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COMPREHENSIVE ORGANOMETALLIC CHEMISTRY III

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

Volume
5

COMPOUNDS OF GROUPS 5 TO 7

Volume Editor
Klaus H. Theopold

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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 for Volume 5 – Klaus H. Theopold, *University of Delaware, Newark, DE, USA*

Klaus H. Theopold was born in Berlin, studied at the Universität Hamburg for his Vordiplom in 1977, and at UC Berkeley, where he obtained his PhD in 1982 under the direction of Professor R. G. Bergman. After spending a year as postdoctoral fellow in the laboratory of Professor R. R. Schrock at MIT, he began his independent career in 1983 as an Assistant Professor at Cornell University. In 1990 he moved to the University of Delaware, where he is currently Professor of Chemistry. His scientific interests encompass synthetic and mechanistic studies of transition metal compounds, in particular paramagnetic organometallics, polymerization catalysis, and coordination compounds relevant to the activation of O_2.

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5.01
Vanadium Organometallics

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5.01.1 Introduction

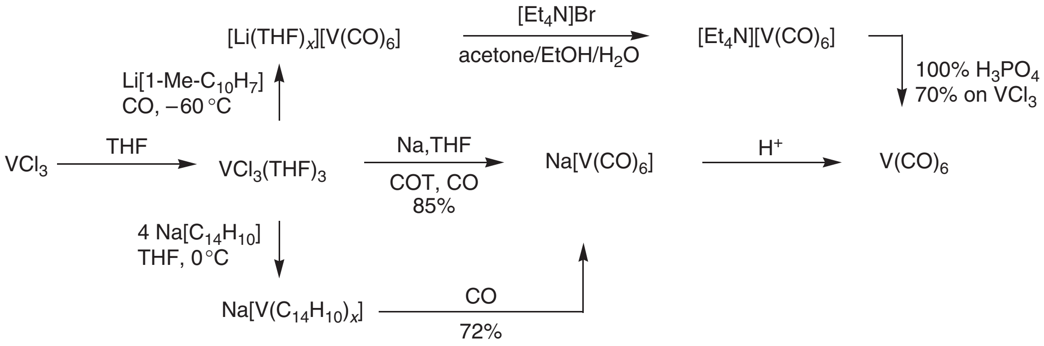
The development of organometallic chemistry of vanadium has lagged behind that of its neighboring group 4 metal analogs. The major reason for this is the strong paramagnetism of many of these vanadium species, which often makes single crystal X-ray diffraction an indispensable tool for their unambiguous characterization. Nevertheless, during the past 15 years, the number of studies of the mid- to high-valent vanadium complexes has dramatically increased, mainly due to the work of a small number of groups, the development of high yield procedures for known or new precursors, and the stabilization of new species by the use of suitable ancillary ligands. Although vanadium compounds are now used as reagents in organic synthesis, materials, polymerization catalysts, and potential drugs, the applications of organovanadium compounds are still rather limited, again probably due to the difficulty in their characterization and handling. This chapter focuses on the synthesis, characterization, reactivity, and applications of organovanadium compounds, and covers the literature since 1993 up to early 2005. For details on organometallic vanadium chemistry prior to 1993, links are always given to the appropriate sections in the two earlier chapters on "vanadium" in COMC (1982) and COMC (1995).[1,2] The contents of this chapter are arranged in sections classified according to the bonding mode of the hydrocarbon ligand. Attempts have been made to extensively include the whole literature (except for reactions that generate non-organometallic products), and to highlight the most significant contributions. In general, work in the patent literature is not covered unless it has not been reported elsewhere. In view of the limited space, the reader is referred to comprehensive reviews and more general reviews such as those recently reported on selected aspects of the role of vanadium complexes in alkene polymerization,[3–6] in organic synthesis,[7,8] as magnetic materials,[9–11] or medicinal applications,[12–15] as well as those treating the chemistry of $Cp^*V(CO)_4$[16] and Cp_2V.[17] Progress in the related coordination chemistry of vanadium can be found in the chapter on vanadium in the companion series of *Comprehensive Coordination Chemistry*.[12]

5.01.2 Carbonyl, Isocyanide, Arduengo-Type Carbene and Related Compounds

5.01.2.1 $V(CO)_6$ and Derivatives

5.01.2.1.1 Synthesis, structure, and bonding

Significant improvements in the synthesis of $[V(CO)_6]^-$ and $V(CO)_6$ have been made, which will certainly help to revive the chemistry and applications of $V(CO)_6$ and its derivatives. The general synthesis of $V(CO)_6$ is a two-step procedure that requires the initial preparation of $[V(CO)_6]^-$ by the reductive carbonylation of $VCl_3(THF)_3$ (Scheme 1) (for a complete description, see COMC (1982) (Volume 3, Chapter 24, Section 24.2.1.1)[2] and COMC (1995) (Volume 5, Chapter 1, Section 5.01.2.4)[1]). $V(CO)_6$ is obtained via oxidation of $[V(CO)_6]^-$ with an acid



Scheme 1

(anhydrous HCl[18] or crystalline 100% H_3PO_4[19,20]). While the original synthesis of $Na[V(CO)_6]$ required high CO pressure and elevated temperatures,[21] an improved and safer procedure was developed by performing the atmospheric pressure reductive carbonylation of $VCl_3(THF)_3$ with sodium in THF in the presence of a fairly large amount of 1,3,5,7-cyclooctatetraene (V/COT molar ratio 0.5) (Scheme 1).[22]

To overcome the use of considerable amounts of the expensive cycloolefin catalyst, in particular in large-scale preparation, a useful alternative to this method has recently been described.[23] It involves the initial reduction of $VCl_3(THF)_3$ by 4 equiv. of sodium anthracenide under an atmosphere of argon, followed by addition of carbon monoxide, affording $Na[V(CO)_6]$ in 72% yield (Scheme 1). A homoleptic anthracene vanadate $[V(C_{14}H_{10})_x]^-$ is postulated as an intermediate. Less successfully, the substitution of anthracene in the previous procedure by naphthalene for the sodium reductive carbonylation of $VCl_3(THF)_3$ afforded lower yields of $Na[V(CO)_6]$ (yield 40–50%, respectively, in THF or DME).[23] The strong reducing nature of the $[V(C_{10}H_8)_x]^-$ intermediate *versus* $[V(C_{14}H_{10})_x]^-$ would explain the difference. Following the same trend, the stronger reducing agent $[V(C_6H_6)_2]^-$ has been reported to react with carbon monoxide to give only ill-defined CO reduction products and no vanadium carbonyls.[24]

Nevertheless, the anthracene- or naphthalene-aided procedures are suitable for the synthesis of rather small quantities (1–2 g) of $Na[V(CO)_6]$. By employing lithium 1-methylnaphthalenide as the reducing agent in the carbonylation of $VCl_3(THF)_3$ (−60 °C, atmosphere CO pressure), the alkali metal polyarene route to $[V(CO)_6]^-$ is easily scaled up by a factor of 10 (Scheme 1). For purification reasons, the $Li[V(CO)_6]$ formed needs further cation exchange by metathesis with $[NEt_4]Br$ to provide $[NEt_4][V(CO)_6]$ in 70% yield (based on VCl_3).[25] The same authors developed an improved procedure for the conversion of $[NEt_4][V(CO)_6]$ into $V(CO)_6$ by 100% H_3PO_4, based on the use of a specially designed Schlenk apparatus that provides $V(CO)_6$ in 86% yield.[25]

Furthermore, preliminary investigations show that bis(naphthalene) vanadium(0) (see Sections 5.01.2.4 and 5.01.6.1) is an excellent precursor to other zerovalent vanadium complexes, and, in particular, report is made that in cyclohexane it quickly combines with CO at normal pressure and 20 °C to give high yields of $V(CO)_6$.[26] Although no experimental details are given, such direct carbonylation would be highly desirable.

A new route to carbonyl–phosphine complexes is the exchange of dinitrogen ligands in N_2 complexes $Na[V(N_2)_n(PMe_2Ph)_{6-n}]$ ($n = 1$ or 2) (prepared by reduction of $VCl_3(THF)_3$ in THF by Na/Hg under dinitrogen atmosphere in the presence of PMe_2Ph). Exposing a solution of a mixture of these complexes to normal pressure of CO at 40 °C results after ca. 50 min in the substitution of all N_2 ligands for CO with the formation of *trans*-$[V(CO)_2(PMe_2Ph)_4]^-$ and small amounts of $[V(CO)_6]^-$.[27] After prolonged exposure to CO (3 days), the main product is *cis*-$[V(CO)_4(PMe_2Ph)_2]^-$ with minor amounts of $[V(CO)_5(PMe_2Ph)]^-$ and $[V(CO)_6]^-$. The diphosphine analog $Na[V(N_2)_n(dmpe)_{4-n}]$ ($n = 1$ or 2) behaves similarly under CO exposure with the formation of *cis*-$[V(CO)_4(dmpe)]^-$ with minor products $[V(CO)_5(dmpe)]^-$ and $[V(CO)_6]^-$. For spectroscopic investigations (^{7}Li NMR) to study close contact ion-pair interactions,[27] the related complex $Li[V(CO)_2(dmpe)_2]$ was prepared by the reduction of $VCl_3(THF)_3$ by excess Li foil in the presence of dmpe followed by addition of CO (^{51}V NMR: −1063 ppm, $J_{VP} = 161$ Hz. $\nu_{CO} = 1731\ cm^{-1}$).

Sodium naphthalenide reduction of (trimpsi)VCl_3(THF) (trimpsi = $Bu^tSi(CH_2PMe_2)_3$) in the presence of CO provides, after salt metathesis with $[Et_4N][Cl]$ and suitable workup, very low yield (5%) of $[Et_4N][(trimpsi)V(CO)_3]$ selectively separated from hydrido derivative (trimpsi)$V(H)(CO)_3$ and structurally established [(trimpsi)V(μ-Cl)$_3$V(trimpsi)][(η^2-trimpsi)$V(CO)_4$].[28] This ligand environment has found particular interest in the development of stable nitrosyl–vanadium chemistry (see Section 5.01.2.3).

The molecular structure of $[Na(THF)_6][V(CO)_6]$ has been determined in the solid state at 298 K (space group $R\bar{3}$).[29] Interatomic distances (V–C 1.91(2) Å, C–O 1.18(3) Å) and angles (V–C–O 174(2)°) in the anion compare well with previous determination on related $[PPN]^+$ salt.[30] Being the only homoleptic transition metal carbonyl that exists near room temperature as free radical, $V(CO)_6$ has been investigated intensively. Its ground-state structure is subject to dynamical Jahn–Teller distortion and has nearly octahedral geometry at room temperature (see COMC (1982), Volume 3, Chapter 24, Section 24.2.1.1). The molecular and spectroscopic properties of $V(CO)_6$ have been studied with different improved techniques.[31–36] According to the most recent studies by means of an extensive array of experimental and theoretical methods,[35] $V(CO)_6$ isolated in Ne, Ar, or CO matrix shows a static Jahn–Teller distortion to D_{3d} symmetric structure. The occurrence of the previously suggested D_{4th} distortion mode is ruled out.

5.01.2.1.2 Carbonyl substitution

Due to the facile tendency to disproportionate in the presence of donor molecules (COMC (1995) Volume 5, Chapter 1, Section 5.01.2.1.2), the direct substitution of $V(CO)_6$ proceeding without change in the metal oxidation state has been limited almost exclusively to the synthesis of mixed CO–phosphine and CO–phosphite vanadium(0) derivatives, as well as to homoleptic isocyanide and mixed CO–isocyanide complexes which are discussed in Section 5.01.2.4. Carbonyl exchange in $V(CO)_6$, $[V(CO)_6]^-$, and $HV(CO)_6$ is well documented (COMC (1982) Volume 3, Chapter 24, Section 24.2.1.2 and COMC (1995) Volume 5, Chapter 1, Section 5.01.2.1.3), and in particular phosphine substitution reactions occur readily in non-donor solvents with the replacement of a variable number of CO ligands to form complexes of the type $V(CO)_{6-n}L_n$ (L = phosphine or phosphite). The crystal structure of the known $[Et_4N][V(CO)_5(PPh_3)]$[37] has been elucidated.[38] The anion has a slightly distorted octahedral geometry with an angle $P–V–CO_{trans}$ of 175.9°. The distance $V–CO_{trans}$ (1.889(4) Å) is shorter by about 5 pm than the distance $V–CO_{cis}$, due to the weaker π-accepting capability of PPh_3, inducing stronger M–CO π-backbonding to the CO_{trans} competing for the same metal d_π-orbitals.

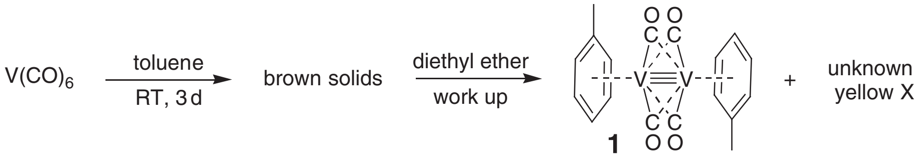
The complexes $Na[V(CO)_3P_m]$ (P_m multidentate phosphine ligands) are prepared by carbonyl substitution in $V(CO)_6$ with 1 equiv. of P_m that initially yields $[V(P_m)_2][V(CO)_6]_2$. Refluxing the latter for 12 h gives neutral $V(CO)_3P_m$ which is subsequently transformed into $[V(CO)_3P_m]^-$ by one-electron reduction with excess sodium sand in THF.[39]

The triphosphorus macrocycle 1,5,9-triethyl-1,5,9-triphosphanecyclododecane ($12[ane]P_3Et_3$) reacts with $[V(CO)_6]^-$ under photolytic conditions to produce orange *fac*-$[(12[ane]P_3Et_3)V(CO)_3]^-$ in 71% yield.[40] This vanadium(−I) complex can be oxidized to the yellow vanadium(0) derivative *fac*-$(12[ane]P_3Et_3)V(CO)_3$ by $[Cp_2Fe]^+$ in 61% yield. The derivative has a low spin d^5-configuration ($\mu_{eff} = 2.3\ \mu_B$).

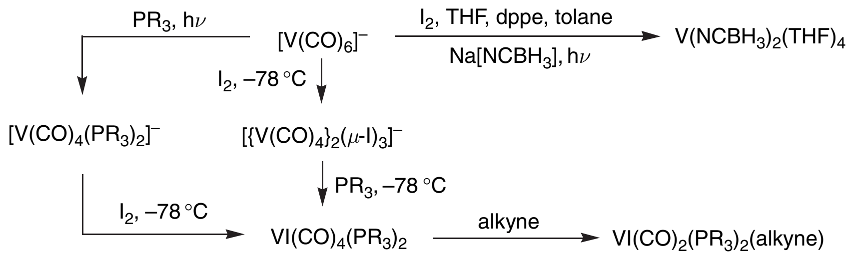
Reactions of $V(CO)_6$ with arenes were reported to involve one-electron oxidation; complexes of the type $[(arene)V(CO)_4]^+[V(CO)_6]^-$ were isolated from the brown solids formed.[41] Interestingly, with toluene as arene, treatment of these brown solids with diethyl ether resulted in gas evolution and after workup, the arene complex **1** was obtained in low yield (10%) (Scheme 2).[42] This is a rare example of a vanadium compound in which a triple bond between vanadium atoms is suggested. Each vanadium atom is involved in a V≡V linkage (V–V = 2.388(2) Å), a nearly planar η^6-toluene ligand (V–centroid distance 1.825 Å), and semibridging carbonyls [two strong V–CO bonds (1.896(5) and 1.954(5) Å) and two weaker V–CO interactions (2.509(5) and 2.660(5) Å)]. Photolysis of a 1 : 1 mixture of $NaV(CO)_6$ with tri-*tert*-butylcyclopropenium tetrafluoroborate gives the deep-blue $[(C_3Bu^t{}_3)V(CO)_4]$ in 50% yield.[43] An X-ray study reveals an η^2-coordinated mode for the cyclopropene with partial scission of one C–C bond in the carbocycle and concomitant partial insertion of the vanadium into the cyclopropenyl ring.

5.01.2.1.3 Redox reactions

Redox reactions in the presence of isocyanide are presented in the section dedicated to isocyanide complexes (Section 5.01.2.5). $V(CO)_6$ is easily reduced by cobaltocene (or decamethylcobaltocene) to $[V(CO)_6]^-$.[44] The voltammetry of the $[V(CO)_6]^{0/-}$ system has been examined for solid $[Na(diglyme)_2][V(CO)_6]$ mechanically attached



Scheme 2



Scheme 3

to electrodes that are immersed in aqueous (electrolyte) media, and shows distinct relationship to the voltammetry of dissolved $[V(CO)_6]^-$.[45] Electron transfer involving $[V(CO)_6]^-$ and neutral $V(CO)_6$ has been studied using spectroscopic methods as well as DFT methods.[36,46–48] Ion pair $[CoCp_2]^+[V(CO)_6]^-$ has been shown to undergo electron transfer upon photooxidation.

$V(CO)_6$ is known for its capability to promote the oxidation of M(−1) carbonylmetallates via outer-sphere electron transfer (see COMC (1995), Volume 5, Chapter 1, Section 5.01.2). Similarly, $Cr(CNFc)_6$ (Fc = ferrocenyl) is readily oxidized by $V(CO)_6$ in dichloromethane to afford the ion pair $[Cr(CNFc)_6]^+[V(CO)_6]^-$,[49] characterized by an X-ray structure. The bond distances V–C (1.935(3)–1.974(3) Å) and C–O (1.147(4)–1.160(4) Å) are very close to other structurally characterized $[V(CO)_6]^-$ anions.

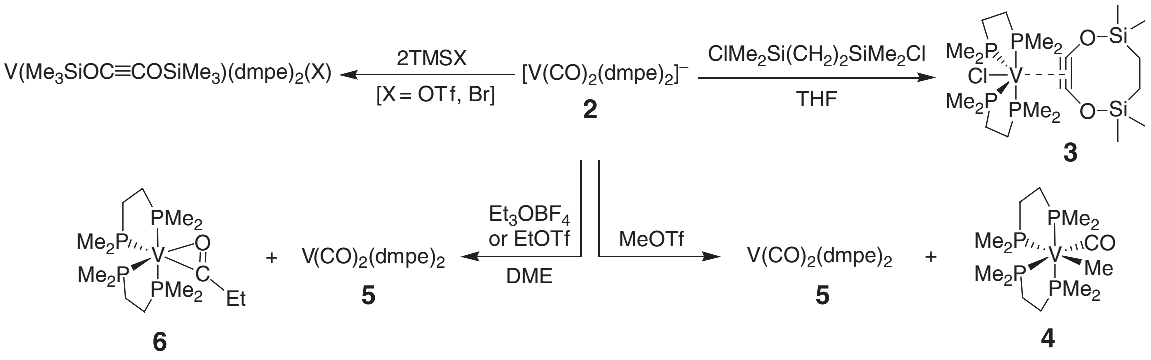
Irradiation of $V(CO)_6$ in low temperature matrices containing O_2 leads to the disappearance of the IR CO absorption and the formation of a novel superoxovanadium species alongside free CO_2.[50] Isotopic substitution experiments with $^{18}O_2$ indicate that this compound is the dioxide–superoxide $[VO_2(\sigma\text{-}O_2)]$ complex.

Crystalline $VI_2(dmpe)_2$ is isolated as a minor product (no yield is reported) in an attempt to prepare σ-alkyl complexes from $[V(CO)_4(dmpe)]^-$ and perfluoro-isopropyl iodide in THF.[51] Reaction of yellow $[V(CO_6)]^-$ with iodine or bromine (X_2) in THF at −78 °C leads to a red solution apparently containing $[\{V(CO)_4\}_2(\mu\text{-}X)_3]^-$ (X = I, Br) as the main component (IR evidence) (Scheme 3). On addition of phosphine PEt_3 or PMe_2Ph, red $VX(CO)_4(PR_3)_2$ is formed.[52] This intermediate can also be generated by the reaction between $[V(CO)_4(PR_3)_2]^-$ and X_2. Alternatively, $VBr(CO)_4(P_m)$ (P_m multidentate phosphine) and other monobromo derivatives $VBr(CO)_3(P_m)$ and $VBr(CO)_2(P_m)$ are obtained by the reaction of $[V(CO_6]^-$ with pyridinium bromide and the corresponding bi-, tri-, and tetradentate phosphine ligands.[51] Addition of alkyne to $[VX(CO)_4(PR_3)_2]^-$ provides a general route to green *trans*-$[VX(CO)_2(PR_3)_2(alkyne)]^-$ species.[52] A molecular structure reveals that the two PR_3 and the two CO ligands are mutually *trans*, a fact that is corroborated by the observation of a single CO stretch in the range 1900–1930 cm^{-1} in pentane solution.

Electron-rich vanadium carbonyl $Na[V(CO)_2(dmpe)_2]$ **2** is able to promote carbon monoxide reductive coupling when reacted with TMS reagents to provide acetylenic products of the type $V(TMS\text{–}O\text{–}C{\equiv}C\text{–}O\text{–}TMS)(dmpe)_2X$ (X = OTf, Br).[53] Similarly, treatment of **2** with the electrophile 1,2-bis(chlorodimethylsilyl)ethane in THF results in the formation of the coupled product **3** which has been shown by single crystal X-ray study to contain a cyclic eight-membered heterocyclic acetylene ligand (Scheme 4) with C–C and V–C bond distances of 1.308(6) and 1.985(3) Å, respectively, and C–V–C angle of 38.5(2)°.[54] Surprising differences of reactivity of **2** with the nature of the alkylating agents are observed. MeOTf alkylates **2** with the formation of the methyl derivative **4** and neutral **5**, whereas the reactions of **2** with EtOTf or Et_3OBF_4 afford a mixture of comparable amounts of the η^2-acyl complex **6** and neutral **5** (Scheme 4).[55] As direct electrophilic attack on the carbon atom of a coordinated CO ligand is extremely rare,[56] the authors instead suggest that ethylation proceeds via initial O-alkylation of the terminal CO ligands followed by subsequent migration of the Et group to form the acyl species. Selected geometrical parameters determined by X-ray analysis follow: V–CO 1.869(8) Å, $V\text{–}C_{acyl}$ 1.956(7) Å, $V\text{–}O_{acyl}$ 2.213(5) Å, $VC_{acyl}O_{acyl}$ 83.8(5)°.

5.01.2.1.4 Applications

The applications of $V(CO)_6$ and its derivatives are limited due to its toxicity. Owing to its intrinsic volatile nature, $V(CO)_6$ has found growing interest for applications in material science, as precursor of vanadium-carbide or -oxide films[57] (link to OMCVD Chapter 12.02) and for the synthesis of thin-film V-based magnets.[58] In solution, $V[TCNE]_x{\cdot}y(CH_2Cl_2)$ ($x \sim 2$, $y \sim 0.3$) can be prepared via the reaction of $V(CO)_6$ (or $V(C_6H_6)_2$) with TCNE. To form thin films and eliminate the detrimental effect of the solvent, $V[TCNE]_x$ films are grown from the gas phase



Scheme 4

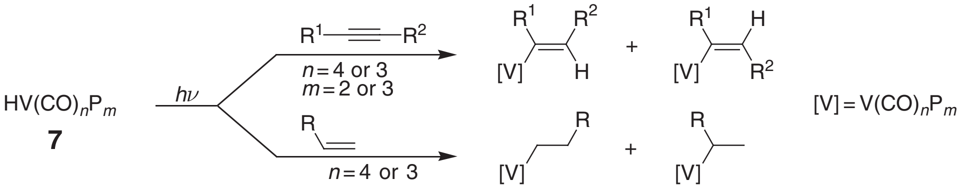
reaction of $V(CO)_6$[58] (or $V(C_6H_6)_2$)[59] and TCNE and could be deposited on various supports. Magnetic properties of such materials (with TCNE and other electron-acceptor ligands) are far beyond the scope of this review; interested readers are advised to consult original articles cited in comprehensive reviews,[9–11] and Chapter 12.07.

5.01.2.2 Carbonyl Hydrides, Allyls, Alkyls, or Alkenyls

The photo-elimination of a carbonyl ligand in $Na[V(CO)_6]$ in the presence of an excess of allyl chloride, followed by addition of the olefinic phosphine $P(C_7H_7)_3$ ($C_7H_7 = 1$-cyclohepta-2,4,6-trienyl), generates the complex (η^3-C_3H_5)$V(CO)_4[P(C_7H_7)_3]$ in which the olefinic phosphine behaves as a conventional two-electron ligand.[60]

The synthesis, characterization, and structure of neutral seven-coordinated hydrido complexes of vanadium are well established, and various hydride complexes stabilized by phosphine ligands $HV(CO)_nL_m$ have been prepared by various methods (COMC (1995) Volume 5, Chapter 1, Section 5.01.2.2). The related deuteride $DV(CO)_4$(ppb) (ppb-1,2-bis(diphenylphosphino) benzene) is prepared by the treatment of $[NEt_4][V(CO)_4(ppb)]$ with D_2O.[39] Hydrido complexes $HV(CO)_nP_m$ **7** (P_m multidentate phosphine) react photochemically with alkenes to form σ-alkyl complexes by hydrovanadation of the C=C bond, and give in most cases the anti-Markovnikov isomer as the main (or sometimes the only) product (see Scheme 5).[61] 4-Methyl-1-pentene and 2,3-dimethyl-1-butene, when reacted with $HV(CO)_4$(dppe), yield methyl derivative $V(Me)(CO)_4$(dppe), through α-and β-alkyl migration, respectively, from the intermediately formed V(4-Me-1-pentyl)$(CO)_4$(dppe) and V(2,3-Me-1-butyl)$(CO)_4$(dppe).[39] Selected spectroscopic data are presented in Table 1. The second way to generate σ-alkyl–carbonyl vanadium $[V(R)(CO)_4(dmpe)]$ consists in the alkylation of $[V(CO)_4(dmpe)]^-$ with RI.[62]

Similarly, complexes **7** ($n = 3$ or 4, P_m bidentate or tridentate phosphine) react with excess alkyne under UV irradiation to afford σ-alkenyl complexes V(σ-alkenyl)$(CO)_n(P_m)$.[51] These complexes are present as a single isomer (*Z*-isomer, $n = 4$) or two isomers (isomers *Z* and *E*) with the *Z*-isomer always dominating (Scheme 5). This stereoselectivity suggests a mechanism involving hydride transfer from a hydride–alkyne intermediate. In the absence of a molecular structure for this series of complexes, the ^{1}H NMR spectra clearly indicate the presence of olefinic hydrogen on Cβ at ca. 5.9 ppm, thus proving the presence of sp^2 carbons. Representative data are given in Table 1. In addition, the chloro complex $V(Cl)(CO)_2(pepe)_2$ (pepe = Ph_2P-$(CH_2)_2$-PEt_2) is synthesized by the treatment of hydrido precursor $V(H)(CO)_4$(pepe) with $[Et_4N][Cl]$.[51]



Scheme 5

Table 1 Selected spectroscopic data for σ-alkyl and σ-alkenyl–carbonyl vanadium complexes of the type R–V(CO)$_4$(dppe)[39,51,61]

R–V(CO)$_4$(dppe) complex	ν_{CO} (cm^{-1})	δ (^{51}V)[a]	δ (^{1}H)
R = 3,3-dimethyl-1-butyl	1930, 1840, 1825	−1044 (AM), −1077 (M)	
4-methyl-1-pentyl	1925, 1840, 1826	−1065 (AM), −1058 (M)	
methyl		−1031	
2-butenyl	1932, 1850, 1829, 1801	−1061 (*Z*)	5.59
1-hexenyl	1930, 1850, 1833, 1801	−1064 (*Z*)	5.58

[a] The isomers anti-Markovnikov (AM), Markovnikov (M), and *Z* (*Z*) are given within the parentheses.

5.01.2.3 Carbonyl–Nitrosyl Derivatives

Most nitrosylating agents are potent oxidizers or potential oxygen-atom sources, which, together with the strong oxophilicity of vanadium metal, may explain the relatively poorly developed chemistry of vanadium–nitrosyl complexes. Synthesis, structure, and spectroscopic data of binary nitrosyl–carbonyl vanadium compounds by CO displacement reaction have been described in COMC (1995) (Volume 5, Chapter 1, Section 5.01.2.5). To overcome the problem of stability of nitrosyl–carbonyl vanadium complexes, and following earlier studies with tridentate phosphine derivatives,[63] tripodal phosphines Bu^{t}Si(CH$_2$PMe$_2$)$_3$ (trimpsi) have been elegantly employed as supporting ligand in this chemistry. Treatment of [Et$_4$N][V(CO)$_6$] with [NO][BF$_4$] in dichloromethane at −35 °C generates the thermally unstable V(CO)$_5$(NO) (see COMC (1995) Volume 5, Chapter 1, Section 5.01.2.5), which upon addition of 1 equiv. of trimpsi at −35 °C followed by warming to room temperature results in gas evolution and formation of (η^2-trimpsi)V(CO)$_3$(NO) (IR evidence).[28] Further reflux in THF affords (trimpsi)V(CO)$_2$(NO) 8 in moderate yield (59%), fully characterized by IR and NMR spectroscopies (see Table 2), X-ray, and cyclic voltammetry measurements ($E_{1/2}$−0.74 V vs. [Cp$_2$Fe]$^{0/+}$). Indeed, the oxidation of 8 with [Cp$_2$Fe][BF$_4$] at ambient temperature in dichloromethane results in the IR and EPR spectroscopically characterized [8][BF$_4$] (Scheme 6).

Treatment of 8 with halogens or halogen sources (Br$_2$, I$_2$, PhICl$_2$, C$_2$Cl$_6$, ClNO, AgCl) produces (trimpsi)V(NO)X$_2$ 9.[64] Alkylation of 9 with dialkylmagnesium reagents in THF affords the monoalkyl derivatives (trimpsi)V(NO)(R)X [R = Me, CH$_2$SiMe$_3$, CH$_2$CMe$_3$] (see also Scheme 6).[65] A crystal structure of (trimpsi)V(NO)(CH$_2$SiMe$_3$)Cl reveals a linear nitrosyl ligand and a V–C bond distance of 2.123(7) Å. These studies demonstrate that the (trimpsi)V(NO) fragment is thermally stable when bound to a variety of co-ligands.

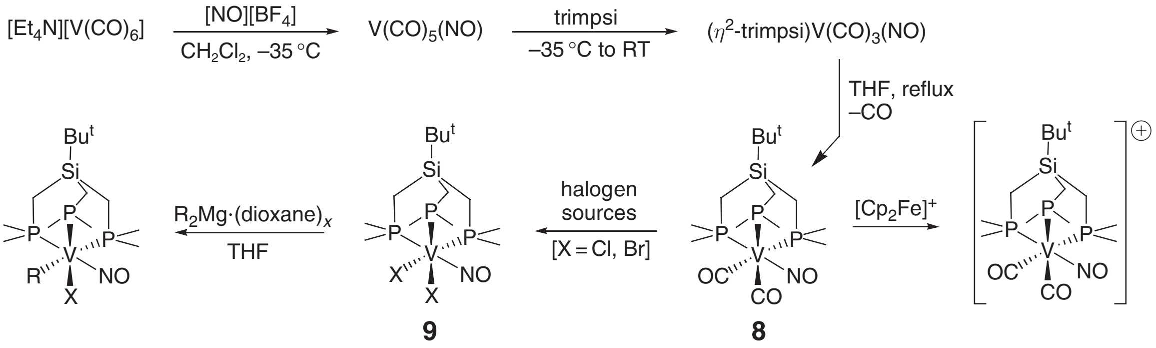
5.01.2.4 Miscellaneous Carbonyl Complexes

The sodium amalgam reduction of the d^0-imido–vanadium(V) compound V(=NAr)Cl$_3$(dme) (Ar = 2,6-Pr$_2^i$-C$_6$H$_3$) in the presence of PMe$_3$, under 2–3 atm of CO, gives the orange complex V(=NAr)Cl(CO)$_2$(PMe$_3$)$_2$, a rare example of an imido complex of trivalent vanadium.[66] Spectroscopic data and DFT calculations support a *trans*, *trans*-configuration of the CO and PMe$_3$ ligands.

Table 2 Selected spectroscopic data for (trimpsi)V(NO) complexes[28,64]

Complex	ν_{CO} (cm^{-1})[a]	ν_{NO}[a] (cm^{-1})	δ ($^{31}P\{^{1}H\}$) *or EPR*
(η^2-trimpsi)V(CO)$_3$(NO)	1990, 1904, 1813[b]	1600[b]	
(trimpsi)V(CO)$_2$(NO) 8	1910, 1920	1543	+5.0 (oct, J_{PV} 220 Hz, 2P), −10.0 (oct, J_{PV} 130 Hz, 1P)
[(trimpsi)V(CO)$_2$(NO)]$^+$	1977,1895[c]	1596[c]	g 2.0035, A(^{51}V) 56 G, a(^{31}P)$_{trans/NO}$ 15 G, a(^{31}P)$_{cis/NO}$ 28 G
(trimpsi)V(NO)Cl$_2$ **9a**		1601	−0.1 (br s, 2P), −24.5 (br s, 1P)
(trimpsi)V(NO)(Me)Cl		1543	−1.3 (br s, 1P), −4.4 (br s, 1P), −23.4 (br s, 1P)

[a] In nujol.
[b] In THF.
[c] In dichloromethane.



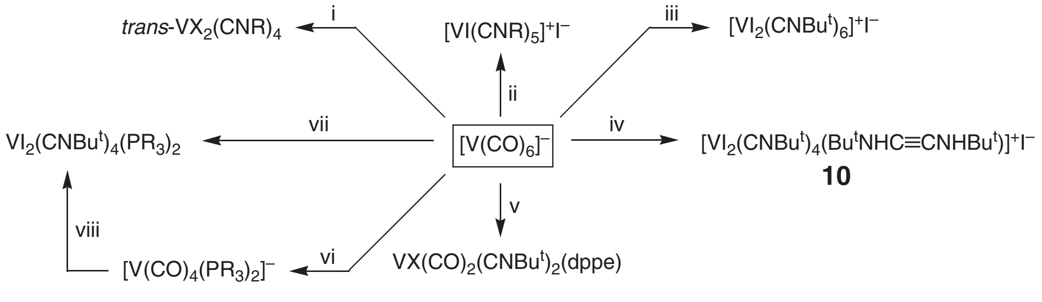
Scheme 6

The homoleptic electron-rich tris(iminoacyl) vanadium(III) compound V(η^2-C(Mes)=NBu^t)$_3$ irreversibly coordinates carbon monoxide to form the unusual, monocarbonyl adduct V(η^2-C(Mes)=NBu^t)$_3$(CO).[67] This complex is a diamagnetic 16-valence-electron compound, and its infrared spectrum exhibits a CO band at 1867 cm^{-1}.

5.01.2.5 Isocyanide Complexes

[V(CO)$_6$]$^-$ serves as a precursor compound for reactions leading to isocyanide–vanadium complexes which, depending on the conditions, yield seven-coordinate complexes of vanadium(I), hexacoordinate complexes of vanadium(I, II, and III), or octacoordinate complexes of vanadium(III). The oxidation of V(-I) to higher-valent vanadium complexes is carried out with iodine or bromine; the V/isocyanide and V/iodine (or V/bromine) stoichiometry, reaction conditions, and workup of the reaction conditions critically determine the precise outcome of each reaction and the compounds generated (Scheme 7). The neutral vanadium(II) complexes *trans*-VX$_2$(CNR)$_4$ (X = I, Br; R = Bu^t, Cy, 2,6-Me$_2$-C$_6$H$_3$, CH$_2$Tos) are prepared in THF from [Et$_4$N][V(CO)$_6$] and X$_2$ in the presence of isonitrile in a molar ratio of V : CNR : X$_2$ of 1 : 4 : 1.5.[68,69] This series of compounds presents a $\mu_{\text{eff}} = 3.89$–$4.07\ \mu_B$, typical of high spin d^3-systems with spin-only contribution to the susceptibility. The same reaction carried out in dichloromethane yields the ionic [VI(CNBu^t)$_5$]$^+$[I]$^-$.[69] The eight-coordinate vanadium(III) complex [V(I)$_2$(CNBu^t)$_6$]$^+$I$^-$ is obtained in dry THF from [V(CO)$_6$]$^-$, I$_2$, CNBu^t used in a ratio V : CNR : I$_2$ of 1 : 6 : 2, while the coupling product **10** is formed when water is added to the reaction.[68]

Similar reactions of [NEt$_4$][V(CO)$_6$] in the presence of the diphosphine dppe, *tert*-butyl isocyanide, and X$_2$ in a molar ratio V : dppe : CNR : X of 1 : 1 : 2 : 1 gave the seven-coordinate carbonyl–isocyanide vanadium(I) complexes VX(CO)$_2$(CNBu^t)$_2$(dppe) with moderate yields (46% (Br), 56% (I)).[68] If the molar ratio V : I$_2$ is 1 : 1.5, which is in between the conditions pertinent for the formation of the V(I) complexes (V : I$_2$ = 1 : 1) and the vanadium(III)



Conditions: i, X$_2$, RNC, THF [R = Bu^t, Cy, Xyl, Bz]; ii, I$_2$, RNC, CH$_2$Cl$_2$ [R = Bu^t, Cy]; iii, I$_2$, Bu^{t}NC, THF; iv, I$_2$, dppe, Bu^{t}NC, H$_2$O; v, X$_2$, dppe, Bu^{t}NC, THF; vi, PR$_3$, $h\nu$; vii, I$_2$, Bu^{t}NC, PR$_3$ (PR$_3$ = PPh$_3$, dppe), THF; viii, I$_2$, Bu^{t}NC [R = PMe$_2$Ph], THF

Scheme 7

Table 3 Selected IR spectroscopic data for isocyanide vanadium complexes

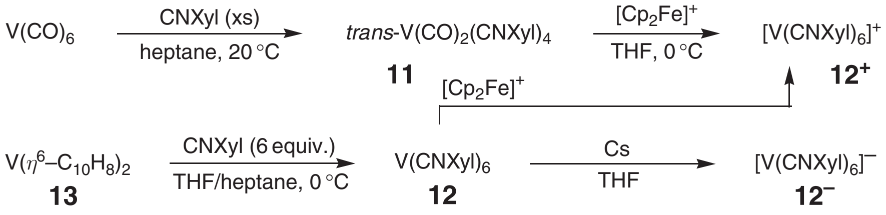
Complex	ν_{CN} (cm^{-1})[a]	ν_{CO} (cm^{-1})[a]	*Other*[a]	*References*
$VI(CO)_2(CNBu^t)_2(dppe)$	2168, 2098	1889, 1842		68
$V(CO)_2(CNXyl)_4$	2011, 1986	1897, 1808		70
$V(CNXyl)_6$	1939			70
$VBr_2(CNBu^t)_4$	2174[b]			69
$[VI_2(CNBu^t)_4(Bu^tNHC{\equiv}CNHBu^t)]I$	2208		3204 (NH), 1561 (C=N)	68
$[VI_2(CNBu^t)_6]I$	2173			68
$VI_2(CNBu^t)_2(PPh_3)_2$	2171			68
$VBr_2(CNBu^t)_2(dppe)$	2155, 2145			68
$[V(CNBu^t)_2(dppe)_2]^-$	2077[b]			27
$[VI(CNBu^t)_5]I$	2195, 2175, 2159			69
$[CpVTp(CNBu^t)][BAr_4]$	2212		2501 (B–H)	71
$Cp^*V(CO)_3(CNBu^t)$	2092[c]	1955, 1979, 1837		72
$Cp^*V(CO)_3(CNCy)$	2084[c]	1957, 1979, 1839		72
$Cp^{Me}VCl_2(CNBu^t)_2$	2208, 2168			73
$V[SeSi(SiMe_3)_3]_3(CNXyl)$	2126			76
$V[(N(C_6F_5)CH_2CH_2)_3N]_3(CNBu^t)$	2180			77
$V[(SCH_2CH_2)_3N](CNBu^t)$	2173			78

[a] In KBr or Nujol.
[b] In THF.
[c] In hexane.
For comparison: $CNBu^t$ 2136 cm^{-1}, CNCy 2136 cm^{-1}, CNXyl 2115 cm^{-1}.

complexes (1 : 2), complexes with vanadium at the oxidation state +II are formed. While a stoichiometry of the reagents in a V : phosphine : Bu^tNC : X_2 ratio as 1 : 2 : 2.2 : 1.5 gives the isocyanide–phosphine complexes $VX_2(Bu^tNC)_2(PR_3)_2$ (X = I and $PR_3 = PPh_3$; or X = Br and $(PR_3)_2$ = dppe). Such hexacoordinate vanadium(II) complexes are also accessible by the oxidation of the anions $[V(CO)_4(PMe_2Ph)_2]^-$ with I_2, but with lower yields.[68] With monophosphines, these compounds are supposed to have the all-*trans* arrangement as only a single ν_{CN} is observed, whereas with the chelating dppe which prevents this configuration, the IR spectrum shows two ν_{CN} bands. Stepwise substitution of N_2 in $Na[V(N_2)_n(dmpe)_{4-n}]$ ($n = 1, 2$) by $CNBu^t$ affords $[V(CNBu^t)_2(dmpe)_2]^-$.[27] Relevant IR stretches for *tert*-butyl isocyanide–vanadium complexes are reported in Table 3.

Surprisingly, no disproportionation event occurred in the reaction of $V(CO)_6$ with excess xylyl isocyanide conducted at room temperature in heptane for 3 days (Scheme 8). This reaction results in the remarkable displacement of four carbonyls from $V(CO)_6$ with the efficient formation of *trans*-$[V(CO)_2(CNXyl)_4]$ **11** as a dark red solid in 80% yield.[70] The vanadium center has an octahedral arrangement, with *trans* V–CO units. As expected, the V–CO bonds (av. V–CO = 2.001(6) Å) are shorter than the V–CN distances (av. V–CN = 2.044(2) Å). Structure **11** has a μ_{eff} of 1.75 μ_B (22 °C), and ESR spectroscopy (frozen toluene) has been recorded: $g_{av} = 2.023$ ($g_\perp = 2.038$, $g\| = 1.993$) and $A_{av} = 47$ G ($A_\perp = 31$ G, $A\| = 80$ G). Pertinent IR data are reported in Table 3 and compared to other isocyanide complexes. Attempts to substitute the remaining carbonyls failed, leading to decomposition products, while oxidation of **11** with 1 equiv. of $[Cp_2Fe]^+$ in THF afforded the homoleptic isocyanide cationic $[\mathbf{12}]^+$. The latter has also been prepared by another route from $V(\eta^6\text{-naphthalene})_2$ (see below).

Upon treatment with $CNBu^t$, the mixed sandwich cationic complex $[CpVTp][BAr_4]$ [Ar = 3,5-$(CF_3)_2C_6H_3$], which is described in Section 5.01.4.2.1, formed the light blue adduct $[CpVTp(CNBu^t)][BAr_4]$.[71] Orange monoisonitrile complexes $Cp^*V(CO)_3(CNR)$ [R = Bu^t, Cy] are prepared via photoinduced substitution of one carbonyl ligand in $Cp^*V(CO)_4$.[72]



Scheme 8

Table 4 Comparison of infrared and structural parameters in $[V(CNXyl)_6]^z$

$[V(CNXyl)_6]^z$	$\nu_{C\equiv N}$ (cm^{-1})[a]	*V–C* (Å)[b]	*C–NXyl* (Å)[b]	*C–N–C* (°)[b]
$Z = 1+$	2033	2.07(2)	1.169(6)	173(2)
$Z = 0$	1939	2.026(7)	1.186(5)	163(4)
$Z = 1-$	1817	1.98(3)	1.20(2)	158(10)

[a] In THF.

[b] Average distance or angle.

Adapted from Barybin, M. V.; Young, V. G. Jr.; Ellis, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 4678–4691 with permission from The American Chemical Society.

Treatment of $VCl_3(THF)_3$ with $NaCp^{Me}$, in the presence of *tert*-butylisocyanide, produces the bis(isocyanide) complex $Cp^{Me}VCl_2(CNBu^t)_2$ along with structurally established byproduct $[Cp^{Me}{}_2V(CNBu^t)_2][VCl_4(THF)_2]$ (see also Section 5.01.4.2.1).[73] All these complexes exhibit typical IR stretching bands for isocyanide ligands (see Table 3).

Bis(η^6-naphthalene)vanadium(0) and its methyl ring-substituted derivative bis(η^6-1-Me-naphthalene)vanadium(0) react with 6 equiv. of xylyl isocyanide in THF/heptane at 0 °C to give high yields of the unprecedented homoleptic zerovalent $V(CNXyl)_6$ **12**, as depicted in Scheme 8.[70,74] This compound is paramagnetic with a low spin d^5-configuration ($\mu_{eff} = 1.76\,\mu_B$). The bulky nature of the xylyl isocyanide ligand appears to be of critical importance for the stabilization of this thermally stable complex. Structure **12** can be reduced into unsolvated Cs[**12**] with Cs/graphite in THF, and is oxidized by $[Cp_2Fe][PF_6]$ to afford [**12**]$[PF_6]$. The members of this family of homoleptic isocyanides $[V(CNXyl)_6]^z$ ($z = +1$, 0, -1) have been structurally characterized, which allows a comparison of structural and infrared data (Table 4) and clearly follow the trend of the π-accepting property of the isocyanide ligand.

Several paramagnetic isocyanide vanadium(III) complexes of general formula LV(CNR) [R = Bu^t, Cy, Xyl] are formed upon addition of the corresponding isocyanide ligand to the appropriate trivalent vanadium precursors $V[N(adamantyl)(3,5\text{-}Me_2C_6H_3)]_3$,[75] $V[SeSi(SiMe_3)_3]_3$,[76] *in situ* generated $V[(N(C_6F_5)CH_2CH_2)_3N]$,[77] and displacement of NH_3 in $V[(SCH_2CH_2)_3N](NH_3)$.[78] All these compounds are high spin d^2-species, and present a characteristic νCN band listed in Table 3.

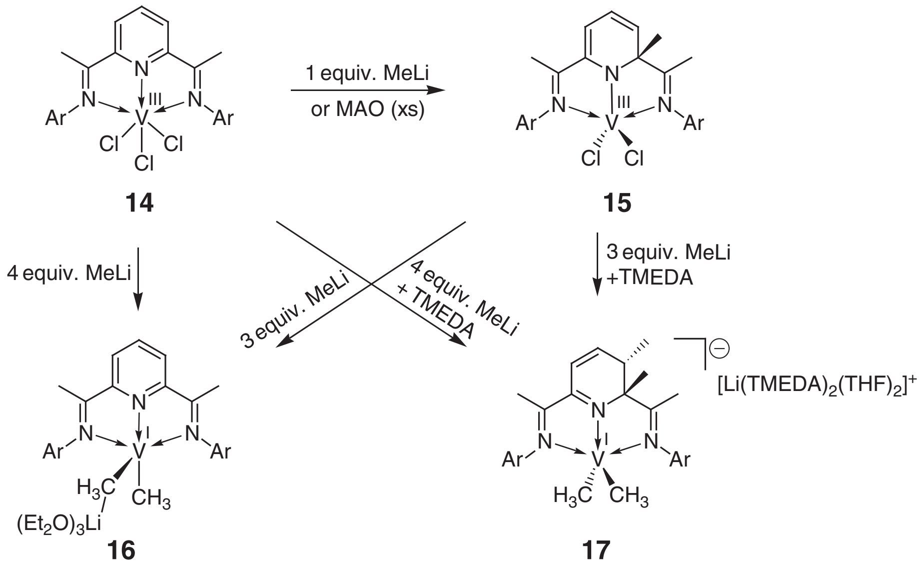
5.01.2.6 N-heterocyclic (Arduengo-type) Carbene (NHC) Complexes

Despite the ever-growing use of N-heterocyclic carbenes as ligand systems for various transition metals, examples of N-heterocyclic carbene complexes of vanadium remain extremely rare. Treatment of divalent $VCl_2(TMEDA)_2$ with 4 equiv. of 1,3-dimethylimidazol-2-ylidene (L^1) in THF generates the substitution product $VCl_2L^1{}_4$.[79] The reaction of the anionic 3-borane-1-methylimidazol-2-ylidene (L^2Li, 3 equiv.) with $VCl_3(THF)_3$ at low temperature results in the formation of a purple solution, from which red paramagnetic ion pair $[LiPy_4]^+[VL^2{}_4]^-$ has been crystallized upon addition of pyridine (V–C 2.119–2.132(6) Å).[80] The remarkably air stable deep red 1 : 1 adduct $V(=O)Cl_3(IMes)$ is formed in 76% yield from the reaction of $VOCl_3$ with 1,3-dimesitylimidazol-2-ylidene (IMes) in toluene.[81] The molecular structure reveals a V–C bond distance of 2.137(2) Å and displays strong $Cl\cdots C_{carbene}$ interactions (Cl–C 2.849 and 2.887(2) Å) between the chlorides *cis* to the carbene and the vacant molecular orbitals of the $C_{carbene}$. Treatment of the bis(carbene)pyridine ligand 2,6-bis[1-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine with $VCl_3(THF)_3$ affords the chelate complex [bis(carbene)pyridine]VCl_3 in quantitative yields as an orange-brown solid.[82] This compound, when activated with MAO, presents a very high activity in the room temperature catalytic polymerization of ethylene (activity: 1280 mg mmol^{-1} bar^{-1} h^{-1}) and produces high density polyethylene.

5.01.3 σ-Bonded Alkyl, Aryl, Alkylidene, and Alkylidyne Complexes

5.01.3.1 Vanadium(I) and Vanadium(II) Complexes

Examples of vanadium(I) alkyls and alkenyls stabilized by both CO and phosphine ligands have already been discussed in Section 5.01.2.2 dedicated to the vanadium carbonyls. A few σ-alkylvanadium(II) complexes may also



Scheme 9

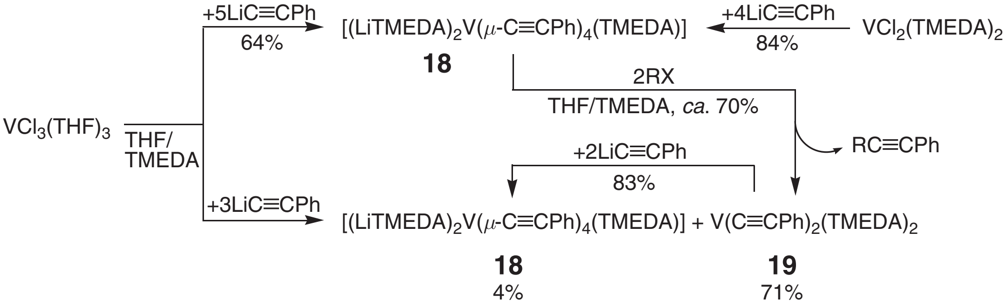
be obtained from the reduction of the tris(mesityl) vanadium(III) precursor $VMes_3(THF)$ and are discussed in the section dedicated to the reactivity of homoleptic σ-alkylvanadium(III) complexes (Section 5.01.3.2.1).[83]

Treatment of diimine/pyridine vanadium(III) complex $\{2,6\text{-bis}[ArN{=}C(Me)]_2(C_5H_3N)\}VCl_3$ **14** ($Ar = 2,6\text{-}Pr^i_2\text{-}C_6H_3$) or its pyridine ring *ortho*-methylated analog **15** with 4 or 3 equiv. of MeLi, respectively, yields two different compounds (Scheme 9), which are selectively separated by suitable workup in the presence/absence of TMEDA. In the absence of TMEDA, the unprecedented monovalent and anionic vanadium dialkyl complex **16** is isolated.[84] This d^4-complex has a square-pyramidal geometry, and surprisingly, does not have the methyl group originally present on the pyridine ring *ortho*-carbon atom. Workup in the presence of TMEDA produces the anionic monovalent dimethyl derivative **17** with a second methyl group on the *meta*-position of the pyridine ring, as shown by an X-ray structure elucidation (see Table 5 which presents selected relevant data for these complexes). Both processes imply two-electron reduction of the metal center and formation of the corresponding vanadium(I) derivatives ($\mu_{eff} = 2.54$ and $2.64\ \mu_B$, respectively). As expected, these complexes, either with or without co-catalyst, are inert toward ethylene polymerization, and may be involved during the polymerization with diimine/pyridine–vanadium(III) catalyst with methylaluminoxane (MAO) in a possible reduction pathway of the V-center with consequent deactivation (see Chapter 11.20).

Neutral dimethylvanadium(II) complex *trans*-$VMe_2(dmpe)_2$ has been prepared by the addition of MeLi to $VCl_2(dmpe)_2$.[85] This method appeared unsuitable for the preparation of other alkyl derivatives such as CH_2SiMe_3.[86] Fortunately, treatment of the divalent tetrahydroborate vanadium precursor *trans*-$V(\eta^1\text{-}BH_4)_2(dmpe)_2$ with Me_3SiCH_2Li results in the clean replacement of the two borohydride groups and gives the new 15-electron

Table 5 Relevant data for alkylvanadium(I) and alkylvanadium(II) complexes

Complex	μ_{eff} (μ_B)	*V–C distances* (Å)	*Other distances* (Å) *or angles* (°)	*References*
$\{2,6\text{-bis}[ArN{=}C(Me)]_2(C_5H_3N)\}V(CH_3)(\mu\text{-}CH_3)Li(Et_2O)_3$ **16**	2.54	$V\text{–}C_{Li}$ 2.118(7), $V\text{–}C_{axial}$ 2.093(9)		84
$[\{2,6\text{-bis}[ArN{=}C(Me)]_2(2,3\text{-}Me_2\text{-}C_5H_3N)\}V(CH_3)_2][Li(THF)_2(TMEDA)_2]$ **17**	2.64	$V\text{–}C_{axial}$ 2.075(11), 2.115(10)		84
trans-$VMe_2(dmpe)_2$	3.7	2.310(5)	V–P (Å) 2.462(5), 2.448(7)	85,86
cis-$V(CH_2SiMe_3)_2(dmpe)_2$	3.8	2.253(3)	V–P (Å) 2.550(1), 2.552(1), C–V–C 92.3°(1)°	86
$[(LiTMEDA)_2V(\mu\text{-}C{\equiv}CPh)_4(TMEDA)]$ **18**		2.186(6), 2.122(8), 2.175(6), 2.128(7)	C≡C (Å) 1.220(9), 1.22(1), 1.210(9), 1.24(1)	87
$V(C{\equiv}CPh)_2(TMEDA)_2$ **19**		2.18(1), 2.18(1)	C≡C (Å) 1.21(1), 1.20(1)	87
$V(C{\equiv}CBu^t)_2(TMEDA)_2$		2.179(2)	C≡C (Å) 1.207(3)	87



Scheme 10

vanadium(II) alkyl *cis*-$V(CH_2SiMe_3)_2(dmpe)_2$ in 50% yield, with an unexpected *cis*-configuration of the alkyl groups rationalized on steric grounds. This borohydride starting material also appeared suitable for the synthesis of the known *trans*-$VMe_2(dmpe)_2$ and the geometry of the latter was confirmed by an X-ray structure determination. Relevant distances and angles are listed in Table 5; the differences are attributed to the differing *trans*-influences of R and phosphine ligands, and steric congestion in the CH_2SiMe_3 complex. The vanadium(II) tetrakis- and bis(alkynyl) complexes 18 and 19[87] are synthesized from the reaction of $VCl_3(THF)_3$ and $LiC{\equiv}CPh$ in THF in the presence of TMEDA as shown in Scheme 10. The four phenylacetylides in 18 are bridged at the α-carbon between the vanadium center and two tetrahedral lithium cations. These complexes present one (for 19) or two (for 18) $\nu_{C\equiv C}$ bands in the expected $2000\,cm^{-1}$ region. The related $V(C{\equiv}CBu^t)_2(TMEDA)_2$ is the only product isolated from an analogous reaction with $LiC{\equiv}CBu^t$. V–C bond distances in these compounds range between 2.122–2.186 Å (Table 5). Reduction of vanadium occurs during these reactions, and use of vanadium(II) precursor $VCl_2(TMEDA)_2$ gives the same alkynyl complexes in higher yields. The alkynyl ligands in these complexes react with organic electrophiles at the α-carbon. Treatment of 18 with RX (Me_3SiCl or MeI) results in the formation of 19 along with $RC{\equiv}CPh$. Insertions of phenylisocyanate in $V(C{\equiv}CBu^t)_2(TMEDA)_2$, and CO_2 in 18 and 19, are also reported and generate after hydrolysis $Bu^tC{\equiv}C(O)NHPh$ and $PhC{\equiv}CCO_2H$, respectively.

5.01.3.2 Vanadium(III) Complexes

5.01.3.2.1 Homoleptic vanadium(III) alkyl complexes

5.01.3.2.1.(i) Synthesis and structure

Previously, homoleptic organovanadium(III) $[VR_4]^-$ [R = Mes[88] or 2,6-MeO-C_6H_3[89]] and VR_3 [R = Mes,[83] $C(CN)_3$,[90] or $CH(SiMe_3)_2$[91]] have been isolated, but structural information is not available for any of them. The reaction of $VCl_3(THF)_3$ with 8 equiv. of $Li(C_6Cl_5)$ at −78 °C followed by salt metathesis with $[Bu_4N][Br]$ allows the isolation of $[Bu_4N][V(C_6Cl_5)_4]$,[92,93] a remarkably stable homoleptic alkylvanadium(III) compound. The solid-state structure of the anion indicates a slightly distorted tetrahedral geometry, with C–V–C angles ranging between 98.1(2)–117.6(2)°, and V–C distances ranging from 2.142(5) to 2.158(5) Å. In contrast, the same arylation using $Li(C_6F_5)$ in place of $Li(C_6Cl_5)$ gave the unprecedented five-coordinate homoleptic vanadium(III) complex $[Bu_4N]_2[V(C_6F_5)_5]$.[93] Attempted similar synthesis of the homoleptic analog with the highly electron-withdrawing 2,4,6-tris-(trifluoromethyl)phenyl aryl ligand, from the reaction of $VCl_3(THF)_3$ with 3.5 equiv. of LiAr (Ar = 2,4,6-$(CF_3)_3$-C_6H_2)), failed with the isolation of the EPR-silent oxo-vanadium(IV) complex $[VAr_3(\mu\text{-}O)][Li(THF)_3]$[94] that contains a linear oxo bridged to a lithium atom attended by three THF molecules. Using only 3 equiv. of LiAr produces the diarylated complex $VAr_2Cl(THF)$, a pseudo-octahedral species due to two weak V···F interactions (V···F 2.306(2) and 2.378(2) Å) and with mutually *cis*-aryl groups (V–C = 2.145(4) and 2.159(4) Å).

5.01.3.2.1.(ii) Reactivity of $VMes_3$ and derivatives

As previously highlighted in COMC (1995) (Volume 5 Chapter 1, Section 5.01.3.3.2), the reactivity of vanadium(III) alkyls is dominated by the reactivity of the thermally stable trismesityl complex $VMes_3(THF)$, prepared by reacting $VCl_3(THF)_3$ with 3 equiv. of MesMgBr in THF.[95–98] Its rich reactivity includes: protolysis reactions (with HCl, RCO$_2$H, ROH, R$_3$SiOH, etc.), oxidative addition (with M=O, C=O, epoxides, NO, etc), insertion reactions (with RNC, RNCO, CO$_2$, etc.), and dinitrogen fixation.

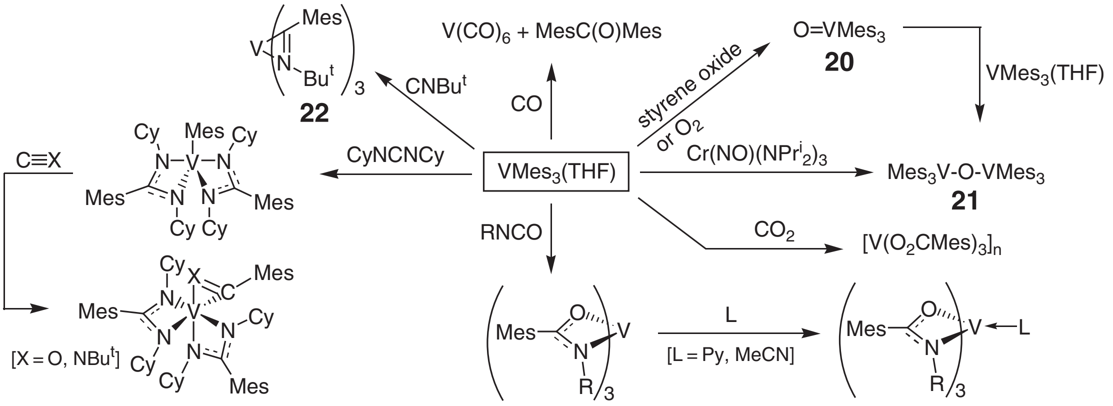
Reaction of VMes$_3$(THF) with Bu^{t}OH in toluene affords the purple mixed valence V(III)–V(IV) complex V(OBu^t)$_2$(μ-OBu^t)(μ-O)V(OBu^t)$_2$(THF) ($\mu_{\mathrm{eff}} = 2.71\,\mu_{\mathrm{B}}$).[99] The same product is obtained using the alkylvanadium(II) dimeric precursor [V(2,6-(MeO)$_2$-C$_6$H$_3$)$_2$(THF)]$_2$. In these two reactions, oxidation of the metal occurs, and the oxygen probably comes from metal-promoted deoxygenation of the aryloxide. Various aryloxide-, mesityl- or mixed aryloxide–mesityl vanadium(III) complexes have been prepared from protolysis reactions of VMes$_3$(THF) with *ortho*-substituted phenols ArOH (2-Pr^i-C$_6$H$_4$OH, 2-Bu^t-C$_6$H$_4$OH, MesOH) and 2,2′-biphenol (biphen). According to the stoichiometry, the partially and fully phenolate-substituted vanadium(III) complexes VMes$_2$(OAr)(THF), VMes(OAr)$_2$(THF)$_2$, V(OAr)$_3$(THF)$_2$, and V$_2$(biphen)$_3$(THF)$_4$ are formed.[100] Treatment of the latter with MesLi gives [Li(THF)$_2$][VMes(biphen)$_2$]. Mixed mesityl–phenolate complexes [Li(DME)$_n$(THF)][VMes$_2$(OAr)$_2$] and [Li(DME)$_2$][VMes(OMes)$_3$] are also obtained by the addition of MesLi to VMes(OAr)$_2$(THF)$_2$ or VCl$_{3-n}$(OMes)$_n$(THF)$_2$ complexes ($n = 2$ or 3). Direct addition of LiOMes or Li$_2$biphen(Et$_2$O)$_4$ to VMes$_3$(THF) leads to [Li(THF)$_4$][VMes$_3$(OMes)] and [Li(DME)][VMes$_2$(biphen)]. Three of these mesityl complexes have been structurally characterized, the V–C distances range 2.09–2.14 Å (cf., av. V–C in VMes$_3$(THF) is 2.108 Å).[101] Oxidation with *p*-chloranil C$_6$Cl$_4$O$_2$ of some of these vanadium(III) complexes in the series [VMes$_{4-n}$(OMes)$_n$]$^-$ produces the neutral corresponding mesityl vanadium(IV) [VMes$_{4-n}$(OMes)$_n$] derivatives (see Section 5.01.3.3.1).[100] Similarly, mixed silyloxide–mesityl complexes of vanadium(III) and vanadium(IV) have been prepared.[102] The protolysis of VMes$_3$(THF) is also found very useful for the metallation of the monomethoxycalix[4]arene [*p*-Bu^t-calix[4]-(OMe)(OH)$_3$] that leads to the trivalent dimer [V{μ-*p*-Bu^t-calix[4]-(OMe)(O)$_3$}]$_2$.[103] Note that these mixed alkoxide- (or aryloxide) alkyl trivalent species are an important class of compounds due to their potential activity in alkene polymerization.[3,4,104–108] (See Chapter 11.20)

Room-temperature fluoridation of VMes$_3$(THF) with the fluoride-transfer agent F$_2$P(NEt$_2$)$_3$ generates ionic [FP(NEt$_2$)][VMes$_3$F].[109] This d^2-vanadium(III) complex ($\mu_{\mathrm{eff}} = 2.73\,\mu_{\mathrm{B}}$) has been characterized by means of multinuclear NMR spectroscopy (for the cation only), IR ($\nu_{\mathrm{VF}} = 583\,\mathrm{cm}^{-1}$, $\nu_{\mathrm{VC}} = 536$ and $511\,\mathrm{cm}^{-1}$), and X-ray structure determination (av. V–C 2.118 Å).

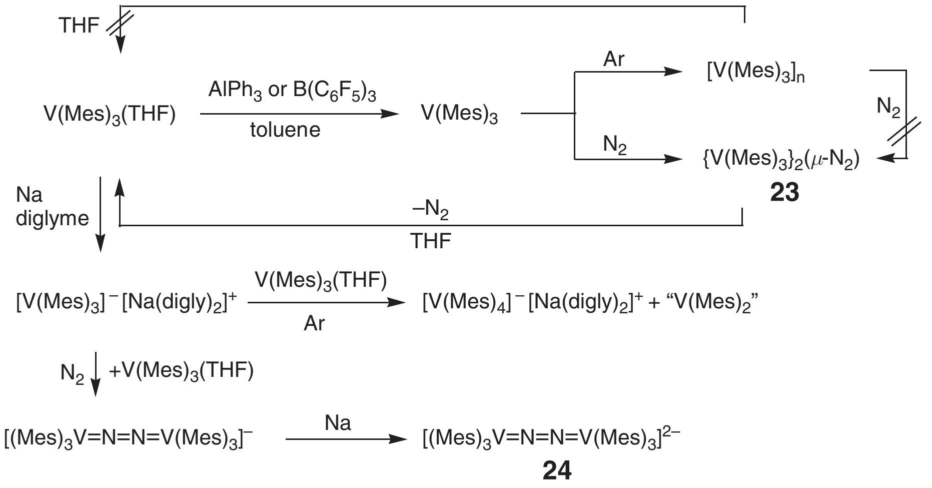
The oxidation of VMes$_3$(THF) by the use of either epoxides or oxo-metals is a useful tool for the preparation of rare higher-valent alkyl complexes. VMes$_3$(THF) smoothly deoxygenates styrene oxide to give the diamagnetic vanadium(V) derivative **20**.[110,111] This oxo-metal complex readily combines with VMes$_3$(THF) to give the paramagnetic vanadium(IV) μ-oxo dimer **21** (Scheme 11), which is further discussed in Section 5.01.3.3.1.

On the same principle, deoxygenation of the nitrosyl complex Cr(NO)(NPr$^i_2$)$_3$ by 2 equiv. of VMes$_3$(THF) gives rise to the nitride derivative Cr(N)(NPr$^i_2$)$_3$ and **21**,[112,113] while the triamido-tungsten(III) carbonyl [N$_3$N$_F$]W(CO) ([N$_3$N$_F$]$^{3-}$ = [(C$_6$F$_5$NCH$_2$CH$_2$)$_3$N]$^{-3}$) reacts with VMes$_3$(THF) in toluene to yield black [N$_3$N$_F$]W(CO)VMes$_3$. The tetrahedral vanadium center has been oxidized by one electron, and thus the complex is best described as a vanadoxyalkylidyne complex with almost linear W$^{\mathrm{VI}}$≡C–O–V$^{\mathrm{IV}}$, V–C bond distances ca. 2.05 Å and alkoxide-type V–O linkage (1.824(14) Å) and W–C of 1.88(2) Å.[114]

The insertions of organic functionalities into the V–C bonds of VMes$_3$(THF) are used for making novel vanadium(III) organometallic derivatives (Scheme 11). *tert*-Butyl isosocyanide inserts into all three V–Mes bonds to



Scheme 11



Scheme 12

afford exclusively the trivalent tris(η^2-iminoacyl) vanadium derivative V(η^2-[N,C]- Bu^{t}NCMes)$_3$ **22**.[67,111] The reactivity of **22** toward insertion reactions (CO_2, isocyanates, CO, isocyanides, etc.), hydrogenolysis, hydrolysis, and oxidation has been extensively studied.[67] Other representative examples of insertion reactions involving VMes$_3$(THF) are depicted in Scheme 11.[67] Furthermore, VMes$_3$(THF) undergoes reductive elimination when reacted with carbon monoxide, producing MesC(O)Mes and probably V(CO)$_6$. VMes$_3$(THF) is completely unreactive toward dinitrogen; however, when the THF molecule is removed using an appropriate Lewis acid ($AlPh_3$ or $B(C_6F_5)_3$),[83,115] the metal center reacts by either oligomerizing forming [VMes$_3$]$_n$ (under argon) or binding dinitrogen (under N_2) leading to the formation of the diamagnetic d^2–d^2 complex [Mes$_3$V(μ-N_2)VMes$_3$] **23** (Scheme 12), which easily loses N_2 upon treatment with THF, reforming VMes$_3$(THF). The reaction of VMes$_3$(THF) with N_2 also occurs under reducing conditions using either sodium or potassium metals, via intermediate formation of the vanadium(II) desolvated anion [VMes$_3$]$^-$. In the case of K, [VMes$_3$]$^-$ reacts with N_2 and in the presence of VMes$_3$ leads to the d^1–d^0 compound {[Mes$_3$V(μ-N_2)VMes$_3$]$^-$[K(digly)$_3$]$^+$}, which depending on the conditions, undergoes a further reduction to d^1–d^1 derivative {[K(digly)$_3$(μ-Mes)$_2$(Mes)V]$_2$(μ-N_2)} (see Scheme 12). Similarly, the reduction of VMes$_3$(THF) with Na under a dinitrogen atmosphere gives the d^1–d^1 dianion [Mes$_3$V(μ-N_2)VMes$_3$]$^{2-}$ **24** with a cumulenic structure [V═N═N═V], which depending on the workup mode has been isolated as {[Mes$_3$V(μ-N_2)VMes$_3$]$^{2-}$[Na(digly)$_2$]$_2$$^{2+}$} or {[Mes$_3$V($\mu$-$N_2$)($\mu$-Na)VMes$_3$]$^-$[Na(digly)$_2$]$^+$}. The d^n-configurations in these complexes are supported by structural evidence (Table 6). Protonation of these dinitrogen complexes shows that only the neutral d^2–d^2 **23** releases exclusively N_2 on protonation, while the other complexes with more reduced dinitrogen ligands release N_2, N_2H_4, and NH_3. This chemical reactivity compares well with the electrochemical studies performed under both N_2 and Ar atmospheres.

Analogous dinitrogen fixation is also achieved in the low temperature reaction of VCl$_3$(THF)$_3$ with 3 equiv. of neopentyllithium in diethyl ether under dinitrogen. The resulting diamagnetic vanadium(III) complex Np$_3$V(μ-N_2)VNp$_3$ easily loses its N_2 ligand upon treatment with donors L (Py, MeCN, RNC), breaking the dimeric structure and forming the corresponding adduct Np$_3$V(L).[116] Relevant structural parameters for Np$_3$V(μ-N_2)VNp$_3$ are listed in Table 6, and compare well with Mes derivatives, the V–Np bond is among the shortest reported for

Table 6 Structural parameters for alkyl-dinitrogen vanadium complexes

Complex	*V–C* (Å)	*V–N* (Å)	*N═N* (Å)	*V–N–N* (°)	*References*
{[Mes$_3$V(μ-N_2)VMes$_3$][K(digly)$_3$]}	av. 2.085	av. 1.756	1.222(4)	180.0	83
{[K(digly)$_3$(μ-Mes)$_2$(Mes)V]$_2$(μ-N_2)}	av. 2.124	1.744(6)	1.233(8)	178.3(8)	83
{[Mes$_3$V(μ-N_2)VMes$_3$][Na(digly)$_2$]$_2$}	av. 2.189	av. 1.767	1.225(7)	180.0	83
{[Mes$_3$V(μ-N_2)(μ-Na)VMes$_3$][Na(digly)$_2$]}	av. 2.173	1.757(6)	1.271(8)	174.7(10)	83
Np$_3$V(μ-N_2)VNp$_3$	2.026(2)	1.725(2)	1.250(3)	180.0	116

such V–C bonds. The dinitrogen complex is also converted to rare oxo-alkylvanadium(V) complex $V({=}O)Np_3$ by reaction with styrene oxide, and releases NpH and N_2 upon protonation with HCl. These complexes have been characterized by NMR and IR spectroscopies (i.e., $Np_3V(\mu\text{-}N_2)VNp_3$: ^{51}V NMR δ 1237, $\nu(N_2)$ 858 [$\nu(^{15}N_2)$ 839]). Interestingly, these two Np species decompose in solution at 20 °C giving NpH and species which are moderately active in the ring-opening metathesis polymerization ROMP of norbornene (1–2 mol Nb/mol V/h).

5.01.3.2.2 Heteroleptic vanadium(III) alkyl complexes

The involvement of trivalent alkyl complexes of vanadium in dinitrogen fixation/activation and even more importantly in olefin polymerization has driven the quest for the synthesis of σ-alkyl complexes. Many different ligands including cyclopentadienyls (see Section 5.01.4.2.1), and O- or N-donor ligands have stabilized these vanadium hydrocarbyls. Mixed alkoxyde–alkyl trivalent species have been discussed in the section treating the reactivity of homoleptic VR_3 (section 5.01.3.2.1). The dinitrogen species $[Mz_2V(Py)]_2(\mu\text{-}N_2)$[117] ($Mz = o\text{-}Me_2NCH_2C_6H_4$) reacts smoothly with 1 equiv. of CuCl to release N_2 and concomitantly forms the trivalent $Mz_2VCl(Py)$ as a deep-red crystalline solid, an octahedral compound with V–C bonds of 2.107(5) and 2.125(5) Å (*trans* to Cl) significantly longer than in the vanadium(II) precursor (V–C *trans* to N_2 2.204(4) Å).[118] The related 1,2-N,N-dimethylaminomethylferrocenyl (FcN) vanadium(III) complex $VCl(FcN)_2$ is prepared from $VCl_3(THF)_3$ and 2 equiv. of Li(FcN).[119–121] This compound adopts a trigonal-bipyramidal geometry in the solid state, probably to minimize steric constraints and to accommodate five-membered rings around the metal center with a V–C of 2.087(3) Å. Varying the stoichiometry of the reactants allows the preparation of the parent complex $VCl_2(FcN)$ and the homoleptic $V(FcN)_3$, which have been investigated by Mössbauer spectroscopy.[122]

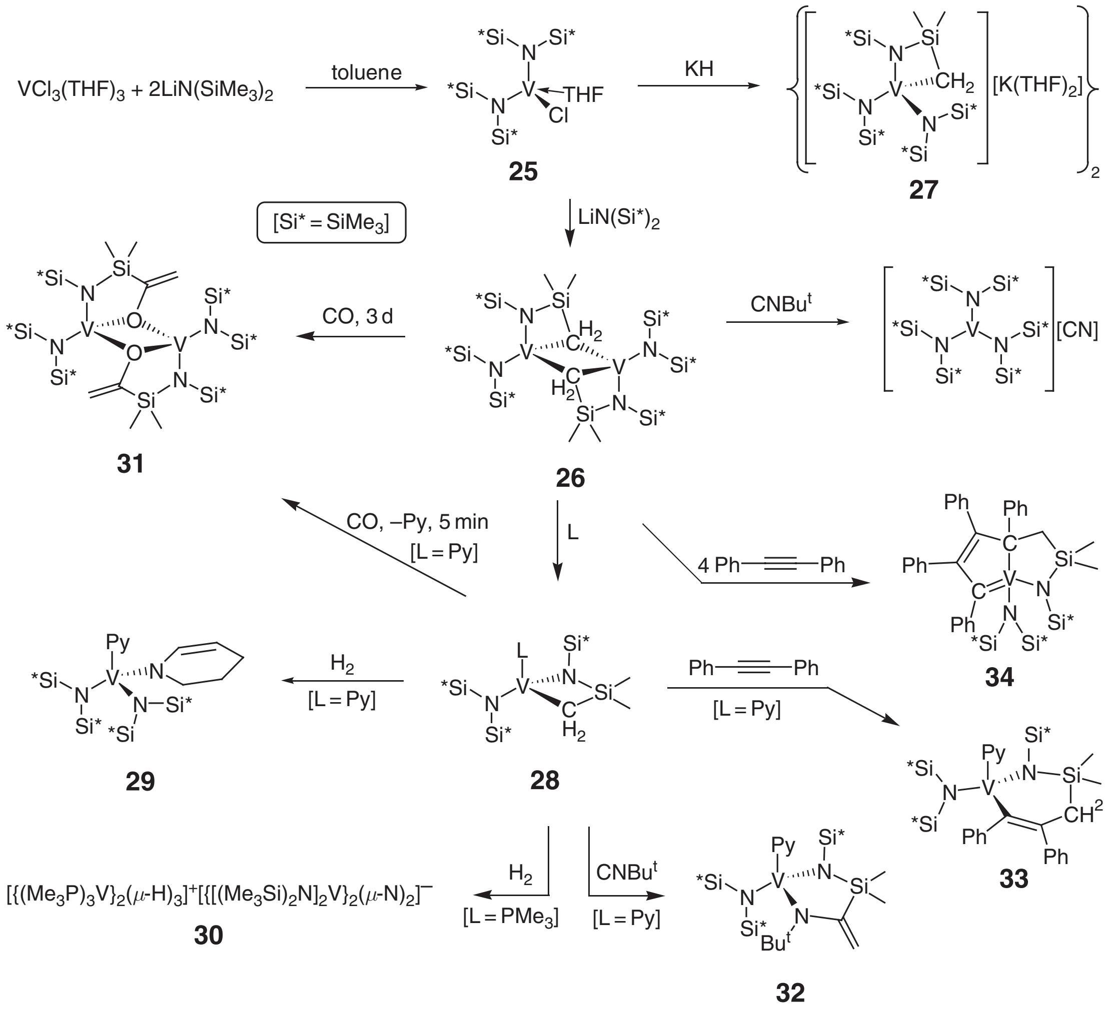
Although not isolated, R_2VCl (R = allyl, crotyl) and $V(O)R_3$ complexes, prepared by the transmetallation of VCl_3 and $VOCl_3$ with RMgCl,[123] afford good regioselectivities in the C–C bond forming reactions of carbonyl compounds.[124] Alkylvanadium species are also suspected to be involved in the geminal diallylation of propiophenone with allyl bromide by vanadium halides in the presence of Zn.[125]

The bis(trimethylsilyl)amido vanadium–nitrogen bond in low- to medium-valent species has been at the origin of the development of a rich chemical reactivity of this functionality. The reaction of $VCl_3(THF)_3$ with 3 equiv. of $LiN(SiMe_3)_2$ does not give the expected homoleptic tris(amido) complex, as observed when using the tris(amine) $VCl_3(NMe_3)_2$ as starting material,[126] but instead initially affords the green monomeric $V[N(SiMe_3)_2]_2Cl(THF)$ **25** which further reacts with 1 equiv. of $LiN(SiMe_3)_2$ to form the blue-violet dimer $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ **26** in 80% yield (see Scheme 13).[127] The X-ray structure analysis confirms the dimeric structure with a four-membered azasilavanadacyclobutane group, and magnetic susceptibility studies indicate antiferromagnetically coupled vanadium atoms ($\mu_{eff} = 2.31\ \mu_B$ per dimer). When reacted with excess KH, **25** leads to a similar dinuclear complex **27**, composed of two moieties held together via K–H agostic interactions with two potassium cations.[128]

The chemical reactivity of the metallacyclic dimer **26** has been explored with respect to the coordination of bases, hydrogenation, and insertion reactions. The dinuclear structure is cleaved by donor molecules (L) such as PMe_3, pyridine, or collidine, affording monomeric $[(Me_3Si)_2N]V[CH_2SiMe_2N(SiMe_3)](L)$ complexes with the conservation of the metallacyclic structure (see Table 7 for selected structural data).[129,130] Hydrogenolysis of the V–C bond in monomeric $[N(SiMe_3)_2]V[CH_2SiMe_2N(SiMe_3)](Py)$ **28a** with H_2 (60 bar) in the presence of pyridine gives the unprecedented enamido vanadium(III) derivative **29** in 36%. Unfortunately, this unusual example of regioselective homogeneous hydrogenation of pyridine is not catalytic.[130] Under the same conditions, the phosphine adduct $[(Me_3Si)_2N]V[CH_2SiMe_2N(SiMe_3)](PMe_3)$ **28b** yields the unprecedented mixed-valent complex **30** in 45%, composed of two separate trihydro–divanadium(II) and nitrido–divanadium(IV–V) fragments with a $\mu_{eff} = 3.27\ \mu_B$.[129]

The reaction of the dimer **26** and monomer **28a** with carbon monoxide proceeds at room temperature, and the same trivalent dinuclear enolate complex **31** is isolated via insertion of CO in the Si–CH_2 bond of the metallacycle.[131] In contrast, the reaction of **26** and **28a** with 1 equiv. of Bu^tNC under identical conditions takes different pathways. Structure **26** eliminates neopentane and neopentene and affords the ionic vanadium(IV) $[V(N(SiMe_3)_2)_3]^+[CN]^-$ in very low yield (20%).[131] Although no other compounds have been isolated, this complicated reaction probably results in the formation of other species. Structure **28a** gives a fast reaction with the formation of the insertion product **32** in 49% yield, a vanadium(III) metallacyclic complex with a vinyl group arising, as previously shown with CO, from the insertion of the isocyanide into the Si–CH_2 bond.

The difference of reactivity between **26** and **28a** is also apparent in the reaction with alkynes. Diphenylacetylene and bis(trimethylsilyl)acetylene insert into the V–CH_2 bond of **28a** to give ring expansion and formation of the paramagnetic vanadium(IV) complex $[(Me_3Si_2)N]V[\eta^2\text{-}[C,N]\text{-}C(R){=}C(R)CH_2SiMe_2N(SiMe_3)](Py)$ (R = Ph **33**, Me_3Si) containing a six-membered metallacyclic ring.[130] By contrast, the reaction of the dimer **26** with 4 equiv. of



$[\{(Me_3P)_3V\}_2(\mu\text{-}H)_3]^+[\{[(Me_3Si)_2N]_2V\}_2(\mu\text{-}N)_2]^-$

30

Scheme 13

Table 7 Relevant structural data for silylamido vanadium complexes

Complex	*V–C* (Å)	*V–N*$_{cycle}$ (Å)	*Other distances*	*References*
$\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ **26**	av. 2.210	av. 1.928		127
$\{[(Me_3Si)_2N]_2V[CH_2SiMe_2N(SiMe_3)][K(THF)_2]\}_2$ **27**	2.190(6)	1.985(5)		128
$[(Me_3Si)_2N]V[CH_2SiMe_2N(SiMe_3)](Py)$ **28a**	2.15(1)	1.735(4)		130
$[(Me_3Si)_2N]V[\eta^2\text{-}[C,N]\text{-}C(Ph){=}C(Ph)CH_2SiMe_2N(SiMe_3)](Py)$ **33**	2.093(3) V–C(Ph)			130
$[(Me_3Si)_2N]V[{=}C(Ph)C(Ph){=}C(Ph)C(Ph)CH_2SiMe_2N(SiMe_3)]$ **34**	2.092(7) V–C(Ph)		V=C 1.876(7)	132
$V[N(SiMe_3)_2]_2Me(THF)$ **35a**	2.095(4)			134
$V[N(SiMe_3)_2]_2Ph(Py)$	ca. 2.1[a]			135
$V[N(SiMe_3)_2]_2(o\text{-}Me_2NCH_2C_6H_4)$	2.210(2)			135
$\{V[N(SiMe_3)_2]_2Me_2\}^-$	2.096(8), 2.124(8)			133
$\{V[N(SiMe_3)_2]_2Me\}_2(\mu\text{-}O)$	2.054(3)			134

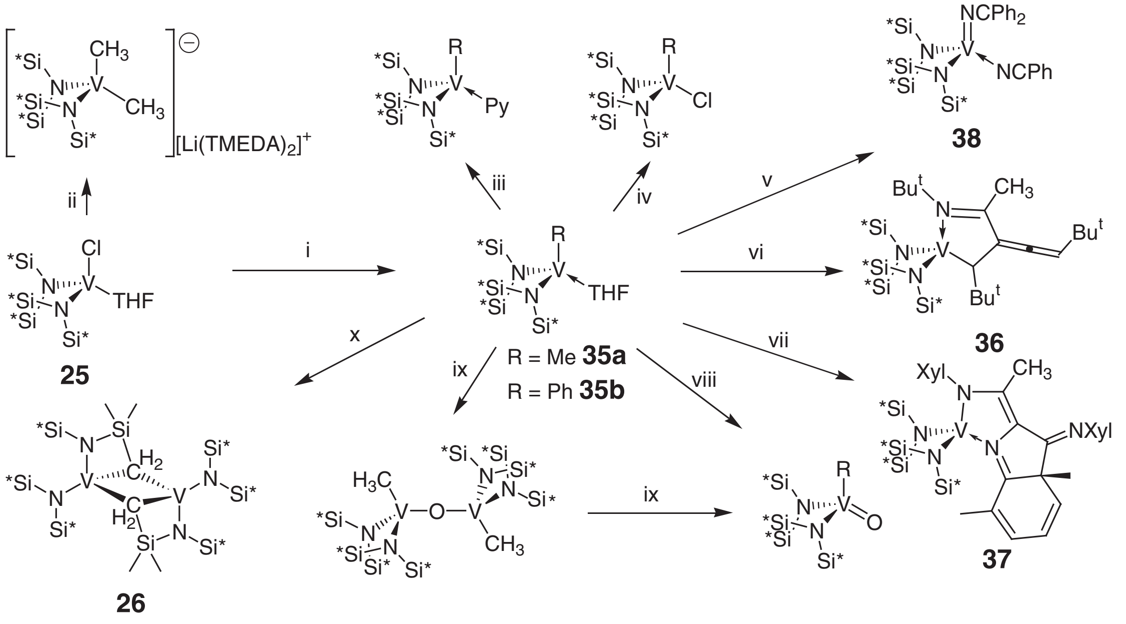
[a] Disorder with Py.

diphenylacetylene affords, after insertion of two alkyne molecules and tautomeric reorganization, a unique diamagnetic vanadium(V) bicyclic carbene–amide complex **34** in up to 44% yield.[132] A crystallographic study reveals a V=C bond distance of 1.87(7) Å and a V–C(Ph) distance of 2.092(7) Å (see Table 7) Alternatively, the same product could be obtained from $V[N(SiMe_3)_2]_2(BH_4)(THF)$ and diphenylacetylene.[136]

Alkylations of **25** with R_2Mg ($R = Ph$, Me) or RLi ($R = Me$, o-$Me_2NCH_2C_6H_4$, C_4H_3S) afford the corresponding rare Cp-free vanadium hydrocarbyl complexes $V[N(SiMe_3)_2]_2R(THF)$ **35**,[133–135] in which the THF is readily displaced by nitrogen donors (pyridine, lutidine) (see Scheme 14). Alkylation with 2 equiv. of MeLi in the presence of TMEDA gives the anionic $\{V[N(SiMe_3)_2]_2Me_2\}^-$.[133] Thermolysis of the monoalkyls $V[N(SiMe_3)_2]_2R(THF)$ ($R = Me$ **35a**, Ph **35b**) results in the loss of the coordinated THF and elimination of RH to provide the vanadium(III) dimer **26**.[133,134] One-electron oxidation of **35a** and **35b** with CuCl affords the vanadium(IV) d^1-species $V[N(SiMe_3)_2]_2R(Cl)$ in moderate yield, whereas 1 equiv. of styrene oxide oxidizes **35a** and **35b** into oxo-vanadium(V) $V(=O)R[N(SiMe_3)_2]_2$. In the case of $R = Me$, the μ-oxo vanadium(IV) intermediate $\{V[N(SiMe_3)_2]_2Me\}_2(\mu\text{-}O)$ is isolated when using only 0.5 equiv. of the epoxide.[133] Relevant structural parameters are reported in Table 7 for a comparison with other alkylvanadium(III) complexes supported by the same silylamido ligand. Insertion of three isocyanide molecules into the V–Me bond in **35a** gives the trivalent diazavanadacyclic products **36** and **37**, as illustrated in Scheme 14.[134,135] In contrast, addition of 3 equiv. of benzonitrile to **35b** affords the trivalent azaalkenylidene derivative **38** resulting from a monoinsertion of PhCN. Surprisingly, the reaction of $VCl_3(THF)_3$ with 6 equiv. of the less bulky Pr^i_2NLi gives the paramagnetic ($\mu_{eff} = 2.89\ \mu_B$) vanadaaminocyclobutane $\{(Pr^i_2N)_2V(\mu\text{-}CH_2C(=CH_2)NPr^i)(Li)\}$ associated in a dimer through a bridging tricoordinated lithium cation and with a V–C bond distance of 2.150(3) Å. The reaction proceeds via C–H bond metathesis in a hypothetical homoleptic $[(Pr^i_2N)_4V]^-$ intermediate, and dehydrogenation of the ligand.[136]

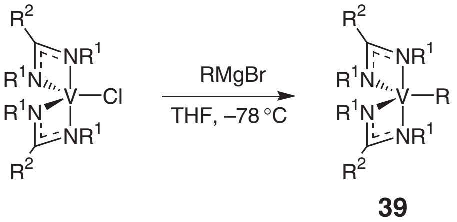
Amidinates have also been found to be suitable ancillary ligands for electron-deficient vanadium(III) hydrocarbyl species. Neutral paramagnetic ($S = 1$) 12-electron bis(amidinate) vanadium(III) alkyls **39** have been prepared from the parent chloride precursors (Scheme 15).[137,138] η^3-Allyl congeners have been prepared similarly. These neutral alkyl systems are thermally robust and catalyze slowly the oligomerization of ethene to linear alkenes without the need of added co-catalyst.

Treatment of mono-(β-diiminato) precursor $[ArNC(R^1)CHC(R^1)NAr]VCl_2(THF)_n$ [$Ar = Ph$, 2,6-Pr^i_2-C_6H_3, 2,4,6-Me_3-C_6H_2; $R^1 = Me$, Bu^t; $n = 0$ or 2 with $R^1 = Ph$] with alkyllithium reagents affords surprisingly stable



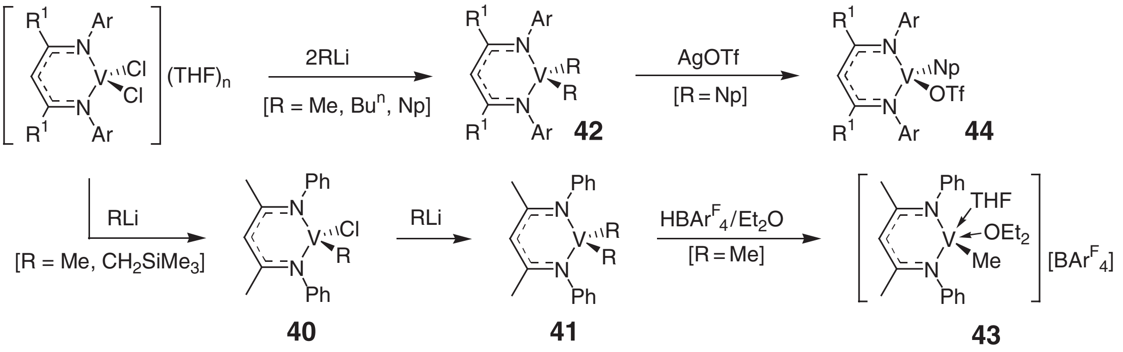
[Si* = SiMe$_3$]; i, 1/2 MgR_2 [$R = CH_3$, Ph]; ii, 2LiMe, 2TMEDA; iii, Py; iv, CuCl; v, PhCN [$R = Ph$]; vi, 3CNBu^t [$R = CH_3$]; vii, 3CNXyl [$R = CH_3$]; viii, 1 styrene oxide [$R = CH_3$, Ph]; ix, 1/2 styrene oxide [$R = CH_3$]; x, Δ, –RH [$R = CH_3$, Ph]

Scheme 14



R \ R^1,R^2	(Pr^i,Bu^t)	($SiMe_3$,Ph)	($SiMe_3,C_6F_5$)
Me	34%	61%	52%
Et		66%	
allyl	72%	68%	

Scheme 15



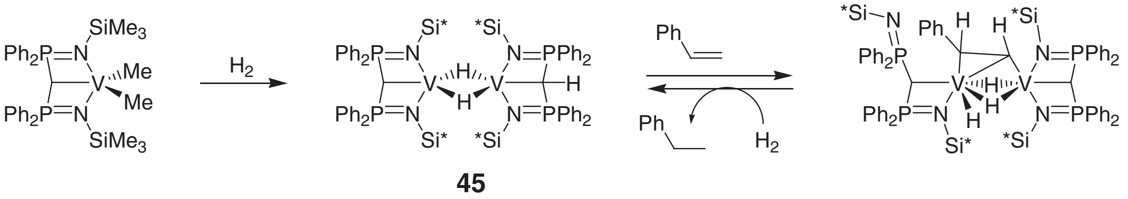
(Ar, R^1, n) = (2,4,6-Me_3-C_6H_2, Me, 0), (2,6-Pr^i_3-C_6H_3, Me, 0), (Ph, Me, 0),(2,4,6-Me_3-C_6H_2, Bu^t, 2)

Scheme 16

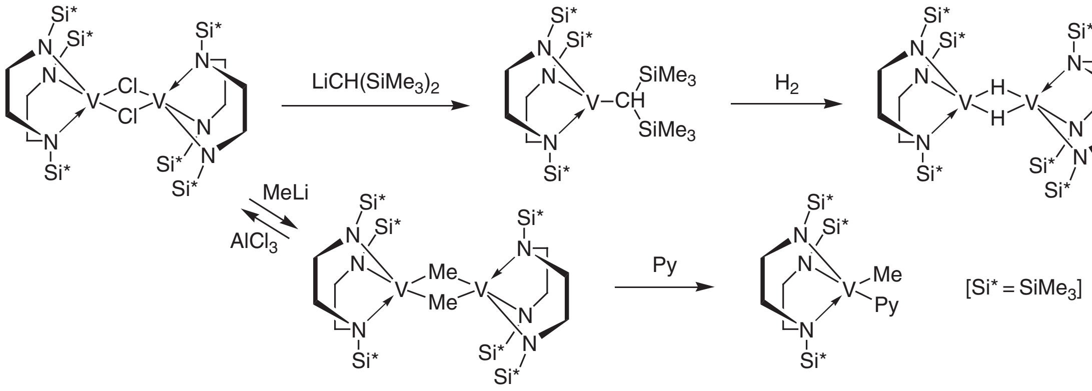
dialkylvanadium(III) complexes [$ArNC(R^1)CHC(R^1)NAr]VR_2$ **41 and 42** (R = Me,[139–141] Bu^n,[139] CH_2SiMe_3,[140,141] CH_2Bu^t[142]) as well as monoalkyl complex **40** (see Scheme 16). Vanadium–carbon bond distances in dimethyl derivative [PhNC(Me)CHC(Me)NPh]VMe_2 are found to be 2.080(4) and 2.126(4) Å.[140] Controversial polymerization activity is reported for these systems. In one study, [$ArNC(R^1)CHC(R^1)NAr]VMe_2$ does not seem to present any significant ethylene polymerization activity with MAO, $EtAlCl_2$, or $B(C_6F_5)_3$ co-catalysts, in the case of Al cocatalysts due to possible ligand transfer to Al.[139] However, the precursor [PhNC(Me)CHC(Me)NPh]$VCl_2(THF)_2$ and MAO does polymerize ethylene as well as slowly co-polymerize ethylene and propylene.[140,141] In this case, although the resulting polyethylene has similar properties with the one prepared from $VCl_3(THF)_3$, transfer of the diiminate to aluminum has been ruled out by spectroscopic studies, corroborated by further observations that [PhNC(Me)CHC(Me)NPh]VMe_2/$B(C_6F_5)_3$ mixtures yielded an active catalyst, as does the cationic **43** in the absence of added co-catalyst.

When reacted with AgOTf, [ArNC(Me)CHC(Me)NAr]$V(CH_2Bu^t)_2$ gives the trivalent, structurally characterized (V–C (Bu) = 2.062(5) Å) **44** in 78% yield, while an extremely rare example of alkylidene-vanadium species is formed upon oxidation using $AgBPh_4$ (this vanadium(IV) compound is further discussed in Section 5.01.3.3.2).[142] Related titanium and chromium chemistry using β-diiminate ligands is treated in Chapters 4.05 and 5.05.

The monoanionic "pincer"-type phosphinimine ligand $((Me_3Si)N{=}PPh_2)_2CH$ affords stabilization of trivalent dialkyls $[((Me_3Si)N{=}PPh_2)_2CH]VMe_2$ (Scheme 17) with V–Me bond distances of 2.070(4) and 2.120(3) Å.[143] Upon hydrogenolysis conditions (60 atm), the dimethyl derivative gives the extremely air sensitive, dinuclear hydride



Scheme 17



46

Scheme 18

complex **45**. This divalent hydride complex underwent oxidative additions of the styrene β-C–H bond affording a dinuclear trivalent vinyl hydride complex, a reaction that could produce ethylbenzene catalytically under H_2.[144]

Particularly robust vanadium(III) monoalkyl complexes incorporating the tridendate diamido ligand $[(Me_3Si)N(CH_2CH_2N(SiMe_3))_2]^{2-}$ have been generated by means of salt metathesis from the chloride precursor (Scheme 18). Although no crystal structure is available for these complexes formulated as $[(Me_3Si)N(CH_2CH_2N(SiMe_3))_2]VR$ (R = Me,[145] $CH(SiMe_3)_2$[146]), the $CH(SiMe_3)_2$ derivative is most probably monomeric, whereas the less bulky methyl congener would be a dimer. The latter is cleaved upon addition of pyridine to afford the monomeric adduct **46**, with a trigonal-bipyramidal V center attached to a Me group at a V–C distance of 2.118(3) Å. Ligand abstraction and metal reduction with various aluminum co-catalysts have been studied,[145] in relation to the property of these diamido systems to catalyze olefin polymerization.[3,4,6,145,147]

An unexpected macrocyclic *n*-butylvanadium(III) complex has been isolated from the reaction of tetralithium salt of the octaethyl porphyrinogen $[Li_4(OEPG)]$ with $VCl_3(THF)_3$.[148] The resulting hydrocarbyl complex possesses a V–C bond distance of 2.077(5) Å. Another tetradentate macrocyclic ligand, that is, *meso*-octaethyl bis(pyridine)–bis(pyrrole) $(N_2N'_2)$ has been shown to stabilize trivalent methylvanadium porphyrinogen complex $(N_2N'_2)VMe$, which undergoes migratory insertion of isocyanides and CO.[149,150] The trivalent vanadium compound $[p\text{-Bu}^t\text{-calix[4]}(OMe)_2(O)_2]VCl$ undergoes alkylation to the corresponding stable, paramagnetic vanadium(III) derivatives $[p\text{-Bu}^t\text{-calix[4]-}(OMe)_2(O)_2]VR$ (R = Me, Bz, p-Me-C_6H_4).[151] CO and isocyanides insert into these alkyl and aryl groups leading to the corresponding η^2-acyl and η^2-iminoacyl derivatives. Careful oxidative demethylation with iodine opens an interesting synthetic route to vanadium(IV) organometallic derivative $[p\text{-}^t\text{Bu-calix[4]-}(OMe)(O)_3]VR$ (R = p-Me-C_6H_4), a remarkable oxidation process that does not affect the V–C bond.

5.01.3.3 Vanadium(IV) and Vanadium(V) Complexes

As for their vanadium(III) analogs, several vanadium(IV) and vanadium(V) alkyls have been stabilized by employing various ancillary O- or N-donor ligands, and these reactive species could lead to the preparation of uncommon alkylidene and alkylidyne vanadium complexes.

5.01.3.3.1 Alkyl complexes supported by oxo and alkoxo ligands

As already highlighted in the section treating the reactivity of homoleptic alkylvanadium(III) complexes (Section 5.01.3.2.1), oxidation of trivalent alkyl complexes $VMes_3(THF)$ or $Np_3V(\mu\text{-}N_2)VNp_3$ with epoxides affords the corresponding pentavalent oxo-vanadium complexes $V(=O)R_3$.[110,116] The reaction of $V(=O)Mes_3$ with $VMes_3(THF)$ gives the μ-oxo vanadium(IV) paramagnetic dimer $Mes_3V–O–VMes_3$, which decomposes with donor solvents. Indeed, ligand redistribution occurs in the presence of pyridine affording the extremely rare terminal oxo-vanadium(IV) organometallic compound $V(=O)Mes_2(Py)_2$ in 46% yield.[110] ^{17}O-enriched oxo complex $V(O^*)(CH_2SiMe_3)_3$ was synthesized from $V(CH_2SiMe_3)_4$ and isotopically enriched water.[152] Relevant IR and structural data are given in Table 8.

Table 8 Some characteristics of alkyl vanadium(IV/V) complexes supported by oxo ligands

Complex	*IR* (cm^{-1})	$\delta^{51}V$	μ_{eff}	V–C (Å)	V–O (Å)	*References*
$\mathrm{V({=}O)Mes_3}$	1029 (V=O)			av. 2.059	1.575(4)	110
$\mathrm{V({=}O)Np_3}$	984 (V=O)	+1212				116
$\mathrm{Mes_3\ V{-}O{-}V\ Mes_3}$	680 (V–O–V)		1.81			110
$\mathrm{V({=}O)Mes_2(Py)_2}$	1012 (V=O)		1.65	2.141(7)	1.593(8)	110
$\mathrm{[Li(THF)_3V(O)Mes_3(THF)]}$				av. 2.107	1.612(3)	153
$\mathrm{[V({=}O)(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)\text{-}(C_6F_5)]_2}$		−481		2.069(5)	1.569(4) (V=O)	154
$\mathrm{V({=}O)(CBr_3)(OBu^t)_2}$	1011 (V=O)	−453				158

Other oxo-vanadium(IV) alkyl complexes are prepared via ligand substitution with 3 equiv. of MesLi on $\mathrm{[Li(THF)_2V(O)(OMes)_3(THF)]}$, resulting in the formation of $\mathrm{[Li(THF)_3V(O)Mes_3(THF)]}$ (34% yield) and $\mathrm{[Li(THF)_2V(O)Mes_2(OMes)(THF)]}$ (16% yield).[153] Alkylvanadium(IV) complexes have also been prepared by oxidation of the parent anionic trivalent alkoxide-mesityl vanadium complexes $\mathrm{V(OR)}_n\mathrm{(Mes)}_{4-n}$ (OR = aryloxide or silanolate) with *p*-chloranil ($\mathrm{C_6Cl_4O_2}$).[100,102]

Remarkably, treatment of the oxo-vanadium(V) complex $\mathrm{[V({=}O)(OCH_2CF_3)_3]_2}$ with the Lewis acid $\mathrm{B(C_6F_5)_3}$ leads to alkoxy/aryl exchange and formation of the unexpected organometallic oxo-vanadium(V) dimer $\mathrm{[V({=}O)(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)(C_6F_5)]_2}$ in 64% yield, while the more basic $\mathrm{V({=}O)(NEt_2)_3}$ gives the Lewis adduct $\mathrm{(C_6F_5)_3B{\cdot}(O{=})V(NEt_2)_3}$ with coordination of the borane to the oxo ligand.[154] A complete series of pentavalent oxo-vanadium complexes with the formula $\mathrm{V({=}O)(CH_2SiMe_3)}_n\mathrm{(OSiPh_3)}_{3-n}$ was reacted with $\mathrm{Al(CH_2SiMe_3)_3}$, and appeared to form similar Lewis adducts derived from the coordination of Al to the oxygen atom of the oxo group,[152] as shown by mutinuclear NMR spectroscopic studies (see Table 9). This suggests that the oxo ligand is the more Lewis basic site in all these molecules; the coordination of Al reduces the degree of π-donation from the oxo ligand to vanadium and facilitates insertion of ethylene into the V–C bonds of alkylvanadates during polymerization with these systems. A correlation between ^{51}V NMR chemical shift and ethylene polymerization activity for such oxo-vanadium(V) catalysts has been suggested.[155,156]

Oxidative demethylation of calix[4]arene complex [*p*-Bu^t-calix[4]-(OMe)$_2$(O)$_2$]VR (R *p*-Me-$\mathrm{C_6H_4}$) by a controlled amount of iodine affords the vanadium(IV) organometallic derivative [*p*-Bu^t-calix[4]-(OMe)(O)$_3$]VR (R = *p*-Me-$\mathrm{C_6H_4}$).[151] The co-deposition of acetone with $\mathrm{VOCl_3}$ in argon matrices leads initially to the formation of a rather strongly bounded adduct, which upon photochemical irradiation and cleavage of a C–C bond in acetone affords methyl derivative $\mathrm{Cl_3V(CH_3)(OC(O)CH_3)}$.[157] The air sensitive and thermally labile $\mathrm{V({=}O)(CBr_3)(OBu^t)_2}$ is formed upon addition of carbon tetrabromide/Bu^{n}Li solution to $\mathrm{V({=}O)Cl(OBu^t)_2}$ at low temperature.[158]

5.01.3.3.2 Alkyl, alkylidene, and alkylidyne complexes stabilized by imido, amido and other anionic N-donor ligands

As already evidenced in the σ-alkylvanadium(III) section (Section 5.01.3.2.2), anionic N-donor ligand systems (e.g., amides, imides, β-diiminates) provide convenient and accessible alternatives to the tremendously popular

Table 9 IR and NMR data for oxo-vanadium(V) complexes.[152] Adapted with permission of The American Chemical Society from Feher, F. J.; Blanski, R. L. *Organometallics*, **1993**, *12*, 958–963

Complex	$\delta\ ^{51}V$ [$w_{1/2}$, Hz]	*oxo* $\delta\ ^{17}O$ [$w_{1/2}$, Hz]	$\delta\ ^{29}Si$ [$w_{1/2}$, Hz]
$\mathrm{V({=}O)(CH_2SiMe_3)_3}$	+1205 [50]	1138 [366]	0.1
$\mathrm{V({=}O)(CH_2SiMe_3)_2(OSiPh_3)}$	+627 [500]	1130 [325]	2.1, −11.2 [90]
$\mathrm{V({=}O)(CH_2SiMe_3)(OSiPh_3)_2}$	−47 [400]	1144 [430]	3.9, −8.7 [90]
$\mathrm{V({=}O)(OSiPh_3)_3}$	−723 [100]	1189 [430]	
$\mathrm{V({=}O)(CH_2SiMe_3)_3{\cdot}Al(CH_2SiMe_3)_3}$	+1575 [111]	857 [650]	
$\mathrm{V({=}O)(CH_2SiMe_3)_2(OSiPh_3){\cdot}Al(CH_2SiMe_3)_3}$	+883 [1350]	830 [360]	6.6, 0.5, −1.5 [26]
$\mathrm{V({=}O)(CH_2SiMe_3)(OSiPh_3)_2{\cdot}Al(CH_2SiMe_3)_3}$	+43 [2100]	843 [375]	7.6, 0.3, 0.1
$\mathrm{V({=}O)(OSiPh_3)_3{\cdot}Al(CH_2SiMe_3)_3}$	−779 [525]	903 [415]	1.9 [55], 0.2

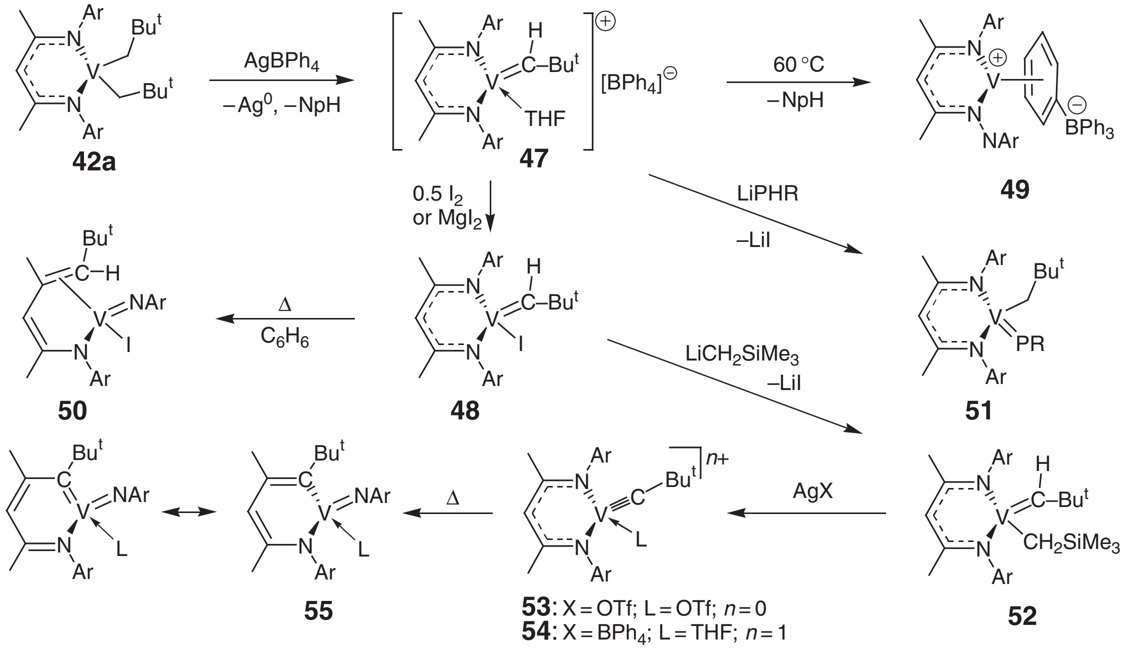
Table 10 Spectroscopic data for alkylvanadium-oxo derivatives

Complex	*v(V–O)* (cm^{-1})	*δ* ^{51}*V NMR* (ppm)	*References*
$\{V[N(SiMe_3)_2]_2Me\}_2(\mu\text{-}O)$	709		133
$V({=}O)Me[N(SiMe_3)_2]_2$	1014	222	133
$V({=}O)Ph[N(SiMe_3)_2]_2$	1011	101	133

cyclopentadienyl ligand. These systems contribute to the development of a rich organometallic vanadium chemistry with stabilization of reactive alkyl, alkylidene, and alkylidyne species described in this section.

The synthesis of alkyl- and oxo-alkylvanadium complexes supported by two bis(trimethylsilyl)amido ligands $[[(Me_3Si)_2N]_2VR(Cl)$, $[(Me_3Si)_2N]_2V({=}O)(R)$, and $\{[(Me_3Si)_2N]_2VMe\}_2(\mu\text{-}O)$ (with R = Me, Ph)] has been discussed in detail in Section 5.01.3.2.2.[133,137] Pertinent spectroscopic data for these alkylvanadium-oxo complexes are listed in Table 10.

Alkylation of tetravalent $(R_2N)_2VCl_2$ (R = Cy, Pr^i), obtained by a surprising disproportionation reaction of $VCl_3(THF)_3$ with 1 equiv. of R_2NLi, proceeds rapidly at −20 °C with alkyllithium reagents to produce the corresponding, moderately stable, dialkylvanadium(IV) derivatives $(R_2N)_2V(R^1)_2$ (R^1 = Np, Ph, Bz).[159] The Np derivative has been characterized by an X-ray structure determination which reveals V–C$_{Np}$ bond distances of 2.088(3) and 2.095(3) Å. Chemical oxidation of bis(neopentyl) complex $[nacnac]V(CH_2Bu^t)_2$ **42a** (nacnac = [ArNC(Me)CHC(Me)NAr], Ar = 2,6-$^iPr_2C_6H_3$) with $AgBPh_4$ leads to the formation of a silver mirror and to an extremely rare example of cationic vanadium(IV)-alkylidene complex **47** in 74% yield (Scheme 19).[142] The X-ray structure reveals a very short V═C bond (1.795(3) Å) and a distorted Np ligand suggesting α-agostic CH interaction with the metal center. Anion exchange in this cationic **47** with 0.5 equiv. I_2 or excess MgI_2 produces neutral, four-coordinate vanadium(IV)-alkylidene complex **48** with extremely short V═C bond of 1.787(3) Å. Thermolysis of **47** at 60 °C affords, after extrusion of NpH, the zwitterionic vanadium(II) complex **49**, while for neutral **47** a "Wittig-like" reactivity is observed which results in the formation of an imido-vanadium(IV) species **50** (see Scheme 19). When neutral **47** is treated with LiPHR (R = 2,4,6-Pr^i_3-C_6H_2 or 2,4,6-Bu^t_3-C_6H_2), the phosphinidene–alkylvanadium(IV) complex **51** is formed.[160] This reaction probably involves α-H migration in a putative phosphide intermediate $[nacnac]V({=}CHBu^t)(PHR)$. Alkylation of **47** with $LiCH_2SiMe_3$ gives the neopentylidene-alkyl species **52** in 72% yield.[161] One-electron oxidation of the latter with AgX (X = OTf, BPh_4) yields the neutral **53** or cationic **54** four-coordinate alkylidyne complexes. These compounds



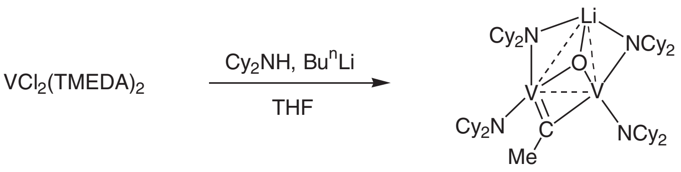
Scheme 19

Table 11 Spectroscopic and structural data for nacnac [ArNC(Me)CHC(Me)NAr] vanadium(IV/V) complexes[142,160,161]

Complex	μ_{eff}	*EPR or* δ $^{51}V/^{13}C$	*V–C* (Å)	*V–C*$_\alpha$*–C*$_\beta$ (°)
{[nacnac]V(=CHBu^t)(THF)}{BPh$_4$} **47**	1.87	$g_{iso} = 1.982$, $A_{iso} = 88$ G	V=C 1.795(3)	159.8(4)
[nacnac]V(=CHBu^t)(I) **48**	1.94	$g_{iso} = 1.976$, $A_{iso} = 64$ G	V=C 1.787(3)	158.7(3)
[nacnac]V(=P-2,4,6-Pr$^i_3$-C$_6$H$_2$)(CH$_2$Bu^t) **51a**	2.09	$g_{iso} = 1.960$	V=P 2.174(4)	130.8(3)
		$A_{iso} = 70$ (V), 40 (P) G	V–C 2.034(4)	
[nacnac]V(=P-2,4,6-Bu$^i_3$-C$_6$H$_2$)(CH$_2$Bu^t) **51b**	2.14	$g_{iso} = 1.963$	V=P 2.1602(6)	132.5(5)
		$A_{iso} = 70$ (V), 40 (P) G	V–C 2.053(2)	
[nacnac]V(=CHBu^t)(CH$_2$SiMe$_3$) **52**	1.90	$g_{iso} = 1.960$	V=C 1.791(6)	V=C–C 163.1(4)
		$A_{iso} = 72$ G	V–C$_{Si}$ 2.092(4)	V–C–Si 130.9(3)
[nacnac]V(≡CHBu^t)(OTf) **53**		−882/375	V≡C 1.674(2)	177.6(2)
{[nacnac]V(≡CHBu^t)(THF)}{BPh$_4$} **54**		−956/374	V≡C 1.696(3)	175.8(3)

represent the first terminal alkylidyne complexes of vanadium; they are stable as solids but transform slowly in solution to imido–vanadium complexes **55** supported by a chelating amido-vinyl ligand resulting from a cross-metathesis transformation (Scheme 19). Alkylidyne **53** is reported to polymerize phenylacetylene in the presence of LiNp, to afford $M_n \sim 7000$. Relevant spectroscopic and structural parameters are given in Table 11.

Addition of divalent VCl$_2$(TMEDA)$_2$ to 2 equiv. of *in situ* prepared Cy$_2$NLi leads to the formation of a complicated mixture of products instead of the known[162a] homoleptic vanadium(II) amide complex.[162b] Surprisingly, from this mixture was crystallized the only known example of vanadium complex with a bridging ethylidyne function **56** (Equation (1)). This dinuclear vanadium(IV) complex results from the unexpected fragmentation of THF probably promoted by a vanadium(II) amide intermediate. The ethylidyne fragment is unsymmetrically coordinated (V–C = 1.79(1) and 2.05(1) Å) which indicates two non-equivalent V–C bonds (double vs. single).



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(1)

Surface organometallic chemistry (see Chapter 12.10) of tetravalent and pentavalent vanadium has been examined. When (Bu^{t}N=)VNp$_3$ is allowed to react at 373 K with dehydroxylated silica, (≡SiO)$_2$V(=*N*Bu^t)Np is the major surface species formed, with minor (≡SiO)$_2$V(NHBu^t)Np$_2$.[163] At 423 K, neopentane adds to the V=N bond of the imido derivative via C–H addition. Similarly, silica-supported bis(alkyl) complex of vanadium(IV) (≡SiO)$_2$V(CH$_2$SiMe$_3$)$_2$ is accessible from precursor V(CH$_2$SiMe$_3$)$_4$.[164,165] It undergoes surprisingly clean thermal (58 °C) α-H elimination of SiMe$_4$ to generate the supported alkylidene (≡SiO)$_2$V(=CHSiMe$_3$). When exposed to excess of styrene at room temperature, this alkylidene species affords trimethylvinylsilane by metathetical exchange.

The imido ligand [NR]$^{2-}$ is currently having a considerable impact on organometallic chemistry either as ancillary ligand isolobal to Cp$^-$ or as a reactive functionality. Easy access to various tetravalent[166–168] or pentavalent[169,170] terminal imido–vanadium precursors contributes to the development of this chemistry that has found applications in olefin polymerization,[104,167,171–176] hydroamination,[177] reaction with PCR,[178] and C–H activation,[179] all these reactions involving V–C bonds, and are discussed below. The imido function has proved to stabilize alkyl groups in both V(IV) and V(V) complexes. Pentavalent V(=NAr)Bn$_3$ may be prepared by chlorine substitution from trichloro derivative V(=NAr)Cl$_3$(THF) with BnMgCl (Ar = 2,6-Pr$^i_2$-C$_6$H$_3$).[176] This compound, which represents the first structurally characterized vanadium(V) trialkyl complex (see relevant structural parameters in Table 12), is a valuable synthetic precursor to a series of other vanadium(V) dialkyl derivatives with supporting alkoxide, aryloxide, and amido functionalities. The bulky nature of the arylimido ligand affords steric protection around the metal center, and the benzyl groups may provide extra stability to the tris(benzyl) species. Of particular interest, mixed aryloxide-dibenzyl V(=NAr′)Bn$_2$(OAr) (Ar = 2,6-Me$_2$-C$_6$H$_3$, Ar′ = 2,6-Pr$^i_2$-C$_6$H$_3$) catalyzes ROMP of norbornene.[173] The choice of the supporting imido ligand is critical. Both reduction and aryl/alkylation are involved in similar reactions of aryl and alkyl

Table 12 ^{51}V NMR data and structural parameters for imido complexes

Complex	*δ ^{51}V*	*V–C* (Å)	*V=N* (Å)	*References*
$V(=NBu^t)(CH_2SiMe_3)_3$	+878			180
$V(=NBu^t)(Np)_3$	+879			181
$V(=NBu^t)(Np)_2(NHBu^t)$	+367			180
$V(=NBu^t)(Np)_2(O\text{-}2,6\text{-}Pr^i\text{-}C_6H_3)$	+378			168
$V(=NBu^t)(Np)_2(OBu^t)$	+293			181
$V(=NBu^t)(Np)(OBu^t)_2$	−324			181
$V(=NBu^t)(OBu^t)_3$	−751			181
$[(\mu\text{-}Bu^tN)VMe_2]_2$	+1604			180
$[(\mu\text{-}Bu^tN)VMe(N(SiMe_3)_2)]_2$	+1291			168
$[(\mu\text{-}Bu^tN)VMe(O\text{-}2,6\text{-}Pr^i\text{-}C_6H_3)]_2$	+1247			168
$V(=N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)Bn_3$	+1008	2.061(7), 2.079(7)[a], 2.086(8)	1.641(6)	176
$V(=N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)Bn_2(O\text{-}2,6\text{-}Pr^i\text{-}C_6H_3)$	+548	2.048(7), 2.084(6)	1.669(5)	176
$V(=N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)Bn_2(OC(CF_3)_3)$	+835	2.026(7), 2.032(7)	1.638(5)	176
$V(=N\text{-}2,6\text{-}Pr^i{}_2\text{-}C_6H_3)Bn_2(NPhMe)$	+289	2.075(9), 2.103(8)[a]	1.658(7)	176

[a] η^2-Coordinated benzyl group.

Grignard reagents with the less bulky terminal (imido)vanadium(V) complex $(ArN{=})VCl_3(THF)_2$ (Ar = 4-Me-C_6H_4) to form vanadium(IV) dimer species $[(\mu\text{-}ArN{=})VR_2]_2$ (R = Bn, Mes). These cyclodivanadazene-type species are diamagnetic, with a V–V bond of 2.45–2.49 Å, and V–C bonds span the range 2.05–2.08 Å.

Alkylation of the vanadium(IV) precursor $(Bu^tN)VCl_2(dme)$ affords either the corresponding vanadium(IV) dialkyl derivative $[(\mu\text{-}Bu^tN)VMe_2]_2$[180] or the vanadium(V) tris(alkyl) complexes $V(=NBu^t)R_3$ (R = CH_2SiMe_3, Np)[168,181] after disproportionation reaction. Amido–alkyl or alkoxo–alkyl derivatives are accessible via alkylation of parent amido or alkoxo compound, or by unexpected photochemical decomposition.[168,180]

The imide–phosphinimide vanadium(V) complex $(ArN{=})V(N{=}PR_3)Cl_2$ [Ar = Ph, 2,6-$Pr^i{}_2$-C_6H_3; R = Pr^i, Bu^t, Ph] is transformed with MeLi and PhMgBr in diethyl ether into the corresponding dialkyl pentavalent species in yields ranging from 36% to 76%.[182] The reaction of the closely related imide–ketimide vanadium(V) complex $(ArN{=})V(N{=}CBu^t{}_2)Cl_2$ [Ar = 2,6-Me_2-C_6H_3] with 2 equiv. of $LiCH_2SiMe_3$ in hexane affords the corresponding dialkyl species $(ArN{=})V(N{=}CBu^t{}_2)(CH_2SiMe_3)_2$ in 95% yield.[183] Interestingly, α-H elimination in this dialkyl complex occurs in the presence of PMe_3 at 80 °C leading to the alkylidene-vanadium(V) complex $(ArN{=})V({=}CHSiMe_3)(N{=}CBu^t{}_2)(PMe_3)$. This complex has a distorted tetrahedral geometry around the metal center with bond distances of 1.860(2) (V=C) and 1.679(2) Å (V=N) (see Table 13 for a comparison with other carbene complexes). Both the dialkyl and the alkylidene complexes exhibit remarkable catalytic activity for ROMP of norbornene giving high molecular weight polymers with unimodal distribution in high yield.

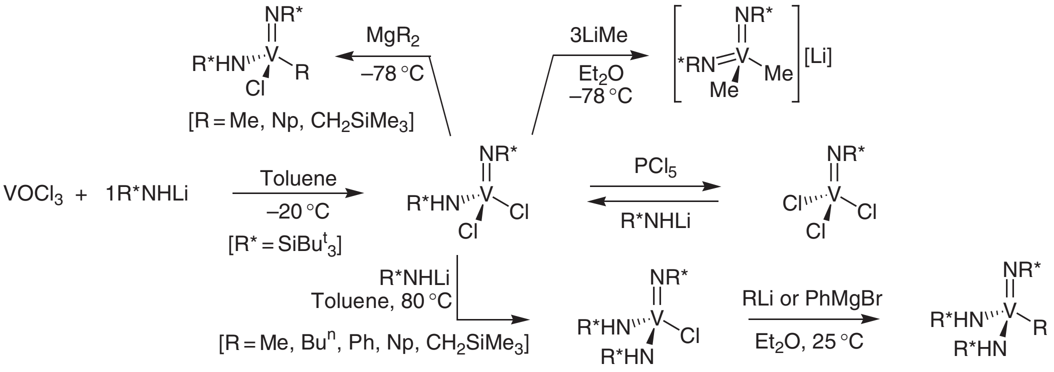
The use of the very bulky imido ligand $[Bu^t{}_3SiN]^{2-}$ has allowed the development of a family of thermally robust hydrocarbyl vanadium(V) complexes, which show remarkable C–H bond activation. These complexes $(Bu^t{}_3SiN{=})V(NHSiBu^t{}_3)_2R$ (R = Me, Bu^n, Np, CH_2SiMe_3)[179,184] stabilized by three bulky nitrogen ligands (one

Table 13 V=C bond distances in vanadium alkylidene and Fischer carbene complexes

Complex	*V=C* (Å)	*References*
$CpV(=CHCMe_3)(dmpe)$ **66**	1.809(3)	218
$CpV(=NAr)(=CHPh)(PMe_3)$ **83**	1.922(6)	240
$[Cp_2Zr]\{\mu\text{-}[O,O]\text{-}OC(C_4H_8)CH_2CHCH{=}CH_2C[{=}VCp(CO)_3]O\}$	2.096(2)	216
$[Cp_2Hf]\{\mu\text{-}[O,O]\text{-}OC(C_4H_8)CH_2CHCH{=}CH_2C[{=}VCp(CO)_3]O\}$	2.086(5)	215
$(ArN{=})V({=}CHSiMe_3)(N{=}CBu^t{}_2)(PMe_3)$[a]	1.860(2)	183
$\{[ArNC(Me)CHC(Me)NAr]V({=}CHBu^t)(THF)\}\{BPh_4\}$ **47**[b]	1.795(3)	142
$[ArNC(Me)CHC(Me)NAr]V({=}CHBu^t)(I)$ **48**[b]	1.787(3)	142
$[ArNC(Me)CHC(Me)NAr]V({=}CHBu^t)(CH_2SiMe_3)$ **52**[b]	1.791(6)	161

[a] Ar = 2,6-$Me_2C_6H_3$.

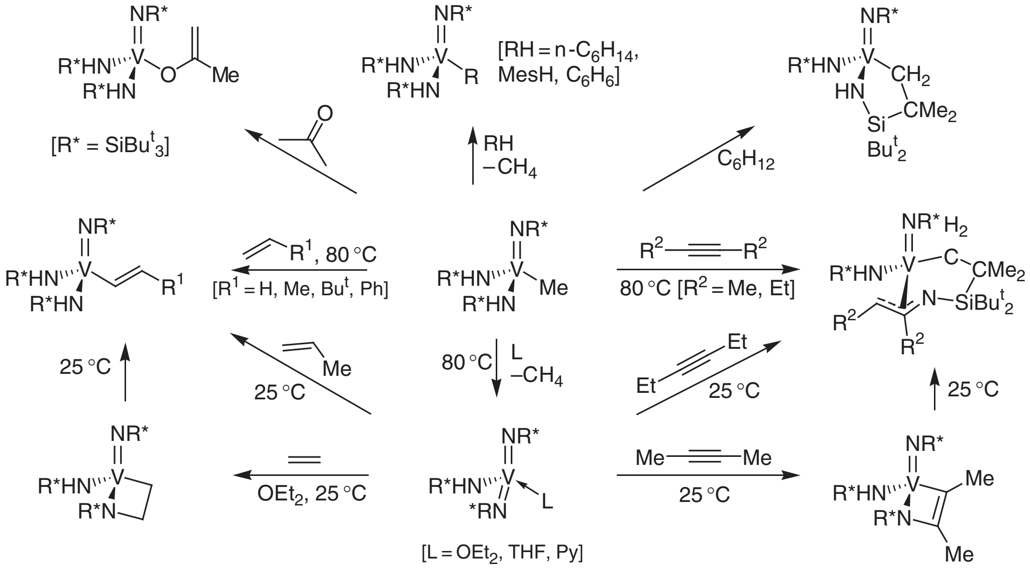
[b] Ar = 2,6-$Pr^i{}_2C_6H_3$.



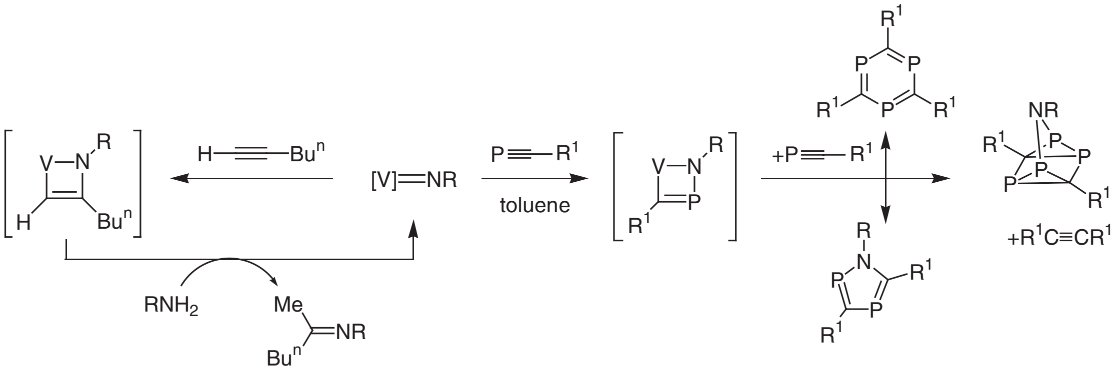
Scheme 20

imido, two amido) are obtained in good yield in two steps from readily available[185] $(Bu^t_3SiN{=})V(NHSiBu^t_3)Cl_2$ (Scheme 20). On thermolysis (80 °C), methyl complex $(Bu^t_3SiN{=})V(NHSiBu^t_3)_2Me$ activates C–H bonds of alkanes/arenes with clean formation of alkyl/aryl species (Scheme 21). As confirmed by theoretical calculations,[186] this novel reactivity is supposed to proceed by C–H addition across the metal–imido bond (i.e., $[2\sigma + 2\pi]$ addition) of an unstable three-coordinated intermediate $[V({=}NSiBu^t_3)_2(NHSiBu^t_3)]$, rather than by simple σ-bond metathesis mechanism. Indeed, this sterically and electronically unsaturated intermediate may be trapped with Lewis bases to afford the corresponding adducts $V({=}NSiBu^t_3)_2(NHSiBu^t_3)(L)$ ($L = Et_2O$, THF, or Py), or with alkynes/alkenes to produce novel cycloaddition compounds, which cleanly rearrange to unusual C–H activation products (Scheme 21).

The imido function has also been involved in the reactivity with phosphaalkynes $P{\equiv}CR$, which depending on the experimental conditions give 3-aza-1,2,4,6-tetraphosphaquadricyclanes, 1,3,5-triphosphabenzenes, or 1,2,4-azadiphospholes. A four-membered ring species depicted in Scheme 22 is the key intermediate in these transformations.[178,187–189] A similar metallacyclic intermediate resulting from [2 + 2] cycloaddition of an alkyne $C{\equiv}C$ and the metal–imido function is proposed to be the key intermediate in the catalytic hydroamination of alkynes with vanadium(IV)–imido complexes (Scheme 22).[177]



Scheme 21



Scheme 22

5.01.4 Mono(η^5-Cyclopentadienyl) Complexes

5.01.4.1 Vanadium(I) Mono(η^5-Cyclopentadienyl) Complexes

5.01.4.1.1 CpV(CO)$_4$ and its derivatives

5.01.4.1.1.(i) Synthesis, structure, and ring substitution

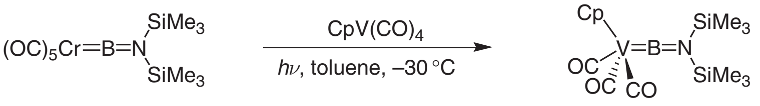
The chemistry of Cp*V(CO)$_4$ and its derivatives has been reviewed elsewhere.[16] Several synthetic approaches have been reported for the preparation of half-sandwich tetracarbonyl vanadium complex CpV(CO)$_4$ and its ring-substituted derivatives in previous editions of COMC (COMC (1982) Volume 3, Chapter 24, Section 24.5.1.1; and COMC (1995) Volume 5, Chapter 1, Section 5.01.4.1.1) and no new methods have been reported over the last 12 years. CpV(CO)$_4$ is prepared from the reduction of Cp$_2$V with potassium followed by addition of carbon monoxide, while substituted cyclopentadienyl derivatives are best obtained from the direct reaction of V(CO)$_6$ with the corresponding substituted cyclopentadiene. The molecular structure of CpV(CO)$_4$ has been determined by gas phase electron diffraction at 95 °C,[190] but the position of the Cp ring relative to the V(CO)$_4$ fragment could not be determined unequivocally. This suggests as expected that there is a very low barrier to internal rotation of the Cp group, as already evidenced by disorder in the solid-state structure.[191] Non-rigidity of the V(CO)$_4$ fragment by means of low frequency CO bending modes has also been suggested to explain the anomalies observed in the microwave spectrum of CpV(CO)$_4$.[192] Gas phase photoelectron spectroscopic studies and DFT calculations reveal that the strong delocalization of electron density from the d^4-metal to the CO ligands dominates the bonding electronic structure of this molecule.[193] The molecular structure of Cp*V(CO)$_4$ has been determined by X-ray crystallography and consists of a four-legged piano stool geometry with mean V–CO and V–Cp$_c$ (Cp$_c$ = centroid of the Cp ligand) bond distances of 1.935 and 1.915 Å, respectively.[194]

5.01.4.1.1.(ii) Reactivity at the metal center

The photoinduced carbonyl substitution of CpV(CO)$_4$ and its ring-substituted derivatives by various donor ligands is well documented and has been extensively described in COMC (1995) (Volume 5, Chapter 1, Section 5.01.4.2). Thus, only the few new studies are presented below. According to IR spectroscopic studies of a variety of ring-substituted half-sandwich tetracarbonyl vanadium complexes in low temperature (ca. 12 K) matrices (Ar, CH$_4$), ring dechelation/ring slippage pathway may play a significant part in the thermal and photochemical reactions of CpV(CO)$_4$ and its derivatives.[195] In addition, photolysis of Cp*V(CO)$_4$ in O$_2$ matrices[195] or argon matrices in the presence of O$_2$[196] led to the formation of Cp*V(CO)$_3$(η^2-O$_2$) with a side-on bonded O$_2$ ligand. In N$_2$ matrices, mono- and bis(dinitrogen) species are formed,[195] while only the mono(dinitrogen) complex CpV(CO)$_3$(N$_2$) is observed in xenon (lXe) or *n*-heptane solutions.[197] Similarly, organometallic alkane[198] and noble-gas (Xe)[199] complexes CpV(CO)$_3$(*n*-heptane) and CpV(CO)$_3$(Xe) have been characterized by time-resolved IR spectroscopy in solution (*n*-heptane) or in supercritical fluids (Xe). UV photolysis of CpV(CO)$_4$ and H$_2$ in liquid Xe (lXe) results in the formation of non-classical dihydrogen complex of vanadium CpV(CO)$_3$(η^2-H$_2$) ($\nu_{\text{H–H}} = 2642\,\text{cm}^{-1}$).[197,200] Similarly, spectroscopic data suggest that reaction of CpV(CO)$_4$ with silane HSiEt$_3$ in solution (lXe, *n*-heptane)[197] or in neat silane[201] results in the formation of labile CpV(CO)$_3$(η^2-HSiEt$_3$) complex. In contrast, reaction with HSiCl$_3$ and HSiEtCl$_2$ led to full oxidative addition and formation of $CpV(CO)_3(H)(SiR_3)$. IR spectroscopy in solution (IXe) with perfluoro-*tert*-butyl alcohol indicates that $Cp^*V(CO)_4$ is sufficiently basic to undergo V–CO···HO hydrogen bonding interactions.[202]

Dimethylsulfide substitution in $CpV(CO)_3(SMe_2)$ and $Cp^*V(CO)_3(SMe_2)$ by the olefinic phosphine $P(C_7H_7)_3$ (C_7H_7 = 1-cyclohepta-2,4,6-trienyl) generates the 18-electron complexes $CpV(CO)_3[P(C_7H_7)_3]$ and $Cp^*V(CO)_3[P(C_7H_7)_3]$, in which the olefinic phosphine ligand is coordinated as a conventional phosphine ligand.[60]

The first half-sandwich complex **57** with a terminal borylene ligand is formed via photochemically induced intermetal borylene transfer upon irradiation of $Cr({=}B{=}N(SiMe_3)_2)(CO)_5$ in the presence of $CpV(CO)_4$ for 4 days at −30 °C in toluene (Equation (2)).[203] An X-ray diffraction study reveals a linear V–B–N arrangement (177.9(4°)) with a short B–N distance of only 1.378(7) Å and a V–B distance of 1.959(6) Å. It can be assumed from NMR spectroscopy and DFT calculations that in solution the borylene ligand displays free rotation even at low temperature, due to an energy difference of only 19 kJ mol^{-1} between the horizontal and the vertical orientation.



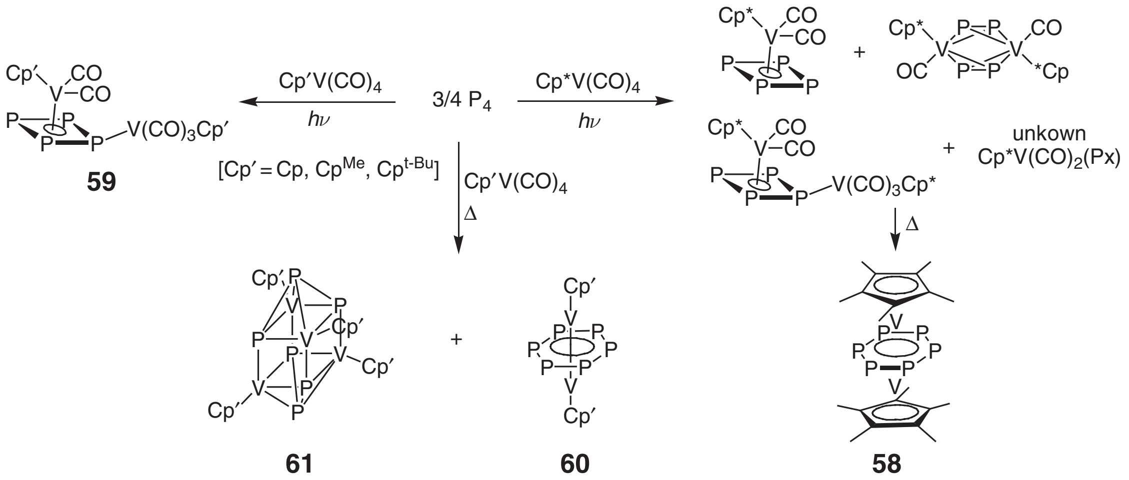
57

(2)

The triphosphane macrocycle 12[ane]P_3Et_3 reacts with $CpV(CO)_4$ thermally or photochemically to produce diamagnetic *cis*-[(η^2-12[ane]P_3Et_3)$CpV(CO)_2$] with the macrocycle, acting as a bidentate ligand, and two *cis*-carbonyl ligands.[40]

As previously reported with $CpV(CO)_4$ in COMC (1995) (Volume 5, Chapter 1, Section 5.01.4.1.2), the photoinduced replacement of one CO in pentamethyl-substituted analog $Cp^*V(CO)_4$ may also be achieved with isonitriles (see Section 5.01.2.5), thioethers, or pyridines.[72] The photoinduced decarbonylation of $Cp^*V(CO)_4$ in THF solution in the presence of white phosphorus, P_4, affords four products (see Scheme 23), two of which have a P_4-ring ligand system.[204,205] All these compounds are converted upon thermal treatment into known[206] tripledecker $Cp^*V(\mu,\eta^6\text{-}P_6)VCp^*$ **58** which is considered to be the thermodynamically stable end product in the $Cp^*V(CO)_4/P_4$ system. In contrast, the unsubstituted complex $CpV(CO)_4$ upon similar irradiation with P_4 gives only the binuclear P_4-bridged product **59**, while thermolysis (145 °C) produces a mixture of the tripledecker **60** and a pseudocubane cluster $Cp_4V_4(P_3)_2$ **61**.

The reaction of $Cp^*V(CO)_4$ and Me_3SiN_3 has been shown to proceed, either under irradiation (argon) or under oxygen, with the formation of various pentavalent vanadium species containing oxo, silyloxo, imido, or azido groups.[207] Excess of Me_3SiN_3 leads to the triazido-vanadium(IV) complex $[Cp^*V(\mu\text{-}N_3)(N_3)_2]_2$. The imido–zirconium complex $Cp_2Zr({=}NBu^t)(THF)$ when treated with $CpV(CO)_4$ in THF-d^8 affords the binuclear complex $\{Cp_2Zr\}_2(\mu\text{-}NBu^t)(\mu\text{-}O)$ along with the corresponding deoxygenated metal–carbonyl isocyanide known[208] complex $CpV(CO)_3(CNBu^t)$.[209]



Scheme 23

5.01.4.1.1.(iii) Applications

Although $CpV(CO)_4$ in the presence of N-methylpyrrolidinone is an effective catalyst for the O_2-allylic oxidation of cyclohexene into cyclohexenone,[210] it is mainly used for its reductive properties. Highly stereoselective room-temperature reduction of *gem*-dibromocyclopropanes to bromocyclopropanes is catalyzed by $CpV(CO)_4$ in combination with zinc in the presence of diethylphosphonate.[211] A related catalytic system based on the use of $CpV(CO)_4$ in the presence of zinc powder and trimethylchlorosilane in DME at room temperature is efficient for C–C bond formation in the reductive coupling of aldehydes to 1,3-dioxolanes.[212] By switching the solvent from DME to THF, the product selectivity dramatically changed, providing 1,2-diols.[213] The pinacol coupling of secondary aliphatic aldehydes is achieved with excellent diastereoselectivity. Similarly, the system $CpV(CO)_4/PhMe_2SiCl/Zn$ catalyzes the reductive coupling of aldimines into 1,2-diamines with high *meso*-selectivity.[214]

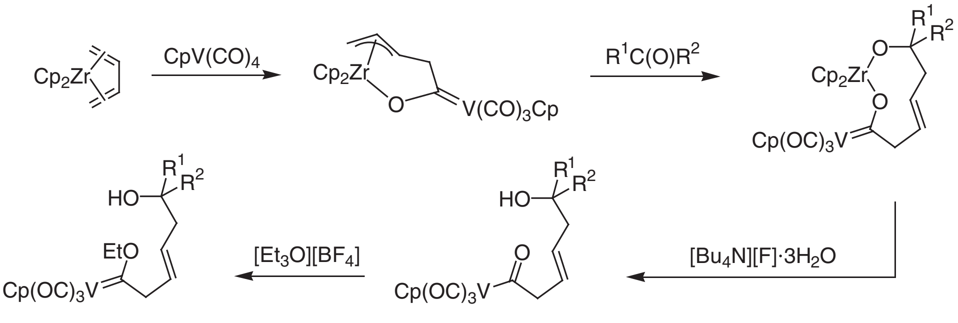
5.01.4.1.2 Polynuclear carbonyls

Highly reactive group 4 (butadiene)metallocene (Zr, Hf) reacts with $CpV(CO)_4$ to yield a π-allyl metalloxycarbene vanadium complex (see Scheme 24), which has been trapped with ketones, aldehydes, or nitriles to give the nine-membered metallacyclic metalloxycarbene vanadium complex.[215–217] X-ray structure determinations reveal V═C distance of 2.096(2) in the Zr complex and 2.086(5) in the Hf analog. Subsequent hydrolysis gives the Zr/Hf-free acyl–vanadate complex that can be O-alkylated with $[Et_3O][BF_4]$ to yield the Fischer-type (alkoxycarbene)vanadium complex.

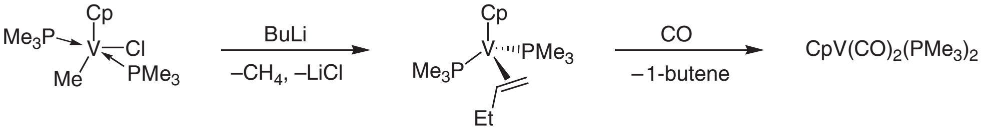
The reaction of $Cp^*V(CO)_2(\eta^4\text{-}P_4)$ with $Cr(CO)_5(THF)$ gives a mixture of binuclear $Cp^*V(CO)_2(\eta^4\text{-}P_4)[Cr(CO)_5]$ and trinuclear $Cp^*V(CO)_2(\eta^4\text{-}P_4)[Cr(CO)_5]_2$ in which the chromium atom is attached to one phosphorus atom of the P_4-ring.[205]

5.01.4.1.3 Monocyclopentadienyl derivatives supported by ligands other than CO

Reaction of vanadium(III) complex $CpV(Me)Cl(PMe_3)_2$ with BuLi produces the 1-butene monovalent complex $CpV(\eta^2\text{-}CH_2{=}CHEt)(PMe_3)_2$ through β-hydrogen abstraction and reductive elimination.[218] A similar ethylene complex was already obtained from analogous reaction with ethyl Grignard reagent.[219] Further exposure of a solution of the alkene complex to CO affords 1-butene and $CpV(CO)_2(PMe_3)_2$ (Scheme 25).



Scheme 24



Scheme 25

5.01.4.2 Other Mono(η^5-Cyclopentadienyl) Complexes

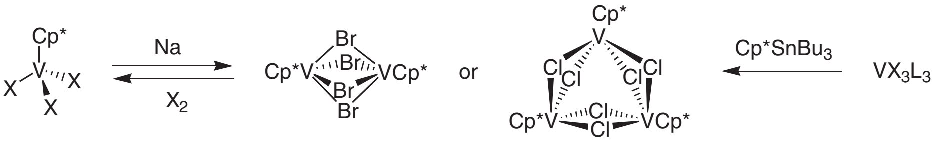
5.01.4.2.1 Vanadium(II) and vanadium(III) complexes

5.01.4.2.1.(i) Halide derivatives

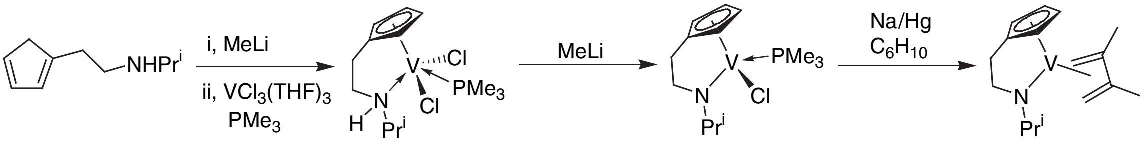
Reductive oligomerization of (η^5-C_5Me_4R)VX_3 [R = Me, Et; X = Br, Cl] with Na/Hg (1 equiv.) in toluene yields the organodivanadium(III) bromide complex [(η^5-C_5Me_4R)V(μ-Br)$_2$]$_2$ or the organotrivanadium(III) chloride cluster [(η^5-C_5Me_4R)V(μ-Cl)$_2$]$_3$ in 90% and 71% yields, respectively.[220] The nuclearity is halide dependent, and both oligomers can be prepared more conveniently and directly, by the addition of Sn(C_5Me_4R)Bu^n_3 to dichloromethane solution of VX_3L_3 [X = Br, L = tetrahydrothiophene, X = Cl, L = THF] at room temperature, in 60% and 80% yields, respectively (Scheme 26).[220] The complete synthesis and physical properties of [Cp*VCl_2]$_3$ have also been reported by two other separate groups.[221–223] Alternatively, [Cp*V(μ-Cl)$_2$]$_3$ has been prepared by slight variations in the reaction conditions (solvent, temperature): addition of Sn(C_5Me_4R)Bu^n_3 to a warm (60 °C) toluene solution of VCl_3(THF)$_3$,[221,222] or the reverse RT addition of the same reagents in toluene:benzene, followed by heating at 55 °C.[223] These experimental conditions, not only for reaction but also crystallization, greatly determine the purity of the sample (and complicate the magnetic properties) that can contain variable amounts of VCl_3 and THF,[220] and has been shown to crystallize in a mixture of crystals of two different forms.[224] Treating [Cp*V(μ-Cl)$_2$]$_3$ with Me_3SnF affords [Cp*V(μ-F)$_2$]$_4$, whose tetrameric arrangement has been elucidated via an X-ray analysis.[225] Furthermore, these Cp*–halide complexes are useful synthons for the development of organovanadium chemistry, giving access to alkyl (Section 5.01.4.2.1), oxo (Section 5.01.4.3.1), nitrido (Section 5.01.4.3.1), and higher-valent halide (Section 5.01.4.3.1) derivatives that are described in the appropriate sections of this chapter.

Cyclopentadienyl or monoalkyl substituted cyclopentadienyl derivatives appear to have lower stability than their Cp* analogs (COMC (1995) Volume 5, Chapter 1, Section 5.01.5.1.1), and have only been obtained as phosphine adducts Cp′VX_2(PR_3)$_2$ [Cp′ = Cp, Cp^{Me}, Cp^{Et}] from the reaction of VCl_3(THF)$_3$ and Cp′M [M = Tl, Na, 1/2Mg, $SnBu^n_3$] in the presence of phosphine to prevent disproportionation. When activated with MAO co-catalyst, Cp′VCl_2(PEt_3)$_2$ [Cp′ = Cp, Cp^{Me}] and indenyl and fluorenyl related complexes have been reported to catalyze 1,3-diene polymerization, leading to polymers with predominantly *cis*-1,4 structure.[226,227] A related reaction between VCl_3(THF)$_3$ and $NaCp^{Me}$, but using *tert*-butylisocyanide instead of phosphine ligands, produces an isocyanide analog $Cp^{Me}VCl_2(CNBu^t)_2$ along with structurally characterized byproduct [$Cp^{Me}_2V(CNBu^t)_2$][VCl_4(THF)$_2$],[73] while in the absence of *tert*-butylisocyanide and using a molar ratio V/NaCp of 1:2, a mixture of Cp^{Me}_2V, $Cp^{Me}_2VCl_2$, and $Cp^{Me_2}VCl$ is obtained.

Similar salt metathesis synthetic routes are used to prepare linked-Cp-amino ancillary paramagnetic vanadium(III) complexes [η^5,η^1-$C_5H_4(CH_2)_2NR_2$]$VCl_2(PMe_3)$ [NR_2 = NMe_2,[228] $NHPr^i$ **62**[229]] (Scheme 27). The X-ray structure confirms the intramolecular coordination of the amine nitrogen atom *trans* to the PMe_3 ligand. However, the amino linkage in these complexes may not be that strong (see item (iv) below, namely "σ-Bonded alkyl, allyl, alkynyl, and alkylidene derivatives") as other very similar amino-substituted cyclopentadienyl ligands are reported to give complexes (such as [η^5-$C_5H_4(CH_2)_2N(CH_2)_5$]$VCl_2(PMe_3)_2$) in which the amino-functionalized side-chain does not



Scheme 26



62 **63** **64**

Scheme 27

coordinate to the metal center.[230,231] Such complexes are reported to behave as butadiene polymerization catalysts (MAO co-catalyst) very differently (in stereoselectivity) from their non-functionalized Cp counterparts, which bears further evidence of the influence of the pendant arm. Further reaction of **62** with MeLi in THF affords the trivalent, paramagnetic, Cp–amide complex **63** (Scheme 27), which can be reduced with Na/Hg in the presence of 2,3-dimethyl-1,3-butadiene into divalent paramagnetic diene complex **64**.[229] Interestingly, the latter could also be prepared from a one-pot reaction starting with $VCl_3(THF)_3$ and the same reagents. Pyridine-substituted cyclopentadienyl complex [5-((2-pyridyl)methyl)-C_5Me_4]VCl_2 is obtained starting from $VCl_3(THF)_3$ and the corresponding lithium salt of the substituted Cp in dichloromethane at 0 °C, and has been used with MAO co-catalyst for ethylene-1-hexene co-polymerization.[232] The synthesis and ethylene polymerization activity of the alkylaminophosphanyl-substituted half-sandwich complex $[\eta^5\text{-}(C_5Me_4(PBu^tNEt_2))]VCl_2(PMe_3)_2$ and its analogs have been reported;[233] however, the amine function in this compound does not bind to the metal center.

5.01.4.2.1.(ii) Carboxylato derivatives

Dinuclear tetra-bridged carboxylato vanadium(III) complexes are generally obtained from the reaction of the corresponding vanadocene or from $CpV(CO)_4$ (COMC (1982) Volume 3, Chapter 24, Section 24.5.4 and COMC (1995) Volume 5, Chapter 1, Section 5.01.5.1.2). The reaction between hindered vanadocene $V(\eta^5\text{-}C_5HPh_4)_2$ and trifluoroacetic acid in benzene under forcing conditions (120 °C, 3.5 atm, 40 h) produces the carboxylate-bridged dimer $(\eta^5\text{-}C_5HPh_4)V(\mu\text{-}O_2CCF_3)_4V(\eta^5\text{-}C_5HPh_4)$, characterized by X-ray diffraction.[234] No reaction is observed with the less acidic benzoic acid.

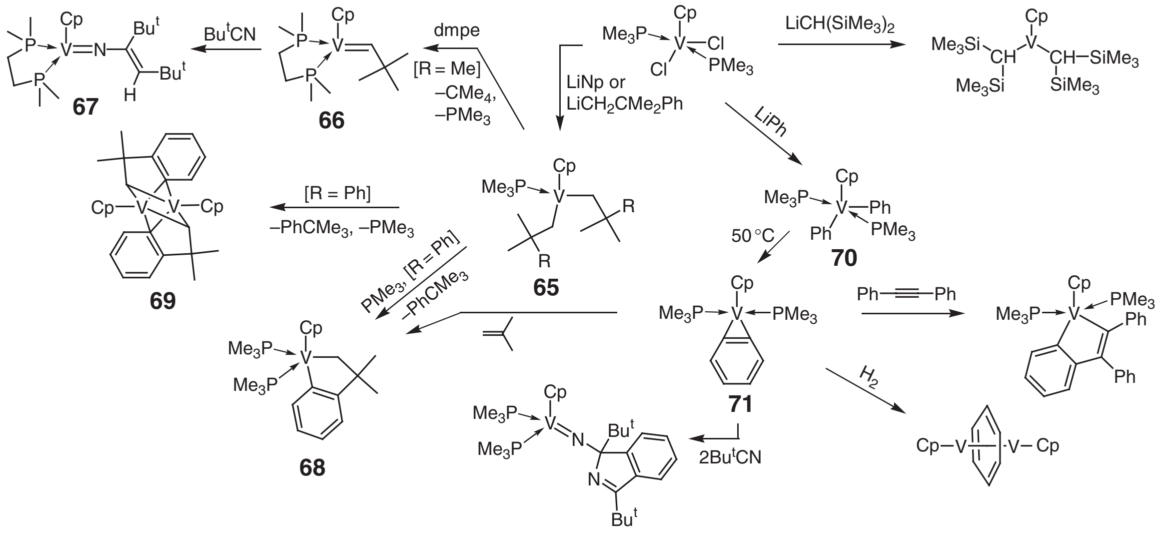
5.01.4.2.1.(iii) Chalcogeno derivatives

Stepwise oxidative decarbonylation of $Cp'V(CO)_4$ [$Cp' = Cp$, Cp^*] with diorganodichalcogenides REER, into diamagnetic $\{Cp'V(CO)_2(\mu\text{-}ER)\}_2$ and paramagnetic $\{Cp'V(\mu\text{-}ER)_2\}_2$, has been extended to tellurides and ferrocenyl-substituted chalcogenolato-bridging compounds [E = S, Se, Te; R = Me, Ph, Fc].[235] Analogous 1,2-benzenedithiolate vanadium(III) dimer complex is also accessible, but from a non-photoinduced route.[236] Bridging sulfido and tellurido bimetallic vanadium(III) complexes $\{Cp'V(CO)_2(\mu\text{-}E)\}_2$ [$Cp' = Cp$, $\eta^5\text{-}C_5H_4Me$; E = S, Te] are prepared from similar synthetic routes either by photolysis of $Cp'V(CO)_4$ or from thermal reaction starting with $Cp'V(CO)_3(SMe_2)$ precursor, and appropriate chalcogenido source H_2S or $TePBu^n{}_3$.[237] Thermolysis (50 °C) of the methyl-substituted above dinuclear species affords tetranuclear pseudocubane clusters $\{Cp'V(\mu^3\text{-}E)\}_4$. These compounds are also prepared by chalcogen abstraction with $PBu^n{}_3$ or $NiCp_2$ in pentachalcogenide $Cp'_2V_2E_5$ (E = Se) or tetrachalcogenide $Cp'_2V_2E_4$ [$Cp' = Cp$, $\eta^5\text{-}C_5H_4Me$; $E_4 = Se_4$, Se_2S_2, Te_2S_2].

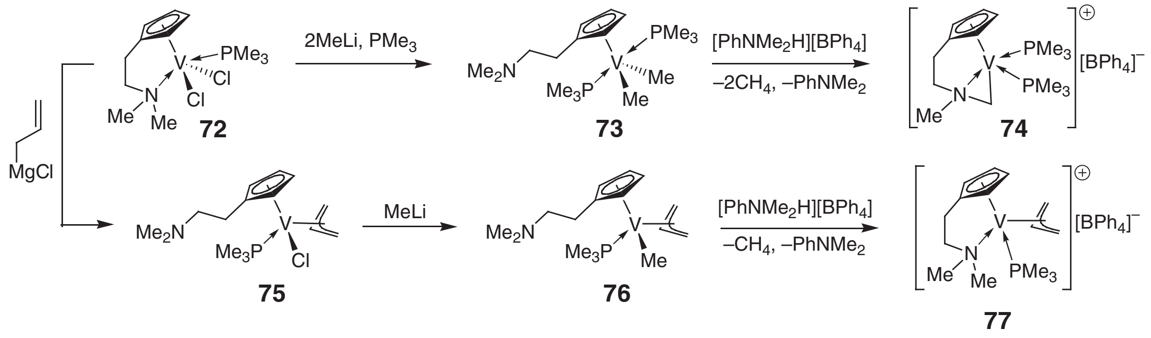
5.01.4.2.1.(iv) σ-Bonded alkyl, allyl, alkynyl, and alkylidene derivatives

Halide replacement with alkyl reagents in easily available $CpVCl_2(PMe_3)_2$ led to a range of organovanadium derivatives of general formula $CpVR_2(PMe_3)_2$, which have been the subject of an extensive research activity (COMC (1995) Volume 5, Chapter I, Section 5.01.5.1.4). Further new developments of the reactivity of such species have been described and are detailed here. By the use of sterically more demanding alkyl groups, electron-deficient paramagnetic vanadium(III) dialkyls $CpV(CH_2CMe_2R)_2(PMe_3)$ **65** [R = Me, Ph] and $CpV[CH(SiMe_3)_2]_2$ have been synthesized (Scheme 28).[218] At ambient temperature, $CpV(CH_2CMe_3)_2(PMe_3)$ **65a** decomposes through α-hydrogen abstraction to produce, in the presence of dmpe, the first vanadium(III) alkylidene **66** with a short V═C bond length of 1.809(3) Å indicative of a true alkylidene complex. A summary of V═C bond distances in vanadium alkylidene or Fischer carbene complexes is presented in Table 13 (along with a comparison with complexes described in Sections 5.01.4.1.2, and 5.01.4.3.1, and 5.01.3.3.2). Reactivity of the alkylidene complex **66** with Bu^tCN leads to the formation of the rare imido complex of trivalent vanadium **67**. In contrast, $CpV(CH_2CMe_2Ph)_2(PMe_3)$ **65b** decomposes in the presence of excess PMe_3 through orthometallation of the aryl substituent to give the metallacycle complex **68**. In the absence of excess PMe_3, the $(\mu\text{-alkyl})_2(\mu\text{-aryl})_2$ dimer **69** is formed, with a short metal–metal distance (2.313(2) Å).

The diphenyl analog $CpVPh_2(PMe_3)_2$ **70** decomposes at 50 °C through β-H abstraction and elimination of benzene to give the first-isolated vanadium–benzyne complex **71** in 50% yield (Scheme 28).[238] Spectroscopic data and structural parameters indicate that this compound can best be described as a high spin d^2-vanadium(III) benzometallacyclopropene complex. The cyclopropene character is expressed in the reactivity of this complex, showing insertion of unsaturated substrates (diphenylacetylene, terminal alkenes, *tert*-butylisonitrile) to produce C,C-coupled products. The benzyne complex also reacts with H_2 to form the known triple-decker $CpV(\eta^6\text{-}C_6H_6)VCp$ through partial hydrogenation of the benzyne ligand. Starting from the same precursor $CpVCl_2(PMe_3)_2$, paramagnetic



Scheme 28



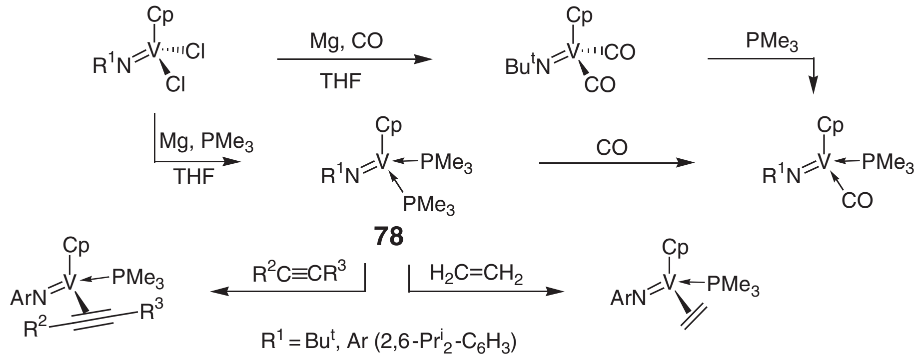
Scheme 29

phenylethynyl complexes $CpVCl_{2-n}(C{\equiv}CPh)_n(PMe_3)_2$ [$n = 1, 2$] are also synthesized and appear to be thermally more stable than other Cp–vanadium(III) hydrocarbyl complexes.[238] The mixed alkynyl–chloride complex reacts with 1 equiv. of $LiBH_4$ to produce the trivalent vanadium borohydride complex $CpV(\eta^2\text{-}BH_4)(C{\equiv}CPh)(PMe_3)$.

Alkylation of the the Cp–amine vanadium(III) **72** with 2 equiv. of MeLi in the presence of PMe_3 yields the corresponding dimethyl **73**,[228] in which the pendant amine arm is now decoordinated in favor of the binding of a second phosphine ligand, as confirmed by X-ray analysis (Scheme 29) (see also item (i), namely "Halide derivatives"). This neutral dimethyl compound reacts with $[NHMe_2Ph][BPh_4]$ but does not generate the expected cationic monomethyl derivative. Instead, 2 equiv. of methane are released with concomitant formation of ionic **74**, in which an Me group of the pendant NMe_2 arm is metallated. With the same ligand set, neutral allyl and mixed methyl–allyl complexes, **75** and **76**, are being prepared by similar methods. Protonation of the latter with $[NHMe_2Ph][BPh_4]$ occurs exclusively at the Me group to yield the ionic allyl complex **77**.[228] DFT studies suggest that these systems have potential high catalytic activity for ethylene polymerization.[239]

5.01.4.2.1.(v) Half-sandwich and mixed sandwich complexes

Reduction of half-sandwich imido–vanadium(V) dichloride $CpV({=}NAr)Cl_2$ [$Ar = 2,6\text{-}Pr^i{}_2C_6H_3$] with magnesium in the presence of trimethylphosphine yields the diamagnetic vanadium(III) bis(trimethylphosphine) complex $CpV({=}NAr)(PMe_3)_2$ **78** (Scheme 30) which represents a rare example of a trivalent imido–vanadium compound.[240] One of the PMe_3 ligands in this complex can be substituted by CO, ethylene, or diphenylacetylene, to give the corresponding π-acceptor (L) vanadium(III) complexes $Cp({=}NAr)(L)(PMe_3)$. Analogous $CpV({=}NBu^t)L_2$ [$L = PR_3$, $P(OR)_3$, CO] are prepared by similar reductive dehalogenation of the parent dichloride precursor with Mg in the



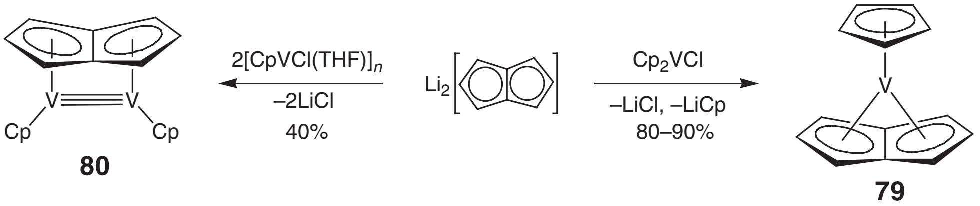
Scheme 30

presence of L,[241] and the bis(phosphine) complex presents similar coordination chemistry toward addition of donors (CO, alkenes, alkynes, phosphaalkynes, nitriles, ketones). Alkylidene transfer from phosphorane $Ph_3P{=}CHPh$ to **78** proceeds with the loss of PMe_3 and PPh_3, and produces the first vanadium(V) alkylidene complex $CpV({=}NAr)({=}CHPh)(PMe_3)$[240] (see the Section 5.01.4.3.1).

The known[242] CpVTp has been obtained with improved yield (57%) by slight modification[71] of the workup procedure in the reaction of Cp_2VCl and KTp in THF, which involves reduction of the metal center and displacement of one Cp ligand. CpVTp shows temperature-independent magnetic moment of 3.69 μ_B consistent with a high spin d^3-configuration, and isotropic room-temperature EPR spectrum, with $g_{iso} = 1.993$ and $A_{iso} = 59.2$ G.[243] Oxidation of CpVTp with $[FeCp_2][BAr^F_4]$ [Ar^F = 3,5-bis(trifluoromethyl)phenyl] in dichloromethane yields the vanadium(III) 14-electron species $[CpVTp][BAr^F_4]$, which upon treatment with donors L affords the corresponding adducts $[CpVTp(L)][BAr^F_4]$ (L = PMe_3, $CNBu^t$).[71] $[CpVTp][BAr^F_4]$ has a $\mu_{eff} = 2.84$ μ_B, close to the spin-only value for an $S = 1$ species.[243]

Treatment of vanadocene monohalides Cp_2VX [X = Cl, Br] with the dilithium salt of the pentalene dianion $Li_2[C_8H_6]$, or its methyl-substituted analog, proceeds with the elimination of one Cp and the halide ligand, and results in the formation of the diamagnetic trivalent complex $CpV(\eta^8\text{-}C_8H_6)$ **79** as illustrated in Scheme 31.[244,245] The corresponding trimethylsilylcyclopentadienyl-, pentamethylcyclopentadienyl-, and indenyl-pentalene congeners are prepared similarly starting from the appropriate precursors. These complexes are all obtained in high yields (80–90%) as thermally stable and sublimable solids. Remarkably, as pointed out by X-ray analyses, the 10-electron dianionic ligand in these complexes adopts a new mode of coordination of pentalene in which all eight carbon atoms are coordinated to one metal center. A direct consequence of the η^8-coordination is the strong folding of the bicyclic π-ligand by 137° toward the vanadium along the central carbon–carbon bond between the bridgehead carbon atoms. DFT studies could reproduce this fold angle.[246] A subsequent article by the same authors reports similar structural features in related Ti- and Zr-pentalene complexes.[247] (See Chapters 4.04 and 4.07.)

Bimetallic pentalene-bridge complex $[CpV]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_8H_6)$ **80** is generated by the reaction of $Li_2(C_8H_6)\cdot x$DME with 2 equiv. of divalent $[CpVCl(THF)]_n$.[248] In contrast to the above η^8-pentalene vanadium complexes, **80** exhibits a rare *syn*-coordination of the two metal centers to the same face of the pentalene (Scheme 31), which now requires a folding away from planarity. According to an X-ray study, it presents an unusually short V–V bond (2.5380(5)Å), which is suggested on the basis of DFT calculations to be a rare example of a V–V triple bond. ^{1}H NMR and magnetic studies



Scheme 31

indicate that, both in solution and in the solid state, the complex exhibits a high spin/low spin equilibrium. Unstable in solution at room temperature, 80 decomposes over a period of days to complex 79, presumably by disproportionation.

The stabilizing tricarbadecaboranyl ligand enabled the synthesis of air- and water-stable, 16-electron vanadium(III) monobromide tricarbadecaboranyl complex [1-Cp-1-Br-2-Ph-1,2,3,4-$C_3B_7H_9$], obtained by the reduction of $CpVBr_3$ with [Li][6-Ph-5,6,9-$C_3B_7H_9$].[249] This tricarbadecaboranyl vanadium complex has been reported to be a potent cytotoxic agent against murine and human leukemia and lymphoma growth, as well as HeLa suspended uterine carcinoma, and most significantly inhibits the growth of cultured human solid tumors.[250] The tricarbadecaboranyl anion [6-Me-*nido*-5,6,9-$C_3B_7H_9$]$^-$ reacts with VBr_2 in refluxing toluene to give [6-Me-$C_3B_7H_9$]$_2$V in 47% yield,[251] which can be regarded as an analog of Cp_2V. Preparative thin-layer chromatography (TLC) allows the separation of five vanadatricarbadecaboranyl isomers with a sandwich-like structure, all being structurally characterized. Unlike high spin Cp_2V, these compounds have a low spin configuration with one unpaired electron, and due to the strong stabilization of the tricarbadecaboranyl ligands, they are surprisingly air- and water-stable and do not react with oxidants (Br_2, Ag^+). Electrochemical studies confirm that behavior. Unexpectedly, using VCl_3 and VCl_4 precursors (in place of VBr_2) lead to the same [6-Me-$C_3B_7H_9$]$_2$V complexes instead of the expected bis(tricarbadecaboranyl) halides.

5.01.4.2.2 Vanadium(IV) and vanadium(V) complexes

5.01.4.2.2.(i) Halide derivatives

The very air sensitive monomeric $Cp'VX_3$ ($Cp' = Cp$, Cp^*, Cp^{Me}, C_5Me_4Et) is prepared by oxidation of $Cp'V(CO)_4$ with X_2 or by treatment of $Cp_2'VX_2$ with $SOCl_2$ as described in COMC (1995) Volume 5, Chapter 1, Section 5.01.5.2.1). Interestingly, $SOCl_2$ could be substituted by chlorine gas in the reaction with $Cp_2'VCl_2$ ($Cp' = Cp$, Cp^{Me}) that can be used for large-scale (39 g) production of $Cp'VCl_3$ and with reasonable yields (52%).[252] Halogenation of $[(C_5Me_4R)VX_2]_n$ ($X = Br$, $n = 2$; $X = Cl$, $n = 3$) with X_2 gives the corresponding $(C_5Me_4R)VX_3$ in good yield.[220] $CpVCl_3$ is easily converted into $CpVBr_3$ upon treatment with BBr_3.[253]

The reaction of Cp^*VX_3 with large excess of Me_3SiN_3 results in a stepwise substitution of the chlorine atoms by azido ligands, leading to the paramagnetic azido-bridged complexes $[Cp^*VCl_2(\mu\text{-}N_3)]_2$, $[Cp^*VCl(N_3)(\mu\text{-}N_3)]_2$, and $[Cp^*V(N_3)_2(\mu\text{-}N_3)]_2$.[254] The latter is also formed in lower yield from $Cp^*V(CO)_4$ and excess Me_3SiN_3 in pentane (see Section 5.01.4.1.1).[207] When activated with an aluminum or a borate co-catalyst, $CpVX_3$ complexes ($X = Cl$, OR, NR_2) and ring-substituted analogs are known to catalyze the polymerization of conjugated dienes giving rubbers with ca. 90% *cis*-1,4-microstructure.[255,256]

Linked Cp–amide tetravalent vanadium complex $[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2NPr^i]VCl_2$ is prepared by reacting the corresponding divalent diene complex $[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2NPr^i]V(\text{diene})$ (diene $= \eta^4\text{-}C_6H_{10}$) with $PhICl_2$.[229] Although details on the preparation and yield are not reported, a disproportionation reaction is probably at the origin of the formation of the analogous complex $[\eta^5,\eta^1\text{-}C_5Me_4(SiMe_2)NBu^t]VCl_2$ from $VCl_3(THF)_3$ and the disodium salt of the Cp–amide ligand.[257] When activated with MAO, both of these "constrained-geometry" catalysts polymerize ethylene[229] and 1,3-pentadiene.[257]

5.01.4.2.2.(ii) Oxo derivatives

Oxo-vanadium(IV) and (V) complexes containing an additional Cp ligand have been obtained by multiple routes that have been described earlier; one of these routes involves the oxidative chlorination (with O_2/HCl or O_2/Cl_2) of lower-valent cyclopentadienyl precursors into $CpV({=}O)Cl_2$ or its ring-alkylated derivatives. (COMC (1995) Volume 5, Chapter 1, Section 5.01.5.2.1). Oxidative decarbonylation of $CpV(CO)_4$ with thionyl chloride affords the monomeric pentavalent dichloride complex $CpV({=}O)Cl_2$ in 72% yield.[258] As for the permethylated Cp analog $Cp^*V({=}O)Cl_2$,[259] an X-ray structure analysis of $CpV({=}O)Cl_2$ reveals a pseudo-tetrahedral "piano stool" configuration for the metal center with a V=O bond distance of 1.590(1) Å. Relevant spectroscopic data are reported in Table 14. Although commercially available $VOCl_3$ has been used with Cp_2Mg for the synthesis of $CpV({=}O)Cl_2$, this procedure suffered from problems of reduction that needed a further step (treatment with O_2/HCl) and only low yields (23%) were obtained.[260] Recently, it was shown that DME helps to stabilize the oxidation state +V of vanadium in such alkylation reactions, and indeed, the adduct $VOCl_3$·DME reacts with CpLi in benzene at room temperature to afford $CpV({=}O)Cl_2$ in 52% yield.[261] This makes simple $VOCl_3$·DME a very convenient starting material for such a transformation, which should also be suitable for the synthesis of ring-substituted congeners.

Decarbonylation of $Cp^*V(CO)_4$ with dioxygen in pentane leads to tetrameric vanadium(IV) dioxide complex $[Cp^*V({=}O)(\mu\text{-}O)]_4$,[194] which is a precursor of the octanuclear aggregate $Cp^*_6V_8O_{17}$. The tetrameric structure has been established by single crystal X-ray diffraction, and consists of an eight-membered ring of alternating $Cp^*V({=}O)$ units and oxo bridges with V=O av. = 1.613(8) and V–O av. = 1.802(8) Å (Cp^*–V = 2.039 Å). A comparative summary

Table 14 Spectroscopic data for $CpV({=}O)Cl_2$ and $Cp^*V({=}O)Cl_2$

Complex	*IR* (cm^{-1})	*Solvent/NMR*	δ^1H	$\delta^{13}C$	$\delta^{51}V$	*References*
$CpV({=}O)Cl_2$	968	C_6D_6	5.71	[a]		258
$Cp^*V({=}O)Cl_2$	967	$CDCl_3$[b]	2.31–2.33	13.3, 133.5	−31	221
$[Cp^*V({=}O)(\mu\text{-}O)]_4$	959, 927(V=O) 800, 722 (V–O)	C_6D_6	2.21, 2.14, 2.10[c]		−628, −649[d]	194

[a] $CDCl_3$ 120.7 ($\delta^{13}C$).
[b] C_6D_6 1.80(δ^1H), −49($\delta^{51}V$)[223].
[c] Ratio 1 : 2 : 1.
[d] Ratio 3 : 1.

of pertinent spectroscopic data is listed in Table 14. Organometallic high spin clusters $(CpV)_4O_4$, $(CpV)_5O_6$, and $(CpV)_6O_n$ ($n = 6$–8) are generated by photochemical reaction of $CpV(CO)_4$ in dichloromethane with fine control of dioxygen concentration.[262] $(CpV)_4O_6$ and related compounds have also stimulated theoretical studies based upon *ab initio*[263] and extended Hückel[264] calculations. In a more or less similar way, oxo-vanadium(V) complexes are formed in the reaction of $Cp^*V(CO)_4$ with trimethylsilylazide in the presence of oxygen.[207]

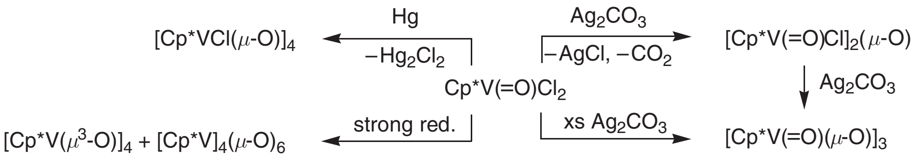
The new high yield preparation of $\{Cp^*V(\mu\text{-}Cl)_2\}_3$ (see Section 5.01.4.2.1) makes its oxidation by O_2 a very convenient and efficient way to synthesize $Cp^*V({=}O)Cl_2$ (yield 65–93%).[221–223] The fluoride precursor $\{Cp^*V(\mu\text{-}F)_2\}_4$ reacts with O_2 in toluene in a similar way, but a mixture of $Cp^*V({=}O)F_2$ and $\{Cp^*V({=}O)F\}_2(\mu\text{-}O)$ is obtained.[225]

Reduction of $Cp^*V({=}O)Cl_2$ with strong reductants (Na, K, Mg, Ca, or their amalgams) gives a mixture of three products: black cubane-like paramagnetic cluster $[Cp^*V(\mu^3\text{-}O)]_4$ ($\mu_{eff} = 2.35\,\mu_B$), black-green adamantane-like diamagnetic cluster $[Cp^*V]_4(\mu\text{-}O)_6$, and purple $\{Cp^*V(\mu\text{-}Cl)_2\}_3$ or an unidentified black material (Scheme 32).[265] The key intermediate is assumed to be the dimer $[Cp^*V({=}O)Cl]_2$. The reductant does not modify the ratio of these species, but the solvent greatly influences the reaction; the formation of $[Cp^*V(\mu^3\text{-}O)]_4$ being favored in THF, whereas $[Cp^*V]_4(\mu\text{-}O)_6$ is favored in toluene. Reduction of $Cp^*V({=}O)Cl_2$ with the milder reductant mercury affords paramagnetic ($\mu_{eff} = 4.51\,\mu_B$) $[Cp^*VCl(\mu\text{-}O)]_4$ as brown needles in 65% yield. Treatment of $Cp^*V({=}O)Cl_2$ with equimolar amounts of Ag_2CO_3 produces the known dark-green vanadium(V) $[Cp^*V({=}O)Cl]_2(\mu\text{-}O)$ in higher yield (64%)[265] than the previously reported[266] synthesis involving the reaction of Cp^*VCl_3 with $Cp^*V(CO)_4/O_2$. With an excess of Ag_2CO_3, $Cp^*V({=}O)Cl_2$ is converted into trinuclear $[Cp^*V({=}O)(\mu\text{-}O)]_3$, presumably via the intermediacy of $[Cp^*V({=}O)Cl]_2(\mu\text{-}O)$.[265]

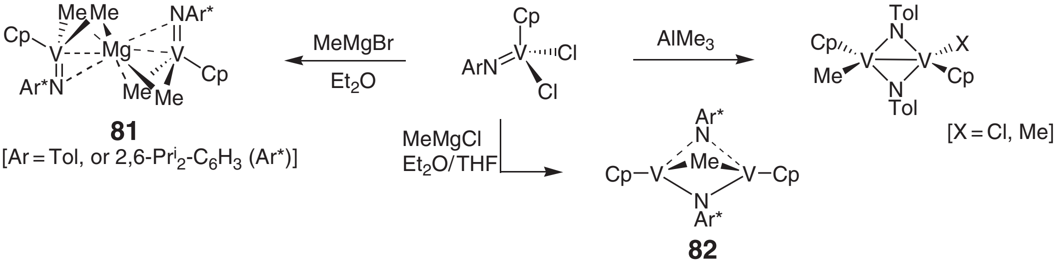
5.01.4.2.2.(iii) Imido derivatives

Pentavalent Cp–imido vanadium derivatives $(RN{=})VCpCl_2$ have been obtained upon treatment of $(RN{=})VCl_3$ with CpLi [R = Bu^t][170] or $CpSiMe_3$ [R = aryl][240,267]. Indenyl analog $(Bu^tN{=})V(\eta^5\text{-}C_9H_5)Cl_2$[268] and other ring-alkylated cyclopentadienyl derivatives $(Bu^tN{=})VCp^RCl_2$[269] are prepared similarly. Arylimido $(ArN{=})VCpCl_2$ derivatives can also be prepared by an imido exchange route from *tert*-butylimido precursor;[270,271] this strategy has been used for covalently attaching Cp–vanadium catalyst to amino-functionalized polystyrene resins.[272] Pentavalent $(Bu^tN{=})VCpCl_2$ and $(Bu^tN{=})VCpCl_2(PMe_3)$ are also formed by disproportionation reaction of tetravalent $V(NBu^t)Cl_2L$ [L = DME, $2PMe_3$].[168,170] Highly oxophilic dimer $[(Me_3SiN{=})VCp^*(\mu\text{-}NSiMe_3)]_2$, which contains both terminal and bridging imido groups, is formed upon addition of 2 equiv. of $LiN(SiMe_3)_2$ to $Cp^*V({=}O)Cl_2$.[207] Many of these Cp–imido vanadium compounds are active catalysts in olefin polymerization[174,272–275] as are their non-Cp parent complexes.[167,173,176,276,277]

Mixed alkoxides, amides, phosphides, or amidinates of the type $(Bu^tN{=})VCpCl(X)$ (X = OR, NR_2, amidinate, PR_2) are readily accessible by further chloride replacement in $(RN{=})VCpCl_2$ with the corresponding lithium reagents,[278–280] or from the reaction of the alkoxo/amido precursors $(Bu^tN{=})VCl_2(X)$ with LiCp (Cp = Cp, indenyl).[180,268,280]



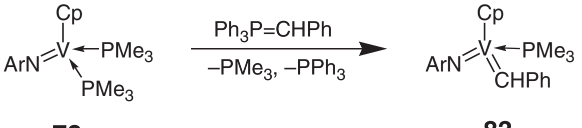
Scheme 32



Scheme 33

Attempted direct dialkylation of arylimido (ArN=)VCpCl$_2$ [Ar = 2,6-Pr^i-C$_6$H$_3$] with alkylating reagents did not allow the isolation of the pure dialkyl complexes but showed extensive reduction/decomposition of the (ArN=)VCp fragment (Scheme 33).[267] Using Grignard reagent MeMgBr affords the tetravalent complex **81** with two methyl groups bridging the vanadium atom of the (ArN=)VCp fragment and the Mg core.[270] In contrast, in Et$_2$O/THF (ArN=)VCpCl$_2$ reacts with an excess of MeMgCl to produce the very unusual, paramagnetic, mono μ-Me complex **82**. These two products provide an explanation for the rapid deactivation of such Cp–imido procatalysts observed during ethylene polymerization. Reduction of (p-Tolyl-N=)VCpCl$_2$ to mixtures of half-sandwich imido-bridged vanadium(IV) dimers [CpV(μ-N-p-Tolyl)]$_2$(Me)(X) [X = Cl or Me] is also reported when using AlMe$_3$ in toluene.[267] Treatment of this mixture with HCl leads to pure diamagnetic tetravalent chloride complex [CpV(μ-N-p-Tolyl)Cl]$_2$ which can be further methylated with MeLi to afford diamagnetic [CpV(μ-N-p-Tolyl)Me]$_2$. The latter is surprisingly unreactive toward Brœnsted acids and small molecules, but does react slowly with CO to generate η^2-acyl complexes. Multinuclear (^{51}V and ^{14}N) NMR spectroscopy has proved to be a useful tool for the electronic environment and structure assignment in these Cp–imido vanadium(V) and diamagnetic vanadium(IV) complexes.[267,281] A comparison of structural parameters in Cp–imido–vanadium complexes is given in Table 15.

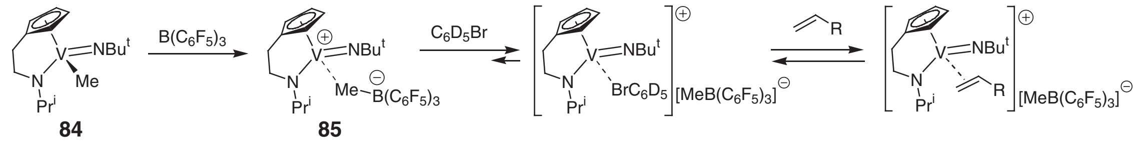
Oxidation of vanadium(III) precursors CpV(=NBu^t)(PMe$_3$)$_2$ with S$_8$, Se, Te, or I$_2$ produces diamagnetic dinuclear imido–vanadium(IV) complexes [VCp(μ-NBu^t)]$_2$(μ-E) (E = S, Se, Te), [VCp(μ-NBu^t)]$_2$(μ,η^1-E$_2$) (E = Se, Te), [VCp(μ-NBu^t)I]$_2$, or vanadium(V) complexes CpV(=NBu^t)(S$_5$) and CpV(=NBu^t)I$_2$.[282,283] Alkylidene transfer from phosphorane Ph$_3$P=CHPh to the arylimido vanadium(III) analog **78** proceeds with loss of PMe$_3$ and PPh$_3$ (Equation (3)), and produces the first vanadium(V) alkylidene complex **83**,[240] the structure of which has been established by X-ray study (Table 15). Due to its coordinative and electronic saturation and lack of phosphine dissociation, this benzylidene complex presents no activity in ROMP of norbornene and no reaction with acetone.



78 **83** (3)

Table 15 Selected structural parameters in Cp–imido–vanadium complexes

Complex	*V–N*$_{imido}$ (Å)	*V–Cp*$_c$ (Å)	*Other* (Å)	*References*
(PhN=)VCpCl$_2$	1.653(4)	1.968(6)		271
[(ArN=)VCp(μ-Me)]$_2$(μ-Mg) **81**	1.724(6)		V–Me 2.200, 2.227(7)	270
[CpV(μ-NAr)]$_2$(μ-Me) **82**	1.867, 1.882(3)		V–Me 2.215, 2.310(4) V–V 2.324(1)	270
[CpV(μ-N-p-Tolyl)Me]$_2$	1.851(2)		V–Me 2.090(4) V–V 2.5095(6)	267
(Bu^{t}N=)V(η^5-C$_9$H$_5$)(OBu^t)Cl	1.640(3)	2.067(2)		268
[η^5,η^1-C$_5$H$_4$(CH$_2$)$_2$NPr^i]V(=NBu^t)Me **84**	1.656(2)		V–Me 2.103(3) V–N$_{amido}$ 1.854(2)	284
CpV(=NAr)(=CHPh)(PMe$_3$) **83**	1.679(5)	1.990(3)	V=C 1.922(6)	240

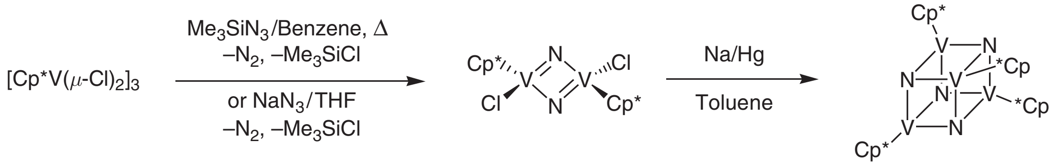


Scheme 34

Dimethylamine elimination in the reaction of the imido complex (Bu^{t}N═)VCl(NMe$_2$)$_2$ with C$_5$H$_5$(CH)$_2$NHPr^i affords the Cp–amido vanadium(v) complex [η^5,η^1-C$_5$H$_4$(CH$_2$)$_2$NPr^i]V(═NBu^t)Cl, which is easily converted with MeLi into the corresponding methyl derivative **84** (Scheme 34).[284] Further reaction with B(C$_6$F$_5$)$_3$ generates the ionic **85**. As indicated by ^{19}F NMR spectroscopy, the latter is present in C$_6$D$_6$ as contact ion pair with substantial interaction between the Me group of the anion and the cationic metal center, while in C$_6$D$_5$Br the anion is displaced to give a solvated cationic species that can strongly and reversibly coordinate olefins upon addition of ethylene or propylene.

5.01.4.2.2.(iv) Nitrido derivatives

Oxidation of [Cp*V(μ-Cl)$_2$]$_3$ with Me$_3$SiN$_3$ in refluxing benzene,[285] or NaN$_3$ in THF,[221] produces the symmetric dimeric vanadium(v) nitrido complex [Cp*V(μ^2-N)Cl]$_2$ in good yield (Scheme 35). An azido derivative of this nitrido compound, [Cp*V(μ^2-N)(N$_3$)]$_2$, is formed upon addition of HN[(SiMe$_2$)$_2$(CH$_2$)$_2$] at room temperature to the triazido complex [Cp*V(N$_3$)$_2$(μ-N$_3$)]$_2$.[207] The X-ray diffraction analysis of these two nitrido species indicates a planar, almost-square V$_2$N$_2$ core, with multiple bonding of the nitrido group to the metal centers (see Table 16 for structural and spectroscopic data). The absence of reactivity of this compound towards strong donors (Py, PMe$_3$) or Me$_3$SiCl is indicative of a strong and stable V–N–V interaction. Reduction of [Cp*V(μ^2-N)Cl]$_2$ with sodium amalgam gives the diamagnetic cubane cluster [Cp*V(μ^3-N)]$_4$, which has a shorter V–N bond than in the parent compound (Table 16).[286a] The structural parameters, in conjunction with ^{51}V NMR data, suggest a very strong V–N nitride bond, whereas DFT calculations[286b] suggest the possible contribution of metal–metal bonding interactions. [Cp*V(μ^3-N)]$_4$ can be reversibly reduced electrochemically at +0.16 V.



Scheme 35

Table 16 Spectroscopic and structural data for nitrido–vanadium complexes

Complex	*δ ^{1}H*	*δ ^{13}C*	*δ ^{51}V*	$\nu_{V–N}$ (cm^{-1})	*X-ray*[c]	*References*
[Cp*V(μ^2-N)Cl]$_2$	2.05[a]		−144[a]	720	V–N 1.771(2), V···V 2.561(2), V–N–V 92.6(2), N–V–N 87.4(2)	221,285
[Cp*V(μ^2-N)(N$_3$)]$_2$	1.80[a]	124.8, 11.2[a]	−377[a]	730	V–N 1.769(3)[d], V···V 2.5633(14), V–N–V 92.60(14), N–V–N 87.40(14)	207
[Cp*V(μ^3-N)]$_4$	1.75[b]	114.3, 12.6[b]	+19.2[b]	441	av. V–N 1.87(2), av. V···V 2.674(8)	286

[a] In C$_6$D$_6$.
[b] In CDCl$_3$.
[c] Bond distances in (Å), and angles in degres.
[d] N is the nitrogen atom of the nitride group.

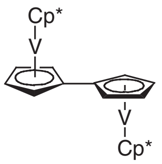
5.01.5 Bis(η^5-Cyclopentadienyl) Complexes

5.01.5.1 Bis(Cyclopentadienyl) Vanadium(II) Complexes

5.01.5.1.1 Synthesis and properties of vanadocenes and ring-substituted derivatives

The unique and stable vanadocene as well as some of its ring-substituted derivatives are easily accessible through a general synthetic procedure which involves the *in situ* reduction of vanadium chlorides (e.g., VCl_3, with Zn, $LiAlH_4$, LiCp) and subsequent reaction with the appropriate alkali metal cyclopentadienide salt. The more convenient and higher yield (80%) procedure for the preparation of Cp_2V in large quantities (ca. 50 g) consists of reacting $[V_2Cl_3(THF)_6]_2[ZnCl_6]$ with NaCp.[287] Since no new methods have come up, for details and comparisons of the various methods available, the reader is referred to the previous editions of COMC (COMC (1982), Volume 3, Chapter 24, Section 24.6.1; COMC (1995), Volume 5, Chapter 1, Section 1.6.1). Recent studies on such VCl_3/Zn/KCp^{ni} mixtures ($Cp^{ni} = C_5(Pr^i)_nH_{5-n}$ with $n = 3$ and 4) leading to the formation of sterically bulky vanadocenes $(Cp^{ni})_2V$ suggest that zincocenes are likely intermediates (Scheme 36), and that zinc complexes will be isolated only when certain Cp rings and temperature conditions are used.[288] A convenient and efficient method for the isolation of pure ring alkylated vanadocenes $(Cp^R)_2V$ [R = Me, Pr^i, Bu^t] (which are often oils of low volatility) involves the drybox purification by chromatography on anhydrous silica gel (yield 55–60%).[289]

The above general procedure of salt metathesis has also been used to prepare a series of amino-functionalized vanadocenes from various amino-substituted cyclopentadienide sodium salts and $[V_2Cl_3(THF)_6]_2[ZnCl_6]$ or $VCl_3(THF)_3/LiAlH_4$ systems.[230,231] Similarly, the reaction of zinc-reduced $VCl_3(THF)_3$ with the dilithium salt of the fulvalene anion and Cp*Li produces, after removing some $Cp^*{}_2V$ by sublimation, the paramagnetic dinuclear fulvalene bridge decamethylvanadocene 86 with 25% yield, in which the two metal centers are weakly antiferromagnetically coupled ($J = -1.6\,cm^{-1}$).[290] Trinuclear metallocenes 87 having terminal ferrocenes or nickelocenes and a central vanadocene, which are Cp-bridged by two adjacent Me_2Si groups, are synthesized using a building-block concept involving in the last step the reaction of $VCl_3(THF)_3$/Zn with the anion of the corresponding metallocene derivative.[291] An X-ray analysis reveals that the bridging ligand is bent, and solid-state magnetic measurements on the NiVNi system show that the interaction is antiferromagnetic with $J = -3.08\,cm^{-1}$. The same bridging ligand is reacted with $[CpVCl(PEt_3)]_2$ to produce dinuclear divalent bridged vanadocenes.[292] Co-condensation of electron-beam generated vanadium vapor with Bu^{t}CP affords the paramagnetic ($\mu_{eff} = 3.58\,\mu B$) complex $V(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)$ in 20–30% yield, in which the phosphorus-containing ring systems result from oligomerization of the phosphaalkyne at the vanadium center.[293]



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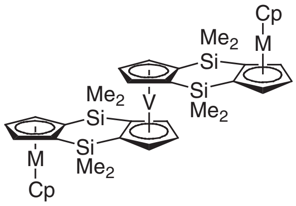

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Multitemperature (108–357 K) X-ray study of vanadocene crystal with careful analysis of the anisotropic displacement parameters suggests a dynamic disorder of the Cp ring.[294] Cp_2V is totally ordered at 108 K, while disorder starts above ca. 170 K. At 108 K, structural parameters (mean V–C 2.269, mean C–C 1.417, V–Cp$_c$ 1.923 Å) are close to those found in the gas phase by electron diffraction.[295] An electron density distribution study was also undertaken on Cp_2V at 108 K,[296] and the electronic structure has been studied using a broad range of DFT methods and compared to other first-row transition metal metallocenes,[297,298] which confirms that the D_{5h} symmetry is the genuine minimum with η^5-Cp ligands. The crystal structures of $[1,3\text{-}(Me_3Si)_2C_5H_3]_2V$[299] and $[Bu^tC_5H_4]_2V$[300] have been reported to exhibit typical sandwich-like structure with almost-planar cyclopentadienyl rings. Structural parameters are listed in Table 17 with a comparison to the few other vanadocenes that have been structurally characterized, including Cp_2V,[301] $Cp^*{}_2V$,[302] and $[C_5HPh_4]_2V$.[303]

$$2VCl_3 + Zn \xrightarrow{THF} 1/2\,[V_2Cl_3]_2[Zn_2Cl_6] \xrightarrow[-2\,MCl]{MCp^{ni}} \{[Cp^{ni}{}_2Zn] + 2\,\text{“}VCl_2\text{”}\} \xrightarrow{\Delta} Cp^{ni}{}_2V + ZnCl_2$$

Scheme 36

Table 17 Comparison of structural parameters in vanadocenes

Complex	*V–C*	*V–Cp$_c$*[a]	*Cp$_c$–V–Cp$_c$*[a]	*C–C*	*References*
Cp_2V[b]	2.269	1.923	180	1.417	294
Cp_2V[c]	2.26	1.92	180	1.42	301
$Cp^*{}_2V$[d]		1.91	177.2		302
$[C_5HPh_4]_2V$	2.268	1.922	180	1.416	303
$[1,2,4\text{-}Pr^i{}_3\text{-}C_5H_2]_2V$	2.274	1.928	180	1.417	288
$[Bu^tC_5H_4]_2V$	2.274	1.935	180	1.404	300
$[1,3\text{-}(Me_3Si)_2C_5H_3]_2V$	2.267	1.92	173.0	1.420	299
$[(MeN(CH_2CH_2)_2CH)C_5H_3]_2V$	2.269	1.93	180	1.41	230

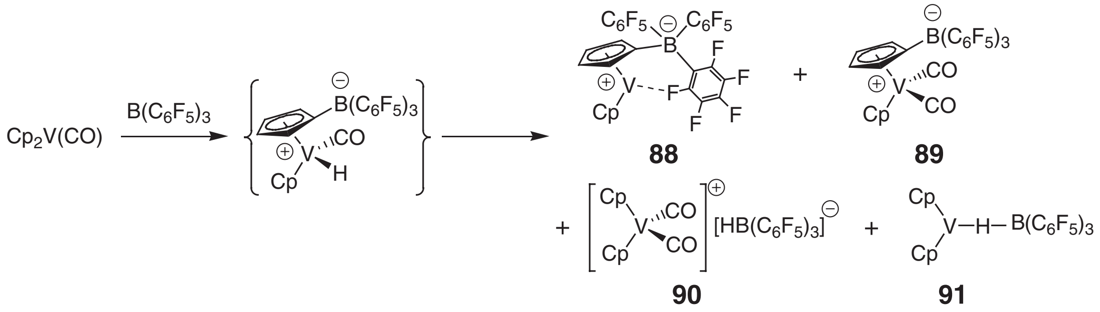
[a] Cp_c denotes the centroid.
[b] At 108 K.
[c] At 295 K.
[d] Disorder prevents accuracy.
All distances are average distances.

5.01.5.1.2 Coordination compounds

5.01.5.1.2.(i) Carbonyl complexes and reactivity of $Cp_2V(CO)$

As illustrated in Scheme 37, the divalent $Cp_2V(CO)$ reacts with the borane $B(C_6F_5)_3$, affording mixtures of the unprecedented zwitterionic ring-borylated vanadium(III) complexes $CpCp^BV$ **88** and $CpCp^BV(CO)_2$ **89** [$Cp^B = \eta_5\text{-}C_5H_4B(C_6F_5)_3$], the ionic vanadium(III) $[Cp_2V(CO)_2][HB(C_6F_5)_3]$ **90**,[304] as well as the neutral $[Cp_2V\text{–}H\text{–}B(C_6F_5)_3]$ **91** with an intriguing hydride bridging the metal center and the boron atom (V–H = 1.87(2) Å, H–B = 1.34(2) Å).[17] Careful separation allowed their isolation and full characterization by means of magnetic measurements, spectroscopic methods (see relevant data in Table 18), and X-ray analysis; the latter reveals that an *ortho*-fluorine atom of one perfluoro phenyl group of the borane in **88** is coordinated to the metal center (V–F = 2.1568(14) Å). These complicated redox and disproportionation reactions are suggested to involve the intermediacy of the hydride $\{CpCp^BV(H)(CO)\}$ generated by the electrophilic addition of the borane $B(C_6F_5)_3$ at the Cp ring of $Cp_2V(CO)$. This reactivity of $Cp_2V(CO)$ toward $B(C_6F_5)_3$ appears very different from that observed with the parent $Cp_2Ti(CO)_2$ which, under identical conditions, was shown to react at the carbonyl function to form unprecedented acylborane complexes.[56]

Reexamination of the reaction between Cp_2V and $V(CO)_6$ that leads, under argon, to ionic $[Cp_2V(CO)_2][V(CO)_6]$ allowed the IR-based characterization, in solution (and by comparison with the permethylated analog, the structure of which has been established by crystallography[305]), of the transient μ-isocarbonyl species $Cp_2V(\mu\text{-}OC)V(CO)_5$.[306] This intermediate is also obtained from the reaction of trivalent Cp_2VCl and $Na[V(CO)_6]$. Experiments conducted with $V(^{13}CO)_6$ followed by treatment with ^{12}CO give $[Cp_2V(^{12}CO)_2][V(^{13}CO)_6]$ and indicate that no distribution of the carbonyl occurs between the two metal centers during the formation of the ionic compound. Reinvestigation of the reaction between Cp_2V and $Co_2(CO)_8$[307,308] allowed to characterize $Cp_2VCo(CO)_4$,[306] whose IR spectrum does not possess bridging carbonyls and thus is proposed to have a V–Co bond. $Cp_2VCo(CO)_4$ slowly decomposes in solution into $[Cp_2V(CO)_2][Co(CO)_4]$, characterized by X-ray, and undergoes charge separation on addition of Lewis bases L (CO, THF, water) and CF_3CO_2H affording the ionic or neutral derivatives of general formula $[Cp_2VL_n]^{0/+}$. The behavior of the permethylated vanadocene parallels that of vanadocene, but low wavenumber absorption in the



Scheme 37

Table 18 Relevant spectroscopic data and magnetic properties for vanadocene complexes resulting from the reaction $Cp_2V(CO) + B(C_6F_5)_3$[304]

Complex	μ_{eff}	δ^1H	$\delta^{19}F$	$\delta^{11}B$	$\delta^{51}V$	*IR* (cm^{-1})
$CpCp^BV$ **88**	2.85					
$CpCp^BV(CO)_2$ **89**	diamagnetic	5.19 (Cp); 5.36, 5.49 (Cp^B)	−52.9, −86.2, −91.0	−14.9	−1652	2050, 2004 (CO)
$[Cp_2V(CO)_2][HB(C_6F_5)_3]$ **90**	diamagnetic	5.59 (Cp); 3.63 (BH)	−58.9, −88.8, −92.0	−25.5	−1661	2038, 1990 (CO); 3123 (BH)
$Cp_2V(\mu\text{-}H)B(C_6F_5)_3$ **91**	2.71					1905 (br, VH)

IR spectrum (1766 cm^{-1}) suggests the presence of a bridging carbonyl and the compound has been postulated to be $Cp^*{}_2V(\mu\text{-}CO)Co(CO)_3$.

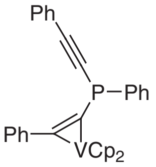
5.01.5.1.2.(ii) Reaction of Cp_2V with unsaturated molecules

The 15-electron vanadocene is an electronically and coordinatively unsaturated molecule that behaves as a carbene-like unit, adding to many organic functional groups. Part of this reactivity has been reviewed elsewhere.[17]

The known[309] $Cp_2V(\eta^2\text{-}CH_2O)$ is formed upon addition of paraformaldehyde to a toluene solution of Cp_2V. Higher yields (77%) are obtained when the reaction is conducted for only 20 h.[310] Reaction of this formaldehyde complex with the electrophilic rhenium compounds *cis*-$Re(CO)_4(L)(F\text{–}BF_3)$ [$L = PPh_3$ or $P(OPh)_3$] leads to the formaldehyde-bridged bimetallic cationic species $[Cp_2V(CH_2O)Re(CO)_4(L)]^+[BF_4]^-$.[310] In contrast, trifluoroacetic anhydride reacts with $Cp_2V(\eta^2\text{-}CH_2O)$ with cleavage of the metallaoxirane ring to produce (trifluoroacetoxy)methyl derivative $Cp_2V(OCOCF_3)(CH_2OCOCF_3)$. In a similar way, the reaction of Cp_2V with 1 equiv. of thionyl chloride in toluene affords the green paramagnetic metallacyclic $Cp_2V(\eta^2\text{-}OSCl_2)$, only characterized by EPR spectroscopy ($A(^{51}V) = 47$ G, $g = 1.998$).[311] Bis(trifluoromethyl)ketene reacts with Cp_2V to give the adduct $Cp_2V\{\eta^2\text{-}(C,O)\text{-}(CF_3)_2C{=}C\text{-}O\}$ containing an η^2-(C,O)-bonded heteroallene as confirmed by single crystal X-ray diffraction (V–O 2.024(8) Å, C–O 1.290(11) Å, V–C 2.034(9) Å, O–C–C 131.2(10)°).[312]

Complexes of vanadocene containing an O,O′-coordinated 1,10-phenanthroline-5,6-dione bound to the Cp_2V can be prepared by direct reaction of the dione with Cp_2V and have been characterized by infrared spectroscopy.[313] Further reaction with $TiCl_4$ or $HfCl_4$ affords the corresponding bimetallic derivatives with the group 4 tetrahalide N,N′-coordinated to the phenanthroline ligand. The vanadium center in these complexes has been oxidized to the formal oxidation state +IV, as corroborated by their magnetic moments.

The oxidative addition of a carbon–carbon triple bond of alkynes to Cp_2V (COMC (1982), Section 24.6.4.2) has been extended to polyynes. When reacted with Cp_2V, diynes,[314,315] triynes,[316] or tetraynes[317] gave the corresponding mono- or bimetallic complexes such as **92–97**, which have been characterized by IR, magnetism, and X-ray analyses. In general, these compounds have one (or two) d^1-vanadium(IV) center(s) with a cyclopropene structure. In only one example, namely in the reaction of the triyne $Me_3Si(C{\equiv}C)_3SiMe_3$ with 2 equiv. of Cp_2V, the expected classical V^{IV} cyclopropene structure is not observed; instead, the metal centers in $(Cp_2V)_2(3\eta{:}4\eta\text{-}Me_3Si(CC)_3SiMe_3)$ **95** have an oxidation state +III and are coordinated to the internal carbon atoms of the triyne via a single σ-type V–C bond (V–C 2.165 Å).[316] Protonation of the coordinated alkynes with anhydrous HCl generally produces a mixture of *E*- and *Z*-isomers of the corresponding alkene with concomitant formation of Cp_2VCl_2.[315,317,318]



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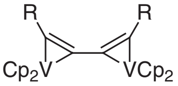

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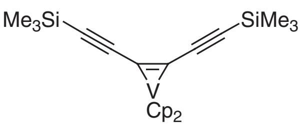

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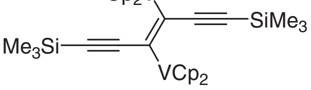

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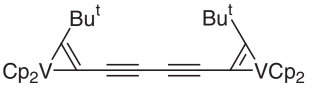

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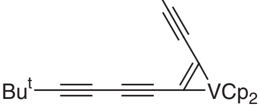

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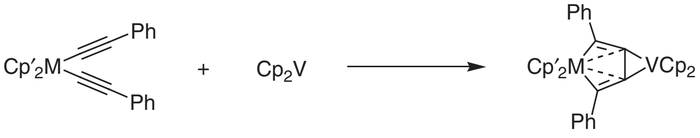
Remarkably, the reaction of bis-alkynyl $Cp'_2M(C{\equiv}CPh)_2$ [M = Ti, Zr; Cp′ = (η^5-C_5H_4R) with R = H, Me, Bu^t, $SiMe_3$] with Cp_2V affords heterobimetallic complexes **98** (Equation (4)).[319,320] According to an X-ray analysis, the Cp_2V is coordinated to the butadiene framework through the two internal carbon atoms, whereas the group 4 metallocene is attached to both internal and external carbon atoms. As a result, the two internal C atoms of the butadiene are planar and tetracoordinated, which has been confirmed by theoretical studies (electron localization function (ELF) analysis).



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(4)

Lewis-acid activated nitriles have been demonstrated to enhance the reactivity of Cp_2V toward C≡N bonds. Adducts of nitriles with Lewis acid BX_3 (X = Cl, Ph, C_6F_5, 2,6-$F_2C_6H_3$, 3,4,5-$F_3C_6H_2$), $RC{\equiv}N{\cdot}BR_3$, react with vanadocene to yield the borane adduct of vanada(IV)azirine complexes $Cp_2V\{\eta^2\text{-(C,N)-}RC{=}N{\cdot}BR_3\}$ (R = Me, 4-CF_3-C_6H_4) as illustrated in Scheme 38.[321,322] These complexes are paramagnetic d^1-species characterized by IR (ν_{CN} 1725–1722 cm^{-1}), EPR ($A(^{51}V) = 41$–44 G), magnetism, and X-ray analysis (V–C 2.02–2.05 Å, V–N 2.07–2.12 Å, N–C 1.23–1.25 Å). Interestingly, an intramolecular C–F···V interaction between boranes that have *ortho*-fluorine atoms on the phenyl ring and the vanadium center was evidenced by EPR spectroscopy. Analogous homobimetallic d^1–d^1 complexes are prepared from similar reactions with dinitriles.[322]

5.01.5.1.2.(iii) Reaction of Cp$_2$V with miscellaneous reagents

Oxidation occurs during the reaction of Cp_2V with the bis(amino) phenol 2,6-$(CH_2NMe_2)_2$-4-Me-C_6H_2OH (ArOH) leading to the trivalent trisphenolate complex $V(OAr)_3$, a pentacoordinated vanadium compound with two η^2-N,O bidentate bis(amino) phenolate ligands and a third η^1-O monodentate ligand.[104]

Vanadium(IV) bis-cyclopentadienyl ditriflate is prepared in 92% yield by the addition of 2 equiv. of silver triflate to a dichloromethane solution of Cp_2V, with concomitant formation of silver.[323] An alternative preparation of this complex consists of reacting Cp_2VCl_2 with 2 equiv. of AgOTf.[324]

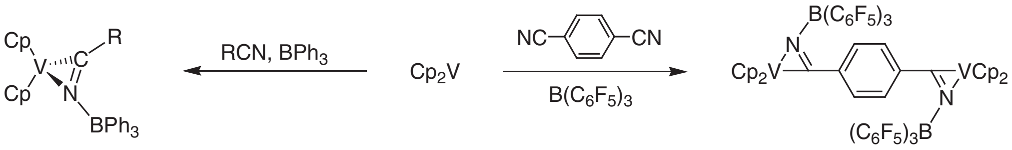
5.01.5.1.3 Applications of Cp$_2$V

Owing to the strong dependence of its paramagnetic ^1H and ^{13}C NMR shift, Cp_2V can serve as a new NMR signal shift thermometer in variable-temperature NMR studies in both the solution and solid states.[325]

Cp_2V has been shown to transform the molybdenum complex $CpMo(CO)_2(\mu\text{-SMe})_2MoCp(CO)_2$ into $CpMo(CO)_2(\mu\text{-H})(\mu\text{-SMe})_2MoCp(CO)_2$ with the possible involvement of a vanadium(III) hydride species.[326]

Exploiting its reducing properties, Cp_2V has been used as an organometallic route for the preparation of polyvinylpyrrolidone-stabilized nanoparticles of Fe^0,[327] Rh^0,[328] and Pd^0 [329] by reduction of chloride precursors $FeCl_2$, $[Rh(\mu\text{-Cl})(C_2H_4)_2]_2$, and $[Pd(allyl)_2Cl]_2$, respectively (see Chapter 12.03).

Due to its high volatility, vanadocene and *tert*-butyl ring-substituted derivatives are suitable precursors for OMCVD[300,330] and plasma-assisted CVD[331] preparation of thin-film ceramic materials (carbides or carbonitrides) (see Chapter 12.02). Reduction of 1,3,5-tris(β,γ-dibromopropyl)-2,4,6-trioxo-1,3,5-triazine with 3 equiv. of Cp_2V gives the corresponding triallyl isocyanurate derivative with precipitation of Cp_2VBr.[332] A catalytic system based on Cp_2V (or Cp_2VCl_2 or $CpV(CO)_4$), Zn and Me_3SiCl is effective for the reductive coupling of aldehydes into dioxolanes.[212]



Scheme 38

5.01.5.2 Bis(Cyclopentadienyl) Vanadium(III), Vanadium(IV) and Vanadium(V) Complexes

Bis-cyclopentadienyl complexes of vanadium(III) and vanadium(IV) obtained by oxidative addition of unsaturated molecules (alkynes, formaldehyde, thionyl chloride, nitriles, CO) to Cp_2V are described in the appropriate section devoted to the reactivity of Cp_2V (Section 5.01.5.1.2).

5.01.5.2.1 Halides, pseudohalides and ring-substituted derivatives

5.01.5.2.1.(i) Halides

Vanadocene halides Cp_2VX_n ($n = 1, 2$; X = Cl, Br, I) and their ring-substituted derivatives are useful precursors to various synthetic compounds, and have attracted considerable interest for their application as magnetic materials, alkene polymerization catalysts, reductive coupling reagents, or potential anti-tumor activity. As described in COMC (1982) (Volume 3, Chapter 24, Section 24.6.8) and COMC (1995) (Volume 5, Chapter 1, Section 5.01.6.3.1), Cp_2VX and its ring-substituted analogs can be prepared by the oxidation of the corresponding vanadocene with alkyl halides, CH_2X_2 (X = Cl, Br), X_2 (X = Cl, I), HCl, $PbCl_2$, or equimolar amount of Cp_2VCl_2.[1,2] Generally, these routes produce only low yields of the desired material, but easy access to various substituted vanadocene precursors (see Section 5.01.5.1.1) makes these routes very valuable. Recently, PCl_3 has also been reported to convert ring-alkylated vanadocenes to a mixture of $Cp^R{}_2VCl$ and $Cp^R{}_2VCl_2$ [R = Me, Pr^i, Bu^t] which are easy to separate.[289] This protocol proved extremely useful for the high yield chlorination of bis-1,1-amino-functionalized vanadocene: using 1 equiv. of PCl_3 gives the vanadium(III) monochloride complex $Cp^N{}_2VCl$, while 2 equiv. of PCl_3 convert the vanadocene into vanadium(IV) dichloride corresponding derivative $Cp^N{}_2VCl_2$ [$Cp^N = \{\eta^5\text{-}C_5H_4CH(CH_2)_4NMe\}$ and $\{\eta^5\text{-}C_5H_4(CH_2)_2N(CH_2)_5\}$].[231]

The direct reaction of VCl_3 with alkali metal cyclopentadienides has met with limited success due to apparent problems of disproportionation. Although the reaction of VCl_3 and 2 equiv. of TlCp in boiling THF represents the best, high yield, synthetic method of preparation of Cp_2VCl,[333] the use of NaCp (see Section 5.01.5.1.1) or $NaCp^*$[302] yields the divalent vanadocene derivative (ratio V : NaCp 1 : 3) or Cp_2VCl_2 after disproportionation (ratio V : NaCp 1 : 2).[334] Similarly, disproportionation occurs in the case of $NaCp^{Me}$ with the formation of $Cp^{Me}{}_2VCl_2$, plus ca. 25% of $Cp^{Me}{}_2VCl$ that arises from non-redox salt metathesis reaction.[73]

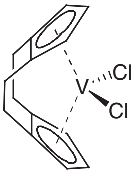
Vanadocene dihalides and ring-substituted derivatives are still prepared by halide substitution in VX_4 with 2 equiv. of an appropriate cyclopentadienide reagent (for details, see COMC (1982) Volume 3, Chapter 24, Section 24.6.8 and COMC (1995) Volume 5, Chapter 1, Section 5.01.6.3.1). The 1,1′-ring-substituted vanadocene dichlorides $(\eta^5\text{-}C_5H_4R)_2VCl_2$ (R = Bu^t, $SiMe_3$, $SiEt_3$) have been prepared in low yields (10–20%) in this way using lithium reagents.[335] The molecular structure of the TMS derivative reveals staggered Cp rings with two bulky TMS groups located in *anti*-positions (Cp_c–V 1.97 Å, V–Cl 2.412 Å, Cp_c–V–Cp_c 131.6°, Cl–V–Cl 86.8°) and compared to the structure of the parent non-substituted Cp_2VCl_2 (Cp_c–V 1.970 Å, V–Cl 2.417 Å, Cp_c–V–Cp_c 134.3°, Cl–V–Cl 85.4°). The standard molar enthalpy of sublimation of Cp_2VCl_2 at 298.15 K is $140.1 \pm 7.4\ \mathrm{kJ\ mol^{-1}}$.[336] The EPR spectrum of magnetically diluted polycrystalline Cp_2VCl_2 presents resolved super-hyperfine splitting (6–10 MHz) due to the interaction of the unpaired electron with the nuclear spin of the two chlorine atoms.[337] Several examples tend to demonstrate that the structure of vanadocene(IV) complexes can be assigned based on comparison of experimental and theoretical (DFT, B3PW91) hyperfine coupling tensors.[338] The electrochemistry of Cp_2VCl_2 has been investigated in the presence of light (300–400 nm) and the kinetics and mechanism of the photochemical dehalogenation have been established.[339] Complete ligand field calculations have been carried out for Cp_2VCl_2 in C_{2v} symmetry;[340] the experimental *d*–*d* transition energies have been assigned, and the ground state is $^2A_1(1a_1)$ with the *d*-orbital energy order following $1a_1 < b_1 < b_2 < 2a_1 < a_2$. Raman spectroscopy can be used as a simple tool for the detection of bent metallocene fragments $[Cp_2V]^{2+}$.[253]

5.01.5.2.1.(ii) Pseudohalides

As described earlier (COMC (1982) Volume 3, Chapter 24, Section 24.6.8 and COMC (1995) Volume 5, Chapter 1, Section 5.01.6.3.3), the pseudohalide complexes Cp_2VY_2 (Y = N_3, CN, NCO, NCS, etc.,) are prepared from the corresponding dichloride complex and the appropriate salt, or from oxidation of Cp_2V with HN_3, $(CN)_2$, or $(SeCN)_2$. Mixed complexes Cp_2VXY are obtained by reacting Cp_2V with $(NC)N_3$ or XCN (X = Cl, Br, I). Sodium dicyanamide $Na[N{\equiv}CNC{\equiv}N]$ reacts with vanadocene dichloride in aqueous solution to form the paramagnetic (g_{iso} 1.984, A_{iso} 70.2 G) pseudohalide complex $Cp_2V(NCNCN)_2$.[341] An X-ray structure elucidation indicates that the dicyanamide ligands are monodentate and coordinated through the terminal nitrogen atom at a V–N distance of ca. 2.05 Å, and with almost linear V–N–C angle (av. 175.1°). In addition, the dicyanamide fragment is almost unaffected by coordination to the metal center with structural parameters close to those of the sodium dicyanamide precursor. Structural parameters for the bis-vanadocene(IV) pseudohalides $Cp^{Me}{}_2V(NCO)_2$[342] and $Cp_2V(N_3)_2$[343] present similar features (V–Cp_c ca 1.97 Å; Cp_c–V–Cp_c ca. 134°; V–N ca. 2.04–2.08 Å) with almost linear NCO and N_3 fragments (ca. 178°).

5.01.5.2.1.(iii) ansa-Bis(cyclopentadienyl) compounds

A few *ansa*-vanadocene complexes have been synthesized which possess six different bridging units: bis-ethanediyl **99**,[344] tetramethylethane **100**,[345,346] EMe_2 **101**,**102** (E = C,[347] Si,[348] Ge[348]), and biphenyl **103**.[349] Their general synthesis is based on the procedures described for the non-bridged analogous systems (Section 5.01.5.2.1) using VCl_3/PCl_3 or VCl_4 and the dilithium or magnesium salt of the bridging ligand, or from $V(acac)_2Cl$ and $V(acac)_3$ precursors[350] followed by oxidation with PCl_3. In some cases, the trivalent monochloride intermediate has been isolated and characterized before its oxidation with PCl_3,[350] or after reduction of the tetravalent dichloride with 1 equiv. of $LiAlH_4$ or tetrakis(dimethylamino)ethene,[345] whereas using 2 equiv. of $NaBH_4$ affords the corresponding vanadium(III) borohydride complex.[346] Determination of *rac/meso* ratio in tetramethylethano-bridged alkyl-substituted vanadocene dichlorides **100** is possible by standard ^1H NMR methods after conversion to diamagnetic corresponding di(*tert*-butylisonitrile) complexes, and separation of *meso*- and *rac*-isomers is achieved via corresponding binaphtolate complexes.[350] An *ansa*-bisCp–imido vanadium(V) complex **102** has been prepared by treatment of $V(NBu^t)Cl_3Py_2$ with the dilithium salt $[\{Li(C_5H_4)\}_2CMe_2]$.[347] Although strongly related to their group 4 *ansa*-metallocene analogs, their olefin polymerization behavior is not reported.



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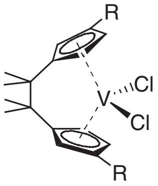

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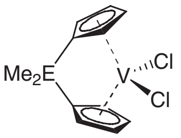

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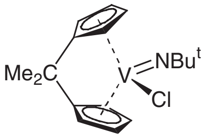

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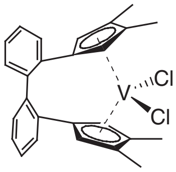

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5.01.5.2.2 Coordination chemistry of halides, CO, and isonitrile derivatives

Following an analogous procedure reported for the synthesis of the rare N-bonded tetracyanoethylene (TCNE) complex $Cp_2VX(\eta^1\text{-TCNE})$ [X = Cl, Br, I],[351] addition of 1 equiv. of TCNE to permethylated $Cp^*{}_2VBr$ produces the diamagnetic vanadium(IV)-d^1-($TCNE^{1-}$) complex $Cp^*{}_2VBr(\eta^1\text{-TCNE})$ in 69% that appears slightly more stable and more soluble than the Cp analog.[352] Varying the stoichiometry of the reactants (V : TCNE ca. 2 : 1) affords the dinuclear d^1-($TCNE^{2-}$)–d^1 complex $[Cp^*{}_2VBr]_2(\mu\text{-TCNE})$ in 54%, with magnetically weakly coupled d^1-centers. The absence of $C{=}C_{TCNE}$ bands in the IR spectrum and the presence of only two main nitrile bands (2172 and 2099 cm^{-1}) suggest a *trans*-1,2-dicoordination of a considerably reduced TCNE ligand.

Reaction of Cp_2VCl_2 with the Lewis acid $FeCl_3$ in acetonitrile yields the cationic complex $[Cp_2VCl(NCCH_3)][FeCl_4]$ in 91%.[353] Infrared data of the coordinated nitrile (ν_{CN} 2319 and 2291 cm^{-1}) and structural parameters as determined by X-ray crystallography [Cp_c–V av. 1.957 Å, Cp_c–V–Cp_c 134.10(4)°, V–N 2.0873(16) Å, V–N–C 178.70(17)°] are comparable with those observed in the methyl derivative $[Cp_2VMe(NCCH_3)][BPh_4]$ (see Section 5.01.5.2.5).[354] The unsolvated 14-electron cation $[Cp_2V]^+$ is formed upon one-electron oxidation of Cp_2V by $[Cp_2Fe]^+$.[306] Due to its extreme sensitivity to air, it was only characterized by IR and from its chemical reactivity with Lewis bases and CO.

Several trivalent zwitterionic ring-borylated and ionic, vanadium complexes have been generated in the reaction of $Cp_2V(CO)$ with $B(C_6F_5)_3$ (see Section 5.01.5.1.2).[304]

Reaction of $Cp_2V(OTf)_2$, generated *in situ* from the parent dichloride complex and AgOTf, with 2,2′-bipyridine and phenanthroline affords $[Cp_2V(bipy)][OTf]_2$ and $[Cp_2V(phen)][OTf]_2$, respectively.[324] These compounds are paramagnetic d^1-species ($\mu_{eff} = 1.66$ and 1.68 μ_B; EPR: $g = 1.996$, $A = 61.1\ cm^{-1}$ and $g = 1.980$, $A = 62.7\ cm^{-1}$, respectively) and have relatively low V^{IV}/V^{III} reduction potentials (ca. −0.62V vs. $Cp_2Fe^{+/0}$ in CH_3CN). The V–N bond distances in these pseudo-tetrahedral complexes average 2.13 Å.

tert-Butyl isocyanide reacts with *ansa*-vanadocene monochlorides[345,350] and tetrakis(dimethylamino)ethene reduced dichlorides[349] to provide, after ligand exchange, the diisocyanide cationic complexes [(*ansa*-Cp_2)$V(CNBu^t)_2$]Cl. Analogous dicarbonyl cationic [(*ansa*-Cp_2)$V(CO)_2$][BPh_4] is obtained from reduction of complexes (*ansa*-Cp_2)VCl_2 with $LiAlH_4$ followed by exposure to CO and cation exchange with $NaBPh_4$.[349]

5.01.5.2.3 Compounds containing O-donor ligands

5.01.5.2.3.(i) Carboxylate, triflate, amino acid, phosphate, and carbonate derivatives

Biscarboxylate complexes $Cp_2V(O_2CR)_2$ [R = H, CCl_3, CF_3] are readily synthesized upon addition of the corresponding carboxylic acid to an aqueous solution of Cp_2VCl_2.[355] These d^1-paramagnetic complexes (EPR: *g* 1.981, *A* ca. 80 G) present in infrared a ν_{COO} at 1632–1691 cm^{-1}, and an X-ray structure of $Cp_2V(O_2CCCl_3)_2$ indicates a V–O bond distance of 2.0313(15) Å. Chelating dicarboxylic acids are prepared similarly.

Bis(cyclopentadienyl) ditriflate $Cp_2V(OTf)_2$ can be obtained in 92% yield by oxidative addition of 2 equiv. of silver triflate to a dichloromethane solution of Cp_2V, with concomitant formation of silver.[323] An alternative preparation of this complex consists of reacting Cp_2VCl_2 with 2 equiv. of AgOTf.[324] The latter protocol also applies for the preparation of *ansa*-vanadocene ditriflate.[350] The reaction of Cp_2VCl_2 and α-amino acids (aa = gly, L-ala, L-val) in aqueous methanol (0.5–1% water) at 40 °C, followed by neutralization with aq. NaOH, gives α-amino acid complexes $[Cp_2V(aa)]Cl$.[356] Infrared spectra suggest that the amino acid is coordinated to the vanadium center through both carboxylic and amino groups (ν_{COO} 1614–1653 cm^{-1}, ν_{NH2} 3317–3368 cm^{-1}).

EPR studies suggest that in aqueous solution Cp_2VCl_2 interacts with phosphates in phosphate-buffered saline to form the chelate species $Cp_2V(O_2PO_2H)$ [$A_{iso}(V) = 68.0$ G $a_{iso}(P) = 29.3$ G, $g = 1.9862$].[357]

The carbonate complex $Cp_2V(O_2CO)$ is prepared by treating an aqueous solution of the formiate precursor $Cp_2V(OOCH)_2$ with $CaCO_3$.[358] IR data (ν_{CO} 1659 and 1624 cm^{-1}) and EPR study on ^{13}C-labeled carbonate complex support a bidentate coordination mode of the carbonate ligand, as already suggested in the related permethyl analog $Cp^*{}_2V(O_2CO)$ (obtained from oxidation of $Cp^*{}_2V(CO)$ with O_2 or N_2O).[359] Nevertheless, the value of the isotropic coupling constant is inexplicably very different in these two compounds ($A_{iso}(^{51}V)$ 63 G and 32 G, respectively, for the Cp and Cp^* derivative).

5.01.5.2.3.(ii) Oxo, alkoxo, and aryloxo derivatives

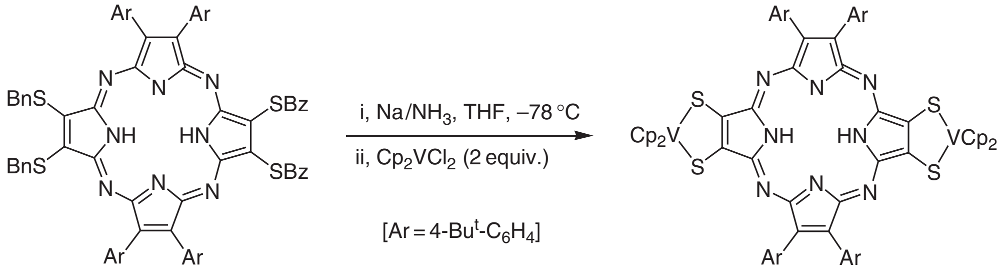
A series of cationic bis(cyclopentadienyl) vanadium(IV) complexes with additional acetylacetonate ligands substituted in the 3-position $[Cp_2V(3\text{-}R\text{-}acac)][OTf]$ (R = Me, Et, Cl, NO_2) have been prepared upon addition of the corresponding 3-R-2,4-pentanedione to *in situ* generated $Cp_2V(OTf)_2$.[360] The structure of the non-substituted $[Cp_2V(acac)][OTf]$ has been confirmed by single crystal X-ray determination [V–C av. 2.294 Å, Cp_c–V 1.97 Å, V–O 1.996(3) and 2.001(3) Å]. These complexes have been characterized by UV–VIS spectroscopy, EPR, and electrochemical studies that show one reversible V^{IV}/V^{V} couple in acetonitrile that follows a clear trend [$E_{1/2} = +0.95, +0.97, +1.09, +1.14, +1.59$ (V vs. $[Cp_2Fe]^{+/0}$), respectively, for R = Me, Et, H, Cl, NO_2]. The biological activity (lipid peroxidation) of this series of complexes correlates to their V^{IV}/V^{V} redox potential. Similar ligand exchange reaction on related *ansa*-vanadocene dichlorides affords acetylacetonato cationic complexes, a reaction that is reversible upon addition of $MgCl_2$ in THF.[350] The binaphtolate *ansa*-vanadocene complexes $[Me_4C_2(3\text{-}R\text{-}C_5H_3)_2]V(binol)$ [R = H, Bu^t] are prepared by addition of 1,1′-binaphtol to the parent dichloride precursor **100** in the presence of triethylamine.[350] Functionalization of a dendrimeric silanol with Cp_2MCl_2 (M = Ti, V, Mo, W) yields the corresponding metal-containing dendrimer $Si[CH_2CH_2SiMe_2OMCp_2Cl]_4$ in which the metal is covalently attached via silyloxy bond.[361] After incorporation in a silica matrix by sol–gel method, and calcination, the resulting metallosilicates exhibit good activity and selectivity in the heterogeneous epoxidation of alkenes with *tert*-butylhydroperoxide.

A great variety of oxo complexes and clusters have been obtained by oxidation of Cp_2VCl_n ($n = 0$–2) with various oxidants (NO, N_2O, O_2, Ag_2CO_3, Ag_2O, Me_3NO, etc.,) (see COMC (1982) Volume 3, Chapter 24, Section 24.6.7 and COMC (1995) Volume 5, Chapter 1, Section 5.01.6.3.6). Exposing a hexane solution of $Cp^*{}_2V$ to nitrous oxide (4 atm) yields paramagnetic ($\mu_{eff} = 1.95$, EPR $g_{iso} = 1.9844$, $A_{iso} = 25$ G) complex $Cp^*{}_2V(O)$ in 45% with concomitant formation of the known[362] $Cp^*{}_4V_4(\mu\text{-}O)_6$ cluster.[363] As indicated by MS and IR data ($\nu_{V=O}$ 855 cm^{-1}, $\nu_{V={}^{18}O}$ 820 cm^{-1}), $Cp^*{}_2V(O)$ is expected to be monomeric; the titanium analog has been trapped with Lewis base. This complex decomposed to form $Cp^*{}_4V_4(\mu\text{-}O)_6$, and decomposition studies on ^{18}O-labeled $Cp^*{}_2V(^{18}O)$ are consistent with the assumption that the assembly of the cluster occurs predominantly from biscyclopentadienylvanadyl species.

Reaction of the trioxo anion $[Cp^*WO_3]^-$ with Cp_2VCl_2 affords the heterobimetallic μ-oxo-bridged complex $Cp_2V(\mu\text{-}O)W(O)_2Cp^*$ in 66% yield (IR: $\nu_{V\text{–}O\text{–}W}$ 793, $\nu_{W=O}$ 904 + 849 cm^{-1}).[364] This complex reversibly binds diethyl ether to form the ionic complex $[Cp_2V(Et_2O)(\mu\text{-}O)W(O)_2Cp^*]Cl$ (IR: $\nu_{V\text{–}O\text{–}W}$ 783, $\nu_{W=O}$ 911 + 868 cm^{-1}).

5.01.5.2.4 Compounds containing S-, Se-, and P-donor ligands

Covalent attachment of one or two vanadocenes to a dithiolene binding site on porphyrazines affords soluble, peripherically metallated, porphyrazines such as the one described in Equation (5).[365] The electron spins of the two d^1-centers in *trans*-divanadium porphyrazines exhibit through-bond exchange coupling (15-line EPR pattern with $A_{iso} = 30$ G), though the metal atoms are separated by a 14.5 Å distance (X-ray). Other bisCp vanadium complexes with two dithiolene[366] or diselenolate[367] ligands are being prepared from the reaction of Cp_2VCl_2 and the corresponding dithiolate and diselenolate. Structurally characterized (V–Cp_c = 1.965 Å, Cp_cVCp_c = 134.6°, V–S = av. 2.470 Å) dithiocarbamate vanadium(IV) complex $[Cp_2V(S_2CNEt_2)][BF_4]$ has been shown to exhibit sperm immobilizing effects that extend vanadocenes as potent spermicidal agents (see Section 5.01.5.2.6).[368]



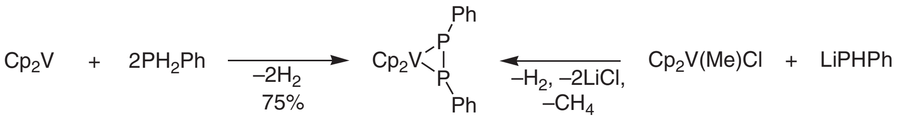
(5)

The thio–oxo complex $[Cp^{Me}{}_2V(\mu\text{-}S)_2VCp^{Me}]_2(\mu\text{-}O)$ has been isolated from the RT reaction of Na-reduced cyclo$(CH_3AsS)_{3,4}$ and $Cp^{Me}{}_2VCl_2$ in THF, which may result from hydrolysis of intermediate thio complex $Cp^{Me}{}_2V(\mu\text{-}S)_2VCp^{Me}Cl$.[369] Its structure consists of two $Cp^{Me}{}_3V_2S_2$ units with asymmetrical V–S bond distances ($Cp^{Me}{}_2$V–S 2.36–2.39 Å vs. Cp^{Me}V–S 2.17–2.21 Å), which O-bridged through two mono-Cp^{Me} vanadium atoms (V–O 1.794(9) Å, V–O–V 166.7(6)°). The compound is diamagnetic in solution, which may be explained either by the presence of V^{IV}–V^{IV} interaction (in the solid state: V–V 3.043(4) Å) or by the presence of mixed oxidation states V^{III}–V^{V} which could also rationalize the asymmetrical V–S bond distances observed.

The reaction of Cp_2V with PH_2Ph proceeds to yield black paramagnetic vanadium(IV) **104** (Scheme 39), probably via the intermediacy of the phosphinidene complex $Cp_2V({=}PPh)$.[370] Alternatively, this compound was prepared from $Cp_2V(Me)Cl$ and LiPHPh, and its structure was confirmed by X-ray crystallography (V–P av. 2.54 Å, P–P 2.160(5) Å). In contrast, Cp_2VMeCl, when reacted with PH_2Ph in presence of $NaBPh_4$, affords the cationic vanadium(III) bis-phosphine complex $[Cp_2V(PH_2Ph)_2][BPh_4]$ with V–P bond distances of ca 2.40 Å.

5.01.5.2.5 σ-Bonded alkyl and aryl derivatives

In relation with its applications as precursor to Ziegler–Natta catalysts, Cp_2VMe_2 was reacted with different boron activators and in different solvents. The cationic complex $[Cp_2VMe(NCMe)][BPh_4]$ **105** was obtained as a pale violet precipitate from the protonolysis reaction of Cp_2VMe_2 with $[NHMe_2Ph][BPh_4]$ in acetonitrile.[371] This adduct is a d^1-paramagnetic ($\mu_{eff} = 1.88$ μ_B) species, and represents the first structurally characterized cationic alkyl complex of vanadium(IV) (V–C 2.221(5) Å, V–N 2.096(4) Å, Cp_c–V av. 1.955 Å, Cp_c–V–Cp_c 136.69°).[354] When conducted in THF (at RT or −80 °C) instead of MeCN, the same reaction leads to the blue-violet vanadium(III) ($\mu_{eff} = 2.75$ μ_B) complex $[Cp_2V(THF)][BPh_4]$, which is explained by disproportionation and redox reactions with concomitant formation of Cp_2VMe_2 and oxidation of BPh_4^- counteranion to BPh_3 and PhPh (see Scheme 40). The transient complex $[Cp_2VMe(THF)][BPh_4]$ could however be characterized by EPR ($g = 1.995$, $A_{iso} = 69.7$ G) by the addition of THF to **105**, before its transformation into Cp_2VMe_2 and EPR-silent $[Cp_2V(THF)][BPh_4]$. Phosphines react similarly on **105** with initial formation of the corresponding cationic vanadium(IV) adduct $[Cp_2VMe(PR_3)][BPh_4]$ ($PR_3 = PMe_2Ph$, $PMePh_2$) [$g = 2.007$, $A(^{51}V) = 61.2$ G, $A(^{31}P) = 30.8$ G, $A(^1H) = 6.25$ G when $PR_3 = PMe_2Ph$] that further evolves in 3 to 4 days into $[Cp_2V(PR_3)][BPh_4]$ (δ ^{31}P NMR 37.9). In dichloromethane, chloride abstraction from the solvent occurs with the formation of Cp_2VCl, BPh_3, and $[N(CH_2Cl)Me_2Ph][BPh_4]$. Similarly, mixing Cp_2VMe_2 and $B(C_6F_5)_3$ in THF gives the vanadium(III) ($\mu_{eff} = 2.80$ μ_B) complex $[Cp_2V(THF)][MeB(C_6F_5)_3]$ after disproportionation and



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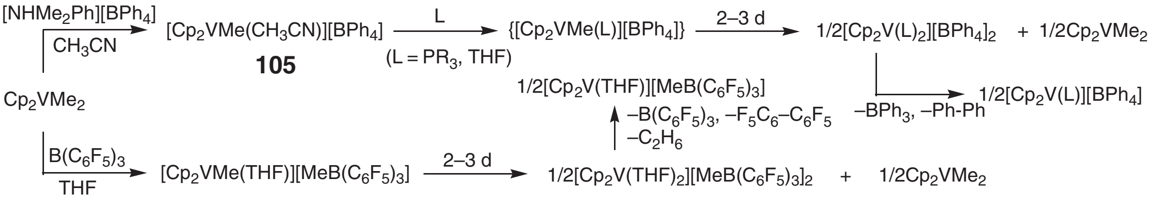
Scheme 39



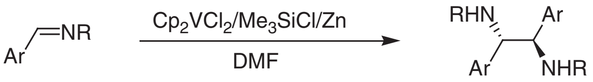
Scheme 40

redox reaction with concomitant formation of Cp_2VMe_2, ethane, and F_5C_6–C_6F_5 (see Scheme 40),[354] and again, EPR evidence accounts for the intermediate formation of the paramagnetic complex $[Cp_2VMe(THF)][MeBPh_3]$ ($g = 1.991$, $A(^{51}V) = 73.2$ G, $A(^1H) = 5.1$ G). The interaction of Cp_2VCl_2 with three different aluminum co-catalysts (MAO, $EtAlCl_3$, $Al_2Et_3Cl_3$) in various V : Al ratios has been monitored by EPR spectroscopy.[372] These studies confirm previous EPR experiments on similar catalyst systems,[373] and suggest the initial formation of $Cp_2VCl(\mu$-Cl)(μ-Et)$AlCl_2$ and $Cp_2VCl(\mu$-Cl)(μ-Et)AlCl(Et) which would further give the vanadium(III) active species.

5.01.5.2.6 Applications

Major applications of Cp_2VX_2 derivatives concern catalytic organic reactions, polymerization of olefins (most is patented and is not discussed here), OMCVD, spermicidal, antiviral and anti-tumor properties. The anti-tumor activity of vanadocenes has been reported in COMC (1995) (Volume 5, Chapter 1, Section 5.01.6.3.4). Subsequently, and due to its low toxicity in combination with the screening of new, more potent and better tolerated complexes, continuous effort has been devoted to vanadium compounds as effective non-platinum anti-tumor agents. Because of the large number of contributions, and also because it is not strictly restricted to vanadium compounds containing a V–C bond, it is beyond the scope of this review to discuss the new developments in this field. Readers are referred to more specialized recent reviews that provide access to various aspects on this topic.[14,15,374–376]

Cp_2VCl_2 is used in catalytic amount in presence of trimethylchlorosilane and zinc (or aluminum) for the coupling of aldehydes[7,212,213,377] or aldimines[214,377] with *meso*-selectivity. The same catalytic system performs the diastereoselective cyclodimerization of arylidene malonitriles into the corresponding cyclopentene derivatives.[378] Examples of reactions catalyzed by the $Cp_2VCl_2/Me_3SiCl/Zn$ system are illustrated in Equations (6) and (7). Perylene is formed in quantitative yield in the reaction of Cp_2VCl_2 with (1,8-naphthalenediyl)magnesium.[379]



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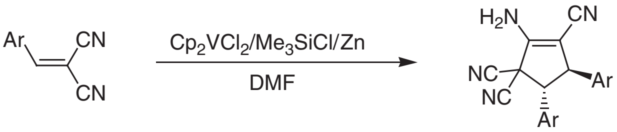


(7)

Cp_2VCl_2 (and to a lesser extent Cp_2V) acts as a source of cyclopentadienyl ligand in its thermal reaction with $Re_2(CO)_{10}$ to afford $CpRe(CO)_3$.[380]

Polymerization of vinyl ether was carried out with Cp_2VCl_2,[381] affording polymers with 63% (isobutyl vinyl ether) and 56% (*tert*-butyl vinyl ether) dyad isotacticity but in low yields. A catalytic system based on Cp_2VCl/MAO polymerizes 1,3-dienes (butadiene, isoprene) into polymers with predominantly *cis*-1,4-structrure.[226]

Cp_2VCl_2 has been grafted onto mesoporous silicates MCM-48,[382], MCM-41,[383] and SBA-15.[384] The resulting V-MCM-48 is active for the liquid phase oxidation of 2,6-di-*tert*-butyl phenol with aqueous H_2O_2, giving high TON and good selectivity; although it suffers substantial leaching. The V-MCM-41 has been used to selectively oxidize alkanes into ketones with various oxidants, isobutyraldehyde/dioxygen affording the best results.

Ceramic thin films containing Ti–V–C–N are obtained by OMCVD of $CpTiCl_2(N(SiMe_3)_2)$ with Cp_2VMe_2.[385,386] (See Chapter 12.02.) The effect of Cp_2VCl_2 and ring-substituted derivatives on the crystal growth of hydroxyapatite, calcium carbonate, and calcium phosphate has been investigated in relation to their potential drug applications and anti-inflammatory and anti-arthritic activity.[387–389] A novel, *in vitro* anticalcification process based on treatment of porcin and human heart valves with Cp_2VCl_2 and other metallocene dichlorides has been developed, which reduced mineralization of the valves by ca. 30%.[390] Several bis(cyclopentadienyl)–V(IV) compounds have been screened for spermicidal activity using computer-assisted semen analysis (human, boar) and intravaginal administration (mice, rabbits). Although the presence of the two Cp ligands on the metal center is not necessarily required for their spermicidal activity,[391] these investigations show evidence that vanadocene halides and pseudohalides, and particularly their chelate complexes (such as $[Cp_2V(acac)]^+$, $[Cp_2V(bipy)]^{2+}$, and $[Cp_2V(S_2CNEt_2)]^+$), are rapid inhibitors of sperm mobility and induce spermatozoa apoptosis.[368,392–395] The mechanism of action is suggested to involve vanadocene-catalyzed generation of reactive oxygen species through Fe^{2+}-initiated lipid peroxidation.[396] Indeed, $[Cp_2V(S_2CNEt_2)]^+$ was shown to alter the membrane by intercalation; it also induces Fe^{2+}-initiated lipid peroxidation.[360,397] Furthermore, this spermicidal activity is not associated with systematic toxic and inflammatory effects, and does not adversely affect the reproductive performance of mice, which may make vanadocenes useful as a new class of safe and effective vaginal contraceptives.[398–400]

5.01.6 Arene and Polyene Complexes

5.01.6.1 Bis(η^6-Arene) Complexes

Bis(η^6-arene)vanadium(0) complexes are classically obtained from the following general synthetic routes: (i) Friedel–Crafts reduction of vanadium(III) or vanadium(IV) chlorides with $Al/AlCl_3$ in refluxing arene, followed by hydrolysis of the salt $[V(\eta^6\text{-}C_6H_6)_2][AlCl_4]$ to form the neutral arene product, (ii) reaction of arenes with metal vapor that necessitates specialized apparatus, and (iii) ring substitution via lithiation of bis(benzene) vanadium. These procedures are extensively discussed in COMC (1982) (Volume 3, Chapter 24, Section 24.7.1.1) and COMC (1995) (Volume 5, Chapter 1, Section 5.01.7.1.1), and the following sections will focus on new developments in the field of bis(arene) compounds.

5.01.6.1.1 Synthesis

A procedure for the preparation of bis(arene) vanadium from vanadium(V) precursor $VOCl_3$ has been patented.[401] It consists of a reaction with $Al/AlCl_3$ in liquid arene to form $[V(\eta^6\text{-arene})_2][AlCl_4]$, which is reduced to $[V(\eta^6\text{-arene})_2]$ in a subsequent reaction with cyclic or acyclic ethers (typically THF/DME). With this procedure, bis(toluene)- and bis(mesitylene)vanadium are obtained in 68% and 94%, respectively (based on $VOCl_3$).

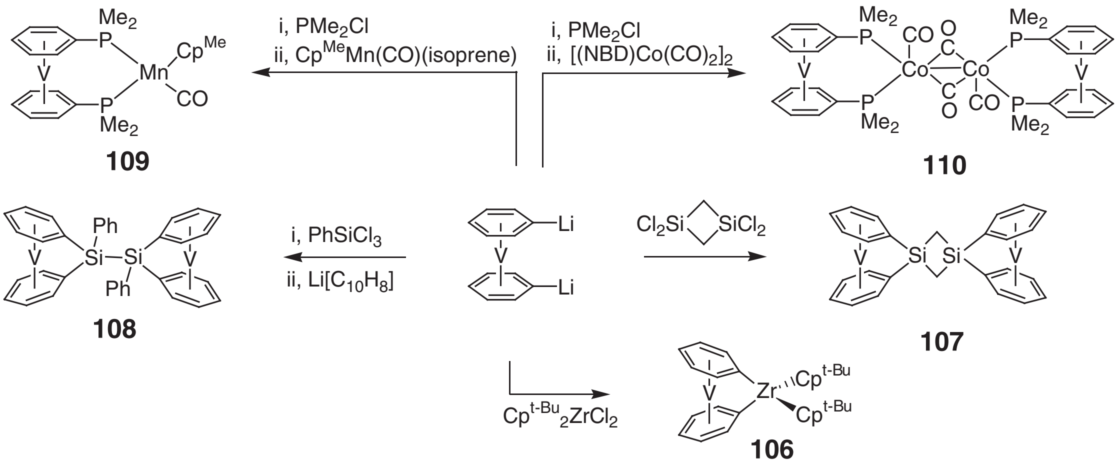
Although an earlier report claimed the possibility to prepare bis(naphthalene) vanadium(0) from the reduction of VCl_3 with lithium naphthalenide,[402] the complex was not isolated and only detected by EPR spectroscopy, and was later prepared by metal-atom vapor method.[403] As depicted in Scheme 41, reaction of 4 equiv. of sodium naphthalenide with $VCl_3(THF)_3$ in THF gives, after oxidation of the (naphthalene)vanadate with alumina (or PF_3), the highly reactive bis(naphthalene) vanadium(0) in 29% (or 19%),[26] and with a more accessible route than the metal-atom vapor technique. It has been fully characterized by UV–VIS (THF: 366 nm, $\varepsilon = 1209\ \mathrm{L\ mol^{-1}\ cm^{-1}}$), mass, IR ($\nu_{C=C}$ 1597 cm^{-1}), EPR ($g = 1.9884$, $A(^{51}V) = 66$ G) spectra and its structure was unambiguously established by X-ray diffraction (av. V–C = 2.21(4) Å, av. C–C 1.39(4) Å). Heating a mixture of DyI_2 with Cp_2V in benzene at 85 °C can afford a small amount of $(\eta^6\text{-}C_6H_6)_2V$ (15% yield).[404]

Bis(η^6-arene) complexes bearing peripheral boryl ($–B(OPr^i)_2$; $–BMes_2$)[405] and organostannyl ($–SnR_3$, R = Me, Ph)[406] substituents are prepared by means of metal-atom ligand-vapor co-condensation technique as well as by lithiation and subsequent reaction with Mes_2BF and R_3SnCl. Similarly, analogous compounds with organogermyl ($–GeR_3$, R = Me, Ph)[407] and phosphine ($–PMe_2$)[408] substituents are synthesized by reaction with R_3GeCl and PMe_2Cl, respectively. The redox and EPR properties of these neutral radical species have been examined in detail.

A great deal of effort has been expended in order to prepare ring-bridged bis(η^6-arene) complexes (Scheme 42) and to study the influence exerted by distortion of the sandwich unit on chemical and spectroscopic properties. The lithiation route is used to introduce one-atom bridging units (SiR_2,[409] GeR_2[407], $ZrCp^{t\text{-}Bu}{}_2$[410]). Ring tilt induced by

$$VCl_3(THF)_3 \;+\; 4Na[C_{10}H_8] \xrightarrow[-70\ \text{to}\ 0\,^\circ C]{THF} \{\,Na[V(C_{10}H_8)_x]\,\} \xrightarrow[0\,^\circ C]{\text{alumina}} \underset{29\%}{V(\eta^6\text{-}C_{10}H_8)_2}$$

Scheme 41



Scheme 42

these Si or Ge short bridges spans 14–20° as determined by X-ray structure characterization. The bending of the sandwich axis and the loss of axial symmetry in these compounds generates an orthorhombic *g*-tensor, and a decrease of A(^{51}V). In contrast, the Zr–V bimetallic complex **106** exhibits only very small bending of the sandwich structure (angle arene$_{\text{centroid}}$-V-arene$_{\text{centroid}}$ = 176.3°). Following the same synthetic strategy, the choice of an appropriate spacer allows the preparation of homodinuclear bis(η^6-arene)vanadium(0) species **107** and **108**, which were shown by EPR spectroscopy to present intermetallic communication despite the non-conjugated nature of the bridges.[409,411] Me$_2$P-substituted bis(arene)vanadium can also act as a ligand to form heterobimetallic V–Mn[408] **109** and {V–Co}$_2$[412] **110** complexes. Interactions within these di- and tetranuclear species have been studied by EPR and electrochemical methods.

5.01.6.1.2 Reactivity

The disproportionation reaction of [V(η^6-Mes)$_2$]$^+$ (see COMC (1995) Volume 5, Chapter 1, Section 5.01.7.1.1) in ether solvent such as THF or DME into vanadium(II) compounds and V(η^6-Mes)$_2$ has been investigated in more detail. The tendency to disproportionate depends on the nature of both the arene and the counteranion, and [V$_2$(μ-X)$_3$(THF)$_6$]$^+$ and V(η^6-Mes)$_2$ are the products formed in the treatment of [V(η^6-Mes)$_2$][AlX$_4$] with THF at room temperature.[413]

V(η^6-Mes)$_2$ is oxidized to VX$_2$(DME)$_n$ by Ph$_3$CX in DME [X = Cl, $n \leq 2$; X = Br or I, $n = 2$].[413,414] V(η^6-Mes)$_2$ reacts at room temperature in heptane with fluorine-substituted carboxylic acids CRF$_2$CO$_2$H (R = H, F) with the evolution of 0.5 mol H$_2$ to afford the monovalent derivative [V(η^6-Mes)$_2$][CRF$_2$CO$_2$].[415] When reacted with two additional equivalents of CF$_3$CO$_2$H in THF, [V(η^6-Mes)$_2$][CRF$_2$CO$_2$] is further oxidized to divalent [H(THF)$_n$][V(OCOCF$_3$)$_3$], probably via the intermediacy of [V(OCOCF$_3$)$_2$(CF$_3$CO$_2$H)]. Indeed, a compound of this type has been isolated in the related reaction of V(η^6-Mes)$_2$ with CF$_3$SO$_3$H. The reaction of 1,10-phenanthroline-5,6-dione with V(η^6-Mes)$_2$ occurs with complete displacement of the arenes and formation of the homoleptic coordination compound trisquinone V(O,O′-C$_{12}$H$_6$N$_2$O$_2$)$_3$.[313]

Bis(naphthalene)vanadium(0) and its methyl derivative bis(1-Me-naphthalene)vanadium(0) react with xylyl isocyanide to give the unprecedented homoleptic zerovalent V(CNXyl)$_6$, a paramagnetic low spin d^5-species which is described in the section dedicated to isocyanide complexes (Section 5.01.2.5)[70,74]

Reactions of [V(η^6-arene)$_2$]^n (arene = 1,3,5-C$_6$H$_3$R$_3$ with R = Me or Bu^t; n = 0, +1, +2) and [TCNE]^y (y = 0, −1) have been examined in order to elucidate the mechanism of the formation of the room temperature magnet [V(TCNE)$_x$]·yCH$_2$Cl$_2$ ($x \sim 2$; $y \sim 1/2$)[416] from V(η^6-C$_6$H$_6$)$_2$ and TCNE. This study suggests a mechanism in which two independent one-electron transfer reactions occur with TCNE as the oxidant, and a vanadium(II) species [V$^{\text{II}}$(η^6-arene)$_2$]$^{2+}$ arising from the oxidation of [V$^{\text{I}}$(η^6-arene)$_2$]$^+$ by TCNE would be the key intermediate in a subsequent reaction with [TCNE]$^{\cdot-}$ leading to the [V(TCNE)$_x$] magnet.[417] In addition, reacting [V(η^6-1,3,5-C$_6$H$_3$Bu$^t{}_3$)$_2$] with TCNE produces the monovalent [V(η^6-1,3,5-C$_6$H$_3$Bu$^t{}_3$)$_2$]$^+$[TCNE]$^{\cdot-}$ which has been structurally and magnetically characterized.

5.01.6.1.3 Physical properties

The gas phase infrared spectra of $[V(C_6H_6)_m]^+$ ($m=1$, 2) present strong bands near 770 and 1430 cm^{-1}, and weaker bands near 1000 cm^{-1}.[418,419] The mono(benzene) cationic species has an additional weaker band at 1565 cm^{-1} and the bis(benzene) has a broad band near 1300 cm^{-1}. All bands have been assigned and compared with the condensed phase spectrum of $V(C_6H_6)_2$ and theory. Unexpectedly, and contrary to the prediction of the 18-electron rule, investigations of the electronic structure of the anion $[V(\text{arene})_m]^-$ ($m=1$, 2) by photoelectron spectroscopy, and confirmed by theoretical studies, indicate that $V(C_6H_6)_2$ has a negative electron affinity and cannot exist in the gas phase.[420]

5.01.6.1.4 Applications

The main applications of bis(arene)vanadium complexes are in the field of material chemistry. As already mentioned in Section 5.01.6.1.2, and in the section dedicated to $V(CO)_6$ (Section 5.01.2.1.4), bis(benzene)vanadium is used to generate room temperature magnet $[V(TCNE)_x]$. Complexes $[V(\eta^6\text{-Mes})_2][X]$ ($X=OCOCF_3$, BPh_4) have been shown to catalyze the room temperature oligomerization of ethylene (1 bar) into 1-hexene.[421]

Vanadium carbide coatings have been deposited on steel substrates by low temperature MOCVD using bis(arene)vanadium precursors (arene = benzene; toluene), and carbonitrides V–C–N are formed in the presence of NH_3.[422,423] A composite of bis(benzene)vanadium and mesoporous niobium oxide has been prepared,[424] and the material exhibited a conductivity of 10^{-4} ohm^{-1} cm^{-1} attributed to the low-dimensional bis(arene) phase in the pores. Bis(arene)vanadium-containing polyacrylonitrile materials have been obtained by the reaction of $V(\text{arene})_2$ (arene = benzene, Mes, $C_6H_4Et_2$) with acrylonitrile in the presence of a catalytic amount of TCNE.[425,426] Such materials form transparent films on coating from CH_3CN solution, and their thermolysis gives naphthyridine-type polymers containing ca. 16% V and presenting third-order non-linear optical properties.

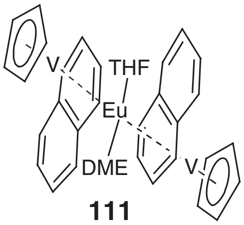
5.01.6.2 Mono(η^6-Arene), Half-sandwich, Mixed Sandwich, Multidecker Complexes, and Their Physical Properties

The reader is referred to COMC (1995) (Volume 5, Chapter 1, Section 1.4.5) and the recent review by Beck and O'Hare[427] for the synthesis and reactivity of triple-decker compounds. The known triple-decker $CpV(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)VCp$[428] has been obtained through partial hydrogenation with H_2 of the benzyne ligand in vanadium–benzyne complex $CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$.[238]

Reaction of $V(CO)_6$ with toluene gives a brown solid, which, upon treatment with diethyl ether, results in gas evolution and after workup, the arene dimer complex $[(\eta^6\text{-toluene})V(CO)_2]_2$ is obtained in low yield (10%). A triple bond between vanadium atoms is suggested in this molecule (for more details, see Section 5.01.2.1.2).[42]

Variable-temperature solid-state magnetic studies indicate that the paramagnetic 26-valence electron triple-decker $CpV(\eta^6\text{-}C_6H_6)VCp$ obeys the Curie–Weiss law between 10–300 K.[429] The room-temperature magnetic moment (4.81 μ_B) is consistent with the presence of four unpaired electrons ($S_T=2$) resulting from magnetic coupling of two intermediate-spin d^4-metal centers ($S_1=S_2=1$). The single crystal molecular structure of the known[430] related building block $CpV(\eta^6\text{-}C_6H_6)$ reveals that the vanadium atom is slightly closer to the benzene ring than the Cp one (V–centroid distances are 1.72 and 1.89 Å for benzene and Cp, respectively), and both ligands are almost parallel (interplanar angle 1.4°).[429] The magnetic moment of this mixed sandwich monovalent complex is 2.81 μ_B in agreement with an intermediate-spin d^4-system.

The tetra-decker bimetallic complexes $[CpV(C_{10}H_8)]_2Ln(THF)(DME)$ (Ln = Eu **111** and Sm) are formed by reacting $LnI_2(DME)_3$ with KCp and $KCpV(C_{10}H_8)$ in DME, followed by treatment with THF.[431] Removal of the solvent leads to the corresponding coordination polymers $[CpV(C_{10}H_8)Ln(THF)Cp(THF)]_n$.



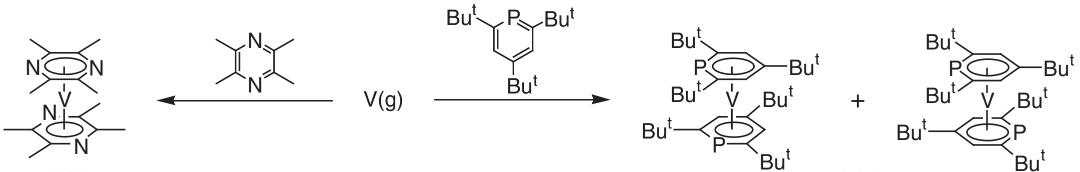
111

Monoarene complexes V(η^6-C_6H_6) and V(η^6-C_6D_6) have been obtained by co-depositing C_6H_6 and C_6D_6 with vanadium atoms in an argon matrix at 15 K, and their EPR spectra were examined in detail by means of experimental studies and simulations in order to determine the electronic structure and ground state of these molecules.[432] EPR analysis of the more complicated V(η^6-1,3,5-F_3-C_6H_3), although randomly oriented, reveals magnetical inequivalency of the three F centers, and suggests that the half-sandwich does not freely rotate arounds its C_3-axis of symmetry when isolated in the Ar matrix.[433] In addition, local density functional (LDF) calculations predict that the molecule is metastable in the gas phase with the ^2E and $^2A_1$ states being nearly degenerate.

Vanadium benzene clusters $V_n(C_6H_6)_m$ are prepared by gas phase reaction of laser-vaporized vanadium atoms with benzene vapor.[434,435] They have been characterized by MS to exhibit magic number behavior at $m = n + 1$ ($n = 1$–5), and ion-mobility experiments, consistent with multiple decker sandwich structure of alternating V atoms and benzene molecules. Quantum chemical calculations indicate the interaction to be of donor–acceptor type.[436] Total spin conservation during growth process plays an important role, and the formation of lower spin species is preferable. The large size dependence of the ionization energies of $V_n(C_6H_6)_{n+1}$ is attributed mainly to the delocalization of metal $d\delta$ electrons via the LUMOs of the benzene molecules, and suggests that much longer size clusters are thermodynamically stable which should make one-dimensional materials possible.[437] Other DFT studies show that vanadium–benzene complexes clearly prefer the sandwich structures rather than the rice-ball structures.[438] The same laser vaporization technique allows the preparation of ring-substituted vanadium(arene) clusters with similar multiple decker sandwich structure.[439] Regarding the configurations of the $V_n(C_6H_6)_m$ complexes ($n = 1$–6), the most recent DFT calculations highlight a change of the D_{6h} symmetry of the energetically most preferred structure when $n = 1$–3 to lower D_2-symmetry in the size range $n = 4$–6.[440] Of interest, the structure of these clusters is predicted to be chiral when $n \geq 4$. The magnetic moments of the sandwich species $V_n(C_6H_6)_m$, measured in the gas phase by a molecular beam magnetic deflection technique, increase with the number of V atoms in the cluster (0.8 μ_B for n, $m = 1, 2$ to 2.1 μ_B for n, $m = 3, 4$),[441] in agreement with the unpaired electrons, coupled ferromagnetically. DFT calculations on $V_n(C_6H_6)_m$ sandwich clusters ($n = 1$–6) show a good overall agreement with the previous experimental effective magnetic moments: the magnetic moments of the V atoms are slightly larger than 1 μ_B, and the total magnetic moment of the complexes increases linearly with their size.[440] Other theoretical investigations suggest this ferromagnetic interaction to be due to an interatomic exchange coupling within the metal d-orbitals along with a partial charge transfer between the $d\delta$ and the LUMO of benzene.[437]

5.01.6.3 Heteroarenes

Metal–ligand vapor co-condensation techniques allow the preparation of several bis(heteroarene) vanadium complexes. By this way, the trisubstituted bis(η^6-phosphabenzene) complex **112** was prepared in low yields (Scheme 43).[442] The bulky *tert*-butyl groups block rotational interconversion and, according to EPR spectroscopy, the two rotamers are present in a synclinal/antiperiplanar ratio close to the statistical ratio of 2 : 1. The full assignment of the EPR spectra of both of these rotamers suggests that the non-substituted parent complex V(η^6-C_5H_5P)$_2$[443] assumes the antiperiplanar conformation in rigid solution. Bis(arsabenzene) complex V(η^6-C_5H_5As)$_2$ is also accessible by the vapor technique,[444] and examination of the hyperfine coupling constant A(^{51}V) confirms that the η^6-arsabenzene, compared to benzene, is a superior η^6-ligand. Bis(η^6-pyrazine) sandwich complex **113** has been prepared by analogous metal vapor synthesis.[445,446] It has been studied by cyclic voltammetry, EPR spectroscopy, and a crystal structure analysis reveals that the pyrazine rings are twisted by ca. 44° relative to each other, and that the V–C and V–N bond distances are ca. 2.20 and 2.11 Å, respectively. The large difference in V–C and V–N bond lengths results in a significant folding of the six-membered ring along the pyrazine N–N vectors. Photoelectron spectroscopic studies of the known[447,448] sandwich-type η^6-dimethylpyridine complex V(η^6-2,6-Me_2-C_5H_3N)$_2$ confirm its electronic similarities to V(η^6-C_6H_6)$_2$, and indicate that the η^6-dimethylpyridine ligand is a better δ-acceptor than benzene.[449]



113 **112**

Scheme 43

5.01.6.4 Dienyl Complexes (“Open-Vanadocene”)

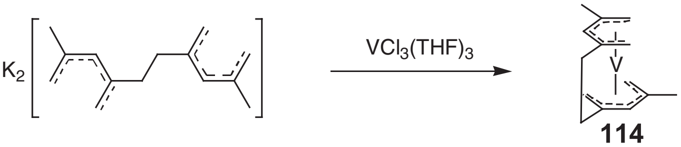
The 15-electron bis(dienyl) complexes (dienyl $=\eta^5$-pentadienyl and η^6-cyclohexadienyl) are typically prepared from *in situ* generated $[V_2Cl_3(THF)_6][Zn_2Cl_6]$ with 2 equiv. of the appropriate dienyl anion, and these complexes are known to form mono-adducts with CO, phosphines, and phosphites (see COMC(1995), Volume 5, Chapter 1, Section 5.01.7.4).

5.01.6.4.1 Pentadienyl

The PF_3 adduct of the bis(dimethylpendadienyl) open-vanadocene, $V(\eta^5\text{-}2,4\text{-}Me_2\text{-}C_5H_5)_2(PF_3)$,[450] has been found by X-ray analysis to adopt a *syn*-eclipsed conformation, with the Lewis base situated by the open edges of the two π-bonded dienyl ligands (V–P = 2.246(1) Å, av. V–C = 2.274 Å).[451]

The open-vanadocene $V(\eta^5\text{-}1,5\text{-}(Me_3Si)_2\text{-}C_5H_5)_2$ has been prepared following the above-mentioned procedure and appropriate potassium 1,5-bis(trimethylsilyl)pentadienide.[452] This complex has a low spin configuration with one unpaired electron ($\mu_{eff} = 1.72\ \mu_B$) and displays typical EPR 8-line pattern with $A_{iso} = 81.5$ G (g 1.970). CO adduct cannot be isolated upon exposure to CO due to the increased steric demands of the TMS subtituents; nevertheless, EPR monitoring of the reaction indicates reversible coordination of CO.

The reaction of the bridged bis(pentadienyl) dianion $K_2[4,4'\text{-}(CH_2)_2(2\text{-}Me\text{-}C_5H_5)]$ with VCl_3/Zn slurry leads to the structurally characterized bridged open-vanadocene complex **114** (Equation (8)).[453] The bridging unit between two pentadienyl groups introduces a significant distortion of the ligand skeleton that leads to conformational changes and alters the stability and reactivity as compared to the unbridged systems.



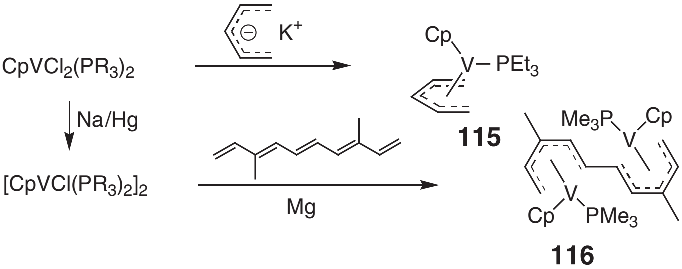
114

(8)

Mono-adducts of half-open vanadocenes CpV(Pdl)(PR_3) such as **115** are prepared from the reaction of $CpVCl_2(PR_3)_2$, or $CpVI_2$ in the presence of PR_3, and various potassium pentadienyls (Pdl $= C_5H_7$, 3-C_6H_9, 2,4-C_7H_{11}) (Scheme 44).[454] The PEt_3 ligand in these complexes can be replaced by CO, phosphites, or isocyanides leading to the corresponding adducts. All these 17-electron species have one unpaired electron (μ_{eff} ca. 1.6–1.7 μ_B) and have been studied by IR and EPR spectroscopies ($A_{iso}(^{51}V) = 61$–69 G, $A_{iso}(^{31}P) = 26$–45 G). An alternative approach has been used to prepare the paramagnetic open-fulvalene complex **116** from 3,8-Me_2-$C_{10}H_{10}$ and $[CpVCl(PMe_3)_2]_2$ in the presence of magnesium.[455]

5.01.6.4.2 Cyclooctadienyl

The reaction of 3 equiv. of K[*c*-C_8H_{11}] with $VCl_3(THF)_3$ gives the green “edge-bridged” open-metallocene $V(\eta^5\text{-}c\text{-}C_8H_{11})_2$.[456] Magnetic susceptibility measurements (one unpaired electron) and EPR spectroscopy ($A_{iso} = 76.6$ G) are in agreement with those of other bis(pentadienyl) systems. The edge-bridged complex adopts a staggered conformation with V–C av. = 2.199 Å. In addition, $V(\eta^5\text{-}c\text{-}C_8H_{11})_2$ forms adducts with both CO and cage phosphites, and infrared data of the carbonyl derivative $V(\eta^5\text{-}c\text{-}C_8H_{11})_2(CO)$ ($\nu_{CO} = 1870\ cm^{-1}$) indicate that the η^5-cyclooctadienyl ligand is a substantially better electron donor than typical pentadienyl ligands.[457]



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116

Scheme 44

5.01.6.5 Trienyl Complexes

5.01.6.5.1 η^7-Cycloheptadienyl complexes

The thermal reaction between $V(CO)_6$ and cycloheptatriene in hexane is known to afford a mixture containing low yields (15–21%) of the green η^7-cycloheptatrienyl complex $(\eta^7\text{-}C_7H_7)V(CO)_3$ and larger quantities of the brown anionic $[V(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_7H_8)][V(CO)_6]$.[458,459] Recent studies have shown that longer reflux time (90 min) leads to improved yields (34%) of the diamagnetic $(\eta^7\text{-}C_7H_7)V(CO)_3$.[460] In analogy to its cyclopentadienyl counterpart $CpV(CO)_4$, $(\eta^7\text{-}C_7H_7)V(CO)_3$ undergoes carbonyl exchange by various phosphines and phosphites either under irradiation in THF or via the photo-generated labile acetonitrile complex $(\eta^7\text{-}C_7H_7)V(CO)_2(NCMe)$.[60,460] Disubstituted complexes $(\eta^7\text{-}C_7H_7)V(CO)(PR_3)_2$ are only available with sterically less demanding ligands (R = Me, OMe). Similarly, photolysis in the presence of diphosphines affords the corresponding chelate complexes as well as binuclear species with bridging diphosphines. A summary of pertinent spectroscopic characterizations is listed in Table 19.

The reaction of $VCl_3(THF)_3$ with 3 equiv. of cyclopheptatrienyl anion $K[\eta^7\text{-}C_7H_7]$ in THF produces a complex $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_7H_9)$ in 54% yield that contains one aromatic η^7-cycloheptatrienyl ligand and one η^5-cycloheptadienyl ligand as evidenced by an X-ray determination.[461]

5.01.6.5.2 Trovacene ((η^7-tropylium)vanadium(η^5-cyclopentadienyl)) and its derivatives

The general synthesis and properties of the paramagnetic ($S = 1/2$) purple trovacene ((η^7-tropylium)vanadium(η^5-cyclopentadienyl)) have been described in COMC(1982) (Volume 3, Chapter 24, Section 24.8.1.1). It is usually prepared from the thermal reaction of $CpV(CO)_4$ and cyclohetatriene, a method that allows the preparation of cycloheptatrienyl-substituted derivatives ([7]trovacenyl complexes), or from the reaction of $CpVCl_3$ and cycloheptatriene in the presence of $i\text{-}C_3H_7MgBr$.

The trovacene structure has been determined more accurately by an X-ray diffraction analysis at 150 K, and this study was complemented by electron density distribution analysis.[462] The following are the important average bond lengths (in Å): Cp ligand C–C 1.42, V–C 2.26, V–Cp_c 1.92; $(\eta^7\text{-}C_7H_7)$ ligand C–C 1.42, V–C 2.19, V–(C_7H_7) 1.46. The nature of the $(\eta^7\text{-}C_7H_7)$–V bond, and comparison with other transition metal analogs, has been studied by means of photoelectron spectroscopy, in conjunction with theoretical considerations as well as electrochemical, spectroscopic (EPR, UV–VIS), and X-ray techniques.[463–466] Part of this work has also been discussed in Green's review on early transition metal complexes with cycloheptatriene and -enyl ligands.[467] In contrast to the predominantly ionic Cp–V bond, the interaction of $(\eta^7\text{-}C_7H_7)$ and vanadium (also Ti, Nb, Ta, Cr) has a significant covalent character. Furthermore, neither the +1 or −3 formalism for the charge of the $(\eta^7\text{-}C_7H_7)$ ring is an accurate description for the metal–C_7 ring bonding. It is proposed that the $(\eta^7\text{-}C_7H_7)$ ligand is best described as a seven-electron donor ligand, and that three valence electrons from the metal are required to form the V–$(\eta^7\text{-}C_7H_7)$ bonding.

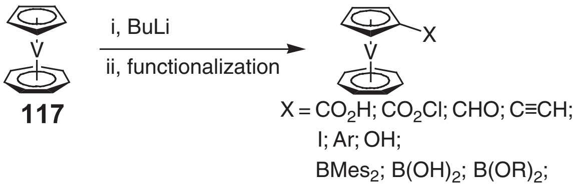
5.01.6.5.2.(i) [5]Trovacenyl complexes

Trovacene $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_5)$ **117** undergoes selective monolithiation at the Cp ring,[468] which enables its functionalization using classical organic chemistry. Various cyclopentadienyl-monosubstituted derivatives

Table 19 Selected spectroscopic data for η^7-cycloheptatrienyl vanadium complexes

Compound	*IR* ν_{CO} (cm^{-1})[a]	δ ^{51}V[b]	δ ^{31}P (Hz)[a]	^1J (^{51}V, ^{31}P)[a]	*References*
$(\eta^7\text{-}C_7H_7)V(CO)_3$	1983, 1913	−1518			460
$(\eta^7\text{-}C_7H_7)V(CO)_2(NCMe)$	1927, 1860	−795[c]			460
$(\eta^7\text{-}C_7H_7)V(CO)_2(PMe_3)$	1913, 1847	−1346	10.2	258	460
$(\eta^7\text{-}C_7H_7)V(CO)(PMe_3)_2$	1800	−855	10.2	258	460
$[(\eta^7\text{-}C_7H_7)V(CO)_2]_2(\mu^2\text{-diphosphine})$					460
Diphosphine = *cis*-$Ph_2PCH{=}CHPPh_2$	1925, 1862	−1188	67.3	258	460
$Me_2PCH_2CH_2PMe_2$	1913, 1844	−1354		258	460
$(\eta^7\text{-}C_7H_7)V(CO)$(*cis*-$Ph_2PCH{=}CHPPh_2$)	1813	−1206	54.4	258	460
$(\eta^7\text{-}C_7H_7)V(CO)(Me_2PCH_2CH_2PMe_2)$	1857	−1123	68.1	258	460

[a] ν_{CO} in THF.
[b] In C_6D_6.
[c] THF/MeCN (external lock).



117

118

Scheme 45

([5]trovacenyl complexes) $(\eta^7\text{-C}_7\text{H}_7)\text{V}[\eta^5\text{-C}_5\text{H}_4(\text{X})]$ have been prepared by this way (Scheme 45), with the functional groups X being $\text{-CO}_2\text{H}$,[469] -COCl,[469] -CHO,[470] -C≡CH,[470] -I,[470] -Ar,[471,472] -BMes_2,[473] -B(OR)_2,[474] -B(OH)_2,[474] and -OH.[475] As for bis(η^6-arene)vanadium(0) complexes, EPR spectroscopy has proved to be a valuable tool in the study of the mononuclear d^5-trovacenyl derivatives as substituent effects and structural distortions are assessed by $A(^{51}\text{V})$ hyperfine analysis, as well as to established monomer–dimer equilibrium in $(\eta^7\text{C}_7\text{H}_7)\text{V}[\eta^5\text{C}_5\text{H}_4(\text{CO}_2\text{H})]$ through weak hydrogen bonds. EPR data for selected [5]trovacenyl complexes are presented in Table 20.

5.01.6.5.2.(ii) [5–5]Bi-, tri-, and tetratrovacenes

The same monolithiation route as above, followed by Li/I exchange with iodocyclohexane, and Pd(ddpf)Cl_2-catalyzed homocoupling, affords (μ-η^5:η^5-fulvalenediyl)bis[(η^7-cycloheptatrienyl)vanadium **119** ([5–5]bitrovacene).[472] Other [5-5]bitrovacene complexes **120** (see Scheme 46) containing [5]trovacenyl units that are linked with various spacers between the two cyclopentadienyl rings have been prepared by suitable reactions.[469–471,473] Tri- and tetranuclear complexes are being synthesized with borane,[473] boroxine,[474] 1,3,5-benzene,[476] 1,3,5-methoxybenzene,[476] and 1,2,4,5-benzene[477] linkers. Intramolecular magnetic communication (which takes the form of antiferromagnetic interaction) in these oligonuclear complexes has been studied in the molecular level by EPR spectroscopy and in the bulk by magnetic susceptometry, by determining the exchange coupling constant J (see Table 21 with a comparison with intramolecular V···V bond distances), as well as by cyclic voltammetry.

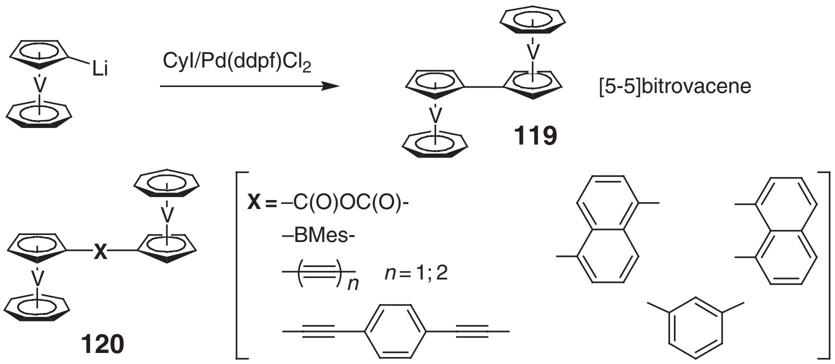
5.01.6.5.2.(iii) [7–7]Bitrovacene

Thermal rearrangement of dicycloheptatriene and subsequent reaction with CpV(CO)_4 yields [7-7]bitrovacene, $(\mu\text{-}\eta^7\text{:}\eta^7\text{-H}_6\text{C}_7\text{-C}_7\text{H}_6)[\text{VCp}]_2$, in which the sandwich complexes are connected via the seven-membered rings.[478] In the solid state, [7-7]bitrovacene is composed of 10 different rotamers, due to steric repulsion of the *ortho*-H of the dicyclopentadienyl ligand, which differ in the torsion angle and inter-vanadium distance. As shown in Table 21, it also presents more pronounced exchange coupling interactions ($J = -24.1\ \text{cm}^{-1}$) than [5-5]bitrovacene.

Table 20 EPR data for [5]trovacenyl $(\eta^7\text{-C}_7\text{H}_7)\text{V}[\eta^5\text{-C}_5\text{H}_4(\text{X})]$ and *ansa*-trovacene complexes[a]

Complex	g_{iso}	A_{iso}	$g_1/g_2[g\|\|]/g_3[g\perp]$	$A_1/A_2[A\|\|]/A_3[A\perp]$	*References*
$(\eta^7\text{-C}_7\text{H}_7)\text{V}[\eta^5\text{-C}_5\text{H}_4(\text{X})]$ X = H **117**	1.9866	69.8	2.0030, 1.9784	13.9, 96.1	473
CO_2H	1.9809	73.4			469
COCl	1.9829	73.5	1.9948, 1.9769	18.5, 101.0	469
BMes_2	1.9789	73.5	1.9970, 1.9688	12.7, 103.5	473
Ph	1.9829	71.8	2.0020, 1.9733	10.2, 102.6	472
OH	1.983	70.6	1.973, 1.975, 1.996	100.0, 100.6, 12.2	475
B(OH)_2	1.983	72.4			474
C≡CH	1.981	73.1			470
$\text{V}[(\eta^7\text{-C}_7\text{H}_6)\text{SiMe}_2(\eta^5\text{-C}_5\text{H}_4)]$ **121**[b]	1.985	68			480
$\text{V}[(\eta^7\text{-C}_7\text{H}_6)\text{SiPh}_2(\eta^5\text{-C}_5\text{H}_4)]$ **122**	1.9832	67.6	1.974, 1.972, 1.999	96.2, 100.8, 6.0	479
$\text{V}[(\eta^7\text{-C}_7\text{H}_6)\text{-Pt(PEt}_3)_2\text{-SiMe}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]$ **124**[b]	1.987	71			480
$\text{V}[(\eta^7\text{-C}_7\text{H}_6)(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_4)]$ **123**	1.9816	70.3	1.9724, 1.9718, 1.998	101.9, 103.6, 5.3	479

[a] EPR in fluid (295 K) and rigid toluene. $A(^{51}\text{V})$ is $|A(^{51}\text{V})|$ in G.
[b] In hexane solution.



Scheme 46

Table 21 EPR and magnetic data for bitrovacenes

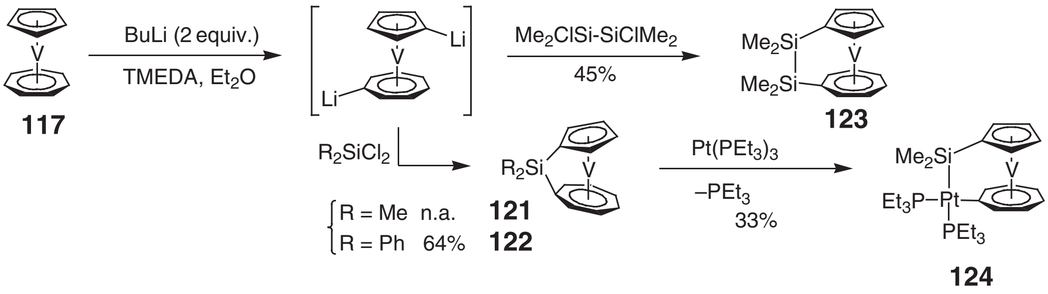
Complex	*V···V* (Å)[a]	g_{iso}	$\lvert A_{iso}\rvert$ (G)	J_{EPR} (cm^{-1})	J_χ (cm^{-1})	*References*
[5–5]Bitrovacene **119**	5.501	1.9816	71.8	−1.5	−2.78	472
Spacer = C≡C	7.602	1.984	72.8	−0.92	−1.45	470
C≡C–C≡C	9.432	1.985	72.7	−0.56	−3.84	470
C≡C–C_6H_4–C≡C	17.27	1.987	72.7	−0.005		470
C(O)OC(O)	6.66	1.9819	73.2	−0.345		469
BMes	5.893	1.9785	73.2	−1.43	−0.96	473
1,8-naphtalene	7.067	1.9789	71.7	−2.22	−1.04	471
1,5-naphtalene		1.9782	72.2	−0.63		471
1,3-C_6H_4	7.2535	1.982	72.0	−0.48	−1.66	471
[7–7]Bitrovacene	4.93–5.53[b]	1.9832	71.9		−24.1	478

[a] Intramolecular bond distance determined by X-ray analysis (note that in some complexes intermolecular V···V distances are shorter).

[b] Range for the 10 rotamers.

5.01.6.5.2.(iv) *ansa*-Trovacene

Heteroannular double lithiation of **117** with BuLi/TMEDA followed by treatment of the intermediate dilithio complex with R_2SiCl_2 [R = Me,[479,480] Ph[479]] produces the corresponding silicon-bridged [1]silatrovacenophane complex V[(η^7-C_7H_6)SiR_2(η^5-C_5H_4)], **121** and **122**, as depicted in Scheme 47. Similar reaction with $(Me_2SiCl)_2$ gives the corresponding [2]silatrovacenophane derivative **123**.[479] Both complexes with $SiPh_2$ and $(Me_2SiCl)_2$ links have been structurally characterized, and present interplanar angles of 17.3° and 3.8°, respectively, and considerable strain in the C_7 ring–link–C_5 ring region. As a consequence, the strained **121** shows irreversible redox behavior



Scheme 47

probably caused by cleavage of the bridge. When reacted with Pt(PEt_3)$_3$, **121** undergoes oxidative addition and regioselective insertion of a Pt(PEt_3)$_2$ moiety into the Si–C bond of the seven-membered ring to afford the structurally characterized [2]platinasilatrovacenophane **124** (Scheme 47), with 33% yield as a blue-grey paramagnetic complex that shows an interplanar angle of 10.6°.[480] Pertinent EPR data for these *ansa*-trovacene complexes are reported in Table 20.

5.01.7 Conclusion

Although the last 15 years have seen the investigations into vanadium organometallic chemistry grow significantly, it is still true to say that at the beginning of the twenty-first century the organovanadium chemistry remains underdeveloped as compared to the neighboring group 4/6 transition metals. One of the major difficulties encountered with vanadium compounds is the often occurring paramagnetism and the inability to control vanadium to move around several oxidation states via disproportionation or redox reactions. However, as is obvious in some sections, the use of new ligands provides suitable environment for the stabilization of reactive functions and has opened the door to new potential developments in homogeneous catalysis. Applications are still limited (organic synthesis, olefin polymerization, medicinal chemistry, material chemistry), but should benefit from the recent advances and the almost infinite possibilities in the design of new ligands. Because of such disproportionation or redox reactions, vanadium remains today a challenging, and always surprising, center for organometallic chemistry, and it is to be hoped that continued investigation of these systems will yield new insights and applications over the next decade.

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5.02
Niobium Organometallics

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5.02.1 Introduction and Organization

5.02.1.1 Coverage and Overview

This chapter encompasses most of the organometallic chemistry of niobium reported in the scientific literature between 1993 and 2004. A few papers that were published in 2005 have also been included. Two chapters that focused on niobium and tantalum chemistry appeared in COMC (1982) and COMC (1995), and these were written by Labinger[1] and Wigley and Gray,[2] respectively. In this edition, the organometallic chemistry of the two metals will be considered separately.

In the last 11 years, and to a lesser extent the preceding ones, the organometallic chemistry of niobium has been dominated by the tendency to attain the highest oxidation state. This state is stabilized in most cases through the formation of Nb–O, Nb–N, or similar multiple bonds, although an appreciable number of complexes in the intermediate +3 oxidation state have also been described – particularly with cyclopentadienyl (Cp) or related ligands such as tris-pyrazol-1-ylborates (Tp). New examples of complexes with η^1-ligands, especially cyclopentadienyl-containing alkyl, silyl, and hydride derivatives, have been isolated, and, in some cases, unexpected structures (e.g., hypervalent situations for silicon in silyl-containing niobocenes) and different modes of reaction have been found. It is also worth noting the large number of examples involving insertion processes into Nb–alkyl bonds, especially in reactions with isocyanides. These reactions mostly give rise to either η^2-iminoacyl derivatives or different types of related niobacycle-containing species. The chemistry of cyclopentadienyl systems with different types of substituted Cp rings, namely, bis-cyclopentadienyl and monocyclopentadienyl derivatives with different kinds of ancillary ligands, has also been at the forefront in this area. In this respect, a large number of new classes of complexes – some of which exhibit rich reactivity – have been described in detail. Furthermore, progress in the study of new classes of cyclopentadienyl-containing complexes is also worthy of note (e.g., *ansa*-niobocene) and has opened up new possibilities in terms of reactivity studies. For example, the isolobal relationship between Cp(NR)Nb and Cp_2M (M = group 4 metal) fragments has been described, and different olefin polymerization catalytic studies based on the cyclopentadienyl-imido niobium unit have been considered. As a continuation of previous studies compiled in COMC (1995), new examples of niobium complexes have proved beneficial in terms of modeling and understanding certain catalytic processes, including the aforementioned olefin polymerization. Finally, a number of complexes have proved useful in different organic reactions in the field of metal-mediated organic synthesis, especially in C–C bond formation and hydrogenation of arenes processes based on the use of lower-valent niobium complexes.

The reader is referred to the corresponding chapters in COMC (1982) and COMC (1995) for a thorough introduction to this field and for a complete overview of the different families of Nb and Ta organometallic complexes reported prior to 1993. Several relevant review articles have appeared over the years, and these are mentioned in the corresponding section. The chapter on group 5 and group 6 metallocenes in the book *Metallocenes* and the chapter devoted to the coordination chemistry of Nb and Ta in COMC (1995) are of particular interest.[3,4]

5.02.1.2 Organization

One or more tables of complexes have been included in each section, and these provide a framework around which discussions are focused. These tables constitute an essential part of the chapter, since they contain exhaustive information concerning the different classes of complexes. Each table contains a “comments” section, which in some cases contains preparative details (denoted as “prep”) and spectroscopic and structural (denoted as X-ray) data as well as additional information that the reader may find useful. In order to maintain consistency with the approach previously used in the chapters in COMC (1982) and COMC (1995), complexes containing more than one type of ligand (i.e., heteroleptic complexes) will only be listed in one section. Such compounds are listed in accordance with the previously established set of “classification priorities”: (i) alkylidenes and alkylidynes, (ii) π-bonded ligands other than Cp, (iii) η^1-ligands, (iv) carbonyls and isonitriles, and (v) cyclopentadienyls. Note that complexes are not described in this order of priority, but are rather classified in a progression according to complexity, as outlined in the table of contents.

5.02.2 Carbonyl and Isocyanide Complexes

5.02.2.1 Carbonyl Derivatives

In the years since 1993, the carbonyl chemistry of Nb has been developed. New examples of complexes in low oxidation states, especially with cyclopentadienyl ligands, have been reported. (see Table 1)

Table 1 Carbonyl complexes of niobium

Compound	*Comments*	*References*
$Cs_3[Nb(CO)_5]$	$Na[Nb(CO)_6] + 3Na \xrightarrow{NH_3(-70\,°C)} \xrightarrow{3CsI/NH_3(-70\,°C)} Cs_3[Nb(CO)_5]$	11
$Na_3[Nb(CO)_5]$	Characterized by ^{93}Nb and ^{13}C NMR spectroscopy	11
$[Et_4N]_2[Nb(CO)_5H]$		11
$[Et_4N]_2[Nb(CO)_5SnPPh_3]$		11
$[Ph_4As][Nb(CO)_5(NH_3)]$		11
$[Ph_4N][Nb(CO)_5(CN^tBu)]$		11
$Nb(CO)_2(dppe)_2X$	X = Cl, Br, I, H	12
$[Nb(CO)_2(dppe)_2X]^+$	X = Cl, Br, I, H; X = Cl EPR(−78 °C); 10-line pattern, $g = 2.04$, $A = 115$ G; X = H EPR(77 K); 10-line pattern, $g = 2.05$, $A = 113$ G	12
cis-$[Nb(CO)_2(CNR)_2(dppe)I]$	R = ^{t}Bu, Cy (X-ray)	14
$Nb(CO)_3(PR_3)_3X$	$PR_3 = PEt_3$, PMe_2Ph, X = Cl, Br, I	14
$Nb(CO)_4(dppe)_2X$	X = Cl, Br, I	14
$Nb(CO)_4(NN)X$	X = Cl, I; NN = ethylenediamine(en), dimethylethylenediamine(dmen), tetramethylenediamine(tmen), 2,2′-dipyridyl(2,2′-dipy), 4,4′-dipyridyl(4,4′-dipy)	15
$Nb(CO)_2(depe)_2Cl$	depe = 1,2-bis(diethylphosphino)ethane	16
$Nb(CO)_2(dbpe)_2Cl$	dbpe = 1,2-bis(dibutylphosphino)ethane	16
$Nb(CO)_2(trimpsi)(NO)$	trimpsi = $^tBuSi(CH_2PMe_2)_3$	17
$(\eta^5\text{-}C_5H_4R)Nb(CO)_4$	R = $COCH_3$,CO_2CH_3(X-ray), $CO_2C_2H_5$, COC_6H_5, $COCH_2C_6H_5$, $C(CH_3){=}CH_2$	19
$(\eta^5\text{-}C_9H_7)Nb(CO)_4$	C_9H_7 = indenyl (X-ray)	19
$(\eta^5\text{-}9\text{-}Ph\text{-}C_{13}H_9)Nb(CO)_4$	$C_{13}H_9$ = 9-Ph-fluorenyl, X-ray	21
$CpNb(CO)_3$	Photochemically generated in matrices (under He)	22
$CpNb(CO)_2$	Photochemically generated in matrices (under He)	22
$CpNb(CO)_3(N_2)$	Photochemically generated in matrices (under N_2)	22
$CpNb(CO)_2(N_2)_2$	Photochemically generated in matrices (under N_2)	22
$CpNb(CO)_3H_2$	Under photochemical conditions	22
$CpNb(CO)_3(\eta^2\text{-}H_2)$	Under photochemical conditions	22
$(C_9H_7)Nb(CO)_3(\eta^2\text{–}H_2)$	Under photochemical conditions	22
$CpNb(CO)_3(Xe)$	Characterized by fast time-resolved infrared (TRIR)	24
$[^RP_2Cp]Nb(CO)Cl_2$	$^RP_2Cp = C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PR_2)_2$, R = i-Pr, Ph; X-ray	26
$[Cp_2(CO)Nb(\mu\text{-}Cl)B(C_6F_5)_3]$	$Cp = C_5H_4SiMe_3$	27
$[Cp_2(CO)Nb(\mu\text{-}H)B(C_6F_5)_3]$	$Cp = C_5H_4SiMe_3$	27
$[Cp_2(CO)_2Nb][HB(C_6F_5)_3]$	$Cp = C_5H_4SiMe_3$	27
$Cp_2Nb(CO)(\eta^1\text{-}pz\text{-}N)$	$Cp = C_5H_4SiMe_3$, pz = pyrazolyl	28
$[Cp_2Nb(L)]_2Hg$	$Cp = C_5H_4SiMe_3$, L = CO, PMe_3 (X-ray)	29
$Cp_2Nb(L)$	L = CO, EPR, $g = 2.097$, $A_{Nb} = 1.72$G	29
$Cp_2Nb(CO)(SePh)$	$Cp = C_5H_4SiMe_3$	30
$[CpNb(\mu\text{-}CO)_2Fe(CO)Cp]$	$Cp = C_5H_4SiMe_3$; X-ray	30
$Cp_2Nb(CO)(\mu\text{-}PR_2)Fe(CO)_4$	R = Me, Ph; prep: $Cp_2Nb(CO)(PR_2) + Fe_2(CO)_9$	31
$Cp_2Nb(\mu\text{-}CO)(\mu\text{-}PR_2)Fe(CO)_3$	R = Me, Ph (X-ray)	31
$Cp_2Nb(CO)(\mu\text{-}PR_2)Fe(CO)_3(PMe_2Ph)$	R = Me, Ph	31
$Cp_2Nb(CO)(\mu\text{-}PPhH)Fe(CO)_4$		32

(*Continued*)

Table 1 (Continued)

Compound	*Comments*	*References*
$Cp_2Nb(\mu\text{-}CO)(\mu\text{-}PPhH)Fe(CO)_3$		32
$Cp_2Nb(\mu\text{-}CO)(\mu\text{-}PPh_2)M(CO)_3(PMe_2H)$	M = Cr (X-ray), W	33
$Cp_2Nb(CO)(\mu\text{-}SeEt)M(CO)_n$	M = Fe, $n = 4$(X-ray); M = Mo, W, $n = 5$; prep:$Cp_2Nb(CO)(SEt) + Fe_2(CO)_9$ or $M(CO)_5(THF)$	34
$Cp_2Nb(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}PR_2S)ML_n$	R = Me, Ph: $ML_n = Cr(CO)_5$; $Mo(CO)_5$; $W(CO)_5$; $CpMn(CO)_2$; $Fe(CO)_4$	35
$[Cp_2Nb(CO)]_3Co_9(CO)_8Te_6$	$Cp = {}^tBuC_5H_4$; prep:$Cp_2NbTe_2H + Co_2(CO)_8$	36
$[Cp_2Nb(CO)]_3Co_9(CO)_8Te_6{\cdot}3Cr(CO)_5$	X-ray	36

5.02.2.2 Carbonyls

In addition to the small number of well-known zerovalent compounds synthesized by metal vaporization techniques,[5–7] attempts to synthesize $Nb(CO)_6$ or related Nb(0) species by either reductive carbonylation of metal salts or oxidation of carbonylate complexes $[Nb(CO)_{6-n}L_n]^{n-}$ have proved unsuccessful – as in previous years.[8] Other approaches, such as the abstraction of hydrogen atoms from hydrides of the type $[Nb(CO)_{6-n}(PR_3)_nH]$, which have been successfully employed to prepare Ta(0) complexes[9] like $[Ta(CO)_4(dmpe)]$, have not yet been attempted. In terms of the development of the chemistry of carbonyls and substituted carbonyls, new examples of complexes in low oxidation states and the reactivities of these systems have been described. New and improved procedures to prepare the key precursor in the study of Nb carbonyls and associated low-valent Nb chemistry, that is, $[Nb(CO)_6]^-$, have been described. A higher-pressure version of this process has also been reported.[10] Reductive carbonylations of $NbCl_4(THF)_2$, mediated by sodium naphthalene or anthracene, provide $[Nb(CO)_6]^-$ as the tetraethylammonium salt in the highest yields known for atmospheric pressure syntheses of this carbonylate (Equation (1)).[11] The anion $[Nb(PF_3)_6]^-$ was prepared in a similar reaction by using PF_3 instead of CO.[11]

$$NbCl_4(THF)_2 + 5[C_{14}H_{10}]^- \xrightarrow{\text{THF, }-40\,^\circ C} \xrightarrow{CO(1\text{ atm})} [Nb(CO)_6]^- + 5C_{14}H_{10} \qquad (1)$$

This complex was subsequently used to synthesize the thermally unstable hydride derivative $[Nb(PF_3)_6H]$. $[Nb(CO)_5]^{3-}$ was prepared by treatment of $[Nb(CO)_6]^-$ with sodium in liquid ammonia, and the species was isolated as $Cs_3[Nb(CO)_5]$. Protonation of the trianion gave $[Nb(CO)_5H]^{2-}$.

Ellis *et al.*[12] carried out both electrochemical and spectroelectrochemical studies of the substituted carbonyl complexes $Nb(CO)_2(dppe)_2X$, which were prepared using an improved version of a method described in COMC (1995). These compounds exhibit a one-electron reversible oxidative process that generates stable (at least on the electrochemical timescale) 17-electron species of the type $[Nb(CO)_2(dppe)_2X]^+$ (Equation (2)). Chemical oxidation of some of these complexes by treatment with different oxidizing agents, such as $[(Ph)_3C][PF_6]$ or ferrocenium hexafluorophosphate, proved unsuccessful.

$$Nb(CO)_2(dppe)_2X \longrightarrow [Nb(CO)_2(dppe)_2X]^+ + e^- \qquad (2)$$

In the same way, an improved method to prepare $Nb(CO)_2(dppe)_2H$ was also reported.[12] Oxidative halogenation of $[Nb(CO)_6]^-$ led to the preparation of new families of halide–carbonyl complexes containing phosphine, amine, isocyanide, and alkyne ligands.[13,14,15,16] In an elegant study, Legzdins *et al.* prepared the first nitrosyl complex of Nb, namely, $Nb(CO)_2(trimpsi)$ (NO) (trimpsi = *tert*-$BuSi(CH_2PMe_2)_3$),[17] and subsequently studied its reactivity.[18]

5.02.2.3 Cyclopentadienyl Carbonyl Complexes

An efficient synthetic route to prepare monocyclopentadienyl–tetracarbonyl complexes, some of which were reported in COMC (1995), has been developed, and involves the reaction of $Na[Nb_2(\mu\text{-}Cl)_3(CO)_8]$ with different NaC_5H_4R, NaC_9H_7, and Li(9-phenylfluorenyl) species.[19,20,21] As a continuation of COMC (1995), photochemical processes involving $CpNb(CO)_4$ and $(C_9H_7)Nb(CO)_4$ were considered, and photolytic substitution by different ligands of one or more of the carbonyl ligands took place.[20,22–24] For example, photolysis of $(C_9H_7)Nb(CO)_4$ led to the non-classical complex $(C_9H_7)Nb(CO)_3(\eta^2\text{-}H_2)$, whereas irradiation of $CpNb(CO)_4$ resulted in both $CpNb(CO)_3H_2$ and $CpNb(CO)_3(\eta^2\text{-}H_2)$.[22] Gas-phase photoelectron spectroscopy was used to investigate bonding between Nb and carbonyl, and cyclopentadienyl ligands in the molecules (η^5-C_5H_4R)Nb(CO)$_4$.[25] Nb(III) is the lowest oxidation state commonly observed in carbonyl-containing niobocene compounds, and this gives rise to numerous types of complexes with the formula $Cp_2Nb(CO)X$ (X = monoanionic ligand). Most classes of these complexes are considered in subsequent sections. Electron-rich $Cp_2Nb(CO)X$ (X = Cl, H) react with the strong Lewis acid $B(C_6F_5)_3$ to give the zwitterionic compounds $[Cp_2(CO)Nb(\mu\text{-}X)B(C_6F_5)_3]$.[27] Nb–Hg compounds $[Cp_2Nb(L)]_2Hg$ serve as stable precursors to the short-lived Nb(II) radicals Cp_2NbL and, in addition, reaction of the binuclear complex, in which L = CO, with several reagents gives rise to a series of heterobimetallic compounds.[29,30] Different types of new heterobimetallic complexes containing the $Cp_2Nb(CO)$ moiety have also been prepared.[31–35] For example, metallaphosphines such as $Cp_2Nb(CO)(PR_2)$ are able to bind unsaturated organometallic fragments to give μ-phosphido-bridged complexes, such as $Cp_2Nb(\mu\text{-}PR_2)(\mu\text{-}CO)M(CO)_xL_y$. Metal telluride clusters composed of niobocene carbonyl moieties have also been described.[36]

5.02.2.4 Isocyanide Derivatives

In a similar way to the carbonyl chemistry, an appreciable number of isocyanide derivatives of niobium contain ancillary cyclopentadienyl ligands, as can be seen from Table 2.

5.02.2.4.1 Isocyanides

The number of isocyanide or substituted isocyanide complexes of niobium reported to date is small. The first homoleptic isocyanide of Nb, namely, $[Nb(CNXylyl)_7][BF_4]$, was isolated in 1999 through oxidation of $[Nb(CO)_6]^-$ with Ag^+ as the oxidizing agent (Equation (3)).[37] Furthermore, direct nitrosylation of $[Nb(CO)_6]^-$ with 2 equiv. of NO^+ in the presence of CNXylyl gave *cis*-$[Nb(CNXylyl)_4(NO)_2]^+$.[38]

$$[Nb(CO)_6]^- + 2Ag^+ + 7CNXylyl \xrightarrow{\text{THF, –60 to 20 °C}} [Nb(CNXylyl)_7]^+ \qquad (3)$$

New complexes have been prepared from $[Nb(CO)_6]^-$ through oxidation with halogens in the presence of the appropriate isocyanide.[13,39] Depending on the reaction conditions, the process yields seven-coordinate complexes of Nb(I), six-coordinate complexes of Nb(I) and Nb(III), or eight-coordinate complexes of Nb(III). In contrast to the corresponding vanadium chemistry, isocyanide complexes of Nb(II) have not been described to date. The oxidation of Nb(–I) to Nb(I) or (III) has been carried out with iodine (or bromine in some cases).

5.02.2.4.2 Cyclopentadienyl isocyanide complexes

Isocyanide-containing niobocene complexes of stoichiometry $Cp_2Nb(CNR)X$ (X = monoanionic ligand) are also well documented, and some of these compounds will be considered in subsequent sections. Fewer monocyclopentadienyl derivatives have been reported;[40,41] although insertion processes involving isocyanides in alkyl monocyclopentadienyl niobium derivatives to give iminoacyl derivatives have been widely studied.

Table 2 Isocyanide complexes of niobium

Compound	*Comment*	*References*
$[Nb(CNXyl)_7][BF_4]$		37
$Nb(CNXyl)_6I$		37
$[Nb(CNXyl)_4(NO)_2][BF_4]$	X-ray	38
$Nb(CO)_2(CNR)_4X$	X = Br, I; R = ^{t}Bu, Cy, 2,6-$Me_2C_6H_3$; intermediate products	39
$[Nb(CNR)_6I_2]I$	R = ^{t}Bu, Cy	39
$Nb(CNR)_3X_3$	X = Br, I	39
$[Nb(CN^tBu)_3(\eta^2\text{-}PhC{\equiv}CPh)I_2]I$		38
$CpNbCl_4{\cdot}(CNR)$	Cp = C_5Me_5; R = ^{t}Bu; 2,6-$Me_2C_6H_3$ (X-ray)	40
$CpNbCl_2(CNR)_3$	Cp = C_5Me_5; R = ^{t}Bu; 2,6-$Me_2C_6H_3$ (X-ray)	40
$CpNbCl_4{\cdot}(CNR)$	Cp = C_5Me_5; R = 2,4,6-$Me_3C_6H_2NC$	41

5.02.2.5 CO and CNR Reductive Coupling Reactions

In the years covered in this review, new studies have been carried out on the reductive coupling of two CO or CNR groups in Nb carbonyl and isonitrile complexes to form η^2-alkyne or related complexes.[13,39,42–44] Carbyne-containing complexes have been proposed as intermediates in these processes. For example, it has been shown that reaction of a siloxycarbyne precursor, [Nb(COSiR$_3$)(CO)(depe)$_2$], with carbon-based electrophiles, such as acetyl chloride (AcCl), gives the mixed-siloxy-/-alkoxyacetylene-coupled products such as [Nb(η^2-R$^1{}_3$SiOC$\equiv$COMe)(depe)$_2$Cl].[43]

5.02.3 η^1-Complexes

The complexes described in this section are those that contain alkyl, aryl, hydride, or related ligands coordinated to the metal center in a σ-fashion; metallacycles with at least one Nb–carbon bond will be considered in Section 6.

5.02.3.1 Alkyls, Aryls, and Related σ-Complexes

The organometallic chemistry of Nb with σ-bonded carbon ligands was covered in great detail in COMC (1995). In the intervening years, several studies have focused on the reactivity of cyclopentadienyl-containing alkyl/aryl niobium complexes toward insertion processes involving unsaturated molecules.

5.02.3.1.1 Alkyl and aryl complexes without cyclopentadienyl ligands

New homoleptic alkyl complexes have not been described in recent years. However, a general study of the geometries of certain d^0-complexes showed that [NbMe$_6$]$^-$ has a slight distortion from an ideal trigonal-prismatic geometry.[45] In general, new classes of mixed-alkyl(aryl) complexes were prepared from halide d^2- or d^0-precursors containing alkoxide, imido, macrocyclic, or related ancillary ligands by metathetical reactions with main group alkylating agents. For example, during the course of a systematic study of niobium chemistry based on a macrocyclic ligand, the (*meso*-octaalkylporphyrinogen)Nb(V) complex [(η^5:η^1:η^5:η^1-Et$_8$N$_4$)NbMe] was prepared by alkylation of the halide precursor.[46,47] Fryzuk *et al.* have extensively studied the coordination chemistry of Nb(III) with bis-(amidophosphine) macrocyclic ligands. These studies led to the preparation of a series of paramagnetic alkyl complexes such as ^{R}[P$_2$N$_2$]NbR^1 (R = Cy, Ph; R^1 = CH$_2$SiMe$_3$, CH(SiMe$_3$)$_2$).[49,50] Hydrogenolysis of some of these complexes in aromatic solvents led to hydride addition to the aromatic solvent, resulting in the formation of the π-bonded complexes.[52] Alkyl complexes containing imido ligands have also been reported.[54,55]

5.02.3.1.2 Cyclopentadienyl alkyl and aryl complexes

Alkyl(aryl)-containing cyclopentadienyl complexes are summarized in Table 3. The synthesis of half-sandwich complexes has continued to be an active area of research. For example, in the high oxidation state, new complexes of the type CpNbR$_n$X$_{4-n}$ have been prepared using similar methods to those described in COMC (1995).[41,56] However, the most extensively studied class of complexes corresponds to mixed-ligand systems containing imido ligands with the stoichiometries CpNbXR(NR^1) and CpNbR$_2$(NR^1).[57–65] Imido ligands have largely been employed as ancillary groups to support high oxidation state metal centers by virtue of the organic R group, the steric and electronic properties of which can be readily modified. The behavior of these complexes in insertion reactions to give acyl and iminoacyl derivatives and the intra- or intermolecular rearrangement processes of the resulting insertion products are discussed in Section 5.02.5.3. Bis(cyclopentadienyl) alkyl/aryl derivatives constitute a common family of compounds, and their chemistry, especially for Nb(V), (IV), and (III) oxidation states, was thoroughly reviewed in COMC (1995). In the high oxidation state, new complexes of the type Cp$_2$NbR(=E), where E is a dianionic ligand, have been reported, with imido-containing compounds well represented.[67–73] A number of oxo-alkyl complexes have also been prepared. For example, Cp$_2$NbR(O) complexes were isolated by thermolysis of Cp$_2$NbR(η^2-CO$_2$)[74] and, in an alternative way, the adducts Cp$_2$NbR(η^2-CO$_2$-B(C$_6$F$_5$)$_3$) evolve with the loss of CO to give the corresponding oxo-alkyl-containing complexes.[75] Compounds of the type Cp$_2$NbR(L), where L = π-acid ligand such as CO, CNR, and PR$_3$, have continued to be prepared by either the reaction of Cp$_2$NbH(olefin) with the appropriate L or the metathetical process of Cp$_2$NbX(L) with alkylating agents.

Table 3 Alkyls and aryl complexes

Compound	*Comments*	*References*
$[Li(OEt_2)_3][NbMe_6]$	X-ray	45
$\{(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)\}NbCl$	Et_8N_4 = *meso*-octaalkylporphyrinogen	46
$\{(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)\}NbMe$	X-ray	47
$\{p\text{-}^tBu\text{-calix[4]-(O)}_4\}\text{-Nb-}CH_2Ph$	Prep: $[\{p\text{-}^tBu\text{-calix[4]-(O)}_4\}_2Nb_2Cl_2] + Mg(CH_2Ph)_2$	48
$^R[P_2N_2]NbR^1$	$^R[P_2N_2] = RP(CH_2SiMe_2NSiMe_2CH_2)_2PR$, R = Cy, Ph; $R^1 = CH_2SiMe_3$ (X-ray), $CH(SiMe_3)_2$ (X-ray), Me; paramagnetic species	49,50
$^R[P_2N_2]NbMe(py)$		50
$(^R[P_2N_2]NbMe)_2(\mu\text{-}N_2)$	R = Cy (X-ray), Ph (X-ray); diamagnetic species	50
$CyPh[NPN]NbMe_3$	$CyPh[NPN] = CyP(CH_2SiMe_2NPh)_2$	51
$[Nb(R\text{-}L)Me_2]_2$	R-L = 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenoxy (X-ray); 2,6-bis(4-ethyl-6-*tert*-butylsalicyl)-4-*tert*-butylphenoxy	53
$[\{NbLR_3\}_2(\mu\text{-}1,n\text{-}NC_6H_4N)]$	$L = CH_3CN$, $R = CH_2SiMe_3$ (X-ray); CH_2CMe_3; CH_2CMe_2Ph; L = THF, $R = CH_2SiMe_3$; CH_2CMe_3; CH_2CMe_2Ph; *n* = 4, 3	54,55
Monocyclopentadienyl derivatives		
$CpNbMe_2Cl_2$	$Cp = C_5Me_5$	41
$CpNbMe_4$	$Cp = C_5Me_5$	56
$[\{CpNbMe_3\}_2(\mu\text{-}O)]$	$Cp = C_5Me_5$	56
$CpNbMeCl_3L$	$Cp = C_5Me_5$; $L = PMe_2Ph$	56
$CpNbMe_3Cl$	$Cp = C_5Me_5$	56
$CpNbMe_2(NMe_2)_2$	$Cp = C_5H_5$	56
$CpNbMe_2(N^tBu)$	$Cp = C_5Me_5$	57
$CpNbR_2(R^1{}_2C_2B_4H_4)$	$Cp = C_5H_5$, C_5Me_5; R^1 = Et (X-ray), $SiMe_3$, Me; carborane moiety	58
$CpNbRCl(NR^1)$	$Cp = C_5H_4SiMe_3$, C_5Me_5, $R^1 = 2,6\text{-}Me_2C_6H_3$, R = Me	59
$CpNbR_2(NR^1)$	$Cp = C_5H_4SiMe_3$, $R^1 = 2,6\text{-}Me_2C_6H_3$, R = Me, CH_2SiMe_3, CH_2CMe_3, NMe_2, $CH_2C_6H_5$	59
$CpNbMe_2(NR)$	$Cp = C_5Me_5$; $R = 2,6\text{-}Pr^i{}_2C_6H_3$; studied as precursor of cationic alkyl catalyst	60
$CpNbR(NH^tBu)(NR^1)$	R = Me, ^nBu, NH^tBu, $R^1 = {}^tBu$; R = Me, $R^1 = 2,6\text{-}Pr^i{}_2C_6H_3$	61
$CpNbXY\{N(2,6\text{-}Me_2C_6H_3)\}$	X = Me, $NH(2,6\text{-}Me_2C_6H_3)$; Y = Cl, $NH(2,6\text{-}Me_2C_6H_3)$ (X-ray)	62
$[CpNbMe(\mu\text{-}NR)]_2$	$R = 2,6\text{-}Pr^i{}_2C_6H_3$; prep: $CpNbMe_2(NR) + H_2$	63
$CpNb(CH_2Ph)_2(N^tBu)$	$Cp = C_5H_4(SiClMeX)$, X = Me, Ph; $Cp = C_5H_4[Si(CH_2Ph)MeX]$, X = Me, Ph	64
$CpNb(CH_2Ph)Cl(N^tBu)$	$Cp = C_5H_4(SiClMe_2)$	64
$[MeNb\{(\mu\text{-}C_5H_4)(CH_2)_3N\}\text{-}\{\mu\text{-}NCH(CH_2)_2C_5H_4\}NbMe_2]$	A bridging η^2,κ N-C(H) = N alkenylideneamide system is present	65
$CpNb(CH_2CRCH_2)(N^tBu)Cl$	R = H, Me	66
Bis(cyclopentadienyl) derivatives		
$Cp_2NbR(N^tBu)$	R = Me, CH_2Ph, $\sigma\text{-}C_3H_5$	67
$[(C_5H_4)CMe_2(C_5H_4)]NbMe(N^tBu)$	Prep: $[(C_5H_4)CMe_2(C_5H_4)NbCl(N^tBu)] + MeLi$	68
$Cp_2NbR(NPh)$	$Cp = C_5H_4SiMe_3$; R = Me, Et, ^iPr	69
$[\{Cp_2NbR\}_2(\mu\text{-}1,n\text{-}N_2C_6H_4)]$	$Cp = C_5H_4SiMe_3$; n = 3, 4; R = Me, Et, ^iPr	69
$[(C_5H_4)SiMe_2(C_5H_4)]NbR(N^tBu)$	R = Me, Et, CH_2Ph, $CH_2CH{=}CH_2$	70
$Cp_2NbMe(NR)$	$R = 2,6\text{-}Me_2C_6H_3$	62
$Cp_2Nb(C{\equiv}CR)(NR^1)$	$Cp = C_5H_5$; R = Me, $SiMe_3$, ^tBu, CH_2Ph; $R^1 = {}^tBu$, $C_6H_4Me\text{-}4$; $Cp = C_5H_4SiMe_3$; R = $SiMe_3$, ^tBu, Ph (X-ray); $R^1 = {}^tBu$, Ph, $C_6H_4Me\text{-}4$, $C_6H_4OMe\text{-}4$, $2,6\text{-}Me_2C_6H_3$	71,72
$[(C_5H_4)SiMe_2(C_5H_4)]Nb(C{\equiv}CR)(N^tBu)$	R = $SiMe_3$, ^tBu; prep: $[(C_5H_4)SiMe_2(C_5H_4)]NbCl(N^tBu) + Mg(C{\equiv}CR)_2$	71
$[Cp_2Nb(C{\equiv}CR)(NHR^1)]^+$	$Cp = C_5H_5$, $R = SiMe_3$, $R^1 = {}^tBu$; $Cp = C_5H_4SiMe_3$, R = Ph, R^1 = Ph	71
$Cp_2NbR(NR^1)$	R = Et, CH_2SiMe_3, $R^1 = {}^tBu$; R = Me, Et, CH_2Ph, CH_2SiMe_3, $CH_2CH{=}CH_2$, $R^1 = C_6H_4Me\text{-}4$	73
$Cp_2NbR(O)$	$Cp = C_5H_4Me$; R = Me, CH_2SiMe_3, CH_2CMe_3, CH_2Ph	74
$Cp_2NbR(O\text{-}B(C_6F_5)_3)$	$Cp = C_5H_4SiMe_3$; $R = CH_2CH_3$, $CH_2CH_2C_6H_5$	75
$Cp_2Nb(CH_2CR{=}CH_2)(O)$	$Cp = C_5H_4SiMe_3$; R = H, Me	66

(*Continued*)

Table 3 (Continued)

Compound	*Comments*	*References*
$Cp_2NbR(O)$	$Cp=C_5H_4SiMe_3$; $R=CH_2CH_3, CH_2CH_2Ph$; prep: $Cp_2NbH(\eta^2\text{-}CH_2{=}CHR)+O_2$	76
$Cp_2NbMe(O)$	Prep: $Cp_2NbMe(NC_6H_4Me\text{-}4)+H_2O$	73
$Cp_2Nb(CH_2CR{=}CH_2)Cl$	$R=Me, H$; paramagnetic species (ESR spectra)	66
$[Cp_2Nb(C\equiv CR)L]^{\cdot +}[BPh_4]$	$Cp=C_5H_4SiMe_3$; $R=Ph, {}^tBu, Ph$; $L=CO, PMe_2Ph$; cation-radical species (ESR spectra)	77
$Cp_2NbMe(\eta^1\text{-}NNCPh_2)$		78
$Cp_2NbR(CO)$	$Cp=C_5H_4SiMe_3$; $R=Et, CH_2CH_2C_6H_5$	75
$Cp_2Nb(CH_2CR{=}CH_2)(L)$	$Cp=C_5H_4SiMe_3$; $R=H, Me$; $L=CO, CN(2,6\text{-}Me_2C_6H_3)$; prep: $Cp_2NbCl(L)+ClMg(CH_2CR{=}CH_2)$	66
$Cp_2Nb(C\equiv CR)(L)$	$Cp=C_5H_4SiMe_3$; $R=Ph, SiM_3, {}^tBu$; $L=CO, PMe_2Ph, P(OEt)_3, CN(2,6\text{-}Me_2C_6H_3)$	77,72
$Cp_2NbR(CNR^1)$	$Cp=C_5H_4SiMe_3$; $R=Et, CH_2CH{=}CHSiPh_3$; $R^1={}^tBu, 2,6\text{-}Me_2C_6H_3, Bu$	79

5.02.3.2 Hydride Complexes

The field of hydride complexes constitutes an important area in the chemistry of Nb and a variety of new complexes, particularly those containing cyclopentadienyl as ancillary ligands, has emerged since the last review in COMC (1995). (see Table 4).

