Å) RuRu bonds. In this case, the PC_4 chain is the result of head-to-head coupling of the ynyl fragments. The bonding of the C_4 unit to the Ru_4 frame poses a conundrum for conventional bonding descriptions as the two central C atoms of the unit are five coordinate. The ligand can simplistically be considered as a nine-electron donor to give 224 64 c.v.e. whereas 66 c.v.e. (3 MM bonds) would make it electron precise.

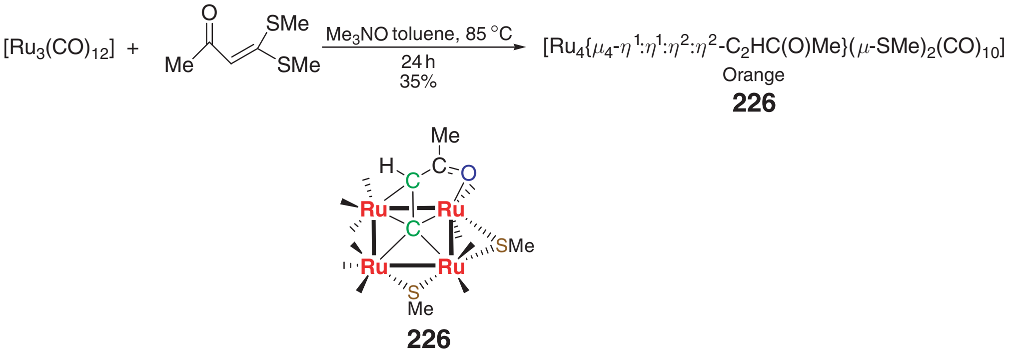
Bubbling CO through a solution of 223 at room temperature causes its rapid and clean conversion to $[Ru_4\{\mu_4\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{:}\eta^3\text{-}PPh_2C[C(O)]CPhCCPh\}(\mu\text{-}PPh_2)(CO)_{11}]$ 225. This facile carbonylation is fully reversible by purging the solution with air or nitrogen (Scheme 26). The CO addition occurs at the unsaturated spike Ru atom in 223 to give four bound carbonyls in the product compared to two in the starting compound. Cleavage of the spike RuRu bond accompanies the addition. The



Scheme 26

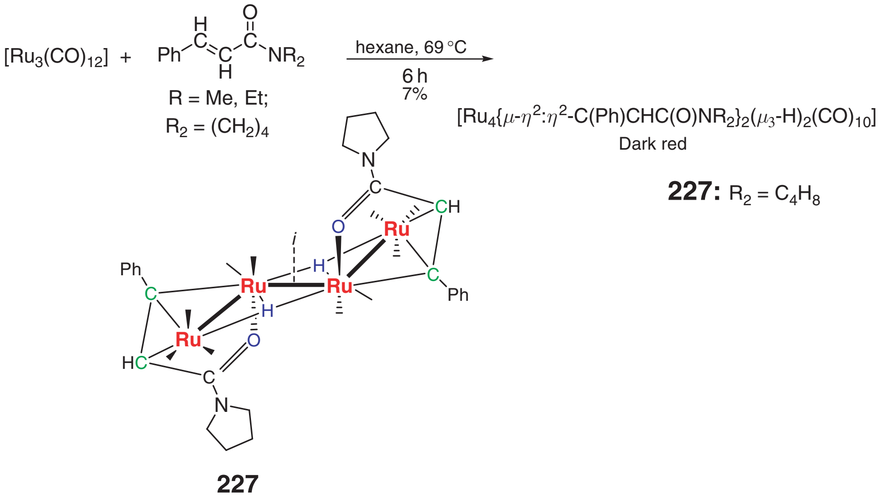
most unusual feature of this reaction, however, is the insertion of CO into the RuC (alkylidene) bond to give new RuC (length 2.14(1) Å) and CC (length 1.52(1) Å) bonds.[160]

Both CS bonds are cleaved in the reaction of $MeC(O)CH{=}C(SMe)_2$ with $[Ru_3(CO)_{12}]$ in the presence of Me_3NO to give $[Ru_4\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C_2HC(O)Me\}(\mu\text{-}SMe)_2(CO)_{10}]$ **226** (Equation (167)).[161] The central Ru_4 unit has a distorted rectangular geometry; the RuRu bonds bridged by the SMe ligands are slightly shorter than the other two metal–metal bonds (2.787(2) and 2.801(1) vs. 2.831(1) and 2.923(2) Å). The RuC lengths are 2.14(1), 2.14(1), and 2.21(1) (σ-bonds), and 2.00(2) and 2.21(1) Å (π-bonds); the RuO distance is 2.11(1) Å.



(167)

The thermal reaction of $[Ru_3(CO)_{12}]$ in solution with *N*-substituted cinnamic amides $PhCH{=}CHC(O)NR_2$ (R = Me, Et; $R_2 = (CH_2)_4$) gives $[Ru_4\{\mu\text{-}\eta^2{:}\eta^2\text{-}CPhCHC(O)NR_2\}_2(\mu_3\text{-}H)_2(CO)_{10}]$ ($R_2 = (CH_2)_4$ **227**; (Equation (168)) as one of the two products.[162] The structure of **227**, which has a crystallographic inversion center, has a planar Z-shaped Ru_4 chain with outer RuRu bonds of length 2.926(1) Å and a central RuRu bond of length 3.011(1) Å. The RuC lengths to the oxadiene ligand are 2.059(4) (σ-bond), and 2.121(4) and 2.223(1) Å (π-bonds); the RuO distance is 2.115(3) Å. The H atoms, located in the diffraction study, bridge three Ru atoms in a planar T-type coordination; the RuH distances are 1.73(7), 1.93(7), and 1.96(7) Å. The molecule has 64 c.v.e. rather than the 66 c.v.e. expected for a complex with three RuRu bonds.[162]

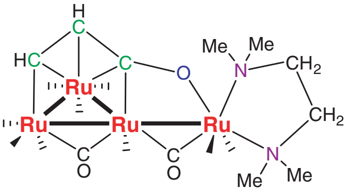


(168)

In an attempt to facilitate the reaction of CaC_2 with $[Ru_3(CO)_{12}]$ (i.e., Equation (103)), tetramethyldiaminoethane (tmeda) was added to the reaction solution. This did not affect the yield of the major product, but the compound $[Ru_4(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-OCCHCH})(\mu\text{-CO})_2(CO)_9(\text{tmeda})]$ **228** (Equation (169)) was isolated and characterized.[115] The Ru_4 geometry is a spiked triangle with RuRu lengths in the range 2.770(1)–2.891(1) Å. The structure carries a CHCHCO unit formed by a carbonyl ligand and an acetylene molecule (presumed to be derived from CaC_2). The unit is bound to the Ru_3 triangle via two RuC σ-bonds (range 2.030(3)–2.089(3) Å, two independent molecules) and two RuC π-bonds (range 2.224(3)–2.387(2) Å). The O atom of the unit is bound to the spike Ru atom (RuO = 2.073(2), 2.075(2) Å). The molecule is a rare example of a ruthenium cluster containing the tmeda ligand; the RuN distances are in the range 2.230(2)–2.250(2) Å.[115]

$$[Ru_3(CO)_{12}] + CaC_2 + Me_2NCH_2CH_2NMe_2 \xrightarrow[\text{overnight}\\ 17\%]{\text{THF, 66 °C}}$$

$[Ru_4(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-OCCHCH})(\mu\text{-CO})_2(CO)_9(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)]$
Dark red
228

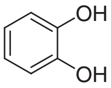


228

(169)

The reactions of $[Ru_3(CO)_{12}]$ with catechol ($1,2\text{-}C_6H_4(OH)_2$) and with 3,5-di-*t*-butyl-1,2-benzoquinone yield compounds of formula $[Ru_4(\mu_3\text{-}\eta^8\text{-}1,2\text{-}O_2C_6H_2R_2)(CO)_8]$ (R = H **229**; R = Bu^t **230**), which differ in the arrangement of the Ru atoms but contain μ_3-semiquinone ligands coordinated via terminal and bridging O atoms and an η^6-C_6 unit (Equations (170) and (171)).[163] Complexes **229** and **230** are rare examples of 68 c.v.e. clusters and as such have just two RuRu bonds (see Section 6.23.1). The two metal bonds may be separated to give two Ru_2 moieties (the 2 : 2 isomer) or joined to give a linear Ru_3 unit and a solitary Ru fragment (the 1 : 3 isomer). The RuRu lengths in these compounds are normal. In 1:3 **229**, the RuRu bonds have crystallographically identical lengths of 2.846(1) Å. In 2:2 **230**, the RuRu bonds also have crystallographically identical lengths of 2.791(1) and 2.787(1) Å (two independent molecules). The RuO terminal bonds are marginally shorter (2.061(4) Å, 1:3 **229**; 2.083(7), 2.092(7) Å 2:2 **230**) than the corresponding bonds to the bridging O atoms (2.120(4), 2.223(4) Å, 1:3 **229**; 2.192(2), 2.204(6), molecule A; 2.193(5), 2.198(7) Å, molecule B, 2:2 **230**). Aspects of the chemistry of **230** are shown in Scheme 27.[163]

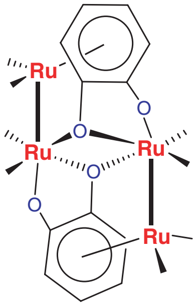
$[Ru_3(CO)_{12}]$ +



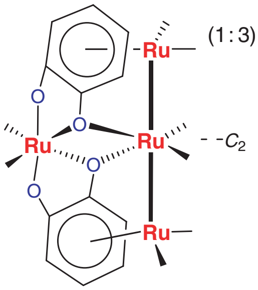
$$\xrightarrow[\text{3 h}]{\text{toluene, 111 °C}}$$

(2 : 2) $[Ru_4(\mu_4\text{-}\eta^2\text{:}\eta^1\text{:}\eta^6\text{-}1,2\text{-}O_2C_6H_4)_2(CO)_8]$ +
Yellow-brown, insoluble, ~90%
229
2 : 2

(1 : 3) $[Ru_4(\mu_3\text{-}\eta^6\text{:}\eta^1\text{:}\eta^2\text{-}1,2\text{-}O_2C_6H_4)_2(CO)_8]$
Red, soluble, ~5%
229
1 : 3

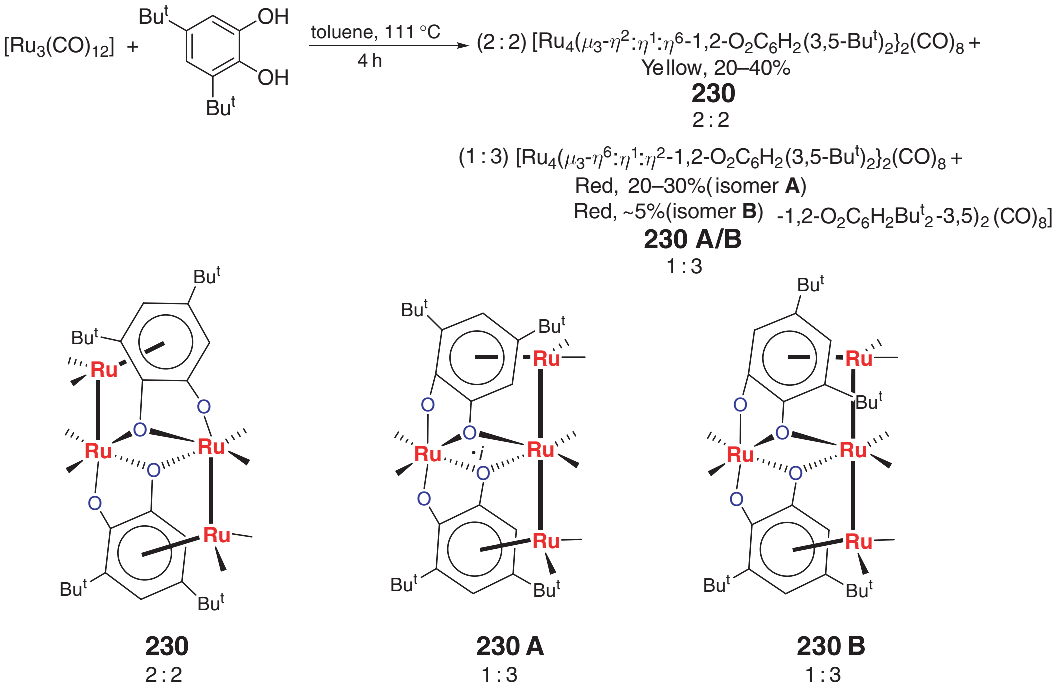


229
2 : 2



229
1 : 3

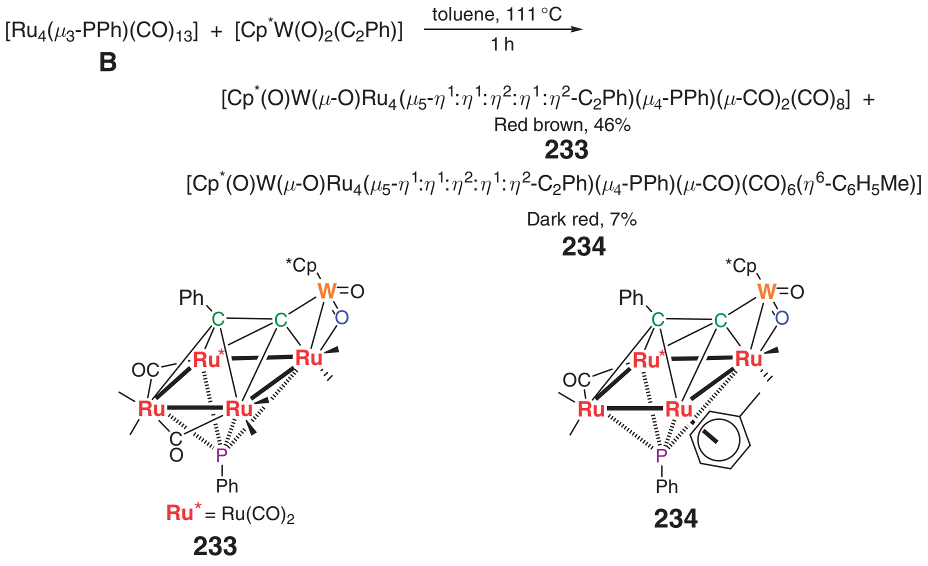
(170)



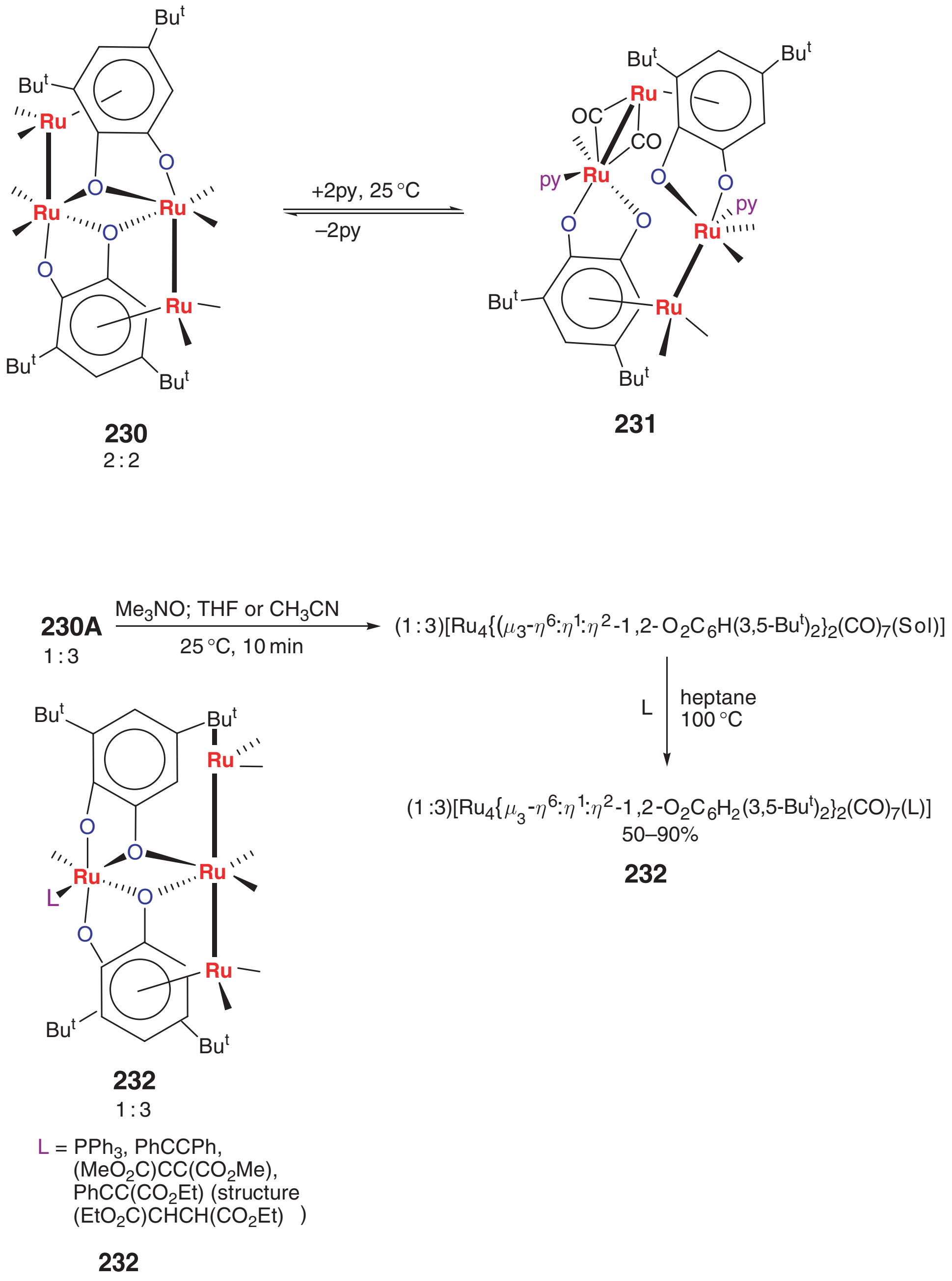
(171)

One product from the reaction of $[Ru_3(CO)_{12}]$ with dibenzylideneacetone (PhCH═CHCOCH═CHPh) in refluxing heptane is $[Ru_4\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^6\text{-}OC(CH{=}CHPh){=}CHCPhCH(CH_2Ph)C(O)CH{=}CHPh\}_2(CO)_8$. The structure has a central Ru_2O_2 ring; the RuO bonds in the compound are in the range 2.094(5)–2.259(5) Å. There are no RuRu bonds in the compound, which readily breaks apart in acetone.[164]

Some interesting examples of early high oxidation state–late low oxidation state mixed metal–metal organometallics with Ru_4 unit have been prepared.[165–168] An example is shown in Equation (172).[165]



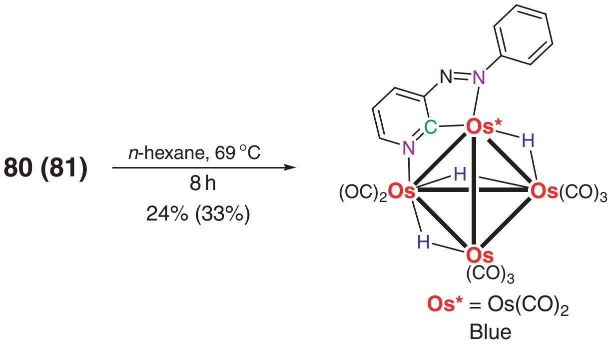
(172)



Scheme 27

6.23.6.2 Osmium Derivatives

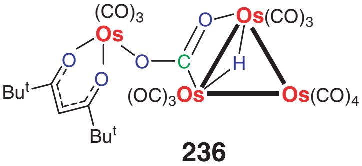
Thermolysis of $[Os_4(\mu\text{-}H)_4(CO)_{11}\{NC_5H_4(N{=}N)Ph\}]$ 80 or $[Os_4(\mu\text{-}H)_4(CO)_{10}(NMe_3)\{NC_5H_4(N{=}N)Ph\}]$ 81 in refluxing *n*-hexane affords $[Os_4(\mu\text{-}H)_3(CO)_{10}\{\mu\text{-}\eta^3\text{-}NC_5H_3(N{=}N)Ph\}]$ 235 in 24% and 33% yields, respectively (Equation (173)).[71] The pyridyl ring bridges an OsOs vector through a nitrogen and a carbon atom (OsN = 2.06(2) Å; OsC = 2.13(3) Å), while an azo nitrogen is bonded to the same osmium atom as the carbon (OsN = 2.10(3) Å). This results in four- and five-membered metallacyclic rings with a dihedral angle of 5.57°. The pyridyl and phenyl rings are highly twisted (dihedral angle of 57.68°).[71]



235

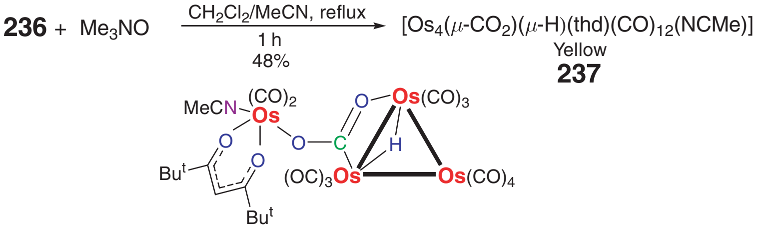
(173)

The synthesis of $[Os_4(\mu\text{-}H)(\mu\text{-}CO_2)(thd)(CO)_{13}]$ **236** (thdH = 2,2,6,6-tetramethyl-3,5-heptandione) is given in Equation (53).[58] Two metal-containing molecular entities are uniquely connected by a bridging CO_2 ligand (OCO angle of 118° with an average CO bond length of 1.27 Å). The OsOs bond lengths of the triosmium $Os_3(\mu\text{-}H)(CO)_{10}$ fragment are in the range of 2.849(1)–2.890(1) Å with the hydride ligand believed to bridge the same OsOs edge (2.890(1) Å) as the CO_2 ligand. The Os atom in the monometallic $Os(CO)_3(thd)(O)$ unit has an octahedral environment composed of three oxygen atoms (from the CO_2 and thd ligands) and three facial CO ligands. The CO_2 ligand is bridged in a parallel fashion to the OsOs edge of the Os_3 triangle (OsC = 2.082(11) Å; OsO = 2.082(7) Å). Lastly, the bidentate thd ligand is symmetrically coordinated to the osmium atom of the $Os(CO)_3(thd)$ unit (OsO = 2.049(7) and 2.051(7) Å). The compound is stable at 110 °C for 30 min.



236

When **236** is allowed to react with freshly sublimed Me_3NO in a mixture of CH_2Cl_2 and MeCN at reflux for 1 h, $[Os_4(\mu\text{-}H)(\mu\text{-}CO_2)(thd)(CO)_{12}(NCMe)]$ **237** is obtained in moderate yield (Equation (174)).[58] The geometric structure of **237** is essentially the same as **236** except that an acetonitrile ligand has replaced the carbonyl ligand at the position opposite to the CO_2 ligand (average CO bond length of 1.28 Å). This compound is believed to be stabilized by the weakly coordinated acetonitrile ligand. The OsOs bond lengths are in the range of 2.8698(4)–2.8931(4) Å. The thd ligand is also symmetrically bound to the osmium atom (OsO = 2.076(5) and 2.066(5) Å). However, the CO_2 ligand is not exactly parallel to the OsOs edge (OsC = 2.091(7) Å; OsO = 2.131(5) Å) as in **236**.[58]



237

(174)

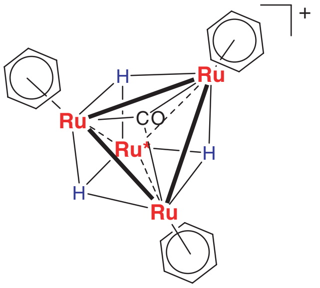
6.23.7 Compounds without CO Ligands

The electron-deficient (58 c.v.e.) cluster cation $[(\eta\text{-}C_6H_6)_4Ru_4(\mu_3\text{-}H)_4]^{2+}$ reacts with CO in water to give the purple, electron-precise (60 c.v.e.) $[(\eta\text{-}C_6H_6)_4Ru_4(\mu_3\text{-}H)_3(\mu_3\text{-}CO)]^+$ **238**, Equation (175)).[169]

$$[Ru_4(\mu_3\text{-}H)_4(\eta\text{-}C_6H_6)_4](Cl)_2 + \underset{(\sim 50\ \text{atm})}{CO} \xrightarrow[\substack{14\ \text{h} \\ 67\%}]{H_2O,\ 50\ ^\circ C} [Ru_4(\mu_3\text{-}H)_3(\mu_3\text{-}CO)(\eta\text{-}C_6H_6)_4]Cl \tag{175}$$

Purple

Cation = **238**



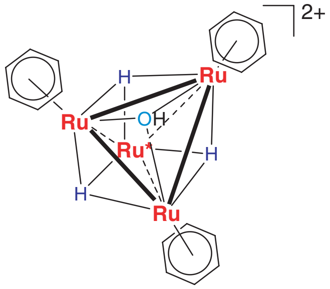
Ru* = Ru(η-C_6H_6)

238

The cation also reacts with water (NaN_3 catalyst) or alcohols to yield $[(\eta\text{-}C_6H_6)_4Ru_4(\mu_3\text{-}H)_3(\mu_3\text{-}OR)]^{2+}$ (R = H **239**, Me, Et, Ph, etc.) (Equation (176)).

$$[Ru_4(\mu_3\text{-}H)_4(\eta\text{-}C_6H_6)_4](Cl)_2 + ROH \xrightarrow[\substack{1\ \text{h} \\ 100\%}]{NaN_3,\ 50\ ^\circ C} [Ru_4(\mu_3\text{-}H)_3(\mu_3\text{-}OR)(\eta\text{-}C_6H_6)_4](Cl)_2 \tag{176}$$

Black-brown, R = H, Cation = **239**, Me, Et



Ru* = Ru(η-C_6H_6)

239

The structures of $[(\eta\text{-}C_6H_6)_4Ru_4(\mu_3\text{-}H)_3(\mu_3\text{-}CO)]Cl$ and $[(\eta\text{-}C_6H_6)_4Ru_4(\mu_3\text{-}H)_3(\mu_3\text{-}OH)]Cl_2$ confirmed the ligand arrangement. The RuRu distances range from 2.732(1) - 2.772(1) Å in **238** and from 2.725(1) - 2.752(1) Å in **239**. Both molecules have a crystallographic mirror plane. The alkoxo clusters are air-stable black-brown solids that dissolve in water and polar solvents such as THF, MeCN, and MeOH.[169]

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6.24
Medium- and High-nuclearity Clusters of Ru/Os

M G Humphrey and M P Cifuentes, Australian National University, Canberra, ACT, Australia

6.24.1 Introduction

6.24.1.1 General Comments

The previous edition of this work, COMC (1995), summarized the development of medium- (M_n, $n = 5$ or 6) and high-nuclearity (M_n, $n > 6$) ruthenium and osmium cluster chemistry. The present work summarizes published reports since then; as was the case in 1993, while this field is dominated by ruthenium clusters, the area of very high-nuclearity (M_n, $n > 10$) clusters is still dominated by osmium clusters. Since the publication of COMC (1995), considerable progress has been achieved in specific areas, for example, arene chemistry of penta- and hexaruthenium clusters and the chemistry of phosphinoalkyne fragment-stabilized pentaruthenium clusters, but, with the exception of tetracapped octahedral and edge-fused bioctahedral decaruthenium clusters, there has been little systematic exploration of the field of high-nuclearity clusters and, indeed, activity with $M_{\geq 10}$ clusters has waned over the past few years.

Syntheses of medium- and high-nuclearity ruthenium and osmium clusters continue to be largely by thermolyses of lower nuclearity precursors, but surface-mediated methods have also been employed; the use of inorganic oxides or zeolites in the preparation of metal carbonyl clusters, including pentaosmium and hexaruthenium carbido clusters, and the decaosmium complexes $[H_5Os_{10}(CO)_{24}]^-$ and $[Os_{10}(\mu_6\text{-C})(CO)_{24}]^{2-}$, has been reviewed.[1]

Advances in spectroscopic characterization continue to drive the development of the field. A number of studies describing the mass spectrometry of medium- and high-nuclearity ruthenium and osmium carbonyl clusters have been reported, including UV-laser desorption,[2–4] laser desorption/ionization time-of-flight[5,6] and energy-dependent electrospray ionization;[7–11] the last mentioned has been shown to resolve mixtures of cluster compounds.

6.24.1.2 Cluster Geometries and Electron Counts

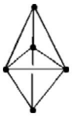
Electron counts and geometries of transition metal clusters have been the subject of considerable discussion; for an explanation of the various approaches to rationalize structure and electron counting, the reader is directed to Ref: 12.

Structurally characterized pentametallic clusters, listed in Table 1, almost all conform to the effective atomic number (EAN) rule. The few exceptions, indicated in Table 1, possess edge-bridged square or spiked square geometries. The edge-bridged squares $Ru_5(\mu_4\text{-NH})(\mu_4\text{-}\eta^2\text{-HC}_2\text{Ph})(\mu\text{-CO})(CO)_{13}$ **72** and $Ru_5(\mu_4\text{-C}{\equiv}\text{CMe})(\mu_3\text{-SEt})(\mu\text{-C}{\equiv}\text{CMe})(\mu\text{-SEt})(CO)_{12}$ **82** are electron deficient and electron rich, respectively, if a metal-only core is considered, but electron precise if main group vertices are included, the former consisting of an edge-bridged pentagonal bipyramid and the latter a trigonal prism. The electron-rich edge-bridged square clusters $Ru_5\{\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-CCC(C}{\equiv}\text{CPh)CPh}\}(\mu_3\text{-SMe})(\mu\text{-PPh}_2)_2(\mu\text{-SMe})(CO)_9$ **118** and $Ru_5\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^4{:}\eta^2\text{-CC[C(C}{\equiv}\text{CPh)CPh]C(C}{\equiv}\text{CPh)CPh}\}(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_8$ **120** both possess two long Ru–Ru bonds (>3.0 Å), a feature characteristic of clusters with bridging *P*- and *S*-ligands, where occupancy of the low-lying LUMOs is not sufficiently localized to result in M–M cleavage. The spiked square $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-CCC}{\equiv}\text{CBu}^t)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-C}{\equiv}\text{CC}{\equiv}\text{CBu}^t)(\mu\text{-CO})(\mu\text{-PPh}_2)_2(CO)_{11}$ **126** is very electron poor, but possesses one short Ru–Ru bond and a distorted $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1$-diynyl ligand. The same 13 core geometries are observed as those reported in COMC (1995); while all ruthenium examples with ≥78 c.v.e. contain μ_5- or μ_4-ligands, which stabilize open geometries, this is not the case for the few known osmium examples **2, 6, 8, and 9**.

Crystallographically characterized hexametallic clusters are listed in Table 2, together with their polyhedral skeletal electron-pair theory (PSEPT)-predicted electron counts. While most clusters conform to this electron counting protocol, adherence to the rules decreases for the more open geometries. The fused square $Ru_6\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-CCHC(O)Me}\}_2(CO)_{16}$ **269** is two electrons deficient but contains one very short Ru–Ru bond (2.656(2) Å) which may be considered a metal–metal double bond. In contrast, $Ru_6(\mu\text{-H})(\mu_5\text{-S})\{\mu_3\text{-}\eta^2\text{-SC(NHPh)NPh}\}(CO)_{15}(PPh_3)$ **279** and $Ru_6(\mu_6\text{-C}_{10}\text{H}_6)(\mu_3\text{-PPh})(CO)_{14}$ **264** are two electrons deficient without obvious localized double bonds. $Os_6(\mu_3\text{-S})_2(\mu\text{-dppm})(CO)_{14}$ **272**, $Ru_6(\mu_6\text{-C})(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-MeC}_2\text{Me})_3(CO)_{12}$ **201**, $Os_6(\mu_4\text{-O})(\mu\text{-OH})_2(\mu\text{-CO})_2(CO)_{16}$, **268**, $Ru_6(\mu_4\text{-S})\{\mu_3\text{-}\eta^2\text{-SC(NHEt)NEt}\}\{\mu_3\text{-}\eta^2\text{-C(NHEt)NEt}\}(\mu\text{-CO})_2(CO)_{14}$ **276**, $Ru_6(\mu_4\text{-S})(\mu_3\text{-pyS})(\mu\text{-SH})(\mu\text{-CO})_2(CO)_{15}$ **280**, and $M_6(\mu_3\text{-E})_4(\mu\text{-dppm})_2(CO)_{12}$ (**271**; M = Ru, E = S; M = Os, E = Se) are all electron rich, the excess electron density being accommodated in low-lying antibonding orbitals and manifested by a corresponding increase in M–M distances. Twenty-eight different core geometries are observed, with variations from those in the earlier work, but the most common by far is octahedral, all examples bar two possessing a μ_6-carbido ligand.

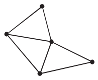
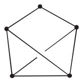
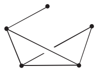
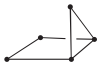
Crystallographically characterized clusters with seven or more metal atoms are listed in Table 3. $[Ru_8(\mu_8\text{-P})(\mu\text{-CO})_2(CO)_{20}]^-$ is four electrons deficient, and can be reduced to the corresponding cluster penta-anion, while $Ru_9(\mu_3\text{-H})(\mu\text{-H})_2(\mu_7\text{-P})(\mu_3\text{-PBu}^t)_3(CO)_{20}$ possesses two electrons more than predicted by either EAN or PSEPT procedures, and contains a long non-hydrido-bridged Ru–Ru bond. Both $[H_2Ru_{10}(\mu_3\text{-CO})(\mu\text{-CO})_4(CO)_{20}]^{2-}$ and $Os_{11}(\mu_4\text{-O})_3(CO)_{30}$ are electron rich without localized bond lengthening. $[Os_{20}(CO)_{40}]^{2-}$ is very electron deficient by PSEPT, which has been explained by the presence of metal–metal bonding and antibonding orbitals in the Os_{10} planes that can be filled or depopulated, resulting in a "breathing" of the cluster framework without bond cleavage.[13]

Table 1 M_5 clusters crystallographically characterized from 1993–2004

EAN	*Core structure*	*Core name*	*Compound*	*Comp. no.*
72		Trigonal bipyramid	$Os_5(CO)_{15}(PMe_3)$ axial, equatorial	4,5
			$Os_5(CNBu^t)(CO)_{15}$	7
			$H_7Ru_5R_5$ ($R = Cp, Cp'$)	60
			$H_7Ru_5Cp_4Cp^*$	61
			$Os_5(\mu\text{-}H)_4(CO)_{11}(\eta^6\text{-}C_6H_6)$	62
			$Os_5(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{11}(\eta^6\text{-}C_6H_5Me)$	64
			$Os_5(\mu\text{-}H)_2(CO)_{13}(\eta^4\text{-}C_6H_8)$	66
			$Os_5\{\overline{S(CH_2)_4C}H_2\}(CO)_{15}$	283
74		Edge-bridged tetrahedron	$Ru_5(\mu_4\text{-}\eta^2\text{-}CC{=}CPh_2)(CO)_{15}$	50
			$Ru_5(\mu_4\text{-}CCH_2)(CO)_{15}$	52
			$Os_5(\mu\text{-}H)_4(CO)_{12}(\eta^6\text{-}C_6H_6)$	63
			$Os_5(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{11}(PMePh_2)(\eta^6\text{-}C_6H_6)$	65
			$Os_5(\mu\text{-}H)_3(\mu\text{-}\overline{NCH_2CH_2C})(CO)_{14}$	73
74		Square pyramid	$[Ru_5(\mu_3\text{-}H)_2(\mu_4\text{-}COH)(\mu\text{-}CO)_3(CO)_{11}]^-$	1
			$Ru_5(\mu_5\text{-}C)(CO)_{14}L$ [$L = PCy_3$, $P(4\text{-}C_6H_4OMe)_3$, $P(4\text{-}C_6H_4F)_3$]	10
			$Ru_5(\mu_5\text{-}C)(CO)_{13}\{P(OCH_2)_3CEt\}_2$	11
			$Ru_5(\mu\text{-}H)(\mu_5\text{-}C)\{\mu\text{-}C(\eta\text{-}C_5H_4)FeCp\}(CO)_{13}$	12
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,3\text{-}C_6H_8)(CO)_{13}$	15
			$Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{12}$	16
			$Ru_5(\mu_5\text{-}C)(CO)_{12}(\eta^6\text{-}C_6H_6)$	17
			$Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,3\text{-}C_6H_8)(CO)_{10}$	19
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,3\text{-}C_6H_8)(CO)_{10}(\eta^6\text{-}C_6H_6)$	20
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)_4(CO)_7(\eta^4\text{-}1,3\text{-}C_6H_8)_2$	21
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,4\text{-}C_6H_8)(CO)_{13}$	22
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,4\text{-}C_6H_8)_2(CO)_{11}$	23
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_{11}(\eta^4\text{-}C_4Ph_4)$	24
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_8Cp_2$	26
			$M_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})(CO)_{11}(PPh_3)$ ($M = Ru, Os$)	27
			$Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})(\mu\text{-}P_2)(CO)_{10}$ (P_2 = dppe, dppf)	28
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}dppf)(CO)_{13}$	29
			$Os_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60})(CO)_{12}(PPh_3)$	30
			$Os_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_{60})(CNCH_2Ph)(CO)_{11}(PPh_3)$	32
			$Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})(CNCH_2Ph)(CO)_{10}(PPh_3)$	33
			$Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(SiEt_3)(CO)_{14}$	34
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)(\mu\text{-}GePh_2)_3(CO)_{11}$	36
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}GePh_2)_4(CO)_{11}$	37
			$Ru_5(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}GePh_2)_4(CO)_{10}$	38
			$Ru_5(\mu_3\text{-}H)(\mu_4\text{-}CH)(\mu_3\text{-}GePh)_2(\mu\text{-}GePh_2)_2(CO)_{10}$	39
			$\{(CH_2)_4N(CH_2PPh_2)_2[Ru_5(\mu_5\text{-}C)(CO)_{12}]\}_2$	46
			$\{Os_5(\mu_5\text{-}C)(CO)_{14}\}_2(\mu\text{-}dppf)$	47
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^1\text{-}12S3)(CO)_{13}$	48
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^3\text{-}12S3)(CO)_{11}$	49
			$[Ru_5(\mu_4\text{-}PNPr^i{}_2)(\mu\text{-}NO)(CO)_{13}]^-$	69
			$Ru_5(\mu_4\text{-}NH)(\mu_3\text{-}PNPr^i{}_2)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{10}$	70
			$Ru_5(\mu_5\text{-}N)\{\mu\text{-}P(R)NPr^i{}_2\}(CO)_{13}$ ($R = OMe, F$)	71
			$Ru_5(\mu_4\text{-}\eta^2\text{-}PC_6H_4\text{-}2\text{-}PPh_2)(CO)_{14}$	75
			$Ru_5(\mu_4\text{-}ECF_3)(CO)_{15}$ ($E = P, As$)	77
			$Ru_5(\mu_4\text{-}PR)(CO)_{15}$ ($R = NCy_2$, F, OMe, Bu^t)	77
			$[NH_2Cy_2][Ru_5(\mu_4\text{-}PO)(CO)_{15}]$	78
			$Ru_5(\mu_4\text{-}PEt)(\mu\text{-}CO)(CO)_9Cp_2$	79
			$Ru_5(\mu_4\text{-}PEt)(CO)_{12}(\eta^6\text{-}C_6H_5Me)$	80
			$Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}CCHPh)(\mu\text{-}PPh_2)(CO)_9Cp^*$	123
			$Ru_5(\mu_5\text{-}C)(\mu\text{-}dppf)(CO)_{13}$	131

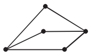
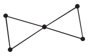
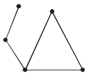
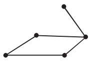
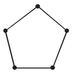
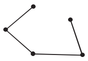
(Continued)

Table 1 (Continued)

EAN	*Core structure*	*Core name*	*Compound*	*Comp. no.*
76		Edge-bridged butterfly	$Os_5(\mu-CO)(CO)_{16}(PMe_3)$	3
			$Ru_5(\mu_5-\eta^3-CCCPhMe)(\mu-CO)(CO)_{14}$	51
			$Ru_5(\mu_3-H)(\mu_4-\eta^1:\eta^1:\eta^3:\eta^3:-C_3H_2Ph)(\mu-CO)(CO)_{13}$	55
			$Os_5(\mu-H)(\mu_3-SePh)(CO)_{15}$	85
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^2:\eta^1:\eta^1-C_2PPh_2)(\mu-dppm)-(\mu-PPh_2)(CO)_{11}$	97
			$Ru_5(\mu_3-\eta^1:\eta^1:\eta^2-C{=}CHR)(\mu_3-SMe)_2(\mu-PPh_2)_2(CO)_{10}$ (R = H, CH=CHMe, CH=CHPh)	106
			$Ru_5(\mu_3-CMe)(\mu_3-SMe)(\mu-Cl)(\mu-PPh_2)_2(\mu-SMe)(CO)_9$	107
76		Wingtip-bridged butterfly	$Ru_5(\mu_5-C)\{\mu-\eta^1:\eta^1:\eta^2-(MeO_2C)CHCH(CO_2Me)\}(CO)_{13}$	13
			$Ru_5(\mu_5-C)\{\mu-\eta^2-(MeO_2C)C_2(CO_2Me)\}(\mu-CO)(CO)_{14}$	14
			$Ru_5(\mu_5-C)(CO)_{13}(\eta^6-C_6H_6)$	18
			$Ru_5(\mu-H)(\mu_5-C)(CO)_{13}Cp$	25
			$Os_5(\mu_5-C)(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})(CNCH_2Ph)(CO)_{11}(PPh_3)$	31
			$Ru_5(\mu-H)(\mu_5-C)(SiEt_3)(CO)_{15}$	35
			$Ru_5(\mu_5-C)(\mu-\eta^2-NO_2)(CO)_{13}(\eta^3-C_3H_5)$	41
			$Ru_5(\mu_5-C)(CO)_{14}(\eta^2-bipy)$	43
			$Ru_5(\mu_5-C)(\mu-\eta^3-N_2C_{10}H_7)(CO)_{13}$	44
			$Ru_5(\mu_5-C)(CO)_{14}(\eta^2-phen)$	45
			$Ru_5(\mu-H)_2\{\mu_4-CC(Me)C(O)OEt\}(CO)_{14}$	57
			$Ru_5(\mu-H)_2\{\mu_4-\eta^1:\eta^1:\eta^2:\eta^2-CC(H)C(O)Me\}(CO)_{14}$	58
			$Ru_5\{\mu_4-\eta^1:\eta^1:\eta^2:\eta^2-CC(H)C(O)Me\}(\mu_4-\eta^1:\eta^2:\eta^2:\eta^1-HC_2CH_2Me)(\mu-CO)(CO)_{12}$	59
			$HOs_5(\mu_5-B)(CO)_{16}$	68
			$Ru_5(\mu_4-PPh)\{\mu_4-\eta^2-(PPh)_2CH_2\}(\mu_3-PPh)(CO)_{11}$	81
			$Ru_5(\mu_4-S)_2(\mu-\eta^1-CNEt_2)_2(CO)_{11}$	84
78		Spiked butterfly	$Ru_5(\mu_5-\eta^5-CHCHCCH_2)(CO)_{15}$	53
			$Ru_5(\mu_5-\eta^2-C{\equiv}C)(\mu-dppm)(\mu-CO)_2(CO)_7(\eta-C_5H_4R)_2$ (R = H, Me)	54
			$Ru_5(\mu-H)_2(\mu_4-\eta^3-BH_2)(CO)_{13}Cp^*$	67
			$Os_5(\mu-H)(CO)_{17}\{\eta^2-N(C_6F_5)NN(C_6F_5)\}$	74
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^2:\eta^1:\eta^1-C_2PPh_2)(\mu-PPh_2)(CO)_{12}(dppm)$	98
78		Edge-bridged square	$Ru_5(\mu_4-NH)(\mu_4-\eta^2-HC_2Ph)(\mu-CO)(CO)_{13}$ (76 c.v.e.)	72
			$Ru_5(\mu_4-C{\equiv}CMe)(\mu_3-SEt)(\mu-C{\equiv}CMe)(\mu-SEt)(CO)_{12}$ (80 c.v.e.)	82
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^2:\eta^1:\eta^1-C_2H)(\mu-CO)(\mu-NHC_6H_4-2-PPh_2)-(\mu-PPh_2)(CO)_{10}$	99
			$Ru_5(\mu_4-\eta^1:\eta^1:\eta^3:\eta^2-CCCCHBu^t)(\mu_3-SMe)(\mu-PPh_2)_2-(\mu-SMe)(CO)_{10}$	110
			$Ru_5\{\mu_4-\eta^1:\eta^1:\eta^2:\eta^4-CC(CHCSiMe_3)C({=}CHSiMe_3)(CO)\}-(\mu_3-SMe)_2(\mu-PPh_2)_2(CO)_8$	111
			$Ru_5\{\mu_5-\eta^2:\eta^1:\eta^2:\eta^1:\eta^3-CC[C(O)SMe]CHCR\}(\mu-PPh_2)_2(\mu-SMe)(CO)_{10}$	112
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^1:\eta^2:\eta^2-CCCPhCPh)(\mu-PPh_2)_2(\mu-SMe)_2(CO)_{10}$	114
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^1:\eta^2:\eta^4-CCCPhCPh)(\mu_3-SMe)(\mu-PPh_2)_2-(\mu-SMe)(CO)_9$	115
			$Ru_5\{\mu_5-\eta^1:\eta^1:\eta^1:\eta^2:\eta^3-CC[C_2(SiMe_3)]C(SiMe_3)C(SiMe_3)\}-(\mu_3-SMe)(\mu-PPh_2)_2(CO)_{10}$	116
			$Ru_5\{\mu_5-\eta^1:\eta^1:\eta^1:\eta^2:\eta^4-CCC(C{\equiv}CPh)CPh\}(\mu_3-SMe)-(\mu-PPh_2)_2(\mu-SMe)(CO)_9$ (80 c.v.e.)	118
			$Ru_5\{\mu_5-\eta^2:\eta^1:\eta^2:\eta^1:\eta^3-CC(SMe)C(C{\equiv}CPh)CPh\}(\mu-PPh_2)_2-(\mu-SMe)(CO)_{10}$	119
			$Ru_5\{\mu_4-\eta^1:\eta^2:\eta^4:\eta^2-CC[C(C{\equiv}CPh)CPh]C(C{\equiv}CPh)CPh\}-(\mu_3-SMe)_2(\mu-PPh_2)_2(CO)_8$ (80 c.v.e.)	120
			$Ru_5(\mu_5-C)(\mu-Br)_2(\mu-\eta^3-C_3H_5)(CO)_{11}(\eta^3-C_3H_5)$	189
			$Ru_5(\mu-H)_3(\mu_4-NH)(\mu_3-OMe)(CO)_{13}$	257
			$Ru_6(\mu_5-N)(\mu_3-NH)(\mu_3-OMe)\{\mu_3-\eta^2-C(O)OMe\}_2-(\mu-CO)(CO)_{13}$ (linked cluster)	258

(Continued)

Table 1 (Continued)

EAN	*Core structure*	*Core name*	*Compound*	*Comp. no.*
78		Diagonally-bridged square	$Ru_5(\mu_5-C)(\mu-NO)(\mu-\eta^2-NO_2)(CO)_{11}(NO)(\eta^3-C_3H_5)$	**40**
			$Ru_5(\mu_5-C)(\mu-NO)(\mu-\eta^2-NO_2)(CO)_{13}(PPh_3)$	**42**
			$[Ru_5(\mu_5-C)(\mu-\eta^2-COMe)(\mu-I)I(CO)_{13}]^-$	**190**
			$Ru_5(\mu_5-C)(\mu-Br)_2(CO)_{14}$	**192**
78		Bow-tie	$Os_5(CO)_{18}L$ ($L = PMe_3$, $CNBu^t$)	**2, 6**
			$Ru_5(\mu_5-\eta^1:\eta^2:\eta^3:\eta^3-C_{14}H_8-\eta^1-PPh)(CO)_{13}$	**76**
			$Ru_5(\mu-H)_2\{\mu_5-\eta^1:\eta^1:\eta^2:\eta^3:\eta^2-PPh_2C_2CH{=}C(2-C_6H_4PPh_2)\}(\mu-PPh_2)(CO)_{11}$	**101**
			$Ru_5(\mu_3-\eta^1:\eta^1:\eta^2-C_6H_6)(\mu_3-SMe)_2(\mu-PPh_2)_2(CO)_{10}$	**108**
80		Double-spiked triangle	$Ru_5\{\mu_5-C(Ph)CC(Ph)C\}(\mu_2-SEt)_2(\mu-CO)(CO)_{12}$	**83**
			$Ru_5(\mu_4-\eta^1:\eta^2:\eta^2:\eta^1-C_2PPh_2)(\mu-PPh_2)(\mu-\eta^3:\eta^3-C_6H_8)(\mu-\eta^1:\eta^3-C_3H_4)(\mu-CO)(CO)_9$	**102**
			$Ru_5(\mu_4-\eta^1:\eta^2:\eta^2:\eta^1-C_2PPh_2)(\mu-PPh_2)(\mu-\eta^3:\eta^3-C_6H_8)(\mu-\eta^1:\eta^3-C_3H_4)(CO)_9\{P(OMe)_3\}$ 3 isomers	**102a**
80		Spiked square	$Ru_5(\mu_5-\eta^2:\eta^1:\eta^1:\eta^2:\eta^4-CCCPhCPh)(\mu-PPh_2)_2(\mu-SMe)_2(CO)_{11}$	**113**
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^1:\eta^1:\eta^3-CCCCH_2)(\mu-PPh_2)_2(\mu-SMe)_2(CO)_{11}$	**117**
			$Ru_5(\mu_4-PPh)(\mu_4-\eta^1:\eta^1:\eta^2:\eta^1-C_{13}H_{12}O)(\mu-PPh_2)(CO)_{11}Cp$	**122**
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1-CCC{\equiv}CBu^t)(\mu_3-\eta^1:\eta^1:\eta^1-C{\equiv}CC{\equiv}CBu^t)(\mu-CO)(\mu-PPh_2)_2(CO)_{11}$ (76 c.v.e.)	**126**
80		Pentagon	$Ru_5(\mu_5-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1-C_2)(\mu-PPh_2)_2(\mu-SMe)_2(CO)_{10}(L)$ ($L = CNBu^t$, $P(OMe)_3$)	**87a**
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1-C_2)(\mu-PPh_2)_2(\mu-SMe)_2(CO)_{11}$	**91**
			$Ru_5(\mu_5-C_2)(\mu-SMe)_2(\mu-PPh_2)_2(CO)_{11}(CNBu^t)$	**96**
			$Ru_5(\mu_5-\eta^1:\eta^2:\eta^2:\eta^1:\eta^1-C_2)(\mu-Cl)_2(\mu-PPh_2)_2(CO)_{11}$	**104**
			$Ru_5(\mu-H)\{\mu_5-\eta^1:\eta^1:\eta^1:\eta^1:\eta^2-CC(PPh_2)\}(\mu-Cl)(\mu-PPh_2)(CO)_{12}$	**105**
			$Ru_5(\mu_5-\eta^1:\eta^2:\eta^1:\eta^4:\eta^2-CCCHCR)(\mu-PPh_2)_2(\mu-SMe_2)_2(CO)_{10}$ ($R = Ph$, $SiMe_3$)	**109**
82		Chain	$Os_5(\mu-Cl)_2(CNBu^t)_2(CO)_{16}$	**8**
			$Os_5Cl_2(CNBu^t)_2(CO)_{18}$	**9**
			$Ru_5(\mu-H)(\mu_5-\eta^1:\eta^1:\eta^2:\eta^2:\eta^6-C_{13}H_7CHC)(\mu_3-OH)(\mu-CO)(CO)_{11}$	**56**
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^2:\eta^2:\eta^1-C_2PPh_2)(\mu-PPh_2)(\mu-SMe)_2(CO)_{13}$	**88**
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^2:\eta^1:\eta^1-C_2PPh_2)(\mu_3-SMe)(\mu-PPh_2)(\mu-SMe)(CO)_{12}$	**89**
			$Ru_5(\mu_5-\eta^1:\eta^2:\eta^2:\eta^1:\eta^1-C_2)(\mu-PPh_2)_2(\mu-SMe)_2(CO)_{12}$	**90**
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^2:\eta^2:\eta^1-C_2PPh_2)(\mu_3-SMe)(\mu-PPh_2)(\mu-SMe)(CO)_{12}$	**92**
			$Ru_5(\mu_5-\eta^1:\eta^1:\eta^2:\eta^1:\eta^1-C_2)(\mu-PPh_2)_2(\mu-SMe)_4(CO)_{10}$	**93**

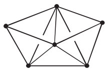
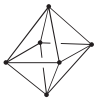
Beyond M_7, only M_{10} has many examples, all ruthenium-containing, while higher nuclearities over this period have been exclusively osmium-containing. The one common motif through these structures is the octahedral unit, many higher nuclearity examples corresponding to (multi)capping of this geometry.

6.24.2 M_5 Clusters

6.24.2.1 Simple Carbonyls, Carbonyl Hydrides, and their Substitution Products

No simple carbonyls or carbonyl hydrides of pentaruthenium clusters have been definitively identified. One candidate, which is obtained in low yields from the reaction of $[Ru_3(CO)_9BH_4]^-$ with $\{RuCl_2Cp^*\}_n$ ($Cp^* = \eta^5-C_5Me_5$), $\{RuCl_2(\eta^6-MeC_6H_4–4-CHMe_2)\}_2$, or $W(CO)_4(NCMe)_2$,[14] was initially proposed to be $[HRu_5(CO)_{15}]^-$.[15] However, subsequent structural analysis has revealed that the cluster is $[Ru_5(\mu_3-H)_2(\mu_4-COH)(\mu-CO)_3(CO)_{11}]^-$ **1** with a square-pyramidal

Table 2 M_6 structures crystallographically-characterized 1993–2004

PSEPT	*Core structure*	*Core name*	*Compound*	*Comp. no.*
84		Bicapped tetrahedron	$Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)$	232
			$Os_6(\mu\text{-}CO)(CO)_{14}(\eta^6\text{-}C_6H_5Me)$	233
			$Os_6(\mu\text{-}H)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{11}(\eta^6\text{-}C_6H_6)$	234
			$Os_6(\mu\text{-}CO)(CO)_{11}(\eta^6\text{-}C_6H_6)_2$	235
			$Os_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_8H_5N_3Me)(CO)_{14}$	253
			$Os_6(\mu_3\text{-}S)_2(\mu\text{-dppm})(CO)_{14}$ (88 c.v.e.)	272
			$Os_6\{\mu\text{-}\overline{S(CH_2)_4CH_2}\}\{\overline{S(CH_2)_4CH_2}\}(CO)_{15}$	282
			$Os_6\{\mu\text{-}\overline{S(CH_2)_3SCH_2}\}(CO)_{16}$	284
			$Os_6\{\mu\text{-}\overline{S(CH_2)_2SCH_2CH_2}\}_2(CO)_{16}$	285
			$Os_6(\mu_3\text{-}\eta^2\text{-}S\overline{CH_2SCH_2SCH_2})(\mu\text{-}CO)(CO)_{14}$	286
			$Os_6\{\mu\text{-}\overline{S(CH_2)_2OCH_2CH_2}\}(\overline{S(CH_2)_2OCH_2CH_2})(CO)_{15}$	287
			$Os_6\{\mu\text{-}\overline{S(CH_2)_2OCH_2CH_2}\}(CO)_{16}$	288
86		Octahedron	$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}CH)(\mu\text{-}PPh_2)_2(CO)_{10}Cp$	121
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(\mu\text{-dppm})_2(CO)_{11}$	128
			$Ru_6(\mu_6\text{-}C)\{\mu\text{-}PH_2(CH_2)_nPPh_2\}(\mu\text{-}CO)(CO)_{14}$ (n = 1, 2, 3)	129
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2\{\mu\text{-}P(NPr^i{}_2)_2\}(CO)_{13}]^-$	132
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}PEt_2)_2(CO)_{14}$	133
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}PEt_2)(CO)_{13}Cp$	134
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{14}\{PPh_2(CH_2)_3Ph\}$	135
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{12}\{\mu\text{-}\eta^1{:}\eta^6\text{-}PPh_2(CH_2)_3Ph\}$	136
			$Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^1{:}\eta^6\text{-}PPh_2(Ph)\}(\mu\text{-}CO)_2(CO)_{11}$	137
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5H_4)(\mu\text{-}CO)_2(CO)_{12}$	139
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{10}Cp_2$	140
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)(\mu\text{-}CO)(CO)_{13}$	141
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^5\text{-}C_5H_4PPh_3)$	142
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_5H_4CPh_2)(CO)_{15}$	143
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}C_5H_4CMe_2)(\mu\text{-}CO)(CO)_{13}$	144
			$Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^3{:}\eta^5\text{-}C_5H_4C(CH_2)_2\}(\mu\text{-}CO)_2(CO)_{11}$	145
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{10}(\eta^5\text{-}C_5H_4CMe_2H)(\eta^5\text{-}C_5H_4CMe_2OH)$	146
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{12}(\eta^6\text{-}C_6H_3R_3\text{-}1,3,5)$ ($R_3 = Me_2H$, Et_3)	147
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_5R)$ ($R = CHMe_2$, Bu)	148
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}\{\eta^6\text{-}Ph(CH_2)_nPh\}$ (n = 0,1)	149
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{13}\{\eta^6\text{-}Ph(CH_2)_2Ph\}$	150
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}R^1C_6H_4R^2)$ ($R^1 = Ph$, $R^2 = Me$; $R^1 = Me$, Et, $R^2 = Ph$)	151,152
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)$	153
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_4C_{18}H_{28}O_8)$	154
			$[PhCH_2NH_2CH_2Ph][Ru_6(\mu_6\text{-}C)(CO)_{13}\text{-}(\eta^6\text{-}C_6H_4C_{12}H_{24}O_8C_6H_4)]$	155
			$[H_3N(CH_2)_8NH_3][Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]_2$	156
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{12}\{\eta^6\text{-}C_6H_4(CO_2Me)_2\text{-}1,4\}$	157
			$Ru_6(\mu_6\text{-}C)\{\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_4(CO_2Me)_2\text{-}1,4\}(\mu\text{-}CO)(CO)_{13}$	158
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}PhCHMePh)$	159
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})(\mu\text{-dppm})(\mu\text{-}CO)_2(CO)_{10}$	160
			$Os_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_6)$	161
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{11}Cp]^-$	162
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R^3)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_6H_4R^1R^2)$ ($R^1 = Me$, $R^2 = H$, $R^3 = Me$; $R^1 = Me$, $R^2 = R^3 = H$; $R^1 = R^2 = Me$, $R^3 = H$)	163
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}1,3\text{-}C_6H_4Me_2)_2$	164
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_6H_5Me)(\eta^6\text{-}C_6H_4Me_2)$	165,166
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(CO)_{14}$	167
			$Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-}C_6H_6)$	168
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(\mu\text{-}CO)(CO)_{11}$	169

(Continued)

Table 2 (Continued)

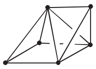
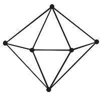
PSEPT	*Core structure*	*Core name*	*Compound*	*Comp. no.*
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(CO)_{12}(\eta^6\text{-}C_6H_6)$	170
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}CO)(CO)_{13}$	171
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_{16}H_{16})$	172
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)(CO)_{11}$	173
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{16}H_{15}NH_2)(\mu\text{-}CO)(CO)_{13}$	175
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{15}Br)(\mu\text{-}CO)(CO)_{13}$	176
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}\textit{meta}\text{-}C_{16}H_{16})$	177
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}\textit{para}\text{-}C_{24}H_{24})$	178
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{14}(\eta^4\text{-}ENBD)$	179
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_7H_8)(\mu\text{-}CO)(CO)_{13}$	180
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^3\text{-}C_7H_8)(\mu\text{-}CO)(CO)_{10}(\eta^5\text{-}C_7H_9)$	181
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{-}MeC_2Me)(CO)_{12}(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2\text{-}1,3$, $C_6H_3Me_3\text{-}1,3,5$)	182
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu_3\text{-}\eta^2\text{-}MeC_2Me)(CO)_{12}$	183
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_4R_2\text{-}1,4)$ (R = Ph, Me)	184
			$[Ru_6(\mu\text{-}H)(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{12}]^-$	185
			$[Ru_6H(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_{12}]^-$	186
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}CO)(CO)_{14}]^-$	187
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}C_5H_7CCCHC_5H_8)(\mu\text{-}CO)(CO)_{13}$	193
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^1{:}\eta^3\text{-}CHC_7H_{11})(\mu\text{-}CO)(CO)_{14}$	195
			$Ru_6(\mu_6\text{-}C)\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}C_8H_{12}CHCHCHC(OH)C_8H_{14}\}(\mu\text{-}CO)(CO)_{13}$	197
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_{12}(\eta^5\text{-}C_5H_3Ph_2)$	198
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^4\text{-}CPhCHCHCPh)(\mu\text{-}CO)(CO)_{13}$	199
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}MeC_2Me)_3(CO)_{12}$ (88 c.v.e.)	201
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}PhC_2Ph)_2(CO)_{13}$	202
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\textit{s-cis,s-cis,trans}\text{-}1,2\text{-}\eta^2\text{-}3\text{-}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)\text{-}(\mu\text{-}CO)_2(CO)_{12}$	203
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\textit{s-trans,s-cis,trans}\text{-}1,2\text{-}\eta^2\text{-}3\text{-}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)(\mu\text{-}CO)_2(CO)_{12}$	204
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_8H_{12})(CO)_{15}$	205
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}CO)(CO)_{13}(NO)$	206
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_4CO_2Me)(\mu\text{-}CO)_3(CO)_{11}(NO)$	207
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SO_2)(CO)_{14}]^-$	208
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)(CO)_{16}$	209
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)(\mu\text{-}CO)_2(CO)_{13}]^{2-}$	210
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)_2(\mu\text{-}CO)_2(CO)_{12}]^{2-}$	211
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)(\mu\text{-}CO)(CO)_{13}(NO)]^-$	212
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2Me)(\mu\text{-}CO)_2(CO)_{13}]^-$	213
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}SO)(CO)_{15}$	214
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}[12]aneS_3)(\mu\text{-}CO)_2(CO)_{11}$	218
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^2\text{-}[16]aneS_4)(\mu\text{-}CO)(CO)_{14}$	219
			$Ru_6(\mu_6\text{-}C)(\eta^3\text{-}[9]aneS_3)(\mu\text{-}CO)(CO)_{13}$	220
			$Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^3\text{-}\textit{cis}\text{-}SCH_2CHMe(CH_2SCH_2CHMe)_2CH_2\}\text{-}(\mu\text{-}CO)_2(CO)_{11}$	222
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}SePh)_2(CO)_{14}$	223
			$Ru_6(\mu_6\text{-}C)(\mu\text{-}SePh)(\mu\text{-}\eta^3\text{-}C_3H_5)(CO)_{14}$	224
			$Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^3\text{-}\textit{trans}\text{-}SCH_2CHMe(CH_2SCH_2CHMe)_2CH_2\}\text{-}(\mu\text{-}CO)_2(CO)_{11}$	
			$Ru_6(\mu_6\text{-}B)(\mu\text{-}H)(\mu\text{-}CO)_2(\mu\text{-}dppm)(CO)_{13}$	239
			$H_2Ru_6(\mu_3\text{-}PBu^t)_3(CO)_{12}$	262
86		Capped square pyramid	$Os_6(\mu\text{-}H)_2(CO)_{18}$	127
			$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}MeC_2Me)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2R_2)(CO)_{14}$(R = Me, Ph)	200
			$Os_6(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(\mu\text{-}CO)(CO)_{14}(NC_5H_5)(NCMe)$	250
			$Ru_6(\mu_4\text{-}PBu^t)(\mu_3\text{-}PBu^t)_3(CO)_{11}$	263
86		Three fused butterflies	$Os_6(\mu\text{-}H)_3(\mu_6\text{-}B)(CO)_{16}$	238

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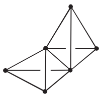
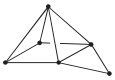
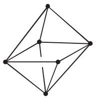
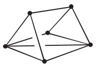
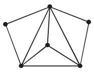
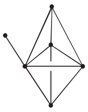
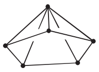
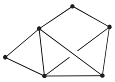
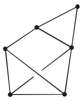
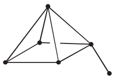
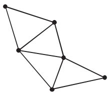
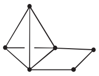
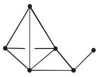
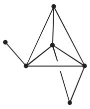
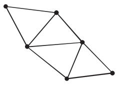
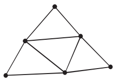
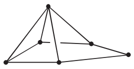
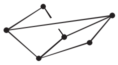
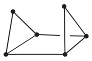
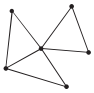
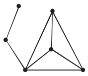
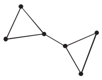
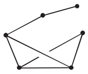
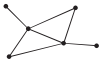
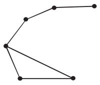
Table 2 (Continued)

PSEPT	*Core structure*	*Core name*	*Compound*	*Comp. no.*
86		Edge-fused tetrahedra	$Os_6(\mu\text{–}H_2)_2\{\mu\text{-}\overline{S(CH_2)_2OCH_2C}H_2\}\{\overline{S(CH_2)_2OCH_2C}H_2\}(CO)_{15}$	289
88		Edge-bridged square pyramid	$Ru_6(\mu_6\text{-}C)(\mu\text{-dppf})(\mu\text{-}CO)_2(CO)_{13}$	130
			$Ru_6(\mu_5\text{-}C)(\mu_3\text{-}S)(CO)_{16}$	215
			$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-apyPh-}N,N)(\mu\text{-}CO)_2(CO)_{14}$	240
			$Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\eta^3\text{-apy}C_6H_4\text{-}N,N,C)(\mu\text{-}CO)_3(CO)_{13}$	241
			$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy-}N,N)(\mu\text{-}CO)_2(CO)_{13}L$ (L = CO, PPh_3)	242
			$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy-}N,N)(\mu\text{-}CO)_2(CO)_{13}(PPh_3)$	243
			$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy-}N,N)(\mu\text{-}CO)_2(CO)_{11}(L)(PPh_3)_2$ (L = CO, PPh_3)	244
			$Ru_6(\mu\text{-}H)_2\{\mu_5\text{-}\eta^2\text{-NC(O)OMe}\}(\mu\text{-}CO)_2(CO)_{14}$	260
			$Ru_6(\mu_4\text{-}S)\{\mu_4\text{-CCHCH=C(Me)Bu}^t\}(CO)_{16}$	275
88		Bond-opened octahedron	$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{12}(\eta^4\text{-}C_4Ph_4)$	138
			$[Ru_6(\mu_6\text{-}C)(\mu\text{-}Br)(\mu\text{-}CO)_2(CO)_{14}]^-$	191
88		Trigonal prism + bond	$Ru_6(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-CCHC}_5H_6)_2(\mu\text{-}CO)_2(CO)_{12}$	194
88		Bi-edge-bridged tetrahedron	$Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(\mu\text{-}CO)(CO)_{12}(\eta^6\text{-}C_6Me_6)$	229
			$Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(\mu\text{-}CO)(CO)_{12}(\eta^5\text{-}C_5R)$ (R = H_4Me, Me_5)	230
			$Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(\mu\text{-}CO)(CO)_{12}(\eta^5\text{-}C_5H_3C_3H_6)$	231
88		Spiked trigonal bipyramid	$Os_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{15}(NC_5H_5)_3$	248
			$Os_6(\mu\text{-}H)(\mu\text{-SeH})(CO)_{18}$	273
88		Pentagonal pyramid	$Ru_6(\mu_6\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_2C{\equiv}CBu^t)(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{13}$	265
90		Bibridged butterfly	$Ru_6(\mu_5\text{-}C)(\mu_3\text{-}\eta^1{:}\ \eta^2{:}\ \eta^2\text{-}C_{16}H_{16}\text{-}\mu\text{-}O)(\mu\text{-}CO)(CO)_{14}(\eta^6\text{-}C_{16}H_{16})$	174
			$Ru_6(\mu\text{-}H)_2(\mu_6\text{-}C)(\mu_3\text{-}S)(CO)_{16}$	216
			$Ru_6(\mu\text{-}H)(\mu_5\text{-}N)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(CO)_{13}$	261
90		Spiked square pyramid	$Ru_6(\mu_5\text{-}C)(\mu_3\text{-}\eta^3\text{-}SCH_2CH_2SCH_2CH_2S)(CO)_{14}$	221
90		Edge-fused butterflies	$Ru_6(\mu_4\text{-}\eta^1{:}\ \eta^1{:}\ \eta^1{:}\ \eta^2\text{-}CCH_2)_2(CO)_{16}$	225
			$Ru_6(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}CCH_2)_2(\mu\text{-dppm})_2(CO)_{12}$	227
			$Ru_6(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}Bu^tCH{=}CHC_2PPh_2)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(CO)_{13}$	266
			$Ru_6(\mu_3\text{-}H)_2(\mu_4\text{-}\eta^2\text{-}L)_2(CO)_{14}$ [HL = (4*S*, 5*S*)-(−)-2-methyl-5-phenyl-2-oxazoline-4-methanol]	270
90		Fused tetrahedron + square	$Ru_6(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^2\text{-}PhCHC_3C_6H_4)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhCHC_3C_6H_4)(CO)_{15}$	228
90		Tetrahedron + fused spiked triangle	$Ru_6(\mu\text{-}H)(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6\text{-}R)(\mu\text{-}CO)(CO)_{14}$ (R = $C_{12}H_{11}$, $C_{12}H_{13}$)	236
			$Ru_6(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^3{:}\eta^6\text{-}C_{13}H_7CHC)(CO)_{15}$	237
90		Spiked edge-bridged tetrahedron	$Os_6(\mu\text{-}H)(\mu_3\text{-}O)(\mu\text{-}\eta^2\text{-}NC_5H_4)(\mu\text{-}CO)(CO)_{15}(NC_5H_5)$	249

(Continued)

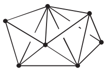
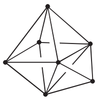
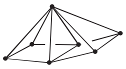
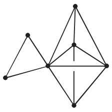
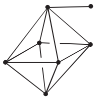
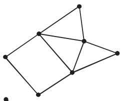
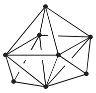
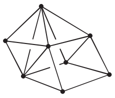
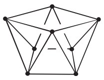
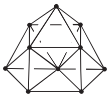
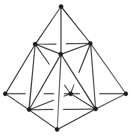
Table 2 (Continued)

PSEPT	*Core structure*	*Core name*	*Compound*	*Comp. no.*
90		Raft	$Os_6(\mu_3-\eta^2-2-NC_5H_4S)_2(CO)_{16}$ $Os_6(\mu_4-\eta^2-2-NC_5H_4S)(CO)_{17}$ $Ru_6\{\mu_6-C(Me)CCC(Me)\}(\mu-SEt)_2(CO)_{14}$	251 252 274
90		Raft	$Ru_6(\mu_6-C_{10}H_6)(\mu_3-PPh)(CO)_{14}$ (88 c.v.e.)	264
90		Bond-opened edge-bridged square pyramid	$Ru_6(\mu_6-C_2CH{=}CHBu^t)(\mu_3-C_2Bu^t)(\mu-PPh_2)_2(\mu-CO)(CO)_{12}$	267
92		Fused squares + bond	$Ru_6(\mu_4-\eta^1:\eta^1:\eta^2:\eta^4-CCHR)_2(CO)_{14}$ ($R = C_7H_{10}, C_8H_{12}$)	196
92		Bi-edge-bridged square	$Ru_6(\mu-H)_4(\mu_5-C)(\mu_3-S)(CO)_{16}$ $Ru_6(\mu-H)(\mu_3-\eta^2-ampy-N,N)(\mu-CO)_2(CO)_{15}$ $Ru_6(\mu-H)(\mu_4-NH)\{\mu_3-\eta^2-C(O)OMe\}(\mu-CO)(CO)_{16}$ $Ru_6(\mu-R)(\mu_4-NH)(\mu-OMe)(\mu-CO)_2(CO)_{16}$ (R = H, OMe, NCO) $Ru_6(\mu_4-NH)\{\mu_3-\eta^2-NHC(O)OMe\}(\mu-OMe)(\mu-CO)_2(CO)_{15}$ $Os_6(\mu_4-O)(\mu-OH)_2(\mu-CO)_2(CO)_{16}$ (94 c.v.e.) $Ru_6(\mu_4-S)\{\mu_3-\eta^2-SC(NHR)N(R)\}\{\mu_3-\eta^2-C(NHR)NR\}(\mu-CO)_2(CO)_{14}$ (R = Et, Ph) (94 c.v.e.) $Ru_6(\mu-H)(\mu_5-S)\{\mu_3-\eta^2-SC(NHPh)NPh\}(CO)_{16}$ (L = CO, CNBu^t) $Ru_6(\mu-H)_6\{\mu_3-\eta^2-SC(NHPh)NPh\}_2(CO)_{14}$ $Ru_6(\mu_4-S)(\mu_3-pyS)(\mu-SH)(\mu-CO)_2(CO)_{15}$ (94 c.v.e.)	217 246 255 256 259 268 276 277 278 280
92		Vertex-fused butterfly and triangle	$Ru_6(\mu-H)(\mu_4-\eta^1:\eta^1:\eta^2:\eta^2-C)(\mu_4-C_2Me)(\mu-CO)(CO)_{16}$	226
92		M_2-spiked tetrahedron	$Os_6(\mu-H)(\eta^2-C_6F_5NNNC_6F_5)(\mu-CO)(CO)_{19}$	254
94		Fused squares	$Ru_6(\mu_6-\eta^1:\eta^1:\eta^2:\eta^2:\eta^1:\eta^1-C_2)(\mu-PPh_2)_2(\mu-SMe)_2(CO)_{14}$ $Ru_6\{\mu_4-\eta^1:\eta^1:\eta^2:\eta^2-CC(H)C(O)Me\}_2(CO)_{16}$ (92 c.v.e.)	124 269
94		Linked triangles	$Ru_6(\mu-H)(\mu_3-\eta^2-ampy-N,N)_2(\mu-CO)_2(CO)_{16}$ $Ru_6(\mu-H)(\mu_5-S)\{\mu_3-\eta^2-SC(NHPh)N(Ph)\}(CO)_{15}(PPh_3)$ (92 c.v.e.)	245 279
94		M_2-spiked butterfly	$Os_6(\mu-H)(\mu-\eta^3-NC_5H_4CH{=}CH)(CO)_{20}$	247
94		2M-spiked butterfly	$M_6(\mu_3-E)_4(\mu-dppm)_2(CO)_{12}$ (M = Ru, E = S; M = Os, E = Se) (96 c.v.e.)	271
96		M_3-spiked triangle	$Os_6(\mu_4-S)(CO)_{20}(NCMe)$	281

metal core, and one significantly longer C–O bond distance, suggesting a μ_4-COH ligand. An attempt to form the carbido cluster $Ru_5(\mu_5-C)(CO)_{15}$ by protonation of 1 with CF_3COOH under CO resulted in the formation of a cluster anion, suggested to be $[HRu_5(CO)_{16}]^-$ on the basis of ^1H NMR and FAB MS.[14]

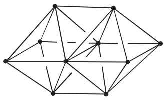
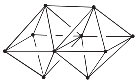
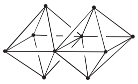
Pentaosmium cluster carbonyls and related anions, hydrides, and substitution products, available from studies by Lewis and co-workers, are summarized in COMC (1995).[16]

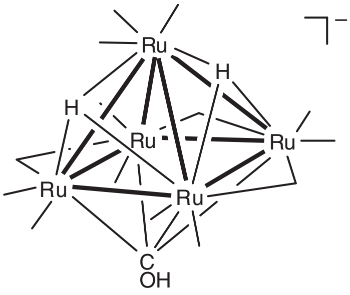
Table 3 M ≥ 7 clusters crystallographically-characterized 1993–2004

M_7				
96		Tri-capped tetrahedra	$Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)$ $Os_7\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}_2(CO)_{16}$ $Os_7\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}(CO)_{17}\ (S(CH_2)_2OCH_2CH_2)$ $Os_7\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}(CO)_{18}$	293 302 303 304
98		Capped octahedron	$[Os_7(CO)_{20}]^{2-}$ $Os_7(CO)_{20}(CNBu^t)$ $Ru_7(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_{10}Cp_2$ $[Ru_7(\mu_6\text{-}C)(\mu_3\text{-}CO)(\mu\text{-}CO)_4(CO)_{11}Cp]^-$	290 291 294 295
100	-		$Ru_7(\mu_4\text{-}PBu^t)_2(\mu_3\text{-}PBu^t)_2(CO)_{14}$	298
100		Face-sharing square pyramids	$Ru_7(\mu_4\text{-}PPh)_2\{(\mu_2\text{-}PPh)_2CH_2\}(CO)_{15}$ (2 isomers)	300,301
102		Triangle + trigonal bipyramid	$Os_7H_2(CO)_{21}\{P(OMe)_3\}$	292
102		Spiked octahedron	$Ru_7(\mu_6\text{-}C)\{\mu_3\text{-}\eta^2{:}\eta^6{:}\eta^6\text{-}(C_6H_4)_2CH_2\}(CO)_{14}$ $Ru_7(\mu_6\text{-}C)(\mu_4\text{-}\eta^4{:}\eta^2{:}\eta^2{:}\eta^2\text{-}R)(\mu\text{-}CO)_2(CO)_{14}$ (R = C_9H_8, $C_{12}H_{12}$)	296 297
106		Fused square + bow-tie	$Ru_7(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}CCCHMe\ \{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CCHC(O)Me\}(CO)_{19}$	299
108		Edge-bridged fused squares	$Ru_7(\mu_6\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{15}$	125
M_8				
110		Bicapped octahedron	$Os_8(CO)_{20}(\eta^6\text{-}C_6H_6)$ $HRu_8(\mu_3\text{-}H)_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_{16}(\eta^6\text{-}R)$ (R = C_6H_6, $C_{16}H_{16}$)	306 307
112		Fused capped trigonal prism and tetrahedron	$Os_8(\mu_6\text{-}C)(CO)_{22}$	305
114	-		$Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})$	308
114	-		$Ru_8(\mu_6\text{-}\eta^2\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{18}(\eta^6\text{-}C_{16}H_{16})$	309
118		Square antiprism	$[Ru_8(\mu_8\text{-}P)(\mu\text{-}CO)_2(CO)_{20}]^-$ (114 c.v.e.)	310
M_9				
130	-		$Ru_9(\mu_3\text{-}H)(\mu\text{-}H)_2(\mu_7\text{-}P)(\mu_3\text{-}PBu^t)_3(CO)_{20}$ (132 c.v.e.)	311
$M_{\geq 10}$				
132		Bicapped octahedron + bicapped square	$[H_2Ru_{10}(\mu_3\text{-}CO)(\mu\text{-}CO)_4(CO)_{20}]^{2-}$ (134 c.v.e.)	317
134		Tetracapped octahedron	$[Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24}]^-$ $[Ru_{10}(\mu_6\text{-}C)(CO)_{24}]^{2-}$ $[Ru_{10}(\mu_6\text{-}N)(CO)_{24}]^-$ $[Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{23}(PPh_3)]^-$ $[Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{22}\{P(OMe)_3\}_2]^-$ $[H_5Os_{10}(CO)_{24}]^-$	312 313 314 315 316 318

(Continued)

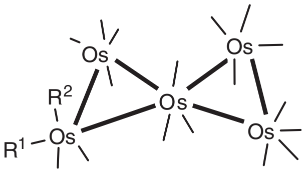
Table 3 (Continued)

M_7				
134		Edge-sharing octahedra + 2 bonds	$Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_{20}(\eta^2{:}\eta^2\text{-nbd})$ $[Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_3H_4)(\mu\text{-}CO)_4(CO)_{18}]^{2-}$ $[Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_3H_4)_2(\mu\text{-}CO)_4(CO)_{16}]^{2-}$	323 324 325
136		Edge-sharing octahedra + 1 bond	$Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}CO)_4(CO)_{19}$ $Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}CO)_4(CO)_{19}(\eta^2{:}\eta^2\text{-nbd})$ $Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}CO)_4(CO)_{17}(\eta^2{:}\eta^2\text{-nbd})$	320 321 322
138		Edge-sharing octahedra	$[Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}CO)_4(CO)_{20}]^{2-}$	319
150	-		$[Os_{11}(\mu_6\text{-}C)(\mu\text{-}Cl)(CO)_{27}]^-$	328
156	-		$Os_{11}(\mu_4\text{-}O)_3(CO)_{30}$ (160 c.v.e.)	327
156	-		$Os_{12}(CO)_{30}$	329
210	-		$[Os_{17}(CO)_{36})]^{2-}$	330
248	-		$[Os_{20}(CO)_{40})]^{2-}$ (242 c.v.e.)	331

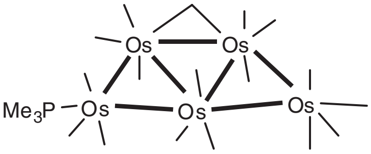


1

Pomeroy and co-workers have prepared ligand-substituted pentaosmium clusters by the nucleophilic attack of $Os(CO)_4(L)$ ($L = PMe_3$,[17] $CNBu^t$[18]) at $Os_4(CO)_{14}$, including three geometric isomers of $Os_5(CO)_{15}(L)$. $Os_5(CO)_{18}(PMe_3)$ **2** is formed in good yield at room temperature; it consists of a bow-tie arrangement of osmium atoms, similar to the binary cluster $Os_5(CO)_{19}$, with the phosphine ligand occupying an equatorial site on an outer osmium atom. Thermolysis of **1** at 43 °C gives $Os_5(\mu\text{-}CO)(CO)_{16}(PMe_3)$ **3**, an edge-bridged butterfly with the phosphine in an equatorial site. The axial **4** and equatorial **5** isomers of the trigonal-bipyramidal cluster $Os_5(CO)_{15}(PMe_3)$ are formed by thermolysis of **3** at 63 °C and 110 °C, respectively, and exist in equilibrium at ca. 80 °C.[17] The related $Os_5(CNBu^t)(CO)_{18}$ **6** contains an axially coordinated isocyanide ligand with a metal core arrangement similar to **2**. Thermolysis of **6** at ca. 45 °C over 3 days affords the spectroscopically characterized $Os_5(CNBu^t)(CO)_{17}$ in almost quantitative yield. Thermolysis of the latter at 65–70 °C gives $Os_5(CNBu^t)(CO)_{15}$ **7**, with the isocyanide ligand located on the most sterically hindered osmium atom of the trigonal-bipyramidal core.[18]



2: $R^1 = PMe_3$; $R^2 = CO$
6: $R^1 = CO$; $R^2 = CNBu^t$



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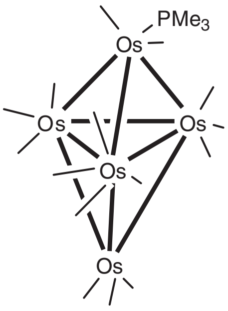

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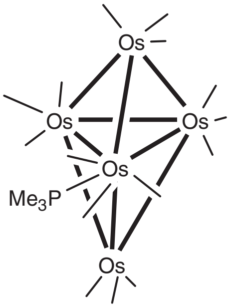

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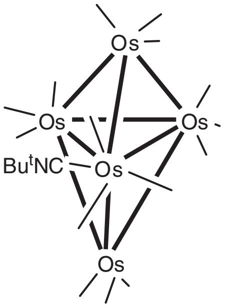
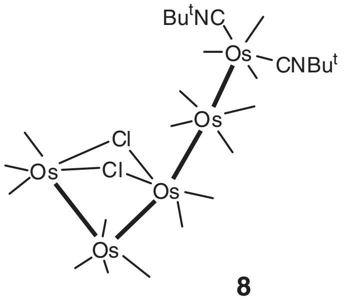