Table 4 Hydride complexes

Compound	*Comments*	*References*
Non-Cp complexes		
$[Nb(H)_2(OC_6HCy_2\text{-}2,6\text{-}Ph_2\text{-}3,5)_2(PMe_3)_2]$	X-ray. Paramagnetic species (ESR spectrum)	81
$NbH(PF_3)_6$	Prep: protonation of $Nb(PF_6)^-$ by H_2SO_4	11
$[\{(Ph_2N)_2Nb\}_2[\mu\text{-}NPh(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)\}(\mu\text{-}H)]Li(TMEDA)_2$	X-ray	82
$Nb(\eta^2\text{-}Me_2C{=}NAr)(\eta^3\text{-}BH_4)(NRAr)_2$	X-ray; $R={}^iPr$; $Ar=3,5\text{-}C_5H_3Me_2$	83
$Nb(\eta^2\text{-}Me_2C{=}NAr)(H)(NRAr)_2$	Transient species	83
$Nb(\eta^2\text{-}{}^tBu(H)\text{-}(C{=}NAr)(H)(N(Np)Ar)_2$	X-ray; Np = neopentyl; $Ar=3,5\text{-}C_5H_3Me_2$	84
$NbH(CO)_2(triphos)(PEt_3)$	X-ray; triphos = $PhP(CH_2CH_2PPh_2)_2$	87
Cyclopentadienyl complexes		
$[(Cp_2NbH_3)M]^+$	$Cp=C_5H_5, C_5H_4SiMe_3, C_5H_3(SiMe_3)_2$; $M=Cu, Ag, Au$ (X-ray)	88
$Cp_2NbH(SiMe_2X)_2$	$Cp=C_5H_5$; $X=Cl$ (X-ray), Ph, H, F (X-ray), Br (X-ray)	96
$Cp_2NbH_2SiR_3$	$Cp=C_5H_5$; $R_3=(OEt)_3, Me_2Ph, Me_2Cl$ (X-ray)	96
$Cp_2NbH(SiMe_2EPh_n)_2$	$Cp=C_5H_5$; $E=S$, $n=1$; $E=P$, $n=2$	98
$Cp_2NbH(SiMe_2X)$	$Cp=C_5H_5$; $X=OTfl, OMe$ (X-ray)	98
$Cp_2NbH_2(SiMe_2PPh_2)$	$Cp=C_5H_5$; X-ray	98
$[Cp_2NbH_2Al(\mu\text{-}H)_2]_2$	$Cp=C_5H_5$; X-ray	98
$Cp_2NbH_2(SiCl_nR_{3-n})$	$Cp=C_5H_5$; $R=Me, Ph$; $n=1, 2$	99
$Cp_2NbH_2(SiCl_3)$	$Cp=C_5H_5$;	99
$Cp_2NbH(SiCl_3)_2$	$Cp=C_5H_5$; X-ray	99
$Cp_2NbH(SiMe_2H)(SiMe_2X)$	$Cp=C_5H_5$; $X=F$, Cl (X-ray), Br (X-ray), I	100
$Cp_2NbH_2(SnMe_2Cl)$	$Cp=C_5H_5$	101
$Cp_2NbH_2(PbMe_2Cl)$	$Cp=C_5H_5$	102
$Cp_2NbH(GeR_3)$	$Cp=C_5H_5$; $R=Me, Ph$	103
$Cp_2NbH(GeMe_3)(GeMe_2Cl)$	$Cp=C_5H_5$	103
$Cp_2NbH_2(SiR_3)$	$Cp=C_5H_4SiMe_3$; $R_3=Me_2Ph, MePh_2, PhH_2, Ph_2H$ (X-ray), Ph_3	104
$Cp_2NbH_2(ER_3)$	$Cp=C_5H_4SiMe_3$; $ER_3=GePh_3$ (X-ray), $GePh_2H, GeEt_3, Ge(C_6H_{13})_3, Ge^iAm_3$ (${}^iAm=CH_2CH_2CH(CH_3)_2$), $Ge(C_6H_{13})_2Cl, Ge^iAm_2Cl, Ge(C_6H_{13})_2H, SnPh_3$(X-ray)	105

(*Continued*)

Table 4 (Continued)

Compound	*Comments*	*References*
$[CpNb(\eta^3\text{-}N(Ar)SiMe_2\text{-}H)\text{-}X(PMe_3)]$	$Cp = C_5H_5$; $Ar = 2,6\text{-}{}^iPr_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$; $X = Cl$ (X-ray), OTf, I	107
$CpNbH(SiPh_2X)(NAr)(PMe_3)$	$Cp = C_5H_5$; $X = Cl$ (X-ray)	108
$CpNbH(SiCl_3)(NAr)(PMe_3)$	$Cp = C_5H_5$	108
$Cp_2Nb(pz)(pzH)$	$Cp = C_5H_4SiMe_3$; pzH = pyrazole	109
$Cp_2NbH(PPh)_2$	$Cp = C_5H_5$, $C_5H_4SiMe_3$	109
$[Cp_2NbH_2(PPh_2H)]Cl$	$Cp = C_5H_5$, C_5H_4Me	111
$Cp_2NbH_2(ER_2)$	$Cp = C_5H_5$; $E = P$, As	112
$[Cp_2NbH_2(PR_2H)]Cl$	$Cp = C_5H_5$; $R = Bu$, ${}^iPr$, ${}^tBu$	113
$Cp_2NbH(PR_2H)$	$Cp = C_5H_5$; $R = Bu$, ${}^iPr$, ${}^tBu$	113
$Cp_2NbH(PR_2H)$	$Cp = C_5H_5$; $R = Me$, Ph	114
$Cp_2NbH(PPh_2H)$	$Cp = C_5H_4SiMe_3$	116
$Cp_2Nb(H_2BR_2)$	$Cp = C_5H_5$; $R_2 = O_2C_6H_4$ (X-ray), C_8H_{14} (X-ray)	117
$Cp_2Nb(H_2BR_2)$	$Cp = C_5Me_5$; $R_2 = O_2C_6H_4$, $O_2C_6H_3\text{-}4\text{-}{}^tBu$ (X-ray), H_2 (X-ray)	118
$Cp_2NbH(BR_2)_2$	$Cp = C_5H_5$; $R_2 = O_2C_6H_4$	119
$Cp_2NbH(\eta^2\text{-}HBR_2)$	$Cp = C_5H_5$; $R_2 = O_2C_6H_4$; transient complex	119
$Cp_2Nb(H_2BR_2)$	$Cp = C_5H_4SiMe_3$; $R_2 = O_2C_6H_4$, C_8H_{14} (X-ray), H_2, theoretical study of dynamic behaviour	120
$Cp_2NbH(P(OR)_3)$	$Cp = C_5H_4SiMe_3$; $R = Me$, Et, Ph	121
$Cp_2NbH(CNR)$	$Cp = C_5H_4SiMe_3$; $R = {}^tBu$, Cy, $2,6\text{-}Me_2C_6H_3$	122
$[Cp_2Nb(\eta^2\text{-}H_2)L]CF_3CO_2$	$Cp = C_5H_4SiMe_3$; $L = P(OEt)_3$, PMe_2Ph; H–D, isotopomers were prepared; species stable at low temperature	123
$[Cp_2Nb(\eta^2\text{-}H_2)(CNR)]CF_3CO_2$	$Cp = C_5H_4SiMe_3$; $R = {}^tBu$, Cy, $2,6\text{-}Me_2C_6H_3$; H–D, isotopomers were prepared; species stable at low temperature	122
$[Cp_2Nb(\eta^2\text{-}H_2)L]CF_3CO_2$	$Cp = C_5H_4SiMe_3$; $L = PHPh_2$; H–D, isotopomer was prepared; species stable at low temperature	116
$[(Cp_2Nb(CO)(\mu\text{-}H))_2M]X$	$Cp = C_5H_4SiMe_3$; $M = Cu$ (X-ray), Ag, Au; $X = BF_4$, PF_6	124
$[Cp_2Nb(L)(\mu\text{-}H)(AuPPh_3)]PF_6$	$Cp = C_5H_4SiMe_3$; $L = P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$	44
$[(Cp_2NbH_2)_2Yb(diglyme)]$	$Cp = C_5H_5$; (X-ray)	125
$Cp_2NbH(Te_2)\cdot Cr(CO)_5$	$Cp = C_5H_4{}^tBu$	126
$[Cp_2Nb(\mu\text{-}H)L(BR_3)]$	$Cp = C_5H_4SiMe_3$; $L = CNR$ ($R = Cy$, Xylyl), CO; $R = B(C_6F_5)_3$, BF_3; prep: $Cp_2NbHL + B(C_6F_5)_3$	127,127a
$[Cp_2NbL_2][HB(C_6F_5)_3]$	$Cp = C_5H_4SiMe_3$; $L = CNR$ ($R = Cy$, Xylyl)	127,127a
$[Cp_2NbH(\mu\text{-}H)(\mu\text{-}PR_2)M'(CO)_4]$	$Cp = C_5H_5$; $R = Me$, Ph; $M' = Cr$, Mo, W	115

5.02.3.2.1 Hydride complexes without cyclopentadienyl ligands

Hydride complexes without a Cp ligand are rare. It has been claimed that hydrides supported by bulky aryloxo ligands catalyze the homogeneous hydrogenation of arenes.[80] These hydrides are generated in a general procedure that involves the high-pressure hydrogenolysis of hydrocarbon solutions of mixed-alkyl/aryl oxides in the presence of a phosphine ligand. However, the resulting compounds are generally thermally unstable, and hence have not been widely studied. For example, treatment of a benzene solution of $[Nb(CH_2SiMe_3)_2(OC_6HPh_4\text{-}2,3,5,6)_2]$/ $[Nb({=}CHSiMe_3)(OC_6HPh_4\text{-}2,3,5,6)_2]$ and PMe_3 under H_2 at a pressure of 1,200 psi produced the d^1-di(hydride), $[Nb(H)_2(OC_6HCy_2\text{-}2,6\text{-}Ph_2\text{-}3,5)_2(PMe_3)_2]$.[81] Formation of this compound involves not only hydrogenolysis of niobium alkyl/alkylidene bonds but also the intramolecular hydrogenation of the *ortho*-phenyl rings of the aryloxide ligands. In an intringuing reaction of the Nb(II) complex $(TMEDA)_2Nb_2Cl_5Li(TMEDA)$ with $KNPh_2$, one of the three resulting products was the dinuclear d^2-Nb(III) hydride, $[\{(Ph_2N)_2Nb\}_2\{\mu\text{-}NPh(\mu\text{–}\eta^1{:}\eta^2\text{-}C_6H_4)\}(\mu\text{-}H)]Li(TMEDA)_2$, formed by oxidative addition of Nb(II) in an intermediate to the C–H bond of one of the aromatic rings.[82] Cummins *et al.* performed a series of elegant studies,[83–86] and described the chemistry of niobaziridine complexes that exhibit interesting reactivity. For example, the hydride complex $Nb(\eta^2\text{-}{}^tBu(H)(C{=}NAr)(H)(N(Np)Ar)_2$ was prepared, and this proved to have a rich small-molecule activation chemistry.

5.02.3.2.2 Cyclopentadienyl hydrides

Cyclopentadienyl niobium hydrides constitute the largest family of this type of complex, and they have long been of interest due to their high reactivity and their spectroscopic properties. The cyclopentadienyl hydrides are summarized in Table 4.

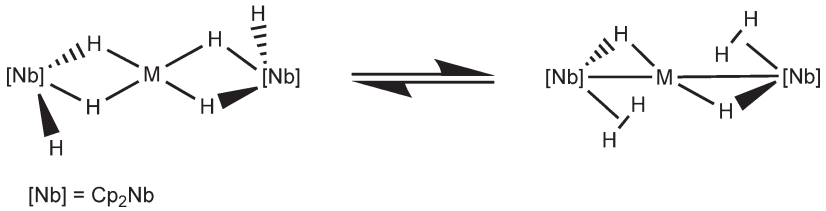
5.02.3.2.2.(i) Hydrogen-exchange coupling in Cp_2NbH_3 complexes

The niobocene trihydrides Cp_2NbH_3 ($Cp = C_5H_5$, C_5Me_5, $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$, and related substituted cyclopentadienyl rings) are probably the most useful starting materials in bis-cyclopentadienyl hydride niobium chemistry. References concerning the preparation and the unusual NMR properties of these compounds were reviewed in COMC (1995). In particular, the ^1H NMR properties of these complexes were found to be anomalous in many ways. In this respect, an exhaustive study[88] was carried out on niobium trihydrides containing silylated Cp rings, which show large exchange coupling in their high-field ^1H NMR spectra due to a hydride-tunneling phenomenon. A number of *ab initio* electronic-energy calculations using a one-dimensional tunneling model were also carried out on metallocenes $[Cp_2MH_3]^{n+}$, M = Mo, W ($n = 1$) and M = Nb, Ta ($n = 0$). On the basis of these calculations, it was established that the stability of the η^2-H_2 structure relative to the minimum energy trihydride is the main parameter governing the magnitude of the exchange coupling.[89] In the search for a means of chemical discrimination between a purely vibrational mechanism and one involving rotational tunneling of dihydrogen, the addition of a Lewis-acidic coinage cation to the niobocene trihydrides containing silylated Cp rings was carried out,[88,90] and adducts of the type $[(Cp_2NbH_3)M]^+$ (M = Cu, Ag, Au) were isolated. Different exchange coupling values were observed, and these were larger for the gold complexes. An explanation for the variations is based on a model that assumes two isomeric states, one involving two bridging and one terminal hydride on Nb, and the other involving one bridging hydride and a dihydrogen molecule (see Scheme 1).

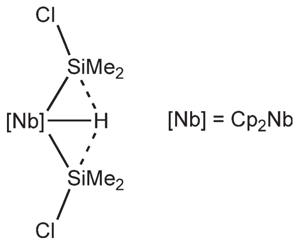
Several theoretical studies have been carried out concerning the stabilization of the η^2-H_2-containing state as a thermally accessible state in the niobocene trihydrides. In a series of elegant studies, Lledos *et al.*[91–93] presented *ab initio* calculations that indicate that the formation of an adduct between a trihydride complex, Cp_2NbH_3, and a Lewis acid (boranes such as BH_3, catecholborane, 9-borabicyclononane and AlH_3) converts the dihydrogen structure into a stable complex. It therefore seems that the strength of the Lewis acid influences the ease of the dihydrogen elimination process. Furthermore, the incoherent contribution to the tunneling exchange of hydrogen pairs in $(C_5H_3(SiMe_3)_2)NbH_3$ has been investigated by ^1H NMR line-shape analysis and two-dimensional ^1H NMR exchange spectroscopy.[94]

5.02.3.2.2.(ii) σ-Bond activation by niobocene hydrides

Trihydride and related derivatives react with hydrosilanes to give the appropriate silyl hydride derivatives. In a series of papers Nikonov *et al.*[95–103] described a series of mono- and bis(silyl) niobocene hydride complexes with functionalized silyl ligands, some of which involve a non-classical interligand interaction between the silyl and hydride ligands (IHI = interligand hypervalent interaction) (Scheme 2).



Scheme 1

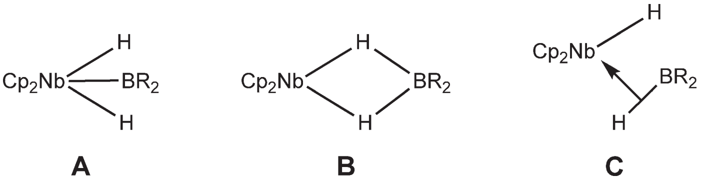


Scheme 2

This type of non-classical interligand hypervalent interaction, that is, X–Si···H (IHI), was thoroughly studied by X-ray diffraction (including single crystal neutron diffraction), density functional theory (DFT) method, and NMR relaxation procedures. On the basis of the results obtained it was established that the interligand interaction emerges because of the transfer of electron density from the electron-rich Nb–H bond to the Si–X antibonding orbital. This kind of bonding can be described as a $4c–4e^-$ interaction in the case of mono(silyl) complexes and $6c–6e^-$ (or $5c–6e^-$ in the coordination sphere of the Nb atom) in the case of bis(silyl) complexes (Scheme 2). Furthermore, the main structural trends due to IHI are: (i) the metal–silicon bonds are shorter than those normally observed, (ii) the silicon–halogen bonds are longer than normal, (iii) Si–H contacts are present, and (iv) in the bis(silyl) complexes the observed Si–Nb–Si bond angles are smaller than expected. For example, a neutron diffraction study of $Cp_2NbH(SiMe_2Cl)_2$[97] indicates that the presence of a neighboring $SiMe_2Cl$ ligand increases the Nb–hydride bond length remarkably, probably through the mechanism outlined above. A series of dihydride niobocene derivatives containing group 14 fragments, namely, $Cp_2NbH_2(ER_3)_2$, has also been described,[105] and these were prepared by reacting Cp_2NbH_3 with several organogermanium hydrides, $HGeR_3$, or $HSnPh_3$. On the other hand, the reactivity of hydride-, silyl-, germyl-, or stannyl-containing niobocene complexes toward the hydrides $HEPh_3$ (E = Si, Ge, Sn) in σ-bond metathesis reactions of d^0-Nb–E bonds with H–E′ bonds has been studied.[105] Reactions of half-sandwich complexes of the formula $CpNb(NAr)(PMe_3)_2$ with silanes were also considered, and two classes of complexes were isolated, namely, unstretched β-agostic (Si–H···Nb) d^2-silylamide [$CpNb(\eta^3\text{-}N(Ar)SiMe_2\text{–}H)X(PMe_3)$] and silylhydrido $CpNbH(SiPh_2X)(NAr)(PMe_3)$ species.[106–108] A number of other main group element–hydrogen bonds can be activated by the trihydride niobocene complex.[28,109] The insertion of group 15 halogenides into the Nb–H bond is an alternative route to bond activation for the synthesis of main group element-substituted niobocene–hydrido complexes. Cp_2NbH_3 was found to react with chlorophosphines to afford the phosphonium salts, and, depending on the nature of the phosphine substituent, deprotonation of these salts leads to either hydride(phosphine) $Cp_2NbH(PR_2H)$ or hydride(phosphide) $Cp_2NbH_2(PR_2)$ complexes.[110–116] Niobocene complexes containing boron moieties, that is, $Cp_2Nb(H_2BR_2)$ and related systems, have been prepared by the reaction of Cp_2NbH_3 or $Cp_2Nb(CH_2{=}CH(R))H$ substrates with the appropriate hydroboranes.[117–120] In these cases, three limiting forms can be used to describe the H_2BR_2 coordination. These include d^0-boryl (A), d^2-borohydride (B), and d^2-agostic borane (C) structures (Scheme 3). In some cases, for example, catechol-containing niobocene derivatives, equilibria between situations A and B have been proposed on the basis of spectroscopic data and isotopic perturbations in the NMR spectra.

5.02.3.2.2.(iii) The chemistry of d^2-hydride niobocene derivatives

An extensive family of niobocene hydrides corresponds to the 18-electron d^2-Cp_2NbHL (L = π-acid ligand). A range of complexes with different classes of π-acid ligands has been described, with the ligands obtained by several different types of preparation process. A large number of these complexes, particularly those with CO and phosphine ligands, were collected in COMC (1995). The most important process for the preparation of these complexes involves heating Cp_2NbH_3 species in the presence of L.[121] In one example it was surprising to find that the thermal treatment of Cp_2NbH_3 with isocyanides gave the complexes $Cp_2NbH(CNR)$ as stable species, without observing insertion reactions of this type of ligand into Nb–H bonds.[122] Another interesting type of reactivity was found in the protonation processes of some of the Cp_2NbHL complexes at low temperatures, in that certain systems yield dihydrogen-containing niobocenes, namely $[Cp_2Nb(\eta^2\text{-}H_2)L]^+$.[116,122,123] NMR studies showed coupling constants J_{HD} of ca. 30 Hz in the deuterated isotopomer species, which verified the presence of an H–D bond and provided evidence of the presence of unstretched dihydrogen complexes. One of the most interesting points concerns the fact that activation barriers for the rotation of H_2 are surprisingly high (ca. 10 kcal mol^{-1}), and, as a consequence, the rotation of the dihydrogen molecule seems to be blocked on the NMR timescale.



Scheme 3

5.02.3.2.2.(iv) Heterometallic complexes containing cyclopentadienyl hydride niobium moieties

Heterometallic hydride complexes of Nb containing different classes of heteroatoms have been prepared. In some cases Cp_2NbH_3 and Cp_2NbHL, with the latter type acting as a two-electron donor toward a coordinatively unsaturated $M(CO)_x$ fragment, have been employed as excellent niobium substrates. An extensive collection of complexes of this type was compiled in COMC (1995). For example, the cationic complexes $[(Cp_2Nb(CO)(\mu\text{-}H))_2M]^+$ (M = Cu, Ag, Au) are the result of the reaction between $Cp_2NbH(CO)$ and $[Cu(MeCN)_4](BF_4)$, $[Cu(PPh_3)Cl]/TlPF_6$, $AgBF_4$, $[Ag(PPh_3)Cl]/TlPF_6$, or $[Au(THT)Cl]/TlPF_6$. In these complexes the coinage cation is only linked to the hydride of each Nb center.[124] Green *et al.* prepared[125] the interesting lanthanide-containing heterometallic complex $[(Cp_2NbH_2)_2Yb(diglyme)]$. The X-ray crystal structure of this complex contains a central Nb–Yb–Nb core and two bridging hydrides located symmetrically on each side of the Nb–Yb vector. Reaction of $Cp_2NbH(Te_2)$, prepared from Cp_2NbH_3 and Te powder, with the unsaturated synthon $Cr(CO)_5$, gave the complex $Cp_2NbH(Te_2)Cr(CO)_5$, where a Te_2 unit and a hydride are coordinated to a bent niobocene moiety; the $Cr(CO)_5$ group is attached to the lateral Te atom.[126]

5.02.4 Alkylidene and Alkylidyne Complexes

Since the first group 5 transition metal complexes containing a multiple metal–carbon bond were discovered,[127] interest in the field of alkylidene ($M{=}CR_1R_2$) and alkylidyne ($M{\equiv}CR$) complexes has grown considerably – especially with respect to the use of these complexes as metathesis catalysts for alkenes and alkynes.[128] Alternative uses of alkylidene complexes include C–H bond-activation systems and catalysts in alkyne polymerizations and ring-opening metathesis polymerizations (ROMPs) of cyclic alkenes, all of which were reviewed in COMC (1995). In this section the synthesis and reactivity of new niobium alkylidene and alkylidyne complexes is considered. The alkylidene, alkylidyne, and related complexes under discussion are summarized in Table 5.

Table 5 Alkylidene, alkylidyne and related complexes of niobium

Compound	*Comments*	*References*
Alkylidene complexes		
$[CpNb({=}CHPh)\{N(2,6\text{-}{}^iPr_2C_6H_4\}(PMe_3)]$	$Cp = C_5Me_5$ (X-ray)	129
$[Cp_2Nb({=}CHPh)(THF)][BPh_4]$	$Cp = C_5H_4{}^tBu$	130
$CpNb({=}CH_2)(\eta^4\text{-}C_4H_6)$	$Cp = C_5Me_5$; transient species	131
$Nb({=}CHSiMe_3)(OAryl)_2X$	$OAryl = OC_6HPh_4\text{-}2,3,5,6$; $X = Cl$, CH_2SiMe_3	81
$[(silox)_3Nb{=}CH(CH{=}CH)_2N{=}Nb(silox)_3]$	X-ray; silox = ${}^tBu_3SiO$	132
$[\{(silox)_3Nb\}_2(\eta^1;\eta^2\text{-}4,5\text{-}C_8H_6)]$	X-ray	133
$(silox)_3Nb\{{=}\overline{C(CH_2)_4CH_2}\}$		133
$(silox)_3Nb\{{=}C(CH_2)_2CH_3\}$		133
$CpNb({=}CHPPh_3)(N^tBu)Cl$	X-ray	134
$[\{p\text{-}{}^tBu\text{-}calix[4]\text{-}(O)_4\}Nb({=}CR_1R_2)]^-$	$R_1 = R_2 = Ph$; $R_1 = Ph$, $R_2 = Me$; $R_1 = Ph$, $R_2 = CH_2Ph$; $R_1 = Pr$, $R_2 = H$; $R_1 = Cp_2Fe$, $R_2 = Me$ (X-ray); $R_1{=}Ph$, $R_2{=}H$ (X-ray)	48
$Cp_2NbX\{{=}C\overline{S(R)C{=}C(R)S}\}$	$Cp = C_5H_4SiMe_3$; X = Cl, Et, CH_2CH_2Ph; $R = CF_3$, CO_2Me, $CO_2({}^tBu)$	135
$[Cp_2(CO)Nb{=}C{=}C(CH_3)(CH_3)C{=}C{=}Nb(CO)Cp_2]^{2+}$	$Cp = C_5H_4SiMe_3$ (X-ray)	136
$[Cp_2({}^tBuNC)Nb{=}C{=}C(CH_3)(CH_3)C{=}C{=}Nb({}^tBuNC)Cp_2]^{2+}$	$Cp = C_5H_4SiMe_3$	137
$[Cp_2Nb({=}C{=}CHR)L][BPh_4]$	$Cp = C_5H_4SiMe_3$; $R = {}^tBu$, Ph; L = CO, PMe_2Ph	77
Alkylidyne complexes		
$[(L\text{-}N)_2Nb(\mu\text{-}CSiMe_3)_2Nb(N\text{–}L)_2]$	$L\text{–}N = C_{12}H_8N$ (X-ray); $L\text{–}N = C_{12}H_{12}N$; $L\text{–}N = C_{16}H_{16}N$	139
$[(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)(\mu\text{-}XylylNC{=}CSiMe_3)Nb(N\text{–}L)_2]$	$L\text{–}N = C_{12}H_8N$; $L\text{–}N = C_{12}H_{12}N$; $L\text{–}N = C_{16}H_{16}N$	
$[(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)\{\mu\text{-}C(R)C(R^1)C(SiMe_3)\}Nb(N\text{–}L)_2]$	$L\text{–}N = C_{12}H_8N$; $R = R' = Et$; $R = Me_3Si$, $R^1 = H$, (X-ray)	140
$[(Me_3P)_2ClNb(\mu\text{-}CSiMe_3)_2NbCl(CH_2SiMe_3)_2]$	X-ray	141
$[\{p\text{-}{}^tBu\text{-}calix[4]\text{-}(O)_4\}Nb(\mu\text{-}CPh)_2Nb\{p\text{-}{}^tBu\text{-}calix[4]\text{-}(O)_4\}]^{4-}$	X-ray	48

5.02.4.1 Alkylidene Complexes

In the last few years, few stable new alkylidene complexes of niobium have been reported. It is known that the most commonly employed strategy for the preparation of alkylidene complexes is the abstraction of an α-hydrogen from an alkyl ligand. This α-H abstraction can take place by either (i) intermolecular deprotonation of an alkyl ligand using an external base or (ii) intramolecular α-H transfer in a sterically congested bis(alkyl) complex to afford an alkylidene ligand and a free alkane. For example, $CpNb(CH_2Ph)_2\{N(^iPr_2C_6H_3\text{-}2,6)\}$ can be dehydrogenated to provide $[CpNb({=}CHPh)\{N(^iPr_2C_6H_3\text{-}2,6)\}(PMe_3)]$ only upon addition of PMe_3, as indicated in Equation (4).[129] Oxidation of $Cp_2Nb(CH_2Ph)_2$ with $AgBPh_4$ in THF gives a cationic benzylidene complex $[Cp_2Nb({=}CHPh)(THF)]BPh_4$, as shown in Equation (5). This reaction probably proceeds through an intermediate cationic Nb(V) dibenzyl complex in which α-hydrogen abstraction takes place, perhaps induced by coordination of THF.[130] Intramolecular α-H abstraction occurs upon thermolysis of the dimethyl complex $[CpNbMe_2(\eta^4\text{-}C_4H_6)]$ to give a transient methylene species, "$[CpNb({=}CH_2)(\eta^4\text{-}C_4H_6)]$," which was trapped with norbornene or acenaphthylene (Equation (6)).[131] Thermolysis or photolysis gave rise to trimethylsilylmethyleneniobium aryloxide complexes (Equation (7)).[81]

$$CpNb(CH_2Ph)_2\{N(C_6H_3Pr^i_2\text{-}2,6)\} \xrightarrow{PMe_3,\ 65\,^\circ C} CpNb({=}CHPh)\{N(C_6H_3Pr^i_2\text{-}2,6)\}(PMe_3) \tag{4}$$

$$Cp_2Nb(CH_2Ph)_2 \xrightarrow[-\,Ag,\ -toluene]{Ag^+/THF} [Cp_2Nb({=}CHPh)(THF)][BPh_4] \tag{5}$$

$$CpNbMe_2(\eta^4\text{-}C_4H_6) \xrightarrow[-CH_4]{50\,^\circ C,\ THF} \text{“}CpNb({=}CH_2)(\eta^4\text{-}C_4H_6)\text{”} \tag{6}$$

$$Nb(CH_2SiMe_3)_2(OAryl)_2X \xrightarrow[-SiMe_4]{100\,^\circ C,\ C_6D_6} Nb({=}CHSiMe_3)(OAryl)_2X \tag{7}$$

Alkylidene-containing complexes have also been prepared from Nb(III) substrates. For example, heating of $(silox)_3Nb(\eta^2\text{-}NC\text{–}py)$ ($silox = {}^tBu_3SiO$) yielded a bimetallic alkylidene/imido complex in modest yield (Equation (8)).[132] Another (silox)-containing Nb system has proved to be effective in the preparation of alkylidene derivatives. For example, H_2-catalyzed rearrangement of the alkyne/alkene complex $[\{(silox)_3Nb\}_2(\eta\text{-}1,2{:}\eta\text{-}5,6\text{-}C_8H_6)]$ to the alkylidene–yne complex $[\{(silox)_3Nb\}_2(\eta^1{:}\eta^2\text{-}4,5\text{-}C_8H_6)]$ was observed.[133] In the same way, it was also found that $(silox)_3Nb(\eta^2\text{-cyclohexene})$ rearranged to $(silox)_3Nb(\text{cyclohexylidene})$ (Equation (9)).[133]

$$(silox)_3Nb(\eta^2\text{-}N,C\text{-}py) \xrightarrow{70\,^\circ C} (silox)_3Nb{=}CH(CH{=}CH)_2N{=}Nb(silox)_3 \tag{8}$$

$$(silox)_3Nb(\eta^2\text{-}C_6H_{10}) \xrightarrow{85\,^\circ C} (silox)_3Nb\{{=}\overline{C(CH_2)_4CH_2}\} \tag{9}$$

Dehydrohalogenation of an intermediate ylide complex also led to the formation of an α-phosphonio(methylidene)niobium complex (Equation (10)).[134]

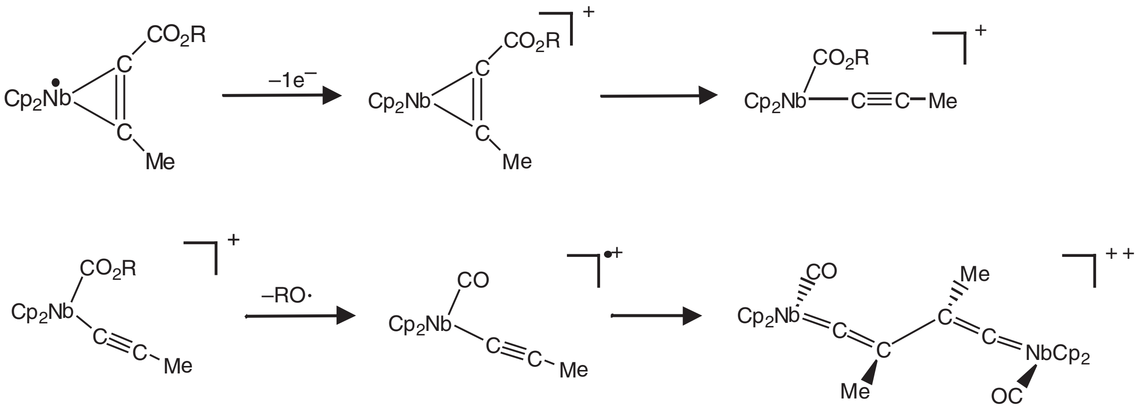
$$CpNb(N^tBu)Cl_2 \xrightarrow[-[MePPh_3]Cl]{2Ph_3P{=}CH_2} CpNb({=}CHPPh_3)(N^tBu)Cl \tag{10}$$

A direct synthesis of niobium alkylidenes and alkylidynes from compounds with some of the most common organic functionalities, namely ketones and aldehydes, was developed by Floriani *et al.*[48] Indeed, the active compound $[\{p\text{-}^tBu\text{-calix[4]-(O)}_4\}_2Nb_2Na_2]$, an $[Nb(III){=}Nb(III)]$ dimer, reacted with aldehydes and ketones through metathesis of the Nb═Nb bond with the carbonyl functionality, as depicted in Equation (11).

$$[(Nb{=}Nb)]^{2-} + R_1COR_2 \longrightarrow [Nb({=}CR_1R_2)]^- + [Nb{=}O] \tag{11}$$

The reaction of CS_2-containing niobocenes with activated alkynes yielded a series of dithiocarbene species. It is not clear whether this type of carbene under these circumstances should be viewed as a dianionic alkylidene ligand bound to Nb(V) or as a neutral carbene bound to Nb(III) (Equation (12)).[135]

$$Cp_2NbX(\eta^2\text{-}CS_2) + RC{\equiv}CR \longrightarrow Cp_2NbX\{{=}\overline{CS(R)C{=}C(R)S}\} \tag{12}$$



Scheme 4

Attempts to oxidize alkyne-containing niobocenes [$Cp_2Nb\{\eta^2\text{-}MeO_2CC{\equiv}CMe\}$] at room temperature (RT) led to an unexpected divinylidene binuclear d^2-niobocene complex (Equation (13)).[136]

$$Cp_2Nb\{\eta^2\text{-}(C,C)\text{-}MeO_2CC{\equiv}CMe\} \xrightarrow[CH_3CN]{2[FeCp_2][BPh_4]} [Cp_2(CO)Nb{=}C{=}C(CH_3)(CH_3)C{=}C{=}Nb(CO)Cp_2]^{2+} \quad (13)$$

Studies aimed at gaining an insight into the mechanism for the formation of the binuclear niobocene divinylidene moiety were also published and the proposed mechanism is depicted in Scheme 4.[137]

There was evidence to confirm that the formation of the complex takes place through carbon–carbon coupling of alkynyl radical cations.[77]

5.02.4.2 Alkylidyne Complexes

Alkylidyne complexes of niobium still remain very rare. In the last few years only a small number of new bridging bis(alkylidyne) niobium complexes has been reported, and these were prepared from another bridging bis(alkylidyne), previously reported in COMC (1995). The 1,3-dimetallacyclobutadiene compound [$(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2$][138] shows interesting reactivity patterns toward protic reagents; protonolysis reaction of this compound with carbazole ligands (L–NH) gives rise to tetrasubstituted derivatives (Equation (14))[139] that undergo addition of 2,6-dimethylphenyl isocyanide (XylylNC) to give [$(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)(\mu\text{-}XylylNC{=}CSiMe_3)Nb(N\text{–}L)_2$] by migratory insertion of organic isocyanides into the transition metal–alkylidyne bond. The alkylidyne-bridged carbazole compounds [$(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)_2Nb(N\text{–}L)_2$] react with alkynes to give insertion into a single alkylidyne bridge (Equation (15)).[140] Bridging bis(alkylidyne) ligands are normally observed in coordinatively unsaturated complexes. Such bridging ligands usually adopt symmetric bonding to the two metal atoms, as in [$(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2$]. Complexes with unsymmetrical bridging bis(alkylidyne) ligands are rarely seen with any metal. The complex [$(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2$] reacted with PMe_3 and HCl to give the first niobium complex containing such unusual unsymmetrically bridged bis(alkylidyne) ligands, which return to a symmetrical bridging arrangement in the bis(alkylidyne) complex upon reaction with Me_3SiCH_2Li (Equations (16) and (17)).

$$[(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2] \xrightarrow[-4TMS]{+4L\text{–}NH} [(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)_2Nb(N\text{–}L)_2] \quad (14)$$

$$[(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)_2Nb(N\text{–}L)_2] \xrightarrow{CR{\equiv}CR^1} [(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)\{\mu\text{-}C(R)C(R^1)C(SiMe_3)\}Nb(N\text{–}L)_2] \quad (15)$$

$$[(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2] \xrightarrow[-4TMS]{\substack{\text{i, 2HCl}\\ \text{ii, exc. PMe}_3}} [(Me_3P)_2ClNb(\mu\text{-}CSiMe_3)_2NbCl(CH_2SiMe_3)_2] \quad (16)$$

$$[(Me_3P)_2ClNb(\mu\text{-}CSiMe_3)_2NbCl(CH_2SiMe_3)_2] \xrightarrow[-2LiCl]{+2LiCH_2Me_3} [(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2] \quad (17)$$

Bridging niobium alkylidynes can be obtained by deprotonation of a niobium alkylidene with sodium naphthalenide (Equation (18)),[48] which can quite easily be protonated back to the niobium alkylidene.

$$\mathrm{Na[Nb({=}CPhH)]} \xrightleftharpoons[+\mathrm{H}^+]{\text{sodium naphthalenide}} \mathrm{Na_4[Nb(\mu\text{-}CPh)_2Nb]} \qquad (18)$$

5.02.5 η^2-Complexes

5.02.5.1 Alkene Complexes

Alkene-containing complexes of Nb have continued to be an important class of organometallic species for this element, because of the role they play in important processes involving alkenes, such as catalytic polymerization, metathesis, and ROMP. In the majority of cases, these complexes have been stabilized in a d^2-niobocene unit, with complexes of the type $Cp_2NbH(\eta^2\text{-alkene})$ being of particular interest. The latter complexes are 18-electron species that have been utilized to investigate olefin insertion into the Nb–H bond. The different classes of complex are summarized in Table 6.

5.02.5.1.1 Alkene complexes without cyclopentadienyl ligands

Examples of this class of complex are very rare. Some complexes have been prepared from Nb precursors that contain bulky alkoxides. For example, reduction of the niobium dichloride $Nb(OC_6H_3{}^iPr_2\text{-}2,6)_3Cl_2$ gives the complex $Nb(OC_6H_3{}^iPr\text{-}\eta^2\text{-}CMe{=}CH_2)(OC_6H_3{}^iPr_2\text{-}2,6)_2(THF)$, which contains an α-methylvinyl group strongly η^2-bound to the niobium center.[142] This ligand results from the facile dehydrogenation of an isopropyl group, and the pathway for dehydrogenation is believed to proceed through a cyclometallation process. In common with many related early transition metal olefin complexes, the niobacyclopropane ring in this complex undergoes ring expansion (coupling) with a variety of unsaturated substrates to give a series of niobacycles (see Section 5.02.6). Wolczanski *et al.* described[133,143,144] the preparation of a series of olefin complexes with the $(silox)_3Nb$ unit ($silox = {}^tBu_3SiO$). Two methods have been used to prepare this class of niobium–olefin complex. The most practical preparation of $(silox)_3Nb(\eta^2\text{-alkene})$ involves Na/Hg reduction of $(silox)_3NbCl_2$ in the presence of an excess of olefin. An alternative methodology involves treatment of $(silox)_3Nb(\eta^2\text{-N,C–NC}_5H_4CH_3(\text{picoline}))$ with a slight excess of olefin, although 4-picoline can be a competitive binder in cases where the olefin is bulky or coordinates poorly for other reasons.

Table 6 Alkene complexes of niobium

Compound	*Comments*	*References*
Without cyclopentadienyl ligands		
$Nb(OC_6H_3{}^iPr\text{-}\eta^2\text{-}CMe{=}CH_2)(OC_6H_3{}^iPr_2\text{-}2,6)_2L_x$	L = THF, $x = 1$ (X-ray); py, $x = 2$; CN^tBu, $x = 2$	142
$(silox)_3Nb(\eta^2\text{-}CH_2CHR)$	R = H, Me, Et, Ph, ^tBu, C_6H_4-p-OMe, C_6H_4-p-CF_3	143, 144
$(silox)_3Nb(\eta^2\text{-}CHMeCHMe)$		143, 144
$[\{(silox)_3Nb\}_2(\mu{:}\eta^2,\eta^2\text{-}C_6H_6)]$	X-ray	144
$(silox)_3Nb(\eta^2\text{-}C_4H_8)$		133
$[\{(silox)_3Nb\}_2(\eta\text{-}1,2{:}\eta\text{-}5,6\text{-}C_8H_6)]$	C_8H_6 = cyclooctatrieneyne (X-ray)	133
Cyclopentadienyl complexes		
$Cp_2NbH(\eta^2\text{-}CH_2{=}CHR)$	Cp = $C_5H_4SiMe_3$; R = Ph, p-MeC_6H_4, p-$MeOC_6H_4$	145, 75
$Cp_2NbH(\eta^2\text{-}CH_2{=}CHR)$	Cp = $C_5H_4SiMe_3$; R = H	75
$[Cp_2Nb(N^tBu)(\eta^2\text{-}C_2H_4)][B(C_6F_5)_4]$	Cp = C_5H_5; characterized by NMR spectroscopy	146
$[\{(\eta^5\text{-}C_5H_4)CMe_2(\eta^5\text{-}C_5H_4)\}Nb(N^tBu)(\eta^2\text{-}CH_2CHR)]\text{-}[B(C_6F_5)_4]$	R = H, Me; characterized by NMR spectroscopy	146
$[Cp(\eta^5\text{-}C_5H_4SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2))NbR]$	Cp = C_5H_5; R = Me, CH_2Ph, CH_2SiMe_3	147
$[Cp(\eta^5\text{-}C_5H_4SiMe_2(CH_2\text{–}CH{=}CH_2))NbRL]$	Cp = C_5H_5; R = Me, CH_2Ph, CH_2SiMe_3; L = CO, CN^tBu, CNxylyl	147
$[\{(\eta^5\text{-}C_5H_4)\,Si\,Me_2(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)\}NbH(\eta^2\text{-}CH_2{=}CHR^1)]$	R = $CHMe_2$, CMe_3 (X-ray); R^1 = H (X-ray), Ph (X-ray)	148
rac- and *meso*-$[\{(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)SiMe_2(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)\}NbH(\eta^2\text{-}CH_2{=}CH_2)]$	R = CMe	148

Alternatively, $(\mathrm{silox})_3\mathrm{Nb(PMe_3)}$ can be used as a source of "$(\mathrm{silox})_3\mathrm{Nb}$", but the expense of this reagent has limited its application to a few olefin adducts (see Equation (19)). Some of these alkene complexes rearrange to form the corresponding alkylidene species (see Section 4.1).

$$(\mathrm{silox})_3\mathrm{Nb(PMe_3)} + \text{alkene (excess)} \longrightarrow (\mathrm{silox})_3\mathrm{Nb}(\eta^2\text{-alkene}) + \mathrm{PMe_3} \qquad (19)$$

$$\text{alkene} = \mathrm{H_2C{=}CH^tBu,\ C_5H_8}$$

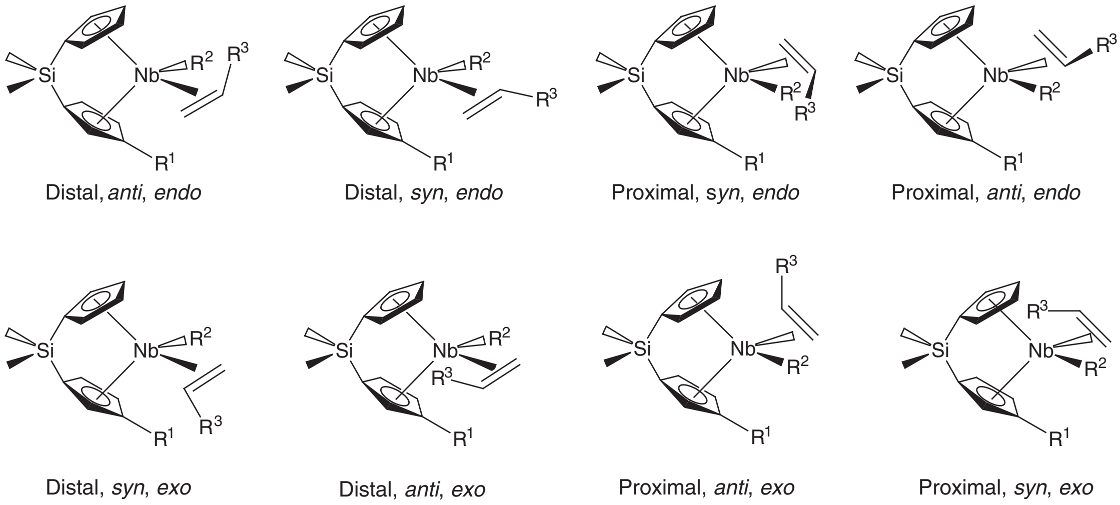
5.02.5.1.2 Cyclopentadienyl alkene complexes

The remarkable stabilizing effect of the cyclopentadienyl ligand has been used to prepare a series of alkene-containing niobium complexes. The study of olefin hydride bis(cyclopentadienyl) niobium complexes has continued. This type of complex has been proposed as a ground-state analog to model the carbon–hydrogen or carbon–carbon bond-forming transition states of a group 4 metallocene catalyst in the stereospecific olefin polymerization process. Numerous hydrido-alkene niobocenes have been isolated by the reaction of the alkene with $\mathrm{Cp_2NbH_3}$ derivatives. Similar compounds were also isolated by the alkylation of $\mathrm{Cp_2NbCl_2}$ complexes with β-hydrogen-containing alkyl groups and simultaneous reduction to give $\mathrm{Cp_2NbR}$, which are transformed into the corresponding alkene-hydrido derivatives $\mathrm{Cp_2NbH}(\eta^2\text{-alkene})$ by β-hydrogen elimination. In this way, $\mathrm{Cp_2NbH}(\eta^2\text{-}\mathrm{CH_2{=}CHR})$ complexes are obtained in the reaction of the corresponding complex $\mathrm{Cp_2NbH_3}$ with the appropriate alkene.[145,75] The process takes place through elimination of $\mathrm{H_2}$ followed by coordination of the olefin to the $\mathrm{Cp_2NbH}$ species. Both *endo*- and *exo*-isomers are formed in this process. The mechanism of the formation of $\mathrm{Cp_2NbH}(\eta^2\text{-}\mathrm{CH_2{=}CHPh})$ has been discussed[145] in terms of a model that involves a consecutive reaction with a reversible step and a first-order dependence with respect to the precursor $\mathrm{Cp_2NbH_3}$. The kinetics of the olefin-hydrido insertion were also studied by ^{1}H NMR spectroscopy using coalescence techniques. In addition, the starting complex $[\mathrm{Cp_2NbCl}]_2$ has been reported to react with 1 equiv. of RMgX to generate at RT the complexes $\mathrm{Cp_2NbH}(\eta^2\text{-}\mathrm{CH_2{=}CHR})$ (*endo*-isomer)[75] through a highly stereoselective β-elimination from the initially formed monoalkyl species $\mathrm{Cp_2Nb(CH_2{-}CH_2R)}$, which was not detected. Interesting d^0-alkene complexes have been described by Green *et al.*[146] In fact, the introduction of an atmosphere of ethene into NMR samples of $[\mathrm{Cp_2Nb(N^tBu)}][\mathrm{B(C_6F_5)_4}]$ and $[\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{CMe_2}(\eta^5\text{-}\mathrm{C_5H_4})\}\mathrm{Nb(N^tBu)}][\mathrm{B(C_6F_5)_4}]$ gave the corresponding alkene-containing derivatives $[\mathrm{Cp_2Nb(N^tBu)}(\eta^2\text{-}\mathrm{C_2H_4})][\mathrm{B(C_6F_5)_4}]$ and $[\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{CMe_2}(\eta^5\text{-}\mathrm{C_5H_4})\}\mathrm{Nb(N^tBu)}(\eta^2\text{-}\mathrm{C_2H_4})][\mathrm{B(C_6F_5)_4}]$, respectively. Complexes $\mathrm{Cp}(\eta^5\text{-}\mathrm{C_5H_4SiMe_2(CH_2}\text{-}\eta^2\text{-}\mathrm{CH{=}CH_2}))\mathrm{NbR}$, which contain a chelating alkene ligand tethered to a cyclopentadienyl ring, have been synthesized by alkylation with reductive elimination of the corresponding dichloride $[\mathrm{Cp}(\eta^5\text{-}\mathrm{C_5H_4SiMe_2(CH_2}\text{-}\eta^2\text{-}\mathrm{CH{=}CH_2}))\mathrm{NbCl_2}]$.[147] In order to examine the effects of cyclopentadienyl and olefin substitution on the preferred stereochemistry, Bercaw *et al.*[148] performed an elegant study in which they prepared a series of singly $\mathrm{SiMe_2}$-bridged *ansa*-niobocene olefin–hydrido complexes $[\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{SiMe_2}(\eta^5\text{-}\mathrm{C_5H_3}\text{-3-R})\}\mathrm{NbH}(\eta^2\text{-}\mathrm{CH_2{=}CHR^1})]$ and *rac*- and *meso*-$[\{(\eta^5\text{-}\mathrm{C_5H_3}\text{-3-R})\mathrm{SiMe_2}(\eta^5\text{-}\mathrm{C_5H_3}\text{-3-R})\}\mathrm{NbH}(\eta^2\text{-}\mathrm{CH_2{=}CH_2})]$ by reduction and alkylation of the corresponding dichloride complexes. The preferred structures of these low-symmetry complexes were examined in terms of the important stereodirecting interactions between the coordinated olefin and the cyclopentadienyl substituents by means of conventional NMR and X-ray diffraction experiments. Selected results are represented in Scheme 5 for one of the enantiomers of $[\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{SiMe_2}(\eta^5\text{-}\mathrm{C_5H_3}\text{-3-R^1})\}\mathrm{Nb}]$. In addition, the rates of hydrogen exchange for olefin-insertion, C–C bond rotation and β-hydrogen elimination have been measured for this class of complex.[149]

The data indicate that both the steric bulk and the location of the cyclopentadienyl substituents have large effects on the energy barrier for hydrogen exchange. Exchange rates decrease by three orders of magnitude as the steric bulk is increased for those niobocenes with unsymmetrical substitution. Furthermore, it was found that the singly bridged *ansa*-niobocenes exchange up to three orders of magnitude faster than unbridged complexes (see Scheme 6). The "*ansa*-effects" were investigated by DFT calculations on model complexes.

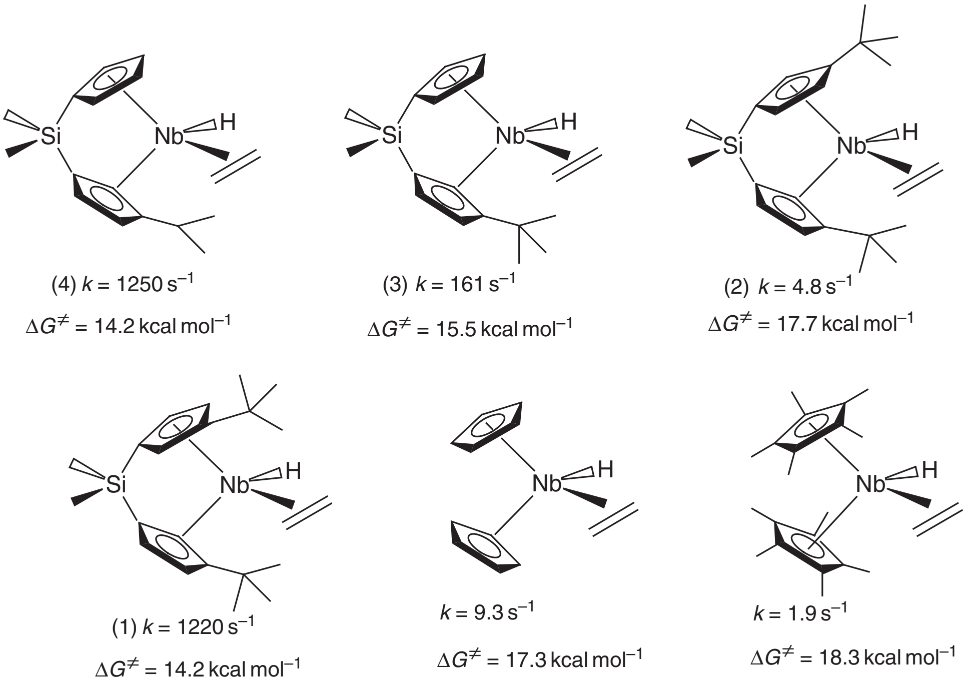
5.02.5.2 Alkyne Complexes

Alkyne-containing complexes of Nb are well known, and in recent years a range of different types of complexes have been prepared, particularly with the cyclopentadienyl ring or tris(pyrazol-1-yl)borate (Tp) group as an ancillary ligand. The alkyne complexes of Nb are summarized in Table 7.



Distal, *anti*, *endo*
Distal, *syn*, *endo*
Proximal, *syn*, *endo*
Proximal, *anti*, *endo*
Distal, *syn*, *exo*
Distal, *anti*, *exo*
Proximal, *anti*, *exo*
Proximal, *syn*, *exo*

Scheme 5



(4) $k = 1250\ s^{-1}$
$\Delta G^{\neq} = 14.2\ kcal\ mol^{-1}$

(3) $k = 161\ s^{-1}$
$\Delta G^{\neq} = 15.5\ kcal\ mol^{-1}$

(2) $k = 4.8\ s^{-1}$
$\Delta G^{\neq} = 17.7\ kcal\ mol^{-1}$

(1) $k = 1220\ s^{-1}$
$\Delta G^{\neq} = 14.2\ kcal\ mol^{-1}$

$k = 9.3\ s^{-1}$
$\Delta G^{\neq} = 17.3\ kcal\ mol^{-1}$

$k = 1.9\ s^{-1}$
$\Delta G^{\neq} = 18.3\ kcal\ mol^{-1}$

Scheme 6

5.02.5.2.1 Alkyne complexes without cyclopentadienyl ligands

Alkyne-functionalized complexes have been prepared by reductive coupling of two CO or CNR groups from carbonyl and isonitrile derivatives in low oxidation states (see Section 5.02.2.3).[16,43,13,39] Alkyne complexes in low oxidation states have also been prepared from Nb(I) carbonyl species $Nb(CO)_3(PR_3)_3X$ through the displacement of one CO and one PR_3 by a four-electron donating alkyne.[14] The one-electron oxidation of $Nb(mes)_3$ (mes = 1,3,5-trimethylbenzene) produces the 16-electron $[Nb(mes)_2]^+$ species, which adds disubstituted symmetrical alkynes to give the ionic Nb(I) species $[Nb(mes)_2(alkyne)]^+$.[151] These complexes contain bent η^6-mesitylene units, and a coordination position is occupied by an alkyne as a formal two-electron donor. Thermal treatment of these compounds led to mesitylene displacement, and formation of the neutral covalent Nb(I) compounds containing the uninegative

Table 7 Alkyne complexes of niobium

Complex	*Comments*	*References*
Whithout Cp ligands		
$Nb(\eta^2\text{-}Me_3SiOC\equiv COSiMe_3)(depe)_2Cl$	depe = 1,2-bis(diethylphosphino)ethane	16
$Nb(\eta^2\text{-}Me_3SiOC\equiv COSiMe_3)(depe)_2OTf$		16
$Nb(\eta^2\text{-}Me_3SiOC\equiv COSiMe_3)(dbpe)_2Cl$	dbpe = 1,2-bis(dibutylphosphino)ethane	16
$Nb(\eta^2\text{-} Me_3SiOC\equiv COSiMe_3)(dbpe)_2OTf$		16
$Nb(\eta^2\text{-}AcOC\equiv COSi^tBuPh_2)(dmpe)_2Cl$		43
$[Nb(\eta^2\text{-}{}^tBuNHC\equiv CNH^tBu)(CN^tBu)_4X_2]X$	X = Br, I, resulting from reductive coupling of two CNR groups	13, 39
$Nb(CO)_2(\eta^2\text{-}RC\equiv CR^1)(PR_3)_2X$	$PR_3 = PMe_2Ph$, X = Cl, Br, I; $R = R^1 = H$, Et, Ph; R = H, $R^1 = Ph$ $PR_3 = PEt_3$, X = I, $R = R^1 = Pr$; R = H, $R^1 = Bu$, Ph; R = Me, $R^1 = Et$ (for X = I X-ray)	14
$Nb(CO)_2(\eta^2\text{-}PhC\equiv CPh)(dppe)X$	X = Br, I	14
$[Nb(CN^tBu)_3(\eta^2\text{-}PhC\equiv CPh)I_2]I$		39
$Nb(CO)_2(\eta^2\text{-}PhC\equiv CH)(PEt_3)_2I$	X-ray; alkyne acting as a 4-electron donor	87
$Nb(CO)_2(diyne)(PR_3)_2I$	$PR_3 = PEt_3$, diyne = 2,4-hexadiyne (X-ray); 1,5-hexadiyne; $PR_3 = PMe_2Ph$, diyne = 2,6-octadiyne	150
$Nb(CO)_2(\eta^2\text{-}Ph_2PC\equiv CPPh_2)(PMe_2Ph)_2$	X-ray	150
$[Nb(mes)_2(\eta^2\text{-}alkyne)]Y$	Alkyne = $MeC\equiv CMe$, $Y = BPh_4$, $B(p\text{-}FC_6H_4)_4$, $B(3,5\text{-}(CF_3)_2C_6H_3)_4$; alkyne = $PhC\equiv CPh$, $Y = BPh_4$, $B(p\text{-}FC_6H_4)_4$ (X-ray)	151
$Nb(\eta^2\text{-}RC\equiv CR)(\eta^6\text{-}C_6H_4X)_2B(C_6H_4X)_2$	R = Me, X = H (X-ray), p-F(X-ray); R = Ph, X = H	151
$Nb(trisAP\text{-}4,6)(\eta^2\text{-}PhC\equiv CSiMe_3)$	trisAP-4,6 = $HC(SiMe_2NC_5NH_2\text{-}4,6\text{-}Me_2)_3$	153
$Nb\{N(SiMe_3)C_5H_3N\text{-}6\text{-}SiMe)\}_3(\eta^2\text{-}PhC\equiv CSiMe_3)$		154
$Nb\{N(SiMe_3)C_5H_3N\text{-}2\text{-}SiMe)\}_2(\eta^2\text{-}PhC\equiv CSiMe_3)$ X	X = Cl, Me (X-ray)	154
$[Nb\{N(SiMe_3)C_5H_3N\text{-}2\text{-}SiMe_3)\}_2(\eta^2\text{-}PhC\equiv CSiMe_3)][MeB(C_6F_5)_3]$	X-ray	154
$Nb(L\text{-}L)(\eta^2\text{-}RC\equiv CR^1)Cl_3$	$R = R^1 = Ph$, L-L = bpzm(bis-(pyrazol-1-yl)methane), bdmpzm(bis(3,5-dimethylpyrazol-1-yl)methane), btpzm(bis(5-trimethylsilyl-pyrazol-1-yl)methane); $R = R^1 = CO_2Me$, L-L = btpzm; $R = R^1 = Me$, L-L = bpzm, bdmpzm, btpzm	155
$[Nb(L\text{-}L\text{-}L)(\eta^2\text{-}RC\equiv CR^1)Cl_2][BF_4]$	$R = R^1 = Ph$, L-L-L = tpzm(tris(pyrazol-1-yl)methane), tdmpzm(tris(3,5-dimethylpyrazol-1-yl)methane); $R = R^1 = Ph$, L-L-L = tpzm, tdmpzm	155
$Nb(\eta^2\text{-}RC\equiv CR^1)(S_2CNR^2{}_2)_3$	$R = R^1 = Ph$, Me, Et, $SiMe_3$; $R^2 = Me$ (X-ray), Et,	156
$Nb(\eta^2\text{-}RC\equiv CR^1)(2\text{-}TCMP)Cl_3$	$R = R^1 = Ph$, $R = R^1 = Me$, $R = R^1 = Et$, R = Ph, $R^1 = Me$, R = Ph, $R^1 = Et$, R = Ph, $R^1 = Pr$ (X-ray), R = Ph, $R^1 = SiMe_3$; 2-TCMP = [{2-thiazolylcarbonyl}methylene]triphenyl-phosphorane	157
$[Nb(\eta^2\text{-}F_3CC\equiv CCF_3)(py)Br_4][Et_4N]$		158
$[P_2N_2]Nb(\eta^2\text{-}HC\equiv CPh)$	$P_2N_2 = PhP\ (CH_2SiMe_2NSiMe_2CH_2)_2PPh$; EPR spectrum ($g = 1.985$; $a(^{93}Nb) = 108.4\ G$)	159
Monocyclopentadienyl or related		
$CpNb(\eta^2\text{-}R^1C\equiv CR^1)Cl_2$	$Cp = C_5H_4SiMe_3$; $R^1 = SiMe_3$	160
$CpNb(\eta^2\text{-}R^1C\equiv CR^2)R_2$	$Cp = C_5H_4SiMe_3$; R = Me, CH_2SiMe_3, CH_2CMe_3, $CH_2C_6H_5$	160
$CpNb(\eta^2\text{-}(R)NAr)(\eta^2\text{-}R^1C\equiv CR^2)R$	$Cp = C_5H_4SiMe_3$; R = Me, CH_2SiMe_3, CH_2CMe_3; Ar = 2,6-$Me_2C_6H_3$	160
$CpNb(NR)(\eta^2\text{-}R^1C\equiv CR^1)(PMe_3)$	$Cp = C_5H_5$, C_5Me_5; $R = C_6H_4{}^tBu\text{-}2,C_6H_3{}^iPr_2\text{-}2,6$; $R^1 = R^1 =$ Ph(X-ray); $R^1 = Ph$, $R^1 = H$	129
$CpNbCl_2(\eta^2\text{-}RC\equiv CR^1)$	$Cp = C_5Me_5$; $R = R^1 = Me$, $SiMe_3$; R = Me, $R^1 = Et$; R = Ph, $R^1 = SiMe_3$	40
Tp=hydrotris(3,5-dimethylpyrazol-1-yl)borate		
$TpNb(\eta^2\text{-}RC\equiv CR^1)Cl_2$	Tp; $RC\equiv CR^1 = PhC\equiv CCH_3$ (X-ray), $PhC\equiv CCH_2CH_2CH_3$, $PhC\equiv CCH_2CH_3$, $CH_3C\equiv CCH_3$, $PhC\equiv CPh$	161
$TpNb(\eta^2\text{-}RC\equiv CR^1)R^2{}_2$	Tp; $R^2 = CH_3$, $RC\equiv CR^1 = PhC\equiv CCH_3$, $PhC\equiv CCH_2CH_3$, $PhC\equiv CCH_2CH_2CH_3$; $R^2 = CH_2Ph$, $PhC\equiv CCH_3$	161

(*Continued*)

Table 7 (Continued)

Complex	*Comments*	*References*
TpNb(η^2-PhC$\equiv$CR)Cl(OCH$_3$)	Tp; R = Me, Et	163
TpNb(η^2-PhC$\equiv$CR)(R^1)(OCH$_3$)	Tp; R^1 = Me, R = Me, Et; R^1 = Ph, R = Et	163
TpNb(η^2-PhC$\equiv$CR)Cl(CH$_2$R^1)	Tp; R^1 = Me, R = Me, Et (X-ray), n-Pr; R^1 = Et, R = Me, Et; R^1 = SiMe$_3$, R = Me (X-ray); R^1 = H, R = Et, n-Pr, CH$_2$SiMe$_3$	164, 165
TpNb(η^2-PhC$\equiv$CMe)(CO)$_2$	Tp	169
TpNb(η^2-PhC$\equiv$CMe)(RCCR^1)(CO)	Tp; R = Ph, PPh$_2$; R^1 = Me, Ph	169
TpNb(η^2-PhC$\equiv$CMe)(CO)(PMe$_2$Ph)	Tp	170
TpNb(η^2-PhC$\equiv$CMe)$_2$(CO)	Tp	170
TpNb(η^2-PhC$\equiv$CMe)(CO)(RCN)	Tp; R = Me, Et (X-ray), PhCH$_2$, 4-MeOC$_6$H$_5$, Ph,4-CF$_3$C$_6$H$_5$; an equilibrium between η^2(3e)-nitrile/η^2(3e)-alkyne form is present	170, 171
TpNb(η^2-MeC$\equiv$CMe)X(R)	Tp; X = Cl, R = c-C$_3$H$_5$ (X-ray), X = Br, R = c-C$_3$H$_5$ (X-ray), X = Cl, R = c-C$_5$H$_9$, X = Cl, R = c-C$_6$H$_{11}$	172
[TpNb(η^2-MeC$\equiv$CMe)Me(L)]BAr$_{f4}$	Tp; L = OEt$_2$, PMe$_2$Ph, PEt$_3$	173
TpNb(η^2-RC$\equiv$CR^1)Cl$_2$	Tp pyrazol; R = Ph, R^1 = Me (X-ray); R = R^1 = Me, Et, SiMe$_3$, Ph	174
TpCpNb(η^2-PhC$\equiv$CMe)Cl	Tp = hydrotris(pyrazol-1-yl)borate; Cp = C$_5$H$_5$ (X-ray)	174
(bdmpzx)Nb(η^2-RC$\equiv$CR^1)Cl$_2$	X = a (bis(3,5-dimethylpyrazol-1-yl)acetate, R = R^1 = Me, Et, Ph, SiMe$_3$; R = Ph, R^1 = Me (X-ray); R = Ph, R^1 = Et; R = Ph, R^1 = SiMe$_3$; x = e (2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide, R = R^1 = Me, Et, Ph; R = Ph, R^1 = Me; R = Ph, R^1 = Et; R = Ph, R^1 = SiMe$_3$	175, 176
(dpmpza)Nb(η^2-RC$\equiv$CR^1)Cl$_2$	dpmpza = (3,5-diphenylpyrazol-1-yl-3′,5′-dimethylpyrazol-1-yl)acetate, R = R^1 = Me, SiMe$_3$; R = Ph, R^1 = Me; R = Ph, R^1 = Et	177
Bis-cyclopentadienyl		
Cp$_2$Nb(η^2-RC$\equiv$CR^1)Cl	Cp = C$_5$H$_4$SiMe$_3$; R = H, R^1 = COOMe; R = Me, R^1 = COOMe; R = R^1 = COOMe	178
{(C$_5$R$_4$)SiMe$_2$(C$_5$R$^1{}_4$)}Nb(η^2-R^{2}C$\equiv$CR^2)Cl	R = R^1 = H, R^2 = Me, Ph(X-ray); R$_4$ = R$^1{}_4$ = H$_3$SiMe$_3$, R^2 = Me, Ph (mixture of *meso*- and *rac*- isomers); R$_4$ = Me$_4$, R$^1{}_4$ = H$_4$, R$^2{}_4$ = Me, Ph	70, 179, 180
Cp$_2$Nb(η^2-RC$\equiv$CR^1)	Cp = C$_5$H$_4$SiMe$_3$; R = R^1 = Ph; R = H, R^1 = Ph; R = H, R^1 = COOMe; R = Me, R^1 = COOMe (paramagnetic species characterized by ESR spectroscopy)	178
Cp$_2$Nb(η^2-MeO$_2$CC$\equiv$CCO$_2$Me)(pz-N)	Cp = C$_5$H$_4$SiMe$_3$; pz = pyrazolyl	28
[Cp$_2$Nb(η^2-RC$\equiv$CR^1)L][BPh$_4$]	Cp = C$_5$H$_4$SiMe$_3$; L = CH$_3$CN, R = R^1 = Ph, R = R^1 = CO$_2$Me, R = R^1 = Me, R = Me, R^1 = CO$_2$Me; L = ^{t}BuCN, R = R^1 = Ph, R = R^1 = CO$_2$Me, R = R^1 = Me, R = Me, R^1 = CO$_2$Me; L = ^{t}BuNC, R = R^1 = Ph, R = R^1 = CO$_2$Me, R = R^1 = Me; L = THF, R = R^1 = Me, R = Me, R^1 = CO$_2$Me; L = Py, R = R^1 = Me	136, 137
Cp$_2$Nb(η^2-RC$\equiv$CR^1)R^2	Cp = C$_5$H$_4$SiMe$_3$; R = R^1 = Ph, R^2 = Me; R = R^1 = R^2 = Me; R = H, R^1 = Ph, R^2 = Me; R = R^1 = Me, R^2 = Et; R = R^1 = Me, R^2 = CH$_2$Ph; R = H, R^1 = Ph, R^2 = CH$_2$Ph (X-ray); R = H, R^1 = Ph, R^2 = CH$_2$CH=CH$_2$	137
Cp$_2$Nb(η^2-RC$\equiv$CR^1)Cl	Cp = C$_5$H$_4$SiMe$_3$; R = C$\equiv$CSiMe$_3$, R^1 = SiMe$_3$; R = C$\equiv$CPh, R^1 = Ph (X-ray); R = CH$_2$CH$_2$C$\equiv$CH, R^1 = H; R = CH$_2$CH=CH$_2$, R^1 = Ph; R = CH$_2$CH=C(CH$_3$)$_2$, R^1 = Ph (X-ray); R = CH$_2$C(CH$_3$)=CH$_2$, R^1 = Ph; R = C(CH$_3$)=CH$_2$, R^1 = H	181
Cp$_2$Nb(η^2-RC$\equiv$CR^1)	Cp = C$_5$H$_4$SiMe$_3$; R = C$\equiv$CSiMe$_3$, R^1 = SiMe$_3$, paramagnetic species	181
Cp$_2$Nb(η^2-RC$\equiv$CR^1)R^2	Cp = C$_5$H$_4$SiMe$_3$; R = C$\equiv$CSiMe$_3$, R^1 = SiMe$_3$R^2 = Me; R = CH$_2$CH=CH$_2$, R^1 = Ph, R^2 = CH$_2$Ph; R = CH$_2$CH=C(Me)$_2$, R^1 = Ph, R^2 = Me	181
Cp$_2$Nb(η^2-RC$\equiv$CR^1)Cl	Cp = C$_5$H$_4$SiMe$_3$; R = CH$_2$CH$_2$CH$_3$, R^1 = Ph; R = CH$_2$CH$_2$CH(CH$_3$)$_2$, R^1 = Ph; R = C$\equiv$CPh(Co(CO)$_3$)$_2$, R^1 = Ph	181

tetraarylborato ligand, with the product having the formula Nb(η^2-RC≡CR) (η^6-$C_6H_4X)_2B(C_6H_4X)_2$. This ligand interacts as a 12-electron donor through an interannular boron-bridged system.[151] Different classes of alkyne niobium(III) complexes have been prepared using the well-known and useful precursors $NbCl_3$(dme) (η^2-RC≡CR^1).[152] Several types of complexes of this kind were described in COMC (1995). For example, an interesting type of reactivity has been described for this class of complex and concerns the reactions of the complexes with aminopyridinato ligands. For example, the reaction of $NbCl_3$(dme)(η^2-PhC≡CSiMe$_3$) with the trilithiated salt of HC(SiMe$_2$NHC$_5$NH$_2$-4,6-Me$_2$)$_3$, Li$_3$(trisAP-4,6), gave rise to Nb(trisAP-4,6)(η^2-PhC≡CSiMe$_3$) in which the trisAP-4,6 acts as a pentadentate ligand.[153] The reactivity of the precursors with N ligands based on pyrazole rings has also been considered. For example, bis(pyrazol-1-yl)methane derivatives (bpzm) have been reported[155] to react with $NbCl_3$(dme)(η^2-RC≡CR^1) complexes to give the corresponding alkyne-containing complexes Nb(bpzm)(η^2-RC≡CR^1)Cl$_3$. In this class of compound the alkyne behaves as a four-electron ligand, and a simple rotation of this unit around the bisector of the metal–alkyne isosceles triangle has been proposed as an explanation for their fluxional behavior. The rotational activation barrier $\Delta G^\ddagger$ was calculated to be ca. 11 kcal mol^{-1}. The reaction of phenylacetylene with the paramagnetic dinuclear dinitrogen complex ([P$_2$N$_2$]Nb)$_2$(μ-N$_2$) displaces the dinitrogen fragment to generate an Nb(IV) paramagnetic alkyne complex [P$_2$N$_2$]Nb(η^2-HC≡CPh).[159]

5.02.5.2.2 Alkyne complexes with cyclopentadienyl and related ligands

This class of complexes constitutes a large family of niobium compounds. Mono- and bis-cyclopentadienyl complexes have been prepared, and in most cases these correspond to CpNb(η^2-RC≡CR^1)X$_2$ and Cp$_2$Nb(η^2-RC≡CR^1)X stoichiometries, where X$^-$ can be a wide variety of anionic ligands. A new type of complexes, namely, TpNb(η^2-RC≡CR^1)X$_2$, Tp = hydrotris(pyrazol-1-yl)borate or related scorpionate ligands, has also been extensively studied, and these compounds exhibit a rich chemistry.

5.02.5.2.2.(i) Monocyclopentadienyl and related alkyne complexes

The number of new complexes of the type CpNb(η^2-RC≡CR^1)X$_2$ is very small. An interesting series of alkyl–alkyne complexes CpNb(η^2-R^{1}C≡CR^2)R$_2$ has been described,[160] and these were prepared by treating CpNb(η^2-R^{1}C≡CR^2)Cl$_2$ derivatives with the appropriate alkylating reagents. Reaction of the dialkyl–alkyne complexes with 2,6-Me$_2$C$_6$H$_3$NC resulted in migration of only one of the two alkyl groups to give the alkyl–alkyne–iminoacyl complexes CpNb(η^2-C(R)NAr)(R^{1}C≡CR^2)R, but led to different coupling products depending on the nature of R (see Section 5.02.6). Furthermore, imido-containing complexes have also been described. For example, complexes of the type CpNb(NR)(η^2-R^{1}C≡CR^2)(PMe$_3$) were formed upon treatment of complexes CpNb(NR)(PMe$_3$)$_2$ with the appropriate alkyne.[129] Interest in the organometallic chemistry of Nb with hydrotris(pyrazol-1-yl)borates has been renewed since Etienne *et al.*[161] discovered an efficient route to niobium(III) complexes containing four-electron donor alkynes TpNb(η^2-RC≡CR^1)X$_2$. This type of complex has proved useful as a starting material in a broad range of reactions.[162] In all cases the alkyne occupies the molecular mirror plane, as shown in Figure 1. The barrier to alkyne rotation is high, and it was established on the basis of qualitative arguments that the structure of these complexes is essentially governed by steric interactions. In some cases interesting bonding modes have been found. For example, the complexes TpNb(η^2-PhC≡CR)Cl(CH$_2$R^1)[164,165] were found to exhibit an α-hydrogen agostic interaction, and for steric reasons this is established preferentially over the more conventional β-agostic interaction. The electronic structure of these systems has been studied in depth using the hybrid QM/MM methodology.[166–168] These fundamental studies have shed some light on the factors that control agostic bonding, and have highlighted the fact that the presence of unusual types of agostic bonding may be a result of steric factors that disfavor alternative structures rather than any intrinsically strong electronic driving force. Interesting behavior was also found upon thermal activation,

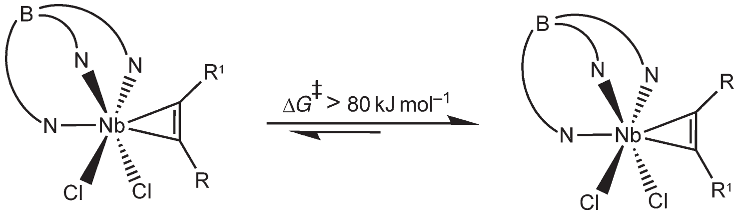
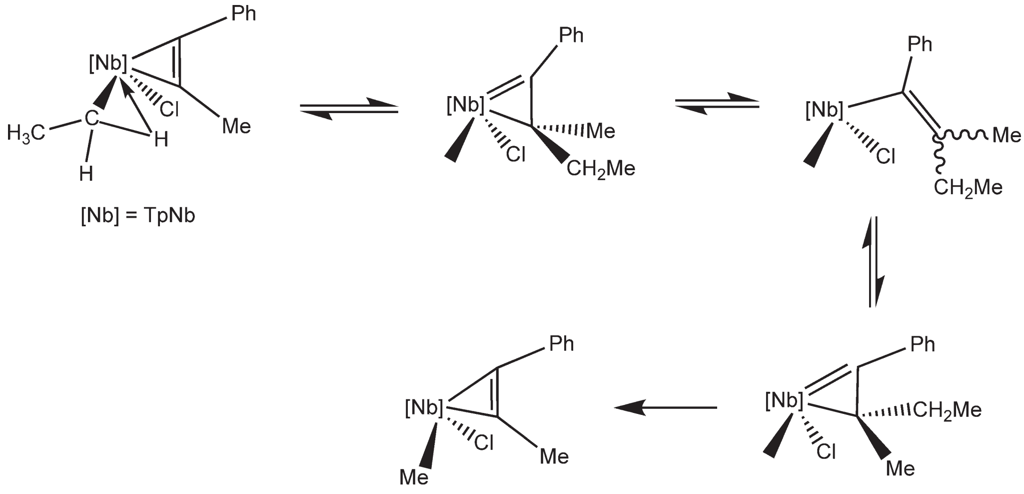


Figure 1



Scheme 7

when some of these complexes undergo a rearrangement in which the niobium-bound alkyl group and the alkyne alkyl group are exchanged. This rearrangement is based on the reversible migratory insertion of the alkyl group onto the alkyne. A transient unsaturated alkenyl species is generated, and this can either undergo intramolecular C–C bond activation (leading to the alkyl switch) or be trapped with appropriate reagents (Scheme 7). Kinetic and trapping data indicate that the migratory insertion of the alkyl group is the rate-determining step of the whole process. An interesting class of complexes that contain a heteroscorpionate ligand related to the tris(pyrazol-1-yl)methane system, namely, (bdmpzx)Nb(η^2-RC$\equiv$CR^1)Cl$_2$ has been described.[175,176] A six-coordinate arrangement has been assumed for these complexes in which the alkyne occupies a single site and exhibits dynamic behavior based on a single rotation of the alkyne ligand around the bisector of the metal–alkyne isosceles triangle (see Figure 2).

5.02.5.2.2.(ii) Bis-cyclopentadienyl alkyne complexes

Complexes of the stoichiometry Cp$_2$Nb(η^2-RC$\equiv$CR^1)X have been prepared through the chemical or electrochemical reduction of Cp$_2$NbX$_2$ species in the presence of the appropriate alkyne.[178] For example, a new type of complex containing *ansa*-cyclopentadienyl ligands (e.g., {(C$_5$R$_4$)SiMe$_2$(C$_5$R$^1_4$)}Nb(η^2-R^{2}C$\equiv$CR^2)Cl, has been synthesized by following this procedure.[70,179,180] Stable cationic d^2-derivatives [Cp$_2$Nb(η^2-RC$\equiv$CR^1)L]$^+$ have also been prepared by the oxidation of paramagnetic complexes Cp$_2$Nb(η^2-RC$\equiv$CR^1) in the presence of an appropriate Lewis base L.[136,137,181] Furthermore, an interesting type of reactivity has been described for some paramagnetic complexes upon treatment with organic halides.[137] Indeed, the reaction with R^{2}X gave rise to mixtures of niobocene alkyl–alkyne

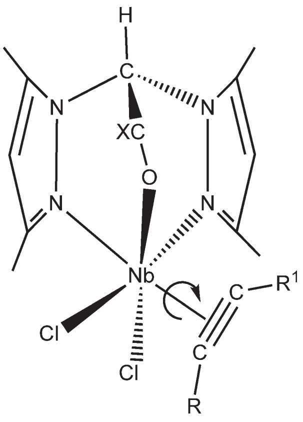


Figure 2

complexes $Cp_2Nb(\eta^2\text{-}RC{\equiv}CR^1)R^2$ and halo-alkyne species $Cp_2Nb(\eta^2\text{-}RC{\equiv}CR^1)X$, probably through the interaction of the unpaired electron of the Nb paramagnetic species with the appropriate radical, $R^{2\cdot}$ or $X^{\cdot}$, which results in the homolytic cleavage of the carbon–halogen bond. An interesting η^1-vinylidene-η^2-alkyne rearrangement was observed in vinylidene d^2-niobocene species of the type $[Cp_2Nb({=}C{=}CHR)(CO)]^+$. In solution, these materials undergo an unexpected isomerization process to give the corresponding η^2-alkyne derivatives $[Cp_2Nb(\eta^2\text{-}HC{\equiv}CR)(CO)]^+$. DFT calculations were carried out on a model system in order to gain an insight into this rearrangement.[77] Calculations showed that the η^1-vinylidene and the η^2-alkyne complexes are isoenergetic. The process takes place through an intraligand 1,2-hydrogen-shift mechanism involving η^2-(C–H)–alkyne species.[77]

5.02.5.3 η^2-Acyls, η^2-Iminoacyls, and Related η^2-complexes

5.02.5.3.1 η^2-Acyls and η^2-iminoacyls

Complexes containing acyl, $NbC({=}O)R$, and iminoacyl, $NbC({=}NR)R$, moieties have been prepared – mainly from alkyl-containing precursors by insertion processes. In some cases these complexes are versatile reactive intermediates in a number of transition metal-promoted stoichiometric and catalytic transformations. In some acyl derivatives, the ligand coordinates in an η^1-fashion, particularly for Nb(III), and this class of complex is also considered in this section. Other compounds included in this section are those that contain other types of η^2-ligands coordinated through both the carbon and heteroatom, for example, carbon dioxide, ketene, ketenimine, and isocyanate. The complexes considered here are shown in Table 8. Acyl-containing complexes are relatively rare. Protonation of the η^2-(C,O)–ketene complexes has

Table 8 η^2–Acyls, η^2-iminoacyls, and related η^2-complexes

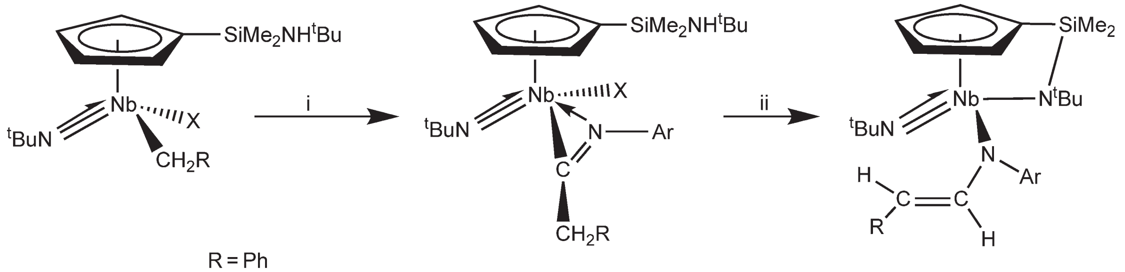
Compound	*Comments*	*References*
Acyl complexes		
$[Cp_2NbMe(\eta^2\text{-}C(O)CHPh_2)][BF_4]$	$Cp = C_5H_4SiMe_3$	182
$[Cp_2NbCl(\eta^2\text{-}C(O)C(R){=}CR^1R^2)][BF_4]$	$Cp = C_5H_4SiMe_3$; $R = Ph$, $R^1 = H$, $R^2 = Me$ (X-ray); $R = Me$, $R^1 = R^2 = H$; $R = Et$, $R^1 = H$, $R^2 = Me$; $R = Et$, $R^1 = R^2 = H$ (isomeric mixture); $R = Me$, $R^1 = H$, $R^2 = Me$ (isomeric mixture)	184
$Cp_2NbCl_2(\eta^2\text{-}C(O)RR^1)$	$Cp = C_5H_4SiMe_3$; $R = R^1 = Ph$; $R = Me$, $R^1 = Ph$, transient species in the electroreduction of acyl chlorides by Cp_2NbCl_2	185
$Cp_2Nb(CO)(\eta^1\text{-}C(O)CH_2CH_2R)$	$Cp = C_5H_4SiMe_3$; $R = H$, Ph	75
$Cp_2Nb(O)(\eta^1\text{-}C(O)CH_2CH_2R)$	$Cp = C_5H_4SiMe_3$; $R = H$, Me	76
$Cp_2Nb(O)(\eta^1\text{-}C(O)OCF_3)$	$Cp = C_5H_4SiMe_3$, X-ray	76
$(R[P_2N_2]Nb)_2(\mu\text{-}C(O)Me)_2$	$(R[P_2N_2] = RP(CH_2SiMe_2NSiMe_2CH_2)_2PR$, $R = Ph$, Cy; prep: $(R[P_2N_2]NbMe)_2(\mu\text{-}N_2) + CO$	50
Iminoacyl complexes		
$[Cp_2Nb(OR)(\eta^2\text{-}C(NPh)CHR^1Ph)][BPh_4]$	$Cp = C_5H_4SiMe_3$; $R = H$, Me; $R^1 = Me$, Et, Ph	186
$[Cp_2NbX(\eta^2\text{-}C(NPh)CHRPh)][BF_4]$	$Cp = C_5H_4SiMe_3$; $X = H$, Me; $R = Me$, Et, Ph	182
$Cp_2Nb(\eta^1\text{-}C(NR)R^1)(CNR)$	$R = Bu$, $2,6\text{-}Me_2C_6H_3$; $R^1 = Et$, $CH_2CH{=}CHSiPh_3$, $CH_2CH{=}CH_2$	79
$CpNbMe(\eta^2\text{-}C(NR)Me)(\eta^2\text{-}PhC{\equiv}CPh)$	$R = Bz$, ${}^tBu$	187
$[C_5H_4(SiMeXY)NbR(\eta^2\text{-}C(NAr)CH_2Ph)]$	$R = CH_2Ph$, Cl; $X = CH_2Ph$, Cl; $Y = Me$, Ph; $Ar = 2,6\text{-}Me_2C_6H_3$	64
$(\eta^5\text{-}C_5H_4\text{-}SiMe_2(NH^tBu))NbX(\eta^2\text{-}C(NAr)CH_2Ph)(N^tBu)$	$X = Cl$, CH_2Ph; $Ar = 2,6\text{-}Me_2C_6H_3$	188
$(\eta^5\text{-}C_5H_4\text{-}SiMe_2(\eta^1\text{-}N^tBu))Nb(\eta^2\text{-}C(NAr)CH_2Ph)(N^tBu)$	$Ar = 2,6\text{-}Me_2C_6H_3$	188
$CpNbX(\eta^2\text{-}C(NAr)R)(N^tBu)$	$X = Cl$, Me, CH_2SiMe_3, CH_2CMe_3, CH_2Ph; $R = Me$, NMe_2 CH_2SiMe_3, CH_2CMe_3, CH_2Ph; $Ar = 2,6\text{-}Me_2C_6H_3$	189
$(\eta^5\text{-}C_5H_4SiMe_2(\eta^1\text{-}N^tBu))Nb(\eta^2\text{-}C(NAr)CH_2Ph)$	$Ar = 2,6\text{-}Me_2C_6H_3$	190
$CpNbR(\eta^2\text{-}C(NAr)R)(\eta^2\text{-}R^1C{\equiv}CR^1)$	$Cp = C_5H_4SiMe_3$; $R = Me$, CH_2SiMe_3, CH_2CMe_3; $R^1 = SiMe_3$; $Ar = 2,6\text{-}Me_2C_6H_3$	160

(*Continued*)

Table 8 (Continued)

Compound	*Comments*	*References*
[{CpNb(η^2-C(NAr)R)R}$_2$(μ-1,x-NC$_6$H$_4$N)]	Cp = C$_5$H$_4$SiMe$_3$; x = 3,4; Ar = 2,6-Me$_2$C$_6$H$_3$; R = Me, CH$_2$Ph, CH$_2$SiMe$_3$	191
[{CpNb(η^2-Me$_2$NC=NAr)Me}$_2$(μ-1,4-NC$_6$H$_4$N)]	Cp = C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$	191
[{Nb(η^2-C(NAr)R)$_2$R}$_2$(μ-1,x-NC$_6$H$_4$N)]	R = CH$_2$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$	191
[(η^5:η^1:η^1:η^1-Et$_8$N$_4$)Nb(CN^{t}Bu)(η^2-C(NBu^t)Me]	Et$_8$N$_4$ = (*meso*-octaalkylporphyrinogen)	47
[TpNb(η^2-C(NH)Ph)(η^2-PhC≡CMe)(CO)][BF$_4$]	Tp = Hydridotris(3,5-dimethylpyrazolyl)borate	170
CO$_2$, ketene, ketenimine and related complexes		
Cp$_2$NbR(η^2-CO$_2$)	Cp = C$_5$H$_4$Me; R = Me, CH$_2$Ph, CH$_2$CMe$_3$; CH$_2$SiMe$_3$	74
Cp$_2$NbR(η^2-CO$_2$)	Cp = C$_5$H$_4$SiMe$_3$; R = Et, CH$_2$CH$_2$Ph, CH$_2$CH$_2$C$_6$H$_4$Me, CH$_2$CH$_2$C$_6$H$_4$OMe	75
Cp$_2$NbCl(η^2-CO$_2$)	Cp = C$_5$H$_4$SiMe$_3$, C$_5$Me$_5$; prep: Cp$_2$NbCl$_2$ + Na/Hg + CO$_2$	192
Cp$_2$Nb(η^2-CO$_2$)	Cp = C$_5$H$_4$SiMe$_3$, C$_5$Me$_5$, electrochemically generated, ten-line ESR spectra g = 2.0228(1.9958), A = 54(46.9) G	192
Cp$_2$NbR(η^2-CS$_2$)	Cp = C$_5$H$_4$SiMe$_3$; R = Et (X-ray), CH$_2$CH$_2$Ph	135
Cp$_2$NbCl(η^2- OCC(R)CH=CH$_2$)	Cp = C$_5$H$_4$SiMe$_3$; R = Et, Ph	184
Cp$_2$NbCl(η^2-OCC(Me)CH$_2$X)	Cp = C$_5$H$_4$SiMe$_3$; X = OMe, NEt$_2$	184
Cp$_2$NbX(η^2-OCC(R)Ph)	Cp = C$_5$H$_4$SiMe$_3$; X = H, Me (X-ray), Et	182
Cp$_2$NbX(η^2-NPhC≡C(R)Ph)	Cp = C$_5$H$_4$SiMe$_3$; X = H, Me, Et	182
[Cp$_2$Nb(η^2-NPhCC(R)Ph)(L)][BPh$_4$]	Cp = C$_5$H$_4$SiMe$_3$; R = Me, Ph (X-ray); L = CH$_3$CN, ^{t}BuCN, PhCN, ^{t}BuNC	186
TpNb(CO)(η^2-PhC≡CMe)(η^2-C(N)R)	Tp = hydridotris(3,5-dimethylpyrazolyl)borate; R = Me, Et (X-ray), CH$_2$Ph, C$_6$H$_5$OMe-4	170
Cp$_2$NbX(η^2-RCN)	Cp = C$_5$H$_4$SiMe$_3$, C$_5$H$_3$(SiMe$_3$)$_2$; X = Cl, Br; R = Me, Ph	193
Cp$_2$NbCl(η^2-RNCO)	Cp = C$_5$H$_4$SiMe$_3$; R = Ph, ^{t}Bu, ^{n}Pr, ^{i}Pr	194
[{CpNbCl}$_2$(η^2-μ-1,x-(OCN$_2$C$_6$H$_4$))]	Cp = C$_5$H$_4$SiMe$_3$; x = 3, 4	69
CpNb(η^2-CMe$_2$N(2,6-Me$_2$C$_6$H$_3$))	Cp = C$_5$Me$_5$	56
(silox)$_3$Nb(η^2-NC-py)	Silox = ^{t}Bu$_3$SiO	132
Cp$_2$NbCl(η^2-CH$_2$O)	Cp = C$_5$H$_4$SiMe$_3$ (X-ray)	195
Cp$_2$Nb(η^2-CH$_2$O)	Cp = C$_5$H$_4$SiMe$_3$; ESR spectrum	195
Cp$_2$NbH(η^2-CH$_2$O)	Cp = C$_5$H$_4$SiMe$_3$	195

been used to prepare η^2-acyl derivatives. For example, Cp$_2$NbMe(η^2-OCCPh$_2$) was easily protonated by HBF$_4$·Et$_2$O to give [Cp$_2$NbMe(η^2-C(O)CHPh$_2$)][BF$_4$].[182] In the same way, η^2-enacyl derivatives [Cp$_2$NbCl(η^2-C(O)C(R^1)=CHR)](BF$_4$) were prepared[183] by transfer of a γ-hydride from the niobium ketene complexes Cp$_2$NbCl(η^2-OCC(R^1)CH$_2$R) to an appropriate triarylcarbenium salt. The cationic enacyls are strong electrophiles, and are susceptible to conjugate addition reactions and [4 + 2]-cycloadditions. Treatment with a suitable base converts these enacyls into the η^2-vinylketene complexes Cp$_2$NbCl(η^2-OCC(R^1)CH=CH$_2$). These compounds are relatively electron rich, and the vinyl terminus constitutes a site for the addition of electrophiles.[183,184] The first neutral acylniobocene complexes Cp$_2$Nb(CO)(η^1-C(O)CH$_2$CH$_2$R) were prepared by the reaction of olefin–hydride complexes Cp$_2$NbH(η^2-RHC=CH$_2$) with CO.[75] The oxidation of these acyl complexes with O$_2$ gave the oxoacyl derivatives Cp$_2$Nb(O) (η^1-C(O)CH$_2$CH$_2$R).[76] In an interesting type of reactivity, cationic iminoacyl derivatives [Cp$_2$Nb(η^2-C(NPh)CRPh)(CH$_3$CN)]$^+$ in wet acetone and methanol evolve to hydroxo/methoxo iminoacyl complexes [Cp$_2$Nb(OR)(η^2-C(NPh)CHRPh)]$^+$ derived from both formal protonation at the β-carbon atom of the ketenimine ligand and a hydroxide(methoxide)-acetonitrile exchange.[186] Most of the iminoacyl complexes were obtained through the insertion processes of isonitriles into Nb–C bonds of cyclopentadienyl-containing derivatives. For example, insertion of CN(Me$_2$C$_6$H$_3$-2,6) into (η^5-C$_5$H$_4$–SiMe$_2$(NH^{t}Bu))NbX(CH$_2$Ph)(N^{t}Bu) gave the corresponding iminoacyl complexes (η^5-C$_5$H$_4$–SiMe$_2$(NH^{t}Bu))NbX(η^2-C(NAr)CH$_2$Ph)(N^{t}Bu).[188] Subsequent heating effected an isomerization that



R = Ph
i, CN–Ar (Ar = $C_6H_3Me_2$-2,6), hexane, 1–2 h; ii, –160 °C, 3 d, hexane

Scheme 8

gave the vinylamido complex (η^5-C_5H_4–$SiMe_2$(η^1-N^{t}Bu))Nb(NAr)(CH=CHPh)(N^{t}Bu) (Scheme 8). A rare example of the deinsertion of isocyanide was observed when the benzyl η^2-iminocarbamoyl-amido silyl compound (η^5-$C_5H_4SiMe_2$(N^{t}Bu-η^2-C=NAr))Nb(CH_2Ph)(N^{t}Bu) was transformed into the η^2-iminoacyl-η^1-amido-silyl derivative (η^5-$C_5H_4SiMe_2$(η^1-N^{t}Bu))Nb(η^2-C(NAr)CH_2Ph) by heating it in solution.[190]

5.02.5.3.2 CO_2, ketene, ketenimine, and related complexes

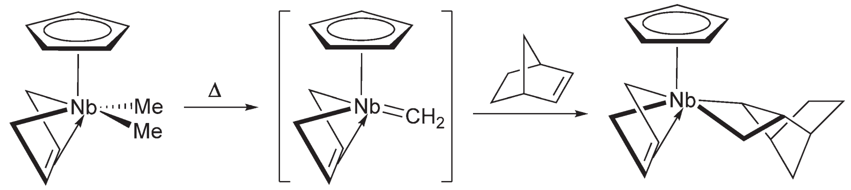
The preparation of CO_2-containing niobocene complexes has continued to attract attention. A previously described procedure (see COMC (1995)) was used by Nicholas *et al.* to prepare new CO_2 complexes $Cp_2NbR(\eta^2\text{-}CO_2)$.[74] This type of complex was also prepared by reaction of olefin–hydride niobocene complexes with CO_2.[75] The preparation of new ketene or ketenimine niobocene complexes has also been carried out. For example, cationic ketenimine-containing species were prepared by oxidation of the appropriate Nb(IV) compounds $Cp_2Nb(\eta^2\text{-}NPhCC(R)Ph)$ with Cp_2Fe^+ in the presence of nitriles or isonitriles.[186] An interesting structural arrangement was found in the nitrile adducts of the type TpNb(CO)(η^2-PhC≡CMe)(RCN), where η^2-coordination and an unprecedented formal three-electron donor ($3e^-$) behavior was found for both the alkyne and the nitrile. This phenomenon occurs through an equilibrium between the η^2-($3e^-$)-nitrile/η^2-($3e^-$)-alkyne form.[170] Furthermore, η^1-nitrile species $Cp_2NbX(\eta^1\text{-}RCN)$ were found to evolve at RT to the more thermodynamically stable η^2-nitrile-containing complexes $Cp_2NbX(\eta^2\text{-}RCN)$.[193] Isocyanate-containing niobocene complexes $Cp_2NbCl(\eta^2\text{-}RNCO)$ have been prepared by reaction of the appropriate free isocyanates with the 16-electron unit Cp_2NbCl.[194,69] Reaction of $CpNbCl_2Me_2$ with 2,6-$Me_2C_6H_3NC$ resulted in a double methyl group migration to give the azaniobacyclopropane complex CpNb(η^2-$CMe_2N(Me_2C_6H_3$-2,6)).[56] Treatment of $(silox)_3NbCl_2$ with Na/Hg in pyridine afforded the complex $(silox)_3Nb(\eta^2\text{-}NC\text{–}py)$.[132] Interesting reactivity was also found in $[Cp_2NbCl]_2$, which reacted with paraformaldehyde to yield the η^2-formaldehyde complex $Cp_2NbCl(\eta^2\text{-}CH_2O)$.[195]

5.02.6 Metallacyclic Complexes

Niobium metallacyclic complexes have played an important role in understanding the stoichiometric transformation of organic molecules. The intermediacy of these species has been demonstrated, for example, in the insertion processes of unsaturated molecules. In recent years some carbon–carbon bond-forming processes mediated by niobium complexes have been found to proceed via metallacyclic intermediates. In this section, the formation and reactivity of niobacyclic complexes in which the metallacyclic units have at least one carbon atom bound to the metal are considered. These compounds have been classified on the basis of the number of members in the metallacyclic moiety (Table 9).

5.02.6.1 Four-membered Metallacycles

The reaction of a mixture of chloro bis/tris-aryloxide niobium complexes with $^nBu_3SnH$ in the presence of 2-vinylpyridine led to insertion of 2-vinylpyridine olefin into the metal–hydride bond, which resulted in the formation of the four-membered pyridylalkyl metallacycle $Nb(OC_6H_3{}^iPr_2\text{-}2,6)_3(\eta^2\text{-}C_7H_8N)Cl$.[196] Furthermore, thermolysis of the dimethylniobium complex $CpNb(\eta^4\text{-}C_4H_6)(CH_3)_2$ afforded a nascent methylidene species that was trapped by norbornene or acenaphthylene to give metallacyclobutane derivatives (Equation (20)).[131] Niobium amido compounds can also be used as precursors for four-membered metallacycles, such as the complex $Cp_2Nb\{(\eta^2\text{-}N,C)N(SiMe_3)SiMe_2CH_2\}$, which presumably results from amido-ligand γ-hydrogen-bond activation.[197]



(20)

Table 9 Metallacyclic complexes of niobium

Compound	*Comments*	*References*
Four-membered metallacycle		
$Nb(OC_6H_3{}^iPr_2\text{-}2,6)_3(\eta^2\text{-}C_7H_8N)Cl$	X-ray	196
$Cp(\eta^4\text{-}C_4H_6)Nb\{CH_2CH(C_5H_8)CH\}$	$Cp = C_5Me_5$, X-ray	131
$Cp(\eta^4\text{-}C_4H_6)Nb\{CH_2CH(C_{10}H_6)CH\}$	$Cp = C_5Me_5$	131
$Cp_2Nb\{N(SiMe_3)SiMe_2CH_2\}$	X-ray	197
$[(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)_2Nb(N\text{–}L)_2]$	$L\text{–}N = C_{12}H_8N$ (X-ray); $L\text{–}N = C_{12}H_{12}N$; $L\text{–}N = C_{16}H_{16}N$	139
$[(L\text{–}N)_2Nb(\mu\text{-}CSiMe_3)(\mu\text{-}XylylNC{=}CSiMe_3)Nb\ (N\text{–}L)_2]$	$L\text{–}N = C_{12}H_8N$; $L\text{–}N = C_{12}H_{12}N$; $L\text{–}N = C_{16}H_{16}N$	139
$[(Me_3P)_2ClNb(\mu\text{-}CSiMe_3)_2NbCl(CH_2SiMe_3)_2]$	X-ray	141
$[(calix)Nb(\mu\text{-}CPh)_2Nb(calix)]^{4-}$	X-ray	48
$Cp_2Nb\{N(SiMe_3)C({}^tBu)CH_2\}$	$Cp = C_5H_4SiMe_3$	66
$CpNb\{\eta^2\text{-}(O)CMe_2\text{-}(CNAr)\}(Me,Ph\text{–}DAD)$	$Cp = C_5H_4SiMe_3$, (Me, Ph–DAD = 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene)	199
$Cp_2Nb(HPPhC_6H_4\text{-})$		111
Five-membered metallacycle		
$H({}^tBu_3SiO)_2Nb\{OSi{}^tBu_2CMe_2CH_2\}$	Two isomers	201
$({}^tBu_3SiO)_2({}^tBuCH_2CH_2)Nb(\eta^2\text{-}O,C\text{-}OSi{}^tBu_2CMe_2CH_2)$	Observed in ^1H NMR	143
$Nb(OC_6H_3{}^iPr\text{-}CMeCH_2CPh_2O)(OC_6H_3{}^iPr_2\text{-}2,6)_2$		142
$Nb(OC_6H_3{}^iPr\text{-}CMeCH_2CPh{=}CPh)(OC_6H_3{}^iPr_2\text{-}2,6)_2$	X-ray	142
$Nb(OC_6H_3{}^iPr\text{-}CMeCH_2CPh{=}CH)(OC_6H_3{}^iPr_2\text{-}2,6)_2$		142
$Nb(OC_6H_3Pr^i\text{-}CMe_2)(OC_6H_3{}^iPr_2\text{-}2,6)_3$	X-ray	142
$Nb(OC_6H_3{}^iPr\text{-}CMe_2)(OC_6H_3{}^iPr_2\text{-}2,6)_2\text{-}(NHPh)$		142
$CpNb(NAr)\{\eta^4\text{-}CH_2C(Me){=}C(SiMe_3)CH(SiMe_3)\}$	$Cp = C_5H_4SiMe_3$, $Ar = 2,6\text{-}Me_2C_6H_3$	199
$CpNb\{\eta^2\text{-}(O)CMe_2\text{-}(CNAr)_2\}(Me,Ph\text{–}DAD)$	$Cp = C_5H_4SiMe_3$	199
$TpClNb\{{=}C(Ph)C(R)C(H)CH(CH_3)\}$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl) borate, R = Ph, X-ray; R = Me	202
$Tp(CH_2CH_3)Nb\{{=}C(Ph)C(CH_3)CHCH_2\}$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl) borate	161
$[TpFNb\{{=}C(Ph)C(CH_3)CPhNH\}]$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl) borate	170
$TpFNb\{{=}C(Ph)C(CH_3)CO(CCH_3{=}CPhH)\}$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl) borate	170
Other metallacycle		
$CpNb(NAr)\{\eta^2\text{-}CH_2CMe_2CH_2CH\text{-}(CH_2CMe_3)C(SiMe_3){=}C(SiMe_3)\}$	$Cp = C_5H_4SiMe_3$	199
$CpNb(NAr)\{\eta^4\text{-}CH(SiMe_3)C(SiMe_3)\text{-}C(CH_2SiMe_3){=}CH(SiMe_3)\}$	$Cp = C_5H_4SiMe_3$, X-ray	199

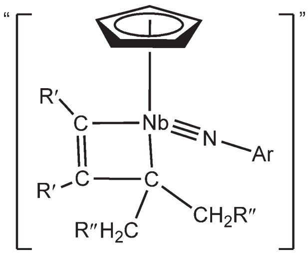
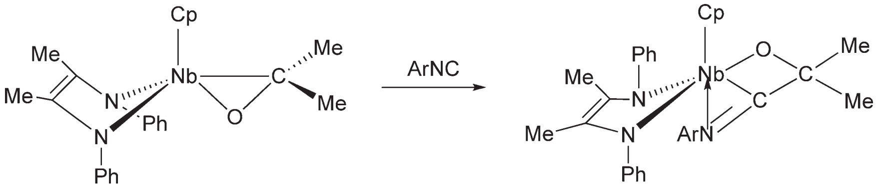


Figure 3

Bridging bis(alkylidyne)niobium complexes show distinct reactivity patterns that lead to a variety of terminally substituted 1,3-dimetallacyclobutadienes. These processes are discussed in Section 5.02.4.2 (Alkylidyne complexes).[139,141,48] Reactions involving $[Cp_2NbCl]_2$ and $[Li\{\eta^3\text{-}N(SiMe_3)C(^tBu)\text{–}CH_2\}]_3$ that give 1-azaallyl complexes of niobium with a four-membered metallacyclic moiety have been described.[66]

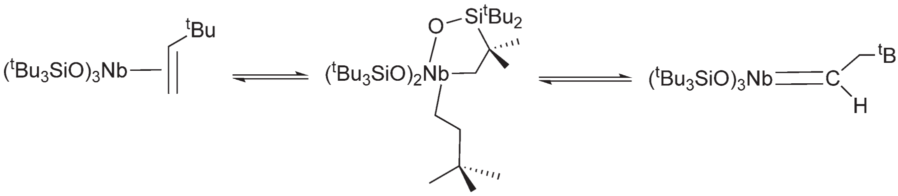
Niobium alkyne complexes have provided convenient routes to study carbon monoxide and isocyanide coupling reactions via metallacyclic intermediates.[198] For example, reactions of dialkyl alkyne derivatives $CpNbR_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ with isocyanides led initially to azametallacyclopropane intermediates, but these species are gradually transformed into different imido niobacycle complexes. The rearrangement of azametallacyclopropanes to the final complexes probably takes place through imido niobacyclobutene intermediates (Figure 3).[160] Furthermore, the insertion reaction of isocyanide into oxaniobacyclopropane, $CpNb\{\eta^2\text{-}(O)CMe_2\}$(Me,Ph–DAD) (Me,Ph–DAD = 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene), affords a complex with a four-membered metallacyclic moiety, namely, $CpNb\{\eta^2\text{-}(O)CMe_2\text{–}(CNAr)\}$(Me,Ph–DAD) (Equation (21)).[199]

 (21)

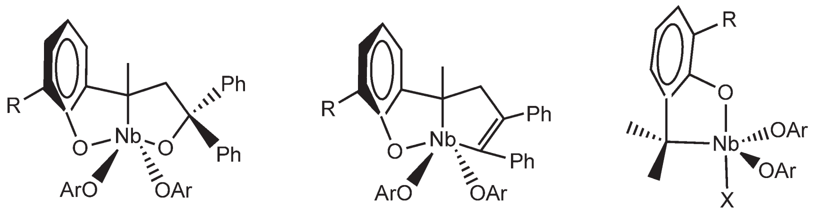
Thermolysis of $Cp_2NbH(HPPh_2)$ leads to the formation of the metallacycle $Cp_2Nb(HPPhC_6H_4\text{–})$ by loss of dihydrogen.[111]

5.02.6.2 Five-membered Metallacycles

Very few new five-membered metallacyclic niobium complexes have been described, but some of these species are of considerable importance as intermediates in deoxygenation studies.[200] Deoxygenation of $(^tBu_3SiO)_3W(NO)$ with $(^tBu_3SiO)_3Nb$(4-picoline) leads to the formation of a mixture of products that contains the cyclometallated niobium product $H(^tBu_3SiO)_2\{NbOSi^tBu_2CMe_2CH_2\}$ (two isomers). The same complex has been observed in the deoxygenation of R_3PO (R = Me, Ph) with $(^tBu_3SiO)_3Nb$(4-picoline).[201] In addition, a five-membered metallacyclic species was observed as an intermediate in the thermolysis of $(^tBu_3SiO)_3Nb(\eta^2\text{-}C_2H_3{}^tBu)$ to the alkylidene $(^tBu_3SiO)_3Nb({=}CHCH_2{}^tBu)$ (Equation (22)).[143]

 (22)

In complexes of the type $Nb(OC_6H_3{}^iPr\text{-}\eta^2\text{-}CMe{=}CH_2)(OC_6H_3{}^iPr_2\text{-}2,6)_2(L)_x$, which contain both five-membered metallacycle and niobacyclopropane moieties,[142] the niobacyclopropane ring undergoes ring expansion (coupling) with a variety of unsaturated substrates, including benzophenone and PhC≡CPh. Furthermore, addition of



Scheme 9

2,6-diisopropylphenol or aniline to the starting complexes leads to the corresponding aryloxide and phenylamido derivatives containing a five-membered metallacycle, which is formed by protonation of the η^2-$\mathrm{CMe{=}CH_2}$ methylene carbon atom of the metallacyclopropane ring (Scheme 9).[142]

Imidoniobacyclopent-3-enes have been isolated from niobacyclobutene intermediates through the migration of hydrogen.[199] In the same way, the insertion of 2 equiv. of isocyanide into oxaniobacyclopropane $\mathrm{CpNb\{\eta^2\text{-}(O)CMe_2\}(Me,Ph\text{–}DAD)}$ affords a complex with a five-membered metallacycle moiety, $\mathrm{CpNb\{\eta^2\text{-}(O)CMe_2\text{–}(CNAr)_2\}(Me,Ph\text{–}DAD)}$.[199] Treatment of $\mathrm{TpNbCl_2(\eta^2\text{-}PhC{\equiv}CR)}$ with 1 equiv. of allylmagnesium chloride at low temperature leads to niobacycle complexes $\mathrm{TpClNb\{{=}C(Ph)C(R)C(H)CH(CH_3)\}}$; these compounds result from the coupling of the four-electron-donor alkyne with a rearranged allyl group, a process that involves a 1,3-hydrogen shift.[202] Addition of 2 equiv. of ethylmagnesium chloride to $\mathrm{TpNbCl_2(\eta^2\text{-}PhC{\equiv}CCH_3)}$ gives a five-membered niobacycle, $\mathrm{Tp(CH_2CH_3)Nb\{{=}C(Ph)C(CH_3)CHCH_2\}}$.[161] Protonation of $\mathrm{TpNb(CO)(\eta^2\text{-}PhC{\equiv}CCH_3)(NCPh)}$ at low temperature with tetrafluoroboric acid leads to the azaniobacycle $\mathrm{TpFNb\{{=}C(Ph)C(CH_3)CPhNH\}}$, which is formed in a regioselective nitrile/alkyne coupling reaction.[170] Similarly, protonation of $\mathrm{TpNb(CO)(\eta^2\text{-}PhC{\equiv}CCH_3)_2}$ leads to the oxaniobacycle $\mathrm{TpFNb\{{=}C(Ph)C(CH_3)CO(CCH_3{=}CPhH)\}}$.[170]

5.02.6.3 Other Metallacycles

Reaction of dialkyl alkyne derivatives, $\mathrm{CpNb(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)R_2}$, with isocyanides leads, in the first step, to azametallacyclopropane species, similar to those discussed above for four- and five-membered metallacycles. These species are gradually transformed into different imido metallacycle niobium complexes that lead to different coupling products depending on the nature of R. When $\mathrm{R = CH_2CMe_3}$, initial formation of the unstable η^2-iminoacyl complex is followed by spontaneous conversion into the imido niobacyclohept-2-ene complex $\mathrm{CpNb(NAr)\{\eta^2\text{-}CH_2CMe_2CH_2CH(CH_2CMe_3)C(SiMe_3){=}C(SiMe_3)\}}$.[199] When $\mathrm{R = CH_2SiMe_3}$, an imido niobacyclopropane(vinyl), $\mathrm{CpNb(NAr)\{\eta^4\text{-}CH(SiMe_3)C(SiMe_3)C(CH_2SiMe_3){=}CH(SiMe_3)\}}$, is isolated.[199]

5.02.7 Complexes with –Ene and –Enyl Ligands

5.02.7.1 η^3-Complexes

The relatively few η^3-complexes of niobium are outlined in Table 10. The chemistry of η^3-allyl complexes of transition metals is well documented.[203] However, there is only a relatively small number of η^3-allyl complexes of niobium despite the fact that the synthesis of the first complex, $\mathrm{Cp_2Nb(\eta^3\text{-}C_3H_5)}$, was reported in 1970.[204] The

Table 10 η^3-Complexes of niobium

Compound	*Comments*	*References*
$\mathrm{\{\eta^5\text{-}\sigma\text{-}(C_5H_4)(CH_2)_3N\}Nb\{\eta^3\text{-}CH_2C(CH_3)CH_2\}_2}$	$\mathrm{Cp = C_5H_4}$	205
$\mathrm{Cp_2Nb\{\eta^3\text{-}CH_2C(R)CH_2\}}$	$\mathrm{Cp = C_5H_4SiMe_3}$, R = H, Me	66
$\mathrm{Cp_2Nb\{\eta^3\text{-}CH(R)CHCH(R^1)\}}$	$\mathrm{Cp = C_5H_4SiMe_3}$, $\mathrm{R = R^1 = SiMe_2{}^tBu}$ (X-ray), R = H, $\mathrm{R^1 = SiPh_3}$	79
$\mathrm{\{\eta^5{:}\eta^3Cp\text{-}C(CH_3)_2\text{-}R\}Nb\{N(CH_3)_2\}\text{-}({=}N\text{-}{}^iPr_2C_6H_3\text{-}2,6)}$	$\mathrm{Cp = C_5H_4}$, $\mathrm{R = \eta^3\text{-}CHCHCH_2}$; $\mathrm{Cp = C_5H_4}$, $\mathrm{R = \eta^3\text{-}CH\text{-}Ph}$	206
$\mathrm{Cp_2Nb\{\eta^3\text{-}N(SiMe_3)C({}^tBu)CH_2\}}$	$\mathrm{Cp = C_5H_4SiMe_3}$	66
$\mathrm{CpNb(\eta^4\text{-}C_4H_6)\ (\eta^3\text{-}C_8H_8)}$	$\mathrm{Cp = C_5Me_5}$ (X-ray)	207

most common method to obtain η^3-allyl niobium complexes is by reaction of halide-containing niobium complexes with allyl Grignard reagents. For example, the addition of (2-methylallyl)MgCl to {η^5-σ-(C$_5$H$_4$)(CH$_2$)$_3$N}NbCl$_2$ gave {η^5-σ-(C$_5$H$_4$)(CH$_2$)$_3$N}Nb{η^3-CH$_2$C(CH$_3$)CH$_2$}$_2$.[205] Furthermore, the allyl complexes Cp$_2$Nb{η^3-CH$_2$C(R)CH$_2$} were prepared by the reaction between [Cp$_2$NbCl]$_2$ and the corresponding Grignard reagents.[66] In addition, η^3-allyl imido amido niobium complexes were obtained by an uncommon intramolecular C–H activation process that involved heating {Cp–C(CH$_3$)$_2$–R}Nb{N(CH$_3$)$_2$}(═N-^{i}Pr$_2$C$_6$H$_3$-2,6).[206] The first example of a 1-azaallyl complex of niobium was synthesized by the reaction of [Cp$_2$NbCl]$_2$ and [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$.[66]

Some of the earliest examples of η^3-complexes of niobium were unusual cyclooctatetraene species that are highly fluxional in solution; for example, treatment of CpNb(η^4-C$_4$H$_6$)(CH$_3$)$_2$ with 1 equiv. of cyclooctatetraene at 50 °C resulted in the formation of CpNb(η^4-C$_4$H$_6$)(η^3-C$_8$H$_8$) through a reductive elimination process.[207] The cyclooctatetraene ligand was coordinated to the niobium center in a dynamic mode in solution, but was found to be bound in an η^3-fashion in the crystal.[207]

5.02.7.2 η^4-Complexes

The η^4-ligands are not particularly common in niobium complexes, and, in this respect, their chemistry has mainly focused on η^4-butadiene complexes or similar complexes with 1,3-diene ligands. Interest in diene complexes of group 5 (Nb, Ta) metals stems from their unique catalytic ability, which is similar to that of group 4 metallocene complexes. Such systems are useful catalysts in the polymerization of ethylene to yield polyethylene with extremely narrow polydispersity, and the stereoselective ROMP of norbornene.[208–210] The formation and reactivity of niobium complexes with η^4-ligands are considered in this section and the compounds are summarized in Table 11.

5.02.7.2.1 η^4-Butadiene complexes

The most important and the most widely studied η^4-complexes of niobium are the η-butadiene species, which are prepared by methods that were reviewed in great detail in COMC (1995). For example, CpNb(η^4-2,3-Me$_2$C$_4$H$_6$)Cl$_2$[208,211] is prepared by reaction of CpNbCl$_4$ with 1 equiv. of the appropriate allylMgCl (2,3-dimethylbut-2-enyl Grignard reagent).[212] Furthermore, CpNb(η^4-C$_4$H$_6$)(CH$_3$)$_2$[131] is prepared by the reaction of CpNb(η^4-C$_4$H$_6$)Cl$_2$[212] with 2 equiv. of MeMgI. This dimethyl complex has been used as a starting material to yield

Table 11 η^4-Complexes of niobium

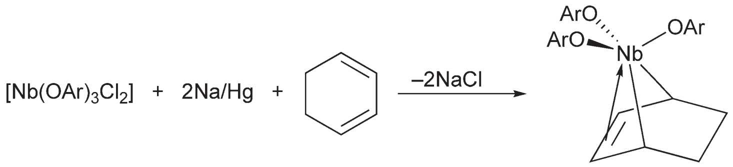
Compound	*Comments*	*References*
CpNb(η^4-2,3-Me$_2$C$_4$H$_4$)Cl$_2$	Cp = C$_5$M$_5$Me	208,211
CpNb(η^4-C$_4$H$_6$)(CH$_3$)$_2$	Cp = C$_5$M$_5$Me	131
Cp Nb(η^4-C$_4$H$_6$)(C$_8$H$_8$)	Cp = C$_5$M$_5$Me, X-ray	207
CpNb(η^4-isoprene) Cl$_2$	Cp = C$_5$M$_5$Me	40
CpNb{*o*-(CH$_2$)$_2$C$_6$H$_4$}Cl$_2$	Cp = C$_5$M$_5$Me, X-ray	207
[ML$_n$][Nb(1,4-η^4-anthracene)$_3$]	ML$_n$ = K(THF)$_x$	213
	ML$_n$ = K(18-crown-6)(THF), X-ray	
	ML$_n$ = Na(triglyme)$_2$	
[K(18-crown-6)(THF)][Nb(1,4-η^4-anthracene)$_2${P(OMe)$_3$}$_2$]	X-ray	213
Nb(OC$_6$H$_3$Ph-η^4-C$_6$H$_7$)(OC$_6$H$_3$Ph$_2$-2,6)$_2$	X-ray	214
Nb(OC$_6$H$_2$Ph$_2$-η^4-C$_6$H$_7$)(OC$_6$H$_2$Ph$_3$-2,4,6)$_2$		214
Nb(OC$_6$H$_3^i$Pr$_2$-2,6)$_2$Cl(η^4-C$_6$H$_8$)	X-ray	215,216
Nb(OC$_6$H$_2$Pr$^i{}_2$-2,6)$_3$(η^4-C$_6$H$_8$)	X-ray	215,216
CpNb{η^4-C$_6$H$_4$(NSiMe$_3$)$_2$}Cl$_2$	Cp = C$_5$H$_3$(SiMe$_3$)$_2$	217
CpNb (η^4-*p*-MeOC$_6$H$_4$-DAD)Cl$_2$	Cp = C$_5$H$_5$, C$_5$Me$_5$ (X-ray)	218
CpNb(CH$_2$Ph)$_2$(η^4-*p*-MeOC$_6$H$_4$-DAD)	Cp = C$_5$Me$_5$	218
CpNb(═CHPh)(η^4-*p*-MeOC$_6$H$_4$-DAD)	Cp = C$_5$Me$_5$	218
CpNb(η^2-N,N′-*p*-MeOC$_6$H$_4$-DAD)(η^4-1,3-butadiene)	Cp = C$_5$H$_5$, C$_5$Me$_5$ (X-ray)	218
CpNb (η^4-Me, Ph-DAD)Cl$_2$	Cp = C$_5$H$_4$SiMe$_3$	199
CpNb{η^4-O(R)C═C(R)O}Cl$_2$	Cp = C$_5$H$_4$SiMe$_3$, R = Me, Ph	199
CpNbR$_2$(η^4-Me, Ph-DAD)	Cp = C$_5$H$_4$SiMe$_3$, R = Me, CH$_2$SiMe$_3$, CH$_2$Ph	199

different complexes such as the methoxy, carbene, and metallacyclobutane derivatives reviewed in other sections.[131] Treatment of $CpNb(\eta^4\text{-}C_4H_6)(CH_3)_2$ with 1 equiv. of cyclooctatetraene results in the formation of $CpNb(\eta^4\text{-}C_4H_6)(C_8H_8)$.[207] The complex $CpNb(\eta^4\text{-isoprene})Cl_2$ can be prepared by the above method, or by reduction of $CpNbCl_4$ with sodium amalgam in the presence of isoprene.[40]

5.02.7.2.2 Other η^4-ligands

In recent years, the aforementioned interest in diene complexes of group 5 metals has led to investigations in the electronic and steric effects of dienes such as *o*-xylylene and anthracene as alternative η^4-1,3-diene ligands with the appropriate $p\pi$-conjugation. Thus, reaction of $CpNbCl_4$ with *o*-$C_6H_4(CH_2MgCl)_2$ gave an *o*-xylylene complex of niobium, $CpNb\{o\text{-}(CH_2)_2C_6H_4\}Cl_2$.[207] The first tris(arene) niobium complex, $[ML_n][Nb(1,4\text{-}\eta^4\text{-anthracene})_3]$, was obtained by reduction of $NbCl_4(THF)_2$ with excess potassium anthracene.[213] Furthermore, a variety of acceptor ligands, including organophosphanes, phosphates, polyenes, and other systems also combines with $[Nb(1,4\text{-}\eta^4\text{-anthracene})_3]^-$ to displace one or more anthracene groups. For example, treatment of $[Nb(1,4\text{-}\eta^4\text{-anthracene})_3]^-$ with an excess of COT and trimethylphosphite led to a rapid reaction that gave a mixture of compounds from which the unprecedented complex $[Nb(1,4\text{-}\eta^4\text{-anthracene})_2\{P(OMe)_3\}_2]^-$ was isolated.[213]

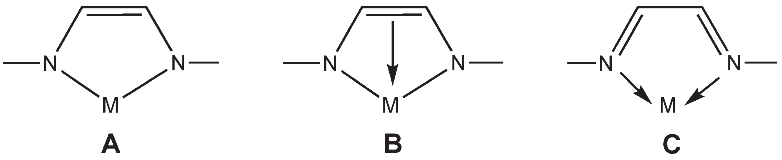
Only a few transition metal systems are able to carry out the homogeneous hydrogenation of arene rings. Studies of the organometallic chemistry of early transition metal aryloxide compounds have shown that mixed-hydrido/aryl oxide derivatives of niobium are able to carry out the hydrogenation of a variety of arene substrates, with an η^4-cyclohexadiene niobium complex isolated as an intermediate in the pathway of the hydrogenation reactions.[214] For example, reduction of $Nb(OAr)_3Cl_2$ by sodium amalgam under an atmosphere of H_2 leads to the η^4-cyclohexadiene complexes $Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2\text{-}2,6)_2$ and $Nb(OC_6H_2Ph_2\text{-}\eta^4\text{-}C_6H_7)(OC_6H_2Ph_3\text{-}2,4,6)_2$,[214] which are formed by stoichiometric intramolecular hydrogenation of one of the *o*-phenyl substituents of a 2,6-diphenylphenoxide ligand attached to niobium. An alternative synthetic route to η^4-cyclohexadiene derivatives of niobium involves reduction of mixed-chloro/aryl oxides in the presence of 1,3-cyclohexadiene (Equation (23)).[215,216]



(23)

In recent years, various 1,4-diaza-1,3-butadiene (DAD) complexes of niobium have been isolated. The DAD ligand is known to exhibit a unique coordination feature in that it binds to the metal center in several modes (Scheme 10), with the σ^2,π-mode **B** being similar to butadiene in terms of bonding capabilities.

Thus, reaction of $CpNbCl_4$ with the lithium salt $Li_2[C_6H_4(NSiMe_3)_2\text{-}1,2]$ gives the complex $CpNb\{\eta^4\text{-}C_6H_4(NSiMe_3)_2\}Cl_2$.[217] In a similar way, the reaction with the dilithium salt of 1,4-bis(*p*-methoxyphenyl)-1,4-diaza-1,3-butadiene (*p*-$MeOC_6H_4$-DAD) led to the formation of the corresponding 1,4-diaza-1,3-butadiene niobium complexes $CpNb(\eta^4\text{-}p\text{-}MeOC_6H_4\text{-DAD})Cl_2$,[218] and subsequent reaction of these complexes with $Mg(CH_2Ph)_2$ gave the corresponding dibenzyl complexes. The dibenzyl complexes are thermally stable in the solid state, but in solution these complexes gradually decompose to give the corresponding benzylidene complexes.[218] The treatment of $CpNb(\eta^4\text{-}p\text{-}MeOC_6H_4\text{-DAD})Cl_2$ with excess butadiene–magnesium adduct afforded mixed-ligand DAD–butadiene complexes $CpNb(\eta^2\text{-}N,N'\text{-}p\text{-}MeOC_6H_4\text{-DAD})(\eta^4\text{-}1,3\text{-butadiene})$.[218] Similar complexes can be obtained by a ligand-exchange reaction between $CpNbCl_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ and 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene (Me,Ph–DAD) or diketones R–CO–CO–R (R = Me, Ph).[199]



Scheme 10

5.02.7.3 η^5-Complexes

The different types of η^5-cyclopentadienyl complexes without other carbon-bonded ligands are considered in this section. Many complexes containing cyclopentadienyl ligands have been described in previous sections. In order to clarify the discussion, the complexes have been divided into mono- and bis-cyclopentadienyl derivatives.

5.02.7.3.1 Monocyclopentadienyl complexes

Perhaps the most useful starting materials for the preparation of monocyclopentadienyl niobium complexes are the d^0-species $CpNbX_4$. Efficient synthetic methods to prepare this class of complex were described in COMC (1995), and are based on the use of different types of non-reducing tin or silicon cyclopentadienyl reagents with NbX_5 derivatives. In the last decade, a few examples of new $CpNbX_4$ have been reported. For example, the reaction of $NbCl_5$ with 1-(SiClMeX)-1-($SiMe_3$)C_5H_4 gave (η^5-C_5H_4(SiClMeX))$NbCl_4$.[64] An interesting half-sandwich boryl-cyclopentadienyl niobium complex has also been prepared by reacting $B(C_5H_4SiMe_3)(C_6F_5)_2$ with $NbCl_5$.[220]

Half-sandwich imido complexes of the type $CpNb(NR)Cl_2$ have continued to be widely studied in recent years due to their relationship with bent metallocenes of group 4 metals. The concept of the cyclopentadienyl imido ligand analogy[221,222] was introduced to explain surprising similarities in the structural features and reactivity of these two classes of complex. Variation of the ancillary substituent R at the imido function offers a way to fine-tune the steric demand and electronic properties of these ligands. Several examples of this type of complex with different classes of substituted cyclopentadienyl rings have been prepared. In most cases the reaction pattern consists of the interaction between the appropriate precursor $CpNbCl_4$ with (i) a lithium amide LiNHR in the presence of a base such as an amine NR_3, (ii) a primary amine RNH_2 with or without a base, or (iii) a silyl amide $NHRSiMe_3$. The use of an analogous synthetic route led to complexes containing both imido and amido ligands, namely, $CpNb(NR)(NHR^1)_xCl_{2-x}$. Green *et al.* used some of these methods to perform a systematic study, and, during the course of this work, interesting structural parameters and reactivity patterns of a large family of these complexes as well as niobocenes and *ansa*-niobocenes (see below) were found.[61,62,223,224] Herrmann *et al.* prepared a series of complexes $CpNb(NR)(NMe_2)_2$ and *ansa*-niobocenes (see below) through a general process that involved deprotonation by an amido ligand from the parent compound $Nb(NR)(NMe_2)_3$ of the appropriate cyclopentadiene ring.[206,225,226] The catalytic activity in olefin-polymerization processes was tested for some of these types of complex. For example, $CpNb(N(C_6H_4{}^tBu\text{-}2))Cl_2$ was tested as a procatalyst for the polymerization of ethylene in combination with diethylaluminium chloride or methylaluminoxane (MAO) co-catalyts, with relatively low activities found under all test conditions.[60]

A few families of related complexes containing scorpionate ligands have also been described. Extended Hückel molecular-orbital (EHMO) calculations support the statement that monoanionic six-electron N-donor ligands, such as Tp (tris(pyrazol-1-yl)borate), possess similar σ,2π-bonding interactions with metal *d*-orbitals as an η^5-cyclopentadienyl ring.[230] For example, the tetrachloro species (κ^3-bdmpzx)$NbCl_4$, bdmpzx = heteroscorpionate NNO-donor ligand, were prepared from $NbCl_5$ and the appropriate heteroscorpionate lithium salt.[231] Different classes of complexes with oxo, alkoxide, and imido ancillary ligands are well known.

5.02.7.3.2 Bis-cyclopentadienyl complexes

Niobocene complexes of this type have been extensively studied, and will be considered on the basis of the nature of the ancillary ligand(s) (see Table 12).

5.02.7.3.2.(i) Halide complexes

Niobocene dihalides Cp_2NbX_2 represent a class of widely investigated organometallic species, and they have been used in metathetical reactions as well as in chemical or electrochemical reduction processes to give a wide variety of d^1-Cp_2NbY_2 and d^2-Cp_2NbXL, L = π-acid ligand, derivatives, respectively. This type of chemistry was reviewed in depth in COMC (1995). New examples of dihalide species, especially with functionalized cyclopentadienyl rings, have appeared in recent years. In some cases, the synthetic procedure involves the reduction of a d^0-precursor. For example, the reduction of $NbCl_5$ with $NaBH_4$ in the presence of (C_5Me_4Et)Li gave (η^5-C_5Me_4Et)$_2NbCl_2$. An evaluation of the reduction chemistry of this complex in comparison to lower substituted niobocene derivatives was also carried out.[235] Cationic d^0-species $[Cp_2NbX_2]^+$ have been obtained in an oxidation process from d^1-precursors. For example, the oxidation of (η^5-$C_5H_4{}^tBu$)$_2NbCl_2$ with $CuCl_2$ afforded the species [(η^5-$C_5H_4{}^tBu$)$_2NbCl_2$]($CuCl_2$).[237]

Table 12 η^5-Cyclopentadienyl complexes of niobium

Compound	*Comments*	*References*
Monocyclopentadienyl and related		
$CpNbCl_4$	$Cp = C_5H_4(SiClMeX)$; $X = Me, Ph$	64
$[(C_5H_4)_2(Me_2SiOSiMe_2)(NbCl_2)_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$	X-ray	64
$CpNbCl_4$	$Cp = C_5H_4SiMe_2(CH_2CH{=}CH_2)$	219
$CpNbCl_4$	$Cp = C_5H_4B(C_6F_5)_2$	220
$CpNbCl_4{\cdot}py$	$Cp = C_5H_4B(C_6F_5)_2$ (X-ray)	220
$CpNb(NO^tBu)Cl_2$	$Cp = C_5H_5$ (X-ray), C_5H_4Me	223
$CpNb(NNMeR^1)X_2$	$Cp = C_5H_5$, C_5H_4Me; $NNMeR^1$ = hydrazido ligand; $R^1 = Me, Ph$; $X = Cl$ (X-ray), O^tBu, NMe_2	224
$CpNb(NNMe_2)Cl_2(PR_3)$	$Cp = C_5H_5$, C_5H_4Me; $R = OMe$ (X-ray), Me	224
$[CpNb(NNMe_2)Cl(PMe_3)_2]PF_6$	$Cp = C_5H_4Me$	224
$CpNb(NR)(NH^tBu)X$	$Cp = C_5H_5$; $R = {}^tBu$, $X = Cl$ (X-ray); $R = {}^tBu$, $X = NH^tBu$; $R = C_6H_3{}^iPr^2,2,6$, $X = Cl$ (X-ray); $R = {}^tBu$, $X = NEt_2$	61
$CpNb\{N(C_6H_3Me_2,2,6)\}XY$	$Cp = C_5H_5$; $X = Y = Cl$ (X-ray), $X = Cl$, $Y = NH(C_6H_3Me_2,2,6)$; $X = Y = NH(C_6H_3Me_2,2,6)$ (X-ray)	62
$CpNb(NR)(NMe_2)_2$	$Cp = C_5H_5$; $C_5H_4R^1$, $R^1 = C_3H_5, C_6H_5, CH_2C_6H_5, CMe_2C_9H_7$; $R = C_6H_3^iPr_2,2,6$	206, 225, 226
$CpNb(NR)Cl_2$	$Cp = C_5R^1{}_5$, $R^1 = H,Me$, $R = {}^tBu$; $Cp = C_5Me_5$, $R = SiMe_3$	57, 227
$CpNb(NR)Cl_2$	$Cp = C_5H_5$, $C_5H_4SiMe_3$; $R = {}^tBu$, C_6H_4Me-4; prep: from $Nb(NR)Cl_3(py)_2$ and NaC_5H_5	228
$CpNb(NR)Cl_2$	$Cp = C_5H_4(SiClMeX)$; $X = Me,Ph$	64
$CpNb(NR)Cl_2$	$Cp = C_5H_4SiMe_3$; $R = C_6H_3Me_2,2,6$; $C_6H_3{}^iPr_2,2,6$	59
$CpNb(NR)ClX$	$Cp = C_5H_4SiMe_2Cl$, $R = {}^tBu$, $X = Cl$; $C_5H_4SiMe_2(NH^tBu)$, $R = {}^tBu$, $X = Cl$, (X-ray), NH^tBu	188
$[(CpNbCl_2)_2(\mu\text{-}1,i\text{-}NC_6H_4N)]$	$Cp = C_5H_4SiMe_3$, $i = 4,3,2$; $Cp = C_5Me_5$, $i = 4,3$	229
$(\kappa^3\text{-bdmpzx})NbCl_4$	bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate; bdmpze = bis(3,5-dimethylpyrazol-1-yl)ethoxide	231
$(\kappa^3\text{-bdmpzx})Nb(O)Cl_2$	bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate; bdmpze = bis(3,5-dimethylpyrazol-1-yl)ethoxide (X-ray)	231
$(\kappa^3\text{-bdmpza})Nb(OR)Cl_3$	bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate; $R = Me, Et, {}^iPr, {}^tBu$	231
$TpNb(O)ClX$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl)borate; $X = Cl$, $OR(Me, Et)$	232
$[(TpNb(O)Cl)_2(\mu\text{-}O)]$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl)borate (X-ray)	232
$TpNb(O)(NHSiMe_3)_2$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl)borate (X-ray)	232
$TpNb(NR)Cl_2$	Tp = hydridotris(3,5-dimethylpyrazol-1-yl)borate; $R = {}^tBu,SiMe_3$	233, 227
$(\kappa^3\text{-bdmpzx})Nb(NR)Cl_2$	bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate; bdmpze = bis(3,5-dimethylpyrazol-1-yl)ethoxide; $R = {}^tBu$, C_6H_4Me, $C_6H_3{}^iPr^2,2,6$	234
Bis-cyclopentadienyl and related halide complexes		
Cp_2NbX_2	$Cp = C_5Me_4Et$, $X = Cl$ (X-ray); EPR ($g = 1.999$, $A = 115.4$ G); $X = F$; EPR($g = 1.956$, $A = 114.2$ G)	235
$CpCp'NbCl_2$	$Cp = C_5H_5$, $Cp' = C_5H_4BCl(C_6F_5)_2$; $Cp = C_5H_4SiMe_3$, $Cp' = C_5H_4BCl(C_6F_5)_2$ (X-ray); zwitterionic structures	220
$CpCp'NbCl_2$	$Cp = C_5Me_5$; $Cp' = C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$	236
$CpCp'NbCl_2$	$Cp = C_5H_5$, C_5Me_5;$Cp' = C_5H_4SiMe_2(CH_2CH{=}CH_2)$	219
$[Cp_2NbXY]Z$	$Cp = C_5H_4{}^tBu$; $X = Y = Cl$, $Z = CuCl_2$ (X-ray); $X = Cl$, $Y = F$, $Z = BF_4$ (X-ray)	237
$[Cp_2NbXY][PF_6]$	$Cp = C_5Me_4Et$; $X = Y = F$ (X-ray); $X = Y = Cl$; $X = Cl$, $Y = (Cl, F)$ (X-ray)	235
$[Cp_2NbCl_2]Z$	$Cp = C_5H_5$; $Z = UF_6$; $Z = WF_6$	238, 239
$[\{Cp_2NbCl_2\}^+]_4[WF_6]^{2-}[WCl_6]^{2-}$	$Cp = C_5H_5$; (X-ray)	239
$[(C_5H_4)\ Si\ Me_2(C_5H_4)]NbCl_2$	EPR($g = 2.0034$, $A = 100.0$ G)	179
$[(C_5H_4)CMe_2(C_5H_4)]NbCl_2$	EPR($g = 1.992$, $A = 90.5$ G)	240
$[(C_5H_3SiMe_3)SiMe_2(C_5H_3SiMe_3)]NbCl_2$	EPR($g = 1.9847$, $A = 104.3$ G); mixture of *meso* and *rac*-isomers	70
$[X(C_5H_3Y)_2]NbCl_2$	$X = CEt_2$, $C(C_5H_{10})$, C_2Me_4, $Y = H$; $X = C_2Me_4$, $Y = {}^tBu$	241

(*Continued*)

Table 12 (Continued)

Compound	*Comments*	*References*
$[(C_5Me_4)SiMe_2(C_5H_3R)]NbCl_2$	R = H, Me, $SiMe_3{}^iPr$, PPh_2, oxidation and reduction potentials have been measured	180
$[(C_5H_3\text{-}3R)SiMe_2(C_5H_3\text{-}3R^1)]NbCl_2$	R = H, $R^1 = CHMe_2$, CMe_3; $R = R^1 = CMe_3$	148
Oxygen and sulfur donor complexes		
$Cp_2Nb(X)Cl$	Cp = (R,R)-(+)-bis[2,3-(1,1′-binaphthyl-2,2′-dimethyl)cyclopenta-2,4-dienyl], indenyl; X = O, O–O, catalysts enantioselective epoxidation of olefins	243
$Cp_2Nb(O)X$	$Cp = C_5Me_5$; X = H, Cl, OH, OMe	244, 245
$[Cp_2Nb(OH)F][BF_4]$	$Cp = C_5Me_5$; (X-ray)	244
$Cp_2Nb(O\text{-}O)Cl$	$Cp = C_5H_4SiMe_3$	246
$[Cp_2NbCl]_2(\mu\text{-}O)$	$Cp = C_5H_4SiMe_3$	246
$[Cp_2Nb(OR)Cl][BF_4]$	$Cp = C_5H_4SiMe_3$; $R = CH_2CPh_3$ (X-ray), Me; prep: reaction of $Cp_2Nb(\eta^2\text{-}CH_2O)Cl$ with $(Ph_3C)BF_4$ or $HBF_4{\cdot}OEt_2$	247
$Cp_2Nb(O{\cdot}BF_3)Cl$	$Cp = C_5H_4SiMe_3$ (X-ray)	247
$Cp_2Nb(S_2)X$	$Cp = C_5Me_5$, X = H (X-ray), SH; $Cp = C_5Me_4Et$, X = I	248, 249
$Cp_2Nb(S)(SH)$	$Cp = C_5Me_5$	248
$Cp_3Nb_3S_x$	$Cp = C_5Me_5$, $x = 7,12$; $Cp = C_5Me_4Et$, $x = 7$ (X-ray), 12	248, 249
$[Cp_2NbS_2]_2M$	$Cp = C_5Me_5$, M = Fe (X-ray), Co; $Cp = C_5Me_4Et$, M = Co	250
$Cp_2Nb(S_2)H{\cdot}Cr(CO)_5$	$Cp = C_5Me_4Et$	251
$Cp_2Nb(Se_2H)$	$Cp = C_5Me_{5,}$, C_5Me_4Et	252
$Cp_2Nb(O)(\kappa^1\text{-}O_2CH)$	$Cp = C_5H_4Me$, R = H	253
$Cp_2Nb(\kappa^2\text{-}X_2CR)$	$Cp = C_5H_4SiMe_3$, R = H, Me, X = O; R = H, X = S	254, 121
$Cp_2Nb(\kappa^1\text{-}O_2CH)(L)$	$Cp = C_5H_4SiMe_3$, R = H, $L = CS_2$, CO, $CNC_6H_3Me_2\text{-}2,6$; R = Me, $L = CS_2$,SCNPh, $PhNC{\equiv}CPhEt$, $MeO_2CC{\equiv}CCO_2Me$, CN^tBu,CO	254
$Cp_2Nb(\kappa^2\text{-}MeCOCHCOMe)$	$Cp = C_5H_4SiMe_3$	254
$Cp_2Nb(\kappa^1\text{-}XC(H)NPh)L$	$Cp = C_5H_4SiMe_3$, X = O, S, L = CO, $CNC_6H_3Me_2\text{-}2,6$,CNCy	255
$Cp_2Nb(\kappa^1\text{-}O_2CCF_3)L$	$Cp = C_5H_4SiMe_3$, L = CO, $CNC_6H_3Me_2\text{-}2,6$, CNCy	255
$Cp_2Nb(\kappa^2\text{-}OC(H)NPh)$	$Cp = C_5H_4SiMe_3$	255
$Cp_2Nb(\kappa^1\text{-}S_2CH)L$	$Cp = C_5H_4SiMe_3$, L = CO, $PHPh_2$	121, 116
$Cp_2Nb(\kappa^2\text{-}OOC(C_6H_3(NH_2)_2))$	$Cp = C_5H_4SiMe_3$	256
$Cp_2Nb(\kappa^1\text{-}OOC(C_6H_3(NH_2)_2))L$	$Cp = C_5H_4SiMe_3$, $L = CNC_6H_3Me_2\text{-}2,6$	256
$Cp_2Nb(\kappa^2\text{-}OCOOCO)$	$Cp = C_5H_4SiMe_3$	257
$Cp_2Nb(\kappa^2\text{-}OCOCH_2OCO)$	$Cp = C_5H_4SiMe_3$	257
$Cp_2Nb(\kappa^2\text{-}O(C)OO)^-$	$Cp = C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$	258
$Cp_2Nb(\kappa^2\text{-}O(C)OO)$	$Cp = C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$ (ESR spectrum; $g = 1.977$, $A = 54$ G)	258
$Cp_2Nb(S(R)S)$	$Cp = C_5H_5$; S(R)S = dmit(1,3-dithiol-2-thione-4,5-dithiolate and related(dmio,dddt)	259
$[Cp_2Nb(S(R)S)]I$	$Cp = C_5H_5$	259
$Cp_2Nb(\text{dithiolene})$	$Cp = C_5H_4{}^tBu$,$C_5H_4SiMe_3$; dithiolene = $C_3S_5{}^{2-}$ (X-ray), $C_3OS_4{}^{2-}$, dddt^{2-}	260
$Cp_2Nb(\kappa^2\text{-}(N,S \text{ or } N,O)L)$	$Cp = C_5H_4SiMe_3$; $L = S(C_5H_4N)$, $S(C_4H_3N_2)$, $S(C_6H_7N_2)$ (X-ray) $O(C_5H_4N)$, $O(C_6H_6N)$, $O(C_6H_7N_2)$, $O(C_9H_6N)$, $HN(C_5H_4N)$, $NH(C_7H_8N)$, $NH(C_6H_7N_2)$	261
$(\eta^5\text{-}C_5H_4R)(\eta^3\text{-}C_5H_4R)Nb(\kappa^2\text{-}ArNO)X_2$	R = H, $SiMe_3$; X = Cl, Br; Ar = Ph, $o\text{-}CH_3C_6H_4$, $p\text{-}(CH_3)_2NC_6H_4$; paramagnetic species	262
Nitrogen donor complexes		
$(C_5H_4(CH_2)_3N)(C_5H_5)Nb(\eta^1\text{-}C_5H_5)$		205
$[(C_5H_4)CMe_2(\eta^1\text{-}C_5H_4)]Nb(N^tBu)(NH^tBu)$		61
$Cp_2Nb(NNMe_2)X$	$Cp = C_5H_5$, C_5H_4Me (X-ray), X = Cl; $X = \eta^1\text{-}C_5H_4R$, R = H, Me	263
$[Cp_2Nb(NNMe_2)(THF)][BPh_4]$		263
$[Cp_2Nb(N^tBu)(O_3SCF_3)]$	$Cp = C_5H_5$ (X-ray)	146
$[Cp_2Nb(N^tBu)(PMe_3)](O_3SCF_3)$	$Cp = C_5H_5$ (X-ray)	146
$[Cp_2Nb(N^tBu)]X$	$Cp = C_5H_5$; $X = MeB(C_6F_5)_3$, $B(C_6F_5)_4$	146
$[(C_5H_4)CMe_2(C_5H_4)]Nb(N^tBu)(O_3SCF_3)$		146

(*Continued*)

Table 12 (Continued)

Compound	*Comments*	*References*
$[(C_5H_4)CMe_2(C_5H_4)]Nb(N^tBu)[B(C_6F_5)_4]$		146
$Cp_2NbN(C_6H_3Me_2\text{-}2,6)Cl$	$Cp = C_5H_5$	62
$Cp_2Nb(NR)Cl$	$Cp = C_5H_4SiMe_3$, $R = Ph$ (X-ray), ^tBu, ^nPr, ^iPr, $C_6H_4Me\text{-}4$, $C_6H_4OMe\text{-}4$ (X-ray); $Cp = C_5H_5$, $R = SiMe_3$	194, 228, 6, 221
$(C_5R_5)(C_5H_4SiMe_2(CH_2\text{-}CH{=}CH_2)Nb(N^tBu)Cl$	$R = H$, Me	219
$[\{Cp_2NbCl\}_2(\mu\text{-}1,x\text{-}N_2C_6H_4)]$	$Cp = C_5H_4SiMe_3$; $x = 3,4$	69
$[(C_5H_4)CMe_2(C_5H_4)]Nb(NR)X$	$R = SiMe_3$, $X = Cl$ (X-ray); $R = {}^tBu$, $X = Cl$ (X-ray), Br (X-ray), I (X-ray)	68
$[(C_5H_3R)SiMe_2(C_5H_3R)]Nb(N^tBu)Cl$	$R = H$ (X-ray); $R = SiMe_3$ (isolated as the *meso*-isomer)	70
$[(C_5Me_4)SiMe_2(C_5H_3R)]Nb(N^tBu)Cl$	$R = H$, Me (X-ray), $SiMe_3$, ^iPr (X-ray)	264
$[(C_5Me_4)GeMe_2(C_5H_4)]Nb(N^tBu)Cl$		265
$[(C_5Me_4)SiMe_2(C_5H_3PPh_2)]Nb(N^tBu)Cl$		266
$[(C_5H_4)CMe_2(\eta^1\text{-}C_5H_4)]Nb(NC_6H_4{}^iPr\text{-}2,6)(NMe_2)$	(X-ray)	225
$[(C_5H_4)CMe_2(C_5H_4)]Nb(NC_6H_4{}^iPr_2\text{-}2,6)Cl$	(X-ray)	225, 267
$[(C_5H_4)CMe_2(\eta^1\text{-}C_9H_6)]Nb(NC_6H_4{}^iPr_2\text{-}2,6)(NMe_2)$		226
$[(C_5H_4)CMe_2(C_5H_4)]Nb(NC_6H_4{}^iPr_2\text{-}2,6)(NMe_2)$		267
$\{[(C_5H_4)CMe_2(C_5H_4)]Nb(NC_6H_4{}^iPr_2\text{-}2,6)(NHMe_2)\}[B(C_6F_5)_4]$	(X-ray)	267
Phosphorus donor complexes		
$[Cp_2Nb(PHPh_2)_2]Cl$	$Cp = C_5H_4Me$	111
$Cp_2Nb(PPh_2)(PHPh_2)$	$Cp = C_5H_4Me$; C_5H_5 (X-ray)	111, 268
$Cp_2Nb(PPh_2)_2M$	$Cp = C_5H_4Me$; $M = Na,Li$	111
$Cp_2Nb(PPh_2)(dmpm)$	$Cp = C_5H_5$; $dmpm = PMe_2CH_2PMe_2$	269
$Cp_2Nb(CO)PPhH(O)$	$Cp = C_5H_5$	32
$Cp_2Nb(CO)PPh(OMe)$	$Cp = C_5H_5$	32
$Cp_2Nb(PPh_2)L$	$Cp = C_5H_5$; $L = P(OMe)_3$, PMe_2H	270
$Cp_2Nb(AsEt_2)(PH^iPr_2)$	$Cp = C_5H_5$	112
$Cp_2Nb(\mu\text{-}PPh_2)(\mu\text{-}dmpm)M(CO)_4$	$Cp = C_5H_5$; $dmpm = PMe_2CH_2PMe_2$; $M = Cr$, Mo (X-ray), W	269
$Cp_2Nb(\mu\text{-}PPh_2)Rh(C_2H_4)$	$Cp = C_5H_5$ (X-ray), C_5H_4Me	271
$Cp_2Nb(L)(\mu\text{-}PPh_2)M(CO)_5$	$Cp = C_5H_5$; $M = Cr$, $L = CO$, $P(OMe)_3$ (X-ray), PMe_2H (X-ray); $M = Mo$, W, $L = CO$, $P(OMe)_3$, PMe_2H	270

A new family of complexes, the *ansa*-niobocene dichlorides, $[(C_5H_4)XR_2(C_5H_4)]NbCl_2$, has emerged recently, and this type of complex has been used as a precursor in different processes, such as alkylation and chemical and/or electrochemical reduction. The most extensive preparative method involves the reaction of $NbCl_4(THF)_2$ with the appropriate salt of the corresponding *ansa*-ligand, $[R_2X(C_5H_4)_2]Y$, $R = $ alkyl group, $X = C$ or Si, $Y = Li_2$, K_2, Tl_2, $(MgCl)_2$.[70,148,179,180,240,241] Other classes of niobocene halide complexes containing additional ancillary ligands will be considered in the following sections.

5.02.7.3.2.(ii) Oxygen- and sulfur-donor complexes

Oxo- and sulfido niobocene complexes are well known, and these systems were widely described in COMC (1995). New examples have, however, been reported since that time. The use of quantum chemical theoretical methods has shown that the oxo ligand in $Cp_2Nb(O)Cl$ derivatives exhibits a strong electron-donor effect supported by a through-space interaction between the oxygen atom and the Cp rings.[242] Oxo-niobocenes, $Cp_2Nb(O)X$ ($X = H$, Cl, OH, OMe), were isolated from the reaction of Cp_2NbCl_2 with sodium or barium hydroxides under different experimental conditions.[244,245] The preparation includes oxidation from Nb(IV) to Nb(V), and the existence of several Nb(IV) intermediates has been postulated. The oxidation process of the electron-rich Nb(III) system $[Cp_2NbCl]_2$[194] to give the oxo complex $Cp_2Nb(O)Cl$ has been studied.[246] New sulfido and disulfide niobocene complexes have also been prepared. For example, the reaction of $Cp_2Nb(BH_4)$

with S_8 gave a mixture of three isomers, namely, $Cp_2Nb(\eta^2\text{-}S_2)H$, $Cp_2Nb(S)(SH)$, and $Cp_2Nb(\eta^2\text{-}S_2)(SH)$.[248,249] Some of these disulfide complexes have been employed in the preparation of heterometallic complexes. For example, the irradiation of $Cp_2Nb(\eta^2\text{-}S_2)H$ in the presence of $Fe(CO)_5$ gave the complex $[Cp_2NbS_2]_2Fe$, which contains an FeS_4 tetrahedron that is ligated by two niobocene ligands.[250]

A broad family of niobocene derivatives containing carboxylato or thiocarboxylato ancillary ligands has also emerged in this period. Several d^0-, d^1-, and d^2-species are well represented, and a wide variety of synthetic procedures were used in their preparation. In this respect, Nicholas *et al.* reported the first example of formato generation, $Cp_2Nb(O)(\kappa^1\text{-}O_2CH)$, by oxidation of the hydrido niobium carbonyl complex $Cp_2NbH(CO)$.[253] Insertion of heterocumulenes into the Nb–H bonds of hydride d^0- or d^2-species has also been a productive procedure to prepare this type of complex. For example, the complex $Cp_2NbH(CO)$ reacted with $PhN{=}C{=}O$ to give the formamido complex $Cp_2Nb(\kappa^1\text{-}OC(H)NPh)(CO)$.[255] In an alternative route, the complexes were prepared by electrochemical reduction of Cp_2NbCl_2 species in the presence of the appropriate carboxylic acid.[256]

5.02.7.3.2.(iii) Nitrogen-donor complexes

The imido ligand has found widespread use in the chemistry of the early transition metals. The literature concerning imido-niobocene and *ansa*-niobocene complexes, $Cp_2Nb(NR)Cl$ and $[(C_5H_4)XR_2(C_5H_4)]Nb(NR^1)Cl$, respectively, during this period is extensive. In several cases, imido-niobocene complexes were prepared by the reaction of the corresponding half-sandwich complexes with the appropriate sodium or lithium cyclopentadienide.

Suitable alternative routes have also been described for the preparation of these complexes. For example, the electron-rich parent complex $[Cp_2NbCl]_2$ reacts with amines RNH_2 to afford the corresponding imido derivatives $Cp_2Nb(NR)Cl$ in accordance with a sequence involving initial oxidative addition of the amine, which gives rise, presumably, to an amido intermediate that subsequently undergoes thermolytic expulsion of H_2 to afford the imido derivatives.[194] Thermal treatment of isocyanate-containing niobocene complexes has also been employed as an efficient method to prepare imido derivatives.[194,69] A large family of *ansa*-niobocene complexes with the imido ancillary ligand has received a significant amount of attention.[264–267] The most useful preparative method consists of the interaction of $Nb(NR)Cl_3(py)_2$ with the appropriate salt of the corresponding *ansa*-ligand, $[R_2X(C_5H_4)_2]Y$ ($R =$ alkyl group; $X = C$ or Si; $Y = Li_2$, K_2, Tl_2). In several cases, for both classes of complex, the imido ligand acts as a four-electron donor. The formal electron count is therefore 20 electrons, and this fact may have an effect on the lengthening of the Nb–Cent distances of these formally "20-electron" complexes in comparison to their 18- and 17-electron analogs. However, it has been established that the surplus electrons in these "high electron" complexes are located in essentially ligand-based orbitals, and thus the 18-electron rule is not violated.[228,264]

5.02.7.3.2.(iv) Phosphorus-donor complexes

Several types of phosphine-containing d^2-niobocene complexes, $Cp_2NbX(PR_3)$ ($X =$ anionic ligand), were described in COMC (1995). In the period since then, several new classes of niobocene-containing phosphorus-donor ancillary ligands have been prepared. For example, d^2-phosphido complexes $Cp_2Nb(PR_2)(L)$ are well known, and their reactivity as metallophosphines to give a wide variety of heterometallic complexes has been studied.[269–271] The reaction of Cp_2NbHL derivatives with halophosphines PR_2Cl has proved to be a useful procedure to prepare these complexes, and it has been claimed that the process involves insertion of PR_2Cl into the Nb–H bond.[111,268,271]

5.02.7.4 η^6- and η^7-Complexes

Although arene niobium chemistry was reported some years ago, in the last few years, the chemistry of η^6-arene of niobium has seen little further development. The greater part of new arene–niobium complexes reported during recent years come from arene–niobium complexes previously reported. Table 13 summarizes the η^6-complexes of niobium. Thus, a new arene–niobium(V) complex could be isolated, when $(\eta^6\text{-}C_6H_5Me)_2Nb$[272] reacted with ethylediamine solutions of K_4Sn_9 to give low but reproducible yields of $[(\eta^6\text{-}C_6H_5Me)NbSn_6Nb(\eta^6\text{-}C_6H_5Me)]^{2-}$, whose structure can be viewed as an Sn_6^{12-} Zintl ion, which requires fully oxidized Nb^{5+} centers.[273] An unusual mixed-valence Nb(IV)/Nb(0) complex, $[(Ph_2N)_2Nb\{(\mu\text{-}NPh(\eta^6\text{-}C_6H_5))\}_2Nb]$, was isolated by heating of $[\{(Ph_2N)_2Nb\}_2[\mu\text{-}NPh(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)\}(\mu\text{-}H)]Li(TMEDA)_2$ in toluene.[82]

The low first ionization potential (5.18 eV) of bis(η^6-mes)niobium[274] and a large negative halfware potential (-0.495 eV vs. standard calomel electrode (SCE)) for the $[(\eta^6\text{-}C_6H_3Me_3)_2Nb]/[(\eta^6\text{-}C_6H_3Me_3)_2Nb]^+$ couple[275] indicate that this complex is a high-energy, electron-rich and, therefore, very reactive 17-electron complex. Thus, $(\eta^6\text{-}C_6H_3Me_3)_2Nb$ reacts with elemental iodine to lead a dinuclear d^{3-} d^3-niobium complex, $[(\eta^6\text{-}C_6H_3Me_3)_2Nb_2(\mu\text{-}I)_4]$,

Table 13 η^6-Complexes of niobium

Compound	*Comments*	*References*
$[K(2,2,2\text{-crypt})]_2[(\eta^6\text{-}C_6H_5Me)NbSn_6Nb(\eta^6\text{-}C_6H_5Me)]$	X-ray	273
$[(Ph_2N)_2Nb\{(\mu\text{-}NPh(\eta^6\text{-}C_6H_5))\}_2Nb]$	X-ray	82
$[(\eta^6\text{-}C_6H_3Me_3)_2Nb_2(\mu\text{-}I)_4]$	X-ray	275
$[(\eta^6\text{-}C_6H_3Me_3)_2Nb_2(\mu\text{-}I)_4]I$		275
$[(\eta^6\text{-}C_6Me_6)_2Nb_2Cl_4]$		277
$[(\eta^6\text{-}C_6Me_6)Nb(O_2CN\text{-}Pr^i{}_2)_2]_2$		277
$[(\eta^6\text{-}C_6H_3Me_3)_2Nb(\eta^2\text{-}RC{\equiv}CR)][Y]$	$R = CH_3$, $Y = BPh_4$, $B(p\text{-}FC_6H_4)_4$, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$ $R = Ph$, $Y = BPh_4$, $[B(p\text{-}FC_6H_4)_4$, X-ray]	151
$[(\eta^6\text{-}C_6H_3Me_3)_2Nb(CO)][Y]$	$Y = BPh_4$, $B(p\text{-}FC_6H_4)_4$, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$	151
$[Nb(\eta^2\text{-}RC{\equiv}CR)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2]$	$R = CH_3$, $X = H$ (X-ray), *p*-F (X-ray) $R = Ph$, $X = H$	151
$Nb(CO)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2$	$X = H$ (X-ray), *p*-F	151
“$[Nb(\eta^6\text{-}C_6H_6)]$”	IR study	279

forming a Nb–Nb single bond.[275] Oxidation of $[(\eta^6\text{-}C_6H_3Me_3)_2Nb_2(\mu\text{-}I)_4]$ with iodine yields an iodide salt of the $[(\eta^6\text{-}C_6H_3Me_3)_2Nb_2(\mu\text{-}I)_4]^+$.[275]

A variation of the Fischer–Hafner preparation[276] leads with substantially quantitative yield to $[(\eta^6\text{-}C_6Me_6)_2Nb_2Cl_4]$.[277] The reaction of this compound with a CO_2-saturated solution of diisopropylamine affords a mixed-ligand arene–carbanate complex $[(\eta^6\text{-}C_6Me_6)Nb(O_2CN\text{–}Pr^i{}_2)_2]_2$.[277]

Cationic bis(arene) niobium complexes of general formula $[(\eta^6\text{-}C_6H_3Me_3)_2Nb(\eta^2\text{-}RC{\equiv}CR)][Y]$[151] were isolated by reaction of $[(\eta^6\text{-}C_6H_3Me_3)_2Nb][Y]$[278] with excess of RC≡CR. The acetylenic derivatives of niobium(I), when R = Me, react with CO at atmospheric pressure to lead $[(\eta^6\text{-}C_6H_3Me_3)_2Nb(CO)][Y]$ by displacement of but-2-yne by carbon monoxide;[151] some of these cationic alkyne complexes containing the tetraarylborato counteranion undergo a thermal rearrangement affording niobium(I) complexes containing the 12-electron-donor tetraarylborato ligand, $[Nb(\eta^2RC{\equiv}CR)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2]$,[151] where there are two of the four phenyl rings of the $[BPh_4]$ coordinated to niobium atom. In these complexes the but-2-yne is easily substituted by CO to give new carbonyl derivative.[151]

Zerovalent $Nb(C_6H_6)$ complex can be prepared from niobium atoms, produced by laser ablation, with benzene vapor in an argon matrix.[279] The IR spectra of the reaction products shows that the primary product is the $Nb(C_6H_6)$ and sandwich $Nb(C_6H_6)_2$ species.[279]

The chemistry of η^7-complexes of niobium remains undeveloped, and in recent years this has not changed substantially. Only some papers about theoretical investigation of the molecular structure,[280] electronic structure,[281] or nature of the niobium–cycloheptatrienyl bond,[282,283] of the mixed-ring sandwich complex $Nb(\eta^7\text{-}C_7H_7)$ $(\eta^5\text{-}C_5H_5)$ have been reported.

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5.03
Tantalum Organometallics

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5.03.1 Introduction and Organization

5.03.1.1 Overview

Organoametallic chemistry of tantalum developed in the last two decades is attributed to the introduction of appropriate bulky ligands for stabilizing not only various unstable intermediate species in organic and catalytic reactions but also unsaturated species with low oxidation states and low coordination numbers. Although tantalum compounds have a general tendency to form dinuclear or cluster compounds, the bulky ligands prevent the formation of higher nuclearity cluster complexes and hence highly unsaturated organometallic compounds are isolated and characterized. The structure and fundamental reactivity of tantalum complexes continues to provide important insights into the understanding of chemical bonding nature including metal–ligand multiple bonds and models for Fischer–Tropsch catalysts and alkene metathesis catalysts. Notable new developments are the catalytic applications of organotantalum compounds for polymerization and oligomerization of ethylene and hydroamination. Tantalum favors the highest oxidation state (+5, d^0-configuration), for which NMR is a useful tool to characterize compounds, being advantageous compared with niobium complexes that are more readily reduced to +4 oxidation state. Thermodynamically stable metal–ligand multiple bonds induce the cleavage of the carbon–nitrogen and carbon–oxygen bond of organic compounds as well as nitrogen–nitrogen bond of N_2.

The reader is referred to the chapter of COMC (1982) written by Labinger 1980[1] and that of COMC (1995) by Wigley and Gray in 1995,[2] who gave an excellent historical context and an extensive collection of organometallic compounds of niobium and tantalum. Several relevant review articles have appeared over the years and these reviews and general reference works for specific ligand or compound types are noted in each section.

5.03.1.2 Organization and Coverage

The main part of this chapter is a series of tables for compounds. Homoleptic compounds are automatically classified into one part of this chapter, while heteroleptic compounds, which contain more than one type of ligand, are usually described in only one section, according to the "classification priorities" as described in Table 1, which has been adapted from COMC (1982) by Labinger[1] and COMC (1995) by Wigley and Gray.[2] Thus, alkylidene complexes are described in the alkylidene section because of the highest priority of alkylidene complexes among any types of complexation. Although the priority is applied for tables, compounds are not discussed in a progression according to ligand type or nuclearity, as outlined in the table of contents. Larger tables are subdivided according to the ancillary

Table 1 Classification priorities for heteroleptic complexes[a]

Priority	*Carbon ligand*	*Comments*
1	Alkylidenes and alkylidynes	Includes Ta=CHR and Ta≡CR ligands. M=C bonds in metallacyclic environments described as metallacycles.
2	π-Bonded ligands other than cyclopentadienyl	π-Ligand must have at least one carbon directly bound to metal.
3	η^1-Ligands	Alkyls are higher priority than hydrides. All metallacycles are excluded here and described in parts of metallacycles. Compounds with Ta–Si bond are covered here.
4	Carbonyls and isocyanides	CO or CNR must be bound to Ta in heterobimetallic complexes.
5	Cyclopentadienyls as the last	Other η^5-ligands are included here, e.g., carborane η^5-$Et_2C_2B_4H_4$, and $[\eta^5\text{-}C_2B_9H_{11}]^{2-}$ (dicarbollide), Tp Tp*

[a] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

ligand set, formal oxidation state, or some other convenient classification. Each table includes a "comments" section, in which the synthetic route is briefly summarized and a compound characterized by X-ray analysis is specified as a term of "X-ray." This chapter covers organometallic chemistry of tantalum from 1993 to early 2005; all references dating from 1993 are included.

5.03.2 Carbonyls, Nitrosyl, and Isocyanides

5.03.2.1 Carbonyls and Substituted Carbonyls

5.03.2.1.1 Carbonyl complexes without cyclopentadienyl ligands

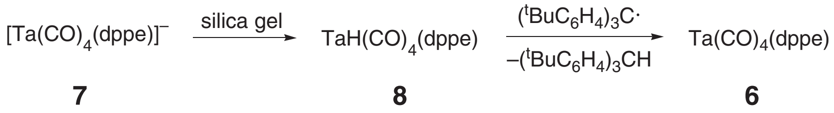
An anionic homoleptic complex, $[Ta(CO)_6]^-$ **1**, whose oxidation state is −1, is a versatile starting compound for preparing carbonyl derivatives. The effective synthetic method of **1** under mild conditions (atmospheric pressure of CO) was reported in 1983 by Ellis *et al.* who used reductive carbonylation of $TaCl_5$ by alkali metal naphthalenides,[3] and by Calderazzo *et al.* who used a reducing system based on Mg–Zn in pyridine.[4] The improved synthesis of **1** is described by Ellis,[5] and more recently, carbonylation of the isolated homoleptic naphthalenide compound, $[Ta(\eta^4\text{-naphthalene})_3]^-$, is reported as another convenient synthetic method.[6]

The anionic homoleptic tantalum carbonyl compound **1** is inert to substitution reaction. It is a special exception that all carbonyl ligands of $[NEt_4][Ta(CO)_6]$ can be replaced by Hhpp (=1,3,4,6,7,8-hexahydro-*2H*-pyrimido[*1,2-a*]-pyrimidine) to give $[Ta(hpp)_4][Ta(CO)_6]$.[7] Ellis reports the extensive synthesis of monosubstituted compounds $[Ta(CO)_5L]^{n-}$ **2** ($n = 1$ for L = CN^tBu, $P(OMe)_3$, PMe_3, $SbPh_3$, $AsPh_3$; $n = 2$ for L = CN) starting from a monosubstituted metal carbonyl anion $[Ta(CO)_5(NH_3)]^-$ **3**, where ammonia acts as a labile ligand.[8] Treatment of $Na_3[Ta(CO)_5]$ **4** in liquid ammonia with 1 equiv. of NH_4Cl or ethanol affords an anionic hydride compound $Na_2[TaH(CO)_5]$ **5**,[5,9] which is further treated by additional equivalent of NH_4Cl to give complex **3** (Scheme 1).[8]

Although $V(CO)_6$ is well known, the corresponding homoleptic tantalum(0) carbonyl complex has not been isolated. Neutral $Ta(CO)_6$ has been tentatively identified in argon matrices by comparison with the IR spectrum of $V(CO)_6$. The first mononuclear Ta(0) carbonyl complex, $Ta(CO)_4(dppe)$ **6**, is prepared stepwise according to Scheme 2.[10,11] A solution of anionic **7** in acetonitrile is passed through a silica gel column to give hydride compound **8**, which is then treated with Eisenberg's stable radical reagent, $(^tBuC_6H_4)_3C\cdot$ to form the 17-electron

$$\underset{\mathbf{4}}{Na_3[Ta(CO)_5]} \xrightarrow[\text{liq. }NH_3]{NH_4Cl} \underset{\mathbf{5}}{Na_2[TaH(CO)_5]} \xrightarrow[\text{liq. }NH_3]{NH_4Cl} \underset{\mathbf{3}}{Na[Ta(CO)_5(NH_3)]}$$

Scheme 1



Scheme 2

compound **6**, which probably exists in equilibrium with a metal–metal bonded diamagnetic dimer because of the absence of EPR signal in solid and broadening EPR signal in solution. Compound **6** is thermally very unstable in a variety of solvents and decomposition occurs. Reaction of **6** with alkyl halides proceeds with the abstraction of halogen atoms: the rate of reaction increases as the strength of the R–X bond decreases, that is, I > Br > Cl, *t*Bu > *i*Pr·Et > Me; benzylic and allylic halides also react quickly, producing $TaX(CO)_4(dppe)$. Electrochemical studies of $TaX(CO)_4(dppe)$ (X = Br, I) and $TaX(CO)_2(dppe)_2$ exhibit a two-electron reduction, indicating that the (+1) and (−1) oxidation states for tantalum are more stable compared to the (0) oxidation state.[12] The oxidation behavior of these two compounds differs: the tetracarbonyl compound exhibits an irreversible process, while the one-electron oxidation of the dicarbonyl compound results in the formation of 17-electron species $[TaX(CO)_2(dppe)_2]^+$, which has not been isolated.[12]

Since the (+1) and (−1) oxidation states of tantalum are stable and the (0) oxidation state is unstable, redox reactions can induce substitution of hexacarbonyltantalate(−1), mainly giving products with the (+1) oxidation state. Reaction of $Na[Ta(CO)_6]$ with 2 equiv. of methylviologen iodide, MV-I_2, in the presence of bidentate nitrogen base ligands such as dmen (=*N*,*N*′-dimethylenthlenediamine) and tmen (=*N*,*N*,*N*′, *N*′-tetramethylethylenediamine) gives the corresponding derivatives of formula $TaI(CO)_4(NN)$ (NN = dmen and tmen).[13] The reaction of $Na[Ta(CO)_6]$ with 2 equiv. of methylviologen iodide (MV-I_2) involves first the formation of $Na[Ta_2(\mu\text{-}I)_3(CO)_8]$ **9**, which quantitatively affords the products upon treatment with NN ligands. More directly, $TaX(CO)_4(NN)$ complexes can be obtained by the reaction of $Na[Ta(CO)_6]$ with HX adducts of the corresponding NN ligands.[13] Similar oxidative substitution reaction of $[Ta(CO)_6]^-$ with iodine in the presence of ${}^tBuNC$ affords $TaI(CO)_3(CN^tBu)_3$ and $[TaI_2(CN^tBu)_6]I$.[14]

The first nitrosyl complex (trimpsi)Ta(NO)$(CO)_2$ **10** has been prepared: addition of a tripodal phosphine, trimpsi [=${}^tBuSi(CH_2PMe_2)_3$], to $Na[Ta_2(\mu\text{-}I)_3(CO)_8]$ **9** in DMF at −78 °C affords a tricarbonyl compound, (trimpsi)Ta$(CO)_3$I,[15] whose reduction in DME by sodium amalgam leads to the formation of Na[(trimpsi)Ta$(CO)_3$] followed by treatment at −78 °C with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide gives **10** (Table 2).[15]

5.03.2.1.2 Cyclopentadienyl carbonyl complexes

Continuous research has been conducted on half-sandwich carbonyls in the last decade. Monocyclopentadienyl carbonyl complexes of general formula $(\eta^5\text{-}C_5H_4R)Ta(CO)_4$ (R = COOMe, COOEt, COMe, COPh, $COCH_2Ph$, C(Me)=CH_2) and indenyl derivatives have been prepared in excellent yield by the reaction of $Na[Ta_2(\mu\text{-}Cl)_3(CO)_8]$ **9** with 2 equiv. of the C_5H_4R anion.[17] The fluorenyl derivative is similarly obtained.[18] Another synthetic method is the reductive carbonylation of half-sandwich tetrachlorides: $Cp'Ta(CO)_4$ (Cp′ = Cp and indenyl) are obtained by treating $Cp'TaCl_4$ with Zn/Mg under CO (1600 psi) at 60 °C followed by sublimation.[19]

Photochemical liberation of carbonyl ligands is also extensively studied. Photolysis of $CpTa(CO)_4$ under H_2 in supercritical xenon at room temperature leads to the oxidative addition of H_2 to a nascent $CpTa(CO)_3$, giving dihydride complex $CpTa(CO)_3H_2$, in contrast to the formation of non-classical dihydrogen complexes in the cases of vanadium and niobium carbonyls,[20] while nitrogen affords $CpTa(CO)_3(N_2)$.[20] Irradiation of $Cp'Ta(CO)_4$ (Cp′ = Cp and indenyl) in frozen Nujol yields the unsaturated CO-loss products, $Cp'Ta(CO)_3$ and $Cp'Ta(CO)_2$.[19] In *n*-heptane solution or supercritical Xe solution at room temperature, $Cp'Ta(CO)_3(L)$ (L = *n*-heptane or Xe) are detected.[21–23] The indenyl–*n*-heptane complex is much more reactive toward CO, H_2, or N_2 than the Cp complex.[21] Kinetic study of CO substitution reaction of $Cp'Ta(CO)_4$ with PBu_3 is reported.[24]

The photochemically generated unsaturated species derived from $Cp^*Ta(CO)_4$ is reactive toward oxidants such as REER, giving oxidatively added products $[Cp^*Ta(CO)_2]_2(\mu\text{-}ER)_2$ (ER = TeMe, SPh, SePh, TepH, SFc, SeFc, TeFc,

Table 2 Carbonyl complexes without Cp ligands[a]

Compound	*Comments*	*References*
$A[Ta(CO)_6]$	Prep:$TaCl_5 + CO + Na[C_{10}H_8]$; A = NEt_4, $Na(diglyme)_2$	3, 5, 10
$A_3[Ta(CO)_5]$	Prep: A = Na: $\{Na(diglyme)_2\}[Ta(CO)_6]$ + Na in liq NH_3; A = Cs, treatment with CsI [*Caution*: the filter cake contains pyrophoric $Na_2C_2O_2$]	5
$[Et_4N]_2[Ph_3SnTa(CO)_5]$	Prep: $Na_3[Ta(CO)_5] + Ph_3SnCl$, then Et_4NBr	5
$[(Ph_3PAu)_3Ta(CO)_5]$	Prep: $[Et_4N]_2[TaH(CO)_5] + 3Ph_3PAuCl$	5
$A_2[TaH(CO)_5]$	Prep: $Na_3[Ta(CO)_6]$ with ethanol; A = Na, NEt_4	5,9
$A[Ta(CO)_6]$	Prep: $A[Ta(\eta^4\text{-naphtharene})_3]$ + ex. CO; A = Na(THF) or Na(crypt 2.2.2)	6
$[Ta(hpp)_4][Ta(CO)_6]$	Prep: $[NEt_4][Ta(CO)_6]$ + Hhpp, Hhpp = 1,3,4,6,7,8-hexahydro-*2H*-pyrimido [*1,2-a*]pyrimidine	7
$[P(Ph)_4][Ta(CO)_6]$	X-ray	7
$[Ta(CO)_5L]^{n-}$	Prep: $[Ta(CO)_5(NH_3)]^- + L$; n = 1 for L = CN^tBu, $P(OMe)_3$, PMe_3, $SbPh_3$, $AsPh_3$; *n* = 2 for L = CN	8
$[Et_4N][Ta(CO)_4(dppe)]$	Prep: photochem. of $[Et_4N][Ta(CO)_6]$ with dppe	10
$TaH(CO)_4(dppe)$	Prep: silica gel/$[Et_4N][Ta(CO)_4(dppe)]$ in acetonitrile	10
$Ta(CO)_4(dppe)$	Prep: $TaH(CO)_4(dppe) + (^tBuC_6H_4)_3C$ radical	10
$TaH(CO)_2(dppe)_2$	Prep: $Na[Ta(CO)_2(dppe)_2]$ + EtOH	12
$TaX(CO)_4(dppe)$	Electrochemistry, X = I, Br	12
$TaX(CO)_2(dppe)_2$	Electrochemistry, X = H, I, Br, Cl	12
$TaI(CO)_4(NN)$	Prep: $Na[Ta(CO)_6]$ + NN + MV-I_2; MV-I_2 = methylviologen iodide, NN = dmen and tmen (X-ray)	13
$TaI(CO)_4(2,2'\text{-dipy})$	Prep: $Na[Ta(CO)_6] + [2,2'\text{-dipy-}H_2]I_2$	13
$TaCl(CO)_4(NN)$	Prep: $Na[Ta(CO)_6] + [NN\text{-}H_2]Cl_2$, NN = dmen, 4,4′-dipy	13
$TaCl(CO)_4(NN)$	Prep: $TaCl(CO)_4(4,4'\text{-bipy})$ + NN, NN = en, dmen, tmen, 2,2′-dipy,	13
$TaI(CO)_3(CN^tBu)_3$	Prep: $[Ta(CO)_6]^-$ + iodine + 3 ^tBuNC	14
$TaI(CO)_3(CN^tBu)(dppe)$	Prep: $TaI(CO)_3(CN^tBu)_3$ + dppe	14
$(trimpsi)Ta(CO)I$	Prep: $Na[Ta_2(\mu\text{-I})_3(CO)_8]$ + trimpsi; trimpsi = $^tBuSi(CH_2PMe_2)_3$	15
$Na[(trimpsi)Ta(CO)_3]$	Prep: (trimpsi)Ta(CO)I + Na/Hg	15
$TaCl(CO)_2(dbpe)_2$	Prep: $TaCl_5$ + Na/Hg + dbpe + CO, dbpe = 1,2-bis(dibutylphosphino)ethane	16

[a] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

S^nBu, S^tBu).[25] Halogens are much more reactive oxidants: the reaction of $Cp^*Ta(CO)_4$ with chlorine leads to Cp^*TaCl_4, whereas the corresponding reactions with bromine or iodine give the oxo-bridged dinuclear complexes $[Cp^*TaX_3]_2(\mu\text{-O})$ (X = Br, I), which in air are converted into mononuclear complexes $Cp^*Ta(O)X_2$.[26]

Metallocene carbonyl phosphido compounds provide unique stable fragments for supporting heterobimetallic compounds. The dimethylphosphido compound $Cp_2TaPMe_2(CO)$ reacts with $M(CO)_5(THF)$ (M = Cr, W) under irradiation to give a heterobimetallic carbonyl complex $Cp_2Ta(\mu\text{-CO})(\mu\text{-PMe}_2)M(CO)_4$, which reacts with phosphines to give $Cp_2Ta(CO)(\mu\text{-PMe}_2)Cr(CO)_4(L)$ (L = PMe_2Ph or PPh_3).[27,28] Under similar conditions, reaction of a racemic bimetallic complex $CpCp''Ta(\mu\text{-CO})(\mu\text{-PMe}_2)W(CO)_4$ ($Cp'' = C_5H_2\text{-1-}^tBu\text{-3,4-Me}_2$), which is obtained by treating $CpCp''Ta(CO)(PMe_2)$ with $W(CO)_5(THF)$ under irradiation, reacts with an optically active phosphine ligand, (R)-(+)-phenyl(*o*-anisyl)methylphosphine, to give two diasteroisomers, which can be separated and characterized by X-ray analyses.[29] A similar chromium complex is also reported by the same group.[30] Reaction of $Cr(CO)_5(THF)$ with metallophosphinite complex $Cp(\eta^5\text{-}C_5Me_4Et)Ta(CO)[PPh(OMe)]$ gives heterobimetallic compound $Cp(\eta^5\text{-}C_5Me_4Et)Ta(CO)[\mu\text{-PPh(OMe)}]Cr(CO)_5$ as the only stereoisomer.[31]

The phosphido complexes $Cp_2Ta(PR_2)(CO)$ (R = Me, Ph) react with H_2O_2 or S_8 to induce the oxidation or sulfurization of the phosphido ligands, giving the corresponding $Cp_2Ta[P({=}X)R_2](CO)$ (X = O or S).[32,33] The oxo- and thiophosphido moieties exhibit similar reactivities toward organic electrophilic reagents such as MeI and MeCOCl, giving rise to the corresponding cationic compounds with the general formula $[Cp_2Ta[P(XE)R_2](CO)]+$ (X = O or S; E = Me or MeCO). The sulfur derivative can coordinate to metal carbonyls to give $Cp_2Ta(CO)[\mu,\eta^1{:}\eta^1\text{-P(S)R}_2][ML_n]$ [ML_n = $Fe(CO)_4$, $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $CpMn(CO)_2$], while the oxo derivative coordinates to an oxophilic organotin compound, that is, Bu_3SnCl.[32,33] The corresponding dihydride derivatives including heterobimetallic complexes have been reported (Table 3).[34]

Table 3 Carbonyl complexes with Cp ligands[a]

Compound	*Comments*	*References*
Half-sandwich complexes		
$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Ta(CO)}_4$	Prep: $\text{Na[Ta}_2(\mu\text{-Cl})_3\text{(CO)}_8] + \text{NaC}_5\text{H}_4\text{R}$; $\text{C}_5\text{H}_4\text{R} = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{COOMe}$ (X-ray), $\text{C}_5\text{H}_4\text{COOEt}$, $\text{C}_5\text{H}_4\text{C(Me)}{=}\text{CH}_2$, $\text{C}_5\text{H}_4\text{COCH}_2\text{Ph}$, $\text{C}_5\text{H}_4\text{COMe}$, $\text{C}_5\text{H}_4\text{COPh}$, Indenyl	17
$(\eta^5$-9-Phenylfluorenyl$)\text{Ta(CO)}_4$	Prep: $\text{Na[Ta}_2(\mu\text{-Cl})_3\text{(CO)}_8]$ + Li(9-phenylfluorenyl)	18
CpTa(CO)_4	Prep: CpTaCl_4 + Zn/Mg + CO (1600 psi) at 60 °C; X-ray	19
$(\eta^5\text{-C}_5\text{H}_4\text{COPh})\text{Ta(CO)}_4$	X-ray	19
$(\eta^5$-Indenyl$)\text{Ta(CO)}_4$	X-ray	19
$\text{Cp}'\text{Ta(CO)}_3(\text{N}_2)$	Photolysis under N_2; Cp' = Cp and Indenyl	20, 21, 35
$\text{Cp}'\text{Ta(CO)}_3\text{H}_2$	Photolysis under H_2; Cp' = Cp and indenyl	20, 21, 35
$\text{CpTa(CO)}_3\text{(Xe)}$	Photolysis in supercritical Xe solution	22, 23
$\text{Cp}'\text{Ta(CO)}_3$(*n*-heptane)	Photolysis in *n*-heptane; Cp' = Cp and indenyl	21, 23
$\text{Cp}'\text{Ta(CO)}_3(\text{PBu}_3)$	Kinetics; Cp' = Cp and indenyl	24
$[\text{Cp}^*\text{Ta(CO)}_2]_2(\mu\text{-ER})_2$	Prep: Photolysis of $\text{Cp}^*\text{Ta(CO)}_4$ + REER, ER = TeMe, SPh, SePh, TePh, SFc, SeFc, TeFc, S^nBu, S^tBu	25
$\text{Cp}'\text{Ta(CO)}_3$	Photolysis at low temperature; Cp' = Cp and indenyl	35
$\text{Cp}'\text{Ta(CO)}_2$	Photolysis at low temperature; Cp' = Cp and indenyl	35
$\text{Cp}^*\text{Ta}({=}\text{NC}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)\text{(H)(CO)[Si(SiMe}_3)_3]$	Prep: $\text{Cp}^*\text{Ta}({=}\text{NC}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)\text{(H)[Si(SiMe}_3)_3]$ + CO at −40 °C, X-ray	36
$\text{Cp}^*\text{Ta(CO)}_4$	Prep: $\text{Cp}^*\text{Ta}(\eta^3\text{-Ph-1-C}_3\text{H}_4)_2$ + CO	37, 38
Metallocene complexes		
$\text{Cp}_2\text{Ta(CO)(PR}_2)$	$\text{Cp}_2\text{Ta(H)(CO)} + \text{ClPR}_2$ + KOH, R = Me, Ph	27, 39
$\text{CpCp}''\text{Ta(CO)(PMe}_2)$	Prep: $\text{CpCp}''\text{Ta(CO)H} + \text{ClPMe}_2$ + KOH, $\text{Cp}'' = \text{C}_5\text{H}_2\text{-1-}^t\text{Bu-3,4-Me}_2$	29
$\text{Cp}_2\text{Ta[P(}{=}\text{X)R}_2\text{](CO)}$	Prep: $\text{Cp}_2\text{Ta(PR}_2\text{)(CO)} + \text{H}_2\text{O}_2$ or S_8, R = Me, Ph; X = O, S	32, 33
$[\text{Cp}_2\text{Ta[P(XMe)R}_2\text{](CO)]I}$	Prep: $\text{Cp}_2\text{Ta[P(}{=}\text{X)R}_2\text{](CO)}$ + MeI, R = Me, Ph; X = O, S	32
$[\text{Cp}_2\text{Ta[P(XCOMe)R}_2\text{](CO)]Cl}$	Prep: $\text{Cp}_2\text{Ta[P(}{=}\text{X)R}_2\text{](CO)}$ + MeCOCl, R = Me, Ph; X = O, S	32
$\text{Cp}^*{}_2\text{TaCl(CO)}$	Prep: $[\text{Cp}^*{}_2\text{TaCl}](\mu\text{-N}_2)$ + CO or $\text{Cp}^*{}_2\text{TaCl(THF)}$ + CO	40, 41
$\text{Cp}^*(\eta^5\text{-C}_4\text{H}_4\text{BN}^i\text{Pr}_2)\text{Ta(CO)}_2$	Prep: $\text{Cp}^*(\eta^5\text{-C}_4\text{H}_4\text{BN}^i\text{Pr}_2)\text{TaCl}_2$ + Mg + CO, X-ray	42
$\text{Cp}_2\text{Ta}[\eta^2\text{-CH}_2\text{B(C}_6\text{F}_5)_2](\text{L})$	Prep: $\text{Cp}_2\text{(Me)Ta[CH}_2\text{B(C}_6\text{F}_5)_2](\mu\text{-H})$ + L, L = CO (X-ray), *t*BuNC (X-ray)	43, 44
$\text{Cp}^*[\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_3)_2]\text{Ta(H)(CO)}$	Prep: $\text{Cp}^*[\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_3)_2]\text{TaH}_3$ + CO	45
ansa-$[\text{Me}_2\text{Si(C}_5\text{Me}_4)_2]\text{TaH(CO)}$	Prep: *ansa*-$[\text{Me}_2\text{Si(C}_5\text{Me}_4)_2]\text{TaH}_3$ + CO	.46
$(\eta^5\text{-C}_5\text{H}_4{}^t\text{Bu})_2\text{Ta(CO)(SH)}$	Prep: $(\eta^5\text{-C}_5\text{H}_4{}^t\text{Bu})_2\text{TaH(CO)}$ + 1/8 S_8	47
$\text{Cp}^*(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)\text{Ta(CO)(PPh}_2)$	Prep: $\text{Cp}^*(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)\text{Ta(H)(CO)} + \text{ClPPh}_2$, and then aq-KOH	48
Heterobimetallic carbonyl complexes		
$\text{Cp}_2\text{Ta}(\mu\text{-CO})(\mu\text{-PMe}_2)\text{M(CO)}_4$	Prep: $\text{Cp}_2\text{Ta(CO)(PMe}_2) + \text{M(CO)}_5\text{(THF)}$ + irradiation, M = Cr, W	27, 28
$\text{Cp}_2\text{Ta(CO)}(\mu\text{-PMe}_2)\text{Cr(CO)}_4\text{(L)}$	Prep: $\text{Cp}_2\text{Ta}(\mu\text{-CO})(\mu\text{-PMe}_2)\text{Cr(CO)}_4$ + L, L = PPh_3 (trans), PMe_2Ph (*cis*, 60%), dmpm (*trans*, 77%), dmpe (*trans*, 77%), CN*t*Bu (*cis*), CNC6H3-2,6-Me2 (*cis*), CNC^*HMePh (*cis*)	27, 28
$\text{Cp}_2\text{Ta(CO)}(\mu\text{-PMe}_2)\text{W(CO)}_4\text{(L)}$	Prep: $\text{Cp}_2\text{Ta}(\mu\text{-CO})(\mu\text{-PMe}_2)\text{Cr(CO)}_4$ + L, L = PPh_3 (*trans*, 5%), PMe_2Ph (*cis*), P^*MePh-*o*-An (*cis*), dmpm (*cis*), dmpe (*cis*), CN*t*Bu (*cis*), CNC6H3-2,6-Me2 (*cis*), CNC^*HMePh (*cis*)	28
$\text{CpCp}''\text{Ta}(\mu\text{-CO})(\mu\text{-PMe}_2)\text{W(CO)}_4$	Prep: $\text{CpCp}''\text{Ta(CO)(PMe}_2) + \text{W(CO)}_5\text{(THF)}$ + irradiation, $\text{Cp}'' = \text{C}_5\text{H}_2\text{-1-}^t\text{Bu-3,4-Me}_2$	29
$\text{CpCp}''\text{Ta(CO)}(\mu\text{-PMe}_2)\text{W(CO)}_4(\text{L}^*)$	Prep: $\text{CpCp}''\text{Ta}(\mu\text{-CO})(\mu\text{-PMe}_2)\text{W(CO)}_4 + \text{L}^*$, $\text{Cp}'' = \text{C}_5\text{H}_2\text{-1-}^t\text{Bu-3,4-Me}_2$, L^* = (R)-(+)-phenyl(*o*-anisyl)methylphosphine, diastereoisomers can be separated and both isomers were characterized by X-ray analyses	29
$\text{Cp}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Ta(CO)}[\mu\text{-PPh(OMe)}]\text{Cr(CO)}_5$	Prep: $\text{Cp}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Ta(CO)[PPh(OMe)]} + \text{Cr(CO)}_5\text{(THF)}$, X-ray	31
$\text{Cp}_2\text{Ta(CO)}[\mu,\eta^1{:}\eta^1\text{-P(S)R}_2][\text{ML}_n]$	Prep: $\text{Cp}_2\text{Ta[P(}{=}\text{S)R}_2\text{](CO)}$ + metal carbonyls, R = Me, Ph; $[\text{ML}_n = \text{Fe(CO)}_4$, Cr(CO)_5, Mo(CO)_5, W(CO)_5, CpMn(CO)_2, X-ray for R = Me and $\text{ML}_n = \text{W(CO)}_5$	32, 33
$\text{Cp}_2\text{Ta(CO)}[\mu,\eta^1{:}\eta^1\text{-P(S)Me}_2]\text{SnBu}_3\text{Cl}$	Prep: $\text{Cp}_2\text{Ta[P(}{=}\text{O)Ph}_2\text{](CO)} + \text{Bu}_3\text{SnCl}$	32
$\text{Cp}^*(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)\text{Ta(CO)}(\mu\text{-PPh}_2)\text{M(CO)}_4$	Prep: $\text{Cp}^*(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)\text{Ta(CO)(PPh}_2) + \text{Cr(CO)}_4$(NBD) or $\text{W(CO)}_4\text{(MeCN)}_2$, M = Cr, W	48, 49

[a] Cp = $\eta^5\text{-C}_5\text{H}_5$, Cp* = $\eta^5\text{-C}_5\text{Me}_5$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

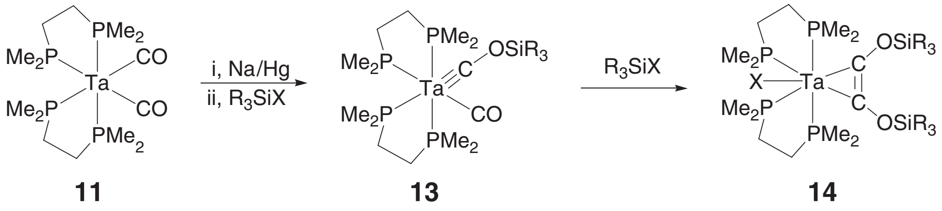
5.03.2.2 CO Reductive Coupling

Reductive coupling reaction of carbonyl and/or isocyanide ligands was reviewed in 1993.[50] The reaction pathway for $Ta(CO)_2(dmpe)_2$ **11** is summarized in Scheme 3, in which the initially formed reduced dicarbonyl-tantalum(−1) compound $Na[Ta(CO)_2(dmpe)_2]$ **12** can be trapped by Me_3SiCl, giving rise to the carbyne–CO compound $Ta(\equiv COSiMe_3)(CO)(dmpe)_2$ (**13**: R = Me), and the second reaction with Me_3SiCl resulted in the formation of bis(siloxyacetylene) complex $Ta(Me_3SiOC\equiv COSiMe_3)(dmpe)_2Cl$ (**14**: $R = R^1 = Me$). Siloxycarbyne complexes $Ta(\equiv COSiR_3)(CO)(dmpe)_2$ **13** ($SiR_3 = Si^iPr_3$, $SiPh_2{}^tBu$, $SiPh_3$) can be isolated by treating **12** with sterically bulky trialkylsilyl halide. Addition of Me_3SiCl or Et_3SiCl to **13** gives the asymmetric acetylene complexes $Ta(R_3SiOC\equiv COSi(R)^1{}_3)(dmpe)_2Cl$ **14** ($R^1 = Me$, Et). The reaction rate was measured for the reaction between $Ta(\equiv COSi^iPr_3)(CO)(dmpe)_2$ (**13**: $R = {}^iPr$) and Me_3SiCl, being first order in both reagents. Large rate enhancement by salt are observed in this reaction, suggesting that, prior to the C–C coupling reaction, the silylation of the CO ligand yields a cationic carbene–carbyne intermediate $[Ta(\equiv COSiR_3)(=C=OSiMe_3)(dmpe)_2]^+$, which is further probed by the isolation of $Ta(\equiv COSiR_3)(COAlEt_3)(dmpe)_2$.[51,52]

The steric demands of the chelating diphosphine ligand such as depe show a minimal effect on the coupling reaction.[53] O-Alkylation of siloxycarbyne complexes **13** and its depe analog with EtOTf in DME gives $Ta(EtOC\equiv COSiR_3)(dmpe)_2OTf$ and $Ta(EtOC\equiv COSiR_3)(depe)_2OTf$, respectively, while the addition of Et_3OBF_4, BnBr, or allyl iodide to **13** produces yellow solution of $Ta(CO)_2(dmpe)_2X$ and the addition of MeOTf affords $Ta(CO)_2(dmpe)_2Me$.[53] Similarly, reactions of siloxycarbynes with MeC(O)Cl and $ClCO_2Me$ afford the corresponding acyl- and formate-capped acetylene complexes. Direct acylation of the reduced dicarbonyl species results in the formation of bis(acyl)-capped acetylene complexes.[53]

5.03.2.3 Isocyanides and Nitrosyl Complexes

Some isocyanide and nitrosyl complexes have been prepared mainly by oxidative substitution reaction of carbonyl compounds and reduction of halides in the presence of ligands. Reported isocyanide compounds are listed in Table 4. A few nitrosyl complexes have been prepared. Addition of $NOBF_4$ to $[Bu_4N][Ta(CO)_6]$ in the presence of an excess of XylNC affords $[Ta(NO)_2(CNXyl)_4][BF_4]$.[54]



Scheme 3

Table 4 Isocyanide and nitrosyl complexes

Compound	*Comments*	*References*
$[TaI_2(CN^tBu)_6]I$	Prep: $[Ta(CO)_6]^- + 2$ iodine + 6 ^tBuNC	14
$TaCl_2(CNCy)_4$	Prep: $TaCl_5 +$ Na/Hg, then + 4CNCy	14
$Cp^*TaCl_2(=N^tBu)(CN^tBu)$	Prep: $Cp^*TaCl_2(=N^tBu) + CN^tBu$	55
$Cp^*TaCl_2(CNXyl)_3$	Prep: $Cp^*TaCl_2(=N^tBu)$ + ex. CNXyl	55
$[Cp_2Ta(\eta^2$-butadiene)(CNR)]-$[CH_3B(C_6F_5)_3]$	Prep: $[Cp_2Ta($*s-trans*-η^4-butadiene)]$[CH_3B(C_6F_5)_3]$ + RNC; R = Bu, Cy	56
$[Cp_2Ta(CNR)_2][CH_3B(C_6F_5)_3]$	Prep: Photolysis of $[Cp_2Ta($*s-trans*-η^4-butadiene)]$[CH_3B(C_6F_5)_3]$ in the presence of an excess of RNC; R = Bu, Cy (X-ray)	56
(trimpsi)Ta(NO)$(CO)_2$	Prep: Na[(trimpsi)Ta$(CO)_3$] + *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide; trimpsi = $^tBuSi(CH_2PMe_2)_3$, (X-ray)	15
$[Ta(NO)_2(CNXyl)_4][BF_4]$.	Prep: $NOBF_4 + [Bu_4N][Ta(CO)_6]$ + ex. XylNC	54

5.03.3 η^1-Complexes

5.03.3.1 Alkyls, Aryls, and Related σ-Complexes without Cp Ligand

5.03.3.1.1 Homoleptic complexes

Although a simple homoleptic pentabenzyl complex, $\mathrm{Ta(CH_2Ph)_5}$ **15**, was originally reported by Schrock in 1976,[57] its 4-methylbenzyl derivative $\mathrm{Ta(CH_2C_6H_4\text{-}4\text{-}Me)_5}$ **16** was isolated and crystallographically characterized.[58] Four of the five 4-methylbenzyl ligands of **16** are σ-bound to the tantalum, while one ligand coordinates in an η^2-fashion to the tantalum atom with an acute Ta–C–$\mathrm{C_{ipso}}$ angle; however, in solution these ligands are equivalent. Recently, Kol *et al.* reported a much more straightforward synthetic method: a slow addition of benzylMgCl to $\mathrm{TaCl_5}$ in ether followed by workup affords pure **15** in 60% yield, which can be stored at −35 °C for weeks without any decomposition.[59] Structural feature of **15** determined by X-ray analysis is quite the same as that of **16**.[59] The reaction of $\mathrm{TaCl_2(CH_2SiMe_3)_3}$ with 2 equiv. of $\mathrm{Me_3SiCH_2MgCl}$ is reported to give peralkylated tantalum(V) complex $\mathrm{Ta(CH_2SiMe_3)_5}$, which can be isolated at −78 °C but decomposed at 52 °C to give $\mathrm{Ta({=}CHSiMe_3)(CH_2SiMe_3)_3}$.[60] Anionic hexaalkynyl complexes were isolated by using a bulky terminal group on an ethynyl ligand: treatment of $\mathrm{TaCl_5}$ with $\mathrm{LiC{\equiv}CSi^tBu_3}$ resulted in the formation of $\{\mathrm{Li(^tBu_3SiC{\equiv}C)_3}\}\mathrm{Ta(C{\equiv}CSi}t\mathrm{Bu_3)_3}$, where a lithium cation interacts with three C≡C bonds.[61] Its metathesis reaction with KOTf forms $\mathrm{K[Ta(C{\equiv}CSi}t\mathrm{Bu_3)_6]}$. These complexes are six-coordinate homoleptic d^0-compounds and adopt trigonal prismatic geometry.

5.03.3.1.2 Alkyl halide complexes

Treatment of dichlorides $\mathrm{TaCl_2(CH_2R)_3}$ (R = Ph, *p*-Tol, $\mathrm{SiMe_3}$) with 2 equiv. of $\mathrm{Bu_3SnF}$ produced the corresponding difluoride compounds $\mathrm{TaF_2(CH_2R)_3}$.[62] Similar treatment of $\mathrm{TaCl_4[CH(SiMe_3)_2]}$ affords tetrafluoride $\mathrm{TaF_4[CH(SiMe_3)_2]}$.[62] Reaction of $\mathrm{[TaCl_3(CH_3CN)_2]_2(\mu\text{-}1,\mathit{n}\text{-}NC_6H_4N)}$ with 6RMgX (R = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2CMe_3}$, $\mathrm{CH_2CMe_2Ph}$) produced dinuclear complexes $\mathrm{[(CH_3CN)(R)_3TaCl](\mu\text{-}1,\mathit{n}\text{-}NC_6H_4N)}$.[63]

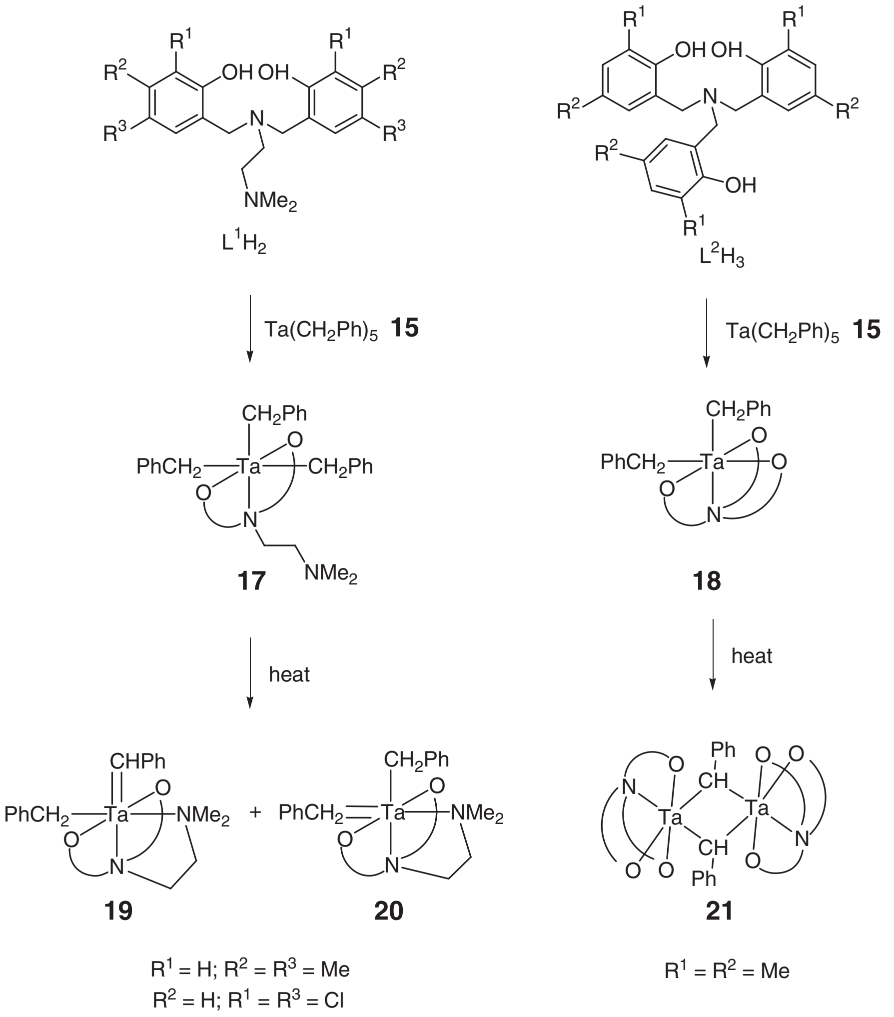
5.03.3.1.3 Alkoxo and aryloxo complexes

Structure **15** serves as a starting material for preparing tantalum alkyl derivatives and can react with alcohols and phenols with the elimination of toluene. Reaction of **15** with bis(phenol) produces tribenzyl **17** and dibenzyl complexes **18** (Scheme 4).[59,64,65] Upon heating of **17**, α-hydrogen abstraction reaction gives a mixture of alkyl–alkylidene complexes **19** and **20**, while the thermolysis of **18** affords dinuclear complex **21**, which has two bridging benzylidene ligands.[64,65]

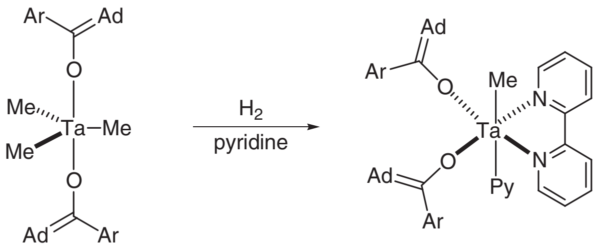
More direct and comprehensive syntheses of bulky aryloxo–alkyl complexes have been reported by Rothwell and his co-workers.[66,67] Trialkyl and dialkyl compounds $\mathrm{Ta(CH_2SiMe_3)_3(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2}$ and $\mathrm{Ta(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)_3}$ were prepared by the reactions of the corresponding chlorides with $\mathrm{LiCH_2SiMe_3}$.[66,68] Thermolysis of $\mathrm{Ta(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)_3}$ results in aromatic C–H bond activation to give cyclometallated compound $\mathrm{T\overline{a[OC_6H_3\text{-}6\text{-}Ph\text{-}2\text{-}(C}_6\mathrm{H_4\text{-}2)](CH_2SiMe_3)(OC_6H_3\text{-}2,6\text{-}Ph_2)_2}$.[66,68] Trimethyl and tribenzyl compounds bearing a chelating bis(phenoxy) ligand, $\mathrm{TaR_3}$[2,2′-ethylenebis(6-isopropylphenoxo)] (R = Me, $\mathrm{PhCH_2}$), are prepared by treating trichloride $\mathrm{TaCl_3}$[2,2′-ethylenebis(6-isopropylphenoxo)] with the corresponding Grignard reagents.[69] Alkyl compounds $\mathrm{TaR_2[(O_2C_{20}H_{12})\text{-}3,3'\text{-}(SiMe_3)_2]}$ containing two chirally resolved 3,3′-di(trimethylsilyl)-1,1′-bi-2,2′-naphthoxide ligands were prepared by two routes: alkylation of $\mathrm{[NH_2Et_2][TaCl_2(O_2C_{20}H_{12})\text{-}3,3'\text{-}(SiMe_3)_2]}$ with 2RMgCl (R = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2Ph}$, *c*-$\mathrm{C_5H_9}$) or treatment of $\mathrm{Ta(CH_2SiMe_3)_3(NMe_2)_2}$ with 2 equiv. of the corresponding binaphthol with concomitant release of amine.[70]

A unique coupling reaction of pyridine was reported for the hydrogenolysis (at atmospheric pressure) of trimethyl compound $\mathrm{TaMe_3(O\text{–}C[Ad]Ar)_2}$ (Ad = 2-adamantylidene, Ar = $\mathrm{C_6H_3\text{-}3,5\text{-}Me_2}$) in pyridine, giving a monomethyl pyridine–bipyridine compound (Scheme 5), although $\mathrm{TaMe_3(O\text{-}C[Ad]Ar)_2}$ exhibits no reaction with dihydrogen at elevated temperature.[71] The intermediate may posses multistep pathway involving a double *ortho*-C–H bond activation of coordinated pyridine and following reductive elimination.

Treatment of $\mathrm{(^tBu_3SiO)_2TaCl_2(\eta^1\text{-}NR_2)}$ [$\mathrm{NR_2}$ = $\mathrm{\overline{N(CH_2)_3CH_2}}$,$\mathrm{\overline{N(CH_2)_4CH_2}}$ with 2 equiv. of R′MgX gives $\mathrm{(^tBu_3SiO)_2TaR'_2(\eta^1\text{-}NR_2)}$ (R′ = Me, Et).[72] Thermolysis of $\mathrm{(^tBu_3SiO)_2TaMe_2(\eta^1\text{-}\overline{N(CH_2)_4CH_2})}$ released methane and an η^2-imine complex, $\mathrm{(^tBu_3SiO)_2TaR(\eta^2\text{-}NC_5H_9)}$, while thermolysis of $\mathrm{(^tBu_3SiO)_2TaEt_2}$ $\mathrm{(\eta^1\text{-}\overline{N(CH_2)_3CH_2})}$ produced the ethylene complex $\mathrm{(^tBu_3SiO)_2Ta(\eta^2\text{-}C_2H_4)(\eta^1\text{-}\overline{N(CH_2)_3CH_2})}$.[72] Exposure of the ethylene complex to excess of ethylene results in the formation of a tantalacyclopentane.[72]

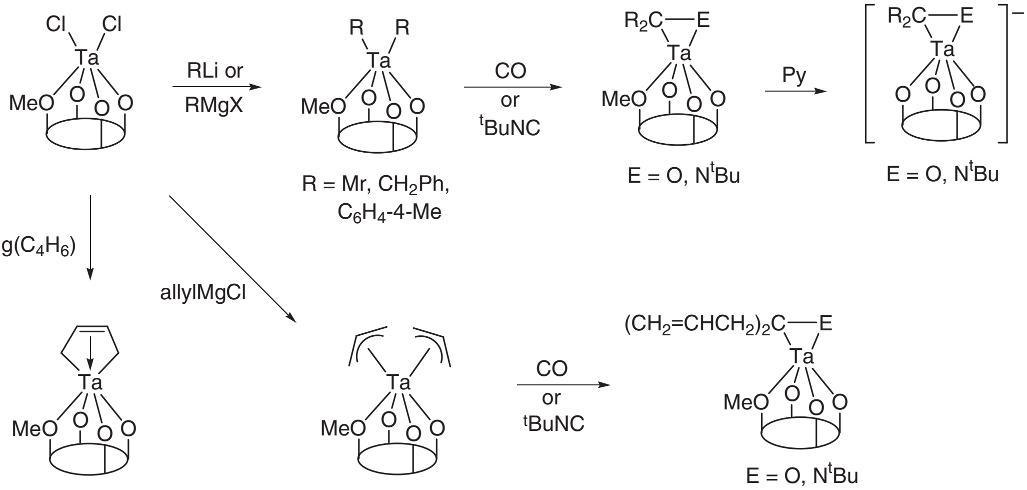


Scheme 4



Scheme 5

Calix[4]arene acts as a ligand stabilizing various organotantalum species (Scheme 6).[73,74] Dialkyl compounds TaR_2{*p*-R-calix[4]arene-OMe} (R = Me, CH_2Ph, C_6H_4-4-Me), bis(allyl), and butadiene complexes were isolated and their migratory insertion reactions reported.[73] Dimeric monoalkyl compounds {TaR[*p*-R-calix[4]arene]}$_2$, which are derived from the demethylation of the ligand, are in equilibrium with their corresponding monomeric forms.[73]



Scheme 6

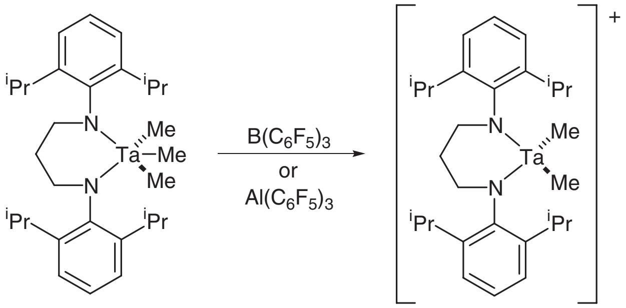
5.03.3.1.4 Amido and imido complexes

TaMe$_5$ can react with triamine ligands, for example, (Me$_3$SiNHCH$_2$CH$_2$)$_2$NH, (C$_6$F$_5$NHCH$_2$CH$_2$)$_2$NH, and (Me$_3$SiNH-2-C$_6$H$_4$)$_2$NH to give dimethyl complexes, [(Me$_3$SiNCH$_2$CH$_2$)$_2$N]TaMe$_2$, [(C$_6$F$_5$NCH$_2$CH$_2$)$_2$N]TaMe$_2$, and [(Me$_3$SiN-2-C$_6$H$_4$)$_2$N]TaMe$_2$, respectively, with the release of methane.[75] Addition of AlMe$_3$ to [(Me$_3$SiNCH$_2$-CH$_2$)$_2$N]TaMe$_2$ produces the zwitterionic adduct, [(Me$_3$SiNCH$_2$CH$_2$)$_2$NAl$^-$Me$_3$]Ta$^+$Me$_2$.[75]

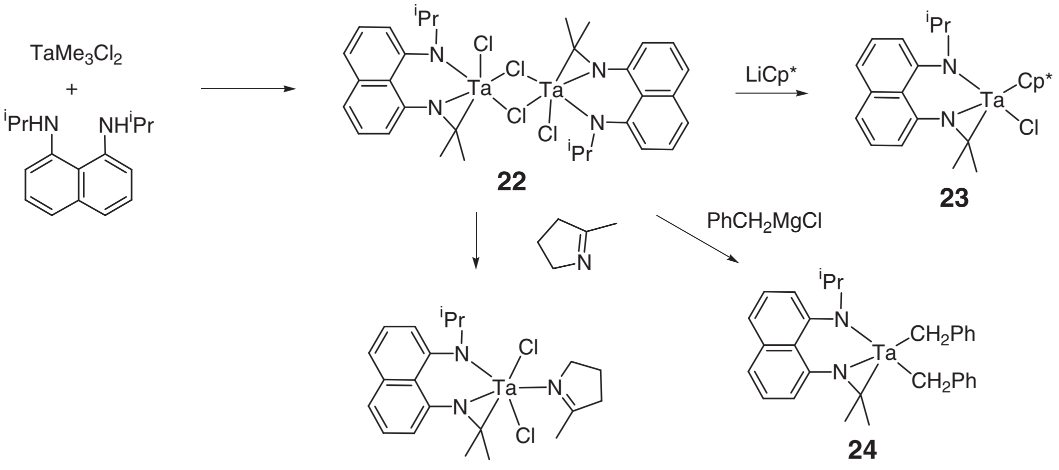
One-pot reaction of TaCl$_5$, ArNH(CH$_2$)$_3$NHAr (Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$), and 5 equiv. of MeMgBr in ether affords a trimethyl complex, TaMe$_3$[ArN(CH$_2$)$_3$NAr].[76] The corresponding cationic complex {TaMe$_2$[ArN(CH$_2$)$_3$NAr]}-[MeB(C$_6$F$_5$)$_3$] is obtained by the addition of B(C$_6$F$_5$)$_3$, while the similar reaction with Al(C$_6$F$_5$)$_3$ results in a mixture of {TaMe$_2$[ArN(CH$_2$)$_3$NAr]}[MeAl(C$_6$F$_5$)$_3$] and {TaMe$_2$[ArN(CH$_2$)$_3$NAr]}[(C$_6$F$_5$)$_3$AlMeAl(C$_6$F$_5$)$_3$] (Scheme 7). Reaction of TaMe$_3$[ArN(CH$_2$)$_3$NAr] with an imidazolide aluminum compound [HNMe(C$_{18}$H$_{37}$)$_2$][(C$_6$F$_5$)$_3$Al(μ-C$_3$H$_3$N$_2$)Al(C$_6$F$_5$)$_3$] gives {TaMe$_2$[ArN(CH$_2$)$_3$NAr]}[(C$_6$F$_5$)$_3$Al(μ-C$_3$H$_3$N$_2$)Al(C$_6$F$_5$)$_3$], which exhibits low activity for co-polymerization of ethylene and 1-octene.[76]

As shown in Scheme 8, reaction of TaMe$_3$Cl$_2$ with 1,8-bis(isopropylamino)naphthalene produces a metallaaziridene complex **22** via β-hydrogen activation.[77] The reaction of **22** with LiCp* and benzyl Grignard reagent affords the corresponding compounds **23** and **24** while maintaining the tantalaaziridene moiety.[77]

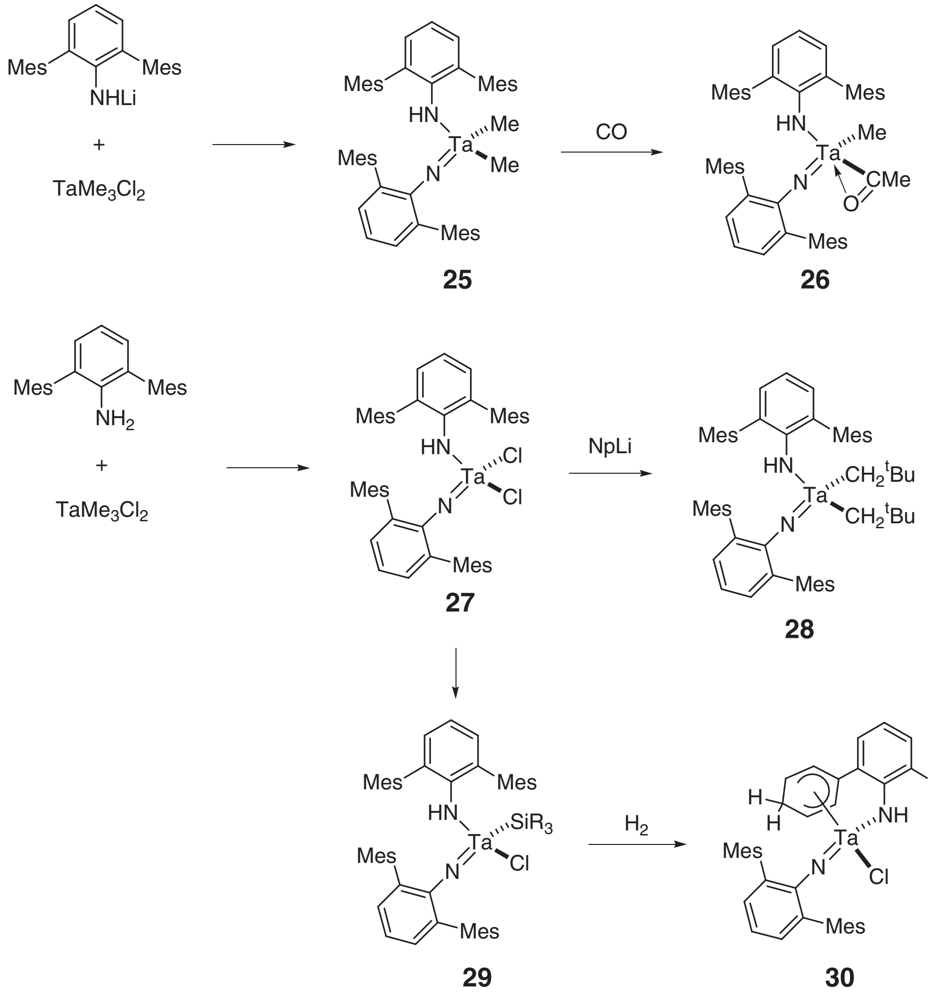
Tantalum alkyl and silyl complexes supported by sterically demanding amido and imido ligands have been reported (Scheme 9).[78] The reaction of TaMe$_3$Cl$_2$ with 2 equiv. of LiNHC$_6$H$_3$-2,6-Mes$_2$ (Mes = 2,4,6-trimethylphenyl) affords (ArN=)(ArNH)TaMe$_2$ (Ar = 2,6-Mes$_2$C$_6$H$_3$) **25**. Addition of CO and PMe$_3$ afforded the corresponding acyl complex (ArN=)(ArNH)-TaMe(η^2-COMe) **26** and phosphine adduct (ArN=)(ArNH)TaMe$_2$(PMe$_3$). (ArN=)(ArNH)TaMe$_2$ rapidly reacts with B(C$_6$F$_5$)$_3$ to form a cationic compound, [(ArN=)(ArNH)TaMe][MeB(C$_6$F$_5$)$_3$]. The free amine directly reacts with TaMe$_3$Cl$_2$ to yield (ArN=)(ArNH)TaCl$_2$ **27**, which is a starting material for preparing the other alkyl complex (ArN=)(ArNH)Ta(CH$_2$^{t}Bu)$_2$ **28** as well as silyl complexes **29**, which then convert to **30** upon hydrogenolysis.[78]



Scheme 7



Scheme 8

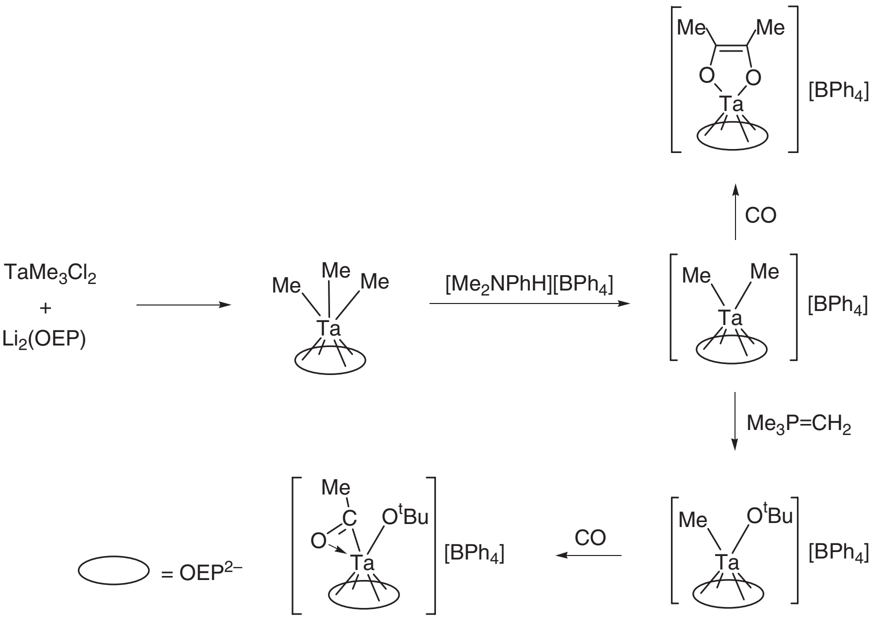


Scheme 9

Addition of Me_3TaCl_2 to 2 equiv. of $LiNHSi^tBu_3$ gives the dimethyl imido compound, $(^tBu_3SiNH)Me_2Ta({=}NSi^tBu_3)$, whose thermolysis in THF or pyridine affords $(L)_2MeTa({=}NSi^tBu_3)_2$ (L = THF, py).[79] Thermolysis of $(^tBu_3SiNH)_2RTa({=}NSi^tBu_3)$ (R = Me, Ph, $PhCH_2$, $^tBuCH_2$) affords a transient bis(imido) species "$(^tBu_3SiNH)Ta({=}NSi^tBu_3)_2$", which can undergo C–H bond activation: in the particular case of R = Ph, 1,4-ditanta-phenyl derivative, $[(^tBu_3SiNH)_2Ta({=}NSi^tBu_3)](\mu\text{-}\eta^1{:}\eta^1\text{-}1,4\text{-}C_6H_4)$ is obtained.[79] The reaction of an anionic dipyrrolide complex $\{[Ph_2C(C_4H_3N)_2]_2TaCl_2\}^-$ with MeLi afforded an anionic dimethyl derivative, $\{[Ph_2C(C_4H_3N)_2]_2TaMe_2\}^-$.[80] Reduction by $NaHBEt_3$ gave a mixture of $\{[Ph_2C(C_4H_3N)_2]Ta[(1,4\text{-}\eta^1;\eta^1\text{-}2,3\text{-}\eta^2\text{-}C_6H_7)(Ph)C(C_4H_3N)_2]\}^-$, (which is a product of the partial hydrogenation of aromatic ring and coordinates to the tantalum as an η^4-diene) and $\{[Ph_2C(C_4H_3N)_2]_3Ta\}^{2-}$.[80] Alkylation of a diamido-pyridine compound $Ta({=}N^tBu)Cl(py)[\kappa^3\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$[81] by $LiCH_2SiMe_3$, $LiCH(SiMe_3)_2$, MeLi, and (allyl)MgCl affords the corresponding monoalkyl complexes with κ^2- or κ^3-ligation of the diamido-pyridine ligand, $Ta({=}N^tBu)(CH_2SiMe_3)(py)[\kappa^3\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$, $Ta({=}N^tBu)(CH_2SiMe_3)(py)[\kappa^2\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$, $Ta({=}N^tBu)[CH(SiMe_3)_2](py)[\kappa^2\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$, $Ta({=}N^tBu)(Me)(py)\text{-}[\kappa^2\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$, and $Ta({=}N^tBu)(\eta^1\text{-allyl})(py)[\kappa^2\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$.[82–84] Diamido-donor ligands that contain the central nitrogen donor moieties can coordinate to the tantalum center. Trimethyl tantalum complexes *mer*-$TaMe_3[(ArNCH_2CH_2)_2NMe]$ and *fac*-$TaMe_3[(ArNCH_2)_2C(Me)Py]$ (Ar = C_6H_3-3,5-Cl_2) were prepared by the reaction of $TaCl_2Me_3$ with $Li_2[(ArNCH_2CH_2)_2NMe]$ and $Li_2[(ArNCH_2)_2C(Me)Py]$, respectively.[85] Monobenzyl and dibenzyl complexes of cyclometallated aryltantalum complexes such as $TaCl_3(C_6H_4\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)$, $TaCl_3(C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)$, $TaCl_2(C_6H_4\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)_2$, $TaCl_2(C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)_2$, $TaCl_2\{(R/S)\text{-}C_6H_4\text{-}2\text{-}CHMeNMe_2\}(CH_2Ph)_2$, and $TaCl_2(CH_2C_6H_4\text{-}2\text{-}NMe_2)(CH_2Ph)_2$ have been prepared.[86]

Fryzuk *et al.* have prepared a methyl complex with a multidentate nitrogen- and phosphine-containing ligand $^R[NPN]TaMe_3$ ($^R[NPN] = RP(CH_2SiMe_2NPh)_2$, R = Ph, Cy), by the reaction of $TaMe_3Cl_2$ with $Li_2(THF)_2\{^R[NPN]\}$.[87–89] Similarly, $[PhP(CH_2SiMe_2NSiMe_2)_2PPh]TaMe_3$ is prepared by the reaction of $TaMe_3Cl_2$ with $Li_2(dioxane)[PhP(CH_2SiMe_2NSiMe_2)_2PPh]$.[90] Photolysis of this trimethyl compound produces methylidene compound $[PhP(CH_2SiMe_2NSiMe_2)_2PPh]Ta({=}CH_2)Me$. Cationic and neutral dimethyl complexes $\{$*trans*-$TaMe_2[PhP(CH_2SiMe_2NSiMe_2)_2PPh]\}X$ (X = BF_4, $B(C_6F_5)_4$) and $Ta(F)Me_2[PhP(CH_2SiMe_2NSiMe_2)_2PPh]$ were reported.[90]

Porphyrins can serve as supporting ligands of tantalum alkyl complexes. Reaction of dilithium octaethylporphyrin and $TaCl_2Me_3$ gives $Ta(OEP)Me_3$ (Scheme 10).[91] One methyl group is removed by 1 equiv. of $[Me_2NHPh][BPh_4]$ to



Scheme 10

yield cationc dimethyl compound $[Ta(OEP)Me_2][BPh_4]$, which does not react with ethylene, acetone, or CO_2, but inserts CO into two Ta–Me bonds to give an enediolate compound. The monomethyl derivative can react with CO to give an acyl compound.[91]

5.03.3.1.5 Amidinate and guanidinate complexes

Amidinate and guanidinate have been used as supporting ligands for alkyltantalum compounds (Scheme 11). Advantages of these ligands are readily accessible and easy to handle, and, moreover, increase the solubility and stability of alkyl complexes. Bis(amidinate) alkyl complexes are usually synthesized by the reaction of soluble alkyl precursors $TaCl_2(CH_2R)_3$ (R = H and Ph) with $Li[ArC(NSiMe_3)_2]$ (Ar = Ph, Tol).[92] The other synthetic route to $TaMe_3[PhC(NSiMe_3)_2]$ is the reaction of Me_2Mg with $TaF_3[PhC(NSiMe_3)_2]$.[93] The addition of Ph_2Mg results in the formation of $Ta(F)Ph_2[PhC(NSiMe_3)_2]$ and $TaF_2Ph[PhC(NSiMe_3)_2]$.[93] Monobenzyl compound $Ta(NMe_2)_3(CH_2Ph)[(^iPrN)_2CN(SiMe_3)^iPr]$, where the guanidinate ligand acts as a monoanion, is obtained by the reaction of $Ta(NMe_2)_3Cl[(^iPrN)_2CN(SiMe_3)^iPr]$, which is obtained from the reaction of $Ta(NMe_2)_3[(^iPrN)_2C{=}N^iPr]$ with Me_3SiCl, with benzyl Grignard reagent.[94]

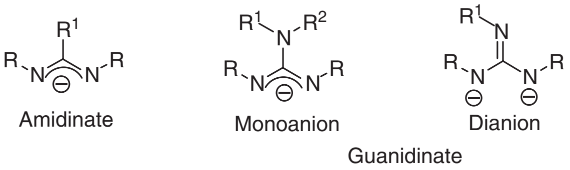
5.03.3.1.6 Silyl complexes

Silyl complexes have been extensively studied. Monosilyl complexes $(Me_2N)_3Ta(SiR_3)Cl$ and $(Me_2N)_4Ta(SiR_3)$ ($SiR_3 = Si(SiMe_3)_3$, $SiPh_2{}^tBu$) were prepared by the reaction of the corresponding chlorides with $LiSiR_3$.[95] Oxidation of $(Me_2N)_4Ta[Si(SiMe_3)_3]$ results in oxygen atom insertion into Ta–N and Ta–Si bonds, giving $(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)[OSi(SiMe_3)_3]$ (Scheme 12). Bis(silyl) compound $(Me_2N)_3Ta[Si(SiMe_3)_3]_2$ adopts a trigonal-bipyramidal structure with two silyl groups in axial positions.[96] Mononuclear imido disilyl complex $[(Me_3Si)_2N](Me_3SiN{=})\text{-}Ta(SiPh_2{}^tBu)_2$ was prepared by the reaction of $\{Ta(\mu\text{-}Cl)Cl({=}NSiMe_3)[N(SiMe_3)_2]\}_2$ with 4 equiv. of $Li(THF)_3SiPh_2{}^tBu$, while stepwise reaction with 2 equiv. of $LiNMe_2$ and 2 equiv. of $Li(THF)_3SiPh_2{}^tBu$ afforded an imido silyl complex, $(Me_2N)[(Me_3Si)_2N](Me_3SiN{=})Ta(SiPh_2{}^tBu)$ (Table 5).[97]

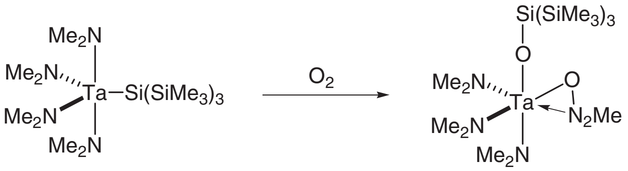
5.03.3.2 Alkyls, Aryls, and Related σ-donors Combined with Cp ligands

Treatment of $Cp'TaCl_4$ [$Cp' = \eta^5\text{-}C_5Me_5$, $\eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$] with Al_2Me_6 in toluene at −40 °C afforded monomethyl or dimethyl derivatives depending on the amounts of the aluminum compound.[114] $Cp^*TaCl_2R_2$ ($R = CH_2SiMe_3$, CH_2CMe_2Ph, CH_2CMe_3, CH_2Ph) can be prepared by treating Cp^*TaCl_4 with $2RMgX$ or R_2Mg.[115]

Cp^*TaMe_4 **31** has been utilized as a starting material, which reacts with various protic substrates or undergoes insertion reactions. Reaction of **31** with silanetriol at 130–140 °C affords tantalum siloxane complex **32** with methane evolution (Scheme 13).[116] Complex **31** reacts with a partially dehydroxylated silica at 700 °C to form $(surface{\equiv}SiO)TaCp^*Me_3$.[117]



Scheme 11



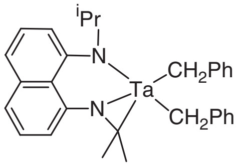
Scheme 12

Table 5 Alkyl, aryl, and related complexes without Cp ligands[a]

Compound	*Comments*	*References*
Homoleptic and halide complexes		
$\mathrm{Ta(CH_2C_6H_5)_5}$	Prep: $\mathrm{TaCl_5}$ + benzylMgCl, X-ray	59
$\mathrm{Ta(CH_2C_6H_4\text{-}4\text{-}Me)_5}$	Prep: $\mathrm{TaCl_2(CH_2C_6H_4\text{-}4\text{-}Me)_3 + Mg(CH_2C_6H_4\text{-}4\text{-}Me)_2}$, X-ray	58
$\mathrm{TaCl_2(CH_2C_6H_4\text{-}4\text{-}Me)_3}$	Prep: $\mathrm{TaCl_5 + Zn(CH_2C_6H_4\text{-}4\text{-}Me)_2}$	58
$\mathrm{Ta(CH_2SiMe_3)_5}$	Prep: $\mathrm{TaCl_2(CH_2SiMe_3)_3 + 2\ Me_3SiCH_2MgCl}$ at −78 °C	60
$\mathrm{\{Li({}^tBu_3SiC{\equiv}C)_3\}Ta(C{\equiv}CSi\mathit{t}Bu_3)_3}$	Prep: $\mathrm{TaCl_5 + 6Li(C{\equiv}CSi{}^tBu_3)}$, X-ray	61
$\mathrm{K[Ta(C{\equiv}CSi\mathit{t}Bu_3)_6]}$	Prep: $\mathrm{\{Li({}^tBu_3SiC{\equiv}C)_3\}Ta(C{\equiv}CSi\mathit{t}Bu_3)_3 + KOTf}$	61
$\mathrm{[K(crypt\ 2.2.2)][Ta(C{\equiv}CSi\mathit{t}Bu_3)_6]}$	X-ray	61
$\mathrm{TaF_2(CH_2R)_3}$	Prep: $\mathrm{TaCl_2(CH_2R)_3 + 2Bu_3SnF}$; R = Ph, *p*-Tol (X-ray), $\mathrm{SiMe_3}$	62
$\mathrm{TaCl_4[CH(SiMe_3)_2]}$	Prep: $\mathrm{TaCl_5 + 1/2\ Zn[CH(SiMe_3)_2]_2}$, X-ray	62
$\mathrm{TaF_4[CH(SiMe_3)_2]}$	Prep: $\mathrm{TaCl_4[CH(SiMe_3)_2] + Bu_3SnF}$, X-ray	62
$\mathrm{[(CH_3CN)(R)_3TaCl](\mu\text{-}1,\mathit{n}\text{-}NC_6H_4N)}$	Prep: $\mathrm{[TaCl_3(CH_3CN)_2]_2(\mu\text{-}1,\mathit{n}\text{-}NC_6H_4N) + 6RMgX}$; R = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2CMe_3}$, $\mathrm{CH_2CMe_2Ph}$	63
Alkoxo and aryloxo complexes		
$\mathrm{Ta(CH_2Ph)_3(L^1)}$	Prep: $\mathrm{Ta(CH_2C_6H_5)_5 + L^1H_2}$ (see Scheme 140), X-ray	59
$\mathrm{Ta(CH_2Ph)_2(L^2)}$	Prep: $\mathrm{Ta(CH_2C_6H_5)_5 + L^2H_3}$ (see Scheme 140), X-ray	59, 64, 65
$\mathrm{Ta(CH_2{}^tBu)_4(L^2H_2)}$	Prep: $\mathrm{Ta({=}CH{}^tBu)(CH_2{}^tBu)_3 + L^2H_3}$ (see Scheme 140), X-ray	65
$\mathrm{TaCl(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)_2}$	Prep: $\mathrm{TaCl_3((OC_6H_3\text{-}2,6\text{-}Ph_2)_2 + 2\ LiCH_2SiMe_3}$	66
$\mathrm{Ta(CH_2SiMe_3)_3(OC_6H_3\text{-}2,6\text{-}Ph_2)_2}$	Prep: $\mathrm{TaCl(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)_2 + LiCH_2SiMe_3}$	66
$\mathrm{Ta(CH_2SiMe_3)_3(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2}$	Prep: $\mathrm{TaCl_3(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2 + 3LiCH_2SiMe_3}$; R = H, Ph, Me; (X-ray), ^{i}Pr (X-ray)	66,68
$\mathrm{Ta(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)_3}$	Prep: $\mathrm{TaCl_2(OC_6H_3\text{-}2,6\text{-}Ph_2)_3 + 2\ LiCH_2SiMe_3}$, X-ray	66
$\mathrm{Ta[OC_6H_3\text{-}6\text{-}Ph\text{-}2\text{-}(C_6H_4\text{-}2)]\text{-}(CH_2SiMe_3)(OC_6H_3\text{-}2,6\text{-}Ph_2)_2}$	Prep: Thermolysis of $\mathrm{Ta(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)_3}$	66
$\mathrm{Ta[OC_6H_3\text{-}6\text{-}Ph\text{-}2\text{-}(C_6H_4\text{-}2)]\text{-}(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)}$	Prep: Thermolysis of $\mathrm{Ta({=}CHSiMe_3)(CH_2SiMe_3)(OC_6H_3\text{-}2,6\text{-}Ph_2)_2}$	66
$\mathrm{TaCl_2(CH_2Ph)(OC_6H\text{-}2,3,5,6\text{-}Ph_4)}$		67
$\mathrm{TaCl(CH_2Ph)_2(OC_6H\text{-}2,3,5,6\text{-}Ph_4)}$		67
$\mathrm{TaCl_2(CH_2SiMe_3)(OC_6H_3\text{-}2,6\text{-}Ph_2)}$	X-ray	67
$\mathrm{TaCl(CH_2SiMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)}$	X-ray	67
$\mathrm{TaCl_2(R)(OC_6H_3\text{-}2,6\text{-}Ph_2)}$	R = cyclopentyl (X-ray), cyclohexyl (X-ray)	67
$\mathrm{TaCl_2(cyclohexyl)(OC_6H\text{-}2,3,5,6\text{-}Ph_4)}$		67
$\mathrm{TaR_3}$[2,2′-ethylenebis(6-isopropylphenoxo)]	Prep: $\mathrm{TaCl_3}$[2,2′-ethylenebis(6-isopropylphenoxo)] + RMgCl; R = Me, $\mathrm{PhCH_2}$ (X-ray)	69
$\mathrm{TaR_2[(O_2C_{20}H_{12})\text{-}3,3'\text{-}(SiMe_3)_2]}$	Prep: $\mathrm{Ta(CH_2SiMe_3)_3(NMe_2)_2}$ + 3,3′-di(trimethylsilyl)-1,1′-bi-2,2′-naphthol or $\mathrm{[NH_2Et_2][TaCl_2(O_2C_{20}H_{12})\text{-}3,3'\text{-}(SiMe_3)_2] + 2RMgCl}$; R = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2Ph}$, *c*-$\mathrm{C_5H_9}$	70
$\mathrm{TaMe_3(O\text{-}C[Ad]Ar)_2}$	Prep: $\mathrm{TaMe_3Cl_2}$ + K O–C[Ad]Ar; Ad = 2-adamantylidene; Ar = $\mathrm{C_6H_3\text{-}3,5\text{-}Me_2}$ (X-ray), $\mathrm{C_6H_2\text{-}2,4,6\text{-}Me_3}$	71
$\mathrm{TaMe(py)(bipy)[O\text{-}C[Ad]C_6H_3\text{-}3,5\text{-}Me_2]_2}$	Prep: $\mathrm{TaMe_3[O{-}C[Ad]C_6H_3\text{-}3,5\text{-}Me_2]_2 + H_2}$ in pyridine, X-ray	71
$\mathrm{({}^tBu_3SiO)_2TaEt_2(N(CH_2)_3CH_2)}$	Prep: $\mathrm{({}^tBu_3SiO)_2TaCl_2(N(CH_2)_3CH_2) + 2\ EtMgCl}$	72
$\mathrm{({}^tBu_3SiO)_2TaMe_2(N(CH_2)_4CH_2)}$	Prep: $\mathrm{({}^tBu_3SiO)_2TaCl_2(N(CH_2)_4CH_2) + 2\ EtMgBr}$	72
$\mathrm{TaMe_2}${*p*-R-calix[4]arene-OMe}	Prep: $\mathrm{TaCl_2}${*p*-R-calix[4]arene-OMe} + MeLi	73, 74
$\mathrm{Ta(CH_2Ph)_2}${*p*-R-calix[4]arene-OMe}	Prep: $\mathrm{TaCl_2}${*p*-R-calix[4]arene-OMe} + $\mathrm{(PhCH_2)Mg}$, X-ray	73, 74
$\mathrm{Ta(C_6H_4\text{-}4\text{-}Me)_2}${*p*-R-calix[4]arene-OMe}	Prep: $\mathrm{TaCl_2}${*p*-R-calix[4]arene-OMe} + $\mathrm{2ClMg(C_6H_4\text{-}4\text{-}Me)}$	73, 74
{TaR[*p*-R-calix[4]arene]}$_2$	Prep: demethylation of $\mathrm{TaR_2}${*p*-R-calix[4]arene-OMe} in pyridine or alkylation of {TaCl[*p*-R-calix[4]arene]}$_2$; R = Me, $\mathrm{CH_2Ph}$, $\mathrm{C_6H_4\text{-}4\text{-}Me}$ (X-ray)	73, 74
$\mathrm{Ta(C_6H_4\text{-}4\text{-}Me)_2}${*p*-R-calix[4]arene-OMe}	Prep: $\mathrm{TaCl_2}${*p*-R-calix[4]arene-OMe} + 2LiCCPh	73
$\mathrm{({}^tBu_3SiO)_3Ta(H)(CH_2CH_3)}$	Prep: $\mathrm{({}^tBu_3SiO)_3Ta(H)_2 + C_2H_4}$	98, 99
$\mathrm{({}^tBu_2PhSiO)_3TaMe_2}$	Prep: $\mathrm{({}^tBu_2PhSiO)_3TaCl_2 + MeMgBr}$	100

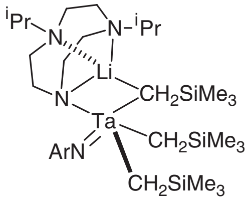
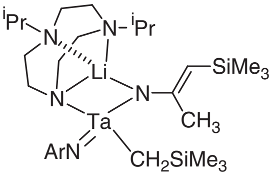
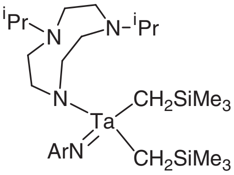
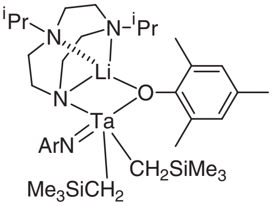
(*Continued*)

Table 5 (Continued)

Compound	*Comments*	*References*
$(^tBu_3SiO)_3Ta(H)(CH_2CH_2CH_3)$	Prep: $(^tBu_3SiO)_3Ta(H)_2 + C_3H_6$	99
$(^tBu_3SiO)_2(H)$ $Ta(OSi(^tBu)_2C(Me)_2CH_2)$	Prep: thermolysis of $(^tBu_3SiO)_3Ta(H)_2$ or $(^tBu_3SiO)_3Ta + {}^tBu_3PO$ at 85 °C	98, 101, 102
$[(^tBu_3SiO)_2Ta(Et)]_2(\mu\text{-}O)_2$	Prep: $[(^tBu_3SiO)_2TaH]_2(\mu\text{-}O)_2 + C_2H_4$	98
$[(^tBu_3SiO)_2TaH(C_2H_5)]_2$	Prep: $[(^tBu_3SiO)_2TaH_2]_2 + C_2H_4$	103
$[(^tBu_3SiO)_2TaH(C_2H_5)](\mu\text{-}H)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2H_3)[Ta(^tBu_3SiO)_2]$	Prep: $[(^tBu_3SiO)_2TaH(C_2H_5)]_2 + C_2H_4$, X-ray	103
$[(^tBu_3SiO)_3Ta(H)](\mu\text{-}OCH_2CH_2CH_2CH_2)[Ta(H)\text{-}(^tBu_3SiO)_3]$	Prep: $(^tBu_3SiO)_3Ta(H)I$ + Na/Hg in THF	98
Amido and imido complexes		
$[(Me_3SiNCH_2CH_2)_2N]TaMe_2$	Prep: $TaMe_5 + (Me_3SiNHCH_2CH_2)_2NH$	75
$[(C_6F_5NCH_2CH_2)_2NH]TaMe_3$	Prep: $TaMe_5 + (C_6F_5NHCH_2CH_2)_2NH$	75
$[(C_6F_5NCH_2CH_2)_2N]TaMe_2$	Prep: $TaMe_5 + (C_6F_5NHCH_2CH_2)_2NH$	75
$[(Me_3SiN\text{-}2\text{-}C_6H_4)_2N]TaMe_2$	Prep: $TaMe_5 + (Me_3SiNH\text{-}2\text{-}C_6H_4)_2NH$	75
$TaMe_3[ArN(CH_2)_3NAr]$	Prep: $TaCl_5$, $ArNH(CH_2)_3NHAr$ ($Ar = C_6H_3\text{-}2,6\text{-}{}^iPr_2$), and 5MeMgBr	76
$[\eta^3\text{-}(Me_2CN)(\mathit{i}PrN)C_{10}H_6]Ta\text{-}(CH_2Ph)_2$  	Prep: $\{[\eta^3\text{-}(Me_2CN)(\mathit{i}PrN)C_{10}H_6]TaCl\}_2(\mu\text{-}Cl)_2 + 4PhCH_2MgCl$	77
$(ArN{=})(ArNH)Ta(CH_2{}^tBu)_2$	Prep: $(ArN{=})(ArNH)TaCl_2$ + 3 $LiCH_2^tBu$; $Ar = 2,6\text{-}Mes_2C_6H_3$, X-ray	78
$(ArN{=})(ArNH)TaMe_2(PMe_3)$	Prep: $(ArN{=})(ArNH)TaMe_2 + PMe_3$; $Ar = 2,6\text{-}Mes_2C_6H_3$	78
$(ArN{=})(ArNH)TaMe_2$	Prep: $TaMe_3Cl_2 + 2LiNHAr$; $Ar = 2,6\text{-}Mes_2C_6H_3$, X-ray	104, 78
$(ArN{=})(ArNH)TaMe(OTf)$	Prep: $(ArN{=})(ArNH)TaMe_2 + AgOTf$; $Ar = 2,6\text{-}Mes_2C_6H_3$	104, 78
$(ArN{=})(ArNH)Ta(hexane)(OTf)$	Prep: $(ArN{=})(ArNH)Ta(H)(OTf)$ + 1-hexene; $Ar = 2,6\text{-}Mes_2C_6H_3$	104, 78
$(^tBu_3SiNH)Me_2Ta({=}NSi^tBu_3)$	Prep: $Me_3TaCl_2 + 2LiNHSi^tBu_3$	79
$(L)_2MeTa({=}NSi^tBu_3)_2$	Prep: thermolysis of $(^tBu_3SiNH)Me_2Ta({=}NSi^tBu_3)$ in THF or Py; L = THF, Py (X-ray)	79
$(^tBu_3SiNH)_2MeTa({=}NSi^tBu_3)$	Prep: $(^tBu_3SiNH)_2ClTa({=}NSi^tBu_3) + AlMe_3$	79
$(^tBu_3SiNH)_2PhTa({=}NSi^tBu_3)$	Prep: $(^tBu_3SiNH)_2ClTa({=}NSi^tBu_3) + PhLi$	79
$(^tBu_3SiNH)_2(PhCH_2)Ta({=}NSi^tBu_3)$	Prep: $(^tBu_3SiNH)_2ClTa({=}NSi^tBu_3) + PhCH_2K$	79
$(^tBu_3SiNH)_2(^tBuCH_2)Ta({=}NSi^tBu_3)$	Prep: $(^tBu_3SiNH)_2ClTa({=}NSi^tBu_3) + {}^tBuCH_2Li$	79
$(^tBu_3SiNH)(^tBu_3SiO)Me\text{-}Ta({=}NSi^tBu_3)$	Prep: $(^tBu_3SiNH)_2MeTa({=}NSi^tBu_3) + {}^tBuSiOH$	79
$[(^tBu_3SiNH)_2Ta({=}NSi^tBu_3)](\mu\text{-}\eta^1\text{:}\eta^1\text{-}1,4\text{-}C_6H_4)$	Prep: thermolysis of $(^tBu_3SiNH)_2RTa({=}NSi^tBu_3)$ in benzene	79
$\{[Ph_2C(C_4H_3N)_2]_2TaMe_2\}^-$	Prep: $\{[Ph_2C(C_4H_3N)_2]_2TaCl_2\}^- + MeLi$, X-ray	80
$Ta({=}N^tBu)(CH_2SiMe_3)(py)[\kappa^3\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$	Prep: $Ta({=}N^tBu)Cl(py)[\kappa^3\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2] + LiCH_2SiMe_3$	83
$Ta({=}N^tBu)(CH_2SiMe_3)(py)[\kappa^2\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$		
$Ta({=}N^tBu)[CH(SiMe_3)_2](py)[\kappa^2\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$	Prep: $Ta({=}N^tBu)Cl(py)[\kappa^3\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2] + LiCH(SiMe_3)_2$	83
$Ta({=}N^tBu)(Me)(py)[\kappa^2\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$	Prep: $Ta({=}N^tBu)Cl(py)[\kappa^3\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2] + MeLi$	84
$Ta({=}N^tBu)(\eta^1\text{-allyl})(py)[\kappa^2\text{-}MeC\text{-}(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$	Prep: $Ta({=}N^tBu)Cl(py)[\kappa^3\text{-}MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]$ + allylMgCl	84
$TaMe_3[(ArNCH_2CH_2)_2NMe]$	Prep: $TaCl_2Me_3 + Li_2[(ArNCH_2CH_2)_2NMe]$; $Ar = C_6H_3\text{-}3,5\text{-}Cl_2$, X-ray	85
$TaMe_3[(ArNCH_2)_2C(Me)Py]$	Prep: $TaCl_2Me_3 + Li_2[(ArNCH_2)_2C(Me)Py]$; $Ar = C_6H_3\text{-}3,5\text{-}Cl_2$, X-ray	85
$TaCl_3(C_6H_4\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)$	Prep: $TaCl_4(C_6H_4\text{-}2\text{-}CH_2NMe_2)$ + 1/2 $Zn(CH_2Ph)_2$	86
$TaCl_2(C_6H_4\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)_2$	Prep: $TaCl_4(C_6H_4\text{-}2\text{-}CH_2NMe_2) + Zn(CH_2Ph)_2$, X-ray	86
$TaCl_3(C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)$	Prep: $TaCl_4(C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}CH_2NMe_2)$ + 1/2 $Zn(CH_2Ph)_2$	86

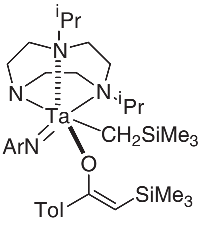
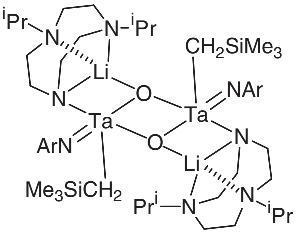
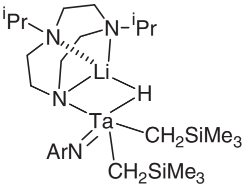
(*Continued*)

Table 5 (Continued)

Compound	*Comments*	*References*
$\mathrm{TaCl_2(C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}CH_2NMe_2)(CH_2Ph)_2}$	Prep: $\mathrm{TaCl_3(CH_2Ph)_2 + 1/2\ Zn(C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}CH_2NMe_2)_2}$	86
$\mathrm{TaCl_2\{(\mathit{R/S})\text{-}C_6H_4\text{-}2\text{-}CHMeNMe_2\}(CH_2Ph)_2}$	Prep: $\mathrm{TaCl_3(CH_2Ph)_2 + 1/2\ Zn\{(\mathit{R/S})\text{-}C_6H_4\text{-}2\text{-}CHMeNMe_2\}_2}$	86
$\mathrm{TaCl_2(CH_2C_6H_4\text{-}2\text{-}NMe_2)(CH_2Ph)_2}$	Prep: $\mathrm{TaCl_3(CH_2Ph)_2 + 1/2\ Zn\{CH_2C_6H_4\text{-}2\text{-}NMe_2\}_2}$	86
$\mathrm{TaCl_2(1\text{-}C_{10}H_6\text{-}8\text{-}NMe_2)(CH_2Ph)_2}$	Prep: $\mathrm{TaCl_3(CH_2Ph)_2 + Li(1\text{-}C_{10}H_6\text{-}8\text{-}NMe_2)}$	86
$\mathrm{^R[NPN]TaMe_3}$	Prep: $\mathrm{TaMe_3Cl_2 + Li_2(THF)_2\{^R[NPN]\}}$; $\mathrm{^R[NPN] = RP(CH_2SiMe_2NPh)_2}$; R = Ph (X-ray), Cy	87–89
$\mathrm{\{^R[NPN](propyl)Ta\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)}$	Prep: $\mathrm{\{^R[NPN]Ta\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)(\mu\text{-}H)_2}$ + propene; R = Ph (X-ray)	89
$\mathrm{[PhP(CH_2SiMe_2NSiMe_2)_2PPh]TaMe_3}$	Prep: $\mathrm{TaMe_3Cl_2 + Li_2(dioxane)[PhP(CH_2SiMe_2NSiMe_2)_2PPh]}$, X-ray	90
$\mathrm{Ta(F)Me_2[PhP(CH_2SiMe_2NSiMe_2)_2PPh]}$	Prep: $\mathrm{\{\mathit{trans}\text{-}TaMe_2[PhP(CH_2SiMe_2NSiMe_2)_2PPh]\}(BF_4)}$ + base	90
$\mathrm{Ta(OEP)Me_3}$	Prep: $\mathrm{TaCl_2Me_3 + Li_2(OEP)}$	91
$\mathrm{Ta(NMe_2)_3(CH_2Ph)[(^iPrN)_2CN(SiMe_3)^iPr]}$	Prep: $\mathrm{Ta(NMe_2)_3Cl[(^iPrN)_2CN(SiMe_3)^iPr] + PhCH2MgCl}$, X-ray	94
$\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaMe_2}$	Prep: $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaCl_2 + 2\ MeLi}$	105
$\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaMe(OTf)}$	Prep: $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaMe_2 + [Cp_2Fe][OTf]}$, X-ray	105
$\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaMeCl}$	Prep: $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaMe(OTf) + NEt_4Cl}$	106
$\mathrm{[(Me_3SiNCH_2CH_2)_3N]Ta(Et)Cl}$	Prep: $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaCl_2 + EtMgCl}$	106
$\mathrm{[(Me_3SiNCH_2CH_2)_3N]Ta(Et)Me}$	Prep: $\mathrm{[(Me_3SiNCH_2CH_2)_3N]Ta(Et)Cl_2 + MeMgCl}$, X-ray	106
$\mathrm{[(Me_3SiNCH_2CH_2)_2N]\text{-}[N(CH{=}CH_2)SiMe_3]Ta(R)}$	Prep: $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaCl_2 + 2RMgX}$; R = $\mathrm{^nPr}$, $\mathrm{^nBu}$, isopentyl, neohexyl	106
$\mathrm{[(Et_3SiNCH_2CH_2)_2N]\text{-}[N(CH{=}CH_2)SiEt_3]TaMe}$	Prep: thermolysis of $\mathrm{[(Et_3SiNCH_2CH_2)_3N]TaMe_2}$	107
$\mathrm{[(Et_3SiNCH_2CH_2)_2N]\text{-}[N(CH{=}CH_2)SiEt_3]TaEt}$	Prep: thermolysis of $\mathrm{[(Et_3SiNCH_2CH_2)_3N]Ta(\eta^2\text{-}CH_2{=}CH_2)}$, X-ray	107
$\mathrm{(Me_3SiCH_2)_2[(C_6H_3\text{-}2,6\text{-}^iPr_2)N{=}]Ta(\mu\text{-}CH_2SiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^iPr_2\text{-}TACN)}$ 	Prep: $\mathrm{[(C_6H_3\text{-}2,6\text{-}^iPr_2)N{=}]Ta\ (^iPr_2\text{-}TACN) + 3Me_3SiCH_2Li}$, X-ray	108
	Prep: $\mathrm{(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^iPr_2\text{-}TACN) + CH_3CN}$	109
	Prep: $\mathrm{(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^iPr_2\text{-}TACN) + PyHCl}$	109
	Prep: $\mathrm{(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^iPr_2\text{-}TACN) + C_6H_2\text{-}2,4,6\text{-}Me_2\text{-}OH}$	109

(Continued)

Table 5 (Continued)

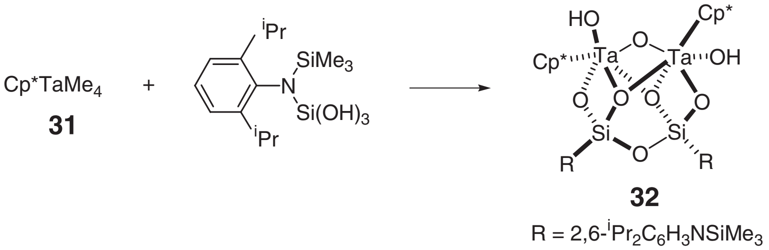
Compound	*Comments*	*References*
	Prep: $(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}{}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe3)(\mu\text{-}\eta^1{:}\eta^3\text{-}{}^iPr_2\text{-}TACN) + TolCOCl$	109
	Prep: $(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}{}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe3)(\mu\text{-}\eta^1{:}\eta^3\text{-}{}^iPr_2\text{-}TACN) + Ph_2CO$	110
	Prep: $(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}{}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe3)(\mu\text{-}\eta^1{:}\eta^3\text{-}{}^iPr_2\text{-}TACN) + H_2$	109
$\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaMe_3$	Prep: $\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl_3 + 3MeMgBr$	111
$Cp^*TaMe_3(SC_6H_7N_2)$	Prep: Cp^*TaMe_4 + 2-mercapto-4,6-dimethylpyrimidine $HSC_6H_7N_2$	112
Amidinate and guanidinate complexes		
$[ArC(NSiMe_3)_2]_2TaR_3$	Ar = Ph, Tol; R = Me, CH_2Ph, X-ray for Ar = Tol and R = Me	92
$[PhC(NSiMe_3)_2]_2TaMe_2(OTf)$	X-ray	92
$[PhC(NSiMe_3)_2]TaMe_3$	Prep: $TaF_3[PhC(NSiMe_3)_2]$ + ex. Me_2Mg	93
$[TolC(NSiMe_3)_2]TaMe({=}O)$	Prep: $[TolC(NSiMe_3)_2]TaMe({=}CH_2)$ + pyridine N-oxide	113
$[PhC(NSiMe_3)_2]Ta(F)Ph_2$	Prep: $TaF_3[PhC(NSiMe_3)_2] + 1.5\ Ph_2Mg$, 4 h	93
$[PhC(NSiMe_3)_2]TaF_2Ph$	Prep: $TaF_3[PhC(NSiMe_3)_2] + 1.5\ Ph_2Mg$, 2 days, X-ray	93
Cationic alkyl complexes		
$\{TaMe_2[ArNH(CH_2)_3NHAr]\}[MeB(C_6F_5)_3]$	Prep: $TaMe_3[ArNH(CH_2)_3NHAr]$ and $B(C_6F_5)_3$	76
$\{TaMe_2[ArNH(CH_2)_3NHAr]\}[(C_6F_5)_3AlMeAl(C_6F_5)_3]$	Prep: $TaMe_3[ArNH(CH_2)_3NHAr]$ and $2Al(C_6F_5)_3$	76
$\{TaMe_2[ArNH(CH_2)_3NHAr]\}[(C_6F_5)_3AlMeAl(C_6F_5)_3]$	Prep: $TaMe_3[ArNH(CH_2)_3NHAr]$ and $2Al(C_6F_5)_3$	76
$\{[PhC(NSiMe_3)_2]_2TaMe_2\}[BPh_4]$	Prep: $[PhC(NSiMe_3)_2]_2TaMe_3 + Me_2NPhHBPh_4$	92
$[Ta(OEP)Me_2][BPh_4]$	Prep: $Ta(OEP)Me_3 + Me_2NPhHBPh_4$	91
$[Ta(OEP)Me(O^tBu)][BPh_4]$	Prep: $[Ta(OEP)Me_2][BPh_4] + {}^tBuOH$	91
$[(ArN{=})(ArNH)TaMe][MeB(C_6F_5)_3]$	Prep: $(ArN{=})(ArNH)TaMe_2 + B(C_6F_5)_3$; Ar = 2,6-$Mes_2C_6H_3$	104, 78
$\{trans\text{-}TaMe_2\text{-}[PhP(CH_2SiMe_2NSiMe_2)_2PPh]\}\text{-}(BF_4)$	Prep: $[PhP(CH_2SiMe_2NSiMe_2)_2PPh]TaMe_3 + [Ph_3C][BF_4]$	90
$\{trans\text{-}TaMe_2\text{-}[PhP(CH_2SiMe_2NSiMe_2)_2PPh]\}[B(C_6F_5)_4]$	Prep: $[PhP(CH_2SiMe_2NSiMe_2)_2PPh]TaMe_3 + [PhNMe_2H][B(C_6F_5)_4]$	90
$[(Me_3SiNCH_2CH_2)_2NAl^-Me_3]\text{-}Ta^+Me_2$	Prep: $[(Me_3SiNCH_2CH_2)_2N]TaMe_2 + AlMe_3$, X-ray	75
$\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}\text{-}[MeB(C_6F_5)_3]$	Prep: $[(C_6F_5NCH_2CH_2)_2NH]TaMe_3 + B(C_6F_5)$, X-ray	75

(Continued)

Table 5 (Continued)

Compound	*Comments*	*References*
Silyl complexes		
$(Me_2N)_3Ta(SiR_3)Cl$	Prep: $(Me_2N)_3TaCl_2 + LiSiR_3$; $SiR_3 = Si(SiMe_3)_3$ (X-ray), $SiPh_2{}^tBu$ (X-ray)	95, 96
$(Me_2N)_4Ta(SiR_3)$	Prep: $(Me_2N)_4TaCl + LiSiR_3$; $SiR_3 = Si(SiMe_3)_3$, $SiPh_2{}^tBu$ (X-ray)	95
$(Me_2N)_3Ta[Si(SiMe_3)_3]_2$	Prep: $(Me_2N)_3TaCl_2 + 2LiSi(SiMe_3)_3$	96
$[(Me_3Si)_2N](Me_3SiN{=})Ta(SiPh_2{}^tBu)_2$	Prep: $\{Ta(\mu\text{-}Cl)Cl({=}NSiMe_3)[N(SiMe_3)_2]\}_2 + 4Li(THF)_3SiPh_2{}^tBu$	97
$(Me_2N)[(Me_3Si)_2N](Me_3SiN{=})Ta(SiPh_2{}^tBu)$	Prep: $\{Ta(\mu\text{-}Cl)Cl({=}NSiMe_3)[N(SiMe_3)_2]\}_2 + 2LiNMe_2 + 2Li(THF)_3SiPh_2{}^tBu$	97
$(ArN{=})(ArNH)Ta(SiR_3)Cl$	Prep: $(ArN{=})(ArNH)TaCl_2 + LiSiR_3$; $SiR_3 = Si(SiMe_3)_3$, $SiPh_2({}^tBu)$, $SiHMes_2$; Ar = 2,6-$Mes_2C_6H_3$	78

[a] $Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

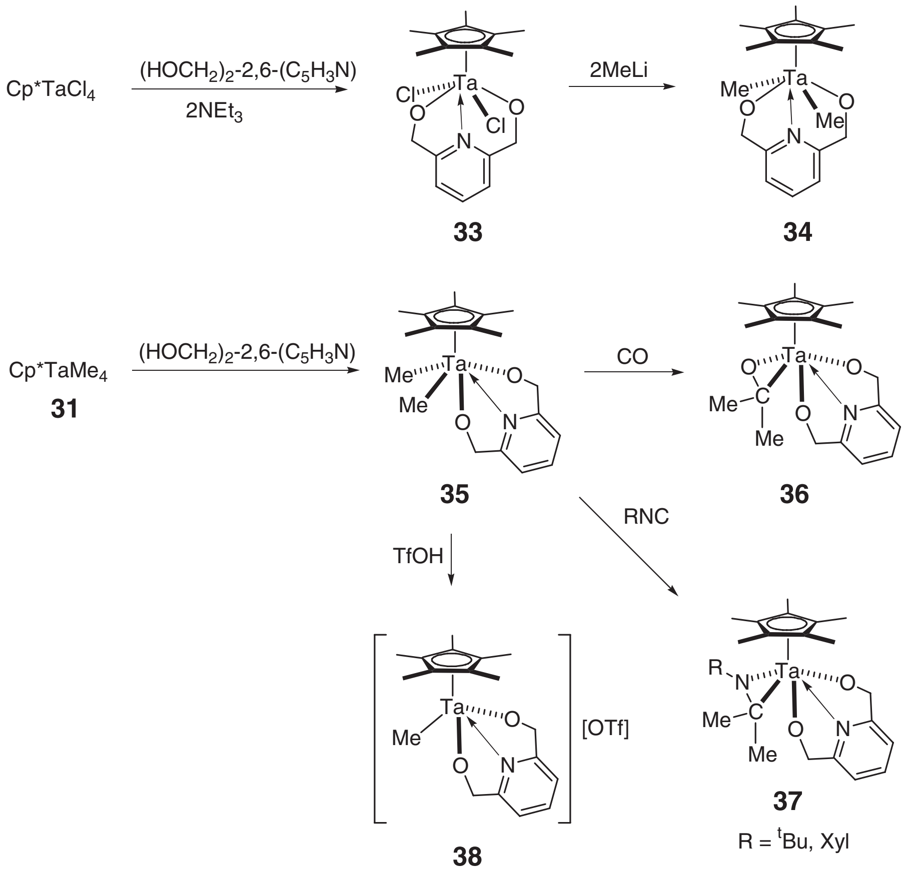


Scheme 13

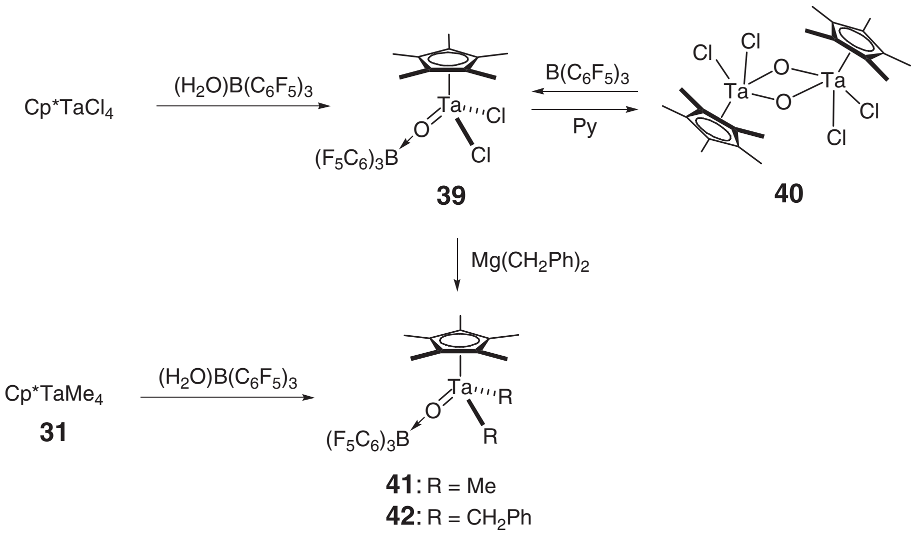
Reaction of **31** with 2-mercapto-4,6-dimethylpyrimidine ($HSC_6H_7N_2$) in toluene produces $Cp^*TaMe_3(SC_6H_7N_2)$.[112] Di-2-pyridyl ketone inserted into a Ta–Me bond of **31** to give an alkoxo complex, $Cp^*TaMe_3(OCMePy_2)$.[118] The dialkoxide ligand bearing pyridine skeleton is a tridentate meridional ligand, which coordinates in a pincer fashion to the metal center (Scheme 14). Reaction of **31** with 2,6-di(hydroxymethyl)pyridine gives *cis*-$Cp^*TaMe_2[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]$ **35**, while its *trans*-derivative **34** can be derived from the alkylation of a dichloro compound.[119] These two complexes showed a difference in reactivity to carbonylation: the *trans*-isomer **34** does not react, while the *cis*-isomer **35** smoothly reacts with atmospheric pressure of carbon monoxide to give an η^2-acetone complex, $Cp^*Ta(\eta^2\text{-}Me_2CO)[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]$ **36**.[119] The similar insertion reaction of isocyanide affords an azatantalacyclopropane complex, $Cp^*Ta(\eta^2\text{-}Me_2C{=}NR)[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]$ (R = ${}^tBu$, $C_6H_3\text{-}2,6\text{-}Me_2$) **37**.[119] Both reactions proceed through acyl or iminoacyl intermediates. Reaction of **35** with triflic acid in acetonitrile affords a cationic methyl complex **38**.

Half-sandwich oxo-chloro compounds have a tendency to make dinuclear or polynuclear oxo-bridged structure. Although unstable dibromo and diiodo tantalum compounds, $Cp^*TaX_2({=}O)$, have been characterized to be mononuclear, the corresponding dichloro compound has been found to be an oxo-bridged dinuclear compound. Royo *et al.* used bulky Lewis acid to stabilize the mononuclear oxo compounds (Scheme 15). Treatment of Cp^*TaMe_4 **31** with $(H_2O)B(C_6F_5)_3$, a unique oxo-transfer reagent, cleanly afforded $Cp^*TaMe_2(\mu\text{-}O)B(C_6F_5)_3$ **41**. The analogous dibenzyl compound $Cp^*Ta(CH_2Ph)_2(\mu\text{-}O)B(C_6F_5)_3$ **42** was also prepared by treating $Cp^*TaCl_2(\mu\text{-}O)B(C_6F_5)_3$ **39** with $Mg(CH_2Ph)_2(THF)_2$.[120]

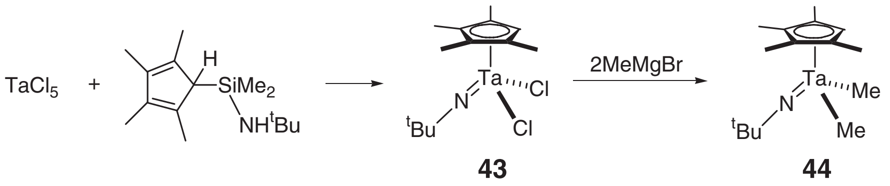
Imido alkyls of half-sandwich complexes are isoelectronic and have frontier orbitals similar to alkylmetallocene complexes of group 4 metals. Treatment of $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}{}^iPr_2)Cl_2$ with an excess of methyl Grignard reagent afforded $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}{}^iPr_2)Me_2$ in good yield.[121] Imido dimethyl complex, $(\eta^5\text{-}C_5Me_4H)TaMe_2({=}N^tBu)$ **44** was derived from the reaction of the corresponding dichloride **43**, which is an unprecedented product of the reaction of $TaCl_5$ with $(C_5Me_4H)SiMe_2(NH^tBu)$, a constrained-geometry ligand (Scheme 16).[76] In contrast to the C–Si bond cleavage, the reaction of $(C_5H_5)SiMe_2(NHPh)$ with $Ta(NMe_2)_5$ produces a constrained geometry catalyst (CGC)-type compound, $[\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NPh]Ta(NMe_2)_3$, which turns to an imido compound, $[\eta^5\text{-}C_5H_4SiMe_2(NMe_2)]Ta({=}NPh)(NMe_2)_2$, after photochemical Si–N bond cleavage.[122] Upon activation with



Scheme 14



Scheme 15

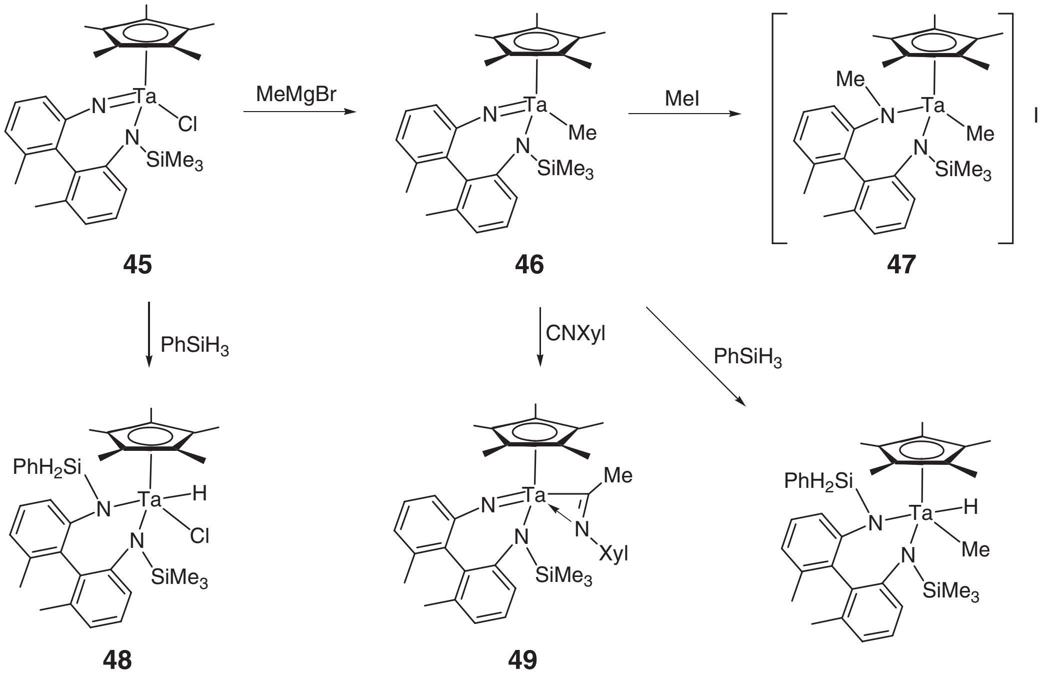


Scheme 16

aluminum imidazolide $[HNMe(C_{18}H_{37})_2]$-$[(C_6F_5)_3Al(\mu\text{-}C_3H_3N_2)Al(C_6F_5)_3]$, **44** becomes a catalyst for co-polymerization of ethylene and 1-octene.[76]

Imido mono- and dialkyl compounds $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}Me_2)(R)Cl$ ($R = CH_2SiMe_3$, CH_2CMe_2Ph, $C_6H_4\text{-}2\text{-}CH_2NMe_2$, CH_2Ph, $CH_2{}^tBu$), $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}Me_2)R_2$ ($R = CH_2SiMe_3$, CH_2CMe_2Ph, C_6H_5, CH_2Ph, $CH_2{}^tBu$), and $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}Me_2)(R)Me$ ($R = CH_2SiMe_3$, CH_2CMe_2Ph, $C_6H_4\text{-}2\text{-}CH_2NMe_2$, CH_2Ph, $CH_2{}^tBu$, C_6H_5) are directly obtained by treating $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}Me_2)Cl_2$ or $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}Me_2)Cl(Me)$ with alkylating reagents.[123] Tantalum methyl complexes with chelating imido–amido ligands have been reported.[124] As summarized in Scheme 17, the methyl compound $Cp^*\ \overline{Ta[{=}N(C_6H_3Me)_2N}SiMe_3]Me$ **46**, which is derived from the methylation of the corresponding monocloride **45**, reacts with methyl iodide and phenylsilane at the nucleophilic imido nitrogen atom to give a cationic **47** and methyl hydride compounds **48**, respectively. Reaction of **46** with xylylisonitrile resulted in the formation of iminoacyl **49**.

Thermolysis of $Cp^*TaMe(NH^tBu)({=}N^tBu)$ generates "$Cp^*Ta({=}N\textit{t}Bu)_2$," which can be trapped by benzene or toluene to give the corresponding compounds $Cp^*Ta({=}N^tBu)(NH^tBu)(Ph)$ and $Cp^*Ta({=}N^tBu)(NH^tBu)(C_6H_4Me)$ via C–H bond activation.[55] $Cp^*Ta({=}N^tBu)(NH^tBu)(Me)$ and $Cp^*Ta({=}N^tBu)(NMe_2)(Me)$ react with carbon dioxide to give carbamate compounds $Cp^*Ta({=}N^tBu)(O_2CNH^tBu)(Me)$ and $Cp^*Ta({=}N^tBu)(O_2CNMe_2)(Me)$.[125] XylNC can insert into the methyl–Ta bond to give η^2- or η^1-iminoacyl compounds, namely $Cp^*Ta({=}N^tBu)(\eta^1\text{-}O_2CNMe_2)(\eta^2\text{-}CMe{=}NXyl)$, $Cp^*Ta({=}N^tBu)(\eta^1\text{-}O_2CNH^tBu)(\eta^2\text{-}CMe{=}NXyl)$ and $Cp^*Ta({=}N^tBu)(\eta^2\text{-}O_2CNH^tB)(\eta^1\text{-}CMe{=}NXyl)$.[125]



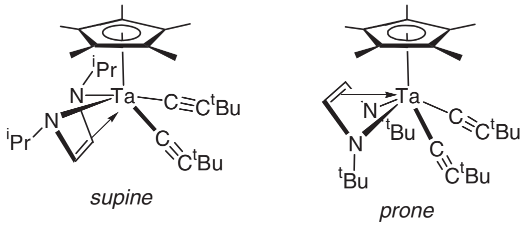
Scheme 17

The dilithium salt of triphenyltriazamethylenemethane reacts with $Cp^*TaMe_2Cl(OTf)$ to give $Cp^*TaMe_2[\eta^2$-*N*,*N*′-$C(NPh)_3]$.[126] Amidinate complex $Cp^*Ta[MeC(N^iPr)_2]Me_3$ has a pseudo-octahedral geometry and the orientation of the amidinate NCN plane is perpendicular to that of Cp^* ligand.[127] The *ansa*-type monomethyl imido compound *ansa*-$[\eta^5:\eta^5-(C_5H_4)_2CMe_2]Ta(=N^tBu)Me$ was obtained by the reaction of the corresponding chloride with MeLi.[128]

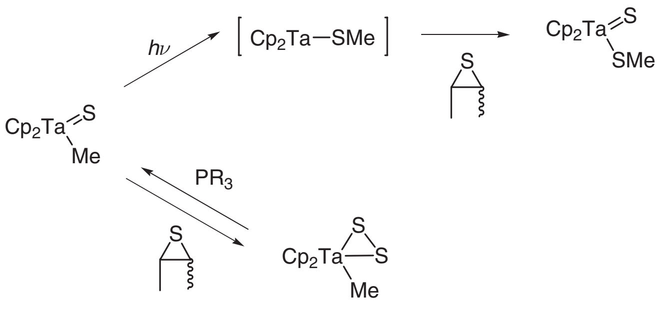
Reactions of dichloro-1,4-diazadiene compounds $Cp^*TaCl_2(\eta^4$-*supine*-$^iPrN{=}CHCH{=}N^iPr)$ and $Cp^*TaCl_2(\eta^4$-*prone*-$^tBuN{=}CHCH{=}N^tBu)$ with 2 equiv. of $LiC{\equiv}C^tBu$ gave the corresponding diacetylide complexes in keeping with the orientation of the DAD ligand, while the methylation of both compounds resulted in the selective formation of prone-dimethyl complexes, $Cp^*TaMe_2(\eta^4$-*prone*-$RN{=}CHCH{=}NR)$ ($R = {}^iPr, {}^tBu$) (Scheme 18).[129]

Irradiation of $Cp_2Ta(C_2H_4)Me$ **50** or thermolysis of $Cp_2Ta(PMe_3)Me$ **51** cleanly generates an intermediate species "Cp_2TaMe," which efficiently abstracts heteroatoms from oxiranes, thiiranes, and aziridines to give $Cp_2Ta(=X)Me$ ($X = O$, S, NR) with retention of stereochemistry of the alkenes produced.[130–133] The reaction of **50** and **51** with azoarene produced imido complex $Cp_2Ta(=NAr)Me$ together with η^2-diazene complex, $Cp_2Ta(\eta^2\text{-NAr–NAr})Me$, which does not convert to the imido complex.[134] Further treatment of $Cp_2Ta(=S)Me$ with thiirane in the dark gave $Cp_2Ta(\eta^2-S_2)Me$, which upon treatment with phosphine regenerated $Cp_2Ta(=S)Me$ along with $S{=}PR_3$, while photolysis of $Cp_2Ta(=S)Me$ in the presence of thiirane afforded a different product, that is, $Cp_2Ta(=S)(SMe)$, presumably through the intramolecular migration of a methyl group to the sulfur ligand (Scheme 19).[132,133] In contrast, photolysis of $Cp_2Ta(C_2H_4)Me$ in the presence of half an equivalent of thiiranes or $S{=}PMe_3$ results in the formation of $Cp_2MeTa(\mu-S)TaCp_2Me$.[132] Treatment of **51** with PhN_3 affords the terminal phenyl azide complex $Cp_2Ta(=N–N=NPh)Me$,[135] whose thermolysis causes evolution of N_2 and the formation of imido complex $Cp_2Ta(=NPh)Me$, via the intramolecular coordination of the Nγ-atom to the tantalum center with the extrusion of N_2.[135] The intramolecular thermal isomerization of $Cp^*{}_2Ta(\eta^2-TeCH_2)(H)$ results in the formation of a methyl complex, $Cp^*{}_2Ta(=Te)Me$.[136] Cationic alkyl complex $[Cp_2TaMe_2][(C_6F_5)_3AlMeAl(C_6F_5)_3]$ shows catalytic activity for syndiospecific methyl methacrylate (MMA) polymerization but is inactive for olefin polymerization.[76]

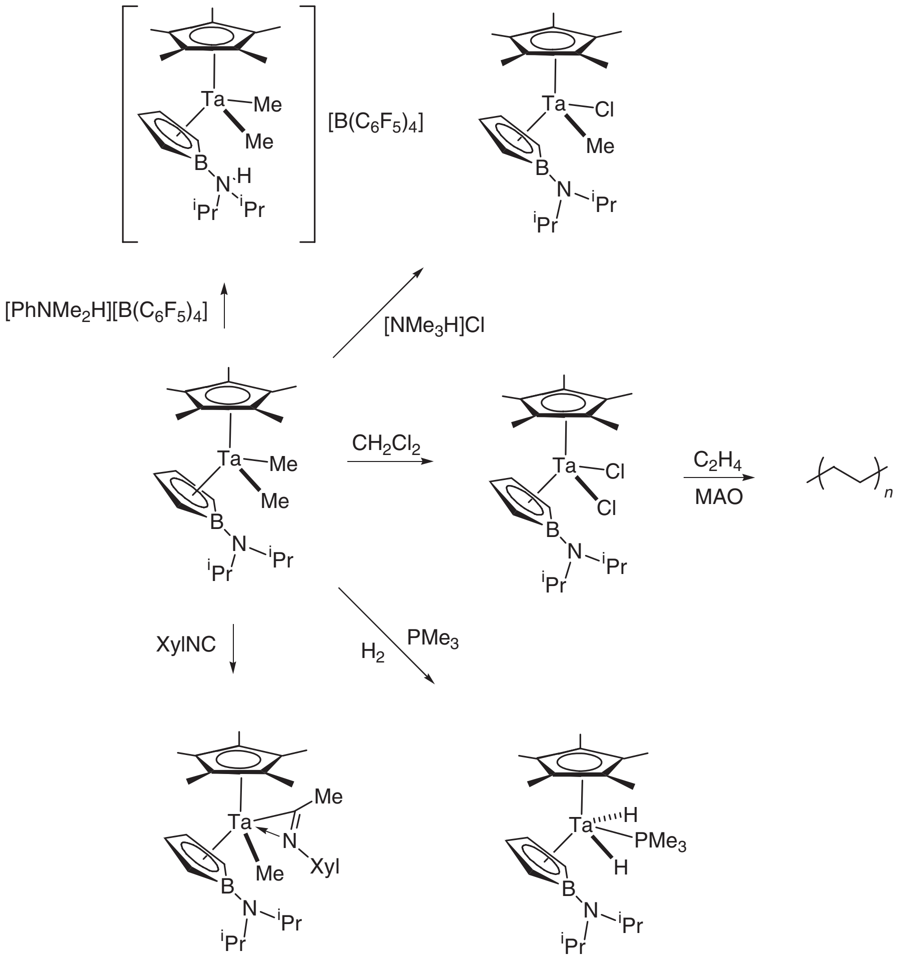
Borollide ligands are close structural relatives of the Cp ligand and can be introduced by the reaction of $Cp^*TaMe_2Cl(OTf)$ with $Li_2(C_4H_4BN^iPr_2)$, giving $Cp^*(\eta^5-C_4H_4BN^iPr_2)TaMe_2$, whose reactivity—including ethylene polymerization catalysis—is shown in Scheme 20.[137–139] Reaction of Me_3TaCl_2 with the dilithium salt of $C_4H_4BiN^iPr_2$ afforded a unique borollide-bridged dinuclear compound, $(\eta^5-C_4H_4BiN^iPr_2)TaMe_2(\mu-\eta^5:\eta^5-C_4H_4BiN^iPr_2)TaMe_4$, while the same reaction in the presence of PMe_3 produced the mononuclear compound $(\eta^5-C_4H_4BiN^iPr_2)TaMe_3(PMe_3)$.[140] Direct reaction of $TaCl_5$ and the dilithium salt of $C_4H_4BiN^iPr_2$ in the presence



Scheme 18



Scheme 19



Scheme 20

of 2 equiv. of $AlCl_3$ resulted in the formation of (η^5-$C_4H_4BiN^iPr_2$)$TaCl_3$.[42] Methylation of (η^5-$C_4H_4BiN^iPr_2$)$TaCl_3$ gives a mixture of (η^5-$C_4H_4BiN^iPr_2$)$TaMe_2$(μ-η^5:η^5-$C_4H_4BiN^iPr_2$)$TaMe_4$ and (η^5-$C_4H_4BiN^iPr_2$)$TaMe_3$. Magnesium reduction of (η^5-$C_4H_4BiN^iPr_2$)$TaCl_3$ in the presence of PMe_3 results in the formation of (η^5-$C_4H_4BiN^iPr_2$)$Ta(PMe_3)_3$(Cl) and its dinitrogen-bridged dinuclear compound upon exposure to dinitrogen.[42] LiCp′ and Li(C_5H_5BR) afford the corresponding compounds, Cp^*(η^5-$C_4H_4BN^iPr_2$)$TaCl_2$, (η^5-C_5H_4Me)$_2$Ta(η^2-$C_4H_4BiNH^iPr_2$)Cl, and (C_5H_5BR)(η^5-$C_4H_4BiNH^iPr_2$)$TaCl_2$.[42]

Hydrogenolysis of a mixed ligand compound (C_5H_5BPh)(η^5-$C_4H_4BN^iPr_2$)$TaMe_2$ in the presence of phosphine donors gives dihydride complexes (C_5H_5BPh)(η^5-$C_4H_4BN^iPr_2$)TaH_2(L) (L = PEt_3, P^iPr_3).[139]

Half-sandwich carborane dichloride complexes (η^5-C_5R_5)(η^5-$(R^1)_2C_2B_4H_4$)$TaCl_2$ (R = H, Me; R^1 = Me, Et, $SiMe_3$) and (η^5-C_5R_5)[η^5-$Cp^*Co(Et_2C_2B_3H_3)$]$TaCl_2$ (R = H, Me) can be alkylated by appropriate alkylating agents: mild alkylation agents give rise to monoalkyl complexes and more powerful nucleophiles achieve dialkylation.[141] Versatile insertion reactions are reported for these complexes.[142] The carborane ligand coordinated to the [CpTa] fragment of Cp(η^5-$Et_2C_2B_4H_4$)$TaCl_2$ can be halogenated by elemental chlorine, bromine, or iodine at room temperature, giving mono- and dihalogenated products. Halogenation of Cp(η^5-$Et_2C_2B_4H_4$)$TaCl_2$ using *N*-halosuccinimides results in the selective formation of monohalogenated compound Cp(η^5-$Et_2C_2B_4H_3X$)$TaCl_2$, while the reaction of Cp[η^5-$Cp^*Co(Et_2C_2B_3H_3)$]$TaCl_2$ with NBS gives tribrominated compound Cp[η^5-$Cp^*Co(Et_2C_2B_3Br_3)$]$TaCl_2$.[143] Brominated carborane complexes can be alkylated or phenylated at metal and cage positions, for example, the reaction of Cp(η^5-$Et_2C_2B_4H_3Br$)$TaCl_2$ with an excess MeMgBr affords Cp(η^5-$Et_2C_2B_4H_3Me$)$TaMe_2$.[143] Anionic bis(dicarbollide) dimethyl complex [PPN][(η^5-$C_2B_9H_{11}$)$_2TaMe_2$] adopts a bent-metallocene structure (Table 6).[144]

Table 6 Alkyl and aryl complexes with Cp ligand or analog[a]

Compound	*Comments*	*References*
Half-sandwich tetramethyl complex		
Cp^*TaMe_4	Prep: Cp^*TaF_4 + ex. Al_2Me_6	145
Half-sandwich halide complexes		
$Cp'TaMeCl_3$	Prep: Al_2Me_6; $Cp' = \eta^5\text{-}C_5Me_5$, $\eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$	114
$Cp'TaMe_2Cl_2$	Prep: Al_2Me_6; $Cp' = \eta^5\text{-}C_5Me_5$ (X-ray), $\eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$	114,146
$Cp^*TaCl_2R_2$	Prep: $Cp^*TaCl_4 + 2RMgX$ or R_2Mg; $R = CH_2SiMe_3$, CH_2CMe_2Ph, CH_2CMe_3, CH_2Ph	115
Aryloxo and alkoxo complexes		
$Cp^*TaMe_3(OCMePy_2)$	Prep: Cp^*TaMe_4 + di-2-pyridyl ketone, X-ray	118
trans-$Cp^*TaMe_2[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]$	Prep: *trans*-$Cp^*TaCl_2[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)] + 2MeLi$, X-ray	119
cis-$Cp^*TaMe_2[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]$	Prep: $Cp^*TaMe_4 + [(HOCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]$	119
$Cp^*Ta(CH_2SiMe_3)_3(OPh)$	Prep: $Cp^*Ta({=}CHSiMe_3)(CH_2SiMe_3)_2 + PhOH$	147
$[Cp^*Ta(CH_2SiMe_3)_2(O)]_n$	Prep: $Cp^*Ta({=}CHSiMe_3)(CH_2SiMe_3)_2 + H_2O$	147
$Cp^*Ta(CH_2SiMe_3)_2(O_2C_6H_3Me)$	Prep: $Cp^*Ta({=}CHSiMe_3)(CH_2SiMe_3)_2 + (HO)_2C_6H_3Me$	147
$Cp^*Ta(CH_2SiMe_3)_3[\eta^2\text{-}O(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)]$	Prep: $Cp^*Ta({=}CHSiMe_3)(CH_2SiMe_3)_2 + HOC_6H_3\text{-}2,6\text{-}Me_2$, X-ray	147
$Cp^*TaMe_2[(SCH_2CH_2)_2X]$	Prep: $Cp^*TaMe_4 + X(CH_2CH_2SH)_2 + NEt_3$; $X = O$ (X-ray), S (X-ray)	148
Amido, imido, and related complexes		
$Cp^*Ta(=N^tBu)(NH^tBu)(Ph)$	Prep: Thermolysis of $Cp^*TaMe(NH^tBu)(=N^tBu)$ in benzene	55
$Cp^*Ta(=N^tBu)(NH^tBu)(C_6H_4Me)$	Prep: Thermolysis of $Cp^*TaMe(NH^tBu)(=N^tBu)$ in toluene	55
$(\eta^5\text{-}C_5Me_4H)Ta(=N^tBu)Me_2$	Prep: $(\eta^5\text{-}C_5Me_4H)TaCl_2(=N^tBu) + 2MeMgBr$	76
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)Me_2$	Prep: $Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)Cl_2 + 2MeMgCl$	121
	Prep: $[Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(Cl)]_2(\mu\text{-}H)_2 + 2MeMgBr$	149
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)R_2$	Prep: $Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)Cl_2 + 2LiR$ or $1Mg(CH_2Ph)_2$; $R = CH_2SiMe_3$, CH_2CMe_2Ph, C_6H_5, CH_2Ph, $CH_2{}^tBu$	123
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)(R)Cl$	Prep: $Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)Cl_2 + 1\ LiR$ or $0.5\ Mg(CH_2Ph)_2$; $R = CH_2SiMe_3$, CH_2CMe_2Ph, $C_6H_4\text{-}2\text{-}CH_2NMe_2$, CH_2Ph, $CH_2{}^tBu$	123
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)(R)Me$	Prep: $Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)Cl(Me) + 1LiR$ or $0.5\ Mg(CH_2Ph)_2$; $R = CH_2SiMe_3$, CH_2CMe_2Ph, $C_6H_4\text{-}2\text{-}CH_2NMe_2$, CH_2Ph, $CH_2{}^tBu$, C_6H_5	123
$Cp^*Ta[=N(C_6H_3Me)_2NSiMe_3]Me$	Prep: $Cp^*Ta[=N(C_6H_3Me)_2NSiMe_3]Cl + MeMgBr$	124
$Cp^*Ta[N(SiH_2Ph)(C_6H_3Me)_2NSiMe_3]\text{-}(X)(H)$	Prep: $Cp^*Ta[=N(C_6H_3Me)_2NSiMe_3](X) + PhSiH_3$; $X = Cl$, Me	124
$Cp^*Ta[=N(C_6H_3Me)_2N(SiH_2Ph)]\text{-}(X)(H)$		124
$Cp^*Ta(=N^tBu)(O_2CNH^tBu)(Me)$	Prep: $Cp^*Ta(=N^tBu)(NH^tBu)(Me) + CO_2$	125
$Cp^*Ta(=N^tBu)(O_2CNMe_2)(Me)$	Prep: $Cp^*Ta(=N^tBu)(NMe_2)(Me) + CO_2$	125
$Cp^*Ta(=N^tBu)(NH^tBu)(Me)$	Prep: $Cp^*TaCl(Me)(=N^tBu) + LiNH^tBu$	125
$Cp^*Ta(=N^tBu)(NMe_2)(Me)$	Prep: $Cp^*TaCl(Me)(=N^tBu) + LiNMe_2$	125
$Cp_2Ta(=N\text{–}N{=}NPh)Me$	Prep: $Cp_2TaMe(PMe_3) + PhN_3$, X-ray	135
$Cp_2Ta(=NPh)Me$	Prep: thermolysis of $Cp_2Ta(=N\text{–}N{=}NPh)Me$	135
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)MeX$	$X = Cl$, NMe_2, N^iPr_2, NH^tBu	150
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(Me)[Si(SiMe_3)_3]$	Prep: $Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(Cl)[Si(SiMe_3)_3] + MeMgBr$, unstable and decomposes to give a dimethyl compound	149
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}Me_2)\{C_6H_4\text{-}2\text{-}[N(SiMe_3)_2]\}_2$		150
$Cp^*Ta(=N^tBu)MeCl$	Prep: $Cp^*Ta(=N^tBu)Cl_2 + ZnMe_2$	150, 151
$Cp^*Ta(=N^tBu)MeX$	Prep: $Cp^*Ta(=N^tBu)MeCl + MX$; $M = Li$, Na; $X = Cl$, OMe, $OCMe_3$, $NHCMe_3$	150, 151
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(Cl)(SiR_3)$	Prep: $Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(Cl)(SiR_3) + (THF)_3LiSiR_3$; $SiR_3 = Si(SiMe_3)_3$, $SiPh_3$, $SiHMes_2$	149
$Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(O^iPr)[Si(SiMe_3)_3]$	Prep: $Cp^*Ta(=NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(H)[Si(SiMe_3)_3]$ + acetone	149
$Cp^*Ta(=N^tBu)Me_2$	Prep: $Cp^*Ta(=N^tBu)Cl_2 + 2MeLi$	151, 152
$Cp^*Ta(=N^tBu)(CH_2Ph)_2$	Prep: $Cp^*Ta(=N^tBu)Cl_2 + 2PhCH_2MgCl$	153

(*Continued*)

Table 6 (Continued)

Compound	*Comments*	*References*
Cp$_2$Ta(=N^{t}Bu)Me	Prep: Cp$_2$Ta(=N^{t}Bu)Cl + MeLi	152
Cp*Ta(=NC$_6$H$_3$-2,6-Ar$_2$)Me$_2$	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-Ar$_2$)Cl$_2$ + 2MeLi; Ar = C$_6$H$_2$-2,4,6-Me$_3$, C$_6$H$_2$-2,4,6-^{i}Pr$_3$	154
Cp*Ta[=NSi(^{t}Bu)$_3$]Me$_2$	Prep: Cp*TaMe$_3$Cl + LiNHSi(^{t}Bu)$_3$	155
Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)Me(OTf)	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)Me$_2$ + AgOTf	154
Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)(CH$_2$^{t}Bu)(H)	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)(H)Br + LiCH$_2$^{t}Bu; Ar = C$_6$H$_2$-2,4,6-^{i}Pr$_3$	154
Cp*Ta(=NC$_6$H$_3$-2,6-Ar$_2$)(CH$_2$^{t}Bu)(H)	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)(H)(OTf) + LiCH$_2$^{t}Bu	154
Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)(Cl)-[Si(SiMe$_3$)$_3$]	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)Cl$_2$ + KSi(SiMe$_3$)$_3$	154
Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)(H)-[Si(SiMe$_3$)$_3$]	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)Cl$_2$ + KSi(SiMe$_3$)$_3$	154
Cp*TaMe(=NXyl)-[N(Xyl)C(Me)=CMe$_2$]	Prep: Cp*TaMe$_2$[η^2-C(Xyl)=CMe$_2$] + XylNC or Cp*TaMe$_4$ + 2XylNC; Xyl = C$_6$H$_3$-2,6-Me$_2$	156
Cp*TaMe$_2$[η^2-C(Xyl)=CMe$_2$]	Prep: Cp*TaCl$_2$[η^2-C(Xyl)=CMe$_2$] + 2MeLi; Xyl = C$_6$H$_3$-2,6-Me$_2$	157
Cp*Ta(Me)(Cl)[η^2-C(Xyl)=CMe$_2$]	Prep: Cp*TaMe(=NXyl)[N(Xyl)C(Me)=CMe$_2$] + HCl; Xyl = C$_6$H$_3$-2,6-Me$_2$	157
Cp*Ta(Me)(OC$_6$H$_3$-2,6-Me$_2$)[η^2-C(Xyl)=CMe$_2$]	Prep: Cp*TaMe(=NXyl)[N(Xyl)C(Me)=CMe$_2$] + HOC$_6$H$_3$-2,6-Me$_2$; Xyl = C$_6$H$_3$-2,6-Me$_2$	157
Cp*Ta(=N^{t}Bu)(Me)(NR$_2$)	Prep: Cp*Ta(=N^{t}Bu)(Me)(Cl) + LiNR$_2$; R = Ph, SiMe$_3$	158
Cp*Ta(=N^{t}Bu)(Me)(NHMe) + Cp*Ta(=NMe)(Me)(NH^{t}Bu)	Prep: Cp*Ta(=N^{t}Bu)(Me)(Cl) with LiNHMe	158
[Cp′TaR$_2$]$_2$(μ-1,*n*-NC$_6$H$_4$N)	Prep: [Cp′TaCl$_2$]$_2$(μ-1,4-NC$_6$H$_4$N) + MeLi, Me$_3$SiCH$_2$MgCl, or (PhCH$_2$)$_2$Mg; Cp′ = η^5-C$_5$H$_4$SiMe$_3$, Cp*; R = Me, CH$_2$SiMe$_3$ (X-ray for Cp*, *n* = 4), CH$_2$Ph	159
[Cp′Ta(Me)Cl]$_2$(μ-1,*n*-NC$_6$H$_4$N)	Prep: [Cp′TaCl$_2$]$_2$(μ-1,4-NC$_6$H$_4$N) + ZnMe$_2$; Cp′ = η^5-C$_5$H$_4$SiMe$_3$, Cp*	159
[Cp′Ta(Me)(NMe$_2$)]$_2$(μ-1,*n*-NC$_6$H$_4$N)	Prep: [Cp′Ta(Me)Cl]$_2$(μ-1,*n*-NC$_6$H$_4$N) + LiNMe$_2$; Cp′ = η^5-C$_5$H$_4$SiMe$_3$, Cp*	159
Cp*Ta(C$\equiv$C^{t}Bu)$_2$(η^4-*supine*-^{i}PrN=CHCH=N^{i}Pr)	Prep: Cp*TaCl$_2$(η^4-*supine*-^{i}PrN=CHCH=N^{i}Pr) + 2LiC$\equiv$C^{t}Bu, X-ray	129
Cp*Ta(C$\equiv$C^{t}Bu)$_2$(η^4-*prone*-^{t}BuN=CHCH=N^{t}Bu)	Prep: Cp*TaCl$_2$(η^4-*prone*-^{t}BuN=CHCH=N^{t}Bu) + 2 LiC$\equiv$C^{t}Bu, X-ray	129
Cp*TaMe$_2$[η^2-*N*,*N*′-C(NPh)$_3$].	Prep: Cp*TaMe$_2$Cl(OTf) + dilithium salt of triphenyltriazamethylenemethane	126
Cp*TaMe$_2$[η^2-*N*,*N*′-C(NPh)$_3$]	Prep: Cp*TaMe$_2$Cl(OTf) + Li$_2$[C(NPh)$_3$], X-ray	126
Cp*Ta[MeC(N^{i}Pr)$_2$]Me$_3$	Prep: Cp*Ta[MeC(N^{i}Pr)$_2$]Me$_3$ + ex. MeMgCl, X-ray	127
Cp*(R$_3$PN)TaMe$_3$	Prep: Cp*TaCl$_3$(NPR$_3$) + 3MeLi; R = ^{t}Bu (X-ray), ^{i}Pr	160
Cp*(R$_3$PN)TaCl$_2$(CH$_2$Ph)	Prep: Cp*TaCl$_3$(NPR$_3$) + PhCH$_2$MgCl; R = ^{t}Bu (X-ray), *i*Pr	160
Cp*(R$_3$PN)TaMe$_2$(CH$_2$Ph)	Prep: Cp*(R$_3$PN)TaCl$_2$(CH2Ph) + 2MeLi; R = *t*Bu, *i*Pr	160
Tp*Ta(CH$_2$^{t}Bu)(Cl)(=NAr)	Prep: Tp*Ta(=CH^{t}Bu)X$_2$ + KNHAr; Ar = Ph, C$_6$H$_3$-2,6-^{i}Pr$_2$	161
Carborane, borollide, and related complexes		
(η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)TaMe$_3$	Prep: (η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)TaCl$_3$ + 3MeMgCl	42
(η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)Ta[CH(SiMe$_3$)$_2$]Cl$_3$	Prep: (η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)TaCl$_3$ + 3MeMgCl	42
(η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)TaMe$_2$(μ-η^5:η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)TaMe$_4$	Prep: Li$_2$[C$_4$H$_4$B*i*N^{i}Pr$_2$](THF) + Me$_3$TaCl$_2$, X-ray	140
	Prep: (η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)TaCl$_3$ + 3MeMgCl	42
(η^5-C$_4$H$_4$B*i*N^{i}Pr$_2$)TaMe$_3$(PMe$_3$)	Prep: Li$_2$[C$_4$H$_4$B*i*N^{i}Pr$_2$](THF) + Me$_3$TaCl$_2$ + PMe$_3$	140
Cp*(η^5-C$_4$H$_4$BN^{i}Pr$_2$)TaMe$_2$	Prep: Cp*TaMe$_2$Cl(OTf) + Li$_2$(C$_4$H$_4$BN^{i}Pr$_2$), X-ray	137
Cp*(η^5-C$_4$H$_4$BMe)TaMe$_2$	Prep: Cp*(η^5-C$_4$H$_4$BMe)TaMeCl + ex. AlMe$_3$, X-ray	138
Cp*(η^5-C$_4$H$_4$BN^{i}Pr$_2$)TaMe(Cl)	Prep: Cp*(η^5-C$_4$H$_4$BN^{i}Pr$_2$)TaMe$_2$ + [NHMe$_3$]Cl	137
[Cp*(η^5-C$_4$H$_4$BNH^{i}Pr$_2$)TaMe$_2$][B(C$_6$F$_5$)$_4$]	Prep: Cp*(η^5-C$_4$H$_4$BN^{i}Pr$_2$)TaMe$_2$ + [PhNMe2H][B(C$_6$F$_5$)$_4$], X-ray	137
Cp(η^5-R$_2$C$_2$B$_4$H$_4$)TaCl(R^1)	Prep: Cp(η^5-R$_2$C$_2$B$_4$H$_4$)TaCl$_2$ + 2 equiv. of alkylating agents (Al$_2$Me$_6$, Me$_2$Zn, EtMgBr, Zn(CH$_2$Ph)$_2$, Np$_2$Mg); R = Et, SiMe$_3$; R^1 = Me, Et, CH$_2$Ph, CH$_2$^{t}Bu	141
Cp*(η^5-Et$_2$C$_2$B$_4$H$_4$)TaCl(R)	Prep: Cp*(η^5-Et$_2$C$_2$B$_4$H$_4$)TaCl$_2$ + 2 equiv. of alkylating agents (Al$_2$Me$_6$, Me$_2$Zn, Zn(CH$_2$Ph)$_2$, Np$_2$Mg); R = Me, CH$_2$Ph, CH$_2$^{t}Bu	141
Cp(η^5-R$_2$C$_2$B$_4$H$_4$)Ta(R^1)$_2$	Prep: Cp(η^5-R$_2$C$_2$B$_4$H$_4$)TaCl$_2$ + 2 equiv. of alkylating agents (MeMgBr, PhLi, PhCH$_2$MgBr, NpLi); R = Et, SiMe$_3$; R^1 = Me, Ph (X-ray), CH$_2$Ph, CH$_2$^{t}Bu	141, 162

(*Continued*)

Table 6 (Continued)

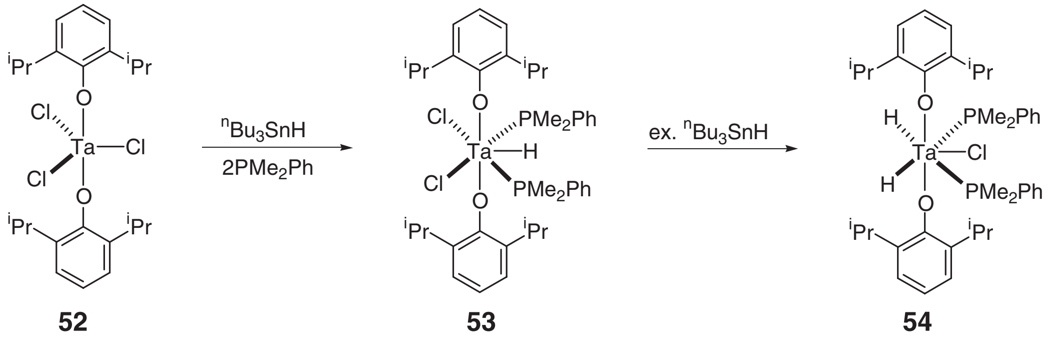
Compound	*Comments*	*References*
$Cp^{*}(\eta^5\text{-}Et_2C_2B_4H_4)TaR_2$	Prep: $Cp^{*}(\eta^5\text{-}Et_2C_2B_4H_4)TaCl_2 + 2$ equiv. of alkylating agents ($MeMgBr$, $PhCH_2MgBr$, $NpLi$); $R = Me$, CH_2Ph, $CH_2{}^tBu$	141
$Cp[\eta^5\text{-}Cp^{*}Co(Et_2C_2B_3H_3)]TaClR$	Prep: $Cp[\eta^5\text{-}Cp^{*}Co(Et_2C_2B_3H_3)]TaCl_2 + 2$ equiv. of alkylating agents (Me_2Zn, Al_2Me_6, $Zn(CH_2Ph)_2$, Np_2Mg); $R = Me$, CH_2Ph (X-ray), $CH_2{}^tBu$	141
$Cp[\eta^5\text{-}Cp^{*}Co(Et_2C_2B_3H_3)]TaR_2$	Prep: $Cp[\eta^5\text{-}Cp^{*}Co(Et_2C_2B_3H_3)]TaCl_2 + 2$ equiv. of alkylating agents ($MeLi$, $MeMgBr$, $PhCH_2MgBr$, $NpLi$); $R = Me$ (X-ray), CH_2Ph, $CH_2{}^tBu$	141
$Cp(\eta^5\text{-}Et_2C_2B_4H_4)\text{-}MeTa[C(R){=}C(R)Me]$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaMe_2 +$ alkynes	142
$Cp(\eta^5\text{-}Et_2C_2B_4H_4)MeTa[N{=}C(R)Me]$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaMe_2 + RCN$; $R = Me$, Et	142
$Cp(\eta^5\text{-}Et_2C_2B_4H_3X)TaR_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_3X)TaCl_2 + 2RMgBr$; $R = Me$, Ph	143
$Cp(\eta^5\text{-}Et_2C_2B_4H_3R)TaR_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_3X)TaR_2 + RMgBr$; $R = Me$, Ph	143
$Cp(\eta^5\text{-}Et_2C_2B_4H_3Bu)TaMe_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_3X)TaMe_2 + 3BuMgBr$	143
$Cp(\eta^5\text{-}Et_2C_2B_4HBr_3)TaMe_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4HBr_3)TaCl_2 + 2MeMgBr$	143
$Cp(\eta^5\text{-}Et_2C_2B_4HMe_3)TaMe_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4HBr_3)TaCl_2 +$ ex. MeMgBr	143
$Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaMe(I)$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaMe_2 + I_2$	143
$Cp[\eta^5\text{-}Cp^{*}Co(Et_2C_2B_3H_3I)]TaCl_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaMe(I) + I_2$	143
$[PPN][(\eta^5\text{-}C_2B_9H_{11})_2TaMe_2]$	Prep: $[PPN][(\eta^5\text{-}C_2B_9H_{11})_2TaCl_2] + 2MeLi$, X-ray	144
$Cp(Et_2C_2B_4H_4)TaCl(CH_2CH_2Ph)$	Prep: $[Cp(Et_2C_2B_4H_4)Ta(H)]_2(\mu\text{-}Cl)_2 +$ styrene	163
$Cp(Et_2C_2B_4H_4)TaCl(CH{=}CHTol)$	Prep: $[Cp(Et_2C_2B_4H_4)Ta(H)]_2(\mu\text{-}Cl)_2 + HCCTol$	163
$\{(\mu\text{-}H)(C_2B_9H_{10})_2\}TaCl(Me)$	Prep: $\{(\mu\text{-}H)(C_2B_9H_{10})_2\}TaCl_2 + ZnMe_2$	164
Metallocene complexes		
$Cp^{*}(\eta^5\text{-}C_5H_4SiMe_3)Ta({=}NC_6H_3\text{-}2,6\text{-}Me_2)X$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Me_2)Cl(X) + LiC_5H_4SiMe_3$; $X = Cl$ (X-ray), Me	123
ansa-$[\eta^5{:}\eta^5\text{-}(C_5H_4)_2CMe_2]Ta({=}N^tBu)Me$	Prep: *ansa*-$[\eta^5{:}\eta^5\text{-}(C_5H_4)_2CMe_2]Ta({=}N^tBu)Cl + MeLi$	128
$Cp_2Ta({=}O)Me$	Prep: photolysis of $Cp_2Ta(C_2H_4)Me$ or thermolysis of $Cp_2Ta(PMe_3)Me$ in the presence of 1 equiv. of oxirane	130–133
$Cp_2Ta(\eta^2\text{-}S_2)Me$	Prep: $Cp_2Ta({=}S)Me +$ thiirane in the dark, X-ray	132, 133
$Cp_2Ta({=}NR)Me$	Prep: photolysis of $Cp_2Ta(C_2H_4)Me$ or thermolysis of $Cp_2Ta(PMe_3)Me$ in the presence of aziridine; $R = Me$, Bu, Ph	132, 133
$Cp_2Ta({=}NAr)Me$	Prep: photolysis of $Cp_2Ta(C_2H_4)Me$ or thermolysis of $Cp_2Ta(PMe_3)Me$ in the presence of azoarene; $Ar = p\text{-}Tol$, Ph	134
$Cp_2Ta(\eta^2\text{-}NAr\text{–}NAr)Me$	Prep: photolysis of $Cp_2Ta(C_2H_4)Me$ or thermolysis of $Cp_2Ta(PMe_3)Me$ in the presence of azoarene; $Ar = p\text{-}Tol$ (X-ray), Ph	134
$Cp_2Ta({=}S)Me$	Prep: photolysis of $Cp_2Ta(C_2H_4)Me$ or thermolysis of $Cp_2Ta(PMe_3)Me$ in the presence of thiirane or $S{=}PMe_3$	132,133
$Cp_2Ta({=}S)(SMe)$		
$Cp_2MeTa(\mu\text{-}S)TaCp_2Me$	Prep: 0.5 equiv. of thiirane or $S{=}PMe_3$	132,133
$Cp^{*}{}_2Ta({=}Te)Me$	Prep: thermal isomerization of $Cp^{*}{}_2Ta(\eta^2\text{-}TeCH_2)(H)$	136
$Cp_2MeTa(\mu\text{-}O)Re(CR{=}CH_2)(CO)_4$	Prep: $Cp_2Ta({=}CH_2)Me + RRe(CO)_5$; $R = Me$, Ph (X-ray)	165
$Cp_2MeTa(\mu\text{-}O)Re[C({=}CH_2)C(Me){=}CH_2](CO)_4$	Prep: $Cp_2Ta({=}CH_2)Me + Re(CMe{=}CH_2)(CO)_5$	166
$Cp_2MeTa^{+}[\mu\text{-}\eta^1{:}\eta^1\text{-}OC({=}CH_2)]Re^{-}(C_3F_7)(CO)_4$	Prep: $Cp_2Ta({=}CH_2)Me + Re(C_3F_7)(CO)_5$, X-ray	166
$Cp_2(Me)Ta[CH_2B(C_6F_5)_2](\mu\text{-}H)$	Prep: $Cp_2Ta({=}CH_2)(CH_3) + HB(C_6F_5)_2$ at −78° C	43, 44
$Cp_2(H)Ta[CH_2B(C_6F_5)_2](\mu\text{-}H)$	Prep: $Cp_2(Me)Ta[CH_2B(C_6F_5)_2](\mu\text{-}H) + HB(C_6F_5)_2$, X-ray	43, 44
$Cp'_2Ta[CH_2B(C_6F_5)_3](CH_3)$	Prep: $Cp'_2Ta({=}CH_2)(CH_3) + B(C_6F_5)_3$; $Cp' = Cp$ (X-ray), C_5H_4Me	167
Cationic alkyl complexes		
$[Cp_2TaMe_2][MeE(C_6F_5)_3]$	Prep: $Cp_2TaMe_3 + E(C_6F_5)_3$; $E = B$, Al	76
$[Cp_2TaMe_2][(C_6F_5)_3AlMeAl(C_6F_5)_3]$	Prep: $Cp_2TaMe_3 + 2Al(C_6F_5)_3$	76
$[Cp_2TaMe_2][B(C_6F_5)_4]$	Prep: $Cp_2TaMe_3 + Ph_3C[B(C_6F_5)_4]$	76
$\{Cp^{*}TaMe[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]\}(OTf)$	Prep: *cis*-$Cp^{*}TaMe_2[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)] + HOTf$	119
$\{Cp^{*}Ta[NMe(C_6H_3Me)_2NSiMe_3]Me\}I$	Prep: $Cp^{*}Ta[{=}N(C_6H_3Me)_2NSiMe_3]Me + MeI$	124

[a] $Cp = \eta^5\text{-}C_5H_5$, $Cp^{*} = \eta^5\text{-}C_5Me_5$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

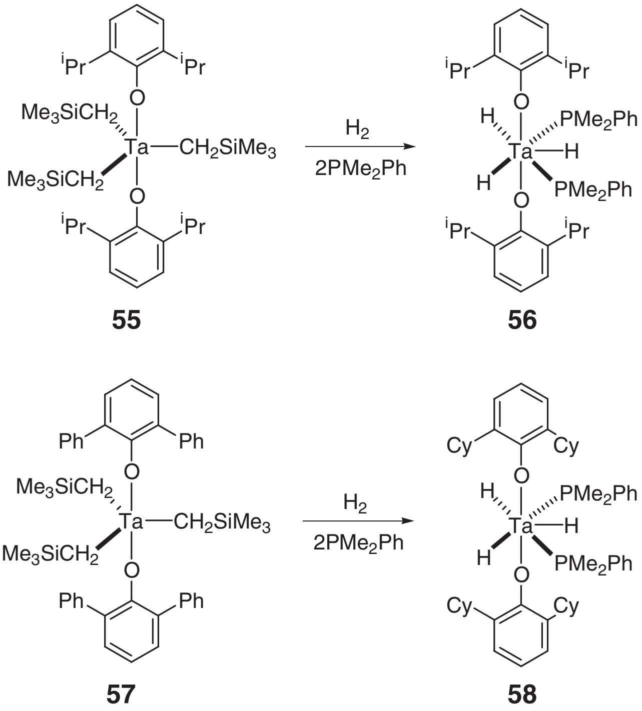
5.03.3.3 Hydride Complexes

5.03.3.3.1 Hydride complexes without cyclopentadienyl ligands

Rothwell and co-workers have prepared a series of hydride complexes of tantalum supported by aryloxide ligands and have demonstrated their catalytic activity for the hydrogenation of a variety of arene substrates.[168] These hydride complexes are isolated by two methods: the first method is the addition of ^{n}Bu$_3$SnH to chloro aryloxides in the presence of appropriate phosphine donors and the second one is the initial formation of the alkyl complexes followed by hydrogenolysis in the presence of a suitable phosphine ligand.[169] The addition of ^{n}Bu$_3$SnH to the trichloride compound Ta(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$Cl$_3$ **52** in the presence of an excess of PMe$_2$Ph leads to the sequential formation of the seven-coordinated mono and dihydrido complexes **53** and **54** (Scheme 21).[170] The formation of the dihydride complex requires an excess of ^{n}Bu$_3$SnH and the final chloride cannot be replaced. The corresponding trihydride **55** is obtained by the hydrogenolysis of the tris(trimethylsilylmethane) compound **56** (Scheme 22). For the 2,6-diphenylphenoxide compound, the hydrogenolysis of the corresponding trialkyl **57** results in the formation of the 2,6-dicyclohexylphenoxide



Scheme 21



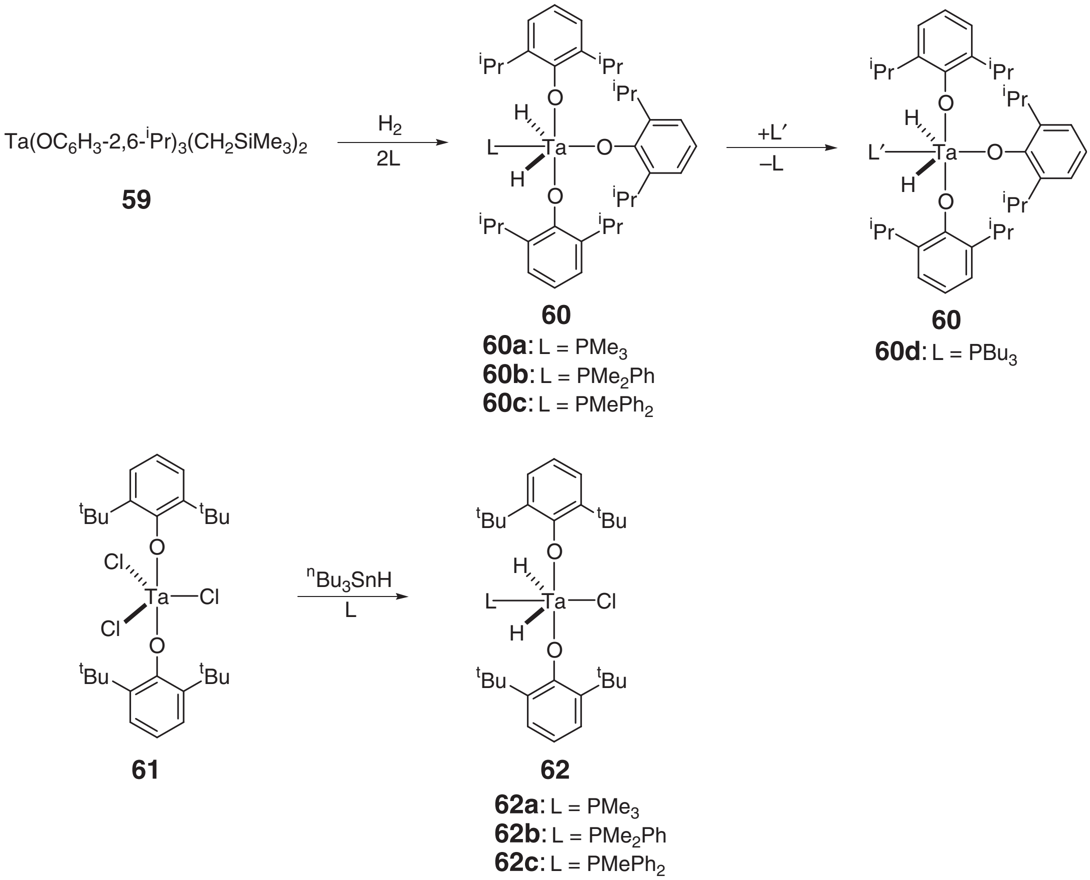
Scheme 22

trihydride derivative **58**, after the intramolecular hydrogenation of the *ortho*-phenyl rings. The hydrogenolysis method is applied for the preparation of the dihydride compound **54**, and the corresponding 2,6-diphenylphenoxide compound, which keeps the phenyl groups unchanged. The seven-coordinated compounds are shown by X-ray analysis to adopt a pentagonal-bipyramidal arrangement of ligands about the tantalum metal center.

In sharp contrast, the X-ray analyses of the octahedral dihydride compounds **60** and **62**, which are prepared as outlined in Scheme 23, intriguingly showed that the *trans*-hydride ligands bend away from an octahedral geometry by ca. 20–30°, the H–Ta–H bond angle being much less than 180°.[169] The deformation of two *trans*-hydride ligands toward a bulky phosphine ligand could not be rationalized on the basis of a simple steric argument predicting a bending toward to the less bulky ligand, Cl or phenoxy ligands, and was able to be estimated by *ab initio* calculations to be due to the π-donor (acceptor) properties of the ligands (a pseudo-second-order Jahn–Teller distortion).[171–173] The hydride ligands are shown to bend toward the stronger π-acceptor and away from the strongest π-donor.

The seven-coordinated mono-, di-, and trihydride complexes adopt a pentagonal-bipyramidal structure with *trans*-axial aryloxide oxygen atoms. When a bulky binaphthoxide ligand is employed, monohydride TaCl$_2$(H)(PMe$_3$)$_2$(3,3′-di(SiMe$_3$)$_2$-1,1′-bi-2,2′-naphtoxido) adopts the seven-coordinate pentagonal-bipyramidal structure but with axial oxygen and chloride atoms.[174] The reactions of TaCl(H)$_2$(PMe$_3$)$_2$(OC$_6$H$_3$-2,6-Ph$_2$)$_2$ with styrene and 3-hexyne are summarized in Scheme 24.[175,176]

Bulky siloxides have been utilized as supporting ligands that stabilize low-coordinate, low-valent tantalum compounds.[177] Sodium amalgam reduction of (^{t}Bu$_3$SiO)$_3$TaCl$_2$ **63** under dihydrogen affords the dihydride (^{t}Bu$_3$SiO)$_3$Ta(H)$_2$ **64**, while the reduction of (^{t}Bu$_3$SiO)$_2$TaCl$_3$ **65** under the same condition gives [(^{t}Bu$_3$SiO)$_2$TaH$_2$]$_2$ **66**.[98] Some typical reactions of hydride compounds **64** and **66** are summarized in Scheme 25 and 26, respectively. Various siloxides (Cy$_3$SiO, ^{t}Bu$_2$PhSiO, ^{t}Bu$_2$MeSiO, ^{i}Pr$_2{}^t$BuSiO, ^{i}Pr$_3$SiO, ^{t}Bu$_2$HSiO) are used for the preparation of tantalum trissiloxides.[100] Insertion of H$_2$C═CH(OR) (R = Me, Et, ^{n}Pr, ^{i}Pr, CH═CH$_2$, Ph) into **64** affords



59

60

60a: L = PMe$_3$
60b: L = PMe$_2$Ph
60c: L = PMePh$_2$

60

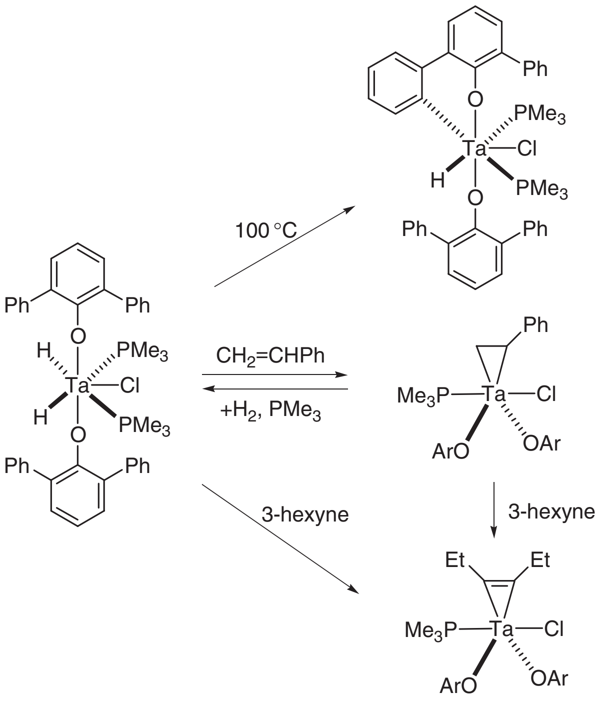
60d: L = PBu$_3$

61

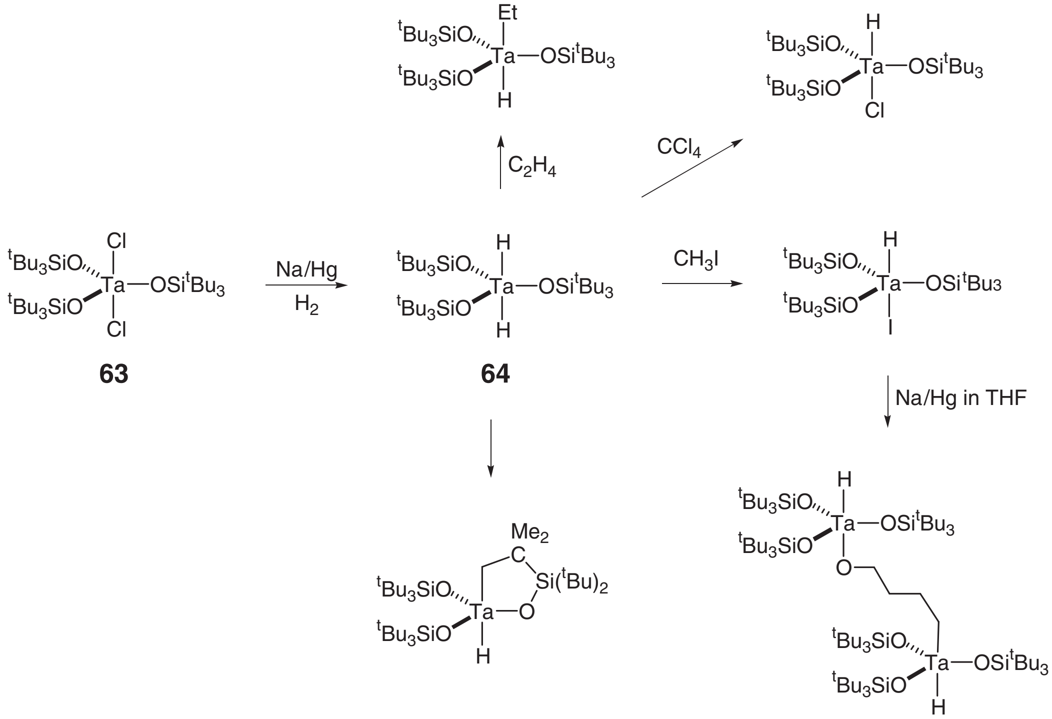
62

62a: L = PMe$_3$
62b: L = PMe$_2$Ph
62c: L = PMePh$_2$

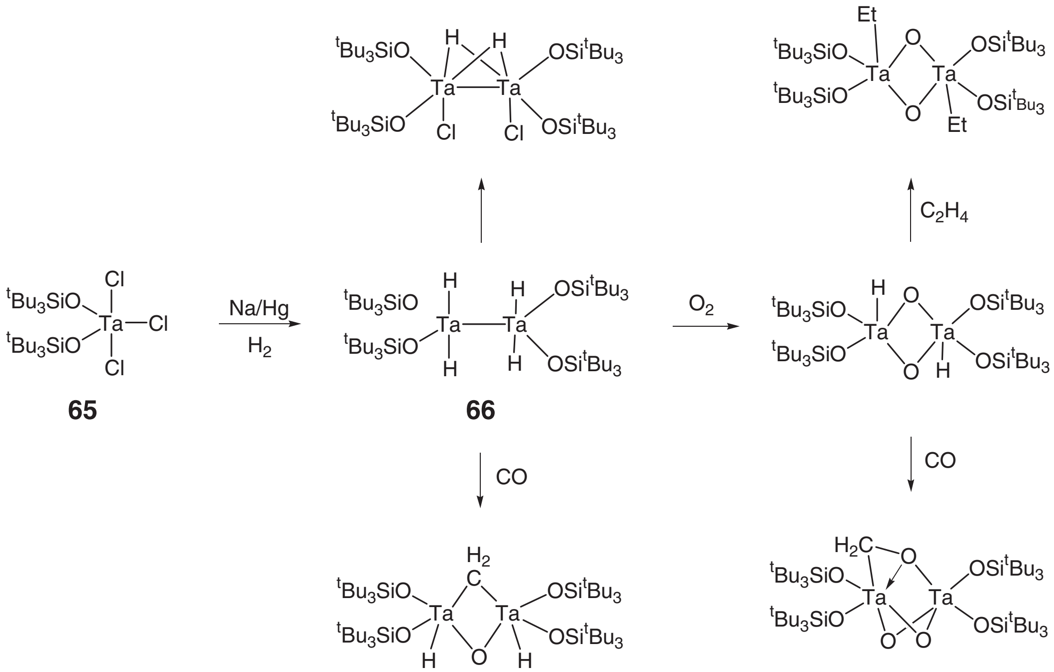
Scheme 23



Scheme 24



Scheme 25



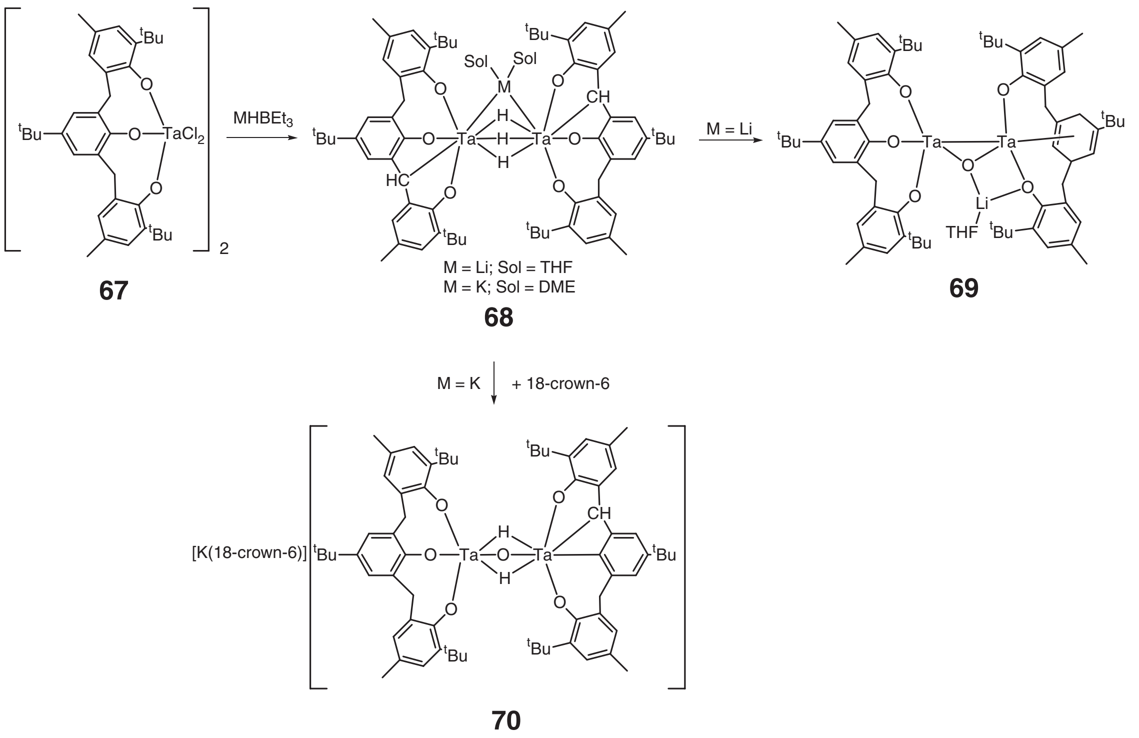
Scheme 26

(^{t}Bu$_3$SiO)$_3$Ta(H)(CH$_2$CH$_2$OR), which undergoes β-OR elimination to give ethylene and (^{t}Bu$_3$SiO)$_3$Ta(H)(OR).[99] Carbonylation of these hydride species demonstrates CO cleavage, giving oxo-methylene-bridged compound. Dinuclear hydride compound **66** reacts with ethylene to give [(^{t}Bu$_3$SiO)$_2$TaH(C$_2$H$_5$)]$_2$ and further reaction results in the formation of [(^{t}Bu$_3$SiO)$_2$TaH(C$_2$H$_5$)](μ-H)$_2$(μ-η^1:η^2-C$_2$H$_3$)[Ta(^{t}Bu$_3$SiO)$_2$].[103] Exposure of "(^{t}Bu$_3$SiO)$_3$Ta" to 1 equiv. of PhEH$_2$ (E = N, P, As) affords hydrides (^{t}Bu$_3$SiO)$_3$Ta(H)(EHPh), which lose dihydrogen to form (^{t}Bu$_3$SiO)$_3$Ta=EPh.[178] Oxidative addition of aryl C–N and related C–O bonds to (^{t}Bu$_3$SiO)$_3$Ta is reported: reaction with H$_2$NC$_6$H$_4$X affords an N–H addition product and also a C–N activation product, (^{t}Bu$_3$SiO)$_3$Ta(C$_6$H$_4$X)(NH$_2$).[179]

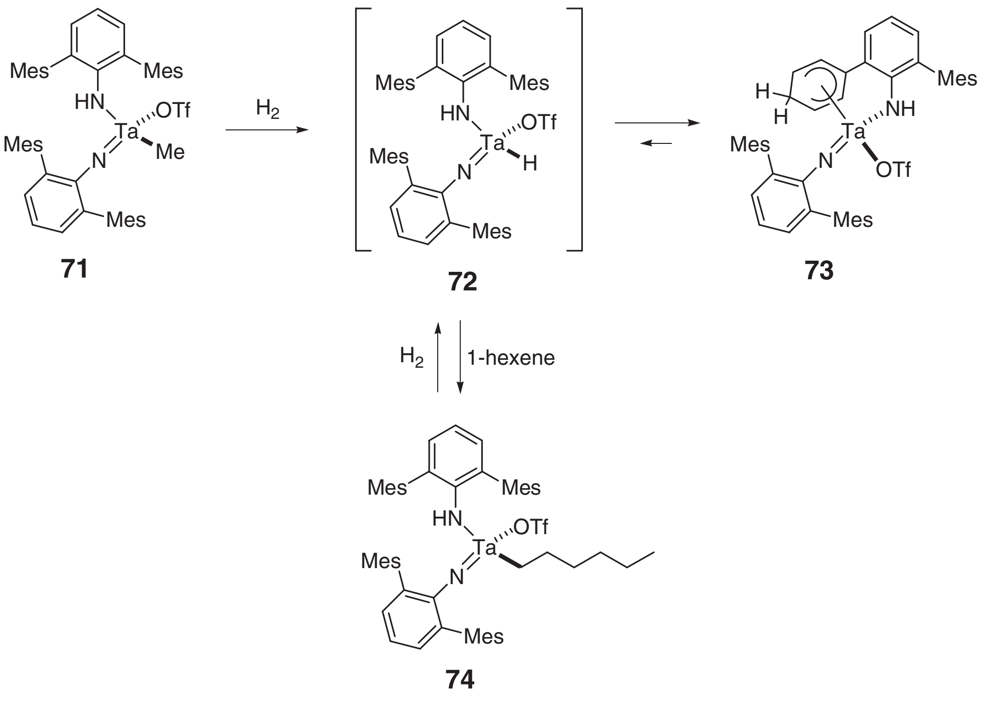
Scheme 27 shows the synthesis of ditantalum complexes **68** supported by a tridentate aryloxide ligand and the C(aryl)–O bond cleavage of the supporting ligand.[180,181] Treatment of [LTaCl$_2$]$_2$ **67** {L = 2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxylbenzyl)-4-*tert*-butyl-phenol} with LiHBEt$_3$ or KHEt$_3$ affords thermally unstable complexes **68**, which involve an intromolecular methylene C–H bond activation. From **68**, two μ-oxo ditantalum complexes **69** and **70** are derived through the transient formation of ditantalum dihydride species that can cleave the C—O bond.

Reversible intramolecular hydride transfer between tantalum and an aromatic ring is observed (Scheme 28).[104] Hydrogenolysis of a monomethyl compound, (ArN=)(ArNH)TaMe(OTf) (**71**: Ar = 2,6-Mes$_2$C$_6$H$_3$) gives an imido–amido η^5-cyclohexadienyl compound **73**. The hydride of the cyclohexadienyl moiety, as a masked hydride, is reversibly transferred to the tantalum center to establish an equilibrium with hydride compound (ArN=)(ArNH)TaH(OTf) **72**, which can react with 1-hexene to give a hexyl compound **74**.[104] Thus, the masked hydride compound **73** can catalyze the hydrogenation of alkenes.[78]

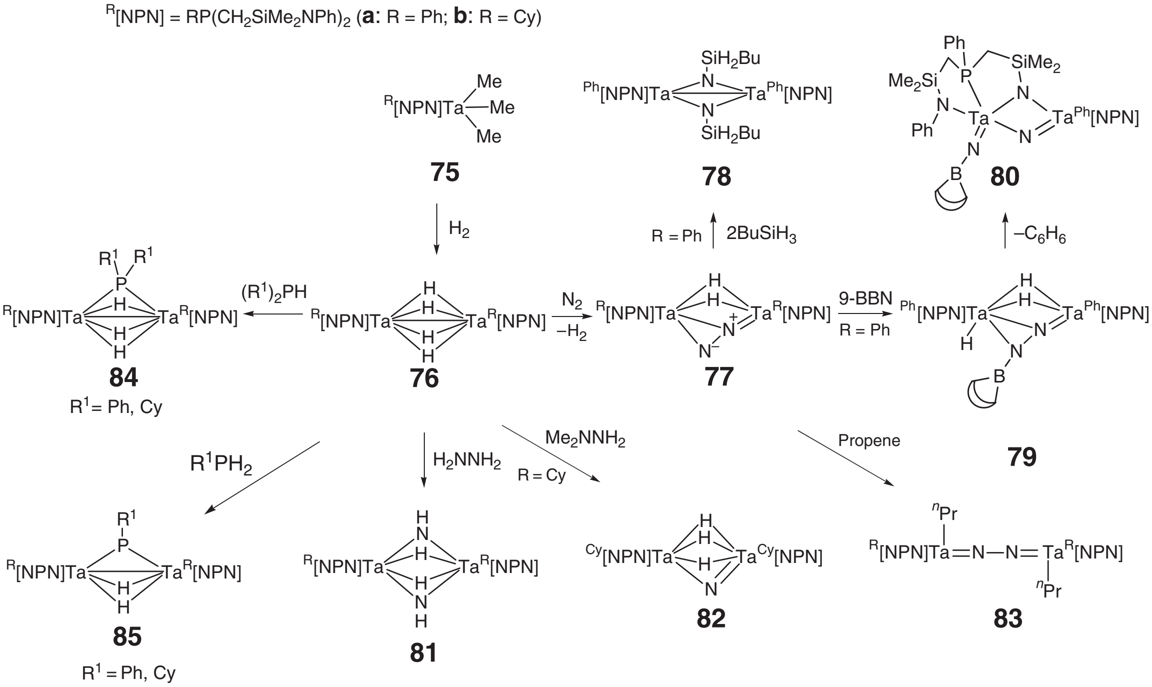
Dinuclear tetrahydride complexes {^{R}[NPN]Ta}$_2$(μ-H)$_4$ (^{R}[NPN] = RP(CH$_2$SiMe$_2$NPh)$_2$, **76a**: R = Ph; **76b**: R = Cy) are prepared by treating the corresponding mononuclear trimethyl complexes ^{R}[NPN]TaMe$_3$ **75** with dihydrogen (1–4 atm) along with the elimination of methane.[87–89] The tetrahydride complexes release dihydrogen to generate coordinatively unsaturated dinuclear dihydride (Ta=Ta) species, which can be trapped by PMe$_3$, or they activate the *ortho*-C–H bond of phenyl group of the NPN ligand.[182] Upon exposure to nitrogen gas, **76a** turns to a dihydride dinitrogen compound **77a**, which reacts with 2 equiv. of butylsilane and 9-BBN to give a disilylimide complex **78a** and a borylimide nitride complex **80** through the cleavage of N–N bond (Scheme 29).[87,89,183–188] Spectroscopic properties and quantum chemistry-based normal coordinate analysis for **77a** have been reported.[189] Lewis acids such as AlMe$_3$, GaMe$_3$, and B(C$_6$F$_5$)$_3$ can coordinate to the nitrogen atom of **77a** to form adducts, {^{Ph}[NPN]Ta}$_2$(μ-η2:η^1-N(L)N)(μ-H)$_2$ (L = AlMe$_3$, GaMe$_3$, and B(C$_6$F$_5$)$_3$).[190] Addition of 1 equiv. of hydrazine to



Scheme 27



Scheme 28



Scheme 29

76b results in the clean formation of $(^{Cy}[NPN]Ta)_2(\mu\text{-}NH)_2(\mu\text{-}H)_2$ **81b**, while similar reaction of **76a** is complicated because of the contamination of free ligand, producing 30% yield of the analog of **81b**.[191] Reaction of **76b** with 1,1-dimethylhydrazine affords nitride **82b**.[191] Propene inserts into the Ta–H bonds of **77a** to give an alkyl dinuclear $\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2$ complex **83**.[89] Addition of primary and secondary phosphines to the tetrahydride complexes produces the corresponding phosphide **84** and phosphinidene complexes **85**.[88]

Fryzuk *et al.* also prepared hydride compounds with a tridentate $[P_2N_2]$ ligand ($[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2)_2PPh$). Hydrogenolysis of $TaMe_3[P_2N_2]$ produces a dinuclear compound $\{[P_2N_2]Ta\}_2(\mu\text{-}H)_4$.[192] During the hydrogenolysis of the trimethyl compound, a trihydride is generated: this can be trapped by PMe_3 to give $[P_2N_2]TaH_3(PMe_3)$.[193] Reaction of $\{[P_2N_2]Ta\}_2(\mu\text{-}H)_4$ with MeI produces a cationic tetrahydride $\{([P_2N_2]Ta)_2(\mu\text{-}H)_4\}I$ along with methyl radical.[192]

Bridging hydride complexes have been reported: reaction of $TaCl_5$ with 4 equiv. of Cy_2NLi afforded two complexes: one is a mononuclear azametallacyclopropane $(Cy_2N)_2TaCl[\eta^2\text{-}N(C_6H_{10})Cy]$ and the other is a dinuclear hydride-bridging compound, that is, $[(Cy_2N)_2ClTa](\mu\text{-}H)_2$ (Table 7).[194,195]

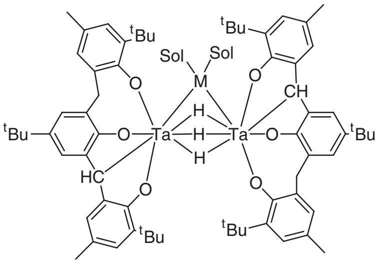
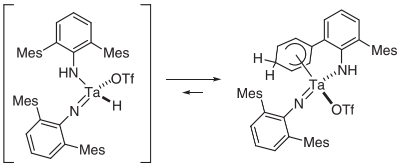
5.03.3.3.2 Hydride complexes with Cp ligands

Protonation of $Cp'_2Ta(H)(CO)$ (**86**: Cp′ = Cp, $C_5H_4{}^tBu$) with stoichiometric amounts of $HBF_4(Et_2O)$ in dichloromethane at −78 °C affords a mixture of two isomers (Scheme 30): the major complexes **87** contain *cis*-η^2-dihydrogen bound to the tantalum center and the minor complexes **88** are *trans*.[196–198] The corresponding *cis*-dihydride complex bearing a phosphite ligand *cis*-$\{Cp_2Ta(H)(D)[P(OMe)_3]\}^+$ is characterized by dynamic NMR analysis and DFT calculation, indicating that the exchange coupling of H–D resulted from the exchange through a dihydrogen transition state (16.6 kcal mol^{-1}).[197,198]

A similar protonolysis of dihydride silyl complex **89** by $(Et_2O)_2HB[C_6H_3(CF_3)_2]_4$ led to the formation of a dinuclear cationic complex **90**, which contains one bridging hydride (Scheme 31).[198]

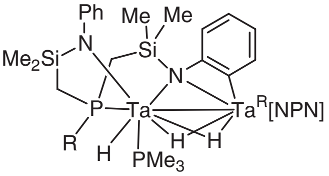
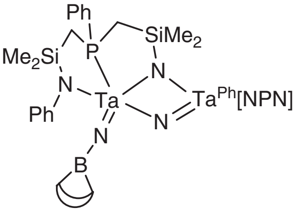
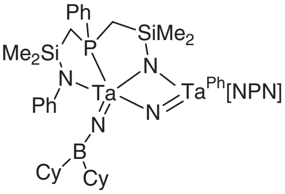
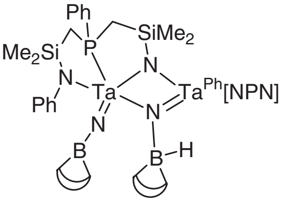
Scheme 32 shows some reactions of a trihydride complex, Cp'_2TaH_3 (**91**: Cp′ = $C_5H_4{}^tBu$), eliminating dihydrogen.[199] Reaction with a protic reagent, CF_3COOH, leads to the formation of dicarboxylate tantalum complex **92** with the loss of two hydride ligands. Addition of an excess of $HBF_4(Et_2O)$ to a solution of the complex **91** affords a transient cationic dihydride species, $[Cp'_2Ta(H)_2]^+$, which can be trapped by dimethylsulfide to give a complex **93** (L = SMe_2). Oxidative formation of the transient species is achieved by using trityl cation or ferrocenium cation. Similarly, oxidative treatment of a trihydride complex with pendant dimethylamino group, $Cp^*(\eta^5\text{-}C_5H_4CH_2CH_2NMe_2)TaH_3$, generated a cationic

Table 7 Hydride complexes without Cp ligands[a]

Compound	*Comments*	*References*
$TaH(PF_3)_6$	Prep: $[Et_4N][Ta(PF_3)_6]$ + ex. conc. H_2SO_4	5
$Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2H(Cl)_2(PMe_2Ph)_2$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2Cl_3 + {}^{n}Bu_3SnH$ + ex. PMe_2Ph, X-ray	169
$Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2(H)_2(Cl)(L)_2$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2(CH_2SiMe_3)_2Cl + H_2$ + ex. L; L = PMe_3, PMe_2Ph (X-ray), $PMePh_2$	169
	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2Cl_3 + {}^{n}Bu_3SnH$ + ex. PMe_2Ph	170
$Ta(OC_6H_3\text{-}2,6\text{-}Ph_2)_2(H)_2(Cl)(PMe_3)_2$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}Ph_2)_2(CH_2SiMe_3)_2Cl + H_2$ + ex. PMe_3	169
$Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2(H)_3(L)_2$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2(CH_2SiMe_3)_3 + H_2$ + ex. L; L = PMe_3, PMe_2Ph	169
$Ta(OC_6H_3\text{-}2,6\text{-}Cy_2)_2(H)_3(L)_2$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}Ph_2)_2(CH_2C_6H_4\text{-}4\text{-}Me)_3 + H_2$ + ex. L; L = PMe_2Ph (X-ray), $PMePh_2$	169
$Ta(OC_6H\text{-}3,5\text{-}Ph_2\text{-}2,6\text{-}Cy_2)_2(H)_3(PMe_2Ph)_2$	Prep: $Ta(OC_6H\text{-}2,3,5,6\text{-}Ph_4)_2(CH_2SiMe_3)_3 + H_2$ + ex. PMe_2Ph	169
$Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_3(H)_2(L)$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_3(CH_2C_6H_4\text{-}4\text{-}Me)_2 + H_2$ + ex. L; L = PMe_3, PMe_2Ph (X-ray), $PMePh_2$	169
$Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_3(H)_2(PBu_3)$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_3(H)_2(L) + PBu_3$	169
$Ta(OC_6H_3\text{-}2,6\text{-}^{i}Pr_2)_3(H)_2(L)$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}Ph_2)_2(L)_3$ (L = PMe_2Ph, $PMePh_2$) + H_2 (1200 psi) at 90 °C; L = PMe_2Cy, $PMePhCy$, $PMeCy_2$	169
$Ta(OC_6H_3\text{-}2,6\text{-}^{t}Bu_2)_2(H)_2(Cl)(L)$	Prep: $Ta(OC_6H_3\text{-}2,6\text{-}^{t}Bu_2)_2Cl_3 + {}^{n}Bu_3SnH$ + ex. L; L = PMe_3, PMe_2Ph, $PMePh_2$ (X-ray)	169
$TaCl_2(H)(PMe_3)_2[3,3'\text{-}(SiMe_3)_2\text{-}1,1'\text{-bi-}2,2'\text{-}(C_{10}H_5O)_2]$	Prep: $TaCl_3(NHMe_2)[3,3'\text{-}(SiMe_3)_2\text{-}1,1'\text{-bi-}2,2'\text{-}(C_{10}H_5O)_2] + {}^{n}Bu_3SnH$ + ex. PMe_3	174
$(^{t}Bu_3SiO)_3Ta(H)_2$	Prep: $(^{t}Bu_3SiO)_3TaCl_2$ + Na/Hg + H_2	98
$(^{t}Bu_2PhSiO)_3Ta(H)_2$	Prep: $(^{t}Bu_2PhSiO)_3TaCl_2$ + Na/Hg + H_2	100
$(^{t}Bu_3SiO)_3Ta(H)Cl$	Prep: $(^{t}Bu_3SiO)_3Ta(H)_2 + CCl_4$	98
$(^{t}Bu_3SiO)_3Ta(H)I$	Prep: $(^{t}Bu_3SiO)_3Ta(H)_2 + CH_3I$	98
$[(^{t}Bu_3SiO)_2Ta(Cl)]_2(\mu\text{-}H)_2$	Prep: $(^{t}Bu_3SiO)_2Ta(Cl)_2(CH_2Ph) + H_2$	98
$[(^{t}Bu_3SiO)_2TaH_2]_2$	Prep: $(^{t}Bu_3SiO)_2TaCl_3$ + Na/Hg + H_2 X-ray	98
$[(R_3SiO)_3Ta]_2(\mu\text{-}H)_2$	Prep: $(R_3SiO)_3TaCl_2$ + Na/Hg + H_2; $R_3Si = {}^{t}Bu_2MeSi$, $^{i}Pr_3Si$	100
$[(^{t}Bu_3SiO)_2TaH]_2(\mu\text{-}O)_2$	Prep: $[(^{t}Bu_3SiO)_2TaH_2]_2 + O_2$	98
$[(R_3SiO)_3TaH]_2(\mu\text{-}O)_2$	Prep: $[(R_3SiO)_3Ta]_2(\mu\text{-}H)_2 + O_2$; $R_3Si = {}^{t}Bu_2MeSi$, $^{i}Pr_3Si$	100
$[(^{t}Bu_3SiO)_2TaH]_2(\mu\text{-}O)(\mu\text{-}H)_2$	Prep: $[(^{t}Bu_3SiO)_2TaH_2]_2 + Me_3NO$	98
$(^{t}Bu_3SiO)_3Ta(H)(EHPh)$	Prep: $(^{t}Bu_3SiO)_3Ta + 1PhEH_2$; E = N, P, As	178
$(^{t}Bu_3SiO)_3Ta(H)(CH_2CH_2OR)$	Prep: $(^{t}Bu_3SiO)_3Ta(H)_2 + H_2C{=}CH(OR)$; R = Me, Et, ^{n}Pr, ^{i}Pr, $CH{=}CH_2$, ^{t}Bu (X-ray), Ph	99
$(^{t}Bu_3SiO)_3Ta(H)(OR)$	R = Me, Et, ^{n}Pr, ^{i}Pr, $CH{=}CH_2$, $CHEtCH{=}CH_2$, $CH_2CH{=}CH_2$, Ph	99
$(^{t}Bu_3SiO)_3Ta(H)(X)$	X = F, Cl, Br	99
 M = Li; Sol = THF M = K; Sol = DME	Prep: $[LTaCl_2]_2 + MHBEt_3$; M = Li, Na; L = 2,6-bis(3-^{t}Bu-5-methyl-2-hydroxylbenzyl)-4-^{t}Bu-phenol	180
 	Prep: $(ArN{=})(ArNH)TaMe(OTf) + H_2$; Ar = 2,6-$Mes_2C_6H_3$, X-ray	104
$\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4$	Prep: $TaMe_3\{^{R}[NPN]\} + H_2$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; R = Ph (X-ray), Cy	87–89
$\{^{R}[NPN]\ Ta\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)(\mu\text{-}H)_2$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + N_2$; R = Ph (X-ray)	87, 89

(*Continued*)

Table 7 (Continued)

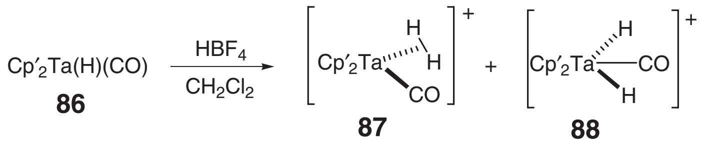
Compound	*Comments*	*References*
$\{^{R}[NPN]BrTa\}(\mu\text{-}\eta^2{:}\eta^1\text{-}NNCH_2Ph)\text{-}(\mu\text{-}H)_2\{Ta^{R}[NPN]\}$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)(\mu\text{-}H)_2 + PhCH_2Br$; R = Ph (X-ray)	89
$\{^{R}[NPN]Ta\}_2(\mu\text{-}NH)_2(\mu\text{-}H)_2$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + N_2H_4$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; R = Ph (X-ray), Cy	191
$\{^{R}[NPN]Ta\}_2(\mu\text{-}NR^1)_2(\mu\text{-}H)_2$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + R^1HNNHR^1$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; R = Ph; R^1 = Me, Ph	191
$\{^{R}[NPN]Ta\}_2(\mu\text{-}N)(\mu\text{-}H)_3$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + Me_2NNH_2$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; R = Cy (X-ray)	191
$\{^{R}[NPN]Ta\}_2(\mu\text{-}NSiH_2Bu)_2$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}NH)_2(\mu\text{-}H)_2 + 2BuSiH_3$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; R = Ph (X-ray)	183
$\{^{R}[NPN]Ta(PMe_3)\}_2(\mu\text{-}H)_2$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + 2PMe_3$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; Cy in solution at −80 °C	182
	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + PMe_3$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; Ph, Cy (X-ray)	182
$\{^{R}[NPN]Ta\}_2(\mu\text{-}P(R^1)_2)(\mu\text{-}H)_3$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + HP(R^1)_2$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; R = Ph, Cy; R^1 = Ph, Cy, X-ray for R = Ph, R^1 = Cy	191
$\{^{R}[NPN]Ta\}_2(\mu\text{-}PR^1)(\mu\text{-}H)_2$	Prep: $\{^{R}[NPN]Ta\}_2(\mu\text{-}H)_4 + HP(R^1)_2$; $^{R}[NPN] = R(CH_2SiMe_2NPh)_2$; R = Ph, Cy; R^1 = Cy, Ad, X-ray for R = Cy, R^1 = Ad	191
$\{[P_2N_2]Ta\}_2(\mu\text{-}H)_4$	Prep: $TaMe_3[P_2N_2] + H_2$; $[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2)_2PPh$, X-ray	192
$\{([P_2N_2]Ta)_2(\mu\text{-}H)_4\}I$	Prep: $\{[P_2N_2]Ta\}_2(\mu\text{-}H)_4 + MeI$, X-ray	192
$[P_2N_2]TaH_3(PMe_3)$	Prep: $[P_2N_2]TaMe_3 + H_2 + PMe_3$	193
$\{^{Ph}[NPN]Ta(H)\}[\mu\text{-}\eta^2{:}\eta^1\text{-}N(BC_8H_{14})N](\mu\text{-}H)_2\{^{Ph}[NPN]Ta\}$	Prep: $\{^{Ph}[NPN]Ta\}_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2$ + 9-BBN, X-ray	184
	Prep: thermolysis of $\{^{Ph}[NPN]Ta(H)\}[\mu\text{-}\eta^2{:}\eta^1\text{-}N(BC_8H_{14})N]\text{-}(\mu\text{-}H)_2\{^{Ph}[NPN]Ta\}$	184
$\{^{Ph}[NPN]Ta(H)\}[\mu\text{-}\eta^2{:}\eta^1\text{-}N(BC_8H_{14})N](\mu\text{-}H)_2\{^{Ph}[NPN]Ta\}$	Prep: $\{^{Ph}[NPN]Ta\}_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2 + Cy_2BH$	188
$\{^{Ph}[NPN]Ta(H)\}[\mu\text{-}\eta^2{:}\eta^1\text{-}N(B(H)C_6H_{13})N](\mu\text{-}H)_2\{^{Ph}[NPN]Ta\}$	Prep: $\{^{Ph}[NPN]Ta\}_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2 + H_2BCMe_2CHMe_2$	188
	Prep: thermolysis of $\{^{Ph}[NPN]Ta(H)\}[\mu\text{-}\eta^2{:}\eta^1\text{-}N(BC_8H_{14})N](\mu\text{-}H)_2\{^{Ph}[NPN]Ta\}$	188
	Prep: $\{^{Ph}[NPN]Ta\}_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2$ + ex. 9-BBN	188

(*Continued*)

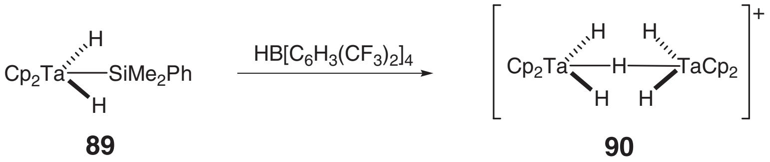
Table 7 (Continued)

Compound	*Comments*	*References*
$\{^{Ph}[NPN]Ta\}_2[\mu\text{-}\eta^2\text{:}\eta^1\text{-}N(L)N](\mu\text{-}H)_2$	Prep: $\{^{Ph}[NPN]Ta\}_2(\mu\text{-}\eta^2\text{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2 + L$; L = $AlMe_3$ (X-ray), $GaMe_3$ (X-ray), $B(C_6F_5)_3$ (X-ray)	190
$\{^{Ph}[NPN]Ta\}_2[\mu\text{-}\eta^2\text{:}\eta^1\text{-}N(L)N](\mu\text{-}H)_2$	Prep: $\{^{Ph}[NPN]Ta\}_2(\mu\text{-}\eta^2\text{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2 + L$; L = $HB(C_6F_5)_2$	188
$[(Cy_2N)_2ClTa](\mu\text{-}H)_2$	Prep: $TaCl_5 + 4Cy_2NLi$, X-ray	194, 195

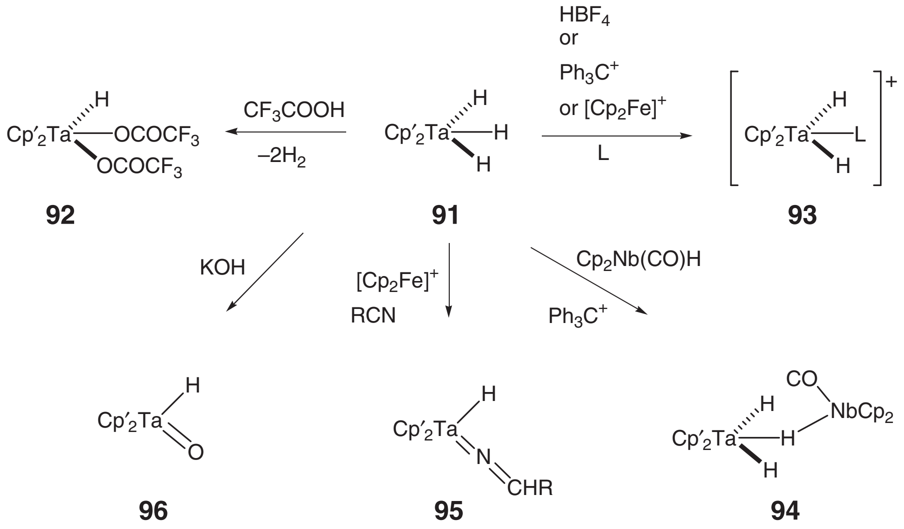
[a] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.



Scheme 30



Scheme 31



Scheme 32

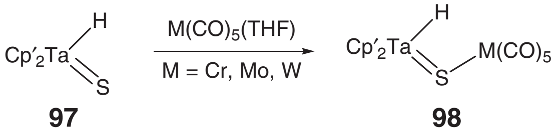
dihydride compound, *trans*-$[Cp^*(\eta^5\text{-}C_5H_4CH_2CH_2NMe_2)TaH_2]PF_6$, where the amino group coordinated to the tantalum center.[200] $[Cp'_2Ta(H)_2]^+$ is trapped by donor molecules or anions to give cationic complexes 93 (L = SMe_2, THT, CN^tBu, PMe_2Ph, CO) or neutral complexes *trans*-$[Cp'_2TaH_2(X)]$ (X = CN and SEt). Reactions with $Cp_2NbH(CO)$ and nitriles afford a cationic heterodinuclear complex 94 and azaalkenylidene complexes 95 (R = Me, ^{t}Bu). Reaction with KOH affords an oxo–hydride complex 96, which may involve nucleophilic attack to form an unstable hydroxide complex. $Cp'_2Ta(H)_2(SH)$, which is accessible by the reaction of the corresponding trihydride with elemental sulfur,[47,201] is found to decompose upon heating in solution to revert to the sulfide complex $Cp'_2Ta({=}S)H$ **97**.[202] The reaction of the trihydride complex Cp'_2TaH_3 **91** with an excess of ethylene sulfide upon heating in toluene gives $Cp'_2Ta({=}S)(SEt)$.[203] The transient cationic dihydride species, $[Cp'_2Ta(H)_2]^+$, is reported to react with L–XH (2-aminobenzoic acid, 2-aminobenzenethiol, 2-thiopyridine, dibenzolylmethane, and acetylacetone), giving the corresponding cationic monohydride complexes, $Cp'_2Ta(H)(L\text{–}X)]^+$, after dihydrogen evolved.[204] The Ta═S bond can be protonated or alkylated, and also served as a donor for $W(CO)_5$ or $W(CO)_4$ moieties.[203] Reaction of $Cp'_2Ta({=}S)H$ **97** with $M(CO)_5(THF)$ (M = Cr, Mo, W) gives heterobimetallic complexes **98** bridged by an unsupported four-electron sulfur ligand (Scheme 33).[205]

Treatment of Cp'_2TaH_3 **91** with an excess of selenium in toluene solution led to the formation of $Cp'_2Ta(\eta^2\text{-}Se_2)H$ **99** (Scheme 34).[206] Abstraction of one selenium atom by triethylphosphite afforded the monoselenide complex $Cp'_2Ta({=}Se)H$ **100**, the analog of **97**. Complexes **101–103** are derived in the same manner as thio analogs.

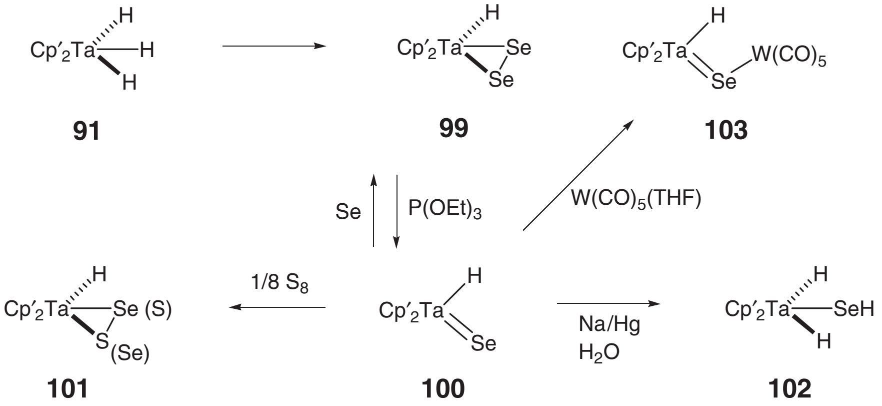
Permethyltantalocene analogs of **99** and **100** containing a Cp^*_2Ta fragment are prepared starting from $Cp^*_2TaH_3$.[207] The permethyltantallocene fragment Cp^*_2Ta is also suited for stabilizing formaldehyde and thioaldehyde complexes. A telluroformaldehyde complex, $Cp^*_2Ta(\eta^2\text{-}TeCH_2)(H)$ **104**, is formed by the addition of tellurium to $Cp^*_2Ta({=}CH_2)H$.[136] Complex **104** can be quantitatively converted to the telluride–methyl derivative, $Cp^*_2Ta({=}Te)Me$. The direct reaction of a trihydride complex $Cp^*_2TaH_3$ with elemental tellurium affords a ditellurido derivative $Cp^*_2Ta(\eta^2\text{-}Te_2)H$, which is further converted to a telluride–hydride complex upon treatment with mercury in the presence of tellurium-trapping reagent, PMe_3.[136] It was reported that $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$ existed in an equilibrium with Cp^*_2TaH, which was trapped by sulfur to give a mixture of $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Ta(\eta^2\text{-}S_2)$ and $Cp^*_2Ta(\eta^2\text{-}S_2)H$.[208] Chlorination and iodination of $Cp^*_2TaH_3$ are reported to give mono- and dihalogenated hydrides, while perfluorination of $Cp^*_2TaH_3$ proceeds to $Cp^*_2TaF_3$.[209]

Addition of a Lewis acid such as $B(C_6F_5)_3$ to Cp_2TaH_3 results in the formation of $Cp_2TaH_2(\mu\text{-}H)B(C_6F_5)_3$, in which $B(C_6F_5)_3$ is hopping between all three hydrides.[210] Similar complexation behavior is observed for $Cp_2TaH_3(LiBEt_4)$ that is simply obtained from Cp_2TaH_3 and $LiBEt_4$.[211] Some hydride complexes $Cp_2TaH_3(LiAlH_4)$, $Cp_2Ta(AlH_4)(THF)$, and $[Cp_2Ta(\mu\text{-}H)_2(AlH_2)]_2(\mu\text{-}OBu)_2$ containing aluminum hydride moieties are prepared.[211]

Hydricity of tantalocene hydrides was evaluated by thermodynamic measurements of the hydride-transfer reaction between $Cp_2TaH(L)$ (L = CO, PEt_3, $(H)_2$) or $Cp^*_2TaH(L)$ (L = $(H)_2$, ═O) and $[(p\text{-}MeOC_6H_4)Ph_2C][BF_4]$ in



Scheme 33



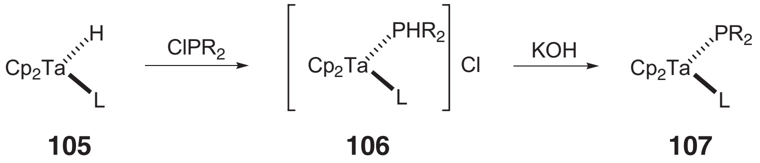
Scheme 34

acetonitrile, giving hydride-transfer free energies ranging from 74 to 95 kcal mol^{-1}.[212] These data indicate that Cp* is a much more efficient donor than Cp, and that phosphine is a better donor than carbonyl despite being a good hydride donor of the trihydride species, thus being consistent with the known donor properties of these ligands.[212] Hydrogen exchange and some reactivities of metallocene hydride complexes of tantalum are reviewed.[213] *ansa*-[$Me_2Si(C_5Me_4)_2$]TaH_3 reacts with CO and ethylene to give the corresponding compounds much faster than $Cp^*_2TaH_3$ does, indicating that the Me_2Si *ansa*-bridge strongly promotes reductive elimination of H_2.[46] *Ab initio* calculations for Cp_2TaH_3 explain the exchange coupling process proceeding through a dihydrogen-like transition state.[214] Reaction of trihydride Cp_2TaH_3 with diphenyldiazomethane quickly proceeds to give a monohydride complex, $Cp_2Ta(H)(\eta^1\text{-}NNCPh_2)$.[215,216] The mechanism of dihydrogen addition to a tantalocene complex such as $Cp^*_2Ta(H)$(benzyne), giving Cp^*TaH_3 and benzene through $Cp^*Ta(H)_2(Ph)$, is elucidated by using parahydrogen induced polarization (PHIP).[217] Pairwise addition of dihydrogen to the 16-electron tantalum(III) intermediate is proposed.

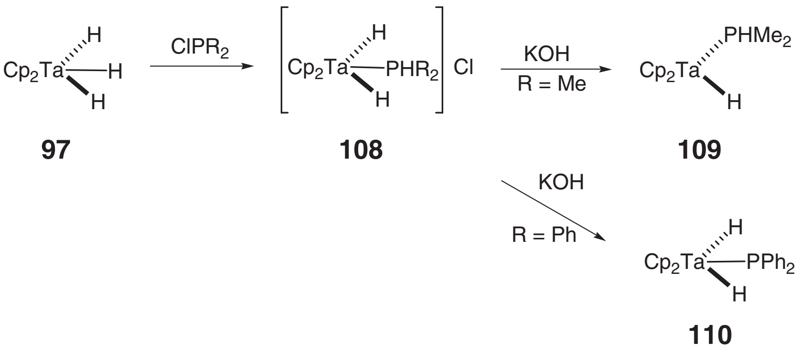
The phosphido or phosphine complexes of tantalocene have been prepared by the direct reactions of monohydride $Cp_2Ta(L)H$ **105** and trihydride Cp_2TaH_3 **97** with $ClPR_2$ followed by treatment with base. Monohydride complexes $Cp_2Ta(H)(L)$ [**105**: L = CO, $P(OMe)_3$, and $PPh(OMe)_2$] react with chlorophosphines $ClPR_2$ (R = Me or Ph) to give phosphonium salts **106**, from which, after deprotonation by KOH, the phosphido complexes $Cp_2TaPR_2(L)$ **107** are obtained (Scheme 35).[27,39]

It is reasonable that the trihydride complex is a better precursor of a transient "Cp_2TaH" intermediate. Two research groups have demonstrated that $ClPPh_2$ smoothly inserts into the central Ta–H bond of **97** to yield an ionic compound *trans*-[$Cp_2TaH_2(HPPh_2)$]Cl (**108**: R = Ph) (Scheme 36).[218–220] Deprotonation of **108** in aqueous NaOH resuls in the selective formation of a neutral dihydride phosphido complex, *trans*-$Cp_2TaH_2(PPh_2)$ **110**.[220] Prolonged heating of **110** in the presence of $HPPh_2$ with periodic removal of dihydrogen produced a mixture of $Cp_2Ta(PHPh_2)(PPh_2)$ and $Cp_2Ta(H)[\eta^2\text{-}P(Ph)P(Ph)]$.[220] In sharp contrast to $ClPPh_2$, a similar deprotonation of an ionic salt *trans*-[$Cp_2TaH_2(HPMe_2)$]Cl (**108**: R = Me) derived from the reaction with $ClPMe_2$ exclusively affords the hydrido-phosphine $Cp_2Ta(H)(PMe_2H)$ **109** (Scheme 36).[218,219] Since similar hydride-phosphine niobocene complexes have been prepared, the deprotonation depends not only on the kind of metal but also on the ligand nature, including substituents on the phosphine atom as well as the cyclopentadienyl moiety.[219–223] For the PMe_2 system, strong electron-donor Cp ligands favor the formation of Ta–phosphido complexes.[219,223] The reaction of Cp_2TaH_3 with RPH_2 (R = Ph, Cy) or P4 affords the corresponding diphosphanato complexes $Cp_2TaH[\eta^2\text{-}(PR)_2]$ and $Cp_2TaH[\eta^2\text{-}(PH)_2]$.[224]

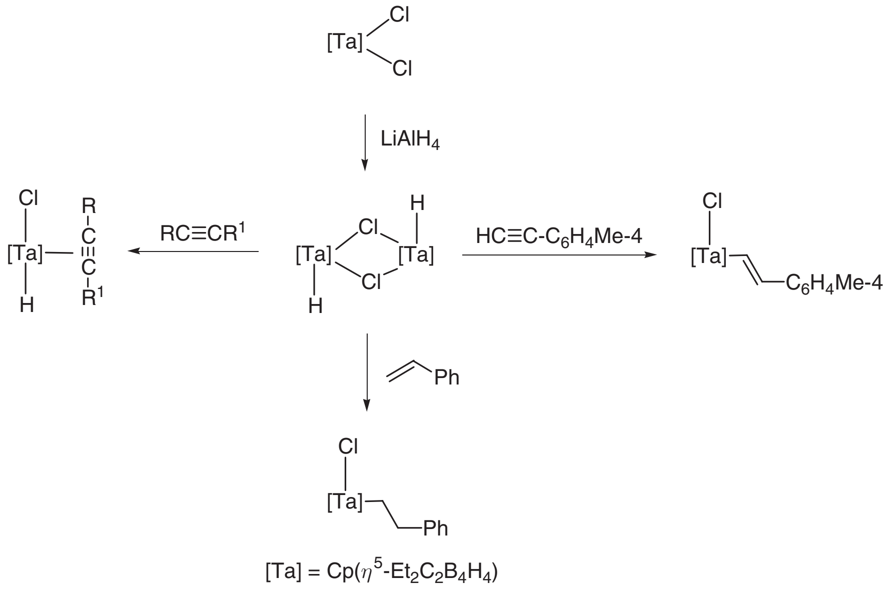
The hydride derivative of tantalacarborane, [$Cp(Et_2C_2B_4H_4)Ta(H)$]$(\mu\text{-}Cl)_2$, which can be made by the reduction of $Cp(Et_2C_2B_4H_4)TaCl_2$ with $LiAlH_4$, is an analog of Schwartz's reagent, exhibiting different insertion reactions, as summarized in Scheme 37. Internal alkynes such as diphenylacetylene and phenylmethylacetylene result in the formation of alkyne hydride compounds, while *p*-tolylacetylene and styrene can insert into a Ta–H bond.[163]



Scheme 35



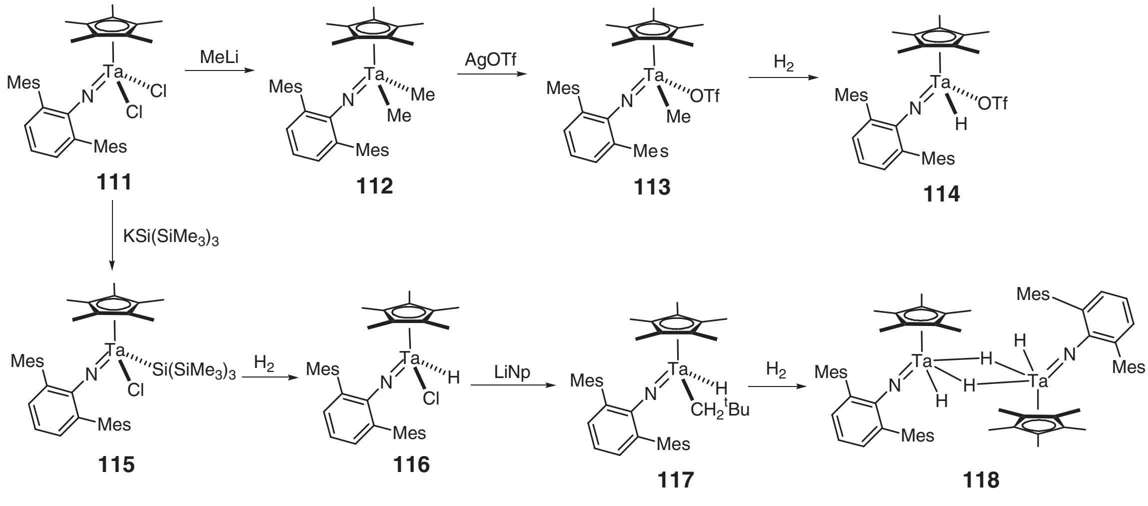
Scheme 36



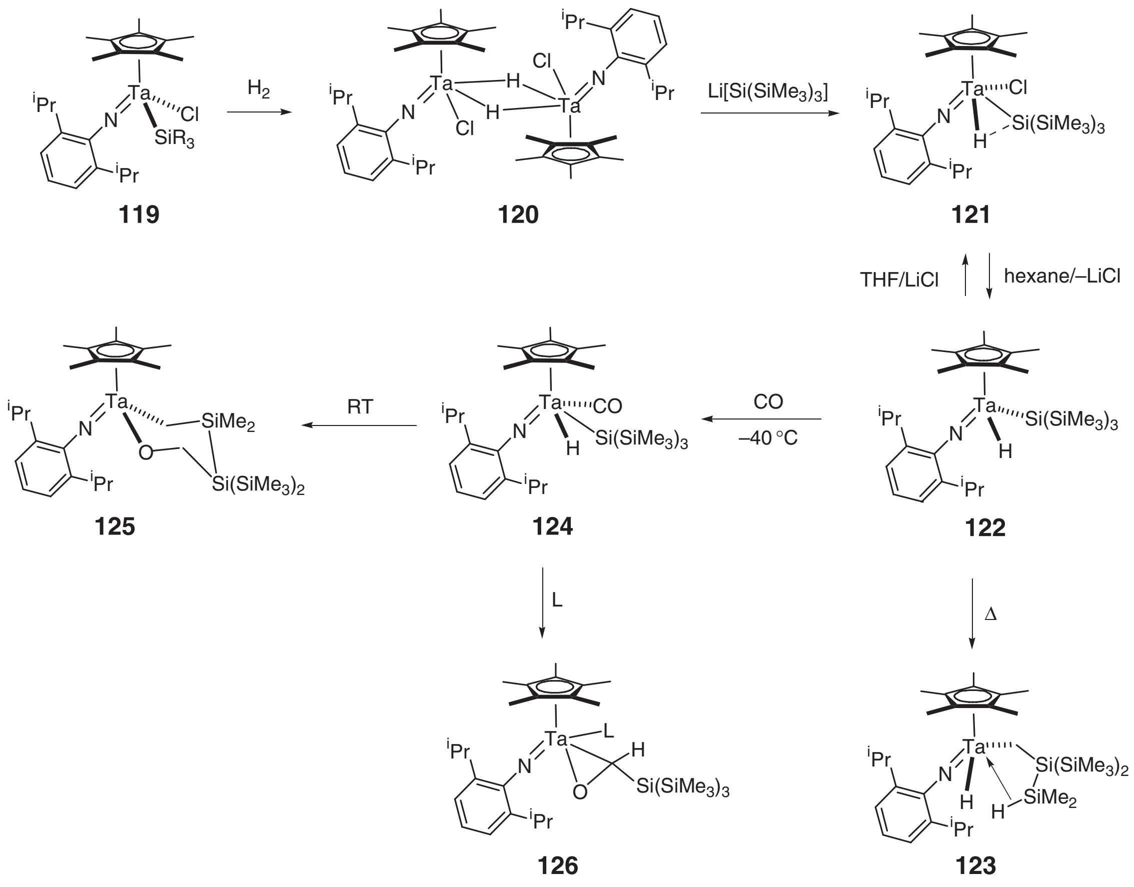
Scheme 37

Half-sandwich complexes with bulky imido moiety stabilize some hydride complexes (Scheme 38). Hydrogenolysis of Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)Me$_2$ **112** proceeds very slowly, while its triflate derivative Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)Me(OTf) **113** readily reacts with dihydrogen to give a monohydride compound Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)H(OTf) **114**.[154] Hydrogenolysis of the hydrido alkyl compound **117** by thermolysis gives a dinuclear hydrogen-bridged compound [Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)(H)]$_2$(μ-H)$_2$ **118**.[154] The very bulky imido compound Cp*Ta(=NC$_6$H$_3$-2,6-Ar$_2$)Me$_2$ (Ar = C$_6$H$_2$-2,4,6-^{i}Pr$_3$) reacts with dihydrogen to give a mononuclear dihydride compound Cp*Ta(=NC$_6$H$_3$-2,6-Ar$_2$)(H)$_2$.[154]

The Ta–Si bond of less bulky imido complexes, Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(Cl)(SiR$_3$) **119**, can be cleaved by dihydrogen to give a hydride-bridged complex, [Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(Cl)]$_2$(μ-H)$_2$ **120**[149] (Scheme 39). Addition of (THF)$_3$LiSi(SiMe$_3$)$_3$ to a THF slurry of **120** produces the anionic compound Li(THF)$_3$[Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(Cl)(H)Si(SiMe$_3$)$_3$] **121** containing a three-center Ta···Si···H interaction, which turns to a neutral hydride–silyl complex, Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)[Si(SiMe$_3$)$_3$] **122**, upon dissolution in hexane or toluene.[149] Compound **122** decomposes at room temperature to give Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)[CH$_2$Si(SiMe$_3$)$_2$SiMe$_2$H] **123** after the



Scheme 38



Scheme 39

conversion of Si(SiMe$_3$)$_3$ to CH$_2$Si(SiMe$_3$)$_2$SiMe$_2$H presumably through an intermediate silylene species. Unsaturated organic compounds [acetonitrile (azomethine complex), isonitrile (acyl complex), ketone (isopropoxide)] insert into the Ta–Si bond of 122, while ethylene (tantalacyclopentane) and diphenylacetylene (tantalacyclopentadiene) react with unsaturated Ta(III) species.[149] Hydrogen and dichloromethane, respectively, afford a dinuclear hydride-bridged compound and a dichloride.[149] Carbonylation of 122 produces an oxametallacyclic compound, Cp*(2,6-^{i}Pr$_2$-C$_6$H$_3$N═)-$\overline{\mathrm{Ta[OCH_2Si(SiMe_3)_2SiMe_2CH_2]}}$ 125, through carbonyl–hydride Cp*Ta(═NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)(CO)[Si(SiMe$_3$)$_3$] 124 and acyl species Cp*Ta(═NC$_6$H$_3$-2,6-^{i}Pr$_2$)(L){η^2-CO(H)[Si(SiMe$_3$)$_3$]} (126: L = CO or PMe$_3$), each of which is isolated.[36] Reaction of the hydride-silyl compound Cp*Ta(═NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)[Si(SiMe$_3$)$_3$] 122 with PhSiH$_3$ produces three dinuclear complexes, [Cp*Ta(═NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)]$_2$(μ-H)$_2$, an analog of 118, Cp$^*_2$Ta$_2$(═NC$_6$H$_3$-2,6-^{i}Pr$_2$)(μ-H)$_2$[μ-Ph(H)SiN(C$_6$H$_3$-2,6-^{i}Pr$_2$)] **127**, and Cp$^*_2$Ta$_2$(H)(μ-H)[μ-Ph(H)SiN(C$_6$H$_3$-2,6-^{i}Pr$_2$)]$_2$ **128**.[225] Complexes **127** and **128** contain the silaimine ligand Ph(H)SiN(C$_6$H$_3$-2,6-^{i}Pr$_2$) from the coupling of imido ligand and PhSiH$_3$. Reaction of CpTa(═NAr)(PMe$_3$)$_2$ (Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$) with HSiClMe$_2$ affords d^0-silyl hydride CpTa(═NAr)(PMe$_3$)(H)(SiMe$_2$Cl), which has a short Ta–Si bond and Si–Cl bonds;[226,227] its crystal structure shows an interligand hypervalent interaction between the silyl and hydride ligands.

The reaction mechnism of the reaction between (η^5-C$_5$Me$_4$R)TaCl$_4$ (R = Me, Et) and 2 equiv. of Bu$_3$SnH, giving a hydride-bridging ditantalum(IV) compound [(η^5-C$_5$Me$_4$R)TaCl$_2$]$_2$(μ-H)$_2$, is reported.[228] Cyclometallated phosphine hydride complex Cp*Ta(PMe$_3$)H$_2$(η_2-CHPMe$_2$) **129** reacts with alcohols to afford the corresponding alkoxides, Cp*Ta(OR)$_4$ (R = Me, ^{i}Pr, Ph), while the reaction with sterically demanding phenols gives Cp*TaH$_2$(OAr)$_2$ (Ar = C$_6$H$_3$-2,6-Me$_2$, C$_6$H$_2$-2,4,6-Me$_3$, C$_6$H$_3$-2,6-^{i}Pr$_2$).[229] Heterocumulenes such as CO$_2$ and RNCO (R = Ph, *p*-Tol) can insert into the Ta–H bond(s) of **129** to give the corresponding bis(formato) Cp*Ta(PMe$_3$)(η^2-OCHO)(η^1-OCHO)(η_2-CHPMe$_2$) and mono(formamido) Cp*Ta(PMe$_3$)H(η^2-OCNR)(η_2-CHPMe$_2$) compounds (Table 8).[230]

Table 8 Hydride complexes with Cp ligands[a]

Compound	*Comments*	*References*
Metallocene complexes		
Cp$_2$TaH$_3$	*ab initio* calculation	214
cis-Cp$^*_2$TaH$_2$Cl	Prep: Cp$^*_2$TaCl(THF) + H$_2$	40
cis-Cp$^*_2$TaHCl$_2$		
trans-Cp$^*_2$TaH$_2$Cl		40, 209
cis-Cp$^*_2$Ta(I)$_2$(H)	Prep: Cp$^*_2$Ta(=Se)(SeH) + MeI	207
	Prep: Cp$^*_2$TaI(H)$_2$ + MeI	209
trans-Cp$^*_2$Ta(H)$_2$(I)	Prep: Cp$^*_2$TaH$_3$ + MeI	209
trans-Cp$^*_2$Ta(H)$_2$(Cl)	Prep: Cp$^*_2$TaH$_3$ + HCl or CCl$_4$ or CHCl$_3$	209
cis-Cp$^*_2$Ta(H)Cl$_2$	Prep: *trans*-Cp$^*_2$Ta(H)$_2$(Cl) + HCl or CCl$_4$ or CHCl$_3$, X-ray	209
Cp*(η^5-C$_5$H$_4$SiMe$_3$)TaH$_3$	Prep: Cp*(η^5-C$_5$H$_4$SiMe$_3$)TaCl$_2$ + ex. LiAH$_4$	45
Cp*[η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$]TaH$_3$	Prep: Cp*[η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$]TaCl$_2$ + ex. LiAH$_4$	45
Cp*(η^5-C$_5$H$_4$PPh$_2$)TaH$_3$	Prep: Cp*(η^5-C$_5$H$_4$PPh$_2$)TaCl$_2$ + NaAl(H$_2$)(OCH$_2$CH$_2$OMe)$_2$	48
Cp*(η^5-C$_5$H$_4$CH$_2$CH$_2$NMe$_2$)TaH$_3$	Prep: Cp*(η^5-C$_5$H$_4$CH$_2$CH$_2$NMe$_2$)TaCl$_2$ + NaAl(H$_2$)(OCH$_2$CH$_2$OMe)$_2$	200
ansa-[Me$_2$Si(C$_5$Me$_4$)$_2$]TaH$_3$	Prep: TaCl$_5$ + *ansa*-[Me$_2$Si(C$_5$Me$_4$)$_2$](SnBu$_3$)$_2$ + LiAlH$_4$	46
Cp$_2$TaH(L)	Hydride-transfer reaction with [(*p*-MeOC$_6$H$_4$)Ph$_2$C][BF$_4$]; L = CO, PEt$_3$, (H)$_2$	212
Cp$^*_2$TaH(L)	Hydride-transfer reaction with [(*p*-MeOC$_6$H$_4$)Ph$_2$C][BF$_4$];L = (H)$_2$, =O	212
Cp*(η^5-C$_5$H$_4$PPh$_2$)TaH(CO)	Prep: Cp*(η^5-C$_5$H$_4$PPh$_2$)TaH$_3$ + CO	48
cis-[Cp$'_2$Ta(η^2-H$_2$)(CO)]Y and its isotomers	Prep: Cp$'_2$Ta(H)(CO) + HY; Cp$'$ = Cp, C$_5$H$_4$^{t}Bu; Y = BF$_4$, B[C$_6$H$_3$(CF$_3$)$_2$]$_4$	196–198
trans-[Cp$'_2$Ta(H)$_2$(CO)]Y	Prep: Cp$'_2$Ta(H)(CO) + HY; Cp$'$ = Cp, C$_5$H$_4$^{t}Bu; Y = BF$_4$, B[C$_6$H$_3$(CF$_3$)$_2$]$_4$ (X-ray)	196, 198
cis-{Cp$'_2$Ta(H)$_2$[P(OMe)$_3$]}$^+$ and its isotomers	NMR and DFT analysis	197, 198
[(Cp$_2$TaH$_2$)$_2$(μ-H)]B[C$_6$H$_3$(CF$_3$)$_2$]$_4$	Prep: 2Cp$_2$Ta(H$_2$)(SiMe$_2$Ph) + HB[C$_6$H$_3$(CF$_3$)$_2$]$_4$	198
Cp$_2$TaH$_2$(μ-H)B(C$_6$F$_5$)$_3$	Prep: Cp$_2$TaH$_3$ + B(C$_6$F$_5$)$_3$	210
trans-[(η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_2$(SMe$_2$)]BF$_4$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + HBF$_4$ + SMe$_2$	199
trans-[Cp*(η^5-C$_5$H$_4$CH$_2$CH$_2$N$^+$Me$_2$H)-TaH$_2$(SMe$_2$)](BF$_4$)$_2$	Prep: Cp*(η^5-C$_5$H$_4$CH$_2$CH$_2$NMe$_2$)TaH$_3$ + HBF$_4$ + SMe$_2$	200
cis-(η^5-C$_5$H$_4$^{t}Bu)$_2$TaH(OCOCF$_3$)$_2$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + ex. CF$_3$COOH	199
cis-[Cp*(η^5-C$_5$H$_4$CH$_2$CH$_2$N$^+$Me$_2$H)-TaH(OCOCF$_3$)$_2$](CF$_3$COO)	Prep: Cp*(η^5-C$_5$H$_4$CH$_2$CH$_2$NMe$_2$)TaH$_3$ + ex. CF$_3$COOH, X-ray	200
[(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)(O$_2$CC$_6$H$_4$-2-NH$_2$)]PF$_6$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + [Ph$_3$C]PF$_6$ + 2-aminobenzoic acid, X-ray	204
[(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)(RC(O)CHC(O)R)]BF$_4$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + [Ph$_3$C]BF$_4$ + acacH or dibenzoylmethane	204
trans-[(η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_2$(L)]PF$_6$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + [Cp$_2$Fe]PF$_6$ or [Ph$_3$C]PF$_6$ + L; L = SMe$_2$, THT, CN^{t}Bu, PMe$_2$Ph, CO	199
Cp$_2$TaH$_3$(LiBEt$_4$)	Prep: Cp$_2$TaH$_3$ + LiBEt$_4$	211
Cp$_2$TaH$_3$(LiAlH$_4$)	Prep: Cp$_2$TaH$_3$ + LiAlH$_4$	211
[Cp$_2$Ta(μ-H)$_2$(AlH$_2$)]$_2$(μ-OBu)$_2$Cp$_2$Ta(AlH$_4$)(THF)	Prep: Cp$_2$TaCl$_2$ + LiAlH$_4$ in THF	211
trans-[(η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_2$(X)]	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + [Cp$_2$Fe]PF$_6$ + NaX; X = CN, SEt	199
(η^5-C$_5$H$_4$^{t}Bu)$_2$TaH(=O)	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + [Cp$_2$Fe]PF$_6$ + KOH	199
Cp$^*_2$Ta(=O)(H)	Prep: Cp$^*_2$TaCl(THF) + NaOH	40, 41
(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)$_2$(SH)	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(=S)H + Na/Hg + water or (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + 1/8 S$_8$	202, 47
(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)(η^2-S$_2$)	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + 3/8 S$_8$	47, 231
Cp$^*_2$Ta(=S)(SH)	Prep: photochemical conversion of Cp$^*_2$Ta(η^2-S$_2$)(H)	208
[(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)(SC$_6$H$_4$-2-NH$_2$)]PF$_6$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + [Ph$_3$C]PF$_6$ + 2-aminobenzenethiol, X-ray	204
[(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)(SC$_5$H$_4$N)]PF$_6$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + [Ph$_3$C]PF$_6$ + 2-thiopyridine, X-ray	204
(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)(μ-S)M(CO)$_5$	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(H)(=S) + M(CO)$_5$(THF); M = Cr, Mo, W (X-ray)	205
(η^5-C$_5$H$_4$^{t}Bu)$_2$Ta(η^2-Se$_2$)(H)	Prep: (η^5-C$_5$H$_4$^{t}Bu)$_2$TaH$_3$ + Se	206

(Continued)

Table 8 (Continued)

Compound	*Comments*	*References*
$(\eta^5-C_5H_4{}^tBu)_2Ta(=Se)(H)$	Prep: $(\eta^5-C_5H_4{}^tBu)_2Ta(\eta^2-Se_2)(H) + P(OEt)_3$	206
$Cp^*_2Ta(\eta^2-Se_2)(H)$	Prep: $Cp^*_2TaH_3 + Se$	207
$Cp^*_2Ta(=Se)(H)$	Prep: $Cp^*_2Ta(\eta^2-Se_2)(H) + PMe_3$	207
$Cp^*_2Ta(=Se)(SeH)$	Prep: photochemical conversion of $Cp^*_2Ta(\eta^2-Se_2)(H)$	207
trans-$(\eta^5-C_5H_4{}^tBu)_2Ta(SeH)(H)_2$	Prep: $(\eta^5-C_5H_4{}^tBu)_2Ta(=Se)(H) + Na/Hg +$ water, X-ray	206
$Cp^*_2Ta(\eta^2-TeCH_2)(H)$	Prep: $Cp^*_2Ta(=CH_2)(H) + Te$, X-ray	136
$Cp^*_2Ta(\eta^2-Te_2)H$	Prep: thermal isomerization of $Cp^*_2Ta(\eta^2-TeCH_2)(H)$, X-ray	136
$Cp^*_2Ta(=Te)H$	Prep: $Cp^*_2Ta(\eta^2-Te_2)H + Hg + PMe_3$	136
trans-$[Cp^*(\eta^5-C_5H_4CH_2CH_2NMe_2)TaH_2]PF_6$	Prep: $Cp^*(\eta^5-C_5H_4CH_2CH_2NMe_2)TaH_3 + [Cp_2Fe]PF_6$, X-ray	200
$[(\eta^5-C_5H_4{}^tBu)_2TaH(N=CHR)]PF_6$	Prep: $(\eta^5-C_5H_4{}^tBu)_2TaH_3 + [Cp_2Fe]PF_6 + RCN$; $R = Me$, ^tBu	199
$Cp^*_2Ta(=NR)(H)$	Prep: $Cp^*_2TaCl(THF) + Li(NHR)$; $R = Ph$, ^tBu	41
$Cp^*[\eta^5-C_5H_4SiMe_2(CH_2CH= CH_2)]-Ta(H)(=NtBu)$	Prep: $Cp^*[\eta^5-C_5H_4SiMe_2(CH_2-\eta^2-CH=CH_2)]TaCl + LiNH^tBu$	232
$Cp_2Ta(H)(\eta^1-NNCPh_2)$	Prep: $Cp_2TaH_3 + N_2CPh_2$, X-ray	215, 216
trans-$[Cp_2TaH_2(PHR_2)]Cl$	Prep: $Cp_2TaH_3 + ClPR_2$; $R = Ph$, Me	219, 220
trans-$Cp_2TaH_2(PPh_2)$	Prep: $[Cp_2TaH_2(HPPh_2)]Cl +$ aq-NaOH, X-ray	220
trans-$[Cp'Cp''TaH_2(PHR_2)]Cl$	Prep: $Cp'Cp''TaH_3 + ClPR_2$; $Cp' = Cp'' = Cp$; $Cp' = Cp$, $Cp'' = C_5H_2-1-{}^tBu-3,4-Me_2$; $Cp' = Cp$, $Cp'' = Cp^*$; $Cp' = Cp'' = Cp^*$; $R = Ph$, Me, X-ray for $Cp' = Cp$, $Cp'' = C_5H_2-1-{}^tBu-3,4-Me_2$ and $R = Me$ after Cl was replaced by PF_6	223
$Cp_2TaH(PHMe_2)$	Prep: $[Cp_2TaH_2(HPMe_2)]Cl +$ aq-KOH	219, 223
trans-$Cp'Cp''TaH_2(PR_2)$	Prep: *trans*-$[Cp'Cp''TaH_2(PHR_2)]Cl +$ strong base $Cp' = Cp'' = Cp$; $R = Ph$ $Cp' = Cp$; $Cp'' = Cp^*$; $R = Me$	223
trans-$[Cp'Cp''TaH_2(PR_2)]Cl$ and $Cp'Cp''TaH(PHR_2)$	$Cp' = Cp$; $Cp'' = C_5H_2-1-{}^tBu-3,4-Me_2$; $R = Me$	
$Cp_2Ta(PHPh_2)(PPh_2)$ and $Cp_2Ta(H)[\eta^2-P(Ph)P(Ph)]$	Prep: thermolysis of *trans*-$Cp_2TaH_2(PPh_2)$	220
$Cp_2Ta(H)[R_2P(CH_2)_nPR_2]$	Prep: $Cp_2TaH_3 + R_2P(CH_2)_nPR_2$ ($n = 1$ or 2)	233
trans-$Cp^*(\eta^5-C_5H_4PPh_2)TaH_2(PPh_2)$	Prep: $Cp^*(\eta^5-C_5H_4PPh_2)TaH_3 + ClPPh_2$, and then aq-KOH	48
$Cp_2TaH[\eta^2-(PR)_2]$	Prep: $Cp_2TaH_3 + RPH_2$; $R = Ph$, Cy (X-ray)	224
$Cp_2TaH[\eta^2-(PH)_2]$	Prep: $Cp_2TaH_3 + P_4$, X-ray	224
Half-sandwich complexes		
$[(\eta^5-C_5Me_4R)TaCl_2]_2(\mu-H)_2$	Mechanism: $(\eta^5-C_5Me_4R)TaCl_4 + 2Bu_3SnH$; $R = Me$, Et	228
$(C_5H_5BPh)(\eta^5-C_4H_4BN^iPr_2)Ta(H)_2(L)$	Prep: $(C_5H_5BPh)(\eta^5-C_4H_4BN^iPr_2)TaMe_2 + H_2 + L$; $L = PEt_3$ (X-ray), P^iPr_3	42, 139
$Cp^*TaH_2(OAr)_2$	Prep: $Cp^*Ta(PMe_3)H_2(\eta_2-CHPMe_2) + 2ArOH$; $Ar = C_6H_3-2,6-Me_2$, $C_6H_2-2,4,6-Me_3$, $C_6H_3-2,6-{}^iPr_2$	229
$Cp^*Ta(=NC_6H_3-2,6-Mes_2)H(OTf)$	Prep: $Cp^*Ta(=NC_6H_3-2,6-Mes_2)Me(OTf) + H_2$	154
$Cp^*Ta(=NC_6H_3-2,6-Mes_2)H(Cl)$	Prep: $Cp^*Ta(=NC_6H_3-2,6-Mes_2)Cl[Si(SiMe_3)_3] + H_2$	154
$[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(Cl)]_2(\mu-H)_2$	Prep: $Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)Cl(SiR_3) + H_2$; $SiR_3 = Si(SiMe_3)_3$, $SiPh_3$, $SiHMes_2$	149
$[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)]_2(\mu-H)_2$	Prep: $Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)Si(SiMe_3)_3 + H_2$	149
$Li(THF)_3[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(Cl)(H)Si(SiMe_3)_3]$	Prep: $[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(Cl)]_2(\mu-H)_2 + (THF)_3LiSi(SiMe_3)_3$ in THF, X-ray	149
$Li(THF)_3[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(Cl)(H)Si(SiPh_3)]$	Prep: $[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(Cl)]_2(\mu-H)_2 + (THF)_3LiSiPh_3$ in THF	149
$Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)[Si(SiMe_3)_3]$	Prep: $Li(THF)_3[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(Cl)(H)Si(SiMe_3)_3]$ dissolved in hexane, X-ray	149
$Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)(CH_2C_6H_2-3,5-Me_2-2-SiHMes_2)$	Prep: $[Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(Cl)]_2(\mu-H)_2 + (THF)_2LiSiHMes_2$ in diethyl ether, X-ray	149
$Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)[\eta^1-N=C(Me)Si(SiMe_3)_3]$	Prep: $Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)[Si(SiMe_3)_3] +$ acetone	149
$Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)[CH_2Si(SiMe_3)_2SiMe_2H]$	Isomerization of $Cp^*Ta(=NC_6H_3-2,6-{}^iPr_2)(H)Si(SiMe_3)_3$	149

(*Continued*)

Table 8 (Continued)

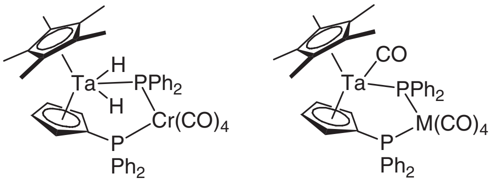
Compound	*Comments*	*References*
$Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)\text{-}(OCHPh_2)[CH_2Si(SiMe_3)_2SiMe_2H]$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(H)[CH_2Si(SiMe_3)_2SiMe_2H] + Ph_2CO$	149
$Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(H)(CH_2CMe_3)$	Prep: $[Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(Cl)]_2(\mu\text{-}H)_2 + 2Me_3CH_2MgCl$, X-ray	149
$[Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(Me)]_2(\mu\text{-}H)_2$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(Me)[Si(SiMe_3)_3] + H_2$	149
$Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Mes_2)(SiH_2Ph)(H)$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Mes_2)(CH_2{}^{t}Bu)(H) + PhSiH_3$	154
$[Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Mes_2)(H)]_2(\mu\text{-}H)_2$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Mes_2)(CH_2{}^{t}Bu)(H) + H_2$	154
$[Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(H)]_2(\mu\text{-}H)_2$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(H)[Si(SiMe_3)_3] + PhSiH_3$	225
$Cp^{*}{}_2Ta_2({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(\mu\text{-}H)_2[\mu\text{-}Ph(H)SiN(C_6H_3\text{-}2,6\text{-}^{i}Pr_2)]$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(H)[Si(SiMe_3)_3] + PhSiH_3$, X-ray	225
$Cp^{*}{}_2Ta_2(H)(\mu\text{-}H)[\mu\text{-}Ph(H)SiN(C_6H_3\text{-}2,6\text{-}^{i}Pr_2)]_2$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}^{i}Pr_2)(H)[Si(SiMe_3)_3] + PhSiH_3$, X-ray	225
$Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Ar_2)(H)_2$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Ar_2)Me_2 + H_2$; $Ar = C_6H_2\text{-}2,4,6\text{-}^{i}Pr_3$	154
$Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Ar_2)(H)Br$	Prep: $Cp^{*}Ta({=}NC_6H_3\text{-}2,6\text{-}Ar_2)(H)_2 + C_6H_5Br$; $Ar = C_6H_2\text{-}2,4,6\text{-}^{i}Pr_3$	154
$CpTa({=}NAr)(PMe_3)(H)(SiMe_2Cl)$	Prep: $CpTa({=}NAr)(PMe_3)_2 + HSiClMe_2$; $Ar = C_6H_3\text{-}2,6\text{-}^{i}Pr_2$, X-ray	226, 227
$CpTa({=}NAr)(PMe_3)(H)(SiMe_2X)$	Prep: $CpTa({=}NAr)(PMe_3)(H)(SiMe_2Cl) + Me_3SiX$; $X = OTf, I$; $Ar = C_6H_3\text{-}2,6\text{-}^{i}Pr_2$	227
$CpTa({=}NAr)(PMe_3)(H)(SiMe_3)$	Prep: $CpTa({=}NAr)(PMe_3)(H)(SiMe_2Cl) + MeLi$; $Ar = C_6H_3\text{-}2,6\text{-}^{i}Pr_2$	227
$Cp^{*}(\eta^5\text{-}C_4H_4BN^{i}Pr_2)Ta(H)_2(PMe_3)$	Prep: $Cp^{*}(\eta^5\text{-}C_4H_4BN^{i}Pr_2)TaMe_2 + H_2 + PMe_3$	137, 139
$Cp^{*}TaH(PPh_2)_3$	Prep: $Cp^{*}TaMe(PPh_2)(\eta^2\text{-}CH_2{=}CH_2) + H_2 + PPh_2H$	234
$[(\eta^5\text{-}C_4H_4BN^{i}Pr_2)Ta(PMe_3)_2Cl](m\text{-}H)[(\eta^5\text{-}C_4H_4BN^{i}Pr_2)Ta(H)(PMe_3)Cl]$	Prep: $(\eta^5\text{-}C_4H_4BN^{i}Pr_2)Ta(PMe_3)_3Cl + H_2$, X-ray	42
$(C_5H_5BPh)(\eta^5\text{-}C_4H_4BN^{i}Pr_2)Ta(H)_2(PMe_3)$	Prep: $(C_5H_5BPh)(\eta^5\text{-}C_4H_4BN^{i}Pr_2)Ta(H)_2(L) + \text{ex. } PMe_3$	139
$Cp^{*}(\eta^5\text{-}C_4H_4BMe)Ta(H)_2(PMe_3)$	Prep: $Cp^{*}(\eta^5\text{-}C_4H_4BMe)TaMe_2 + H_2 + PMe_3$	138, 139
$Cp^{*}Ta(PMe_3)(\eta^2\text{-}OCHO)(\eta^1\text{-}OCHO)(\eta_2\text{-}CHPMe_2)$	Prep: $Cp^{*}Ta(PMe_3)H_2(\eta_2\text{-}CHPMe_2) + CO_2$	230
$Cp^{*}Ta(PMe_3)H(\eta^2\text{-}OCNR)(\eta_2\text{-}CHPMe_2)$	Prep: $Cp^{*}Ta(PMe_3)H_2(\eta_2\text{-}CHPMe_2) + RNCO$; $R = Ph$, *p*-Tol	230
Carborane complexes		
$[Cp(Et_2C_2B_4H_4)Ta(H)]_2(\mu\text{-}Cl)_2$	Prep: $Cp(Et_2C_2B_4H_4)TaCl_2 + LiAlH_4$	163
$Cp(Et_2C_2B_4H_4)TaCl(H)(RCCR^1)$	Prep: $[Cp(Et_2C_2B_4H_4)Ta(H)]_2(\mu\text{-}Cl)_2 + RCCR^1$; $R = R^1 = Ph$; $R = Me$, $R^1 = Ph$	163

[a] $Cp = \eta^5\text{-}C_5H_5$, $Cp^{*} = \eta^5\text{-}C_5Me_5$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

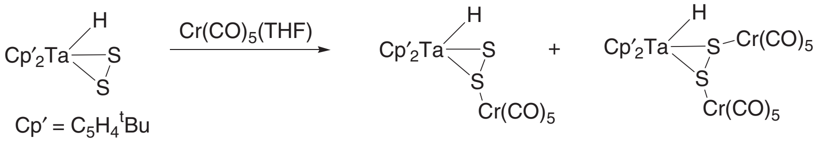
5.03.3.3.3 Heterobimetallic hydride complexes

Insertion of $ClPPh_2$ followed by deprotonation of the hydride carbonyl complex $Cp^{*}(\eta^5\text{-}C_5H_4PPh_2)TaH(CO)$ and the trihydride $Cp^{*}(\eta^5\text{-}C_5H_4PPh_2)TaH_3$ provides the corresponding phosphido complexes $Cp^{*}(\eta^5\text{-}C_5H_4PPh_2)Ta(CO)(PPh_2)$ and *trans*-$Cp^{*}(\eta^5\text{-}C_5H_4PPh_2)TaH_2(PPh_2)$, which can act as bidentate ligands for $M(CO)_4$ fragments through two phosphine atoms (Scheme 40).[48,49]

The reaction of $Cp'_2Ta(\eta^2\text{-}S_2)H$[231] with an excess of $Cr(CO)_5(THF)$ gives heterobimetallic complexes $Cp'_2TaH(S_2)[Cr(CO)_5]$ and $Cp'_2TaH(S_2)[Cr(CO)_5]_2$ ($Cp' = \eta^5\text{-}C_5H_4{}^{t}Bu$) (Scheme 41).[235] Heterobimetallic



Scheme 40



Scheme 41

complexes $Cp_2TaH_2(\mu\text{-}H)M(CO)_5$ are prepared by a simple reaction of Cp_2TaH_3 and $M(CO)_5$ (M = Cr, Mo, W) precursors.[236] The central hydride ligand of Cp_2TaH_3 bound to group 6 metal and the fluxionality of the hydride ligands are characterized spectroscopically. Bimetallic complexes $[Cp'_2TaH(\mu\text{-}H)_2M(PPh_3)]PF_6$ (M = Cu, Au) containing two bridging hydride ligands are products of the reaction of $Cp'TaH_3$ with $[M(PPh_3)]PF_6$.[237]

Thermal displacement of dihydrogen from the trihydride Cp_2TaH_3 in the presence of 1 equiv. of diphosphine $R_2P(CH_2)_nPR_2$ ($n = 1$ or 2) affords the cooresponding monohydride complexes $Cp_2Ta(H)[R_2P(CH_2)_nPR_2]$: one phosphine could coordinate to the tantalum center, while the other remains free, giving $Cp_2Ta(\mu\text{-}H)[\mu,\eta^1{:}\eta^1\text{-}R_2P(CH_2)_nPR_2]M(CO)_4$ (M = Cr, Mo, W).[233] The phosphido- and hydride-bridged heterobimetallic complexes, $Cp_2TaH(\mu\text{-}H)[\mu\text{-}PR_2]M(CO)_4$ (R = Me, Ph; M = Cr, Mo, W), are obtained from the corresponding hydride phosphido complexes and metal carbonyls $M(CO)_4(L)_2$ (M = Cr, Mo, W; I_2 = NBD; L = piperidine).[218,219] Similar treatments of $Cp_2TaH_2(PPh_2)$ and $CpCp^*TaH_2(PMe_2)$ with $Fe(CO)_3(BDA)$ (BDA = benzylideneacetone) afforded the corresponding heterobimetallic complexes $Cp_2TaH(\mu\text{-}H)(\mu\text{-}PPh_2)Fe(CO)_3$ and $CpCp^*TaH(\mu\text{-}H)(\mu\text{-}PMe_2)Fe(CO)_3$[223] (Table 9). $Cp_2TaH(\mu\text{-}H)(\mu\text{-}PMe_2)M(CO)_4$ reacts with phosphines or diphosphines L [L = PMe_2Ph, PPh_2Me, $Me_2P(CH_2)PMe_2$ (dmpm), or $Me_2PCH_2CH_2PMe_2$ (dmpe)] to give open-structured complexes, *trans*-$Cp_2TaH_2(\mu\text{-}PMe_2)[M(CO)_4(L)]$ with the *cis*-arrangement at M as major or sole products.[27,238] In the case of diphosphine ligands, the intact phosphine part of $Cp_2TaH_2(\mu\text{-}PMe_2)M(CO)_4[Me_2P(CH_2)_nPMe_2]$ (M = Mo, W; $n = 1$ or 2) is coordinated by an additional $Cr(CO)_5$ fragment, giving linear trimetallic complexes, $Cp_2TaH_2(\mu\text{-}PMe_2)M(CO)_4[\mu\text{-}\eta^1{:}\eta^1\text{-}Me_2P(CH)_nPMe_2][Cr(CO)_5]$.

Table 9 Heterobimetallic hydride complexes[a]

Compound	*Comments*	*References*
$(\eta^5\text{-}C_5H_4{}^tBu)_2Ta(H)(\mu\text{-}Se)W(CO)_5$	Prep: $(\eta^5\text{-}C_5H_4{}^tBu)_2Ta({=}Se)(H) + W(CO)_5(THF)$, X-ray	206
$Cp'_2TaH(S_2)[Cr(CO)_5]$	Prep: $Cp'_2Ta(\eta^2\text{-}S_2)H$ + ex. $Cr(CO)_5(THF)$, X-ray	235
$Cp'_2TaH(S_2)[Cr(CO)_5]_2$		235
$Cp_2TaH_2(\mu\text{-}H)M(CO)_5$	Prep: $Cp_2TaH_3 + M(CO)_5(THF)$; M = Cr, Mo, W	236
$[Cp'_2TaH(\mu\text{-}H)_2M(PPh_3)]PF_6$	Prep: $Cp'TaH_3 + [M(PPh_3)]PF_6$; M = Cu, Au	237
$[(\eta^5\text{-}C_5H_4{}^tBu)_2TaH_2(\mu\text{-}H)Nb(CO)Cp_2]PF_6$	Prep: $(\eta^5\text{-}C_5H_4{}^tBu)_2TaH_3 + [Cp_2Fe]PF_6 + Cp_2Nb(H)(CO)$	199
$Cp_2Ta(\mu\text{-}H)[\mu,\eta^1{:}\eta^1\text{-}R_2P(CH_2)_nPR_2]M(CO)_4$	Prep: $Cp_2Ta(H)[R_2P(CH_2)_nPR_2] + M(CO)_4(piperidine)_2$; $n = 1$ or 2; M = Cr, Mo, W	233
$Cp_2TaH(\mu\text{-}H)[\mu\text{-}PR_2]M(CO)_4$	Prep: *trans*-$Cp_2TaH_2(PPh_2)$ or $Cp_2TaH(PHMe_2) + M(CO)_4(L)_2$ (L_2 = NBD, L = piperidine); R = Me, Ph; M = Cr, Mo, W, X-ray for R = Me, M = Cr	218, 219
$Cp_2TaH(\mu\text{-}H)(\mu\text{-}PPh_2)Fe(CO)_3$	Prep: *trans*-$Cp_2TaH_2(PPh_2) + Fe(CO)_3(BDA)$, X-ray	223
$CpCp^*TaH(\mu\text{-}H)(\mu\text{-}PMe_2)Fe(CO)_3$	Prep: *trans*-$CpCp^*TaH_2(PMe_2) + Fe(CO)_3(BDA)$	223
$Cp_2TaH_2(\mu\text{-}PMe_2)M(CO)_4(L)$	Prep: $Cp_2TaH(\mu\text{-}H)(\mu\text{-}PMe_2)M(CO)_4$ + L; M = Cr, Mo, W; L = PMe_2Ph, PPh_2Me, $Me_2P(CH_2)PMe_2$ (dmpm), or $Me_2PCH_2CH_2PMe_2$ (dmpe)	27,238
$Cp_2Ta(H)_2[\mu,\eta^1{:}\eta^1\text{-}P(S)R][ML_n]$	Prep: $Cp_2Ta[P({=}S)Me_2]H_2$ + metal carbonyls; R = Me, Ph; $[ML_n] = Fe(CO)_4$, $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $CpMn(CO)_2$	34
$Cp_2TaH_2(\mu\text{-}PMe_2)M(CO)_4[\mu\text{-}\eta^1{:}\eta^1\text{-}Me_2P(CH_2)_nPMe_2][Cr(CO)_5]$	Prep: $Cp_2TaH_2(\mu\text{-}PMe_2)M(CO)_4[Me_2P(CH)_nPMe_2] + Cr(CO)_5(THF)$; M = Mo, W; $n = 1$, 2	27, 238
trans-$Cp^*(\eta^5\text{-}C_5H_4\overline{PPh_2)Ta(H)_2(\mu\text{-}PPh_2)Cr}(CO)_4$	Prep: *trans*-$Cp^*(\eta^5\text{-}C_5H_4PPh_2)TaH_2(PPh_2) + Cr(CO)_4(NBD)$	48, 49

[a] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

5.03.4 Alkylidenes and Alkylidynes

5.03.4.1 Alkylidene Complexes without Cp Ligand

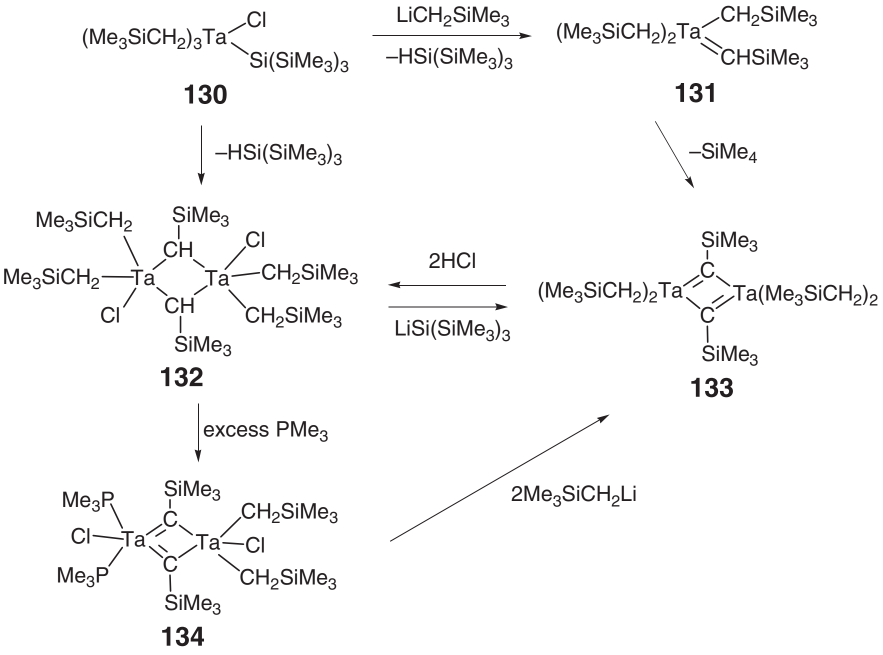
Schrock has reviewed recent developments in the chemistry of alkylidene and alkylidyne complexes.[239–242] Calorimeter was used for the intramolecular α-hydrogen abstraction reaction of the isolated $Ta(CH_2SiMe_3)_5$ to give $Ta({=}CHSiMe_3)(CH_2SiMe_3)_3$,[243] which gradually decomposed in second-order kinetics to the dimeric alkylidyne complex $(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2$.[60] $(^tBuCH_2)_3Ta{=}CH^tBu$ reacts with ammonia to give a pentamer $[(^tBuCH_2)_2TaN]_5$, which is a precursor of TaN.[244]

Silane elimination to form metal–carbon multiple bonds is reported to be much preferred over alkane elimination.[245–249] Treatment of $(Me_3ECH_2)_3TaCl_3$ (E = Si, C) with 2 equiv. of $LiSi(SiMe_3)_3$ yielded $(Me_3ECH_2)_2Ta({=}CHEMe_3)(Si(SiMe_3)_3)$ (E = Si,C) along with the release of silane $HSi(SiMe_3)_3$. Treatment of $(Me_3SiCH_2)_3TaCl_3$ with 1 equiv. of $LiSi(SiMe_3)_3$ affords unstable $(Me_3SiCH_2)_3TaCl(Si(SiMe_3)_3)$ **130**, which decomposes to give a dimeric alkylidene-bridged complex **132** (Scheme 42).[246,250,251] Reaction of **130** with $LiCH_2SiMe_3$ gives a mononuclear alkylidene complex **131**, which turns into a dimeric bis(alkylidyne) complex **133**. Treatment of **132** with an excess of PMe_3 results in the formation of **134**.

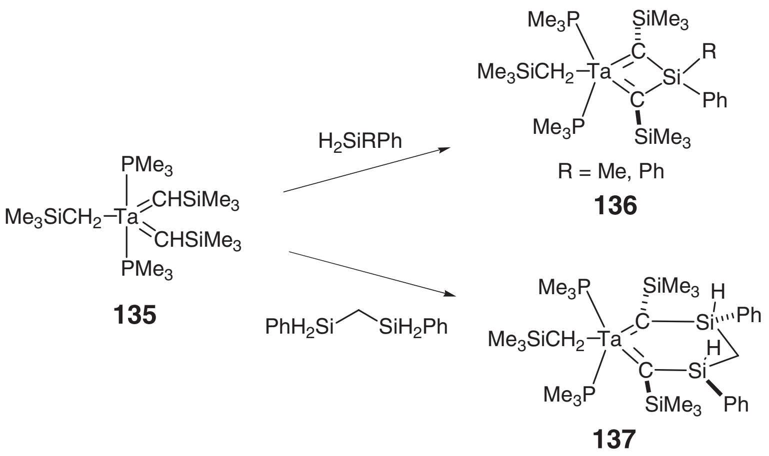
Silane Si–H bonds react with π-bonds in the Ta=CHR moiety to result in the silylation of the alkylidene carbon. Tantalum alkylidene $(Me_3SiCH_2)_3Ta({=}CHSiMe_3)(PMe_3)$ reacted with phenyl silanes $PhSiRH_2$ (R = Me, Ph) to produce bis(silyl)-substituted alkylidene complexes $(Me_3SiCH_2)_3Ta[{=}C(SiMe_3)SiPhRH]$.[252,253] Similar reaction of $(Me_3SiCH_2)Ta({=}CHSiMe_3)_2(PMe_3)_2$ **135** with the corresponding silanes afforded metallasilacyclobutadiene **136** and metalladisilacyclohexadiene **137** complexes (Scheme 43).[253]

Bulky aryloxo ligands can stabilize mononuclear complexes. Treatment of $TaCl_3(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}^tBu_2)_2$ with $LiCH_2SiMe_3$ leads to the formation of the alkylidene complex $(Me_3SiCH_2)(Me_3SiCH{=})Ta(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}^tBu_2)_2$.[66] The analogous alkylidene compounds $(Me_3SiCH_2)(Me_3SiCH{=})Ta(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2$ (R = H, Me, ^{i}Pr, Ph) are generated by photolysis of trialkyls $(Me_3SiCH_2)_3Ta(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2$.[66] Thermolysis of $(Me_3SiCH_2)(Me_3SiCH{=})Ta(OC_6H_3\text{-}2,6\text{-}Ph_2)_2$ results in a cyclometallated compound.[66]

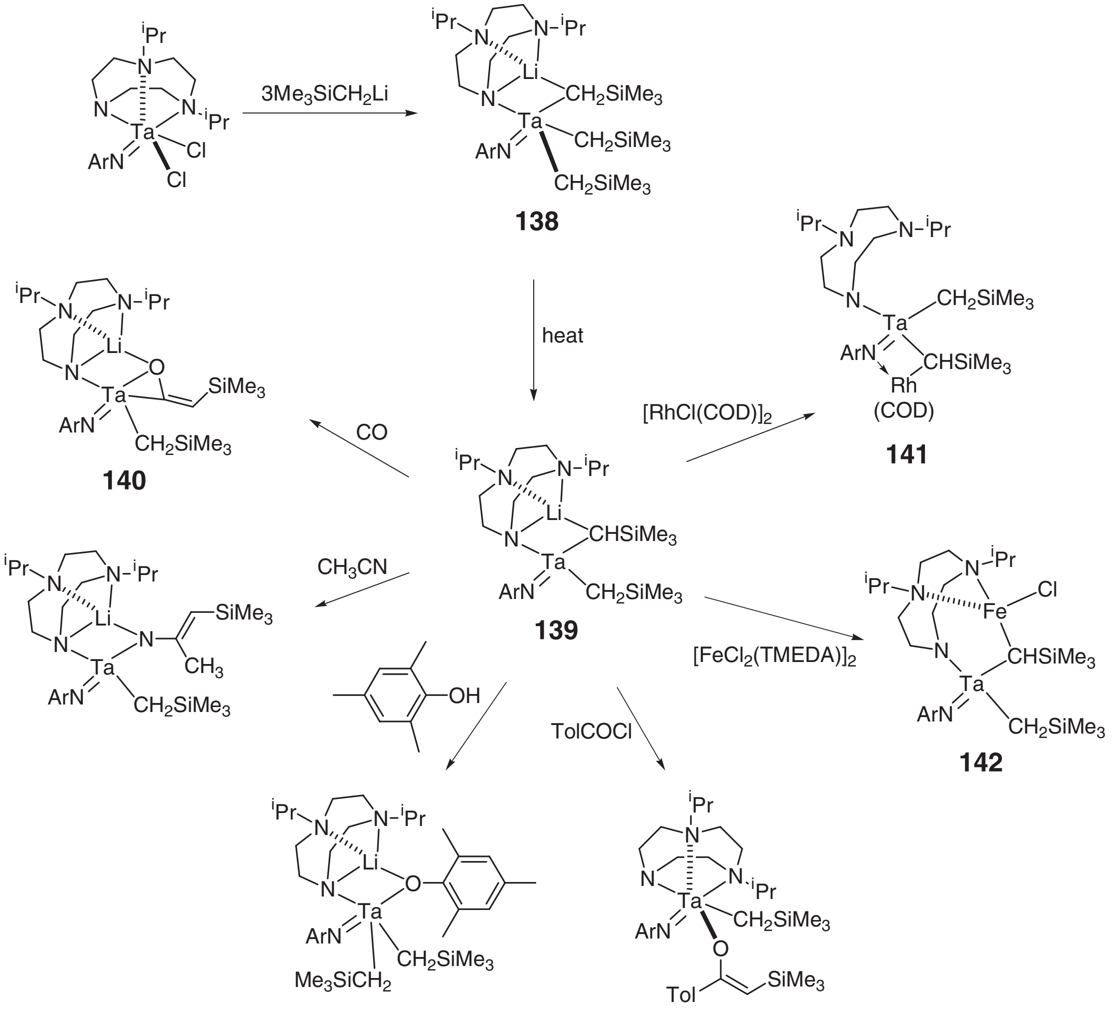
An anionic triazacyclononane ligand can stabilize some alkylidene complexes.[108–110] Treatment of $Ta({=}NAr)Cl_2(^iPr_2\text{-}TACN)$ ($^iPr_2$-TACN = *N*,*N′*-bis(isopropyl)-1,4,7-triazacyclononanyl anion; Ar = $C_6H_3\text{-}2,6\text{-}^iPr_2$) and 3 equiv. of Me_3SiCH_2Li results in the formation of trialkyl complex **138**, which has one alkyl group bridging between tantalum and lithium.[108] Structure **138** undergoes α-hydrogen abstraction upon heating to give the alkylidene **139** with the elimination of $SiMe_4$ (Scheme 44).[108] The reactions of **57** toward protic substrates, nitriles,



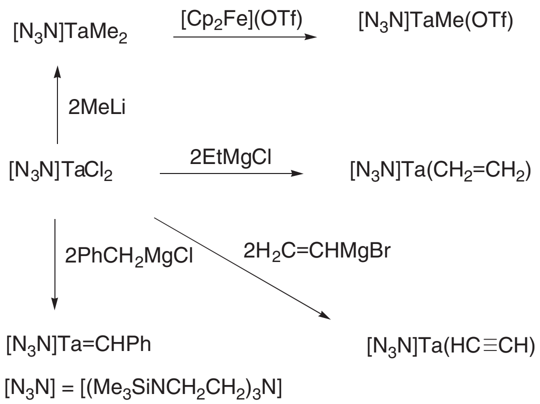
Scheme 42



Scheme 43



Scheme 44



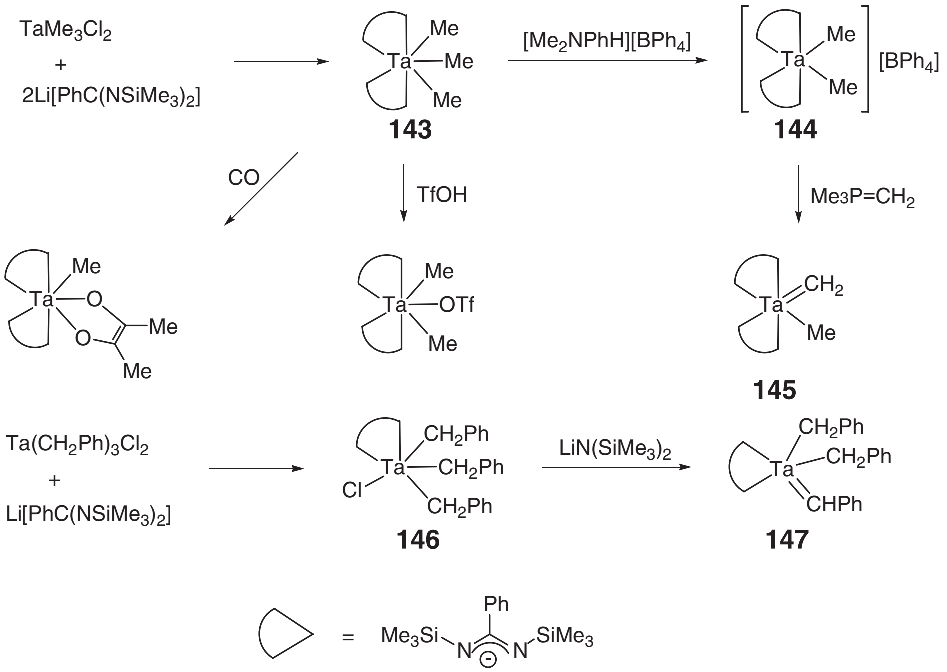
Scheme 45

and other unsaturated electrophiles, including metal chlorides, have been demonstrated for estimating the effect of the lithium anion (Scheme 16).[109,110] Carbonylation of **139** afforded the ketene complex **140**. Reactions of **139** with $[RhCl(COD)]_2$ and $[FeCl_2(TMEDA)]_2$ result in the formation of heterobimetallic compounds **141 and 142**, respectively, which contain a bridging alkylidene moiety.

Multidentate ligands uniquely stabilize some organotantalum species. Scheme 45 shows the case of triamidoamine ligand $[(RNCH_2CH_2)_3N]^{3-}$ with sterically bulky R groups ($R = SiMe_3$, $SiEt_3$).[105,106] A convenient starting material is $[(Me_3SiNCH_2CH_2)_3N]TaCl_2$, which could be alkylated to give dimethyl, benzylidene, ethylene, and acetylene complexes, depending on the alkylating reagents.[105,106] Upon treatment with $PhPH_2$, the ethylene complex is converted to ethylidene complex $[(Me_3SiNCH_2CH_2)_3N]Ta{=}CHMe$.[105,106] The ethylene complex is not stable in solution, but gradually decomposes to give an ethyl compound, $[(Me_3SiNCH_2CH_2)_2N][N(CH{=}CH_2)SiMe_3]Ta(Et)$ via cleavage of one N–C bond of the ligand.[106] Similarly, dialkylation of $[(Me_3SiNCH_2CH_2)_3N]TaCl_2$ produces the corresponding monoalkyl compounds $[(Me_3SiNCH_2CH_2)_2N][N(CH{=}CH_2)SiMe_3]Ta(R)$ ($R = {}^nPr$, ${}^nBu$, isopentyl, neohexyl) together with the corresponding alkylidene compounds $[(Me_3SiNCH_2CH_2)_3N]Ta{=}CHCH_2R^1$ ($R^1 = CH_3$, CH_2CH_3, $CH(CH_3)_2$, CMe_3).[106] The greater solubility of triethylsilyl derivatives versus trimethylsilyl derivatives is expected and almost the same chemistry is reported.[107] Amalgam reduction of $Ta({=}CHR)Cl_2[N(SiMe_2CH_2P^iPr_2)_2]$ ($R = {}^tBu$, Ph) under dinitrogen generates dinuclear complexes $\{Ta({=}CHR)[N(SiMe_2CH_2P^iPr_2)_2]\}_2(\mu\text{-}N_2)$, in which dinitrogen is bound in an end-on mode.[254] Another multidentate ligand supports the trimethyl complex $[P_2N_2]TaMe_3$ ($[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2)_2PPh$), whose photolysis results in the formation of the methyl–methylidene compound $[P_2N_2]Ta({=}CH_2)Me$.[90] Exposure of this methylidene compound to ethylene gives two alkyl ethylene products, namely $[P_2N_2]TaMe(\eta^2\text{-}C_2H_4)$ and $[P_2N_2]TaEt(\eta^2\text{-}C_2H_4)$.[193] The complex $[P_2N_2]TaEt(\eta^2\text{-}C_2H_4)$ can be alternatively prepared by the reaction of $[P_2N_2]TaH_3(PMe_3)$ with ethylene.[193]

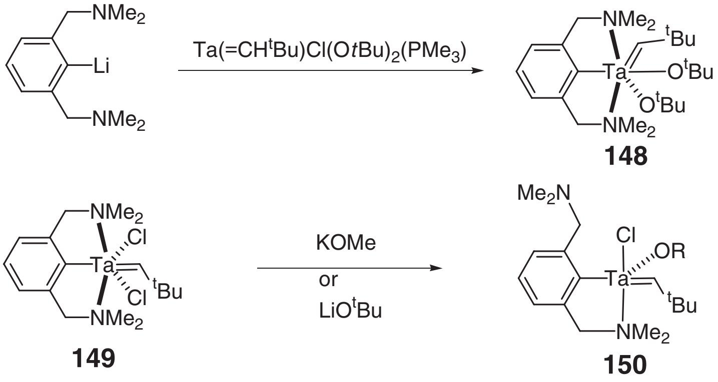
The reactions of appropriate coordinatively unsaturated species with carbene precursors such as $Me_3P{=}CH_2$ have been utilized for the preparation of $Cp_2TaMe({=}CH_2)$.[255,256] A similar strategy is applied for cationic bis(amidinate) dimethyl complex, $\{[PhC(NSiMe_3)_2]_2Ta(CH_3)_2\}[BPh_4]$ **144**, which is derived from $[PhC(NSiMe_3)_2]_2Ta(CH_3)_3$ **143** with $[Me_2NPhH][BPh_4]$. Reaction of **144** with $Me_3P{=}CH_2$ or $Et_3P{=}CH(SiMe_3)$ gives methylidene complex $[PhC(NSiMe_3)_2]_2Ta(CH_3)({=}CH_2)$ **145** (Scheme 46).[92] Treatment of mono(amidinate) tribenzyl compound $[PhC(NSiMe_3)_2]TaCl(CH_2Ph)_3$ **146** with $LiN(SiMe_3)_2$ affords the benzylidene compound $[PhC(NSiMe_3)_2]Ta({=}CHPh)(CH_2Ph)_2$ **147**.[92] An amidinate methylidene complex, $[TolC(NSiMe_3)_2]_2Ta({=}CH_2)Me$, acts as the methylene-transfer reagent.[113] $[TolC(NSiMe_3)_2]_2Ta({=}CH_2)Me$ does not react with weak oxidants such as styrene oxide and triphenylphosphine oxide; however, it reacts with pyridine N-oxides to yield $[TolC(NSiMe_3)_2]_2Ta({=}O)Me$ and regioselective methylation of pyridine N-oxides.[113]

Alkylidene complex $Ta({=}CH^tBu)X_3(THF)_2$ ($X = Cl$ or Br) is a starting compound for the preparation of $Tp^*Ta({=}CH^tBu)X_2$ ($X = Cl$, Br).[161] Bis(alkoxide) compounds $Ta({=}CH^tBu)[\eta^3\text{-}C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2](O^tBu)_2$ **148** and $Ta({=}CH^tBu)[\eta^2\text{-}C_6H_4\text{-}2\text{-}(CH_2NMe_2)](O^tBu)_2$ can be derived from the reactions of $Ta({=}CH^tBu)Cl(O^tBu)_2(PMe_3)$ and $Li[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]$ and sequential reaction of $Ta({=}CH^tBu)Cl_3$ with 1/2 $Zn[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]_2$ and $2LiO^tBu$, respectively (Scheme 46).[257] The 1:1 reaction of $Ta({=}CH^tBu)[\eta^3\text{-}C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]Cl_2$ and $ZnCl(CH_2CMe_3)$ produces a bimetallic alkylidyne complex $TaCl_2[\eta^3\text{-}C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2](\mu\text{-}C^tBu)(\mu\text{-}ZnCl)$, which

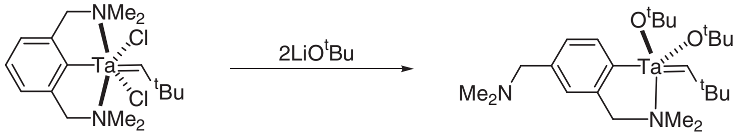


Scheme 46

converts into alkylidyne compound Ta(≡C^{t}Bu)Cl[η^3-C_6H_3-2,6-(CH_2NMe_2)$_2$] upon treatment with TMEDA.[258] Reaction of Ta(=CH^{t}Bu)[η^3-C_6H_3-2,6-(CH_2NMe_2)$_2$]Cl_2 **149** with LiO^{t}Bu and KOMe gives monoalkoxide compounds Ta(=CH^{t}Bu)[η^2-C_6H_3-2,6-(CH_2NMe_2)$_2$]Cl(OR) (**150**; R = Me, ^{t}Bu), which have a free NMe_2 moiety and adopt tbp coordination (Scheme 47).[257] Ta(=CH^{t}Bu)[η^2-C_6H_3-2,6-(CH_2NMe_2)$_2$]Cl(O^{t}Bu) undergoes the metathesis reaction with vinylsilane to give Ta(=$CHSiMe_3$)[η^2-C_6H_3-2,6-(CH_2NMe_2)$_2$]Cl(O^{t}Bu) (Scheme 48).[257] Ta(=CH^{t}Bu)Cl_3(THF)$_2$ and TaCl(O^{t}Bu)$_2$ (=CHR)(PMe_3) (R = ^{t}Bu, CMe_2Ph) are used for the preparation of Ta(=CH^{t}Bu)Cl_2[C_6H_4-2-($CH_2NMeCH_2CH_2NMe_2$)] and Ta(=CHR)(O^{t}Bu)$_2$[C_6H_4-2-($CH_2NMeCH_2CH_2NMe_2$)].[259] Alkylidene compounds Ta(=CH^{t}Bu)(O^{t}Bu)$_2$[C_6H_4-2-($CH_2NMeCH_2CH_2NMe_2$)] and Ta(=$CHCMe_2Ph$)(O^{t}Bu)$_2$-[C_6H_4-2-($CH_2NMeCH_2CH_2NMe_2$)] react with ethylene to give the metallacyclobutane Ta($CH_2CH_2CH_2$)(O^{t}Bu)$_2$-[C_6H_4-2-($CH_2NMeCH_2CH_2NMe_2$)] and/or an ethylene compound Ta(η^2-C_2H_4)(O^{t}Bu)$_2$-[C_6H_4-2-(CH_2NMeCH_2-CH_2NMe_2)].[259]



Scheme 47



Scheme 48

Tantalum alkylidene $Ta(=CHCMe_3)(CH_2CMe_3)_3$ reacts with the surface hydroxyl groups of silica to form $(surface{\equiv}SiO)Ta(=CHCMe_3)(CH_2CMe_3)_2$ or $(surface{\equiv}SiO)_2Ta(=CHCMe_3)(CH_2CMe_3)$, depending on whether the silica was previously dehydroxylated at 700 or 300 °C, respectively.[117,261,262] Treatment with hydrogen provides surface tantalum(III) hydride, $(surface{\equiv}SiO)_2TaH$, which can react with PMe_3 to form phosphine–hydride species $(surface{\equiv}SiO)_2TaH(PMe_3)$,[263] and undergo C–H bond activation of methane and cycloalkanes to give the corresponding surface tantalum–methyl and tantalum–cycloalkyl derivatives,[264,265] $(surface{\equiv}SiO)_2TaH$ catalyzes some catalytic reactions: the H/D exchange between CH_4 and CD_4,[266] the hydrogenolysis of C–C bonds of alkanes,[267,268] and alkane metathesis.[117,269–273] Thermal treatment of $(surface{\equiv}SiO)_2TaH$ up to 500 °C leads to the formation of $(surface{\equiv}SiO)_2Ta$.[274]

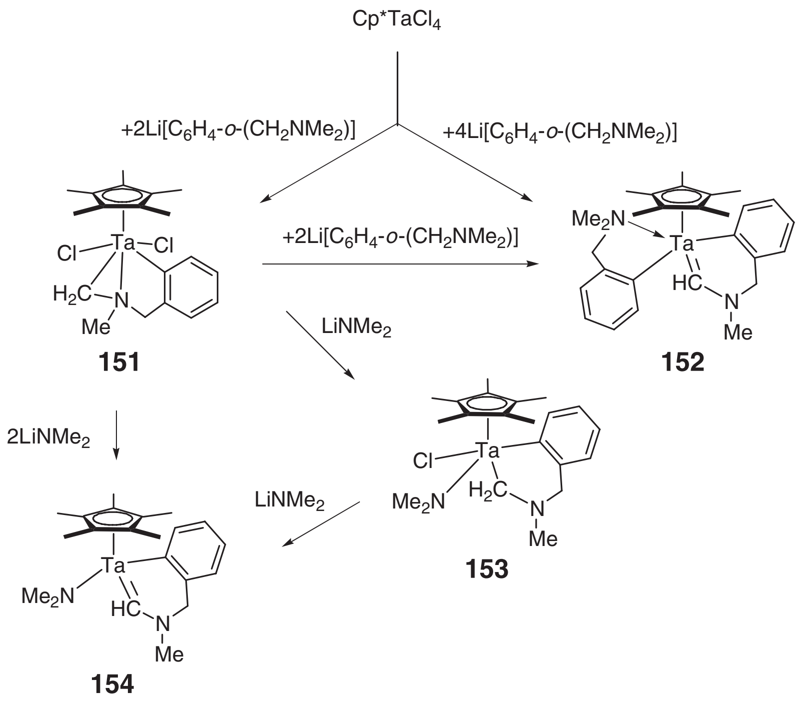
5.03.4.2 Alkylidene Complexes with Cp Ligands

Half-sandwich fragments have stabilized the alkylidene moiety. The reaction of $CpTaCl(NEt_2)_2$ with 2 equiv. of MeLi afforded a cyclopentadinenylidene complex, $CpTa(=C_5H_4)(NEt_2)_2$, in low yield.[275] $CpTa(=N^tBu)Cl_2$ reacts with 2 equiv. of $Ph_3P{=}CH_2$ to give a phosphonio(methylidene) complex $Cp(Cl)Ta(=N^tBu)(=CHPPh_3)$.[276] The reaction of lithiated ylide $Li(CH_2)_2PPh_2$ with $Cp^*Ta(=N^tBu)Cl_2$ affords the chelating compound, $Cp^*(Cl)(^tBuN=)Ta[CH_2P(Ph)_2CH_2]$, which further reacts with a second $Li(CH_2)_2PPh_2$ to give $Cp^*(^tBuN=)Ta(=CHPPh_2Me)_2$ via an intramolecular α-hydrogen migration.[276] Benzylation of phosphinimide complexes $Cp^*Ta(NPR_3)Cl_3$ ($R = {}^tBu, {}^iPr$) affords the corresponding benzylidene complexes $Cp^*(R_3PN)Ta(=CHPh)(CH_2Ph)$, which are robust and fail to react with a variety of reagents including $AlMe_3$, MeLi, PhCN, acetylenes, and olefins.[160] In the case of MeI, $Cp^*(^tBu_3PN)Ta(=CHPh)(CH_2Ph)$ reacts upon heating in benzene to give an unexpected styrene complex, $Cp^*(^tBu_3PN)Ta(\eta^2\text{-}CH_2{=}CHPh)(CH_2Ph)$, in 19% yield as a product of nucleophilic attack on methyl iodide by the benzylidene ligand followed by β-hydride elimination.[160] Reaction of Cp^*TaCl_4 with the stable phosphavinyl Grignard reagent (*Z*)-$MgCl(OEt_2)\{C(^tBu){=}PCy\}$ induces the phosphavinyl-coupling reaction to give 2,4-diphosphabicyclo[1.1.0]butane, $Cy_2P_2C_2{}^tBu_2$.[277] In this reaction, $\{Cp^*TaCl_2[=C(t\mathrm{Bu})P(Cy)\text{-}]\}_2$ is isolated and characterized as an intermediate.[277] The reactions of $Cp^*Ta(=CHSiMe_3)(CH_2SiMe_3)_2$[278] with XylNC and phenol give η^2-iminoacyl complexes, $Cp^*Ta(=CHSiMe_3)(CH_2SiMe_3)\{\eta^2\text{-}C(CH_2SiMe_3){=}NXyl\}$ and $Cp^*Ta(CH_2SiMe_3)_3(OPh)$, respectively.[147]

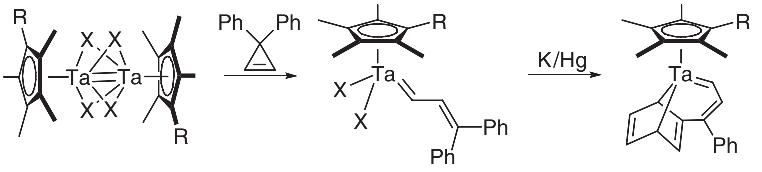
The reaction of Cp^*TaCl_4 and 4 equiv. of $Li[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]$ affords the cyclic alkylidene complex **152** as a product of double C–H bond activation of a methyl group on nitrogen (Scheme 49).[279] The same reaction with 2 equiv. of the anion results in the formation of η^2-imine complex **151**, which further reacts with dimethylamide to give **153** and **154**.[279]

Alkyne coordinated to the tantalum center can be converted to a cyclic alkylidene complex upon treatment with CO and isonitrile: reaction of $Cp^*TaMe_2(\eta^2\text{-}PhC{\equiv}CPh)$ with *tert*-butylisonitrile gives the monomethy–iminoacyl complex, which, upon heating, rearranges to a cyclic alkylidene compound $Cp^*MeTa{=}CH(Ph)C(Ph){=}C(Me)N^tBu$.[280] Similar reaction with carbon monoxide affords the corresponding oxametallacycle $Cp^*MeTa{=}CH(Ph)C(Ph){=}C(Me)O$.[280] $[(\eta^5\text{-}C_5Me_4R)Ta]_2(\mu\text{-}X)_4$ ($R = Me$, Et; $X = Cl$, Br) reacts with 3,3-diphenylcyclopropene to give the corresponding mononuclear compounds $(\eta^5\text{-}C_5Me_4R)Ta(=CHCH{=}CPh_2)$, which can be reduced by potassium amalgam to give tantalanorbornadiene complexes (Scheme 50).[281] Reaction of $[Cp^*Ta]_2(\mu\text{-}X)_4$ ($X = Cl$, Br) with allene leads to the alkylidene compound, whose reduction by sodium amalgam induced double C–H activation of allene ligand to give propynylidene compound (Scheme 51).[282]

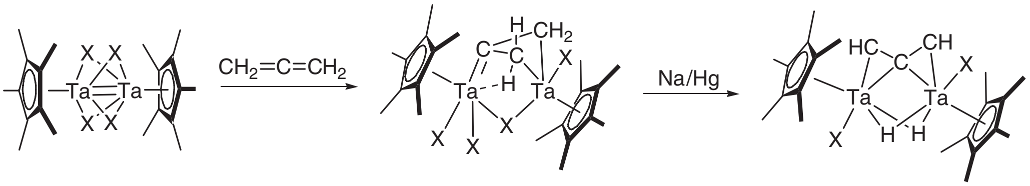
Benzylidene complexes containing an η^4-diene ligand are prepared by α-hydrogen abstraction of the bis(benzyl) species.[283,284] Benzylidene complexes $Cp'Ta(=CHPh)(PMe_3)$(supine-*s*-*cis*-η4-butadiene) ($Cp' = Cp$, Cp^*) are prepared by thermolysis of $Cp'Ta(CH_2Ph)_2$(supine-*s*-*cis*-η4-butadiene) in the presence of PMe_3.[283,284] *o*-Xylylene



Scheme 49



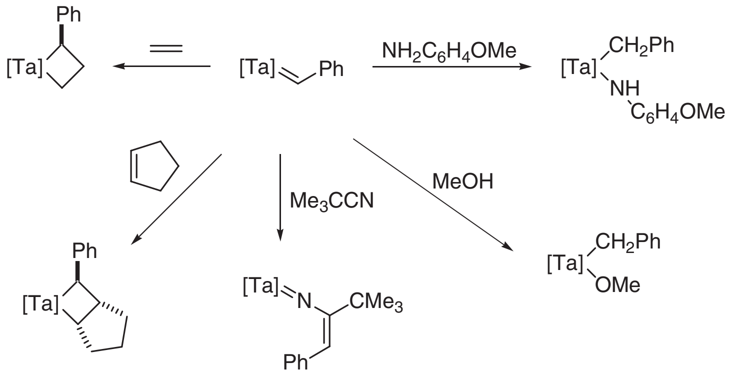
Scheme 50



Scheme 51

benzylidene compound Cp*Ta(=CHPh)[η^4-C$_6$H$_4$(CH$_2$)$_2$-1,2] is also obtained in a similar manner from Cp*Ta(CH$_2$Ph)$_2$[η^4-C$_6$H$_4$(CH$_2$)$_2$-1,2].[284] These dibenzyl compounds are unique catalyst precursors for ring opening metathesis polymerization (ROMP) of norbornene: the butadiene compound with Cp* produces *cis*-poly(norbornene), while the *o*-xylylene compound affords *trans*-poly(norbornene), but no stereoselectivity is found for the polymerization by Cp–butadiene precursor.[283,284] Reaction of Cp*TaCl$_2$(supine-*s-cis*-η^4-2,3-dimethylbutadiene) with 2 equiv. of PhCH$_2$MgCl results in the spontaneous formation of Cp*Ta(=CH$_2$Ph)(supine-*s-cis*-η^4-butadiene), whose reactions with ethylene, cyclopentene, Me$_3$CCN, MeOH, and *p*-methoxyaniline have been reported (Scheme 52).[285] Thermolysis of Cp*Ta(CH$_2$Ph)$_2$(η^2-C,N-AD) (AD = 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene) gives Cp*Ta(=CHPh)(supine-η^4-AD).[286]

Intramolecular hydride migration to an alkene bound to the metallocene fragment is possible: treatment of Cp$_2$Ta(H)(η^2-C$_2$H$_4$) with (CF$_3$)$_2$CFI or C$_6$F$_5$I gives an ethylidene complex, Cp$_2$Ta(=CHMe)(I).[287] It is notable that this reaction is the same as that of the isolectronic tungsten analog [Cp$_2$W(H)(η^2-C$_2$H$_4$)]$^+$, which is oxidized by



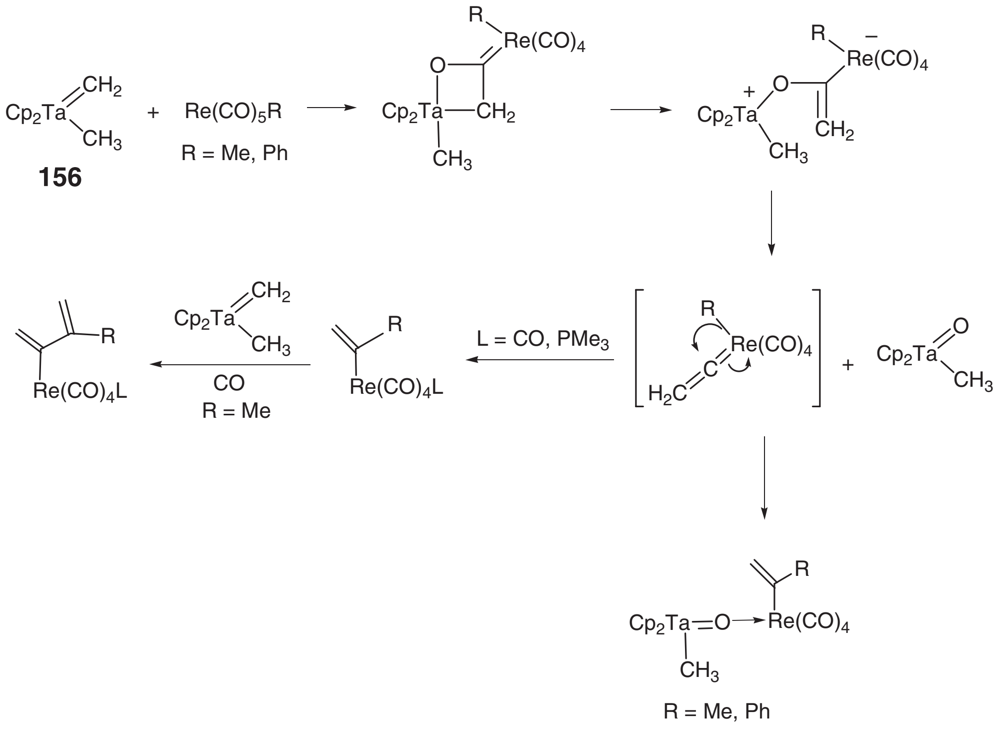
[Ta] = TaCp*(*supine*-η^4-2,3-dimethyl-1,3-butadiene)

Scheme 52

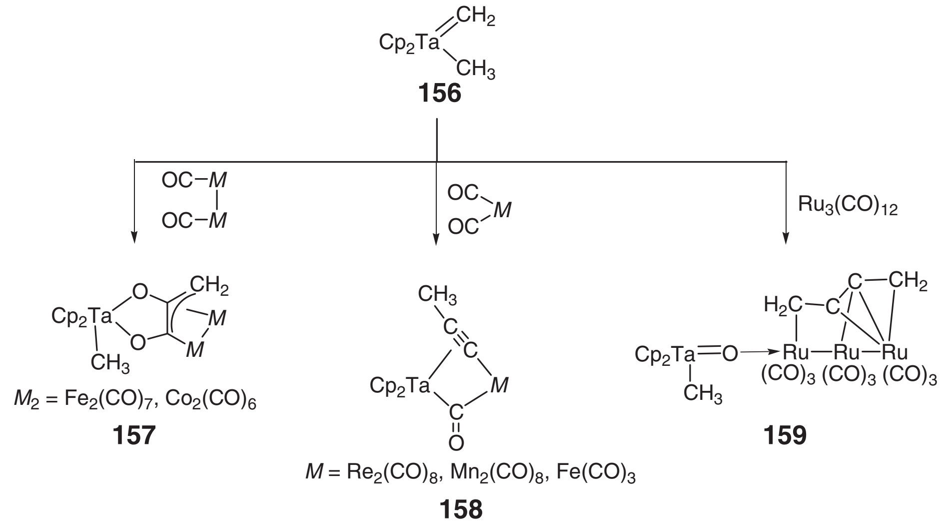
iodine to give the corresponding $[Cp_2W({=}CHMe)(I)]^+$.[288] Permethyltantallocene(III) complex $Cp^*_2TaCl(THF)$ reacts with LiMe or CH_2PMe_3 to give methylidene complexes, $Cp^*{}_2Ta({=}CH_2)Cl$ and $Cp^*Ta({=}CH_2)(H)$.[41] Alkylation of $Cp^*(\eta^5\text{-}C_5H_4SiMe_3)TaCl_2$ with 1 equiv. of $Mg(CH_2Ph)_2$ or 2 equiv. of $LiCH_2R$ ($R = SiMe_3$, CMe_3, CM_2Ph) affords bis-μ-alkylidene complexes $[Cp^*(\eta^5\text{-}C_5H_4SiMe_3)Ta(\mu\text{-}CHR^1)]_2$ ($R^1 = Ph$, $SiMe_3$, CMe_3) via α-hydrogen abstraction and the hydride tantalabenzocyclo-2-pentene, $Cp^*(\eta^5\text{-}C_5H_4SiMe_3)(H)\text{-}\overline{Ta(CH_2CMe_2\text{-}o\text{-}C}_6H_4)$ as a result of intramolecular C–H bond activation.[289] $Cp'_2Ta({=}CH_2)(CH_3)$ ($Cp' = Cp$, C_5H_4Me) react with $B(C_6F_5)_3$ at the methylene ligand to give zwitterionic tantalocene compounds $Cp'_2Ta[CH_2B(C_6F_5)_3](CH_3)$, in which the tantalum center is stabilized by a strong α-agostic interaction of the methylene moiety.[167] ^tBuNC inserts into the Ta–methylene bond to form imine compounds $Cp'_2Ta[\eta^2\text{-}N(^tBu){=}CCH_2B(C_6F_5)_3](CH_3)$.[167] Similar reaction of $Cp_2Ta({=}CH_2)(CH_3)$ with 1 equiv. of $HB(C_6F_5)_2$ results in the production of the neutral compound $Cp_2(Me)Ta[CH_2B(C_6F_5)_2](\mu\text{-}H)$ at −78 °C, which further reacts with $HB(C_6F_5)_2$ to give $Cp_2(H)Ta[CH_2B(C_6F_5)_2](\mu\text{-}H)$ along with $MeB(C_6F_5)_2$.[43] The reactivity of the borataalkene moiety is quite similar to alkene moiety bound to early transition metals. *In situ* generated $Cp'_2Ta[\eta^2\text{-}CH_2B(C_6F_5)_2]$ ($Cp' = Cp$, C_5H_4Me) can be trapped by alkynes $R^1C{\equiv}CR^2$ to give zwitterionic metallacyclic compounds, $Cp'_2\text{-}\overline{Ta[C(R^1){=}C(R^2)\text{-}B(C_6F_5)_2CH_2}]$, or vinylalkylidene complexes $Cp'_2\,\overline{Ta[{=}C(R^1)\text{-}C(R^2){=}CH\text{-}B(C_6F_5)_2H}]$ depending on the steric bulk of the alkynes.[290] Reactions of $Cp_2(Me)Ta[CH_2B(C_6F_5)_2](\mu\text{-}H)$ with CO or *t*BuNC afford borataalkene compounds $Cp_2Ta[\eta^2\text{-}CH_2B(C_6F_5)_2](L)$ (L = CO, *t*BuNC) with the release of methane.[43,44] In sharp contrast, two moles of isonitrile RNC (R = Cy, CH_2Ph) can insert into the B–C bond of the η^2-borataalkene ligand of $Cp_2(Me)Ta[CH_2B(C_6F_5)_2](\mu\text{-}H)$ to give $Cp_2Ta\{\eta^3\text{-}CH_2C[C(B(C_6F_5)_2)NR]NR\}$ which has an η^3-azaallyl ligand incorporating an iminoacyl boryl fragment of the central carbon atom.[291] The mechanism of H_2-addition to $Cp^*{}_2Ta({=}CH_2)H$ giving $Cp^*{}_2TaH_3$ is examined by PHIP and ^{13}C-labeling experiments: the addition of H_2 takes place following the formation of a Ta(III) methyl intermediate.[292]

5.03.4.3 Reaction of Carbene Complexes with Metal Carbonyls

Bergman *et al.* have demonstrated that the tantalocene methylidene–methyl complex $Cp_2Ta({=}CH_2)Me$ **156** is a unique starting material for preparing heterobimetallic complexes by two categories of reactions. The first reaction is based on the Wittig-like reactivity of the carbene moiety. Reaction of **156** with a carbonyl ligand of $RRe(CO)_5$ (R = Me, Ph) gives oxo-bridging heterobimetallic complexes $Cp_2MeTa(\mu\text{-}O)Re(CR{=}CH_2)(CO)_4$ (Scheme 53).[165,166] This reaction may involve an initial formation of oxametallacycle followed by ring opening to oxotantalum and vinylidene complexes. The rapid conversion of the vinylidene moiety by R-group migration generates an alkenyl complex, which is trapped by the oxotantalum species or donor ligands, CO or PMe_3. The trapped alkenyl complex can further react with **156**, giving rise to the butadienyl complexes, $Cp_2MeTa(\mu\text{-}O)Re[C({=}CH_2)C(Me){=}CH_2](CO)_4$ in THF and $Re[C({=}CH_2)C(Me){=}CH_2](CO)_5$ upon exposure to CO. In the case of $R = C_3F_7$, a zwitterionic intermediate with a bridging ketene ligand can be isolated and crystallographically characterized.[166]



Scheme 53

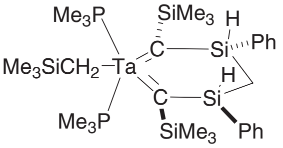
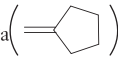
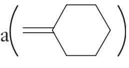
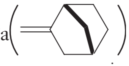
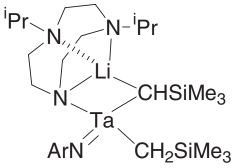


Scheme 54

Reaction of **156** with dinuclear metal carbonyls such as $Co_2(CO)_8$ and $Fe_2(CO)_9$ gives the corresponding metallacyclic complexes **157**, and reaction with $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ gives carbonyl–methylacetylide bridging binuclear complexes, $Cp_2Ta(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}MeC_2)M$ (**158**: $M = Re_2(CO)_8$, $Mn_2(CO)_8$, $Fe(CO)_3$) (Scheme 54).[131,166] Double Wittig-type reaction of carbonyls bound to $Ru_3(CO)_{12}$ proceeds and a unique cluster compound, $Cp_2MeTa(\mu\text{-}O)Ru_3(\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-}C_4H_4)(CO)_9$ **159**, bearing a butatriene ligand is obtained.[293]

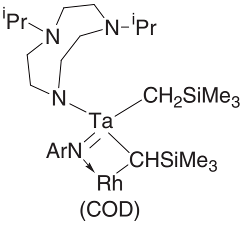
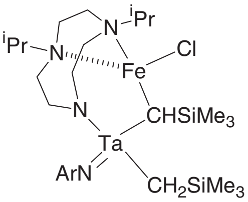
A second reaction of **156** is the C–H bond activation of the methyl group of **156**, which serves as a versatile starting compound for preparing double methylene-bridged heterobimetallic complexes. Heterobimetallic bis(μ-methylene) complex $Cp_2Ta(\mu\text{-}CH_2)_2CoCp$ has its unpaired electron localized on the cobalt center. Reaction with aromatic disulfides rapidly affords the corresponding diamagnetic monothiolate complexes by keeping the heterobimetallic skeleton, $Cp_2Ta(\mu\text{-}CH_2)_2Co(SAr)Cp$ (Ar = C_6H_4-4-X; X = Me, MeO, H, CF_3; Ar = C_6H_3-2,6-Me_2).[294] Reactions of $Cp_2Ta({=}CH_2)Me$ with (indenyl)$Ir(CO)_2$ and $[RhCl(CO)_2]_2$ afford $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ and $Cp_2Ta(\mu\text{-}CH_2)_2Rh(CO)_2$.[295] The oxidative addition of $HSiR_3$ (R = Me, Et, Ph) with $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ is reported to give $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2(H)(SiR_3)$ and the oxidative addition of H_2 to $Cp_2Ta(\mu\text{-}CH_2)_2Ir(H_2)(CO)(PPh_3)$ gives $Cp_2Ta(\mu\text{-}CH_2)_2Ir(H_2)(CO)(PPh_3)$.[295,296] These reactions are reversible, and ethylene hydrosilation is catalyzed by $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$.[296] Another heterobimetallic bis(μ-methylene) complex, $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$, is prepared by treating $Cp_2Ta(\mu\text{-}CH_2)Me$ with $CpPd(\eta^3$-allyl).[297,298] The unique reaction of $Cp_2Ta(\mu\text{-}CH_2)_2PdCp$ is due to the lability of Cp ligand on the palladium center: addition of donor ligands in dichloromethane or acetonitrile to give $[Cp_2Ta(\mu\text{-}CH_2)_2Pd(L_2)]X$ (X = Cl, C_5H_5; L = PMe_3, $P(OMe)_3$; L_2 = DMPE) and $Cp_2Ta(\mu\text{-}CH_2)_2Pd(P(OMe)_3)(CH_2CN)$ (Table 10).[297,298]

Table 10 Alkylidene complexes[a]

Compound	*Comments*	*References*
Without Cp ligand		
$Ta({=}CHSiMe_3)(CH_2SiMe_3)_3$	Prep: thermolysis of $Ta(CH_2SiMe_3)_5$	60
$Ta({=}CHSiMe_3)_2(CH_2SiMe_3)(PMe_3)_2$		299
$(Me_3ECH_2)_2Ta({=}EH^tBu)[Si(SiMe_3)_3]$	E = Si (X-ray), C (X-ray)	245, 246
$(Me_3SiCH_2)(Me_3SiCH{=})Ta(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2$	Prep: photolysis of $(Me_3SiCH_2)_3Ta(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2$; R = H, Me, Ph	68
$(Me_3SiCH_2)(Me_3SiCH{=})Ta(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}R_2)_2$	R = H, Me, ^{i}Pr, ^{t}Bu, Ph	66
$(Me_3SiCH_2)_3Ta[{=}C(SiMe_3)SiPhRH]$	R = Me, Ph	252, 253
$(Me_3P)_2(Me_3SiCH_2)Ta[C(SiMe_3)Si(Ph)(R)C(SiMe_3)]$	R = Me (X-ray), Ph (X-ray)	252, 253
	X-ray	252, 253
$(^tBuCH_2)(^tBuCH{=})$- $Ta\text{-}N(^tBu){=}B(CH_2^tBu)N(^tBu)SiMe_2CH_2$		300
$Ta(CH_2Ph)({=}CHPh)(L^1)$	L^1 (see Scheme 4), X-ray	59
$[Ta(\mu\text{-}CHPh)(L^2)]_2$	L^2 (see Scheme 4), X-ray	65
$Me_3SiCH{=}CHC(SiMe_3){=}TaCl_3(TMEDA)$	Prep: $\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}TaCl_4 + 2TMEDA$, X-ray	301
$(^tBu_3SiO)_3Ta({=}CHR)$	Rearrangement of $(^tBu_3SiO)_3Ta(\eta^2$-alkene): R = Me, Et, *n*Pr, CH_2Ph, $CH_2C_6H_4$-*p*-OMe, $CH_2C_6H_4$-*p*-CF_3	302
$(^tBu_3SiO)_3Ta$ 	Rearrangement of $(^tBu_3SiO)_3Ta(\eta^2$-cyclopentene)	302
$(^tBu_3SiO)_3Ta$ 	Rearrangement of $(^tBu_3SiO)_3Ta(\eta^2$-cyclohexene)	302
$(^tBu_3SiO)_3Ta$ 	Rearrangement of $(^tBu_3SiO)_3Ta(\eta^2$-norbornene)	302
$(Me_3SiCH_2)[(C_6H_3)\text{-}2,6\text{-}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^iPr_2\text{-}TACN)$ 	Prep: thermolysis of $(Me_3SiCH_2)_2[(C_6H_3\text{-}2,6\text{-}^iPr_2)N{=}]\text{-}Ta(\mu\text{-}CH_2SiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^iPr_2\text{-}TACN)$, X-ray	108

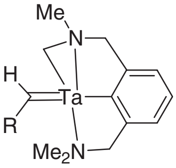
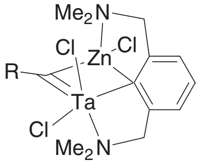
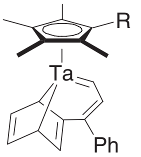
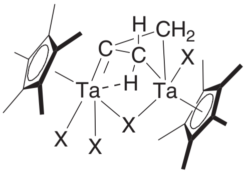
(*Continued*)

Table 10 (Continued)

Compound	*Comments*	*References*
	Prep: $(Me_3SiCH_2)[(C_6H_3-2,6-{}^iPr_2)N{=}]Ta(\mu-CHSiMe_3)(\mu-\eta^1{:}\eta^3-{}^iPr_2-TACN) + [RhCl(COD)]_2$, X-ray	110
	Prep: $(Me_3SiCH_2)[(C_6H_3-2,6-{}^iPr_2)N{=}]Ta(\mu-CHSiMe_3)(\mu-\eta^1{:}\eta^3-{}^iPr_2-TACN) + [FeCl_2(TMEDA)]_2$, X-ray	110
$[PhC(NSiMe_3)_2]_2Ta(CH_3)({=}CH_2)$	Prep: $\{[PhC(NSiMe_3)_2]_2Ta(CH_3)_2\}^+ + Me_3P{=}CH_2$ or $Et_3PCHSiMe_3$	92
$[PhC(NSiMe_3)_2]Ta(CH_2Ph)_2({=}CHPh)$	Prep: $[PhC(NSiMe_3)_2]TaCl(CH_2Ph)_3 + LiN(SiMe_3)_2$	92
$[(Me_3SiNCH_2CH_2)_3N]Ta{=}CHR$	Prep: $[(Me_3SiNCH_2CH_2)_3N]TaCl_2 + 2PhCH_2MgCl$ and $2Me_3SiCH_2Li$; R = Ph, $SiMe_3$	105, 106
$[(Me_3SiNCH_2CH_2)_3N]Ta{=}CHMe$	Prep: $[(Me_3SiNCH_2CH_2)_3N]Ta(\eta^2-CH_2{=}CH_2) + PhPH_2$	105
$[(Me_3SiNCH_2CH_2]_3N]Ta({=}CHR)$	Prep: $Ta(CH_2R)_2Cl_3 + Li_3[(Me_3SiNCH_2CH_2)_3N]$; R = Ph, CMe_3	106
$[(Me_3SiNCH_2CH_2)_3N]Ta{=}CHCH_2R^1$	Prep: $[(Me_3SiNCH_2CH_2)_3N]TaCl_2 + RMgX$ (R = ^{n}Pr, ^{n}Bu, isopentyl, neohexyl); $R^1 = CH_3$, CH_2CH_3, $CH(CH_3)_2$, CMe_3	106
$[(Et_3SiNCH_2CH_2]_3N]Ta({=}CHCH_2R)$	Prep: $[(Et_3SiNCH_2CH_2)_3N]TaCl_2 + 2RCH_2CH_2MgX$; R = H, Me, Et, $CHMe_2$	107
$[(Et_3SiNCH_2CH_2]_3N]Ta({=}CHR)$	Prep: $[(Et_3SiNCH_2CH_2)_3N]TaCl_2 + 2RCH_2MgX$; R = $SiMe_3$, Ph	107
$[(Et_3SiNCH_2CH_2)_3N]Ta({=}CHCH_2)\}_2$	Prep: $[(Et_3SiNCH_2CH_2)_3N]TaCl_2 + 2CH_2{=}CHMgBr$	107
$(ArN)(Me_3SiCH_2)(Me_3SiCH{=})Ta[(N^iPr)_2(CH_2CH_2)_3NLi]$		108–110
$[\{(^iPr)_2NCH_2SiMe_2\}_2N]Ta({=}CHR)Cl_2$	R = Ph, ^{t}Bu	254
$\{[\{(^iPr)_2NCH_2SiMe_2\}_2N](RCH{=})Ta\}_2(\mu-N_2)$	R = Ph, ^{t}Bu	254
$Ta({=}CH^tBu)[\eta^2-C_6H_3-2,6-(CH_2NMe_2)_2]Cl(OR)$	Prep: $Ta({=}CH^tBu)[\eta^3-C_6H_3-2,6-(CH_2NMe_2)_2]Cl_2 + LiO^tBu$ or KOMe; R = Me, ^{t}Bu (X-ray)	257, 260
$Ta({=}CHSiMe_3)[\eta^3-C_6H_3-2,6-(CH_2NMe_2)_2]Cl(O^tBu)$	Prep: $Ta({=}CH^tBu)[\eta^2-C_6H_3-2,6-(CH_2NMe_2)_2]Cl(O^tBu) + CH_2{=}CHSiMe_3$	257
$Ta({=}CH^tBu)[\eta^3-C_6H_3-2,6-(CH_2NMe_2)_2](O^tBu)_2$	Prep: $Ta({=}CH^tBu)Cl(O^tBu)_2(PMe_3) + Li[C_6H_3-2,6-(CH_2NMe_2)_2]$, X-ray	257
$Ta({=}CH^tBu)[\eta^3-C_6H_4-2-(CH_2NMe_2)](O^tBu)_2$	Prep: $Ta({=}CH^tBu)Cl_3 + 1/2\ Zn[C_6H_4-2-(CH_2NMe_2)]_2 + 2LiO^tBu$	257
$TaCl_2[C_6H_3-2,6-(CH_2NMe_2)_2](\mu-C^tBu)(\mu-ZnCl)$	Prep: $Ta({=}CH^tBu)[C_6H_4-2,6-(CH_2NMe_2)_2]Cl_2 + ZnCl(CH_2CMe_3)$ or $[TaCl_2(dme)(\mu-C^tBu)(\mu-Cl)]_2Zn + Li[C_6H_4-2,6-(CH_2NMe_2)_2]$, X-ray	258
$Ta({=}CH^tBu)[\eta^2-C_6H_3-2,4-(CH_2NMe_2)_2](O^tBu)_2$	Prep: $Ta({=}CH^tBu)[\eta^3-C_6H_3-2,6-(CH_2NMe_2)_2]Cl_2 + 2LiO^tBu$ at 80 °C	260
$Ta({=}CH^tBu)[\eta^2-C_6H_3-2,4-(CH_2NMe_2)_2]Cl(O^tBu)$	Prep: $Ta({=}CH^tBu)[\eta^3-C_6H_3-2,6-(CH_2NMe_2)_2]Cl(O^tBu)$ at 80 °C	260
$Ta({=}CH^tBu)[\eta^2-C_6H_3-2,4-(CH_2NMe_2)_2](O^tBu)_2$	Prep: $Ta({=}CH^tBu)[\eta^3-C_6H_3-2,4-(CH_2NMe_2)_2]Cl(O^tBu) + LiO^tBu$	260
$Ta({=}CH^tBu)Cl_2[C_6H_4-2-(CH_2NMeCH_2CH_2NMe_2)]$	Prep: $TaCl_3({=}CH^tBu)(THF)_2 + Li[C_6H_4-2-(CH_2NMeCH_2CH_2NMe_2)]$, X-ray	259

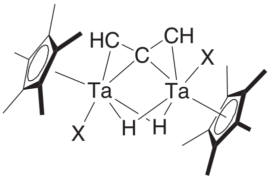
(Continued)

Table 10 (Continued)

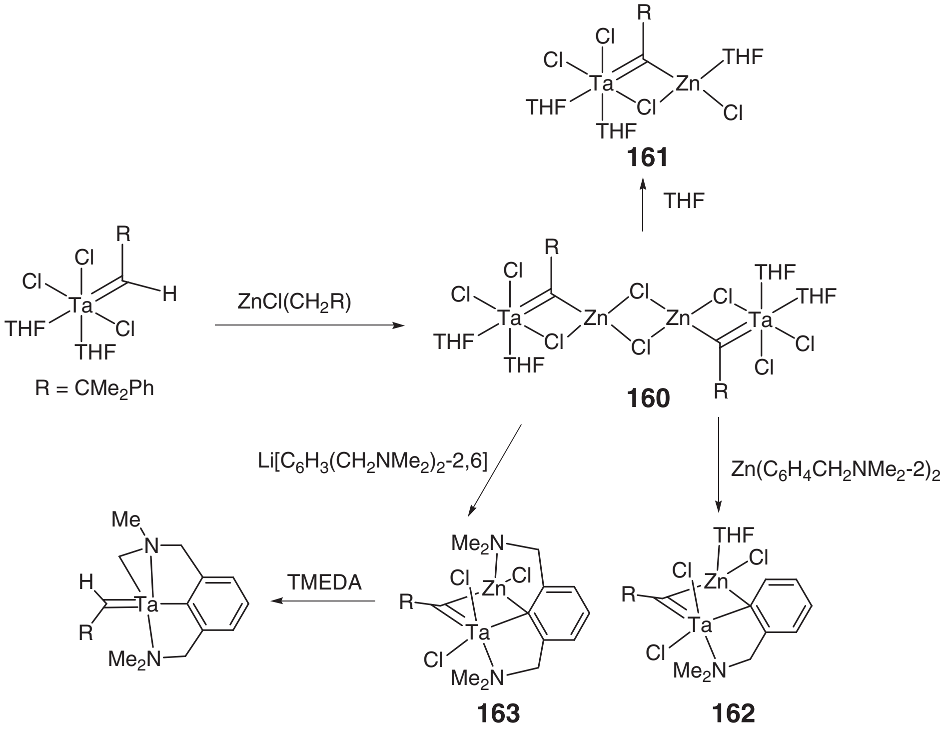
Compound	*Comments*	*References*
$Ta(=CHR)(O^tBu)_2[C_6H_4\text{-}2\text{-}(CH_2NMeCH_2CH_2NMe_2)]$	Prep: $TaCl(O^tBu)_2(=CHR)(PMe_3) + Li[C_6H_4\text{-}2\text{-}(CH_2NMeCH_2CH_2NMe_2)]$; R = ^{t}Bu, CMe_2Ph	259
	 Prep: +TMEDA	303
$\{Ta(=CHR)[N(SiMe_2CH_2P^iPr_2)_2]\}_2(\mu\text{-}N_2)$	Prep: $Ta(=CHR)Cl_2[N(SiMe_2CH_2P^iPr_2)_2] + Na/Hg + N_2$; R = ^{t}Bu, Ph	254
$[P_2N_2]Ta(=CH_2)Me$	Prep: photolysis of $[P_2N_2]TaMe_3$; $[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2)_2PPh$, X-ray	90
$[(Ph_2PCH_2)_2C(Me)O]Ta(=CH^tBu)Cl_2$		304
Stabilized carbene		
$TaCl_4[\overline{CN(Me)CH=CHN}(Me)]_{22}$	Prep: $TaCl_4(THF)_2$ + 1,3-dimethylimidazolin-2-ylidene	305
$Cp^*TaCl_4[C(Me)=N(H)Ar]$	Prep: $Cp^*Ta[\eta^2\text{-}C(Me)=NAr]Cl_3 + HCl$; Ar = $C_6H_3\text{-}2,6\text{-}Me_2$ (X-ray), $C_6H_2\text{-}2,4,6\text{-}Me_3$	306
With Cp ligands		
$CpTa(=C_5H_4)(NEt_2)_2$		275
$Cp^*Me\overline{Ta=CH(Ph)C(Ph)=C(Me)X}$	X = O (X-ray), N^tBu	280
$Cp^*(Me_2NCH_2\text{-}o\text{-}C_6H_4)\overline{Ta=CHN(Me)CH_2\text{-}o\text{-}C}_6H_4$	Prep: $Cp^*TaCl_4 + 4Li[C_6H_5\text{-}o\text{-}(CH_2NMe_2)]$	279
$Cp^*(Me_2N)\overline{Ta=CHN(Me)CH_2\text{-}o\text{-}C}_6H_4$		279
$Cp(Cl)Ta(=N^tBu)(=CHPPh_3)$	Prep: $CpTa(=N^tBu)Cl_2 + 2Ph_3P=CH_2$	276
$Cp^*(Cl)(^tBuN=)\overline{Ta[CH_2P(Ph)_2CH_2}]$	Prep: $CpTa(=N^tBu)Cl_2 + Li(CH_2)_2PPh_2$	276
$Cp^*(^tBuN=)Ta(=CHPPh_2Me)_2$	Prep: $Cp^*(Cl)(^tBuN=)\overline{Ta[CH_2P(Ph)_2CH_2}]_{+} + Li(CH_2)_2PPh_2$	276
$Cp^*(R_3P=N)Ta(=CHPh)(CH_2Ph)$	Prep: $Cp^*TaCl_3(NPR_3) + 3PhCH_2MgCl$; R = ^{t}Bu (X-ray), ^{i}Pr	160
$CpCl\overline{Ta=C(^tBu)B(^iPr)N}(^iPr)$		307
$Cp^*Ta(\eta^4\text{-butadiene})(=CHPh)(PMe_3)$	X-ray	283
$Cp^*Ta(\eta^4\text{-o-xylylene})(=CHPh)$	X-ray	284
$Cp^*Ta(\eta^4\text{-2,3-dimethylbutadiene})(=CHPh)$	X-ray	285
$(\eta^5\text{-}C_5Me_4R)Ta(=CHCH=CPh_2)$	Prep: $[(\eta^5\text{-}C_5Me_4R)Ta]_2(\mu\text{-}X)_4$ + 3,3-diphenylcyclopropene; R = Me, Et; X = Cl, Br	281
	Prep: $(\eta^5\text{-}C_5Me_4R)Ta(=CHCH=CPh_2) + K/Hg$; R = Me (X-ray), Et	281
	Prep: $[Cp^*Ta]_2(\mu\text{-}X)_4$ + allene; X = Cl, Br	282

(Continued)

Table 10 (Continued)

Compound	*Comments*	*References*
	Prep: allene adduct + Na/Hg	282
$\mathrm{Tp^*Ta({=}CH^tBu)X_2}$	Prep: $\mathrm{Ta({=}CH^tBu)X_3(THF) + Tp^*K}$; X = Cl, Br	161
$\mathrm{Tp^*Ta({=}CH^tBu)(Cl)Y}$	Prep: $\mathrm{Tp^*Ta({=}CH^tBu)X_2 + MY}$ (M = Li or Na); Y = OMe, $\mathrm{O^iPr}$, $\mathrm{NMe_2}$	161
$\mathrm{Cp_2Ta({=}CHMe)(I)}$	Prep: $\mathrm{Cp_2TaH(\eta^2\text{-}C_2H_4) + (CF_3)_2CFI}$, X-ray	287
$\mathrm{Cp^*{}_2Ta({=}CH_2)Cl}$	Prep: $\mathrm{Cp^*{}_2TaCl(THF) + CH_2PMe_3}$	41
$\mathrm{Cp^*{}_2Ta({=}CH_2)H}$	Prep: $\mathrm{Cp^*{}_2TaCl(THF) + CH_3Li}$	41
$\mathrm{\{Cp^*TaCl_2[{=}C(\mathit{t}Bu)P(Cy\text{-})]\}_2}$	Prep: $\mathrm{Cp^*TaCl_4}$ + (Z)-$\mathrm{MgCl(OEt_2)\{C(^tBu){=}PCy\}}$, X-ray	277
ansa-$\mathrm{[(Me_2Si)_2(\eta^5\text{-}C_5H_3\text{-}4\text{-}^tBu)(\eta^5\text{-}C_5H_2\text{-}3,5\text{-}^iPr_2)]TaMe({=}CH_2)}$	Prep: $\mathrm{K_2\{[(Me_2Si)_2(\eta^5\text{-}C_5H_3\text{-}4\text{-}^tBu)(\eta^5\text{-}C_5H_2\text{-}3,5\text{-}^iPr_2)]\} + TaMe_3Cl_2}$, X-ray	308
$\mathrm{[Cp^*(\eta^5\text{-}C_5H_4SiMe_3)Ta(\mu\text{-}CHR^1)]_2}$	Prep: $\mathrm{Cp^*(\eta^5\text{-}C_5H_4SiMe_3)TaCl_2}$ + 1 equiv. of $\mathrm{Mg(CH_2Ph)_2}$ or 2 equiv. of $\mathrm{LiCH_2R}$ (R = $\mathrm{SiMe_3}$, $\mathrm{CMe_3}$; $\mathrm{R^1}$ = Ph, $\mathrm{SiMe_3}$, $\mathrm{CMe_3}$)	289
$\mathrm{Cp^*(\eta^5\text{-}C_5H_4SiMe_3)(H)\text{-}Ta(CH_2CMe_2\text{-}\mathit{o}\text{-}C_6H_4)}$	Prep: $\mathrm{Cp^*(\eta^5\text{-}C_5H_4SiMe_3)TaCl_2}$ + 2 equiv. of $\mathrm{LiCH_2CMe_2Ph}$, X-ray	289
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Co(SAr)Cp}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2CoCp + ArSSAr}$; Ar = $\mathrm{C_6H_4\text{-}4\text{-}X}$; X = Me, MeO, H, $\mathrm{CF_3}$; Ar = $\mathrm{C_6H_3\text{-}2,6\text{-}Me_2}$ (X-ray)	294
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)Me + (indenyl)Ir(CO)_2}$	295
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)(PPh_3)}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2 + PPh_3}$	295
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Rh(CO)_2}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)Me + 1/2\ [RhCl(CO)_2]_2}$	295
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Rh(CO)(PPh_3)}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)Me + RhCl(CO)(PPh_3)_2}$	295
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2(H)(SiR_3)}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2 + HSiR_3}$; R = Me, Et, Ph	296
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_3}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_3 + CO}$	295
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(H_2)(CO)(PPh_3)}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)(PPh_3) + H_2}$	295
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2PdCp}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)Me + CpPd(\eta^3\text{-}allyl)}$	297, 298
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2PdCp^*}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)Me + Cp^*Pd(\eta^3\text{-}allyl)}$	298
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2Pd(Cl)(L)}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2PdCp + L}$ in $\mathrm{CH_2Cl_2}$; L = $\mathrm{PMe_3}$, $\mathrm{P(OMe)_3}$	297, 298
$\mathrm{[Cp_2Ta(\mu\text{-}CH_2)_2Pd(L_2)]Cl}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2PdCp + 2L}$ in $\mathrm{CH_2Cl_2}$; L = $\mathrm{PMe_3}$, $\mathrm{P(OMe)_3}$; $\mathrm{L_2}$ = DMPE (X-ray)	297, 298
$\mathrm{[Cp_2Ta(\mu\text{-}CH_2)_2Pd(DMPE)](C_5H_5)}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2PdCp}$ + DMPE in $\mathrm{CH_3CN}$, X-ray	297, 298
$\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2\text{-}Pd(P(OMe)_3)(CH_2CN)}$	Prep: $\mathrm{Cp_2Ta(\mu\text{-}CH_2)_2PdCp + P(OMe)_3}$ in $\mathrm{CH_3CN}$	297, 298
$\mathrm{Cp'_2Ta[C(R^1){=}C(R^2)\text{-}B(C_6F_5)_2CH_2]}$	Prep: $\mathrm{Cp'_2MeTa[CH_2B(C_6F_5)_2H] + R^1C{\equiv}CR^2}$; $\mathrm{R^1 = R^2}$ = Me; $\mathrm{R^1}$ = H, $\mathrm{R^2}$ = Ph (kinetic product); $\mathrm{R^1}$ = Ph, $\mathrm{R^2}$ = H (thermodynamic product), Cp′ = Cp, $\mathrm{\eta^5\text{-}C_5H_4Me}$, X-ray for $\mathrm{\eta^5\text{-}C_5H_4Me}$ and $\mathrm{R^1 = R^2}$ = Me; X-ray for $\mathrm{\eta^5\text{-}C_5H_4Me}$ and $\mathrm{R^1}$ = Ph, $\mathrm{R^2}$ = H	290
$\mathrm{Cp'_2Ta[{=}C(R^1)\text{-}C(R^2){=}CH\text{-}B(C_6F_5)_2H]}$	Prep: $\mathrm{Cp'_2MeTa[CH_2B(C_6F_5)_2H] + R^1C{\equiv}CR^2}$; $\mathrm{R^1 = R^2}$ = Et; $\mathrm{R^1 = R^2}$ = Ph; $\mathrm{R^1}$ = Ph, $\mathrm{R^2}$ = Me; Cp′ = Cp, $\mathrm{\eta^5\text{-}C_5H_4Me}$, X-ray for Cp and $\mathrm{R^1}$ = Ph, $\mathrm{R^2}$ = Me	290
$\mathrm{Cp'Ta({=}CHPh)(PMe_3)}$(supine-*s-cis*-$\eta^4$-butadiene)	Prep: thermolysis of $\mathrm{Cp'Ta(CH_2Ph)_2}$(supine-*s-cis*-η^4-butadiene) + $\mathrm{PMe_3}$, Cp′ = Cp, $\mathrm{Cp^*}$ (X-ray)	283, 284
$\mathrm{Cp^*Ta({=}CH_2Ph)}$(supine-*s-cis*-$\eta^4$-butadiene)	Prep: $\mathrm{Cp^*TaCl_2}$(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + $\mathrm{2PhCH_2MgCl}$, X-ray	285
$\mathrm{Cp^*Ta({=}CHPh)[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]}$	Prep: thermolysis of $\mathrm{Cp^*Ta(CH_2Ph)_2[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]}$, X-ray	284
$\mathrm{Cp^*Ta({=}CHPh)}$(supine-h4-AD)	Prep: thermolysis of $\mathrm{Cp^*Ta(CH_2Ph)_2(\eta^2\text{-}C,N\text{-}AD)}$; AD = 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene	286

[a] Cp = η^5-$\mathrm{C_5H_5}$, Cp* = η^5-$\mathrm{C_5Me_5}$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.



Scheme 55

5.03.4.4 Alkylidyne Complexes

In the course of reductive coupling of the coordinated carbonyls, alkylidyne complexes $Ta(\equiv COSiR_3)(CO)(dmpe)_2$ and $Ta(\equiv COSiR_3)(COAlEt_3)(dmpe)_2$ have been isolated and characterized.[16,51,52] Zinc alkyl species $ZnCl(CH_2CMe_2Ph)$ react with alkylidene compound $Ta(=CHCMe_2Ph)Cl_3(THF)_2$ to give an alkylidyne-bridged compound $(THF)_2Cl_2Ta(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)Zn(\mu\text{-}Cl)_2Zn(\mu\text{-}Cl)(\mu\text{-}CCMe_2Ph)Ta(THF)_2Cl_2$ **160** via H-abstraction from the alkylidene moiety.[303] Structure **160** can convert to some alkylidyne and alkylidene compounds **161–163** as outlined in Scheme 55.[303]

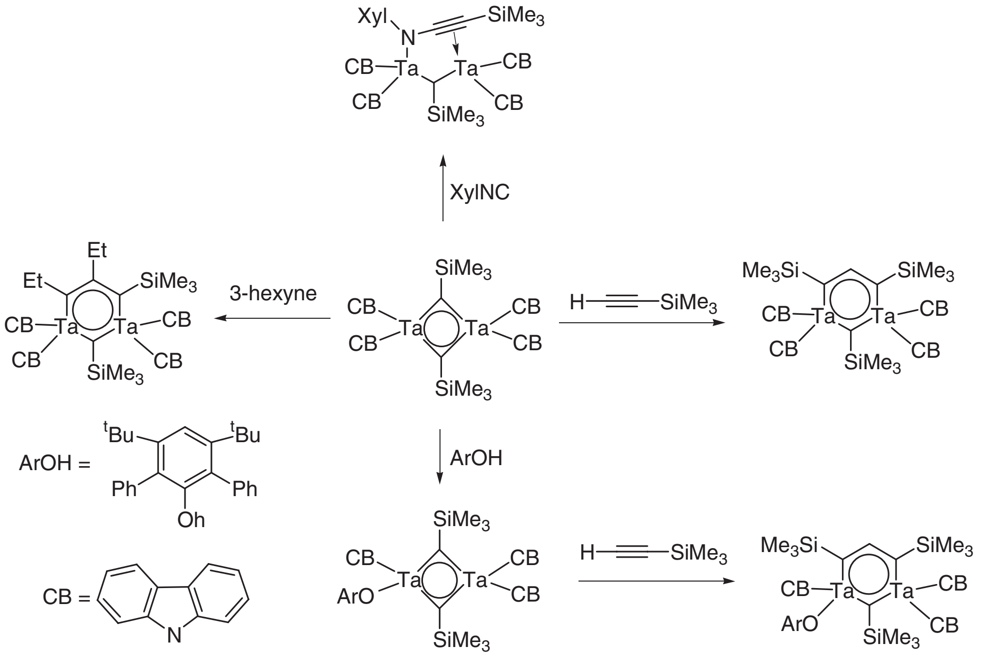
1,3-Ditantalacyclobutadiene $Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$, first isolated by Wilkinson and his co-workers, is thermally stable, but the terminal alkyl moieties can be substituted with protic reagents. In the case of bulky substituted phenol derivatives, monosubstituted compounds $(Me_3SiCH_2)(ArO)Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2$ are obtained (Scheme 56).[309,310] Four alkyl moieties are fully replaced by carbazoles (R_2N; carbazole, tetrahydrocarbazole, 3-^{t}Bu-carbazole) to give $(R_2N)_2Ta(\mu\text{-}CSiMe_3)_2Ta(NR_2)_2$.[311] Xylylisocyanide can insert into the tantallacyclobutadiene to give an amido–alkyne-bridged compound $(CB)_2Ta[\mu\text{-}\eta^1\text{:}\eta^2\text{-}(Xyl)NC\equiv CSiMe_3](\mu\text{-}CSiMe_3)Ta(CB)_2$ (CB = carbazole).[311] Alkynes can insert into the tantallacyclobutadiene moieties of $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)_2$ and its monophenoxide $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)(OAr)$ $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)_2$ (CB = carbazole, Ar = 3,5-di-*t*Bu-2,6-diphenylphenyl) to form 1,3-ditantallabenzene derivatives (Scheme 730).[313] Thermolysis of a decaline solution of $(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}{}^tBu_2)Ta(CO)_4$ and $(PhAs)_6$ affords $[(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}{}^tBu_2)Ta]_3(\mu\text{-}O)_2(\mu_3\text{-}CPh)(As_3)$, which contains a triply bridged carbyne ligand (Table 11).[312]

5.03.5 η^2-Complexes

5.03.5.1 Alkene Complexes

5.03.5.1.1 Alkene complexes without cyclopentadienyl ligands

Sodium amalgam reduction of $(^tBu_2PhSiO)_3TaCl_2$ in the presence of ethylene affords an ethylene complex, while the less bulky precursors $(^iPr_3SiO)_3TaCl_2$ and $(^tBu_2MeSiO)_3TaCl_2$ give metallacyclopentanes.[100] These three compounds upon reduction in the presence of 2-butyne give the corresponding 2-butyne complexes.[100] Some alkene



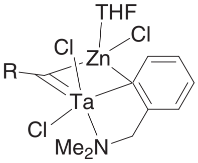
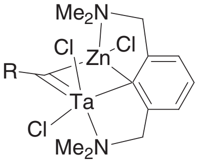
Scheme 56

Table 11 Alkylidyne complexes[a]

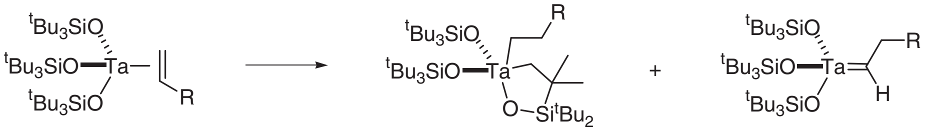
Compound	*Comments*	*References*
Without Cp ligand		
$Ta(\equiv COSiR_3)(CO)(dmpe)_2$	Prep: $Ta(CO)_2(dmpe)_2 + ClSiR_3$; $SiR_3 = SiPh_2{}^tBu$ (X-ray), $SiPh_3$	51, 52
$Ta(\equiv COSiPh_2{}^tBu)(CO)(depe)_2$	Prep: $Ta(CO)_2(depe)_2 + Na/Hg + ClSiPh_2{}^tBu$	16
$Ta(\equiv COSiR_3)(COAlEt_3)(dmpe)_2$	Prep: $Ta(\equiv COSiR_3)(CO)(dmpe)_2 + AlR^1{}_3$; $SiR_3 = Si^iPr_3$, $SiPh_2{}^tBu$ (X-ray), $SiPh_3$	51, 52
$Ta(\equiv COSiR_3)(COAlEt_3)(dmpe)_2$	$SiR_3 = Si^iPr_3$, $SiPh_2{}^tBu$ (X-ray), $SiPh_3$	51, 52
$Ta(\equiv C^tBu)Cl[C_6H_4\text{-}2,6\text{-}(CH_2NMe_2)_2]$	Prep: $TaCl_2[C_6H_4\text{-}2,6\text{-}(CH_2NMe_2)_2](\mu\text{-}C^tBu)(\mu\text{-}ZnCl) + TMEDA$ or $Ta(=CH^tBu)Cl_2[C_6H_4\text{-}2,6\text{-}(CH_2NMe_2)_2] + MeLi$	258
$(Me_3SiCH_2)(ArO)Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2$	Prep: $Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4 + ArOH$; ArOH = 2,6-diphenylphenol (X-ray), 2,3,5,6-tetraphenylphenol, 2,6-diphenyl-3,5-dimethylphenol, 2,6-diphenyl-3,5-di(*tert*-butyl)phenol, 2-(1-naphthyl)-3,5,6-triphenylphenol, 2,6-bis(1-naphthyl)phenol (X-ray), 2,6-bis(1-naphthyl)-3,5-diphenylphenol, 2,6-bis(1-naphthyl)-3,5- di(*tert*-butyl)phenol, 2-phenyl-4,6-di(*tert*-butyl)phenol, 2-(1-naphthyl)-4, 6-di(*tert*-butyl)phenol	309, 310
$(R_2N)_2Ta(\mu\text{-}CSiMe_3)_2Ta(NR_2)_2$	Prep: $Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4 + R_2N\text{–}H$; R_2N = carbazole, tetrahydrocarbazole, 3-^{t}Bu-carbazole	311
$(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)(OAr)$	Prep: $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)_2 + ArOH$; CB = carbazole; Ar = 3,5-di-*t*Bu-2,6-diphenylphenyl	313
$(CB)_2Ta[\mu\text{-}\eta^1{:}\eta^2\text{-}(Xyl)NC{\equiv}CSiMe_3](\mu\text{-}CSiMe_3)Ta(CB)_2$	Prep: $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)_2 + XylNC$; CB = carbazole	311
$(CB)_2Ta(\mu\text{-}CSiMe_3)[\mu\text{-}C(SiMe_3)CHC(SiMe_3)]Ta(CB)(OAr)$	Prep: $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)(OAr) + HC{\equiv}CSiMe_3$; CB = carbazole, Ar = 3,5-di-*t*Bu-2,6-diphenylphenyl, X-ray	313
$(CB)_2Ta(\mu\text{-}CSiMe_3)[\mu\text{-}C(SiMe_3)CHC(SiMe_3)]Ta(CB)_2$	Prep: $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)(OAr) + HC{\equiv}CSiMe_3$; CB = carbazole, X-ray	313

(*Continued*)

Table 11 (Continued)

Compound	*Comments*	*References*
$(CB)_2Ta(\mu\text{-}CSiMe_3)[\mu\text{-}C(SiMe_3)C(Et)C(Et)]Ta(CB)_2$	Prep: $(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)(OAr) + EtC{\equiv}CEt$; CB = carbazole, X-ray	313
$(THF)_2Cl_2Ta(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)Zn(\mu\text{-}Cl)_2Zn(\mu\text{-}Cl)(\mu\text{-}CCMe_2Ph)Ta(THF)_2Cl_2$	Prep: $Ta({=}CHCMe_2Ph)Cl_3(THF)_2 + ZnCl(CH_2CMe_2Ph)$	303
$(THF)_2Cl_2Ta(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)ZnCl(THF)$	Prep: $(THF)_2Cl_2Ta(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)Zn(\mu\text{-}Cl)_2Zn(\mu\text{-}Cl)(\mu\text{-}CCMe_2Ph)Ta(THF)_2Cl_2 + THF$	303
	Prep: $(THF)_2Cl_2Ta(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)Zn(\mu\text{-}Cl)_2Zn(\mu\text{-}Cl)(\mu\text{-}CCMe_2Ph)Ta(THF)_2Cl_2 + 1/2\ Zn(C_6H_4CH_2NMe_2\text{-}2)_2$	303
	Prep: $(THF)_2Cl_2Ta(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)Zn(\mu\text{-}Cl)_2Zn(\mu\text{-}Cl)(\mu\text{-}CCMe_2Ph)Ta(THF)_2Cl_2 + \{Li[C_6H_3(CH_2NMe_2)_2\text{-}2,6]\}_2$	303
With Cp ligand		
$[(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}{}^tBu_2)Ta]_3(\mu\text{-}O)_2(\mu_3\text{-}CPh)(As_3)$	Prep: thermolysis of $(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}{}^tBu_2)Ta(CO)_4$ and $(PhAs)_6$, X-ray	312

[a] $Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.



164 **165** **166**

Scheme 57

complexes $(Bu_3SiO)_3Ta(\eta^2\text{-alkene})$ **164** are prepared by the reaction of $({}^tBu_3SiO)_3Ta$ with alkene (alkene = C_2H_4, C_3H_6, 1-butene, *c*-pentene, *c*-hexene, norbornene; $H_2C{=}CHC_6H_4\text{-}p\text{-}X$; X = H, OMe, CF_3).[302] Thermolysis of **164** produces two compounds: one is the C–H activated alkyl species **165** and the other is alkylidene compound **166** (Scheme 57).[302]

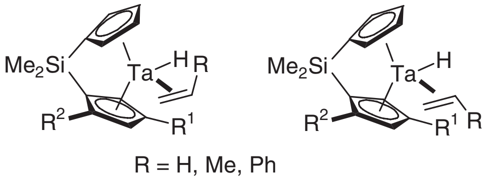
$[P_2N_2]TaH_3(PMe_3)$ or $[P_2N_2]Ta({=}CH_2)Me$ reacts with ethylene to afford an ethyl–ethylene complex, $[P_2N_2]Ta(Et)(\eta^2\text{-}C_2H_4)$, which shows a β-agostic interaction between the ethyl group and the tantalum center.[193]

5.03.5.1.2 Mono(cyclopentadienyl) alkene complexes

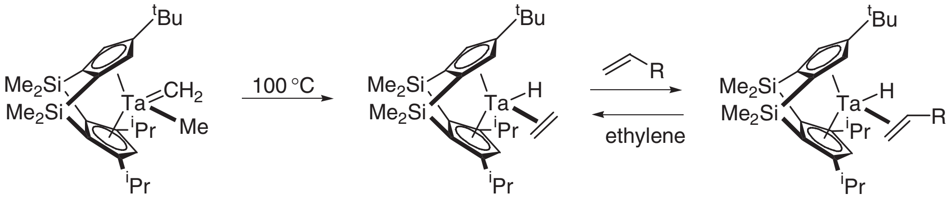
Dialkyl compounds $Cp^*Ta({=}NXyl)R_2$ (R = Et, Pr) are thermally unstable and react with PMe_3 to give alkene complexes $Cp^*Ta({=}NXyl)(\eta^2\text{-}CH_2{=}CHR)(PMe_3)$ (R = H, Me) after β-elimination and reductive elimination of alkanes.[314] Similar compounds $Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(\eta^2\text{-}CH_2{=}CHR)(PMe_3)$ (R = H, Me) are prepared.[315] Reaction of $Cp^*TaMe_2(\eta^2\text{-}CH_2{=}CH_2)$ with PPh_2H gives $Cp^*TaMe(PPh_2)(\eta^2\text{-}CH_2{=}CH_2)$, which can further react with H_2 in the presence of PPh_2H to afford $Cp^*TaH(PPh_2)_3$.[234]

5.03.5.1.3 Bis (cyclopentadienyl) alkene complexes

Reaction of $Cp^*{}_2TaCl(THF)$ with ethylMgBr afforded $Cp^*Ta(\eta^2\text{-}C_2H_4)(H)$ in 72% yield,[41] which is comparable to the previous report for the treatment of $Cp^*{}_2TaCl_2$ with 2 equiv. of ethylMgBr.[315] Similar alkylation of singly



Scheme 58



167 **168** **169**

Scheme 59

SiMe$_2$-bridged *ansa*-tantalocene dichlorides with 2 equiv. of RCH$_2$CH$_2$MgX (R = H, Me, Ph) affords the corresponding hydride olefin complexes.[308] Propylene and styrene coordinate to the metal center avoiding the bulkiness of the substituent on the Cp ligand and with the olefin substituent directed toward the hydride ligand (*endo*-) (Scheme 58), unlike the parent Cp$_2$TaH(olefin) complexes that contain approximately equal *endo*- and *exo*- isomers.[308] *ansa*-[Me$_2$Si(C$_5$Me$_4$)$_2$]TaH(η^2-C$_2$H$_4$) is obtained by the reaction of *ansa*-[Me$_2$Si(C$_5$Me$_4$)$_2$]TaH$_3$ with excess ethylene, with a rate that is ca. 4000 times faster than that of the corresponding Cp* analog, Cp$^*_2$TaH$_3$.[46]

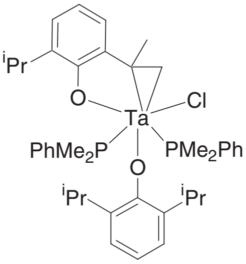
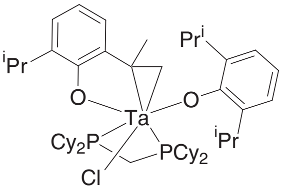
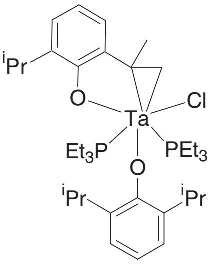
Ethylene derivative **168** of doubly SiMe$_2$-bridged *ansa*-tantalocene is obtained by thermolysis of the corresponding methyl–methylidene compound **167** (Scheme 59).[308] Addition of excess propylene or styrene results in olefin exchange and the formation of the corresponding hydride olefin compounds. The rate of ethylene insertion for these *ansa*-type hydride–ethylene complexes is determined by dynamic NMR spectroscopic studies (line broadening and magnetization transfer): the rate for *ansa*-[Me$_2$Si(C$_5$Me$_4$)$_2$]TaH(η^2-C$_2$H$_4$) is much faster (ca. 760 times) than that for the corresponding unbridged complex Cp$^*_2$TaH(η^2-C$_2$H$_4$),[46] while the rate of the doubly Me$_2$Si-bridged complex is comparable to that of Cp$^*_2$TaH(η^2-C$_2$H$_4$).[316] Trihydride compound Cp$_2$TaH$_3$ reacts with C$_{60}$ to give Cp$_2$Ta(H)(η^2-C$_{60}$). [317] Reduction and subsequent alkylation of Cp′[η^5-C$_5$H$_4$SiMe$_2$(CH$_2$CH=CH$_2$)]TaCl$_2$ (Cp′ = Cp, Cp*) result in the formation of η^2-alkene compounds, Cp*[η^5-C$_5$H$_4$SiMe$_2$(CH$_2$-η^2-CH=CH$_2$)]TaCl and Cp′[η^5-C$_5$H$_4$SiMe$_2$(CH$_2$-η^2-CH=CH$_2$)]TaR (R = Me, CH$_2$Ph, CH$_2$SiMe$_3$) (Table 12).[232]

5.03.5.2 Alkyne and Benzyne Complexes

5.03.5.2.1 Alkyne complexes without cyclopentadienyl ligands

Zinc dust reduction of TaCl$_5$ in the presence of internal alkynes in DME and toluene has been reported to generate *in situ* alkyne species of formula TaCl$_3$(DME)(RC≡CR^1),[321–323] which were recently isolated and fully characterized.[324,325] The DME ligand is readily replaced by nitrogen donor ligands such as pyridine, bipyridine, and TMEDA.[324] These alkyne compounds react with carbonyl compounds, giving allyl alcohols upon hydrolysis. [324] TaCl$_3$(DME)(EtC≡CEt), TaCl$_3$(DME)(HC≡CSiMe$_3$), and TaCl$_3$(py)$_2$(EtC≡CEt) can catalyze the cyclotrimerization of 1-alkynes.[326] Terminal olefins bearing adjacent hydroxyl group and metallo-imines react with *in situ* generated tantalum–alkyne compounds.[327,328] Reaction of TaCl$_3$(DME)(PhC≡CMe) with 1 equiv. of KTp* affords Tp*TaCl$_2$(PhC≡CMe), whose alkylations produce symmetric and unsymmetric alkyl complexes, Tp*TaMe$_2$(PhC≡CMe), Tp*Ta(Et)(Cl)(PhC≡CMe), and Tp*Ta(Et)(Me)(PhC≡CMe).[325,329] Tantalum ethyl complex Tp*Ta(Et)(Cl)(PhC≡CMe) is kinetically stable in sharp contrast to the observed rearrangement of the corresponding niobium ethyl compound to Tp*Nb(Me)Cl(PhC≡CEt).[330] Ethyl moieties of both ethyl complexes Tp*Ta(Et)(Cl)(PhC≡CMe) and Tp*Ta(Et)(Me)(PhC≡CMe) have an α-agostic interaction.

Table 12 Alkene complexes[a]

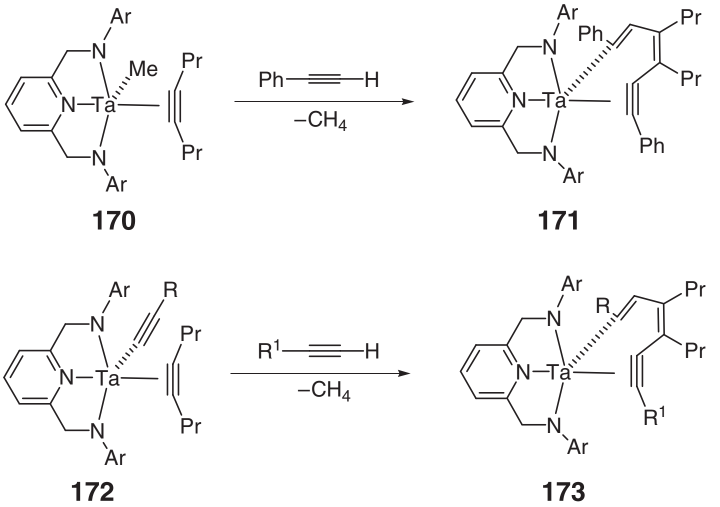
Compound	*Comments*	*References*
Alkene complexes without Cp ligand		
$(^tBu_3SiO)_2Ta(\eta^2\text{-}C_2H_4)(\eta^1\text{-}\overline{N(CH_2)_3CH_2})$	Prep: thermolysis of $(^tBu_3SiO)_2TaEt_2(\eta^1\text{-}\overline{N(CH_2)_3CH_2})$	72
$(^tBu_2PhSiO)_3Ta(\eta^2\text{-}C_2H_4)$	Prep: $(^tBu_2PhSiO)_3TaCl_2 + Na/Hg + C_2H_4$	100
$(^tBu_3SiO)_3Ta(\eta^2\text{-alkene})$	Prep: $(^tBu_3SiO)_3Ta$ + alkene; alkene = C_2H_4, C_3H_6, 1-butene (X-ray), *c*-pentene, *c*-hexene, norbornene; $H_2C{=}CHC_6H_4\text{-}p\text{-}X$; X = H, OMe, CF_3	302
	Prep: $TaCl(H)_2(PMe_2Ph)_2(OAr)_2$ + 1,3-cyclohexadiene or styrene; Ar = $C_6H_3\text{-}2,6\text{-}^iPr_2$	175, 176, 318
	Prep: $TaCl_3(\eta^1\text{-}Cy_2PCH_2PCy_2)(OAr)_2 + Na/Hg$; Ar = $C_6H_3\text{-}2,6\text{-}^iPr_2$, X-ray	319
	Prep: $TaCl_3(PMe_2Ph)_2(OAr)_2 + HSnBu_3 + PEt_3$; Ar = $C_6H_3\text{-}2,6\text{-}^iPr_2$, X-ray	175
$TaCl(PMe_3)(\eta^2\text{-}CH_2{=}CHPh)(OC_6H_3\text{-}2,6\text{-}Ph_2)_2$	Prep: $Ta(H)_2Cl(PMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)$ + styrene, X-ray	175, 176
$Ta(\eta^2\text{-}C_2H_4)(O^tBu)_2[C_6H_4\text{-}2\text{-}(CH_2NMeCH_2CH_2NMe_2)]$	Prep: $Ta({=}CHCMe_2Ph)(O^tBu)_2[C_6H_4\text{-}2\text{-}(CH_2NMeCH_2CH_2NMe_2)] + C_2H_4$, X-ray	259
$[(Me_3SiCH_2CH_2)_3N]Ta(\eta^2\text{-}CH_2{=}CH_2)$	Prep: $[(Me_3SiNCH_2CH_2)_3N]TaCl_2 + 2EtMgCl$	105, 106
$[(Et_3SiNCH_2CH_2]_3N]Ta(\eta^2\text{-}CH_2{=}CH_2)$	Prep: $[(Et_3SiNCH_2CH_2)_3N]TaCl_2 + 2CH_3CH_2MgCl$	107
$[P_2N_2]Ta(Me)(\eta^2\text{-}C_2H_4)$	Prep: $[P_2N_2]Ta({=}CH_2)Me + C_2H_4$	193
$[P_2N_2]Ta(Et)(\eta^2\text{-}C_2H_4)$	Prep: $[P_2N_2]Ta({=}CH_2)Me + C_2H_4$ or $[P_2N_2]TaH_3(PMe_3) + C_2H_4$, X-ray	193
Alkene complexes with Cp ligand		
$Cp^*[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]Ta(H)(\eta^2\text{-}C_2H_4)$	Prep: $Cp^*[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]TaH_3 + C_2H_4$	45
$Cp^*Ta({=}NXyl)(\eta^2\text{-}CH_2{=}CHR^1)(PMe_3)$	Prep: $Cp^*Ta({=}NXyl)Cl_2$ RMgX (R = Et, Pr) + PMe_3; R^1 = H (X-ray), Me	314
$Cp^*Ta({=}NC_6H_3\text{-}2,6\text{-}^iPr_2)(\eta^2\text{-}CH_2{=}CHR^1)(PMe_3)$	Prep: $Cp^*Ta({=}NXyl)Cl_2$ RMgX (R = Et, Pr) + PMe_3; R^1 = H, Me	315
$Cp^*TaMe(PPh_2)(\eta^2\text{-}CH_2{=}CH_2)$	Prep: $Cp^*TaMe_2(\eta^2\text{-}CH_2{=}CH_2) + PPh_2H$	234
$Cp^*(^tBu_3PN)Ta(\eta^2\text{-}CH_2CHPh)(CH_2Ph)$	X-ray	160
$Cp^*(R_3PN)Ta(\eta^2\text{-}C_2H_4)Cl$	Prep: $Cp^*TaCl_3(NPR_3) + 2EtMgCl$; R = ^tBu (X-ray), ^iPr	160
$Cp^*(R_3PN)ClTa(\mu\text{-}C_2H_4)B(C_6F_5)_3$	Prep: $Cp^*(R_3PN)Ta(\eta^2\text{-}C_2H_4)Cl + B(C_6F_5)_3$; R = ^tBu (X-ray)	160

(Continued)

Table 12 (Continued)

Compound	*Comments*	*References*
$Cp^*(R_3PN)Ta(\eta^2\text{-}C_2H_4)Et$	Prep: $Cp^*TaCl_3(NPR_3) + 3EtMgCl$; R = ᵗBu, ⁱPr	160
$Cp^*{}_2Ta(\eta^2\text{-}C_2H_4)(H)$	Prep: $Cp^*_2TaCl(THF) + EtMgBr$	41,315
$Cp_2Ta(H)(\eta^2\text{-}C_{60})$	Prep: $Cp_2TaH_3 + C_{60}$	317
ansa-$[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)]Ta(\eta^2\text{-}C_2H_4)(H)$	Prep: $[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)]TaCl_2 + 2EtMgBr$; R = ⁱPr, ᵗBu	308
ansa-$[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_2\text{-}2,4\text{-}{}^iPr_2)]Ta(\eta^2\text{-}C_2H_4)(H)$	Prep: $[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_2\text{-}2,4\text{-}{}^iPr_2)]TaCl_2 + 2EtMgBr$; two isomers	308
ansa-$[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)]Ta(\eta^2\text{-}CH_2CHMe)(H)$	Prep: $[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)]TaCl_2 + 2CH_3CH_2CH_2MgCl$; R = ⁱPr (two isomers), ᵗBu	308
ansa-$[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)]Ta(\eta^2\text{-} CH_2CHPh)(H)$	Prep: $[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)]TaCl_2 + 2PhCH_2CH_2MgBr$; R = ⁱPr (three isomers), ᵗBu	308
ansa-$[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_2\text{-}2,4\text{-}{}^iPr_2)]Ta(\eta^2\text{-}CH_2CHPh)(H)$	Prep: $[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_2\text{-}2,4\text{-}{}^iPr_2)]TaCl_2 + 2PhCH_2CH_2MgBr$; two isomers	308
ansa-$[(Me_2Si)_2(\eta^5\text{-}C_5H_3\text{-}4\text{-}{}^tBu)(\eta^5\text{-}C_5H_2\text{-}3,5\text{-}{}^iPr_2)]Ta(\eta^2\text{-}C_2H_4)(H)$	Prep: thermolysis of *ansa*-$[(Me_2Si)_2(\eta^5\text{-}C_5H_3\text{-}4\text{-}{}^tBu)(\eta^5\text{-}C_5H_2\text{-}3,5\text{-}{}^iPr_2)]TaMe({=}CH_2)$	308,316
ansa-$[(Me_2Si)_2(\eta^5\text{-}C_5H_3\text{-}4\text{-}{}^tBu)(\eta^5\text{-}C_5H_2\text{-}3,5\text{-}{}^iPr_2)]Ta(\eta^2\text{-}CH_2CHR)(H)$	R = Me, Ph	308
ansa-$[Me_2Si(C_5Me_4)_2]TaH(\eta^2\text{-}C_2H_4)$	Prep: *ansa*-$[Me_2Si(C_5Me_4)_2]TaH_3 + C_2H_4$	46
$Cp^*[\eta^5\text{-}C_5H_4SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)]TaCl$	Prep: $Cp^*[\eta^5\text{-}C_5H_4SiMe_2(CH_2CH{=}CH_2)]TaCl_2 + Na/Hg$	232
$Cp^*[\eta^5\text{-}C_{5'}H_4SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)]TaR$	Prep: $Cp^*[\eta^5\text{-}C_5H_4SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)]TaCl + RMgX$; R = CH_2SiMe_3, CH_2Ph	232
$Cp'[\eta^5\text{-}C_5H_4SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)]TaR$	Prep: $Cp'[\eta^5\text{-}C_5H_4SiMe_2(CH_2CH{=}CH_2)]TaCl_2 + 2RMgX$; Cp′ = Cp, Cp*; R = Me, CH_2Ph, CH_2SiMe_3	232
$(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)Ta(\eta^2\text{-}butadiene)$	Prep: $CpTaCl_2$(*s-cis*-η^4-butadiene) + CpNa	320

[a] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.



Scheme 60

Sodium amalgam reduction of *mer*-$\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl_3}$ in the presence of internal alkynes yields the five-coordinate Ta(III) alkyne complexes $\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl(\eta^2\text{-}RC{\equiv}CR)}$ (R = Pr, Et, Ph).[111,331] When methyl derivative $\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}Ta(Me)(\eta^2\text{-}PrC{\equiv}CPr)}$ **170** reacts with an excess of phenylacetylene, methane elimination and double alkyne insertion produce **171** (Scheme 60).[331] The reaction involves the initial formation of alkynyl compounds **172**, which are alternatively prepared by the reaction of $\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl(\eta^2\text{-}PrC{\equiv}CPr)}$ with $\mathrm{LiC{\equiv}CR}$, and successive insertion of terminal alkynes results in the formation of the corresponding metallacyclic products **173**.[331] The internal alkynes such as 4-octyne and 3-hexyne did not react even at 110 °C.

5.03.5.2.2 Cyclopentadienyl alkyne complexes

Phosphaalkynes can donate four electrons to the tantalum atom: treatment of $\mathrm{Cp^*TaCl_2(CO)_2(THF)}$ and $\mathrm{RC{\equiv}P}$ affords $\mathrm{Cp^*TaCl_2(\eta^2\text{-}RC{\equiv}P)}$ (R = ^{t}Bu, adamantly), which reacts with $\mathrm{KO^tBu}$ to give the corresponding bis(alkoxo) compounds.[332]

5.03.5.2.3 Benzyne complexes

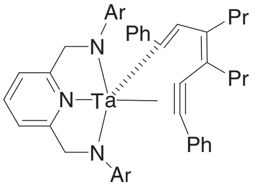
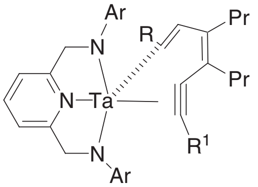
Reaction of $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaCl_2}$ with 2 equiv. of PhLi or reaction of $\mathrm{[(Me_3SiNCH_2CH_2)_3N]Ta(Me)Cl}$ with 1 equiv. of PhMgBr produces the benzyne compound, $\mathrm{[(Me_3SiNCH_2CH_2)_3N]Ta(\eta^2\text{-}C_6H_4)}$; during these reactions, $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaPhCl}$ or $\mathrm{[(Me_3SiNCH_2CH_2)_3N]TaPh(Me)}$ are observed (Table 13).[106]

Table 13 Alkyne and benzyne complexes[a]

Compound	*Comments*	*References*
Alkyne complexes without cyclopentadienyl ligand		
$\mathrm{(R_3SiO)_3Ta(\eta^2\text{-}MeC{\equiv}CMe)}$	Prep: $\mathrm{({}^tBu_2PhSiO)_3TaCl_2 + Na/Hg}$ + 2-butyne; $\mathrm{R_3Si = {}^tBu_2PhSi}$	100
$\mathrm{TaCl_3(DME)(RC{\equiv}CR^1)}$	Prep: $\mathrm{TaCl_5 + Zn + RC{\equiv}CR^1}$; $\mathrm{R = R^1 = Et}$ (X-ray); $\mathrm{R = R^1 = \textit{n}\text{-}C_5H_{11}}$; $\mathrm{R = Ph, R^1 = Me}$ (X-ray); $\mathrm{R = R^1 = Ph}$	324
$\mathrm{TaCl_3(py)_2(RC{\equiv}CR^1)}$	Prep: $\mathrm{TaCl_3(DME)(RC{\equiv}CR^1)}$ + pyridine; $\mathrm{R = R^1 = Et}$ (X-ray); $\mathrm{R = R^1 = \textit{n}\text{-}C_5H_{11}}$; $\mathrm{R = Ph, R^1 = Me}$; $\mathrm{R = R^1 = Ph}$	324
$\mathrm{TaCl_3(bipy)(EtC{\equiv}CEt)}$		324
$\mathrm{TaCl_3(TMEDA)(EtC{\equiv}CEt)}$	X-ray	324
$\mathrm{TaCl_3(DME)(HC{\equiv}CSiMe_3)}$		326
$\mathrm{TaCl_3(DME)(PhC{\equiv}CMe)}$		325
$\mathrm{Tp^*TaCl_2(PhC{\equiv}CMe)}$	Prep: $\mathrm{TaCl_3(DME)(PhC{\equiv}CMe) + KTp^*}$, X-ray	325, 329
$\mathrm{Tp^*TaMe_2(PhC{\equiv}CMe)}$	Prep: $\mathrm{Tp^*TaCl_2(PhC{\equiv}CMe) + 2MeLi}$	325
$\mathrm{Tp^*Ta(Et)(Cl)(PhC{\equiv}CMe)}$	Prep: $\mathrm{Tp^*TaCl_2(PhC{\equiv}CMe) + EtMgCl}$, X-ray	325
$\mathrm{Tp^*Ta(Et)(Me)(PhC{\equiv}CMe)}$	Prep: $\mathrm{Tp^*Ta(Et)(Cl)(PhC{\equiv}CMe) + MeLi}$	325
$\mathrm{Ta(R_3SiOC{\equiv}COSi(R^1)_3)(dmpe)_2Cl}$	$\mathrm{SiR_3 = Si^iPr_3, SiPh_2{}^tBu, SiPh_3; R^1 = Me, Et}$	52
$\mathrm{Ta(Me_3SiOC{\equiv}COSiMe_3)(depe)_2X}$	X = Cl, OTf	16
$\mathrm{Ta(Me_3SiOC{\equiv}COSiMe_3)(dbpe)_2X}$	X = Cl, OTf	16
$\mathrm{Ta(Me_2\overbrace{SiOC{\equiv}COSi}^{CH_2CH_2}Me_2)(depe)_2Cl}$	X-ray	16
$\mathrm{Ta(EtOC{\equiv}COSiR_3)(dmpe)_2OTf}$	$\mathrm{SiR_3 = Si^iPr_3, SiPh_2{}^tBu}$	53
$\mathrm{Ta(EtOC{\equiv}COSiR_3)(depe)_2OTf}$	$\mathrm{SiR_3 = Si^iPr_3, SiPh_2{}^tBu, SiMe_3}$	53
$\mathrm{Ta(AcOC{\equiv}COSiPh_2{}^tBu)(depe)_2Cl}$	X-ray	53
$\mathrm{Ta(AcOC{\equiv}COSiPh_2{}^tBu)(dmpe)_2Cl}$		53
$\mathrm{Ta(MeO_2COC{\equiv}COSiPh_2{}^tBu)(dmpe)_2Cl}$		53
$\mathrm{Ta(AcOC{\equiv}COAc)(dmpe)_2Cl}$	X-ray	53
$\mathrm{Ta(AcOC{\equiv}COAc)(depe)_2Cl}$		53
$\mathrm{TaCl(PMe_3)(\eta^2\text{-}EtC{\equiv}CEt)(OC_6H_3\text{-}2,6\text{-}Ph_2)_2}$	Prep: $\mathrm{Ta(H)_2Cl(PMe_3)_2(OC_6H_3\text{-}2,6\text{-}Ph_2)}$ + 3-hexyne, X-ray	175
$\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl(\eta^2\text{-}RC{\equiv}CR)}$	Prep: $\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl_3 + RC{\equiv}CR + Na/Hg}$; R = Pr (X-ray), Et, Ph	111, 331
$\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl(\eta^2\text{-}PhC{\equiv}CH)}$	Prep: $\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl_3 + PhC{\equiv}CH + Na/Hg}$	331
$\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}Ta(Me)(\eta^2\text{-}PhC{\equiv}CH)}$	Prep: $\mathrm{\{C_5H_3N\text{-}2,6\text{-}[CH_2N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2\}TaCl(\eta^2\text{-}RC{\equiv}CR) + MeMgBr}$	331

(Continued)

Table 13 (Continued)

Compound	*Comments*	*References*
	Prep: $[C_5H_3N\text{-}2,6\text{-}(CH_2NAr)_2]Ta(Me)$ (η^2-$PrC{\equiv}CPr$) + ex. $PhC{\equiv}CH$; Ar = C_6H_3-2,6-$^iPr_2$	331
$[C_5H_3N\text{-}2,6\text{-}(CH_2NAr)_2]Ta(C{\equiv}CR)(\eta^2\text{-}PrC{\equiv}CPr)$	Prep: $[C_5H_3N\text{-}2,6\text{-}(CH_2NAr)_2]TaCl$ (η^2-$PrC{\equiv}CPr$) + $RC{\equiv}CLi$; Ar = C_6H_3-2,6-$^iPr_2$; R = Ph, Bu, $SiMe_3$, C_6H_4-2-$SiMe_3$	331
	Prep: $[C_5H_3N\text{-}2,6\text{-}(CH_2NAr)_2]Ta(C{\equiv}CR)(\eta^2\text{-}PrC{\equiv}CPr)$ + $R^1C{\equiv}CH$; Ar = C_6H_3-2,6-$^iPr_2$; R = R^1 = Ph; R = R^1 = Bu, R = R^1 = $SiMe_3$; R = Ph, R^1 = Bu; R = Ph, R^1 = $SiMe_3$	331
$[(Me_3SiNCH_2CH_2)_3N]Ta(\eta^2\text{-}HC{\equiv}CH)$	Prep: $[(Me_3SiNCH_2CH_2)_3N]TaCl_2$ + $2CH_2{=}CHMgBr$, X-ray	105, 106
$[(Et_3SiNCH_2CH_2)_3N]Ta(\eta^2\text{-}HC{\equiv}CH)$	Prep: $[(Et_3SiNCH_2CH_2)_3N]TaCl_2$ + $2CH_2{=}CHMgBr$	107
Alkyne complexes with cyclopentadienyl ligand		
$Cp^*Ta(X)(Y)(\eta^2\text{-}PhC{\equiv}CPh)$	X = Y = Me; X = Cl, Y = Me; X = Cl, Y = NMe_2	280
$[Cp^*TaCl(\eta^2\text{-}PhC{\equiv}CPh)]_2$		280
$Cp_2Ta(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^1\text{-}MeC{\equiv}C)M$	Prep: $Cp_2Ta({=}CH_2)Me$ + $(CO)_2M$; M = $Re_2(CO)_8$, $Mn_2(CO)_8$, $Fe(CO)_3$	166
$Cp^*TaCl_2(\eta^2\text{-}RC{\equiv}P)$	Prep: $Cp^*TaCl_2(CO)_2(THF)$ + $RC{\equiv}P$; R = ^tBu (X-ray), adamantly	332
$Cp^*Ta(O^tBu)_2(\eta^2\text{-}RC{\equiv}P)$	Prep: $Cp^*TaCl_2(\eta^2\text{-}RC{\equiv}P)$ + $2KO^tBu$; R = ^tBu, adamantly	332
Benzyne complexes		
$Cp^*Ta(\eta^4\text{-butadiene})(\eta^2\text{-}C_6H_4)$	Prep: thermolysis of $Cp^*Ta(\eta^4\text{-butadiene})Me(Ph)$; X-ray	333
$Cp(\eta^5\text{-}Et_2C_2B_4H_4)Ta(\eta^2\text{-}C_6H_4)(PMe_3)$	Prep: thermolysis of $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaPh_2$ + PMe_3	162
$[(Me_3SiNCH_2CH_2)_3N]Ta(\eta^2\text{-}C_6H_4)$	Prep: $[(Me_3SiNCH_2CH_2)_3N]TaCl_2$ + 2PhLi or $[(Me_3SiNCH_2CH_2)_3N]Ta(Me)Cl$ + PhMgBr	106

[a] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

5.03.5.3 Acyls, Iminoacyls, and Related η^2-Complexes

5.03.5.3.1 Formyl and acyl complexes

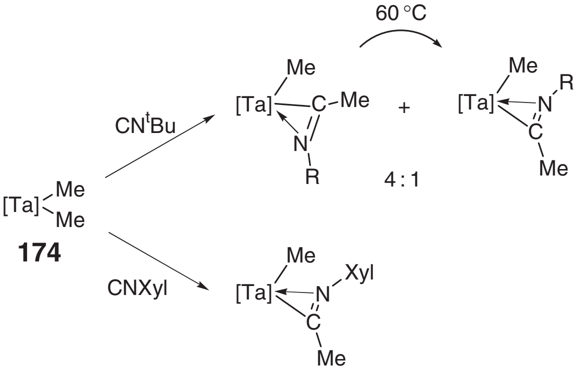
Carbonylation of a cationic methyl porphyrin compound $[Ta(OEP)Me(O^tBu)][BPh_4]$ affords the acyl $[Ta(OEP)(\eta^2\text{-}COMe)(O^tBu)][BPh_4]$.[91] Carbonylation of $(^tBu_3SiO)_3Ta(R)H$ (R = H, Et) or treatment of $(^tBu_3SiO)_3Ta$ with RCHO affords $(^tBu_3SiO)_3Ta[\eta^2\text{-}C(H)(R)O]$.[98] Treatment of dimeric hydride compounds, $[(^tBu_3SiO)_2TaCl]_2(\mu\text{-}H)_2$, $[(^tBu_3SiO)_2TaH_2]_2$, and $[(^tBu_3SiO)_2TaH]_2(\mu\text{-}O)_2$ with CO affords $[(^tBu_3SiO)_2TaCl]_2(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^2\text{-}CHO)$, $[(^tBu_3SiO)_2Ta]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}CHO)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH_2O)$, and $[(^tBu_3SiO)_2Ta]_2(\mu\text{-}\eta^2{:}\eta^1\text{-}CH_2O)(\mu\text{-}O)_2$.[98]

5.03.5.3.2 Iminoacyl complexes

η^2-Iminoacyl complexes of tantalum have been prepared by the insertion of isocyanide into Ta–C bond because they are easily accessible and less reactive compared with the related η^2-acyl derivatives.[334] Isonitrile CNXyl inserts into Ta–C bond of dialkyl compounds $Cp^*Ta({=}NXyl)R_2$ (R = Et, Pr, CH_2SiMe_3, CH_2CMe_3, CH_2Ph, Ph) and monoalkyl compounds $Cp^*Ta({=}NXyl)(R)Cl$ (R = Me, Et, Pr, CH_2SiMe_3, CH_2CMe_2Ph, CH_2CMe_3, CH_2Ph, C_6H_4-2-(CH_2NMe_2), NMe_2) to give iminoacyl compounds $Cp^*Ta({=}NXyl)(R)[\eta^2\text{-}C(R){=}N(Xyl)]$ and $Cp^*Ta({=}NXyl)(Cl)[\eta^2\text{-}C(R){=}N(Xyl)]$.[314,335] The insertion reaction of methyl–alkyl imido compounds $Cp^*Ta({=}NXyl)(R)Me$ (R = CH_2SiMe_3, CH_2CMe_2Ph, CH_2CMe_3, CH_2Ph, Ph, C_6H_4-2-(CH_2NMe_2), NMe_2) affords the corresponding η^2-iminoacyl compounds of XylNC insertion into the methyl or alkyl bond.[335]

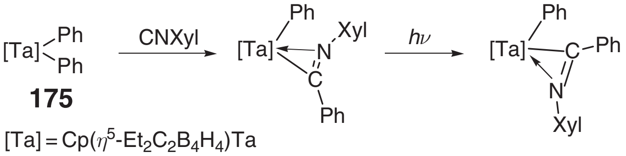
Dimethyl carborane complex, Cp(η^5-$Et_2C_2B_4H_4$)$TaMe_2$ **174**, is stable in acetonitrile; however, under irradiation, acetonitrile inserted into a Ta–Me bond, forming Cp(η^5-$Et_2C_2B_4H_4$)MeTa(N═CMe_2).[142] In contrast, isonitriles can insert rapidly at room temperature into Ta–C bonds of **174** and its phenyl analog **175**, giving η^2-iminoacyl complexes (Schemes 61 and 62).[142] In each reaction, the inner nitrogen complexes (*exo*/*endo*) are thermodynamically more stable. Thermal or photochemical isomerizations between the inner and outer isomers are observed.[142] The amido(methyl) complexes $Cp^*Ta({=}N^tBu)(Me)(NR_2)$ (R = Ph,$SiMe_3$) are derived by the reaction of $Cp^*Ta({=}N^tBu)(Me)(Cl)$ with lithium amides.[158] Hydrogen exchange between amido and imido ligands is observed for the reaction of $Cp^*Ta({=}N^tBu)(Me)(Cl)$ with LiNHMe, resulting in the mixture of $Cp^*Ta({=}N^tBu)(Me)(NHMe)$ and $Cp^*Ta({=}NMe)(Me)(NH^tBu)$.[158] Insertion of CNXyl into Ta–Me bond of $Cp^*Ta({=}N^tBu)(Me)(NR_2)$ (R = Ph, $SiMe_3$) affords the η^1-iminoacyl derivatives $Cp^*Ta({=}N^tBu)(NR_2)(\eta^1\text{-}CMe{=}NXyl)$ (R = Ph, $SiMe_3$), while CNXyl insert into Ta–N(Me)R bond of $Cp^*Ta({=}N^tBu)(Me)(NMeR)$ (R = H, Me) to give η^2-iminocarbamoyl compounds $Cp^*Ta({=}N^tBu)(Me)[\eta^2\text{-}C(NMeR){=}NXyl]$ (R = H, Me).[158]

Double insertion of isonitrile into $Cp^*TaMeX(N^tBu)$ **176** is reported (Scheme 63).[151] Two XylNC also insert into the Ta–Me bonds of (η^5-$C_4H_4BiN^iPr_2$)$TaMe_3(PMe_3)$ to give a bis(iminoacyl) compound (η^5-$C_4H_4BiN^iPr_2$)$TaMe[\eta^2\text{-}C(Me){=}NXyl]_2$, which further reacts with XylNC to give (η^5-$C_4H_4BiN^iPr_2$)$TaMe[\eta^2\text{-}C(Me){=}NXyl][\eta^3\text{-}N(Xyl){=}CHCH_2C(Me)NXyl]$.[140] This reaction involves an iminoacyl-coupling reaction and C–H activation of a methyl group. Two equivalents of XylNC (Xyl = 2,6-dimethylphenyl) insert into the Ta–N bonds of $Ta(NMe_2)_3$-$[(^iPrN)_2C{=}N^iPr]$, giving the bis(iminocarbamoyl) product $Ta(NMe_2)(\eta^2\text{-}XylN{=}CNMe_2)_2[(^iPrN)_2C{=}N^iPr]$.[94]



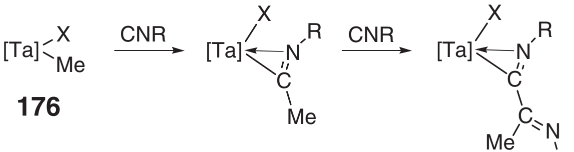
[Ta] = Cp(η^5-$Et_2C_2B_4H_4$)Ta

Scheme 61



[Ta] = Cp(η^5-$Et_2C_2B_4H_4$)Ta

Scheme 62



[Ta] = Cp*Ta(N^{t}Bu); R = 2,6-$Me_2C_6H_3$
X = Me, Cl, OMe, O^{t}Bu, NH^{t}Bu

Scheme 63

Dimethyl complex Cp*TaMe$_2$[(SCH$_2$CH$_2$)$_2$O] reacts with XylNC to give an imine complex Cp*Ta[η^2-N(Xyl)=CMe$_2$][(SCH$_2$CH$_2$)$_2$O], which further react with XylNC to give a cyclic η^1-iminoacyl compound Cp*Ta[N(Xyl)CMe$_2$C(=NXyl)][(SCH$_2$CH$_2$)$_2$O].[148] Similarly, Cp*TaMe$_3$(SC$_6$H$_7$N$_2$) further reacts with 2 equiv. of XylNC to give four-membered metallacyclic compound Cp*(SC$_6$H$_7$N$_2$)Me Ta[N(Xyl)CMe$_2$C(=NXyl)].[112] In the case of ^{t}BuNC, η^2-imine compound, Cp*(SC$_6$H$_7$N$_2$)MeTa[η^2-CMe$_2$=N(^{t}Bu)], is detected in an NMR tube reaction.[112] The insertion of isonitriles RNC (R = ^{t}Bu, Cy, CH$_2$Ph) occurs exclusively into the Ta–CH$_2$ bonds of zwitterionic compounds Cp$'_2$Ta[CH$_2$B(C$_6$F$_5$)$_3$](Me) (Cp$'$ = Cp, C$_5$H$_4$Me), which also have a strong α-agostic interaction, to give the corresponding iminoacyl compounds, while the insertion of the same isonitriles into a Ta–Me bond of the non-zwitterionic analog [Cp$_2$TaMe$_2$][B(C$_6$F$_5$)$_4$] occurs much more rapidly to form the corresponding iminoacyl compounds.[336]

Monohydride compounds Ta(H)Cl$_2$(PMe$_2$Ph)$_2$(OC$_6$H$_3$-2,6-^{i}Pr$_2$) supported by bulky aryloxo ligands react with isocyanides CNC$_6$H$_3$-2,6-^{i}Pr$_2$, CNXyl, or ^{t}BuNC to give η^2-iminoacyl compounds TaCl$_2$(η^2-C(H)(PMe$_2$Ph)NR)(OC$_6$H$_3$-2,6-^{i}Pr$_2$) (R = C$_6$H$_3$-2,6-^{i}Pr$_2$, Xyl, ^{t}Bu) in which phophine binds to the carbon of the iminoacyl moiety.[337,338] Reaction with 3 equiv. of ^{t}BuNC results in the formation of (2,6-^{i}Pr$_2$-C$_6$H$_3$O)$_2$Cl$_2$Ta[N(^{t}Bu)C(=C=N^{t}Bu)CH=N(^{t}Bu)]·[337,338]

Dinuclear trialkyl bis(imido) complex, [Ta(CH$_2$SiMe$_3$)$_3$(CH$_3$CN)]$_2$(μ-1,4-NC$_6$H$_4$N), reacts with XylNC to give [Ta(η^2-C(CH$_2$SiMe$_3$)=NXyl)$_2$(CH$_2$SiMe$_3$)]$_2$(μ-1,4-NC$_6$H$_4$N).[339] Bridged iminoacyl compounds (η^1-dmpm)Cl$_2$Ta(μ-NTol)[μ-η^2-C(H)=NTol](μ-dmpm)TaCl(η^2-DTolF) and (η^2-DTolF)Cl$_2$Ta(μ-NPh)(μ-η^2-CH=NTol)Ta(η^2-DTolF)$_2$ (dmpm = bis(dimethylphosphino)methane, DTolF = di-p-tolylformamidinate anion) are prepared.[340,341]

5.03.5.3.3 Imine complexes

The direct synthesis of imine complexes from TaCl$_5$ is reported: treatment of TaCl$_5$ with zinc dust in DME and toluene followed by addition of PhCH$_2$N=CHPh affords TaCl$_3$(DME)[η^2-N(CH$_2$Ph)=CHPh], which reacts with carbonyl compounds and isocyanate.[342] An imine complex, Tp*Ta(η^2-CH$_2$=NPh)(CH$_2$^{t}Bu)(Cl), is obtained by an intramolecular transfer of a proton from the methyl group of an N-methylanilide complex.[161]

The dimethyl tantalum complex Cp*TaCl$_2$Me$_2$ reacts with CO and isocyanides CNAr (Ar = C$_6$H$_3$-2,6-Me$_2$, C$_6$H$_2$-2,4,6-Me$_3$) to form the acetone Cp*TaCl$_2$[η^2-O=CMe$_2$] and imine compounds Cp*TaCl$_2$[η^2-N(Ar)=CMe$_2$].[156,157,306] The imine compounds react further with HCl to give Cp*TaCl$_3$[N(Ar)CHMe$_2$].[156,306] Cp*TaCl$_2$[η^2-C(Xyl)=CMe$_2$] (Xyl=C$_6$H$_3$-2,6-Me$_2$) can be methylated by MeLi to give the dimethyl complex Cp*TaMe$_2$[η^2-C(Xyl)=CMe$_2$].[156,306] Further insertion of XylNC into these imine compounds results in the formation of the corresponding imido complexes Cp*TaCl$_2$(=NXyl) and Cp*TaMe(=NXyl)-[N(Xyl)C(Me)=CMe$_2$][156,343] Treatment of Cp*TaMe$_3$(X) with CNXyl affords Cp*Ta(X)Me[η^2-C(Xyl)=CMe$_2$], which further reacts with CNXyl stepwise to give Cp*Ta(X)-(=NXyl)[N(Xyl)C(Me)=CMe$_2$] and Cp*Ta(X)(=NXyl)[η^2-N(Xyl)=CCMe$_2$CMe=NXyl].[343] Isocyanides CNAr (Ar = C$_6$H$_3$-2,6-Me$_2$, C$_6$H$_2$-2,4,6-Me$_3$) also insert into the Ta–Me bond of Cp*TaCl$_3$Me to give iminoacyl compounds, Cp*Ta[η^2-C(Me)=NAr]Cl$_3$, which react with HCl to give carbene complexes Cp*TaCl$_4$[C(Me)=N(H)Ar].[306] Carbonylation of Cp*Ta(=NXyl)Me$_2$ gives the corresponding acyl compound, Cp*MeTa(=NXyl)[η^2-C(Me)=O], which gives a dinuclear ene diolate complex, [Cp*Ta(=NXyl)(Me)]2[μ-OC(Me)=C(Me)], by intermolecular coupling reaction between two acyl carbon atoms.[157] In the carbonylation of Cp*Ta(=NXyl)Me(Cl), the expected imido acyl compound is not obtained, but oxo η^2-iminoacyl complex Cp*Ta(Cl)(O)[η^2-C(Me)=N(Xyl)] is obtained.[157] Similarly, carbonylation of dialkyl compounds Cp*Ta(=NXyl)R$_2$ (R = CH$_2$SiMe$_3$, CH$_2$CMe$_3$, CH$_2$Ph, CH$_2$CMe$_2$Ph), monoalkyl compounds Cp*Ta(=NXyl)(R)Cl (R = CH$_2$CMe$_2$Ph, NMe$_2$), and methyl–alkyl imido compounds Cp*Ta(=NXyl)(R)Me (R = CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$, CH$_2$Ph) affords the corresponding η^2-acyl or carbamoyl compounds.[335] Insertion of XylNC into dialkyls Cp*TaCl$_2$R$_2$ (R = CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$, CH$_2$Ph) results in the formation of η^2-iminoacyl compounds Cp*TaCl$_2$R[η^2-C(R)=N(Xyl)], which upon standing at room temperature give rise to an imido compound Cp*TaCl$_2$(=NXyl).[115] Monoalkylated compound Cp*TaCl(CH$_2$SiMe$_3$)[η^2-N(Xyl)=CMe$_2$] slowly decomposes to give Cp*TaCl(C(Me)=CH$_2$)(=NXyl).[146]

Heterocyclic imine compounds (η^2-quinoline)Ta(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_3$, (η^2-6-methylquinoline)Ta(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_3$, and (η^2-6-methylquinoline)TaCl(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$(ether) are obtained by amalgam reduction of TaCl$_2$(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_3$(η^1-quinoline), (η^2-quinoline)Ta(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_3$, and (η^1-6-methylquinoline)TaCl$_3$(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$.[344] In the presence of excess pyridine, amalgam reduction of (^{t}Bu$_3$SiO)$_2$TaCl$_2$(η^1-NR$_2$) [NR$_2$ = N(CH$_2$)$_3$CH$_2$, N(CH$_2$)$_4$CH$_2$]] affords the corresponding η^2-pyridine complexes (^{t}Bu$_3$SiO)$_2$Ta(η^2-NC$_5$H$_4$)(η^1-NR$_2$) (Table 14).[72]

Table 14 η^2-Acyl, η^2-iminoacyl, and related η^2-complexes of tantalum[a]

Compound	*Comments*	*References*
Formyl, acyl, and related complexes		
[Ta(OEP)(η^2-COMe)(O^{t}Bu)][BPh$_4$]	Prep: [Ta(OEP)Me(O^{t}Bu)][BPh$_4$] + CO	91
(ArN=)(ArNH)TaMe(η^2-COMe)	Prep: (ArN=)(ArNH)TaMe$_2$ + CO; Ar = 2,6-Mes$_2$C$_6$H$_3$	78
Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(Me)[η^2-COSi(SiMe$_3$)$_3$]	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(Me)[Si(SiMe$_3$)$_3$] + CO	149
Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(L){η^2-CO(H)[Si(SiMe$_3$)$_3$]}	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)(CO)[Si(SiMe$_3$)$_3$] + L; L = CO or PMe$_3$	36
(^{t}Bu$_3$SiO)$_3$Ta[η^2-C(H)(R)O]	Prep: (^{t}Bu$_3$SiO)$_3$Ta(R)H + CO or (^{t}Bu$_3$SiO)$_3$Ta + RCHO; R = H, Et	98
[(^{t}Bu$_3$SiO)$_2$TaCl]$_2$(μ-H)(μ-η^2:η^2-CHO)	Prep: [(^{t}Bu$_3$SiO)$_2$TaCl]$_2$(μ-H)$_2$ + CO	98
[(^{t}Bu$_3$SiO)$_2$Ta]$_2$(μ-η^2:η^2-CHO)(μ-η^1:η^2-CH$_2$O)	Prep: [(^{t}Bu$_3$SiO)$_2$TaH$_2$]$_2$ + CO	98
[(^{t}Bu$_3$SiO)$_2$Ta]$_2$(μ-η^2:η^1-CH$_2$O)(μ-O)$_2$	Prep: [(^{t}Bu$_3$SiO)$_2$TaH]$_2$(μ-O)$_2$ + CO	98
Cp*MeTa(=NXyl)[η^2-C(Me)=O] [Cp*Ta(=NXyl)(Me)]$_2$[μ-OC(Me)=C(Me)O]	Prep: Cp*Ta(=NXyl)Me$_2$ + CO	157
Cp*Ta(=NXyl)(R)[η^2-C(R)=O]	Prep: Cp*Ta(=NXyl)R$_2$ + CO; R = CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$, CH$_2$Ph	335
Cp*Ta(=NXyl)(Cl)[η^2-C(R)=O]	Prep: Cp*Ta(=NXyl)(R)Cl + CO; R = CH$_2$CMe$_2$Ph (X-ray), NMe$_2$	335
Cp*Ta(=NXyl)(Me)[η^2-C(R)=O]	Prep: Cp*Ta(=NXyl)(R)Me + XylNC; R = CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$	335
Ketones, aldehydes, and related complexes		
Ta[η^2-OC(allyl)$_2$]{*p*-R-calix[4]arene-OMe}	Prep: Ta(allyl)$_2${*p*-R-calix[4]arene-OMe} + CO	73
Ta[η^2-OC(R)$_2$]{*p*-R-calix[4]arene-OMe}	Prep: TaR$_2${*p*-R-calix[4]arene-OMe} + CO; R = Me, CH$_2$Ph (X-ray), C$_6$H$_4$-4-Me	73
[PyMe]{Ta[η^2-OC(CH$_2$Ph)$_2$](*p*-R-calix[4]arene)}	Prep: Ta[η^2-OC(CH$_2$Ph)$_2$]{*p*-R-calix[4]arene-OMe} + py	73
(Me$_2$N)$_3$Ta(η^2-ONMe$_2$)[OSi(SiMe$_3$)$_3$]	Prep: (Me$_2$N)$_4$Ta(SiR$_3$) + O$_2$, X-ray	95
Cp*Ta(η^2-Me$_2$CO)[(OCH$_2$)$_2$-2,6-(C$_5$H$_3$N)]	Prep: Cp*TaMe$_2$[(OCH$_2$)$_2$-2,6-(C$_5$H$_3$N)] + ex. CO, X-ray	119
Cp*Ta(η^2-Me$_2$C=NR)[(OCH$_2$)$_2$-2,6-(C$_5$H$_3$N)]	Prep: Cp*TaMe$_2$[(OCH$_2$)$_2$-2,6-(C$_5$H$_3$N)] + RCN; R = ^{t}Bu, C$_6$H$_3$-2,6-Me$_2$	119
TaTa(η^2-O=$\overline{\mathrm{CCH_2CHRCH_2}}$))(O^{t}Bu)$_2$[C$_6H_4$-2-(CH$_2$NMeCH$_2CH_2NMe_2$)]	Ta($\overline{\mathrm{CH_2CHRCH_2}}$)(O^{t}Bu)$_2$[C$_6H_4$-2-(CH$_2$NMeCH$_2CH_2NMe_2$)] + CO; R = H (X-ray), Me, Ph	345
Iminoacyl complexes		
Ta[η^2-(^{t}Bu)N=C(allyl)$_2$]{*p*-R-calix[4]arene-OMe}	Prep: Ta(allyl)$_2${*p*-R-calix[4]arene-OMe} + ^{t}BuNC	73
Ta[η^2-(^{t}Bu)N=C(R)$_2$]{*p*-R-calix[4]arene-OMe}	Prep: TaR$_2${*p*-R-calix[4]arene-OMe} + ^{t}BuNC; R = Me, CH$_2$Ph, C$_6$H$_4$-4-Me	73
[PyMe]{Ta[η^2-(^{t}Bu)N=C(R)$_2$](*p*-R-calix[4]arene)}	Prep: Ta[η^2-(^{t}Bu)N=(CH$_2$Ph)$_2$]{*p*-R-calix[4]arene-OMe} + py; R = CH$_2$Ph (X-ray), C$_6$H$_4$-4-Me	73
[PyMe]{Ta[η^2-(^{t}Bu)N=C(C$_4$H$_6$)]{(*p*-R-calix[4]arene)}	Prep: Ta(η^4-C$_4$H$_6$){*p*-R-calix[4]arene-OMe} + py; R = CH$_2$Ph (X-ray), C$_6$H$_4$-4-Me	73
Cp*TaCl$_2$R[η^2-C(R)=N(Xyl)]	Prep: Cp*TaCl$_2$R$_2$ + XylNC; R = CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph (X-ray), CH$_2$CMe$_3$, CH$_2$Ph	115
Cp$^*\overline{\mathrm{Ta[=N(C_6H_3Me)_2N}}$SiMe$_3$][$\eta^2$-C(Me)=NXyl]	Prep: Cp$^*\overline{\mathrm{Ta[=N(C_6H_3Me)_2N}}$SiMe$_3$]Me + XylNC	124
Cp*Ta(=N^{t}Bu)(η^1-O$_2$CNMe$_2$)(η^2-CMe=NXyl)	Prep: Cp*Ta(=N^{t}Bu)(O$_2$CNH^{t}Bu)(Me) + XylNC	125
Cp*Ta(=N^{t}Bu)(η^1-O$_2$CNH^{t}Bu)(η^2-CMe=NXyl)	Prep: Cp*Ta(=N^{t}Bu)(O$_2$CNMe$_2$)(Me) + XylNC in C$_6$D$_6$ or CDCl$_3$	125
Cp*Ta(=N^{t}Bu)(η^2-O$_2$CNH^{t}B)(η^1-CMe=NXyl)	Prep: Cp*Ta(=N^{t}Bu)(O$_2$CNMe$_2$)(Me) + XylNC in hexane	125
Cp*(η^5-C$_4$H$_4$BN^{i}Pr$_2$)TaMe(η^2-C(Me)=NXyl)	Prep: Cp*(η^5-C$_4$H$_4$BN^{i}Pr$_2$)TaMe$_2$ + XylNC	137
(η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaMe[η^2-C(Me)=NXyl]$_2$	Prep: (η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaMe$_3$(PMe$_3$) + 2XylNC	140
(η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaMe[η^2-C(Me)=NXyl][η^3-N(Xyl)=CHCH$_2$C(Me)NXyl]	Prep: (η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaMe[η^2-C(Me)=NXyl]$_2$ + XylNC, X-ray	140

(*Continued*)

Table 14 (Continued)

Compound	*Comments*	*References*
Cp(η^5-Et$_2$C$_2$B$_4$H$_4$)TaMe[η^2-C(Me)=NR]	Prep: Cp(η^5-Et$_2$C$_2$B$_4$H$_4$)TaMe$_2$ + RNC; R = ^{t}Bu, Xyl, X-ray for two isomers, outer and inner nitrogen isomers with R = ^{t}Bu	142
Cp(η^5-Et$_2$C$_2$B$_4$H$_4$)TaPh[η^2-C(Ph)=NXyl]	Prep: Cp(η^5-Et$_2$C$_2$B$_4$H$_4$)TaPh$_2$ + XylNC, X-ray	142
Cp*Ta(CH$_2$SiMe$_3$)(=CHSiMe$_3$)[η^2-C(CH$_2$SiMe$_3$)=N(Xyl)]	Prep: Cp*Ta(=CHSiMe$_3$)(CH$_2$SiMe$_3$)$_2$ + CNXyl; Xyl = C$_6$H$_3$-2,6-Me$_2$	147
Cp*Ta[N(Xyl)CMe$_2$C(=NXyl)][(SCH$_2$CH$_2$)$_2$O]	Prep: Cp*Ta[η^2-N(Xyl)=CMe$_2$][(SCH$_2$CH$_2$)$_2$O] + XylNC, X-ray	148
Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H){η^2-C[Si(SiMe$_3$)$_3$]=NXyl}	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)[Si(SiMe$_3$)$_3$] + CNXyl	149
Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H){η^2-C[CH$_2$Si(SiMe$_3$)$_2$SiMe$_2$H]=NXyl}	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)[CH$_2$Si(SiMe$_3$)$_2$SiMe$_2$H] + CNXyl	149
Cp*Ta(=N^{t}Bu)X[η^2-C(Me)=NR]	R = 2,6-Me$_2$C$_6$H$_3$; X = Me, Cl, OMe, O^{t}Bu, NH^{t}Bu	151
Cp*Ta(=N^{t}Bu)X{η^2-C[(Me)=NR]=NR}	R = 2,6-Me$_2$C$_6$H$_3$, double insertion of CNR; X = Me, Cl (X-ray), OMe, O^{t}Bu, NH^{t}Bu	151
Cp*Ta(=N^{t}Bu)Cl{η^2-C(NH^{t}Bu)=NR}	R = 2,6-Me$_2$C$_6$H$_3$	151
Cp*Ta(X)[η^2-C(Me)=N(Xyl)](=NXyl)	Cp*Ta(=NXyl)(X)Me + CNXyl; Xyl = C$_6$H$_3$-2,6-Me$_2$; X = Me (X-ray), Cl	157
Cp*Ta(Cl)(O)[η^2-C(Me)=N(Xyl)]	Prep: Cp*Ta(=NXyl)Me(Cl) + CO, X-ray	157
Cp*Ta(=N^{t}Bu)(NR$_2$)(η^1-CMe=NXyl)	Prep: Cp*Ta(=N^{t}Bu)(Me)(NR$_2$) + CNXyl; R = Ph, SiMe$_3$	158
Cp*Ta(=N^{t}Bu)(Me)[η^2-C(NMeR)=NXyl]	Prep: Cp*Ta(=N^{t}Bu)(Me)(NMeR) + XylNC; R = H, Me (X-ray)	158
Cp*TaMe(η^2-PhC≡CPh)[η^2-C(Me)=NR]	R = Me, ^{t}Bu	280
Cp*Ta(η^2-C(Me)=NAr)Cl$_3$	Cp*TaCl$_3$Me + CNAr; Ar = C$_6$H$_3$-2,6-Me$_2$, C$_6$H$_2$-2,4,6-Me$_3$	306
Cp*Ta(=NXyl)(R)[η^2-C(R)=N(Xyl)]	Prep: Cp*Ta(=NXyl)R$_2$ + XylNC; R = Et, Pr, CH$_2$SiMe$_3$, CH$_2$CMe$_3$, CH$_2$Ph, Ph	314, 335
Cp*Ta(=NXyl)(Cl)[η^2-C(R)=N(Xyl)]	Prep: Cp*Ta(=NXyl)(R)Cl + XylNC; R = Me (X-ray), Et, Pr, CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$, CH$_2$Ph, C$_6$H$_4$-2-(CH$_2$NMe$_2$), NMe$_2$	314, 335
Cp*Ta(=NXyl)(Me)[η^2-C(R)=N(Xyl)] and Cp*Ta(=NXyl)(R)[η^2-C(Me)=N(Xyl)]	Prep: Cp*Ta(=NXyl)(R)Me + XylNC; R = CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$, CH$_2$Ph, Ph, C$_6$H$_4$-2-(CH$_2$NMe$_2$), NMe$_2$	335
TaCl$_2$(η^2-C(H)(PMe$_2$Ph)NR)(OC$_6$H$_3$-2,6-^{i}Pr$_2$)	Prep: Ta(H)Cl$_2$(PMe$_2$Ph)$_2$(OC$_6$H$_3$-2,6-^{i}Pr$_2$) + RNC C; R = C$_6$H$_3$-2,6-^{i}Pr$_2$, Xyl, ^{t}Bu	337, 338
TaCl$_2$[η^2-C(H)(PMe$_3$)N(C$_6$H$_3$-2,6-^{i}Pr$_2$)](OC$_6$H$_3$-2,6-^{i}Pr$_2$)	X-ray	337, 338
(2,6-^{i}Pr$_2$-C$_6$H$_3$O)$_2$Cl$_2$	X-ray	337, 338
Ta[N(^{t}Bu)C(=C=N^{t}Bu)CH=N(^{t}Bu)]· Cp*Ta(X)(=NXyl)[η^2-N(Xyl)=CCMe$_2$CMe=N(Xyl)]	Prep: Cp*TaX(=NXyl)[N(Xyl)CMe=CMe$_2$] + XylNC; Xyl = C$_6$H$_3$-2,6-Me$_2$; X = Cl, Me (X-ray)	343
[Ta(η^2-C(CH$_2$SiMe$_3$)=NXyl)$_2$(CH$_2$SiMe$_3$)]$_2$(μ-1,4-NC$_6$H$_4$N)	Prep: [Ta(CH$_2$SiMe$_3$)$_3$(CH$_3$CN)]$_2$(μ-1,4-NC$_6$H$_4$N) + 4XylNC	339
(η^1-dmpm)Cl$_2$Ta(μ-NTol)[μ-η^2-C(H)=NTol](μ-dmpm)TaCl(η^2-DTolF)	Prep: Ta(SMe$_2$)$_3$Cl$_6$ + Zn, DMPM + LiDTolF; DMPM = bis(dimethylphosphino)methane; DTolF = di-*p*-tolylformamidinate anion	340
(η^2-DTolF)Cl$_2$Ta(μ-NPh)(μ-η^2-CH=NTol)Ta(η^2-DTolF)$_2$	Prep: Ta(SMe$_2$)$_3$Cl$_6$ + 4LiDTolF; DTolF = di-*p*-tolylformamidinate anion, X-ray	341
Ta(η^2-N(^{t}Bu)=CCH$_2$CHRCH$_2$)(O^{t}Bu)$_2$[C$_6$H$_4$-2-(CH$_2$NMeCH$_2$CH$_2$NMe$_2$)]	Ta(CH$_2$CHRCH$_2$) (O^{t}Bu)$_2$[C$_6$H$_4$-2-(CH$_2$NMeCH$_2$CH$_2$NMe$_2$)] + ^{t}BuNC; R = H, Me, Ph (X-ray)	345
Cp$'_2$Ta{η^2-C[CH$_2$B(C$_6$F$_5$)$_3$]=NR}(Me)	Prep: Cp$'_2$Ta[CH$_2$B(C$_6$F$_5$)$_3$](Me) + RCN; R = ^{t}Bu, Cy, CH$_2$Ph; Cp$'$ = Cp, C$_5$H$_4$Me	336
[Cp$'_2$Ta(η^2-CMe=NR)(Me)][B(C$_6$F$_5$)$_4$]	Prep: [Cp$_2$TaMe$_2$][B(C$_6$F$_5$)$_4$] + RCN; R = ^{t}Bu, Cy, CH$_2$Ph	336

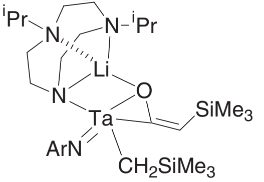
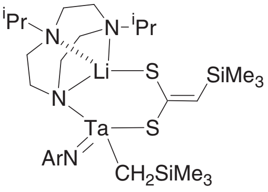
(*Continued*)

Table 14 (Continued)

Compound	*Comments*	*References*
η^2-Imine and related complexes		
$({}^t\mathrm{Bu_3SiO})_2\mathrm{TaR}(\eta^2\text{-}\mathrm{NC_5H_9})$	Prep: thermolysis of $({}^t\mathrm{Bu_3SiO})_2\mathrm{TaMe_2}(\eta^1\text{-}\overline{\mathrm{N(CH_2)_4CH_2}})$	72
$({}^t\mathrm{Bu_3SiO})_2\mathrm{Ta}(\eta^2\text{-}\mathrm{NC_5H_4})(\eta^1\text{-}\mathrm{NR_2})$	Prep: $({}^t\mathrm{Bu_3SiO})_2\mathrm{TaCl_2}(\eta^1\text{-}\mathrm{NR_2})$ + pyridine + Na/Hg; $\mathrm{NR_2} = \overline{\mathrm{N(CH_2)_3CH_2}}$ and $\overline{\mathrm{N(CH_2)_4CH_2}}$	72
$\{[\eta^3\text{-}(\mathrm{Me_2CN})({}^i\mathrm{PrN})\mathrm{C_{10}H_6}]\mathrm{TaCl}\}_2(\mu\text{-}\mathrm{Cl})_2$	Prep: $\mathrm{Me_3TaCl_2} + 1,8\text{-}({}^i\mathrm{PrHN})_2\mathrm{C_{10}H_6}$, X-ray	77
$[\eta^3\text{-}(\mathrm{Me_2CN})({}^i\mathrm{PrN})\mathrm{C_{10}H_6}]\mathrm{TaCl_2(NC_5H_9)}$	Prep: $\{[\eta^3\text{-}(\mathrm{Me_2CN})({}^i\mathrm{PrN})\mathrm{C_{10}H_6}]\mathrm{TaCl}\}_2(\mu\text{-}\mathrm{Cl})_2$ + 2-methylpyrroline, X-ray	77
$[\eta^3\text{-}(\mathrm{Me_2CN})({}^i\mathrm{PrN})\mathrm{C_{10}H_6}]\mathrm{TaClCp^*}$	Prep: $\{[\eta^3\text{-}(\mathrm{Me_2CN})({}^i\mathrm{PrN})\mathrm{C_{10}H_6}]\mathrm{TaCl}\}_2(\mu\text{-}\mathrm{Cl})_2 + \mathrm{LiCp^*}$, X-ray	77
$\mathrm{Ta(NMe_2)}(\eta^2\text{-}\mathrm{ArN{=}CNMe_2})_2[({}^i\mathrm{PrN})_2\mathrm{C{=}N}{}^i\mathrm{Pr}]$	Prep: $\mathrm{Ta(NMe_2)_3}[({}^i\mathrm{PrN})_2\mathrm{C{=}N}{}^i\mathrm{Pr}]$ + 2ArNC, X-ray	94
$\mathrm{Cp^*(SC_6H_7N_2)Me}\ \overline{\mathrm{Ta[N(Xyl)CMe_2C}}\mathrm{({=}NXyl)]}$	$\mathrm{Cp^*TaMe_3(SC_6H_7N_2)}$ + 2 XylNC	112
$\mathrm{Cp^*(SC_6H_7N_2)MeTa}[\eta^2\text{-}\mathrm{CMe_2{=}N}({}^t\mathrm{Bu})]$	$\mathrm{Cp^*TaMe_3(SC_6H_7N_2)} + {}^t\mathrm{BuNC}$	112
$\mathrm{Cp^*TaCl(CH_2SiMe_3)}[\eta^2\text{-}\mathrm{N(Xyl){=}CMe_2}]$	Prep: $\mathrm{Cp^*TaCl(CH_2SiMe_3)}[\eta^2\text{-}\mathrm{N(Xyl){=}CMe_2}] + \mathrm{LiCH_2SiMe_3}$	146
$\mathrm{Cp^*TaCl(C(Me){=}CH_2)({=}NXyl)}$	Prep: thermolysis of $\mathrm{Cp^*TaCl(CH_2SiMe_3)}[\eta^2\text{-}\mathrm{N(Xyl){=}CMe_2}]$	146
$\mathrm{Cp^*Ta}[\eta^2\text{-}\mathrm{N(Xyl){=}CMe_2}][\mathrm{(SCH_2CH_2)_2O}]$	Prep: $\mathrm{Cp^*TaMe_2[(SCH_2CH_2)_2O]}$ + XylNC	148
$\mathrm{Cp^*TaCl_2}[\eta^2\text{-}\mathrm{C(Ar){=}CMe_2}]$	Prep: $\mathrm{Cp^*TaCl_2Me_2}$ + CNAr; Ar = $\mathrm{C_6H_3}$-2,6-$\mathrm{Me_2}$, $\mathrm{C_6H_2}$-2,4,6-$\mathrm{Me_3}$	156, 306, 343
$(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})\mathrm{TaCl_2}[\eta^2\text{-}\mathrm{C(Xyl){=}CMe_2}]$	Prep: $(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})\mathrm{TaCl_2Me_2}$ + CNXyl	146
$\mathrm{Cp^*TaMe_2}[\eta^2\text{-}\mathrm{C(Xyl){=}CMe_2}]$	Prep: $\mathrm{Cp^*TaCl_2}[\eta^2\text{-}\mathrm{C(Xyl){=}CMe_2}]$ + 2MeLi; Xyl = $\mathrm{C_6H_3}$-2,6-$\mathrm{Me_2}$, X-ray	156, 306
$\mathrm{Cp^*Ta(X)(Me)}[\eta^2\text{-}\mathrm{C(Xyl){=}CMe_2}]$	Prep: $\mathrm{Cp^*Ta(X)Me_3}$ + CNXyl; X = Cl, Me; Xyl = $\mathrm{C_6H_3}$-2,6-$\mathrm{Me_2}$	156, 343
$\mathrm{Tp^*Ta}(\eta^2\text{-}\mathrm{CH_2{=}NPh})(\mathrm{CH_2}{}^t\mathrm{Bu})(\mathrm{Cl})$	Prep: $\mathrm{Tp^*Ta({=}CH}{}^t\mathrm{Bu})\mathrm{X_2}$ + KN(Me)Ph, X-ray	161
$\mathrm{Cp'_2Ta}[\eta^2\text{-}\mathrm{N}({}^t\mathrm{Bu})\mathrm{{=}CCH_2B(C_6F_5)_3}](\mathrm{CH_3})$	Prep: $\mathrm{Cp'_2Ta[CH_2B(C_6F_5)_3](CH_3)}$ + *t*BuNC; Cp′ = Cp, $\mathrm{C_5H_4Me}$ (X-ray)	167
$[(\mathrm{Cy_2N})_2\mathrm{ClTa}(\eta^2\text{-}\mathrm{N(C_6H_{10})Cy}]$	Prep: $\mathrm{TaCl_5} + 4\mathrm{Cy_2Li}$, elimination of $\mathrm{Cy_2NH}$, X-ray	194
$\mathrm{Cp^*Ta}[\eta^2\text{-}\mathrm{CH_2{=}N(Me)CH_2}\text{-}o\text{-}\mathrm{C_6H_4}]\mathrm{Cl_2}$	Prep: $\mathrm{Cp^*TaCl_4} + 2\mathrm{Li[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]}$, X-ray	279
$\mathrm{TaCl_3(DME)}[\eta^2\text{-}\mathrm{N(CH_2Ph){=}CHPh}]$	Prep: $\mathrm{TaCl_5}$ + Zn + $\mathrm{PhCH_2N{=}CHPh}$, X-ray	342
(η^2-quinoline)$\mathrm{Ta(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3}$	Prep: $\mathrm{TaCl_2(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3}$($\eta^1$-quinoline) + Na/Hg	344
(η^2-6-methylquinoline)$\mathrm{Ta(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3}$	Prep: $\mathrm{TaCl_2(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3}$($\eta^1$-6-methylquinoline) + Na/Hg	344
(η^2-quinoline)$\mathrm{Ta(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3(PMe_3)}$	Prep: (η^2-quinoline)$\mathrm{Ta(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3 + PMe_3}$	344
(η^2-6-methylquinoline)$\mathrm{Ta(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3(PMe_3)}$	Prep: (η^2-6-methylquinoline)$\mathrm{Ta(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3 + PMe_3}$, X-ray	344
(η^2-6-methylquinoline)$\mathrm{TaCl(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_2}$(ether)	Prep: (η^1-6-methylquinoline)$\mathrm{TaCl_3(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_2}$ + Na/Hg, X-ray Prep: $(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{TaCl(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_2}$ + 6-methylquinoline	344
[3,3,3-(η^2-$\mathrm{N(Cy){=}CNMe_2}$)$_3$-*closo*-3,1,2-$\mathrm{TaC_2B_9H_{11}}$]	Prep: [3,3,3-$\mathrm{(NMe_2)_3}$-*closo*-3,1,2-$\mathrm{TaC_2B_9H_{11}}$] + 3CNCy	346
$\mathrm{(ArO)_2Ta}(\eta^2\text{-}\mathrm{N,C\text{-}C_5H_2N\text{-}2,4,6\text{-}{}^tBu_3})(\mathrm{O}{}^t\mathrm{Bu})$	Prep: $\mathrm{(ArO)_2ClTa}(\eta^2\text{-}\mathrm{N,C\text{-}C_5H_2N\text{-}2,4,6\text{-}{}^tBu_3}) + \mathrm{KO}{}^t\mathrm{Bu}$, X-ray	347
$\mathrm{(ArO)_2Ta}(\eta^2\text{-}\mathrm{N,C\text{-}C_5H_2N\text{-}2,4,6\text{-}{}^tBu_3})(\mathrm{S}{}^t\mathrm{Bu})$	Prep: $\mathrm{(ArO)_2ClTa}(\eta^2\text{-}\mathrm{N,C\text{-}C_5H_2N\text{-}2,4,6\text{-}{}^tBu_3}) + \mathrm{LiS}{}^t\mathrm{Bu}$, X-ray	347
$\mathrm{Cp^*TaCl_2}(\eta^2\text{-}\mathrm{C,N\text{-}ArN{=}CHCH{=}NAr})$	Prep: $\mathrm{Cp^*TaCl_4}$ + $\mathrm{Li_2}$ salt of ArN=CHCH=NAr; Ar = $\mathrm{C_6H_3\text{-}2,6\text{-}{}^iPr_2}$	348
$\mathrm{Cp^*TaCl_2}$(supine-η^2-1-*o*,*o*′-xylyl-4-phenyl-1-aza-1,3-diene)	Prep: $\mathrm{Cp^*TaCl_4}$ + 1-o,o′-xylyl-4-phenyl-1-aza-1,3-diene + Al + cat. $\mathrm{HgCl_2}$	286
$\mathrm{Cp^*TaMe_2}(\eta^2\text{-}\mathrm{C,N\text{-}AD})$	Prep: $\mathrm{Cp^*TaCl_2}$(supine-η^4-AD) + $\mathrm{MgMe_2}$; AD = 1,4-diphenyl-1-aza-1,3-diene, 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene (X-ray)	286, 349

(Continued)

Table 14 (Continued)

Compound	*Comments*	*References*
$Cp^*Ta(CH_2Ph)_2(\eta^2\text{-C,N-AD})$	Prep: $Cp^*TaCl_2(\text{supine-}\eta^4\text{-AD}) + 2(PhCH_2)_2Mg$; AD = 1,4-diphenyl-1-aza-1,3-diene (X-ray), 1-*p*-methoxylphenyl-4-phenyl-1-aza-1,3-butadiene, 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene (X-ray)	349, 350
Other complexes		
	$(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}{}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}{}^iPr_2\text{-TACN}) + CO$, X-ray	109, 110
	Prep: $(Me_3SiCH_2)[(C_6H_3\text{-}2,6\text{-}{}^iPr_2)N{=}]Ta(\mu\text{-}CHSiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}{}^iPr_2\text{-TACN}) + CS_2$	109

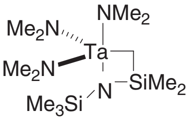
[a] $Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

5.03.6 Metallacyclic Complexes

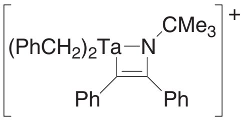
5.03.6.1 Four-membered Metallacycles and Their Heteroatom Derivatives

Four-membered metallacycles are intermediates in the alkene metathesis reaction. By choosing appropriate supporting ligands, tantalacyclobutanes can be isolated. Reaction of $Ta({=}CHSiMe_3)[\eta^2\text{-}C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]Cl(O^tBu)$ with ethylene produces the tantalacyclobutane compound $\overline{Ta[CH(SiMe_3)CH_2CH_2]}[\eta^2\text{-}C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]Cl(O^tBu)$.[257] A metallacyclobutane $\overline{Ta(CH_2CH_2CH_2)}(O^tBu)_2[C_6H_4\text{-}2\text{-}(CH_2NMeCH_2\text{-}CH_2NMe_2)]$ reacts with 1-alkenes such as propene and styrene to give $\overline{Ta(CH_2CHRCH_2)}(O^tBu)_2[C_6H_4\text{-}2\text{-}(CH_2NMeCH_2CH_2NMe_2)]$ (R = Me, Ph) as metathesis products.[345] Carbonylation and isonitrile insertion into these metallacyclobutanes afford ketone and η^2-iminoacyl compounds, respectively.[345]

An azametallacyclobutane has been prepared. Treatment of $(Me_2N)_3TaCl[N(SiMe_3)_2]$ with 1 equiv. of $Li(THF)_2SiPh_2{}^tBu$ leads to the silyl complex, $(Me_2N)_3Ta(SiPh_2{}^tBu)[N(SiMe_3)_2]$, which converts thermally to metallaheterocycle **177**.[351,352] Cationic azametallacyclobutene **178** is prepared and spectroscopically characterized.[353] Complex **178** is thought to be an intermediate of the addition of aniline to diphenylacetylene.[353]



177

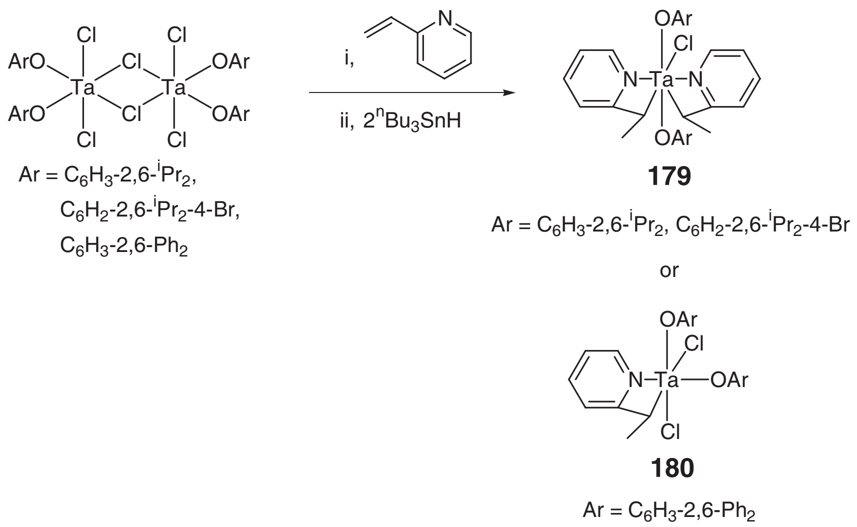


178

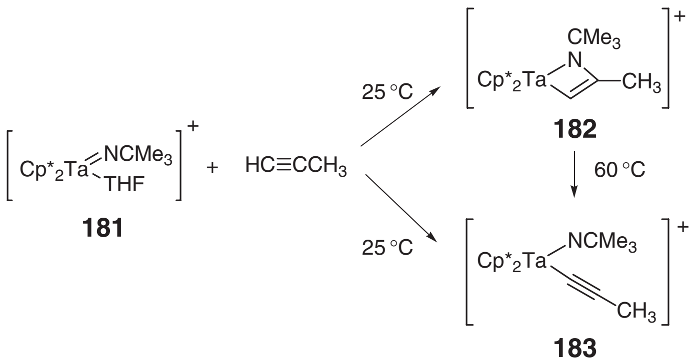
Regioselective insertion of 2-vinylpyridine to *in situ* generated hydride species supported by aryloxo ligands affords pyridyl metallacyclobutenes **179** and **180**[354] (Scheme 64).

Reaction of THF adduct $[Cp^*{}_2Ta({=}NCMe_3)(THF)]$ **181** with propyne gives an initial mixture of the [2 + 2] cycloaddition product **182**, azametallacyclobutene, and the C–H activated propynyl complex **183**[355] (Scheme 65).

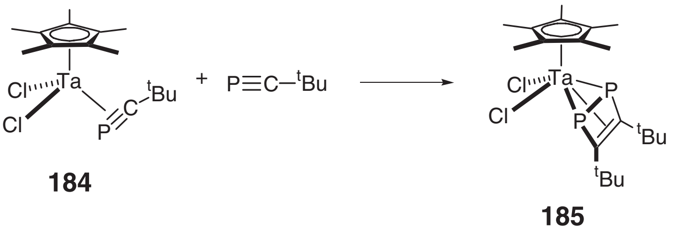
$Cp^*TaCl_2(\eta^2\text{-}{}^tBuC{\equiv}P)$ **184** reacts with $^tBuC{\equiv}P$ to give 1,2-diphosphacyclobutadiene complex, $Cp^*TaCl_2(\eta^1,\eta^1,\eta^2\text{-}1,2\text{-}P_2C_2{}^tBu_2)$ **185** (Scheme 66).[332]



Scheme 64



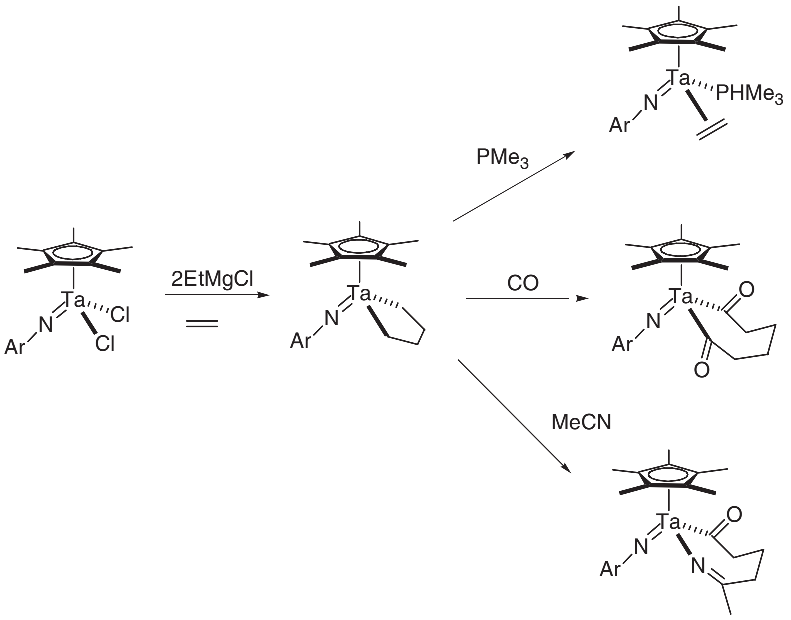
Scheme 65



Scheme 66

5.03.6.2 Five-Membered Metallacycles and Their Heteroatom Derivatives

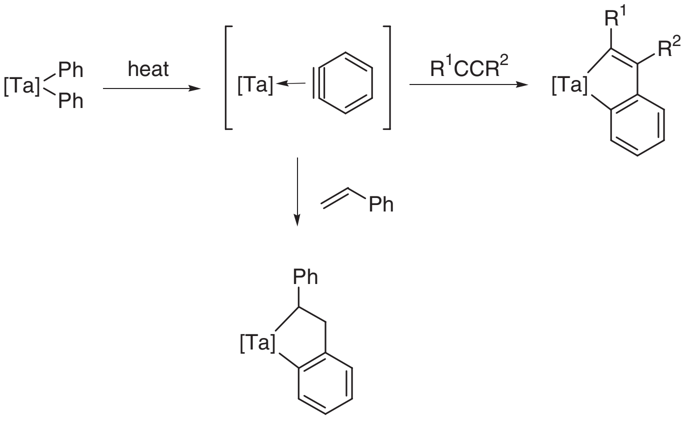
Half-sandwich imido compound Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)Cl$_2$ shows group 4 metallocene-like reactivity. Scheme 67 shows the synthesis of alkene and metallacyclic complexes.[315] Half-sandwich imido compound Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)[Si(SiMe$_3$)$_3$] reacts with ethylene and diphenylacetylene to give tantalacyclopentane and tantalacyclopentadiene through the reductive elimination of HSi(SiMe$_3$)$_3$.[149]



Scheme 67

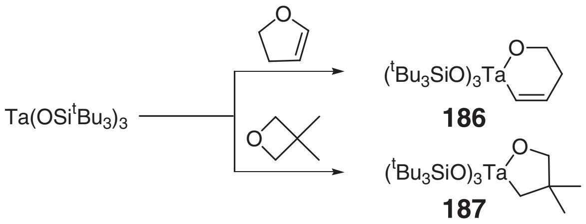
Insertion of alkynes and styrene into Cp(η^5-$Et_2C_2B_4H_4$)$TaPh_2$ gives metallacyclic compounds as shown in Scheme 68 through a nacent benzyne species that can be trapped by the addition of PMe_3 to give Cp(η^5-$Et_2C_2B_4H_4$)Ta(η^2-C_6H_4)(PMe_3),[162] while the photochemical reaction with the dimethyl complex Cp(η^5-$Et_2C_2B_4H_4$)$TaMe_2$ afforded a vinyl–methyl complex, Cp(η^5-$Et_2C_2B_4H_4$)MeTa(C(R)═C(R)Me.[142,356]

Heterometallacycles are derived from the C–O bond fission of cyclic oxa compounds. Reactions of highly reactive $(^tBu_3SiO)_3Ta$ with 1,2-dihydrofuran and 3,3-dimethyloxetane cleanly cleave the C–O bond to give oxametallacycles **186** and **187**, respectively (Scheme 69).[179] Reactions of $(^tBu_3SiO)_3Ta(H)_2$ with ethyl vinyl ketone and acrolein give the hydride $(^tBu_3SiO)_3Ta(H)(OCH(R)CH{=}CH_2)$ (R = H, Et), which at elevated temperature turns to oxatantalacyclopentanes, $(^tBu_3SiO)_3\ \overline{Ta(OCH(R)CH_2CH_2)}$.[99] Double carbonylation of a cationic dimethyl porphyrin compound $[Ta(OEP)Me_2][BPh_4]$ affords 2,5-dixoametallacyclopentene $[Ta(OEP)(OC(Me){=}C(Me)O)][BPh_4]$.[91] Carbonylation of bis(amidinate) trimethyl complex, $[PhC(NSiMe_3)_2]_2Ta(CH_3)_3$ affords a similar compound $[PhC(NSiMe_3)_2]_2$-$Ta(CH_3)(OC(Me){=}C(Me)O)$.[92]

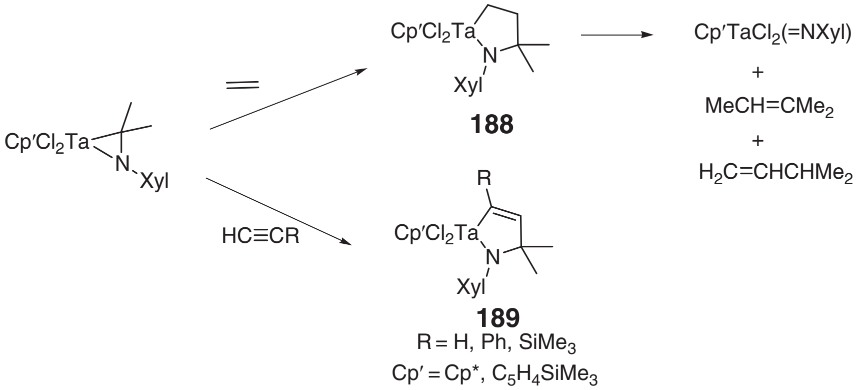


[Ta] = Cp(η^5-$Et_2C_2B_4H_4$)Ta

Scheme 68



Scheme 69

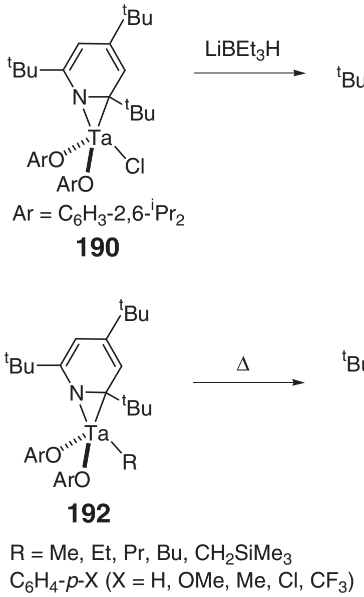


Scheme 70

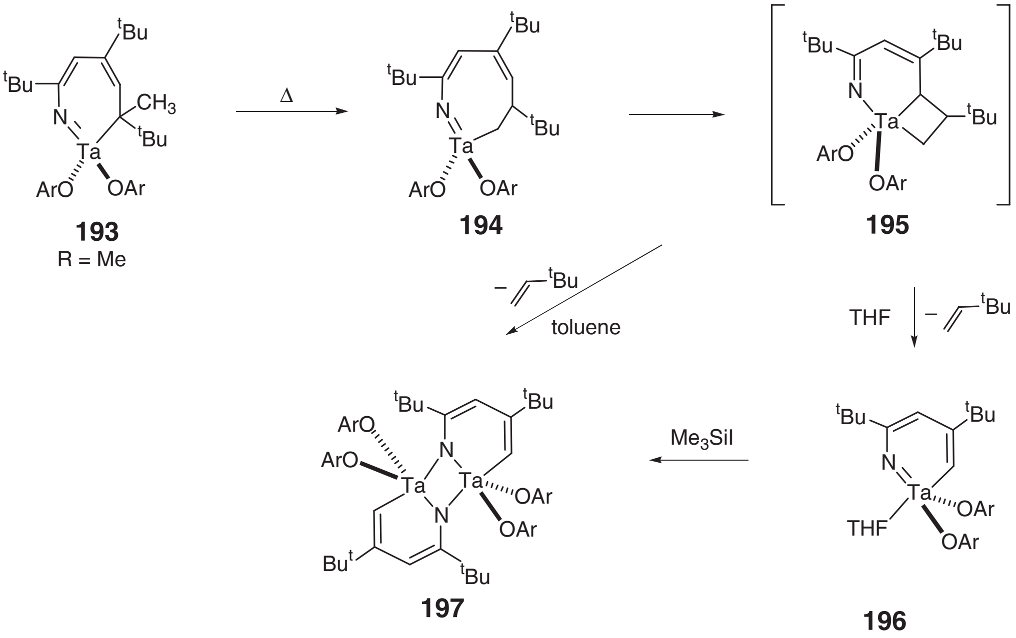
Treatment of Cp′TaCl$_2$[η^2-N(Xyl)═CMe$_2$] (Cp′ = Cp*, η^5-C$_5$H$_4$SiMe$_3$) with ethylene and 1-alkynes gives rise to 188 and 189, respectively (Scheme 70).[146] The azametallacyclopentane 188 decomposes to give Cp′TaCl$_2$(═NXyl).[146]

5.03.6.3 Six-membered or Higher Metallacycles and Their Heteroatom Derivatives

Wigley *et al.* have investigated carbon–nitrogen bond cleavage in an η^2-N,C-pyridine complex, hydride or alkyl addition reaction leading to metallacyclic ompounds with a Ta═N bond as a model of hydrodenitrogenation catalysts.[357] Treatment of η^2-*N,C*-pyridine complex, (ArO)$_2$ClTa(η^2-N,C-C$_5$H$_2$N-2,4,6-^{t}Bu$_3$) 190 (Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$), with LiBEt$_3$H spontaneously affords the C–N bond scission product (ArO)$_2$-$\overline{\mathrm{Ta({=}NC^tBu{=}CHC^tBu{=}CHCH}}\mathrm{^tBu)}$ 191 (Scheme 71).[358] The reactions of 190 with carbon nucleophiles provide the alkyl and aryl derivatives (ArO)$_2$(R)Ta(η^2-N,C-C$_5$H$_2$N-2,4,6-^{t}Bu$_3$) 192, whose thermolysis affords the corresponding C–N bond cleavage compounds (ArO)$_2$ $\overline{\mathrm{Ta[{=}NC^tBu{=}CHC^tBu{=}CHC}}\mathrm{^tBu(R)]}$ 193 (R = Me, Et, Pr, CH$_2$SiMe$_3$, Ph, C$_6$H$_4$-*p*-X) after an intramolecular alkyl or aryl migration from the metal to the imino carbon of the ligand (Scheme 71).[358,359] In the case of methyl complex (ArO)$_2$ $\overline{\mathrm{Ta[{=}NC^tBu{=}CHC^tBu{=}CHC}}\mathrm{^tBu(Me)]}$ (193: R = Me), further decomposition in toluene proceeds to give a dimer of tantalapyridine complex, [(ArO)$_2$]$_2$ $\overline{\mathrm{Ta({=}NC^tBu{=}CHC^tBu{=}CH)}}$]$_2$ 197 involving eight-membered metallacycle 194 and its bicycle intermediate 195 as outlined in Scheme 72.[358] Upon thermolysis of 193 (R = Me) in THF, a monomeric tantalapyridine complex (ArO)$_2$(THF) $\overline{\mathrm{Ta({=}NC^tBu{=}CHC^tBu{=}CH)}}$ 196 is isolated.[360, 361] THF of the monomeric compound 196 can be replaced by pyridine to give a monomeric pyridine adduct, (ArO)$_2$(py)$_2$ $\overline{\mathrm{Ta({=}NC^tBu{=}CHC^tBu{=}CH)}}$, while ^{t}BuNCO and ^{i}PrN═C═N^{i}Pr can insert into the Ta–C bond to form eight-membered metallacyclic compounds, (ArO)$_2$ and (ArO)$_2$ $\overline{\mathrm{Ta[{=}NC^tBu{=}CHC^tBu{=}CHC({=}N^tBu)O]}}$ respectively.[361] Two η^2-*N,C*-pyridine complexes, (ArO)$_2$Ta(η^2-N,C-C$_5$H$_2$N-2,4,6-^{t}Bu$_3$)(O^{t}Bu) $\overline{\mathrm{Ta[{=}NC^tBu{=}CHC^tBu{=}CHC}}\overline{\mathrm{({=}N^iPr)}}\mathrm{N^iPr]}$, and (ArO)$_2$Ta($\eta^2$-N,C-C$_5H_2$N-2,4,6-^{t}Bu$_3$)(S^{t}Bu) are prepared and the S^{t}Bu ligand is a better σ,π-donor overall than OAr or O^{t}Bu.[347]



Scheme 71

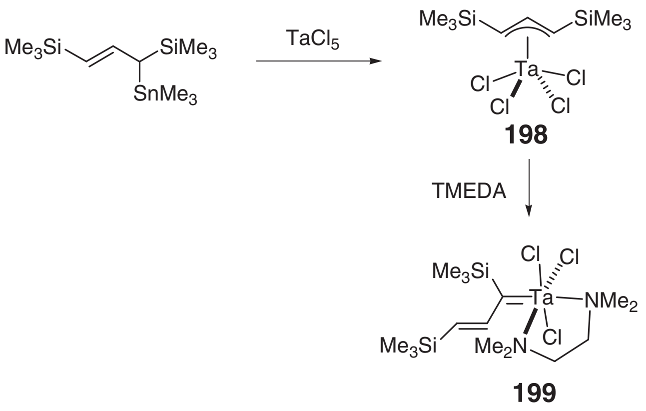


Scheme 72

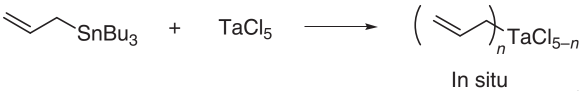
5.03.7 π-Complexes of Carbocyclic Ligands

5.03.7.1 η^3-Complexes

A bis(allyl) complex of tantalum(III), $Cp^*Ta(\eta^3\text{-Ph-1-}C_3H_4)_2$, which exhibits *supine–supine* geometry, is prepared by treating Cp^*TaCl_4 with 4 equiv. of 1-phenylallylMgCl.[37,38] Bis(allyl) complexes $Cp^*(RN{=})Ta(\eta^1\text{-allyl})(\eta^3\text{-allyl})$ [$R = Si(^tBu)_3$ and $C_6H_3\text{-2,6-}^iPr_2$] supported by half-sandwich imido fragments, which are prepared by treating $Cp^*Ta({=}NR)Cl_2$ with 2 equiv. of allylmagnesium bromide, have σ-allyl and π-allyl moieties.[155] Treatment of



Scheme 73



Scheme 74

$\mathrm{Me_3SiCH{=}CHCH(SiMe_3)(SnMe_3)}$ with $\mathrm{TaCl_5}$ produces the allyl compound $\{\eta^3\text{-}\mathrm{C_3H_3(SiMe_3)_2\text{-}1,3}\}\mathrm{TaCl_4}$ 198, to which addition of 2 equiv. of TMEDA afforded a tantalum alkylidene complex, $\mathrm{Me_3SiCH{=}CHC(SiMe_3){=}TaCl_3(TMEDA)}$ 199 as a product of dehydrochlorination by TMEDA (Scheme 73).[301] This is the first example of an allyl-to-alkylidene transformation.

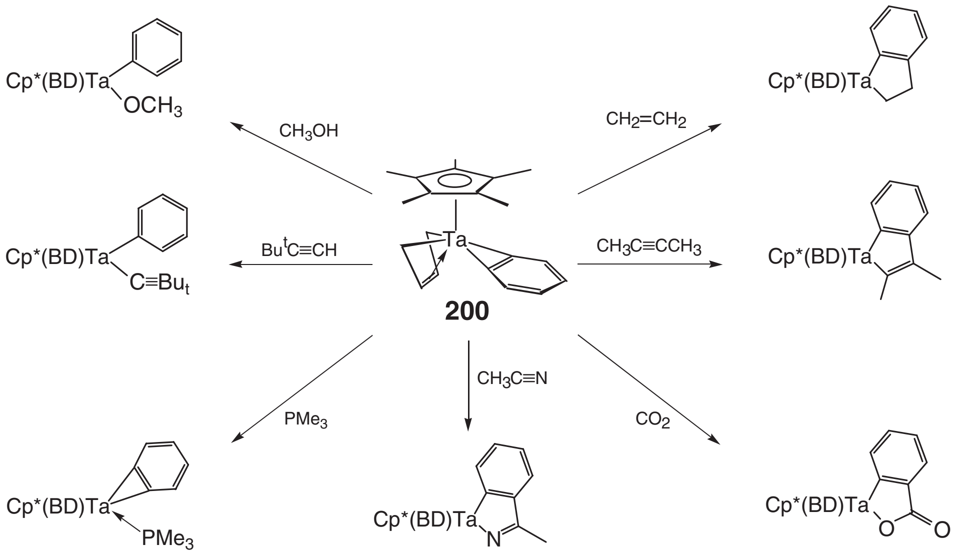
Transmetallation of allyltin compounds with $\mathrm{TaCl_5}$ afforded tantalum allyl species (Scheme 74), which reacted with enones and imines to give the corresponding β-allylated ketones and homoallylamines.[362,363]

5.03.7.2 η^4-Complexes

5.03.7.2.1 η^4-Diene complexes

Coordination modes of mono(butadiene) and bis(butadiene) to half-sandwich fragments of tantalum have been summarized in COMC (1995): tantalum favors the metallacyclopentene structure rather than an *s-cis*-η^4-butadiene structure, and *supine* (exo) and *prone* (endo) geometry as well as *s-trans*-coordination mode have been observed for bis(diene) complexes.[364–367] Since the CpTa(diene) fragment is isoelectronic and isolobal to $\mathrm{Cp_2Hf}$, alkyl,[368,369] ethylene,[370] benzyne,[333] and alkylidene complexes[283,284] together with their catalytic applications are reported.[371–373]

The tantalum–benzyne complex $\mathrm{Cp^*Ta}$(supine-*s-cis*-η^4-butadiene)(η^2-$\mathrm{C_6H_4}$) 200 is prepared by thermolysis (70 °C) of the methyl phenyl complex $\mathrm{Cp^*Ta(Me)(Ph)}$(supine-*s-cis*-η^4-butadiene), which is formed by successive treatments of $\mathrm{Cp^*TaCl_2}$(supine-*s-cis*-η^4-butadiene) with 1 equiv. of PhMgI and 1 equiv. of MeMgI.[333] Scheme 75 shows some reactions of the benzyne compound 200. Ethylene and 2-butyne insert into the tantalum benzyne bond of the benzyne compound to form the metallacycles $\mathrm{Cp^*}$(*supine-s-cis*-η^4-butadiene) $\overline{\mathrm{Ta(C_6H_4CH_2CH_2})}$ and $\mathrm{Cp^*}$(*supine-s-cis*-η^4-butadiene) $\overline{\mathrm{Ta[C_6H_4C(Me){=}C(Me)}}]$, respectively. Acetonitrile and carbon dioxide give $\mathrm{Cp^*}$(*supine-s-cis*-η^4-butadiene) $\overline{\mathrm{Ta[C_6H_4C(Me){=}N}}]$ and $\mathrm{Cp^*}$(*supine-s-cis*-η^4-butadiene) $\overline{\mathrm{Ta[C_6H_4C({=}O)O}}]$, respectively. Protolysis by methanol and 3,3-dimethyl-1-butyne affords phenyl complexes $\mathrm{Cp^*}$(*supine-s-cis*-η^4-butadiene)Ta(OMe)(Ph) and $\mathrm{Cp^*}$(*supine-s-cis*-η^4-butadiene)$\mathrm{Ta(C{\equiv}CCMe_3)(Ph)}$, respectively. Ethylene compounds $\mathrm{Cp'Ta}$(*supine-s-cis*-η^4-butadiene)(η^2-$\mathrm{C_2H_4}$)($\mathrm{PMe_3}$) ($\mathrm{Cp'} = \mathrm{Cp}$, $\mathrm{Cp^*}$) are prepared by the reaction of $\mathrm{Cp'TaCl_2}$(supine-*s-cis*-η^4-butadiene) with 2 equiv. of EtMgI in the presence of $\mathrm{PMe_3}$.[370] Ethylene ligand is labile and carbonylation of CpTa(*supine-s-cis*-η^4-butadiene)(η^2-$\mathrm{C_2H_4}$)($\mathrm{PMe_3}$) produces a mixture of CpTa(*supine-s-cis*-η^4-butadiene) (CO)($\mathrm{PMe_3}$) and CpTa(supine-*s-cis*-η^4-butadiene)$\mathrm{(CO)_2}$.[370]



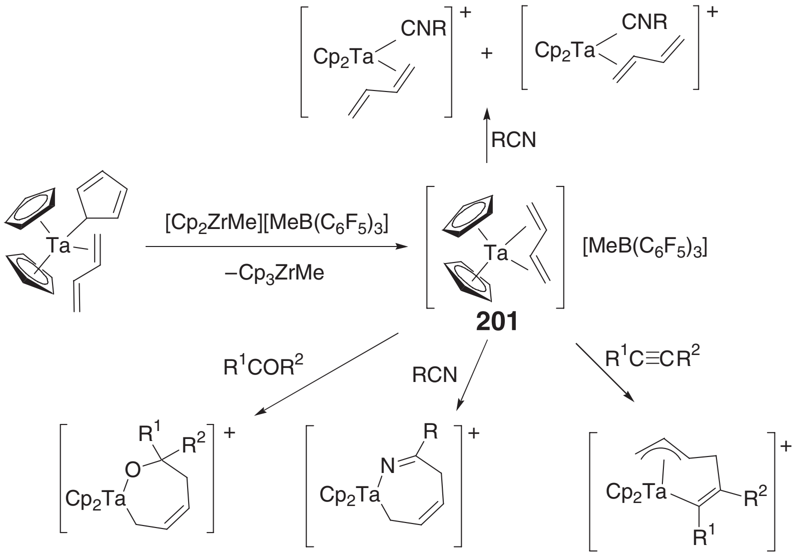
Scheme 75

Bis(butadiene) complexes $Cp'Ta(1,3\text{-butadiene})_2$ ($Cp' = Cp, Cp^*$) have two different diene ligands with *supine* and *prone* geometries. One of two diene ligands is labile. Treatment of bis(butadiene) complex $Cp'Ta$(*s-cis*-η^4-butadiene)$_2$ with ArN=CHCH=NAr (Ar = *p*-$MeOC_6H_4$) affords $Cp'Ta$(*supine-s-cis*-η^4-butadiene)(ArNCH=CHNAr),[374] which can be alternatively prepared by the reaction of $Cp'TaCl_2$(ArNCH=CHNAr) with Mg(1,3-butadiene) adduct.[348] The reaction of CpTa(supine-*s-cis*-η^4-butadiene)$_2$ with 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) gives CpTa(*supine-s-cis*-η^4-butadiene)(OTf)$_2$.[375]

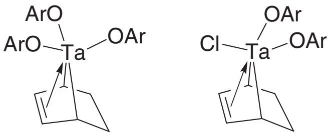
Dichloride and dimethyl complexes $Cp'TaR_2$(supine-*s-cis*-η^4-diene) ($Cp' = Cp$, Cp^*; R = Cl, Me; diene = butadiene, isoprene, 2,3-dimethylbutadiene) as well as bis(diene) complexes $Cp'Ta(\text{diene})_2$ are unique catalyst precursors for a living polymerization of ethylene upon activation by an excess of MAO.[368,369] Monoalkyl and dialkyl compounds of butadiene or *o*-xylylene ligand are prepared by the alkylation of the corresponding dichlorides $Cp'TaCl_2$(supine-*s-cis*-η^4-butadiene) ($Cp' = Cp$, Cp^*) or $Cp^*TaCl_2[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]$. Dibenzyl compounds $Cp'Ta(CH_2Ph)_2$(supine-*s-cis*-η^4-butadiene) and $Cp^*Ta(CH_2Ph)_2[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]$ thermally decompose to give the corresponding benzylidene compounds, which catalyze the ring-opening metathesis polymerization of norbornene.[283,284] Under the thermolysis conditions of $Cp^*Ta(CH_2Ph)_2[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]$, the nascent benzylidene species can be trapped by acenaphthylene to give $Cp^*[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]\ \overline{Ta[CHPhCH(C_{10}H_6)CH]}$.[284] Treatment of Cp^*TaCl_4 with 1 equiv. of *o*-$C_6H_4(CH_2MgCl)_2$ afforded *o*-xylylene complex, $TaCl_2(\eta^4\text{-}o\text{-}(CH_2)_2C_6H_4)Cp^*$,[284] which becomes a catalyst for ethylene polymerization upon activation by MAO.[376]

$Cp'TaCl_2$(*supine-s-cis*-η^4-butadiene) ($Cp' = Cp$, C_5H_4Me, Cp^*) reacts with cyclooctatetraene dianion to give $Cp'Ta$(*supine-s-cis*-η^4-butadiene)(prone-η^3-C_8H_8).[377] Treatment of Cp^*Ta(*supine-s-cis*-η^4-butadiene)(prone-η^3-C_8H_8) with $B(C_6F_5)_3$ gives a unique zwitterion complex, Cp^*Ta(*supine-s-cis*-η^4-butadiene){8-B$(C_6F_5)_3$-η^5-bicyclo[5.1.0]-octadienyl}.[377] Cationic *s-trans*-butadiene compound $[Cp_2Ta$(*s-trans*-η^4-butadiene)$]^+$ **201** is prepared by treating $(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)Ta(\eta^2\text{-butadiene})$ with $(Cp_2ZrMe)^+[CH_3B(C_6F_5)_3]^-$ (Scheme 76).[320] Ketones, nitriles, and alkynes can react with the diene compound **201**, giving seven-membered σ-allyl cyclic compounds and metallacyclic π-allyl compounds, while the reaction with isocyanides gives $[Cp_2Ta(\eta^2\text{-butadiene})(CNR)]^+$.[56,320] Cationic *s-trans*-butadiene compound $[CpCp^*Ta$(*s-trans*-η^4-butadiene)$][CH_3B(C_6F_5)_3]$ is also derived from $CpCp^*Ta(\eta^2\text{-butadiene})Cl$ and shows the same reactivity toward ketones and nitriles.[378] Magnesium butadiene reacted with borollide compound $Cp^*(\eta^5\text{-}C_4H_4B\text{-}N^iPr_2)TaCl_2$ to give $Cp^*(\eta^5\text{-}C_5H_5B\text{-}N^iPr_2)Ta$(*s-trans*-$\eta^4$-butadiene), in which a butadiene moiety coordinates in *s-trans*-mode.[379]

Sodium amalgam reduction of $TaCl_2(OC_6H_3\text{-}2,6\text{-}^iPr_2)_3$ and $TaCl_3(OC_6H_3\text{-}2,6\text{-}^iPr_2)_2$ in the presence of 1,3- or 1,4-hexadiene leads to the corresponding 1,3-cyclohexadiene compounds $Ta(OC_6H_3\text{-}2,6\text{-}^iPr_2)_3(\eta^4\text{-}1,3\text{-}C_6H_8)$ **202** and $TaCl(OC_6H_3\text{-}2,6\text{-}^iPr_2)_2(\eta^4\text{-}1,3\text{-}C_6H_8)$ **203** (Scheme 77).[318,380]



Scheme 76

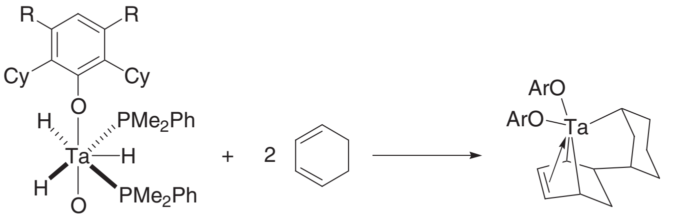


202 **203**

Ar = C_6H_3-2,6-$^iPr_2$

Scheme 77

Various tantalum hydride compounds react with 1,3-cyclohexadiene: the 2,6-dicyclohexyl substituted phenoxo compounds $Ta(H)_3(PMe_2Ph)_2(OC_6H_3\text{-}2,6\text{-}Cy_2)$ and $Ta(H)_3(PMe_2Ph)_2(OC_6H\text{-}2,6\text{-}Cy_2\text{-}3,5\text{-}Ph_2)$ produce the diene coupling products **204** (Scheme 78), while the reaction of dihydride with 1,3-cyclohexadiene results in the C–H activation of isopropyl group of phenoxy ligands, giving an η^2-olefin compound **205** (Scheme 79).[318] Cyclometallated compounds **206** are also formed in the reaction of $TaCl(H)_2(PMe_2Ph)(OC_6H_3\text{-}2,6\text{-}^tBu_2)$ with cyclohexadiene, styrene, and phenylacetylene.[175,318]

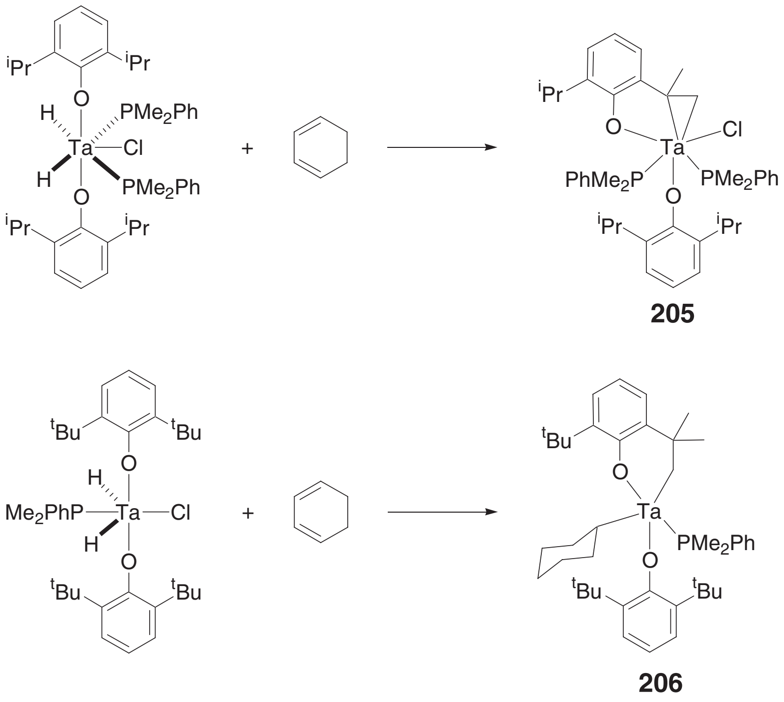


204

Ar = C_6H_3-2,6-Cy_2, C_6H-2,6-Cy_2-3,5-Ph_2

R = H, Ph

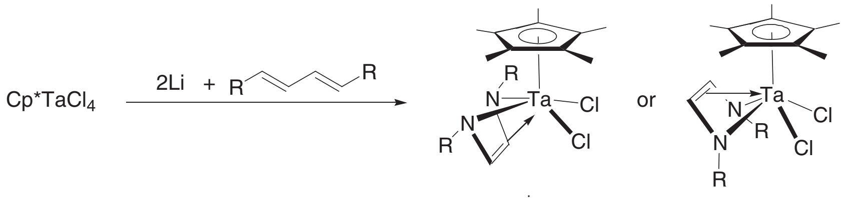
Scheme 78



Scheme 79

5.03.7.3 η^4-Heterodiene Complexes

Supine and prone orientation of 1-aza-1,3-diene and 1,4-diaza-1,3-diene are also observed for half-sandwich tantalum compounds.[365] Reaction of Cp*TaCl$_4$ with the dilithium salts of 1,4-diaza-1,3-butadiene afford the corresponding diazadiene complexes. Depending on the substituents at the nitrogen atoms and tantalum center, supine **207** and prone **208** compounds are obtained (Scheme 80).[129,348,374] In the case of bulky substituted DAD ligand, an η^2-imine complex Cp*TaCl$_2$(η^2-C,N-ArN═CHCHNAr) (Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$) is isolated.[348] Treatment of the dichloro compounds Cp*TaCl$_2$(supine-*s-cis*-η^4-RN═CHCH═NR) (R = *p*-MeO-C6H4, *o*-Tol, Cy) with MgMe$_2$ or Mg(CH$_2$Ph)$_2$ produces the corresponding dialkyl compounds Cp*Ta(CH$_2$R^1)$_2$(prone-*s-cis*-η^4-RN═CHCH═NR) (R^1 = H, Ph), while the monoalkylation maintains the supine geometry.[348] Thermolysis of bis(benzyl) complex Cp*Ta(CH$_2$Ph)$_2$(prone-*s-cis*-η^4-RN═CHCH═NR) (R = *p*-MeO-C6H4, Cy) provides the benzylidene complexes, Cp*Ta(═CH$_2$Ph)(prone-*s-cis*-η^4-RN═CHCH═NR), with the *anti*-geometry around the Ta═CHPh moiety.[348] Theoretical study of the bonding mode of 1,4-diaza-1,3-butadiene ligand bound to a "CpTaCl$_2$" fragment shows that the donation of DAD ligand is dominated by the nitrogen atoms and the interaction between the tantalum center and the carbon atoms of the ligand is not significant.[381] The reaction of the dilithium salt of *o*-C$_6$H$_4$(NSi^{i}Pr$_3$)$_2$ with



Scheme 80

$\mathrm{Cp^*TaCl_4}$ affords $\mathrm{Cp^*TaCl_2[C_6H_4(NSi^iPr_3)_2\text{-}1,2]}$.[382] A similar reaction of $\mathrm{Li_2[C_6H_4(NSiMe_3)_2\text{-}1,2]}$ with $\mathrm{Cp''TaCl_4}$ ($\mathrm{Cp''=C_5H_3(SiMe_3)_2\text{-}1,3}$) affords $\mathrm{Cp''TaCl_2[C_6H_4(NSiMe_3)_2\text{-}1,2]}$.[383] Anionic compound $\mathrm{Li[Ta(^tBuN{=}CHCH{=}N^tBu)_3]}$ is prepared by treating $\mathrm{TaCl_5}$ with 3 equiv. of $\mathrm{[Li(OEt_2)]_2[^tBuN{=}CHCH{=}N^tBu]}$.[384]

Half-sandwich 1-aza-1,3-diene complexes of tantalum, $\mathrm{Cp^*TaCl_2}$(supine-η^4-AD) (AD = 1,4-diphenyl-1-aza-1,3-diene, 1-*p*-methoxylphenyl-4-phenyl-1-aza-1,3-butadiene, 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene), are prepared by treating $\mathrm{[Cp^*TaCl_2]_2}$ with the corresponding AD ligands.[286,349] Dimethyl compound $\mathrm{Cp^*TaMe_2}$(supine-η^4-1,4-diphenyl-1-aza-1,3-diene) is readily prepared by the reaction of the dichlorides with $\mathrm{Mg(CH_3)_2}$, while the reaction with $\mathrm{Mg(CH_2Ph)_2}$ is more complicated. Reaction with $\mathrm{Mg(CH_2Ph)_2}$ produces two compounds, $\mathrm{Cp^*Ta(CH_2Ph)_2}$($\eta^2$-C,N-AD) and $\mathrm{Cp^*(CH_2Ph)\,\overline{Ta[{=}CPhCH{=}C}HNPh]}$.[286,349] Reaction of $\mathrm{Cp^*Ta(CH_2Ph)_2}$(supine-$\eta^4$-AD) (AD = 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene) with Mg(butadiene) affords $\mathrm{Cp^*Ta}$(supine-η^4-butadiene)(η^2-C,N-AD).[286] Intramolecular coupling reaction of η^2-azadiene ligand and iminoacyl moiety, which is derived from the insertion of XylNC to $\mathrm{Cp^*Ta(CH_2Ph)_2}$($\eta^2$-C,N-AD) (AD = 1,4-diphenyl-1-aza-1,3-diene, 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene), results in the formation of an amido–imide compound $\mathrm{Cp^*Ta({=}NAr)\{N(Xyl)C(CH_2Ph){=}CHCH{=}CHPh\}(CH_2Ph)}$.[350]

Addition of 1,4-diisopropyl-1,4-diazabuta-1,3-diene to the *in situ* generated Ta(0) species by treating $\mathrm{TaCl_5}$ with 5 equiv. of Na/naphthalene in 1,2-dimethoxyethane affords 17-electron Ta(1,4-$^i\mathrm{Pr_2}$-1,4-diazabuta-1,3-diene)$_3$, which can be oxidized by adding $\mathrm{AgBPh_4}$ to give 16-electron [Ta(1,4-$^i\mathrm{Pr_2}$-1,4-diazabuta-1,3-diene)$_3$][$\mathrm{BPh_4}$], though both complexes contain three planar diazadiene ligands with diazametallacyclopentene structure.[385]

Polymerization of MMA is catalyzed by bis(butadiene) compounds $\mathrm{Cp'Ta}$(η^4-1,3-butadiene)$_2$ ($\mathrm{Cp'=Cp, Cp^*}$) in the presence of co-catalyst $\mathrm{AlMe(OC_6H_2\text{-}2,6\text{-}(^tBu)2\text{-}4\text{-}Me)_2}$.[386] Methyl methacrylate can coordinate in an η^4-fashion to the tantalum center. Treatment of $\mathrm{[Cp^*TaCl_2]_2}$ with MMA affords MMA complex $\mathrm{Cp^*TaCl2}$(supine-η^4-MMA), which further reacts with the dilithium salt of RN=CHCH=NR (R = Cy, *p*-$\mathrm{MeOC_6H_4}$) to give $\mathrm{Cp^*Ta}$(supine-η^4-MMA)(η^2-RN=CHCH=NR).[387] These MMA compounds upon activated by $\mathrm{AlR_3}$ become catalysts for a living polymerization of MMA.[387]

5.03.7.3.1 Other η^4-ligands

Ellis has succeeded in the preparation of tris(η^4-naphthalene)- and tris(1-4-η^4-anthracene)tantalite(−1), which are the first homoleptic complexes and highly pyrophoric.[6] Anthracene complexes $\mathrm{Cp^*TaCl_2}$(1-4-η^4-anthracene) and $\mathrm{Cp^*Ta(CH_2Ph)_2}$(1-4-$\eta^4$-anthracene) are reported to have a supine geometry with the coordination of 1–4 positions of anthracene to the tantalum center.[388] Trimethylenemethane can coordinate in an η^4-fashion to tantalum. Treatment of $\mathrm{TaCl_2Me_3}$ with the dilithium salt of tribenzylidenemethane affords $\mathrm{(TBM)TaMe_3}$ (TBM = tribenzylidenemethane), which is treated with $\mathrm{ZnCl_2}$ to give $\mathrm{(TBM)TaMe_2Cl}$ **209**.[389] Treatment of **209** with $\mathrm{Li(C_5R_5)}$ (R = H, Me) produces (η^5-$\mathrm{C_5R_5}$)(TBM)$\mathrm{TaMe_2}$.[389,390] Reaction of **209** with a lithium salt of boratabenzene $\mathrm{Li[C_5H_5B\text{-}NMe_2]}$ gives (η^4-TBM)(η^5-$\mathrm{C_5H_5B\text{-}NMe_2}$)$\mathrm{TaMe_2}$, which has a metallocene-like coordination environment.[379]

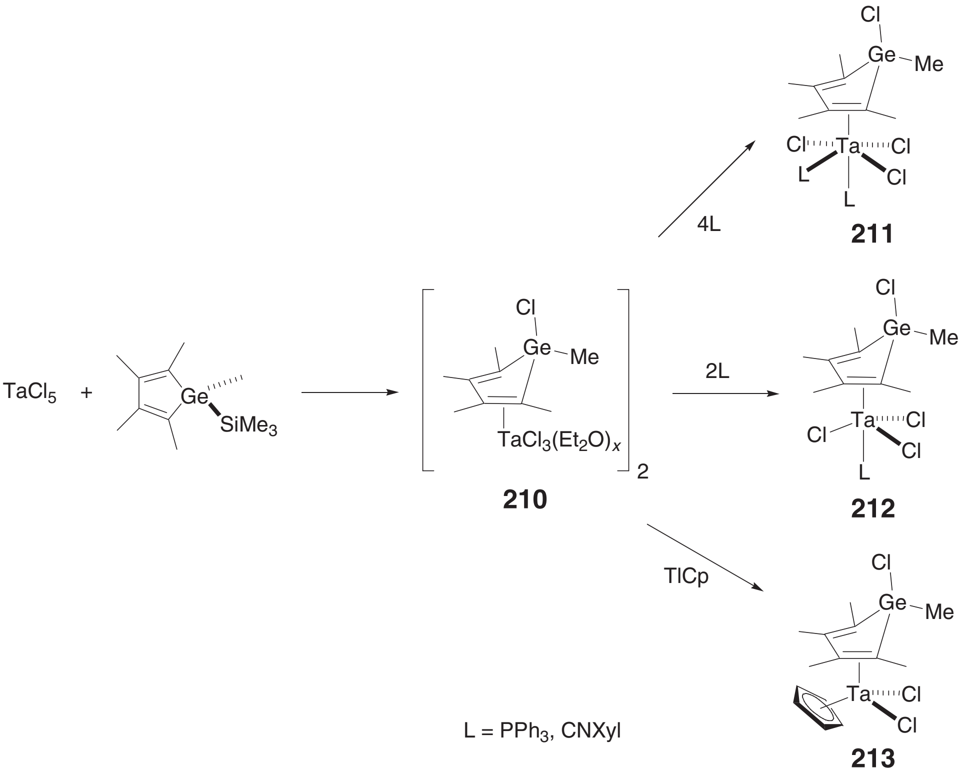
Germole can coordinate in an η^4-fashion to tantalum: reaction of $\mathrm{TaCl_5}$ with $\mathrm{C_4Me_4Ge(Me)(SiMe_3)}$ in dichloromethane results in the immediate formation of $\{[\eta^4\text{-}\mathrm{C_4Me_4Ge(Me)(Cl)]TaCl_3(Et_2O)_{\mathit{x}}}\}_2$ **210**.[391] Addition of two electron donor molecules to **210** gives stable adducts $[\eta^4\text{-}\mathrm{C_4Me_4Ge(Me)(Cl)]TaCl_3(L)}$ **211** and $[\eta^4\text{-}\mathrm{C_4Me_4Ge(Me)(Cl)]TaCl_3(L)_2}$ **212** (L = $\mathrm{PPh_3}$, CNXyl).[391] Addition of TlCp to **210** affords $\mathrm{Cp}[\eta^4\text{-}\mathrm{C_4Me_4Ge(Me)(Cl)]TaCl_2}$ **213**[391] (Scheme 81).