7

Reaction of $Os_3(\mu\text{-}X)_2(CO)_{10}$ (X = Cl, Br) with 2 equiv. of $Os(CNBu^t)(CO)_4$ at 60 °C over 7 days forms pentanuclear clusters $Os_5(\mu\text{-}X)_2(CNBu^t)_2(CO)_{16}$ (X = Cl **8**, Br) in good yields. The complex has a chain of osmium atoms related to the parent trisomium cluster by replacement of one of the carbonyl ligands with an $Os_2(CO)_7(CNBu^t)_2$ unit.[19] A similar reaction with $Os_3X_2(CO)_{12}$ affords the linear clusters $Os_5X_2(CNBu^t)_2(CO)_{18}$ (X = Cl **9**, Br, I). These remarkably stable complexes are the first group 8 metal clusters containing unbridged dative Os–Os bonds. The tetraosmium chain can be prepared using an equimolar amount of $Os(CNBu^t)(CO)_4$.[20]



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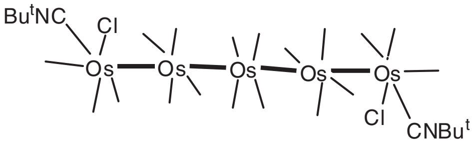
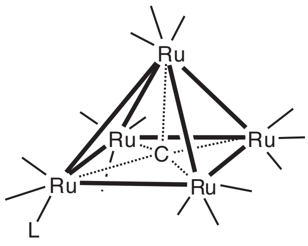


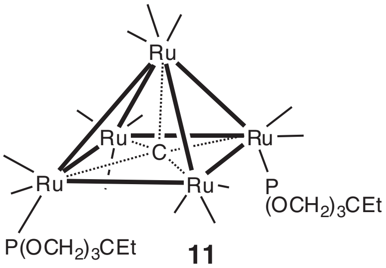
9

6.24.2.2 Carbido Clusters

The earlier chemistry of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ and $Ru_6(\mu_6\text{-}C)(CO)_{17}$ has been reviewed.[21] Poë and co-workers have clarified aspects of the substitution chemistry of pentaruthenium carbido clusters by comprehensive kinetic, thermodynamic, and structural studies. Stopped-flow kinetic measurements and thermodynamic studies on the reversible addition of MeCN to $Ru_5(\mu_5\text{-}C)(CO)_{15}$ provide quantitative data for the structural change from square-pyramidal to bridged butterfly geometries resulting from Ru–Ru bond cleavage.[22] Substitution at $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with small phosphines occurs by two well-separated steps involving adduct formation and CO dissociation, whereas reaction with larger phosphines occurs through a second-order one-step process.[23] Average Ru–Ru separations in phosphine-substituted pentaruthenium carbido clusters $Ru_5(\mu_5\text{-}C)(CO)_{14}L$ **10** [L = $P(4\text{-}C_6H_4OMe)_3$, $P(4\text{-}C_6H_4F)_3$, PCy_3], $Ru_5(\mu_5\text{-}C)(CO)_{13}(etpb)_2$ **11** [etpb = $P(OCH_2)_3CEt$], and other $Ru_5(\mu_5\text{-}C)(CO)_{15-n}L_n$ examples are similar, but the individual values span a wide range; Ru–Ru bonds *cis* to PR_3 substituents are longer than other Ru–Ru distances, but a clear dependence on cone angle of PR_3 is not observed. In contrast, the Ru–P distances increase with cone angle. As PR_3 basicity increases, the carbido atom is found further out from the basal Ru_4 plane.[24] Substitution at $Ru_5(\mu_5\text{-}C)(CO)_{14}\{P(OPh)_3\}$ and $Ru_5(\mu_5\text{-}C)(CO)_{14}(PCy_3)$ occurs by an associative pathway to give products containing the two ligands at ruthenium atoms on opposite vertices of the basal plane,[25] while bidentate ligands such as dppf coordinate diaxially **29**.[26] The ferrocenyl pentaruthenium carbido cluster $Ru_5(\mu\text{-}H)(\mu_5\text{-}C)\{\mu\text{-}C(\eta\text{-}C_5H_4)FeCp\}(CO)_{13}$ **12**, with a bridging ferrocenyl alkylidene ligand, is prepared in 10% yield from the thermolysis of $Ru_4\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}(OHC)CC(\eta\text{-}C_5H_4)FeCp\}(CO)_{12}$ in toluene.[27]



10: L = P(4-$C_6H_4OMe)_3$, P(4-$C_6H_4F)_3$, P($C_6H_{11})_3$



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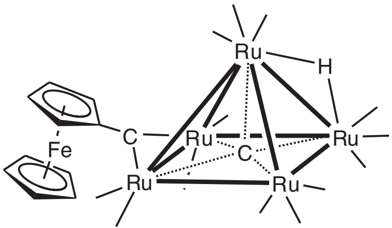
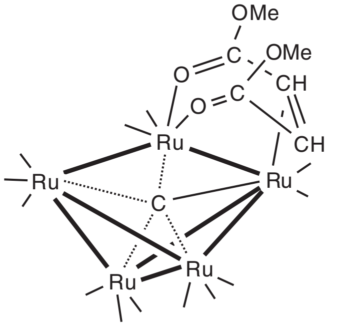


12

$Ru_5(\mu_5\text{-}C)(CO)_{15}$ reacts with Me_3NO followed by dimethyl maleate or dimethyl acetylenedicarboxylate to give the wingtip-bridged butterfly complexes $Ru_5(\mu_5\text{-}C)\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}(MeO_2C)CHCH(CO_2Me)\}(CO)_{13}$ **13**, 51% or $Ru_5(\mu_5\text{-}C)\{\mu\text{-}\eta^2\text{-}(MeO_2C)C_2(CO_2Me)\}(\mu\text{-}CO)(CO)_{14}$ **14**, 8%, respectively. No reaction occurs with dimethyl fumarate, in which the CO_2Me groups are arranged (*E*) with respect to the C=C bond.[28]



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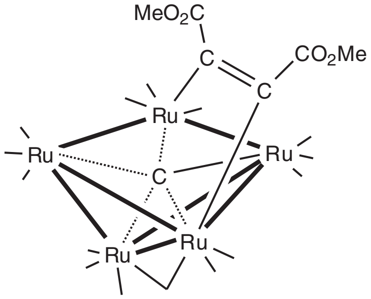
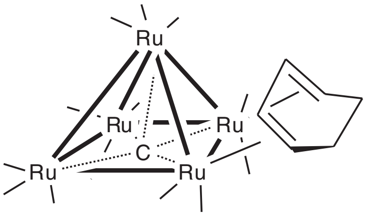


14

Ruthenium carbido clusters containing carbocyclic ligands are available from the work of Johnson and co-workers, and can be prepared by direct substitution of carbonyl or other cluster-bound ligands with an unsaturated organic ligand, or by capping reactions using cyclopentadienyl-containing precursors. These routes have been used successfully to prepare a number of penta- and hexametallic carbido complexes. Some of the earlier work in this area has been reviewed.[29–33] A survey of the structures of M_5 and M_6 clusters (M = Ru, Os) containing cyclopentadienyl or η^6-arene ligands emphasizes the different geometries of the cores. The former are derived from t.b.p. frameworks by cleavage of M–M edges. The M_6 geometries are based on octahedral or bicapped tetrahedral frameworks. Extensive statistical analyses of the steric and electronic factors determining the positions of the carbocyclic rings and the ligand polyhedra and related low-energy fluxional processes have been given.[34]

Reactions of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with cyclohexa-1,3- and -1,4-diene afford derivatives bearing cyclohexadiene and benzene ligands; the interconversion of the observed η^6-terminal and $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-face-capping coordination modes has been studied in detail. Reaction with cyclohexa-1,3-diene in the presence of 2 equiv. of Me_3NO affords the $\mu\text{-}\eta^2{:}\eta^2$-diene complex $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,3\text{-}C_6H_8)(CO)_{13}$ **15**, which reacts with a further equivalent of Me_3NO to give isomeric clusters $Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{12}$ **16** and $Ru_5(\mu_5\text{-}C)(CO)_{12}(\eta^6\text{-}C_6H_6)$ **17**, containing a face-capping and an η^6-bound benzene ligand, respectively. CO addition to the latter gives the bridged-butterfly cluster $Ru_5(\mu_5\text{-}C)(CO)_{13}(\eta^6\text{-}C_6H_6)$ **18**; loss of CO from **18** affords **17** via the spectroscopically characterized apical isomer $Ru_5(\mu_5\text{-}C)(CO)_{12}(\eta^6\text{-}C_6H_6)$. The face-capped isomer **16** converts irreversibly into the η^6-basal-bound complex **17** on warming, without any evidence for the formation of the η^6-apical cluster intermediate.[35] Irradiation of **17** (in a PMMA film) gives the face-capped complex **16** via the η^6-apical complex, suggesting a heterolytic bond fission pathway for the thermolytic conversion and a homolytic fission pathway for the photolytic reaction.[36]



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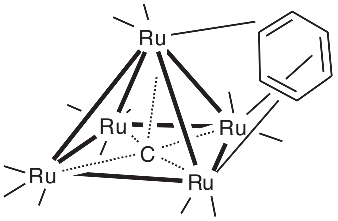

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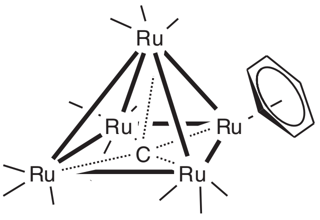

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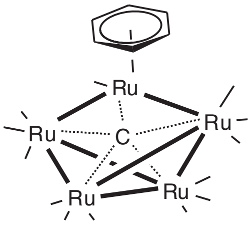
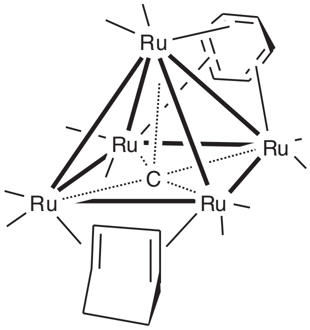


18

Isomeric clusters **16** and **17** react further with cyclohexa-1,3-diene to give benzene–diene complexes $Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,3\text{-}C_6H_8)(CO)_{10}$ **19** and $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,3\text{-}C_6H_8)(CO)_{10}(\eta^6\text{-}C_6H_6)$ **20**, containing an η^4-diene and face-capping or η^6-benzene ligands, respectively. In contrast to the facile interconversion of **16** and **17**, isomerization of **19** to **20** requires high temperatures, and is accompanied by extensive decomposition. The bis(η^4-diene) cluster $Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)_4(CO)_7(\eta^4\text{-}1,3\text{-}C_6H_8)_2$ **21** results from reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with the diene and 3 equiv. of Me_3NO, and converts into **16** on reaction with CO.[37] Reaction using cyclohexa-1,4-diene affords $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,4\text{-}C_6H_8)(CO)_{13}$ **22**, the structural analog of the 1,3-diene cluster **15**, which reacts with a second diene molecule to give $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}1,4\text{-}C_6H_8)_2(CO)_{11}$ **23**.[38,39]



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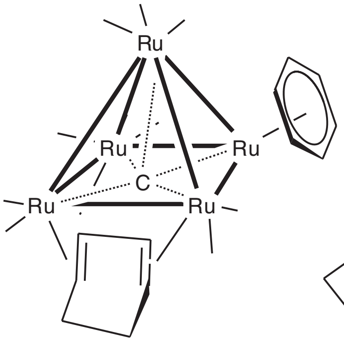

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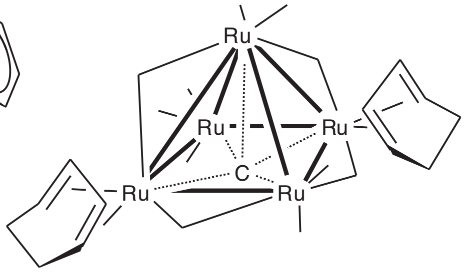

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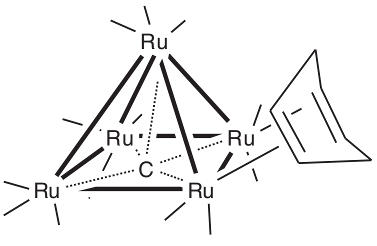

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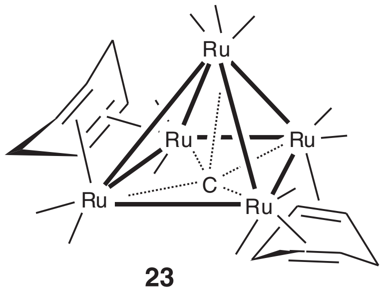
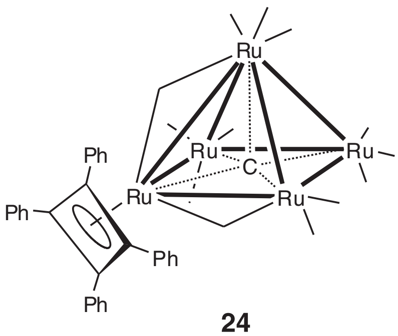


23

The cyclobutadiene complex $Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_{11}(\eta^4\text{-}C_4Ph_4)$ **24** is formed from a redox-mediated ligand transfer between $Ru_5(\mu_5\text{-}C)(CO)_{15}$ and $[Pd(acetone)_3(\eta^4\text{-}C_4Ph_4)]^{2+}$. The hexaruthenium analog **138** is prepared in a similar manner.[40,41] The cyclopentadienyl cluster $Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(CO)_{13}Cp$ **25** is formed from reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with sodium cyclopentadienide followed by protonation with HBF_4, and contains a hydride ligand bridging the butterfly hinge metal bond. Attempts to form the square-pyramidal isomer of **25**, or the cyclopentadienyl analog of **17**, were unsuccessful.[42] The reaction of cyclopentadiene and Me_3NO with $Ru_5(\mu_5\text{-}C)(CO)_{15}$ is less selective, giving the bis(cyclopentadienyl) clusters $Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_8Cp_2$ **26** and **140**, among a number of unidentified products.[43]



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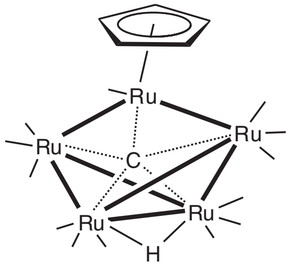

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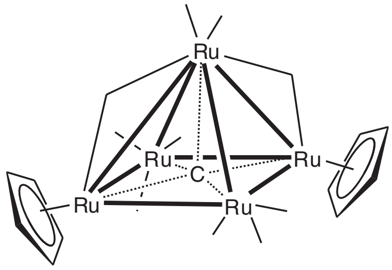
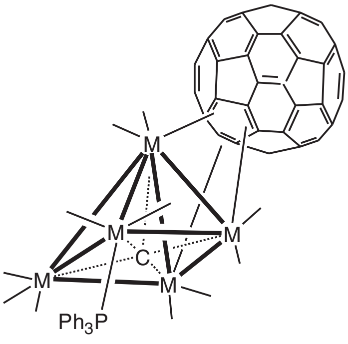
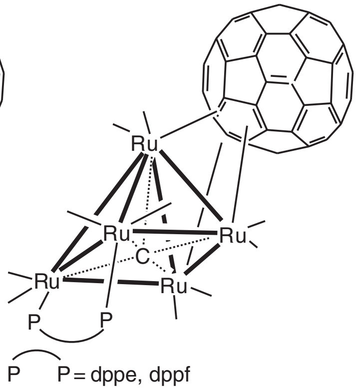


26

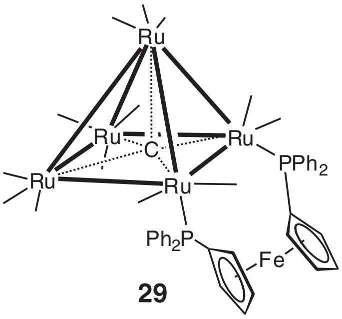
The chemistry of pentanuclear group 8 carbido clusters with C_{60} has been developed by Shapley (ruthenium) and Park (osmium), and their co-workers. The first example was prepared from the reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with C_{60} in refluxing chlorobenzene to give a brown, sparingly soluble solid with an IR spectrum similar to that of a pentaruthenium carbido complex containing a face-capping benzene ligand, suggesting formation of $Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})(CO)_{12}$. Addition of PPh_3, dppe or dppf to the brown reaction mixture affords $Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})(CO)_{11}(PPh_3)$ **27** and $Ru_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})(\mu\text{-}P_2)(CO)_{10}$ ($P_2 =$ dppe, dppf; **28**), respectively, the dppf example by way of an η^1-dppf intermediate. The C_{60} ligand caps one triangular face, as in **16**, and the phosphine ligands occupy axial positions on basal ruthenium atoms on the metal face opposite to the C_{60} site. The complexes are available in slightly better yields from the direct reactions of C_{60} with the corresponding phosphine-substituted pentaruthenium precursors, $Ru_5(\mu_5\text{-}C)(CO)_{15-n}(L)$ ($n = 1$, $L = PPh_3$; $n = 2$, $L =$ dppe, dppf **29**). The hexaruthenium analog **160** containing a coordinated dppm ligand has also been prepared.[26,44]



M = Ru, Os
27

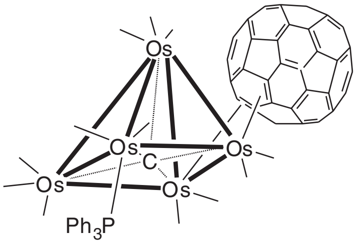


P = dppe, dppf
28



29

Reaction of C_{60} with $Os_5(\mu_5\text{-}C)(CO)_{12}(NCMe)_2(PPh_3)$ affords a mixture of $Os_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})(CO)_{11}(PPh_3)$ (**27**, $M = Os$) and $Os_5(\mu_5\text{-}C)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_{60})(CO)_{12}(PPh_3)$ **30**, containing the C_{60} ligand in face-capping and $\eta^2\text{:}\eta^2$-edge-bridging geometries, respectively. The two forms can be interconverted by thermolysis or carbonylation, the C_{60} ligand undergoing a 180° rotation with respect to the Os_3 face on interconversion between the two forms. Complex **27** ($M = Os$) can also be prepared by decarbonylation of $Os_5(\mu_5\text{-}C)(CO)_{14}(PPh_3)$ with Me_3NO and subsequent treatment with C_{60}. The isocyanide complexes $M_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})(CNCH_2Ph)(CO)_{11}(PPh_3)$ ($M = Ru$, Os **31**) have been prepared, the osmium example containing a wingtip-bridged butterfly arrangement of osmium atoms, obtained by Os–Os bond rupture on ligand addition. Thermolysis of **31** (M = Os) affords $Os_5(\mu_5\text{-}C)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_{60})(CNCH_2Ph)(CO)_{11}(PPh_3)$ **32**, which converts reversibly into the isomer $Os_5(\mu_5\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})(CNCH_2Ph)(CO)_{10}(PPh_3)$ (**33**, M = Os) by CO loss/addition. Thermolysis of the ruthenium isomer of **31** affords **33** (M = Ru), with no evidence for a $\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_{60}$ intermediate; the Ru_5C–C_{60} interaction is thought to be considerably stronger than the Os_5C–C_{60} bonding, precluding M–C bond scission in favor of carbonyl loss.[45,46] The C_{60}-substituted complexes **27** and **28** (P_2 = dppf) are reduced at significantly more positive potentials than the precursor phosphine–carbido clusters, consistent with the strong electronegative character of the face-capping C_{60} ligand.[47]



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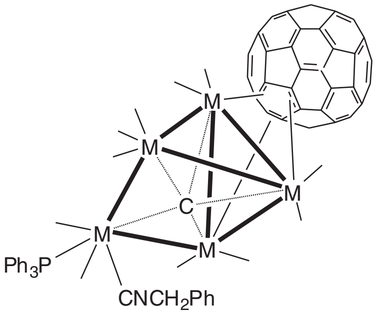
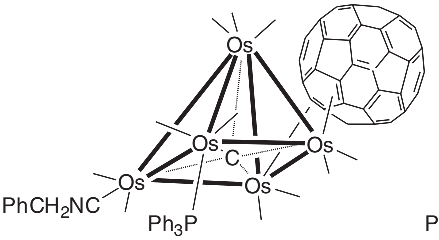


M = Ru, Os
31



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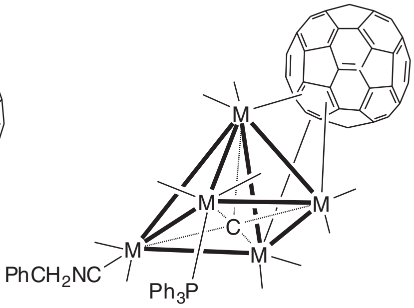
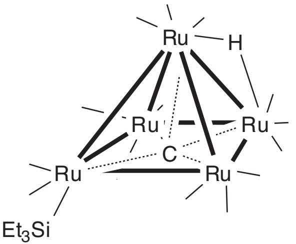


M = Ru, Os
33

The products from the photolytic reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with triethylsilane, square-pyramidal $Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(SiEt_3)(CO)_{14}$ **34**, and the wingtip-bridged butterfly complex $Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(SiEt_3)(CO)_{15}$ **35** can be interconverted, carbonylation of **34** affording **35**, and thermolysis of **35** giving **34**.[48] Reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with triphenylgermane at 150 °C affords square-pyramidal $Ru_5(\mu_5\text{-}C)(\mu\text{-}CO)(\mu\text{-}GePh_2)_3(CO)_{11}$ **36** and $Ru_5(\mu_5\text{-}C)(\mu\text{-}GePh_2)_4(CO)_{11}$ **37**; addition of $GeHPh_3$ to **36** also affords **37**. Complex **37** reacts with H_2 at 150 °C to initially give the dihydride $Ru_5(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}GePh_2)_4(CO)_{10}$ **38**, prolonged reaction affording $Ru_5(\mu_3\text{-}H)(\mu_4\text{-}CH)(\mu_3\text{-}GePh)_2(\mu\text{-}GePh_2)_2(CO)_{10}$ **39**, which contains a μ_4-methylidyne ligand derived from the interstitial carbon atom.[49]



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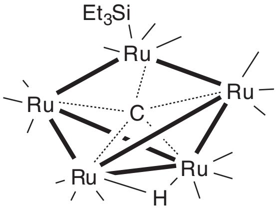

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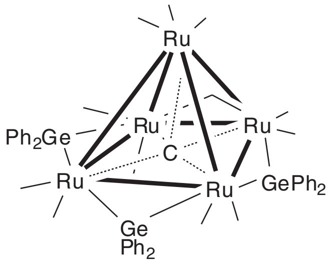

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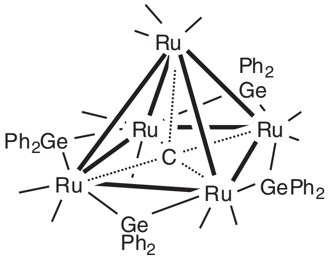

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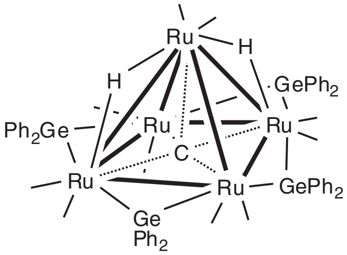

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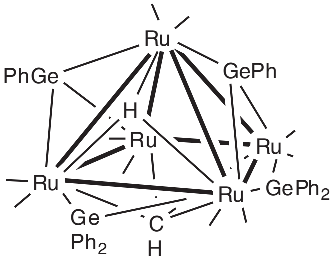
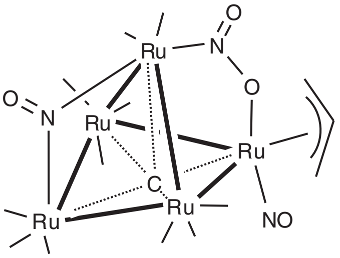


39

Nitric oxide reacts with anionic ruthenium clusters to give nitrosyl products by redox-type reactions involving the replacement of a carbonyl ligand and a single negative charge with an NO unit, and reacts with neutral nitrosyl clusters to give products bearing NO_2 ligands. The hexanuclear allyl cluster $[Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(CO)_{15}]^-$ reacts with NO to form the nitrosyl complexes $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}CO)(CO)_{13}(NO)$ **206** and $Ru_5(\mu_5\text{-}C)(\mu\text{-}NO)(\mu\text{-}\eta^2\text{-}NO_2)(CO)_{11}(NO)(\eta^3\text{-}C_3H_5)$ **40**. The former contains a terminal nitrosyl ligand, while the pentaruthenium product has both a terminal NO, and bridging NO and NO_2 ligands. Complex **206** reacts further with NO with loss of a ruthenium atom to give $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2\text{-}NO_2)(CO)_{13}(\eta^3\text{-}C_3H_5)$ **41**. The related anionic nitrosyl cluster $[Ru_6(\mu_6\text{-}C)(CO)_{15}(NO)]^-$, derived from $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ and NO, reacts further with NO with loss of a ruthenium atom to give pentanuclear $Ru_5(\mu_5\text{-}C)(\mu\text{-}NO)(\mu\text{-}\eta^2\text{-}NO_2)(CO)_{14}$, characterized as the PPh_3 adduct **42**, with the same bridged-square metal geometry as **40**. Complexes **40–42** retain a μ_5-carbido ligand which probably aids in stabilizing the metal core, similar reaction with the non-carbido dianion $[Ru_6(CO)_{18}]^{2-}$ leading only to decomposition products.[50,51]



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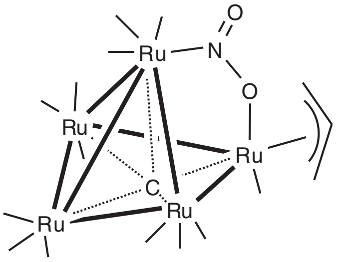

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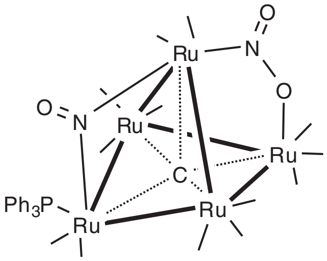
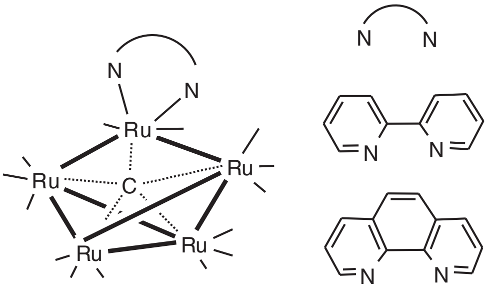


42

Reaction between $Ru_5(\mu_5\text{-}C)(CO)_{15}$ and 2,2′-bipyridyl (bipy) in the presence of Me_3NO affords the wingtip–bridged butterfly complexes $Ru_5(\mu_5\text{-}C)(CO)_{14}(\eta^2\text{-bipy})$ **43** and $Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}\eta^3\text{-}N_2C_{10}H_7)(CO)_{13}$ **44**, the latter being the orthometallated derivative of the former. Reaction with 1,10-phenanthroline (phen) affords the analogous complexes **45** and $Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}\eta^3\text{-phen–H})(CO)_{13}$.[52]



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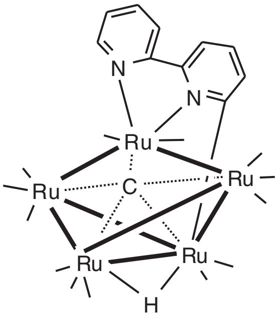
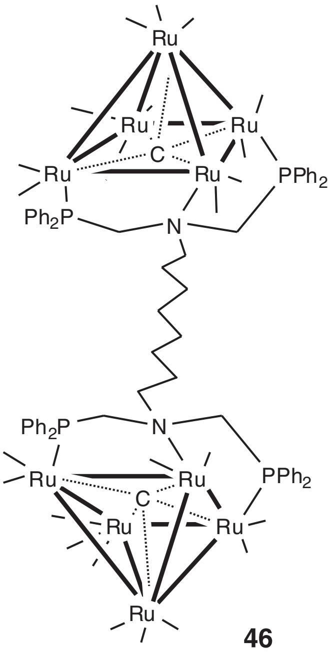


44

$Ru_5(\mu_5\text{-}C)(CO)_{12}$ has been attached to the tridentate terminal phosphine groups of the organic third-generation dendrimer DAB-dendrimer-$\{N(CH_2PPh_2)_2\}_{16}$ (DAB = diaminobutane); the model complex $\{Ru_5(\mu_5\text{-}C)(CO)_{12}\}_2\text{-}\{\mu\text{-}[N,P,P\text{-}(Ph_2PCH_2)_2N]_2(CH_2)_8\}$ **46**, containing two pentaruthenium square-based pyramids linked by the bis-tridentate ligand, has also been prepared.[53] The bridged pentaosmium dimer $\{Os_5(\mu_5\text{-}C)(CO)_{14}\}_2(\mu\text{-dppf})$ **47** forms from the thermolysis of the mixed-metal complex $Os_5Pd(\mu_6\text{-}C)(\mu\text{-dppf})(CO)_{14}$.[54]



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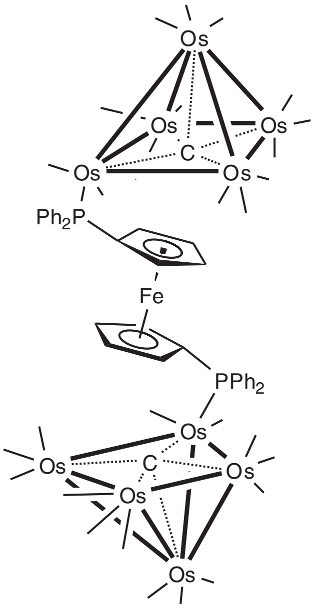

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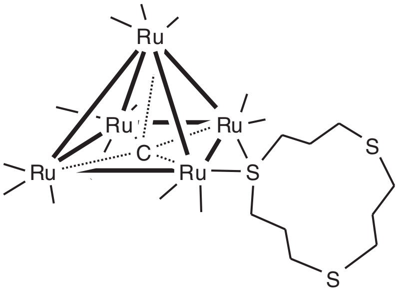
The polythiaether macrocycle 1,5,9-trithiacyclododecane (12S3) reacts with $Ru_5(\mu_5\text{-}C)(CO)_{15}$ in refluxing hexane to give $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^1\text{-}12S3)(CO)_{13}$ **48**, and in refluxing octane to give $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^3\text{-}12S3)(CO)_{11}$ **49**; the former is converted into the latter at 125 °C.[55]



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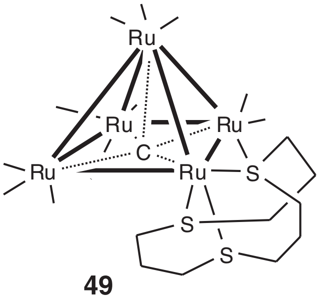

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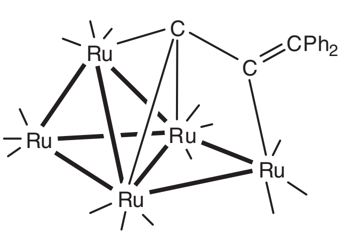
6.24.2.3 Clusters Containing Hydrocarbon Ligands

Acid-induced dehydration of the triruthenium hydroxyalkyne complex $Ru_3\{\mu_3\text{-}\eta^2\text{-}CH{=}CCPh(R)(OH)\}(\mu\text{-}CO)(CO)_9$ (R = Me, Ph) affords small amounts of the allenylidene complexes $Ru_5(\mu_4\text{-}\eta^2\text{-}CC{=}CPh_2)(CO)_{15}$ **50** and $Ru_5(\mu_5\text{-}\eta^3\text{-}CCCPhMe)(\mu\text{-}CO)(CO)_{14}$ **51**. Complex **50** contains an edge-bridged tetrahedral metal structure, whereas **51** has an edge-bridged butterfly core.[56]



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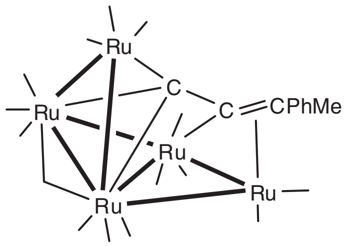
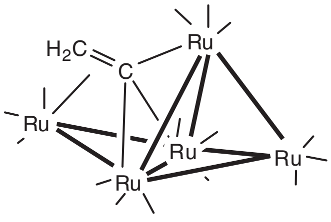


51

The room-temperature reaction between $Ru_3(CO)_{10}(NCMe)_2$ and ethyne to form $Ru_3(\mu_3\text{-}\eta^2\text{-}HC_2H)(\mu\text{-}CO)(CO)_9$ also gives trace amounts of the pentanuclear complex $Ru_5(\mu_4\text{-}\eta^2\text{-}CCH_2)(CO)_{15}$ **52**. Thermolysis of $Ru_3(\mu_3\text{-}\eta^2\text{-}HC_2H)(\mu\text{-}CO)(CO)_9$ in hexane affords slightly more of **52** along with small amounts of $Ru_5(\mu_5\text{-}\eta^4\text{-}CHCHCCH_2)(CO)_{15}$ **53** and two hexanuclear clusters 225 and 226; the spiked butterfly complex **53** contains a C_4 chain resulting from coupling of two ethyne molecules.[57,58] Cluster expansion of $Ru_3(\mu\text{-dppm})(CO)_{10}$ using the ethyne-1,2-diyl complexes $\{Ru(CO)_2(\eta^5\text{-}C_5H_4R)\}_2(\mu\text{-}C{\equiv}C)$ (R = H, Me) affords $Ru_5(\mu_5\text{-}\eta^2\text{-}C{\equiv}C)(\mu\text{-dppm})(\mu\text{-}CO)_2(CO)_7(\eta^5\text{-}C_5H_4R)_2$ **54**. The C_2 ligand in **54** bridges a spiked butterfly cluster in which the butterfly is considerably flattened (dihedral ca. 140°). Addition of CO to **54** (R = Me) affords tetranuclear $Ru_4(\mu_4\text{-}\eta^2\text{-}C{\equiv}C)(\mu\text{-dppm})(CO)_9(\eta^5\text{-}C_5H_4Me)$ with concomitant formation of $\{Ru(CO)_2Cp'\}_2$.[59,60]



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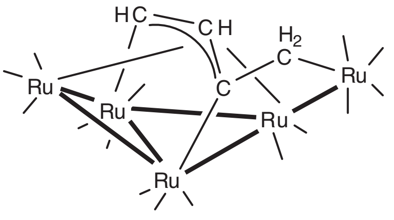

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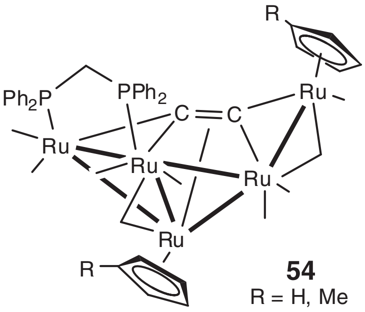
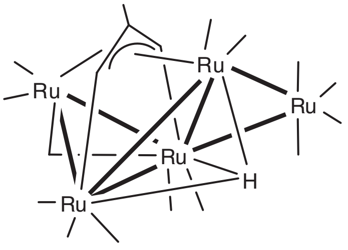


54
R = H, Me

The reaction of $Ru_3(CO)_{12}$ with isopropenylbenzene affords trace amounts of $Ru_5(\mu_3\text{-}H)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}C_3H_2Ph)(\mu\text{-}CO)(CO)_{13}$ **55**, with the hydrocarbyl ligand located between the wings of a butterfly component of the metal core, forming two η^3-π-interactions with the wingtip ruthenium atoms. Attempts to form **55** by reaction of $Ru_3(CO)_{12}$ with the other π-allylic reaction product, $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C_3H_2Ph)(CO)_9$, gave only the known hexanuclear carbido complex $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{-}C_2HPh)(CO)_{15}$.[61]

$Ru_3(CO)_{12}$ reacts with 9-ethynylfluoren-9-ol to give $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6\text{-}CCHC_{13}H_7)(\mu_3\text{-}OH)(\mu\text{-}CO)(CO)_{11}$ **56** and hexanuclear 237. Complex **56** contains an unusual bent chain, open chain of five ruthenium atoms.[62]



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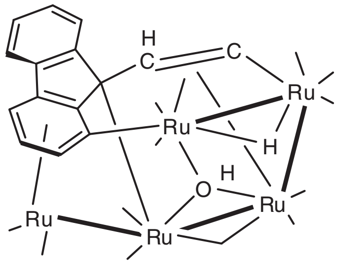
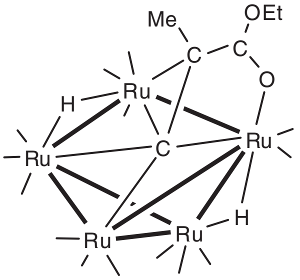


56

Reaction of $Ru_3(CO)_{12}$ with ethyl methacrylate affords the edge-bridged butterfly complex $Ru_5(\mu\text{-}H)_2\{\mu_4\text{-}CC\text{-}MeC(O)OEt\}(CO)_{14}$ **57**.[63] A series of clusters with nuclearities between 4 and 7 are formed from the reaction of

$Ru_3(CO)_{12}$ with but-3-yn-2-ol in refluxing cyclohexane, including pentanuclear complexes $Ru_5(\mu\text{-}H)_2\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CCHC(O)Me\}(CO)_{14}$ **58** and $Ru_5\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CCHC(O)Me\}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HC_2CH_2Me)(\mu\text{-}CO)(CO)_{12}$ **59**.[64]



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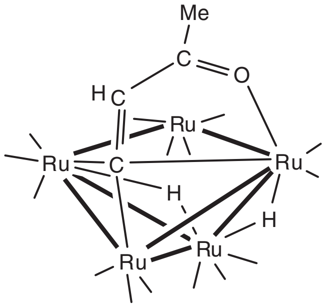

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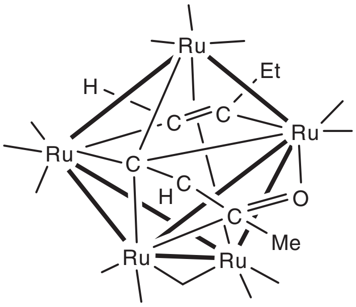
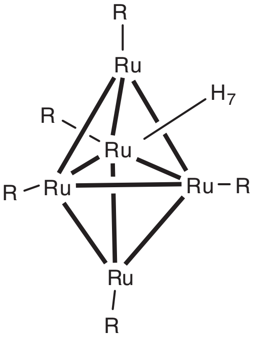
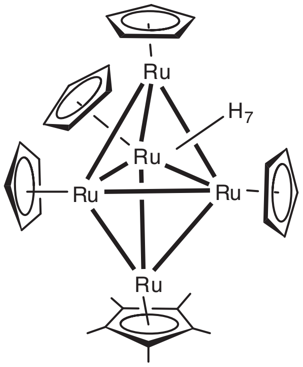


59

The pentaruthenium polyhydride complexes $H_7Ru_5R_5$ (**60**, R = Cp, η^5-C_5H_4Me) are prepared by treatment of RuCl(tmeda)Cp (tmeda = tetramethylethylenediamine) or $RuCl_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_4Me)$, respectively, with $LiAlH_4$. Similar reaction with RuCl(tmeda)Cp/$LiAlH_4$ and Ru(acac)Cp* (acac = acetylacetonate) affords the mixed ligand cluster $H_7Ru_5Cp_4Cp^*$ **61**. All complexes contain trigonal-bipyramidal metal frameworks, the last mentioned with the Cp* ligated to an apical ruthenium atom. Treatment of **60** (R = Cp) with $PHPh_2$ affords the spectroscopically characterized $H_5Ru_5(\mu_4\text{-}PPh)Cp_5$, presumably containing a square-pyramidal metal core. Fluxionality studies on **60** using ^1H NMR spectroscopy indicate an exchange process between the RuCp groups in the apical and equatorial sites, possibly involving a reversible Ru–Ru bond cleavage and reformation process similar to the Berry pseudo-rotation.[65]



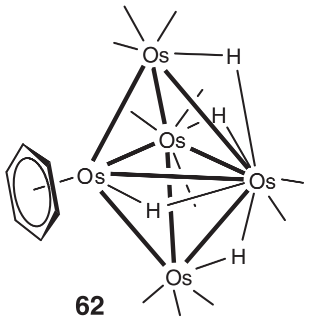
60: R = Cp, (η^5-C_5H_4Me)



61

Cluster-capping reactions of tetraosmium precursors using $[M(NCMe)_3(\eta^6\text{-}C_6H_5R)]^{2+}$ (M = Ru, Os; R = H, Me) afford η^6-arene-containing pentanuclear clusters; pentaosmium products from $[H_4Os_4(CO)_{11}]^{2-}$ include $Os_5(\mu\text{-}H)_4(CO)_{11}(\eta^6\text{-}C_6H_6)$ **62** and $Os_5(\mu\text{-}H)_4(CO)_{12}(\eta^6\text{-}C_6H_6)$ **63**.[66] Similar reactions with the reduction product of $H_2Os_4(CO)_{13}$ afford the axially ligated, spectroscopically characterized $H_2Os_5(CO)_{12}(\eta^6\text{-}C_6H_5R)$ (R = H, Me), which convert on standing into the more stable equatorial isomers $Os_5(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{11}(\eta^6\text{-}C_6H_5R)$ (**64**, R = Me). Reactions of the axial isomers with CO afford $H_2Os_5(CO)_{13}(\eta^6\text{-}C_6H_5R)$ (R = H, Me), and with $PMePh_2$ give the addition product $Os_5(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_{11}(PMePh_2)(\eta^6\text{-}C_6H_6)$ **65**; hydrogenation gives the tetrahydride complex $H_4Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)$. Attempts to interconvert **62 and 63** by thermolytic or photochemical means were unsuccessful.[67]

The reaction between the lightly stabilized tetraosmium hydrido cluster $Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2$ and cyclohexa-1,3-diene affords the trigonal-bipyramidal $Os_5(\mu\text{-}H)_2(CO)_{13}(\eta^4\text{-}C_6H_8)$ **66** together with a number of tetraosmium products.[68]



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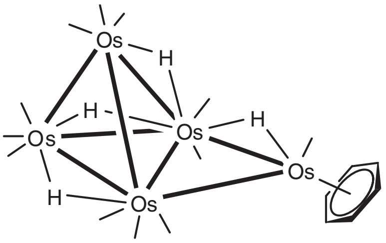

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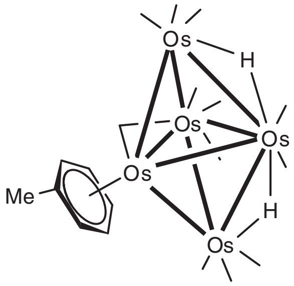

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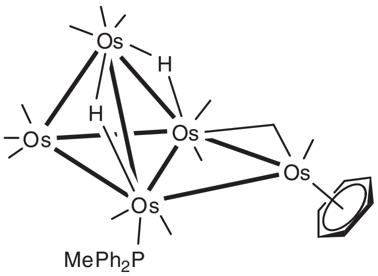

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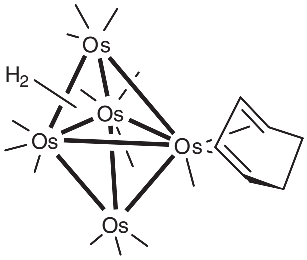
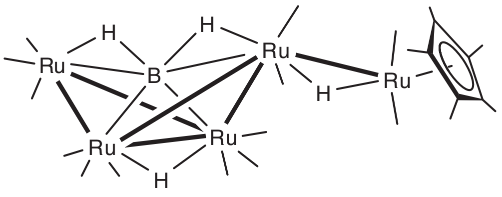


66

6.24.2.4 Clusters Containing Heteroatom Ligands

6.24.2.4.1 Clusters containing *B*, *N*, *P*, *S*, or *Se* ligands

$\{RuCl_2Cp^*\}_n$ adds to anionic $[Ru_3(CO)_9(BH_4)]^-$ to give $Ru_5(\mu\text{-}H)_2(\mu_4\text{-}BH_2)(CO)_{13}Cp^*$ **67**. Reaction of **67** with PPh_3 leads to loss of the spike ruthenium unit.[15] The boride cluster $HOs_5(\mu_5\text{-}B)(CO)_{16}$ **68** is formed from the thermolysis of $H_3Os_3(CO)_9(BCO)$ in toluene, along with $Os_4(\mu\text{-}H)(\mu_4\text{-}BH_2)(CO)_{12}$.[69]



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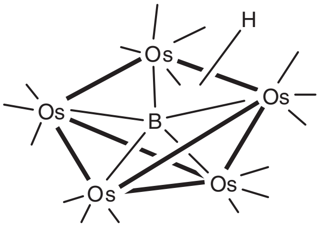
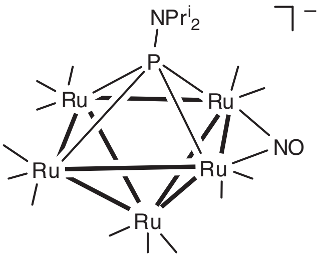


68

The cluster-bound nitrosyl ligand is transformed into nitrene or nitrido ligands in electrophilic reactions of the mixed nitrosyl–phosphinidene cluster anion $[Ru_5(\mu_4\text{-}PNPr^i{}_2)(\mu\text{-}NO)(CO)_{13}]^-$ **69**, formed by treating the aminophosphinidene cluster $Ru_5(\mu_4\text{-}PNPr^i{}_2)(CO)_{15}$ with $[PPN]NO_2$ ($[PPN]^+ = [Ph_3P{=}N{=}PPh_3]^+$). Complex **69** reacts with acids by N–O bond cleavage to form the nitrene cluster $Ru_5(\mu_4\text{-}NH)(\mu_3\text{-}PNPr^i{}_2)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{10}$ **70** when treated with $HOSO_2CF_3$, or nitrido clusters $Ru_5(\mu_5\text{-}N)\{\mu\text{-}P(R)NPr^i{}_2\}(CO)_{13}$ (**71**, R = OMe, F) with $MeSO_2CF_3$ or HBF_4, respectively. The formation of **70** from **69** is the first example of the conversion of a μ-NO ligand into a μ_4-NH group.[70,71] Thermolysis of the nitrene cluster $Ru_3(\mu_3\text{-}NOMe)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_9$ in *n*-octane leads to trace amounts of the pentanuclear $Ru_5(\mu_4\text{-}NH)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)(CO)_{13}$ **72** among a number of tetraruthenium complexes. The origin of the proton of the NH group was not determined, possible sources including cleavage of the cluster-bound methoxynitrido unit. A similar reaction with the diphenylacetylene analog affords the hexaruthenium complex **261**, also in low yield.[72]



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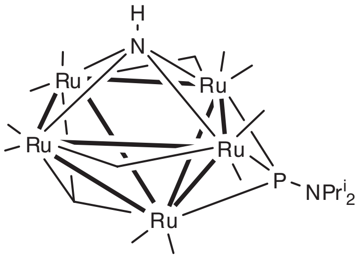

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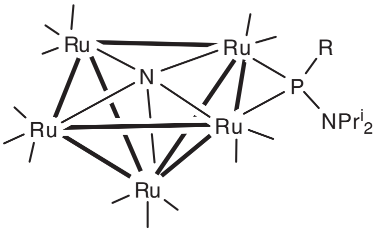

R = OMe, F

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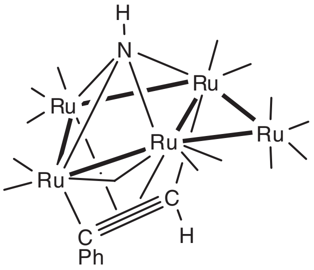
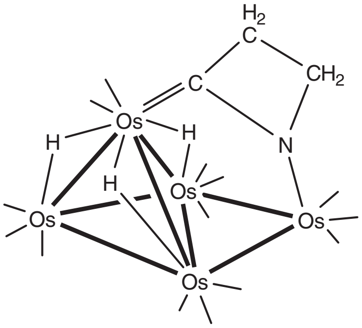


72

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with azetidine affords $Os_3(\mu\text{-H})(\mu\text{-}\overline{NCH_2CH_2C}H_2)(CO)_{10}$, which forms a small amount of the pentaosmium complex $Os_5(\mu\text{-H})_3(\mu\text{-}\overline{NCH_2CH_2C})(CO)_{14}$ **73**, along with triosmium products, when heated in octane. Complex **73** contains the azetidine ligand spanning an edge-bridged tetrahedral metal core.[73] The linear triosmium hydrido complex $Os_3H(CO)_{11}\{\eta^2\text{-N}(C_6F_5)NN(C_6F_5)\}$ reacts with $Os_3(CO)_{10}(NCMe)_2$ at room temperature to give the spectroscopically characterized hexaosmium complex $Os_6(\mu\text{-H})(CO)_{21}(NCMe)\text{-}\{\eta^3\text{-N}(C_6F_5)NN(C_6F_5)\}$, thought to contain a triangular arrangement of osmium atoms with an equatorial Os_3 linear spike. This complex readily converts into the spiked butterfly cluster $Os_5(\mu\text{-H})(CO)_{17}\{\eta^2\text{-N}(C_6F_5)NN(C_6F_5)\}$ **74** at room temperature, and both complexes form $Os_5(CO)_{16}$ on heating.[74]



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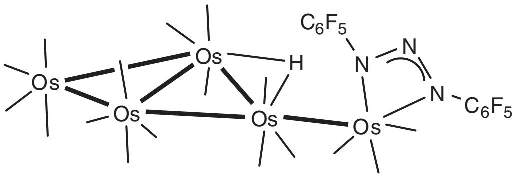
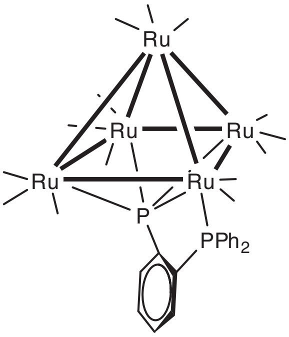


74

$Ru_5\{\mu_4\text{-}\eta^2\text{-}(PC_6H_4PPh_2\text{-}2)\}(CO)_{14}$ **75** is formed in low yield from the reaction between $Ru_3(CO)_{12}$ and 1,2-bis(phenylphosphino)benzene. The complex contains a phosphinidene ligand thought to originate from a small amount of the isomeric 1-phosphino-2-diphenylphosphinobenzene, which is present on distillation of the phosphine reagent.[75] Reaction of $Ru_3(CO)_{12}$ with diphenyl(9-anthracenyl)phosphine affords $Ru_5(\mu_5\text{-}\eta^1\text{:}\eta^2\text{:}\eta^3\text{:}\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-PPh})(CO)_{13}$ **76** in 5% yield; the cluster contains a skewed bow-tie metal configuration.[76] The square-pyramidal phosphinidene complex $Ru_5(\mu_4\text{-PBu}^t)(CO)_{15}$ (**77**, E = P, R = Bu^t) was prepared in trace amounts from the reaction of $Ru_3(CO)_{12}$ with the cyclic phosphine $P_4Bu^t_4$.[77] Similarly, reactions with $P_4(CF_3)_4$, CF_3EH_2, or $(CF_3)_2EH$ (E = P, As) give small amounts of $Ru_5\text{-}(\mu_4\text{-ECF}_3)(CO)_{15}$ (**77**, E = P, As) among a number of lower-nuclearity products.[78–80] A high yield route into functionalized phosphinidene pentaruthenium complexes has been developed using the aminophosphinidene clusters $Ru_4\text{-}(\mu_3\text{-PNR}_2)(CO)_{13}$ (R = Cy, Pr^i) as precursors, cluster expansion with $Ru_3(CO)_{12}$ or $Ru(CO)_5$ giving $Ru_5(\mu_4\text{-PR})(CO)_{15}$

(**77**, E = P, R = $\mathrm{NCy_2}$, $\mathrm{NPr^i{}_2}$) in 70–95% yield. Subsequent treatment with anhydrous $\mathrm{HBF_4}$ gives the fluorophosphinidene analog **77** (E = P, R = F), whereas reaction with $\mathrm{HBF_4}$ in water gives a mixture of **77** (R = F) and $[\mathrm{Ru_5(\mu_4\text{-}PO)(CO)_{15}}]^-$ **78**, containing the first example of a μ_4-PO ligand. Attempts to convert **77** (E = P, R = F) into **78** by reaction with hydroxide, a route previously demonstrated for the related $\mathrm{Ru_4(\mu_3\text{-}PF)(CO)_{13}}$, were unsuccessful. Reaction with alcohols affords **77** (E = P, R = OMe, OEt, $\mathrm{OPr^i}$), but treatment with $\mathrm{H_2O}$, $\mathrm{HNR_2}$, and MeLi gave no reaction.[81,82]



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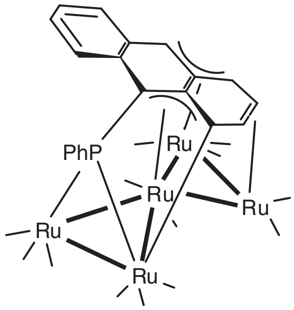

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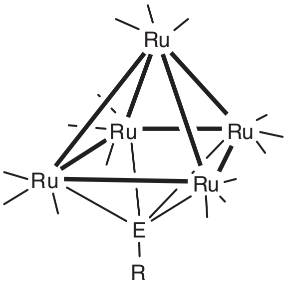
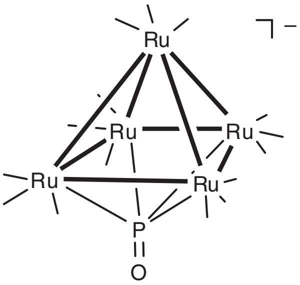


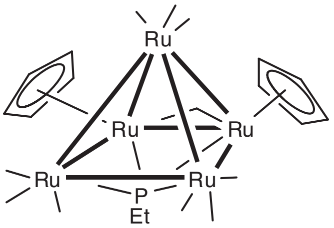
E = P; R = $\mathrm{Bu^t}$, $\mathrm{CF_3}$, $\mathrm{NCy_2}$, $\mathrm{NPr^i{}_2}$,F, OMe, OEt, $\mathrm{OPr^i}$
E = As; R = $\mathrm{CF_3}$

77



78

Thermolysis of $\mathrm{Ru_3(CO)_{12}}$ and the ferrocenylphosphine $\mathrm{PEt_2Fc}$ (Fc = ferrocenyl) in octane proceeds by loss of iron-containing fragments to give small amounts of square-pyramidal $\mathrm{Ru_5(\mu_4\text{-}PEt)(\mu\text{-}CO)(CO)_9Cp_2}$ **79**, along with the hexanuclear carbido clusters **133 and 134**. A similar reaction with $\mathrm{PEtFc_2}$ in toluene gives $\mathrm{Ru_5(\mu_4\text{-}PEt)(CO)_{12}(\eta^6\text{-}C_6H_5Me)}$ **80**, containing a coordinated toluene molecule derived from the reaction solvent.[83] The cyclic carbophosphine 1,2,3,4-tetraphenyl-1,2,3,4-tetraphospholane reacts with $\mathrm{Ru_3(CO)_{12}}$ to give the wingtip-bridged butterfly cluster $\mathrm{Ru_5(\mu_4\text{-}PPh)\{\mu_4\text{-}\eta^2\text{-}(PPh)_2CH_2\}(\mu_3\text{-}PPh)(CO)_{11}}$ **81** in 18% yield, along with the heptanuclear clusters **300 and 301**. All the P–P bonds in the phosphine reagent are cleaved to form two phosphinidene ligands and a μ_4-η^2-$\mathrm{PhPCH_2PPh}$ unit in which one of the phosphorus $\mathrm{PR_2}$ groups bridges three ruthenium atoms.[84]



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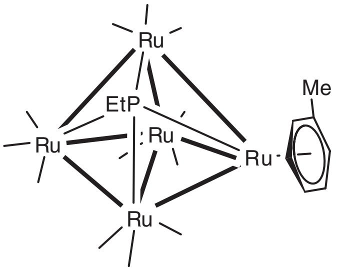

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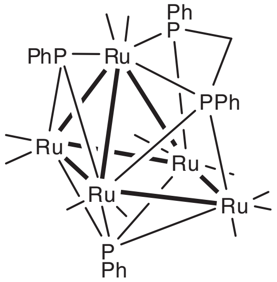
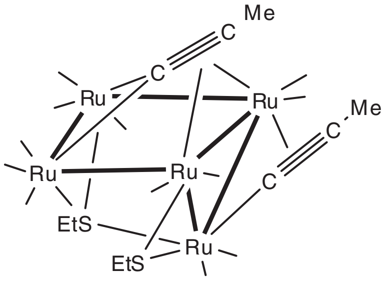


81

The reactions of $Ru_3(CO)_{12}$ with the ethylthioalkynes $RC{\equiv}CSEt$ (R = Me, Ph) proceed with C–S bond cleavage to afford a series of clusters of nuclearity between three and six, including pentanuclear $Ru_5(\mu_4\text{-}C{\equiv}CMe)(\mu_3\text{-}SEt)(\mu\text{-}C{\equiv}CMe)(\mu\text{-}SEt)(CO)_{12}$ 82 and $Ru_5\{\mu_5\text{-}C(Ph)CC(Ph)C\}(\mu\text{-}SEt)_2(\mu\text{-}CO)(CO)_{12}$ 83. Both 82 and 83 contain two coordinated alkynyl units, which are coupled in the latter to form a four-carbon chain.[85]



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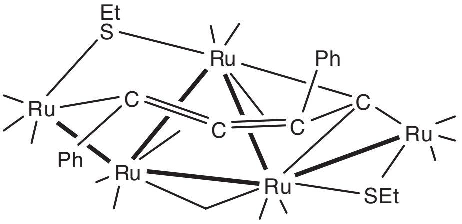
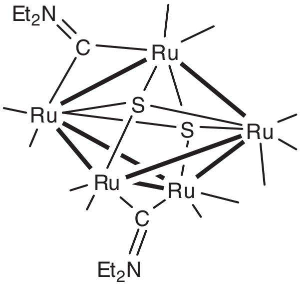


83

The mononuclear complex *cis*-$[Ru(CO)_2(\eta^2\text{-}S,S\text{-}S_2CNEt_2)_2]$ reacts with $Ru_3(CO)_{12}$ in refluxing xylene to give $Ru_5(\mu_4\text{-}S)_2(\mu\text{-}\eta^1\text{-}CNEt_2)_2(CO)_{11}$ 84, a reaction corresponding to the desulfurization of both dithiocarbamato ligands.[86]

Reaction of $[Os_5H(CO)_{15}]^-$ with PhSeCl affords $Os_5(\mu\text{-}H)(\mu_3\text{-}SePh)(CO)_{15}$ 85, in which the phenylselenido ligand caps an edge-bridged butterfly arrangement of osmium atoms.[87]



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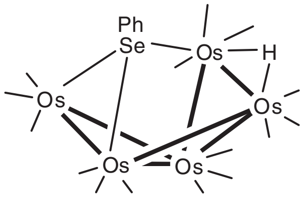
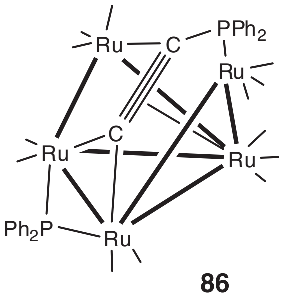


85

6.24.2.4.2 Phosphinoalkyne-derived clusters

The open pentaruthenium clusters $Ru_5(\mu_5\text{-}\eta^3\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ 86, prepared by thermolysis of the linked cluster $\{Ru_3(CO)_{11}\}_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)$, and $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}$ 87, available from reaction of 86 with dimethyl disulfide, have afforded a rich chemistry that has been developed by Bruce and co-workers, some of which have been reviewed.[16,88,89]

The formation of 87 has been studied in detail, and several intermediates isolated. Reaction under mild conditions affords the dicarbide chain complex $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}SMe)_2(CO)_{13}$ 88 together with small amounts of $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_2PPh_2)(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)(\mu\text{-}SMe)(CO)_{12}$ 89, while warming 88 gives $Ru_5(\mu_5\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{12}$ 90 in 64% yield, together with small amounts of $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}$ 91 and $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_2PPh_2)(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)(\mu\text{-}SMe)(CO)_{12}$ 92, and reaction of 91 with further dimethyl disulfide affords $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_4(CO)_{10}$ 93.[90]



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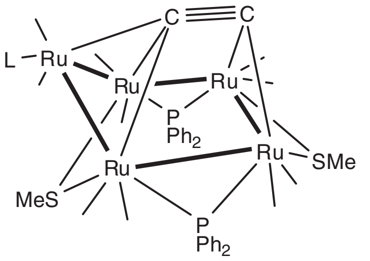
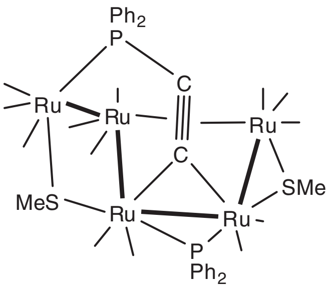


87: L = CO

87a: L = CNBu^t, P(OMe)$_3$



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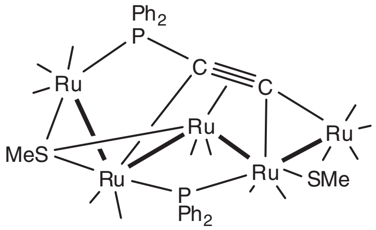

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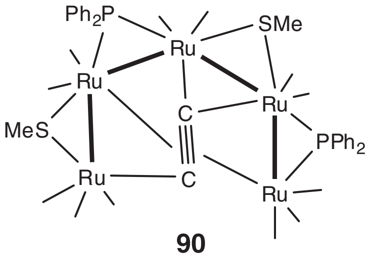

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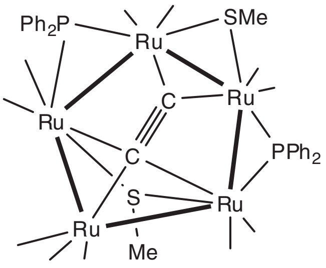

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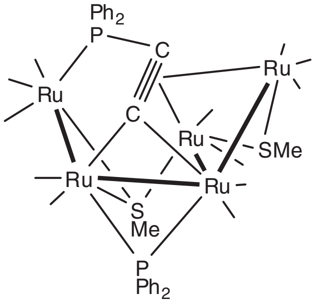

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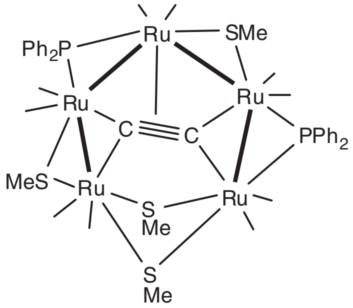
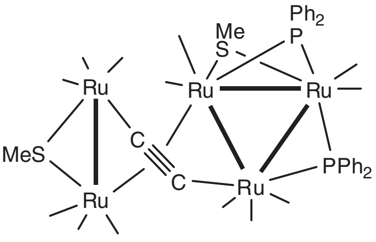


93

Thermolysis of 87 under 30 atm of carbon monoxide results in Ru–Ru metal bond cleavage to give 94 and 95, where fragments of the original cluster are linked via the C_2 unit.[91] Addition of CNBu^t to 87 results in a reorganization of the C_2 unit and flattening of the Ru_5 pentagon to give 96; decarbonylation occurs on heating, restoring the original cluster geometry (87a, L = CNBu^t).[92] The related MeCN complex 87a (L = NCMe) is formed from reaction of 87 and Me_3NO/MeCN, but no evidence for the formation of the analog of 96 was seen. Facile substitution of MeCN by PPh_3 and $P(OMe)_3$ [87a, L = $P(OMe)_3$] occurs; extension to dppa gives "dumb-bell" clusters containing two PPh_2-substituted clusters bridged by a C≡C moiety. While CO substitution occurs in 87 with NH_2Bu^n, only the known vinylidene complex 106 is obtained in reactions with $NHEt_2$ or NEt_3.[93]



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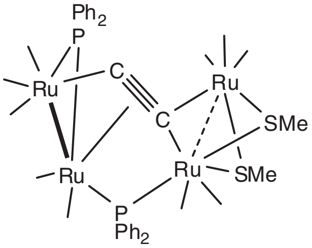

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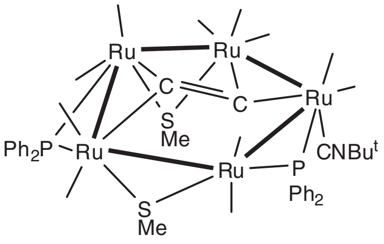
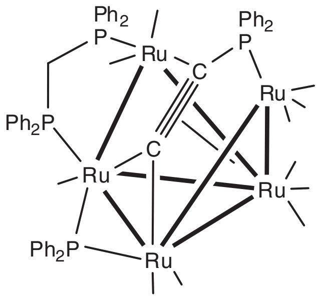


96

The reactions of 86 with phosphines afford a range of complexes including $Ru_5(\mu_5\text{-}\eta^1:\eta^1:\eta^2:\eta^1:\eta^1\text{-}C_2PPh_2)(\mu\text{-dppm})(\mu\text{-}PPh_2)(CO)_{11}$ 97 and the spiked butterfly complex $Ru_5(\mu_5\text{-}\eta^1:\eta^1:\eta^2:\eta^1:\eta^1\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(dppm)$ 98 from reaction with dppm, and the edge-bridged square cluster $Ru_5(\mu_5\text{-}\eta^1:\eta^1:\eta^2:\eta^1:\eta^1\text{-}C_2H)(\mu\text{-}CO)(\mu\text{-}NHC_6H_4\text{-}2\text{-}PPh_2)(\mu\text{-}PPh_2)_2(CO)_{10}$ 99 from the reaction with $PPh_2(2\text{-}C_6H_4NH_2)$. The butterfly complex $Ru_4\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}C_2PPh_2[Ru(\mu\text{-}OH)(C,P\text{-}2\text{-}CHMeC_6H_4PPh_2)(CO)_2]\}(\mu\text{-}PPh_2)(CO)_{10}$ 100 is formed via Ru–Ru bond cleavage on reaction with $PPh_2(2\text{-}C_6H_4CH{=}CH_2)$, the fifth ruthenium atom being attached to the cluster by μ-OH and $\mu\text{-}PPh_2C_2$ ligands. Trace amounts of the bow-tie complex $Ru_5(\mu\text{-}H)_2\{\mu_5\text{-}\eta^1:\eta^1:\eta^2:\eta^3:\eta^2\text{-}PPh_2C_2CH{=}C(2\text{-}C_6H_4PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ 101 are also obtained from the reaction with the alkenyl phosphine. This complex contains a diphosphine four-carbon chain derived from the original PPh_2 cluster-bound ligand and the alkenyl side chain from the incoming ligand.[94,95]



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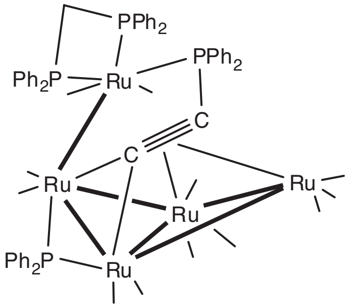

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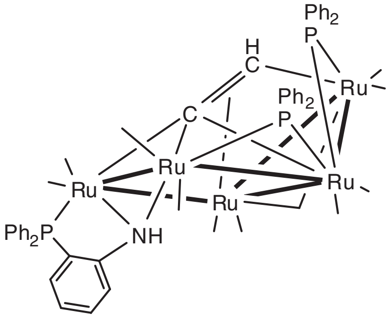

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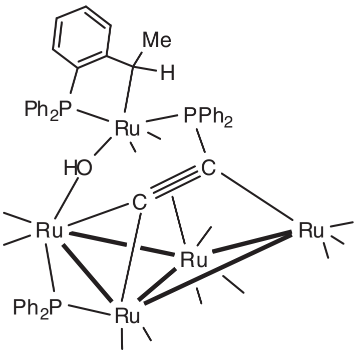

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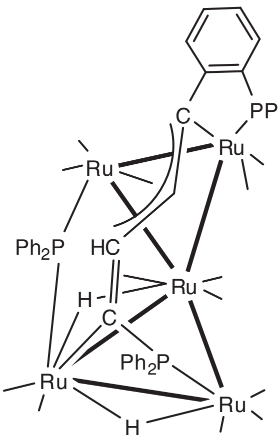
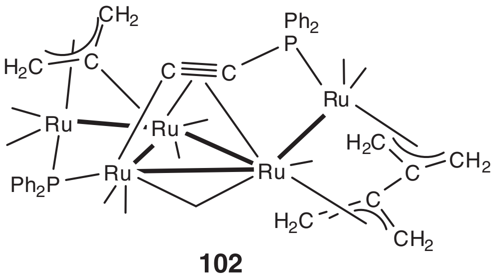


101

Reactions of 86 with allene afford $Ru_5(\mu_4\text{-}\eta^1:\eta^2:\eta^2:\eta^1\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}\eta^3:\eta^3\text{-}C_6H_8)(\mu\text{-}\eta^1:\eta^3\text{-}C_3H_4)(\mu\text{-}CO)(CO)_9$ 102 and $Ru_4\{\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_2PPh_2[Ru(CO)_2]\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^4\text{-}C_9H_{12})(\mu\text{-}\eta^1:\eta^3\text{-}C_3H_4)(CO)_8$ 103, and with 5-chloro-4-chloromethyl-2,4-dimethylpent-1-ene give $Ru_5(\mu_5\text{-}\eta^1:\eta^2:\eta^2:\eta^1:\eta^1\text{-}C_2)(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ 104 and $Ru_5(\mu\text{-}H)\{\mu_5\text{-}\eta^1:\eta^1:\eta^1:\eta^1:\eta^2\text{-}CC(PPh_2)\}(\mu\text{-}Cl)(\mu\text{-}PPh_2)(CO)_{12}$ 105. Complexes 102 and 103 contain dimerized and trimerized allene molecules coordinated to an open ruthenium framework that results from Ru–Ru metal bond cleavage, while complex 104 is the analog of the open dicarbide derivative 87, with chloride ligands in place of the SMe groups. Three isomers of $Ru_5(\mu_4\text{-}\eta^1:\eta^2:\eta^2:\eta^1\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}\eta^3:\eta^3\text{-}C_6H_8)(\mu\text{-}\eta^1:\eta^3\text{-}C_3H_4)(CO)_9\{P(OMe)_3\}$ **102a** have also been prepared, with cores analogous to 102.[96,97]



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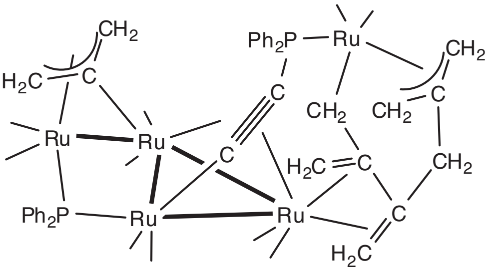

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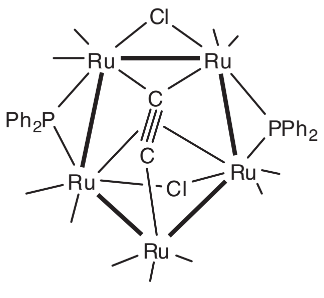

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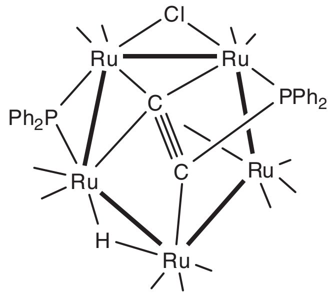
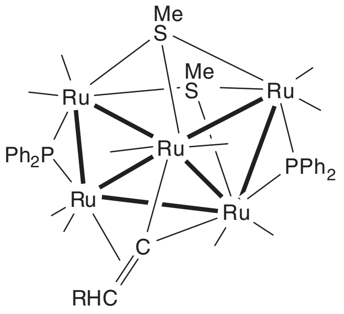
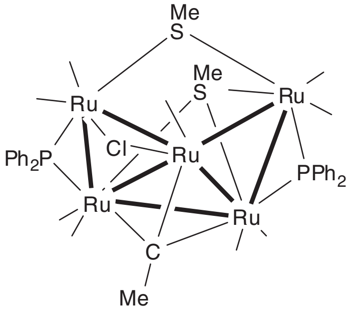


105

Reaction of **87** with hydrogen or alkenes is characterized by insertion of the C_β into the H–R bond (R = H, C) of the incoming reagent. Thus, the parent vinylidene cluster $Ru_5(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (**106**, R = H) forms from the reaction of **87** with dihydrogen, and analogous complexes result from reactions with alkenes ($H_2C{=}CHR$, R = H, Me, Ph, $CHCO_2Et$). Complex **106** (R = H) reacts with HCl to give the carbyne complex $Ru_5(\mu_3\text{-}CMe)(\mu_3\text{-}SMe)(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(CO)_9$ **107**.[98,99] Reaction of **87** with 1,3-butadiene affords $Ru_5(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_6H_6)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ **108**, an electron-rich M_5 cluster with 80 c.v.e. containing a $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2$-cyclohex-1-yne-4-ene ligand formed from the cycloaddition of the incoming diene to the C_2 unit.[100]



106: R = H, $CH{=}CH_2$, $CH{=}CHMe$, $CH{=}CHPh$, $CH{=}CHCO_2Et$



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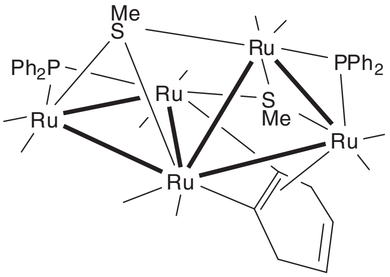
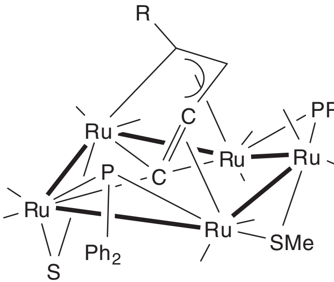


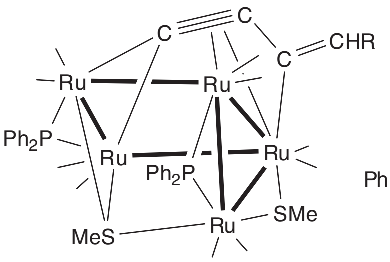
108

Terminal alkynes react with **87** by coupling with the C_2 unit, frequently in concert with other bond formation. Treatment with $HC{\equiv}CR$ (R = Ph, Bu^t, $SiMe_3$)[101,102] affords the pentagonal cluster $Ru_5(\mu_5\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^4{:}\eta^2\text{-}CCCHCR)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe_2)_2(CO)_{10}$ **109** as the major product, with $Ru_5(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^2\text{-}CCCCHBu^t)(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(CO)_{10}$ (**110**, R = Bu^t) also isolated in the 3,3-dimethylbut-1-yne case.[103] The same reaction with ethynyltrimethylsilane at slightly higher temperatures and reaction times also produces a small amount of $Ru_5\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^4\text{-}CC(CHCSiMe_3)C({=}CHSiMe_3)CO\}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_8$ **111**, containing a bicyclic diruthenacycle formed from the C_2 unit and a cluster-bound CO ligand. Complex **109** (R = Ph, $SiMe_3$) is carbonylated to give minor amounts of $Ru_5\{\mu_5\text{-}\eta^2{:}\eta^1{:}\eta^2{:}\eta^1{:}\eta^3\text{-}CC[C(O)SMe]CHCR\}(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(CO)_{10}$ **112**, the combination of the C_4 ligand of **92** with a CO and an SMe group having given a thiocarboxylate ligand; the major product is $Ru_5(\mu_5\text{-}\eta^2{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}CCCPhCPh)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}$ **113**, in which one ruthenium atom of the precursor has been extruded from the metal core but retained by bridging ligand coordination. Thermolysis of **113** gives only minor amounts of the decarbonylation product **109**, the major product being the spectroscopically characterized $Ru_5(\mu_5\text{-}CCCHCR)(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(CO)_9$.



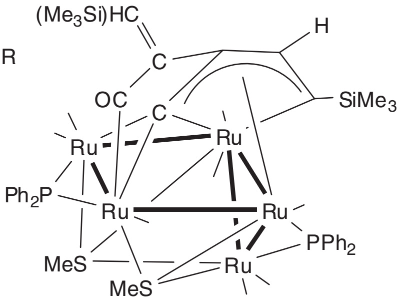
R = Ph, $SiMe_3$, Bu^t

109



R = Bu^t, $SiMe_3$, H

110



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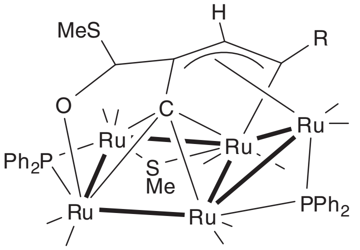
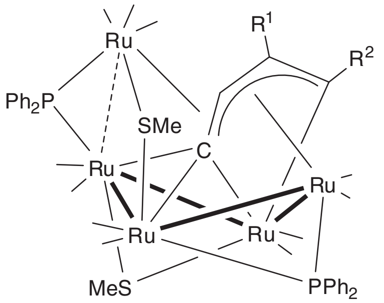


R = Ph, $SiMe_3$

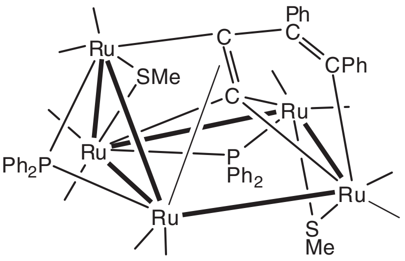
112



$R^1 = R^2 = Ph$
$R^1 = H$, $R^2 = Ph$, $SiMe_3$

113

The major products from reactions of 87 with internal alkynes result from addition of an alkynyl carbon to one of the carbon atoms of the dicarbide unit. Reaction with diphenylethyne gives $Ru_5(\mu_5\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-CCCPhCPh})(\mu\text{-}PPh_2)_2(\mu\text{-SMe})_2(CO)_{10}$ **114** and $Ru_5(\mu_5\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^4\text{-CCCPhCPh})(\mu_3\text{-SMe})(\mu\text{-}PPh_2)_2(\mu\text{-SMe})(CO)_9$ (**115**, R = Ph) (**114** giving **115** on heating), whereas reaction with but-2-yne affords **115** (R = Me) only. Carbonylating **115** (R = Ph) gives **113** (R, R^1 = Ph), which affords a mixture of **114** and **115** on heating.[101,104]



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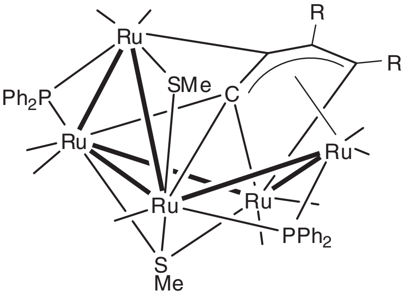
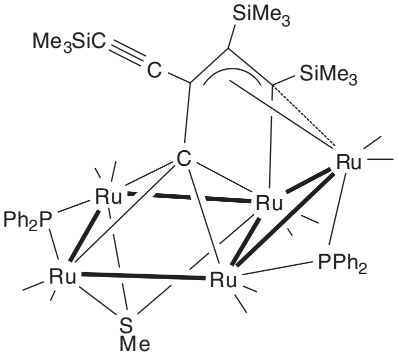


115

The reaction of 87 with bis(trimethylsilyl)ethyne affords an isomeric mixture of **110** (R = $SiMe_3$), together with $Ru_5\{\mu_5\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^3\text{-CC}[C_2(SiMe_3)]C(SiMe_3)C(SiMe_3)\}(\mu_3\text{-SMe})(\mu\text{-}PPh_2)_2(CO)_{10}$ **116**, in which an SMe ligand has been lost from the precursor. Treating the isomers with KOH results in desilylation and formation of **110** (R = H), subsequent carbonylation giving $Ru_5(\mu_5\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-CCCCH}_2)(\mu\text{-}PPh_2)_2(\mu\text{-SMe})_2(CO)_{11}$ **117**. Clusters **110** (R = H) and **117** contain a butatrienylidene ligand formed by end-to-end coupling of the C_2 moiety with the vinylidene $C{=}CH(SiMe_3)$.[103,105]



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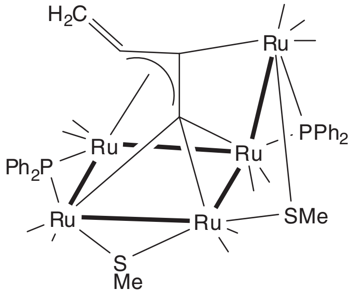
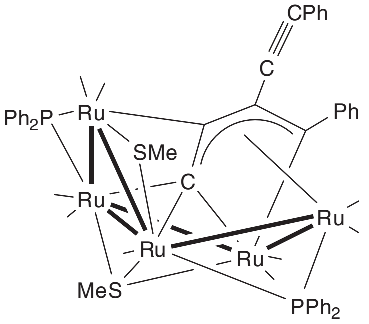


117

Reaction of **87** with 1,4-diphenylbuta-1,3-diyne results in insertion of one C≡C unit into the dicarbide ligand to give $Ru_5\{\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}CCC(C{\equiv}CPh)CPh\}(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(CO)_9$ **118**, $Ru_5\{\mu_5\text{-}\eta^2{:}\eta^1{:}\eta^2{:}\eta^1{:}\eta^3\text{-}CC(SMe)\text{-}C(C{\equiv}CPh)CPh\}(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(CO)_{10}$ (**119**, $R^1 = R^2 = Ph$; two isomers), $Ru_5\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^4{:}\eta^2\text{-}CC[C(C{\equiv}CPh)\text{-}CPh]C(C{\equiv}CPh)CPh\}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_8$ **120**, along with analogs of a number of known related complexes. In complex **120**, insertion of two diyne molecules produces a multi-branched 10-carbon chain. Both **118** and **120** have 80 c.v.e., two more than expected for a pentanuclear cluster with six M–M bonds.[106]



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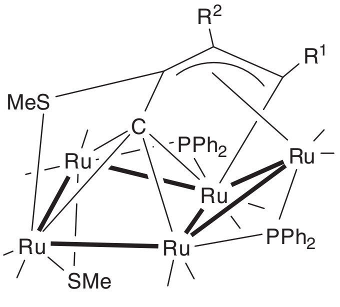
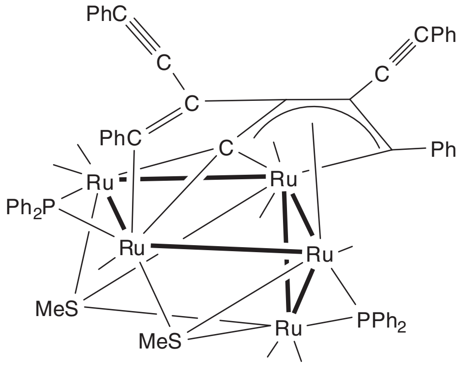


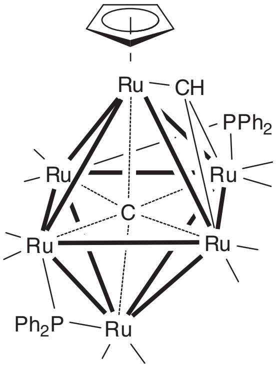
R^1, R^2 = Ph, C≡CPh

119



120

Complex **87** reacts with cyclopentadienes to give hexanuclear carbido clusters $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}CH)\text{-}(\mu\text{-}PPh_2)_2(CO)_{10}(\eta\text{-}C_5R_5)$ ($R_5 = H_5$ **121**, H_4Me, Me_5) as the main products, along with pentanuclear byproducts $Ru_5(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{13}H_{12}O)(\mu\text{-}PPh_2)(CO)_{11}Cp$ **122** and $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}CCHPh)(\mu\text{-}PPh_2)(CO)_9\text{-}Cp^*$ **123** for the cyclopentadiene and pentamethylcyclopentadiene examples, respectively. Formation of cluster **121** involves relatively rare C–C bond cleavage of the PPh_2C_2 ligand of the precursor cluster, forming the methylidyne ligand and, presumably, the interstitial carbide atom. Complex **122** contains a tetracyclic ligand formed from the incorporation of CO and a C_2 fragment with two molecules of the cyclopentadiene.[107]



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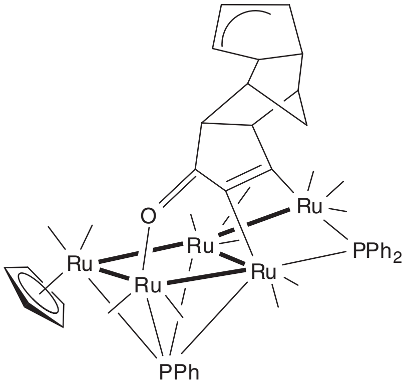

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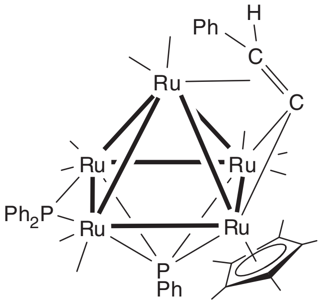
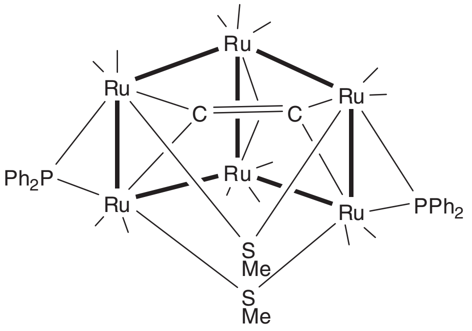


123

The reaction between **87** and $Ru(CO)_5$ results in incorporation of the metal atom to give hexanuclear $Ru_6(\mu_6\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{14}$ **124** and heptanuclear $Ru_7(\mu_6\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(\mu\text{-}CO)(CO)_{15}$ **125**. The metal core of **124** consists of two edge-sharing squares; in **125**, the seventh metal atom bridges the outer edge of one square.[108]



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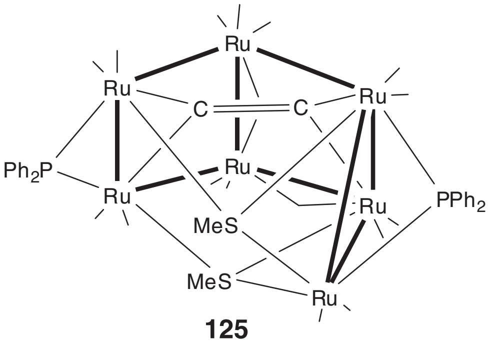

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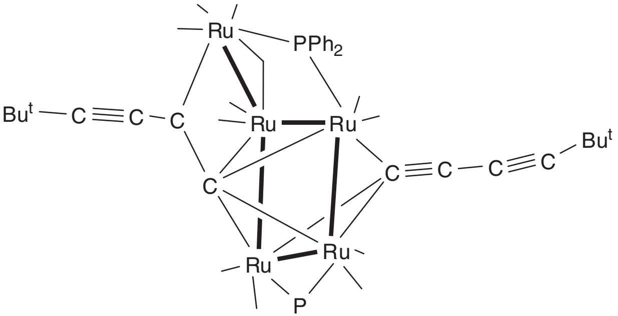


126

Molecular orbital calculations on some of these C_2 pentaruthenium clusters have shown that bonding can be explained using the Dewar–Chatt–Duncanson model, with electron-donating interactions from the occupied orbitals of the dicarbide unit to vacant metal orbitals and back-donation from the filled metal orbitals to the C_2 π^*-orbitals.[109]

Thermolysis of the diynylphosphine clusters $Ru_3(CO)_{11}(Ph_2PC{\equiv}CC{\equiv}CR)$ ($R = Bu^t$, Ph, $SiMe_3$) results in P–C and Ru–Ru bond cleavage, affording products with nuclearities from 2 to 6, including the alkylidyne–carbido clusters $Ru_5(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}CCC{\equiv}CBu^t)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-}C{\equiv}CC{\equiv}CBu^t)(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(CO)_{11}$ **126** and hexanuclear

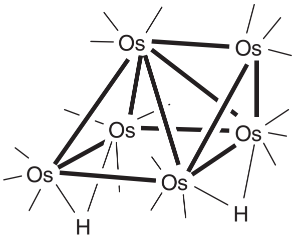
265 from the *t*-butyl precursor. Complex **126** contains a pendant μ_3-η^1-diyne ligand and, with 76 c.v.e., is four electrons deficient for a spiked square metal geometry.[110]

6.24.3 M_6 Clusters

6.24.3.1 Simple Carbonyls, Carbonyl Hydrides, and their Substitution Products

The early chemistry of hexanuclear carbonyl clusters, including those of ruthenium and osmium, has been reviewed.[111] The hexaruthenium dianion $[Ru_6(CO)_{18}]^{2-}$ is prepared inside NaX–zeolite cages in 80–90% yields by treatment of $[Ru(NH_3)_6]^{3+}$/NaX with CO and H_2. Oxidation of the supported dianion results in cluster degradation to mononuclear ruthenium products, a process that is reversible on re-exposure to CO/H_2.[112] A redetermination of the crystal structure of $Os_6(CO)_{18}$, as its chloroform solvate, confirms the bicapped tetrahedral metal core seen with the unsolvated cluster.[113]

Spontaneous decarbonylation of $Ru_6(\mu\text{-H})_2(CO)_{18}$ to afford $Ru_6(\mu\text{-H})_2(CO)_{17}$ occurs on standing (solid state, dynamic vacuum, several weeks). The latter was first identified by X-ray methods, the physical properties of both compounds being very similar (proton NMR chemical shifts differ by only 0.02 ppm). Rapid degradation to Ru_3 and Ru_4 clusters occurs in solution. Treatment of $Ru_6(\mu\text{-H})_2(CO)_{17}$ with BH_3SMe_2 affords an improved synthesis (21%) of $Ru_6(\mu\text{-H})(\mu_6\text{-B})(CO)_{17}$.[114] A neutron diffraction study has shown that the hydride ligands on the capped square-pyramidal cluster $Os_6(\mu\text{-H})_2(CO)_{18}$ **127** bridge the opposite basal Os–Os bonds.[115]



127

Addition of $Os_3(CO)_{10}(NCMe)_2$ to $H_2\{Os(CO)_4\}_n$ ($n = 1$–3) leads to cluster expansion to give a series of spectroscopically characterized addition products with nuclearities from 4 to 9.[116] The planar raft cluster $Os_6(CO)_{20}(NCMe)$ reacts with *P*-donor ligands by rapid initial formation of the adducts $Os_6(CO)_{20}(L)(NCMe)$ in a pre-equilibrium step, followed by slow dissociation of NCMe; the equilibrium and rate constants vary systematically with the electronic and steric properties of L.[117]

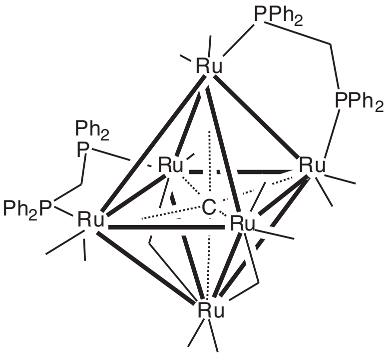
6.24.3.2 Carbido Clusters

6.24.3.2.1 Carbido clusters with carbonyl and hydrido ligands, and their simple substitution products

A high yield synthesis of the hexaruthenium carbido dianion $[Ru_6(\mu_6\text{-C})(CO)_{16}]^{2-}$ has been developed. $RuCl_3 \cdot nH_2O$ is carbonylated in ethylene glycol at 110 °C/1 atm CO, the resulting mixture of tri- and dicarbonyl ruthenium(II) species being reductively carbonylated in the presence of a 10-fold excess of potassium carbonate; reproducible yields of around 80% can be achieved.[118] Electrochemical reduction of $Ru_6(\mu_6\text{-C})(CO)_{17}$ under strictly anaerobic conditions affords $[Ru_6(\mu_6\text{-C})(CO)_{16}]^{2-}$. However, an infrared spectroelectrochemical study of the same reduction process under O_2 has shown that the reaction proceeds with concomitant formation of 1.1–1.3 molecules of CO_2 per cluster, in addition to degradation products, $Ru_6(\mu_6\text{-C})(CO)_{17}$ being regenerated in the presence of CO.[119]

Hexaruthenium phosphine clusters $Ru_6(\mu_6\text{-C})(CO)_{16}(PPh_3)$, $Ru_6(\mu_6\text{-C})(CO)_{15}(PPh_3)_2$, and $Ru_6(\mu_6\text{-C})(\mu\text{-dppm})_2(\mu\text{-CO})_2(CO)_{11}$ **128** are formed from the reaction of the mixed-metal complex $Ru_6Pt(\mu_6\text{-C})(CO)_{16}(\eta^4\text{-COD})$ (COD = 1,5-cyclooctadiene) with PPh_3 or dppm.[120] The η^1-phosphine complex $Ru(CO)_4(\eta^1\text{-dppp})$ [dppp = 1,3-bis(diphenylphosphino)propane] reacts with $Ru_5(\mu_5\text{-C})(CO)_{15}$ to give $Ru_6(\mu_6\text{-C})(\mu\text{-dppp})(CO)_{16}$ as the main product, probably via the bridged intermediate $\{Ru_5(\mu_5\text{-C})(CO)_{14}\}(\mu\text{-dppp})\{Ru(CO)_4\}$.[121] The phosphine-substituted series of clusters $Ru_6(\mu_6\text{-C})\{\mu\text{-PPh}_2(CH_2)_nPPh_2\}(\mu\text{-CO})(CO)_{14}$ (**129**, $n = 1$–3) forms from $Ru_6(\mu_6\text{-C})(CO)_{17}$ and the relevant bidentate phosphine. Two spectroscopically characterized products obtained from the reaction with

1,4-bis(diphenylphosphine)butane ($n = 4$) include a complex with the phosphine in a pendant coordination mode, thought to be a result of the increasing conformational strain within the ligand on increasing the chain length.[122]



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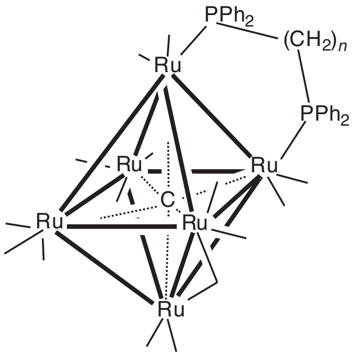


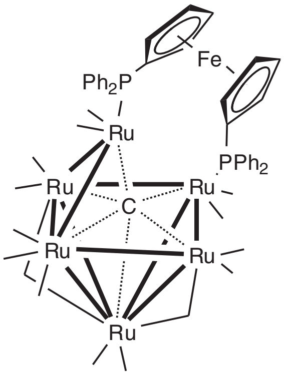
$n = 1–3$

129

The water-soluble monophosphine complex $\mathrm{Ru_6(\mu_6\text{-}C)(CO)_{16}\{P(C_6H_4SO_3Na\text{-}3)_3\}}$ is an effective pre-catalyst for the water-gas shift reaction.[123]

Bis(diphenylphosphino)acetylene has been used to link hexaruthenium clusters to form a cluster polymer formulated as $\mathrm{\{Ru_6(\mu_6\text{-}C)(CO)_{15}(Ph_2PC_2PPh_2)\}}_n$. Conductivity increases with time under the electron beam, suggesting that the metal clusters aggregate following carbonyl loss, forming a conducting chain.[124]

Substitution of CO in $\mathrm{Ru_6(\mu_6\text{-}C)(CO)_{17}}$ by dppf first affords the spectroscopically characterized $\mathrm{Ru_6(\mu_6\text{-}C)(CO)_{16}}$(dppf-*P*), which slowly converts into paramagnetic $\mathrm{Ru_6(\mu_6\text{-}C)(\mu\text{-}dppf)(\mu\text{-}CO)_2(CO)_{13}}$ **130**, in which the Ru···Ru vector bridged by the diphosphine and the adjacent apical–equatorial Ru–Ru bond have cleaved to give a hinged square-based pyramid. The paramagnetism is 35% of that expected from a spin triplet state as a result of weak antiferromagnetic coupling between the ferrocene nucleus and the $\mathrm{Ru_6(\mu_6\text{-}C)}$ cluster. Electronically, this complex is related to paramagnetic $\mathrm{[Co_6(\mu_6\text{-}C)(CO)_{14}]^-}$. Irreversible two-electron reduction (−0.65 V vs. Ag/AgCl) and one-electron oxidation (+1.15 V) waves are found for **130** at 223 K, the former being cluster-based and the latter being associated with the ferrocene nucleus. Thermolysis of **130** results in decapping of the cluster to give $\mathrm{Ru_5(\mu_5\text{-}C)(\mu\text{-}dppf)(CO)_{13}}$ **131**, also obtained from $\mathrm{Ru_5(\mu_5\text{-}C)(CO)_{15}}$ and dppf; one-electron oxidation and two-electron reduction occur at +1.06 and −1.05 V, respectively. The related ligand $\mathrm{Co(\eta^5\text{-}C_5H_4PPh_2)_2}$ (dppc) reacts with $\mathrm{Ru_6(\mu_6\text{-}C)(CO)_{17}}$ to give (possibly) $\mathrm{[dppc^+]_2[Ru_6(\mu_6\text{-}C)(CO)_{16}]}$ together with $\mathrm{Ru_5(\mu_5\text{-}C)(\mu\text{-}dppc)(CO)_{13}}$, also prepared directly from $\mathrm{Ru_5(\mu_5\text{-}C)(CO)_{15}}$. The magnetic properties, EPR and variable-temperature ^{31}P NMR spectra indicate that a single unpaired electron is present.[125,126] An unusual cluster ion pair, $\mathrm{[Ru_3\{\mu\text{-}P(NPr^i{}_2)_2\}_3(CO)_9][Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2\{\mu\text{-}P(NPr^i{}_2)_2\}(CO)_{13}]}$, has been prepared by the addition of $\mathrm{PCl(NPr^i{}_2)_2}$ to $\mathrm{[Ru_4(CO)_{13}]^{2-}}$. The cation consists of an almost-planar, 50-electron triruthenium triangle, with a phosphido ligand symmetrically bridging each Ru–Ru bond. The anion **132** consists of an octahedral hexaruthenium carbido cluster with a symmetrically bridging phosphido ligand.[127]



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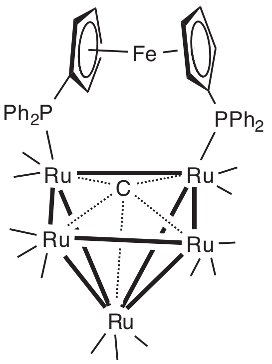

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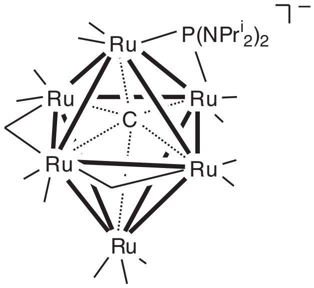

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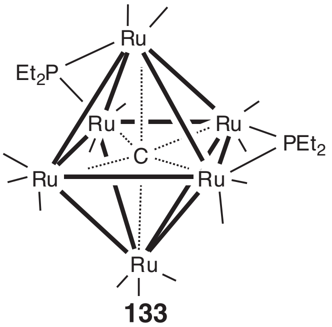
Thermolysis of $Ru_3(CO)_{12}$ with PEt_2Fc (Fc = ferrocenyl) results in P–C(Fc) bond cleavage, rather than P–C(Et) cleavage, and loss of the iron unit to give hexaruthenium carbido clusters $Ru_6(\mu_6\text{-}C)(\mu\text{-}PEt_2)_2(CO)_{14}$ **133** and $Ru_6(\mu_6\text{-}C)(\mu\text{-}PEt_2)(CO)_{13}Cp$ **134**, along with pentanuclear cluster **79**. The Cp ligand transferred to the cluster framework in the formation of **134** can be derived from either the Cp or C_5H_4 groups of the ferrocenylphosphine, the latter also involving proton abstraction from the solvent.[83]



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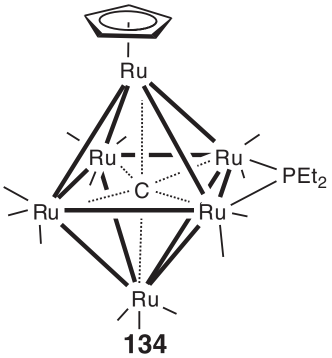

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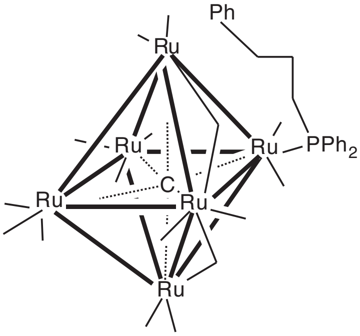
$Ru_6(\mu_6\text{-}C)(CO)_{17}$ has been reacted with 2 equiv. of the monodentate phosphine $PPh_2(CH_2)_3Ph$ in an attempt to create a cluster analog of ferrocene by inducing η^6-coordination of the carbon-bound phenyl ring of a phosphine ligand. Stepwise reaction affords the *P*- and *P*,η^6- products $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{14}\{PPh_2(CH_2)_3Ph\}$ **135** and $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{12}\{\mu\text{-}P,\eta^6\text{-}PPh_2(CH_2)_3Ph\}$ **136**, respectively. Surprisingly, the phosphorus-bound phenyl ring preferentially coordinates to the cluster core. Analogous reactions with the related pentaruthenium cluster $Ru_5(\mu_5\text{-}C)(CO)_{15}$ afford the spectroscopically characterized monosubstituted complex, and unidentified bis-phosphine complexes, which do not contain η^6-coordinated arene.[128] Thermolyses of the monophosphine complexes $Ru_6(\mu_6\text{-}C)(CO)_{16}(PR_2Ph)$ afford $Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^1{:}\eta^6\text{-}PR_2Ph\}(\mu\text{-}CO)_2(CO)_{11}$ [R = Ph **137**, Me] with the same coordination of ligands as in **136**. The reaction is reversible under CO at room temperature.[129]



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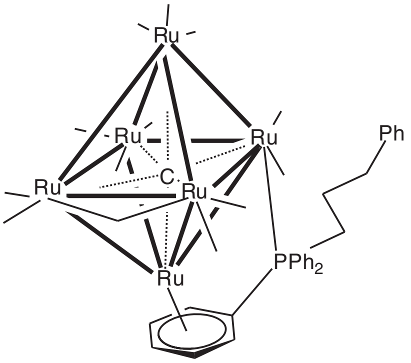

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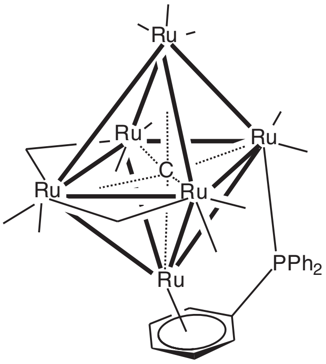
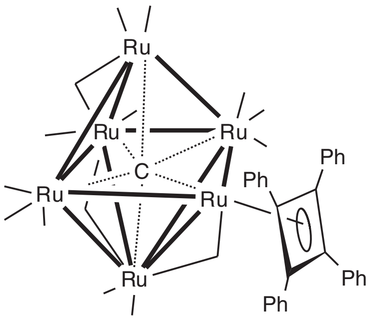


137

6.24.3.2.2 Carbido clusters with arene ligands

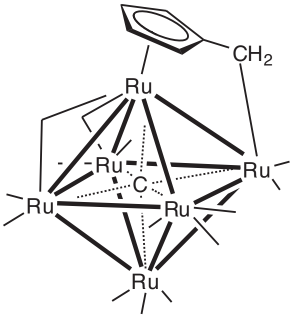
Carbido complexes with coordinated arene ligands are available from studies by Johnson and co-workers, and form the best-studied group of hexaruthenium clusters; the early work has been summarized.[29,31,130] These complexes are generally prepared by one of the three routes: the thermolytic reaction of $Ru_3(CO)_{12}$ with the desired arene or polyunsaturated reagent, thermolysis of the preformed $Ru_6(\mu_6\text{-}C)(CO)_{17}$ with the organic reagent, or capping of pentaruthenium carbido precursors with appropriate monometallic η-arene reagents. Structural analyses show that a graphite-like crystallographic packing in these clusters affords maximum interaction between arene groups on adjacent molecules, with the bridging carbonyl ligand of one molecule slipping into the tetragonal cavity formed by four CO ligands of the neighboring molecule. Resulting head-to-tail chains are seen in both mono- and bis-arene derivatives, with little difference observed in the alternative coordination modes, namely $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$- face capping or η^6-apical.

The cyclobutadiene complex $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{12}(\eta^4\text{-}C_4Ph_4)$ **138** is formed from redox-mediated ligand transfer between $[Pd(acetone)_2(\eta^4\text{-}C_4Ph_4)]^{2+}$ and $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$. The metal core consists of a bond-opened octahedron, with the η^4-organic ligand bound to a basal ruthenium atom.[41]



138

The reaction between $Ru_6(\mu_6\text{-}C)(CO)_{17}$ and cyclopentadiene in the presence of Me_3NO affords a minor amount of $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5H_4)(\mu\text{-}CO)_2(CO)_{12}$ **139**, along with the pentanuclear cluster **26** and the bis-arene complex $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{10}Cp_2$ **140**. Complex **139** contains a chelating $\eta^1{:}\eta^5\text{-}CH_2C_5H_4$ ligand, the CH_2 unit presumably derived from nucleophilic addition of the cyclopentadienide anion to a carbonyl ligand followed by H^+/H^- transfer.[43,131] Reaction of $Ru_6(\mu_6\text{-}C)(CO)_{17}$ with pentamethylcyclopentadiene in refluxing heptane affords $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)(\mu\text{-}CO)(CO)_{13}$ **141**, an analog of **139**,[132] whereas reaction of the same cluster with 3 equiv. of Me_3NO and $C_5H_4PPh_3$ leads to the formation of the zwitterionic complex $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^5\text{-}C_5H_4PPh_3)$ **142**.[133] The reactions of $Ru_6(\mu_6\text{-}C)(CO)_{17}/Me_3NO$ with fulvenes give products containing both facially and terminally bonded five-membered rings, rather than the possible six-membered ring products. Complexes $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_5H_4CPh_2)(CO)_{15}$ **143** and $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}C_5H_4CR_2)(\mu\text{-}CO)(CO)_{13}$ ($R = Ph$, Me; **144**) are obtained from reactions with 6,6-diphenylfulvene (dpf) and 6,6-dimethylfulvene (dmf). Thermolysis of **144** ($R = Me$) in acetonitrile yields $Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^3{:}\eta^5\text{-}C_5H_4C(CH_2)_2\}(\mu\text{-}CO)_2(CO)_{11}$ **145**, containing an $\eta^3{:}\eta^5$-bound cyclopentadienyl ligand, whereas further reaction with dmf in the presence of water gives $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{10}(\eta^5\text{-}C_5H_4CMe_2H)(\eta^5\text{-}C_5H_4CMe_2OH)$ **146**.[131,134]



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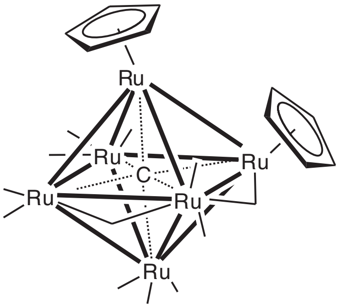

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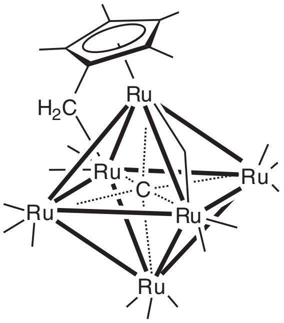

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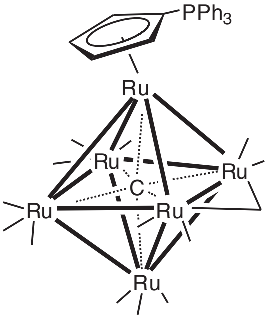

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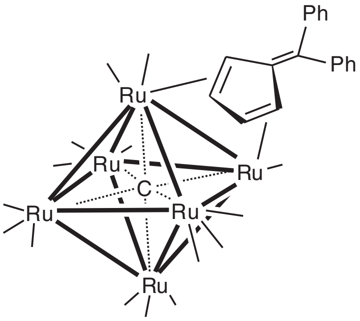

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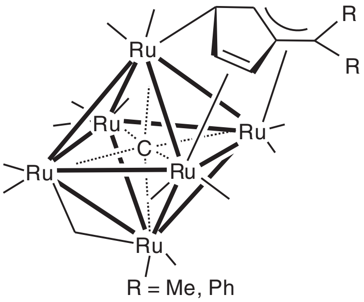

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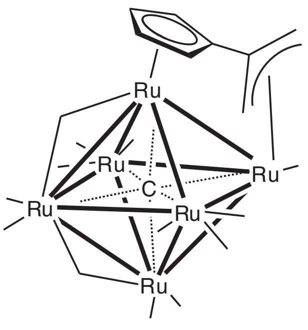

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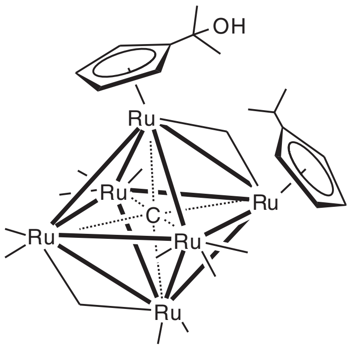
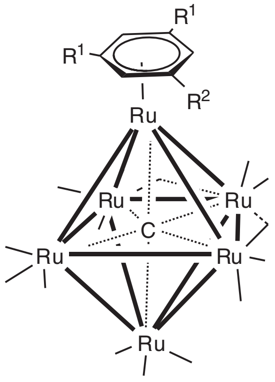


146

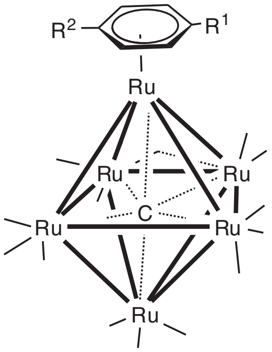
$Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{12}(\eta^6\text{-}C_6H_3R_3\text{-}1,3,5)$ (**147**; $R_3 = Me_2H$) contains two rotamers in the unit cell; the more sterically demanding **147** ($R_3 = Et_3$) contains ethyl groups pointing vertically which allows intermolecular interlocking in the crystal lattice.[135] Reactions between $Ru_3(CO)_{12}$ and unsaturated arene reagents isopropenylbenzene, 4-phenyl-1-butene, and allylbenzene afford $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_5R)$ [$R = CHMe_2$, Bu **148**, Pr, $CH{=}CHMe$] in 3–5% yield; similar reactions with the corresponding saturated reagents improve yields to 10–15%.[136] Similarly, reactions with styrene, 4-methyl- or 4-trifluoromethylstyrene, give a mixture of products, including trace amounts of $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}MeC_6H_4R)$ [$R = Me$ **148**, H, CF_3] and the spectroscopically characterized $Ru_6(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HC_2C_6H_4R)(CO)_{15}(\eta^6\text{-}EtC_6H_4R)$, with a doubly bridged tetrahedral metal core and a hydrogenated vinyl ligand.[137]

Bicyclic arene compounds react with $Ru_3(CO)_{12}$ to give $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}\{\eta^6\text{-}Ph(CH_2)_nPh\}$ ($n = 0$, 1; **149**), $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{12}\{\eta^6\text{-}Ph(CH_2)_2Ph\}$ **150**, $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}R^1C_6H_4R^2)$ [$R^1 = Ph$, $R^2 = Me$ **151**, Et, Ph; $R^1 = Me$, Et, $R^2 = Ph$ **152**], and $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}Ph\text{-}1\text{-}C_6H_3\text{-}3,5\text{-}Ph_2)$. The isolation of both **151 and 152** ($R = Me$) suggests a subtle balance between the steric and electronic factors governing product distribution in these examples, although crystal packing was shown to be more efficient in the latter.[138–140] Reactions of $Ru_3(CO)_{12}$ with biphenyl or diphenyl ether give $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}R)$ ($R = C_6H_5C_6H_5$, PhOPh),[141] and the reaction of $Ru_6(\mu_6\text{-}C)(CO)_{17}$ with *trans*-stilbene gives $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}\text{-}(\eta^6\text{-}PhCH{=}CHPh)$.[138]



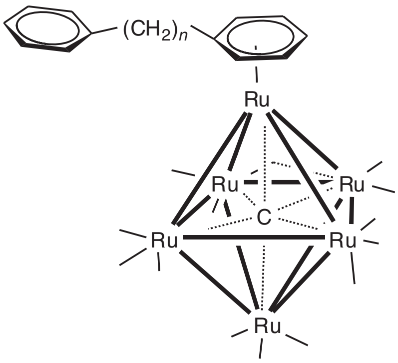
$R^1 = Me$, $R^2 = H$
$R^1 = R^2 = Et$

147



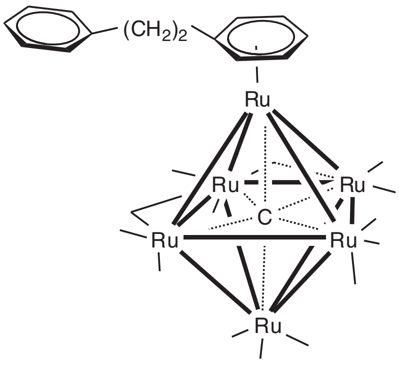
$R^1 = CHMe_2$, Bu; $R^2 = H$
$R^1 = R^2 = Me$

148



n = 0, 1

149



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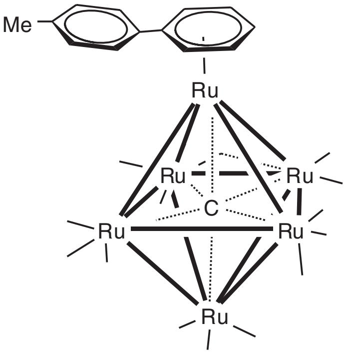

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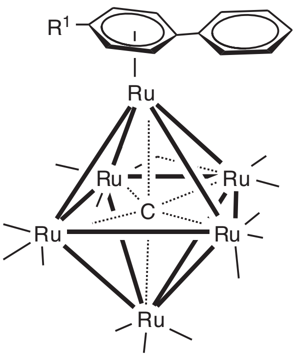
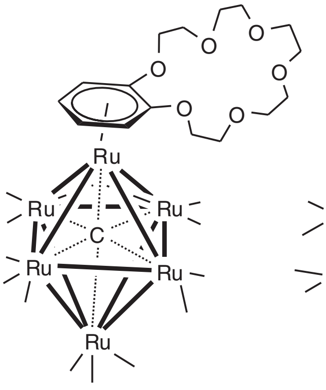


R^1 = Me, Et

152

Aryl crown ethers coordinate to $Ru_6(\mu_6\text{-}C)(CO)_{17}$ by the aryl group to give $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_4R)$ [$R = C_{10}H_{20}O_6$ **153**, $C_8H_{16}O_5$, $C_{18}H_{28}O_8$ **154**], the usual redox activity of the clusters being modified by addition of Na^+ or NH_4^+ ions. The anodic shift found on addition of Na^+ is consistent with the formation of a host–guest complex involving the crown ether, and the solid-state structure of the NH_4^+ adduct reveals the cation H-bonded to the ether O atoms. Treatment of the larger crown ether complex **154** with $[NH_2(CH_2Ph)_2]^+$ gives a cationic "pseudo-rotaxane" **155**, where the amine has been threaded through the macrocyclic cavity to give a π-stacking arrangement of three arene rings. In contrast, the smaller cluster **153** reacts with the diprotonated diamine $[NH_3(CH_2)_8NH_3]^{2+}$ to give the dicationic N–H· · ·O bound, linked dicluster system **156**, with the cluster units arranged in a *trans*-configuration.[142,143] Complex **153** and $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ (and $[H_2Ru_{10}(CO)_{25}]^{2-}$) have been used as transmission electron microscopy probes to determine the position of ammonium-functionalized tethers on mesoporous silica.[144,145]



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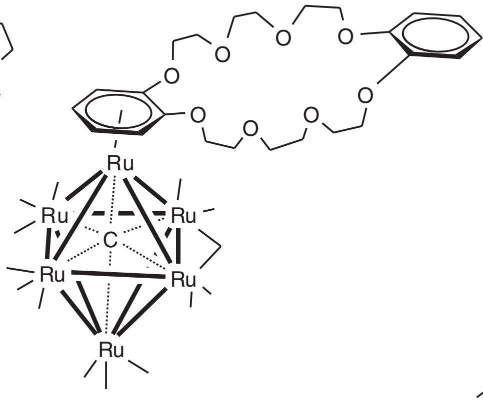

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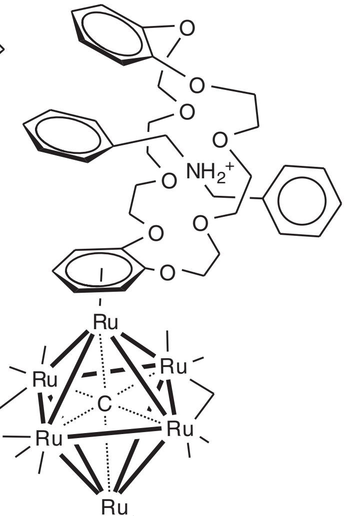

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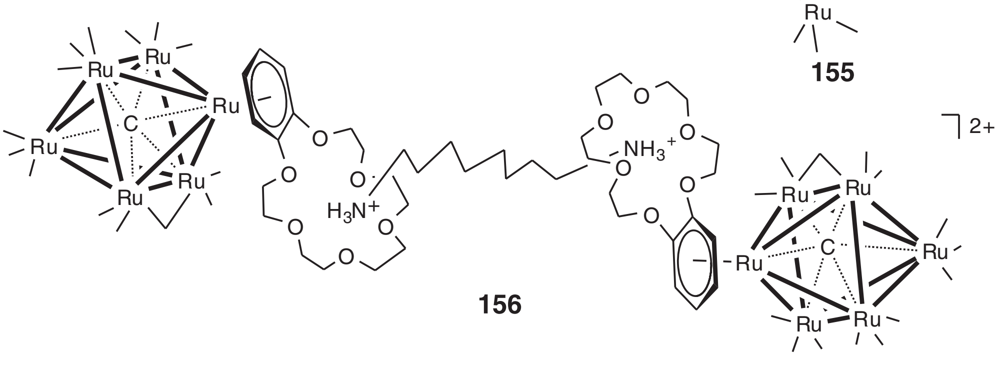
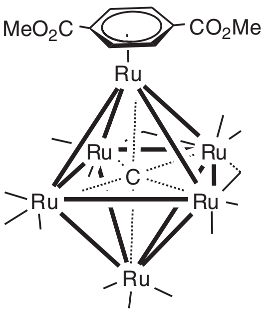


156

The complexes $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{12}\{\eta^6\text{-}C_6H_4(CO_2Me)_2\text{-}1,4\}$ **157** and $Ru_6(\mu_6\text{-}C)\{\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_4(CO_2Me)_2\text{-}1,4\}(\mu\text{-}CO)(CO)_{13}$ **158** are the first examples of coordination isomers of the same arene ligand on the $Ru_6(\mu_6\text{-}C)(CO)_{14}$ framework, and are formed by the reaction of $Ru_6(\mu_6\text{-}C)(CO)_{17}$ with the substituted arene $1,4\text{-}C_6H_4(CO_2Me)_2$. The formation of the relatively unusual face-capping arene ligand is thought to be due to the increased electron-withdrawing properties of this arene.[146]



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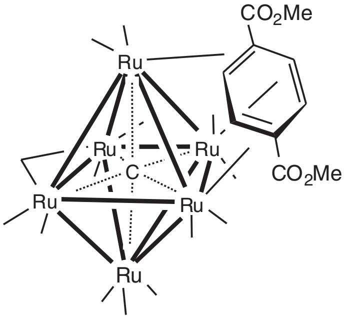
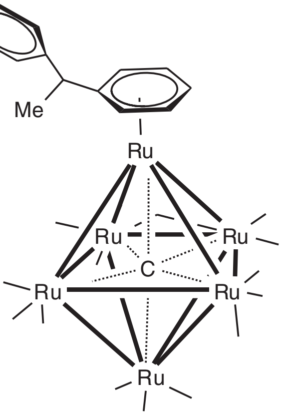


158

Reaction of 1,1-diphenylethene with $Ru_3(CO)_{12}$ affords low yields of $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}PhCHMePh)$ **159**, containing the hydrogenated alkene, and the spectroscopically characterized $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}PhCH{=}CHPh)$, containing the unsaturated ligand, but no linked clusters. Trace amounts of the heptanuclear species **296** are also isolated.[147]

In a reaction analogous to that of $Ru_5(\mu_5\text{-}C)(CO)_{15}$, $Ru_6(\mu_6\text{-}C)(CO)_{17}$ reacts with C_{60} in chlorobenzene followed by treatment with dppm to give $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})(\mu\text{-}dppm)(\mu\text{-}CO)_2(CO)_{10}$ **160**.[44]

Hexanuclear arene complexes can also be prepared by ionic coupling reactions on a preformed pentametallic carbido cluster core. Reaction of $[Os_5(\mu_5\text{-}C)(CO)_{14}]^{2-}$ with $[Os(NCMe)_3(\eta^6\text{-}C_6H_6)]^{2+}$ affords $Os_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_6)$ **161** in 30% yield,[148] and the dianionic cluster $[Ru_5(\mu_5\text{-}C)(CO)_{14}]^{2-}$ reacts with 2 equiv. of $[Ru(NCMe)_3Cp]^+$ to give the hexanuclear ionic complex $[Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{11}Cp]^-$ **162**, along with the heptanuclear complex **294**, each in around 40% yield.[149]



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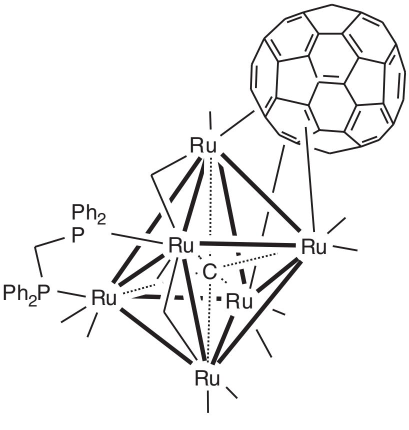

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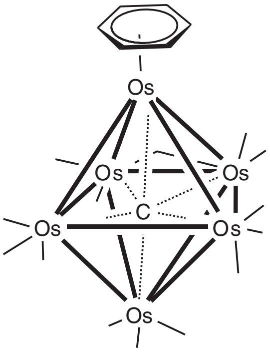

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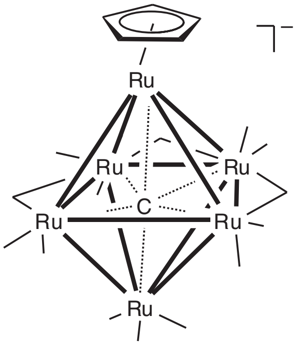
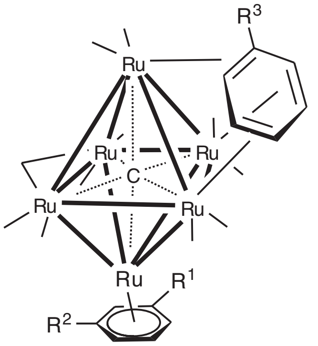


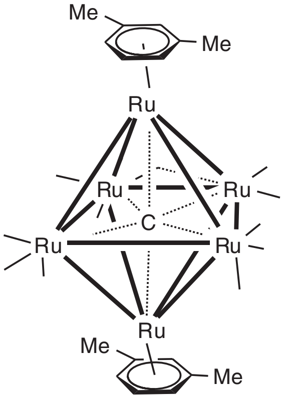
162

Clusters containing two arene units have been prepared by two routes. Activation of the relevant monoarene complex $Ru_6(\mu_6\text{-}C)(CO)_{11}(\eta^6\text{-arene})$ with Me_3NO, followed by addition of a dihydroarene, gives $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^4\text{-dihydroarene})(CO)_{11}(\eta^6\text{-arene})$. The bis(arene) cluster is then formed by the removal of a further CO ligand, with concomitant dehydrogenation of the second ring. Alternatively, where the hydrogenated arene is not available, treatment of the monoarene cluster with 3 equiv. of Me_3NO followed by the relevant arene has been successful. Solutions of the bis-toluene complex $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_5Me)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_6H_5Me)$ (**163**; $R^1 = Me$, $R^2 = H$, $R^3 = Me$) show interchange between the crystallographic form and the bis-apical isomer $Ru_6(\mu_6\text{-}C)(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2$.[150] The bis-xylene complex $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)_2$ **164** is prepared from the monoadduct $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}1,3\text{-}C_6H_4Me_2)$ and xylene; solutions containing both complexes afford co-crystals consisting of alternating stacks of bimolecular layers formed from molecules of the same type.[151] The *cis-* and *trans-*isomers of the mixed bis-arene complexes $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_6H_5Me)(\eta^6\text{-}C_6H_4Me_2)$ **165** and **166** are formed from the xylyl cluster $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_4Me_2)(CO)_{14}$ and dihydrotoluene. A third isomer, $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_5Me)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_6H_4Me_2)$, was characterized by IR spectroscopy and mass spectrometry.[152]



$R^1 = Me$, $R^2 = H$; $R^3 = Me$
$R^1 = Me$, $R^2 = R^3 = H$
$R^1 = R^2 = Me$; $R^3 = H$

163



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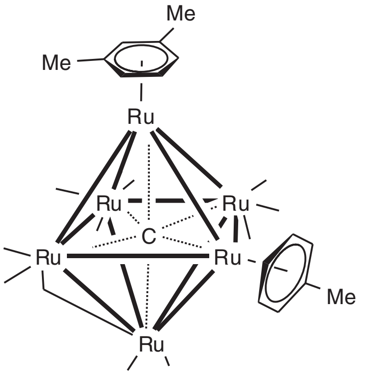

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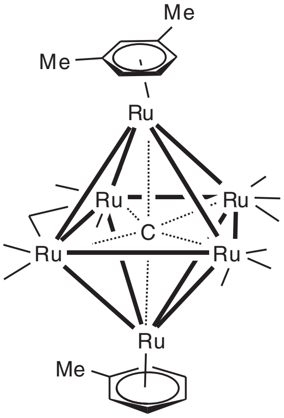
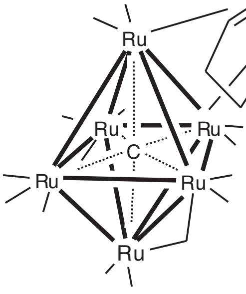


166

Bis-arene complexes can be prepared in a stepwise manner by reaction of 1,3- or 1,4-cyclohexadiene with $Me_3NO/Ru_6(\mu_6\text{-}C)(CO)_{17}$ to give the monodiene and monoarene complexes $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8)(CO)_{14}$ **167** and $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-}C_6H_6)$ **168**, the 1,4-diene isomerizing to the 1,3-diene on coordination to the cluster. Addition of further 1,3- or 1,4-diene and 2 equiv. of Me_3NO to **168** affords a mixture of the isomers

$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(\mu\text{-}CO)(CO)_{11}$ **169** and $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(CO)_{12}(\eta^6\text{-}C_6H_6)$ **170**, along with the previously reported $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{11}(\eta^6\text{-}C_6H_6)$. Addition of Me_3NO to **167** affords **168**, and mild thermolysis of **169** results in migration of the benzene unit from $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$- or face capping to η^6- or terminal coordination to give **170**, a transformation also observed in the related pentaruthenium system. The complex $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{11}(\eta^6\text{-}C_6H_6)$ is also prepared from **170** upon addition of Me_3NO, or from the reaction of the benzene/dienyl intermediate $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_6H_7)(CO)_{12}(\eta^6\text{-}C_6H_6)$, formed on reaction of **170** with Ph_3C^+, followed by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[153]



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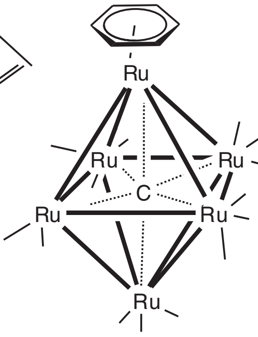

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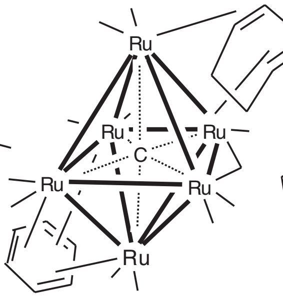

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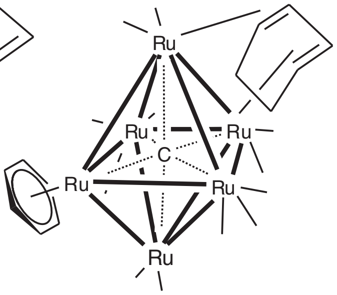
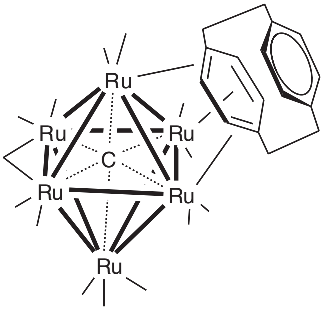


170

Similarly, the preformed monoarene complexes $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, 1,3-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$) react with Me_3NO and 1,3- or 1,4-cyclohexadiene to give the series of arene–diene complexes $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(CO)_{12}(\eta^6\text{-arene})$. Subsequent reaction with Me_3NO results in dehydrogenation of the diene to give the arene–benzene derivatives, $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-arene})$ (**163**; $R^1 = Me$, $R^2 = R^3 = H$; $R^1 = R^2 = Me$, $R^3 = H$). These clusters reversibly isomerize on standing at −25 °C to the bis-terminal arene isomers $Ru_6(\mu_6\text{-}C)(CO)_{11}(\eta^6\text{-arene})(\eta^6\text{-}C_6H_6)$, where the arenes are located on mutually *cis*- ruthenium atoms.[154]

The chemistry of hexaruthenium carbido clusters ligated by arene groups within paracyclophane ligands has also been extensively studied by Johnson and co-workers,[155,156] with the aim of forming linked cluster complexes. The series $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}CO)(CO)_{13}$ **171**,[135] $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}CO)(CO)_{10}(\eta^6\text{-}C_{16}H_{16})$ **172**, and $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)(\mu\text{-}CO)(CO)_{11}$ **173** are formed from the reaction between $Ru_3(CO)_{12}$ and [2.2]paracyclophane.[157] A fourth product, $Ru_6(\mu_5\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)(\mu\text{-}CO)(CO)_{14}$ **174**, is also obtained in 5% yield. Thermolysis of **174** produces **171** almost quantitatively, suggesting **174** is an intermediate en route to **171**.[158,159]



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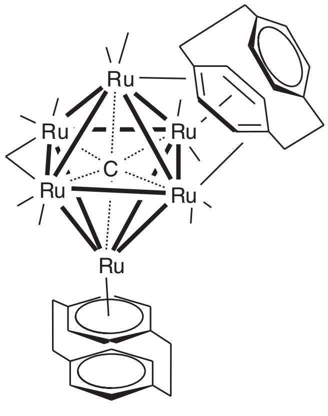

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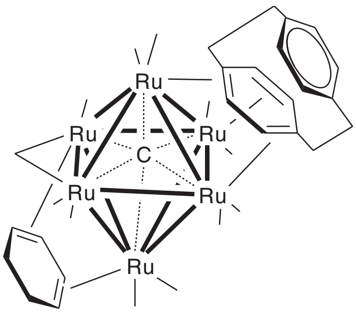

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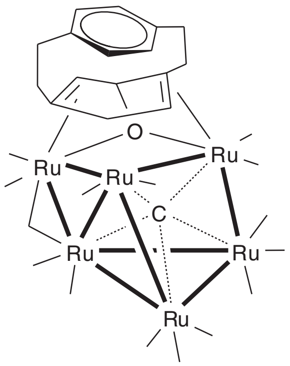
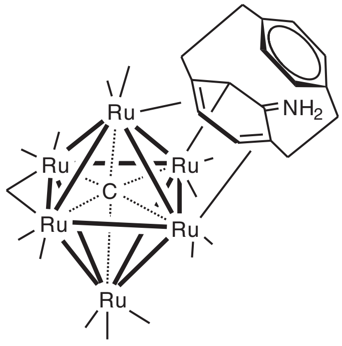


174

Similarly, heating $Ru_3(CO)_{12}$ with 4-amino[2.2]paracyclophane or 4-bromo[2.2]paracyclophane in refluxing octane affords $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{16}H_{15}NH_2)(\mu\text{-}CO)(CO)_{13}$ **175** and $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{15}Br)(\mu\text{-}CO)(CO)_{13}$ **176**, respectively, with the paracyclophane ring in the former product coordinated via the aniline ring in the unusual $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2$-mode; the cluster coordinates to the most activated (or least deactivated) of the paracyclophane rings.[160] Similar reactions with [2.2]*ortho*-, *anti*-[2.2]*meta*-, and [2.2.2]paracyclophanes afford complexes containing the ligand in an apical η^6-coordination mode, with $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}meta\text{-}C_{16}H_{16})$ **177** and $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}para\text{-}C_{24}H_{24})$ **178** being structurally verified. The difference in coordination modes is likely due to a combination of steric and electronic reasons, the orientation of the aromatic C–H bonds and of the π-orbitals favoring interaction with the metal face in the case of [2.2]paracyclophane. The [2.2]paracyclophane adduct can also be prepared by the ionic coupling of $[Ru_5(\mu_5\text{-}C)(CO)_{14}]^{2-}$ with $[Ru(NCMe)_3(\eta^6\text{-}C_{16}H_{16})]^{2+}$, presumably by rearrangement of the less stable $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_{16}H_{16})$.[161]



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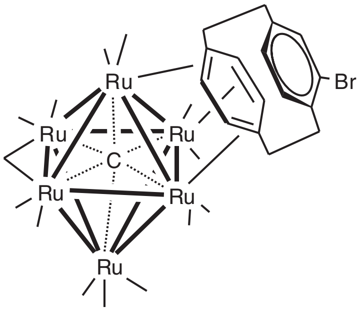

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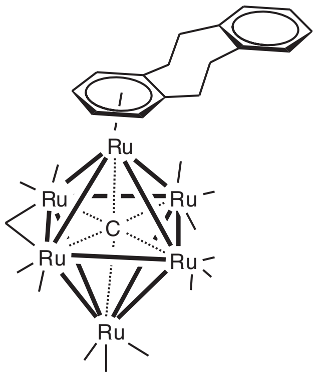

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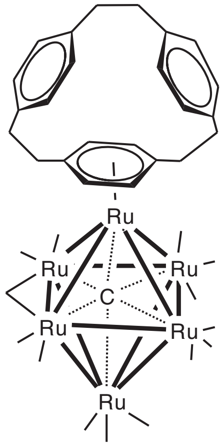

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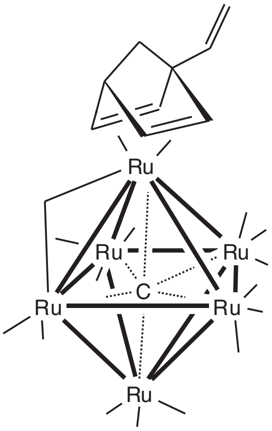
Products obtained from the reaction of $Ru_6(\mu_6\text{-}C)(CO)_{17}$ with cycloheptatriene retain the Ru_6C cluster core and contain organic fragments in a variety of coordination modes: $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{14}(\eta^4\text{-}ENBD)$ (ENBD = ethenylnorbornadiene) **179** contains a C_9 ethenylnorbornadiene ligand, the origin of the additional C_2 unit being unknown; $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_7H_8)(\mu\text{-}CO)(CO)_{13}$ **180** is isoelectronic with the elusive arene complex $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{14}$, the carbocyclic ligand being almost parallel to the triangular metal face; and $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^3\text{-}C_7H_8)(CO)_{10}(\eta^5\text{-}C_7H_9)$ **181** has two carbocyclic ligands, in apical and face-capping coordination modes. Cluster-mediated ring contraction also affords the η^6-toluene-containing complex.[162]



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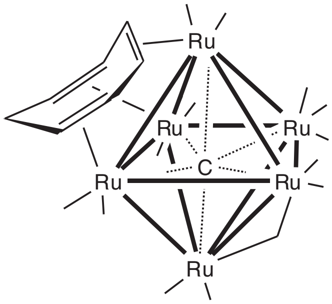

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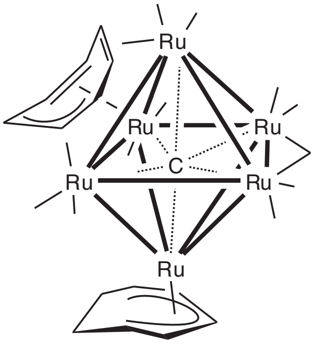
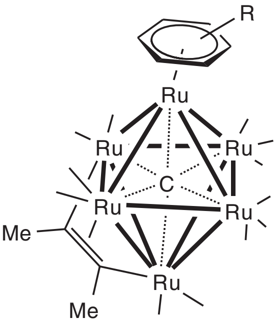


181

Reactions of $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, 1,3-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$) and of $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu\text{-}CO)(CO)_{13}$ **171** with 2 equiv. of Me_3NO in the presence of but-2-yne afford $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{-}MeC_2Me)(CO)_{12}(\eta^6\text{-arene})$ **182**, together with $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu_3\text{-}\eta^2\text{-}MeC_2Me)(CO)_{12}$ **183**. The presence of two μ_3-bound ligands in **183** contrasts with trinuclear complexes, where migration of the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6$ to form $\eta^6\text{-}C_6H_6$ is observed on reaction with alkyne.[163]

The η^6-coordinated arene ligands in $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-}C_6H_6)$ **168**, $Ru_6(\mu_6\text{-}C)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(CO)_{12}(\eta^6\text{-}C_6H_6)$ **170**, and $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{11}(\eta^6\text{-}C_6H_6)$ display electrophilic character. Nucleophilic addition of LiPh affords the anionic intermediates $[Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^4\text{-}C_6H_6Ph_2)]^{2-}$, $[Ru_6(\mu_6\text{-}C)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(CO)_{12}\text{-}(\eta^5\text{-}C_6H_6Ph)]^-$, and $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{11}(\eta^5\text{-}C_6H_6Ph)]^-$, respectively. Subsequent hydride abstraction with $[CPh_3]^+$ gives $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_4Ph_2\text{-}1,4)$ (**184**; R = Ph), and the spectroscopically characterized $Ru_6(\mu_6\text{-}C)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(CO)_{12}(\eta^6\text{-}C_6H_5Ph)$ and $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{11}(\eta^6\text{-}C_6H_5Ph)$, respectively. Similar treatment of **168 and 170** with MeLi affords the analogous complexes, with $Ru_6(\mu_6\text{-}C)\text{-}(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_4Me_2\text{-}1,4)$ (**184**; R = Me) being structurally verified.[164,165]



R = H, Me, 1,3-Me_2, 1,3,5-Me_3

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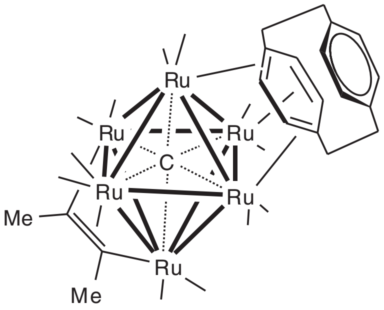

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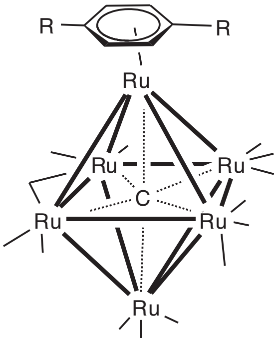


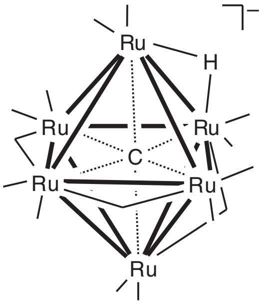
R = Ph, Me

184

6.24.3.2.3 Carbido clusters with other hydrocarbon ligands

Iwasawa and co-workers have defined the decarbonylated structures and catalytic activity of hexaruthenium carbido species. Metal oxide-supported $[Ru_6(\mu_6\text{-}C)(CH_3)(CO)_{16}]^-$ maintains its metal framework at 470–520 K under CO or CO/H_2, producing methane on heating in a vacuum, or acetaldehyde in the presence of CO/H_2. In contrast, the same cluster in solution or the SiO_2-supported non-carbido cluster anion $[Ru_6(CO)_{18}]^{2-}$ react to form only methane. The supported cluster is selective for ethene hydroformylation.[166–168] Methane production on MgO is accompanied by the release of two CO molecules per cluster, to give $Ru_6(\mu_6\text{-}C)(CO)_{14}$/MgO, which reversibly loses or adds CO, with concomitant shrinkage and expansion of the metal–carbido framework.[169,170] Time-resolved energy-dispersive X-ray absorption fine-structure studies of $Ru_6(\mu_6\text{-}C)(CO)_{14}$/MgO show that it forms $Ru_6(\mu_6\text{-}C)(CO)_6$/MgO on heating *in vacuo*. Carbonylation occurs by way of two $Ru_6(\mu_6\text{-}C)(CO)_6$ intermediates with differing Ru–Ru bond distances. Initial coordination of six CO molecules to the hexaruthenium framework is followed by an Ru–Ru bond expansion, and subsequent addition of another five CO molecules to give $Ru_6(\mu_6\text{-}C)(CO)_{11}$. Decarbonylation occurs in two steps, with concomitant cluster shrinkage. The $Ru_6(\mu_6\text{-}C)(CO)_{11}$/MgO system is a better catalyst for the conversion of CO/H_2 into oxygenated products than is $Ru_6(\mu_6\text{-}C)(CO)_{14}$/MgO.[171]

$[Ru_6(\mu_6\text{-}C)(CH_3)(CO)_{16}]^-$ is catalytically active for hydrogenation and isomerization of alkenes. Hydrogenation at 100 °C/100 atm H_2 affords the unsaturated hydrido cluster $[Ru_6(\mu\text{-}H)(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{12}]^-$ **185**, which is carbonylated to $[Ru_6H(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_{12}]^-$ **186**, containing a terminal hydride ligand. A similar hydrogenation of $[Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(CO)_{15}]^-$ at 130 °C also produces **185**.[172]



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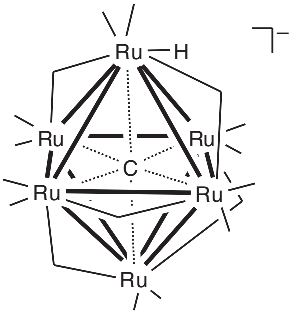

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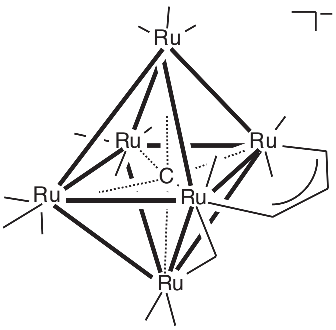
Carbido clusters with alkyl or allyl ligands are available from studies by Chihara and co-workers. A second solid-state isomer of the anionic complex $[Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}CO)(CO)_{14}]^-$ **187** has been isolated by crystallization from methanol. The isomers differ in the number of bridging CO ligands, the known isomer **188** having one bridging and one semi-bridging CO ligand, whereas the new isomer has a single bridging CO and a slight shift in the position of the allyl group.[173] Anion **187** reacts with allyl bromide to form $Ru_5(\mu_5\text{-}C)(\mu\text{-}Br)_2(\mu\text{-}\eta^3\text{-}C_3H_5)(CO)_{11}(\eta^3\text{-}C_3H_5)$ **189**. The related alkyl cluster anion $[Ru_6(\mu_6\text{-}C)(Me)(CO)_{15}]^-$ reacts with methyl iodide to form $[Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2\text{-}COMe)(\mu\text{-}I)I(CO)_{13}]^-$ **190**. The anionic bromo cluster $[Ru_6(\mu_6\text{-}C)(\mu\text{-}Br)(\mu\text{-}CO)_2(CO)_{14}]^-$ **191** is formed from $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ by bromination or treatment with $PhCH_2Br$, and reacts with further $PhCH_2Br$ to give $Ru_5(\mu_5\text{-}C)(\mu\text{-}Br)_2(CO)_{14}$ **192** with a geometry analogous to that of **190**.[174]



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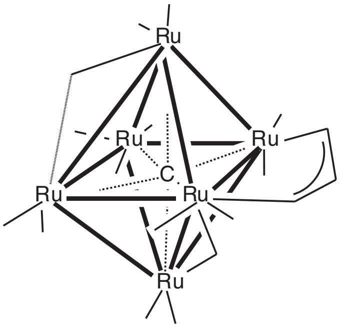

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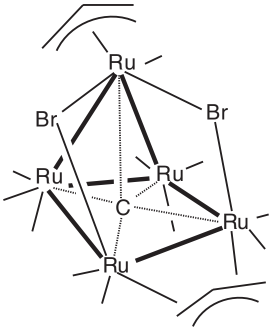

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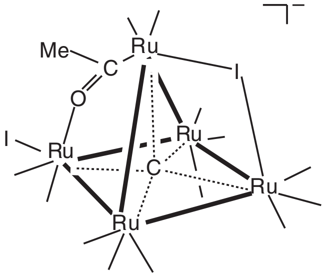

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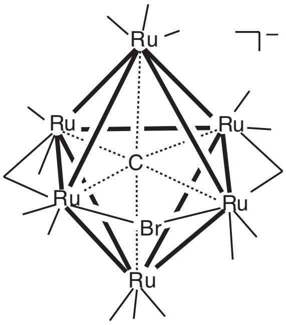

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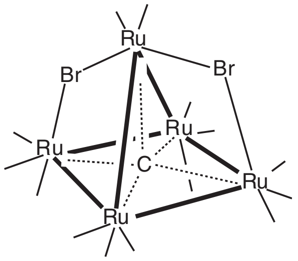
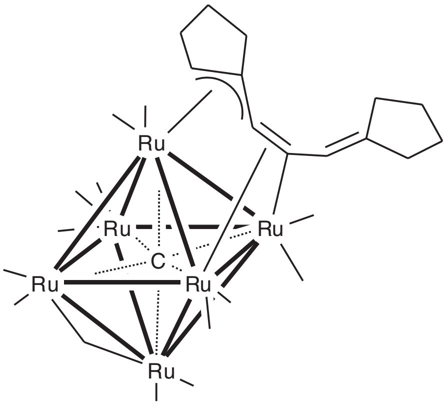


192

Reactions of $Ru_3(CO)_{12}$ with the hydroxyalkynes HC≡CROH ($R = C_5H_8$, C_7H_{12}, C_8H_{14}) give $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}C_5H_7CCCHC_5H_8)(\mu\text{-}CO)(CO)_{13}$ **193**, $Ru_6(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}CCHC_5H_6)_2(\mu\text{-}CO)_2(CO)_{12}$ **194**, $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^1{:}\eta^3\text{-}CHC_7H_{11})(\mu\text{-}CO)(CO)_{14}$ **195**, $Ru_6(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}CCHR)_2(CO)_{14}$ (**196**, $R = C_7H_{10}$, C_8H_{12}), and $Ru_6(\mu_6\text{-}C)\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}C_8H_{12}CHCHCHC(OH)C_8H_{14}\}(\mu\text{-}CO)(CO)_{13}$ **197**. Complexes **193** and **194** are formed from 1-ethynylcyclopentanol; the former contains a ligand formed from the coupling of two alkyne units with concomitant loss of water, while the latter consists of a distorted trigonal prism with an additional Ru–Ru bond across the square base, with two alkynyl ligands bound to opposite faces. The reaction with 1-ethynylcycloheptanol affords **195** and **196** ($R = C_7H_{10}$), the latter with a metal core made up of two linked distorted square-planar units and containing two alkyne ligands in similar bonding mode to **194**. Similar reaction with 1-ethynylcyclooctanol yields **196** and **197**, the latter containing a 1,2,3,4-hexatetraene chain.[175]



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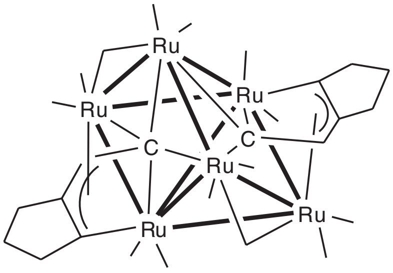

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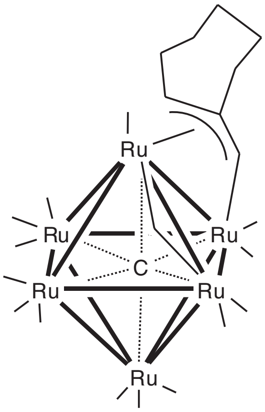

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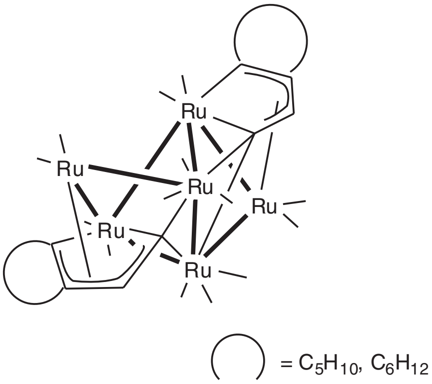

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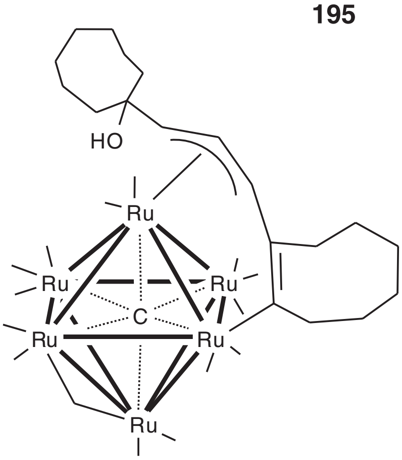
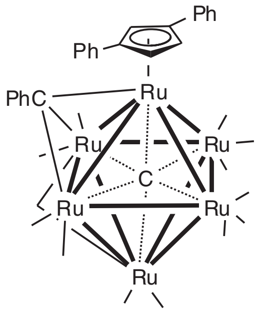


197

$Ru_6(\mu_6\text{-}C)(CO)_{17}$ reacts with $HC{\equiv}CPh/Me_3NO$ to give $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{-}PhC_2H)(CO)_{15}$ as the major product, along with minor amounts of $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_{12}(\eta^5\text{-}C_5H_3Ph_2)$ **198**, and isomeric clusters $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^4\text{-}CPhCHCPhCH)(\mu\text{-}CO)(CO)_{13}$ and $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^4\text{-}CPhCHCHCPh)(\mu\text{-}CO)(CO)_{13}$ **199**. Formation of the η^5-diphenylcyclopentadienyl ligand and face-capping alkylidyne group in complex **198** requires phenylacetylene C≡C bond cleavage and condensation of two alkyne units with the residual CH unit. The organic fragment in the isomeric clusters is derived from the head-to-tail and head-to-head coupling of the alkyne units, respectively, while the spectroscopically characterized $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^4\text{-}CPhCHCPhCH)(\mu\text{-}CO)(CO)_{13}$ is thought to be the precursor of **198**.[176,177]

Similar reaction with $MeC{\equiv}CMe$ affords $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}MeC_2Me)(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_2Me)(CO)_{14}$ **200**, resulting from a rearrangement of the metal framework to give a face-capped square-pyramidal cluster and octahedral $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}MeC_2Me)(CO)_{15}$. The latter reacts further with $MeC{\equiv}CMe$ to give **200** and the tris-alkyne cluster $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}MeC_2Me)_3(CO)_{12}$ **201**, where the octahedral metal core is maintained; **201** can also be formed from **200**. Complex **200** is electron precise, assuming that the $\mu\text{-}\eta^2{:}\eta^2$-alkyne functions as a two-electron donor; in contrast, complex **201** is an 88 c.v.e cluster, with the three alkyne ligands donating four electrons each.[178] $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}PhC_2Ph)_2(CO)_{13}$ **202** is obtained from the reactions of $Ru_5Pt(\mu_5\text{-}C)(CO)_{16}$ or $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}PhC_2Ph)(CO)_{15}$ with diphenylacetylene.[179]



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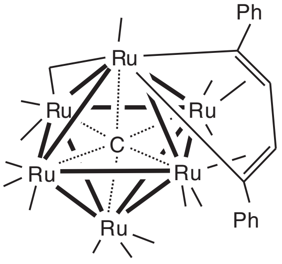

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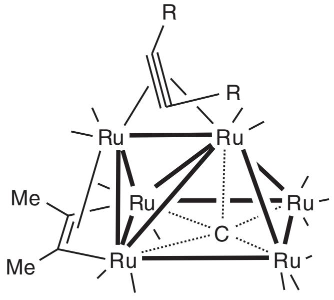
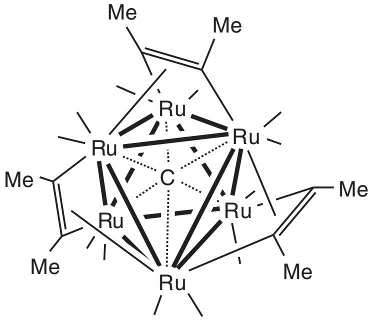


R = Me, Ph

200



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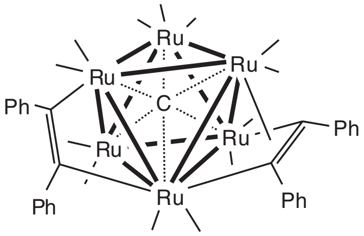
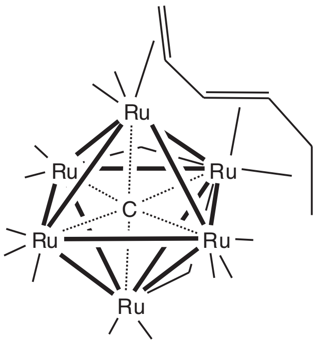


202

$Ru_6(\mu_6\text{-}C)(CO)_{17}$ reacts with a mixture of the *cis-* and *trans-*isomers of 1,3,5-hexatriene to give isomeric $Ru_6(\mu_6\text{-}C)(\mu\text{-}s\text{-}cis,s\text{-}cis,trans\text{-}1,2\text{-}\eta^2\text{-}3\text{-}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)(\mu\text{-}CO)_2(CO)_{12}$ **203** and $Ru_6(\mu_6\text{-}C)(\mu\text{-}s\text{-}trans,s\text{-}cis,trans\text{-}1,2\text{-}\eta^2\text{-}3\text{-}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)(\mu\text{-}CO)_2(CO)_{12}$ **204**, along with $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^4\text{-}trans\text{-}MeCHCHCHCHMe)(CO)_{15}$ and $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_6)$, the former probably resulting from trace impurities in the organic reagent. Conversion of **203** into **204** occurs in 16% yield; attempts to convert **204** into **203** by thermolysis in a closed system were unsuccessful.[180]

Reaction of $Ru_3(CO)_{12}$ with cyclooctene affords $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_8H_{12})(CO)_{15}$ **205** in 27% yield, resulting from dehydrogenation of the reagent. In contrast, reaction with cyclooctatetraene results in cluster degradation to give a binuclear complex, $Ru_2(\mu\text{-}\eta^4{:}\eta^4\text{-}C_8H_8)(CO)_5$.[181]



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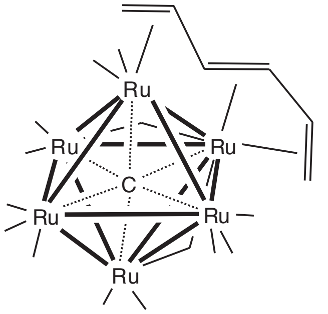

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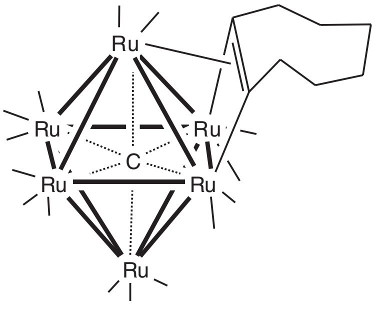
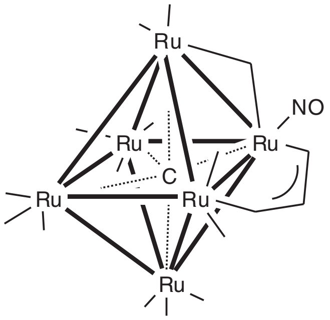


205

6.24.3.2.4 Carbido clusters with heteroatom donor ligands

The reactivity of the hexaruthenium carbido clusters $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$, $Ru_6(\mu_6\text{-}C)(CO)_{17}$, and the methyl and allyl derivatives, $[Ru_6(\mu_6\text{-}C)(Me)(CO)_{16}]^-$ and $[Ru_6(\mu_6\text{-}C)(CO)_{15}(\eta^3\text{-}C_3H_5)]^-$, toward NO and SO_2 has been the subject of studies by Wakatsuki and co-workers, some of which have been reviewed.[182] Gaseous NO has been used as a route into nitrosyl complexes. Reaction with the dianionic cluster affords $[Ru_6(\mu_6\text{-}C)(CO)_{15}(NO)]^-$ in 85% yield, while reaction with the allyl-containing cluster anion gives the neutral cluster $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)$-$(\mu\text{-}CO)(CO)_{13}(NO)$ **206**, containing a terminal NO bonded to the same metal atom as the allyl unit. Further reaction of these nitrosyl complexes with NO results in cluster degradation and formation of pentaruthenium carbido clusters $Ru_5(\mu_5\text{-}C)(CO)_{14}(NO)(NO_2)$ and $Ru_5(\mu_5\text{-}C)(\mu\text{-}\eta^2\text{-}NO_2)(CO)_{13}(\eta^3\text{-}C_3H_5)$ **41**. $[Ru_6(\mu_6\text{-}C)(CO)_{15}(NO)]^-$ also reacts with bromine to give the neutral adduct $Ru_6(\mu_6\text{-}C)Br(CO)_{14}(NO)$. The 2-methoxycarbonylallyl analog of **206**, $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_4CO_2Me)(\mu\text{-}CO)_3(CO)_{11}(NO)$ **207**, has also been prepared, using a similar reaction between NO and the precursor cluster $[Ru_6(\mu_6\text{-}C)(CO)_{15}(\eta^3\text{-}C_3H_4CO_2Me)]^-$.[183] Reaction of SO_2 with the allyl cluster $[Ru_6$-$(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(CO)_{16}]^-$ proceeds to give $[Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SO_2)(CO)_{14}]^-$ **208**.[50,51,184] ^1H NMR spectroscopy reveals that activation parameters for ligand mobility in **206–208** are independent of the steric and electronic character of the allyl group, suggesting that the NO and SO_2 groups are mobile around the cluster, while the allyl unit remains stationary.[183]



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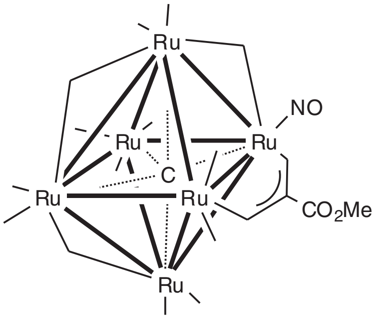

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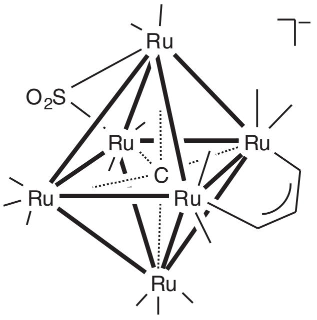
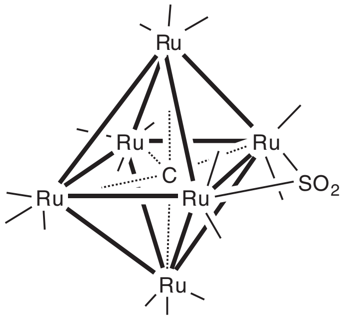


208

Gaseous SO_2 reacts with $Ru_6(\mu_6\text{-}C)(CO)_{17}$ at room temperature by substitution of one CO ligand to give $Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)(CO)_{16}$ **209**; the reaction is readily reversible, converting into the starting cluster almost quantitatively on standing under a CO atmosphere. The dianionic cluster $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ reacts with SO_2/Me_3NO to give the substitution product $[Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)(\mu\text{-}CO)_2(CO)_{13}]^{2-}$ **210**, which reacts further to give the bis-substitution product $[Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)_2(\mu\text{-}CO)_2(CO)_{12}]^{2-}$ **211**. Attempts to introduce a third SO_2 ligand were unsuccessful. Complex **210** reacts with gaseous NO to give $[Ru_6(\mu_6\text{-}C)(\mu\text{-}SO_2)(\mu\text{-}CO)(CO)_{13}(NO)]^-$ **212**, bearing both SO_2 and NO ligands. The alternative route to this cluster, reaction of the nitrosyl complex $[Ru_6(\mu_6\text{-}C)(CO)_{15}(NO)]^-$ with SO_2/Me_3NO, was unsuccessful. Methylation of **210** with $MeOSO_2CF_3$ results in S–O bond cleavage to give $[Ru_6(\mu_6\text{-}C)$-$(\mu\text{-}SO_2Me)(\mu\text{-}CO)_2(CO)_{13}]^-$ **213**, which reacts further to give the moisture sensitive $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}SO)(CO)_{15}$ **214**, containing a face-capping SO ligand.[184]



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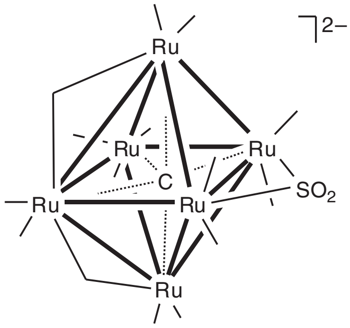

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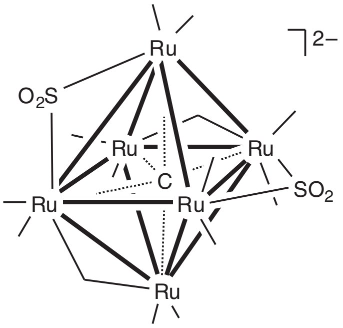

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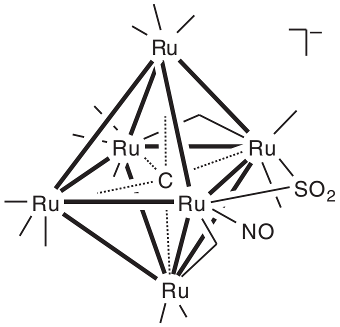

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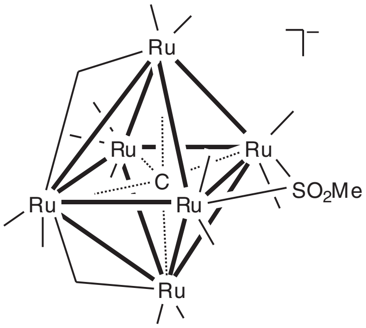

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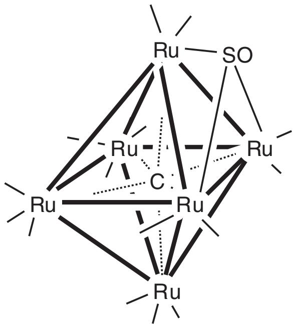
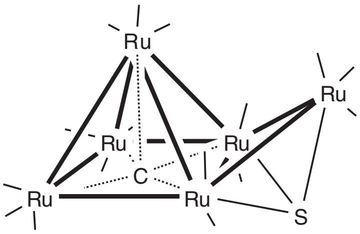


214

$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}S)(CO)_{16}$ **215** is formed in good yield from **214** under 1 atm of CO at 70 °C, reduction of the SO ligand being accompanied by addition of CO and cleavage of two Ru–Ru bonds. Reaction of **214** with 10 atm H_2 and 1.5 equiv. of CO yields interconvertible $Ru_6(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu_3\text{-}S)(CO)_{16}$ **216** and $Ru_6(\mu\text{-}H)_4(\mu_5\text{-}C)(\mu_3\text{-}S)(CO)_{16}$ **217** (15 atm H_2, 2 weeks, **216** → **217**; Ar, 4 days, **217** → **216**). Attempts to reduce the SO_2 ligands of the related clusters **209** and **211** were unsuccessful.[185]



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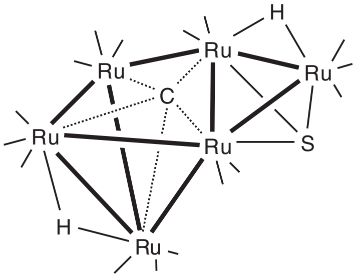

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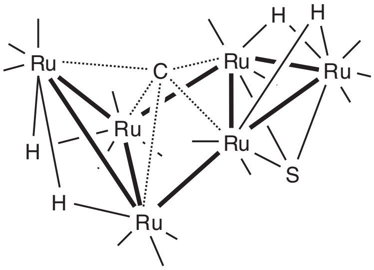
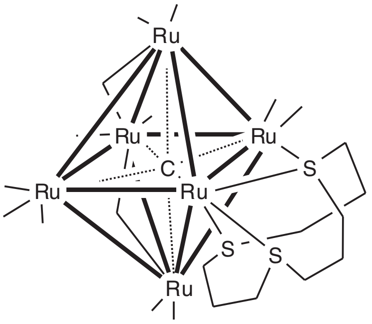


217

The series of octahedral hexaruthenium complexes **218–220** containing polythiaether macrocyclic ligands has been prepared from $Ru_6(\mu_6\text{-}C)(CO)_{17}$. $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^3\text{-}[12]aneS_3)(\mu\text{-}CO)_2(CO)_{11}$ **218** contains a trithiacycle where the three sulfur atoms are coordinated across an Ru–Ru bond. The tetrathiacyclic ligand in $Ru_6(\mu_6\text{-}C)(\mu\text{-}\eta^2\text{-}[16]aneS_4)(\mu\text{-}CO)(CO)_{14}$ **219** is also bridging an Ru–Ru bond, in this case leaving two uncoordinated sulfur atoms. In contrast, the smaller trithiacyclic ligand in $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta^3\text{-}[9]aneS_3)$ **220** chelates a single ruthenium atom. Thermolysis of **220** or reaction of **218** with [9]aneS_3 affords $Ru_6(\mu_5\text{-}C)(\mu_3\text{-}\eta^3\text{-}SCH_2CH_2SCH_2CH_2S)(CO)_{14}$ **221**, containing a thiolato ligand formed by elimination of ethene and coordinated to four of the ruthenium atoms. The loss of ethene from **220** is more facile than loss of CO, which would give a product analogous to **218**.[186]

$Ru_6(\mu_6\text{-}C)(CO)_{17}$ also reacts with a mixture of *cis*- and *trans*-3,7,11-trimethyl-1,5,9-trithiacyclododecane to give $Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^3\text{-}cis\text{-}SCH_2CHMe(CH_2SCH_2CHMe)_2CH_2\}(\mu\text{-}CO)_2(CO)_{11}$ 222 and two isomers of $Ru_6(\mu_6\text{-}C)\{\mu\text{-}\eta^3\text{-}trans\text{-}SCH_2CHMe(CH_2SCH_2CHMe)_2CH_2\}(\mu\text{-}CO)_2(CO)_{11}$.[187]



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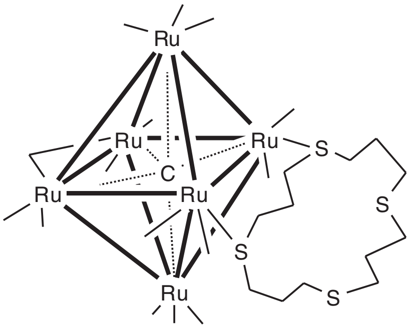

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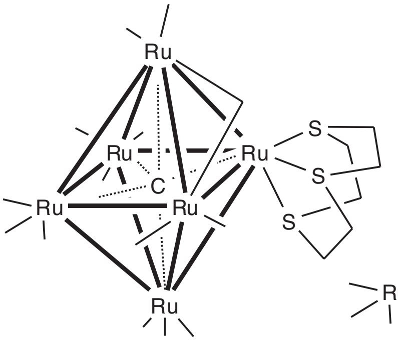

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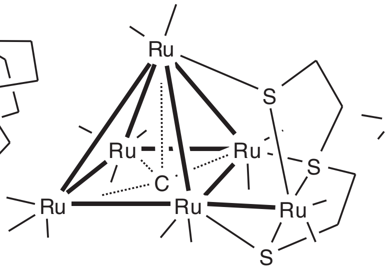

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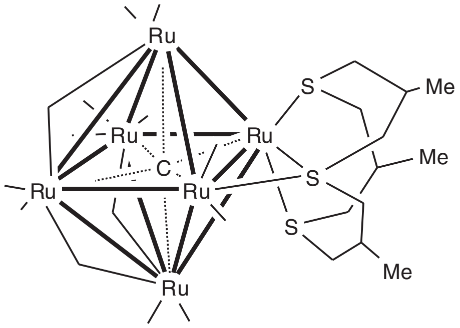