The C–H activation of methyl group of $\mathrm{Cp^*}$ proceeds in the reaction of $\mathrm{Cp^*TaCl_4}$ with 3 equiv. of KCB (CB = carbazole) to give (η^1:η^3-$\mathrm{CH_2C_5Me_4}$)Ta(X)(CB)$_2$, which can be alkylated by $\mathrm{PhCH_2MgCl}$ and $\mathrm{Me_3SiCH_2Li}$, giving (η^1:η^3-$\mathrm{CH_2C_5Me_4}$)$\mathrm{Ta(CH_2R)(CB)_2}$ (R = Ph, $\mathrm{SiMe_3}$).[392] Both chloride and alkylated compounds adopt the bonding as η^1:η^3-$\mathrm{CH_2C_5Me_4}$ (Table 15).[392]

5.03.7.4 η^5-Complexes

5.03.7.4.1 Mono(cyclopentadienyl) complexes

Half-sandwich trichloride compounds (η^5-$\mathrm{C_5R_5}$)$\mathrm{TaCl_4}$ (R = H, Me) are versatile starting materials. The most convenient synthetic method is the reaction between cyclopentadienyltrimethylsilane and $\mathrm{TaCl_5}$ in dichloromethane. Bis(pentafluorophenyl)borylsubstituted cyclopentadiene ligand can also be introduced by this method.[394] Phosphine adducts [*rac*-$\mathrm{Fe(C_5H_4)CMe_2P(H)(R)](Cp^*TaCl_4)_2}$ and $\mathrm{Cp^*TaCl_4(PH_2R)}$ (R = ^{t}Bu, Ad, Cy, Ph, Mes) of $\mathrm{Cp^*TaCl_4}$ are reported.[395,396] Reduction of $\mathrm{Cp^*TaCl_4(PH_2R)}$ with 1,8-diazabicyclo[5.4.0]undec-7-ene (= DBU) produces a Ta(IV) compound $\mathrm{[Cp^*TaCl_4][H(DBU)]}$.[397] Addition of donors to $\mathrm{Cp^*TaCl_4}$ gives $\mathrm{Cp^*TaCl_4(L)}$ (L = $\mathrm{CNC_6H_3\text{-}2,6\text{-}Me_2}$, CN $\mathrm{C_6H_2\text{-}2,4,6\text{-}Me_3}$, ^{t}BuNC, $\mathrm{PhNH_2}$).[398] Amalgam reduction of $\mathrm{Cp^*TaCl_4(CNC_6H_3\text{-}2,6\text{-}Me_2)}$ affords



Scheme 81

Table 15 η^3-Allyl and η^4-diene and related complexes[a]

Compound	*Comments*	*References*
η^3-Allyl complexes		
$Cp^*Ta(\eta^3\text{-Ph-l-}C_3H_4)_2$	Prep: $Cp^*TaCl_4 + 4$ 1-phenylallylMgCl, X-ray	37,38
$\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-1,3}\}TaCl_4$	Prep: $Me_3SiCH{=}CHCH(SiMe_3)$-$(SnMe_3) + TaCl_5$	301
$Cp^*(RN{=})Ta(\eta^1\text{-allyl})(\eta^3\text{-allyl})$	Prep: $Cp^*Ta({=}NR)Cl_2 + 2$allylmagnesium bromide; $R = Si(^tBu)_3$ (X-ray) and $C_6H_3\text{-2,6-}^tPr_2$	155
$Ta(\eta^3\text{-allyl})_2\{p\text{-R-calix[4]arene-OMe}\}$	Prep: $TaCl_2\{p\text{-R-calix[4]arene-OMe}\} + 2$-allylMgCl	73
η^4-Diene complexes		
$Cp^*Ta(\eta^4\text{-butadiene})(CH_2Ph)_2$	Prep: $Cp^*Ta(\eta^4\text{-butadiene})Cl_2 + 2PhCH_2MgCl$, X-ray	283
$Cp'Ta(\textit{supine-s-cis-}\eta^4\text{-butadiene})(\text{prone-}\eta^3\text{-}C_8H_8)$	$Cp'TaCl_2(\textit{supine-s-cis-}\eta^4\text{-butadiene})(Cp' = Cp$, C_5H_4Me, $Cp^*) +$ cyclooctatetraene dianion	377
$Cp^*Ta(\textit{supine-s-cis-}\eta^4\text{-butadiene})\{8\text{-}B(C_6F_5)_3\text{-h 5-bicyclo[5.1.0]octadienyl}\}$	Prep: $Cp^*Ta(\textit{supine-s-cis-}\eta^4\text{-butadiene})(\text{prone-}\eta^3\text{-}C_8H_8) + B(C_6F_5)_3$	377
$[Cp_2Ta(\textit{s-trans-}\eta^4\text{-butadiene})][CH_3B(C_6F_5)_3]$	Prep: $(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)Ta(\eta^2\text{-butadiene}) + (Cp_2ZrMe)^+[CH_3B(C_6F_5)_3]^-$, X-ray	320
$[CpCp^*Ta(\textit{s-trans-}\eta^4\text{-butadiene})][CH_3B(C_6F_5)_3]$	Prep: $CpCp^*Ta(\eta^2\text{-butadiene})Cl + (Cp_2ZrMe)^+[CH_3B(C_6F_5)_3]^-$, X-ray	378

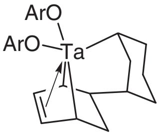
(Continued)

Table 15 (Continued)

Compound	*Comments*	*References*
CpTa(*supine-s-cis*-η^4-butadiene)(OTf)$_2$	Prep: CpTa(*s-cis*-η^4-butadiene)$_2$ + 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate)	375
Cp$'$Ta(*supine-s-cis*-η^4-butadiene)(ArNCH=CHNAr)	Prep: Cp$'$Ta(*s-cis*-η^4-butadiene)$_2$ + ArN=CHCH=NAr or Cp$'$TaCl$_2$(*s-cis*-η^4-ArN=CHCH=NAr)$_2$ + Mg(butadiene); Cp$'$ = Cp, Cp*; Ar = *p*-MeOC$_6$H$_4$ (X-ray for Cp), Cy(X-ray for Cp*), *p*-Tol	348,374
Cp$'$Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_2$H$_4$)(PMe$_3$)	Prep: Cp$'$TaCl$_2$(supine-*s-cis*-η^4-butadiene) + 2EtMgI + PMe$_3$; Cp$'$ = Cp, Cp*	370
CpTa(supine-*s-cis*-η^4-butadiene)(CO)(PMe$_3$) + CpTa(supine-*s-cis*-η^4-butadiene)(CO)$_2$	Prep: CpTa(supine-*s-cis*-η^4-butadiene)(η^2-C$_2$H$_4$)(PMe$_3$) + CO	370
CpTa(supine-*s-cis*-η^4-butadiene)(2-PhCCPh))(PMe$_3$)	Prep: CpTa(supine-s-cis-η^4-butadiene)(η^2-C$_2$H$_4$)(PMe$_3$) + diphenylacetylene	370
Cp$'$TaMe$_2$(supine-*s-cis*-η^4-butadiene)	Prep: Cp$'$TaCl$_2$(supine-*s-cis*-η^4-butadiene) + 2MeMgI; Cp$'$ = Cp, Cp*	368, 369
Cp$'$TaMe$_2$(supine-*s-cis*-η^4-isoprene)	Prep: Cp$'$TaCl$_2$(supine-*s-cis*-η^4-isoprene) + 2MeMgI, Cp$'$ = Cp, Cp*	368, 369
Cp$'$TaMe$_2$(supine-*s-cis*-η^4-2,3-dimethylbutadiene)	Prep: Cp$'$TaCl$_2$(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + 2MeMgI; Cp$'$ = Cp, Cp*	368, 369
Cp*TaMe(OTf)(supine-*s-cis*-η^4-isoprene)	Prep: Cp$'$TaMe$_2$(supine-*s-cis*-η^4-isoprene) + TfOH, X-ray	369
Cp*Ta(Me)(Ph)(supine-*s-cis*-η^4-butadiene)	Prep: Cp*TaCl$_2$(supine-*s-cis*-η^4-butadiene) + PhMgI + MeMgI	333
Cp*TaCl(Ph)(supine-*s-cis*-η^4-butadiene)	Prep: Cp*TaCl$_2$(supine-*s-cis*-η^4-butadiene) + PhMgI	333
Cp*Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_6$H$_4$)	Prep: thermolysis (70 °C) of Cp*Ta(Me)(Ph)-(supine-*s-cis*-η^4-butadiene), X-ray	333
Cp*(supine-*s-cis*-η^4-butadiene)$\mathrm{Ta\overline{(C_6H_4CH_2CH_2}})$	Prep: Cp*Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_6$H$_4$) + ethylene	333
Cp*(*supine*-s-*cis*-η^4-butadiene) $\mathrm{Ta\overline{[C_6H_4C(Me){=}C(Me)}]}$	Prep: Cp*Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_6$H$_4$) + 2-butyne, X-ray	333
Cp*(*supine-s-cis*-η^4-butadiene) $\mathrm{Ta\overline{[C_6H_4C(Me){=}N}]}$	Prep: Cp*Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_6$H$_4$) + CH$_3$CN, X-ray	333
Cp*(*supine-s-cis*-η^4-butadiene) $\mathrm{Ta\overline{[C_6H_4C({=}O)O}]}$	Prep: Cp*Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_6$H$_4$) + CO$_2$	333
Cp*(*supine-s-cis*-η^4-butadiene)Ta(OMe)(Ph)	Prep: Cp*Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_6$H$_4$) + methanol, X-ray	333
Cp*(*supine-s-cis*-η^4-butadiene)Ta(C≡CCMe$_3$)(Ph)	Prep: Cp*Ta(supine-*s-cis*-η^4-butadiene)(η^2-C$_6$H$_4$) + 3,3-dimethyl-1-butyne, X-ray	333
Cp$'$Ta(CH$_2$Ph)$_2$(supine-*s-cis*-η^4-butadiene)	Prep: Cp$'$TaCl$_2$(supine-*s-cis*-η^4-butadiene) + 2PhCH$_2$MgCl; Cp$'$ = Cp, Cp* (X-ray)	283, 284
CpTa(CH$_2$Ph)$_2$(supine-*s-cis*-η^4-2,3-dimethylbutadiene)	Prep: CpTaCl$_2$(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + 2PhCH$_2$MgCl	285
Cp*(supine-*s-cis*-η^4-2,3-dimethylbutadiene) $\mathrm{Ta\overline{[CHPhCH_2CH_2}]}$	Prep: Cp*Ta(=CHPh)(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + C$_2$H$_4$	285
Cp*(supine-*s-cis*-η^4-2,3-dimethylbutadiene) $\mathrm{Ta\overline{[CHPhCH(C_3H_6)CH}]}$	Prep: Cp*Ta(=CHPh)(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + cyclopentene	285
Cp*Ta[=NC(CMe$_3$)=CHPh](supine-*s-cis*-η^4-2,3-dimethylbutadiene)	Prep: Cp*Ta(=CHPh)(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + Me$_3$CCN, X-ray	285
Cp*Ta(CH$_2$Ph)(OMe)(supine-*s-cis*-η^4-2,3-dimethylbutadiene)	Prep: Cp*Ta(=CHPh)(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + MeOH	285

(Continued)

Table 15 (Continued)

Compound	*Comments*	*References*
$Cp^*Ta(CH_2Ph)(NHC_6H_4$-4-OMe)(supine-*s-cis*-η^4-2,3-dimethylbutadiene)	Prep: $Cp^*Ta({=}CHPh)$(supine-*s-cis*-η^4-2,3-dimethylbutadiene) + *p*-methoxyaniline, X-ray	285
$Cp^*Ta(CH_2Ph)({=}NC_6H_4$-4-OMe)(h^1-2,3-dimethyl-2-butene)	Prep: thermolysis of $Cp^*Ta(CH_2Ph)(NHC_6H_4$-4-OMe)(supine-*s-cis*-η^4-2,3-dimethylbutadiene), X-ray	285
$Cp^*TaCl(CH_2EMe_3)$(supine-*s-cis*-η^4-butadiene)	Prep: Cp^*TaCl_2(supine-*s-cis*-η^4-butadiene) + Me_3ECH_2MgCl; E = C, Si	284
$Cp^*Ta(Me)(CH_2EMe_3)$(supine-*s-cis*-η^4-butadiene)	Prep: Cp^*TaCl_2(supine-*s-cis*-η^4-butadiene) + MeMgI; E = C, Si	284
$Cp^*TaCl_2[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]$	Prep: Cp^*TaCl_4 + 1,2-$C_6H_4(CH_2MgCl)_2$, X-ray	284
$Cp^*Ta(CH_2Ph)_2[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]$	Prep: $Cp^*TaCl_2[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]$ + $2PhCH_2MgCl$	284
$Cp^*[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]\ \overline{\text{Ta[CHPhCH(C}_{10}\text{H}_6\text{)CH]}}$	Prep: $Cp^*Ta({=}CHPh)[\eta^4\text{-}C_6H_4(CH_2)_2\text{-}1,2]$ + acenaphthylene, X-ray	284
Cp^*Ta(supine-η^4-butadiene)(η^2-C,N-AD)	Prep: $Cp^*Ta(CH_2Ph)_2$(supine-η^4-AD) + Mg(butadiene); AD = 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene	286
$Cp^*(\eta^5\text{-}C_5H_5B\text{-}N^iPr_2)Ta$(*s-trans*-butadiene)	Prep: $Cp^*(\eta^5\text{-}C_5H_5B\text{-}N^iPr_2)TaCl_2$ + $(C_4H_6)Mg$, X-ray	379
$\{[Ph_2C(C_4H_3N)_2]Ta[(1,4\text{-}\eta^1;\eta^1\text{-}2,3\text{-}\eta^2\text{-}C_6H_7)(Ph)C(C_4H_3N)_2]\}^-$	Prep: $\{[Ph_2C(C_4H_3N)_2]_2TaMe_2\}^-$ + $NaHBEt_3$, X-ray	80
$Ta(\eta^4\text{-}1,3\text{-}C_6H_8)$\{*p*-R-calix[4]arene-OMe\}	Prep: $TaCl_2$\{*p*-R-calix[4]arene-OMe\} + $Mg(C_4H_6)$	73
$Ta(OC_6H_3\text{-}2,6\text{-}^iPr_2)_3(\eta^4\text{-}1,3\text{-}C_6H_8)$	Prep: $TaCl_2(OC_6H_3\text{-}2,6\text{-}^iPr_2)_3$ + Na/Hg + 1,3- or 1,4-hexadiene	318, 380
$TaCl(OC_6H_3\text{-}2,6\text{-}^iPr_2)_2(\eta^4\text{-}1,3\text{-}C_6H_8)$	Prep: $TaCl_3(OC_6H_3\text{-}2,6\text{-}^iPr_2)_2$ + Na/Hg + 1,3-hexadiene	318
	Prep: $Ta(H)_3(PMe_2Ph)_2(OAr)_2$ + 1,3-cyclohexadiene; Ar = C_6H-2,6-Cy_2-3,5-R_2; R = H (X-ray), Ph	318
η^4-Heterodiene complexes		
Cp^*TaCl_2(η^4-*supine*-$^iPrN{=}CHCH{=}N^iPr$)	Prep: Cp^*TaCl_4 + Li_2 salt of $^iPrN{=}CHCH{=}N^iPr$, X-ray	129
Cp^*TaCl_2(η^4-*prone*-$^tBuN{=}CHCH{=}N^tBu$)	Prep: Cp^*TaCl_4 + Li_2 salt of $^tBuN{=}CHCH{=}N^tBu$	129
$Cp'TaCl_2$(η^4-*supine*-RN=CHCH=NR)	Prep: Cp^1TaCl_4 + Li_2 salt of RN=CHCH=NR, Cp′ = Cp, Cp^*; R = Cy, *p*-MeO—C_6H_4 (X-ray for Cp), *p*-Tol, *o*-Tol	348, 374
$Cp^*Ta(CH_2R^1)_2$(prone-*s-cis*-η^4-RN=CHCH=NR)	Prep: Cp^*TaCl_2(supine-*s-cis*-η^4-RN=CHCH=NR) + $Mg(CH_2R^1)_2$; R = *p*-MeO—C_6H_4 (X-ray for R^1 = H), *o*-Tol, Cy (X-ray for R^1 = Ph); R^1 = H, Ph	348
$Cp^*TaCl(CH_2Ph)$(supine-*s-cis*-η^4-RN=CHCH=NR)	Prep: Cp^*TaCl_2(supine-*s-cis*-η^4-RN=CHCH=NR) + 1/2 $Mg(CH_2Ph)_2$; R = *o*-Tol, X-ray	348
$Cp^*Ta({=}CHPh)$(prone-*s-cis*-η^4-RN=CHCH=NR)	Prep: thermolysis of $Cp^*Ta(CH_2Ph)_2$(prone-*s-cis*-η^4-RN=CHCH=NR); R = *p*-MeO—C_6H_4, Cy	348
$Cp^*Ta(S^tBu)_2(\eta^2\text{-C,N-}^tBuN{=}CHCH{=}N^tBu)$	Prep: Cp^*TaCl_2(η^4-*prone*-$^tBuN{=}CHCH{=}N^tBu$) + $2LiS^tBu$	129
$Cp^*Ta({=}S)$(η^4-*prone*-$^tBuN{=}CHCH{=}N^tBu$)		129
$Cp''TaCl_2[C_6H_4(NSiMe_3)_2\text{-}1,2]$	Prep: $Li_2[C_6H_4(NSiMe_3)_2\text{-}1,2]$ + $Cp''TaCl_4$ (Cp'' = $C_5H_3(SiMe_3)_2$-1,3), X-ray	383
$Cp^*TaCl_2[C_6H_4(NSi^iPr_3)_2\text{-}1,2]$	Prep: $Li_2[C_6H_4(NSi^iPr_3)_2\text{-}1,2]$ + Cp^*TaCl_4, X-ray	382
$Cp^*TaMe_2[C_6H_4(NSi^iPr_3)_2\text{-}1,2]$	Prep: $Cp^*TaCl_2[C_6H_4(NSi^iPr_3)_2\text{-}1,2]$ + 2MeMgBr	382
$Li[Ta(^tBuN{=}CHCH{=}N^tBu)_3]$	Prep: $TaCl_5$ + $3[Li(OEt_2)]_2$-$[^tBuN{=}CHCH{=}N^tBu]$	384

(Continued)

Table 15 (Continued)

Compound	*Comments*	*References*
Cp*TaCl$_2$(supine-η^4-AD)	Prep: [Cp*TaCl$_2$]$_2$ + AD; AD = 1,4-diphenyl-1-aza-1,3-diene (X-ray), 1-*p*-methoxylphenyl-4-phenyl-1-aza-1,3-butadiene, 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene (X-ray)	286, 349
Cp*TaCl(CH$_2$Ph)(supine-η^4-AD)	Prep: Cp*TaCl$_2$(supine-η^4-AD) + 1/2 (PhCH$_2$)$_2$Mg; AD = 1,4-diphenyl-1-aza-1,3-diene, 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene	286, 349
Cp*(CH$_2$Ph) $\overline{\text{Ta[=CPhCH=CHN}}$Ar]	Prep: Cp*TaCl$_2$(supine-η^4-AD) + 2(PhCH$_2$)$_2$Mg; AD = 1,4-diphenyl-1-aza-1,3-diene, 1-*p*-methoxylphenyl-4-phenyl-1-aza-1,3-butadiene; Ar = Ph, *p*-MeOC$_6$H$_4$	349
Cp*Ta(=NAr){N(Xyl)C(CH$_2$Ph)=CHCH=CHPh}(CH$_2$Ph)	Prep: Cp*Ta(CH$_2$Ph)$_2$(h2-C,N-AD) + XylNC; AD = 1,4-diphenyl-1-aza-1,3-diene, 1-*o*-tolyl-4-phenyl-1-aza-1,3-diene; Ar = Ph, *o*-Tol (X-ray)	350
Cp*TaCl$_2$(supine-η^4-MMA)	Prep: [Cp*TaCl$_2$]$_2$ + MMA, X-ray	387
Cp*Ta(supine-η^4-MMA)(η^2-RN=CHCH=NR)	Prep: Cp*TaCl$_2$(supine-h4-MMA) + the dilithium salt of RN=CHCH=NR; R = Cy (X-ray), *p*-MeOC$_6$H$_4$	387
η^4-Naphthalene and anthracene complexes		
A[Ta(η^4-C$_{10}$H$_8$)$_3$]	Prep: TaCl$_5$ + 6Na(C$_{10}$H$_8$); A = Na(THF), Na(crypt 2.2.2)	6
A[Ta(η^4-C$_{14}$H$_{10}$)$_3$]	Prep: A[Ta(η^4-C$_{10}$H$_8$)$_3$] + C$_{14}$H$_{10}$; A = Na(THF)$_2$, Na(crypt 2.2.2)	6
Cp*TaCl$_2$(1-4-η^4-anthracene)	Prep: Cp*TaCl$_4$ + Mg(anthracene)(THF)$_3$	388
Cp*Ta(CH$_2$Ph)$_2$(1-4-η^4-anthracene)	Prep: Cp*TaCl$_2$(1-4-η^4-anthracene) + 2PhCH$_2$MgCl, X-ray	388
η^4-Trimethylenemethane complexes		
(TBM)TaMe$_3$	Prep: TaCl$_2$Me$_3$ + Li$_2$[TBM]; TBM = tribenzylidenemethane	389, 390
(^{t}Bu-TBM)TaMe$_3$	Prep: TaCl$_2$Me$_3$ + Li$_2$[^{t}Bu-TBM]; ^{t}Bu-TBM = dibenzylidene-4-^{t}Bu-benzylidenemethane, X-ray	389, 390
(TBM)TaMe$_2$Cl	Prep: (TBM)TaMe$_3$ + ZnCl$_2$, X-ray	389
(TBM)TaMe$_2$(NPh$_2$)	Prep: (TBM)TaMe$_2$Cl + LiNPh$_2$, X-ray	390
Cp(TBM)TaMe$_2$	Prep: (TBM)TaMe$_2$Cl + LiCp or (TBM)TaMe$_2$(OTf) + LiCp, X-ray	389, 393, 390
Cp*(TBM)TaMe$_2$	Prep: (TBM)TaMe$_2$Cl + LiCp*, X-ray	389, 390
(η^5-C$_5$H$_4$Me)(TBM)TaMe$_2$	Prep: (TBM)TaMe$_2$Cl + Li(C$_5$H$_4$Me), X-ray	390
(η^5-Flu)(TBM)TaMe$_2$	Prep: (TBM)TaMe$_2$Cl + LiFlu; Flu = fluorenyl, X-ray	390
Tp(TBM)TaMe$_2$	Prep: (TBM)TaMe$_2$Cl + NaTp, X-ray	390
[H$_2$B(pz)$_2$](TBM)TaMe$_2$	Prep: (TBM)TaMe$_2$Cl + K[H$_2$B(pz)$_2$], X-ray	390
Tp*(TBM)TaMe$_2$	Prep: (TBM)TaMe$_2$Cl + KTp*, X-ray	390
(η^4-TBM)(η^5-C$_5$H$_5$B-NMe$_2$)TaMe$_2$.	Prep: (TBM)TaMe$_2$Cl + Li[C$_5$H$_5$B-NMe$_2$]	379
Other η^4-ligands		
Ta(1,4-^{i}Pr$_2$-1,4-diazabuta-1,3-diene)$_3$	Prep: TaCl$_5$ + 5 Na[Naph] + 1,4-^{i}Pr$_2$-1,4-diazabuta-1,3-diene	385
[Ta(1,4-^{i}Pr$_2$-1,4-diazabuta-1,3-diene)$_3$][BPh$_4$]	Prep: Ta(1,4-^{i}Pr$_2$-1,4-diazabuta-1,3-diene)$_3$ + AgBPh$_4$	385
(η^1:η^3-CH$_2$C$_5$Me$_4$)Ta(X)(CB)$_2$	Prep: Cp*TaCl$_4$ + 3KCB; CB = carbazole, X-ray	392
(η^1:η^3-CH$_2$C$_5$Me$_4$)Ta(CH$_2$SiMe$_3$)(CB)$_2$	Prep: (η^1:η^3-CH$_2$C$_5$Me$_4$)Ta(X)(CB)$_2$ + Me$_3$SiCH$_2$Li, X-ray	392
(η^1:η^3-CH$_2$C$_5$Me$_4$)Ta(CH$_2$Ph)(CB)$_2$	Prep: (η^1:η^3-CH$_2$C$_5$Me$_4$)Ta(X)(CB)$_2$ + PhCH$_2$MgCl, X-ray	392
{[η^4-C$_4$Me$_4$Ge(Me)(Cl)]TaCl$_3$(Et$_2$O)$_x$}$_2$	Prep: TaCl$_5$ + C$_4$Me$_4$Ge(Me)(SiMe$_3$); x = 0.5–1.0	391

(Continued)

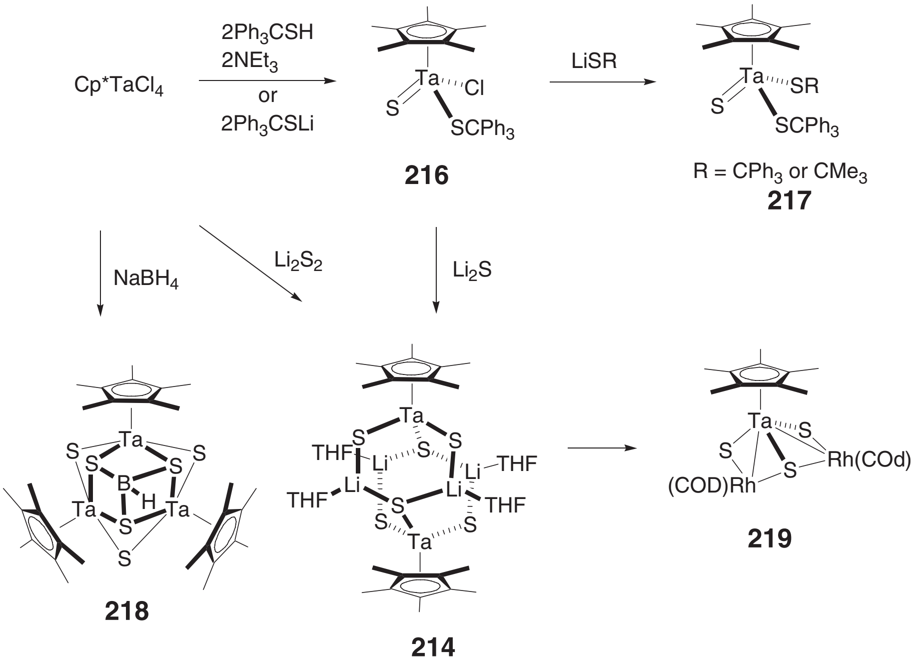
Table 15 (Continued)

Compound	*Comments*	*References*
$[\eta^4\text{-}C_4Me_4Ge(Me)(Cl)]TaCl_3(L)$	Prep: $\{[\eta^4\text{-}C_4Me_4Ge(Me)(Cl)]TaCl_3(Et_2O)_x\}_2 + 2L$; L = PPh_3, CNXyl	391
$[\eta^4\text{-}C_4Me_4Ge(Me)(Cl)]TaCl_3(L)_2$	Prep: $\{[\eta^4\text{-}C_4Me_4Ge(Me)(Cl)]TaCl_3(Et_2O)_x\}_2 + 4L$; L = PPh_3, CNXyl (X-ray)	391
$Cp[\eta^4\text{-}C_4Me_4Ge(Me)(Cl)]TaCl_2$	Prep: $\{[\eta^4\text{-}C_4Me_4Ge(Me)(Cl)]TaCl_3(Et_2O)_x\}_2$ + TlCp, X-ray	391

[a] Cp = $\eta^5\text{-}C_5H_5$, Cp* = $\eta^5\text{-}C_5Me_5$, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

$Cp^*TaCl_2(CNC_6H_3\text{-}2,6\text{-}Me_2)_3$.[398] Reactions of Cp^*TaCl_4 with 4,6-dimethyl-2-mercaptopyrimidine and 3-cyano-2-hydroxy-4,6-dimethylpyridine in the presence of triethylamine give the corresponding trichloro compounds, $Cp^*TaCl_3(\eta^2\text{-}SC_6H_7N_2)$ and $Cp^*TaCl_3(\eta^2\text{-}OC_8H_7N_2)$.[112] Pyridylalkoxide complexes $Cp^*TaCl_3(OCRPy_2)$ (R = Me, Py) were synthesized by the reaction of Cp^*TaCl_4 with the corresponding Li salts.[118] Bulky phenoxo ligand can be introduced into the half-sandwich moiety: $Cp^*TaCl_3(OC_6H\text{-}2,3,5,6\text{-}Ph_4)$ is prepared by the reaction of Cp^*TaCl_4 with $LiOC_6H\text{-}2,3,5,6\text{-}Ph_4$.[399] Calix[4]arene complexes Cp^*Ta(*p*-R-calix[4]arene) (R = H, ^{t}Bu) are obtained by treating the potassium salt of calix[4]arene with Cp^*TaCl_4.[400] The *endo*-calix site is a cavity for stabilizing the coordination of water and acetonitrile to the electron-deficient metal center. Metallasiloxane compound $^tBu_2Si(O)_2[Cp^*TaCl]_3(\mu\text{-}Cl)(\mu\text{-}O)_2(\mu^3\text{-}O)$ is prepared by the reaction of Cp^*TaCl_4 with $^tBu_2Si(OLi)_2$.[401] Treatment of Cp^*TaMe_4 with $^tBuP(O)(OH)_2$ produces $\{Cp^*Ta[OP(OH)_2{}^tBu]\}_2(\mu\text{-}O)_2[\mu\text{-}O_2P(O)^tBu]_2$.[402] Clear reaction of $CpTaCl_4$ with tris(2-hydroxyphenyl)amine and tris(2-hydroxy-4,6-dimethylbenzyl)amine afforded the corresponding monochloro trialkoxo complexes, adopting a pseudo-octahedral geometry.[403]

The sulfide complexes $[Cp^*Ta(S)_3Li_2(THF)_2]_2$ **214** and $[Cp^*Ta(S)_2]_3Li_2(THF)_2$ **215** are synthesized by the reactions of Cp^*TaCl_4 with 3–5 equiv. of Li_2S_2 or Li_2S, respectively.[404] Treatment of Cp^*TaCl_4 with triphenylmethanethiol in the presence of base causes C–S bond cleavage to give a sulfide complex, $Cp^*Ta({=}S)(SCPh_3)Cl$ **216**.[405] The reactions of **216** with LiSR (R = CPh_3 or CMe_3), Li_2S, and $NaBH_4$ give the corresponding compounds, $Cp^*Ta({=}S)(SCPh_3)(SR)$ **217**, **214**, and a BH- capped trinuclear cluster $[Cp^*Ta(S)_2]_3(BH)$ **218** (Scheme 82).[405]



Scheme 82

Trisulfidotantalum compound **214** reacts smoothly with $[\mathrm{Rh}(\mu\text{-Cl})(\mathrm{COD})]_2$ and $\mathrm{RuHCl(PPh_3)_3}$ to give the trinuclear clusters, $\mathrm{Cp^*TaS_3\{Rh(COD)\}_2}$ **219** and $\mathrm{Cp^*TaS_3\{RuH(PPh_3)_2\}_2}$ **220**.[406] $\mathrm{Cp^*Ta(S\textit{t}Bu)_3(OBu)}$ is a minor product of the reaction of $\mathrm{Cp^*TaCl_4}$ and $\mathrm{^tBuSLi}$ in THF: the butoxy moiety comes from the solvent THF.[407] Bis (dithiolate) compound $\mathrm{Cp^*Ta(ndt)_2}$ (ndt = norbornane-*exo*-2,3-dithiolate) is derived by treating $\mathrm{Cp^*TaCl_4}$ with $\mathrm{2Li_2(ndt)_2}$.[408] Dinuclear thiolate compound $[(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{TaCl_2}]_2(\mu\text{-}\eta^2{:}\eta^2\text{-EDT})(\mu\text{-O})$ is prepared by treating $(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{TaCl_4}$ with $\mathrm{Na_2EDT}$ (EDT = ethylene dithiolate).[409] Other oxo-bridged heterobimetallic compounds are prepared by treating $\mathrm{Cp^*TaMe_4}$ with 2 equiv. of hydroxide dimers of rhodium and iridium, $[\mathrm{M}(\mu\text{-OH})(\mathrm{COD})]_2$ (M = Rh, Ir) to give $\mathrm{Cp^*Ta}(\mu_3\text{-O})_4[\mathrm{M(COD)}]_4$.[410]

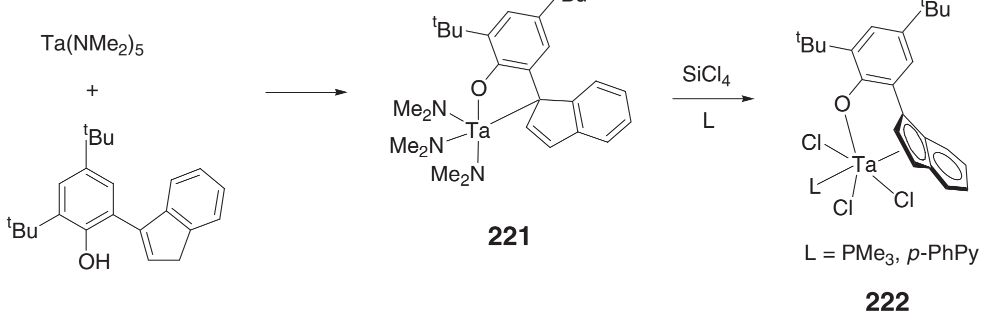
$\mathrm{Ta(NMe_2)_5}$ reacts with inden-3-ylphenol $\mathrm{HOC_6H_2}$-2-(inden-3-yl)-4,6-$\mathrm{^tBu_2}$ to initially form the tetrakis(dimethylamidophenoxo compound, which upon heating to 100 °C turns into η^1-indenyl compound **221** (Scheme 83).[411] Replacement of three amido groups by chloride groups is achieved by a reaction with $\mathrm{SiCl_4}$ in the presence of donor ligands, giving **222**.[411]

Thermolysis of $(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta(CO)_4}$ and $\mathrm{As_4}$ gives $[(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta}]_2(\mu\text{-}\eta^4{:}\eta^4\text{-}\mathrm{As_8})$ together with $[(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta}]_3(\mathrm{As_6})$.[412] Photolysis of $(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta(CO)_4}$ and $\mathrm{P_4}$ affords a mixture of some clusters $(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta(CO)_2}(\eta^4\text{-}\mathrm{P_4})$, $[(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})(\mathrm{CO})\mathrm{Ta}]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{P_2})_2$, and $(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})_3\mathrm{Ta_3(P_2)_2}$,[413] while thermolysis of $(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta(CO)_4}$ and $\mathrm{Cp^*FeP_5}$ affords trinuclear cubane-like mixed cluster $(\mathrm{Cp^*Fe})[(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta}](\mathrm{P})_5$ together with $[(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta}]_3(\mathrm{P})_5$ and $[(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta}]_4(\mathrm{P_3})_2$.[414] The same reaction with $\mathrm{Cp^*FeAs_5}$ affords $(\mathrm{Cp^*Fe})[(\eta^5\text{-}\mathrm{C_5H_3}\text{-1,3-}\mathrm{^tBu_2})\mathrm{Ta}](\mathrm{As})_5$.[413]

Phosphinidene-bridged ditantalum(IV) complexes $[\mathrm{Cp^*TaCl}]_2(\mu\text{-PR})_2$ (R = Cy, ^{t}Bu, Ph, Mes) and $[(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{TaCl}]_2(\mu\text{-PMes})_2$ are prepared by $\mathrm{Cp^*TaCl_4}$ or $(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{TaCl_4}$ with 2LiPHR.[415,416] $[(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{Ta(PPh_2)}]_2(\mu\text{-PPh_2})_2$ is obtained by the reaction of $(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{TaCl_4}$ with $\mathrm{KPPh_2(dioxane)_2}$.[416] The reaction of $[\mathrm{Cp^*TaCl}]_2(\mu\text{-PPh})_2$ with XylNC gives $[\mathrm{Cp^*Ta(CNXyl)_4Cl}]\mathrm{Cl}$.[415] The reaction of oxo-bridged $[\mathrm{Cp^*TaCl_3}]_2(\mu\text{-O})$ with $\mathrm{Cy_2P_2H_2}$ gives $[\mathrm{Cp^*TaCl_2}]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{P_2Cy_2})(\mu\text{-O})$.[415] Imido-bridged ditantalum(IV) complexes $[\mathrm{Cp^*TaCl}]_2(\mu\text{-NPh})_2$ are derived by the reduction of $\mathrm{Cp^*Ta({=}NPh)Cl_2}$ by magnesium.[417]

Imido–amido half-sandwich compound $\mathrm{Cp^*Ta({=}NSiMe_3)[N(SiMe_3)_2]Cl}$ is prepared by the reaction of $\mathrm{Cp^*TaCl_4}$ with $\mathrm{LiN(SiMe_3)_2}$.[418] Its treatment with $\mathrm{N_3SiMe_3}$ and $\mathrm{HN{=}PEt_3}$ affords $\mathrm{Cp^*Ta({=}NSiMe_3)[N(SiMe_3)_2](N_3)}$ and $\mathrm{Cp^*Ta({=}NSiMe_3)[N(SiMe_3)_2](N{=}PEt_3)}$, respectively.[418] 1,2,3-Triazole complexes $\mathrm{Cp^*Ta(N_3)_2Cl[N_2N(Me)\text{-}C(COOMe)C(COO)]}$ and $\mathrm{Cp^*TaPh_3[N_3C_2(COOMe)_2]}$ are prepared by the [2 + 3] cycloaddition of azido complexes$\{\mathrm{Cp^*TaCl(N_3)_2}(\mu\text{-}\mathrm{N_3})\}_2$ and $\mathrm{Cp^*TaPh_3(N_3)}$ with dimethyl acetylenedicarboxylate, respectively.[419] Reactions of $\mathrm{Cp^*TaCl_4}$ with 2, 3 and 4 equiv. of $\mathrm{LiNH^tBu}$ give the corresponding imido complexes $\mathrm{Cp^*TaCl_2({=}N^tBu)}$, $\mathrm{Cp^*TaCl(NH^tBu)({=}N^tBu)}$, and $\mathrm{Cp^*Ta(NH^tBu)_2({=}N^tBu)}$.[55] $\mathrm{Cp^*TaCl_2({=}N^tBu)}$ reacts with CNtBu and CNXyl to give $\mathrm{Cp^*TaCl_2({=}N^tBu)(CN^tBu)}$ and $\mathrm{Cp^*TaCl_2(CNXyl)_3}$.[55]

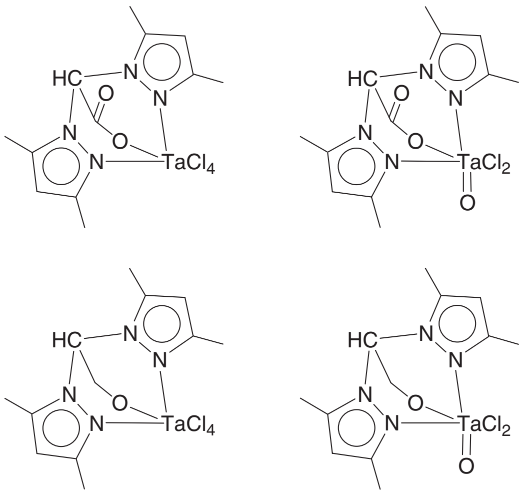
Half-sandwich carborane complexes $(\eta^5\text{-}\mathrm{C_5R_5})(\eta^5\text{-}(\mathrm{R^1})_2\mathrm{C_2B_4H_4})\mathrm{TaCl_2}$ (R = H, Me; $\mathrm{R^1}$ = Me, Et, $\mathrm{SiMe_3}$) and $(\eta^5\text{-}\mathrm{C_5R_5})[\eta^5\text{-}\mathrm{Cp^*Co(Et_2C_2B_3H_3)}]\mathrm{TaCl_2}$ (R = H, Me) have been prepared by the disproportionation reaction of $(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{TaCl_4}$ with 2 equiv. of the corresponding *nido*-carborane monoanions, being far more efficient than an earlier approach involving reactions with carborane dianions.[141] Carborane complexes $\mathrm{Cp(R_2C_2B_4H_4)TaCl_2}$ (R = Me, Et, $\mathrm{SiMe_3}$) are reported to be potent cytotoxic agents against tumors.[420] An anionic compound $[\mathrm{PPN}][(\eta^5\text{-}\mathrm{C_2B_9H_{11}})_2\mathrm{TaCl_2}]$ is prepared by the reaction of $(\mathrm{C_2B_9H_{11}})\mathrm{TaCl_3}$ with $[\mathrm{PPN}][\mathrm{Tl(C_2B_9H_{11})}]$.[144] Reaction of the dilithium salt of 1,2-$\mathrm{C_2B_9H_{10}}$ with $\mathrm{TaCl_5}$ in refluxing toluene yields $\{(\mu\text{-H})(\mathrm{C_2B_9H_{10}})_2\}\mathrm{TaCl_2}$.[164]



Scheme 83

Hughes *et al.* have reported systematic syntheses of dicarbollide amide complexes by amine elimination reaction: $Ta(NMe_2)_5$ reacts with *nido*-$C_2B_9H_{13}$ or $[NHMe_3]$[*nido*-$C_2B_9H_{12}$] to yield carborane–amide complexes $Ta(NMe_2)_3(C_2B_9H_{11})$ with icosahedral 3,1,2-, 2,1,7-, and 2,1,12-TaC_2B_9 cages depending on three icsosahedral carborane precursors containing 1,2-, 1,7-, and 1,12-$C_2B_9H_{12}$ cages.[421–423] Boron methylate 11-Me-*nido*-12,7-$C_2B_9H_{12}$ also produces [4,4,4-$(NMe_2)_3$-*closo*-3-Me-4,1,2-$TaC_2B_9H_{10}$].[424] The polar multiple bonds in CO_2, CS_2, isonitrile, and acetonitrile insert into Ta–N bonds of [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] to give the corresponding inserted products, while protic substrates proceed with amine elimination.[346,422] The silollide ligand reacts with $Ta(NMe_2)_5$ to give $[NEt_4][Ta(MeSiB_{10}H_{10})(NMe_2)_3]$, which reacts with dichloromethane or dibromoethane to give $[NEt_4][Ta(MeSiB_{10}H_{10})(NMe_2)_2Cl]$ or $[NEt_4][Ta(MeSiB_{10}H_8)(\mu\text{-}NMe_2)_2Br_3]$.[425] A silsesquioxane ligand, $(Cy_7Si_7O_{12})$, is introduced into "$Ta(C_2B_9H_{11})$" by amine elimination reaction.[426,427]

Pyrazolylborate compounds $Tp^*Ta({=}O)Cl_2$ and $Tp^*Ta({=}N^tBu)Cl_2$ are directly derived from the reaction of KTp^* with $[TaOCl_3]_x$ and $Ta({=}N^tBu)Cl_3(py)_2$, respectively.[428] Direct reaction of $TaCl_5$ and $Tp^*Sn(Cl)Bu_2$ produces $[Tp^*TaCl_3][TaCl_6]$.[429,430] Otero and his co-workers have prepared new monoanionic heteroscorpionate ligands, which can coordinate by two nitrogen atoms and one oxygen atom to the tantalum (Scheme 84) (Table 16).[431]



Scheme 84

Table 16 Mono(Cp) complexes[a]

Compound	*Comments*	*References*
Halogen complexes		
Cp^*TaCl_4	Prep: $Cp^*Ta(CO)_4 + Cl_2$X-ray	26, 396
Cp^*TaCl_4(chiral phosphine)	Chiral phosphines are $PhP(C_5Me_4)_2$, $PhP(C_4H_6$-2,5-$Me_2)$	432
$Cp^*TaCl_4(L)$	Prep: $Cp^*TaCl_4 + L$; L = CNC_6H_3-2,6-Me_2 (X-ray), CN C_6H_2-2,4,6-Me_3, ^tBuNC, $PhNH_2$	398
$Cp'TaCl_4(PH_2R)$	Prep: $Cp'TaCl_4 + PRH_2$; $Cp' = C_5H_4Me$, Cp^*; R = Cy, *t*Bu, Ph, C_6H_2-2,4,6-$^iPr_3$, X-ray for Cp^* and C_6H_2-2,4,6-$^iPr_3$	433
$Cp^*TaCl_2(CNC_6H_3$-2,6-$Me_2)_3$	Prep: $Cp^*TaCl_4(CNC_6H_3$-2,6-$Me_2)$ + Na/Hg	398
$CpTaCl_4[\eta^1$-$PPh_2CH_2C({=}O)NPh_2]$	Prep: $CpTaCl_4 + Ph_2PCH_2C({=}O)NPh_2$	434
$CpTaCl_4[\eta^1$-$O{=}C(Me)NHPPh_2]$	Prep: $CpTaCl_4 + Ph_2PNHC({=}O)Me$	434
$[\eta^5$-$C_5H_4B(C_6F_5)_2]TaCl_4$	Prep: $TaCl_5 + Me_3SiC_5H_4B(C_6F_5)_2$	394
$[\eta^5$-$C_5H_4B(C_6F_5)_2(py)]TaCl_4(py)$	Prep: $[\eta^5$-$C_5H_4B(C_6F_5)_2]TaCl_4$ + ex. Py	394
[*rac*-$Fe(C_5H_4)CMe_2P(H)(R)](Cp^*TaCl_4)_2$	Prep: $2Cp^*TaCl_4$ + *rac*-$Fe[(C_5H_4)CMe_2P(H)(R)]_2$; R = Ph (X-ray), Mes	395
$Cp^*TaCl_4(PH_2R)$	Prep: $Cp^*TaCl_4 + PH_2R$; R = ^tBu (X-ray), Ad (X-ray), Cy (X-ray), Ph (X-ray), Mes (X-ray)	396

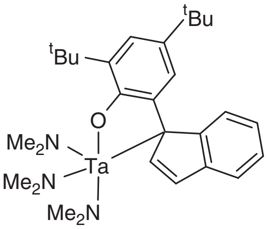
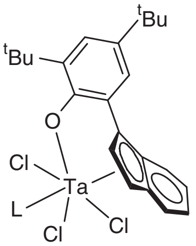
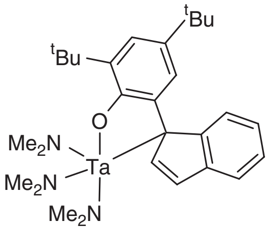
(*Continued*)

Table 16 (Continued)

Compound	*Comments*	*References*
[(η^5-C$_5$H$_4$Me)Ta(PPh$_2$)]$_2$(μ-PPh$_2$)$_2$	Prep: (η^5-C$_5$H$_4$Me)TaCl$_4$ + KPPh$_2$(dioxane)$_2$, X-ray	416
(η^5-C$_5$H$_4$Me)TaCl$_4$(PH$_2$Mes)	Prep: (η^5-C$_5$H$_4$Me)TaCl$_4$ + PH$_2$Mes, X-ray	416
[(η^5-C$_5$H$_4$Me)TaCl]$_2$(μ-PMes)$_2$	Prep: (η^5-C$_5$H$_4$Me)TaCl$_4$(PH$_2$Mes) + DBU, X-ray	416
[Cp*TaCl$_4$][H(DBU)]	Prep: Cp*TaCl$_4$(PH$_2$R) + DBU; R = ^{t}Bu, Ad, Ph, Mes, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, X-ray	397
[Cp*Ta(CNXyl)$_4$Cl]Cl	Prep: [Cp*TaCl]$_2$(μ-PPh)$_2$ + ex. XylNC, X-ray	415
Amide and amidinate complexes		
Cp*TaCl$_3$[MeC(N^{i}Pr)$_2$]	X-ray	127
{Cp*TaCl$_2$[MeC(N^{i}Pr)$_2$]}[SbF$_6$]	X-ray	127
CpTaCl$_3${(Me$_3$SiN)$_2$CC$_6$H$_2$-2,4,6-^{i}Pr$_3$}	Prep: TaCl$_4${(Me$_3$SiN)$_2$CC$_6$H$_2$-2,4,6-^{i}Pr$_3$} + Cp$_2$Mg, X-ray	435
Imido and related complexes		
CpTa(=NAr)Cl$_2$	Prep: CpTaCl$_4$ + ArNHSiMe$_3$; Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$	227
[CpTa(=NAr)Cl]$_2$	Prep: thermolysis of CpTa(=NAr)H(SiMe$_2$Cl)(PMe$_3$); Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$	227
CpTa(=NAr)(PMe$_3$)$_2$	Prep: CpTa(=NAr)Cl$_2$ + 2PMe$_3$ + Mg; Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$	227
[CpTa(=NAr)(PMe$_3$)$_2$Cl]OTf	Prep: CpTa(=NAr)(PMe$_3$)(H)(SiMe$_2$Cl) + AgOTf; Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$	227
CpTa(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(NMe$_2$)$_2$	Prep: Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(NMe$_2$)$_3$ + C$_5$H$_6$	436, 437
Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)Cl$_2$	Prep: Cp*Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(H)Si(SiMe$_3$)$_3$ + CH$_2$Cl$_2$	149
	Prep: Cp*TaCl$_4$ + 2 LiNH C$_6$H$_3$-2,6-^{i}Pr$_2$	438
Cp*TaCl$_2$(=NAr)	Prep: Cp*TaCl$_2$[η^2-C(Ar)=CMe$_2$] + ArNC; Ar = C$_6$H$_3$-2,6-Me$_2$, C$_6$H$_2$-2,4,6-Me$_3$	156, 343
	Prep: thermolysis of Cp*TaCl$_2$[η^2-C(Ar)=CMe$_2$]; Ar = C$_6$H$_3$-2,6-Me$_2$, C$_6$H$_2$-2,4,6-Me$_3$	306
Cp*Ta(=NC$_6$H$_3$-2,6-Mes$_2$)Cl$_2$	Prep: Cp*TaCl$_4$ + LiNH C$_6$H$_3$-2,6-Mes$_2$ + NEt$_3$, X-ray	154
Cp*Ta(=NC$_6$H$_3$-2,6-Trip$_2$)Cl$_2$	Prep: Cp*TaCl$_4$ + LiNH C$_6$H$_3$-2,6-Trip$_2$ + NEt$_3$; Trip = 2,4,6-triisopropylphenyl	154
Cp*TaCl$_2$(=NXyl)	Prep: Cp*TaCl$_4$ + LiNH(C$_6$H$_3$-2,6-Me$_2$)	55
	Prep: Cp*TaCl$_2$R$_2$ + XylNC; R = CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$, CH$_2$Ph	115
Cp*Ta(=NPh)Cl$_2$	Prep: Cp*TaCl$_4$(PhNH$_2$) + 2LiNEt$_2$	398
CpTa(=N^{t}Bu)Cl$_2$	Prep: CpTaCl$_4$ + 2^{t}BuNH$_2$ + LiN^{t}Bu(SiMe$_3$)	152
Cp*Ta(=N^{t}Bu)Cl$_2$	Prep: Cp*TaCl$_4$ + 2LiNH^{t}Bu	55
	Prep: Cp*TaCl$_4$ + ^{t}BuNH$_2$ + LiN^{t}Bu(SiMe$_3$)	152
Cp*Ta[=NSi(^{t}Bu)$_3$]Cl$_2$	Prep: Cp*Ta[=NSi(^{t}Bu)$_3$]Me$_2$ + 2[^{i}Pr$_2$EtNH]Cl	155
Cp*Ta(=NSiMe$_3$)Cl$_2$	Prep: Cp*TaCl$_4$ + LiN(SiMe$_3$)$_2$	439
Cp*Ta(=NSiMe$_3$)[N(SiMe$_3$)$_2$]Cl	Prep: Cp*TaCl$_4$ + LiN(SiMe$_3$)$_2$	418
Cp*Ta(=NSiMe$_3$)[N(SiMe$_3$)$_2$](N$_3$)	Prep: Cp*Ta(=NSiMe$_3$)[N(SiMe$_3$)$_2$]Cl + N$_3$SiMe$_3$	418
Cp*Ta(=NSiMe$_3$)[N(SiMe$_3$)$_2$](N=PEt$_3$)	Prep: Cp*Ta(=NSiMe$_3$)[N(SiMe$_3$)$_2$]Cl + HN=PEt$_3$	418
Cp*Ta(X)(=NXyl)[N(Xyl)CMe=CMe$_2$]	Prep: Cp*Ta(X)Me$_3$ + 2 XylNC; Xyl = C$_6$H$_3$-2,6-Me$_2$; X = Cl, Me (X-ray)	156,343
Cp*TaCl(=NXyl)[η^2-N(Xyl)=CCMe$_2$CMe=N(Xyl)]	Prep: Cp*TaCl(=NXyl)[N(Xyl)CMe=CMe$_2$] + XylNC; Xyl = C$_6$H$_3$-2,6-Me$_2$	343
Cp*TaCl(NH^{t}Bu)(=N^{t}Bu)	Prep: Cp*TaCl$_4$ + 3LiNH^{t}Bu	55
Cp*Ta(NH^{t}Bu)$_2$(=N^{t}Bu)	Prep: Cp*TaCl$_4$ + 4LiNH^{t}Bu	55
(η^5-C$_5$Me$_4$H)TaCl$_2$(=N^{t}Bu)	Prep: TaCl$_5$ + (C$_5$Me$_4$H)SiMe$_2$(NH^{t}Bu)	76
[η^5,η^1-C$_5$H$_4$SiMe$_2$NPh]Ta(NMe$_2$)$_3$	Prep: (C$_5$H$_5$)SiMe$_2$(NHPh) + Ta(NMe$_2$)$_5$	122
[η^5-C$_5$H$_4$SiMe$_2$(NMe$_2$)]Ta(=NPh)(NMe$_2$)$_2$	Prep: photolysis of [(η^5-C$_5$H$_4$)SiMe$_2$N(Ph)]Ta(NMe$_2$)$_3$	122
[Cp*TaCl]$_2$(μ-NPh)$_2$	Prep: Cp*Ta(=NPh)Cl$_2$ + Mg	417
[Cp*Ta(N$_3$)$_2$Cl](μ-N$_3$)$_2$	Prep: Cp*TaCl$_4$ + ex. Me$_3$SiN$_3$	418
[Cp*Ta(N$_3$)$_3$](μ-N$_3$)$_2$	Prep: Cp*TaCl$_4$ + ex. Me$_3$SiN$_3$	418
Cp*Ta(N$_3$)$_2$Cl[N$_2$N(Me)C-(COOMe)C(COO)]	Prep: [Cp*Ta(N$_3$)$_2$Cl](μ-N$_3$)$_2$ + MeO$_2$CC≡CCO$_2$Me	419
Cp*TaPh$_3$(N$_3$)	Prep: Cp*TaPh$_3$Cl + Me$_3$SiN$_3$	419
Cp*TaPh$_3$[N$_3$C$_2$(COOMe)$_2$]	Prep: Cp*TaPh$_3$(N$_3$) + MeO$_2$CC≡CCO$_2$Me	419
Cp*TaCl$_3$[N(Ar)CHMe$_2$]	Prep: Cp*TaCl$_2$[η^2-C(Ar)=CMe$_2$] + HCl	306

(*Continued*)

Table 16 (Continued)

Compound	*Comments*	*References*
Alkoxo and aryloxo complexes		
$Cp^*TaCl_3(OCRPy_2)$	Prep: $Cp^*TaCl_4 + LiOCRPy_2$; R = Me, Py (X-ray)	118
$Cp^*TaCl_3(OC_8H_7N_2)$	Prep: Cp^*TaCl_4 + 3-cyano-2-hydroxy-4,6-dimethylpyridine $HOC_8H_7N_2 + NEt_3$	112
$CpTa(L)Cl$	Prep: $CpTaCl_4 + LH_3$; $L = N(C_6H_4\text{-}2\text{-}O)_3$, $N(C_6H_4\text{-}3,5\text{-}Me_3\text{-}2\text{-}CH_2O)_3$	403
$Cp^*TaCl_2[(OCH_2)_2\text{-}2,6\text{-}(C_5H_3N)]$	Prep: $Cp^*TaCl_4 + (HOCH_2)_2\text{-}2,6\text{-}(C_5H_3N) + 2NEt_3$, X-ray	119
$Cp^*Ta(OR)_4$	Prep: $Cp^*Ta(PMe_3)H_2(\eta_2\text{-}CHPMe_2) + 4ROH$; R = Me, ${}^iPr$, Ph	229
$Cp^*Ta(p\text{-}R\text{-}calix[4]arene)$	Prep: $Cp^*TaCl_4 + K_4\{p\text{-}R\text{-}calix[4]arene\}$; R = H, ${}^tBu$, X-ray	400
$Cp^*Ta(p\text{-}R\text{-}calix[4]arene)(L)$	R = H, ${}^tBu$; L = H_2O, CH_3CN, X-ray	400
$Cp^*Ta(S{}^tBu)_3(OBu)$	Prep: $Cp^*TaCl_4 + {}^tBuSLi$ in THF, X-ray	407
$(\eta^5\text{-}C_5R_5)Cl_3\,Ta[PPh_2CH\text{--}C(\text{--}O)Ph]$	Prep: $\eta^5\text{-}C_5R_5)TaCl_4 + Ph_2PCH_2C({=}O)Ph$; R = H, Me	434
	Prep: $Ta(NMe_2)_5 + HOC_6H_2\text{-}2\text{-}(inden\text{-}3\text{-}yl)\text{-}4,6\text{-}{}^tBu_2$, X-ray	411
	 Prep: + $SiCl_4$ + L; L = PMe_3, p-Ph-py (X-ray)	411
$Cp^*TaCl_3(OC_6H\text{-}2,3,5,6\text{-}Ph_4)$	Prep: $Cp^*TaCl_4 + LiOC_6H\text{-}2,3,5,6\text{-}Ph_4$	399
${}^tBu_2Si(O)_2[Cp^*TaCl]_3(\mu\text{-}Cl)(\mu\text{-}O)_2(\mu^3\text{-}O)$	Prep: ${}^tBu_2Si(OLi)_2 + Cp^*TaCl_4$, X-ray	401
$\{Cp^*Ta[OP(OH)_2{}^tBu]\}_2(\mu\text{-}O)_2[\mu\text{-}O_2P(O){}^tBu]_2$	Prep: $Cp^*TaMe_4 + {}^tBuP(O)(OH)_2$, X-ray	402
Oxo complexes		
$Cp^*TaCl_2(\mu\text{-}O)B(C_6F_5)_3$	Prep: $Cp^*TaCl_4 + (H_2O)B(C_6F_5)_3$ or $[Cp^*TaCl_2(\mu\text{-}O)]_2 + B(C_6F_5)_3$, X-ray	120
$[Cp^*TaCl_2(\mu\text{-}O)]_2$	Prep: $Cp^*TaCl_2(\mu\text{-}O)B(C_6F_5)_3$ + py	120
$[Cp^*TaX_3]_2(\mu\text{-}O)$	Prep: $Cp^*Ta(CO)_4 + X_2$; X = Br (X-ray), I	26
$Cp^*Ta({=}O)X_2$	Prep: $[Cp^*TaX_3]_2(\mu\text{-}O)$ + air	26
$[Cp^*TaCl(\mu\text{-}O)]_3(\mu_3\text{-}O)(\mu\text{-}O_2PHPh)$	Prep: $[Cp^*TaCl]_2(\mu\text{-}PPh)_2$ + moisture acetone, X-ray	415
$Cp^*TaCl_3(OR)$	Prep: $Cp^*TaCl_4 + LiOR$; R = ${}^tBu$, $SiPh_3$, $C_6H_3\text{-}2,6\text{-}Me_2$	147
$Cp^*TaCl_2(OR)_2$	Prep: $Cp^*TaCl_4 + 4LiOR$; R = ${}^tBu$, $SiPh_3$, $C_6H_3\text{-}2,6\text{-}Me_2$	147
$Cp^*TaCl(OSiMe_3)_3$	Prep: $Cp^*TaCl_4 + 4NaOSiMe_3$	147
$Cp^*Ta(\mu_3\text{-}O)_4[M(COD)]_4$	Prep: Cp^*TaMe_4 2 $[M(\mu\text{-}OH)(COD)]_2$; M = Rh, Ir	410
Sulfido and thiolate complexes		
$Cp^*Ta({=}S)(SCPh_3)Cl$	Prep: $Cp^*TaCl_4 + 2Ph_3CSH + 2NEt_3$ or $Cp^*TaCl_4 + 2Ph_3CSLi$, X-ray	405
$Cp^*Ta({=}S)(SCPh_3)(SR)$	Prep: $Cp^*Ta({=}S)(SCPh_3)Cl + LiSR$; R = CPh_3, CMe_3	405
$Cp^*Ta(S)_3Li_2(THF)_2$	Prep: $Cp^*Ta({=}S)(SCPh_3)Cl + Li_2S$ or $Cp^*TaCl_4 + Li_2S_2$	405 404, 440
$Cp_3^*Ta_3(S)_3(S_3BH)$	Prep: $Cp^*Ta({=}S)(SCPh_3)Cl + NaBH_4$, X-ray	405
$CpTaCl_3\{\kappa^2\text{-}S,S'\text{-}B(H)(Cl)(mt)_2\}$	mt = methimazolyl	441
$Cp^*TaS_3\{Rh(COD)\}_2$	Prep: $Cp^*Ta(S)_3Li_2(THF)_2 + [Rh(\mu\text{-}Cl)(COD)]_2$, X-ray	406
$Cp^*TaS_3\{RuH(PPh_3)_2\}_2$	Prep: $Cp^*Ta(S)_3Li_2(THF)_2 + RuHCl(PPh_3)_3$, X-ray	406
$Cp^*Ta(ndt)_2$	Prep: $Cp^*TaCl_4 + 2Li_2(ndt)_2$; ndt = norbornane-*exo*-2,3-dithiolate	408
$[(\eta^5\text{-}C_5H_4Me)TaCl_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}EDT)(\mu\text{-}O)$	Prep: $(\eta^5\text{-}C_5H_4Me)TaCl_4 + Na_2EDT$; EDT = ethylene dithiolate	409

(*Continued*)

Table 16 (Continued)

Compound	*Comments*	*References*
(η^5-C$_5$H$_4$Me)Ta(3,4-S$_2$C$_6$H$_3$Me)$_2$	Prep: (η^5-C$_5$H$_4$Me)TaCl$_4$ + 2,3,4-(TlS)$_2$C$_6$H$_3$Me	409
Cp*TaCl$_2$[(SCH$_2$CH$_2$)$_2$X]	Prep: Cp*TaCl$_4$ + X(CH$_2$CH$_2$SH)$_2$ + 2NEt$_3$, X = O, S (X-ray)	148
Cp*TaCl$_3$(SC$_6$H$_7$N$_2$)	Prep: Cp*TaCl$_4$ + 2-mercapto-4,6-dimethylpyrimidine HSC$_6$H$_7$N$_2$ + NEt$_3$, X-ray	112
P$_n$, As$_n$, and related complexes		
[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta]$_2$(μ-η^4:η^4-As$_8$)	Prep: thermolysis of (η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta(CO)$_4$ with As$_4$, X-ray	412
[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta]$_3$(As$_6$)	X-ray	
(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta(CO)$_2$(η^4-P$_4$)	Prep: photolysis of (η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta(CO)$_4$ with P$_4$, X-ray	413
[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)(CO)Ta]$_2$(μ-η^2:η^2-P$_2$)$_2$	X-ray	
(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)$_3$Ta$_3$(P$_2$)$_2$		
(Cp*Fe)[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta](As)$_5$	Prep: thermolysis of (η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta(CO)$_4$ and Cp*FeAs$_5$, X-ray	413
(Cp*Fe)[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta](P)$_5$	Prep: thermolysis of (η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta(CO)$_4$ and Cp*FeP$_5$	414
[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta]$_3$(P)$_5$		
[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta]$_4$(P$_3$)$_2$		
(Cp*Fe)[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta]-(P)$_5$[Mo(CO)$_5$]	Prep: (Cp*Fe)[(η^5-C$_5$H$_3$-1,3-^{t}Bu$_2$)Ta](P)$_5$ + Mo(CO)$_5$(THF), X-ray	414
[Cp*TaCl]$_2$(μ-PR)$_2$	Prep: Cp*TaCl$_4$ + 2LiPHR; R = Cy (X-ray), ^{t}Bu (X-ray), Ph (X-ray), Mes (X-ray)	415
[(η^5-C$_5$H$_4$Me)TaCl]$_2$(μ-PMes)$_2$	Prep: (η^5-C$_5$H$_4$Me)TaCl$_4$ + 2LiPHMes, X-ray	415
[Cp*TaCl$_2$]$_2$(μ-η^2:η^2-P$_2$Cy$_2$)(μ-O)	Prep: [Cp*TaCl$_3$]$_2$(μ-O) with Cy$_2$P$_2$H$_2$, X-ray	415
Tp and related complexes		
Tp*Ta(=NAr)Cl$_2$	Prep: Ta(=NAr)Cl$_3$(THF)$_2$ + KTp*; Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$	442
Tp*Ta(=NAr)Cl(OBu)	Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$, X-ray	442
Tp*Ta(=O)Cl$_2$	Prep: [TaOCl$_3$]$_x$ + KTp*	428
Tp*Ta(=N^{t}Bu)Cl$_2$	Prep: Ta(=N^{t}Bu)Cl$_3$(py)$_2$ + KTp*	428
Tp*Ta(μ-Cl)$_2$(μ-THT)TaCl$_3$	Prep: [TaCl$_2$(THT)]$_2$(μ-Cl)$_2$(μ-THT) + KTp*	329
Tp*Ta(=NSiMe$_3$)Cl$_2$	Prep: Ta(=NSiMe$_3$)Cl$_3$(py)$_2$ + KTp*, X-ray	439
[Tp*TaCl$_3$][TaCl$_6$]	Prep: 2TaCl$_5$ + Tp*Sn(Cl)Bu$_2$, X-ray	429, 430
TaCl$_4$(κ^3-bdmpze)	Prep: bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) + BuLi + TaCl$_5$	431
TaCl$_4$(κ^3-bdmpza)	Prep: lithium salt of bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) + TaCl$_5$	431
TaCl$_3$(κ^3-bdmpza)(OR)	Prep: TaCl$_4$(κ^3-bdmpza) + HOR; R = Me, Et, ^{i}Pr, ^{t}Bu	431
Ta(=O)Cl$_2$(κ^3-bdmpze)	Prep: TaCl$_4$(κ^3-bdmpze) + THF	431
Ta(=O)Cl$_2$(κ^3-bdmpza)	Prep: TaCl$_4$(κ^3-bdmpza) + THF	431
Carborane and borollide complexes		
(η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaCl$_3$	Prep: TaCl$_5$ + Li$_2$[C$_4$H$_4$BiN^{i}Pr$_2$] + 2AlCl$_3$, X-ray	42
(η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaCl(PMe$_3$)$_3$	Prep: (η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaCl$_3$ + Mg + ex. PMe$_3$	42
[(η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaCl(PMe$_3$)$_2$]2(μ-N$_2$)	Prep: (η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaCl$_3$ + Mg + ex. PMe$_3$ + N$_2$	42
(η^5-C$_4$H$_4$BiNH^{i}Pr$_2$)Ta(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)Cl$_2$	Prep: (η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaCl$_3$ + H$_2$NC$_6$H$_3$-2,6-^{i}Pr$_2$ + 2NEt$_3$, X-ray	42
(η^5-C$_4$H$_4$BiNH^{i}Pr$_2$)Ta[OC(Me)$_2$CH$_2$C(=O)Me]Cl$_3$	Prep: (η^5-C$_4$H$_4$BiN^{i}Pr$_2$)TaCl$_3$ + 2acetone, X-ray	42
[PPN][(η^5-C$_2$B$_9$H$_{11}$)$_2$TaCl$_2$]	Prep: (C$_2$B$_9$H$_{11}$)TaCl$_3$ + [PPN][Tl(C$_2$B$_9$H$_{11}$)]	144
[PPN][(η^5-C$_2$B$_9$H$_{11}$)$_2$TaF$_2$]	Prep: [PPN][(η^5-C$_2$B$_9$H$_{11}$)$_2$TaCl$_2$] + 2AgPF$_6$	144
{(μ-H)(C$_2$B$_9$H$_{10}$)$_2$}TaCl$_2$	Prep: Li$_2$[1,2-C$_2$B$_9$H$_{10}$] + TaCl$_5$, X-ray	164
[2,2,2-(NMe$_2$)$_3$-*closo*-2,1,12-TaC$_2$B$_9$H$_{11}$]	Prep: Ta(NMe$_2$)$_5$ + *nido*-2,9-C$_2$B$_9$H$_{13}$, X-ray	423
[2,2,2-(NMe$_2$)$_3$-*closo*-2,1,7-TaC$_2$B$_9$H$_{11}$]	Prep: Ta(NMe$_2$)$_5$ + [NHMe$_3$][*nido*-7,9-C$_2$B$_9$H$_{12}$], X-ray	423
[3,3,3-(NMe$_2$)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$]	Prep: Ta(NMe$_2$)$_5$ + *nido*-1,2-C$_2$B$_9$H$_{13}$, X-ray	422
[3,3,3-(η^2-O$_2$CNMe$_2$)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$]	Prep: [3,3,3-(NMe$_2$)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$] + 3CO$_2$, X-ray	422
3,3′-[3,3-(NMe$_2$)$_2$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$]$_2$(μ-O)	Prep: [3,3,3-(NMe$_2$)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$] + H$_2$O,-ray	443
[2-Br-2,2-(NMe$_2$)$_2$-*closo*-2,1,12-TaC$_2$B$_9$H$_{11}$]	Prep: [2,2,2-(NMe$_2$)$_3$-*closo*-2,1,12-TaC$_2$B$_9$H$_{11}$] + CH$_2$Br$_2$	443
[3,3,3-(η^2-S$_2$CNMe$_2$)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$]	Prep: [3,3,3-(NMe$_2$)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$] + 3CS$_2$	422

(Continued)

Table 16 (Continued)

Compound	*Comments*	*References*
$[3,3,3\text{-}(\eta^1\text{-N}{=}\text{C(R)NMe}_2)_3\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}]$	Prep: $[3,3,3\text{-}(\text{NMe}_2)_3\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}] + 3\text{RCN}$; R = Me (X-ray), $p\text{-FC}_6\text{H}_4$ (X-ray)	346
$[3,3,3\text{-(SPh)}_3\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}]$	Prep: $[3,3,3\text{-}(\text{NMe}_2)_3\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}] + 3\text{PhSH}$	346
$[3,3,3\text{-}(\text{OC}_6\text{H}_2\text{-}2,6\text{-Me}_2)_3\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}]$	Prep: $[3,3,3\text{-}(\text{NMe}_2)_3\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}] + 3\text{HOC}_6\text{H}_2\text{-}2,6\text{-Me}_2$, X-ray	346
$[4,4,4\text{-}(\text{NMe}_2)_3\text{-}closo\text{-}3\text{-Me-}4,1,2\text{-TaC}_2\text{B}_9\text{H}_{10}]$	Prep: $\text{Ta(NMe}_2)_5 + 11\text{-Me-}nido\text{-}12,7\text{-C}_2\text{B}_9\text{H}_{12}$, X-ray	424
$[3,3,3\text{-}(\eta^1\text{-N}{=}\text{C(R)NMe}_2)_2\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}]_2(\mu\text{-O})$	Prep: hydrolysis of $[3,3,3\text{-}(\eta^1\text{-N}{=}\text{C(R)NMe}_2)_3\text{-}closo\text{-}3,1,2\text{-TaC}_2\text{B}_9\text{H}_{11}]$, X-ray	444
$[\text{NEt}_4][\text{Ta(MeSiB}_{10}\text{H}_{10})(\text{NMe}_2)_3]$	Prep: $\text{Ta(NMe}_2)_5 + [\text{NEt}_4][\text{Ta(MeSiB}_{10}\text{H}_{12})]$	425
$[\text{NEt}_4][\text{Ta(MeSiB}_{10}\text{H}_{10})(\text{NMe}_2)_2\text{Cl}]$	Prep: $[\text{NEt}_4][\text{Ta(MeSiB}_{10}\text{H}_{10})(\text{NMe}_2)_3]$ + dichloromethane	425
$[\text{NEt}_4][\text{Ta(MeSiB}_{10}\text{H}_8)\ (\mu\text{-NMe}_2)_2\text{Br}_3]$	Prep: $[\text{NEt}_4][\text{Ta(MeSiB}_{10}\text{H}_{10})(\text{NMe}_2)_3]$ + dichloromethane	425
$(\text{C}_2\text{B}_9\text{H}_{11})\text{Ta(Cy}_7\text{Si}_7\text{O}_{12})$	Prep: $[(\text{NMe}_2)_3\text{TaC}_2\text{B}_9\text{H}_{11}] + \text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})_3$	426

[a] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

5.03.7.4.2 Bis(cyclopentadienyl) complexes

The paramagnetic mixed ring dichloro complexes $\text{Cp}^*[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)]\text{TaCl}_2$ and $\text{Cp}^*[\eta^5\text{-C}_5\text{H}_3\text{-}1,3\text{-}(\text{SiMe}_3)_2]\text{TaCl}_2$ were prepared from Cp^*TaCl_4 and the lithium salt of the corresponding Cp derivatives with sodium amalgam.[45] These compounds can be oxidized by PCl_5 to give air sensitive diamagnetic trichloro compounds, soluble in most organic solvents (Scheme 85).

The *ansa*-type metallocene complexes of group 4 metals have been utilized as catalyst precursors for stereospecific polymerization of α-olefins. The synthetic route using metal amides is successfully applied to synthesize η^5:η^1- and η^5:η^5-*ansa*-metallocene complexes of tantalum (Scheme 86).[436, 437] Tris(amido)imido complex **223** with cyclopentadiene and its bridged derivative Cp-CMe$_2$-Cp in toluene at 90–110 °C afford half-sandwich complex **224** and η^5:η^1-*ansa*-metallocene complex **225** as a result of deprotonation by amine ligand. A fast η^5:η^1–η^1:η^5 interchange of the Cp-CMe$_2$-Cp ligand is observed. Replacement of NMe$_2$ ligand of **203** by ClSiMe_3 in toluene resulted in the formation of η^5:η^5-*ansa*-complex **226**. Cationic *ansa*-η^5:η^5 complex **227** is prepared by treating **225** with 1 equiv. of $[\text{HNMe}_3]\text{-}[\text{B}(\text{C}_6\text{F}_5)_4]$ in THF at low temperature.

Treatment of $\text{Ta}({=}\text{NEMe}_3)\text{Cl}_3(\text{py})_2$ (E = C, Si) with 3 equiv. of CpNa affords $(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)\text{Ta}({=}\text{NEMe}_3)$, while the reaction of $\text{Ta}({=}\text{NSiMe}_3)\text{Cl}_3(\text{py})_2$ with KTp^* gives $\text{Tp}^*\text{Ta}({=}\text{NSiMe}_3)\text{Cl}_2$.[152,439,445] Reduction of $\text{Cp}_2\text{Ta}({=}\text{N}^t\text{Bu})\text{Cl}$ by C_8K affords dimer $(\text{Cp}_2\text{Ta})_2(\mu\text{-N}^t\text{Bu})_2$, which involes an equilibrium between four η^5-Cp coordination compound **228** and three η^5/one η^1-coordination compound **229**.[446] Similarly, an imido-bridged compound $[\text{CpTaCl}]_2(\mu\text{-N}^t\text{Bu})_2$ is prepared by the C_8K reduction[152] (Scheme 87).

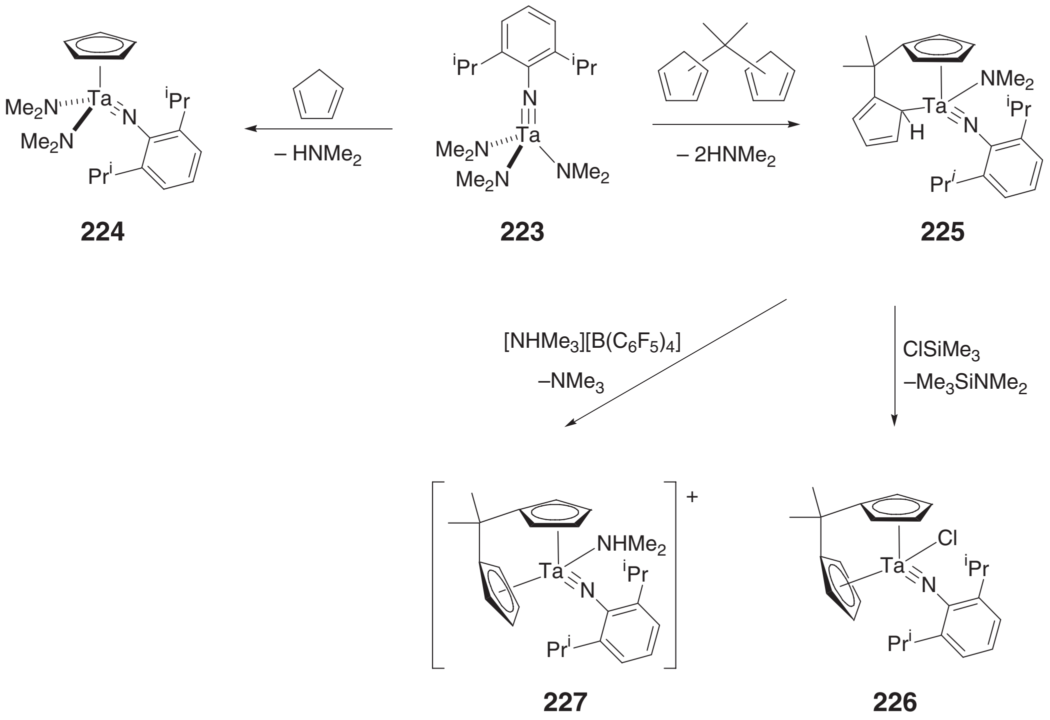
Eisenberg and his co-workers have reported a dinucler dinitrogen complex, $[\text{Cp}^*{}_2\text{TaCl}]_2(\mu\text{-N}_2)$ **230**, with the nitrogen molecule coordinated in an end-on fashion to each tantalum center.[40] Sodium amalgam reduction of $\text{Cp}^*{}_2\text{TaCl}_2$ has been reported to give a transient "$\text{Cp}^*{}_2\text{TaCl}$" species[41] which under nitrogen atmosphere converts to **230**. Dinitrogen is readily replaced by CO and H_2, giving $\text{Cp}^*{}_2\text{TaCl(CO)}$ and $\text{Cp}^*{}_2\text{TaH}_2\text{Cl}$ contaminated by $\text{Cp}^*{}_2\text{TaHCl}_2$ and $\text{Cp}^*\text{Ta}({=}\text{O})\text{H}$.[40]

Tantalocene complex $\text{Cp}^*(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{TaCl}_2$ containing an aminoethyl-functionalized ligand is prepared from the reaction of $\text{Cp}^*\text{TaCl}_3(\text{PMe}_3)$ **231** with $\text{LiC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2$,[200] according to Bercaw's method.[447] Similarly, $\text{Cp}^*(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)\text{TaCl}_2$ is also obtained from **231** and $\text{LiC}_5\text{H}_4\text{PPh}$.[48] Reaction of $[\text{TaCl}_3(\text{L})_2]_2(\mu\text{-}1,\text{n-NC}_6\text{H}_4\text{N})$ with 4 equiv. of $\text{Li}(\text{C}_5\text{H}_4\text{SiMe}_3)$ affords $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{TaCl}](\mu\text{-}1,\text{n-NC}_6\text{H}_4\text{N})$,[63] while the reaction with 2 equiv. of $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$ or Cp^*SiMe_3 gives half-sandwich type products $[\text{Cp}'\text{TaCl}_2]_2(\mu\text{-}1,\text{n-NC}_6\text{H}_4\text{N})$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ and Cp^*).[159] $[(\text{Cp}')\text{TaCl}_2]_2(\mu\text{-}1,n\text{-NC}_6\text{H}_4\text{N})$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ and Cp^*) can also be

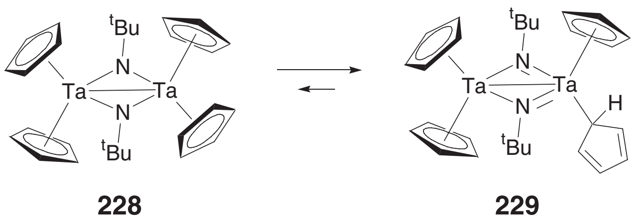
$$\text{Cp}^*\text{Cp}''\text{TaCl}_2 \;+\; \text{PCl}_5 \longrightarrow \text{Cp}^*\text{Cp}''\text{TaCl}_3$$

$$\text{Cp}'' = \eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3) \text{ and } \eta^5\text{-C}_5\text{H}_3\text{-}1,3\text{-}(\text{SiMe}_3)_2$$

Scheme 85



Scheme 86



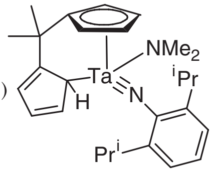
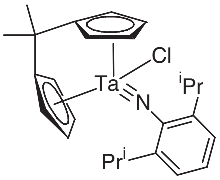
Scheme 87

prepared by treating Cp′TaCl$_4$ with 0.5 equiv. of $(Me_3Si)_2NC_6H_4N(SiMe_3)_2$.[159] Alkylations of [Cp′TaCl$_2$](μ-1,4-NC_6H_4N) by MeLi, Me_3SiCH_2MgCl, or $(PhCH_2)_2Mg$ give the corresponding alkylated products, [(η^5-$C_5H_4SiMe_3$)TaR$_2$]$_2$(μ-1,4-NC_6H_4N) (R = Me, CH_2SiMe_3, CH_2Ph).[159] In the reaction with $ZnMe_2$, monomethylated product can be selectively obtained.[159] Intramolecular Arbuzov rearrangement of $Cp_2Ta(PPh_2)(P(OMe)_2R)$ (R = Ph and OMe), which were derived from the sequential treatment of $Cp_2TaH(P(OMe)_2R)$ with $ClPPh_2$ followed by OH-, afforded the corresponding tantalaphosphonates, $Cp_2Ta(PPh_2Me)(P({=}O)(OMe)R)$.[39] The phosphoryl oxygen of the corresponding niobocene was reported to bind unsaturated metal carbonyl, $Cr(CO)_5$, giving a heterobimetallic complex.[39] $Cp^*{}_2Ta({=}Se)I$ served as a useful synthetic precursor for organoselenium derivatives: methylation afforded $Cp^*{}_2Ta(\eta^2\text{-}SeCH_2)H$ and $Cp^*{}_2Ta({=}Se)Me$ (Table 17).[207]

5.03.7.5 η^6-Complexes

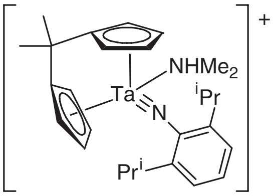
An improved synthesis of $[(\eta^6\text{-}C_6Me_6)Ta(Cl_2)]_2$ is reported.[450] The combination of $[(\eta^6\text{-}C_6Me_6)Ta(Cl_2)]_2$, CO_2, and NH^iPr_2 results in the formation of a dinuclear carbamate compound $[(\eta^6\text{-}C_6Me_6)Ta(O_2CN^iPr_2)_2]_2$.[450] A series of η^6-hexamethylbenzene alkyl and aryl complexes of tantalum(III) supported by aryloxide and arenethiolate ligands are prepared (Table 18).[451] The reaction of $(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Cl$ (Ar = C_6H_3-2,6-$^iPr_2$) with MeMgBr affords

Table 17 Metallocene complexes[a]

Compound	*Comments*	*References*
Ta(III) complexes		
$Cp^*_2TaCl(THF)$	Prep: Na/Hg + Cp^*TaCl_2 in THF	41
$[Cp^*_2TaCl]_2(\mu-N_2)$	Prep: Na/Hg + $Cp^*TaCl_2 + N_2$, X-ray	40
$[(\eta^5-Cp)_2Ta](\mu-N^tBu)_2[Ta(\eta^5-Cp)(\eta^1-Cp)]$	Prep: $Cp_2Ta({=}N^tBu)Cl + C_8K$, X-ray	446
$[CpTaCl]_2(\mu-N^tBu)_2$	Prep: $CpTa({=}N^tBu)Cl_2 + C_8K$	152
Ta(IV) complexes		
$Cp^*(\eta^5-C_5H_4PPh_2)TaCl_2$	Prep: $Cp^*TaCl_3(PMe_3) + LiC_5H_4PPh_2$	48
$Cp^*[\eta^5-C_5H_4(SiMe_3)]TaCl_2$	Prep: $Cp^*TaCl_4 + Li[C_5H_4\ (SiMe_3)]$ + Na/Hg, X-ray	45
$Cp^*[\eta^5-C_5H_3-1,3-(SiMe_3)_2]TaCl_2$	Prep: $Cp^*TaCl_4 + Li[C_5H_3-1,3-(SiMe_3)_2]$ + Na/Hg	45
$Cp'[\eta^5-C_5H_4SiMe_2(CH_2CH{=}CH_2)]TaCl_2$	Prep: $Cp'TaCl_4 + Li\ [C_5H_4SiMe_2(CH_2CH{=}CH_2)]$ + Na/Hg; $Cp' = Cp, Cp^*$	448
Ta(V) complexes		
$Cp^*_2TaF_3$	Prep: $Cp^*_2TaH_3 + Py(HF)_x$	209
$[Cp^*_2TaF_5]$-	Prep: $Cp^*_2TaH_3 + Et_3N(HF)_3$	209
cis-$Cp^*_2TaF(CN)_2$	Prep: $Cp^*_2TaF_3 + Me_3SiCN$	209
$Cp^*[\eta^5-C_5H_4(SiMe_3)]TaCl_3$	Prep: $Cp^*[\eta^5-C_5H_4(SiMe_3)]TaCl_2 + PCl_5$	45
$Cp^*[\eta^5-C_5H_3-1,3-(SiMe_3)_2]TaCl_3$	Prep: $Cp^*[\eta^5-C_5H_3-1,3-(SiMe_3)_2]TaCl_2 + PCl_5$	45
ansa-$[Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_3-3-R)]TaCl_3$	Prep: $TaCl_5 + [Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_3-3-R)](SnBu_3)_2$; $R = {}^iPr, {}^tBu$	308
ansa-$[Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_2-2,4-{}^iPr_2)]TaCl_3$	Prep: $TaCl_5 + [Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_2-2,4-{}^iPr_2)](SnBu_3)_2$	308
ansa-$[Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_3-3-R)]TaCl_2$	Prep: *ansa*-$[Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_3-3-R)]TaCl_3$ + Zn dust; $R = {}^iPr, {}^tBu$	308
ansa-$[Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_2-2,4-{}^iPr_2)]TaCl_2$	Prep: *ansa*-$[Me_2Si(\eta^5-C_5H_4)(\eta^5-C_5H_2-2,4-{}^iPr_2)]TaCl_3$ + Zn dust	308
ansa-$[Me_2C(\eta^5-C_5H_4)(\eta^1-C_5H_4)]Ta({=}NC_6H_3$- $2,6-{}^iPr_2)(NMe_2)$ 	Prep: $Ta({=}NC_6H_3-2,6-{}^iPr_2)(NMe_2)_3 + Me_2C(C_5H_5)_2$, X-ray	436,437
ansa-$[Me_2C(\eta^5-C_5H_4)_2]Ta({=}NC_6H_3$- $2,6-{}^iPr_2)Cl$ 	Prep: [*ansa*-$Me_2C(\eta^5-C_5H_4)(\eta^1-C_5H_4)]Ta({=}NC_6H_3-2,6-{}^iPr_2)(NMe_2) + Me_3SiCl$,X-ray	436, 437
$(\eta^5-C_5H_5)_2(\eta^1-C_5H_5)Ta({=}NEMe_3)$	Prep: $Ta({=}NEMe_3)Cl_3(py)_2$ + 3CpNa; E = C (X-ray), Si (X-ray)	439
$Cp_2Ta({=}N^tBu)Cl$	Prep: $Ta({=}N^tBu)Cl_3(py)_2$ + 2NaCp	152
$CpCp^*Ta({=}N^tBu)Cl$	Prep: $Cp^*Ta({=}N^tBu)Cl_2$ + NaCp	152
ansa-$[Me_2C(\eta^5-C_5H_4)_2]Ta({=}N^tBu)Cl$	Prep: $K_2[(C_5H_4)_2CMe_2] + Ta({=}N^tBu)Cl_3(py)_2$	128
$(\eta^5-C_5H_4{}^tBu)_2Ta({=}S)(SEt)$	Prep: $(\eta^5-C_5H_4{}^tBu)_2TaH_3$ + ethylene sulfide	203
$(\eta^5-C_5H_4{}^tBu)_2Ta({=}S)(S^iPr_2)$	Prep: $(\eta^5-C_5H_4{}^tBu)_2TaH_3$ + propylene sulfide, X-ray	203
$[(\eta^5-C_5H_4{}^tBu)_2Ta(SR)(SR^1)]^+$	$R = R^1 = Et$; $R = H$, $R^1 = {}^iPr$; $R = Me$, $R^1 = {}^iPr$	203
$(\eta^5-C_5H_4{}^tBu)_2(S^iPr)Ta(\mu-S)W(CO)_5$	Prep: $(\eta^5-C_5H_4{}^tBu)_2Ta({=}S)(S^iPr) + W(CO)_5(THF)$	203
$(\eta^5-C_5H_4{}^tBu)_2Ta(\mu-S^iPr)(\mu-S)W(CO)_4$	Prep: $(\eta^5-C_5H_4{}^tBu)_2Ta({=}S)(S^iPr) + W(CO)_4(pip)$	203
$Cp^*(\eta^5-C_5H_4CH_2CH_2NMe_2)TaCl_2$	Prep: $Cp^*TaCl_3(PMe_3) + LiC_5H_4CH_2CH_2NMe$	200
$Cp_2TaPR_2(L)$	$Cp_2Ta(H)(L) + ClPR_2 + OH$-; $L = P(OMe)_3$ and $PPH(OMe)_2$	39
$Cp_2Ta(PPh_2Me)(POR^1R^2)$	$R^1 = R^2 = OMe$; $R^1 = OMe$, $R^2 = Ph$	39
$Cp_2Ta(PPh_2Me)(POR^1R^2)$	$R^1 = R^2 = OMe$; $R^1 = OMe$, $R^2 = Ph$	39
$Cp^*_2Ta({=}NPh)Cl$	Prep: $Cp^*_2TaCl(THF) + PhN_3$, X-ray	41
$Cp^*_2Ta({=}O)Cl$	Prep: $Cp^*_2TaCl(THF) + N_2O$	41
$Cp^*_2Ta({=}Se)(I)$	Prep: $Cp^*_2Ta(\eta^2-Se_2)(H)$ + MeI	207
$[Cp^*_2TaCl]_n$		41

(Continued)

Table 17 (Continued)

Compound	*Comments*	*References*
$[(\eta^5\text{-}C_5H_4SiMe_3)_2TaCl]_2(\mu\text{-}1,n\text{-}NC_6H_4N)$	Prep: $[TaCl_3(L)_2]_2(\mu\text{-}1,n\text{-}NC_6H_4N) + 4Li(C_5H_4SiMe_3)$, X-ray for $n = 4$	63
$[Cp'TaCl_2]_2(\mu\text{-}1,n\text{-}NC_6H_4N)$	Prep: $[TaCl_3(L)_2]_2(\mu\text{-}1,n\text{-}NC_6H_4N) + 2C_5H_4(SiMe_3)_2$ or $2Cp^*SiMe_3$; $Cp' = \eta^5\text{-}C_5H_4SiMe_3$, Cp^* (X-ray for $n = 4$) Prep: $2\ Cp'TaCl_4 + (Me_3Si)_2NC_6H_4N(SiMe_3)_2$	159
$Cp^*[\eta^5\text{-}C_5H_4SiMe_2(CH_2CH{=}CH_2)]Ta({=}N^tBu)Cl$	Prep: $Cp^*Ta({=}N^tBu)Cl_2 +$ Li $[C_5H_4SiMe_2(CH_2CH{=}CH_2)]$	448
Carborane, carbollide, and related complexes		
$Cp^*(\eta^5\text{-}C_4H_4BN^iPr_2)TaCl_2$	Prep: $Cp^*(\eta^5\text{-}C_4H_4BN^iPr_2)TaMe_2 + CH_2Cl_2$ or $CHCl_3$	137
	Prep: $(\eta^5\text{-}C_4H_4BiN^iPr_2)TaCl_3 + LiCp^*$	42
$(\eta^5\text{-}C_5H_4Me)_2Ta(\eta^2\text{-}C_4H_4BiNH^iPr_2)Cl$	Prep: $(\eta^5\text{-}C_4H_4BiN^iPr_2)TaCl_3 +$ ex. LiC_5H_4Me, X-ray	42
$(C_5H_5BR)(\eta^5\text{-}C_4H_4BiNH^iPr_2)TaCl_2$	Prep: $(\eta^5\text{-}C_4H_4BiN^iPr_2)TaCl_3 + Li[C_5H_5BR]$; $R = Ph, NMe_2, N^iPr_2$ (X-ray)	42
$Cp(\eta^5\text{-}R_2C_2B_4H_4)TaCl_2$	Prep: $CpTaCl_4 + 2[R_2C_2B_4H_5]^-$; $R = Me, Et, SiMe_3$ (X-ray)	141
$Cp^*(\eta^5\text{-}Et_2C_2B_4H_4)TaCl_2$	Prep: $Cp^*TaCl_4 + 2\ [Et_2C_2B_4H_5]^-$, X-ray	141
$(\eta^5\text{-}C_5R_5)[\eta^5\text{-}Cp^*Co(Et_2C_2B_3H_3)]TaCl_2$	Prep: $CpTaCl_4 + 2\ [Cp^*Co(Et_2C_2B_3H_4)]^-$; $R = H, Me$ (X-ray)	141
$Cp(\eta^5\text{-}Et_2C_2B_4H_3X)TaCl_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaCl_2 + X_2$ or NXS	143
$Cp(\eta^5\text{-}Et_2C_2B_4H_2X_2)TaCl_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaCl_2 + X_2$	143
$Cp(\eta^5\text{-}Et_2C_2B_4HBr_3)TaCl_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaCl_2 + 10Br_2$	143
$Cp(\eta^5\text{-}Et_2C_2B_4HBr_3)TaCl_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaCl_2 + 10Br_2$	143
$Cp[\eta^5\text{-}Cp^*Co(Et_2C_2B_3Br_3)]TaCl_2$	Prep: $Cp[\eta^5\text{-}Cp^*Co(Et_2C_2B_3H_3)]TaCl_2 + NBS$	143
$Cp(\eta^5\text{-}Et_2C_2B_4H_4)ClTa[N{=}C(R)Me]$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaCl(Me) + RCN$; $R = Me, Et$	142
$Cp(\eta^5\text{-}Et_2C_2B_4H_4)Ta(OPh)_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaCl_2 + 2PhONa$	141
$[Cp(\eta^5\text{-}Et_2C_2B_4H_4)Ta(NCMe)_2](BF_4)_2$	Prep: $Cp(\eta^5\text{-}Et_2C_2B_4H_4)TaMe_2 + 2HBF_4$ in CH_3CN	141
$Cp^*(\eta^5\text{-}C_4H_4BN^iPr_2)Ta(PMe_3)_2$	Prep: $Cp^*(\eta^5\text{-}C_4H_4BN^iPr_2)TaMe_2 + H_2 + PMe_3$	138
$Cp^*(\eta^5\text{-}C_4H_4BMe)Ta(PMe_3)_2$	Prep: $Cp^*(\eta^5\text{-}C_4H_4BMe)TaMe_2 + H_2 + PMe_3$	138
Cationic complexes		
$[Cp^*_2TaF_2][BF_4]$	Prep: $Cp^*_2TaF_3 + Et_2OBF_3$, X-ray	209
$[Cp^*_2TaMe(OH)][B(OH)(C_6F_5)_3]$	X-ray	449
$\{[ansa\text{-}Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4)]Ta({=}NC_6H_3\text{-}2,6\text{-}^iPr_2)(NHMe_2)\}^+$  	Prep: $[ansa\text{-}Me_2C(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)]Ta({=}NC_6H_3\text{-}2,6\text{-}^iPr_2)(NMe_2) + [NHMe_3][B(C_6F_5)4]$	436, 437

^{a}Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Tp = tris(pyrazolyl)borate, Tp* = tris(3,5-dimethylpyrazolyl)borate, dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphosphino)ethane.

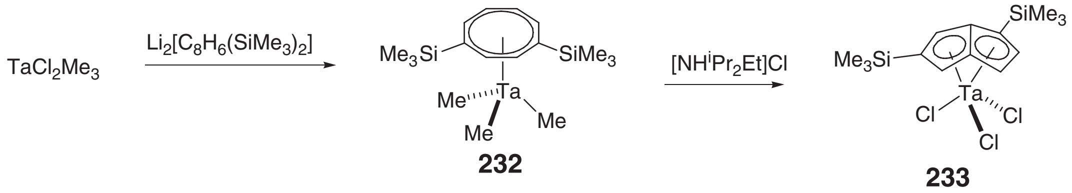
$(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Me$, while the reations of $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ with RMgBr or RLi form dialkylated compounds $(\eta^6\text{-}C_6Me_6)Ta(OAr)R_2$ ($R = Me, Et, CH_2SiMe_3, Ph$) and monoalkylated compounds $(\eta^6\text{-}C_6Me_6)Ta(OAr)R(X)$ ($R = Me, Et, CH_2SiMe_3, Ph$).[451] Arenethiolate derivatives are also prepared by reacting $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ with LiSAr ($Ar = C_6H_2\text{-}2,4,6\text{-}i\text{Pr}_3$, $C_6H_2\text{-}2,4,6\text{-}Me_3$).[451] The reduction of $Cp^*_2TaCl(THF)$ using $LiBHEt_3$ induces C–H bond activation of one methyl group of the Cp^* ligand, giving $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$.[41]

5.03.7.6 η^8-Complexes

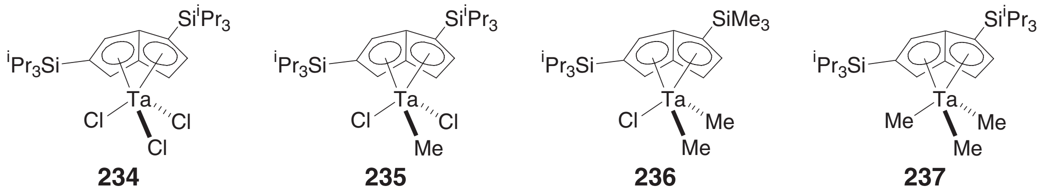
Ligand replacement of an anionic homoleptic anthracene compound, $[Ta(1\text{-}4\text{-}\eta^4\text{-anthracene})_3]$-, with COT in THF resulted in high yield of the known compound, $[Ta(COT)_3]$-.[6] The unique intramolecular conversion of mononuclear η^8-cyclooctatetraene complex 232 into mononuclear η^8-coordinated pentalene complex 233 was reported[452] (Scheme 88). Reaction of $TaCl_2Me_3$ with the dianion of 1,4-bis(trimethylsilyl)cyclooctatetraene affords 232, which is treated with $[NH^IPr_2Et]Cl$ in dichloromethane; sublimation affords 233 in low yield. The crystallographic

Table 18 η^6-Arene and related complexes

Compound	*Comments*	*References*
$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{AlCl}_4)_2$	Prep: $\text{TaCl}_5+\text{C}_6\text{Me}_6+\text{Al}+\text{AlCl}_3$	450
$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{Cl}_2)]_2$	Prep: $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{AlCl}_4)_2+\text{THF}$	450
$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{O}_2\text{CN}^i\text{Pr}_2)_2]_2$	Prep: $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{Cl}_2)]_2+4[\text{NH}_2^i\text{Pr}_2][\text{O}_2\text{CN}^i\text{Pr}_2]$	450
$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})_2\text{Me}$	Prep: $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})_2\text{Cl}+\text{MeMgBr}$; $\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$	451
$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{R}_2$	Prep: $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{Cl}_2+2\text{RMgBr}$ or RLi; R = Me, Et (X-ray), CH_2SiMe_3, Ph; $\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$	451
$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{R}(\text{X})$	Prep: $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{Cl}_2+\text{RMgBr}$ or RLi; R = Me, Et, CH_2SiMe_3, Ph; $\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$	451
$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{R}(\text{H})$	Prep: $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{R}(\text{X})+\text{RMgBr}$ or RLi; R = Et, CH_2SiMe_3; $\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$	451
$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})(\text{CH}_2\text{SiMe}_3)(\text{Ph})$	Prep: $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{CH}_2\text{SiMe}_3(\text{Cl})+\text{PhLi}$; $\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$	451
$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})(\text{SAr}')\text{Cl}$	Prep: $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{OAr})\text{Cl}_2+\text{LiSAr}'$; $\text{Ar}'=\text{C}_6\text{H}_2\text{-2,4,6-}i\text{Pr}_3$, $\text{C}_6\text{H}_2\text{-2,4,6-Me}_3$; $\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$	451
$\text{Cp}^*(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{TaH}_2$	Prep: $\text{Cp}^*_2\text{TaCl}(\text{THF})+\text{LiBHEt}_3$	41



Scheme 88



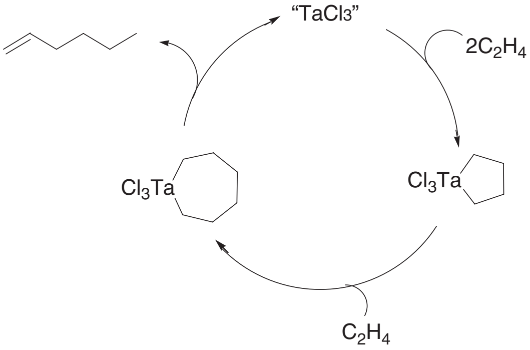
Scheme 89

characterization revealed that 233 is the pentalene complex with all eight carbons coordinated to the tantalum center. Some pentalene complexes 234–237 were alternatively prepared from the reaction of TaCl_2Me_3 with the dipotassium salt of $\text{C}_8\text{H}_6\text{-1,4-(Si}^i\text{Pr}_3)_2$ followed by addition of BX_3 or 1 or 2 equiv. of $[\text{NH}^i\text{Pr}_2\text{Et}]\text{Cl}$[453] (Scheme 89).

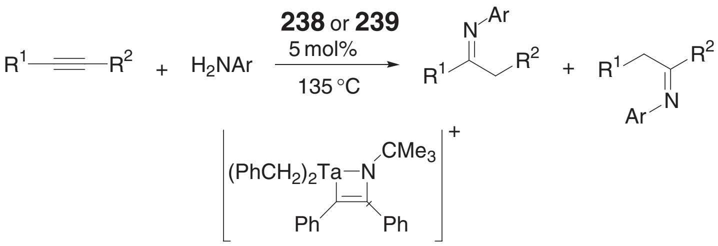
5.03.8 Tantalum Complexes in Catalysis and Organic Synthesis

5.03.8.1 Polymerization of Alkenes

Some tantalum complexes have been utilized as catalysts for polymerization of ethylene, but not for α-olefins. The attractive report in this topic is the living polymerization of ethylene by using tantalum diene complexes that are isolelectronic to metallocene complexes of hafnium,[368,369] and activity is improved when niobium analogs are used as catalysts.[454] Some imido complexes are also reported to catalyze the ethylene polymerization.[76,153,155,455] Bis(2-benzylaminopyridinato) complexes were reported to have high activities for ethylene polymerization.[456] MMA is polymerized by MMA compounds of tantalum.[387]



Scheme 90



178

Scheme 91

5.03.8.2 Trimerization of Ethylene

Alkylation of $TaCl_5$ by $SnMe_4$, $AlMe_3$, or $ZnMe_2$ in chlorobenzene generates an active catalyst for ethylene trimerization, selectively giving 1-hexene (up to 99% selectivity).[457] Although it has been reported that these methylation agents can produce $TaCl_3Me_2$ and its derivatives,[57] a Ta(III) species generated initially via reductive reaction reacts with 2 equiv. of ethylene to give tantalacyclopentane, which further reacts with ethylene to give a metallacycloheptane intermediate (Scheme 90). Activity and selectivity are almost the same as for a chromium catalyst system.[458] Theoretical calculation showed that the trimerization process involves stepwise formation of tantalacycloalkanes and the conversion of tantalacycloheptane to 1-hexene adduct of $TaCl_3$ occurs as a concerted process with relatively low free energy (25.5 kcal mol^{-1}), whereas the dimerization process is not favorable because of the non-existence of a concerted reductive elimination process of tantalacyclopentane.[459]

5.03.8.3 Hydroamination

Neutral and cationic alkyltantalum imido complexes, $Me_3CN{=}Ta(CH_2R)_3$ (**238**: R = Ph, ^{t}Bu) and $[Me_3CN{=}Ta(CH_2Ph)_2]B(C_6F_5)_4$ **239**, serve as catalysts for hydroamination of internal and terminal alkynes and allene.[353] As a controlled reaction, the cationic complex **239** reacts with diphenylacetylene to give an azametallacyclobutene **178**, which also catalyzes the addition of aniline to diphenylacetylene (Scheme 91).

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5.04
Chromium Compounds with CO or Isocyanides

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5.04.1 General Remarks

The field of chemistry involving the syntheses, structures, reactions, and molecular dynamics of molecules possessing at least one chromium–carbonyl linkage is vast. The previous editions, COMC (1982) and COMC (1995), covered the important developments up to mid-1993, and this chapter attempts to highlight the more important advances and also to suggest areas for future investigation. It became evident that, in addition to the expected gradual improvements in experimental techniques, there has been a major trend to combine observation with theory. Of particular relevance is the ready accessibility of high-level computational approaches, derived not merely from the availability of better software but also from the continually enhanced power and speed of personal computers. Thus, many publications describe combined synthetic and calculation studies that provide a theoretical underpinning for the observed phenomena.

As the range of chromium carbonyl complexes continues to burgeon, one is not only faced with the decision to focus on the topics which have not been comprehensively reviewed recently, but also to provide literature entries to those extremely well-developed areas that have attracted the attention of numerous reviewers. Thus, in recent years, there has been a major effort to link chromium carbonyl moieties to almost all of the main group elements, and much of this work is summarized herein. In addition, arene chromium tricarbonyls have been very widely exploited, not only to take advantage of the modified properties of the complexed arene ring and its attached substituents, but also for their stereodirecting characteristics. In these cases, the reader is provided with a list of relevant reviews as well as a number of selected examples that highlight the particular reaction type. Similarly, chromium carbene complexes have become classic reagents for the construction of polycyclic aromatics and, once again, we cite important reviews and also provide some examples to illustrate the versatile chemistry of these systems.

Even the researcher already familiar with the general trends in organochromium chemistry, and who is comfortable with today's technology, may find an initial web-based search of the area somewhat daunting since it may merely reveal an enormous mass of indigestible information. Nevertheless, a search for the synthesis or properties of any specific chromium carbonyl compound is likely to be most readily accomplished via the web; this is especially true for X-ray crystallographically determined structures where the Cambridge Crystallographic Database provides an extremely valuable resource.

We have also attempted to gather and correlate the less readily available information on the chemical, physical, spectroscopic, and structural properties of molecules containing chromium carbonyl linkages, as well as noting their potential applications. However, we emphasize once again the need to place this chapter in the context of the previous reports in COMC (1982), chapters 26.1 and 26.2, and in COMC (1995), chapters 3–8.

5.04.2 Neutral, Cationic and Anionic Chromium Carbonyls

Previous work on $Cr(CO)_6$ and related species has been covered in COMC (1982) and COMC (1995).[1,2]

5.04.2.1 Computational Studies and Spectroscopic Measurements

The octahedral (O_h) and square pyramidal (C_{4v}) structures of $Cr(CO)_6$ and $Cr(CO)_5$ have been optimized at high levels of theory including the modified coupled-pair functional (MCPF), single and double excitation coupled-cluster (CCSD), and CCSD(T) levels of theory (including a perturbational estimation for connected triple excitations).[3] The sequential bond energies of $[Cr(CO)_x]^+$, $x = 1$–6, have been determined by collision-induced dissociation in a guided ion beam tandem mass spectrometer. The sum of these bond dissociation energies, 4.99 ± 0.14 eV, is in good agreement with literature thermochemistry. The observation that the relative bond strengths vary non-monotonically with the number of ligands was discussed in terms of spin conservation and ligand field theory.[4]

A combined theoretical and experimental study on $Cr(CO)_6$ using core electron spectroscopy has been reported with some previous assignments being revised.[5] Spectrally resolved sonoluminescence, specifically atomic line emission from metal atom excited states, has been observed upon ultrasonic irradiation of $Cr(CO)_6$ in silicone oil solutions. This phenomenon arises from acoustic cavitation (the formation, growth, and implosive collapse of bubbles), which produces localized hot spots with extreme temperatures and pressures and very short lifetimes, thus stripping CO from the metal complexes and thermally populating electronic excited states of the metal atoms.[6]

Several studies have been reported of known and as-yet unknown dichromium species that will provide challenges for the experimentalists. Thus, the optimized geometries, net charges, and Mulliken bond orders of the super-reduced chromium carbonyl anions $[Cr(CO)_5]^{2-}$, $[Cr(CO)_4]^{4-}$, $[Cr(CO)_3]^{6-}$ have been studied at the density functional theory (DFT) level. As expected, from the conventional orbital model of enhanced backdonation from an electron-rich metal into π^*-orbitals on the carbonyl ligands, the calculated C–O distances are lengthened monotonically with increasing anionic charge, but the M–C distances are significantly lengthened only in the higher reduced states. Moreover, the DFT calculations show that although the Mulliken net charges on the M, C, and O atoms all increase, the excess anionic charge is mainly located on the central metal atom.[7]

DFT calculations were used to obtain the first structural characterization of the unsaturated dichromium carbonyl $Cr_2(CO)_9$, which is predicted to have a remarkably short metal–metal bond length of 2.31 (B3LYP) or 2.28 Å (BP86). This chromium–chromium distance is essentially identical to the known value for the Cr≡Cr triple bond in $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$. The dissociation energy to the fragments $Cr(CO)_4$ and $Cr(CO)_5$, which involves cleavage of Cr–Cr and Cr–C linkages, was evaluated as 134 (B3LYP) or 180 kJ mol^{-1} (BP86), whereas $Cr_2(CO)_{10}$ and the saturated $Cr_2(CO)_{11}$ system have negligible dissociation energies. The minimum-energy structure for $Cr_2(CO)_9$ structure is of C_s-symmetry with the two chromium atoms asymmetrically bonded to the bridging carbonyls. However, a structure of C_2-symmetry, and also a D_{3h}-isomer analogous to $Fe_2(CO)_9$, lie within 4 kJ mol^{-1}, and so $Cr_2(CO)_9$ is expected to be highly fluxional.[8] DFT has also been used to investigate the conformations and thermochemistry of the singlet and triplet potential energy surfaces (PES) of $Cr_2(CO)_{10}$. The global minimum-energy structure for the lowest singlet state of C_{2h}-symmetry is consistent with a model of two interacting $Cr(CO)_5$ fragments in which one carbonyl in each fragment acts as an asymmetric four-electron donor bridging carbonyl, with chromium–chromium distances of 2.93 (B3LYP) or 2.83 Å (BP86). Avoiding a Cr···Cr bond by incorporating four-electron donor CO groups in this way allows each chromium atom in singlet $Cr_2(CO)_{10}$ to attain the favored 18-electron configuration by using, in a simple picture of the bonding, only the six octahedral sp^3d^2-hybrids. The dissociation energy to two $Cr(CO)_5$ fragments, or to $Cr(CO)_6$ and $Cr(CO)_4$ fragments, is predicted to be 42 kJ mol^{-1}.

The lowest triplet state of $Cr_2(CO)_{10}$ is predicted to lie approximately 42 kJ mol^{-1} above the singlet global minimum. In the case of triplet $Cr_2(CO)_{10}$, the lowest energy minima were found to be of C_2- and C_{2h}-symmetry, with similar energies. The chromium–chromium distances in triplet $Cr_2(CO)_{10}$ were found to be shorter than those in the corresponding singlet structures, namely 2.81 (B3LYP) or 2.68 Å (BP86) suggesting a $\sigma + 2(1/2)\pi$ Cr═Cr double bond similar to the O═O bond in O_2, or the Fe═Fe bond in the experimentally observed triplet state system $(C_5Me_5)_2Fe_2(\mu\text{-}CO)_3$.[9]

Most recently, DFT has been used to provide the first structural characterization of the highly unsaturated dichromium carbonyl $Cr_2(CO)_8$ which is predicted to have a short metal–metal bond length of 2.30 (B3LYP) or 2.28 Å (BP86). The minimum-energy structure exhibits distorted C_s-symmetry, with non-equivalent chromium atoms and two equivalent asymmetrically bridging carbonyls. A high-symmetry (D_{2d}) structure with a nominal chromium–chromium quadruple bond lies approximately 92 kJ mol^{-1} higher in energy. The dissociation energy of $Cr_2(CO)_8$ to the fragments $2Cr(CO)_4$, or $Cr(CO)_3$ plus $Cr(CO)_5$, is predicted to be about 142 (B3LYP) or 184 kJ mol^{-1} (BP86), indicating that $Cr_2(CO)_8$, like $Cr_2(CO)_9$ but unlike $Cr_2(CO)_{10}$ and $Cr_2(CO)_{11}$, is stable with respect to dissociation into its fragments.[10]

The structure of the binuclear metal carbonyl ion $[Cr_2(CO)_6]^+$ found in laser ablation-molecular beam (LAMB) experiments has been examined by DFT calculations. Three different conformations were optimized: a D_{3d}-structure with three terminal carbonyl groups on each chromium atom, a D_{2h}-isomer with two bridging carbonyl groups and two terminal carbonyl groups on each chromium atom, and finally a molecule of D_{4h}-symmetry with four bridging carbonyl groups and one terminal carbonyl group on each chromium atom. Of these, the most stable conformation is the D_{3d} which is 36.76 and 286.44 kJ mol^{-1} lower in energy than the D_{2h}- and D_{4h}-structures, respectively.[11]

5.04.2.2 Experimentally Determined Structures

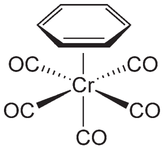
Several structures have been reported for the decacarbonyldichromate(2−) ion, $[Cr_2(CO)_{10}]^{2-}$. The dianion was prepared by naphthalenide reduction of a Cr(0) precursor, and was characterized as its bis-[bis(triphenylphosphine)-iminium] salt $[(Ph_3P)_2N]_2[Cr_2(CO)_{10}]$ in which a non-coordinating countercation was used.[12] The $[Cr_2(CO)_{10}]^{2-}$ dianion is structurally similar to that in a previously characterized compound with a $[K(DME)_2]^+$ counterion (DME = dimethoxyethane), despite the loss of the solid-state ion pairing present in the $[K(DME)_2]^+$ salt. This dianion has also been obtained by reduction of $Cr(CO)_6$ with sodium/thallium amalgam in DMF followed by addition of 2,2,2-crypt in ethylenediamine solvent. The geometric parameters observed differ significantly from those reported previously for the $[K(DME)_2]^+$ and $[(Ph_3P)_2N]^+$ salts, reflecting the weaker coordinating nature of the [2,2,2-crypt-Na]$^+$ cation.[13]

5.04.3 Chromium Carbonyls with Very Weakly Bonded Ligands

Metal–dinitrogen bond energies have been calculated for the series $Cr(CO)_{6-n}(N_2)_n$, where $n = 1$–6, by using DFT.[14] In all cases, the metal–N_2 bond is weaker than the metal–CO bond because CO is both a better donor and a better acceptor of electron density. The calculated bond energies for Cr–N_2 bonds for the lowest energy isomers of the chromium complexes were 100, 96, 92, 88, 84, and 105 kJ mol^{-1} for $n = 1$–6, respectively. The trend of decreasing bond energy with added N_2 ligands was attributed to weaker orbital interactions. The exception was $Cr(N_2)_6$, which was predicted to be more stable than the carbonyl-containing complexes and was ascribed to the absence of a CO *trans*-effect.[15]

Photolysis of $Cr(CO)_6$ in low-temperature, rare-gas solutions gives transient organometallic complexes $LCr(CO)_5$, where L is a weak ligand such as CO_2, N_2O, Xe, or Kr. The short-lived species were detected by time-resolved IR spectroscopy at 150–200 K.[16] Subsequently, *ab initio* quantum mechanical calculations at the MP2 and CCSD(T) level of theory using effective core potentials for the heavy atoms, as well as density functional calculations using various gradient corrections, have been reported for the noble gas complexes $(OC)_5Cr$–Ng (Ng = Ar, Kr, Xe). The optimized geometries show increasing Cr–noble gas distances in the order Ar < Kr < Xe, and metal–Ng bond energies in close accord with experimentally observed data.[17]

The gas-phase reactions of benzene and of C_6D_6 with $Cr(CO)_5$ were studied by use of time-resolved IR spectroscopy. Presumably, the product is (η^2-benzene)$Cr(CO)_5$, **1**, in which benzene coordinates to the metal via an isolated double bond. The temperature dependence of the rate of dissociative loss of benzene from **1** revealed a bond-dissociation energy of 38.5 ± 3.3 kJ mol^{-1}.[18] In a more recent study, displacement of the benzene ligand from photolytically generated $(OC)_5Cr(\eta^2$-benzene) by THF and a series of methyl-substituted tetrahydrofurans was studied by using laser flash photolysis. The activation enthalpy of 47.7 ± 4.6 kJ mol^{-1} was considered to be a lower estimate of the $(CO)_5Cr$–(η^2-benzene) bond-dissociation enthalpy.[19]



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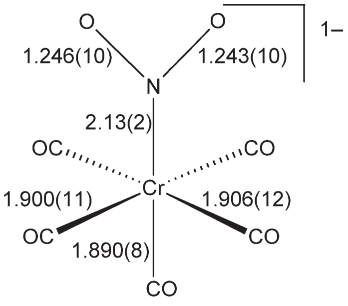
An interesting development has been the use of a miniature flow reactor for photochemical reactions in supercritical fluids. Thus, $[Cr(CO)_5(\eta^2\text{-}C_2H_4)]$ was isolated, for the first time on a preparative scale, by the UV photolysis of $[Cr(CO)_6]$ in supercritical C_2H_4 at room temperature.[20] Similarly, the propene complex $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ has also been isolated as a stable solid.[21] In related work, the kinetics of the replacement of the weakly bound alkene ligand in (η^2-(*Z*)-cyclooctene)$Cr(CO)_5$ by tetracyanoethylene to give (TCNE)$Cr(CO)_5$ suggest that the rate-determining step is the cleavage of the metal–olefin bond in the starting material. The large positive value of the activation entropy is consistent with the dissociative nature of reaction.[22]

5.04.4 Nitro and Nitroso Chromium Carbonyls

$Cr(CO)_6$ reacts with Me_3NO in CH_2Cl_2 in the presence of $[(Ph_3P)_2N][NO_2]$ to yield the carbonyl nitro monoanion $[Cr(CO)_5(NO_2)]^{1-}$ that was fully characterized in solution by IR spectroscopy, and in the solid state by a single crystal X-ray diffraction study of the salt $[PPh_4][Cr(CO)_5(NO_2)]$. The ion was revealed to adopt the expected octahedral structure such that the nitro group is *N*-bonded, as in **2**.[23] Considering the known chromium nitrosyls, $Cr(NO)_4$ is tetrahedral,[24] while $Cr(CO)_3(NO)_2$ has only been observed in a matrix isolation study.[25] The structure of the deep red crystalline salt $[(Ph_3P)_2N][Cr(CO)_4NO]$ has now been shown to be a distorted trigonal bipyramid. As expected, the nitrosyl group is equatorial, and the major distortion in the $[Cr(CO)_4NO]^{1-}$ anion involves the axial CO groups which bend away from the NO ligand to make an angle C_{ax}–Cr–C_{ax} of 159°. This distorted structure is not attributed to lattice effects, since high-level molecular orbital calculations show a similar geometry for the isolated $[Cr(CO)_4NO]^{1-}$ anion. Interestingly, these calculations revealed that the isoelectronic $[Mn(CO)_5]^{1-}$ anion is fluxional, whereas no other low-energy structure was available to $[Cr(CO)_4NO]^{1-}$.[26]



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5.04.5 Chromium Carbonyl Hydrides and Hydrogen Complexes

As noted in COMC (1995),[27] the carbonyl hydrides $[CrH(CO)_5]^{1-}$ and $[(\mu\text{-}H)Cr_2(CO)_{10}]^{1-}$ have been widely studied, and an improved practical procedure for the selective preparation of $KHCr(CO)_5$ has been described.[28] The possible existence of several other molecules of this type has been investigated by DFT, using both BP86 and B3LYP functionals. In particular, the relative stabilities of several dichromium carbonyls, $[Cr_2(CO)_{11}]$, $[(\mu\text{-}H)Cr_2(CO)_{10}]^{1-}$, $[(\mu\text{-}H)_2Cr_2(CO)_9]^{2-}$, and $[(\mu\text{-}H)_2\text{-}Cr_2(CO)_8]^{2-}$, have been evaluated. Homoleptic chromium carbonyl structures of the formula $Cr_2(CO)_{11}$ appear to be thermodynamically unstable with respect to dissociation to the fragments $Cr(CO)_6$ and $Cr(CO)_5$, and only slightly metastable with respect to the transition state leading to these dissociated fragments. In contrast, both the BP86 and B3LYP functionals predict the known $[(\mu\text{-}H)Cr_2(CO)_{10}]^{1-}$ to have significant stability with respect to the fragments $Cr(CO)_5 + [Cr(CO)_5H]^{1-}$. While $[(\mu\text{-}H)_2Cr_2(CO)_9]^{2-}$ remains unknown, the related structure $[(\mu\text{-}H)_2Cr_2(CO)_8]^{2-}$ is predicted to be stable with respect to its fragments and is indeed isolable. Overall, it is suggested that the BP86 method is preferable to B3LYP for this particular class of compounds.[29]

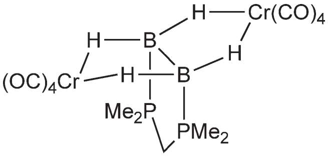
In 1995, the equilibrium geometries, vibrational frequencies, and metal–dihydrogen bond energies of $M(CO)_5H_2$ (M = Cr, Mo, and W) were studied with MP2 and CCSD(T) calculations.[30] In 1998, the interaction between H_2 and $M(CO)_n(PH_3)_{5-n}$ (M = Cr, Mo, W; $n = 0, 3, 5$) metal fragments was studied by means of CCSD(T)//B3LYP calculations. Three steps in the dihydrogen addition path starting from the separated ML_5 and H_2 fragments leading to a stable dihydride have been considered: (i) dihydrogen coordination; (ii) cleavage of the H–H bond in a dihydrogen-like structure, leading to a pentagonal-bipyramidal *cis*-dihydride; and (iii) reorganization of the initial isomer into a more stable dihydride structure. It was concluded that for $Cr(CO)_5H_2$ and $Cr(CO)_3(PH_3)_2H_2$ only the dihydrogen complexes would be observable, whereas for $Cr(PH_3)_5H_2$ there should exist an equilibrium between the dihydrogen complex and the pentagonal-bipyramidal dihydride.[31]

The complex $Cr(CO)_3(PPr^i_3)_2(\eta^2\text{-}H_2)$ has a side-bonded dihydrogen ligand with H–H = 0.67(5) Å (by X-ray crystallography), and the ^1H NMR spectrum of the HD isotopomer showed a J(HD) value of 35 Hz. The complex completely dissociates H_2 in solution to give $Cr(CO)_3(PPr^i_3)_2$, which contains an agostic C–H interaction.[32] Very recently, it has been reported that photolysis of a dichloromethane solution of $Cr(CO)_6$ at low temperature in the presence of hydrogen gas affords $Cr(CO)_5(H_2)$ that was characterized as a dihydrogen complex based on a short T_1 value for the hydride ^1H NMR resonance, and a large H–D coupling constant of 35.8 Hz in the monodeutero derivative.[33]

5.04.6 Other Bridging Hydrides to Chromium Carbonyls

In a somewhat related study, the energetics of the formation of intermolecular agostic Cr–H–C linkages has been reported. This involved the use of actinometry and photoacoustic calorimetry to monitor the photochemistry of $M(CO)_6$ (M = Cr, Mo) whereby a carbonyl ligand was substituted by piperidine in heptane. Flash photolysis data have been interpreted in terms of an initial formation of (heptane)$M(CO)_5$ with subsequent displacement of heptane by piperidine.[34]

In accord with earlier extended Hückel molecular orbital calculations,[35] DFT data on the bonding and structural features of $[(\eta^n\text{-}BH_4)Cr(CO)_4]^{1-}$ ($n = 1$–3) complexes showed that the ground state is bidentate,[36] in good agreement with experimental results.[37] A review of this topic has appeared.[38] The reaction of $Cr(CO)_6$ with borane–phosphine adduct $H_3B{\leftarrow}PMe_2CH_2PMe_2{\rightarrow}BH_3$ yielded the dichromatetraborane **3** in which the cyclic diborane(4)–diphosphine acts as a tetradentate ligand by coordinating to each of the two $Cr(CO)_4$ fragments in a bidentate fashion through vicinal BH's.[39] This cluster can be depicted as a derivative of tetraborane in which the wingtip BH_2^+ groups in B_4H_{10} have been replaced by isolobal $Cr(CO)_4$ fragments, and the two terminal hydrides attached to the basal borons have been replaced by the diphosphine.



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5.04.7 Chromium Carbonyl Complexes of Groups 13–16

The vacant coordination site in $Cr(CO)_5$ has been occupied by a wide variety of ligands, thus generating an enormous number of complexes of the type $LCr(CO)_5$, in particular, where L is a phosphorus-based ligand or a carbene.[40,41] Such systems will be discussed later in this chapter. However, in recent years, considerable effort has been expended so as to incorporate ligands whereby the chromium has been attached to almost every element in groups 13 through 16. Earlier work has been summarized in COMC (1982)[42] and in COMC (1995).[43]

5.04.7.1 Chromium Carbonyl Complexes of Boron, Aluminum, Gallium, Indium, and Thallium

An early report described the photochemical reaction of $Cr(CO)_6$ with Lewis base adducts of borane, $L{\cdot}BH_3$, where $L = Me_3P$, Ph_3P or Me_3N, to form terminal borylene complexes $[(L{\cdot}BH_3)Cr(CO)_5]$. In contrast, photolysis of $R_2NH{\cdot}BH_3$ with $Cr(CO)_6$ led only to borazoles.[44] Subsequently, it was found that the reaction of $Na_2Cr(CO)_5$ with $Br_2B–N(SiMe_3)_2$ furnished $(OC)_5Cr{=}B{=}N(SiMe_3)_2$, **4**, in 30% yield.[45] Moreover, photolysis of the tungsten analog, $(OC)_5W{=}B{=}N(SiMe_3)_2$, with $(OC)_5Cr(NMe_3)$ gave the intermetallic borylene transfer product **4** almost quantitatively.[46] The boron–nitrogen length of 1.353 Å and the chromium–boron bond length of 1.996 Å suggest double bonds in both cases.

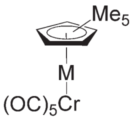
$$(OC)_5Cr{=}B{=}N(SiMe_3)_2$$

4

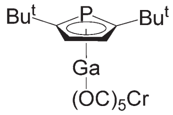
$d(Cr{=}B) = 1.996$ Å

$d(B{=}N) = 1.353$ Å

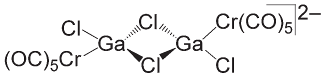
To investigate the bonding of the carbene-like ligand $AlCp^*$ ($Cp^* = C_5Me_5$) toward a transition metal, $Cp^*Al–Cr(CO)_5$, **5**, the first structurally characterized coordination compound containing direct Al–Cr bonding was prepared from $(COT)Cr(CO)_5$ and $AlCp^*$.[47] The corresponding gallium complex, $Cp^*Ga–Cr(CO)_5$, **6**, has also been synthesised by an analogous route.[48] Moreover, [2,5-bis(*t*-butyl)–phospholyl]gallium and $(COD)Cr(CO)_5$ yielded $[(Bu^t)_2C_4H_2P]Ga–Cr(CO)_5$, **8**.[49] Other gallium–chromium systems include dimeric $\{[(OC)_5Cr]_2Ga_2Cl_4\}^{2-}$, **9**, and $\{[(OC)_5Cr]_2Ga_2Cl_2R_2\}^{2-}$, **10**, prepared from $Na_2Cr(CO)_5$ and $GaCl_3$ or $RGaCl_2$. The presumed dimers derived from R_2GaCl, where R = Me or Et, lose trialkylgallium to form $\{[(OC)_5Cr]_2GaMe\}^{2-}$, **11**.[50]



5: M = Al; *d*(Cr=Al) = 2.376 Å
6: M = Ga; *d*(Cr=Ga) = 2.405 Å
7: M = In; *d*(Cr=In) = 2.585 Å



8: *d*(Cr=Ga) = 2.390 Å



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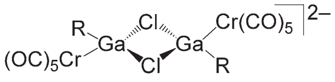

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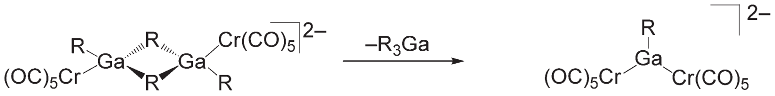

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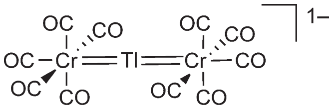
Even the heaviest members of group 13 are known to bond directly to chromium. Thus, the reaction of Cp*In with the chromium-transfer agent (COD)Cr(CO)$_5$ results in the formation of Cp*In–Cr(CO)$_5$, 7, in which Cp*In acts as an electron-pair donor; however, the Cp*In–Cr linkage is not linear in the solid state, but is rather 158°.[51] The chromium–aluminum, chromium–gallium, and chromium–indium distances in 5, 6, 7, and 8 are 2.376, 2.405, 2.585, and 2.390 Å, respectively. Haloderivatives of indium bonded to the chromium pentacarbonyl moiety are also known. Thus, the reactive In(I)-complexes $[\{(OC)_5Cr\}InX\cdot THF]$ (X = Cl, Br) react with an excess of $[Ph_4P]X$ to give the corresponding trihaloindate complexes $[Ph_4P]_2[\{(OC)_5Cr\}InX_3]$ in which In has a formal oxidation state of +1. ^{115}In NMR spectra of Cr(CO)$_5$-substituted indium species are reported for the first time.[52]

Finally, $[(OC)_5Cr{=}Tl{=}Cr(CO)_5]^{1-}$, 12, a complex with linear, doubly coordinated thallium, has been prepared from $K_2Cr(CO)_5$ and $TlCl_3$ in the presence of THF and [2,2,2]-cryptand.[53] The complex anion 12 has D_{4h}-symmetry with chromium–thallium distances of 2.64 Å, and is isoelectronic with the trimetallic cumulene complex $[(OC)_4Fe{=}Tl{=}Fe(CO)_4]^{1-}$.[54] In 12, the chromium–thallium bond is markedly shorter than that found in $[Tl\{Cr(CO)_5\}_3]$, where the 2.87 Å linkage can be regarded as the measure for a Cr–Tl single bond.

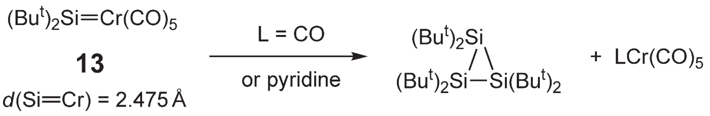


d(Tl=Cr) = 2.64 Å

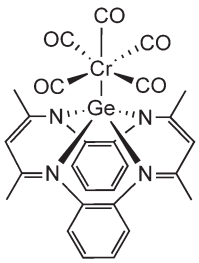
12

5.04.7.2 Chromium Carbonyl Complexes of Silicon, Germanium, Tin, and Lead

The salt adduct $[(Bu^t)_2Si:Cr(CO)_5]\cdot[CF_3SO_3Na]\cdot 2THF$ 13 possesses a chromium–silicon double bond (2.475 Å); however, the triflate does not coordinate rigidly to 13 but exchanges rapidly in non-polar solvents (^{29}Si NMR 150.7 ppm). Upon treatment with pyridine or CO, di(*t*-butyl)silylene is eliminated and trimerizes to give cyclic $[(Bu^t)_2Si]_3$. Adduct 13 reacts with hexamethylphosphoramide to yield $(Bu^t)_2(HMPA)Si{=}Cr(CO)_5$, in which the Cr–Si bond distance is now 2.527 Å.[55]



Ge(tmtaa), where (H_2tmtaa = dibenzotetramethyltetraaza[14]annulene), reacts with (THF)Cr$(CO)_5$ to give (tmtaa)GeCr$(CO)_5$, **14**, in which the local geometries around chromium and germanium are octahedral and square pyramidal, respectively, and the equatorial Cr$(CO)_4$ and GeN_4 moieties are arranged in an eclipsed fashion.[56] Somewhat analogous systems have been reported whereby Ge(II), Sn(II), or Pb(II) salen complexes [salen = 2,2′-*N*,*N*′-bis(salicylidene)ethylenediamine] yield mono- and *cis*-disubstituted chromium carbonyls (salen)M═Cr$(CO)_5$ and [(salen)M]$_2$Cr$(CO)_4$, **15** and **16**, respectively. The X-ray crystal structure of the complex **15**, M = Sn, reveals a pentacoordinated tin in which the Sn–Cr bond distance of 2.557 Å is one of the shortest known for transition metal divalent Sn complexes.[57]



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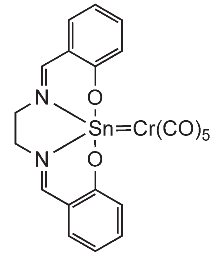
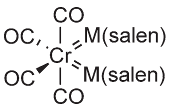


15

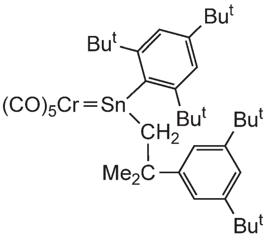
d(Sn═Cr) = 2.557 Å



M = Sn, Pb

16

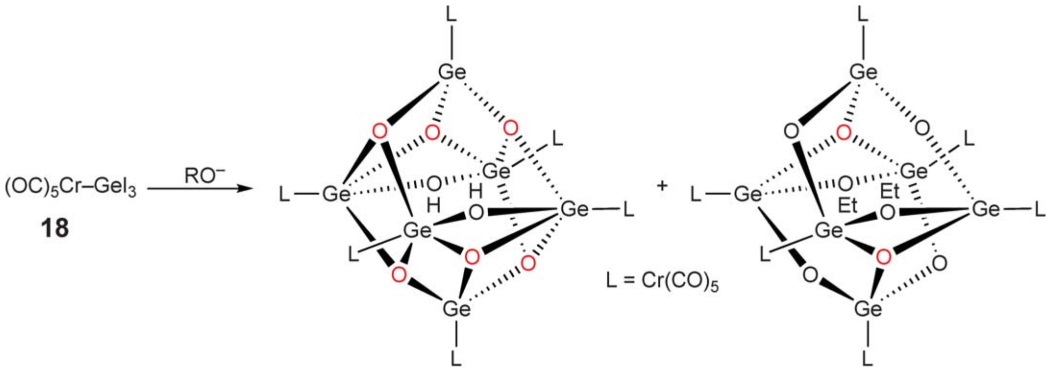
Analogous to the silylene complex **13**, reaction of (THF)Cr$(CO)_5$ with the alkylaryl stannylene RR^1Sn (R = 2,4,6-$Bu^t_3C_6H_2$, $R^1 = CH_2C(CH_3)_2$-3,5-$Bu^t_2C_6H_2$) furnishes the donor-free stannylene complex $[(OC)_5Cr{=}SnRR^1]$ **17**. The three-coordinate tin atom is in a strictly planar environment with an acute C–Sn–C angle of 91°, and a tin–chromium double bond of 2.614 Å.[58]



17

d(Sn=Cr) = 2.614 Å
Φ(C-Sn-C) = 91°

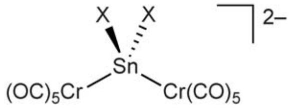
Group 14 halides react with chromium carbonyls, or chromium carbonyl anions, to yield a variety of different products. Thus, $Na_2Cr_2(CO)_{10}$ and $GeCl_4$ react to form $[(OC)_5Cr–GeCl_3]^{1-}$; the corresponding iodo complex $[(OC)_5Cr–GeI_3]^{1-}$, **18**, can be prepared from (THF)Cr$(CO)_5$ and GeI_2 in the presence of iodide. Molecule **18** reacts with alcoholates to produce the cage compounds $[\{(OC)_5Cr\}_6Ge_6(\mu_2\text{-OH})_2(\mu_3\text{-O})_6]^{2-}$, **19**, and $[\{(OC)_5Cr\}_6Ge_6(\mu_2\text{-OEt})_2(\mu_2\text{-O})_4(\mu_3\text{-O})_2]^{2-}$, **20**, such that an octahedral arrangement of six Ge atoms, each bearing a Cr$(CO)_5$ protecting group, is held together by μ_3-O, μ_2-O, and μ_2-OR bridges.[59] In a similar manner, $Na_2Cr_2(CO)_{10}$ and SnX_2 can yield $[(OC)_5Cr–SnX_3]^{1-}$, or dianions of the type $[\{(OC)_5Cr\}_2SnX_2]^{2-}$ **21** (X = Cl, Br), as relatively unreactive $[Ph_4P]^+$ or $[Bu_4N]^+$ salts. They have been characterized as alkali metal (12-crown-4) or [2,2,2]-cryptand salts, confirming their structures as possessing bridging $SnCl_2$ moieties with Cr–Sn–Cr-angles close to 130°.[60] Moreover, in the presence of oxygen and water, they are readily transformed into the rhombododecahedral cage compound $[\{(OC)_5Cr\}_6Sn_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$, **22**, closely analogous to the germanium systems **19** and **20**. In the dichromium species **21**, the halides can be replaced by oxinate, quinolinate, or acetate, and the lead analogs $[\{(CO)_5Cr\}_2Pb(OAc)_2]^{2-}$ have also been characterized crystallographically. ^{119}Sn NMR data are presented for all the tin compounds.[61]



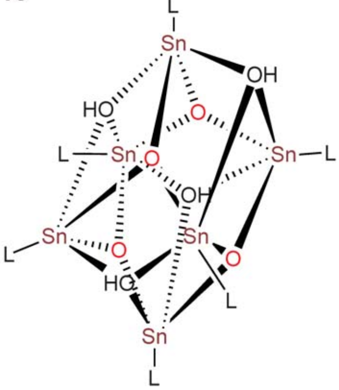
18

R = H
19

R = Et
20

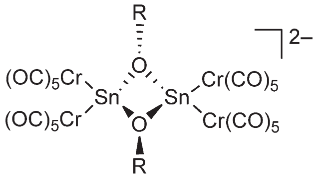


X = Cl, Br
21



L = Cr(CO)5
22

Inidene complexes of the general type $[L_nM\overset{\cdots}{-}E(X)\overset{\cdots}{-}ML_n]^{x-}$, such as $[\{(CO)_5Cr\}Sn(OR)\{Cr(CO)_5\}]^{1-}$ (R = Et, Pr^i), derived from **21**, have been shown to dimerize via alkoxy-donor Sn-acceptor bonding by which a planar Sn_2O_2 ring is formed. The Sn–$\{Cr(CO)_5\}$ bonds in **23** are aligned vertical to this ring, whereas the R–O groups are almost coplanar with the Sn_2O_2 ring, leading to idealized D_{2h}-symmetry.[62]



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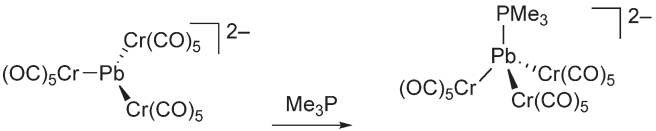
In $[PPh_4]_2[\{(OC)_5Cr\}_3Pb]$, **24**, prepared by the reaction of $Pb(NO_3)_2$ with $Na_2Cr_2(CO)_{10}$ in THF, the lead atom is approximately in the plane of the three chromium atoms, and the Pb–Cr bond length of 2.73 Å suggests a degree of multiple bonding. Upon addition of trimethylphosphine to give $[PPh_4]_2[\{(OC)_5Cr\}_3Pb(PMe_3)]$, **25**, the lead atom is now 0.38 Å out of the plane toward the PMe_3 ligand, but still deviates strongly from an ideal tetrahedron with bond angles of 101° for P–Pb–Cr and 117° for Cr–Pb–Cr, and the Pb–Cr distance has now lengthened to 2.82 Å. ^{207}Pb NMR data of $Cr(CO)_5$-bound Pb species are reported for the first time.[63,64] The reaction of $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(CH_2NMe_2)\}]_2Pb$ with $(THF)Cr(CO)_5$ affords the heterotrimetallic plumbylene adduct **26** in excellent yield. Interestingly, **26** exists solely as the *meso*-diastereomer, both in the solid state and in solution, even though in solution it consists of a mixture of interconverting *rac*- and *meso*-diastereomers.[65]

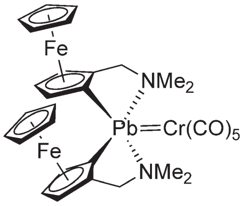


24

d(Cr–Pb) = 2.73 Å

25

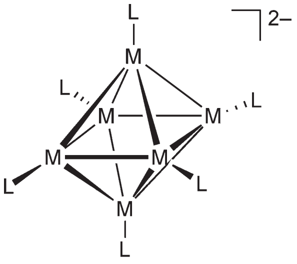
d(Cr–Pb) = 2.82 Å
Φ(Cr–Pb–Cr) = 117°



26

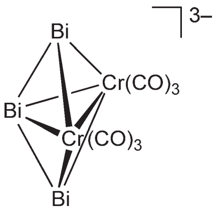
5.04.7.3 Zintl Ions Stabilized by Chromium Carbonyl Moieties

The borane anion $[B_6H_6]^{2-}$ is the archetypical octahedral *closo*-cluster possessing seven skeletal electron pairs as required by Wade's rules.[66,67] However, even though the structures of many borane cages or clusters are parallelled by Zintl ions, the first such *closo*-octahedral cluster to be characterized arose from the reaction of $K_2[Cr(CO)_5]$ with $SnCl_2$ in THF in the presence of [2,2,2]-cryptand (L) to give $[KL]_2[Sn_6\{Cr(CO)_5\}_6]$ **27**. The anionic cluster consists of six tin atoms in a regular octahedron with Sn–Sn distances of 2.93–2.96 Å; each Sn atom is ligated by an *exo*-skeletal $Cr(CO)_5$ moiety with a Cr–Sn bond ranging from 2.608 to 2.613 Å.[68] Subsequently, the analogous hexagermanium cluster $(Ph_4P)_2[Ge_6\{Cr(CO)_5\}_6]$, **28**, was prepared from GeI_2 and $Na_2[Cr_2(CO)_{10}]$ in the presence of 2,2′-bipyridine. The Ge–Ge and Ge–Cr distances range from 2.42 to 2.52 Å and from 2.395 to 2.426 Å, respectively.[69]



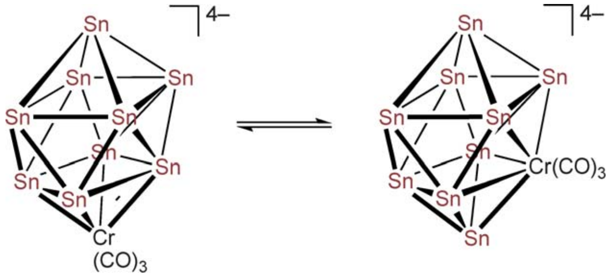
L = $Cr(CO)_5$
27: M = Sn
28: M = Ge

Recently, the anionic Zintl species $[Bi_3Cr_2(CO)_6]^{3-}$, **29**, in which the potassium countercation is encapsulated in an aza-crypt, were prepared by reaction of an ethylenediamine solution of K_5Bi_4 and the crypt with solid (mesitylene)$Cr(CO)_3$. The anion is a trigonal-bipyramidal cluster in which the $Cr(CO)_3$ fragments are equatorial, and the shape and electron count of the cluster are consistent with a *closo*-deltahedron possessing six skeletal electron pairs.[70]



29

In contrast, the Sn_9^{4-} monocapped square-antiprismatic Zintl ion has been known for some time.[71] This nine-vertex system is an example of a *nido*-cluster with 11 skeletal electron pairs in accord with the PSEPT model.[72] Treatment with (mesitylene)$Cr(CO)_3$ and 2,2,2-cryptand in an ethylenediamine/toluene solvent mixture forms the bicapped square-antiprismatic 10-vertex 22-electron *closo*- $[Sn_9Cr(CO)_3]^{4-}$ cluster, **30**, in which the $[\eta^4\text{-}Cr(CO)_3]$ unit now occupies the formerly vacant site, as shown by X-ray crystallography. However, the variable-temperature ^{119}Sn and ^{13}C NMR data reveal the existence of a fluxional process that interconverts the $\eta^4\text{-}C_{4v}$ and $\eta^5\text{-}C_s$ structures **30** and **31**, respectively, possibly proceeding via a triangular-face rotation mechanism.[73] It is, of course, well known that in Sn_9^{4-} itself interconversion of the C_{4v}-square-antiprismatic and the D_{3h}-tricapped trigonal-prismatic isomers is facile.[71]



30 **31**

5.04.7.4 Phosphorus Derivatives of Chromium Carbonyls

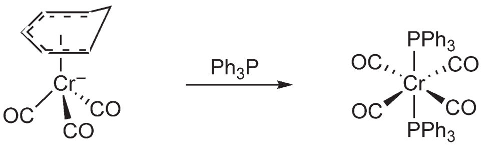
The number of chromium carbonyl complexes containing a ligand in which one or more phosphorus atoms act as donors to the metal is truly enormous. The early work has, of course, been thoroughly covered in COMC (1982)[42] and in COMC (1995).[74] In this section, an attempt has been made to categorize the more recently studied compounds in terms of the number of direct phosphorus–chromium linkages and the novelty of the *P*-containing ligand.

5.04.7.4.1 Phosphine complexes of chromium carbonyls

Although a large number of relatively routine X-ray crystallographic structural determinations to establish molecular geometries have been reported, in many cases there is an underlying problem that required an accurate knowledge of the molecular geometry. Typically, in the tris-(*ortho*-tolyl)phosphine complex, $[\{(o\text{-}Me\text{–}C_6H_4)_3P\}Cr(CO)_5]$, the most favored conformation, and also the barriers to both P–aryl and P–Cr rotation, had been evaluated by molecular mechanics calculations.[75] Nevertheless, reliable structural data were necessary to compare with the theoretical predictions. Similarly, to test the steric limits of ligand complexation, $Cr(CO)_5$ complexes of tris(trimethylsilyl)phosphine and of mono- and bis-(1-adamantyl)phosphine have been prepared and structurally characterized.[76,77] Other crystallographically characterized systems containing simple phosphines include $[\{\eta^2\text{-}Me_2P(CH_2)_2\text{-}PMe_2\}Cr(CO)_4]$,[78,79] $[\{\eta^2\text{-}Me_2PCH_2PMe_2\}Cr(CO)_4]$,[80] $[\{(o\text{-}MeO\text{–}C_6H_4)_3P\}Cr(CO)_5]$,[81] $[\{Ph_2(C_2F_5)P\}_2Cr(CO)_4]$,[82] and $[\{\eta^2\text{-}Ph_2P(CH_2)_5PPh_2\}Cr(CO)_4]$.[83]

The majority of such complexes has been synthesized by thermal or photochemical replacement of a weakly bonded ligand—very commonly THF, Me_3N, norbornadiene (nbd), or cyclooctene (COE). Interestingly, the microwave-assisted synthesis of compounds such as $Cr(CO)_4L$ (where L = bipy, en, dppm, dppe) from $Cr(CO)_6$ and L results in increased yields and a very marked reduction in reaction times by factors ranging from 5 to >500.[84]

However, numerous other routes have also been explored. Thus, the reaction of triphenylphosphine with the intermediate $[(\eta^5\text{-cyclohexadienide})Cr(CO)_3]^{1-}$ anion (produced by reduction of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$) resulted in cyclohexadienide loss and formation of the unexpected product, *trans*-$[Cr(CO)_4(PPh_3)_2]$, **32**, whose structure was secured by X-ray crystallography.[85] The question of the preferred isomer (*cis* or *trans*) was reinvestigated, and the molecular geometry redetermined in a different space group; it was concluded that although the structure is dominated by steric interactions, in the gas phase the *cis*-isomer is more stable.[86]



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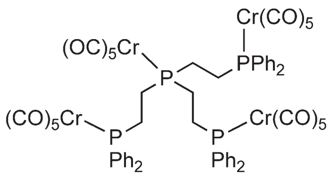
A number of simple phosphine complexes have now been generated by the reaction of the anionic chromium species $K[HCr(CO)_5]$ with PR_3 ($R = Et, Ph, NMe_2$) in THF at 65 °C. These reactions proceed first by generating the monosubstituted hydridotetracarbonylchromates, $[HCr(CO)_4PR_3]^{1-}$, with subsequent substitution of the hydride ligand to give the disubstituted derivatives *trans*-$Cr(CO)_4(PR_3)_2$.[87] However, at −80 °C, $[HCr(CO)_5]^{1-}$ reacts with PBr_3 to give $(H_3P)Cr(CO)_5$ and $K[BrCr(CO)_5]$, which further reacts with PBr_3 only above −20 °C to give $(Br_3P)Cr(CO)_5$. PCl_3 behaves similarly. In contrast, $K\{(\mu\text{-}H)[Cr(CO)_5]_2\}$ reacts with PBr_3 only at 25 °C, affording selectively $Cr(CO)_5(PBr_3)$.[88]

A number of potentially multidentate phosphines have been used initially as unidentate ligands and subsequently attached either to the same metal (chelating) or to a different metal (bridging), thus linking centers of quite a different character. Typically, the unicoordinated diphosphines, $Cr(CO)_5(\eta^1\text{-P–P})$ (P–P = 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), or 1,4-bis(diphenylphosphino)benzene (dppb)), were prepared by amine oxide-induced phosphine substitution of $Cr(CO)_6$. The systems with pendant phosphine groups were then converted into the bridged heterobimetallic complexes $(OC)_5Cr(\mu\text{-P–P})M(CO)_5$ (M = Mo, W) upon treatment with $(MeCN)M(CO)_5$.[89]

The tri- and tetradentate ligands phenylbis(diphenylphosphinoethyl)phosphine $PhP(CH_2CH_2PPh_2)_2$ (Pf–Pf–Pf) and tris(diphenylphosphinoethyl)phosphine $P(CH_2CH_2PPh_2)_3$ ($P\text{–}Pf_3$), respectively, display remarkable versatility. Not only can they form complexes whereby each phosphorus is bonded to a $Cr(CO)_5$ moiety, as in $[(P\text{–}Pf_3)\{Cr(CO)_5\}_4]$, **33**, but also they yield systems whereby a $Cr(CO)_4$ fragment is chelated either by a terminal and a central phosphorus (giving a five-membered ring **34**) or to two terminal phosphines (giving an eight-membered ring **35**).[90–92] The M–P bond lengths, M–P–C and P–C–C bond angles in the eight-membered ring are greater than the corresponding ones in the five-membered ring, revealing the larger ring strain in the former case. Nine-membered rings containing chromium have been obtained from 1,4,8,11-tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane which yields the bis-$Cr(CO)_4$ complex **36** as well as the tetrakis-$Cr(CO)_5$ system **37**.[93]



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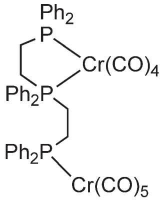

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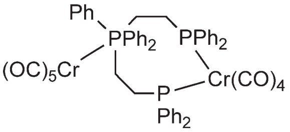

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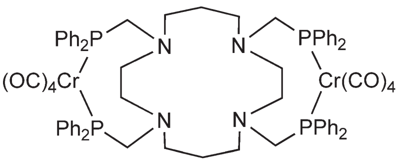

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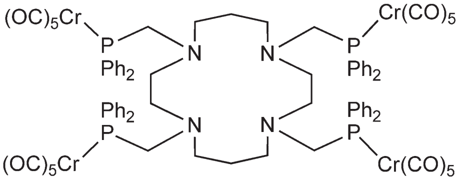
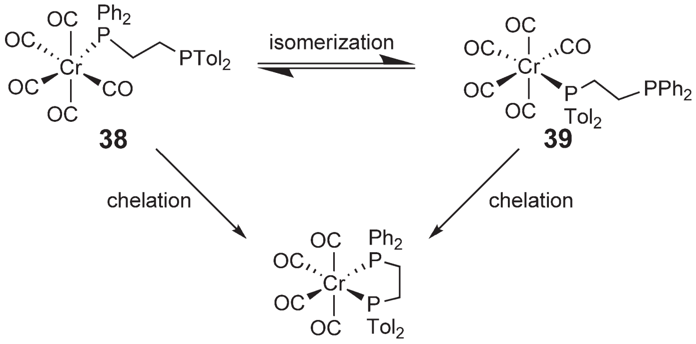


37

The kinetics of the chelate ring-closure reaction in $(\eta^1\text{-dppm})Cr(CO)_5$ have been studied by ^{31}P NMR. The data revealed a large negative activation entropy implying that the mechanism of chelate ring-closure reaction is associative.[94,95] In a more recent investigation, the dangling phosphine complexes $(OC)_5Cr[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$, **38**, and $(OC)_5Cr[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$, **39**, were synthesized, thus providing a pair of linkage isomers. The kinetics of isomerization and of chelation were studied, and it was found that the position of equilibrium favors ditolylphosphino coordination. Moreover, the results suggest that the transition states for both isomerization and chelation are significantly associative, and become more so in descending order through group 6.[96] In related work, the thermal substitution kinetics of 1,5-cyclooctadiene in (COD)Cr$(CO)_4$ by the chelating diphosphines $Ph_2P(CH_2)_nPPh_2$, where $n = 1–3$, were studied by quantitative FT-IR spectroscopy. In the proposed mechanism, the rate-determining step is the cleavage of one metal–olefin bond of the COD ligand, and the observed activation parameters support an associative process.[97]



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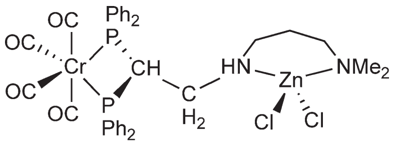
39

The difunctional phosphine $(Ph_2P)_2CHCH_2NH(CH_2)_3NMe_2$ reacts successively with chromium carbonyl, and then with zinc chloride, to yield **40** in which the diphosphine chelates to chromium and the two amine centers coordinate to zinc.[98]



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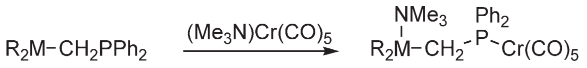
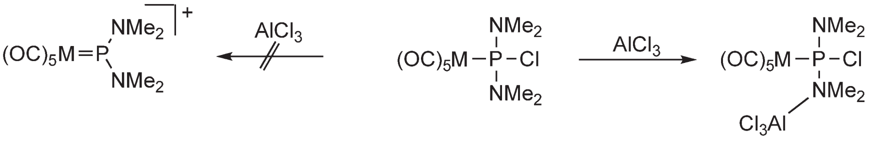
In a somewhat related fashion, the group 13 compounds $R_2MCH_2PPh_2$ ($R = CH_2CMe_3$ or CH_2SiMe_3; M = Ga or In) reacted readily with $(Me_3N)Cr(CO)_5$ in benzene to form $(OC)_5Cr[PPh_2CH_2MR_2{\cdot}NMe_3]$, **41**. In contrast, when the phosphine was attached directly to the group 13 element, as in R_2MPPh_2 ($R = CH_2CMe_3$, CH_2SiMe_3; M = Al, Ga, In), only the two aluminum compounds and $(Me_3CCH_2)_2GaPPh_2$ yielded $(OC)_5Cr[PPh_2MR_2{\cdot}NMe_3]$. However, the bis(trimethylsilylmethyl)gallium and -indium ligands reacted with $[NEt_4][Cr(CO)_5Cl]$ to form $[NEt_4][Cr(CO)_5(PPh_2MR_2Cl)]$.[99] In a similar vein, $(OC)_5Cr\{P(NMe_2)_2Cl\}$ has been synthesized and treated with $AlCl_3$ in an attempt to form coordinated phosphenium cation complexes by chloride abstraction; unexpectedly, however, the adduct $M(CO)_5L–AlCl_3$, **42**, was produced.[100] Donor/acceptor ligands of the type $Me_2PCH(R)OSnMe_3$ (R = H, Me, or Ph) have been prepared by the reaction of Me_3SnCl with $HOCH(R)PMe_2$ or by insertion of RCHO into the Sn–P bond of the stannylphosphine Me_3SnPMe_2. These new ligands, and also the ethylene-bridged analog $Me_2PCH_2CH_2SnMe_3$, yield the corresponding phosphorus-bonded pentacarbonylchromium complexes.[101]



M = Al, Ga, In

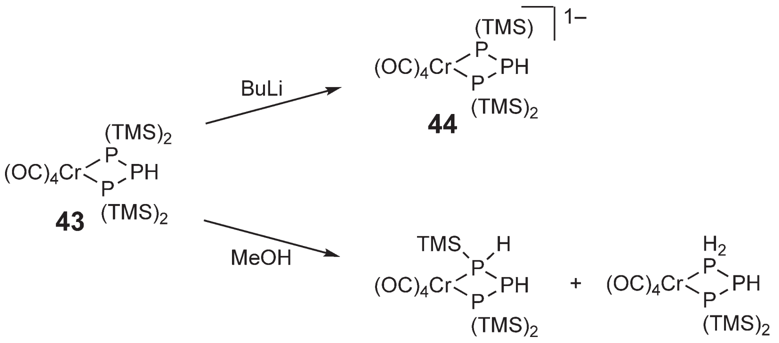
41



M = Cr

42

Phosphorus-rich phosphines and bulky silyl phosphines, such as $[(\mathrm{TMS})_2\mathrm{P}]_2\mathrm{PH}$, $(\mathrm{TMS})(\mathrm{Bu}^t)\mathrm{P}$-PH-$\mathrm{P}(\mathrm{TMS})_2$, $[(\mathrm{Bu}^t)_2\mathrm{P}]_2\mathrm{PH}$, and $[(\mathrm{TMS})_2\mathrm{P}]_2\mathrm{PMe}$, react with $(\mathrm{THF})\mathrm{Cr(CO)}_5$ via their terminal phosphorus sites to give the corresponding $(\eta^1\text{-L})\mathrm{Cr(CO)}_5$, and eventually the chelates $(\eta^2\text{-L})\mathrm{Cr(CO)}_4$, **43**.[102] Complexation to chromium affects the reactivity of these ligands; for example, $[(\mathrm{TMS})_2\mathrm{P}]_2\mathrm{PH}$ undergoes lithiation at the central PH unit but, when the chelate **43** is treated with BuLi, cleavage of the silicon–phosphorus bond adjacent to the metal occurs to give **44**. The resulting phosphines, $(\mathrm{TMS})\mathrm{PH}$-PH-$\mathrm{P}(\mathrm{TMS})_2$ and PH_2-PH-$\mathrm{P}(\mathrm{TMS})_2$, are stable when coordinated to $\mathrm{Cr(CO)}_4$ but apparently not as a free ligand.[103]



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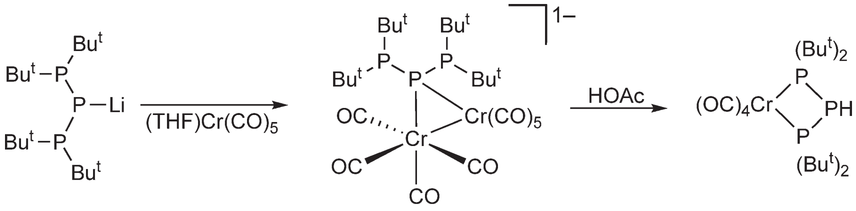
44

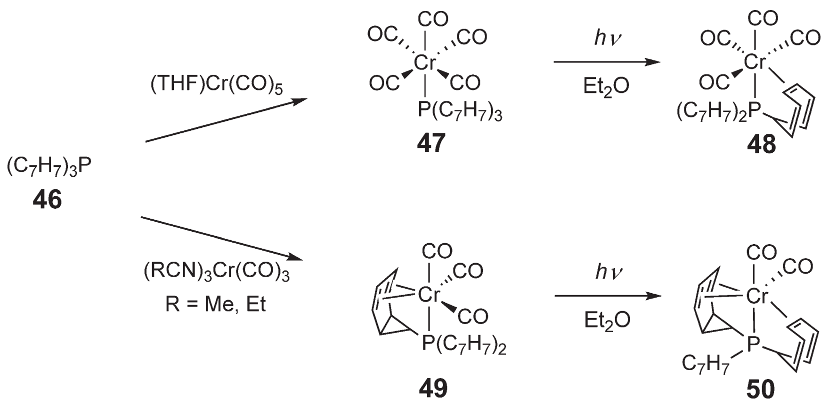
The closely related salt $[\mathrm{Li(THF)}_2][(\mathrm{Bu}^t{}_2\mathrm{P})_2\mathrm{P}]$ and $(\mathrm{THF})\mathrm{Cr(CO)}_5$ yield the anion $[(\mathrm{OC})_4\mathrm{Cr}\{\eta^2\text{-}(\mathrm{Bu}^t{}_2\mathrm{P})_2\mathrm{P}\}\eta^1\text{-}\mathrm{Cr(CO)}_5]^{1-}$, **45**, that reacts with acetic acid to furnish the neutral species $[(\mathrm{OC})_4\mathrm{Cr}\{\eta^2\text{-}(\mathrm{Bu}^t{}_2\mathrm{P})_2\mathrm{PH}\}]$. All compounds were characterized by ^{1}H, ^{13}C, ^{31}P, and ^{7}Li NMR spectroscopy, and **45** by X-ray crystallography.[104] Interestingly, a similar ligand possessing a central nitrogen atom, that is, $(\mathrm{Ph}_2\mathrm{P})_2\mathrm{NH}$, when treated with $\mathrm{Cr(CO)}_6$ in the presence of $\mathrm{Me}_3\mathrm{NO}$ and subsequently with KH in THF, yields the stable salt $[\mathrm{K(THF)}_3][\mathrm{Cr(CO)}_4\{\eta^2\text{-}(\mathrm{Ph}_2\mathrm{P})_2\mathrm{N}\}]$, which in the solid state forms infinite chains via isocarbonyl bridges.[105]



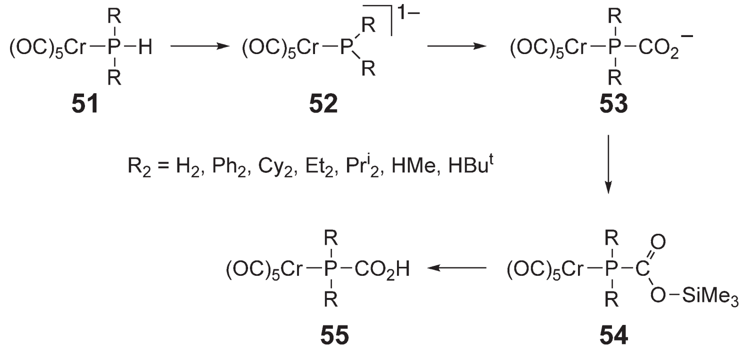
45

Diphosphine complexes may be formed through coupling processes by removal of HCl from $(\mathrm{OC})_5\mathrm{Cr(RPHCl)}$, where R = Ph or NEt_2 to give the bridged species $(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-PPh(H)-PPh(Cl)}\}\mathrm{Cr(CO)}_5$ and $(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-PH(NEt}_2)\text{-P(NEt}_2)\mathrm{Cl}\}\mathrm{Cr(CO)}_5$. Similarly, treatment of $(\mathrm{OC})_5\mathrm{Cr(PHCl}_2)$ with NEt_3 furnished $(\mathrm{OC})_5\mathrm{Cr}(\mu\text{-Cl}_2\mathrm{PPCl}_2)\mathrm{Cr(CO)}_5$. Further reaction of these three diphosphines with $\mathrm{Bu}_4\mathrm{NF}$, HCl, or MeOH gave $(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-PPh(H)-PPh(F)}\}\mathrm{Cr(CO)}_5$, $(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-PHCl-PCl}_2\}\mathrm{Cr(CO)}_5$, and $(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-P(OMe)}_2\text{-P(OMe)}_2\}\mathrm{Cr(CO)}_5$, respectively. Except for $\mathrm{Cl}_2\mathrm{PPCl}_2$, these diphosphine ligands are unknown in the free state. Attempts to abstract HCl from $(\mathrm{OC})_5\mathrm{Cr(PhPHCl)}$ to generate $(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-PhP=PPh}\}\mathrm{Cr(CO)}_5$ failed.[106] The bridging $\mathrm{P}_2\mathrm{Cl}_4$ ligand, as found in $(\mathrm{OC})_5\mathrm{Cr}(\mu\text{-Cl}_2\mathrm{PPCl}_2)\mathrm{Cr(CO)}_5$, is also formed in the reaction of $[\mathrm{Cr(CO)}_5(\mathrm{PCl}_3)]$ with $\mathrm{Na}_2[\mathrm{Cr}_2(\mathrm{CO})_{10}]$.[107] Furthermore, $[\mathrm{Cr(CO)}_5(\mathrm{PCl}_3)]$ and $\mathrm{Li}[\mathrm{PPh}_2\mathrm{Cr(CO)}_5]$ react to give $[\{(\mathrm{OC})_5\mathrm{Cr}\}(\mathrm{H})\mathrm{P}\{\mathrm{PPh}_2\mathrm{Cr(CO)}_5\}_2]$.[108]

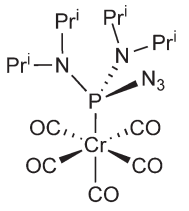
Tris(cycloheptatrienyl)phosphine, **46**, exhibits an extraordinary range of reactions with chromium carbonyls. At room temperature, $(\mathrm{THF})\mathrm{Cr(CO)}_5$ yields the expected normal phosphine complex $[(\mathrm{C}_7\mathrm{H}_7)_3\mathrm{P}]\mathrm{Cr(CO)}_5$, **47**. However, upon irradiation in ethereal solution, **47** is converted into the tetracarbonyl derivative $[(\eta^2\text{-C}_7\mathrm{H}_7)(\mathrm{C}_7\mathrm{H}_7)_2\mathrm{P}]\mathrm{Cr(CO)}_4$, **48**, in which one of the three cycloheptatrienyl substituents of the ligand is symmetrically coordinated as a stable monoolefinic side chain. Moreover, donor-stabilized $(\mathrm{RCN})_3\mathrm{Cr(CO)}_3$ reacts with **46** to yield $[(\eta^4\text{-C}_7\mathrm{H}_7)(\mathrm{C}_7\mathrm{H}_7)_2\mathrm{P}]\mathrm{Cr(CO)}_3$, **49**, such that one of the three ring substituents is now coordinated in the η^4-norcaradiene form. Subsequent irradiation of **49** in ethereal solution led to $[(\eta^4\text{-C}_7\mathrm{H}_7)(\eta^2\text{-C}_7\mathrm{H}_7)(\mathrm{C}_7\mathrm{H}_7)\mathrm{P}]\mathrm{Cr(CO)}_2$, **50**, where **46** is acting as an eight-electron ligand.[109]



The ability of a $Cr(CO)_5$ moiety to stabilize the otherwise unavailable species has been exploited in the preparation of phosphinoformic acids, the unknown *P*-analogs of carbamic acids. The synthesis follows the sequence chromium–phosphine, **51**, –phosphido anion, **52**, –phosphinocarboxylate, **53**, –phosphinosilyl ester, **54**, and finally phosphinocarboxylic acid, **55**. The silylated ligand $R_2PCO_2SiMe_3$, **54**, decomposes readily in protic media to form Me_3SiOH, CO_2, and R_2PH; however, on silica gel, the corresponding chromium complex can be desilylated to furnish the required carboxylic acid. The structure of $(OC)_5Cr(PH_2CO_2H)$ has been elucidated by X-ray crystallography, and matches well with high-level calculations on the predicted geometry of the still unknown free ligand.[110,111]



Another example is that of $(Pr^i_2N)_2PN_3$, which, when photolyzed with $Cr(CO)_6$ in THF solution, furnishes $[(Pr^i_2N)_2P(N_3)]Cr(CO)_5$, **56**. Unlike most azides, **56** is stable to ultraviolet irradiation.[112] A particularly illustrative case involves the first synthesis of a *para*-diphosphaquinone, that was isolated as its bis(pentacarbonylchromium) derivative.[113] Treatment of the *p*-chloro(aryl)phosphino-disubstituted benzene **57** with zinc, and subsequently with $(THF)Cr(CO)_5$, yielded the chromium-stabilized diphosphaquinone, **58**, as both (*E*)- and (*Z*)-isomers. It was necessary to use a particularly bulky aryl substituent, in this case the super-mesityl group, 2,4,6-tri-(*t*-butyl)phenyl.



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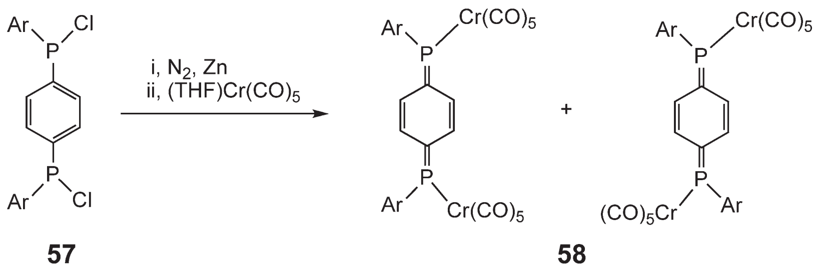
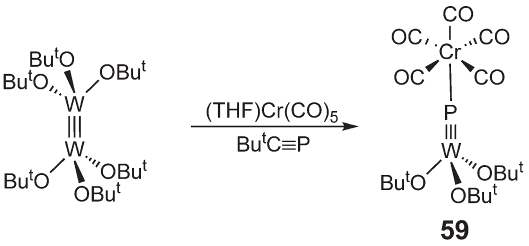
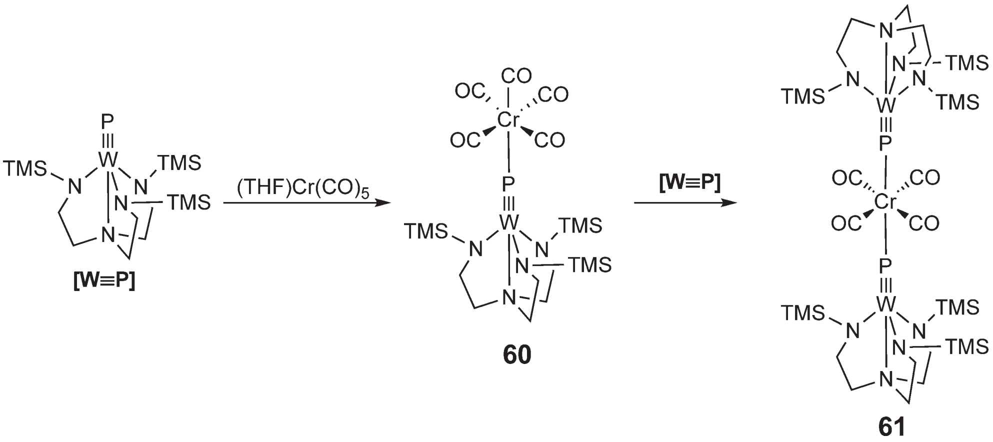


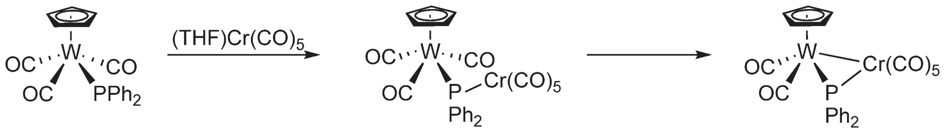
Although metal–nitrogen triple-bonded systems, $L_nM{\equiv}N$, are a well-developed area of chemistry, the corresponding metal–phosphorus triple-bonded analogs, $L_nM{\equiv}P$, are of much more recent vintage. Treatment of the metal–metal triple-bonded precursor $(Bu^tO)_3W{\equiv}W(O\text{-}Bu^t)_3$ with $Bu^tC{\equiv}P$ in the presence of $(THF)M(CO)_5$, where M is Cr or W, provided the first examples of formal tungsten–phosphorus triple-bonded compounds, $(Bu^tO)_3W{\equiv}P\text{-}M(CO)_5$, **59**.[114] Subsequently, this was extended to phosphido- (or arsenido-) tungsten trisaminatoethylamine complexes, whereby the phosphorus (or arsenic atoms) are terminal ligands and react with $(THF)Cr(CO)_5$ to produce the mono- and bis-coordinated chromium systems **60 and 61**. In the latter, the N–W–P–M–P–W–N axis is linear and the tungsten adopts a distorted trigonal-bipyramidal geometry.[115] This area has since been reviewed.[116]

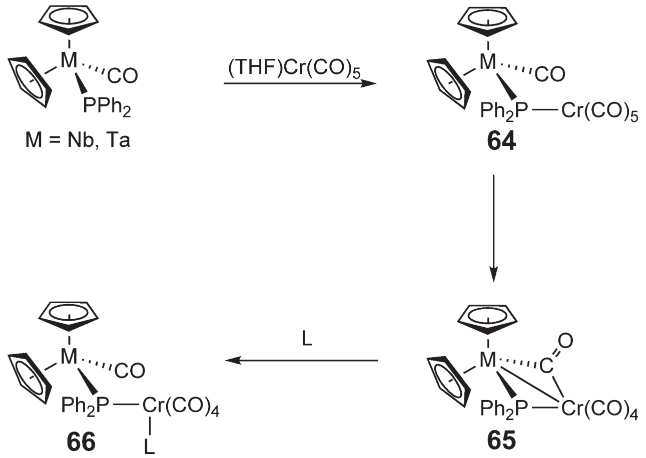


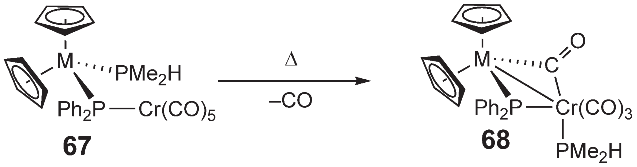


5.04.7.4.2 Metal-chromium phosphido-bridged complexes

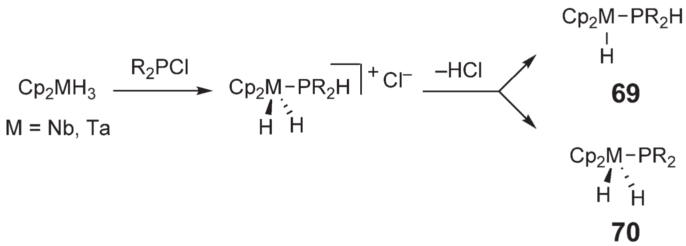
The chemistry of metal–metal-bonded phosphido-bridged species has been studied in some depth in recent years. Thus, the reaction of $CpW(CO)_3PPh_2$ with $(THF)Cr(CO)_5$ yields $CpW(CO)_3(\mu\text{-}PPh_2)Cr(CO)_5$, **62**, that loses a carbonyl from tungsten to form $CpW(CO)_2(\mu\text{-}PPh_2)Cr(CO)_5$, **63**, possessing a dative Cr–W bond (3.09 Å) and a semi-bridging carbonyl which undergoes exchange on the NMR timescale with the other equatorial ligands on chromium.[117] Analogously, the heterobimetallic phosphido-bridged complexes $Cp_2M(L)(\mu\text{-}PR_2)Cr(CO)_5$ (M = Ta, R = Me, L = CO; M = Nb, R = Ph, L = CO, $P(OMe)_3$, Me_2PH) were prepared by the reaction of the appropriate terminal phosphido complex $Cp_2M(CO)(PR_2)$ with $(THF)Cr(CO)_5$, and subsequent replacement of the M–CO ligand by a phosphine.[118–120] In $Cp_2Nb(L)(\mu\text{-}PPh_2)Cr(CO)_5$ (L = CO, $P(OMe)_3$), **64**, the metallic centers in both complexes are tethered by a single bridge. The large Nb–P–Cr angles (126° and 129°) and the long Nb–Cr distances (4.653 and 4.758 Å), respectively, clearly show the absence of a metal–metal interaction. However, photolytic elimination of one CO from the monobridged complexes produced the dibridged systems $Cp_2M(CO)(\mu\text{-}PR_2)Cr(CO)_4$, **65**, whereupon addition reactions of Lewis bases L (L = phosphines, diphosphines, isonitriles) led to $Cp_2M(CO)(\mu\text{-}PR_2)Cr(CO)_4(L)$, **66**, with L regiospecifically coordinating to chromium. In some cases, the reaction may be stereospecific, since the coordination of L can lead to *cis*- or *trans*-arrangements with respect to the PR_2 bridge. Interestingly, photolysis of $Cp_2Nb(PMe_2H)(\mu\text{-}PPh_2)Cr(CO)_5$, **67**, yields the di-bridged species $Cp_2Nb(\mu\text{-}PPh_2)(\mu\text{-}CO)Cr(CO)_3(PMe_2H)$, **68**, whereby the dimethyl–phosphine ligand that was originally bonded to niobium has migrated into chromium; moreover, the Nb–Cr distance of 3.02 Å clearly indicates the presence of a direct metal–metal bond.[120] Use of the 1,2-dimethyl–4-*tert*-butyl–cyclopentadienyl ligand led to the chiral metallophosphine $Cp'CpTa(CO)PMe_2$, which possesses an asymmetric Ta center; this metalloligand reacts with a $Cr(CO)_5$ fragment giving the chiral bimetallic derivative $Cp'CpTa(CO)(\mu\text{-}PMe_2)Cr(CO)_5$.[121]

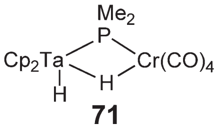






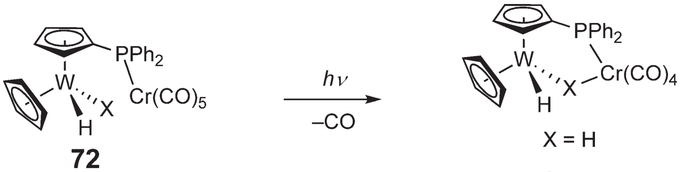
In somewhat analogous fashion, the trihydrides Cp_2MH_3 (M = Nb, Ta) react with chlorophosphines PR_2Cl (R = Me, Ph) affording phosphonium salts $[Cp_2MH_2(PR_2H)]Cl$. Deprotonation of these salts leads either to hydride phosphine $Cp_2MH(PR_2H)$ or to hydride phosphido $Cp_2TaH_2(PPh_2)$ metalloligands, 69 or 70, respectively. These two kinds of complexes are able to bind $[Cr(CO)_5]$ or $[Cr(CO)_4]$ organometallic fragments to give mono- or dibridged heterobimetallic systems; of these, $Cp_2Ta(H)(\mu\text{-}H)(\mu\text{-}PMe_2)Cr(CO)_4$, 71, has been characterized crystallographically, but the authors suggest that the Ta···Cr distance of 3.293 Å is not indicative of a metal–metal bond.[122]





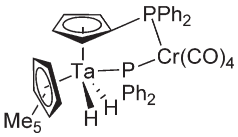
71

These studies have been extended to tungstenocene complexes whereby one of the cyclopentadienyl rings bore a phosphine substituent, as in $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4PPh_2]WHX$ (X = H or Cl), and led ultimately to the binuclear compound 72. Photolysis and loss of a chromium carbonyl yielded the cyclic bridged hydride complex $(\eta^5\text{-}C_5H_5)WH(\mu\text{-}H)[\eta^5\text{-}C_5H_4PPh_2{\cdot}Cr(CO)_4]$, 73, in which the Cr···W separation of 3.30 Å precludes a direct metal–metal bond.[123] The corresponding chloro-bridged complex (η^5-C_5H_5)WCl(μ-Cl)[η^5-$C_5H_4PPh_2$·Cr(CO)$_4$] has also been reported.[124]



72 **73**

The two concepts of having a phosphorus donor group attached either directly to the metal or as a substituent in a cyclopentadienyl ring have been combined in the new bidentate metalloligands derived from tantalocene, (C_5Me_5)(C_5H_4X)Ta(H_2)(PPh_2) and (C_5Me_5)(C_5H_4X)Ta(CO)(PPh_2) (X = PPh_2 or $CH_2CH_2NMe_2$). These molecules can act as chelating bidentate ligands affording bimetallic complexes, notably the Ta(V) complex (C_5Me_5)($C_5H_4PPh_2$)TaH_2(μ-PPh_2)Cr(CO)$_4$, **74**, or the Ta(III) species (C_5Me_5)($C_5H_4PPh_2$)Ta(CO)(μ-PPh_2)-Cr(CO)$_4$, **75**.[125,126]



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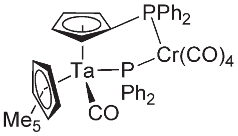

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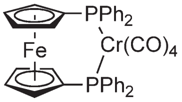
5.04.7.4.3 Ferrocenylphosphines and phosphaferrocenes

A number of chromium carbonyl complexes of 1,1′-bis(diphenylphosphino)ferrocene (dppf) and of 1′-(diphenylphosphino)ferrocenylcarboxylic acid have been reported. In particular, the dimetallic species **76** and **77**, as well as the trimetallic system **78**, have been structurally characterized and also studied by cyclic voltammetry.[127,128]



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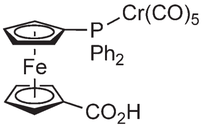

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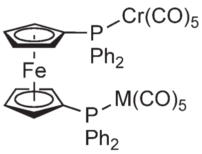
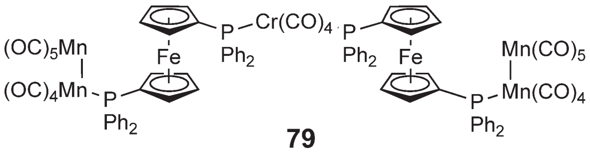


M = Cr, Mo, W

78

This has been extended to the syntheses of a series of oligomeric complexes [(OC)$_x$M(μ-L–L)Cr(CO)$_4$(μ-L–L)M(CO)$_x$], where (L–L) is 1,1′-bis(diphenylphosphino)ferrocene, Fe($C_5H_4PPh_2$)$_2$, or $Ph_2P(CH_2)_mPPh_2$ ($m = 2,3$), and M(CO)$_x$ = Cr(CO)$_5$, Mo(CO)$_5$, W(CO)$_5$, Fe(CO)$_4$, or $Mn_2(CO)_9$. Thus, the repeating units are ferrocenyl or alkyl chain diphosphine and metal carbonyl fragments, and sometimes the oligomeric chains are supported by an M–M bond. The longest polymeric chain described consists of seven metal atoms in (OC)$_5$Mn-Mn(CO)$_4$($Ph_2PC_5H_4$)Fe($C_5H_4PPh_2$)Cr(CO)$_4$($Ph_2PC_5H_4$)Fe($C_5H_4PPh_2$)Mn(CO)$_4$-Mn(CO)$_5$, **79**.[129] Other very interesting heteropolymetallic complexes made in this fashion include (OC)$_5$Cr($Ph_2PC_5H_4$)Fe($C_5H_4PPh_2$)AuCl, **80** (by displacement of the labile ligand from (Me_2S)AuCl), and the trimetallic pentanuclear system *trans*-[(OC)$_5$Cr($Ph_2PC_5H_4$)Fe($C_5H_4PPh_2$)]$_2$MCl_2 (M = Pd or Pt), **81**. All of these complexes were examined by cyclic voltammetry which revealed a chemically reversible phosphinoferrocene-based oxidation, followed by an irreversible oxidation of the molecule.[130]



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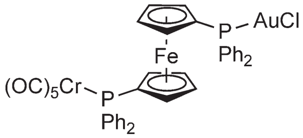

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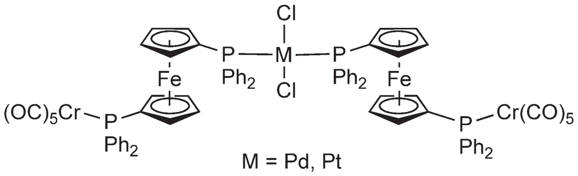
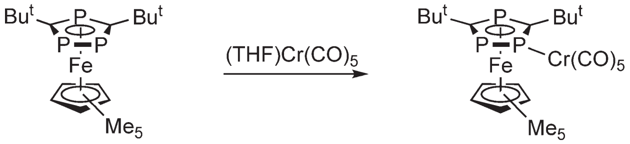


M = Pd, Pt

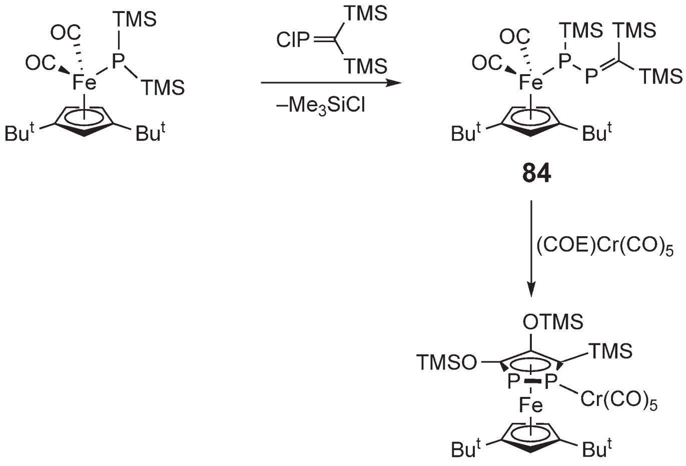
81

The two adjacent phosphorus atoms of the 1,2,4-triphosphacyclopentadienyl ring in [(η^5-C_5Me_5)Fe(η^5-3,5-$(Bu^t)_2C_2P_3$)], 82, can ligate to other metal centers to afford novel bi- and trimetallic complexes. Thus, treatment with (THF)$Cr(CO)_5$ yields [(η^5-C_5Me_5)Fe(η^5-3,5-$(Bu^t)_2C_2P_3$)]$Cr(CO)_5$, 83.[131]



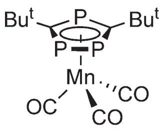
82 **83**

The reaction of (η^5-1,3-$(Bu^t)_2C_5H_3$)$(CO)_2$FeP$(TMS)_2$ with bis(trimethylsilyl)methylenechlorophosphine proceeds with loss of chlorotrimethylsilane to afford the 3-metallo-2,3-diphosphapropene (η^5-1,3-$(Bu^t)_2C_5H_3$)$(CO)_2$FeP(TMS)-P=C$(TMS)_2$, 84. Subsequent treatment with [(*Z*)-cyclooctene]$Cr(CO)_5$ furnished the 1,2-diphosphaferrocene 85, whereby the diphosphapropene moiety has coupled with the two carbonyl ligands to form the diphosphacyclopentadienyl ring, the carbonyl oxygens have combined with trimethylsilyl groups (providing a strong thermodynamic driving force for the rearrangement), and the pentacarbonylchromium group is attached to a ring phosphorus.[132]



85

Analogous complexes derived from (triphosphacyclopentadienyl)tricarbonylmanganese are also known. Thus, triphenylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole reacted with bromopentacarbonylmanganese(I) in THF to give a 61% yield of the triphosphole manganese complex 86, which, on treatment with (THF)Cr(CO)$_5$, furnished the chromium complex 87.[133]



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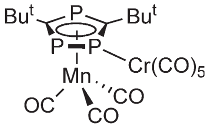
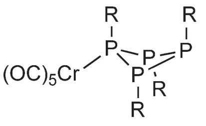


87

5.04.7.4.4 Phosphorus rings linked to chromium carbonyls

The use of chromium carbonyls for the stabilization and X-ray crystallographic characterization of cyclic phosphorus-containing systems is widespread. These include not only P$_n$ rings but also those containing a wide variety of main group elements (B, C, Ge, Sn, N, As, Sb, O, S, Se, Te) and transition metals (Fe, Co, Mn, Mo, Ir).

(1,2,3,4-Tetracyclohexylcyclotetraphosphane)pentacarbonychromium, 88, has been structurally characterized; in each case, the cyclohexyl chair binds to phosphorus via an equatorial site, the P$_4$-ring is bent and the cycloalkyl substituents adopt an *all-trans*-configuration with respect to the P$_4$-ring.[134] In related work, (pentaphenylcyclopentaphosphane)pentacarbonylchromium, (P$_5$Ph$_5$)Cr(CO)$_5$, 89, has been crystallographically characterized in both its triclinic and monoclinic forms.[135,136] The bis[pentamethylcyclopentadienyl]tricyclohexaphosphine, 90, reacts with (THF)Cr(CO)$_5$ to give the zwitterionic trimetallic complex 91, whose basic structure resembles the cuneane motif found in the Hittorf allotrope of phosphorus.[137]



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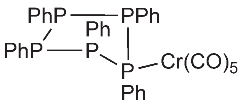

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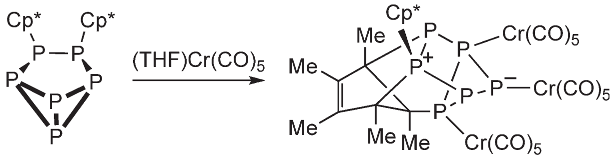
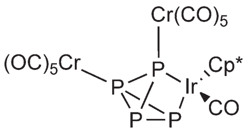


90 **91**

The reaction of [Cp*Ir(CO)$_2$] with white phosphorus under photochemical or thermal conditions produced two bicyclotetraphosphine complexes and a cuneane-type complex that were characterized as the chromium carbonyl complexes 92, 93, and 94, respectively.[138] In a related study, it was found that the photolysis of a range of substituted (cyclopentadienyl)cobalt dicarbonyls with P$_4$ in the presence of (THF)Cr(CO)$_5$ at ambient temperature yielded initially the bicyclotetraphosphine complexes 95. Subsequent loss of the second carbonyl ligand led to formation of the square-pyramidal cages 96 in which the P$_4$-ring bears four Cr(CO)$_5$ substituents. When the cyclopentadienyl ring contains several very bulky substituents, there is a high tendency to lose one or more Cr(CO)$_5$ fragments, as in 97.[139] Similarly, the photochemical reaction of [(C$_5$H$_4$Bu^t)Mo(CO)$_3$]$_2$ with white phosphorus in the presence of (THF)Cr(CO)$_5$ led to the open-cage structure 98 in which the molybdenum is linked to three members of a P$_4$-ring, each atom of which is linked to a Cr(CO)$_5$ moiety.[140]



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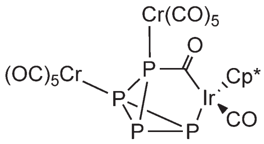

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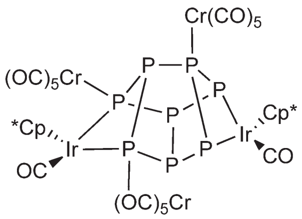

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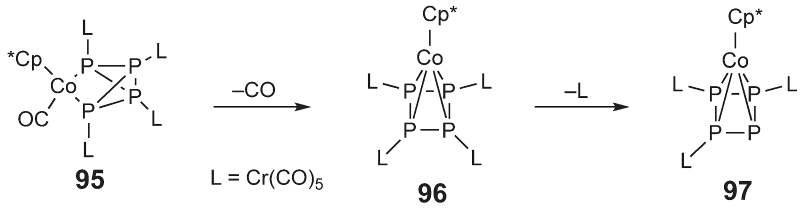
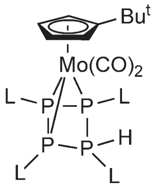


95 L = Cr(CO)$_5$ **96** **97**

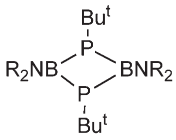


L = Cr(CO)$_5$

98

5.04.7.4.5 Phosphorus–boron-containing rings linked to chromium carbonyls

The reaction of LiP(H)Bu^t with R$_2$NBCl, where R = Et, Pr^i, yields 1,3-diphospha-2,4-diboretanes 99 that form mono- and bis-Cr(CO)$_5$ complexes when treated with (THF)Cr(CO)$_5$. However, if the substituents are sterically demanding, cycloreversion is observed with formation of [(aminoborylidene)phosphinyl-*P*]pentacarbonylchromium compounds as in [(tmp)B=P(Bu^t)]Cr(CO)$_5$ (tmp = 2,2,6,6-tetramethypiperidino), which adopts an allene-like structure 100.[141] Interestingly, (nbd)Cr(CO)$_4$ and 1,2-di-*tert*-butyl-3-(diisopropylamino)-4-(dimethylamino)-1,2,3,4-diphosphadiboretane, 101, yield a complex in which the ligand is isomerized such that the 1,3,2,4-diphosphadiboretane binds in a dihapto fashion to the metal in 102. This process is accompanied by a change of the *tert*-butyl groups from an *anti*-orientation to a *syn*-orientation. Presumably, this rearrangement occurs via a monomeric aminoborylidenephosphine analogous to 100.[142] The cage compounds (Btmp)$_2$P$_2$GeR$_2$ (R = Ph or Me) have also been characterized as the Cr(CO)$_5$ complexes 103.[143]



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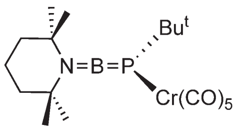

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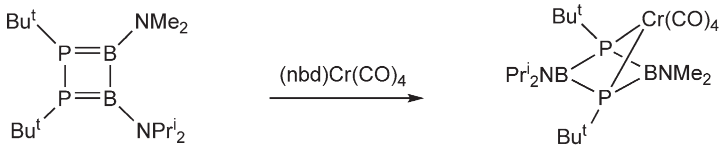
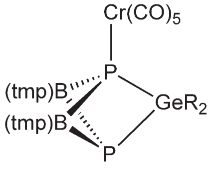
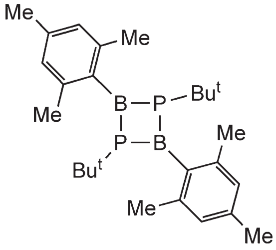


101 **102**



103

Photolysis of the very bulky diphosphadiboretane **104** with (THF)Cr$(CO)_5$ led to the square-pyramidal complex **105** in which the Cr$(CO)_4$ moiety is bonded in an η^4-fashion. Furthermore, the corresponding triphosphatriborin behaves as a six-electron donor when treated with $(CH_3CN)_3Cr(CO)_3$ to yield **106**, which adopts the piano-stool structure conventionally found for (arene)Cr$(CO)_3$ systems.[144,145]



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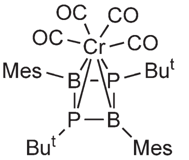
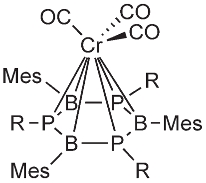


Mes = 2,4,6-$Me_3C_6H_2$

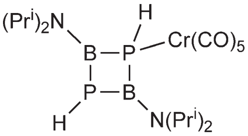
105



R = Bu^t, Ph

106

Structures have also been determined for the chromium carbonyl complexes derived from the diphosphadiboretane $(Pr^i{}_2NBPH)_2$ and the aminodiphosphanylborane $Pr^i{}_2NB(PH_2)_2$. These ligands reacted with $(Me_3N)Cr(CO)_5$ to give **107** and **108**, respectively.[146]



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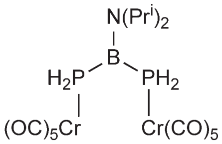
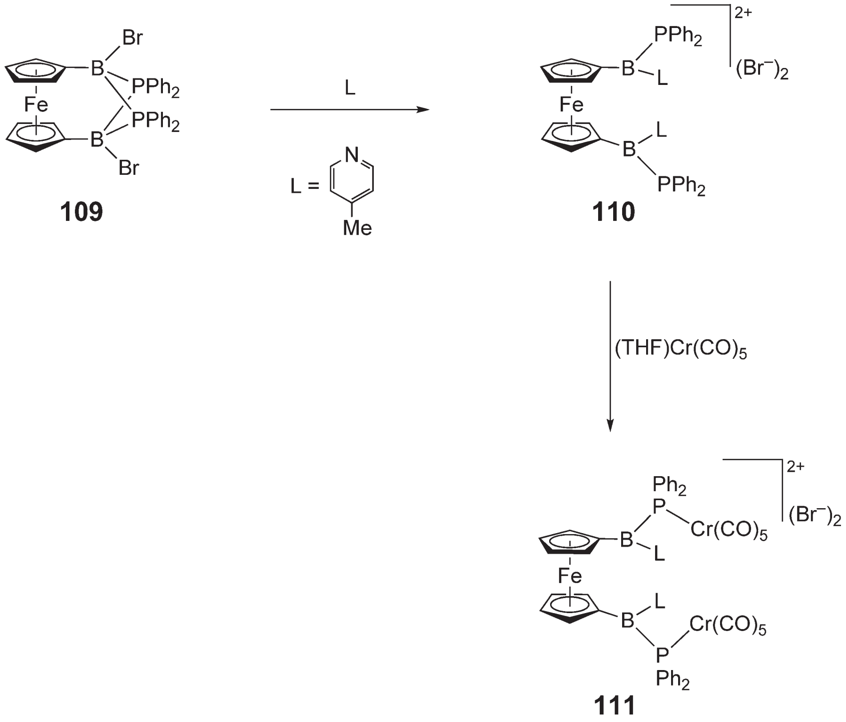


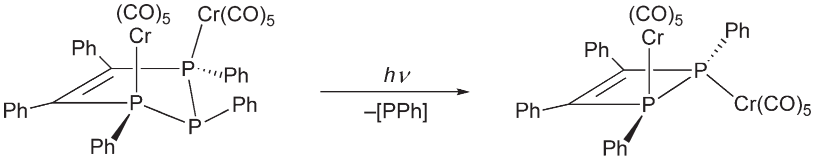
108

When the boron–phosphorus-linked *ansa*-ferrocene **109** was treated with excess γ-picoline, bridge opening occurred with loss of bromide to form the ionic species **110**. The presence of three-coordinate phosphorus centers in **110** was confirmed by their ability to bind Cr$(CO)_5$ fragments, which afforded the trimetallic complex **111**.[147]

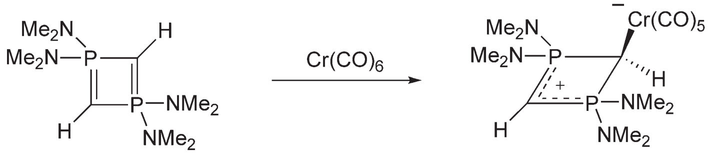


5.04.7.4.6 Phosphorus–carbon-containing rings linked to chromium carbonyls

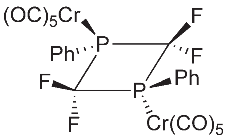
The reaction of (THF)Cr(CO)$_5$ with 1,2,3,4,5-pentaphenyl-1,2,3-triphospholene affords a single stereoisomer of the dichromium complex **112**. Visible light photolysis of **112** generates the ring contraction product [(*trans*-tetraphenyl-1,2-η-1,2–diphosphetene){Cr(CO)$_5$}$_2$], **113**, with loss of a PPh moiety. The structures were all secured by X-ray crystallography.[148] In contrast, 1,1,3,3-tetrakis(dimethylamino)–1λ5,3λ5-diphosphete, **114**, reacts with Cr(CO)$_6$ to yield zwitterionic {1,1,3,3-tetrakis(dimethylamino)-1λ5,3λ5-diphosphete}Cr(CO)$_5$, **115**, that was also characterized by X-ray crystallography.[149] The saturated P_2C_2 ring system in *trans*-2,2,4,4-tetrafluoro–1,3-diphenyl-1,3-diphosphetanediyl-1,3-bis[pentacarbonylchromium(0)], **116**, displays inversion symmetry. The P–CF$_2$ bond is somewhat lengthened on complexation, and the phenyl-diphosphetane interplanar angle is reduced from 89° in the free ligand to 61° in the complex.[150]



112 **113**

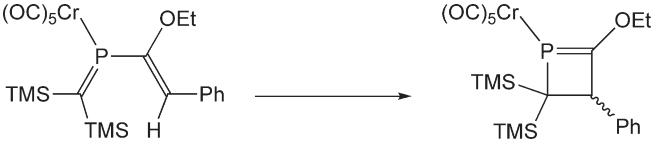


114 **115**



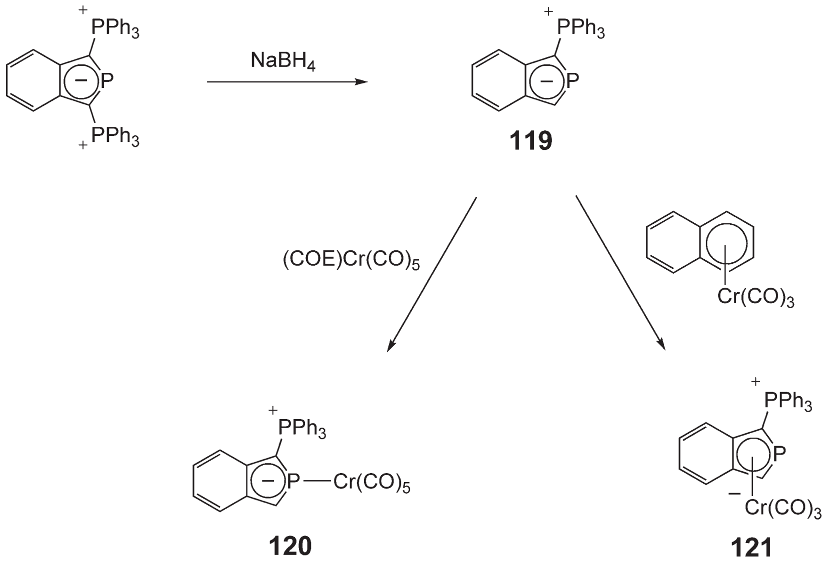
116

Another route to a P_2C_2 ring system begins with the carbene complex [benzyl(ethoxy)methylene]pentacarbonylchromium PhCH$_2$(OEt)C=Cr(CO)$_5$. The complex, after being deprotonated by BuLi, was allowed to react with ClP=C(TMS)$_2$, which, after rearrangement, formed the 2-phosphabutadiene (TMS)$_2$-C=P[Cr(CO)$_5$]-C(OEt)=CHPh, **117**. When warmed to 70 °C in toluene, **117** underwent electrocyclization to form the dihydrophosphete complex **118**.[151]



117 **118**

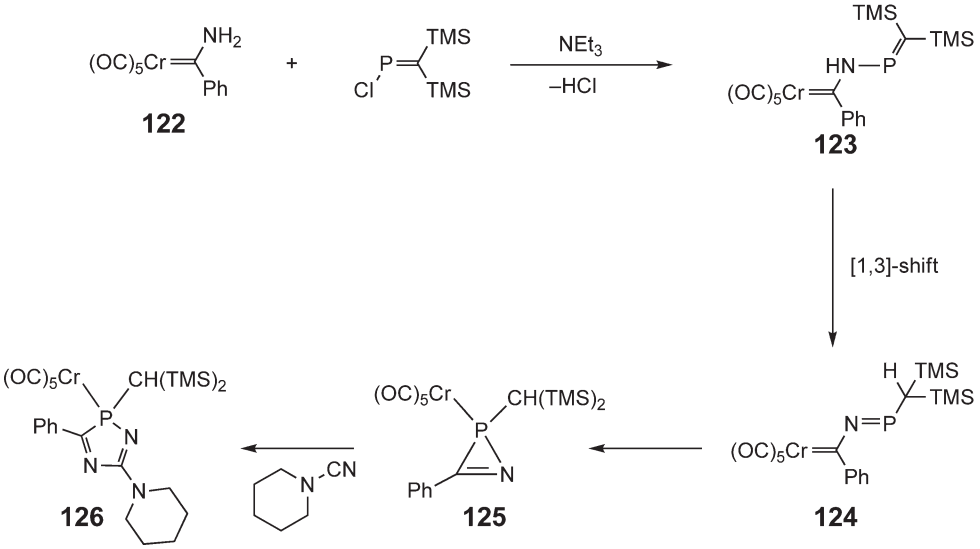
The first example of a π-complex of a 10π-electron phosphorus heterocycle bonded to a *d*-block metal was provided by the 1-triphenylphosphoniobenzo[*c*]phospholide, **119**, which is accessible via the borohydride reduction of 1,3-bis(triphenylphosphonio)benzophospholide. The zwitterion **119** displays an ambident coordination ability similar to a phosphinine, as shown by its reactions with (COE)Cr(CO)$_5$ and (naphthalene)Cr(CO)$_3$, which gave the σ- and π-bonded complexes **120 and 121**, respectively.[152] The products were unambiguously characterized by X-ray crystallography. (η^5-3,5-Di-*t*-butyl-1,2,4-triphosphole)Cr(CO)$_3$ has also been synthesized and structurally characterized and its aromatic character discussed.[153]



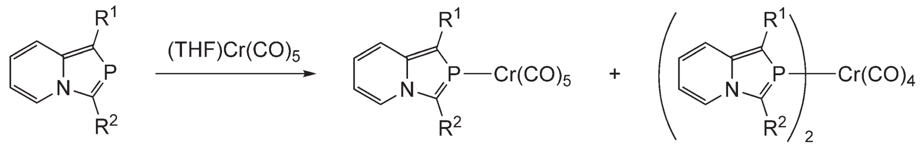
5.04.7.4.7 Phosphorus–nitrogen-containing rings linked to chromium carbonyls

The reaction of the carbene complex **122** with $ClP{=}C(TMS)_2$ in the presence of a base yields initially the P–N-coupled product **123**, which undergoes a 1,3-hydrogen shift, thus generating the P=N double-bonded species **124**. Subsequent cyclization and migration of the pentacarbonylchromium moiety from carbon to phosphorus leads finally to the 3-phenyl-2*H*-azaphosphirene complex **125**.[154] As shown in Scheme 1, further reaction at ambient temperature, using 1-piperidinonitrile as solvent in the presence of tetracyanoethylene, brought about regioselective insertion of 1-piperidinonitrile into the P–N bond of the 2*H*-azaphosphirene complex **125**; the final product is the (2*H*-1,4,2-diazaphosphole)-$Cr(CO)_5$ complex **126**.[155]

In a manner analogous to the behavior of **119**, the 2-phospha-indolizines **127** ($R^1 = Me$; $R^2 = CO{-}Bu^t$, COPh, CO_2Me or CO_2Et), react with $(THF)Cr(CO)_5$, or $(nbd)Cr(CO)_4$, to give the σ-complexes $(L)Cr(CO)_5$ or *cis*-$L_2Cr(CO)_4$, **128** or **129**, respectively.[156]



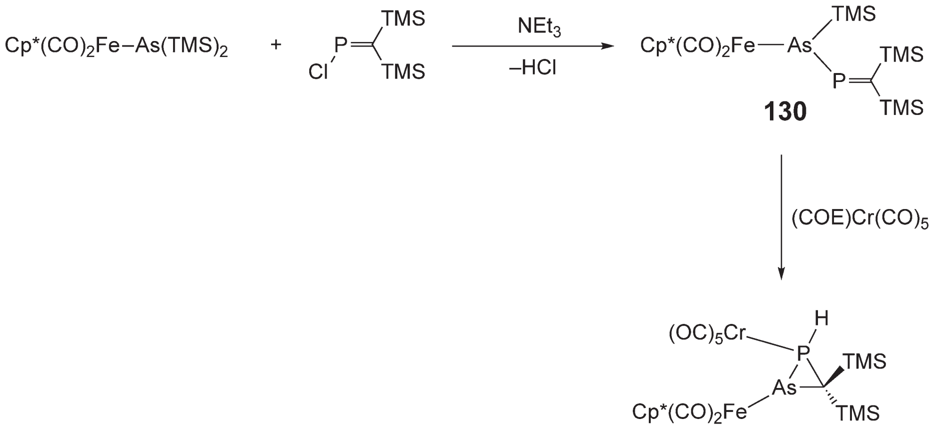
Scheme 1



127 **128** **129**

5.04.7.4.8 Phosphorus rings containing arsenic, antimony, selenium, tellurium, or tin

(η^5-C_5Me_5)(CO)$_2$FeAs(TMS)$_2$ and ClP═C(TMS)$_2$ react with the elimination of chlorotrimethylsilane to form the 1-metallo-1-arsa-2-phosphapropene **130**. Subsequent treatment with [(*Z*)-cyclooctene]Cr(CO)$_5$ furnished the phosphaarsirane-[Cr(CO)$_5$] adduct **131** that was characterized by X-ray crystallography.[157] The compounds (CO)$_5$Cr-EPhH$_2$, where E = P or As, react with RP(C≡CH)$_2$ (R = Bu^t, Bz) via insertion into the E–H bonds to give 1,4-diheterocyclohexa-2,5-diene complexes **132**. Similarly, the dialkynyltin Me$_2$Sn(C≡CPh)$_2$ and (CO)$_5$CrEPhH$_2$ yield the corresponding P–Sn or As–Sn cyclic systems. The 1-phospha-4-arsacyclohexa-2,5-diene can also function as a bridge between two different metals by reaction of the chromium complex **132** with (THF)Mo(CO)$_5$, as depicted in Scheme 2.[158]



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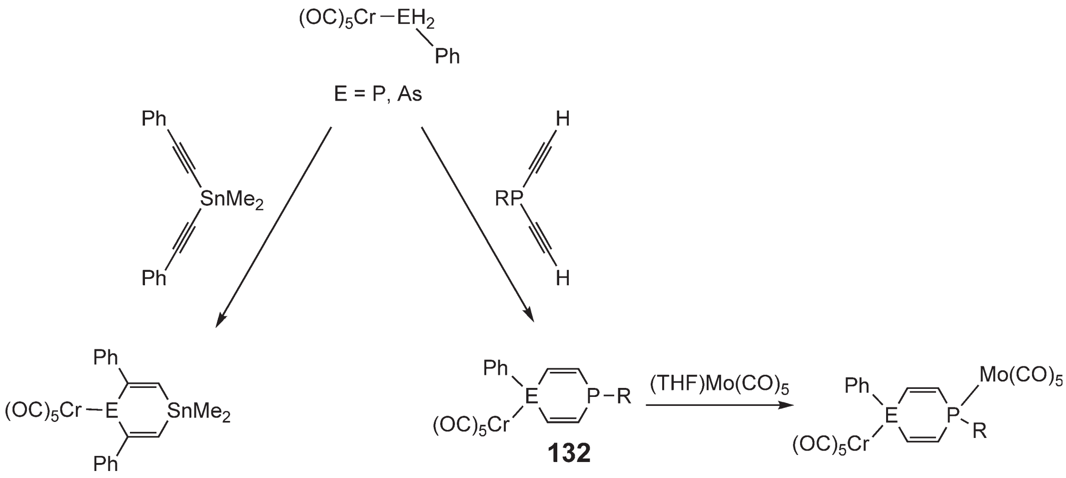
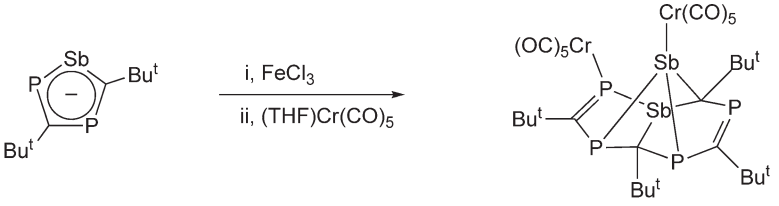
131



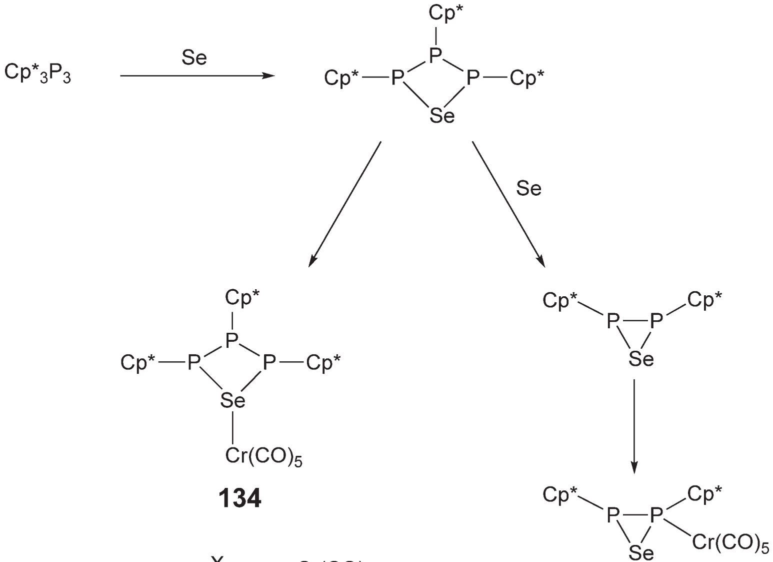
Scheme 2

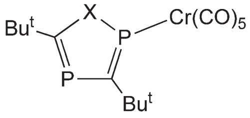
When the antimony-containing cage compound $\mathrm{P_4Sb_2C_4Bu^t{}_4}$ was treated with an excess of $\mathrm{(THF)Cr(CO)_5}$, the product was the 2 : 1 adduct **133** whereby one $\mathrm{Cr(CO)_5}$ fragment was coordinated to an unsaturated phosphorus center while the other is bonded to an antimony center.[159]



133

1,2,3-Tris(pentamethylcyclopentadienyl)cyclotriphosphine reacted with elemental selenium to form the insertion product 2,3,4-tris(pentamethylcyclopentadienyl)selenatriphosphetane, which was trapped as the selenium-coordinated pentacarbonylchromium complex **134**. Subsequent reaction of **134** with more selenium yields the selenadiphosphirane that was also characterized as its $\mathrm{Cr(CO)_5}$ complex **135**.[160] The incorporation of a $\mathrm{Cr(CO)_5}$ moiety allowed the first structural characterizations of the 1,2,4-selenadiphosphole and the 1,2,4-telluradiphosphole aromatic ring systems **136**. Coordination occurs at the phosphorus atom adjacent to the chalcogen in the ring.[161]





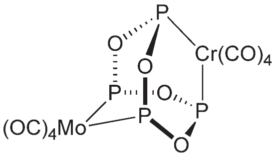
X = Se, Te

136

5.04.7.4.9 Phosphorus–oxygen-containing rings linked to chromium carbonyls

Cyclotetrakis[bis(diisopropylamino)phosphoxane] $\mathrm{[(Pr^i{}_2N)_2P]_4O_4}$ forms a heterobimetallic $\mathrm{Cr(CO)_4}$-$\mathrm{Mo(CO)_4}$ adamantanoid cage, **137**, comprised of four $\mathrm{P_3O_2M}$ six-membered rings.[162,163] However, in the dichromium complex

138, each metal atom is *cis*-coordinated to two phosphorus atoms of the tetraphosphoxane ring to form a four-membered Cr–P–O–P chelate ring, and the eight-membered phosphoxane heterocycle adopts a novel twist-boat-twist-boat configurational isomer of the alternative adamantanoid cage such that the molecule possesses an inversion center.[164]



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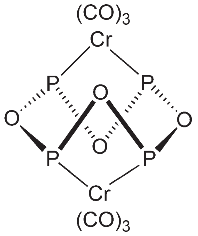

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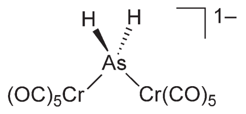
5.04.7.4.10 DFT studies on chromium carbonyl complexes of phosphinidenes and 1,4-diphosphabutadiyne

Calculations at the DFT level have been carried out for the phosphinidene transition metal complexes $(OC)_5Cr\text{-}PR$, where M = Cr, Mo, and W, and R = H, Me, Ph, SiH_3, OH, SH, NH_2, and PH_2. The free phosphinidenes R–P have triplet ground states, but their $M(CO)_5$ complexes prefer singlet states because of the substantial stabilization of the unoccupied phosphorus $p\pi$-acceptor orbital. It was shown that the investigated ligands are strong π-acceptors and even stronger σ-donors. In the case of unsubstituted PH complexes, the ground state is a singlet due to strong preferential stabilization by π-backdonation into the empty phosphorus $p\pi$-orbital. When substituents are present, the situation is somewhat more complex. Although significant π-backdonation is observed for the $(OC)_5Cr\text{-}PCH_3$ and $(OC)_5Cr\text{-}PSiH_3$ complexes, this occurs to a lesser extent in the case with $(OC)_5Cr\text{-}POH$, $(OC)_5Cr\text{-}PSH$, $(OC)_5Cr\text{-}PNH_2$; indeed, the backbonding almost disappears for $(OC)_5Cr\text{-}PPH_2$. Hence, the π-backdonation from the metal fragment decreases accordingly due to competition with this substituent π-donation but remains effective in further preferentially stabilizing the singlet.[165,166]

DFT calculations have also been used to assess the viability of 1,4-diphosphabutadiyne (PCCP) as a target for synthesis. The molecule is apparently a thermodynamically stable, linear P≡C–C≡P dimer that is best considered as having partial triple bond character, similar to the bonding in NC–CN. However, the relatively low HOMO–LUMO gap of 2.5 eV in 1,4-diphosphabutadiyne (vs. 5.6 eV in NCCN) is indicative of kinetic instability, suggesting the high probability of a strong tendency toward polymerization. Nevertheless, coordination of the terminal phosphorus atoms to a transition metal fragment, such as $[Cr(CO)_5]$, enhances the stability of the system, and side-on coordination provides additional stabilization.[167]

5.04.7.5 Chromium Carbonyl Complexes of Arsenic, Antimony, and Bismuth

A very large number of complexes of the general type $R_3ECr(CO)_5$, where E is P, As, Sb, or Bi, have been reported.[168,169] In a typical example, a series of such systems have been prepared, and properties such as the electro-optical Kerr effect, electric dipole moments, and the stereostructural preferences with regard to orientations about the Cr–E bond and Ph group rotations have been studied.[168] However, a variety of chromium complexes incorporating much more novel ligands have also been reported. Thus, $[H_2As\{Cr(CO)_5\}_2]^{1-}$, **139**, $[HE\{Cr(CO)_5\}_3]^{2-}$, **140** (E = As), or **141** (E = Sb), are the first examples of group 6 complexes containing E–H fragments. The dianion **140** reacts with benzyl or propargyl bromides to yield the RX addition products $[(R)(Br)As\{Cr(CO)_5\}_2]^{1-}$; in contrast, **141** forms the halosubstituted complexes $[XSb\{Cr(CO)_5\}_3]^{2-}$ (X = Br or Cl).[170]



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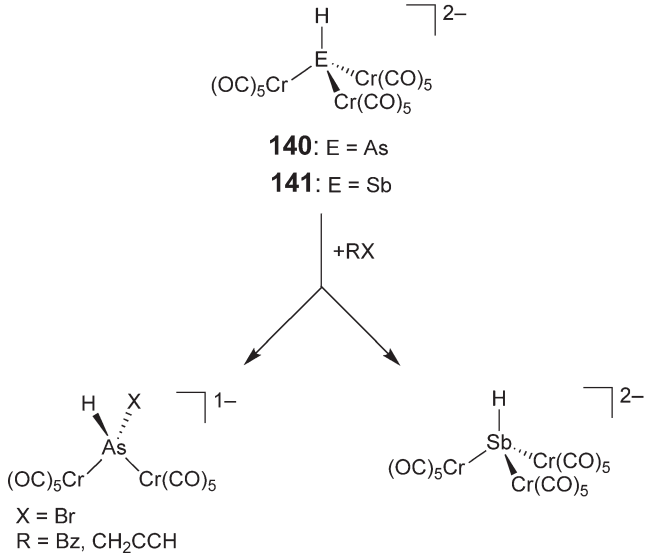


140: E = As

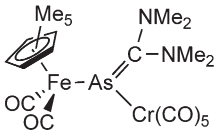
141: E = Sb

+RX

X = Br

R = Bz, CH_2CCH

The metalloarsaalkene $[(\eta^5\text{-}C_5Me_5)(CO)_2FeAs{=}C(NMe_2)_2]$ reacts with $(cod)Cr(CO)_5$ to yield $[(\eta^5\text{-}C_5Me_5)(CO)_2FeAs\{Cr(CO)_5\}{=}C(NMe_2)_2]$, **142**. Interestingly, the analogous metallophosphaalkene complex **143** loses dimethylamine to furnish the iron–phosphorus heterocycle, **144**, in which the P–Cr linkage is retained.[171]



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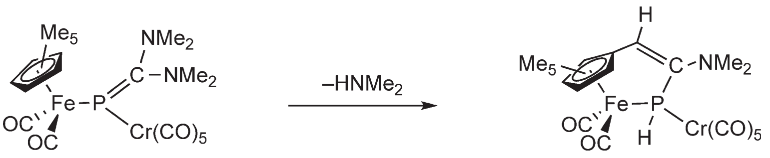


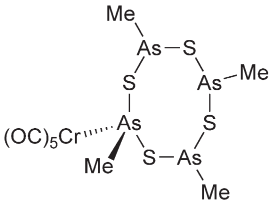
–$HNMe_2$

143

144

As noted previously (in Section 05.04.7.4.1), phosphido- and arsenido-tungsten trisaminatoethylamine complexes, in which the phosphorus and arsenic atoms are terminal ligands, react with $(THF)Cr(CO)_5$ to produce the mono- and bis-coordinated chromium systems **60** and **61**.[115]

Arsenic forms a number of cyclic ligands that can coordinate to chromium in a variety of ways. In the η^3-cyclotriarsenido complex $[(\eta^5\text{-}C_5H_5)Cr(CO)_2(\eta^3\text{-}As_3)]$, the average As–As distance in the triangular ligand was found to be 2.338 Å.[172] Photolysis of the *cyclo*-methylarsathianes, $(MeAsS)_n$, $n = 3$ or 4, with $Cr(CO)_6$ in THF furnished the complexes $[(OC)_5Cr\text{-}\eta^1\text{-}cyclo\text{-}(MeAsS)_4]$, **145**, and $[(OC)_3Cr\text{-}\eta^3\text{-}cyclo\text{-}(MeAsS)_5]$, **146**, in which the As–S ring system had expanded to give metal-stabilized 8- and 10-membered rings, respectively, with alternating arsenic and sulfur atoms. In **146**, the metal coordinates to both the arsenic and sulfur atoms of the ring, thus better accommodating octahedral symmetry at the metal atom.[173]



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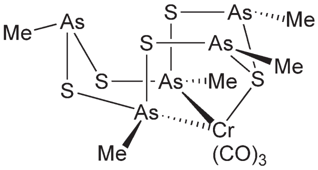
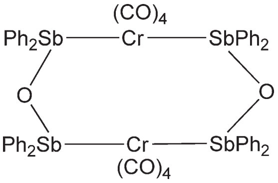


146

Similarly, tetrameric phenylcycloarsoxane $(PhAsO)_4$ exhibits a boat-chair conformation in the solid state but reaction with $Cr(CO)_6$ confirms its capability to undergo metal-mediated ring expansion. Thus, in $\{[cyclo\text{-}(C_6H_5AsO)_6][Cr(CO)_3]_2\}$, the 12-membered As–O rings are stabilized by the participation of alternating arsenic atoms in the coordination spheres of opposite facial chromium tricarbonyl fragments.[174] Other arsenic ligands include the chalcogen-bridged species as in $[(\eta^2\text{-}Ph_2AsOAsPh_2)]Cr(CO)_4$ and $[(\eta^2\text{-}Ph_2AsSAsPh_2)]Cr(CO)_4$.[175]

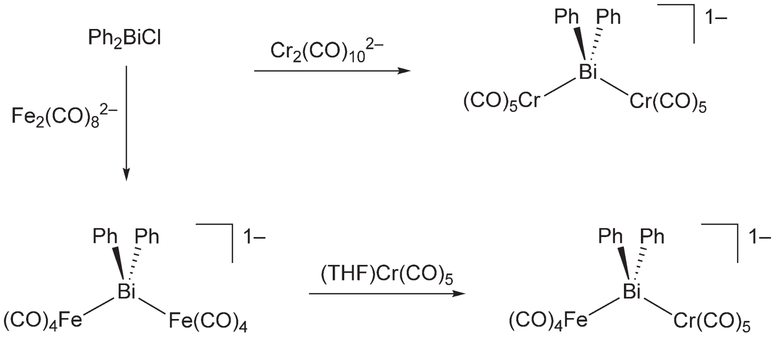
The distibinomethane ligands $R_2SbCH_2SbR_2$ (R = Ph, dpsm; R = Me, dmsm) yield monodentate and bridging bidentate complexes $[M(CO)_5(\eta^1\text{-dpsm})]$ (M = Cr, Mo, W), $[(OC)_5M(\mu\text{-dpsm})M(CO)_5]$, $[(OC)_5M(\mu\text{-dmsm})M(CO)_5]$, and *fac*-$[M(CO)_3(\eta^1\text{-dpsm})_3]$. However, no examples with chelating distibinomethanes were prepared.[176] Recently, however, chromium carbonyl complexes of the di-, tri-, and tetrastibanes $(Bu^t)_2SbSb(Bu^t)_2$, $(Bu^t)_2Sb(SbMe)_nSb(Bu^t)_2$ ($n = 1$ or 2), and $Mes_2Sb(SbPh)_nSbMes_2$ ($n = 1$ or 2) have been prepared. These multidentate antimony systems can function as bridging or as chelating ligands, as in $[(OC)_5Cr](Me_2SbSbMe_2)[Cr(CO)_5]$ or $[Cr(CO)_4(Ph_2Sb\text{-}SbPh\text{-}SbR\text{-}SbPh_2)]$ ($R = CH_2SiMe_3$), which have been characterized by X-ray crystallography.[177] ^{121}Sb Mössbauer spectra of several $[Cr(CO)_5(SbR_3)]$ complexes have been interpreted in terms of the degree of electron transfer from antimony to the transition metal.[178] Thermolysis of $(\eta^4\text{-norbornadiene})Cr(CO)_4$, or photolysis of $Cr(CO)_6$, with the stibines Ph_2SbCl and $(Ph_2Sb)_2X$ (X = O or S) gives rise to $Ph_2Sb(Cl)\text{-}Cr(CO)_5$ and $[(Ph_2Sb)_2X\text{-}Cr(CO)_4]_2$, respectively. In the latter cases, the eight-membered rings **147** are formed.[179] Another noteworthy result involves the gas-phase reaction of $[Sb_2]^{1-}$, formed by laser ablation of elemental antimony, with neutral group 6 and group 8 metal carbonyls to produce the first antimony-to-transition metal triple bonds, as exemplified by $[Sb{\equiv}Cr(CO)_4]^{1-}$; *ab initio* calculations show it to be consistent with a primarily covalent triple bond.[180]



147

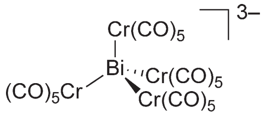
Another interesting series of multiply bonded antimony–chromium carbonyl complexes are the cationic species that arose from the abstraction of chloride by Lewis acid reagents from the stibinidene complexes $[\{(\eta^6\text{-arene})Cr(CO)_2\}_2SbCl]$ (arene = Me_6C_6, 1,3,5-$Me_3C_6H_3$, C_6H_6) to produce the allene-type dichromastibacumulenium ions $[(arene)Cr(CO)_2{=}Sb{=}Cr(CO)_2(arene)]^+$, which were detected spectroscopically in solution. Their stability is enhanced with an increasing number of methyl substituents on the arene ligand.[181]

The ditertiary bismuthine *p*-$Ph_2BiC_6H_4BiPh_2$ reacts to yield mono- and dicomplexed chromium carbonyls $[(p\text{-}Ph_2BiC_6H_4BiPh_2)Cr(CO)_5]$ and $[(p\text{-}Ph_2BiC_6H_4BiPh_2)\{Cr(CO)_5\}_2]$. A survey of $BiPh_3$ and its compounds established that the C–Bi–C angles increase upon complex formation.[182] Treatment of Ph_2BiCl with the anion $[Cr_2(CO)_{10}]^{2-}$ produces $[Ph_2Bi\{Cr(CO)_5\}_2]^{1-}$. The analogous reaction of Ph_2BiCl with $[Fe_2(CO)_8]^{2-}$ yields $[Ph_2Bi\{Fe(CO)_4\}_2]^{1-}$ that, upon further reaction with $(THF)Cr(CO)_5$, generates the heterometallic cluster $[Ph_2Bi\{Fe(CO)_4\}\{Cr(CO)_5\}]^{1-}$ **148**.[183]



148

A series of novel pentacarbonylchromium derivatives of bismuth has been prepared by reactions of sodium bismuthate with $Cr(CO)_6$ in KOH/MeOH solutions.[184] At room temperature, the highly charged anion $[Bi\{Cr(CO)_5\}_4]^{3-}$, **149**, is formed, in which the central bismuth atom is tetrahedrally coordinated to four $[Cr(CO)_5]$ groups. However, at 80 °C, the product is the methyl complex $[MeBi\{Cr(CO)_5\}_3]^{2-}$, **150**, presumably via the C–O activation of MeOH. Further reactions of **149** with CH_2Cl_2 or propargyl bromide yield the halosubstituted complexes $[XBi\{Cr(CO)_5\}_3]^{2-}$ (X = Cl or Br), whereas with alkyl iodides **149** furnish $[RBi\{Cr(CO)_5\}_3]^{2-}$ (R = Me, Et).[184] The formation of these products may involve the intermediate bismuthinidene $[Bi\{Cr(CO)_5\}_3]^{1-}$, or possibly the trianion $[Bi\{Cr(CO)_5\}_3]^{3-}$, the former being isoelectronic with the previously discussed lead(IV) analog $[Pb\{Cr(CO)_5\}_3]^{2-}$ in **25**.[63,64]



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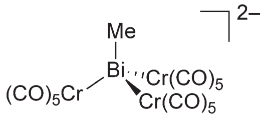


150

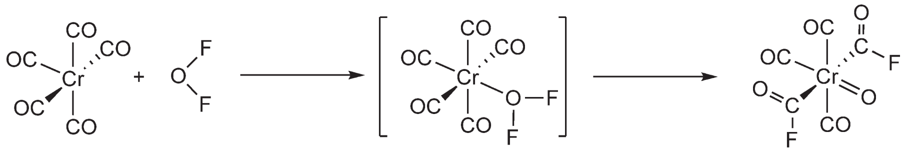
5.04.7.6 Chromium Carbonyl Complexes of Group 16

5.04.7.6.1 Reaction of pentacarbonylchromium with oxygen difluoride

DFT was used to calculate the reaction of OF_2 with the fragment $Cr(CO)_5$. Unlike SF_2 or SeF_2, OF_2 does not show simple ligand behavior but reacts with the transition metal fragment via an oxidative addition process leading to a d^2 Cr(IV)–oxo complex, **151**, and transforming two *cis*-carbonyls into fluoroformyl ligands, as shown in Scheme 3. This reaction was calculated to proceed without any major activation barrier, and to be exothermic by approximately 100 kcal mol^{-1}.[185]

5.04.7.6.2 Chromium carbonyl complexes of sulfur, selenium, and tellurium

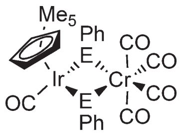
The potentially tridentate trithio-, triseleno-, and tritelluro-ethers $MeC(CH_2EMe)_3$, where E = S, Se, or Te, yield *fac*-$[M(CO)_3L_3]$ complexes of Cr, Mo, or W. However, the Cr complexes of Se and Te are prone to decompose into *cis*-$[Cr(CO)_4\{\eta^2\text{-}MeC(CH_2EMe)_3\}]$. In contrast, the complexes $[Cr(CO)_3(L_3)]$, where L_3 = 1,4,7-trithiacyclononane or 1,4,7-trithiacyclodecane, are stable.[186] The iridium carbonyl half-sandwich complexes $Cp^*Ir(CO)(EPh)_2$ (E = S, Se)



151

Scheme 3

behave as neutral chelating ligands as in $Cp^*Ir(CO)(\mu\text{-}EPh)_2[Cr(CO)_4]$, **152**. A phosphine analog, $Cp^*Ir(PMe_3)(\mu\text{-}SeMe)_2[Cr(CO)_4]$, was also obtained. X-ray data suggest that there is no direct metal–metal interaction.[187]



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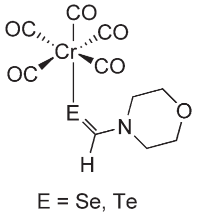
Other complexes in which selenium or tellurium is directly linked to a chromium carbonyl moiety include the seleno- or telluro-amides derived from the reactions of 4-(selenoformyl)morpholine or 4-(telluroformyl)morpholine with $(pyridine)Cr(CO)_5$, as in **153**.[188] Moreover, the diferrocenylthio-, seleno-, and telluro- ketones, **154**, which are synthesized by the reaction of diferrocenyl ketone with P_4S_{10}, $(Me_2Al)_2Se$ or $(Me_2Al)_2Te$, respectively, react with $(THF)Cr(CO)_5$ to yield the corresponding complexes $[(Fc)_2C{=}E][Cr(CO)_5]$, **155**. However, for E = Te, detelluration takes place, and tetraferrocenylethylene $(Fc)_2C{=}C(Fc)_2$ is obtained quantitatively.[189]



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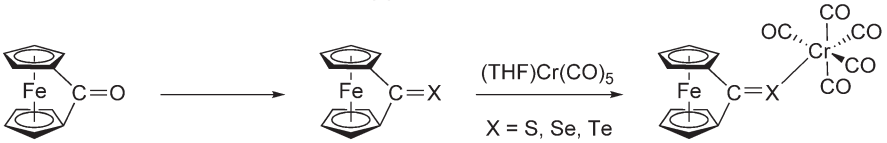
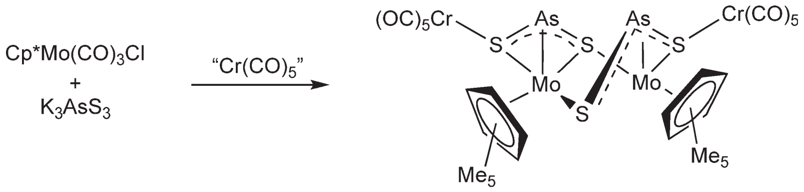


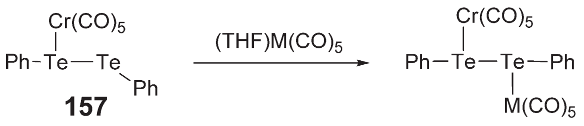
154 **155**

The reaction of $[Cp^*Mo(CO)_3Cl]$ ($Cp^* = C_5Me_5$) with K_3AsS_3 has been investigated under different conditions. At 56 °C, the already known compounds $[Cp^*{}_2Mo_2S_4]$, $[Cp^*{}_2Mo_2As_2S_3]$, and $[Cp^*{}_2Mo_2S_4H_2]$ are formed along with $[Cp^*{}_2Mo_2(CO)_2As_2S_4]$ that was characterized as its bisadduct $[\{Cp^*{}_2Mo_2(CO)_2As_2S_4\}\cdot 2Cr(CO)_5]$, **156**. An X-ray crystallographic study of **156** reveals the presence of two novel AsS_2 ligands, bridging two Mo atoms in a pseudoallylic manner. The $Cr(CO)_5$ fragments are coordinated to both the outer sulfur atoms; thus, each AsS_2 ligand in **156** acts as a seven-electron ligand.[190]



156

The reaction of 1 or 2 equiv. of $(THF)Cr(CO)_5$ with Ph_2Te_2 gives $(Ph_2Te_2)Cr(CO)_5$, **157**, or $[(\mu\text{-}Ph_2Te_2)\{Cr(CO)_5\}_2]$, **158**, respectively; further reaction of **157** with $(THF)W(CO)_5$ yielded $(CO)_5Cr(\mu\text{-}Te_2Ph_2)W(CO)_5$, **159**. The products were characterized by X-ray diffraction and by ^{125}Te NMR.[191,192] The reaction of K_2Te_4 with different stoichiometries of $Cr(CO)_6$ and 2,2,2-crypt in ethylenediamine gives dark brown $[K(2,2,2\text{-crypt})]_2[Cr(CO)_5Te_3]$ and orange $[K(2,2,2\text{-crypt})]_2[\{Cr(CO)_5\}_2Te_2]$. These end-bonded polytellurides were characterized by X-ray crystallography.[193]

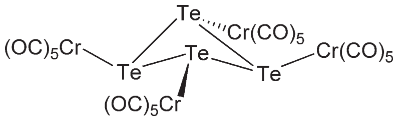


157

158: M = Cr
159: M = W

Subsequently, it was found that the monotelluride-bridged species $[Et_4N]_2[Te\{Cr(CO)_5\}_n]$ ($n = 2$ or 3) are preparable by the reaction of Te powder with 3 equiv. of $Cr(CO)_6$ in the presence of $[Et_4N]Br$ in concentrated ethanolic KOH solution.[194] The Cr_3 species **160** displays a pyramidal geometry with the Te atom bonded to three $Cr(CO)_5$ fragments, whereas the Cr_2 anion **161** adopts a non-linear structure with the Te atom coordinated to two $Cr(CO)_5$ moieties. In effect, these molecules parallel the structures of H_3O^+ and H_2O, which have one and two non-bonded electron pairs, respectively. Interestingly, a novel C–O activation of MeOH was observed when **160** was treated with methanolic NaOH solution at 70 °C, giving the Te-methylated product **162**. The Cr_2 anion, **161**, also reacts with CH_2Cl_2 to form the CH_2-bridged tetrachromium complex $[CH_2\{TeCr_2(CO)_{10}\}_2]^{2-}$, **163**. In methanol, **161** is transformed into the known tetrachromium tritelluride complex $[Te_3\{Cr(CO)_5\}_4]^{2-}$, **164**;[195] it also undergoes oxidative coupling with Cu(I) to form the dimeric open cluster $[Te_2\{Cr(CO)_5\}_4]^{2-}$, **165**, and reacts with NaOH to give the dimeric ring complex $[Te_2Cr_4(CO)_{18}]^{2-}$, **166**, as shown in Scheme 4.[194]

The reaction of elemental tellurium with Cp''_2NbBH_4 ($Cp'' = C_5Me_5$ or C_5Me_4Et) in THF at 60 °C gave $[Cp''_2Nb(Te_2H)]$, which, upon treatment with $(THF)Cr(CO)_5$, gave $[Te_4\{Cr(CO)_5\}_4]$, **167**, the first organometallic derivative of a tellurium allotrope, in this case *cyclo*-tetratellurium.[196] More recently, it has been reported that the niobocene trihydride $[Cp'_2NbH_3]$ ($Cp' = Bu^t\text{-}C_5H_4$) and Te powder react in THF to give $[Cp'_2Nb(Te_2)H]$, which further reacts with $(THF)Cr(CO)_5$ to give $[Cp'_2Nb(Te_2)HCr(CO)_5]$, in which a Te_2 unit and a hydrogen are coordinated to the bent niobocene moiety, and a $Cr(CO)_5$ group is attached to the lateral Te atom.[197]



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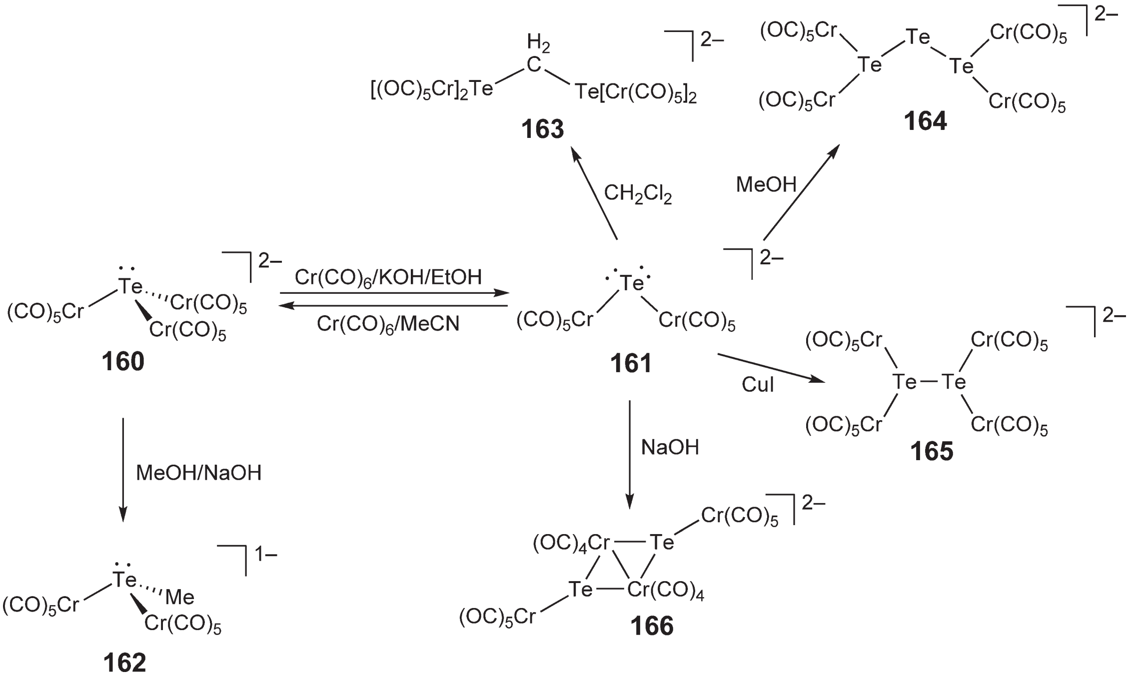
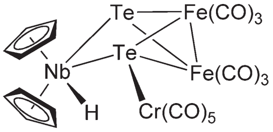


163 **164** **160** **161** **165** **162** **166**

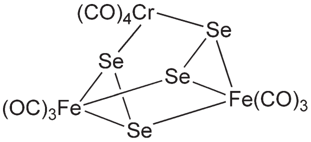
Scheme 4

$[Cp'_2Nb(Te_2)H]$ also reacts with $[Fe_2(CO)_9]$ to give $[\{Cp'_2NbH(Te)_2\}Fe_2(CO)_6]$, which, upon treatment with $(THF)Cr(CO)_5$, furnishes $[\{Cp'_2NbH(Te)_2\}Fe_2(CO)_6Cr(CO)_5]$, **168**, in nearly quantitative yield. The $Fe_2(CO)_6$ unit has added across the Te–Te linkage in a perpendicular fashion, and the incoming $Cr(CO)_5$ fragment bonds to the central Te atom, proximate to the Nb–H moiety. The ^1H NMR spectrum of **168** at −80 °C shows that only the sterically crowded isomer in which the chromium is proximal to the Nb–H had crystallized. Above 0 °C, an additional set of Cp′ and NbH resonances appears, which may be attributed to migration of the $Cr(CO)_5$ fragment from the central to the lateral Te atom.[198]



168

The rich chemistry of clusters containing chromium carbonyls[199] is beyond the scope of this chapter but the novel inorganic quadricyclane, **169**, comprised of a core of iron and selenium (or sulfur) with the latter coordinated to a $Cr(CO)_4$ moiety, is noteworthy.[200]



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5.04.8 Arene Chromium Tricarbonyls

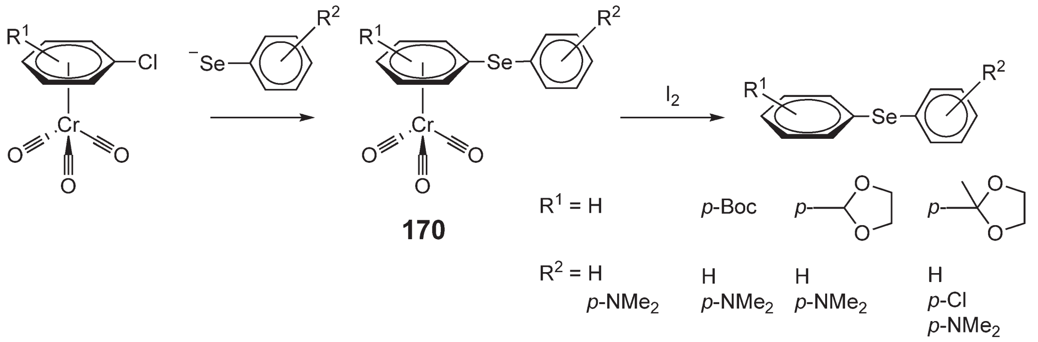
The chemistry of arenes complexed by a chromium carbonyl moiety is one of the most widely studied fields of organometallic chemistry, and completely comprehensive discussion of such an area is not viable within this format. The topic received very extensive coverage in COMC (1982)[201] and COMC (1995)[202] and, in recent years, has again been the subject of numerous reviews. Many truly outstanding studies have been reported, with much emphasis on the exploitation of both planar and axial chirality in organic synthesis. We have cited the leading reviews and have also taken the opportunity to highlight some of the more elegant or widely applicable reaction types.

5.04.8.1 Aromatic Nucleophilic Substitution or Addition Reactions

The π-complexation of a tricarbonylchromium moiety to an arene ring can have a wide variety of consequences. The electron-withdrawing effect of the organometallic tripod renders the ring susceptible to attack by a wide variety of nucleophiles to give cyclohexadienyl–metal complexes. When a suitable leaving group is present in the ring, the nucleophile can be directly incorporated; in other cases, cyclohexadienes are produced. The intermediate cyclohexadienyl complexes can be processed in several ways, leading to several distinct synthesis methods. Thus, the presence of a fluoro or chloro substituent on the arene allows an effective analog of classical S_NAr reactivity, with a wide range of nucleophiles including simple amines, alkoxides, and carbon anions.

Another general process is the addition/protonation protocol, where a hydrogen substituent on the arene is replaced by a nucleophile. This opens new questions of regioselectivity since the typical arene ligand has several hydrogens which are candidates for substitution. This area has been the subject of several comprehensive reviews.[203–206]

A typical straightforward example is the preparation of unsymmmetrical diaryl selenides by nucleophilic displacement of halide by areneselenolates in (η^6-chloroarene)$Cr(CO)_3$ complexes in DMSO at 70 °C. However, the reactivity of the cationic $[(chloroarene)\text{-}Fe(C_5H_5)]^+$ and $[(chloroarene)Mn(CO)_3]^+$ complexes was substantially higher, affording substitution products at ambient temperature in ethanol. Intermediate (arylseleno)arene chromium complexes, **170**, were characterized by ^{77}Se NMR whereby complexation caused a 20–45 ppm downfield shift.[207] Another example involves the reaction of the metallophosphide anions $[(OC)_4FePPh_2]^-$ or $[(OC)_5CrPPh_2]^-$ with tricarbonyl(η^6-fluoroarene)chromium that furnished the dimetallic complexes **171**.[208]



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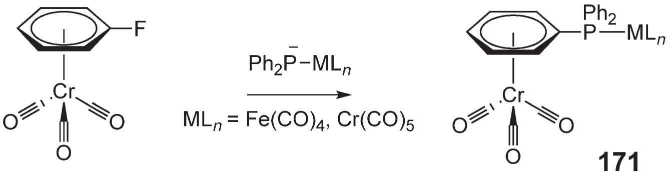
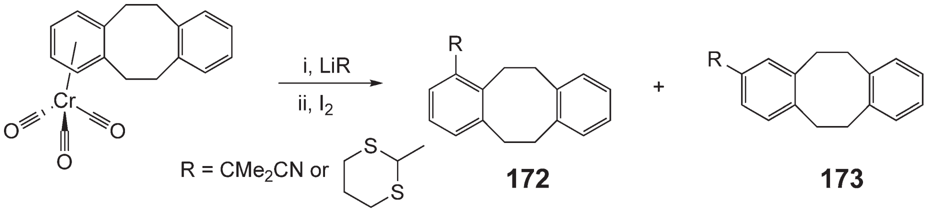


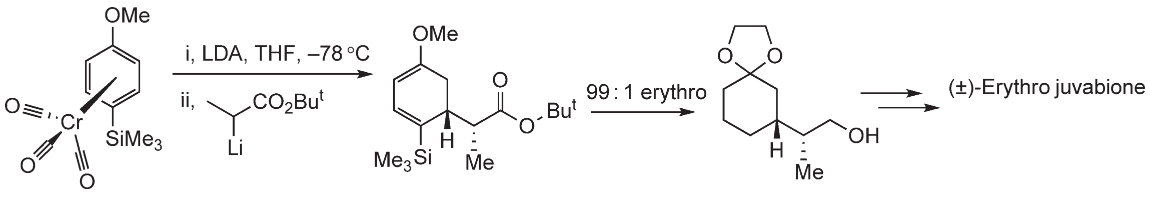
171

Another illustrative reaction involves the generation of 1,2;5,6-dibenzocycloocta-1,5-diene derivatives with α- and β-substituents which are readily accessible from (1,2;5,6-dibenzocycloocta-1,5-diene)$Cr(CO)_3$ via a two-step sequence: initial addition of a nucleophile, followed by oxidation of the intermediate anionic cyclohexadienyl complex. Nucleophiles used included $LiCMe_2CN$, $LiCH_2CN$, and *cyclo*-$S(CH_2)_3SCHLi$. The primary carbanion $LiCH_2CN$ and the *S*-stabilized cyclic carbanion give mixtures of α- and β-substituted products, **172** and **173**, and in both cases, α-isomers were major; in contrast, the opposite regioselectivity was obtained with the tertiary carbanion $LiCMe_2CN$.[209]



172 **173**

A higher level of sophistication arises when the ring is appropriately substituted such that the attachment of a $Cr(CO)_3$ unit differentiates between the faces of a prochiral arene, thus engendering chirality in the molecule.[210] In recent years, a variety of methods have been developed to prepare enantiomerically pure arene–chromium tricarbonyl complexes either en route to complex natural products or as chiral catalysts for asymmetric syntheses. This phenomenon has been exploited in syntheses of cyclohexenones,[211,212] cyclohexadienes,[213,214] lactones,[215] and many others.[216–223] The crucial initial step in the synthesis of (±)-erythro juvabione[224] is a one-pot procedure involving nucleophilic addition, protonation, and decomplexation, and is depicted in Scheme 5.



Scheme 5

5.04.8.2 Cine and Tele Nucleophilic Substitutions in Arene Chromium Carbonyls

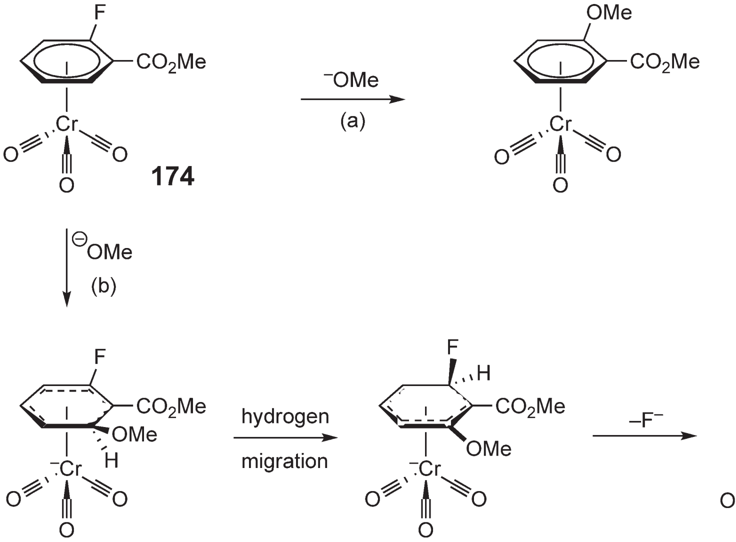
In the reaction of tricarbonyl(η^6-fluoroanisole)chromium with lithium phenylacetylide at low temperature, the overwhelming abundance of *meta*- and *ortho*-products demonstrated that the reaction was not a straightforward S_NAr mechanism. The results provide support for a mechanism in which the nucleophile does not attack at the *ipso* site, but rather at a phenyl ring carbon not bearing the leaving group; subsequent hydrogen migration and finally elimination of the leaving group regenerates aromaticity.[225] In cine-substitution reactions, the entering group attacks a position adjacent to that occupied by the leaving group, whereas in tele-substitutions the entering group takes up a position more than one atom away from the atom to which the leaving group was attached.[204,226,227] This concept can be used to explain a longstanding result from the pioneering days of chiral (arene)tricarbonylchromium chemistry. When the enantiomerically pure methyl ester of (2-fluorobenzoic acid)Cr(CO)$_3$, **174**, was allowed to react with methoxide, the resulting (methyl 2-methoxybenzoate)Cr(CO)$_3$ had partially racemized.[228] This can now be explained by (i) normal nucleophilic displacement of fluoride, that is, *ipso* attack, with retention of stereochemical integrity and (ii) concomitant tele-*meta* attack of the incoming nucleophile at the other site adjacent to the ester functionality, hydrogen migration (possibly via a chromium hydride), and finally elimination of fluoride, as in Scheme 6.

5.04.8.3 Arene Lithiations and Reactions with Electrophiles

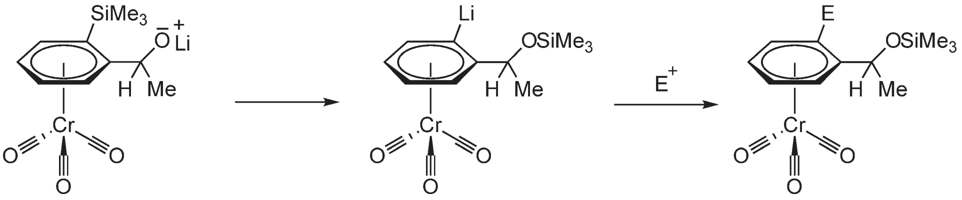
Coordination of an arene to a Cr(CO)$_3$ fragment enhances the acidity of the ring protons which can be removed with strong bases such as LDA and Bu^{n}Li to give (ArLi)Cr(CO)$_3$ complexes. Other methods for producing (ArLi)Cr(CO)$_3$ complexes such as halogen–metal and metal–metal exchange are also known. Even (*o*-chlorophenyl lithium)Cr(CO)$_3$ gives substantial yields of addition instead of benzyne formation, the primary pathway in the absence of the chromium stabilization. In general, the metal-complexed aryllithium derivatives are formed more readily and react like a stabilized version of the free aryllithiums. These (ArLi)Cr(CO)$_3$ complexes react as strong nucleophiles with a variety of electrophiles to provide substituted (arene)Cr(CO)$_3$ species, and this topic has been the subject of several reviews.[229–233]

Another efficient, and elegant, route to lithioarene complexes takes advantage of the activating effect of the Cr(CO)$_3$ unit and combines this with a Brook rearrangement to allow stereoselective bis-functionalizations of arene–chromium systems. Initial nucleophilic addition of an organolithium reagent, for example, MeLi, to the carbonyl moiety in (2-HCOC$_6$H$_4$SiMe$_3$)Cr(CO)$_3$ is followed by a 1,4-carbon-to-oxygen silyl migration and then alkylation of the resultant aryl anion, as depicted in Scheme 7.[234]

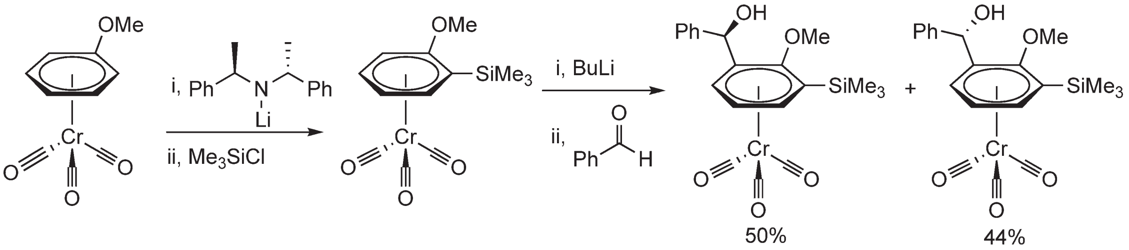
The most significant contributions in recent years involve the development of enantioselective synthetic methods based on the use of chiral lithium amide bases that preferentially abstract protons from particular sites. Typically,



Scheme 6

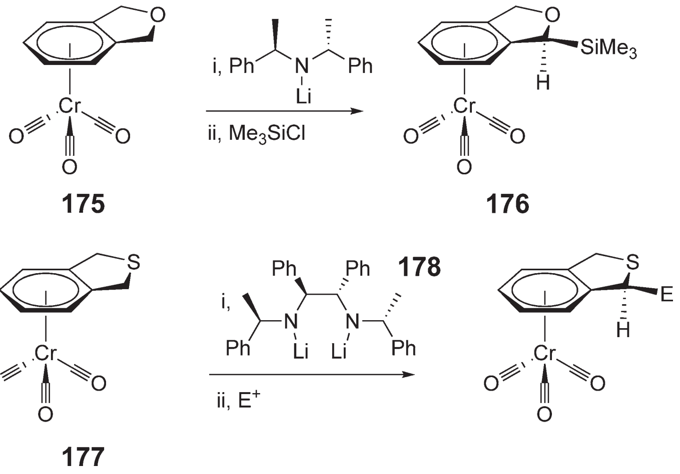


Scheme 7

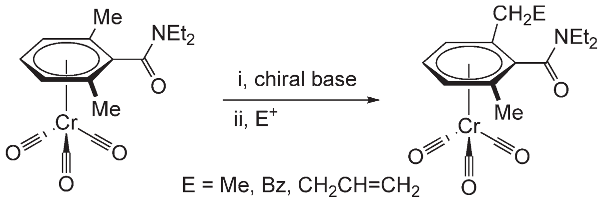


Scheme 8

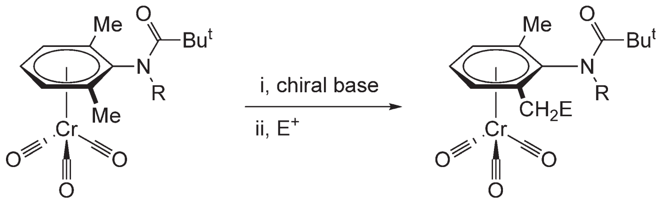
enantiomerically enriched tricarbonyl(η^6-arene)chromium complexes can be obtained in up to 84% ee from the reaction of monosubstituted complexes, for example, (η^6-anisole)Cr(CO)$_3$, with Me$_3$SiCl, mediated by a chiral Li amide base (Scheme 8).[235] Thus, the use of (PhCHMe)$_2$NLi] enables the asymmetric transformation of tricarbonyl[η^6-(1,3-dihydroisobenzofuran]chromium, **175**, into the corresponding *ortho*-silylated complex, **176**, in 82% yield and 76% ee. In the case of tricarbonyl(η^6-1,3-dihydroisobenzothiophene)chromium, **177**, it was necessary to use the bis-Li amide base, (PhCHMe$_2$NLiCHPh)$_2$], **178**, to effect asymmetric substitution with high ee (up to 95%). Decomplexation gave the corresponding chiral products in highly enantiomerically enriched form. In all cases, the absolute stereochemistry of the products was established by X-ray crystallography.[236,237]



Analogously, the axial chiral benzamides, **179**, or anilides, **180**, have been prepared by enantiotopic lithiation at the benzylic methyl of prochiral tricarbonylchromium complexes of *N*,*N*-diethyl-2,6-dimethylbenzamide and *N*-methyl-*N*-acyl–2,6-dimethylaniline with a chiral lithium amide followed by electrophilic substitution. The resulting axially chiral chromium-complexed benzamides and anilides were oxidized in air to give chromium-free axially chiral benzamides and anilides in enantiomerically enriched form without axial bond rotation at room temperature.[238]



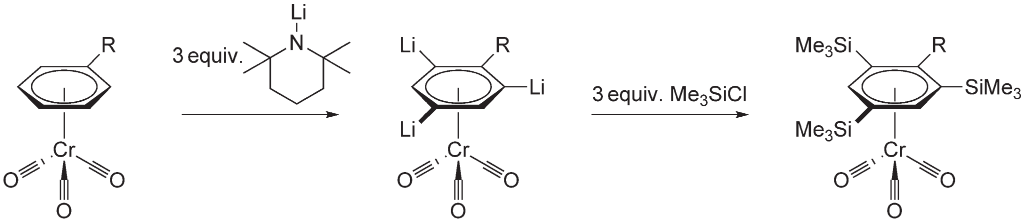
179



R	E
Me	Me, Bz, $CH_2CH{=}CH_2$, CH_2CCMe, CH_2CCPh
Et	Me, Bz
CH_2OMe	Me, Bz

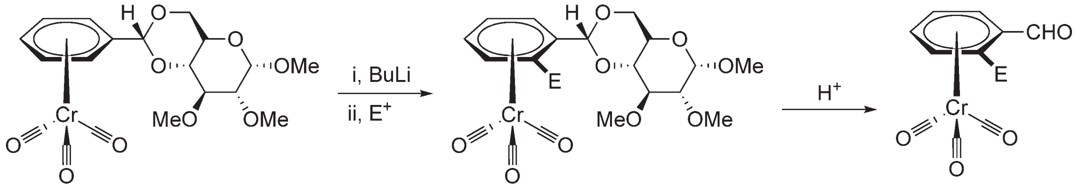
180

The currently known examples of chiral (arene)chromium carbonyls are now very numerous and include the formation of sulfenyl, sulfinyl, sulfonyl, and sultam complexes,[239–243] amides,[244] esters, silylated systems,[245] β-lactones,[246,247] β-aminoesters and β-lactams,[248,249] chiral phosphines,[250] and many others.[251–258] There is also a report of a trianionic species, **181**, whereby the sulfone $(C_6H_5SO_2Bu^t)Cr(CO)_3$ reacted with lithium 2,2,6,6-tetramethylpiperidine in THF at −78 °C followed by a Me_3SiCl quench to give a 50% yield of 2,4,6-$(Me_3Si)_3C_6H_2SO_2Bu^t$.[259,260]

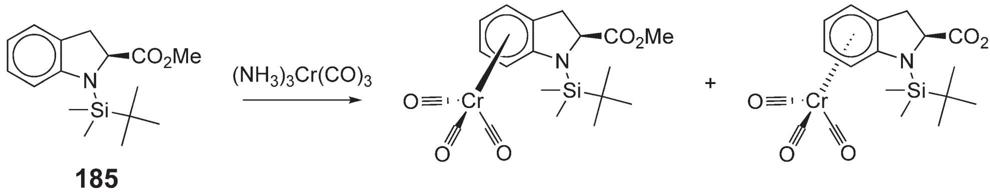


181

An alternative approach used a complex already rendered chiral by the incorporation of a substituent from the chiral pool. Thus, lithiation of the glucopyranoside chromium complex **182** with BuLi in Et_2O followed by treatment with a range of electrophiles gave 65–98% **183** ($E = SiMe_3$, Me, $SnBu_3$, CPh_2OH, SPh, PPh_2, $CH_2{:}CHCH_2$; >98% ee), which on acid hydrolysis gave the aldehyde complexes **184** ($E = SiMe_3$, Me).[261] Similarly, (−)-8-phenylmenthol was prepared and converted to the corresponding tricarbonyl(η^6-arene)chromium complex.[262] Similarly, treatment of enantiomerically pure *N*-*tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester, **185**, with tri(amine)-(tricarbonyl)chromium gave a diastereomeric mixture resulting from addition of the tricarbonyl fragment to either face of the arene. The isomers were separated chromatographically and unambiguously characterized by X-ray crystallography.[263] Another approach involves the use of lipase to effect a kinetic resolution of a series of arene–chromium complexes.[264]



182 **183** **184**



185

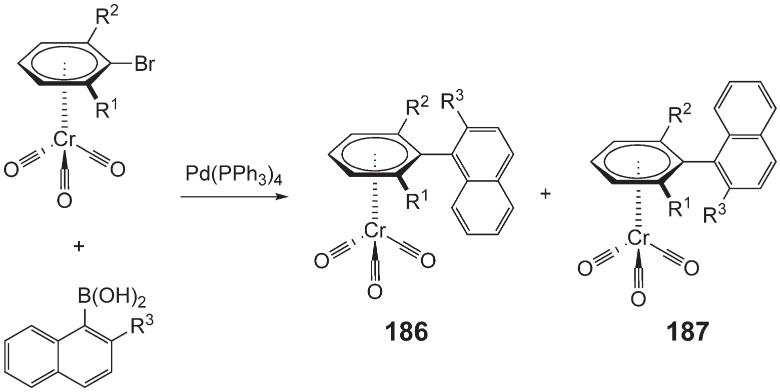
5.04.8.4 Chromatographic Separation of Chiral Arene Chromium Carbonyls

Racemic mixtures of 34 planar chiral disubstituted (η^6-arene)Cr(CO)$_3$ complexes have been examined by HPLC on a chiral stationary phase containing active sites comprised of clefts formed by the perpendicular disposition of π-acidic 3,5-dinitrobenzamide groups relative to π-basic naphthyl groups. Thirty of the 34 showed different retention factors for their enantiomers. To account for the enantiodiscrimination, it was hypothesized that the arene, using the face *anti* to the tricarbonylchromium, enters the cleft and undergoes simultaneous face-to-face and face-to-edge π–π interactions with the aromatic walls of the cleft. Hydrogen bond formation may also provide yet another attractive interaction, thus facilitating enantiodiscrimination.[265]

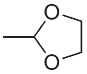
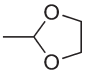
Concurrently, it was established in a different laboratory that most chiral arene–chromium complexes were separable on commercially available Bakerbond Chiralcel HPLC columns of derivatized cellulose on silica gel. Overall the results ranged from good to excellent, and direct resolution of the enantiomers of (ethyl *o*-methoxybenzoate)Cr(CO)$_3$ was performed on a semi-preparative scale with retention times of 77.8 and 179.8 min and optical rotations $[\alpha]_{58921}$ of $+30.0 \pm 4.1°$ and $-29.5 \pm 1.0°$, respectively.[266] Subsequently, enantiomers of chiral tricarbonyl(arene)chromium and cyclopentadienyl-titanium(IV) complexes were separated by HPLC employing a Chiralcel OD (Daicel) column, eluting with hexane/2-propanol mixtures.[267]

5.04.8.5 Palladium Coupling of Arene–Chromium Carbonyls

Axially chiral biaryls have attracted much recent attention.[268] One approach involves nucleophilic displacement of a methoxy group of planar chiral (*o*-methoxybenzoate)chromium complexes with aryl Grignard reagents, but a more widely adopted method invokes Stille or Suzuki palladium-mediated cross-couplings. Typically, diastereomerically axial naphthyl (η^6-phenyl)Cr(CO)$_3$ complexes were prepared by cross-coupling of (arene)chromium complexes with naphthylboronic acids; subsequent axial isomerization from **186** to **187** was accomplished by refluxing of the coupling products in a higher boiling point solvent. The goal of these particular studies was the synthesis of naphthyltetrahydroisoquinoline alkaloids.[269,270]

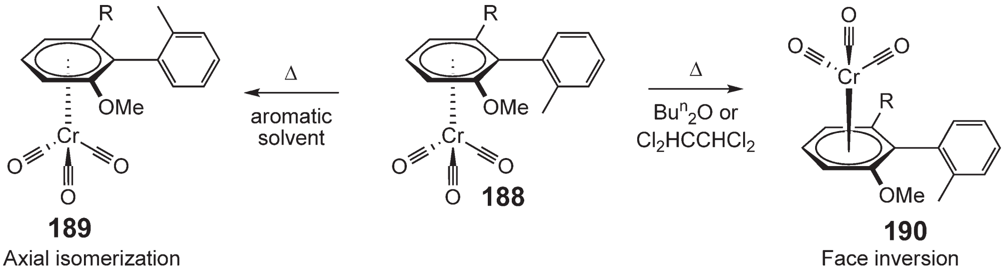


186 **187**

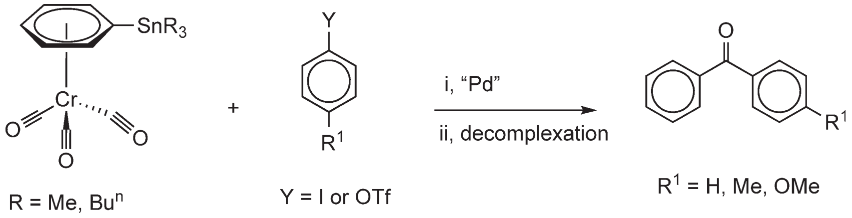
R^1	R^2	R^3
OMe	CHO Me CH_2OH 	H
Me	H	OMe
Me OMe 	H	Me

In a particularly informative study, the factors influencing axial isomerization versus inversion of planar chirality were elucidated. The former process merely requires rotation about the central bond linking the two aryls, whereas the latter involves migration of the organometallic tripod from one face of the arene to the reverse. When an enantiomerically pure sample of a *syn*-biaryl-Cr(CO)$_3$ complex, **188**, with an *ortho*-methyl substituent in the non-complexed ring was heated at reflux in mesitylene, it underwent a central bond rotation to yield the thermodynamically favored *anti*-isomer **189**. In contrast, when heated at reflux in di-*n*-butyl ether, those complexes bearing *ortho*-substituents (e.g., CH_2OMe,CH_2NMe_2) possessing a heteroatom suffer migration of the Cr(CO)$_3$ fragment onto the opposite face of the complexed ring so as to invert the planar chirality, as shown for **190** in Scheme 9. Presumably, this transfer is aided by temporary complexation of the chromium moiety to the heteroatom in the side chain.[271]

Other palladium cross-couplings involving arene–chromium complexes include the incorporation of a wide variety of aryls,[272–274] vinyls,[275] indanes,[276] thiophenes,[277] alkynes,[278] and ketones.[279] In the final case, there is no need to



Scheme 9



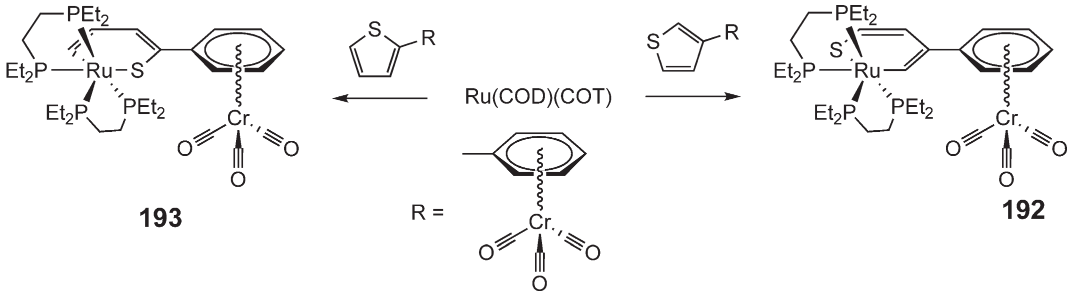
Scheme 10

add CO as it is provided internally by the $Cr(CO)_3$ unit, as in Scheme 10. A particularly fine example demonstrated the use of a planar chiral tricarbonyl(aryl-halide)chromium complex to generate the key intermediate for the formation of the vancomycin AB ring system by a diastereoselective Suzuki–Miyaura coupling.[280]

The enormous importance of arene–chromium carbonyls as versatile intermediates is further exemplified by the syntheses of dihydroisocoumarins,[281] mitosanes whose skeleton mimics the mitomycin family of anti-tumor agents,[282] serrulatane diterpenoids,[283] complexed mustard agents with anti-tumor properties,[284] the marine diterpene helioporin,[285] anti-inflammatory pseudopterosins,[286] hydrophenalenes related to helioporin E and pseudopterosin G,[287] the anti-infective sesquiterpene (1S,4S)-7,8-dihydroxycalamenene,[288] (−)-steganone and the *O*,*O*′-dimethyl derivative of korupensamine A,[289–292] the spirocyclic core of the antitumor agent fredericamycin A,[293] a precursor of (+)-vertin,[294] and (R)-(+)-lasiodiplodin,[295] (+)-ptilocaulin,[296] and the lythraceae alkaloid (−)-lasubine.[297] A number of major reviews describing the use of arene–chromium carbonyls in organic synthesis have appeared.[298–301]

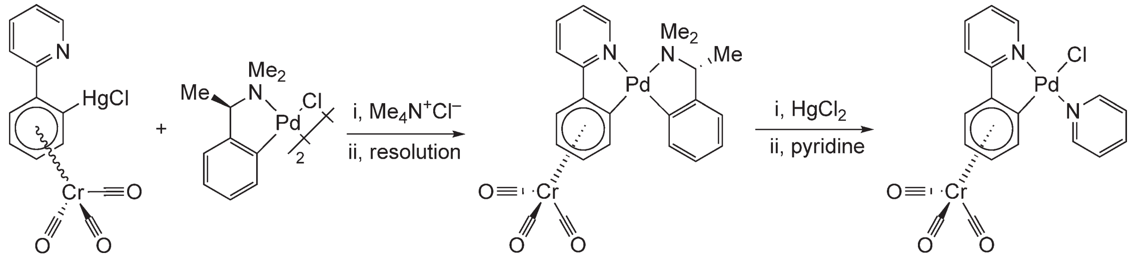
5.04.8.6 *ortho*-Mercurations and -Palladations of Arene Chromium Tricarbonyls

The selective *ortho*-mercurations of tricarbonylchromium derivatives of 2-phenylpyridine, *N*,*N*-dimethylbenzylamine, (1*S*)-1-(dimethylamino)-1-phenylethane, and 2-phenyl-2-oxazoline by $Hg(OAc)_2$ have been reported. The conversion of chloromercurated complexes, for example, $(\eta^6\text{-Ar-HgX})Cr(CO)_3$, into the corresponding homoleptic trinuclear $[(\eta^6\text{-Ar})Cr(CO)_3]_2Hg$ complexes was readily carried out by reaction with Me_4NCl in refluxing acetone. The trimetallic and bimetallic mercurated $(\eta^6\text{-arene})Cr(CO)_3$ complexes were readily converted into cyclopalladated binuclear complexes upon transmetallation with Pd(II) salts. These $(OC)_3Cr$-bound bis-chelated Pd(II) species can be designed for the preparation of enantiopure planar chiral cyclopalladated $(\eta^6\text{-arene})Cr(CO)_3$ complexes. The study of the mechanism of this transmetallation reaction revealed the key role of the excess of chloride salt, which is necessary for the isolation of persistent heteroleptic bis-chelated Pd(II) complexes. Thus, the synthesis has been reported of highly enantioenriched (+) and (−) samples of the *ortho*-chloropalladated 2-[tricarbonyl(η^6-phenyl)chromium]pyridine, **191**, whose enantiopurity was assessed with the aid of diamagnetic Λ and Δ TRISPHAT salts used as chiral shift ^1H NMR agents. The absolute configurations of the two enantioenriched complexes were determined by X-ray diffraction techniques.[302,303]



193 **192**

Scheme 11



191
ee > 96%

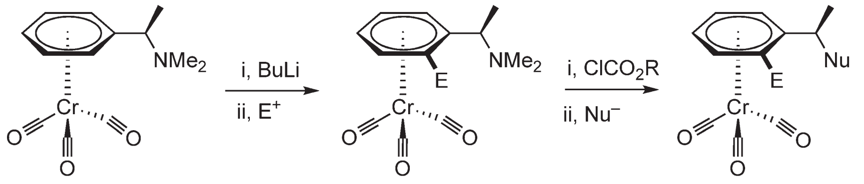
The influence of an (arene)Cr(CO)$_3$ substituent has also been investigated in the insertion of ruthenium into carbon–sulfur bonds. Thiophene bonding and ring-opening modes have been extensively studied as models for the homogeneous hydrodesulfurization (HDS) of petroleum feedstocks. They react with coordinatively unsaturated electron-rich metal complexes to give thiametallacycles. When a thiophene bearing an (arene)Cr(CO)$_3$ substituent at the 3-position is allowed to react with Ru(COD)(COT), the ruthenium inserts into the 1-2 carbon–sulfur bond and the product is stabilized as the bis-diphosphine adduct, **192**, as in Scheme 11. In contrast, when the (arene)Cr(CO)$_3$ substituent is sited at the 2-position, the ruthenium now inserts into the 1-5 carbon–sulfur linkage to yield **193**, that is, the bond attacked is the one less sterically hindered by the presence of the half-sandwich moiety. However, the authors suggest that the electron-withdrawing influence of the arene chromium tricarbonyl may also play an important role in the regioselective insertion of the ruthenium into the carbon–sulfur bond.[304]

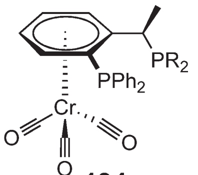
5.04.8.7 Chiral Arene Chromium Complexes as Ligands for Asymmetric Catalysis

Inherently chiral arene–chromium carbonyl moieties have been incorporated into a very wide variety of asymmetric catalytic systems whereby they impose asymmetry on appropriate neighboring transition metal centers. Many such examples of their use as catalysts in asymmetric catalytic synthesis such as chiral hydrogenations, reductions, heterofunctionalizations, and C–C bond formations have now been reported, and the area has been recently reviewed.[305]

Typically, when (*R*)-[{α-(dimethylamino)ethyl}-η^6-benzene]Cr(CO)$_3$ is stereoselectively substituted in the *ortho*-position with PPh$_2$, P(O)Ph$_2$, or CO$_2$R groups, exchange of the amino group for a chloro substituent, and subsequent diastereoselective introduction of a variety of P, N, and O nucleophiles generate bifunctional chelating ligands, as shown in Scheme 12. In particular, the diphosphines, such as **194**, are good catalysts for rhodium-catalyzed enantioselective hydrogenations, while other substitutents give rise to efficient iridium-catalyzed hydroaminations, and palladium-catalyzed allylic sulfonations.[306–308]

Related (arene)tricarbonylchromium-based P–P and P–N ligands attached to arene–ruthenium(II), C$_5$Me$_5$–rhodium(III), and –iridium(III) centers have been characterized by X-ray crystallography, and have been studied in catalytic hydrogen transfer reactions and in the kinetic resolution of racemic alcohols, where they showed good conversion, but low enantioselectivity.[309] Other effective enantioselective hydrogenation catalysts based on an arene–chromium skeleton bear a phospholane substituent[310] or possess aminophosphine–phosphinite ligands derived from tetrahydroisoquinoline. The latter compounds have been examined as chiral auxiliaries in the hydrogenation of functionalized ketones, and a cyclopentyl-substituted *anti*-stereoisomer gave the highest enantioselectivities (up to >99% ee).[311]

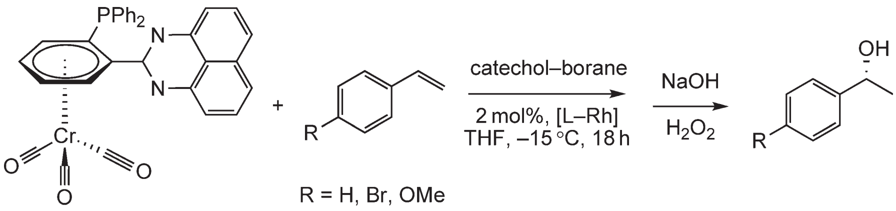




194

E	*R*^{1}	*Nu*	*R*^{2}
CO_2R^1	Me	PR^2_2	Ph Bu^t
$P(O)R^1_2$	Ph	PR^2_2	Ph
PR^1_2	Ph	PR^2_2	Ph Cy Bu^t *p*-C_6H_4F
		OMe	
		NHCHMePh	
		CN	
	Cy	PR^2_2	Ph
	Pr^i		

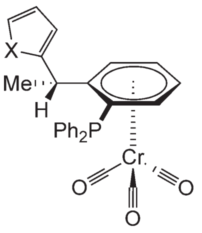
Scheme 12



195

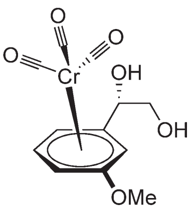
Scheme 13

The versatility of asymmetric catalysts based on the (arene)tricarbonylchromium framework is exemplified by rhodium systems for hydroboration (as in the P–N-complexed Rh derivative of the ligand **195** shown in Scheme 13),[312,313] palladium- or rhodium-based systems containing the furan- or thiophene-containing ligand **196** for the hydrosilylation of styrene or of ketones,[314,315] allylic alkylation of arenes,[316–318] asymmetric addition of diethylzinc to ketones[319–322] (leading to macrolides such as (*R*)-(−)-phoracantholide and (*R*)-(+)-lasiodiplodin[324]), palladium-catalyzed aryl aminations,[325] hydroformylations,[326] hydrogenations,[327] and complexes such as the facial diastereomers of tricarbonyl[(η^6-3-methoxyphenyl)-1,2-ethanediol]chromium, **197**,[328] or of 1,2,3,4-tetrahydronaphthalene-1,2-diol,[329] that can function as π-face selective auxiliaries in Lewis acid-catalyzed Diels–Alder cycloadditions, as in the cycloaddition of methacrolein and cyclopentadiene.[330]



X = O, S, NMe

196



197

5.04.8.8 The Influence of (Arene)tricarbonylchromium Substituents on Cycloaddition Reactions

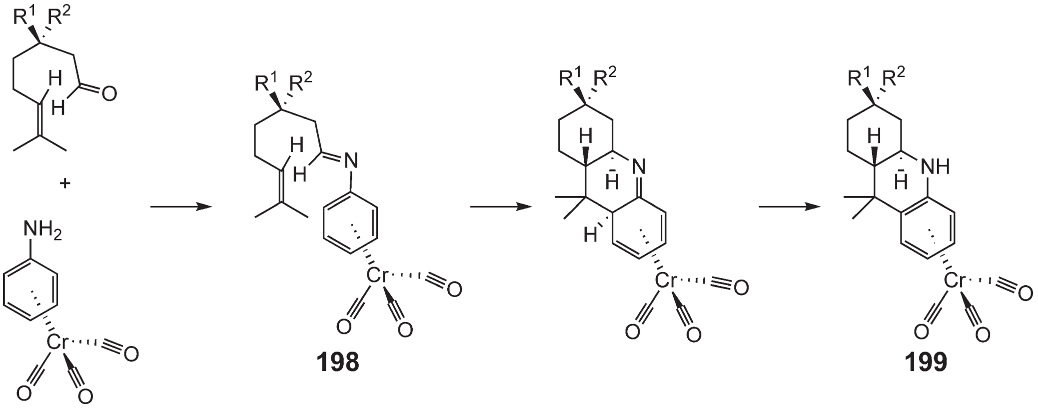
5.04.8.8.1 [2 + 2]-, [3 + 2]-, and [4 + 2]-cycloadditions

The attachment of a bulky (aryl)Cr(CO)$_3$ substituent to one component of a cycloaddition reaction can impose a considerable degree of stereochemical control. Thus, the novel (imino-η^6-arene)chromium complexes, **198**, (R^1, R^2 = H, Me) with non-activated olefins tethered to the 2-azadiene system were found to participate in a diastereoselective intramolecular Lewis acid-catalyzed hetero-Diels–Alder reaction to give the (η^6-octahydroacridine)chromium complexes **199**. As shown in Scheme 14, in the transition state, the tethered dienophile can attack only from the top face of the 2-aza-diene moiety because the lower face is completely shielded by the tricarbonylchromium fragment. The *trans*-nature of the ring junction was verified by a single crystal X-ray structure determination.[331]

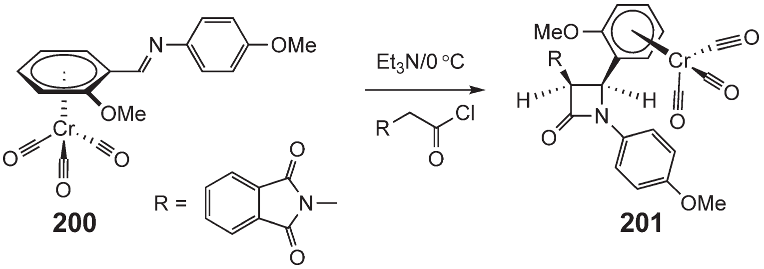
Another good example is provided by the stereoselective [2 + 2]-cycloaddition reaction between the chiral tricarbonyl(η^6arene)chromium-complexed imine, **200**, and phthalimidoketene to afford the chromium-complexed 3-phthalimido-2-azetidinone, **201**, in enantiopure form (Scheme 15). Decomplexation and the cleavage of the phthalimido group furnished the corresponding 3-amino-4-substituted-2-azetidinone, and demonstrates a general route to homochiral β-lactams.[332,333]

Other processes that invoke arene chromium tricarbonyls as stereocontrol agents include the syntheses, via a highly diastereoselective [3 + 2]-cycloaddition, of enantiopure pyrrolidines from acrylates and azomethine ylides linked to a planar chiral chromium,[334] the zinc chloride-promoted stereoselective cyclocondensation of the Danishefsky diene [(E)-MeOCH=CHC(=CH$_2$)OSiMe$_3$] to *ortho*-substituted benzaldehyde- and benzaldimine-Cr(CO)$_3$ complexes to give 2,3-dihydro-4-pyridinone and 2,3-dihydro-4-pyranone derivatives in fairly good (75–90%) yields and with complete stereoselection,[335] and the use of chromium carbonyl derivatives of 8-phenylmenthol acrylates to modulate π-stacking effects in Diels–Alder reactions.[336]

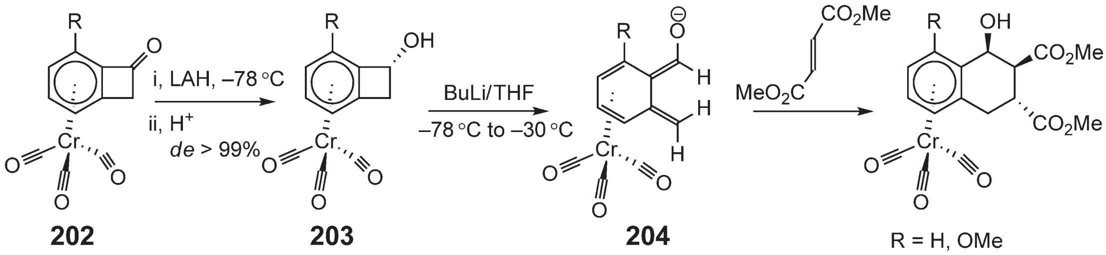
The tricarbonylchromium-complexed benzocyclobutenone, **202**, exhibits much versatile chemistry. Reduction with a hydride source yields the *endo*-alcohol, **203**, which, after deprotonation at −78 °C, ring-opens at approximately −30 °C to an *ortho*-quinodimethane intermediate, **204**, that reacts with a range of dienophiles, as in Scheme 16.



Scheme 14

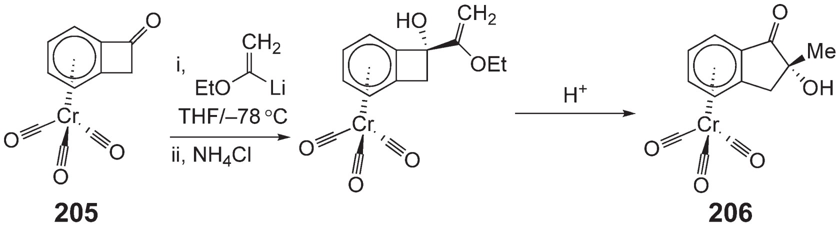


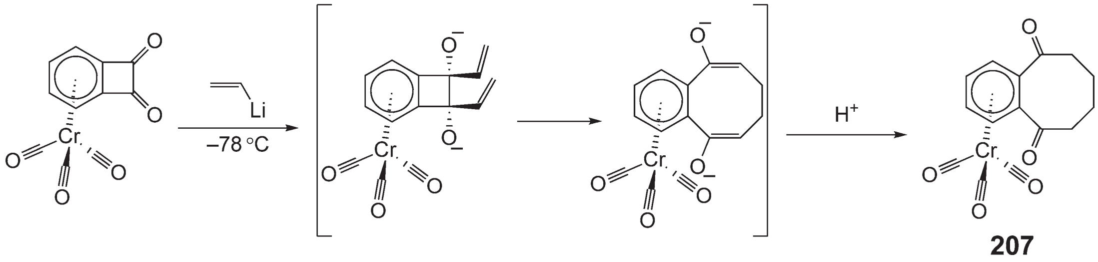
Scheme 15



Scheme 16

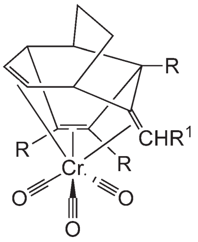
Moreover, treatment of the enantiomerically pure ketone, **205**, with 1-ethoxy-1-lithioethene leads to the exo-vinyl derivative that undergoes acidic hydrolysis to the ring-expansion product, **206**, with complete retention of stereochemical integrity. This procedure has been extended whereby the reaction of excess ethenyllithium with the chromium complex of benzocyclobutenedione yielded the *cis*-1,2-divinyldiolate, that undergoes a dianionic oxy-Cope rearrangement to furnish, eventually, the ring-expanded benzocyclooctenedione, **207**.[337–343] This chemistry and other related reactions in the area have been reviewed recently.[344]





5.04.8.8.2 Higher-order cycloadditions

Transition metal-promoted higher-order cycloaddition reactions have been described. Thus, (η^6-1,3,5-cycloheptatriene)tricarbonylchromium and various substituted derivatives undergo photochemically or thermally initiated [6π + 4π]-cycloaddition with a range of substituted butadiene partners. Electron-rich and electron-deficient dienes participate equally well in the transformation, and only the *endo*-diastereomers were produced.[345,346] 1,3,5-Cycloheptatriene can also undergo stereoselective [6π + 4π]-cycloaddition reactions with conjugated 1,3-dienes to yield substituted, chiral bicyclo[4.4.1]undecatrienes in the presence of chromium carbonyl catalysts.[347] Similarly, UV-photolysis of [η^6-tricarbonyl(*N*-cyanoazepine)chromium] with a range of conjugated dienes gave rise to [6 + 4]-cycloadducts.[348] Furthermore, UV irradiation of the cycloheptadienyl complexes [(η^5-C_7H_8R)Cr(CO)$_3$SnPh$_3$] or cyclohexadienyl complexes [(η^5-C_6H_6R)Cr(CO)$_2$(NO)] and 2 equiv. of 2-butyne or 3-hexyne in toluene or *n*-hexane gave tricyclic complexes, for example, **208** or **209**, (R = Me, R^1 = H; R = Et, R^1 = Me), arising from sequential [5 + 2]- and homo [5 + 2]-cycloadditions of two alkyne molecules to the η^5-dienyl manifold.[349] Cycloadditions involving heptafulvene complexes have been comprehensively reviewed.[350]



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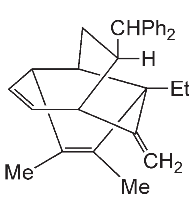
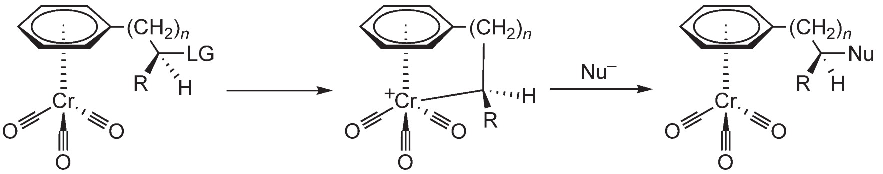


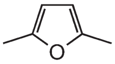
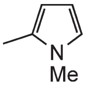
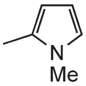
209

5.04.8.9 Chromium-stabilized Benzyl Cations and Related Complexes

The ability of a chromium tricarbonyl fragment to stabilize benzyl cations (or anions, or even radicals) has long been recognized. Indeed, this remarkable property has earned the $Cr(CO)_3$ unit the sobriquet of being hermaphroditic whereby the excess or deficit of electronic charge at the benzylic carbon can be alleviated by differing degrees of backdonation from the metal into the carbonyl vacant π^*-orbitals.[351,352] This phenomenon is, of course, readily monitored via the carbonyl infrared stretching frequencies. The topic has been reviewed, with especial emphasis on the retention of stereochemical integrity during the course of nucleophilic substitutions at the benzylic site,[353] and on the details of the reaction mechanism.[354] Moreover, it has been demonstrated that this stabilization is not restricted to the benzylic (α-) position, but that (η^6-arene)tricarbonylchromium complexes with leaving groups at the β- or γ-positions also undergo nucleophilic substitution reactions with net retention of stereochemistry via neighboring group participation from the coordinatively saturated chromium atom, as depicted in Scheme 17.[355]

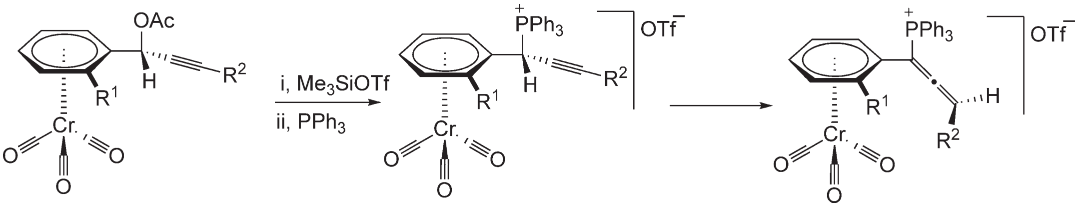
DFT computations have been reported which clarify the structural and energetic effects of tricarbonyl complexation on benzonorbornenyl cations. When the $Cr(CO)_3$ moiety is geometrically confined away from the cationic center, it behaves as an inductively electron-withdrawing group, attenuating the non-classical stabilization provided by the aromatic ring. However, when the Cr atom and the cationic carbon are in close proximity, filled *d*-orbitals on the metal can interact directly with the vacant *p*-orbital on carbon, thus overwhelming and supplanting the traditional non-classical stabilization.[356]



LG	*n*	*R*	*Nu*
I	1	D	OMe
			H
			$CH_2CH{=}CH$
			CH_2CO_2Et
			CH_2COMe
			
			
I	2	Me	
OMs	2	Me	OAc

Scheme 17

Another interesting recent example involves the formation of (arene)$Cr(CO)_3$-substituted σ-propargyl cations, which, upon treatment with Ph_3P, do not yield the expected propargylated phosphonium salts, **210**, but rather furnish allenyl phosphonium salts, **211**, in 69–77% yields via a prototropic isomerization.[357] The synthetic utility of the related (η^6-arene)$Cr(CO)_3$-substituted phosphorylallenes has also been explored.[358–360]



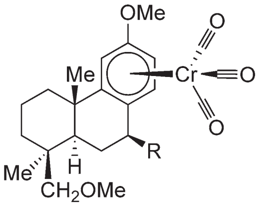
210 **211**

5.04.8.10 Chromium Tricarbonyl Complexes of Polycyclic Hydrocarbons

5.04.8.10.1 Polycyclic aromatics

The range of tricarbonylchromium complexes of polycyclic aromatic hydrocarbons (PAHs) has been considerably extended in recent years. Thus, $Cr(CO)_3$ derivatives of pyrene, fluoranthene, and anthracene have been prepared to supplement the known examples of phenanthrene and naphthalene.[361] Moreover, a study of the complexes derived from 21 substituted PAHs, including phenanthrenes, pyrenes, and partially hydrogenated versions, revealed the regioselectivity of the coordination reactions between PAHs and chromium hexacarbonyl. In contrast to an early report that a $Cr(CO)_3$ moiety always bonds to the terminal aromatic ring of a PAH, it was shown that complexation to 9-methylanthracene and 9,10-dimethylanthracene occurs on the central aromatic ring.[362] X-ray crystal structures of the $Cr(CO)_3$ complexes of pyrene, perylene, chrysene, and 1,2-benzanthracene have been reported. DFT calculations indicated that the topology of the coordination of the $Cr(CO)_3$ fragment and its asymmetry with respect to the coordinating ring may depend on its ability to maintain the maximum aromaticity of the complexed ligand.[363] The aromatic character of chromium-complexed rings is further discussed in Section 05.04.8.15.1.

Tricarbonylchromium complexes of a series of estra-1,3,5(10),6-tetraenes have been reported in which facial selectivity was verified by X-ray crystallography.[364] In the early work involving chromium carbonyl complexation to the steroidal skeleton,[365] there was little stereoselectivity, and it is assumed that in these particular cases the presence of the 6,7-double bond exerts a directive influence on the complexation. Similarly, the stereoselective synthesis of a number of (η^6-arene)tricarbonylchromium complexes, such as **212**, derived from podocarpic acid was achieved in good to excellent yield.[366] The relationship between complexation of a metal to the α-face of a steroidal A-ring and to the β-face of the aromatic ring of the podocarpate framework has been discussed previously.[367]

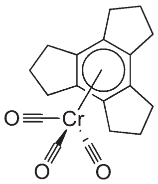


R = OH, OMe, OMOM, OC(O)Me, OTHP

212

5.04.8.10.2 Chromium tricarbonyl complexes of indanes, indenes and related species

The tricarbonylchromium complex of trindane, **213** (the condensation trimer of cyclopentanone), has been prepared and shown to adopt a structure such that the three five-membered rings adopt envelope conformations in which the central methylene groups are bent toward the metal. The possibility of preparing *all-syn*-hexamethyltrindane as a precursor to sumanene was discussed.[368] The tetracyclic system 4*b*,9,9*a*,10-tetrahydroindeno[1,2-a]indene affords two monocomplexes, **214 and 215**, whereby the $Cr(CO)_3$ group can bond to either the convex or concave face of the ligand. Moreover, two bis-complexes have also been isolated in which one or both of the organometallic units are attached to the convex side of the arced molecular skeleton.[369] Even more impressively, the reaction of 9*H*,10*H*-4*b*,9*a*([1,2]benzenomethano)indeno[1,2-*a*]indene (triptindan) with $Cr(CO)_6$ affords a mononuclear complex, together with two bis-complexes and one tris-complex, **216** ($M = Cr(CO)_3$), in which all three organometallic tripods are coordinated in the isoclined orientation with respect to the polar axis of the ligand.[370]



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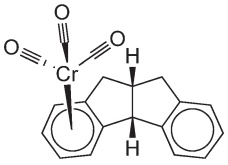

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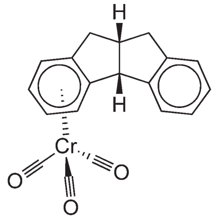

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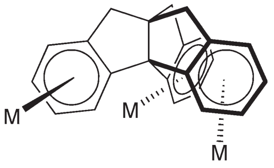
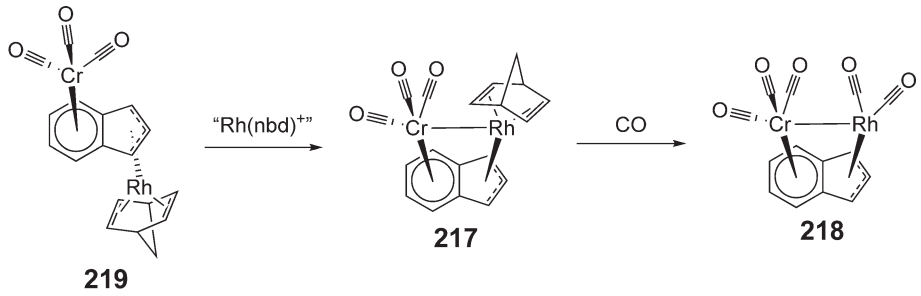


216

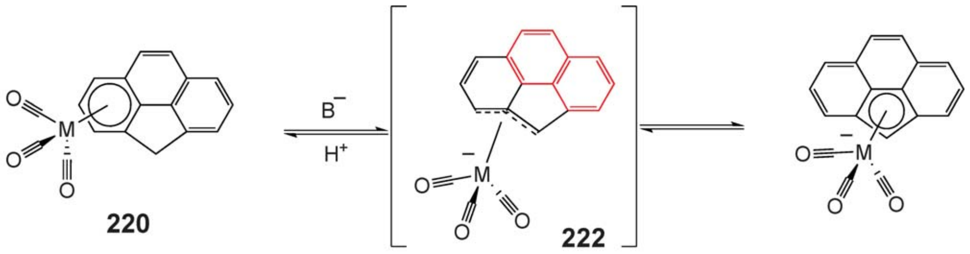
The potassium salt of the [(η^6-indenyl)$Cr(CO)_3$]-anion reacted with $[Rh(Cl)nbd]_2$ (nbd = norbornadiene) at −30 °C in THF to yield *syn*-[$Cr(CO)_3$(indenyl)]Rh(nbd), **217**. When CO was bubbled through the solution, it generated *syn*-[$Cr(CO)_3$(indenyl)]$Rh(CO)_2$, **218**, which adopted a bent indenyl structure clearly coordinated to both metals. The driving force for this distortion probably arises mainly from a metal–metal interaction.[371] In contrast, the analogous *anti*-[$Cr(CO)_3$(indenyl)]Rh(nbd) isomer, **219**, is far less distorted but, when exposed to $Rh(nbd)^+$ in THF, it undergoes a rapid *trans–cis*-isomerization to generate **217**.[372] An electrochemical study of the two isomers of $Cr(CO)_3$(indenyl)Rh(cod) indicated a strong interaction between the metals in the *syn*-case.[373]



5.04.8.11 Haptotropic and Silatropic Shifts Involving Chromium Carbonyl Moieties

5.04.8.11.1 Haptotropic shifts

The early experimental[374,375] and theoretical[376] work on haptotropic shifts was based on the interconversion of η^6- and η^5-isomers of manganese and chromium complexes of indene/indenyl, fluorene/fluorenyl, and related polycyclic aromatics. This has been extended to include the analogous complexes, **220**, of cyclopenta[*def*]phenanthrene and its 9,10-dihydro derivative, **221**.[377] In the latter case, the migration barriers match those observed in the corresponding fluorene complexes, whereas the barriers are considerably lower in **220**, possibly attributable to the 10π-aromatic character of the η^3-structure, **222**, through which the migration occurs.[378] Interestingly, the analogous complexes of η^5-cyclopenta[*l*]phenanthrene, **223**, show no propensity to undergo η^5- to η^6-haptotropic shifts upon protonation.[379]



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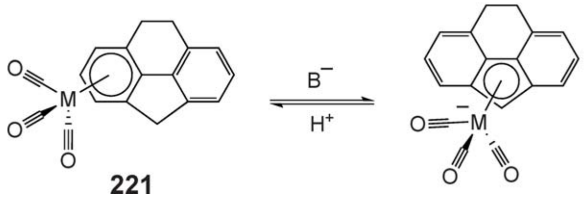
222



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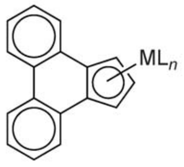
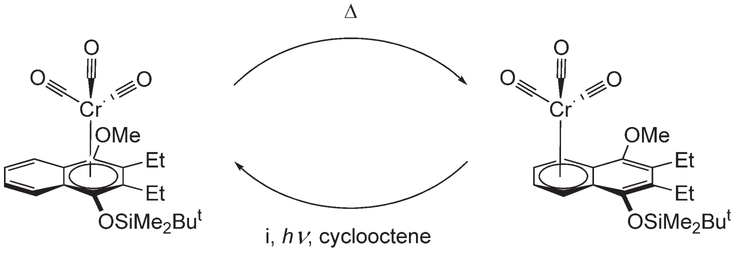


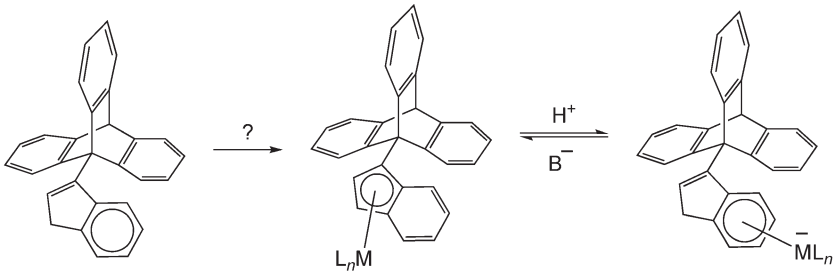
223

There have also been many studies on the η^6-to-η^6-interconversions in naphthalenes and related systems, and this topic has been very comprehensively reviewed.[380] Other (polyaromatic)Cr(CO)$_3$ complexes that have been shown to exhibit haptotropic behavior include (phenalene)Cr(CO)$_3$,[381] (fluoranthene)Cr(CO)$_3$,[382] and dibenzothiophene.[383] Recently, this phenomenon has been exploited with a view to develop an organometallic switching device by means of controlled haptotropic rearrangements in the naphthohydroquinone skeleton. The process is based on the reversible shift of a tricarbonyl chromium fragment between the two six-membered rings. The complexes were synthesized by chromium-templated [3 + 2 + 1]-benzannulation, thus placing the metal tripod initially on the substituted ring, as in **224** but, upon thermolysis, it migrates onto the unsubstituted ring, as in **225**. The process can be reversed by photolysis in the presence of cyclooctene and carbon monoxide.[384] The chromium template may be tuned by incorporating phosphorus co-ligands, which allow the acceleration or deceleration of the isomerization process, and can also be extended from naphthalenes to phenanthrene or tetra- and pentacyclic heteroarene systems.[385–387]



224 **225**

Moreover, the potential use of haptotropic shifts to mediate the behavior of a molecular brake has been suggested. The indenyl-triptycene, **226**, has been prepared with the goal of introducing a metal tripod, the movement of which would block or release the rotation of the three-bladed rotor depending on whether the M(CO)$_3$ unit was η^5- or η^6-bonded.[388] However, incorporation of a Cr(CO)$_3$ unit into **226** occurs preferentially on a blade of the triptycene,[388] and the resulting structure resembles that of previously determined triptycene-CrCO)$_3$ complexes.[389] Very recently, the synthesis and X-ray crystal structure of the tricarbonylchromium derivative, **227**, of a benz[*cd*]azulene was reported; this system raises the possibility that the chromium could adopt an η^5-structure, **228**, the known η^6-isomer, **227**, or even an η^7-mode of attachment, **229**, to the ligand, dependent on whether the charge on the system was uninegative, neutral or unipositive.[390]



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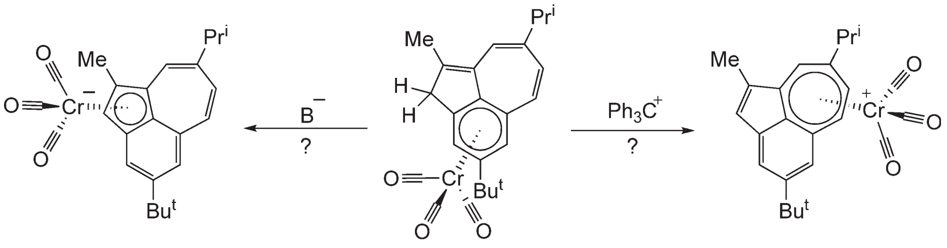
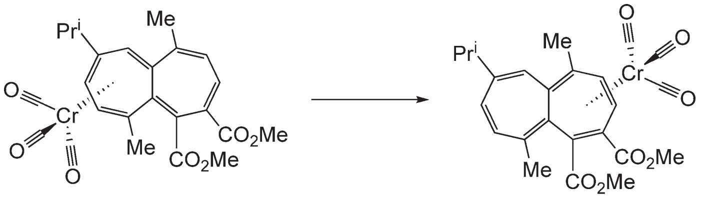


228 **227** **229**

Intramolecular (and intra-ring) migrations in the heptalene system are particularly interesting whereby the η^6-to-η^6 haptotropic shift of a $Cr(CO)_3$ moiety is accompanied by a series of double-bond shifts, as in **230** to **231**. While the occurrence of inter-ring haptotropic migrations of $Cr(CO)_3$ groups has long been established for anellated aromatic systems, this appears to be the first time that such rearrangements have been unequivocally demonstrated for $Cr(CO)_3$ complexes of nonplanar bicyclic [4*n*]-annulenes, such as in the highly twisted heptalene π-manifold.[391,392]

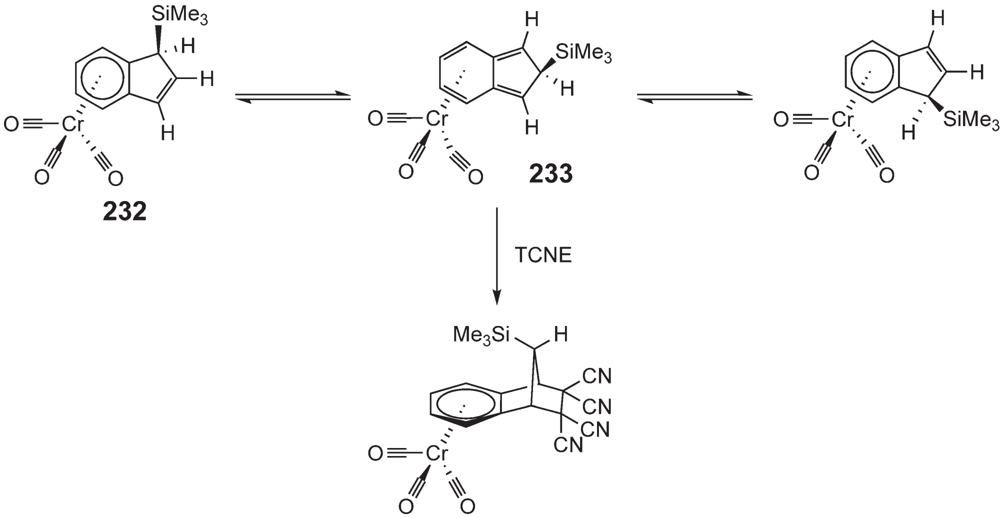


230 **231**

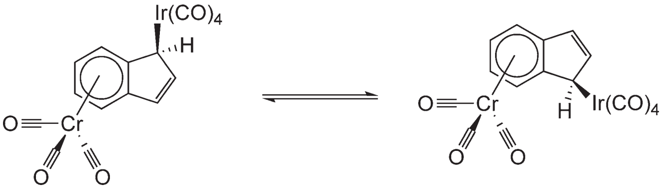
5.04.8.11.2 Silatropic migrations

It has already been shown that the ring opening of benzocyclobutenone, **202**, to the corresponding *ortho*-quinodimethane, **204**, is tolerant to the presence of a coordinated η^6-tricarbonylchromium moiety.[344] In light of the similarity between this ring-opening process and the isomerization of indenes to the corresponding isoindenes, the effect of chromium complexation on the rate of [1,5]-silicon shifts in 1-silylindenes has been examined.[393] Thus, the dynamic behavior of the chromium-complexed indene, **232**, was investigated qualitatively by 2D-EXSY NMR and quantitatively by variable-temperature single selective inversion experiments. The barrier toward the [1,5]-silicon migration was determined to be $\sim 100 \pm 4\,\mathrm{kJ\,mol^{-1}}$, a value indistinguishable from that previously reported for the uncomplexed ligand.[394,395]

The proposed symmetry-allowed [1,5]-suprafacial sigmatropic shift mechanism was confirmed by trapping the intermediate isoindene, **233**, with tetracyanoethylene in a [4 + 2]-cycloaddition process, as shown in Scheme 18. All the products were unambiguously characterized by X-ray crystallography.[393] These data suggest that the dynamic behavior of the indenyl complex of iridium, **234**, can also be rationalized in terms of [1,5]-shifts rather than as [1,3]-symmetry-forbidden shifts as was originally proposed.[396]

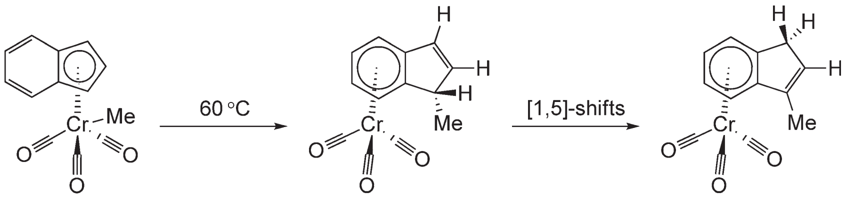


Scheme 18



234

σ-Methyl-(η^5-indenyl)chromium tricarbonyl, 235, rearranges quantitatively into (η^6-1-*endo*-methylindene)chromium tricarbonyl, 236, in C_6D_6 solution at 30–60 °C. DFT calculations suggest that this “ricochet rearrangement” proceeds in two steps of which the methyl group migration from Cr onto the indenyl ligand is rate determining. The barrier to a subsequent hydrogen [1,5]-sigmatropic shift in the indene, to give 237, is essentially unaffected by the presence of the $Cr(CO)_3$ group on the six-membered ring. This parallels the observed silatropic shift behavior in 232.[397]



235 **236** **237**

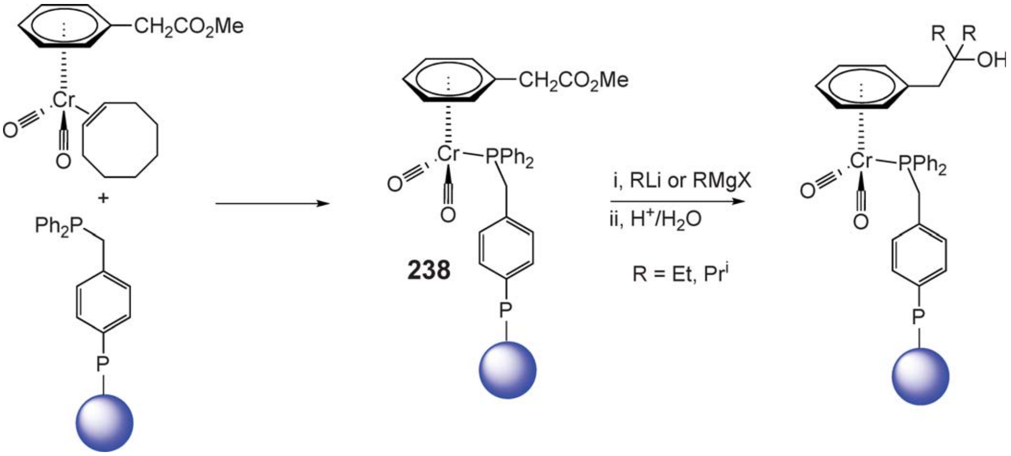
5.04.8.12 Polymer-bound Arene Chromium Carbonyl Complexes

Polymers containing organometallic fragments either in the backbone or attached to functional groups have been widely studied in recent years, notably by ring opening of *ansa*-ferrocenes or other sandwich-based systems.[398] Chromium carbonyls have, of course, been incorporated into polymer precursors, but have also been used to anchor an arene–chromium fragment to a polymer surface and then released from that surface after a reaction has been carried out on the bound fragment. In another materials science-related area, phenylphosphonic acid and diethylzinc reacted in toluene/THF to give a white gel that was dried in air at room temperature for 8 h to give the layered compound $[ZnC_6H_5PO_3]{\cdot}H_2O$. It has been observed that (η^6-C_6H_6)$Cr(CO)_3$ can be incorporated into the gel during the condensation reaction, thus providing a convenient non-aqueous organometallic sol–gel route to a layered metal phosphonate material.[399]

In a related area, organometallic oligomers based on the photolytic replacement of two *cis*-carbonyl ligands in $Cr(CO)_6$ by the ditopic, non-chelating ligand 4,4′-bipyridine (4,4′-bipy) have been prepared in 95% yield. Subsequent photolysis of the *cis*-(4,4′-bipy)$Cr(CO)_4$ with $[M(CO)_6]$ (M = Cr, Mo, W) furnished the homometallic or heterometallic trimetallic complexes $[(OC)_5M$-4,4′-bipy)$Cr(CO)_4$(4,4′-bipy)$M(CO)_5]$. This process could be extended to the analogous pentametallic species, thus providing a general method of preparation for symmetrically substituted oligomers with an odd number of metal atoms and of defined length and composition.[400]

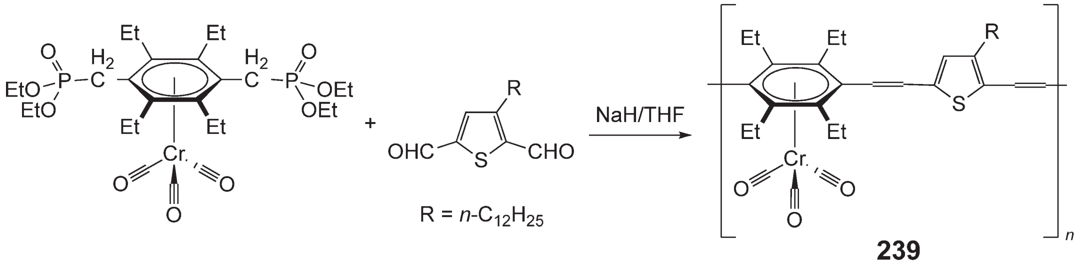
5.04.8.12.1 Chromium carbonyls as traceless linkers

This latter application can include the attachment of a substrate containing an aromatic ring to a polymer-supported triphenylphosphine via a chromium carbonyl linker. Chemical manipulation and subsequent release from the polymer demonstrated the use of π-arene chromium complexes as traceless linkers.[401,402] This concept is exemplified by the reaction of $Cr(CO)_2(L)(\eta^6\text{-}PhCH_2CO_2Me)$, where L is a weakly bound ligand such as cyclooctene, to react with $QPC_6H_4CH_2PPh_2$ (Q = polystyrene cross-linked with 2% divinylbenzene) to give $Cr(CO)_2(QPC_6H_4CH_2PPh_2)(\eta^6\text{-}PhCH_2CO_2Me)$, **238**, in high yield. Treatment of these polymer-bound esters with Grignard or organolithium reagents provides a highly efficient solid-phase synthesis of tertiary alcohols in a traceless manner using this strategy.[403] Decomplexation and release of the desired product from the polymeric surface was achieved by heating to 50 °C with acetonitrile in THF. Extension of this technology involved generation and alkylation of an enolate anion, and substitution via the Mitsunobu reaction; this approach has applications in both synthetic and combinatorial chemistry.[404]



5.04.8.12.2 (Arene)chromium carbonyls as units in the main polymer chain

A novel poly(*p*-phenylenevinylene)-type (PPV-type) conjugated co-polymer, **239**, containing tricarbonyl(arene)-chromium and thiophene units in the main chain, was synthesized by Horner–Wadsworth–Emmons olefination using 2,5-diformyl-3-dodecylthiophene and tricarbonyl{tetraethyl[(η^6-1,4-phenylene)bis(methylene)]bis[phosphonate]}-chromium. [405,406] Analogously, the palladium-catalyzed polymerization of η^6-(1,4-diethynylbenzene)tricarbonyl chromium with 3-alkyl-2,5-dibromothiophene (R = octyl, decyl, dodecyl) yielded the corresponding alternating conjugated co-polymers, **240**, in good yields.[407] Continuing with this theme, π-conjugated polymers, **241**, based on poly(*p*-phenylene–ethynylene) and containing (η^6-arene)$Cr(CO)_3$ units in the main chain were prepared by the Sonogashira coupling of η^6-(1,4-diethynylbenzene)tricarbonylchromium with 1,4-diiodo-2,5-dialkoxybenzenes.[408] Moreover, very recently, a novel organometallic-conjugated polymer, **242**, containing (η^6-arene)$Cr(CO)_3$ and platinum in the main chain was synthesized by dehydrohalogenative coupling of (η^6-1,4-diethylbenzene)tricarbonylchromium with *trans*-$(PBu_3)_2PtCl_2$.[409]



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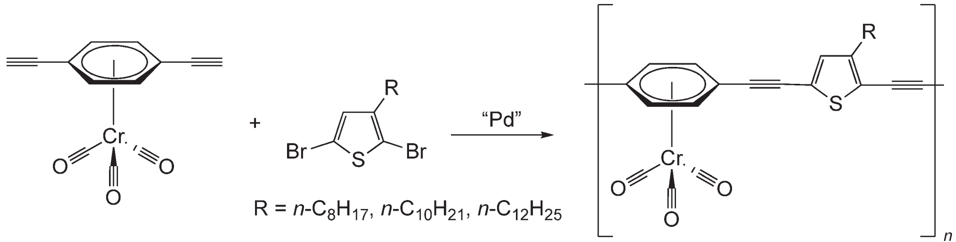

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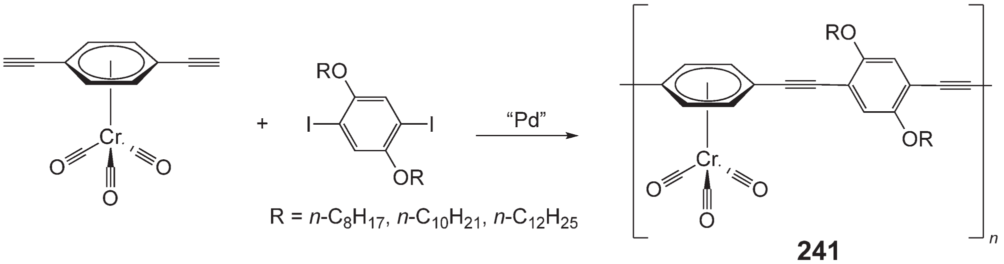

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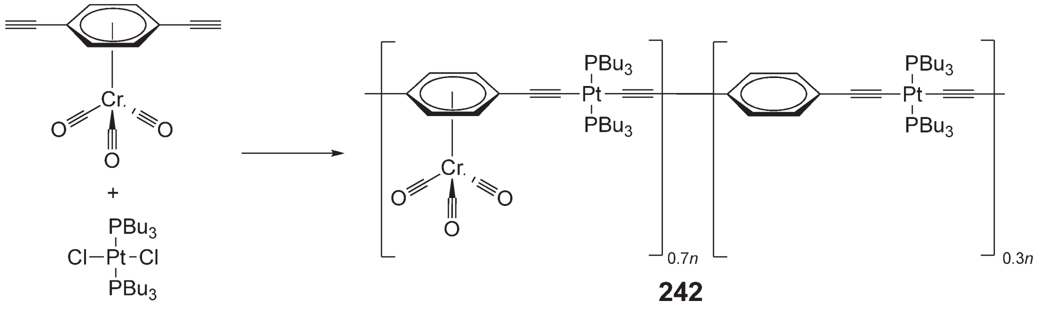

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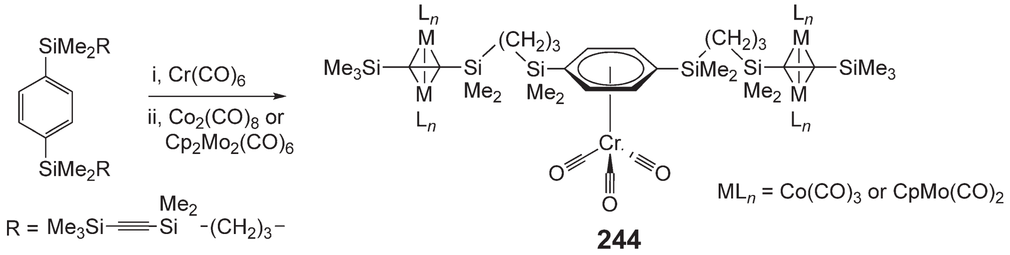
5.04.8.12.3 Chromium carbonyls in silicon-containing polymers

Silsesquioxanes containing (arene)tricarbonylchromium units have been obtained from molecular organosilicon precursors. The hydrolytic sol–gel polymerizations of [η^6-$C_6H_5Si(OMe)_3$]$Cr(CO)_3$, [η^6-1,4-$C_6H_4RR^1$]$Cr(CO)_3$ ($R = R^1 = Si(OMe)_3$; $R = R^1 = CH_2Si(OMe)_3$; $R = R^1 = CH_2CH_2Si(OMe)_3$), and {$\eta^6$-1,3,5-$C_6H_3[Si(OMe)_3]_3$}-$Cr(CO)_3$ under nucleophilic catalysis by fluoride ion led quantitatively to new monophasic hybrid organic–inorganic silica gels. Upon heating the xerogels at 400 °C under an argon flow, weight losses corresponding to complete carbon monoxide elimination were obtained, leading to chromium in a low oxidation state within the solid.[410]

The novel organosilicon dendrimers $Si[(CH_2)_3SiMe_2Ph]_4$ and $Si[(CH_2)_3Si(Me)\{(CH_2)_3SiMe_2Ph\}_2]_4$, that are peripherally functionalized with aromatic rings, were constructed by employing a divergent synthetic approach. The π-coordinating ability of these surface-located arene rings allowed the synthesis of a family of organometallic dendritic macromolecules containing η^6-coordinated $Cr(CO)_3$ moieties at the periphery of the organosilicon dendritic cores.[411] Moreover, reaction of $Me_3SiSiMe_2C_6H_5$ with $Cr(CO)_6$ under thermal conditions afforded (η^6-$Me_3SiSiMe_2$-C_6H_5)$Cr(CO)_3$ with retention of the silicon–silicon bond.[412]

Chromium-containing polymer precursors based on an alkynylsilane or arylsilane backbone have also been described. Typically, the allylethynylsilane, **243**, can be coordinated initially by a $Cr(CO)_3$ unit at the central arene ring, and then by either a $Co_2(CO)_6$ or a $Cp_2Mo_2(CO)_4$ moiety at the alkyne positions, as in **244**. Subsequent hydrosilylation yielded polymers containing chromium and/or cobalt sites. However, complexation of the alkynyldiphenylsilane, **245**, with chromium led to a cyclized product **246** via an intramolecular hydrosilylation. The organometallic complexes were all characterized crystallographically.[413]



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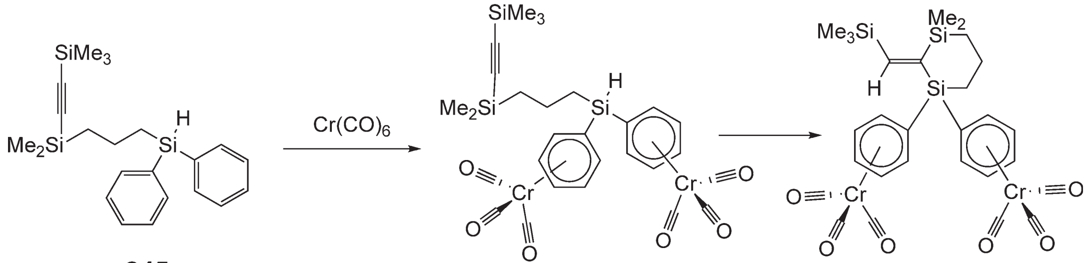

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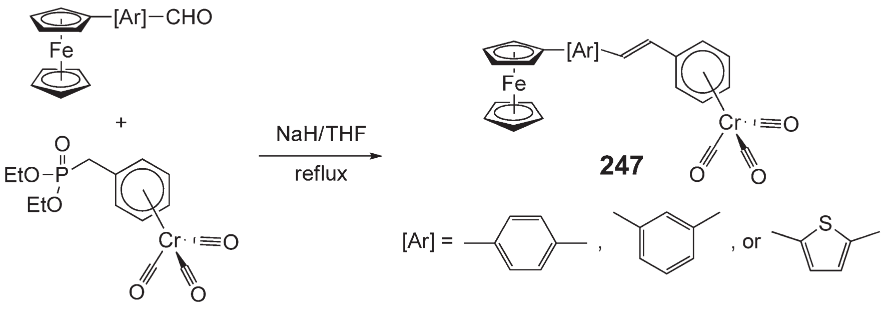
5.04.8.13 Non-linear Optical Applications of Arene Chromium Tricarbonyls

In the search for new materials exhibiting non-linear optical (NLO) properties, workers have focused on the determination of the structural features required to obtain compounds with enhanced quadratic molecular response (hyperpolarizability β). At the molecular level, donor–π-conjugated bridge–acceptor (D–π–A) structures capable of substantial charge transfer, and thus a significant difference between ground-state and excited-state dipole moments, may be viable candidates for NLO, and especially second harmonic generation (SHG).[414] To this end, many organometallics have been evaluated for potential NLO effects, as summarized in several reviews.[415–417]

One approach has been to link tricarbonyl(η^6-arene)chromium and ferrocenyl fragments via a series of aromatic spacers, including *meta*- and *para*-phenyls or thiophenes, as in **247**. These molecules were synthesized via the Horner–Emmons–Wadsworth olefination procedure by treating suitably functionalized ferrocenyl aldehydes with tricarbonylchromium benzyl phosphonates.[418] This work was extended to incorporate nitrile ligands linked to tricarbonyl (η^6-arene)chromium complexes by conjugated spacers such as alkynes and thiophenes, **248**. The synthetic route involved the reactions of a range of bromonitrile derivatives with tricarbonylchromium-complexed phenylacetylene using the palladium-catalyzed Sonogashira coupling procedure.[419–421] These alkynyl–thiophenyl linkers have also been used to connect tricarbonyl (η^6-arene)chromium fragments to (η^5-cyclohexadienyl)iron(1+) complexes, as in **249**, by using Stille and Sonogashira coupling reactions. The synthesis of these novel bimetallic organochromium/organoiron monocation dipoles establishes a general strategy for the synthesis of mixed metal Cr/dipole complexes for evaluation for NLO effects by hyper-Rayleigh scattering.[422]



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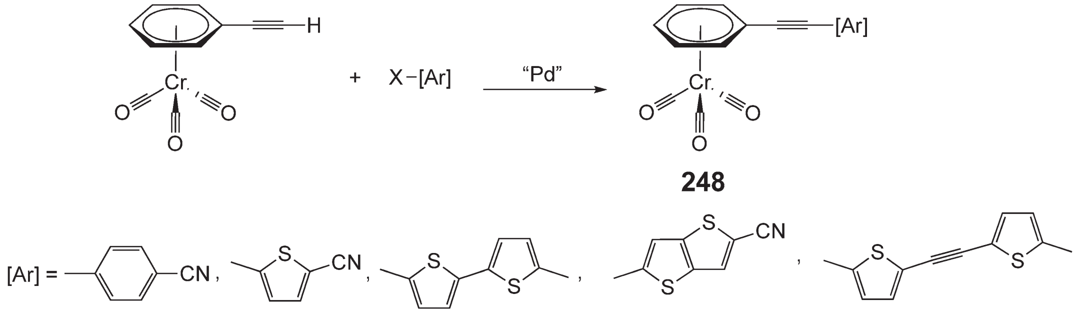

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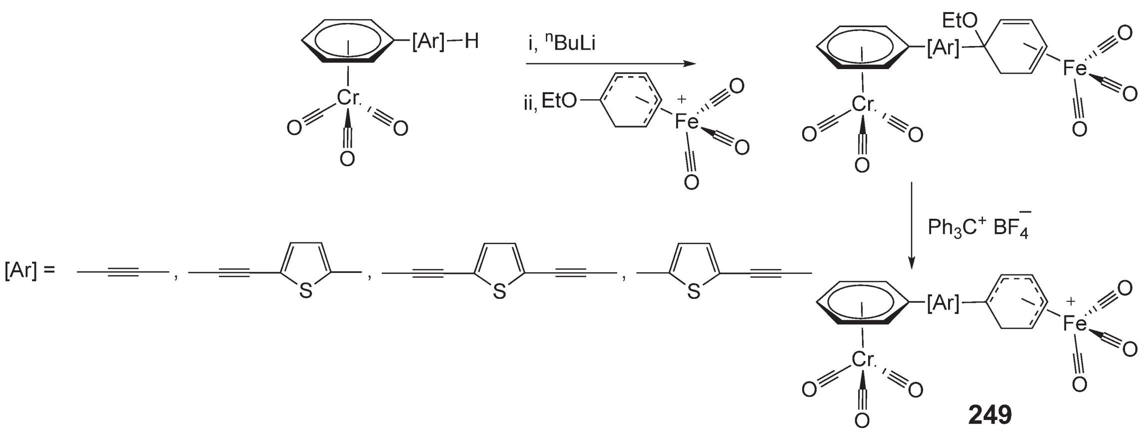

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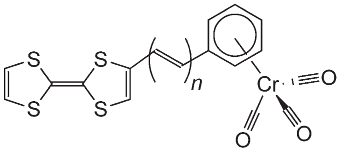
Donor- and acceptor-substituted alkynylated chromium carbonyl arene complexes $(OC)_3Cr(\eta^6\text{-}C_6H_5)(C{\equiv}C)_nR$ ($n = 1$ or 2; $R = p\text{-}C_6H_4\text{-}NMe_2$, $p\text{-}C_6H_4\text{-}NO_2$, ferrocenyl) exhibited UV–VIS spectra and NLO properties (hyper-Rayleigh scattering measurements), which revealed that the chromium carbonyl arene fragment behaved in an electronically amphoteric fashion. As noted previously, this moiety can behave as an electron donor or an electron acceptor, depending on the character of the substituent at the far end of the conjugating bridge.[423] The real and imaginary parts of third-order non-linear optical susceptibilities ($\chi(3)$) of solutions of $[\{Fe_2(CO)_6\}(\mu_3\text{-}E_3P)\text{-}\{Cr(CO)_2Cp\}]$, $E = S$ or Se, were shown to possess nearly three times the second molecular hyperpolarizability values of their corresponding precursor clusters $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$. The results suggest the rich potential of mixed metal, mixed non-metal class of clusters as materials exhibiting large non-linearity.[424]

In 1994, computationally efficient ZINDO calculations were used to elucidate the electronic origins of the second-order NLO response in molecules with extended π-architectures weakly coupled to transition metal fragments. The computed quadratic hyperpolarizabilities of group 6 stilbazole pentacarbonyl derivatives were in good agreement with the experiment. The molecular orbital analysis indicated that the $M(CO)_5$ fragment acted as σ-acceptor, forcing the adjacent pyridine ring to become the site of the molecular LUMO.[425] More recently, DFT calculations were performed to determine the accurate first static hyperpolarizability (β) of nitrogen-bound group 6 metal carbonyls representing the class of chromophores displaying weak coupling between donor and acceptor. The NLO response of this class of second-order NLO metal complexes is dominated by metal-to-ligand charge-transfer excitations involving low-lying, filled metal–carbonyl-based orbitals and empty π^*-orbitals of the nitrogen-bound ligand.[426]

Very recently, the NLO behavior in push–pull tetrathiafulvalene (TTF)–tricarbonyl(arene)chromium complexes has been investigated. In these D–π–A systems, the TTF and π-extended tetrathiafulvalenes act as strong electron donors that are covalently connected to a tricarbonyl(η^6-arene)chromium unit as the acceptor moiety through a systematically increased conjugated bridge of vinylene units. The molecules **250** and **251** ($n = 1$–3) were synthesized by the Wittig–Horner olefination reaction. The electronic spectra as well as the electrochemical data reveal different behavioral patterns for the TTF derivatives and for the extended TTF derivatives. Cyclic voltammetry shows the influence of the tricarbonyl(arene)chromium arene on the oxidation potentials in the former but, as the chain is extended, this effect diminishes. *Ab initio* calculations using the CPHF/6-31G*//B3P86/6-31G* model and time-dependent density functional theory revealed that an intraligand charge-transfer transition (ILCT) and the metal-to-ligand charge-transfer transition (MLCT) are responsible for the non-linear response.[414]



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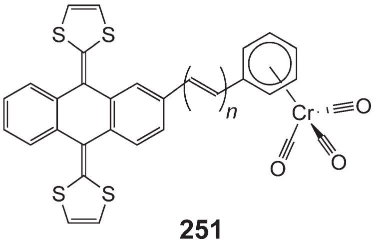

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5.04.8.14 Molecular Modeling and Other Computational Approaches

Calculations to rationalize the structures and dynamics of (arene)tricarbonylchromium complexes have focused on such issues as the tripodal rotation barrier,[427–430] the stabilization of benzylic anions, cations, and radicals,[431] molecular electrostatic potential and electron density topography,[432] conformational analysis,[433,434] harmonic force fields and vibrational frequencies,[435] and estimates of the η^6-bonding capability of C_{60} toward transition metal fragments.[436]

A combined computational (DFT using the B3LYP method) and experimental study of additions of electrophiles, nucleophiles, and radicals to tricarbonylchromium-complexed arenes revealed that the organometallic fragment stabilizes all three types of intermediates. Concerning the mechanisms for electrophilic addition to complexed arenes, the calculations strongly favor a pathway in which the cation initially adds to the metal center rather than to the arene ring.[437]

Ligand repulsive energies calculated using force fields based on both Allinger's MMP2 and Rappe's universal force field (UFF) methods have been found to provide reliable steric parameters for ligands and metal fragments, such as $Cr(CO)_5$, in organometallic systems. The data correlate well with experimental data, such as cone angles.[438]

DFT calculations have also been performed to investigate the functionalization of single-wall carbon nanotubes (SWNTs) with the $Cr(CO)_3$ metal fragment. A circumcoronene molecule ($C_{54}H_{18}$), made by the fusion of 19 hexagonal carbon rings, was used to model a fragment of a graphene sheet, and geometric constraints were imposed to reproduce the curvature of the SWNT surface. The most favorable coordination sites on the hexagonal rings of the carbon atom surface and the electronic properties of the resulting system were evaluated.[439] Similarly, calculations have been carried out to investigate the coordination and haptotropic rearrangement of the $Cr(CO)_3$ fragment on the (6, 0) carbon nanotube sidewalls. The migration of the organometallic fragment between two coordination sites on adjacent hexagonal rings of (6, 0) carbon nanotubes was found to be 68 kJ mol^{-1} above the global minimum structure.[440]

5.04.8.15 Spectroscopic, Kinetic, and Crystallographic Studies on Arene Chromium Carbonyls

5.04.8.15.1 NMR studies on (arene)chromium carbonyls

A number of (arene)tricarbonylchromium complexes were synthesized within the confines of NaX zeolite and studied with diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) and C13 magic angle spinning NMR (MAS NMR) spectroscopy. The arenes benzene, toluene, mesitylene, anisole, and aniline all produce hexahapto π-complexes physisorbed within the zeolite supercage. DRIFTS spectra show three bands in the carbonyl region indicating less than C_{3v}-symmetry, and NMR spectra have narrow carbonyl bands near 240 ppm, which indicate rapidly reorienting complexes within the zeolite.[441] The decomposition of (η^6-benzene)- and (η^6-anisole)-tricarbonylchromium supported on NaX zeolite was studied by DRIFTS, which indicated that the complexes adsorb on NaX zeolite at two different sites. The (arene)tricarbonylchromium decomposes by forming the surface chromium tricarbonyl as the arene becomes detached and CO is evolved when the surface tricarbonyl decomposes. However, upon adding either benzene or anisole to a sample of $Cr(CO)_3$/NaX at approximately 403 K, the half-sandwich compound is reformed within the NaX zeolite.[442]

The barriers to tripodal rotation in systems of the general type (arene)$CrL^1L^2L^3$ have been extensively studied by variable-temperature NMR techniques.[443] In most of the cases studied, when the barrier is primarily steric, the arenes themselves impose pseudo-threefold symmetry on the system, for example, in $[(C_6Et_6)Cr(CO)(CS)(NO)]^+$.[444] Restricted rotation has now been observed in (1,4-di-*tert*-butylbenzene)$Cr(CO)_2PPh_3$ with a barrier of $\sim 32\ kJ\ mol^{-1}$.[445] Furthermore, the series of (arene)$Cr(CO)_2P$(*o*-tolyl)$_3$ complexes exhibit restricted rotation about the phosphorus–carbon bonds in solution. In those cases where planar chirality is present, diastereoisomers may be detected, which differ in the helicity of the phosphine conformation. Such behavior parallels the earlier report on $(C_5Ph_5)Fe(CO)_2(PMe_2H)(CHO)$.[446] Slowed $Cr(CO)_3$ tripodal rotation has also been observed in a Cr–Mn-linked hexadienyl–carbene system.[447]

Although the fast exchange of carbonyls is a common feature for metal carbonyl compounds in solution, in the solid state high interatomic potential energy barriers cause this occurrence to be highly unlikely. However, it has been shown that the compartmentalization of (arene)$Cr(CO)_3$ in the β-cyclodextrin cavity removes any constraint and thereby facilitates the rotation of the $Cr(CO)_3$ group in the solid state.[448]

The relative aromatic character of coordinated arenes, and the associated question concerning ring current-induced chemical shifts, continues to attract attention. A calculation of the aromaticity of benzene relative to (η^6-benzene)$Cr(CO)_3$ based on the exaltation of magnetic susceptibility criterion was carried out using *ab initio* molecular theory. As is well known, benzene exhibits a diamagnetic susceptibility exaltation, $\Lambda(\text{calc}) = -15.1$ ppm cgs, $\Lambda(\text{exp}) = -13.7$ ppm cgs, and is aromatic. In contrast, (η^6-benzene)$Cr(CO)_3$ has a positive susceptibility exaltation, $\Lambda(\text{calc}) = 12.3$ ppm cgs, characteristic of an antiaromatic species.[449]

Subsequently, ring currents in a wide range of organometallics including $(C_6H_6)Cr(CO)_3$ and $(C_6H_6)_2Cr$ were assessed by σ-π-dissected nucleus-independent chemical shift (NICS) calculations. Shielding contributions from the C–C(π) orbitals to the NICS values suggest that there is no quenching of ring current in the complexed benzene rings.[450] Nevertheless, there is much evidence that protons that are sited directly above an arene ring and which experience a shielding effect normally attributed to the ring current exhibit a marked deshielding when the ring is complexed by a tricarbonyl moiety.[451–457]

5.04.8.15.2 Mass spectrometric studies on (arene)chromium carbonyls

The gas-phase reactivity of isomeric $[\text{arene–Cr}]^+$ adduct ions has been studied by tandem mass spectrometry. *Ortho*-, *meta*-, and *para*-(disubstituted arene)Cr ions were generated by electron impact-induced loss of three CO groups from the corresponding (η^6-arene)tricarbonylchromium complexes. Comparison of metastable decomposition and/or collision-induced dissociation spectra allowed the characterization of the *ortho*-isomer through specific fragmentations, often owing to the ability of Cr^+ to form a bridge between the two substituents, and differentiation of the *meta*- from the *para*-isomer.[458] An electron impact ionization mass spectrometric study on [(arene)$Cr(CO)_3$] (arene = C_6H_6, 1,4-$Me_2C_6H_4$, 1,2,4,5-$Me_4C_6H_2$, and C_6Me_6) showed successive loss of CO ligands to give electron-deficient complexes $[(\text{arene})Cr(CO)_{3-x}]^+$ ($x = 0$–3). Analysis of these species using approximate DFT indicates that the loss of CO ligands stabilizes high-spin states, the effect being more marked in the cationic species than in their neutral counterparts.[459]

5.04.8.15.3 Other spectroscopic techniques

The vibrational overtone spectra of gaseous (cycloheptatriene)$Cr(CO)_3$ and (benzene)$Cr(CO)_3$ have been recorded at the third overtone region using photoacoustic spectroscopy and compared to the spectra of the free ligands. The structural information obtained from the spectra was discussed and compared to the results of gas-phase electron diffraction and microwave spectroscopic studies. It was concluded that η^6-bonding is more favorable for (cycloheptatriene)$Cr(CO)_3$.[460] Microwave spectra for four isotopomers of benzene chromium tricarbonyl were measured in the 4–17 GHz range. The ^{53}Cr quadrupole coupling strength was low, indicating a near-octahedral charge distribution around the Cr atom.[461] Penning ionization electron spectra of (η^6-benzene)$Cr(CO)_3$ by collision with metastable He atoms were observed, thus providing information on anisotropic interaction potential energy for the spatial region where the corresponding molecular orbitals extend.[462]

Helium I and helium II ultraviolet photoelectron spectroscopy (UPS) of a series of (arene)$Cr(CO)_3$ derivatives have been reported. Comparisons with the free arenes suggest that, in all the cases studied, the spectra can be interpreted in terms of charge donation from the ring to the $Cr(CO)_3$ group as a whole: electronic effects at chromium are visible at the C and O atoms as shifts in ionization energy (IE).[463] PES studies using variable photon energy have also been reported.[464] Core and valence region X-ray photoelectron spectroscopy (XPS) data on methyl-substituted benzene chromium tricarbonyl complexes have been measured at 170 K, and revealed that the core levels were unchanged by the addition of the electron-donating groups on the ring.[465]

5.04.8.15.4 Kinetic and mechanistic studies

Time-resolved IR spectroscopy was used to identify the first observable species following nanosecond laser photolysis of (benzene)$Cr(CO)_3$ in alkane solution as $(C_6H_6)Cr(CO)_2$(alkane). UV–VIS-monitored laser flash photolysis was used to observe the reaction of this species with CO, whereby it was found that the rate of reaction with CO depends on the alkane solvent and the nature and degree of substitution of the arene ligand. The enthalpies of activation for all reactions were constant ($24 \pm 2\ \mathrm{kJ\ mol^{-1}}$), while the entropy of activation increased upon methyl substitution of the arene, and upon a change in the solvent from cyclohexane to a linear alkane.[466]

Detailed kinetics studies of arene displacement by 1-hexene from the 10 (arene)$Cr(CO)_5$ complexes (arene $= C_6H_{6-n}Me_n$; $n = 2$–5) generated by pulsed laser flash photolysis have been reported. The systematic variations in rate constants for unimolecular dissociation of arenes in the presence of a 1-hexene trap strongly support edge-on bonding of the arene to Cr for the Me-substituted benzene compounds in which there is a C–C ring edge unsubstituted by methyls. Where no such ring edge is present, that is, for mesitylene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, and pentamethylbenzene, the kinetics data suggest that a rapid equilibrium is established between two binding modes, the second possibly through the ring center.[467] Moreover, the kinetics of the reaction of photogenerated (η^1-bromobenzene)$Cr(CO)_5$, in which the arene coordinates weakly to chromium through a dative Br→Cr bond, with more strongly bonding alkenes to give (η^2-alkene)$Cr(CO)_5$ was studied by employing pulsed laser flash photolysis with visible and IR detection. The data are consistent with a single mechanism, involving dissociation of PhBr from (η^1-PhBr)$Cr(CO)_5$, followed by competitive reaction of the $[Cr(CO)_5]$ intermediate thus produced with PhBr or the alkene.[468]

Measurement of the rates of displacement of arene and thiophene ligands from (arene)$Cr(CO)_3$ by PBu_3 or PPh_3 revealed that the reactions are first order in the complex and the incoming ligand. Rates of reaction increase in the order benzene < styrene < triphenylene < pyrene < phenanthrene < dimethylthiophene < naphthalene < thiophene < anthracene and span roughly eight orders of magnitude.[469]

5.04.8.15.5 Database analyses of X-ray crystallographic information

The orientation (eclipsed or staggered) of the tripodal moiety in (arene)$Cr(CO)_3$ systems is frequently attributed to the electronic characteristics of the substituents on the ring. Thus, the strongly donating dimethylamino substituent enhances the electronic density at the *ortho*- and *para*-carbons and so favors the eclipsed carbonyl orientation which places the metal in a pseudo-octahedral environment. However, it was argued from an examination of many structures that more subtle factors, such as crystal packing forces, dictate the carbonyl orientation in these cases, suggesting that *a priori* prediction of the conformation is often unjustified.[470] Another survey of 34 (η^6-arene)tricarbonylchromium complexes retrieved from the Cambridge Structural Database focused essentially on the distortions of the arene ligand caused by the electronic properties of the substituents connected to it. The conclusion drawn was that deviations from the ideal structure, such as chromium-to-*ipso*-carbon and the chromium-to-ring distances, correlated well with the Hammett σ_p and σ_{p+} constants.[471]

The fact that arene ligands experience significant ring expansion upon coordination with chromium tricarbonyl, as established by precise X-ray crystallographic analyses of numerous complexes, has been related to the analogous bond-lengthening behavior in intermolecular 1 : 1 charge transfer complexes of the corresponding series of arenes with nitrosonium cation (NO^+). Such a charge redistribution may thus account for the enhanced reactivity to nucleophilic attack of the arene ligand in various (arene)$Cr(CO)_3$ complexes and related transition metal/arene analogs.[472]

In another thoughtful application of X-ray data, six crystal structures of substituted triphenylmethanol derivatives, either alone or as their mono- or bis-(chromium tricarbonyl) complexes, have been reported. It was demonstrated that, from the X-ray crystal structure of the acentric racemic $(\pm)$-$(1pR,1''R)(1pS,1''S)$-$[Cr(CO)_3(\eta^6\text{-}Bu^tC_6H_3(CMeOMe)CPh_2OH)]$, it was possible to deduce the fourfold helical structure of the corresponding chiral $(-)$-$(1pR,1''R)$-isomer.[473] The bimetallic derivatives reveal the ability to control intermolecular interactions by the positioning of relative stereochemistry.

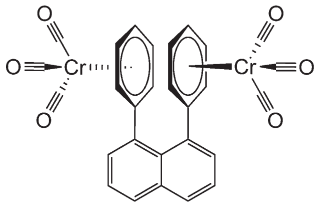
5.04.8.16 Miscellaneous Arene Chromium Carbonyls

Photolytic decarbonylation of a series of (η^6-arene)Cr(CO)$_3$ complexes in the presence of trichlorosilane initially yields (η^6-arene)Cr(CO)$_2$H(SiCl$_3$) and subsequently the disilyl adducts (η^6-arene)Cr(CO)$_2$(SiCl$_3$)$_2$. However, the intermediate dihydride, (η^6-arene)Cr(CO)(H)$_2$(SiCl$_3$)$_2$, has been isolated and crystallographically characterized. The data more strongly support a formulation as Cr(IV) dihydride derivatives as opposed to σ-bonded side-on H-SiCl$_3$ groups and are clearly not η^2-dihydrogen complexes.[474] An analogous study on the photolysis of (η^6-arene)Cr(CO)$_3$ complexes (arene = benzene, toluene, mesitylene, fluorobenzene, and difluorobenzene) with triphenylstannane yielded both (η^6-arene)Cr(CO)$_2$(η^2-HSnPh$_3$) and (η^6-arene)Cr(CO)$_2$(SnPh$_3$)$_2$. The relatively high J(^{119}Sn–Cr–H) and J(^{117}Sn–Cr–H) values as well as the X-ray structural data support the existence of three-center two-electron bonds in the hydrido stannyl complexes.[475,476]

A series of phenylboron ligands, including Ph(CH$_2$)$_3$B(OH)$_2$, [Ph(CH$_2$)$_3$BO]$_3$, form (η^6-arene)Cr(CO)$_3$ complexes which have π-donor π-arene ligands and which also bear a Lewis acid σ-acceptor boron substituent. However, there was no evidence that these boron groups formed ground-state intra- or intermolecular interactions with the Lewis base functions of the carbonyl oxygen atoms.[477]

Electrochemical oxidation of (C$_6$H$_6$)Cr(CO)$_3$ in CH$_2$Cl$_2$/[NBu$_4$][B(C$_6$F$_5$)$_4$] yields the 17-electron cation [(C$_6$H$_6$)Cr(CO)$_3$]$^+$ at room temperature which undergoes facile substitution of CO by PPh$_3$ to form [(C$_6$H$_6$)Cr(CO)$_2$PPh$_3$].[478]

The mono- and bis-Cr(CO)$_3$ complexes of several phenyl-substituted 1,8-diarylnaphthalenes have been prepared and their structures determined by X-ray crystallography. In the monocomplexes, the face-to-face aryl groups adopt a geometry almost identical to that observed in the free ligand. In contrast, in the dichromium species, **252**, the two complexed rings bend away from each other such that the dihedral bend angle out of the naphthalene ring plane increases from 3° to 27°, implying a strongly repulsive interaction between them. In the dinitrophenyl compound, **253**, the ν(CO) stretching frequencies increase by $\sim$10 cm^{-1}, and this phenomenon has been attributed to the marked π-donation from the Cr(CO)$_3$-complexed ring to the electron-deficient dinitrophenyl moiety.[479]



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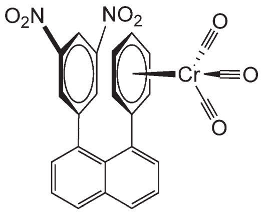

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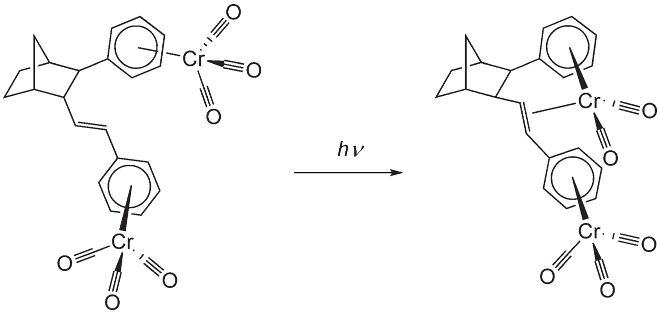
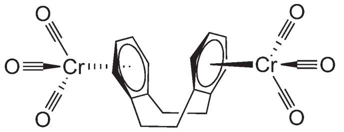
The reaction of Cr(CO)$_6$ with *cis,exo*-2-phenyl–3-(2-(*E*)-phenylethenyl)norbornane yields the bis-arene tricarbonylchromium complex **254**. When photolyzed with visible light, the 2-phenyl undergoes a rotation such that the externally bonded arene–Cr(CO)$_3$ can bind, after a carbonyl displacement, via the double bond to form the η^6,η^2-metal-coordinated complex **255**. This was described as being analogous to molecular tweezers, thus placing a metal into the molecular cavity.[480]



254 **255**

The mono- and bis-(tricarbonylchromium) complexes of 1,2;5,6-dibenzocycloocta-1,5-diene have been structurally characterized. The mono- and *cis*-bis-Cr(CO)$_3$ derivatives exhibit a boat-like geometry, **256**, whereas the bis-*trans*-complex, 257, preferentially adopts a chair structure, presumably to minimize steric interactions between the bulky organometallic tripods.[481]



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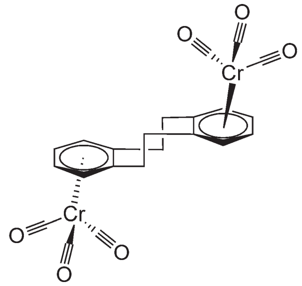

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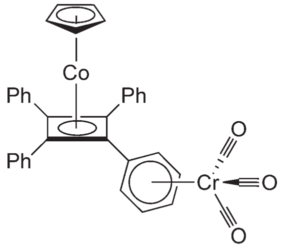
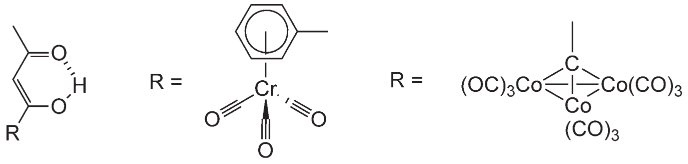
The reaction of (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt with excess $Cr(CO)_6$ led to a number of heterometallic compounds, whereby one or more of the phenyl groups had been transformed into an (η^6-C_6H_5)$Cr(CO)_3$ substituent, as in 258. In the dichromium case, 1,2- and 1,3-isomers were produced.[482] Furthermore, ferrocenes bearing (η^6-C_6H_5)$Cr(CO)_3$ substituents have also been reported.[483]



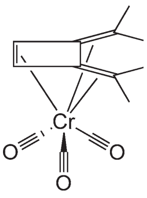
258

Conventional coordination chemistry, as exemplified by the enormous number of acetylacetonate complexes, has been extended into the inorganometallic regime by the incorporation of organometallic fragments into the basic ligand. Thus, the modified acacH systems 259 and 260 containing either a $(C_6H_5)Cr(CO)_3$ or the $CCo_3(CO)_9$ cluster fragment have been crystallographically characterized and subsequently used to form coordination complexes of Co(II), Co(III), and Al(III).[484]



259 **260**

Although not an arene, dimethylenecyclobutene does behave as an η^6-ligand and binds to a tricarbonylchromium tripod. Thus, (η^6-diisopropylidene–cyclobutene)$Cr(CO)_3$, 261, was prepared by reaction of the free ligand with $(CH_3CN)_3Cr(CO)_3$, and was shown by X-ray diffraction to possess two long Cr–C_{exo} bonds (2.482 and 2.590 Å).[485] The structure and dynamics of the parent system, that is, (dimethylenecyclobutene)$Cr(CO)_3$ (and also (triquinacene)$Cr(CO)_3$), were investigated by using a variety of computational methods; however, hybrid HF/DFT methods using sufficiently large basis sets offered the most accurate results in comparison to experiment. Although substantial barriers to rotation about the metal–arene bond were predicted for both, neither barrier was considered high enough to restrict the dynamics to the degree where atropisomerism on the laboratory timescale would be possible.[486]



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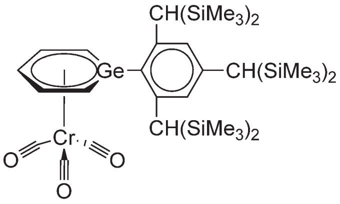
5.04.8.17 Heteroarene Chromium Carbonyls

Chromium carbonyl complexes of numerous heteroarene-type rings, such as pyridines, phosphabenzenes, arsabenzenes, thiabenzene oxides, borazoles, or borathiins, have been described,[487,488] and reference has already been made to complexes derived from $R_3P_3R^1{}_3B_3$.[144,145] In recent years, other systems have been explored. For example, the germabenzene complex, **262**, bearing the bulky protecting group 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl was prepared by reaction of the ligand with $[(MeCN)_3Cr(CO)_3]$ and was fully characterized by X-ray diffraction.[489] An analogous borabenzene complex, $(C_5H_5B\text{-}THF)Cr(CO)_3$, **263**, in which the boron is coordinated by THF has also been described.[490]



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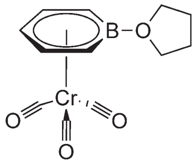

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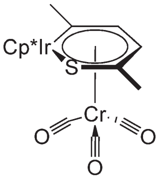
UV photolysis of a hexane solution containing $M(CO)_6$ (M = Cr, Mo, W) and excess thiophene, 2,5-dimethylthiophene, benzothiophene, or dibenzothiophene generates the η^1-sulfur-bonded complexes; however, for the benzo systems, the rather unstable η^6-complexes have also been detected.[491] The iridathiabenzene analog $[Cp^*Ir(C,S\text{-}2,5\text{-dimethylthiophene})]Cr(CO)_3$, **264**, of $(\eta^6\text{-arene})Cr(CO)_3$ has been prepared from $(MeCN)_3Cr(CO)_3$ and $Cp^*Ir(C,S\text{-}2,5\text{-dimethylthiophene})$, whereby the heterocycle has been ring opened.[492]



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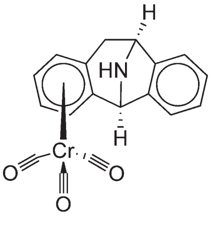
5.04.8.18 Potential Applications of Arene Chromium Carbonyls

The possible uses of $(arene)Cr(CO)_3$ systems as molecular switches, brakes, or as constituents in polymers have already been mentioned. However, their applicability in numerous other areas has also been proposed.

5.04.8.18.1 Biomedical applications

There are several ligand-binding sites that modulate the effect of glutamate binding to the *N*-methyl-D-aspartate (NMDA) receptor complex, one of which is the PDP (phencyclidine) site. The molecules 5-methyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (MK-801), and 10,5-(iminomethano)-10,11-dihydro-5H-dibenzo[*a*,*d*]cycloheptene (IDDC) are potent ligands for the PDP site, and it has been hypothesized that π-stacking may play an important role in their activity. To investigate this further, mono- and bis-$Cr(CO)_3$ complexes such as **265** and **266** were prepared, which retained their activity for this site. It was assumed that, since these ligands are curved such that the amine bridge lies on the convex face, the metal carbonyl fragments were bonded to this face since the concave side would be less accessible.[493] Surprisingly, the assignments are based only on NMR measurements and no X-ray crystallographic data are reported.



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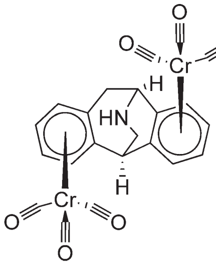

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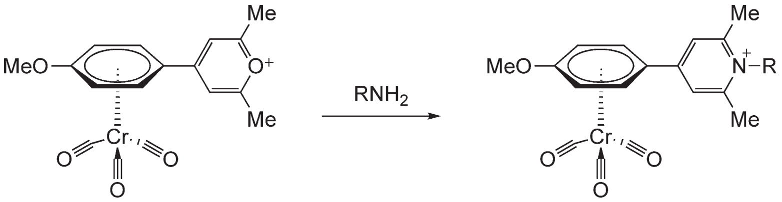
The pyrylium-linked arene–$Cr(CO)_3$ cationic complex, **267**, apparently bears the majority of the positive charge on the heterocyclic ring which does not lean toward the chromium center as is normally the case with metal-stabilized cations.[494] Moreover, **267** reacts readily with benzylamine or with β-alanine methyl ester to produce the corresponding pyridinium salts, **268**.[495,496] It was subsequently demonstrated that a variant of this approach could be used to label lysine residues in proteins such as bovine serum albumin.[497]

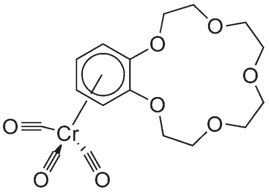


267 **268**

5.04.8.18.2 Analytical applications

The novel technique entitled carbonyl metallo immunoassay (CIMA) is a non-isotopic immunological assay that uses metal carbonyl complexes as tracers and Fourier transform IR spectroscopy (FT-IR) as the detection method. This assay is based on the particular spectral features of these complexes, which show very strong absorption bands in the 1,800–2,200 cm^{-1} spectral range where proteins and organic molecules do not absorb. CIMA has been used to assay three antiepileptic drugs (carbamazepine, phenobarbital, phenytoin) that bear arene-bonded metal carbonyl moieties, such as $Cr(CO)_3$.[498] This methodology extends the utility of chromium carbonyls in bioorganometallic chemistry from its original aim of selective binding to hormonal receptor sites.[365,499]

The ν(CO) modes of [(η^6-benzocrown ether)$Cr(CO)_3$] complexes, such as **269**, in methanol and methanol–water solutions shift to higher wave number with addition of alkali metal salts to the solution; this wave number shift correlates with the cation concentration such that the complexes can be used as FTIR-readable molecular sensors for the alkali metal cations.[500]



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5.04.8.18.3 Liquid crystalline behaviour

In the quest for arene chromium carbonyls exhibiting liquid crystal behaviour, (η^6-hexaalkoxytriphenylene)-$Cr(CO)_3$ complexes with varying alkyl chain lengths (C_5H_{11} to C_9H_{19}) were prepared and studied by DSC, optical polarizing microscopy, and X-ray diffraction. The complexes with alkyl chain lengths C_5 to C_8 displayed isotropic melting behaviour; however, the hexanonyloxy-substituted disk-shaped complex displayed a nematic ND phase between 37 and 58 °C.[501] 1,4,7-Trisubstituted (1,4,7-triazacyclononane)$Cr(CO)_3$ also behave as metallomesogens and exhibit liquid properties. The observed mesophases were characterized as disordered rectangular columnar of a pyramidic type.[502] [Cholesteryl(*p*-methyl)benzoate]$Cr(CO)_3$ has also been shown to exhibit liquid crystal behavior.[503,504]

5.04.9 Cyclopentadienyl Chromium Carbonyls and Related Species

The early chemistry of cyclopentadienyl chromium carbonyls of the general type $CpCr(CO)_3X$ has been very comprehensively reviewed in COMC (1982) and COMC (1995).[505,506] However, the major focus in recent years has been on the chemistry of the dimers $(C_5R_5)Cr_2(CO)_6$ and the propensity of the relatively weak Cr–Cr bond to cleave, yielding radicals which exhibit many fascinating reactions.

5.04.9.1 Synthesis, Properties, and Reactivity of the 17-Electron Species $[(C_5R_5)M(CO)_3\cdot]$

Laser flash photolysis of $[(C_5R_5)M(CO)_3]_2$ (M = W, Mo, and Cr) provides a convenient source of $[(C_5R_5)M(CO)_3\cdot]$, an organometallic free radical with 17 valence electrons. It is a transient and highly reactive species. Depending on the circumstances and the other reagents present, the radical will dimerize, undergo halogen and H-atom-abstraction reactions, and electron-transfer reactions.[507,508] Thermodynamic and activation parameters for the dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ into paramagnetic monomers have been determined from ^{1}H NMR shift and line width measurements. The observed homolytic bond dissociation energies were found to be approximately $64 \pm 2\,\mathrm{kJ\,mol^{-1}}$ for the C_5H_5 system but somewhat less, $\sim 59 \pm 2\,\mathrm{kJ\,mol^{-1}}$, for the more sterically crowded C_5Me_5 dimer.[509] Direct electrochemical characterization of these 17-electron intermediates was also achieved by using photomodulated voltammetry.[510]

The reaction between $Cr(CO)_6$ and $Na(C_5Ph_5)$ and subsequent metathesis yields $[Ph_3P{=}N{=}PPh_3]^+$-$[(C_5Ph_5)Cr(CO)_3]^-$, that upon oxidation by $AgBF_4$ in cold THF under an argon atmosphere produces the $[(C_5Me_5)Cr(CO)_3\cdot]$ radical which was crystallographically characterized as a benzene solvate. The anionic and radical forms of $[(C_5Me_5)Cr(CO)_3]$ form a redox pair connected by a quasi-reversible one-electron process.[511]

The radical $[(C_5Ph_5)Cr(CO)_3\cdot]$ reacts with small, neutral, monodentate Lewis bases (PMe_3, PMe_2Ph, $P(OMe)_3$) in THF at −78 °C to yield the monomeric substitution products $(C_5Ph_5)Cr(CO)_2L(THF)$ as thermally stable solids that were characterized electrochemically and spectroscopically. The frozen-solution ESR spectra of $(C_5Ph_5)Cr(CO)_2L$ in toluene were comparable to those of other low-spin d^5-piano-stool complexes; moreover, rotation of the $Cr(CO)_2L$ moiety relative to the C_5Ph_5 ring was rapid on the ESR timescale in low-temperature liquid solutions. The X-ray crystal structure of the hemisolvate $(C_5Ph_5)Cr(CO)_2PMe_3(0.5THF)$ was determined.[512]

Interestingly, when the photolysis of the Cr≡Cr triple-bonded system $[Cp^*Cr(CO)_2]_2$ in *n*-heptane was monitored by time-resolved IR spectroscopy, it revealed the triply bridged CO-loss intermediate $Cp^*Cr(\mu\text{-}CO)_3CrCp^*$ as the only initial photoproduct; no metal–metal bond fission was observed. Two bridging ν(CO) bands were observed, resulting from the splitting of the E′ mode, which indicated that the CO bridging groups are asymmetrical. The rate of the backreaction with CO was found to be 1,000 times faster than the rate of the analogous backreaction of CO with $CpFe(\mu\text{-}CO)_3FeCp$.[513]

The enthalpies of reaction of the $[(C_5Me_5)Cr(CO)_3\cdot]$ radical and disulfides (RSSR) to form $(C_5Me_5)Cr(CO)_3SR$ (R = Ph, Me) were measured by solution calorimetry, leading to Cr–SR bond strength estimates of 146 and $180\,\mathrm{kJ\,mol^{-1}}$, respectively.[514] Reaction of a large excess of H_2S with 2 mol of $[(C_5Me_5)Cr(CO)_3\cdot]$ gave $(C_5Me_5)Cr(CO)_3H$ and $(C_5Me_5)Cr(CO)_3SH$; kinetic studies showed that two reaction pathways are followed, dependent on the CO pressure.[515] In contrast, the reaction of $[(C_5Me_5)Cr(CO)_3\cdot]$ with dihydrogen to form $(C_5Me_5)Cr(CO)_3H$ proceeds via an oxidative addition, and is not inhibited by added pressure of CO.[516] A kinetic study of the reactions of $[(C_5Me_5)Cr(CO)_3\cdot]$ with pyridine-thiols and -thiones has also been reported.[517]

Detailed kinetic studies of the reactions of the 17-electron species $[CpCr(CO)_3\cdot]$, formed by thermal homolysis of the metal–metal-bonded dimer $[CpCr(CO)_3]_2$, with the non-β-hydrogen-containing organic halides, for example,

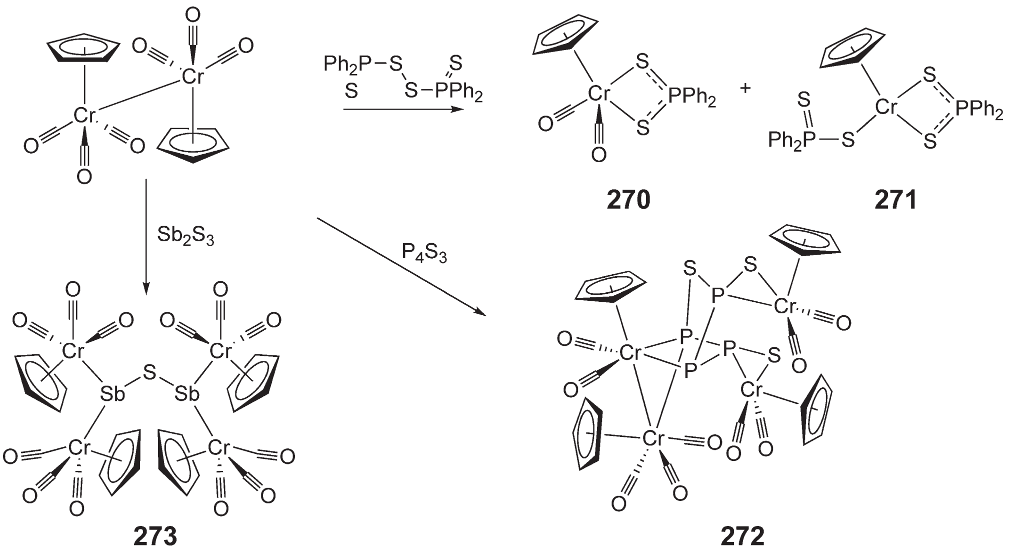
$BrCH_2CN$, $BrCH_2CO_2Me$, CF_3CH_2I, MeI, were consistent with rate-determining steps involving halogen atom transfer from carbon to chromium. The resulting organic radicals then in most cases couple with a second molecule of $[CpCr(CO)_3\cdot]$ to form the corresponding 18-electron, unstable alkylchromium compounds $CpCr(CO)_3R$. However, when a β-hydrogen was available for abstraction, the products were the corresponding alkene plus the metal hydride $CpCr(CO)_3H$.[518]

The rate of H/D exchange between activated olefins methyl methacrylate-d^5 or styrene-d^8, and $(\eta^5\text{-}C_5R_5)Cr(CO)_3H$ (R = H, Me, Ph) was measured to study the mechanism of the complexes as catalysts in radical polymerizations. The data yield a Cr–H bond-dissociation energy of 249 kJ mol^{-1} in $(C_5H_5)Cr(CO)_3H$ bond, a value in agreement with the DFT-calculated value of 243 kJ mol^{-1}.[519]

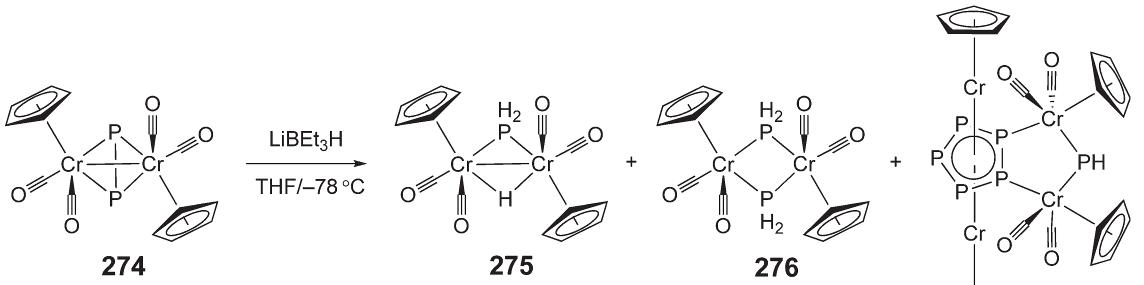
In $[(C_5H_4CO_2Et)Cr(CO)_3]_2Hg$, the central mercury atom lies on a crystallographic inversion center, so that the Cr–Hg–Cr skeleton is exactly linear with an average Cr–Hg bond length of 2.695(1) Å. The coordination polyhedron around each Cr atom approximates to a square-based pyramid with the substituted cyclopentadienyl ring occupying the apical position.[520] Similarly, the analogous benzyl complex $[(\eta^5\text{-}C_5Bz_5)Cr(CO)_3]_2Hg$ was synthesized from the *in situ* reaction of phenylmercuric chloride with $[(\eta^5\text{-}C_5Bz_5)Cr(CO)_3]$ in THF, and was also characterized by X-ray crystallography.[521]

The reaction of $[Cp'Cr(CO)_3]_2$ ($Cp' = \eta^5\text{-}C_5H_4Me$) with anhydrous $SnCl_2$ gave the insertion product $[Cp'Cr(CO)_3]_2SnCl_2$, which in turn was converted to $[Cp'Cr(CO)_3]_2SnCl(C{\equiv}CPh)$ or $[Cp'Cr(CO)_3]_2Sn(TePh)_2$ when treated with lithium phenylacetylenide or NaTePh, respectively.[522] The facile reaction of $[CpCr(CO)_3]_2$ with 1 mole equiv. of $Ph_2P(S)SSP(S)Ph_2$ led to the isolation of purplish brown solid $CpCr(CO)_2(S_2PPh_2)$, **270**, and blue solid $CpCr(S_2PPh_2)_2$, **271**, in 50% and 10% yields, respectively. Variable-temperature ^1H and ^{31}P NMR studies showed the occurrence of very rapid unidentate–bidentate exchange between the ligands in **271** over the range −80 to +60 °C.[523]

The reaction of $[CpCr(CO)_3]_2$ with P_4Se_3 produced $Cp_4Cr_4(CO)_8(P_2Se_2)$, a tetrachromium complex possessing an unusual open-book-like structure, which was characterized by X-ray crystallography.[524] In contrast, after 13 days at ambient temperature, $[CpCr(CO)_3]_2$ and P_4S_3 yielded $Cp_4Cr_4(CO)_9(P_4S_3)$, **272**, as the major product together with traces of $CpCr(CO)_2P_3$ and $[CpCr(CO)_2]_2S$.[525] The reaction of $[CpCr(CO)_3]_2$ with Sb_2S_3 under mild reaction conditions gave $(\mu\text{-}S)(CpCr(CO)_3)_2$, and the novel tetrachromium complex $(\mu\text{-}S)(Sb(CpCr(CO)_3)_2)_2$, **273**, which contains the bare Sb–S bridging ligand with each antimony atom bonded to two chromium atoms.[526]

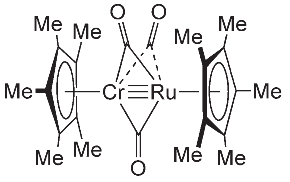


Treatment of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$, **274**, with $LiBEt_3H$ in THF at −78 °C affords the new phosphanido complexes $[\{CpCr(CO)_2\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$, **275**, $[\{CpCr(CO)_2\}_2(\mu\text{-}PH_2)_2]$, **276**, and the paramagnetic triple-decker sandwich complex, **277**, which has a distorted *cyclo*-P_5 middle deck. The EPR spectrum of **277** exhibits a noticeable hyperfine interaction with two of the ^{31}P nuclei.[527]



274 **275** **276** **277**

$[(C_5Me_5)Cr(CO)_3]^-$ and $[(C_5Me_5)Ru(MeCN)_3]^+$ react to produce the heterodimetallic complex $(C_5Me_5)Cr(\mu\text{-}CO)_3Ru(C_5Me_5)$, 278. In the analogous tungsten–ruthenium complex, the W–Ru bond length of 2.41 Å is consistent with the presence of a metal–metal triple bond, while the unsymmetrical bonding mode of the three bridging carbonyl groups reflects the inherent non-equivalence of the two different C_5R_5M units.[528] Treatment of $[L_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ ($L = Ph_3P$, Cy_3P) with an equimolar amount of $[CpCr(CO)_3H]$ afforded the organometallic hydroxo clusters $[L_2Pd_2(Ph)_2(\mu\text{-}OH)(\mu\text{-}CO)_2(\mu_3\text{-}CO)CrCp]$, 279, in high yield. These reactions can be regarded as the neutralization of an acidic transition metal hydride by a basic transition metal hydroxide.[529]



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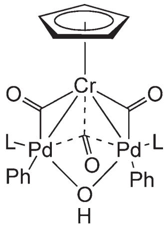

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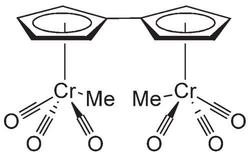
5.04.9.2 Fulvalene and Fulvene Chromium Carbonyls

Fulvalene (Fv) presents two five-membered rings for complexation by metal fragments, and (dialkylfulvalene)$Cr_2(CO)_6$ complexes such as $(\eta^5:\eta^5\text{-}C_{10}H_8)Cr_2(CO)_6Me_2$, 280, have been prepared by stepwise addition of methyl iodide to the salt $(Et_4N)_2[FvCr_2(CO)_6]$; the acyl derivatives are readily obtained via CO insertion upon treatment with 2 equiv. of PMe_2Ph, giving rise to *trans,trans*-$FvCr_2(CO)_2(PMe_2Ph)_2(COMe)_2$.[530] The (fulvalene)dichromium hexacarbonyl dihydrides, $FvCr_2(CO)_4L_2H_2$ ($L = PMe_2Ph$ or PMe_3), hydrogenate isoprene or 1,3,5-hexatriene to give $FvCr_2(CO)_4L_2$. Variable-temperature IR and NMR studies demonstrate the existence of a facile equilibrium between the *trans*-isomers of the Cr–Cr-bonded species, 281, and the novel biradical species $L(CO)_2Cr(\mu\text{-}Fv)Cr(CO)_2L$, 282, at room temperature in solution, as also evidenced by radical reactions with alkyl halides.[531] The evident weakness of the metal–metal bond in these species is reflected in the structure of (fulvalene)dichromiumhexacarbonyl, $(\eta^5:\eta^5\text{-}C_{10}H_8)Cr_2(CO)_6$, 283, which exhibits the longest hitherto known CpCr-CrCp bond (3.471 Å) and constitutes a catalyst for the radical dihydrogenation of conjugated dienes.[532]



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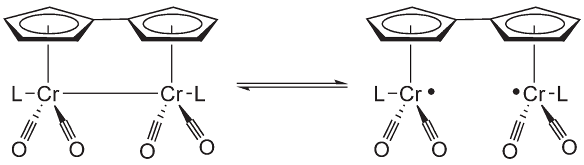
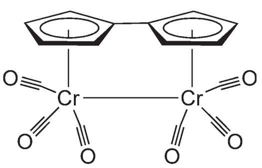


281 **282**



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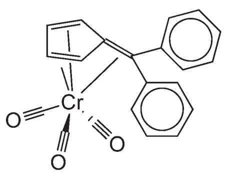
The direct incorporation of a $Cr(CO)_3$ moiety into 6,6-diphenylfulvene yields the isomer, 284, in which the metal preferentially coordinates in an η^6-fashion to the diene and exocyclic double bonds.[533] However, it has recently been shown that condensation of (η^6-benzophenone)tricarbonylchromium with cyclopentadiene gave a different isomer, 285, in which one of the 6-phenyl substituents is the site of coordination by the $Cr(CO)_3$ unit.[534]



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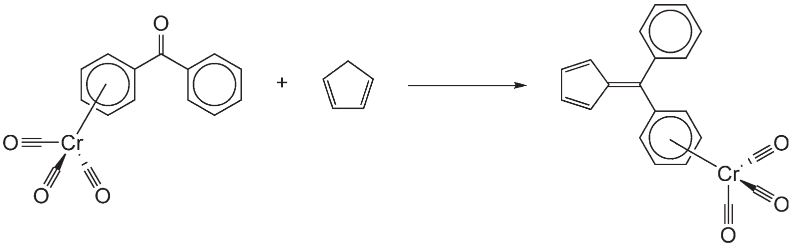

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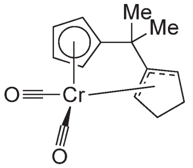
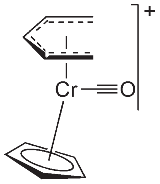
5.04.9.3 Miscellaneous Cyclopentadienylchromium Carbonyls

The reaction of $Cr(CO)_6$ with 2,2-bis(cyclopentadienyl)propane yields several products including the *ansa*-dihydrochromocene dicarbonyl, 286, in which an η^3-pentenyl group is tethered to the η^5-cyclopentadienyl group by a CMe_2 bridge.[535]



286

An electrochemical investigation on 17- and 18-electron complexes of structural type $[(\eta^5\text{-cyclopentadienyl})(\eta^5\text{-pentadienyl})Cr(CO)]^{n+}$, where $n = 0$ or 1, revealed that the 17-electron complex is more stable by approximately 50 kJ mol^{-1} when the pentadienyl ligand is bound in the U conformation, 287, rather than the S conformation. Moreover, rate constants for isomerizations to the more stable isomer have been measured for both 17-electron and 18-electron complexes using digital simulation techniques.[536]



287

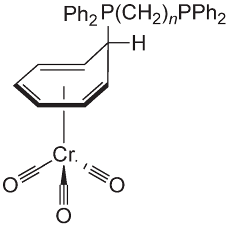
The reaction of the η^2-arylthioxophosphine complex $CpCr(CO)_2(SP(H)Ar)$ with $[CpCr(CO)_3]_2$ at 110 °C led to the isolation of a mixture of new, structurally characterized complexes: hydridophosphido-bridged $Cp_2Cr_2(CO)_4(\mu_2\text{-H})(\mu_2\text{-P(H)Ar})$, bis(phosphido)-bridged Cr=Cr doubly bonded $Cp_2Cr_2(CO)_2(\mu_2\text{-P(H)Ar})_2$, and the μ_3-phosphinidene cubanes $Cp_4Cr_4S_3(\mu_3\text{-PAr})$ and $Cp_4Cr_4S_2(\mu_3\text{-PAr})_2$.[537]

Molecular orbital calculations have been used to examine the bonding in the complexes $CpCr(CO)_2(NX)$ where X = O, S, Se, Te. It was established that there is an increasing Cr–N interaction as X changes from O to S to Se to Te. Bond lengths, bond orders, vibrational frequencies, and heats of reaction all support the conclusion that metal-to-ligand π-backbonding increases down the group from NO to NTe.[538]

5.04.10 Seven-Membered Ring Complexes of Chromium Carbonyls

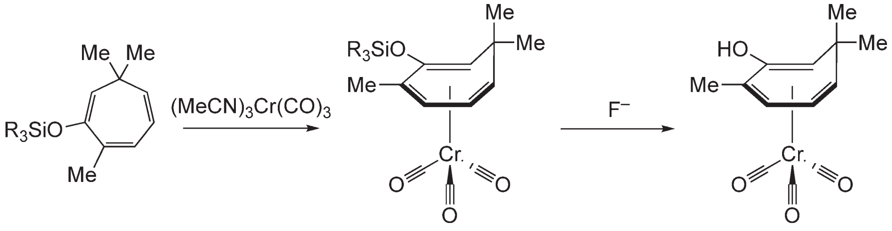
Earlier work on organometallic C_7-derivatives of chromium has been summarized in COMC (1982) and COMC (1995).[539,540] $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]BF_4$ reacts with the diphosphines $Ph_2P(CH_2)_nPPh_2$, $n = 1$–4, at −40 °C to form two types of complexes that are quite different from previous carbonyl substitution products. With diphosphines, where

$n = 1$–3, the products are the 7-*exo*-ring adducts, **288**, whereby one phosphorus is ligating. However, with $Ph_2P(CH_2)_4PPh_2$, the product is the diphosphine ring linked dimer $[(7,7'\text{-}exo\text{-dppb})\{\eta^6\text{-}(C_7H_7)Cr(CO)_3\}_2][BF_4]_2$. The ring carbon-to-phosphorus bond length of 1.852 Å indicates a relatively weak bond, consistent with facile cleavage of these adducts on reaction with nucleophiles such as hydride.[541]



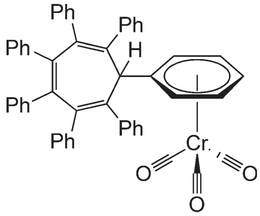
288

The stabilization of vinyl alcohols (as Pd complexes) or the keto form of phenol (as an $Fe(CO)_3$ complex) has long been known and it has now been demonstrated that cycloheptatriene enol complexes, **289**, can prepared by the desilylation of a wide range of (trialkylsilyloxycycloheptatriene)$Cr(CO)_3$ complexes with fluoride. Enantiomerically enriched enol complexes can be accessed by derivatization as chiral, non-racemic esters followed by regeneration of the enol. Biocatalytic resolution has also been achieved.[542]



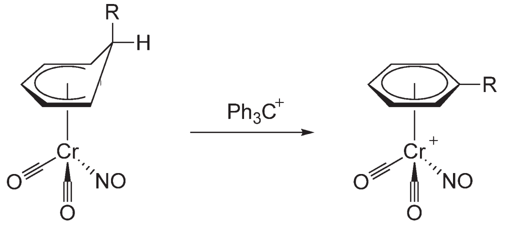
289

The Diels–Alder reaction of tetraphenylcyclopentadienone (tetracyclone) with triphenylcyclopropene followed by thermal elimination of CO produces heptaphenylcycloheptatriene; subsequent reaction with $Cr(CO)_6$ produced $(\eta^6\text{-}C_7Ph_7H)Cr(CO)_3$, **290**, in which the organometallic fragment has been incorporated on a peripheral phenyl substituent rather than on the seven-membered ring.[543]

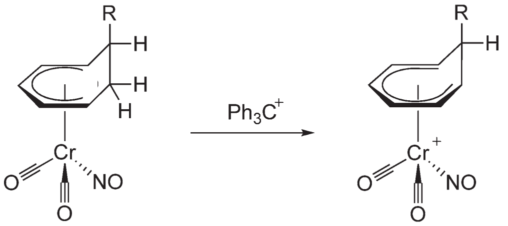


290

The addition of nucleophiles to $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ and $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ followed by treatment with *N*-methyl–*N*-nitroso–*p*-toluenesulfonamide (Diazald) gave the cyclohexadienyl and cycloheptadienyl complexes $[(\eta^5\text{-}C_6H_6R)Cr(CO)_2(NO)]$ and $[(\eta^5\text{-}C_7H_8R)Cr(CO)_2(NO)]$, **291** and **292**, respectively. Abstraction of hydride gave the highly sensitive cations $[(\eta^6\text{-}C_6H_6)Cr(CO)_2(NO)]^+$, **293**, and $[(\eta^6\text{-}C_7H_8)Cr(CO)_2(NO)]^+$, **294**.[544]

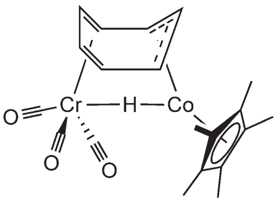


291 **293**



292 **294**

The heterodinuclear system [(OC)$_3$Cr(μ-H)(μ-C$_7$H$_7$)Co(μ-C$_5$Me$_5$)], **295**, was prepared from (η^6-C$_7$H$_8$)Cr(CO)$_3$ and (η^5-C$_5$Me$_5$)Co(C$_2$H$_4$)$_2$ by displacement of the labile ethylenes. The boat-shaped bridging cycloheptatrienyl ligands adopt the η^4(Cr) : η^3(Co) coordination in the solid state. In solution, however, hindered rotation of the C$_7$H$_7$ ring on the NMR timescale was observed.[545]



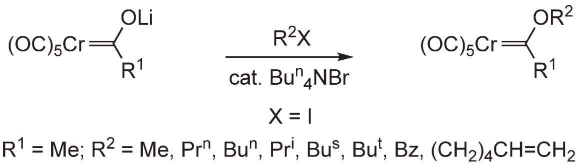
295

5.04.11 Carbene Complexes of Chromium Carbonyls

The synthetic, structural, mechanistic, and reactivity aspects of the chemistry of metal carbenes are of such scope that they were the focus of no less than five chapters in COMC (1995). The major applications to organic synthesis are cyclopropanation,[546] cycloadditions and cyclizations (in particular benzannulation, sometimes known as the Dötz reaction),[547] and their behavior under photolytic conditions.[548] These areas have been frequently and comprehensively reviewed, and so just a few representative reactions are depicted to give a flavor of the rich variety of chemistry that has been reported over the past 10 years. There have also been some computational and experimental studies on the physical organic chemistry of chromium carbene carbonyl complexes.[549–554] The interconversions of chromium-carbenes and chromium-isonitriles are discussed in Section 05.04.12.1.

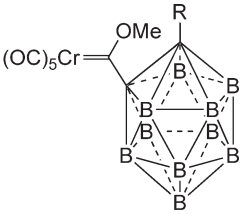
5.04.11.1 Synthetic Aspects

The most common standard procedure for the preparation of Fischer-type chromium carbenes involves nucleophilic addition of an organolithium reagent to a coordinated carbonyl followed by electrophilic alkylation using a reactive species such as a trialkyloxonium salt, for example, Me$_3$O$^+$, or an alkyl triflate. However, it has been shown that alkyl iodides can also function as the electrophile when the process is carried out under phase-transfer conditions, as in Scheme 19. This methodology benefits from the economy of using alkyl iodides, the procedural ease of a "one-pot" preparation and the greater variety of non-trivial alkyl moieties that can be incorporated as part of the alkoxy substituent.[555]



Scheme 19

The number of variations on this theme is very large. For example, the *ortho*-carborane-substituted Fischer-type carbene complexes **296** were prepared from $Cr(CO)_6$ and 1-lithio–2-R-*closo*–1,2-$C_2B_{10}H_{10}$ (R = Me or Ph) in THF and were characterized by their ^{11}B and ^{13}C NMR spectra.[556] The range of substituents to have been incorporated into chromium carbene carbonyl complexes in recent years is extensive,[557–596] and the area has been thoroughly reviewed.[597]

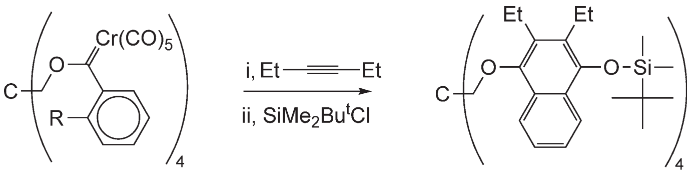


296

5.04.11.2 Benzannulations and Related Cyclizations

The benzannulation reaction involves the combination of the chromium carbene $(OC)_5Cr{=}C(OR)R$ and an alkyne $R^1C{\equiv}CR^2$, which yields substituted, naphthols as shown in Scheme 20. The phenolic substituent arises from the insertion of a carbonyl originally on chromium. The mechanism is believed to proceed via initial formation of a metallacyclobutene that opens to a 1-chroma-butadiene and then rearranges to a ketene complex. Finally, closure to a cyclohexadienone and enolization yields the corresponding naphthol–$Cr(CO)_3$ complex that can exist in two haptomeric forms.[598]

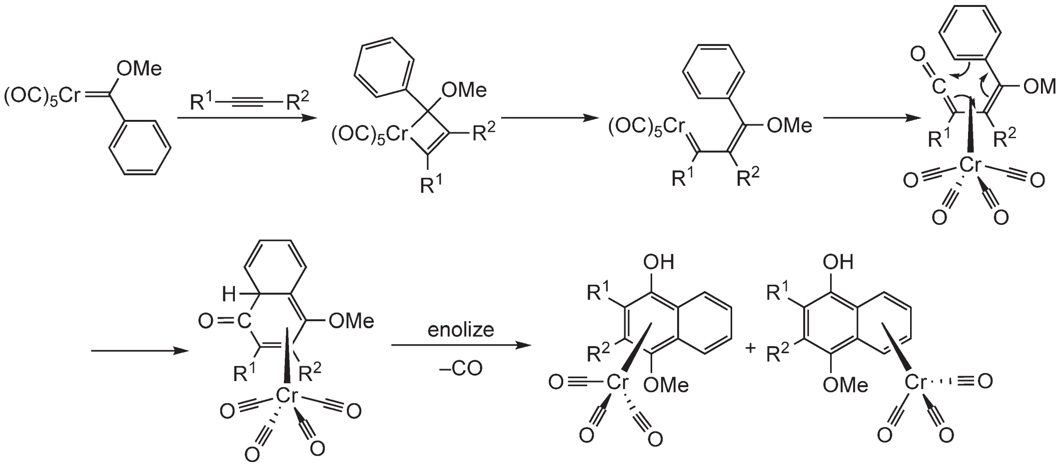
Typically, the tetracarbene complex, **297**, was generated by an acylation/alcoholysis sequence using pentaerythritol, $C(CH_2OH)_4$, as the alcohol. Upon subsequent reaction with 3-hexyne, **297** underwent complete benzannulation at all four carbene centers to produce **299**. However, the analogous (2-methoxyphenyl)carbene complex, **298**, resists benzannulation, which is blocked by the increased steric bulk in the system.[599]



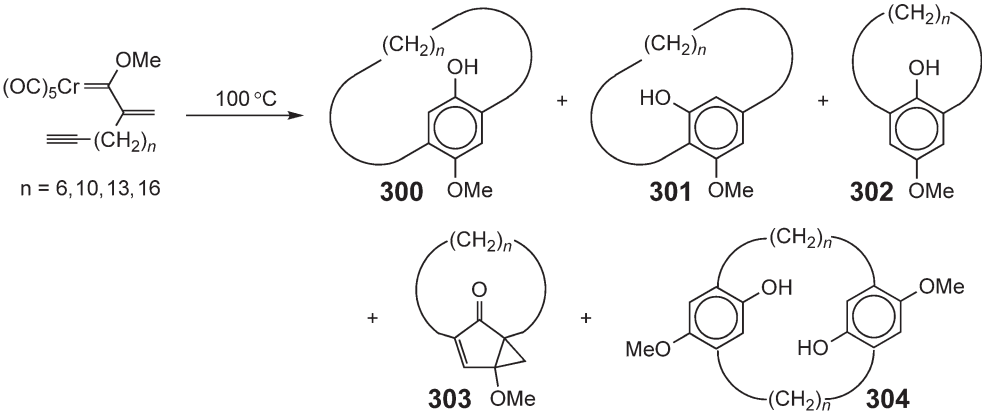
297: R = H
298: R = OMe

299

As shown in Scheme 21, the intramolecular benzannulation of carbene complexes with alkynes tethered to the α-carbon gives the 1,4- and 1,3-disubstituted paracyclophanes **300 and 301**, but, surprisingly, also yields metacyclophanes **302**, tricyclic enones **303**, and *n*,*n*-paracyclophanes **304**. The relative yields of the products depend on the length of the tether and on the nature of the solvent. With a tether length of 16 methylenes, the reaction follows the pattern observed in intermolecular reactions to give paracyclophane **300**. With intermediate tether lengths ($n = 10$, 13), the reaction gives an additional paracyclophane, **302**, in which the two oxygen substituents are *meta* on the arene ring. This unprecedented type of product requires the cleavage of the carbon–carbon bond between the α- and



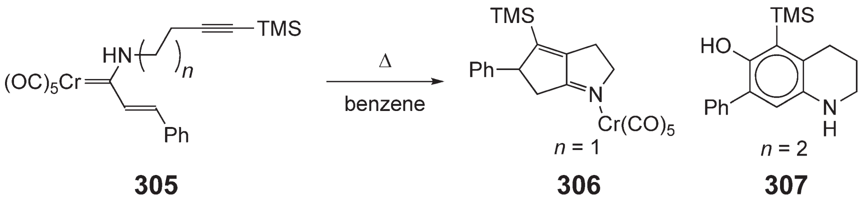
Scheme 20



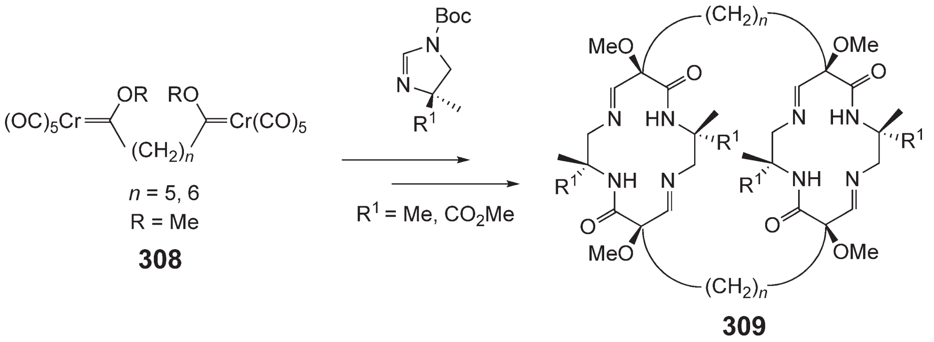
Scheme 21

β-carbons of the vinyl carbene complex. The proposed mechanism involves the crossed intramolecular [2 + 2]-cycloaddition of the alkene and a ketene in a conjugated dienyl ketene to give a benzvalenone paddleane intermediate. When the tether is too short ($n = 6$) to accommodate intramolecular cyclization, the n,n-paracyclophanes **304** are produced.[600]

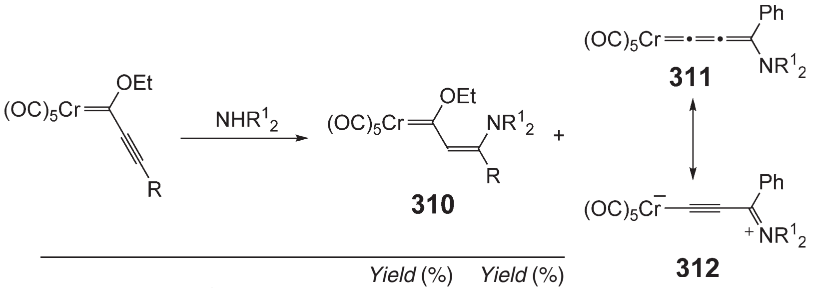
Intramolecular reactions of alkenyl-substituted amino carbene chromium complexes with alkyne functional groups tethered through the nitrogen substituent of the carbene carbon, for example, **305**, where $n = 1$ and R = Ph, H, TMS, gave the 1-azabicyclo[3.3.0]octane complexes, **306**, that resulted from cyclization without CO insertion. In contrast, when $n = 2$, CO insertion does occur and 6-hydroxytetrahydroquinolines, **307**, were produced.[601]

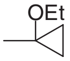


Another carbene-derived novel heterocyclic system arose when the linked bis(chromium carbene) complexes **308** were photolyzed with N-protected imidazolines followed by deprotection and acid-catalyzed dimerization to form the bis(dioxotetraazacyclotetradecadienes), **309**, linked by five- or six-carbon aliphatic chains.[602]

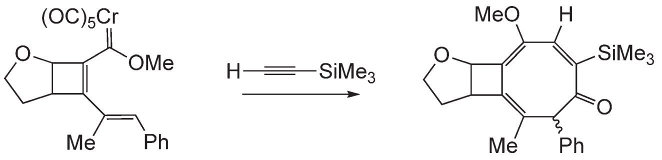


Primary and secondary amines react with pentacarbonyl(1-ethoxy-1-alkynylcarbene)chromium complexes, $(OC)_5Cr{=}C(OEt)C{\equiv}CR$ (R = Ph, cyclopropyl, $SiMe_3$) to give pentacarbonyl[ethoxy(2-aminoethenyl)carbene]-chromium complexes **310** and pentacarbonyl(3-aminoallenylidene)chromium complexes **311** in yields ranging from 0% to 86%, depending on the size of the substituents on the alkyne and the amine, the basicity of the amine, and the temperature.[603] When the reaction was carried out in CS_2/CH_2Cl_2 in the presence of aluminum chloride, the aminoallenylidene complexes were formed in 53–73% isolated yield. Bond distances derived from X-ray data indicate that a polarized iminium-alkynyl structure, **312**, gives a more adequate description than the allenylidene structure, **311**.[604]



R	*R*$^1_2$	*Yield* (%) **310**	*Yield* (%) **311/312**
Ph	Pr^i_2	44	53
	Me_2	94	0
	$(CH_2CH{=}CH_2)_2$	98	0
	Bz_2	99	0
Pr^c	Me_2	96	0
	HCy	86	0
Bu^t	Me_2	84	8
	Bz_2	15	71
TMS	Me_2	27	0
	Bz_2	0	0
	Me_2	85	13
	Bz_2	53	45
	HCy	80	11
CMe_2OEt	Me_2	80	13
	Et_2	22	75
	Pr^i_2	0	68
	$(CH_2CH{=}CH_2)_2$	30	64
	Bz_2	23	74
	HPr^n	58	41
	HCy	30	67
	HPr^i	11	86
CMe_2OTMS	Me_2	87	12

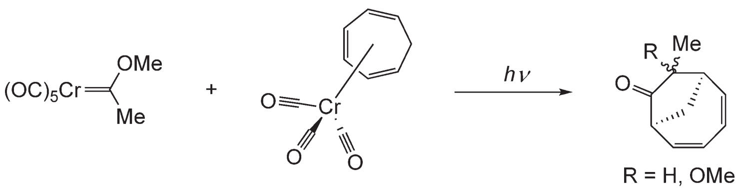
Interestingly, the first Dötz-like reaction between conjugated (dienylcarbene)pentacarbonylchromium complexes, **313**, and terminal alkynes gave eight-membered carbocycles **314**.[605] The area of benzannulations using chromium carbene carbonyl complexes has been extraordinarily well explored,[606–635] and the topic has been comprehensively reviewed.[636,637]



313 **314**

5.04.11.3 Cycloadditions Involving Chromium Carbene Carbonyl Complexes

In common with the higher-order cycloaddition reactions described in Section 05.04.8.8.2, photolytic reaction of pentacarbonyl[(methoxy)–(methyl)carbene]chromium with tricarbonyl(cycloheptatriene)chromium afforded an isomeric mixture of bicyclo[4.2.1]nonanone products, **315**.[638] The area of cycloaddition reactions[639–644] involving chromium carbene carbonyls has been reviewed.[636]



315

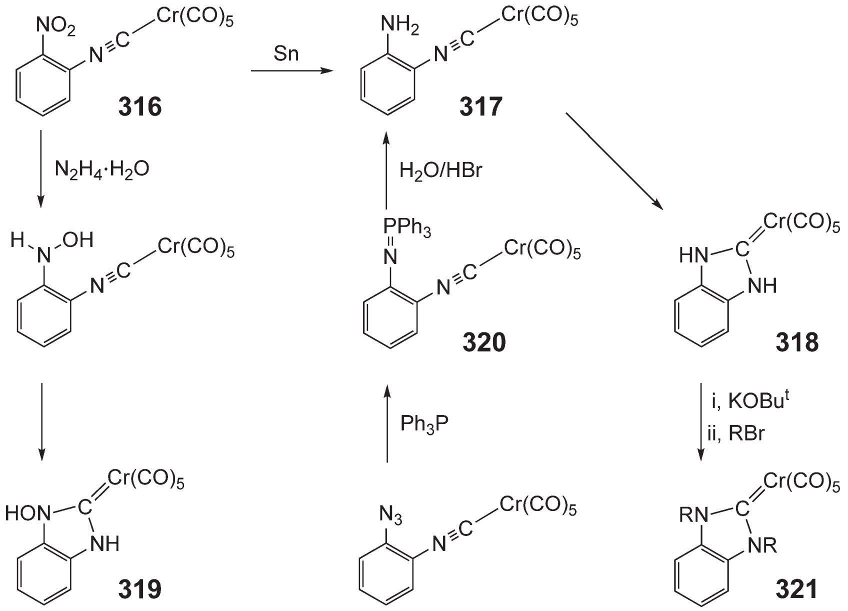
5.04.12 Isonitrile (Isocyanide) Complexes of Chromium

Isonitriles form a wide variety of complexes, both terminal and bridging;[645,646] in many ways, they are comparable to carbonyls as ligands, and the similarities of their bonding characteristics have been explored spectroscopically. A feature of much of the recent work on isonitrile complexes illustrates the interconvertibility with their isomeric carbene complexes. There have also been studies on cyanide/isocyanide linkage isomers, as well as on complexes of fluorinated isonitriles.

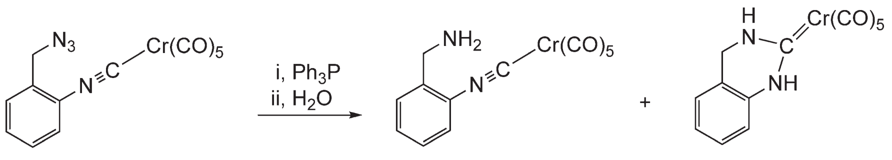
5.04.12.1 Cyclization Reactions of Chromium Isonitriles

The reaction of 2-nitrophenyl isocyanide with (THF)Cr(CO)$_5$ yielded the isocyanide complex **316**, which, upon reduction with elemental tin, gave the corresponding chromium carbonyl derivative, **317**, of the unstable 2-aminophenyl isocyanide ligand. This latter compound spontaneously underwent intramolecular nucleophilic attack of the primary amine at the isocyanide carbon atom to yield the *NH*,*NH*-benzimidazol-2-ylidene system **318**. Use of hydrazine hydrate instead of tin resulted in incomplete reduction of the nitro group, yielding ultimately the *NH*,*NOH*-stabilized benzimidazol-2-ylidene complex, **319**.[647]

In a closely related study, (2-azidophenyl isocyanide)Cr(CO)$_5$ reacts with PPh$_3$ at the azido function to give the 2-triphenylphosphiniminophenyl isocyanide complex, **320**, that can be hydrolyzed with H$_2$O/HBr to afford Ph$_3$P═O and the unstable 2-aminophenyl isocyanide ligand that spontaneously cyclizes as noted already. Double deprotonation of the cyclic *NH*,*NH*-carbene ligand with KOBu^t and reaction with 2 equiv. of allyl bromide yields the *N*,*N*′-dialkylated benzannulated *N*-heterocyclic carbene complex **321**.[648]

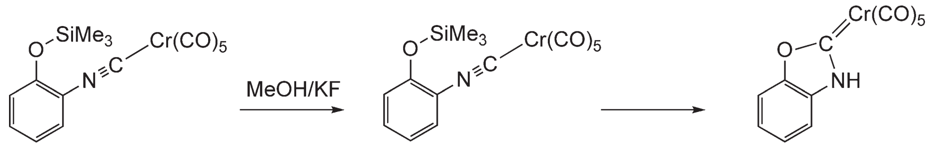


Similarly, the pentacarbonylchromium derivative of 2-(azidomethyl)phenyl isocyanide was also shown to undergo the Staudinger reaction with PPh_3 affording the phosphinimine–isocyanide complex $[(OC)_5Cr\{C{\equiv}NC_6H_4\text{–}2\text{-}(CH_2N{=}PPh_3)\}]$ that in turn reacts with water to afford a mixture of the amino-isocyanide $[(OC)_5Cr\{C{\equiv}NC_6H_4\text{–}2\text{-}(CH_2NH_2)\}]$ and the cyclic carbene complex 322.[649]



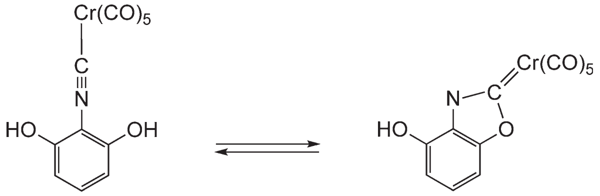
322

Hydrolysis of the Si–O bond in (2-trimethylsiloxyphenyl isocyanide)$Cr(CO)_5$ gives rise to an equilibrium between the complex with a 2-hydroxyphenyl isocyanide ligand and its 2,3-dihydrobenzoxazol–2-ylidene isomer 323.[650]



323

Similarly, the equilibrium between chromium complexes of 2,6-dihydroxyphenyl isocyanide and of the carbene complex derived from 4-hydroxybenzoxazole, 324 and 325, respectively, has been investigated.[651,652]



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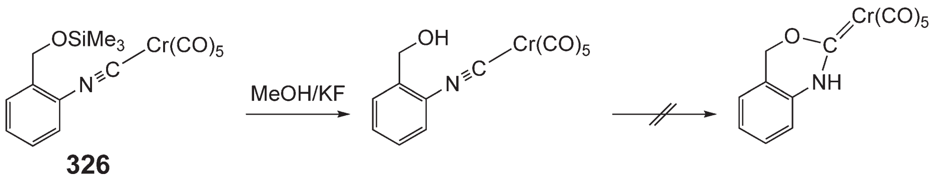
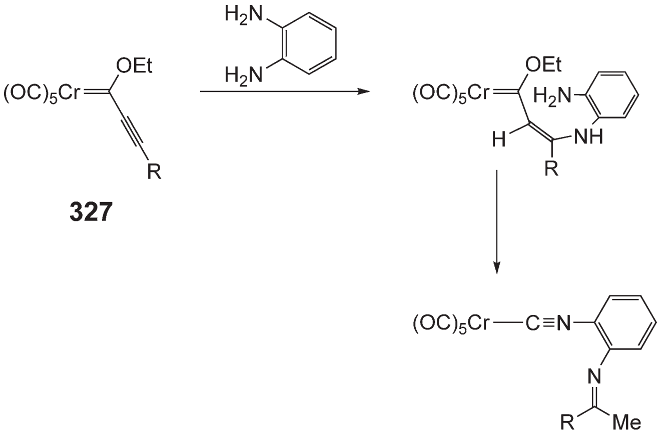
325

In yet another variation on this theme, treatment of [2-(trimethylsiloxymethyl)phenyl isocyanide]$Cr(CO)_5$, 326, with fluoride ions in MeOH gives the corresponding 2-(hydroxymethyl)phenyl isocyanide chromium complex, which does not cyclize.[653]



326

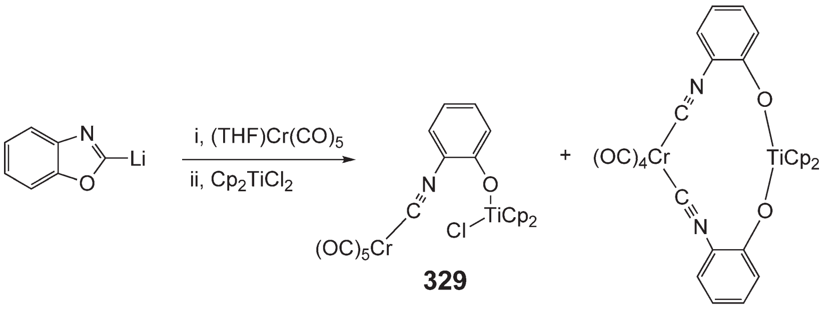
The reaction of 1,2-diaminobenzene with chromium alkynylcarbene complexes, $(OC)_5Cr{=}C(OEt)(C{\equiv}CR)$ (R = Ph, Fc, Pr^n), 327, and subsequent rearrangement to isocyanides, $(OC)_5CrC{\equiv}NC_6H_4N{=}C(Me)R$, 328, occurs either thermally or by SiO_2 catalysis. The reaction presumably proceeds via a Michael addition of 1,2-diaminobenzene across the alkyne linkage, nucleophilic attack at the carbene center by the second amino functionality, and cleavage of the bicyclic carbene intermediate with concomitant loss of EtOH. In support of this proposal, the crystal structure of the initially formed adduct $(OC)_5Cr{=}C(OEt)CH{=}C(Fc)NHC_6H_4NH_2$-2 was determined.[654,655]



327

328

Interestingly, the cyclization process can be reversed in the presence of a strongly oxophilic reagent. Thus, reaction of lithiated benzoxazole with $(THF)Cr(CO)_5$ and subsequently with Cp_2TiCl_2 affords bimetallic systems in which the titanium is *O*-bonded and the group 6 metal isocyanide coordinated. Depending on starting material and reaction conditions, the cyclopentadienyl titanium complex may act as either a mono- or bidentate ligand, as in $[(OC)_5Cr\{CN(o\text{-}C_6H_4)O\}Ti(Cl)Cp_2]$, 329, or in the 12-membered heterometallacyclic ring $[(OC)_4Cr\{CN\text{-}(o\text{-}C_6H_4)O\}_2TiCp_2]$, 330.[656]



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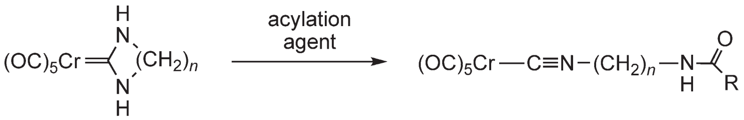
330

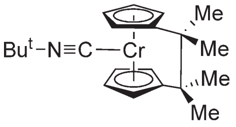
The transformation of cyclic diaminocarbene complexes $(OC)_5Cr{=}CNH(CH_2)_nNH$ ($n = 2$, 3), 331, into the corresponding isocyanide complexes $(OC)_5CrCN(CH_2)_nNHCOR$, 332, can also be achieved in high yields by acylation. Apparently, the *N*-acyl group destabilizes the diaminocarbene complexes and causes the cleavage of a C–N bond, thus forming the isocyanide product.[657]



331 **332**

5.04.12.2 Cyclopentadienyl Chromium Isonitriles

The reaction of $Me_4C_2[\eta^5\text{-}C_5H_4]_2Ca$ with $CrCl_2$ in the presence of 1 equiv. of Bu^{t}NC affords the tetramethylethano-bridged chromocene complex 333, offering a new and convenient synthetic entry into this *ansa*-chromocene system. The isocyanide complex 333 undergoes ligand substitution with CO to form the previously reported $Me_4C_2[\eta^5\text{-}C_5H_4]_2Cr(CO)$, which may also be prepared by allowing $Me_4C_2[\eta^5\text{-}C_5H_4]_2Ca$ to react with $CrCl_2$ under 1 atm of CO.[658]



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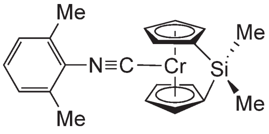
Subsequently, $Me_2Si(C_5Me_4)_2Cr$, the first example of an *ansa*-chromocene containing no additional ligands at chromium, was synthesized from $Me_2Si(C_5Me_4)_2Li_2$ and $CrCl_2(THF)_x$. The complex is paramagnetic and reacts readily with 2,6-xylyl isocyanide to give $Me_2Si(C_5Me_4)_2Cr(CN\text{–}2,6\text{-}Me_2C_6H_3)$, 334, which was characterized by X-ray crystallography.[659]



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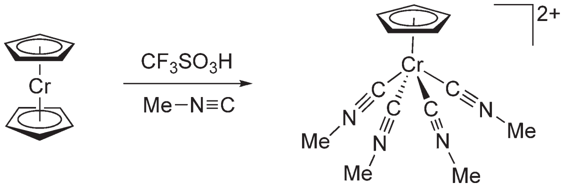
Chromocene, triflic acid, and CH_3NC yield $[CpCr(CNCH_3)_4]^{2+}$, the formerly elusive 17-electron half-sandwich complex of chromium(III); moreover, the corresponding pentamethylcyclopentadienyl analog 335 is preparable from $[(C_5Me_5)CrCl_2]_2$. 335 is also available electrochemically from $[(C_5Me_5)Cr(CNCH_3)_4]^+[PF_6]^-$, which was synthesized by the reaction of $[Cp^*Cr(mesitylene)]^+ [PF_6]^-$ with $CNCH_3$ in 86% yield. The dications were shown by NMR and EPR spectroscopies to contain one unpaired electron in the chromium d_{z^2}-orbital.[660]



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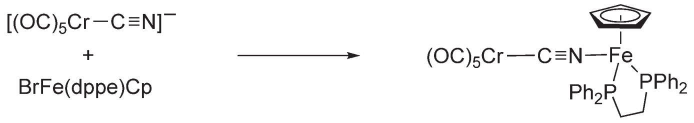
5.04.12.3 Heterometallic Systems with Bridging Isonitriles

The preparation and behavior of cyanide/isocyanide-bridged organometallic complexes is exemplified by the preparations of $[(OC)_5Cr(\mu\text{-}CN)Fe(dppe)Cp]$, 336, and $[(OC)_5Cr(\mu\text{-}NC)Fe(dppe)Cp]$, 337, from $Na[Cr(CO)_5CN]$ with $[BrFe(dppe)Cp]$ or $[(OC)_5Cr(THF)]$ with $[Cp(dppe)FeCN]$ in THF, respectively. These isomers cannot be interconverted thermally up to their decomposition points (~150 °C).[661] Another pair of isomers, 338 and 339, containing Mo–NC–Cr and Mo–CN–Cr linkages, respectively, have been examined by cyclic voltammetry, which revealed a degree of electronic communication between the metal centers in these heterobimetallic complexes.[662]



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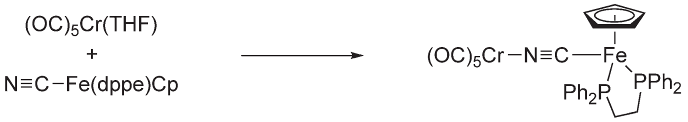

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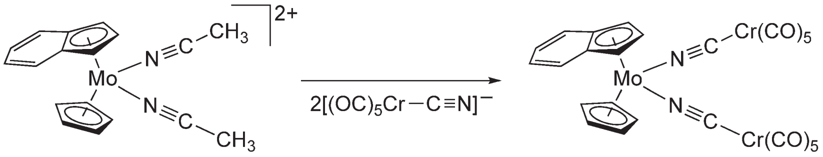

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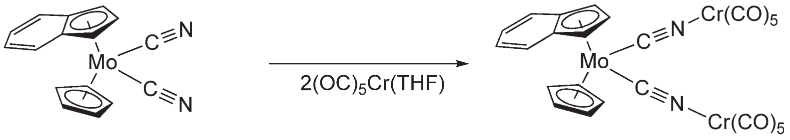

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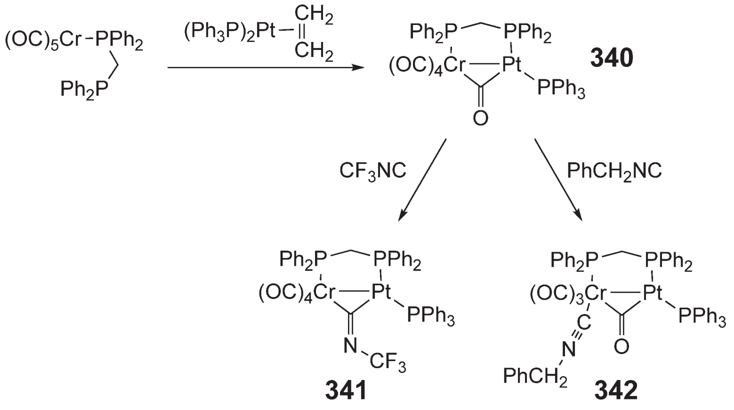
Another chromium–iron system linked by an isonitrile ligand arises from the treatment of aminoferrocene with a mixture of phenyl formate and phenol, and subsequent dehydration of the resulting ferrocenylformamide with $POCl_3$, to produce air and thermally stable isocyanoferrocene in high yield. The reaction of 6 equiv. of FcNC with bis(naphthalene)chromium(0) afforded $Cr(CNFc)_6$ that was characterized crystallographically. Successive one-electron oxidations of $Cr(CNFc)_6$ with Ag^+ produced the corresponding paramagnetic species $[Cr(CNFc)_6]^+$ and $[Cr(CNFc)_6]^{2+}$.[663]

The reaction of $[Cr(CO)_5(\eta^1\text{-dppm})]$ with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ afforded the dppm-bridged heterobimetallic μ-carbonyl platinum–Cr complex $[(OC)_4Cr(\mu\text{-CO})(\mu\text{-dppm})Pt(PPh_3)]$, **340**. Isocyanides with electronegative substituents, for example, $R = CF_3$, afforded the isonitrile-bridged complex $[(OC)_4Cr(\mu\text{-C:NR})(\mu\text{-dppm})Pt(PPh_3)]$, **341**. With less electronegative isocyanides ($R = CH_2Ph$, C_6H_{11}, $CH_2PO(OEt)_2$), the incoming ligand replaces a terminal carbonyl, as in **342**.[664]

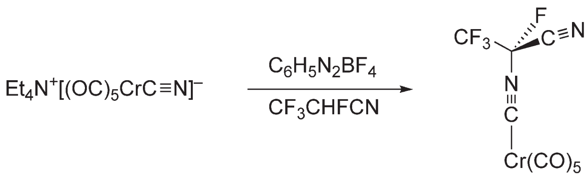


5.04.12.4 Halogenated Chromium Isonitrile Complexes

(Fluoroisocyanoacetonitrile)$Cr(CO)_5$, **343**, was obtained from the reaction of (trifluoroethenyl)isocyanide $Cr(CO)_5$ and ammonia. It was necessary to devise a different route to (2,3,3,3-tetrafluoro-2-isocyanopropionitrile)$Cr(CO)_5$, **344**, which was prepared by radical alkylation of tetraethylammonium [pentacarbonyl(cyano)chromate] in the presence of 2,3,3,3-tetrafluoropropionitrile. The pentacarbonylchromium fragment serves as a protecting group preventing the otherwise facile polymerization of the halogenated isocyanides. The fluorinated isonitriles are powerful π-acceptor ligands.[665]

$$\mathrm{(CF_2{=}CF{-}NC)Cr(CO)_5 \xrightarrow[-2HF]{NH_3} N{\equiv}C{-}CHF{-}N{\equiv}C{-}Cr(CO)_5}$$

343



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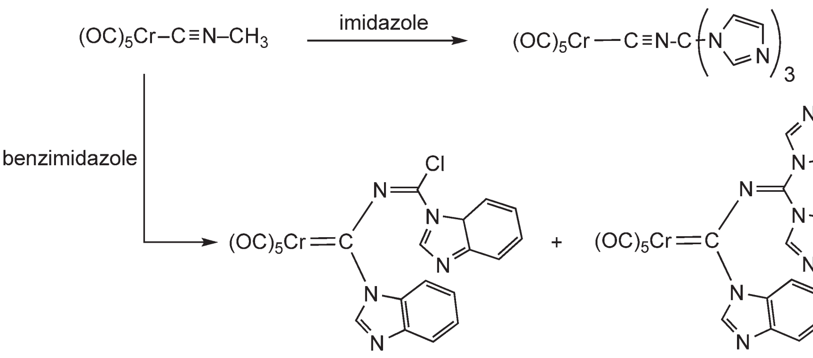
Other fluorinated isocyanide derivatives of chromium include $(C_6F_5NC)Cr(CO)_5$,[666] $(CF_3CH_2NC)Cr(CO)_5$,[667] and (n-$C_7F_{15}CH_2NC)Cr(CO)_5$.[667] $(CHF_2NC)Cr(CO)_5$ is best described as an octahedral complex of Cr(0) whereby the Cr–C bond distance to the difluoromethyl isocyanide ligand (1.956 Å) is longer than the distances to the carbonyl ligands (Cr–CO_{cis} 1.909–1.915 Å, Cr–CO_{trans} 1.900 Å), indicating a smaller π-acceptor/σ-donor ratio for the isocyanide ligand relative to that of the carbonyl ligands.[668] Flash vacuum pyrolysis of $(CHF_2NC)Cr(CO)_5$ at 240 °C generated the free ligand difluoromethyl isocyanide, thus allowing the acquisition of its rotational spectrum and dipole moment.[669]

The radical alkylation of $[Et_4N][Cr(CO)_5(CN)]$ with HCClX–CClFY (X = F, Y = F, Cl; X = Y = Cl) yielded the halogenated ethyl isocyanide complexes $[(CO)_5Cr(CN{-}CClX{-}CClFY)]$. Dehalogenation using Zn in Et_2O gave $[(CO)_5Cr\text{-}(CN{-}CX{=}CFY)]$, which reacted with various nucleophiles exclusively at the difluoromethylene group. Thus, addition of trimethylphosphine produced the unstable phosphorane $[(CO)_5Cr(CN{-}CF{=}CF{-}(PMe_3F))]$, which decomposed thermally, and on hydrolysis yielded (1,2-difluoroethenyl isocyanide)pentacarbonylchromium. A cyano substituent can also be introduced at the β-position of the isocyanide function by reaction with KCN to form $[(CO)_5Cr(CN{-}CX{=}CF{-}CN)]$. The alkenyl isocyanides $CF_2{=}CCl{-}N{\equiv}C$, $CF_2{=}CF{-}N{\equiv}C$, $CFCl{=}CCl{-}N{\equiv}C$, $CFH{=}CF{-}N{\equiv}C$, and $CF(CN){=}CCl{-}N{\equiv}C$ could be obtained by flash vacuum pyrolysis of the appropriate chromium complexes.[670]

$(CCl_3NC)Cr(CO)_5$ reacts with imidazole (*Im*H) with substitution of all three chlorine atoms to give $(CIm_3NC)Cr(CO)_5$, **345**. In contrast, benzimidazole attacks $(CCl_3NC)Cr(CO)_5$ at both the trichloromethyl and the isocyano function, resulting in the formation of the *N*,*N*′-carbene complexes **346** and **347**.[671]



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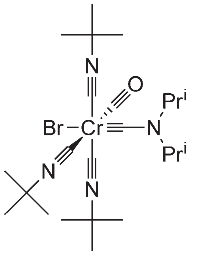
5.04.12.5 Isonitriles as Precursors to Aminocarbene and Aminocarbyne Complexes

N-lithio iminoacylates $(OC)_5Cr{=}C(NRLi)C{\equiv}CR^1$ (R = cyclohexyl, phenyl, *o*- or *p*-tolyl; R^1 = Ph, $SiMe_3$) were obtained by reaction of the appropriate pairs of lithioalkyne and isocyano complex $(OC)_5Cr(CNR)$. Protonation or alkylation, for example, with MeI, produces the aminocarbene complexes $(OC)_5Cr{=}C(NRMe)\text{-}C{\equiv}CR^1$ in 75–90% overall yield. The latter compounds are generated stereoselectively in the (*E*)-configuration ($E:Z = 14:1$ to $29:1$) by kinetic control but are isomerized at 80 °C to give the corresponding (*Z*)-stereoisomers.[672]

High yield syntheses of neutral and cationic aminocarbyne complexes of Cr-bearing isocyanide ligands have been prepared by the replacement of the γ-picoline ligands in $Br(CO)_2(pic)_2Cr{\equiv}CN(Pr^i)_2$ by EtNC or Bu^tNC. At 60 °C in toluene solvent, a third Bu^tNC can be introduced to give the monocarbonyl derivative $Br(CO)(Bu^tNC)_3Cr{\equiv}CN(Pr^i)_2$, **348**. Interestingly, in polar solvents, formation of cationic aminocarbyne complexes is favoured in polar solvents as demonstrated by the reaction of **348** with RNC in refluxing CH_2Cl_2, which leads exclusively to $[(RNC)_4(CO)Cr{\equiv}CN(Pr^i)_2]Br$. Subsequent further reaction with Bu^tNC in refluxing THF affords the cationic aminocarbyne complex $[(Bu^tNC)_5Cr{\equiv}CN(Pr^i)_2]Br$.[673]



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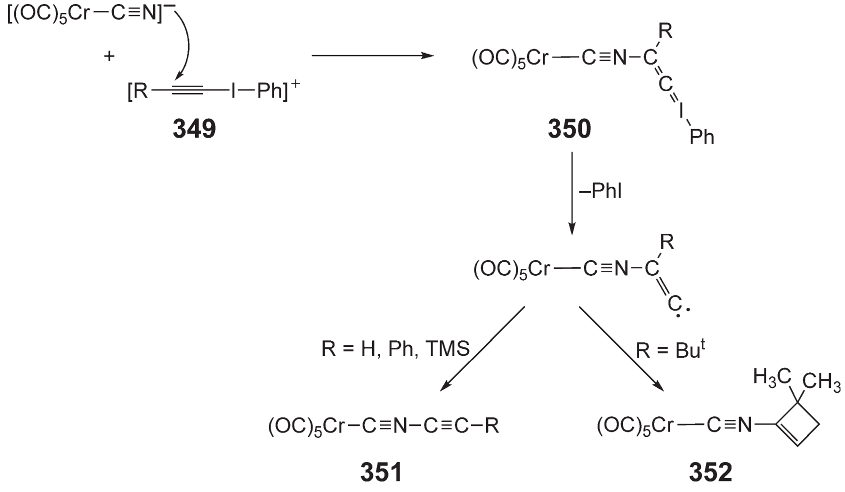
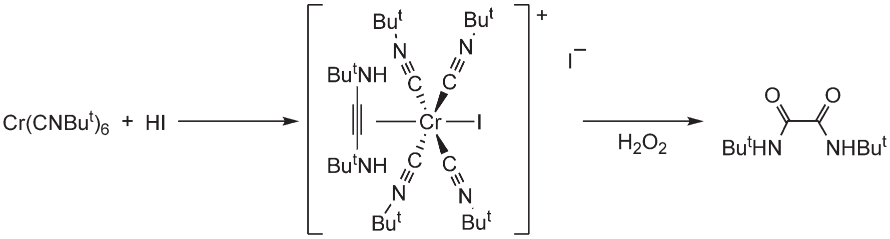
Protonation of chromium aminocarbyne complexes $[(C_5R_5)(OC)_2Cr{\equiv}CNR^1{}_2]$ (R = H, Me; $R^1 = CHMe_2$) with HX (X = Cl, Br) in pentane at −50 °C gave the aminocarbene systems $[(C_5R_5)(CO)_2(X)Cr{=}C(H)NR^1{}_2]$. Substitution of the halide by EtNC or Bu^tNC in the presence of $TlPF_6$ in CH_2Cl_2 gave $[(C_5Me_5)(CO)_2(RNC)Cr{=}C(H)NR^1{}_2]^+[PF_6]^-$, a carbene complex of divalent chromium.[674]

5.04.12.6 Miscellaneous Chromium Isonitrile Complexes

$[Et_4N][Cr(CO)_5CN]$ reacted with $[RC{\equiv}C\text{–}I\text{–}Ph]X$, **349** (R = Ph, H, X = triflate; R = Me_3Si, Bu^t, X = BF_4) to give $[(OC)_5CrC{\equiv}N\text{–}C{\equiv}CR]$ (R = Ph, Me_3Si, H) and $[(OC)_5CrC{\equiv}NR^1]$ (R^1 = 4,4-dimethyl–1-cyclobutenyl).[675] This reaction is believed to proceed by nucleophilic attack of the anionic cyano(pentacarbonyl)chromate at the β-carbon of the alkynyl(phenyl)iodonium salt, **349**, that is in effect a masked alkynyl cation, to yield the ylide **350**. Elimination of iodobenzene generates the vinylidene carbene which can either rearrange to the alkynyl isonitrile complex **351** by migration of the R group, or which can undergo a C–H insertion, as in **352**.



The reductive coupling of two isocyanide ligands to form a coordinated bis(alkylamino)acetylene molecule has been observed as the result of the treatment of [Cr($Bu^tNC)_6$] with 2 equiv. of aqueous HI in THF. The product was characterized X-ray crystallographically as the salt [Cr($Bu^tNHC{\equiv}CNHBu^t$)($Bu^tNC)_4$I]I, **353**. The idealized geometry about the chromium center is capped trigonal prismatic with C_{2v}-symmetry. Treatment of **353** with excess H_2O_2 resulted in the oxidative removal of the coupled acetylene as *N,N'*-di-*tert*-butyloxamide.[676]



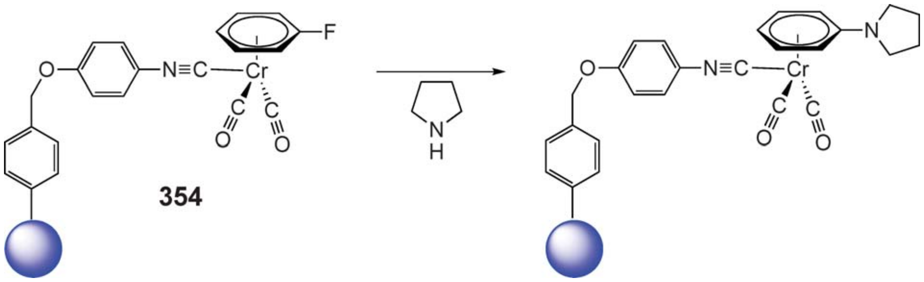
353

The reaction of $ClBR_2$ [R = $CH(SiMe_3)_2$] with $[NEt_4][M(CN)(CO)_5]$ in CH_2Cl_2 or PhMe gives the thermally stable complexes $[(R_2BNC)Cr(CO)_5$. The X-ray crystal structure reveals a linear Cr–C–N–B skeleton with long Cr–C (1.971 Å) and B–N (1.475 Å) bonds and a short C–N bond (1.159 Å), consistent (as are the IR, Raman, and NMR spectra) with its formulation as $[(OC)_5Cr–C{\equiv}N–BR_2]$.[677]

$Cr(NMes)_2(SMes)_2$ (Mes = 2,4,6-$Me_3C_6H_2$) reacts with 2,6-xylylisocyanide (Xyl–NC) to form the five-coordinate Cr(IV) complex Cr(NMes)$(SMes)_2$(Xyl–NC)$_2$ such that the Cr(IV) adopts trigonal-bipyramidal geometry with axial isocyanides. Numerous other isocyanide complexes of chromium in high oxidation states (IV, V, and VI) have been reported.[678,679]

5.04.12.7 Surface-bound Chromium Isonitrile Complexes

As noted in Section 05.04.8.1, haloarenes complexed to a tricarbonyl moiety are readily susceptible to nucleophilic attack with loss of halide. This phenomenon has been exploited by replacing a carbonyl ligand of the tripod by a polymer-bound isocyanide, and then carrying out nucleophilic substitutions (for example, with pyrrolidine, piperidine, or indole) on a supported fluoroarene complex, as in $(C_6H_5F)Cr(CO)_2(CNR)$ (where R = $C_6H_4OCH_2$–4-C_6H_4X and X = polystyrene), **354**.[680] This concept has since been successfully extended to the analogous (1,4-dichlorobenzene)$Cr(CO)_2$(CNR) polymer-bound complexes, which exhibit considerable versatility.[681]



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In a somewhat related study, 4-ferrocenylphenyl isocyanide and 11-mercapto-undecanoylferrocene have been adsorbed onto freshly prepared chromium surfaces with the goal of modifying the surface properties by incorporating electroactive species. The adsorbed layers are stable under nitrogen and in vacuum, but not in air, and desorb when soaked in CH_2Cl_2.[682]

5.04.12.8 Spectroscopic Studies on Chromium Isonitriles

IR and micro-Raman spectra of crystalline $Cr(CO)_5(Bu^tNC)$ and *cis*-$Cr(CO)_4$–$(Bu^tNC)_2$ were recorded in the 3000–390 cm^{-1} region at ambient temperature and selected pressures up to 45 kbar with the aid of diamond-anvil cells. The vibrational data indicate that both the mono- and the disubstituted complex undergo a phase transition at ~11 kbar and ~6 kbar, respectively. The ν(NC) modes are significantly more pressure sensitive in the low-pressure phases than are the ν(CO) modes. The Cr–CO and Cr–CNBu^t π-backbonding interactions are apparently increased in the low-pressure phases by the application of pressure. This effect is greatest for the CO ligands, affording additional evidence for the weaker π-acceptor capacity of the Bu^{t}NC ligand. This interpretation is supported by the fact that the ν(CO) modes involving vibrations of CO groups *trans* to Bu^{t}NC have significantly higher pressure dependences than do the other ν(CO) vibrations.[683]

Eight aryl isocyanides (CNC_6H_4R, R = 2- and 4-CF_3, 4-NO_2, 4- and 2-Cl; 2,4- and 2,6-$CNC_6H_3Cl_2$; and 2,4,6-$CNC_6H_2Cl_3$) containing multiple electron-withdrawing substituents have been synthesized, and the σ-donating and π-accepting abilities of these isocyanides were evaluated by examining the spectroscopic and electrochemical properties of the (isocyanide)Cr$(CO)_5$ derivatives. Linear relations were found between the Hammett parameters of the *para*-substituted isocyanides and their ^{13}C NMR chemical shifts, and also of ν(NC) with the $E_{1/2}$ values.[684]

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5.05
Chromium Compounds without CO or Isocyanides

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5.05.1 Introduction and Scope

The aim of this chapter is to provide a comprehensive review of the synthesis, structure, and reactivity of organochromium compounds, excluding those that contain carbonyl or isocyanide ligands. Carbonyl- and isocyanide-containing species are addressed separately in Chapter 5.04 of this volume. The present chapter summarizes complexes in which the carbon ligands are primarily σ-donors, and this discussion is followed by an extensive review of compounds supported by π-donating η^3-allyl, η^5-Cp, and η^6-arene ligands (and their derivatives). Compounds with imido and nitrido π-ligands are also reviewed, as are complexes supported by σ-donating oxygen, nitrogen, phosphorus, and sulfur atoms; in most instances, these latter ligands contain multiple donors and coordinate in a multidentate fashion. In addition, the small family of discrete heterogeneous organochromium complexes is summarized, followed by a review of theoretical calculations on chromium model systems related to olefin polymerization. Finally, the use of organochromium complexes in oxidation chemistry and organic synthesis is briefly outlined. While the period of coverage is inclusive between 1993 and 2004, a few important references from the first quarter of 2005 are included as well. Over this time period, many pertinent reviews have appeared that address various aspects of organochromium chemistry and these are cited in the appropriate sections. In addition, the reader is referred to a recent review by Poli, which describes open-shell (paramagnetic) organometallic complexes and the impact of spin state on structure and reactivity.[1] Since many of the chromium compounds described in this chapter fall into the "open-shell" category, Poli's review is particularly relevant.

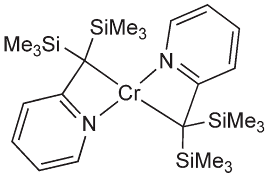
5.05.2 σ-Bonded Alkyl and Aryl Complexes

Numerous examples of chromium(II) and chromium(III) σ-bonded alkyl and aryl compounds, including homoleptic and heteroleptic complexes, have been prepared. The resulting complexes display a wide range of mononuclear and multinuclear structures. Alkyls with additional σ-donor atoms also bind to chromium to form homoleptic and heteroleptic complexes. This chapter has been arranged to first describe the smaller collection of pendant donor σ-alkyl complexes, followed by the more extensive body of work encompassing traditional σ-alkyls and σ-aryl derivatives.

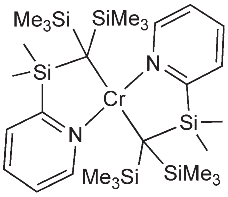
5.05.2.1 σ-Alkyls with Pendant Donor Groups

5.05.2.1.1 Chromium(II) derivatives

The reaction of $CrCl_2$ with 2 equiv. of Li(btsmp) (btsmp = 2-bis(trimethylsilyl)methylpyridine) yields $Cr(btsmp)_2$ **1**, which displays a bidentate square planar ligand arrangement around chromium (C_{2h} symmetry); the ligands adopt a *trans*-configuration.[2] The average Cr–C bond length (2.215 Å) is ca. 0.1 Å longer than that found in typical chromium(II) alkyls, presumably a consequence of the steric strain caused by the four-membered chelate ring. The structurally related alkyl ligand $[C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)]^-$, also with a 2-pyridyl appendage, reacts with $CrCl_2$ to yield the square planar $Cr[C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)]_2$ **2** in which the ligands are also bound in a *trans*-arrangement.[3] The Cr–C bond length (2.303 Å) is even longer than that in **1**, undoubtedly due to interligand steric interactions involving the bulky trimethylsilyl and dimethylsilyl groups. For both **1** and **2**, magnetic moments in the solid and solution state are consistent with high spin ($S = 2$) ground-state configurations, a very common feature of square planar chromium(II) complexes.

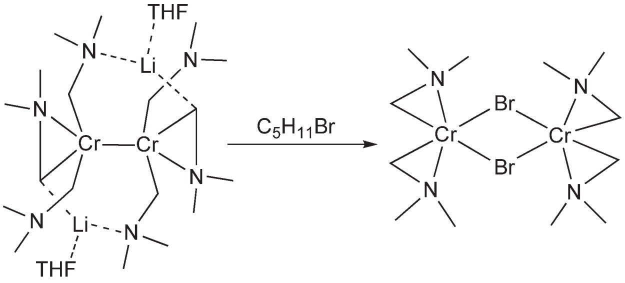


1



2

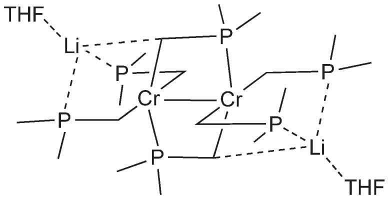
A homoleptic dimethylaminomethyl chromium(II) complex, $[Cr_2(CH_2NMe_2)_6][Li(THF)]_2$ **3** has been prepared by Steinborn *et al.* via reaction of $CrCl_2$ with 3 equiv. of $LiCH_2NMe_2$.[4] The complex displays a dimeric structure with a "super" short (1.884 Å), unsupported Cr–Cr quadruple bond, giving rise to largely diamagnetic behavior (0.67 μ_B/Cr) at room temperature. Each chromium atom is ligated by three CH_2NMe_2 ligands, two with η^1- and one with η^2-coordination. The Cr–Cr bond in **3** is reactive and is cleaved by oxidation with 1-bromopentane, yielding a bromide-bridged chromium(III) dimer, $[Cr(\eta^2\text{-}CH_2NMe_2)_2(\mu\text{-}Br)]_2$ **4**, which displays distorted octahedral coordination geometries at chromium. The reduced magnetic moment of **4** (2.97 μ_B/Cr) indicates significant antiferromagnetic coupling between the chromium atoms, presumably via exchange through the bridging bromides.



3

4

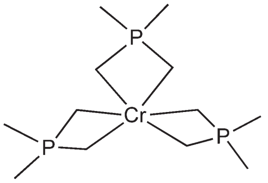
In related work, Steinborn has prepared the dimethylphosphinomethyl chromium(II) complex, $[Cr_2(CH_2PMe_2)_6][Li(THF)]_2$ **5**, via reaction of $CrCl_2(THF)_2$ with 3 equiv. of $LiCH_2PMe_2$.[5] The compound displays low residual paramagnetism (0.81 μ_B/Cr) at room temperature and contains a short Cr–Cr bond (1.950 Å) although this bond is substantially longer than that in the dimethylaminomethyl analog **3**. Furthermore, the Cr–Cr quadruple bond in **5** is bridged by two dimethylphosphinomethyl ligands in a μ-$\eta^1:\eta^1$-arrangement, in contrast to the unsupported quadruple bond in **3**. Each chromium atom is further coordinated by two η^1-CH_2PMe_2 ligands. Reaction of $[Cr_2(CH_2PMe_2)_6][Li(THF)]_2$ with TMEDA results in TMEDA coordination at Li (replacement of THF) but leaves the Cr–Cr bond intact. In contrast, chromium(II) alkyls without pendant donor groups undergo significant structural reorganization upon addition of TMEDA (Section 5.05.2.2).



5

5.05.2.1.2 Chromium(III) derivatives

A chromium(III) derivative incorporating a phosphorus-containing alkyl has also been structurally characterized. In this case, the phosphorus atom is not coordinated to chromium, but rather the ligands in $Cr[(CH_2)_2PMe_2]_3$ **6** are symmetrically bound (nearly equivalent Cr–C bond lengths) to form 1-chroma-3-phosphacyclobutane structures.[6] Other chromium(III) alkyls with pendant donors include a trinuclear, mixed metal complex that is formed upon reaction of $CrCl_3(THF)_3$ with a tetranuclear Grignard reagent, $[(Me_2NCH_2CH_2CH_2)Mg_2Cl_3(THF)_2]_2$.[7] In the resulting trinuclear complex, $[\{(Me_2NCH_2CH_2CH_2)_2Cr(\mu\text{-}Cl)_2\}_2Mg]$ **7**, the two $(Me_2NCH_2CH_2CH_2)_2Cr$ fragments are coordinated to a central Mg atom via four bridging chloride ligands. The steric strain imposed by the five-membered chelate rings creates a distorted octahedral geometry around chromium, although the steric strain is not manifested in unusual Cr–C (2.025–2.09 Å) and Cr–N (2.161–2.218 Å) bond lengths; these values are quite typical of other chromium(III) complexes. A similar synthesis to that just described, except using $Li(CH_2CH_2CH_2NMe_2)$ in place of the Grignard reagent, leads to an air stable μ_4-oxo-centered cubane complex, $[Cr_4(CH_2CH_2CH_2NMe_2)_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6]$, in which each octahedral chromium(III) ion is ligated by a bidentate $CH_2CH_2CH_2NMe_2$ ligand, three bridging chlorides, and the μ_4-oxo ligand.[8] In this latter complex, the Cr–C (2.08 Å–2.09 Å) and Cr–N (2.19 Å–2.20 Å) bond lengths are similar to those of the chromium–magnesium complex **7**. The source of the bridging oxo ligand has not been definitively established.



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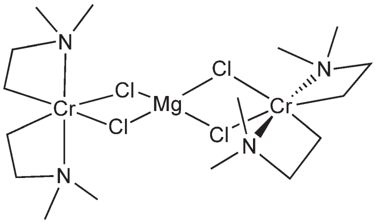

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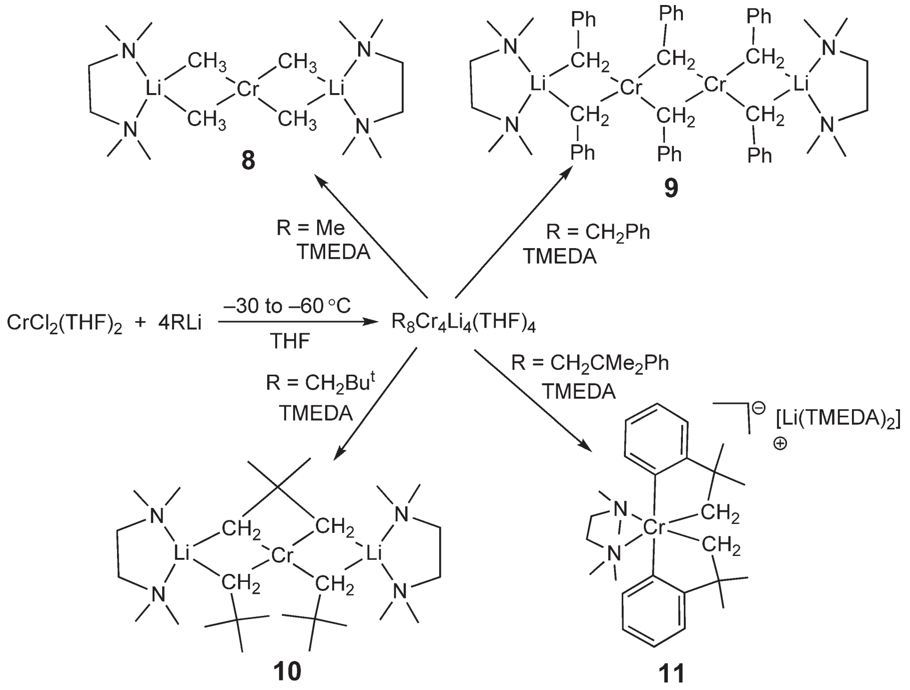
5.05.2.2 Chromium(II) and Chromium(III) σ-Alkyls without Pendant Donor Groups

Gambarotta has described an extensive family of chromium(II) and chromium(III) σ-alkyl complexes resulting from the reaction of $CrCl_2(THF)_2$ with various equivalents of RLi (R = Me, CH_2Ph, CH_2Bu^t, $CH_2C(Ph)Me_2$).[9] As will be seen, the exquisite sensitivity of these structures to the identity of the alkyl group—and to the type of coordinating Lewis base—has made this an incredibly rich area of study. For a 4 : 1 RLi : Cr ratio, the initially formed, thermally labile chromium alkyls are characterized as the nearly diamagnetic species $R_8Cr_2Li_4(THF)_4$. Depending on the identity of R, subsequent treatment with N,N,N′,N′-tetramethylethylenediamine (TMEDA) yields a variety of chromium(II) and chromium(III) complexes (Scheme 1). For R = Me, monomeric $Me_4Cr[Li(TMEDA)]_2$ **8** is produced, while dimeric (and diamagnetic) $(PhCH_2)_6Cr_2[Li(TMEDA)]_2$ **9** results from the benzyl derivative. Furthermore, addition of TMEDA to $(Bu^tCH_2)_8Cr_2Li_4(THF)_4$ induces cyclometallation to form the structurally characterized chromacyclobutane $(Bu^tCH_2)_2(CH_2CMe_2CH_2)Cr[Li(TMEDA)]_2$ **10**. In **8–10**, the alkyl ligands bridge between the distorted square planar chromium atoms and the peripheral lithium ions. In yet another example,

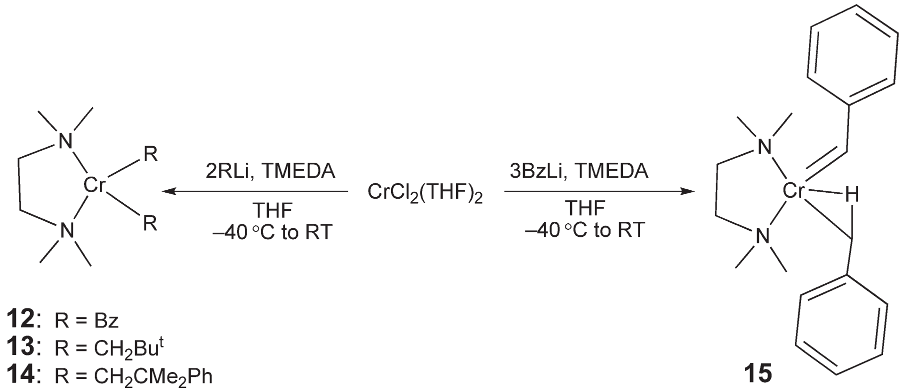


Scheme 1

addition of TMEDA to $(\mathrm{PhMe_2CCH_2})_8\mathrm{Cr_2Li_4(THF)_4}$ leads to a five-membered cyclometallated chromium(III) product, $[o\text{-}\mathrm{C_6H_4CMe_2CH_2}]_2\mathrm{Cr(TMEDA)[Li(TMEDA)_2]}$ **11**, which displays distorted octahedral geometry around chromium. The oxidant has not been identified.

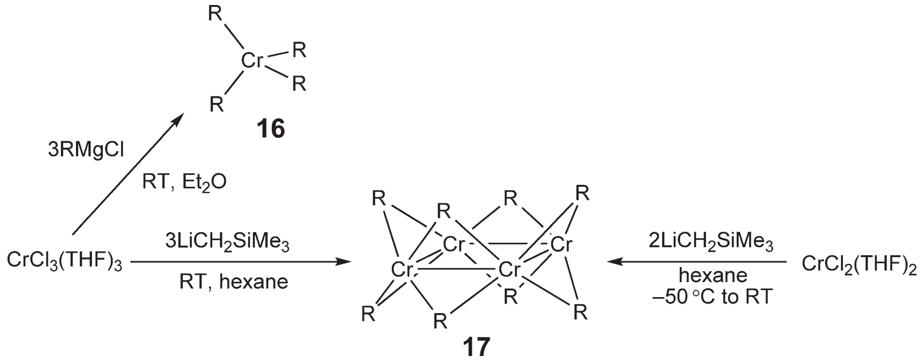
Changing the RLi : Cr ratio from 4 : 1 to 2 : 1 yields paramagnetic ($S = 2$) dialkyls of the type $(\mathrm{TMEDA})\mathrm{CrR_2}$ (R = Bz **12**, $\mathrm{CH_2Bu^t}$ **13**, $\mathrm{CH_2C(Ph)Me_2}$ **14**, Scheme 2). Derivatives **12** and **14** have been structurally characterized and display similar tetrahedrally distorted square planar geometries and similar Cr–C bond lengths (2.177 Å, 2.185 Å for **12** and 2.146 Å for **14**). In the case of benzyl derivative chemistry, a 3 : 1 RLi : Cr ratio yields a square planar product with similar Cr–C bond lengths (2.169 Å and 2.170 Å) to those for **12**, but which has been formulated as an unprecedented chromium(III) carbene complex, $(\mathrm{TMEDA})\mathrm{Cr}(=\mathrm{CHPh})(\mathrm{CH_2Ph})$ **15**, on the basis of X-ray crystallographic and magnetic susceptibility data ($\mu_{\mathrm{eff}} = 3.96\,\mu_{\mathrm{B}}$). In the crystal structure, one C–H bond of the benzyl ligand participates in an agostic interaction with chromium and this hydrogen atom is also loosely associated with the benzylidene carbon.

Additional homoleptic chromium alkyls have been prepared by Gambarotta via the reaction of $\mathrm{CrCl_3(THF)_3}$ with Grignard and alkyllithium reagents (Scheme 3).[10] Reaction of $\mathrm{CrCl_3(THF)_3}$ with 3 equiv. of RMgCl



12: R = Bz
13: R = $\mathrm{CH_2Bu^t}$
14: R = $\mathrm{CH_2CMe_2Ph}$

Scheme 2

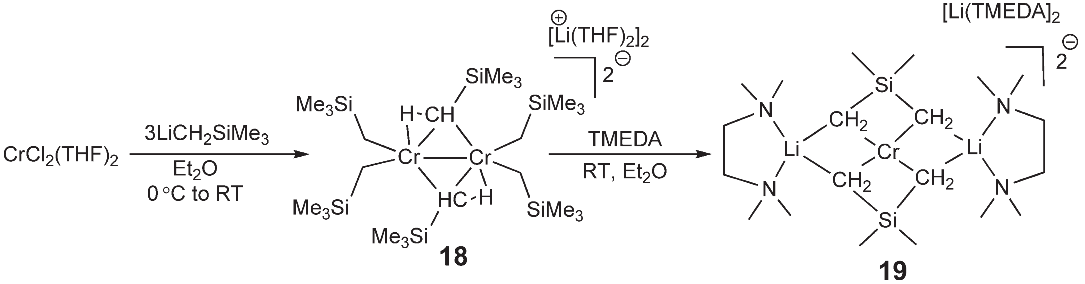


Scheme 3

(R = CH_2Bu^t or CH_2SiMe_3) yields the previously synthesized[11,12] tetravalent CrR_4 **16** complexes, which have been structurally characterized. In the solid state, these paramagnetic ($S = 1$) compounds adopt tetrahedral geometries with relatively short Cr–C bond lengths (1.954 Å–2.031 Å) consistent with the Cr(IV) oxidation state. Solutions of CrR_4 do not react with ethylene until AlR_3 co-catalysts are added, after which rapid formation of high molecular weight polyethylene ensues (activity = 1.1 g PE/(mmol-Cr h bar)). Switching from Grignard to alkyllithium reagents causes a dramatic shift in product composition. Reaction of $CrCl_3(THF)_3$ with 3 equiv. of $LiCH_2SiMe_3$ yields the previously prepared[13] tetrameric, metal–metal bonded $[(Me_3SiCH_2)_2Cr]_4$ **17**. Detailed X-ray structural characterization shows **17** to be a nearly regular square planar arrangement of four chromium atoms bridged above and below by eight trimethylsilylmethyl groups. Alternatively, the molecule can be viewed as a cubane structure with eight trimethylsilylmethyl groups occupying the cube's corners and the four chromium atoms in face-centered positions; in this description, the top and bottom faces of the cube are unoccupied.

Complex **17** is paramagnetic at room temperature (1.61 μ_B) but shows only low residual paramagnetism at 2 K (0.3 μ_B). This behavior is consistent with antiferromagnetic coupling between chromium atoms due to superexchange via the bridging alkyl groups, coupled with strong metal–metal bonding interactions (Cr–Cr distances 2.331 to 2.402 Å). An isotropic spin Hamiltonian model with strong antiferromagnetic exchange between the four metal centers adequately reproduces the magnetic data with J ranging from $J = -510$ to $-475\,cm^{-1}$, depending on whether the chromium atoms are presumed to be in high spin or low spin d^4 configurations. In contrast to the inertness of CrR_4 towards ethylene, $[(Me_3SiCH_2)_2Cr]_4$ polymerizes ethylene without requiring co-catalysts. In the same study, Gambarotta has confirmed earlier work[13] showing that $[(Me_3SiCH_2)_2Cr]_4$ is also prepared by the reaction of $CrCl_2(THF)_2$ with 2 equiv. of $LiCH_2SiMe_3$.

However, in another example of uncanny sensitivity to reagent ratios, Girolami has shown that the reaction of $CrCl_2(THF)_2$ with 3 equiv. of $LiCH_2SiMe_3$ yields the dinuclear chromium(II) alkyl $[Cr_2(CH_2SiMe_3)_6][Li(THF)_2]$ **18**, in which two CH_2SiMe_3 ligands bridge the Cr–Cr quadruple bond and each chromium atom is further ligated by two terminal CH_2SiMe_3 groups (Scheme 4).[14] The bridging ligands display α-agostic C–H···Cr interactions. Treatment of **18** with TMEDA leads to ligand C–H activation along with cleavage of the Cr–Cr bond to generate the monomeric bis(metallacycle) complex $[Cr(\kappa^2C,C'\text{-}CH_2SiMe_2CH_2)_2][Li(TMEDA)]_2$ **19**. This high spin ($S = 2$) compound bears a



Scheme 4

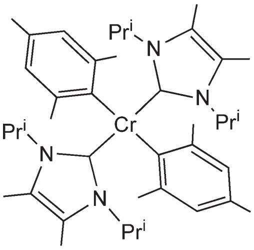
striking resemblance to neopentyl derivative **10** prepared by Gambarotta, except that **10** possesses only one metallocyclobutane ring resulting from γ C–H activation.

5.05.2.3 Chromium(II) and Chromium(III) σ-Aryls

Several chromium σ-aryl derivatives were previously prepared and these have been reviewed in COMC (1982) and COMC (1995). A few additional chromium σ-aryl complexes have been prepared recently, including heteroleptic and homoleptic derivatives.

5.05.2.3.1 Heteroleptic derivatives

A bis(carbene) complex **20** incorporating both 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene and σ-bound mesitylene ligands (mes = 2,4,6-$Me_3C_6H_2$) is produced by reacting $Cr(mes)_2(THF)_3$ with 2 equiv. of carbene.[15] The chromium(II) center displays square planar geometry and the aryl and carbene Cr–C bond lengths (2.175 Å and 2.178 Å, respectively) are statistically indistinguishable. Fluorinated aryl ligands have also been used to prepare chromium(II) bisphosphine complexes. In one example, Gibson has reacted $CrCl_2(THF)_2$ with 2 equiv. of $[2,4,6\text{-}(CF_3)_3C_6H_2]Li$ in the presence of PMe_3 to yield square planar $Cr(PMe_3)_2(2,4,6\text{-}(CF_3)_3C_6H_2)_2$ **21**; the bulky fluorinated aryl ligands are disposed in mutually *trans*-positions.[16] The structure is analogous to the previously reported non-fluorinated version, $Cr(PMe_3)_2(2,4,6\text{-}Me_3C_6H_2)_2$,[17] except for slightly longer Cr–C (2.184 Å) and Cr–P (2.519 Å) bonds due to the larger steric requirements of the fluorinated ligand.



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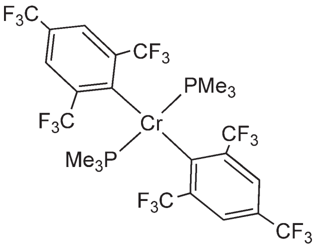

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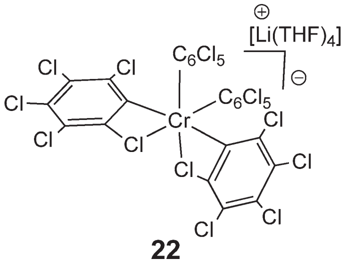
5.05.2.3.2 Homoleptic derivatives

Homoleptic chromium aryls have also been prepared and structurally characterized, including a rare case wherein chromium oxidation states II, III, and IV are effectively stabilized by the same halogenated aryl ligand. The Forníes group has been particularly active in this area and has reported that the reaction of $CrCl_3(THF)_3$ with 5 equiv. of perchlorinated LiC_6Cl_5 yields monomeric $[Cr(C_6Cl_5)_4][Li(THF)_4]$ **22**, which displays magnetic behavior ($\mu_{eff} = 3.75\,\mu_B$) consistent with a high spin chromium(III) center.[18] The coordination geometry is best described as distorted octahedral with two monodentate and two bidentate C_6Cl_5 ligands; the bidentate ligands coordinate via the *ipso* carbons and one of the *ortho*-Cl atoms (Cr–Cl bond lengths of 2.818 Å and 3.001 Å). The Cr–C bond lengths range from 2.073 Å to 2.173 Å, with shorter Cr–C bonds opposite the weakly coordinated chlorine atoms. In a subsequent, more extensive report, Forníes and co-workers have shown that chemical oxidation of $[Cr(C_6Cl_5)_4]^-$ yields the neutral chromium(IV) species $Cr(C_6Cl_5)_4$,[19] which displays $S = 1$ magnetic behavior and presumably adopts a tetrahedral geometry analogous to other reported CrR_4 complexes.

Furthermore, reaction of $CrCl_2(THF)_2$ with 5 equiv. of LiC_6Cl_5 yields a thermally labile chromium(II) complex, $[Cr(C_6Cl_5)_4][\{Li(THF)_3\}_2(\mu\text{-}Cl)]_2$ **23**, which includes an unusual chloride-bridged $\{Li(THF)_3\}^+$ cation. The Cr–C bond length (2.208 Å) in **23** is slightly longer than that in **22**, which is consistent with the observed high spin $S = 2$ ($\mu_{eff} = 4.77\,\mu_B$) chromium(II) center. It should be noted that the chromium(II) and chromium(III) aryl structures display discrete anions and cations, in contrast to homoleptic chromium(II) alkyls, such as **8–11**, wherein the chromium anion and lithium cation are invariably bridged via alkyl groups. The stabilization of structures with chromium(II), (III), and (IV) oxidation states with the same ligand is presumably due to the electron-withdrawing nature of the ligand, along with its ability to form secondary interactions (via Cl atoms) with chromium. Extension of this work to fluorinated aryl ligands has been accomplished by low temperature reaction of $CrCl_3(THF)_3$ with 5 equiv. of LiC_6F_5. Subsequent cation exchange yields $[Cr(C_6F_5)_5][n\text{-}Bu_4N]_2$ **24**, which displays an unusual, five-coordinate square pyramidal geometry for chromium(III).[20] The Cr–C_{ipso} bond lengths partition into four long bonds

(2.140 to 2.185 Å) along the basal plane and one short apical bond (2.088 Å). Two *ortho* C–F bonds appear to offer some protection to the open coordination site; however, there is no overwhelming evidence for direct Cr–F bonding. Even with this unusual geometry, the chromium(III) ion retains its usual high spin ($S=3/2$) electronic state.



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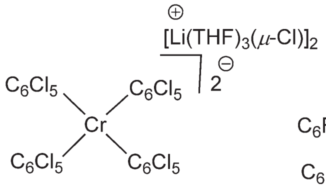

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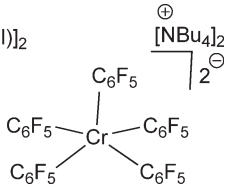

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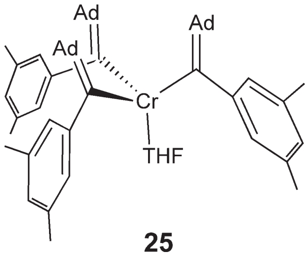
5.05.2.4 Chromium(III) σ-Alkenyls

A tris(alkenyl)chromium(III) complex has been prepared by Cummins using a sterically demanding alkenyl ligand.[21] The bulky bromoolefin BrC(=Ad)(Ar) (Ad = 2-adamantylidene, Ar = 3,5-$Me_2C_6H_3$) is converted to the Grignard reagent and reacted with anhydrous $CrCl_3$. Residual THF from the Grignard reagent also coordinates to chromium yielding the monomeric complex Cr(THF)[C(=Ad)(Ar)]$_3$ **25**, which possesses a magnetic moment (3.67 μ_B) consistent with a high spin chromium(III) ion. This extremely electron-deficient (formally 11-electron) complex reacts with pyridine (displacing THF) but other potential ligands, such as TMEDA and PEt_3, do not react and are presumably too large to fit in the protective pocket provided by the bulky alkenyl ligands.



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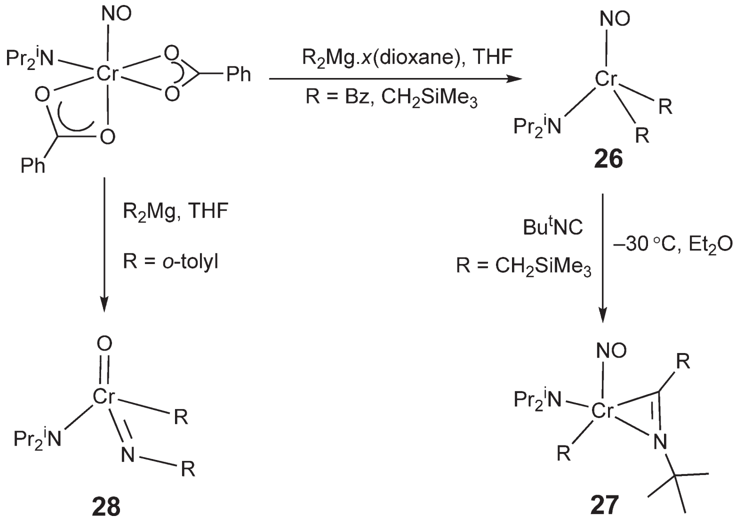
5.05.2.5 Nitrosyl-containing Chromium σ-Alkyl and σ-Aryl Compounds

The chemistry of chromium–nitrosyl complexes is extensive, primarily consisting of derivatives with Cp ancillary ligands. The Cp-containing nitrosyls are addressed later in this chapter (Section 5.05.4.1), however some non-Cp nitrosyl derivatives have also been prepared and deserve mention (Scheme 5). For example, the bis-benzoate $Cr(NO)(N^iPr_2)(O_2CPh)_2$ complex yields formally 14-electron dialkyl derivatives $Cr(NO)(N^iPr_2)R_2$ **26** via a reaction with 2 equiv. of R_2Mg (R = Bz, CH_2SiMe_3).[22] Spectroscopic data and X-ray structural analysis are consistent with significant Cr–NR_2 π-bonding, indicating that the amido ligands are best described as four-electron donors. In addition, some 14-electron derivatives, such as $Cr(NO)(N^iPr_2)(Bz)_2$, show crystallographic evidence for η^2-benzyl coordination and an agostic C–H···Cr interaction with the isopropyl C–H bond; both observations are consistent with significant coordinative and electronic unsaturation. Complex **26** displays reactivity with unsaturated C–N bonds; treatment of **26** with Bu^tNC forms the isonitrile insertion product **27**. Surprisingly, reaction of $Cr(NO)(N^iPr_2)(O_2CPh)_2$ with 2 equiv. of Ar_2Mg (Ar = *o*-tolyl) does not yield the expected bis-aryl analog, $Cr(NO)(N^iPr_2)(Ar)_2$, but rather forms an oxo-imido product $Cr(NAr)(O)(N^iPr_2)(Ar)$ **28**, resulting from N–O bond cleavage.[23] Finally, brown precipitates characterized as $[Cr(NO)_2(OEt)_2(EtAlCl_2)_2]$ and $[Cr(NO)_2(CHMe)(OEt)_2(AlCl_2)_2]_n$ have been isolated from the reactions of $[Cr(NO)_2(OEt)_2]_n$ and $EtAlCl_2$.[24]

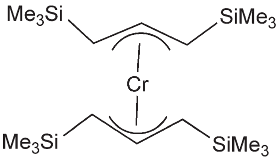


Scheme 5

5.05.3 π-Allyl Complexes

5.05.3.1 Chromium(II) Complexes

The chemistry of π-bonded chromium(II) allyl compounds has yielded numerous mononuclear and multinuclear complexes. For example, the homoleptic chromium(II) bis(π-allyl) complex **29** is prepared by the reaction of 2 equiv. of 1,3-bis(trimethylsilyl)allyl anion with $CrCl_2$.[25] The thermally stable, 12-electron monomeric complex has been structurally characterized and displays η^3-allyl ligands with staggered trimethylsilyl substituents. Use of the 1,1′,3-tris(trimethylsilyl)allyl anion yields an analogous monomeric chromium(II) complex **30**, while the less sterically encumbered 1-(trimethylsilyl)allyl anion affords a dimeric metal–metal bonded derivative **31**. Each chromium atom in **31** is bound by an η^3-allyl; the remaining two allyl ligands serve to bridge the Cr–Cr quadruple bond (Cr–Cr = 1.9784 Å).[26] Each of the monomeric complexes displays magnetic behavior consistent with isolated $S = 2$ systems. On the other hand, dimeric **31** is diamagnetic, consistent with extensive metal–metal bonding interactions.



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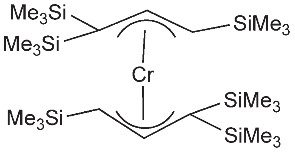

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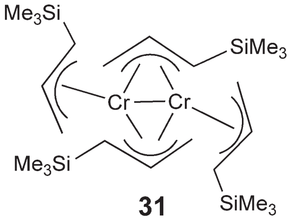

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5.05.3.2 Chromium(III) Complexes

Structural studies on homoleptic chromium(III) tris(π-allyl) complexes have been hampered, in part, by their thermal instability. In lieu of detailed crystallographic information, Blom and Swang have performed density functional theory (DFT) and *ab initio* calculations on tris(allyl)chromium and tris(2-methylallyl)chromium derivatives;[27] in addition, the latter compound had sufficient thermal stability to also be examined via variable-temperature NMR spectroscopy.[28] Calculations suggest ground-state C_{3h} geometries for both complexes; however, the NMR data for the 2-methylallyl derivative indicates that lower symmetry conformers likely exist in solution. Perhaps the moderately bulky 1-(trimethylsilyl)allyl or 1,3-bis(trimethylsilyl)allyl ligands (used to stabilize chromium(II) derivatives **29** and **31**) would produce sufficiently stable chromium(III) allyl complexes that would be amenable to crystallographic characterization.

5.05.4 Mono(η^5-Cyclopentadienyl) Complexes and Derivatives

The stability imparted by the coordination of Cp ligands (and derivatives thereof) allows for the preparation of chromium compounds containing a wide variety of additional neutral and anionic ligands. The reader is referred to the relevant chapters in COMC (1982) and COMC (1995) for excellent summaries of this rich and diverse field. Additional reviews published since 1993 are mentioned at the appropriate point in the paragraphs that follow. The following section describes the synthesis, structure, and reactivity of mono-Cp chromium complexes. Since many of these compounds serve as models for, or improvements upon, commercial polymerization catalysts (*vide infra*), the reactivity discussions will often focus on ethylene polymerization catalysis.

5.05.4.1 Nitrosyl Complexes

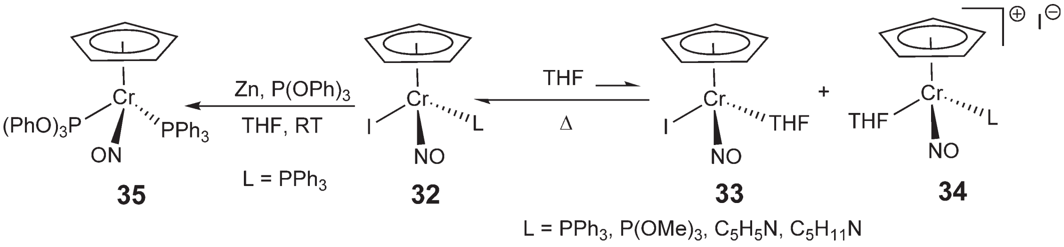
Transition metal–nitrosyl complexes, both classical coordination compounds and organometallic complexes, have received renewed interest partly due to the biological impacts of NO, including its role in blood pressure regulation. In fact, the potential use of metal–nitrosyl complexes as cardiovascular therapeutic agents has been explored.[29] Legzdins has written an extensive review of metal–nitrosyl complexes prepared up through 2001 and has included a discussion of organochromium species.[30] The present chapter addresses the synthesis, characterization, and unusual physical and chemical properties of organochromium nitrosyl complexes that have appeared since 1993. As a general rule, carbonyl-containing compounds are not described in detail; carbonyl-containing complexes are addressed in the Chapter 5.04.

5.05.4.1.1 Mononitrosyl derivatives

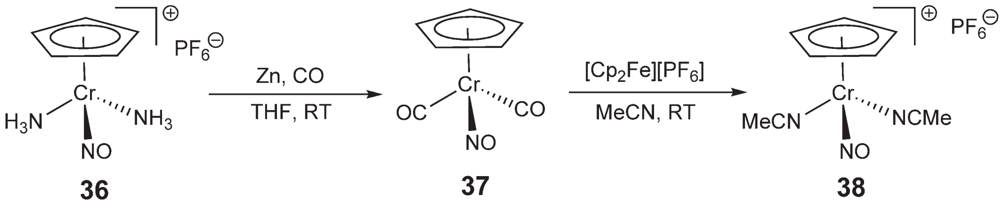
Organochromium nitrosyl chemistry is dominated by Cp-containing complexes. Beginning with mononitrosyl complexes, dimeric species such as $[Cp'Cr(NO)I]_2$ have been converted to monomeric Cp′Cr(NO)(L)I **32** by a reaction with various σ-donor ligands ($Cp' = Cp$ or Cp^*, $L = PPh_3$, $P(OMe)_3$, $P(OPh)_3$, pyridine, piperidine) in CH_2Cl_2.[31] These 17-electron complexes display EPR spectra consistent with an $S = 1/2$ ground state and undergo partial ligand substitution reactions in donor solvents, such as THF, to form small amounts of Cp′Cr(NO)(THF)I **33**. Furthermore, heating **32** in THF also generates, in addition to **33**, small but detectable (by EPR) quantities of cationic [Cp′Cr(NO)(L)(THF)][I] **34**, which is formed by dissociation of I^- (Scheme 6). However, in both cases, the solvolysis equilibria favor the parent complex **32**. On the other hand, electrochemical reduction of **32** to its 18-electron redox partner **32**$^-$ is irreversible and coincides with complete loss of iodide. This result indicates that the reduced 18-electron complex is "more" substitutionally labile than its 17-electron counterpart; this behavior is unusual given that 17-electron complexes typically display greater substitution lability than 18-electron, closed-shell derivatives. In keeping with this unusual observation, chemical reduction of **32** ($Cp' = Cp$, $L = PPh_3$) by Zn in the presence of $P(OPh)_3$ leads to complete loss of I^- and generation of the 18-electron mixed phosphine–phosphite $CpCr(NO)(PPh_3)(P(OPh)_3)$ **35** (Scheme 6).

5.05.4.1.1.(i) Influence of σ- and π-donor ligands

In a series of papers, Legzdins *et al.* have described how the nature of the neutral donor ligand influences the stability and reactivity of nitrosyl compounds. For example, the 17-electron cationic bis(ammine) complex $[CpCr(NO)(NH_3)_2][PF_6]$ **36**, which is formed by dehalogenation of $[CpCrNO(\mu\text{-}I)]_2$ with $AgPF_6$ in the presence of σ-donating NH_3, does not undergo substitution reactions with π-accepting CO. However, an 18-electron intermediate, formed by reduction of **36** with Zn, readily loses NH_3 and coordinates CO to form the known dicarbonyl, $CpCr(NO)(CO)_2$



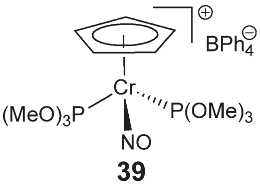
Scheme 6



Scheme 7

37 (Scheme 7).[32] Furthermore, one-electron oxidation of **37** with $[Cp_2Fe][PF_6]$ in acetonitrile leads to loss of CO and coordination of σ-donating MeCN to form the nitrile adduct $[CpCr(NO)(NCMe)_2][PF_6]$ **38**.

From these observations, Legzdins concluded that σ-donors (e.g., NH_3, MeCN) favor cationic 17-electron configurations, while π-acceptor ligands, such as CO, stabilize neutral 18-electron complexes.[32] Extension of this work to include σ-donating alkylamine and π-accepting isocyanide ligands further confirms the σ-donor/π-acceptor preference noted above.[33] Furthermore, use of intermediate ligands, such as $P(OMe)_3$, allows for isolation of both 17- and 18-electron complexes (**39** and **40**, respectively). Somewhat surprisingly at first glance, the Cr–P bonds in **40** are 0.11 Å shorter than in **39**; however, this is entirely consistent with greater π-backbonding interactions in the 18-electron derivative.



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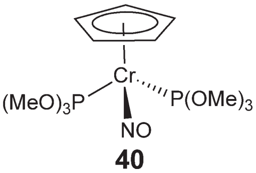
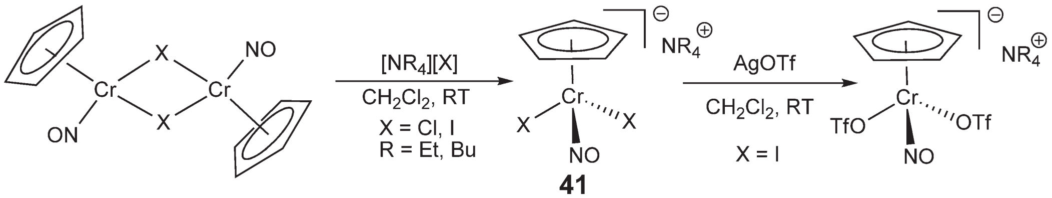


40

The stabilizing impact of π-acceptor ligands has been examined via extended Hückel calculations.[34] For 18-electron complexes, π-acceptor ligands are required to stabilize the doubly occupied HOMO. One-electron oxidation (thereby depopulating the HOMO) results in a weaker metal–ligand interaction and enhanced ligand dissociation (consistent with experimental observations). For 17-electron complexes coordinated by σ-donor ligands, the HOMO is largely non-bonding and only singly occupied. In this case, the half-filled non-bonding HOMO does not disturb metal–ligand bonding interactions, and such complexes are predicted to be stable and relatively substitution-inert.

5.05.4.1.1.(ii) Dihalide complexes

Anionic 17-electron dihalide complexes of the type $[CpCr(NO)X_2]^-$ ($X = I^-$, Cl^-) have been pursued as possible precursors (via oxidation) to neutral, 16-electron $CpCr(NO)X_2$ species. Toward this end, reaction of $[CpCr(NO)X]_2$ with $[NR_4][X]$ ($R = Et$, Bu^n; $X = I^-$, Cl^-) generates $[CpCr(NO)X_2][NR_4]$ **41**.[35] In the case of diiodide complexes, removal of iodide with AgOTf ($OTf^- = O_3SCF_3^-$) provides complexes with weakly bound triflate ligands (Scheme 8). The triflates are then readily displaced by bromide, providing access to the $[CpCr(NO)Br_2]^-$ derivative. Unfortunately, one-electron oxidation of **41** does not lead to the expected 16-electron $CpCr(NO)X_2$ but rather to products that are consistent with NO liberation.



Scheme 8

The source of the instability of $CpCr(NO)Cl_2$ was examined via extended Hückel theoretical calculations.[35] A proposed high spin ($S=1$) configuration for the $CpCr(NO)Cl_2$ intermediate avoids spin pairing by promoting a metal–nitrosyl π-bonding electron to a non-bonding energy level. The resulting loss of π-bonding interactions weakens the Cr–NO bond, leading to increased nitrosyl lability. Additional detailed theoretical calculations at the DFT level indicate a tendency toward unusually long Cr–NO bond lengths in these $S=1$ complexes, consistent with weaker Cr–NO interactions and with the experimentally observed lability of NO.[36]

5.05.4.1.1.(iii) Alkyl complexes

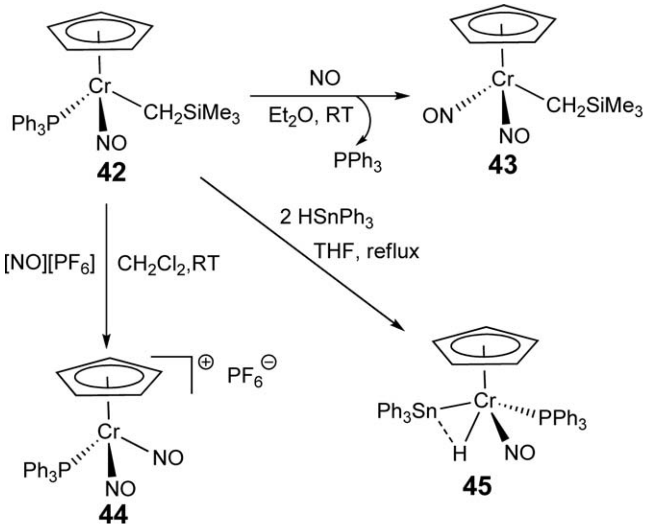
The previously described triphenylphosphine-ligated **32** ($Cp'=Cp$, $L=PPh_3$) can be alkylated to form $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ **42** in a process that involves phosphine loss prior to alkyl-for-iodide exchange.[37] Previously inaccessible alkyl derivatives CpCr(NO)(L)(R) ($L=C_5H_{11}N$, NH_2Bu^t; $R=CH_2SiMe_3$, CH_2Ph) are prepared by similar routes. Cyclic voltammetry experiments have shown that alkyl derivatives such as **42** are unstable in their cationic 16-electron and anionic 18-electron configurations, precluding reactivity studies of these even-electron complexes. With regard to 17-electron derivatives, **42** is unreactive with CO, H_2, and C_2H_4, yet it reacts readily with NO and $[NO][PF_6]$ to form $CpCr(NO)_2CH_2SiMe_3$ **43** and $[CpCr(NO)_2(PPh_3)][PF_6]$ **44**, respectively (Scheme 9). Moreover, treatment of **42** with 2 equiv. of $HSnPh_3$ results in loss of the alkyl ligand with addition of the Sn–H bond to generate $CpCr(NO)(PPh_3)(H)(SnPh_3)$ **45**.[38] Finally, while PPh_3-ligated **42** is unreactive towards CO, CpCr(NO)(L)(R) analogs with smaller donors, such as $L=$piperidine (pip), do react with CO to give CpCr(NO)(pip)(CO) and $CpCr(NO)(CO)_2$ via formal expulsion of alkyl radical (R·).[38]

5.05.4.1.1.(iv) Sulfido and selenido complexes

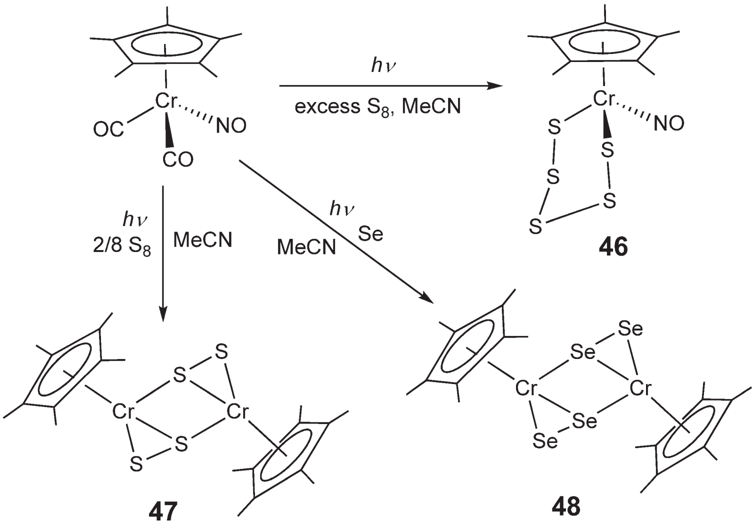
Poly-sulfido and -selenido nitrosyl complexes are prepared via photochemical decarbonylation of $CpCr(NO)(CO)_2$ in the presence of elemental sulfur or selenium (Scheme 10).[39] Use of excess sulfur leads to the cyclopentasulfido complex **46**, whereas limiting the sulfur input leads to the dimeric, bridging disulfido **47**. The bridging diselenido compound **48** is formed irrespective of the amount of available selenium. An extensive family of Cp-containing sulfido and selenido complexes is described in Section 5.05.4.4.

5.05.4.1.1.(v) Cp-containing complexes from non-Cp precursors

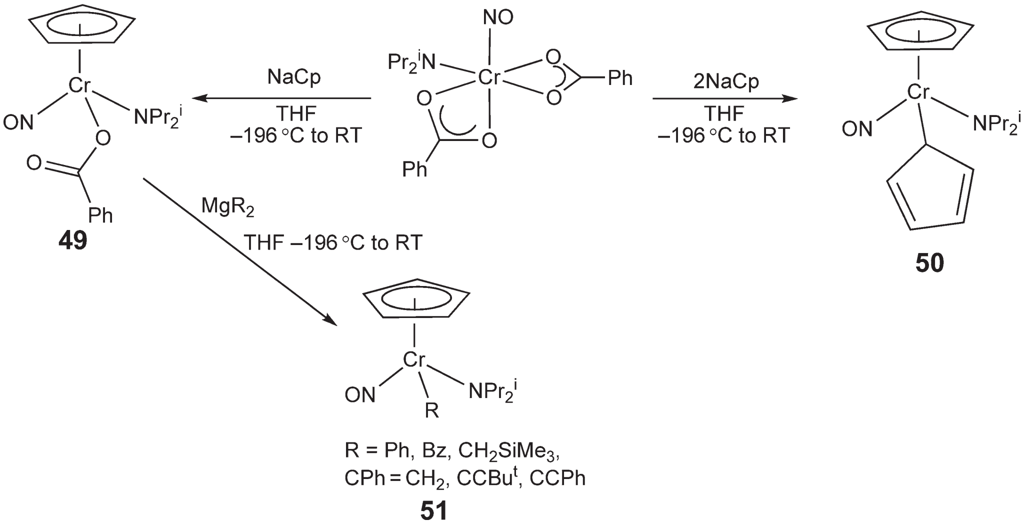
Chromium–nitrosyl complexes without Cp-supporting ligands can serve as useful starting materials to make Cp-containing derivatives (Scheme 11). For example, reaction of $Cr(NO)(N^iPr_2)_3$ with benzoic acid leads to bis-benzoate $Cr(NO)(N^iPr_2)(O_2CPh)_2$. The bis-benzoate derivative reacts with NaCp to effect a Cp-for-benzoate exchange, resulting in $CpCr(NO)(N^iPr_2)(O_2CPh)$ **49**. Addition of a second equivalent of NaCp yields $CpCr(NO)(N^iPr_2)(\eta^1\text{-}Cp)$ **50**. The second benzoate can also be removed upon reaction with R_2Mg to form the



Scheme 9

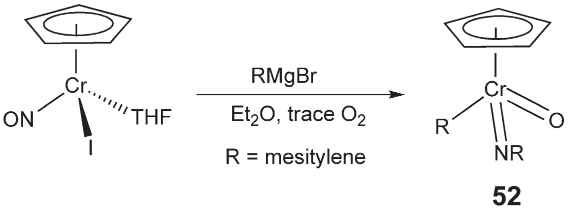


Scheme 10



Scheme 11

organometallic alkyl derivatives $\mathrm{CpCr(NO)(N^iPr_2)(R)}$ **51**.[40] Finally, reaction of CpCr(NO)(THF)I with the sterically demanding Grignard reagent, (mes)MgBr (mes = 2,4,6-$\mathrm{C_6H_2Me_3}$), leads to N–O bond cleavage and formation of CpCr(O)(N-mes)(mes) **52** (Scheme 12).[41] Similar N–O bond breaking to form oxo-imido complexes has been noted previously in the synthesis of non-Cp nitrosyl derivative 28.



Scheme 12

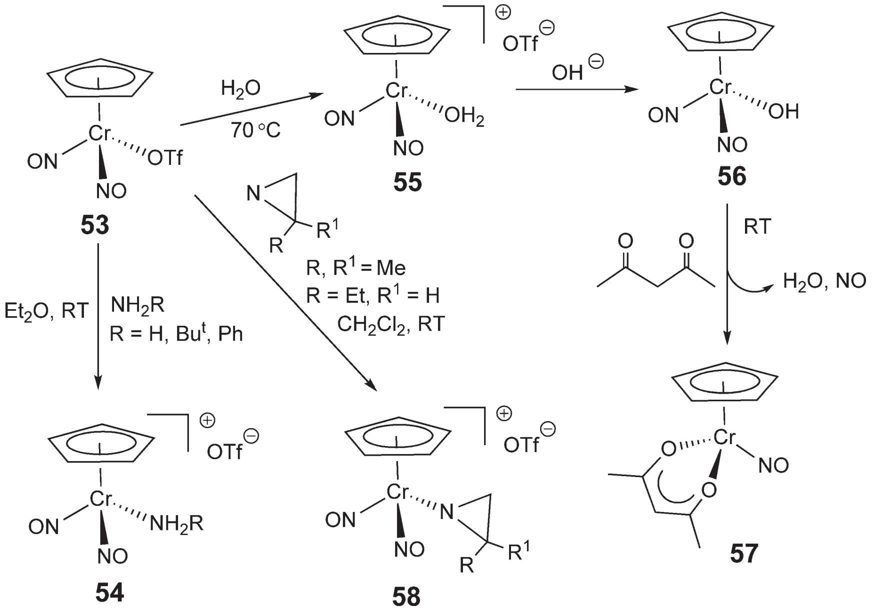
5.05.4.1.2 Dinitrosyl derivatives

Dinitrosyl complexes of the type $CpCr(NO)_2Cl$ have been converted to triflate-bound derivatives **53** with AgOTf, and the weakly bound triflate is readily displaced by σ-donor ligands, such as primary amines forming **54**, and even water forming **55** (Scheme 13).[42] In this study, detailed analysis of the aqueous chemistry of $[CpCr(NO)_2]^+$ unveils surprisingly stable $[CpCr(NO)_2(H_2O)]^+$ **55** and $[CpCr(NO)_2(OH)]$ **56** derivatives, the latter of which is basic enough to react with weak acids such as acetylacetone, forming 17-electron mononitrosyl CpCr(NO)(acac) **57**, with simultaneous liberation of NO (Scheme 13). X-ray structural analysis confirms the chelating nature of the acetylacetonate (acac) ligand. Using a similar dehalogenation strategy, reaction of $CpCr(NO)_2Cl$ with AgX ($X = BF_4^-$, OTf^-) in the presence of 2,2-dimethylaziridine or 2-ethylaziridine leads to the cationic adducts $[CpCr(NO)_2(Az)][X]$ **58**.[43]

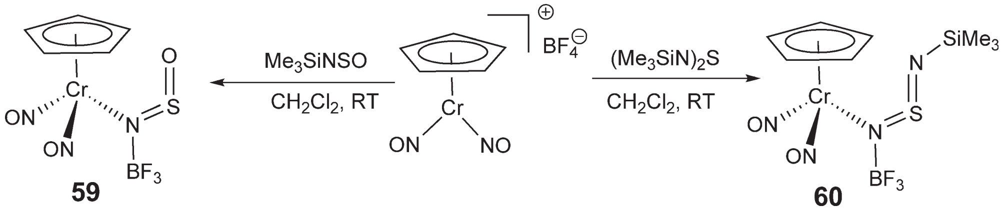
Further examples of dinitrosyl complexes include $CpCr(NO)_2[N(BF_3)SO]$ **59** and $CpCr(NO)_2[N(BF_3)SNSiMe_3]$ **60**, which are formed by the reaction of $[CpCr(NO)_2][BF_4]$ with Me_3SiNSO and $S(NSiMe_3)_2$, respectively (Scheme 14).[44] In both cases, X-ray crystallographic analysis confirms that the byproduct BF_3 is coordinated to nitrogen, forming borane-imino adducts. Finally, reaction of $CpCr(NO)_2Cl$ with the sodium salt of 4,6-dimethylpyrimidin-2-thiol leads to expulsion of 1 equiv. of NO and formation of **61** with bidentate coordination of the pyrimidine-2-thiolate (Scheme 15).[45]

5.05.4.2 π-Allyl Complexes

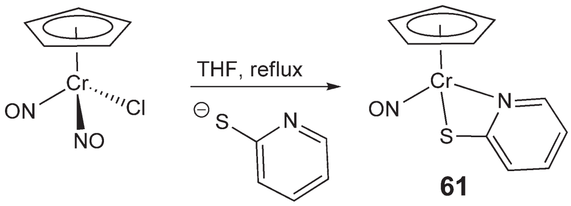
Cyclopentadienylchromium bis(π-allyl) complexes of the type $Cp'(\eta^3\text{-}C_3H_5)_2Cr$ **62** ($Cp' = Cp$, Cp^*, indenyl) have been prepared by low temperature (−30 °C) reaction of $[Cp'CrCl_2]_2$ with a slight excess of C_3H_5MgCl.[46] Complex **62** reacts further upon warming to give the allyl-bridged dimer **63**. Bis(allyl) **62** also reacts with small phosphine or phosphite



Scheme 13



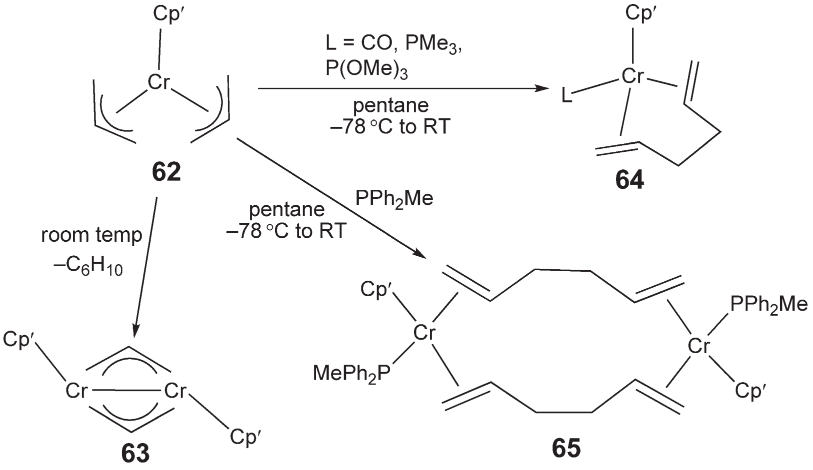
Scheme 14



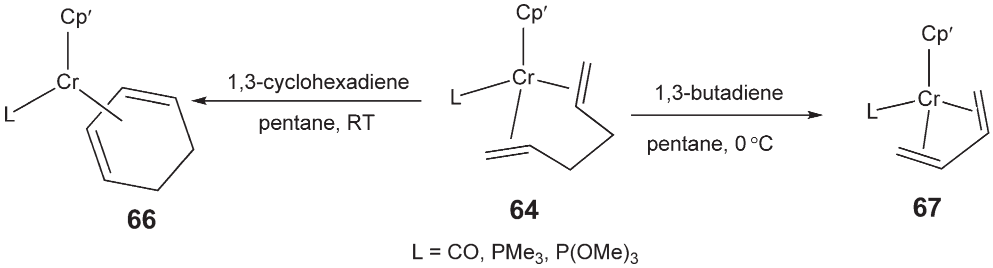
Scheme 15

donors causing reductive coupling of the allyl groups and formation of monomeric 1,5-hexadiene-coordinated species **64** (Scheme 16). Use of more sterically demanding phosphines (e.g., Ph_2PMe) leads to the formation of dinuclear 1,5-hexadiene-bridged compounds **65**. The 1,5-hexadiene ligand in **64** is readily displaced by 1,3-cyclohexadiene or butadiene to form the η^4-1,3-cyclohexadiene **66** and η^4-1,3-butadiene **67** complexes, respectively (Scheme 17).

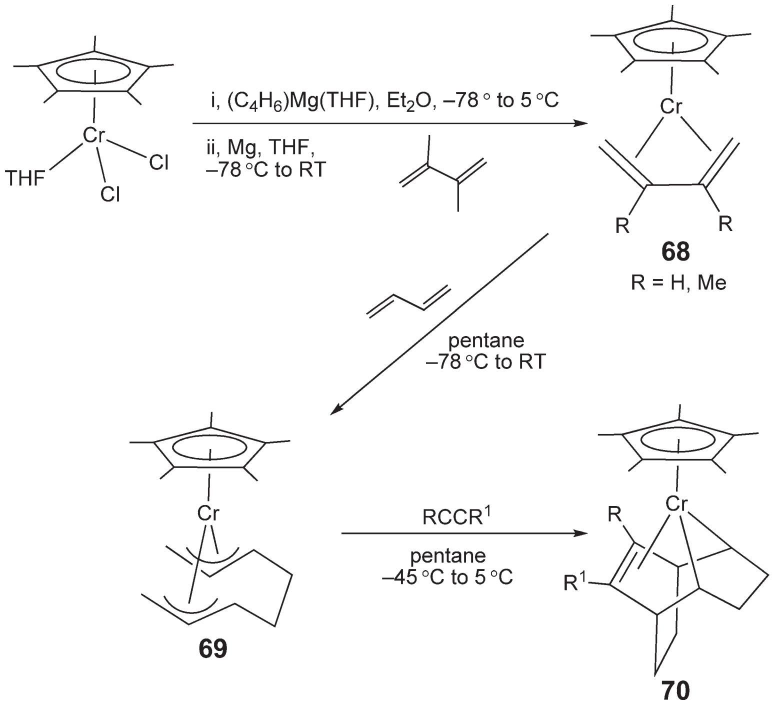
Donor-free diene derivatives (**68**; R = H, Me) are formed via the reaction of $Cp^*CrCl_2(THF)$ with metallated dienes such as $(C_4H_6)Mg(THF)_2$ or via the reduction of $Cp^*CrCl_2(THF)$ with activated Mg in the presence of 2,3-dimethylbutadiene (Scheme 18).[47] Alternatively, direct reaction of $Cp'(\eta^3\text{-}C_3H_5)_2Cr$ with the appropriate diene also provides donor-free **68**. The coordinative unsaturation of 68 is demonstrated by its ready acceptance of an additional donor ligand such as CO or PMe_3 to form the previously described **67** derivatives. Complex **68** also reacts with additional 1,3-butadiene, causing coupling of 1,3-butadiene to octadiene, and formation of monomeric $Cp^*(\mu\text{-}\eta^3,\eta^3\text{-}C_8H_{12})Cr$ **69** (Scheme 18). The latter compound reacts with disubstituted alkynes (RC_2R^1; R, R^1 = Me, Et) by addition at the 2,7-positions of the bound octadienyl ligand; the resulting coupled ligand is bound both η^1- and η^2- to the chromium atom **70** (Scheme 18). Reaction of the sterically unencumbered $Cp(\eta^3\text{-}C_3H_5)_2Cr$ with excess butadiene leads to a diamagnetic complex, $(CpCr)_2(\mu\text{-}\eta^3,\eta^3\text{-}C_8H_{12})$, in which the octadienyl fragment bridges both chromium atoms.[47]



Scheme 16



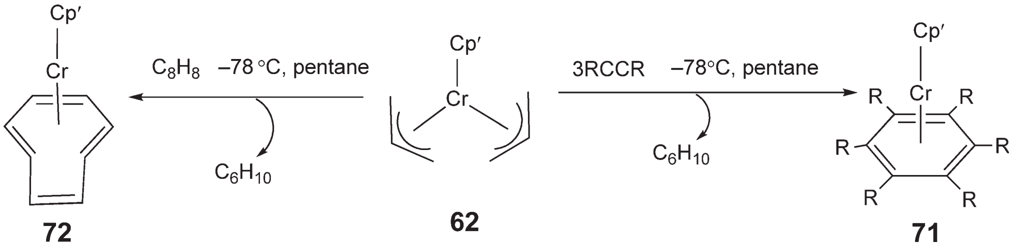
Scheme 17



Scheme 18

5.05.4.3 Complexes with η^6-Arene and η^6-Triene Supporting Ligands

Reaction of Cp′(η^3-C_3H_5)$_2$Cr complexes (Cp′ = Cp, MeCp, Bu^{t}Cp, indenyl) with various alkynes (RC_2R) (R = H, Me, Et, Ph) results in reductive coupling of the bound allyls to form 1,5-hexadiene, with concomitant cyclotrimerization of alkyne to form substituted arenes (Scheme 19). The arene subsequently displaces 1,5-hexadiene to form the unsymmetrical mixed ligand complexes Cp′(η^6-C_6R_6)Cr **71**.[48] In related reactions, treatment of Cp′(η^3-C_3H_5)$_2$Cr with cyclooctatetraene also results in allyl coupling followed by 1,5-hexadiene loss, leading to Cp′(η^6-C_8H_8) **72**; an X-ray crystal structure confirms IR evidence that one of the tetraene's double bonds remains unbound. A similar reaction of Cp′(η^3-C_3H_5)$_2$Cr with cycloheptatriene leads ultimately to the diamagnetic Cp′(η^7-C_7R_7)Cr, presumably via H-atom abstraction from the ligand. An alternative route to **71** (Cp′ = Cp*) involves heating [Cp*CrCl$_2$]$_2$ and C_6R_6 (R = H, D, Me) with the Lewis-acidic reducing agents $AlCl_3$/Al or a mixture of AlX_3 (X = Cl, Et), Al and $LiAlH_4$.[49] In this synthesis, the Lewis acid serves to cleave the bridging-chloride dimer while Al reduces chromium from Cr(III) to Cr(I). The mixed Cp′Cr(arene) complexes display paramagnetic NMR spectra and possess magnetic moments consistent with $S = 1/2$ species. Oxidation of Cp*Cr(η^6-arene) with [Cp_2Fe][PF_6] generates stable paramagnetic ($S = 1$) monocations. The monocations display appreciable delocalization of spin onto the π-ligands, and the authors claim that these are attractive candidates for building ferromagnetic donor–acceptor stacks by pairing with the appropriate π-anion.

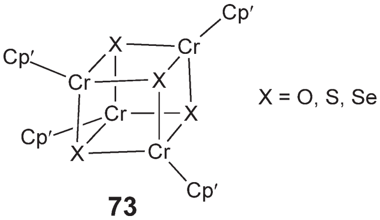


Scheme 19

5.05.4.4 Chalcogenide Complexes

5.05.4.4.1 Cubane clusters

Organochromium cubane clusters, $(Cp'Cr)_4X_4$ clusters (73; X = O, S, Se), in which the metal atoms occupy alternate corners in a distorted cube structure have been known for several years. Their chemistry was reviewed in COMC (1995)[50] and the reader is referred to this excellent summary for background information.



73

5.05.4.4.1.(i) Theoretical studies

More recently, general periodic trends in $(CpM)_4X_4$ complexes (M = Cr 73, Mo; X = O, S) have been examined using broken symmetry DFT.[51] This approach accurately reproduces the rhombic distortion displayed by $(CpCr)_4O_4$ (two short and four long Cr–Cr distances) and the near-perfect tetrahedral structure of $(CpCr)_4S_4$ (six equivalent Cr–Cr distances). The calculations further demonstrate that the three metal valence electrons remain localized in $(CpCr)_4O_4$ (no appreciable Cr–Cr bonding) but are fully delocalized over the cubane structure in $(CpCr)_4S_4$; the different bonding scenarios result from the competing effects of orbital overlap (favoring delocalization) and spin polarization energy (favoring localization). In the case of $(CpCr)_4Se_4$, solid-state ^{77}Se NMR spectroscopy showed two axially symmetric resonances, which is consistent with two different Se environments within a single distorted cubane molecule or with two different $(CpCr)_4Se_4$ structures within the crystal lattice;[52] the available data do not distinguish between these two possibilities. Finally, mixed tellurium/oxygen-containing clusters $(CpCr)_4Te_nO_{4-n}$ (n = 1–3) have been prepared by prolonged thermolysis of $CpCr(CO)_3(TePh)$.[53]

5.05.4.4.1.(ii) Oxidized clusters

Electrochemical experiments on $(Cp'Cr)_4O_4$ (Cp′ = Cp, Cp*, C_5H_4Me) have shown that derivatives with Cp′ = Cp* and C_5H_4Me undergo successive oxidations to the mono- and dications, whereas the Cp-ligated complex is oxidized to the monocation only.[54] Chemical oxidation of $(Cp^*Cr)_4O_4$ with $AgBF_4$ or 7,7,8,8-tetracyanoquinodimethane (tcnq) yields the salts $[(Cp^*Cr)_4O_4][BF_4]$ and $[(Cp^*Cr)_4O_4]$[tcnq], respectively. Magnetic measurements are consistent with $S = 1/2$ ground states for both monocations; the spin state results from strong antiferromagnetic exchange between the three $S = 3/2$ and one $S = 1$ chromium ions in the cluster. In the case of $[(Cp^*Cr)_4O_4]$[tcnq], additional antiferromagnetic coupling between the $S = 1/2$ cation and the $S = 1/2$ tcnq anion is observed below 110 K.

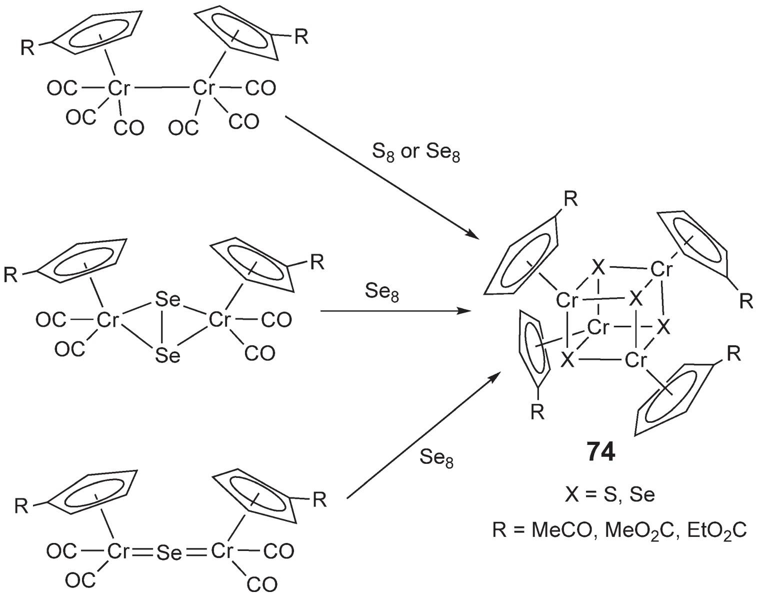
5.05.4.4.1.(iii) Derivatized Cp ligands

More recently, $(Cp'Cr)_4X_4$ (X = S, Se) derivatives 74 containing functionalized Cp′ ligands (Cp′ = $MeC(O)C_5H_4$, $MeO_2CC_5H_4$, $EtO_2CC_5H_4$) have been prepared by the reaction of the appropriate carbonyl dimer, $[Cp'Cr(CO)_3]_2$, with excess elemental sulfur or selenium.[55] As shown in Scheme 20, the linear Cr_2Se complex $[Cp'Cr(CO)_2]_2Se$ and the butterfly complex $[Cp'Cr(CO)_2]_2Se_2$ also serve as useful precursors to $(Cp'Cr)_4Se_4$ upon reaction with elemental selenium.[56] In the case of $[(MeC(O)C_5H_4)Cr]_4X_4$, the carbonyl group can be converted to an imine by reaction with excess 2,4-dintrophenylhydrazine. Other reactions at the peripheral acetyl group also leave the cubane structure intact. For example, the pendant carbonyl group of $[(MeC(O)C_5H_4)Cr]_4Se_4$ reacts with $NaBH_4$ to give the secondary hydroxy derivative $[MeCH(OH)C_5H_4]_4Cr_4Se_4$, or with MeMgI, to form the tertiary hydroxy complex $[Me_2C(OH)C_5H_4]_4Cr_4Se_4$. Furthermore, the carbonyl group reacts with the Wittig reagent $Ph_3P{=}CHPh$ to give $[PhCH{=}C(Me)C_5H_4]_4Cr_4Se_4$.

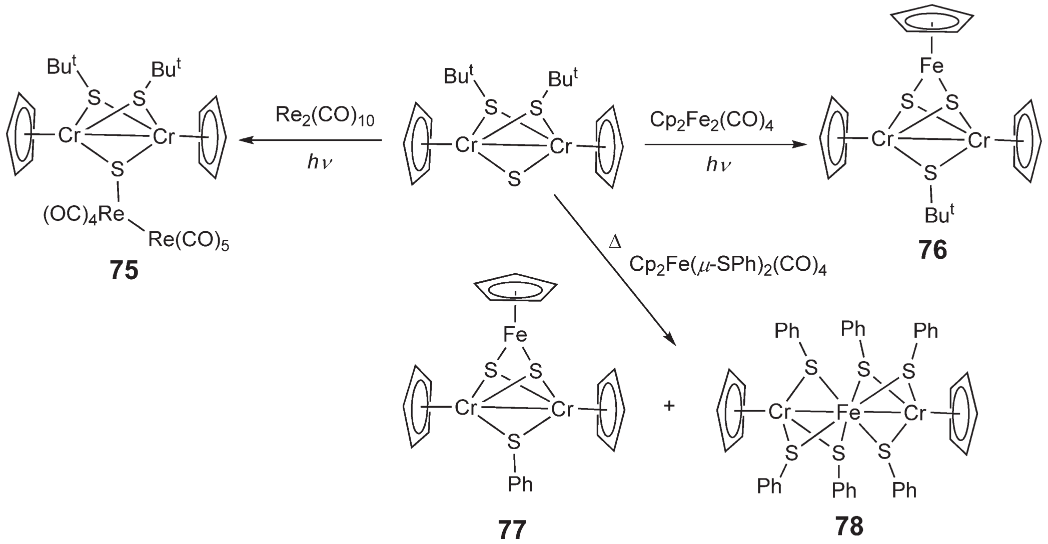
5.05.4.4.2 Thiolate-bridged derivatives

5.05.4.4.2.(i) Iron- and rhenium-containing complexes

The thiolate- and sulfide-bridged dimer, $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$, first prepared in 1979,[57] has been used as a metal-containing ligand to prepare heteronuclear clusters (Scheme 21). For example, photochemical reaction of



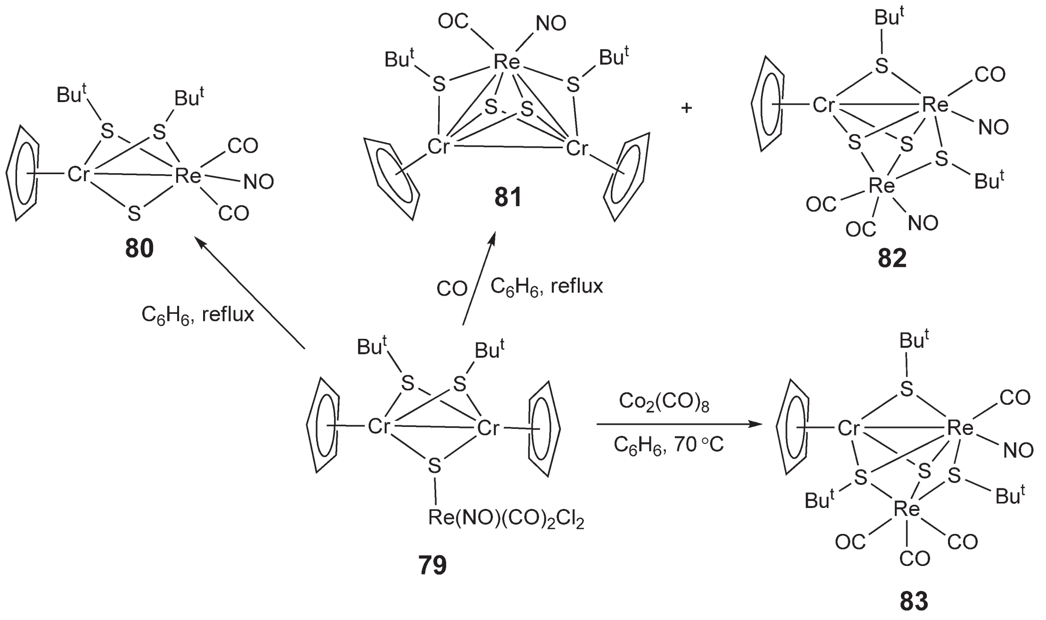
Scheme 20



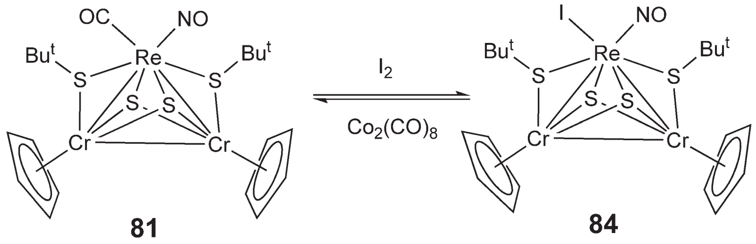
Scheme 21

$Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ with $Re_2(CO)_{10}$ yields the structurally characterized $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)Re_2(CO)_9$ **75**.[58] Similarly, prolonged photochemical reaction of $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ and $Cp_2Fe_2(CO)_4$ leads to triangular diamagnetic complex $Cp_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2FeCp$ **76**.[59] Thermal reaction of $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ and $Cp_2Fe_2(CO)_2(\mu\text{-}SPh)_2$ affords triangular $Cp_2Cr_2(\mu\text{-}SPh)(\mu_3\text{-}S)_2FeCp$ **77** and linear trimer $CpCr(\mu\text{-}SPh)_3Fe(\mu\text{-}SPh)_3CrCp$ **78**.

In another thermal example, reaction of $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ with dimeric $[(NO)(CO)_2ReCl(\mu\text{-}Cl)]_2$ results in cleavage of the rhenium dimer and formation of both *cis*- and *trans*-$Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)Re(NO)(CO)_2Cl_2$ **79**.[60] Thermolysis of the $ReCr_2$ trimer **79** leads to dinuclear $CpCr(\mu\text{-}SBu^t)_2(\mu\text{-}S)Re(NO)(CO)_2$ **80** and trinuclear $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)_2Re(NO)(CO)$ **81**, the latter displaying a relatively long Cr–Cr interaction (Cr–Cr = 3.010 Å) (Scheme 22). Each compound possesses low residual paramagnetism at 77 K (ranging from 0.32 to 0.75 μ_β/Cr), due to antiferromagnetic exchange between the chromium(III) ions. Triangular clusters with $CrRe_2$ and Cr_2Re cores are



Scheme 22



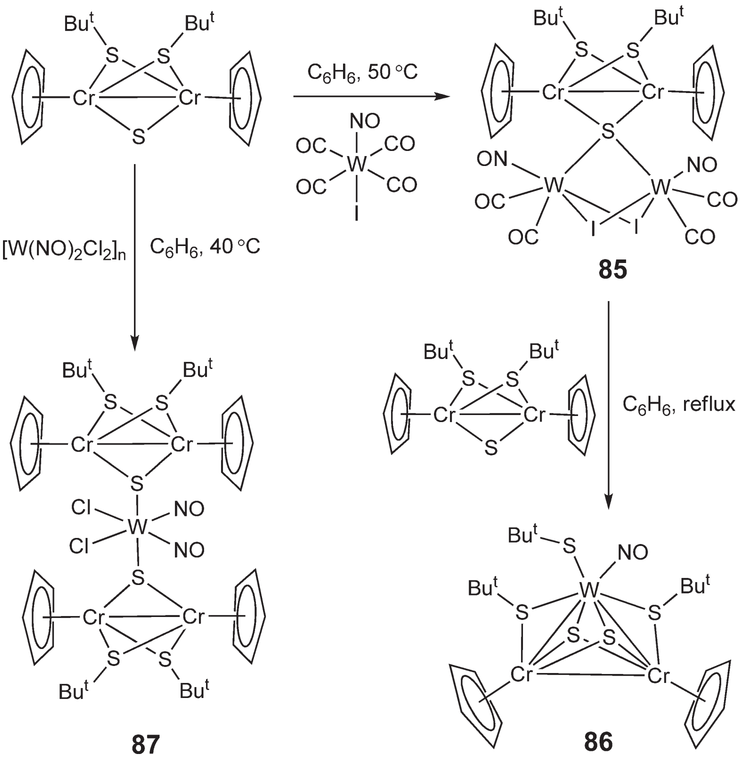
Scheme 23

prepared by thermolysis of **79** forming intermediate $[CpCr(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)Re(NO)(CO)]_2$, followed by carbonylation with CO to generate **81** and paramagnetic ($S=3/2$) $CpCr(\mu\text{-}SBu^t)Re(NO)(CO)(\mu_3\text{-}S)_2(\mu\text{-}SBu^t)Re(NO)(CO)_2$ **82** (Scheme 22).[61] Alternatively, carbonylation with $Co_2(CO)_8$ forms the paramagnetic ($S=3/2$) $CpCr(\mu\text{-}SBu^t)Re(NO)(CO)(\mu_3\text{-}S)(\mu_3\text{-}SBu^t)(\mu\text{-}SBu^t)Re(CO)_3$ **83**. Oxidation of **81** with I_2 leads to $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)_2Re(NO)I$ **84**, which can be reduced back to **81** with $Co_2(CO)_8$ (Scheme 23).[61]

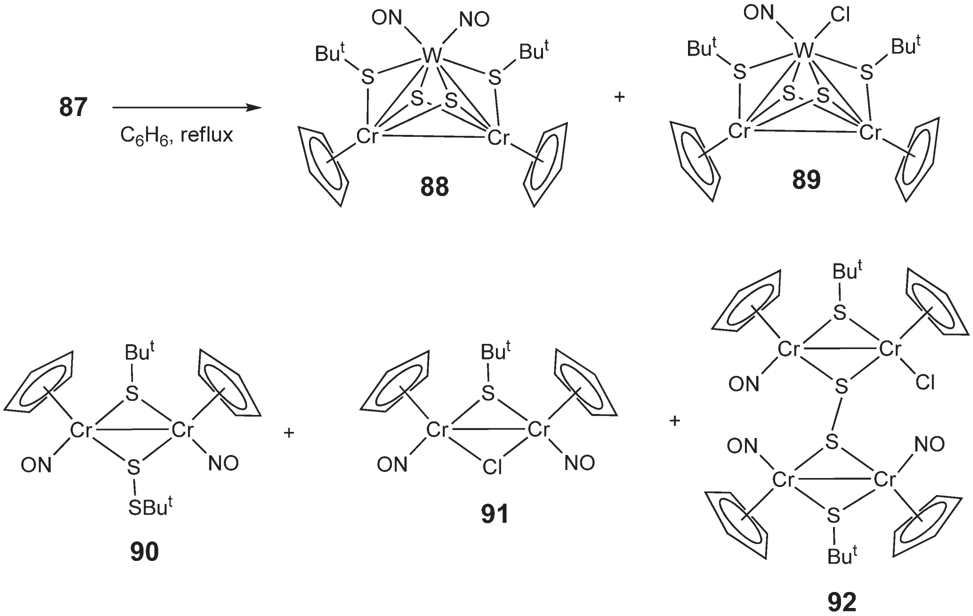
5.05.4.4.2.(ii) Tungsten-containing complexes

Reaction of $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ with *trans*-$W(CO)_4(NO)I$ leads to CO loss and formation of the tetranuclear $[CpCr(\mu\text{-}SBu^t)]_2(\mu_4\text{-}S)[W(CO)_2(NO)(\mu\text{-}I)]_2$ **85**, wherein the sulfide group bridges all four metal atoms (Scheme 24).[62] In **85**, the CpCr–CrCp moiety is nearly linear, which results in a relatively short Cr–Cr bond (2.764 Å) due to effective σ-bonding interactions within the linear CpCr–CrCp arrangement. Further treatment of **85** with $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ forms the trinuclear $[CpCr(\mu\text{-}SBu^t)(\mu_3\text{-}S)]_2W(NO)(SBu^t)$ **86** as the principal product. The trimer **86** is structurally related to **81**, including a relatively long Cr–Cr interaction (3.027 Å). Formation of other tungsten–nitrosyl complexes is accomplished by reacting $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ with polymeric $[W(NO)_2Cl_2]_n$ to afford the pentanuclear complex $[Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$ **87** (Scheme 24).[63]

Thermolysis of **87** yields diamagnetic triangular clusters $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)_2W(NO)_2$ **88** and $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu_3\text{-}S)_2W(NO)Cl$ **89**, as well as non-tungsten complexes $Cp_2Cr_2(NO)_2(\mu\text{-}SBu^t)(\mu\text{-}SSBu^t)$ **90**, $Cp_2Cr_2(NO)_2(\mu\text{-}SBu^t)(\mu\text{-}Cl)$ **91**, and $Cp_4Cr_4(NO)_3Cl(\mu\text{-}SBu^t)_2(\mu_4\text{-}S_2)$ **92** (Scheme 25). The non-tungsten complexes **90 and 91**, as well as $CpCr(NO)(\mu\text{-}SBu^t)_2Cr(Cl)Cp$ **93** are also obtained directly via the reaction of $Cp_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)$ with

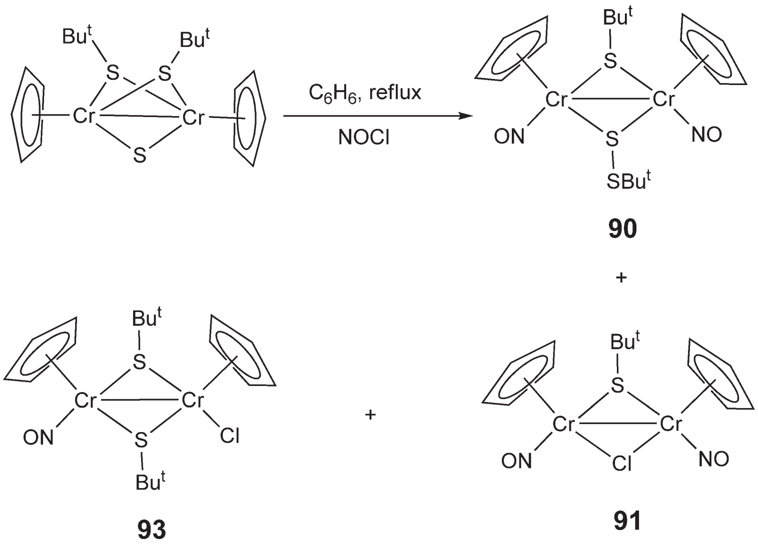


Scheme 24



Scheme 25

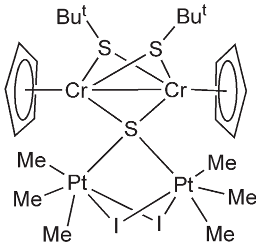
NOCl (Scheme 26). Each of the nitrosyl complexes **90–93** displays a bent CpCr–CrCp moiety, in contrast to the linear CpCr–CrCp arrangement found in the precursor $Cp_2Cr_2(\mu\text{-SBu}^t)_2(\mu\text{-S})$. As observed previously, the bent arrangement presumably does not allow for effective σ-orbital Cr–Cr interactions, which in turn leads to relatively long Cr–Cr bonds (ranging from 2.959 Å to 3.116 Å in **90–93**).



Scheme 26

5.05.4.4.2.(iii) Platinum-containing complexes

Extension of heterometallic complexes to include the platinum group is achieved by the reaction of Cp$_2$Cr$_2$(μ-SBu^t)$_2$ (μ-S) with [PtMe$_3$I]$_4$ to form the tetranuclear [CpCr(μ-SBu^t)]$_2$(μ_4-S)[PtMe$_3$(μ-I)]$_2$ **94**.[64] The overall structure of **94** is similar to that of tungsten analog **85** wherein the sulfide group bridges all four metal atoms; in keeping with the trend noted previously, the nearly linear CpCr–CrCp fragment in **94** displays a relatively short Cr–Cr bond (2.761 Å).



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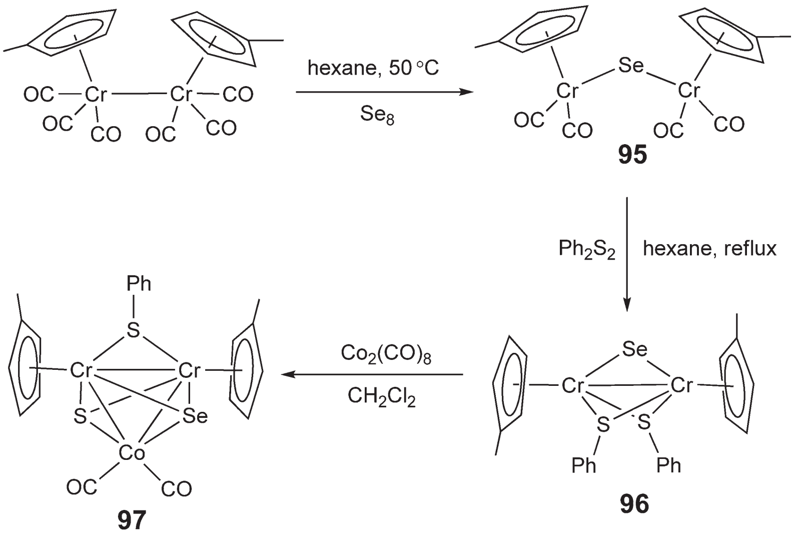
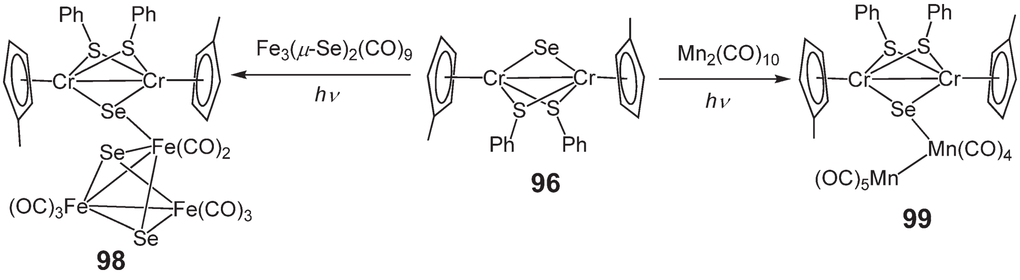
5.05.4.4.2.(iv) Selenium- and tellurium-bridged complexes

Heterochalcogenide complexes containing both sulfur and selenium atoms have also been prepared (Scheme 27). Reaction of [Cp′Cr(CO)$_3$]$_2$ (Cp′ = MeCp) with Se powder results in decarbonylation with the formation of [Cp′Cr(CO)$_2$]$_2$(μ-Se) **95**.[65] Subsequent treatment of **95** with Ph$_2$S$_2$ yields [Cp′Cr(μ-SPh)]$_2$(μ-Se) **96**. Complex **96** reacts further with Co$_2$(CO)$_8$ to give the mixed metal, mixed chalcogenide Cp′$_2$Cr$_2$(μ-SPh)(μ_3-S)(μ_3-Se)Co(CO)$_2$ **97**. Both **96** and **97** are diamagnetic and display short Cr–Cr bonds (2.730 Å and 2.624 Å, respectively) typical of the linear CpCr–CrCp arrangement. An analogous sulfur–tellurium mixed chalcogenide complex has been prepared by reacting [Cp′Cr(μ-SPh)]$_2$(μ-Te) with Co$_2$(CO)$_8$.[66]

Furthermore, heterometallic selenium-bridged complex **98** results from photochemical reaction of **96** with Fe$_3$(μ_3-Se)$_2$(CO)$_9$ while manganese complex **99** forms upon photolysis of a mixture of **96** and Mn$_2$(CO)$_{10}$ (Scheme 28).[66] Both compounds are effectively diamagnetic and possess nearly linear CpCr–CrCp arrangements and relatively short Cr–Cr bonds (2.763 Å and 2.835 Å, respectively). Higher temperature photolysis of [Cp′Cr(μ-SPh)]$_2$(μ-Se) and Mn$_2$(CO)$_{10}$ gives the paramagnetic dinuclear complex Cp′Cr(μ-SPh)$_3$Mn(CO)$_3$, which displays a magnetic moment consistent with three unpaired electrons.



Scheme 27



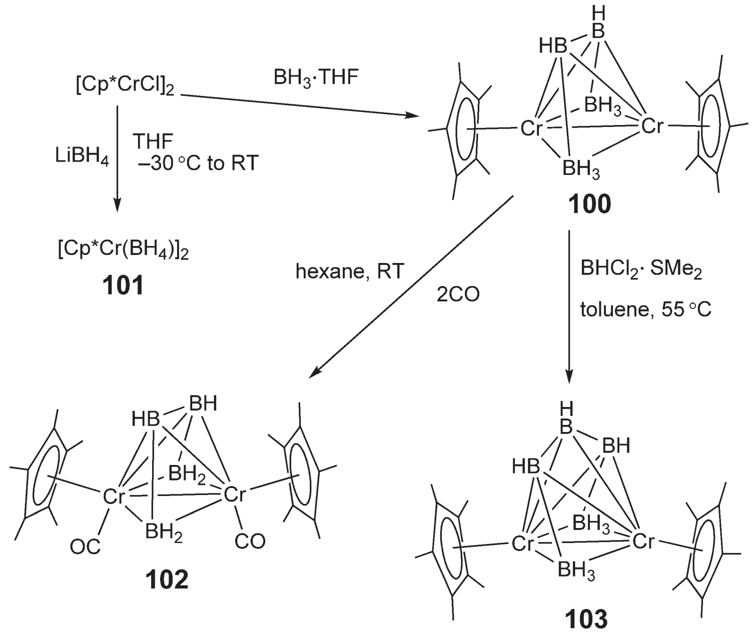
Scheme 28

5.05.4.5 Borane-containing Clusters

Organochromium metallaboranes consisting of Cp–chromium groups bridged by various borane entities have been prepared. A brief overview of metallaborane chemistry has appeared, including a discussion of chromaborane derivatives.[67] This chapter will focus on the synthesis of selected chromaboranes and will reference molecular orbital studies that describe the detailed bonding interactions. The reader is referred to these latter works for more in-depth discussions on cluster bonding.

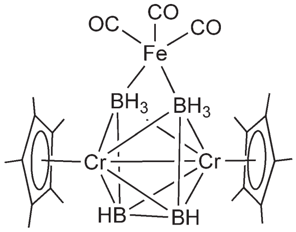
The electronically unsaturated cluster $(Cp^*Cr)_2B_4H_8$ **100** is prepared by treating $[Cp^*CrCl]_2$ with $BH_3{\cdot}THF$, while reaction of $[Cp^*CrCl]_2$ with $LiBH_4$ produces the paramagnetic $[Cp^*CrBH_4]_2$ **101** in high yield (Scheme 29).[68] Heating **101** results in disproportionation to **100** and an unidentified Cp^*Cr hydride. The structure of **100** displays a Cr–Cr single bonding interaction (2.870 Å), with the Cp^*Cr fragments bridged by an asymmetric B_4H_8 ring. The unsaturated nature of **100** is demonstrated by the rapid uptake of CO by each chromium center to form $(Cp^*CrCO)_2B_4H_6$ **102**.[69] Another metallaborane cluster, $(Cp^*Cr)_2B_5H_9$ **103**, is produced by reaction of **100** with $BHCl_2{\cdot}SMe_2$,[70] a common source of the BH fragment. Complex **103** displays Cp^*Cr centers bridged by a B_5H_9 ring system. In contrast to **100**, which shows rather dissimilar B–B bond lengths (ranging from 1.61 to 1.75 Å), the B–B bonds in **103** are more uniform (ranging from 1.661 Å to 1.694 Å); moreover, the NMR spectral properties are consistent with the retention of this structure in solution.[71] Additional NMR studies on $(Cp^*M)_2B_5H_9$ (M = Cr, Mo, W) derivatives find that ^{11}B NMR chemical shifts correlate with the sum of the metal's ionization potential and electron affinity.[72]

Further reactions of **100** include treatment with $Fe_2(CO)_9$ leading to the formation of mixed metal metallaborane $(Cp^*Cr)_2B_4H_8Fe(CO)_3$ **104**[73] and reduction with Na/Hg yielding the one-electron reduced species $Na[(Cp^*Cr)_2B_4H_8]$ **105**.[74] Paramagnetic ^{11}B NMR spectra of mixtures of **100** and **105** indicate that the two structures are closely related. Complex **100** also reacts with CS_2, resulting in hydroboration of CS_2 to a methanedithiolato ligand,



Scheme 29

which is incorporated into **106**.[75] In **106**, the $\mathrm{Cp^*Cr}$ centers are bridged by a seven-membered $\mathrm{CH_2S_2B_4H_6}$ ring, with each sulfur atom bridging a Cr–B bond.



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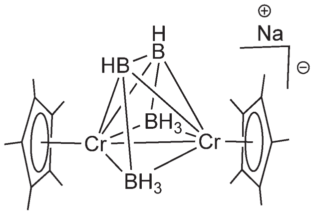

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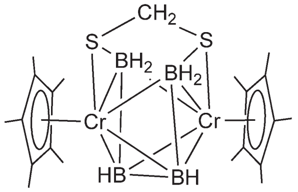

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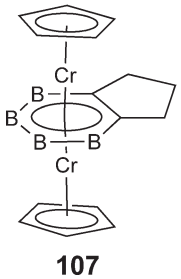
Fenske–Hall molecular orbital calculations have been carried out on unsaturated $\mathrm{(Cp^*Cr)_2B_4H_8}$ **100** and on its CO, $\mathrm{Fe(CO)_3}$, and $\mathrm{CH_2S_2}$ adducts.[76,77] These calculations indicate that extensive electronic delocalization over the metallaborane cluster permits stable structures with two fewer and two additional skeletal electrons than formally allowed by Wade's rules. Transitioning between these variable electron count structures proceeds without skeletal bond formation or breaking, which correlates well with the minimal structural changes observed experimentally upon addition of CO, $\mathrm{CS_2}$, and $\mathrm{Fe(CO)_3}$ fragments to the $\mathrm{(Cp^*Cr)_2B_4H_8}$ core.

Finally, attempts to prepare the Cp analog of **100** leads instead to a triple-decker complex **107** with two CpCr fragments sandwiching a substituted tetraborabenzene ligand $\mathrm{C_2B_4H_6}$.[78] Fenske–Hall calculations on **107** are consistent only with its formulation as a $\mathrm{[CpCr^{III}–Cr^{III}Cp]^{4+}}$ dimer bridged by a planar 6π-electron $\mathrm{C_2B_4H_6^{4-}}$ ion.



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5.05.4.6 Chromium(II) and Chromium(III) Halides, Alkyls, and Aryls

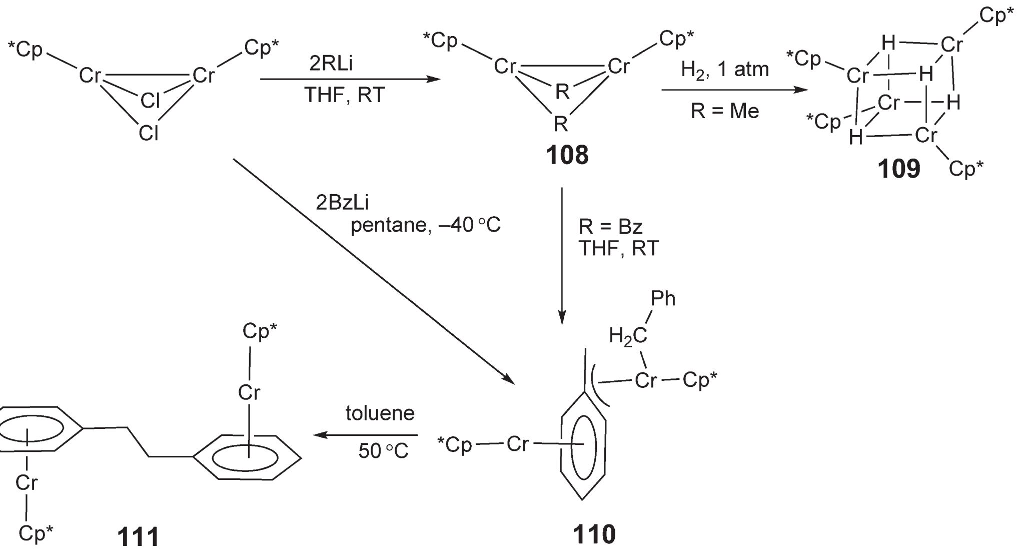
A key motivation for studying mono-Cp chromium complexes is their relevance to commercial ethylene polymerization catalysts, particularly the Union Carbide catalyst for making high density polyethylene (HDPE). This heterogeneous catalyst results from the reaction between chromocene and the silanol (Si–OH) groups of dehydroxylated silica (SiO_2), presumably forming a mono-Cp chromium complex bound to silica.[79,80] The exact structure of the catalyst, including the nature (number and type) of the other ligands, remains open to debate. Discrete mono-Cp chromium compounds can help shed light on this subject by serving as structural and reactivity models of these important catalysts.

Several research groups have taken advantage of the special stability imparted by Cp and Cp^* ligands to generate an extensive family of chromium(II) and chromium(III) complexes, many of which serve as effective polymerization catalysts. Theopold has summarized the synthesis, structure, and polymerization behavior of numerous Cp-containing chromium complexes in several reviews,[81,82,83] and Jolly has also summarized advances in organochromium π-complexes, primarily those containing Cp rings and other π-ligated organic fragments.[84] This chapter will focus on the synthesis, structure, and reactivity (especially related to polymerization catalysis) of mono-Cp chromium halide, alkyl, and aryl complexes prepared since 1993. Of special significance are compounds with an additional neutral donor tethered to the Cp ring. As will become apparent, binding of the tethered donor often imparts enhanced reactivity to the resulting polymerization catalyst.

5.05.4.6.1 Multinuclear chromium(II) derivatives

Recently prepared dinuclear mono-Cp chromium(II) complexes include $[Cp^*Cr(\mu\text{-Cl})]_2$ and $[Cp^*Cr(\mu\text{-R})]_2$ **108** (R = Me, Et, *n*-Bu, Ph, CH_2SiMe_3) (Scheme 30).[85] These compounds typically display short Cr–Cr distances, small magnetic moments, and reduced reactivity (e.g., no reaction with ethylene is observed), due to significant metal–metal bonding interactions. While the reactivity is attenuated overall, $[Cp^*Cr(\mu\text{-Me})]_2$ does react with hydrogen to form a chromium hydride cubane cluster $[Cp^*Cr(\mu_3\text{-H})]_4$ **109**, which was previously reported.[86] A derivative of the chromium hydride cluster, $[Cp'Cr(\mu_3\text{-H})]_4$ ($Cp' = C_5Me_4Et$), reacts further with high pressure H_2 to form $[Cp'_4Cr_4(\mu_3\text{-H})_5(\mu_3\text{-H})_2]$.[87] This septahydride displays high paramagnetism ($S = 7/2$) resulting from ferrimagnetic interactions between three $S = 3/2$ spins aligned antiparallel with the unique $S = 1$ center.

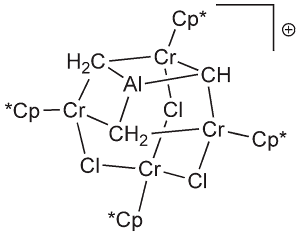
In addition to the alkyl and aryl derivatives mentioned above, a benzyl derivative of **108** has also been prepared and it displays unusual reactivity.[88] For example, **108** (R = Bz) rearranges at room temperature to give a mixed valent Cr(I)–Cr(III) complex $[Cp^*Cr(\eta^1\text{-Bz})(\mu\text{-}\eta^3:\eta^6\text{-Bz})CrCp^*]$ **110** (Scheme 30). Further decomposition of **110** upon heating forms a dibenzyl-bridged Cr(I)–Cr(I) dimer $[(Cp^*Cr)_2\text{-}\mu\text{-}\eta^6\text{:}\eta^6\text{-Bz-Bz}]$ **111**, in which each 17-electron chromium center is sandwiched between one Cp^* and one η^6-arene ring ligand. Of the bridging benzyl complexes



Scheme 30

described, only the Cr(I)/Cr(III) complex polymerizes ethylene (no activity numbers were reported, however), presumably via coordination and insertion at the chromium(III) center. The lack of ethylene polymerization reactivity for **108** and **111** supports earlier observations and assertions by Theopold that chromium(III) complexes are preferred for effective polymerization catalysts.[327]

Tetranuclear chromium(II) clusters have been prepared by the reaction of $[Cp^*Cr(\mu\text{-}Cl)]_2$ or $Cp^*CrCl_2(HNPPr^i_3)$ with excess $AlMe_3$.[89] For both chromium reagents, identical tetranuclear cations $[(Cp^*Cr)_4(\mu\text{-}Cl)_2(\mu\text{-}CH_2)_3AlMe]^+$ **112** are formed. However, the structure of the aluminum-containing anion depends on the chromium source, with $[Cp^*Cr(\mu\text{-}Cl)]_2$ yielding the bridging oxo anion, $[(Me_2Al)(\mu_3\text{-}O)(AlCl_2Me)(AlMe_2Cl)]^-$, and $Cp^*CrCl_2(HNPPr^i_3)$ generating the bridging methine anion $[(Me_2Al)_2(\mu_4\text{-}CH)(AlCl_2Me)_2]^-$. The structure of the aluminum-based anions is thought to model certain structural aspects of methylalumoxane (MAO), which is formed by controlled (partial) hydrolysis of $AlMe_3$ and is the common activator for organometallic polymerization catalysts.



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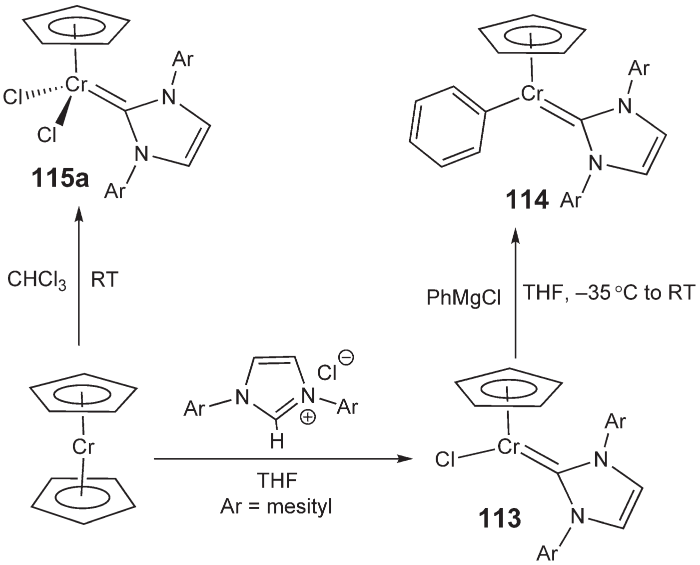
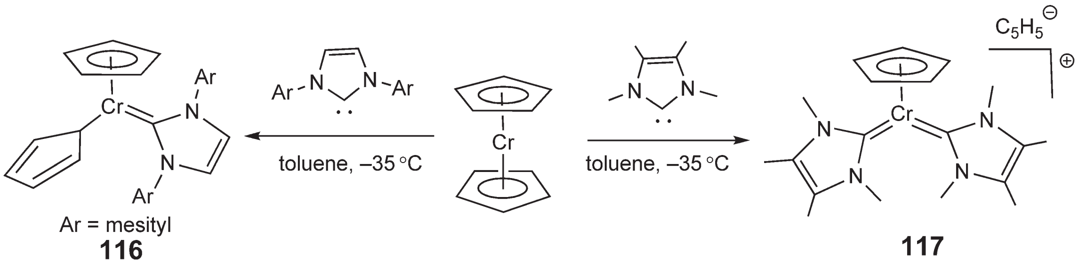
5.05.4.6.2 Chromium(II) and chromium(III) carbene derivatives

Other Cp–chromium(II) complexes include a chlorocarbene derivative **113** obtained by the reaction of Cp_2Cr with 1,3-dimesitylimidazolium chloride (Scheme 31);[90] this complex displays a relatively rare high spin ($S=2$) ground state. Carbene complex **113** is converted to the phenyl analog **114** by a reaction with PhMgBr and is readily oxidized to the $S=3/2$ chromium(III) dichlorocarbene **115a** in trichloromethane. The Cr–C(carbene) bond length (2.123 Å) in **114** is similar to those found in other Fischer-type carbenes.[91]

Additional examples of Cp–chromium(II) carbenes are prepared by direct reaction of chromocene with various substituted carbenes; the substitution pattern of the carbene dictates whether monocarbene **116** or cationic dicarbene **117** products are formed (Scheme 32).[92] The spin states of **116** and **117** have not been reported, so it is unclear

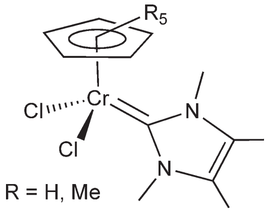


Scheme 31



Scheme 32

whether the unusual high spin ($S = 2$) configuration observed in **113** is also observed for these complexes. Further examples of Cp–chromium(III) carbenes, such as **115b**, have been prepared by displacement of THF from $CpCrCl_2(THF)$ or $Cp^*CrCl_2(THF)$ by 1,2,3,4-tetramethylimidazol-2-ylidene.[93] Alkylation of **115b** with 2 equiv. of MeLi generates the dialkyl analog. Unfortunately, complex **115b**, in the presence of MAO, displays "disappointing" polymerization catalyst activity (no quantitative activity was provided), although the polymer is described as highly branched on the basis of its low melting point (80–120 °C).

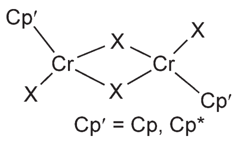


115b

5.05.4.6.3 Dinuclear chromium(III) derivatives

Numerous dinuclear Cp–chromium(III) compounds were prepared prior to 1993 and their chemistry has been summarized in the previously mentioned reviews by Theopold[81–83] and Jolly[84] as well as in Volume 5 of COMC (1995).

With regard to recent work on dimeric $[Cp'Cr(\mu\text{-}X)X]_2$ derivatives (**118**; X = halide, alkyl; Cp′ = Cp, Cp*), Janiak has outlined a frontier molecular orbital description for chromium(III) dimers that qualitatively explains the impact of bridging ligand type (alkyl vs. halide) on the Cr–Cr bond length and on the observed magnetic moment.[94] In addition, sterically encumbered pentaphenylcyclopentadienyl (C_5Ph_5) ligated chromium(III) dimers have been prepared by halogenation of $(C_5Ph_5)Cr(CO)_3$, which results in the formation of $[(C_5Ph_5)Cr(\mu\text{-}X)X]_2$ (**119**, X = Cl, Br, I); the dimers can be cleaved with THF to form monomeric $(C_5Ph_5)CrX_2(THF)$ complexes.[95] The structure of **119** is similar to that of relatively unencumbered Cp- and Cp*- based complexes indicating that the phenyl rings have minimal steric impact.



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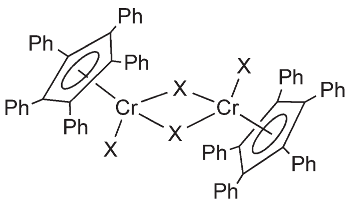

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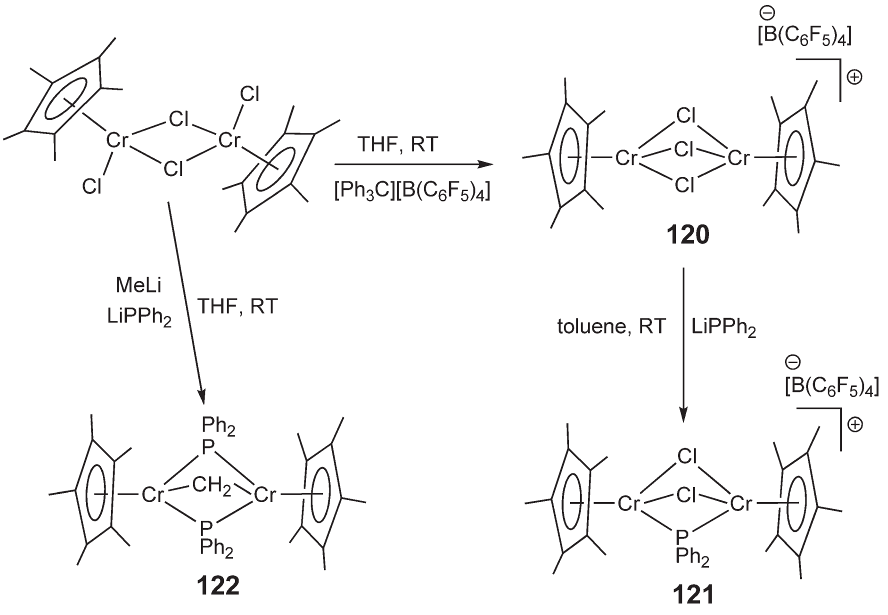
Other dinuclear chromium(III) complexes include a variety of cationic and neutral chloro- and phosphido-bridged species (Scheme 33). Among these are the cationic, triply bridged $[(Cp^*Cr)_2(\mu\text{-}Cl)_3][B(C_6F_5)_4]$ **120**, which is formed



Scheme 33

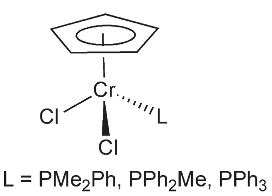
by treating $[Cp^*CrCl(\mu\text{-}Cl)]_2$ with a chloride abstractor such as $[Ph_3C][B(C_6F_5)_4]$.[96] The phosphido-bridged $[(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)_2][B(C_6F_5)_4]$ **121** is produced upon addition of $LiPPh_2$ to **120**. In addition, neutral, triply bridged $(Cp^*Cr)_2(\mu\text{-}PPh_2)_2(\mu\text{-}Me)$ **122** and $(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Me)(\mu\text{-}Cl)$ are obtained by the reaction of $[Cp^*CrCl(\mu\text{-}Cl)]_2$ with a combination of MeLi and $LiPPh_2$. Among complexes **120–122**, the derivatives with bridging methyl groups display the shortest Cr–Cr bond lengths (ranging from 2.5517 Å to 2.6134 Å), which is consistent with trends noted by Janiak.[94] However, none of the bridged phosphido derivatives were evaluated as polymerization catalysts.

5.05.4.6.4 Monomeric chromium(III) derivatives

As mentioned previously for complex **119**, chromium(III) halide-bridged dimers are readily cleaved with strong σ-donors and/or by the reaction with bulky metal alkyls, thus making the dimers useful precursors to 13- and 15-electron monomeric complexes. A large family of 15-electron monomeric $CpCrX_2(L)$ compounds (L = σ-donor ligand, X = halide, triflate) have been prepared by Köhler and characterized by NMR spectroscopy.[97] The monomeric compounds typically adopt a three-legged piano stool structure and invariably display high spin ($S = 3/2$) electronic states.

5.05.4.6.4.(i) Phosphine-ligated 15-electron complexes

Poli *et al.* have explored the chemistry of phosphine-ligated complexes, including $CpCrCl_2(L)$ (**123**; L = PMe_2Ph, $PMePh_2$, PPh_3).[98] Upon reduction with sodium, these high spin ($\mu_{eff} = 3.73$ to $3.81\,\mu_B$) phosphine derivatives undergo chloride loss with concomitant disproportionation to chromocene and uncharacterized chromium(II) phosphine complexes. Attempts to prepare 17-electron $CpCrX_2(\eta^2\text{-P–P})$ (X = Cl, Me) complexes using potentially bidentate $Me_2PCH_2PMe_2$ (dmpm), $Me_2PCH_2CH_2PMe_2$ (dmpe), and $Ph_2PCH_2CH_2PPh_2$ (dppe) ligands do not produce 17-electron species, but rather form bridged dimeric $CpCrX_2(\eta^2\text{-P–P})CrCpX_2$ **124** or monomeric 15-electron $CpCrX_2(\eta^1\text{-P–P})$ **125** species with one dangling, uncoordinated phosphine.[99] The apparently strong structural preference for 15-electron complexes has been examined using DFT calculations and is found to be due to the high energy cost of electron pairing that accompanies ligand binding (15-e^- spin quartet → 17-e^- spin doublet), which outweighs the energy gain from forming a new Cr–P bond.[100] Additional DFT calculations on phosphine exchange in $CpCrCl_2(PR_3)$ systems suggests that a 17-electron bis(phosphine) activated complex, $CpCrCl_2(PR_3)_2$, does indeed form during the associative substitution process, but that it does so without crossover to the 17-electron spin doublet state.[101] The predicted associative (S_N2) substitution mechanism agrees with stopped-flow studies that show clear second-order kinetics.[101]



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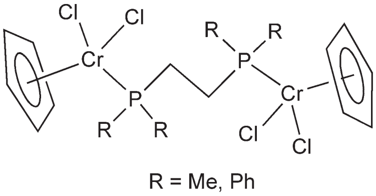

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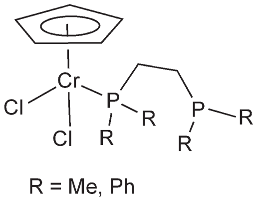

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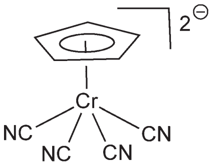
5.05.4.6.4.(ii) Evidence for 17-electron complexes

While stable 17-electron $CpCrCl_2(L–L)$ complexes have proved to be somewhat elusive, the use of more strongly bonding cyanide ligands in place of chloride allows for observable 17-electron $[CpCr(CN)_4]^{2-}$ **126** species. Equilibrium amounts of $[CpCr(CN)_4]^{2-}$ (formed by $[CpCr(CN)_3]^- + CN^- \rightarrow [CpCr(CN)_4]^{2-}$) are observed using EPR spectroscopy.[102] Additionally, 17-electron $[CpCr(CN)_2(L_2)]$ complexes (L = phosphine donor) are also observed by EPR upon reaction of $[CpCr(CN)_3]^-$ with monodentate or bidentate tertiary phosphines. Using DFT calculations, the stability of 17-electron cyanide complexes (relative to chloride complexes) was explained by a smaller pairing energy in the case of CN^- ligation, which makes formation of $[CpCr(CN)_2(L_2)]$ derivatives more favorable.[103] However, stable, isolable 17-electron Cp–chromium(III) adducts are only generated with strong-field isonitrile ligands **127**.[104]



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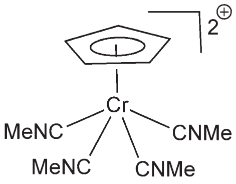

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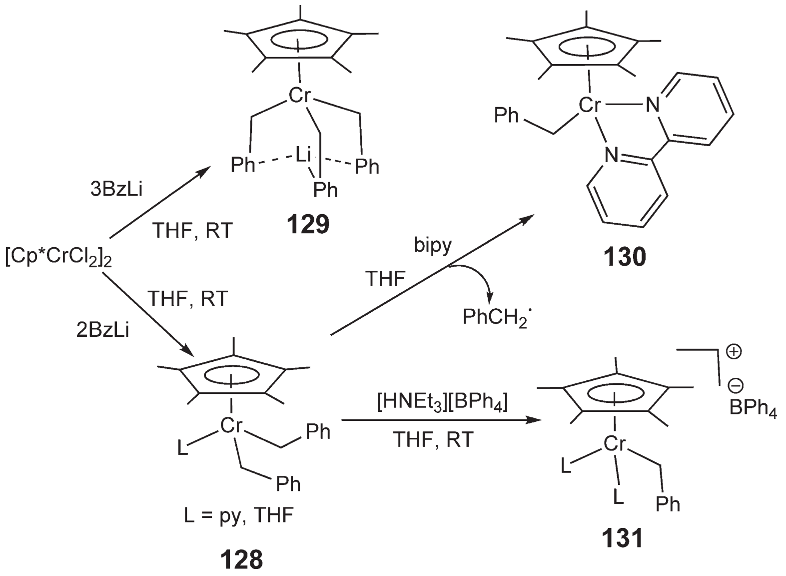
5.05.4.6.5 Monomeric chromium(III) derivatives relevant to olefin polymerization

Monomeric Cp–chromium(III) complexes, such as $[Cp^*CrMe(THF)_2][BPh_4]$, have been shown to be effective ethylene polymerization catalysts.[293] Subsequent work in this area has explored the impact of differing alkyl/aryl substituents, as well as the effect of alternative donor ligands (or the lack thereof), on compound structure and catalyst performance. The following paragraphs summarize recent work in this area, with special emphasis paid to olefin polymerization behavior.

5.05.4.6.5.(i) Benzyl complexes

In some recent examples, reaction of the chloro-bridged dimer $[Cp^*CrCl(\mu\text{-}Cl)]_2$ with 2 equiv. of BzMgCl yields $Cp^*Cr(Bz)_2(L)$ (**128**; L = THF, pyridine) (Scheme 34).[105] Alternatively, addition of 3 equiv. of BzLi produces $Li[Cp^*Cr(Bz)_3]$ **129** in which the three benzyl aromatic rings surround the Li counterion. Reaction of **128** with bipyridine (bipy) results in the loss of one benzyl ligand by homolytic Cr–C bond cleavage, generating the chromium(II) complex $Cp^*Cr(Bz)(bipy)$ **130**. Additionally, reaction of **128** with $[HNEt_3][BPh_4]$ generates the cationic $[Cp^*Cr(Bz)(THF)_2][BPh_4]$ **131**. Complexes **128** (2.2 g PE/(mmol-Cr h bar)), **129** (2.0 g PE/(mmol-Cr hr bar)), and **131** (5.6 g PE/(mmol-Cr hr bar)) are moderately active polymerization catalysts. While the cationic **131** is the most active, even the anionic, coordinately saturated **129** displays activity. The latter complex presumably eliminates



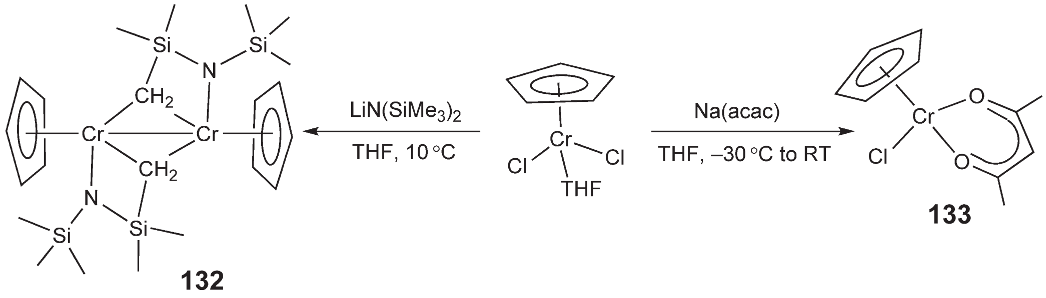
Scheme 34

one equivalent of BzLi to generate 13-electron Cp*Cr(Bz)$_2$, which then coordinates and inserts ethylene to initiate the polymerization reaction. The polymerization reaction using **129** is inhibited by added BzLi, thereby supporting the proposed mechanism.

5.05.4.6.5.(ii) Complexes with additional multidentate ligands

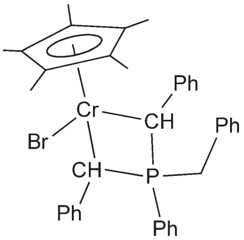
Mono-Cp chromium complexes supported by additional multidentate ligands are also known and some have been evaluated as polymerization catalysts. For example, treatment of CpCrCl$_2$(THF) with excess LiN(SiMe$_3$)$_2$ yields a dinuclear complex **132**, with the resulting metal–metal bond (Cr–Cr = 2.662 Å) spanned by a bidentate (N–Si–CH$_2$)$^{2-}$ ligand (Scheme 35).[106] The dimer alone is ineffective as a catalyst, which is not surprising given its coordination saturation and metal–metal bonding interactions. However, reaction of **132** with an alkylaluminum reagent (type not specified) affords an active catalyst, although no activity data or polymer details have been provided. Other bidentate ligand derivatives are known, such as Cp′Cr(acac)Cl (**133**; acac = acetylacetonate, Cp′ = Cp, Cp*), which is prepared by the reaction of [Cp′CrCl(μ-Cl)]$_2$ with sodium acetylacetonate (Scheme 35).[107] These $S = 3/2$ ($\mu_{\text{eff}} = 3.4$ to $3.78\,\mu_\beta$) compounds display moderate ethylene polymerization activity (24 g PE/(mmol-Cr hr bar)) after activation with MAO.

Finally, the bidentate phosphoniodiylide complex, [(C$_5$Me$_5$)CrBr{η^2-PhP(CHPh)$_2$(CH$_2$Ph)}] **134**, is formed upon the reaction of [Cp*CrBr(μ-Br)]$_2$ with Li$_2$[PhP(CHPh)$_3$].[108] Presumably, the targeted tridentate complex,



Scheme 35

$(C_5Me_5)Cr\{PhP(CHPh)_3\}$, is unstable or is readily protonated by solvent impurities leaving **134** as the only isolable product. The olefin polymerization activity of this compound is not known.



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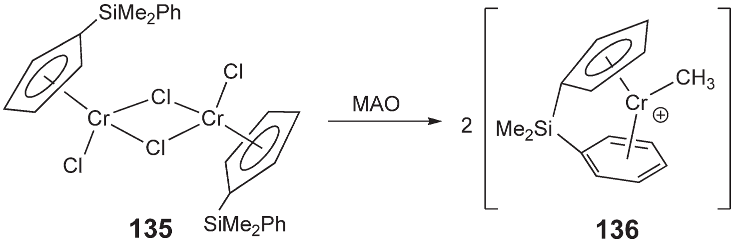
The ability of donor ligands (π- or σ-donors) to enhance the polymerization performance of organometallic catalysts is an active area of interest. The following paragraphs will summarize work on complexes containing σ- and π-donors, including the impact of such donors on catalyst performance. The continued exploration of alternative donors will likely yield further polymerization catalyst improvements.

5.05.4.6.5.(iii) Complexes with π-donors

With regard to π-donors, reaction of $CrCl_3$ with $Li[PhMe_2SiCp]$ affords the chloro-bridged dimer $[PhMe_2SiCpCrCl_2]_2$ **135**.[109] An X-ray structure determination confirms the dimeric structure with an unbound phenyl ring. Ethylene polymerization activity of up to 220 g PE/(mmol-Cr hr bar) is obtained when **135** is combined with MAO. The authors suggest that a chromium-phenyl π-donor interaction, as depicted in **136**, is responsible for the enhanced activity; comparative data on an analogous alkylsilyl–Cp derivative would help support this claim. Similar π-donor interactions and catalyst enhancements have been observed (or inferred) in group 4 metallocene catalysts.[110,111]



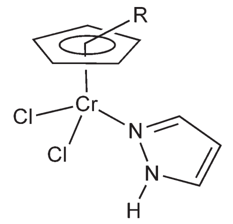
135 **136**

5.05.4.6.5.(iv) Complexes with exogenous σ-donors

The significant impact of strong σ-donor ancillary ligands on compound structure and polymerization catalyst performance has been demonstrated with various σ-donors. In one example, pyrazole ligands cleave the $[Cp'CrCl_2]_2$ dimer ($Cp' = Cp^*$, Me_3SiCp, $H_2C{=}C(Me)CH_2Cp$) to form monomeric $Cp'CrCl_2(pyrazole)$ **137** complexes.[112] Addition of MAO yields active ethylene polymerization catalysts (37 to 44 g PE/(mmol-Cr hr bar)). In addition, a dimeric dppe-bridged complex, similar to complex **124** prepared by Poli,[99] has been prepared and displays three-fold higher polymerization activity (140 g PE/(mmol-Cr hr bar)) compared to its pyrazole-based counterpart. However, it is unclear whether phosphine ligation, or the dimeric structure, or a combination of both factors is responsible for enhanced catalytic performance.

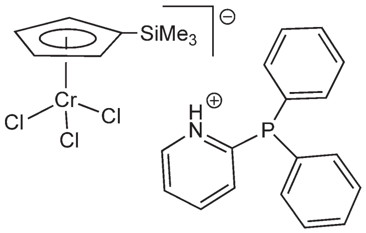
Potentially bidentate 2-pyridylphosphine ligands have been examined in combination with Me_3SiCp–chromium complexes. Reaction of $(Me_3SiCp)CrCl_2(THF)$, which is prepared *in situ* from $Me_3SiCpLi$ and $CrCl_3$ in THF, with $Ph_2P(2\text{-}C_5H_4N)$ leads to the predominant formation of $[(Me_3SiCp)CrCl_3][Ph_2P(2\text{-}C_5H_4NH)]$ **138**, along with small amounts of a compound formulated as the neutral pyridyl-ring adduct $(Me_3SiCp)CrCl_2[Ph_2P(2\text{-}C_5H_4N)]$.[113] Ionic complex **138**, which shows the expected $S = 3/2$ magnetic behavior, exists as discrete anions and cations in the solid state. Complex **138** displays high ethylene polymerization activity when activated by MAO

(260 g PE/(mmol-Cr hr bar)); however, it is unclear how (or if) the pyridylphosphine ligand coordinates to the active catalyst. It is not known whether the neutral phosphine adduct is an active polymerization catalyst.



R = Me$_5$, SiMe$_3$, CH$_2$C(Me) = CH$_2$

137



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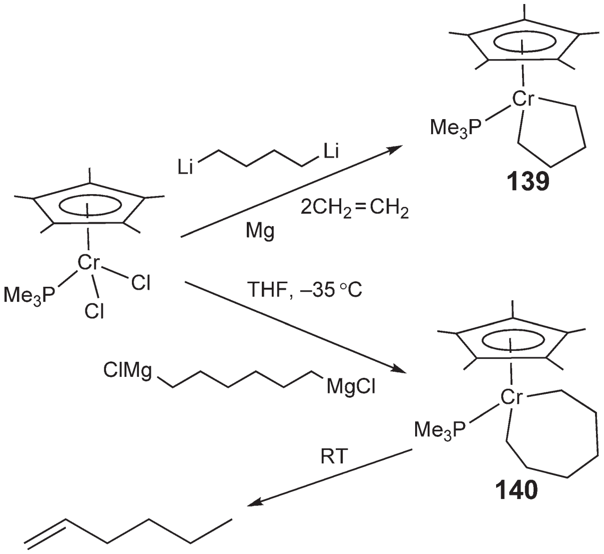
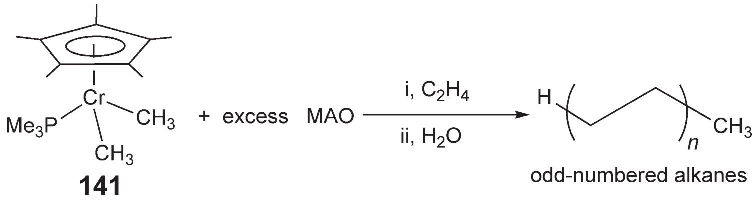
Jolly has also examined the impact of phosphine coordination on reactivity. Phosphine-ligated chromacyclopentane **139** and chromacycloheptane **140** derivatives have been prepared by reacting Cp*CrCl$_2$(PR$_3$) (R = Me, Et) with 1,4-dilithiobutane and 1,6-dichloromagnesiohexane, respectively (Scheme 36).[114] Moreover, **139** can be prepared in high yield by reacting the dichloride with active Mg in the presence of ethylene, presumably via a Cr(η^2-CH$_2$═CH$_2$) intermediate. Support for such an intermediate comes with the trapping of CpCr(PMe$_3$)$_2$(η^2-CH$_2$═CH$_2$) upon reduction of CpCrCl$_2$(THF) with active Mg in the presence of ethylene and excess PMe$_3$. Chromacycloheptane **140** liberates 1-hexene upon warming to room temperature (Scheme 36), supporting the involvement of metallacycloheptane complexes in selective 1-hexene formation. Other chromium complexes involved in ethylene trimerization, and further discussion of the trimerization mechanism, are described in Section 5.05.9.5.

In addition to increased polymerization activity observed with phosphine ligation, polymer product properties (e.g., molecular weight) are also affected. For example, Bazan has prepared highly active ethylene oligomerization catalysts based upon Cp*CrMe$_2$(PMe$_3$) **141**.[115] Activation with MAO yields oligomerization catalysts that produce almost exclusively odd-numbered alkanes after aqueous workup. A mechanism involving chain growth at chromium, followed by chain transfer to aluminum is consistent with the observed products. Initial insertion of ethylene into a Cr–Me bond (the latter formed by catalyst activation with MAO) accounts for the odd-numbered carbon products. In a more extensive study,[116] Bazan reports that treatment of **141** with a combination of B(C$_6$F$_5$)$_3$ and AlMe$_3$ also produces odd-numbered alkanes with a product distribution similar to that obtained



Scheme 36

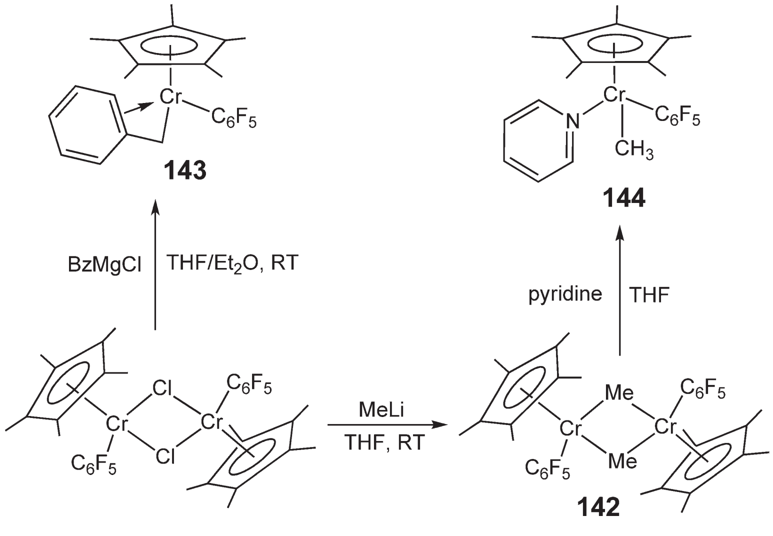
with **141**/MAO, although the activity using MAO is nearly double that of $B(C_6F_5)_3/AlR_3$ (280 vs. 150 g oligomer/(mmol-Cr hr bar)). Finally, replacement of $AlMe_3$ with $AlEt_3$ in the borane-activated systems produces even-numbered alkane products, again consistent with a mechanism involving chain growth at chromium followed by chain transfer to aluminum.



5.05.4.6.5.(v) Complexes with perfluorophenyl (C_6F_5) ligation

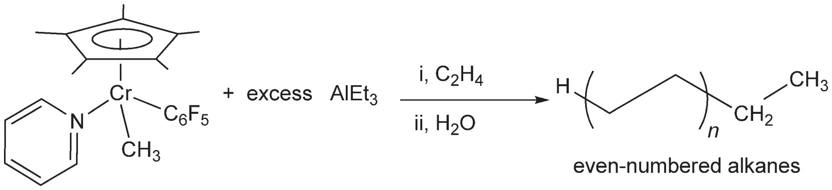
In addition to Bazan's phosphine-ligated complexes, incorporation of a perfluorinated phenyl ring into the basic Cp^*–chromium(III) structure yields complexes that are especially effective ethylene oligomerization and polymerization catalysts (Scheme 37). For example, Gabbai reports that $[Cp^*Cr(C_6F_5)(\mu\text{-Me})]_2$ **142**[117] behaves as a single-component ethylene polymerization catalyst, even though the dimer is coordinatively saturated and displays metal–metal bonding interactions (Cr–Cr distance = 2.697 Å). That **142** is an effective catalyst implies that the dimer readily dissociates in hydrocarbon media in the presence of ethylene to give reactive, presumably 13-electron, catalytic species. An even more effective catalyst is the monomeric benzyl analog $Cp^*Cr(C_6F_5)(\eta^3\text{-Bz})$ **143**.[118] This complex possesses exceptionally high polymerization activity (241 g PE/(mmol-Cr hr bar)), especially when considering that it does not require activation via co-catalysts. In the case of **143**, the benzyl ligand apparently slips to η^1-ligation, allowing ethylene to bind and subsequently insert into the growing alkyl chain.

As shown in Scheme 37, dimeric **142** is readily converted to the pyridine adduct $Cp^*Cr(C_6F_5)(Me)(py)$ **144**. As expected, **144** is not an active single-component catalyst due to ethylene's inability to compete with pyridine for access to the chromium center. However, for both **142** and **144**, addition of excess $AlEt_3$ in the presence of ethylene results in effective oligomerization catalysts, each producing a Poisson distribution of even-numbered alkane oligomers (C_6 to C_{32}) after hydrolysis. As with Bazan's phosphine-promoted system **141**, a mechanistic scheme involving chain growth at chromium followed by rapid chain transfer to aluminum accounts for the narrow (Poisson)



Scheme 37

product distribution. Here initial ethylene insertion into a Cr–Et bond, which is formed by catalyst activation with $AlEt_3$, explains the exclusive formation of even-numbered carbon products.



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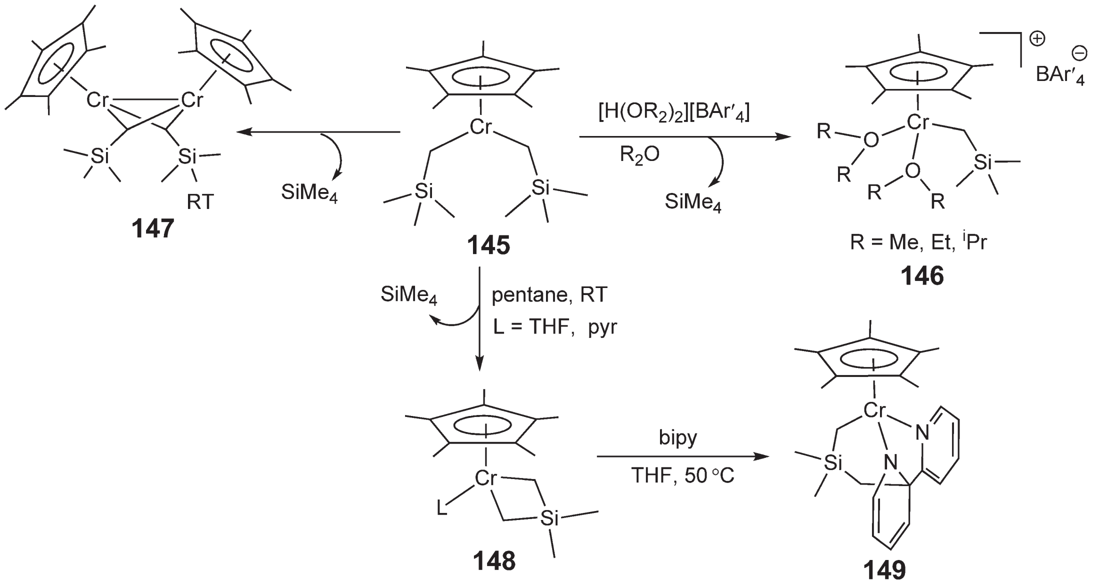
5.05.4.6.5.(vi) Complexes capable of higher olefin polymerization

Cp–chromium complexes, like those just described, typically display high selectivity for inserting ethylene over higher α-olefins. This behavior mimics that of the heterogeneous Union Carbide catalyst (Cp_2Cr/SiO_2), although the reasons for the unusually high selectivity remain somewhat obscure (however, see Section 5.05.11 for theoretical insights). The ability to incorporate higher olefins would allow chromium catalysts to manufacture commercially useful linear low density polyethylene (LLDPE), a product that is now produced almost exclusively by group 4 catalysts (Ziegler–Natta and metallocenes).

While Cp–chromium complexes are reticent to incorporate higher α-olefins, Heitz has demonstrated that dimeric chromium(III) complexes of the type $[Cp'CrMeCl]_2$ (Cp′ = Cp, Cp*, indenyl, fluorenyl), in combination with MAO, mediate the homopolymerization of norbornene as well as the co-polymerization of ethylene and norbornene.[119,120] The authors observe trends toward higher activity as the electron-donating nature of Cp′ increases, and toward decreased polynorbornene crystallinity as the steric bulk of Cp′ increases. Even with the successful polymerization of norbornene, the failure of Cp–chromium complexes to polymerize traditional α-olefins, such as propylene and 1-hexene, is still quite prevalent.

Reasoning that this effect might be steric in origin, and that higher olefins might not compete effectively with THF (or other moderate strength donors) for access to the chromium center, Theopold has prepared cationic complexes with weakly bound ether donors. For example, reaction of $Cp^*Cr(CH_2SiMe_3)_2$ **145** and $[H(OR_2)_2][BAr'_4]$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$; R = Me, Et, ^iPr) generates $[Cp^*Cr(CH_2SiMe_3)(OR_2)_2][BAr'_4]$ **146** (Scheme 38). At room temperature, cationic **146** displays relatively high ethylene polymerization activity (57 g PE/(mmol-Cr hr bar)) for a single-component catalyst. More significantly, **146** was the first Cp–chromium complex



Scheme 38

to also homopolymerize higher olefins such as propylene and 1-hexene, yielding relatively low molecular weight oligomers.[121] However, even with the successful polymerization of higher olefins, highly electrophilic complex **146** is still relatively selective for ethylene.

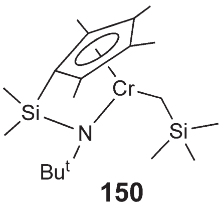
The 13-electron **145** also polymerizes ethylene at extremely low temperatures; however, its thermal instability precludes detailed polymerization evaluations. Nevertheless, its instability leads to some interesting rearrangements as outlined in Scheme 38. For example, **145** decomposes at room temperature to produce a bridging alkylidene (μ-$CHSiMe_3$) dimer **147** in the absence of coordinating ligands and a metallacyclobutane, $Cp^{*}Cr(CH_2)_2SiMe_2(L)$ **148**, when σ-donors are present.[122] Metallacyclobutane formation involves formal loss of $SiMe_4$ and is proposed to occur through a terminal alkylidene intermediate. Attempts to trap the chromium(III) alkylidene by thermolysis of **145** in the presence of a diphosphine do not generate a monomeric alkylidene, but instead lead to dimeric, phosphine-linked metallacyclobutanes. In addition, attempted trapping of the alkylidene by the reaction of **148** with 2,2′-bipyridine (bipy) results in alkylation of bipy via trimethylsilylmethyl group transfer[123] and coordination of the new CNN ligand to form **149**. Oxidation of **149** either chemically or electrochemically[124] leads to rapid dimerization of the initially formed cation with the formation of a complex dicationic species linked by oxidatively coupled bipy ligands.

5.05.4.6.6 Monomeric chromium(III) derivatives with tethered σ-donors

Even with the modest higher olefin polymerization success mentioned in the previous section, Cp–chromium compounds, in general, still exhibit high selectivity for ethylene; thus, extensive work has targeted complexes with improved higher olefin reactivity. Several groups have explored the use of donor-modified Cp ligands, in the hope of making the metal center more receptive to larger α-olefins. In group 4 metallocene complexes, use of Cp ligands tethered to donor atoms via silyl or hydrocarbyl linkages has produced the so-called “constrained-geometry” complexes that display exceptional reactivity for higher olefins.[125] The tied-back nature of the constrained-geometry ligand exposes the “frontside” of the metal center, where olefin binding and insertion occur, making the catalyst more accommodating to larger monomers. Given the success in group 4 complexes, several groups have tested Cp-tethered donor ligands in chromium systems.

5.05.4.6.6.(i) Complexes with anionic tethered σ-donors

Theopold has used the silyl-bridged Cp*-amido ligand to prepare constrained-geometry chromium complexes **150 and 151**.[126] While **150** appears to possess an open and accessible metal center, co-polymerization of ethylene and higher olefins (e.g., 1-hexene) does not lead to any higher olefin incorporation, even when conducted in a solvent mixture containing 50 vol.% of the higher olefin. In addition, propylene homopolymerization experiments yield only the dimeric product 2-methyl-1-pentene, indicating that the linked Cp-amido framework does not facilitate higher olefin binding and insertion. Hey-Hawkins has also examined the potential of phosphanylalkylcyclopentadienyl ligands in which the Cp and phosphorus donors are connected by a single carbon bridge to form constrained-geometry complexes.[127] Reaction of $CrCl_3(THF)_3$ with $Li[(C_5H_4)CMe_2PHR)]$ ($R = Ph, Bu^t$) yields a phosphido-bridged dimer **152** rather than the desired monomeric complex; apparently, activation of the P–H bond and loss of HCl generates **152**. Mononuclear complexes, such as **153**, can be obtained by starting with $CrCl_3(PMe_2Ph)_3$ but the tethered phosphine remains unbound. Both **152 and 153** are moderately active ethylene polymerization catalysts when activated by MAO (2.0 to 4.6 g PE/(mmol-Cr hr bar)).



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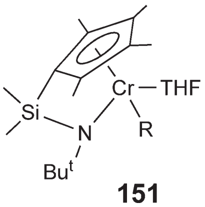

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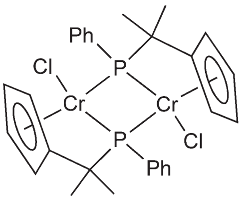

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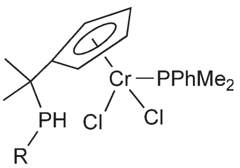

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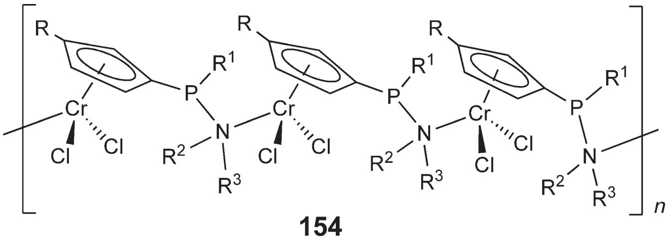
5.05.4.6.6.(ii) Complexes with neutral tethered σ-donors

Other attempts to obtain “constrained-geometry” chromium complexes have utilized neutral donors tethered to the Cp ligand. For example, alkylaminocyclopentadienylphosphanes, $Cp^{R}P(R^1)NR^2R^3$ (R, R^1, R^2, and R^3 = alkyl, aryl), where the Cp and nitrogen donor ligands are linked by a single phosphorus atom, have been employed.[128] However, mass spectrometry and solubility data indicate that only dimeric and perhaps polymeric chromium species **154** are formed via intermolecular, rather than the desired intramolecular, N→Cr coordination. Nevertheless, **154** is activated by MAO to form a high activity ethylene polymerization catalyst (up to 290 g PE/(mmol-Cr hr bar)). Although no co-polymerization data was reported, **154** would not be expected to improve olefin accessibility to the chromium center.



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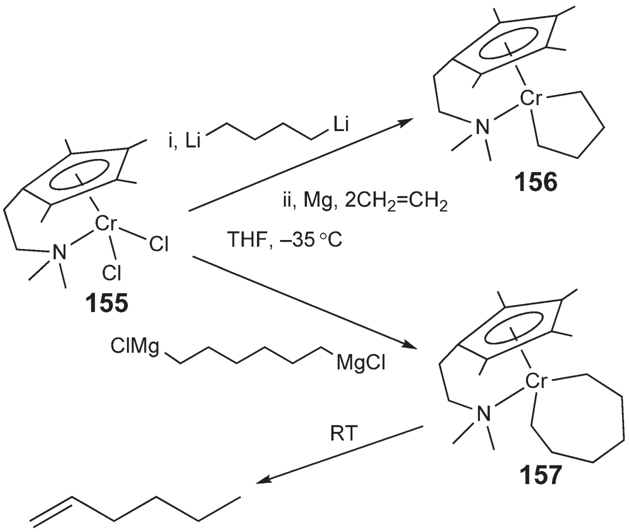
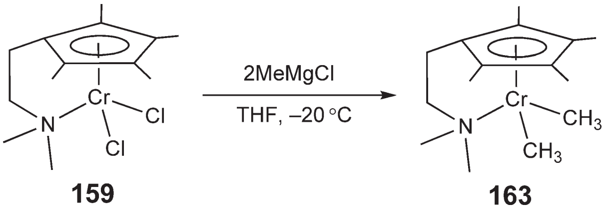
Other research groups have focused on using neutral donors tethered to the Cp ring via two-carbon (ethylene) bridges. For example, Jolly has used an amine-substituted Cp ligand to prepare chromacyclopentane (and chromacycloheptane) derivatives by treating dichloride **155** with 1,4-dilithiobutane and 1,6-dichloromagnesiohexane, respectively (Scheme 39).[114] Moreover, chromacyclopentane **156** can be formed by reacting dichloride **155** with activated Mg in the presence of ethylene. These syntheses mirror those of the previously described phosphine-ligated complexes **139** and **140**.[114] Presumably, **156** is generated by reduction of **155** to a chromium(I) intermediate, followed by oxidative coupling of two molecules of ethylene. Thermolysis of the chromacycloheptane complex **157** eliminates primarily 1-hexene, which again supports a metallacycloheptane species as a viable intermediate in selective 1-hexene formation. This topic, along with several other complexes involved in selective oligomerization of ethylene to 1-hexene and 1-octene are discussed further in Section 5.05.9.

In addition to amine-substituted Cp ligands, Jolly has used imine-, alkoxy-, and alkylthio-substituted Cp donors to prepare an extensive family of chromium(III) dichloride complexes ligated both by the Cp ring and the ethylene-bridged donor atom (e.g., complexes **155** and **158–162**).[129] In compounds such as **158** and **159**, the Cr–N distances (2.1–2.2 Å), determined by X-ray crystallography, confirm the intramolecular amine ligation. However, in some instances, polymeric chromium complexes appear to form, especially when more flexible tethers and more sterically demanding amines are used. Impressively, the monomeric compounds polymerize ethylene with exceptionally high activities (up to 5000 g PE/(mmol-Cr hr bar)) even with low MAO loadings (100 : 1 Al : Cr). These complexes are among the highest activity chromium-based catalysts prepared to date. Specific activity enhancements result from alkyl-substituted cyclopentadienyl rings and by converting Cr–Cl linkages to Cr–Me; the latter transformation is readily accomplished with 2 equiv. of MeMgCl to form **163** (Scheme 40).

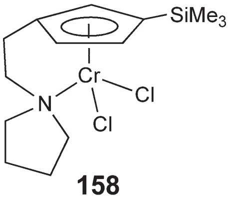


Scheme 39



Scheme 40

Somewhat surprisingly, in contrast to constrained-geometry complexes 150 and 151, catalysts based upon pyrollidine-substituted 155 incorporate significant amounts of 1-hexene during ethylene/1-hexene co-polymerization experiments. Yasuda has also used the Cp-tethered amine complexes, including some supported on silica, to prepare high activity ethylene polymerization catalysts that are also able to homopolymerize propylene and 1-hexene and co-polymerize ethylene and these higher monomers.[130,131] The co-polymerization reactivity reported by Yasuda and Jolly for complexes 155–162, and the complete lack thereof for constrained-geometry compounds 150 and 151, is quite extraordinary. The Cp(centroid)–Cr–N angles, which describe the ligand's bite angle and provide a measure of the accessibility of the metal's front side, are quite similar for 158/159 (113°–114°)and 150 (115.9°). Thus, while these compounds have similar degrees of "openness" at the metal center, they display very different abilities to polymerize higher olefins. The impact of ligand electronic differences (anionic N donor in 150 vs. neutral N donor in 158 and 159 on polymerization performance has not been completely explained.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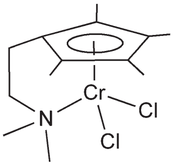
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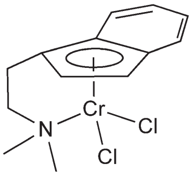
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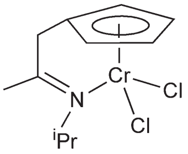
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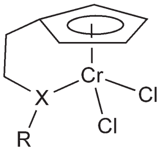
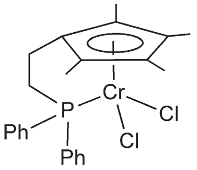
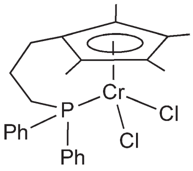

X = O, S
R = Me, *t*-Bu

162

Jolly has extended the range of donor-ligated Cp–chromium complexes to include ethylene-bridged dialkyl- and diarylphosphines 164 and 165[132,133,134] and arsines 166.[134] The ligation of phosphorus and arsine to chromium has been confirmed via X-ray crystallography. The Cr–P distances (2.45–2.47 Å) are typical of chromium(III)–phosphorus single bonds and the length of the alkyl spacer has no impact on Cr–P distance. The longer Cr–As bond length (2.537 Å) in 166 is consistent with arsine's larger atomic radius. Increased steric requirements at phosphorus result in longer Cr–P bonds, and these steric effects correlate with catalyst activity and polymer product properties; namely, small phosphine substituents correlate with higher catalyst activity and lower product molecular weight. In this same study, DFT calculations were performed on olefin binding and insertion steps for compounds such as 164.[134] The results indicate that the β-hydrogen transfer and chain propagation steps have comparable rates for complexes with small phosphine substituents, leading to oligomeric products. However, chain propagation is increasingly favored (β-hydrogen transfer is increasingly disfavored) for larger phosphorus substituents, leading to higher molecular weight polymeric products. The authors argue that the larger steric requirements of the six-membered β-hydrogen transfer transition state (compared to the more compact four-membered insertion transition state) cause greater steric interactions as the size/cone angle of the phosphine increases. Additional theoretical examinations of organochromium polymerization catalysts are summarized in section 5.05.11.



164



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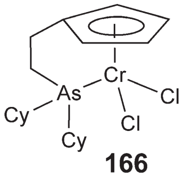
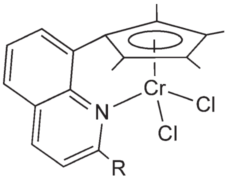
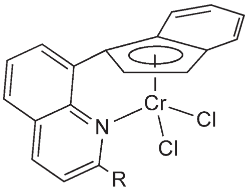


166

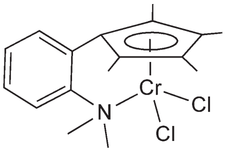
The Enders group has examined rigid two-carbon bridges between the Cp and the neutral donor by using N,N-dimethylanilyl- and 8-quinolyl-functionalized cyclopentadienyl ligands. The rigid linker avoids the formation of polymeric chromium species (as observed in some ethylene-bridged complexes) and promotes the formation of mononuclear chromium complexes **167–169**.[135,136,137] X-ray structural analysis confirms that monomeric complexes form, with Cr–N bonds (2.10 to 2.25 Å) in the expected range for chromium(III) complexes. While Cp(centroid)–Cr–N angles for **167–169** have not been reported, one might expect these to be similar to those found in ethylene-bridged complexes **158** and **159**. As observed in other Cp-containing systems, the use of alkyl-substituted Cp rings yields higher catalyst activity: 3500 g PE/(mmol-Cr hr bar) for C_5Me_4 compared to only 950 g PE/(mmol-Cr hr bar) for C_5H_4. Moreover, substitution at the quinoline ring (R = Me) leads to lower activity (670 g PE/(mmol-Cr hr bar)), presumably due to unfavorable interactions between the quinoline substituent and the olefin binding and insertion region. Interestingly, attempted alkylation at the metal center yields both a chromium alkyl **170** and a product from reaction at the quinoline ligand **171** (Scheme 41).



R = H, Me
167

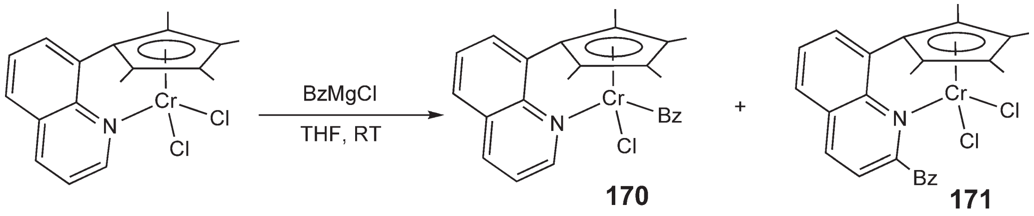


R = H, Me
168

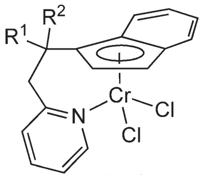


169

Finally, Huang *et al.* have recently reported the synthesis of nitrogen-functionalized Cp–chromium complexes **172**, **173** containing a three-carbon spacer between the Cp and nitrogen substituent.[138] As with the previously mentioned quinolyl- and anilyl-substituted Cp derivatives, X-ray crystallographic analysis shows that the nitrogen atoms are clearly bound to the metal center (Cr–N = 2.11–2.12 Å). Moreover, polymerization studies indicate that indenyl systems and ligands with increased steric bulk in the bridging atoms (R^1 and R^2) lead to enhanced ethylene polymerization activity (up to 2000 g PE/(mmol-Cr hr bar)). Similar reactivity trends have been noted for ethylene–hexene co-polymerizations. Finally, similar to the complexes prepared by Enders and Jolly **158–166**, and in contrast to constrained-geometry complexes **150** and **151**, catalysts based upon **172** and **173** incorporate significant levels of 1-hexene in co-polymerization experiments.

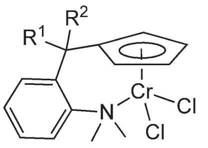


Scheme 41



R^1, R^2 = Me
R^1 = Me, R^2 = Et

172



R^1, R^2 = Me
R^1 = Me, R^2 = Et
R^1, R^2 = c-C_5H_9, c-C_6H_{11}

173

5.05.4.6.7 Boratabenzene complexes

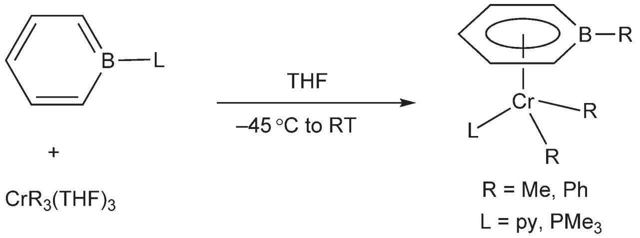
Complexes containing boratabenzene ligands (anionic C_5H_5B–R species) bear structural and reactivity similarities to Cp complexes due to the isoelectronic relationship between boratabenzene and cyclopentadienide. In the case of chromium complexes, Bazan has shown that the direct reaction between Li(C_5H_5B–R) and $CrCl_3(THF)_3$ does not lead to chromium(III) products, but rather to reduction of the metal with subsequent isolation of bis(boratabenzene)chromium(II), a structural relative of chromocene.[139] However, chromium(III) complexes are obtained by reacting chromium–carbon σ-bonded species with borabenzene adducts (C_5H_5B–L). For example, reaction of C_5H_5B–PMe_3 with $CrPh_3(THF)_3$ (or "$CrMe_3$") leads to transfer of the phenyl (or methyl) group to boron with concomitant transfer of PMe_3 to chromium (Scheme 42).[140] The net result is the formation of an anionic η^6-coordinated boratabenzene ligand (C_5H_5B–Ph), with the chromium complex **174** assuming the typical three-legged piano stool geometry. Active polymerization catalysts are formed by the reaction of $B(C_6F_5)_3$ with **174** ligated by either pyridine (65 g PE/(mmol-Cr hr bar)) or trimethylphosphine (72 g PE/(mmol-Cr hr bar)).

5.05.5 Bis(η^5-Cyclopentadienyl)chromium (Chromocenes) and Related Complexes

Since its original synthesis in the 1950's, chromocene (Cp_2Cr) has been the subject of numerous theoretical studies, including a recent comparative account of Cp_2M complexes of the first transition series.[141] Chromocene's importance is further underscored by its use in Union Carbide's silica-supported ethylene polymerization catalyst (Cp_2Cr/SiO_2). In this application, chromocene was the first metallocene to find widespread use in olefin polymerization. This chapter summarizes developments in the synthesis, spectroscopic characterization, and reactivity of chromocene and its analogs, including substituted bis(cyclopentadienyl), *ansa*-bis(cyclopentadienyl), bis(indenyl), as well as various pentadienyl, cyclooctadienyl, and cycloheptatrienyl derivatives.

5.05.5.1 Chromocene and Derivatives Incorporating Substituted Cyclopentadienyl Rings

An alternative, high yield (92%) synthesis of Cp_2Cr **175** has been reported involving the reaction of NaC_5H_5 with the cationic nitrile adduct $[Cr(NCPh)_4][BF_4]_2$.[142] A high resolution crystal structure analysis of Cp_2Cr has been reported by Flower,[143] which shows the η^5-Cp ligands to be in a staggered configuration with an average Cr–C bond length of 2.151 Å. A separate solid-state ^1H and ^{13}C NMR study[144] of Cp_2Cr indicates that all molecules in the crystalline sample



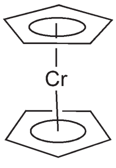
174

Scheme 42

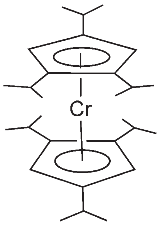
are magnetically equivalent, in agreement with the aforementioned crystal structure determination. However, in the same NMR study, analysis of decamethylchromocene ($Cp^*{}_2Cr$) reveals splitting of both the ^1H and ^{13}C signals, suggesting the presence of two magnetically inequivalent molecules in the crystal lattice. An X-ray crystallographic analysis of $Cp^*{}_2Cr$ has clarified the observed inequivalency; two crystallographically and magnetically distinct molecules are found in the unit cell, with the independent molecules oriented nearly orthogonal to each other.[144] Additional NMR studies on $(MeCp)_2Cr$ have appeared, including an examination utilizing natural abundance ^2H nuclei.[145]

5.05.5.1.1 Cyclopentadienyl derivatives with bulky alkyl substituents

Chromocene is highly air and moisture sensitive and displays intermediate spin ($S=1$) magnetic behavior. Several efforts have been made to alter the stability and the electronic properties of chromocene derivatives. Toward this end, chromocene complexes with bulky cyclopentadienyl ligands have been prepared by the reaction of $CrCl_2$ with various isopropyl and *t*-butyl-substituted cyclopentadienes, including $(1,2,4\text{-}Pr^i{}_3C_5H_2)_2Cr$ **176** and $(Pr^i{}_4C_5H)_2Cr$ **177**.[146] X-ray structural analysis of **176** reveals that the rings are perfectly staggered to reduce ring–ring interactions. However, even with these large protective substituents, the chromium(II) compounds typically remain air and moisture sensitive and possess intermediate spin ($S=1$) ground states in solution ($\mu_{eff}=2.94$ to $3.17\,\mu_B$). However, octaisopropyl derivative **177** does display unusual magnetic behavior in the solid state; it transitions from intermediate spin $S=1$ at low temperature to high spin $S=2$ at room temperature.[147] In contrast, previous magnetic studies on $Cp^*{}_2Cr$ showed that substitution with methyl groups alone is insufficient to cause a spin transition; permethylated $Cp^*{}_2Cr$ remains intermediate spin up to room temperature.[148] Thus, these findings indicate that both electron donation and steric bulk on the Cp ligand are necessary to effect spin state modifications. More detailed discussions of the impact of cyclopentadienyl ligand structure on metal complex spin multiplicity have appeared, including summaries of Cp_2Cr and its derivatives.[149,150] The more striking impact of indenyl substituents on the structural and electronic properties of bis(indenyl)chromium complexes are given in detail in Section 5.05.5.3.



175



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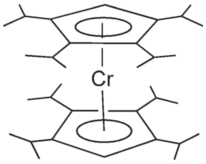
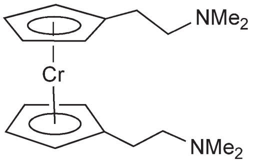


177

5.05.5.1.2 Heteroatom-substituted cyclopentadienyl derivatives

Chromocene analogs and related structures with heteroatom-containing ligands have also been synthesized, including a bis(cyclopentadienyl) derivative incorporating tethered dimethylamino groups **178**.[151] The compound was not structurally characterized but NMR spectroscopic evidence indicates that the dimethylamino groups are unbound. Additionally, the mixed $Cp^*(Tp)Cr$ complex (**179**; Tp = hydrotris(pyrazolyl)borate) forms upon treatment of $[Cp^*Cr(\eta\text{-}Cl)]_2$ with KTp. The solid-state structure of **179** reveals significant Jahn–Teller distortion, in agreement with DFT calculations for the (relatively rare) $S=2$ ground state; the distortion is manifested in one long Cr–N bond (2.439 Å).[152]



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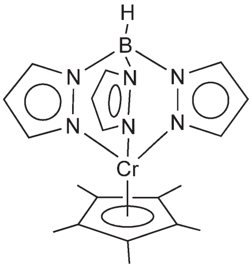
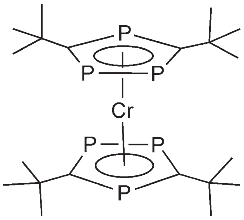


179

Other heteroatom-substituted chromocene analogs incorporate phosphorus atoms at one or more vertices of the five-membered ring. Vapor phase reaction of chromium atoms and the phosphaalkyne *t*-BuCP (metal vapor synthesis technique) has allowed Cloke *et al.* to prepare [3,5-Bu^t_2-1,2,4-P_3C_2]$_2$Cr **180** in low yield;[153] the yield is similar to that obtained using more conventional organolithium synthetic techniques.[154] A monophosphorus phosphacyclopentadienyl derivative (Tmp)$_2$Cr (**181**; Tmp = 2,3,4,5-Me_4-1-phosphacyclopentadienyl) is prepared in high yield by the reaction of KTmp with $CrCl_2$.[155] The solid-state structure of **181** contains rings in the expected staggered configuration, with diametrically opposed P atoms. Similar to Cp^*_2Cr, **181** displays typical intermediate spin ($S = 1$) magnetic behavior and undergoes reversible one-electron oxidation to a high spin $S = 3/2$ chromium(III) monocation. In another phosphorus-containing derivative, an improved synthesis of the previously reported[156] triple-decker complex [$Cp^*Cr(\mu_2{:}\eta^5\text{-}P_5)CrCp^*$] **182** has been described.[157] Oxidation of **182** with [Cp_2Fe][SbF_6] yields the corresponding cationic derivative, which displays a significantly longer (by 0.46 Å) Cr–Cr interaction than its reduced counterpart **182**; this behavior is consistent with the removal of an electron from a Cr–Cr bonding orbital upon oxidation. The cationic complex possesses complicated magnetic behavior, including an abrupt spin crossover transition at 23 K; at this temperature, the complex transitions from two weakly antiferromagnetically coupled chromium(II) centers to one characterized by a completely diamagnetic state.



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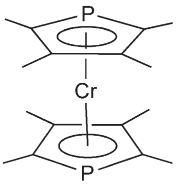

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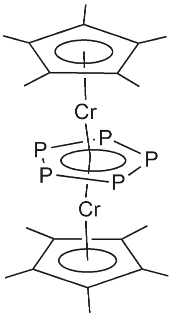

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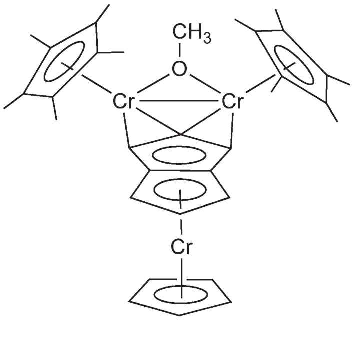
5.05.5.1.3 Derivatives with pentalene ligands

Another chromocene analog is prepared by the reaction of [$Cp^*Cr(\eta\text{-}Cl)$]$_2$ with the pentalene dianion, $Li_2C_8H_6{\cdot}x$ DME (DME = dimethoxyethane), resulting in the formation of trinuclear complex **183**.[158] Here, the pentalene ligand is bound as a five-electron cyclopentadienyl-like π-donor to one chromium center and as a three-electron, bridging allyl-like ligand to the other two chromium atoms. The additional bridging methoxy ligand presumably results from the decomposition of dimethoxyethane. The magnetic behavior of **183** is consistent with an isolated $S = 1$ chromocene-like species (lower part of structure **183**) combined with two antiferromagnetically coupled ($J = 356\ cm^{-1}$) chromium(II) ions (upper part of structure **183**).



183

5.05.5.2 Ansa-Bis(cyclopentadienyl) Chromium Complexes (ansa-Chromocenes)

Bridged or *ansa*-chromium(II) metallocenes are interesting synthetic targets because the bent or tilted ring structures expose the chromium center, thereby making it more reactive with (and receptive to) donor ligands. The following sections describe attempts to prepare both unligated and donor-ligated *ansa*-chromocenes.

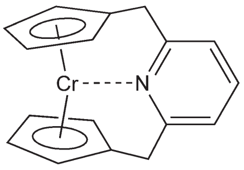
5.05.5.2.1 Theoretical considerations

Theoretical calculations by Green indicate that 16-electron Cp_2Cr displays a strong preference for the triplet ($S=1$) configuration, which is associated with parallel Cp rings. The loss of spin-pairing energy upon coordination of ligands such as CO, yielding bent diamagnetic 18-electron Cp_2CrCO complexes, is thermodynamically unfavorable.[159] On the other hand, for 16-electron *ansa*-chromocenes, the preference for the triplet state is not nearly so pronounced; the physical constraints of the bridged Cp rings make them unable to adopt a parallel ring ($S=1$) geometry and the diamagnetic bent singlet state becomes more accessible. Thus, loss of spin-pairing energy upon ligand binding is no longer an issue (for bent complexes, both 16- and 18-electron complexes are diamagnetic) and binding of σ-donor ligands becomes more favorable.

5.05.5.2.2 Chromium(II) derivatives and reactions with σ-donors

The first well-characterized *ansa*-chromocene without external σ-donor ligands, prepared by Paolucci and Ossola,[160] utilizes a bis-Cp ligand built upon a 2,6-lutidine backbone **184**. The Cp rings are canted 29.1° with respect to each other, giving a Cp(centroid)–Cr–Cp(centroid) angle of 163.3°. The position of the pyridine ring results in a long Cr–N(pyridine) interaction (2.512 Å). In **184**, the pyridine ring blocks the approach of any external ligands, thus precluding the coordination of other donors.

Shapiro *et al.*, utilizing a chromium for calcium metal replacement strategy, have prepared bridged chromium(II) metallocenes by the reaction of $CrCl_2$ with a preformed calcium metallocene (calcocene).[161] When prepared in the presence of *tert*-butyl isocyanide or CO, 18-electron complexes **185** are formed. The L = CO complex is identical to one prepared and structurally characterized by Brintzinger, which displays a Cp–Cr–Cp angle of 143.3°.[162] As with Brintzinger's earlier work, uncharacterizable, presumably polymeric, products are formed in the absence of σ-donor ligands. Shapiro has prepared other bis(indenyl) and bis(cyclopentadienyl) *ansa*-calcocene precursors via reductive coupling of substituted fulvenes and indenylidenes.[163,163a–163c] Some of these *ansa*-calcocenes have been used to prepare *ansa*-chromocene derivatives **186a–c** that contain more elaborately substituted bridging groups.[164] In these cases, the presence of an external donor ligand (L) is still required to prevent the formation of insoluble, polymetallic species. The structure of **186c** is similar to that of **185**, including a nearly identical Cp–Cr–Cp angle of 143.4°. Monomeric **186a–c** display reversible or quasi-reversible oxidations to the Cr(III) monocations and the redox potentials are moderately sensitive to the nature of the bridging substituents and donor ligand.[164]



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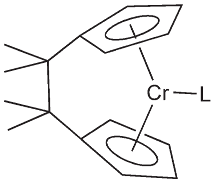
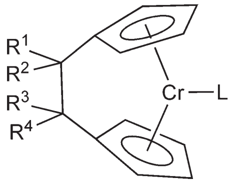


L = CO, CNBu^t

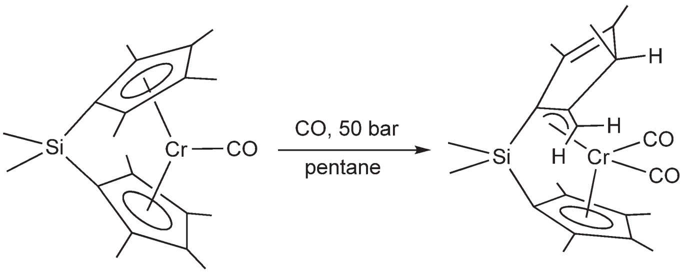
185



186a: $R^1=R^2=R^3=R^4=Me$
186b: $R^1=R^4=Ph$; $R^2=R^3=H$
186c: $R^1=R^4=3,4\text{-}(MeO)_2C_6H_3$; $R^2=R^3=H$

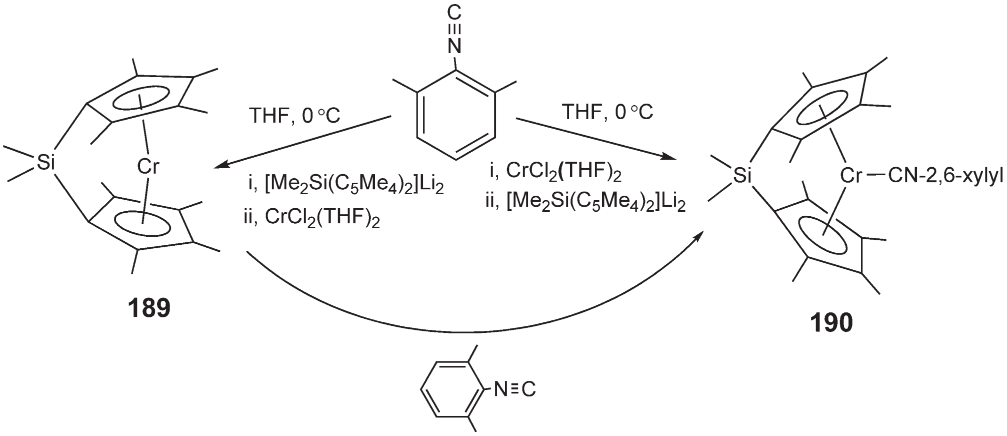
Brintzinger has reported the combined benefits of using silyl-bridged and permethylated Cp groups to enhance the stability of *ansa*-chromium(II) metallocenes.[165] For example, reaction of $Li_2[Me_2Si(C_5Me_4)_2]$ with $CrCl_2(THF)_2$ under a CO atmosphere forms the stable 18-electron CO adduct **187**. Exposure of this monocarbonyl derivative to elevated CO pressure produces a dicarbonyl adduct **188** in which one of the permethylated Cp rings rearranges to an unusual η^3-coordinated $C_5(H)Me_3CH_2$ ligand (Scheme 43). In the same study, detailed kinetic and NMR investigations have shown that the ring-slipped complex **188** undergoes subsequent isomerizations to various η^3-tautomers.

The above reactions all require an external donor to complete the 18-electron configuration and there were no examples of 16-electron (ligand-free) *ansa*-chromocenes (except perhaps for **184** until Brintzinger prepared $Me_2Si(C_5Me_4)_2Cr$[166] **189** in 2004. The unusual synthesis of **189** is sensitive to the order of reactant addition and requires the presence of 2,6-xylyl isocyanide for **189** to form, yet **189** does not incorporate the isocyanide in any way (Scheme 44). Reversing the order of reactant addition (right hand side of Scheme 44) leads to isonitrile adduct **190**. For the generation of **189**, the authors propose that initial trimerization of the isocyanide produces an anionic, bidentate ligand that transiently sequesters chromium, and that the bidentate ligand is subsequently displaced from chromium by $[Me_2Si(C_5Me_4)_2]Li_2$ to afford **189**. The crystal structure of **189** shows a severely distorted silyl-bridged



187 **188**

Scheme 43



189 **190**

Scheme 44

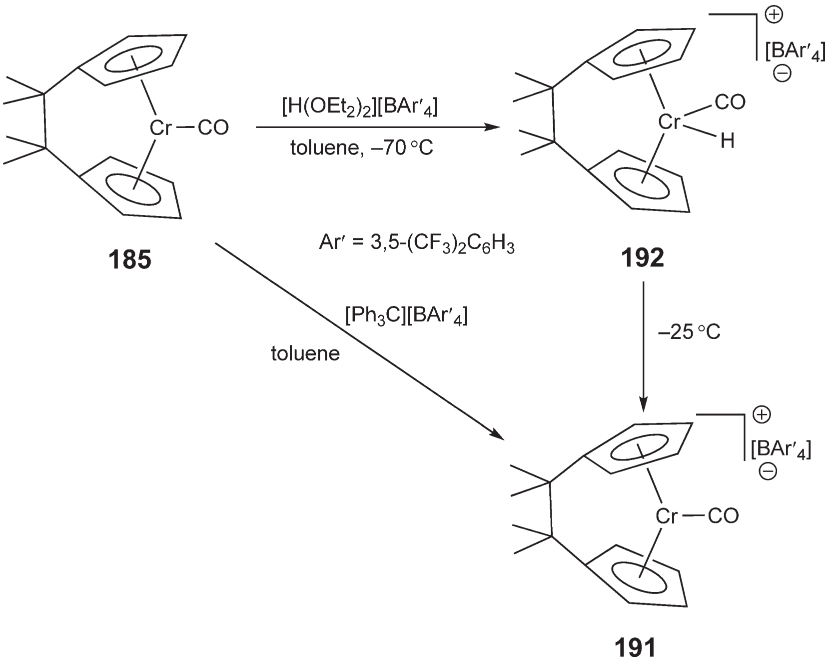
ligand, presumably a consequence of the preference for chromium(II) metallocenes to adopt co-planar ring orientations; indeed the Cp–Cr–Cp angle increases from 143.4° in **185** to 158.3° in **189**. Ligand-free complex **189** readily binds free 2,6-xylyl isocyanide to form **190**; in the case of **190**, the Cp–Cr–Cp linkage reverts to a more acute angle (146.1°). Somewhat surprisingly, **189** does not bind phosphines, phosphites, acetonitriles, or trialkylamines at the metal center.

5.05.5.2.3 Chromium(III) and chromium(IV) derivatives

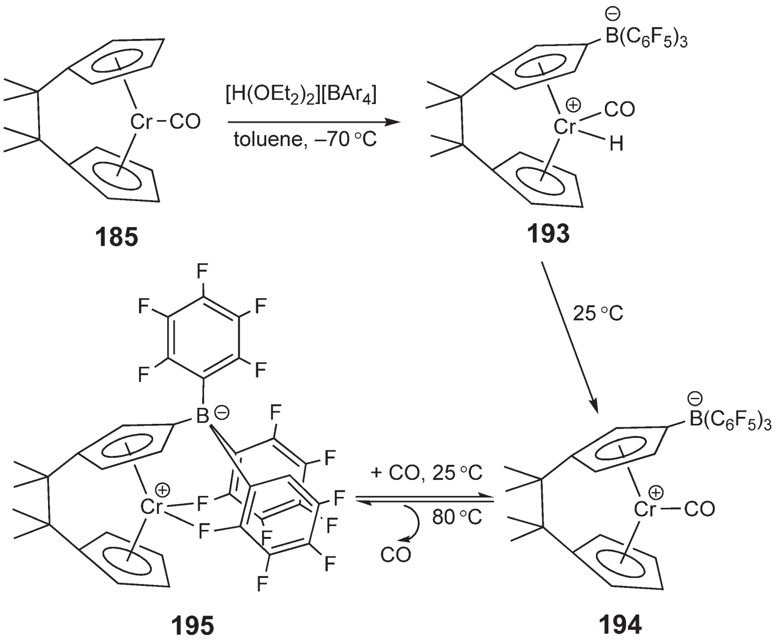
While chromium(II)-based *ansa*-chromocenes have been the most heavily studied, bridged complexes capable of stabilizing chromium(III) and chromium(IV) oxidation states are also known. For example, Shapiro has synthesized an *ansa*-chromocene(III) carbonyl cation [Me$_4$C$_2$(C$_5$H$_4$)$_2$CrCO][BAr$'_4$] **191** by low temperature reaction of **185** with [H(Et$_2$O)$_2$][BAr$'_4$] (Ar$'$ = (3,5-(CF$_3$)$_2$C$_6$H$_3$)) to give an intermediate diamagnetic chromium(IV) hydride **192** that subsequently decomposes at −25 °C to give **191** (Scheme 45).[167] A more straightforward synthesis of **191** involves chemical oxidation of **185** with [Ph$_3$C$^+$][BAr$'_4$] to give the somewhat unusual low spin $S = 1/2$ chromium(III) cation (Scheme 45). Complexes **185** and **191** possess similar solid-state structures, including similar Cp–Cr–Cp angles (143.3° and 142.2°, respectively).

Treatment of **185** with [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] instead of [H(Et$_2$O)$_2$][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] gives a ring-borylated zwitterionic chromium(IV) hydride **193**[168] that decomposes to zwitterionic chromium(III) carbonyl complexes (**194**, L = CO) (Scheme 46). Further heating of **194** evolves CO and forms **195** in which two fluorinated aryl rings are bound to the chromium center via Cr–F linkages.

Shapiro has also shown that **194** (L = CNXyl) can be oxidized to a diamagnetic, 18-electron chromium(IV) isocyanide/cyanide complex **196** with AgCN (Scheme 47).[169] For **196**, the resulting Cp–Cr–Cp angle of 133.6° indicates that the Cp rings have tilted back to accommodate the additional ligand.



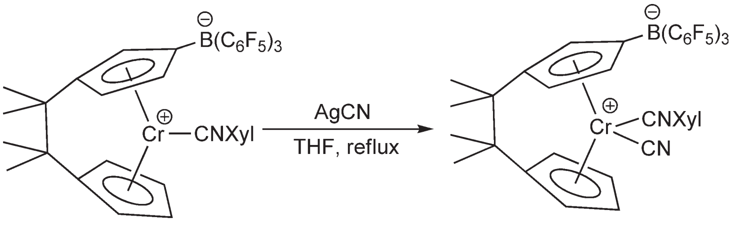
Scheme 45



Scheme 46

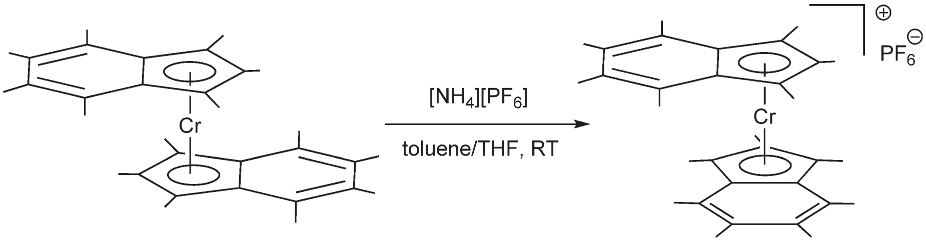
5.05.5.3 Bis(indenyl)chromium Complexes

Bis(indenyl) chromium complexes are structural relatives of chromocenes; however, recent work has shown that the structures and resulting electronic properties of bis(indenyl) derivatives are more variable than their chromocene counterparts. Reaction of 2 equiv. of permethylated indenide (C_9Me_7)Li with $CrCl_2$ generates monomeric (C_9Me_7)$_2$Cr **197**, which can be oxidized to a chromium(III) cation **198** with NH_4PF_6 (Scheme 48).[170] Structural



194 **196**

Scheme 47



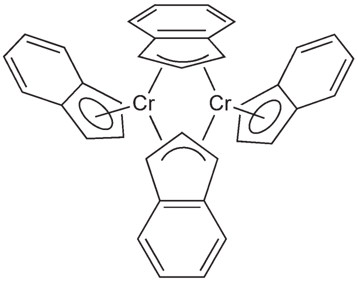
S = 1
197

S = 3/2
198

Scheme 48

analysis shows the indenyl rings to be coordinated in a fully staggered orientation for **197** (rotation angle = 180°) giving a ground-state triplet ($S = 1$); on the other hand, the $S = 3/2$ cation **198** adopts a *gauche* indenyl arrangement (rotation angle = 89°).

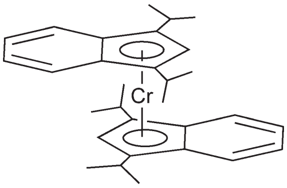
The monomeric nature of permethylated **197** contrasts with that of the parent bis(indenyl)chromium, first prepared in 1978,[171] which Jolly has recently determined to be a dimer **199** in the solid state;[172] the solid-state structure of **199** displays two conventional η^5-and two unconventional bridging μ-η^3-indenyl ligands. The dimer is a relatively low activity (<1 g PE/(mmol-Cr h bar)) single-component catalyst for ethylene polymerization; the observed reactivity is attributed to the relatively easy slippage of the bridging indenyl ligand.



199

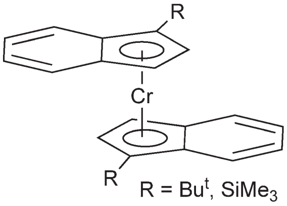
The impact of indenyl substitution on ring conformations and electronic ground states has been explored as a way to tailor specific magnetic properties. While the permethylindenyl complex **197** adopts an intermediate spin configuration ($S = 1$) with staggered rings, Hanusa has found that partial substitution of the indenyl rings leads to variable spin state behavior. For example, $[1,3\text{-}Pr^i_2C_9H_5]_2Cr$ **200**, which is formed by the reaction of $Li[1,3\text{-}(Pr^i_2)C_9H_5]$ with $CrCl_2$, possesses staggered indenyl ligands (rotation angle = 180°) as is observed for **197**.[173] However, **200** adopts a high spin ($S = 2$) electronic configuration in stark contrast to intermediate spin **197**.

In a subsequent more extensive study, Hanusa has examined several mono- and disubstituted indenyl systems.[174] Monosubstituted compounds such as $[1\text{-}Bu^tC_9H_6]_2Cr$ and $[1\text{-}(Me_3Si)C_9H_6]_2Cr$ **201** possess staggered configurations (rotation angles = 180°) and high spin ($S = 2$) electronic ground states. On the other hand, disubstituted compounds with large substituents, such as $[1,3\text{-Bu}^t{}_2C_9H_5]_2Cr$ and $[1,3\text{-}(Me_3Si)_2C_9H_5]_2Cr$ **202**, are forced, by inter-ring steric interactions, to adopt *gauche* indenyl conformations (rotation angles = 87°) and these display intermediate spin ($S = 1$) behavior. The desire to control high spin (staggered) intermediate spin (*gauche*) transitions, and the demonstrated correlation between ligand conformation and spin state multiplicity, indicates that further ligand modifications could lead to tailored magnetic properties.



$S = 2$

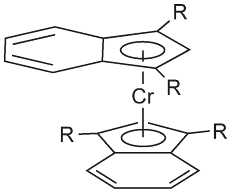
200



R = Bu^t, SiMe$_3$

$S = 2$

201



R = Bu^t, SiMe$_3$

$S = 1$

202

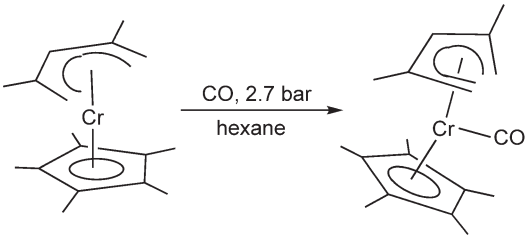
Finally, the reaction chemistry of bis(indenyl)Cr complexes with σ-donor ligands has apparently not been heavily explored. However, the structural preferences of various bis(indenyl)CrL$_2$ (L = CO, Cl, H) complexes have been examined theoretically via DFT calculations.[175]

5.05.6 π-Dienyl and π-Trienyl Complexes

5.05.6.1 Bis(pentadienyl) Complexes (Open-ring Chromocenes)

Bis(pentadienyl)chromium complexes, the open-ring analogs of chromocene, as well as certain mixed pentadienyl–cyclopentadienyl derivatives have been examined as potentially more reactive relatives of Cp$_2$Cr. For mixed systems, Waymouth reports that $Cp^*(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)Cr$ (**203**; $\eta^5\text{-}2,4\text{-}Me_2C_5H_5$ = 2,4-dimethylpentadienyl) undergoes carbonylation to form $Cp^*(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)CrCO$ **204**.[176] In both **203** and **204**, the pentadienyl ligand binds more strongly to chromium than does Cp* as evidenced by shorter (by ca. 0.068 Å) Cr–C(pentadienyl) bonds. In the 18-electron **204**, the normally U-shaped pentadienyl ligand adopts an S-shaped geometry upon coordination of CO (Scheme 49); in other mixed systems, similar U → S transformations have been observed upon ligand binding.[177] Previous work by Basolo and Ernst showed that one-electron oxidation of 18-electron adducts, such as $Cp(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)CrCO$, generates 17-electron cationic species in which the open dienyl ligand reverts to the U-shaped configuration.[178] More recent cyclic voltammetry and bulk electrolysis experiments by Geiger and Ernst confirm that the U and S structures interconvert via redox-induced isomerizations and that the 17- and 18-electron complexes favor U and S configurations, respectively.[179]

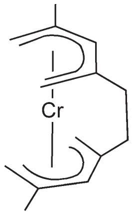
With regard to *ansa*-pentadienyl complexes, Ernst has reported the synthesis of an ethylene-bridged bis(pentadienyl) complex **205**.[180] In this case, the ligand coordinates in a *gauche* conformation, with the U-shaped pentadienyls oriented nearly orthogonal to each other (rotation angle = 92.2°). The magnetic properties were not disclosed. Spectroscopic data indicates the metal center readily binds alkylphosphines to form 18-electron, monoligand complexes or 2 equiv. of CO to form a dicarbonyl complex. In the dicarbonyl complex, one pentadienyl ligand slips to an η^3-binding mode to accommodate the additional CO. Non-bridged bis(pentadienyl) complexes are also known, including $[1,5\text{-}(Me_3Si)_2C_5H_5]_2Cr$ **206a** and unsymmetrical $[(1\text{-}Me_3Si\text{-}3\text{-}Me)C_5H_5]_2Cr$



203 **204**

Scheme 49

206b derivatives.[181] Similar to *ansa*-pentadienyl complex **205**, the 1,5-$(Me_3Si)_2C_5H_5$ ligands in **206a** coordinate to chromium in a *gauche* configuration (rotation angle = 78.7°); however, as with **205**, the spin state of **206a** was not disclosed. In the same study, a mixed Cp–pentadienyl system, Cp(2,4-$Me_2C_5H_5$)Cr, was structurally characterized. Here, as in mixed complex **203**, the open-ring 2,4-$Me_2C_5H_5$ ligand binds more tightly to chromium than does the Cp (0.063 Å shorter Cr–C bonds).



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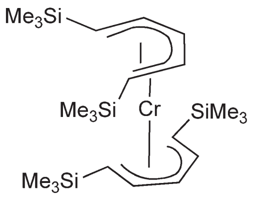
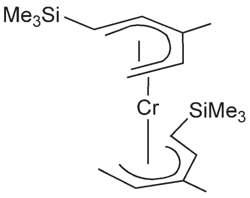


206a



206b

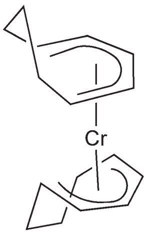
Finally, the relatively labile pentadienyl ligands in $(2,4\text{-}Me_2C_5H_5)_2Cr$ are readily removed by reaction with triethylphosphine telluride, yielding a hexachromium molecular cluster $Cr_6Te_8(PEt_3)_6$. Subsequent pyrolysis of the cluster forms the ferromagnetic material Cr_3Te_4,[182] thus demonstrating that organometallic complexes can serve as useful precursors to novel inorganic materials.

5.05.6.2 Bis(cyclooctadienyl) Complexes

Ernst has also prepared bis(octadienyl) complexes by reacting $CrCl_2$ with 2 equiv. of potassium cyclooctadienide KC_8H_{11}.[183] The $C_8H_{11}^-$ anion can be viewed as an "edge-bridged" pentadienyl ligand with a three-carbon bridge linking pentadienyl positions 1 and 5. The structural similarity between cyclooctadienyl and pentadienyl ligands thus translates into similar chromium ligand bonding scenarios. For example, the cyclooctadienyl ligands in $(C_8H_{11})_2Cr$ **207** are bound in a *gauche* configuration with a rotation angle (84°) and Cr–C bond lengths similar to those found in other open-ring chromocenes.[184] Presumably, the reactivity of bis(pentadienyl) and bis(octadienyl) derivatives should also be similar; however, the reactivity of **207** with σ-donor ligands has not been extensively explored.

5.05.6.3 Cycloheptatrienyl Complexes

The attempted synthesis of bis(cycloheptadienyl)chromium, $(C_7H_9)_2Cr$, by the reaction of $CrCl_3$ with 3 equiv. of KC_7H_9 leads, unexpectedly, to the mixed cycloheptatrienyl–cycloheptadiene complex $(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})Cr$-**208**.[185] The authors suggest that the stability of the highly delocalized η^7-C_7H_7 ligand drives this "disproportionation" reaction. In **208**, the C_7H_7 fragment is nearly planar and the η^4-cycloheptadiene ligand is bound in an enediyl fashion. Some mixed arene–cycloheptatrienyl complexes, such as $[(\eta^6\text{-arene})(\eta^7\text{-}C_7H_6R)Cr][PF_6]$ (**209a**; arene = C_6H_5Me, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$; R = H, 4-MeC_6H_4), have been prepared by refluxing $[(\eta^7\text{-}C_7H_6R)Cr(CO)_3][PF_6]$ in the appropriate aromatic solvent.[186,187] The 18-electron monocations are readily oxidized to the 17-electron radical dications **209b** with $[Cp_2Fe][PF_6]$ (Scheme 50). For the structurally characterized **209a–209b** redox pair (arene = C_6H_5Me; R = 4-MeC_6H_4), oxidation causes only a small increase in metal–ring distances, which is consistent with a HOMO that is essentially non-bonding with respect to metal–carbon interactions. Finally, the geometric and electronic properties of mixed cyclopentadienyl–cycloheptatrienyl complexes, $(\eta^5\text{-Cp})(\eta^7\text{-}C_7H_7)M$ (M = group 4–6), have been examined using relativistic DFT.[188]



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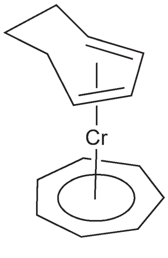

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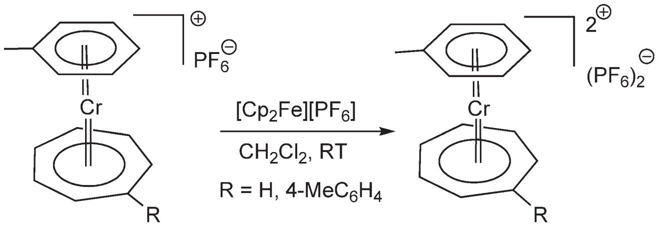


209a **209b**

Scheme 50

5.05.7 Bis(η^6-Arene) Complexes

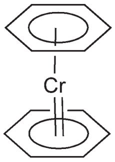
Bis(η^6-arene)chromium complexes such as the parent compound $(C_6H_6)_2Cr$ **210** have been actively studied since the middle of the twentieth century. Excellent reviews by Uhlig[189] in 1993 and more recently by Seyferth[190,191] in 2002 have provided thorough historical accounts of the synthesis and characterization of these and other organochromium complexes. With 2005 representing the fiftieth anniversary of the discovery of this important compound class, Seyferth's two comprehensive reviews covering the synthesis of various organochromium compounds, including the ultimate synthesis and characterization of $(C_6H_6)_2Cr$ (and its derivatives), are especially relevant. This section of the chapter will highlight recent advances in this field, primarily in the use of new arene ligands and synthetic procedures to produce heteroatom-substituted bis(arene)chromium complexes. Use of chromium–arene complexes in forming solid-state materials is also addressed.

5.05.7.1 Theoretical Considerations

Bis(η^6-benzene)chromium complexes often serve as model compounds when testing and refining theoretical calculation techniques. For example, a semi-empirical PM3 model, augmented with two-electron interactions, provides calculated bond dissociation energies, ground-state geometries, and ionization potentials for $(C_6H_6)_2Cr$ that are in reasonable agreement with experimental results.[192] In another work, a DFT analysis of $(C_6H_6)_2Cr$ and its cation $[(C_6H_6)_2Cr]^+$ has yielded calculated ligand binding energies that compare well with experimental data.[193] Finally, the detailed nature of metal–ligand binding in $(C_6H_6)_2Cr$ has been further explored with DFT calculations. The results indicate that metal–ligand bonding in $(C_6H_6)_2Cr$ is primarily covalent and that the largest orbital contribution comes from Cr → benzene δ backdonation,[194] leading to the description of $(C_6H_6)_2Cr$ as a δ-bonded molecule.

5.05.7.2 Compounds with Hydrocarbon-substituted Arenes

Diamagnetic, 18-electron bis(arene) complexes are often prepared by metal vapor synthesis (MVS), a technique first utilized by Timms in 1969.[195] In this procedure, chromium and ligand vapor are co-condensed in a cooled (77 K) reaction chamber and the condensate reacts upon warming to form air sensitive bis(arene) products. Using the MVS technique, several new bis(arene)chromium compounds have been prepared, including sandwich complexes with polycyclic aromatic hydrocarbons such as fluorene **211**,[196] triphenylene **212**,[196] and fluoranthrene **213**.[197] In the case of complex **213**, NMR data is consistent with chromium bound to the more π-donating benzene ring fragment. Stable, one-electron oxidization products of **211–213** have also been prepared. Other hydrocarbon-substituted derivatives include alkyl-substituted complexes $[1,4\text{-}(Bu^t)_2C_6H_4]_2Cr$ **214**[198] and $[1,2,4,5\text{-}Me_4C_6H_2]_2Cr$ **215**.[199] Somewhat surprisingly, **215** displays eclipsed benzene rings (D_{2h} symmetry) in the solid state; however, gas-phase electronic absorption spectra are most consistent with a staggered ring configuration (D_{2d} symmetry). Detailed analysis of Rydberg transition data for **215** and for other arene ring-substituted complexes[200,201] indicates that the first ionization potential (originating from the non-bonding chromium $3d_{z^2}$ orbital) decreases linearly with an increase in the number of methyl groups; this trend is consistent with the methyl group's inductive effect and with an increase in polarizability of the complex upon methylation.



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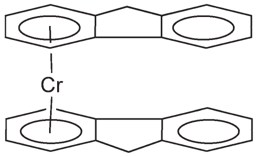

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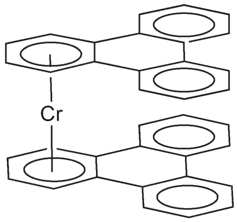

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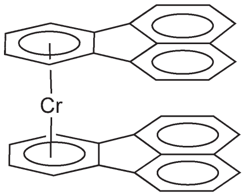

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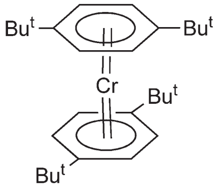

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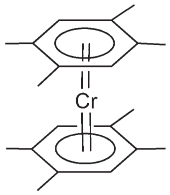

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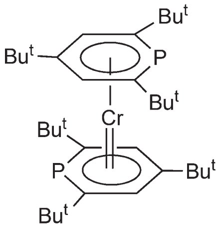
5.05.7.3 Compounds with Heteroatom-substituted Arenes

While the MVS technique has proved to be relatively functional group tolerant, there is a limit to the type of heteroatom that can be introduced via this method. Fortunately, additional functionalized bis(arene)chromium complexes can be prepared by more traditional organolithium-based synthetic techniques. These methods are summarized in the following paragraphs. To describe more easily these routes, we have segregated the substituted arenes into (i) those with the heteroatom as an integral part of the six-membered ring, and (ii) those with the heteroatom on the ring's periphery.

5.05.7.3.1 Derivatives with heteroatoms integral to the ring

Phosphabenzene (C_5H_5P) and arsabenzene (C_5H_5As) are representative ligands with the heteroatom within the six-membered arene ring. For phosphabenzenes, use of sterically hindered derivatives such as 2,4,6-$Bu^t{}_3C_5H_2P$ and 2-(Me_3Si)-3-MeC_5H_3P is required for the formation of the η^6-complexes **216** and **217**,[202,203] respectively, by the MVS technique. By comparison, use of unsubstituted phosphabenzene (phosphinine) yields only the nearly perfectly octahedral, hexakis P-bound (η^1-C_5H_5P)$_6$Cr **218**.[204,205] In the case of **216** and **217**, the steric bulk introduced by the adjacent *t*-butyl or trimethylsilyl groups prevents direct phosphorus coordination to chromium. However, the interaction of these large substituents with those on neighboring rings sometimes results in complex isomeric mixtures (multiple rotamers), which complicates product identification and purification. In contrast to phosphabenzene, reaction of chromium atoms with the less σ-donating C_5H_5As produces (η^6-C_5H_5As)$_2$Cr **219** directly.[206] Boratabenzene ligands, (C_5H_5B-R)$^-$, are also members of this heteroatom-substituted ligand set. However, as noted previously, their chemistry and methods of synthesis more closely resemble those of Cp complexes; thus, boratabenzene derivatives were previously discussed along with Cp-containing compounds in Section 5.05.4.6.7.



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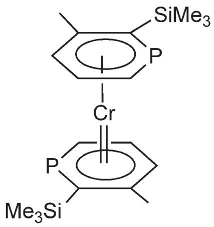

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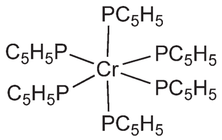

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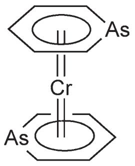


219

5.05.7.3.2 Derivatives with heteroatoms on the periphery

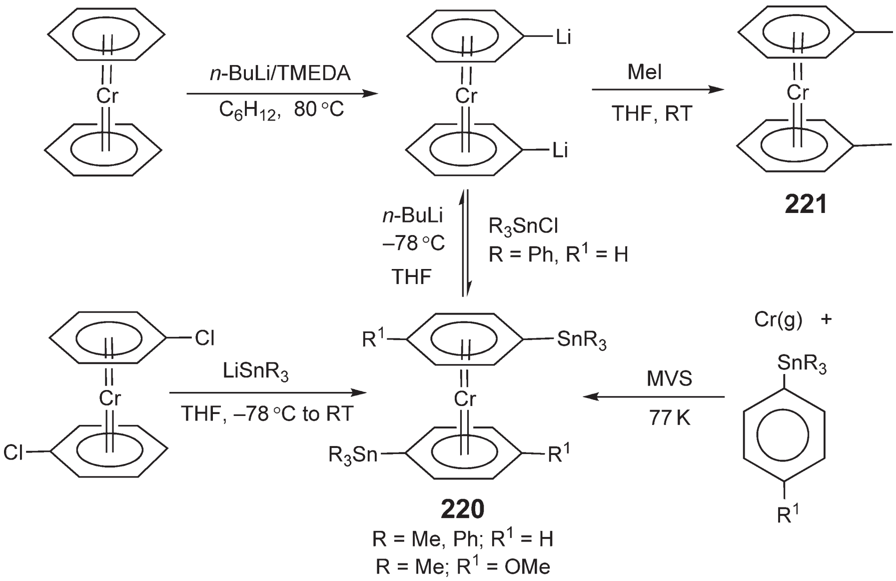
Several bis(η^6-arene)chromium complexes with heteroatoms on the periphery of the arene ring have been prepared, including those containing tin, germanium, silicon, boron, nitrogen, phosphorus, and sulfur atoms.

5.05.7.3.2.(i) Tin-substituted derivatives

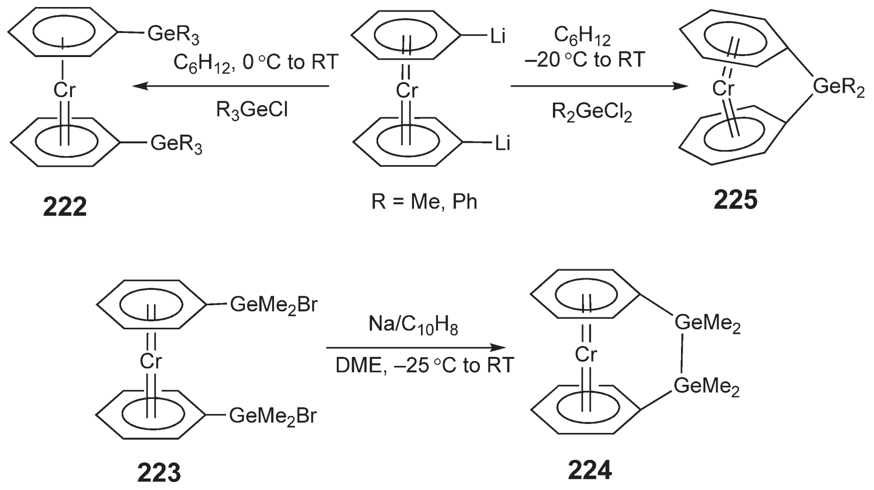
Tin complexes are outlined first since their preparation methods encompass many of the synthetic avenues available (Scheme 51). For example, the traditional MVS route has been used to prepare stannyl derivatives $(4\text{-}R_3SnC_6H_4R^1)_2Cr$ (**220**: R = Me, Ph; R^1 = H and R = Me, R^1 = OMe).[207] The trimethylstannyl- and triphenylstannyl-substituted complexes can also be prepared by low temperature reaction between $LiSnR_3$ (R = Me, Ph) and $(C_6H_5Cl)_2Cr$. In yet another synthetic strategy, stannyl-substituted arene rings are produced by dilithiation of $(C_6H_6)_2Cr$ (using *n*-BuLi and TMEDA) to form $[(C_6H_5)_2Cr]^{2-}$, followed by treatment with 2 equiv. of Ph_3SnCl, yielding **220** (R = Ph, R^1 = H). Even with large tin substituents like $\text{-}SnPh_3$, the strict coplanarity of the arene ligands is retained. Consistent with the structural similarities between unsubstituted **210** and tin-substituted **220**, the electronic perturbations caused by organotin substitution are relatively minor as measured by EPR spectroscopy and electrochemical reduction potentials. In a final synthetic method, stannyl groups are readily removed and replaced with alkyl substituents by reaction of **220** with *n*-BuLi, yielding intermediate $[(C_6H_5)_2Cr]^{2-}$, which subsequently reacts with MeI to form **221**. This destannylation method has been touted as a useful way to prepare the synthetically useful $[(C_6H_5)_2Cr]^{2-}$ without the need for, or contamination by, an auxiliary base like TMEDA.

5.05.7.3.2.(ii) Germanium-substituted derivatives

Moving upward from tin to germanium in group 14, it is possible to prepare Ge-substituted bis(arene) compounds (Scheme 52). For example, the MVS technique yields $(R_3GeC_6H_5)_2Cr$ (**222**; R = Me) and $(BrMe_2GeC_6H_5)_2Cr$ **223**.[208] Further reaction of **223** with sodium naphthalenide results in coupling of the arene systems via a Ge–Ge bridge to form **224**. Sandwich complexes **222** (R = Me, Ph) are also prepared by the reaction of $[(C_6H_5)_2Cr]^{2-}$ with Me_3GeCl and Ph_3GeCl, respectively. This synthetic method is analogous to that used to prepare the $\text{-}SnMe_3$ and $\text{-}SnPh_3$ complexes (**220**; R = Me, Ph; R^1 = H) described earlier. And, as observed with the tin-substituted complexes, only minor structural and electronic perturbations are caused by placement of germanium on the periphery of the arene ring. On the other hand, formation of germanium-bridged (*ansa*-) species such as **225** (R = Me, Ph) by the reaction of $[(C_6H_5)_2Cr]^{2-}$ with Me_2GeCl_2 and Ph_2GeCl_2, respectively, causes significant electronic, structural, and reactivity differences to emerge. X-ray structural analysis of **225** (R = Ph) shows that incorporation of a single Ge atom bridge atom produces a 14.4° tilting of the arene rings with respect to each other. This distortion, coupled with a



Scheme 51

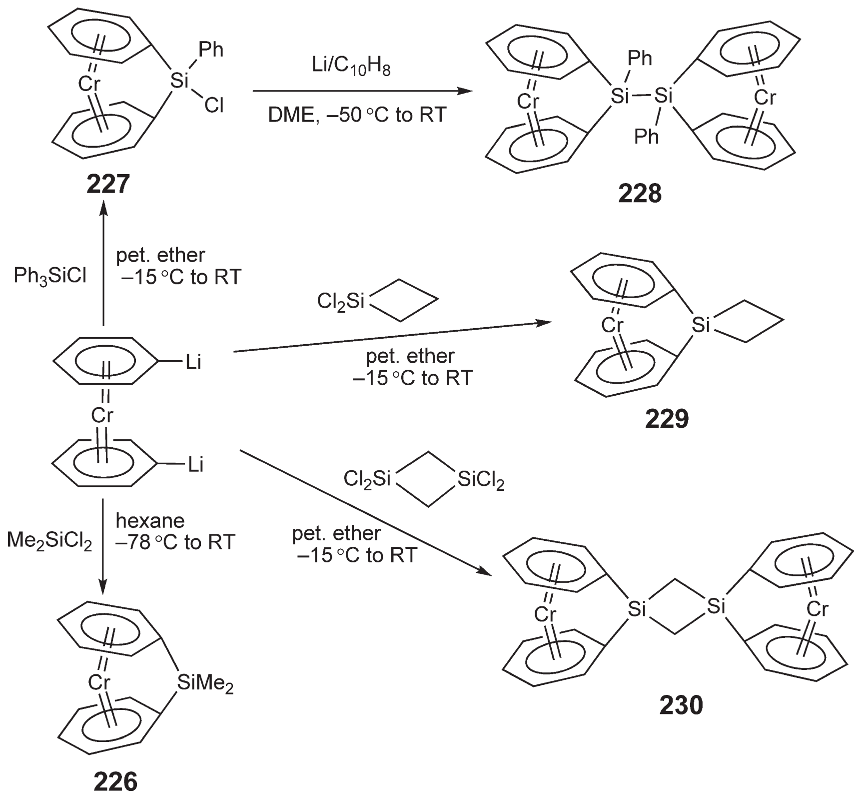


Scheme 52

relatively weak C_{ipso}–Ge bond, renders the radical cations **225**$^+$ unstable and prone to oxidative degradation, presumably via cleavage of the Ge–C bond.

5.05.7.3.2.(iii) Silicon-substituted derivatives

Continuing upward in group 14, *ansa*-silylene species, such as **226**[209] and **227**,[210] have been prepared by the reaction of $[(C_6H_5)_2Cr]^{2-}$ with the appropriate di- or trichlorosilane (Scheme 53). For **226**, X-ray structural analysis shows the arene rings to be tilted by 14.4°, identical to that observed in the solid-state structure of Ge complex **225** (R = Ph). In

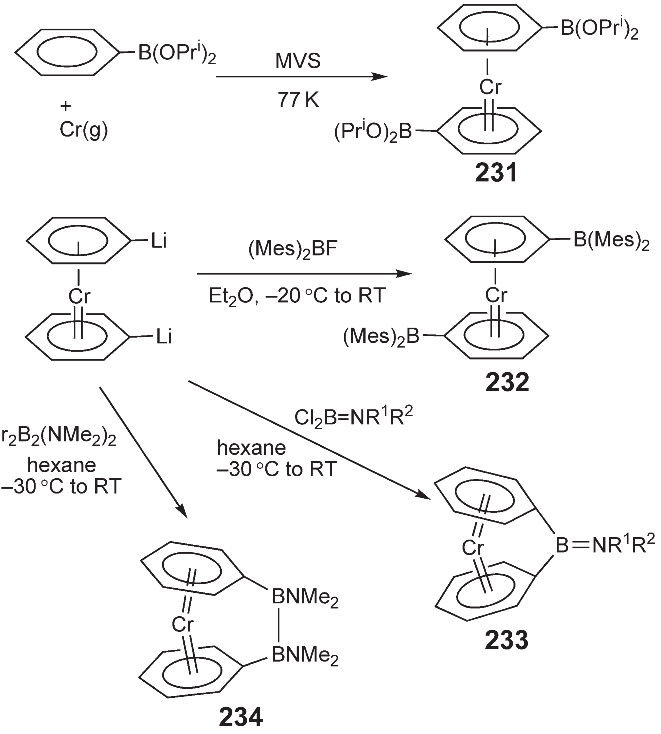


Scheme 53

the case of 227, reductive coupling with lithium naphthalenide results in the bimetallic disilane 228. Mononuclear silacyclobutane-bridged 229 and dinuclear 1,3-disilacyclobutane-bridged 230 complexes are also known.[211] While crystal structures of these *ansa*-silylenes have not been determined, the solid-state structures of analogous vanadium compounds display the arene ring tilt expected for single-atom-bridged complexes, and the chromium compounds are expected to follow suit. For dinuclear compounds 228 and 230, it was of interest to study the extent of electronic communication between the metal centers through the respective Si–Si and 1,3-disilacyclobutane bridges. Unfortunately, oxidation of 228 and 230 produces unstable radical cations that cannot be examined by EPR. However, detailed EPR studies (including spectral simulation) on neutral bimetallic vanadium analogs (note that neutral vanadium centers and chromium radical cations both possess one unpaired electron) show weak electronic coupling between the two $S = 1/2$ metal centers. Interestingly, electronic exchange is even observed across the 1,3-disilacyclobutane bridge. Further accounts of electronic communication between metal centers are described below in the section covering phosphine-substituted complexes.

5.05.7.3.2.(iv) Boron-substituted derivatives

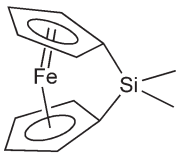
Moving to group 13 heteroatom substituents, boron-containing sandwich complexes are prepared by co-condensation of Cr vapor with bis(isopropoxy)borylbenzene to form 231,[212] or by reaction of $[(C_6H_5)_2Cr]^{2-}$ with Mes_2BF (mes = 1,3,5-trimethylphenyl) to afford 232 (Scheme 54). As with other chromium complexes with co-planar arene rings, the radical cation 232^+ is stable, as is the radical anion, 232^-. Detailed EPR simulations indicate that oxidation to the radical cation state is a metal-centered process, while reduction to the radical anion is centered on the boryl ligand. *ansa*-Boryl and *ansa*-diboryl species are prepared by the reaction of $[(C_6H_5)_2Cr]^{2-}$ with the appropriate boron or diboron halide, forming 233 and 234, respectively (Scheme 54).[213] Complex 233, with a single boron atom bridge, displays the largest arene tilt angle (26.6°) of any bridged species prepared to date (compared to 14.4° for germyl and silyl derivatives 225 and 226; as a result, 233 is extremely air and moisture sensitive and is even unstable in polar organic solvents. Unfortunately, incompatibility with polar solvents 233 does not allow for electrochemical and EPR investigations. While the diboron-bridged 234 shows a much smaller tilt angle of 10.1°, the authors did not comment on its moisture sensitivity.



Scheme 54

5.05.7.3.2.(v) Ring-opening polymerization reactions

For germyl, silyl, and boryl-bridged complexes such as 225–227 and 233, the ring strain, as manifested in large arene tilt angles, is proposed to translate into enhanced ring-opening polymerization (ROP) activity. Successful ROP of bridged bis(arene) complexes can lead to transition metal-containing polymers linked by an arene backbone structure and such metal-containing organic polymers could have interesting electrical and mechanical properties. For example, earlier work by Manners has shown that ferrocenophanes, such as 235, undergo ROP (either thermal or anion initiated) to form high molecular weight poly(ferrocenylsilanes).[214] In attempts to extend ROP to strained bis(arene) chromium complexes, the silylene-bridged 226 is found to randomly co-polymerize (thermally at 140 °C or via *n*-BuLi initiation) with 235 to produce a heterobimetallic co-polymer 236.[208] Attempts to homopolymerize 226 by anionic initiation leads to products that are consistent with ring opening, but no characterizable polymeric products are isolated. However, in more recent work, Manners has successfully used a Pt(0) catalyst to effect ROP of 226 to polychromarenylsilane, an air sensitive polymer 237 with $M_n = 4100$ as determined by solid-state ^{13}C and ^{29}Si NMR spectroscopy.[215]



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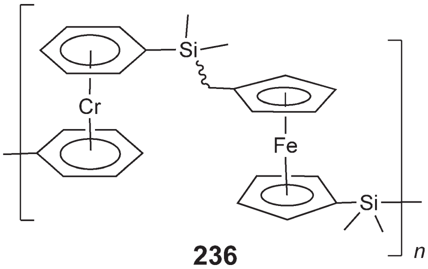

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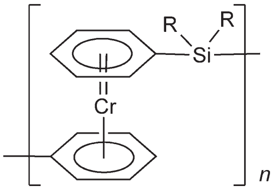

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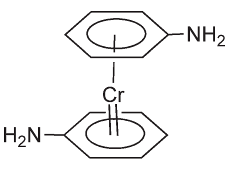
The ring-strained germanium complexes 225 have not been subjected to ROP conditions. However, thermolysis of the vanadium analogs leads to decomposition (to free ligand and vanadium metal) without undergoing ROP, suggesting a similar fate would await chromium derivatives. The boron-bridged complex 233 is especially appealing for ROP applications given its large tilt angle (26.6°) and associated ring strain. Ring opening of 233 with BuLi was successful but the products are limited to dimeric species; thermally induced ROP does not produce polymeric products. Given the successful formation of polychromarenylsilane 237, the Pt(0)-catalyzed route may yet provide a viable pathway to high molecular weight Ge- and B-containing organochromium polymers.

Bis(arene) complexes modified with nitrogen, phosphorus, and sulfur σ-donor atoms on the periphery have also been prepared. If properly oriented, such compounds are potentially useful for constructing heterometallic complexes by bridging through the peripheral donor atoms.

5.05.7.3.2.(vi) Nitrogen-substituted derivatives

Beginning with nitrogen-containing complexes, Elschenbroich's group has prepared bis(aniline) derivative 238, by the reaction of the silyl-protected aniline, $(Me_3Si)_2NC_6H_5$, and chromium vapor, followed by desilylation to give 238.[216] Other nitrogen-containing compounds including $[1,4\text{-}(Me_2N)_2C_6H_4]_2Cr$ 239 and $\{1,4\text{-}[(Me_3Si)\text{-}NH]_2C_6H_4\}_2Cr$ 240 are prepared by the co-condensation route.[217] Notably, complex 240 adopts an eclipsed ring orientation that is stabilized by inter-ring hydrogen bonding interactions. While it appears that 238–240 could potentially bind other metals through the nitrogen donor atoms, heterometallic complexes incorporating these chelating ligands have not yet been reported.



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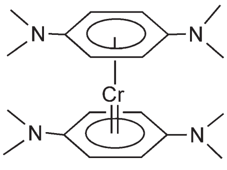

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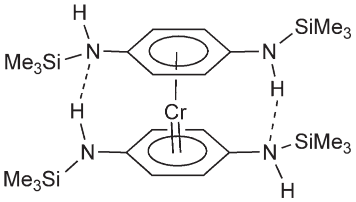

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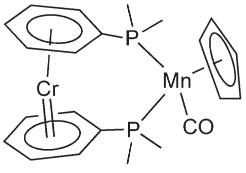
5.05.7.3.2.(vii) Phosphorus-substituted derivatives

In contrast to nitrogen-based substituents, bis(arene)chromium complexes with phosphorus donor groups have proved to be useful in forming heterometallic complexes. Some representative multinuclear compounds include those incorporating Mn **241**,[218] Mo **242**,[219] and Co **243**, **244**;[220,221] these are typically prepared via photochemical carbonyl substitution reactions. In addition to synthetic details, the references above also examine the extent of electronic communication between the metal centers, using combined cyclic voltammetry and EPR spectroscopic experiments.



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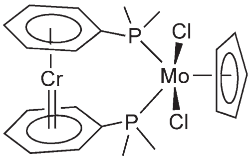

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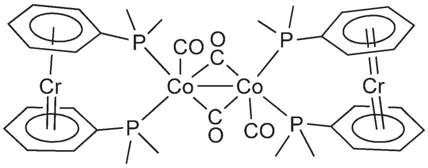

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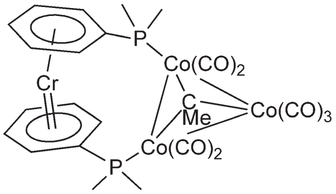

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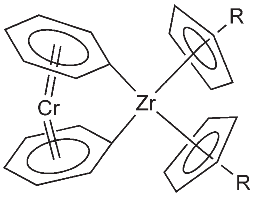
5.05.7.3.2.(viii) Miscellaneous derivatives

Another bimetallic complex, zircona[1]chromacyclophane **245**, has been prepared by the reaction of zirconocene dichloride with $[(C_6H_5)_2Cr]^{2-}$.[222] While the reaction of $[(C_6H_5)_2Cr]^{2-}$ with a metal dihalide appears to be a general route to prepare mixed metal systems, it seems that only the zirconium metallocenes have been synthesized to date. In addition, sulfur-containing complexes based upon a 2-R-benzo[b]thiophene ligand (**246**; R = H, Me, $SiMe_3$) are formed by the co-condensation of chromium atoms and the thiophene ligand.[223] The methyl derivative crystallizes as the *meso*-isomer with the thiophene ligands in nearly perfectly eclipsed orientations, presumably due to favorable π-stacking effects. However, NMR data suggest that both *meso*- and racemic isomers exist in solution. While the thiophene sulfur atoms are not oriented properly to bind other metals, the synthesis of **246** extends the MVS technique to include sulfur-containing arene ligands.



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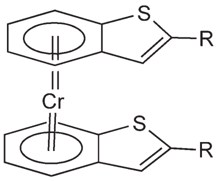

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Finally, a recently reported method uses mixed alkali metal/alkyl-magnesium piperidide bases to selectively deprotonate one arene ring of $(C_6H_6)_2Cr$, which forms $\{NaMg[Cr(C_6H_5)(C_6H_6)(TMP)_2]\cdot TMEDA\}$ (TMP = tetramethylpiperidide) and leaves the other arene ring untouched.[224] This route may provide a general preparative method to functionalized bis(arene) structures in which only one arene ring is substituted.

5.05.7.4 Applications of Bis(arene)chromium Complexes

5.05.7.4.1 Engineered materials

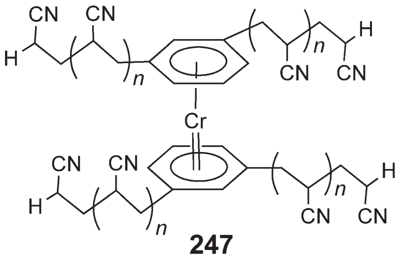
There has been much recent interest in using organometallic complexes to design crystalline and/or polymeric structures with predictable properties—the so-called “engineered materials.” These structures are expected to have interesting magnetic (ferromagnetic or antiferromagnetic) and, perhaps even, non-linear optical properties.

5.05.7.4.1.(i) Covalent interactions

The chromium-containing polymers formed via ROP (described in the previous section) represent a case of extended polymer networks linked via covalent interactions. In another example, bis(arene)chromium complexes with polyacrylonitrile appendages have been prepared by polycyanoethylation of the arene rings. The star-shaped polymers consist of a central bis(arene)chromium complex with up to four polyacrylonitrile arms **247**.[225] Thermolysis at 160 °C decomposes **247** to yield a room temperature ferromagnet.

5.05.7.4.1.(ii) Non-covalent interactions

Non-covalent interactions, such as hydrogen bonds, can also be used to design organochromium-containing network structures. For example, a bis(benzene)chromium derivative with carboxylic acid substituents, $(C_6H_5CO_2H)_2Cr$, is formed by the reaction of $[(C_6H_5)_2Cr]^{2-}$ and CO_2 followed by acidic workup.[226] The neutral diacid forms hydrogen-bonded dimers **248** in the solid state. More impressively, its oxidized derivative, $[(C_6H_5CO_2H)_2Cr][PF_6]$, forms an extended stair-step lattice of chromium-containing chains **249** via intermolecular hydrogen bonding. Other examples of engineered crystalline structures incorporate $[(C_6H_6)_2Cr]^+$ as counterions encapsulated in a hydrogen-bonded framework of anionic cyclohexane-1,3-dione[227] or in an ordered array of hydrogen-bonded squaric acid monoanions.[228]



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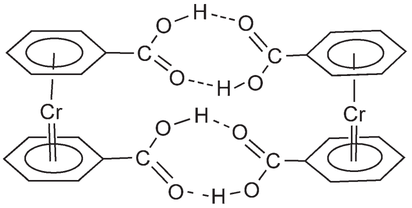

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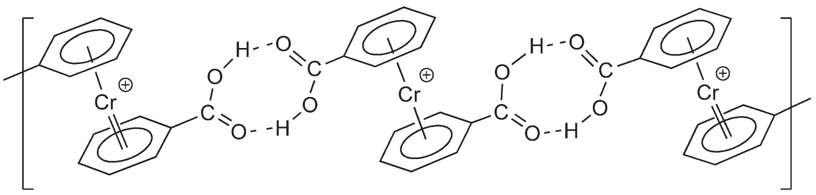

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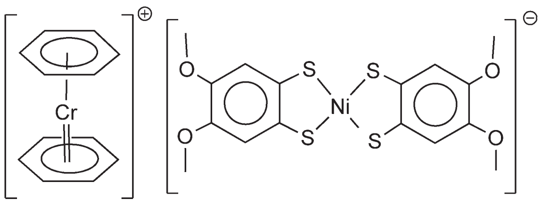
5.05.7.4.1.(iii) Charge transfer salts

In yet another example, $(C_6H_6)_2Cr$ and hexafluorobenzene form a charge transfer stacked crystalline network $[(C_6H_6)_2Cr{\cdot}C_6F_6]$.[229] Crystals consisting of interpenetrating sublattices of $[(C_6H_6)_2Cr]^+$ and bis(4,5-dimethoxy-1,2-benzenedithiolato)nickel(III) **250** are also known.[230] In **250**, the $S = 1/2$ chromium(I) and nickel(III) centers become ferromagnetically ordered below 3.4 K.



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5.05.7.4.2 Miscellaneous applications

In addition to the polymeric and crystalline materials mentioned above, a few other important uses of bis(arene)chromium compounds deserve mention. It was recently discovered that $(C_6H_6)_2Cr$ functions as an efficient radical (R·) scavenger, forming 17-electron $(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_6R)Cr$ species.[231] Bis(benzene)chromium is also an efficient catalyst (in the presence of air) for the hydrosilylation of ketones and aldehydes (forming alkoxysilanes), and for dehydrocoupling of silanes and primary alcohols to afford organosilanes.[232] Finally, bis(arene)chromium complexes can be used to form hard chromium carbide coatings via chemical vapor deposition at 300–600 °C;[233] the latter example represents another case of organochromium complexes serving as useful precursors to novel inorganic materials.

5.05.8 Organochromium Complexes Supported by Imido and Nitrido Ligands

A recent review by Leung has summarized successful attempts to employ π-donating organoimido ligands in the synthesis of high-valent chromium(IV, V, VI) complexes.[234] Furthermore, the formation of organoimido derivatives by the reaction of certain nitrosyl-containing compounds with metal alkyl reagents was previously described in this chapter (Section 5.05.2.5). In the present section, we will focus on the synthesis and reactivity of organometallic organoimido and nitrido chromium complexes containing well-characterized chromium–carbon bonds.

5.05.8.1 Monomeric Chromium(VI) Complexes

5.05.8.1.1 Alkylidene derivatives

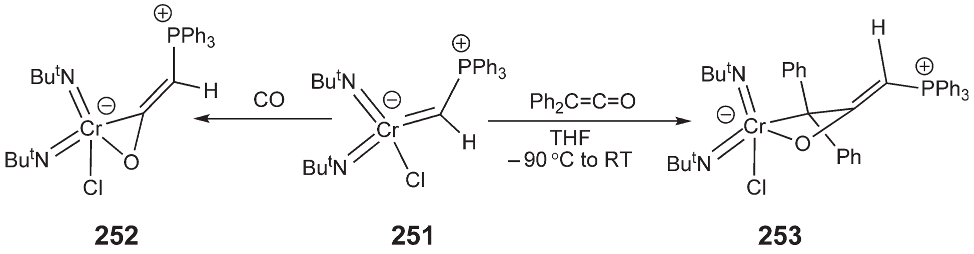
Sundermeyer has prepared a chromium alkylidene complex, $Cr(NBu^t)_2[{=}C(H)(PPh_3)]Cl$ **251**, by the reaction of $Cr(NBu^t)_2Cl_2$ with 2 equiv. of phosphorus ylide $Ph_3P{=}CH_2$.[235] The resulting carbene ligand reacts with CO and isonitriles to form η^2-acyl **252** and η^2-iminoacyl complexes, respectively (Scheme 55). In addition, cycloaddition of the carbene with diphenylketene yields a four-membered metallacyclobutane **253** with an exocyclic α-phosphoniomethylidene.

5.05.8.1.2 σ-Alkyl and σ-aryl derivatives

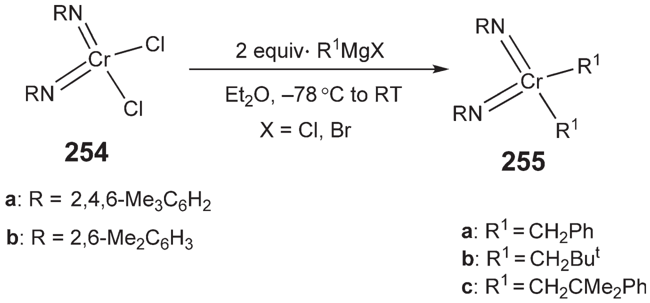
5.05.8.1.2.(i) Synthesis and insertion reactions

Bis(alkylimido) and bis(arylimido) complexes with sterically hindered substituents (e.g., Bu^t, 2,4,6-$Me_3C_6H_2$, or 2,6-$Me_2C_6H_3$) have been used to prepare chromium(VI) complexes containing σ-alkyl or σ-aryl groups. Wilkinson and Hursthouse report that bis(aryl)imido complexes can be prepared using an aryl- for alkyl-imido exchange strategy; reaction of $Cr(NBu^t)_2Cl_2$ with the appropriate substituted aryl isocyanate produces $Cr(NR)_2Cl_2$ (**254a**: R = 2,4,6-$Me_3C_6H_2$; **254b**: R = 2,6-$Me_2C_6H_3$).[236] Reaction of **254a** with selected Grignard reagents, R^1MgBr ($R^1 = CH_2Ph$, CH_2Bu^t, CH_2CMe_2Ph), affords the respective dialkyls $Cr(NR)_2R^1_2$ **255a–c** (Scheme 56). These dialkyls undergo insertion reactions with R^2NC ($R^2 = Bu^t$, 2,6-$Me_2C_6H_3$) to give η^2-iminoacyl derivatives.

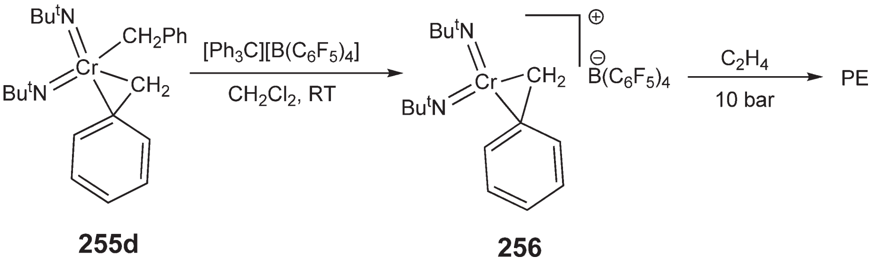
Gibson's group has also synthesized bis(imido)chromium(VI) dialkyls by the reaction of $Cr(NR)_2Cl_2$ (R = Bu^t, 2,6-$Pr^i{}_2C_6H_3$)[237] with 2 equiv. of R^1MgCl ($R^1 = CH_3$, CH_2Ph).[238] The dibenzyl complex $Cr(NBu^t)_2(CH_2Ph)_2$ (**255d**; R = Bu^t, $R^1 = CH_2Ph$) displays both η^1- and η^2-benzyl ligands in the solid and solution states. Subsequent addition of $[Ph_3C][B(C_6F_5)_4]$ affords the η^2-benzyl cation, $[Cr(NBu^t)_2(CH_2Ph)][B(C_6F_5)_4]$ **256**, which is a rare example of a well-defined, homogeneous chromium(VI) ethylene polymerization catalyst (activity = 25 to 66 g PE/(mmol-Cr h bar)) (Scheme 57). Gibson *et al.* have also reported additional syntheses of bis(arylimido) complexes, alternative catalyst activation procedures, and more extensive polymerization testing data.[239,240] For example, activation of $Cr(NBu^t)_2Cl_2$ with Et_2AlCl or MAO provides only moderate activity catalysts (9.0 and 4.4 g PE/(mmol-Cr h bar), respectively). On the other hand, bis(imido) dialkyl precatalysts such as **255e** (R = 2,6-$Pr^i{}_2C_6H_3$, $R^1 = CH_2Ph$) typically provide much more active catalytic species. Several dialkyl complexes can be readily activated with boron



Scheme 55



Scheme 56



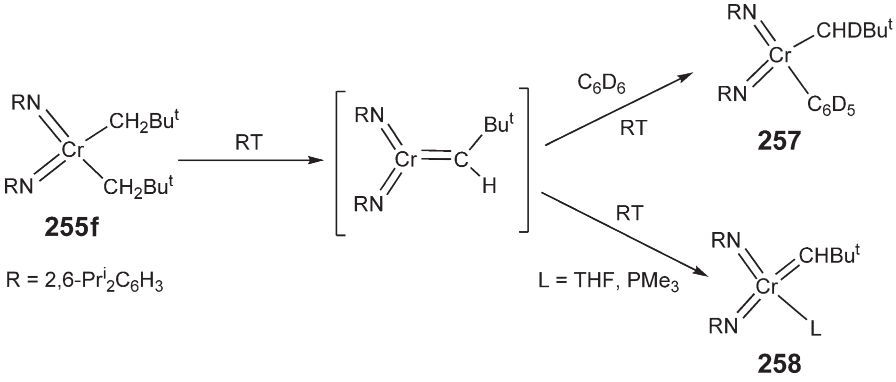
Scheme 57

reagents $[PhNMe_2H][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$, and $B(C_6F_5)_3$, producing catalysts with activities ranging from 20 to 66 g PE/(mmol-Cr h bar).