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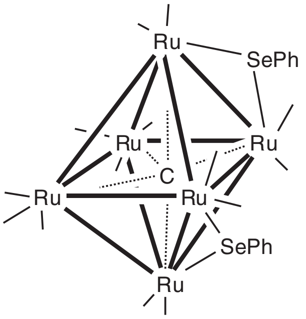
The selenyl cluster $[Ru_6(\mu_6\text{-}C)(SePh)(CO)_{15}]^-$ is obtained from treating $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ with phenylselenyl chloride, thermolysis affording $Ru_6(\mu_6\text{-}C)(\mu\text{-}SePh)_2(CO)_{14}$ 223, and reaction with allyl bromide giving $Ru_6(\mu_6\text{-}C)(\mu\text{-}SePh)(\mu\text{-}\eta^3\text{-}C_3H_5)(CO)_{14}$ 224.[188]



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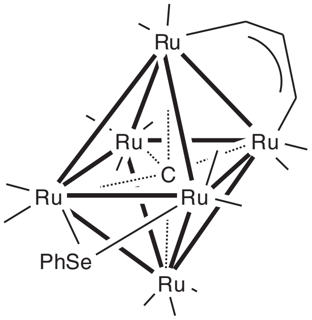
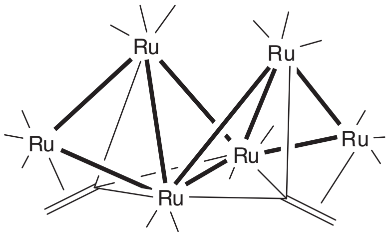


224

6.24.3.3 Clusters Containing Hydrocarbon Ligands

Thermolysis of $Ru_3(\mu_3\text{-}\eta^2\text{-}HC_2H)(\mu\text{-}CO)(CO)_9$ in hexane gives a number of complexes ranging in nuclearity from 3 to 6, including small amounts of pentanuclear clusters 52 and 53, and hexanuclear complexes $Ru_6(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}CCH_2)_2(CO)_{16}$ 225 and $Ru_6(\mu\text{-}H)(\mu_4\text{-}C)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C_2Me)(\mu\text{-}CO)(CO)_{16}$ 226. The metal framework of 225 consists of a "ladder" configuration made up of two edge-sharing butterflies, each containing a μ_4-CCH ligand; the shared Ru–Ru bond is unusually short. The hydrido cluster **226** contains a butterfly metal core with an Ru_2 unit fused to a hinge atom; the μ_4-carbide and methylethynyl ligands are formed by a disproportionation of the two ethyne molecules.[57,58] Thermolysis of $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}C_2SiMe_3)(\mu\text{-dppm})(CO)_7$ in the presence of KF gives $Ru_6(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}CCH_2)_2(\mu\text{-dppm})_2(CO)_{12}$ **227** in 80% yield, containing a μ_4-CCH_2 vinylidene ligand in each of the butterfly clefts of the raft metal geometry. The complex is closely related to **225**, the dppm ligand resulting in slightly longer metal–metal bond lengths in **227**.[189] Thermolysis of $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)(\mu\text{-CO})(CO)_9$ results in dimerization of the cluster to give $Ru_6(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^2\text{-}PhCHC_3C_6H_4)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhCHC_3C_6H_4)(CO)_{15}$ **228**. The organic ligands are formed by attack of an alkynyl carbon at one of the phenyl groups, with migration of an H atom from the aromatic ring to the C_4 chain.[190]



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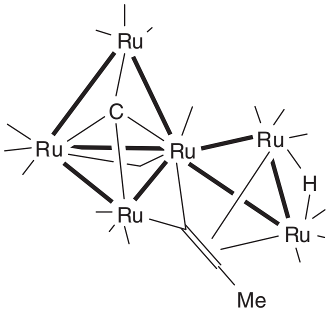

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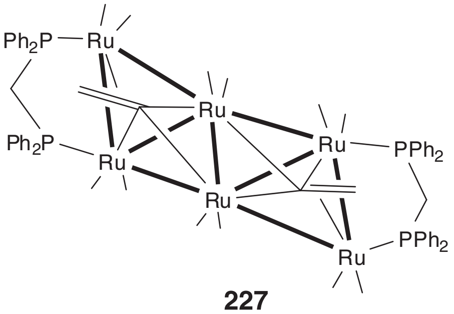

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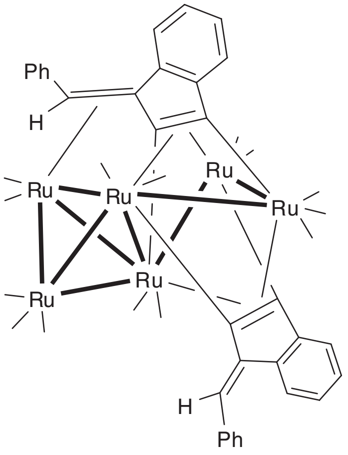

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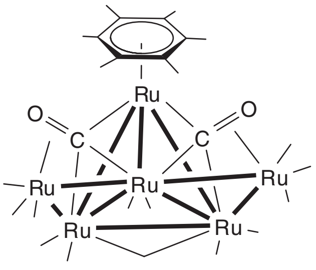
Thermolysis of $Ru_3(CO)_{12}$ with hexamethylbenzene affords $Ru_6(\mu_4\text{-}\eta^2\text{-CO})_2(\mu\text{-CO})(CO)_{12}(\eta^6\text{-}C_6Me_6)$ **229**.[191] The reactions between $Ru_3(CO)_{12}$ and cyclohexene or cycloocta-1,3-diene are characterized by formation of products involving ring contraction. Reaction with cyclohexene gives $Ru_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\mu\text{-CO})(CO)_{12}(\eta^5\text{-}C_5H_4Me)$ (**230**, $R_5 = H_4Me$) among a number of products. The triply-bridging hydride ligand lies beneath the basal plane of the central tetrahedron of ruthenium atoms. Similar thermolysis with cycloocta-1,3-diene gives $Ru_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2\text{-}(\mu\text{-CO})(CO)_{12}(\eta^5\text{-}C_5H_3C_3H_6)$ **231**. Complexes **229–231** have the same double-bridged tetrahedral structure and two μ_4-bridging carbonyl ligands as the mesitylene complex $Ru_6(\mu_4\text{-}\eta^2\text{-CO})_2(\mu\text{-CO})(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$ but, unlike the mesitylene complex, attempts to form the corresponding hexaruthenium carbido–arene complexes were unsuccessful, probably due to steric reasons. The mechanism for the ring transformations is uncertain, although it is likely that the process involves an initial contraction of the cluster-bound ligand, followed by dehydrogenation.[192,193] Analogous complexes $Ru_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\mu\text{-CO})(CO)_{12}(\eta^5\text{-}C_5R_5)$ [**230**, $R_5 = H_5$, Me_5, $H_4(SiMe_3)$] are prepared using nickelocene, Cp^*H, or $C_5H_5(SiMe_3)$ as the C_5 reagent.[194,195]



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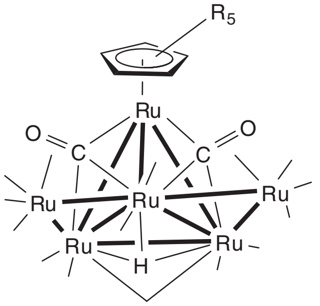
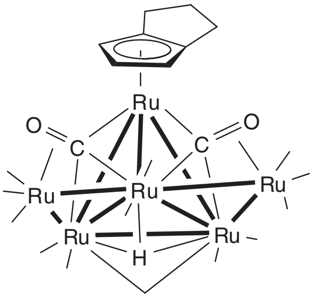


$R_5 = H_4Me, Me_5, H_5, H_4(SiMe_3)$

230



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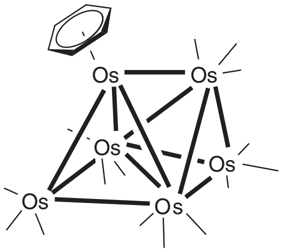
The dicationic (arene)osmium-capping fragments $[Os(NCMe)_3(\eta^6\text{-}C_6H_6)]^{2+}$ and $[Os(CF_3SO_3)_2(\eta^6\text{-}C_6H_5Me)]^{2+}$ are precursors for hexaosmium clusters containing both terminal and face-capping arene ligands, the monoarene complexes $Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)$ 232 and $Os_6(\mu\text{-}CO)(CO)_{14}(\eta^6\text{-}C_6H_5Me)$ 233 being derived from $[Os_5(CO)_{15}]^{2-}$ and containing bicapped tetrahedral metal cores.[196] Bis-arene clusters are prepared in a similar manner. $Os_6(\mu\text{-}H)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(CO)_{11}(\eta^6\text{-}C_6H_6)$ 234 is formed from $Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)$, and contains benzene ligands in the two different coordination modes. The bis-terminal cluster $Os_6(\mu\text{-}CO)(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ 235, formed from $[Os_4H_2(CO)_{12}]^{2-}$ via the pentanuclear intermediate $Os_5H_2(CO)_{12}(\eta^6\text{-}C_6H_6)$, has the same metal core geometry.[197,198]



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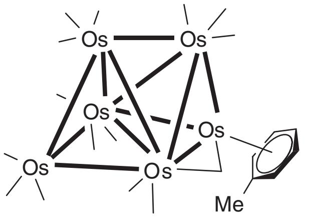

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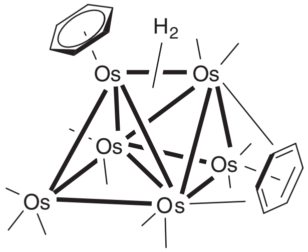

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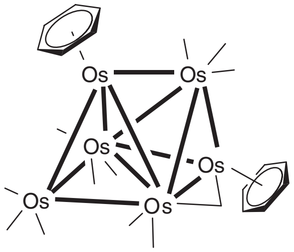
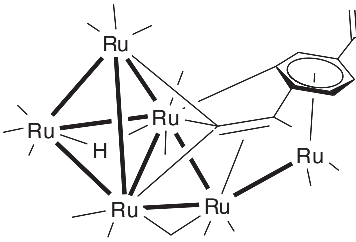


235

1,4-Diisopropenylbenzene reacts with $Ru_3(CO)_{12}$ to give a range of products, including hexanuclear clusters $Ru_6(\mu\text{-}H)(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6\text{-}C_{12}H_{11})(\mu\text{-}CO)(CO)_{14}$ 236 and $Ru_6(\mu\text{-}H)(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6\text{-}C_{12}H_{13})(\mu\text{-}CO)(CO)_{14}$ isolated as a mixture in 3% yield, and the spectroscopically characterized carbido cluster $Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{11}H_{10})(CO)_{15}$. A crystallographic study suggests a random distribution of the two hydrido complexes in the crystal in approximately equal proportions; the former 236 contains an isopropenyl group, which has been hydrogenated in the latter. The structure of the carbido complex is based on that of a related tetranuclear cluster $Ru_4(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{12}H_{14})(CO)_{10}$, which has been shown to be a precursor to the carbido cluster.[199] $Ru_3(CO)_{12}$ reacts with 9-ethynylfluoren-9-ol to give 56 and $Ru_6(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^3{:}\eta^6\text{-}C_{13}H_7CHC)(CO)_{15}$ 237, along with a number of lower-nuclearity complexes. The hexanuclear cluster has the same metal core as 236, with the organic fragment similarly interacting with five of the ruthenium atoms.[62]



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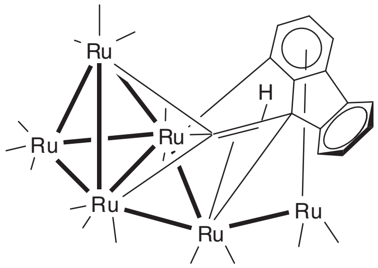


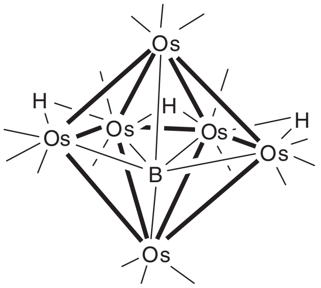
237

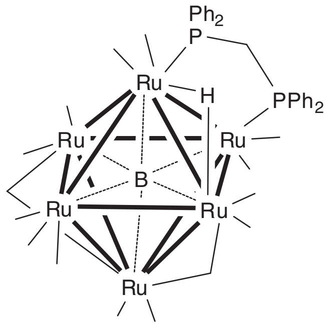
6.24.3.4 Clusters Containing Heteroatom Ligands

6.24.3.4.1 Boron-containing clusters

Reaction of $[Ru_3(\mu_3\text{-}\eta^2\text{-}B_2H_5)(CO)_9]^-$ with the activated clusters $Ru_3(CO)_{12-n}(NCMe)_n$ ($n = 2, 3$) affords a mixture of products, including both octahedral $[Ru_6(\mu_6\text{-}B)(CO)_{17}]^-$ (10%) and trigonal-prismatic $[Ru_6(\mu\text{-}H)_2(\mu_6\text{-}B)(CO)_{18}]^-$ (20%).[200,201] Reaction of the tris-acetonitrile cluster $Ru_3(CO)_9(NCMe)_3$ with BH_3 is an improved route to $Ru_6(\mu\text{-}H)(\mu_6\text{-}B)(CO)_{16}$ (60% yield). Treatment of $Ru_6(\mu\text{-}H)_2(CO)_{17}$ with BH_3SMe_2 affords $Ru_6(\mu\text{-}H)(\mu_6\text{-}B)(CO)_{17}$ (21%), which can be carbonylated to give spectroscopically characterized $HRu_5(\mu_5\text{-}B)(CO)_{15}$ and $HRu_5(\mu_5\text{-}B)(CO)_{16}$.[114]

Thermolysis of $H_3Os_3(CO)_9(BCO)$ in toluene affords $Os_6(\mu\text{-}H)_3(\mu_6\text{-}B)(CO)_{16}$ **238**; the 86 c.v.e. cluster adopts a geometry based on a pentagonal bipyramid with a vertex removed and containing an interstitial boride, a novel geometry for 86 c.v.e. hexaosmium clusters, but duplicating that observed for the 84 c.v.e. $Os_6(CO)_{18}$, with an additional interstitial boron.[202] Up to four CO groups in $[Ru_6(\mu_6\text{-}B)(CO)_{17}]^-$ can be replaced by $P(OMe)_3$ ligands, although the reaction stops at monosubstitution with PPh_3. Acidification (CF_3CO_2H) of the latter gives the expected hydrido cluster, but the corresponding reaction of the mono-$P(OMe)_3$ anion affords $Ru_6(\mu_6\text{-}B)\{\mu\text{-}P(OMe)_2\}(CO)_{16}$.[203] $[Ru_6(\mu_6\text{-}B)(CO)_{17}]^-$ reacts with dppm, subsequent protonation giving $Ru_6(\mu\text{-}H)(\mu_6\text{-}B)(\mu\text{-}CO)_2(\mu\text{-}dppm)(CO)_{13}$ **239**.[204]



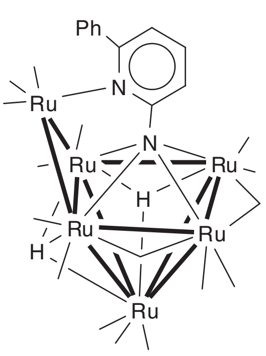


(hydride ligands not located in structural study)

238 **239**

6.24.3.4.2 *N*-ligands

Cabeza and co-workers have developed hexaruthenium cluster chemistry with aminopyridine ligands. $Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}apyPh\text{-}N,N)(\mu\text{-}CO)_2(CO)_{14}$ **240** and $Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\eta^3\text{-}apyC_6H_4\text{-}N,N,C)(\mu\text{-}CO)_3(CO)_{13}$ **241** are isolated from a number of products in the reaction between $Ru_3(CO)_{12}$ and 2-amino-6-phenylpyridine (H_2apyPh). Both complexes consist of an edge-bridged square-pyramidal metal core, the apyPh ligand being cyclometallated in **241**. Complex **240** is also formed by reaction of the co-product $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_9$ with $Ru_3(CO)_{12}$ or in small yields from the hydrogenation of **241**. Thermolysis of **240** gives only a small amount of **241** among other unidentified products.[205] Similar reactions using 2-aminopyridine (H_2apy) or 2-amino-6-methyl-pyridine, where the 2,6-substitution of the aryl ring prevents the formation of orthometallated cluster products, afford a high yield route into these clusters, with $Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}ampy\text{-}N,N)(\mu\text{-}CO)_2(CO)_{14}$ (**242**, $L = CO$) and $Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}apy\text{-}N,N)(\mu\text{-}CO)_2(CO)_{14}$ produced in 77% yields. Carbonyl substitution on **242** with PPh_3 gives a mixture of two isomers of $Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy-}N,N)(\mu\text{-}CO)_2(CO)_{13}(PPh_3)$, one being **242** ($L = PPh_3$) where the phosphine ligand is *cis*- to the pyridine N atom on the bridging ruthenium atom. Heating the isomeric mixture or treating **242** ($L = CO$) with 1 equiv. of PPh_3 results in the formation of **243**, where the phosphine ligand is transferred to the apical ruthenium atom. The di- and trisubstituted products, $Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy-}N,N)(\mu\text{-}CO)_2(CO)_{12}(PPh_3)_2$ (**244**, $L = CO$) and $Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy-}N,N)(\mu\text{-}CO)_2(CO)_{11}(PPh_3)_3$ (**244**, $L = PPh_3$), can also be prepared.[206,207]



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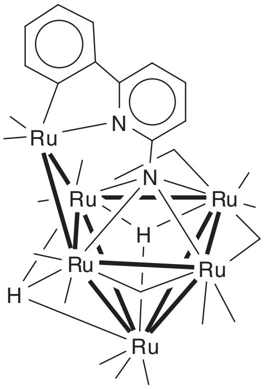

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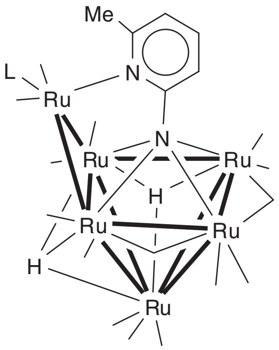
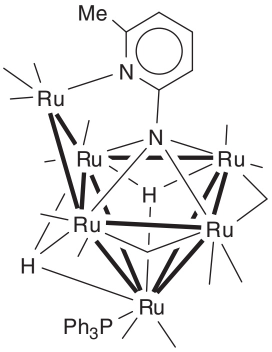


L = CO, PPh3

242



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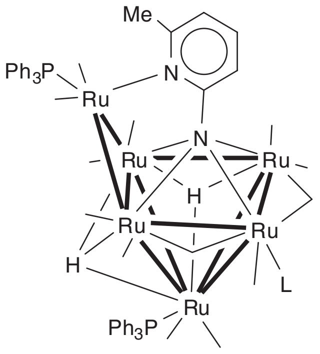
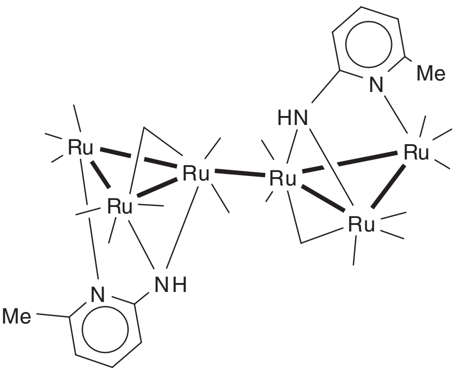


L = CO, PPh3

244

Cluster condensation of the cationic trinuclear complex $[Ru_3(\mu_3\text{-}\eta^2\text{-ampy-}N,N)(CO)_{10}]^+$ on reaction with OH^-[208] or $[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-}$[209] affords $Ru_6(\mu_3\text{-}\eta^2\text{-ampy-}N,N)_2(\mu\text{-}CO)_2(CO)_{16}$ **245** and $Ru_6(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-ampy-}N,N)\text{-}(\mu\text{-}CO)_2(CO)_{15}$ **246**, respectively. The 94 c.v.e dimeric cluster **245** is also prepared by reduction of the cationic precursor with zinc dust, and by reaction with $[Ru_3(\mu_3\text{-ampy})(CO)_9]^-$.



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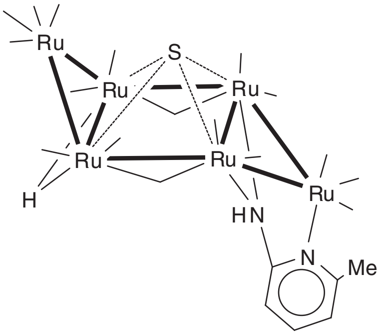

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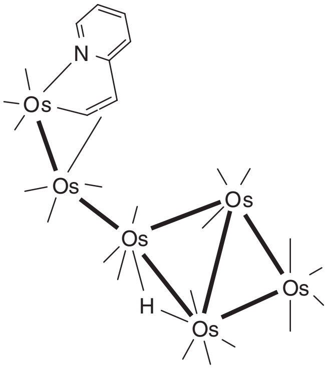
Reaction of $H_2Os_3(\mu_3\text{-}CNC_5H_4\text{-}2\text{-}CH{=}CH_2)(CO)_9$ and $Os_3(CO)_{10}(NCMe)_2$ affords $Os_6(\mu\text{-}H)(\mu\text{-}\eta^3\text{-}NC_5H_4CH{=}CH)(CO)_{20}$ **247**, which consists of an almost-planar Os_4 butterfly with an Os_2 spike.[210] Treating $Os_6(CO)_{16}(NCMe)_2$ with an equimolar amount of pyridine affords the series $Os_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{15}(NC_5H_5)_3$ **248**, $Os_6(\mu\text{-}H)(\mu_3\text{-}O)(\mu\text{-}\eta^2\text{-}NC_5H_4)(\mu\text{-}CO)(CO)_{15}(NC_5H_5)$ **249**, and $Os_6(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(\mu\text{-}CO)(CO)_{14}(NC_5H_5)(NCMe)$ **250**. Complex **248** contains a $\mu_4\text{-}\eta^2$-CO ligand, while in **249** the oxygen atom is μ_3-coordinated in a T-shaped coordination mode.[211] Similarly, reacting $Os_6(CO)_{16}(NCMe)_2$ with di-2-pyridyl disulfide affords the pyridine-2-thione raft clusters $Os_6(\mu_3\text{-}\eta^2\text{-}2\text{-}NC_5H_4S)_2(CO)_{16}$ **251** and $Os_6(\mu_4\text{-}\eta^2\text{-}2\text{-}NC_5H_4S)(CO)_{17}$ **252**, the latter with a puckered raft geometry resulting from an osmium atom folding up to coordinate to the organic unit.[212]



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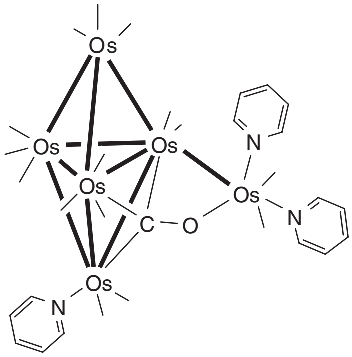

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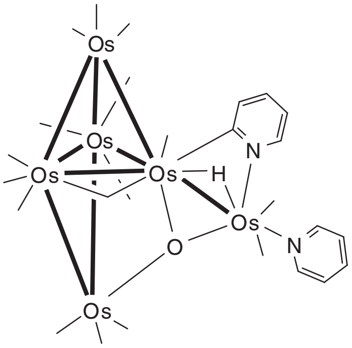

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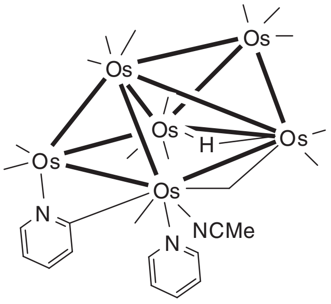

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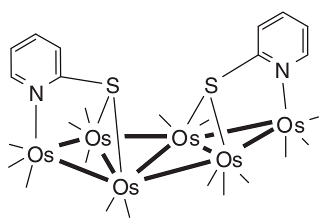

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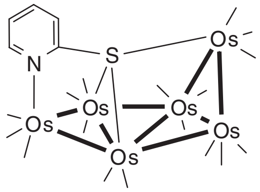

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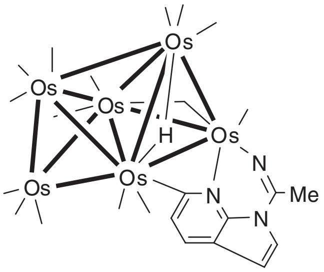
Reaction of $Os_6(CO)_{16}(NCR)_2$ (R = Me, Et) with 7-azaindole affords $Os_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_8H_5N_3R)(CO)_{14}$ (R = Me **253**, Et) with a bicapped tetrahedral metal core containing a metallaheterocyclic organic unit formed from the coupling of the coordinated acetonitrile ligand with the incoming azaindole. Complex **253** (R = Me) forms the spectroscopically characterized anionic cluster $[Os_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_8H_4N_3Me)(CO)_{14}]^-$ reversibly on treatment with acid/base.[213] A series of clusters with Os_2 or Os_3 spikes is formed in low yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with the triazene $C_6F_5N{=}NNHC_6F_5$. The initially formed isomers of $Os_6(\mu\text{-}H)(\eta^2\text{-}C_6F_5NNNC_6F_5)(CO)_{20}(NCMe)_2$ are unstable, and slowly form $Os_6(\mu\text{-}H)(\eta^2\text{-}C_6F_5NNNC_6F_5)(\mu\text{-}CO)(CO)_{19}$ **254** via loss of NCMe and Os–Os bond formation. The spectroscopically characterized isomers are thought to have a triangular metal core with an Os_3 spike located on an equatorial position either *cis* or *trans* to the bridging hydride, whereas **254** has a tetrahedral metal core and an Os_2 spike; in each case, the terminal spike-metal atom bears the chelating organic unit.[214]



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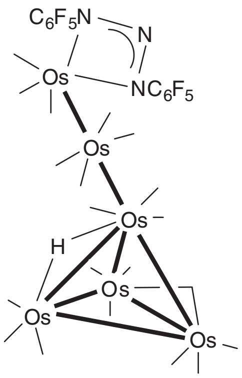
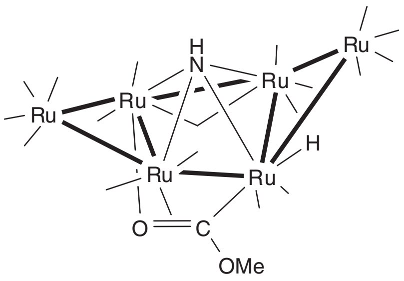


254

Hexaruthenium nitrene clusters are prepared from triruthenium nitrosyl precursors. Methylation of $[Ru_3(\mu\text{-NO})(CO)_{10}]^-$ with CF_3SO_3Me affords trace amounts of $Ru_6(\mu\text{-H})(\mu_4\text{-NH})\{\mu_3\text{-}\eta^2\text{-C(O)OMe}\}(\mu\text{-CO})(CO)_{16}$ **255**, containing a μ_3-η^2-methoxycarbonyl group. Hydrogenation of the major product, $Ru_3(\mu_3\text{-CO})(\mu_3\text{-NOMe})(CO)_9$, in the presence of $Ru_3(CO)_{12}$, yields the bi-edge-bridged square cluster $Ru_6(\mu\text{-H})(\mu_4\text{-NH})(\mu\text{-OMe})(\mu\text{-CO})_2(CO)_{16}$ (**256**, R = H), and pentanuclear $Ru_5(\mu\text{-H})_3(\mu_4\text{-NH})(\mu_3\text{-OMe})(CO)_{13}$ **257**, related to **256** by loss of a bridging ruthenium atom. Thermolysis of $Ru_3(\mu_3\text{-CO})(\mu_3\text{-NOMe})(CO)_9$ at 90 °C gives the dimethoxy complex $Ru_6(\mu_4\text{-NH})(\mu\text{-OMe})_2(\mu\text{-CO})_2(CO)_{16}$ (**256**, R = OMe) in low yield, whereas heating in refluxing *n*-octane gives $Ru_6(\mu_5\text{-N})(\mu_3\text{-NH})(\mu_3\text{-OMe})\{\mu_3\text{-}\eta^2\text{-C(O)OMe}\}_2(\mu\text{-CO})(CO)_{13}$ **258**, containing an edge-bridged square metal core with a sixth ruthenium atom attached via the coordinating ligands, and containing both nitrene and nitrido ligands. Pyrolysis of the related hydrido cluster $Ru_3(\mu\text{-H})_2(\mu_3\text{-NOMe})(CO)_9$ affords $Ru_6(\mu_4\text{-NH})\{\mu_3\text{-}\eta^2\text{-N(H)C(O)OMe}\}(\mu\text{-OMe})(\mu\text{-CO})_2(CO)_{15}$ **259**, $Ru_6(\mu\text{-H})_2\{\mu_5\text{-}\eta^2\text{-NC(O)OMe}\}(\mu\text{-CO})_2(CO)_{14}$ **260**, and $Ru_6(\mu_4\text{-NH})(\mu\text{-OMe})(\mu\text{-NCO})(\mu\text{-CO})_2(CO)_{16}$ (**256**, R = NCO).[215–217] Thermolysis of the nitrene complex $Ru_3(\mu_3\text{-NOMe})(\mu_3\text{-}\eta^2\text{-PhC}_2\text{Ph})(CO)_9$ in *n*-octane leads to cluster condensation to give pentanuclear **72**, and the hexanuclear complex $Ru_6(\mu\text{-H})(\mu_5\text{-N})(\mu_3\text{-}\eta^2\text{-PhC}_2\text{Ph})_2(CO)_{13}$ **261** in 6% yield. The metal framework consists of a bridged, wingtip-bridged butterfly structure with the nitrido atom semi-encapsulated within the bridged-butterfly metal unit, rather than the square-pyramidal-based cores usually seen in complexes with interstitial nitrogen atoms.[72]



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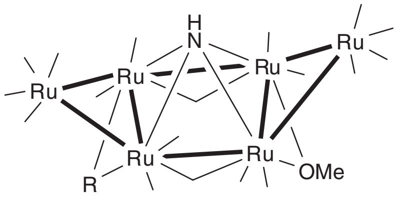
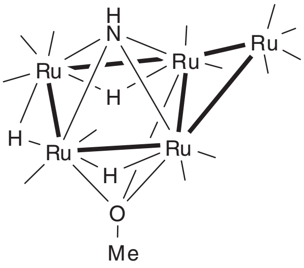


R = H, OMe, NCO

256



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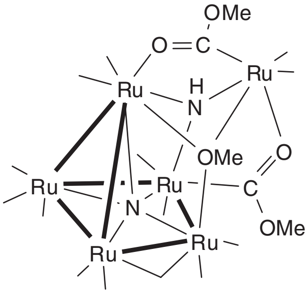

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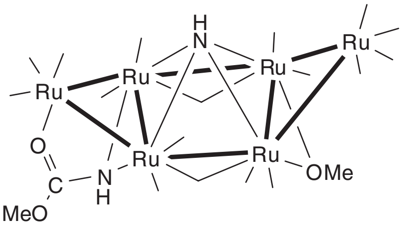

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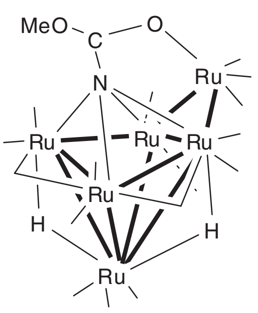

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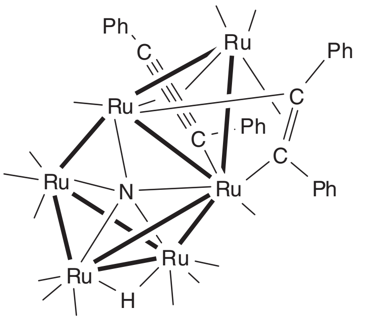

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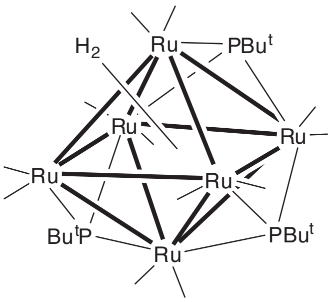
6.24.3.4.3 *P*-ligands

The octahedral phosphinidine complex $H_2Ru_6(\mu_3\text{-PBu}^t)_3(CO)_{12}$ **262** is prepared in 7% yield from $Ru_4(\mu\text{-H})_4(CO)_{12}$ and the cyclic phosphine $P_4Bu^t{}_4$, a space-filling model of the complex suggesting that the hydrides are located in bridging and interstitial positions.[77] The same phosphine reacts with $Ru_3(CO)_{12}$ to give the capped square-pyramidal cluster $Ru_6(\mu_4\text{-PBu}^t)(\mu_3\text{-PBu}^t)_3(CO)_{11}$ **263**, as well as higher-nuclearity clusters **298** and **311**.[218] $Ru_3(CO)_{12}$ also reacts with (1-naphthyl)diphenylphosphine to give the spectroscopically characterized pentanuclear $Ru_5(PPh)(C_{10}H_5PPh_2)(CO)_{12}$ and the 88 c.v.e. hexanuclear cluster $Ru_6(\mu_6\text{-}C_{10}H_6)(\mu_3\text{-PPh})(CO)_{14}$ **264** in 8% yield, among a number of products. The puckered raft cluster contains an eight-electron donor naphthalene unit, formed by P–C bond cleavage, interacting with each of the six ruthenium atoms.[219]



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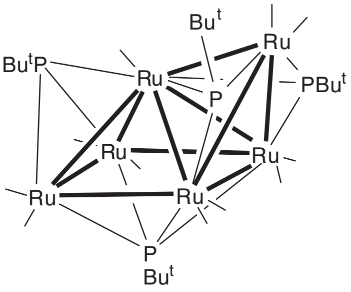

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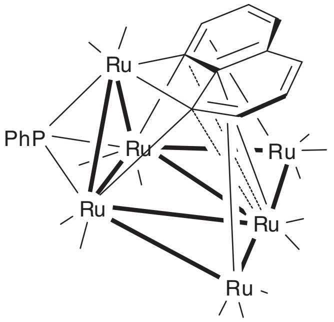
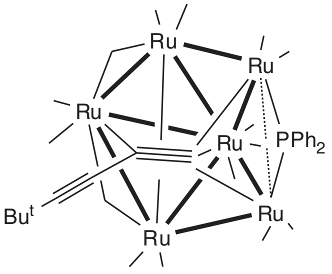


264

$Ru_6(\mu_6\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_2C{\equiv}CR)(\mu\text{-PPh}_2)(\mu\text{-CO})_2(CO)_{13}$ ($R = Bu^t$ **265**, Ph), with an unusual pentagonal-pyramidal metal core, is formed in low yield from the thermolysis of $Ru_3(CO)_{11}(Ph_2PC{\equiv}CC{\equiv}CR)$.[110,220] Thermolysis of the linked dicluster complex $\{Ru_3(\mu\text{–H})(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_8\}_2(\mu\text{-dppa})$ affords two hexaruthenium products, $Ru_6(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-}Bu^tCH{=}CHC_2PPh_2)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Bu^t)(\mu\text{-PPh}_2)(CO)_{13}$ **266**, with a ladder arrangement of metal atoms, and $Ru_6(\mu_6\text{-}C_2CH{=}CHBu^t)(\mu_3\text{-}C_2Bu^t)(\mu\text{-PPh}_2)_2(\mu\text{-CO})(CO)_{12}$ **267**, with a $C_2CH{=}CHBu^t$ "alkylidene–carbide" ligand coordinated in a similar manner to the $C_2C{\equiv}CBu^t$ ligand in complex **265**.[221]



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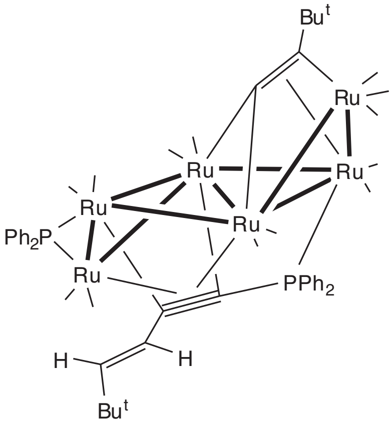

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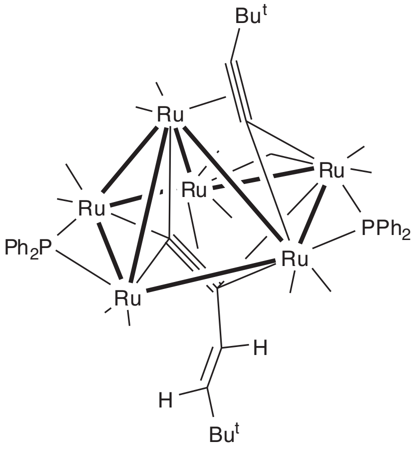
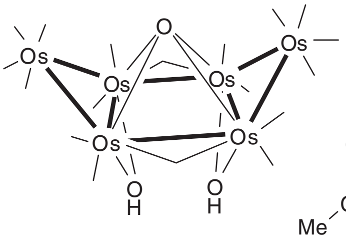


267

6.24.3.4.4 *O*-ligands

The reaction between $Os_3(CO)_{11}(NCMe)$ and molecular oxygen yields the hexametallic oxo cluster $Os_6(\mu_4\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}CO)_2(CO)_{16}$ **268** in 55% yield. The 94 c.v.e. cluster contains two electrons more than expected for a bi-bridged square metal geometry. The extra electrons are thought to occupy antibonding orbitals associated with the bridging OH ligands, resulting in slightly longer bonds between the osmium atoms bearing these ligands. Vacuum pyrolysis of **268** affords the high-nuclearity osmium cluster **329**.[222]

A series of clusters containing between four and seven metal atoms (see **58**, **59** and **299**) is obtained from reaction between $Ru_3(CO)_{12}$ and but-3-yn-2-ol in refluxing cyclohexane. The hexanuclear product $Ru_6\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CCHC(O)Me\}_2(CO)_{16}$ **269** is obtained in 15% yield, and contains an unusual fused square metal framework. The cluster has two electons fewer than the 94 c.v.e. expected, suggesting some double bond character associated with the significantly short central Ru–Ru bond [2.656(2) Å]. The organic fragments are formed via dehydrative condensation and are coordinated on opposite faces of each metal square, forming metallacycloketonic rings similar to the organic ligands in the related pentanuclear clusters **58** and **59**.[64] The dihydrido cluster $Ru_6(\mu_3\text{-}H)_2(\mu_4\text{-}\eta^2\text{-}L)_2(CO)_{14}$ [**270**, HL = (4*S*,5*S*)-(−)-2-methyl-5-phenyl-2-oxazoline-4-methanol] is formed in low yield from $Ru_3(CO)_{12}$ and HL, and contains two ruthenium triangles held together by the four capping ligands and weak Ru–Ru bonds (av. 3.061 Å), resulting in a cluster core comprising edge-sharing butterflies.[223] 4-Methoxyphenol reacts with $Ru_3(CO)_{12}$ to give the spectroscopically characterized hexaruthenium raft cluster $Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu_5\text{-}\eta^7\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}$, along with two tetranuclear products. A similar reaction with 2-naphthol affords the related $Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu_5\text{-}\eta^7\text{-}OC_{10}H_6)(CO)_{16}$.[224]



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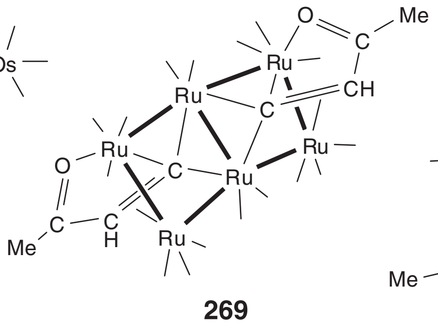

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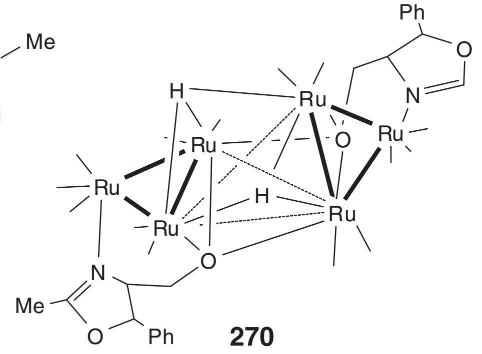

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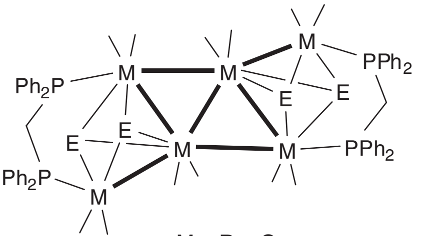
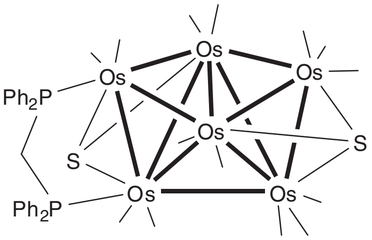
6.24.3.4.5 *S*- and *Se*-ligands

Thermolysis of Ru$_3$(μ_3-Se)$_2$(μ-dppm)(CO)$_7$ results in cluster condensation to give Ru$_6$(μ_3-E)$_4$(μ-dppm)$_2$(CO)$_{12}$ (271, M = Ru, E = Se), with a doubly-spiked butterfly core. The cluster is electron-rich (96 c.v.e.), the extra electron density probably associated with the antibonding MOs of the central Ru$_4$ core, which has significantly longer butterfly hinge-wingtip Ru–Ru bond distances compared to the other Ru–Ru bonds.[225] Similar reactions with Os$_3$(μ_3-E)$_2$(μ-dppm)(CO)$_7$ (E = S, Se) afford the spectroscopically characterized analog Os$_6$(μ_3-S)$_4$(μ-dppm)$_2$(CO)$_{12}$ and 271 (R = Os, E = Se); treatment of the latter with CO regenerates the starting cluster. The reaction between Os$_3$(μ_3-S)(μ-dppm)(CO)$_7$ and Os$_3$(CO)$_{10}$(NCMe)$_2$ gives Os$_6$(μ_3-S)$_2$(μ-dppm)(CO)$_{14}$ 272, containing a bicapped tetrahedral metal core. The cluster is also electron-rich (88 c.v.e.), the extra electron density probably residing in the central Os$_4$ core.[226,227] Treatment of Os$_6$(CO)$_{18}$ with equimolar sodium borohydride, followed by addition of PhSeCl to the resulting [HOs$_6$(CO)$_{18}$]$^-$, affords the neutral Os$_6$(μ-H)(μ-SeH)(CO)$_{18}$ 273, a spiked trigonal-bipyramidal cluster with a bridging SeH ligand presumably derived by loss of benzene in the presence of the excess NaBH$_4$.[87]



M = Ru, Os
E = S, Se

271



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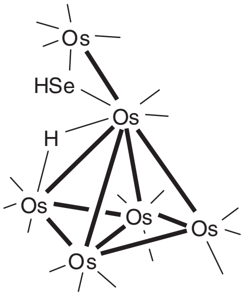
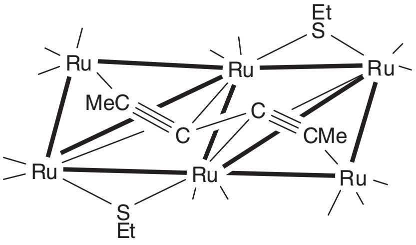


273

The raft cluster Ru$_6$(μ_6-CMeCCCMe)(μ-SEt)$_2$(CO)$_{14}$ 274 is formed in trace amounts in the reaction between Ru$_3$(CO)$_{12}$ and MeC≡CSEt, where two acetylide fragments have combined to form a hexa-2,4-diyne. Interestingly, the coupling of the acetylide units is the opposite to that observed in the related complex 83, that is, C(R)CCC(R) for 274 and C(R)CC(R)C for 83.[85]

Ru$_3$(CO)$_{12}$ reacts with 4-*t*-butyl-4-methyl-1-(phenylthio)cyclobutene to give Ru$_6$(μ_4-S){μ_4-CCHCH=C(Me)Bu^t}-(CO)$_{16}$ 275 in trace amounts. The bridged square-pyramidal cluster contains the sulfido ligand capping the square face and a μ_4-substituted vinylidene ligand.[228]



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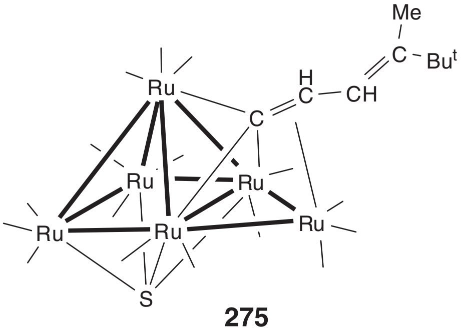
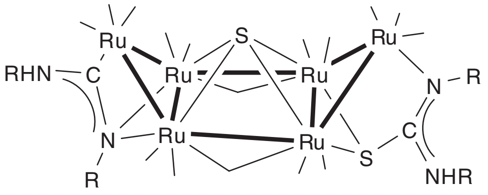


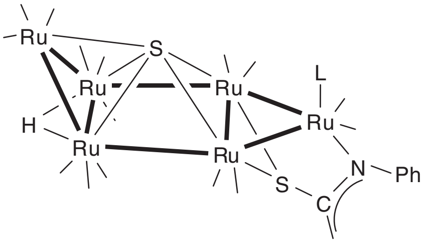
275

Heating Ru$_3$(CO)$_{12}$ with the thioureas SC(NHR)$_2$ (R = Et, Ph) results in cluster condensation to give bi-edge-bridged square clusters Ru$_6$(μ_4-S){μ_3-η^2-SC(NHR)N(R)}{μ_3-η^2-C(NHR)N(R)}(μ-CO)$_2$(CO)$_{14}$ (276, R = Et) and Ru$_6$(μ-H)(μ_5-S){μ_3-η^2-SC(NHPh)N(Ph)}(CO)$_{16}$ (277, L = CO), respectively. Complex 276 consists of a boat configuration of metal atoms and is electron-rich, with compensating elongated Ru–Ru bonds in the Ru$_4$ square core. Complex 277 also contains elongated bonds in the basal square, and an unusual μ_5-bound sulfur atom.[229] Thermolysis of Ru$_3$(μ-H){μ_3-η^2-SC(NHPh)N(Ph)}(CO)$_9$ in cyclohexane also affords complexes 276 (R = Ph) and 277 (L = CO). Hydrogenation of 277 (L = CO) gives Ru$_6$(μ-H)$_6${μ_3-η^2-SC(NHPh)N(Ph)}$_2$(CO)$_{14}$ 278, along with the known trinuclear cluster Ru$_3$(μ-H)$_2$(μ_3-S)(CO)$_9$. The reaction presumably proceeds via breakdown of 277 to give the trinuclear intermediate which then dimerizes to give the hexanuclear product.[230] The reactivity of 277 ($L = CO$) toward two-electron donors has been investigated. Substitution with PPh_3 results in cleavage of an elongated Ru–Ru bond and formation of $Ru_6(\mu\text{-}H)(\mu_5\text{-}S)\{\mu_3\text{-}\eta^2\text{-}SC(NHPh)NPh\}(CO)_{15}(PPh_3)$ 279, where the phosphine is coordinated to an apical site on the *S*-bound ruthenium atom. In contrast, Me_2S, PBu^n_3, $P(OMe)_3$, $P(OPh)_3$, and $CNBu^t$ substitute at an axial site of an apical metal atom, the structurally characterized example being 277 ($L = CNBu^t$). Complex 279 is a 92 c.v.e. cluster, two electrons deficient for a compound with seven M–M bonds, but reaction with CO results in fragmentation to the trinuclear $Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}SC(NHPh)(NPh)\}(CO)_9$.[231]



R = Et, Ph

276



L = CO, CNBu^t

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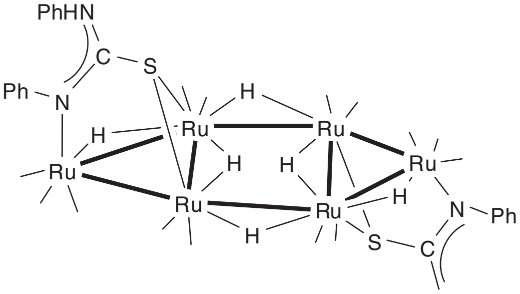

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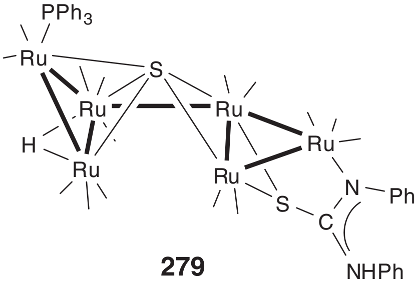

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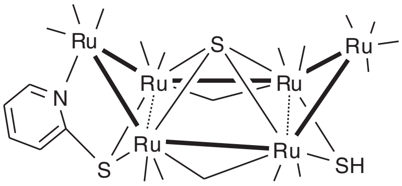
Thermolysis of $Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_9$ (pyS = pyridine-2-thionato) in refluxing *n*-decane affords $Ru_6(\mu_4\text{-}S)(\mu_3\text{-}pyS)(\mu\text{-}SH)(\mu\text{-}CO)_2(CO)_{15}$ 280 in 5% yield, with a geometry similar to that of the thiourea complexes 276. In contrast, thermolysis in hexane affords a trimer of trinuclear clusters $\{Ru_3(\mu_3\text{-}H)(\mu_4\text{-}pyS)(CO)_7\}_3$.[232]

Reaction between $Os_3(CO)_{10}(NCMe)_2$ and *N*-(*p*-methoxybenzoyl)-*S*-benzoylsulfenamide results in desulfurization of the organic reagent and formation of $Os_6(\mu_4\text{-}S)(CO)_{20}(NCMe)$ 281, an Os_3-spiked triangular cluster surrounding a μ_4-sulfido ligand and retaining a coordinated acetonitrile ligand. Interestingly, the cluster is stable toward H_2, CO, and PPh_3 substitution. Thermolysis of 281 in chloroform affords $Os_5(\mu_4\text{-}S)(CO)_{15}$ and $Os_6(\mu_3\text{-}S)(CO)_{19}$.[233]



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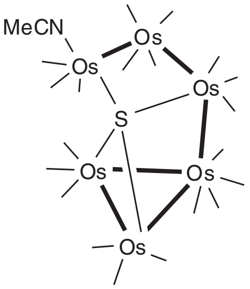

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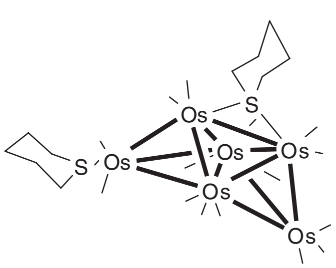
Reaction between $Os_6(CO)_{16}(NCMe)_2$ and cyclic thioethers and thioxanes affords 282, 283 $[S(CH_2)_4CH_2]$, 284 $[S(CH_2)_3SCH_2]$, 285 $[S(CH_2)_2SCH_2CH_2]$, 286 $(SCH_2SCH_2SCH_2)$, 287 $[S(CH_2)_2OCH_2CH_2]$, and the spectroscopically characterized $Os_6\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}\{O(CH_2)_2SCH_2CH_2\}(CO)_{15}$. Thermolysis of 282 results in conversion to the pentanuclear co-product 283. Carbonylation of 287 gives 288 and $Os_6(CO)_{18}$, and hydrogenation affords the dihydrido cluster 289.[234]



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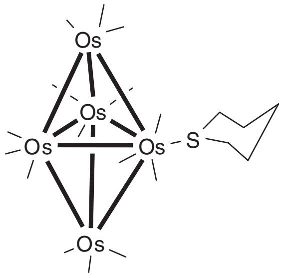

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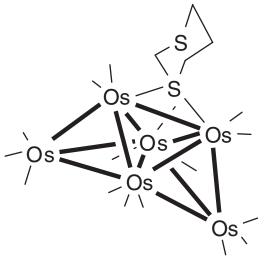

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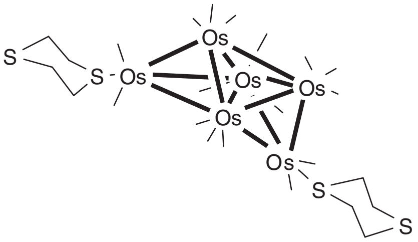

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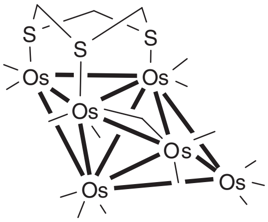

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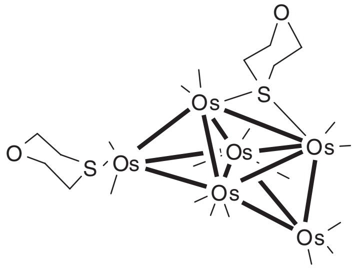

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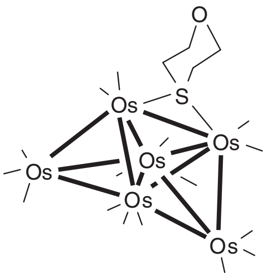

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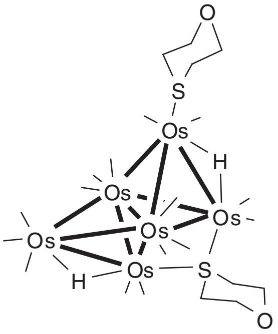
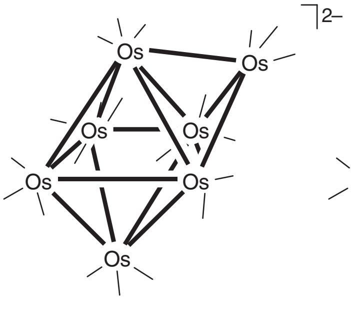


289

6.24.4 Clusters Containing more than Six Metal Atoms

6.24.4.1 M$_7$ Clusters

The face-capped octahedral cluster dianion $[Os_7(CO)_{20}]^{2-}$ **290** forms in 70% yield from the reduction of $Os_7(CO)_{21}$ with BH_4^-.[235] Addition of $Os(CNBu^t)(CO)_4$ to $Os_6(CO)_{18}/Me_3NO$ affords $Os_7(CO)_{20}(CNBu^t)$ **291** in 25% yield.[236] Phosphite addition to $Os_7H_2(CO)_{21}$ affords $Os_7H_2(CO)_{21}\{P(OMe)_3\}$ **292**, the core consisting of a fused triangle and trigonal bipyramid, with the phosphite ligand coordinated to one of the outer osmium atoms.[237]



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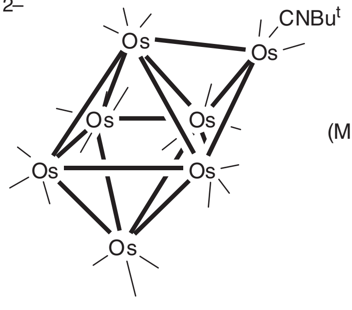

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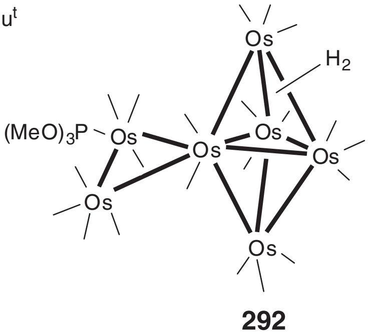

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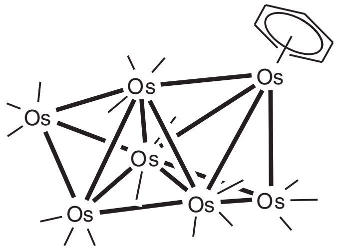
Reactions between the arene–osmium-capping reagents $[Os(L)_n(\eta^6\text{-}C_6H_5R)]^{2+}$ [$R = H$, $L_n = (NCMe)_3$; $R = Me$, $L_n = (CF_3SO_3)_2$] and $[Os_6(CO)_{17}]^{2-}$ afford $Os_7(CO)_{17}(\eta^6\text{-}C_6H_5R)$ ($R = H$ **293**, Me) in yields of around 25%; the same products are obtained in trace amounts from $Os_7(CO)_{21}/Me_3NO$ and an excess of the relevant diene C_6H_7R. The metal core consists of four face-fused tetrahedra, the arene ligand apparently migrating from the capping osmium.[196] A similar reaction of $[Ru(NCMe)_3Cp]^+$ with $[Ru_5(\mu_5\text{-}C)(CO)_{14}]^{2-}$ affords $Ru_7(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_{10}Cp_2$ **294** in 40% yield, together with the hexanuclear cluster **162**, whereas reaction with $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ affords the anionic product $[Ru_7(\mu_6\text{-}C)(\mu_3\text{-}CO)(\mu\text{-}CO)_4(CO)_{11}Cp]^-$ **295** in 60% yield, along with 12% of **294**. Both clusters contain a capped octahedral metal core, the latter with a face-capping CO ligand associated with the capping ruthenium atom. The formation of a small amount of the bis-Cp complex **294** in the reaction with the hexaruthenium precursor suggests that the Cp ligand has been transferred from the mononuclear reagent to the cluster.[149] Thermolysis of $Ru_3(CO)_{12}$ with 1,1-diphenylethene affords the hexanuclear cluster **159**, together with $Ru_7(\mu_6\text{-}C)\{\mu_3\text{-}\eta^2{:}\eta^6{:}\eta^6\text{-}(C_6H_4)_2CH_2\}(CO)_{14}$ (**296**; 102 c.v.e.), which has a spiked octahedral core. The organic reagent has undergone C=C bond cleavage, followed by hydrogenation of the remaining "carbene" fragment to give a methylene group. Intermolecular contacts in the latter involve both graphitic and CO…HC interactions.[147] The related spiked octahedral clusters $Ru_7(\mu_6\text{-}C)(\mu_4\text{-}\eta^4{:}\eta^2{:}\eta^2{:}\eta^2\text{-}R)(\mu\text{-}CO)_2(CO)_{14}$ ($R = C_9H_8$, $C_{12}H_{12}$; **297**,) in which a five-membered metallacycle incorporating the spike ruthenium atom is fused to a six-membered arene, are formed in trace amounts from the reaction of $Ru_3(CO)_{12}$ and isopropenyl- or 1,3-diisopropenyl-benzene, respectively,[238] and $Ru_7C(C_{12}H_{12})(CO)_{16}$ is produced in 3% yield among a number of products, including **236**, from the reaction between $Ru_3(CO)_{12}$ and 1,4-diisopropenylbenzene.[199]



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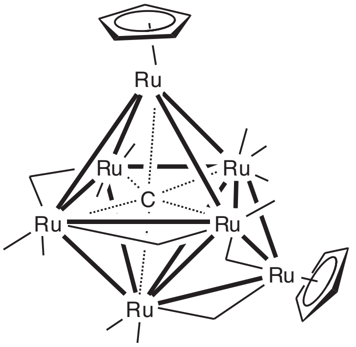

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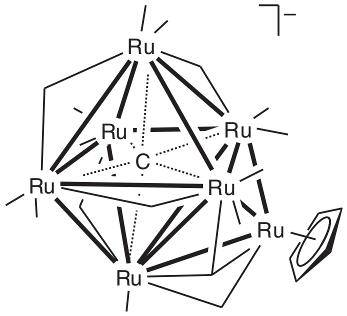

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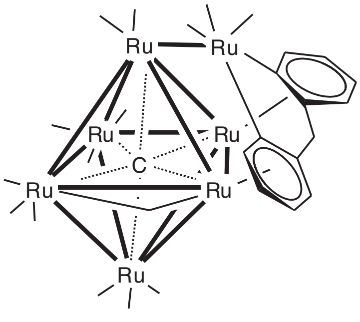

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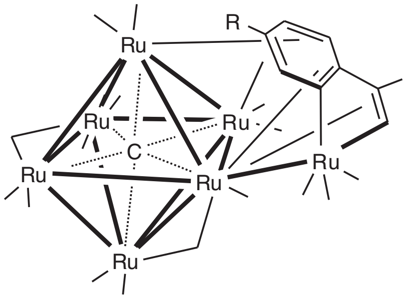
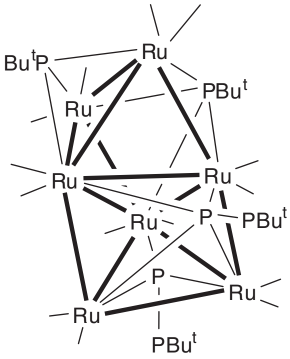


$R = C_9H_8$, $C_{12}H_{12}$

297

The cyclic phosphine $P_4Bu^t{}_4$ reacts with $Ru_3(CO)_{12}$ to give the capped square-pyramidal cluster **263**, as well as $Ru_7(\mu_4\text{-}PBu^t)_2(\mu_3\text{-}PBu^t)_2(CO)_{14}$ **298**, and the nonanuclear cluster **311**. Complex **298** is a 100 c.v.e. cluster with a metal core made up of two square-pyramidal units fused via a triangular face;[218] **298** is the major product from reaction of $Ru_4(\mu_4\text{-}H)_4(CO)_{12}$ with the same phosphine.[77] $Ru_7(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}CCCHMe)\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CCHC(O)Me\}(CO)_{19}$ **299** is formed in low yield (8%) from reaction between $Ru_3(CO)_{12}$ and an excess of but-3-yn-2-ol, along with a number of lower-nuclearity complexes including **58**, **59**, and **269**. The heptanuclear cluster contains an allenylidene ligand, and has an unusual distorted square-planar Ru_4 fragment sharing an edge of an edge-bridged

Ru_4 butterfly.[64] The cyclic carbophosphine 1,2,3,4-tetraphenyl-1,2,3,4-tetraphospholane reacts with $Ru_3(CO)_{12}$ to give two isomers of $Ru_7(\mu_4\text{-}PPh)_2\{(\mu_2\text{-}PPh)_2CH_2\}(CO)_{15}$ **300** and **301**, as well as the pentanuclear cluster **81**. The complexes consist of two face-sharing square pyramids, differing in the arrangement of the metal atoms—in **300** the two square pyramids share a common vertex, whereas in **301** they have different apices.[84]



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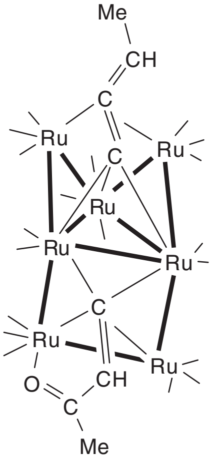

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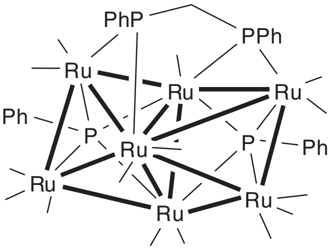

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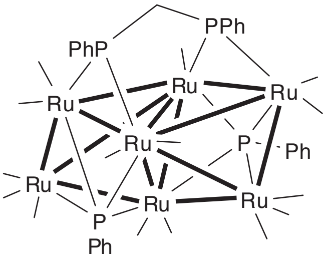
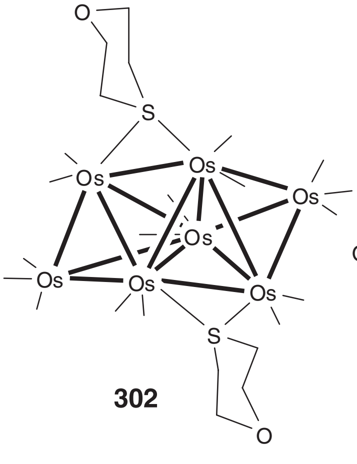


301

Sulfur-containing heptanuclear clusters have been prepared from the reaction of $Os_7(CO)_{17}$-$(NCMe)_2$ with 1,4-thioxane. The three complexes $Os_7\{\mu\text{–}S(CH_2)_2OCH_2CH_2\}_2(CO)_{16}$ **302**, $Os_7\{\mu\text{–}S(CH_2)_2OCH_2CH_2\}(CO)_{17}\{S(CH_2)_2OCH_2CH_2\}$ **303**, and $Os_7\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}(CO)_{18}$ **304**, each contain metal cores consisting of four fused tetrahedra, but attempts to convert **302** into **303** or **304** by addition of CO were unsuccessful. Carbonylation of **303** gives the spectroscopically characterized $Os_7\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}(CO)_{18}$, but attempts to form this complex from **304** were also unsuccessful.[239]



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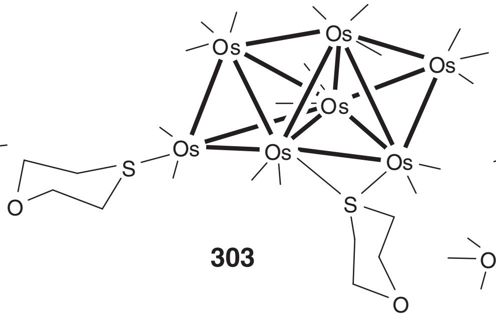

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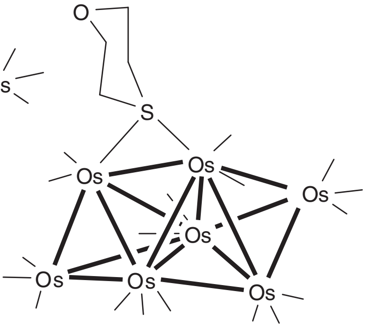
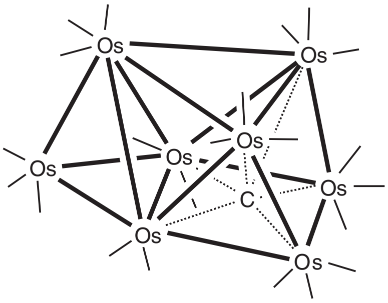


304

6.24.4.2 M_8 Clusters

Vacuum pyrolysis of $H_3Os_3(\mu_3\text{-COMe})(CO)_9$ affords a mixture of products from which $Os_8(\mu_6\text{-C})(CO)_{22}$ **305** has been isolated in 15% yield. The metal core geometry is related to that of the known cluster $[Os_{11}(\mu_6\text{-C})(CO)_{27}]^{2-}$ by loss of three $Os(CO)_3$ capping groups.[240] Cluster buildup of $[Os_7(CO)_{21}]^{2-}$ with $[Os(NCMe)_3(\eta^6\text{-}C_6H_6)]^{2+}$ affords $Os_8(CO)_{20}(\eta^6\text{-}C_6H_6)$ **306** in 30% yield. The complex consists of a bicapped octahedral metal core, with the arene ligand terminally bonded to one of the capping osmium atoms.[235]



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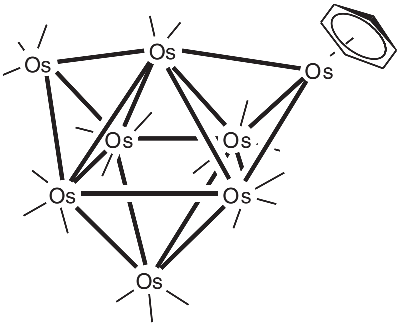

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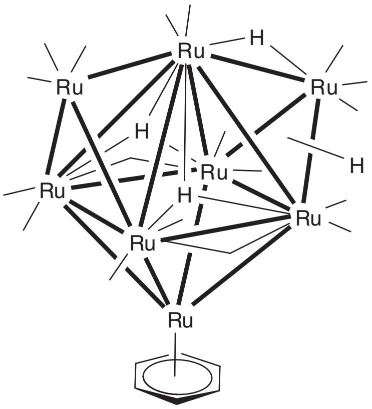
Thermolysis of $Ru_3(CO)_{12}$ in octane with cyclohexene or [2.2]paracyclophane affords $HRu_8(\mu_3\text{-H})_2(\mu\text{-H})(\mu\text{-CO})_2(CO)_{16}(\eta^6\text{-R})$ (**307**; $R=C_6H_6$, 10%; $C_{16}H_{16}$, 3%). The bicapped octahedral geometry contains two hydride ligands capping opposite faces on the octahedral core, and a bridging hydride on one of the ruthenium caps. The fourth hydride ligand was not located, and is thought to be disordered over the different cluster sites. Reaction with CO results in degradation to $Ru_3(CO)_{12}$ and $Ru_6(\mu_6\text{-C})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(CO)_{14}$ **171** for the cyclophane cluster, and $Ru_4(\mu\text{-H})_4(CO)_{12}$ and $Ru_4(\mu\text{-H})_2(CO)_{13}$ in the benzene case.[241,242] A similar reaction between $Ru_3(CO)_{12}$ and [2.2]paracyclophane in refluxing *n*-heptane produces $Ru_8(\mu\text{-H})_2(\mu_6\text{-}\eta^2\text{-CO})(CO)_{19}(\eta^6\text{-}C_{16}H_{16})$ **308** and $Ru_8(\mu_6\text{-}\eta^2\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})(CO)_{18}(\eta^6\text{-}C_{16}H_{16})$ **309** in trace amounts ($\leq$1%), and containing the first examples of $\mu_6\text{-}\eta^2$-coordinated CO ligands. Both clusters possess 116 c.v.e. and an edge-bridged *nido*-dodecahedron metal core. Complex **308** contains a η^2-CO ligand in the central cavity of the metal core, coordinated to six metal atoms, and **309** has a second η^2-CO group interacting with the four ruthenium atoms of a metal butterfly unit.[243,244]

The octaruthenium phosphido cluster anion $[Ru_8(\mu_8\text{-P})(\mu\text{-CO})_2(CO)_{20}]^-$ **310** is produced in around 30% yield from the thermolysis of $Ru_3(\mu\text{-H})(\mu\text{-NC}_5H_4)(CO)_{10}$ and chlorodiphenylphosphine in chlorobenzene. The square-antiprismatic cluster contains an interstitial phosphorus atom (δ_P 600–800), and 114 c.v.e., four electrons less than expected. Cyclic voltammetric studies show an uptake of four electrons in three steps; the third two-electron reduction step is irreversible, suggesting that a structural change may occur.[245]



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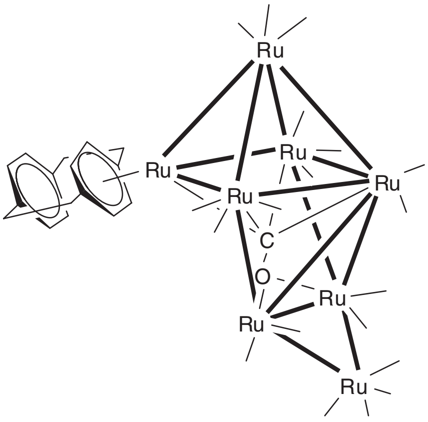

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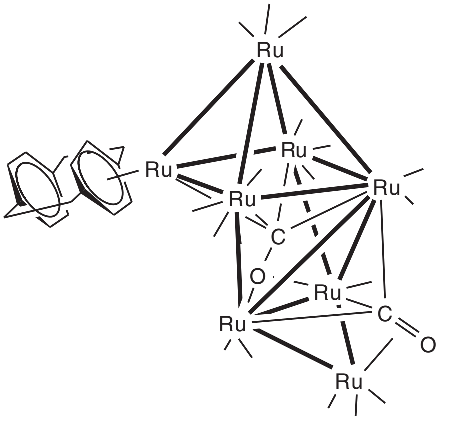

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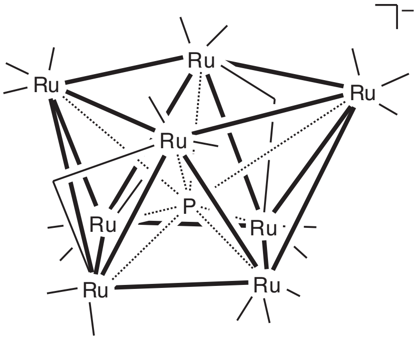

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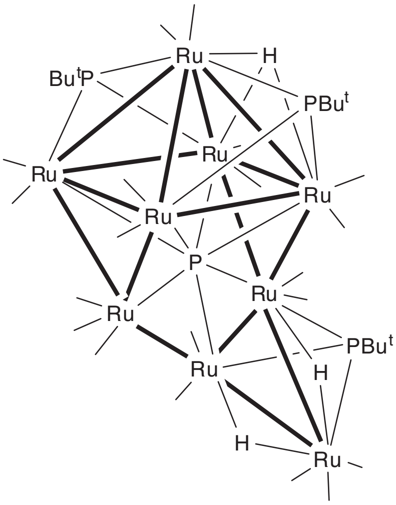
6.24.4.3 M_9 Clusters

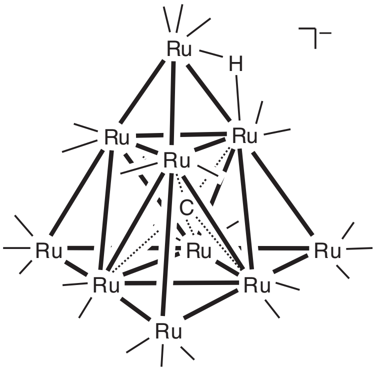
Thermolysis of $Ru_3(CO)_{12}$ with 3 equiv. of the cyclic phosphine $P_4Bu^t{}_4$ in xylene affords a mixture of products, including nonanuclear $Ru_9(\mu_3\text{-H})(\mu\text{-H})_2(\mu_7\text{-P})(\mu_3\text{-PBu}^t)_3(CO)_{20}$ **311**, hexanuclear **263**, and heptanuclear **298**. The metal core is based on a dibridged square-pyramidal geometry, with two additional ruthenium atoms forming an arch across the square face. The phosphorus atom is bound to seven metal atoms in a semi-encapsulated position. The complex contains 132 c.v.e., two more than predicted.[218]



311

6.24.4.4 M_{10} Clusters

The decaruthenium hydrido cluster anion $[Ru_{10}(\mu\text{-H})(\mu_6\text{-C})(CO)_{24}]^-$ **312** is formed as the PPN^+ salt in 35% yield among a mixture of products from the extended thermolysis of $Ru_3(CO)_{12}$ in mesitylene, followed by stirring at room temperature with [PPN]Cl.[246,247] Thermolysis of the trinuclear pyridyl cluster $Ru_3(\mu\text{-H})(\mu\text{-NC}_5H_4)(CO)_{10}$ in chlorobenzene over 40 min affords **312** with a diruthenium cation, $[Ru_2(\mu\text{-H})(\mu\text{-NC}_5H_4)_2(CO)_4(Hpy)_2]^+$, in yields of around 80%; the same reaction in the presence of $[PPh_4][BF_4]$ affords the decaruthenium anion as the $[PPh_4]^+$ salt (45%).[248,249] The cluster anion **312** is deprotonated to the related dianion $[Ru_{10}(\mu_6\text{-C})(CO)_{24}]^{2-}$ **313** by stirring with dbu (95%), or by refluxing the solid obtained from the initial mesitylene thermolysis in an acetone–methanol solution containing [PPN]Cl (35% from $Ru_3(CO)_{12}$); the dianion can also be reprotonated with HCl gas.[246] In contrast, the diruthenium–decaruthenium salt is deprotonated by stirring at room temperature with [PPN]Cl, providing a facile route to the dianionic cluster, $[PPN]_2[Ru_{10}(\mu_6\text{-}C)(CO)_{24}]$ (80%).[248,249] Structural analyses of the anion and dianion show that the clusters consist of a tetracapped octahedral metal core, with a μ_6-carbon atom in the central cavity;[247,248] the hydride ligand in the former was located indirectly and bridges an outer Ru–Ru bond.[248] The related nitrido cluster anion $[Ru_{10}(\mu_6\text{-}N)(CO)_{24}]^-$ **314** is prepared by thermolysis of $Ru_3(CO)_{12}$ and $[PPN]N_3$ in diglyme, followed by addition of silica, giving a mixture of **312–314**. A better route involves condensation of the preformed hexaruthenium nitrido cluster anion $[Ru_6(\mu_6\text{-}N)(CO)_{16}]^-$ with $Ru_3(CO)_{12}$ followed by the addition of silica, giving **233** in 69% yield. The cluster contains the same metal core geometry as **312** and **313**.[247]



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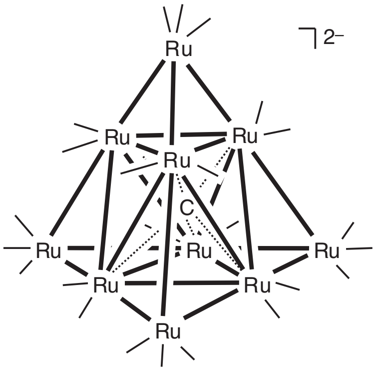

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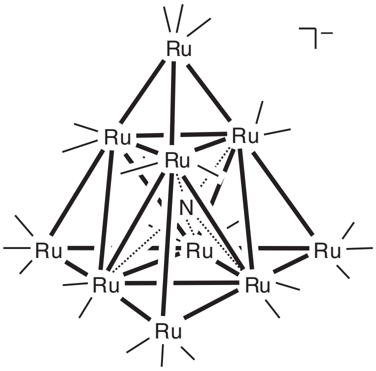
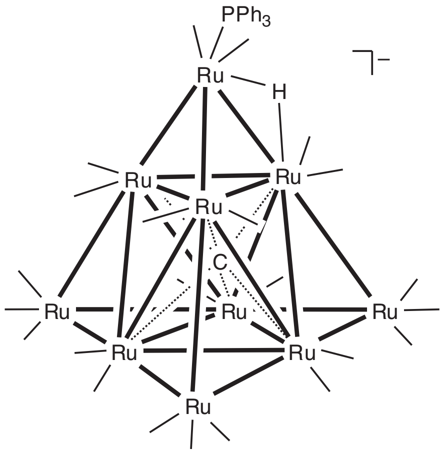


314

The reactivity of the carbido clusters has been examined. Reaction of **313** with CO at room temperature results in cluster degradation to give quantitative yields of the hexaruthenium carbido cluster dianion $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$ and $Ru_3(CO)_{12}$, thermolysis of this mixture in diglyme re-forming **313**. Similarly, treating **312** or **314** with CO gives mixtures of $Ru_3(CO)_{12}$ with $[HRu_6(\mu_6\text{-}C)(CO)_{16}]^-$ or $[Ru_5(\mu_5\text{-}N)(CO)_{14}]^-$, respectively.[247] A study into the reactivity of both the diruthenium and $[PPh_4]^+$ salts of the hydrido cluster **312** toward phosphines and phosphites has resulted in the series $[Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24-n}(PR_3)_n]^-$ ($n = 0$–4, R = Ph, OMe), with crystallographically verified examples of the monophosphine **315** and bis-phosphite **316** complexes. The facile substitution of the carbonyl ligands can be carried out in a stepwise manner, with inital replacement at the ruthenium apex associated with the hydrido ligand. Interestingly, replacement of the decaruthenium carbonyl ligands occurs before substitution of the pyridine ligands in the case of the diruthenium cation. The linked icosaruthenium cluster dianion, $[\{Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24}\}_2\text{-}(\mu\text{-dppa})]^{2-}$ [dppa = bis(diphenylphosphino)acetylene], is formed from reaction of **312** with dppa. Hydrido and carbonyl ligand fluxionality studies on the series of cluster anions have been reported.[248–251]



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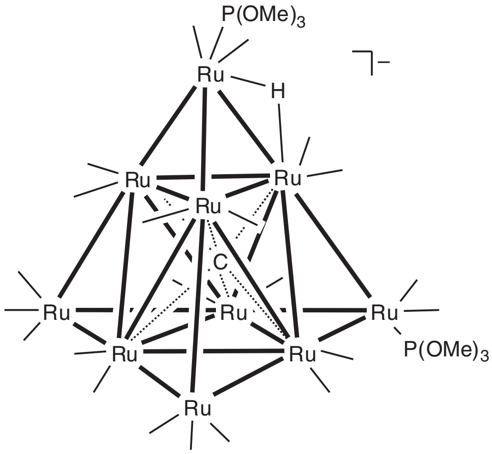
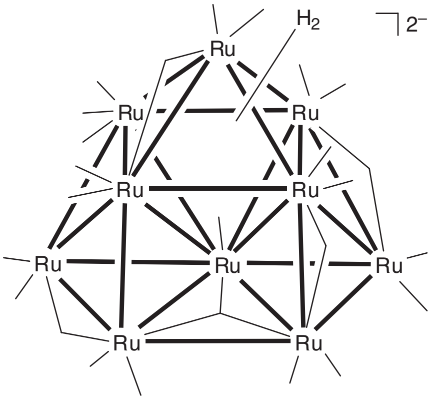


316

The electrochemical properties of $[Ru_{10}(\mu\text{-H})(\mu_6\text{-C})(CO)_{24}]^-$ and $[Ru_{10}(\mu_6\text{-C})(CO)_{24}]^{2-}$ have been examined using cyclic voltammetry and UV–VIS spectroelectrochemical techniques. Both complexes show a two-electron reduction associated with a structural change at low temperature, probably an Ru–Ru bond cleavage, which is reversible at room temperature.[252] *In situ* IR spectroelectrochemical studies of the analogous decaosmium cluster anion $[Os_{10}(\mu_6\text{-C})(CO)_{24}]^{2-}$ show a series of five oxidation states, $[Os_{10}(\mu_6\text{-C})(CO)_{24}]^{n-}$ ($n = 0$–4), with no apparent structural changes associated with the reduction processes.[253] Electronic spectroscopy, magnetic susceptibility, EPR studies, and local density functional (LDF) calculations indicate that the decaruthenium anion and dianion have "molecular" rather than "mesometallic" character.[254]

The dihydrido decaruthenium cluster dianion $[H_2Ru_{10}(\mu_3\text{-CO})(\mu\text{-CO})_4(CO)_{20}]^{2-}$ **317** is formed in 27% yield by thermolysis of $Ru_3(CO)_{12}$ in ethanol followed by addition of silica, whereas thermolysis of the same precursor in a methanol–water mixture also affords the undecaruthenium cluster **326**. Complex **317** consists of a bicapped octahedron fused with a bicapped square pyramid; the hydride ligands were not located.[255] This cluster has been used as a transmission electron microscopy probe to determine the position of the functionalized groups in mesoporous silica.[145] A high yield route to the decaosmium hydrido clusters $[H_5Os_{10}(CO)_{24}]^-$ and $[H_4Os_{10}(CO)_{24}]^{2-}$ has been developed. Hydrogenation (1 atm, 200 °C) of silica-supported $\{Os(CO)_3(OH)_2\}_n$ affords the pentahydrido cluster anion in 65% yield, whereas heating the same precursor in ethylene glycol gives the tetrahydrido species in excellent yield (80%). A similar yield of the tetrahydrido cluster is obtained by thermolysis of $\{Os(CO)_3Cl_2\}_2$ with Na_2CO_3 in ethylene glycol under hydrogen.[256] The hydride ligands in $[H_5Os_{10}(CO)_{24}]^-$ **318** are proposed to be located in three bridging and two face-capping sites using variable-temperature X-ray crystallographic studies and potential energy calculations.[257]



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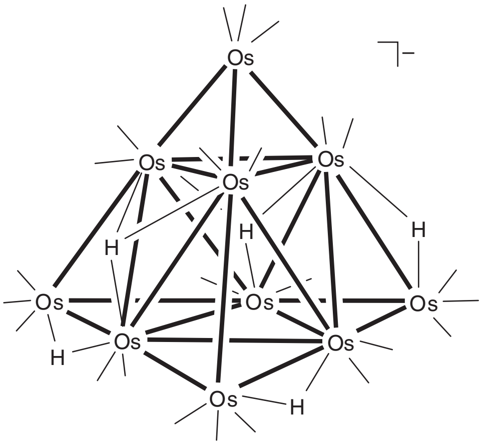
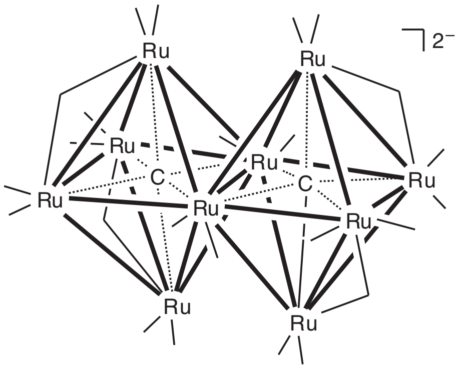


318

A high yield route to the dicarbido decaruthenium dianionic cluster, $[Ru_{10}(\mu_6\text{-C})_2(\mu\text{-CO})_4(CO)_{20}]^{2-}$ **319**, has been developed using CaC_2 as the carbide source, thermolysis with $Ru_3(CO)_{12}$ in THF followed by stirring with [PPN]Cl affording the dianion in 60% yield. A similar reaction using $Ru_3(\mu\text{-dppm})(CO)_{10}$ as the metal precursor affords only the known hexanuclear vinylidene cluster $Ru_6(\mu_4\text{-CCH}_2)_2(\mu\text{-dppm})(CO)_{12}$.[258]

Oxidation of **319** (as the PPN^+ or $NEt_4{}^+$ salts) with $[FeCp_2]^+$ in the presence of disubstituted alkynes affords the neutral alkynyl derivatives $Ru_{10}(\mu_6\text{-C})_2(\mu\text{-}\eta^2\text{-}R^1C_2R^2)(\mu\text{-CO})_4(CO)_{19}$ ($R^1 = R^2 = Ph$ **320**, tol; R^1, $R^2 = Ph$, Me). Reduction with methanolic hydroxide produces the cluster dianion $[Ru_{10}(\mu_6\text{-C})_2(CO)_{22}(PhC_2Ph)]^{2-}$.[259] Norbornadiene (nbd) and diphenylacetylene occupy different positions on the cluster. In $[Ru_{10}(\mu_6\text{-C})_2(CO)_{22}(nbd)]^{2-}$ and $Ru_{10}(\mu_6\text{-C})_2(\mu\text{-CO})_4(CO)_{19}(\eta^4\text{-nbd})$ **321**, obtained by oxidative ($[FeCp_2]^+$) carbonylation of $[Ru_{10}(\mu_6\text{-C})_2(CO)_{22}(nbd)]^{2-}$ or oxidative substitution of the parent dianion, the diene chelates an outer Ru atom. In contrast, the alkyne in $[Ru_{10}(\mu_6\text{-C})_2(CO)_{22}(PhC_2Ph)]^{2-}$ and $Ru_{10}(\mu_6\text{-C})_2(CO)_{23}(PhC_2Ph)$ is located between the apical Ru atoms. The ligands occupy the same relative positions in $Ru_{10}(\mu_6\text{-C})_2(\mu\text{-}\eta^2\text{-PhC}_2\text{Ph})(\mu\text{-CO})_4(CO)_{17}(\eta^4\text{-nbd})$ **322**, best obtained via carbonyl substitution on **321** with diphenyacetylene (81%).[260]



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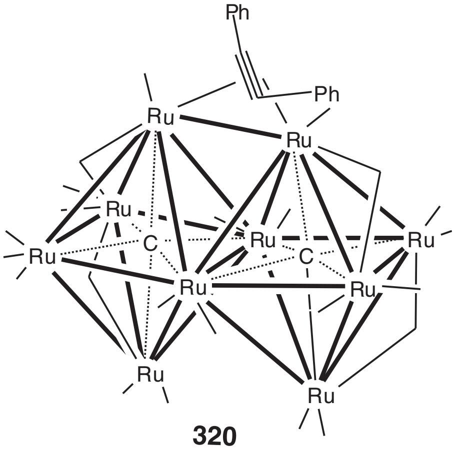

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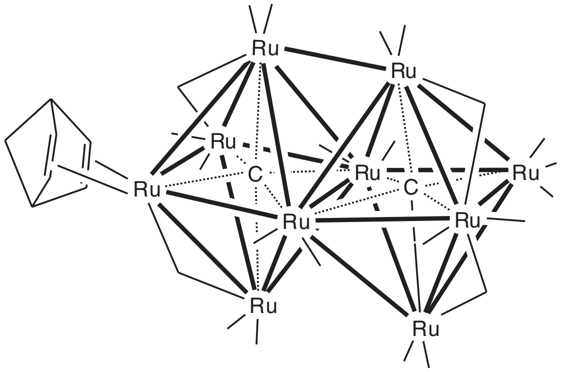

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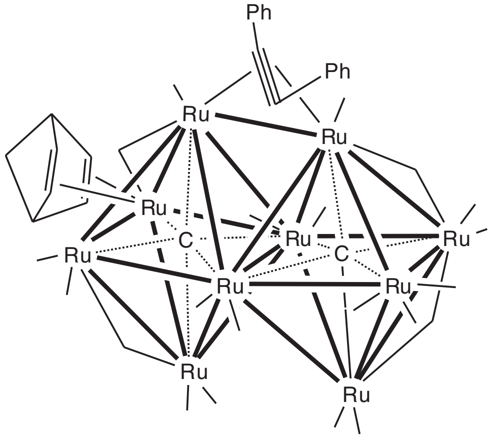
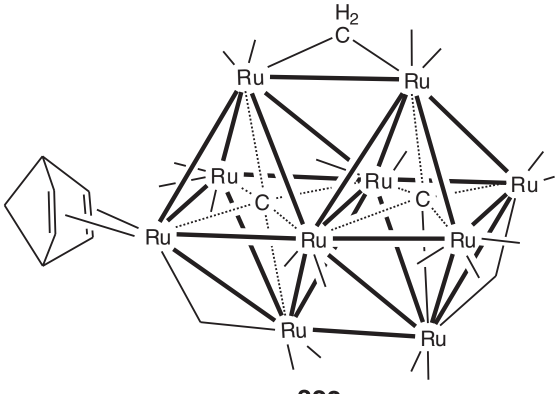


322

Reaction of $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{22}(nbd)]^{2-}$ with $CH_2N_2/[FeCp_2]^+$ gives $Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_{20}(\eta^4\text{-}nbd)$ (**323**, 33%), where the CH_2 group bridges two apical Ru atoms. At 80 °C, reversible formation of the hydrido-methylidyne tautomer occurs.[261] Both mono- and disubstitution of $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{24}]^{2-}$ by allene has been observed, with one, in $[Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_3H_4)(\mu\text{-}CO)_4(CO)_{18}]^{2-}$ **324**, or two, in $[Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_3H_4)_2\text{-}(\mu\text{-}CO)_4(CO)_{16}]^{2-}$ **325**, allene ligand(s) spanning apical Ru atoms.[262]



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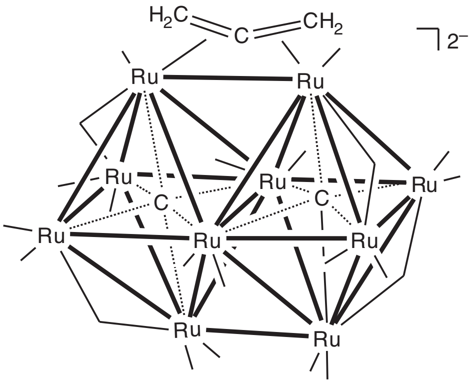

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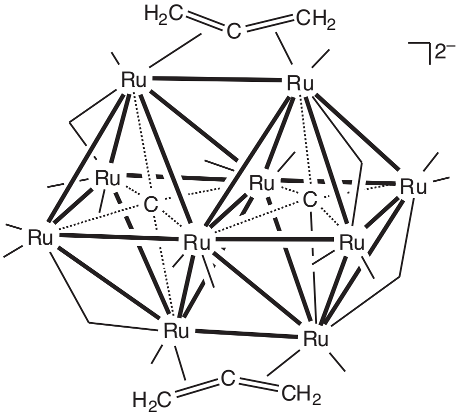
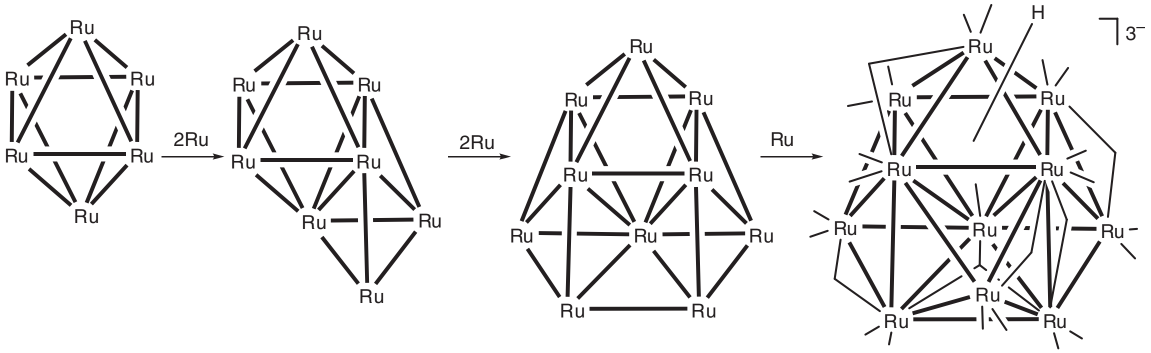


325

6.24.4.5 M_{11} Clusters

Thermolysis of $Ru_3(CO)_{12}$ in a mixture of methanol and water affords the trianionic cluster $[HRu_{11}(\mu_3\text{-}CO)(\mu\text{-}CO)_6(CO)_{21}]^{3-}$ **326** in 15% yield among a mixture of products; thermolysis over a period of days in acetonitrile containing traces of water affords almost quantitative yields. The metal core geometry is related to that of one of the co-products, the decaruthenium cluster **317**, by addition of an extra ruthenium atom to the square face. Complex **326** completes the series of complexes having core geometries built up by sequential addition of ruthenium atoms from octahedral ($[Ru_6H(CO)_{18}]^-$) to the fused octahedral trigonal bipyramid ($[Ru_8H_2(CO)_{21}]^{2-}$) to bicapped octahedron fused with a bicapped square pyramid **317** to **326** (Scheme 1).[255]

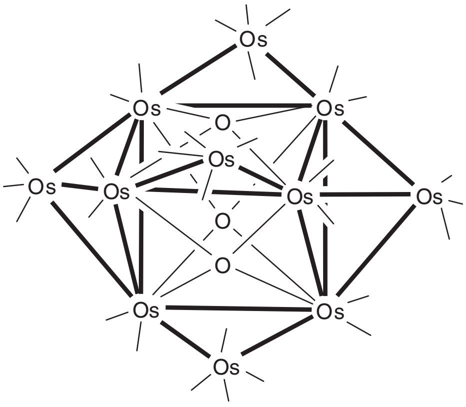
Vacuum pyrolysis of the hydroxy-bridged $Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}$ at 240 °C affords $Os_{11}(\mu_4\text{-}O)_3(CO)_{30}$ **327** among a number of products. The metal core is based on a trigonal-prismatic geometry with additional capping (two) and bridging (three) metal atoms, and three μ_4-oxo ligands located over the square faces of the trigonal prism. The complex is electron-rich, with 160 c.v.e. instead of the predicted 156.[263] Vacuum pyrolysis of $Os_3(CO)_{12}$ at 260 °C over 3 days affords a mixture of products; extraction of the residue with methanol/acetone solutions of [PPN]Cl affords $[Os_{11}(\mu_6\text{-}C)(\mu\text{-}Cl)(CO)_{27}]^-$ **328** in around 8% yield. The complex contains the same metal core as $[Os_{11}(\mu_6\text{-}C)(CO)_{27}]^-$, with a bridging chloride ligand replacing an Os–Os bond; it forms the



317 **326**

Scheme 1

decaosmium dianion $[Os_{10}(\mu_6\text{-}C)(CO)_{24}]^{2-}$ readily on standing over a period of 5 days, or more rapidly in the presence of pyridine or dbu.[264]



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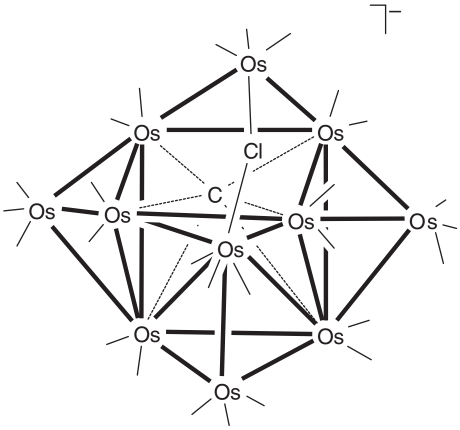
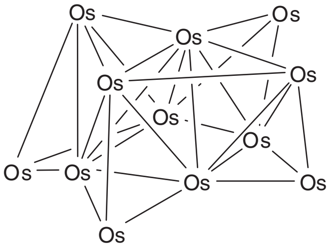


328

6.24.4.6 $M_{\geq 12}$ Clusters

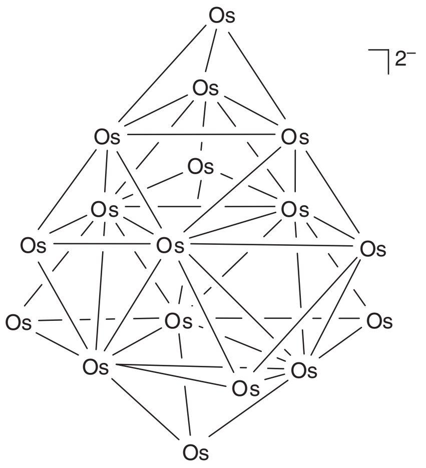
Vacuum pyrolysis of $Os_6(\mu_4\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}CO)_2(CO)_{16}$ **268** at temperatures of over 210 °C gives the dodecaosmium neutral cluster $Os_{12}(CO)_{30}$ **329** in 32% yield. The 156 c.v.e. electron-precise cluster contains an irregular metal geometry based on a distorted square pyramid, with three edge-sharing tetrahedra and an osmium atom capping a triangular-pyramidal face.[222]



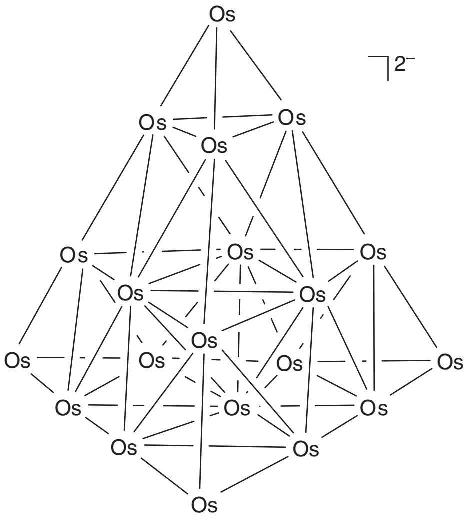
329

* CO ligands omitted for clarity

Osmium cluster dianions $[Os_{17}(CO)_{36}]^{2-}$ **330** and $[Os_{20}(CO)_{40}]^{2-}$ **331** are formed in up to 10 and 20% yields, respectively, by vacuum pyrolysis of $Os_3(CO)_{10}(NCMe)_2$ at temperatures above 260 °C. Complex **330** contains a close-packed arrangement of 16 metal atoms, with the additional Os breaking the otherwise threefold symmetry of the metal core. The two osmium atoms with metal connectivities of 8 and 9 have significantly shorter Os–Os bond distances (2.663 Å), comparable to that of the bulk metal (2.6754 Å). The cluster is electron-precise, with 210 c.v.e. The electron-deficient complex **331** consists of a cubic close-packed arrangement of metal atoms, and has been characterized by IR spectroscopy in five oxidation states.[13]



330*



331*

* CO ligands omitted for clarity

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6.25
Heterometallic Ru/Os-containing Compounds

W-T Wong, University of Hong Kong, Hong Kong, People's Republic of China

6.25.1 Introduction

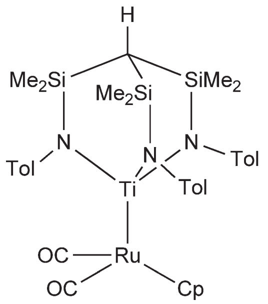
Heterometallic compounds that contain ruthenium or osmium as one of their constituents occupy an important position in organometallic chemistry because of their good balance of reactivity and stability. These group 8 metals form metal–metal bonds with most of the transition metals, as well as the group 11 and 12 elements. They are often sufficiently stable to allow for full characterization by spectroscopic and crystallographic techniques, and examples of their novel reactivity to small molecules, such as unsaturated hydrocarbons, are commonplace in the literature. The cooperative activation and synergistic interaction of mixed-metal systems has long been a research focus in organometallic chemistry, and their potential in the field of catalysis is equally important. It is well known that bimetallic complexes, and in particular cluster compounds, can be valuable precursors to supported bimetallic catalysts, because they contain metal components with well-defined stoichiometries, which allows better control of the nature of the bimetallic particles that are formed.[1] Recent studies have shown that bimetallic nanoparticles with intriguing catalytic behavior can be obtained.[2] This is certainly an added impetus for the investigation of the chemistry of heterometallic complexes. Several review articles on the syntheses, structural properties, and reactivity studies of mixed-metal clusters that contain ruthenium or osmium are available,[3–6] in addition to relevant sections in the annual survey of organometallic metal cluster chemistry[7–16] and the Royal Society of Chemistry's specialist report on organometallic chemistry.[17]

6.25.2 Dinuclear Compounds

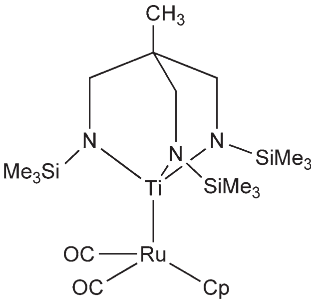
Dinuclear Ru/Os mixed-metal compounds with known structures reported within this reviewing period are listed in Tables 1–8.

6.25.2.1 Ru/Os Heterodinuclear Compounds Containing Group 4 Elements

The isolation of a series of novel early–late heterometallic Ru/Ti mixed-metal compounds by the coupling of a series of tripodal amido titanium halide complexes with K[CpRu(CO)$_2$] has been reported. Complexes **1** and **2** were prepared by reacting [CH(SiMe$_2$NTol)$_3$TiBr] or [CH$_3$C(CH$_2$NSiMe$_3$)$_3$TiBr] with K[CpRu(CO)$_2$] in toluene at −70 °C.[18,19] The Ru–Ti bond of **1** (2.503(4) Å) is significantly shorter than that of **2** (2.573(1) Å) because the Ru–Ti is less shielded.

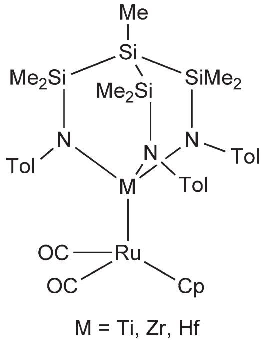


1



2

The tetra-Si tripodal amido metal halide complexes of Ti, Zr, and Hf were also reacted with K[CpRu(CO)$_2$] in a similar manner at −60 °C to yield complexes **3** (Table 1).

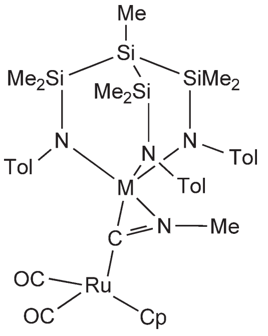


3

Table 1 Ru/Os mixed-metal compounds containing group 4 elements with known structures

Formula	*References*
[RuTi{η^3-CH(SiMe$_2$NTol)$_3$}(CO)$_2$Cp]	18
[RuTi{η^3-CH$_3$C(CH$_2$NSiMe$_3$)$_3$}(CO)$_2$Cp]	19
[RuTi{η^3-SiMe(SiMe$_2$NTol)$_3$}(CO)$_2$Cp]	21
[RuZr{η^2-CH$_2$(SiMe$_2$NTol)$_2$}(CO)$_2$Cp]	25
[RuZr{η^3-SiMe(SiMe$_2$NTol)$_3$}(μ-η^2-C=NTol)(CO)$_2$Cp]	21
[RuZr{η^3-SiMe(SiMe$_2$NTol)$_3$}(μ-CO$_2$)(OSMe$_2$)(SMe$_2$)(CO)$_2$Cp]	22

Methyl isocyanide reacted with **3** through insertion into the metal–metal bond, which is possible due to its high polarity to give **4**. Metal–metal bond rupture was observed with the two metals that are bridged by the cyanide carbon. This may be regarded as the first example of a metal analog of the α-addition reaction to the carbon of the isocyanide.[20,21]



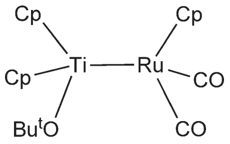
M = Ti, Zr, Hf

4

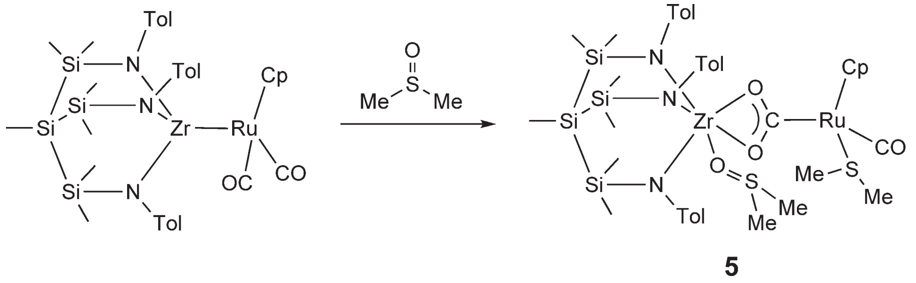
In addition to isocyanide, methyl sulfoxide also reacted with the Ru–Zr complex to give the CO_2-linked dinuclear compound **5**, as depicted in Scheme 1.[21,22] The oxygen in the sulfoxide was transferred to the carbon monoxide under the joint influence of Ru and Zr. Other functional groups, such as isocyanate, lactone, and dithione, were also added to the polar Ru–Zr bond in a way similar to the sulfoxide.[23] Similar additions to the polar Ru–Zr bond have been observed in dinuclear complexes with Zr stabilized by Cp ligands alone.[24]

In addition to the tripodal amido ligand, the chelating amido ligand-stabilized Zr complex was also employed to prepare a Ru–Zr mixed-metal cluster **6** which was converted into the dinuclear complex **7**, as shown in Scheme 2.[25]

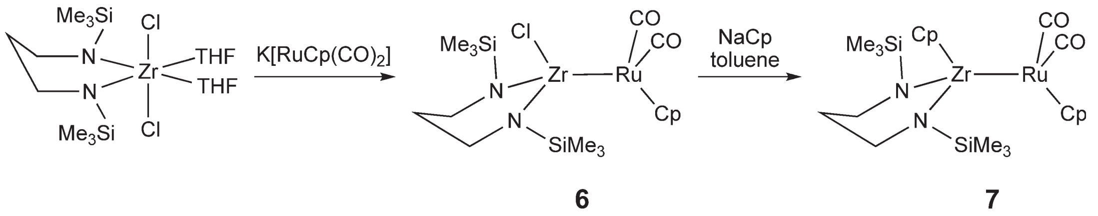
UV photolysis ($\lambda > 420$ nm) of the Ru dimer $\{CpRu(CO)_2\}_2$ with $[Cp_2Ti(OBu^t)]$ in toluene at $-10\,°C$ yielded the dinuclear complex $[RuTi(OBu^t)Cp_3(CO)_2]$ **8**. The reaction also took place in the dark or upon heating.[26]



8



Scheme 1



Scheme 2

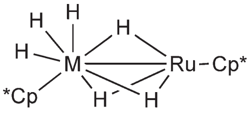
Amine elimination between [CpRu(CO)$_2$H] and [Cp*Ti(NMe)$_3$] gave a new Ru–Ti dinuclear complex, [RuTi(NMe)$_2$-Cp*Cp(CO)$_2$] 9, in moderate yield. This mixed-metal complex is stable in an inert atmosphere both in solution and in solid form, but decomposes to [Cp$^*_4$Ti$_4$O$_6$], {CpRu(CO)$_2$}$_2$, and NMe$_3$ upon exposure to oxygen and moisture.[27]

6.25.2.2 Ru/Os Heterodinuclear Compounds Containing Group 5 Elements

No bimetallic dinuclear complex with a structure determined by X-ray analysis was reported for Ru/Os with group 5 elements in this review period.

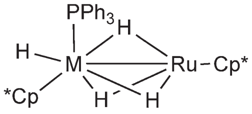
6.25.2.3 Ru/Os Heterodinuclear Compounds Containing Group 6 Elements

Novel bimetallic Ru–group 6 metal complexes were prepared from the reduction of {Cp*RuCl}$_4$ and [Cp*MCl$_4$] (M = Mo and W) by LiBH$_4$ in diethyl ether at room temperature. Complex **10** was isolated in moderate yield upon addition of methanol at −78 °C. These complexes are the first examples of polyhydride complexes that contain Ru and group 6 metals. Organic ligands such as phosphine, amine, and acetylacetone react with **10** to give a series of hydride-substituted bimetallic clusters **11–13**. The nucleophiles only attacked the terminal hydrides, and left the bridge hydrides unaltered.[28]



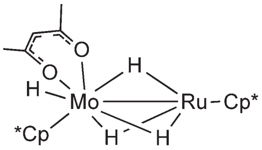
M = Mo, W

10

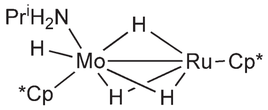


M = Mo, W

11

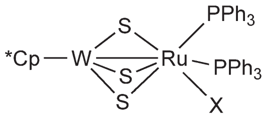


12



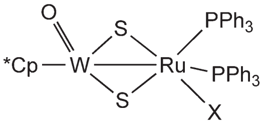
13

Tastsumi *et al.* reported a series of sulfido-bridged Ru–W dinuclear complexes **14–16** in high yield from the reaction of PPh$_4$[WS$_2$(E)] (E = S, NPh or PPh$_3$) with [RuClX(PPh$_3$)$_3$] (X = Cl or H) in CH$_3$CN at room temperature.



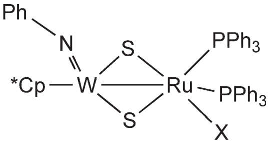
X = Cl, H

14



X = Cl, H

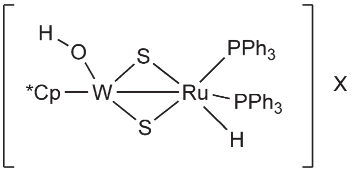
15



X = Cl, H

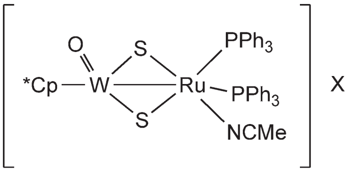
16

Complex **15** (X = H) was protonated by two acids [H(OEt$_2$)$_2$][BAr$^F_4$] (Ar$^F_4$ = 3,5-(CF$_3$)$_2$(C$_6$H$_3$)) and HOTf in THF to yield complex **17**. The further reaction of **17** with CH$_3$CN in THF led to H$_2$ evolution and complex **18**.



X = BAr$^F_4$, OTf

17



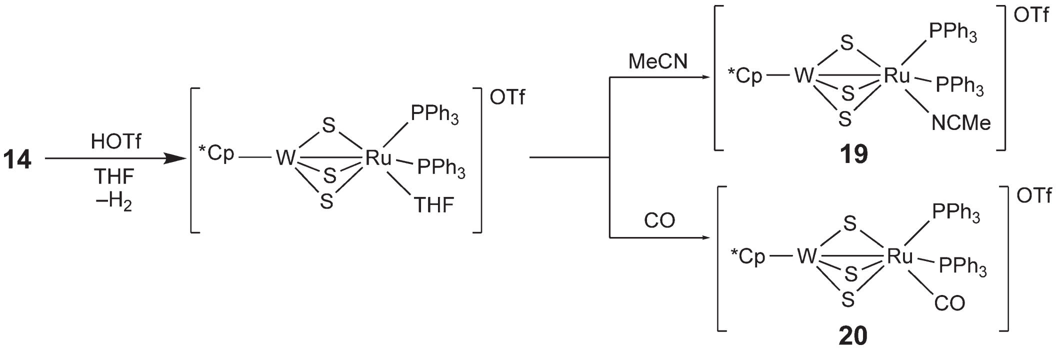
X = BAr$^F_4$, OTf

18

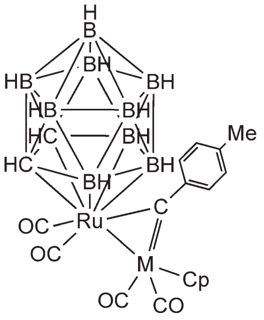
H$_2$ evolution was also observed in the protonation of complex **14** (X = H) by HOTf in THF. Subsequent reaction with CH$_3$CN yielded complex **19**, and reaction with CO gave complex **20**, as shown in Scheme 3.

A deuterium exchange ^{1}H NMR experiment showed that complexes **14**, **15** (X = H), and **17** (X = BAr$^f_4$) underwent H/D exchange with D$_2$ atmosphere to produce HD and H$_2$, which suggests a possible intermediate with an η^2-D$_2$ moiety. Among the three complexes, **17** showed the easiest exchange.[29]

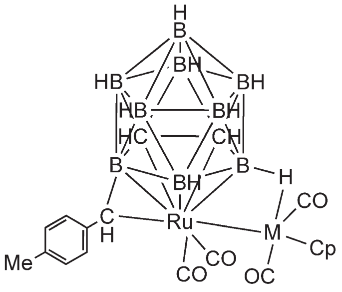
The reactions of [RuE(THF)Cp(CO)$_2$] (E = η^5-7,8-C$_2$B$_9$H$_{11}$, η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_{11}$, and [M(CTol)Cp(CO)$_2$] (M = Mo, W) yielded a series of novel carborane Ru–Mo and Ru–W complexes, including **21–27**.[30] Molecular structures that are similar to those of **26** and **27** have not been observed in the literature before.



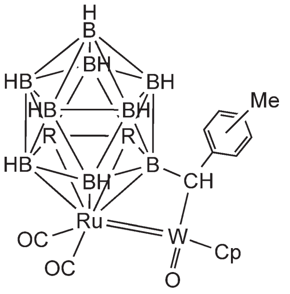
Scheme 3



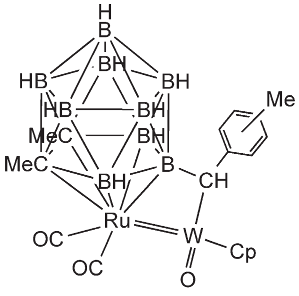
21 M = W, Mo



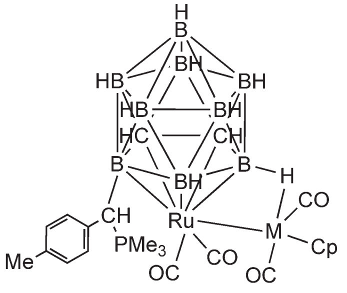
22 M = W, Mo



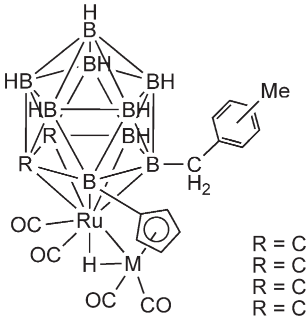
23 R = CH Me-4
R = CMe Me-2



24 Me-4, Me-2

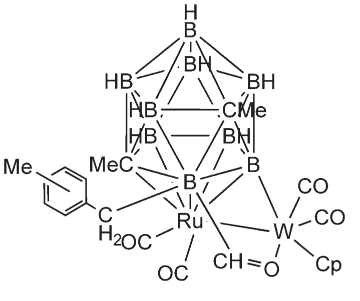


25 M = W, Mo



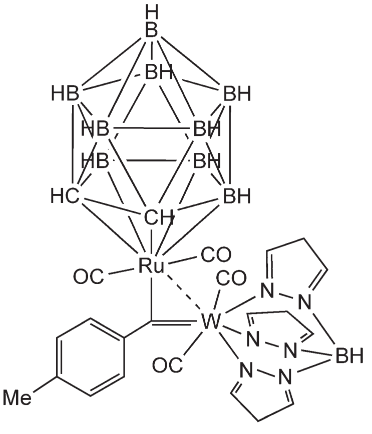
R = CMe, M = W Me-4
R = CMe, M = Mo Me-4
R = CMe, M = Mo Me-2
R = CH, M = W Me-4
R = CH, M = Mo Me-4

26

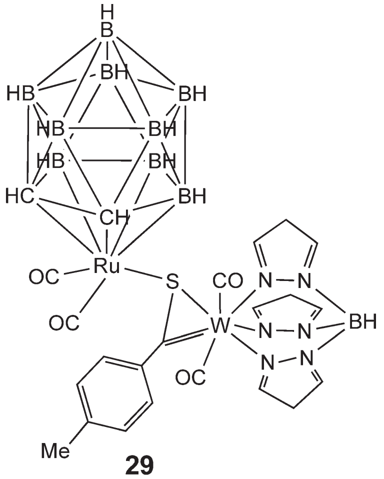


27 Me-4 ,Me-2

In similar reactions with other group 6 metal complexes, [M{κ^3-HB(pz)$_3$}(CTol)(CO)$_2$] (M = Mo, W) gave a different series of Ru mixed-metal complexes. Complex 28 showed an abnormally long (about 3 Å) Ru–W bond which was readily broken by sulfur in CH_2Cl_2 to give complex 29. The structure demonstrates a unique η^2-coordinated thioacyl group.[31]

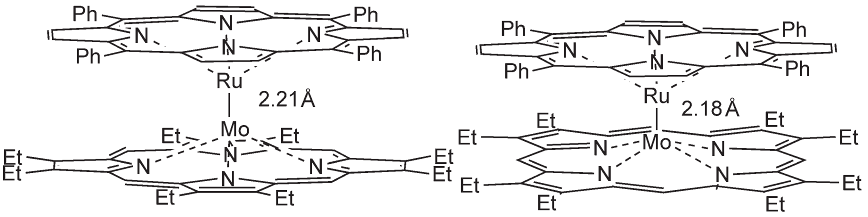


28



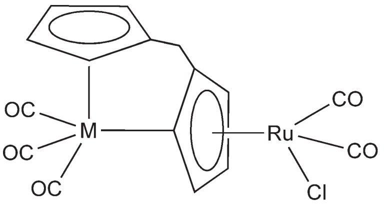
29

Porphyrins that contain Ru–Mo and Os–Mo dinuclear complexes was reported by Collman *et al.*[32] One of the isolated complexes, [RuMo(OEP)(TPP)][PF_6] 30 (OEP = octaethylporphyrin, TPP = tetraphenylporphyrin), possesses a unique deformational isomerism. The Ru–Mo metal–metal bonds of the two molecules in the asymmetric unit are of different lengths.[33]



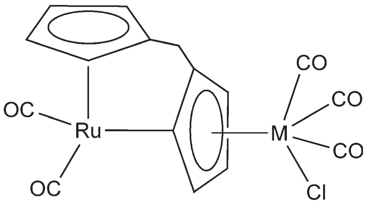
30

Heck *et al.* reported an Ru–group 6 metal bimetallic system that was stabilized with bis(cyclopentadienyl) ligands.[34–35] The two metal centers were first coordinated by the cyclopentadiene, and intramolecular metathesis was carried out to join the two metal centers. In contrast to the common η^5-coordination, a unique η^1:η^5 coordination of the cyclopentadiene in the Ru–Mo and Ru–W systems (complexes 31 and 32) was observed by Bitterwolf *et al.*[36]



M = Mo, W

31



M = Mo, W

32

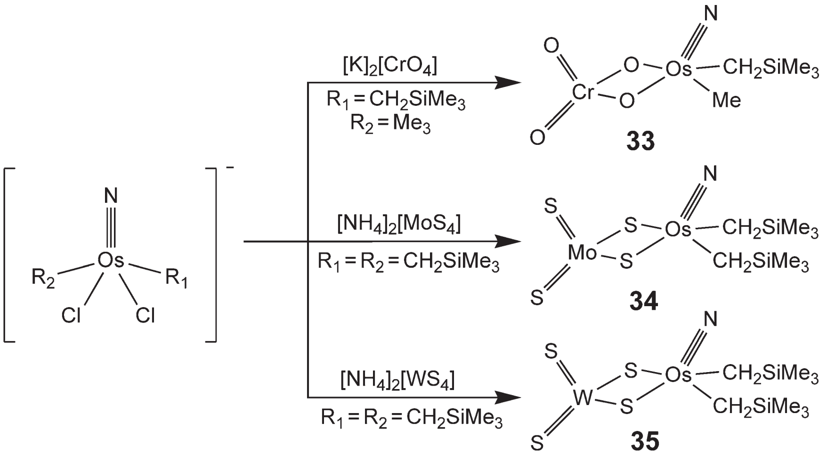
The ionic coupling of the sodium salt of ruthenium and group 6 metal halides was also found to be an effective way to derive dinuclear complexes. Examples include [RuM(μ-dppm)(CO)$_3$Cp′Cp] (M = Mo or W; Cp′ = Cp or Cp*),[37] [RuM(CO)$_5$Cp′Cp] (M = Cr, Mo or W, Cp′ = Cp; M = Mo, Cp′ = Cp*),[38] [RuCr(μ-η^6,η^1-C_7H_7)(CO)$_5$Cp],[39] and [RuCr{KCO-η^7-N($C_2H_4OC_2H_4OCH_3$)$_3$}(μ-H)$_3$(PPh$_3$)$_3$(CO)$_2$] (see Table 2).[40]

Table 2 Ru/Os mixed-metal compounds containing group 6 elements with known structures

Formula	*References*
$[RuCr(\mu\text{-}O)_2O_2N(CH_2SiMe_3)_2][NBu^n{}_4]$	41
$[RuCr(CO)_5Cp_2]$	38
$[RuCr\{KCO\text{-}\eta^7\text{-}N(C_2H_4OC_2H_4OCH_3)_3\}(\mu\text{-}H)_3(PPh_3)_3(CO)_2]$	40
$[OsCr(\mu\text{-}O)_2O_2(N)(CH_2SiMe_3)_2][PPh_4]$	41
$[OsCr(\mu\text{-}dmpe)(CO)_8]$	45
$[RuMo(\mu\text{-}\eta^2\text{-}acac)(\mu\text{-}H)_3Cp^*{}_2]$	28
$[RuMo(\mu\text{-}dppm)(\mu\text{-}H)(CO)_3Cp_2][BF_4]$	37
$[RuMo(\mu\text{-}dppm)(CO)_3CpCp^*]$	37
$[RuMo(\mu\text{-}dppm)(CO)_3Cp_2]$	37
$[RuMo(\mu\text{-}H)_3H_3Cp^*{}_2]$	28
$[RuMo(CO)_5Cp_2]$	38
$[RuMo(CO)_5CpCp^*]$	38
$[RuMo(NH_2Pr^i)(\mu\text{-}H)_3HCp^*{}_2]$	28
$[RuMo(OEP)(TPP)][PF_6]$	33
$[RuMo\{\mu\text{-}\eta^5,\eta'^1:\eta'^5\text{-}(C_5H_4)CH_2(C_5H_3)\}Cl(CO)_5]$	36
$[RuMo\{\mu\text{-}\eta^5,\eta'^5\text{-}Me_2CpCH_2TolC_2B_9H_7\}(\mu\text{-}H)(CO)_5]$	30
$[RuMo\{\sigma,\eta^5\text{-}(CHTol)C_2B_9H_{10}\}(CO)_4Cp]$	30
$[RuW(\mu\text{-}dppm)(\mu\text{-}H)(CO)_3Cp_2]Cl$	37
$[RuW(\mu\text{-}dppm)(CO)_3CpCp^*]$	37
$[RuW(\mu\text{-}dppm)(CO)_3Cp_2]$	37
$[RuW(\mu\text{-}H)_3H_3Cp^*{}_2]$	28
$[RuW(\mu\text{-}S)_2(CH_3CN)(PPh_3)_2Cp^*][OTf]$	29
$[RuW(\mu\text{-}S)_2(O)(CH_3CN)(PPh_3)_2Cp^*][OTf]$	29
$[RuW(\mu\text{-}S)_2(O)Cl(PPh_3)_2Cp^*]$	29
$[RuW(\mu\text{-}S)_2(OH)H(PPh_3)_2Cp^*][BAr^F{}_4]$	29
$[RuW(\mu\text{-}S)_2(OH)H(PPh_3)_2Cp^*][OTf]$	29
$[RuW(\mu\text{-}S)_3(PPh_3)_2COCp^*][OTf]$	29
$[RuW(\mu\text{-}S)_3Cl(PPh_3)_2Cp^*]$	29
$[RuW(\mu\text{-}S)_3H(PPh_3)_2Cp^*]$	29
$[RuW(CO)_5Cp_2]$	38
$[RuW\{\mu\text{-}\sigma,\eta^5\text{-}(CHTol)C_2B_9H_{10}\}(O)(CO)_2Cp]$	30
$[RuW\{\mu\text{-}\sigma,\eta^5Me_2(CH_2Tol)C(H)OC_2B_9H_6\}(CO)_4Cp]$	30
$[RuW\{\mu\text{-}\sigma,\eta^5\text{-}Me_2(CHTol)C_2B_9H_8\}(O)(CO)_2Cp]$	30
$[RuW\{\mu\text{-}\eta^5,\ \eta'^1:\eta'^5\text{-}(C_5H_4)CH_2(C_5H_3)\}Cl(CO)_5]$	36
$[RuW\{\mu\text{-}\eta^5,\eta'^5\text{-}(C_5H_4)CMe(C_5Me_4)\}(CO)_5]$	35
$[RuW\{\mu\text{-}\eta^5,\eta'^5\text{-}(C_5H_4)C(O)(C_5Me_4)\}(CO)_5]$	34
$[RuMo\{\mu\text{-}\eta^5,\eta'^5\text{-}C(CH_3)_2(C_5H_4)_2\}(CO)_5]$	36
$[RuW\{\mu\text{-}\eta^5,\eta'^5\text{-}CH_2(C_5H_4)_2\}(CO)_5]$	36
$[RuW(\mu\text{-}1\kappa C^\alpha,1{:}2\kappa S\text{-}SCTol)(\eta^5\text{-}C_2B_9H_{11})\{\kappa^3\text{-}HB(pz)_3\}(CO)_4]$	31
$[RuW\{\kappa^3\text{-}HB(pz)_3\}(\eta^5\text{-}C_2B_9H_{11})(CO)_4]$	31
$[RuW\{\eta^5\text{-}9\text{-}CH(PMe_3)C_2B_9H_{10}\}Cp]$	30
$[OsW(\mu\text{-}Cl)Cl(phen)(CO)_6]$	43
$[OsW(\mu\text{-}S)_2S_2(N)(CH_2SiMe_3)_2][NBu^n{}_4]$	42
$[OsW(\mu\text{-}dmpe)(CO)_8]$	45
$[OsW(PMe_3)_2(CO)_8]$	45
$[OsW\{P(CH_2O)_3CMe\}_2(CO)_8]$	45
$[OsW\{P(CH_2O)_3CMe\}(PMe_3)(CO)_8]$	45
$[OsW\{P(OMe)_3\}(PMe_3)(CO)_8]$	45

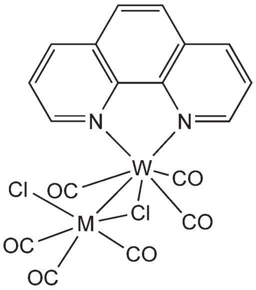
Shapley *et al.* showed that the reactions of nitrido complexes of Ru and Os with CrO_4^{2-}, MoS_4^{2-}, and WS_4^{2-} give a range of oxygen- and sulfur-bridging bimetallic complexes **33–35**, as depicted in Scheme 4.[41,42] Catalysis studies of the Os–Cr complex in the oxidation of benzyl alcohol showed that the alcohol first coordinated to the Os metal, which was then followed by β-hydrogen elimination.

Pizzotti *et al.* employed $[fac\text{-}RuCl_2(CO)_3]$ and $[fac\text{-}OsCl_2(CO)_3]$ with $[W(phen)(pyz)(CO)_3]$ (phen = 1,10-phenanthroline and pyz = pyrazine) in THF at 0–5 °C to yield Ru–W and Os–W bimetallic complexes **36** in good yields. The heterometallic metal–metal bonds of these complexes were found to be weak, as the $W(phen)(CO)_3$ group was easily



Scheme 4

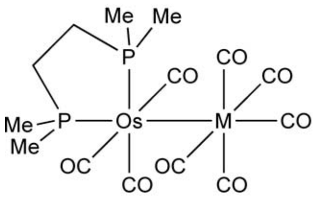
substituted by soft ligands, such as PPh_3, CO, and pyridine.[43] A similar finding that $[OsW(PMe_3)(CO)_9]$ was photolyzed with UV at 400 nm to give $W(CO)_5$ was reported by Tyler *et al.*[44]



M = Ru, Os

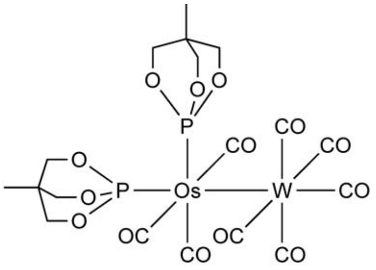
36

A comparison of the different coordinated phosphines on the stability of Os–W dinuclear complexes was reported by Pomeroy *et al.*[45] Complex **37** was prepared from the reaction of $[W(CO)_5THF]$ with the corresponding $Os(PR_3)_2(CO)_3$ in CH_2Cl_2 or *n*-hexane at room temperature. Attempts to synthesize the Cr analogs of **38**–**41** failed due to steric effects. The reactivity of **38**, **39**, and **41** with PPh_3 in CH_2Cl_2 to give $W(CO)_5(PPh_3)$ and $Os(CO)_3(PR_3)(PR'_3)$ is in the order of **39** > **41** > **38**.

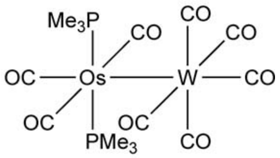


M = Cr, W

37



38



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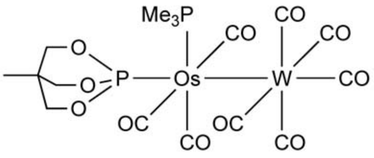

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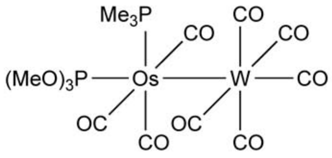
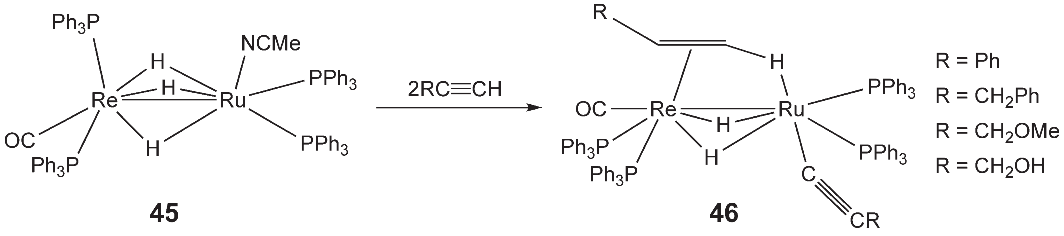


41

6.25.2.4 Ru/Os Heterodinuclear Compounds Containing Group 7 Elements

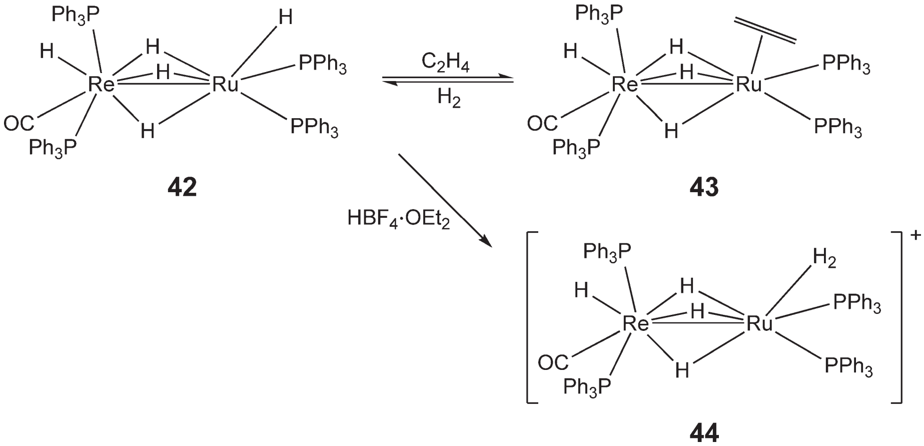
Bimetallic polyhydride complexes are an important class of catalysts due to their ability to eliminate molecular hydrogen from coordinated ligands to give unsaturated organic molecules. In this context, a series of Ru–Re mixed-metal dinuclear complexes that contain polyhydrides was extensively investigated by Mathieu *et al.*, and the reaction of K[Re(PPh_3)$_2$$H_6$] with RuHCl($PPh_3$)$_3$CO gave **42** in good yield. Complex **42** is inert to alkynes, but readily undergoes substitution by ethylene to give [RuRe(μ-H)$_3$(C_2H_4)(PPh_3)$_4$CO] **43**. Upon protonation by HBF_4, complex **42** reacted to yield the first heterometallic complex to contain molecular hydrogen, [RuRe(μ-H)$_3$-(H_2)(PPh_3)$_4$CO][BF_4] **44**[46] (see Scheme 5). As the steric and electronic properties of the phosphine ligands govern the formation of the Ru–Re complexes, the investigation of a series of different phosphines was also undertaken by Mathieu.[47] An increase in the steric bulk of the phosphine ligands caused the rate of the reaction to drop, and a higher temperature was needed for a complete reaction.

To facilitate the reactivity of the alkynes with the Ru–Re complexes, complex **42** was activated by substituting the two terminal hydrogens with CH_3CN to give **45**, which reacted with a series of alkynes to give the novel η^1,η^2-alkenyl Ru–Re complexes **46**.[48]



45 **46**

The synthesis and spectroscopy of [RuMn(Pr^i-DAB)Me(CO)$_7$] **47** (Pr^i-DAB = *N*,*N*′-diisopropyl-1,4-diaza-1,3-butadiene) and [RuMn(Pr^i-PyCa)Me(CO)$_7$] **48** (Pr^i-PyCa = pyridine-2-carbaldehyde-*N*-isopropylimine) were reported by Stufkens *et al.* (see Table 3).[49] The complexes were prepared by reacting KMn(CO)$_5$ with [Ru(Pr^i-DAB)(I)Me(CO)$_2$] or [Ru(Pr^i-PyCa)(CF_3SO_3)$_2$Me(CO)$_2$] in THF at room temperature. The lowest energy absorption band of the RuMn complex was assigned to Ru(d_π) to Pr^i-PyCa or Pr^i-DAB (π^*) using resonance Raman spectroscopy.

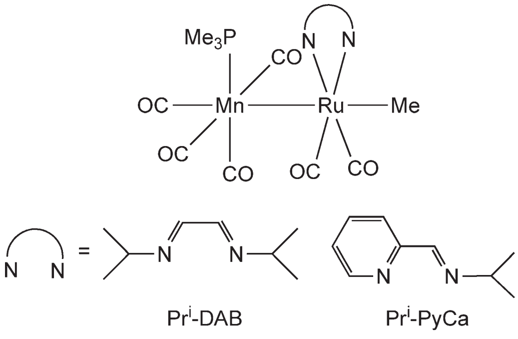


42 **43** **44**

Scheme 5

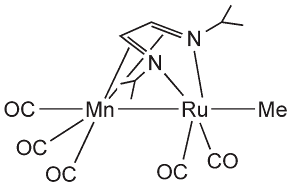
Table 3 Ru/Os mixed-metal compounds containing group 7 elements with known structures

Formula	*References*
$[\mathrm{RuMn}(\mu\text{-}\sigma,\sigma,\eta^2\text{-Pr}^i\text{-pyCa})\mathrm{Me(CO)_5}]$	50
$[\mathrm{RuMn}(\mathrm{Pr}^i\text{-PyCa})\mathrm{Me(CO)_7}]$	49
$[\mathrm{RuMn(SnPPh_3)(iPr\text{-}DAB)(CO)_7}]$	52
$[\mathrm{OsMn(CNBu^t)(CO)_8}][\mathrm{I}]$	54
$[\mathrm{RuRe}(\mu\text{-H})_2\{\mu\text{-}\eta^1,\eta^2\mathrm{CH_2CHCH_2OMe}\}\mathrm{(CHCCH_2OMe)(PPh_3)_4CO}]$	48
$[\mathrm{RuRe}(\mu\text{-H})_3\mathrm{(H)_2(PPh_3)_4CO}]$	46
$[\mathrm{RuRe}(\mu\text{-H})_3\mathrm{(PMePh_2)_2(PPh_3)_3CO}]$	47
$[\mathrm{OsReMe(CO)_9}]$	53



47 **48**

The photolysis of 47 and 48 using UV with energy that is equal to their lowest energy absorption band in hexane was studied. The photolyzed products obtained were $[\mathrm{RuMn}(\mu\text{-}\sigma,\sigma,\eta^2,\eta^2\text{-Pr}^i\text{-DAB})\mathrm{Me(CO)_5}]$ 49 and $[\mathrm{RuMn}(\mu\text{-}\sigma,\sigma,\eta^2\text{-Pr}^i\text{-PyCa})\mathrm{Me(CO)_5}]$ 50. However, when the hexane was replaced with CH_2Cl_2 or $CHCl_3$, the isolated products were $[\mathrm{Mn(CO)_5Cl}]$ and $[\mathrm{Ru(Pr^i\text{-}DAB)ClMe(CO)_2}]$ or $[\mathrm{Ru(Pr^i\text{-}PyCa)ClMe(CO)_2}]$.[50] Ru–Mn complexes with structures that are closely related to the photolyzed products 49 and 50 were reported by Elsevier *et al.*[51] Other Ru–Mn dinuclear complexes that contain halides and $SnPh_3$ like $[\mathrm{RuMnBr(iPr\text{-}DAB)(CO)_7}]$ and $[\mathrm{RuMn(SnPPh_3)(iPr\text{-}DAB)(CO)_7}]$ are also known.[52]



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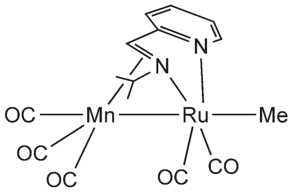
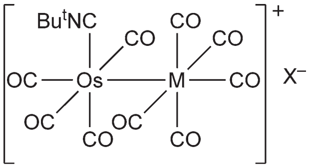


50

Only a few examples of Os–Mn and Os–Re complexes have been encountered.[53,54] A novel metal chain compound with Os–Mn and Os–Re monomers was investigated by Pomeroy *et al.* The bimetallic complexes were prepared by reacting $[\mathrm{Os(CNBu^t)(CO)_4}]$ with $[\mathrm{Mn(CO)_5I}]$ or $\{\mathrm{Re}(\mu\text{-Cl})\mathrm{(CO)_4}\}_2$ to yield, under an inert atmosphere, $[\mathrm{OsMn(CNBu^t)(CO)_8}]\mathrm{I}$ or $[\mathrm{OsRe(CNBu^t)(CO)_8}]\mathrm{Cl}$ 51.

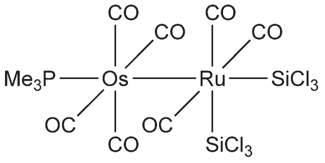


M = Mn, X = I
M = Re, X = Cl

51

6.25.2.5 Ru/Os Heterodinuclear Compounds Containing Group 8 Elements

Pomeroy *et al.* reported the only examples of Ru–Os mixed-metal dinuclear complexes in this review period. [*cis*-$Ru(SiCl_3)_2(CO)_4$] reacted with [$Os(PMe_3)(CO)_4$] or [$Os(CNBu^t)_2(CO)_3$] to give [$RuOs(PMe_3)(SiCl_3)_2(CO)_7$] **52** or [$RuOs(CNBu^t)_2(SiCl_3)_2(CO)_6$] **53** (Table 4).[55]



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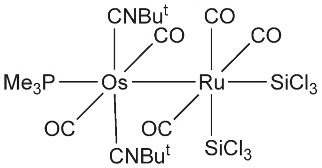

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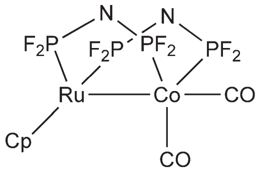
6.25.2.6 Ru/Os Heterodinuclear Compounds Containing Group 9 Elements

Mixed-metal complexes of Ru/Os with group 9 elements have been more intensely investigated than any other group. A number of reported synthetic routes have involved the use of bridging phosphine ligands to stabilize the metal–metal bonds. Mague *et al.* reported that the reactions of [$RuCl\{\eta^1\text{-}MeN(PF_2)_2\}_2Cp$] and group 9 metal carbonyl complexes ([$Co_2(CO)_8$], $\{RhCl(CO)_2\}_2$, and [$IrCl(PPh_3)_2(CO)$]) in toluene at room temperature yielded the di-bridging phosphine complexes **54–56**.[56]



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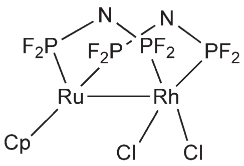

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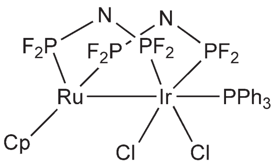
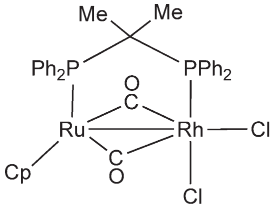


56

A similar preparation that employed [RuCl(2,2-dppp)Cp] (dppp = $Ph_2PCMe_2PPh_2$) and half an equivalent of $\{RhCl(CO)_2\}_2$ in toluene to give [$RuRh(\mu\text{-}CO)_2(2,2\text{-}dppp)Cl_2Cp$] **57** in good yield was reported by Smith *et al.*[57] Ru–Ir analogs **58** with the bridging phosphines dppm (dppm = $Ph_2PCH_2PPh_2$), dppen (dppen = $CH_2{=}C(PPh_2)_2$, and dppa (dppa = $Ph_2PNHPPh_2$) were isolated by Nawar.[58]



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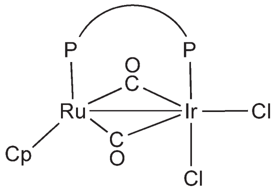

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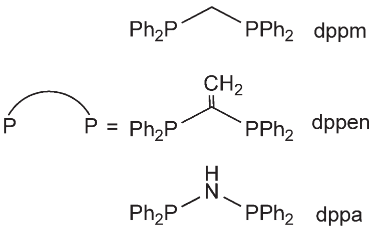
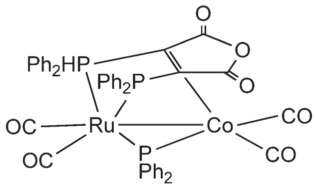


Other than bidentate-bridging phosphines, a series of mixed-metal complexes that contain bidentate non-bridging phosphines was also reported.[59] An interesting compound [$RuCo(\mu\text{-}\eta^2,\eta^2\text{-}bma)(\mu\text{-}PPh_2)(CO)_4$] **59** (bma = 2,3-bis(diphenylphosphino)maleic anhydride) was reported by Richmond *et al.* (Table 5)[60,61] The two phosphines are coordinated to the Ru atom and do not bridge across the Ru–Co metal bond, which is rare in this class of compounds.

Table 4 Ru/Os mixed-metal compounds containing group 8 elements with known structures

Formula	*References*
[$RuOs(CNBu^t)_2(SiCl_3)_2(CO)_6$]	55
[$RuOs(PMe_3)(SiCl_3)_2(CO)_7$]	55

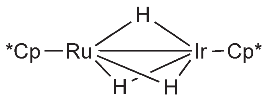


59

Table 5 Ru/Os mixed-metal compounds containing group 9 elements with known structures

Formula	*References*
[RuCo(μ-η^2,η^2-bma)(μ-PPh$_2$)(CO)$_4$]	60
[RuCo(μ-CO)(CNBu^t)(CO)$_4$Cp*]	64
[RuCo(μ-CO)(CO)$_5$Cp*]	64
[RuCo(μ-CO)$_2$(μ-dppm)(CO)$_2$Cp*]	64
[RuCo(SnPh$_3$)(Pr^i-DAB)(CO)$_6$]	52
[RuCo{μ-η^2,η^4-C(Tol)CHC(Tol)CH}(CO)$_3$Cp*]	63
[RuCo{μ-η^3-Ph$_2$PC(CO$_2$Me)C(CO$_2$Me)}{(Z)-Ph$_2$PCH=CHPPh$_2$}(μ-CO)(CO)$_3$]	61
[RuCo{η^2-MeC=CHCH=NPr^i}(μ-CO)(CO)$_5$]	51
[RuCo{(Z)-Ph$_2$PCH=CHPPh$_2$}(μ-PPh$_2$)(CO)$_5$]	61
[OsRh(η^2-C$_4$H$_8$)(μ-dppm)$_2$(CO)$_3$][BF$_4$]	72
[OsRh(η^6-*p*-cymeme)(μ-pz)$_2$(CO)$_2$][BPh$_4$]	67
[OsRh(η^6-*p*-cymeme)(μ-pz)$_2$Cl(CO)$_2$]	67
[OsRh(η^6-*p*-cymeme)(μ-pz)$_2$I(CO)]	67
[OsRh(μ-CO)(μ-H)(CF$_3$SO$_3$)(μ-dppm)$_2$(CO)$_3$][CF$_3$SO$_3$]	73
[OsRh(μ-CO)(C(Me)=CH$_2$)(μ-dppm)$_2$(CO)$_2$]	76
[OsRh(μ-CO)(η^1-CH$_2$CN)(dppm)$_2$(CO)$_2$]	75
[OsRh(μ-CO)(CH$_3$)(dppm)$_2$(CO)$_2$]	75
[OsRh(μ-CO)$_2${C(Me)=C(Me)$_2$}(CH$_3$)(μ-dppm)$_2$CO][CF$_3$SO$_3$]	76
[OsRh{μ-η^1,η^2-HCCH(PMe$_3$)}(μ-CO)Cp(CO)$_3$]	79
[OsRh{μ-CMeO}(μ-CO)(CF$_3$SO$_3$)(μ-dppm)$_2$(CO)$_2$][CF$_3$SO$_3$]	73
[OsRh{μ-CMeO}(CF$_3$SO$_3$)(dppm)$_2$(CO)$_2$][CF$_3$SO$_3$]	73
[RuRh(μ-η^1,η^1-(MeCO$_2$)C=C(CO$_2$Me))(μ-dppm)$_2$(CO)$_2$][BF$_4$]	71
[RuRh(μ-η^1,η^1-CF$_3$C=CCF$_3$CH$_2$)(μ-dppm)$_2$(CO)$_3$][CF$_3$SO$_3$]	71
[RuRh(μ-η^2,η^4-(CH=C(CH$_2$OH)CH=(CH$_2$OH)CH$_2$)(μ-dppm)$_2$(CO)$_2$][CF$_3$SO$_3$]	71
[RuRh(η^4-C$_8$H$_{12}$)(μ-pz)(μ-H)(PPr$^i{}_3$)$_2$(CO)$_2$][BF$_4$]	65
[RuRh(μ-CH$_2$)(μ-CO)(μ-dppm)$_2$(CO)$_3$][BF$_4$]	70
[RuRh(μ-CH$_2$)(PMe$_3$)(μ-dppm)$_2$(CO)$_3$][BF$_4$]	70
[RuRh(μ-CO)(μ-PBu$^t{}_2$)(μ-dppm)(CO)$_3$]	59
[RuRh(μ-CO)(μ-PBu$^t{}_2$)(μ-HPBu$^t{}_2$)(CO)$_4$]	59
[RuRh(μ-CO)$_2$(dppp)Cl$_2$Cp]	57
[RuRh(μ-dppm)$_2$(CO)$_4$][BF$_4$]	70
[RuRh{μ-MeN(PF$_2$)$_2$}$_2$(PMe$_2$Ph)Cl$_2$Cp]	56
[RuRh{(*S*)-μ-η^2-O$_2$CCH(OH)Ph}(μ-H)PhCp][ClO$_4$]	81
[RuIr(μ-η^1,η^2-CH=CH$_2$)$_2$HCp$^*{}_2$]	62
[RuIr(η^6-*p*-cymeme)(μ-pz)$_2$(μ-CO)Cl(PPh$_3$)(CO)]	66
[RuIr(η^6-*p*-cymeme)(μ-pz)$_2$I(CO)$_2$]	67
[RuIr(μ-CH$_2$)(μ-CO)(μ-dppm)$_2$(CO)$_3$][BF$_4$]	69
[RuIr(μ-CH$_2$)(PMe$_3$)(μ-dppm)$_2$(CO)$_3$][BF$_4$]	69
[RuIr(μ-CO)(μ-dppm)$_2$H(CO)$_3$]	69
[RuIr(μ-CO)$_2$(μ-dppa)Cl$_2$Cp]	58
[RuIr(μ-H)(μ-η^2,η^4-MeCH=CHC$_6$H$_4$)Cp$^*{}_2$]	62
[RuIr(μ-H)$_3$Cp$^*{}_2$]	62
[OsIr(μ-η^2,η^2-B$_3$H$_3$)(μ-H)$_4$(PPh$_3$)$_2$(CO)Cp*]	77
[OsIr(μ-η^3,η^3-B$_4$H$_3$Cl)(μ-H)$_2$(PPh$_3$)$_2$(CO)Cp*]	77
[OsIr(μ-η^4,η^4-B$_5$H$_5$)(H)(PPh$_3$)$_3$CO]	77
[OsIr(η^6-*p*-cymeme)(μ-pz)$_2$(μ-CO)(PPh$_3$)(CO)][BPh$_4$]	66
[OsIr(GeCl$_3$)Cl(CO)$_5$Cp]	80
[OsIrBr$_2$(CO)$_5$Cp]	80

Ionic coupling of $[RuCp^*(MeCN)_3][BF_4]$ with $Li[IrCp^*H_3]$ in THF at room temperature afforded the polyhydrido Ru–Ir complex $[RuIr(\mu\text{-}H)_3Cp^*_2]$ **60**. Complex **60** was reacted with ethene, PhC≡CMe, and PhC≡CPh to give $[RuIrH(\mu\text{-}\eta^1:\eta^2\text{-}CH{=}CH_2)_2Cp^*_2]$ **61**, $[RuIr(\mu\text{-}H)(\mu\text{-}\eta^2:\eta^4\text{-}MeCH{=}CHC_6H_4)Cp^*_2]$ **62**, and $[RuIr(\mu\text{-}H)_2(\mu\text{-}\eta^1:\eta^2\text{-}(Z)\text{-}CPh{=}CHPh)Cp^*_2]$ **63**, respectively.[62]



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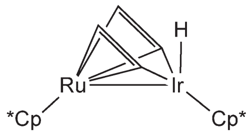

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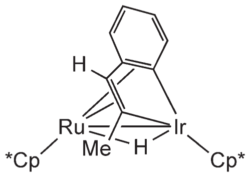

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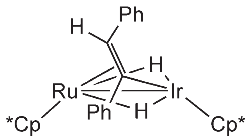
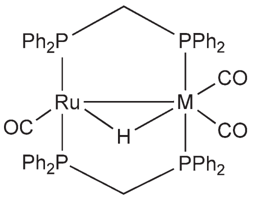


63

The interaction of $[RuCp^*Cl(CO)_2]$ and $Na[Co(CO)_4]$ in THF at 60 °C afforded $[RuCo(\mu\text{-}CO)Cp^*(CO)_5]$ **64** in good yield. Various CO substitution reactions to give **65–67** were demonstrated by Matsuzaka *et al.*, and are depicted in Scheme 6.[63,64] The catalytic activity of complex **64** in the head-to-head coupling of methyl propiolate to give $[(E)\text{-}(MeO_2C)CH{=}CH(C{\equiv}CCO_2Me)]$ was investigated.

A series of Ru–Rh pyrazolate-bridged dinuclear complexes **68–74** were isolated by Oro *et al.*[65] The preparation involved the coupling of Ru-pyrazolate cations with Rh olefin complexes. The pyrazolate-bridged Ru/Os–group 9 mixed-metal complexes were able to undergo stereospecific substitution with PPh_3 as shown in Scheme 7.[66,67] A review of pyrazolate-bridged mixed-metal complexes that includes a number of different bimetallic systems was prepared by Akita.[68]

Ru–Rh and Ru–Ir complexes containing bridging CH_2 groups were extensively studied by Cowie *et al.*[69,70] The mixed-metal complexes were prepared by the coupling of $[PPN][HRu(CO)_4]$ with $[M(dppm)_2Cl]$ in THF to yield $[RuM(\mu\text{-}H)(dppm)_2(CO)_3]$ **75** (M = Ir or Rh). Complex **75** was further reacted with HBF_4, followed by the addition of CO at the Ru atom to give $[RuM(dppm)_2(CO)_4][BF_4]$ **76**. Diazomethane was then employed to yield $[RuM(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2(CO)_3][BF_4]$ **77**. Compound **77** reacted with PMe_3 through the substitution of the μ-CO to give $[RuM(\mu\text{-}CH_2)(dppm)_2(PMe_3)(CO)_3][BF_4]$ **78**.



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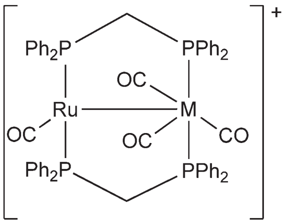

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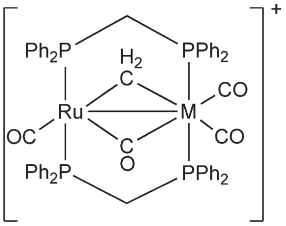

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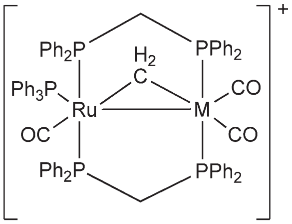
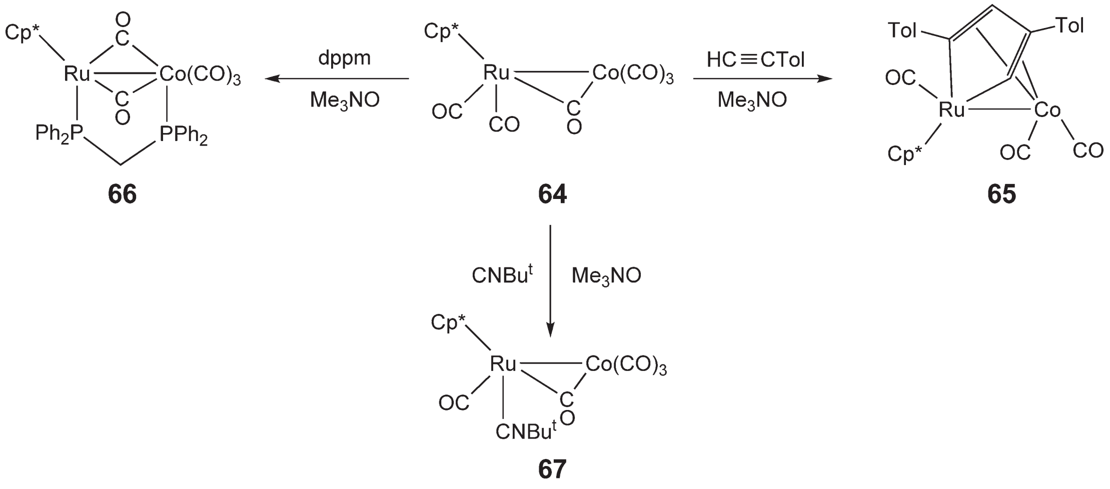
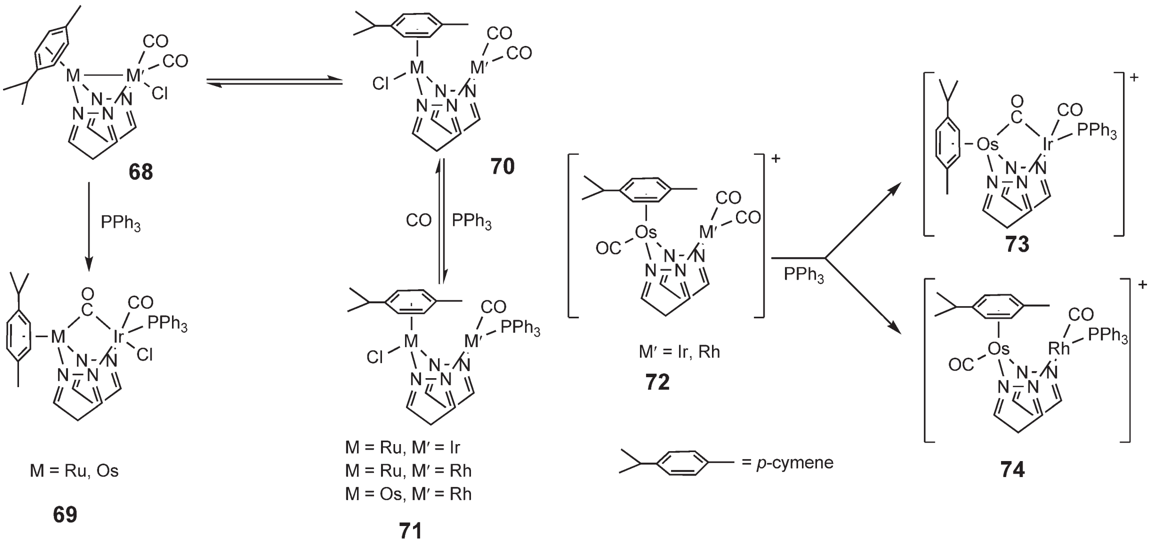


M = Rh, Ir

78

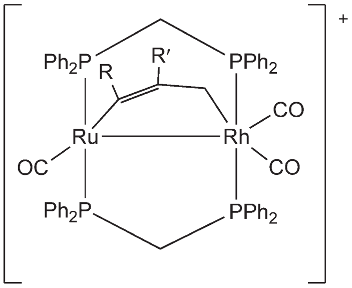


Scheme 6



Scheme 7

The interaction of a range of alkynes with complex 77 (M = Rh) was investigated, and bimetallic complexes [RuRh(μ-η^1,η^1-RC=CR′CH$_2$)(dppm)$_2$(CO)$_3$][CF$_3$SO$_3$] 79 (R = R′ = CO$_2$Me, CF$_3$, CO$_2$Et or R = CH$_3$; R′ = CH(OEt)$_2$, CH$_2$OH) were isolated. The CH$_2$ group was inserted into the alkynes to form a C$_3$ moiety that bridges the Ru–Rh bond with the vinylic end bonded to Rh and the alkyl end bonded to Ru, which is a good model for C$_3$H$_6$-bridging intermediates for the bulk Rh/Os system. C$_2$(CO$_2$Me)$_2$ reacts with 76 (M = Rh) in the presence of Me$_3$NO to give 80, which in the reaction with CH$_2$N$_2$ did not give the expected CH$_2$-inserted complex but instead complex 81 was isolated.[71]



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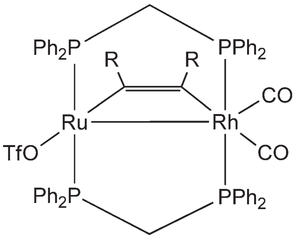
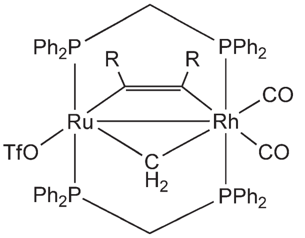


R = CO$_2$Me

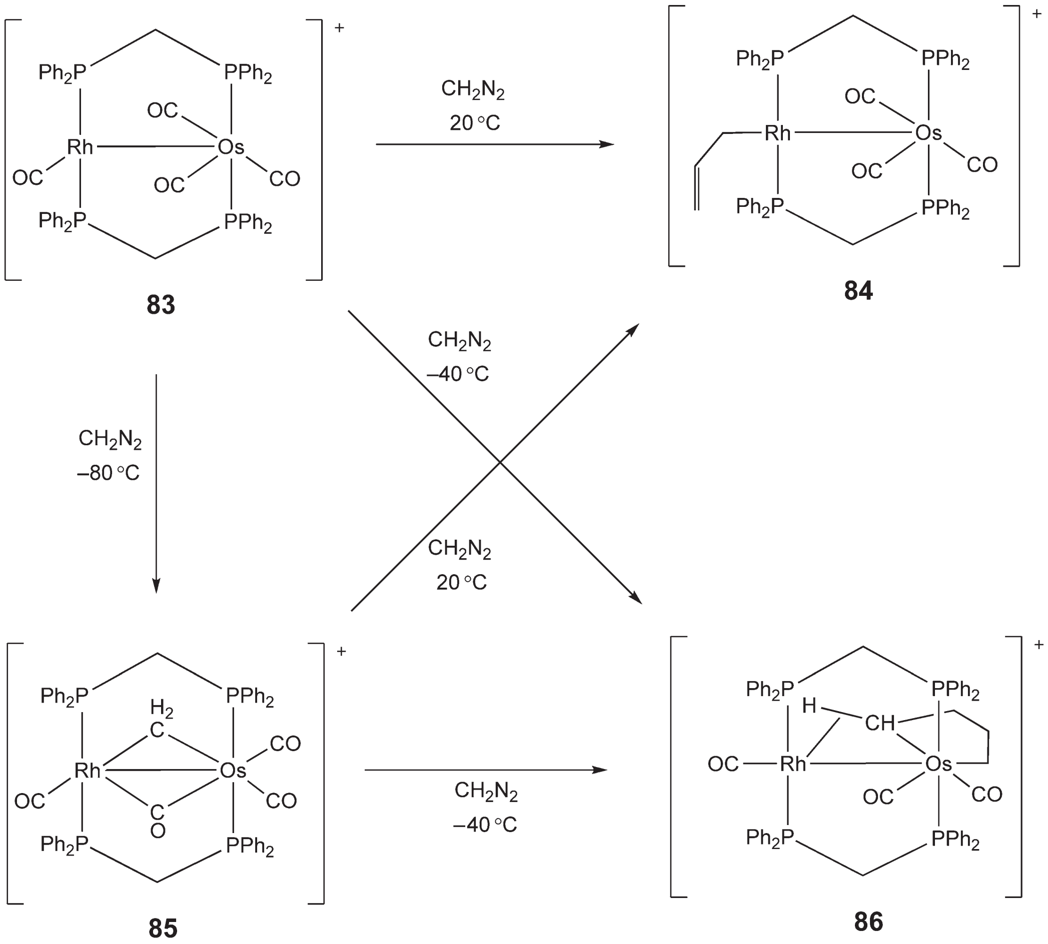
80



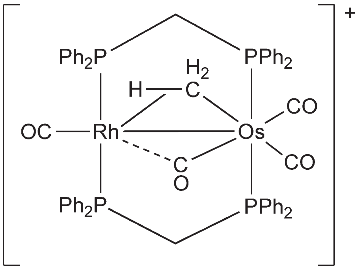
81

An analogous methylene-bridged Os–Rh system was also reported from the reaction of [PPN][HOs(CO)$_4$] with [Rh(dppm)$_2$Cl] to give [OsRh(μ-H)(dppm)$_2$(CO)$_3$] **82**, which was then reacted with HBF$_4$ and then CO to yield [OsRh(dppm)$_2$(CO)$_4$][BF$_4$] 83. Diazomethane was employed at different temperatures to give complexes 83–86, as shown in Scheme 8. Depending on the temperature of the reaction, C$_3$ or C$_4$ fragments were made through the coupling of the μ-CH$_2$ groups. By ^{13}C-enriched labeling, the sequence of the reactions was investigated by ^{13}C-NMR.[72]

The protonation of methylene-bridged 85 with triflic acid at −80 °C yielded a new methyl-containing complex 87. This was then warmed to −40 °C to form 88 with the migration of the methyl group from Os to the Rh metal. Further warming of 88 up to 25 °C caused the semibridging carbonyl to interact with the methyl group to give the acetyl-bound complex 89. Attempts to reduce the acetyl group to ethanol by the reaction of 89 with diazomethane, PMe$_3$, or carbon monoxide were not successful.[73]



Scheme 8



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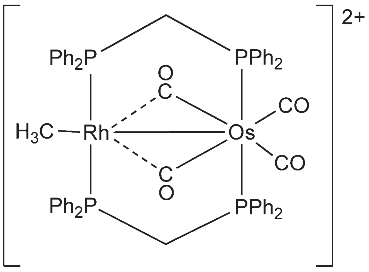

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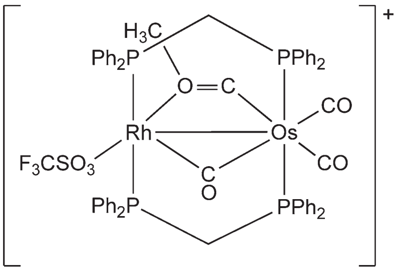
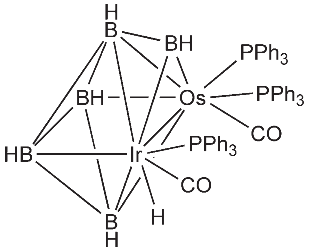


89

It has been suggested that Os–Rh complexes possess a suitable binding affinity with hydrocarbon fragments, but are still sufficiently labile for methylene insertion.[74] In addition to the bridging methylene, Cowie *et al.* also reported a detailed study on alkyl and hydrido Os–Rh complexes that show a site-specific reductive elimination of methane[75] and vinyl, allyl Os–Rh complexes with vinyl to carbene transformations.[76]

Barton *et al.* reported an interesting series of Os–Ir boranes complexes with a *pileo-closo-nido* structural sequence. $[Os(B_5H_9)(PPh_3)_2CO]$ was reacted with $^{n}BuLi$ and a 0.5 equiv. of $[(Cp^{*}IrCl_2)_2]$ in THF at −35 °C to give complexes 90–92.[77,78]



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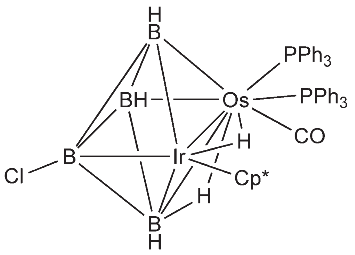

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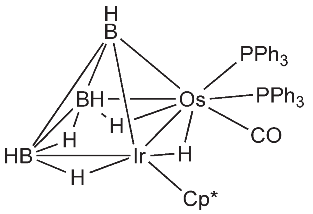
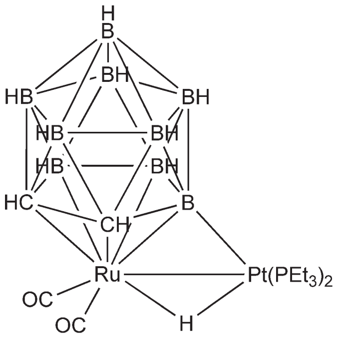


92

The substitution of the carbonyl ligands of Os carbonyl complexes with Ir/Rh aryl complexes was investigated, and simple coupling products were formed.[79,80]

6.25.2.7 Ru/Os Heterodinuclear Compounds Containing Group 10 Elements

Ru–Pt and Ru–Ni carborane complexes were isolated by Stone *et al.* The reaction between $[K(18\text{-crown-}6)][Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})H(CO)_2]$ and $[PtHCl(PEt_3)_2]$ in THF in the presence of $TlPF_6$ gave a bimetallic complex **93**.[82] A similar reaction was reported by Kim *et al.* using *nido*-$[Ru(6\text{-}\eta^6\text{-}Pr^iC_6H_4Me)B_9H_{13}]$, KH, and $[PtCl_2(PMe_2Ph)_2]$.[83,84] In contrast, the cationic Ni carborane complex *closo*-$[NEt_4][(4,1,6\text{-}Ni\text{-}\eta^5\text{-}C_2B_{10}H_{12})(4\text{-}\eta^3\text{-}C_3H_5)]$ reacts with $[Ru(PPh_3)_2Cl_2]$ in THF to give complex **94**. No direct metal–metal bond was observed in the solid-state structure of **94**. The Ru is bonded to the carborane cage through a B–H–Ru agostic interaction (see Table 6).[85]



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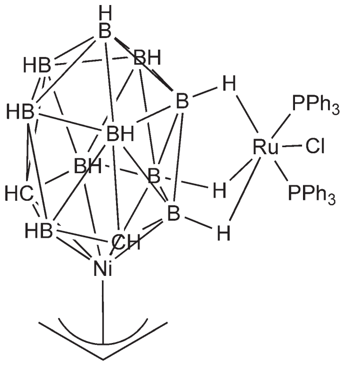
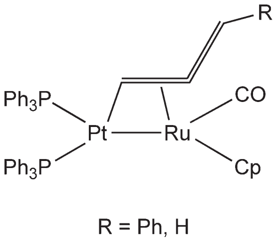