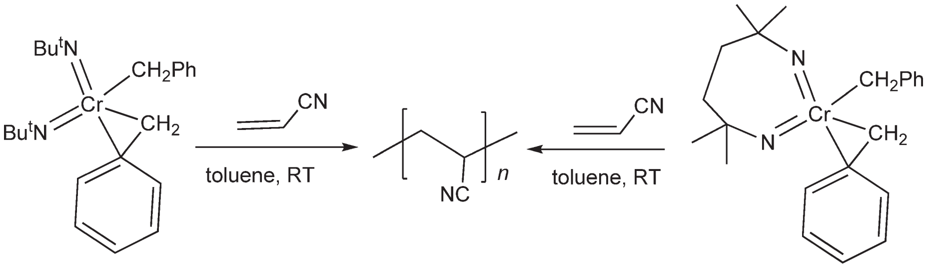
Finally, the bis(neopentyl) derivative, **255f** ($R = 2,6\text{-}Pr^i{}_2C_6H_3$, $R^1 = CH_2Bu^t$), undergoes clean elimination of CMe_4 at room temperature to form a chromium(VI) alkylidene, which reacts rapidly with the C–D bond of C_6D_6, forming $(2,6\text{-}Me_2C_6H_3N)_2Cr(CHDBu^t)(C_6D_5)$ **257**, and with donor ligands to form adducts $(2,6\text{-}Me_2C_6H_3N)_2Cr(CHBu^t)(L)$ **258** (Scheme 58).[241] Somewhat surprisingly, the intermediate alkylidene does not react with ethylene or norbornene.

5.05.8.1.2.(ii) Insertion reactions of functionalized monomers

Siemeling *et al.* have extended the polymerization potential of bis(imido) complexes to include polar monomers. Specifically, **255d** ($R = Bu^t$, $R^1 = CH_2Ph$) and the *ansa*-bis(imido) complex, $Cr(NCMe_2CH_2CH_2CMe_2N)(CH_2Ph)_2$ **259**, are effective single-component catalysts for the homopolymerization and co-polymerization of functionalized monomers such as acrylonitrile, methylmethacrylate, and vinylacetate;[242,243] note that these reactions do not require separate addition of co-catalyst (Scheme 59). *ansa*-Complex **259** and its unbridged benzyl analog **255d** are structurally similar, including the now familiar η^1- and η^2-benzyl ligation; however, **259** is more thermally robust than its



Scheme 58



255d **259**

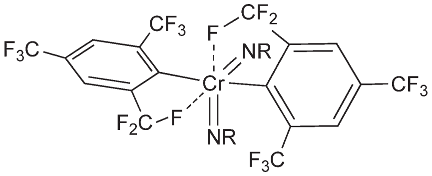
Scheme 59

unbridged counterpart. Nevertheless, benzyl derivatives **255d** and **259** produce polymers with similar properties. Of particular note, the polyacrylonitrile product possesses unusually high molecular weight ($M_w = 1{,}200{,}000$) with relatively narrow polydispersity ($M_w/M_n = 2.8$).

5.05.8.1.2.(iii) Bis(adamantylimido) derivatives

Readily crystallizable bis(adamantylimido) chromium(VI) complexes have also been prepared, including bis(alkyl) derivatives $Cr(NAd)_2R^1_2$ (R = Ad = adamantyl; $R^1 = CH_2Ph$, CH_2Bu^t, CH_2CMe_2Ph).[244] As with the previously described benzyl complexes, the bis(adamantylimido) derivative possesses both η^1- and η^2-benzyl ligands. Furthermore, the bis(neophyl) complex $Cr(NAd)_2(CH_2CMe_2Ph)_2$ shows evidence of α-agostic C–H···Cr interactions in the solid state. Apparently, the ethylene polymerization performance of bis(adamantylimido) complexes has not been examined.

Gibson's group has also prepared and structurally characterized $Cr(NR)_2(fmes)_2$ (**260**; R = Bu^t, Ad; fmes = 2,4,6-tris(trifluoromethyl)phenyl), which incorporates the sterically hindered (and electron-withdrawing) fluorinated aryl ligand.[245,246] The solid-state structure of **260** exhibits distorted tetrahedral coordination along with weak Cr···F interactions (2.421 to 2.468 Å) involving the two *ortho*-CF_3 groups, giving rise to pseudo-six-coordinate geometry at chromium; similar geometries have been noted previously for non-fluorinated analogs.[247] No further reactivity or polymerization studies of these fluorinated compounds have been described.



R = Bu^t, Ad

260

5.05.8.1.2.(iv) Halogenated bis(arylimido) derivatives

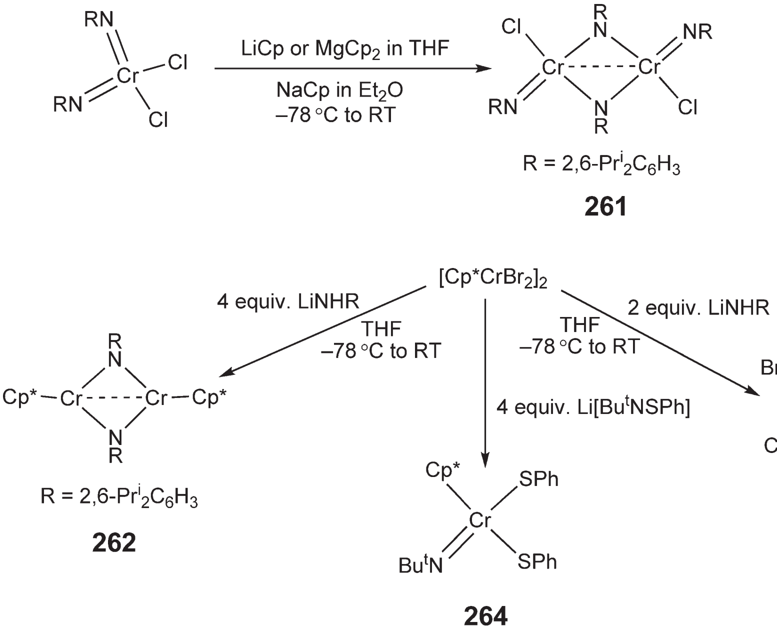
Halogenated bis(arylimido) complexes $Cr(NR)_2Cl_2$ (R = 2,6-$Cl_2C_6H_3$, 2,4,6-$Br_3C_6H_2$) are effective cyclopropanation catalysts. Reaction of ethyldiazoacetate with various substituted styrenes in the presence of catalytic (<1 mol.%) amounts of $Cr(NR)_2Cl_2$ produces cyclopropanated products in moderate to high yields depending on the structure of the styrene; α-methylstyrene provides cyclopropanated product in 64% yield whereas 4-chlorostyrene yields the corresponding product in 91% yield.[248]

5.05.8.2 Cyclopentadienyl Chromium Imido Derivatives

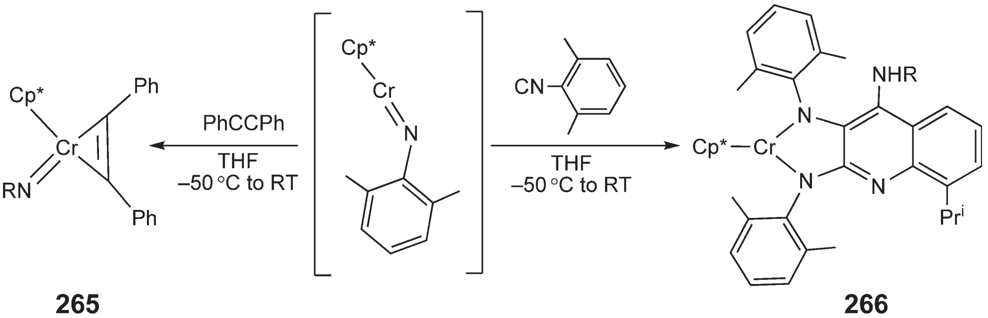
Chromium(V) mono(imido) organometallic complexes have been prepared, including those with Cp-supporting ligands. For example, treatment of $Cr(NBu^t)Cl_3(dme)$ (dme = dimethoxyethane) or $[PPh_4][Cr(NBu^t)Cl_4]$ with TlCp gives the paramagnetic ($\mu_{eff} = 1.7\ \mu_B$) $CpCr(NBu^t)Cl_2$.[249] However, attempts to prepare the Cp* analog, by using LiCp^* in place of TlCp, have been unsuccessful and there are no reported attempts to prepare Cr–C σ-bond derivatives via chloride replacement reactions with organolithium or Grignard reagents.

Attempts to prepare chromium(VI) half-sandwich complexes $\mathrm{CpCr(NR)_2X}$ by the reaction of $\mathrm{Cr(NR)_2X_2}$ with LiCp, NaCp, or $\mathrm{MgCp_2}$ leads instead to metal reduction and formation of a dimeric chromium(V) derivative $\mathrm{[Cr(NR)(\mu\text{-}NR)Cl]_2}$ **261** (Scheme 60).[250] On the other hand, metal–metal bonded chromium(III) complexes $\mathrm{[Cp^*Cr(\mu\text{-}NR)]_2}$ **262** are produced by the reaction of $\mathrm{[Cp^*CrBr_2]_2}$ with 4 equiv. of a sterically encumbered LiNHR ($\mathrm{R = 2,4,6\text{-}Bu^t_3C_6H_2}$, $\mathrm{2,6\text{-}Pr^i_2C_6H_3}$).[251] Significant metal–metal bonding and/or electronic exchange through the bridging imido groups results in antiferromagnetic interactions and low residual paramagnetism. Reaction of $\mathrm{[Cp^*CrBr_2]_2}$ with 2 equiv. of less bulky lithium amides, such as $\mathrm{LiNHC_6H_{11}}$ or LiNHPh, yields the corresponding chromium(IV) dimers $\mathrm{[Cp^*CrBr(\mu\text{-}NR)]_2}$ **263**, presumably via disproportionation, although the low-valent chromium co-product has not been identified. In addition, Wilkinson and Hursthouse have prepared the monomeric chromium(V) imido-thiolato complex $\mathrm{Cp^*Cr(NBu^t)(SPh)_2}$ **264** by the reaction of $\mathrm{[Cp^*CrBr_2]_2}$ with 4 equiv. of $\mathrm{Li(Bu^tNSPh)}$.[252] Various substituted arylimido derivatives, $\mathrm{Cp^*Cr(NAr)(SPh)_2}$, can be synthesized using similar reaction schemes.[253]

For bulky imido substituents such as $\mathrm{R = 2,6\text{-}Pr^i_2C_6H_3}$, the chromium(III) imido intermediate "CpCrNR" can be trapped with diphenylacetylene, providing monomeric $\mathrm{Cp^*Cr(NR)(PhCCPh)}$ **265** (Scheme 61).[251] The short Cr–N bond (1.659 Å) and nearly linear Cr–N–C angle (165.8°) strongly suggest that the imido ligand functions as a



Scheme 60

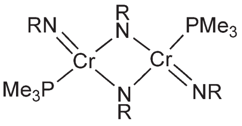


Scheme 61

six-electron donor. Attempted trapping of the chromium(III) imido with 2,6-xylyl isocyanide does not lead to a simple isocyanide adduct, but rather to the quinolineamido ligated complex **266** via a complex isocyanide–imido coupling reaction.

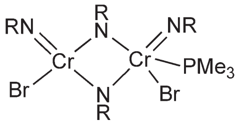
5.05.8.3 Additional Dinuclear Chromium(IV) and Chromium(V) Complexes

Wilkinson and Hursthouse have prepared several other imido-based dinuclear chromium complexes. The temperature-induced reduction of bis(imido) dialkyls **255a–c** ($R = 2,4,6\text{-}Me_3C_6H_2$, $R^1 = CH_2Ph$, CH_2Bu^t, CH_2CMe_2Ph) in the presence of PMe_3 results in alkyl group loss and the formation of a chromium(IV) bridging imido dimer $[Cr(NC_6H_2\text{-}2,4,6\text{-}Me_3)(\mu\text{-}NC_6H_2\text{-}2,4,6\text{-}Me_3)(PMe_3)]_2$ **267**.[236] In another reaction, attempted alkylation of bis(imido) dichloride **254a** ($R = 2,4,6\text{-}Me_3C_6H_2$) with BrMgEt, in the presence of PMe_3, does not lead to the expected chromium(VI) dialkyl, but rather to reduction of the chromium center with the formation of an unsymmetrical chromium(V) complex **268**. Furthermore, attempted alkylation of **254a** ($R = 2,4,6\text{-}Me_3C_6H_2$) with $ClMg(CH_2\text{-}4\text{-}C_6H_4CMe_3)$ does not produce a dialkylated product, but rather a symmetrical chromium(IV) bridging imido dimer **269** in which each chromium is coordinated by a mixed benzyl/aryl amido ligand. The mixed amido group presumably forms upon transfer of the benzyl group to an arylimido ligand with concomitant reduction of chromium from Cr(VI) → Cr(IV). In both dinuclear compounds, the presence of chromium–chromium bonding interactions and/or electronic exchange through the bridging ligands renders the complexes diamagnetic.



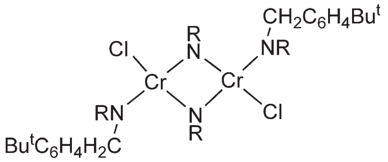
$R = 2,4,6\text{-}Me_3C_6H_2$

267



$R = 2,4,6\text{-}Me_3C_6H_2$

268

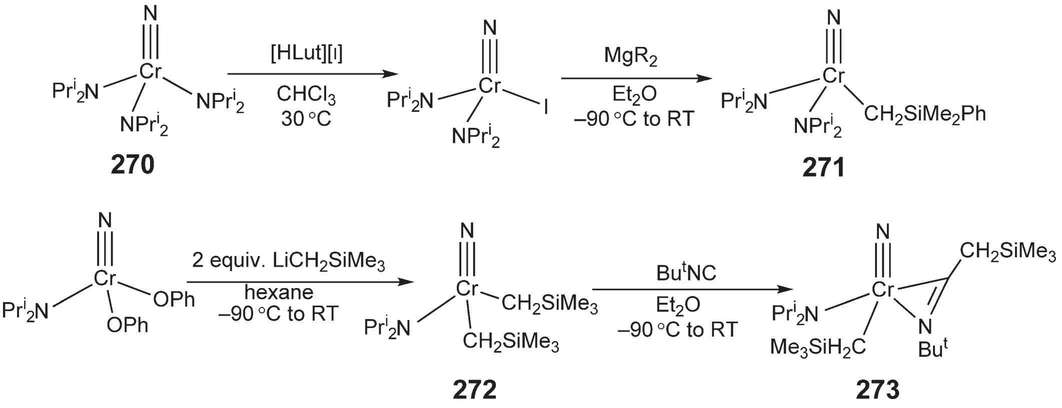


$R = 2,4,6\text{-}Me_3C_6H_2$

269

5.05.8.4 Organochromium Complexes with Nitrido Ligands

Only a few examples of organochromium complexes incorporating nitrido ligands have been reported (Scheme 62). In one example, Cummins describes the conversion of $[(Pr^i_2N)_3Cr(N)]$ **270** to the iodide derivative $[(Pr^i_2N)_2Cr(N)(I)]$ with 2,6-lutidinium iodide, followed by reaction with $Mg(CH_2SiMe_2Ph)_2$ to form the chromium(VI) organometallic derivative $[(Pr^i_2N)_2Cr(N)(CH_2SiMe_2Ph)]$ **271**.[254] The chromium–nitrido distances in **270** and **271** are similar (1.544 Å and 1.535 Å, respectively), whereas the chromium–amido distances are notably shorter (by 0.033 Å) in **271**; these trends are consistent with the better match provided by the two π-donor amido



Scheme 62

groups in **271** and the two symmetry-allowed π-bonding $N(p\pi) \rightarrow Cr(d\pi)$ interactions. A dialkyl derivative, $[(Pr^i_2N)Cr(N)(CH_2SiMe_3)_2]$ **272**, has been prepared from $[(Pr^i_2N)Cr(N)(OPh)_2]$ and 2 equiv. of $LiCH_2SiMe_3$ (Scheme 62).[255] Complex **272** reacts with Bu^{t}NC to afford the η^2-iminoacyl derivative $\{(Pr^i_2N)Cr(N)[\eta^2\text{-}C(NBu^t)(CH_2SiMe_3)](CH_2SiMe_3)\}$ **273**. Insertion of a second equivalent of Bu^{t}NC into the remaining Cr–alkyl bond has not been observed.

5.05.9 Chromium Complexes Supported by Ligands Containing O, N, P, and S Heteroatoms

The preparation of transition metal compounds containing non-Cp ligands has experienced renewed interest, driven in large part by the success of certain nickel and palladium bis(imine)[256] and iron pyridinebis(imine)[257,258] complexes to serve as olefin polymerization catalysts. The success in late transition metal complexes has fueled interest in non-Cp organometallic compounds across the transition metal series; two excellent reviews by Gibson have described recent advances in this field.[259,260] This chapter will summarize developments in chromium complexes supported by non-Cp ligands containing oxygen, nitrogen, phosphorus, and sulfur donor atoms; most often these ligands are multidentate. The primary focus will be on the structure, electronic properties, and reactivity of these complexes, especially as they relate to olefin polymerization. Many of the compounds described in the following sections do not contain chromium–carbon bonds. However, their use as precursors to olefin polymerization catalysts indicates that metal–carbon bonds can be supported by these ligand sets. The large impact that subtle ligand changes can have on polymerization performance (*vide infra*) ensures that this will continue to be a fruitful area of research. Even though there is a heavy emphasis on polymerization applications in the subsequent discussion, reactivity with small molecules (e.g., CO, H_2, alkynes, etc.,) will be highlighted where appropriate.

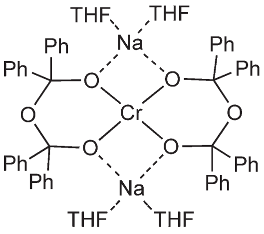
5.05.9.1 Anionic Monodentate [O], Bidentate [O$_2$], and Tetradentate [O$_4$] Supporting Ligands

5.05.9.1.1 Monodentate [O] derivatives

Organochromium complexes with exclusively monodentate aryloxy- or alkyloxy-ligands have not been extensively characterized by structural methods. However, the reaction products of chromium(III) tris(2-ethylhexanoate) and various hindered 2,6-substituted phenol ligands are effective ethylene trimerization catalysts when activated by $AlEt_3$ in aromatic ether solvents;[261] activities up to 32 g oligomer/(mmol-Cr h bar) and selectivities for 1-hexene within the C_6 fraction of up to 98% are observed. Presumably, substitution of hexanoate by aryloxy occurs, however, no characterization of the aryloxy-containing species has been provided. In addition, the reaction products of chromium(III) tris(2-ethylhexanoate) and sterically hindered cyclopentadienes (e.g., C_5Ph_5H, $C_5Ph_4H_2$) have been evaluated as catalysts in combination with $AlEt_3$; these mixtures display ethylene trimerization activity up to 50 g oligomer/(mmol-Cr h bar), with up to 93% selectivity for hexenes.[262] As in the previous case, the structures of the reaction products are not currently known.

5.05.9.1.2 Bidentate [O$_2$] derivatives

Chromium complexes with certain bidentate oxy ligands, such as disiloxanes and bis(phenoxide) derivatives, have been more completely characterized. For example, reaction of $CrCl_2$ with 2 equiv. of the disiloxane $Na_2[(OSiPh_2)_2O]$ yields $[Na(THF)_2]_2Cr[(OSiPh_2)_2O]_2$ **274**, which contains co-planar siloxane rings and square planar geometry at chromium.[263] Reaction of **274** with $AlEt_3$ produces a low activity (1.7 g PE/(mmol-Cr h bar)) ethylene polymerization catalyst. The related but more sterically hindered bis(phenoxide), 3,3′-bis(triphenylsilyl)-biphenoxide ($^{TPS}LO_2$), has been used to prepare monomeric $(^{TPS}LO_2)Cr(THF)_2$ **275**; this complex adopts a highly distorted square planar geometry at the chromium(II) center due to the bulky triphenylsilyl substituents.[264] The impact of such distortions on ethylene polymerization activity would be of interest but has not been examined. In another example, treatment of $CrCl_3(THF)_3$ with the relatively unhindered *rac*-Li_2(binol) (binol = 1,1′-bis-2-naphtholate) produces an octahedral tris-chelate chromium(III) complex **276** in low yield.[265] The compound's propeller-like geometry has been confirmed by X-ray crystallography; the average Cr–O bond length (1.988 Å) is relatively long in comparison to that of other chromium(III) derivatives, presumably due to the three formal negative charges on the hexacoordinate chromium center. When combined with MAO or Et_2AlCl, complex **276** displays moderate ethylene polymerization activity (15 g PE/(mmol-Cr h bar)).



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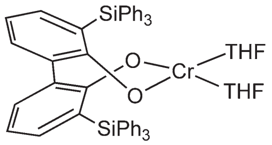

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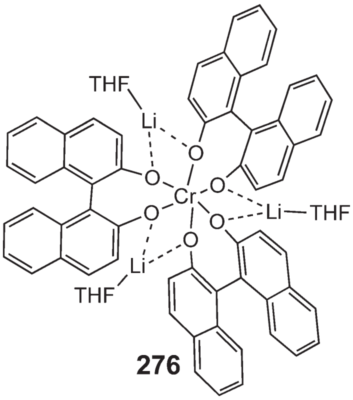

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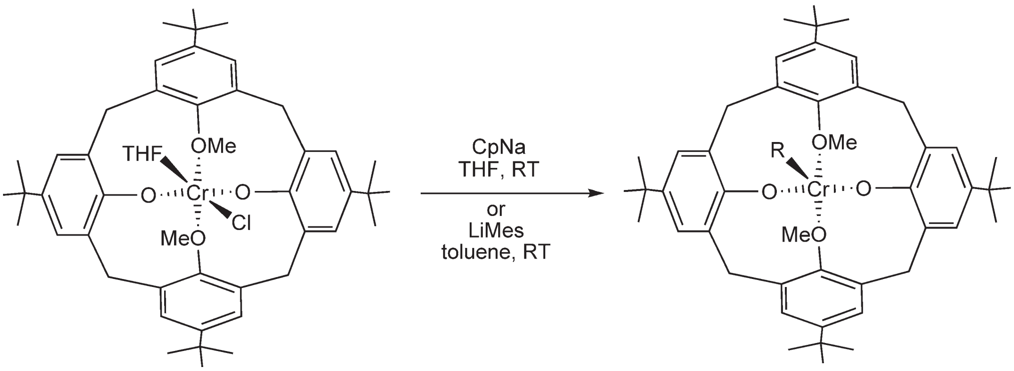
Bidentate acetylacetonate (acac) ligands have also been used in the context of chromium(III) chemistry. While no discrete acac-ligated organochromium complexes have been isolated or structurally characterized, they are used to form homogeneous $Cr(acac)_3/AlR_3$ catalyst mixtures for polymerizing ethylene[266] and 4-methyl-1-pentene.[267] Furthermore, heterogeneous $Cr(acac)_3/MgCl_2/AlR_3$ mixtures catalyze the formation of polyethylene,[268] polypropylene,[269] ethylene–propylene random co-polymers,[270] and ethylene–propylene block co-polymers.[271]

5.05.9.1.3 Tetradentate [O_4] derivatives

A series of discrete chromium(III) calix[4]arene complexes has been prepared by treating $CrCl_3(THF)_3$ with the potentially tetradentate *p*-Bu^{t}calix[4]$(ONa)_2(OMe)_2$.[272] Most notably, a useful high spin ($S = 3/2$) monochloro THF adduct **277** is formed, which can be subsequently converted into organochromium species. Gibson's group has also prepared a chromium(III) calix[4]arene complex; however, in the latter case, the chromium center is fully encapsulated by two fused calix[4]arene ring systems and is not amenable to further derivatization.[273] On the other hand, monomeric **277** serves as a useful precursor to five-coordinate mesitylene and Cp derivatives **278** (Scheme 63). Complex **277** is also readily reduced with sodium naphthalinide to form a high spin ($S = 2$) square pyramidal chromium(II) complex with the calix[4]arene ligand serving as a tetradentate donor and THF occupying the apical site. Furthermore, addition of O_2 to the reduced complex forms a structurally characterized di-μ-oxo chromium(IV) dimer. None of the aforementioned calix[4]arene complexes have been auditioned as ethylene polymerization catalysts; however, a mixture of lithiated *p*-Bu^{t}calix[4]arene, $CrCl_3(THF)_3$, and $AlEt_3$ is useful for polymerizing ethylene to low molecular weight polyethylene.[274]



R = Cp, Mes

277 **278**

Scheme 63

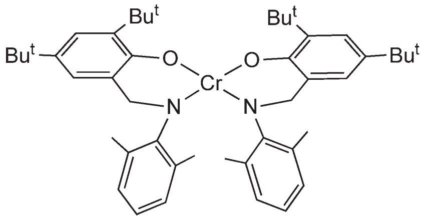
5.05.9.2 Anionic Monodentate [N] Supporting Ligands

The previously prepared $[N(SiMe_3)_2]_2Cr(THF)_2$[275] **279** is oxidized with I_2 to form a tetrahedral chromium(IV) complex, $[N(SiMe_3)_2]_2CrI_2$ **280**, and with dicumyl peroxide to give the trigonal planar chromium(III) derivative $[N(SiMe_3)_2]Cr(OCMe_2Ph)_2$ **281** (Scheme 64).[276] Complexes **279–281** are all similarly active for ethylene polymerization (40–50 g PE/(mmol-Cr h bar)) when treated with alkylaluminum co-catalysts, in spite of the significant variation in oxidation state (ranging from chromium(II) to chromium(IV)) and coordination geometry.

5.05.9.3 Anionic Bidentate [NO] and Tridentate [N$_2$O] Supporting Ligands

5.05.9.3.1 Bidentate [NO] ligand derivatives

Monomeric chromium complexes supported by sterically encumbered, anionic aza–oxy [NO] ligands have been prepared and examined as ethylene polymerization catalysts. For example, reaction of $CrCl_3(THF)_3$ with lithium and sodium salts of the reduced Schiff base ligand, $3,5\text{-}Bu^t{}_2\text{-}2\text{-}(OH)C_6H_2CH_2NH(2,6\text{-}Me_2C_6H_3)$, produces bis(ligand) chromium(II) and mono(ligand) chromium(III) complexes upon addition of one and two ligand equivalents, respectively.[277] The chromium(II) bis(ligand) structure **282** displays distorted square planar geometry with *cis*-coordinated oxygen and nitrogen atoms. In contrast to the typical high spin ($S=2$) behavior of square planar chromium(II) complexes, **282** possesses an intermediate spin ($S=1$) ground state ($\mu_{\text{eff}}=2.6\,\mu_B$). Upon isolation from acetonitrile, the high spin ($S=3/2$) chromium(III) mono(ligand) species **283** adopts a distorted octahedral arrangement around chromium with *trans*-chloride and *cis*-acetonitrile ligands completing the coordinate sphere. Both **282 and 283** are active ethylene polymerization catalysts when combined with MAO or Et_2AlCl, affording linear polyethylene. Complex **283** (chromium(III)) is especially active (130 g PE/(mmol-Cr h bar)) when combined with Et_2AlCl.



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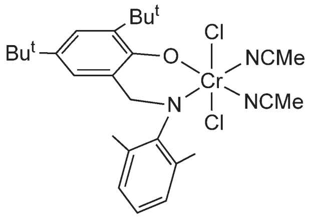

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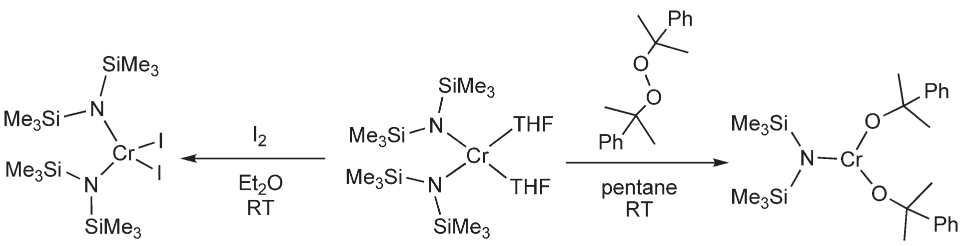
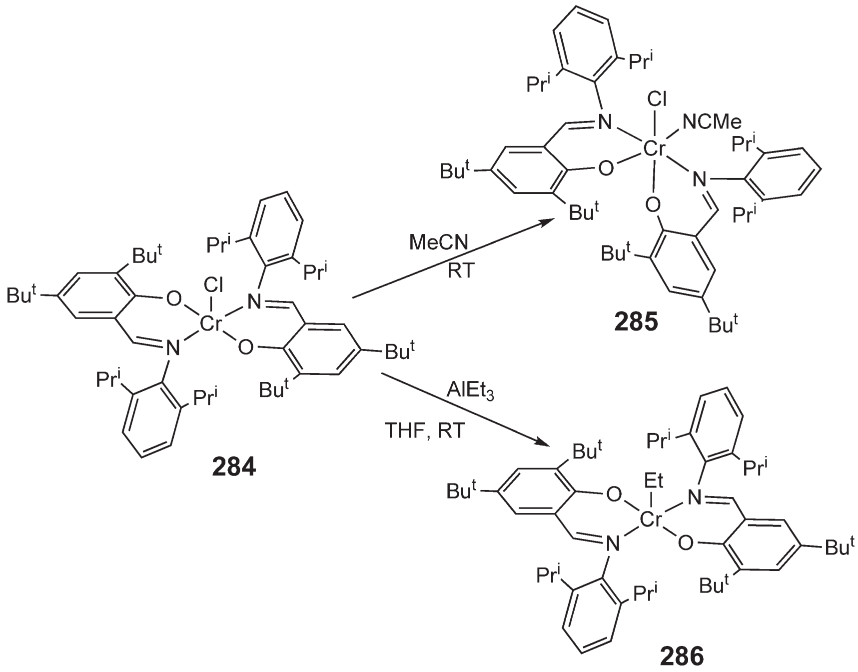
Salicylaldiminato-ligated compounds, oxidized ligand analogs of the reduced Schiff base compounds just described, are also known (Scheme 65). Reaction of 2 equiv. of $Li[3,5\text{-}Bu^t{}_2\text{-}2\text{-}(O)C_6H_2CHN(2,6\text{-}Pr^i{}_2C_6H_3)]$ with $CrCl_3(THF)_3$ leads to the bis(ligand) complex $[3,5\text{-}Bu^t{}_2\text{-}2\text{-}(O)C_6H_2CHN(2,6\text{-}Pr^i{}_2C_6H_3)]_2CrCl$ **284**.[278] Addition of acetonitrile to **284** generates the octahedral acetonitrile adduct **285**, which possesses bidentate [NO] ligands in a *cis*-arrangement. Alkylation of **284** with $AlEt_3$ leads to the $S=3/2$ ethyl derivative **286**, which displays square pyramidal geometry and *trans*-disposed [NO] ligands. The chromium–ethyl bond length in **286** is rather typical (2.065 Å) of other $S=3/2$ chromium(III) alkyls. Complexes **284–286** are active ethylene polymerization catalysts (50–100 g PE/(mmol-Cr h bar)), especially when combined with Et_2AlCl, and produce high molecular weight (up to $1.7\times10^6\,\text{g mol}^{-1}$) polyethylene.

A chromium(II) pyridyl enolate complex **287** has been prepared by the reaction of $CrCl_2(THF)_2$ with the potentially tridentate ligand $Na[(O)(Bu^t)C(2\text{-}CH_2NC_5H_3Me\text{-}6)_2]$.[279] This 6-Me substituted [N$_2$O] ligand undergoes fragmentation



280 **279** **281**

Scheme 64

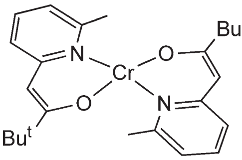


Scheme 65

via loss of 2,6-dimethylpyridine, generating the transient bidentate [NO] pyridyl enolate which subsequently reacts with $CrCl_2$ to form 287. The resulting [NO] ligands are bound in a *trans*-fashion with square planar geometry around chromium. The complex is presumably $S = 1$, although the measured magnetic moment ($\mu_{eff} = 3.2\,\mu_B$) is somewhat high for this spin state. Activation of 287 with Et_2AlCl generates a moderately active (35 g PE/(mmol-Cr h bar)) ethylene polymerization catalyst. Interestingly, attempts to use analogous 3-, 4-, and 5-Me substituted [N_2O] ligand derivatives result in oxidation to chromium(III) and generation of only high spin ($S = 3/2$), tris-chelated derivatives 288. This finding implies that the 6-Me group in 287 protects the chromium center from approaching pyridyl enolate ligands. Indeed, only with prolonged heating of 287 in toluene does oxidation to a 6-Me tris-chelate (analogous to 288) occur.

5.05.9.3.2 Tridentate [N_2O] ligand derivatives

An extensive library of chromium(III)–Schiff base complexes, some with additional donor appendages, has been prepared using high throughput screening techniques.[280] The ligand library has been generated by condensing substituted salicylaldehydes (typically containing bulky *ortho*-substituents) with 55 commercial amines. Reaction of the ligands *in situ* with (*p*-tolyl)$CrCl_2$(THF) generates [NO]- and [N_2O]-chelated complexes that have been screened for ethylene polymerization activity (after MAO activation). Complexes with [N_2O] ligation such as 289 are especially active catalysts (up to 6970 g PE/(mmol-Cr h bar)) and produce relatively low molecular weight polyethylene ($M_w = 1100\ \mathrm{g\,mol^{-1}}$). Complexes with bidentate salicylaldimine [NO] ligands, on the other hand, are also highly active but tend to produce higher molecular weight polymer ($M_w > 1 \times 10^6\ \mathrm{g\,mol^{-1}}$).



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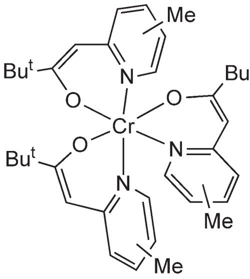

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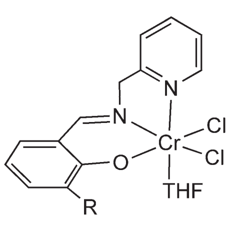


R = anthracenyl, triptycenyl

289

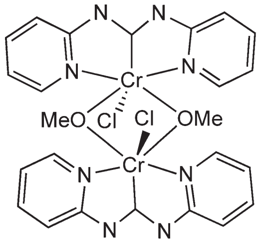
5.05.9.4 Anionic Bidentate [N_2] Supporting Ligands

5.05.9.4.1 Formamidinate derivatives

Formamidinate ligands, RNC(H)NR, typically bridge metal–metal bonded species via the nitrogen donor atoms. In an unusual reaction, treatment of $CrCl_2$ with the anion of N,N′-di(2-pyridyl)formamidine (HDpyF), followed by workup in methanol, yields the methoxy-bridged chromium(III) dimer $Cr_2(\mu\text{-OMe})_2(\eta^3\text{-N,C,N}'\text{-}H_2DpyF)_2Cl_2$ **290**.[281] In this case, metal ligation occurs via the pyridyl nitrogens and the sp^3-hybridized central carbon atom rather than through the ligand's inner nitrogen atoms. The chromium–carbon bond lengths (2.059 Å and 2.068 Å) are typical for chromium(III) complexes.

5.05.9.4.2 Diamido ligand derivatives

The chelating disiloxane-1,3-diamido ligand, $\{[(NBu^t)SiMe_2]_2O\}^{2-}$, reacts with $CrCl_2$ to produce a divalent chromium species formulated as the dimeric $Cr_2\{[(NBu^t)SiMe_2]_2O\}$ **291** based upon mass spectrometry results.[282] Similar reaction of $CrCl_3$ with the disiloxane-1,3-diamido ligand yielded the structurally characterized **292**, wherein one disiloxanediamido ligand bridges the two chromium(III) centers. Both **291** and **292** are activated with Et_2AlCl to form moderately productive (1.8 to 23 g PE/(mmol-Cr h bar)) ethylene polymerization catalysts.



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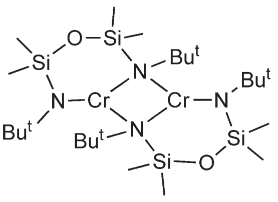

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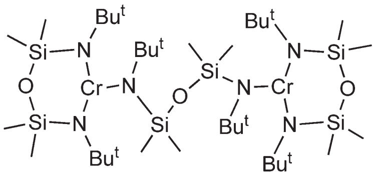

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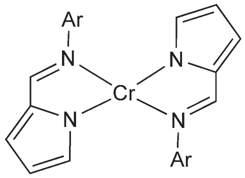
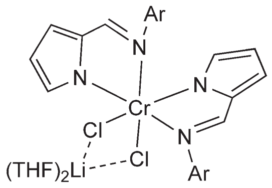
5.05.9.4.3 Iminopyrrolyl ligand derivatives

The bidentate iminopyrrolyl ligand family has been widely used in transition metal chemistry and the field was recently reviewed.[283] With regard to chromium chemistry, chromium(II) and chromium(III) complexes supported by bulky mono-anionic iminopyrrolyl ligands have been prepared by Gibson *et al.*[284] For example, reaction of lithium iminopyrrolyl with $CrCl_2$ yields **293**, which possesses the expected square planar geometry at chromium(II) with *trans*-oriented ligands. The chromium(III) product **294** displays octahedral geometry with *cis*-disposed chloride ligands. Apparently, the bulky iminopyrrolyl structure prevents tris-ligation to chromium(III). Alkylation of **294** with AlR_3 (R = Me, Et) yields neutral, coordinatively unsaturated alkyl derivatives **295**, wherein the alkyl ligand occupies the apical position in the square pyramidal structure. The alkyl derivatives do not polymerize ethylene in the absence of an activator. However, addition of 30 equiv. of Me_2AlCl to **293–295** produces high activity catalysts (up to 120 g PE/(mmol-Cr h bar)) for making high molecular weight polyethylene.



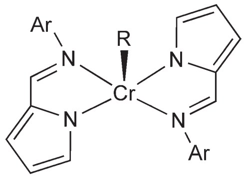
Ar = 2,6-$Pr^i_2C_6H_3$

293



Ar = 2,6-$Pr^i_2C_6H_3$

294



R = Me, Et
Ar = 2,6-$Pr^i_2C_6H_3$

295

5.05.9.4.4 Diketiminate ligand derivatives

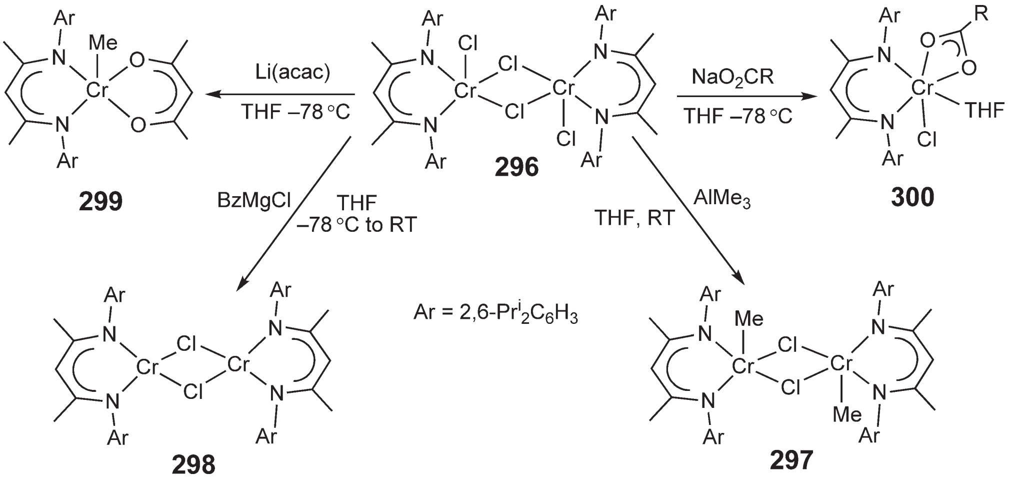
Monoanionic β-diketiminato ligands, based primarily upon the N,N-diaryl-2,4-pentanediimine structure, have received considerable recent attention. These ligands can be viewed as more versatile analogs of their β-diketonato (acac) relatives by virtue of the steric protection provided by appropriately chosen nitrogen substituents. A very thorough review by Lappert describes the synthesis, structure, and catalytic properties of group 1–14 metal β-diketiminates.[285] The present chapter will summarize recent work on organochromium derivatives and their olefin polymerization activity. For simplicity, we will utilize the "nacnac" acronym to describe β-diketiminate-substituted metal complexes; the term has been coined by Theopold to emphasize the structural similarity between β-diketiminato and β-diketonato ligands.

Gibson *et al.* report that bridging chloride derivative $\{[(2,6\text{-Pr}^i{}_2\text{Ph})_2\text{nacnac}]\text{CrCl}(\mu\text{-Cl})\}_2$ **296**, is prepared by treating $\text{CrCl}_3(\text{THF})_3$ with 1 equiv. of $\text{Li}[(2,6\text{-Pr}^i{}_2\text{Ph})\text{nacnac}]$.[286] Further reaction of **296** with AlMe_3 generates **297**, which is formed by methyl substitution at the apical position (Cr–C bond length = 2.037 Å) while leaving the bridging chloride structure intact (Scheme 66). Attempted alkylation of **296** with BzMgCl does not form the expected benzyl derivative, but leads instead to chromium reduction and formation of the chromium(II) dimer $\{[(2,6\text{-Pr}^i{}_2\text{Ph})_2\text{nacnac}]\text{CrCl}\}_2$ **298**.[287] Addition of bidentate ligands, such as β-diketonates or carboxylates, to **296** results in dimer cleavage and formation of monomeric compounds; five-coordinate square pyramidal structures **299** prevail for β-diketonate ligation, whereas six-coordinate, THF-ligated species **300** are formed upon carboxylate addition (Scheme 66). Compounds **296–300** are effective ethylene polymerization catalysts (up to 93 g PE/(mmol-Cr h bar)) after treatment with alkylaluminum reagents such as Me_2AlCl.

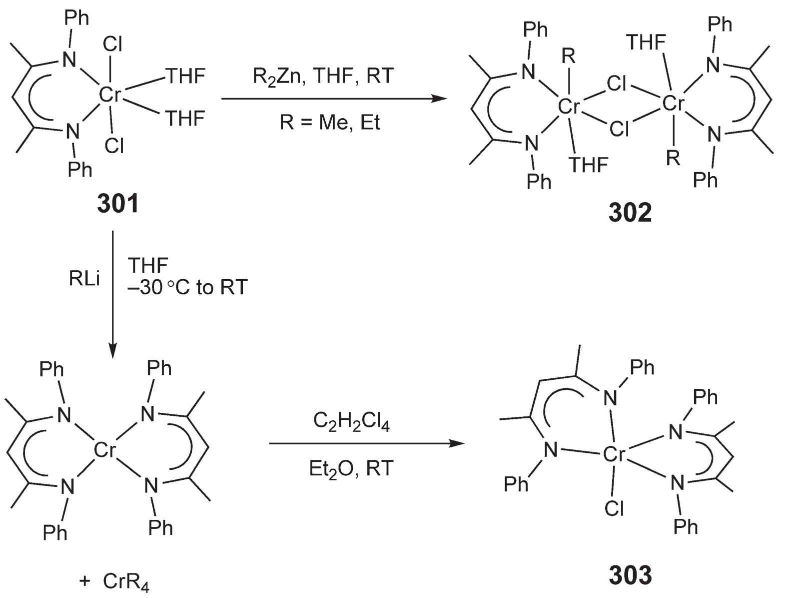
In complementary work, Theopold has shown that 1 equiv. of relatively unhindered $[(\text{Ph})_2\text{nacnac}]\text{Li}$ reacts with $\text{CrCl}_3(\text{THF})_3$ to give monomeric $[(\text{Ph})_2\text{nacnac}]\text{CrCl}_2(\text{THF})_2$ **301** with *trans*-disposed chloride ligands.[288] In contrast to the more hindered bridging chloride dimer **296**, monomeric **301** forms because THF effectively competes with chloride to fill the remaining chromium coordination sites. Thus, this represents a relatively unusual case of a less hindered ligand favoring a monomeric structure. Activation of **301** with MAO (130 equiv.) generates a moderately active ethylene polymerization catalyst (34 g PE/(mmol-Cr h bar)) capable of producing high molecular weight polyethylene ($M_w = 1.1 \times 10^6\ \text{g mol}^{-1}$).

In a more extensive study, Theopold has described transformations of **301** leading to various organometallic derivatives.[289] For example, monoalkyl $\{[(\text{Ph})_2\text{nacnac}]\text{CrR}(\mu\text{-Cl})(\text{THF})]\}_2$ **302** is prepared via alkylation of **301** with R_2Zn (R = Me, Et) (Scheme 67). Attempted alkylation with 2 equiv. of alkyllithium reagents results in disproportionation to CrR_4 and $[(\text{Ph})_2\text{nacnac}]_2\text{Cr}$; due to interligand steric effects, the chromium(II) complex adopts a distorted tetrahedral structure rather than the square planar geometry typically observed for compounds of this type. In a further reaction, oxidative chlorination of $[(\text{Ph})_2\text{nacnac}]_2\text{Cr}$ with $\text{C}_2\text{H}_2\text{Cl}_4$ yields the trigonal bipyramidal chromium(III) derivative $[(\text{Ph})_2\text{nacnac}]_2\text{CrCl}$ **303**.

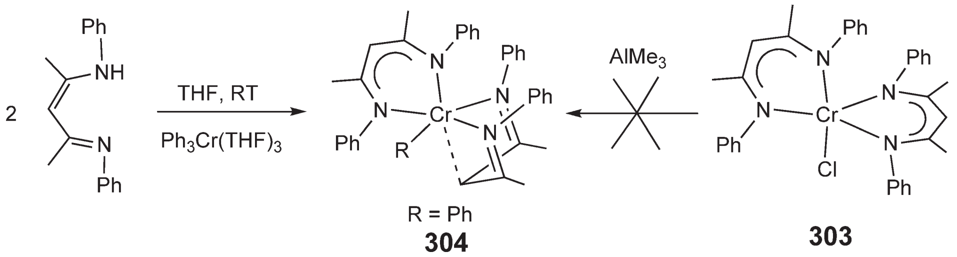
Attempts to substitute the chloride ligand in **303** via reaction with AlR_3 do not produce the desired chromium(III)–alkyl derivative, but rather a five-coordinate *ortho*-metallated product is formed, $(\text{Ph})_2\text{nacnac}(\eta^1\text{-C}_6\text{H}_4\text{-Ph})\text{nacnacCr}$,



Scheme 66



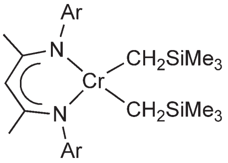
Scheme 67



Scheme 68

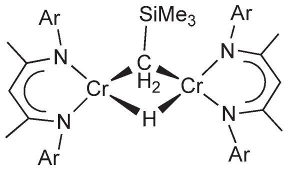
probably via σ-bond metathesis of the initially formed [(Ph)$_2$nacnac]$_2$CrR intermediate. However, [(Ph)$_2$nacnac]$_2$-CrPh **304** can be prepared by treating CrPh$_3$(THF)$_3$ with 2 equiv. of the parent (Ph)$_2$nacnacH ligand (Scheme 68). The structure of **304** is that of a distorted square pyramid; one nacnac ligand is bound in the usual planar η^2-manner, while the central carbon atom of the other ligand folds back toward the chromium center (Cr–C bond length = 2.56 Å), indicating that the latter ligand functions as an η^3-donor. Ethylene polymerization studies on **301–304** demonstrate that, with the notable exception of **304**, the chromium(III) derivatives are highly active catalysts when combined with MAO (132 to 1470 g PE/(mmol-Cr h bar)) and produce broad molecular weight distribution polymers. As often observed for organochromium-based catalysts, these particular chromium–nacnac catalysts do not incorporate significant amounts of propylene or 1-hexene during ethylene/α-olefin co-polymerization experiments.

In a separate study, Theopold found that use of the more hindered (2,6-Me$_2$Ph)$_2$nacnac ligand allows for the generation of stable dialkyl [(2,6-Me$_2$Ph)$_2$nacnac]Cr(CH$_2$SiMe$_3$)$_2$ **305**, which adopts a distorted tetrahedral structure.[290] Despite its 11-electron configuration, **305** surprisingly does not polymerize ethylene in the absence of additional co-catalysts. However, **305** is reactive with H$_2$; hydrogenation leads to reduction to chromium(II), liberation of SiMe$_4$, and formation of a bridging alkyl hydride dinuclear complex [(2,6-Me$_2$Ph)$_2$nacnacCr]$_2$(μ-CH$_2$SiMe$_3$)(μ-H) **306**.[291] The structure of **306** displays a butterfly core configuration due to interligand steric repulsions; its reduced magnetic moment (1.8 μ_B/Cr at 294 K) is consistent with significant antiferromagnetic coupling via the bridging ligands and/or metal–metal bonding (Cr–Cr distance = 2.6026 Å) interactions. A related bridging dihydride [(2,6-Me$_2$Ph)$_2$nacnacCr]$_2$(μ-H)$_2$ **307** is formed during attempted preparation of [(2,6-Me$_2$Ph)$_2$nacnac]CrEt$_2$, apparently via β-H elimination from the unstable diethyl intermediate. The chromium(II) dihydride dimer also displays a reduced magnetic moment ($1.2\,\mu_B$/Cr at 294 K) and significant metal–metal bonding (Cr–Cr = 2.6207 Å).



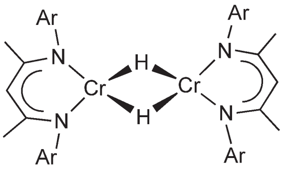
Ar = 2,6-$Me_2C_6H_3$

305



Ar = 2,6-$Me_2C_6H_3$

306

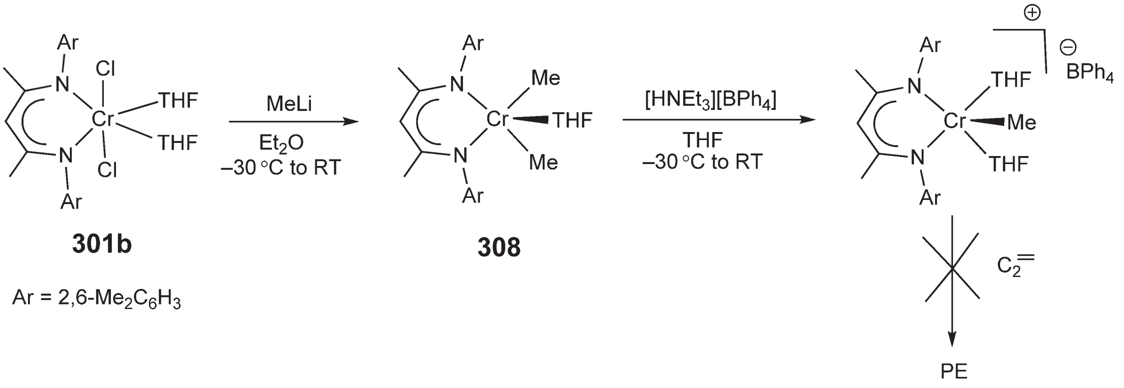


Ar = 2,6-$Me_2C_6H_3$

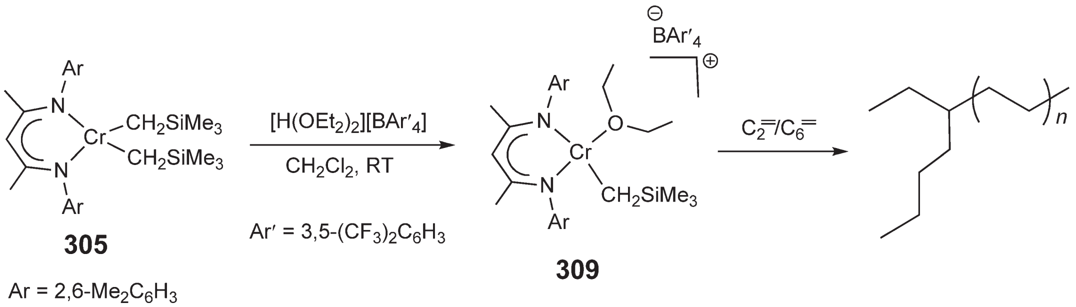
307

The hindered (2,6-$Me_2Ph)_2$nacnac ligand has also been used to prepare other alkyl derivatives.[292] For example, reaction of [(2,6-$Me_2Ph)_2$nacnac]$CrCl_2(THF)_2$ **301b** with 2 equiv. of MeLi yields the neutral dialkyl [(2,6-$Me_2Ph)_2$nacnac]$CrMe_2$(THF) **308**. Protonation of the **308** with [$HNEt_3$][BPh_4] generates cationic {[(2,6-$Me_2Ph)_2$nacnac]CrMe$(THF)_2$}[BPh_4], which surprisingly fails to display polymerization activity (Scheme 69). This lack of activity is in stark contrast to the related Cp* analog [Cp*CrMe$(THF)_2$][BPh_4],[293] which was previously shown to be an effective single-component polymerization catalyst.

However, in very recent work, ethylene polymerization activity has been observed for diethyl ether-ligated derivatives.[292] In this case, protonation of dialkyl **305** with [$H(OEt_2)_2$][$BAr^F{}_4$] ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) yields the stable ether-ligated monoalkyl {[(2,6-$Me_2Ph)_2$nacnac]Cr(CH_2SiMe_3)(Et_2O)}[$BAr^F{}_4$] **309**, which readily loses Et_2O to form an active ethylene polymerization catalyst (Scheme 70). While catalyst activity is only moderate (22 g PE/(mmol-Cr h bar)), the polymeric product is extremely uniform as evidenced by its low polydispersity ($M_w/M_n = 1.2$). Furthermore, polymer molecular weight increases with ethylene conversion, indicating that **309** displays some attributes of a living polymerization system. Also notable is the ability of **309** to incorporate high



Scheme 69



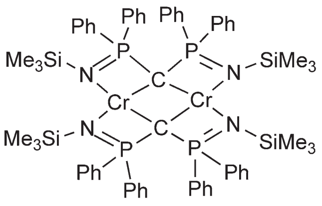
Scheme 70

levels of 1-hexene (103 branches per 1000 C atoms) during ethylene/1-hexene co-polymerization experiments. This co-polymerization behavior contrasts with that of most organochromium catalysts studied to date, but is similar to that displayed by the commercial Phillips (Cr/SiO_2) catalyst; thus, monomeric **309** is purported to serve as a reasonable structural and reactivity model for the commercial Cr/SiO_2 system. For comparative purposes, the reader is referred to a recent review that summarizes the current understanding of the commercial Phillips catalyst (structure and reactivity).[294]

5.05.9.4.5 Bis(phosphoranimine) ligand derivatives

Dianionic bis(phosphoranimine)methandiide donors represent another family of anionic [N_2] ligands. Cavell *et al.* have recently summarized the synthesis and reactivity of early metal complexes incorporating bis(phosphoranimine)-methandiide ligands.[295] With regard to chromium complexes, reaction of $CrCl_2(THF)_2$ with $Li_2\{C(Ph_2P{=}NSiMe_3)_2\}$ forms the dimeric bis(ligand) complex $\{C(Ph_2P{=}NSiMe_3)_2\}_2Cr_2$ **310**.[296] The dimer displays a central square planar Cr_2C_2 core with relatively short Cr–C interactions (2.128 Å to 2.150 Å). The remainder of the ligand protrudes above and below the Cr_2C_2 plane to produce distorted tetrahedral geometries at each chromium center.

In related work, Stephan *et al.* have utilized a mono-anionic bis(phosphoranimine)methanide ligand derivative, $Li\{HC(Ph_2P{=}NSiMe_3)_2\}$, to prepare the chromium(II) dimer $\{[HC(Ph_2P{=}NSiMe_3)_2]Cr(\mu\text{-}Cl)\}_2$ **311**.[297] X-ray crystallography reveals that, in the asymmetric unit, one dimer possesses trigonal bipyramidal chromium centers with chromium bound to the each ligand's central carbon atom (Cr–C = 2.264 Å), while the other dimer possesses distorted square planar geometry at chromium without significant Cr–C interactions (Cr–C = 2.921 Å). In any event, MAO activation of **311** yields a moderately effective ethylene polymerization catalyst (60 g PE/(mmol-Cr h bar)) that produces broad molecular weight distribution polymer.



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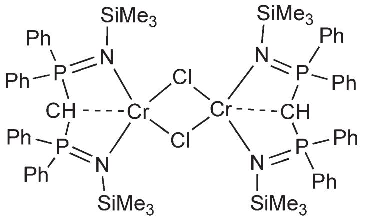
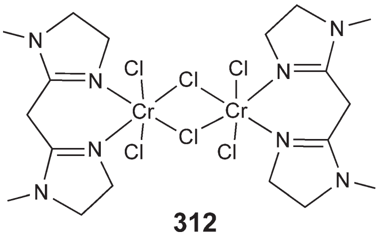


311

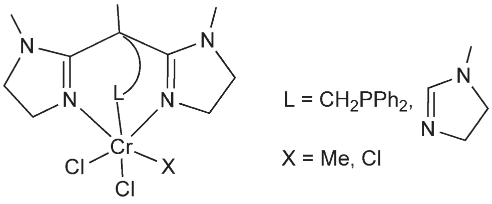
5.05.9.5 Neutral Bidentate [N_2] and Tridentate [N_3] Supporting Ligands

5.05.9.5.1 Bis(imidazolyl) ligand derivatives

Chromium(III) complexes containing bis(imidazolyl)methane-based chelates are formed by the reaction of $MeCrCl_2(THF)_3$ or $CrCl_3(THF)_3$ with the appropriate substituted ligand.[298,299] Bis(imidazolyl)methane ligands without an additional coordinating donor atom produce bridging chloride dimers **312** upon reaction with $CrCl_3(THF)_3$, whereas ligands with an additional donor (imidazole or $\text{-}CH_2PPh_2$ linkage) yield monomeric chromium(III) complexes **313** as indicated by mass spectrometry and magnetic susceptibility data. The dimeric structures can be cleaved with coordinating solvents (e.g., MeCN) to form monomeric complexes. Activation of monomeric or dimeric complexes with MAO yields relatively low activity (typically <5 g oligomer/(mmol-Cr h bar)) ethylene oligomerization catalysts.



312



313

5.05.9.5.2 Triazacyclohexane and triazacyclononane ligand derivatives

The tridentate η^3-coordinating behavior of cyclic triaza ligands such as 1,3,5-triazacyclohexane (TACH) and 1,4,7-triazacyclononane (TACN) has been exploited to prepare numerous facially coordinated chromium complexes.

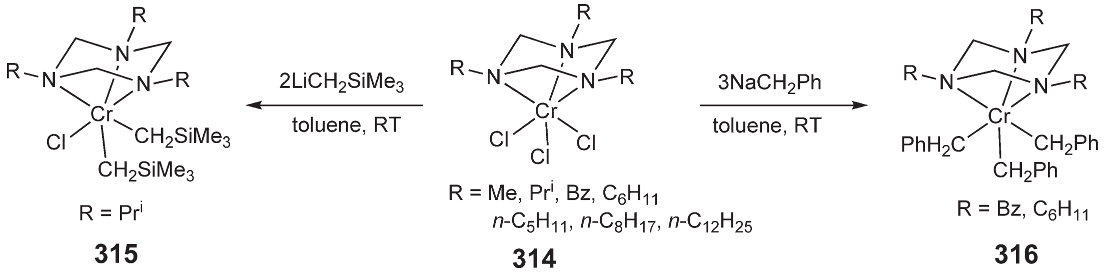
5.05.9.5.2.(i) R_3TACH ligated complexes

With regard to TACH compounds, substitution at nitrogen has provided a wide variety of R_3TACH ligands and several have been used to prepare chromium(0) carbonyl and chromium(III) halide complexes. Included in this set are chromium derivatives with N-alkyl ligand substituents (R = Me, Et, Bu^t),[300,301] plus those with pendant hydroxy (R = CH_2CH_2OH, $CH_2C_6H_4$-2-OH)[302] and alkyne (R = $CH_2CH_2CH_2C{\equiv}CH$)[303] substituents. In the latter two cases, metal binding of the hydroxy and alkyne functionalities was not observed. Köhn and co-workers have been particularly active in this area and have reported the straightforward synthesis of (R_3TACH)$CrCl_3$ complexes **314** by addition of R_3TACH (R = Me, Pr^i, Bz, C_6H_{11}) to $CrCl_3(THF)_3$.[304,305] Subsequent treatment of (Pr^i_3TACH)$CrCl_3$ with 2 equiv. of $LiCH_2SiMe_3$ produces dialkyl (Pr^i_3TACH)$CrCl(CH_2SiMe_3)_2$ **315** (Scheme 71).[303] Similarly, alkylation of (Bz_3TACH)$CrCl_3$ and (Cy_3TACH)$CrCl_3$ (Cy = C_6H_{11}) with 3 equiv. of NaBz provides the stable tribenzyl derivatives; the crystal structures of **315** and (R_3TACH)$CrBz_3$ (**316**; R = C_6H_{11})[304] reveal fairly typical Cr(III)–C bond lengths (averaged 2.083 Å and 2.122 Å, respectively). Activation of (R_3TACH)$CrCl_3$ complexes (R = Me, *n*-C_5H_{11}, *n*-C_8H_{17}, *n*-$C_{12}H_{25}$) with MAO yields high activity ethylene polymerization catalysts (450 to 720 g PE/(mmol-Cr h bar)); increased activity correlates loosely with larger/longer R groups.[306] The (R_3TACH)$CrCl_3$/MAO system displays some selectivity toward 1-hexene formation and is also able to effectively co-polymerize ethylene and 1-hexene. Thus, the (R_3TACH)$CrCl_3$/MAO catalyst resembles the previously described cationic chromium(III)–nacnac complex **309** and certain donor-functionalized Cp derivatives (e.g., **155–162**) in its ability to polymerize α-olefins.

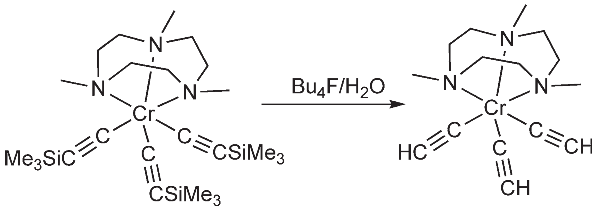
The selective olefin trimerization potential of (R_3TACH)$CrCl_3$/MAO systems has been extended to include propylene, 1-hexene, and styrene monomers[307] as well as 1-decene and 1-dodecene.[308] The latter two olefins are readily trimerized to C_{30} and C_{36} oligomers, respectively. These olefinic products can be subsequently hydrogenated to form alkanes with useful viscosity indices for synthetic lubricant applications. Interestingly, during oligomerization of 1-decene and 1-dodecene, branching at the α-position of the catalyst amino substituent (R) tends to suppress the desired trimerization reaction and enhance the undesired olefin isomerization process; thus, straight chain aliphatic substituents are preferred. In addition to standard MAO co-catalysts, complex **314** is also activated with a combination of $AlBu^i_3$ and $[PhNMe_2H][B(C_6F_5)_4]$, yielding similar olefin trimerization behavior.[309] In this same report, catalyst deactivation studies in arene solvents indicate that transfer of R_3TACH to aluminum and formation of bis(arene)chromium(I) cations are key deactivation steps. The isolation of chromium(I) species is consistent with an olefin trimerization mechanism that involves reductive elimination of 1-hexene with concomitant formation of a chromium(I) intermediate during the catalytic cycle.

5.05.9.5.2.(ii) R_3TACN ligated complexes

With respect to substituted 1,4,7-triazacyclononane ligands (R_3TACN), chromium(III) complexes have been prepared, including derivatives with pendant 2-pyridylmethyl[310] and carboxamide[311] donors. Unfortunately, in these latter cases, the pendant donors are also bound to chromium, forming five- and six-coordinate structures,



Scheme 71



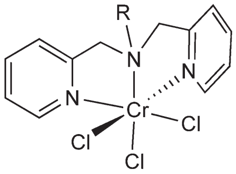
317a **317b**

Scheme 72

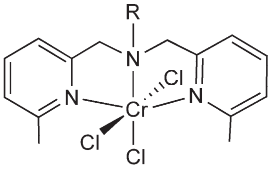
which hampers their subsequent derivatization or conversion to organometallic derivatives. In one final example, a chromium(III) tris(trimethylsilylacetylide) complex, $[(Me_3TACN)Cr(C{\equiv}CSiMe_3)_3]$ **317a**, has been produced upon the reaction of $[(Me_3TACN)Cr(CF_3SO_3)_3]$ with excess $LiC{\equiv}CSiMe_3$.[312] Deprotection of **317a** to form the triacetylide **317b** is accomplished with wet Bu_4NF (Scheme 72). The acetylide ligands are able to coordinate potassium and cesium ions, forming binary (dichromium) and ternary (trichromium) complexes with the respective alkali metal.

5.05.9.5.3 Bis(2-pyridylmethyl)alkylamine ligand derivatives

Octahedral chromium(III) complexes supported by unsubstituted and 6-methyl substituted bis(2-pyridylmethyl)alkylamines adopt *fac*-**318a** and *mer*-**318b** coordination geometries, respectively.[313] After activation by MAO, the *fac*-complexes display moderate ethylene polymerization activity (up to 18 g PE/(mmol-Cr h bar)) and are 30–40 times more active than their *mer*-counterparts. Furthermore, *fac*-complexes tend to produce significant quantities of lower molecular weight polymer. The preferential adoption of a *fac*-coordination geometry has also been proposed to account for the selective trimerization of ethylene using a chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/$AlEt_3$/alkyl halide catalyst mixture.[314]



R = n-C_3H_7, n-C_6H_{13}
318a



R = n-C_3H_7, n-C_6H_{13}
318b

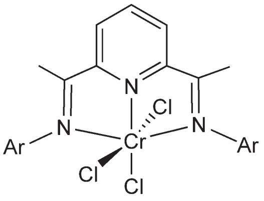
5.05.9.5.4 Pyridinebis(imine) and related ligand derivatives

Tridentate pyridine-2,6-bis(imine) ligands (PBI = $2,6\text{-}[ArN{=}C(Me)]_2C_5H_3N$; Ar = substituted aryl) have received significant recent attention due to their ability to support highly active late transition metal (Fe, Co) polymerization catalysts,[315,316] including some with the ability to polymerize propylene stereoselectively.[317] The PBI ligand family has been subsequently applied to chromium complexes. For example, Gambarotta *et al.* have prepared $(PBI)CrCl_3$ **319** utilizing a PBI ligand with Ar = $2,6\text{-}(Pr^i)_2C_6H_3$.[318] The crystal structure of **319** shows the expected *mer*-coordination geometry, with the aryl rings oriented nearly perpendicular to the PBI plane. Attempted alkylation of **319** with $AlMe_3$ forms does not lead to new chromium–carbon bonds; instead a pentacoordinate chromium(II)–PBI complex is formed with $ClAlMe_3^-$ ligands in the remaining two coordination positions. Attempted alkylation of **319** with BzMgCl also does not lead to chromium–benzyl species, but results in reduction to chromium(II), alkylation of the pyridine ring, and subsequent coupling of the alkylated pyridyl rings to form a complex bridged dimeric structure.

In complementary work, Esteruelas and co-workers have extended chromium–PBI chemistry by preparing numerous $(PBI)CrCl_3$ derivatives **319** with a wide range of N-aryl ring substitution patterns. For ethylene polymerization purposes, especially useful substitutions were those at the aryl 2,6-positions (*ortho*-positions).[319] Upon treatment with MAO, **319** derivatives form high activity ethylene polymerization catalysts and the resulting catalyst activity and polymer properties depend primarily on the identity (number and size) of the *ortho*-substituents. The highest activities (up to 2500 g PE/(mmol-Cr h bar)) are achieved with two small *ortho*-substituents; however, bulkier substituents tend to produce higher molecular weight product.

Small *et al.* have examined other chromium(II) and chromium(III) PBI derivatives and reported that single substitution at the *ortho*-position yields ethylene dimerization catalysts selective for 1-butene. The dimerization behavior switches to ethylene oligomerization and then to polymerization as the size and number of *ortho*-substituents increases.[320] Moreover, this same study shows that chromium(II) and chromium(III) PBI complexes combine with MAO to produce nearly identical catalyst activities and polymer properties. Moreover, the activated catalysts display identical UV–vis spectra suggesting that similar catalytic species are formed upon MAO activation regardless of the initial chromium oxidation state. However, the exact structure of this catalytic species remains ambiguous.

Chromium complexes supported by *mer*-coordinating ligands that are structurally related to PBI have also been prepared. In one case, (PYBOX)$CrCl_3$ **320** is formed by the reaction of $CrCl_3(THF)_3$ with 2,6-bis[(4*S*)-Pr^i-2-oxazolin-2-yl]pyridine (PYBOX).[321] Similar to PBI-ligated complexes, **320** displays *mer*-geometry in the solid state. However, in contrast to the highly active **319**/MAO systems, **320**/MAO is only a moderately active ethylene polymerization catalyst (5.2 g PE/(mmol-Cr h bar)). The reasons for this dramatic shift in activity are not entirely clear given the structural similarity between **319** and **320**. In another related example, pyridinebis(carbene) chromium(III) complexes **321** have been prepared upon the reaction of $CrCl_3(THF)_3$ with the appropriate substituted pyridinebis(carbene) ligand (R = Pr^i, 2,6-$Pr^i_2C_6H_3$, adamantyl).[322,323] These compounds display extremely high ethylene oligomerization activity in the presence of MAO, producing up to 40 000 g oligomer/(mmol-Cr h bar) for R = 2,6-$Pr^i_2C_6H_3$. The oligomeric product forms with Schulz–Flory constants in an industrially relevant range (K = 0.75–0.80) and the K value is somewhat sensitive to steric bulk on the carbene ligand; larger R groups tend to produce higher molecular weight product. Thus, the product slate can be adjusted by judicious choice of ligand substituents.



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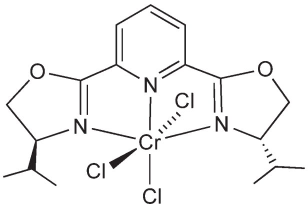

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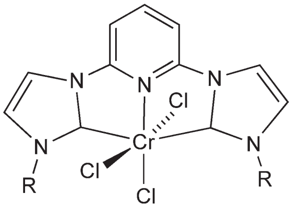

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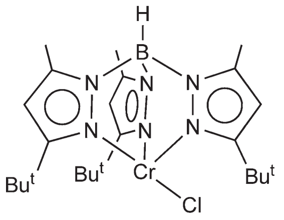
5.05.9.6 Anionic Tridentate [N_3] Supporting Ligands

The trispyrazolylborate (Tp) ligand and its many substituted analogs have served as a remarkably versatile tridentate ligand in transition metal chemistry.[324,325] Recently, this ligand class, especially sterically encumbered derivatives, has been employed in organochromium chemistry.

5.05.9.6.1 Chromium(II) derivatives

With respect to chromium(II) chemistry, reaction of $CrCl_2$ with $KTp^{tBu,Me}$ ($Tp^{tBu,Me}$ = hydrotris(3-Bu^t-5-Me-pyrazolyl)borate) generates the chromium(II) complex ($Tp^{tBu,Me}$)CrCl **322**.[326] A similar reaction with added pyridine produces ($Tp^{tBu,Me}$)CrCl(py) **323**. In both cases, residual 3,5-substituted pyrazole (from the initial preparation of $KTp^{tBu,Me}$) leads to the formation of some pyrazole-ligated complex ($Tp^{tBu,Me}$)CrCl(pyrazole) as well. The solid-state structure of **322** displays a remarkable distortion from idealized C_{3v} symmetry; the Cl atom is positioned nearly *trans* to one of the pyrazole nitrogens. This arrangement leaves two open *cis*-coordination sites producing the so-called "*cis*-divacant" octahedral geometry. The reaction of pyridine-ligated **323** with Grignard reagents produces chromium(II) alkyl (R = Et, CH_2SiMe_3) and aryl (R = Ph) species ($Tp^{tBu,Me}$)CrR **324** which no longer coordinate pyridine; in the solid state, the R = Et and Ph derivatives possess fairly typical chromium(II)–carbon bond lengths (2.111 Å and 2.129 Å, respectively) and the same "*cis*-divacant" coordination geometry as observed in **322**. Alkyl derivatives **324** do not polymerize ethylene, which further supports the contention that divalent chromium species are incompatible with high olefin polymerization activity.[327]



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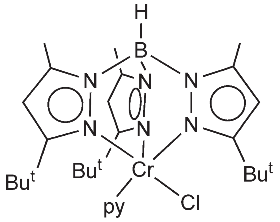

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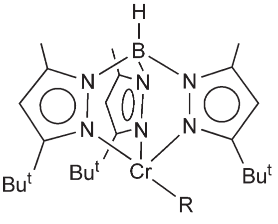
5.05.9.6.2 Chromium(III) derivatives

For chromium(III) complexes, reaction of $(Tp^{Me2})CrCl_2(DMAP)$[328] with 2 equiv. of MeLi or BzMgCl generates the dialkyl derivatives $(Tp^{Me2})CrR_2(DMAP)$ **325** (R = Me, Bz; Tp^{Me2} = hydrotris(3,5-Me_2-pyrazolyl)borate; DMAP = N,N-dimethylaminopyridine).[329] Both dialkyl derivatives are air stable and display slightly distorted octahedral geometries with facially coordinated Tp^{Me2} and *cis*-disposed alkyl ligands. The Cr–C bond lengths (2.07 Å to 2.13 Å) are fairly typical of chromium(III) complexes. Polymerization catalyst evaluation data has been reported. An unsubstituted Tp-containing derivative has been formed by addition of $CrCl_3(THF)_3$ to KTp followed by salt metathesis with Ph_4PBr to form $[Ph_4P][TpCrCl_3]$.[330] This octahedral complex is activated with MAO to yield a moderately active (15 g PE/(mmol-Cr h bar)) ethylene polymerization catalyst.



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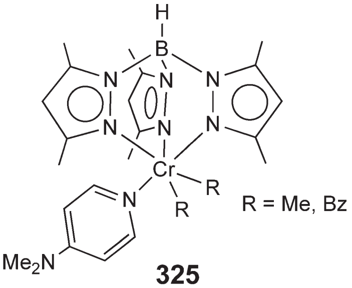

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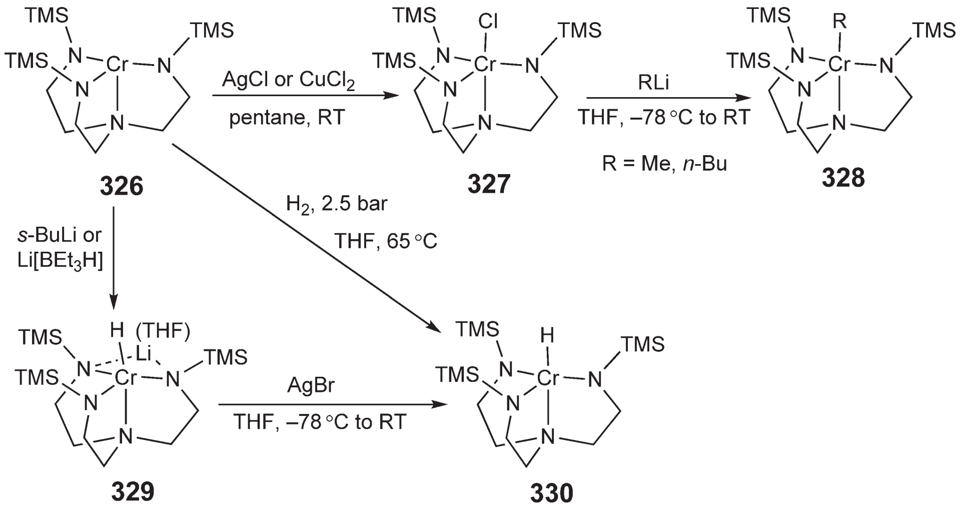
Finally, a brief review by Gade has outlined the use of numerous tridentate nitrogen-based ligands to support group 4 complexes.[331] Such neutral, triaza ligands, including diamidopyridyl derivatives, should also be effective ligands for organochromium complexes, however, their use to date in chromium chemistry has been limited.

5.05.9.7 Anionic and Neutral Tetradentate [N_4] Supporting Ligands

5.05.9.7.1 Triamidoamine-ligated derivatives

Triamidoamines, $[(RN(H)CH_2CH_2)_3N]$, can be deprotonated to form tetradentate, trianionic [N_4] ligands that bind transition metals with enforced trigonal pyramidal coordination geometry. Such coordination environments are atypical for chromium(III) and chromium(IV), which normally adopt octahedral and tetrahedral geometries, respectively. Thus, the steric enforcement of unnatural coordination geometries might be expected to impart unusual reactivity to the chromium centers.

Toward this end, treatment of $CrCl_3(THF)_3$ with a slight excess of $Li_3[(RNCH_2CH_2)_3N]$ affords $[(RNCH_2CH_2)_3N]Cr$ (**326**, R = $SiMe_3$).[332] A related derivative with R = Bu^tMe_2Si was prepared earlier by Schrock but was not structurally characterized.[333] The solid-state structure of **326** shows the chromium(III) ion in a rare trigonal pyramidal environment with the trimethylsilyl groups forming a protective pocket above the chromium atom. Oxidation of **326** with AgCl, $PhICl_2$, or $CuCl_2$ yields a trigonal bipyramidal chromium(IV) chloride $[(RNCH_2CH_2)_3N]CrCl$ **327**, wherein the protective pocket houses the Cr–Cl bond (Scheme 73). Both **326** and **327** are high spin, possessing magnetic moments consistent with $S = 3/2$ and $S = 1$ ground spin states, respectively.



Scheme 73

Additional trigonal bipyramidal chromium(IV) $[(RNCH_2CH_2)_3N]CrX$ derivatives are prepared (X = CN, Br, F, I) using analogous synthetic routes.[334] Alkylation of 327 can be accomplished with RLi (R = Me, Bu^n), yielding high spin $[(Me_3SiNCH_2CH_2)_3N]CrR$ derivatives 328.[335] The chromium(IV) alkyls 328 are unreactive toward ethylene, much like their homoleptic chromium(IV)–alkyl (CrR_4) counterparts. It is also noteworthy that the stability of $[(Me_3SiNCH_2CH_2)_3N]Cr(Bu^n)$ is somewhat unusual, given the tendency of many chromium–alkyls, albeit typically in lower metal oxidation states, to undergo β-hydride elimination. Indeed, attempted alkylation of 326 or 327 with *s*-BuLi leads not to an alkylation product, but rather to the chromium(III) hydridochromate, (THF)-$Li[(Me_3SiNCH_2CH_2)_3N]CrH$ 329, presumably via β-hydride elimination from an unstable *s*-butylchromate intermediate (Scheme 73).[336] Hydridochromate 329 can also be prepared from 326 and traditional hydride sources, such as $LiBEt_3H$. The corresponding chromium(IV) hydride, $[(RNCH_2CH_2)_3N]CrH$ 330, is obtained by oxidation of 329 with AgBr or by direct reaction of 326 with H_2; the latter route represents the only known oxidative addition of H_2 to a chromium(III) center. Both high spin chromium(III) and (IV) hydrides 329 and 330 have been structurally characterized and each exhibits trigonal bipyramidal geometry in the solid state with similar Cr–H bond lengths (1.58 Å and 1.56 Å, respectively).

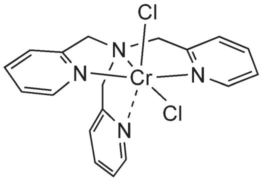
5.05.9.7.2 Porphyrin-ligated derivatives

With regard to planar $[N_4]$ ligands, organometallic porphyrin complexes (TTP)CrR (TTP = meso-tetra-*p*-tolylporphyrin; R = Ph, $p\text{-}Bu^tC_6H_4$, CH_2SiMe_3) have been prepared via the reaction of (TTP)CrCl with RLi reagents.[337] In deuterated solvent, (TTP)CrR reacts with O_2 to generate (TTP)Cr(O) species and RD, indicating that homolysis of the Cr–R bond occurs with subsequent trapping of R by the deuterated solvent. The Cr–R bond in (TTP)CrR is stable to heat but can be cleaved with acid or halogenating agents. No polymerization data has been reported.

5.05.9.7.3 Tris(2-pyridylmethyl)amine-ligated derivatives

The potentially tetradentate tris(2-pyridylmethyl)amine (TPA) has been used to form stable chromium(II) and chromium(III) complexes.[338] Reaction of $CrCl_2$ with TPA generates the monomeric $(TPA)CrCl_2$ 331, which displays significant Jahn–Teller distortion (long axial Cr–Cl and Cr–N bonds) in the solid state, consistent with its high spin ($S = 2$) electronic ground state. Chromium(III)–TPA derivatives have also been prepared by the reaction of $CrCl_3(THF)_3$ with 1 equiv. each of TPA and $NaBAr_4$ (Ar = Ph, 3,5-$(CF_3)_2C_6H_3$), generating $[(TPA)CrCl_2][BAr_4]$ 332; complex 332 possesses the octahedral geometry expected of an $S = 3/2$ chromium(III) center. Whereas attempted alkylation of chromium(II) 331 with Grignard or RLi reagents leads to intractable oils, reaction of $[(TPA)CrCl_2][BAr_4]$ with RMgCl (R = Me, Ph) generates stable cationic alkyl and aryl derivatives $[(TPA)CrR_2][BAr_4]$ 333. The organometallic complexes display fairly typical chromium(III)–carbon bond lengths

(2.078 Å and 2.095 Å for R = Me; 2.074 Å and 2.102 Å for R = Ph). The chromium(II) and chromium(III)–TPA complexes **331–333** are moderately active ethylene polymerization catalysts in the presence of MAO (10 to 22 g PE/(mmol-Cr h atm)), producing low to moderate molecular weight polyethylene.



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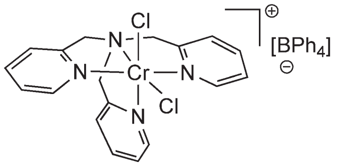

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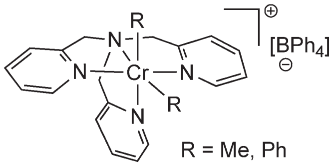

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5.05.9.8 Tridentate [S_3], Tetradentate [S_4], and Mixed Tridentate [NS_2] Ligands

5.05.9.8.1 Tridentate and tetradentate thioether derivatives

A few chromium(III) compounds supported by tridentate and tetradentate thioether ligation have been prepared in which the thioether forms a part of a macrocyclic ring. Included in this set are ([9]aneS_3)$CrCl_3$ and [([14]aneS_4)$CrCl_2$][PF_6] complexes.[339,340] X-ray structural analysis of the latter complex shows it to possess *cis*-disposed chloride ligands; however, organometallic derivatives have apparently not been prepared nor has any polymerization activity data been reported.

5.05.9.8.2 Tridentate mixed amine–thiolate/amine–thioether derivatives

Chromium complexes supported by tridentate aminebis(thiolate)and aminebis(thioether) ligands have been prepared. In an example using the former ligand, reaction of bridging bromide dimer [Cp^*CrBr_2]$_2$ with the aminebis (thiolate) $HN(CH_2CH_2SNa)_2$ produces $Cp^*Cr(\eta^3\text{-}NH(CH_2CH_2S)_2)$ **334**.[341] Attempts to convert the bound ligand to an aminebis(thioether) by the reaction of **334** with MeI in methanol forms [$Cp^*CrI(\mu\text{-}OMe)$]$_2$ as the only isolable chromium species; oxidation and methylation of the ligand forms the disulfide $(MeSCH_2CH_2NHCH_2CH_2S)_2$, which is subsequently displaced from the metal.

Chromium(III) chloride complexes supported by neutral aminebis(thioether) ligands have been prepared by the reaction of $CrCl_3(THF)_3$ with $HN(CH_2CH_2SR)_2$ (**335**; R = Me, Et, Bu^n, *n*-decyl).[342] X-ray structural analysis of the R = Et derivative confirms the *mer*-coordination geometry. Activation of **335** with MAO yields ethylene trimerization catalysts that are highly active (up to 200 g hexene/(mmol-Cr h bar)) and highly selective for 1-hexene (up to 99.8%). The remarkable 1-hexene selectivity of **335** allows this catalyst to be coupled with group 4 metallocene catalysts (similarly activated by MAO) to produce LLDPE using ethylene as the only monomer source.[343]

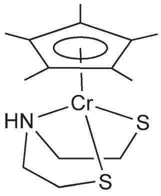
5.05.9.9 Phosphine-based Supporting Ligands

Phosphine ligands have been used extensively to support organochromium complexes in both chromium(II) and chromium(III) oxidation states. The phosphine ligands include anionic and neutral bidentate [P_2] structures as well as neutral tridentate [P_3] derivatives.

5.05.9.9.1 Anionic and neutral bidentate [P_2] ligated derivatives

5.05.9.9.1.(i) Chromium(II) complexes

Deprotonation of the methylene bridge in diphenylphosphinomethane (dppm) provides the diphosphinomethanide ion [$Ph_2PCHPPh_2$]$^-$, a formally six-electron diphosphine donor. Reaction of this anionic diphosphine with $CrCl_2(THF)_2$ produces a bridging chloride dinuclear complex **336**, which displays one pentacoordinate (square pyramidal) and one tetracoordinate (square planar) chromium(II) center.[344]



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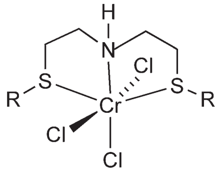

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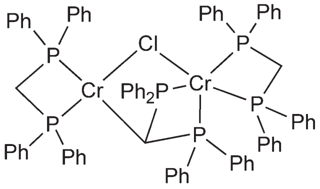
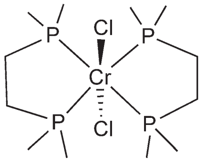


336

Chromium(II) complexes with more traditional neutral chelating diphosphine ligands, such as $CrCl_2(dmpe)_2$ and $CrMe_2(dmpe)_2$ **337** (dmpe = dimethylphosphinoethane), are effective catalysts for 1,3-diene polymerization when combined with MAO or $AlEt_3$. The chemo- and stereoselectivity of the polymer is determined largely by the monomer structure.[345] For example, 1,3-butadiene is polymerized to 1,2-syndiotactic polybutadiene, whereas isoprene and (*E*)- and (*Z*)-1,3-pentadiene form 3,4-amorphous polyisoprene, *cis*-1,4-isotactic poly[(*E*)-pentadiene] and *cis*-1,4-atactic poly[(*Z*)-pentadiene], respectively. A proposed active site structure with one dmpe ligand and an η^3-bonded growing polymer chain **338** allows the entering monomer to insert at C1 or C3, giving rise to the differing polymer structures.

A more extensive series of octahedral chromium(II) complexes supported by bis(dimethylphosphino)methane (dmpm), 1,2-bis(diethylphosphino)ethane (depe), 1,3-bis(diethylphosphino)propane (depp), and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) has been examined.[346] X-ray crystallography shows that the $CrCl_2(depe)_2$ derivative adopts the expected octahedral structure with *trans*-disposed chlorides. The Cr–P distances in $CrCl_2(depe)_2$ are 0.037 Å longer than those found in $CrCl_2(dmpe)_2$, indicative of weaker ligand binding in the depe complex. The polymerization of 1,3-butadiene by $CrCl_2(dmpm)_2$–MAO produces primarily 1,2-isotactic structures, whereas $CrCl_2(depe)_2$–MAO and $CrCl_2(depp)_2$–MAO yield 1,2-syndiotactic polymers, as does the previously described $CrCl_2(dmpe)_2$–MAO system. The much more hindered phosphine system, $CrCl_2(dcpe)_2$–MAO, exhibits low activity and poor chemoselectivity (both 1,2- and *cis*-1,4-polybutadiene structures are formed). Collectively, these polymerization results indicate that modest ligand bulk at phosphorus favors 1,2-syndiotactic polymeric structures, whereas less bulky phosphines, such as dmpm, produce 1,2-isotactic sequences. Wilkinson and Hursthouse have prepared similar *trans*-$CrCl_2(diphos)_2$ **339** complexes with relatively unhindered 1,2-bis(phosphino)benzene and 1,2-bis(isopropylphosphino)benzene, as well as 1,2-bis(dimethylphosphino)benzene ligands.[347] The polymerization of 1,3-butadiene by these latter complexes has not been explored; however, the lack of significant steric bulk at phosphorus would presumably favor the generation of 1,2-isotactic polybutadiene.



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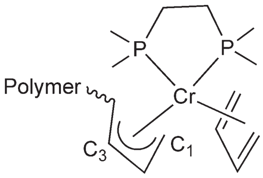

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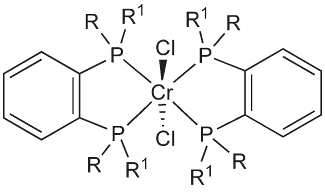


R = H, Me
R^1 = H, Me, Pr^i

339

5.05.9.9.1.(ii) Chromium(III) complexes and their ethylene oligomerization behavior

As mentioned previously in this chapter, catalysts capable of selectively oligomerizing ethylene to highly valued 1-hexene and 1-octene fractions are of special interest. A comprehensive review of ethylene trimerization technology has appeared, which includes the important role that chromium compounds have played.[348] Among the chromium-derived oligomerization catalysts, many supported by phosphine-based ligands are particularly effective and these are described in the paragraphs that follow.

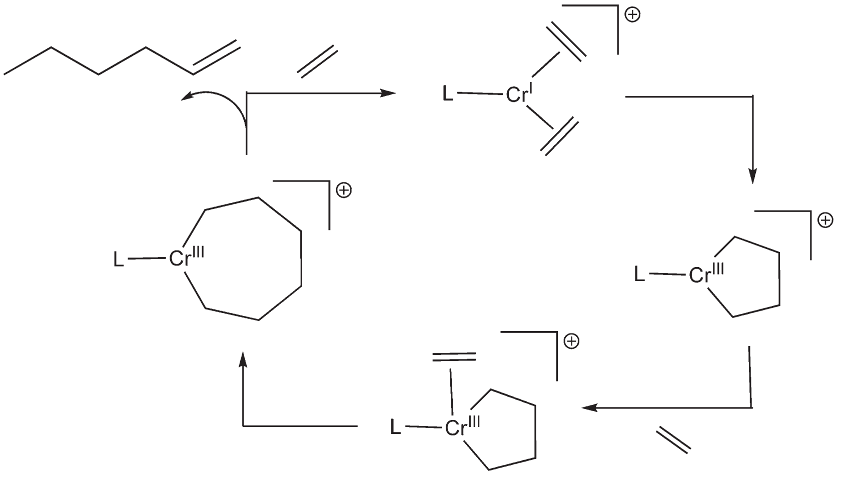
For example, in work completed at BP Chemical, bidentate diphosphinoamine ligands (PNP^{OMe}) of the type $Ar'_2PN(Me)PAr'_2$ (**340**; Ar′ = *ortho*-methoxy substituted aryl group; $R^1 = R^2 = R^3 = R^4 =$ OMe, $R^5 =$ Me) combine *in situ* with $CrCl_3(THF)_3$ to produce highly active ethylene trimerization catalysts after activation with MAO; activities up to 2700 g oligomer/(mmol-Cr h bar) have been obtained.[349] The oligomerization products are typically >80%

hexenes, with the selectivity toward 1-hexene (within the C_6 fraction) often being >99.5%. Under BP Chemical's test conditions, *ortho*-methoxy aryl substituents in **340** are absolutely necessary for catalyst activity as is the PNP backbone structure; complexes formed by using methylene ($Ar'_2PCH_2PAr'_2$) and ethylene ($Ar'_2PCH_2CH_2PAr'_2$) bridged diphosphine ligands are ineffective catalysts. Note that in **340**, the central nitrogen atom does not bind to the metal center but merely serves as a bridge between the two phosphorus donors.

Bercaw's group has isolated discrete (PNP^{OMe})$CrCl_3$ and (PNP^{OMe})$CrPh_3$ complexes[350] by reacting PNP^{OMe} with $CrCl_3(THF)_3$ and $CrPh_3(THF)_3$ **341**, respectively. Complex **341** has been structurally characterized and displays (P,P,O)-κ^3 coordination of the diphosphine ligand, wherein a single *ortho*-methoxy group binds to chromium to complete the octahedral coordination. Treatment of **341** with $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ produces an active catalyst that displays turnover frequency and selectivity for 1-hexene similar to that of MAO-activated catalysts. Moreover, the Bercaw group has shown that a 1 : 1 molar mixture of C_2D_4 and C_2H_4 produces only 1-hexenes C_6D_{12}, $C_6D_8H_4$, $C_6D_4H_8$ and C_6H_{12} in a 1 : 3 : 3 : 1 ratio. This very significant experiment provides clear and convincing evidence for a mechanism involving metallacycloheptane intermediates as shown in Scheme 74.

Very similar, and in some cases identical, catalyst systems have been examined by a research group at Sasol. However, in stark contrast to BP Chemical's requirement for *ortho*-methoxy groups, the Sasol team has found that **340** derivatives with *ortho*-alkyl groups ($R^1 = R^2 = R^3 = R^4 =$ Me, Et, Pr^i, $R^5 =$ Me, Pr^i) are very productive oligomerization catalysts (up to 350 g oligomer/(mmol-Cr h bar)).[351] Sasol's reaction conditions were different from those employed by BP, including higher pressure, lower temperature and a 1 : 2 (rather than 1 : 1) Cr : ligand ratio; still the difference in polymerization performance is striking. In the Sasol work, hexene and octene are the primary products formed, and these usually represent >90 wt.% of the total product mass. Bulkier *ortho*-alkyl groups favor the formation of 1-hexene over 1-octene as does the introduction of steric bulk at the bridging nitrogen.

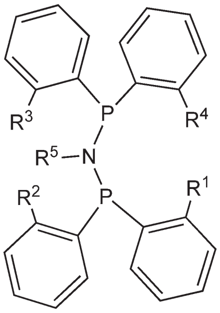
Even without *ortho*-substituents on the ligand's aryl rings (**340**; $R^1 = R^2 = R^3 = R^4 =$ H, $R^5 =$ Me), high oligomerization activities are still obtained (up to 680 g oligomer/(mmol-Cr h bar)) and the product slate shifts primarily to a C_8 composition; typically >95% selectivity for 1-octene is observed within the C_8 fraction.[352] A discrete chromium–$[P_2]$ ligand complex has been isolated as part of this study; the compound adopts a dimeric $[Cr(Ph_2PN(Ph)PPh_2)Cl_2(\mu\text{-}Cl)]_2$ **342** structure with each chromium atom displaying distorted octahedral geometry. Importantly, complex **342** is catalytically competent when combined with MAO, yielding activity and α-olefin selectivity comparable to that of *in situ* prepared catalysts; these findings indicate that the dimer and the *in situ* prepared complex likely form similar catalytic species. Moreover, the Sasol team found that diphosphine ligands of the type $Ph_2PN(Me)N(Me)PPh_2$ and $Ph_2PCH_2CH_2PPh_2$ (dppe) also provide active oligomerization catalysts when combined with a suitable chromium(III) source and MAO, although the amount of undesired polyethylene side-product became substantial. Finally, altering the aryl substitution pattern in **340** from *ortho* to *meta* to *para* changes the catalytic behavior from selective trimerization to predominantly tetramerization.[353] The authors assert that steric bulk in the vicinity of the metal center (*ortho*-substitution) forces the metallacycloheptane intermediate into a conformation favorable for β-hydride



L = multidentate ligand

Scheme 74

elimination, leading to preferential 1-hexene production. Without such constraints, olefin insertion is more competitive with elimination, skewing the product distribution toward 1-octene. Also, with *ortho*-methoxy substituents, competitive binding of the methoxy donor to chromium can retard ethylene binding and insertion, again favoring 1-hexene formation.



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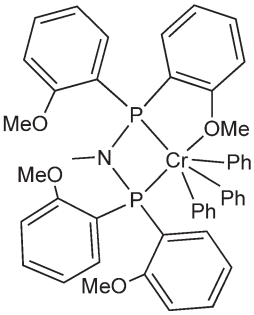

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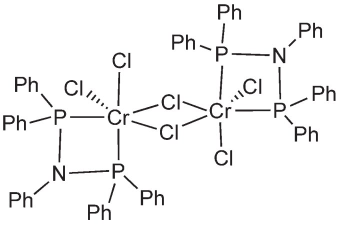

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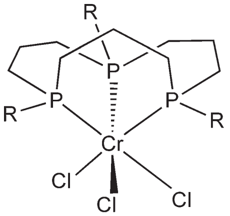
5.05.9.9.2 Neutral tridentate [P_3] ligated derivatives

Chromium complexes containing the triphosphorus macrocycle [12]aneP_3R_3 ([12]aneP_3R_3 = 1,5,9-R_3-1,5,9-triphosphacyclodecane; R = Et, Ph, C_3H_6OMe) have been prepared and explored as ethylene polymerization catalysts.[354] Reaction of $CrCl_3(THF)_3$ with 1 equiv. of [12]aneP_3R_3 yields the desired ([12]aneP_3R_3)$CrCl_3$ **343** complex. Alternatively, chlorination of ([12]aneP_3R_3)$Cr(CO)_3$ with Cl_2 provides another route to **343**.[355] X-ray structural analysis of **343** (R = Et, C_3H_6OMe) shows facially capped octahedral structures with average P–Cr–P angles (91.02° and 90.49°, respectively) close to ideal octahedral values. Ethylene polymerization experiments with **343** (R = Et, Ph) display low to moderate catalytic activities (4 to 14 g PE/(mmol-Cr h bar)) when combined with MAO or trialkylaluminum co-catalysts.[352] Related complexes with pendant methoxy groups (**343**; R = C_3H_6OMe) tend to favor oligomerization (forming C_8 to C_{24} products) over polymerization catalysis. Additional chromium(0) carbonyl complexes have been prepared using macrocyclic triphosphines with pendant donor (N, P, O, S) groups, although these have not been converted to their chromium(III) chloride analogs nor have they been auditioned as catalysts.[356,357] Finally, an acyclic, linear triphosphine, $Pr^nP(C_2H_4PEt_2)_2$, combines with $CrCl_3(THF)_3$ to form *mer*-[$Pr^nP(C_2H_4PEt_2)_2$]$CrCl_3$ **344**; the compound has been structurally characterized; however, no metrical details were provided in the patent citation.[358] After MAO activation, **344** oligomerizes ethylene with modest activity (9 g oligomer/(mmol-Cr h bar)) and high (96%) selectivity for 1-hexene.



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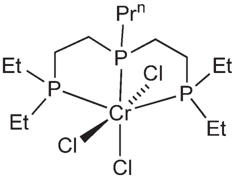
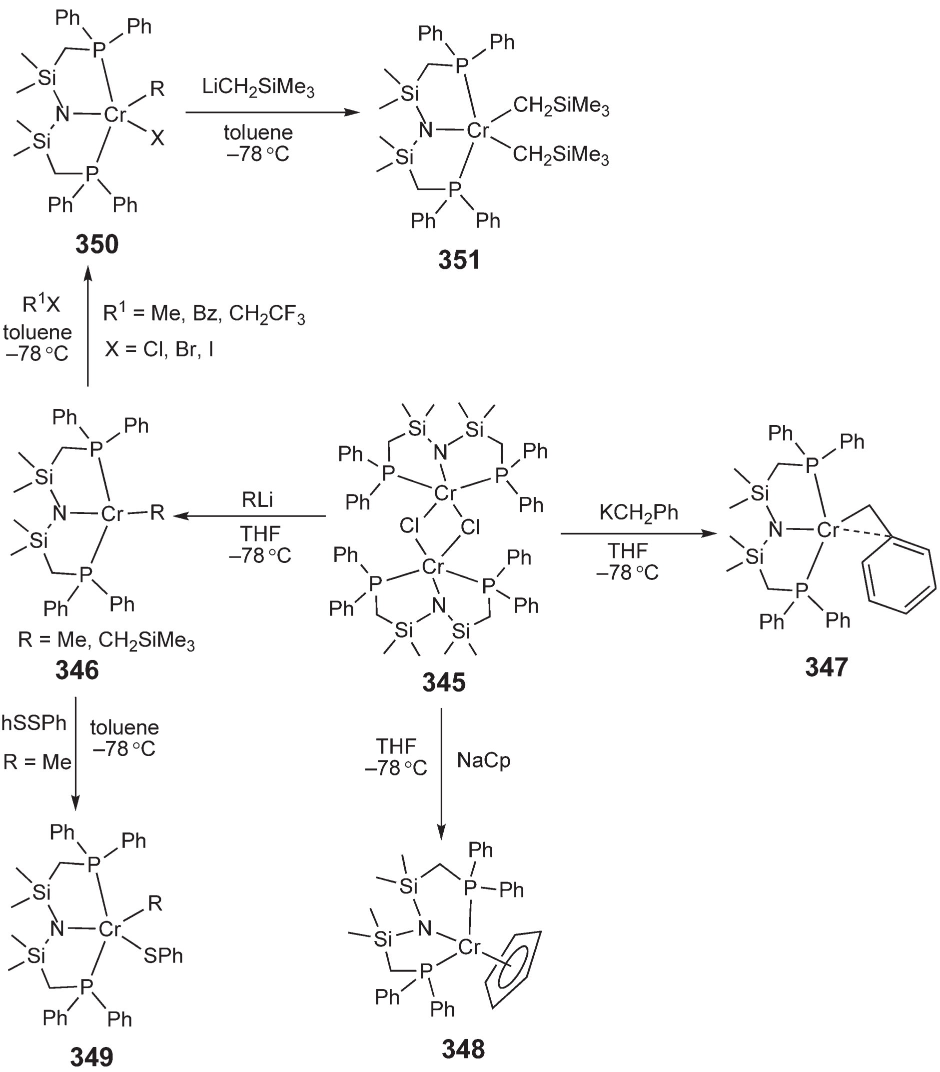


344

5.05.9.9.3 Anionic and neutral tridentate [NP_2] ligated derivatives

5.05.9.9.3.(i) Chromium(II) complexes

Chromium(II) complexes supported by the tridentate, anionic ligand, $[N(SiMe_2CH_2PPh_2)_2]^-$, have been prepared and structurally characterized. For example, reaction of $CrCl_2(THF)_2$ with 1 equiv. of $LiN(SiMe_2CH_2PPh_2)_2$ produces the bridging chloride dimer **345**,[359] which is subsequently converted to various monomeric alkyl (**346**;



Scheme 75

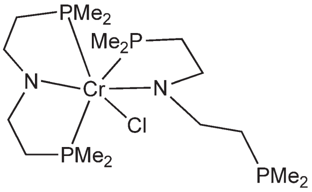
R = Me, CH_2SiMe_3), η^2-benzyl **347**, and Cp **348** derivatives (Scheme 75).[360] Both **346 and 347** display meridional ligand coordination and nearly planar geometry around each high spin ($S = 2$) chromium(II) ion. Derivative **348**, on the other hand, possesses distorted facial geometry at chromium and an intermediate spin ($S = 1$) electronic configuration. Interestingly, the Cr–Me bond does not insert ethylene, consistent with Theopold's earlier claims that chromium(II) centers are not ideally suited for traditional olefin polymerization.[327] Despite this lack of reactivity, the Cr–Me bond does react with hydrogen to form a bridging hydride dimer, with CO to form the acyl derivative, and with acetylene to form polyacetylene.

Complex **346** can be oxidized with diphenyl disulfide (PhSSPh) forming the high spin ($S = 3/2$) chromium(III) complex $[N(SiMe_2CH_2PPh_2)_2]CrMe(SPh)$ **349**,[361] which displays a five-coordinate geometry at the chromium(III) center (Scheme 75). The steric bulk of the diphenylphosphine moieties appears to avert the formation of octahedral chromium(III) centers by preventing normally favorable bridging sulfur interactions. Oxidation of square planar **346** (R = Me, CH_2SiMe_3) with various R^1X species (MeI, CF_3CH_2I, MeBr, BzCl) yields one-electron oxidation products $[N(SiMe_2CH_2PPh_2)_2]CrR(X)$ (**350**; R = Me, CH_2SiMe_3; X = Br, Cl),[362] which also display five-coordinate structures. Interestingly, the Cr–Me and Cr–N bonds in **350** (R = Me, X = Br) are 0.030 Å longer and 0.108 Å shorter, respectively, than in the chromium(II) starting material. These bond lengths imply that the amido lone pair plays a significant π-donor role in stabilizing the chromium(III) center, perhaps by functioning as a full four-electron donor.

Although theoretically possible, no dialkyl complexes $[N(SiMe_2CH_2PPh_2)_2]Cr(R)(R^1)$ have been isolated from the reaction of high spin **346** with R^1X. Instead only alkyl halide complexes **350** are obtained. However, complex **350** ($R = CH_2SiMe_3$, $X = Cl$) can be alkylated with $LiCH_2SiMe_3$ to form the formally 13-electron chromium(III) dialkyl $[N(SiMe_2CH_2PPh_2)_2]Cr(CH_2SiMe_3)_2$ **351** (Scheme 75); attempts to prepare dimethyl analogs of **351** have been unsuccessful. Interestingly, Cp-ligated **348** is able to form both alkyl, $Cp[N(SiMe_2CH_2PPh_2)_2]Cr(CH_2Ph)$, and halide, $Cp[N(SiMe_2CH_2PPh_2)_2]CrCl$, products upon reaction with $PhCH_2Cl$. Finally, dialkyl **351** catalyzes the formation of a small amount of white solid—presumably polyethylene—upon exposure to 1 atm of ethylene; however, the amount of solid and its properties have not been reported.

5.05.9.9.3.(ii) Chromium(III) complexes

Both monomeric and dimeric chromium(III) complexes are supported by the anionic diphosphinoamido ligand $[N(CH_2CH_2PMe_2)_2]^-$.[363] Reaction of $CrCl_3(THF)_3$ with 2 equiv. of $LiN(CH_2CH_2PMe_2)_2$ (in toluene–Et_2O solvent) yields monomeric **352**, which contains one tridentate and one bidentate ligand. Use of 1.5 equiv. of $LiN(CH_2CH_2PMe_2)_2$ (in toluene solvent) yields an asymmetric dinuclear complex **353** in which one phosphorus-bound methyl group has been metallated to form a Cr–C σ-bond. Furthermore, reaction of $CrCl_3(THF)_3$ with 1 equiv. of the more sterically demanding isopropyl derivative, $LiN(CH_2CH_2PPr^i{}_2)_2$, yields yet another asymmetric compound **354**, which displays one tridentate (spanning both chromium centers) and one bidentate ligand. None of the compounds **352–354** have been evaluated as polymerization catalysts.



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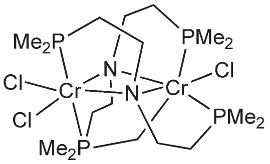

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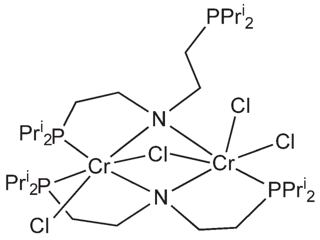


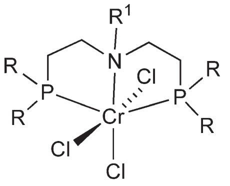
354

Chromium(III) complexes **355** supported by neutral diphosphinoamine ligands, $(R_2PC_2H_4)_2NR^1$ ($R = Et$, Ph, C_6H_{11}; $R^1 = H$), are prepared by treating $CrCl_3(THF)_3$ with 1 equiv. of the appropriate ligand. X-ray structural analysis of **355** ($R = Ph$ and C_6H_{11}) shows the ligand to be bound in a tridentate, meridional manner.[364] The $R = Ph$ complex oligomerizes ethylene in the presence of MAO with moderate activity (6 g oligomer/(mmol-Cr h bar)) and high (98%) selectivity for hexene. Use of more basic and sterically demanding $R = C_6H_{11}$ substituents leads to decreased catalyst activity and formation of a product slate shifted toward polyethylene. Less sterically demanding $R = Et$ substituents provide the best combination of activity (48 g oligomer/(mmol-Cr h bar)) and hexene selectivity (97%). The similar solid-state structures for $R = Ph$ and C_6H_{11} derivatives, as revealed by X-ray crystallography, contrasts with their very different catalytic behavior. Thus, it has been proposed that, in the active catalyst, the ligand binds in a manner that is sensitive to steric bulk (i.e., facially).

5.05.9.9.4 Mixed donor tridentate [NPS] ligated derivatives

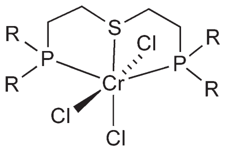
In an extension of their work on $[NP_2]$[364] and $[NS_2]$[342] ligands, McGuinness and Wasserscheid have prepared chromium(III) complexes supported by various tridentate $(R_2PCH_2CH_2)_2NR^1$ (**355**; R = alkyl, aryl; $R^1 = H$, Me, Bz) and $(RSCH_2CH_2)_2NR^1$ (**335**; R = alkyl, $R^1 = H$) ligands, including derivatives with propyl rather than ethyl spacer groups between donor atoms.[365] Compounds incorporating tridentate ligands with secondary amines and with small, basic sulfur or phosphorus donors, such as **335** and **355** ($R^1 = H$), yield the best combination of catalyst activity (up to 280 g hexene/(mmol-Cr h bar)) and hexene selectivity (99.7%). Complexes supported by ligands with tertiary amines (**355**; $R^1 = Me$, Bz) are much less active (<1 g product/(mmol-Cr h bar)) and less selective for hexene (<40%), indicating that deprotonation of the central amine nitrogen (by MAO) might be a critical step in catalyst formation. For aminebis(thioether) ligands, expanding the chelate ring size (from ethyl to propyl spacers) also diminishes catalyst performance. In addition, this same report describes the preparation of chromium(III) complexes incorporating tridentate $[SP_2]$ and $[PS_2]$ donor sets.[365] Among these compounds, $[(R_2PCH_2CH_2)_2S]CrCl_3$ (**356**; R = Et, Ph) and $[(EtSCH_2CH_2)_2PPh]CrCl_3$ **357** display only moderate activity

(<30 g product/(mmol-Cr h bar)) with reduced hexene selectivity; this data underscores the need for a central secondary amine for optimal catalyst activity.



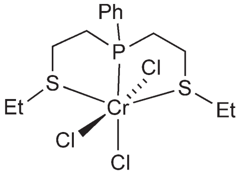
R = Et, Ph, C_6H_{11}
R^1 = H, Me, Bz

355



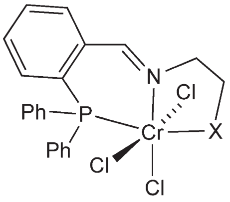
R = Et, Ph

356



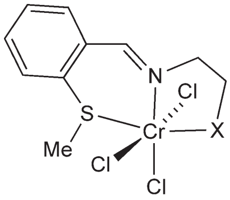
357

Very recently, Bluhm and co-workers have described the synthesis and characterization of chromium(III) complexes supported by various [NP_2], [NS_2], [NPS], [N_2P], and [ONS] ligands; in each case, nitrogen serves as the ligand's central donor atom.[366] Chromium(III) complexes supported by imino 358 and 359 and amino 360-based ligands are readily prepared by reacting the appropriate tridentate ligand with $CrCl_3(THF)_3$ in THF. Several of these compounds have been structurally characterized and, in each case, the ligand adopts a meridianal coordination geometry. Ethylene polymerization studies (MAO co-catalyst) indicate that catalyst performance is sensitive to the donor atom type and to polymerization temperature. Notably, hexene selective (up to 98% selective) catalysts result from imino-based [NP_2] or [NPS] ligand sets, while other donor combinations, including those with an amino central nitrogen, tend to produce polyethylene under similar conditions. Interestingly, complex 358 ($X = PPh_2$) shifts from producing primarily hexene at room temperature to primarily polyethylene at 85 °C.



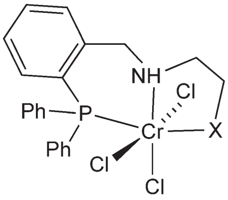
358

X = NMe_2, 2-C_5H_4N
OMe
PPh_2
SEt



359

X = NMe_2
OMe
PPh_2
SEt



360

X = PPh_2
SEt

5.05.10 Heterogeneous Organochromium Complexes

The immobilization of organometallic compounds on solid supports often provides discrete complexes that can serve as models for industrially relevant heterogeneous catalysts. Thus, the study of heterogeneous organometallic species, and the reactions leading to these surface-bound complexes, has emerged as an area of active interest. In a recent review, Basset *et al.* have provided an excellent summary of surface organometallic chemistry and its applications to various catalytic reactions.[367] The present chapter focuses on recent reports describing the physical and structural characterization of heterogeneous organochromium species.

5.05.10.1 Cyclopentadienyl-containing Complexes

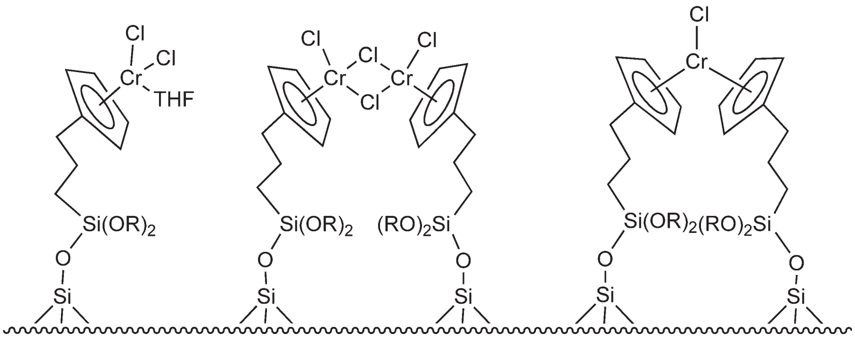
The reaction product of Cp_2Cr with dehydroxylated silica (SiO_2) is known to generate an active ethylene polymerization catalyst (Union Carbide catalyst).[79,80] In this deposition reaction, surface silanol groups (≡Si–OH) serve to protonate one Cp ligand, leading to its liberation from chromium and the formation of surface-bound mono-Cp species, ≡Si–O–CrCp. However, precise structural details are lacking. In an effort to obtain structural information, Blümel *et al.* have studied this reaction product using solid-state ^{1}H NMR spectroscopy.[368] By analogy to ^{1}H NMR spectra of Cp–chromium(II) and Cp–chromium(III) model complexes, resonances of the Cp_2Cr/SiO_2 reaction product have been assigned to the Cp hydrogens in bridged dimeric chromium(II) (25 ppm), half-sandwich monomeric chromium(III) (282 ppm), and dimeric chromium(III) (148 ppm) surface species. Of these three, only the monomeric chromium(III) is presumed to be catalytically active. As the Cp_2Cr loading increases, the 148 ppm resonance intensifies, which is consistent with enhanced dimer formation as the surface density of chromium increases. A separate EXAFS investigation of the Cp_2Cr/SiO_2 reaction product reveals that the average surface species is most consistent with Cp–chromium(III) dimers (Cr–Cr separation of 2.95 Å), which are presumably bridged by oxygen atoms from nearby surface siloxanes (≡Si–O–Si≡).[369]

Heterogeneous Cp-containing complexes can also be prepared by the reaction of $CrCl_3(THF)_3$ with cyclopentadienyl-modified silica surfaces.[370] Solid-state ^{13}C CPMAS NMR and diffuse reflectance infrared (DRIFTS) spectroscopic data confirm the initial cyclopentadiene surface modification. After cyclopentadiene deprotonation and addition of $CrCl_3(THF)_3$, a series of monomeric mono-Cp, monomeric bis-Cp, and chloride-bridged structures are assumed to form (Scheme 76); unfortunately, the paramagnetism of chromium(III) prevents the observation of ^{13}C NMR resonances for any chromium-containing species. Ethylene polymerization tests reveal that these supported species are modest catalysts, forming both polyethylene and oligomeric products.

Deposition of pre-formed Cp–chromium(III) complexes onto solid supports represents another route to surface-bound organochromium(III) species. For example, addition of $Cp^*CrMe_2(pyr)$ to dehydrated MCM-22 zeolite supports liberates 1 equiv. of methane per chromium atom; infrared and powder EPR spectra are consistent with a chromium(III) organometallic complex **361** bound to the surface via a chromium–oxygen bond.[371] Zeolites with higher aluminum content yield higher activity ethylene polymerization catalysts (up to 84 g PE/(mmol-Cr h bar)) after activation with MAO, and the polyethylene products are of high molecular weight (M_w = ca. 4×10^6 g mol^{-1}) and relatively narrow molecular weight distribution ($M_w/M_n = 3.5$), which is consistent with reasonably uniform ≡SiO–Cr(Me)Cp^* sites.

Immobilization of Cp–chromium(III) complexes onto $MgCl_2$ supports has also been reported.[372] In this case, the amine-tethered Cp complex, $(Me_2NCH_2CH_2C_5Me_4)CrCl_2$ (**155**, previously described in Section 5.05.4.6.6), can be deposited onto solid $MgCl_2/AlR_n(OEt)_{3-n}$. While extensive catalyst characterization data have not been provided, the supported catalysts display high activity (up to 2690 g PE/(mmol-Cr h bar)) and produce polymers with high molecular weight and uniform spherical particle morphology.

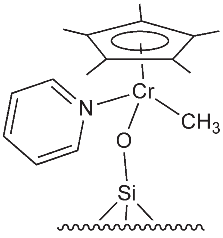
The oxidized Phillips catalyst (CrO_3/SiO_2) is known to react with CO to form reduced Cr(II)–SiO_2 species. The reaction of reduced Phillips catalysts with ethylene at high temperature (300 °C) yields supported, albeit catalytically inactive, Cp–chromium complexes.[373] The Cp rings are proposed to result from chromium-assisted coupling of ethylene, either with or without C–C bond cleavage. In related work by the same group, reaction of Cr(II)–SiO_2 with ethylene at lower temperatures (ambient to 100 °C) produces π-bound ethylene–chromium species (observed by DRIFTS); however, no spectroscopic evidence for ethylene coupling to form metallacycles was obtained at these low temperatures.[374] Yet at 300 °C, organochromium compounds are formed and these can be removed from the silica surface by reaction with methanolic HCl. A wide array of $(R_nCp)CrCl_2(CH_3OH)$ species have been characterized by XPS, ^{1}H, and ^{2}H NMR spectroscopy and mass spectrometry results. In addition, the isolation and crystallographic characterization of $[(1,2,3\text{-}Me_3Cp)CrCl_2]_2$ from the product mixture lends support to the proposed oxidative coupling reaction scheme.



Scheme 76

5.05.10.2 Chromium(III) Allyl and Alkyl Complexes

Silica-supported chromium(III) allyl complexes have been prepared by the reaction of Cr(2-Me-allyl)$_3$ with silica dehydrated at various temperatures (200–800 °C).[375] The tris(allyl)chromium precursor reacts with surface hydroxyl groups to release isobutene; the amount of liberated isobutene depends on the initial hydroxyl concentration. Analysis of DRIFTS data indicates σ-bonded allyls **362** are present in all samples, but that π-bonded allyls **363** are observed only for those samples prepared using highly dehydroxylated (800 °C) silica. Moreover, ethylene polymerization studies show that samples prepared on 800 °C silica form highly methyl-branched polyethylenes, whereas only unbranched polymers resulted from catalysts prepared using silica dehydrated at lower temperatures; the reasons for this product shift are not readily apparent. In a separate study, Cr[CH(SiMe$_3$)$_2$]$_3$ has been deposited on dehydrated silica (600 °C) and is an effective ethylene polymerization catalyst without the need for further activation;[376] the detailed structure and bonding of the supported complex have not been determined.



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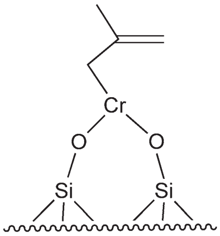

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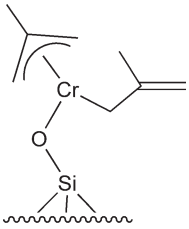

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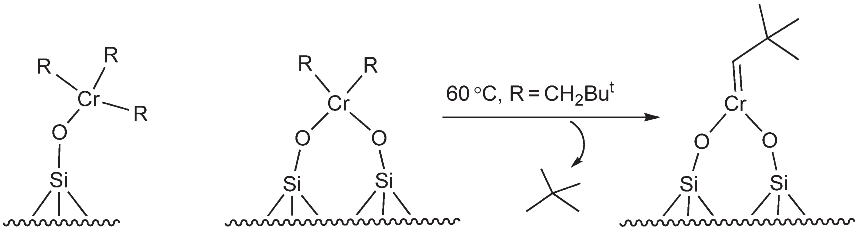
5.05.10.3 Chromium(IV) Alkyl Complexes

With regard to chromium(IV) species, Scott *et al.* found that deposition of homoleptic chromium(IV) alkyls, CrR$_4$ (R = CH$_2$SiMe$_3$, CH$_2$Bu^t), onto dehydrated silica (500 °C) liberates 1 equiv. of RH to generate ($\equiv$SiO)Cr(CH$_2$Bu^t)$_3$ **364**.[377] Use of silica dehydrated at lower temperature (200 °C) liberates 2 equiv. of RH. On the basis of this reaction chemistry, along with EPR and magnetic susceptibility ($\mu_{\mathrm{eff}} = 2.68\,\mu_\beta$) measurements, the latter surface species is formulated as the chromium(IV) dialkyl, ($\equiv$SiO)$_2$CrR$_2$ **365**, which is grafted to the surface via two $\equiv$Si–O–Cr linkages (Scheme 77). The reactivity and product formulation are consistent with lower surface silanol density at higher dehydration temperatures.

Thermolysis of **365** (R = CH$_2$Bu^t) cleanly liberates neopentane (Scheme 77) and forms a product formulated as the chromium(IV) alkylidene ($\equiv$SiO)$_2$Cr=CHBu^t **366**;[378] this relatively rare chromium alkylidene is apparently stabilized by deposition on the silica surface. The observed reactivity of **366** with Br$_2$ and acetone, forming Bu^{t}CHBr$_2$ and Me$_2$C=CHBu^t, respectively, is consistent with its formulation as a terminal alkylidene. For the formation of the alkylidene, isotope labeling and kinetic studies are consistent with the expected mechanism involving first-order intramolecular α-H elimination of alkane.[379]

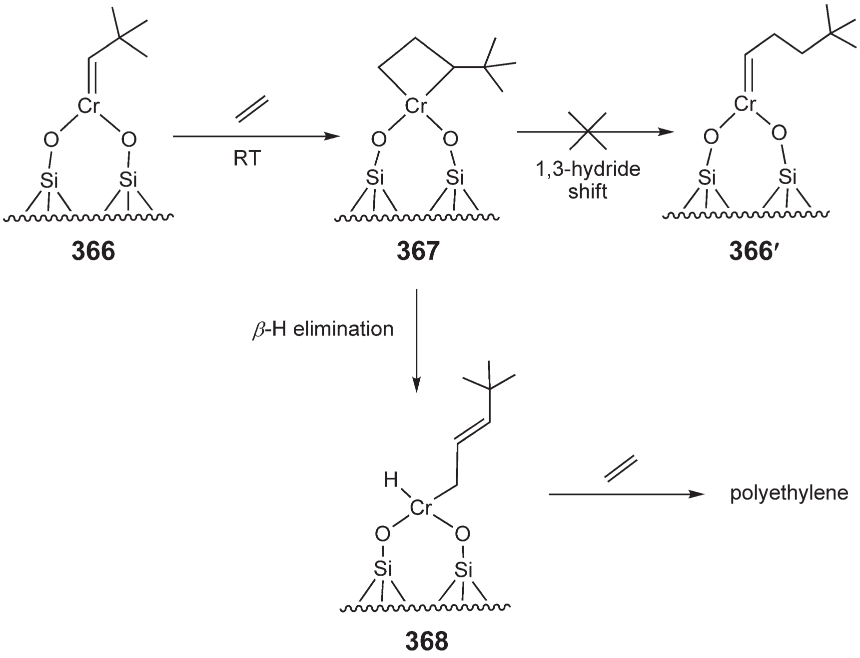
With regard to further reactivity, surface-bound **366** catalyzes the polymerization of ethylene and 1-hexene without additional activation (Scheme 78). Moreover, the first-order dependence of polymerization rate on both monomer pressure



364 **365** **366**

R = CH$_2$Bu^t, CH$_2$SiMe$_3$

Scheme 77



Scheme 78

and total Cr loading, the observed kinetic isotope effect ($k(C_2H_4)/k(C_2D_4) = 1.29$), and the temperature dependence of the second-order rate constants all favor a migratory insertion pathway at an alkyl chromium(IV) center rather than an alternating alkylidene–metallacyclobutane (366 → 367 → 366′) chain propagation mechanism.[380] The small positive kinetic isotope effect is most consistent with α-H agostic assistance during migratory insertion and such agostic interactions are well known to be involved in metallocene-based migratory insertion polymerization mechanisms.[381] While the alkylidene–metallacyclobutane–alkylidene sequence (366 → 367 → 366′) is not a likely pathway in normal chain propagation, initial metallacyclobutane formation followed by β-H elimination is proposed to account for the formation of a chromium(IV) alkyl hydride 368, which readily inserts ethylene to initiate the polymer chain.[382] The energetics of this transformation have been examined theoretically and further details are provided in the following section.

5.05.11 Theoretical Aspects of Organochromium-catalyzed Olefin Polymerization

Because of their industrial relevance to olefin polymerization catalysis, model complexes representing both supported and homogeneous chromium catalysts have been the subject of numerous theoretical studies examining three critical polymerization steps: olefin binding, olefin insertion, and chain termination. The following paragraphs outline recent work on chromium(III) complexes, including Cp and diiminate ligated species, as well as chromium(IV) bis(amide), chromium(IV) bis(siloxide), and chromium(VI) bis(imido) structures.

5.05.11.1 Chromium(III) Species

5.05.11.1.1 Model complexes containing simple σ-donors

Initial work by Jensen and Børve has examined relatively simple cationic chromium(III) complexes, $[CrCl(H_2O)CH_3]^+$, using several theoretical treatments including Hartree–Fock, second-order perturbation theory (MP2), local spin density approximation (LSDA), and gradient-corrected DFT.[383] Ethylene adducts with bent pyramidal structures and weak agostic C–H interactions are predicted to be the stable intermediates. Ethylene binding (olefin complex) energies (Δ_{OC}) are large and exothermic ($\Delta_{OC} = -22$ to $-28\,\mathrm{kcal\,mol^{-1}}$) and depend somewhat on the calculation method. Calculations based on DFT predict an insertion barrier of $8.4\,\mathrm{kcal\,mol^{-1}}$; this barrier is slightly higher than that calculated for group 4 metallocenes, but is in excellent agreement with the experimental value for chromium complexes (8 ± 1 kcal mol^{-1}).[384]

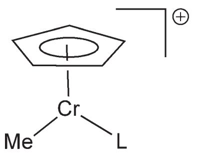
5.05.11.1.2 Model complexes containing cyclopentadienyl ligands

Further DFT calculations by Jensen *et al.* have examined [CpCrMe(L)]$^+$ (**369**, L = H_2O, THF, imidazol-2-ylidene) and [($R_2NC_2H_4C_5H_4$)CrMe]$^+$ (**370**, R = H, Me) complexes, which serve as active site models of previously synthesized complexes (e.g., **370** models **155**).[385] The calculations predict similar charge densities at the chromium centers and similar barriers to ethylene insertion (e.g., 6.4 kcal mol^{-1} for **369** (L = THF) and 10.2 kcal mol^{-1} for **370** (R = H)), regardless of the identity of the donor ligand. There is no apparent correlation between the calculated insertion barriers and the experimentally observed activities, or between activity and the respective Cr–donor bond strengths. However, activity does correlate with the presence of a tethered donor group, suggesting that a locally high concentration of the donor ligand is important to catalyst performance, perhaps by impacting the energetics of monomer coordination. A related comparative study of ethylene insertion with [($H_2NC_2H_4C_5H_4$)M(III)R]$^+$ (M = Sc–Co, R = Me) complexes suggests that Sc, V, and Co complexes should also display high activity—comparable to that of Cr(III)—whereas Mn(III) complexes are not expected to be particularly active.[386]

In complementary work, Doren *et al.* have used DFT calculations to examine the exceptional selectivity of **369** (L = THF) and related systems for the insertion of ethylene over higher α-olefins.[387] Calculations on [CpCr(propyl)(THF)]$^+$ predict an ethylene insertion barrier of 9.4 kcal mol^{-1}, in good agreement with the experimentally derived value (8 ± 1 kcal mol^{-1}) reported by Theopold.[384] The calculations also suggest that [CpCrMe(THF)]$^+$ should not co-polymerize ethylene and propylene because of relatively poor (and thus reversible) olefin binding and a 5 kcal mol^{-1} higher insertion barrier for propylene relative to ethylene. Thus, for Cp–chromium complexes, weak (reversible) olefin binding, coupled with a higher propylene insertion barrier relative to ethylene, works in concert to favor ethylene insertion and disfavor ethylene–propylene co-polymerization. On the other hand, the authors note that complexes with large olefin binding energies and small insertion barriers would maintain the insertion transition state energy below the barrier to olefin dissociation. Such a situation (essentially irreversible olefin binding) promotes the insertion of whichever monomer is complexed and favors co-polymerization. Some examples of ligand families that promote strong olefin binding are mentioned in the paragraphs that follow.

5.05.11.1.3 Model complexes containing diiminate ligands

Cationic chromium(III) diiminate model complexes **371** have also been examined by Ziegler *et al.*;[388] calculations indicate that alkyl complexes with this ligand family adopt structures with the nitrogen lone pairs perpendicular to the N–Cr–N plane and with β-agostic C–H···Cr interactions. Complexes without bulky nitrogen substituents display strong olefin binding ($\Delta_{OC} = -12.5$ kcal mol^{-1}). In addition, the difference between insertion (10.4 kcal mol^{-1}) and termination (19.0 kcal mol^{-1}) barriers indicates that these catalysts should behave as polymerization (rather than oligomerization) catalysts, consistent with the experimental findings of Gibson[286] and Theopold.[289] Strong olefin binding (i.e., irreversible) and a modest insertion barrier also suggest that **371** might serve as an effective co-polymerization catalyst; the recently reported excellent co-polymerization performance of Theopold's chromium(III) diiminate (**309**, Section 5.05.9.4.4)[292] supports this prediction. In addition, the preference for insertion over termination (via β-hydrogen transfer (BHT) to ethylene) can be amplified by increasing steric bulk at nitrogen; the steric bulk serves to destabilize the sterically demanding BHT transition state relative to olefin insertion, thus promoting propagation over termination.



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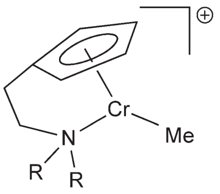

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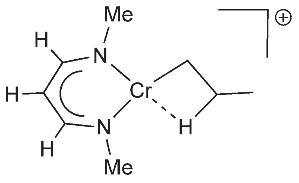

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Finally, in the same study, a bulky bridged diamide ligand, which possesses nitrogen lone pairs lying in the N–Cr–N plane, has also been examined. In the case of chromium(III) compounds, however, relatively poor olefin binding (−0.9 kcal mol^{-1}) and a high ethylene insertion barrier (15.4 kcal mol^{-1}) make this a rather unattractive catalyst candidate.

5.05.11.2 Chromium (IV) Species

5.05.11.2.1 Model complexes containing diamido ligands

Schmid and Ziegler have used DFT calculations to examine $[Cr(L)(L')R]^+$ complexes ($L,L' = NH_3, NH_2^-$) with electron configurations ranging from d^2 to d^4.[389] The calculated olefin binding energy declines linearly with increasing d-electron count due to less favorable $\pi \rightarrow d$ donation from ethylene to chromium. The d^2 or chromium(IV) case, $[Cr(NH_2)_2Et]^+$, is predicted to be an especially promising candidate, especially for higher olefin polymerization, since it possesses high olefin binding energy ($\Delta_{OC} = -18.4$ kcal mol^{-1}) and a relatively small insertion barrier (6.3 kcal mol^{-1}). As pointed out earlier by Doren,[387] the combination of strong olefin binding and a low insertion barrier should generate catalysts capable of polymerizing higher olefins. Also for the d^2 (chromium(IV)) case, diamide ligands with nitrogen lone pairs lying in the N–Cr–N plane are predicted to be competent polymerization catalysts as these yield low insertion/high termination barriers, thus favoring the formation of high molecular weight polymeric product. Note that this behavior contrasts with that expected for chromium(III) diamide derivatives described in the Section 5.05.11.1.3.

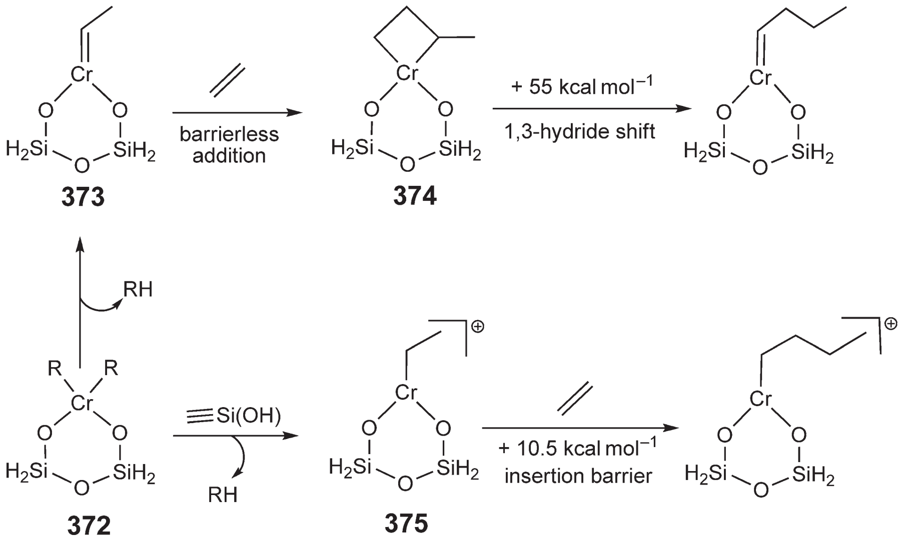
5.05.11.2.2 Model complexes containing disiloxide ligands

Using DFT techniques, Schmid and Ziegler have examined a chromium(IV) disiloxide structure, $(OSiH_2\text{-}OSiH_2O)CrR_2$ **372**,[390] as a model for the silica-bound chromium(IV) alkyls prepared by Scott *et al.*[377–380] Calculations indicate that polymerization mechanisms arising from neutral bis(alkyl) or alkylidene structures suffer from high activation barriers. While the monomeric alkylidene **373** readily inserts ethylene to form the metallacyclobutane **374** (the transformation is barrierless and exothermic by ca. 40 kcal mol^{-1}), the subsequent 1,3-hydrogen shift, which is required to regenerate the alkylidene, has a prohibitively high activation energy (55 kcal mol^{-1}); thus, this route is not predicted to be a viable polymerization pathway (Scheme 79).

On the other hand, cationic Cr(IV) alkyls **375**, which presumably can form by protonation of the neutral alkylidene by surface acidic sites (Si–OH), display strong ethylene binding ($\Delta_{OC} = -18.3$ to -23.1 kcal mol^{-1} relative to the separated reactants) and a reasonable ethylene insertion barrier (10.5 kcal mol^{-1}) (Scheme 79). This combination yields an insertion transition state energy below that of the separated reactants, suggesting that such chromium compounds should serve as useful co-polymerization catalysts. Indeed, the ethylene–hexene co-polymerization behavior exhibited by Scott's surface-supported complex **366**[379] lends support to these calculations.

5.05.11.2.3 Model complexes containing amine–bis(amide) ligands

Cationic chromium(IV) amine-bis(amide) model complexes, $[(NH_3)(NH_2)_2CrEt]^+$, have also been studied by Ziegler *et al.*[391] Binding of ethylene is predicted to be moderately exothermic ($\Delta_{OC} = -5.2$ kcal mol^{-1}) and the insertion barrier is relatively large (12.5 kcal mol^{-1}). In this case, the insertion transition state energy is above that of the

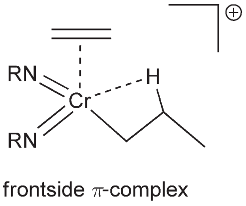


Scheme 79

separated reactants (reversible ligand binding scenario) and such systems should not effectively co-polymerize ethylene and higher olefins. Tethering the amine and amide groups via ethyl linkers improves ethylene binding energy ($\Delta_{OC} = -15.3\,\text{kcal mol}^{-1}$) and increases the difference between insertion ($12.1\,\text{kcal mol}^{-1}$) and termination ($25.6\,\text{kcal mol}^{-1}$) barriers; the $13.5\,\text{kcal mol}^{-1}$ difference between termination and insertion barriers makes the tethered ligand complex a good candidate for a living polymerization system.

5.05.11.3 Chromium(VI) Species

Jensen and Børve have examined cationic chromium(VI) bis(imido) systems, $[Cr(NH)_2R]^+$,[392] which serve as models of Gibson's catalytically active cationic bis(imido) complex $[Cr(NBu^t)_2(CH_2Ph)]^+$ (**256**, Section 5.05.8.1.2).[238] Frontside ethylene binding to $[Cr(NH)_2R]^+$ yields a stable π-complex **376**, but one which displays a high subsequent ethylene insertion barrier ($16\,\text{kcal mol}^{-1}$ for the R = propyl derivative). In an alternative, binding mode, backside ethylene coordination (forming π-complex **377**) requires significant ligand reorganization, making such direct binding unlikely. However, a pathway involving isomerization of frontside to backside π-complexes by inversion of **376** to **377**, followed by ethylene insertion into **377**, proceeds with an overall activation energy comparable to that of direct insertion into the frontside π-complex. Nevertheless, these calculated activation energies are still large relative to the high observed activity of **256**.



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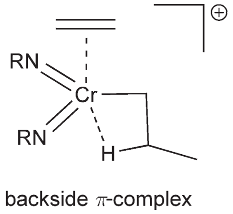
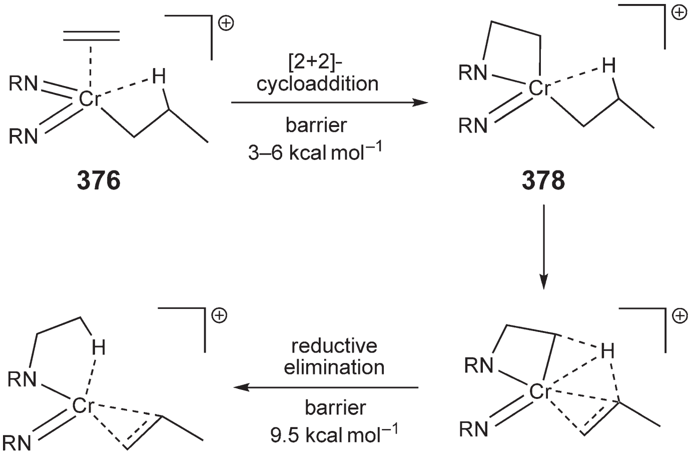
versus



377

In an alternative mechanism, ethylene undergoes [2 + 2]-cycloaddition to the Cr═N bond of **376** forming azametallacyclobutane **378**. This cycloaddition proceeds with low activation energy ($3–6\,\text{kcal mol}^{-1}$) and suggests that the active catalytic species in chromium(VI) bis(imido) complexes might involve ligand modification. In a subsequent report, Jensen and Børve also identified a relatively low energy reductive elimination pathway (Scheme 80) involving the [2 + 2]-cycloaddition intermediate;[393] thus, catalysis involving chromium(VI) bis(imido) precursors might also involve chromium in a reduced oxidation state.



Scheme 80

5.05.11.4 Model Complexes for Olefin Trimerization

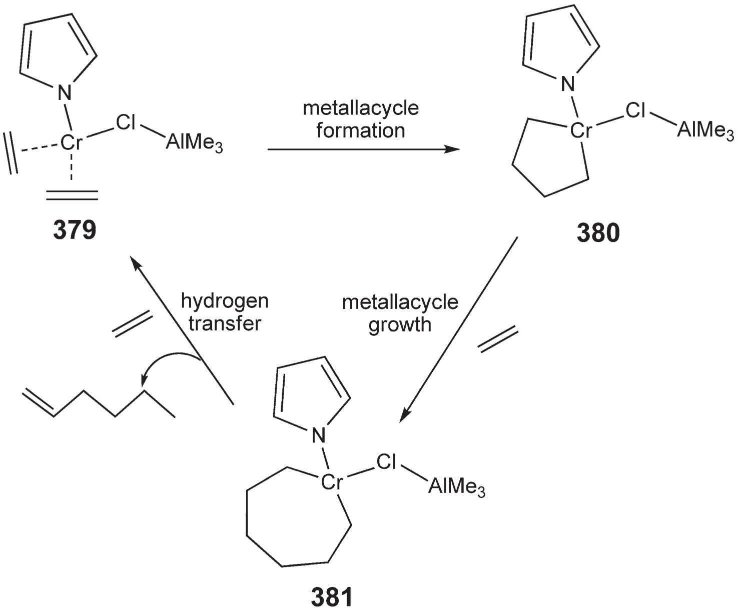
Phillips has commercialized a process for selective ethylene trimerization based upon a Cr–pyrrolyl–AlR_3 catalyst mixture,[394] and the mechanism for this transformation has been explored with DFT calculations.[395] The catalytic pathway used for the calculations involves a catalyst resting state consisting of a chromium(II) center **379** ligated by anionic pyrrolyl and $ClAlMe_3^-$ groups along with two π-bound ethylene molecules (Scheme 81). Oxidative coupling of the bound ethylene forms a chromium(IV) metallacyclopentane **380**; subsequent coordination and insertion of a third ethylene monomer generates the metallacycloheptane intermediate **381**. Reductive elimination of 1-hexene (via hydrogen transfer within the metallacycloheptane framework) from **381** and coordination of ethylene completes the cycle by regenerating **379**. The calculations indicate that all steps in the catalytic cycle (Scheme 81) are energetically favorable with insertion of the third ethylene monomer (**380**→**381**) serving as the rate-determining step. Variable pyrrolyl ligation modes (η^1 or η^5) were also considered for each step, with η^5-ligation being preferred for ethylene coupling (**379**→**380**) and the η^1-coordination mode being favored during ring expansion (**380**→**381**). Thus, pyrrolyl ring slippage may aid in the catalytic process. Moreover, inclusion of the more relevant $ClAlMe_3^-$ fragment, rather than simple Cl^-, in the chromium coordination sphere lowers the insertion barrier for rate-determining metallacycle growth (**380**→**381**) by 11.3 kcal mol^{-1}, indicating that chloroaluminate ions may also help enhance catalyst activity.

5.05.12 Organochromium Complexes in Oxidation Chemistry

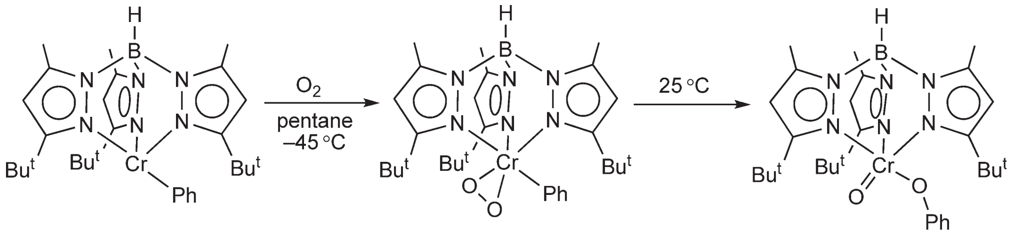
The use of high-valent chromium–oxo complexes, such as CrO_3 and CrO_2Cl_2, to effect the oxidation of organic fragments is well known. This extensive chemistry is beyond the scope of the present review. Instead, this chapter will mention some recent chromium-mediated oxidation chemistry involving complexes and intermediates with well-characterized chromium–carbon bonds.

5.05.12.1 Tris(pyrazolyl)borate Ligated Complexes

The synthesis of chromium(II) alkyl and aryl species coordinated by sterically encumbered tris(pyrazolyl)borate ligands, such as $(Tp^{tBu,Me})CrR$ (**324**, R = Et, Ph), has already been described in Section 5.05.9.6.1; these compounds display unusual "*cis*-divacant" coordination geometries and appear poised to accept additional ligands or to bind small



Scheme 81

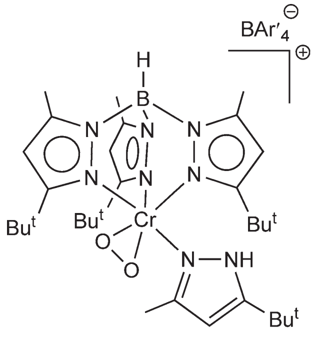


324 **382**

Scheme 82

reactive molecules.[326] Along these lines, reaction of **324** (R = Ph) with dioxygen yields a chromium(IV) oxo–phenoxy derivative **382**, which forms by migratory insertion of oxygen into the Cr–phenyl bond via an intermediate chromium(III) η^2-superoxo complex (Scheme 82); the superoxo intermediate has been observed by low temperature infrared spectroscopy.[396] Compound **382** represents an unusual example of a paramagnetic ($\mu_{\text{eff}} = 2.6\,\mu_{\text{B}}$) mono-oxo complex and its formation demonstrates the ability of chromium to direct the intramolecular oxidation of chromium–carbon bonds. The intramolecular mechanism depicted in Scheme 82, rather than a free-radical based process, is supported by the lack of crossover products generated during oxidation of an equimolar mixture of $(\text{Tp}^{\text{tBu,Me}})\text{CrC}_6\text{D}_5$ and $(\text{Tp}^{\text{tBu}})\text{CrC}_6\text{H}_5$.

The "side-on" superoxo intermediate proposed in Scheme 82 is further supported by the successful isolation and structural characterization of a pyrazole-ligated η^2-superoxo complex $[(\text{Tp}^{\text{tBu,Me}})\text{Cr}(\text{O}_2)(\text{pz}'\text{H})][\text{BAr}'_4]$ (**383**, $\text{pz}'\text{H} = 3\text{-Bu}^{\text{t}}\text{-5-Me-pyrazole}$, $\text{Ar}' = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$).[397] In contrast to chromium(II) complexes containing the $\text{Tp}^{\text{tBu,Me}}$ ligand (e.g., **324**), superoxo intermediates are not observed during the reaction of oxygen and chromium complexes ligated by Tp^{iPr2}, presumably because $(\text{Tp}^{\text{iPr2}})\text{CrX}$ complexes cannot adopt the "*cis*-divacant" structure.[398,399] Finally, a structurally related chromium(IV) oxo complex $[(\text{Tp}^{\text{tBu,Me}})\text{Cr(O)}(\text{pz}'\text{H})][\text{BAr}'_4]$ **384** has been prepared by treatment of pyrazolyl-ligated $[(\text{Tp}^{\text{tBu,Me}})\text{Cr}(\text{pz}'\text{H})][\text{BAr}'_4]$ with PhIO. Complex **384** reacts with weak R–H bonds ($D_{\text{R-H}} < 92\,\text{kcal mol}^{-1}$) to form the chromium(III) hydroxy complex $[(\text{Tp}^{\text{tBu,Me}})\text{Cr(OH)}(\text{pz}'\text{H})][\text{BAr}'_4]$ **385**.[400]



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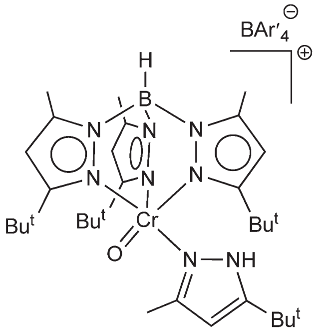

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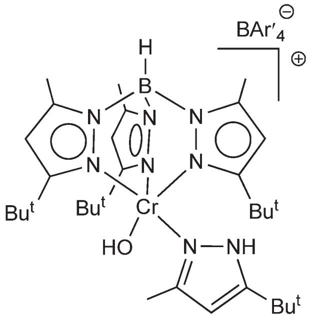

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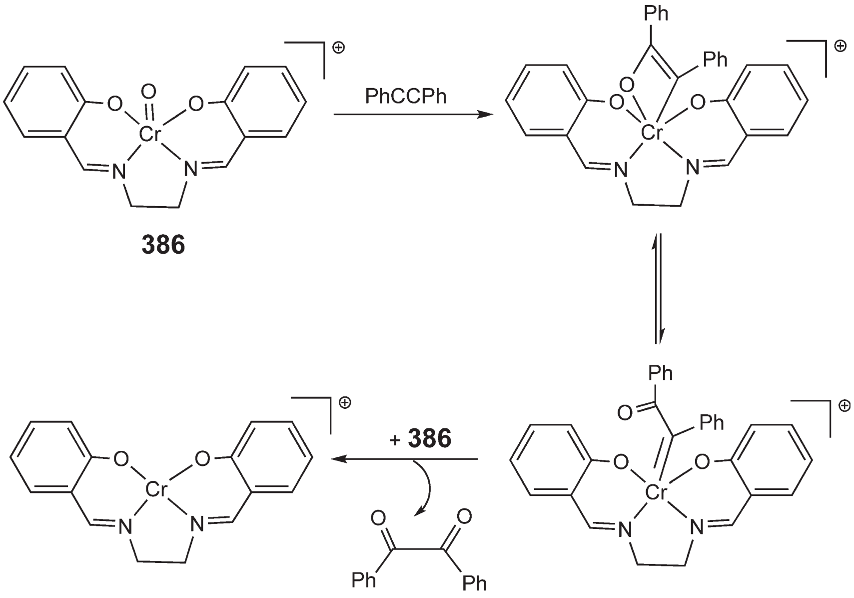
5.05.12.2 Salen-Ligated Complexes

The oxidation of alkenes via metal–oxo complexes can proceed via direct oxygen atom transfer from the metal to the alkene or via intermediate metallaoxetane species. Alkynes, on the other hand, do not form stable products from direct oxygen atom transfer and are thought to proceed via four-membered metallaoxetene or carbene intermediates. This chemistry has been explored via the oxidation of alkynes (e.g., PhC≡CPh) by $[(\text{salen})\text{CrO}][\text{OSO}_2\text{CF}_3]$ **386** to form 1,2-diones. Kinetic data is consistent with a rate-limiting, second-order reaction between **386** and PhC≡CPh, forming a metallaoxetene or carbene intermediate, which is then proposed to react with a second equivalent of **386** to generate the 1,2-dione (Scheme 83).[401]



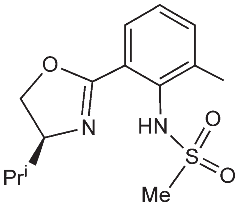
Scheme 83

5.05.12.3 Cyclopentadienyl-ligated Complexes

Cyclopentadienyl chromium–oxo compounds can be used as efficient stoichiometric olefin epoxidation reagents. Exposure of $[\mathrm{Cp'CrCl_2}]_2$ ($\mathrm{Cp'} = \mathrm{Cp}$, $\mathrm{Cp^*}$) to dry oxygen provides high yields of chromium(V) oxo complexes $\mathrm{Cp'Cr(O)Cl_2}$.[402] Computational work (DFT) suggests that $\mathrm{CpCr(O)Cl_2}$ should epoxidize olefins more readily than its $\mathrm{Cp^*}$ counterpart and experimental work in this same report confirms this prediction. A mechanism involving direct oxygen atom transfer from chromium to olefin is favored rather than one proceeding via [2 + 2]-cycloaddition (requiring an oxametallacyclobutane intermediate). The calculations also indicate that the spin state change required upon oxygen atom transfer does not impede the reaction (no "spin blocking" is observed), but rather it opens a lower energy pathway. In complementary work, Ziegler *et al.* have examined the oxidation of ethylene with $\mathrm{CrO_2Cl_2}$[403] and find that [2 + 2]-cycloaddition (forming an oxametallacyclobutane) is not an energetically viable route to the formation of epoxides. However, Limberg *et al.* have suggested that an oxametallacyclobutane intermediate may be involved in the formation of acetaldehyde during the oxidation of ethylene with $\mathrm{CrO_2Cl_2}$,[404] although direct oxygen atom transfer to ethylene was also suggested.

5.05.13 Organochromium Complexes in Organic Synthesis

The use of organochromium(III) reagents to facilitate carbon–carbon bond forming reactions is an extensive field and has been recently summarized in separate reviews by Fürstner,[405,406] Avalos *et al.*,[407] Hodgson,[408] and Wessjohann.[409] One of the most useful reactions in this class – the Nozaki–Hiyama–Kishi coupling reaction – involves insertion of chromium(II) species into alkenyl-, alkynyl-, allyl-, propargyl-, or aryl halides to afford organochromium(III) reagents that can couple with electrophiles such as aldehydes in extremely chemoselective transformations. Recently, this reaction has been rendered catalytic in chromium by using manganese (rather than chromium) as a less toxic stoichiometric reductant, and $\mathrm{Me_3SiCl}$ to facilitate catalyst turnover.[410] In some cases, the use of $\mathrm{Cp_2Cr}$ or $\mathrm{CpCrCl_2(THF)}$, in place of simple chromium(II) halide salts, has been found to improve catalytic efficiency in chromium,[411,412] suggesting that other discrete organochromium complexes might be useful in this regard (see Section 5.05.13.1). Moreover, combinations of chiral ligands and chromium(II) salts have been shown to effect stereoselective coupling reactions. In some cases, such as with chiral sulfonamide 387[413] and bis(8-quinolinolato) 388[414] ligands, the chromium–ligand complex has been isolated and structurally characterized. A recent review by Denmark and Fu provides an excellent summary of catalytic enantioselective addition reactions, including those mediated by chromium.[415] In addition to the references cited above, the reader is also referred to Volume 12 in this series, which provides comprehensive coverage of the use of organometallic reagents in organic synthesis.



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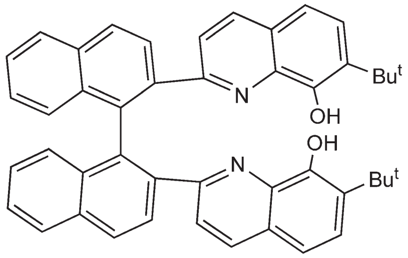

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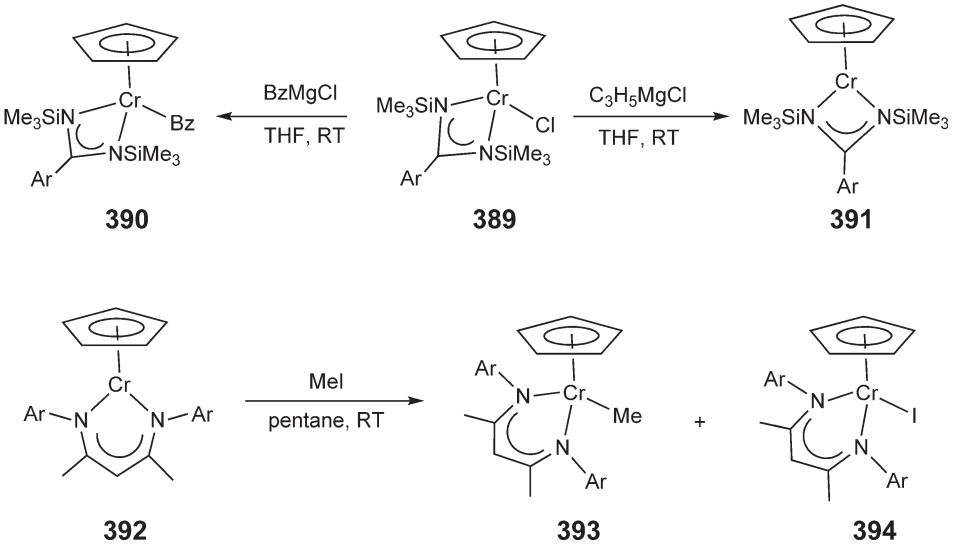
Two additional applications of organochromium reagents in organic synthesis deserve mention: the use of (i) discrete organochromium complexes to examine the initial steps in organohalide activation, and (ii) chromium(III)–butyllithium reaction products to effect a variety of organic transformations.

5.05.13.1 Organohalide Activation

The first step in chromium-mediated coupling reactions, such as the Nozaki–Hiyama–Kishi reaction, involves reduction of R^1X with 2 equiv. of Cr(II) to form Cr(III)–R^1 and Cr(III)–X species via single-electron transfer events. However, very few chromium(III) products from this step have been isolated and characterized. Among previously mentioned complexes (Section 5.05.9.9.3), $[N(SiMe_2CH_2PPh_2)_2]CrR$ **346** produced chromium(III) $[N(SiMe_2CH_2PPh_2)_2]CrR(X)$ **350** and $[N(SiMe_2CH_2PPh_2)_2](Cp)Cr$ **348** formed both $[N(SiMe_2CH_2PPh_2)_2](Cp)CrX$ and $[N(SiMe_2CH_2PPh_2)_2](Cp)CrR^1$ upon reaction with R^1X.[362] Complex **348** thus models alkyl halide activation by providing both Cr(III)–R and Cr(III)–X reaction products. Smith *et al.* have extended this chemistry to include Cp–chromium derivatives supported by benzamidinato ligands.[416] Reaction of $CpCrCl_2(THF)$ with $Li(TMEDA)[ArC(NSiMe_3)_2]$ ($Ar = 4\text{-}C_6H_4CF_3$) yields $CpCr[ArC(NSiMe_3)_2]Cl$ **389**, which undergoes alkylation with BzMgCl to form $CpCr[ArC(NSiMe_3)_2]Bz$ **390** and reduction with C_3H_5MgCl to yield the chromium(II) derivative $CpCr[ArC(NSiMe_3)_2]$ **391** (Scheme 84). Alkyl halide activation was examined by the reaction of **391** with BzCl, which generates both **389** and **390** (products identified by ^{19}F NMR spectroscopy). Smith's group has also demonstrated that β-diketiminato-ligated $Cp[(2,6\text{-}Pr^i_2Ph)_2nacnac]Cr$ **392**, formed by the reaction of $\{[(2,6\text{-}Pr^i_2Ph)_2nacnac]CrCl\}_2$ (**298**, Section 5.05.9.4.4) with NaCp, activates MeI to form both $Cp[(2,6\text{-}Pr^i_2Ph)_2nacnac]CrMe$ **393** and $Cp[(2,6\text{-}Pr^i_2Ph)_2nacnac]CrI$ **394** (Scheme 84).[417] Thus, both **391** and **392** model



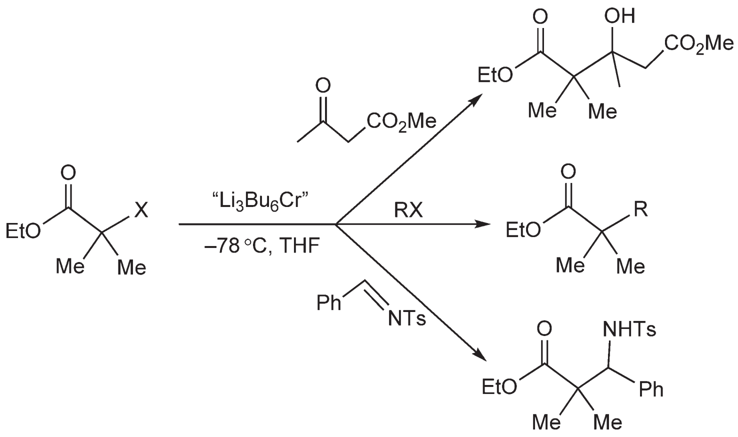
Scheme 84

the initial step of alkyl halide activation by producing both Cr–R and Cr–X (X = Cl, I) species. The reactivity of **348**, **391**, and **392** is also significant since primary alkyl halides are typically unreactive toward traditional aprotic chromium(II) reagents. The enhanced reductive power of **348**, **391**, and **392** allows for the activation of alkyl halides (MeI, MeBr, BzCl), and this superior reactivity may prove useful in organic synthesis. Finally, Smith has summarized single-electron transfer reactions, including those involving chromium(II), in a recent review.[418]

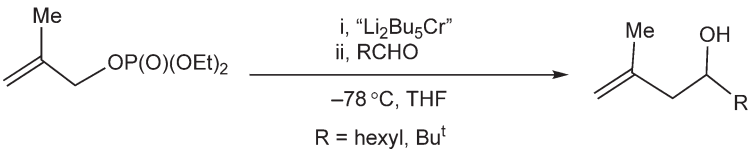
5.05.13.2 Use of Chromium–Butyllithium Reagents

Low-valent chromium(III)–butyllithium reaction products have been used to effect a variety of useful organic transformations. For example, reaction of $CrCl_3$ with 6 equiv. of BuLi at −78 °C generates an intermediate, formulated by Hosami *et al.* as the chromium(III)-ate reagent Bu_6CrLi_3, although the structure and stoichiometry are still in some doubt.[419] Nonetheless, this intermediate reacts with ketones or esters bearing a leaving group α to the carbonyl to form enolates, which subsequently react with a variety of electrophiles such as aldehydes, ketones, and alkyl halides to form new C–C bonds as outlined in Scheme 85. Hosami *et al.* have also shown that Bu_5CrLi_2 (produced from $CrCl_3$ and 5 equiv. of BuLi at −78 °C) generates allylic nucleophiles upon reaction with allylic phosphates[420] and that these nucleophiles react with aldehydes and ketones to form homoallylic alcohols in high yield; a representative reaction is shown in Scheme 86.

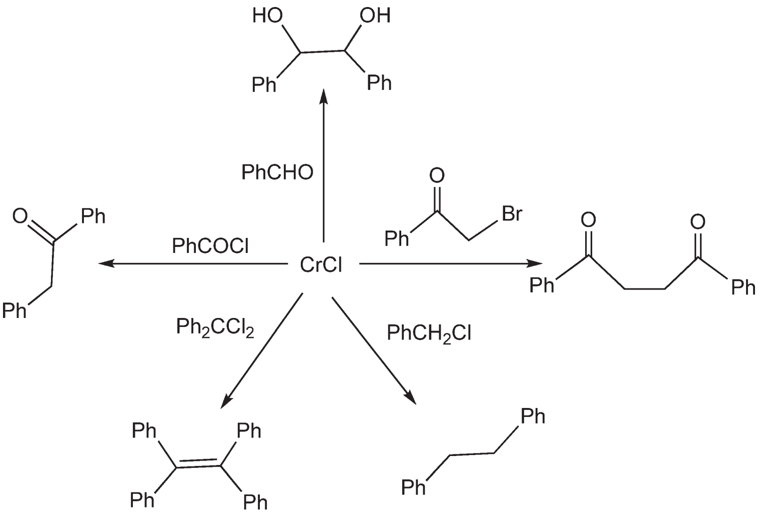
In related work, Eisch *et al.* have produced low-valent chromium complexes upon reaction of $CrCl_3$ with 2 equiv. of BuLi and have demonstrated that different chromium reagents result from reactions in cold THF versus those performed in hot toluene.[421] The complex formed in THF is formulated as CrCl, and this chromium(I) reagent effects the reductive dimerization of aldehydes, acyl halides, and benzylic halides (Scheme 87). On the other hand, the reactive product formed in toluene is described as Bu_2CrCl and behaves as a hydride transfer agent and cleaves carbon–heteroatom σ- and π-bonds (Scheme 88). Finally, the Eisch group has produced the soluble chromium(I) dihydride $LiCrH_2$ by a reaction of $CrCl_3$ and 4 equiv. of BuLi in THF.[422] The dihydride expands the scope of chromium-mediated organic chemistry by serving as a useful reagent for several reduction, dimerization, cyclization, and polymerization reactions; representative examples of such reactions are outlined in Scheme 89.



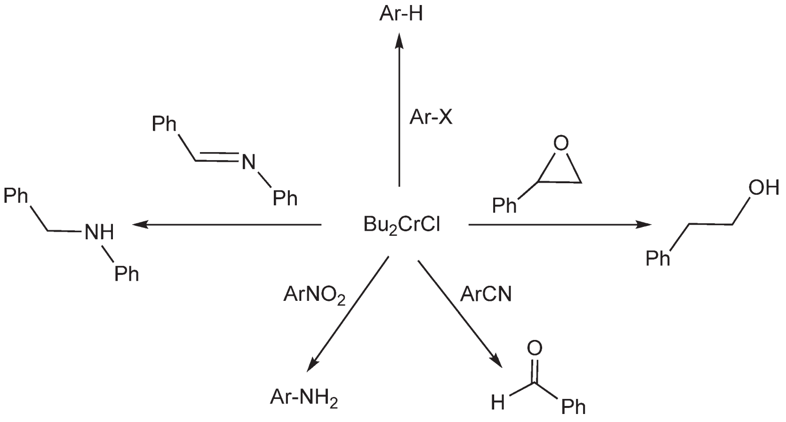
Scheme 85



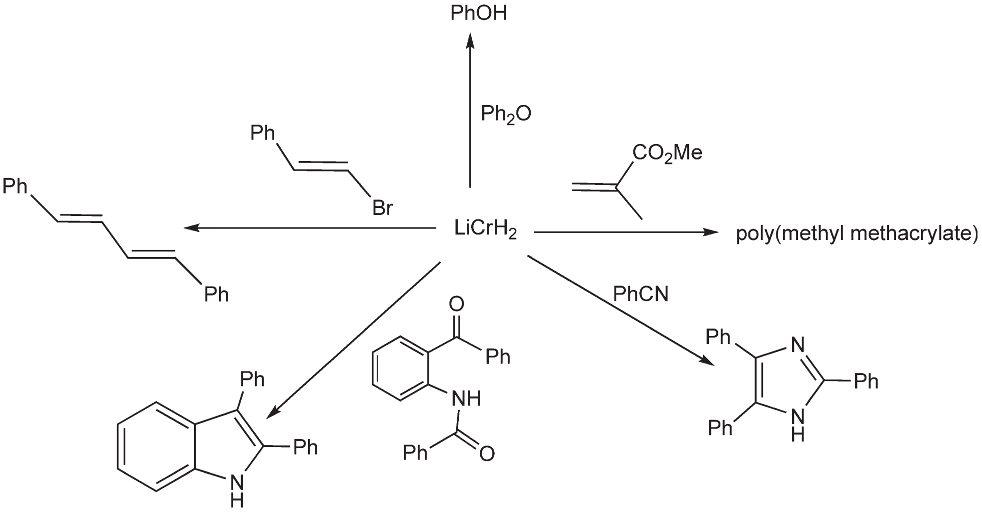
Scheme 86



Scheme 87



Scheme 88



Scheme 89

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5.06
Molybdenum Compounds with CO or Isocyanides

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The chemistry of the Mo–CO and Mo–CNR fragments is treated in this chapter. This work is a sequel to COMC II (1995), and as such the literature from 1993 to the end of 2004 is surveyed. Some relevant review articles from 2005 are also included. Not discussed in this chapter is the chemistry of transition metal cluster compounds, complexes containing the carborane ligand, and the use of molybdenum compounds in organic transformations. Complexes containing the nitrile ligand have been included in *Comprehensive Coordination Chemistry II*.[1] The organization of this chapter broadly follows those in previous volumes of COMC II (1995), so that [Mo(CO)$_6$] and σ-donor/π-acceptor carbon-based ligands are treated together, followed by compounds that do not contain π-bonded ligands. These are treated in Section 5.06.3 and are classified according to the hapticity of the metal ligand interactions. Finally, molybdenum complexes with isocyanide ligands are reviewed in Section 5.06.4. For an overview of the use of group 6 metals in organic synthesis, the reader is referred to the series *Science of Synthesis*, which includes preparative details for a wide variety of common molybdenum compounds,[2] and Volumes 10 and 11 of this work.

5.06.1 Molybdenum Hexacarbonyl and Other Carbonyl Complexes with Carbon Based σ-Donor and σ-Donor/π-Acceptor Bonded Ligands

5.06.1.1 Spectroscopic and Theoretical Studies on Molybdenum Hexacarbonyl

The physical properties and synthetic details of [Mo(CO)$_6$] have been thoroughly treated in COMC (1982)[3] and COMC (1995).[4] Developments since 1993 revolve around more sophisticated spectroscopic and theoretical calculations. In addition to previous studies on vibrational spectroscopy, the far IR spectrum ($500-10\,\text{cm}^{-1}$) of gaseous [Mo(CO)$_6$] has been recorded and agrees with the O_h symmetry observed in the crystal structure.[5] By using a combination of continuous low-pressure supersonic jet and high-resolution FTIR spectroscopy, Asselin and co-workers were able to carry out detailed ro-vibrational studies on the ν_6 fundamental band of [Mo(^{12}CO)$_6$]. The natural abundance of [Mo(^{13}CO)(^{12}CO)$_5$] was also studied.[6] Vibrational spectra of group 6 metal hexacarbonyls in the solid state have also been analyzed using the oriented gas and latent symmetry approaches.[7] Theoretical studies on the vibrational spectra of [Mo(CO)$_6$] have also been reported.[8,9] In particular, time-dependent DFT calculations have shown that weak bands in the absorption spectra of [M(CO)$_6$] can be assigned to forbidden metal to ligand charge transfer (MLCT) bands and not, as has previously been stated, ligand field excitations.[10] Theoretical and spectroscopic methods for examining ground-state [Mo(CO)$_6$] have also been forthcoming.[11,12] Charge decomposition analysis (CDA) studies of [Mo(CO)$_5$L] (L = CO, SiO, CS, N$_2$, NO$^+$, CN$^-$, NC$^-$, HCCH, CCH$_2$, CH$_2$, CF$_2$, and H$_2$) have also shown that this technique can be considered as a quantitative expression of the Dewar–Chatt–Duncanson model.[13] Other techniques reported include electron momentum spectroscopy,[14] X-ray absorption spectroscopy,[15] and X-ray photoelectron spectroscopy.[16,17]

Gas phase spectroscopy has produced interesting association products. [Mo$_2$(CO)$_n$]$^+$ (n = 0–11) and higher Mo clusters have been observed. Compounds with n = 10 or 11 would be predicted to be unstable, as the long Mo–Mo bond length is unfavorable for bridging CO ligands. Therefore, it is an interesting development that polynuclear

Table 1 Bond dissociation energies of $[Mo(CO)_n]$ measured by PIE spectroscopy

Bond dissociated	*Experimental BDE* (kJ mol^{-1})
$[Mo(CO)_6]^+$	137.0 ± 8
$[Mo(CO)_5]^+$	129.3 ± 6
$[Mo(CO)_4]^+$	167.9 ± 21
$[Mo(CO)_3]^+$	140.9 ± 21
$[Mo(CO)_2]^+$	$\leq 160.2 \pm 30$
$[Mo(CO)]^+$	>42.3

Adapted from Chen, Y.-J.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys*. 1997, *107*, 4527–4536, with permission.

clusters can be observed starting from $[Mo(CO)_6]$.[18] Gas phase dissociations of the carbonyl ligands have also been studied by experiment[19–22] and theory[23–29] (first dissociation energies for $[Mo(CO)_6] = 137$–186 kJ mol^{-1} and 114–220 kJ mol^{-1}, respectively). Photoionization efficiency (PIE) spectroscopy has given the bond dissociation energies (BDEs) for $[Mo(CO)_6]^+$ through $[Mo(CO)]^+$ which are listed in Table 1; the highest BDE being for $[Mo(CO)_4]^+$.[22] A report on the laser ablation of Mo atoms with CO in a neon matrix also gives unsaturated neutral, anionic, and cationic $[Mo(CO)_n]$ species ($n = 1$–6) observed from the photodissociation experiments. These species have been characterized by IR spectroscopy and by DFT calculations.[30] A review on the synthesis and characterization of neutral, anionic, and cationic binary metal carbonyls has also appeared.[31]

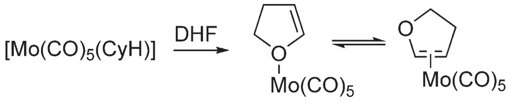
^{95}Mo NMR spectroscopy has gained prominence as an analytical technique during the last two decades, and it is now almost routine to measure these spectra; this area has been reviewed recently.[32,33] Solid-state NMR spectra of stationary and spinning samples of $[Mo(CO)_6]$ have only recently been reported[34] as they have been hampered by the relatively low gyromagnetic ratio and abundance of the ^{95}Mo isotope. However, the authors were able to detect a $^{13}C/^{12}C$ isotope effect on ^{95}Mo shielding, and the results agree with predictions made from a crystal structure determination. A further paper detailed the measurement of the $^{12}C/^{13}C$ isotope effect.[35] This has been expanded to a single crystal NMR study.[36] The NMR shielding tensor has also been subject to a theoretical investigation using a scalar relativistic approach, and the calculated ^{95}Mo chemical shift (−1804 ppm) is remarkably close to the experimental value (−1857 ppm). In this study, it was found that the inclusion of relativistic effects was important in 4*d* compounds and essential in 5*d* compounds.[37] Further studies on ^{95}Mo NMR spectroscopy[38,39] and ^{13}C and ^{17}O NMR spectroscopy[40,41] using other computational methods have also been described.

5.06.1.2 Photochemistry of Molybdenum Hexacarbonyl

The understanding of weakly solvated species such as $[Mo(CO)_5(alkane)]$, obtained by photolysis in an appropriate solvent, is of obvious importance as a common synthetic approach is the substitution of carbonyl ligands with an appropriate ligand under photolytic activation (Equation (1)). The reaction is now thought to proceed by very fast (femtosecond timescale) reactive decay to give a vibrationally excited pentacoordinate species $\{Mo(CO)_5\}^*$, followed by vibrational cooling and trapping by a solvent molecule to give $[Mo(CO)_5(solv)]$. This is followed by a slower second-order reaction with added ligands to form $[Mo(CO)_5L]$. Alkane (linear or cyclic), alkene, or alkyne solvents have been studied. An extensive review on transition metal alkane complexes has been published.[42]

$$[Mo(CO)_6] \xrightarrow[-CO]{h\nu} \{Mo(CO)_5\}^* \xrightarrow{+solv} [Mo(CO)_5(solv)] \xrightarrow[-solv]{+L} [Mo(CO)_5L] \qquad (1)$$

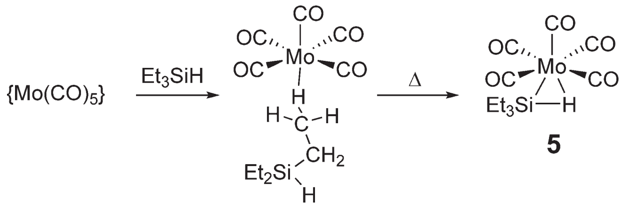
The initial photolysis has been studied using a variety of techniques and the vibrational relaxation measured between 20–50 ps.[23,43–45] The reaction of $[M(CO)_5(solv)]$ with L has also been examined using time-resolved optical and infrared spectroscopy for L = CO in cyclohexane solutions.[46] This gave the thermodynamic parameters $k_{CO} = 4.6 \pm 0.2 \times 10^6\ M^{-1}s^{-1}$, and $\Delta H^{\ddagger}_{CO} = 32.6 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger}_{CO} = -7.3 \pm 11$ J mol^{-1} K^{-1}. Similar values have been obtained using actinometry, photoacoustic calorimetry (PAC), and optoacoustic spectrometry in the study of the reactions of $[Mo(CO)_5(alkane)]$ with piperidine,[47] THT,[48] and THF.[49] It was shown that the molybdenum–alkane bond energy was very low (56 kJ mol^{-1}) while the Mo–THF (104 kJ mol^{-1}), Mo–piperidine (142 kJ mol^{-1}), and Mo–THT (155 kJ mol^{-1}) energies were also measured. Finally, the reaction of DHF (DHF = 2,3- and 2,5-dihydrofuran) with $[Mo(CO)_5(CyH)]$, **1**, has been studied using TRIR spectroscopy. The DHF molecule initially forms a complex through the oxygen as the kinetic product, 2, but this undergoes a reversible intramolecular linkage isomerization to give an equilibrium mixture of the η^1- and η^2-product, 3 (Equation (2)). The activation enthalpy for the linkage isomerization is ~40–60 kJ mol^{-1} while activation entropies are near zero.[50]



1 2 3

(2)

The enthalpy changes of the reactions $[M(CO)_6] \rightarrow [M(CO)_5(L)]$ (L = *n*-heptane, H_2, and N_2) have also been studied by PAC using high pressures of H_2 or N_2. The enthalpy change for L = *n*-heptane is 105 kJ mol^{-1}, consistent with measurements from low-pressure PAC, whereas for H_2 and N_2 the enthalpy change is 87 and 86 kJ mol^{-1}, respectively.[51] From PAC studies, it has been shown that an associative mechanism operates for the initial coordination of the solvent.[52] Pulsed laser flash photolysis shows that the desolvation process goes via a dissociative mechanism;[53] however, time-resolved optical and infrared spectroscopy suggests an interchange mechanism for desolvation.[47] This work has also been extended to the photolysis of $[Mo(CO)_6]$ in Et_3SiH (Equation (3)). The $\{Mo(CO)_5\}$ fragment is solvated (<2 ps) by the C–H bonds of the silane, 4, which then undergoes a rearrangement to form the silyl hydride species 5 (few ns). The mechanism is thought to be dissociative.[54]



5

4

(3)

The examination of the reactivity of $BH_3{\cdot}L$ (L = NMe_3, PMe_3 or PPh_3) with $[M(CO)_6]$ is of relevance to this discussion as it is isoelectronic with CH_4, studied in earlier matrix isolation experiments. Whilst for Cr and W stable examples of η^1-H-$BH_2{\cdot}L$ complexes were isolated, under identical conditions $[Mo(CO)_5(\eta^1\text{-H-}BH_2{\cdot}L)]$ could not be, as the backreaction with liberated CO was fast.[55] Pulsed laser flash photolysis has also been used to study the reactions of $[Mo(CO)_6]$ in CCl_4 solution, the initial product being $[Mo(CO)_5(\eta^1\text{-}ClCCl_3)]$, where one chloride ligand is bonded to the molybdenum.[56] This decomposes in the presence of an alkene trap by second-order rate kinetics and is indicative of a displacement or interchange mechanism. Matrix isolation studies have also been used to investigate the reactivity of $[Mo(CO)]_6$ with alkynes.[57] This is of interest as there is a tautomerization process to give vinylidene species, a common synthetic pathway to metallacumulenes (see Section 5.06.1.6.3). However, due to the limitations of the matrix isolation technique, solvent effects were not studied and the initial coordination steps not investigated. Further work using the techniques described above should shed more light on the solvation of $\{Mo(CO)_5\}$ with alkynes and the resulting rearrangement to vinylidene species. Some experimental reactivity studies suggest that a vinylidene species is formed.[58] Polyethylene matrix studies have also been used to study reactive intermediates from photolysis.[59]

5.06.1.3 Studies on Supported $[Mo(CO)_6]$

As described in COMC (1995),[5] the use of $[Mo(CO)_6]$ adsorbed onto zeolites, alumina, and other supports has been a topic of much interest and has been reviewed recently.[60,61] Therefore, only selected important results will be presented here. Detailed kinetic measurements of the anchoring and decarbonylation of $[Mo(CO)_6]$ in Na56Y zeolite show that these processes occur at the same rate and probably via the common intermediate, $(\sim\text{Si–O–OC})_3Mo(CO)_3(Na^+)_n$ (~Si–O = zeolite). The decarbonylation process is thought to form a complex $(CO)_3Mo(O)_3$, where the coordinated zeolite ligand $(O)_3$ is a triangular face of three oxide ions.[62] The thermodynamic data show very low enthalpies and extremely negative entropies ($\Delta H = 40 \pm 3$ kJ mol^{-1} and $\Delta S = -185 \pm 9$ J mol^{-1} K^{-1}) for anchoring and decarbonylation. In a study on the adsorption of $[Mo(CO)_6]$ onto partially dehydroxylated or hydroxylated Al_2O_3 using IR and UV spectroscopy, it was found that $[Mo(CO)_6(ads)]$ loses CO reversibly with an apparent single rate constant $k = 1.8 \times 10^{-4}\ s^{-1}$ at 298 K to form $[Mo(CO)_5(ads)]$. Upon removal of the released CO under vacuum, $[Mo(CO)_5(ads)]$ loses two additional molecules of CO to form $[Mo(CO)_3(ads)]$. On hydroxylated alumina, physisorbed $[Mo(CO)_6]$ undergoes nucleophilic attack by hydroxyl groups, forming $[Mo(CO)_5(L)]$

(L = surface hydroxyl). This species then loses additional carbonyl ligands to form lower subcarbonyls.[63] The characterization of $[Mo(CO)_5(ads)]$ is of importance as this species has been postulated in numerous studies but had not previously been detected.

5.06.1.4 Kinetics and Reactivity of $[Mo(CO)_6]$

There are two main reactivity patterns that $[Mo(CO)_6]$ undergoes: (i) substitution and (ii) oxidation. Substitution of one or more carbonyl ligands via photolytic, thermal, or chemical activation is one of the most widely studied reaction pathways. Results from 1993 onward are described in this chapter, although given the volume of work that has been published some selectivity has been applied. A relatively new development is microwave-assisted syntheses, which reduces reaction times dramatically and in some examples increases yields over methods that are more conventional. Examples with mono-, bi-, and tridentate ligands have been reported.[64,65] Chemical activation has been primarily achieved using Me_3NO, which oxidizes a carbonyl ligand to CO_2 and, in the absence of any other ligands, the liberated Me_3N coordinates to form $[Mo(CO)_5(NMe_3)]$. Other reagents can also accomplish this transformation, and the reaction of hydroxylamine in place of Me_3NO gives $[Mo(CO)_5(NH_3)]$. The reaction kinetics were studied and show first-order kinetics in both $[Mo(CO)_6]$ and $[NH_2OH]$ concentrations. Further analysis suggests that the oxidation of CO is via a four-centered mechanism and the liberated ammonia then coordinates to the unsaturated $[Mo(CO)_5]$ intermediate.[66] A further chemical activation technique that has proved successful is the use of catalytic $NaBH_4$ in refluxing EtOH, first described by Chatt and co-workers.[67]

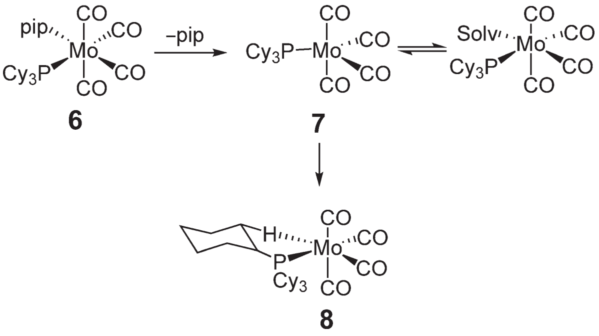
By substitution of two carbonyl ligands the *cis*- and *trans*-isomers can be formed, with the *trans*-isomer being the thermodynamically stable product, and a large body of work on the kinetics of these reactions has been published. While numerous efforts have been made to correlate reactivities of *cis*-isomers to their solid-state structures, very little work has been done on the *trans*-isomer.[68] For the synthesis of *cis*-compounds, the commonly used precursors are $[Mo(CO)_4(pip)_2]$ or bidentate diene ligands such as norbornadiene (nbd) or cyclooctadiene (cod); however, the displaced ligand may be non-innocent.[69] Kinetic studies on the substitution of cyclooctadiene for bidentate phosphine ligands have been carried out. When the phosphine is dppm, it was found that the reaction rate exhibits a first-order dependence on the concentration of $[Mo(CO)_4(cod)]$, while the observed rate constant depends on the concentrations of both the cod and phosphine.[70] The rate constant and activation parameters showed little variation with the length of the phosphine chain.[71,72] This implies that the rate-determining step is the cleavage of one of the two metal–olefin bonds. Similar results have been obtained from the study of the substitution of norbornadiene for 2,2′-bipyridyl in the complex $[Mo(CO)_4(nbd)]$, and the activation parameters suggest an associative mechanism in the transition state.[73]

The kinetics of Equation (4) (where L and L^1 are phosphine, phosphite donors) has been investigated. All reactions cleanly follow a mechanism involving initial Mo–pip bond breaking, followed by competition between pip and L^1 for the resulting five-coordinate $[(L)Mo(CO)_4]$ intermediate. The activation parameters for Mo–pip bond breaking have been obtained. The enthalpies and entropies of activation for trialkyl phosphite support intramolecular N–H···O–P hydrogen bonding when compared to those for trialkyl phosphine. The data have been interpreted in terms of a "fundamental" ligand exchange, involving $[(L)Mo(CO)_4]$ and L^1.[74]

$$\textit{cis}\text{-}[Mo(CO)_4(pip)L] + L^1 \longrightarrow \textit{cis,trans}\text{-}[Mo(CO)_4LL^1] + pip \tag{4}$$

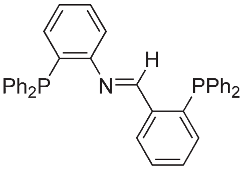
Piperidine dissociation from *cis*-$[(Cy_3P)(pip)Mo(CO)_4]$, **6**, has also been studied and shown to produce *cis*-$[(\eta^2\text{-}Cy_3P)Mo(CO)_4]$, **8**, where PCy_3 forms a five-membered ring bonded to molybdenum via phosphorus at one end and hydrogen (agostic bond) at the other end. Results from kinetic studies suggest that loss of piperidine from *cis*-$[(Cy_3P)(pip)Mo(CO)_4]$ takes place via a dissociative mechanism, where the electronically unsaturated species *cis*-$[(\eta^1\text{-}PCy_3)Mo(CO)_4]$, **7**, is formed during the reaction (Scheme 1).[75]

Formation of chelated complexes from $[Mo(CO)_5(\eta^1\text{-}NN)]$ (NN = phen, substituted phen) has been studied by laser flash photolysis and the observed kinetic effects can be accounted for by an interchange ligand substitution mechanism during which CO is displaced by the chelate.[76] In contrast, linkage isomerization in $[Mo(CO)_5(\eta^1\text{-}PP^1)]$ ($PP^1 = Ph_2PC_2H_4P(p\text{-}Tol)_2$) has been shown to proceed via an associative mechanism, and the transition state becomes more associative as group 6 is descended.[77] The ring-closing reaction of $[Mo(CO)_5(\eta^1\text{-}NN)]$ (NN = phen) has also been studied in supercritical CO_2 and ethane. The activation volume was described to be highest just above the critical point of these solvents, demonstrating the large repulsive contribution to activation volumes of these supercritical solvents.[78] For synthesis of $[Mo(CO)_3L_3]$, the starting materials of choice are $[Mo(CO)_3(NCR)_3]$ (R = Me, Et), $[(cht)Mo(CO)_3]$, or $[(aryl)Mo(CO)_3]$ (aryl = C_6H_6, Mes, etc), all of which give



Scheme 1

the *fac*-substituted tricarbonyl. One of the drawbacks of $[Mo(CO)_3(NCR)_3]$ is its air sensitivity, and the use of pyridine as an alternative ligand has been reported to be significantly more air stable.[79] The *fac*- to *mer*-isomerization has been studied in the complex $[Mo(CO)_3(\mathbf{9})]$ and activation parameters suggest either a dissociative or twist mechanism for this process.[80]



9

The second reactivity pathway of oxidation has also been studied in great detail as the resulting Mo(II) species often show activity in catalytic applications. Many reagents can be used for the oxidation, and work up to 1996 has been covered in two extensive reviews.[81,82] In general, the oxidizing agent also acts as an incoming ligand. Some examples are shown in Equations (5)–(7),[83–85] and more can be found in Section 5.06.2.3.3.

$$[Mo(CO)_3(NCMe)_3] + Br_2 \xrightarrow[\text{MeCN}]{-78\,°C} [MoBr_2(CO)_3(NCMe)_2] \tag{5}$$

$$[Mo(CO)_4(NN)] + HgCl_2 \longrightarrow [MoCl(HgCl)(CO)_3(dmp)] \tag{6}$$

$$[MoBr_2(CO)_2(PPh_3)_2] + AgBF_4 \longrightarrow [(Ph_3P)_2(CO)_2Mo(\mu\text{-}F)_3Mo(CO)_2(PPh_3)_2][BF_4] \tag{7}$$

5.06.1.5 Carbonyl Metallates

A review on homoleptic metal carbonyl anions of the transition metals has appeared.[86] $[Mo(CO)_5]^-$, $[Mo(CO)_5]^{2-}$, and $[Mo_2(CO)_{10}]^{2-}$ are all known compounds but few synthetic or spectroscopic studies have been forthcoming since the publication of COMC II (1995).[4] The reaction of $[Mo(CO)_6]$ with $C(NMe_2)_4$ gives rise to the anionic compounds $[C(NMe_2)_3]_2[Mo_2(CO)_{10}]$ and $[C(NMe_2)_3][(CO)_4Mo(O_2CNMe_2)]$, both of which have been structurally characterized.[87] The $[PPN]_2[Mo_2(CO)_{10}]$ salt has also been structurally characterized (Mo–Mo = 3.153(2) Å).[88] In addition, a new synthetic procedure for $[M(CO)_5]^{2-}$ (M = Mo, W) has been reported by the reduction of $[M(CO)_6]$ with KC_8 under dilute condition that avoids the formation of the dimeric $[Mo_2(CO)_{10}]^{2-}$ salt.[89] The metallate anions have found a variety of uses by salt elimination, and these will be described in the appropriate chapters. The first example of a cationic molybdenum carbonyl complex, $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3][Sb_2F_{11}]$, has been synthesized by the oxidation of $[Mo(CO)_6]$ with liquid SbF_5. This shows the highest carbonyl stretching frequency for any known Mo(II) species (2110 cm^{-1}). Structural characterization shows it to exist as a coordination polymer in the solid state.[90]

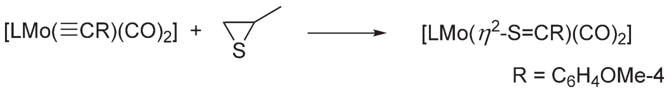
5.06.1.6 Molybdenum Carbonyl Complexes with σ-Donor/π-Acceptor Carbon Ligands

5.06.1.6.1 Molybdenum–carbon single bonds

The insertion of CO into a metal–alkyl bond to form an acyl is a fundamental step in many industrially relevant carbonylation reactions. Few examples of molybdenum acyl species have been reported since COMC (1995).[4] There are three different types of bonding modes commonly observed, η^1, η^2, and agostic (Scheme 2). The chemistry of agostic acyls up to 1995 has been covered in a review,[91] and they are only observed with dithiocarbamate co-ligands. In addition, theoretical calculations have been carried out and the agostic stabilization is 53.2 kJ mol^{-1}.[92] Additional substitution chemistry of η^2-agostic species has also been presented.[93,94] Further migratory reactions of acyl species are rare, partly due to the increased M–C bond strength of the acyl ligand. However, it has been reported that acyl groups can migrate to coordinated secondary phosphine ligands to give $[\mathrm{CpMo(CO)_2(PPh_2COR^1)R^2}]$ ($\mathrm{R^1, R^2 = Me, Et}$) upon treatment with a base. The mechanism postulated for this migration is firstly deprotonation of the secondary phosphine, followed by an intramolecular nucleophilic attack on the acyl carbon atom by the anionic phosphido ligand, then alkylation of the metal with $\mathrm{R^2I}$.[95] This has been corroborated by reactivity studies with alkynes to form vinylphosphine or η^3-acryloyl ligands depending on the reaction conditions.[96]

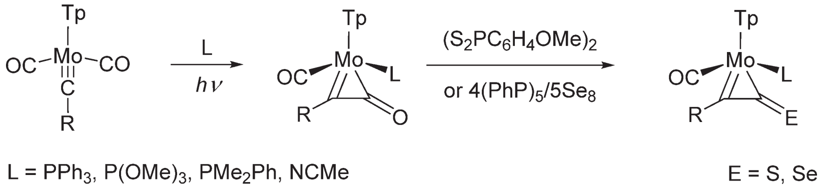
The one-pot reaction of $[\mathrm{Mo(CO)_6}]$, $\mathrm{LiNPr^i_2}$, $\mathrm{I_2}$, and $\mathrm{PPh_3}$ affords the carbamoyl complex $[\mathrm{Mo}(\eta^2\text{-}\mathrm{OCNPr^i_2})\mathrm{I(CO)_3(PPh_3)}]$ which has been used as a starting point for ligand substitution reactions.[97] Imino–acyl complexes are synthesized from isocyanides and are discussed in Section 5.06.4.3. Thioacyl complexes $[\mathrm{L}_n\mathrm{M}(\eta^2\text{-}\mathrm{SCX})\,(\mathrm{CO})_2]$ (L = Tp, bipy, etc.; X = NMe$_2$, OR) have been prepared via two different methods (Equations (8) and (9)) and their reactivity explored.[98–101]

$$[\mathrm{LMo(CO)_3}]^- + \mathrm{XC(=S)Cl} \longrightarrow [\mathrm{LMo}(\eta^2\text{-S=CX})(\mathrm{CO})_2] \qquad (8)$$



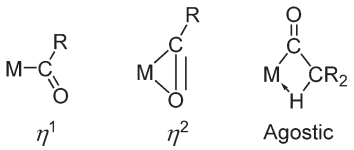
(9)

Thioketenyl complexes of the type $[\mathrm{TpMo}(\eta^2\text{-SCCR})(\mathrm{CO})\mathrm{L}]$ (L = P(OMe)$_3$, PMe$_2$Ph, PPh$_3$; R = C$_6$H$_4$Me-4) have been prepared,[102] and one example of a selenoketenyl complex has been reported (Equation (10)).[103]



(10)

There are very few examples of alkyl and aryl complexes of any group 6 metal in the zero oxidation state, and molybdenum examples are the most scarce. A complex with a bridging carbide ligand has been synthesized, $[(\mathrm{Cy_3P})_2(\mathrm{Cl})_2\mathrm{Ru{\equiv}C \rightarrow Mo(CO)_5}]$, but due to its instability could not be isolated. ^{13}C NMR data suggest that there is a localized Ru≡C triple bond and a single bond to the molybdenum.[104] The chemistry of pentafluorophenyl derivatives of molybdenum carbonyl has been explored, and the complexes *cis,mer*-$[\mathrm{Mo(CO)_2(C_6F_5)\{P(OMe)_3\}_3}][\mathrm{Na}]$ have been synthesized[105] and found to react with CO or ^{t}BuNC to give *mer-trans*-$[\mathrm{Mo(C_6F_5)(CO)_2(L)\text{-}\{P(OMe)_3\}_2}][\mathrm{N(PPh_3)_2}]$ after anion exchange. For L = CO, a structural characterization was presented.[106] A convenient synthesis of the required precursors has only recently been developed. Thus, the reaction of $\mathrm{AgC_6F_5}$ with $[\mathrm{PPN}][\mathrm{Mo(CO)_5Cl}]$ gives the salt $[\mathrm{PPN}][\mathrm{Mo(CO)_5(C_6F_5)}]$ in good yields. This has also been structurally characterized and is stable to air in the solid state for up to 2 weeks.[107] An electrochemical study was also carried out and a slow chemical reaction after one electron oxidation was observed. Simulation of the cyclic voltammograms and chemical

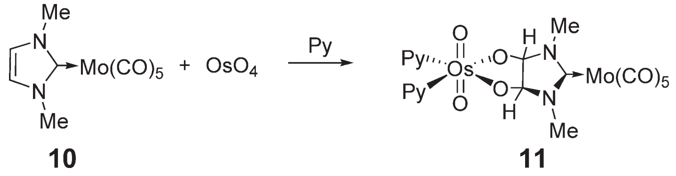


Scheme 2

oxidation in the presence of nucleophiles show that this reaction is the cleavage of the Mo–aryl bond and the formation of [Mo(CO)$_5$L]. The rate constant in the presence of pyridine is approximately 700 $\mathrm{M^{-1}\,s^{-1}}$.[108]

It has been shown that Mo(0) can insert into a C–F bond of a suitably designed Schiff's base ligand to form oxidative addition products that are stable, and this has been reviewed.[109] This concept has been further extended to oxidative addition reactions with C–Cl bonds, e.g., *o*-ClC$_6$H$_4$CH=NCH$_2$CH$_2$NMe$_2$, at room temperature. The design features of the ligand make this process very facile. Additional reactivity studies with alkynes showed they undergo a migratory insertion reaction resulting in net replacement of a C–Cl bond by a C–C bond.[110]

Also of note is the synthesis of complexes of N-heterocyclic carbene (NHC) ligands. These are included in this section, as it is known that the ligand is purely a σ-donor due to the partial occupation of the *p*-orbital on the carbon by the lone pairs on the two nitrogen atoms. This ligand has been the subject of intense research interest and has been reviewed,[111–113] so only recent developments will be reported here. [Mo(CO)$_5$(NHC)] (NHC = :C{N(R)C(H)}$_2$; R = ^{i}Pr, Mes) has been alternatively synthesized by the reaction of the triethylborane adduct of the imidazol-2-ylidene ligand with [Mo(CO)$_6$], demonstrating the synthetic potential of these air stable synthons.[114] The coordinated NHC ligand also undergoes some reactivity, for example, on the treatment of **10** with OsO$_4$, osmylation of the C=C bond occurs to give bimetallic redox stable compound **11**, whereas the Mo–C bond is not affected (Equation (11)).[115] A more recent development is the synthesis of acyclic singlet carbenes, which have properties similar to the NHC ligands.[116,117] Complex **12** has been synthesized but found to be very unstable with regard to loss of CO, and could only be characterized under an atmosphere of CO (Equation (12)).[118] Earlier synthetic strategies for the synthesis of these electron-rich cyclic carbenes have been reported,[119–121] and examples of group 6 complexes used as carbene-transfer reagents also disclosed.[122] σ-Bonded alkynyl complexes are also known for molybdenum and the reader is referred to reviews in this area.[123,124] A comprehensive review on heterobimetallic systems bridged by unsaturated hydrocarbons has been published.[125]



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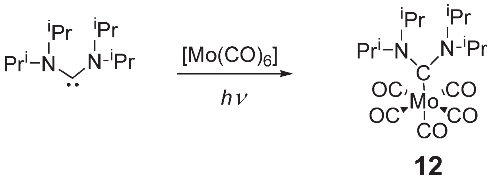
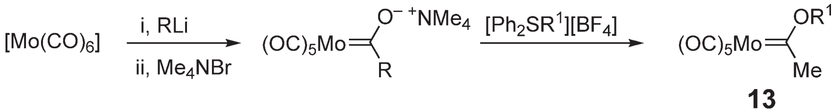


(12)

5.06.1.6.2 Molybdenum–carbon double bonds

By far the most extensive Mo=C species are of the Fischer carbene type. These have been divided into oxycarbene Mo=C(OR)R^1, aminocarbene Mo=C(NR)R^1, and other substituted carbene ligands. The syntheses of these compounds are generally well established (see examples in COMC I (1982)[3] and COMC II (1995)[4]), and the major focus is now on their use in organic synthesis. This area has been reviewed[126] and is included in Volumes 10 and 11 of this edition.[3] A further area of interest of Fischer carbenes is their use as building blocks for bi- and polymetallic species. This area has been recently reviewed.[127] Several aspects of Fischer carbene chemistry are also included in the reviews cited in Section 5.06.1.6.3.

Synthesis – alkoxycarbenes. A new synthetic technique for synthesizing alkoxy Fischer-type carbenes such as **13** has been reported by treating [(OC)$_5$Mo=C(O)R][NMe$_4$] with dialkyl sulfonium salts (Equation (13); R, R^1 = various alkyl groups).[128,129] Neutral alkoxy Fischer carbenes have been prepared in a modified reaction of [(OC)$_5$M=C(OLi)R] with alkyl iodides under phase-transfer conditions or in aqueous media. The advantages of this method are that complex alkyl groups can be incorporated very simply.[130] Although this method works well for Cr, it gives low yields of the expected products for Mo and W. An unusual carbene **15** was formed by the reaction of a germacyclopropabenzene **14** (R = 2,4,6-{(Me$_3$Si)$_2$CH}$_3$C$_6$H$_2$; R^1 = 2,6-Pr$^i_2$C$_6$H$_3$) with [Mo(CO)$_6$] (Equation (14)). The mechanism of this reaction was thought to proceed via CO insertion toward the cyclopropabenzene derivative.[131] Bimetallic alkoxycarbene compounds that contain a thiophene linker have been synthesized and structurally characterized, for example, [(OC)$_5$Mo=C(OEt)(C$_8$H$_6$S$_2$)(OEt)C=Mo(CO)$_5$].[132] Bi- and heterometallic heteroatom-stabilized metal carbene complexes of this type have recently been reviewed.[128] Diazo-functionalized Fischer carbene complexes have been synthesized, although they are not particularly stable, possibly because the electrophilic Fischer carbene may interact with the nucleophilic diazo-substituted carbene, facilitating N_2 loss and subsequent decomposition.[133] Conjugated enyne–carbonyl compounds such as **16** react with $[Mo(CO)_5(NEt_3)]$ via a cycloisomerization reaction to form a Fischer carbene **17** (Equation (15)).[134]



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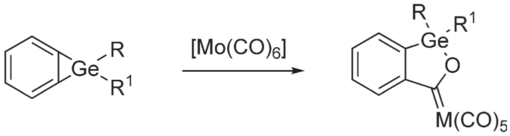
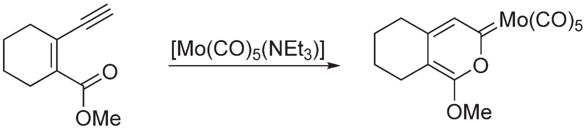
(13)



14 **15**

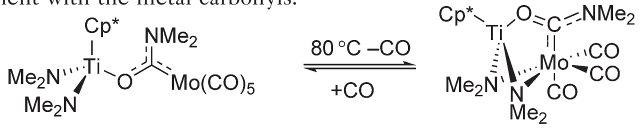
(14)



16 **17**

(15)

Fischer carbenes have also been synthesized by the insertion of $[M(CO)_6]$ (M = Cr, Mo, W) into the Ti–N bond of $[Cp^*Ti(NMe_2)_3]$ to form **18** which is bridged by an $\{O(Me_2N)C\}$ unit, and the carbon atom forms a Fischer carbene-like complex with M. Heating these complexes forms **19**, which reacts with CO to regenerate **18** (Equation (16)).[135] Further titanocene-substituted Fischer carbenes can be synthesized by trapping the vinylidenetitanocene $[Cp^*_2Ti{=}C{=}CH_2]$ fragment with the metal carbonyls.[136]

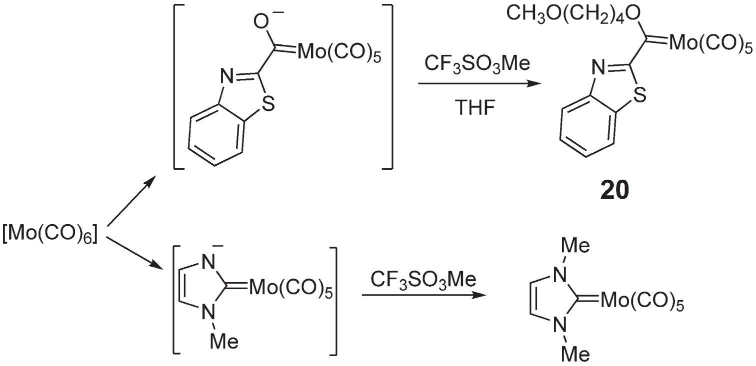


18 **19**

(16)

A series of lithiated pyrazole or imidazole ligands has been reacted with $[Mo(CO)_5L]$ (L = CO, THF, X^-) to give alkoxy fisher carbenes, for example, **20**, or an imidazole-type carbene **21** (Scheme 3).[137]

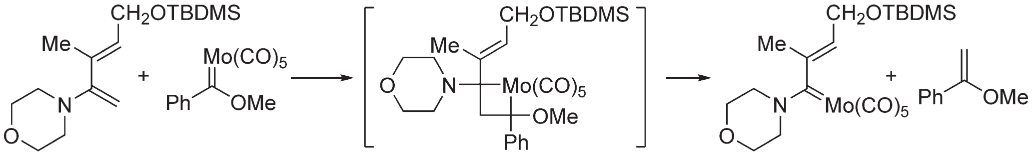
Synthesis – amino carbenes. Vinylaminocarbenes **23** can be readily synthesized by the [2 + 2]-cycloaddition reaction of 2-amino-1,3-butadienes **22** and phenylmethoxycarbenes (Equation (17)). These carbenes react with electron-deficient alkenes to give vinyl ketones via a cyclopropanation mechanism.[138]



20

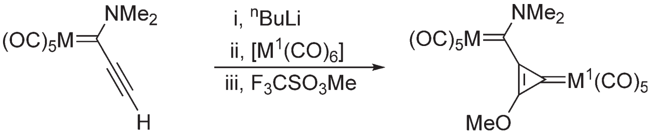
21

Scheme 3



22 **23** (17)

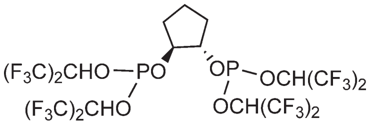
The sequential reaction of the (dimethylamino)ethynylcarbene complex **24** with ^{n}BuLi, $[M^1(CO)_6]$ ($M \neq M^1 = Cr$, Mo, W), and $CF_3SO_3CH_3$ affords heterobinuclear complexes **25** which feature an aminocarbene–cyclopropenylidene bridging ligand (Equation (18)).[139] These results demonstrate the facile migration of carbonyl metal fragments along a carbon chain, something that has been frequently proposed. Notably, if this reaction is carried out using THF as a solvent, different products are obtained that do not contain a second metal.[140]



24 **25** (18)

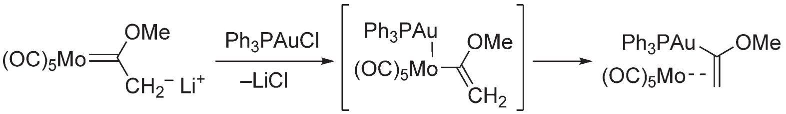
Pyrrole-substituted Fischer carbene analogs have been synthesized and show reactivity more akin to alkoxycarbenes rather than aminocarbenes.[141]

Properties – alkoxycarbenes. The oxycarbene $[(OC)_5Mo{=}C(OMe)Ph]$ reacts with an enantiomerically pure diphosphite **26** to give *fac*-$[(OC)_3Mo\{{=}C(OMe)Ph\}$(**26**)], which unusually can be isomerized to the *mer*-isomer by heating under an atmosphere of CO. The facile formation of chiral, non-racemic Fischer carbene derivatives holds exciting opportunities for organic synthesis.[142]



26

The addition of the $[(Ph_3P)Au]^+$ electrophile to deprotonated Fischer-type alkoxy(methyl)carbene complexes of pentacarbonyl group 6 metals leads to the formation of **27**, a novel vinyl ether complex of gold coordinated to the pentacarbonylmetal moiety (Equation (19)). The bonding in these complexes has also been studied crystallographically and by DFT calculations.[143]



27 (19)

The reaction of $[(OC)_5Mo{=}C(OMe)SiMePh_2]$ with silanes gives the expected Si–H insertion product for Mo, but Cr and W give other products.[144]

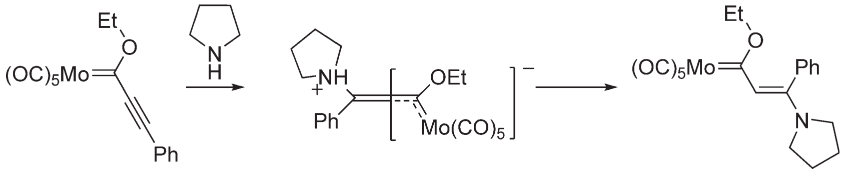
A potentially useful application of Fischer carbenes has been demonstrated in the labeling of peptides with the easily detected $[M(CO)_5]$ fragment.[145] There has been much interest in the functionalization of sugars with Fischer carbenes as this may affect the conformation of the organic sugar.[146,147] The reaction of $BF_3{\cdot}OEt_2$ with lithiated Fischer carbenes $[(OC)_5Mo{=}C(OLi)R]$ (R = Bu, Ph, 2-Naph, PhCH═CH, PhC≡C) gives rise to unstable $[(OC)_5Mo{=}C(OBF_2)R]$ which decomposes above −60 °C to generate acyl radicals.[148] Treatment of dialkyl- or diaminoboranes with oxy-stabilized Fischer carbenes gave the corresponding dialkylboroxy and diaminoboroxy Fischer carbene complexes and subsequently leads to oxaborolane and oxazaborolidine derivatives via C–H insertion reactions on warming to room temperature.[149]

The Fischer carbene $[Li][(CO)_5M\{{=}C(OMe)CH_2\}]$ reacts with the cationic ruthenium alkylidene at the C_γ atom of the unsaturated chain to afford the neutral bimetallic σ-alkynyl $[(\eta^5\text{-Ind})(PPh_3)_2Ru(C{\equiv}CC(Ph)_2$-

$\{CH_2C(OMe){=}Mo(CO)_5\})]$.[150] The catalytic polymerization of alkynes in the presence of $[(CO)_5Mo{=}C(O)R][NMe_4]$, Et_3OBF_4, and $AlCl_3$ (R = Ph, thiophenyl, furanyl) has been reported.[151]

Properties – amino carbenes. The reaction of iminocarbenes with alkenes[152] and alkynes[153] under photolytic conditions has been investigated and forms pyrroline and 2*H*-pyrroles, respectively. The mechanism for reaction with alkenes is postulated to involve an initial cyclopropanation followed by a light-induced [1,3]-sigmatropic rearrangement. In contrast, the reaction with alkynes undergoes initial dissociation of a carbonyl group, coordination of an alkyne moiety, ring enlargement and subsequent reductive elimination. The reaction of the Fischer carbene $[(OC)_5M{=}C(NH_2)Ph]$ with $ClP{=}C(SiMe_3)_2$ gives rise to an azaphosphirene via a cascade reaction, which has been structurally characterized.[154] Also isolated from the reaction with bis(diisopropylamino)chlorophosphine is $[(CO)_5M\{C(N(H)PR_2)R^1\}]$ (M = Cr, Mo, W; $R = NPr^i{}_2$; R^1 = Me, Ph), which has also been structurally characterized.[155]

The acidity of Fischer carbenes has been measured via a kinetic approach, and the pK_a of $[(OC)_5Mo{=}C(OMe)Me]$ was 12.81 in a 50 : 50 mix of CH_3CN and H_2O.[156] Rate constants for the deprotonation of the carbene complexes by OH^- and amine bases were also measured. Interestingly, the pK_a and rate constants vary little in comparison to Cr and W. A kinetic study of the reaction of secondary amines to α,β-unsaturated Fischer carbenes was undertaken (Equation (20)). It was shown to obey a second-order rate law whereby the first step involves attack on the alkoxy oxygen followed by nucleophilic attack of a second amine on the carbenic carbon. The activation parameters were $\Delta G^{\ddagger}{}_{298} = 44.4\ \mathrm{kJ\ mol^{-1}}$, $\Delta H^{\ddagger} = 4.4 \pm 0.1\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S^{\ddagger} = -134 \pm 1\ \mathrm{J\ mol^{-1}\ K^{-1}}$.[157]

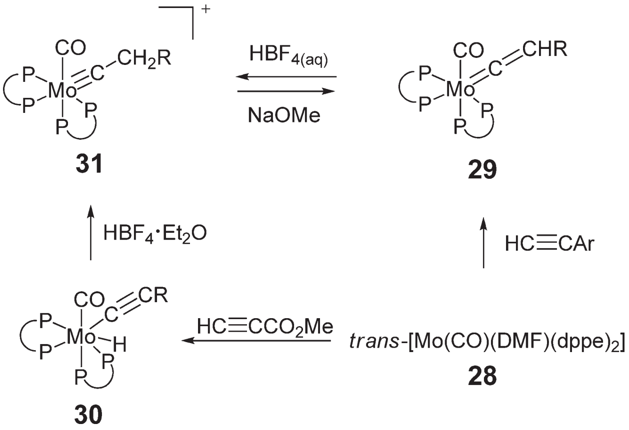


(20)

Computational studies on Fischer carbenes have been forthcoming. One study highlights the importance of including relativistic effects in the calculations.[158] It has been shown that in $[(OC)_5M{=}CH_2]$ the intrinsic σ-bond strengths are in the order W > Cr > Mo.[159]

5.06.1.6.3 Metallacumulene ligands

Less well studied are the metallacumulene-type ligands. Vinylidene, allenylidene, and higher metallacumulene derivatives have all been reported for group 6 metals, although examples of Mo(0) are rather scarce in comparison with Cr and W. This topic has been the subject of several comprehensive reviews on synthetic[160–163] and mechanistic aspects,[164] so a representative example will be given here which includes typical reactions of vinylidene species (Scheme 4). Treatment of *trans*-$[Mo(CO)(DMF)(dppe)_2]$, **28**, with arylacetylenes gives vinylidene complexes *cis*-$[Mo({=}C{=}CHR)(CO)(dppe)_2]$, **29**, (R = Ph, 4-$MeC_6H_4$) whereas treatment with $HC{\equiv}CCO_2Me$ afforded an alkynylhydrido complex $[Mo(C{\equiv}CCO_2Me)H(CO)(dppe)_2]$, **30**. Structure **29** reacts with aqueous HBF_4 to form an

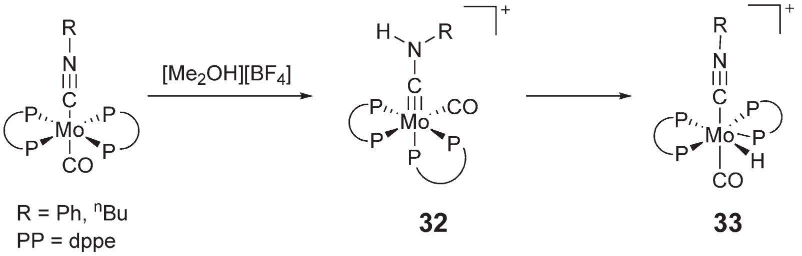


Scheme 4

alkylidyne complex *cis*-[Mo(≡CCH_2Ph)(CO)$(dppe)_2$][BF_4], **31**. The reaction of **30** with $HBF_4{\cdot}OEt_2$ also gives complex **31**. Structure **29** can be readily synthesized from **31** by the reactions with NaOMe. These compounds were further characterized by X-ray diffraction.[165] The electronic structure, bonding, and reactivity of [$L_nM({=}C)_nH_2$] ($n = 4$, 5) has been studied by density functional theory. It was shown that the HOMO has contributions from the metal and even-numbered carbon atoms, while the LUMO has contributions from carbon atoms in odd positions. This explains the regioselectivity of nucleophilic and electrophilic attack that has been observed experimentally.[166] Additionally, the [TpMo$(CO)_2$] framework has been used to stabilize Mo–C multiply bonded species, and this is discussed in Section 5.06.2.4.2.(i).

5.06.1.6.4 Molybdenum alkylidyne species

As is the case for metallacumulenes, the chemistry of molybdenum alkylidyne species has been somewhat neglected in comparison to its chromium and tungsten counterparts. Since the publication of COMC II (1995),[4] there have been few examples of new [$(OC)_nMo{\equiv}CR$] species. These have also been covered in several reviews,[167–173] so only a brief discussion is included here. A convenient one-pot synthesis of [(bipy)$(CO)_2$Mo(≡CAr)Br] has been reported and an investigation into its reactivity to form thioacyls performed.[174] Protonation of isocyanides has also been shown to form carbyne complexes such as **32** (Equation (21)) and structural characterization (where R = Ph) reveals a delocalization of electron density from the nitrogen *p*-orbital into a *p*-orbital of the carbyne. This compound is unstable in solution however and isomerizes into the hydridoisocyanide complex **33**.[175] Protonation reactions have been studied on a variety of molybdenum carbynes and two distinct products have been observed, either protonation at the carbyne carbon (the kinetic product) or at the metal (thermodynamically favored). Thus, in the presence of π-acidic ligands, the thermodynamic product **34** was isolated, while sequential replacement of the CO ligands with phosphites enables the kinetic product **35** to be isolated (Equation (22)).[176] Further examples containing Tp ligands are discussed in Section 5.06.2.4.2.(i).



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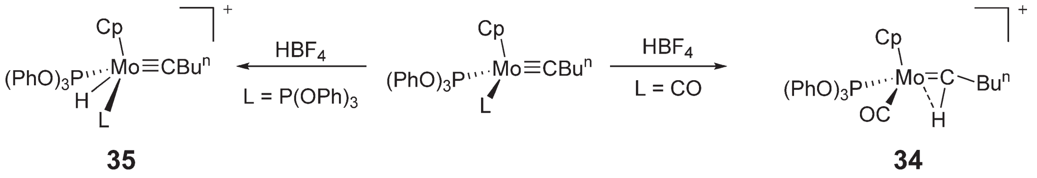


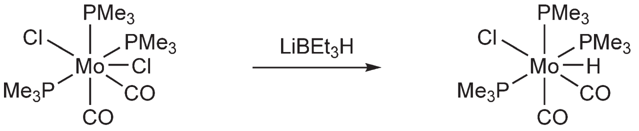
(22)

5.06.2 Carbonyl Complexes of Noncarbon-Bonded Ligands to Molybdenum

5.06.2.1 Molybdenum Hydride and Dihydrogen Complexes

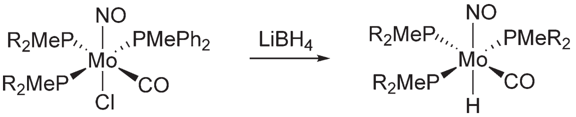
5.06.2.1.1 Hydrides

Synthesis. Molybdenum hydrides can be synthesized via a number of different ways. The reaction of [$MCl_2(CO)_2(PMe_3)_3$], **36**, with super hydride gives the monohydride [$MH(Cl)(CO)_2(PMe_3)_3$], **37**, although the reaction is somewhat sensitive to the exact conditions used (Equation (23)).[177] It is a well-known fact that the strength of the M–H bond depends on the electronegativity of the metal center. It is also known that nitrosyl groups can lower the orbital electronegativity of transition metal compounds,[178] and the addition of strongly σ-donating phosphine ligands enhances this effect. To this end, the compounds *mer*-[Mo(H)(CO)(NO)$(PMePh_2)_3$], **39**,[179] *mer*-[Mo(H)(CO)(NO)$(PMe_3)_3$], **40**,[180] and the deuteride *mer*-[Mo(D)(CO)(NO)$(PMe_3)_3$],[181] **40**^{D}, have been prepared from the reaction of **38** with $LiBH_4$, although the synthesis of **40** proceeded via a BH_4 intermediate which could be isolated (Equation (24)). These complexes are reported to be thermally stable. Protonation reactions can also be used to synthesize molybdenum carbonyl hydrides. For example, treatment of the dinitrogen or nitrile complexes [Mo(CO)(L)(dppe)$_2$], where L = N$_2$, **41**; NCR, **42** (R = Me, Et, ^{n}Pr), with aqueous HBF$_4$ gives [MoH(CO)(OH$_2$)(dppe)$_2$]$^+$, **43** or [MoH(CO)(NCR)(dppe)$_2$]$^+$, **44** respectively (Equation (25)).[182]



36 **37**

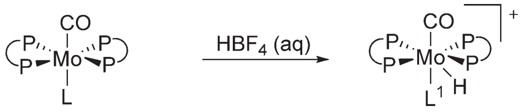
(23)



38

39: R = Ph
40: R = Me

(24)



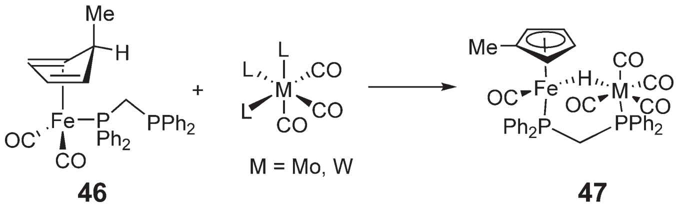
41: L = N$_2$
42: L = NCR

43: L^1 = OH$_2$
44: L^1 = NCR

(25)

Reactivity studies of a series of unsaturated [M$_2$(μ-H)$_2$] (M = M) fragments have been a fruitful area of research for many metals. Group 6 examples are not so well studied, as a simple synthetic technique for [Et$_4$N]$_2$[Mo$_2$(CO)$_8$(μ-H)$_2$] has only recently been developed. Thus, treatment of [(TMEDA)Mo(CO)$_4$] with [Et$_4$N][BH$_4$] under carefully controlled conditions affords the unsaturated species in modest yields. This simple synthetic technique should allow a deeper investigation into the chemistry of these species.[183]

There are many examples of a hydride bridging to a second transition metal. Rhenium and ruthenium hydrides give a variety of products upon treatment with [(diglyme)Mo(CO)$_3$] to form the compounds [(Ph$_3$P)$_3$M(μ-H)$_3$Mo(CO)$_3$]$^-$ (M = Re,[184] Ru[185]) or [ReMo$_3$H$_4$(CO)$_{12}$]$^{3-}$ with [ReH$_9$]$^{2-}$.[186] Cp$_2$TaH$_3$ or [Cp$_2$MH$_2$(PR$_2$H)][Cl] (M = Nb, Ta) react with [Mo(CO)$_5$] or [Mo(CO)$_4$(nbd)] to give the expected heterobimetallic compounds [Cp$_2$Ta(H)$_2$(μ-H)Mo(CO)$_5$],[187] **45** or [Cp$_2$MoH(μ-H)(μ-PR$_2$)M(CO)$_4$],[188] respectively. Reaction of [(η^4-MeC$_5$H$_5$)Fe(CO)$_2$(η^1-dppm)], **46**, with [M(CO)$_3$L$_3$] (M = Mo, W; L$_3$ = (NCEt)$_3$, (THF)$_3$, C$_7$H$_8$) gave [(η^5-MeC$_5$H$_4$)Fe(CO)(μ-η^1:η^1-dppm)(μ-H)M(CO)$_4$], **47**, via coordination of the monodentate dppm to M and CO migration from Fe to M with a sequential or concerted oxidative addition of the *endo*-C–H bond of the η^4-MeC$_5$H$_5$ ligand. Trapping of the Fe–H bond by M forms a six-membered heterocyclic ring (Equation (26)).[189]



46 **47**

(26)

Properties. Complex **37** shows dynamic rearrangement in solution involving exchange of phosphine groups and CO ligands, as deduced by variable-temperature NMR spectroscopy. The structure proposed is roughly pentagonal bipyramidal with a phosphine and CO ligand in the axial positions and the two remaining phosphines transoid. The solid-state structure of the W analog was also reported. However, these are thermally sensitive and decompose to **36** and other unidentified products. Loss of PMe$_3$ has been postulated in this decomposition as the thermal stability is increased if this ligand is added.[177] Spectroscopic characterization of **39** suggests that the hydride is *trans* to the NO group, based on ^{13}C NMR and IR spectroscopic measurements.[179] This was confirmed in a structural determination of **40**. Additionally, this complex showed a very low ν(M–H) band in the infrared spectrum at 1609 cm^{-1} (hexane solutions at −70 °C), suggesting that the M–H bond is weak. DFT analysis gives an Mo–H bond strength of

296 kJ mol^{-1}.[180] **40**^{D} was also studied by ^{2}H NMR spectroscopy.[181] Complex **43** displays an extremely low ν(CO) stretch in its infrared spectrum at 1776 cm^{-1}, due to the good σ- and π-donating OH_2 group in the *trans*-position and no other π-acidic ligands. Both complexes **43** and **44** have been structurally characterized.[182]

In order to fully characterize the known compounds $[M(CO)_2(\eta^2\text{-PP})_2H][SO_3CF_3]$ (M = Cr, Mo, W; η^2-PP = dppm, dppe), electrochemical methods have been used.[190] It was shown that the oxidation proceeds via an electrochemical–chemical–electrochemical–chemical (ECEC) mechanism with M–H bond cleavage. The use of the corresponding deuteride revealed a normal isotope effect, suggesting that reactivity at the M–H bond is an important kinetic or thermodynamic component of the oxidation reaction. Additionally, the oxidized species $[M(CO)_2(\eta^2\text{-PP})_2H]^{2+}$ can be viewed as extremely strong acids [pK_a(MH$^+$)-pK_a(MH^{2+}) = 27.9 (dppm) and 26.2 (dppe)].

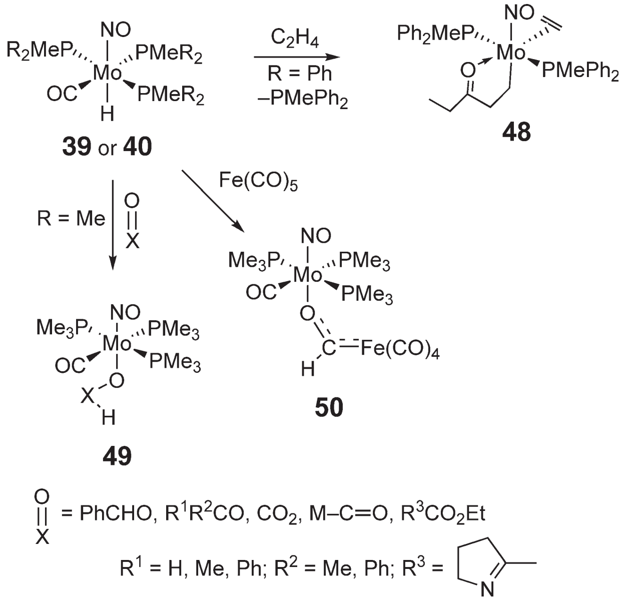
$[ReMo_3H_4(CO)_{12}]^{3-}$ shows unusual variable-temperature NMR spectra whereby the carbonyl ligands exchange but not the hydride ligands. A turnstile mechanism was postulated and the barrier to this process was estimated at 44.40 ± 0.12 kJ mol^{-1}.[186] Compound **45** has been subject to detailed variable-temperature NMR and IR studies, and on the basis of T_1 measurements a structure was proposed in which the central hydride was bonded to the Mo center which is dynamic in solution and goes through a dihydrogen intermediate.[187]

Reactivity. The chloride ligand in **37** can be replaced by a variety of anionic bidentate ligands (S_2CNMe_2, $S_2COCHMe_2$, S_2COMe, acac). The ^{1}H NMR spectra unequivocally prove that the hydride ligand is still bonded to the Mo center and the structure $[MH(\eta^2\text{-SS})(CO)_2(PMe_3)_2]$ is postulated.[177] Complex **39** shows unusual reactivity toward alkenes, with **48** formed by reversible insertion into the M–H bond after coordination to the metal center. This has implications for the mechanism of CO–olefin co-polymerization.[179] Compound **40** also reacts with aldehydes, ketones, and CO_2 via an insertion mechanism to form **49**. CO does not insert into the M–H bond, rather substitution of one of the phosphine ligands is observed. However, formyl complexes such as **50** can be obtained using $Fe(CO)_5$ or $Re_2(CO)_{10}$ (Scheme 5).[180] The heterobimetallic complex $[RhMo(H)(CO)_4(\mu\text{-dppm})_2]$ also displays reactivity toward alkynes.[191]

The reactivity of unsupported bridged hydrides and analogs with bridging phosphine ligands has been investigated with NO$^+$ salts and found to substitute a carbonyl ligand for NO cleanly, although these are considerably less stable than the tungsten analogs.[192]

5.06.2.1.2 Dihydrogen compounds

Since the discovery of the first dihydrogen complex by Kubas in 1980, this field of research has expanded rapidly. Group 6 metal complexes have been at the heart of this interest, as exemplified by the discussion in COMC (1995).[193] The interest in these σ-bonded ligands has been expanded to examples with Si–H, B–H, Sn–H, and C–H bonds, where oxidative addition or reversible/irreversible binding has been observed. Due to the interest, this



Scheme 5

Table 2 Spectroscopic and structural properties of some Mo–(η^2-H_2) complexes

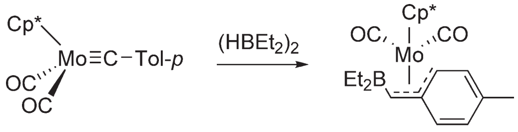
Complex	δ_H (ppm)	J_{H-D} (Hz)	T_1 (ms)	d_{H-H} (Å)	*References*
$[(dppe)_2Mo(CO)(\eta^2\text{-}H_2)]$	−4.7	34	20	0.736(10)[a]	203
$[\{(m\text{-}Tol)_2PC_2H_4P(m\text{-}Tol)_2\}Mo(CO)(\eta^2\text{-}H_2)]$	−5.38	30	10	0.85 ± 0.03[b]	204
$[(dppe)_2Mo(CNPh)(\eta^2\text{-}H_2)]$	−4.8		17		205

[a] From a neutron diffraction study.
[b] From solution T_1 NMR methods.

field has been the subject of a number of reviews on synthetic[194–199] and theoretical aspects[200,201] and an excellent book[202] has also been published, to which the reader is referred. Notable compounds prepared include $[(dppe)_2Mo(CO)(\eta^2\text{-}H_2)]$, which has been additionally characterized by neutron diffraction. The stability of the η^2-H_2 linkage critically depends on the amount of backbonding into the H_2 σ^*- orbital and the analogous compounds with $R_2PC_2H_4PR_2$ (R = Et, Bu^i) are sufficiently electron rich to form the dihydride compounds via oxidative addition. Surprisingly, the complex $[(dppe)_2Mo(CNAr)(\eta^2\text{-}H_2)]$ is stable toward oxidative addition, and this has been ascribed to steric effects. Selected spectroscopic data are given in Table 2.

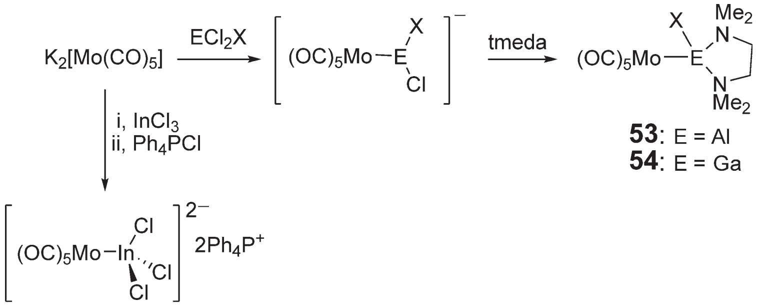
5.06.2.2 Molybdenum Carbonyl Complexes Containing Group 13 Ligands

There are few examples of group 13-based ligands coordinated to the $\{Mo(CO)_n\}$ fragment. The carbollide fragment has been well studied, and an improved synthesis and structural characterization of the tricarbonylmolybdacarborane species $[(C_2B_9H_{11})Mo(CO)_3]^{2-}$ has been reported.[206] A decarbonylation reaction with sulfur donor reagents affords new precursors for high-valent molybdacarboranes, while one-electron oxidation of the PPN salt affords a dimer with a long Mo–Mo bond.[207] An interesting report on the hydroboration of carbenes such as **51** to form **52** has appeared (Equation (27)).[208] In comparison to hydroboration of C≡C species, M≡C examples are more complex; however, new opportunities can be envisioned using these methodologies.



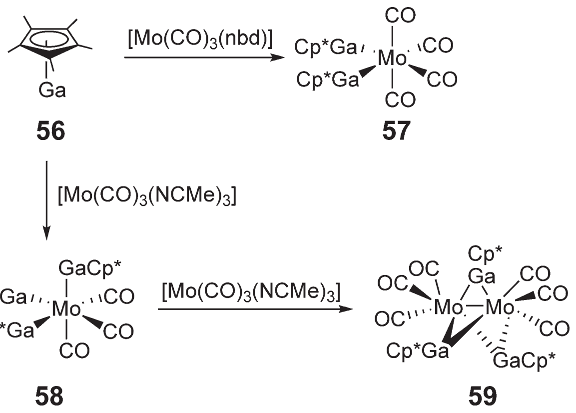
51 **52** (27)

The reactions of carbonyl metallates with ECl_3 or ECl_2X (E = Al, Ga) have been studied (Scheme 6). The compounds $[(CO)_5Mo\text{–}E(X)L_2]$ (E = Al **53**, Ga **54**; X = Cl, Et; L_2 = tmeda) were isolated by treating the intermediate monoanionic solvent-free salt with the appropriate base.[89] Structure **53** is a rare example of an unbridged terminal transition metal–aluminum bond. The infrared spectra reveal that the chloride ligands shift ν(CO) to higher energy compared to the alkyl ligands, because the donor ability of the halide fragment to the metal is lower. Similar reactivity was observed with $InCl_3$ in the presence of $[Ph_4P]Cl$ to give the In(I) derivative **55**, and the authors postulate that the intermediate is $[(CO)_5Mo\text{–}In(Cl)THF]$ (Scheme 6). This compound was characterized structurally



55

Scheme 6



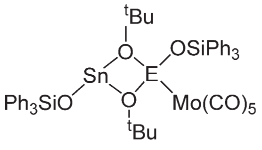
Scheme 7

(Mo–In = 2.7466(1) Å) and in solution by ^{119}In NMR spectroscopy.[209] The reactivity of Cp*Ga, **56**, as a ligand has also been investigated as it is isolobal with CO (Scheme 7). Thus, displacement of norbornadiene from [Mo(CO)$_4$(nbd)] gives **57**,[210] while **58** or **59** can be isolated from reactions with [Mo(CO)$_3$(NCMe)$_3$].[211] Spectroscopic and structural evidence suggest that the Cp*Ga ligand acts as a strong σ-donor.

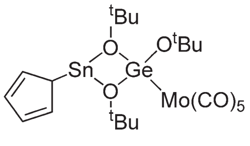
5.06.2.3 Molybdenum Carbonyl Complexes Containing Si, Ge, Sn, and Pb

5.06.2.3.1 Mononuclear σ-donor ligands

Synthesis. Bimetallic complexes containing silyl or siloxyl ligands have been reviewed.[212] Salt metathesis reactions of the [Mo(CO)$_5$I]$^-$ anion with the potassium salt of undecamethylcyclohexasilane give the expected [Mo(CO)$_5$Si$_6$Me$_{11}$]$^-$ anion.[213] As part of the interest in new mixed metal siloxide materials, the ligand [{E(μ-OBu^t)(OSiPh$_3$)}$_2$] (E = Ge, Sn, Pb) has been synthesized and reacted with [Mo(CO)$_6$] under reflux conditions. The isolated compounds show the binding of the Mo(CO)$_5$ fragment to one of the Ge **60** or Sn **61** atoms, whereas attempts to make the lead analog failed and only lead elemental was observed.[214] In a similar vein, the ligand [(C$_5$H$_5$)Sn(η^2-OBu^t)$_2$Ge(OBu^t)] also reacts with [Mo(CO)$_6$] to give **62**, where the Ge atom is coordinated to the Mo fragment.[215]

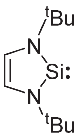


60: E = Ge
61: E = Sn



62

The bisaminosilylene and germylene ligands have attracted much attention, as they are isoelectronic to the Arduengo-type carbenes. The synthesis of the molybdenum carbonyl adducts of stable bisaminosilylenes have been reported in an effort to compare the electronic properties of these ligands. The silylene ligands **63** and **64** were reacted in a 2 : 1 ratio with [Mo(CO)$_6$] under photolytic conditions and *trans*-[Mo(CO)$_4$(**63**)$_2$] or *trans*-[Mo(CO)$_4$(**64**)$_2$] isolated in good yields.[216] Both are also isolated when less than 2 equiv. of the ligand is used, and there was no evidence of the formation of the *cis*-isomer. Two equivalents of silylene **65** react with [Mo(CO)$_4$(nbd)] to form the *cis*- and *trans*-isomers of [Mo(CO)$_4$(**65**)$_2$] in a 30 : 70 ratio.[217] Treatment of diaminogermane **66** with [Mo(CO)$_4$(NCEt)$_2$] affords only *cis*-[Mo(CO)$_4$(**66**)$_2$] along with small amounts of *fac*-[Mo(CO)$_3$(**66**)$_3$].[218]



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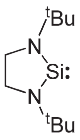

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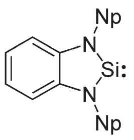

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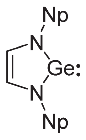
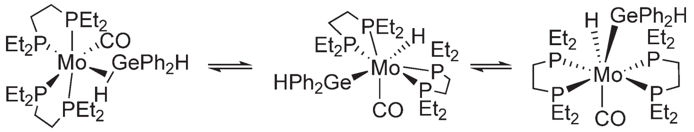


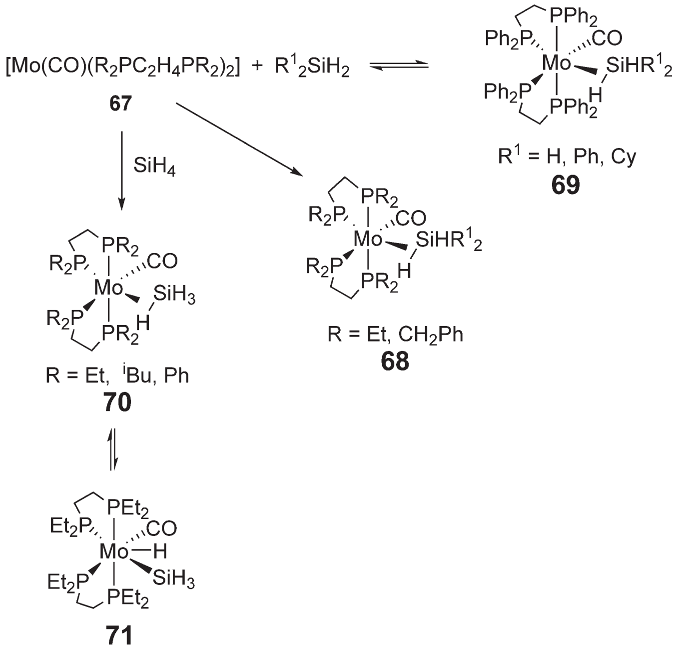
66

There is much interest in σ-bonded complexes of E–H (E = H, C, Si, Ge) and the 16-electron agostic [Mo(CO)($R_2PC_2H_4PR_2$)$_2$] fragment, **67**, has been used to good effect (Scheme 8). Critically, the nature of the phosphine determines the nature of the isolated product. For example, the first example of an η^2 σ-bound Si–H fragment **68** was synthesized by treatment of [Mo(CO)($R_2PC_2H_4PR_2$)$_2$] (R = Et, CH_2Ph) with secondary silanes $R^1{}_2SiH_2$ (R^1 = Ph, Cy, H), whereas **69** (R = Ph) was shown to be in equilibrium with the starting material.[219] This has been ascribed to insufficient Mo($d\pi$) to Si–H(σ^*) backdonation due to the less basic phosphine. The reactivity was further expanded to SiH_4 and again the nature of the phosphine was found to be important as **70** (R = Ph or ^{t}Bu) was isolated, which is the first example of an η^2-SiH_4 fragment, but using the ligand $Et_2PC_2H_4PEt_2$ the product was found to be in equilibrium with the seven-coordinate hydrosilyl tautomer **71**.[220] This has obvious implications for the study of methane activation. In both examples, the CO and the Si–H fragment are *cis* to each other due to the high π-accepting nature of the Si–H fragment being electronically favored to be *cis* to the strongly π-accepting CO ligand. These species have also been the subject of theoretical calculations.[221] Extension of this methodology has also led to the synthesis of the analogous germyl **72**, which is the first structurally characterized σ-germane compound, and again the nature of the phosphine dictates the isolated products so that oxidative addition products **73** and **74** are also observed (Equation (28)). In addition, theoretical studies on the silyl and germyl compounds indicate that oxidative addition of the Ge–H bond is easier than the Si–H bond because of their *trans*-orientation with respect to the CO ligand, which in turn weakens the binding and activation of the σ-ligand. The E–H bond lengths (E = Si, Ge), although not directly comparable, show Ge complexes to be more hydridic in character with shorter E–H bonds.[222]



72 **73** **74** (28)

Properties. The IR and structural data of $[Mo(CO)_5Si_6Me_{11}]^-$ suggest that there is a buildup of negative charge on the silicon that is bound to the metal center as the Mo–Si bond length (2.666(1) Å) and the resonance for the bound Si is shifted to high field in the ^{29}Si NMR spectrum.[213] The complexes of the homo-[214] and heteroleptic[215] tin alkoxide ligands have been characterized by multinuclear NMR, and both Sn complexes have additionally been structurally characterized.



Scheme 8

Table 3 Selected spectroscopic and structural data for NHSi and NHGe compounds

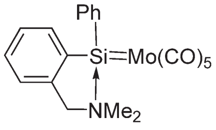
Complex	*IR* (cm^{-1})	^{29}*Si NMR* (ppm)	*Mo–Si/Ge* (Å)	*References*
trans-[Mo(CO)$_4$(**63**)$_2$]	2016, 1947[a]	119.3	2.471	216
trans-[Mo(CO)$_4$(**64**)$_2$]	2009, 1937[a]	155.3	2.480	216
trans-[Mo(CO)$_4$(**65**)$_2$]	1910[b]	156.5	2.4472(6)	217
cis-[Mo(CO)$_4$(**65**)$_2$]	1958, 1932, 1895, 1873[b]	153.7		217
cis-[Mo(CO)$_4$(**66**)$_2$]	2026, 1940, 1923, 1892[b]			218
fac-[Mo(CO)$_3$(**66**)$_3$]	1961, 1853[b]		2.5369	218

[a] Benzene.
[b] Nujol.

IR and Raman spectroscopic studies suggest that the electronic properties of the silylene and germylene ligands are roughly equivalent to PPh$_3$. The crystal structures of *trans*-[Mo(CO)$_4$(**63**)$_2$], [Mo(CO)$_4$(**64**)$_2$], [Mo(CO)$_4$(**65**)$_2$],[216,217] and *fac*-[Mo(CO)$_3$(**66**)$_3$][218] have been reported and selected spectroscopic and structural data are shown in Table 3. For [Mo(CO)$_4$(**65**)$_2$], the *cis*-and *trans*-isomers do not interconvert as the same ratio is observed when the sample is heated to 100 °C. Also of note, the synthesis of the *cis*-isomer is the first example of an octahedral bis[bis(amino)-silylene] metal carbonyl complex, as the large cone angle of the Arduengo-type silylene carbenes generally makes this arrangement unfavorable on steric grounds. The shorter than expected Mo–Ge bond length and the increase in N–Ge bond lengths also suggest that the coordinated germylene is a strong π-acceptor ligand.

5.06.2.3.2 Multiply bonded group 14 complexes

Synthesis. Multiply bonded complexes featuring the heavier group 14 elements are of interest, as they are isoelectronic with the carbon-based Fischer carbene and alkylidene ligands. The Si, Sn, and Pb multiply bonded species have been prepared by photolysis or substitution reactions. The reaction of [Mo(CO)$_6$] with the dihydrosilane ligand [2-{(dimethylamino)methyl}phenyl]phenylsilane under photolytic conditions gives rise to the aminoarylsilanediyl complex **75**, where the central silicon is further stabilized by intramolecular coordination of the amino group.[223] Compounds **76**[224] and **77**[225] were synthesized from the free metal–ylene and [Mo(CO)$_5$(THF)]. Also relevant to this discussion is the synthesis of [{(CO)$_5$Mo}$_2$Sn(NN)] (**79**, NN = (Py)$_2$, bipy, phen, or 2,2′-bipyrimidine) which can be considered as the base-stabilized organometallic cumulene [(OC)$_5$Mo=Sn=Mo(CO)$_5$] that is too unstable to be isolated in its free state. This has been made from the reaction of the PPN salt with NaBPh$_4$ to form the more reactive [Na]$_2$**78**, in the presence of pyridine or bidentate nitrogen donors (Equation (29)).[226] Of note is the fact that the central tin atom is in the formal oxidation state of zero.



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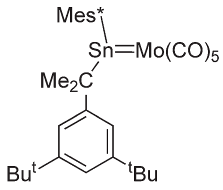

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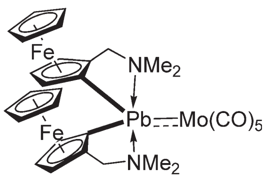

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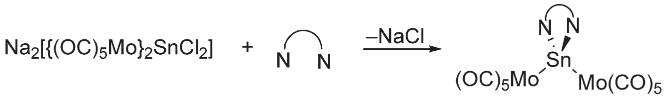


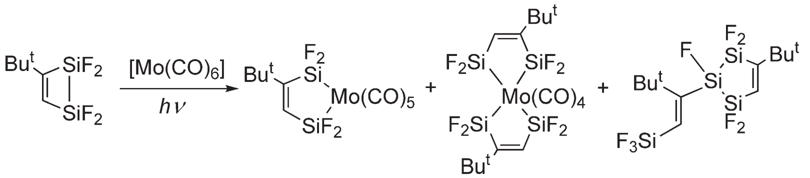
78 **79** (29)

The reaction of a disilacyclobutene **80** with [Mo(CO)$_6$] under photolysis has been studied and shown to give three products, namely the disilylmetallacycles, **81** and **82**, in addition to a ligand dimerization product **83** (Equation (30)).[227] The bisgermavinylidene ligand, **84**, reacts with [Mo(CO)$_5$(THF)] to give a small amount of the molybdenum germacyclopropane **85** (Equation (31)).[228] The mechanism of formation was postulated to involve the addition of an Mo(CO)$_5$ moiety across the Ge=C double bond to form a C–Ge–Mo three-membered ring. The germanium then coordinates to an Mo(CO)$_5$ fragment to form the observed structure. The metallagermacyclopropane ring rearranges with the elimination of "[Mo(CO)$_5$Ge]" to form the carbene pincer complex **86**.

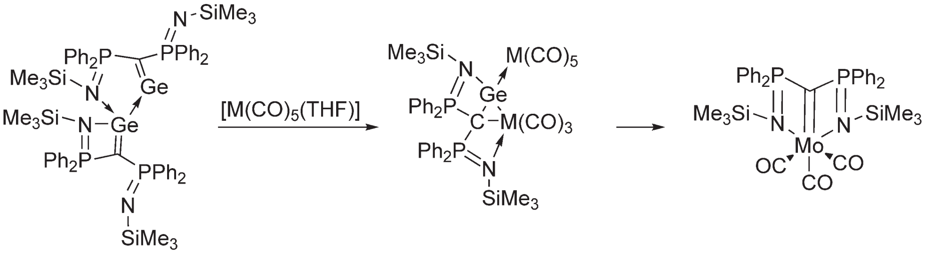
Table 4 Selected spectroscopic and structural data for complexes 75–77

Complex	*M NMR* (ppm)	*M–Mo* (Å)	*IR* (cm^{-1})	*References*
75	+111.2		2055, 1926[a]	223
76	+928.5	2.756(1)	2060, 1981, 1933[b]	224
77		2.8531(13)	2060, 1986, 1936, 1916[c]	225

[a] $CDCl_3$.
[b] KBr.
[c] THF.



80 **81** **82** **83** (30)



84 **85** **86** (31)

Properties. Spectroscopic and metric parameters of 75–77 are shown in Table 4. ^{13}C NMR studies on 75 show only one resonance for the carbonyl ligands indicating rapid exchange of the equatorial and axial CO ligands, whereas the ^{29}Si NMR chemical shift is typical for the formation of an Si═Mo double bond.[223] Structure 76 was structurally characterized and shows a planar *sp*^{2} tin atom.[224] The NMR spectra of 77 show a dynamic process involving dissociation and re-coordination of one of the N–Pb bonds, whereas the room-temperature ^{13}C NMR spectrum shows that the $^2J_{C–Pb}$ coupling constant in the transoid carbonyl ligand is roughly double that seen for the cisoid (153 and 82 Hz, respectively). Crystallographic data also show asymmetric Pb–N bond lengths and the short Pb–Mo bond length indicates some π-character. IR spectroscopic studies suggest that the $(FcN)_2Pb$ ligand in 77 is not only a strong donor ligand but also a π-acceptor ligand which is comparable to phosphine ligands.[225] Electrochemical studies on $[(OC)_5M{=}EX_2(THF)]$ (M = Cr, Mo, W; E = Ge, Sn; X = Cl, Br, I) in acetonitrile solutions show irreversible reduction and oxidation processes, indicating that the radical ions were unstable. It also showed that the electronic structures of these heavy carbenes are similar to those of the Fisher carbenes.[229]

Structure 78 has been structurally characterized as the Ph_4P salts[230] and the significantly more reactive alkali metal (12-crown-4)$_2$ or [2,2,2]cryptand salts can be synthesized.[231] Structural data for 79 are recorded, whereas ^{119}Sn NMR spectroscopy suggests an equilibrium with decoordination of one of the nitrogen donors.

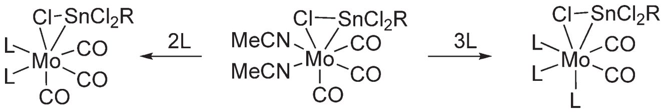
5.06.2.3.3 Mo(ii) carbonyl complexes of Ge and Sn

Synthesis. The uses of main group tetrahalides as oxidizing agents have been investigated, and recent results are described. The reaction of $[Mo(CO)_3(NCMe)_3]$ with $GeCl_4$ was first described using acetonitrile as the solvent to form $[Mo(Cl)(GeCl_3)(CO)_3(NCMe)_2]$, 87,[232] but ^{13}C NMR spectroscopy suggested a number of different compounds. $[Mo(CO)_4(NCMe)_2]$ was also found to react with $GeCl_4$ in CH_2Cl_2[233] to give the same product. In this report, it was shown that mono- and binuclear species with varying numbers of carbonyl and nitrile ligands were also formed, although the monomeric species can be restored by recrystallisation from the corresponding nitrile. $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$, 88, was also observed and the authors postulate that this is formed in a disproportionation reaction along with $[MoCl_2(CO)_2(NCMe)_2]$.

The reaction of $SnCl_4$ with $[Mo(CO)_3(NCMe)_3]$ in acetonitrile was first reported in 1989 and the spectroscopic data suggested the formation of isomers of $[Mo(Cl)(SnCl_3)(CO)_3(NCMe)_2]$, **89**.[234] $[Mo(CO)_4(NCMe)_2]$ was also found to react with $SnCl_4$ in CH_2Cl_2[235] to give the same product, but as for the germanium example, a number of other compounds with differing carbonyl and nitrile ligands could also be identified including $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$, **90**. The analogous compounds $[Mo(CO)_3(NCMe)_2(SnRCl_2)Cl]$, **91**, (R = Me,[236] ^{n}Bu,[237] Ph[236,237]) can be prepared in a similar way.

The photochemical reaction of $[Mo(CO)_6]$ with $SnCl_4$ gives rise to the trimetallic species $[(CO)_4Mo(\mu\text{-}Cl)_3Mo(SnCl_3)(CO)_3]$, **92**, and treatment with MeCN forms the complexes $[MoCl_2(CO)_3(NCMe)_2]$ and **89**.[238] The reactions of many examples of the oxidation of neutral Mo(0) compounds $[Mo(CO)_3(\eta^2\text{-}LL)L^1]$ with $SnCl_4$ give heterobimetallic compounds of the type *fac*-$[Mo(CO)_3(SnCl_3)(\eta^2\text{-dppm})][SnCl_5]$, where LL = dppm and L^1 = CO. Where LL = bipy, phen and $L^1 = \eta^1$-dppm, $[Mo(CO)_3(SnCl_3)(Cl)(\eta^2\text{-NN})]$ or $[Mo(CO)_2(SnCl_3)(\eta^2\text{-NN})(\eta^2\text{-dppm})][SnCl_5]$ were isolated depending on the reaction conditions.[239] Finally, the polymer-supported $[\{2\text{-}(4\text{-}ROC_6H_4N{=}CH)pyridine\}Mo(CO)_4]$ (R = H, polystyrene-Si^iPr_2)[240,241] compound also undergoes oxidative addition of $PhSnCl_3$, which has been characterized both on the support and by liberation and subsequent X-ray crystallography.

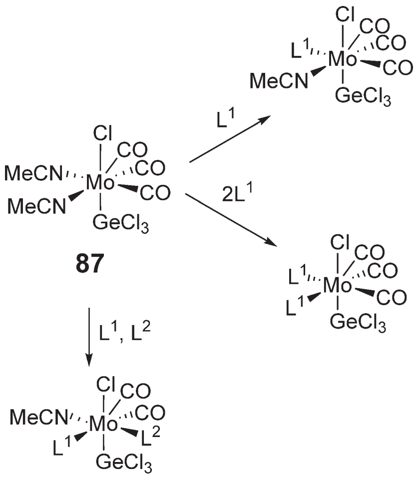
Reactivity. These compounds typically show substitution of the labile nitrile and/or CO ligands typically using mono- and bidentate group 15 donor ligands (Scheme 9). The compounds $[Mo(Cl)(GeCl_3)(CO)_3(MeCN)L]$,[232,242] $[Mo(Cl)(GeCl_3)(CO)_3L_2]$,[232,242,243,244] $[Mo(Cl)(GeCl_3)(CO)_2LL^1{}_2]$,[232,242,243] $[Mo(Cl)(GeCl_3)(CO)_2LL^1L^2]$,[232] $[Mo(\mu\text{-}Cl)(SnCl_2R)(CO)_3L_2]$,[237,239,245–253] $[Mo(\mu\text{-}Cl)(SnRCl_2)(CO)_2LL^1{}_2]$[237,254,255] (Equation (32)), and $[Mo(CO)_3(NCMe)(S_2PX_2)(SnRCl_2)]$[256] have all been synthesized by substitution reactions. Specific examples are given in Table 5.



91 (32)

In addition, some of these compounds are also pre-catalysts for allylic substitution with β-dicarbonyl nucleophiles,[257] polymerization of alkynes to give polyacetylenes and cyclic oligomers (mainly aromatic *cyclo*-trimers),[233,235,258] co-polymerization of norbornene and *tert*-butyl acetylene,[259] and in C–C coupling reactions, for example, allylic substitution in glycals,[260] electron-rich aromatics,[261] aldehydes, and ketones,[262] and β-dicarbonyl nucleophiles.[257] Compound **89** is also an active catalyst for the ROMP of norbornene, norbornadiene,[263] and halogenated norbornenes.[265] Complex **92** was found to react with alkynes.[264,265]

Properties. All the Ge and Sn compounds are described as being very air sensitive, both in solution and in the solid state, whereas the alkyl- and aryl-substituted tin compounds are also light sensitive. Infrared and NMR spectroscopy have been used to characterize the compounds **87** and **89**, and the carbonyl ligands show three bands in the IR



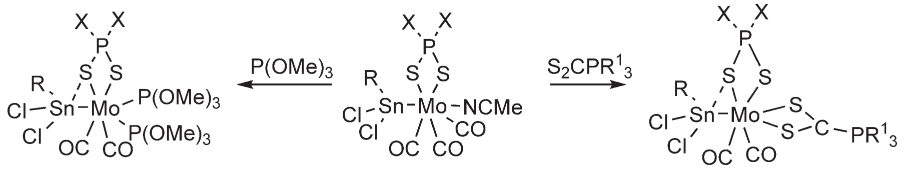
Scheme 9

Table 5 Some examples of complexes of the type $[MoCl(ECl_2R)(CO)_2LL^1L^2]$

E	*R*	*L*	*L^1*	*L^2*	*Comments*	*References*
Ge	Cl	CO	MeCN	EPh_3	E = P–Sb	232
Ge	Cl	MeCN	PPh_3	PPh_3		232
Sn	^{n}Bu	$P(OMe)_3$	$P(OMe)_3$	$P(OMe)_3$	X-ray	237
Ge	Cl	CO	bipy			243
Sn	Ph	CO	MeCN	PPh_3	Mössbauer	246
Sn	Ph	CO	$H_2C(4\text{-}BrPz)_2$		X-ray	252
Sn	Cl, Me, Ph	$P(o\text{-}FC_6H_4)_3$	phen		Mössbauer	254
Sn	Ph, ^{n}Bu	S_2PX_2	$S_2CP(R^1)_3$		X-ray	266
Sn	Ph	$2\text{-}(4\text{-}HOC_6H_4N{=}CH)Py$	CO	CO	X-ray	241

spectrum and a single resonance for the carbonyl ligands in the ^{13}C NMR spectra indicating a symmetric structure.[233,235] Compounds **88** and **90** can be distinguished by a downfield shift of the carbonyl resonances in the ^{13}C NMR spectra.[233,235] Complex **91** shows an unsymmetrical structure with different nitrile and CO ligands, as evidenced by ^1H, ^{13}C, and IR spectroscopy.[236] An important consideration of these seven-coordinate compounds is the geometry observed in the solid-state structures. ^{119}Sn Mössbauer spectroscopy of **91** showed a five-coordinate tin center, indicating that the chloride ligand is bridging between the tin and molybdenum metals.[236] The crystal structure of the complexes $[Mo(Cl)(SnCl_3)(CO)_3(NCEt)]$ confirms this bridging environment.[238] The structure is best described as a distorted capped octahedron with the tin occupying the capping position. The Sn–Mo bond length is quite short at 2.694(1) Å, and the authors suggest that it may contain some double bond character.

The compounds $[Mo(CO)_2\{P(OMe)_3\}(SnBu^nCl_2)Cl]$[237] and **93**[256] have both been structurally characterized. Both show fluxional ^{31}P NMR spectra indicating a dynamic process at room temperature. Further substitution reactions of **93** with $P(OMe)_3$ or $S_2CPR^1_3$ gives **94** and **95** (R = Ph, ^{n}Bu; X = OEt, Ph; R^1 = Cy, ^{i}Pr),[266] for which $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)]$ was structurally characterized and showed that one of the sulfur atoms of the S_2CPR_3 groups bridge to the tin (Equation (33)).

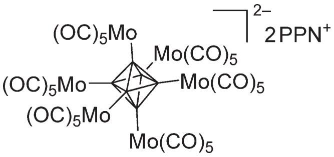


94 **93** **95** (33)

In relation to the ring-opening polymerization reactions, complexes $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_n(\eta^4\text{-}C_7H_8)(NCMe)]$ ($n = 2$,[267] 3[268]) have been structurally characterized.

5.06.2.3.4 Cluster compounds containing group 14 elements

Cluster compounds containing tin or lead are an important class of compounds. Electron-precise **96** which are $[E_6]^{2-}$ (E = Ge, Sn) clusters with six $Mo(CO)_5$ groups as protecting units can be synthesized in reasonable yield by the reaction of a threefold excess of the carbonyl metallate $[Mo_2(CO)_{10}]^{2-}$ with GeI_2. This is the first time that the Mo analog has been prepared and both Sn and Ge analogs have been structurally characterized as their PPN salts. These complexes retain their structure in solution, as shown by IR and ^{119}Sn NMR spectroscopy.[269] In contrast to the synthesis of the Cr and W analogs, the Mo compound could not be made in the pure form by the reduction of $[(CO)_5MoI_2Ge\text{–}GeI_2Mo(CO)_5]$, although the synthesis and structure of the related $[(OC)_5MoGeCl_3]^-$ and $[(OC)_5MoGeI_3]$ have been reported.[270] The thermal decomposition of the neutral $[(OC)_5MoGeCl_2(THF)]$ moiety has also been studied and compared with other Ge(II) and Ge(IV) species.[271] The *closo*-$[Sn_9Mo(CO)_3]^{4-}$ anion has been prepared and characterized by multinuclear NMR and structurally characterized. In solution, there is a dynamic equilibrium between the η^4- and η^5-structures that proceeds via a triangular face rotation mechanism.[272] The reaction of the Pb_9^{4-} anion with $[Mo(CO)_3(\eta^6\text{-mesitylene})]$ gives rise to the *closo*-$[1\text{-}Mo(CO)_3(\eta^4\text{-}Pb_9)]^{4-}$ cluster anion, which has been characterized by X-ray crystallography and by multinuclear (^{95}Mo and ^{207}Pb) NMR spectroscopy. It was shown by a theoretical study that the Pb_9 cluster was acting as a π-donor to the $Mo(CO)_3$ fragment and the IR stretch for the CO ligands is one of the lowest yet reported; however, it was noted that for E_9^{4-} cages the position of the CO bands may not be the best measure of electron donation ability.[273]



96

Vertex = Ge or Sn

5.06.2.4 Molybdenum Carbonyl Complexes Containing Group 15 Ligands

5.06.2.4.1 σ-Donor nitrogen ligands

Spectroscopic and theoretical studies on the nature of the bond between simple NR_3 ligands and transition metals are discussed along with phosphorus examples in Section 5.06.2.4.3.(i). The synthesis and characterization of a series of Mo(0), Mo(I), and Mo(II) complexes of bis(2-picolyl)amine (bpa) have been reported, with special emphasis on the potential of $[Mo(bpa)(CO)_3]$ as a marker group in bio-organometallic chemistry.[274] 1-Borylimidazole compounds of $[Mo(CO)_5]$ have been prepared and structurally characterized.[275] Macrocyclic complexes containing the triazacyclohexane ligand have been prepared.[276]

5.06.2.4.2 π-Acceptor nitrogen ligands

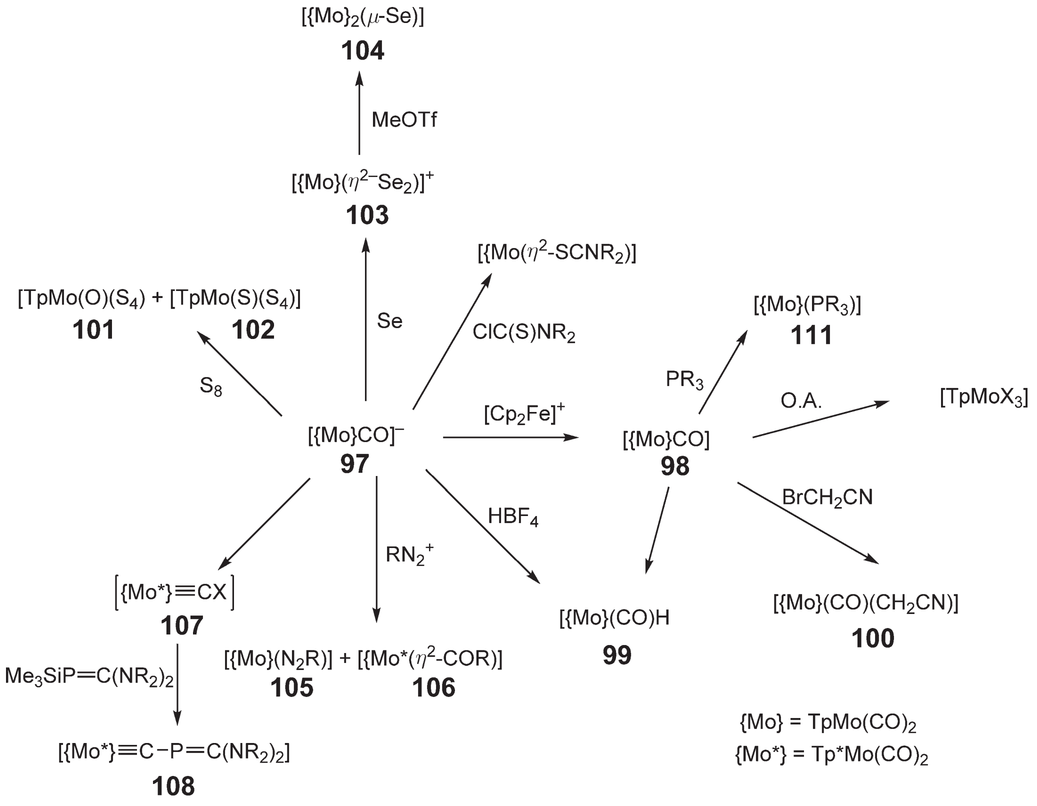
This section includes donor ligands such as bipy, phen, and terpy and also the widely studied Tp ligands. The spectroscopy, photochemistry, and electrochemistry of zerovalent α-diimine ligands,[277] bis(pyrazolyl)alkanes,[278] tris(pyrazolyl)alkanes,[279] the chemistry of N_2, NNH, NNH_2, and NNH_3 ligands,[280] bis(pyridyl)amine ligands,[281] and metal NO compounds[282] have been subject to reviews to which the reader is referred.

5.06.2.4.2.(i) Tp complexes

Synthesis. Transition metal complexes of the Tp ligand have been extensively studied[283] as it is well known to stabilize unusual metal systems, perhaps best exemplified by complex $[Tp^*PtMe_2H]$, which is stable at ambient temperatures.[284] The substitution of pyrazole rings also affects the reactivity, steric effects are important but also electronic effects are observed, for example, Tp^* is a better electron donor than Tp. Three types of molybdenum Tp compounds have been synthesized: anionic, neutral, and radical systems. All these display considerable reactivity. The complex $[TpMo(CO)_3]^-$, **97**, can be readily synthesized from the reaction of the Tp salt with $[Mo(CO)_6]$;[285] this reaction also works well for substituted Tp ligands.[286] In this way, the compounds $[Tp'Mo(CO)_3]^-$ and $[Tp^*Mo(CO)_3]^-$ have been prepared (Tp = hydridotris(pyrazolyl)borate, Tp′ = tetrakis(pyrazolyl)borate, Tp^* = hydridotris(3,5-dimethylpyrazolyl)borate). Other examples feature a ferrocene group attached to the boron[287] and phenyl groups tethered to one of the pyrazole rings.[288] The BH fragment has been replaced with an SiR group[289] and this has allowed metallo-dendrimers to be synthesized.[290]

The reactivity of a number of Mo complexes toward Tp anions has been reported. For example, Hill and co-workers have synthesized a range of thiocarbamoyl and alkoxythiocarbamoyl Mo(II) compounds, some of which are stabilized by the Tp fragment, and further investigated their reactivity.[99–101] The thiocarbamoyl complex $[TpMo(CO)_2(\eta^2\text{-}C(S)NMe_2)]$ has also been structurally characterized,[291] as has the dithiocarbamate compound $[TpMo(CO)_2(\eta^2\text{-}S_2CNEt_2)]$.[292] Both these compounds show bidentate C(S)–S coordination to the molybdenum. Complexes containing an η^3-dienyl ligand can also be synthesized from $[Mo(CO)_3(Py)_3]$, allenic electrophiles, and KTp, or by addition of enynes and subsequent decarbonylation of $[TpMo(CO)_3H]$.[293]

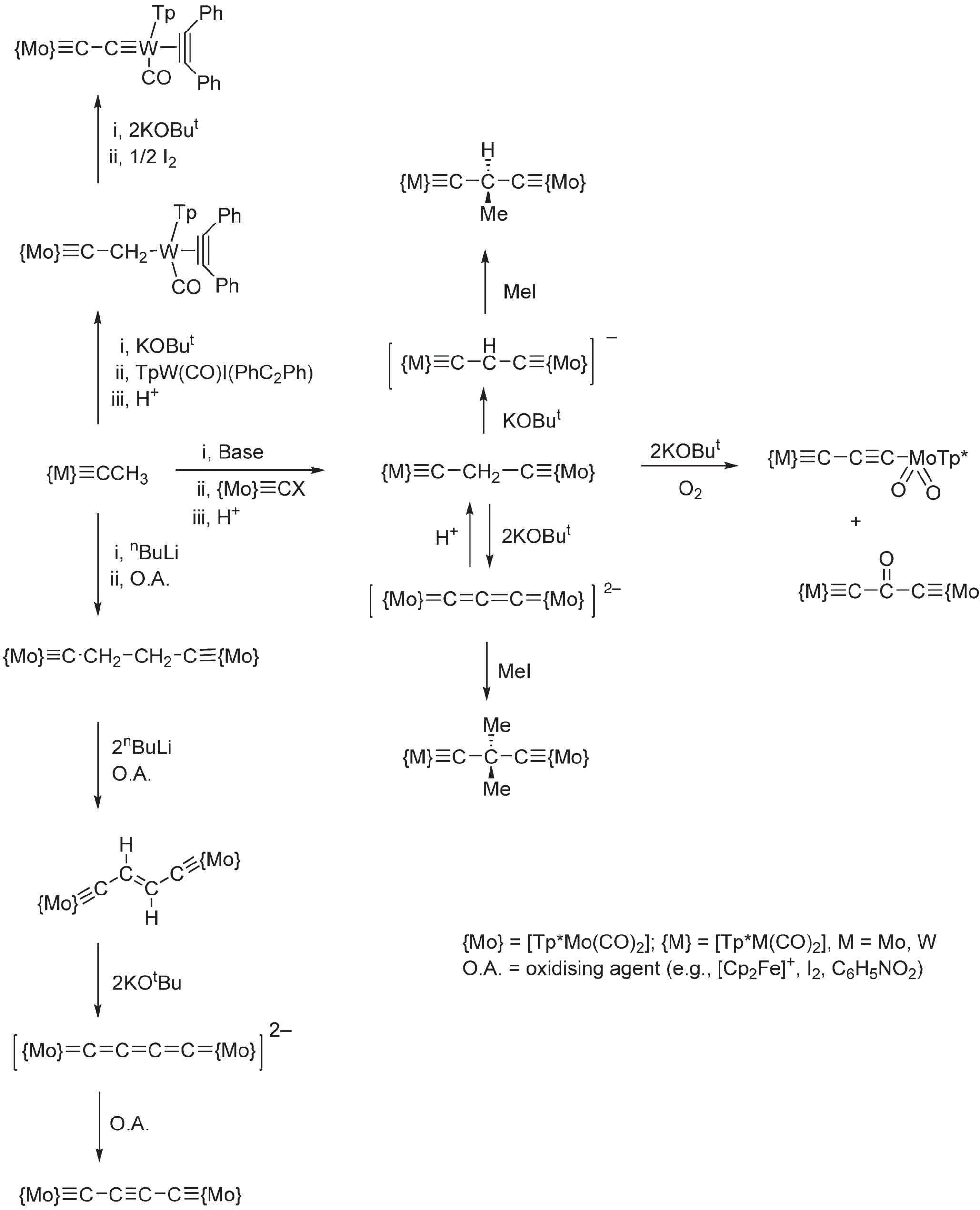
Reactivity. The reactivity of $[TpMo(CO)_2]$ fragment is summarized in Scheme 10. Oxidation of **97** with ferrocenium salts affords the neutral 17-electron radical $[TpMo(CO)_3]$ (**98**, Tp = substituted Tp ligands). Protonation of the anionic salts affords the hydride **99**. $[TpMo(CO)_3]$ and the anionic salt reacts with bromoacetonitrile to afford the first example of an alkyl-substituted complex, $[TpMo(CO)_2CH_2CN]$, **100**.[285] Compound **98** has also been shown to be an effective catalyst for chain transfer during free radical polymerization of methyl methacrylate.[294] The reactivity of Et_4N[**97**] toward sulfur and selenium has been investigated. Whilst for S_8 oxidation was observed forming **101** and **102**,[295] elemental Se gave **103**[296] due to the weaker oxidizing ability of selenium. Upon treatment of **103** with



Scheme 10

MeOTf, **104** can be isolated. Oxidation of $[\mathrm{Tp^*Mo(CO)_3}]^-$ with various oxidants such as $SOCl_2$, Br_2, I_2, and HNO_3 affords a variety of mononuclear Mo(III and VI) complexes $\mathrm{Tp^*MoX_3}$ (X = Cl, Br, I, and O).[297] The reaction of $[\mathrm{TpMo(CO)_3}]^-$ with diazonium salts yields the expected aryldiazenido products $[\mathrm{TpMo(CO)_2(N_2R)}]$ (R = Ph, C_6H_4X-4 {X = CN, COMe, CF_3}, C_6H_4X-3 {X = NO_2, COMe}), **105**, via CO substitution; however, Tp* gives different products depending on the solvent. Thus, $[\mathrm{Tp^*Mo(CO)_3}]^-$ gives **98** and $[\mathrm{Tp^*Mo(CO)_2}(\eta^2\text{-COR}^1)]$, **106**, via oxidative formation of aryl radicals in acetonitrile, but the known chlorocarbyne and new bromo- and iodocarbynes $[\mathrm{Tp^*M(CO)_2}(\equiv\mathrm{CX})]$, **107**, (X = Cl, Br or I) are formed in haloalkane solvents. The carbonyl stretching frequencies decrease I > Br > Cl, indicating that π-donation from the halogens makes an important contribution to the ground state of these molecules. It was also shown that the oxidation of $[\mathrm{Tp^*Mo(CO)_3}]^-$ by diazonium salts are dictated by the steric effect of the methyl groups on the pyrazole ring, and not electronic effects, and further substitution causes a reversion to the carbonyl substitution pathway.[298] The chlorocarbyne complex **107** has also been the subject of further reactivity studies.[299] Especially interesting is the reaction with phospa- and arsa-alkenes. Thus, $\mathrm{Me_3SiP{=}C(NR_2)_2}$ (R = Me, Et) gives **108**, which has small contributions from two other mesomeric forms, as shown by spectroscopy and a crystal structure determination.[300] Further reactivity has been summarized in a recent review.[301] The known alkylidyne complex $[\mathrm{Tp(CO)_2Mo{\equiv}CCH_3}]$ can be deprotonated to form a vinylidene intermediate, and elegant work by Templeton and co-workers has enabled the synthesis and characterization of a variety of binuclear metallacumulene species (Scheme 11).[302–305] The synthesis of a series of alkyne complexes has also been reported, and investigated with regard to the coordination of ketones.[306] The redox pair $[\mathrm{TpMo(CO)_2}(\eta^2\text{-PhC{\equiv}CPh})]^{0/+}$ has been structurally characterized and shows a shortening of the M–C(alkyne) bond and lengthening of the C≡C bond. This is opposite to the expected Dewar–Chatt–Duncanson model of alkyne bonding and can be explained if the HOMO is the antibonding M–alkyne $\pi_\perp$-orbital. This example suggests that the metal alkyne fragment can be regarded as an electron sink and stable complexes with d^4, d^5, and d^6 configurations could be formed. There is also the possibility of these interconverting through electron-transfer processes.[307]

Complex **97** reacts with $\mathrm{I(CH_2)_3I}$ to give the acyl species **109** via deprotonation of an η^2-acyl intermediate, thus inducing a cyclization (Scheme 12). The acyl intermediate also reacts with RNC via an insertion mechanism to form



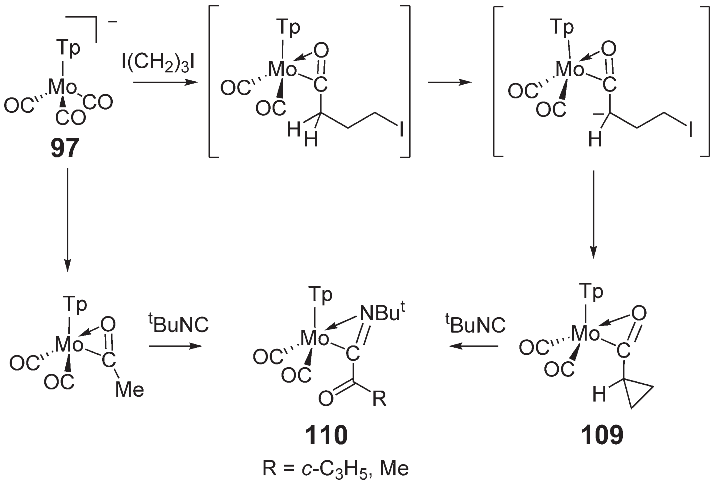
{Mo} = [Tp*Mo(CO)$_2$]; {M} = [Tp*M(CO)$_2$], M = Mo, W
O.A. = oxidising agent (e.g., [Cp$_2$Fe]$^+$, I$_2$, C$_6$H$_5$NO$_2$)

Scheme 11

110. Further reactivity on the tungsten analog confirms the mechanistic steps.[308] Photoinitiated oxidation of 1,3-dimethyladamantane by oxygen catalyzed using [TpMo(CO)$_3$H] has also been reported.[309]

Properties. One of the big advantages of the [TpMo(CO)$_2$L] fragment is its stability to air, especially in comparison with the Cp analog, and ease of synthesis. It is not surprising, therefore, that this has been used in a series of organic transformations.[310–314]

The reaction of [Tp*Mo(CO)$_3$H] with [TpMo(CO)$_3$] and [TpMo(CO)$_3$]$^-$ was examined by NMR spectroscopy in order to obtain information on the rates of hydrogen atom transfer, proton transfer, and electron transfer between the same metal complexes. An extremely detailed NMR spectroscopic study revealed rate constants for all three processes. Additionally, the pK_a and bond dissociation enthalpies were calculated.[286] Similar studies were carried out for [TpMo(CO)$_3$H].[315] A further method of quantifying kinetic acidities of [TpMo(CO)$_3$H] via the quenching of

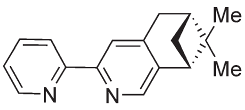


Scheme 12

the excited state of *trans*-[ReO$_2$(Py)$_4$]$^+$ has also been reported.[316] The 17-electron species [TpMo(CO)$_2$L], **111** (L = CO, tertiary phosphines; Scheme 10), have also been studied by EPR spectroscopy.[285] All these compounds have also been subject to structural analysis. A crystal structure determination of [TpMo(CO)$_2$CH$_2$CN] has also been carried out and is the first example of this class of compounds.[285] [FcB(pz)$_3${Mo(CO)$_3$}$_2$]$^{2-}$ has been studied by CV and shows that the two molybdenum atoms are non-communicating.[287] Compound **105** has been structurally characterized by single crystal X-ray diffraction studies.[298]

5.06.2.4.2.(ii) Complexes containing bipy and terpy ligands

Synthesis. Few further examples of bipy and terpy complexes have come forward since 1993. Compounds with two bipy ligands have been reviewed recently.[317] The chemistry of terpy ligands is relatively undeveloped compared to the copious research involving bipy, phen, and substituted ligands. Molybdenum carbonyl complexes [Mo(CO)$_4$(L)] containing *R*/*R* and *S*/*S* enantiomers of **112**,[318] **113**, **114**,[319] and achiral **115** and **116**[320] have been prepared. One of the major uses for bipy-type ligands is in the synthesis of large molecular arrays and some Mo species have been synthesized with this aim in mind.[321] Molybdenum complexes containing terpy ligands are fluxional in solution, this process involves decoordination of one of the pyridyl rings. Two studies using unsubstituted terpy[322] and 4,4′,4″-^{t}Bu$_3$-2,2′ : 6′,2″-terpy[247] report $\Delta G^{\ddagger} \sim 50\,\mathrm{kJ\,mol^{-1}}$ for this process. The oxidation of [Mo(CO)$_4$(nbd)] with I$_2$ or CuBr$_2$ followed by treatment with bipy ligands gives [Mo(CO)(nbd)(bipy)X$_2$];[323] analogous reactions using terpy have also been reported to give [Mo(CO)(nbd)(terpy)X]X (terpy = 2,2′:6′,2″-terpyridine or 4,4′,4″-^{t}Bu$_3$-2,2′:6′,2″-terpyridine; X = Br, I).[324] [M(CO)$_4$(L)] (L = 4′-phenyl-2,2′:6′,2″-terpyridine) has been reported to contain a bidentate terpyridyl ligand,[325] while seven-coordinate cationic Mo(II) examples with terpy acting as a tridentate ligand are known.[326]



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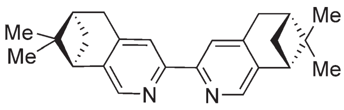

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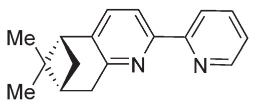

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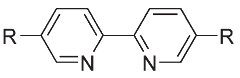

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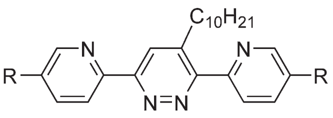
R = N=CHFc



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Properties. [Mo(CO)$_4$(**112**)] has been studied by circular dichroism spectroscopy in the visible range and shows weak Cotton effects.[318] Further electronic absorption spectroscopic studies have been carried out on

$[M(CO)_4(n,n'\text{-}X_2\text{-bipy})]$ ($M = Cr$, Mo, W; $n,n' = 3, 4, 5, 6$; $X = Me$, CN, CO_2Me; bipy = 2,2′-bipyridine) in an attempt to correlate the molar absorptivities with solvent polarity but the effects of geometric distortion precluded a simple explanation of the observations in terms of a single parameter.[327]

Reactivity. $[Mo(CO)_4(\eta^2\text{-NN})]$ (η^2-NN = bipy, phen) reacts with CuCl to give the heterobimetallic species $[Mo(CO)_4(\eta^2\text{-NN})(CuCl)]$, and spectroscopic studies suggest it has a polymeric structure.[328] Similar reactivity has been observed with $HgCl_2$ to give $[Mo(CO)_3(\eta^2\text{-NN})(HgCl)(Cl)]$ (NN = bipy, phen, 2,9-dimethylphenathroline) and its reactivity toward tin halides examined. The crystal structure of $[Mo(CO)_3(\eta^2\text{-NN})(HgCl)(Cl)]$ has been determined and shown to be seven coordinate with a Cl capping one face and a typical Mo–Hg σ-bond.[329] $[Mo(CO)_4(\mathbf{114})]$ has also been tested in asymmetric allylic substitution with poor enantioselectivity.[319] The same reaction with non-chiral phen ligands has been reported to give good selectivity for alkylation of *Z*-allyl acetates.[330]

5.06.2.4.3 Phosphorus ligands

The electronic properties of many phosphine ligands have traditionally been deduced by comparing the infrared spectra of the appropriate adduct of nickel carbonyl. In recent years, the molybdenum carbonyl fragment has become increasingly favored due to the ease of handling $[Mo(CO)_6]$ compared with the toxic, gaseous $[Ni(CO)_4]$, and the low bond dissociation energies for $[Mo(CO)_6]$ mean that substitution of one or more carbonyl ligand is facile. As a consequence of this, there are many examples of phosphine adducts $[Mo(CO)_n(P)_{6-n}]$ reported in the literature since 1993. For the purpose of this chapter, some selectivity has been applied so that only representative examples from the field are given. In particular, unusual synthesis, reactivity, or structural properties will be highlighted, along with more fundamental aspects of bonding. In lieu of this selectivity, the reader is referred to reviews on zwitterionic $^+$P–C–E–X (betaines, E = P, As),[331] phosphenium,[332] *trans*-spanning diphosphine,[333] tri- and tetradentate polyphosphine ligands,[334] reactivity of phosphaalkyne species toward metal carbene complexes,[335] phospinine[336] ligands, ligands containing low-coordinate phosphorus,[337] cyclopentadienyl complexes bearing pendant phosphorus ligands,[338] phosphabenzenes and phosphaferrocenes,[339] phosphinidenes,[340,341] azaphosphirenes,[342] and a themed issue of *Chemical Reviews*.[343]

As discussed in Section 5.06.1.4, many synthetic strategies exist for the substitution of one, two, or three carbonyl ligands. The synthetic methods generally follow one of the following pathways:

(a) substitution of $[Mo(CO)_6]$;
(b) substitution of labile donor ligands such as $[Mo(CO)_5(THF)]$, $[Mo(CO)_4(pip)_2]$ or $[Mo(CO)_3(NCMe)_3]$;
(c) reaction of coordinated P-X (X = halide, hydride) species;
(d) reaction of coordinated phosphides; and
(e) reaction of uncoordinated phosphides.

For clarity, the discussion will be divided into two sections PY_3 and PY_2 as the chemistry of PY has been reviewed recently[344] (Y = any atom). Representative examples of each of these methodologies are given in Table 6. PY_3 class of compounds is by far the most common; therefore, this is subject to the most selectivity. Given the similarity in reactivity, molybdenum phosphide complexes are also included in this section. PY_2 examples are mainly made up of heterocyclic compounds (e.g., phospholes, phosphabenzene), phosphinidene (RP^{2-}), or phosphaalkenes. One of the questions arising from the study of heterocyclic compounds is their bonding mode, as σ-donation or π-donation from the heterocycle are both possible.

5.06.2.4.3.(i) PY_3 complexes: phosphines and phosphides

Synthesis. The study of the coordination chemistry of primary and secondary phosphines has not received the same attention as tertiary phosphines, primarily because, on complexation, the P–H bond weakens, making then susceptible to deprotonation resulting in the formation of phosphides (*vide infra*). There have been some examples in the literature of molybdenum and tungsten carbonyl complexes of primary and secondary phosphines, and spectroscopic and structural data suggest that despite the differences in cone angles the geometry of the molybdenum is not affected to any great degree.[345–347]

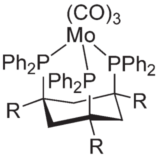
A variety of tripodal and macrocyclic polyphosphines has been synthesized. There are many examples of functionalized tripod ligands, so only representative examples are given. $RC(CH_2PPh_2)_3$ ($R = H_3C$,[348] $H_2C{=}CHCH_2OCH_2$,[349] $HOCH_2CH_2OCH_2$,[350] $HOC_6H_4CH_2$,[351] $PhCOOCH_2$[352]), tripod ligands with three different substituents[353] and *cis,cis*-1,3,5-tris(phosphino)-1,3,5-tris(alkyl)cyclohexane, **117**, act as facially capping tridentate triphosphine ligands.[354–356] Complexes containing chiral,[357,358] diastereomeric,[359] and water-soluble[360] tripodal ligands have also been synthesized.

Table 6 Synthesis of selected phosphine complexes (for synthetic details see text)

Complex	*Method*	*Comments*	*References*
$[Mo(CO)_{6-n}(\mathbf{124})_n]$	a, b	$n = 1$–3 ^{95}Mo NMR study	381
$[Mo(CO)_4(pip)(\mathbf{125})]$	b		382
$[Mo(CO)_{6-n}\{P(C_7H_7)_3\}_n]$	a, b	Also shows olefin bonding modes	383
$[Mo(CO)_5(\mathbf{126})]$	b	Ferromagnetically coupled	384
$[Mo(CO)_5\{(C_2F_5)_2PR\}]$	a	R = Ph, Me, NEt_2	385
$[Mo(CO)_5\{(C_2F_4)_2PPh\}]$	a	Also $Ph_2P(C_2F_4)$	386
$[Mo(CO)_5(dppa)]^a$	b	Both η^1 and chelate formed	387
$[\{TriphosCo(P_3)\}\{Mo(CO)_5\}_2]^b$	a	Fluxional NMR spectra	388
$[\{TriphosCo(P_3)\}Mo(CO)_5]^b$	a	Fluxional NMR spectra	389
$[Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}]$	a	Grafted onto alumina	390
$[\{Mo(CO)_5\}_4Si\{O(CH_2)_3(SiMe_2)(OCH_2PPh_2)_4\}]$	a	Dendrimeric structures	391
fac-$[Mo(CO)_3\{P(C{\equiv}CPh)_3\}_3]$	b	X-ray structure	392
fac-$[\{C_3H_5OPX_2\}_3Mo(CO)_3]$	b	X = F, Cl	393
fac-$[Mo(CO)_3(\mathbf{127})]$	b	X-ray structure, tetracarbonyl adduct also prepared	394

[a] dppa = $HN(PPh_2)_2$.
[b] Triphos = $MeC(CH_2PPh_2)_3$.

Applications include sol–gel synthesis to form stationary phase polymers that display useful reactivity toward transmetallation reactions to form catalytically active rhodium compounds.[361,362] Phosphacavitand ligands **118** have also been synthesized and $Mo(CO)_5$ complexes formed.[363–366] Tetraazatetraphosphadimolybdacyclophanes[367] $[CH_2(4,4'\text{-}(OC)_4Mo(Ph_2PNHC_6H_4)_2)]_2$, **119**, and $[CH_2(4,4'\text{-}(OC)_4Mo(Ph_2PCH_2NHC_6H_4)_2)]_2$ are readily synthesized, and tetraphosphorus-substituted calixarene ligands **120** and the molybdenum carbonyl complex have been prepared where **120**, and the corresponding calix[3]arene, act as an η^3-ligand.[368,369] Macrocyclic phosphine ligands are a rare class of compounds and the coordination chemistry is relatively unknown. Mathey and co-workers have shown that tetrameric phospholes can be converted into a series of tetraphosphorus macrocyles, and some molybdenum carbonyl complexes have been prepared and structurally characterized.[370] 1,4,7-Triphospha-2,3,5,6,8,9-hexasilacyclononane, **121**, and its molybdenum carbonyl complex have been reported.[371] The most comprehensive study of triphosphacyclododecane **122** has been carried out by Edwards and co-workers. Secondary,[372] tertiary,[373–375] and pendant donor examples[376] of $[([12]aneP_3R_3)Mo(CO)_3]$ (R = Et, ^{i}Pr, ^{i}Bu, CH_2SiMe_3) and $[([12]aneP_3R_3)Mo(CO)_2X_2]$[377,378] (R = C_2H_4OMe, $CH_2C_4H_3O$) have been reported.



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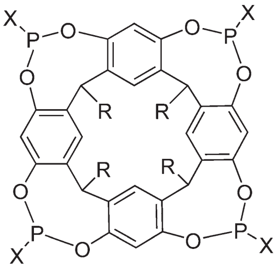

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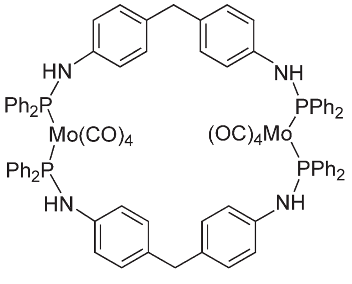

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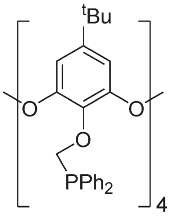

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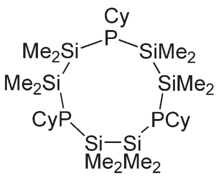

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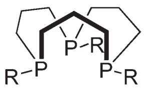

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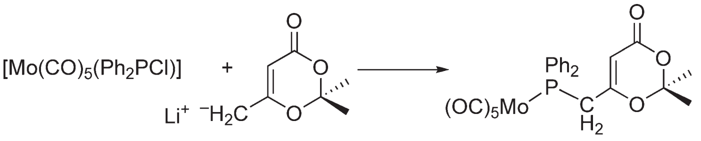
An example of type c synthesis is the dehydrohalogenation of [Mo(CO)$_5$(HPPhCl)] with Et$_3$N, which gave [(CO)$_5$MoPh(H)PP(Cl)PhMo(CO)$_5$].[379] [Mo(CO)$_5$(PPh$_2$Cl)] also reacts with carbon-based anions to form functionalized phosphines, for example, the use of the anion derived from 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one gives the substituted phosphine **123** in good yield (Equation (34)).[380]



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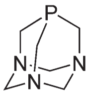
(34)

Phosphorus rings and cages are an important class of compounds, with applications ranging from coordination to materials chemistry. There are many general methods for the synthesis of L$_n$M(R$_2$NPO)$_n$M^{1}L$_n$, for example, the homoleptic **128**. Examples of P$_3$O$_3$ and P$_4$O$_4$ cages synthesized from bis(dialkylamino)phosphine oxides are known, whereby the steric effects of the secondary amine plays a pivotal role in the assembly of these cages.[395] [Mo(CO)$_4${(^{i}Pr)$_2$NPO}]$_4$ has been synthesized in a different manner, namely by elimination of the Mo(II) vertex in the mixed-valent, adamantanoid cage complex [Mo(CO)$_4${(^{i}Pr)$_2$NPO}$_4$Mo(CO)$_2$I$_2$] with NaS$_2$CNMe$_2$.[396,397]



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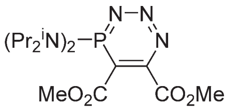

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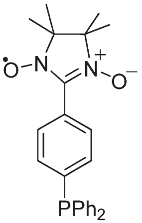

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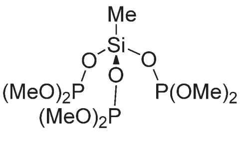

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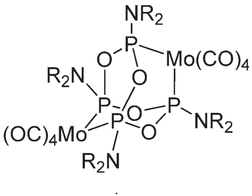


R = ^{i}Pr, Cy

128

Homo- and heterobimetallic complexes can be readily formed using phosphines or phosphides as bridging ligands. There have been many examples reported in the literature, and some examples are shown in Table 7. The synthesis of [Mo(CO)$_5$(η^1-PP)] is typically via methods a or b, followed by treatment with the second metal. Rigid phosphines generally form bimetallic complexes in one reaction step.[398] Examples of multidentate phosphines with the uncoordinated phosphorus donor atom forming bimetallic species are also well represented.

Syntheses of phosphide complexes (methods d and e) have also been investigated in detail. New syntheses of the phosphide-bridged complexes [(OC)$_4$Mo(μ-PR$_2$)$_2$Mo(CO)$_4$] (R = Me,[406] Ph[407]) have been forthcoming. Heterobimetallic complexes have been extensively studied. Some examples are shown in Table 8. The syntheses of [CpW(CO)$_2$(μ-PPh$_2$)Mo(CO)$_5$][408] from [CpW(CO)$_3$PPh$_2$] and [Mo(CO)$_4$(nbd)], and [CpFe(CO)$_2$(μ-PPh$_2$)-Mo(CO)$_5$][409] from [CpFe(CO)$_2$I] and Li[Mo(CO)$_5$PPh$_2$] have been reported and both of these compounds have been structurally characterized and show rich reactivity. Uniquely, [(CO)$_3$Fe(μ-PPh$_2$)$_2$Mo(CO)$_4$] has been synthesized from *trans*-[(CO)$_3$Fe(Ph$_2$PH)$_2$] with [Mo(CO)$_6$].[410]

Properties. The electronic properties of phosphine and arsine ligands continue to be the subject of much debate. Especially controversial are the role of M–P π-backbonding, particularly which orbital acts as the acceptor for the

Table 7 Synthesis of homo- and heterobimetallic complexes containing phosphine donor ligands as the bridge

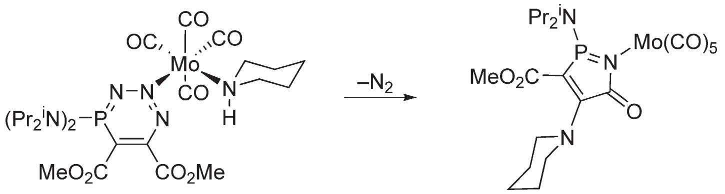
Ligand	*Metal*	*Comments*	*References*
Ph$_2$P(CH$_2$)$_8$PPh$_2$	Mo	X-ray structure	399
dppe	W, Cr	Also dppp, dppb	400
dppf	Cr, Mo, W	Trimeric	401
Ph$_2$PCH$_2$P(O)Ph$_2$	Mo	η^6-arene and P coordination	402
[WI$_2$(CO)$_3$(η^2-triphos)]	Mo		403
[CpRuCl{(Ph$_2$P)$_2$CHCH$_2$PPh$_2$}]	Mo		404
[Mo(CO)$_4${(PPh$_2$)$_2$CHPPh$_2$}]	AuX	X = Cl, C$_6$F$_5$	405

Table 8 Synthesis of heterobimetallic $[Cp_2M(\mu\text{-}PR_2)(\mu\text{-}X)Mo(CO)_4]$ complexes with phosphide bridging groups (Ar = 2,4,6-triisopropylphenyl)

M	*R*	*X*	*Comments*	*References*
Mo, W	Ph	H	Also monobridged	411
Nb	Ph	dppm	X-ray	412
Zr	$(SiMe_3)_2$	$P(SiMe_3)_2$	X-ray	413
Zr	HAr	PHAr	Racemic isomer	414
Nb	Ph	CO	Monobridged in PR_3 examples	415
Ta	Me		Photolysis gives CO bridged	416

electron density, and the relative σ- and π-contributions to this bond. For example, the difficulties in separating σ- and π-effects in determining the π-acidity of PCl_3 have been discussed.[417] The relative order of π-accepting ligands has also been a topic of much discussion. For a good description of this problem, the reader is referred to work by Frenking and co-workers.[418] Various experimental techniques have been used including spectroscopic, crystallographic, and others, and the consensus appears to be that there is an important π-component in M–P and M–As bonding in $[M(CO)_5L]$ but as yet no convincing evidence for involvement of either P–X or P–C σ^*-antibonding orbitals has been forthcoming.[419] The use of theoretical methods in this area has been recently reviewed.[420] ^{95}Mo NMR spectroscopy has become routine and has been used to probe the steric and electronic effects of molybdenum phosphorus compounds. As steric effects will influence the paramagnetic shielding term, the ^{95}Mo NMR spectra of a variety of $[Mo(CO)_{6-n}(PY_3)_n]$ complexes were analyzed.[421] An important result was the correlation of $\delta(^{95}Mo)$ with Tolman's cone angle, which can provide an empirical estimate of the bulkiness of any phosphite ligand from its NMR spectrum. A series of solid-state and single crystal ^{31}P NMR studies has been carried out to examine the ^{31}P chemical shift tensor.[422–425] The majority of examples show that the principal component roughly corresponds to the direction of the M–P bond, but subtle variations in electronic structure and local symmetry can dictate the orientation of the tensor. Theoretical methods have also been used and agree well with experimentally derived values.[426,427] The compound $[Mo(CO)_3(PF_3)_3]$ has been re-examined by ^{19}F and ^{31}P NMR spectroscopy both in solution and in the gas phase. The results show that the complex exists both as *fac*- and *mer*-isomers.[428]

Ligand **124** has been shown to be a good σ-donor and π-acceptor by ^{95}Mo NMR spectroscopy. Both the ligand and complex are air stable.[381] For the unusual ligand **125**, spectroscopic and structural studies indicate that there are no significant geometric and electronic differences between coordinated and uncoordinated ligands.[382] In solution, this complex slowly decomposes via migration of the coordinated piperidine ligand (Equation (35)).



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The potentially multihapto $P(C_7H_7)_3$ ligand also forms oligomeric compounds via η^2-, η^4- or η^6-bonding modes from the unsaturated C_7H_7 moiety.[429] In contrast, the complex of an allylphosphite ligand $C_3H_5OPX_2$ (X = F, Cl) shows no secondary allyl interactions.[393] Fluorinated ligands have been the subject of increasing interest and those described in Table 6 show electronic properties similar to those of phosphite ligands. The complex $[Mo(CO)_5\{Ph_2P(C_2F_3)\}]$ has been structurally characterized.[430] The triphosphite ligand **127** is less electron releasing than tertiary phosphine analogs and more closely resembles the π-arenes of $[Mo(CO)_3(\eta^6\text{-}C_6H_6)]$ in its electronic character.[394]

The molybdenum carbonyl complexes of the dppa ligand $\{dppa = HN(PPh_2)_2\}$ show NH··NCMe hydrogen-bonded interactions in the solid state. In the chelate complex, there is an acute P–Mo–P angle [65.29(6)°].[387] $[\{(Triphos)CoP_3\}Mo(CO)_5]$ is a good example of the use of unusual ligands in organometallic synthesis and both the mono- and the bis- $Mo(CO)_5$ complexes show highly fluxional NMR spectra. The activation parameters $\Delta H^\ddagger = 61.6\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^\ddagger = 96.0\ \mathrm{J\ mol^{-1}K^{-1}}$, $\Delta G^\ddagger{}_{298} = 33.1\ \mathrm{kJ\ mol^{-1}}$ for {(triphos)M} rotation about its C_3 axis and $\{Mo(CO)_5\}$ scrambling over the P_3 cycle have been measured.[389] Similar compounds with Cp instead of triphos have also been prepared and show similar properties.[431]

The study of water-soluble phosphines and their use in catalysis is of ongoing interest.[432] One of the most popular ligands is $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS) and the kinetics of phosphine dissociation in $[Mo(CO)_5(TPPTS)]$ and $[Mo(CO)_4(TPPTS)_2]$ have been examined.[433] It was found that both reactions proceed via a dissociative mechanism which is first order in $[Mo(CO)_{6-n}(TPPTS)_n]$ ($n=1$, 2). The activation parameters were also measured, and it was found that for $n=1$ they were very similar to PPh_3 and for $n=2$ when the sodium ions were "solvated" with kryptofix-211 the dissociation was enhanced compared to PPh_3, presumably due to larger steric requirements. There was also a 10 : 1 selectivity for CO over TPPTS in organic solvents due to electrostatic repulsions in the five-coordinate $[Mo(CO)_4(TPPTS)]$. $[Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}]$ has been grafted onto alumina surface by binding through phosphonate groups to form a monolayer. Other examples of water-soluble phosphines are known.[434,435]

As described in the synthesis section, bidentate phosphine ligands have been used to synthesize heterobimetallic species. The heat of protonation of the uncoordinated or dangling phosphorus in $[M(CO)_5(\eta^1\text{-dppm})]$ and the more electron-rich $[M(\eta^2\text{-NN})(CO)_3(\eta^1\text{-dppm})]$ (η^2-NN = bipy, phen) have been measured as a way of determining the basicity of the phosphorus. It was found that the ligands show increasing basicity from $dppmH^+ < [M(CO)_5(\eta^1\text{-dppm})](M = Cr < Mo < W) < dppm \leq fac\text{-}[Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})] < fac\text{-}[Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})] \sim fac\text{-}[W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})]$; H^+ is more electron withdrawing than $M(CO)_5$, and $[Mo(CO)_3(phen)]$ and $[W(CO)_3(bipy)]$ enhance the basicity of the dangling phosphorus compared with dppm.[436]

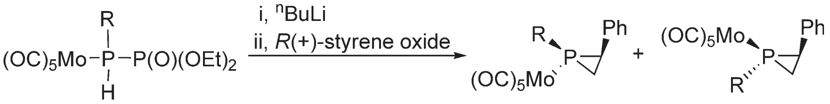
In systems where both phosphine ligands and carbonyl ligands are present, it is thought that CO is preferentially lost upon photolysis (see COMC I (1982)[3] and COMC II (1995)).[4] New results, however, suggest that this is not always the case, and photovoltammetry has been used to study the photolysis of *fac*-$[Mo(CO)_3\{(Ph_2PC_2H_4)_2PPh\}]$.[437] This isomerizes to the *mer*-isomer rather than CO dissociation and corroborates experimental work by Davies and co-workers.[438,439]

The compound $[(OC)_4Mo(\mu\text{-}PR_2)_2Mo(CO)_4]$ has also been studied by electrochemistry and theory. The results are consistent with progressive cleavage of the metal–metal bond in one-electron steps. The second step is rate limiting due to a larger part of the structural change. Theoretical calculations suggest that the redox-active orbital is a metal–metal σ^*-orbital with substantial bridging ligand character that decreases markedly in energy on passing from the metal–metal bonded $[M(I)]_2$ state to non-bonded $[M(0)]_2$.[440]

EHMO calculations on $[Cp_2Mo(\mu\text{-}PH_2)(\mu\text{-}H)Mo(CO)_n]$ ($n=4$, 5) suggest that there is a metal–metal bond,[411] and crystallography shows a dative M–M bond in $[CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_4]$, with a semi-bridging carbonyl ligand. $[(CO)_3Fe(\mu\text{-}PPh_2)_2Mo(CO)_4]$ is reported to contain an M–M bond on the basis of spectroscopic and structural studies, although the Fe–Mo bond length is long at 2.854(1) Å.[410] The complex $[CpFe(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5]$ has no metal–metal bond on the basis of X-ray crystallography[409] and has also been studied by Mössbauer spectroscopy.[441] Additionally, $[CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5]$ shows fluxional behavior in the ^{13}C NMR spectrum attributed to exchange of the carbonyl ligands.[408] This process involves a cleavage and reformation of the Mo–W bond, but this is reported to be faster than the NMR timescale. Such processes are commonplace amongst phosphide-bridged M–M bonded systems.

Reactivity. The reactivity of coordinatively unsaturated $[Mo(CO)_3(PR_3)_2]$ and $[Mo(CO)(PP)_2](PP = (PCy_3)_2$, depe, dppe) has been studied, as the agostic interactions are weak and can be easily substituted. Thus, $[Mo(CO)_3(PCy_3)_2(\eta^1\text{-}P_4)]$, $[Mo(CO)_3(PCy_3)_2(\eta^1\text{-}P{\equiv}CMes^*)]$,[442] *trans,mer*-$[(R_3P)_2(CO)_3M(L)]$ (M = Mo, W; R = ^{i}Pr, Cy; L = THF, η^2-H_2), and *trans,mer*-$[(R_3P)_2(CO)_3M]_2(\mu\text{-}L)$(R = ^{i}Pr, Cy; μ-L = pyrazine, 4,4′-bipyridine, and 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine) have been synthesized via this methodology, and the latter complexes studied by electrochemical and EPR spectroscopy.[443]

There are examples of ligand coupling reactions using $Mo(CO)_n$ fragments as a template. The synthesis and liberation of optically active phosphiranes have been achieved on a molybdenum template, the other enantiomer formed with *S*(-)-styrene oxide (R = ^{t}Bu, Menthyl in Equation (36)).[444] The first example of a 6a-thiathiophthen metal complex has been prepared from $[Mo(CO)_5(PPh_2CS_2CH_2C{\equiv}CH)]$ and structurally characterized (Equation (37)).[445] It has also been shown that the alkenyl functions of $Ph_2P(C_2H_3)$ can be coupled to form dppe and ethyne when coordinated to $Mo(CO)_4$.[446] Addition of KO^{t}Bu and PPh_2H to $[M(CO)_4\{(Ph_2PCH_2)_2C{=}CH_2\}]$ (M = Cr, Mo, W) leads to *cis*-$[M(CO)_4\{Ph_2PCH{=}C(Me)CH_2PPh_2\}]$ and *fac*-$[M(CO)_3\{(Ph_2PCH_2)_2C(Me)PPh_2\}]$. The geometry of the products crucially depends on the original form of the ligand, and marked differences were therefore observed in the chelate ring conformation and in the position of the C=C bond (exocyclic or endocyclic). *cis*-$[Mo(CO)_4\{Ph_2P(CH_2)_3PPh_2\}]$ with no C=C bond was also characterized.[447]



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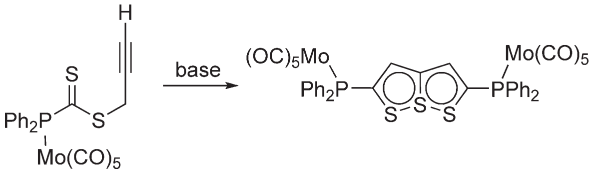

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$[(OC)_4Mo(\mu\text{-}PMe_2)_2W(CO)_4]$ has been found to be a good precursor to MoO_3/WO_3 oxides or Mo/W alloys under MOCVD conditions.[406] $[(OC)_4Mo(\mu\text{-}PR_2)_2Mo(CO)_4]$ (R = Me, Ph) reacts with tri-*n*-butylphosphine to give mono- and bis-substituted species. The kinetics of this reaction were investigated, and it was found that the overall substitution rate depends on the rate of CO dissociation, the backreaction (k_1 and k_{-1}), and on $[PBu^n{}_3]$. The nature of the substituents at the phosphido bridge markedly affects the value of k_1, which is higher for R = Ph compared with R = Me. This is mainly due to a lower activation enthalpy ($\Delta H_1^{\ddagger} = 125$ (Ph) and 141 (Me) kJ mol^{-1}), which may reflect a weakening of the Mo–CO bond in the presence of a more electron-withdrawing ligand in *trans*-position. The values of the competition rate ratio k_1/k_2 (<1) show that attack of the small CO is favored with respect to the large $PBu^n{}_3$. This suggests that the steric crowding observed on the molecular structure of the starting seven-coordinate complexes should play an important role also in the reactivity of their six-coordinate intermediates.[448]

Heterobimetallic complexes are of much interest as they may display properties that are different from the individual metal ions, and a general review on this area has been published.[449] There are two structural forms that have been identified, those without a metal–metal interaction and those with a direct metal–metal bond. The reactivity of $[CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5]$ has been investigated in some detail and can be explained by the Mo donating two electrons from its filled t_{2g} orbitals to the adjacent metal through a dative M–M bond, as has been suggested for other systems.[450] The effect of this will be to weaken the bonding to the equatorial carbonyl groups enhancing the lability. In addition, the electron density around the carbons will be reduced leading to an increase in the electrophilicity of these carbonyls and greater reactivity toward nucleophilic reagents. Thus, on addition of Lewis bases such as phosphines or CO, coordination to the molybdenum *cis* to the phosphide bridge is observed, resulting in the cleavage of the M–M bond.[408] The reaction of phosphine imines eliminates triphenylphosphine oxide and forms isocyanide derivatives *cis* to the phosphide bridge.[451] The use of bidentate phosphines has been reported and in this case, substitution of two CO ligands on the Mo center takes place and the M–M bond is retained.[452] Further reactivity with thiolates has some relevance to catalytic hydrodesulfurization reactions.[453,454] The regioselectivity of binding of incoming nucleophiles has also been demonstrated in the reactivity of phosphines toward $[Cp_2TaH(\mu\text{-}PMe_2)(\mu\text{-}H)Mo(CO)_4]$, although it was demonstrated that steric bulk of the incoming ligand can affect this reaction.[455,416]

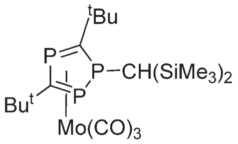
Deprotonation of coordinated phosphines in the complex $[Mo(CO)_5(PR_2H)]$ is a common strategy to synthesize heterobimetallic species and examples of $[(OC)_5Mo(\mu\text{-}PR_2)ML_n]$, where MLn = $PtCl_2$,[456,457] $[X(\eta^5\text{-}C_5H_4)_2M]$ (X = $SiMe_3$, CMe_2; M = Mo, W)[458] and $Hg(PBu^t{}_2)$[459] are known. However, other products have been noted where attack of the phosphide is at a Cp center in substituted molybdocene and tungstocene dichlorides.[460,461] A different synthetic approach is to react $LiPR_2$ with $[Mo(CO)_6]$ to form directly the coordinated phosphide. The reactivity toward alkyl halides has been investigated. Spectroscopic data indicate that the DBP (DBP = dibenzophospholide) ligands are better π-acceptors than the $RPPh_2$ ligands, but invariant toward the alkyl substituents.[462] The reactivity of the complex $[(DBPLi)Mo(CO)_5]$ has been further investigated including the synthesis of an asymmetric 1,2-diphospholylethene which was confirmed by an X-ray structure.[463]

Despite the potential uses in catalysis, few of these compounds have been tested and these only in olefin polymerization.[464,465] This should prove a fruitful area for future research.

5.06.2.4.3.(ii) PY_2 complexes

Synthesis. Phospholes are generally non-aromatic systems, although there is one report of the di-*tert*-butylphosphole forming a π-complex $[(PC_4H_2{}^tBu_2\text{-}2,5)Mo(CO)_2]_2$, which shows properties like the analogous Cp system.[466] However, on sequential replacement of a C=C bond for a P=C bond the aromatic character increases. Thus, the ligand 1,2,4-triphosphole does indeed form the η^5-complex **129** on treatment of the ligand with $[Mo(CO)_3(cht)]$.[467] Interestingly, no other bonding modes were detected, and this was studied using theoretical calculations. The ligand 1,2,4-thiadiphosphole forms the η^5-complex **130** on reaction with $[Mo(CO)_3(cht)]$,[468,469] or an η^1-complex on treatment with $[Mo(CO)_5(THF)]$.[469] An unprecedented synthesis of $P_3C_2Bu^t{}_2CBu^t$(imidazolin-2-ylidene) has been reported, and it forms the η^5-complex **131**, when treated with $[Mo(CO)_3(cht)]$. The crystal structure shows it to be significantly delocalized.[470] 4,5-Diphenyl-1,2,3-triphospholide complexes of Mo have been reported, and form bis- and tris-adducts, where the phosphorus is bonding in a σ-fashion.[471] The coordination chemistry of heterophospholes has only recently been studied in any detail. The benzaphosphole complexes such as **132** have been synthesized and the ligand binds through the phosphorus atom. NMR studies suggest that the ligand is a weak donor but good acceptor ligand.[472] This has been further corroborated by the isolation of **133**, where the coordination to the poorly σ-basic phosphorus is preferred over the sulfur, due to the superior $d(\mathrm{M}) \rightarrow \pi^*$ interactions.[473] Changing the annulated five-membered ring for **134** ($R^1 = H$, Me; $R^2 = COBu^t$, COPh, CO_2Et, CO_2Me, CN; $R^3 = H$; $R^4 = H$, Me) featuring a six-membered ring does not affect the electronic properties of these ligands. In this case, *fac* and *mer*-$[Mo(CO)_3L_3]$ from the reaction of the ligand and $[Mo(CO)_3(cht)]$ were also isolated, and a possible π-complex observed by ^{31}P NMR spectroscopy.[474] The synthesis and reactivity of the aromatic anion C_4P^- has been investigated with a variety of metals. The chemistry of the phosphaferrocene derivatives has been recently reviewed[475] and the chemistry of diphosphaferrocene examined.[476] As expected, the adducts formed with $[Mo(CO)_5]$ are similar to those with other alkyl and aryl phosphines.

The coordination chemistry of the triphosphabenzene moiety is discussed in Section 5.06.3.1.12 and diphosphacyclobutadiene (diphosphete) ligands are treated in Section 5.06.3.1.7. Phosphaalkene complexes of molybdenum carbonyl have been the subject of a theoretical study.[477] A phosphaalkene bearing a pendant phosphine donor group reacts with $[Mo(CO)_4(nbd)]$ to give **135** where both phosphine ligands donate in a σ-fashion.[478] Diphosphabutadiene **136** reacts with molybdenum hexacarbonyl to form $[Mo(CO)_4(\mathbf{136})]$, where the low-coordinate phosphorus center is protected with bulky aryl groups.[479,480] The photolytic reaction in the presence of oxygen oxidizes the backbone of the ligand, but not the P=C or Mo–P centers.[481] A study on the isomerization of these diphosphabutadiene ligands has also been reported.[482] 2,2′-Bisphosphinine complexes of group 6 metals have also been synthesized.[483]



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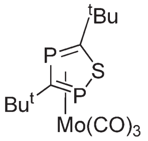

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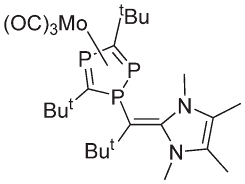

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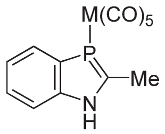

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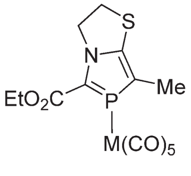

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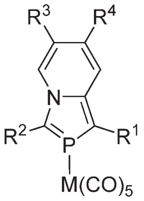

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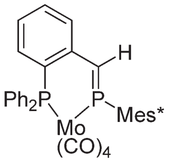

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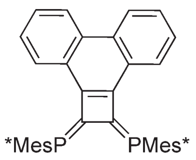

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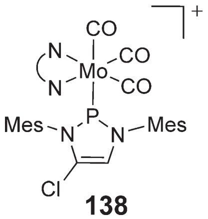
Phosphinidene examples include two theoretical studies;[484,485] examples where phosphinidenes have been formed as transient intermediates[486,487] and a series of phosphenium cations which has been synthesized, and the reactivity studied. These are included here as cationic phosphenium compounds which can be described by the two limiting resonance forms $L_nM \leftarrow PR_2^+$ or $LnM^+{=}PR_2$, the latter being a phosphinidene. New synthetic methods have been reported for **137** (NN = bipy, dppe, phen)[488] and *fac*-$[M(LL)(CO)_3(P\{OCMe_2\}_2)]^+$.[489] A series of complexes *fac*-$[(bipy)(CO)_3M\{PXY(OMe)\}]$ (M = Cr, Mo, W; XY = $(NEt_2)_2$; $N(Me)CH_2CH_2O$; (NEt_2) (OMe); $OCMe_2CMe_2O$; $(OMe)_2$) has also been prepared in order to probe the stability of these species. It was found that the stability can be increased by either going to a heavier congener, increasing the number of amino substituents on the phosphenium center, or adding an ethylene bridge between X and Y.[490] More recently, the unsaturated analog **138** (L = OTf, PPh_3) has been prepared via a different route.[491]



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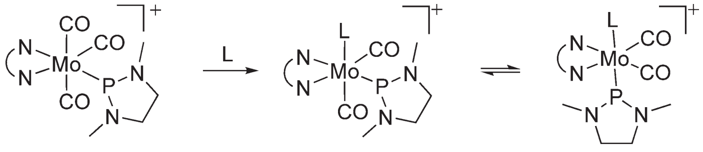
Properties. The kinetic product **137** isomerizes to the thermodynamically more stable *mer*-isomer, and the isomerization rate is dependent on the metal (Cr > Mo > W and bipy > dppe). This can be easily explained by the strong π-acceptor ability of the phosphenium species.[488] ^{95}Mo NMR spectroscopy has been used to further characterize these phosphenium species, and corroborates the M$=$P double bond character.[492] Structural and theoretical arguments[493] suggest that there is little N → P(phosphenium) π-donation. Theoretical calculations also support the strong π-electron-accepting character, which is calculated to be stronger than that of CO. Complex **138** has been shown to exist only as the *fac*-isomer and spectroscopic and structural characterization reveal considerable M$=$P double bond character.[492] This ligand is a better π-acceptor than the saturated systems described above.

Reactivity. The reactivity of **137** has been investigated in some detail. Thus, reaction with L(L $=$ PR$_3$, ROP{N(Me)CH$_2$}$_2$), MeOP{N(Me)C$_2$H$_4$O} forms *cis*-**139** and *trans*-**139** (Equation (38)) which exist in equilibrium. Some of these complexes have been structurally characterized and show a short Mo–P(phosphenium) bond length indicating some double bond character.[491] Migrations of OR, NR, and SR moieties to the phosphenium phosphorus have also been examined.[494]

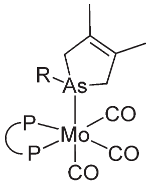


137 *cis*-**139** *trans*-**139** (38)

5.06.2.4.4 Complexes containing arsenic, antimony, and bismuth donors

5.06.2.4.4.(i) Monodentate ligands

Synthesis. The complexes *cis*-[Mo(CO)$_4$(E^{1}Me$_3$)(EMe$_2$SiMe$_3$)] (E, E^1 $=$ P, As) have been prepared from substitution of a carbonyl ligand in [Mo(CO)$_5$L]. Thermal substitution was also achieved but accompanied by considerable isomerization to the *trans*-isomer. IR and NMR spectroscopic data suggest that the monodentate ligands are very similar to the bidentate examples.[495] The monodentate arsine As(C$_6$H$_4$OMe-*p*)$_3$ has been developed as an "electrospray-friendly" ligand as it facilitates the observation of the [M + H]$^+$ peak in ESMS studies on metal carbonyl and halide species.[496] 3-Arsolene ligands have been prepared and reacted with [Mo(CO)$_5$(NCMe)] or [Mo(CO)$_3$(η^2-PP)(NCMe)] (PP $=$ dppe, dppm) via displacement of the nitrile ligands to give **140** (R $=$ H, Me, $^{\rm t}$Bu, Ph), which were spectroscopically characterized.[497] The cyclic ligand 1-phospha-4-arsacyclohexa-2,5-diene also coordinates to the Mo(CO)$_5$ fragment to form **141**, as the arsenic still has a lone pair available for bonding.[498] Penta- and tetracarbonyl adducts of Ph$_2$SbCl and (Ph$_2$Sb)$_2$X (X $=$ O, S) have been prepared.[499] The cyclic Sb$_4$$^{\rm t}Bu_4$ acts as a ligand to form [Mo(CO)$_5$L], which has been structurally characterized.[500] The unusual antimony cage compound P$_4$Sb$_2$C$_4$Bu$^{\rm t}_4$ reacts with [Mo(CO)$_5$(THF)] to form **142** which bonds through both the P and Sb center.[501] The unsaturated tertiary phosphine and arsine complexes of [(R$_3$E)Mo(CO)$_5$] (R$_3$E $=$ H$_3$CC$\equiv$CEPh$_2$ or H$_2$C$=$C$=$CH(DBP) (DPB $=$ dibenzophosphole) or Ph$_2$E-*trans*-CH$_2$CH$=$CHCH$_3$; E $=$ P, As) have been shown to undergo hydrophosphination and hydroarsination[502] or intramolecular [4 + 2]-Diels–Alder cycloaddition reactions[503] in the coordination sphere of the transition metal to give a variety of products, depending on reaction conditions.



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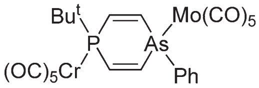

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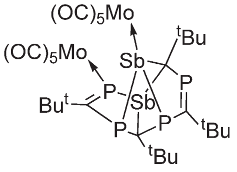

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The compound [(OC)$_4$Mo$\equiv$Sb]$^-$ has been characterized in the gas phase using Fourier transform ion cyclotron resonance spectroscopy, and *ab initio* calculations show the Mo–Sb bond to be a primarily covalent triple bond.[504]

Properties. A re-examination of the simple structures [$Mo(CO)_5(EPh_3)$] (E = As, Sb,[505] Bi[506]) and [$Mo(CO)_4(AsPh_3)_2$][507] coupled with other theoretical treatments[508–510] has allowed a further understanding of the σ-and π-properties of these ligands and stereostructural preferences regarding orientations about the Mo–E bond and phenyl group rotations. Detailed analysis of IR and Raman spectra[511] suggest little involvement of the E–Y σ^*-orbitals in π-backbonding. ^{121}Sb Mössbauer spectroscopy has also been reported for R = Ph and Me and indicates that the stibine ligands are poor π-acids.[512] A ^{13}C NMR spectroscopic study suggests that the $BiPh_3$ ligand has a very low *trans*-influence, as expected for a very poor σ-donor ligand.[506] This was further confirmed by the inability to synthesize the same compound under thermal activation and the bis ligand complex, [$Mo(CO)_4(BiPh_3)_2$], was inaccessible.

The isolation of the compounds with monodentate distibine ligands allows a comparison to be made for the series of P, As, and Sb donor ligands, and IR spectroscopy shows little change in the position of the carbonyl bands suggesting that σ-donation and π-acceptance decreases down the group so overall small electron density changes in the metal results. Additionally, the inability for chelate formation is due to the strain in the four-membered ring, and fits in with the observation that some chelates are formed with the As analog, but that this shows a great deal of strain.[517]

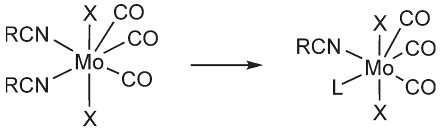
5.06.2.4.4.(ii) Bi- and tridentate ligands

The potentially bidentate diarsine ligand $Ph_2AsEAsPh_2$ (E = O, S) on reaction with [$Mo(CO)_4(nbd)$] leads to monodentate bonding in the formation of [$Mo(CO)_4(\eta^1\text{-}L)_2$], although DFT calculations suggest that a bidentate binding mode should be stable.[513] A hexaethylcyclohexaarsoxane complex [[$Mo(CO)_3]_2$[*cyclo*-$(EtAsO)_6$]] was prepared by reaction of $(EtAsO)_n$ with molybdenum hexacarbonyl and spectroscopically characterized. These results suggest that alkylcycloarsoxane is present in solution as a mixture of trimers and tetramers and metal-assisted ring expansion is postulated as forming the hexamer.[514] In contrast, the phenyl derivative exists as tetramers but undergoes a ring expansion also to form {[$Mo(CO)_3]_2$[*cyclo*-$(C_6H_5AsO)_6$]}.[515] Bidentate distibine ligands have been developed and the coordination chemistry explored,[516] but discrepancies between workers have been noted. The ligand $R_2Sb(CH_2)SbR_2$ (R = Ph, dpsm; Me, dmsm) reacts with [$Mo(CO)_5(THF)$] or [Et_4N][$Mo(CO)_5Br$] to give the compounds [$Mo(CO)_5(\eta^1$-dpsm)], [$(OC)_5Mo(\mu$-dmsm)$Mo(CO)_5$], *cis*-[$(OC)_4Mo(\mu$-dpsm)$_2Mo(CO)_4$], *cis*-[$(OC)_4Mo(\mu$-dmsm)$_2Mo(CO)_4$], and *fac*-[$M(CO)_3(\eta^1$-dpsm)$_3$], while η^1-complexes of dmsm were too unstable to be isolated.[517] A further molybdenum carbonyl complex of the bidentate distibine ligand 1,2-$C_6H_4(CH_2SbMe_2)_2$ has been synthesized.[518] The tripodal $MeC(CH_2SbPh_2)_3$ ligand forms a complex *fac*-[$Mo(CO)_3L$] upon reaction with [$Mo(CO)_6$] and $NaBH_4$ in refluxing EtOH or in an impure form with [$Mo(CO)_3(MeCN)_3$]. Structural and spectroscopic data suggest that the tripodal tristibine ligand is a weaker σ-donor than the corresponding phosphine.[519] As of the time of writing, there are no examples of macrocyclic antimony ligands.

The reactions of the carbonyl metallates with Ph_2BiCl result in the formation of [$Ph_2Bi\{Mo(CO)_5\}_2]^-$ anion that has been structurally characterized as its PPN salt. It was shown crystallographically that the bismuth center is in a tetrahedral environment indicating that the lone pair is coordinating to a second metal center, that is, it is not chemically inert.[520]

5.06.2.4.4.(iii) Seven-coordinate Mo(II) species

Further interest in seven-coordinate Mo(II) species has allowed the preparation of a number of adducts arising from ligand substitution from [$MoBr_2(CO)_3(NCMe)_2$],[521] [$MoI_2(CO)_3L$], (L = $(NCR)_2$, R = Ph;[522] 1,2-C_6H_4-$(CH_2CN)_2$[523]), or [$MoBrI(CO)_3(NCMe)_2$][524] to give adducts of the type [$MoX_2(CO)_3(NCR)L$] (Equation (39); L = PPh_3, $AsPh_3$, $SbPh_3$). When X = Br, stirring in CH_2Cl_2 causes dimerization to give [$Mo(\mu\text{-}I)Br(CO)_3L]_2$. The mixed halide species was found to be much more unstable compared with the diiodide derivative. A series of bis-ligand complexes [$MoBrI(CO)_3LL^1$] (L, L^1 = EPh_3, dppm, dppe, dppp, phen) were also synthesized.[525] Reaction of [$MI_2(CO)_3(NCMe)_2$] with 1 equiv. of L followed by 1 equiv. of pyrazole yields the complexes [$MI_2(CO)_3(pz)L$] (L = PPh_3, $AsPh_3$, $SbPh_3$).[248] Similar reactivity was observed for imidazole and 4-methylimidazole ligands.[525] The seven-coordinate Mo(II) species [$MoX_2(CO)_2L_2$] (L = MeCN, PPh_3, $AsPh_3$)[526] have been investigated in ring-opening polymerization of norbornene (X = I) and polymerization of substituted acetylenes (X = Cl).[527]

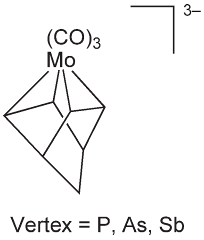


(39)

5.06.2.4.4.(iv) Clusters

Few examples of Mo–As clusters have been presented. Reaction of [Mo(CO)$_6$] with NaAsO$_2$ in MeOH or EtOH gives [Et$_4$N]$_2$[(OC)$_5$MoAsMo$_3$(CO)$_9$(μ_3-OR)$_3$Mo(CO)$_3$] (R = Me, Et). This has been structurally characterized and shown to consist of a tetrahedral AsMo$_3$ core. An Mo(CO)$_3$ fragment is bonded to the Mo$_3$ base via three triply bridging methoxy ligands. The structure is completed by an Mo(CO)$_5$ fragment which is bonded to the lone pair of the As. Extended Hückel calculations on an idealized model with C_{3v} symmetry showed that the extra electron pair is located in an a_2 orbital, equally delocalized over the three Mo atoms of the Mo$_3$ base.[528] [Mo(CO)$_6$] reacts with NaBiO$_3$ in MeOH to give a BiMo$_4$ cluster, [Et$_4$N]$_2$[BiMo$_4$(CO)$_{12}$(η^3-OMe)$_3$], probably by adventitious oxidation. This has been structurally characterized, and the authors describe one of the methoxy groups as donating three electrons to make a stable *closo*-cluster.[529] Heterobimetallic clusters of the type [(Cp*Co)$_n${Mo(CO)$_3$}As$_6$] (n = 2,3) have also been reported.[530]

Clusters containing the Zintl ions E$_7^{3-}$ (E = P, As, Sb) form complexes **143**.[531] The compounds comprise distorted norbornadiene-like η^4-E$_7^{3-}$ groups bound to C_{3v} Mo(CO)$_3$ centers. The bonding is described as E$_7$ π-type interactions with the metal center. For E = Sb, the crystal structure has been reported.[532] K$_5$Bi$_4$ reacts with [Mo(CO)$_3$(cht)] to give a *closo*-deltahedron cluster, **144**.[533] It consists of bent [Bi$_3$]$^{3-}$ molecules coordinated to two neutral M(CO)$_3$ moieties. The trimer [Bi$_3$]$^{3-}$ can be considered to be isoelectronic and isostructural with ozone.



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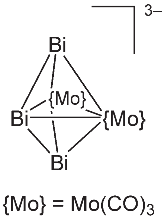
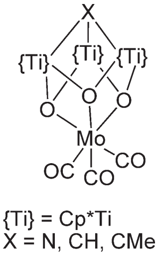


144

5.06.2.5 Molybdenum Carbonyl Complexes Containing Group 16 Ligands

5.06.2.5.1 Oxygen donor ligands

There are surprisingly few examples of these species in the literature from 1993. Reaction of [TpMo(CH$_3$)(CO)-(η^2-MeC≡CMe)] with *p*-anisaldehyde in the presence of H[B(ArF)$_4$] affords a σ-bonded anisaldehyde derivative and no evidence was found for the π-bonded arene complex. This is in contrast to the situation for the tungsten analog that has been studied by variable-temperature IR and NMR spectroscopy and the identification of a σ-π equilibrium established.[534] The reaction of [Mo(CO)$_3$(mesitylene)] with a titanium-containing heterocubane [{Cp*Ti(μ-O)}$_3$(μ_3-X)] (X = N, CH, CMe) displaces the arene and forms **145** in good yields. DFT studies suggest that there is no change in oxidation state, but that there is some delocalization of electron density through metal–metal interactions.[535]



145

A variety of O–O and N–O ligands based on a semiquinone core have been found to react with [Mo(CO)$_6$] to give [Mo$_2$O$_4$(CO)$_2$L$_2$] and other higher oxidation state species that do not contain carbonyl ligands.[536–538] Schiff's base ligands also react with $[Mo(CO)_6]$ to form oxymolybdenum carbonyl compounds.[539] $[(CO)_3Mo(\mu\text{-}OH)_3Mo(CO)_3]^{3-}$ has been synthesized by treatment of $[Mo(CO)_6]$ with hydroxide ions under solid–liquid biphasic conditions.[540] The reaction of $[Mo(CO)_2(PPh_3)_2Br_2]$ with AgO_3SCF_3 gives the bis(triflate) complex $[Mo(CO)_2(PPh_3)_2(O_3SCF_3)_2]$, which can be considered as a precursor for the 12-electron system $[Mo(CO)_2(PPh_3)_2]^{2+}$. Spectroscopic evidence suggests that one triflate anion acts as a chelating ligand, but can be displaced readily to give examples of alkyne-and nitrile-substituted products.[541]

The reaction of the allyl complex $[(\eta^3\text{-}C_3H_4Me\text{-}2)Mo(CO)_2(phen)Cl]$ with $Na[B(ArF)_4]$ in the presence of water affords the unusual aquo complex $[(\eta^3\text{-}C_3H_4Me\text{-}2)Mo(CO)_2(phen)(OH_2)][B(ArF)_4]$, while the neutral hydroxyl species $[(\eta^3\text{-}C_3H_4Me\text{-}2)Mo(CO)_2(phen)(OH)]$ has also been prepared.[542] The reactivity of the hydroxyl complex toward organic electrophiles[543] CS_2,[544] and alkenes[545] has been investigated.

5.06.2.5.2 Sulfur donor ligands

Group 6 – group 10 heterobimetallic compounds with sulfur ligands,[546] chalcogen-bridged metal carbonyl complexes,[547] coordination chemistry of transition metals with hydrogen chalcogenide and hydrochalcogenido ligands,[548] terminal chalcogenido complexes of transition metals,[549] selonolate and tellurolate ligands,[550] and binuclear thiolato-bridged compounds[551] have been reviewed.

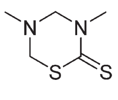
Synthesis. There are many methods to synthesize molybdenum thiol and thiolate complexes, both featuring monodentate, bidentate, and bridging bonding modes. Representative examples are shown in Table 9. They generally follow one of the following pathways:

(a) $[Mo(CO)_6]+L$
(b) $[Mo(CO)_5(THF)]+L$
(c) $[Mo_2(SR)_2(CO)_8]$ and Bu_4NX
(d) $[Mo(CO)_3(NCMe)_3]+L$
(e) $[Mo(CO)_4(pip)]+L$
(f) $[MoI_2(CO)_3(NCMe)_2]+L$
(g) $[MX_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]+L$

The di(1-cyclohepta-2,4,6-trienyl)sulfane ligand, $S(C_7H_7)_2$, has been synthesized and its reactivity investigated. Both penta- and tetracarbonyl derivatives can be synthesized with the latter displaying an η^2-interaction with one of the C=C bonds of the cht ring. Somewhat unusually, at higher reaction temperatures, isomerization takes place to form $[Mo(CO)_5\{S(CH_2Ph)(C_7H_7)\}]$.[553] The reaction of a potentially tridentate tripodal ligand $\{RCH_2C(CH_2PPh_2)(CH_2X)(CH_2Y)\}$ (R = H, OMe; X, Y = SAlkyl, SH) with $[Mo(CO)_3(NCMe)_3]$ affords **147** whereby the SH function is uncoordinated. However, deprotonation of the ligand to form the corresponding thiolate and subsequent reaction with $[Mo(CO)_3(NCMe)_3]$ does afford the η^3-complex **148**, which is significantly more stable if isolated as the [2,1,1]cryptand or [2,2,2]cryptand salts of the alkali metals. Reaction of **148** with RX (R = Me, Et, Bz) affords the thioether derivatives in good yields.[568] Of interest is the synthesis of **149**, as it allows a comparison of the Cp, Tp, and Tm ligands. The results of spectroscopic and structural comparisons reveal that the Tm ligand is a strong π-donor, Tp is a strong σ-donor, and Cp a good π-acceptor ligand.[571] The phosphazane ligands **150** and **151** form different compounds containing the $[Mo(CO)_n]$ fragment depending on which starting material is used.[577,578] A series of [9]aneS_2P and [10]aneS_2P macrocycles has been synthesized using an $Mo(CO)_3$ fragment as a template, starting from $[Me_4N]_2[Mo(CO)_3\{PhP(CH_2CH_2S)_2\}]$. The ligand can be oxidatively removed from the Mo template by treatment with elemental sulfur.[574] A further method for the synthesis of carbonyl thiolates is by reaction of precursor complexes with CO, as exemplified by the formation of 16-electron complexes **152** and **153** (Equation (40)). Structural determinations were carried out, and distortions from octahedral and trigonal-prismatic geometries were due to electronic effects. π-Donation from the sulfur atoms to molybdenum was also inferred from short Mo–S bond lengths.[579] An improved method of thiolate-transfer reagents for the synthesis of dithiolate complexes has been reported using $[Ni(S_2C_2Me_2)_2]$.[580] This method has been used to synthesize dithiolate alkyne complexes $[Cp_2Mo_2\text{-}\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}S_2C_2Ph_2)_2]$.[581]

Table 9 Synthetic routes to molybdenum thiols and thiolates (for synthetic details see text)

Complex	*Synthesis*	*Comments*	*References*
$[Mo(CO)_5(\mathbf{146})]$	a		552
$[M(CO)_5\{S(C_7H_7)_2\}]$	a	M = Cr, Mo, W	553
$[Bu_4N][M(CO)_5(SR)]$	a	R = 2-mercaptobenzimidazolyl, 2-mercaptobenzothiazolyl, 2-mercaptobenzoxazolyl	554
$[Et_4N][M(CO)_5(SCPh_3)]$	a, b	Kinetics of CO substitution with $P(OEt)_3$	555
$[Et_4N][M(CO)_5(SCOPh)]$	b	Kinetic study	556
$[Mo_2(SCy)_2(CO)_8]$	a	X-ray structure	557
$[Bu_4N][Mo_2Br(SCy)_2(CO)_6]$	c	X-ray structure	558
$[Bu_4N][Mo_2(\mu\text{-}SPh)_2(\mu\text{-}Cl)(CO)_6]$	c		559
$[Et_4N][Mo_2(SPy)_3(CO)_5]$	a	Mixed valent Mo	560
$[Bu_4N]_2[Mo_2(CO)_8(SHex^n)_2]$		X-ray structure	561
$[Et_4N]_2[Mo_2(STol\text{-}o)_2(CO)_8]$	a	X-ray structure and CV	562
$[Mo_2(\mu\text{-}SPy)_2(CO)_{6-n}(PPh_3)_n]$	d	$n = 1, 2$	563
$[Mo(CO)_4\{R_2P(S)P(S)R_2\}]$	a	R = Me, Et, ^{n}Pr, ^{n}Bu, Ph	564,565
cis-$[Mo(CO)_4\{S(C_7H_7)(\eta^2\text{-}C_7H_7)\}]$	a	X-ray structure	553
$[Et_4N][Mo(CO)_4\{\eta^2\text{-}S_2P(OEt)_2\}]$	e	X-ray structure	566
$[Mo_2(CO)_{10}\{\mu\text{-}Ph_2P(S)P(S)Ph_2\}]$	a	R = Me, Et, ^{n}Pr, ^{n}Bu, Ph	564, 567
147	d	Pendant CH_2SH function	568
$[Mo(CO)_4(Ph_2PN(Ph)PPh_2(E)\text{-}P,E)]$	b	E = S, Se	569
$[MoI_2(CO)_3\{Ph_2P(S)CH_2P(S)Ph_2\text{-}S,S'\}]$	f		570
149	a	X-ray structure	571
$[MoI(CO)([9]aneS_3)(\eta^2\text{-}RC_2R)_2]I$	g	X-ray structure	572
$[MI(CO)(ttn)(\eta^2\text{-}RC_2R)]I$	g	ttn = $MeS(CH_2)_2S(CH_2)_2SMe$	572
$[Me_4N]_2[Mo(CO)_3\{PPh(C_6H_4S\text{-}2)_2\}]$	a	X-ray structure	573
$[Me_4N]_2[Mo(CO)_3\{PPh(CH_2CH_2S)_2\}]$	d		574
fac-$[Mo(CO)_3(SPPhPy_2\text{-}S,N_2)]$	a	X-ray structure	575
148	d		568
$[Mo_3(CO)_6(\mu\text{-}SPy)_2(\mu_3\text{-}SPy)_2]$	d	X-ray structure	576



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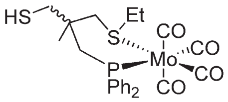

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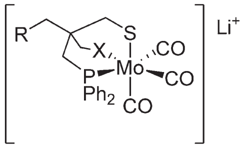
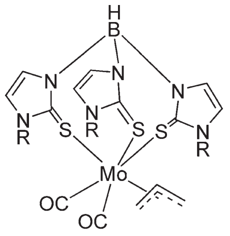


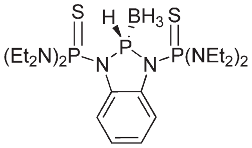
X = PPh$_2$; R = H
X = S; R = OCH$_3$

148



R = Me

149



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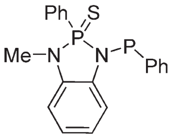

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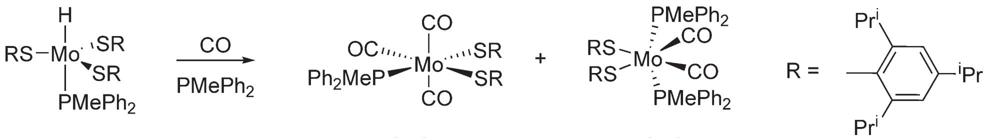
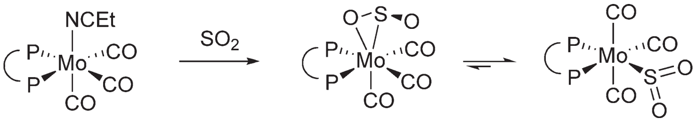
 (40)

152 **153**

Few examples of SO_2 complexes have been reported. Reaction of $[Mo(CO)_3(NCEt)(\eta^2\text{-PP})]$ (PP = dppm, dppe, dppp, dppf) with SO_2 afforded first the *fac*-isomer which rearranged slowly into the *mer*-isomer (Equation (41)). The stability of the *mer*-isomer is due to the effective overlap between the LUMO of the SO_2 molecule and a high, metal-centered HOMO of the metal compound. The isomerization process likely follows a trigonal twist mechanism, and the inflexible dppf ligand displays the slowest isomerization rate.[582] $[Mo(CO)_2(dmpe)(PPh_3)(SO_2)]$ has been prepared and structurally characterized.[583]



(41)

The main method for the synthesis of thiocarbamate ligands is by simple salt metathesis reactions of an Mo–X species with anionic S_2CX (X = PR_3, etc.).[292,584–587] Insertion of CS_2 into an Mo–N bond of $[(pip)_2M(CO)_4]$ in the presence of ^nBuLi has been reported as an alternative method.[588]

Properties. The kinetics of CO substitution in $[Et_4N][M(CO)_5(SCOPh)]$ (Equation (42); L = $P(OPr^i)_3$; M = Mo, W) have been investigated.

$$[M(CO)_5(SCOPh)]^- + L \longrightarrow cis\text{-}[M(CO)_4(L)(SCOPh)]^- + CO \tag{42}$$

Activation parameters are $\Delta H^\ddagger = 102.9(8)\,kJ\,mol^{-1}$, $\Delta S^\ddagger = 8.2(6)\,eu$; M = W, $\Delta H^\ddagger = 118.8(8)\,kJ\,mol^{-1}$, $\Delta S^\ddagger = 11.3(5)\,eu$.[556] A kinetic investigation of the substitution of PPh_3 and SO_2 in Equations (43) and (44) has been reported and the activation parameters are $\Delta H^\ddagger = 51.4\,kJ\,mol^{-1}$ (dmpe); $69.8\,kJ\,mol^{-1}$ (dppe) $\Delta S^\ddagger = -126.7\,J\,mol^{-1}\,K^{-1}$ (dmpe); $-68.6\,J\,mol^{-1}\,K^{-1}$, suggesting an intramolecular associative mechanism. The substitution of SO_2 on the other hand proceeds via both associative and dissociative mechanisms.[584]

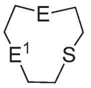
$$[Mo(CO)_2(\eta^1\text{-PP})(PPh_3)_2(SO_2)] \longrightarrow [Mo(CO)_2(\eta^2\text{-PP})(PPh_3)(SO_2)] + PPh_3 \tag{43}$$

PP = dpme, dppe

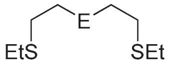
$$[Mo(CO)_3(\eta^2\text{-L})(\eta^2\text{-}SO_2)] + PR_3 \longrightarrow [Mo(CO)_3(\eta^2\text{-L})(PR_3)] + SO_2 \tag{44}$$

L = bipy, dppm

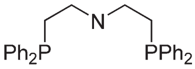
A series of 16- and 18-electron carbonyl complexes based on 1,2-disubstituted benzene rings with N, O, and S donor atoms has been prepared in order to examine the π-donor characteristics of the ligands. It was found that the equatorial site for the most effective π-donor is preferred over the axial position. Theoretical calculations suggest that the unoccupied d_{xy} orbital lies in the equatorial plane; thus, stabilization via a π-donor ligand in this position is favored. The axial position exhibits a filled/filled repulsion as both orbitals available for π-bonding are filled.[589] Titration calorimetry has been used to study a series of cyclic and acyclic tridentate N, S, and P donor ligand complexes of $[H\text{–}M(CO)_3(L)]^+$ (M = Cr, Mo, W; L = TACN, **154**, **155**, **156**). The metal basicity increases as the ligand donor group basicity increases, but the large difference between the pK_a values of thioethers (−6.8) and phosphines (6.25) suggests that thioether donor groups should be much weaker donors than phosphines. The observation that thioether groups contribute nearly as much as phosphine groups to the basicity of the metal in the $[H\text{–}M(CO)_3(L)]^+$ has been explained by suggesting that repulsion between the π-symmetry lone electron pair on sulfur and the filled metal *d*-orbitals increases the energies of the *d*-orbitals thereby making the metal more basic than expected from only the σ-donor ability of the sulfur. Acyclic ligands add approximately $6.7 \pm 1.2\,kJ\,mol^{-1}$ to the basicity of the metal.[590]



E = S; E^1 = PPh, NEt
E = E^1 = NEt
154



E = S, PPh, NEt
155



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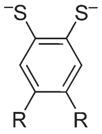
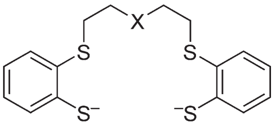
The complexes $[M(CO)_2(S_2C_2Me_2)_2]^{0/1-/2-}$ (M = Mo, W) have been studied by a combination of X-ray crystallography, CV, and EPR spectroscopy, and additionally by DFT calculations and it has been shown that going from

0 to 2-, the M–S, S–C, and C–O bond distances increase while the M–C, chelate ring C–C, and ν (CO) values decrease. Calculations ascribe this to the non-innocent behavior of the ligand.[591] In relation to molybdenum enzymes, a series of compounds containing the $S_2C_2Me_2$ ligand has been synthesized,[580] including some carbonyl complexes containing Mo(IV), and studied by EXAFS spectroscopy; good agreement between the EXAFS and crystallographic data has been achieved. These results raise the possibility that reduced enzyme sites could bind CO.[592] Other complexes that have been synthesized in order to model the active sites of enzymes include $[Mo\{S(CH_2)_2S\}(CO)_2(PEt_3)_2]$,[593] $[Mo(CO)_2(PCy_3)($**157**$)]$,[594] and $[Mo(CO)_2($**158**$)]$.[595]


R = H, ${}^tBu$

157

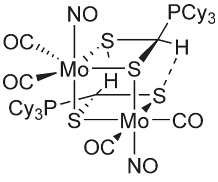

X = NH, O, S

158

Reactivity. Dinuclear species of the type $[Mo_2(SPh)_2(CO)_8]$ can add a further equivalent of SR^- to form $[Et_4N][Mo_2(SR)_3(CO)_6]$ which features a planar Mo_2S_2 unit coordinated by a third SCR bridging ligand; for R = Ph or S_2CNEt_2, additional characterization by electrochemical methods has been reported.[596] Other carbonyl substitution reactions have been examined, most notably with phosphine ligands[597] or carboxylates.[598]

$[Mo(NCMe)(\eta^3\text{-}C_3H_5)(CO)_2\{\eta^2\text{-}S_2P(OEt)_2\}]$, **159**, has been prepared from the reaction of $[Et_4N][Mo(CO)_4\{\eta^2\text{-}S_2P(OEt)_2\}]$ with allyl chloride, and shown to exist in equilibrium with **160**; the interconversion is probably via a trigonal twist mechanism. Further reactivity has been examined (Scheme 13), most interesting of which is the insertion of CS_2 into the Mo–N bond in **161** forming **162**, possibly due to the greater π-acceptor character of the $S_2CNC_5H_{10}{}^-$ ligand compared to the $S_2P(OEt)_2{}^-$ ligand.[566] Compound **159** reacts with dppm to form stereochemically rigid complexes **163** and **164**.[599] Complex **165** shows a rare example of an η^1-diethyldithiophosphate ligand,[600] which has also been implied in the formation of **166**.[567]

The reaction of Mo(0) dithiocarbamato carbonyl complexes, $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$, with Et_4NMoS_4 in MeOH affords a trinuclear mixed valence Mo–S complex, $[Et_4N]_2[(OC)_4MoS_2MoS_2Mo(CO)_4]$, which has been spectroscopically and structurally characterized and contains a trimetallic MoS_2MoS_2Mo core with two Mo_2S_2 planes sharing an Mo atom.[601] Reaction of nitrosyl molybdenum complex $[MoBr(NO)(CO)_2(\kappa^2\text{-}S_2CPCy_3)]$[602] with $LiBHEt_3$ or $NaBH_4$ gives **167**. A crystal structure study shows the central part of the molecule can be described as a quasicubane cage formed by two Mo, four S, and two CS···H–C interactions thus conferring greater stability to the dimer.[603]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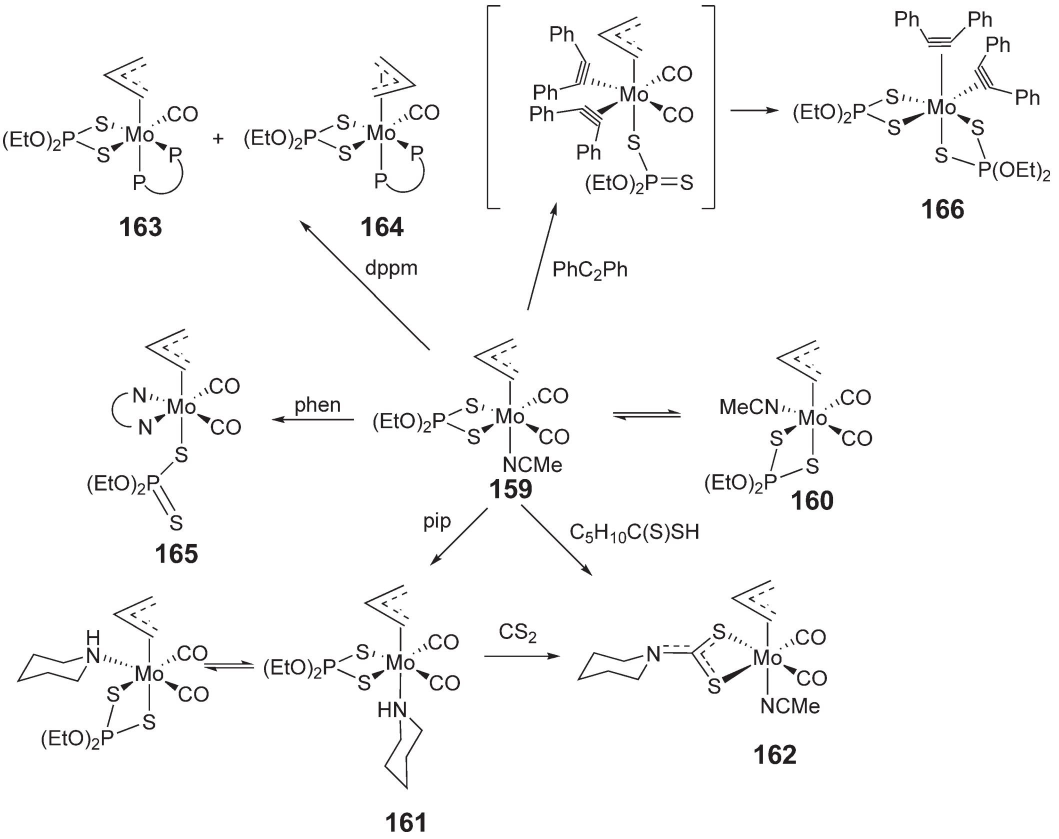
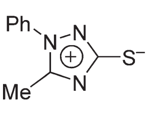
5.06.2.5.3 Selenium and tellurium donor ligands

5.06.2.5.3.(i) Monodentate ligands

Synthesis. The compound $[Mo(CO)_5L]$ ($L = (p\text{-}CH_3OC_6H_4)_2Te$) has been synthesized by a novel oxygen transfer from the corresponding telluroxide with concomitant elimination of CO_2; the kinetics of the reaction have been investigated and the reaction obeys a second-order rate law.[604] Ligands based on a pyrazole, tetrazole, and imidazole framework such as **168**, **169** (E = S, Se),[605] and **170** (alkyl = Me, ${}^iPr$; E = S, Se, Te)[606] form monodentate complexes $[LMo(CO)_5]$. From spectroscopic data, the relative donor ability follows the trend Te > Se > S. In contrast to these stable imidazole-based ligands, tellurocarbonyl ligands are rather more unstable, and the ligands **171** (E = Se, Te) form monoadducts with $[Mo(CO)_5]$. While both compounds have been characterized spectroscopically, the tellurium example was reported to decompose rapidly.[607]



Scheme 13



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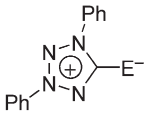

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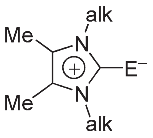

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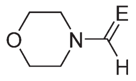
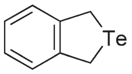


171

The reactions of Ph_2E_2 (E = Se, Te) with $[Mo(CO)_3(NCMe)_3]$ afford the oxidative addition Mo(I) compound $[Mo(CO)_3(NCMe)(\mu\text{-}EPh)]_2$. The structure of the tellurium example has been presented. Further reactivity studies on these compounds suggest that the selenium derivative can be further oxidized by Ph_2Se_2 to give the poorly characterized $[Mo_2(CO)_5(NCMe)(SePh)_4]$.[608] Ph_2Te_2 also reacts with $[Mo(CO)_6]$ to give $[Mo_2(CO)_{10}(\mu\text{-}Ph_2Te_2)]$, $[Mo(CO)_3(NCMe)(\mu\text{-}TePh)]_2$, and $[\{Mo(CO)_3\}_2(\mu\text{-}TePh)(\mu\text{-}Ph_2N_2)]$ all of which were structurally characterized and show Mo–Mo bond bridged by the chalcogenide.[609] Significant differences in reactivity were observed using Py_2Se_2. The oxidative addition of the Se–Se bond occurs to give mononuclear seven-coordinate Mo(II) species $[Mo(CO)_3(\eta^2\text{-}SePy)_2]$ which shows the SePy ligand binding through both the soft Se and hard N atoms.[610] A series of compounds containing the monodentate tellurium ligand 1,3-dihydrobenzo[c]tellurophane, $[Mo(CO)_{6-n}(\mathbf{172})_n]$ ($n = 1,2,3$), has also been reported.[611]



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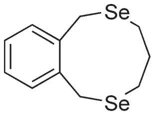
Properties. Based on IR and multinuclear (^{95}Mo, ^{125}Te) NMR spectroscopy it was deduced that **172** bonds through the lone pair on the tellurium atom and not as an arene. The spectroscopic characterization of the three compounds $[Mo(CO)_{6-n}(\mathbf{172})_n]$ ($n = 1,2,3$) has also allowed the trends in ^{95}Mo and ^{121}Te NMR spectra to be determined. Both the NMR chemical shifts move to higher frequency by ~200 ppm on sequential replacement of a CO ligand. This same trend is observed for other ligands such as phosphines and thioethers and is indicative of increasing electron density on the molybdenum center. For *cis*-$[Mo(CO)_4(\mathbf{172})_2]$, a crystal structure analysis was also reported and the bond lengths of the CO ligands *trans* to the telluroether ligands are approximately 0.1 Å shorter than those *trans* to a carbonyl ligand. This trend is in agreement with those observed for phosphine ligands.[611]

5.06.2.5.3.(ii) Bi- and tri-dentate ligands

Some heterodifunctional ligands containing Se have come forward, but these are typically not basic enough to displace two carbonyl ligands, so coordination of the softer Se donor requires substitution of weakly bonded groups on the molybdenum center. The reaction of $(Ph_2P)_2NPh$ with Se gives the mono-oxidized ligand $Ph_2PN(Ph)P({=}Se)Ph_2$ that acts as a bidentate P,Se ligand when reacted with $[Mo(CO)_4(pip)]$.[569] Using the same synthetic methodology, it was possible to synthesize the monoselenide of 1,8-bis(diphenylphosphino)naphthalene that forms the bidentate P,Se-coordinated $[Mo(CO)_4L]$ when treated with $[Mo(CO)_4(nbd)]$. This is somewhat unstable in solution and decomposes via elimination of elemental Se and the formation of the bis-phosphine adducts, but has been structurally characterized.[612]

Synthesis. The compounds $[Mo(CO)_4(RE(CH_2)_nER)]$ (E = S, R = Me, *n* = 2, 3; E = Se, R = Me, *n* = 2, 3; E = Te, R = Me, *n* = 2, 3) have been synthesized by substitution reactions of $[Mo(CO)_4(nbd)]$.[613] The ligands *o*-$C_6H_4(TeMe)_2$[613] and *o*-$C_6H_4(CH_2TeMe)_2$[614] also form similar compounds. Linear potentially tridentate telluroether ligands $Te(C_3H_6TeR)_2$ (R = Ph, Me) have been synthesized, and it was found that the *fac*-$[Mo(CO)_3L]$ was only isolable for R = Me, and even then the complex was unstable.[615] The tripodal ligands $MeC(CH_2EMe)_3$ (E = S, Se, Te) have also been reported to form *fac*-$[Mo(CO)_3L]$ by reaction with $[Mo(CO)_3(NCMe)_3]$, but for S and Se these are somewhat unstable and decompose to *cis*-$[Mo(CO)_4(\eta^2\text{-}L)]$, all of which have been spectroscopically characterized.[616] Macrocyclic thioethers have been known for some time, but the corresponding seleno- and telluroethers have only recently been developed. In contrast to the unstable tripodal compounds described above, the macrocyclic systems are much more robust. These have been synthesized by the reaction of $[Mo(CO)_6]$ with $[9]aneS_3$ or $[10]aneS_3$ and $NaBH_4$ in refluxing EtOH. The formed *fac*-$[Mo(CO)_3L]$ has been characterized by IR and multinuclear NMR (^1H, ^{13}C, ^{95}Mo) spectroscopy.[616] Other cyclic systems reported are $[Mo(CO)_4([8]aneSe_2)]$ and seven-coordinate Mo(II) species $[\{Mo(X)_2(CO)_3\}_2([16]aneSe_4)]$ and $[Mo(X)_2(CO)_3(\mathbf{173})]$ (X = Br, I) formed from **173** and $[\{Mo(X)_2(CO)_4\}_2]$.[617] The Mo(II) species proved to be insoluble, suggesting a bridging coordination mode. A mixed macrocycle **174** has also been prepared and reactions with $[Mo(CO)_6]$ afforded low yields of *cis*-$[Mo(CO)_4(\eta^2\text{-}\mathbf{174})]$, which was also prepared from $[Mo(CO)_4(nbd)]$. Spectroscopic data suggest the macrocycle coordinates through one S and Te donor atoms.[618]



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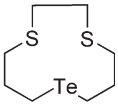
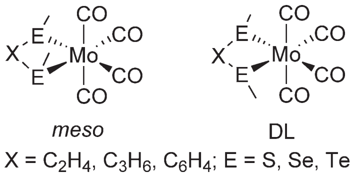


174

Properties. A comprehensive comparison of the electronic effects of a series of dithio-, diseleno-, and ditelluroether ligands based on the compounds $[Mo(CO)_4(\eta^2\text{-EE})]$ has been reported.[613] IR and multinuclear (^1H, ^{13}C, ^{77}Se, ^{125}Te, and ^{95}Mo) NMR spectroscopic studies show that the σ-donor ability increases $S < Se < Te$ and the σ-donor ability of the ligands is in the order *o*-$C_6H_4(CH_2TeMe)_2 \sim C_6H_4(TeMe)_2 > MeTe(CH_2)_3TeMe$,[614] while there is negligible π-bonding in the series; this is in line with earlier predictions. Also noted in these studies is that the inversion barrier of the group 16 elements also increases in the same order, albeit dependent on other factors such as chelate ring size, to such an effect that the two invertomers (*meso* and DL) can be observed spectroscopically for the Te complexes and some Se complexes, but the S show only an averaged signal (Scheme 14). This is indicative of a higher barrier to inversion for Te. Finally, due to unfavorable interactions between the phenyl group and axial carbonyl ligand, the DL isomer is present in >70% for the compound $[Mo(CO)_4(PhTe(CH_2)_3TePh)]$ while in the other example the ratio is 50 : 50.

5.06.2.5.3.(iii) Clusters

The $[Se_2MoCr_2(CO)_{10}]^{2-}$ cluster has been prepared from the reaction of $[Se_2Cr_3CO_{10}]^{2-}$ with $[Mo(CO)_6]$,[619] whereas $[Te_2Cr_2Mo_2(CO)_{18}]^{2-}$ and $[Te_2CrMo_2(CO)_{10}]^{2-}$ have been prepared via a similar strategy.[620] The iron



Scheme 14

compound $[Fe_2(CO)_6(\mu\text{-EE}')]$ shows a rich variety of cluster compounds when reacted with $[Mo(CO)_5(THF)]$. The structures obtained depend on the nature of E and E^1. $[Fe_4Mo(CO)_{14}(\mu_3\text{-E})_2(\mu_3\text{-E}^1)_2]$ and $[Fe_3Mo(CO)_{11}(\mu_3\text{-E})(\mu_3\text{-E}^1)(\mu\text{-E}^1\text{–E}^1)]$ (E, E^1 = S, Se, Te),[621] $[Fe_2Mo(CO)_{10}(\mu_3\text{-Se})_2]$,[622] $[Fe_4Mo(CO)_{14}(\mu_3\text{-Se}_2)(\mu_3\text{-Te})_2]$,[623] $[Fe_2(CO)_6(\mu_3\text{-Se})_2Mo(CO)_2(\mu_3\text{-Te})_2Fe_2(CO)_6]$,[624] $[Fe_2M(CO)_{10}(\mu_3\text{-S})(\mu_3\text{-Te})]$[625] have been prepared. Similarly, $[Ru_3(\mu_3\text{-Se})_2(CO)_7(PPh_3)_2]$ also reacts with $[Mo(CO)_3(MeCN)_3]$ to give the cluster $[MoRu_3(\mu_4\text{-Se})_2(\mu\text{-CO})_4(CO)_6(PPh_3)_2]$.[626,627] Solvothermal synthesis can also be used to synthesize $[Fe_2MoTe_3(CO)_{11}]$ from $[Fe_3(CO)_{12}]$, $[Mo(CO)_6]$, and Na_2Te_2 in methanol. The crystal structure showed a Te bridging between an $Mo(CO)_5$ fragment and an $Fe_2(CO)_6Te_2$ fragment.[628]

5.06.2.6 Halogenide Ligands

The oxidative addition chemistry of halogens and pseudohalogens has been covered in two comprehensive reviews, to which the reader is referred.[81,82] $[Mo(CO)_5X]^-$ has been the subject of DFT calculations in order to study the electronic structure and CO ligand dissociation energies. These indicate that CO loss is most facile from the *cis*-position; the dissociation energies increase along the series $X = NH_2 < OH < F < Cl < Br < I < CH_3 < H$. These results agree with experimental data. Trends in CO dissociation are related to the ability of X to stabilize the unsaturated $16e^-$ $[M(CO)_4X]^-$, while π-destabilization of the ground-state $[M(CO)_5X]^-$ species is equally significant. The electronic structure of the $18e^-$ species shows that X_π–d_π four-electron destabilization results in hybridization at the metal center that enhances *trans*-M–CO but reduces *cis*-M–CO π-backdonation. Strong π-donation from X also induces σ-antibonding interactions between the metal and the *cis*-CO ligands. A fragment analysis reveals that these effects are strongest for the hard fluoride, hydroxide, and amide ligands.[629] Electrochemical investigation of $[Mo(CO)_2(dppe)_2F]PF_6$ reveals that carbonyl fluoride complexes may exist in a wide range of oxidation states and confirm that fluoride is relatively strongly bound in these types of systems.[630] The potentially useful molybdenum(II) complex $[Mo(CO)_5OTf]^+$ has been prepared by oxidation of $[Mo(CO)_5X]^-$ with AgOTf and subsequent disproportionation, as characterized by electrochemical and EPR spectroscopic studies.[631]

5.06.2.7 Molybdenum Carbonyl Complexes of the Noble Gases

The observation of noble gases interacting with the $[M(CO)_5]$ fragments has been made previously and little work has since been carried out. A general review on this subject has been written.[632] One of the difficulties in studying these systems is the fact that photogenerated $[Mo(CO)_5]$ reacts with inert solvents such as alkanes within picoseconds of being generated and thus the very weakly bound complexes of the noble gases cannot be studied in solution (see Section 5.06.1.2). There are two experimental approaches that avoid this problem: (i) studying the reactions in the gas phase, and (ii) in liquefied noble gases where the reactant and solvent are the same. Infrared spectroscopic characterization of the van der Waals complexes $Mo(CO)_6Rg$ (Rg = Ar, Kr, Xe) formed in supersonic jet expansions has also been carried out and from the results, the authors showed that the structure is a C_3 symmetric top with the M–Rg distance slightly larger than the van der Waals radius.[633] As an alternative to the matrix isolation techniques supercritical fluids can also be used. $[Mo(CO)_5Kr]$, $[Mo(CO)_5Xe]$, and $[Mo(CO)_5(CO_2)]$ have been observed in supercritical fluids using time-resolved IR spectroscopy. The second-order rates of reaction with CO have also been measured and Kr ($k_2 = 4.3 \times 10^8\,mol^{-1}\,dm^3\,s^{-1}$) is much more easily displaced than the Xe analog ($k_2 = 1.1 \times 10^7\,mol^{-1}\,dm^3\,s^{-1}$) which is comparable to CO_2 ($k_2 = 7.7 \times 10^6\,mol^{-1}\,dm^3\,s^{-1}$).[634,635] In addition, the weak bonding between the noble gas and the $[Mo(CO)_5]$ fragment has been examined using DFT calculations. The orbital interaction has also been calculated and is dominated by the *p*-orbitals on the noble gas and orbitals of the equatorial carbonyl ligands.[636]

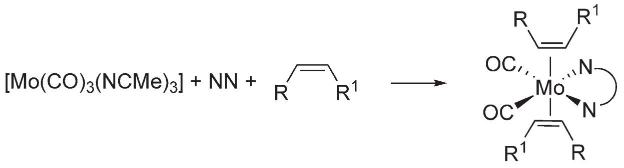
5.06.3 π-Complexes of Molybdenum Carbonyls

5.06.3.1 Carbon-based η^2-Ligands

5.06.3.1.1 Alkene compounds

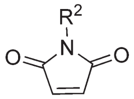
Few examples of alkene–molybdenum carbonyl complexes are known. This is generally because of the lability of the olefin; however, this has been overcome by using polymer supported olefins, for example, polystyrene supports.[637]

Photochemical reaction of $[M(CO)_6]$ (M = Cr, Mo, W) with $RCH{=}CHCO_2Me$ ($R = H$, Ph, MeO_2C) gives $[M(CO)_5(\eta^2\text{-}RCH{=}CHCO_2Me)]$, whilst thermal substitution of $[M(CO)_6]$ gives $[M(CO)_4(\eta^4\text{-}MeO_2CCH{=}CHCO_2Me)]$ which has additional coordination through the oxygen moieties. The factors governing η^2- and η^4-coordination were probed using theoretical calculations.[638] A series of octahedral d^6-bis(alkene) complexes has been prepared from the reaction of $[Mo(CO)_3(NCMe)_3]$[639–643] with a bidentate N-donor ligand and an appropriate alkene or $[Mo(CO)_4(dpphen)]$[644] and the alkene (Equation (45)). These are of interest due to the conformation the alkenes take, the favored one having the N or O atom pointing towards a carbonyl group. In addition, weak interactions between the N or O atoms and a carbonyl ligand have been inferred from solid-state structures. The other important observation from the crystal structures of a variety of alkenes is that the C=C bond is longer, due to the competition for the metal $d\pi$-electrons between the π^* CO and C=C orbitals. Other examples with TCNE as the olefin have been published and the spectroscopic data interpreted in terms of metal → ligand π-interactions.[645] $[M(CO)_5(\eta^2\text{-vinylferrocene})]$ (M = Cr, Mo, W) has been prepared by photolysis of $[M(CO)_6]$ and vinylferrocene, although the Mo and Cr examples were not stable enough to be isolated as pure products, and decomposition products included polymerization of the vinylferrocene moiety.[646] An unusual example is the platinacyclobutenone **175** that also features an η^2-interaction with a $CpMo(CO)_2$ fragment has been reported and the reactivity explored (Scheme 15).[647]



NN = bipy, phen, o-phenylenediamine, dpphen, $(NCMe)_2$
$R = R^1 = CO_2Me$, CO_2Bu^n
$R = CO_2Me$, $R^1 = OCOMe$
$R = H$, $R^1 = CO_2Me$

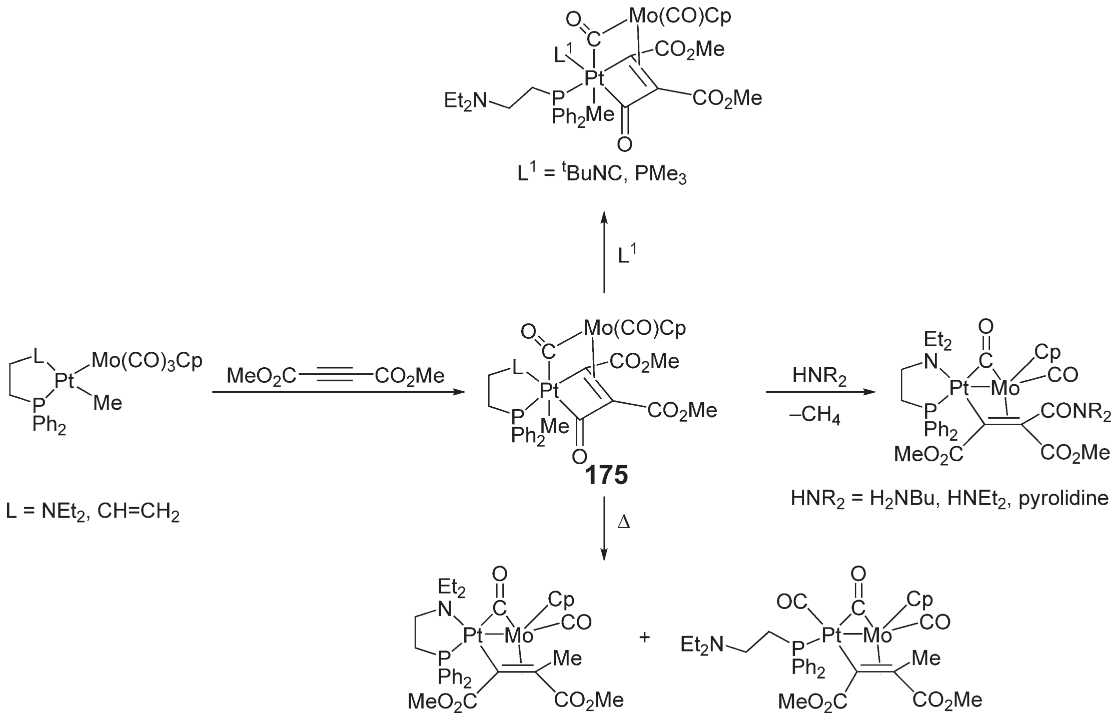
(45)



R^2 = Me, Ph

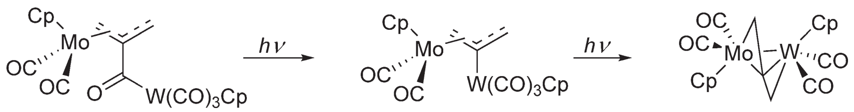
5.06.3.1.2 Molybdenum complexes of allenes

There are few reports of the synthesis and reactivity studies of the allene ($R_2C{=}C{=}CR_2$) ligand, probably due to the lack of general interest in these compounds. Some publications regarding the use of Mo-mediated allene reactions have been reported in, for example, the Pauson–Khand reaction[648–650] and intramolecular allene–alkyne [2 + 2]-cycloadditions.[651] Bimetallic species bridged by allenes have been synthesized from photolysis of dinuclear complexes containing a μ-η^3:η^1-β-carbonylallylic bridging ligand (Equation (46)).[652] A novel synthesis of allene compounds has been described by treatment of propargyl complexes with trityl salts (Equation (47)).[653] Unusual cyclization reactions occur on addition of PPh_3, and further chemistry of the coordinated dihydronaphthalene has been presented.[654] The fluorinated allene 1,1-difluoroallene reacts with $[CpMo(CO)_2]_2$ in a manner similar to the synthesis of other alkenes to form **176** in low yield. This has been spectroscopically and structurally characterized and shows metric data similar to the known non-fluorinated example.[655] The binuclear fulvalene complex $[Mo_2(CO)_6(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ reacts with allene photochemically to afford three complexes **177**, **178** and **179** (Scheme 16). Compound **179** can be synthesized from **177** by photolysis in the presence of excess allene, whilst **177** rearranges at room temperature to form **180**. Complex **178** shows hindered allene rotation deduced from NMR spectroscopy and $\Delta G^{\ddagger}_{303} = 57.4 \pm 2\ \text{kJ mol}^{-1}$.[656] The reaction of $[CpMo(CO)_3]^-$ with



Scheme 15

$R_2C{=}C{=}CCH_2OTs$ (R = H, Me, Ph) has been investigated by Welker and co-workers[657–659] (Scheme 17) and forms a complexed cyclobutenone 181 via a CO insertion followed by alkene insertion into the Mo–C bond of the allene. In contrast however, using the softer $[CpMo(CO)_2(PR_3)]^-$ allows the isolation of the σ-bonded allene complex 182. The use of substituted allenes affords a mixture of cyclobutenone 183 and allyl complexes 184 and 185; the ratios and stereochemistry are dependent on the counterion. A small amount of 186 formed by S_N2'-addition was also observed for R^1 = Ph, indicating that for this substituent CO insertion and CO loss results in almost identical yield of products. Some further reaction chemistry of 183 has been studied so that oxidative demetallation to form 187 or reduction to form 188 can be achieved in good yields.



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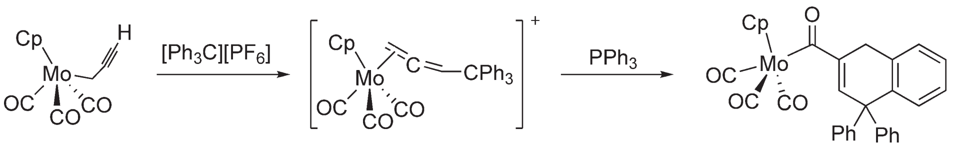

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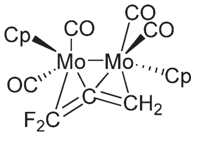

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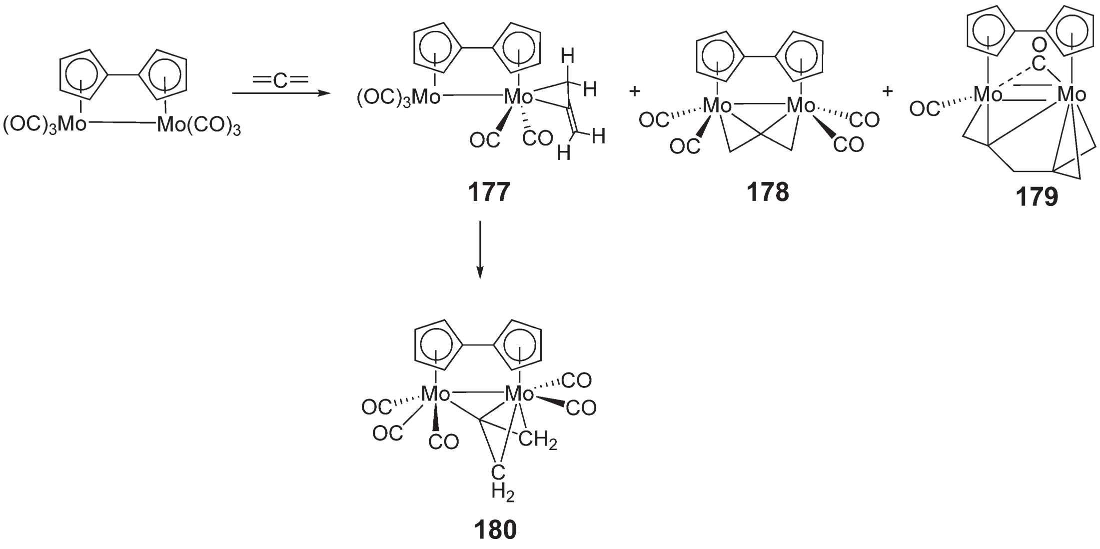
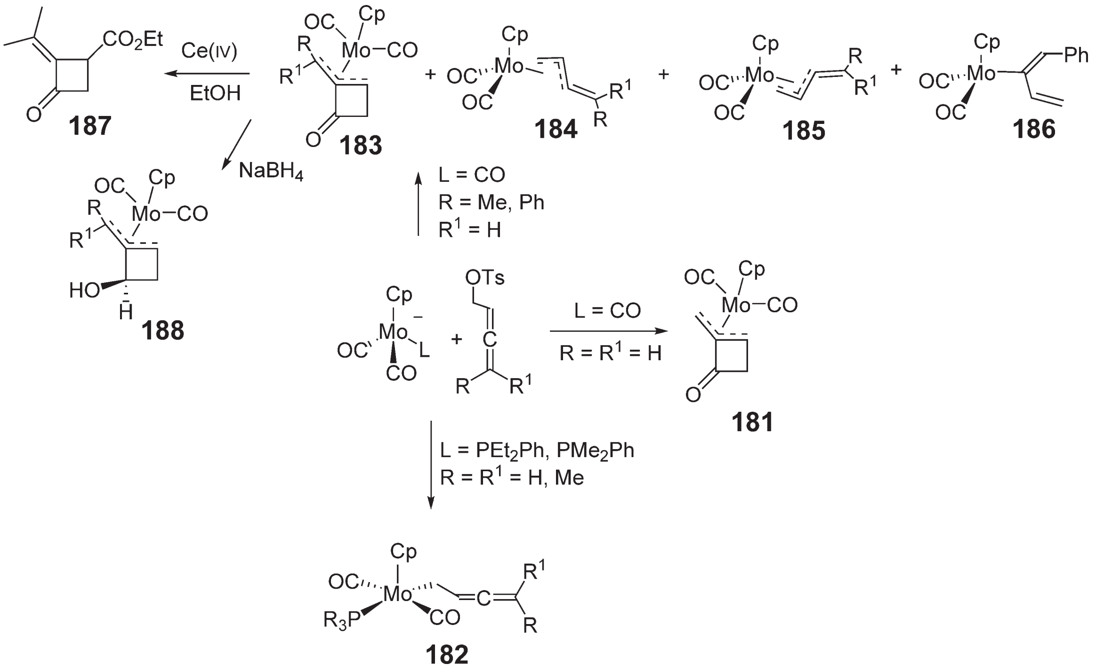


Scheme 16



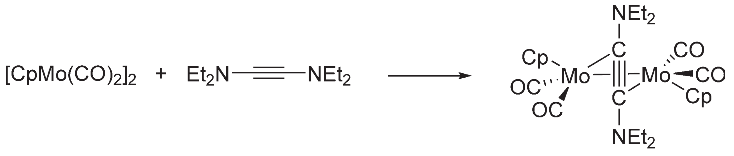
Scheme 17

5.06.3.1.3 Alkyne compounds

The use of alkynes in molybdenum chemistry is vast. Not included in this section is the use of alkyne ligands in the formation of mixed metal clusters. However, there are a number of reviews to which the reader is referred. The bonding of metal–alkyne complexes is a very important topic and has been reviewed.[660,661] Homo- and heterobinuclear complexes which feature a four-electron bridging ligand have been reviewed,[662] as has the reactivity of dimetal acetylides towards η^2-side-on coordination of further transition metal fragments[663] and the use of bis(alkyne) transition metals in the formation of bimetallic "tweezer" molecules.[664] Halocarbon complexes of Mo(II) including alkynes have also been reviewed.[81] The use of alkynes in transition metal-catalyzed reactions such as amination[665] and the Pauson–Khand reaction[666] or their use in the synthesis of polysubstituted benzene[667] and pyridine[668] derivatives, the addition of heteroatom-H bonds to alkynes,[669] and the synthesis of carbocyclic and heterocyclic moieties[670] have been reviewed. Cyclynes (rings containing alkyne moieties) have also been reviewed.[671] A common reaction for metal alkyne complexes is the tautomerization to form metal vinylidene species, and mechanistic aspects have been reviewed.[164] σ-Bonded alkynyl complexes have also been reviewed.[123,124]

Synthesis. The synthesis of tetrahedrane complexes of the type $[\{CpMo(CO)_2\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC{\equiv}CR^1)]$ has been well established in previous volumes of COMC (1982)[672] and COMC (1995)[673] and such compounds are readily accessible. Further work has mainly focused on the synthesis of functionalized Cp ligands, and some examples are given in Table 10.

Complex **190** has been synthesized by reaction of $[CpMo(CO)_2]_2$ with the metalloalkyne $[CpRu(\eta^1\text{-}C{\equiv}CR)(CO)_2]$ and demonstrates that the metalloalkyne acts as a simple organo-substituted alkyne under these conditions. A study of the VT NMR spectra reveals that the fluxional process observed is due to disruption of the central Mo_2C_2 core. In contrast, when the iron analog is used Fe–C bond cleavage occurs and the known complexes where R = Me, Ph and R^1 = H are isolated. The alkynyl silyl species where R = $SiMe_2C_3H_5$ and R^1 = $SiMe_3$ or $SiMe_2C_3H_5$ have been synthesized in an effort to observe a metal stabilized silyl cation on protonation.[677] Terthiophenes have been appended to an alkyne and the tetrahedrane molybdenum complex **189** can be polymerized under electrochemical conditions.[678] Unusually, analogous reactions with the alkyne $Et_2NC{\equiv}CNEt_2$ affords the η^1-product $[\{CpM(CO)_2\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}Et_2NC{\equiv}CNEt_2)]$, **191**, which has been structurally characterized (Equation (48)).[683] An unusual method of synthesizing tetrahedrane examples is the reaction of $[M_2(\mu\text{-}\eta^1{:}\eta^2C{\equiv}CPh)(CO)_4(Cp)_2]^-$ with gold halides to form good yields of $[M_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_2AuPR_3)(CO)_4(Cp)_2]$ (M = Mo, W; R = Ph, Me) (Equation (49)).[684]



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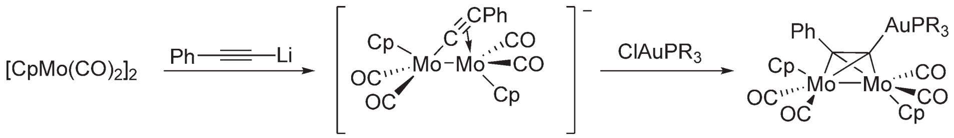

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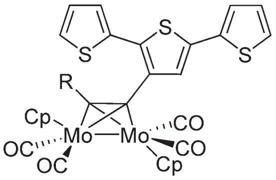
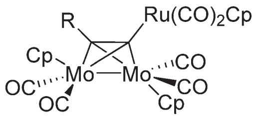


R = H, Ph

189



R = Me, Ph

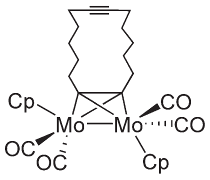
190

Homobimetallic compounds with bridging cyclic diynes, **192, 193 and 194**, have been prepared via a number of different ways.[685] Heterobimetallic species have also been reported, and representative examples are given in

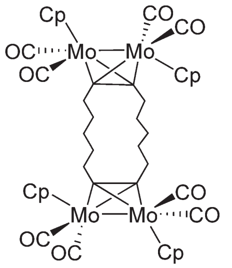
Table 10 Synthesis of compounds of the type $[\{CpMo(CO)_2\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC{\equiv}CR^1)]$

Cp	*R*	*R^1*	*Comments*	*References*
$^tBuC_5H_4$	Me, Et, Ph	H, Et, Ph	Photochemistry	674
$C_5H_4C(O)R^2$	H	H	R^2 = Me, Ph, OMe, OEt	675,676
Cp	$SiMe_2$allyl	$SiMe_3$, $SiMe_2$allyl		677
Cp	H	Terthiophene	**189**	678
Cp, CpMe	H	Fp	Fp = $CpFe(CO)_2$, $Cp^*Fe(CO)_2$, $Cp'Fe(CO)_2$, $(C_5H_4SiMe_3)Fe(CO)_2$	679
Cp	Me, Ph	$Ru(CO)_2Cp$	**190**	680
Cp	$SiMe_3$	$C{\equiv}C\text{–}SiMe_3$		681
Cp	$SiMe_3$	$Mo(CO)_3Cp$		681
Cp	Ph	$Fe(\eta^5\text{-}C_5H_4)_2Si(Me)$	X-ray structure	682

Table 11. Using the isolobal principle, $[\{(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_2\text{MoCo}(\text{CO})_3\}(\mu\text{-R}^1\text{C}{\equiv}\text{CR}^2)]$ ($\text{R}=\text{CH}_3\text{CO}$, CH_3CO_2; $\text{R}^1=\text{Ph}$, Tol; $\text{R}^2=\text{H}$, Ph, Tol) have been prepared by salt metathesis[686] or by reaction of the MoCo cluster with the alkyne.[687] The synthesis of the MoNi complex goes through an intermediate (Equation (50)).[688]



192



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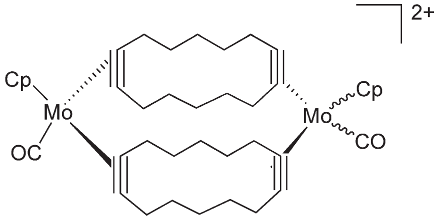
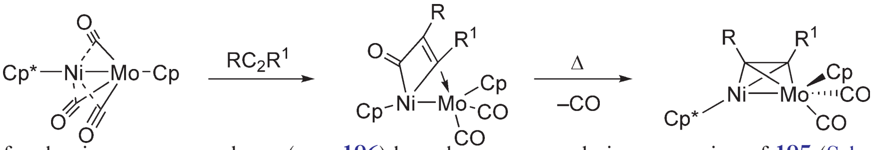


syn : *anti*
3 : 1
194

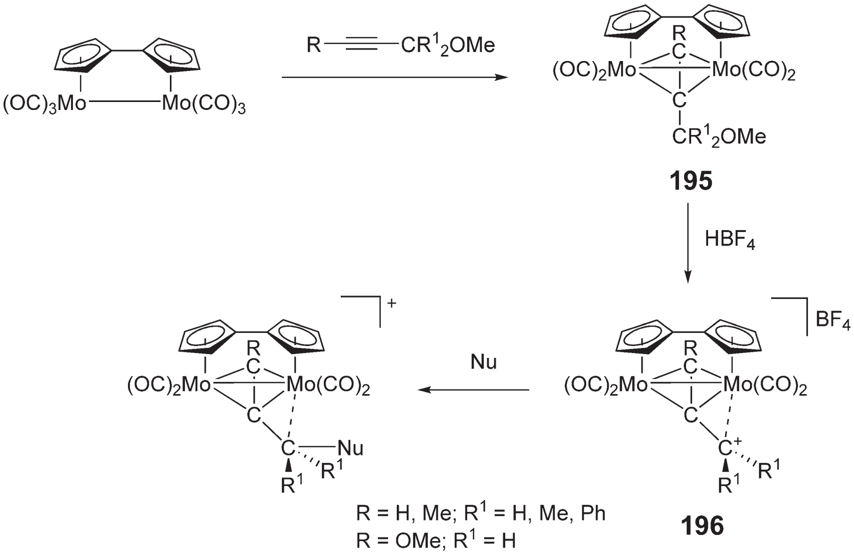


(50)

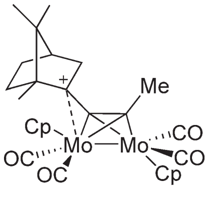
A number of carbenium type complexes (e.g., **196**) have been prepared via protonation of **195** (Scheme 18).[695–698] Better yields of **196** are obtained by using 1 equiv. of Me_3NO along with the alkyne. Compound **197** has been prepared with a bornyl cation and this is stable with respect to the Wagner–Meerwein rearrangement to the 4-alkynylcamphenyl cation. The preferential stabilization of the cation over the Mo center has been examined by theoretical calculations.[699] Other examples, **198**[700] and **199**,[701] have been reported and synthetic and spectroscopic aspects reviewed.[702]

Table 11 Synthesis of compounds of the type $[\text{CpMo(CO)}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-RC}{\equiv}\text{CR}^1)\text{ML}_n]$

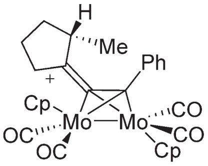
Cp	*R*	*R*^{1}	*ML*$_n$	*References*
Cp, Cp′	H, Me, Et, Ph	Me, Et, Ph, CMe_2OMe	NiCp*	688,689,690
$\text{C}_5\text{H}_4\text{C(O)Me}$	Ph	Ph	NiCp	691
Cp	CH_2OH	CH_2OH	Co(CO)_3	692
Cp	H	Me, Ph, CH_2OH	Co(CO)_3	693
$\text{C}_5\text{H}_4\text{CO}_2\text{Me}$, $\text{C}_5\text{H}_4\text{C(O)Me}$	H	H	CpW(CO)_2	694



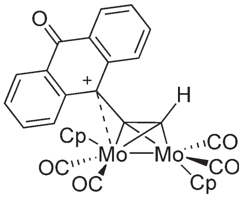
Scheme 18



197



198



199

A series of d^6-molybdenum bis(alkyne) complexes has also been synthesized with strongly electron withdrawing alkynes, for example, [Mo(CO)$_2$(η^2-NN)(alkyne)$_2$] (alkyne = RO$_2$CC≡CCO$_2$R (R = Me, Et), PhC≡CCO$_2$Et; NN = en, phenylenediamine, 2-NH$_2$CH$_2$Py, bipy, phen).[703]

Properties. The photochemistry of [(η^5-C$_5$H$_4$Bu^t)$_2$Mo$_2$(CO)$_4$(μ-η^2:η^2-RC≡CR^1)] (R = Me, Et, Ph, R^1 = Et, Ph, H) has been examined in Nujol matrices and the carbonyl loss products [(η^5-C$_5$H$_4$Bu^t)$_2$Mo$_2$(CO)$_2$(μ-η^1:η^2-CO) (μ-η^2:η^2-alkyne)] and [(η^5-C$_5$H$_4$Bu^t)$_2$Mo$_2$(μ-CO)$_3$(μ-η^2:η^2-alkyne)] identified by IR spectroscopy.[674] Some structurally characterized examples of *trans*-bis(alkyne) species have been forthcoming, for example, [Mo(CO)$_2$(HPz)$_2$(DMAD)$_2$].[704] [Mo(CO)$_2$(NN)(alkyne)$_2$] also feature *trans*-alkynes as shown by a crystal structure determination and spectroscopic characterization. NMR spectroscopy has been used to probe the mechanism of alkyne rotation.[703]

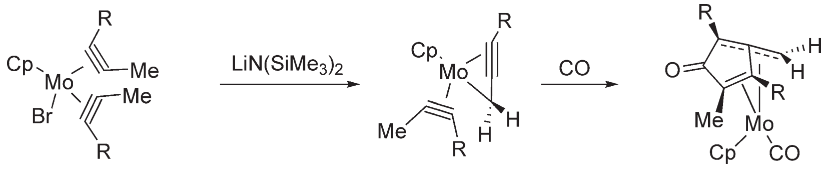
Electrochemical and spectroscopic methods have been used to probe the reduction of [Cp^{R}M(L)(RC$_2$R)$_2$]$^+$ (M = Mo, W; R = Me, Ph; Cp^R = Cp, Cp*, C$_5$Ph$_4$H; L = NCMe, CO). It was found that for L = NCMe a one-electron reduction to [Cp^{R}M(NCMe)(RC$_2$R)$_2$] occurs, which rapidly loses MeCN to give the 17-electron complexes [Cp^{R}M(RC$_2$R)$_2$]. However, for L = CO two sequential one-electron reductions are observed, the first of which is reversible and gives the 19-electron metal based radical species [Cp^{R}M(CO)(RC$_2$R)$_2$]. The second reduction affords [Cp^{R}M(CO)(RC$_2$R)$_2$]$^-$.[705] The carbenium complexes [{CpMo(CO)$_2$}$_2$(μ-η^2:η^3-HC≡C–C(R^1)(R^2))]$^+$ show dynamic NMR spectra which have been ascribed to rotation of the C–C$^+$ bond and interconversion of the Mo–C$^+$ bond. These compounds have additionally been investigated electrochemically and by theoretical methods. It was found that the reactivity is dependent on the Mo–C$^+$ bond distances which in turn are dependent on the R^1 and R^2 substituents.[706] A second electrochemical study was also reported with different conclusions.[707]

Reactivity. Alkyne displacement has been observed upon treating bis(alkyne) Mo(II) species with phosphite donors (Equation (51)).[708,709] It is likely that the mechanism is associative, with a concomitant change in the number of electrons donated to the metal by the alkyne ligand. Addition of 2 equiv. of a phosphite affords the bis-(phosphite) complex [MI$_2$(CO){P(OR)$_3$}$_2$(η^2-R^{1}C$_2$R^2)] which is initially formed as the *cis*-isomer and rearranges to the thermodynamically stable *trans*-isomer via a trigonal twist mechanism. Notably, however, the *cis*-isomer where R^1 = R^2 = Me has been structurally characterized. Additionally, the barrier to rotation in the butyne substituted example has been measured to be ~55 kJ mol^{-1} from NMR spectroscopic investigations. Addition of 3 equiv. of a phosphite affords the cyclotrimerisation product in good yield.

$$[\mathrm{MoI_2(CO)(NCMe)}(\eta^2\text{-}\mathrm{EtC_2Et})_2] + \mathrm{P(OR)_3} \xrightarrow{-\mathrm{EtC_2Et}} [\mathrm{MoI_2(CO)(NCMe)\{P(OR_3)\}}(\eta^2\text{-}\mathrm{EtC_2Et})] \qquad (51)$$

$$\mathrm{R = Ph,\ {}^iPr}$$

Deprotonation of complexes of the type [CpMoBr(η^2-RC$_2$Me)$_2$] (R = Me, Ph) affords a novel prop-2-ynyl complex **200** (Equation (52)).[710] Theoretical and reactivity studies on this complex have been reported.[711,712]

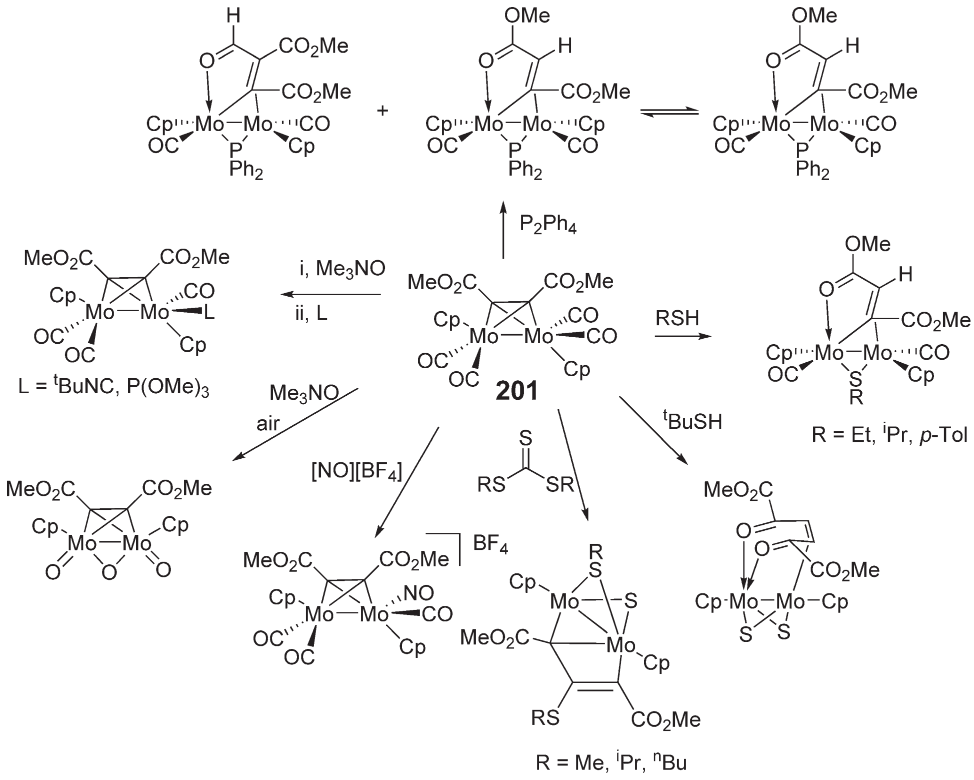


200

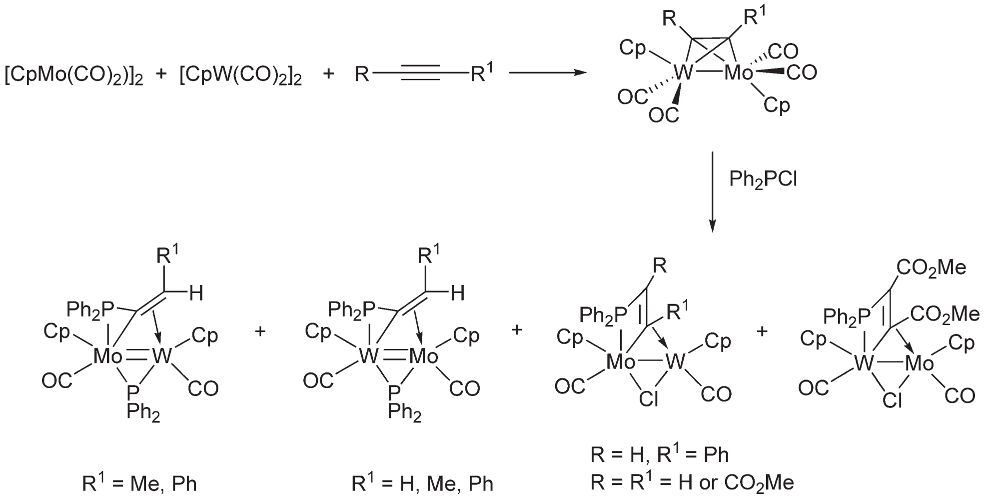
(52)

The complex [{CpMo(CO)$_2$}$_2$(μ-C$_2$R$_2$)] (R = CO$_2$Me), **201**, shows unusual reactivity toward P$_2$Ph$_4$, RSH,[713] substitution of carbonyls, oxidation,[714,715] and desulfurization of thiols has been observed (Scheme 19).[716–718] Similar reactivity was found for analogous MoCo[719–721] and MoW[722] compounds (Scheme 20).

A unique example of an alkyne binding parallel to the Mo–Mo bond has been synthesized by the reaction of [{CpMo(CO)$_2$}$_2$(μ-C$_2$Ph$_2$)] with ^{i}PrSH affording [Mo$_2$(μ-η^1:η^1-C$_2$Ph$_2$)(μ-S)(μ-SPr^i)$_2$Cp$_2$]. EHMO analysis suggests

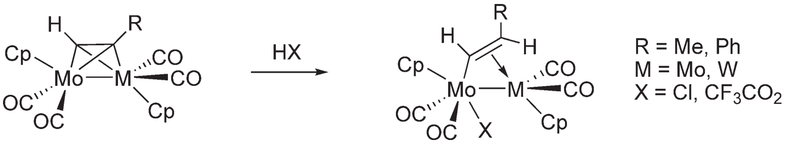


Scheme 19



Scheme 20

that this bonding mode is preferred as it maximizes the overlap between the alkyne and metal orbitals, as well as reducing repulsive interactions with the bridging thiolate ligands.[723] Reactions with $[Co_2(CO)_8]$ afford tetranuclear clusters of the type $[Co_2Mo_2(\mu_4\text{-}R^1C_2R^2)(\mu\text{-}CO)_4(CO)_4Cp_2]$[724]and $[Co_3Mo(\mu_4\text{-}R^1C{\equiv}CR^2)(CO)_9Cp]$,[725] as well as hexanuclear $[Co_4Mo_2(\mu_4\text{-}CR)_2(\mu\text{-}CO)_2(CO)_8Cp_2]$ and heptanuclear $[Co_5Mo_2(\mu_4\text{-}CR)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ clusters.[726] The butterfly Mo_2Co_2 cluster has also been formed by thermolysis of $[\{CpMo(CO)_2\}_2(\mu\text{-}C_2Ph_2)]$ with $[\{Co(CO)_3\}_2(\mu\text{-}C_2Ph_2)]$ and is formed by dissociation of the alkyne from the Co fragment, coupling of the free alkyne ligand with the Mo complex, and subsequent reaction with the $Co_2(CO)_6$ fragment.[727] Protonation of MoW bimetallic species has been studied and forms a complex that contains a σ- and π-bonded vinyl ligand (Equation (53)).[728] An example of C≡C activation has been observed in the reaction of $[\{CpMo(CO)_2\}_2(\mu\text{-}RC{\equiv}CR^1)]$ (R = H, Me, R^1 = H, Me, Ph) with $Ru_3(CO)_{12}$ to form an Mo_2Ru_4 cluster.[729]



(53)

5.06.3.1.4 Carbon-based η^3-ligands

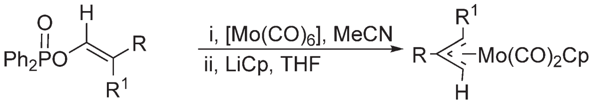
5.06.3.1.4.(i) Molybdenum cyclo-C_3 complexes

Cyclopropenyl complexes of the group 6 metals are extremely limited. Despite the previously reported examples of molybdenum carbonyl complexes reported in COMC I (1982)[672] and COMC II (1995),[673] there has been little further work on these compounds. During the time frame for this volume, only two examples have been forthcoming. A theoretical study of the bonding interactions between both $[CpRuBr_2]$ and $[CpMo(CO)_2]$ fragments and the *cyclo*-$[C_3H_3]$ ligand has been reported,[730] whilst M_3C_3 compounds containing the $CpMo(CO)_3$ fragment have been synthesized in poor yield by the reaction of $K[CpMo(CO)_3]$ with $[C_3Cl_3][SbF_6]$. NMR evidence shows free rotation around the M–C bond, but these complexes are surprisingly unreactive.[731]

5.06.3.1.4.(ii) $[(\eta^3\text{-allyl})Mo(CO)_2]$ complexes

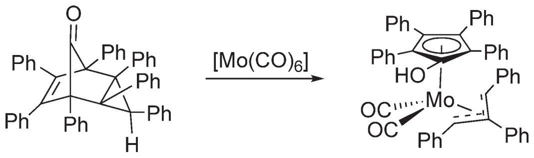
Complexes of the type $[CpMo(\eta^3\text{-allyl})\ (CO)_2]$ are well known and used extensively in organic synthesis. Aspects of this work have been the subject of several reviews[670,732–735] and are included in Volumes 10 and 11 of this series.[3]

Synthesis. A new efficient synthesis for $[CpMo(\eta^3\text{-allyl})(CO)_2]$ has been reported from the reaction of $[Mo(CO)_6]$ or $[Mo(CO)_3(NCMe)_3]$ with allylic diphenylphosphinates followed by treatment with cyclopentadienyllithium (Equation (54)).[736] Planar, chiral cationic η^3-allyl molybdenum complexes have been synthesized from chiral allylic benzoates and *cis*-$[Mo(CO)_4(Py)_2]$; for example, $[Mo(CO)_2(OBz)(\eta^3\text{-}C_3H_5)(Py)_2]$ has been synthesized from (S)-4-phenylbut-3(E)-en-2-yl benzoate. Structural and mechanistic studies have been reported.[737] The use of the $[CpMo(\eta^3\text{-allyl})\ (CO)_2]$ fragment as a marker for bioorganometallic chemistry has been reported, and the Cp ring substituted with amino acids and dipeptides synthesized.[738] A new synthesis for $[(CpMo(\eta^3\text{-allyl})(CO)(NO)]^+$ by treatment of $[CpMo(\eta^3\text{-allyl})(CO)_2]$ with $[NO][PF_6]$ in DME has been reported.[739] This is of use as the cation has been found to be more active for a number of stereo- and regio-controlled organic transformations. Substitution of the Cp ligand for the isoelectronic Tp ligand has also been reported, and additional stability was obtained using the $B(ArF)_4$ counterion.[740] The Diels–Alder reaction of tetraphenylcyclopentadienone with triphenylcyclopropene yields the expected adduct **202** with an *endo* hydrogen at C(7). On reaction with $[Mo(CO)_6]$, a retro-Diels–Alder reaction occurs to form **203** (Equation (55)).[741] Mono- and dinuclear bipyridyl derivatives of the $\{(\eta^3\text{-}C_3H_5)Mo(CO)_2\}$ fragment have been synthesized in order to ascertain the effect of changing the ligands on structural and solution dynamics. NMR evidence showed that the equatorial isomers were most favored and the binuclear compound $[\{(\eta^3\text{-}C_3H_5)Mo(CO)_2(2,2'\text{-bipy})\}_2(\mu\text{-}4,4'\text{-bipy})][PF_6]_2$ was shown by X-ray diffraction to form large channels with rectangular sections.[742]



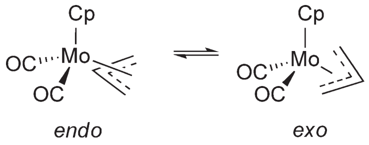
(54)

R, R^1 = various alkyls and cycloalkyls



202 **203**

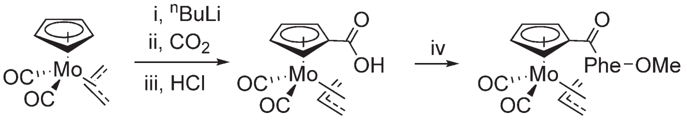
(55)



Scheme 21

Properties. *Exo-endo* isomerization is a common feature of all these complexes in solution, whilst the *exo*-isomer is almost exclusively observed in solid-state structures (Scheme 21). Recent theoretical investigations suggest that the *endo*-isomer is intrinsically more stable because of a more favorable overlap between the filled d_{xy} orbital of the molybdenum atom and the π_2 orbital of the allyl function and $d_z2-\pi_2$ backbonding interaction. However, there is competition between the allyl ligand and the CO ligand for the backbonding, and this destabilizes the *endo*-isomer so that the *exo*- and *endo*-isomers become comparable in stability.[743] The mechanism for interconversion has also been studied theoretically which has shown that the η^3-η^3-η^3 pathway is preferred, as the η^3-transition state is more stable than the corresponding η^1-transition state.[744]

The first example of a structurally characterized *endo*-allyl group has been recently reported in complex **204**, [Mo(C_5H_4-CO-Phe-OMe)(η^3-C_3H_5)(CO)$_2$] (Phe = phenylalanine; Equation (56)). In solution, however, a mixture of *endo*- and *exo*-conformations was observed and a $\Delta G^{\ddagger}$ value of 60–62 kJ mol^{-1} for the barrier to interconversion was measured.[738]



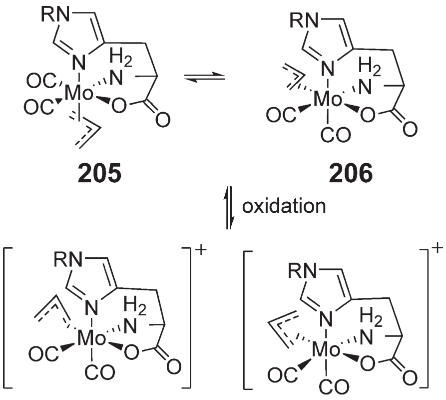
(56)

204

iv, HPhe-OMe, HBTU, Et_3N, DMF

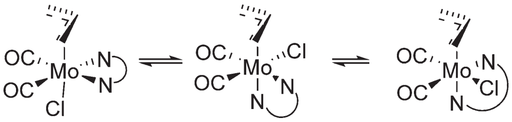
Synthetic studies,[745] variable temperature electrochemistry,[746] theoretical calculations,[747] and circular dichroism spectroscopy[748] have been used to investigate the fluxionality in **205**, **206** and their one-electron oxidized derivatives (Scheme 22).

An indenyl complex with a pendant aminopropyl arm, [{η^5-$C_9H_6(CH_2)_3N(SiMe_3)_2$}Mo(CO)$_2$($\eta^3$-$C_3H_5$)], shows a 2 : 1 *exo* : *endo* ratio whilst the parameters to interconversion were calculated to be $\Delta H^{\ddagger} = 70 \pm 6$ kJ mol^{-1}, $\Delta S^{\ddagger} = 11 \pm 22$ J mol^{-1} K^{-1} and $\Delta G^{\ddagger} = 67.7 \pm 0.1$ kJ mol^{-1}. No evidence for an η^3-η^1-η^3 isomerization mechanism could be observed using spin-transfer NMR experiments.[749] A trigonal twist mechanism has been proposed for pyrazole and acac derivatives of the [(η^3-allyl)Mo(CO)$_2$] fragment.[750] Substituents on the terminal position can also interact with spectator ligands causing severe distortions of the allyl unit, as shown by ^{1}H NMR and X-ray crystallographic studies.[751] For example, CH/π attractive interactions have been implicated in determining conformations of the allyl ligand in [LMo(CO)$_2$(η^3-R^{1}R^{2}C=CHCHR)] (L = bis(3,5-dimethyl-1-pyrazolyl)phosphinate; R^1,



Scheme 22

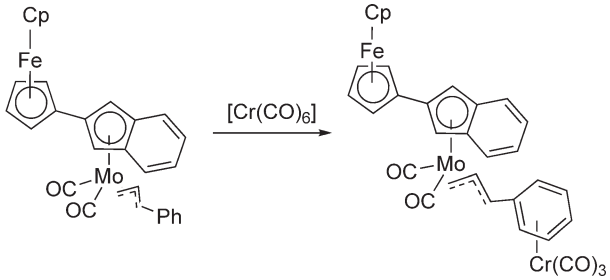
$R^2 = Me$, H; R = Me, Ph, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$).[752] A variety of allyl molybdenum complexes, including $[(CpMo(\eta^3\text{-allyl})(CO)(NO)]^+$, have been studied by DFT methods with respect to their reactivity toward nucleophiles, and the results agree well with experimental findings.[753] $[TpMo(\eta^3\text{-allyl})(CO)(NO)]^+$ has been structurally characterized, and in combination with detailed NMR studies, the authors observe a significant distortion to an η^2-allene type bonding. It was also found that the *endo* : *exo* ratio was strongly dependent on the substituents of the allyl fragment, so for C_3H_5 the ratio was 1 : 5.2, whist exclusively the *endo* form was observed for C_4H_7 and only the *exo* form observed for cyclic allyls C_6H_9 and C_8H_{13}. A proposed mechanism for the formation of these nitrosyl complexes involves the electrophilic addition of NO^+ to the neutral η^3-allyl complexes with concurrent slippage of the allyl to generate a seven-coordinate cationic η^1-allyl complex. This was corroborated by deuterium-labeling studies using $[TpMo(CO)_2(\eta^3\text{-}C_3H_4D)]$ which gave evidence for an η^3 to η^1 mechanism responsible for the formation of *exo*/*endo* isomers.[740] It was also found that this π-σ-π isomerization was valid for a range of $[TpMo(CO)_2(\eta^3\text{-}C_3H_3R_2)]$.[754] The use of substituted allyl ligands adds further isomerisation processes involving *syn-anti* configurations, and this has been studied for a variety of substituents on the $[TpMo(CO)_2(\eta^3\text{-allyl})]$ framework.[755] Three fluxional processes have been identified in the complexes $[(\eta^3\text{-allyl})Mo(CO)_2(PPy_nPh_{3-n}\text{-P,N})Br]$ and $[(\eta^3\text{-allyl})Mo(CO)_2(OPPy_nPh_{3-n}\text{-O,N})Br]$ (Py = 2-pyridyl; *n* = 2, 3) including a trigonal twist mechanism whereby the coordinated N-donor exchanges from axial to equatorial, a "pivoted double switch" mechanism which scrambles two equatorial coordination sites with racemization, but keeping the P donor *trans* to the allyl ligand and a slow dissociative exchange of coordinated and non-coordinated pyridyl ligands.[756] The complex $[(\eta^3\text{-allyl})Mo(CO)_2(bipy^*)Cl]$ ($bipy^* = 4,4'\text{-}{}^tBu_2bipy$) also shows three isomers in solution which interconvert *via* a trigonal twist mechanism (Equation (57)).[757]



(57)

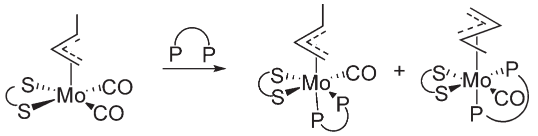
The photochemistry of $[CpMo(\eta^3\text{-allyl})(CO)_2]$ has been investigated and *exo*-*endo* isomerization was observed at wavelengths between 360 and 400 nm. On increasing the energy, CO loss was also observed to give the product formulated as $[CpMo(CO)(n\text{-heptane})(\eta^3\text{-}C_3H_5)]$ via TRIR spectroscopy. When $[CpMo(CO)_2(\eta^3\text{-}C_3H_5)]$ was photolyzed in supercritical ethylene, $[CpMo(CO)(C_2H_4)(\eta^3\text{-}C_3H_5)]$ was formed.[758] The photochemistry of $[CpMo(\eta^1\text{-allyl})(CO)_2]$ has also been investigated in frozen gas matrixes and in solution.[759]

Reactivity. The cyclohexenyl compound $[(CpMo(\eta^3\text{-}C_6H_7)(CO)_2]$, and the cationic cyclohexadiene $[(CpMo(\eta^4\text{-}C_6H_8)(CO)_2][BF_4]$ (Cp = Cp, $C_5H_4SiMe_3$, Ind), have been shown to form 1 : 1 and 2 : 1 inclusion complexes in β-cyclodextrin, for example, $\beta\text{-CD}/[CpMo(\eta^3\text{-}C_5H_7)(CO)_2]$, and comprehensively characterized.[760,761] Significantly, the reaction of $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(\eta^2\text{-NN})Cl]$ (η^2-NN = bipy, phen) with R_2Mg or $LiC{\equiv}CR$ affords $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(\eta^2\text{-NN})R]$ (R = Me, Et, Bz, $C{\equiv}CH$, $C{\equiv}CPh$, $C{\equiv}CSiMe_3$) as opposed to alkylation at the allyl function or elimination of the olefin.[762,763] Substitution of the labile acetonitrile ligands in $[(\eta^3\text{-}C_3H_4R)Mo(CO)_2(NCMe)_2X]$ for water-soluble pyridine ligands affords stable allyl complexes that have varying degrees of water solubility.[764] An interesting synthesis for heterotrimetallic species has been reported from the reaction of the bridged fulvalene species $[CpFe(C_5H_4C_5H_2Me_2)Mo(CO)_2(\eta^3\text{-}C_3H_4Ph)]$ with $[Cr(CO)_6]$ to form a Cr–arene bond (Equation (58)). A series of the bridged fulvalene complexes has also been characterized by cyclic voltammetry studies, and these results suggest a possible interaction between the Fe and Mo centers.[765]



(58)

Dithiocarbamate (S_2CR) ligands have been used extensively in all areas of molybdenum chemistry. The reaction of pyrolidinyldithiocarbamate with $[\{\eta^3\text{-}C_3H_4Me\}Mo(NCMe)_2(CO)_2Br]$ gives good yields of **207** which reacts further with diphosphines to give $[\{\eta^3\text{-}C_3H_4Me\}Mo(\eta^2\text{-}S_2CNC_4H_8)(CO)(diphos)]$ (Equation (59); diphos = dppm, *exo* : *endo* 1 : 20; diphos = dppe, *exo* : *endo* = 2 : 1).[766] $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(S_2PX_2)(NCMe)]$ undergoes simple substitution chemistry to form monomeric or dimeric species.[587] Examples of C–C coupling reactions in the coordination sphere of these Mo(II) species have also been published upon reaction with DMAD (Equation (60)).[767]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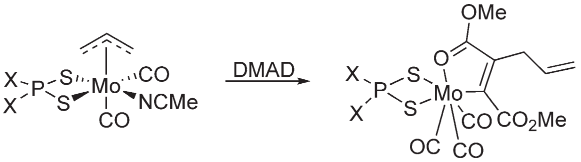
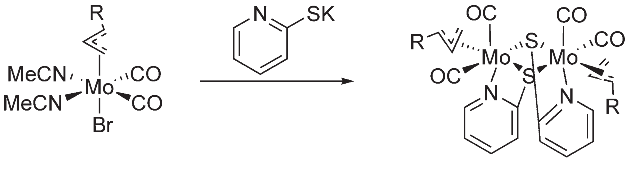
(59)


X = OEt, Ph

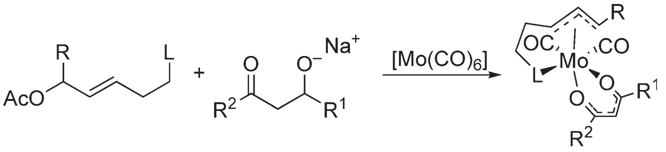
(60)

[(η^3-C_3H_4R)Mo(CO)$_2$(NCMe)$_2$Br] reacts with 2-KSC_5H_4N to give bimetallic **208**, (Equation (61); R = H, Me) which on treatment with the amine $C_5H_{10}NH$ affords a monomeric complex [(η^3-C_3H_4R)Mo(CO)$_2$(η^2-pyS)$_2$(NHC_5H_{10})] which exists in equilibrium as different geometric isomers.[768]


208

(61)

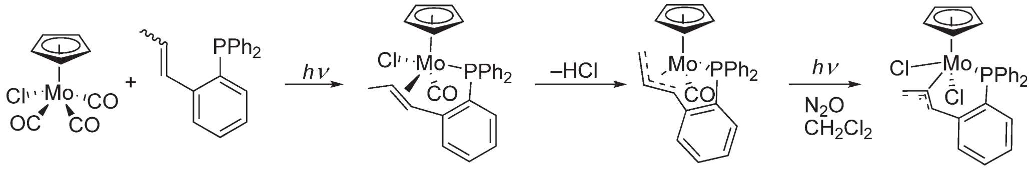
Allyl groups with additional donor functions are known, for example, with aldehydes,[769–771] pendant arm sulfur, or nitrogen donor groups (Equation (62)),[772] and these have been examined in aldehyde allylation reactions.[773]


R = H, Me; L = NMe$_2$, SMe; R^1, R^2 = OEt, Me, CF$_3$

(62)

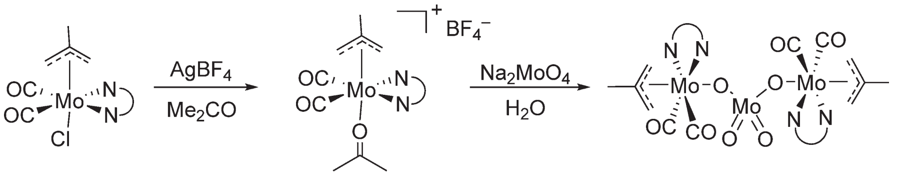
The chemistry of pendant-donor allyl ligands has been extended to the use of phosphine-donor atoms. Thus, treatment of [CpMo(CO)$_3$Cl] with 2-(1-propenyl)phenyldiphenylphosphine affords an η^2-olefin complex that undergoes an intramolecular HCl elimination to form the η^3-allyl complex **209** which exists only as the *endo*-isomer, both in solution and in the solid state. This is thought to be the thermodynamic product as the ligand is preorientated as the *exo*-isomer in the intermediate complex. Oxidation with N_2O in CH_2Cl_2 solutions affords the Mo(IV) species **210**, which is a rare example of a high oxidation state Mo atom bound to a soft allyl ligand (Scheme 23).[774]

The synthesis of Mo complexes with soft allyl ligands in combination with hard oxo-functions has been the subject of study due to the implication of these species in heterogeneous allylic oxidation. Thus, the reaction of


209 **210**

Scheme 23

$[(\eta^3\text{-C}_3\text{H}_4\text{Me})\text{Mo(CO)}_2(\text{bipy})\text{Cl}]$ with AgBF_4 in acetone affords $[(\eta^3\text{-C}_3\text{H}_4\text{Me})\text{Mo(CO)}_2(\text{bipy})(\text{O}{=}\text{CMe}_2)][\text{BF}_4]$ which on treatment with Na_2MoO_4 gives **211**, the first example of an Mo(II)-O-Mo(VI)-O-Mo(II) species (Equation (63)).[775] Substitution of bipy for the bipy* in order to aid solubility, gave a hydrogen bonded network of H_2O and crown-ether molecules between two $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_2(\text{bipy}^*)]$ moieties.[757] Dioxygen activation has been observed on oxidation of $[(\text{allyl})\text{Mo(CO)}_2\text{XL}]$ (L = bis(3,5-dimethylpyrazolyl)methane; allyl = 2-phenyl-2-propenyl, 2-propenyl, X = Br, Cl) to form an Mo_2O_4 core $[\text{MoO}(\mu\text{-O})\text{LX}]_2$.[776] An unusual example of a soft allyl moiety in combination with a hard fluoro ligand has been reported.[777] Further examples of soft allyl ligands in combination with hard amido ligands have been forthcoming, and complex **212** (Ar = Ph, *o*-Tol) isolated, which is a rare example of a complex without amido → metal π-donation. Its reactivity has been investigated (Scheme 24) and four reactivity pathways have been observed: (i) deprotonation of the amido group preferentially to the allyl group to form **213**; (ii) insertion reactions into the Mo–N bond to form **214–216**; (iii) simple acid–base exchange reactions to form **217**; and (iv) oxidation to form **211**.[778]



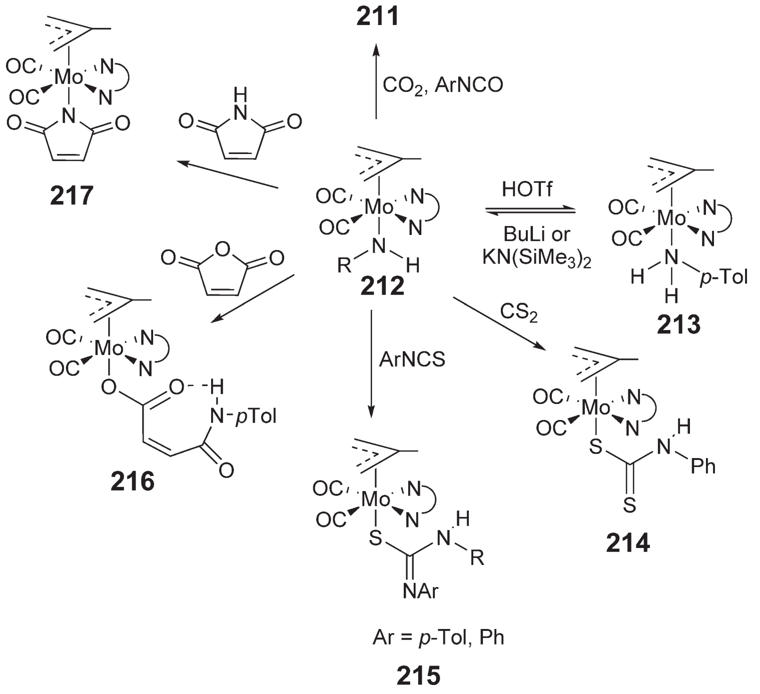
211

(63)

5.06.3.1.4.(iii) η^3-indenyl complexes

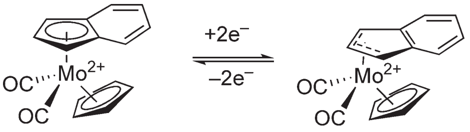
Indenyl ligands are well known to ring-slip to the η^3-hapticity during reactions, which is manifested in rate enhancements; this is commonly called the indenyl effect. However, there are some examples of stable complexes containing the indenyl ligand in a η^3-hapticity, and these are discussed in this section.

Synthesis. $[(\eta^5\text{-Ind})\text{M(CO)}_2\text{L}_2]\text{BF}_4$ (M = Mo or W; L = NCMe or DMF) and an excess of L gives ring-slipped molybdenum complex, $[(\eta^3\text{-Ind})\text{M(CO)}_2\text{L}_3]\text{BF}_4$. Other examples with $\text{L}_3 = \text{HC(pz)}_3[\text{HB(pz)}_4]^-$, Me_3TACN or {en(NCMe)}, OPPh_3, OP(OMe)_3, $(\text{O}_2\text{CCF}_3)^-$, acac^- also afford η^3-indenyl derivatives, whilst for L_2 = bipy, dppe, $(\text{PMe}_3)_2$, $\{\text{P(OMe)}_3\}_2$ or triphos only the η^5-indenyl hapticity was observed.[779,780] In addition, theoretical studies have



Scheme 24

been presented. Redox-induced ring slippage has also been observed in compounds of the general formula $[IndCpMoL_2]^{2+}$ (where L = CO, NCMe, PR_3, bidentate N-donor ligands, isonitriles) by treatment with Cp_2Co. These have also been investigated electrochemically (Equation (64)).[781]



(64)

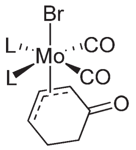
The use of a sterically bulky indenyl ligand, 1-$Me_3SiC_9H_6$, allows the isolation of mixed ring [(η^3-Ind)Mo(η^5-Me_3SiInd)$(CO)_2$] or [(η^3-Me_3SiInd)Mo(η^5-Me_3SiInd)$(CO)_2$], in contrast to [$(Ind)_2Mo(CO)_2$] where hapticity exchange between both rings is observed. These compounds have been characterized by a variety of techniques including cyclic voltammetry and *ab initio* calculations and it was found that the conformation of the Me_3Si group is due to a balance between steric and electronic effects.[782]

5.06.3.1.4.(iv) η^3-cyclopentenyl complexes

Only one example of a cyclopentenyl complex has been reported. Reaction of 2,2-bis(cyclopentadienyl)propane with $[Mo(CO)_6]$ or $[Mo(CO)_3(NCMe)_3]$ affords [$Mo(CO)_2(\eta^5{:}\eta^3\text{-}C_5H_4C(Me)_2C_5H_6)$] as a single isomer. The photochemistry of this species was examined both in a nujol matrix and in solution containing PPh_3.[783]

5.06.3.1.4.(v) η^3-cyclohexenyl complexes

η^3-C_6H_9 species are readily made from the corresponding 1,3-cyclohexadiene complexes by deprotonation, and are discussed in Section 5.06.3.1.6.(ii). The synthesis of [Mo(η^3-C_6H_7O)$(CO)_2(NCMe)_2$Br] has been reported from $[Mo(CO)_6]$ and bromocyclohex-2-enone in acetonitrile. From this, complexes **218** or **219** (L_2 = bipy, dppm) have been prepared. Surprisingly, none of these compounds reacts with trityl salts to form η^4-dienes, which is extremely facile for cyclopentadienone (see Section 5.06.3.1.6.(iii)), and theoretical calculations have been used to rationalize this anomaly.[784]



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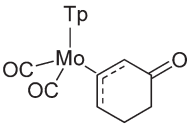
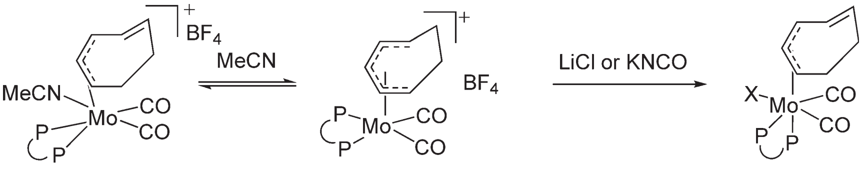


219

5.06.3.1.4.(vi) η^3-cycloheptenyl complexes

There are few reports on the chemistry of the cycloheptenyl ligand. Some examples have been synthesized from the corresponding cycloheptatriene ligands and are detailed in Section 5.06.3.1.11.(ii). Reaction of complex **220** (PP = dppm, dmpe, dppe, η^2-triphos) with LiCl or KNCO gave **221** (X = Cl, NCO), which is quite stable with regard to $\eta^3 \rightarrow \eta^5$ hapticity changes (Equation (65)). In addition, an equilibrium between the η^5-**220** and the ring-slip complex **222** was observed on addition of acetonitrile, and the effect of L on the stability of the η^3-hapticity determined to be bipy > dppe > dppm. The nature of the diene has also been investigated with respect to $\eta^5 \rightarrow \eta^3$ hapticity changes and the order is $C_8H_{11} \geq C_5H_7 > C_7H_9$[785,786]

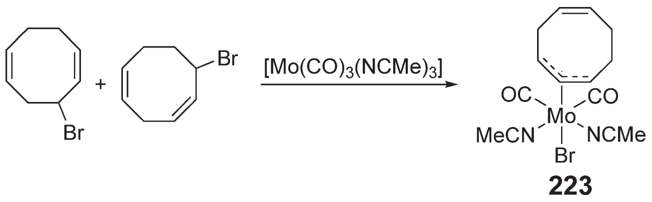


222 **220** **221**

(65)

5.06.3.1.4.(vii) η^3-cyclooctenyl ligands

Synthesis. The chemistry of the cyclooctadiene ligand bound to molybdenum is dominated by the η^3-hapticity, although few new results have been forthcoming during the past 10 years. A new synthesis of η^3-cyclooctenyl substituted molybdenum(II) species has been developed, starting from the bromo-cyclooctadienes and $[Mo(CO)_3(MeCN)_3]$. Thus, $[MoBr(CO)_2(NCMe)_2(1\text{-}3\text{-}\eta{:}^{5,6}\text{-}C_8H_{11})]$, **223**, and $[MoBr(CO)_2(NCMe)_2(1\text{-}3\text{-}\eta{:}^{4,5}\text{-}C_8H_{11})]$, **224**, have been prepared (Equations (66) and (67) respectively).[787,788] Hydride abstraction of derivatives of these compounds with $AgBF_4$ afforded the pentahapto-complexes **225** in good yields (Equation (68)).[789]



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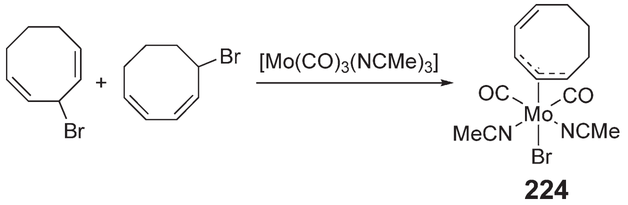

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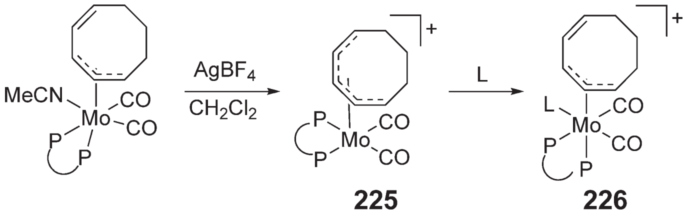


(68)

Properties. Solid-state analysis of **223** shows a twist of the ring, which is also observed in solution by very small proton–proton coupling constants, whilst **224** shows a planar ring. For **225**, NMR studies indicate a substantial barrier to ring rotation.[789] A systematic investigation into the free energy of activation for the trigonal twist mechanism in $[MX(CO)_2(\eta^2\text{-PP})(\eta^3\text{-L})]$ [$M = Mo$ or W; $X =$ halide, NCO or NCS; $PP = Ph_2P(CH_2)_nPPh_2 (n = 1–3)$] has been reported, the results of which are strongly dependent on the nature of the alkene.[790] Further corroborating evidence of the hapticity change has been shown in the complexes $[TpMo(CO)_2(\eta^3\text{-}C_8H_{11})]$ and $[\{9\text{-BBN}(Pz)_2\}Mo(CO)_2(\eta^3\text{-}C_5H_6Ph)]$, whereby weak BH···Mo or CH···Mo interactions prevent interconversion to the pentahapto derivatives.[791]

Reactivity. Compound **224** displays varied substitution chemistry and examples with isonitriles, Cp, phosphine and bipy ligands have been prepared. Significantly, they exclusively show η^3-bonding of the cyclooctadiene ring.[787] Complex **225** also exhibits substitution chemistry (Equation (68)), albeit this time with concomitant η^5-η^3 hapticity shifts to form **226**. Of note is the fact that the $1\text{-}3\text{-}\eta\text{-}C_8H_{11}$ ligand in **223** is less effective at this hapticity shift than the one to five ligand in **224**, possibly due to the enhanced donor capability of the former and/or the configuration of the coordinated carbon atoms.[790]

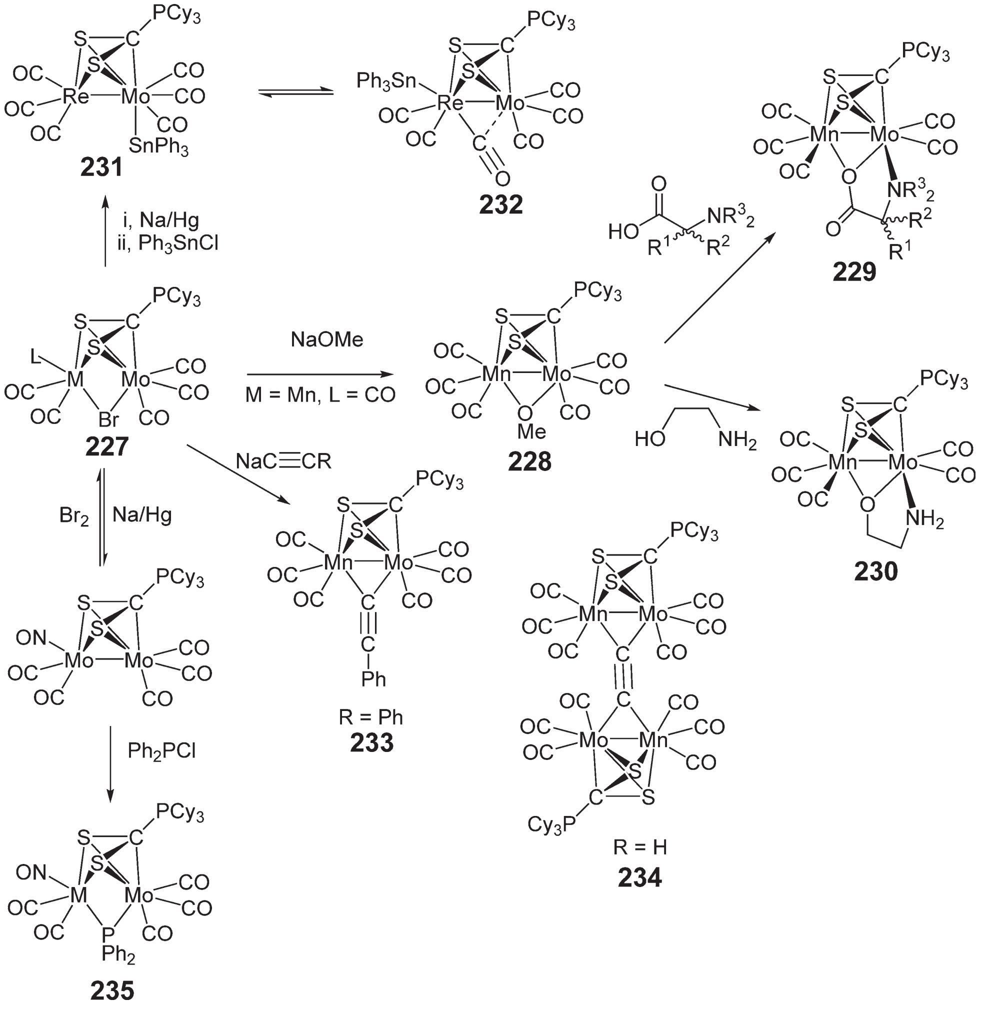
5.06.3.1.5 Heteroatom-substituted η^3-ligands

5.06.3.1.5.(i) Amidinate ligands

Further examples of molybdenum carbonyl compounds of amidinato and the related amidinate ligands have been published. The complex $[Mo(\eta^3\text{-allyl})(\eta^2\text{-amidinato})(CO)_2(pyridine)]$ has been found to be a good starting material for further studies, as the pyridine ligand is more labile than in the analogous acetonitrile complexes. Treatment with monodentate donors has been reported to give simple substitution products.[792] Reaction of $[(\eta^3\text{-allyl})Mo(\eta^2\text{-amidinato})(CO)_2(pyridine)]$ with bidentate N-donor ligands affords examples of η^1-bound amidinato ligands, whilst in contrast, bidentate phosphine-donor ligands give $[\{Mo(\eta^3\text{-allyl})(\eta^2\text{-amidinato})(CO)_2\}_2(\mu\text{-dppe})]$ or mononuclear monocarbonyl complexes $[Mo(\eta^3\text{-allyl})(\eta^2\text{-amidinato})(CO)(\eta^2\text{-dppe})]$, depending on the reaction conditions. The different reactivity toward phen and dppe has been ascribed to the difference in π-acceptor character of the bidentate ligands. The phosphine complex shows fluxional behavior in solution, namely *endo-exo* isomerization. A crystal structure determination showed a disordered allyl group that was modeled as *exo*/*endo*-isomers.[793] Bis(amidine) complexes can be prepared from $[Mo(\eta^3\text{-allyl})(CO)_2(NCMe)_2Cl]$ and 2 equiv. of $ArN{=}C(R)NHAr$ ($R = H$, Me; $Ar = Ph$, $p\text{-}MeC_6H_4$).[794]

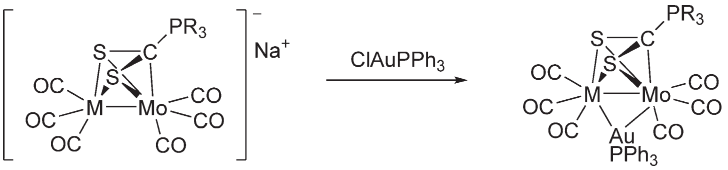
5.06.3.1.5.(ii) Dithiocarboxy ligands

Complexes containing the thiocarboxy ligand $[S_2CR]^-$ display a bonding mode that can be considered as allylic, as experimental and theoretical calculation of complexes containing iron have demonstrated.[795] The first example of mononuclear molybdenum species containing a trihapto-bonded S,S′,C-trimethylphosphonium dithiocarboxylate ligand, $[M(S_2CPMe_3)(CO)_2(PMe_3)_2]$ ($M = Mo$, W) was reported in 1993.[796] Electrophilic attack at the central carbon with protic acids or alkyl-derived electrophiles has been studied. A theoretical study on the dynamic behavior of the Mo species has been reported.[797] Bimetallic systems $[(OC)_3M(\mu\text{-}S_2CPR_3)Mo(CO)_3]^-$ and $[(L)(OC)_2Mo(\mu\text{-}S_2CPCy3)M^1(CO)_3]^-$ ($M = Mn$; Re; $M^1 = Mo$, W; $L = NO$, η^3-allyl)[602,798,799] have been synthesized and their reactivity examined (Scheme 25). Reaction of $[MnMo(CO)_6(\mu\text{-}S_2CPCy_3)(\mu\text{-}Br)]$, **227**,[602] with NaOMe affords $[MnMo(CO)_6\text{-}(\mu\text{-}S_2CPCy_3)(\mu\text{-}OMe)]$, **228**, and treatment with a variety of amino acids eliminates MeOH to form **229**, ($R^1 = H$, Me; $R^2 = H$, Me, Ph, Bz; $R^3 = H$, Me), whilst O–N donor ligands displace one CO ligand giving **230**.[800] Unusually, reduction of $M = Mn$,[801] Re[802] and treatment with Ph_3SnCl affords complexes with Mo-Sn bonds for $M = Mn$ but for $M = Re$ an equilibrium mixture of **231** and **232** is observed whereby the $SnPh_3$ group migrates between the Mo and Re. Reaction



Scheme 25

with acetylides affords **233**, which features a bridging acetylide where both metals are bonded to one carbon atom, and the bonding situation is best described as a three-center two-electron bond, whilst dimeric **234** can be described as a tetrametallic acetylene.[803] Treatment of $[(OC)_3M(\mu\text{-}S_2CPR_3)Mo(CO)_3]^-$ and $[(L)(OC)_2Mo(\mu\text{-}S_2CPCy_3)M^1(CO)_3]^-$ with $ClAuPPh_3$ to form heterotrimetallic $[(OC)_3M(\mu\text{-}S_2CPR_3)(\mu\text{-}AuPPh_3)Mo(CO)_3]$ (Equation (69), M = Mn, Re, R = Cy, ^{i}Pr) and $[(L)(OC)_2Mo(\mu\text{-}S_2CPCy_3)(\mu\text{-}AuPPh_3)M^1(CO)_3]$ (Equation (70), M^1 = Mo, W; L = η^3-allyl, NO). A crystal structure determination of M = Mn, R = Cy conclusively demonstrates the allylic nature of the S_2CPR_3 ligand and significant differences in the $AuMoM^1S_2C$ core were noted in the crystal structures of M^1 = Mo, L = allyl and M^1 = W, L = NO.[804] A further interesting feature of these complexes is the migration of the pseudoallylic fragment of the S_2CPR_3 from Mo to the second metal. For example, reduction of $[MMo(CO)_5(\mu\text{-}Br)(\mu\text{-}PP)(\mu\text{-}S_2CPR_3)]$ (PP = dmpm or tedip) and subsequent treatment with Ph_3SnCl affords $[MMo(SnPh_3)(CO)_4(\mu\text{-}PP)(\mu\text{-}S_2CPR_3)]$ where the central carbon has migrated from Mo to M (M = Mn,[805] Re[806]) and loss of one carbonyl ligand (Equation (71)). Treatment of $[MnMo(CO)_6(\mu\text{-}S_2CPPr^i{}_3)]^-$ with Ph_2PCl also affords this migration to form $[MnMo(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}S_2CPPr^i{}_3)]$, **235**.[807] Similar complexes with bridging PPh_2 ligand have also been prepared for M = Mo, W,[808] whilst for M = Re simple substitution of a carbonyl ligand on the molybdenum center is observed on addition of PR_3 (R = Ph, OMe). Theory has been used to explain this effect on the basis of orbital overlap considerations.[809]



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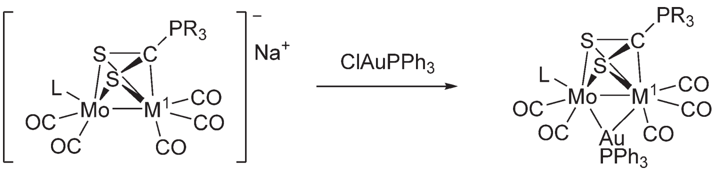

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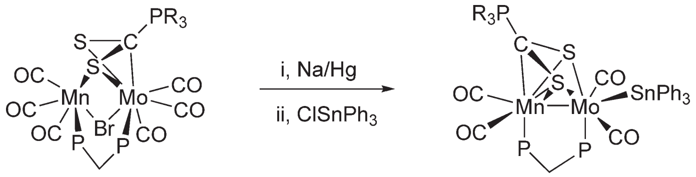


(71)

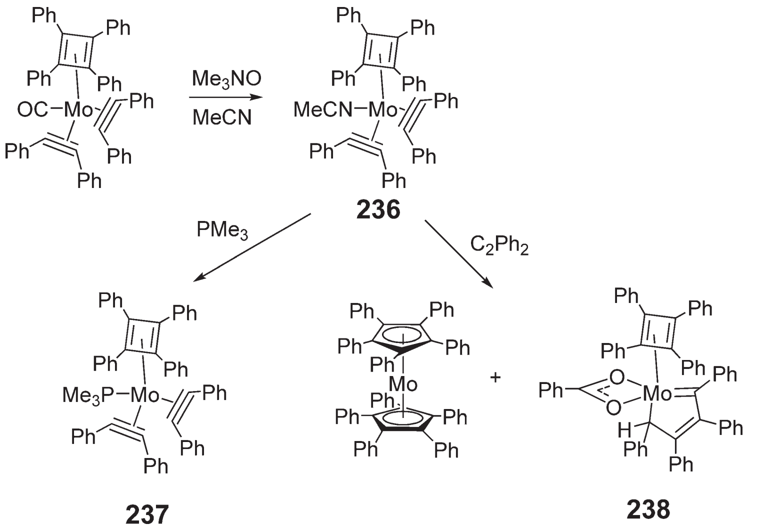
5.06.3.1.6 Carbon-based η^4-ligands

5.06.3.1.6.(i) Molybdenum cyclo-C_4 complexes

As is the case with *cyclo*-C_3 compounds discussed in Section 5.06.3.1.4.(i), synthesis and reactivity studies of cyclobutadiene molybdenum carbonyl compounds are scarce. Only one further example of the reactivity of $[Mo(CO)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)]$ with Me_3NO to give **236** has been reported. This reacts with trimethylphosphine to produce **237** or with diphenylacetylene to produce the sandwich compound $[Mo(C_5Ph_5)_2]$ and **238** (Scheme 26).[810]

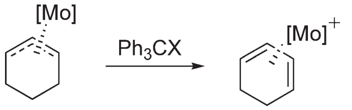
5.06.3.1.6.(ii) η^4-diene ligands

Synthesis. An alternative, high-yielding synthesis for compounds of the type $[CpMo(\eta^4\text{-diene})(CO)_2Br]$ by hydride abstraction from $[CpMo(\eta^3\text{-allyl})(CO)_2]$ using trityl halides, in the presence of hexafluoroisopropanol has been reported.[811,812] It is especially useful for the formation of cyclohexadiene substituents (Equation (72)). Extension of this work to prochiral allyl functions has also been reported, although the enantiomeric excess was modest (~10% ee).[813] The irradiation of $[(CpMo(CO)_2)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-acetylene})]$ in ethylene forms (η^4-butadiene)tricarbonylbis(η^5-cyclopentadienyl)dimolybdenum as well as other products (Equation (73)).[814] Protonation reactions of $[Cp'Mo(CO)_2(\eta^3\text{-allyl})]$ (Cp′ = Cp, Cp*, Ind) in the presence of a variety of cyclic and acyclic dienes give rise to $[Cp'Mo(CO)_2(\eta^4\text{-diene})]^+$ in very good yields (Equation (74)),[815] and the corresponding indenyl complexes can also be prepared.[760] This can also be extended to nucleophilic addition of a hydride ligand to complexes of the type $[Cp_2MoL_2]^{2+}$ (Cp = Cp, Ind; L = 1/2-dppe, PMe_3) to form the compounds $[CpMo(\eta^4\text{-diene})\ (L_2)]^+$ via regioselective attack on the *exo*-face of the Cp ring to



Scheme 26

form the *endo*-isomer. This was conclusively proved from detailed examination of ^{1}H NMR spectra and a crystal structure determination (for L = dppe). Notably, this reaction is reversible and a further equivalent of H^- forms the η^3-allyl-bonded complex. Addition of softer C-, P-, and S-based nucleophiles gives similar reactivity.[816] A further synthetic pathway is by treatment of [Cp*Mo(CO)$_2$(MeCN)$_2$][BF$_4$] with butadienes, as exemplified in Equation (75) by the isolation and further reactivity studies of [Cp*Mo(CO)$_2${η^4-*syn*-s-*cis*-CH$_2$CHCHCH(OAc)}][BF$_4$], **239**.[817] [(Ind)Mo(CO)$_2$] complexes of 1,3-dienes, including spirocyclopentadienes, can be synthesized from 1,3-dienes and [(Ind)Mo(CO)$_2$(NCMe)$_2$][BF$_4$].[818] Tetracarbonyl-η^4-S-*cis*-diene-μ-η^5:η^5-fulvalene-dimolybdenum complexes can be readily formed by photolysis of μ-η^5 : η^5-fulvalene-dimolybdenum with a variety of substituted butadiene ligands.[819] The synthesis of bimetallic "flyover" η^4-diene complexes via a coupling reaction of [CpMo(PhC≡CR)$_2$Cl] (R = Me, Ph) with Co$_2$(CO)$_8$ **240** or Fe$_2$(CO)$_9$ **241** has also been reported (Equation (76)).[820]



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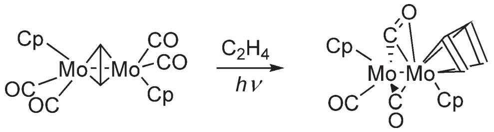

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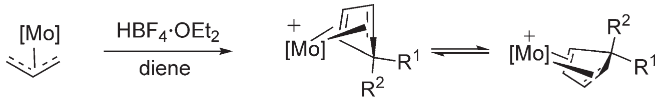

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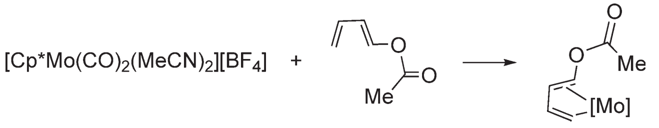

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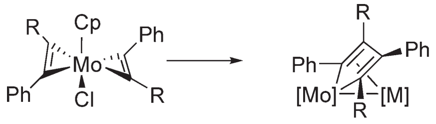


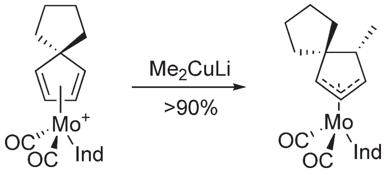
(76)

[Mo] = CpMo(CO)$_2$; [M] = Co(CO)$_2$ **240**, Fe(CO)$_3$ **241**

Properties. The simple complexes [Mo(CO)$_4$(η^4-1,3-butadiene)] and [Mo(CO)$_4$(η^4-1,3-cyclohexadiene)] have been studied by VT NMR spectroscopy and shown to display hindered ligand movements with activation energies of 40–50 kJ mol^{-1}.[821] The structural preferences for a series of [CpMo(η^4-diene)LL]$^+$ have been studied theoretically and experimentally. It was found that all examples known in the literature that have been structurally characterized exhibit an *endo*-conformation of the diene. This form is the preferred one both on steric and on electronic grounds, as ascertained by calculations.[822] The existence of *endo*- and *exo*-isomers of cyclic dienes has been established by variable-temperature NMR spectroscopy.[815] The 19-electron complex **241** is unusual in that it is paramagnetic, with the unpaired electron occupying a delocalized orbital with significant CO π^* contribution.[820] Both examples of "flyover" species can be viewed as an MC$_4$ sandwich π-bound to a second metal, which enhances the transfer of electron density within the C$_4$ fragment in comparison to mononuclear MC$_4$ species. [CpMo(η^4-diene)(L)]$^+$ and their C$_6$ ring congeners [CpMo(η^4-C$_6$H$_8$)(CO)$_2$]$^+$ and [CpMo(η^3-C$_6$H$_9$)(CO)$_2$] have been studied electrochemically, and show irreversible reductions. These species have also been the subject of theoretical studies.[816]

Reactivity. The complexes [Cp′Mo(CO)$_2$(η^4-diene)]$^+$ show very rich reactivity (Scheme 27). For example, mixed ring CpMoCp′ compounds can be synthesized readily, ring-slippage reactions of indenyl and C$_5$H$_4$Me has been investigated, deprotonation of [CpM(η^4-C$_5$Me$_5$H)(CO)$_2$][BF$_4$] to give the allylic complexes [CpM{η^3-C$_5$(CH$_3$)$_4$H(CH$_2$)}(CO)$_2$] (M = Mo, W).[815] Deprotonation of [Cp′Mo(CO)$_2$(η^4-diene)][BF$_4$] (Cp′ = Cp, Ind) occurs at CH$_3$ in a terminal position of the diene ligand to yield the corresponding allyl complex, which has proved to be a more convenient synthesis for [Cp′Mo(CO)$_2$(η^3-C$_6$H$_7$)].[760] [CpMo(CO)$_2$(η^3-C$_6$H$_7$R)][BF$_4$] (R = H, Me, Ph) can also be readily functionalized by electrophilic attack of aldehydes to give isolable examples of cationic η^4-dienes which, after demetallation, functionalized cyclohexadiene compounds can be formed in good yields.[823]

Compound **239** also exhibits varied reactivity, mainly via formation of the η^3-allyl substituted complex, where the Mo center is further coordinated by the aldehyde moiety.[817] Nucleophilic addition of lithium dimethylcuprate to the complexed *spiro*-diene in [(Ind)Mo(CO)$_2$(diene)][BF$_4$] gives the expected η^3-allylmolybdenum complexes in high yield, and this has applications to organic synthesis (Equation (77)).[818] Further cuprate reagents have also been used to afford functionalization at the C4 position.[824,825]



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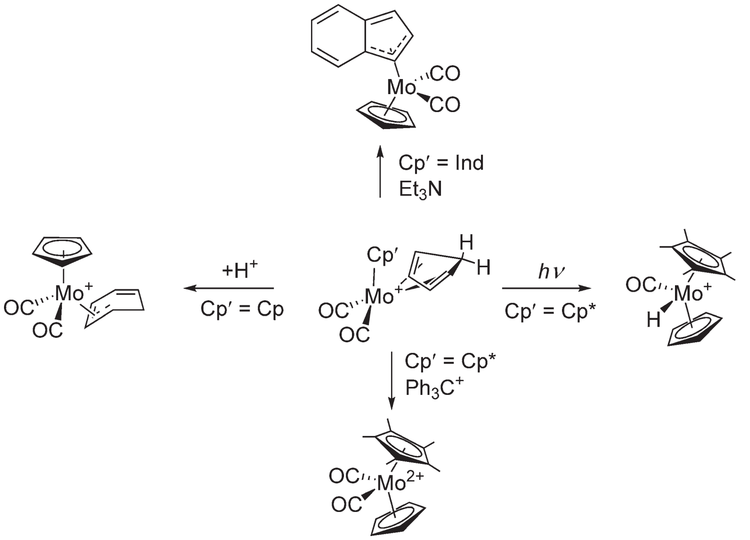
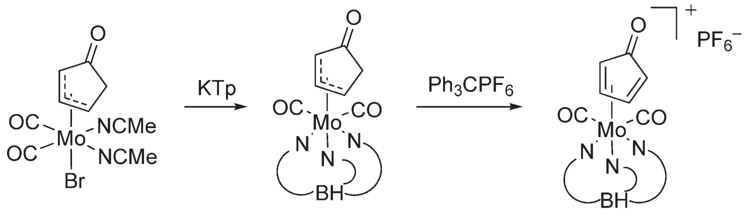


Scheme 27

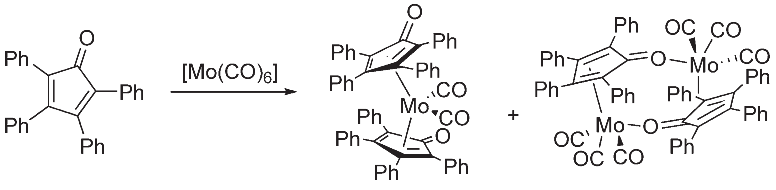
5.06.3.1.6.(iii) η^4-cyclopentadienones

Synthesis. The reaction of $[Mo(CO)_3(NCMe)_3]$ with bromo-cyclopentenone yields the η^3-cyclopentenoyl complex **242** which on treatment with either Tp, bipy or dppm gives the neutral η^3-compounds **243**. Hydride abstraction with trityl salts affords the cationic η^4-cyclopentadienone compounds **244** in good yields (Equation (78)).[826] Reaction of the much bulkier tetraphenylcyclopentadienone with $[Mo(CO)_6]$ or $[Mo(CO)_3(NCMe)_3]$ gives the η^4-diene complex **245** and also small amounts of the dimeric $[\{Mo(CO)_3(\sigma{:}\eta^4\text{-}C_4Ph_4CO)\}_2]_2$ complex **246** which has been structurally characterized (Equation (79)).[827]



242 **243** **244**

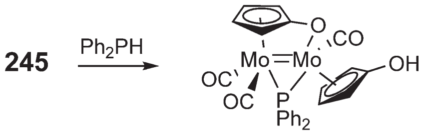
(78)



245 **246**

(79)

Properties and reactivity. Structure **242** has been structurally characterized and shows metric parameters that are typical for η^3-allyl derivatives. Moreover, the only isomer is *exo* to the allyl group.[826] The electrophilic η^4-cyclopentadienone ligand in **244** reacts cleanly with a variety of nucleophilic reagents to give functionalized η^3-cyclopentenoyl complexes in high yield and *anti* to the coordinated metal and exclusively α to the ketonic functional group. Strongly basic nucleophiles deprotonated the methyl group of the analogous complex $[TpMo(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)\ (CO)_2]$ to afford $[TpMo(\eta^3\text{-}C_5H_3OCH_2^-)(CO)_2]$; this process is reversible. Several of the products were structurally characterized.[828] Compound **245** undergoes substitution chemistry to give $[Mo(CO)_nL(\eta^4\text{-diene})]$ ($L = PR_3$, NCMe; $n = 3$; $L =$ dppe, $n = 2$) and unusually, upon treatment with Ph_2PH the dimeric Mo═Mo species $[Mo_2(CO)_3(\mu\text{-}PPh_2)(\mu\text{-}\sigma{:}\eta^5\text{-}C_4Ph_4CO)(\eta^5\text{-}C_4Ph_4COH)]$, **247**, via an oxidative addition of the P–H function and subsequent protonation of one cyclopentadienone ligand (Equation (80)).[827]

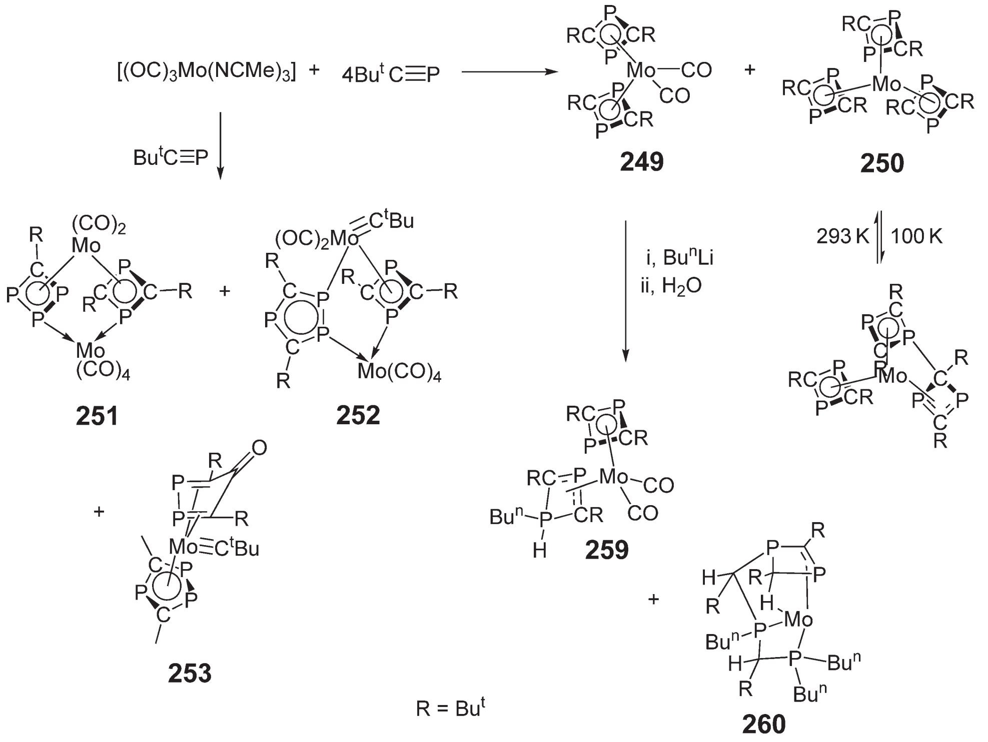


247

(80)

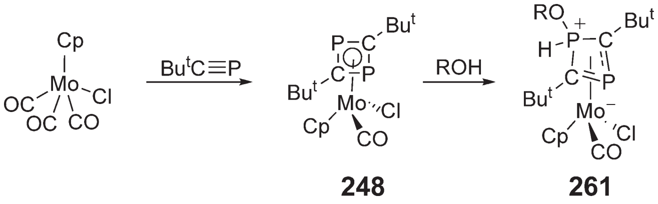
5.06.3.1.7 Heteroatom-substituted η^4-ligands

Synthesis. Cyclodimerization reactions of phosphaalkynes on a variety of molybdenum templates have been studied in order to compare its reactivity with alkynes. What is obvious from these studies is that the products obtained are dependent upon the reaction conditions and metal template used, no doubt due to the high reactivity of the phosphaalkyne. Also of note is that $^tBuC{\equiv}P$ behaves differently to the reactivity of alkynes. Thus, reaction of $^tBuC{\equiv}P$ with $[Cp'Mo(CO)_3Cl]$ ($Cp' = Cp$, Cp^*) affords the diphosphacyclobutadiene complex **248** in good yield (Equation (81)).[829,830] Reacting 4 equiv. of $^tBuC{\equiv}P$ with $[Mo(CO)_3(MeCN)_3]$ affords the bis(diphosphabutadiene) complex **249**, along with homoleptic **250**.[831] With an excess of phosphaalkyne three different compounds **251**–**253** have been isolated; interestingly, **253** must have been formed by CO insertion during cyclodimerization (Scheme 28).[832] $[(cht)Mo(CO)_3]$ also gives complex **251** in addition to the cyclotrimerization product **254** (Equation (82)). Using the cationic $[IndMo(CO)_2(MeCN)_2][BF_4]$ and an excess of $^tBuC{\equiv}P$, a four-membered ring



Scheme 28

is again formed in **255**; however in this case, X-ray crystallographic analysis shows that the bonding is best described as an η^3-phosphaallyl system. In solution, the authors postulate that the P_2C_2 ring could be π-bound in an η^4-fashion (Equation (83)).[833] The cyclodimerization reaction of ${}^tBuC{\equiv}P$ can also be carried out in the presence of alkynes to afford an inclusion product **256** (Equation (84)).[834]



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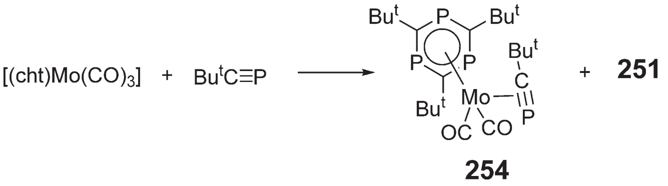

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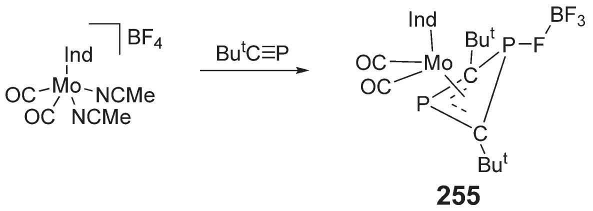

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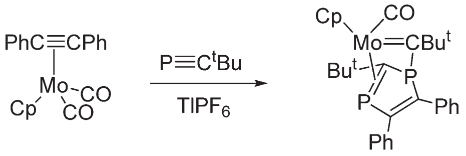
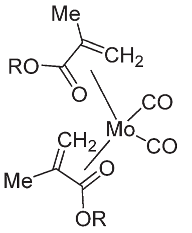


256

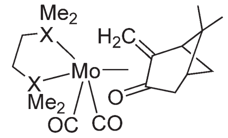
(84)

1-Oxa-1,3-dienes show an η^4-bonding mode when coordinated to molybdenum, as shown by the synthesis of **257**. However, the ligand is very labile and easily displaced by coordinating solvents.[835] Compounds featuring only one oxadiene ligand, for example, **258**, are more stable.[836] A theoretical study has also been presented, and the results agree with published experimental data.[837] Some work has also been published on the analogous 1,3-azadiene ligands.[838]



R = Me, Et

257



X = N, P

258

Properties and reactivity. The diphosphabutadiene complex **248** has been structurally characterized and confirms the π-bound η^4-heterocyclic nature of the ligand.[830] DFT calculations on the bonding and properties of **249** and **250** suggest that along with the inherent nucleophilicity, the diphosphacyclobutadiene ligands also show electrophilic character. This has been shown by the reactivity of **249** with Bu^{n}Li followed by quenching with water to form two products, **259** and **260** (Scheme 28). In these compounds, the bonding situation is difficult to rationalize, but shows that the amphiphilicity of the diphosphabutadiene ligand can lead to interesting phosphorus heterocycles, and no doubt, this work will be expanded and rationalized. An additional point of interest is the observation of a topotatic reaction of the homoleptic complex **250**, which is the first example of a reversible chemical reaction in which single crystals are conserved (Scheme 28).[831] Facile oxidation of one P(III) center in **248** to P(V) by water or methanol in the formation of [CpMoCl(CO){$\eta^3,\lambda^3,\lambda^5$-PC$_2Bu^t{}_2$PH(OR)}], **261** (R = H, Me), has been reported (Equation (81)).[829]

5.06.3.1.8 Carbon-based η^5-ligands

5.06.3.1.8.(i) General remarks

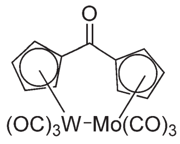
The chemistry of anionic η^5-ligands has been well studied over the past decade, and to follow on from COMC (1995),[839] coverage is from 1995 to 2004. The majority of synthetic and spectroscopic studies have focused primarily on $[CpMo(CO)_3]_2$ which will be discussed first. Reactivity of this and $[CpMo(CO)_2]_2$ to form the fragments $[CpMo(CO)_nL]$, where L is subdivided by periodic group, will be subsequently treated. The photochemistry of linked and unlinked Cp type complexes has been reviewed.[840] Some aspects of the chemistry of binuclear complexes containing the fulvalene ligand have also been reviewed.[125] Synthetic[841] and electrochemical[842] comparisons between Cp and fulvalene ligands in the complexes $[L_2Mo_2(CO)_6]$ have also been reported. In general, the reactivity of indenyl complexes is somewhat similar to that of the Cp derivatives. However, the major difference is the greater ability of the indenyl ligand to ring-slip ($\eta^5 \rightarrow \eta^3$), that is, the indenyl effect. Theoretical calculations[843,844] have been used to probe this effect and numerous experimental studies have been presented.[845–850] Examples of isolated η^3-complexes of indenyl ligands are collated in Section 5.06.3.1.4.(iii).

5.06.3.1.8.(ii) $[CpMo(CO)_3]_2$

Synthesis. Since the publication of COMC II (1995),[839] compounds of this type have been the subject of synthetic investigations, and a number of substituted Cp ligands have been reported using established synthetic methodologies. The synthetic procedures generally involve treatment of $[Mo(CO)_6]$, or analogues with labile ligands, for example, $[Mo(CO)_5(THF)]$, with the required cyclopentadiene or the cyclopentadienyl anion followed by oxidation with, for example, Fe(III) salts. A new method for making $[CpMo(CO)_3]_2$ in a microwave oven has been reported to give yields of >90%.[64] For further discussions, see Ref: 840. A series of linked Cp compounds has also been synthesized and some examples are given in Table 12. Side-reactions leading to de-silylated products are sometimes obtained. Heterobimetallic complexes can also be synthesized, generally starting from the monomeric carbonyl compound with an appropriate Cp ligand. For example, **262**,[851] or **263**[852] have been reported. Unbridged CpMo–RuCp examples have also been synthesized by the reaction of $Na[CpMo(CO)_3]$ with the required ruthenium halide compounds (Equation (85)).[853]

$$Na[CpMo(CO)_3] + [CpRu(CO)_2X] \longrightarrow [Cp(OC)_3Mo\text{–}Ru(CO)_2Cp] \qquad (85)$$

Properties. The doubly bridged Cp complex **264** has been structurally characterized, for example, where $X = CMe_2$, CH_2, and $Y = SiMe_2$ or $X = CMe_2$ and $Y = SiPh_2$. They show significantly elongated Mo–Mo bonds, probably due to the rigid ligand creating unfavorable steric interactions between the carbonyl groups on the two metal centers, and there is an identifiable trend between the metal–metal distances and the centroid–M–M–centroid torsion angle.[854] Studies on the dynamic NMR spectra of **266** have also been reported,[856] and intermetal carbonyl exchange has been observed by ^{13}C NMR spectroscopy in $[CpMo(CO)_3]_2$ and $[Cp_2MoW(CO)_6]$. The mechanism of exchange has been shown to be the same as postulated for $[Cp_2Mo_2(CO)_5(CNMe)]$, and is surprisingly facile with $\Delta G^{\ddagger} = 58.1 \pm 0.8\,kJ\,mol^{-1}$ for the *gauche* isomer and $\Delta G^{\ddagger} = 62.3 \pm 0.8\,kJ\,mol^{-1}$ for the *trans*-isomer (with respect to the Cp ligands) of $[Cp_2Mo_2(CO)_6]$. Rotation around the Mo–Mo bond was found to be a higher energy process with $\Delta G^{\ddagger}{}_{278} = 64.0 \pm 0.8\,kcal\ mol^{-1}$ for the *trans*- to *gauche*-isomerization and $\Delta G^{\ddagger}{}_{278} = 68.8 \pm 0.8\,kJ\,mol^{-1}$ for *gauche*- to *trans*-isomerization.[859] Using the same techniques, CO exchange in the isomers of $[Cp_2Mo_2(CO)_5(CNMe)]$ has also been measured and shown to go via a merry-go-round mechanism and the activation parameters calculated.[860] Vollhardt and co-workers have used the tercyclopentadienyl system **268** to investigate fundamental steps in organometallic displacement reactions and the bond strengths in a series of M–M compounds (Equation (86)). The advantage of this metallomeric equilibrium allows kinetic and thermodynamic data to be obtained on otherwise intractable systems.[861]



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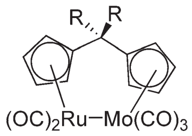
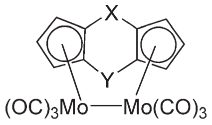


R = H, Me

263



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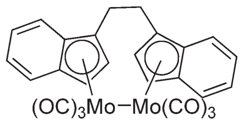

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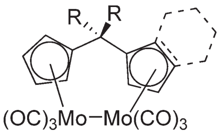
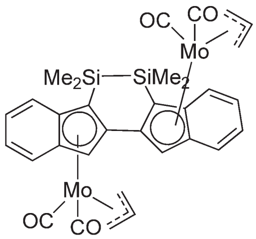


R = H, Me

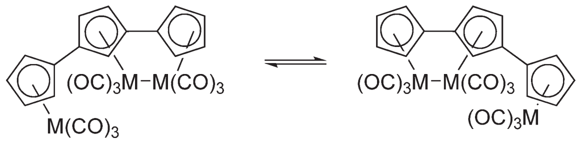
266



267

Table 12 Synthesis of representative examples of bridged Cp compounds

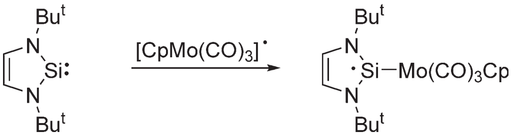
Complex	*Comments*	*References*
264	Mo–Mo = 3.4328(12) Å	854
265	*rac-mer* isomerization	855
266	Mo–Mo = 3.149(1) Å	856
$[(CpCH_2CH_2NMeC(O)(CH_2)_nCH_3)_2Mo_2(CO)_6]$	$n = 3, 8, 18$	857
267	*anti-facial* isomer only	858



268 **268**

(86)

Photolysis of $[\mathrm{CpMo(CO)_3}]_2$ species results in cleavage of the Mo–Mo bond to form short lived 17-electron $[\mathrm{CpMo(CO)_3}]^{\cdot}$ radicals. Time-resolved infrared spectroscopy has been used to study the recombination of photogenerated radicals. The second-order rate constant was found to be $(3 \pm 1) \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$.[862] TRIR spectroscopy has also been used to study $[(\mathrm{Bu^tCp})\mathrm{Mo(CO)_3}]^{\cdot}$ radicals in a variety of solvents (heptane, THF, $\mathrm{Xe_{(l)}}$, $\mathrm{CO_{2(l)}}$) and in this case the second-order rate constants are $(7.9 \pm 0.5) \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$ in Xe; $(3.2 \pm 0.5) \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$ in heptane; $(2.2 \pm 0.8) \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$ in THF; and $(1.7 \pm 0.5) \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$ in $\mathrm{CO_2}$, the anomalously low value for $\mathrm{CO_2}$ is due to the formation of a transient Mo radical–$\mathrm{CO_2}$ complex,[863] which has been the subject of further study.[864] A new method used to characterize these transient species is the electrochemical-based photomodulated voltammetry, and the results agree with previous literature estimates.[865] The reactions of 17-electron species have also been studied with halides and pseudohalides via an atom-transfer mechanism.[866] Of particular note to this discussion is the isolation of thermally stable 17-electron radical species by using the Tp ligand, which is discussed in Section 5.06.2.4.2.(i). The reactivity of these short-lived intermediates has been examined and a detailed account is given in Ref: 840. Rate laws for the hydride abstraction of H by primary, secondary, and tertiary alkyl radicals in $[\mathrm{CpMo(CO)_3H}]$ ($\mathrm{Cp} = \mathrm{Cp}$, $\mathrm{Cp^*}$) have been established.[867] Reaction with the N-heterocyclic silylene gives silicon-centered radicals (Equation (87)).[868]



(87)

5.06.3.1.8.(iii) Reactivity of the $[\mathrm{CpMo(CO)}_n\mathrm{L}]$ fragment

5.06.3.1.8.(iii).(a) $\mathrm{CpMo(CO)_3H}$

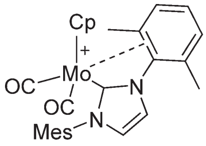
It has long been known that quenching the ionic compounds $[\mathrm{CpMo(CO)_3}]^-$ with acidic substrates affords the respective hydride complexes, and this has been thoroughly covered in COMC I (1982)[672] and COMC II (1995).[839] Further work has mainly concentrated on derivatives of the Cp ligand. One interesting development is the photochemical reaction of dihydrogen with $[\mathrm{CpM(CO)_3}]_2$ ($\mathrm{M} = \mathrm{Mo}$ or W) to give the corresponding metal hydrides, $[\mathrm{CpM(CO)_3H}]$. It was found that hydride formation is only significant when the photolysis wavelengths are in the high-energy regions known to trigger CO loss, and hydride formation is suppressed by adding CO, making it likely that the reaction involves an oxidative addition of $\mathrm{H_2}$ to an electron-deficient, CO-loss intermediate.[869] $[\mathrm{CpMo(CO)_3H}]$ has been studied with microwave spectroscopy, and in conjunction with DFT calculations the Mo–H bond length has been calculated at 1.80(1) Å, in good agreement with structural studies on similar compounds.[870] Oxidation of $[\mathrm{CpMo(CO)_2(PR_3)H}]$ ($\mathrm{R} = \mathrm{Ph}$, Me) with $[\mathrm{Cp_2Fe}]^+$ salts has been investigated,[871] and a series of papers detailing the kinetics of hydride transfer between $[\mathrm{CpMo(CO)_2LH}]$ and trityl salts[872–875] or BzNADH[876] has been published, whilst $[\mathrm{CpMo(CO)_2(PPh_3)H}]$ has been used as a hydride-transfer reagent in the ionic hydrogenation of ketones.[877] These studies have culminated in the use of $[\mathrm{CpMo(CO)_2(PR_3)H}]$ being used as a catalyst for hydrogenation of ketones,[878–881] and expanded to solvent-free catalysis.[882]

5.06.3.1.8.(iii).(b) $\mathrm{CpMo(CO)}_n$ fragment with σ-donor/π-acceptor carbon ligands

Molybdenum-carbon single bonds – synthesis. Molybdenum alkyl complexes are well studied, especially in the formation of $[\mathrm{CpMo(CO)_3Me}]$ via quenching of the corresponding anionic species with MeI. This has been treated in COMC (1982)[672] and COMC II (1995),[839] and a few further developments have been reported recently; these are included in Table 13. All complexes have been made by the reaction of the appropriate $[\mathrm{CpMo(CO)_3}]^-$ anion with alkyl halides. Also included in this section are N-heterocyclic carbene complexes as they are widely believed to be pure σ-donor ligands. The complex $[\mathrm{CpMo(CO)_2(IMes)}][\mathrm{B(C_6F_5)_4}]^-$, **269**, has been reported and unusually one C═C bond of the mesityl substituents has been shown by synchrotron X-ray diffraction methods to be weakly bonded to the molybdenum.[883] A similar weak C═C bonding has also been observed in $[\mathrm{CpMo(CO)_2(PPh_3)}][\mathrm{B(ArF)_4}]$, **270**.[884] Structure **269** is an active catalysts for hydrogenation and hydrosilylation of aldehydes and ketones.[885] σ-Bonded alkynyl complexes have been reviewed.[123,124]

Table 13 Representative examples of [CpMo(CO)$_3$R]

Complex	*Comments*	*References*
[(EtO)$_3$SiC$_3$H$_6$Mo(CO)$_3$Cp]		886
[Cp*Re(CO)(NO)CO$_2$CH$_2$CH$_2$Mo(CO)$_3$Cp]		887
[*o*-C$_6$H$_4$(CH$_2$Mo(CO)$_3$Cp)$_2$]	Structure for Cp = C$_5$H$_4$Me	888
[*p*-C$_6$H$_4$(CH$_2$Mo(CO)$_3$Cp)$_2$]	Stable to air, water, dilute acids and bases	889
[Cp(CO)$_2$(PPh$_m$Me$_{3-m}$)Mo{(CH$_2$)$_n$X}]	Cp = Cp*, Cp; X = Br, I, n = 3, 4; m = 1, 2	890
[Cp(CO)$_3$W(CH$_2$)$_n$Mo(CO)$_3$Cp]	Cp = Cp*, Cp; n = 3, 4	891
[CpMo(CO)$_3$(CH$_2$CO$_2$NS)]	NS = N-succinimidyl	892
[CpMo(CO)$_3$(C$_2$H$_4$Phth)]	Phth = Phthalimide; X-ray structure	893



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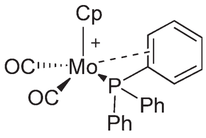
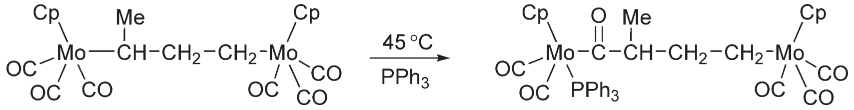


270

Properties of molybdenum-carbon single bonds. Vibrational spectra for partially deuterated isotopomers of [CpM(CO)$_3$Et] (M = Mo or W) have been recorded. The isolated CH stretching frequencies of the CHD$_2$CD$_2$M isotopomers show that the terminal Me groups in all compounds studied have one weak and two stronger C–H bonds which indicate differences of $\sim$0.005 Å in bond length, or 20 kJ mol^{-1} in bond-dissociation energy, between the weaker and stronger C–H bonds. The metal atom substituents weaken all three β-C–H bonds, the *gauche*- bonds and the *trans*-bonds by $\leq$25 kJ mol^{-1}. These bonds are amongst the weakest yet identified in nonagostic alkyltransition-metal compounds.[894]

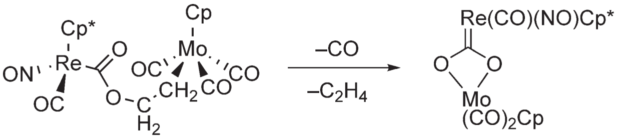
Reactivity of molybdenum–carbon single bonds. Some important results concerning alkyl migration have been forthcoming. Interest in rhodium-catalyzed hydroformylation to give linear or branched products has prompted investigations into the alkyl migration reactions of homodinuclear complexes with one branched alkyl chain and a linear metal terminus. Following standard synthetic procedures, complexes of the type [CpM(CO)$_n${CH(CH$_3$)CH$_2$CH$_2$}-M(CO)$_n$Cp] (M = Mo, n = 3; M = Fe, n = 2) could be isolated and on addition of PPh$_3$ alkyl migration onto a carbonyl ligand occurred. It was found that the branched chains reacted preferentially to the linear terminus, and the authors rationalize this behavior on the conflicting steric and electronic effects in alkyl migration reactions (Equation (88)).[895]



(88)

Uniquely, it has been found that alkyl migration reactions can also be studied in the solid state. Thus, the reaction of [CpMo(CO)$_3$Me)] with PPh$_3$ at a variety of temperatures affords the acyl complex [CpMo(CO)$_2$(η^2-COMe)(PPh$_3$)], and the decarbonylation product [CpMo(CO)$_2$(PPh$_3$)Me)] has also been observed at higher temperatures. A kinetic study suggests that the reaction is pseudo-first-order with k = 5.18 × 10^{-5} s^{-1} (in toluene solutions k = 0.8–2.5 × 10^{-5} s^{-1}, under similar temperatures and reactant ratios).[896] This type of migration has been studied using DRIFTS and optical miscroscopy and shown to follow pseudo-first-order kinetics, both in the solid state and in the melt.[897]

Thermolysis of metal alkyl complexes is of interest as further products can be isolated. For example, **271** rearranges to form the CO$_2$-bridged compound **272** as the major product (Equation (89)).[887] The Cp analog has been additionally characterized by DRIFTS spectroscopy.[898]



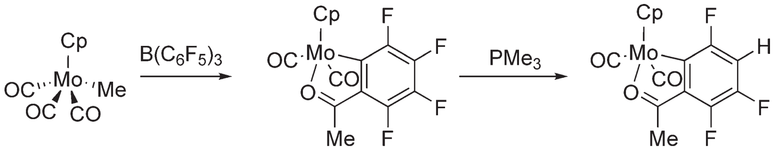
(89)

271 **272**

Examples of transition metal complexes with long-chain alkyl groups are relatively rare, but can be synthesized by the now common procedures. Thus, **273** can be prepared and its reactivity explored.[890] Reaction with NaI affords good yields of **274** and heterobimetallic species **275** can be synthesized via salt elimination (Scheme 29).[891]

Whilst transition metal alkyls are an important part of some catalysts (e.g., group 4 olefin polymerization catalysts), few catalytic applications are known for Mo alkyls. Carbonyl complexes of formula [Cp′M(CO)$_3$R] (Cp′ = Cp, Cp*, M = Mo, W; R = various alkyls) activated by *tert*-butyl hydroperoxide have been applied as very active and selective olefin epoxidation catalysts. It was found that Mo complexes were more active than the analogous tungsten compounds and increasing alkylation of the Cp ligand lowered the catalytic activity.[899]

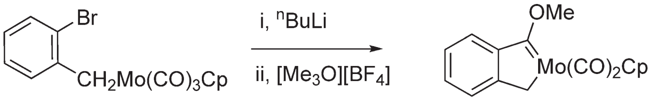
A very unusual reaction has been observed upon treatment of [CpMo(CO)$_3$Me] with the strong Lewis acid [B(C$_6$F$_5$)$_3$]. Complex **276** was isolated and thought to occur via an insertion of tetrafluorobenzyne into the Mo–C acyl bond. Further reactivity with PMe$_3$ affords **277**, which is formed via a highly unusual and specific C–F bond activation (Equation (90)).[900]



276 **277**

(90)

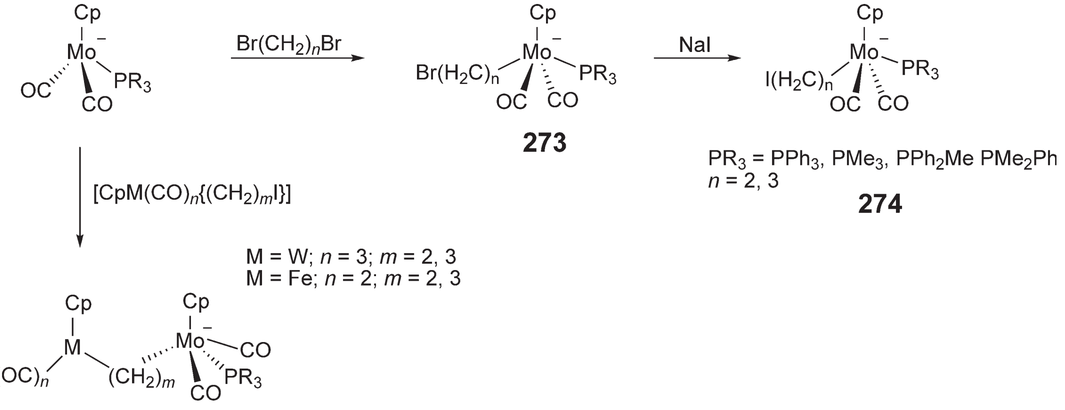
Molybdenum–carbon double bonds. The reviews cited in Section 5.06.1.6.2 are also relevant to this discussion. However, there are fewer Fischer carbene examples with Cp as an ancillary ligand. Reaction of (2-bromobenzyl) σ-complex **278** with Bu^{n}Li and [Me$_3$O][BF$_4$] forms the first example of a stable metallaindene, **279** (Equation (91)).[901] These species undergo fluxional behavior in solution and the authors postulate a pseudo-rotation mechanism to explain the observed dynamic behavior. Notably, these complexes are stable to carbene migratory insertion reactions.



278 **279**

(91)

Cyclic amino-carbenes have been synthesized via an alkyl migration to a coordinated isocyanide. Thus, treatment of [CpMo(CO)$_2$(CNMe)]$^-$ with iodooxiranes gives either the expected carbene complex, **280**, or complex **281** which displays a coordinated pyran moiety (Scheme 30).[902] Dihaloalkanes also react with [CpMo(CO)$_3$]$^-$ to form cyclic carbenes.[903,904] Chiral-at-metal carbene complexes **283** have also been prepared via reaction of complex **282** with furfurylamine followed by alkylation of the amine with MeI or BzBr (Equation (92)). This exists as diastereoisomers (Scheme 31), which have been characterized on the basis of a detailed NMR study. Heating these compounds affords the Diels–Alder products **284**, as diastereoisomers (Equation (92)).[905]

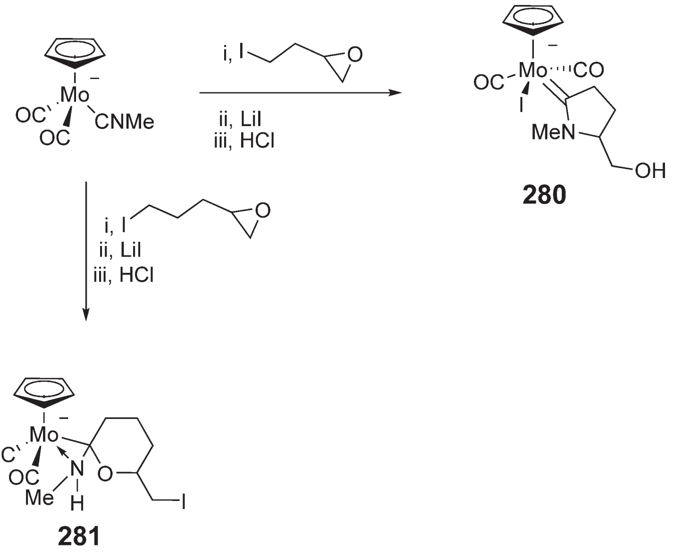


273

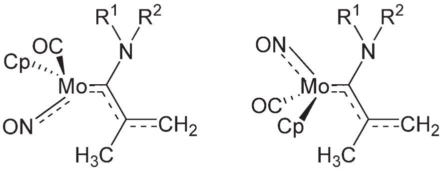
274

275

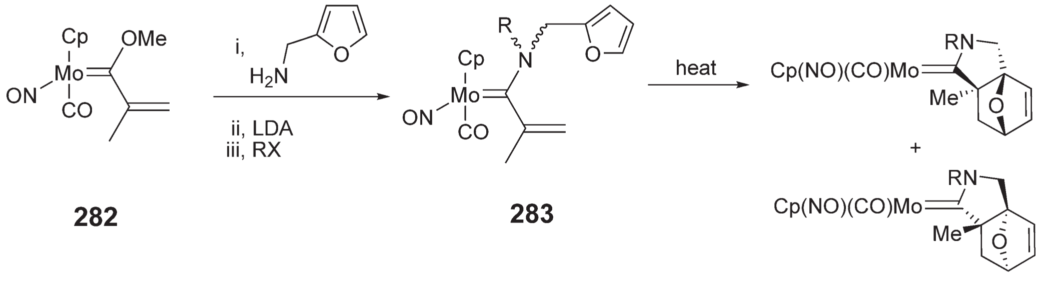
Scheme 29



Scheme 30

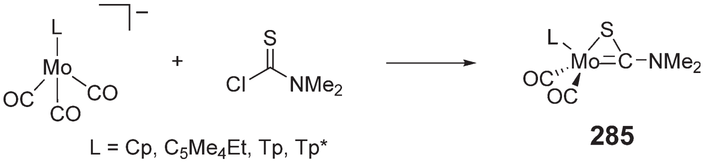


Scheme 31



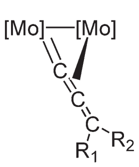
282 **283** **284** (92)

Some thiocarbene complexes have also been reported. For example, reaction of $[LMo(CO)_3]^-$ with $Me_2NC(S)Cl$ affords an η^2-dimethylamino(thio)carbene complex 285, which has been structurally characterized for L = Tp (Equation (93)).[291] A thiocarbene $[Cp(Ph_3Sn)(CO)_2Mo{=}C(SAr)Ph]$ (Ar = Ph, Tol) has been prepared by reaction of the unstable $[Cp(Ph_3Sn)(CO)_2Mo{=}C(OCOMe)Ph]$. Notably, this complex cannot be synthesized by conventional thiolysis methods.[906] η^2-phosphinocarbene complexes have also been prepared.[907]



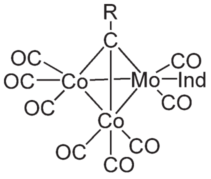
285 (93)

Metallacumulene and molybdenum alkylidynes. Metallacumulene complexes have been the subject of much study, and the comments and reviews cited in Section 5.06.1.6.3 apply here. Molybdenum allenylidene complexes are quite rare, being limited to work published by Kergoat and co-workers. The reaction of a lithium acetylide with $[\{CpMo(CO)_2\}_2(\mu\text{-}\eta^2:\eta^3\text{-}HC{\equiv}CCR^1R^2)][BF_4]$ (R, $R^1 = H$, Me, Et, Cy, Ph) affords **286** via abstraction of the acetylenic proton. When $R^1 = Me$ or Et, the complexes exist as diastereoisomers, but for larger substituents only one isomer is formed. Systematic NMR investigations and a crystal structure for $CR^1R^2 = Cy$ have been used to characterize these complexes.[908] Reactivity and theoretical studies suggest that electrophilic attack is under charge control, whilst nucleophilic attack is under orbital control.[909] Heterometallic compounds with $R^1 = Fc$ have also been reported.[910] Examples of carbyne (μ_3-CR) and carbide ligands bridging in **287**[850] and **288**[911] have been prepared. $Mo{\equiv}C$ species with ancillary Cp ligands are also well represented and covered in the reviews cited in Section 5.06.1.6.4.



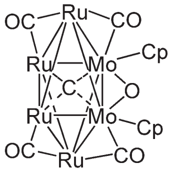
[Mo] = $CpMo(CO)_2$

286



R = H, Me, CO_2Et

287



Ru = $Ru(CO)_2$

288

5.06.3.1.8.(iii).(c) Group 1 and 2 metal complexes

Alkali metal salts of $[CpMo(CO)_3]^-$ are well-known compounds and are one of the main precursors in organomolybdenum chemistry. Whilst the synthetic methods are well documented, few further studies have been carried out. There is only one example of a new Mo–group 2 complex reported since 1994. The reaction of the beryllium complex ArBeCl (Ar = terphenyl ligand) with $Na[CpMo(CO)_3]$ gives rise to a unique example of a beryllium isocarbonyl structure, $[Ar(THF)_2Be(\mu\text{-}OC)Mo(CO)_2Cp]$,[912] in contrast to reactivity with ArGeCl which forms multiply bonded Mo–Ge complexes. The beryllium compound has been structurally characterized and shows structural and spectroscopic features consistent with isocarbonyl linkages.[913]

5.06.3.1.8.(iii).(d) Transition metal complexes of $CpMo(CO)_n$ fragment

Early transition metals, lanthanides and actinides. Few examples of group 4 complexes have been reported during the past decade. $[Cp(CO)_3Mo\text{–}Ti(O^tBu)_3]$ has been prepared by salt metathesis and spectroscopically characterized (Equation (94)).[914] There are no further examples of group 5 metal complexes. Some lanthanide metal compounds have been forthcoming but these involve isocarbonyl linkages (Equations (95)–(97)).[915–917] No examples of actinide molybdenum compounds have been reported.

$$({}^tBuO)_3TiCl + K[CpMo(CO)_3] \longrightarrow [({}^tBuO)_3Ti\text{–}Mo(CO)_3Cp] \tag{94}$$

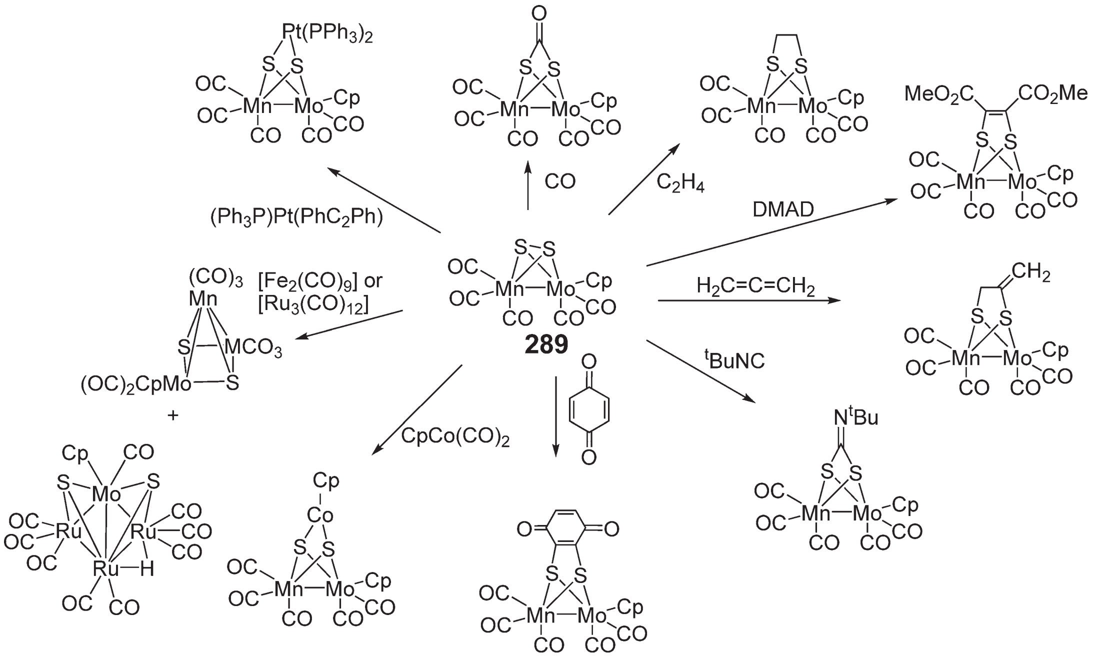
$$SmI_2(THF)_4 + [CpMo(CO)_3]_2Hg \longrightarrow [(THF)_4I_2Sm(\mu\text{-}OC)Mo(CO)_2Cp] \tag{95}$$

$$[Tp_2Sm] + [CpMo(CO)_3]_2 \longrightarrow [Tp_2Sm(\mu\text{-}OC)Mo(CO)_2Cp] \tag{96}$$

$$[TpLnI] + Na[CpMo(CO)_3] \longrightarrow \underset{(Ln = Sm,\ Yb)}{[TpLn(THF)(\mu\text{-}OC)_2Mo(CO)_3Cp]_2} \tag{97}$$

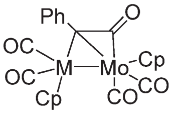
Group 7-10 metals. There are many examples of molybdenum compounds containing metals from groups 7 to 10, either with direct M–M bonds or bridged by other ligands: a review article concerning this topic has been published.[918] An account of metal clusters is outside the scope of this chapter. The chemistry of Mo–Mn species is dominated by reactivity studies of **289** (Scheme 32).

This complex has been synthesized by the reaction of $[Mn_2(CO)_7(\mu\text{-}S_2)]$ with $[CpMo(CO)_3]_2$ and a byproduct $[CpMoMn_3(CO)_{13}(\mu_3\text{-}S)(\mu_4\text{-}S)]$ was also isolated.[919] $[CpMoMn(CO)_5(\mu\text{-}S_2)]$ reacts with alkenes,[920] quinines,[921,922] and Co, Fe, Ru[923] and Pt[924] metal complexes to form new complexes where these fragments have inserted into the S–S bond. The analogous selenido compound has also been reported.[925] Cationic carbyne complexes $[Cp(CO)_2M{\equiv}CC_6H_5]BBr_4$ (M = Mn and Ru) react with $Na[CpMo(CO)_3]$ to form $\eta^1:\eta^2$-ketene complexes **290**,[926] whilst $[(Cp)_2Mo(H)CO][Mn_3(CO)_9(\mu\text{-}SC_6H_5)_4]$ gives the mercapto-carbene complex $[Cp(CO)_2Mn{=}C(SC_6H_5)\text{-}C_6H_5]$ and the thiolato-bridged carbonyl complex $[CpMo(CO)_2(\mu\text{-}SC_6H_5)_2Mn(CO)_3]$.[927] Mixed metal complexes containing iron are common and mainly based on the tetrahedral $[(\mu_3\text{-}S)FeMMo]$ core, **291**. These complexes are

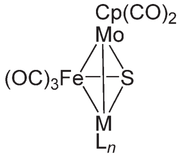


Scheme 32

known for M = Mo,[928–930] Fe,[931] Ru,[932,933] Os,[933] and particularly for M = Co.[934–938] [(μ_3-S)NiRuMo] compounds have been synthesized,[939–941] and selenium analogues are also known for [(μ_3-Se)RuCoMo].[942] There are many examples in the literature of Mo–Co clusters bridged by alkyne ligands; this is outside the scope of this chapter. Of note, however, is an examination of the substitution[943] and photochemistry[944] of the dinuclear complex [CpMo(CO)$_3$-Co(CO)$_4$], where ring-slip reactions of the Cp ligand have been postulated.


M = Mn, Ru

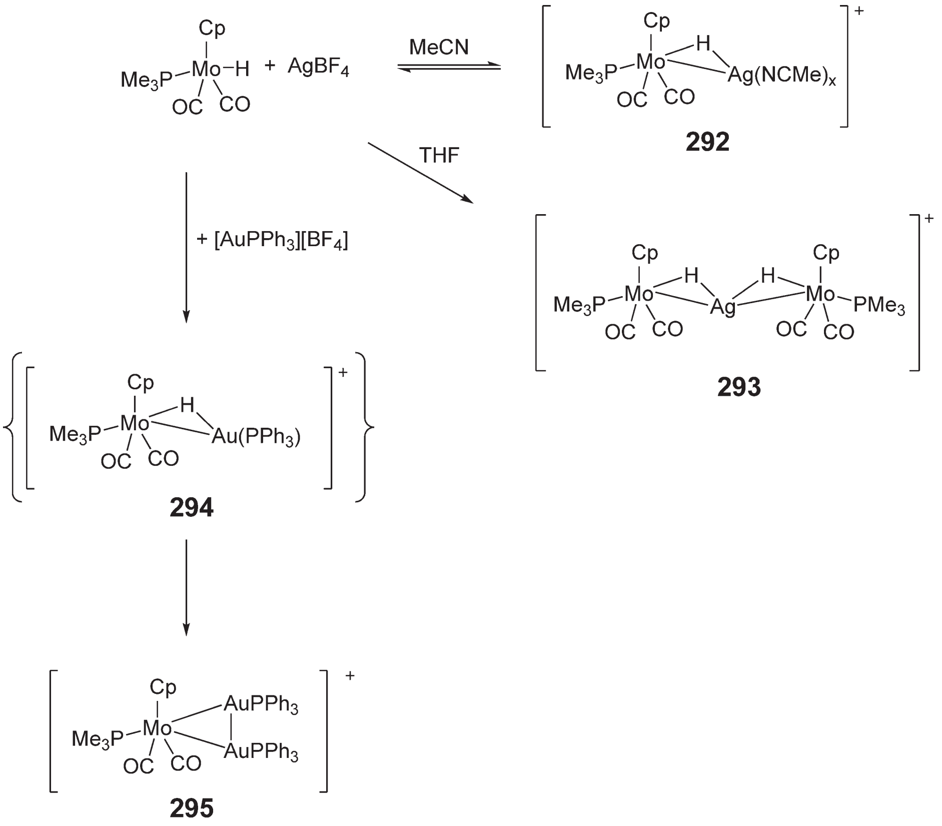
290


M = Mo, Fe, Ru, Os, Co

291

Heterobimetallic Ru–Mo complexes [(η^5-C$_5$R$_5$)Ru(CO)(μ-dppm)MoCp(CO)$_2$][945] and [Ind(CO)$_3$Mo–Ru(CO)$_2$Cp][946] have been used in catalytic CO$_2$ hydrogenation to formic acid or aerobic oxidation of THF to prepare γ-butyrolactone and propylformate. A new synthesis for [Cp*Ni–Mo(CO)$_3$Cp] has been presented, and is useful as a cluster building blocks, for example, [FeNiMo(μ_3-CO)(μ_2-CO)(CO)$_5$(Cp)(Cp*)] has been synthesized and structurally characterized.[947] A number of Ni–Mo bimetallic species are known and their reactions with alkynes have been documented.[948–952] Palladium–molybdenum compounds are known with the bridging η^5-C$_5$H$_4$(CH$_2$)$_n$PR$_2$ ligand (R = alkyl, aryl; n = 0–3).[338,953,954] Complexes with unsupported Mo–Pd[955,956] and Mo–Pt[647,957] bonds are also reported along with Mo–Pd bonded complexes with bridging alkylidene ligands.[958,959]

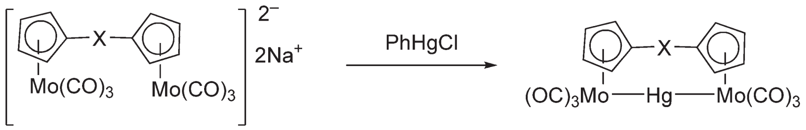
Late transition metals. A copper compound, [Cp*Mo(CO)$_3$Cu(PPh$_3$)], has been isolated in impure form, and the identification is based upon comparison of spectroscopic data with the tungsten analog.[960] Hydride abstraction from [CpMo(CO)$_3$H] with gold alkoxides affords the expected products [Cp(CO)$_3$Mo–AuL] (L = PR$_3$, R, Ar),[961] but the use of AgBF$_4$ affords an equilibrium mixture of 292 or 293 in acetonitrile or THF solutions, respectively (Scheme 33). Structure 292 slowly decomposes in solution with elimination of H$_2$ gas and metallic Ag to form [CpMo(CO)$_2$(PMe$_3$)(MeCN)]BF$_4$. This decomposition could be interpreted as either an inner-sphere electron transfer or an elimination of unstable AgH.[962] The reaction of [CpMoH(CO)$_2$L] (L = PR$_3$, CO) with [AuPPh$_3$][BF$_4$] in THF gives MoAu$_2$ clusters 295, and an intermediate 294 has been identified spectroscopically.



Scheme 33

The crystal structure of [CpMo(CO)$_2$(PMe$_3$)(AuPPh$_3$)$_2$]BF$_4$ has been determined.[963] [CpMo(CO)$_3$(AuPPh$_3$)] has also been obtained by the reaction of Li[CpMo(CO)$_3$] with Ph$_3$PAuCl and has been structurally characterized.[964]

The bulky C$_5$Bz$_5$$^-$ ligand reacts with [Mo(CO)$_6$] and PhHgCl to form [(C$_5$Bz$_5$)Mo(CO)$_3$]$_2$Hg.[965] Bridged Cp ligands have gained prominence in the literature, and heterotrimetallic systems containing Hg have been prepared. It has also been shown that Hg(CN)$_2$ inserts into the M–M bond of [(η^5:η^5-(C$_5$H$_3$CO$_2$Me)$_2$)Mo$_2$(CO)$_6$], and under electrochemical studies the reductive elimination of Hg is seen, resulting in the formation of the dianion [(η^5:η^5-(C$_5$H$_3$CO$_2$Me)$_2$)Mo$_2$(CO)$_6$]$^{2-}$.[966] The reaction of anionic **296** with PhHgCl affords the trimetallic species **297** which has been characterized by X-ray diffraction (Equation (98)).[967] An ^{95}Mo and ^{119}Hg NMR study has been undertaken on bulky or bifunctional Cp ligands in compounds of the type [Cp(OC)$_3$MoHgX] and trends in chemical shifts discussed.[968] The use of the [CpMo(CO)$_3$]Hg fragment in the synthesis of mixed metal clusters has been widely reported, but is outside the scope of this chapter.

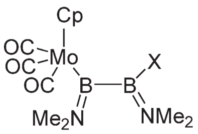


(98)

296 X = (C(O)CH$_2$)$_2$, (CH$_2$CH$_2$)$_2$O **297**

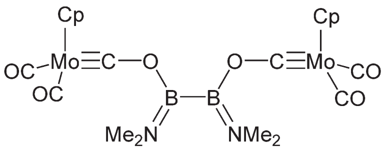
5.06.3.1.8.(iii).(e) Group 13 CpMo carbonyl compounds

Synthesis. The oxidative addition of B–X (X = Hal, H) to metal fragments has been successfully utilized for many years to make metal–element bonds. An example is the reaction of 1,2-dihaloboranes(4) with [CpMo(CO)$_3$]$^-$ to form **298**.[969,970] However, it has also been noted that this reaction can take an unexpected course, and in the case of B$_2$(NMe$_2$)$_2$I$_2$ a novel dinuclear boryloxycarbyne complex **299** was isolated.[971] This is the kinetically favored product and rearranges to the thermodynamically favored **300**.[972]



X = Cl, Br

298



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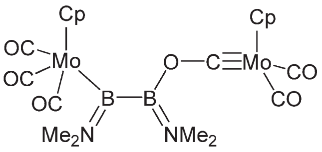
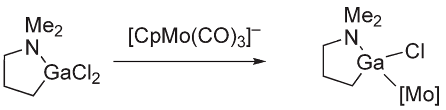


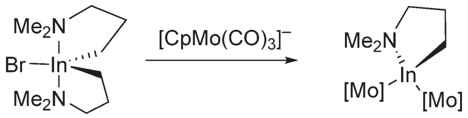
300

The activation of tetracoordinate (sp^3-type) boranes has also been investigated. Thus, the photolytic reaction of $BH_3{\cdot}PMe_3$ with $[Cp^*Mo(CO)_3Me]$ affords $[Cp^*Mo(CO)_3(BH_2{\cdot}PMe_3)]$ in moderate yields. Crystallographic and spectroscopic data suggest there is little $d\pi-p\pi$ backbonding from the metal to the boron and reactivity studies also suggest a polarized $Mo^-–B^+$bond.[973] Of note is the fact that by using $[CpMo(CO)_3Me]$ or $[Mo(CO)_6]$[55] thermally unstable boryl compounds were obtained.

$[CpMo(CO)_3H]$ reacts with $Bu^t{}_3E$ (E = Al, Ga) to form species with M–E bonds. The solid-state structure of $[CpMo(CO)_3(GaBu^t{}_2)]$ shows an additional interaction between the electron-deficient Ga center and one of the carbonyl ligands thus forming dimeric species. Lewis acid–base complexes can be formed by recrystallising these compounds from donor solvents.[974] The reactions of organogallium and organoindium halides with $[CpMo(CO)_3]^-$ gives rise to donor-stabilized **301**[975] and **302**[976] species (Equations (99) and (100)).

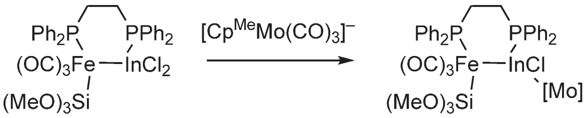


301 (99)

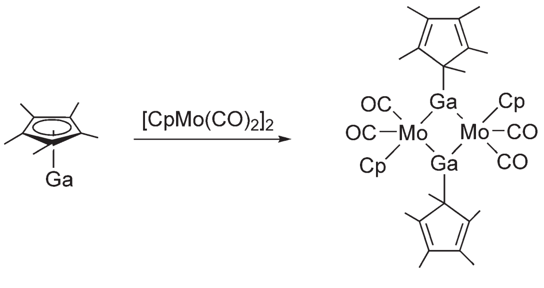


302 (100)

The synthesis of trimetallic **303** has also been reported by the reaction of *mer*-$[\{(MeO)_3Si\}(OC)_3Fe(\mu\text{-dppm})InCl_2]$ with $[CpMo(CO)_3]^-$ (Equation (101)).[977] Salt elimination is not restricted to group 13 halides, as the synthesis of $[\{CpMo(CO)_3\}_2In(NCS)]$ has been reported starting from $In(NCS)_3$.[978] Cp^*Ga has been investigated as a ligand as it can be considered to be isolobal to CO. While $[(Cp^*Ga)_nMo(CO)_{6-n}]$ ($n = 2$, 3) have been prepared as stable complexes (Section 5.06.2.2), the addition of Cp^*Ga to $[CpMo(CO)_2]_2$ gives dimeric **304** with bridging Cp^*Ga units and a long Mo–Mo bond (3.521(7) Å), which the authors postulate is a result of steric crowding.[211] Of interest is the observation that the Cp^* is coordinated in an η^1-fashion to the Ga (Equation (102)).



303 [Mo] = $CpMo(CO)_3$ (101)



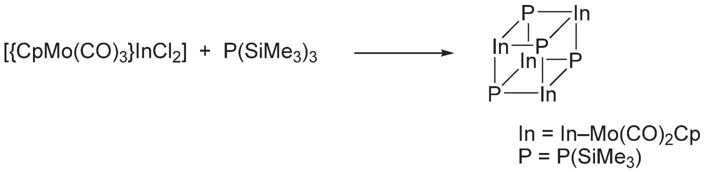
304 (102)

The compounds $[\{CpMo(CO)_3\}_3E]$ (E = Ga, In) have been prepared from $[\{CpMo(CO)_3\}_2BiCl]$ and the corresponding metal.[979]

Properties and reactivity. In a comprehensive study, Hartwig and Waltz have shown that $[Cp^*M(CO)_nB(OR)_2]$ ($M = Fe$, Ru, $n = 2$; Mo, W, $n = 3$) form alkylboronate esters with alkanes under photolytic activation. A detailed mechanistic study was described.[980] Indium chemistry is the most represented in this area. The known compound $[CpMo(CO)_3InCl_2]$ has been structurally characterized[981] and its reactivity investigated (Equations (103) and (104)). Both amide species are monomeric and contain trigonal planar In atoms.[982] In contrast, $[\{Cp(CO)_3Mo\}InCl_2]$ reacts with $P(SiMe_3)_3$ in THF to form the heterocubane $[\{Cp(CO)_3Mo\}_4In_4(PSiMe_3)_4]$ (Equation (105)).[983] Oxidation reactions involving magnesium afford decomposition products.[984] ^{207}Tl NMR spectroscopic studies on a variety of thallium-containing metal compounds have been reported.[985]

$$[\{CpMo(CO)_3\}_2InCl] + LiN(SiMe_3)_2 \longrightarrow [\{CpMo(CO)_3\}_2InN(SiMe_3)_2] \tag{103}$$

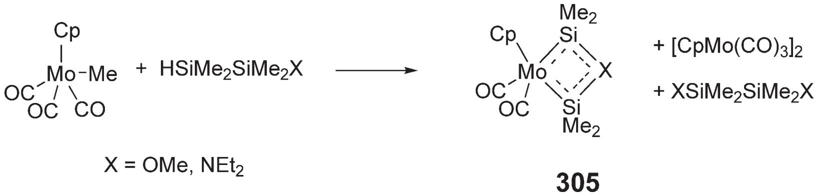
$$[\{CpMo(CO)_3\}InCl_2] + 2LiN(SiMe_3)_2 \longrightarrow [\{CpMo(CO)_3\}In\{N(SiMe_3)_2\}_2] \tag{104}$$



(105)

5.06.3.1.8.(iii).(f) CpMoCO compounds containing Si, Ge, Sn, or Pb

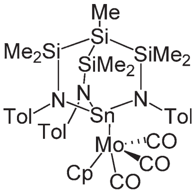
Preparation. The reactions of chlorosilanes with $[CpMo(CO)_2(PMe_3)]^-$ have been well documented[986] to give $[CpMo(CO)_2(PMe_3)(SiR_3)]$ for SiR_3 = halosilane,[987] chlorodisilanes,[988] chlorosiloxanes,[989] and chlorodisilanols.[990] Unsaturated systems have also been studied, and the synthesis of donor-bridged bis(silylene)molybdenum compounds reported. The reaction of $[CpM(CO)_3Me]$ and $HSiMe_2SiMe_2X$ ($X = OMe$, NEt_2) under photolytic activation affords **305**, which is the first isolated example of a molybdenum silylene complex (Equation (106)).[991]



(106)

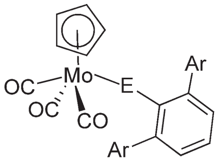
305

Stereoselective oxidative insertion reactions of $GeCl_2$ into M–Cl[992,993] or M–H[994] bonds have also been reported to form *cis*-$[Cp'Mo(CO)_2(PMe)_3(GeCl_2X)]$ ($Cp' = Cp$, Cp^*; $X = H$, Cl), which is a more convenient synthesis for metal–Ge(IV) species. However, photolysis of $[CpMo(CO)_2]_2$ with $HSiMe_2Ph$ affords $[\{CpMo(CO)_2\}_3(\mu_3\text{-}CH)]$[995] or $[\{CpMo(CO)_2\}_3(\mu_3\text{-}CCH_3)]$[996] via reduction of a CO ligand. Using salt metathesis techniques, heterometallic Mo–Sn compounds can be formed from R_2SnCl_2 and $[Cp'Mo(CO)_3]^-$.[997–999] The compound $[\{CpMo(CO)_3\}_2SnI_2]$ has been obtained as the only product from the reaction of the heterobimetallic alkoxides $[I_2Sn\{Al(OPr^i)_4\}_2]$ and $[I_2Sn\{Ti(OPr^i)_5\}_2]$ with $[CpMo(CO)_3]^-$.[1000] The use of a triamidostannate $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3SnLi(OEt_2)]$ as a metalloligand toward a variety of metal fragments has been described. Complex **306** shows restricted rotation ($\Delta G^\ddagger = 67.8 \pm 1.0\,kJ\,mol^{-1}$) around the Mo–Sn bond due to the sterically congested coordination sphere.[1001]

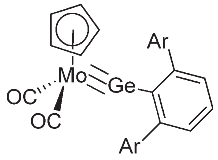


306

Multiple bonding between group 14 elements and transition metal fragments is a topic of much interest. Complexes **307** ($Ar = C_6H_2\text{-}2,4,6\text{-}^iPr_3$, $C_6H_2\text{-}2,6\text{-}Mes_2$)[1002] and **308** ($Ar = C_6H_2\text{-}2,4,6\text{-}^iPr_3$),[1003] synthesized from the reaction of ArEX with $Na[CpMo(CO)_3]$, have been reported. Attempts at the preparation of the analgous Ge example failed and **309** ($Ar = C_6H_2\text{-}2,4,6\text{-}^iPr_3$,[1004] $C_6H_2\text{-}2,6\text{-}Mes_2$[1005]), which remarkably features an M≡Ge triple bond, was isolated due to facile CO elimination. The inability to isolate Sn and Pb triple-bonded examples is due to the greater stability of the lead lone pair (i.e., the inert pair effect) and the larger size of Sn/Pb versus Ge which makes CO elimination less likely.



307: E = Sn
308: E = Pb

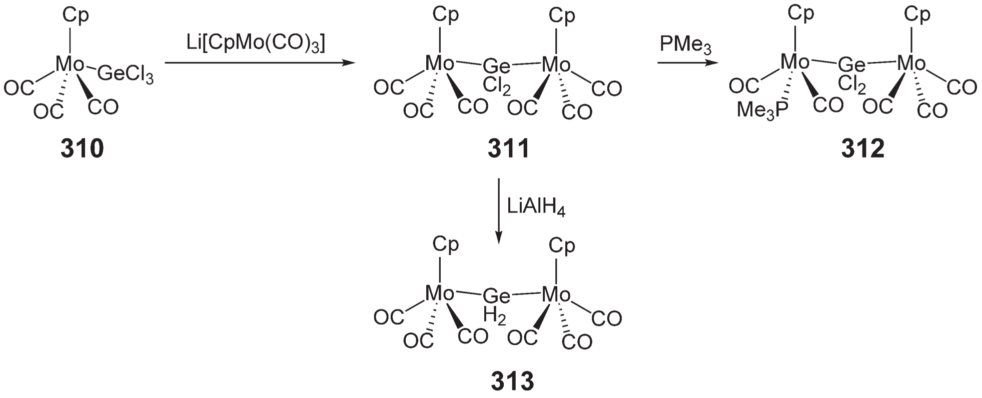


309

Properties. The molybdenum silane compounds $[CpMo(CO)_2(PMe_3)(SiH_3)]$ have been characterized by ^{29}Si NMR spectroscopy and all display resonances typical for metal-bound silicon species. In addition, Raman spectroscopy has been used to obtain information on the M–Si and Si–H force constants.[1006–1008] Compound **305** shows a degree of unsaturation in the M–Si bond, as evidenced from the short Mo–Si bond length and low-field ^{29}Si NMR resonance. Variable-temperature NMR spectroscopic studies also revealed a dynamic process whereby an M═Si intermediate was formed. The electron-rich molybdenum metal donates electron density into the Si–X σ^*-orbital, which weakens this bond and also stabilizes the silyl(silylene) intermediate by backdonation into the empty $p\pi$ orbital of the silylene silicon atom.[991] A series of $[CpMo(CO)_3SnR_3]$ (R = Ph, X) heterobimetallic systems has been studied by ^{119}Sn Mössbauer spectroscopy, and it shows two different tin environments in the solid state, possibly indicating intramolecular association.[1009] $[\{MoCp(CO)_2\}_3(\mu_3\text{-}CH)]$ shows complicated dynamic behavior in solution involving a gear-like and local rotation of the $CpMo(CO)_2$ units with concomitant switching of the semibridging CO ligands.[995]

X-ray diffraction studies revealed an almost linear, two-coordinate Ge geometry and very short Mo–Ge bond distance in **309**,[1004,1005] while **307** shows a two-coordinate V-shaped geometry.[1002] Structure **308** is the first example of a metalloplumbylene, which features a bent two-coordinate lead geometry and long M–Pb bond lengths.[1003] The low coordination number of the tin and lead atoms is also manifested in the low-field chemical shift in the ^{119}Sn and ^{209}Pb NMR spectrum. Theoretical calculations on $[Cp(CO)_2Mo{\equiv}ER]$ (E = Si–Pb, R = H, Me, Ph, terphenyl)[1010] and $[Cp(OC)_nM{\equiv}GeMe]$ (M = Cr, Mo, W, Fe)[1011] have also been reported.

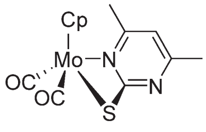
Reactivity. The metallohydridosilanols can be converted into the corresponding chlorosilanols by treatment with CCl_4,[988] and into metallosilanetriols using dimethyldioxirane.[1012,1013] Conversely, treatment of the halosubstituted metallosilanes with $LiAlH_4$ gives the hydridosilanes.[1006] The *trans*-isomer $[CpMo(CO)_2(PMe_3)GeCl_2H]$ is cleanly chlorinated by CH_2Cl_2,[994] whereas the *cis*-isomer $[CpMo(CO)_2(PMe)_3(GeCl_2X)]$ can be converted into the *trans*-isomer by an endothermic isomerization in the melt.[1014] Reaction of the trichlorogermyl complexes **310** (Cp = C_5H_5; M = Mo, W) with $Li[CpM(CO)_3]$ gives bimetallic **311** which undergoes CO displacement or substitution reactions to form **312** or **313**, respectively (Scheme 34).[1015] The reactions of transition metal–stannyl trichlorides with the potassium salts of $B(pz)_4$ or Tp have been reported to give hexacoordinate Sn chelates $[MSnCl_2(L)]$ (M = $W(CO)_3Cp$, $Mo(CO)_3Cp$, $Fe(CO)_2Cp$), but trimetallic complexes Cl_2SnM_2 were obtained from the reactions with $H_2B(pz)_2$.[1016]



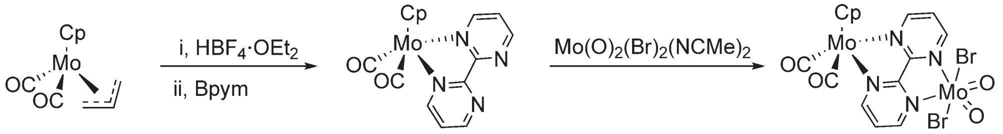
Scheme 34

5.06.3.1.8.(iii).(g) Group 15 complexes

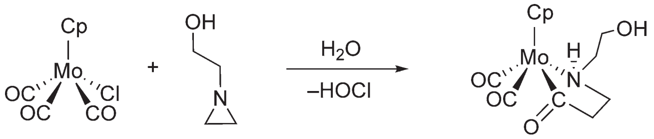
CpMo nitrogen compounds. Monometallic complex **314** is formed upon treatment of the mercaptopyrimidine ligand with $[CpMo(CO)_3]_2$, in contrast to related chemistry of iron compounds of this ligand.[1017] Bipyrimidine complexes of the $[CpMo(CO)_2]$ fragment have been prepared by protonation of an allyl ligand. This complex is ideally suited to the synthesis of bimetallic species as the reaction with the high oxidation state $[Mo(O)_2(Br)_2(NCMe)_2]$ shows (Equation (107)). The bipyrimidine ligand also allows some electronic communication between the metal centers.[1018] ReO_3X (X = Me, Cl) have also been incorporated using this methodology.[1019] Aziridines have been reacted with $[CpMo(CO)_3Cl]$ in an attempt to form cationic η^1-complexes. However, an unusual ring-opening reaction occurs to form a neutral metallacycle (Equation (108)).[1020]



314



(107)

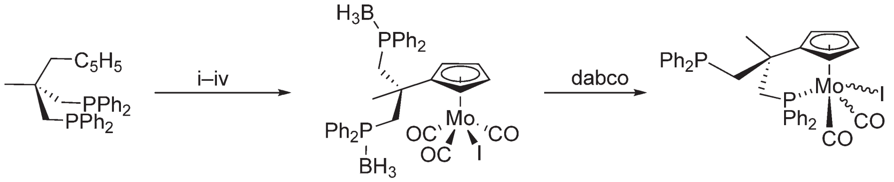


(108)

Some bridging nitrido complexes have also been prepared. The anionic clusters $[Fe_5MN(CO)_{14}Cp]^{2-}$ (M = Mo, W) have been synthesized from $[Fe_4N(CO)_{12}]^-$ and $[CpM(CO)_3]^-$ and X-ray diffraction studies show that they consist of six metal atoms, arranged in octahedral metal cages encapsulating a μ_6-N ligand.[1021] $[Ru_2Mo(\mu\text{-}H)(CO)_8(Cp)(\mu_3\text{-}NOMe)]$ and $[Ru_2Mo(\mu\text{-}H)(CO)_8(Cp)(\mu_3\text{-}NH)]$ have been prepared from $[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)]$ and $[CpMo(CO)_3H]$, while with $[\{CpMo(CO)_3\}_2Hg]$ pentanuclear $[Ru_3(CO)_{10}(\mu\text{-}NH_2)(\mu_3\text{-}Hg\{MoCp(CO)_3\}]$ could be isolated.[1022] A hetero-trimetallic complex $[CpMoFeCo(CO)_8(\mu_3\text{-}NH)]$ has been prepared via a metal exchange reaction of $[FeCo_2(CO)_9(\mu_3\text{-}NH)]$ and $Na[CpMo(CO)_3]$, and ^{14}N NMR data suggest a degree of delocalization over the M_3 core.[1023]

CpMo phosphorus compounds. The format of this section follows that of Section 5.06.2.4.3, and the reviews cited in that section are also valid here. Again, there has been a large body of work published on this subject and this necessitates some selectivity. Consequently, only compounds that display unusual structure, bonding, or reactivity will be included.

Synthesis of PY_3 and phosphide complexes. An unusual method of synthesizing phosphine derivatives is by treatment of the tripodal ligand **315**, which contains a C_5H_5 group (Equation (109)). Protection of the phosphine ligands using BH_3 and oxidation affords **316** with non-coordinating phosphine donors; however, removal of the borane enables coordination of one phosphorus ligand to form **317**.[1024]

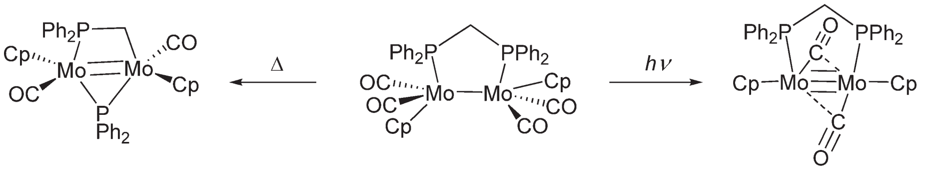


(109)

315 **316** **317**

i, BuLi; ii, $BH_3{\cdot}THF$; iii, $[Mo(CO)_3(NCMe)_3]$; iv, I_2

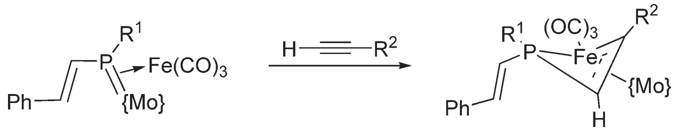
Decarbonylation of the dimolybdenum complexes **318** (Cp = Cp, Cp*) occurs readily upon heating to afford the phosphido complexes **319** (Equation (110)). The irreversible P–C bond cleavage in the backbone of the dppm ligand can be suppressed at lower temperatures, as photochemical decarbonylation of the tetracarbonyl complexes yields the triply bonded dicarbonyl **320** as the major products (Equation (110)).[1025] Decarbonylation of the heterodinuclear complex **321** has also been studied, and **322** isolated from thermal decarbonylation, or **323** under photolytic conditions (Scheme 35). This hydride is thermally unstable, and further photolysis at 10 °C affords **324**. Further reactivity studies have been examined in order to rationalize the proposed mechanism and observed selectivity.[1026] Oxidation of $[Cp_2M_2(CO)_4(\mu\text{-dppm})]$ with $[Cp_2Fe][BF_4]$ or $[Cp_2Fe][PF_6]$ affords the mononuclear $[CpM(CO)_2\text{-}(dppm)]^+$ via the unstable $[Cp_2M_2(CO)_4(\mu\text{-dppm})]^{+\cdot}$ radical cation. This cation also reacts with a second equivalent of the oxidizing agent to form $[Cp_2M_2(CO)_4(\mu\text{-dppm})]^{2+}$, which abstracts fluoride ions from its counterion.[1027] Expansion of this work to the use of the oxidizing agent $[Cp_2Fe][B(ArF)_4]$ has enabled the chemistry of the paramagnetic $[Cp_2M_2(CO)_3(\mu\text{-PP})]^{+\cdot}$ (PP = dmpm, dppm, tedip) to be explored. It was found that the stability depends on the metal (Mo > W) and the diphosphine (dmpm > dppm > tedip), and typical reactivity toward EH (E = HO, MeO PhS) to form *cis*-$[Mo_2Cp_2(\mu\text{-SPh})(\mu\text{-CO})(CO)_2(\mu\text{-PP})](BArF_4)$ or $[Mo_2Cp_2(\mu\text{-OH})(CO)_2\text{-}(\mu\text{-dppm})](BArF_4)$, and no evidence of H-abstraction was observed.[1028]



319 **318** **320**

(110)

Unusual reactivity has been observed upon treating 1-molybda-2-phospha-1,3-dienes with alkynes to form the metalloallylic complex **325** (Equation (111)).[1029]

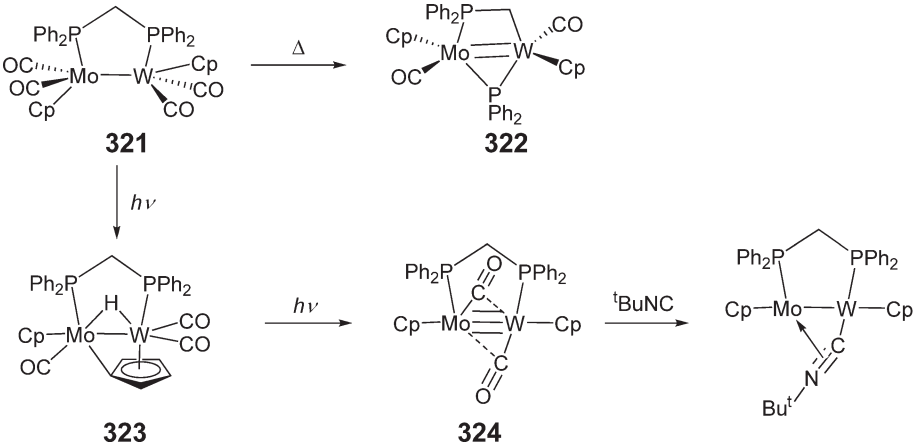


325

{Mo} = $CpMo(CO)_2$; R^1 = 2,4,6-$^tBu_3C_6H_2O$; R^2 = ^nPr, Ph

(111)

Seventeen-electron complexes of Mo-carbonyls are rare, the first examples being prepared in 1996. Using sterically bulky and strongly donating Cp and phosphine ligands, $[CpMoClL(CO)][PF_6]$ {L = dppe, $(PMe_3)_2$} have been



321 **322** **323** **324**

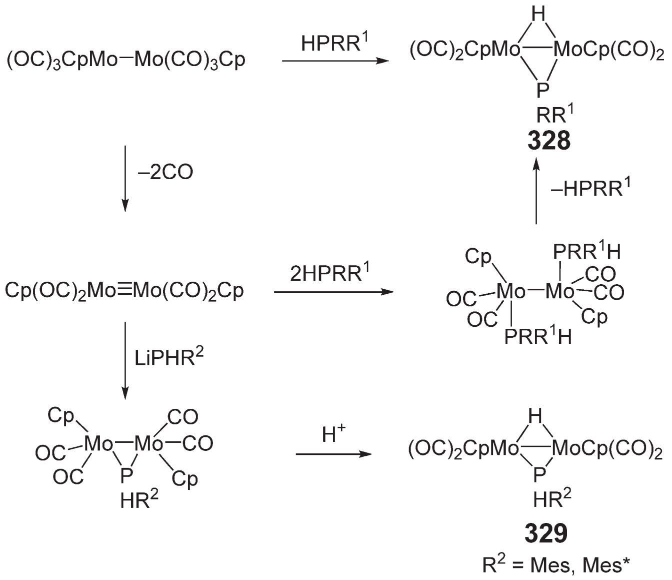
Scheme 35

prepared and characterized by EPR spectroscopy and cyclic voltammetry.[1030] The study of 19-electron complexes is of great interest and the complex [CpMo(CO)$_3${P(OMe)$_3$}] has been studied by DFT calculations. This has been postulated as a key intermediate in photochemical reactions of [Cp$_2$Mo$_2$(CO)$_6$] with P(OMe)$_3$, and loss of P(OMe)$_3$ from the monophosphite [CpMo(CO)$_3${P(OMe)$_3$}] is slightly thermodynamically favorable.[1031] Examples of 19-electron compounds that are water soluble have also been reported.[1032] A second possibility exists when using ligands with low-lying π^*-orbitals, and these have been used to prepare so-called $18+\delta$ complexes, whereby the extra "valence" electron resides in the ligand orbital rather than the M–L antibonding orbital. A series of bidentate phosphorus ligands has been examined by electrochemical, EPR spectroscopic and theoretical calculations, and those that feature a reduction potential more positive than −1 V (vs. SCE) formed long-lived complexes, which can be related to large HOMO–LUMO separations.[1033] A further method of synthesizing metal-based radicals is by the oxidation of [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]$^-$ with [Cp$_2$Fe]$^+$ salts affording a novel 33-electron metal–metal-bonded radical [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]$^\cdot$. This compound is sufficiently stable to enable an investigation into its reactivity, and in all cases the Mo$_2$ unit is intact due to the bridging phosphide group.[1034]

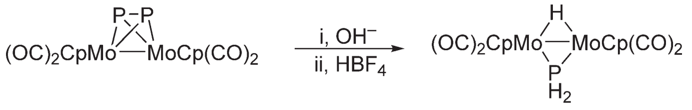
The phosphido complexes [CpMo(CO)$_2${P(Cl)TMP}] (TMP = 2,2,6,6-tetramethyl-1-piperidyl) and [CpMo(CO)$_3$-{P(Cl)NPr$^i_2$}] react with selected transition metal complexes to form hetero- and homobimetallic phosphinidene bridged complexes of the type [CpMo(CO)$_2$(μ-PR)ML$_n$] (ML$_n$ = CpMo(CO)$_2$; Co(CO)$_3$; Mn(CO)$_4$),[1035] and the reaction of [{(R)[(η^2-C≡CPh)Co$_2$(CO)$_6$]}P(Cl)] (R = 2,4,6-^{t}Bu$_3$C$_6$H$_2$O) with Na[CpMo(CO)$_3$] affords the terminal phosphinidene [(R){(η^2-C≡CPh)Co$_2$(CO)$_6$}P═MoCp(CO)$_2$].[1036]

Phosphido-bridged heterobimetallics [CpMo(CO)$_n$(μ-PPh$_2$)Fe(CO)$_4$] (n = 2,3) have been synthesized by the reaction of [CpMo(CO)$_2$PPh$_2$] with Fe$_2$(CO)$_9$. Substitution of CO ligands on the Fe center was observed when L (L = P(OMe)$_3$, PPh$_2$H, PPh$_3$) was added to [CpMo(CO)$_2$(μ-PPh$_2$)Fe(CO)$_4$]; however, the complex where n = 3 failed to react.[1037] Tetrahedrane compounds [CpMo(CO)$_2$]$_3$P[1038] and other phosphorus-rich complexes {(CpMo(CO)$_2$)$_2$(μ-η^2:η^2-P$_2$)[Mo(CO)$_5$]$_2$}[1039] [Cp′Mo(CO)$_2$(η^3-P$_3$)], [Cp″Mo(CO)$_2$(η-P$_3$)], [{Cp′Mo(CO)$_2$}$_2$(μ-η^2:η^2-P$_2$)], [{Cp″Mo(CO)$_2$}$_2$(μ-η^2:η^2-P$_2$)],[1040] (Cp″ = C$_5$H$_3$Bu$^t_2$) [Cp*Mo(μ-η^4:η^2-P$_4$) (μ-η^2:η^2-P$_2$)FeCp*],[1041] [Cp′Mo(CO)$_2$(η^3-P$_4$){Cr(CO)$_5$}$_4$(H)] (Cp′ = C$_5$H$_4$Bu^t),[1042] and [(η^3-P$_3$)MCp′(CO)$_3$][1043] have been reported.

The reaction of the naked phosphorus ligands in **326** with an excess of OH$^-$ followed by protonation affords the new phosphido complex **327** (Equation (112)). This is a much more advantageous synthesis as other methods use PH$_3$ gas.[1044] Compound **327** can also be obtained in a one-pot reaction from [CpMo(CO)$_2$]$_2$, LiP(SiMe$_3$)$_2$, MeOH, and HBF$_4$, although attempts to synthesize the corresponding arsenic derivative failed.[1045] The synthesis of PRR^1-bridged species, for example **328**, has also been reported via two methods, either the addition of a secondary phosphine to [CpMo(CO)$_3$]$_2$ or to [CpMo(CO)$_2$]$_2$, the latter being more useful for volatile phosphines (R = H, Et, ^{t}Bu, Cy, Ph; R^1 = ^{t}Bu, Cy, Ph).[1046] However, this method does not work for bulky phosphines, and a two-step procedure has been published for the synthesis of **329** (R^2 = Mes, Mes*). Of note is that when R = Mes, *cis*- and *trans*-isomers were detected (Scheme 36).[1047]



Scheme 36

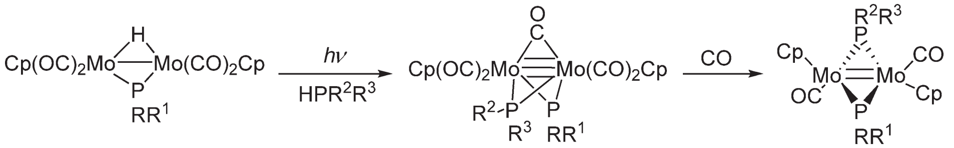


326 **327** (112)

Properties of PY_3 and phosphide complexes. Synthesis and examination of the crystal structures of $[CpMo(CO)_2\{P(OR)_3\}I]$ (R = Me, Et, ^{i}Pr, ^{i}Bu, Np) allowed a series of steric parameters to be measured, and compared to Tolmans cone angle.[1048] Enthalpies for protonation (ΔH_{MHM}) of the Mo–Mo bond in the dinuclear Mo complexes $[Cp_2Mo_2(CO)_4(PR_3)_2]$ have been measured and it was shown that the PMe_3 complex ($-114.6(8)\,kJ\,mol^{-1}$) is significantly more basic than its PMe_2Ph analog ($-79.0(2)\,kJ\,mol^{-1}$). This result indicates that the basisity of the metal is influenced by the ancillary ligands.[1049]

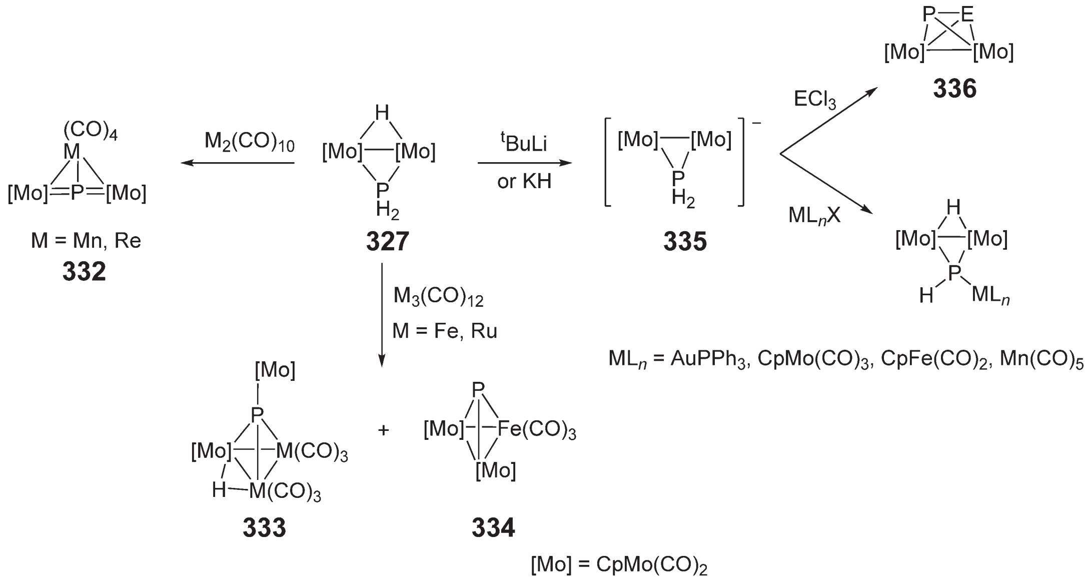
Complex **327** has been the subject of an X-ray diffraction study. The Mo–Mo bond length supports the formulation of an M–M single bond (3.2818(9) Å), whilst the remaining metric parameters are similar to that of the known PPh_2-bridged species, and the small differences ascribed to steric effects.[1045] Fluxional behavior is observed in some examples of **328**; the degree of fluxionality appears to be determined by electronic effects of the phosphide, so that electron withdrawing groups increase the rate of fluxionality.[1046] The nature of the bonding in $[\{CpM(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}PMe_2)]$ and the deprotonated congener has been studied by DFT calculations, and NBO analysis suggests that there is no M–M bond or unpaired electon density around the metal in the bridged hydride compound.[1050]

Reactivity of PY_3 and phosphide complexes. The reactivity of **328** has been examined in some detail. Addition of a further phosphide group is possible under photolytic activation forming **330**, and this can be carbonylated to give **331** (Equation (113)). A mechanism for this reaction was also discussed.[1046]



328 **330** **331** (113)

The reactivity of **327** has been investigated (Scheme 37), and treatment with $[M_2(CO)_{10}]$ (M = Mn, Re) forms **332** which features a linear M_3P triangular cluster, whilst with $[M_3(CO)_{12}]$ (M = Fe, Ru), **333** and **334**, which are rare examples of a naked μ_4-P atom, are isolated.[1051] Deprotonation of **327** cleanly forms anionic **335**, and some reactivity

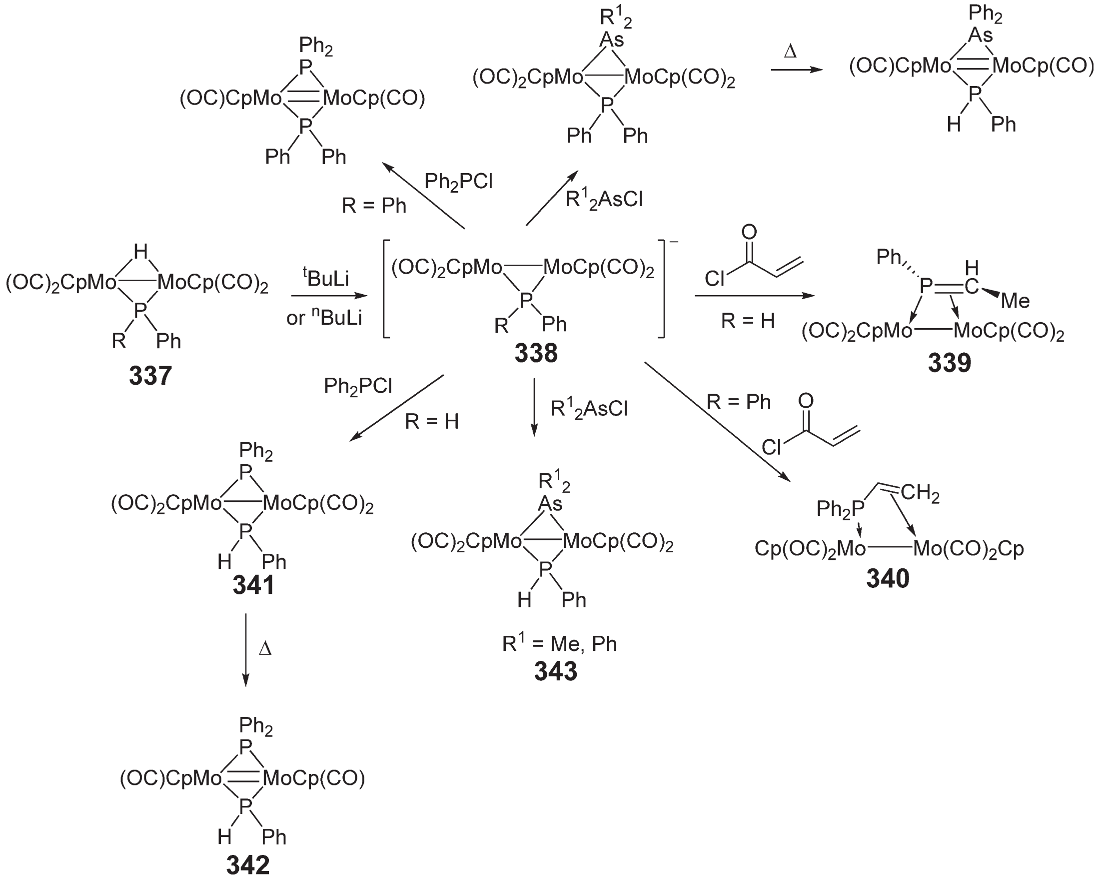


Scheme 37

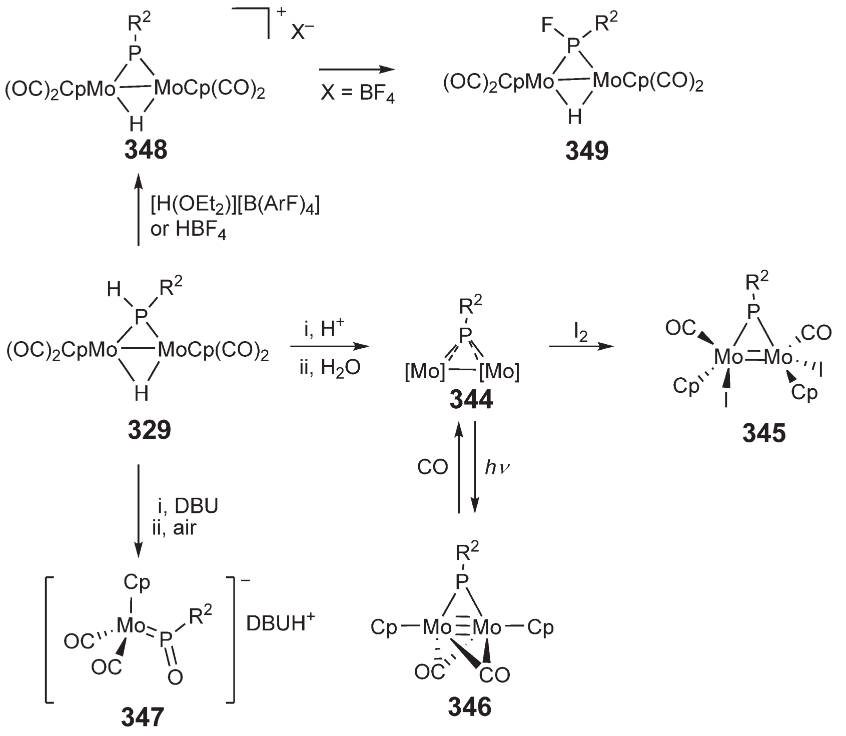
studies have been published. Most unusual is the reaction with ECl_3 (E = P, As, Sb) to form complexes with naked μ-E_2 ligands **336**,[1052] and this has been further expanded to the reaction with $[W(CO)_5(THF)]$, which forms adducts through the phosphorus lone pair.[1053] A μ_3-P atom is seen in the reaction of $[\{CpM(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}PH_2)]$ with $[AuCl(PPh_3)]$ to form $[\{Cp(CO)_2Mo\}_2(\mu\text{-}H)\{\mu_3\text{-}P(H)Au(PPh_3)\}]$,[1054] whilst $[ML_nX]$ (ML_n = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Fe(CO)_2Cp$, $Mn(CO)_5$; X = Cl, Br) also forms similar compounds.[1055] $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}PR_2)(CO)_2]$ (R = Cy, Ph, OEt) can be reduced to give the salts of the triply bonded anions $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}CO)_2]^-$ and the reactivity is similar to that of **335**.[1056]

Deprotonation of **337** (R = H, Ph) is easily achieved, and the resulting anionic **338** shows rich and varied reactivity. For example, treatment with acryloyl chloride gives a rare example of a μ-$\eta^1:\eta^2$-bonded phosphaalkene, **339**, in good yields (Scheme 38). The mechanism is thought to involve elimination of CO from the coordinated acroyl moiety and a rearrangement to form a vinyl phosphine intermediate, followed by a [1,3]-H shift from the coordinated PHPh group. This mechanism is plausible considering the isolation of the vinyl phosphine complex **340** from $[\{CpMo(CO)_2\}_2(\mu\text{-}PPh_2)]^-$, in which the sigmatropic H shift cannot take place. Thermolysis of **339** forms the *cis*-isomer, and both have been structurally characterized.[1057] A DFT study suggests that the π-bond of the phosphaalkene moiety is essentially lost on coordination, with the P═C π- and π^*-orbitals being used in bonding to the metal core.[1058] Compound **338** reacts with R_2PCl to form **341** which can be decarbonylated to give the Mo═Mo double-bonded complex **342**. When treated with $R^1{}_2AsCl$ (R^1 = Me, Ph), **343** is isolated. This is the first example of a complex with a bridging phosphido- and a bridging arsenido group. Similar reactivity is observed for R = Ph.[1059] Upon reaction of **338** with thiols the novel quadruply bridged compounds $[Cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)(\mu\text{-}PPh_2)]$ (R = Et, Pr^i, Bu^t, p-C_6H_4Me, $C_{12}H_{25}$) can be isolated.[1060]

The bulky substituent on the phosphorus atom in **329** (R^2 = Mes, Mes*) allows further interesting chemistry to be pursued (Scheme 39). Protonation, and subsequent treatment of this intermediate with H_2O, affords the known



Scheme 38

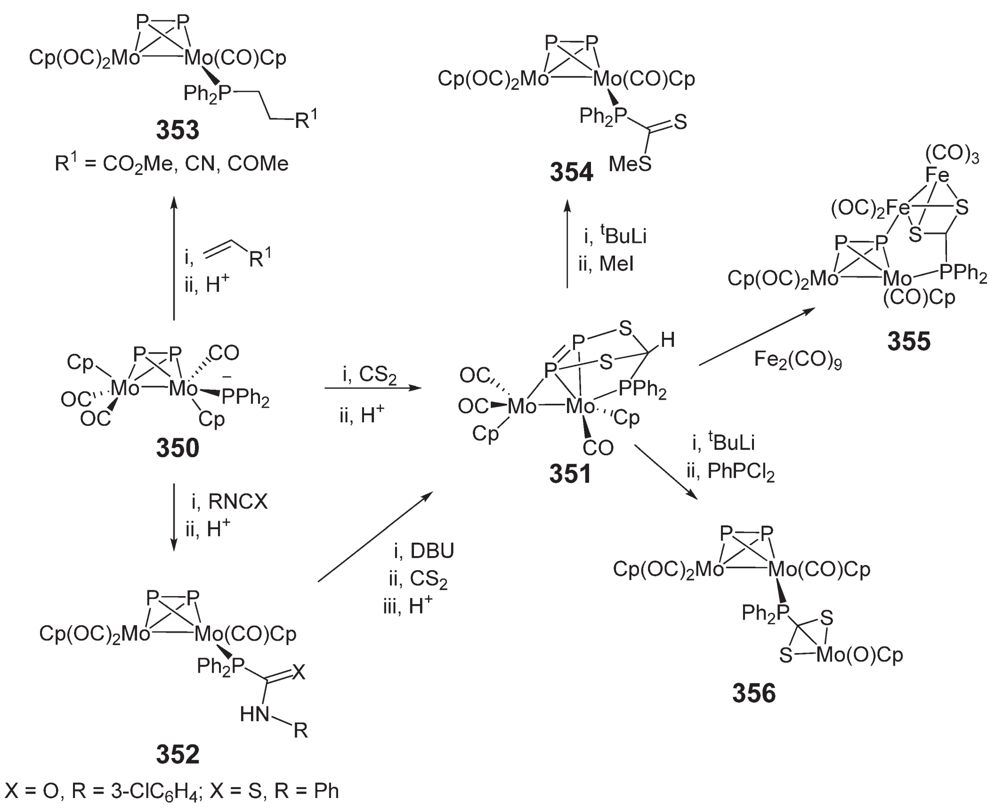


Scheme 39

phosphinidene complex **344** in good yields. The reactivity of this has been studied, and remarkably, addition of I_2 occurs at the metal center forming **345**, a rare example of a phosphinidene spanning an M═M bond. Photolysis of **344** forms **346** where the phosphinidene ligand spans an Mo≡Mo bond; addition of CO regenerates **344**.[1061] Reaction of **329** with DBU followed by exposure to air gives **347**, the first example of an anionic phosphinidene oxide complex. The reactivity of this complex, which displays three different nucleophilic sites, has been investigated.[1062] Protonation of **329** with either $[H(OEt_2)_2][B(ArF)_4]$ or $HBF_4{\cdot}OEt_2$ gives the cationic phosphinidene complexes **348** and concomitant loss of H_2 in good yield. Fluoride abstraction competes with carbonylation when $X = BF_4$ to yield the neutral fluorophosphide hydrides **349**. In contrast, protonation of the hydride compounds with smaller Mes or Cy substituents on phosphorus gives the corresponding unsaturated tetracarbonyls $[Mo_2Cp_2(\mu\text{-}PHR^2)(CO)_4]^+$, which are unstable at room temperature and decompose to give the electron-precise pentacarbonyls $[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4]^+$, also displaying a *cis*-arrangement of the metal fragments.[1047]

The complex $[Cp_2(CO)_3Mo_2(PPh_2H)(\mu\text{-}\eta^2{:}\eta^2\text{-}P_2)]$ can be deprotonated by treatment with ^tBuLi to form anionic **350**, which shows varied reactivity (Scheme 40). For example, quenching with CS_2 affords the novel cyclic complex **351**, which has an unprecedented bridging ligand containing a CSP_2S five-membered ring.[1063] Cumulenes such as $3\text{-}ClC_6H_4NCO$ and PhNCS also react with the anion to form simple addition products **352** after reprotonation, and **353** is formed by reaction with $H_2C{=}CHR^1$. Reaction of **351** with MeI yields **354**, in which ring scission and reformation of the tetrahedral Mo_2P_2 core has taken place. Reaction of this compound with metal carbonyls can also lead to reformation of the Mo_2P_2 moiety, for example, in **355**, whilst deprotonation and reaction with $PhPCl_2$ affords the unusual complex **356**, formed by oxidative scission of the Mo–Mo bond and further reaction with **351**.[1064]

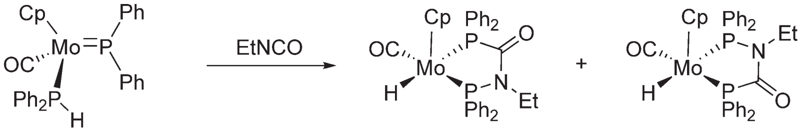
PY_2 and PY complexes – preparation. The reactivity of CpMo compounds toward elemental phosphorus has been subject to much study, and the formation of naked phosphorus ligands[1065] and P_n clusters[1041,1042] has been documented. Cationic phosphenium compounds have also been studied in some detail, and have been recently reviewed.[1066] The use of P═C and P≡C moieties in the synthesis of ring and cage structures assisted by transition metals has also been reviewed.[1067] Examples of $[(\eta^5\text{-}RC_5H_4)_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}P_2)]$ (R = COMe; CO_2Me) have been prepared.[1065] The usual method of synthesizing P═C complexes is either by decarbonylation of M-PHR, or by dehydrohalogenation of bifunctional complexes $[Cp(OC)_2(H_2RP)M\text{-}Cl]$, and both of these methodologies have been used to synthesize $[Cp(OC)_2M{=}PHMes^*]$.[1068] This complex displays further reactivity at the P–H function.



Scheme 40

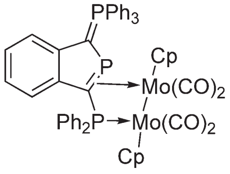
Reactivity of PY$_2$ and PY complexes. [Cp$_2$(CO)$_4$Mo$_2$((μ-η^2:η^2-P$_2$)] reacts with AgOTf, AgNO$_3$ and CuBr to give well-ordered assemblies and one and two-dimensional polymers, where the P$_2$ ligand acts as a bridge. These compounds were characterized crystallographically.[1069] Thermolytic reaction of [Cp(CO)$_2$M(η^3-P$_3$)] with [M$^1{}_2$Cp$_2$(CO)$_4$] (M = M^1 = Mo or W) afforded the dimetallic complexes [Mo$_n$W$_{(2-n)}$Cp$_2$(CO)$_4$(μ-η^2:η^2-P$_2$)] (n = 0–2) and the tri-metallic complexes [Mo$_n$W$_{(3-n)}$Cp$_3$(CO)$_6$(μ_3-P)] (n = 0–3). These trimetallic species were readily oxidized by atmospheric oxygen in solution to the corresponding complexes containing the μ_3-PO ligand, [Mo$_n$W$_{(3-n)}$Cp$_3$-(CO)$_6$(μ_3-PO)] (n = 0–3), some of which have been characterized by X-ray diffraction.[1070]

The reactivity of transition metal phosphenium (M=P) systems is characterized by the reactivity of the M=P double bond. Reaction types typically follow coupling reactions of the phosphorus function. [2 + 2]-Cycloadditions with a variety of different substrates have been observed, for example, [Cp(OC)$_2$M=P(o-Tol)Ph] (M = Mo, W) with the isocyanate EtNCO leads to the formation of the four-membered phosphametallacycles with high diastereoselectivity.[1071] [3 + 2]-Cyclization reactions have been observed upon treating the phosphenium complex [Cp(CO)(HPh$_2$P)M=PPh$_2$] with EtNCO (Equation (114)). The complexes exist in a 5 : 2 ratio, and hydride/halide exchange is observed upon dissolution in CCl$_4$.[1072]



(114)

Five-membered cyclic phosphametallacycles, [Cp(CO)$_2$M{P(^{t}Bu)$_2$N(H)N=C(CO$_2$Et)}], are formed from the reaction of [Cp(OC)$_2$M=P(^{t}Bu)$_2$] (M = Mo, W) with ethyl diazoacetate.[1073] Cycloaddition reactions are also observed with other reactive functional groups present, for example, [Cp(OC)$_2$M=P(H)^{t}Bu] (M = Mo, W), reacts with isothiocyanate, with an additional insertion into the PH bond, yielding the cycloadducts [Cp(OC)$_2$M-P[C(S)NHR](t-Bu)-C(=NR)-S] (M = Mo, W; R = Me, Et, ^{t}Bu) with high diastereoselectivity.[1074] However, it must be noted that the low steric shielding in the compound [Cp(OC)$_2$M=P(H)^{t}Bu] means that the M=P moiety is unstable and only enables this to be used *in situ*. Increasing the steric bulk to an Mes* group enables the isolation of stable H-substituted sp^2 hybridized phosphenium systems, thus allowing the reactivity patterns to be studied in greater detail.[1068] Coordination to the metal through the P═C bond has also been observed in **357** and **358**.[1075]



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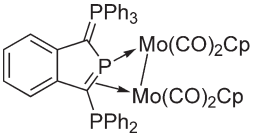
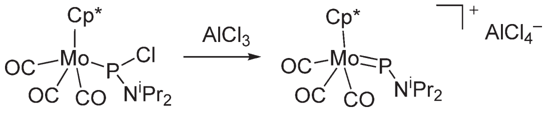


358

Electrophilic phosphinidenes have been synthesized[1076,1077] (Equation (115)) and shown to have reactivity similar to Fischer carbenes, in that nucleophilic attack is at the phosphorus center as opposed to the metal centered attack of nucleophilic phosphinidene complexes. Of note is the decrease in M═P bond length ($\Delta d_{M═P} = 0.069$ Å) on substitution of a carbonyl ligand for Et$_3$P in [Cp*Mo(CO)$_3${PN^{i}Pr$_2$}][AlCl$_4$].[1078]

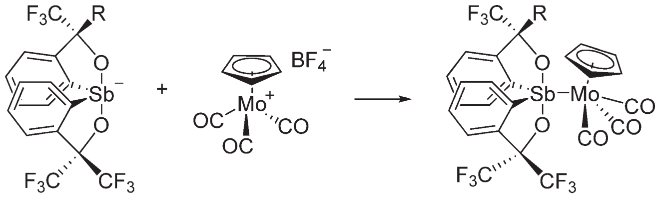


(115)

CpMo As–Bi compounds – preparation. The synthesis and reactivity of transition metal–group 15 element cluster compounds has been the subject of an extensive review.[1079] Also reviewed is the chemistry of mixed group 15–group 16 compounds (e.g., "AsS") and their coordination chemistry.[1080] A synthetic strategy for the preparation of M–Sb bonds via the reaction of Sb(CF$_3$)$_3$ with various Tm–H species has been reported. In the case of CpM(CO)$_3$H (M = Cr, Mo, W), the anticipated compound is formed, but slow decomposition occurs (Equation (116)). Nevertheless, spectroscopic data support the formulation, and a crystal structure analysis of the W compound has been presented.[1081]

$$[\mathrm{CpM(CO)_3H}] + \mathrm{Sb(CF_3)_3} \longrightarrow [\mathrm{Cp(OC)_3M{-}Sb(CF_3)_2}] \tag{116}$$

The coordination chemistry of a series of pentavalent hypercoordinate antimony ligands has been investigated. Thus, **359** reacts with [CpMo(CO)$_3$][BF$_4$] to form stable **360** (Equation (117)).[1082] The complex [{Cp″Mo(CO)$_3$}BiCl$_2$] (Cp″ = C$_5$H$_5$Bu$^t{}_2$) has been prepared via a two-step synthesis as this complex could not be formed from reaction of the [CpMo(CO)$_3$]$_2$ with BiCl$_3$ (Equation (118)).[1083] This compound was also reported to decompose in THF solutions to form the structurally characterized ionic compound [(Cp″Mo(CO)$_2$(μ-Cl)$_3$]$_2$[Bi$_2$Cl$_8$(THF)$_2$]. [CpMo(CO)$_3$]$_2$BiCl and [CpMo(CO)$_3$]BiCl$_2$ have also been prepared by reaction of elemental bismuth with tricarbonylcyclopentadienylmolybdenum chloride in DMSO.[1084] The thiolate group in the bismuth complex Bi(SC$_6$F$_5$)$_3$ can be described as a pseudohalide, which has been demonstrated by the reaction with [{CpMo(CO)$_3$}$_3$Bi] to form [{CpMo(CO)$_3$}$_2$Bi(SC$_6$F$_5$)], which is analogous to the reaction with BiCl$_3$.[1085]



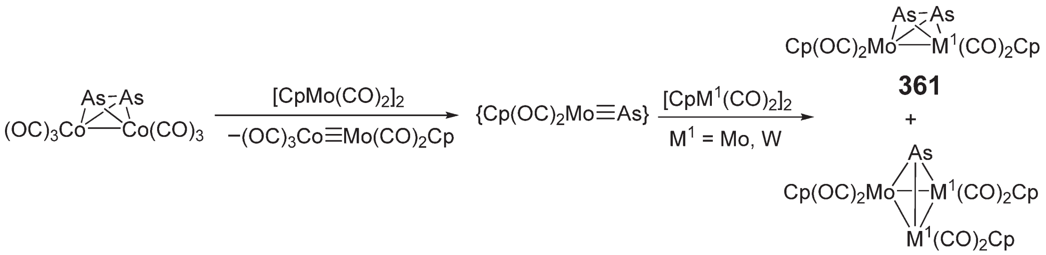
R = CF$_3$, Me

359 **360**

(117)

$$2\mathrm{K[Cp''Mo(CO)_3]} + \mathrm{BiCl_3} \longrightarrow [\{\mathrm{Cp''Mo(CO)_3}\}_2\mathrm{BiCl}] \xrightarrow{\mathrm{BiCl_3}} 2[\{\mathrm{Cp''Mo(CO)_3}\}\mathrm{BiCl_2}] \tag{118}$$

Unsubstituted or "naked" group 15 element complexes are a topic of much interest, as a wide variety of structural motifs are possible. An unusual synthesis of [Mo$_2$(μ-As$_2$)Cp$_2$(CO)$_4$] via transfer of As$_2$ from [Co$_2$(μ-η^2:η^2-As$_2$) (CO)$_6$] has been reported; this is an interesting development as As$_2$ is only available in the vapor phase. Further heterobi- and trimetallic systems can also be formed via this reaction. Co-thermolysis of [CpMo(CO)$_3$]$_2$ with [CpW(CO)$_3$]$_2$ and gray arsenic affords **361** and four trimetallic products, $[MM^1_2(\mu_3\text{-As})Cp_3(CO)_6]$, in low to reasonable yields (Equation (119)). These are thought to progress via M≡As intermediates.[1086] Also studied is the reactivity of K_3ES_3 (E = As,[1087] Sb[1088]) toward $[Cp^*Mo(CO)_3Cl]$ to yield fragments containing the As_2S_3 or SbS moiety amongst others. The products obtained proved to be strongly dependent on reaction conditions. DFT calculations were carried out on $[Cp^*Mo(CO)_3SbS]^-$.[1088] A further report on the synthesis of naked Sb clusters occurs on thermolysis of $[CpM(CO)_3]_2$ (M = Mo, W) with antimony powder to form an unusual complex **362** where coupling of two Cp ligands to form a fulvalene ligand has occurred.[1089]



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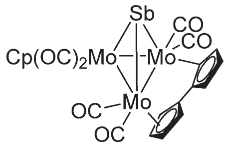
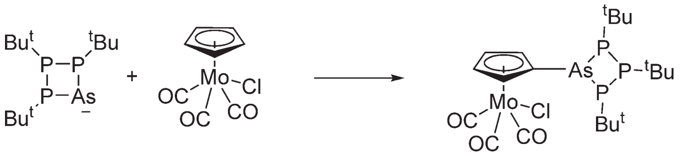


362

The reactions of $[R_nE_n]^-$ anions have been well documented. The reactions of $[(^tBuP)_3As]^-$ anion with $[CpM(CO)_3Cl]$ (M = Mo, W) unexpectedly give **363** as a result of nucleophilic addition to the C_5H_5 ring, rather than the expected substitution product (Equation (120)).[1090] $[(^tBu_3Sb_4)Mo(CO)_3Cp]$ has been formed from the reaction of $^tBu_4Sb_4$ and $[CpMo(CO)_3]_2$,[500] whilst $[CpMo(CO)_2]_2Sb_2$, $[CpMo(CO)_2Sb_3]$ (Cp = Cp, Cp*), and an organo-Sb ring, $[Cp^*Mo(CO)_3(^tBu_3Sb_4)]$, have also been isolated.[1091,1092]



363

(120)

The study of high oxidation state group 15 elements with transition metal fragments is relatively unexplored, probably due to the reducing conditions provided by the transition metal moieties. For example, antimony is reduced when $[SbPh_2BrO]_2$ is treated with $Na[CpMo(CO)_3]$ to produce $[\mu\text{-}SbPh_2]_2[Mo(CO)_2Cp]_2$. The solid-state structure shows bridging diphenylstibido groups between two $CpMo(CO)_2$ moieties giving a central “butterfly” Sb_2Mo_2 ring. The Mo–Sb and Sb–Sb separations are both short, but there is no Sb–Sb bond present.[1093]

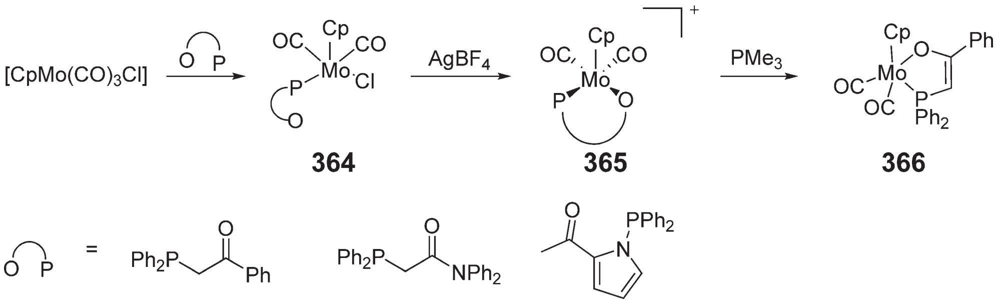
Properties of CpMo As–Bi compounds. The complex $[\{CpMo(CO)_3\}_2BiCl]$ has been structurally characterized and shows weak asymmetric Bi··Cl interactions that aggregate the molecule into dimers. The authors suggest that this interaction is of the same order of magnitude as crystal packing forces, by comparison to the isoelectronic manganese complex.[1094] Complex **360** is of interest because the pseudorotation barrier can be measured by NMR spectroscopic investigations. It was found that the pseudorotation is intramolecular and much higher in energy than in cases with carbon or halide substituents. Also evident was the strongly electron-donating nature of the $CpMo(CO)_3$ fragment and the strong preference for equatorial bonding to the antimony centre.[1082,1095]

Reactivity of CpMo As–Bi compounds. $[\{Cp(CO)_3Mo\}_2SbCl]$ has been reported to react with elemental chalcogens E (E = S, Se) and various chalcogen compounds (e.g., $E(SiMe_3)_2$, Na_2E, NaSeMes, and $LiSe^tBu$) to form a variety of new clusters $[\{Cp(CO)_3Mo\}_2Sb]_2S$, $[\{Cp(CO)_3Mo\}_2Sb_3\{Mo(CO)_2Cp\}]$, $[\{Cp(CO)_2Mo\}_2SeSbCl]$, and $[\{Cp(CO)_2Mo\}_2\text{-}SeSb\{MoCp(CO)_3\}]$. These were characterized by X-ray crystallography.[1096]

The reaction of $[\{Cp''Mo(CO)_3\}BiCl_2]$ with $Na_2[Fe(CO)_4]$ or $Na_2[W(CO)_5]$ affords the *arachno*-cluster $[\{Fe_2(CO)_6\}\{Fe(CO)_4\}\{\mu_3\text{-}BiMo(CO)_3Cp''\}_2]$ or $[\{Cp''Mo(CO)_3\}_2BiCl]$, respectively. The former has been structurally characterized and shows typical Mo–Bi bond lengths (Mo–Bi = 2.915(2) Å), although it displays a different structural motif to the related $[\{Fe_3(CO)_9\}\{\mu\text{-}BiFe(CO)_2Cp''\}_2]$.[1083]

5.06.3.1.8.(iii).(h) Group 16 complexes

CpMoCO compounds of O donor ligands. As is the case for $[Mo(CO)_6]$, there are few examples of oxygen-donor ligands for this class of compound, no doubt because of the relative mismatch between the hard O ligands and the soft transition metal. Reaction of a series of bidentate keto-phosphine ligands with $[CpMo(CO)_3Cl]$ (Cp = Cp, Cp^*) affords first the P-coordinated complex **364**, but the chelation occurs upon treatment with $AgBF_4$ to form **365**. Substitution of the keto-bound group with monodentate phosphines has been observed; however, **366** is formed by deprotonation with PMe_3 (Equation (121)).[1097,1098]

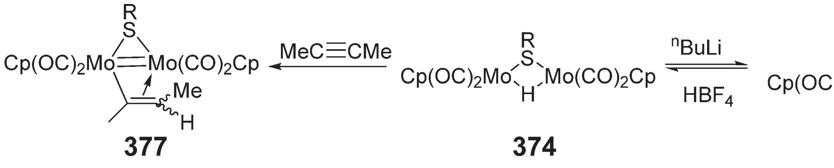


364 **365** **366** (121)

Interesting chemistry has been observed from the reaction of $[CpMo(CO)_2]_2$ with the tetraethyl pyrophosphite ligand $\{(EtO)_2P\}_2O$ (Scheme 41). The simple adduct **367** is first formed which can then be thermally decarbonylated to give **368** via oxidative addition of a P–O bond to the Mo–Mo center. This reacts with CO to give **369** which is thermally or photolytically reversible. Photolytic decarbonylation of **367** is less selective and mixtures of products are formed.[1099] Structure **368** shows addition at the Mo═Mo bond to form **370** and **371**, P–O reductive elimination or insertion into an Mo–P **372** or M–O bond **373**.[1100]

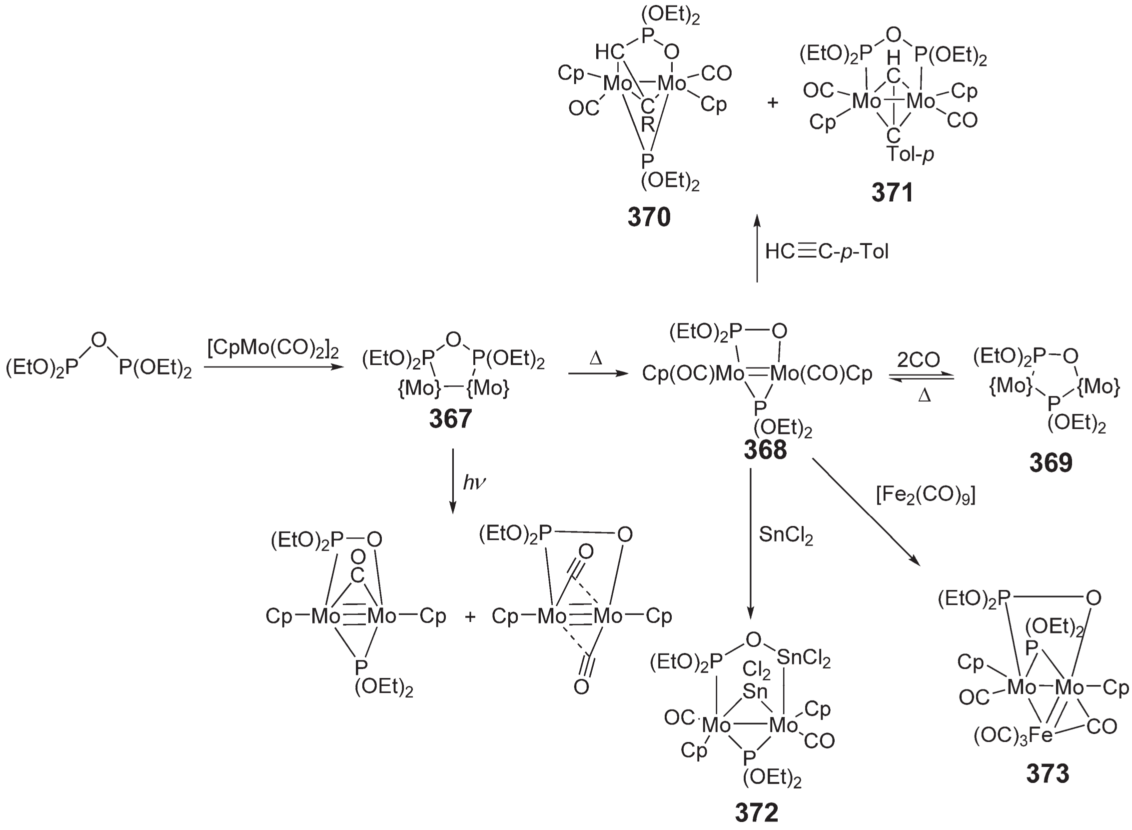
Molybdenum hydroxy compounds are known. For example, treatment of $Mo_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)][B(ArF)_4]$ with water gives the hydroxo complexes $[Mo_2Cp_2(\mu\text{-}OH)(CO)_2(\mu\text{-}dppm)][B(ArF)_4]$ and $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}OH)(CO)_2(\mu\text{-}dppm)][B(ArF)_4](OH)$, the former being an intermediate in the hydrolysis reaction.[1028]

CpMoCO compounds of S donor ligands – synthesis. Oxidative addition of RSH to $[CpMo(CO)_2]_2$ affords good yields of **374** (Equation (122); R = Me, ^{t}Bu, Ph, Bz). The corresponding reaction with $[Cp^*Mo(CO)_2]_2$ does not afford the analogous products.[1101] This study has been extended to oxidative addition of Me_2S_2 to $[Cp^*Mo(CO)_2]_2$ to afford $[\{Cp^*Mo(CO)_2\}_2(\mu\text{-}SMe)(\mu\text{-}S)]$ rather than $[Cp^*Mo(SR)_2]$, the analog of which is obtained using the unsubstituted Cp ligand. The compounds $[\{Cp^*Mo(CO)_2\}_2(\mu\text{-}ER)_2]$ (ER = SPh, SBz, SeMe, SePh) can also be synthesized via the same methodology,[1102] and $[\{CpMo(CO)_2\}_2(\mu\text{-}SBz)_2]$ structurally characterized.[1103] Unusually, the complex $[\{CpMo(CO)_2\}_2(\mu\text{-}SPh)_2]$ has also been synthesized from $[(\eta^5\text{-}RC_5H_4)Mo(CO)_2]_2$ (R = H, MeCO) and the Fe/S butterfly compound $[Fe_2(CO)_6(\mu\text{-}PhS)_2]$ in refluxing xylene. This compound exists as *trans/anti-* and *trans/syn-*isomers (with respect to the relative arrangement of the Cp and CO ligands, and the mutual orientation of the Ph groups on the bridging S atoms) for R = MeCO are interconvertible.[1104] Dinuclear molybdenadithiolate compounds can be prepared in a one-pot reaction of $[CpMo(CO)_3]_2$, elemental sulfur, and DMAD via thermal activation to give $[CpMo(CO)_2\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2MoCp]$, or photolytically to form mainly isomeric $[CpMo(CO)\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2\text{-}Mo(CO)Cp]$.[1105]



377 **374** **378** (122)

The thermal reaction of $[CpMo(CO)_3H]$ with Me_2S_2 and allyl chloride has been reinvestigated. The expected $[Cp_2Mo_2(\mu\text{-}SMe)_3(CO)_2]Cl$ was isolated, along with the new trinuclear complex

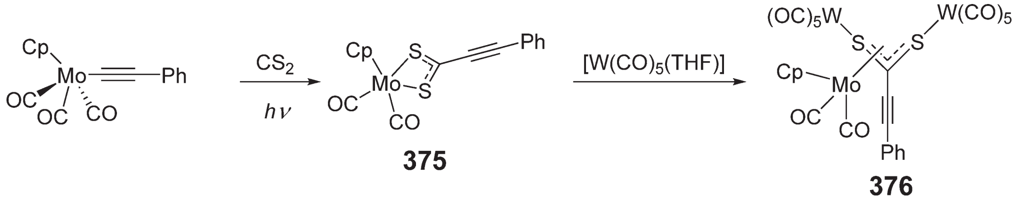


Scheme 41

$[CpMo(CO)(\mu\text{-}SMe)_3Mo(CO)_2(\mu\text{-}SMe)Mo(CO)_2Cp]$. The solid-state structure of this Mo_3 species contains a $Cp(CO)Mo(\mu\text{-}SMe)_3Mo(CO)_2$ core with an $Mo{\equiv}Mo$ bond of normal length (2.800(1) Å), linked to a $CpMo(CO)_2SMe$ unit via the sulfur atom and an unusually long Mo–Mo bond of 3.115(2) Å.[1106] A new method of synthesizing $[CpMo(CO)_3SH]$ by reaction of the corresponding $[C_5R_5M(CO)_3H]$ with $Ph_3Sb{=}S$ has been reported (R = H, Me).[1107] Reaction of $[CpMo(CO)_3Cl]$ with $Tl[SC_6F_4H\text{-}4]$ affords the salt metathesis product $[CpMo(CO)_3(SC_6F_4H\text{-}4)]$ and $Tl[CpMo(CO)_2(SC_6F_4H\text{-}4)_2]$. ^{19}F NMR spectroscopy shows a dynamic process in the Tl complex, which on the basis of previous studies of the SC_6F_5 analogues involves Tl dissociation and aryl rotation and/or sulfur inversion.[1108]

An unusual method of synthesizing molybdenum thiolates has been reported by treatment of $[Mo(CO)_3(NCMe)_3]$ with $[Na][C_5H_4SR]$ (R = Me, Ph, Bz, tol) via C–S bond cleavage to form $[Cp(CO)Mo(\mu\text{-}SR)_3Mo(CO)_3]$ in low yields. When more than 1 equiv. of the thiolate is added, $[Cp(CO)Mo(\mu\text{-}SPh)_3Mo(CO)(SPh)_2]$ can also be isolated.[1109]

Photolysis of the alkynyl complex $[CpMo(CO)_3(C{\equiv}CPh)]$ with CS_2 affords **375**, which has been structurally characterized and confirms the insertion of CS_2 into the M–C bond. Treatment with $\{W(CO)_5\}$ isomerizes the ligand from η^2 to η^3 and the formation of **376** (Equation (123)).[1110]



(123)

Unusual ring opening of cyclic thiolates has been observed upon reaction with $[CpMo(CO)_2]_2$, which is similar to reactivity observed with heterobinuclear compounds (see Scheme 19 in Section 5.06.3.1.3).[1111]

Properties of CpMoCO compounds of S donor ligands. Structure **374** shows dynamic behavior in the NMR spectra. This is thought to involve *cis–trans* isomerization with a low-energy barrier ($\Delta G = 50$–$64\,\mathrm{kJ\,mol^{-1}}$).[1101] The bond strength of the M–S bond in $[(C_5R_5)Mo(CO)_3SPh]$ (R = H, Me) was measured to be ~159–171 $\mathrm{kJ\,mol^{-1}}$ from a thermochemical study.[1112] This study has been expanded to investigate the M–SH bond strengths for the complexes $[Cp^*M(CO)_3SH]$, which increase in the order Cr(192) < Mo(230) < W(263) ($\mathrm{kJ\ mol^{-1}}$). The pK_a value of $[Cp^*Mo(CO)_3SH]$ (pK_a = 13) is at least 4 pK_a units less acidic than that of $[Cp^*Mo(CO)_3H]$ (pK_a = 9.2).[1107] The electrochemical behavior of complexes possessing bridging thioether ligands, for example, $[Cp_2Mo_2(CO)_2(\mu\text{-SMe})(\mu\text{-SMe}_2)]^+$, $[Cp_2Mo_2(CO)_2(\mu\text{-SMe}_2)_2]^{2+}$, and their corresponding Cp* analogues have been reported and shown to go via S–C bond cleavage.[1113,1114]

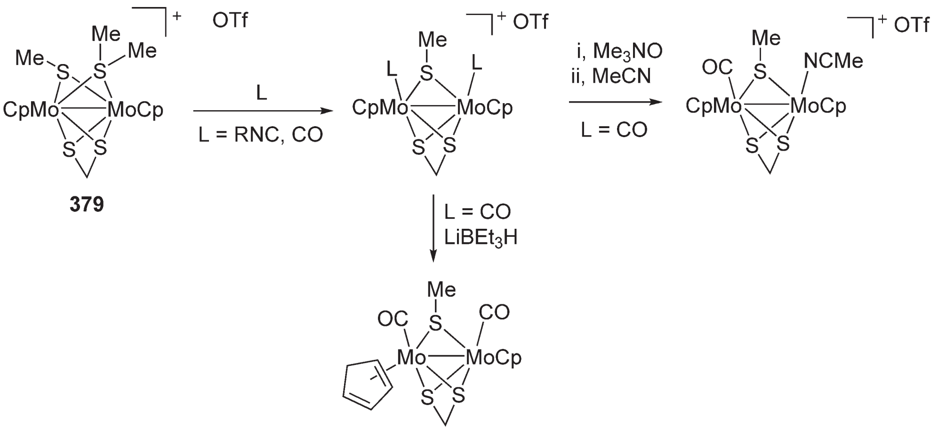
Reactivity of CpMoCO compounds of S donor ligands. The reactivity of **374** (R = Me, Ph) toward alkynes has been examined (Equation (122)). Under photolytic activation in the presence of alkynes, a formal insertion of the alkyne into the Mo–H bond forms **377**. Deprotonation to form **378** and further reactivity has also been studied.[1115]

$[\{Cp^*Mo(CO)_2\}_2(\mu\text{-SMe})(\mu\text{-SMe}_2)_2]^{2+}$ reacts with electrophilic reagents to form $[Cp^*{}_2Mo_2(CO)_2(\mu\text{-SMe})_2(\mu\text{-SH})]X$ (X = BF_4, Cl, F), stereospecifically as the *cis*-isomers.[1102] Reactions with halogens and alkyl halides RCH_2X give $[Cp^*{}_2Mo_2(CO)_2(\mu\text{-SMe})_2(\mu\text{-SR})]X$ (R = I, X = I_5, R = Cl, Br, CN, C≡CH, CO_2Me, ^{i}Pr).[1116] The reactivity of complex **379** with a variety of electron donors has been extensively examined (Scheme 42).[1117]

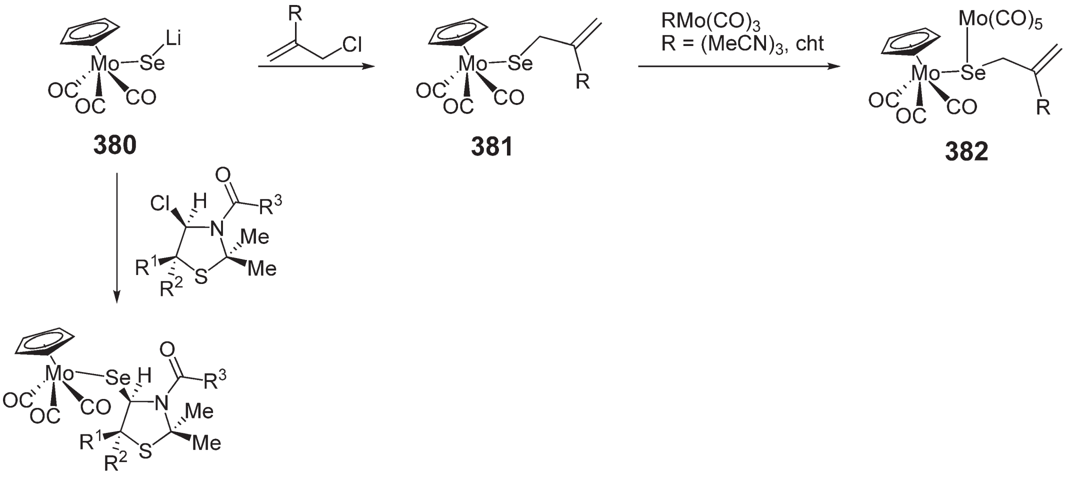
Reaction of $[\{CpMo(CO)_2\}_2(\mu\text{-SR})_2][BF_4]_2$ with cyanide ions gave the corresponding cyanide complexes *trans*-$[Cp_2Mo_2(CO)(CN)(\mu\text{-SR})_2]^-$ (R = Me, ^{i}Pr, ^{t}Bu, Ph, or CF_3). The nature of the R group has crucial influence on the site of the reaction of these cyanide complexes with Me_3O^+. S-methylation occurred with R = Me, ^{i}Pr (*syn*- and *anti*-isomers), or Ph (*anti*-isomer), whereas N-methylation was observed for R = Ph (*syn*-isomer) or CF_3 (*anti*- and both *syn*-isomers). This can be ascribed to electronic effects of the R groups, which control the site of methylation by switching the reaction from orbital control (S-methylation) to charge control (N-methylation).[1118] Reaction of $[\{Cp'Mo(CO)_2\}_2(\mu\text{-SR})_2][BF_4]_2$ with azido species forms isocyanate complexes $[Cp'{}_2Mo_2(NCO)(CO)_3(\mu\text{-SR})_2][BF_4]$ (Cp′ = C_5H_5, R = Me, Ph; Cp′ = C_5Me_5, R = Me).[1119]

$[Mo_2Cp_2(\mu\text{-SMe})_3(NCCH_3)_2][BF_4]$ reacts with $H[BF_4]$ in acetonitrile to give the tetrakis(acetonitrile) complex $[Mo_2Cp_2(\mu\text{-SMe})_2(NCCH_3)_4][BF_4]_2$. However, $[Mo_2Cp_2(\mu\text{-SMe})_3(CO)_2]^+$ does not undergo this reaction, indicating that the electronic properties of the ancillary ligands L in the $[Mo_2Cp_2(\mu\text{-SMe})_3L_2]^+$ moiety govern the activation of a sulfur atom in protonation reactions.[1120]

CpMoCO compounds containing Se or Te. A review on the chemistry of transition metal selenato and telluro compounds[550] and a comprehensive review on the synthesis and properties of telluroether, anionic organotellurium and inorganic tellurium (halotellurium, telluride, and polytellurides) ligands[1121] have been published, to which the reader is referred for general information. The majority of the literature concerning Mo–Se and Mo–Te species refers to heteronuclear cluster compounds, and is outside the scope of this chapter. Reaction of allylic halides (R = H, Me) with **380** affords the monomeric propeneselenato compound **381**, which slowly decomposes in solution to form dimeric $[Cp(OC)_2MoSeCH_2CR{=}CH_2]_2$. Compound **381** also reacts with Mo(0) species to form mixed oxidation state dimer **382**, by an unknown mechanism (Scheme 43).[1122] Complex **380** also reacts with N-acyl-4-chlorothiazolidines (R^1, R^2 = Me, $(CH_2)_5$; R^3 = Me, Ph) to form **383**, which are organometallic derivatives of the biologically



Scheme 42



Scheme 43

relevant thiazolidine N/S-heterocycles.[1123] Reactions of [(η^5-RC_5H_4)$_2$$Mo_2(CO)_6$] (R = CH_3CO, PhCO, CH_3O_2C, EtO_2C) with diphenylditelluride in the presence of $^nBu_4NI$ have been reported to give mononuclear and binuclear complexes [$CpMo(CO)_3Te$] and [Cp_2Mo_2(μ-Te)$_2$(μ-TePh)$_2$] (M=M), depending on the substituents on the Cp rings.[1124] The analogous Mo≡Mo species [(η^5-RC_5H_4)$_2$$Mo_2(CO)_4$] also react with Ph_2Te_2 to give [(η^5-RC_5H_4)$_2$$Mo_2(CO)_4$($\mu$-TePh)$_2$] (R = H, Me_3Si, MeCO), whilst the reaction of [(η^5-MeC_5H_4)$_2$$Mo_2(CO)_4$] with Ph_2Te_2 gives [(η^5-MeC_5H_4)$_2$$Mo_2(CO)_4$-($\mu$-TePh)$_2$] and an unexpected triply bridged complex [(η^5-MeC_5H_4)$Mo_2(CO)_4$(μ-TePh)$_3$].[1125] The thermal reaction of [(η^5-RC_5H_4)$_2$$Mo_2(CO)_4$] with [$Fe_2(CO)_6$($\mu$-PhSe)$_2$] affords selenolato-bridged bimetallic complexes [(η^5-RC_5H_4)Mo(CO)(μ-SePh)]$_2$ (R = MeCO, MeO_2C), whilst under UV irradiation a trimetallic cluster is isolated.[1126]

5.06.3.1.8.(iii).(i) CpMo(CO)$_3$X

Preparation. The standard synthetic routes to halo-compounds are by oxidation of [$CpMo(CO)_3$]$_2$, [$CpMo(CO)_3$]$^-$, or [$CpMo(CO)_3H$] with typical halogenating agents such as X_2, PX_3, alkyl halides, or NBS. Some examples are given in Table 14.

The reactivity of [(C_5Bz_5)$Mo(CO)_3Me$] toward chlorinating agents has been investigated, and the products obtained are dependent on the nature of the chlorinating agent. Thus, with $PhICl_2$ the replacement of the Me group for a Cl is first observed, and on further treatment with $PhICl_2$ decarbonylation occurs to form [(C_5Bz_5)$MoCl_4$]. However, with PCl_5 as the chlorinating agent, the unusual [(C_5Bz_5)Mo(η^2-$COCH_3$)Cl_3] is isolated.[1127] Chiral indenyl compounds have been synthesized, and the oxidation of the lithium salt with iodine affords the expected iodo compound, whilst the use of allyl chloride gives the η^3-allyl derivative.[1128]

The heterogenization of [$CpMo(CO)_3X$] onto silica supports has been reported and these compounds found use in olefin epoxidation catalysis.[1132]

Coordinatively unsaturated compounds of the type [$CpMo(CO)_2X$] have been postulated as intermediates in a number of thermal and photochemical reactions, but have yet to be isolated. Therefore, DFT calculations have been performed on these compounds (X = halogen, H, CN, CH_3) and the dependence on the geometry and substituent effects rationalized.[1133]

Table 14 Synthesis of [(C_5R_5)$Mo(CO)_3X$] complexes

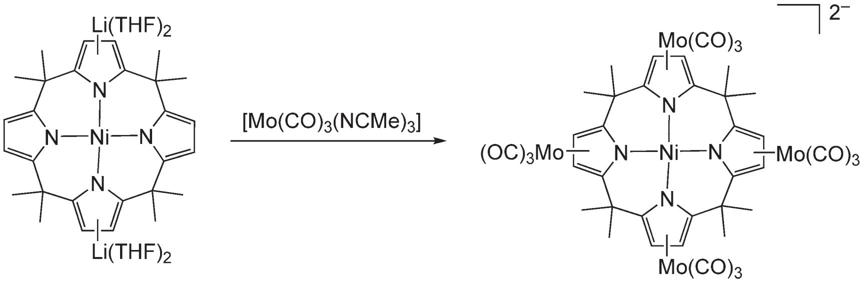
Complex	*Starting material*	*Oxidizing agent*	*Comments*	*References*
[(C_5Bz_5)$Mo(CO)_3Cl$]	[(C_5Bz_5)$Mo(CO)_3Me$]	$PhICl_2$	X-ray structure	1127
[(2-Menthlyindenyl)$Mo(CO)_3I$]	Li[(2-menthlyindenyl)$Mo(CO)_3$]	I_2	X-ray structure	1128
[($C_5H_4{}^tBu$)$Mo(CO)_3Cl$]	[($C_5H_4{}^tBu$)$Mo(CO)_3H$]	CCl_4		1129
[Mo(1,2-$C_5H_3{}^tBu_2$)$(CO)_3Br$]	[M(1,2-$C_5H_3{}^tBu_2$)$(CO)_3$]$_2$	Br_2		1130
[(C_5Ph_5)$Mo(CO)_3Cl$]	Li[(C_5Ph_5)$Mo(CO)_3$]	PCl_3		1131

5.06.3.1.9 Pentadienyl complexes

There have been few reports on the chemistry of pentadienyl molybdenum carbonyl **384**.[1134] It has been shown that in most cases the reactivity is very similar to Cp counterparts, but some unusual products were also observed upon reaction with alkyl halides, probably due to the greater reactivity of these open Cp-type ligands (Scheme 44).

5.06.3.1.10 Heteroatom-substituted η^5-ligands

Few examples of heteroatom-substituted ligands display an η^5-coordination mode. Phospholes have been discussed in Section 5.06.2.4.3.(ii). An example of a pyrrole binding to molybdenum is shown in the reaction of the nickel porphyrin complex **385**, which binds 2 or 4 equiv. of the Mo(CO)$_3$ fragment, for example, **386** (Equation (124)).[1135]



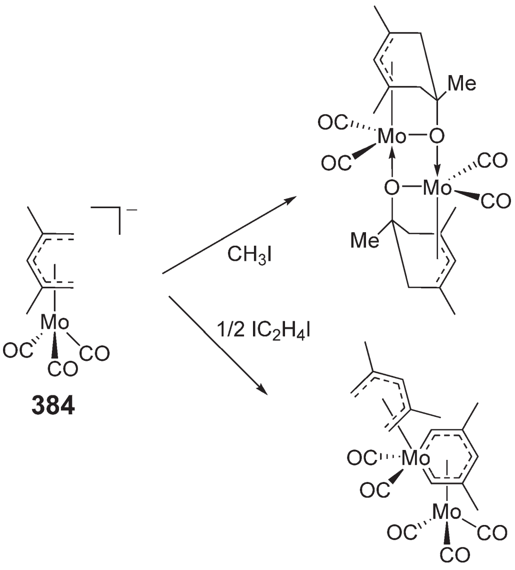
385 **386**

(124)

5.06.3.1.11 Carbon-based η^6-ligands

5.06.3.1.11.(i) Mo η^6-arene compounds

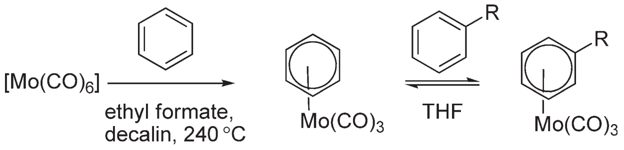
Synthesis. In contrast to the vast amount of literature on Cr–arene complexes, the study of Mo–arene compounds is substantially less well investigated.[1136] One of the major reasons for this is the higher sensitivity toward oxygen and the longer reaction times required in comparison to the Cr derivatives making the thermal syntheses lower yielding. Additionally, the Mo–arene bond is more labile than that of the Cr–arene bond, again complicating the synthesis and isolation of these compounds. The synthesis of **387** has been optimized for almost quantitative isolated yields; from this starting material, improved synthetic procedures have been reported that give high yields for substituted arenes via THF displacement of the aryl ligand in [(C$_6$H$_6$)Mo(CO)$_3$] (Equation (125)).[1137] Other methods have involved the replacement of the labile Py or DMF ligands in [Mo(CO)$_3$L$_3$] with arenes in the presence of the Lewis acid BF$_3$·OEt$_2$ and some examples are given in Table 15.



Scheme 44

Table 15 Synthesis of [(arene)Mo(CO)$_3$] complexes

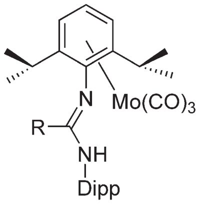
Starting material	*Arene*	*Yield (%)*	*References*
[Mo(CO)$_3$(DMF)$_3$]	1,3,5-Triphenylbenzene	40	1138
[Mo(CO)$_3$(DMF)$_3$]	$C_6F_5CF_3$	56	1138
[Mo(CO)$_3$(MeCN)$_3$]	1,2,4,5-tetrakis(bromomethyl)benzene		1139
[Mo(CO)$_3$(py)$_3$]	$MeC_6H_4EMe_3$ (E = Si, Sn)	40	1140
[Mo(CO)$_6$]	$Me_3SiSiMe_2C_6H_5$	22	1141



387

(125)

Other examples have been reported where η^6-coordination to an arene substituent is favored over coordination by other donor ligands, for example, in guanidine compound 388,[1142,1143] or in [Mo{(Ph)$_2$POC$_6$H$_3$(Ph)(η^6-Ph)}(CO)$_2$].[1144] In other cases, subtle effects can dictate the preferred bonding modes, for example, either η^6-arene coordination in 389 or η^1-N coordination in 390 have been observed on slight changes of the ligand.[1145] Relatively few examples of binuclear complexes are known. The synthesis of [M$_2$(η^6:η^6-C$_6$H$_5$-C$_6$H$_5$)(CO)$_6$] (M = Cr, Mo, W) has been reported (Equation (126)) and these complexes characterized by NMR and CV spectroscopy. The CV spectrum shows that the dimolybdenum complex undergoes a single two-electron reduction at about the same potential as the corresponding dichromium complex, but the Mo dianion is less stable than the Cr analog.[1138]



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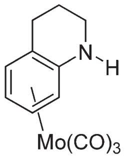

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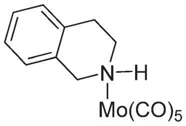


390

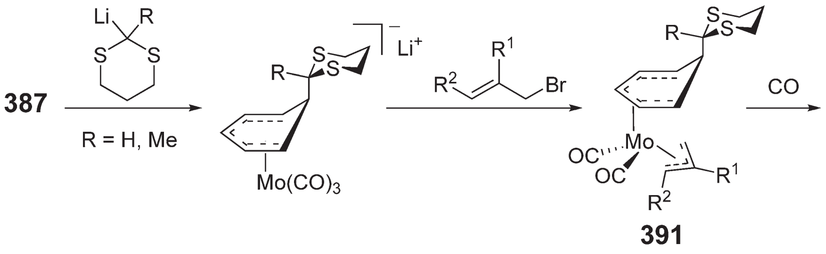
$$[(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3] + [(\eta^6\text{-}C_6H_5\text{-}C_6H_5)Mo(CO)_3] \longrightarrow [Mo_2(\eta^6{:}\eta^6\text{-}C_6H_5\text{-}C_6H_5)(CO)_6] \qquad (126)$$

Properties. [(η^6-arene)Mo(CO)$_3$] (arene = C$_6$H$_5$EMe$_3$; E = C, Si, Ge, Sn) complexes have been studied by multinuclear (^{1}H, ^{13}C, ^{95}Mo) NMR and IR spectroscopy. The substituents on the arene ring influence the ^{95}Mo NMR chemical shifts, and this has been interpreted as a balance between inductive effects and hyperconjugation from the substituents.[1140] ^{13}C and ^{95}Mo CP-MAS spectroscopy have been used to study the chemical shift and electric field gradient tensors, and DFT calculations also aid in the understanding of the small electric field gradient interaction at the central nucleus predicted previously in piano stool complexes.[1146] Additionally, the photoelectron spectra of [(arene)Mo(CO)$_3$] (arene = C$_6$H$_6$, mesitylene) and theoretical calculations on 387 have been reported.[1147] Cyclobutabenzenes and their group 6 complexes have also been studied via NMR spectroscopic techniques.[1148]

The photochemistry of [Mo(CO)$_6$] has been well developed (see Section 5.06.1.2), but in contrast that of [(arene)Mo(CO)$_3$] has been somewhat neglected. This is also surprising, as the chromium analogs have been thoroughly investigated. Using a combination of matrix isolation and time-resolved IR studies, a number of important differences have been observed with regard to [(arene)Cr(CO)$_3$]. The quantum yield of photo-extrusion of a CO molecule is markedly affected by the wavelength used, indicating that more than one excited state is possible for these compounds. The reaction of [(arene)Mo(CO)$_2$(solv)] (solv = range of alkane solvents) with other ligands occurs within 100–300 μs and the activation parameters indicate that an associative mechanism is the best description for the Mo and W cases.[1149] Photolysis of [(Mes)Mo(CO)$_3$] in a polyethylene matrix under high pressures of N$_2$ or H$_2$ affords mono-, bis- and tri-substituted products at room temperature, underlying the stabilizing effect of the mesityl group on N$_2$ and H$_2$ complexes.[59]

The study of [Mo(CO)$_6$] adsorbed onto solid supports have been of interest for a number of years (see Section 5.06.1.3), but only one investigation has been reported for [(arene)Mo(CO)$_3$] and studied by a combination of DRIFTS spectroscopy and Monte Carlo theory.[1150] Theoretical[1151] and experimental[1152] evidence for the η^6-coordination of fullerenes to an {Mo(CO)$_3$} fragment have also been described.

Reactivity. The use of [(arene)Cr(CO)$_3$] in organic synthesis is well documented, but the Mo analogs have been much less thoroughly studied. This is undoubtedly due to the high kinetic lability of the Mo–arene bond. However, it should be possible to identify intermediates that are not observed for the Cr reactions, as the Mo–C and Mo–H bonds are stronger. Indeed, there have been reports on the sequential nucleophilic and electrophilic addition to the benzene ligand in **387** (Equation (127)).[1153] The metal fragment can be removed by carbonylation to yield the *trans*-disubstituted allyl cyclohexadiene **392** in good overall yield. In this regard, it is important to note that the intermediate allyl complex **391** cannot be isolated in the reaction with the Cr analog.



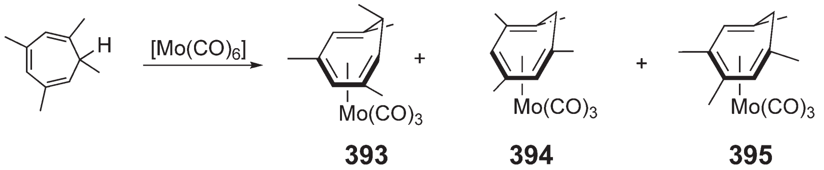
R^1 = R^2 = H; R^1 = Me, R^2 = H; R^1 = H, R^2 = Me

(127)

The use of [(arene)Mo(CO)$_3$] compounds in catalysis has been extensively investigated, and has been found to be an active catalyst for the polymerization of phenylacetylene[1154–1158] and hydrosilylation of dienes.[1159]

5.06.3.1.11.(ii) Cycloheptatriene ligands

Synthesis and properties. η^6-Cycloheptatriene complexes are not as well studied as their η^7-cycloheptatrienyl counterparts, although the preparation is simple enough for undergraduate studies.[1160] 1,3,5,7-Tetramethylcycloheptatriene reacts with [Mo(CO)$_6$] to form an inseparable mixture of three isomers, **394** and **395** arise from [1,5] hydrogen shifts from the original product **393** (Equation (128)). Substituents in the 1-position hinder the proposed transition state and as such, the formation of these isomers can be rationalized.[1161] The [1,5] hydrogen shift is also observed in the regioselective synthesis of molybdenum complexes of phosphine substituted cycloheptatriene ligands **396** (Equation (129)). Spectroscopic and structural characterization for R = Ph[1162] and ^{i}Pr[1163] has been reported. Reductive dimerization of an η^7-cycloheptatrienyl complex affords three isomers (*endo-endo*, *endo-exo*, and *exo-exo* with respect to the protons on the bridging C$_2$) of a bitropyl compound. The isomers have been identified by means of NMR spectroscopy, cyclic voltammetry, and a crystal structure determination of the *endo-endo* isomer **397** as its PPN salt (Equation (130)).[1164]



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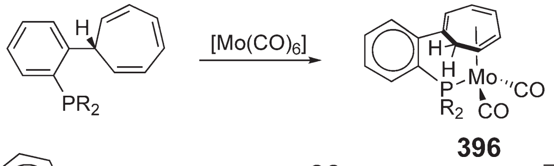

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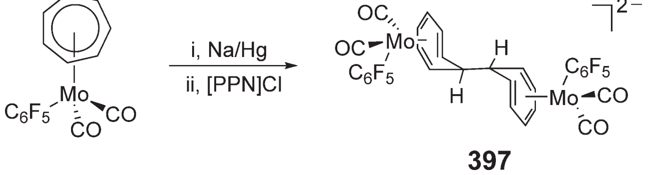
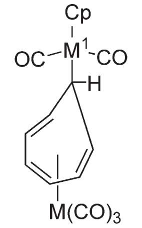


(130)

A series of heterobimetallic complexes has been synthesized based on cycloheptatriene. Reduction of a tropyne complex yields the bimetallic Pt–Mo compound **398**, which has been structurally characterized (Scheme 45).[1165] The 1,2,3,5-cycloheptatriene ring is the first example of this type, although attempts to remove the $Mo(CO)_3$ moiety failed. The two further byproducts **399** and **400** were independently synthesized by arene exchange reaction with the corresponding platinum cycloheptatriene complexes and $[(p\text{-xylene})Mo(CO)_3]$. **398** has also been examined by NMR spectroscopy and shown to be fluxional.[1166] Other examples with a cycloheptatriene ligand acting as an η^6:η^1 bridging ligand, for example, **401**, have been reported for $M = Cr$, Mo, W; $M^1 = Fe$, Ru.[1167] A further bimetallic complex $[(CO)_3M(\mu\text{-H})(\mu\text{-}C_7H_7)CoCp^*]$ has been prepared via a CH activation reaction of $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ and $[Cp^*Co(H_2C{=}CH_2)_2]$.[1168]

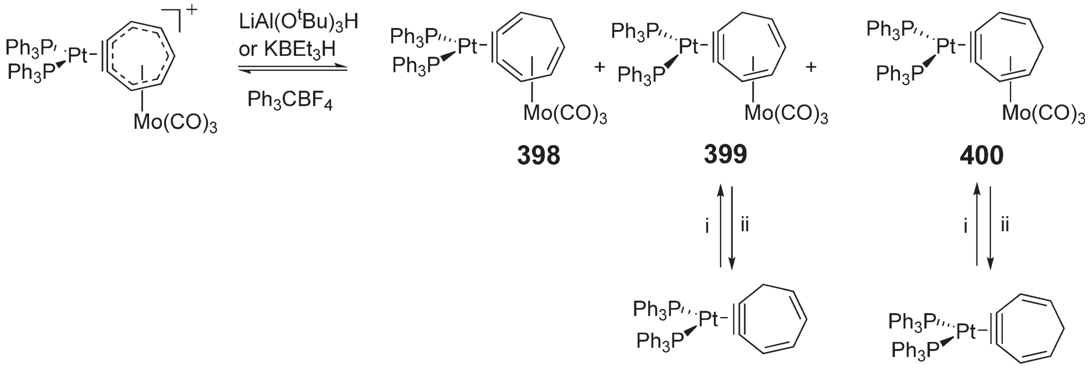


M = Cr, Mo, W; M^1 = Fe, Ru

401

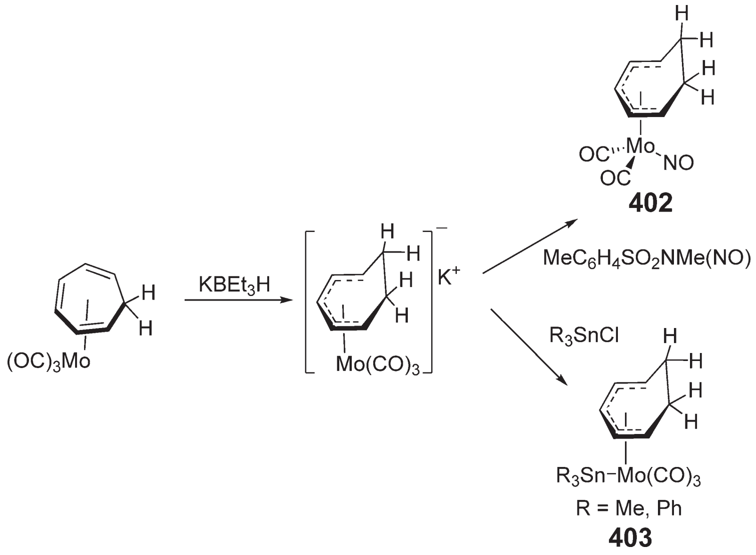
Reactivity. Hydride abstraction to form η^7-cycloheptatrienyl derivatives is a common reactivity pathway, and is described in Section 5.06.3.6. The addition of H^- has also been studied, and extremely temperature sensitive η^5-cycloheptadienyl anions have been characterized by IR spectroscopy. However, stable derivatives can be formed by treatment of these anions with R_3SnCl or Diazald $\{MeC_6H_4SO_2NMe(NO)\}$ to form **402** and **403**, respectively (Scheme 46). Structure **403** shows broad NMR spectra, indicative of a fluxional process presumed to be rotation of the $Mo(CO)_2(NO)$ fragment relative to the cycloheptadienyl ring, by comparison to the chromium analog.[1169]

Protonation reactions under an atmosphere of CO have also been investigated, and an η^5-cycloheptadienyl complex **404** can be isolated. Treatment of this complex with MeCN or ^{t}BuNC affords a ring slip to the η^3-derivative **405**, which is noteworthy for the fact that this is the first observed $\eta^5 \rightarrow \eta^3$ hapticity shift for a group 6 cycloheptatriene complex (Equation (131)). Moreover, comparisons with indenyl systems suggest that the cycloheptadienyl ligand is more susceptible to this ring-slip reaction than indenyl ligands. The substitution chemistry has been investigated and two reaction pathways have been observed, either substitution of the acetonitrile ligands with retention of the η^3 hapticity or a reversion to η^5 bonding mode.[1170]

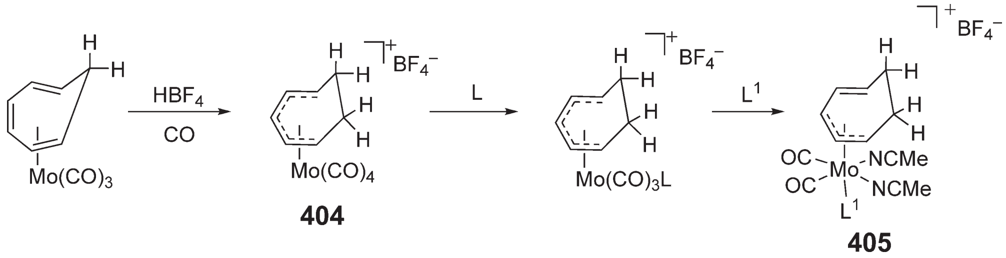


i, [(*p*-xylene)Mo(CO)$_3$]; ii, PPh$_3$ or Phen

Scheme 45



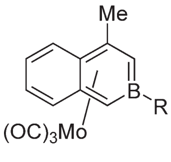
Scheme 46



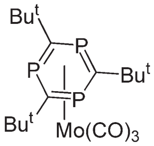
(131)

5.06.3.1.12 Heteroatom-substituted η^6-ligands

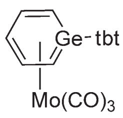
Only a few examples of heteroatom-containing ligands binding in an η^6-fashion have been reported. Azaborines ($C_4H_4B(R)NH$) are isoelectronic with arenes and unsurprisingly they bond in an η^6 mode when complexed to $M(CO)_3$ fragments (M = Cr, Mo), as shown by infrared studies and an X-ray study of the chromium complex.[1171] Boratanaphthalenes have been prepared, and the molybdenum complexes **406** show the expected η^6-interaction. Reactivity studies have also been presented and a series of gold and mercury compounds prepared, along with the first example of a platinum cluster with this ligand type.[1172] The reaction of the triphosphabenzene $P_3C_3{}^tBu_3$ with $[(toluene)Mo(CO)_3]$ affords the π-complex **407** in good yields. No interaction of the phosphorus lone pairs with the metal center is observed by NMR spectroscopy.[1173] The photoelectron spectrum of this complex has also been reported and comparisons made with $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$.[1174] The recently synthesized germabenzene ligand has been discussed with regard to its aromaticity and in conjunction with spectroscopic and theoretical results, the formation of an η^6-complex **408** reveals that it can be considered aromatic (tbt = 2,4,6-tris{bis-(trimethylsilyl)-methyl}phenyl).[1175] N-cyanoazepine coordinates to an $\{M(CO)_3\}$ fragment (M = Cr, Mo, W) in an η^6-manner to form **409**.[1176] The ligands 1-arsanaphthalene and 2-trimethylsilyl-1-arsanaphthalene also react with $[Mo(CO)_3(Py)_3]$ to form **410**, where the η^6-interaction is with the C_5As ring rather than the C_6 ring. There is also no σ-bonding from the As to Mo center, as shown by structural analysis.[1177] There are also some examples of metallobenzene coordinating to molybdenum fragments in an η^6-manner; these have recently been reviewed.[1178] Heteroatom-substituted metallobenzene complexes, for example, iridathiabenzene **411**, have also been synthesized.[1179,1180]



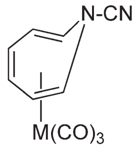
R = NPri$_2$, Me
406



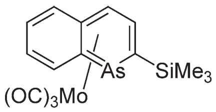
407



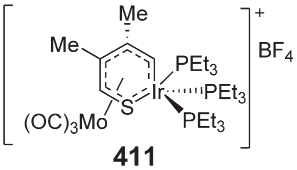
408



409



410

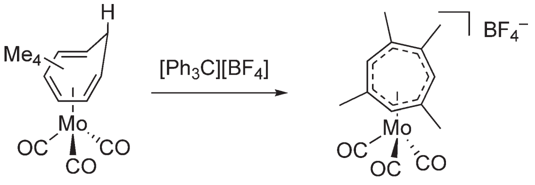


411

5.06.3.2 Carbon-based η^7-Ligands

The study of η^5-cyclopentadienyl and η^6-arene ligands is well developed, but cycloheptatrienyl (cht) is by comparison not as well utilized as a ligand. Group 6 metals are most commonly found as η^6-cycloheptatriene or η^7-cycloheptatrienyl complexes, and work up to 1994 has been included in an excellent review that describes the synthesis, bonding, structure and reactivity.[1181] Since that time, few further bonding considerations have been forthcoming, so this chapter only describes recent synthetic and reactivity studies and the reader is referred to Ref: 1182.

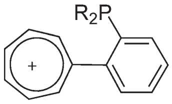
Synthesis. Several routes to substituted cycloheptatrienyl metal complexes are known.[1182] Hydride abstraction from an η^6-cycloheptatriene complex using trityl salts is a general method of synthesizing η^7-cycloheptatrienyl complexes, for example in the synthesis of 1,3,5,7-tetramethylcycloheptatrienyl molybdenum complex **412** (Equation (132)).[1162]



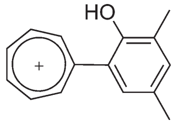
412

(132)

This methodology can also be used to synthesize previously unknown functionalised cht ligands, for example, **413** with pendant phosphine donors.[1163,1164] Other examples of pendant donor ligands include phenol **414**,[1182] cyclopentadiene **415**[1183] and cycloheptatriene **416**[1184], and further reactivity has been explored.



413



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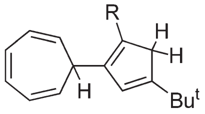
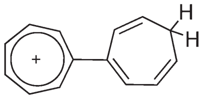
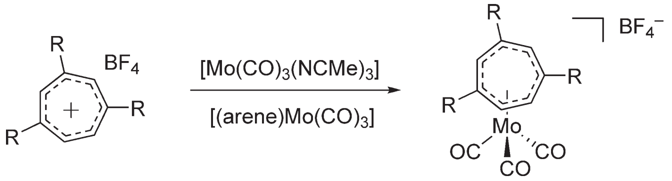


R = H, ^{t}Bu
415



416

A further convenient method of synthesizing substituted cht ligands is by the reaction of tropylium salts with $[Mo(CO)_3(NCMe)_3]$[1185] or, in higher yields, $[(arene)Mo(CO)_3]$.[1186] Thus, reaction of tropylium salts $C_7H_6R^+$ ($R = Me$, ^{t}Bu, *p*-C_6H_4F, $C{\equiv}CPh$)[1185] or $(1,3,5\text{-}C_7H_4R_3)^+$ ($R = {}^tBu$, ^{i}Pr, $SiMe_3$)[1186] affords $[(\eta^7\text{-}C_7H_6R)Mo(CO)_3]^+$ or $[(\eta^7\text{-}C_7H_4R_3)Mo(CO)_3]^+$, **417** (Equation (133)). Other methods have been used, including nucleophilic attack on a coordinated cycloheptatriene moiety, or via treatment of $[Mo(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}OMe)C_7H_7\}]$, with RMgX and subsequent thermolytic rearrangement and hydride abstraction of $[Mo(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}R)C_7H_7\}]$ [$R = Me$, ^{t}Bu, p-C_6H_4F] (Equation (134)). However, these methods do not give pure products, or the yields are quite low.[1185] A further example of nucleophilic attack on the cht ring is shown by treatment of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3][BF_4]$ with an amidine ligand to form **418**.[1188] The reaction of tertiary phosphines with $[(\eta^7\text{-}C_7H_7)Mo(CO)_3][BF_4]$ has been the subject of a kinetic study that supports a mechanism involving direct addition of the P nucleophiles to the tropylium ring, but is inconsistent with initial rate-determining attack at the metal center.[1189] Chiral-at-metal compounds have also been synthesized by reaction of $[(\eta^7\text{-}C_7H_7)Mo(L)(NCMe)]BF_4$ with CO to give a diastereoisomeric mixture of **419**.[1190,1191] The CO ligand can be substituted with other ligands such as PR_3 or RNC.



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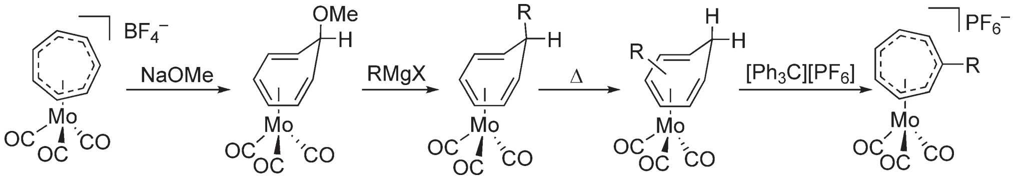

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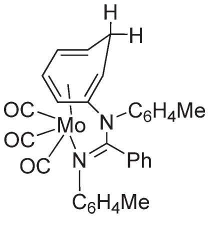
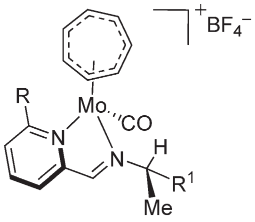


418

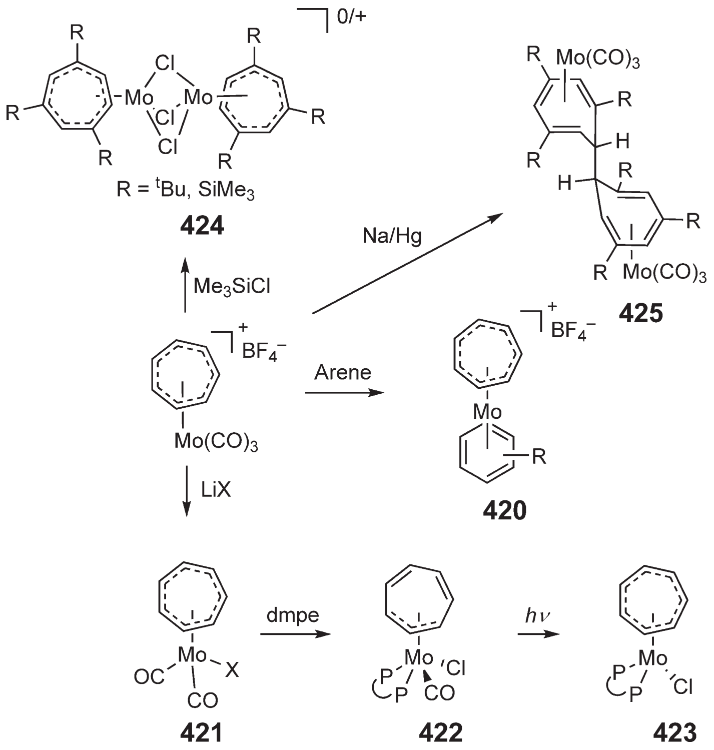


R = H, R^1 = Ph; R = Me, R^1 = Ph; R = H, R^1 = Cy

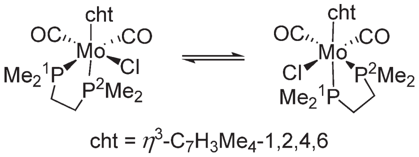
419

Properties and reactivity. A theoretical study that examines the stereo- and regioselectivity of nucleophilic attack on [(η^7-C_7H_7)Mo(CO)$_3$][BF$_4$] has been reported, and the results agree well with experimental work.[1192] The photochemistry of [(η^7-C_7H_7)Mo(CO)$_3$]$^+$ has been the subject of much study and this topic has been reviewed.[1193] Some common reactions of [(η^7-cht)Mo(CO)$_3$]$^+$ are shown in Scheme 47, as is the treatment with arenes to form sandwich complexes **420** (arene = toluene, mesitylene, xylene)[1161,1185,1186,1194] or by reaction with LiX to form **421** (X = Cl, Br).[1161,1185,1186,1195] Addition of dmpe to [(η^7-$C_7H_3Me_4$-1,2,4,6)Mo(CO)$_2$Cl] results in a hapticity change to η^3 and the formation of **422**, which under UV photolysis eliminates two CO molecules to form **423** and a concomitant hapticity change back to η^7 is observed. Compound **422** is fluxional in solution involving a trigonal-twist and 1,2-shift of the Mo atom (Scheme 48); a $\Delta G^\ddagger$ of 53.3 kJ mol^{-1} was estimated for the trigonal-twist mechanism.[1161] [(η^7-1,3,5-$C_7H_4R_3$)Mo(CO)$_3$] reacts with TMSCl to afford the dinuclear halide-bridged compound **424**. Reduction of [(η^7-1,3,5-$C_7H_4R_3$)Mo(CO)$_3$] with Na/Hg affords a bimetallic C–C coupled product **425** as a single diastereoisomer. The postulated mechanism involves an approach of two radical species in a back-to-back fashion with the R groups in a favorable staggered conformation.[1186] The reduction of [(η^7-C_7H_7)Mo(CO)$_3$] gives a similar moiety [{Mo(CO)$_3$}$_2$(μ-η^5:η^5-C_7H_7-C_7H_7)]$^{2-}$, but the dianoinic salt shows η^5-hapticity, and has been structurally characterized as its [PPN] salts.[1196]

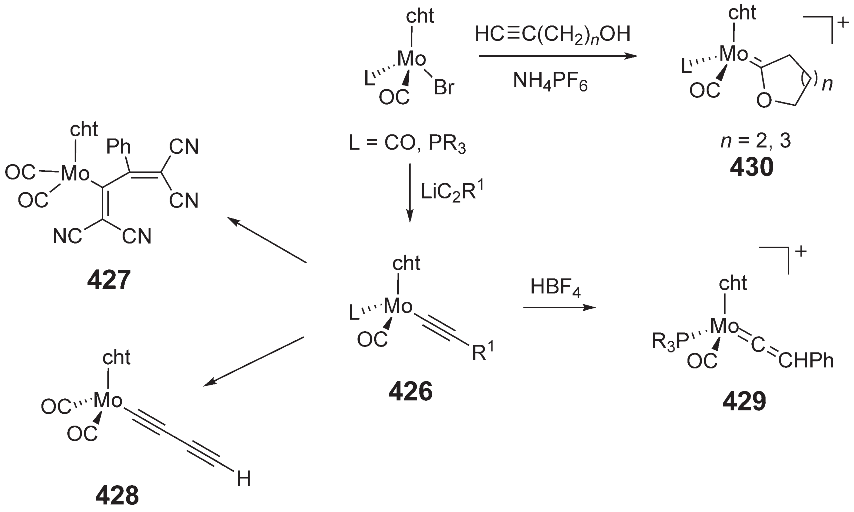
The synthesis of [(η^7-cht)Mo(CO)$_2$X] has also allowed further reactivity to be explored via salt metathesis methodologies. For example, alkynyl complexes **426** (R = Bu^t, SiMe$_3$, CO$_2$Et, C≡CSiMe$_3$) have been prepared from [(η^7-C_7H_7)MoBr(CO)$_2$] and alkynyllithium or copper reagents. From this, σ-butadienyl complex **427** and alkynyl complex **428** have been synthesized and characterized by NMR and IR spectroscopy. Protonation affords the vinylidene complex **429**.[1197] More interestingly, the first examples of stable cycloheptatrienylmolybdenun carbene complexes **430** (R = Me, Ph) have been obtained via reaction of [(η^7-C_7H_7)MoBr(CO)(PR$^1_3$)] with a but-3-yn-1-ol and [NH$_4$][PF$_6$].[1198] Further oxycarbenes have also been prepared using similar methodologies (Scheme 49).[1199] Carbonyl groups can also be substituted with bipy and diazabutadiene ligands to form [(η^7-C_7H_7)Mo(η^2-NN)Br].[1200] The binuclear complex *syn*-*cis*-[(η^7-C_7H_7)Mo(CO)TePh]$_2$ has been synthesized and the bimetallic structure is linked by bridging PhTe groups rather than Mo–Mo bonds.[1201] Alkyl groups can also be included for example to form [(η^7-C_7H_7)MoR(CO)(PR$^1_3$)] (R = Me, Ph, C$_6$F$_5$; R^1 = Me, Ph).



Scheme 47



Scheme 48



Scheme 49

A second reactivity pathway has also been identified, namely ring slip reactions. For example, addition of isonitriles to cht complexes gives [(η^3-C_7H_7)MBr$(CO)_2$(CNBu^t)$_2$] and further reactivity of this complex affords CO and bromide substitution and a hapticity change to η^7.[1202] Further studies have examined the effects of the metal, X, R and the temperature in the reaction depicted in Equation (135) (M = Mo, W; X = NCO, NCS, C≡CPh, C_6F_5, $SnPh_3$, Br; R = H, Me).[1203]

$$[(\eta^7\text{-}C_7H_6R)MX(CO)_2]^{n+} + 2L^1 \longrightarrow [(\eta^3\text{-}C_7H_6R)MX(CO)_2L^1{}_2]^{n+} \qquad (135)$$

The conclusions indicated that a hapticity change is more pronounced for electron-poor metal centers with electron delocalising substituents on the cht ring. A further finding was that the η^7-bonding mode is more favored on increasing temperature. This effect is not specific to mononuclear species as the bimetallic complex [$Mo_2(CO)_4(NCMe)_2(\mu$-η^7:η^7-$C_{14}H_{12})]^{2+}$ also undergoes a hapticity change on treatment with acetonitrile.[1184]

5.06.4 Isocyanide Complexes of Molybdenum

5.06.4.1 General Remarks

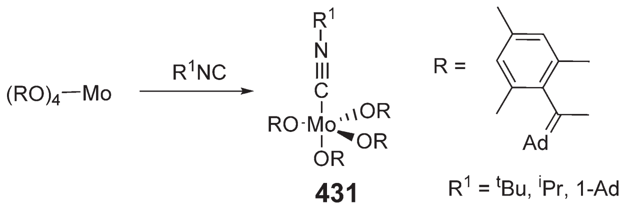
Isocyanides are commonly used ligands in group 6 chemistry, as the electronic properties are similar to those of the CO ligand. A frequent use of isocyanides is in substitution of CO or other labile ligands. There are examples of this simple substitution chemistry in the sections discussed above, and further examples are detailed below. A number of review articles have also been published, to which the reader is referred. The chemistry of β-functional aryl isocyanides[1204] and cyclization reactions to generate coordinated N-heterocyclic carbenes[1205] are common, and this subject has been reviewed. Other common reactions are the formation of aminocarbene complexes by nucleophilic attack at a coordinated isocyanide ligand[1206] or aminocarbyne complexes by electrophilic addition to coordinated isocyanides.[1207] The coordination chemistry of CNH,[1208] CNH_2,[1209] fluorinated isocyanide,[1210] bis(isocyanide) ligands in the formation of polynuclear complexes[1211] and theoretical studies of isocyanide complexes of transition metals have been reviewed.[1212] Coupling reactions of isocyanides have also been reviewed.[1213]

5.06.4.2 Isocyanide Complexes of Mo in Oxidation States (IV)–(0)

Spectroscopic and structural data of representative examples of isocyanide complexes of Mo in various oxidation states are given in Table 16.

5.06.4.2.1 Mo(IV)

There are few examples of isocyanide complexes of Mo(IV). The reaction of an enolate complex [Mo(OC(Ad)Mes)$_4$] (Ad = 2-adamantylidene) with isocyanides gives **431** which exists in a triplet ground state and has been structurally characterized and shown to have a trigonal bipyramidal geometry. Unusually, the Mo–C bond length is quite long at 2.228(9) Å (Equation (136)).[1214] The carborane complex [1,2-μ-{NHC(Me) = NH}-2,2-(CNBu^t)$_n$-2-I-*closo*-2,1-$MoCB_{10}H_{10}$] (n = 1–3) has also been synthesized, and for n = 3 characterized by X-Ray diffraction.[1215]



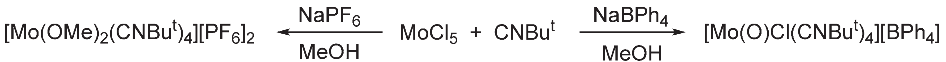
(136)

[Cp*MoCl(N^{t}Bu)(CNXy)] can be formed via reduction of [Cp*Mo(N^{t}Bu)Cl$_2$], and this has been alkylated by MeMgCl to give [Cp*Mo(N^{t}Bu)(CNXy)Me].[1229] Reduction of Mo(V) to Mo(IV) using excess isocyanide has also been reported in the case of the preparation of **432** and **433** (Equation (137)).[1216] The photochemistry of these complexes has been investigated and they show phosphorescence at 77 K and also in solution at room temperature for [MoOCl(CNBu^t)$_4$]$^+$.

Table 16 Spectroscopic and structural characterization of isocyanide complexes

Compound	*M–C* (Å)	*ν(C=N)* (cm^{-1})	μ_{eff}	*References*
431	2.228(9)	2157[a]	2.92	1214
[1,2-μ-{NHC(Me)=NH}-2,2,2-(CNBu^t)$_3$-2-I-*closo*-2,1-MoCB$_{10}$H$_{10}$]	2.098, (average)	2187[b], 2165		1215
432	2.166(5), 2.173(4)	2213[c]		1216
[Mo(H)(Me$_2$C=NAr)(N(Pr^i)Ar)$_2$(CNAd)]		1718[d]		1217
[Mo(H)(Me$_2$C=NAr)(N(Pr^i)Ar)$_2$(CNAd)$_2$]	2.135(11), 2.083(11)	2035[d]	1.76	1217
[Mo(N(^{t}Bu)Ar)$_3$(NCBu^t)]	1.933(6)	1762[d]	1.83	1217
[Mo(N$_3$N)(CNBu^t)][e]		1838[f]	1.74	1218
[CpMo(SPh)(CO)(CN^{t}Bu)$_2$]	2.053(4), 2.086(4)			1219
cis-[Mo(SC$_6$H$_2$Pr^i$_3$-2,4,6)$_2$(CNMe)$_4$]	2.086(5), 2.088(6)	2149[f], 2067, 1907		1220
cis-[Mo(SC$_6$H$_2$Pr^i$_3$-2,4,6)$_2$(CNBu^t)$_4$]	2.083(2), 2.063(3)	2126,[f] 2081, 2035		1220
trans-[{Mo(CO)(NO)(CNBu^t)}$_2${μ-(η^5-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}]	1.89(3)	2124[f]		1221
trans-[{Mo(NO)(CNBu^t)$_2$}$_2${μ-(η^5-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}]	2.046(11), 2.022(12)	2012,[f] 1966		1221
[MoH(CNBu^t){Si(Ph)[Ph$_2$PCH$_2$CH$_2$P(Ph)C$_6$H$_4$o]$_2$}]	2.10(1)	2025[g]		1222
(*S*Mo,*S*C)-[(η^7-C$_7$H$_7$)Mo(L)(CNBu^t)]BF$_4$[h]	2.135(3)	2148[g]		1190
[Mo(CO)$_5$(CNC$_6$H$_4$NO$_2$-2]	2.090(4)	3133[g]		1223
[Mo(CO)$_4${H$_2$C(OC$_6$H$_4$NC-1)$_2$}]		2145[g], 1970		1224
[Mo(CO)$_4$(435)$_2$]	2.116(5)	2135[b], 2067		1225
fac-[Mo(CO)$_3$(CNCH$_2$CF$_3$)$_3$]	2.134(10)	2173[g], 2112		1226
[Mo$_2$(μ-O)(CNXy)$_{10}$]	2.20(1), 2.11 (average)	2062[f]		1227
[Mo(O)F(CNMes)$_4$][BF$_4$]	2.15 (average)	2170[f]		1227
[CpW(CO)$_2$(μ-PPh$_2$)Mo(CO)$_4$(CNPr^1)]	2.120(6)	2169		451
[Mo(dppe)$_2$(CNPh)(N$_2$)]	1.998(3)	1914[g]		1228

[a] C_6D_6.
[b] CH_2Cl_2.
[c] KCl.
[d] Et_2O.
[e] $N_3N = (RNCH_2CH_2)_3N$; R = Me_3Si, C_6F_5.
[f] Nujol.
[g] KBr.
[h] L = 2-PyC(H)=NCH(Me)(Ph).



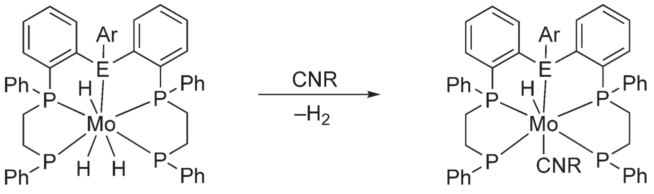
$$[Mo(OMe)_2(CNBu^t)_4][PF_6]_2 \xleftarrow[MeOH]{NaPF_6} MoCl_5 + CNBu^t \xrightarrow[MeOH]{NaBPh_4} [Mo(O)Cl(CNBu^t)_4][BPh_4] \qquad (137)$$

432 **433**

5.06.4.2.2 Mo(III)

Schrock and co-workers have used the triamidoamine ligand to good effect in a variety of unusual complexes with different transition metals. The complex [Mo(N$_3$N)(N$_2$)] (N$_3$N=(RNCH$_2$CH$_2$)$_3$N; R = Me$_3$Si, C$_6$F$_5$) reacts with isocyanides with elimination of N$_2$ to form paramagnetic [Mo(N$_3$N)(CNR)] (R = Bu^t, Xyl) which can be oxidized with [Cp$_2$Fe][OTf] or [Cp$_2$Fe][B(ArF)$_4$].[1218] [Mo(H)(Me$_2$C=NAr){N(Pr^i)Ar}$_2$] (Ar = 3,5-C$_6$H$_3$Me$_2$) and its three-coordinate isomer [Mo{N(Pr^i)Ar}$_3$] is of interest as it undergoes small molecule activation. The reactions with bulky isocyanides have been examined and the 1 : 1 complex of [Mo{N(Pr^i)Ar}$_3$] isolated, whilst [Mo(H)(Me$_2$C=NAr){N(Pr^i)Ar}$_2$] binds two molecules of AdNC.[1217] Structural and spectroscopic data suggest that [Mo{N(Pr^i)Ar}$_3$(CNBu^t)] shows significant multiple bonding between the Mo and C atoms. Additional kinetic and thermochemical measurements were made and it was found that [Mo{N(Pr^i)Ar}$_3$] is not an intermediate in the reaction of [Mo(H)(Me$_2$C=NAr){N(Pr^i)Ar}$_2$] to [Mo{N(Pr^i)Ar}$_3$(CNAd)], but rather that the molybdaziridine hydride opens upon AdNC binding in an associative process. The enthalpies of reaction are −102.9 kJ mol^{-1} for [Mo{N(Pr^i)Ar}$_3$], and −121.7 kJ mol^{-1} for [Mo{N(Bu^t)Ar)$_3$(CNAd)]. The enthalpy of binding of the second equivalent of AdNC to form [Mo{N(Pr^i)Ar}$_3$(CNAd)$_2$] is −42.7 kJ mol^{-1}.