94

Table 6 Ru/Os mixed-metal compounds containing group 10 elements with known structures

Formula	*References*
$[RuNi(\mu\text{-}\eta^3,\eta^3\text{-}C_2B_{10}H_{10})(\eta^3\text{-}C_3H_5)(\mu\text{-}H)_2(PPh_3)_2]$	85
$[RuNi(TP^{\#})(\mu\text{-}\eta^1\text{-}C{=}CHPh)(\mu\text{-}CO)(CO)Cp]$	91
$[RuNi(TP^{\#})(\mu\text{-}CO)_2(PPh_3)Cp]$	91
$[RuNi(TP^{\#})(CO)_2Cp]$	91
$[OsPd(MeCN)(\mu\text{-}\eta^5,\eta^1\text{-}C_5H_3PPh_2)_2]$	92
$[RuPt(\mu\text{-}\sigma,\eta^5C_2B_9H_{10})(\mu\text{-}H)(PEt_3)_2(CO)_2]$	82
$[RuPt(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}HC{=}C{=}CH_2)(PPh_3)_2(CO)Cp]$	86
$[RuPt(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}PhC{=}C{=}CH_2)(PPh_3)_2(CO)Cp]$	86
$[RuPt(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}PhC{=}C{=}CHC(O)NHSO_2Tol)(PPh_3)(CO)Cp]$	88
$[RuPt(\mu\text{-}\eta^1,\eta^1{}_{\alpha,\beta}\text{-}HCC(O)CH_3)(\mu\text{-}H)(PPh_3)_2COCp]$	87
$[RuPt(\mu\text{-}\eta^4,\eta^4\text{-}B_9H_9)(\mu\text{-}H)_2(\eta^5\text{-}Pr^iC_6H_4Me)(PMe_2Ph)_2]$	83
$[RuPt(\mu\text{-}\eta^5,\eta^3\text{-}B_9H_9)(\mu\text{-}\eta^6,\eta^1\text{-}PPh_3)(PMe_2Ph)_2]$	84
$[RuPt(\mu\text{-}\eta^5,\eta^4\text{-}B_9H_9)(\eta^6\text{-}Pr^iC_6H_4Me)(PMe_2Ph)_2]$	83
$[RuPt(Cl)_2(\mu\text{-}dmpm)(PPh_3)Cp][PF_6]$	90
$[RuPt(\mu\text{-}dppm)(\mu\text{-}CO)(Cl)_2(CO)]$	89
$[RuPt\{\mu\text{-}\eta^1,\eta^2\text{-}C{=}CPhN(SO_2Tol)COCH_2\}(PPh_3)(Bu^tCN)(CO)Cp]$	88

Two Ru–Pt complexes with the common formula [RuPt(μ-η^1,$\eta^2_{\alpha,\beta}$-RC = C = CH$_2$)(PPh$_3$)$_2$CpCO] **95** (R = Ph, H) were isolated from the reactions of [Ru(RC = C = CH$_2$)Cp(CO)$_2$] with [Pt(PPh$_3$)$_4$] or [Pt(PPh$_3$)$_2$C$_2$H$_4$] in THF at −78 °C by Wojcicki *et al.*[86] The conversion of the allenyl group in **95** to give the hydrido-alkylidiene group in **96** was achieved by stirring with alumina, silica, or Florisil in CH$_2$Cl$_2$ or CHCl$_3$.[87] The reaction of **95** with *p*-TolSO$_2$NCO in toluene at −78 °C yielded a γ-carbon-substituted product **97** and a [3 + 2]-cycloadduct **98**.[88]



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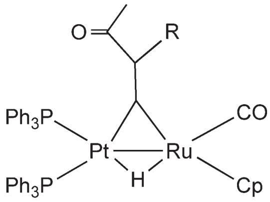

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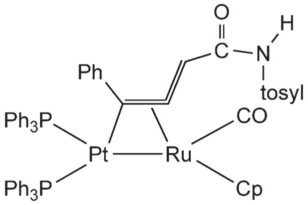

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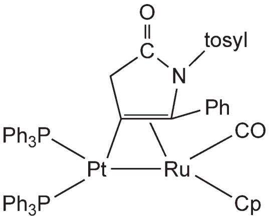
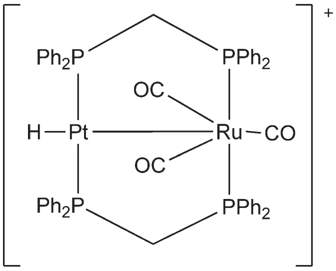


98

Bridging bidentate phosphine-stabilized Pt–Ir complex **99** was prepared from the reaction of [Pt(dppm)$_2$]Cl$_2$ with PPN[HRu(CO)$_4$] in CH$_2$Cl$_2$ at −80 °C. Complex **99** underwent chlorination to yield the neutral complex **100**.[89] A similar Ru–Pt complex was isolated by Mague *et al.*[90]



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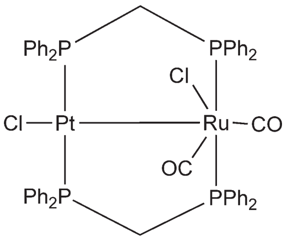
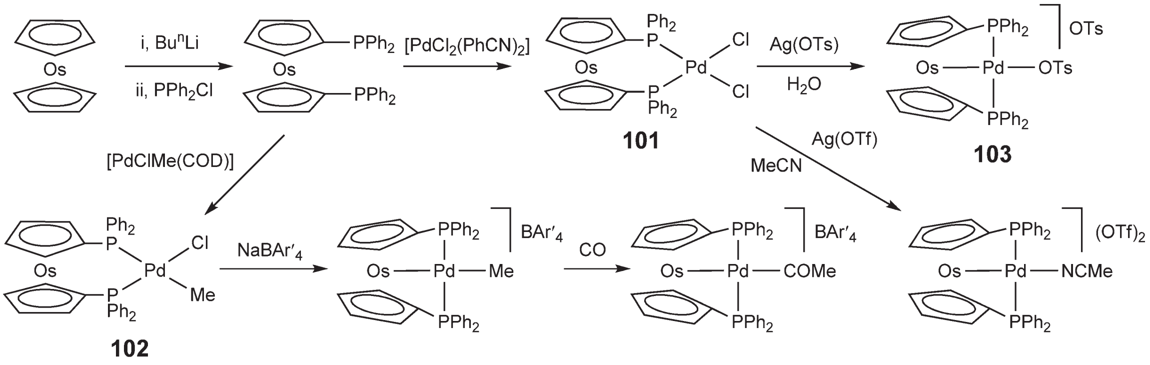


100

Gusev *et al.* reported some rare examples of Os–Pd dinuclear complexes from the reaction of osmocene with [PdCl(Me)(COD)] or [PdCl$_2$(PhCN)$_2$] (COD = 1,5-cyclooctadiene). The resulting Os–Pd complexes **101 and 102** were further reacted to give a series of derivatives, as shown in Scheme 9. The catalysis of the methoxycarbonylation of ethene (TOF = 402) and styrene (TOF = 44) by complex **103** were investigated.[92]

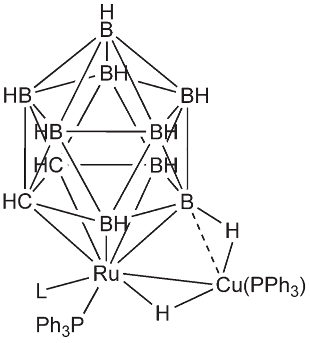


BAr′$_4$ = 3,5-(CF$_3$)$_2$C$_6$H OTf = trifluoromethanesulfonate OTs = *p*-toluenesulfonate

Scheme 9

6.25.2.8 Ru/Os Heterodinuclear Compounds Containing Group 11 Elements

Ionic coupling of [RuH(η^5-7,8-$C_2B_9H_{11}$)L(PPh_3)]$^-$ (L = PPh_3, CO) with [MCl(PPh_3)$_x$] (M = Cu, x = 3; Au, x = 1) in THF at room temperature afforded the bimetallic complexes **104 and 105** in good yields. The bonding in the B–H–Cu moiety can be regarded as a three-center two-electron bond, in which the boron atom is also partially bonded to the Cu atom.[93,94]



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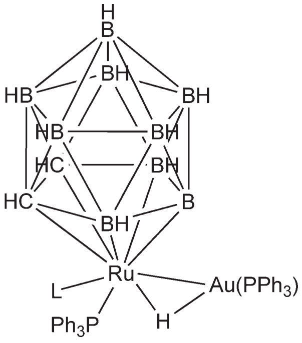
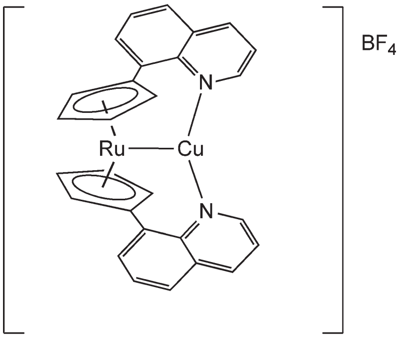


105

L = PPh_3, CO

The first example of an adduct of ruthenocene derivatives with copper was reported by Enders *et al.* (see Table 7).[95] The complex [Ru(qcp)$_2$] (qcp = 8-quinolylcyclopentadienyl) reacts with [Cu(MeCN)$_4$][BF_4] in toluene to yield complex **106** in good yield. The ruthenocene can be regarded as a tridentate ligand to the d^{10} metals ion. Compound **106** is chiral, and has C_2 symmetry. An irreversible pair of cathodic (+0.37 V vs. SCE) and anodic (+1.2 V) events was observed in the cyclic voltammogram. A similar tridentate ruthenium analog *trans*-[RuL_2(CO)$_3$] (L = 2-(Ph_2P)py) reacts with [Ag(CF_3SO_3)] in THF to give complex **107**.[96]



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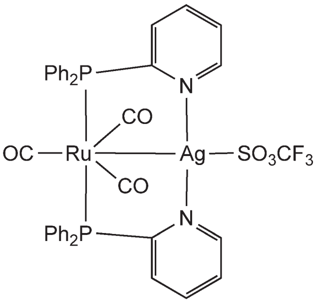


107

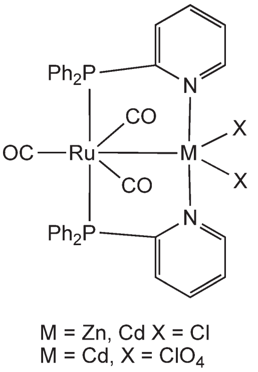
Only one Os–Ag dinuclear complex was reported in this review period. [OsAg(O_2CCF_3)(PPh_3)$_2$(CO)$_3$] **108** was isolated from the reaction of *trans*-[Os(PPh_3)$_2$(CO)$_3$] and [Ag(O_2CCF_3)(PPh_3)$_2$(CO)$_3$] in THF.[97] The oxidation potential of **108** was found to be 0.55 V in CH_2Cl_2 (vs. Ag/Ag$^+$), which is 0.51 V more positive than *trans*-[Os(PPh_3)$_2$(CO)$_3$] under the same conditions. The Ag–Os bond length is 2.712(1) Å, which is consistent with the Os → Ag$^+$ dative bonding situation.[97]

Table 7 Ru/Os mixed-metal compounds containing group 11 elements with known structures

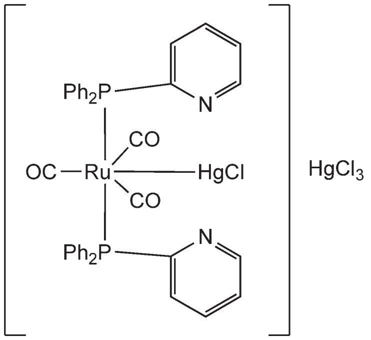
Formula	*References*
[RuCu(μ-η^5,η^1-qcp)$_2$][BF_4]	95
[RuCu(μ-H)$_2$(η^5-$C_2B_9H_{10}$)(PPh_3)$_3$]	93
[OsAg(O_2CCF_3)(PPh_3)$_2$(CO)$_3$]	97
[RuAg(μ-Ph_2Ppy)(CF_3SO_3)(CO)$_3$]	96
[RuAu(μ-H) (η^5-$C_2B_9H_{11}$)(PPh_3)$_2$(CO)]	94
[RuAu(μ-H)(η^5-$C_2B_9H_{11}$)(PPh_3)$_3$]	93

6.25.2.9 Ru/Os Heterodinuclear Compounds Containing Group 12 Elements

A series of bimetallic complexes of Ru with group 12 metals was obtained from the reaction of $[Ru(L)_2(CO)_3]$ (L = 2-(Ph_2P)py, *N*-(Ph_2PCH_2morpholine)) and MCl_2, $M'(ClO_4)_2$, $M''(I)_2$ (M = Zn, Cd, Hg, M′ = Cd, M″ = Cd, Hg) in CH_2Cl_2 at room temperature (Table 8). The mixed-metal complexes **109–111** isolated were found to have common structural features.[96,98]



109



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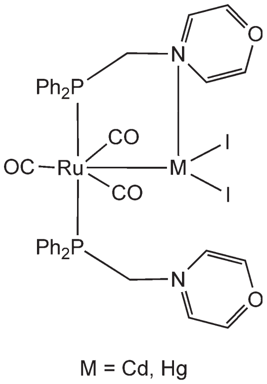
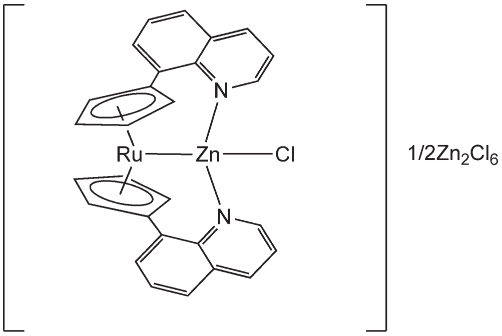


111

Enders *et al.* reported the first example of adduct formation between Zn and ruthenocene derivatives, complex 112, from the reaction of $[Ru(qcp)_2]$ and $ZnCl_2$ in toluene at ambient temperature.[95]



112

6.25.3 Cluster Compounds

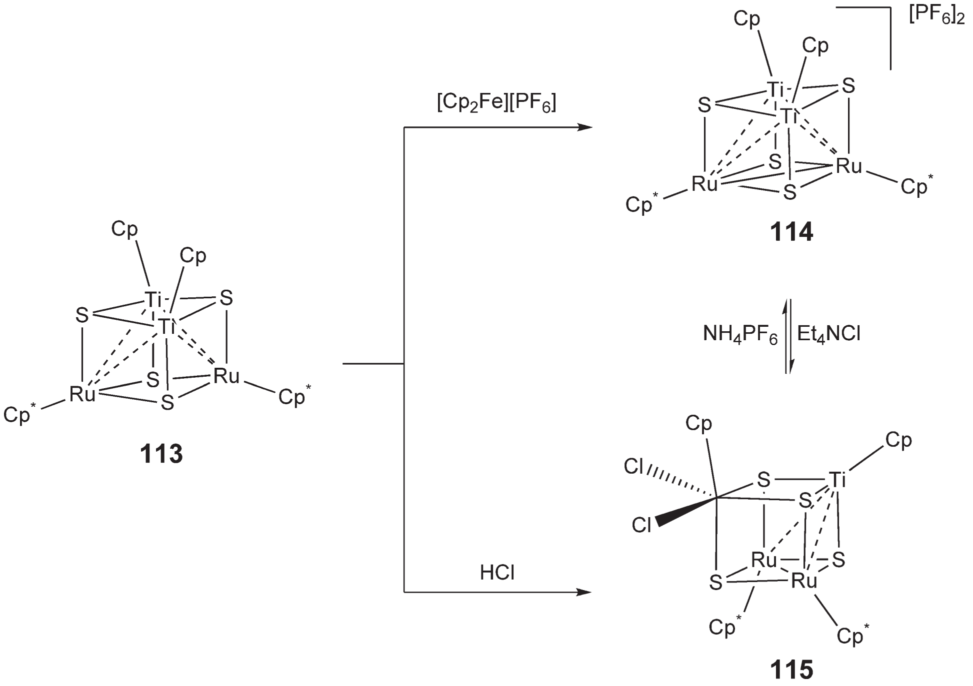
The Ru/Os mixed-metal clusters with known structures reported within this reviewing period are listed in Tables 9–17.

Table 8 Ru/Os mixed-metal compounds containing group 12 elements with known structures

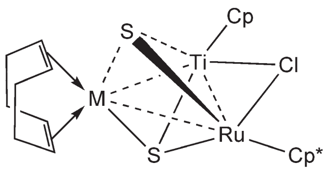
Formula	*References*
$[RuZn(\mu\text{-}\eta^5,\eta^1\text{-qcp})_2][Zn_2Cl_6]_{0.5}$	95
$[RuZn(\mu\text{-}Ph_2Ppy)(Cl)_2(CO)_3]$	98
$[RuCd(\mu\text{-}Ph_2Ppy)(Cl)_2(CO)_3]$	98
$[RuCd(\mu\text{-}Ph_2Ppy)(ClO_4)_2(CO)_3]$	98
$[RuCd\{\mu\text{-}N\text{-}(Ph_2PCH_2\text{morpholine})\}\{N\text{-}(Ph_2PCH_2\text{morpholine})\}I_2(CO)_3]$	96
$[RuHg(Ph_2Ppy)Cl(CO)_3][HgCl_3]$	98
$[RuHg\{\mu\text{-}N\text{-}(Ph_2PCH_2\text{morpholine})\}\{N\text{-}(Ph_2PCH_2\text{morpholine})\}I_2(CO)_3]$	96

6.25.3.1 Ru/Os Mixed-metal Clusters Containing Group 4 Elements

The early–late heterobimetallic cubane-type sulfido clusters, such as **113**, were prepared from the reaction of heterobimetallic complex [RuTi(μ-SH)$_2$ClCp$_2$Cp*] **120** with triethylamine at −78 °C.[99] Compound **113** was also prepared by reacting the [(CpTiS)$_2$(μ-S)$_2$]$^{2-}$ anion with {Cp*Ru(μ_3-Cl)}$_4$ directly.[100] X-ray analysis and extended Hückel molecular calculations have indicated that the compound **113** has four Ru → Ti dative bonds and a weak Ti–Ti interaction. The reaction of **113** with 3 equiv. of [Cp$_2$Fe][PF$_6$] gave the dicationic cluster **114**, which contains an additional Ru–Ru bond. However, the oxidation of **113** with an excess of HCl afforded the neutral dichloride cluster **115**. Interconversion between **114** and **115** can be achieved with a chloride or hexafluorophosphate anion.

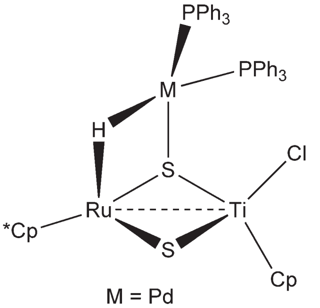


Further chloride substitution of **115** to give [Ru$_2$Ti$_2$(μ_3-S)$_4$Cl$_3$CpCp$^*_2$] **116** was observed in boiling 1,2-dichloroethane.[101] The crossed condensation of the two different hydrosulfide-bridged dinuclear complexes [(Cp*Ru(μ-SH)Cl)$_2$] with [RuTi(μ-SH)$_2$ClCp$_2$Cp*] afforded a novel cubane-type sulfido cluster [Ru$_3$Ti(μ_3-S)$_4$CpCp$_3^*$] **117**. Variable-temperature ^{1}H NMR measurements showed that the Ru–Ru bond in **117** is mobile. In contrast to **113**, cluster **117** underwent oxidation with [Cp$_2$Fe][PF$_6$] or HCl to give dicationic cluster [Ru$_3$Ti(μ_3-S)$_4$CpCp$_3^*$]X$_2$ (X = Cl **118**, X = PF$_6$ **119**).[102] It appears that the synthetic strategy that is based on [RuTi(μ-SH)$_2$ClCpCp*] **120** can be used to generate heterotrimetallic sulfido clusters. A series of trimetallic complexes **121–124** with TiRuM core were prepared and structurally characterized (Table 9).[103]



M = Rh
M = Ir

121
122



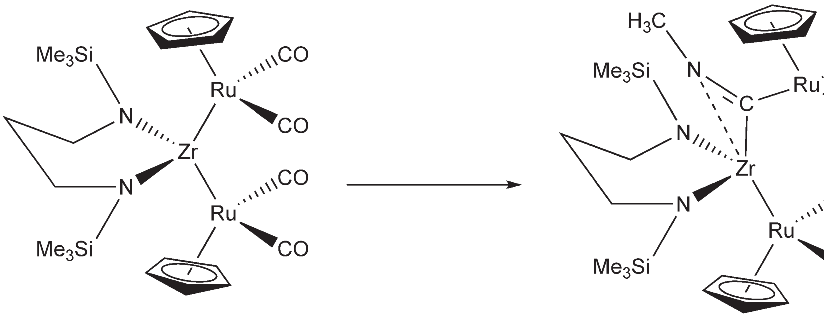
M = Pd
M = Pt

123
124

Table 9 Ru/Os mixed-metal clusters containing group 4 elements with known structure

Formula	*References*
Clusters with two different kinds of metal	
$[Ru_2Ti(PPh_3)_2(\mu_3\text{-}S)_2(\mu\text{-}Cl)_2CpCp^*]$	103
$[Ru_2Ti_2(\mu_3\text{-}S)_4Cl_2Cp_2Cp^*_2]$	101
$[Ru_2Ti_2(\mu_3\text{-}S)_4Cl_3Cp_2Cp^*_2]$	101
$[Ru_2Ti_2(\mu_3\text{-}S)_4Cp_2Cp^*_2]$	99,100
$[Ru_2Ti_2(\mu_3\text{-}S)_4Cp_2Cp^*_2][PF_6]_2$	101
$[Ru_3Ti(\mu_3\text{-}S)_4CpCp^*_3]$	102
$[Ru_3Ti(\mu_3\text{-}S)_4CpCp^*_3]Cl_2$	102
$[Ru_2ZrCH_2(CH_2NSiMe_3)_2(CO)_4Cp_2]$	104
$[Ru_2ZrCH_2(CH_2NSiMe_3)_2(CNMe)(CO)_4Cp_2]$	104
Clusters with three different kinds of metal	
$[RuTiIr(COD)(\mu_3\text{-}S)_2(\mu\text{-}Cl)CpCp^*]$	103
$[RuTiPd(PPh_3)_2(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}H)ClCpCp^*]$	103
$[RuTiPt(PPh_3)_2(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}H)ClCpCp^*]$	103
$[RuTiRh(COD)(\mu_3\text{-}S)_2(\mu\text{-}Cl)CpCp^*]$	103
$[Ru_2Ti_2Pd_2(PPh_3)(\mu_3\text{-}S)_3(\mu\text{-}O)\{\mu_3\text{-}SC(CO_2Me)C(CO_2Me)\}Cp_2Cp^*_2]$	334
$[Ru_2Ti_2Pd_2(PPh_3)(\mu_3\text{-}S)_4(\mu_3\text{-}O)(\mu\text{-}H)_2Cp_2Cp^*_2]$	334

A trinuclear Ru_2Zr complex $[CH_2(CH_2NSiMe_3)_2Zr\{Ru(CO)_2Cp\}_2]$ **125** that possesses two highly polar metal–metal bonds was prepared. The insertion of methylisocyanide into one of the Ru–Zr bonds in **125** to give **126** was observed.[104]

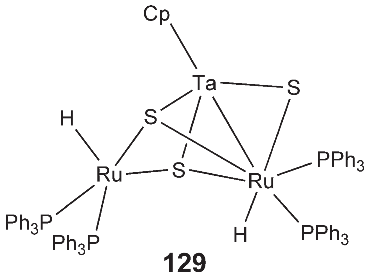


125

126

6.25.3.2 Ru/Os Mixed-metal Clusters Containing Group 5 Elements

Several amphiphilic ruthenium clusters that contain an oxovanadium $[(\eta^6\text{-p-MeC}_6H_4Pr^i)_4Ru_4V_6O_{19}]$ **127** or oxomolybdenum $[(\eta^6\text{-p-MeC}_6H_4Pr^i)_4Ru_4Mo_6O_{16}]$ **128** core were obtained from the reactions of arene ruthenium dichloride dimer with sodium vanadate or sodium molybdate (Table 10).[105] The ^{17}O NMR spectroscopy and partial charge calculations indicated the presence of three different kinds of oxygen atoms in **128**. A new Chevrel-type cluster that contains Ru and Nb has been reported.[106] The synthesis of phases of composition $Nb_xRu_{6-x}Te_8$ $(2.83 \leq x \leq 3.50)$ was confirmed by the X-ray powder method. The reaction of $[\{Cp^*TaS_3Li_2(THF)_2\}_2]$ with 4 equiv. of $[RuH(Cl)(PPh_3)_3]$ in THF gave cluster **129**, in which a short Ta–Ru distance (2.703 Å) was observed.[107]



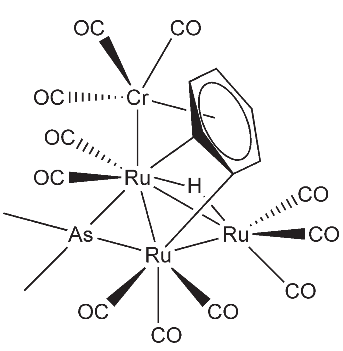
129

Table 10 Ru/Os mixed-metal clusters containing group 5 elements with known structure

Formula	*References*
$[Ru_4V_6(\eta^6\text{-p-MeC}_6H_4{}^iPr)_4O_{19}]$	105
$[Ru_2TaS_3H_2(PPh_3)_4Cp^*]$	107

6.25.3.3 Ru/Os Mixed-metal Clusters Containing Group 6 Elements

Cullen *et al.* reported the isolation of a series of Ru/Cr and Os/Cr mixed-metal clusters from the pyrolysis of $M_3(CO)_{11}[XC_6H_5Cr(CO)_3]$ (M = Ru, Os; X = PPh_2, PPr^i_2, $AsMe_2$) (Table 11).[108,109] An Ru–Cr bond is present in 130. However, no direct Os–Cr bond has been observed in any of the other reported Os/Cr systems.



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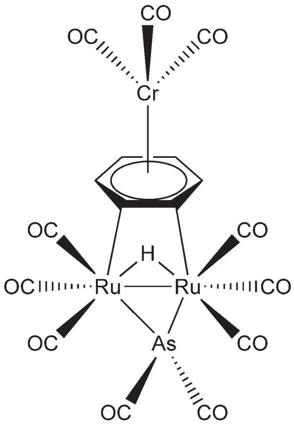
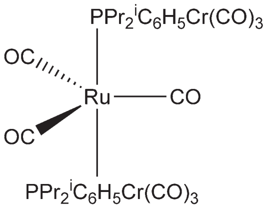


131



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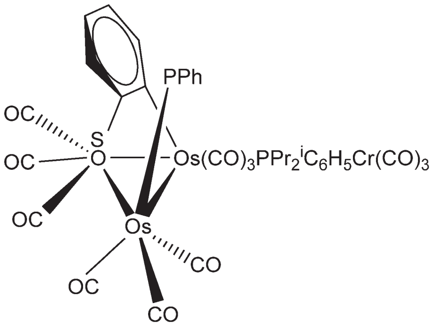
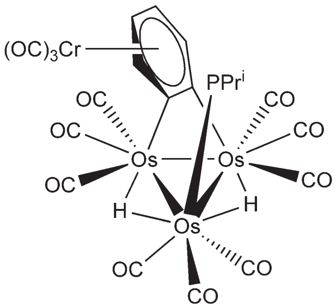
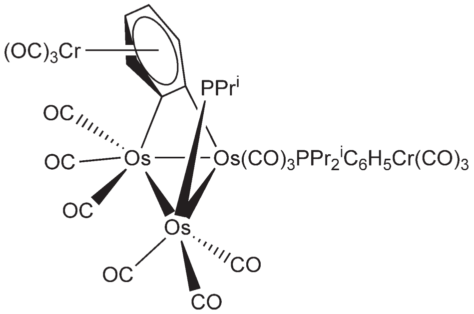


133



134



135

The dimolybdenum alkyne complexes $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)Cp_2]$ (R^1, R^2 = Me; R^1 = H, R^2 = H, Me, Ph) were employed to prepare a number of Ru–Mo mixed-metal clusters with intriguing properties. Morris *et al.* showed

Table 11 Ru/Os mixed-metal clusters containing group 6 elements with known structure

Formula	*References*
Clusters with two different kinds of metal	
$[\mathrm{RuCr(Pr_2{}^iPC_6H_5)Cr(CO)_9}]$	109
$[\mathrm{Ru_2Cr(\mu-H)(\mu-\eta^2-\eta^6-C_6H_4)(\mu-AsMe_2)(CO)_9}]$	108
$[\mathrm{Ru_3Cr(\mu-H)(\mu_3-\eta^2-\eta^6-C_6H_4)(\mu-AsMe_2)(CO)_{11}}]$	108
$[\mathrm{Os_3Cr(PhPC_6H_4)(Ph_2PC_6H_5)(CO)_{11}}]$	109
$[\mathrm{Os_3CrH_2(Pr^iPC_6H_4)(CO)_{12}}]$	109
$[\mathrm{Os_3Cr_2H_2(Pr^iPC_6H_4)(Pr_2{}^iPC_6H_5)(CO)_{14}}]$	109
$[\mathrm{RuMo_2(\eta^6-p-MeC_6H_4Pr^i)O_4\{MeC(CH_2O)_3\}_2}]$	124
$[\mathrm{RuMo_2(\mu_3-C{=}CH_2)(\mu-PPh_2)_2(CO)_4Cp_2}]$	112
$[\mathrm{RuMo_2(\mu_3-C{=}CHMe)(CO)_6(PPh_2Me)Cp_2}]$	112
$[\mathrm{RuMo_2(\mu_3-C{=}CHMe)(CO)_7Cp_2}]$	111
$[\mathrm{RuMo_2(\mu_3-CCH_2Me)(\mu-PPh_2)(CO)_5Cp_2}]$	112
$[\mathrm{RuMo_2(\mu_3-Se)(CO)_7Cp_2}]$	125
$[\mathrm{RuMo_2(\mu-C_2Ph_2)(\mu_3-S)_2(CO)_3Cp_2}]$	117
$[\mathrm{RuMo_3(\mu_3-S)_4(CO)_2(\eta^5-C_5H_4Me)_3}][\mathrm{OTs}]$	122
$[\mathrm{Ru_2Mo(\mu_3-S)(\mu-H)\{\eta^5-C_5H_4(CO_2Me)\}(CO)_8}]$	119
$[\mathrm{Ru_2Mo(\mu_3-S)(\mu-H)\{\eta^5-C_5H_4(COMe)\}(CO)_8}]$	119
$[\mathrm{Ru_2Mo(\mu_3-S)(\mu-H)\{\eta^5-C_5H_4(Me)\}(CO)_8}]$	119
$[\mathrm{Ru_2Mo(\mu-H)\ (\mu_3-NH)(CO)_8Cp}]$	131
$[\mathrm{Ru_2Mo(\mu-H)\ (\mu_3-NOMe)(CO)_8Cp}]$	131
$[\mathrm{Ru_2Mo(\mu-H)(\mu_3-PNPr^i{}_2)(CO)_8Cp}]$	133
$[\mathrm{Ru_2Mo(\mu-H)(\mu_3-PPh)(CO)_8Cp^*}]$	127
$[\mathrm{Ru_2Mo\{\mu-C_6H_4(NH_2)-1,2\}_2(PPh_3)_2(CO)_6}]$	126
$[\mathrm{Ru_2Mo\{\mu-C_6H_4(NH_2)-}\mathit{o}\mathrm{\}_2(PPh_3)_2(CO)_6}][\mathrm{PF_6}]_2$	134
$[\mathrm{Ru_2Mo_2(\mu_3-C_2Ph_2)(\mu_3-S)(\mu-SPr^i)_2(CO)_4Cp_2}]$	117
$[\mathrm{Ru_2Mo_2(\mu_3-S)_2(\mu_3-CO)\{\eta^5-C_5H_4(CO_2Me)\}(CO)_6}]$	118
$[\mathrm{Ru_2Mo_2(\mu_3-S)_2(\mu-SEt)(\mu-PPh_2)(CO)_4Cp_2}]$	116
$[\mathrm{Ru_2Mo_2(\mu_3-S)_2(\mu-SPr^i)_2(CO)_4Cp_2}]$	115
$[\mathrm{Ru_2Mo_2(\mu_3-S)_2\{\eta^5-C_5H_4(COMe)\}_2(CO)_8}]$	119
$[\mathrm{Ru_2Mo_2(\mu_3-S)_4Cl_4(DMF)_2(\eta^5-C_5EtMe_4)_2}]$	120
$[\mathrm{Ru_2Mo_2(\mu_4-Se)_2\ (PPh_3)_2(CO)_{10}}]$	129
$[\mathrm{Ru_2Mo_6(\eta^6-C_6H_5Me)_2O_{20}(OMe)_2}][\mathrm{Bu_4N}]_2$	124
$[\mathrm{Ru_2Mo_6(\eta^6-C_6Me_6)_2O_{18}\{MeC(CH_2O)_3\}_2}][\mathrm{Bu_4N}]_2$	124
$[\mathrm{Ru_2Mo_6(\eta^6-C_6Me_6)_2O_{20}(OMe)_2}][\mathrm{Bu_4N}]_2$	124
$[\mathrm{Ru_2Mo_6(\mu_3-S)_8(\eta^5-C_5H_4Me)_6(\mu-CO)_3}][\mathrm{OTs}]_2$	122
$[\mathrm{Ru_2MoS(\mu-S_2)(\mu-S)(\mu_3-S)Cp^*{}_2}]$	121
$[\mathrm{Ru_3Mo(\mu_3-C{\equiv}C)(\mu-CO)_3(CO)_2Cp_4}]$	130
$[\mathrm{Ru_3Mo(\mu_3-H)(\mu_3-PPh)(CO)_{10}Cp^*}]$	127
$[\mathrm{Ru_3Mo(\mu_3-Hg)(\mu-NH_2)(CO)_{13}Cp}]$	131
$[\mathrm{Ru_3Mo(\mu-H)(CO)_{12}Cp^*}]$	128
$[\mathrm{Ru_3Mo(\mu-H)_2(\mu-PPh_2)(CO)_{10}Cp^*}]$	127
$[\mathrm{Ru_3Mo_2(NC_6H_3Me_2-2,6)_2(CO)_{12}}]$	132
$[\mathrm{Ru_3Mo_2(\mu_3-O)_2(\mu_3-CPh)(\mu-C_3Ph_3)(CO)_8Cp_2}]$	114
$[\mathrm{Ru_4Mo_2(\mu_3-CMe)_2(CO)_{12}Cp_2}]$	110
$[\mathrm{Ru_4Mo_2(\mu_6-C)(\mu-O)(CO)_{12}Cp_2}]$	113
$[\mathrm{Ru_4Mo_2(\mu-PPh)_2(CO)_{12}Cp_2{}^*}]$	127
$[\mathrm{Ru_4Mo_4O_{16}(p-Pr^iC_6H_4Me)_4}]$	123
$[\mathrm{OsMo_2(\mu_3-Se)(CO)_7Cp_2}]$	125
$[\mathrm{Ru_2W(\mu_3-S)(\mu-S)_2(S)(CO)_2Cp^*{}_2}]$	173
$[\mathrm{Ru_2W(\mu-S)_4(C_5Me_4Et)_2(CO)_2}]$	173
$[\mathrm{Ru_2W(\mu-S_2)(\mu_3-S)(\mu-S)SCp^*{}_2}]$	121
$[\mathrm{Ru_2W_2(\mu_3-S)_2(\mu_2-S)_2(CO)_6Cp^*{}_2}]$	172
$[\mathrm{Ru_2W_2(\mu_3-S)_2(\mu-S)_2(CNBu^t)(CO)_5Cp^*{}_2}]$	173
$[\mathrm{Ru_2W_2(\mu_3-S)_3(O)(CO)_6Cp^*{}_2}]$	173
$[\mathrm{Ru_2W_2(\mu_3-S)_3(S)(CO)_6Cp^*{}_2}]$	172
$[\mathrm{Ru_2W_3(\mu_3-CCBu^t)(CO)_9Cp^*{}_3}]$	159
$[\mathrm{Ru_2W_3(\mu_4-C)(\mu_3-CPh)(CO)_9Cp^*{}_3}]$	159
$[\mathrm{Ru_3W(\mu_4-Se)(\mu_3-Se)\{P(CH_2Ph)Ph_2\}_2(CO)_{12}}]$	184

(Continued)

Table 11 (Continued)

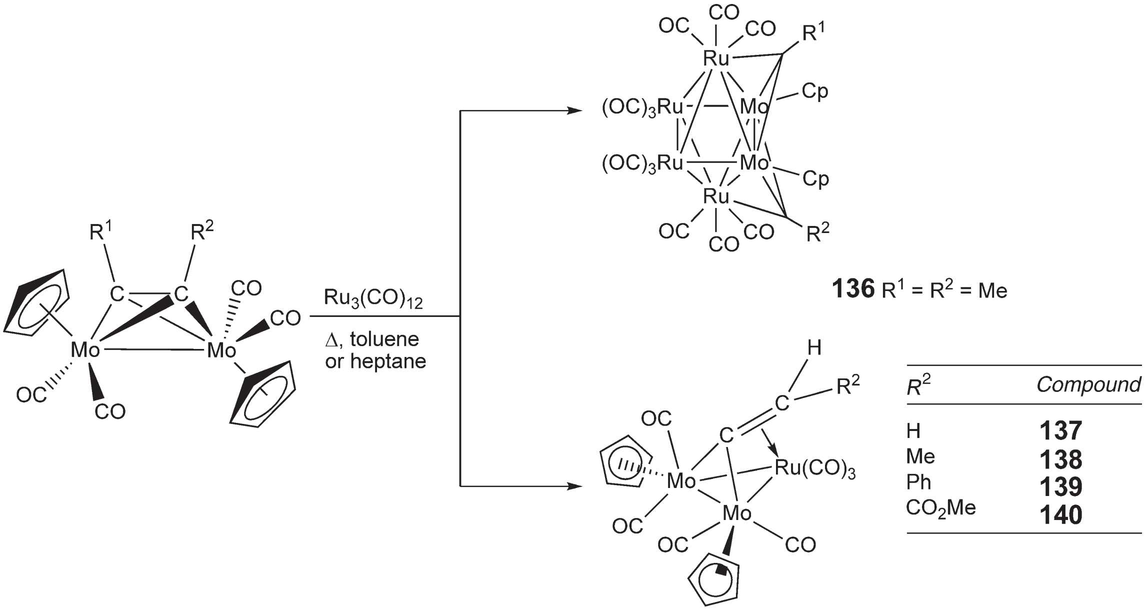
Formula	*References*
$[Ru_3W(\mu_4\text{-Se})_2(\mu\text{-CO})_4(PPh_3)_2(CO)_6]$	184
$[Ru_3W(\mu_4\text{-Se})_2(\mu\text{-CO})_4\{P(OMe)Ph_2\}_2(CO)_6]$	184
$[Ru_3W(\mu_4\text{-Se})_2(\mu\text{-CO})_4\{P(p\text{-MeOC}_6H_4)_3\}_2(CO)_6]$	184
$[Ru_3W(\mu\text{-AuPPh}_3)(\mu\text{-H})_2(CO)_{11}Cp^*]$	165
$[Ru_3W(\mu\text{-AuPPh}_3)(\mu\text{-H})_2(CO)_{11}Cp]$	165
$[Ru_3W(\mu\text{-H})(AuPPh_3)B(CO)_{11}Cp]$	170
$[Ru_3W(\mu\text{-H})(\mu_3\text{-C}_2C{\equiv}C)(CO)_{12}Cp]$	167
$[Ru_3W(\mu\text{-H})(\mu_3\text{-}\eta^1{:}\eta^2\text{-C}_2C{\equiv}C)(\mu\text{-dppm})(CO)_{10}Cp]$	167
$[Ru_3W(\mu\text{-H})(PPh_3)(BH)(CO)_{10}Cp]$	171
$[Ru_3W(\mu\text{-O})_2(\mu_3\text{-NPh})(CCCMe{=}CH_2)(CO)_5(PMe_2Ph)Cp^*]$	162
$[Ru_3W(O)(\mu\text{-O})(\mu_3\text{-NPh})(CCR)(CO)_8Cp^*]$	162
$[Ru_3W(O)_2(\mu_3\text{-NPh})(CCCMe{=}CH_2)(CO)_8Cp^*]$	162
$[Ru_3W_2(C_{10}H_2O_2)(CO)_{14}Cp_2]$	166
$[Ru_3W_2(CO)_{13}Cp_2]$	151
$[Ru_3W_2(\mu\text{-O})(\mu_5\text{-C})(CO)_9CpCp^*]$	152
$[Ru_3W_2(O)(\mu_5\text{-C})(CO)_{11}Cp^*{}_2]$	151
$[Ru_3W_2(O)(\mu_5\text{-C})(CO)_{11}Cp_2]$	152
$[Ru_3W_5(\eta^6\text{-C}_6Me_6)_3O_{18}(H_2O)]$	185
$[Ru_4W(\mu_3\text{-H})(CO)_{14}Cp]$	149
$[Ru_4W(\mu_3\text{-O})F\{\mu_3\text{-}\eta^2\text{-P(O)N(Pr}^i)_2\}(\mu_4\text{-}\eta^2\text{-CCPh})H(CO)_9Cp^*]$	169
$[Ru_4W(\mu_4\text{-PPh})(CCPh)(CO)_{11}Cp^*]$	163
$[Ru_4W(\mu_5\text{-C})(\mu\text{-CPh})(CO)_{12}Cp]$	150
$[Ru_4W(\mu_5\text{-C})(\mu\text{-CPh})(CO)_{12}Cp]$	164
$[Ru_4W(\mu\text{-O})\{\mu_3\text{-}\eta^2\text{-OPN(Pr}^i)_2\}(\mu_4\text{-}\eta^2\text{-CCPh})(\mu\text{-CO})(CO)_9Cp^*]$	168
$[Ru_4W(\mu\text{-O})_2\{\mu_3\text{-PN(Pr}^i)_2\}(\mu_5\text{-}\eta^2\text{-CCPh})(CO)_{10}Cp^*]$	168
$[Ru_4W(O)_2(\mu_4\text{-PPh})(CCPh)(C_7H_8)(CO)_7Cp^*]$	158
$[Ru_4W(O)_2(\mu_4\text{-PPh})(CCPh)(CO)_{10}Cp^*]$	158
$[Ru_4W_2(\mu_4\text{-PPh})(\mu_3\text{-PPh})(CO)_{12}Cp^*{}_2]$	157
$[Ru_4W_4(\eta^6\text{-C}_6Me_6)_4O_{16}]$	185
$[Ru_4W_8(\eta^6\text{-p-MeC}_6H_4Pr^i)_7(\mu\text{-OH})_6(OH)_2(H_2O)_2O_{28}]$	185
$[Ru_5W(\mu_4\text{-C})(\mu_3\text{-CCH}_2Ph)(\mu\text{-H})_4(CO)_{12}Cp^*]$	160
$[Ru_5W(\mu_5\text{-C})(CCPh)(CO)_{13}Cp]$	160
$[Ru_5W(\mu_5\text{-C})(CCPh)(CO)_{15}Cp]$	160
$[Ru_5W(\mu_6\text{-C})(\mu\text{-CCH}_2Ph)(\mu\text{-H})_2(CO)_{13}Cp^*]$	160
$[Ru_5W(\mu_6\text{-C})(\mu\text{-CPh})(CO)_{14}Cp]$	150
$[Ru_5W(\mu_6\text{-C})(\mu\text{-CPh})(CO)_{14}Cp]$	164
$[Ru_5W(\mu\text{-H})(\mu_3\text{-}\eta^2{:}\mu_3\text{-}\eta\text{-C}_2C_2)(CO)_{17}Cp\}]$	167
$[Ru_5W(O)_2(\mu_4\text{-PPh})(CCPh)(CO)_{12}Cp^*]$	158
$[Ru_6W(\mu_3\text{-H})\{C_5H_3(SiMe_3)_2\}(CO)_{18}]$	156
$[Ru_6W(O)_2(\mu_6\text{-C})(CCPh)(CO)_{11}(C_7H_8)Cp^*]$	161
$[Ru_6W(O)_2(\mu_6\text{-C})(CCPh)(CO)_{14}Cp^*]$	161
$[Os_3W(C_2)(C_2Ph)(CO)_9Cp^*]$	190
$[Os_3W(C_2)(OC_2Ph)(CO)_9Cp^*]$	190
$[Os_3W(C{\equiv}CCH_2OMe)(CO)_{11}Cp^*]$	191
$[Os_3W(\mu_3\text{-CH})(CO)_{11}Cp^*]$	187
$[Os_3W(\mu_3\text{-CH})(\mu_3\text{-CCO}_2Pr^i)_2(CO)_9Cp^*]$	195
$[Os_3W(\mu_3\text{-CMe})(CMeCTol)(CO)_{10}Cp]$	189
$[Os_3W(\mu_3\text{-CTol})_3(CO)_9Cp]$	201
$[Os_3W(\mu_3\text{-}\eta^2\text{-C}_2Tol_2)(\mu_3\text{-CTol})(CO)_{10}Cp]$	201
$[Os_3W(\mu_3\text{-S})(\mu_3\text{-CTol})(CO)_{10}Cp]$	205
$[Os_3W(\mu_3\text{-S})(\mu\text{-H})(\mu\text{-CHTol})(CO)_{10}Cp]$	205
$[Os_3W(\mu_4\text{-C})(\mu\text{-CH=CHOMe})(CO)_9Cp^*]$	193
$[Os_3W(\mu_4\text{-C})(\mu\text{-CHCHCH}_2Ph)(CO)_{10}Cp^*]$	200
$[Os_3W(\mu_4\text{-C})(\mu\text{-CPh})(CO)_{10}Cp^*]$	192
$[Os_3W(\mu_4\text{-C})(\mu\text{-CPh})(CO)_{10}Cp^*]$	193
$[Os_3W(\mu_4\text{-C})(\mu\text{-H})(\mu\text{-CCHOMe})(CO)_9Cp^*]$	192
$[Os_3W(\mu_4\text{-C})(\mu\text{-H})_2(\mu\text{-C}_8H_6O)(CO)_9Cp^*]$	193
$[Os_3W(\mu_4\text{-C})(\mu\text{-H})_2(\mu\text{-CCH}_2OMe)(CO)_9Cp^*]$	193

(Continued)

Table 11 (Continued)

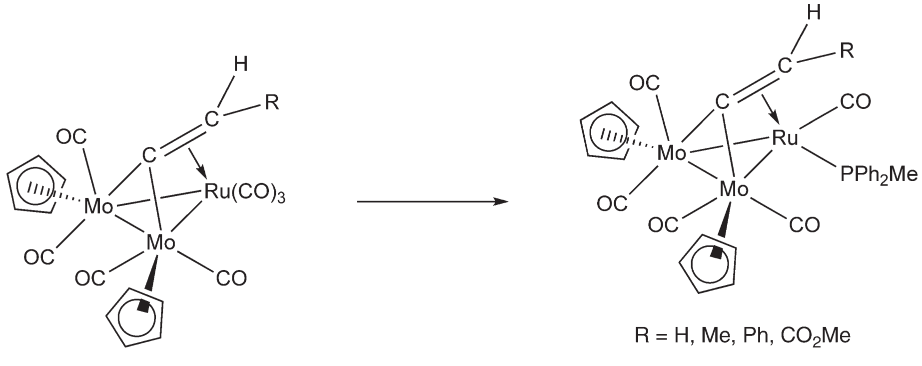
Formula	*References*
$[Os_3W(\mu\text{-}H)\{C_3H(CO_2Pr^i)\}_2\{C_5Me_4(CH_2)\}(CO)_9]$	195
$[Os_3W(\mu\text{-}H)\{\mu_3\text{-}\eta^3\text{-}C(H)C(Ph)C(OH)\}(CO)_{12}]$	199
$[Os_3W(\mu\text{-}H)_2(CCCH_2OMe)(CO)_{10}Cp^*]$	193
$[Os_3W(\mu\text{-}H)_2(\mu_3\text{-}CTol)\ (PPh_3)(CO)_{10}Cp]$	204
$[Os_3W(\mu\text{-}H)_2(\mu_3\text{-}CTol)(CO)_{10}Cp]$	204
$[Os_3W(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)(CO)_{10}Cp]$	186
$[Os_3W(\mu\text{-}O)(\mu_3\text{-}CMe)(CO)_9Cp^*]$	187
$[Os_3W(\mu\text{-}O)(\mu_3\text{-}CTol)(CO)_{10}Cp]$	203
$[Os_3W(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CHTol)(CO)_9Cp]$	202
$[Os_3W(\mu\text{-}O)_2(\mu\text{-}CCPh)(CO)_9Cp^*]$	194
$[Os_3W(\mu\text{-}S)(\mu\text{-}H)(\mu\text{-}CHTol)(CO)_9Cp]$	205
$[Os_3W(\mu\text{-}SCH_3)(\mu_4\text{-}CH)(CO)_{11}Cp]$	206
$[Os_3W(\mu\text{-}SCH_3)(\mu\text{-}CH_2)(CO)_{12}Cp]$	206
$[Os_3W(\mu\text{-}SCH_3)(\mu\text{-}H)_2(\mu_4\text{-}CH)(CO)_9Cp]$	206
$[Os_3W(O)(\mu\text{-}O)(CCPh)(CO)_{11}Cp^*]$	194
$[Os_3W(O)(\mu\text{-}O)(CCPh)(PhC_2Ph)(CO)_8Cp^*]$	196
$[Os_3W(O)(\mu\text{-}O)(CCPhCCHPh)(CO)_8Cp^*]$	196
$[Os_3W(O)(\mu\text{-}O)(CCPhCPhCPh)(CO)_8Cp^*]$	196
$[Os_3W(O)(\mu\text{-}O)(CCPhCPhCPh)(CO)_8Cp^*]$	196
$[Os_3W(O)_2(\mu\text{-}H)\{\mu\text{-}\eta^3\text{-}C({=}CHPh)C{\equiv}C\}(CO)_{10}Cp^*]$	197
$[Os_3W\{C(Me)C(Me)C(Tol)\}(CO)_9Cp]$	189
$[Os_3W\{C_3H(CO_2Pr^i)_2\}(CO)_{10}Cp^*]$	195
$[Os_3W\{CC_2(CO_2Pr^i)_2H\}(CO)_{10}Cp^*]$	195
$[Os_3W\{\mu_3\text{-}CC(CH_2Ph)(CH_2)\}(CO)_{10}Cp^*]$	200
$[Os_3W_2(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}CMe)(CO)_9Cp_2]$	188
$[Os_4W(\mu_3\text{-}O)(\mu_3\text{-}CMe)(CO)_{12}Cp]$	188
$[Os_4W(\mu\text{-}O)(\mu_3\text{-}CMe)(CO)_{12}Cp]$	188
Clusters with three different kinds of metal	
$[RuMoCo(\mu_3\text{-}S)\{C_5H_4C(O)C_6H_4CO_2CH_3\}(CO)_8]$	139
$[RuMoCo(\mu_3\text{-}S)\{C_5H_4C(O)CH_2CH_2CO_2CH_3\}(CO)_8]$	144
$[RuMoCo(\mu_3\text{-}S)\{C_5H_4C(O)CH_3\}(CO)_8]$	137
$[RuMoCo(\mu_3\text{-}S)\{C_5H_4C(O)Ph\}(CO)_8]$	140
$[RuMoCo(\mu_3\text{-}S)\{C_5H_4CO_2Et\}(CO)_8]$	143
$[RuMoCo(\mu_3\text{-}Se)\{C_5H_3(CH_3)(COCH_3)\}\ (CO)_8]$	142
$[RuMoCo(\mu_3\text{-}Se)\{C_5H_3(CH_3)(COCH_3)\}(CO)_8]$	138
$[RuMoCo(\mu_3\text{-}Se)\{C_5H_4C(O)C_6H_4CO_2CH_3\}(CO)_8]$	136
$[RuMoCo(\mu_3\text{-}Se)\{C_5H_4C(O)OEt\}(CO)_8]$	141
$[RuMoCo(\mu_3\text{-}Se)\{C_5H_4C(O)Ph\}(CO)_8]$	136
$[RuMoCo(\mu_5\text{-}S)\{C_5H_4(CH_3CO_2C_6H_4CO)\}(CO)_8]$	135
$[RuMoNi(\mu_3\text{-}S)\{C_5H_4C(NR)CH_3\}(CO)_5Cp]$	146
$[RuMoNi(\mu_3\text{-}S)\{C_5H_4C(O)CH_3\}(CO)_5Cp]$	145
$[RuMoNi(\mu_3\text{-}S)\{C_5H_4C[NNH\text{-}C_6H_3\text{-}2,4\text{-}(NO_2)_2]CH_3\}(CO)_5]$	147
$[RuWCo(\mu_3\text{-}Se)\{C_5H_4C(O)CH_2CH_2C(O)CH_3\}(CO)_8]$	182
$[RuWCo(\mu_3\text{-}Se)\{C_5H_4C(O)CH_2CH_2CO_2CH_3\}(CO)_8]$	183
$[RuWCo(\mu_3\text{-}Se)\{C_5H_4C(O)CH_3\}(CO)_8]$	181
$[RuWCo(\mu_3\text{-}S)(C_5H_4CO_2CH_3)(CO)_8]$	180
$[RuWNi(\mu_3\text{-}S)(C_5H_4CO_2C_6H_4CO_2CH_3)(CO)_5Cp]$	146
$[RuWNi(\mu_3\text{-}S)(C_5H_4COCH_3)(CO)_5Cp]$	177
$[Ru_2W_2Co_2(\mu_3\text{-}S)_2\{C(O)C_6H_4C(O)\}(CO)_{16}Cp_2]$	178
$[Ru_2W_2Co_2(\mu_3\text{-}S)_2\{\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)C_5H_4\text{-}\eta^5\}(CO)_{16}]$	137
$[Ru_2WPt(\mu_3\text{-}S)_2(\mu\text{-}S)_2Me_2(C_5Me_4Et)_2(CO)_2]$	174
$[Ru_2WPt_2(\mu_3\text{-}S)_2(\mu\text{-}S)_2(PPh_3)_2(\mu\text{-}Co)(CO)(C_5Me_4Et)_2]$	175
$[Ru_2WPt_2(\mu_3\text{-}S)_4Me_4(CO)_2Cp^*{}_2]$	174
$[Ru_3Co_2W(\mu_3\text{-}\eta^2{:}\mu_3\text{-}\eta^2\text{-}CCHC_2)(\mu\text{-}CO)(CO)_{16}Cp\}]$	167
$[Ru_{3\text{-}m}Fe_m(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2{:}\mu_3\text{-}\eta^2\text{-}C_2C_2)\{Ru_{2-n}Fe_nW(CO)_8Cp\}]$	167
$[Ru_3WRh_2(\mu\text{-}CO)(CO)_{14}BCp]$	176
$[Os_3WAu(PPh_3)(\mu\text{-}CO)(CO)_{11}Cp^*]$	207
$[Os_3WAu(PPh_3)(\mu\text{-}CO)(CO)_{11}Cp]$	207

that the alkyne complexes reacted with $Ru_3(CO)_{12}$ to give $[Mo_2Ru_4(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)(CO)_{12}Cp_2]$ clusters (for $R^1 = R^2 = Me$; **136**) in addition to the μ_3-vinylidene clusters $[Mo_2Ru(\mu_3\text{-}C{=}CHR^2)(CO)_7Cp_2]$ ($R^2 = H$, Me, Ph, CO_2Me; **137–140**).[110] Cluster **136** represents the first example of the scission of ethyne into two methylidyne fragments on a metal cluster. This octahedral cluster contains 84 cluster valence electrons, which is consistent with the relatively short Mo–Mo distance that was observed.[111] The thermal reactions of **137–140** with PPh_2Me afforded the mono-substituted complexes $[RuMo_2(\mu_3\text{-}C{=}CHR)(CO)_6(PPh_2Me)Cp_2]$ ($R = H$, Me, Ph, CO_2Me; **141**) in excellent yields. A site-selective substitution of a CO ligand at the ruthenium center exclusively was observed.[112]



136 $R^1 = R^2 = Me$

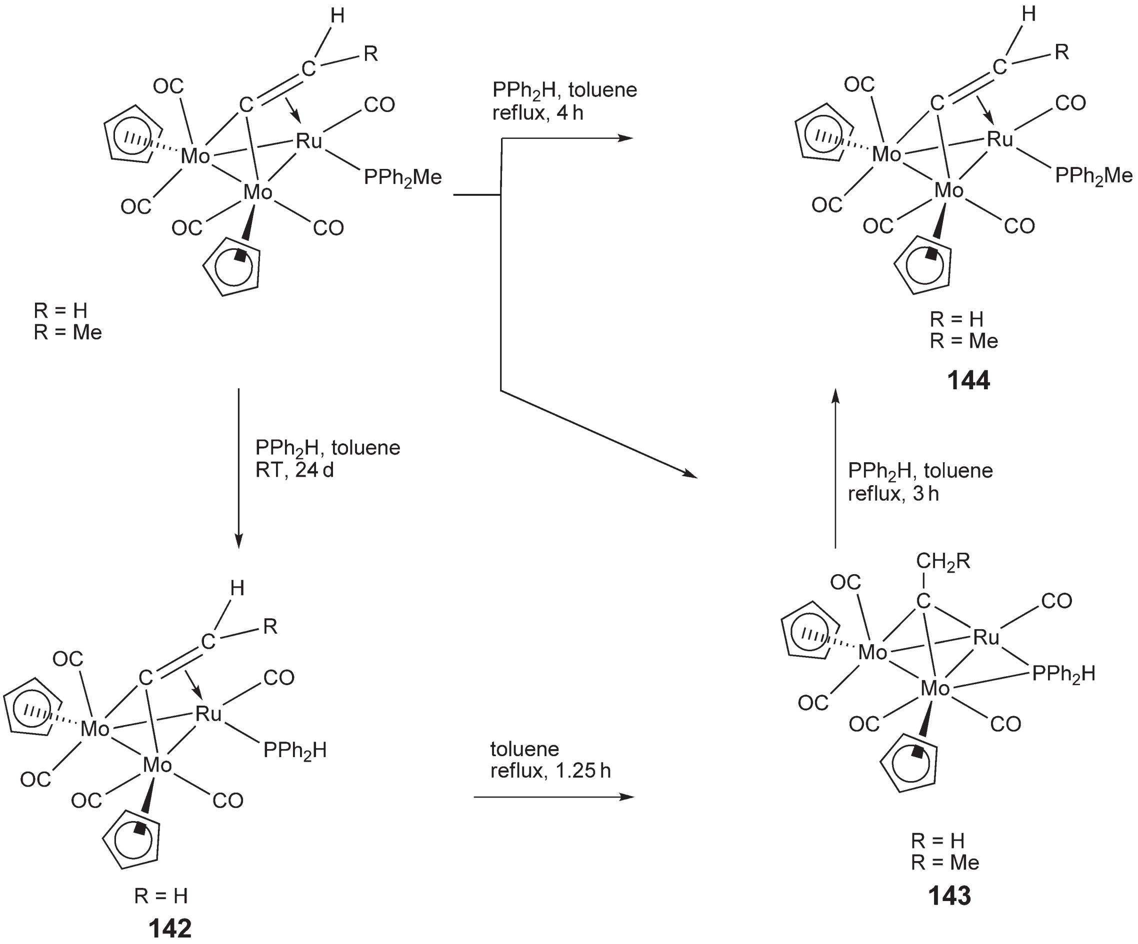
R^2	*Compound*
H	**137**
Me	**138**
Ph	**139**
CO_2Me	**140**

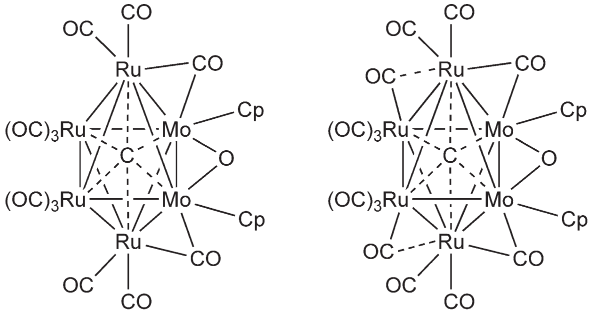


R = H, Me, Ph, CO_2Me

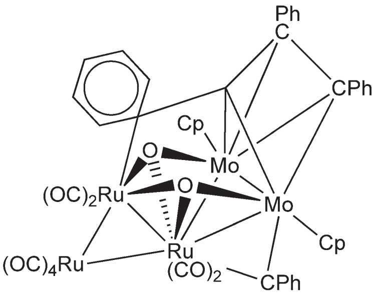
141

The reactions of **137 and 138** with diphenylphosphine led to the formation of **142**, **143**, and **144** in a sequential manner, which thus demonstrates the interconversion of vinylidene and alkylidyne ligands on a metal cluster surface. The carbide-oxo cluster **145** was isolated in 41% yield from the reaction of $Mo_2(CO)_4Cp_2$ and $Ru_3(CO)_{12}$ in refluxing toluene. Two isomeric structures with slightly different CO ligand dispositions were observed in the same crystal.[113] A related pentanuclear μ_3-oxo species **146** with a highly distorted bow-tie structure was isolated in low yield.[114] The mixed-metal clusters $[Ru_2Mo_2(\mu_3\text{-}S)_2(\mu\text{-}SR)(\mu\text{-}X)(CO)_4Cp_2]$ [$X = SR$, $R = Et$, Pr^i **147**[115] or PPh_2 **148**[116]] were prepared by the treatment of **149** or **150** with $Ru_3(CO)_{12}$, which involved the dealkylation of the thiol ligand at the dimolybdenum center.

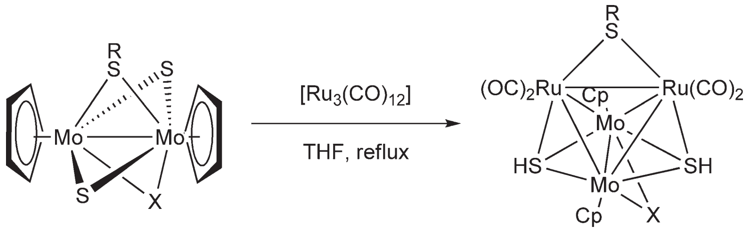




145



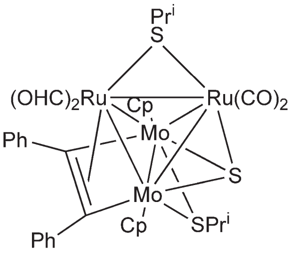
146



X = SR **149**
X = PPh$_2$ **150**

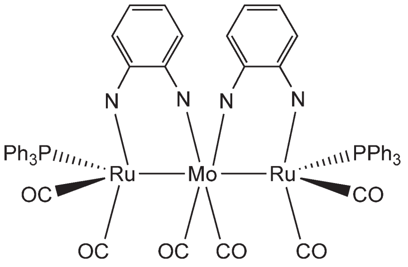
X = SR, R = Et, Pr^i **147**
X = PPh$_2$ **148**

A structurally similar tetrahedral cluster **151** in which a μ_3-S ligand is replaced by a μ_3-C_2Ph_2 alkyne ligand was synthesized.[117] This method of producing Ru–Mo mixed-metal clusters has also been used for other substituted cyclopentadienyl dimolybdenum reagents in which the Mo=Mo doubly bonded dimers are involved.[118–120] Mononuclear tetrathiometallates $[MoS_4]^{2-}$ and the cationic cluster complex $[(\eta^5\text{-}C_5H_4Me)_3Mo_3S_4]^+$ were also used to assemble mixed-metal clusters of ruthenium-molybdenum.[122] Sodium molybdate[123] or oxoalkoxopolymolybdates[124] were used to synthesize amphiphilic organoruthenium oxomolybdenum clusters. These clusters are believed to be important model compounds for heterogeneous catalysis that is derived from organometallic complexes that are adsorbed at the surfaces of metal oxides.

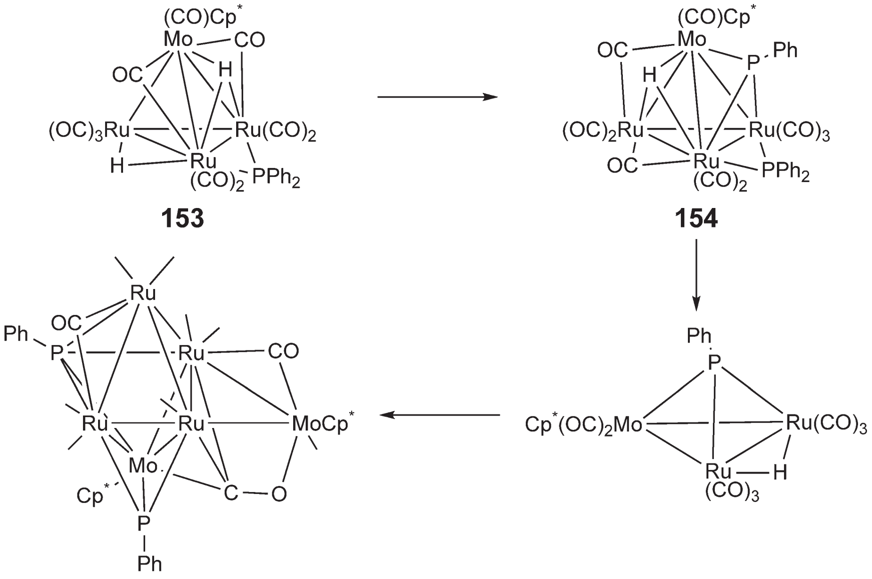


151

$[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)_2(PPh_3)]$ reacts with $Mo(CO)_6$ to give a mixed-metal cluster **152** with an open-chain metal skeleton. It is interesting to note that neither $Cr(CO)_6$ nor $W(CO)_6$ reacted to give mixed-metal clusters. The reaction of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with an excess of molybdenum hydride $Cp^*Mo(CO)_3H$ in refluxing toluene afforded **153** and **154**. Cluster **153** is an intermediate for the formation of **154**. Subsequent treatment of **154** with CO resulted in cluster fragmentation to give the trinuclear **155**. Dimerization of **155** occurred upon thermolysis to afford **156** in moderate yield.[127]



152



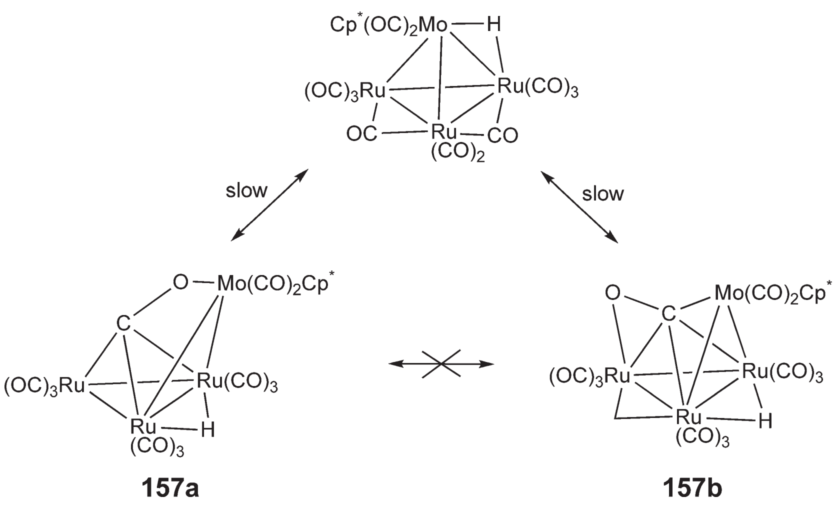
153

154

156

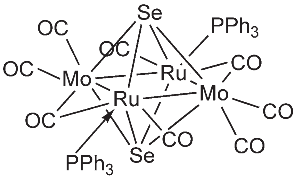
155

Chi *et al*. established a unique isomerization process that involves the quadruple bridging of the CO ligand on **157**.[128] A tetrahedral isomer is believed to be involved in the fluxional process in solution.

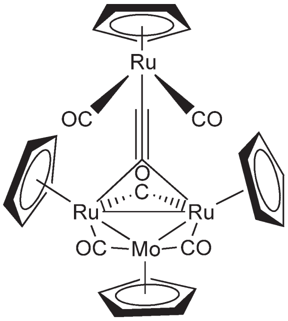


An electron-deficient *closo*-cluster **158** was prepared from the open-triangular *nido*-cluster [$Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2$] with [$Mo(CO)_3(MeCN)_3$] under mild conditions. The unusual stability of this unsaturated complex may be attributable to the strong electron-donating phosphine ligands.[129]

The reaction gave the tetranuclear cluster now formulated as **159** as the major product. It displays a remarkable μ_3-C≡C fragment that is bound to the Ru$_3$ triangle, which is a very rare coordination mode for alkynes.[130]

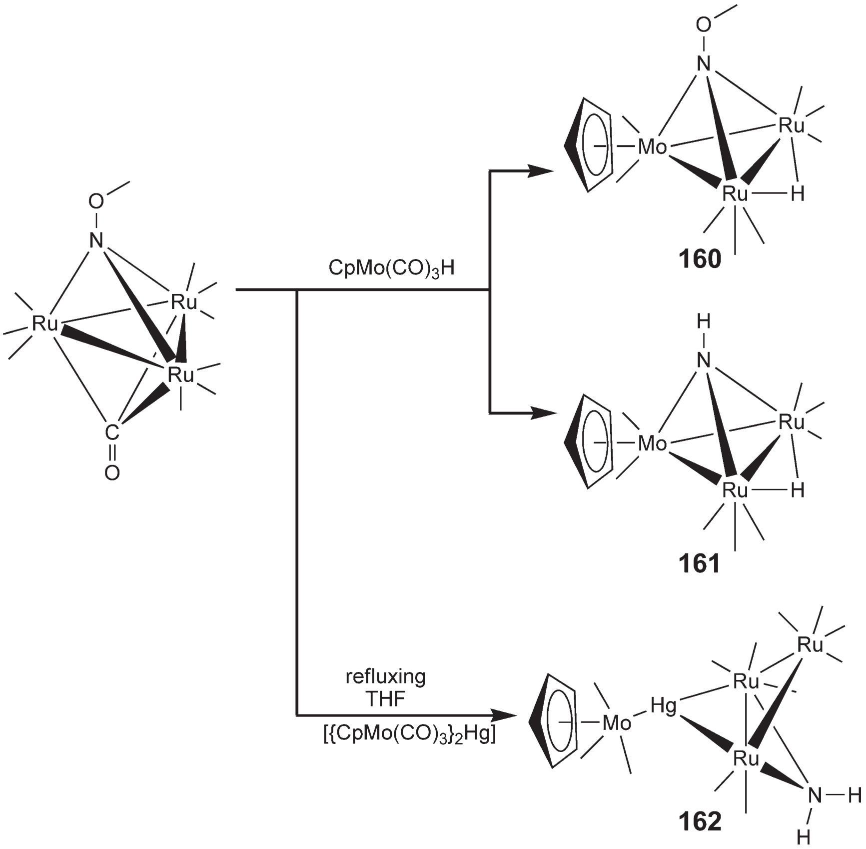


158

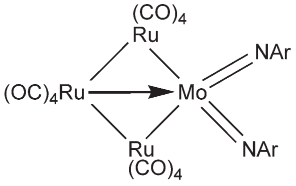


159

Treatment of methoxynitrido cluster [$Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)$] with stoichiometric amounts of the hydrido complex [$CpMo(CO)_3H$] in THF afforded two trinuclear Ru–Mo clusters **160 and 161**, in which metal exchange has occurred. However, the same methoxynitrido cluster when reacted with the organomercurial [$\{CpMo(CO)_3\}_2Hg$] resulted in the formation of a pentanuclear trimetallic species **162**. Although [$CpMo(CO)_3H$] and [$\{CpMo(CO)_3\}_2Hg$] possess the same isolobal "$CpMo(CO)_3$" fragment, their reactivity is rather different.[131]



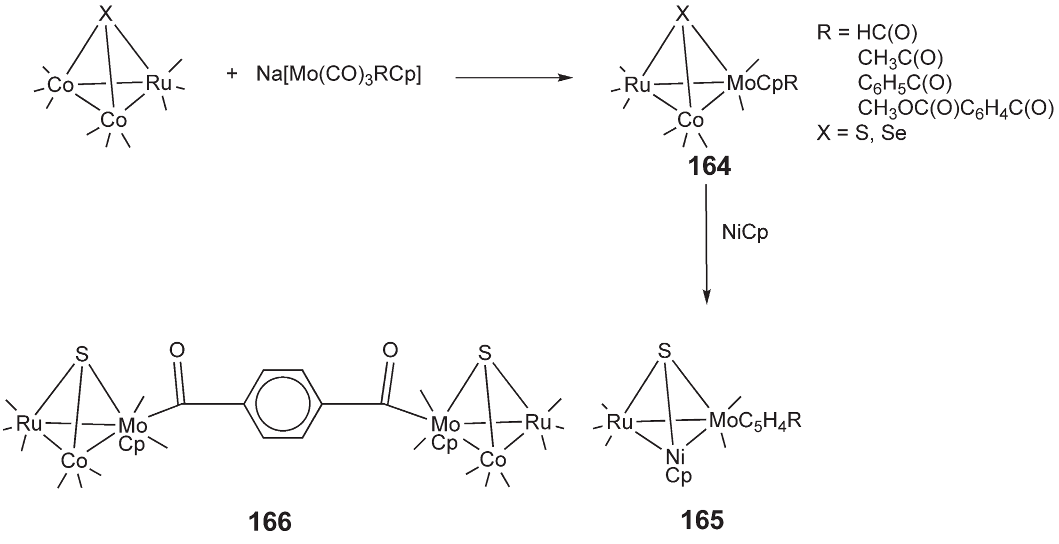
The reaction of $[Ru_3(CO)_{11}]^{2-}$ dianion with molybdenum bis(imido) complexes $[Mo(NAr)_2Cl_2(dme)]$ led to the isolation of new high–low valent clusters $Ru_3(CO)_{12}\{Mo(NAr)_2\}$ (Ar = $C_6H_3Me_2$-2,6; **163**). These compounds are unstable in polar solvents, such as THF, which may reflect the strong polarization of the Ru–Mo bonds and the electron deficiency at the molybdenum center.[132]



Ar = $C_6H_3Me_2$

163

The chemistry of chiral heterotrimetallic clusters of RuMoCo, such as **164**, was investigated in detail by Yin *et al.*[135–144] They established a general synthetic method for this class of compounds by the metal-exchange reactions of $[RuCo(\mu_3\text{-}X)(CO)_9]$ (X = S, Se) with $Na[Mo(CO)_3C_5H_4R]$ (R = ketone, acyl groups). Double tetrahedral clusters, such as **165**, with two RuMoCoS cores that are bridged by bicyclopentadienyl ligands can also be made based on the same principle. It has been shown that cluster **164** can undergo further metal exchange with $NiCp_2$ to give the RuMoNi trimetallic cluster **166**.[145–147]



R = $HC(O)$
$CH_3C(O)$
$C_6H_5C(O)$
$CH_3OC(O)C_6H_4C(O)$
X = S, Se

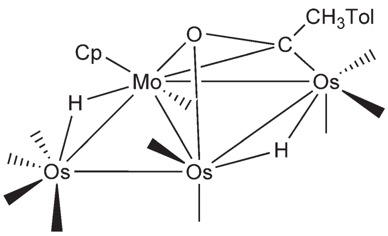
164

166

165

R = $COCH_3$

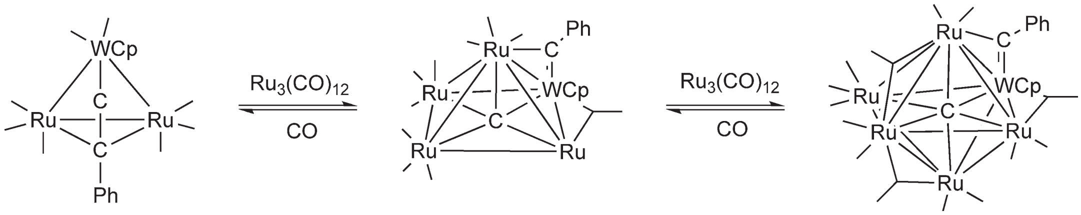
Osmium–molybdenum clusters are not as well studied as the Ru–Mo system. The solution dynamics of **167** have been investigated by VT ^{13}C-NMR spectroscopy, which indicated that the acyl C–O bond in **167** undergoes scission when induced by the hydride ligands.[148]



167

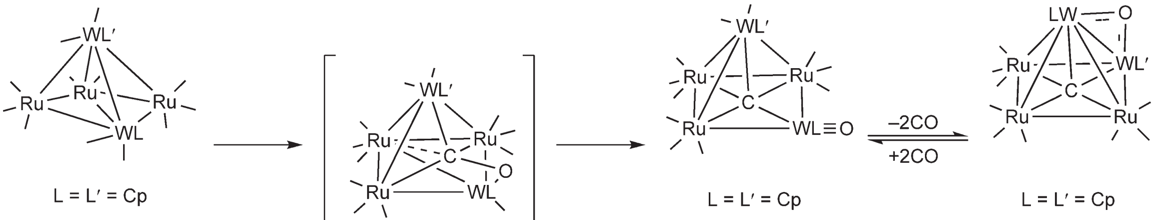
Metal-exchange reactions have been employed to generate Os–Mo and Ru–Mo clusters in low yield from [$FeMo_2(\mu_3$-Se)$(CO)_7Cp_2$] and $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$, respectively.[125]

The chemistry of both Ru–W and Os–W mixed-metal clusters was extensively investigated by Chi *et al.*, and a number of exciting discoveries were made. These include the reversible scission of a coordinated acetylide ligand on the acetylide cluster **168**, which can be prepared from the condensation of $CpW(CO)_3(C_2Ph)$ and $Ru_3(CO)_{12}$ in refluxing toluene.[150] The carbide clusters **169 and 170** were formed when **168** was heated with $Ru_3(CO)_{12}$ in heptane. Interestingly, the reaction sequence can be reversed to regenerate the acetylide cluster **168** in the presence of pressurized CO. This kind of reactivity is seldom observed for semi-encapsulated ruthenium carbide systems.



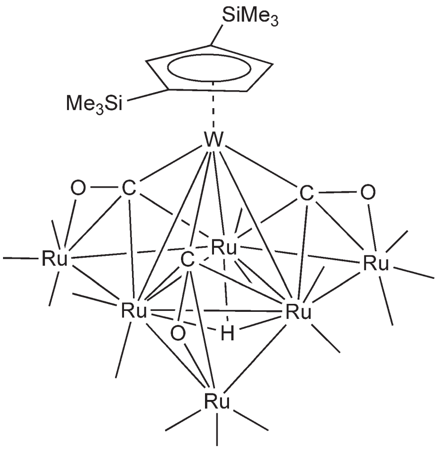
168 **169** **170**

The direct scission of a coordinated CO ligand to give an oxo–carbido cluster has been observed in the synthesis of the Ru–W cluster **172** from a Cp* analog of **171** via an intermediate with a μ_4-CO ligand. X-ray analysis of **172** showed that it adopts a wingtip-bridged butterfly metal skeleton with a penta-coordinated carbide ligand, and that the oxo ligand is coordinated to the Cp*W bridge. The multiple bond nature of the W≡O is supported by a very short W–O distance of 1.697(5) Å. In addition, a ^{17}O-NMR spectroscopic study gave supporting evidence for the direct scission of the CO ligand.[151] Extensive heating of **172** in toluene led to the formation of the μ-oxo species **173**.[152]

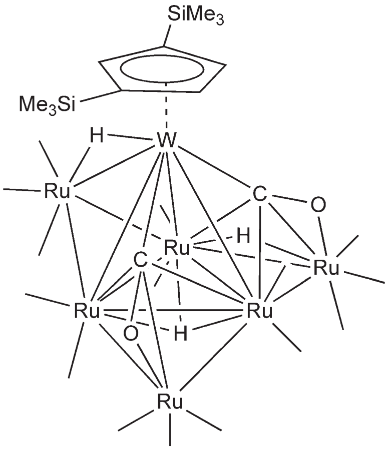


171 **172** **173**

It is widely believed that the transformation of a terminal CO or bridge CO to a quadruply bridging CO is an essential step for the cleavage of the C–O bond in metal clusters and on metal surfaces.[153,154] In connection with this, Chi successfully prepared cluster **174**, which contains three quadruply bridging μ_4-η^2-CO ligands. The hydrogenation of **174** led to the formation of trihydrido cluster **175**, which displays fluxional processes that involve hydride exchange at room temperature. The formation of **174** is in sharp contrast to the condensation reactions that use CpW(CO)$_3$H or Cp*W(CO)$_3$H, which afforded only the tetranuclear species [Ru$_3$W(μ-H)(CO)$_{12}$Cp′] (Cp′ = Cp or Cp*).[128,155] It is believed that the difference in reactivity may result from the steric interaction of the substituents on the Cp ring. Although the mechanistic details are not clear, it is unlikely that a step-by-step cluster building reaction leads to **174**.[156]

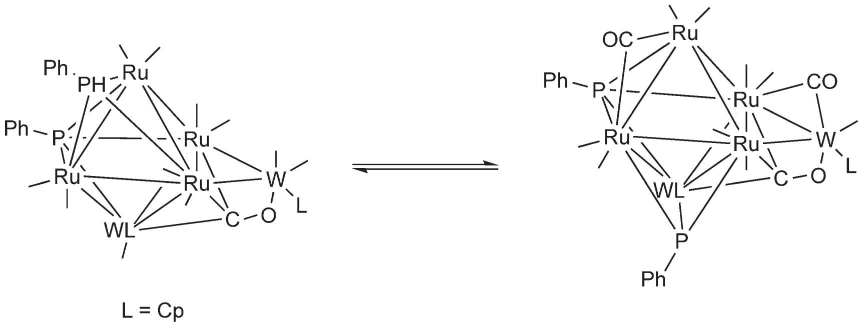


174



175

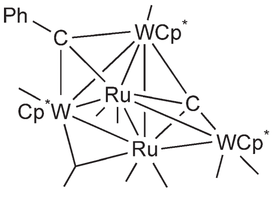
The heating of the heterometallic phosphinidene cluster [Ru$_2$W(μ-H)(μ_3-PPh)(CO)$_8$Cp*] in refluxing toluene afforded two isomeric Ru$_4$W$_2$ clusters **176** and **177**. Isomerization occurs at elevated temperatures for these compounds. Cluster **176** underwent cluster degradation with molecular hydrogen to give [Ru$_3$W(μ-H)(μ_3-PPh)(CO)$_{10}$Cp*] and with CO to give [Ru$_3$(CO)$_9$(μ_3-PPh)$_2$] and [Ru$_4$(CO)$_{11}$(μ_4-PPh$_2$)].[157]



176 **177**

The heterometallic clusters [Ru$_4$W(O)$_2$(μ_4-PPh)(CCPh)(CO)$_{10}$Cp*], [Ru$_4$W(O)$_2$(μ_4-PPh)(CCPh)(CO)$_7$(C$_7$H$_8$)-Cp*], and [Ru$_5$W(O)$_2$(μ_4-PPh)(CCPh)(CO)$_{12}$Cp*], prepared from the condensation of [Ru$_4$(CO)$_{13}$(μ_3-PPh)] and [Cp*W(O)$_2$(CCPh)], feature a class of oxo early-metal organometallics with late-metal compounds. All of them display an Ru–O = W interaction.[158]

The reaction of [Ru$_2$W(CCPh)(CO)$_8$Cp*] with an excess of Cp*W(CO)$_3$H gave the carbide–alkylidyne cluster **178** in low yield, and a similar condensation using *tert*-butyl derivative [Ru$_2$W(CCBu^t)(CO)$_8$Cp*] afforded the acetylide cluster **179**. Both **178** and **179** contain an edge-bridged tetrahedral metal core in which the butterfly crater is occupied by a μ_4-carbide in **178** and a quadruply bridging CO ligand in **179**.[159]



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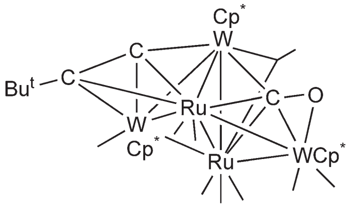
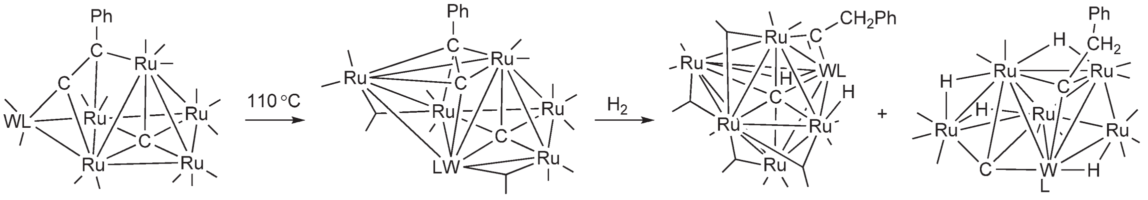


179

Treatment of [Ru$_5$C(CO)$_{15}$] with Me$_3$NO, followed by the addition of [Cp′W(CO)$_3$(CCPh)] (Cp′ = Cp or Cp*), produced the two heterometallic clusters **180** and **181**. Cluster **180** converted into **181** at elevated temperatures, and **181** reacted with hydrogen to give **182** and **183** via a 1,1-addition of H$_2$ to the coordinated acetylide with the concurrent formation of either two or four bridging hydrides.[160]



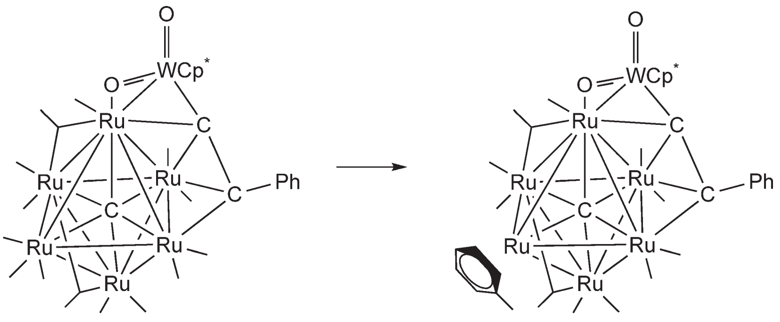
L = Cp, Cp **180**

L = Cp, Cp **181**

L = Cp, Cp **182**

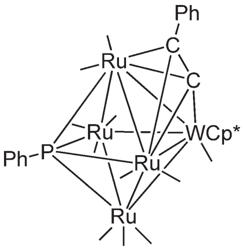
L = Cp, Cp **183**

A similar activation method using Me$_3$NO on [Ru$_6$C(CO)$_{17}$], followed by the addition of the high-valent acetylide complex [Cp*W(O)$_2$(CCPh)], afforded mixed-metal cluster **184**. The extended heating of **184** in toluene gave the toluene-substituted cluster **185**. Both **184** and **185** reacted with CO in refluxing toluene to regenerate the homometallic clusters and tungsten dioxo starting material.[161]



184 **185**

The reactions of imido cluster [$Ru_3(CO)_{10}(\mu_3$-NPh)] with [$Cp^*W(O)_2(CCR)$] (R = Ph and CMe = CH_2) produced [$Ru_3W(O)(\mu$-O)(μ_3-NPh)(CCR)$(CO)_8Cp^*$] in good yields. These clusters consist of an open triangular Ru_3 core with the dioxotungsten unit bonded to the central Ru atom via a W = O → Ru dative interaction.[162] The treatment of phosphinidene cluster [$Ru_4(CO)_{13}(\mu_3$-PPh)] with tungsten acetylide complexes [$Cp'W(CO)_3(CCPh)$] (Cp′ = Cp or Cp^*) afforded interconvertible isomers in different colors of the formula [$Ru_4W(\mu_4$-PPh)(CCPh)$(CO)_{11}Cp'$]. X-ray analysis of the Cp^* derivatives **186 and 187** showed that they both contain a novel Ru_4WP octahedral core in which the acetylide ligand is coordinated to an Ru_2W triangle, but in which the phosphinidene ligand coordination has a different position.[163]



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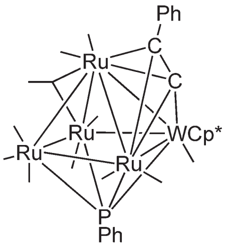
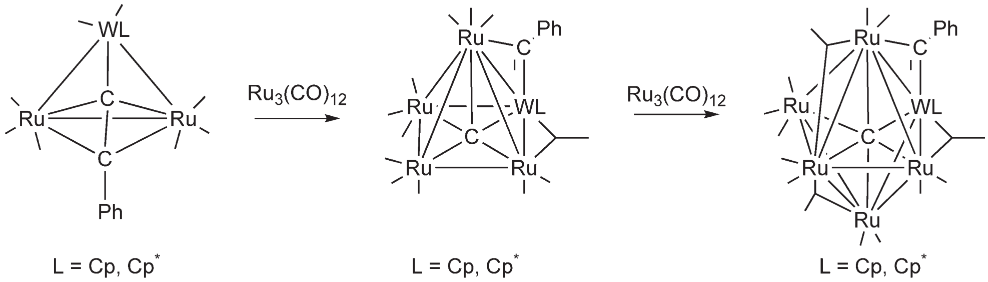


187

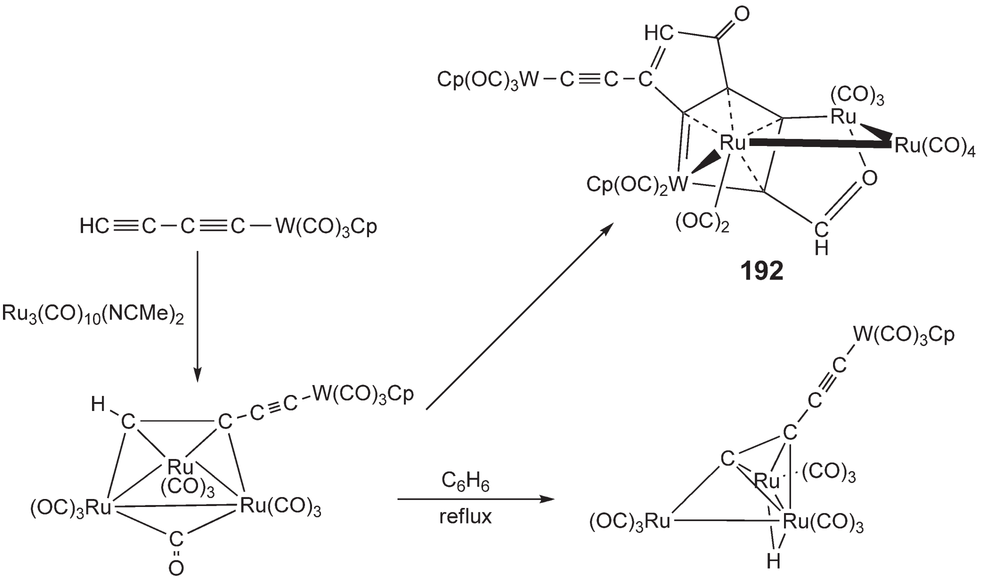
Carbido–alkylidyne clusters **188 and 189** were prepared from interactions of [$Ru_2W(CCPh)(CO)_8Cp'$] (Cp′ = Cp or Cp^*) with [$Ru_3(CO)_{12}$]. This series of compounds illustrates the reversible cleavage of an acetylide carbon–carbon bond that is induced by the cluster-building reaction. Both hydrogenation and reaction of thiophenol with **188** led to derivatives that contain a similar metal core arrangement.[164]



188 **189**

The trimetallic compounds [$Ru_3W(\mu$-$AuPPh_3)(\mu$-$H)_2(CO)_{11}Cp'$] (Cp′ = Cp or Cp^*) were obtained from the hydrogenation of [$Ru_3W(\mu$-$AuPPh_3)(CO)_{12}Cp'$] in refluxing THF. The Cp and Cp^* derivatives show different metal core arrangements in the solid state.[165]

Compounds that contain metal centers bridged by carbon chains are important due to their potential novel material properties. In this context, a series of mixed-metal complexes that contain a tetracarbon (C_4) ligand were extensively investigated by Bruce *et al.* The reaction of [$W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$] with [$Ru_3(CO)_{10}(NCMe)_2$] gave **190** as the initial product, which readily transformed into **191** upon heating in benzene solution. Cluster **190** was reacted with an additional equivalent of tungsten reagent to give **192**. The ligand system on **192** can be rationalized by the dimerization of the diynyl ligand and the incorporation of two CO molecules. Cluster **191** interacted with $Fe_2(CO)_9$, $Co_2(CO)_8$, and $Ru_3(CO)_{12}$ to afford trimetallic/bimetallic complexes.[166,167]



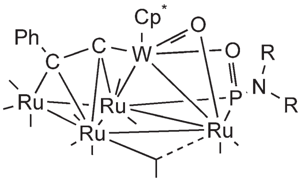
190

191

192

Carty *et al.* reported the reaction of the tungsten oxo acetylide complex [$Cp^*W(O)_2(CCPh)$] with [$Ru_4(CO)_{12-13}\{\mu_3\text{-}PN(R)_2\}$] ($R = Pr^i$ or Cy) to give oxo-bridged mixed-metal clusters 193 and 194. A diisopropylaminophosphinoxo ligand has been found on 193, and is the first example of this kind.[168,169]

Boron containing mixed-metal clusters of ruthenium–tungsten were investigated by Housecroft *et al.* The deprotonation of [$Ru_3W(\mu\text{-}H)(CO)_{11}(BH)Cp$] proceeded by the loss of the proton that bridged a B–H–Ru edge, and the remaining cluster-bound H atom in the corresponding anion is fluxional in solution. The auration of the anion by [Ph_3PAuCl] gave trimetallic cluster 195 in high yield.[170]



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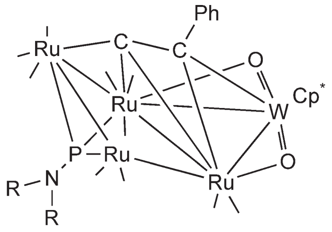

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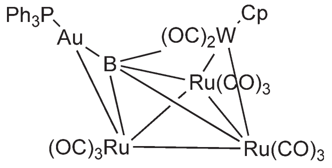
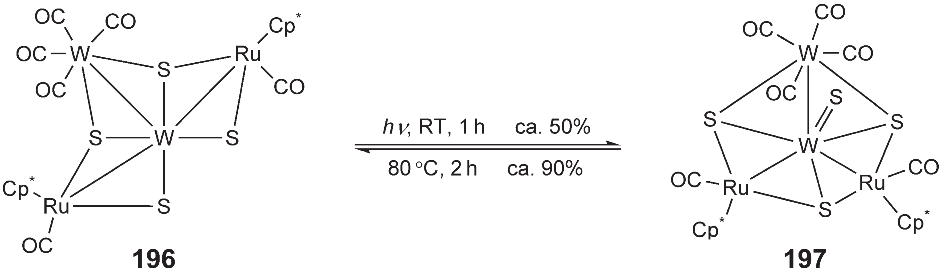


195

Phosphine-substituted cluster [$Ru_3W(\mu\text{-}H)(CO)_{10}(PPh_3)(BH)Cp$] was made by either the reaction of [$Ru_3(\mu\text{-}H)(CO)_8(PPh_3)BH$] with $\{CpW(CO)_3\}_2$ or the PPh_3 substitution of [$Ru_3W(\mu\text{-}H)(CO)_{11}(BH)Cp$] after Me_3NO-MeCN activation.[171]

Ogino *et al.* described cluster construction by the reaction of [$Cp^*_2Ru_2S_4$] with [$W(CO)_3(NCMe)_3$] to give a pair of isomeric tetranuclear Ru–W clusters 196 and 197. Two interesting aspects of this reaction should be noted. In the course of the reaction, the redistribution of the S and CO ligands took place between the Ru and W atoms without loss of any S and CO ligands. Furthermore, thermal and photochemical interconversion between them was observed.[172] The mechanistic pathway for their formation and their redox properties were also examined.[173]



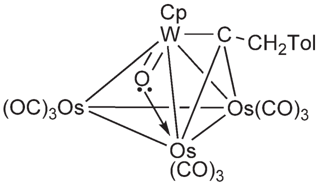
196

197

By a similar synthetic principle, the stepwise construction of trimetallic clusters $[Ru_2WPt(\mu_3\text{-}S)_2(\mu\text{-}S)_2Me(CO)_2(C_5Me_4Et)_2]$ and $[Ru_2WPt_2(\mu_3\text{-}S)_4Me_4(CO)_2Cp^*{}_2]$ was achieved by heating of $[Ru_2W(\mu\text{-}S)_4(CO)_2Cp^*{}_2]$ with $[PtMe_2(COD)]$. The subsequent reaction of the Ru_2WPt_2 complex with an excess of HCl gave monochlorination at one of the Pt centers only.[174,175] In parallel tothe RuMoCo and Ru MoNi[146,177] trimetallic systems, Yin *et al.* also studied the RuWCo and RuWNi clusters that contain sulfido[137,178–180] and selenido[181–183] ligands. Their chemical properties bear a close resemblance to those of the molybdenum analogs. Other Ru–W selenido clusters[184] or oxo clusters[185] are also known.

An important characteristic feature of metal cluster chemistry is the promotion of bond-dissociation and bond-formation reactions that involve attached organic moieties. The Os–W mixed-metal clusters happen to be a neat system to illustrate this characeteristic. A review article on this area has also been written.[208] A large number of Os–W cluster complexes are known, and their chemistry has essentially been uncovered by several research groups, including Shapley, Chi, and Park.

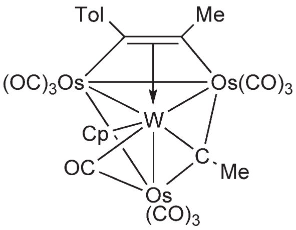
The interconversion of alkylidyne, alkylidene, vinylidene, and alkyne ligand moieties in a single cluster complex has been demonstrated on the oxo–alkylidyne cluster **198** via hydrogenation, protonation, or thermolysis.[186]



198

The heterometallic ketenyl complexes $[Os_3W(\mu\text{-}H)\{C(O)CH_2\}(CO)_3Cp']$ (Cp′ = Cp or Cp*) that possess a pendant $Cp'W(CO)_3$ substituent were prepared by the condensation of $[Os_3(CO)_{10}(NCMe)_2]$ with the metal–aldehyde complex $[Cp'W(CO)_3CH_2CHO]$. Pyrolysis of these ketenyl complexes in the solid state at 185 °C afforded tetranuclear clusters in the case of the Cp* derivative, whereas the Cp system[187] gave pentanuclear species.[188] In both cases, C–O bond scission in the ligated ketene fragment was observed.

The interactions of $[Os_3(CO)_{10}(C_2Me_2)]$ with $[CpW(CO)_2(\equiv CTol)]$ afforded the alkylidyne–alkyne cluster **199** and the dimetalloallyl complex **200**. Heating of **200** resulted in the selective scission of one C–C bond to give another alkylidyne–alkyne cluster **201**. This transformation provides a model of alkyne metathesis through a dimetalloallyl intermediate.[189]



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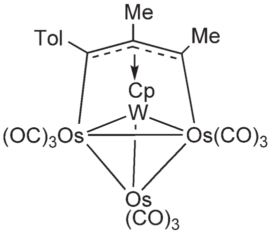

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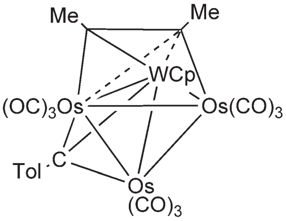
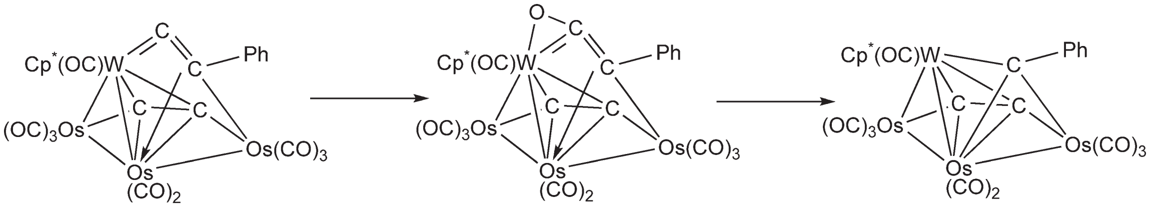


201

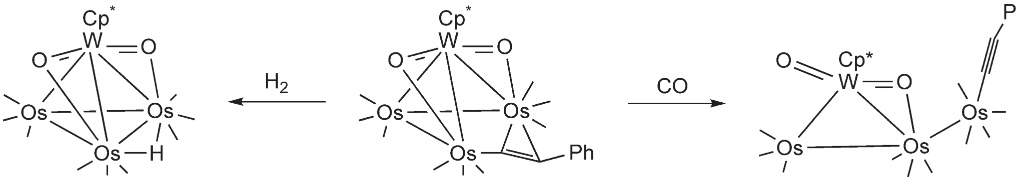
Another interesting transformation that involves the sequential conversion of acetylide into ketenyl and alkylidyne was observed in **202**. The oxidation of **202** in toluene produced the ketenyl complex **203**, which underwent CO dissociation to give the alkylidyne cluster **204**.[190]



202 **203** **204**

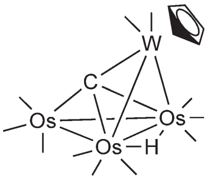
Acetylide migration was observed in $[Os_3W(C\equiv CCH_2OMe)(CO)_{11}Cp^*]$, which was prepared by the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with $[Cp^*W(CO)^3(C\equiv CCH_2OMe)]$.[191]

The tetranuclear acetylide clusters $[Os_3W(CCR)(CO)_{11}Cp^*]$ (R = Bu, Ph, CH_2OMe), depending on the substituents of the acetylide ligand, showed reversible C–C bond scission and C–H bond activation to give the carbide–alkylidyne cluster $[Os_3W(\mu_4\text{-}C)(\mu\text{-}CPh)(CO)_{10}Cp^*]$ (for R = Ph) and the carbide–vinylidene clusters $[Os_3W(\mu_4\text{-}C)(\mu\text{-}H)(\mu\text{-}CCHR')Cp^*]$ (R′ = Pr, OMe), respectively.[192,193] The addition of $[Cp^*W(O)_2(CCPh)]$ to the activated cluster $[Os_3(CO)_{10}(NCMe)_2]$ led to the heterometallic cluster **205**, which contains two edge-bridging oxo groups and an acetylide ligand in μ-η^2 fashion. The hydrogenation and carbonylation of this complex afforded **206** and **207**, respectively.[194]



205 **206** **207**

The high-yield synthesis of carbide mixed-metal cluster **208** and its reactivity with an electron-deficient alkyne (diisopropyl acetylenedicarboxylate) have been reported. Chemical transformations that involve a dimetalla-allyl ligand were observed.[195] The reaction of acetylide cluster **205** with diphenylacetylene yielded two clusters **209** and **210** by alkyne coordination and the cluster-assisted formation of C–C bonds between acetylide and alkyne, respectively. However, the reaction with phenylacetylene gave **211** as the major product.[196] The coupling reaction of $[Cp^*W(O)_2(C\equiv CC\equiv CPh)]$ with the unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ proceeded smoothly to give **212**, in which the organic ligand C≡CC═CHPh was formed by facile hydride transfer reaction. The isomerization of **212** in solution was observed.[197]



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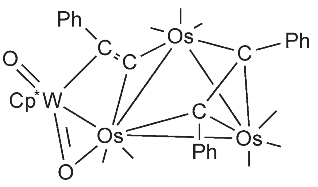

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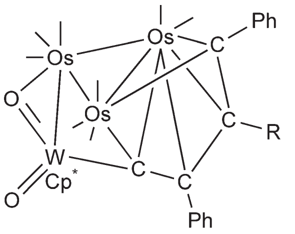
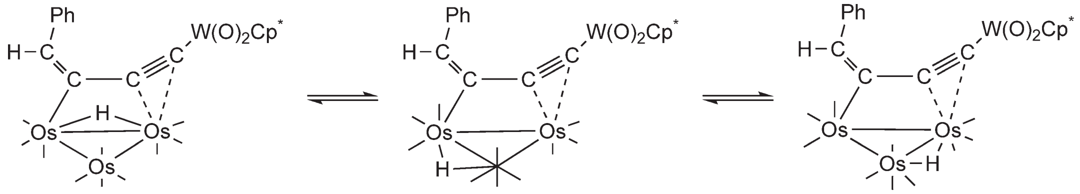


R = Ph **210**
R = H **211**



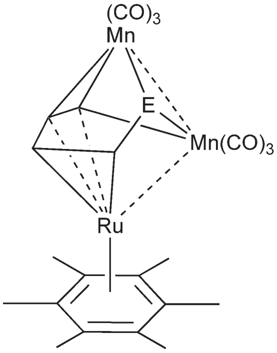
212

The mixed-metal cluster of Os–W without Cp-type ligands was also created. Earlier work by Lewis *et al.* showed that the interaction of the $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ anion with $[W(CO)_3(NCMe)_3]$ afforded the stable $[Os_3W(\mu\text{-}H)(\mu\text{-}CO)(CO)_{13}]^-$ anion in good yield.[198] The reaction of this heterometallic anion with phenylacetylene gave $[Os_3W(\mu\text{-}H)\{\mu_3\text{-}\eta^3\text{-}C(H)C(Ph)C(OH)\}(CO)_{12}]$ in moderate yield. The coupling of a phenylacetylene and a CO ligand has also been observed.[199]

6.25.3.4 Ru/Os Mixed-metal Clusters Containing Group 7 Elements

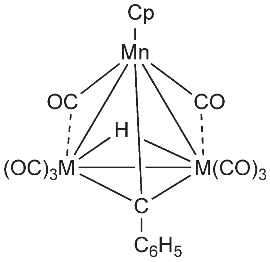
Mixed-metal clusters of these combinations are rather scarce in this review period (see Table 12). A few reports that have featured efforts to open up their chemistry are summarized in the following. Shriver *et al.* ultilized the oxo cluster anion $[Ru_3(CO)_9(\mu_3\text{-}O)]^{2-}$ as a nucleophile with the lightly stabilized complexes $[M(CO)_3(NCMe)_3]^+$ (M = Mn or Re) to prepare the mixed-metal acetamidediato cluster anions $[Ru_3M\{\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3\}]$ (M = Mn or Re).[209] The carbonylcyanometalate $[Mn(C_5H_4Me)(CN)(CO)_2]^-$ reacts with $[Ru_3(CO)_{12}]$ to give a mixed-metal anionic cluster with a CN^- ligand in the $\mu_3\text{-}\eta^2$ bonding mode. The corresponding aurated species with the formula $[Ru_3\{(\mu_3\text{-}\eta^2\text{-}NC)MnCp(CO)_2\}(AuPPh_3)(CO)_{10}]$ was also prepared and structurally characterized.[210] Treatment of $[(\eta^5\text{-}C_4H_4E)Ru(\eta^6\text{-}C_6Me_6)]^{2+}$ (E = S, Se) with cobaltocene and $[(1\text{-methylnaphthalene})Mn(CO)_3]BF_4$ at −78 °C led to the isolation of **213** and **214**, respectively. X-ray analyses revealed manganese insertion into a C–S or C–Se bond and two metal–metal bonds without the formation of bridging CO ligands.[211]

The interaction of the cationic carbyne complex $[Cp(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ with $[PPN]_2[M_3(CO)_{11}]$ (M = Ru, Os) in THF at a low temperature afforded **215** in moderate yield.[212]



E = S
E = Se

213
214



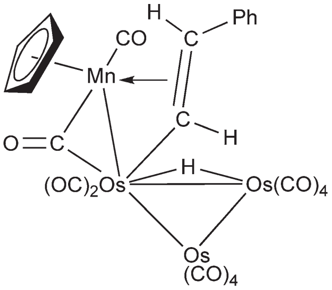
M = Ru, Os

215

Table 12 Ru/Os mixed-metal clusters containing group 7 elements with known structure

Formula	*References*
Clusters with two different kinds of metal	
$[RuMn_2(\eta^6\text{-}C_6Me_6)(SC_4H_4)(CO)_6]$	211
$[RuMn_2(\eta^6\text{-}C_6Me_6)(SeC_4H_4)(CO)_6]$	211
$[Ru_3Mn\{\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3\}(CO)_{12}][PPN]$	209
$[Ru_2Mn(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6Cp]$	212
$[OsMn(CNBu^t)Cl(CO)_8]$	54
$[Os_2Mn(CNBu^t)_2Br(CO)_{11}]$	54
$[Os_3Mn(CNBu^t)_3I(CO)_{14}]$	213
$[Ru_2Re_2(\mu\text{-}H)(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$	216
$[Ru_2Re_2(\mu_3\text{-}S)_4\{S_2C_2(SiMe_3)_2\}_2Cp^*{}_2]$	217
$[Ru_2Re_3(\mu\text{-}H)_3(\mu\text{-}PPh_2C_2)(\mu\text{-}PPh_2)(CO)_{17}]$	221
$[Os_2Re_2(CO)_{14}(CNBu^t)_4]$	219
$[Os_3Re(\mu\text{-}H)(PPh_3)(CO)_{14}]$	218
Clusters with three different kinds of metal	
$[Ru_3MnAu(\mu_3\text{-}\eta^2\text{-}NC)(PPh_3)(CO)_{12}Cp]$	210
$[RuRe_2Ir(\mu_3\text{-}S)_4\{S_2C_2(SiMe_3)_2\}_2Cp^*{}_2][PF_6]$	217
$[Os_3ReCo_2\{\mu_6\text{-}C_2C{=}CH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{14}]$	220

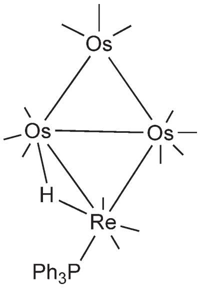
A novel metal-chain extension reaction to give mixed-metal clusters (Os_nMn, $n = 1, 2, 3$) with a linear metal skeleton using $[Os(CO)_4(CNBu^t)]$ and $[Mn(CO)_5X]$ (X = Cl, Br, I) was developed by Pomeroy *et al.*[54,213] The redox behavior of mixed-metal cluster **216** was investigated, and it was found that cluster fragmentation occurs after four-electron reduction to give a triosmium cluster and the $[CpMn(CO)_2]^{2-}$ dianion.[214]



216

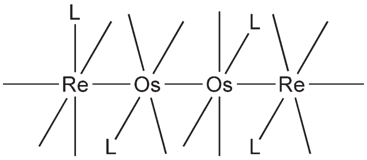
An Ru–Re mixed-metal cluster anion with the formula $[RuRe_6C(CO)_{21}]^{2-}$ was created from a photochemical reaction between the $[Re_6C(CO)_{19}]^{2-}$ anion and $Ru_3(CO)_{12}$.[215] Heterometallic sulfide clusters of Ru–Re with open[216] or cubane[217] structures are also known.

Os–Re cluster **217**, which contains a planar, diamond-like metal skeleton, was prepared by the addition of $[Re(CO)_4(PPh_3)H]$ to $[Os_3(CO)_{10}(cyclooctene)_2]$.[218]



217

Treatment of $[Os(CO)_3(CNBu^t)_2]$ with $[Re_2(\mu\text{-}H)(\mu\text{-}\eta\text{-}C_2H_3)(CO)_8]$ led to the isolation of **218 and 219** in low yields. Both compounds contain an approximately linear $ReOs_2Re$ chain.[219]



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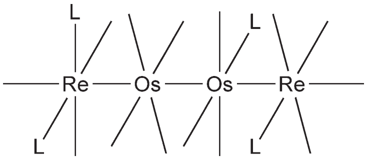


219

L = Bu^{t}NC

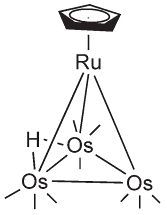
6.25.3.5 Ru/Os Mixed-metal Clusters Containing Group 8 Elements

Mixed-metal clusters of Fe–Ru and Fe–Os will be surveyed in Chapter 6.10, which is dedicated to iron organometallic compounds. Table 13 lists the Ru–Os mixed-metal clusters with known structures.

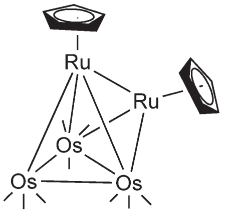
Table 13 Ru/Os mixed-metal clusters containing group 8 elements with known structure

Formula	*References*
$[RuOs_3(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)(CO)_{12}]$	230
$[RuOs_3(\mu_4\text{-}HC_2Me)(CO)_{12}]$	229
$[RuOs_3(\mu\text{-}H)(CO)_{11}Cp]$	223
$[RuOs_3(\mu\text{-}H)(PPh_3)(CO)_{10}Cp]$	224
$[RuOs_3(\mu\text{-}H)(PPh_3)(CO)_{11}Cp]$	224
$[RuOs_3(\mu\text{-}H)_2(CO)_{12}PPh_3]$	231
$[RuOs_4(\mu_5\text{-}C)(\eta^6\text{-}C_6H_6)(CO)_{12}]$	228
$[RuOs_4(\eta^6\text{-}C_6H_6)(CO)_{13}]$	227
$[RuOs_4(\mu\text{-}H)_2(\eta^6\text{-}C_6H_6)(CO)_{13}]$	227
$[RuOs_4(\mu\text{-}H)_3(\mu_3\text{-}\sigma,\sigma,\eta^6\text{-}C_6H_5)(PPh_2Me)(CO)_{12}]$	227
$[RuOs_4(\mu\text{-}H)_3(\mu_3\text{-}\eta^6\text{-}C_6H_5)\{P(OMe)_3\}(CO)_{12}]$	226
$[RuOs_4(\mu\text{-}H)_4(\eta^6\text{-}C_6H_6)(CO)_{11}]$	225
$[RuOs_4(AuPPh_3)(CO)_{13}Cp]$	227
$[RuOs_5(\mu_6\text{-}C)(\eta^6\text{-}C_6H_6)(CO)_{14}]$	228
$[Ru_2Os_3(\mu_3\text{-}CO)_2(CO)_9Cp_2]$	223
$[Ru_2Os_3(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$	221
$[Ru_2Os_3(\mu\text{-}H)\{P(OMe)_3\}(\mu_3\text{-}\eta^5\text{-}C_5H_4)(CO)_{11}Cp]$	224
$[Ru_2Os_5(CO)_{15}Cp_2]$	222

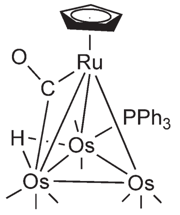
The synthetic strategies for Ru–Os mixed-metal clusters can be broadly classified into two categories: ionic coupling and condensation that is assisted by coordinated alkyne ligands. Lewis *et al.* nicely demonstrated the synthetic value of $[RuCp(MeCN)_3]^+$ [222–224] and $[M(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ (M = Ru, Os)[225–228] cations as capping reagents on monoanionic or dianionic clusters in the preparation of Ru–Os mixed-metal clusters **220–225** and others.



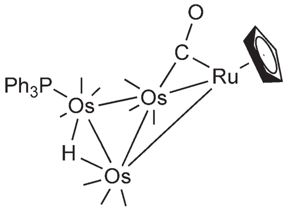
220



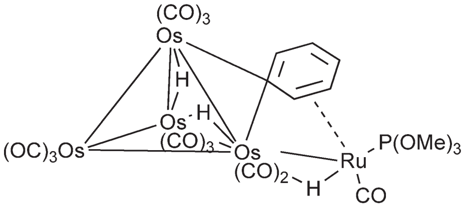
221



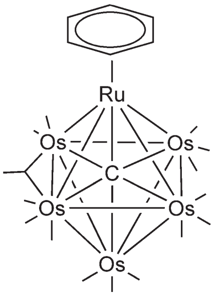
222



223

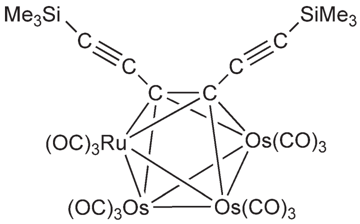


224



225

The reaction of the acetylide cluster $[Os_3(\mu\text{-}H)(\mu\text{-}C{\equiv}Me)(CO)_9]$ with $[Ru_3(CO)_{12}]$ in refluxing hexane gave $[RuOs_3(\mu_4\text{-}HC_2Me)(CO)_{12}]$ with a butterfly metal core.[229] Alkynyl complexes such as $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)]$ also formed mixed-metal clusters **226** when treated with $[Ru_3(CO)_{12}]$ (Table 13).[230]



226

A new synthetic route with high yield (70%) for $[RuOs_3(\mu-H)(CO)_{13}]$, was developed by Leong *et al*. The phosphine substitution of this cluster was also studied.[231]

6.25.3.6 Ru/Os Mixed-metal Clusters Containing Group 9 Elements

Many ruthenium–cobalt and osmium–cobalt cluster complexes are known. One of the simplest examples, $[RuCo_3(\mu-H)(CO)_{12}]$, or in its anionic form $[RuCo_3(CO)_{12}]^-$, was extensively studied by Braunstein *et al*. Site-selective substitution reactions and isomerizations on the tetrahedral $RuCo_3$ core with N, P, S, Se, and Te donor ligands have been reported.[232,233] Skeletal rearrangements of the $RuCo_3$ core that lead to tri- and pentanuclear phosphinidene clusters were observed.[234] Interactions of $[RuCo_3(CO)_{12}]^-$ with various alkynes afforded the butterfly clusters with the formula $[RuCo_3(\mu_4-\eta^2-RC_2R')(CO)_{10}]^-$, in which the Ru atom occupies a hinge position. Selective degradation of these anions to give $RuCo_2$ clusters can be achieved.[235] Substitution by reaction of $[RuCo_3(\mu-H)(CO)_{12}]$ with bulky phosphine,[248–250] multidentate phosphine,[251,252] thiophene,[253,254] and thienylphosphine[255] ligands has been studied. It is interesting to note that the tridentate phosphine-stabilized cobalt cluster $[Co_3(\mu_3-CCl)(CO)_6(tdpm)]$ (tdpm = tri(diphenylphosphino)methane) reacted with $Na[RuCp(CO)_2]$ to produce the mixed-metal cluster $[RuCo_3(\mu_4-C)(CO)_8(tdpm)Cp]$, which contains a tetrahedral sp^3 carbide ligand (Table 14).[256]

The anion $[RuCo_3(CO)_{12}]^-$ has also been used to prepare metallic nanoparticles on mesoporous silica xerogels and MCM-41 type supports.[235,236] Another important synthetic method to Ru–Co clusters is the alkyne-assisted cluster condensation that was established by Bruce *et al*. It was shown that ruthenium alkynes,[237,238] diynes,[220,239,240] or

Table 14 Ru/Os mixed-metal clusters containing group 9 elements with known structure

Formula	*References*
Clusters with two different kinds of metal	
$[RuCo_2(\mu_3-\eta^2-C{=}CHPh)\{PPh_2(C_5H_2O_2)\}(CO)_7]$	250
$[RuCo_2(\mu_3-\eta^2-MeO_2CC_2CO_2Me)(CO)_9]$	235
$[RuCo_2(\mu_3-PCy)(CO)_9]$	234
$[RuCo_2(\mu_3-S)\{CN(Me)SPh\}(CO)_8]$	254
$[RuCo_2(\mu_3-Se)(\mu-dppm)(CO)_7]$	233
$[RuCo_2(\mu_3-Se)\{\mu-Ph_2(2-C_5H_4N)P\}(CO)_7]$	233
$[RuCo_3(\mu_3-C_8H_8)(\mu_3-CO)_3(CO)_3Cp^*]$	260
$[RuCo_3(\mu_4-C)(tdpm)(CO)_8Cp]$	256
$[RuCo_3(\mu_4-\eta^2-Me_3SiC_2C{\equiv}CH)(CO)_{10}][NBu^n{}_4]$	235
$[RuCo_3(\mu_4-\eta^2-Me_3SiC_2C{\equiv}CSiMe_3)(CO)_{10}][Et_4N]$	235
$[RuCo_3(\mu_4-\eta^2-Me_3SiC_2C{\equiv}CSiMe_3)(PPh_3)(CO)_9][Et_4N]$	235
$[RuCo_3(\mu-H)(\mu-CO)_3\{\mu-Ph_2(2-C_5H_4N)P\}(CO)_7]$	233
$[RuCo_3(\mu-H)(PMe_2Ph)_2(CO)_{10}]$	232
$[RuCo_3(\mu-H)(PMe_2Ph)_3(CO)_9]$	232
$[RuCo_3(\mu-H)(SC_4H_8)(CO)_{11}]$	253
$[RuCo_3(\mu-H)\{HC(PPh_2)_3\}(CO)_9]$	251
$[RuCo_3(\mu-H)\{HC(PPh_2)_3\}(PMe_2Ph)(CO)_8]$	252
$[RuCo_3(\mu-H)\{P(SC_4H_3)_3\}(CO)_{11}]$	255
$[RuCo_3\{\mu_4-\eta^2-HC_2-C(CH_3){=}CH_2\}(CO)_{10}][Et_4N]$	235
$[RuCo_3\{\mu_4-\eta^2-HC_2-CH_2OCH_2C{\equiv}CH\}(CO)_{10}][Et_4N]$	235
$[RuCo_4(\mu_4-PCy)(\mu-CO)_2(CO)_{11}]$	234
$[Ru_2Co(CO)_4CpCp^*{}_2]$	261
$[Ru_2Co(\mu_3-CO)(BH_2)_3(CO)_3Cp^*{}_2]$	246
$[Ru_2Co(\mu_3-CO)(\mu_3-NH)(CO)_6Cp^*]$	243
$[Ru_2Co(\mu-CO)_2(PMe_2Ph)B_3H_4(CO)Cp^*{}_2]$	247
$[Ru_2Co(\mu-CO)_2(B_2H_2B)(NC_5H_5)(CO)_2Cp^*{}_2]$	247
$[Ru_2Co(\mu-CO)(B_2H_2)(NC_4H_4C)(CO)_3Cp^*{}_2]$	247
$[Ru_2Co_2(\mu_4-C_2Ph_2)(\mu_3-CO)_2(CO)_4Cp_2]$	257
$[Ru_2Co_4(\mu_3-\eta^2-HC_2CH_2OC_6H_4OCH_2C_2H-\eta^2-\mu_3)(CO)_{18}]$	262
$[Ru_2Co_6(C_6H_4OS)_{10}(PBu^n{}_3)_6]$	258
$[Ru_3Co(\mu_3-C_9H_6Ph)(\mu-CO)_4(CO)_5]$	241
$[Ru_3Co(\mu_3-CO)(BH)_3(CO)_2Cp^*{}_3]$	245

(Continued)

Table 14 (Continued)

Formula	*References*
$[Ru_3Co(\mu-H)(\mu_4-N)(CO)_9Cp^*]$	243
$[Ru_3Co(\mu-H)_2(\mu_4-N)(\mu-I)(CO)_8Cp^*]$	242
$[Ru_3Co(\mu-H)_2\{\mu-\eta^2-C(OMe)O\}(\mu_4-N)I(\mu-I)(CO)_6Cp^*]$	242
$[Ru_3Co(\mu-H)_2\{\mu-\eta^2-C(OMe)O\}(\mu_4-N)I(\mu-I)(CO)_6Cp^*]$	242
$[Ru_3Co(\mu-H)_3(\mu-CO)(PCy_3)(CO)_{10}]$	248
$[Ru_3Co(\mu-H)_3\{HC(PPh_2)_3\}(CO)_9]$	251
$[Ru_3Co(\mu-H)_3\{HC(PPh_2)_3\}(PMe_2Ph)(CO)_9]$	252
$[Ru_3Co_2(\mu_3-CO)(\mu_3-NH)\{\mu_4-\eta^8-C_6H_4C(H)C(Ph)\}(CO)_7Cp^*_2]$	244
$[Ru_3Co_2(\mu_4-C_2Ph)(\mu_3-C_2Ph)(\mu-CO)(\mu-dppm)(CO)_{10}]$	240
$[Ru_3Co_2(\mu_5-\eta^2,\eta^2-PhC_2C_2Ph)(CO)_{14}]$	239
$[Ru_5Co(\mu_6-C)(\mu-CO)_2(CO)_{14}][PPN]$	263
$[Ru_5Co_2C_4(\mu-PPh_2)_2(CO)_{23}]$	220
$[Ru_5Co_4(\mu_{10}-C_2)(\mu_3-SMe)_2(\mu-PPh_2)_2(\mu-CO)_7(CO)_{11}]$	237
$[Ru_6Co(\mu_3-H)(\mu-CO)_3(\mu_4-\eta^2-CO)(\mu_4-N)(CO)_8Cp^*_3]$	243
$[Ru_6Co_2(\mu_7-C_2)(\mu_3-SMe)_2(\mu-PPh_2)_2(\mu-CO)_4(CO)_{13}]$	238
$[Os_6Co_2(\mu-PPh_2)(\mu-PPh_2C_2C_2)(CO)_{24}]$	220
$[RuRh_2(C_2S_4)Cp^*_3]$	294
$[RuRh_2(\mu-CO)_3(\mu_3-CO)(\eta^5-7,8-C_2B_9H_{11})Cp^*_2]$	289
$[RuRh_3(CO)_{12}][PPN]$	277
$[RuRh_3(\mu-H)(SPh_2)_3(CO)_9]$	275
$[RuRh_3(\mu-H)(SPhMe)_3(CO)_9]$	275
$[Ru_2Rh(CO)_4Cp_2Cp^*]$	261
$[Ru_2Rh(\mu_3-S)_3(SCH_2COCH_3)Cp^*_3][BF_4]$	293
$[Ru_2Rh(\mu_3-S)_4(MeCN)Cp^*_3][SbF_6]_2$	293
$[Ru_2Rh(\mu-H)(\mu_3-S)_2Cl_2PPh_3Cp^*_2]$	292
$[Ru_2Rh_2(\mu-CO)_5(CO)_7][PPh_4]_2$	276
$[Ru_2Rh_2(\mu-H)(\mu-CO)_3(CO)_9][PPh_4]$	276
$[Ru_2Rh_6(\mu-H)_2(SC_4H_8)_3(CO)_{18}]$	253
$[Ru_2Rh_6(\mu-H)_2(SEt_2)_3(CO)_{18}]$	275
$[Ru_3Rh(CO)_{13}][PPN]$	277
$[Ru_3Rh(\mu_3-H)(\mu-PBu^t_2)_2(Bu^t_2PH)(\mu-Cl)_2(CO)_7]$	291
$[Ru_3Rh(\mu-H)_2(CO)_{12}][PPN]$	272
$[Ru_3Rh(\mu-H)_2(\mu_4-\eta^2-CO)(\mu-CO)_2(PPh_3)_2(CO)_5Cp^*]$	271
$[Ru_3Rh(\mu-H)_2(PPh_3)(BH)(CO)_8Cp^*]$	281
$[Ru_3Rh_2(\mu_3-H)(\mu-CO)(\mu_3-CO)_2(\mu-\eta^1:\eta^5-CH_2C_5Me_4)(CO)_6Cp^*]$	271
$[Ru_3Rh_2(\mu-H)_2(CO)_{13}(PPh_3)]$	272
$[Ru_4Rh(\mu_5-C)(CO)_{12}Cp^*]$	267
$[Ru_4Rh(\mu_5-C)(\mu-H)(CO)_{11}Cp^*]$	268
$[Ru_4Rh(\mu-H)(BH_2)(CO)_{13}Cp^*]$	282
$[Ru_4Rh(\mu-H)_2(\mu-Cl)B(CO)_{12}Cp^*]$	284
$[Ru_4Rh_2(\mu-H)(nbd)_2B(CO)_{12}]$	287
$[Ru_4Rh_2(nbd)_2B(CO)_{12}][PPN]$	287
$[Ru_4Rh_2B(CO)_{16}][PPN]$	283
$[Ru_5Rh(\mu_6-C)(CO)_{14}Cp^*]$	265,266
$[Ru_5Rh(\mu_6-C)(CO)_9Cp_2Cp^*]$	265
$[Ru_5Rh(\mu-CO)(\mu_4-\eta^2-CO)_2(CO)_{12}Cp^*]$	270
$[Ru_5RhB(CO)_{17}]$	288
$[Ru_6Rh_3B_2(CO)_{23}][PPN]$	283
$[Os_2Rh(\mu-CO)_2(CO)_9Cp^*]$	296
$[Os_2Rh_2(\eta^3-CH_2CHCH_2COO)_2(\mu-CO)_2(CO)_7]$	300
$[Os_3Rh(\mu_3-CCH_3)(\eta^6-C_6H_5CH_3)(CO)_9]$	300
$[Os_3Rh(\mu_3-H)(\mu-Cl)(\mu-CO)(CO)_9Cp^*]$	296
$[Os_3Rh(\mu_4-\eta^2-PhC_2Ph)(\mu-\eta^1:\eta^2-PhC_2PhH)(\mu-CO)(CO)_9]$	297
$[Os_3Rh(\mu-H)_2(\mu-CO)(\mu-I)(bipy)(CO)_8]$	295
$[Os_3Rh(\mu-H)_2(\mu-CO)(\mu-I)(\eta^4-COD)(CO)_8]$	295
$[Os_3Rh(\mu-H)_3(\eta^4-COD)(CO)_{10}]$	295
$[Os_3Rh_2(\mu-H)(\mu-CO)_2(CO)_8(\mu-\eta^5,\eta^1-CH_2C_5Me_4)Cp^*]$	296
$[Os_3Rh_4(\mu_3-\eta^1:\eta^1:\eta^1-C_6H_5CH_3)(CO)_{13}]$	302

(Continued)

Table 14 (Continued)

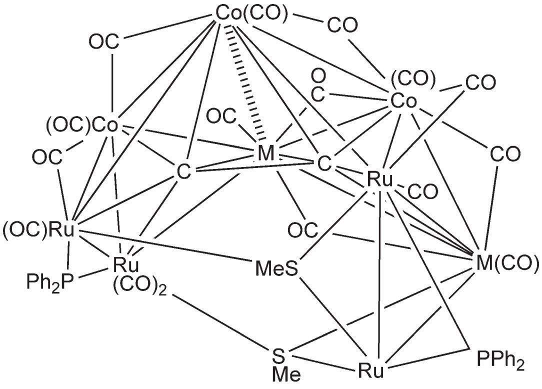
Formula	*References*
$[Os_4Rh(\mu\text{-}H)_2(CO)_{13}Cp^*]$	304
$[Os_4Rh(\mu\text{-}H)_3(MeC{=}NH)(CO)_{11}Cp^*]$	304
$[Os_4Rh(\mu\text{-}H)_4(\eta^2\text{-}NC_5H_4C_2H_2)(CO)_{13}]$	301
$[Os_4Rh_2(\mu\text{-}H)_2(CO)_{11}Cp^*{}_2]$	304
$[Os_4Rh_3(\mu_3\text{-}H)(\mu_3\text{-}CO)(\eta^4\text{-}C_7H_8)_2(CO)_{14}]$	298
$[Os_5Rh(\mu_5\text{-}C)(\mu_3\text{-}CO)(CO)_{13}Cp^*]$	303
$[Os_5Rh_2(\eta^6\text{-}C_6H_5CH_3)(\mu\text{-}CO)(CO)_{16}]$	300
$[Os_6Rh(\mu\text{-}H)_2(CO)_{20}][PPN]$	297
$[Os_6Rh(\mu\text{-}H)_7(\mu\text{-}CO)(CO)_{18}]$	297
$[Os_6Rh(\mu\text{-}H)_9(CO)_{18}]$	297
$[Os_{12}Rh_9(\mu_3\text{-}Cl)(CO)_{44}]$	298
$[RuIr_2(\mu_3\text{-}S)(\mu\text{-}SCH_2CH_2CN)_2(CO)Cp^*{}_3][PF_6]$	325
$[RuIr_2(\mu_3\text{-}S)(\mu\text{-}SCH_2CH_2CN)_2(\mu\text{-}HC{=}CCO_2Me)Cp^*{}_3][PF_6]$	325
$[RuIr_2(\mu_3\text{-}S)(\mu\text{-}SCH_2CH_2CN)_2ClCp^*{}_3]$	324
$[RuIr_2(\mu_3\text{-}S)_2(dppe)(\eta^4\text{-}C_5Me_5CHCl_2)ClCp^*]$	323
$[RuIr_2(\mu_3\text{-}S)_2(\mu\text{-}H)_2(dppe)Cp^*{}_2]$	323
$[RuIr_2(\mu_3\text{-}S)_2(SC_6H_2Pr^i{}_3)_2Cp^*{}_2]$	323
$[RuIr_2(\mu_3\text{-}S)_2Me(dppe)Cp^*{}_2][PF_6]$	323
$[RuIr_2(\mu_3\text{-}S)_2PPh_3Cl_2Cp^*{}_2]$	323
$[Ru_2Ir(\mu\text{-}H)(dppm)_3(CO)_5]$	313
$[Ru_2Ir(\mu\text{-}H)(PCy_3)_3(CO)_6]$	313
$[Ru_2Ir(\mu\text{-}H)(PhC{\equiv}CMe)(CO)_9]$	310
$[Ru_2Ir(\mu\text{-}H)(PhC{\equiv}CPh)(CO)_9]$	310
$[Ru_2Ir(PhC{\equiv}CPh)(CO)_9][PPN]$	310
$[Ru_2Ir_2(\mu\text{-}H)_2(PPh_3)_2(CO)_{10}]$	319
$[Ru_2Ir_2(\mu\text{-}H)Cl(CO)_{12}]$	317
$[Ru_3Ir(CO)_{13}][PPN]$	307
$[Ru_3Ir(\mu_3\text{-}H)(\mu\text{-}PBu^t{}_2)_2(Bu^t{}_2PH)(\mu\text{-}Cl)_2(CO)_8]$	322
$[Ru_3Ir(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)(\mu\text{-}\eta^2\text{-}PhC{=}CHPh)(CO)_{10}]$	309
$[Ru_3Ir(MeC{\equiv}CMe)(CO)_{11}][PPN]$	310
$[Ru_3Ir(\mu\text{-}H)(BH_2)(CO)_{10}Cp^*]$	281
$[Ru_3Ir(\mu\text{-}H)(EtC{\equiv}CEt)(CO)_{11}]$	310
$[Ru_3Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}MeC{\equiv}CMe)(CO)_{11}]$	309
$[Ru_3Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)(CO)_{11}]$	309
$[Ru_3Ir(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{12}][Ru_3Ir(\mu\text{-}H)_2(CO)_{12}][PPN]_2$	308
$[Ru_3Ir(\mu\text{-}H)_2(CO)_{12}][PPN]$	307
$[Ru_3Ir(\mu\text{-}H)_2(\mu\text{-}PBu^t{}_2)_2(Bu^t{}_2PH)(\mu_3\text{-}Cl)(CO)_7]$	321
$[Ru_3Ir(\mu\text{-}H)_2Cl(CO)_{12}]$	316
$[Ru_3Ir(\mu\text{-}H)_2PPh_3(CO)_{11}][PPN]$	312
$[Ru_3Ir(\mu\text{-}H)_3(PPh_3)_2(CO)_{10}]$	319
$[Ru_3Ir(\mu\text{-}H)_3\{P(OPh)_3\}(CO)_{11}]$	312
$[Ru_3Ir(\mu\text{-}H)_3AsPh_3(CO)_{11}]$	312
$[Ru_3Ir(\mu\text{-}H)_3PMe_3(CO)_{11}]$	312
$[Ru_3Ir(\mu\text{-}H)_3PPh_3(CO)_{11}]$	319
$[Ru_3Ir(\mu\text{-}H)PPh_3(CO)_{12}]$	318
$[Ru_3Ir(\mu\text{-}H)PPh_3(CO)_{12}]$	319
$[Ru_3Ir(PhC{\equiv}CMe)(CO)_{11}][PPN]$	310
$[Ru_3Ir(PhC{\equiv}CPh)(CO)_{11}][PPN]$	310
$[Ru_3Ir_2(CO)_{14}][PPh_4]_2$	315
$[Ru_3Ir_2(\mu\text{-}H)(CO)_{14}][PPh_4]$	315
$[Ru_3Ir_7(CO)_{23}][N\{P(C_6H_4Me\text{-}p)_3\}_2]$	320
$[Ru_4Ir(\mu\text{-}H)(\mu_4\text{-}CCH_3)(CO)_{15}]$	311
$[Ru_4Ir_2B(CO)_{16}][PPN]$	280
$[RuIr_2(\mu_3\text{-}S)(\mu\text{-}SCH_2CH_2CN)(\mu_3\text{-}SCH_2CH_2C{=}NH)Cp^*{}_3][PF_6]_2$	325
$[Os_2Ir_2(\mu\text{-}H)_2(PCy_3)_2(CO)_{10}]$	313
$[Os_3Ir(\mu\text{-}H)_3(PCy_3)_3(CO)_8]$	313
$[Os_3Ir(CO)_{13}][PPN]$	314

(*Continued*)

Table 14 (Continued)

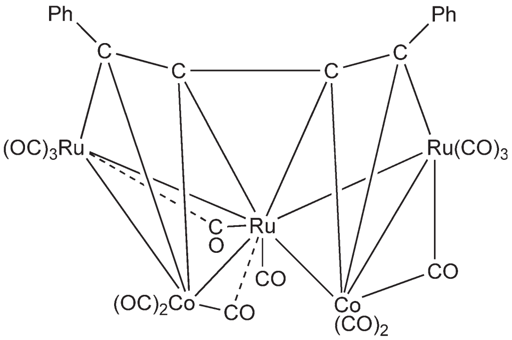
Formula	*References*
Clusters with three different kinds of metal	
$[RuCo_2(NC)Fe(CO)_{12}Cp]$	259
$[RuCo_3Au(PPh_3)(\mu\text{-}CO)_5(CO)_6(PMe_2Ph)]$	249
$[Ru_2Co_4Hg(\mu_5\text{-}C)(CO)_{13}Cp_2]$	256
$[Os_3CoRu(CO)_{13}Cp]$	264
$[Os_3Co_2Re\{\mu_6\text{-}C_2C{=}CH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{14}]$	220
$[RuRh_3Au(PPh_3)(CO)_{12}]$	290
$[Ru_2Rh_2Au(PPh_3)(\mu\text{-}CO)_5(CO)_7][PPh_4]$	276
$[Ru_3Rh_2Au(PPh_3)_2(\mu\text{-}H)(CO)_{13}]$	274
$[Ru_3RhAu(\mu\text{-}H)(\mu\text{-}dppf\text{-}P,P')B(CO)_8Cp^*]$	285
$[Ru_4Rh(AuPPh_3)(\mu\text{-}H)(nbd)B(CO)_{12}]$	284
$[Ru_4Rh_2Au(PCy_3)(CO)_{16}B]$	280
$[Ru_4Rh_2Au(PPh_3)(nbd)_2B(CO)_{12}]$	287
$[Ru_4Rh_2Au(PPh_3)(nbd)B(CO)_{14}]$	287
$[Ru_4Rh_2Au(PPh_3)(PPh_3)_2B(CO)_{15}]$	288
$[Ru_4Rh_2Au(PPh_3)_3B(CO)_{14}]$	286
$[Ru_4Rh_2Au(PPh_3)B(CO)_{16}]$	286
$[Ru_5RhAu(PPh_3)(\mu_6\text{-}C)(COD)(CO)_{14}]$	269
$[Ru_3Ir_6Au(PPh_3)(CO)_{21}][PPh_4]$	320
$[Ru_3Ir_7Au(PPh_3)(CO)_{23}]$	320
$[Ru_4Ir_2Au(PCy_3)B(CO)_{16}]$	280

allenylidene[241] complexes reacted with $[Co_2(CO)_6]$ and other transition metal alkynophiles to give mixed-metal clusters that contain novel organic moieties on the cluster surface. Several remarkable examples are 227, 228, and 229.



M = Co/Ru

227



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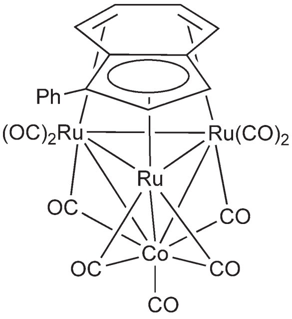
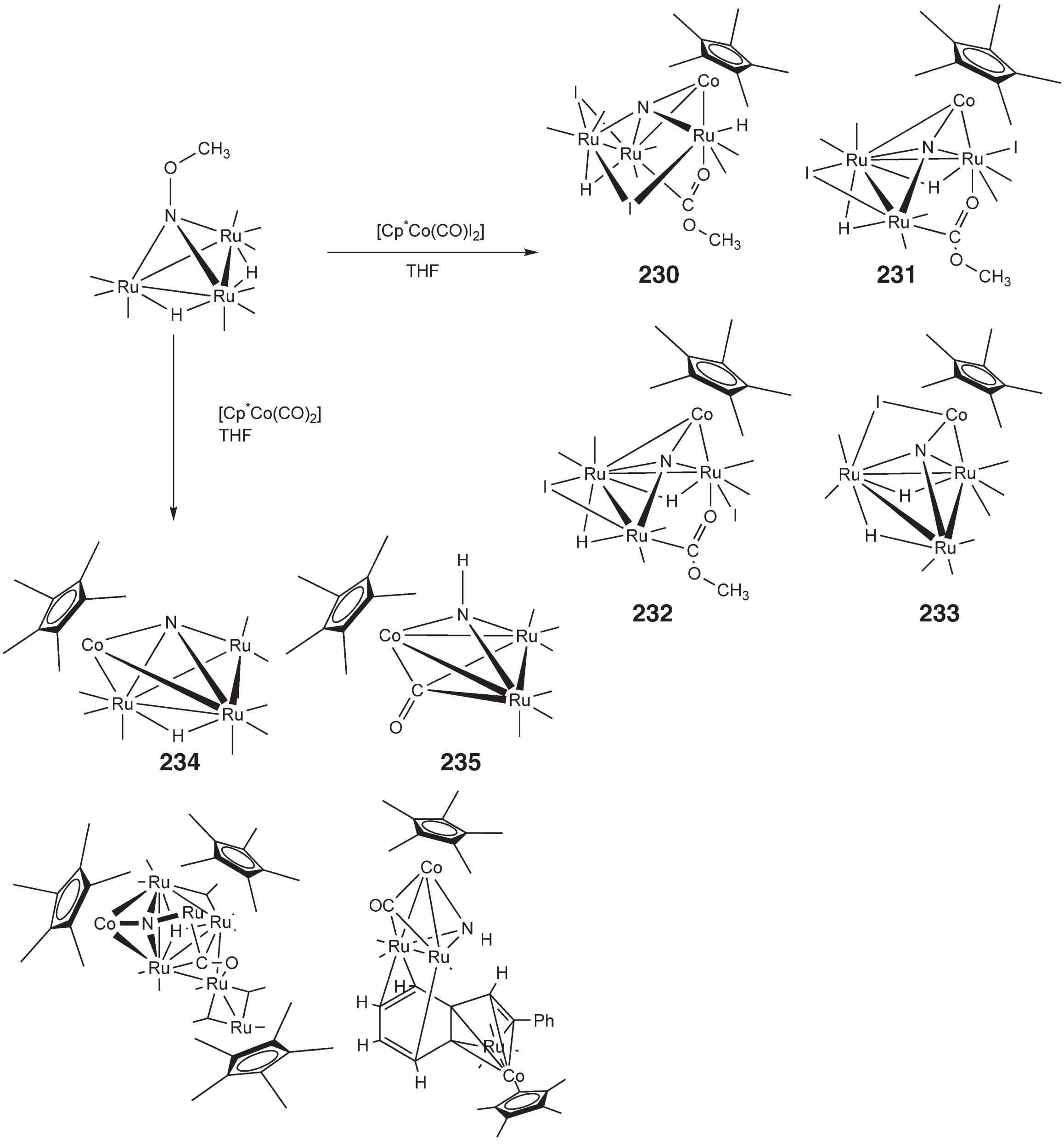


229

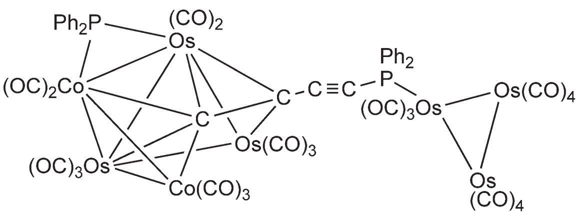
A series of Ru–Co mixed-metal nitride and nitrene carbonyl clusters 230–236 was synthesized from the interactions of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}NOMe)(CO)_9]$ with mononuclear cobalt reagents such as $[Cp^*Co(CO)I_2]$ and $[Cp^*Co(CO)_2]$. The alkyne derivative $[Ru_3(\mu_3\text{-}NOMe)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(CO)_9]$ has also been used. It is interesting to observe the formation of 237, which has a metallacyclopentadiene ring that is derived from the coordinated alkyne ligand and ruthenium metal.[244] In addition to their structural characterization, these mixed-metal clusters have been studied by ^{15}N NMR spectroscopy.[242,243]



230 **231** **232** **233** **234** **235** **236** **237**

Mixed-metal Ru–Co clusters that contain boron were extensively investigated by Fehlner's group. The addition of a cobalt carbonyl moiety to $[(Cp^*Ru)_3(\mu\text{-}H)_2B_3H_6]$ led to hydrogen loss and the formation of the $[Ru_3Co(\mu_3\text{-}CO)(CO)_2(BH)_3Cp_3^*]$ cluster, which has a cubane-type skeleton.[245] The reaction of *nido*-$[1,2\text{-}(Cp^*Ru)_2(\mu\text{-}H)_2B_3H_7]$ with $[Co_2(CO)_8]$ gave *nido*-$[Ru_2Co(\mu_3\text{-}CO)(CO)_3(BH)_3Cp_2^*]$ with an unusual unbridged BH fragment.[246] The reactivity of this *nido*-cluster to *P*- or *N*-donor ligands was also investigated, and it was found that the phosphines attacked the cobalt center while the pyridines substituted at the boron center.[247] Other synthetic strategies for the Ru–Co cluster system that are based on the addition reaction[257–259] and ionic coupling reaction [260–263] have also appeared.

Although the osmium–cobalt cluster anion $[Os_3Co(CO)_{13}]^-$ has been known since 1986, its chemical reactivity has not been well established compared to that of the ruthenium analog. Only a few examples can be found in this review period. Lewis *et al.* showed that the ionic coupling of the $[Os_3Co(CO)_{13}]^-$ anion with $[RuCp(NCMe)_3]^+$ afforded the pentanuclear triheterometallic cluster $[Os_3CoRu(CO)_{13}Cp]$ in 21% yield.[264] Bruce *et al.* reported the clusters **238** and **239** that were obtained from heating osmium–diyne–cobalt or osmium/rhenium–diyne–cobalt complexes.[220]



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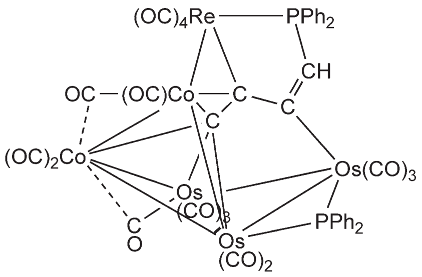
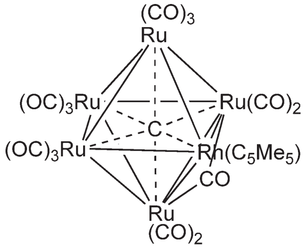


239

Ruthenium–rhodium and osmium–rhodium mixed-metal clusters have been extensively investigated in terms of their synthesis, structure, and reactivity to small molecules. Ionic coupling is by far the most important method for their preparation. For example, the interaction of the dianionic cluster $[Ru_5C(CO)_{14}]^{2-}$ and the dicationic rhodium species $[RhCp^*(MeCN)_3]^{2+}$ afforded the expected hexanuclear mixed-metal cluster $[Ru_5Rh(\mu_6\text{-}C)(CO)_{14}Cp^*]$ **240** in good yield. Subsequent reactions with C_5H_6 or C_6H_8 in the presence of Me_3NO resulted in the formation of $[Ru_5Rh(\mu_6\text{-}C)(CO)_9Cp_2Cp^*]$ and $[Ru_5Rh(\mu_6\text{-}C)(C_6H_6)(CO)_{11}]$, respectively.[265,266]

Treatment of **240** with 80 atm of CO at 80 °C led to the pentanuclear clusters $[Ru_5C(CO)_{15}]$ and $[Ru_4Rh(\mu_5\text{-}C)(CO)_{12}Cp^*]$ **241** in similar yields (~30%).[267] The reaction of **241** with an excess of $[Et_4N][BH_4]$ gave the monoanion $[Ru_4Rh(\mu_5\text{-}C)(CO)_{11}HCp^*]^-$, which can be oxidized by I_2 to give $[Ru_4Rh(\mu_5\text{-}C)(CO)_{11}HICp^*]$. The substitution chemistry of **241** with phosphine ligands has also been investigated.[268]

A similar ionic coupling between the $[Ru_5C(CO)_{14}]^{2-}$ dianion with the $[Rh(COD)_2]^{2+}$ dication gave the COD-bearing mixed-metal cluster in an analogous manner.[269] However, Raithby *et al.* showed that novel products can be obtained from this simple coupling method. The reaction of the $[Ru_6(CO)_{18}]^{2-}$ dianion with the $[RhCp^*(MeCN)_3]^{2+}$ dication led to metal exchange and afforded $[Ru_5Rh(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{12}Cp^*]$, instead of the expected Ru_6Rh complex.[270] Indeed, metal-exchange and skeletal rearrangement are rather commonly encountered in mixed-metal cluster chemistry. The thermolysis of tetranuclear **242** afforded the pentanuclear cluster **243** and the tetranuclear cluster $[Ru_2Rh_2(CO)_8Cp_2^*]$ with different metal core compositions.[271]



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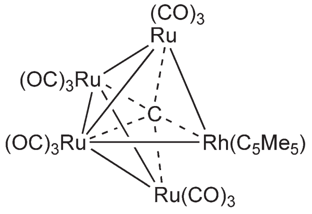

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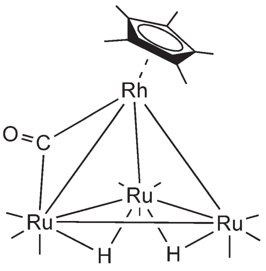

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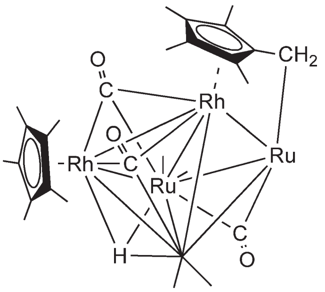
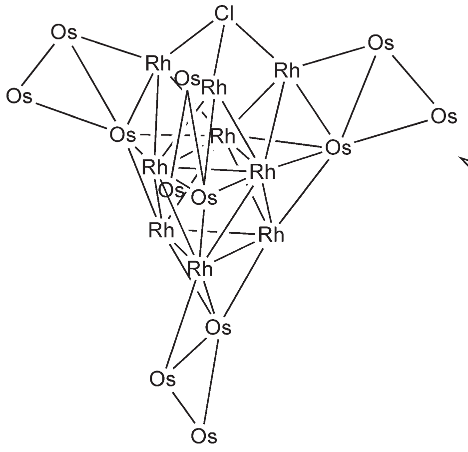


243

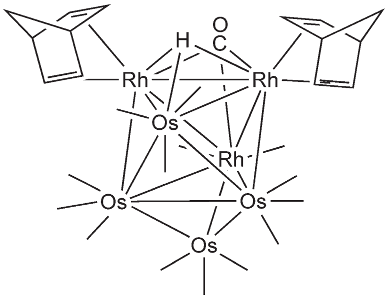
Another convenient entrance into the Ru–Rh mixed-metal cluster chemistry was provided by Pakkanen *et al.* They established a high-yield synthetic route to [PPN]$[H_2Ru_3Rh(CO)_{12}]$ from the interaction of $[HRu_3(CO)_{11}]^-$ anion and $Rh_2(CO)_4Cl_2$,[272] and studied its chemical properties.[273,274] The chemistry of the rhodium-rich system $[RuRh_3(\mu\text{-}H)(CO)_{12}]$ was also investigated by this group.[253,275] Non-hydrido carbonyl clusters, such as the $[Ru_2Rh_2(CO)_{12}]^{2-}$, $[Ru_3Rh(CO)_{13}]^-$, and $[RuRh_4(CO)_{12}]^{2-}$ anions, were also synthesized and studied by Fumagalli *et al.* These cluster anions showed a high degree of fluxional behavior even at low temperatures, as is evidenced from the ^{13}C NMR data.[276,277]

Mixed-metal boride cluster chemistry was extensively investigated by Housecroft *et al.* Cluster expansion around the semi-encapsulated boron atom in the $[Ru_4H(CO)_{12}(BH)]^-$ anion has led to a wide range of heterometallic boride clusters that involve group 11 metals,[278,279] and to the octahedral clusters $[Ru_4Rh_2(CO)_{16}B]^-$ and $[Ru_4Rh_2(CO)_{16}B(AuPPh_3)]$.[280] The use of $[Ru_3(CO)_9BH_4]^-$ and $[Ru_3(CO)_9(B_2H_5)]^-$ as precursors to higher nuclearity boron-containing clusters is also effective. Various mononuclear rhodium reagents have shown good ionic coupling reactions with these boron cluster anions to give mixed-metal clusters.[281–283] In addition, the substitution behavior of many Ru–Rh–B clusters has been studied, which is important for the understanding of the isomerization that is associated with these clusters.[284–288] Carborane Ru–Rh mixed-metal clusters have also been extensively studied, which has arisen because convenient synthetic routes to $Ru(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$-containing complexes are now available.[289] A variety of Ru–Rh mixed-metal clusters that contain phosphine,[290] phosphinidene,[291] and thio[261,292–294] ligands have been prepared and structurally characterized.

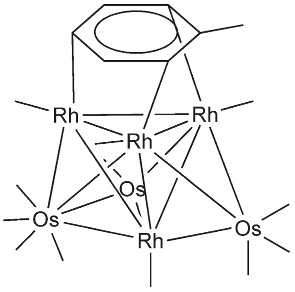
Mixed-metal clusters of osmium and rhodium have attracted considerable interest, because the rhodium tends to show a stable, coordinately unsaturated 16-electron configuration, whereas the osmium clusters display a very rich chemistry and are kinetically stable. In addition, both osmium and rhodium have a well-established background of catalytic applications. Both the nucleophilic addition of rhodium reagents to the coordinatively unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$[295] and the ionic coupling[296,297] method have been explored. The reaction of the $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ anion with $\{Rh(nbd)Cl\}_2$ in the presence of $AgPF_6$ afforded two high-nuclearity clusters $[Os_{12}Rh_9(\mu_3\text{-}Cl)(CO)_{44}]$ and $[Os_4Rh_3(\mu_3\text{-}H)(\mu_3\text{-}CO)(\eta^4\text{-}C_7H_8)_2(CO)_{14}]$ in moderate yields. It is believed that $\{Rh(nbd)Cl\}_2$ undergoes chloride dissociation upon reaction with silver (I) salts to give the active rhodium reagent $[Rh(nbd)]^+$, which then reacts with the osmium cluster anion via a complicated redox condensation, instead of a simple ionic coupling reaction.[298] The reactivity of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ **244** has been extensively studied recently, although it was synthesized much earlier.[299] The reaction of **244** with vinyl compounds in toluene led to cluster build-up, alkylidyne formation, arene substitution, and alkene isomerization.[300,301] An interesting example is the isolation of the cluster **245**, which contains a toluene ligand that is coordinated to the Rh_3 surface in a rarely observed $\mu_3\text{-}\eta^1:\eta^1:\eta^1$ bonding mode.[302]



Metal core of $[Os_{12}Rh_9(\mu_3\text{-}Cl)(CO)_{44}]$



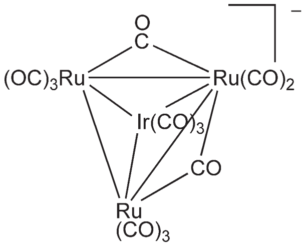
$[Os_4Rh_3(\mu_3\text{-}H)(\mu_3\text{-}CO)(\mu_4\text{-}C_7H_8)_2(CO)_{14}]$



245

Ionic coupling reactions have also proved to be useful for the preparation of carbide,[303] phosphine,[304] and imino[305] clusters of osmium and rhodium.

Significant advances in the chemistry of mixed-metal clusters of Ru–Ir and Os–Ir were made in this review period. The work of Süss-Fink *et al.* on the synthesis, structure, and reactivity of these mixed-metal clusters sheds light on the potential of these compounds as catalysts in the carbonylation of methanol to give acetic acid.[306,307] The reaction of the $[Ir(CO)_4]^-$ anion with Ru_3CO_{12} in refluxing THF gave the first homoleptic mixed-metal Ru–Ir carbonyl anion $[Ru_3Ir(CO)_{13}]^-$ 246 in good yield (85%). Protonation and hydrogenation reactions gave the hydrido derivatives $[Ru_3IrH(CO)_{13}]$ **247**, $[Ru_3IrH_2(CO)_{12}]^-$ **248**, and $[Ru_3IrH_3(CO)_{12}]$ **249**. Cluster 246 was found to be catalytically active in the carbonylation of methanol. The O–H bond of MeOH was activated to give the cluster anion $[Ru_3Ir(\mu\text{-H})(\mu\text{-OMe})(CO)_{12}]^-$ 250, which upon prolonged reaction gave $[Ru_3Ir(\mu\text{-H})_2(CO)_{12}]^-$ 251 and formaldehyde.[308]



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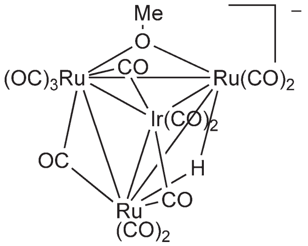

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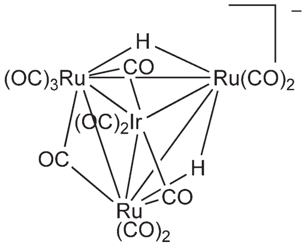


251

The hydrido clusters **247–249** also display a very rich chemistry. Cluster **247** is an excellent catalyst for the hydrogenation of diphenylacetylene to give stilbene with a turnover number of 990. Several mixed-metal clusters that contain alkynes are also active catalysts and have been isolated and structurally characterized in this catalytic reaction.[309,310]

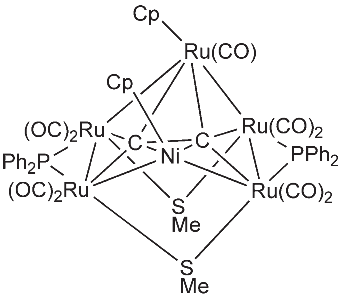
Heating of **247** with ethylene in hexane afforded, in addition to **249**, the pentanuclear cluster $[Ru_4Ir(\mu\text{-H})(\mu_4\text{-CCH}_3)(CO)_{15}]$, in which the ethylidyne ligand is in a rarely observed μ_4-coordination mode.[311] Site-selective substitutions with phosphine, phosphite, and related ligands on 246 and **248** have been observed.[312,313]

Based on a similar strategy, the cluster anion $[Os_3Ir(CO)_{13}]^-$ **252** was prepared in 50% yield from the reaction of $[Ir(CO)_4]^-$ with $[Os_3(CO)_{12}]$, and its use in the catalytic carbonylation of methanol was also studied.[314] The metal-framework degradation reactions of both 246 and **252** with bulky phosphine ligands were investigated.[313] It is interesting to note that the further condensation of $[Ir(CO)_4]^-$ on 246 occurred at a higher reaction temperature to give $[Ru_3Ir_2(CO)_{14}]^{2-}$ anion.[315]

Irdium carbonyl chloride complexes, such as $[Ir(CO)_3Cl]_n$ and $[Ir(CO)Cl(PPh_3)_2]$, were also used to generate Ru–Ir mixed-metal clusters that contain chloride.[316,317] Substitution reactions with phosphine ligands were examined using ^{31}P NMR spectroscopy.[318,319] A series of high-nuclearity Ru–Ir and Ru–Ir–Au clusters were isolated in good yields from the reaction of $[Ir_6(CO)_{15}]^-$ with $[Ru_3(CO)_{12}]$ in the presence of *p*-toluenesulfonic acid. They contain an essentially tetrahedral core that is similar to that observed in the well-known $[Os_{10}C(CO)_{24}]^{2-}$ anion.[320] Boron,[280,281] phosphido,[321,322] and sulfide clusters[323,324] of Ru–Ir have also been established. Both spectroscopic and crystallographic studies of these species have been reported.[325]

6.25.3.7 Ru/Os Mixed-metal Clusters Containing Group 10 Elements

Ru–Ni and Os–Ni clusters are rather rare. A handful of examples for Ru–Ni exist, but no new Os–Ni cluster was structurally characterized in this review period. It is believed that this is a consequence of choice, rather than scientific grounds. The reactions of nickelocene with the open dicarbon cluster $[Ru_5(\mu_5\text{-C}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{11}]$ led to two novel Ru–Ni clusters 253 and 254.[326] Extended Hückel and density functional calculations were carried out on 254 to rationalize the two observed coordination modes of the C_2 unit to the metal framework. The interaction of the diyne complex $[Ru_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^1,\eta^2\text{-C}{\equiv}\text{CC}{\equiv}\text{CBu}^t)(CO)_6]$ with labile nickel reagents $[Ni(COD)_2]$ or $[Ni(CO)_4]$ gave the cluster 255 as the single major product, which can be visualized as the stoichiometric coupling of two Ru_2 molecules together with the incorporation of a single Ni atom.[327] Several other Ru–Ni clusters with a tetrahedral metal core have also been reported (Table 15).[261,328]



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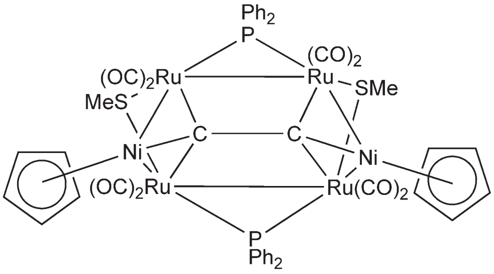

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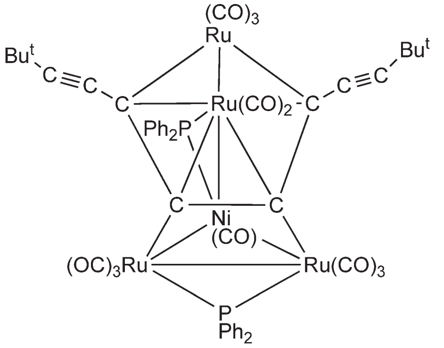

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Table 15 Ru/Os mixed-metal clusters containing group 10 elements with known structure

Formula	*References*
Clusters with two different kinds of metal	
$[Ru_2Ni_2(CO)_2Cp_2Cp^*{}_2]$	261
$[Ru_3Ni(\mu\text{-}H)(CO)_{12}][Ph_4P]$	328
$[Ru_4Ni_2(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_8Cp_2]$	326
$[Ru_4Ni(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^4\text{-}Bu^tC{\equiv}CC_4C{\equiv}CBu^t)(CO)_{12}]$	327
$[Ru_5Ni(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_9Cp_2]$	326
$[Ru_2Pd_2(\mu_3\text{-}S)_2(\mu\text{-}Br)(PPh_3)BrCp^*{}_2]$	335
$[Ru_2Pd_2(\mu_3\text{-}S)_2(\mu\text{-}Cl)(PPh_3)_2Cp^*{}_2]Cl$	335
$[Ru_2Pd_2(\mu_3\text{-}S)_2(\mu\text{-}SPr^i)(PPh_3)BrCp^*{}_2]$	335
$[Ru_2Pd_2(\mu_3\text{-}S)_2(\mu\text{-}SPr^i)(SPr^i)(PPh_3)Cp^*{}_2]$	333
$[Ru_2Pd_2(\mu_3\text{-}S)_2Cl_2(PPh_3)_2(CO)_2Cp^*{}_2]$	335
$[Ru_2Pd_2(PBu^t{}_3)_2(CO)_9]$	329
$[Ru_3Pd_3(PBu^t{}_3)_3(CO)_{12}]$	329
$[Ru_5Pd(\mu_6\text{-}C)(PBu^t{}_3)(CO)_{15}]$	330
$[Ru_5Pd_2(\mu_6\text{-}C)(PBu^t{}_3)_2(CO)_{15}]$	330
$[Ru_6Pd_2(\mu_6\text{-}C)(PBu^t{}_3)_2(CO)_{17}]$	329
$[Ru_6Pd_6(CO)_{24}][Et_4N]_2$	336
$[Ru_{10}Pd_8C_2(C_3H_5)_4(CO)_{27}]$	337
$[Ru_{12}Pd_2C_2(CO)_{30}][PPN]_2$	337
$[Ru_{12}Pd_4C_2(CO)_{32}][PPN]_2$	337
$[Os_2Pd_2(\mu\text{-}I)_4I_4(\mu\text{-}dppf)_2(CO)_4]$	345
$[Os_3Pd_2(bipy)_2(CO)_{12}]$	339
$[Os_4Pd(\mu\text{-}H)_3(\mu\text{-}Cl)_3py(CO)_{11}]$	340
$[Os_4Pd(\mu\text{-}H)_3(\mu\text{-}I)_3(CO)_{12}]$	342
$[Os_4Pd(\mu\text{-}H)_4(\mu\text{-}I)_2(CO)_{12}]$	342
$[Os_4Pd_6(\mu\text{-}dppm)_2(\mu\text{-}CO)_5(\mu_3\text{-}CO)_3(CO)_8]$	344
$[Os_5Pd(\mu_4\text{-}C)(\mu\text{-}Cl)_2(\mu\text{-}PPh_2py)(CO)_{14}]$	346
$[Os_5Pd(\mu_5\text{-}C)(\mu\text{-}Cl)_2(PPh_3)(CO)_{15}]$	347
$[Os_5Pd(\mu_5\text{-}C)(\mu\text{-}Cl)I(\mu\text{-}PPh_2py)(CO)_{14}]$	346

(*Continued*)

Table 15 (Continued)

Formula	*References*
$[Os_5Pd(\mu_5\text{-}C)(\mu\text{-}CO)_2(PPh_3)_2(CO)_{12}]$	347
$[Os_5Pd(\mu_6\text{-}C)(\mu\text{-}dppf)(CO)_{14}]$	345
$[Os_5Pd(\mu\text{-}H)_4(\mu\text{-}Cl)_2(CO)_{16}]$	340
$[Os_5Pd(\mu\text{-}H)_4H(\mu\text{-}Cl)(CO)_{16}]$	340
$[Os_5Pd(\mu\text{-}H)_6(CO)_{16}]$	340
$[Os_5Pd_4(\mu_6\text{-}C)(\mu\text{-}dppm)_2(\mu\text{-}CO)_3(CO)_{12}]$	344
$[Os_5Pd_6(\mu\text{-}dppm)_2(\mu\text{-}CO)_6(CO)_{13}]$	343
$[Os_5Pd_6(\mu\text{-}H)_2(\mu\text{-}dppm)_2(\mu\text{-}CO)_5(CO)_{13}]$	343
$[Os_6Pd(bipy)(CO)_{18}]$	338
$[Os_6Pd(\mu\text{-}H)_8(CO)_{18}]$	342
$[Os_6Pd_2(\mu\text{-}H)_4(\mu\text{-}Cl)_2(CO)_{18}(\mu\text{-}Cl)_2]$	340
$[Os_6Pd_2(\mu\text{-}H)_6(\mu\text{-}I)_2(CO)_{18}]$	342
$[Os_8(\mu_4\text{-}Pd)(\mu_5\text{-}C)_2(\mu\text{-}Cl)_2(\mu\text{-}PPh_2py)(CO)_{22}]$	346
$[Os_8(\mu\text{-}Pd_2Cl_2)(\mu_5\text{-}C)_2(\mu\text{-}Cl)_2(CO)_{24}]$	346
$[Os_8(\mu\text{-}Pd_2I_2)(\mu_5\text{-}C)_2(\mu\text{-}I)_2(CO)_{24}]$	346
$[Os_{18}Pd_3(\mu_6\text{-}C)_2(CO)_{42}][PPN]_2$	348
$[RuPt_2(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(PPh_3)_2(CO)_5]$	382
$[RuPt_3(\mu\text{-}H)(\mu\text{-}dppm)_3(\mu\text{-}CO)_2(CO)_2][PF_6]$	386
$[Ru_2Pt(dppe)(CO)_8]$	383
$[Ru_2Pt(dppe)_2(CO)_6]$	383
$[Ru_2Pt(PBu^t_3)(CO)_9]$	332
$[Ru_2Pt\{\mu\text{-}\eta^2\text{-}C_{10}H_6C_4Ph_2\}_2(CO)_6]$	358
$[Ru_2Pt_2(\mu\text{-}H)_2(PBu^t{}_3)_2(CO)_8]$	332
$[Ru_2Pt_2(PBu^t{}_3)_2(CO)_9]$	332
$[Ru_3Pt(CO)_{11}(PPr^i{}_3)_2]$	373
$[Ru_3Pt(\mu_3\text{-}\eta^3\text{-}PhCCPh)(PPr^i{}_3)(CO)_{10}]$	373
$[Ru_3Pt(\mu_3\text{-}PNPr^i{}_2)(PPh_3)(CO)_{10}]$	379
$[Ru_3Pt(\mu_3\text{-}S)_2(PPh_3)_2(CO)_9]$	377
$[Ru_3Pt(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}PCCCCPh)(dppe)(CO)_{10}]$	385
$[Ru_3Pt(\mu_4\text{-}\eta^2{:}\eta^2\text{-}CCBu^t)(dppe)(CO)_9]$	372
$[Ru_3Pt(\mu_4\text{-}\eta^2{:}\eta^2\text{-}CCBu^t)(\mu\text{-}H)(dppe)(CO)_9]$	372
$[Ru_3Pt(\mu_4\text{-}\eta^2\text{-}CCBu^t)(dppb)(CO)_9]$	372
$[Ru_3Pt(\mu_4\text{-}\eta^2\text{-}CCBu^t)(dppp)(CO)_9]$	372
$[Ru_3Pt(\mu\text{-}H)(\mu_3\text{-}COMe)(PCy_3)(CO)_{10}]$	374
$[Ru_3Pt(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeCCHCMe)(PPr^i{}_3)(CO)_9]$	373
$[Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}NO)(PPr^i{}_3)(CO)_{10}]$	373
$[Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}N)(PPr^i{}_3)(CO)_{10}]$	373
$[Ru_3Pt\{\mu_3\text{-}C(Bu^t)CC(Bu^t)CH_2\}(dppe)(CO)_8]$	371
$[Ru_3Pt\{\mu_4\text{-}C(Bu^t)C(H)CCBu^t\}\{C(H)C(Bu^t)\}\{\mu\text{-}\sigma\text{-}\pi\text{-}C(H){=}C(H)Bu^t\}(dppe)(CO)_7]$	371
$[Ru_3Pt\{\mu_4\text{-}C(Ph)CCC(H)(Bu^t)\}(\mu_4\text{-}Te)(\mu\text{-}TePr^i)(dppe)(CO)_6]$	371
$[Ru_4Pt(\mu_4\text{-}PF)(PPh_3)(CO)_{13}]$	379
$[Ru_4Pt(\mu_4\text{-}PNPr^i{}_2)(PPh_3)(CO)_{13}]$	379
$[Ru_4Pt(\mu_4\text{-}PO)(PPh_3)(CO)_{13}][H_2NPr^i{}_2]$	379
$[Ru_4Pt(\mu_4\text{-}POEt)(PPh_3)(CO)_{13}]$	379
$[Ru_4Pt(\mu_4\text{-}POH)(PPh_3)(CO)_{13}]$	378
$[Ru_4Pt(\mu_4\text{-}S)_2(PPh_3)(\mu\text{-}CO)(CO)_{11}]$	377
$[Ru_4Pt_2(CO)_{18}]$	387
$[Ru_4Pt_2(\mu_6\text{-}C)(COD)_2(CO)_{13}]$	368
$[Ru_4Pt_2\{\mu_5\text{-}C_6H_4(C_2Ph_2)_2\}(CO)_{14}]$	359
$[Ru_4Pt_3(PBu^t{}_3)(CO)_{17}]$	364
$[Ru_5Pt(\mu_5\text{-}C)(\mu\text{-}\eta^2\text{-}EtC_2Et)(\mu_3\text{-}\eta^2\text{-}EtC_2Et)(CO)_{13}]$	355
$[Ru_5Pt(\mu_5\text{-}C)(PBu^t{}_3)(CO)_{15}]$	360
$[Ru_5Pt(\mu_6\text{-}C)(C_{60})(dppe)(CO)_{11}]$	384
$[Ru_5Pt(\mu_6\text{-}C)(CO)_{15}][Ph_4P]_2$	368
$[Ru_5Pt(\mu_6\text{-}C)(COD)(CO)_{14}]$	366
$[Ru_5Pt(\mu_6\text{-}C)(dppe)(CO)_{14}]$	384
$[Ru_5Pt(\mu_6\text{-}C)(\mu\text{-}dppm)(CO)_{14}]$	367
$[Ru_5Pt(\mu_6\text{-}C)(\mu\text{-}dppm)_2(CO)_{12}]$	367
$[Ru_5Pt(\mu_6\text{-}C)(Me_2S)(CO)_{15}]$	362
$[Ru_5Pt(\mu_6\text{-}C)(PMe_2Ph)(CO)_{15}]$	361

(Continued)

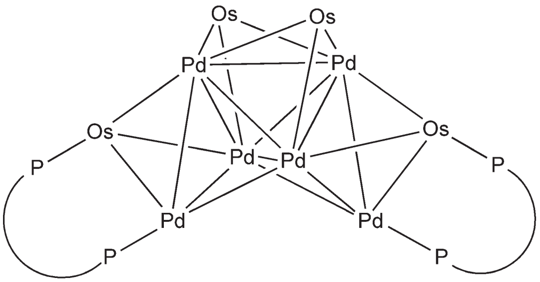
Table 15 (Continued)

Formula	*References*
$[Ru_5Pt(\mu_6\text{-}C)(PMe_2Ph)_2(CO)_{14}]$	361
$[Ru_5Pt(\mu_6\text{-}C)(PPh_3)(CO)_{15}]$	366
$[Ru_5Pt(\mu_6\text{-}C)(PPh_3)_2(CO)_{14}]$	366
$[Ru_5Pt_2(\mu_6\text{-}C)(PBu^t{}_3)(CO)_{16}]$	331
$[Ru_5Pt_2(\mu_6\text{-}C)(PPh_3)_2(CO)_{15}]$	366
$[Ru_5Pt_3(\mu_6\text{-}C)(PBu^t{}_3)_2(CO)_{16}]$	331
$[Ru_5Pt_4(\mu_6\text{-}C)(PPh_3)_3(CO)_{16}]$	368
$[Ru_6Pt(\mu_6\text{-}C)(COD)(CO)_{16}]$	366
$[Ru_6Pt_2(\mu_6\text{-}C)(COD)_2(CO)_{15}]$	366
$[Ru_6Pt_2(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{-}EtC_2Et)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5(Et_4))(\mu\text{-}CO)(CO)_{16}]$	355
$[Ru_6Pt_3(\eta^6\text{-}TolCH_2CH_2Tol)(\mu_3\text{-}H)_4(CO)_{18}]$	349
$[Ru_6Pt_3(\mu_3\text{-}H)(\mu\text{-}H)_3(CO)_{21}]$	351
$[Ru_6Pt_3(\mu_3\text{-}H)(\mu\text{-}H)_3(PPh_3)(CO)_{20}]$	357
$[Ru_6Pt_3(\mu_3\text{-}\eta^6\text{-}PhC_2H_4Ph)(\mu_3\text{-}H)_4(CO)_{18}]$	349
$[Ru_6Pt_3(\mu_3\text{-}PhC_2Ph)(SMe_2)(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{19}]$	350
$[Ru_6Pt_3(\mu_3\text{-}PhC_2Ph)_3(\mu\text{-}H)_6(CO)_{15}]$	349
$[Ru_6Pt_3(\mu_6\text{-}C)(dppm)_2(CO)_{16}]$	367
$[Ru_6Pt_3(\mu\text{-}H)_3(\mu\text{-}CO)(CO)_{20}][Pt(PMe_3)_3H]$	357
$[Ru_6Pt_3\{\mu\text{-}PhCC(H)Ph\}(\mu\text{-}H)(CO)_{21}]$	351
$[Ru_8Pt_2(\mu_3\text{-}\eta^2\text{-}EtC_2Et)_3(\mu\text{-}CO)_2(CO)_{16}]$	356
$[Ru_{10}Pt_2(\mu_6\text{-}C)_2(CO)_{28}][PPN]_2$	369
$[Ru_{10}Pt_3(\mu_6\text{-}C)_2(CO)_{32}][Ph_4P]_2$	368
$[Ru_{12}Pt(\mu_6\text{-}C)_2(MeCN)_2(CO)_{32}]$	369
$[OsPt_2(\mu\text{-}I)_2(\mu\text{-}CO)(PPh_3)_3(CO)_2]$	394
$[Os_2Pt(PPh_3)_2(CO)_8]$	389
$[Os_3Pt(COD)(\mu_4\text{-}FcC_4Fc)(CO)_9]$	392
$[Os_3Pt(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\eta^1\text{-}C{\equiv}CPh)(Bu^t{}_2bipy)(CO)_9]$	393
$[Os_3Pt(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\eta^1\text{-}C{\equiv}CPh)(Me_2bipy)(CO)_9]$	393
$[Os_3Pt(\mu\text{-}H)(\mu\text{-}dppm)\{Si(OMe)_3\}(CO)_{10}]$ two isomers	388
$[Os_4Pt_2(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_4(CO)_8]$	391
$[Os_6Pt_5(CO)_{25}]$	390
Clusters with three different kinds of metal	
$[Ru_5Pd_2Pt(\mu_6\text{-}C)(PBu^t{}_3)_2(CO)_{16}]$	331
$[Ru_5PdPt(\mu_6\text{-}C)(PBu^t{}_3)(CO)_{16}]$	331
$[RuPt(AuPPh_3)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CH_2(CCPh)(PPh_3)_2(CO)Cp][CF_3SO_3]$	381
$[Ru_2Pt_3(\mu_4\text{-}Hg)_2(dppm)_3(CO)_4Cp_2]$	380
$[Ru_3Pt(\eta^2\text{-}dppf)(\mu_4\text{-}S)_2(\mu\text{-}CO)_2(CO)_6]$	376
$[Ru_3Pt(\eta^2\text{-}dppf)(\mu_4\text{-}S)_2(CO)_8]$	376
$[Ru_5PtAu_2(PPh_3)_2(\mu_6\text{-}C)(CO)_{15}]$	368
$[Ru_5Pt(\mu\text{-}GePh_2)(\mu_6\text{-}C)(CO)_{15}]$	363
$[Ru_5Pt(\mu\text{-}PbPh_2)(\mu_6\text{-}C)(CO)_{15}]$	363
$[Ru_5Pt(\mu\text{-}SnPh_2)(\mu_6\text{-}C)(CO)_{15}]$	363
$[Ru_5Pt(\mu\text{-}SnPh_2)(\mu_6\text{-}C)(PMe_2Ph)(CO)_{14}]$	363
$[Ru_6Pt_3Au(PEt_3)(\mu\text{-}H)_3(CO)_{21}]$	353
$[Ru_6Pt_3Au_2(PEt_3)_2(\mu_3\text{-}H)_2(CO)_{21}]$	353
$[Ru_6Pt_3Hg(\mu_3\text{-}H)_2I(CO)_{21}][NBu_4]$	354
$[Ru_6Pt_3Ir(\mu_3\text{-}H)_2(CO)_{21}Cp^*]$	354
$[Os_3Pt_2(COD)(\mu_5\text{-}FcC_4Fc)(CO)_{10}]$	392

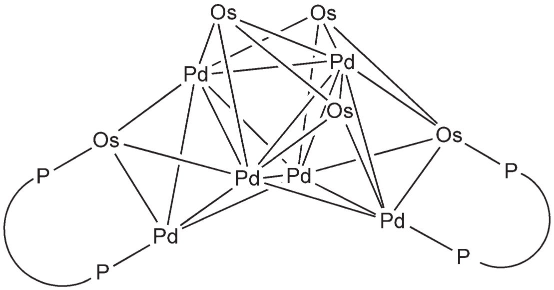
Adams *et al.* showed that Lewis acid–base interactions between metal atoms can be ultilized in the construction of Ru–Pd mixed-metal clusters in an elegant way. The reaction of $[Pd(PBu^t{}_3)_2]$ with $[Ru_3(CO)_{12}]$ or $[Ru_6C(CO)_{17}]$ afforded $[Ru_3Pd_3(PBu^t{}_3)_3(CO)_{12}]$ or $[Ru_6Pd_2(\mu_6\text{-}C)(PBu^t{}_3)_2(CO)_{17}]$, respectively. The addition of the $Pd(PBu^t{}_3)$ fragment to the cluster bears a close resemblance to the protonation of cluster anions. Another remarkable demonstration of the potential of the $Pd(PBu^t{}_3)_2$ reagent in cluster synthesis was obtained from its reaction with $Ru(CO)_5$. The new complex $[Ru_2Pd_2(PBu^t{}_3)_2(CO)_9]$ that was formed in this reaction can be viewed as dipalladium adduct of $Ru_2(CO)_9$, which is known to be very unstable.[329] In a similar procedure, $[Ru_5Pd(\mu_6\text{-}C)(PBu^t{}_3)(CO)_{15}]$ **256** and $[Ru_5Pd_2(\mu_6\text{-}C)(PBu^t{}_3)_2(CO)_{15}]$ **257** can be prepared in moderate yields. The $Pd(PBu^t{}_3)$ groups in **257** were found to undergo a dynamical interchange.[330–332]

Ru–Pd mixed-metal clusters that are derived from disulfide- or hydrosulfide-bridged diruthenium complexes were extensively studied by Hidai *et al.*[333,334] Interesting structural transformations that involve the Pd(PPh_3) moiety have been reported.[335] High-nuclearity Ru–Pd clusters have also been created via redox condensation reactions. The cluster anion $[Ru_6Pd_6(CO)_{24}]^{2-}$[336] and $[Ru_{10}Pd_{18}C_2(C_3H_5)_4(CO)_{27}]$[337] are important examples of this class of interesting compounds.

The first mixed-metal cluster of Os–Pd, $[Os_6Pd(bipy)(CO)_{18}]$, was reported in 1994,[338] and since then a variety of mixed-metal cluster that contain various Os : Pd ratios have been created. Palladium-pyridine complexes appear to be useful reagents in the synthesis of mixed-metal clusters with osmium carbonyl compounds.[339–341] The reaction of the coordinately unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $[Pd(NH_3)_2I_2]$ afforded a number of Os–Pd clusters with a high hydride content.[342] Both palladium phosphine and bidentate phosphine complexes are useful in the preparation of high-nuclearity mixed-metal clusters. The reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $[Pd_2(\mu\text{-}dppm)_2Cl_2]$ gave **258** and **259**, in addition to **260**, with the same metal core,[343] in which the molecule contains a twofold symmetry axis.[344]

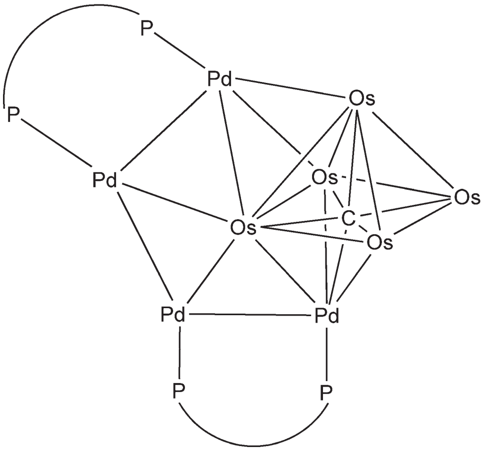


Metal core of **258** and **259**

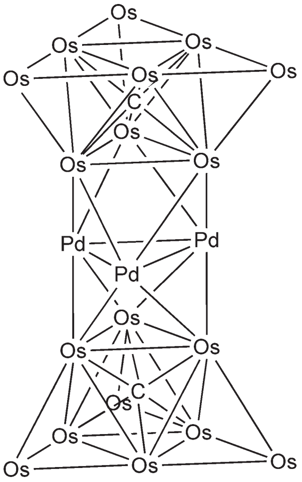


Metal core of **260**

The carbide cluster $[Os_5C(CO)_{15}]$ reacted with $[Pd_2(\mu\text{-}dppm)_2Cl_2]$ to afford $[Os_5Pd_4(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{12}(\mu\text{-}dppm)]$ **261**.[344] Cluster degradation of $[Os_5C(CO)_{15}]$ to the Os_4Pd species has been observed for this robust compound.[347] Treatment of an excess of $[Pd(MeCN)_4](BF_4)_2$ with $[PPN]_2[Os_{10}C(CO)_{24}]$ in CH_2Cl_2 at room temperature yielded the novel Os–Pd cluster anion $[Os_{18}Pd_3(\mu_6\text{-}C)_2(CO)_{42}]^{2-}$ **262**. Cluster **262** can be visualized as a triangular Pd_3 metal unit that is sandwiched between two tricapped octahedral $\{Os_9(\mu_6\text{-}C)(CO)_{21}\}$ subclusters. The naked Pd_3 triangle is relatively exposed and rarely observed in the metal chemistry of this element. Five reversible redox couples were observed for **262** at room temperature, which signifies its electron reservoir behavior.[348]



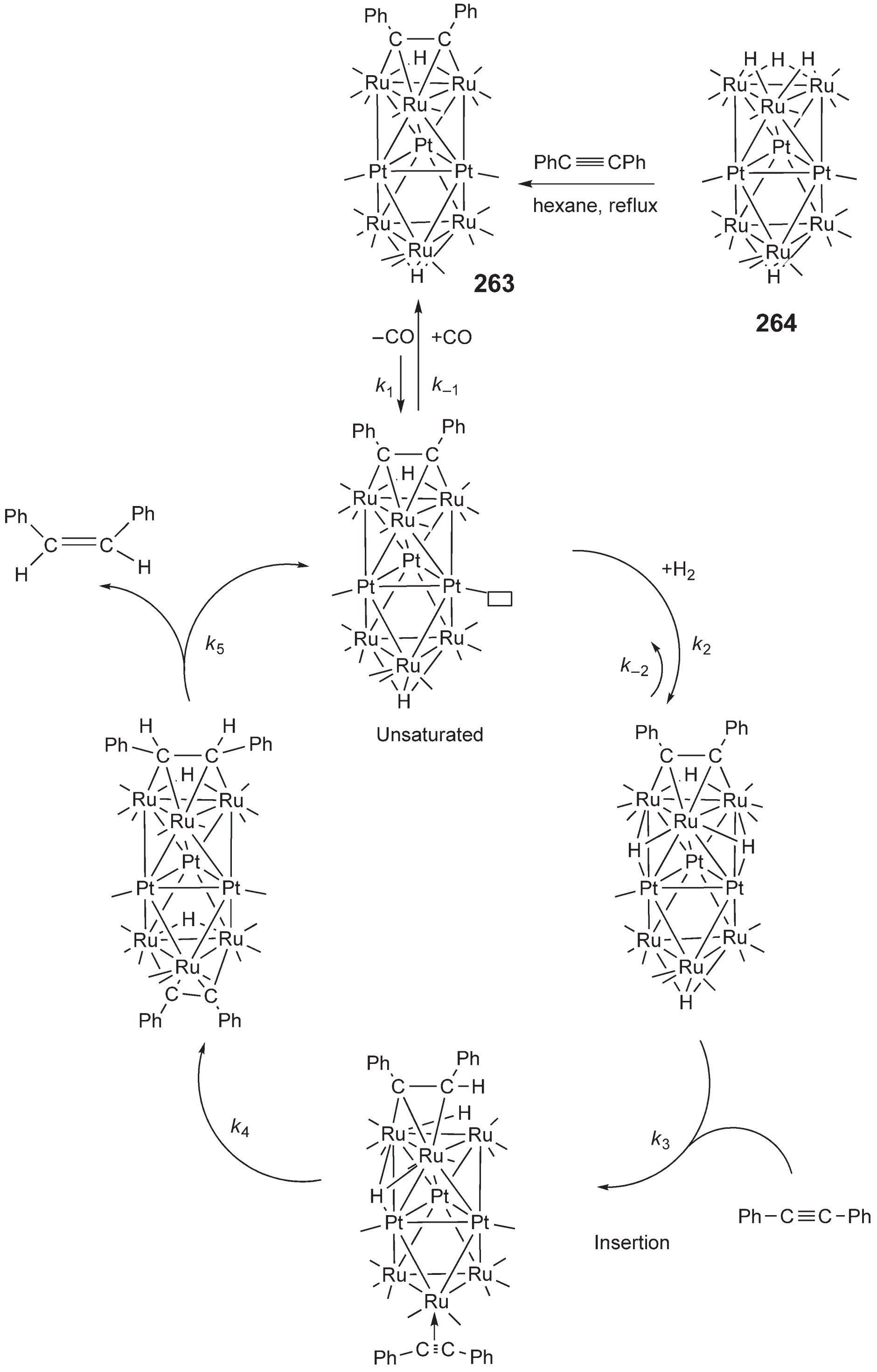
Metal core of **261**



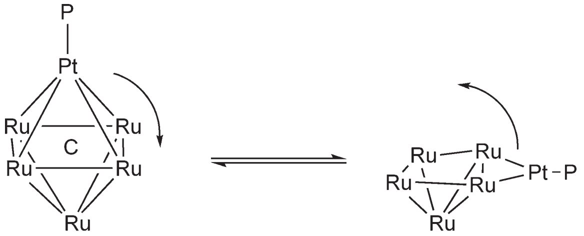
Metal core of **262**

Ruthenium–platinum mixed-metal clusters have received considerable attention in the past 10 years. They have been found to be active bimetallic catalysts for organic reactions, and are also good precursors for the generation of nanoalloys. A classic example of the catalytic study of Ru–Pt clusters was provided by Adams *et al.*, which involved the catalytic hydrogenation of diphenylacetylene to (*Z*)-stilbene at 50 °C and 1 atm of hydrogen by $[Ru_6Pt_3(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{20}]$ **263**. The reaction kinetics were carefully examined, and a mechanism for the catalytic cycle that involves this layer-segregated cluster was reported.[349,350]

Cluster **263** was prepared in high yield by reaction of alkyne with $[Ru_6Pt_3(\mu_3\text{-}H)(\mu\text{-}H)_3(CO)_{21}]$ **264**, which can be obtained from the hydrogenation of $[Ru_4Pt_2(CO)_{18}]$.[351] The catalytic hydrosilylation of diarylalkynes using **263** as a catalyst has also been investigated. A kinetic analysis showed that the reaction is first order in cluster and silane concentrations, but zeroth order in alkyne concentration.[352] Cluster **264** is an important building block for a variety of trimetallic clusters, including Ru–Pt–Au,[353] Ru–Pt–Ir, and Ru–Pt–Hg[354] combinations. In all of these systems, the layer-segregated structure is maintained. To delineate the reaction mechanism of alkyne hydrogenation using **263**, a number of related Ru–Pt clusters were examined for their reactions to alkyne ligands.[355–357] Unusual reactivity patterns, such as the intramolecular coupling of alkynes on a cluster, were observed in some instances.[358,359]



Adams *et al.* also reported a number of interesting molecular dynamic processes for Ru–Pt clusters. The cluster $[Ru_5Pt(\mu_6\text{-}C)(PMe_2Ph)(CO)_{15}]$ was shown to undergo facile intramolecular phosphine ligand exchange between a platinum and ruthenium center at 160 °C.[360] A molecular cluster model for atom hopping on metal surfaces was demonstrated by [$Ru_5Pt(\mu_5\text{-}C)(PBu^t{}_3)(CO)_{15}$] **265**. The mechanism of interconversion involves a reversible breaking and making of two Ru–Pt bonds with a shift of the platinum-phosphine moiety back and forth between the twofold edge-bridging Ru_2 site and the fourfold Ru_4 site.[361]



265

The dynamic intramolecular ligand exchange of phosphine and thioether ligands was observed in $Ru_5Pt(\mu_6\text{-}C)(CO)_{16}$ derivatives, and the thioether ligand was shown to migrate between the metal atoms much faster than the tertiary phosphine ligand.[362] The facile introduction of bridging MPh_2 moieties (M = Ge, Sn, Pb) into Ru–Pt carbide clusters can be achieved. The reaction of $Ru_5Pt(\mu_6\text{-}C)(CO)_{16}$ with Ph_3GeH and Ph_3SnH afforded the trimetallic complexes $Ru_5Pt(\mu\text{-}MPh_2)(\mu_6\text{-}C)(CO)_{15}$ (M = Ge, Sn) in good yields, and an analogous Pb compound was obtained with Pb_2Ph_6 as the starting material.[363] Dipalladium or diplatinum phosphane units were introduced on Ru_5 carbido clusters.[331,332,364] The skeletal rearrangement and dynamic behavior of these compounds were observed by NMR techniques.[330]

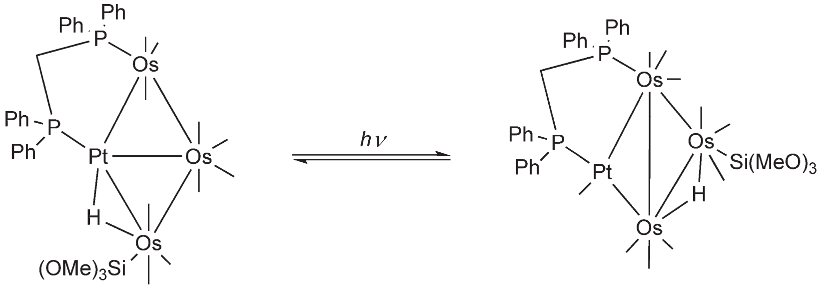
Johnson *et al.* showed cluster-derived Ru–Pt catalysts to be highly active in hydrogenation reactions.[365] In connection with this, a variety of Ru–Pt mixed-metal clusters were synthesized and studied for their reactivity and potential for supported nanocatalysts. High-nuclearity Ru–Pt clusters were obtained from the ionic coupling reactions based on $[Ru_5C(CO)_{14}]^{2-}$ or $[Ru_6C(CO)_{16}]^{2-}$ in the presence of Pt or Au reagents with a chloride scavenger.[366–369]

Shapley *et al.* showed that [$Ru_5Pt(\mu_6\text{-}C)(CO)_{16}$] underwent reductive condensation on carbon support to give bimetallic nanoparticles. The incipient Ru–Pt nanoparticles initially gave a disordered structure at 473 K, in which Pt was at the core of the condensing particles. On further heating to 673 K, the nanoparticles adopted an inverted structure with Pt appearing preferentially at the surface.[370] The usefulness of organometallic mixed-metal clusters for the synthesis of nanoalloys was demonstrated.

The chemistry of Ru–Pt clusters that contain alkyne ligands was investigated by Farrugia *et al.* Coupling reactions between coordinated alkynes,[371,372] NO activation,[373] and CO exchange reactions[374] were observed.

Hor *et al.* successfully demonstrated the use of CO gas as a reducing and desulfurizing agent on metal aggregates to produce metal clusters. The mixed-metal cluster compound [$RuPt_2(\mu_3\text{-}S)_2(PPh_3)_6Cl$]Cl is an example that was prepared using this methodology.[375] Platinum reagents that contain bidentate phosphine ligands have also been used to prepare Ru–Pt mixed-metal clusters. Air-stable Pt(0) complexes [$Pt(\eta^2\text{-dppf})(\eta^2\text{-dba})$] (dba = dibenzylideneacetone) reacted with [$Ru_3(\mu_3\text{-}S)_2(CO)_{10}$] to give a novel square cluster [$Ru_3Pt(\eta^2\text{-dppf})(\mu_4\text{-}S)_2(CO)_8$] in good yield.[376] Many phosphine-containing Ru–Pt clusters have been synthesized, and their structure determined by crystallography.[377–385] The solution dynamic behavior of these compounds has also been investigated.[386]

Photo-induced isomerization is rather common in organometallic clusters. However, the trapping of higher energy photoisomers for detailed analysis, such as crystallographic study, is rare. In this context, Adams *et al.* provided an interesting example of this procedure. The irradiation of [$Os_4Pt(\mu\text{-}H)(\mu\text{-dppm})\{Si(OMe)_3\}(CO)_{10}$] **266** led to a good conversion (43%) to an isomer **267**. Under thermal conditions, **267** reverted to **266** very slowly in a first-order process with $t_{1/2} = 4.6$ h at 47 °C. Clusters **256** and **257** can be separated in pure form for both spectroscopic studies and crystal growth.[388]



266 **267**

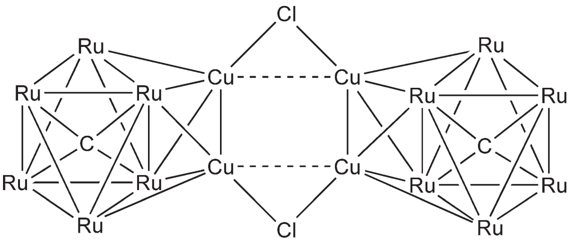
A rational synthesis of Os_2Pt clusters was developed by Takats *et al.* The reaction of $Os_2(CO)_8(C_2H_4)$ with $[Pt(PPh_3)_2(C_2H_4)]$ gave $[Os_2Pt(CO)_8(PPh_3)_2]$ in good yield. Other convenient ways to generate $Os_2Pt(CO)_{10}$ involve the cleavage of $[Os_4Pt_2(CO)_{18}]$ **268** under high pressure of CO or of $[Os_3Pt_2(CO)_{10}(COD)]$ by CO purge.[389]

The hydrogenation reaction of **268** in refluxing octane yielded the high-nuclearity cluster $[Os_6Pt_5(CO)_{25}]$ in 58% yield.[390] Alkyne derivatives of **268** were also prepared.[391] Pre-formed alkyne-containing Os_3 clusters were also used to generate Os–Pt mixed-metal clusters.[392] Platinum alkyne complexes reacted with labile triosmium clusters[393] or osmium carbonyl halides[394] to yield Os–Pt mixed-metal clusters.

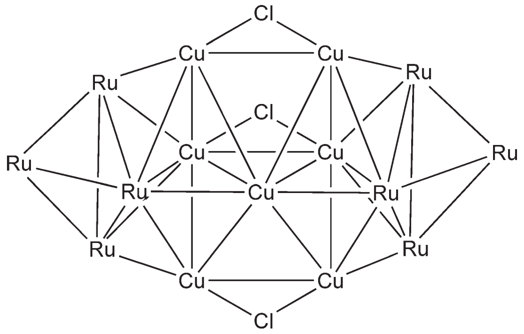
6.25.3.8 Ru/Os Mixed-metal Clusters Containing Group 11 Elements

The usual route for the preparation of Ru–Cu mixed-metal clusters is by the reaction of a cationic copper complex with a cluster anion. Raithby *et al.* prepared high-nuclearity Ru–Cu clusters 269–272 in Ru : Cu ratios of 3 : 1, 8 : 7, 2 : 1, 10 : 3, respectively, and the copper core bridged two units of ruthenium clusters.[395–397] The reaction of CuCl and hexa-ruthenium carbido clusters $[PPN][Ru_6C(CO)_{16}]$ gave a quantitative yield of $[PPN]_2[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]$ 269.[395] The central planar rectangular Cu_4 unit, being end-bridged by two Cl atoms at both ends, linked together the two octahedral Ru_6C units.

Alternatively, the reaction of an excess of $[Cu(MeCN)_4][BF_4]$ with $[PPN][Ru_6H(CO)_{18}]$ in the presence of refluxing CH_2Cl_2 gave $[PPN]_2[Ru_8Cu_7H_2Cl_3(CO)_{24}]$ 270.[396] The tetrahedral Ru_4 units on the two sides were connected by the central Cu_7 units, which appeared as two square pyramids fused on a common triangular face. Each chlorine atom bridged two copper atoms. The only copper atom that was not bonded to any Cl that coordinated to six Cu and two Ru atoms was essentially in a metallic environment.



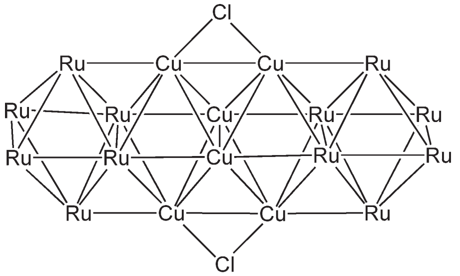
Metal core geometry of **269**



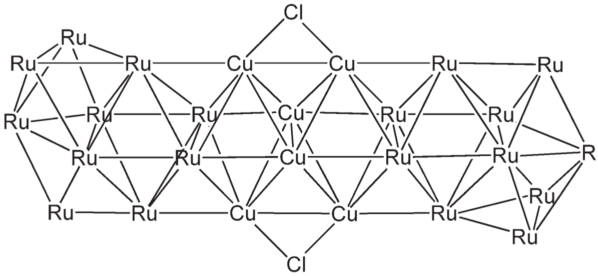
Metal core geometry of **270**

Similarly, $[PPN]_2[Ru_{12}Cu_6H_2Cl_2(CO)_{34}]$ 271 was prepared from $[Ru_6H(CO)_{18}]^-$ in MeCN, with the central Cu_6 unit, which resembled two tetrahedra fused on a common edge, being sandwiched between two octahedral Ru_6 units.[396] The two Cl also bridged the copper atoms at opposite ends.

$[NBu^n{}_4]_4[Ru_{20}Cu_6H_4Cl_2(CO)_{48}]$ 272 represents the highest-nuclearity ruthenium–copper carbonyl cluster that has been structurally characterized so far.[397] The complex showed the same geometry of central Cu_6Cl_2 unit as in 271. The Ru_{10} units appeared as two octahedra that were fused through a common triangular face, which generated three butterflies, one of which was capped. However, the hydrides in complexes 269–272 were unable to be located structurally, nor were they resolved through NMR studies. It seems that the presence of chlorides helped to stabilize the complex from fragmentation reactions.

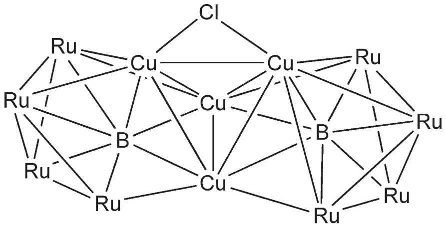


Metal core geometry of **271**



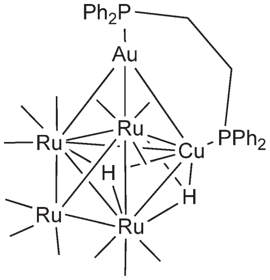
Metal core geometry of **272**

Housecroft *et al.* reported the synthesis of $[PPN][Ru_8Cu_4B_2H_2(\mu\text{-}Cl)_2(CO)_{24}][Cl]$ 273 from $[PPN][Ru_4BH_2(CO)_{12}]$ and $[Cu(MeCN)_4][BF_4]$.[398] Similar to the complexes that have already been described, the two Ru_4 butterfly units were connected by a tetrahedral Cu_4 unit, one edge of which was bridged by a chloro ligand. The two Ru_4 units were twisted with respect to each other by ~38°, and the central boron atom was hepta-coordinated. Although the hydrides in the complex were also unable to be located, it is believed that the complex should be neutral, and that it co-crystallizes with [PPN]Cl.



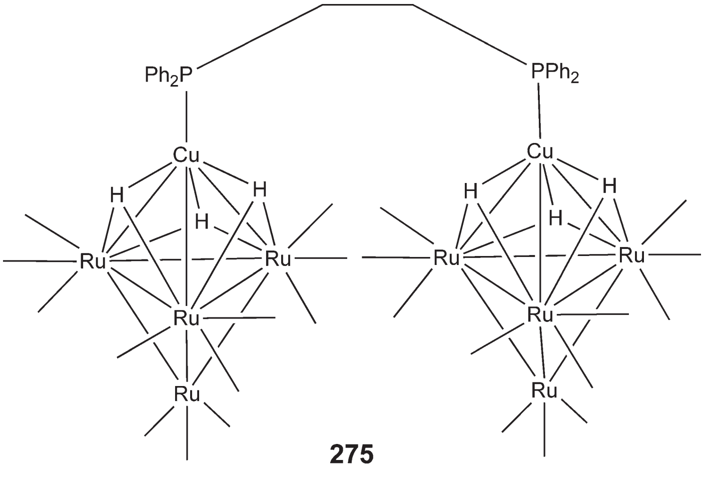
Metal core geometry of **273**

The heteronuclear cluster chemistry of group 11 metals was also studied extensively by Salter. In general, the higher-nuclearity clusters were synthesized by the incorporation of $M(PR_3)$ fragments (where M = Cu, Ag, or Au) into preformed clusters. An alternative method was through exchange reactions. $[M'X(PPh_3)]$ (M′ = Cu/Au, X = Cl; M′ = Ag, X = I) were used to replace one or two $M(PR_3)$ units in a mixed-metal cluster compound (Scheme 10). $[Ru_4CuAu(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ **274** was prepared and structurally characterized.[399] The complex showed an overall capped trigonal-bipyramidal metal core geometry. This method is useful for the preparation of novel trimetallic clusters of the type $[Ru_4MM'(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (M = Cu, M′ = Ag, Au; M = Ag, M′ = Au; n = 1, 2).



274

In addition, Salter also studied the effect of a bidentate diphosphine ligand that links two cluster subunits of identical stoichiometry using $[\{Ru_4Cu(\mu_3\text{-}H)_3(CO)_{12}\}_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}]$ **275**.[400] It is interesting to note that due to differences in crystal packing forces, the differences in the equivalent metal–metal separation of the two subunits in **275** were as high as ca. 0.118 Å for the Cu–Ru distances and up to ca. 0.132 Å for the Ru–Ru distances. NMR studies of **275** at −90 °C revealed that there was a rapid rotation of the whole $\{Ru_4Cu(\mu_3\text{-}H)_3(CO)_{12}\}$ subunit around the Cu–P bond, which showed that the free energy of activation that was available for this fluxional processes was unexpectedly low.



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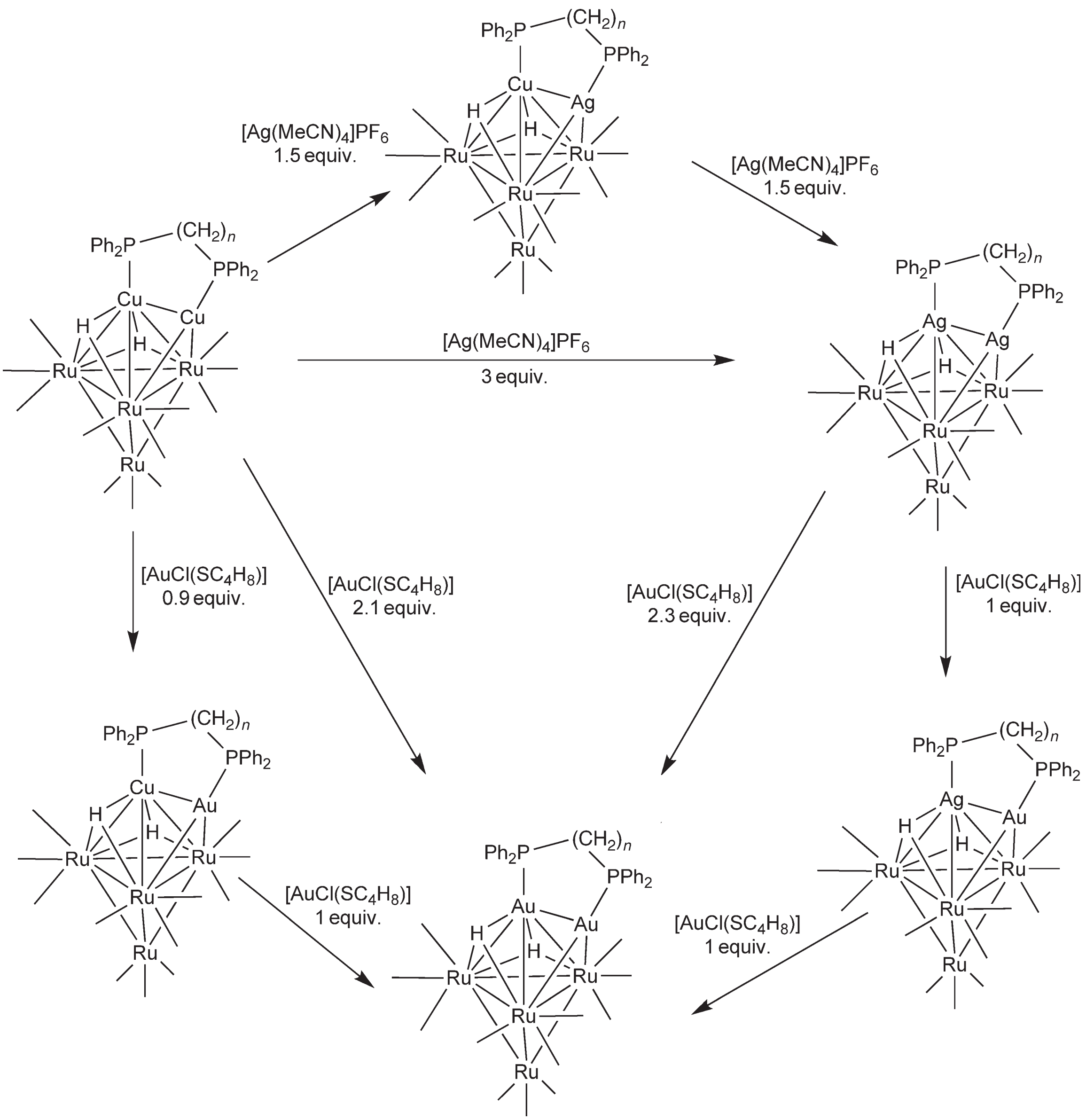
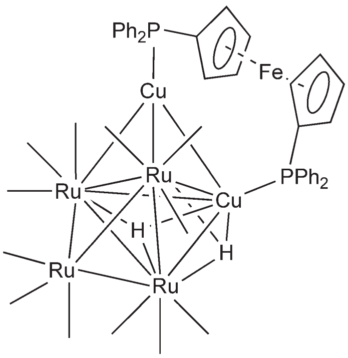


Scheme 10

The dppf analog of **274** was also prepared and studied.[401,402] Although only the di-copper analog $[Ru_4Cu_2(\mu_3\text{-}H)_2(dppf)(CO)_{12}]$ **276** was structurally characterized, it is believed that the Ag_2 and Au_2 analogs share a similar core geometry, as their spectroscopic data closely resemble each other.[401] The metal core of **276** showed the same capped trigonal bipyramidal skeletal geometry as **274**. VT NMR studies of the dynamic behavior of the mixed-metal cluster compounds $[Ru_4MM'(\mu_3\text{-}H)_2(dppf)(CO)_{12}]$ ($M = M' = Cu$, Ag or Au; $M = Cu$, $M' = Au$; dppf $= (\mu\text{-}(Ph_2P\text{-}\eta\text{-}C_5H_4)_2Fe)$ were carried out, and it was found that the dppf ligand undergoes a fluxional process in solution that involves inversion at the P atoms and the twisting of the Cp rings. The $\Delta G^{\ddagger}$ values for this fluxional process were calculated for the Cu_2, Ag_2, and Au_2 complexes. Although the dppf fluxionality was still observable in solution for the trimetallic cluster complex $[Ru_4CuAu(\mu_3\text{-}H)_2(dppf)(CO)_{12}]$ **277**, the metal skeleton of this cluster was stereochemically rigid, in marked contrast to the bimetallic analogs.[402]



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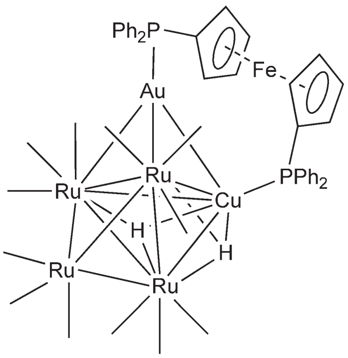
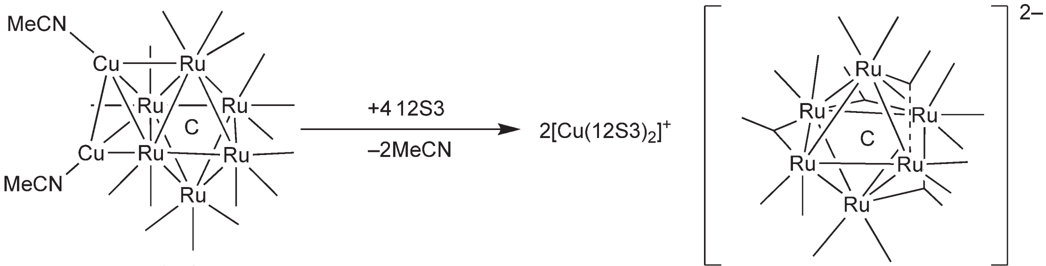


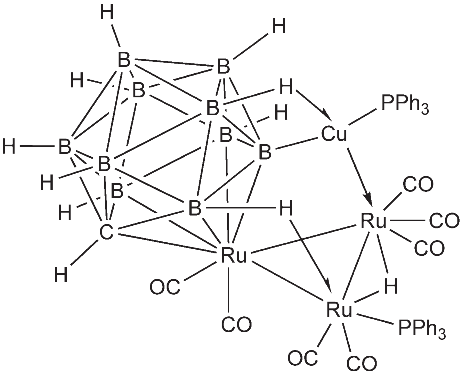
277

In addition to building up mixed-metal clusters from homometallic clusters, Adams *et al.* demonstrated the use of thiacrown ether 1,5,9-trithiacyclododecane (12S3) to selectively and completely abstract the copper atoms from Ru–Cu cluster $[Ru_6Cu_2(\mu_6\text{-}C)(CO)_{16}(MeCN)_2]$ **278** to give $[Ru_6(\mu_6\text{-}C)(CO)_{16}][Cu(\eta^3\text{-}12S3)(\eta^1\text{-}12S3)]_2$.[403] It is suggested that this method may be applied to the regeneration of certain contaminated heterogenous catalysts.



278

Stone *et al.* prepared bimetallic complexes $[Ru_3(\mu\text{-}H)(CO)_7(PPh_3)\{\eta^5\text{-}10\text{-}M(PPh_3)\text{-}7\text{-}CB_{10}H_{10}\}]$ (M = Cu **279**, Ag) from the reaction of $[NHMe_3][Ru_3(CO)_8(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ and $[CuCl(PPh_3)_3]$ in the presence of $Tl[PF_6]$ or $Ag[BF_4]$ and PPh_3 (Table 16).[404] An exopolyhedral three-center two-electron B–H⇀Cu bond that involved the B(2) site in the *nido*-10-Cu(PPh_3)-7-$CB_{10}H_{10}$ cage system was observed in the complex. Similarly, $[Ru_3(\mu\text{-}H)(CO)_8\{\eta^5\text{-}10\text{-}Au(PPh_3)\text{-}7\text{-}CB_{10}H_{10}\}]$ **280** can be prepared from $[AuCl(PPh_3)]$. Interestingly, no analogous B–H⇀Au bond was found in **280**.



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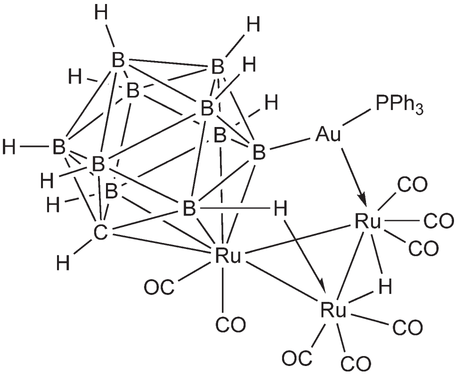


280

Only a very few Os–Cu clusters are known, and most of them contain Os_3 or Os_4 units. Ang *et al.* synthesized the Os_5–Cu cluster $[Os_5Cu(\mu\text{-}H)(CO)_{18}(PPh_3)]$ **281** from $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $CF_3COOCu(PPh_3)$.[405] The

Table 16 Ru/Os mixed-metal clusters containing group 11 elements with known structure

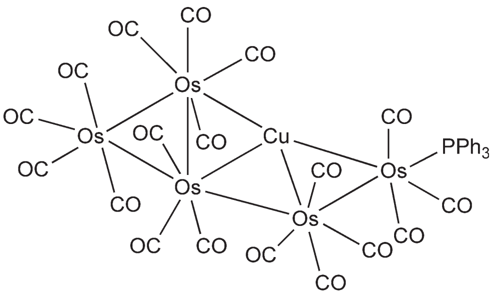
Formula	*References*
Clusters with two different kinds of metal	
$[Ru_3Cu(\mu-H)(CO)_7(PPh_3)\{\eta^5-10-(PPh_3)-7-CB_{10}H_{10}\}]$	404
$[Ru_6Cu_2(\mu_6-C)(CO)_{16}(MeCN)_2]$	403
$[Ru_8Cu_2(\mu_3-H)_6(\mu-dppe)(CO)_{24}]$	400
$[Ru_8Cu_2(\mu_3-H)_6(\mu-dppe_2)(CO)_{24}]$	400
$[Ru_8Cu_4(\mu-Cl_2)(BH)_2(CO)_{24}][PPN]Cl$	398
$[Ru_8Cu_7H_2Cl_3(CO)_{24}][PPN]_2$	396
$[Ru_{12}Cu_4(\mu_6-C)_2Cl_2(CO)_{32}][PPN]_2$	395
$[Ru_{12}Cu_6H_2Cl_2(CO)_{34}][PPN]_2$	396
$[Ru_{20}Cu_6H_4Cl_2(CO)_{48}][NBu^n{}_4]_4$	397
$[Os_5Cu(\mu-H)(PPh_3)(CO)_{18}]$	405
$[Ru_4Ag_2(\mu_3-H)_2\{P(Tol)_3\}_2(CO)_{12}]$	406
$[Ru_6Ag(\mu-C)(CO)_{16}][PPh_4]$	408
$[Ru_6Ag(\mu-C)(CO)_{16}][PPN]$	408
$[Ru_8Ag\{B(\mu-H)_2\}_2(CO)_{24}][PPN]$	398
$[Ru_{10}Ag_3(\mu-C)_2(\mu-Cl)_2(CO)_{28}][AsPh_4]_2$	407
$[Ru_{12}Ag_2(\mu-C)_2(CO)_{30}][PPh_4]$	408
$[Os_3Ag(\mu-PPh_2)(\mu-PMe_2)(CO)_{10}]$	409
$[RuAu_3(PPh_3)_3(\mu-H)_3\{\mu_3-CH_3C(CH_2PPh_2)_3\}][PF_6]_2$	431
$[Ru_2Au\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2(\mu-CO)PPh_3(CO)_4][SbF_6]$	432
$[Ru_3Au(\mu_3-HC_2H)(PPh_3)(CO)_9]$ (butterfly form)	420
$[Ru_3Au(\mu_3-HC_2H)(PPh_3)(CO)_9]$ (tetrahedral form)	420
$[Ru_3Au(\mu-H)(CO)_8\{\eta^5-10-(PPh_3)-7-CB_{10}H_{10}\}]$	404
$[Ru_3Au(\mu-H)(\mu_3-CCCPh_2)(PPh_3)(CO)_9]$	422
$[Ru_3Au_2(\mu_3-C_6H_3R)(\mu-PPh_2)_2(PPh_3)_2(CO)_6]$	427
$[Ru_3Au_2(\mu_3-CEtCMeCPhCPh)(PPh_3)_2(CO)_7]$	428
$[Ru_3Au_2(\mu_3-NPh)(PPh_3)_2(CO)_9]$	427
$[Ru_3Au_2(\mu-dppm)(\mu-H)\ (\mu_3-COMe)(CO)_9]$	414
$[Ru_3Au_2(\mu-Ph_2P(CH_2)_5PPh_2)(\mu-H)\ (\mu_3-COMe)(CO)_9]$	414
$[Ru_3Au_2\{\mu_3-PPhCH_2PPh(C_6H_4-2)\}(P(OMe)_3)_2(CO)_8]$	427
$[Ru_3Au_3(\mu_3-C_2Ph)(PPh_3)_3(CO)_8]$	429
$[Ru_3Au_3(\mu_3-CMeCHCMe)(PPh_3)_3(CO)_8]$	429
$[Ru_3Au_4(\mu_3-CCH_2)(PPh_3)_2(CO)_9]$ (square pyramid form)	420
$[Ru_4Au_2(\mu-Ph_2PCH{=}CHPPh_2)(\mu_3-H)(\mu-H)_2(CO)_{12}]$	413
$[Ru_4Au_2(PMe_3)_2(\mu_4-PCF_3)(CO)_{12}]$	419
$[Ru_4Au_2(PPh_3)_2(\mu_3-PCF_3)(CO)_{12}]$	419
$[Ru_5Au_2(\mu_5-C)(\mu-dppe)(CO)_{14}]$	410
$[Ru_5Au_2(\mu-dppm)(CO)_{15}]$	415
$[Ru_5Au_3(BPPh_3)_3(CO)_{14}]$	426
$[Ru_6Au(B)(PPh_3)\{P(OMe)_3\}(CO)_{16}]$	424
$[Ru_6Au(\mu_3-H)(\mu-O{:}\mu-C{:}\eta^6-OC_6H_3OMe-4)(PPh_3)(CO)_{16}]$	423
$[Ru_6Au_2(\mu_6-C)(CO)_{16}(Ph_2PCH_2)_2NCH_2Ph]$	418
$[Ru_6Au_2(\mu_6-C)(\mu-CO)_2(PPh_3)_2(CO)_{14}]$	427
$[Ru_6Au_2(\mu-dppe)(\mu_6-C)(CO)_{16}]$	415
$[Ru_6Au_2(\mu-H)B(PPh_3)_2(CO)_{16}]$	425
$[Ru_6Au_3(B)\{P(Tol)\}_3(CO)_{17}]$	425
$[Ru_6Au_3B(PPh_3)_3(CO)_{16}]$	425
$[Ru_{10}Au_2(\mu_5-C)_2(Ph_2PCH_2PPh_2)(CO)_{24}]$	416
$[Os_3Au(\mu-PPh_2)(PPh_3)(CO)_{10}]$	409
$[Os_3Au(PPh_3)(\mu-Cl)(CO)_{10}]$	443
$[Os_3Au_2(\mu-S)(PPh_3)_2(CO)_9]$	435
$[Os_4Au(\mu-Cl)(PPh_3)(CO)_{14}]$	442
$[Os_4Au(\mu-H)_3(PPh_3)(CO)_{12}]$	444
$[Os_4Au(\mu-H)_3(PPh_3)(NMe_3)(CO)_{11}]$	445
$[Os_4Au_2(\mu-dppe)(\mu-H)_4(CO)_{11}]$	416
$[Os_4Au_2(\mu-H)_2(PPh_3)_3(CO)_{11}]$	445
$[Os_4Au_3(\mu-H)_3(PPh_3)_3(CO)_{11}]$	445
$[Os_4Au_4(\mu-dppm)_2(\mu-H)_2(CO)_{11}]$	441

(Continued)

Table 16 (Continued)

Formula	*References*
$[Os_4Au_4(\mu\text{-}H)_2(PPh_3)_4(CO)_{11}]$	445
$[Os_6Au_2(\mu\text{-dppm})(CO)_{17}]$	417
$[Os_6Au_2(\mu\text{-dppm})(CO)_{17}]$	417
$[Os_6Au_4(\mu\text{-dppm})_2(CO)_{17}]$	438
$[Os_7Au_2(\mu\text{-dppm})(CO)_{19}]$	439
$[Os_7Au_2(PEt_3)_2(CO)_{20}]$	437
$[Os_8Au_2(\mu\text{-dppb})(CO)_{22}]$	436
$[Os_8Au_2(\mu\text{-}H)_6(\mu\text{-dppe})(CO)_{24}]$	410
$[Os_9Au_2(\mu\text{-dppe})(CO)_{23}]$	440
$[Os_9Au_2(PCy_3)_2(CO)_{24}]$	440
$[Os_{10}Au_4(PPh_2Me)_4(CO)_{24}]$	446
Clusters with three different kinds of metal	
$[Ru_4Cu_2(\mu_3\text{-}H)_2(\mu\text{-dppf})(CO)_{12}]$	401
$[RuAuFe(\mu_4\text{-}\eta^5\text{-}\eta^2\text{-}C_5H_4C{\equiv}C)(PPh_3)(CO)_9Cp]$	434
$[Ru_2Os_6Au_2(\mu\text{-dppm})Cp_2(CO)_{17}]$	417
$[Ru_3AuRh(\mu\text{-}H)(\mu\text{-dppf})(B)(CO)_8Cp^*]$	285
$[Ru_3Au_3(\mu_6\text{-}B)(\mu\text{-}H)(\mu\text{-dppf})(Cl)(CO)_9Cp^*]$	433
$[Ru_3Au_3(\mu_6\text{-}B)(\mu\text{-}H)(\mu\text{-dppf})(Cl)(CO)_9Cp]$	433
$[Ru_4Au_2(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-dppf})(CO)_{12}]$	402
$[Ru_4AuCu(\mu_3\text{-}H)_2(\mu\text{-dppf})(CO)_{12}]$	402
$[Ru_4AuCu(\mu\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$	399
$[Ru_4Au_2Rh(Ph_2PCH_2PPh_2)B(CO)_{14}]$	412
$[Ru_8Au_2Rh_8B_2(\mu\text{-dppp})(CO)_{32}]$	412
$[Os_6Ru_2Au_2(\mu\text{-dppm})Cp_2(CO)_{17}]$	417

heteronuclear metal framework resembles a puckered "ladder-like" geometry based on two butterfly arrangements with the wings fused along an Os–Cu bond. Although the hydride could not be located crystallographically, its presence was evident in the ^1H NMR study.

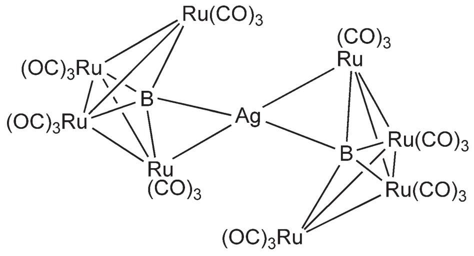


281

$[Ru_4Ag_2(\mu_3\text{-}H)_2(CO)_{12}\{P(C_6H_4Me\text{-}2)_3\}_2]$ **282** was prepared by Salter to study the steric properties of the phosphine ligands.[406] Surprisingly, the marked increase in the cone size of 145° (PPh_3) to 194° ($P\{C_6H_4Me\text{-}2\}_3$) did not alter the geometry of the Ru_4Ag_2 units, which remained capped trigonal bipyramidal. The dynamic exchange of the two Ag sites and of the phosphine ligands between clusters was also observed in solution.

The reaction of $[PPN][Ru_4B(\mu\text{-}H)_2(CO)_{12}]$ and $[Ag(MeCN)_4][BF_4]$ or $AgBF_4$ gave a mixture of the tetra-silver analog of 273 and a mono-silver complex $[PPN][\{Ru_4B(\mu\text{-}H)_2(CO)_{12}\}_2Ag]$, 283, in which the Ag atom linked the two $Ru_4B(\mu\text{-}H)_2(CO)_{12}$ units in a mutually *trans*-orientation.[398]

Johnson *et al.* synthesized $[AsPh_4]_2[Ru_{10}Ag_3(\mu\text{-}C)_2(\mu\text{-}Cl)_2(CO)_{28}]$ 284 from $[Ru_5(\mu\text{-}C)(CO)_{14}]^{2-}$.[407] Mild thermolysis of 284 adsorbed on mesoporous silica gave discrete nanoparticles that catalyzed the hydrogenation of hex-1-ene.



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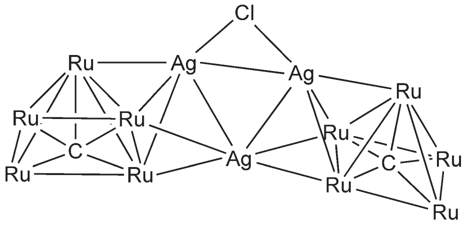
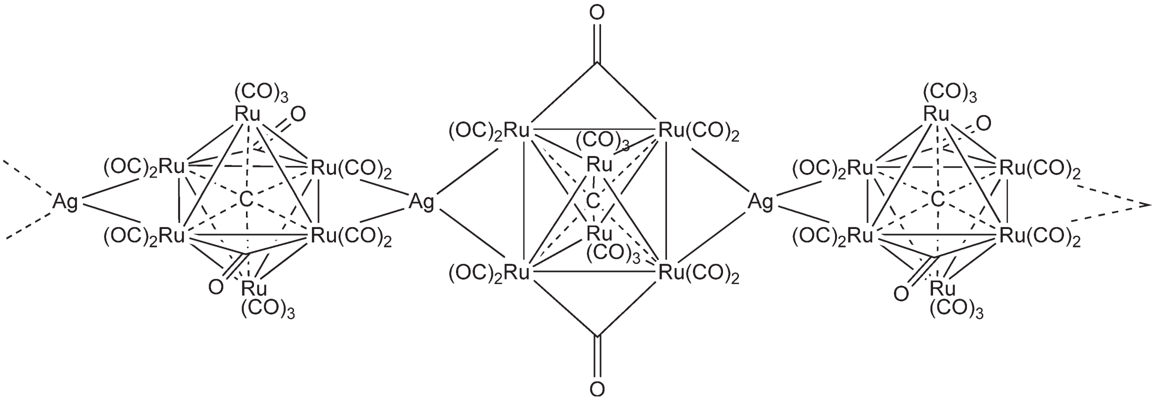


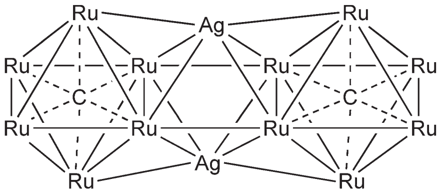
Metal core geometry of **284**

A polymeric chain of high-nuclearity mixed-metal clusters was prepared by Wakatsuki.[408] $[PPN]^+$ 285 and $[PPh_4]^+$ 286 salts of $[Ru_6Ag(\mu_6\text{-}C)(CO)_{16}]^-$ showed a similar pattern of infinite chains of alternating units of the anionic cluster $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^-$ with a cationic Ag that were separated from each other by layers of the PPN or PPh_4 cations. The heating of 286 in MeOH at 60 °C resulted in "depolymerization" to give the di-silver complex $[PPh_4]_2[Ru_{12}Ag_2(\mu\text{-}C)_2(CO)_{30}]$ 287.

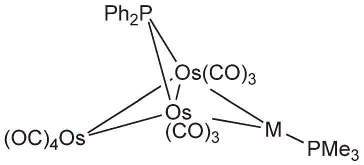
The reactions of $[Os_3(\mu\text{-}PPh_2)(CO)_{10}]^-$ with $[M(PR_3)Cl]$ (M = Ag, R = Me 288; M = Au, R = Ph) in the presence of Tl(OAc) gave the tetranuclear butterfly clusters $[Os_3(\mu\text{-}MPMe_3)(\mu\text{-}PPh_2)(CO)_{10}]$ 288.[409]



Infinite chains of $[Ru_6Ag(\mu_6\text{-}C)(CO)_{16}]^-$ in **285** and **286**



Metal core geometry of **287**

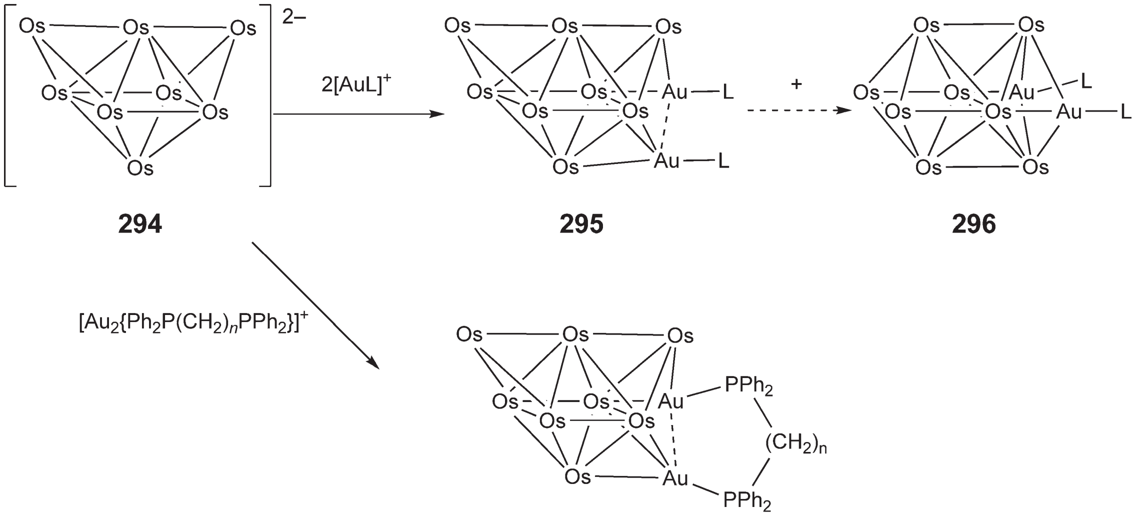


288

Ru–Au clusters that contain various $Ph_2P(CH_2)_nPPh_2$ (L–L) ligands have been extensively studied. Due to the flexibility of the diphosphine ligand, the Au metal may be coordinated to the same Ru cluster, as in $[Ru_5Au_2(Ph_2PCH_2CH_2PPh_2)C(CO)_{14}]$ **289**, or may connect two cluster units, as in $[\{Ru_5C(CO)_{14}\}_2Au_2(Ph_2PCH_2CH_2PPh_2)]$ **290**.[410] The latter is favored if an excess of cluster is used. The versatile nature of the [ClAu(L–L)AuCl] (L–L = dppm, dppe, dppb, dppp, dppa, (*Z*)-dppet) ligand was studied in more detail.[411–414] It was reported that the tendency of forming linked clusters of the form $[\{Ru_6(CO)_{17}B\}_2\{\mu\text{-}Au(L\text{–}L)Au\}]$ increased down the series.[411] Lewis found that the carbido Ru_6 cluster $[Ru_6C(CO)_{16}]^{2-}$ retained its geometry upon auration with $[Au_2(dppm)Cl_2]$ to give $[Ru_6Au_2(dppm)C(CO)_{16}]$ **291**, whereas the non-carbido dianion $[Ru_6(CO)_{18}]^{2-}$ broke down to form $[Ru_5Au_2(dppm)(CO)_{15}]$ **292**.[415] In $[Ru_{10}Au_2(dppm)C(CO)_{24}]$ **293**, the bidentate Au ligand capped two adjacent vertex-sharing triangular faces of the Ru_{10} tetra-capped octahedral core.[416] Various heterotrimetallic clusters that contain Ru–Au were prepared.[412,417] Nanoscale Ru–Au clusters that are assembled around a dendritic core of amino phosphine multi-ligands were prepared and studied by high-resolution transmission electron microscopy, and their monomeric cluster analogs were also studied structurally for comparison.[418]

Due to the isolobal properties of H^+ and $[Au(PR_3)]^+$, Ru–Au clusters were generally prepared by the reaction of $[Au(PR_3)X]$ with Ru cluster anions (R = alkyl, OMe, Ph, C_6H_4-Me-2; X = halide, Me).[419–423,432] Humphrey showed that an edge-bridging hydride may be replaced by a face-capping $Au(PPh_3)$ moiety, as in $[Ru_6Au(PPh_3)(\mu_3\text{-}H)(\mu\text{-}O:\mu\text{-}C\text{-}\eta^6\text{-}OC_6H_3OMe\text{-}4)(\mu\text{-}CO)(CO)_{15}]$.[423] Housecroft investigated the auration of certain boride clusters.[424–426] Trigoldoxonium cation $[O\{Au(PR_3)\}_3]^+$ (R = Me, OMe, Ph, C_6H_4-Me-2) has been widely used to introduce multiple Au atoms into metal clusters.[425–429] Venanzi *et al.* studied the theoretical and spectroscopic aspects of $RuAu_3$ clusters.[430,431] Ferrocene-containing Ru–Au clusters were also studied by several groups.[285,402,433,434]

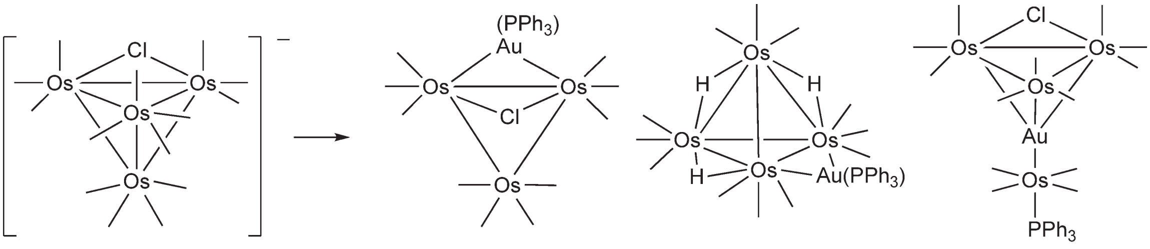
Lewis, Raithby *et al.* extensively studied Os–Au clusters. They showed that the addition of mono-gold electrophiles to the $[Os_8(CO)_{22}]^{2-}$ cluster ion 294 resulted in both the kinetic product 295, in which the bicapped octahedral geometry was retained, and the thermodynamic product 296, which showed a rearrangement of the metal core.[436] The similar reaction of $[Os_7(CO)_{20}]^{2-}$ with $[Au(PEt_3)]^+$ gave $[Os_7\{Au(PEt_3)\}_2(CO)_{20}]$ **297** with the retention of geometry.[437] In contrast, with di-gold electrophiles, such as $[Au_2(dppm)]^+$, the Au atoms lie in close proximity, with retention of the original geometry in most cases.[417,436,438–440] Furthermore, tetra-gold clusters can be obtained with 2 equiv. of $[Au_2(dppm)]^+$.[441]



294 **295** **296**

298

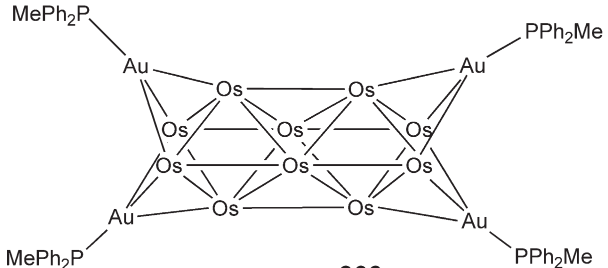
The auration of $[Os_4(\mu\text{-}Cl)(CO)_{13}]^-$ 299 resulted in a mixture of products 300–302, including the insertion of an $Os(CO)_4$ fragment into a gold–phosphine bond 302.[442]



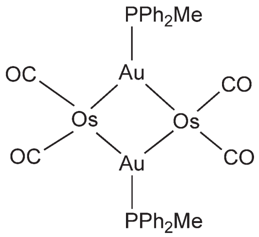
299 **300** **301** **302**

The photochemistry of 300 was studied by Raithby,[443] and the electrochemistry and catalytic reactivity of 301 for oxidative carbonylation of aniline was examined by Wong.[444] The effect of different Os : Au ratios (ranging from 1 to 4) in bimetallic clusters on their catalytic reactivity for carbonylation was also studied.[445] Woods *et al.* prepared various bimetallic metal complexes using the metallophosphanide anions in the form ML_nX (X = halide), including $[Os_3Au(PPh_3)(\mu\text{-}PPh_2)(CO)_{10}]$ 302.[409]

High-nuclearity clusters have attracted much attention because of their high intermetal connectivity and closely packed array of metal atoms. $[Os_{10}\{Au(PPh_2R)\}_4(CO)_{24}]$ (R = Me) 303 was shown to have an open tubular structure in which the equatorial–equatorial interactions were significantly weaker and the axial–axial interactions were stronger compared with a regular Os_6 octahedron.[446]



Side view of **303**



End view of **303**

6.25.3.9 Ru/Os Mixed-metal Clusters Containing Group 12 Elements

Suzuki *et al.* prepared the tetrahedral Ru_3Zn cluster $[Ru_3Zn(\mu_3\text{-}H)(\mu\text{-}H)_3(Et)(\eta^5\text{-}Cp^*)_3]$ **304** from a stoichiometric amount of $[Ru_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3(\eta^5\text{-}Cp^*)_3]$ and diethylzinc. With the incorporation of the triply-bridged Zn or other metal alkyl, the electron density of the Ru center, and thus its reactivity (as reflected through cyclic voltammetry) to C–C/C=C/C–H bond cleavage, could all be finely tuned (Table 17).[447]

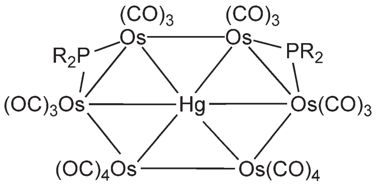
Mercury has shown a rich structural chemistry with the group 8 metals. It serves as a link in mixed-metal clusters, and also participates in a range of multi-center metal–metal bonds. It has been added as an Hg–ligand fragments, as a naked Hg atoms, and as an aggregate of Hg atoms into an extended framework.

Table 17 Ru/Os mixed-metal clusters containing group 12 Elements with known structure

Formula	*References*
Clusters with two different kinds of metal	
$[Ru_3Zn(\mu_3\text{-}H)(\mu\text{-}H)_3(Et)Cp^*{}_3$	447
$[RuHg_2Br_2(CO)_4]$	454
$[RuHg_2(\mu\text{-}\eta^3\text{-}SC_5H_4N)\}_2(CO)_{22}]$	452
$[Ru_2Hg(CO)_8][PPN]_2$	448
$[Ru_2Hg(\eta^5\text{-}Cp)_4][PF_6]$	450
$[Ru_2Hg\{\mu_2\text{-}(ClCH_2COO)_2\}(\mu\text{-}NHC_{10}H_6NH)(PPr^i{}_3)_2(CO)_4]$	451
$[Ru_4Hg_4(CO)_{16}]$	449
$[OsHg_2(Br)_2(CO)_4]$	455
$[Os_2HgCp_4][PF_6]$	450
$[Os_3Hg(\mu\text{-}I)(CF_3)(CO)_{10}]$	456
$[Os_3Hg_2(CF_3)_2(CO)_{11}]$	457
$[Os_6Hg(\mu\text{-}Cl)_2(CO)_{20}]$	461
$[Os_6Hg(\mu\text{-}PPh_2)_2(CO)_{20}]$	459
$[Os_6Hg(\mu\text{-}PPh_2)_2(\mu\text{-}CO)_2(CO)_{18}]$	459
$[Os_6Hg(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(\mu\text{-}H)(CO)_{20}]$	460
$[Os_6Hg(\mu\text{-}\eta^2\text{-}CH{=}CH_2)_2(CO)_{20}]$	460
$[Os_6Hg(\mu\text{-}\eta^2\text{-}CH{=}CHPh)_2(CO)_{20}]$	460
$[Os_6Hg(\mu\text{-}\eta^2\text{-}SC_5H_4N)_2(CO)_{20}]$	452
$[Os_6Hg(\mu\text{-}\eta^2\text{-}SC_7H_4NS)_2(CO)_{20}]$	452
$[Os_6Hg(\mu\text{-}\eta^2\text{-}SC_7H_4NS)_3(CO)_{20}]$	452
$[Os_6Hg\{\mu\text{-}P(Bu^i)_2\}_2(\mu\text{-}CO)_2(CO)_{18}]$	459
$[Os_6Hg\{\mu\text{-}P(Bu^i)_2\}_2(\mu\text{-}CO)_2(CO)_{18}]$ (isomer)	459
$[Os_7Hg(\mu\text{-}\eta^2\text{-}CH{=}CHPh)_2(CO)_{24}]$	460
$[Os_7Hg_2(\mu\text{-}Cl)_2(CO)_{24}]$	461
$[Os_7Hg_2(\mu\text{-}\eta^2\text{-}SC_5H_4N)_2(CO)_{24}]$	452
$[Os_8Hg_2(\mu\text{-}Cl)_2(CO)_{28}]$	461
$[Os_{10}Hg(\mu_5\text{-}C)_2(\mu\text{-}\eta^2\text{-}SC(N{=}NPh)({=}NNHPh)_2(CO)_{28}]$	452
$[Os_{10}Hg(\mu_5\text{-}C)_2(\mu\text{-}\eta^2\text{-}SPh)_2(CO)_{28}]$	452
$[Os_{18}Hg(\mu_6\text{-}C)_2H(CO)_{42}][PPh_3H]_3$	458
Clusters with three different kinds of metal	
$[Ru_3HgMo(CO)_{10}(\mu\text{-}NH_2)(CO)_{13}Cp]$	131
$[Os_3HgMo(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{13}Cp]$	460

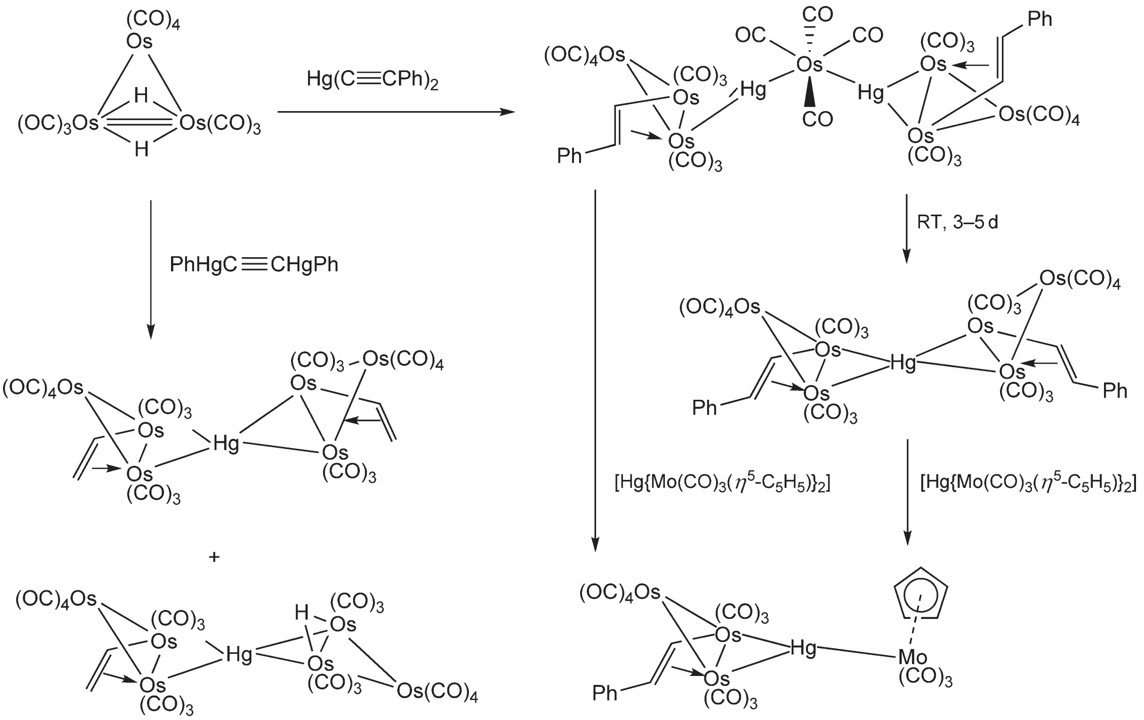
Direct reaction with Hg^{2+} salts or Hg metal usually results in the addition of Hg as a naked atom. As in the case of $K_2[Hg\{Ru(CO)_4\}_2]$ **305** or $[PPN]_2[Hg\{Ru(CO)_4\}_2]$ **306**, Hg serves to link two units of $\{Ru(CO)_4\}$.[448] Similarly, the analogous tetramer, $\{RuHg(CO)_4\}_4$ **307**, was successfully characterized by the X-ray powder diffraction method, despite its poor solubility.[449] In the mercuric salt of ruthenocene, due to steric repulsion, the neighboring metallocenes rotated away from each other in a staggered conformation as in the ferrocene analogue, and the osmocene analog showed the eclipsed conformation.[450] In $[Ru_2\{\mu_2\text{-}Hg(ClCH_2COO)_2\}(\mu\text{-}NHC_{10}H_6NH)\{P(Pr^i)_3\}_2(CO)_4]$ **308**, by contrast, the bis(chloroacetato-Hg) fragments were added onto a Ru dimer.[451] The reaction of $PhHg(SC_5H_4N)$ with $[Ru_3(CO)_{10}(MeCN)_2]$ gave the adducts *cis*-$[Ru(CO)_4\{Ru_3(CO)_9(\mu\text{-}\eta^3\text{-}SC_5H_4N)(\mu\text{-}Hg)\}_2]$ **309**, in which the Hg ligand was inserted separately across two Ru clusters.[452] The hetero-tri-metallic cluster $[Ru_3(CO)_{10}(\mu\text{-}NH_2)(\mu_3\text{-}Hg)\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}]$ **310** was prepared from a methoxynitrido cluster in $[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)]$.[131] Osella *et al.* investigated the electrochemistry of $[\{Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}Bu^t)\}_2Hg]$ **311**, $[\{Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}Bu^t)\}HgRe(CO)_5]$ **312**, and $[\{Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}Bu^t)\}HgMoCp(CO)_3]$ **313**.[453]

High-nuclearity Os–Hg clusters were prepared by Lewis *et al.*[458] They demonstrated the stepwise demercuration of the cluster $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ **314** to $[Os_{18}Hg_xC_2(CO)_{42}]^{y-}$ ($x = 1$–3, $y = 1$–4) through photochemical and redox chemical reactions. A novel μ_6-Hg–Os cluster, $[Os_6(\mu_6\text{-}Hg)(\mu\text{-}PR_2)_2(CO)_{20}]$ **315**,[459] was prepared by Egold.



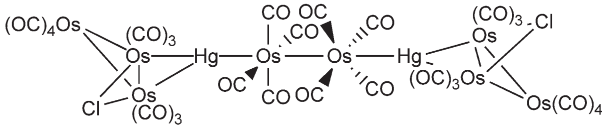
315

Cleavage of the Hg–C bond by the unsaturated cluster $[Os_3H_2(CO)_{10}]$ was examined. It was found that the reaction of $[Hg(C{\equiv}CPh)_2]$ and $[RHgC{\equiv}CHgR]$ with $[Os_3H_2(CO)_{10}]$ gave isostructural products. Trimetallic clusters $[\{Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CHPh)\}(\mu_3\text{-}Hg)\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}]$ **316** can also be prepared from symmetric mercurials such as $[Hg\{M(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ (M = Cr, Mo, W).[460]

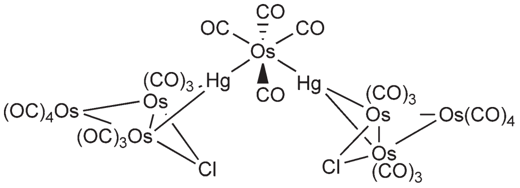


316

Reactions of alkyl or aryl mercurial halides with [Os$_3$(CO)$_{10}$(NCMe)$_2$] gave Os–Hg clusters **317** and **318**, which have unusual metal core geometries.[461]



317



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Abbreviations

acac	acetyl acetone
BAr^F_4	B{3,5-(CF$_3$)$_2$(C$_6$H$_3$)}$_4$
bma	3-bis(diphenylphosphino)maleic anhydride
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadienyl
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
dppa	bis(diphenylphosphino)amine
dppb	1,4-bis(diphenylphosphino)butane
dppet	1,2-bis(diphenylphosphino)ethene
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	bis(diphenylphosphino)propane
Et	ethyl
Pr^i	iso-propyl
Pr^i-DAB	*N*,*N*′-diisopropyl-1,4-diaza-1,3-butadiene
Pr^i-PyCa	pyridine-2-carbaldehyde-*N*-isopropylimine
Me	methyl
Bu^n	butyl
OEP	octaethylporphyrin
OTf	[CF$_3$SO$_3$]$^-$
Ph	phenyl
phen	1,10-phenanthroline
PMe$_3$	trimethylphosphine
P(OMe)$_3$	trimethylphosphite
PPh$_3$	triphenylphosphine
PPN	[N(PPh$_3$)$_2$]$^+$
py	pyridine
pz	pyrazine
qcp	8-quinolylcyclopentadienyl
Bu^t	tert-butyl
Tol	tolyl
$TP^{\#}$	tris(1,3-dimethyl-2-bromopyrazolyl)borate
TPP	tetraphenylporphyrin

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