Reaction of a series of isocyanides with the tetraphosphine molybdenum hydride complexes containing Si or Ge has been documented (Equation (138)). This has enabled a survey of the *trans*-influence of the Si and Ge ligands, and the spectroscopic data suggest that there is a significant amount of backbonding to the metal.[1222]

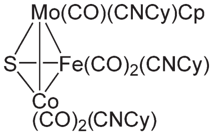


(138)

E = Si; Ar = Ph, C_6F_5, $C_6H_4NMe_2$-4; R = ^tBu, Cy, Ph, Bz, Xyl
E = Ge; Ar = Ph; R = ^tBu

5.06.4.2.3 Mo(II)

The M_3 clusters $[(\mu_3\text{-S})FeMCo(CO)_8(\eta^5\text{-}C_5H_4R)]$ (R = Me, H) react with 1, 2, or 3 equiv. of CyNC to form **434** where first the Mo is coordinated, then the iron, and finally the Co centers are coordinated. These compounds have been comprehensively characterized by IR, ^1H and ^{59}Co NMR, and ^{57}Fe Mössbauer spectroscopy. For the mono-substituted compound, the CN stretch (2183 cm^{-1}) is higher than that of the free isocyanide, and the authors explain this as being due to the synergistic effect of the strongly σ-donating isocyanide and the strong π-acceptor character of the CO ligands.[1230]



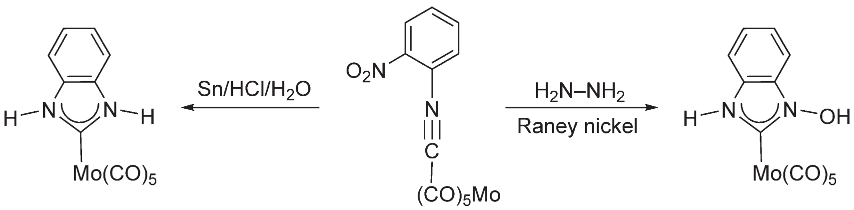
434

Reduction of higher oxidation state Mo complexes in the presence of isocyanides is a convenient method of synthesis. Thus, reduction of $[Cp^*MoCl_3(\eta^2\text{-SS})]$ (SS = $(EtO)_2PS_2$) affords $[Cp^*Mo(CNBu^t)_2(\eta^2\text{-SS})]$.[1231] Reaction of $[MH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (M = Mo or W) or $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ with RNC (R = Me or Bu^t) gave *cis*-$[M(SC_6H_2Pr^i_3\text{-}2,4,6)_2(CNR)_4]$ (M = Mo, R = Me or Bu^t; M = W, R = Me). Some examples have been structurally characterized, and an electrochemical study of these 16-electron complexes has been reported. A single-electron anodically induced *cis–trans* isomerization has been observed which goes via an EC-square mechanism; rate and equilibrium constants have been measured.[1220,1232]

5.06.4.2.4 Mo(0)

Reaction of $[M(CO)_6]$ (M = Cr, Mo, W) with alkyl azide RN_3 (R = heptyl, $PhCH_2$, etc.) and PPh_3 affords mono-isocyanide complexes $[M(CO)_5(CNR)]$. *cis*-$[M(CO)_4(CNR)_2]$ and *fac*-$[Mo(CO)_3(CNR)_3]$ compounds can be obtained by thermal decomposition of the monoisocyanide complexes.[1233] A further synthetic strategy for the synthesis of isocyanides is by treatment of *trans*-$[Mo(N_2)_2(dppe)_2]$ with an excess of benzylideneanilines PhCH=NAr (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) to give *trans*-$[Mo(CNAr)(N_2)(dppe)_2]$.[1228] Reaction with CO, isocyanides, or H_2 displaces the coordinated N_2.[1234] Protonation of the coordinated isocyanide to form amino-carbenes has been studied.[1235] The kinetics of the reactions between HCl and *trans*-$[MoL(CNPh)(Ph_2PCH_2CH_2PPh_2)_2]$ (L = CO, N_2 or H_2) have been studied by stopped-flow spectroscopy and show that in all cases initial protonation is at the isocyanide, the protonation is very complex and the final products are formed by protonation, labilization of *trans*-ligands, and proton dissociation.[1236]

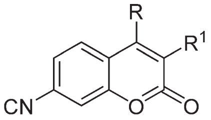
Reaction of $[Mo(CO)_5(THF)]$ with 2-nitrophenyl isocyanide affords the expected complex in good yields. Spectroscopic and structural data reveal little backbonding, and reduction of the NO_2 function with either Sn/HCl or hydrazine hydrate/Raney nickel to form benzannulated N-heterocyclic carbenes via cyclization of the unstable 2-aminophenyl isocyanide (Equation (139)).[1223] The series of complexes $[Mo(CO)_{6-n}(CNXy)_n]$ (n = 1–6) has been investigated by electrochemical and theoretical methods, and rates measured for *cis–trans* and *fac–mer* isomerization.[1237]



(139)

Heterobimetallic compounds have been made via the deprotonation of benzoxazole and treatment with $[M(CO)_5(THF)]$ (M = Cr, Mo, W) and Cp_2TiCl_2. The coordination of the isocyanide to the group 6 metal center was shown by IR spectroscopy and a structural determination of the Cr derivative. The use of an oxophilic early transition metal centre is thought to be the driving force for this reaction.[1238]

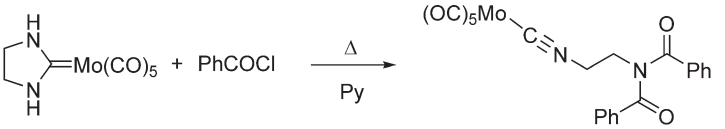
7-Isocyanocoumarin, **435**, has been prepared and complexes $[Mo(CO)_4(\mathbf{435})_2]$ prepared. The spectroscopic data suggest that this family of isocyanides are significantly stronger π-acids than other aryl isocyanides, possibly due to coupling of the low energy π^*-orbital of the coumarin fragment to the metal center through the CN bridge. The photochemistry has been examined and due to low energy MLCT excited state these complexes exhibit emission spectra in solutions, something that is relatively rare for metal carbonyl complexes.[1225]



R = Me, CF_3; R^1 = H, Me, Cl

435

C–N bond cleavage in the stable diaminocarbene molybdenum carbonyl complex has been observed upon treatment with acylating agents (Equation (140)).[1239]

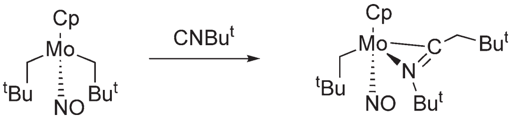


(140)

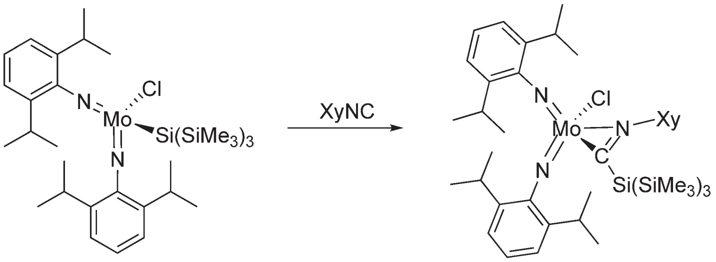
$[Mo(\eta^4\text{-}P_4)(dppe)]$ (P_4 = *meso*-*o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$) reacts with a variety of isocyanides to give mono-, bis-, and tri-substituted complexes, as the phosphine ligand can bind in an η^2 to η^4 hapticity.[1240]

5.06.4.3 Imino–Acyl Complexes of Molybdenum

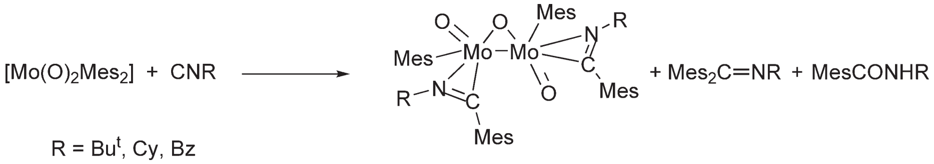
Analogous to the formation of acyls is the insertion of isocyanides into a metal–alkyl bond. However, this is less well studied than acyl chemistry, possibly because other reactions occur, for example, multiple insertions or coupling reactions. However, iminoacyl derivatives of molybdenum have been prepared via a number of methodologies. Insertion into an Mo–C[1241] (Equation (141)) or Mo–Si[1242] (Equation (142)) bond has been observed. An unusual reaction has been observed when treating the high-valent oxymolybdenum species $[Mo(O)_2Mes_2]$ with a series of isocyanides (Equation (143)). This complex is the first example of an η^2-iminoacyl moiety coordinated to a high oxidation state metal together with hard "oxo" ligands.[1243]



(141)



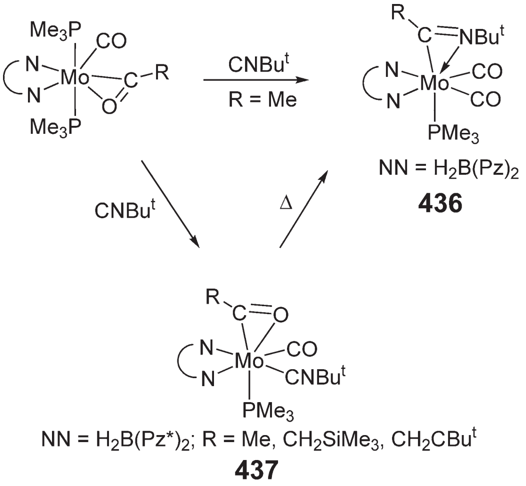
(142)



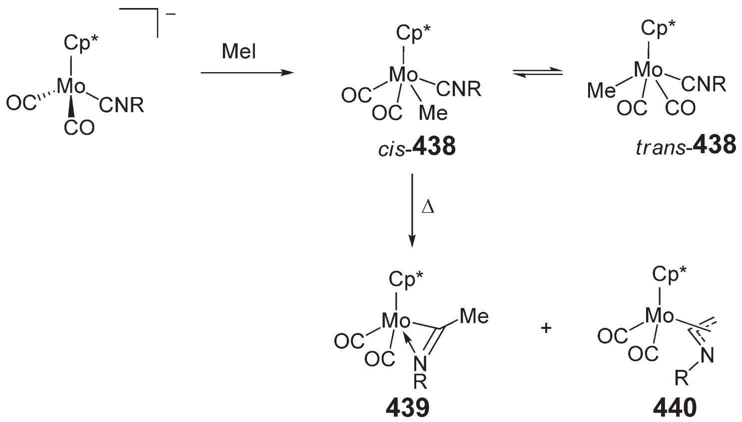
(143)

Isomerization of isocyanide–acyl complexes to the corresponding iminoacyl derivatives has been studied using the system $[(H_2B(Pz')_2)Mo(PMe_3)_2(CO)(\eta^2\text{-}OCR)]$ ($Pz' = Pz, Pz^*$; $R = Me, CH_2SiMe_3, CH_2Bu^t$). Depending on the size of the R groups and the bis(pyrazole) ligand, either the iminoacyl **436** or the isocyanide–acyl complex **437** is observed (Scheme 50). The kinetics of isomerization have been measured for $[(H_2BPz_2)Mo(PMe_3)(CO)(\eta^2\text{-}OCR)(CNBu^t)]$ and the activation parameters are $\Delta H^{\ddagger} = 84.9 \pm 5.8\ \text{kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -72.7 \pm 5.0\ \text{J mol}^{-1}\ \text{K}^{-1}$. A mechanism for the transformation was postulated and it goes via a seven-coordinate alkyl–carbonyl–isocyanide intermediate.[1244] This was further supported by the kinetics of the analogous reactions with CNXy. As expected, this inserts faster than $CNBu^t$, but only by one order of magnitude, indicating that the formation of the seven-coordinate intermediate is the rate-determining step.[1245]

Iminoacyls have also been formed on treatment of $[Cp^*Mo(CO)_2(CNR)]^-$ ($R = {}^tBu, {}^iPr$) with MeI to form *cis*- and *trans*-**438**. Under thermolysis this converts into the corresponding iminoacyl **439** and also an azaallyl derivative **440** (Scheme 51). Monitoring this reaction by VT NMR spectroscopy shows that it is only the *cis*-isomer of **438** that undergoes the migration, but both *cis*- and *trans*-isomers are in equilibrium. In this case, migration is faster than isomerization. It was found that solvent effects are substantial, so that azaallyl formation is favored in non-donating solvents. Also, the use of bulky isocyanides favors the azaallyl formation. Of note is the fact that no formation of any η^2-acyl moieties was observed, indicating that the carbonyl–iminoacyl isomer is thermodynamically favored over the isocyanide–acyl isomer.[1246] The photoelectron spectra of these three compounds have been measured and show a number of points. The destabilization of the MO's of *d*-orbital character indicates that RNC is a better π-donor but poorer π-acceptor than CO, as expected, and that iminoacyl complexes are more electron rich at the metal center than



Scheme 50



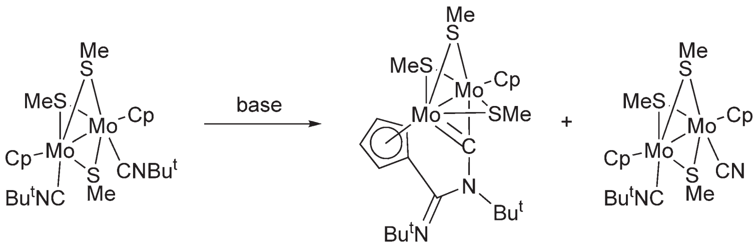
Scheme 51

the azaalkyls. Additionally, the iminoacyl and azaallyl show two bands of equal intensity in the PES experiment which have been ascribed to a filled–filled interaction between the 2*a*' orbital of the CpMo(CO)$_2$ fragment and the stable π orbital of the iminoacyl or azaallyl fragment. This separation is greater in the azaallyl spectrum due to the partial involvement of the filled–filled interaction with a ligand orbital. This has previously been described as an N-based lone pair, but theoretical calculations have now disproved this idea.[1247] The observation of azaallyl isomers has been extended to indenyl analogs, although in this case a preference for the iminoacyl form was observed, and ascribed to an electronic effect of the indenyl ligand.[1248]

A series of N-acylamido complexes [MH{N(R)COR^1-N,O}(dppe)$_2$] has been synthesized by reactions of [MoH$_4$(dppe)$_2$] with N-alkylamides RNHCOR^1 (R = Me, Ph; R^1 = H, Me, Ph). These display further reactivity with alcohols to form [MH$_2$(OR^2)$_2$(dppe)$_2$] (OR^2 = OMe, OEt, catechol), via a coordinatively unsaturated intermediate formed upon release of the N-acylamido ligand.[1249]

5.06.4.4 Coupling Reactions of Isocyanides

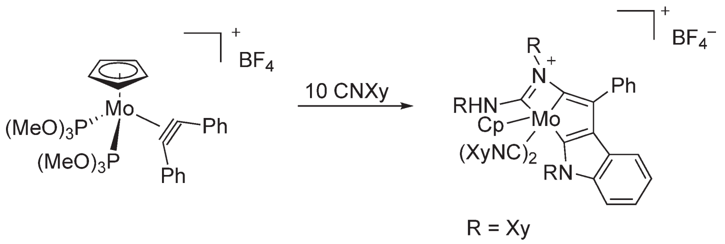
[Mo(CO)$_{6-n}$(CNR)$_n$] (n = 1, 2, 3; R = ^{t}Bu, C$_6$H$_4$NO$_2$-4, Ph, C$_6$H$_4$CO$_2$C$_2$H$_4$(CF$_2$)$_6$CF$_3$-p) have been found to be good catalysts for the stannylation of alkynes.[1250–1254] The product from the reaction of [Et$_2$OH][BF$_4$] with the aminocarbyne complexes *trans*-[M(CNHMe)(CNMe)(dppe)$_2$][BF$_4$] (M = Mo or W) gives the corresponding bis(amino)acetylene compounds *trans*-[MF(η^2-MeHNC≡CNHMe)(dppe)$_2$][BF$_4$] which was previously formulated as *trans*-[M(CNHMe)$_2$(dppe)$_2$][BF$_4$]$_2$.[1255] An unusual coupling reaction of an isocyanide and a Cp ligand has been reported upon addition of a base to **441**. The ratio of the coupled product **442** and a dealkylated nitrile **443** depends on the base, so that with ^{n}BuLi only **443** was observed, whilst using NaOH in the presence of excess isocyanide gave the highest yield of **442** (Equation (144)).[1256]



441 **442** **443** (144)

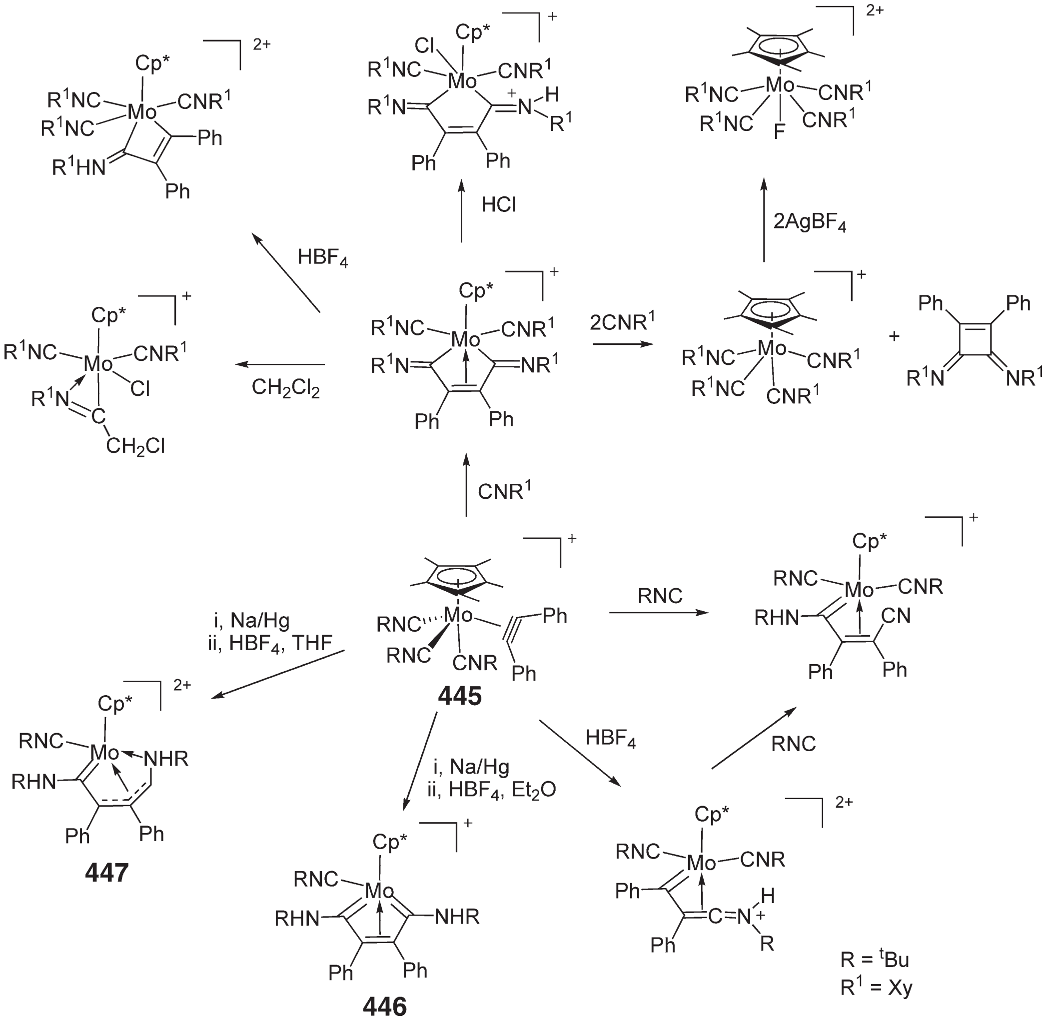
Intermolecular hydroboration has been observed upon thermolysis of [H$_2$B(pz*)$_2$Mo(CO)$_2$(PMe$_3$)-(η^2-^{t}BuN=CMe)] to form [HB(pz*)$_2$Mo(N(Bu^t)CHMe)(CO)$_2$(PMe$_3$)].[1257]

Isocyanide–alkyne coupling reactions are common. Substitution of the phosphite ligands in [CpMo{P(OMe$_3$)}$_2$-(η^2-PhC≡CPh)]$^+$ with XyNC uniquely affords indole **444** via a cascade reaction involving C–H activation and coupling of three isocyanide ligands with the coordinated alkyne (Equation (145)).[1258] Additional ligand-induced isocyanide-coupling reactions have been observed in **445**, and reductively induced isocyanide coupling reactions gives **446**, a rare example of a metallacyclopentatriene, or **447** depending on the choice of solvent.[1259] When XyNC was used, further coupling reactions were observed (Scheme 52).[1260] Reactions between $[M(CO)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ (M = Mo; W) and an excess of $CNBu^t$ in CH_2Cl_2 give $[M(CNBu^t)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ and $[M\{{=}C[N(H)Bu^t]C(Me){=}C(Me)[C(O)N(H)Bu^t]\}(CNBu^t)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$.[1261]



444

(145)



Scheme 52

Acknowledgment

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5.07

Molybdenum Compounds without CO or Isonitrile Ligands

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5.07.1 Introduction

This chapter covers complexes that do not contain either carbonyl or isonitrile ligands directly bonded to a molybdenum center. It is organized based upon the nature of the organic ligand attached to the central molybdenum atom. The cyclopentadienyl or functionalized cyclopentadienyl ligand (Cp^R) is a very common spectator ligand in this type of chemistry. Complexes that contain the spectator Cp^R ligand may therefore appear in sections where precedence is given to other organic ligands that are present rather than in the section concerned specifically with Cp^R-containing complexes.

5.07.2 Complexes Containing σ-Bonded Organic Groups

5.07.2.1 Homoleptic Complexes

In 1973 Wilkinson reported the preparation of the homoleptic methyl-containing compound $[W(CH_3)_6]$.[1] Later, theoretical calculations suggested that this compound should be based upon trigonal-prismatic geometry, rather than octahedral, as is common in six-coordinate coordination chemistry, and the structure of $[W(CH_3)_6]$ was subsequently shown to be strongly distorted C_{3v} trigonal prismatic.[2] The structure is of particular interest because it contains three long W–C bonds at a narrow angle to each other and three shorter W–C bonds at a larger angle. Recently, the compounds $[Mo(CH_3)_5]$, $[Mo(CH_3)_6]$, and $Li[Mo(CH_3)_7]$ have been prepared and structurally characterized (Figures 1–3).[3,4] Blue $[Mo(CH_3)_5]$ is prepared through reaction of $MoCl_5$ with $ZnMe_2$. $[Mo(CH_3)_5]$ is paramagnetic and has a square-pyramidal geometry with Mo–C_{apical} 206.8(1) pm and Mo–C_{basal} 211.1(1) pm. Orange-brown $[Mo(CH_3)_6]$ is prepared on treatment of MoF_6 with $Zn(CH_3)_2$ and is thermally stable up to 10 °C; it is very sensitive toward oxygen. Its solid-state structure is similar to its tungsten analog. The structure is strongly distorted trigonal prismatic with three short Mo–C bonds 211.1(3) pm with C–Mo–C 94.9° and three long Mo–C bonds 219.0(3) pm with C–Mo–C 75.7°. Red $[Li\{O(CH_2CH_3)_2\}][Mo(CH_3)_7]$ was prepared on treatment of $[Mo(CH_3)_6]$ with MeLi, and is isostructural with its tungsten analog $[Li][W(CH_3)_7]$. The structure is best described as a capped octahedron. In none of the reported structures is there any evidence for an α-agostic interaction. Theoretical calculations have been carried out on the homoleptic d^0-complexes $[MMe_6]^{2-}$ (M = Ti, Zr, Hf); $[MMe_6]^-$ (M = V, Nb, Ta); $[MMe_6]$ (M = Cr, Mo, W); $[MMe_6]^+$ (M = Tc, Re); the d^1-complexes $[MMe_6]$ (M = Tc, Re); and the d^2-complexes $[MMe_6]$ (M = Ru, Os).[5] The relative energies of the different stationary points are collected together in Table 1.

A qualitative MO representation for d^0-MH_6 molecules is presented in Figure 4,[6] and by extrapolation has been used to explain why the 18-electron complex $[Mo(CO)_6]$ is octahedral: all orbitals up to and including the t_{2g} are filled. Distortion of the octahedral geometry along a threefold axis affords the trigonal prism with a qualitative increase in

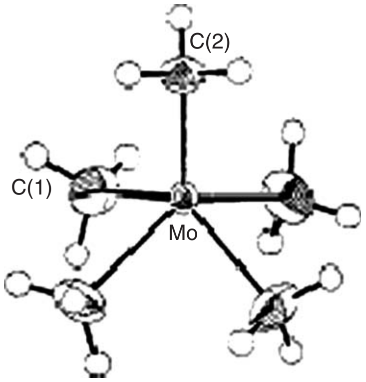

Figure 1 Molecular structure of [MoMe$_5$]. Reproduced by permission of The Royal Society of Chemistry from Roessler, B.; Kleinhenz, S.; Seppelt, K. *Chem. Commun.* **2000**, 1039–1040.

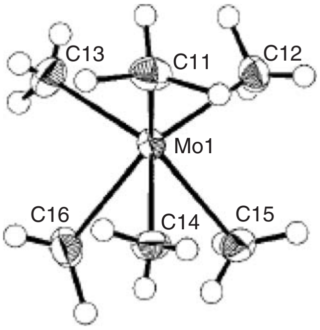

Figure 2 Molecular structure of [MoMe$_6$]. Reproduced from Roessler, B.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1259–1261, with permission from Wiley-VCH.

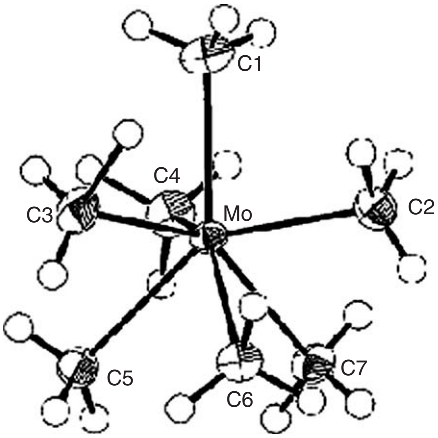

Figure 3 Molecular structure of [MoMe$_7$]$^-$. Reproduced from Roessler, B.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1259–1261, with permission from Wiley-VCH.

Table 1 The relative energies kJ mol^{-1} for the different stationary points on the potential energy surface[a]

Species	*Distorted prism A* (C_3)	*Regular prism B* (D_3)	*Distorted octahedron C* (C_{3v})
$[Ti(CH_3)_6]^{2-}$		0.0	+52.8[b]
$[Zr(CH_3)_6]^{2-}$		0.0	+65.8[b]
$[Hf(CH_3)_6]^{2-}$		0.0	+43.4[b]
$[V(CH_3)_6]^{-}$		0.0	+120.0
$[Nb(CH_3)_6]^{-}$	0.0	+0.8	+125.4
$[Ta(CH_3)_6]^{-}$		0.0	+130.1
$[Cr(CH_3)_6]$	0.0	+11.5	+98.6
$[Mo(CH_3)_6]$	0.0	+39.3	+110.3
$[W(CH_3)_6]$ (OR)	0.0	+24.6	+131.9
$[W(CH_3)_6]$ (NR)	0.0	+52.5	+103.3
$[Tc(CH_3)_6]^{+}$	0.0	+112.2	+90.3
$[Re(CH_3)_6]^{+}$	0.0	+93.0	+110.0
$[Tc(CH_3)_6]$[c]		0.0	+148.1
$[Re(CH_3)_6]$[c]		0.0	+169.5
$[Ru(CH_3)_6]$		0.0[d]	+136.3[e]
$[Os(CH_3)_6]$		0.0[d]	+160.4[e]

[a] Energies relative to the most stable (distorted trigonal prism A if observed otherwise the regular prism B).

[b] Optimizations converged to D_{3d} symmetry.

[c] Doublet states.

[d] Closed-shell singlet states.

[e] Triplet states.

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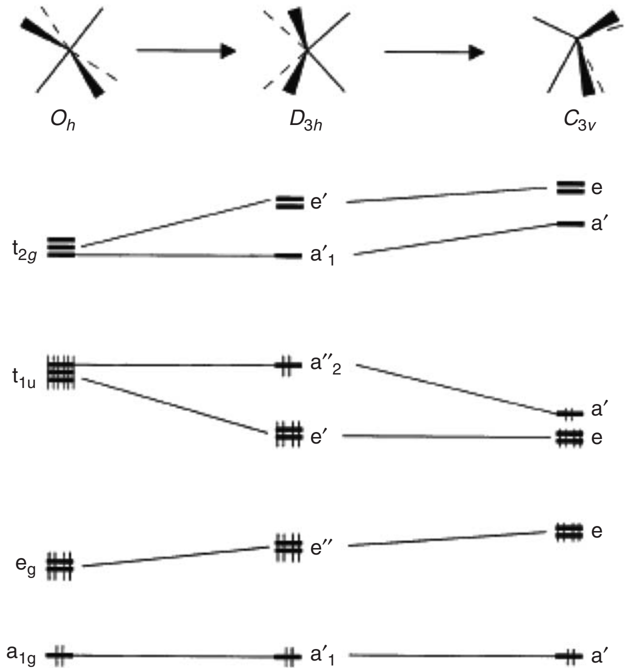


Figure 4 Qualitative molecular orbital diagram for MH_6 systems. Reprinted with permission from Kang, S. K.; Tang, H.; Albright, T. A. *J. Am. Chem. Soc.* **1993**, *115*, 1971–1981. © (1993) American Chemical Society.

energy. For $[MoMe_6]$, however, we have a 12-electron system, so the orbitals are filled to the t_{1u} level, and the same distortion, in this instance, results in stabilization with further distortion to the C_{3v} distorted trigonal prism resulting in additional stabilization and further energy raising of the virtual orbitals. The valence bond model can also be used very effectively and accounts for the observed geometry by addressing the problem of orbital percentage.[7]

If it is considered that the bonding in [$MoMe_6$] is derived solely from *s*- and *d*-orbitals with no *p*-contribution; a picture close to that observed is obtained according to natural bond orbital analysis in *ab initio* and density functional theory (DFT) calculations. A set of sd^5 hybrid orbitals is obtained with angles preferentially at 63° and 117°. The distorted trigonal prism is the most chemically reasonable geometry that can be constructed with these angles and mirrors that observed in the solid-state structure.[4] The factors that largely influence the nature of the structures of d^0-configurations – σ-bonding, ligand repulsion, core polarization, and π-bonding – have been reviewed.[7,8] The nature of the trigonal-prismatic versus octahedral structure has been further investigated through the preparation and structural characterization of the complexes [$MoMe_5(OMe)$], [$MoMe_4(OMe)_2$], [WMe_5Cl], and [$WMe_3Cl(OMe)_3$]. The first three complexes were found to be distorted trigonal prismatic and the last octahedral. What is apparent is that in the presence of less than three π-donor ligands the trigonal-prismatic structure is favored.[9] The preparation of the two homoleptic dimeric complexes [Mo_2R_6] ($R = CH_2CMe_2Ph$, CH_2SiMe_2Ph) has also been described. The molecular structures of both complexes have been determined. The Mo–Mo distances were found to be 217.65(8) and 217.0(2) pm, respectively, and are slightly shorter than for the analogous hexaalkoxide complex [$Mo_2(OCMe_2Ph)_6$], which has an Mo–Mo bond length of 223.88(6) pm. The shorter nature of the bond is not ascribed to the effects of π-donation from the alkoxide ligands, rather the two [MoR_3] fragments repel each other less.[10] The thermal decomposition of [$Mo_2(OR)_6$] and [$Mo_2(OR)_4(CH_2Ph)_2$] has been investigated.[11] The hexaalkoxide gives MoO_2 after sublimation, whereas the mixed alkyl/alkoxide decomposes prior to sublimation to give mainly Mo_2C.

5.07.2.2 Heteroleptic Complexes

5.07.2.2.1 Containing cyclopentadienyl-supporting ligands

5.07.2.2.1.(i) Compounds with phosphine ligands

The preparation of [$CpMo(CH_3)_2(PMe_3)$] has been reinvestigated.[12] The presence of excess phosphine was found to retard the reaction, and a mechanism based upon a single-electron transfer followed by radical addition was proposed. The compound was also characterized by a single crystal X-ray diffraction study. The average Mo–C bond was found to be 226.9(3) pm, which is slightly longer than those reported for [$CpMo(Me)_2(\eta^4\text{-}C_4H_6)$], where the average Mo–C bond length is 224.9(3) ppm.[13,14] The complex was also found to undergo three reversible one-electron oxidations at −2.51, −1.27, and −0.05 V versus Fc, whereas [$CpMo(Me)_2(\eta^4\text{-}C_4H_6)$] only undergoes two reversible one-electron oxidations.[14] Treatment of [$CpMo(Me)_2(\eta^4\text{-}C_4H_6)$] with 1 and 2 molar equiv. of triflic acid selectively cleaves one or two methyl groups to afford the mono- or bistriflate, respectively.[13] The use of [$Cp_2Mo(CH_3)_2$][PF_6]–methylaluminoxane and [$Cp_2Mo(CH_3)_2$]–methylaluminoxane in olefin polymerization has been described, and the different kinetic profiles obtained were accounted for by a methyaluminoxane effect.[15] The crystal structure of [$Cp^*Mo(Me)_4$] has been reported and the geometry about the Mo atom shown to be a square-based pyramid.[16] Its subsequent hydrolysis has been described and shown to generate organometallic oxides that act as models for molybdenum oxide-based catalysis.[17] The reactivity of [$Cp^*Mo(Me)_3$] toward hydrazines has also been described.[18] The compound [$CpMo(N^tBu)Cl(Me)_2$] has been prepared and structurally characterized. The methyl groups are *cis* to each other with Mo–C bond lengths of 225.2(12) and 225.6 (13) pm, respectively.[19]

5.07.2.2.2.(ii) Compounds with nitrosyl ligands

Legzdin's group has carried out detailed studies on complexes of the type [$Cp^*Mo(NO)R_2$], and several review articles are available.[20–23] Theoretical calculations on the reactivity of the [$Cp^*Mo(NO)R_2$] systems have appeared.[24–27] The results obtained from the calculations mirror those observed experimentally for bulkier R groups using the model [$Cp^*Mo(NO)Me_2$]; however, it has been shown experimentally that this coordinatively unsaturated compound undergoes spontaneous rearrangement to [$Cp^*Mo(NMe)(O)Me$] via nitrosyl N–O bond cleavage,[24] so some caution is required in interpretation of the data.

Treatment of the 16-electron complex [$Cp^*Mo(NO)Cl_2$] with 0.5 equiv. of $(Me_3CCH_2)_2Mg\cdot$dioxane at low temperature affords the monoalkyl halo complex [$Cp^*Mo(NO)(CH_2CMe_3)Cl$], and the bis-alkyl complex [$Cp^*Mo(NO)(CH_2CMe_3)_2$] is obtained on treatment with a second 0.5 molar equiv.. The equivalent tungsten complexes can also be prepared and are less Lewis acidic than their Mo counterparts. Treatment of [$Cp^*Mo(NO)(CH_2CMe_3)Cl$] with 0.5 molar equiv. of R_2Mg affords mixed complexes [$Cp^*Mo(NO)(CH_2CMe_3)R$] ($R = CH_2SiMe_3$, *p*-tolyl).[28] The crystal and molecular structure of [$Cp^*Mo(NO)(CH_2CMe_3)_2$] has been determined

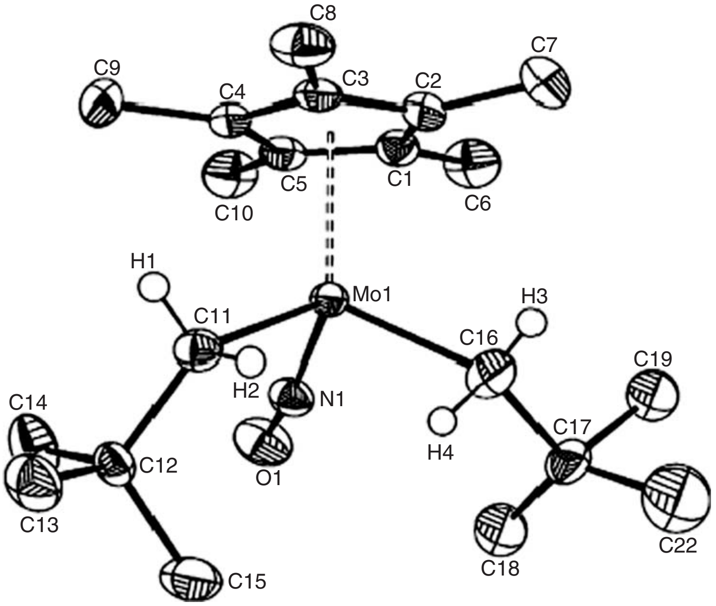
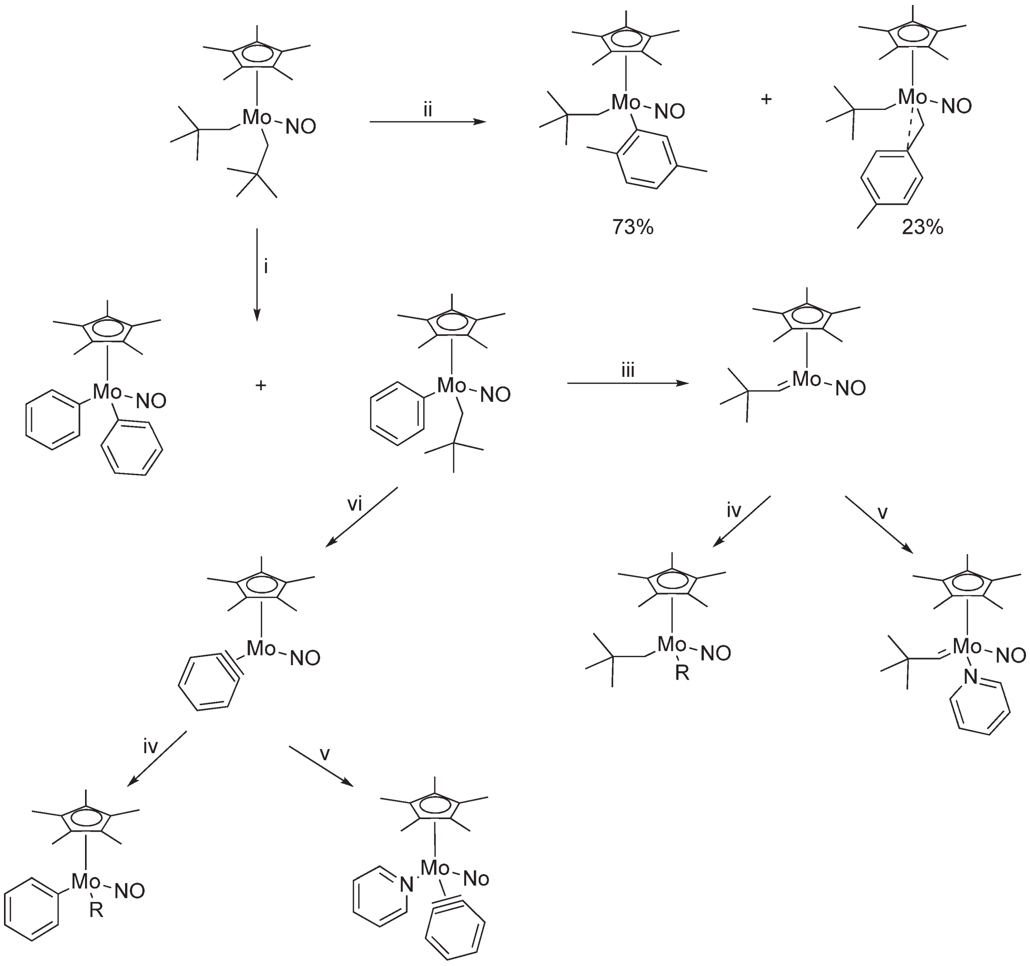


Figure 5 Molecular structure of [Cp*Mo(NO)(CH_2CMe_3)$_2$]. Reprinted with permission from Wada, K.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. *J. Am. Chem. Soc.* **2003**, *125*, 7035–7048. © (2003) American Chemical Society.

(Figure 5),[25] and found to be virtually identical to its tungsten congener. The structure shows clear evidence for a C(16)–H(4) α-agostic interaction Mo(1)···H(4) 218(6) pm; Mo(1)–C(16)–H(4) 81(3)° with a second α-agostic interaction of a more subtle nature also reported Mo(1)···H(2) 218(6) pm; Mo(1)–C(11)–H(2) 99(2)°. This double α-agostic interaction is similar to that obtained for the tungsten analog [Cp*W(NO)(CH_2CMe_3)$_2$]. Of particular note is the ability of these complexes to facilitate C–H activation.[23,25,29] The initial (C–H) activation of [Cp*Mo(NO)(CH_2CMe_3)$_2$] affords the transient alkylidene complex [Cp*Mo(NO)($CHCMe_3$)], which is then able to C–H activate sp^3- and sp^2-C–H bonds, for representative examples (see Scheme 1).

As mentioned previously, the preparation of the complex [Cp*Mo(NO)(Me)$_2$] has proved to be difficult. The rationale given for the difficulty in synthesizing this complex is the strong Lewis acidity of the 16-electron metal center and the poor steric protection offered by the methyl groups. The solid-state spectroscopic evidence suggests that [Cp*Mo(NO)(Me)$_2$] is dimeric and contains bridging isonitrosyl ligands. In the solid-state IR spectrum, no ν(NO) stretching vibration in the normal range 1700–1500 cm^{-1} is observed, although a band at 1377 cm^{-1}, which shifts to 1352 cm^{-1} on isotopic ^{15}N exchange, is observed. This was used to assign the N–O stretching vibration. Addition of simple Lewis bases such as py, PMe_3, NCMe, and THF allows the formation of the simple 18-electron adducts [Cp*Mo(NO)(Me)$_2$L]. [Cp*Mo(NO)(Me)$_2$] can be stored indefinitely under an inert atmosphere at room temperature; however, in solution, a rapid isomerization to [Cp*Mo(NMe)Me(μ-O)Mo(Me)$_2$(NO)Cp*] occurs, which has been confirmed crystallographically (Figure 6).[24]

The Mo–O–Mo linkage is found to be unsymmetrical: Mo–O(1) 213.9(4) and Mo–O(2) 176.0(4) pm, indicating some multiple bond character in the Mo–O(2) bond. The chemistry of the complexes [Cp*Mo(NO)(CH_2Ph)Cl] has also been described, and is somewhat different from the neopentyl-containing complexes.[30–32] The difference in reactivity derives from the nature of one benzyl ligand, which adopts an η^2- bonding mode, making the complexes formally 18 electron. This makes them much more thermally stable than their 16-electron dialkyl analogs. The crystal structure of the hydroxyl-bridged dimer [Cp*$_2$Mo$_2$(μ-OH)$_2$(NO)$_2$(CH_2Ph)$_2$] has also been reported.[33] The reactivity of diaryl complexes toward insertion of heterocumulenes has also been described,[34] as have the crystal and molecular structures of several other related compounds.[35,36] The isomerization of an [Mo$_2$(μ-NO)$_2$] moiety to the unusual [(ON)Mo=N–Mo=O] fragment has also been effected.[37] The reactivity of [Cp*Mo(NO)(R)$_2$] and [Cp*Mo(NO)(R)X] toward a range of lithium reagents has been described,[38–40] with the reactivity observed including deprotonation, metathesis, reduction, alkylidene formation, and ligand scrambling.



i, C_6H_6; ii, 1,4-Me–C_6H_4; iii, –C_6H_6; iv, R–H; v, py; vi, –C_5H_{12}

Scheme 1

The coupling of 1,3-cyclooctadiene has also been achieved on the treatment of $[Cp^*Mo(NO)(CH_2SiMe_3)_2]$ with cyclooctadiene.[41] The preparation and structural characterization of the complexes $[Cp^RMo(NO)_2R]$($Cp^R = Cp$, Cp^*; $R = CH_2Cl$, CH_2Br, CH_2I) has been described.[42] The properties of the halomethyl groups were found to be intermediate of those of halide or methyl. The Mo–C bond lengths for the halomethyl groups in $[Cp^*Mo(NO)_2R]$ are 219.2(10) ($R = CH_2Cl$), 220.0(9) ($R = CH_2Br$), and 219.7(9) pm ($R = CH_2I$), respectively, and when compared to the Mo–C bond lengths in $[CpMo(NO)_2R]$ (218.7(5) ($R = CH_2Cl$) and 217.0(7) pm ($R = CH_3$)), are marginally longer. Controlled oxidation of the halomethyl complexes afforded CH_2O and the halonitrosyl complex $[Cp^RMo(NO)_2X]$, which on further oxidation affords $[Cp^RMoO_2X]$ plus nitrogen oxides.

5.07.2.2.2 Containing nitrogen-supporting ligands

A review article covering alkyl complexes with imido-supporting ligands has appeared.[43]

The complexes $[Mo(NR)_2R^1Cl]$ ($R = 2,6\text{-}^iPr_2C_6H_3$; $R^1 = CH_2CMe_2Ph$, CH_2Me_3) were prepared on treatment of $[Mo(NR)_2Cl_2]$ with RMgX ($R = 2,6\text{-}^iPr_2C_6H_3$; $R^1 = CH_2CMe_2Ph$, CH_2Me_3), and their reactivity was investigated (Scheme 2).[44] Several crystal structures were reported, and all displayed weak α-agostic interactions; for a selected example, see Figure 7. The dimensions of the agostic interaction in this compound are: Mo–C(1) 232.95(5) pm, Mo–H(1A) 246(2) pm; Mo–C(1)–H(1A) 100.0(13)°.

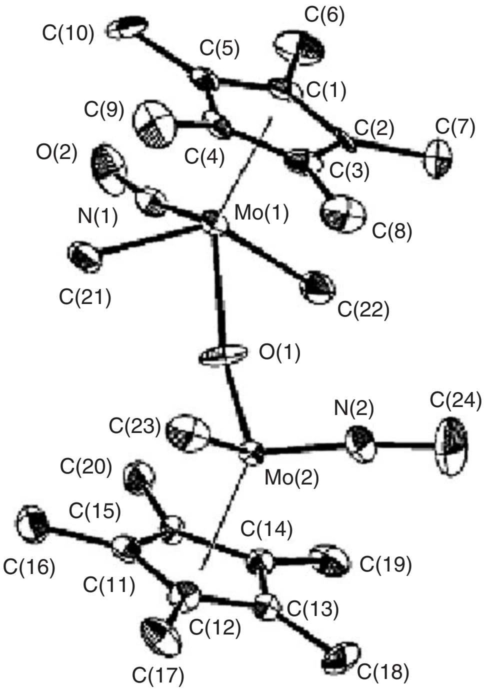
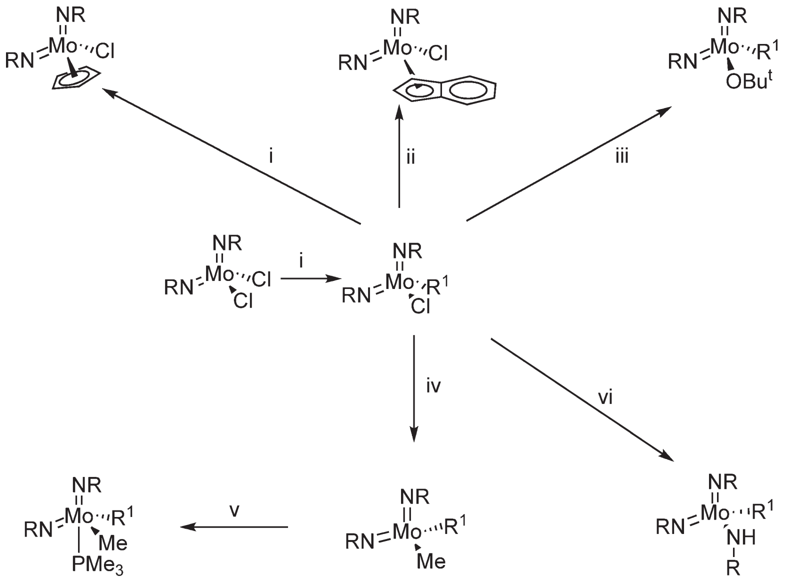


Figure 6 Molecular structure of [Cp*Mo(NMe)Me(μ-O)Mo(Me)$_2$(NO)Cp*]. Reprinted with permission from Sharp, W. B.; Daff, P. J.; McNeil, W. S.; Legzdins, P. *J. Am. Chem. Soc.* **2001**, *123*, 6272–6282. © (2001) American Chemical Society.



R = 2,6-Pr^i–C$_6$H$_3$; R^1 = CH$_2$CMe$_3$
i, LiCp; ii, Li(indenyl); iii, LiOBu^t; iv, MeMgI; v, PMe$_3$; vi, LiNHR

Scheme 2

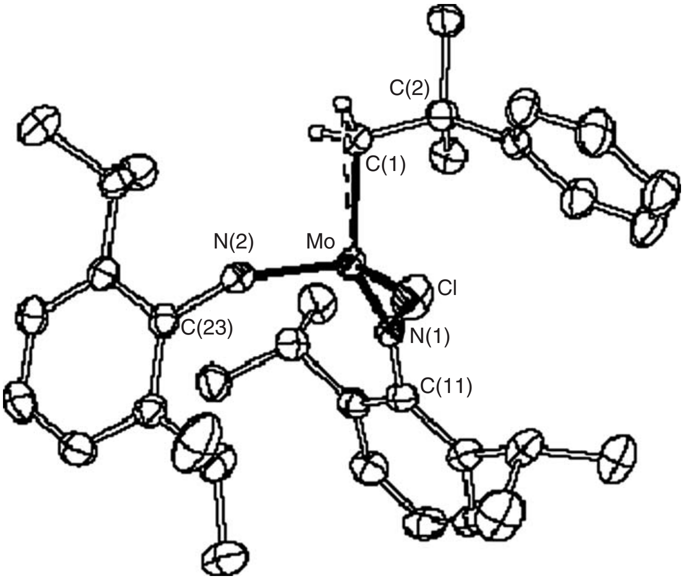


Figure 7 Molecular structure of [Mo(NC$_6$H$_3$–2,6-Pr^i)$_2$Cl(CH$_2$CMe$_2$Ph)] showing the α-agostic interaction. Gibson, V. C.; Redshaw, C.; Walker, G. L. P.; Clegg, W.; Elsegood, M. R. J. *J. Organomet. Chem.* **2004**, *689*, 332–344. Reproduced with permission of Elsevier.

Much interest in the preparation of bis-imido bis-alkyl complexes of the form [Mo(NR)$_2$(R)$_2$] remains.[45–51] The R group bound to the imido nitrogen is usually either ^{t}Bu or a bulky aryl group. These complexes also tend to be tetrahedral in nature.

The crystal structure of the bis-benzyl complex [Mo(N^{t}Bu)$_2$(CH$_2$Ph)$_2$] (Figure 8), shows that the benzyl groups adopt two different coordination modes η^1- and η^2-, respectively, with Mo–C(9) = 218.66(17) pm, Mo–C(10) = 246.73(16) pm, and Mo–C(16) = 219.58(16) pm.[50]

The Mo–C bonds in this class of compound are sensitive to protic cleavage, for example, cleavage of the mesityl bond in [Mo(N^{t}Bu)$_2$(mes)$_2$] has been achieved on treatment with either 8-hydroxyquinoline or

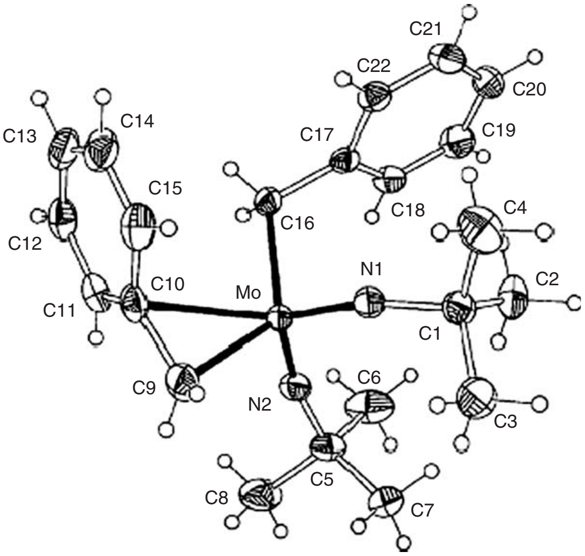


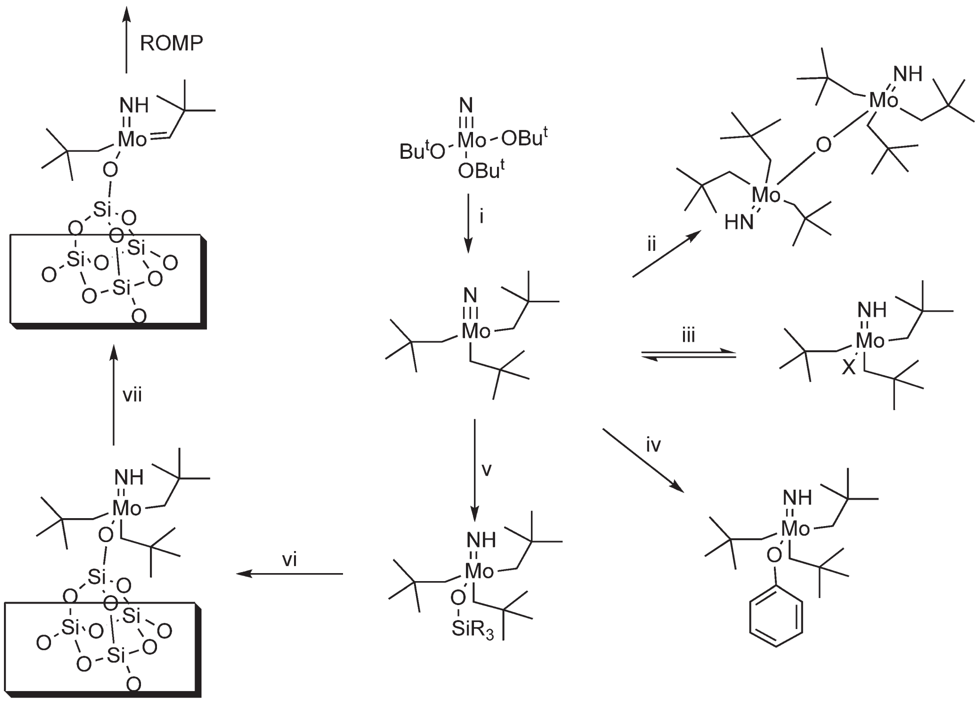
Figure 8 Molecular structure of [Mo(NBu^t)$_2$(CH$_2$Ph)(η^2-CH$_2$Ph)]. Reproduced from Clegg, W.; Elsegood, M. R. J.; Dyer, P. W.; Gibson, V. C.; Marshall, E. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *C55*, 916–918, with permission from IUCr journals.

8-hydroxyquinaldehyde to give the five-coordinate monomesityl-containing products [$Mo(N^tBu)_2(mes)(O–N)$] (O–N = 8-hydroxyquinoline or 8-hydroxyquinaldehyde).[48]

Complexes of the type [$Mo(NMes)R_3$] (R = CH_2CMe_2Ph, CH_2SiMe_3) were prepared on treatment of [$Mo(NMes)(O)Cl_2(dme)$] with 3 equiv. of RMgX.[52] The synthesis of Mo-based clusters containing alkyl or aryl imido groups with methyl groups has also been reported.[53] Complexes containing the isodiazene ligand (NNPh),[54,55] or the pincer N–C–N, C–N, and C–O chelate systems with alkyl or aryl co-ligands are also known.[56–59]

The use of the trisamidoamine ligands $\{N[NR]_3\}^{3-}$ with bulky substituents at the amido nitrogen atoms has continued to develop particularly through the work of Schrock's group.[60–65] The principal feature of these ligands is that they create a sterically protected threefold symmetric pocket, which allows, sterically protected, coordination of other fragments.[66,67] These complexes have been used as precursors for alkylidyne complexes[63] and η^2-acyls formed by CO insertion.[60] More recently, diamidoamine[68,69] ligands have been utilized to prepare alkyl-containing complexes through halide metathesis, and alkylidene complexes were subsequently obtained after α-elimination had taken place.[69]

Herrmann and co-workers reported the preparation of [$Mo(N)(CH_2CMe_3)_3$] (Scheme 3),[70] and from spectroscopic data inferred that it is either oligomeric or polymeric in the solid state, containing MoNMo chains. This compound adds HBr or phenol to give the monomeric complexes [$Mo(NH)(CH_2CMe_3)_3X$] (X = Br, OPh), where X = Br; the complex has been crystallographically characterized. In the case of water, the oxygen-bridged dimer [$(Me_3CCH_2)_3(HN)Mo(\mu\text{-}O)Mo(NH)(CH_2CMe_3)_3$], which has also been structurally characterized, forms. [$Mo(N)(CH_2CMe_3)_3$] also reacts with R_3SiOH bonds in the same fashion to generate [$Mo(NH)(CH_2CMe_3)_3(OSiR_3)$] and in the case of SiO_2, generates after α-elimination the alkylidene complex [$Mo(NH)({=}CHCMe_3)(CH_2CMe_3)(OSilica)$], which was shown to be an effective ring-opening metathesis polymerization (ROMP) catalyst (Scheme 3).[71] Controlled thermolysis of these compounds has been shown to yield phase-pure molybdenum nitrides.[72] Caulton and co-workers have been able to prepare and crystallographically characterize the related monomeric complex [$Mo(N)(mes)_3$][73] (Figure 9). The Mo–C bonds were found to be 214.2(4), 210.0(5), and 213.3(5) pm, respectively. In addition, the complex [$Mo(N)(O^tBu)(\eta^2\text{-}C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$] was also reported and



i, 3MgNpBr; ii, 0.5 H_2O; iii, HX, X = F, Cl, Br, I, O_3SCF_3; iv, PhOH; v, $HOSiPh_3$;
vi, SiO_2, 70 °C, 15 h; vii, $-C_5H_{12}$

Scheme 3

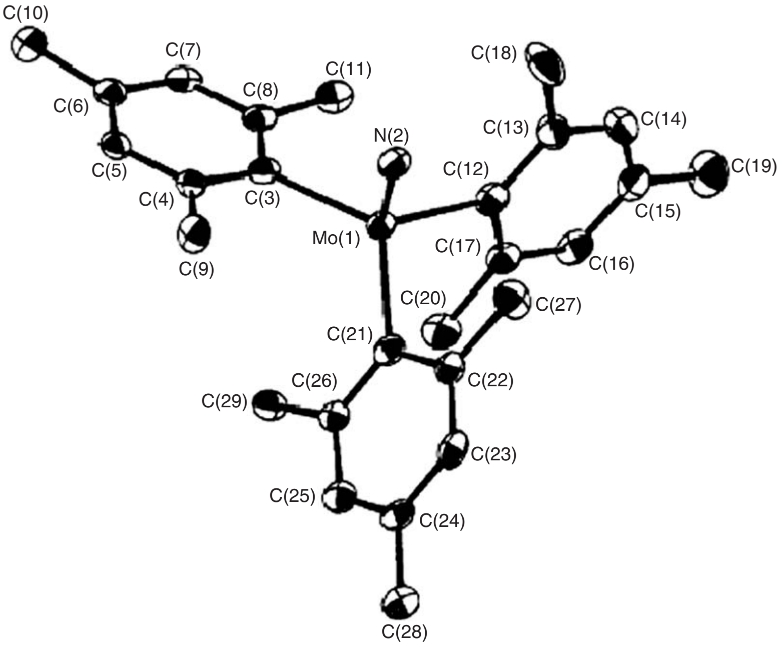


Figure 9 Molecular structure of [MoN(mes)$_3$]. Reprinted with permission from Caulton, K. G.; Chisholm, M. H.; Doherty, S.; Folting, K. *Organometallics* **1995**, *14*, 2585–2588. © (1995) American Chemical Society.

crystallographically characterized. The Mo–C distances are 218.8(3) and 217.6(2) pm. The MoN distances were found to be virtually identical at 164.9(3) and 166.3(4) pm, respectively, and slightly shorter than the observed Mo–NH distance of 172 pm (av.) in Herrmann's structures. The activation of N_2 by Mo(III) complexes of the type [L_3Mo] (L = NH_2, NMe_2, CH_3) has been studied using all electron-generalized DFT calculations. The influence of relativistic effects was found to be particularly high for a 4*d* metal, and this was put down to the strength of the MoN bond.[74]

5.07.2.2.3 Containing oxygen-supporting ligands

Reviews on complexes containing metal oxo-alkyl complexes have appeared covering their synthesis, conversion to alkylidene complexes with subsequent catalytic use,[43,75] and as alkene epoxidation catalysts.[76] The complexes [Mo(bpy)(O)$_2$R$_2$] (R = Br, Me, Et) have been shown to effect ROMP of norbornene in the presence of MeMgBr. Of greater interest is when [Mo(bpy)(O)$_2$Me$_2$] is supported on montmorillonite K10. Catalysis occurs in the absence of the co-catalyst producing a polymer containing a higher *cis* content, with the *cis* and *trans* parts of the polymer being more "blocky" than those prepared in the presence of the co-catalyst.[77] The preparation of [Mo(bpy)(O)$_2$Me$_2$] and analogous compounds containing functionalized bpy ligands has been described, as has their utility as oxidizing agents.[78] A patent has appeared in which compounds of the type [Mo(O)X$_2$R$_2$] (X = halogen R = $C_1 - C_4$ alkyl) are used as epoxidation catalysts.[79] Related complexes containing diazobutadiene ligands, rather than bpy, [Mo(DAB)(O)$_2$(Me)$_2$], have also been prepared and used as ROMP catalysts,[80] as have the coordinatively unsaturated complexes [Mo(O)$_2$(R)$_2$] (R = Me, Et).[81,82] The alkylation of [TpMo(O)$_2$X] (Tp = hydrotris(pyrazolyl)borate) has been described,[83] and in a Raman study on the comparable [Tp*Mo(O)$_2$Me] and [Cp*Mo(O)$_2$Me] complexes, it was shown that the Tp* ligand is a stronger donor than Cp*. This contrasts the observation that Cp is a stronger donor than Tp in carbonyl-containing complexes.[84] The reaction of the quadruply bonded complex [Mo$_2$(^{i}Bu)$_2$(NMe)$_4$] with propanol has been investigated and shown to effect amide for alkoxide exchange with concomitant loss of the ^{i}Bu groups by reductive elimination.[85] The use of related compounds containing diaryloxo ligands in ROMP has been described.[86,87] The preparation of [Mo$_4$(μ-O)$_4$Me]-containing clusters has been described,[53] as have other multimetallic species that contain oxo ligands.[88,89]

5.07.2.2.4 Alkynyl-containing complexes

Metal alkynyl complexes continue to be of interest because of their potential applications in non-linear optics, luminescent materials, molecular devices, and polymer chemistry. The chemistry of homodinuclear σ-alkynyl complexes has recently been reviewed.[90] Compounds of the type $[Mo_2(C{\equiv}CR)_4(PMe_3)_4]$ ($R = Me$, ^iPr, ^tBu, $SiMe_3$, Ph) are readily prepared on treatment of $[Mo_2(PMe_3)_4X_4]$ with 4 molar equiv. of $LiC{\equiv}CR$.[91] The parent acetylide complex $[Mo_2(C{\equiv}CH)_4(PMe_3)_4]$ is readily obtained by desilylation of $[Mo_2(C{\equiv}CSiMe_3)_4(PMe_3)_4]$ with $[^nBu_4N][HF_2]$.[92] Treatment of the complex $[Mo_2Cl_4(dmpm)_2]$ {dmpm = bis(dimethylphosphino)methane} with a mixture of $LiC{\equiv}CSiMe$ and $HC{\equiv}CSiMe$ resulted in a complex that contains σ^1-alkynyl ligands, a (μ-$\eta^2:\eta^2$-$HC{\equiv}CSiMe$) ligand and a (μ-$C{=}C(SiMe_3)$-η^2-$C{\equiv}CSiMe$) ligand derived through multi-ligand coupling.[93] Resonance Raman spectroscopy and X-ray crystallography have been used to study these complexes in an attempt to gain evidence for π-backbonding effects.[94] The X-ray structures confirm D_{2d} symmetry for the $[Mo_2(C{\equiv}CR)_4(PR_3)_4]$ complexes with little variation in the Mo–Mo bond distance (213 pm). The compounds are diamagnetic and have been studied by NMR spectroscopy. Electrochemical investigations that were carried out on $[Mo_2(C{\equiv}CSiMe_3)_4(PR_3)_4]$ revealed a single-electron reduction at −2.13 V (vs. Fc).[95] Other examples of compounds containing alkynyl ligands have been reported.[96–99]

5.07.2.2.5 Other complexes

A review of synthetic procedures used to prepare molybdenum organometallic complexes excluding arene complexes has appeared,[100] as has a review of the use molybdenum organometallics in chemical vapor deposition (CVD).[101] Paramagnetic complexes of the type $[Mo(CH_2SiMe_3)(o\text{-}^iPr_2P\text{-}C_6H_4\text{-}\eta^6\text{-}C_7H_6)]$ have been prepared and characterized by X-ray crystallography, for example.[102] Complexes containing the triscyanomethyl ligand have also been reported.[103] Alkyl transfer from Pt to Mo mediated by oxygen exchange has been described,[104] as has the susceptibility of Mo–C bonds to insertion.[34,105] The behavior of CH_3 radicals on O/Mo (110) surfaces[106] and their catalytic oxidation has been investigated too.[75] Complexes containing heavier group 14 ligands of the type, SiR_3,[107–110] GeR_3,[108–110] and SnR_3[108,111] have been prepared and characterized.

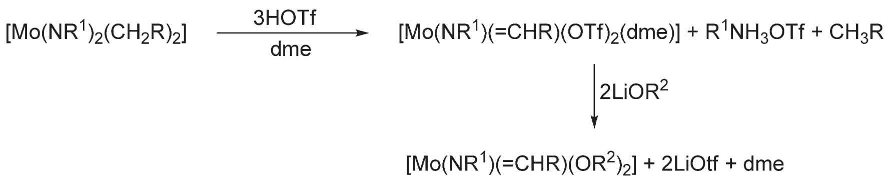
5.07.3 Alkylidene-containing Complexes

By far the most significant development of non-carbonyl-containing organometallic chemistry of molybdenum since 1994 has been in the area of high oxidation state Schrock-type alkylidene complexes. Some are now commercially available, and they are routinely used to effect transformations in mainstream organic natural product synthesis[112–124] and carbohydrate chemistry.[117,125–130] This has recently been recognized by the joint award of the 2005 Nobel prize for chemistry to Chauvin, Grubbs, and Schrock for their contributions to metathesis chemistry. Comprehensive annual surveys on the chemistry of transition metal double and triple bonds have appeared, covering the literature from 1997 to 2002, and are likely to continue to appear on an annual basis.[131–136] This section will concentrate on the synthesis, characterization, and reactivity of well-characterized compounds. A general overview of the catalytic uses of high oxidation state Schrock-type catalysts will be included to a level to define reaction class. Many review articles have appeared covering the following topics: alkylidene complexes,[137] alkylidene complexes as polymerization initiators,[138] metathesis reactions,[139–144] alkene metathesis in organic chemistry,[145–151] enantioselective reactions,[152–155] asymmetric olefin metathesis (AOM),[155–157] asymmetric diene metathesis polymerization (ADMET),[158,159] ROMP,[160,161] ring-closing metathesis (RCM),[162,163] heterogenized alkylidene catalysts,[164,165] preparation of fluorinated block co-polymers,[166] stereoselectivity with acyclic internal alkenes,[167] and alkyne polymerization.[168–170]

5.07.3.1 Schrock-type Alkylidene Complexes

5.07.3.1.1 Synthesis and structure

The use of high oxidation state molybdenum alkylidene-containing complexes in many areas of organic synthesis and polymer chemistry is becoming increasingly common. It has been stated: "No magic catalyst has been discovered that will achieve high activity and enantioselectivity in all circumstances, and it seems highly unlikely that any will be discovered".[142] The inability of one compound to be a cover-all catalyst has driven the synthetic chemist to prepare ever more elaborate systems. To this end, a large number of high oxidation state imido-supported alkylidene complexes of the type $[Mo{=}CHR(NR)(OR)_2]$ have been prepared and fully characterized. They are normally synthesized,[137,155,171–187] as illustrated in Scheme 4. In addition, compounds that contain tethered imido alkylidene



Scheme 4 General route to high oxidation state alkylidene complexes.

functionality have been prepared in a similar fashion.[188,189] For comprehensive listings of the compounds made, see the reviews written by Schrock.[137,155]

The main development in this area over the last decade has been the synthesis of asymmetric variants.[154,155] Initial syntheses of chiral variants were for use in polymer synthesis.[190,191] The structural characteristics of the complexes (Figure 10) are attractive for the design of chiral catalysts, using the method outlined in Scheme 4, for the following reasons: the simple modular mode of preparation and because the imido and alkoxy ligands do not disassociate from the metal center during catalysis. Therefore, changes in catalyst structure affect the catalytic site and influence both selectivity and reactivity. The alkoxy ligands offer the opportunity for incorporation of chirality through non-racemic tethered chiral bis-hydroxy ligands.[156,177] These complexes show appreciable catalytic activity and tolerance to a wide range of functional groups.

Twenty-four complexes of the type $[Mo(NR^1)({=}CR^1R^2)(OR^3)L_n]$ (L = two-electron donor; $n = 0, 1$) have been studied by single crystal X-ray diffraction,[172–175,179,180,188,192–201] and the $Mo{=}C$ bond length varies between 182.7 and 194.9 pm. The presence of *syn*- and *anti*-alkylidyne isomers (Figure 11) has a profound effect on the reactivity of alkylidene complexes.[184] Schrock and co-workers rationalized that the *syn*/*anti*-isomerization had a significant influence on the *cis*/*trans*-double bond content obtained during ROMP of norbornadienes.[184,202] It is generally found that the *syn*-isomer is the most stable with $K_{syn/anti} > 10^3$ (Figure 11). The rate of interconversion is also fast when R is an electron-donating group ($R = {}^tBu$, $k_{syn/anti} = 1\,s^{-1}$) and relatively slow when electron withdrawing ($R = CMe(CF_3)_2$, $k_{syn/anti} = 10^{-5}\,s^{-1}$). In addition, it has been concluded from kinetic data that the *anti*-isomer is at least 100 times more reactive in metathesis reactions than the *syn*-isomer. Detailed NMR studies have been carried out on the ROMP of 2,3-bis(trifluoromethyl)norbornadiene $NBDF_6$ and the data obtained used to rationalize the resulting polymer stereochemistry. The norbornadiene attacks on the CNO face of the alkylidene-containing complex (C = alkylidene C; N = imido N; and O = alkoxide O) using its own *exo*-face. The bridgehead has to be

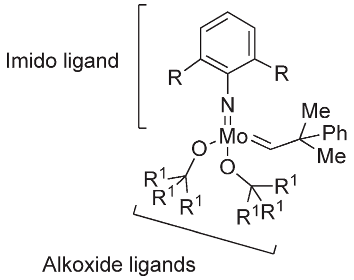


Figure 10 General structure of imido-supported alkylidene complexes.

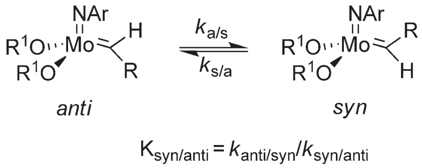
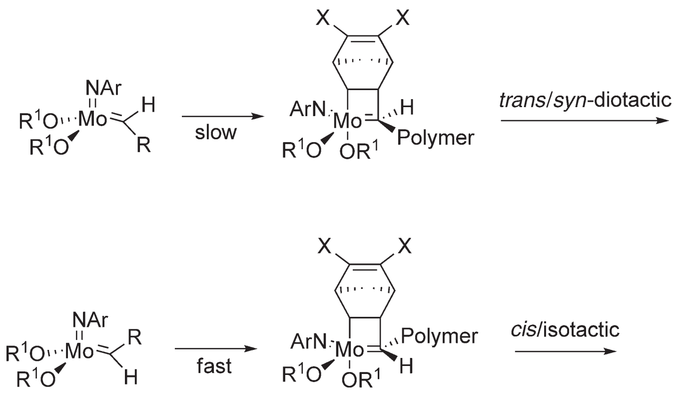


Figure 11 *Syn*- and *anti*-alkylidene rotamers.



Scheme 5 The influence of the *syn*- and *anti*-rotamers on polymer double bonds.

syn to the imido group. The relative stereochemistry then depends on the relative rates of rotamer isomerization and polymerization. The poly-NBDF$_6$ prepared using [Mo(NC$_6$H$_3$-2,6-^{i}Pr)-(CHCMe$_2$Ph)(O^{t}Bu)$_2$] is produced by *syn* insertion of the monomer on the *exo*-face of the unsubstituted norbornadiene double bond of the *anti*-rotamer. This polymerization process was found to be slow meaning that the *anti*-isomer is kinetically accessible at room temperature. Since $K_{\mathrm{syn/anti}} = 10^3$, the *anti*-rotamer has to be in the order of 10^5 times more reactive than the *syn*-rotamer to generate the experimentally observed >99% *trans* double bonds. On modification of the alkoxide ligands to {OCMe(CF$_3$)$_2$}, the rate of polymerization was found to be greater than *syn*/*anti*-isomerization, so the *syn*-rotamer is the active metathesis form and results in the formation of the *cis* double bonds (Scheme 5). This *syn*/*anti*-rotamer accessibility as the origin of the *cis*/*trans* double bonds has been further confirmed through the investigation of the temperature effect.[202] This interpretation of the polymerization process is strongly supported by theoretical calculations.[203]

5.07.3.1.2 Attachment to solid supports

With increasing environmental concerns, the general desire to reduce waste and enhance recyclability attachment of alkylidene complexes to solid supports has been investigated and successfully achieved. The reactivity of the immobilized systems has been investigated.[194,204–210] It has been found that chiral versions are effective in asymmetric catalysis and are competitive with their homogeneous analogs.[204–206]

5.07.3.1.3 Reactions of alkylidene complexes

The most significant advance in the reaction chemistry of these high oxidation state alkylidene complexes is the use of chiral versions in asymmetric synthesis and target-oriented organic synthesis.[155]

5.07.3.1.3.(i) Metathesis reactions

5.07.3.1.3.(i).(a) With alkenes

The different types of metathesis reaction that Schrock-type catalysts are used for are illustrated in Figure 12. It is clear that there is no single catalyst that shows unique efficacy in all metathical reactions, and studies have been carried out to compare the relative efficiencies of the high oxidation state imido-supported Mo alkylidene (Schrock-type) catalysts with the lower oxidation state ruthenium carbene complexes (Grubbs-type catalysts).[129,211–218] The system which produces the most effective catalyst is sometimes counterintuitive, and a catalyst screen is often used to determine which catalyst should be used. What is clear though, is that the Mo systems are tolerant to a wide range of functional groups. It has also been shown that metathesis reactions can be carried out in supercritical CO$_2$.[219] Examples of catalytic enantioselective RCM,[196] tandem asymmetric ROMCM,[220] and asymmetric olefin metathesis in target-oriented synthesis[221] are illustrated in Schemes 6–8.

For other examples, the reader is directed to the following articles, which include asymmetric variants, on ROMP,[130,191,208,222–277] ADMET,[157,278–292] ROCM and cross-metathesis (CM),[217,220,293–299] RCM.[180,195,196,221,300–308] The ability of these systems to tolerate elements from groups 14 to 16 is illustrated in the following selected articles: group 14 precursors, the preparation of allyl silanes by CM,[309] the polymerization of

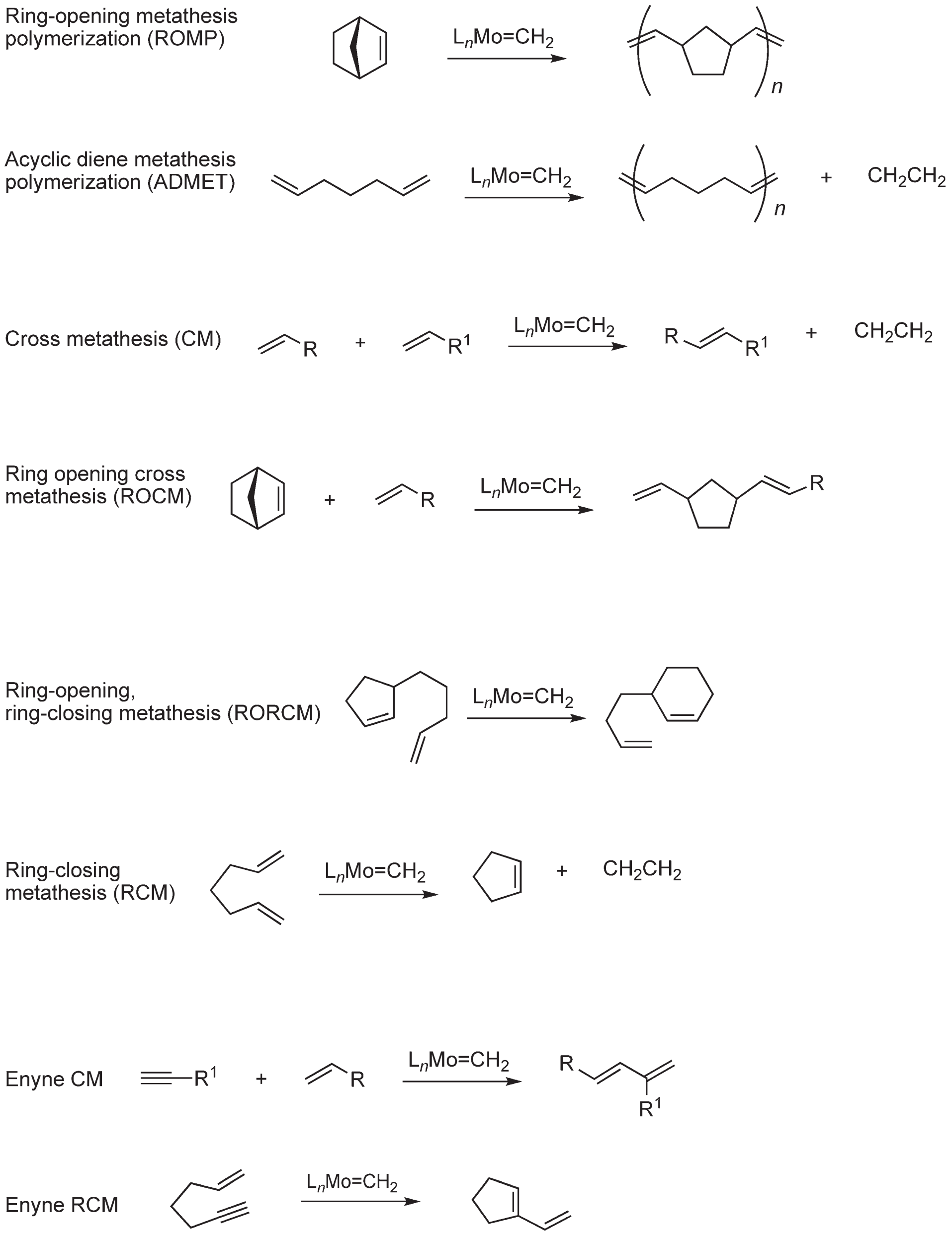
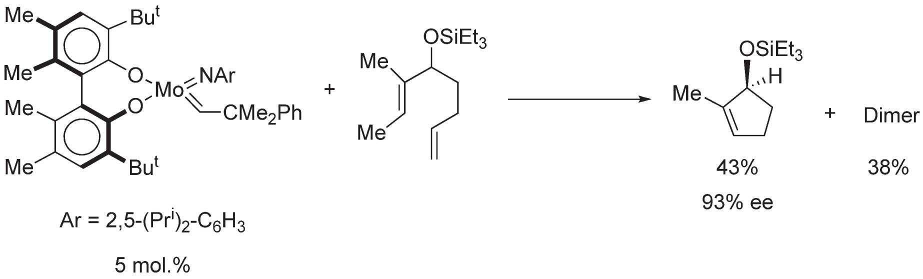
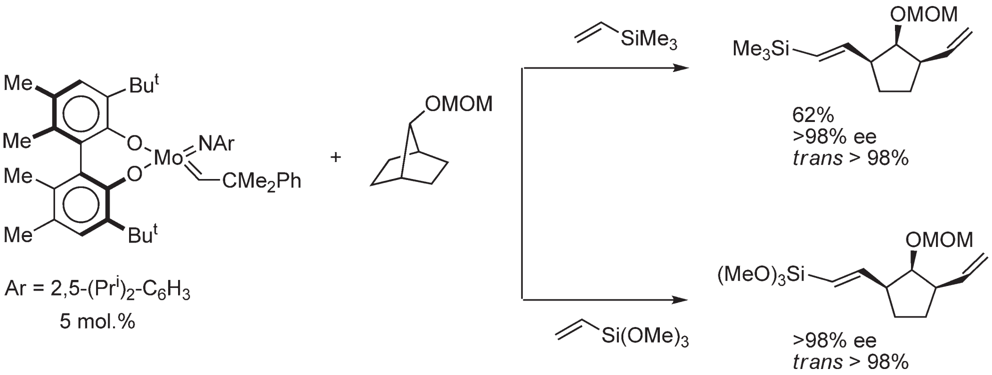


Figure 12 Different types of metathesis reactions.

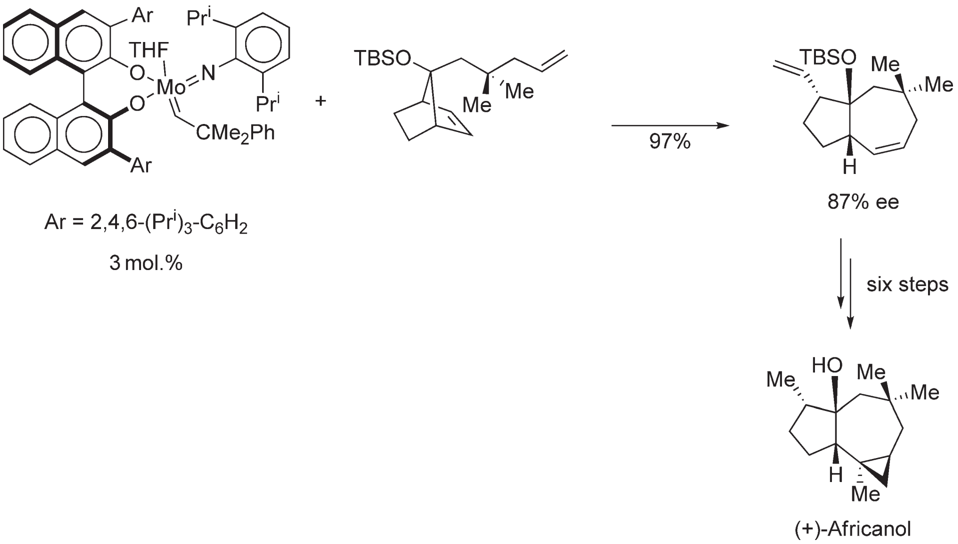
o-trimethylsilylphenylacetylene,[200] diethynyldisilanes,[199] the formation of silicon-containing macrocycles and polymers,[310] carbosilane oligomers,[311] and alkenylsilyl ethers by RCM.[312] Similarly, vinyl[313] and allyl[314] stannanes have been prepared by CM and polycarbostannanes obtained by ADMET;[287,288] group 15 precursors have been used to form cyclic phosphinates,[315] cyclic phopshines RCM,[211] RO of cyclic imines,[192,228] unsaturated amines,[316] mixed imide systems,[317] chiral secondary cyclic amines,[318] and nitrogen heterocycles;[319,320] group 16 precursors have led to the formation of highly substituted alcohols,[321] tertiary alcohols,[322] perhydroxylated alkenes,[323] chiral furans,[324] cyclic-enolethers,[325–327] polyethers,[328] and chromenes[214] are all readily prepared by metathesis reactions. Schrock-type alkylidene complexes have been found to be tolerant to sulfur-based functional groups, and have been used as catalysts in the preparation of sulfur-containing heterocycles by RCM,[329] to effect RCM of vinyl sulfides,[330] and to effect CM of vinyl sulfones and vinyl sulfoxides.[331] Simple alkene isomerization by metathesis has also been described.[332]



Scheme 6 Enantioselective RCM.

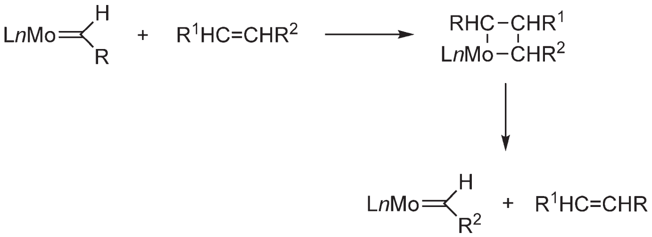


Scheme 7 Enantioselective AROM/CM.



Scheme 8 Enantioselective AROM/RCM to generate a bicyclic product on a synthetic route to (+)-africanol.

Kinetic investigations have also been carried out to try and elucidate the factors that influence methathesis in a variety of different systems.[243,244,333–336] Torsional strain,[337] varying alkene-substitution patterns,[182,338] and *Z*/*E* alkenes and their interaction with both Mo- and W-based catalysts[339] have all been investigated in attempts to obtain a better understanding of the factors that influence the activity observed in these systems.



Scheme 9 Chauvin mechanism for olefin metathesis.

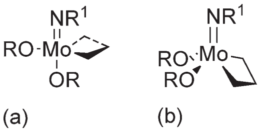


Figure 13 Geometries of intermediate molybdacyclobutanes: (a) Trigonal bipyramidal and (b) Square-based pyramid.

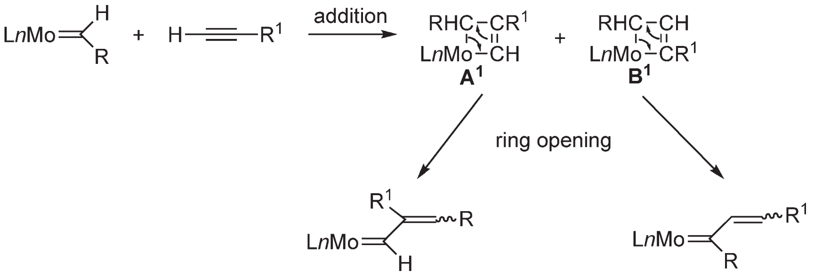
Theoretical calculations. The addition of alkenes to the Mo═CR$_2$ fragment has been studied[203,334,340–342] to model metathesis processes and to elucidate the importance of the molybdacyclobutane intermediate. The generally accepted pathway is illustrated in Scheme 9. The intermediate molybdacyclobutane-containing complex has two possible geometries, either trigonal bipyramidal or a square-based pyramid (Figure 13).

The calculations show that the molybdacyclobutane is stable with respect to decomposition into the alkylidene and free alkene, and that only a small ca. 10 kJ mol^{-1} activation barrier exists for its formation in the [alkylidene + alkene]-reaction. The decomposition energy calculations also inferred that the square-pyramidal geometry is most stable when electron-releasing alkoxide ligands are present, and the trigonal-bipyramidal structure is favored in the presence of electron-withdrawing alkoxides. The reaction pathway was found to be similar for both cases. Initially, the alkene forms a weak adduct with the alkylidene complex. At this point in the reaction coordinate the course of the reaction differs. When electron-releasing alkoxides are present, nucleophilic attack at the metal center followed by nucleophilic attack by the alkylidene carbon on the coordinated alkene occurs. Therefore, a stepwise process to form the molybdacyclobutane takes place, whereas for electron-releasing alkoxides, nucleophilic attack by the alkene at the metal center and alkylidene carbon are simultaneous and the process is, in this instance, concerted. This concerted [$2_\pi + 2_\pi$]-addition (which is symmetry forbidden in organic chemistry) between the alkylidene carbon atom and the alkene is made feasible by non-zero π–π^* overlaps and because there is a considerable energy gap between the $\pi_{\mathrm{alkylidene}}$, π_{alkene}. The π_{olefin} is 4 eV lower in energy. It has been found that the rate of *syn*/*anti* interconversion of the alkylidene ligand is important in stereocontrol during the polymerization process (Scheme 5).[203,341] The Mo═CR$_2$ bond strength has been investigated theoretically and found to be of comparable energy to an MoO bond.[343] The reactivity of the Mo═CH$_2$ fragment, found on metallic surfaces, toward propene addition has been investigated using DFT, and molybdacyclobutanes were found to be part of the reaction pathway, thus mirroring the behavior seen in homogeneous systems.[344] Related studies on the Mo═CH$_2$ group bound to alumina have also appeared.[345–347]

Patent literature. The utility of the high oxidation state imido alkylidene complexes in a wide range of commercially important chemistry over the last 10 years is borne out by the number of patents granted. They include: uses in asymmetric ring-closing metathesis,[348] the manufacture of dental materials[349] polymer purification,[350] alkene and norbornene polymerization[351–356] photochemical ROMP of cyclic alkenes,[357] hydrogenation products derived from ROMP of cyclic alkenes,[352,358] CM for the preparation of fatty acid nitriles and amines,[359] preparation of 14-membered macrolides from leucomycins for the treatment of bacterial infections,[360] as agents for degelling polymerization chambers,[361] preparation of polyenes and conjugated aliphatic compounds,[362] and catalyst precursors.[363]

5.07.3.1.3.(i).(b) With alkynes

In addition to catalyzing metathesis reactions with alkenes, high oxidation state alkylidene complexes have been shown to be effective catalysts for the polymerization of alkynes.[181,193,198,201,364–371] The generation of chiral polyenes from alkynes has been described.[193] This work has also been studied theoretically.[342,372,373] The general mechanism by which alkynes interact with the alkylidene fragment is illustrated in Scheme 10. An unsymmetrical



Scheme 10 Addition of acetylenes to alkylidene complexes.

acetylene can add with two different orientations affording molybdacyclobutenes **A**[1] and **B**[1] (Scheme 10). The transition state structures are trigonal bipyramidal and similar to those observed in alkene addition.[373] The calculated enthalpy of HC_2H addition to $[MoNH(CH_2)(OR^1)_2]$ is 2.5 kJ mol^{-1} for $R^1 = Me$ and 0.6 kJ mol^{-1}, where $R = CF_3$, indicating a significant preference for addition to the fluorinated alkoxide-containing complex. These barriers to addition are slightly higher than those observed in the corresponding ethylene addition. α-Addition (R toward the metal) is found to be intrinsically more favorable than β-addition by over 17 kJ mol^{-1}; however, this preference is reduced by solvent effects. These observations are explained by a destabilizing interaction between the π-orbital of the acetylene and the imido ligand lone pair.

Conrotatory ring opening of the molybdacyclobutene ring has been studied in detail, and the ring can open via an imido “in” or “out” pathway. The outward pathway is found to be favored. Furthermore, this preference is enhanced by the presence of electron-withdrawing alkoxide ligands. The calculations went on to show why the confirmation of the polymer obtained is dependent upon the conformation of the starting alkylidene (*syn* or *anti*).[372]

5.07.3.1.3.(i).(c) Other reactions

Schrock-type alkylidene complexes have been shown to react with calyx[4]arenes,[374] have utility in hydroxyl-directed steroselective olefination of ketones,[375] and also react with phosphaalkynes.[376]

5.07.3.2 Other Alkylidene Complexes

Other types of high oxidation state alkylidene complexes with ancillary imido ligands have been described,[197,377–380] so have complexes with oxo ligands,[381] hydrotris(pyrazolyl)borate,[382–384] cycloheptatrienyl[385] and cyclopentadienyl–nitrosyl,[40,386–388] supporting ligands. A series of vinylidene complexes has been prepared and their reactivity investigated.[389,390] Insertion of alkynes into Mo–C bonds has been found to afford alkylidene complexes as well.[391] A stable alkylidene layer has also been obtained through the reaction of alkenes with MoC surfaces.[392] Alkylidenes on Mo metal surfaces have also been investigated.[393] A molybdenum/alumina system has also been developed as a metathesis catalyst and studied by a variety of techniques including DFT and X-ray photoelectron spectroscopy (XPS).[164,165,344–347]

5.07.4 Alkylidyne-containing Complexes

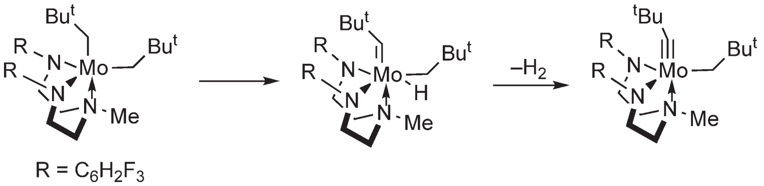
Systems derived from $[Mo(CO)_6]$[394] and their reactivity are beyond the scope of this section, which will concentrate on well-defined alkylidyne complexes. Comprehensive annual surveys on the chemistry of transition metal double and triple bonds have appeared, covering the literature from 1997 to 2002, and are likely to continue to appear on an annual basis.[131–136] In addition, a number of general reviews on complexes containing metal–carbon triple bonds are available.[395–400]

5.07.4.1 Synthesis and Structure

The efficacy of complexes of the type $[Mo(CR)(OR)_3]$ as metathesis catalysts has been known for 20 years, but the full exploitation of these compounds has been prevented due to difficulties associated with their synthesis. The search for short and effective synthetic routes to amido- and alkoxide-supported molybdenum alkylidyne complexes continues to develop, however, with the principal driver being the generation of complexes that will act as well-defined metathesis catalysts.

Schrock and co-workers have carried out detailed studies on complexes containing diamidoamine ligands,[64,65,68,401–404] in particular, the preparation of alkyl complexes derived from them. Of notable significance is the observation of double α-hydrogen elimination[65] at rates that are orders of magnitude faster than β-hydrogen elimination (where the alkyl group carries β-hydrogen atoms), yielding alkylidyne-containing complexes with the loss of dihydrogen, rather than loss of alkene where potential for competition was possible.[69] The reason given for α-elimination taking precedence over the normally favored β-hydrogen elimination in these cases is the lower steric requirement of the alkylidene hydride intermediate versus alkene hydride. The compound $[\{(3,4,5\text{-}F_3C_6H_2NCH_2CH_2)_2NMe\}Mo(\equiv CBu^t)(CH_2Bu^t)_2]$ formed by double α-hydrogen elimination (no β-elimination possible) from $[\{(3,4,5\text{-}F_3C_6H_2NCH_2CH_2)_2NMe\}Mo(CH_2Bu^t)_2]$ (Scheme 11) has been crystallographically characterized[68] (Figure 14), and found to have an Mo≡C bond length of 177.6(3) pm and an Mo–C bond length of 214(3) pm. Confirmation of the double α-elimination followed by loss of hydrogen was confirmed by measurement of the H_2 produced. The alkylidyne ^{13}C resonance was observed at 307.7 ppm, which is typical of this type of d^0-alkylidyne-containing complex.[395]

In addition to compounds containing terminal alkylidyne ligands, examples of bridging alkylidyne ligands are also known.[405] The oxy–carbyne complex $[\{(3,4,5\text{-}F_3C_6H_2NCH_2CH_2)_3NMe\}Mo\equiv COSiMe_3]$ was obtained on reacting the anionic carbonyl-containing complex $[\{(3,4,5\text{-}F_3C_6H_2NCH_2CH_2)_3NMe\}Mo(CO)]^-$ with $SiMe_3Cl$.[406] Cummins and co-workers reported[407] the preparation of the trisamido complex $[Mo\{N^tBu(C_6H_3\text{-}3,5\text{-}Me)\}_3]$, which was then used by Fürstner *et al.* as a catalyst for alkyne metathesis.[408] Subsequently, Cummins *et al.* reported the preparation of well-defined alkylidyne complexes from $[Mo\{N^tBu(C_6H_3\text{-}3,5\text{-}Me)\}_3]$[409] and $[MoH(\eta^2\text{-}Me_2C{=}N(^tBu)C_6H_3\text{-}1,2\text{-}Me_2)(\{N^tBu(C_6H_3\text{-}3,5\text{-}Me)\}_2]$[410–413] (Schemes 12 and 13), and the early chemistry relating to these compounds has been reviewed, and some patented.[414,415] Alcoholysis of these amido complexes yields active, alkoxide-supported, alkyne metathesis catalysts.



Scheme 11 Alkylidyne formation via double α-elimination.

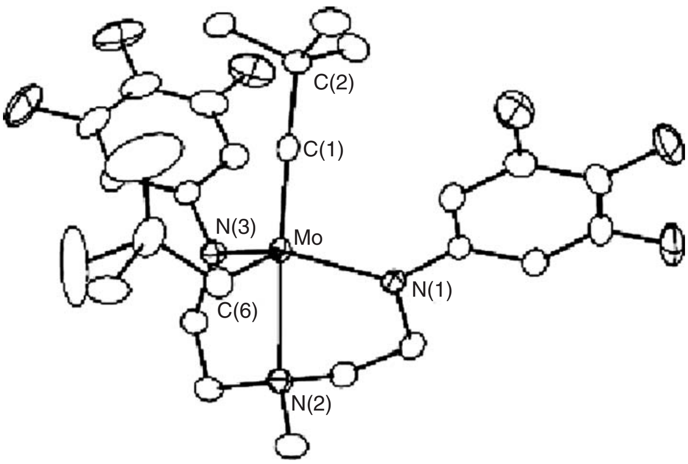
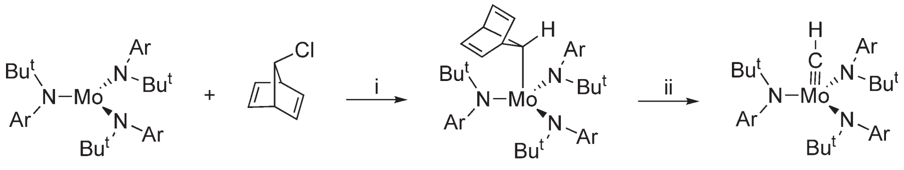
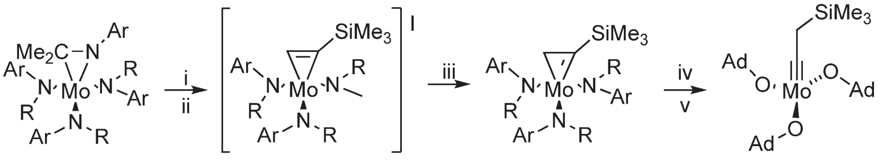


Figure 14 Molecular structure of $[\{(3,4,5\text{-}F_3\text{–}C_6H_2F_3NCH_2CH_2)_2NMe\}Mo(\equiv CBu^t)(CH_2Bu^t)_2]$. Reprinted with permission from Cochran, F. V.; Schrock, R. R. *Organometallics* **2001**, *20*, 2127–2129. © (2001) American Chemical Society.


i, [Ti{N(^{t}Bu)Ar}$_3$]; ii, $-C_6H_6$

Scheme 12


i, HC_2SiMe_3; ii, 0.5 I_2; iii, Li[BHEt$_3$]; iv, 353 K, 12 h; v, AdOH

Scheme 13

Some mixed amido/biphen-containing complexes (biphen^{2-} = 3,3′-di-^{t}butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate) have also been prepared, and when they were reacted with a range of alkynes were found not to effect metathesis; rather metallacyclobutadiene-containing complexes were obtained, which decomposed to η^2-alkyne-containing species, which in one case was crystallographically characterized.[416]

The anions [C≡Mo{N(R)Ar$_3$}]$^-$ {R = C(CD$_3$)$_2$CH$_3$ or ^{t}Bu; Ar = 3,5-C$_6$H$_3$–Me$_2$} containing one-coordinate carbon have been prepared through the deprotonation of the parent alkylidyne by benzylpotassium (Scheme 14). Extremely rapid proton exchange between the alkylidyne and carbide-containing complexes was found to occur in THF ($k = 7 \times 10^6\,M^{-1}\,s^{-1}$). The solid-state structures of the starting alkylidyne and its conjugate base have been determined crystallographically. The Mo≡C bond lengths are 170.2(5) pm[417] and 171.3(9) pm,[418] respectively, and are statistically the same. The ^{13}C{^{1}H}-NMR shift for the carbide carbon is δ 501 ppm versus the parent alkylidyne at δ 282 ppm. The carbide is found to be nucleophilic, and its reactivity is summarized in Scheme 14.

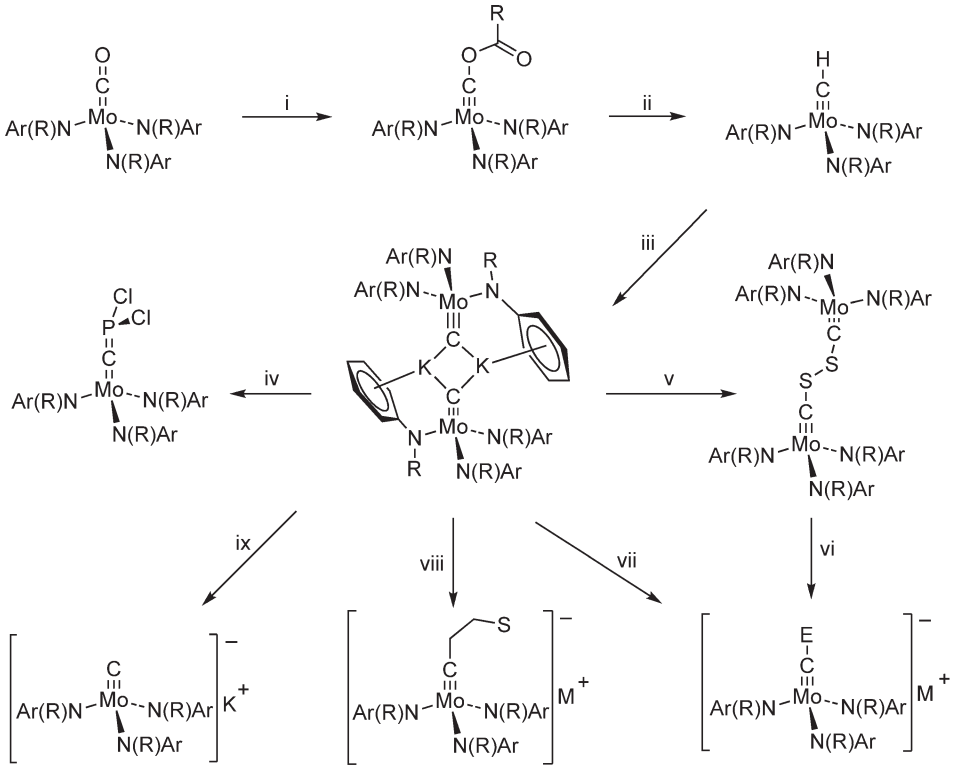
The most significant advance in the preparation of well-defined alkylidyne metathesis catalysts has been reported by Moore and co-workers.[419] Building on the work of Fürstner's group,[408,420,421] who reported the generation of active metathesis catalysts through the treatment of [Mo{N^{t}Bu(C$_6$H$_3$-3,5-Me)}$_3$] with CH$_2$Cl$_2$ that generates mixtures of [MoCl{N^{t}Bu(C$_6$H$_3$-3,5-Me)}$_3$] and, metathetically inactive, [Mo≡CH{N^{t}Bu(C$_6$H$_3$-3,5-Me)}$_3$], coupled with the knowledge that the metathetically inactive complex [Mo≡CH{N^{t}Bu(C$_6$H$_3$-3,5-Me)}$_3$] is known to readily convert into the active alkoxy analogs [Mo≡CH(OR)$_3$] on alcoholysis.[409,411,412,417] Moore recognized, in what proved to be a master stroke, that by the introduction of a reductive recycling strategy for the inactive halide side-product followed by alcoholysis, 100% conversion to active alkylidyne metathesis catalysts would be achieved. Carrying out the reaction in the presence of magnesium gives exclusively the metathesis inert amido/alkylidyne-containing complex which, fortunately, is itself inert toward the Mg. Subsequent alcoholysis generates the alkoxy derivatives that are direct analogs of the known metathesis-active Cummins alkoxide-supported alkylidyne catalysts (Scheme 15). The synthesis of this class of compounds is now straightforward, and their utility in metathesis chemistry is likely to blossom rapidly.

Routes to aminocarbyne-containing complexes and their reactivity have been described,[422] and solid-state 2D NMR spectroscopy has been used to study alkylidyne-containing complexes bound to silica.[423] Protonation of the bis-alkyne-containing complex [Mo(dppe)$_2$(η^2-HC$_2$Me)$_2$] with HBF$_4$·OEt$_2$ was found to give the alkylidyne-containing complex [MoF(CC$_2$Me)(dppe)$_2$] in 42% yield.[424]

5.07.4.2 Alkyne Metathesis

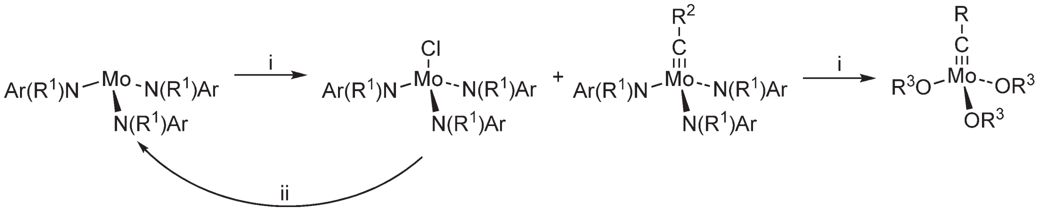
5.07.4.2.1 Alkyne metathesis in synthesis

The use of well-defined molybdenum complexes in alkyne metathesis has been reviewed.[425] One strategy of particular note is the use of RCM of alkynes followed by stereoselective alkyne hydrogenation to give exclusively



i, Na/Hg, RC(O)Cl; ii, Na/THF, MeCN; iii, KCH_2Ph; iv, PCl_3; v, S_8; vi, Na/Hg THF, benzo-12-c-4; vii, Se or Te; viii, SC_2H_4; ix, Kryptofix 222 or benzo-15-c-5

Scheme 14



i, RCH_2Cl (R^1 = H, CH_3, CH_2CH_3); ii, Mg; iii, R^3OH

Scheme 15

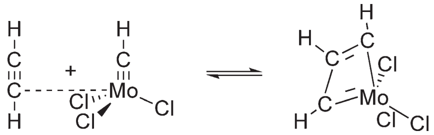
(*Z*)-alkenes,[421,426,427] and this approach has been successfully applied to the synthesis of prostaglandins,[426,428] microbial biosurfactants,[429] marine toxins,[430] and reactions carried out in supercritical CO_2.[431] It overcomes the problem of carrying out RCM on equivalent alkene substrates using Schrock- or Grubbs-type alkylidene complexes,[425] which generally give an (*E*)/(*Z*)-isomeric mixture of the cyclic alkene that then require separation. Using Moore's reductive recycle strategy to generate well-defined alkylidyne complexes, effective alkyne dimerization has been achieved,[432] and further work has shown that by a slight modification of the reaction conditions, a collection of poly(2,5-thienyleneethynylene)s can be prepared[433] by alkyne metathesis with M_n, in some cases, reaching 35 000 with a PDI(M_w/M_n) 2.7.

5.07.4.2.2 Mechanism of alkyne metathesis

Alkyne metathesis is much less studied than alkene metathesis, and this is primarily due to the lack of well-defined initiators. The mechanism of metathesis has been studied using non-local DFT by Ziegler and co-workers.[434] The reaction is considered to occur via the formation of a molybdacyclobutadiene (Scheme 16). The geometries of the starting alkylidyne complex and molybdacyclobutadiene are illustrated in Figure 15 with selected bond lengths and angles.

The major structural changes observed on reaction with the alkyne are: the pyramidal relationship shown by the molybdenum and three chlorine atoms is lost as they become co-planar; the alkylidyne carbon moves out of the coordination plane defined by the $MoCl_3$ fragment by 40°. These data also suggest that there is significant interaction between the $C_\beta(p_\pi)$ and $Mo(d_\pi)$ components in the $1b_2$ orbital of the molybdacyclobutadiene ring. The molybdacyclobutadiene was found to form in a manner similar to the $[\pi^3+\pi^3]$-symmetry-forbidden formation of cyclobutadiene from acetylene, which for the organometallic reaction pathway was found to be symmetry allowed. The activation barrier for molybdacyclobutadiene formation is $10\,kJ\,mol^{-1}$ and, once formed, is found to be $70\,kJ\,mol^{-1}$ more stable than the starting reagents. The tautomeric tetrahedrane $[(\eta^3\text{-cyclopropenyl})MoCl_3]$ complex has also been studied theoretically. Geometry optimization and energy minimization for the eclipsed (A) and staggered (B) conformations (Figure 16) was carried out with the eclipsed conformation, found to be energetically most stable. The study also showed that the direct formation of this tautomer was symmetry forbidden with a $40\,kJ\,mol^{-1}$ electronic barrier; however, the cyclopropenyl complex is $52\,kJ\,mol^{-1}$ more stable than the metallacyclobutadiene.

Chisholm and co-workers have also carried out DFT calculations on Schrock "chop-chop" reactions and gained insights into why tungsten-based systems are more effective than their molybdenum analogs.[435,436]



Scheme 16 Reaction of alkylidyne complex with an acetylene.

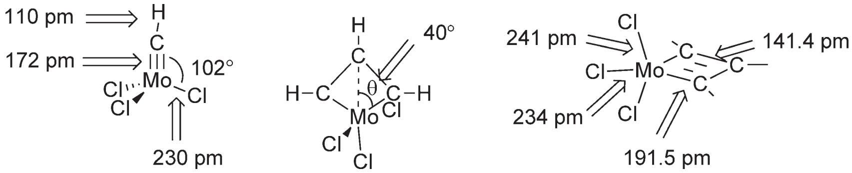


Figure 15 Calculated geometries of starting alkylidyne and molydacyclobutadiene.

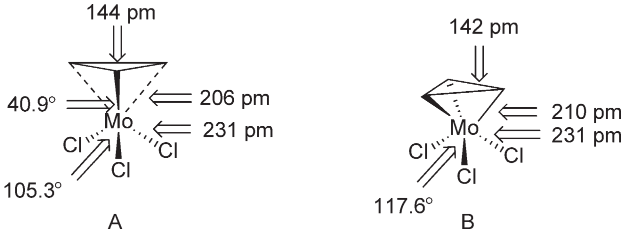


Figure 16 Calculated geometries of eclipsed (A) and staggered (B) cyclopropenyl tautomers.

5.07.4.3 Heavier Main-group 14 Element Triple Bonds

The compounds [Cp*(dmpe)MoH(SiMes)][437] and *trans*-[MoBr(dppe)$_2${Ge(η^1-Cp*)}],[438] which contain "formal" metal-to-silicon and -germanium triple bonds have been described. The Mo≡Si bond length was found to be 221.9(2) pm with Mo–Si–C 170.9(2)° and the Mo≡Ge bond length of 231.85(6) pm with Mo–Ge–C 175.3(4)° and both were shown to display characteristics similar to their carbon analogs the alkylidynes. In the solid-state structure of [Cp*(dmpe)MoH(SiMes)], there was evidence that the Mo–H ligand bridges the Mo≡Si bond, although in solution NMR data suggest the presence of an unbridged Mo≡Si bond. The η^1-Cp* bound to germanium was found to undergo a rapid haptotropic shift. Theoretical calculations suggest a barrier of approximately 10.7 kJ mol^{-1}.

5.07.5 Alkene-containing Complexes

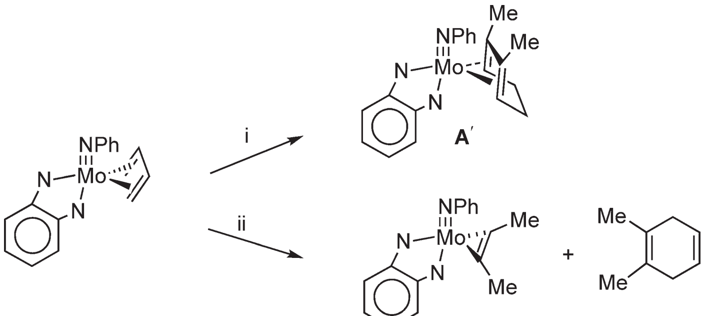
5.07.5.1 Containing Amido- and Imido-supporting Ligands

Gibson and co-workers have reported the preparation of the four- and five-coordinate bis(imido) alkene complexes of the type [Mo(N^{i}Pr)$_2$(PMe$_3$)$_2${η^2-H$_2$C$_2$H(R)}] (R = H, Me, CH = CH$_2$) and [Mo(N^{t}Bu)$_2$(PMe$_3$){η^2-H$_2$C$_2$H(R)}] (R = H, Me) from [Mo(NR)$_2$Cl$_2$(DME)].[439,440] The greater steric demand and reduced steric flexibility of the ^{t}Bu group was given as the reason for four-coordinate preference in the ^{t}BuN-containing complexes. The crystal structures of the complexes [Mo(N^{i}Pr)$_2$(PMe$_3$)$_2${η^2-H$_2$C$_2$H$_2$}] and [Mo(N^{t}Bu)$_2$(PMe$_3$){η^2-H$_2$C$_2$H(Me)}] have been described. For [Mo(N^{i}Pr)$_2$(PMe$_3$)$_2${η^2-H$_2$C$_2$H$_2$}], the structure is described as a distorted trigonal bipyramid about Mo with the two PMe$_3$ ligands axial and the alkene C═C vector parallel to the P–Mo–P axis. The C═C bond length is 137.5(10) pm, implying little π-backbonding to the alkene ligand. The alkene C═C bond vector in [Mo(N^{t}Bu)$_2$(PMe$_3$){η^2-H$_2$C$_2$H(Me)}] points toward the weakest π-donor ligand with an alkene C═C bond length of 143.1(7) pm, implying that it is behaving as a stronger π-acceptor than in its five-coordinate analog. Indeed, the [Mo(N^{t}Bu)$_2$(PMe$_3$)] fragment coordinates the diphosphine [{2,4,6-(CF$_3$)C$_6$H$_2$}$_2$P]$_2$, and, like its alkene congener, the P═P vector points toward the weakest π-donor PMe$_3$.[441] Other similar d^2-imido-containing alkene complexes have been described.[442,443] The preparation of [{N(CH$_2$CH$_2$NSiMe$_3$)$_3$}Mo(η^2-H$_2$C$_2$H$_2$)] has been achieved in two ways: reduction of [{N(CH$_2$CH$_2$NSiMe$_3$)$_3$}MoCl] with Mg in the presence of ethene or ethene displacement of dinitrogen from [{N(CH$_2$CH$_2$NSiMe$_3$)$_3$}Mo(N$_2$)].[406] The complex is paramagnetic with $\mu_B = 1.73$.

Boncella and co-workers have reported the preparation of the Mo(IV) alkene complexes [Mo(NPh){*o*-(Me$_3$SiN)$_2$–C$_6$H$_4$}(η^2-alkene)] through the treatment of [MoCl$_2$(NPh){*o*-(Me$_3$SiN)$_2$–C$_6$H$_4$}(THF)] with Grignard reagents (RMgCl, R = CH$_2$CH$_2$Ph, ^{n}Pr, ^{i}Bu) that contain β-hydrogen atoms.[444] The molecular structure of [Mo(NPh)-{*o*-(Me$_3$SiN)$_2$–C$_6$H$_4$}(η^2-CH$_2$CHPh)] was determined by a single crystal X-ray diffraction study, and the Mo–C alkene bond lengths are 214.5(2) and 219.0(2) pm, respectively, with a C═C distance of 145.2 (3) pm, suggesting the formation of a molybdacyclopropane on alkene complexation. In the reaction with EtMgCl, the molybdacyclopentane complex [Mo(NPh){*o*-(Me$_3$SiN)$_2$–C$_6$H$_4$}(CH$_2$CH$_2$CH$_2$CH$_2$)] is obtained along with an oligomer. Clean formation of the molybdacyclopentane-containing complex can be effected by reaction of [MoCl$_2$(NPh)-{*o*-(Me$_3$SiN)$_2$–C$_6$H$_4$}(THF)] with a stoichiometric amount of EtMgCl under an atmosphere of ethene. The chemistry of these complexes has been developed.[189,445–448] The complex [Mo(NPh){*o*-(Me$_3$SiN)$_2$–C$_6$H$_4$}-(η^4-CH$_2$═CHCH═CH$_2$)] has also been characterized by a single crystal X-ray diffraction study. The Mo–alkene bond lengths show significant Mo-terminal Mo-internal differences: 225.4(3) and 225.7(2) pm versus 233.6(2) and 235.5(2) pm, respectively, with diene CC bonds of 140.1(4), 139.7(4), 140.5(4) pm, respectively. This complex reacts with a stoichiometric amount of but-2-yne to give the cyclohexadiene-containing complex **A′** (Scheme 17), which has been structurally characterized. In the presence of excess but-2-yne, the alkyne-containing complex, which has also been structurally characterized, is produced along with free cyclohexadiene. The mechanism of this coupling reaction was probed and the proposed mechanism is illustrated in Scheme 18. Evidence for the ene–allyl intermediates was obtained from an arsenal of low-temperature NMR experiments.

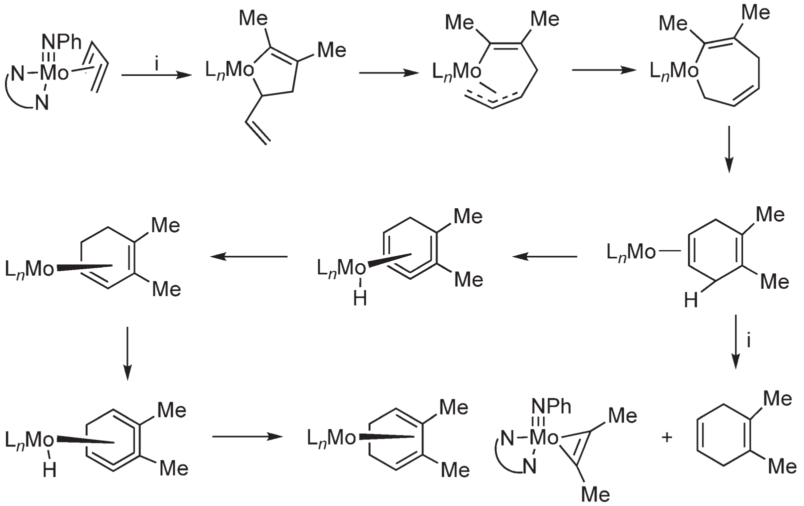
5.07.5.2 Cyclobutadiene-containing Complexes

The molecular structures of [MCl$_2$(η^2-Ph$_4$C$_4$)Cp] (M = Nb, Mo) have been reported.[449] The ^{13}C{^{1}H}-NMR data for the Nb complex indicated that the cyclobutadiene ligand is best considered as a dinegative ligand when applying formal oxidation states. In an extended Hückel molecular orbital (EHMO) study, comparing their relationship to the



i, MeC$_2$Me; ii, 2MeC$_2$Me

Scheme 17



i, MeC$_2$Me

Scheme 18

bent-sandwich complexes [MCl$_2$Cp$_2$], the dinegative nature of the cyclobutadiene ligand was confirmed. The formally 17-electron [MoCl$_2$(η^2-Ph$_4$C$_4$)Cp] displayed an EPR spectrum with a g value of 2.005 and a hyperfine splitting, $A = 36$ G (coupling to 5/2 nuclei of molybdenum atom ($^{95/97}$Mo). The complexes [Mo(η^4-P$_2$C$^t_2$Bu$_2$)$_3$][450] and [Mo{P(OMe)$_2$OB(F)$_2$OP(OMe)$_2$}(η^4-P$_2$C$^t_2$Bu$_2$)Cp][451] which contain the 1,3-diphospha-2,4-^{t}butyl-cyclobutadiene ligand have also been prepared. The homoleptic complex was prepared by co-condensation of Mo atoms and ^{t}BuCP and has been crystallographically characterized. The three rings orientate themselves so as to relieve steric interactions between the ^{t}butyl groups.

5.07.5.3 Containing Cyclopentadienyl-supporting Ligands

A detailed study was carried out to model the structural preferences observed in complexes of the type [CpMoLL(η^4-diene)]$^+$ using molecular mechanics, EHMO calculations, and crystallographic studies to gain insight into the *endo*-*exo*-fluxionality of coordinated dienes in this class of complex.[452] These calculations indicated that the energy differences between the *endo*- and *exo*-conformation for cyclic dienes is small, and that the presence of the *endo*-conformation in the solid state is probably due to crystal packing forces. The crystal structures of [Mo(NCMe)$_2$(η^4-C$_4$H$_6$)Cp][BF$_4$] and [Mo(PMe$_3$)$_2$(η^4-C$_5$H$_6$)Cp][BF$_4$] were also reported, and these structures displayed the normally observed *endo*-orientation of the diene fragment in the solid state (Figure 17).

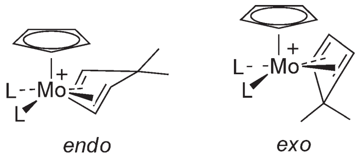
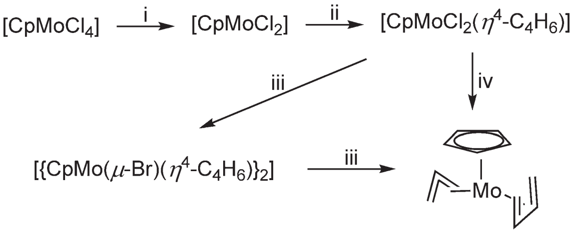


Figure 17 The *endo*- and *exo*-diene orientation on complexation.

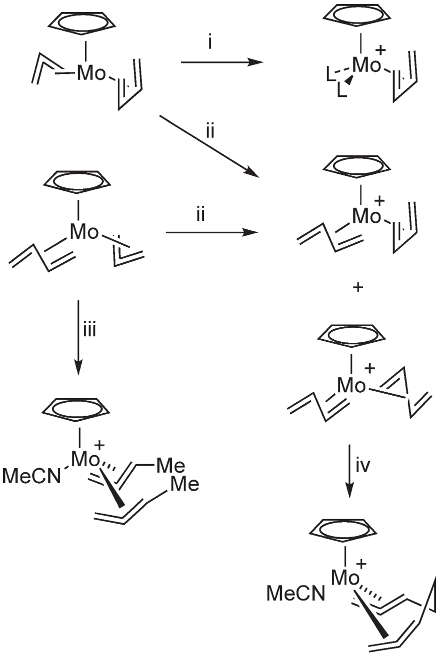
The protonation of cyclopropylcarbynes has been shown to generate diene-containing complexes of the type [CpMoLL(η^4-diene)]$^+$, and as expected the crystal structure of [CpMo{P(OMe)$_3$}$_2${η^4-H$_2$C═CHC(Me)═CH$_2$}]$^+$ displays *endo*-complexation of the diene.[453]

Poli and co-workers have carried out an in-depth study on Mo(II) and Mo(III) complexes that contain only carbon-based ligands, including dienes, allyls, and alkyls in the presence of a spectator Cp ligand.[14,454–458] Some aspects of this work have been reviewed.[459] The synthesis of these compounds and their patterns of reactivity toward electrophiles and nucleophiles are illustrated in Schemes 19–21.



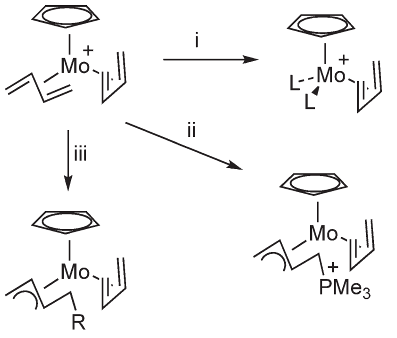
i, Zn; ii, C$_4$H$_6$; iii, CH$_2$CHCHMgBr; iv, 2CH$_2$CHCHMgBr

Scheme 19



i, HBF$_4$, MeCN or CN^{t}Bu; ii, HBF$_4$/THF, C$_4$H$_6$; iii, HBF$_4$/NCMe, C$_4$H$_6$; iv, NCMe

Scheme 20



i, NCMe or CN^{t}Bu; ii, PMe$_3$; iii, LiR (R = Me, CH$_2$CH=CH$_2$)

Scheme 21

Treatment of [CpMoCl$_2$] with a stoichiometric amount of butadiene followed by 1 molar equiv. of allylmagnesium bromide affords the Mo(II) dimer [{CpMo(μ-Br)(η^4-C$_4$H$_6$)}$_2$], which readily reacts with a further molar equivalent of allylmagnesium bromide to give the mixed allyl/diene complex [CpMo(η^3-C$_3$H$_5$)(η^4-C$_4$H$_6$)] that exits as a 98 : 2 mixture of [CpMo(*supine*-η^3-C$_3$H$_5$)(*prone*-η^4-C$_4$H$_6$)] and [CpMo(*supine*-η^3-C$_3$H$_5$)(*supine*-η^4-C$_4$H$_6$)] (Scheme 19).

On heating, isomerization to the [CpMo(*supine*-η^3-C$_3$H$_5$)(*s-trans*-η^4-C$_4$H$_6$)] isomer takes place. On cooling back to room temperature, this complex is found to be confirmationally stable, and has been isolated and crystallographically characterized. Chemical oxidation of [CpMo(η^3-C$_3$H$_5$)(η^4-C$_4$H$_6$)] (98 : 2 mixture) with [Cp$_2$Fe][PF$_6$] affords [CpMo(*supine*-η^3-C$_3$H$_5$)(*supine*-η^4-C$_4$H$_6$)][PF$_6$]. Subsequent reduction back with Cp$_2$Co afforded [CpMo(*supine*-η^3-C$_3$H$_5$)(*supine*-η^4-C$_4$H$_6$)], which has also been characterized crystallographically. However, little useful data could be obtained from the crystal structure because of allyl/butadiene disorder. It was found that these neutral complexes do not react with nucleophiles under mild conditions but readily react with protons.

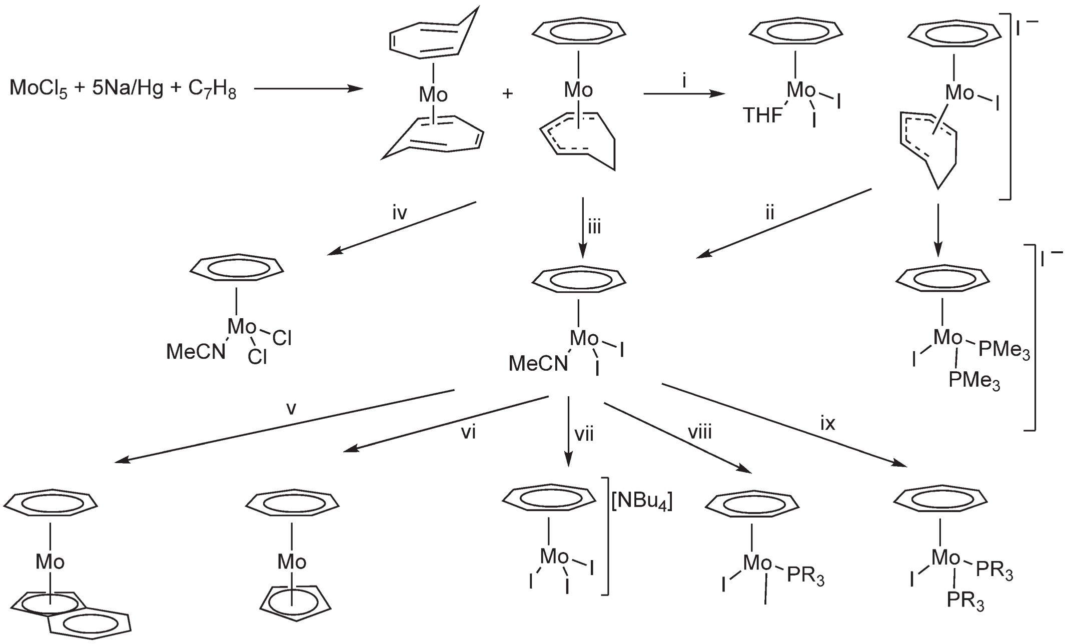
Preferential attack is at the allyl terminus liberating propene. The coordinatively unsaturated fragment [CpMo(*supine*-η^4-C$_4$H$_6$)], which is generated *in situ*, then forms adducts with a variety of donor molecules. Protonation of the *s-trans* butadiene was found to be preferable in NCMe yielding a bis-allyl complex (80%) versus protonation at the allyl terminus (20%). The treatment of the cationic complex [CpMo(*supine*-η^4-C$_4$H$_6$)(*s-trans*-η^4-C$_4$H$_6$)]$^+$ with a variety of nucleophiles has been investigated. Attack results in either displacement of the *s-trans* butadiene ligand or nucleophilic attack at the *endo*-terminal carbon of the *s-trans* butadiene ligand.[458]

The ability of the complexes [MoX$_2$(η^4-diene)(η^5-C$_5$R$_5$)] (R = H, Me; diene = butadiene, isoprene, 2,3-dimethylbutadiene; X = Cl, Me) to act as alkene polymerization catalysts has also been investigated.[454] The most active catalysts contained the Cp* ring. It was found that the Mo catalysts were less active than their Nb analogs even though they had a faster turnover frequency. The reduction in reactivity was put down to the greater covalency of the Mo–C bond and its higher strength relative to the Nb–C bond. The chain-propagation step was found theoretically to take place on the spin doublet surface. It was suggested that more efficient catalysts could be accessible if the π-acidity of the diene co-ligand could be reduced, thereby stabilizing the quartet ground state of a putative [CpMoL$_2$R]$^+$ intermediate. The potential problem with this proposition is the instability of this type of compound. It is well known that the compounds [CpMoR$_2$(PMe$_3$)$_2$], where the diene has been replaced by phosphines, decompose above −20 °C. Clearly though this is an avenue for further exploration.

5.07.5.4 Containing Cycloheptatrienyl Ligands

An improved synthetic route to [Mo(η^7-C$_7$H$_7$)(η^5-C$_7$H$_9$)] has been described, and the chemistry of this complex has been further developed (Scheme 22).[460–463]

The magnetic behavior of several compounds has also been investigated.[460,461] For example, the magnetic behavior of [MoI$_2$(NCMe)(η^7-C$_7$H$_7$)], which model fittings indicated was one-dimensional, is consistent with its crystallographically determined solid-state structure (Figure 18).



i, I_2, THF; ii, NCMe; iii, I_2, NCMe; iv, $PhICl_2$, Toluene, NCMe; v, Li(Ind); vi, LiCp; vii, $[NBu_4]I$; viii, PR_3 (R = Me, PPh_3); ix, Na/Hg, PMe_3

Scheme 22

The complexes $[Mo(\eta^6\text{-}C_6H_5\text{-}Me)(\eta^7\text{-}C_7H_3\text{-}1,2,4,6\text{-}R)][BF_4]$ (R = H, Me) were found to react with a range of thiols to yield the thiolate-bridged dimers $[\{Mo(\mu\text{-}SR^1)_3(\eta^7\text{-}C_7H_3\text{-}1,2,4,6\text{-}R)\}_2][BF_4]$ (R = H, R^1 = Et, Pr, Bu, Ph, CH_2Ph; R = Me, R^1 = Ph).[464] These molecules were found to be fluxional and the fluxionality is due to inversion at pyramidal sulfur. The barriers to inversion ($\Delta G^{\ddagger}$) were found to be in the range 52.9–58.1 kJ mol^{-1} by variable-temperature (VT) ^1H NMR spectroscopy. In related studies, the preparation of neutral imido-bridged complexes has also been described.[465] The syntheses of $[Mo(\eta^6\text{-}C_6H_5\text{–}Me)(\eta^7\text{-}C_7H_3\text{–}1,2,4,6\text{-}Me_4)]$ and $[MoCl(dmpe)(\eta^7\text{-}C_7H_3\text{-}1,2,4,6\text{-}Me_4)]$ from $[Mo(CO)_6]$ have been described along with the simple substitution reaction with Na(acac) (Scheme 23).

The mixed complex $[Mo(\eta^6\text{-}C_6H_3\text{-}1,3,5\text{-}Me_3)(\eta^7\text{-}C_7H_7)][PF_6]$ was prepared by refluxing $[Mo(CO)_3\text{-}(\eta^7\text{-}C_7H_7)][PF_6]$ with 1,3,5-trimethylbenzene.[466] The more sterically demanding arene complex $[Mo(\eta^6\text{-}C_6H_3\text{–}1,3,5\text{-}^tBu_3)(\eta^7\text{-}C_7H_7)][PF_6]$ was prepared via trimerization of $^tBuC_2H$ by $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)][PF_6]$. The 1,3,5-tri-^{t}butylbenzene ligand was found to be inert to substitution and gives a stable dication on oxidation; other molybdenum–arene-based systems were found to be unstable on oxidation.

Tamm and co-workers have recently reported[467] the synthesis of the sterically encumbered cycloheptatrienes, 1,3,5-R–C_7H_5 (R = ^{t}Bu, $SiMe_3$), through ring expansion of the parent, 1,3,5-$R_3C_6H_3$ with CH_2N_2, that then react with $[Ph_3C][BF_4]$ to give the tropylium cations, which readily coordinate to molybdenum (Scheme 24).

The crystal structure of the very sterically crowded dication $[Mo(\eta^6\text{-}C_6H_3\text{-}1,3,5\text{-}^tBu_3)(\eta^7\text{-}C_7H_4\text{-}1,3,5\text{-}^tBu_3)][BF_4]$ has been determined (Figure 19).

The ^{t}Bu groups of the arene and tropylium cation are seen to be staggered offering steric protection to the Mo center. It was found that the π-bound arene was inert to substitution, and mirrors the inert reactivity pattern displayed by the previously reported complex $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)]$. The redox pair $[Mo(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_4\text{-}1,3,5\text{-}^tBu_3)]$ **A**[2] and $[Mo(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_4\text{-}1,3,5\text{-}^tBu_3)][BF_4]$ **B**[2] have also been synthesized and crystallographically characterized (Figure 20).

The Mo–Mo bond is 16.1 pm shorter in the cation {307.81(6) vs. 323.9(1) pm} as expected on removal of an electron from an antibonding molecular orbital. The bonding in this redox pair was also studied using DFT. In a study based upon the isolobal relationship between $[Mo(\eta^7\text{-}C_7H_7)]$ and $[Ru(\eta^5\text{-}C_5H_5)]$, a series of heteroatom-functionalized side arms has been introduced into cycloheptatrienyl ligands,[467–470] which on complexation to molybdenum generate chelate systems analogous to the known ruthenium systems [CpRuL] with the principal aim to see if the molybdenum cycloheptatrienyl-containing complexes display similar catalytic activity. The synthetic protocol for the preparation of a phenol-substituted cycloheptatriene is illustrated in Scheme 25.

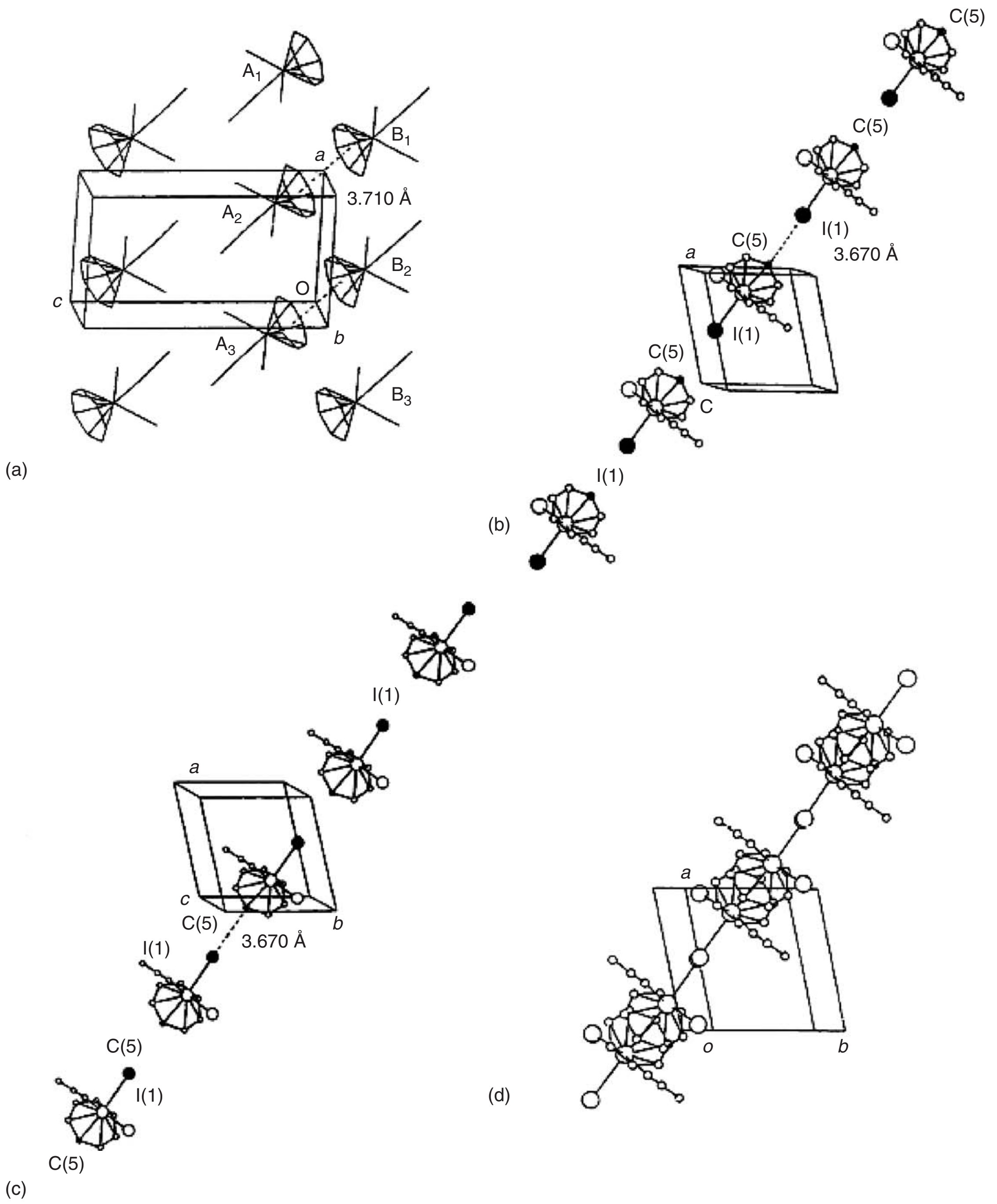
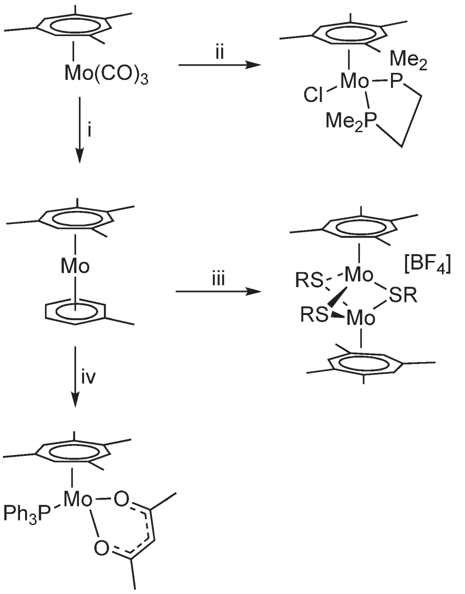


Figure 18 Crystal structure of [$MoI_2(NCMe)(\eta^7\text{-}C_7H_7)$]: (a) along the *b*-axis; (b) of molecules A_x along the *c*-axis; (c) of molecules B_x along the *c* axis; (d) along the *c*-axis. Reproduced by permission of The Royal Society of Chemistry from Green, M. L. H.; Harrison, A.; Mountford, P.; Ng, D. K. P. *J. Chem. Soc.*, *Dalton Trans.* **1993**, 2215–2221.

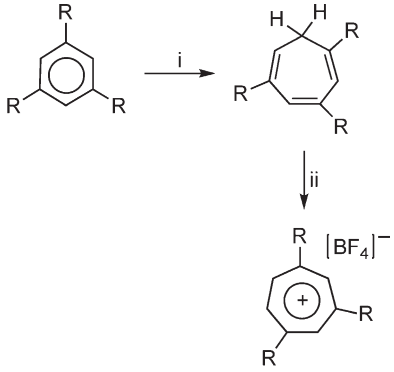
The compound [$Mo\{{=}C(H)SiMe_3\}(\eta^7\text{-}C_7H_6\text{–}C_6H_4\text{-}o\text{-}PPh_2)$], derived from [$MoBr_2(\eta^7\text{-}C_7H_6\text{–}C_6H_4\text{-}o\text{-}PPh_2)$] and $BrMgCH_2SiMe_3$, has been shown to effect ROMP of norbornene[469] and [$Mo(\eta^2\text{-}PhC_2Ph)(\eta^7\text{-}C_7H_6\text{–}C_6H_4\text{-}o\text{-}P^iPr_2)$][$BPh_4$] to trimerize ^{t}BuCH to 1,3,5-tri-^{t}Bu–benzene and 1,2,4-tri-^{t}Bu–benzene.[470]

The preparation of the interesting triple-decker complex [$Mo(\mu\text{-}\eta^5{:}\eta^5\text{-}P_5)(\eta^7\text{-}C_7H_7)FeCp$][$BF_4$] has also been described.[471]



i, PhMe; ii, LiCl, dmpe, *hν*; iii, RSH (R = Pr, Bu, Ph, Bn); iv, Na(acac)

Scheme 23



i, CH$_2$N$_2$; ii, [Ph$_3$C][BF$_4$]

Scheme 24

The sandwich compound [Mo(η^6-C$_7$H$_8$)$_2$], which was first prepared by a co-condensation reaction between Mo atoms and cycloheptatriene,[472] and found to isomerize to [Mo(η^7-C$_7$H$_7$)(η^5-C$_7$H$_9$)] on standing via a hydride shift with a half-life of 200 h, has been reinvestigated theoretically.[473] The available kinetic data indicate that the process is intramolecular with the two possible intermediates, illustrated in Figure 21. DFT calculations also indicate that the isomerization process takes place intramolecularly.[473] The pathway to the neutral complex **A*** was found to have a lower (13 kJ mol^{-1}) activation barrier than the pathway to its cationic 17-electron analog **B***. The rate-determining step was found to be C–H bond breaking to form the respective Mo–H-containing intermediate. The lower rate of conversion to the cationic system is a direct result of weaker hydride binding in the intermediate formed. The rearrangement process was also found to be facilitated by facile ring slippage from η^6 to η^4.

The gas-phase electronic adsorption spectra of [(η^5-C$_5$H$_4$R)Mo(η^7-C$_7$H$_7$)] (R = H, Me) have been recorded and interpreted.[474] Rydberg bands, that disappear when the spectrum is recorded in hexane, were observed, corresponding to the transitions from the non-bonding Mod_{z^2} to Rns, Rnp, and Rnd. Analysis of the data showed the first ionization energies to be 5.69 eV (45,890 cm^{-1}, R = H) and 5.62 eV (45,300 cm^{-1}, R = Me). In addition, methylation of

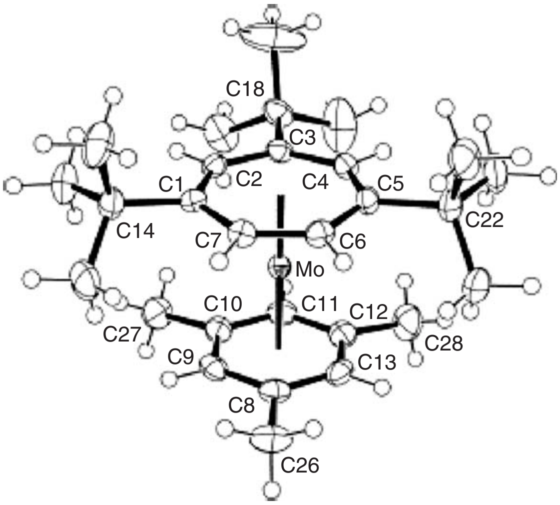


Figure 19 Molecular structure of [Mo(η^6-C_6H_3-1,3,5-^{t}Bu_3)(η^7-C_7H_4-1,3,5-^{t}Bu_3)]$^+$. Reproduced by permission of The Royal Society of Chemistry from Tamm, M.; Bannenberg, T.; Froehlich, R.; Grimme, S.; Gerenkamp, M. *Dalton Trans.* **2004**, 482–491.

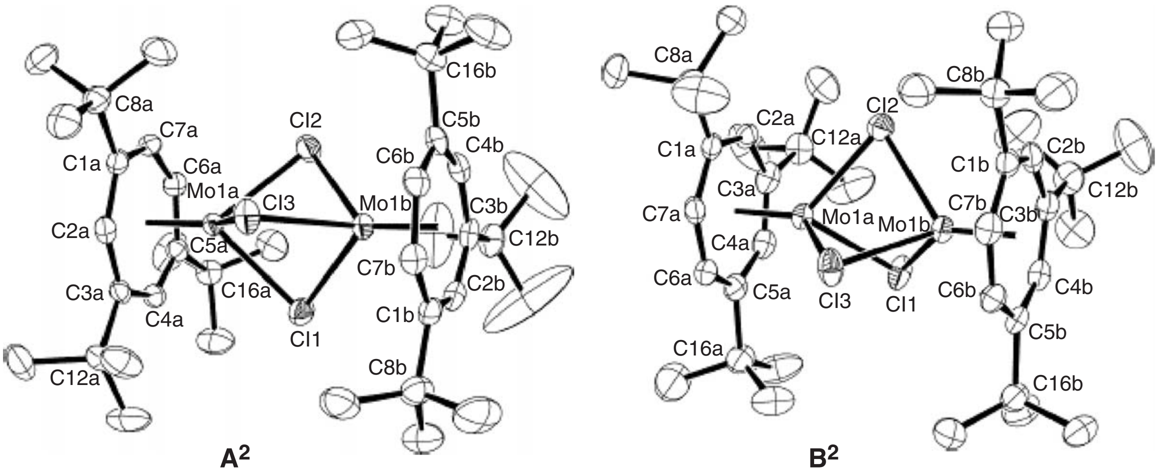
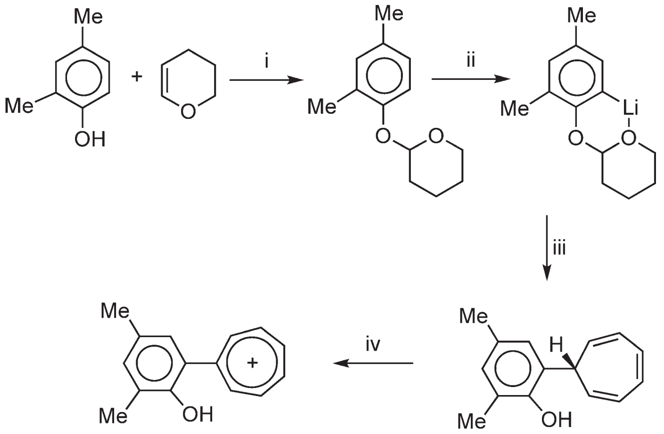


Figure 20 Molecular structures of [Mo(μ-Cl)$_3$(η^7-C_7H_4-1,3,5-^{t}Bu_3)] **A^2** and [Mo(μ-Cl)$_3$(η^7-C_7H_4-1,3,5-^{t}Bu_3)]$^+$ **B^2**. Reproduced by permission of The Royal Society of Chemistry from Tamm, M.; Bannenberg, T.; Froehlich, R.; Grimme, S.; Gerenkamp, M. *Dalton Trans.* **2004**, 482–491.

the Cp ring results in splitting of the $R5p_{x,y}$ and the $R5d_{xz,yz}$ transitions with the appearance of Rd_{xy} and $Rd_{x^2-y^2}$ excitations that is consistent with the reduction of molecular symmetry from $C_{\infty\nu}$ to C_s.

5.07.5.5 Other Alkene-containing Complexes

In a continuing study, looking at the ability of low-valent d^6-metal fragments to act as π-bases, Harman and co-workers have investigated the ability of the fragment [TpMo(NO)L] (Tp = hydrotris(pyrazolyl)borate, L = NH_3, imidazole) to complex unsaturated hydrocarbon fragments.[475–477] Alkenes, alkynes, ketones, polyaromatic hydrocarbons, and aromatic heterocycles are found to η^2-coordinate to the fragment. Complexation in this η^2-manner effectively dearomatizes the aromatic ring systems in a similar manner to previously investigated osmium and rhenium systems. Protonation experiments indicate that the Mo system is more basic. Complexes containing prochiral arenes have been found to exist as a mixture of coordination diastereoisomers in solution. However, on crystallization only one diastereoisomer is evident. The homomorphic nature of the solid state has been used to effect stereoselective solid-state reactions.[476]



i, Me_3SiI; ii, BuLi; iii, $C_7H_7[BF_4]$, EtOH, PPTS; iv, $[Ph_3C][BF_4]$

Scheme 25

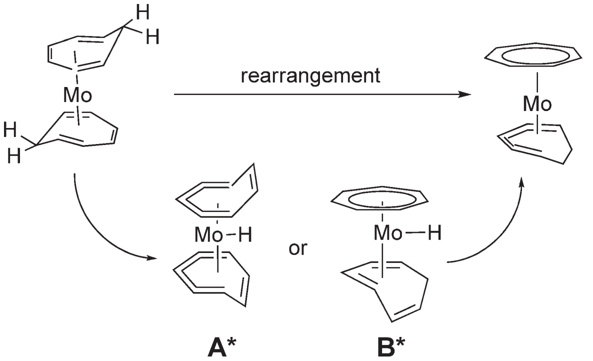


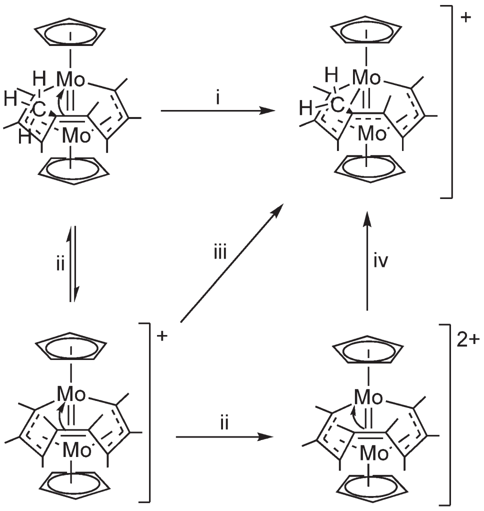
Figure 21 Rearrangement of $[Mo(\eta^6\text{-}C_7H_8)_2]$ to $[Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ showing the possible intermediates **A*** and **B***.

Several sulfur-bridged clusters have been shown to uptake ethene.[478] Treatment of C_{60} with $[Cp_2MoH_2]$ afforded $[Mo(\eta^2\text{-}C_{60})Cp_2]$ which was characterized spectroscopically.[479] The generation of highly active Mo on reduction of $MoCl_5$ by Mg, which had been activated by anthracene, in THF allowed $[Mo(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)_3]$ to be prepared in 40% yield.[480] The homoleptic tris-oxadiene complexes $[Mo\{\eta^4\text{-}Me_2NC({=}O)CH{=}CH_2\}_3]$ and $[Mo\{\eta^4\text{-}MeOC({=}O)C(Me){=}CH_2\}_3]$ have been synthesized and crystallographically characterized. The bonding of the oxadiene is intermediate between η^4 and $\kappa^2{:}\eta^2$.[481,482] Other oxadiene-containing complexes have been described.[483]The redox reaction illustrated in Scheme 26 has been investigated.[484,485]

Cyclic voltammetry shows two oxidation waves, where the second is found to be irreversible. The intermediate monocation is readily isolated on treatment with 1 equiv. of an oxidant, and can then be further oxidized to the dication on treatment with a second equivalent of oxidant. The implication of these observations is that because the process can be effected both electrochemically and chemically, both an EC mechanism or EEC mechanism are possible. The solid-state structure of the monocation was obtained and compared to the neutral starting material. On oxidation there was a lengthening of the Mo–C_{alkene} bonds and a shortening of the C=C bond. This is consistent with the Dewar–Chatt–Duncanson model of alkene bonding. Detailed EPR, NMR, and EHMO studies indicate that the unpaired electron occupies an orbital of a″ symmetry localized on Mo(2) and is involved in π-backbonding to the alkene function of the C_8Me_8 ligand.

5.07.5.6 Gas-phase Reactions

Gas-phase kinetics for the reactions between neutral transition metal atoms and a variety of alkanes and alkenes has been studied experimentally at 300 K and theoretically, with the data obtained from the calculations correlating well



i, $2[Cp_2Fe]^+$, $[CPh_2]^+$; ii, –e; iii, $-H^{\cdot}$; iv, $-H^+$

Scheme 26

with experiment.[486,487] Molybdenum atoms were found not to react with alkanes including cyclopropane, for which the *ab initio* calculations indicated that the barrier to CH insertion remained prohibitively high with a CC insertion activation barrier of 38.9 kJ mol^{-1}. It was found that Mo reacts with alkenes, albeit only with larger ones, and then only slowly. This was explained in terms of the extreme stability of the $4d^5 5s^1$, ^7S ground state of molybdenum, with the excitation energy to the lowest ^5S state requiring 130 kJ mol^{-1}, being too high for the reaction to proceed at any appreciable rate. The reason for the observed reactivity toward heavier alkenes is due to inefficient collisional stabilization of a weakly bound high-spin complex. The gas-phase reaction of Mo^+ toward alkenes has also been investigated.[488] The Mo^+ ion was generated through laser ablation, and the composition of the products analyzed by time-of-flight mass spectrometry. Competition reactions in the presence of Tc^+, Re^+, and Cu^+ were also described with the mixed metal systems obtained by co-ablation. H_2 loss was found to be the major reaction process giving, for example, Mo–C_2H_2 in the reaction of Mo^+ with ethene. For cycloalkenes competing CC bond cleavage was observed. Mo^+ was found to be slightly less reactive than both Tc^+ and Re^+.

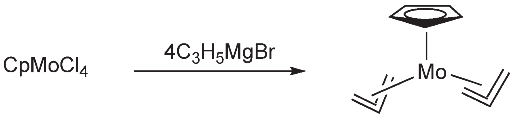
5.07.5.7 Alkene Catalysis

Reviews concerned with alkene epoxidation have appeared.[76,489] The catalytically important alkene insertion into metal–hydrogen bonds has been studied in detail.[490,491] The deactivation of molybdenum/silica catalysts used in alkene metathesis has been studied.[492] The deactivation resulted through the isomerization of the catalytically important intermediate metallacyclobutadiene into π-alkene-containing complexes and associated Mo^{4+} cations.

5.07.6 π-Allyl-containing Complexes

5.07.6.1 Containing Cyclopentadienyl-supporting Ligands

A review of the comparative chemistry of 18-electron Mo(II) and 17-electron Mo(III) systems that only contain carbon-based ligands has appeared.[493] Treatment of $[CpMoCl_4]$ with 4 equiv. of allyl Grignard affords $[CpMo(\eta^3\text{-}C_3H_5)_2]$ (Equation (1)).



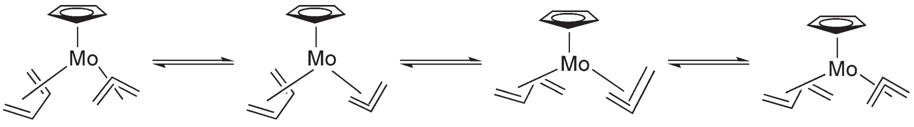
(1)

$[CpMo(\eta^3\text{-}C_3H_5)_2]$ is stable in donor solvents at room temperature, however, warming in NCMe effects hexa-1,5-diene formation via a metal-mediated allyl coupling reaction. Hexa-1,5-diene can also be generated through treatment of $[CpMo(\eta^3\text{-}C_3H_5)_2]$ with $[Cp_2Fe][PF_6]$ at room temperature.[494] The reaction between $[CpMoCl_2\text{-}(\eta^4\text{-}C_4H_6)]$ and allyl Grignard affords an isomeric mixture of [CpMo(*prone*-η^3-C_3H_5)(*supine*-η^4-C_4H_6)] (major 98%) [CpMo(*supine*-η^3-C_3H_5)(*supine*-η^4-C_4H_6)] the orientation of the π-bound ligands was confirmed by nuclear Overhauser enhancement (NOE) experiments (Scheme 27).

Heating in solution generates a third isomer [CpMo(*supine*-η^3-C_3H_5)(*s-trans*-η^4-C_4H_6)]. Oxidation of these Mo(II) complexes can be achieved using $[Cp_2Fe][PF_6]$ to generate the analogous Mo(III) compounds. Crystallographic studies of the Mo(II) species showed the Mo–C bond lengths to lie in the range 221.1–230.0 pm; no bond length data are available for the analogous Mo(III) species because of disorder between the allyl and diene ligands in the crystals studied.[457] The reactivity of these mixed allyl/diene systems toward nucleophilic and electrophilic reagents has been investigated,[456,458,494] reviewed,[493] and discussed in detail in Section 5.07.5.3.

The reactivity of $[Cp_2Mo(\eta^3\text{-}C_3H_5)]^+$ toward nucleophiles has been studied using DFT (B3LYP). Nucleophilic attack was found to take place preferentially at the central allyl carbon atom. The data obtained from the related system $[CpMo(CO)(NO)(\eta^3\text{-}C_3H_5)]^+$, where attack is preferred on the terminal carbon, imply that regioselectivity is governed primarily by orbital interactions.[495] Some allyl-tethered phosphine-containing complexes of Mo have been described, with several being crystallographically characterized. The allyl Mo–$C_{(allyl)}$ bond lengths are found to be in the range 225–230 pm for Mo(II) and 228–236 pm for Mo(IV) complexes.[496] Resolution of the chiral-at-metal complex of [CpMo(NO) (η^3-C_4H_7){(*S*)-(+)-10-camphorsulfonate}] facilitated the preparation of the enantiomerically pure complexes [CpMoX(NO)(η^3-C_4H_7)] (X = Cl, Br, I). The ability of the enantiomerically pure (+) complex [CpMoX(NO)(η^3-C_4H_7)] to react with benzaldehyde was investigated and(*S*)-(−)3-methyl-1-phenyl-3-butene-1-ol was obtained in greater than 98% ee.[497] Several of the resolved compounds have also been crystallographically characterized.[497,498] Other examples of π-allyl complexes being used to effect organic transformations have been described,[499,500] and several review articles covering this material have appeared.[501,502] Some phosphine complexes containing open pentadienyl ligands have been synthesized, and the compound $[Mo(PEt_3)(\eta^5\text{-}C_5H_5\text{-}2,4\text{-}Me_2)_2]$ has been crystallographically characterized. Of particular note is the presence of one sickle *S*-coordinated pentadienyl fragment (Figure 22) with the bonding best described as allyl–ene in nature. The C–C bond connecting the two fragments is long at 148.1(22) pm.[503]

Other pentadienyl-containing complexes have also been described.[504]



Scheme 27 Different allyl diene orientations possible in $[CpMo(\eta\text{-allyl})(\eta\text{-diene})]^{0/1+}$.

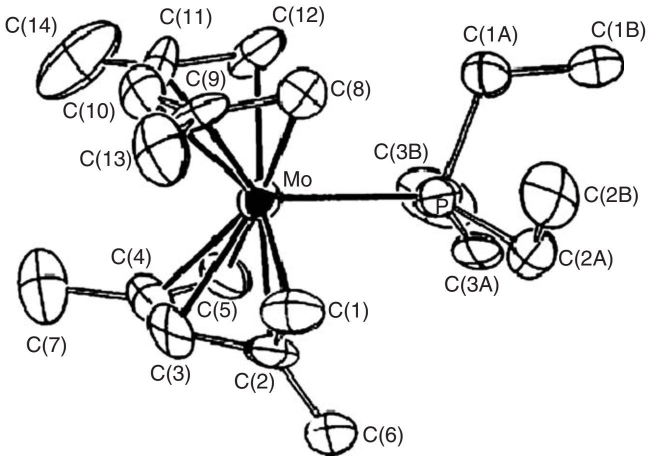


Figure 22 Molecular structure of $[Mo(PEt_3)(\eta^5\text{-}C_5H_5\text{-}2,4\text{-}Me_2)_2]$. Reprinted with permission from Waldman, T. E.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Hutchinson, J. P.; Ernst, R. D. *Organometallics* **1993**, *12*, 1543–1552. © (1993) American Chemical Society.

5.07.6.2 Other Monomeric Complexes

The reactivity of [MoH(dppe)$_2$(η^3-C_3H_5)] toward protic acids has been investigated and found to yield propene, and unusually propyne too.[505] The mechanism of this reaction was established by detailed kinetic studies and product analysis. The crystal structure of [MoH(dppe)$_2$(η^3-C_3H_5)] has also been determined but found to be disordered about the allyl ligand.[506] The related 2-methylallyl complex [MoH(dppe)$_2$(η^3-C_4H_7)] was found to undergo inter- and intramolecular interconversion to an η^4-trimethylenemethane ligand. The reactivity of these compounds toward protons was also investigated,[507] and all of this work has been reviewed.[99]

Treatment of [Mo(N^{t}Bu)$_2$Cl$_2$] with 2-methylallyl Grignard affords the bis-allyl complex [Mo(N^{t}Bu)$_2$(η^1-C_4H_7)(η^3-C_4H_7)]. Two different coordination modes of the allyl ligands are observed: purely σ and ($\sigma+\pi$) which was supported by DFT calculations. The allyl ligands are fluxional and found to rapidly intercovert.[508] Another example of ($\sigma+\pi$) binding of an allyl fragment has also been described.[509] The crystal structure of [Mo{η^3-($\sigma+\pi$)C_3H_5}$_2$(PMe$_3$)$_3$] revealed Mo–C(σ) 224.6(6) and 225.1(7) pm with Mo–C(π) ranging from 231.1(6) to 236.2(1) pm. The structure of [Mo(η^3-allyl)$_4$] has been investigated theoretically by using the molecular mechanics approach and by *ab initio* methods. Both confirm S_4 geometry, and the fluxional nature of the complex is attributed to allyl rotation via a π–σ–π mechanism. The *ab initio* approach predicts a much higher barrier to allyl rotation than does the molecular mechanics calculation.[510]

The use of allyl complexes for the polymerization of vinylpyridines has been described,[511] and the catalytic use of molybdenum–oxo-supported allyl complexes in ammoxidation process has been reviewed.[512] Treatment of the [Mo(η^3-C_3H_4Me)(bipy)(CO)$_2$(OCMe$_2$)]$^+$ cation with an aqueous solution containing [MoO_4^{2-}] solution afforded, after workup, [Mo(η^3-C_3H_4Me)O$_2$], which dimerizes in the solid state and displays short Mo–O···H–C contacts.[513] The use of cyclopropenyl complexes as olefin polymerization catalysts has been patented.[514]

5.07.6.3 π-Allyls Bound to Oxide Surfaces

The nature of the binding of the [Mo(η^3-allyl)$_4$] fragment to silica has been studied theoretically. Two different methods of anchorage of the [Mo(η^3-allyl)$_2$] fragment to the silica were investigated (see Figure 23). The calculations were found to support the presence of π-bound allyl groups at molybdenum centers, and that one of the allyl groups interacts directly with an oxygen atom of the silica support. C–H activation occurs because of this important interaction, and fits nicely with enhanced acidity of all allyl H atoms and the accepted mechanism of alkene metathesis.[515,516] Other related studies on silica-supported [Mo(η^3-allyl)] catalysts have appeared,[517,518] including a review article.[519] Fe(100)–OH has also been reacted with [Mo(η^3-allyl)$_4$] and found ultimately to generate mixed metal oxide catalysts. Initial complexation, however, affords systems with π-bound allyl groups.[520] Treatment of Al_2O_3 with [Mo(η^3-allyl)$_4$] has also come under investigation for the generation of alkene metathesis catalysts.[521–523]

The adsorbtion of allyl iodide onto Mo$_2$C(100) has been investigated by thermal X-ray desorption spectroscopy, photoelectron spectroscopy, and high resolution electron loss spectroscopy (HREELS) between 100 and 1200 K. The allyl iodide adsorbs disassociatively and molecularly on the surface at 100 K giving a chemisorbed layer. Rupture of the C–I bond is complete by 220 K with evidence for the preparation of η^1- and η^3-bound allyl species (HREELS). These fragments are easily hydrogenated to propene. Propylidyne complexes formed by dehydrogenation were also observed.[524]

The interaction of propene with MoO$_3$ has been studied by EPR, and different Mo(V) centers are observed. The most important observation is that the resulting π-bound allyl moiety is complexed a significant distance away from

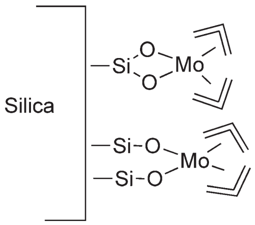


Figure 23 Different modes of attachment of the [Mo(η-allyl)$_2$] fragment to silica.

the simultaneously created Mo(V) center.[525] The charge sensitivity of this process and a bond order analysis of the reactivity trends in the allyl/MoO_3 chemisorption system have been carried out.[526,527] These studies suggested that the selective oxidative addition of the allyl iodide fragment occurs by a concerted mechanism.

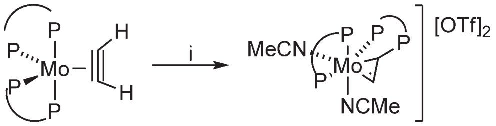
5.07.7 Alkyne-containing Complexes

5.07.7.1 Containing Phosphorus-based Ligands

The crystallographically characterized complexes $[Mo(dppe)_2(\eta^2\text{-}RC_2R)]$ (R = Me;[528] R = H[529]) have been prepared and shown to have trigonal-bipyramidal geometry. The Mo–C bond lengths are 206.1(5) (R = H) and 206.3(13) pm (R = Me) with the $C\equiv C$ bond lengths 126.5(7) and 129.0(14) pm, respectively. In both cases it was found that the $C\equiv C$ bond is parallel to the *trans*-P–Mo–P vector. The reactivity of $[Mo(dppe)_2(\eta^2\text{-}MeC_2Me)]$ toward protonation was investigated and found to yield $[MoCl_2(dppe)_2]$, $[MoH_2Cl_2(dppe)_2]$, but-1-ene (69 ± 6%) and *cis*-but-2-ene (10 ± 2%) and but-2-yne (21 ± 2%). The possible mechanisms were discussed based upon kinetic data, and the protonation of unsaturated hydrocarbon ligands has been reviewed.[99] Treatment of the compound $[Mo(dppe)_2(\eta^2\text{-}HC_2H)]$ with $HBF_4\cdot OEt_2$ was found to give $[MoF(dppe)_2(\eta^2\text{-}HC_2H)][BF_4]$, which could also be obtained by chemical oxidation with $[FeCp_2][BF_4]$ in THF. If the oxidation was effected in THF/NCMe in the presence of NaOTf, a different product resulted $[Mo(NCMe)_2(dppe)(\eta^3\text{-}\{{=}CH\text{–}CHP(Ph)CH_2CH_2PPh_2\})]$ (Scheme 28). The formation of the latter is explained by nucleophilic attack of one phosphorus atom of a dppe ligand at an alkyne contact carbon. This complex was crystallographically characterized.[529]

Protonation of the bis-alkyne compound $[Mo(dppe)_2(\eta^2\text{-}MeC_2Me)_2]$ with excess HX has also been investigated and a variety of products resulted. For example, treatment with $HBF_4\cdot Et_2O$ afforded the *trans*-vinyl-containing complex $[MoF(\sigma\text{-}CH{=}CHMe)(dppe)_2]$ and the alkylidyne-containing complex $[Mo({\equiv}CCH_2Me)F(dppe)_2]$.[424] Treatment of the acetylide complexes $[MoH_3(C\equiv CBu^t)(dppe)_2]$ with anhydrous HCl afforded $[MoH_2Cl_2(dppe)_2]$, dihydrogen, and $HC\equiv CBu^t$ with the formation of $[MoH_3(dppe)_2(\eta^2\text{-}HC_2Bu^t)]$ implicated in the reaction pathway. The consequence of protonation at the metal center or the alkyne ligand was discussed; the former pathway leads to the alkynyl-containing complex and the latter to an alkylidyne-containing complex. Treatment of $[MoH(SAr)_3(PPh_2Me)]$ (Ar = C_6H_2-2,4,6-Me or ^{i}Pr) with either (Tol)$C\equiv CH$ or $PhC\equiv CH$ gave the mixed ylide/alkyne-containing complexes $[Mo(O)(SAr)_2(\eta^2\text{-}HC_2R)\{{=}C(R)CH{=}PMePh_2\}]$ (R = Tol, or Ph), whereas the reaction between the related complex $[MoH(SAr)_3(PMe_2Ph)]$ (Ar = C_6H_2-2,4,6-^{i}Pr) and PhC_2H afforded a crystallographically characterized alkylidyne complex $[Mo(O)(SAr)_3\{{=}C(Ph)CH{=}C(Ph)CH_2PMe_2Ph\}]$.[530] The oxo ligand is believed to have originated from adventitious water present in the reaction mixture.

In a study[470,531] to generate catalytically active cycloheptatrienyl complexes, which are isolobal and isoelectronic with the known catalytically active Ru fragment $[CpRuPR_3]^+$, the compounds $[Mo(\eta^2\text{-}RC_2H)(\eta^7\text{-}C_7H_6\text{–}C_6H_4\text{-}o\text{-}PR^1{}_2)]$ were prepared (when R = Ph, ^{t}Bu; R^1 = ^{i}Pr or Ph) and were crystallographically characterized (where R = Ph, R^1 = ^{i}Pr and Ph; R = Me, R^1 = ^{i}Pr). The compound $[Mo(\eta^2\text{-}RC_2H)(\eta^7\text{-}C_7H_6\text{–}C_6H_4\text{-}o\text{-}PR^1{}_2)$ was also found to catalyze (5 mol.%) the cyclization and linear oligomerization of $PhC\equiv CH$ to give 1,3,5-triphenyl benzene (52%), 1,2,5-triphenyl benzene (28%), and linear oligomers (20%). This clearly illustrates the potential application for this type of complex. An obvious advantage to be gained from developing systems like this further would be cost benefits: molybdenum is significantly cheaper than ruthenium. Related compounds are also discussed in Section 5.07.5.4. The complex $[Mo(PMe_3)(\eta^2\text{-}PhC_2CO_2Et)_3]$ has been prepared, structurally characterized, and studied in detail using EHMO calculations.[532] The dimeric complex $[\{MoCl_2(PMe_3)_2(\mu\text{-}S)(\mu\text{-}\eta^2:\eta^2\text{-}MeC_2Me)\}_2]$ has also been synthesized and structurally characterized.[533]



(P–P = dppe)

i, $[Cp_2Fe][BF_4]$, NCMe, THF, 2NaOTf

Scheme 28

5.07.7.2 Containing Amido- and Imido-supporting Ligands

Using the isolobal relationship between bent metallocenes of group 4 and bis-imido complexes of group 6, the four-coordinate bis-imdo alkyne-containing complexes [Mo(NR^1)$_2$(PMe$_3$)(η^2-R^{2}C$_2$R^3)] (R^1 = ^{t}Bu, R^2 = R^3 = Ph; R^1 = ^{t}Bu, R^2 = Ph, R^3 = H; R^1 = adamantyl, R^2 = R^3 = Ph) were prepared and structurally characterized. For example, in [Mo(NBu^t)$_2$(PMe$_3$)(η^2-PhC$_2$Ph)] (Figure 24), the Mo–C bond lengths are 208.1(8) and 215.9(9) pm, respectively, with the C≡C bond length 131 (1) pm.[440] The C≡C bond length is indicative of π-backbonding, but not to the same extent as in analogous zirconocene complexes. Related mesitylimido complexes have also been described.[443] The alkyne ligand is found to align perpendicular to the plane defined by the metal and the two imido ligands with the alkyne pointing toward the weakest π-donor (Figure 25), and compares directly to what is observed in the related alkene complexes discussed in Section 5.07.5.1. The alkyne-contact carbon closest to the PMe$_3$ was found to display a more substantial $^2J_{\text{P–C}}$ (Ca. 20 Hz) with the ^{13}C resonances comparable to those observed in isolobal ziconium and niobium complexes.

The octahedral complexes [MoCl$_2$(NMes)(PMe$_3$)(η^2-R^{1}C$_2$R^2)] (R^1 = R^2 = Ph; R^1 = H, R^2 = Ph) have also been prepared and, where R^1 = R^2 = Ph, crystallographically characterized.[534] Some mixed amido/imdo complexes of the type [Mo(NPh){(o-SiMe$_3$N)$_2$C$_6$H$_4$}(η^2-R^{1}C$_2$R^2)] (R^1 = CO$_2$Me, R^2 = H; R^1 = Ph, R^2 = Me; R^1 = Me, R^2 = SiMe$_3$; R^1 = R^2 = Ph, SiMe$_3$, Me) have recently been prepared and studied theoretically using two layer ONIOM and the B3LYP hybrid DFT calculations.[447] The compounds, [Mo(NPh){(o-SiMe$_3$N)$_2$C$_6$H$_4$}(η^2-Me$_3$SiC$_2$SiMe$_3$)] (R = SiMe$_3$,[447] Me[446]), have both been characterized crystallographically (Figure 26). The alkyne ligand is found, as in other imido complexes, to be perpendicular to the Mo(NR) vector, which, theoretical calculations confirm, maximizes imido π-donation and minimizes alkyne π-donation, thus enhancing the stronger Mo–N versus Mo–C bond. Another feature to be noted and that is clearly visible in Figure 27 is the amido ligand fold angle of 133° (Table 2). This is the same as that observed for the analogous but-2-yne containing complex[446] and the dialkyl complex [Mo(NPh){(o-SiMe$_3$N)$_2$C$_6$H$_4$}(CH$_2$)$_4$].[444] Theoretical calculations on d^0 diamide imido complexes have

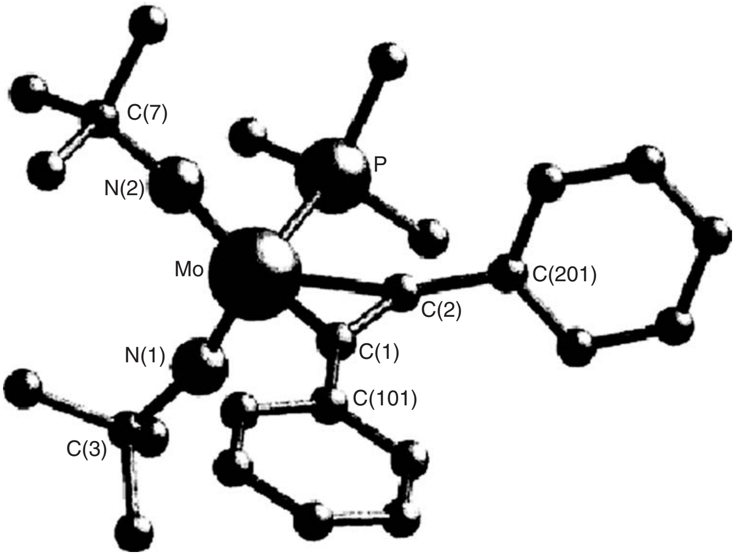


Figure 24 Molecular structure of [Mo(NBu^t)$_2$(PMe$_3$)(η^2-PhC$_2$Ph)]. Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *Polyhedron* **1995**, *14*, 103–111. Reproduced by permission of Elsevier.

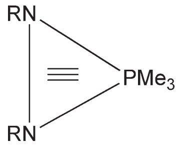


Figure 25 Orientation of the alkyne vector in complexes of the type [Mo(NR)$_2$(PMe$_3$)(η^2-alkyne)].

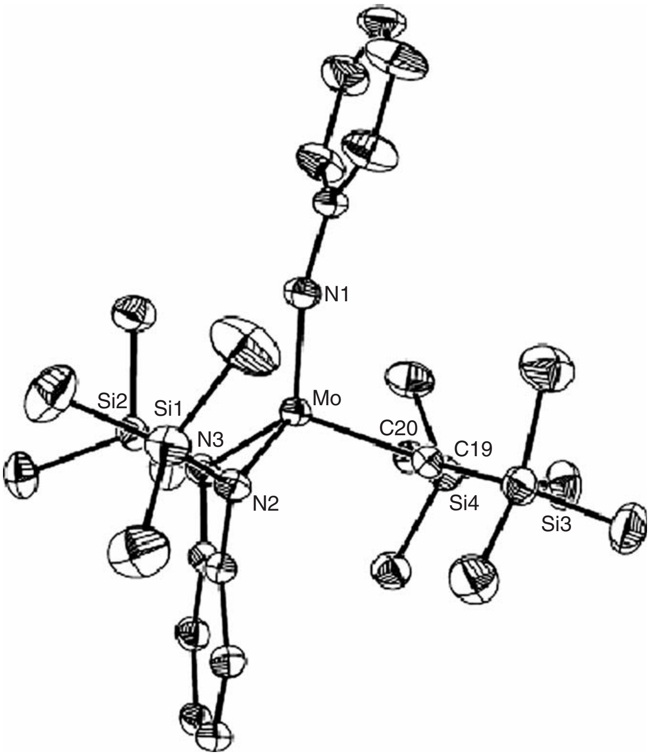


Figure 26 Molecular structure of [Mo(NPh){(o-$SiMe_3N)_2C_6H_4$}(η^2-$Me_3SiC_2SiMe_3$)]. Reprinted with permission from Ison, E. A.; Cameron, T. M.; Abboud, K. A.; Boncella, J. M. *Organometallics* **2004**, *23*, 4070–4076. © (2004) American Chemical Society.

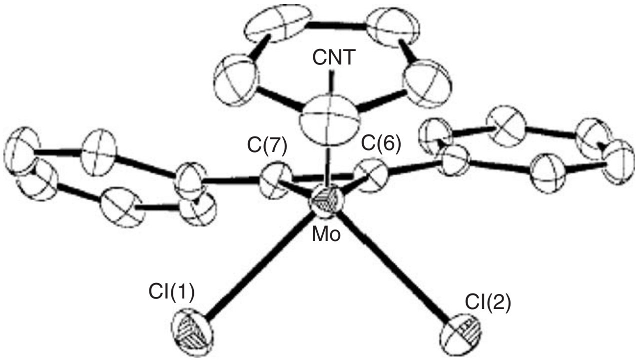


Figure 27 Molecular structure of [$MoCl_2$(η^2-PhC_2Ph)Cp]. Reproduced by permission of The Royal Society of Chemistry from Le Grognec, E.; Poli, R.; Richard, P. *Dalton Trans.* **2000**, 1499–1506.

demonstrated the importance of diamide lone pair donation in the bonding of this type of complex. It has been found that to optimize π-donation, the diamide ligand has to fold to maximize lone pair *p–d* overlap. Since the diamide fold angle is comparable to d^0-alkyl complexes, the alkyne ligands should be considered as dianionic ligands, and the complexes best described as being molybdacyclopropenes with the formal metal oxidation state of (VI). This is supported nicely by the solid-state structure of the pyridine-containing complex [Mo(NPh){(*o*-$SiMe_3N)_2C_6H_4$}$(py)_2$],[535] which has a fold angle of 175.5° (essentially none!) being formally Mo(IV). The ability of alkynes to be considered as dianionic ligands is not new and has been studied theoretically.[536] The coordinated alkynes have also been shown, using VT ^{1}H NMR spectroscopy, to undergo propeller-like rotation with activation barriers of approximately 55 kJ mol^{-1}. These complexes also undergo an alkylaluminum-induced diamide transfer from Mo to Al generating π-bound arene-containing complexes[537] (see Section 5.07.9.2 for a more detailed

Table 2 Fold angles for Mo imido diamido complexes

Compound	*Fold angle* (°)	*References*
$[Mo(NPh)\{(o\text{-}SiMe_3N)_2C_6H_4\}(\eta^2\text{-}Me_3SiC_2SiMe_3)]$	133.0	446
$[Mo(NPh)\{(o\text{-}SiMe_3N)_2C_6H_4\}(\eta^2\text{-}MeC_2Me)]$	133.0	446
$[Mo(NPh)\{(o\text{-}SiMe_3N)_2C_6H_4\}(CH_2)_4]$	132.5	444
$[Mo(NPh)\{(o\text{-}SiMe_3N)_2C_6H_4\}(\eta^2\text{-}H_2CCHPh)]$	129.2	444
$[Mo(NPh)\{(o\text{-}SiMe_3N)_2C_6H_4\}(\eta^2\text{-}py)_2]$	175.5	535
$[Mo(NPh)\{(o\text{-}SiMe_3N)_2C_6H_4\}(\eta^4\text{-}C_4H_6)]$	167.8	444

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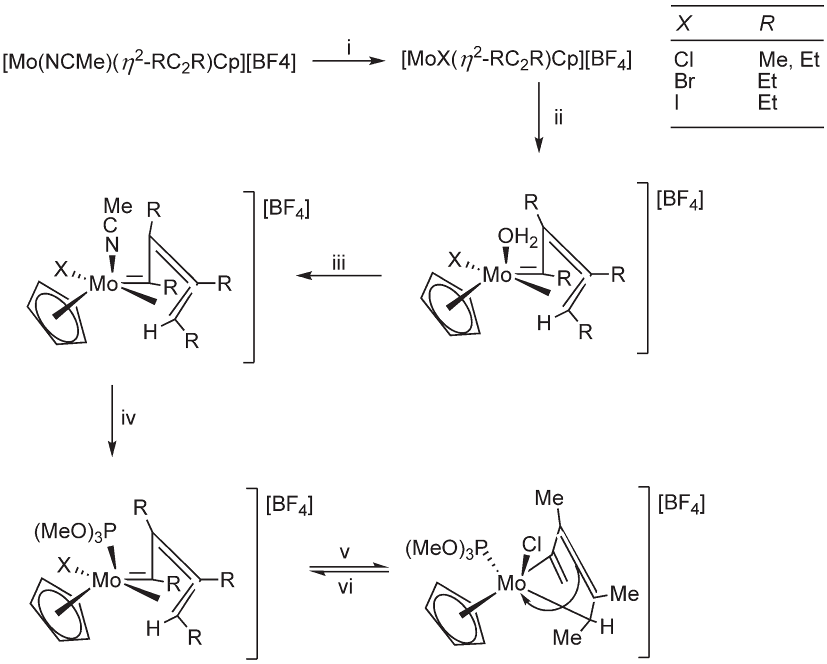
discussion). The complex $[Mo\{N(^iPr)C_6H_3\text{-}3,5\text{-}Me\}_3(\eta^2\text{-}PhC_2Ph)]$ has also been synthesized, where there was an anticipation that C≡C bond scission would occur affording alkylidyne-containing complexes.[410] The same tris-amido-supporting fragment was also found to bind nitriles in an η^2-fashion.[410,538]

5.07.7.3 Containing Cyclopentadienyl-supporting Ligands

Poli and co-workers have reported[539] the preparation of a new class of 17-electron molybdenum(III) alkyne complexes $[MoCl_2(\eta^2\text{-}R^1C_2R^2)Cp]$ ($R^1 = Me$, $R^2 = Et$, Ph; $R^1 = R^2 = Et$, Ph) through the direct thermal reaction of $[\{CpMoCl_2\}_2]$ with 2 equiv. of the respective alkyne. The molecular structure of $[CpMoCl_2(\eta^2\text{-}PhC_2Ph)]$ (Figure 27) shows that the alkyne adopts a conformation almost parallel to the Cp ligand. The tilt angle θ, defined as the angle between the Mo–alkyne plane and the plane defined by Mo, the center of gravity of the Cp ring, and the midpoint of the alkyne bond, is 85.61°, where parallel to the Cp ring plane is 90°.

DFT calculations (B3LYP/LANL2DZ) show that a θ angle of 30° should be expected. The calculations were also carried out with the ethyne ligand forced to adopt a parallel geometry, and it was found that the ethyne orientation had little effect on the overall energy of the complex, and suggests therefore that the parallel orientation is adopted to minimize the steric interaction between the ethyne ligand and the Cp ring. Cyclic voltammetry shows that these compounds also undergo a fully reversible one-electron oxidation and an irreversible one-electon reduction process. When the syntheses of the hex-3-yne and pent-2-yne-containing complexes are carried out in the presence of excess alkyne, an additional product is observed. Crystallographic characterization of this species showed that it was the previously reported compound $[CpMoCl_2(\eta^5\text{-}C_4Et_4H)]$ that contains an η^5-butadienyl ligand.[540] A series of these butadienyl complexes was prepared[540] from the bis-alkyne complexes $[Mo(NCMe)(\eta^2\text{-}RC_2R)_2(L)]$ (R = Me or Et; L = Cp or Ind) in the reaction sequence illustrated in Scheme 29. Deprotonation of the butadienyl fragment in $[MoCl\{{=}CMe\text{-}\eta^3\text{-}[C(Me)C(Me)C(Me)]\}\{P(OMe)_3\}Cp]$, formed by substitution of the NCMe ligand in $[Mo(NCMe)(\eta^2\text{-}RC_2R)_2Cp]$ by $P(OMe)_3$, with $Li(NSiMe_3)_2$ affords $[MoCl\{\eta^4\text{-}CH(Me){=}C(Me){=}C{=}CH_2\}\text{-}\{P(OMe)_3\}Cp]$, which contains a vinyl–allene ligand (Scheme 29). Reprotonation affords the starting butadienyl-containing complex. Treatment with AlH^iBu_2, however, afforded the buta-1,3-diene-containing complex $[MoCl\{\eta^4\text{-}CH(Me){=}C(Me){=}C{=}CH_2\}\{P(OMe)_3\}L]$, which on treatment with $[Ph_3C][BF_4]$ also regenerates the starting butadienyl-containing complex.

In other studies from Green's group, the complexes $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}R^1C_2R^2)Cp]$ ($R^1 = R^2 = Ph$, Me; $R^1 = Me$, $R^2 = Ph$) have been reacted with the Grignard reagents $XMgR^3$ ($R^3 = Me$, Et, CH_2Ph, $CH_2CH{=}CH_2$, $CH{=}CH_2$, and $CH_2\{MgI\}_2$),[541] and deprotonation of $[MoBr(\eta^2\text{-}MeC_2R)Cp]$ (R = Me, Ph) was found to lead to the formation of σ,η^2-prop-2-ynyl-containing complexes $[Mo(\sigma,\eta^2\text{-}CH_2C_2R)(\eta^2\text{-}RC_2Me)Cp]$, which on protonation regenerate the alkyne-containing complexes.[542–544] The σ,η^2-prop-2-ynyl ligand was found crystallographically (R = Ph) to lie in a plane essentially parrallel to the Cp ligand. In an analogous deprotonation reaction with $Li\{N(SiMe_3)_2\}$, $[MoBr\text{-}(\eta^2\text{-}MeC_2Me)(dpps)Cp][BF_4]$ (dpps = *o*-diphenylphosphinostyrene) affords an η^5-pentadienyl-containing complex $[Mo\{\eta^3:\eta^3\text{-}CH_2CHC(Ph)CH{=}C_6H_4PPh_2\text{-}o\}Cp]$ rather than the expected σ,η^2-prop-2-ynyl ligand-containing complex. Subsequent protonation led to the formation of a twisted *trans*-1,3-diene-containing complex.[543] The complex $[Mo(\sigma,\eta^2\text{-}CH_2C_2Me)(\eta^2\text{-}RC_2Me)Cp]$ has been shown to undergo cyclization reactions on treatment with $F_3CC_2CF_3$ and CO.[545] Other cyclization reactions involving molybdenum bis-hexafluorobut-2-yne-containing complexes have been described.[546,547] The complex $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}PhC_2Ph)Cp]$ can be prepared from $[Mo\{P(OMe)_3\}_2\{{=}C(Ph)CHPh\}Cp]$ on treatment with $[Cp_2Fe]^+$ or $[Ph_3C]^+$ via a 17-electron cation that readily



X	R
Cl	Me, Et
Br	Et
I	Et

i, LiX; ii, $HBF_4{\cdot}OEt_2$, CH_2Cl_2; iii, NCMe; iv, $P(OMe)_3$; v, $Li[N(SiMe_3)_2]$; vi, $HBF_4{\cdot}BF_4$

Scheme 29

loses a proton.[548] On effecting the oxidation with $B(C_6F_5)_3$, a competing reaction is observed that leads to the formation of a labile *trans*-stilbene-containing complex.

The phosphaalkyne-containing complex $[Mo\{P(OMe)_3\}_2(\eta^2\text{-PC}{\equiv}\text{Bu}^t)Cp]$ has been prepared and spectroscopically characterized.[549] It shows a $^{13}C\{^1H\}$-NMR shift at $\delta = 334.8$ ppm for the phosphaalkyne contact carbon atom. EHMO and DFT calculations were carried out, and the data indicated a direct correlation with the analogous alkyne complexes. Evidence was presented that the phosphaalkyne readily switches from being a four-electron to two-electron donor. Evidence for four-electron donor phosphaalkyne-containing complexes has been described elsewhere.[550]

5.07.7.4 Bimetallic Complexes

Chisholm's group has investigated the reaction of $[Mo_2(O^tBu)_6]$ with ethyne.[551] At low temperature (−80 °C), polyacetylene is produced; however at −40 °C, two other products are obtained: $[Mo_2(\mu\text{-}HC_2H)(O^tBu)_6]$, which contains a π-bound alkyne, and $[Mo_2(\mu\text{-}C_4H_4)(O^tBu)_6]$, which contains a bridging molybdacyclobutadiene ligand, resulting from the dimerization of ethyne.[551] Both compounds have been crystallographically characterized as methylpyridine and CO adducts, repectively (Figures 28 and 29). The alkyne in $[Mo_2(\mu\text{-}HC_2H)(O^tBu)_6(\text{mepy})]$ is found to bridge perpendicular to the Mo–Mo bond. Neither of these compounds is an intermediate in the formation of polyacetylene. It is believed that polyacetylene formation results from a trace amount of an *in situ* formed alkylidyne-containing complex. Theoretical calculations[435,436] carried out on $[M_2(EH)_6]$ (M = Mo, W; E = O, S) in the Schrock "chop-chop" reaction have explained why alkyne complexes of the type $[Mo_2(\mu\text{-}RC_2R)(OR)_6]$ are isolable, whereas the tungsten analogs tend to undergo alkyne scission leading to alkylidyne complexes. Scission of ethyne at a dimolybdenum center has, however, been documented.[405] The data from these calculations led to the preparation and structural characterization of $[W(\mu\text{-}PhC_2Ph)(SC_6H_4\text{-}2\text{-}Me)_6]$, where, unlike analogous molybdenum complexes where the alkyne is perpendicular to the Mo–Mo vector, the alkyne is skewed (43°) relative to the W–W bond axis.[435]

Morris and co-workers have reported[552] that the reaction between $[Cp_2Mo_2(CO)_4]$ and ^iPrSH affords two separable isomers **A** and **B** (Scheme 30), where the ^iPr substituents are either *syn* or *anti* to the alkyne ligand. Isomer **A** has been crystallographically characterized and displays the first example of a π-bound alkyne parallel to the Mo–Mo bond,

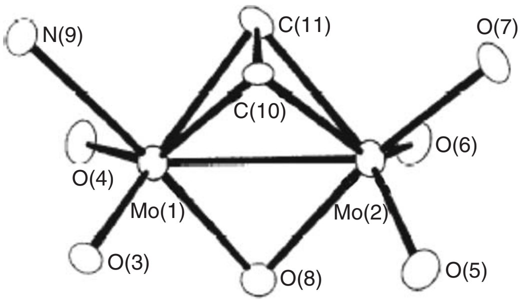


Figure 28 Molecular structure of $[Mo_2(OBu^t)_6(4\text{-Mepy})(\mu\text{-}C_2H_2)]$. Chisholm, M. H.; Hoffman, D. M.; Northius, J. M.; Huffman J. C. *Polyhedron* **1996**, *16*, 839–847. Reproduced with permission of Elsevier.

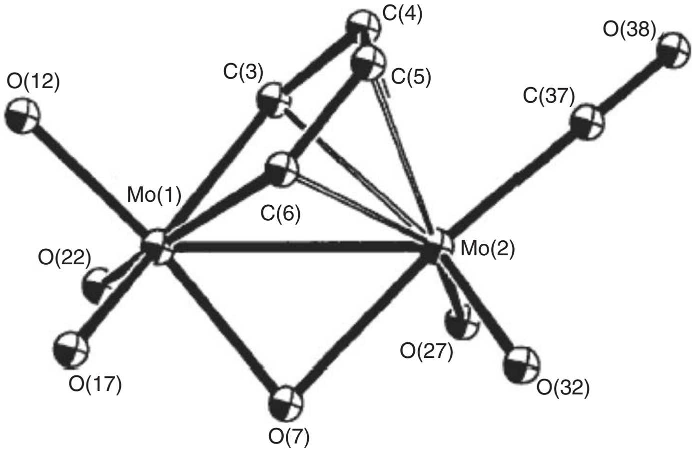
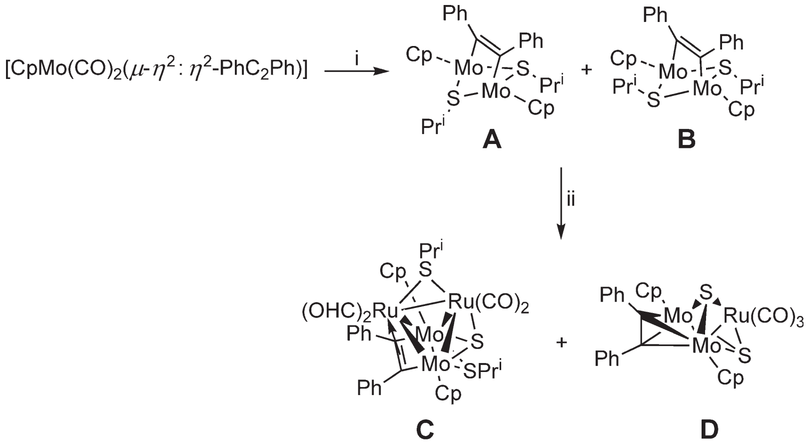


Figure 29 Molecular structure of $[Mo_2(OBu^t)_6(CO)(\mu\text{-}C_4H_4)]$. Chisholm, M. H.; Hoffman, D. M.; Northius, J. M.; Huffman J. C. *Polyhedron* **1996**, *16*, 839–847. Reproduced with permission of Elsevier.

leading to the description of the alkyne ligand as a dimetallated alkene. EHMO calculations were carried out and showed that on going from a parallel to perpendicular orientaion of the alkyne resulted in a 4.0 eV destabilization, with both the $\pi(\psi)$ and $\pi^*(\zeta)$ much less stabilizing in the perpendicular orientation. The calculations also suggested that the alkyne should be considered as a dimetallated alkene with the molybdenum centers becoming formally Mo(IV). It was



i, $5Pr^iSH$; ii, $[Ru_3(CO)_{12}]$

Scheme 30

also found that the $C_{(alkyne)}\cdots S$ repulsive interactions were increased on going from the parallel to perpendicular orientation. The Mo–Mo bond order was found to be ≤1 rather than the possible, and expected, double bond. Treatment of either isomer with $[Ru_3(CO)_{12}]$ afforded two products C and D (Scheme 30). In C, the alkyne retains its parallel orientation to the Mo–Mo bond, whereas in D it resumes the more normal perpendicular orientation. Other work with thiols,[553,554] primary phosphines,[553] dithiolenes,[555] and 1,3-dithiole–thiones[556–558] has been described.

5.07.7.5 Other Complexes

The π-basic fragment [TpMo(NO)L] has been shown to coordinate alkynes as well as arenes, dienes, ketones, and aromatic heterocycles.[477] Some complexes containing thiacycloalkynes[559] and cyclotetradeca-1,8-diyne[560] have been prepared. Alkyne-containing complexes with ancillary cyclobutadiene,[561] diethyldithiophosphate,[562] and porphyrin[563] ligands have also been described. The complexes $[MoCl_3(SEt_2)(\eta^2\text{-}PhC_2SeBu)]$[564] and $[MoCl_3\{S(CH_2)_4\}(\eta^2\text{-}PhC_2R)]$ (R = Ph, Me) were synthesized. Since the overall geometry is *mer*, *trans* and identical to the analogous tungsten complex $[WCl_3(PMe_3)_2(\eta^2\text{-}PhC_2Ph)]$, in which the alkyne bonding is described as a tungstacyclopropene, the molybdenum is also considered as an Mo(v) ion, where the alkyne behaves as a dianionic ligand. Theoretical calculations on related systems also support this proposal.[536] A monomeric MoO_2 fragment has been coordinated in a π-fashion to the two acetylide ligands in the titanium-based complex $[(\eta^2\text{-}C_5H_4\text{–}SiMe_3)_2Ti(CCSiMe_3)_2]$, which has been crystallographically characterized (Figure 30).[565]

5.07.7.6 Electrochemical Studies

Cyclic voltammetry shows that $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)Cp][BF_4]$ undergoes a reversible reduction at −1.25 V vs the saturated calomel electrode (SCE) at a platinum electrode in CH_2Cl_2 affording $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)Cp]$.[566] $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)Cp]$ can also be generated chemically through treatment of a frozen solution of $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)Cp][BF_4]$ with $[CoCp^*_2]$. Both the NMR and EPR spectra of the 18-electron cation and 19-electron neutral species revealed temperature-dependent fluxional processes. Two different processes were described, a rapid alkyne oscillation in the neutral radical and alkyne rotation in the cation, with the barrier to alkyne oscillation significantly lower. EHMO calculations indicate that the singly occupied molecular orbital (SOMO) of the neutral 19-electron species is largely metal based but with significant unpaired electron density on the alkyne ligand. $[Mo(\eta^2\text{-}PhC_2Ph)Cp_2]$ has been shown[567] to undergo a one-electron oxidation to $[Mo(\eta^2\text{-}PhC_2Ph)Cp_2]^+$. The anodic reactions were studied by cyclic voltammetry (CV), linear scan voltammetry (LSV), and bulk electrolysis. The one-electron process was found to be fully reversible (Nernstian). The redox potential was also

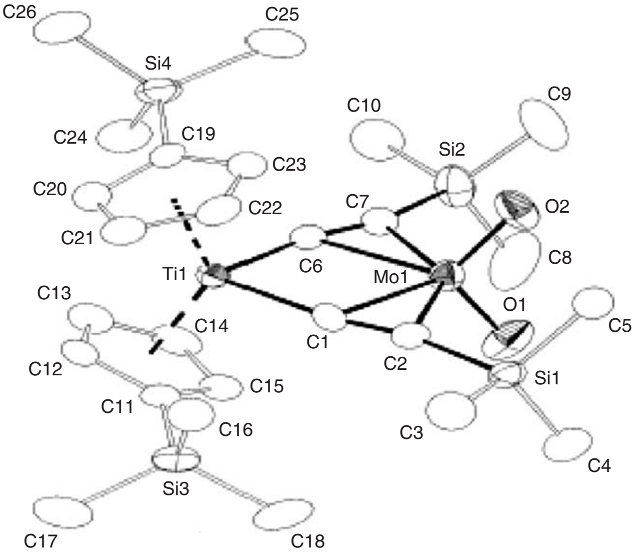
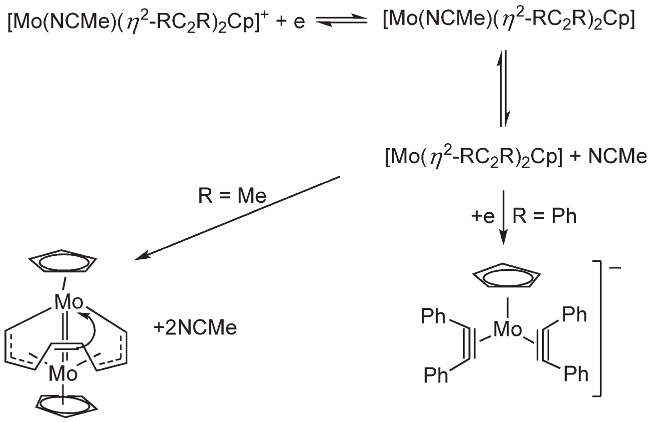


Figure 30 Molecular structure of $[(\eta^5\text{-}C_5H_4\text{-}SiMe_3)_2Ti(C\equiv CSiMe_3)_2\cdot MoO_2]$. Mansilla, N.; Rheinwald, G.; Lang, H. *J. Organomet. Chem.* **2000**, *602*, 72–74. Reproduced by permission of Elsevier.



Scheme 31 The electrochemical reduction of $[CpMo(\eta^2\text{-}RC_2R)_2]$.

found to be similar to that for $[Mo(Me)_2Cp_2]$, leading to the bonding between the alkyne and the molybdenum to be described as a molybdacyclopropene, where again the alkyne ligand is considered as a dianion. Bulk oxidation can also be achieved using ferrocene, and this allowed further spectroscopic investigation; unfortunately however, small amounts of ferrocene were always present in the purified material. The alkyne $\nu(C{\equiv}C)$ was found to increase to 1824 from 1774 cm^{-1} in the parent compound and is consistent with reduced backdonation to the alkyne ligand on oxidation of the metal center. The EPR spectrum afforded a single line at ambient temperature $g_{iso} = 2.049$ and a rhombic spectrum at 120 K in a 1 : 1 $CH_2Cl_2/C_2H_4Cl_2$ glass: $g_1 = 2.142$, $g_2 = 2.009$, $g_3 = 1.996$, $g_{ave} = 2.049$. A single hyperfine splitting was observed and assigned as $A_3(Mo)$ ca. 20 G. The compounds $[Mo(NCMe)(\eta^2\text{-}RC_2R)_2(CpR^1_5)]^+$ (R = Me, Ph; R^1 = H, Me) have been reduced electrochemically, and the products obtained found to be alkyne dependent (Scheme 31).[568]

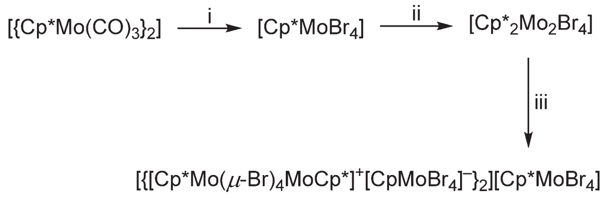
For the diphenylacetylene-containing complexes $[Mo(NCMe)(\eta^2\text{-}PhC_2Ph)_2(CpR^1_5)]^+$ (R = H, Me), the overall electrochemical sequence is ECE, beginning and ending with an 18-electron species. The initially formed 19-electron acetonitrile-containing complexes rapidly lose acetonitrile to give 17-electron species, which are sufficiently stable to allow another one-electron reduction wave, at a more negative potential, to occur, ultimately giving the anionic complexes $[Mo(\eta^2\text{-}PhC_2Ph)_2(CpR^1_5)]^-$. Where the alkyne is but-2-yne, there was no evidence for the 17-electron radical prior to dimerization and alkyne coupling. The 19-electron species $[Mo(NCMe)(\eta^2\text{-}PhC_2Ph)_2(CpR^1_5)]$ (R^1 = H, Me) were also prepared chemically by reduction of $[Mo(NCMe)(\eta^2\text{-}PhC_2Ph)_2(CpR^1_5)]^+$ with $[CoCp_2]$, and investigated by EPR spectroscopy. The virtual lack of metal dependence of the reduction potential for the 17-electron radicals $[CpM(\eta^2\text{-}RC_2R)_2]$ (M = Mo, W) suggests that the half-filled orbital is located mainly on the alkyne ligands. The EPR data obtained are also consistent with this statement. Similar studies have been carried out on the analogous carbonyl-containing compounds $[Mo(CO)(\eta^2\text{-}RC_2R)_2(CpR^1_5)]$ (R^1 = H, Me). In all cases, the 19-electron species was more stable, and little CO dissociation was observed. A further reduction afforded the anionic formally 20-electron species $[Mo(CO)(\eta^2\text{-}RC_2R)_2(CpR^1_5)]^-$ (R^1 = H, Me).

5.07.8 Cyclopentadienyl-containing Complexes

5.07.8.1 Monocyclopentadienyl Complexes

5.07.8.1.1 Containing halide-supporting ligands

The synthesis, structure, and properties of complexes containing the $\{(Cp^R)Mo(\text{III})\}$ fragment have been reviewed.[569] The complexes $[(Cp^R)MoCl_4]$ ($Cp^R = C_5H^iPr_4$, C_5Et_5) have been prepared and shown to have the four-legged piano-stool geometry.[570] The syntheses of $[(\eta^5\text{-}C_5H_4SiMe_2R)MoCl_4]$ (R = Cl, OH) from $[Mo(CO)_3(NCMe)_3]$ have been described,[571] with subsequent reduction in the presence of Na/Hg, affording the dimer $[\{(\eta^5\text{-}C_5H_4SiMe_2R)MoCl\}_2(\mu\text{-}Cl)_4]$. Conversion to the imido-containing complexes $[(\eta^5\text{-}C_5H_4SiMe_2Cl)Mo(NR)Cl_2]$ (R = 2,6-Me_2Ph, ^tBu) was also described. $[CpMoCl_4]$ has been shown to effectively polymerize a variety of substituted acetylenes in the presence of co-catalysts such as EtMgBr, Et_3Al, and BuLi.[572] These catalyst systems were found to be much less



i, PBr_3; ii, Na/H; iii, Br_2

Scheme 32

effective catalysts than $[Mo(O)Cl_4]$, and this was put down to the steric and electronic properties of the Cp ligand. $[Cp^*MoCl_4]$ was, however, found to be less moisture sensitive.[572] Some bimetallic complexes containing silylated cyclopentadienyl ligands have also been described.[573] Halide abstraction from $[Cp^*{}_2Mo_2Cl_6]$ using $AlCl_3$ afforded $[Cp^*{}_2Mo_2Cl_5]^+$ that has a crystallographically determined Mo–Mo bond length of 286.6(2) pm. This distance is noticeably longer than Mo–Mo distances in other Mo(IV)–Mo(IV) systems, and was studied using Fenske–Hall calculations. Another example of halide abstraction using the Lewis acid $SbCl_5$, instead of $AlCl_3$, has been described.[574] Cp^*-containing complexes with bromide and iodide ancillary ligands have been prepared, and their chemistry investigated. Subtle differences in reactivity are noted when compared to their Mo(III) and Mo(IV) chloride counterparts.[575] Conversion of $[\{Cp^*Mo(CO)_3\}_2]$ to the mixed valence compound $[\{[Cp^*Mo(\mu\text{-}Br)_4MoCp][Cp^*MoBr_4]\}_2][Cp^*MoBr_4]$, which contains Mo(III), Mo(IV), and Mo(V) centers has been reported,[576] using the route illustrated in Scheme 32.

Halide complexes containing optically active cyclopentadienyl ligands have also been described.[577]

Three different routes for the preparation of $[Cp^*MoCl_3]$ have been described,[578] namely, thermal decarbonylation of $[Cp^*MoCl_3(CO)_2]$, reduction of $[CpMoCl_4]$, and chlorination of $[\{Cp^*MoCl_2\}_2]$. The use of the thermal decomposition methodology with the complexes $[CpMoX_3(CO)_2]$ (X = Cl, Br, I) allowed preparation of the analogous compounds $[CpMoX_3]$.[579]

The synthesis of the dimer $[\{Cp^*Mo(\mu\text{-}I)_2\}_2]$ through treatment of $[Cp^*MoI_3]$ with PMe_3 has been described. The molecular structure was determined by a single crystal X-ray diffraction study, and the Mo–Mo length of 270.8(3) pm is slightly shorter than that observed in the structure of the dicationic analog $[\{Cp^*Mo(\mu\text{-}I)_2\}_2]^{2+}$ {271.8(3) pm}, and is consistent with the highest occupied molecular orbital (HOMO) being *d* rather than d^* in character.

The Becke–Lee–Yang–Parr (BLYP) and Becke–Perdew–Wang (BPW91) functionals have been used to study a variety of half-sandwich complexes. The two functionals were found to agree very well with each other for the calculated bond distances not involving the metal. In a double-ζ plus polarization quality basis set, both overestimate metal-to-ligand distances by amounts that are similar to those observed in small molecules with equivalent basis sets. No matter what changes were made to the functionals, consistent discrepancies between the calculated bond lengths involving the metal and those determined by experiment were evident in terms of an overestimation.[580]

5.07.8.1.2 Complexes containing group 13-supporting ligands

Treatment of $[Cp^*MoCl_4]$ with 5 molar equiv. of $BH_3{\cdot}THF$ yields $[(Cp^*Mo)_2B_5H_9]$[581,582] and a small amount of the electronically unsaturated cluster $[(Cp^*MoCl)_2B_3H_7]$.[581,583] The molecular structure of $[(Cp^*MoCl)_2B_3H_7]$ was determined by a single crystal diffraction study (Figure 31). The structure is best considered as a trigonal bipyramid, which implies electronic unsaturation; six electron pairs are required for the compound to be electronically saturated. The Mo–Mo distance is 309.6(1) pm, which is 10% longer than in the related saturated cluster $[\{\eta^5\text{-}C_5H_4\text{-}Me)MoCl\}_2B_5H_9]$ and significantly longer than other molybdenum species that contain single Mo–Mo bonds.[584] Fenske–Hall calculations showed the presence of an Mo–Mo σ-bond. The good molybdenum–borane orbital energy match also has an additional stabilizing effect by causing elevation of Mo–B antibonding orbital energies. The variation of the ^{11}B NMR chemical shifts in $[(Cp^*MoCl)_2B_5H_9]$ has been investigated using molecular orbital calculations, and reveal the presence of two high-lying filled molecular orbitals and two low-lying unfilled molecular orbitals, which correlate well with the shift differences observed.[585] Other Mo–borane cluster syntheses have been described.[586] The use of molybdenum–borane clusters in olefin catalysis has also been described and patented.[587]

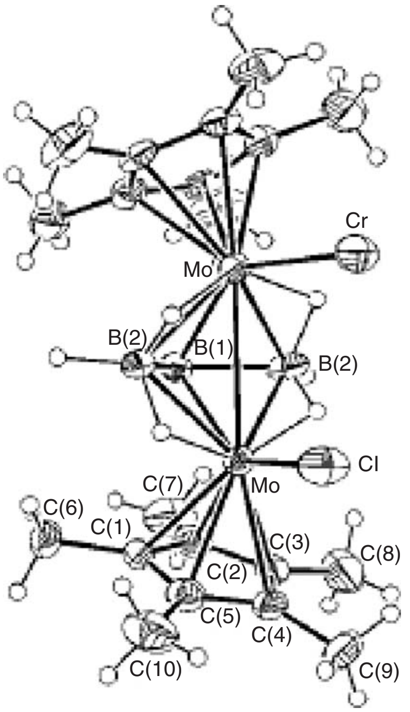


Figure 31 Molecular structure of [(Cp*MoCl)$_2$B$_3$H$_7$]. Reprinted with permission from Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1997**, *119*, 11120–11121. © (1997) American Chemical Society.

5.07.8.1.3 Containing group 15-supporting ligands

5.07.8.1.3.(i) Nitrogen based

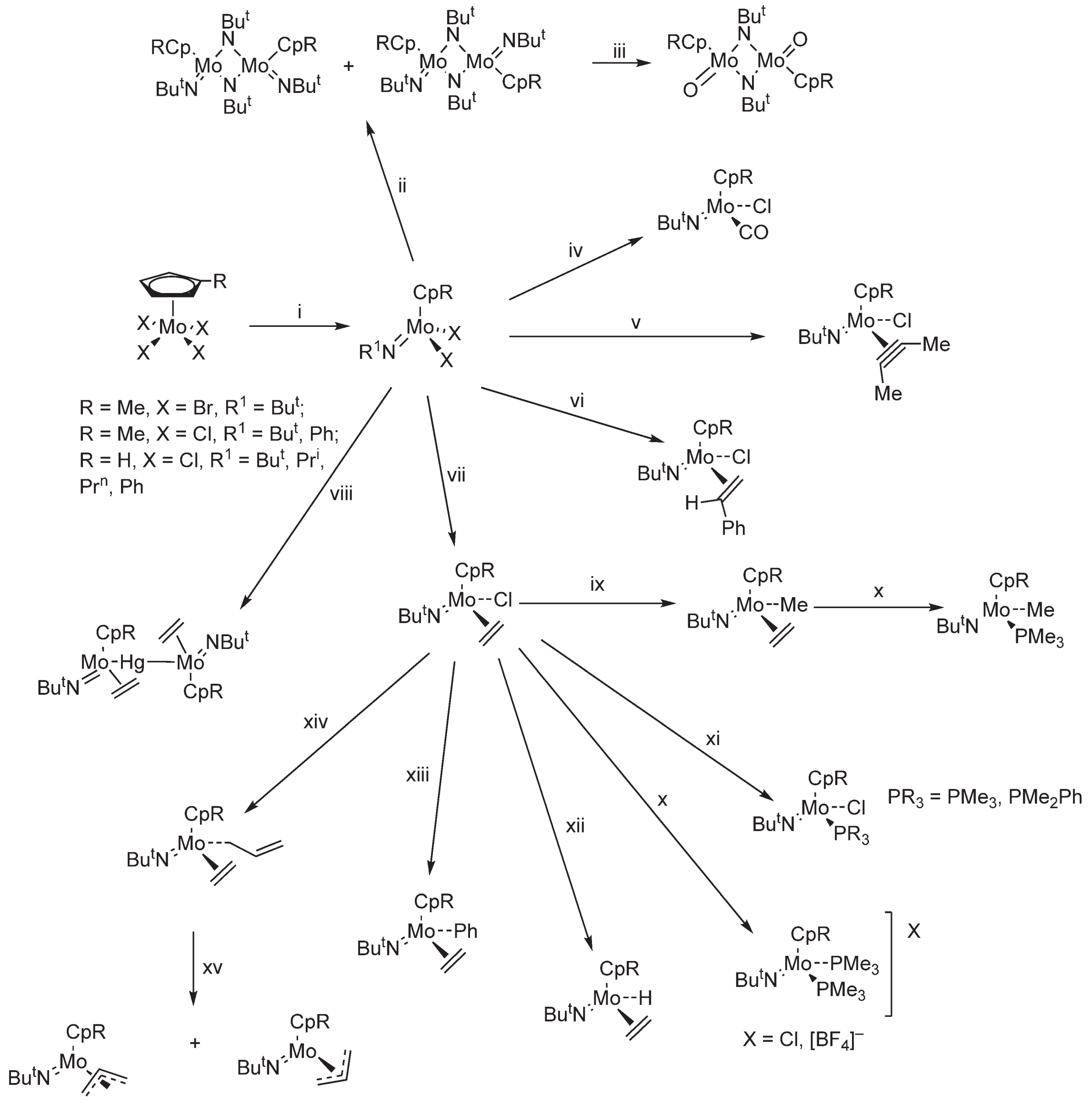
5.07.8.1.3.(i).(a) Amido

The preparation of [CpMo(NMe$_2$)$_3$] has been described.[588] It was studied using NMR, photoelectron spectroscopy, and electron diffraction. The data obtained are consistent with a ground-state structure, in which one of the amido groups lies with the Me groups axial to the Mo–cyclopentadienyl vector and the other two with the Me groups equatorial. DFT calculations also predict this to be the favored conformation. The preparation of Li$_2$[Cp(CH$_2$)$_3$NMe] and its transfer to Mo generating mixed half-sandwich amido complexes has been described.[589] Other half-sandwich compounds that contain chelating bidentate amido[590] or chelating amido alkoxy ligands have been reported. Disproportionation of hydrazine has been shown to generate complexes containing bridging amido ligands.[591] This contrasts the preparation of the mixed Cp bis-organohydrazido complexes [CpMo(NNRPh)$_2$(PPh$_3$)][OTf] (R = Me, Ph), which have been fully characterized.[592] Amido complexes that contain η^5-indenyl ligands have also been prepared and their reactivity investigated.[593]

5.07.8.1.3.(i).(b) Imido

The isolobal relationship between the imido ligand and Cp has been exploited in the preparation of a range of complexes that contain both the η^5-Cp and imido ligands,[508,594–603] and some of this work has been reviewed.[604] A summary of the reactivity shown by these complexes is illustrated in Scheme 33. The molecular structures of many of the new complexes were determined using single crystal X-ray diffraction studies including the trimetallic complex [{CpMo(NBu^t)(η^2-H$_2$C=CH$_2$)}$_2$Hg] (Figure 32). The Mo–Hg, Mo–NBu^t, and Mo–C bond lengths are 269.2(2), 277.3(2), 175(2), 172(2), 228(3), 217(3), 218(3) and 226(2) pm, respectively, and are all in the expected ranges. Bimetallic complexes that contain fluoro-functionalized imido ligands have also been prepared.[605] Mixed compounds of the type [(Cp^R)Mo(OR)(NR)$_2$] have been synthesized, where Cp^R includes indenyl and functionalized Cp ligands.[606,607] Bimetallic imido complexes where the (CpSiMe$_2$Cp) ligand bridges two metal centers have also been prepared and their susceptibility to oxidation investigated.[608]

Half-sandwich imido complexes have been shown to act as ethylene polymerization catalysts,[609] and are useful for the production of polyoxomethylene.[610]



i, 3NH$_2$R^1; ii, LiNHBu^t; iii, alumina column; iv, Na/Hg, CO; v, Na/Hg, MeC$_2$Me; vi, Na/Hg, PhCHCH$_2$; vii, KC$_8$, C$_2$H$_4$; viii, Na/Hg, C$_2$H$_4$; ix, MeLi; x, PMe$_3$, $h\nu$; xi, PR$_3$, $h\nu$; xii, LiBHEt$_3$; xiii, LiPh; xiv, CH$_2$CHCHMgBr; xv, $h\nu$

Scheme 33

5.07.8.1.3.(i).(c) Nitrosyl-containing complexes

The chemistry of the 16-electron fragment [Cp*Mo(NO)Cl$_2$] continues to be developed. A range of alkyl,[21,23–25,27–41] alkylidene,[40,386,387] alkoxide,[611] hydroxy,[33] and amido-containing[612] complexes have been synthesized and their chemistry investigated. The crystal structure of [{CpMo(NO)(μ-Cl)}$_2$] has also been reported.[613] Much of this work has been reviewed,[22] and discussed in Sections 5.07.2.2.1.2 and 5.07.3.2.[20,22] An important potential application of [Cp*Mo(NO)$_2$Cl] as a vascular dilator has been described.[614] The compound performed well in *in vitro* and *in vivo* experiments, and this work has been patented.[615] In related work, the complexes [Cp*Mo(NO)I(L)] (L = amino acid) which contain biologically relevant ligands have been synthesized, and the compound [Cp*Mo(NO)I(leu)] (leu = leucine) was crystallographically characterized with the amino acid found *trans* to the nitrosyl ligand.[616] Treatment of [Cp*Mo(NO)(CO)$_2$] with R$_2$E$_2$ (R = Me, Ph; E = S, Se) under photolytic conditions was found to

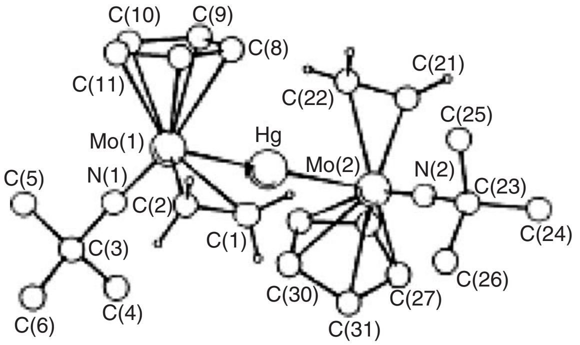


Figure 32 Molecular structure of $[\{CpMo(NBu^t)(\eta^2\text{-}H_2C{=}CH_2)\}_2Hg]$. Reproduced by permission of The Royal Society of Chemistry from Green, M. L. H.; Konidaris, P. C.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1994**, 2851–2859.

afford the compounds $[CpMo(NO)(ER)_2]$ in good yield.[617] The diiodo complex $[Cp^*Mo(NO)I_2]$ has also been reacted with a range of bidentate sulfur-donor ligands such as $[S_2CNR]^-$, $[S_2PMe_2]^-$, $[S_2P(OMe)_2]^-$,[618] and $[(SC_5H_4)_2Fe]^{2-}$.[619]

5.07.8.1.3.(ii) Phosphorus based

5.07.8.1.3.(ii).(a) Phosphine hydrides

The preparation of $[Cp^*MoH_5(PMe_3)]$ on treatment of $[Cp^*MoCl_2(PMe_3)]$ with $LiAlH_4$ has been described. T_1 measurements (780 ms, 230 K, 400 MHz) suggest that the molecule has a classical hydride structure.[620] The protonation of $[Cp^*MoH_5(PMe_3)]$ has also been studied and found to yield $[Cp^*MoH_6(PMe_3)]^+$.[621] T_1 measurements show that there is an η^2-H_2 ligand present, and the complex takes the form $[Cp^*Mo(\eta^2\text{-}H_2)(H)_4(PMe_3)]^+$. These experimental observations were supported by theoretical calculations at the second-order Moeller–Plesset perturbation (MP2) level.

The synthesis and the mechanism of H scrambling in $[CpMoH_3(dppe)]$ has been described.[622] A single crystal X-ray diffraction study showed the structure to be based upon a pseudotrigonal prism (Figure 33) rather than the expected pseudooctahedron, with an average Mo–H distance of 159 (5) pm.

The preparation, solid-state structure, and hydride–deuteride exchange in the related complex $[CpMoH_3(PMe_2Ph)_2]$ have been described along with related theoretical calculations on the model system $[CpMoH_3(PMe_3)_2]$.[623] The

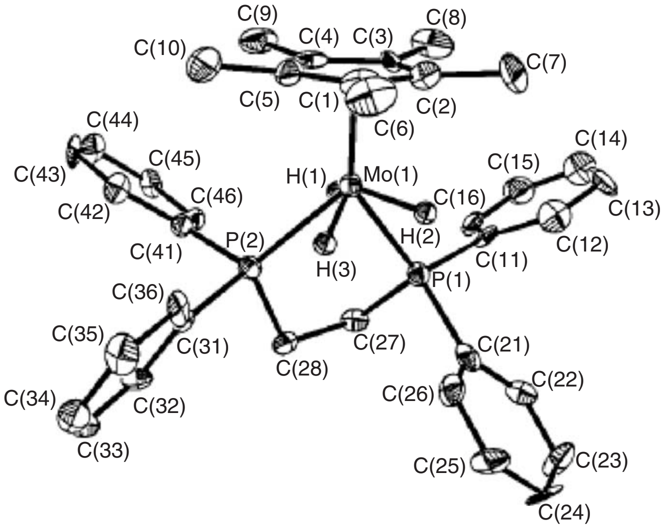


Figure 33 Molecular structure of $[Cp^*Mo(H_3)(dppe)]$. Reprinted with permission from Fettinger, J. C.; Pleune, B.; Poli, R. *J. Am. Chem. Soc.* **1996**, *118*, 4906–4907. © (1996) American Chemical Society.

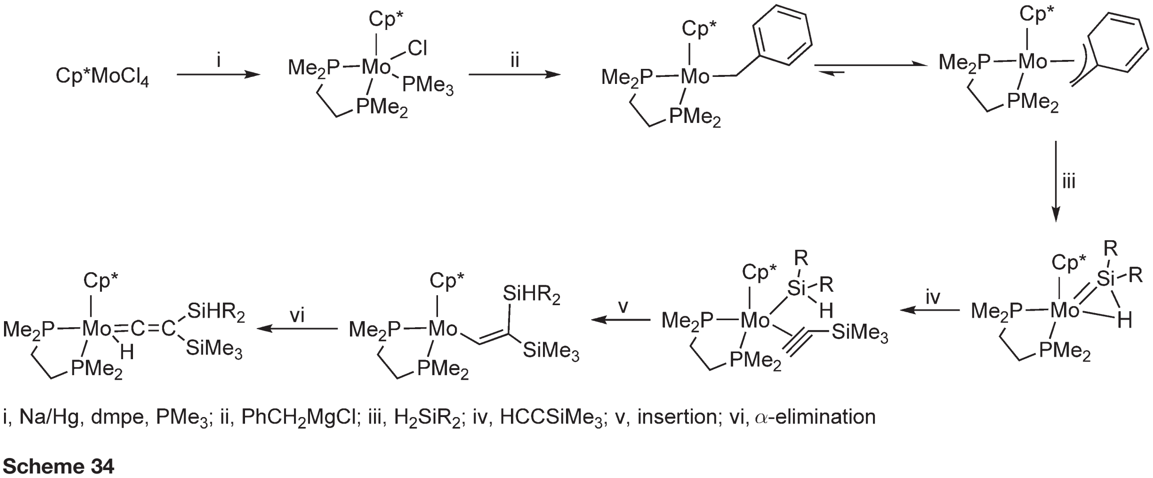
synthesis of [Cp*MoH$_3$(dppe)] has been described.[624] T_1 measurements imply a classical hydride structure, and protonation leads to the unstable tetrahydride [Cp*MoH$_4$(dppe)]$^+$, which also has a classical hydride structure. This was confirmed by T_1 measurements and a single crystal X-ray diffraction study of the tungsten analog. Oxidation[625] with [Cp$_2$Fe][PF$_6$] affords the cationic complex [Cp*MoH$_3$(dppe)][PF$_6$], which is unstable to the reductive elimination of H$_2$ giving [Cp*MoH(dppe)][PF$_6$]. Oxidation of [(η^5-C$_5$R$_5$)MoH$_3$(dppe)] (R = Me, Et) by [Cp$_2$Fe]$^+$ in wet THF gave the complexes [(η^5-C$_5$R$_5$)Mo(OH)$_2$(dppe)], which show a low-potential reversible oxidation wave.[626] The structure of the [(η^5-C$_5$Et$_5$)Mo(OH)$_2$(dppe)] was confirmed by a single crystal X-ray diffraction study and displays a four-legged piano-stool geometry with two terminal OH ligands in a relative *trans*-configuration. The complex [CpMo(OH)(PMe$_3$)$_2$], containing a hydroxyl ligand, is also known.[627] It is a stable monomeric 16-electron organometallic complex with a spin triplet ground state, and was obtained from the reaction of [CpMoCl(PMe$_3$)$_3$] with KOH. DFT (B3LYP) geometry optimizations for the model compound [CpMo(OH)(PH$_3$)$_2$] afford a spin triplet ground state with a bent *endo*-hydroxide ligand. An excited singlet state with a bent *exo*-OH ligand is found 9.5 kJ mol^{-1} higher in energy. Analogous calculations carried out on the related [CpMoX(PH$_3$)$_2$] (X = Cl, H, PH$_2$) systems show a spin triplet ground state for X = Cl and H, and a singlet ground state when X = PH$_2$. The compound [CpMo(OH)(PMe$_3$)$_2$] slowly decomposes in C$_6$D$_6$ in the presence of PMe$_3$ by a process that is initiated by the activation of a solvent C–D bond. This process was found to give a mixture of [CpMoH(PMe$_3$)$_3$] and [CpMo(η^2-CH$_2$PMe$_2$)(PMe$_3$)$_2$]. The oxidation of [CpMoH(PMe$_3$)$_3$] with Ag$^+$ in MeCN to give the 17-electron complex [CpMoH(PMe$_3$)$_3$]$^+$ has been investigated. [CpMoH(PMe$_3$)$_3$]$^+$ is indefinitely stable at low temperature; however, on warming to room temperature it slowly decomposes. Kinetic measurements show that the decomposition follows a second-order rate law. [CpMoH(PMe$_3$)$_3$]$^+$ can also be generated by ferrocenium or anodic oxidation. A bimetallic Mo–Ru cluster containing the {Cp*MoH$_3$} fragment has also been described.[628] [Cp*MoH(PMe$_3$)$_3$] has been shown to abstract CO from CO$_2$, (CHO)$_n$, HCO$_2$H, and MeOH to give [Cp*MoH(CO)(PMe$_3$)$_2$].[629] The silylene hydride-containing complexes [Cp*MoH(=SiR^{1}R^2)(dmpe)] (R^1 = R^2 = Me, Et, Ph; R^1 = Me, R^2 = Ph) have been prepared, as illustrated in Scheme 34.[630] The molecular structure of [Cp*MoH(=SiEt$_2$)(dmpe)] has been determined in a neutron diffraction study (Figure 34). The hydride ligand was located in the difference map and found to bridge the Mo=Si bond. The Mo–H, Mo=Si, and Si–H bond lengths are 184.7(12), 234.3(10), and 168.3(13) pm, respectively. The Mo–H bond distance is 32 pm longer than that observed in the X-ray structure of [Cp*MoH{=C=C(SiMe$_3$)SiEt$_2$}(dmpe)] (Mo–H = 152(8) pm) (Figure 35), obtained on treatment of [Cp*MoH(=SiEt$_2$)(dmpe)] with Me$_3$SiC≡CH (Scheme 34).

5.07.8.1.3.(ii).(b) Phosphine halides

Treatment of [(η^5-C$_5$R$_5$)MoCl(CO)$_2$(PMe$_3$)] (R = H, Me) with PhICl$_2$ afforded the Mo(V) complexes [(η^5-C$_5$R$_5$)MoCl$_4$(PMe$_3$)] in good yield.[631]

The reaction of [(η^5-C$_5$Me$_4$Et)MoCl$_4$] with primary phosphines has been described and found to yield simple monophosphine adducts;[632] other Mo(V) phosphine-containing complexes are also known.[633,634]

The preparation of the complexes [CpMoCl$_3$(PMe$_2$Ph)$_2$] and [Cp*MoCl$_3$L] (L = PMe$_3$, PMe$_2$Ph) have been reported. The Cp*-containing complexes prefer the 16-valence-electron configuration.[635] Theoretical calculations at the MP2 level on the [CpMCl$_3$(PH$_3$)$_n$] (M = Nb or Mo, n = 1 or 2) model systems afforded geometries in good agreement with the experimentally observed data, and were used to explain why it is not possible to compare the



i, Na/Hg, dmpe, PMe$_3$; ii, PhCH$_2$MgCl; iii, H$_2$SiR$_2$; iv, HCCSiMe$_3$; v, insertion; vi, α-elimination

Scheme 34

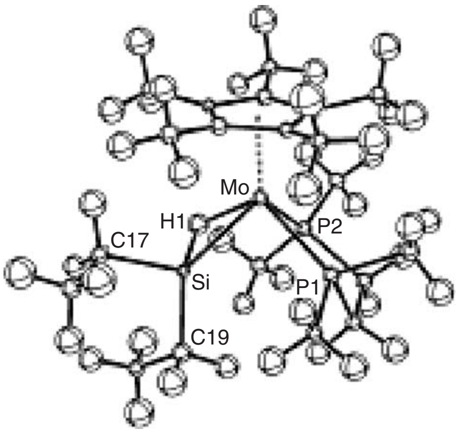


Figure 34 Molecular structure of [Cp*MoH(=SiEt$_2$)(dmpe)]. Reprinted with permission from Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428–10440. © (2004) American Chemical Society.

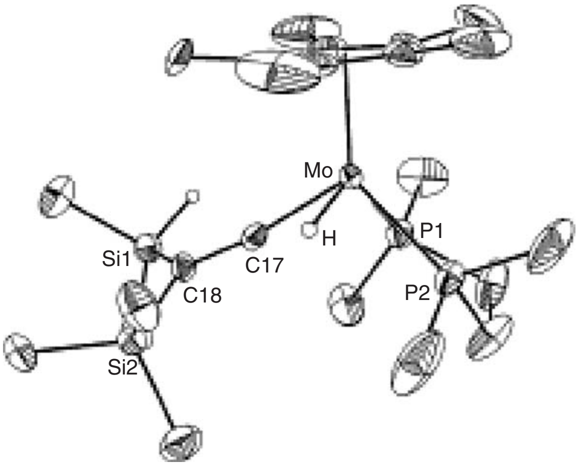


Figure 35 Molecular structure of [Cp*MoH(=SiEt$_2$)(dmpe)]. Reprinted with permission from Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428–10440. © (2004) American Chemical Society.

equilibration between [CpMoCl$_3$(PMe$_2$Ph)$_2$] and [CpMoCl$_3$(PMe$_2$Ph)] in the presence of free PMe$_2$Ph with the equivalent equilibration seen for the analogous niobium complexes [CpNbCl$_3$(PMe$_2$Ph)$_2$] and [CpNbCl$_3$(PMe$_2$Ph)]. The calculated PH$_3$ dissociation energy for M = Nb was 89.5 kJ mol^{-1}, which is in good agreement with the experimentally measured parameters, and for [CpMoCl$_3$(PH$_3$)$_2$], it was found to be stabilized by 138 kJ mol^{-1} relative to the excited 1A′ state and by 99 kJ mol^{-1} relative to the ground 3A″ state. Thus, the regaining of pairing energy upon PH$_3$ dissociation from [CpMoCl$_3$(PH$_3$)$_2$] suggests a stabilization for the 16-electron monophosphine complex of 39 kJ mol^{-1}. The observed differences in bonding parameters on going from Nb to Mo, along with a natural population analysis, suggest that the main reason for stronger Mo–PH$_3$ bonding interactions results from the greater extent of both M←P σ-donation and M→P π-backbonding for the d^2-metal relative to the d^1-metal.[636] The cationic complexes [(η^5-C$_5$R$_5$)MoI$_2$(PMe$_3$)$_2$][BF$_4$] (R = H, Me) were prepared by oxidation of the neural Mo(III) precursors [(η^5-C$_5$R$_5$)MoI$_2$(PMe$_3$)$_2$], and both have been crystallographically characterized.[637]

The complex [Cp*MoCl$_2$(PMe$_2$Ph)$_2$] was prepared[638] either on treatment of [Cp*MoCl$_4$] with PMe$_2$Ph and Na or by a ligand-redistribution process after reduction of [Cp*MoCl$_3$(PMe$_2$Ph)] by Na. The redistribution occurs due to the energetic instability of the intermediate 15-electron complex [Cp*MoCl$_2$(PMe$_2$Ph)]. [Cp*MoCl$_2$(PMe$_2$Ph)$_2$] is oxidized by the CH$_2$Cl$_2$ solvent in the presence of AlCl$_3$ affording [Cp*MoCl$_2$(PMe$_2$Ph)$_2$]AlCl$_4$. Other routes to analogous 17-electron bis-phosphine complexes have been described.[639–641] Theoretical calculations[642,643] MP2 and DFT(B3LYP) have shown that for the compounds [CpMoX$_2$(PH$_3$)$_n$] (X = Cl, Me; n = 1, 2), the 17-electron species are favored over the 15-electron compounds. Of paramount importance is the spin-pairing energy (16.5 kJ mol^{-1}), which is much lower than the energy gain in forming an additional Mo–P bond (51.5 kJ mol^{-1}), affording a spin doublet 17-electron complex. This parallels experimental observation and differs markedly from the analogous Cr complexes where the 15-electron quartet complex is favored. The calculations show that the spin-pairing energy (94.6 kJ mol^{-1}) is much greater than that obtained in forming an additional Cr–P bond (69.3 kJ mol^{-1}). Further calculations[644] have shown that the root mean square (RMS) doublet–quartet spin-orbit coupling (SOC) at the minimum energy crossing point (MECP) is of the order of 250 cm^{-1}, therefore large enough to allow facile surface crossing. Two mechanisms of phosphine dissociation were considered: one totally located in the doublet surface and the other that allowed dissociation to the quartet state. The data presented suggest that far from hindering the rate of phosphine dissociation from [$CpMoCl_2(PH_3)_2$] on going to the quartet state, it appears that it is in fact accelerated by this spin-state change. These data indicate that spin-state changes may affect the rate of solution-state organometallic reactions.

The molecular structure of [Cp^*MoCl_2(dppe)] has been determined by a single crystal X-ray diffraction study and shown to have a four-legged piano-stool geometry, with the dppe ligand occupying relatively *trans*-coordination sites (Figure 36), which contrasts with the previously reported structure for [$CpMoBr_2$(dppe)], which has the more common *cis*-geometry.[645] EPR spectroscopy indicated that a mixture of isomers is present in solution, and the relative amounts of the isomers is both temperature and solvent dependent. The crystal structures of [$CpMoCl(PMe_3)_3$][BF_4] and [$Cp^*MoCl(PMe_3)_3$][PF_6] have been determined.[646] A collection of half-sandwich Mo(III), Mo(IV), and Mo(V) complexes containing the bifunctional ligands Ph_2PCH_2X (X = 2-oxazolinyl or C(O)NPh_2) has been prepared.[647] Analogous complexes containing the $PPh_2CH_2CH_2S^-$ ligand have also been reported.[648]

The Mo(II) complexes [$Cp^*MoCl(L)_2$] (L = tertiary phosphine) have been synthesized and isolated. They are rare examples of stable 16-electron cyclopentadienyl molybdenum(II), and found to have a spin triplet ground state.[649]

The dissociation of PH_3 from [$CpMoX(PH_3)_3$] (X = H, CH_3, F, Cl, Br, I, OH, PH_2) to give the corresponding 16-electron [$CpMoX(PH_3)_2$] fragment has been studied using DFT (BLYP). The triplet spin state is preferred by all X ligands except PH_2 with the singlet–triplet gap varying between 7.1 kJ mol^{-1} for OH to 36.5 kJ mol^{-1} for F. The Mo–PH_3 bond-dissociation energy found on generating the 16-electron ground state varies dramatically across the series from 18.9 kJ mol^{-1} for OH to 98.7 kJ mol^{-1} for H. These calculated data correlate well with experimental data. For the geometry-optimized spin doublet system [$CpMoX(PH_3)_3$], a Mo–PH_3 bond-dissociation energy of 102 kJ mol^{-1} is calculated. The changes in the Mo–PH_3 bond-dissociation energy on the variation of X is influenced by three factors that stabilize the 16-electron product relative to the 18-electron starting material: (i) adoption of the higher (triplet) spin state through release of pairing energy, (ii) Mo–X π-interactions, and (iii) the release of steric pressure. The relative importance of the three effects depends on the nature of X. For double-sided π-donor X

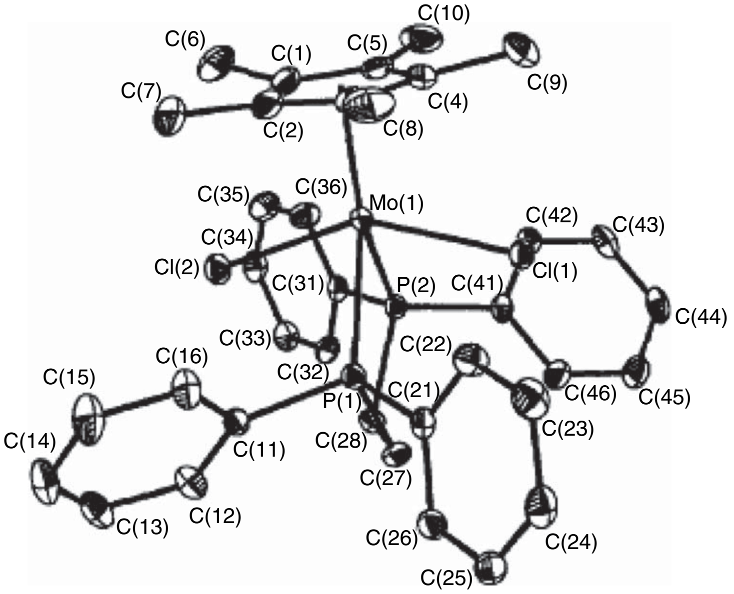


Figure 36 Molecular structure of [Cp*$MoCl_2$(dppe)]. Fettinger, J. C.; Keogh, D. W.; Pleune, B.; Poli, R. *Inorg. Chim. Acta* **1997**, *261*, 1–5. Reproduced by permission of Elsevier.

ligands (F > Cl > Br > I), a larger triplet–singlet gap is seen, whereas for single-sided π-donors the singlet state is favored. The π-stabilization ability was found to follow the order PH_2 > OH > F > Cl > Br > I > H. The major steric interaction in the complexes appears to be related to the presence of inactive lone pairs at X and their orientation and or proximity to the PH_3 ligands (Cl, Br > I, OH > F, PH_2, H, CH_3). The 16-electron Me system shows a significant α-agostic interaction in the singlet state; however, the undistorted triplet configuration remains favored energetically.[650]

A comparative kinetic study on the addition of the isolobal and isosteric CO and N_2 ligands to the spin-triplet organometallic complex [Cp*MoCl(PMe$_3$)$_2$] has been described.[651] The addition of CO is fast, and ultimately gives [Cp*MoCl(CO)$_2$(PMe$_3$)]; however, the addition of N_2 proceeds slowly and incompletely to an equilibrium position, which is temperature dependent. The temperature dependence of the equilibrium gave the following parameters for the reaction: $\Delta H = -95.8 \pm 8.8\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S = -281.4 \pm 29.4\,\mathrm{J\,mol^{-1}\,K^{-1}}$. The activation parameters for addition of CO are $\Delta H^{\dagger} = 21.0 \pm 1.2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\dagger} = -147 \pm 16.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$, and for the addition of N_2 are $\Delta H^{\dagger} = 58.8 \pm 4.2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\dagger} = -84 \pm 12.6\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Extrapolation of the rate data to 25 °C indicated a rate difference of over three orders of magnitude: $k_{CO} = 29 \pm 3\,\mathrm{M^{-1}\,s^{-1}}$ and $k_{N_2} = 0.014 \pm 0.001\,\mathrm{M^{-1}\,s^{-1}}$. The reaction was then studied theoretically using full geometry optimization at the MP2 level on the model systems [CpMoCl(PH$_3$)$_2$] + L (L = CO or N_2). The calculated energetics for the system were found to agree with experiment. The 16-electron complex [CpMoCl(PH$_3$)$_2$] is more stable in the spin-triplet state, with the excited 1A′ state being 45.8 kJ mol^{-1} higher in energy. The Mo–L bond formation was calculated to be exothermic by 117.2 kJ mol^{-1} for N_2 and by 252 kJ mol^{-1} for CO. The calculations for the addition of L along the reaction coordinate show an initial ligand-rearrangement related barrier for both the spin-singlet and the spin-triplet surfaces. After overcoming this barrier, it was found that the spin-singlet curve descends in energy earlier for the addition of CO relative to N_2. As the N_2 ligand continued to approach the metal, it was found that the 3A″ surface becomes increasingly repulsive, contrasting the development of an attractive interaction and a bound triplet state for CO. The addition of N_2 to [CpMoCl(PH$_3$)$_2$] has been further studied using DFT.[652] The optimized transition state and MECPs for the reaction suggest that the rate of addition is controlled by the barrier defined by the spin-triplet transition state (TS), with spin inversion occurring after this point. The calculated activation enthalpy is 28.2 kJ mol^{-1}, based on the spin-triplet TS, and is in excellent agreement with that measured for the reaction of [Cp*MoCl(PMe$_3$)$_2$] with N_2.

The complexes [{MeC(CH$_2$-η^5-C$_5$H$_4$)(CH$_2$PPh$_2$)$_2$}Mo(O)][653] and [Cp*Fe(P)$_6$MoCp]$^+$ have been synthesized and fully characterized.[654]

5.07.8.1.3.(ii).(c) Phosphido

Treatment of [(η^5-C$_5$EtMe$_4$)MoCl$_4$] with lithium phosphides affords Mo(III) complexes of the type [(η^5-C$_5$EtMe$_4$)Mo(μ-Cl)$_3$(μ-PR$_2$)] that contain bridging phosphide ligands.[655] Related compounds have also been prepared from other Mo(III) precursors.[656,657] The reaction of [Mo$_2$(μ-O$_2$CMe)$_4$] with KCp* in the presence of PMe$_3$ gave [{Cp*Mo(μ-O$_2$CMe)}$_2$(μ-PMe$_2$)(μ-Me)] as a result of P–CH$_3$ bond cleavage.[658] This compound has been crystallographically characterized (Figure 37), and shown to have Mo–P bond lengths of 238.8(1) and 238.5(1) pm, respectively, with the Mo–Mo separation of 284.5(5) pm consistent with an Mo–Mo single bond.

The terminal phosphido complex [(η^5-C$_5$EtMe$_4$)Mo{PH(2,4,6-Bu$^t_3$C$_6$H$_2$)}(PMe$_3$)$_2$] was obtained on the treatment of [(η^5-C$_5$EtMe$_4$)MoCl$_2$(PMe$_3$)$_2$] with LiPH(2,4,6-Bu$^t_3$C$_6$H$_2$) in a 1 : 2 molar ratio. Oxidative addition of HPPh$_2$ to [Cp*MoCl(N$_2$)(PMe$_3$)$_2$] was shown to yield the mixed terminal-phosphido, phophine-containing complex [Cp*MoHCl(PPh$_2$)(PMe$_3$)$_2$] in good yield.[659] A range of other complexes containing phosphido ligands is known.[660–663]

5.07.8.1.4 Containing group 16-supporting ligands

5.07.8.1.4.(i) Oxygen based

The complexes [(η^5-C$_5$R$_5$)Mo(O)$_2$Cl] (R = H, Me, CH$_2$Ph) are readily synthesized from the reaction of parent carbonyls [(η^5-C$_5$R$_5$)Mo(CO)$_3$Cl] with *t*-BuOOH (TBHP) in decane. The compound [{η^5-C$_5$(CH$_2$Ph)$_5$}Mo(O)$_2$Cl] can be stored and handled at room temperature without decomposition, which is in contrast to the more temperature sensitive Cp and Cp* analogs. The complexes [(η^5-C$_5$R$_5$)Mo(O)$_2$Cl] (R = H, Me, CH$_2$Ph) catalyze the epoxidation of cyclooctene, styrene, and 1-octene with TBHP as oxidizing agent. The highest activity was found for R = Bz, showing a TOF = 21,000 mol/(mol × h) for cyclooctene in CH$_2$Cl$_2$ at 55 °C with the ratio catalyst : substrate : TBHP = 0.0001 : 1 : 2.5. This activity even surpasses that of the well-known MeReO$_3$/H$_2$O$_2$ system. The stable parent carbonyls can be used as pre-catalysts, since they are transformed into the catalytically active complex [(η^5-C$_5$R$_5$)Mo(O)$_2$Cl] under the operating catalytic conditions.[664] Incorporation of this complex into

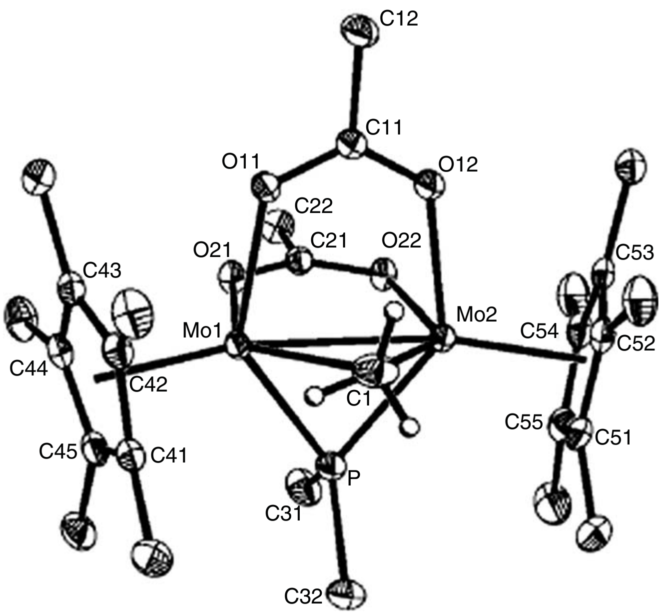


Figure 37 Molecular structure of [{Cp*Mo(μ-O_2CMe)}$_2$(μ-PMe_2)(μ-Me)]. Reproduced by permission of The Royal Society of Chemistry from Shin, J. H.; Parkin, G. *Chem. Commun.* **1998**, 1273–1274.

Zeolite MCM41 has been achieved, and it was shown to still be an effective epoxidation catalyst that could be recycled. Loss of activity occurred, however, in subsequent runs with the greatest decrease between runs 1 and 3.[665] Other routes to complexes of the type [(η^5-C_5R_5)Mo(O)$_2$Cl] have been described.[571,666–669] For example, treatment of [{CpMo(CO)$_3$}$_2$] with $SOCl_2$ has been found to be an efficient route to [CpMo(O)Cl_2].[669] The oxidation of [{Cp*Mo(CO)$_2$}$_2$] with H_2O_2/HCl in $CHCl_3$ has been described and shown to yield [Cp*MoCl(O)$_2$], which could then be efficiently converted into the other oxides such as *anti*-[{Cp*MoCl(O)}$_2$(μ-O)], [Cp*MoCl_2(O)], and *syn*-[{Cp*Mo(O)(μ-O)}$_2$].[668] The monoxide complex [Cp*MoCl_2(O)] has been crystallographically characterized and found to have a short Mo═O bond length of 168.3(2) pm. Some synthetic preparations of high-valent {Cp*Mo}-containing complexes have been presented in *Inorganic Syntheses*.[670]

The synthesis of the silyl-functionalized Cp-containing complex [(η^5-C_5H_4–$SiMe_3$)Mo(O)$_2$Cl] has been described.[671] This complex is nearly 5 times more soluble in supercritical CO_2 than its non-silylated analog. The ability of [(η^5-C_5H_4–$SiMe_3$)Mo(O)$_2$Cl] to carry out the oxidation of PPh_3 using molecular oxygen and the epoxidation of cyclohexene by *t*-butyl hydroperoxide has also been investigated. Complete oxidation of PPh_3 could be achieved in the presence of the catalyst; no oxidation was observed in the absence of catalyst. Epoxidation could be effected in scCO_2, but the overall conversion was poor when compared to the same reaction carried out in conventional solvents. Treatment of [Cp*MoCl_4] with H_2O_2 yields the oxo–peroxo complex [Cp*Mo(O)(O_2)Cl] in high yield. The complex has been crystallographically characterized (Figure 38). The Mo═O and O–O bond lengths were found to be 168.3(3) and 144.5(7) pm, respectively.[672] It was found to slowly decompose on standing in the solid state but can be regenerated on the addition of more H_2O_2. The importance of peroxy-containing complexes derives from their biological relevance, and their utility as epoxidation catalysts and other peroxo complexes have been prepared.[673] Complexes containing the peroxo and superoxo ligands have been reviewed.[674]

The [Cp*Mo(O)$_3$] group has been used as a protecting group in the preparation of mixed molybdate lanthanide metal clusters, several of which have been crystallographically characterized.[675] Routes to organometallic polyoxomolybdates such as [NBu_4][Cp*Mo_6O_{18}] have been described.[676] Other high nuclearity clusters containing the [Cp*Mo(O)$_n$] have also been prepared.[677,678] The chemistry of the high oxidation state compound [Cp$^*_2$$Mo_2(O)_5$] in aqueous solution has been developed, including its synthesis,[679] electrochemical behaviour,[680] a speciation study in 20% MeOH/H_2O in the pH range 0–14,[681] and the generation of bimetallic species;[682] some of this work has been reviewed.[683]

The compound [CpMo(O)(η^3-S_2CC≡CPh)] has been synthesized and fully characterized,[684] as has the dimeric complex [{Cp*Mo}{PhP(O)(OH)$_2$}]$_2$($PhPO_3$)$_2$(μ-O)$_2$], which is prepared on treatment of [Cp*MoCl_4] with PhP(O)(OH)$_2$, and has also been structurally characterized.[685] A number of mixed oxide–sulfide-[686,687] and oxide–thiolate-containing dimers[688] have been prepared and fully characterized as have some heteronuclear

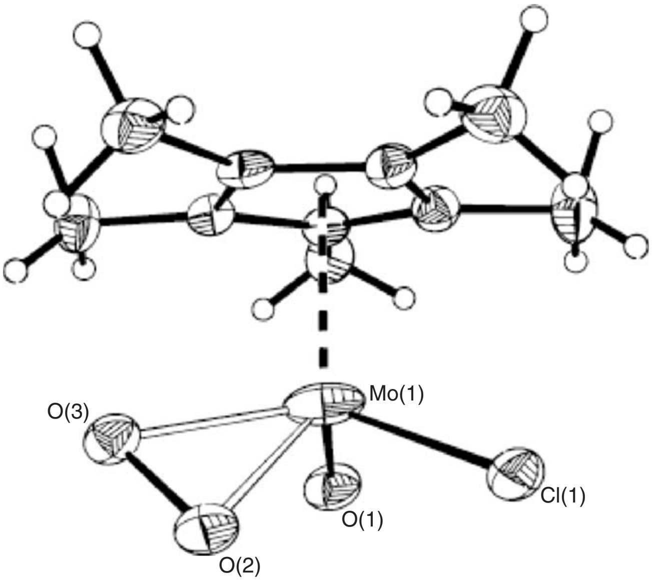


Figure 38 Molecular structure of [Cp*Mo(O)(η^2-O_2)Cl]. Reprinted with permission from Chakraborty, D.; Bhattacharjee, M.; Kraetzner, R.; Siefken, R.; Roesky, H. W.; Uson, I.; Schmidt, H.-G. *Organometallics* **1999**, *18*, 106–108. © (1999) American Chemical Society.

Mo–Ti-containing bimetallics based upon the [Cp*Mo(O)$_n$] fragment.[689] The synthesis, solution-state behavior, and crystal structure of [$Mo_2(OBu^t)_6CpNa(dme)$] have been reported.[690] The Mo≡Mo bond length was found to be 227.6(1) pm.

5.07.8.1.4.(ii) Sulfur based

The synthesis and reactivity of Cp^R-containing complexes with ancillary sulfur ligands has been reviewed.[691,692] Treatment of [Cp*Mo(CO)$_3$Cl] with 4,5-bis(benzoylthio)-1,3-dithiole-2-thione gives [Cp*Mo(DMIT)$_2$]$^{2-}$ in good yield.[693] Other thiolene-containing complexes have been prepared.[694,695] Treatment of [(η^5-L)MoCl$_3$] (L = indenyl, Cp) with [S_2CNEt]$^-$, [$S_2P(OEt)_2$]$^-$, and [acac]$^-$ afford the 16-electron species [(η^5-L)MoCl$_2$(E_2R)] (L = indenyl, Cp; E_2R = [S_2CNEt]$^-$, [$S_2P(OEt)_2$]$^-$, [acac]$^-$), which have been fully characterized,[696] as has the compound [$Cp_2Mo_2Fv(\mu$-$SC_6H_5)$][$Re_2(\mu$-SPh$)_3(CO)_6$] (Fv = fulvalene).[697] The synthesis of the complexes M[CpMo($SC_6F_4H)_4$] (M = K, Rb, Cs) have been described. NMR spectroscopy shows that there is rotation about the Mo–S bonds as well as inversion at pyramidal sulfur.[698] The related perfluorophenyl thiolate-containing complexes Tl[CpMo($SC_6F_5)_4$] have been shown to undergo Tl-for-M-for-[M($PPh_3)_3$] (M = Au, Cu) exchange to give [M($PPh_3)_3$][CpMo($SC_6F_5)_4$].[699] A VT ^{1}H-NMR spectroscopic investigation of the inversion at pyramidal sulfur gave $\Delta G^\dagger = 44\,\mathrm{kJ\,mol^{-1}}$. A new route into high oxidation state [Cp*Mo(S)$_n$] fragments was found on the reaction of [Cp*MoCl$_4$] with thiolates. Many known and new compounds were prepared as a direct result of C–S bond-activation reactions,[700] and some of this work has also been reviewed and includes details on general C–S bond activation.[701] The ability of dinuclear {CpMo(μ-S)} fragments to effect C–S bond cleavage has also been reviewed.[702]

The reaction of {Cp*Mo(S)$_3$} with Cu salts to give the double incomplete cubane clusters of the type [PPh_4]$_2$[Cp*MoS$_3$Cu$_3$X$_3$]$_2$ has been described, as has their subsequent reactivity toward phosphines.[703] Thermal analysis of Cu and Ag clusters derived from {Cp*Mo(S)$_3$} using DG-TGA has been carried out, and shows the presence of a two-stage decomposition pathway.[704] Achar–Brindley–Sharp, Coats–Redfern, Kissinger, and Flynn–Wall–Ozawa equations were used to calculate the non-isothermal kinetic parameters and to determine the most probable mechanisms of cluster degradation. Clusters that are derived from the {Cp*Mo(S)$_3$} fragment and contain Ag and Cu have also been the subject of review articles.[705,706] Treatment of [Cp*Mo(S^{t}Bu)$_3$] with $FeBr_3$ afforded the neutral tetranuclear cluster [Cp$^*_2$Mo$_2$Fe$_2$S$_4$Br$_2$], which has been crystallographically characterized.[707] Clusters that contain Ni have also been described.[708] These clusters were also shown to be effective catalysts, in the presence of NEt_3, for intramolecular cyclization of alkynoic acids to give 95–99% yields of enol lactones. A variety of other polynuclear clusters has also been prepared.[709–712]

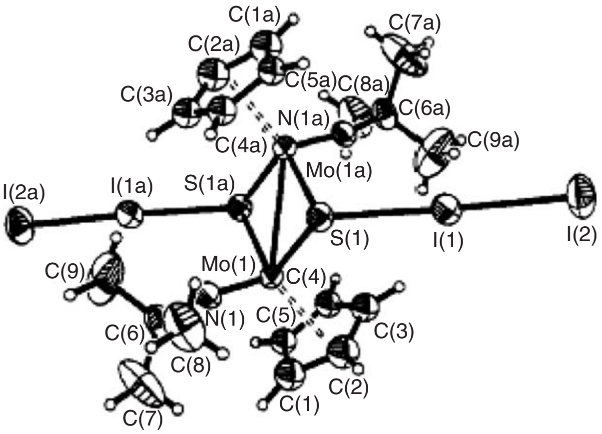


Figure 39 Molecular structure of [{CpMo(N-*t*-Bu)(μ-S·I$_2$)}$_2$]. Reprinted with permission from Allshouse, J.; Haltiwanger, R. C.; Allured, V.; Rakowski DuBois, M. *Inorg. Chem.* **1994**, *33*, 2505–2506. © (1994) American Chemical Society.

Polythiophene has been attached to a Mo-sulfide-based cluster, and its electrochemistry investigated. Electrochroism was observed and attributed to electronic synergistic interactions between the Mo sulfide cluster units and the polythiophene π-backbone.[713] Other thiophenium-[714] and thiophene-[715] containing clusters have been prepared, and the compounds obtained studied as model compounds for the hydrodesulfurization process. Several review articles have also appeared, discussing the nature of hydrodesulfurization.[716–720]

The reaction of [{CpMo(μ-S)(NBu^t)}$_2$] with iodine formed the bis-iodine adduct, [{CpMo(N-*t*-Bu)(μ-S)·I$_2$)}$_2$].[721] The crystal structure of [{CpMo(N-*t*-Bu)(μ-S·I$_2$)}$_2$] showed that a charge-transfer adduct had formed between each sulfido ligand and a linear iodine molecule (Figure 39). Weak intermolecular interactions were also observed between the terminal iodine atoms.

The reaction of [{CpMo(μ-S)(NBu^t)}$_2$] with AgOTf produced a one-dimensional polymeric material, with a repeating unit of the formula [{CpMo(NBu^t)S}$_5$]Ag(NCMe)OTf$_3$[AgOTf]$_2$. The crystal structure of [{CpMo(NBu^t)S}$_5$]Ag(NCMe)OTf$_3$[AgOTf]$_2$ shows that the dinuclear units of [{CpMo(μ-S)(NBu^t)}$_2$] are linked by repeating S–(μ-Ag)$_2$–S rings (Figure 40).

Dinuclear μ-sulfido complexes of molybdenum with (dimethylamino)ethyl-substituted cyclopentadienyl ligands have been synthesized,[722] as have water-soluble sulfide-bridged dimers through the introduction of water-solubilizing Cp^R groups.[723] Dimers that contain bridging sulfide and bridging methylene groups have been studied using EHMO calculations in conjunction with purely sulfur-bridged systems to probe why alkenes do not readily insert into the disulfide analogs.[724] Complexes that contain the sulfhydryl group have been described and their reactivity investigated,[711,725] as has the addition of alkynes to mixed oxo–sulfide clusters.[726] The activation of alkynes by sulfur-rich clusters has also been described,[727] as has the incorporation of alkyne and vinylidene units into tetrazolate groups.[728] Acetonitrile hydration versus Mo oxidation,[729] formation of acetonitrile ligand-rich systems,[730] transformation of hydrazines to diazene and diazenido ligands,[731] preparation of azido moieties,[732] and their thermal decomposition to amido and nitride species in sulfur-rich clusters have all been described. Other reactivity patterns for this class of compound have also been reported.[663,733–735]

The electrochemistry of thiolate bridge-containing systems has been investigated.[736–738] In particular, oxidation of (μ-NR$_2$)[737] and cleavage of N=N bonds[738] have been reported. The electrochemical reduction of N=N and its relevance to nitrogenase activity has also been described.[739] Reviews regarding the development of model systems for molybdenum-based enzymes are also available.[740–744] The electrochemical behavior of clusters containing the {CpMo(μ-SR)$_3$} fragment and additional hydroxyl or oxo ligands has also been reviewed.[745]

The reactions of the alkenes, propene, 1-butene, *cis*- and *trans*-2-butene, and hexene isomers with [{(R–Cp)Mo-(μ-S)}$_2$S$_2$CHX]I (R = H, Me, CO$_2$Na; X = H, CN, Bu^t) have been investigated. Alkene addition to the sulfido ligands resulted in the formation of alkanedithiolate-containing complexes. The complexes were then able to take up additional alkene. The rates of these reactions were monitored using visible spectroscopy. The rate constants (k_{on}) were compared as the dimer substituent and alkene structure were varied. The rate constants for alkene dissociation from the alkanedithiolate complexes (k_{off}) were also determined by NMR spectroscopy. The relative contributions of k_{on} and k_{off} to the equilibrium constants for reversible alkene binding, as inductive and steric effects were varied,

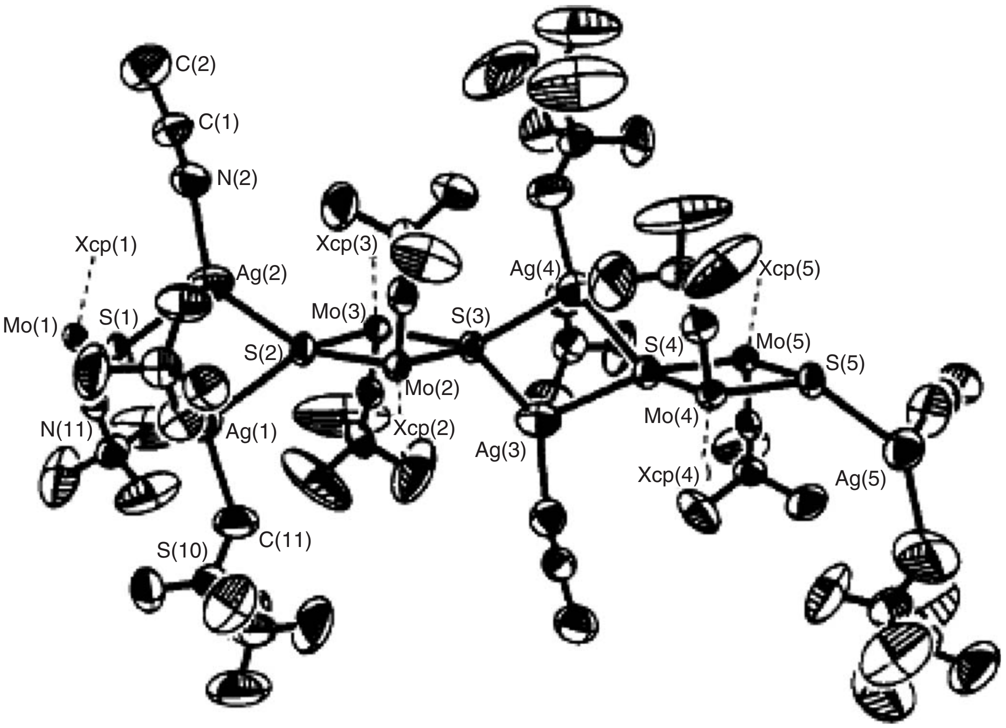


Figure 40 The repeating unit of [{CpMo(N^{t}Bu)S}$_5$][Ag(NCMe)(OTf)] with the Cp rings and the CF_3 groups of OTf on Ag(2) omitted. Reprinted with permission from Allshouse, J.; Haltiwanger, R. C.; Allured, V.; Rakowski DuBois, M. *Inorg. Chem.* **1994**, *33*, 2505–2506. © (1994) American Chemical Society.

suggest there is potential for using these systems in alkene separation. To this end, patents have been filed covering the incorporation of the $[(CpMo)_2(\mu\text{-S})_n]$ fragment into membranes and the utility of these membranes as chemospecific agents for the separation of alkenes.[746,747] The use of the sulfide-bridged systems $[(CpMo)_2(S_2CH_2)(\mu\text{-S})(\mu\text{-SR})][OTf]$ (R = H, Bu^t) for the oligomerization of alkenes has also been described.[748] The use of sulfido-bridged dimolybdenum complexes as catalysts in hydrogenolysis, hydrogenation, substitution, oligomerization, and exchange reactions has also been reviewed.[749]

5.07.8.1.4.(iii) Selenium based

A number of complexes containing bridging selenium atoms and or selonates have been described.[750–754] The synthesis and reactivity of the half-sandwich compounds $[Cp^*Mo\{E_2C{=}C(CN)_2\}_2]^{2-}$ (E = Se, S) have also been reported.[755]

5.07.8.1.4.(iv) Tellurium based

Refluxing $[Cp_2Mo_2Fe_2(CO)_7Te_2]$ and PhN_3 in benzene in the presence of air afforded $[Cp_2Mo_2O_2(\mu\text{-Te})(\mu\text{-NC}_6H_5)]$.[756] The structure of this multimetallic species was crystallographically determined, and can be described as consisting of a [CpMo–MoCp] unit, bridged by a μ-Te atom and an imido ligand. A terminal oxo group is also bonded to each Mo moiety. The tetrakis-bridged complexes $[\{(\eta^5\text{-RC}_5H_4)Mo\}_2(\mu\text{-PhTe})_4]$ (R = MeCO, MeO_2C) and $[\{(\eta^5\text{-RC}_5H_4)Mo\}_2(\mu\text{-Cl})(\mu\text{-PhTe})_3]$ were synthesized on reaction of $[\{(\eta^5\text{-RC}_5H_4)(CO)_2Mo\}_2]$ with Ph_2Te_2 in xylene at 110 °C followed by treatment with $[Cp_2TiCl_2]$. These complexes have been fully characterized, by ^{125}Te NMR spectroscopy, for example. The symmetrically bridged cluster displays a single resonance at −139 ppm and the asymmetrically bridged cluster displays resonances at 113, −9, and −249 ppm relative to Ph_2Te_2. Bis-TePh-bridged complexes could be isolated if the reaction was worked up in the absence of $[Cp_2TiCl_2]$. The dimolybdenum complex $[\{Cp_2Mo_2\}(\mu\text{-S})(\mu\text{-Te})(\mu\text{-SPh})_2]$ has been synthesized and structurally characterized.[757] This complex shows large third-order optical non-linearity as measured by degenerate four-wave mixing with picosecond excitation at 532 nm. A hyperpolarizability (*g*) of 1.2×10^{-30} esu was obtained. The molecular structure was obtained by a single

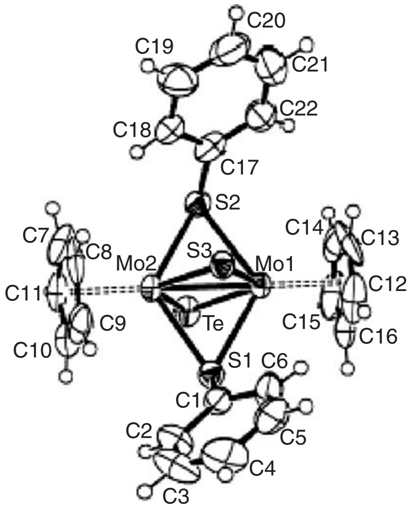


Figure 41 Molecular structure of [{CpMo}$_2$(μ-s)(μ-Te)(μ-SPh)$_2$]. Mathur, P.; Ghose, S.; Trivedi, R.; Gelinsky, M.; Rombach, M.; Vahrenkamp, H.; Banerjee, S.; Philip, R.; Kumar, G. R. *J. Organomet. Chem.* **2000**, *595*, 140–144. Reproduced by permission of Elsevier.

crystal X-ray diffraction study (Figure 41). The Mo–Mo, Mo–Te$_{(ave)}$, Mo–S$_{(ave)}$, and Mo–SPh$_{(ave)}$ are 262.6(2), 270.1(2), 226.5(4), and 248.8 pm, respectively.

5.07.8.2 Dicyclopentadienyl Complexes

5.07.8.2.1 Molybdenocene and its derivatives

Molybdenocene [Cp$_2$Mo] has been prepared by photolysis of [Cp$_2$MoH$_2$] at low temperature and studied by laser-induced fluorescence.[758] The preparation of [(η^5-C$_5$Ph$_5$)$_2$Mo][BF$_4$] and its crystallographically characterized molecular structure have been described (Figure 42).[759] The average bond lengths found for Mo–ring centroid, Mo–C, and C–C

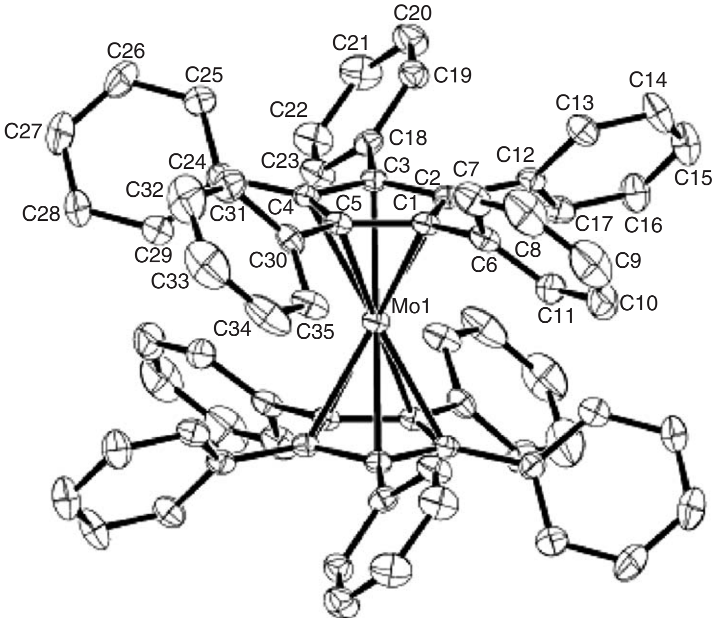


Figure 42 Molecular structure of [(η^5Ph$_5$C$_5$)$_2$Mo]$^+$. Field, L. D.; He, T.; Masters, A. F.; Turner, P. *Polyhedron* **2002**, *21*, 1707–1714. Reproduced by permission of Elsevier.

are 204.0, 237.6, and 143.2 pm, respectively. The electrochemistry of this complex was also described with potentials for the following couples $[(\eta^5\text{-}C_5Ph_5)_2Mo]^{0/+}$ −0.46 V and $[(\eta^5\text{-}C_5Ph_5)_2Mo]^{0/-}$ −1.92 V, respectively, versus Fc.

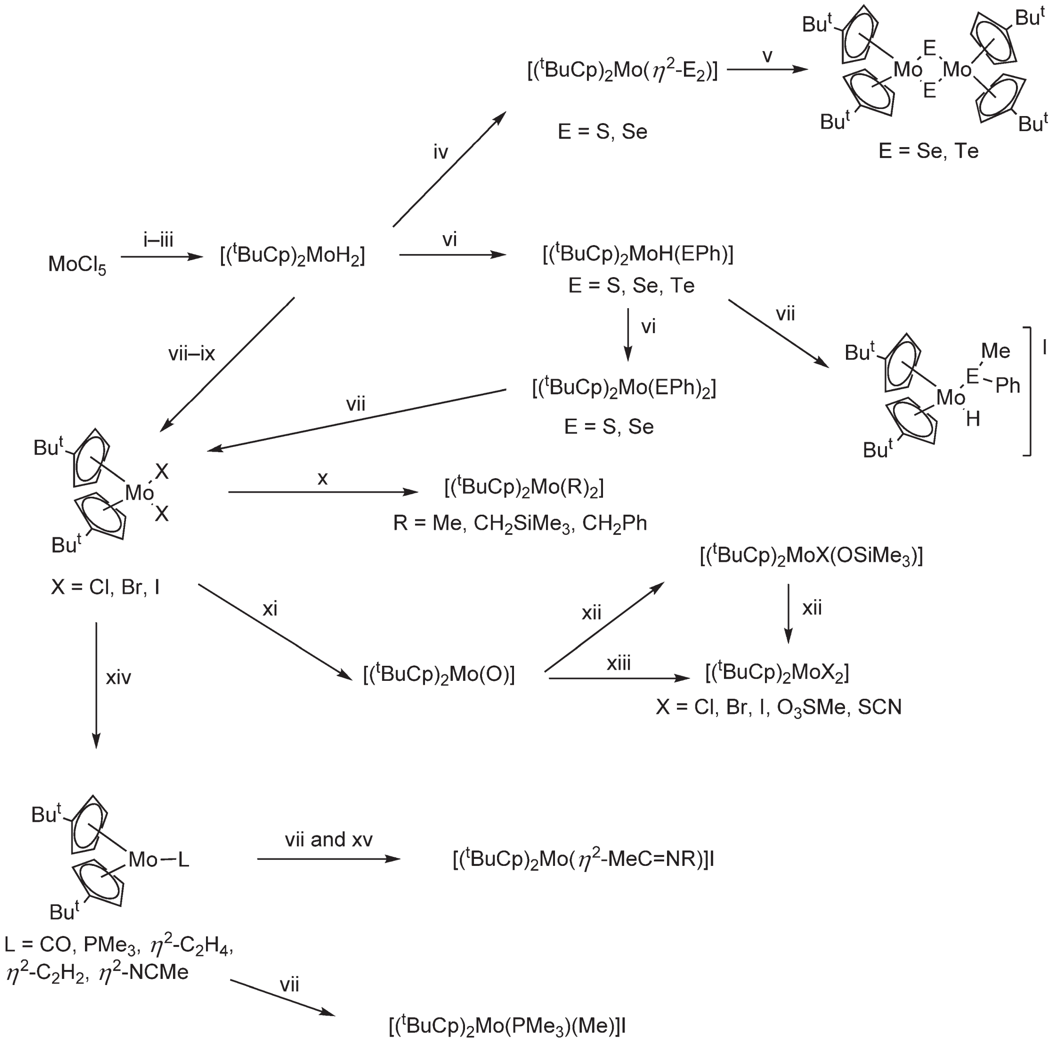
DFT has been used to study the addition of methane to $[Cp_2Mo]$.[760] Theoretical studies have also been carried out on the oxidative addition of methane to metallocenophane compounds.[761] The application of a modified EHMO-ASED formalism to the determination of the structural parameters of molybdenocene has also been described.[762]

Compounds of the type $[Cp_2MoL]$ ($L = CO_2$, C_2H_4) have been prepared, and their reactivity toward halofluorocarbons investigated, ultimately leading to fluoroalkylation of the Cp ring.[763,764] $[Cp_2Mo]$-containing compounds with ancillary heterocyclic carbene ligands,[765] phosphines,[661] η^2-nitriles[766] have been prepared and their reactivity investigated.

5.07.8.2.2 Molydenocene dihydrides and their chemistry

5.07.8.2.2.(i) Monomeric complexes

The preparation of the compounds $[(\eta^5\text{-RCp})_2MoH_2]$ ($R = SiMe_3$[606] and ^tBu[634,767]) has been described. A summary of the reactivity of $[(\eta^5\text{-}^tBuCp)_2MoH_2]$ and its derivatives is shown in Scheme 35.[634] Many of the compounds prepared have



i, ^tBuCpLi, $NaBH_4$; ii, H^+; iii, OH^-; iv, E_n; v, PMe_3; vi, Ph_2E_2; vii, MeI; viii, CCl_4;
ix, CH_2Br_2; x, RLi or RMgX; xi, LiOH; xii, Me_3SiX; xiii, $2Me_3SiX$; xiv, Na/Hg, L; xv, EtI

Scheme 35

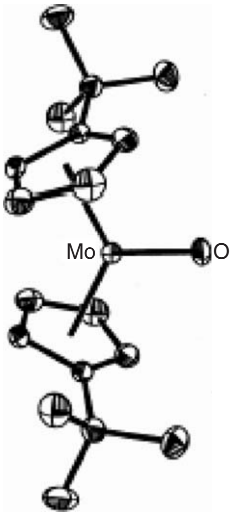


Figure 43 Molecular structure of [^{t}BuCP)$_2$Mo═O]. Reproduced by permission of The Royal Society of Chemistry from Shin, J. H.; Savage, W.; Murphy, V. J.; Bonanno, J. B.; Churchill, D. G.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1732–1753.

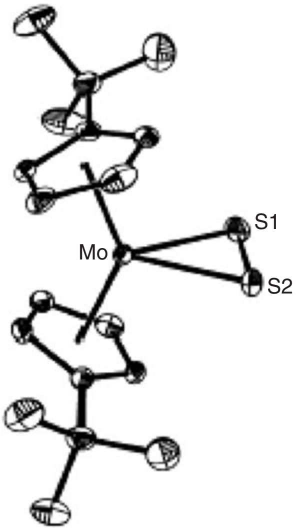


Figure 44 Molecular structure of [(^{t}BuCp)$_2$Mo(η^2-S_2)]. Reproduced by permission of The Royal Society of Chemistry from Shin, J. H.; Savage, W.; Murphy, V. J.; Bonanno, J. B.; Churchill, D. G.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1732–1753.

been crystallographically characterized, for example, [(^{t}BuCp)$_2$Mo(O)] and [(^{t}BuCp)$_2$Mo(η^2-S_2)] (Figures 43 and 44). The Mo═O bond length is 170.5(4) pm, clearly indicating an Mo═O double bond. The average Mo–S bond length in [(^{t}BuCp)$_2$Mo(η^2-S_2)] is 245.4(2) pm with an S–S bond length of 204.3(4) pm, indicating that the (η^2-S_2) ligand behaves as an S_2^{2-} ligand. A directly analogous structure is seen for [(^{t}BuCp)Mo(η^2-S_2)] which has Mo–$Se_{(ave)}$ 259.2(4) and Se–Se 232.2(6) pm, respectively, again indicating that the (η^2-Se_2) ligand behaves as a Se_2^{2-} ligand. The compounds [$Cp_2MoH(O_2CR)$] (O_2CR = chiral carboxylate) were prepared on treatment of the parent dihydride with a chiral carboxylic acid.[768] The monohydride compounds containing sulfonamides [$Cp_2MoH(NO_2SAr)$] have also been described.[769] Reductive elimination of alkanes from the *ansa*-bridged compounds [$(Cp^R)_2Mo(R)H$] have been studied, and the kinetic data show a normal isotope effect, which differs from the tungsten analogs, which show an inverse primary isotope effect.[770] The reaction of [$(Cp^R)_2MoH_2$] (Cp^R = Cp or C_5H_4-Me) with $B(C_6F_5)_3$ has been investigated and found to afford [$(Cp^R)_2Mo(H)(\eta^1\text{-}HB(C_6F_5)_3)$].[771] The treatment of [Cp_2MoH_2] with divalent silicon reagents has also been described.[772–775]

5.07.8.2.2.(ii) Protonation studies

The protonation of [$(Cp^R)_2MoH_2$] (Cp^R = any functionalized Cp ring) has been known since the 1960s, and this protonation reaction continues to generate interest.[776–780] This is due to the utility of these hydride complexes in catalysis. Protonation of [Cp_2MoH_2] by TsOH[781] has been decribed, as has its use for the reduction of imines to amines,[782] to form η^3-crotyl-containing complexes through reaction with allyl alcohols, [783] and to reduce ketones in water.[784–786] The reactivity of [$(\eta^5C_5H_4{-}Me)_2MoH_2$] toward nucleophiles in the presence of H^+ has also been described.[787] Cyclic hydroxypropyl-containing complexes have also been prepared on the treatment of [Cp_2MoH_2] with functionalized allyl alcohols.[779] The reaction with allyl alcohol also generates a π-allyl-containing complex. Some of this work has been reviewed.[786,788,789] Over the last 20 years, it has become clear that there is a balance between classical dihydride coordination and η^2-dihydrogen coordination, and an enhanced understanding of the factors that influence this will lead to a better understanding of catalytic processes. For the [$(Cp^R)_2MoH_3$]$^+$ systems, it has been found that there are significant stability differences in *ansa*-bridged systems versus non-*ansa*-bridged systems.[776] The non-*ansa*-bridged systems are best described as [$(Cp^R)_2Mo(H)_3$], a classical trihydride, and the *ansa*-bridged systems [$(Cp^R)_2Mo(H)\ (\eta^2\text{-}H_2)$], which contain a dihydrogen ligand. The barrier to (η^2-HD) propeller-like rotation has been measured[776] for the complex [$\{Me_2Si(C_5Me_4)_2\}Mo(\eta^2\text{-}HD)H$]$^+$ and found to be 39 kJ mol^{-1}, which is slightly higher than that found[780] for [$\{Me_2C(C_5Me_4)_2\}Mo(\eta^2\text{-}HD)H$]$^+$ at 31.5 kJ mol^{-1}. The *ansa*-bridge also has other marked influences on the acidity of these compounds, and hence accounts for the difference in the ease of dihydrogen loss observed between classical and *ansa*-bridged systems.

5.07.8.2.2.(iii) Multimetallic complexes

The preparation and reactivity of the dimetallic complex [$CpMoH_2(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4{-}C_5H_4)MoH_2Cp$] has been described.[790] Treatment of [Cp_2MoH_2] with a variety of silver[791–795] and copper salts[796] leads to a diverse range of cluster compounds; for selected examples, see Figure 45, many of which have been crystallographically characterized.

Typically the Mo–Ag bond length lies in the range 300 ± 5 pm and the Ag–Ag bond lengths 293 ± 3 pm. Photolysis of [$(\eta^5\text{-}C_5H_4\text{-}Bu^t)_2MoH_2$] affords *trans*-[$\{(\eta^5\text{-}C_5H_4\text{-}Bu^t)Mo(\mu\text{-}\sigma,\eta^5\text{-}C_5H_3Bu^t)H\}_2$].[797] Small clusters have been

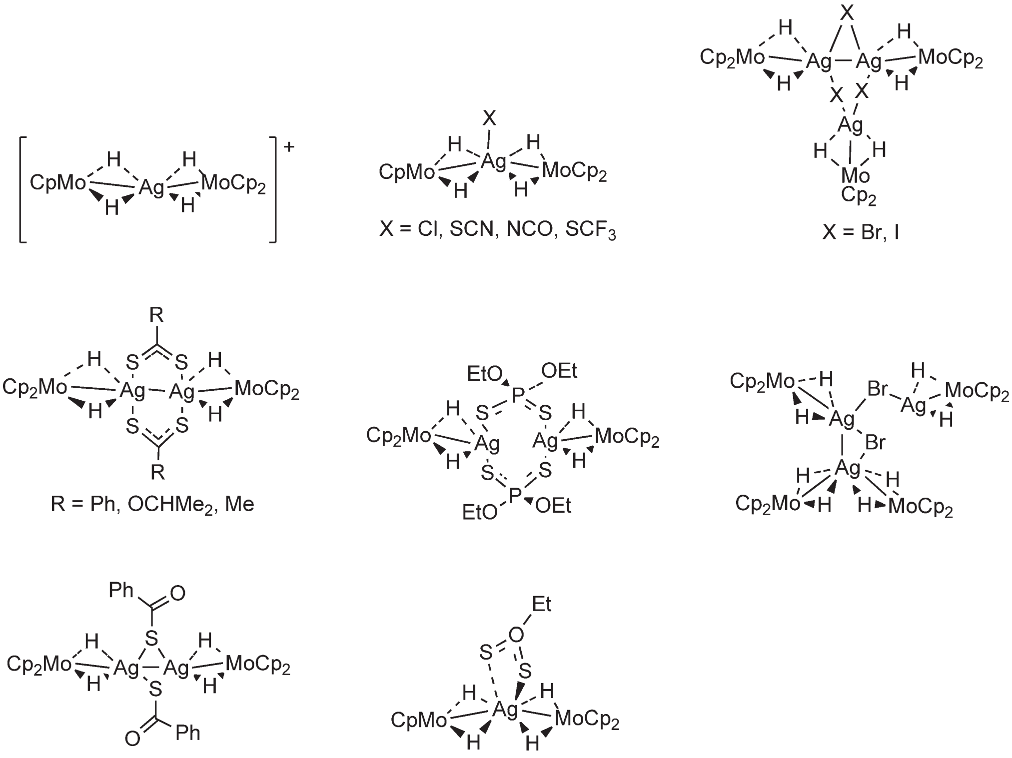
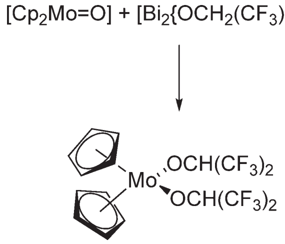
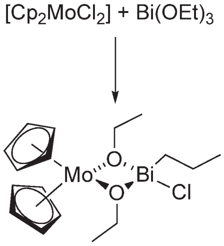


Figure 45 Multimetallic complexes formed on the reaction of [Cp_2MoH_2] with silver salts.



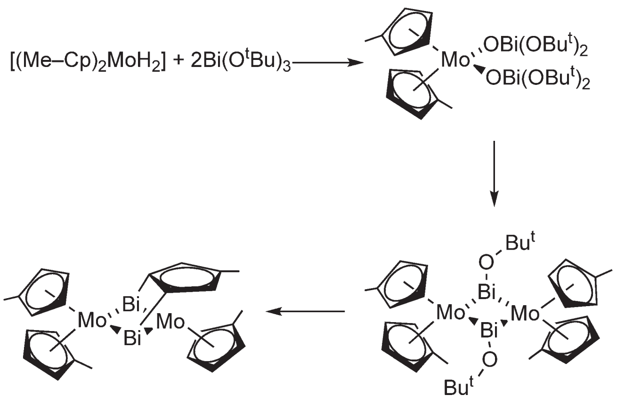
Scheme 36 The first synthesis of a bis alkoxy-containing molybdenocene.



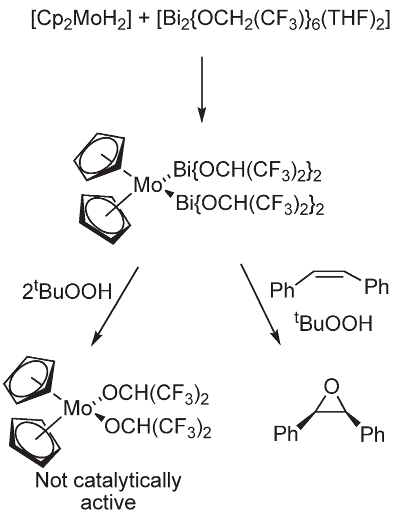
Scheme 37 The synthesis of a di-alkoxy bridged molybdenum–bismuth dimer.

prepared on the treatment of $[Cp_2MoH_2]$ with zirconocenes[798] and $[Fe_2(\mu\text{-}\eta^2\text{-}S_2)(CO)_6]$.[799] The reactivity of $[Cp_2Mo{=}O]$, $[Cp_2MoCl_2]$, and $[Cp_2MoH_2]$ toward $Bi(OR)_3$ have been investigated[800–804] (Schemes 36–38), and shown to afford a diverse range of products including $[CpMo\{OCH(CF_3)_2\}_2]$ (Scheme 36), the first example of a bisalkoxymolybdenocene complex that mirrors the known thiolate analogs and $[(Me\text{–}Cp)Mo(\mu_3\text{-}\eta^5:\eta^1:\eta^1\text{-}Cp\text{–}Me)(\mu\text{-}Bi)_2Mo(Cp\text{–}Me)_2]$ (Scheme 38), where a double C–H activation has occurred forming two new Bi–C bonds.

Many of the compounds prepared have been crystallographically characterized, and the Mo–Bi bond lengths lie in the range 278–297 pm. Detailed DFT, atoms in molecules (AIM), natural bond order (NBO), and electron localization function (ELF) calculations have also been carried out and used to explain the bent nature of the Bi–C bonds that allows the Cp ring to ligate to both the molybdenum and bismuth centers in terms of closed-shell carbanionic carbon atoms interacting with cationic closed-shell bismuth atoms. These compounds are of particular interest because of the utility of bismuth molybdates in the epoxidation of alkenes. Indeed $[Cp_2Mo(Bi\{OCH(CF_3)_2\})_2]$ has been shown to effectively epoxidize *cis*-stilbene (Scheme 39). Of significance though is that under the reaction conditions, cleavage of the Mo–Bi bonds is possible, but the molybdencocene-based and bismuth-based products isolated from a model study were found not to be catalytically active in the epoxidation reaction, implying there is a



Scheme 38 C–H activation to form Bi–C bonds.



Scheme 39 Epoxidation catalyzed by $[Cp_2Mo\{Bi(OCH(CF_3)_2)\}_2]$ and ^tBuOOH.

need to retain the Mo–Bi bond for catalysis to take place.[800] $[CpMoCl_4]$ also reacts with $[Bi_2\{OCH(CF_3)_2\}_6(THF)_2]$ to give the tris-alkoxy-containing complex $[CpMoCl\{OCH(CF_3)_2\}_3]$, which has been crystallographically characterized.[800]

The synthesis and crystal structure of $[CpMoHLi]_3$ has been described and contains a hexagonal Mo_3Li_3 central core.[805] Treatment of $[Cp_2MoHLi]_n$ with S_8 followed by $GdBr_3$ affords the tetrameric cluster compound $[Li(THF)_4][Cp_2MoSGdBr_4(THF)]_2$, which has been crystallographically characterized. The coordination geometry at Mo is tetrahedral and at Gd octahedral.[806] The synthesis and reaction of $[(\eta^5C_5H_4Me)_2MoH_2]$ with $HAlR_2$ (R = Et, ^iBu) has been described. The aluminum-bridged complexes $[\{(\eta^5C_5H_4\text{-}Me)(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4\text{–}Me)Mo(\mu\text{-}AlRH)\}_2]$ (R = ^iBu, Et) were obtained in good yield, and the crystal structure of $[\{(\eta^5C_5H_4\text{–}Me)(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4\text{–}Me)Mo(\mu\text{-}AlBu^iH)\}_2]$ was determined and shown to have a Mo–Al bond length of 263.6(2) pm (Figure 46).[807] The crystal structure of the parent dihydride was also described.

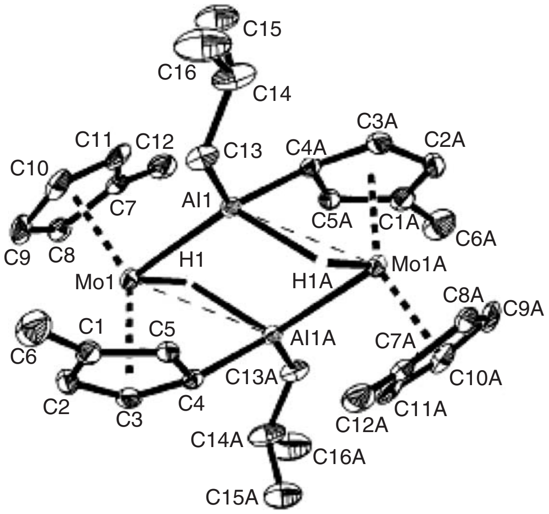


Figure 46 Molecular structure of $[\{Me\text{-}Cp(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_3\text{-}Me)Mo(\mu\text{-}Al^iBuH)\}_2]$. Reproduced from Stander, M.; Oesen, H.; Blaurock, S.; Hey-Hawkins, E. *Z. Anorg. Allg. Chem.* **2001**, *627*, 980–984, with permission from Wiley-VCH.

5.07.8.2.3 Molybdenocene dihalides and their chemistry

5.07.8.2.3.(i) Redox chemistry

The electrochemistry of [$\mathrm{Cp_2MoCl_2}$] has been studied.[808,809] Using photoelectrochemical techniques, with light in the range 300–400 nm, appreciable photocurrents were found to flow at potentials more positive than are required for oxidation. The light absorption was attributed to the cation formed by the one-electron oxidation of [$\mathrm{Cp_2MoCl_2}$] to [$\mathrm{Cp_2MoCl_2}$]$^+$ (Scheme 40).

The preparation of [$\mathrm{Cp_2MoCl_2}$][$\mathrm{BF_4}$] through the NO[$\mathrm{BF_4}$] oxidation of [$\mathrm{Cp_2MoCl_2}$] has been described.[810] This oxidation to the monocation can also be achieved using $\mathrm{WF_6}$. [$\mathrm{CpMoCl_2}$]$^{2+}$ can be synthesized from [$\mathrm{Cp_2MoCl_2}$] using [$\mathrm{(FCN)_3F}$][$\mathrm{BF_4}$] as the oxidizing agent in the presence of a fluoride ion acceptor ($\mathrm{BF_3}$ or $\mathrm{PF_5}$) in $\mathrm{SO_2}$ solution.[811] The crystal structure of the complexes [$\mathrm{Cp^*{}_2Mo(\mu\text{-}I)_4}$][$\mathrm{FeI_4}$] and [$\mathrm{Cp^*MoI_2(\mu\text{-}I)(\mu\text{-}O)}$] has also been described.[812]

5.07.8.2.3.(ii) Bioorganometallic chemistry of molydenocene dichloride

The bioorganometallic chemistry of [$\mathrm{CpMoCl_2}$] has developed significantly over the last decade, and has been reviewed.[813] Interest in this compound stems from its structural similarities to [$\mathrm{Cp_2TiCl_2}$], which is in the process of going through clinical trials. It has been found that all of the metallocene dihalides [$\mathrm{Cp_2MCl_2}$] (M = Ti, V, Nb, Mo), which have similar structural characteristics, have unique biological chemistry. [$\mathrm{Cp_2MoCl_2}$] has been found to have limited antitumor activity.[813,814] Key results that have appeared over the last 10 years include detailed studies on cellular uptake,[815] interactions with nucleic acids,[816–818] thionucleosides and thiobases,[819] amino acids,[820] proteins, thiols, carboxylates, and phosphates,[821,822] DNA,[823–825] spermicidal activity,[826] activity against testicular cancer,[827] inhibition of human topoisomerase II,[828] mechanism of action,[829] novel catalytic reactions that have relevance to biological molecules, that is, the cleavage of phosphate esters,[830–833] which add to earlier studies on hydrolysis.[813] The most significant findings of these studies are that [$\mathrm{Cp_2MoCl_2}$] interacts negligibly with DNA under physiological conditions, while systematic studies of its coordination chemistry have shown simultaneous weak adduct formation with phosphate (*O*) and heterocyclic (*N*) donors (Figure 47).

Strong stable adducts have been found to form with deprotonated thiols and amino acids (Figure 48).

The ability of [$\mathrm{Cp_2MoCl_2}$] to catalyze the hydrolysis of phosphate esters[830–832,834] (Scheme 41), which mimic the stable phosphate diester backbone in DNA, is of particular significance, as it may be related to its antitumor activity. It has, however, been shown that significant catalytic activity is not observed above pH 4, implying that it may not be a relevant mechanism *in vivo*. Since it is known that in certain tumors an acidic environment is present, in these cases, this method of DNA cleavage may not be ruled out. The use of [$\mathrm{Cp_2MoCl_2}$] and other metallocenes as antitumor agents has been patented.[835]

5.07.8.2.3.(iii) Compounds containing the η^5-indenyl ligand

The compounds [$(\eta^5\text{-Ind})\mathrm{CpMoX_2}$] have been prepared[696,836–838] and show comparable reaction chemistry to the parent [$\mathrm{Cp_2MoCl_2}$]. Chemical and electrochemical reduction of complexes of the type [$\mathrm{Cp(Ind)MoL_2}$]$^{n+}$ ($n = 0, 1, 2$) have been studied in detail.[839–841] Indenyl ring slip from η^5- to η^3-binding was found to be affected by sequential one-electron redox reactions.[840] Simple ligand-addition reactions also effect ring slippage and indenyl ring slip, and have been reviewed.[842,843]

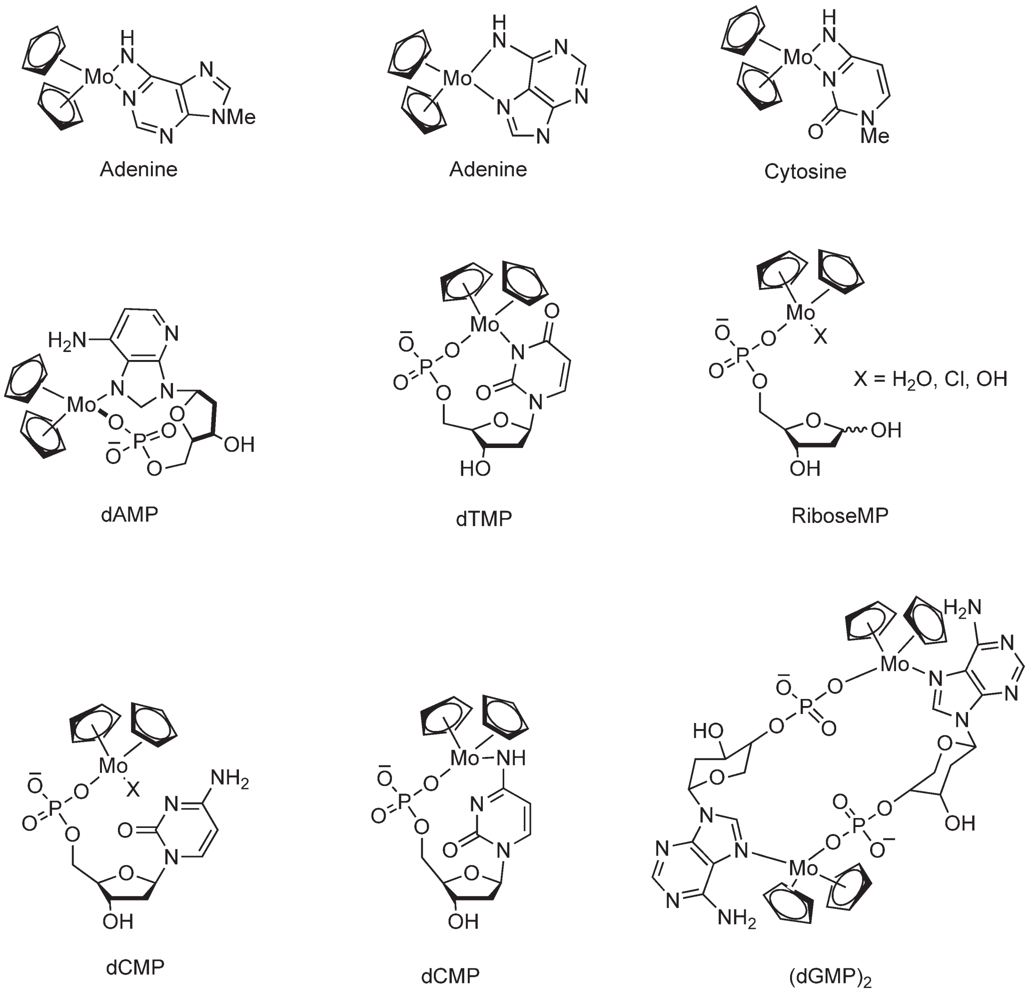
5.07.8.2.3.(iv) Containing *ansa* bridges

The preparation of a variety of *ansa*-bridged molybdenocene dihalides has been described.[844–848] The overall reactivity pattern differs noticeably from that observed in the non-bridged systems, and the difference in reactivity is termed the "*ansa* effect".[845,848] These systems have been used as polymerization catalysis,[847] and as model compounds for hydrodesulfurization.[849] In addition to the dihalo complexes and their reactivity, amido- and imido-containing *ansa*-bridged systems have also been prepared,[850–852] and their utility as catalysts investigated.[852] A short review on *ansa*-based systems is available.[604]

$$[\mathrm{Cp_2MoCl_2}] - e \xrightarrow{\text{i}} [\mathrm{Cp_2MoCl_2}]^+ \xrightarrow{\text{ii}} [\mathrm{Cp_2MoCl(NCMe)}]^+ \xrightarrow{\text{iii}} [\mathrm{Cp_2MoCl(NCMe)}]^{2+}$$

i, NCMe; ii, $h\nu$; iii, −e

Scheme 40



Adenine

Adenine

Cytosine

dAMP

dTMP

X = H_2O, Cl, OH

RiboseMP

dCMP

dCMP

$(dGMP)_2$

Figure 47 Coordination modes between named DNA constituents and $[Cp_2Mo]$. Adapted from Waern, J. B.; Harding, M. M. *J. Organomet. Chem.* **2004**, *689*, 4655–4668.

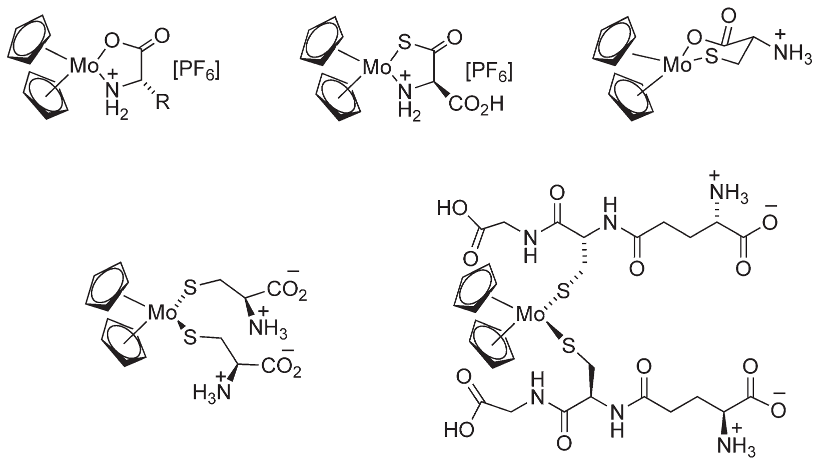
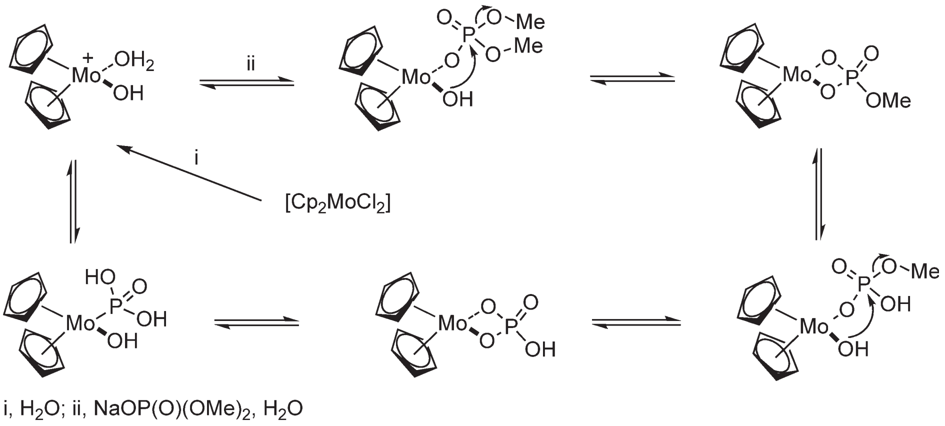


Figure 48 Coordination modes observed between amino acids and the $[Cp_2Mo]$ fragment. Adapted from Waern, J. B.; Harding, M. M. *J. Organomet. Chem.* **2004**, *689*, 4655–4668.



Scheme 41 Catalysis of ester hydrolysis by $[Cp_2MoCl_2]$.

5.07.8.2.3.(v) Other complexes

Routes to mixed Cp ring-containing dihalide complexes have been described.[836,837] A series of metallocenes that contain the PPh_2Cp ligand have been prepared and characterized.[853] The mass spectrum of $[Cp_2MoCl_2]$ has been reported,[854] as have the ^{35}Cl and ^{79}Br NQR spectra of $[Cp_2MoX_2]$ ($X = Cl$, Br).[855] The reactivity of $[Cp_2MoCl_2]$ toward α,ω-thiols,[856] cyclodextrin,[857] 1,8-naphthalenediylmagnesium,[858] and $[(Cp\text{–}R)_2MoCl_2]$ ($R = {}^tBu$, $SiMe_3$) with metallophosphide anions[859] has been described, as has the cleavage of the C–S bond in thiophene.[860] The formation of trimetallic compounds containing the $[Cp_2Mo]$ moiety have also been prepared photolytically.[861]

5.07.8.2.3.(vi) Catalytic activity

$[Cp_2MoCl_2]$ has been supported on silica and used to develop Mo(IV) systems that effect the catalytic dehydrogenation of methanol.[862] Its use as a polymerization catalyst for alkynes in the presence of alkylaluminums has also been described.[863,864] Reductive carbonyl coupling of acetaldehyde and acetone using bimetallic systems obtained from decarbonylative reaction between $[\{CpMo(CO)_3\}_2]$ and silica has been investigated. It was found that acetaldehyde and acetone reductively couple to produce *cis*- and *trans*-2-butenes and 2,3-dimethyl-2-butene, respectively.[865] Patents on the use of the dihalides as polymerization catalysts have also appeared, for example.[866,867]

5.07.8.2.4 Containing group 14-supporting ligands

A collection of papers dealing with the formation of heavier main group element molybdenocene bonds has appeared and includes the formation of Mo–Si bonds through the capping of silanol dendrimers, which were then calcined and used as epoxidation catalysts,[868] and the photochemical reaction of hydrosilanes with $[Cp_2MoH_2]$.[772–775,869] A review article on the preparation and typical reaction patterns of silyl-containing molybdenocene complexes is also available.[775] A series of compounds containing Mo–Sn bonds is also known.[870–872]

5.07.8.2.5 Containing group 15-supporting ligands

5.07.8.2.5.(i) Nitrogen based

A brief review of imido-containing complexes and their reactivity is available.[604]

The compound $[(\eta^3\text{-}Cp^*)_2Mo(N)(N_3)]$ was prepared by thermal elimination of N_2 from the diazide $[(\eta^5\text{-}Cp^*)_2Mo(N_3)_2]$. This reaction was studied theoretically, and the barrier to elimination was found to be strongly influenced by whether the azide ligand was orientated *endo* or *exo*.[873] The X-ray structure of $[(\eta^3\text{-}Cp^*)_2Mo(N)(N_3)]$ (Figure 49) has been determined, and the Mo≡N bond lengths for two independent molecules in the unit cell were found to be 166.0(4) and 167.1(4) pm, and are comparable to the crystallographic database mean of 165 pm. The displacement of the Cp^* rings from their normal η^5-coordination mode results from a strong Mo–N π-interaction perpendicular to the $[Mo(N)(N_3)]$ plane.

The bis-imido complex $[(\eta^5\text{-}Cp)(\eta^1\text{-}Cp)Mo(NBu^t)_2]$ has been synthesized and the complex shown to be at the limit of π-saturation.[597] VT NMR spectroscopy was used to identify three fluxional processes: (i) rotation of the η^1-Cp

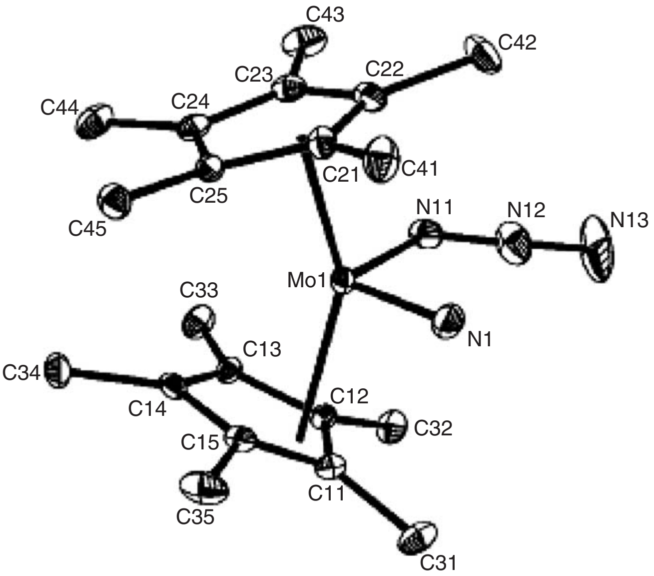


Figure 49 Molecular structure of *endo*-[(η^3-Cp*)$_2$(N)(N$_3$)]. Reprinted with permission from Shin, J. H.; Bridgewater, B. M.; Churchill, D. G.; Baik, M.-H.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2001**, *123*, 10111–10112. © (2001) American Chemical Society.

ligand about the Mo–C$_{ipso}$ bond, (ii) metallotropic migration, sigmatropic rearrangement of the η^1-Cp ring, (iii) hapticity interconversion of the two η^n-Cp rings. This, as in [(η^3-Cp*)$_2$Mo(N)(N$_3$)], shows the ability of the stronger NR π-donor to displace the poorer π-donating Cp ligand.

The preparation of the imido-containing complexes [(η^5-C$_4$H$_4$–R)$_2$Mo(NR^1)] (R, R^1 = Me, Bu^t; H, Bu^t; H, Pr^i; H, Ph) and some analogous indenyl-containing complexes has been described.[598]

5.07.8.2.5.(ii) Phosphorus based

Molybdenocene systems that contain bridging phosphido ligands have been prepared and fully characterized spectroscopically.[662,874,875]

5.07.8.2.6 Containing group 16-supporting ligands

5.07.8.2.6.(i) Oxygen based

The hydrolysis of molybdenocene dihalides has been investigated, and has led to the preparation and isolation of some hydroxyl-bridged complexes, and the mixed hydroxyl–aquo complex [Cp$_2$Mo(OH)(OH$_2$)]$^+$.[834] Inter- and intramolecular H/D exchange has been found to be catalyzed on dissolution of [Cp$_2$MoX$_2$] in water.[876] Other examples of H/D exchange facilitated by [Cp$_2$Mo(OH)(OH$_2$)]$^+$ in water have been reported.[877,878] Several C–H activation mechanisms have been described. The use of [Cp$_2$Mo(OH)(OH$_2$)]$^+$ for the hydration of nitriles to amides has also been achieved.[879] Treatment of [Cp$_2$MoH$_2$] with [Cp$_2$Mo(OTs)$_2$] in aqueous acetone affords [{Cp$_2$Mo-(μ-OH)}$_2$][OTs]$_2$,[880] which readily reacts with alcohols to form alkoxides and phosphines to form adducts.[881] A series of teflate-containing complexes has also been prepared,[882] as has a series of oxo-containing complexes,[883–885] which in some cases have been studied theoretically,[886] had their electronic structure determined,[885] and their utility in water splitting evaluated.[883] The reaction of [Cp$_2$Mo(O)] toward boron-based Lewis acids affording adducts of the type [Cp$_2$Mo(OBR$_3$)] has been described.[887] A speciation study on the complex [Cp$^*{}_2$Mo(O)$_5$] in methanol over the pH range 0–14 using stripped-flow analysis has been described, and the compound was found to be a strong electrolyte.[681] A review covering the nature of terminal metal–chalcogen bonds has also appeared.[888]

5.07.8.2.6.(ii) Sulfur based

A number of dithiolene[889–897] complexes have been prepared, and their optical, electrochemical, and magnetic properties investigated. Charge-transfer salts have been prepared with tetracyanoquinodimethane (TCNQ) giving rise to solids showing one-dimensional antiferromagnetic interactions,[890] and spin ladders in the solid state.[890] Three-dimensional antiferromagnetic spin ladders have also been described.[894,895] The effect of counteranions on the structural parameters has also been investigated.[897] The phase diagram of [Cp_2Mo(dmit)] has also been determined.[896] Several examples of the [Cp_2Mo] fragment fused to a porphyrazine ring system by a dithiolate link have been described, and strong coupling between the molybdenocene moiety and fused ring system is seen.[891–893] Other mono-[898–901] and bimetallic[554,733,902,903] complexes that contain mono- and bidentate terminal and bridging thiolate ligands have been synthesized, and their reactivity investigated. In a study of fold angles in dithiolate complexes, it was found that the interaction of the metal in-plane and sulfur *p*-orbitals is a factor of importance in electron-transfer reactions that regenerate the active sites in molybdenum and tungsten enzymes.[742]

The molecular structure of [Cp_2Mo(mto)] (mto = monothiooxalate) has been determined.[904] Inversion at pyramidal sulfur in dithioether complexes of the type [$Cp_2Mo(RSCH_2CH_2SR)$] has been studied by VT ^{1}H NMR spectroscopy and found to have barriers to inversion of approximately 55 kJ mol^{-1}. EHMO calculations confirmed that the fluxionality definitely resulted from inversion at pyramidal sulfur and could not be accounted for by simple ring flip of the MoS_2C_2 ring.[905] Compounds that contain bridging sulfide ligands have also been synthesized, and their reactivity investigated.[558,722] The oxidation of the compounds [$Cp_2Mo(S)_n$] ($n = 2, 4$) with *m*-chloroperbenzoic acid to give S_nO ligands has been described,[906] as has the insertion of SO_2 into the S–S bond present in these complexes to give dithiosulfate and bis *o*-alkylthiosulfate-containing complexes.[907]

5.07.9 Arene-containing Complexes

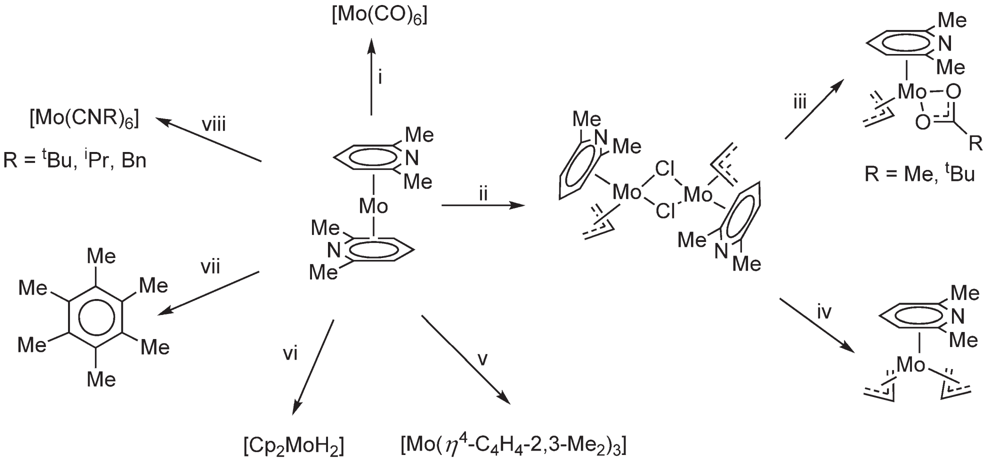
An article covering the synthetic routes available for the preparation of arene-containing complexes has recently appeared.[908]

5.07.9.1 Bis-arene Complexes

Timms and co-workers have reported[909] the first synthesis of bis-arene complexes of molybdenum that contain a π-bound bromobenzene ligand. This was achieved through co-condensation of the molybdenum atoms with a mixture of bromobenzene and hexafluorobenzene to give [$(\eta^6\text{-}C_6F_6)Mo(\eta^6\text{-}C_6H_5Br)$] with a yield of <5%. More success was had, however, with the formation of bromobenzene-containing bis-arene complexes of chromium through mixed ligand-condensation reactions. The complexes [$(\eta^6$-F–arene$)Cr(\eta^6\text{-}C_6H_5Br)$] (F–arene = C_6H_5F, $C_6H_5CF_3$, C_6H_4-1,3-F_2, C_6H_4-1,3-CF_3) were all isolated. These results contrast the normal outcome of of co-condensation of either molybdenum or chromium atoms with bromobenzene, which yield no organometallic product. Based on these observations, Timms proposed a half-sandwich mechanism for the formation of bis-arene complexes. The theory makes use of the following assumptions.

(i) The initial interaction of a metal atom with an arene is to form a half-sandwich compound rather than undergo oxidative addition.
(ii) The rate of addition of the first arene is faster than addition of the second to form the bis-arene, because the metal is a stronger Lewis acid than the half-sandwich compound and because of the steric implications of addition of the second arene.
(iii) Oxidative addition is more facile to the half-sandwich compound as the metal center is more electron rich than the free atom. The bis-arene complexes are still more susceptible to oxidative addition as the metal becomes more electron rich. However, the two arene rings offer steric protection to the metal center offering kinetic stabilization, so the oxidation of the half-sandwich compound is likely to be kinetically favored at low temperature.
(iv) Depending on whether the arene is electron withdrawing or electron releasing, different electronic properties will be imparted to the metal center. The more electron withdrawing the less susceptible to oxidative addition will be the half-sandwich compound.

The implication from these co-condensation reactions is that for molybdenum, only the half-sandwich [$Mo(\eta^6\text{-}C_6F_6)$] is resistant to oxidative addition of the C–Br bond in bromobenzene, whereas for chromium those formed from C_6H_5F, $C_6H_5CF_3$, C_6H_4-1,3-F_2, C_6H_4-1,3-CF are also electron deficient enough to resist oxidative addition. These observations on oxidative addition reactions undergone by half-sandwich compounds were then extended into a broader discussion about C–H-activation reactions seen in other co-condensation reactions to show its broader applicability.



i, CO; ii, $CH_2CHCHCl$; iii, NaO_2CR; iv, $CH_2CHCHMgCl$; v, C_4H_4-2,3-Me_2; vi, C_5H_6; vii, MeC_2Me; viii, CNR

Scheme 42

MVS continues to be used to prepare new bis-arene complexes. The perdeuterocomplexes $[(\eta^6\text{-}C_6D_6)_2Mo]$ and $[(\eta^6\text{-}C_6D_3\text{-}1,3,5\text{-}CD_3)_2Mo]$ have been synthesized,[910] and the latter intercalated into ZnS_2. The arene ring rotation was studied by solid-state ^{2}D NMR. Free rotation was found for C_6D_6 in the temperature range 160–360 K, whereas for $[(\eta^6\text{-}C_6D_3\text{-}1,3,5\text{-}CD_3)_2Mo]$, and its intercalated partner, the ligands were found to be static up to 360 K. MVS has also been used to prepare $[(2\text{-R–benzo}[b]\text{-thiophene})_2Mo]$ ($R = H$, Me, $SiMe_3$), in which the thiophene ligands are π-bound through the arene ring. The complexes are found to be mixtures of diastereoisomers.[911] The preparation of the bis-2,6-dimethylpyridine-containing complex $[(\eta^6\text{-}NC_5H_3\text{-}2,6\text{-}Me)_2Mo]$ has been described several times.[912–914] A photon electron spectroscopy (PES) study[912] on the complexes $[(\eta^6\text{-}NC_5H_3\text{-}2,6\text{-}Me)_2M]$ ($M = Ti$, V, Cr, Mo) showed that they were electronically similar to their purely carbon-based analogs. The 2,6-dimethylpyridine was, however, found to be a better δ-acceptor, implying that the dimethylpyridine ring is more strongly bound. These results concur with earlier work, which showed that the $M \rightarrow L$ δ backdonation ($dxy + dx^2 - y^2 \rightarrow \pi_3$) represents the greatest source of stabilization for this type of complex.[915]

The reactivity of $[(\eta^6\text{-}NC_5H_3\text{-}2,6\text{-}Me)_2Mo]$ has been investigated,[91,914] and is summarized in Scheme 42.

Other conventional syntheses of bis-arene complexes have been described.[916–918] The most useful being the thermal displacement of both benzene rings from $[(\eta^6\text{-}C_6H_6)_2Mo]$ to give access to alkyl-functionalized systems that previously were only available using MVS routes.

Hydroboration of $[(\eta^6\text{-}C_6H_5\text{–}CH_2CH{=}CH_2)_2Mo]$ was carried out with the hope that the Lewis-acidic borane center would interact with molybdenum-centered electron density.[919] This interaction was not observed. More recently, however, the solid-state structure of $[\{\eta^6\text{-}C_6H_5C_6H_3(Ph)OH\}(PMe_3)_3Mo]$ realized the possibility of a Lewis acid interaction with the molybdenum-centered electron density (see Section 5.07.9.2 for a more detailed discussion). A series of bis-arene complexes have also been used as precursors for plasma-enhanced metalloorganic chemical-vapour deposition (MOCVD). The molybdenum film laid down was found to have high hardness and average corrosion resistance.[920]

Some EHMO calculations on the hypothetical complexes $[(\eta^6\text{-arene})(\eta^6\text{-fullerene})Mo]$ and $[(\eta^6\text{-arene})_2Mo]$ have been described;[921] they have also been used to assess ^{1}H NMR data for a series of bis-arene complexes,[922] and DFT calculations have also been carried out to calculate ^{95}Mo NMR shifts.[923,924]

5.07.9.2 Monoarene Complexes

Thermolysis of $[CpMo(CH_2Ph)\{P(OMe)_3\}(\eta^2\text{-}PhC_2Ph)]$ has been shown to give the mixed sandwich compound $[CpMo(\eta^6\text{-}C_6Ph_6)]$.[924] This compound has been studied electrochemically and found to undergo a reversible one-electron oxidation.

A series of $[(\eta^6\text{-arene})MoL_3]$ (arene $= C_6H_6$, $C_6H_5CH_3$, $C_6H_5OCH_3$, $C_6H_5SiMe_3$; $L_3 =$ mono-, bi-, and tridentate phosphines) has been prepared by phosphine displacement of a π-bound arene in the parent bis-arene complex.

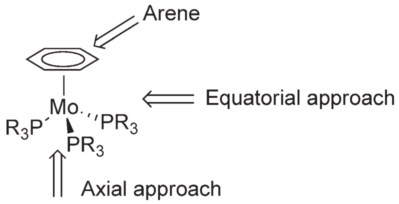


Figure 50 Possible proton approaches.

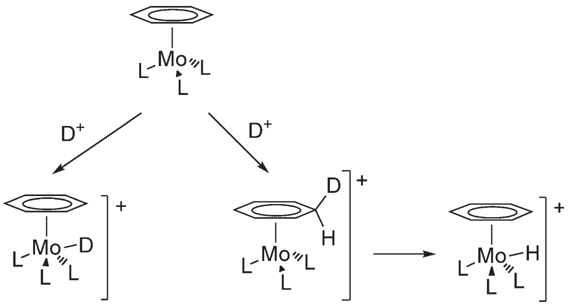
Many of them have been structurally characterized.[925–929] An alternative synthetic route to this type of compound has been reported, namely, the reduction of $[MoCl_3(PhP(CH_2CH_2PPh_2)_2]$ with sodium amalgam in the presence of C_6H_5R (R = H, Me, MeO).[930]

A major interest in these complexes has been their interaction with a proton, and the protonation of unsaturated hydrocarbon ligands has been reviewed.[99] In principal, the proton can attack at three points: the arene; equatorial or axial to the metal (Figure 50).[926]

In the protonation reaction, direct attack at the metal is preferred over initial attack at the arene, which is then followed by proton transfer to the metal if there is little steric congestion. Increasing the steric demand of the phosphine ligands leads to enhanced direct attack at the arene (see Scheme 43) for partitioning of metal versus arene attack by H^+.[926]

This partitioning has been studied theoretically, and sterically accessible frontier orbitals have been mapped. The data from this study showed that proton attack at the *exo*-position of the arene occurs at the same molecular orbital as direct proton attack at the metal center, so it just approaches the same orbital from a different direction.[927]

Treatment of $[Mo(PMe_3)_6]$ with 2,6-diphenylphenol at 70 °C afforded the π-bound arene complex $[Mo(PMe_3)_3\text{-}\{\eta^6\text{-}C_6H_5C_6H_3\text{–}(Ph)OH\}]$, which has been characterized by a single crystal X-ray diffraction study (Figure 51).[931] The most interesting feature of this structure is the hydrogen bond between the phenolic H and the metal-centered electron density: $d(Mo\cdots H) = 276(3)$pm, $d(Mo\cdots O) = 357.1(2)$pm, and Mo–H–O = 172(3)°. This complex subsequently undergoes O–H oxidative addition to the Mo center affording $[(\eta^6:\eta^1\text{-}C_6H_5\text{–}C_6H_3(Ph)O\}MoH(PMe_3)_3]$. DFT calculations show that this non-conventional hydrogen-bond interaction facilitates the oxidative addition. It also relates nicely to the protonation reactions of $[(\eta^6\text{-arene})MoP_3]$, studied in depth by Ashby's group, where protonation is expected to go equatorially.[927]



Ligand	Protonation	
	(%)	(%)
$(PPh_2CH_2)_3CMe$	0	100
$\{Ph_2P(CH_2)_2\}_2PPh$	80	20
$(PPh_2Me)_3$	0	100
$(PPhMe_2)_3$	20	80
$(PMe_3)_3$	40	60

Scheme 43 Relative percentages of protonation.

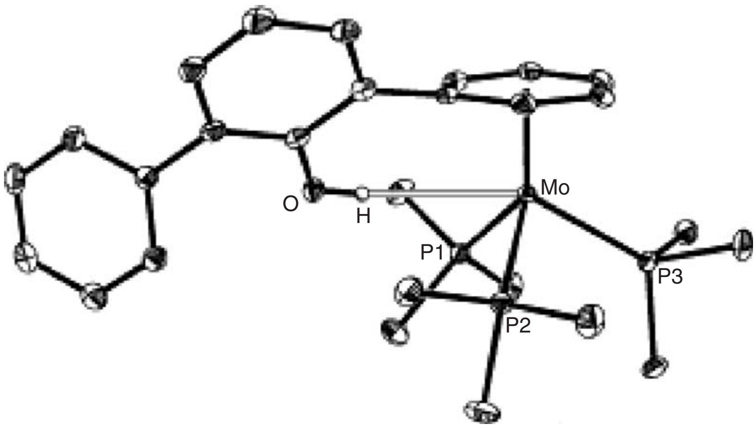
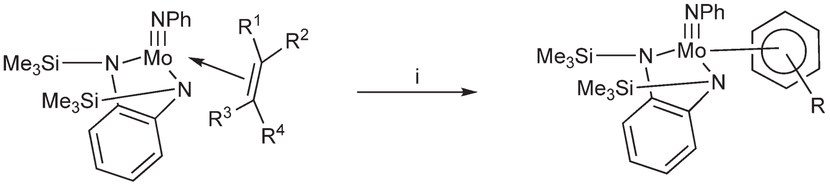


Figure 51 Molecular structure of [Mo(PMe$_3$)$_3${η^6-C$_6$H$_5$C$_6$H$_3$–(Ph)OH}]. Reproduced by permission of The Royal Society of Chemistry from Hascall, T.; Baik, M.-H.; Bridgewater, B. M.; Shin, J. H.; Churchill, D. G.; Friesner, R. A.; Parkin, G. *Chem. Commun.* **2002**, 2644–2645.

The reactivity of the dimeric [{Mo(μ-Cl)(η^3-CH$_2$CHCH$_2$)(η^6-arene)}$_2$] complexes toward heterodifunctional ligands has been described.[932,933] Unusual H/D exchange between methylene protons of an η^2-ketophosphine and D$_2$O was observed. These compounds were also found to catalytically hydrogenate alkenes at 15 psiH$_2$. Many of the complexes prepared were characterized by single crystal X-ray diffraction studies, and showed that the π-bound arene ring distorts significantly from planarity.

Of particular current interest is the preparation of the high oxidation state arene complexes [MoNPh{*o*-(Me$_3$SiN)$_2$C$_6$H$_4$}-(η^6-arene)] (arene = benzene, toluene, *o*-, *m*-, *p*-xylene, diphenylmethane, and bibenzyl) (Scheme 44).[448] The solid-state structures of [MoNPh{*o*-(Me$_3$SiN)$_2$C$_6$H$_4$}(η^6-*m*-xylene)] and [MoNPh{*o*-(Me$_3$SiN)$_2$C$_6$H$_4$}(η^6-*p*-xylene)] suggest that the arene binding is strongly distorted toward a 1,3-butadiene-like interaction with the metal center. For example, in [MoNPh{*o*-(Me$_3$SiN)$_2$C$_6$H$_4$}(η^6-*m*-xylene)], the six Mo–C bond lengths are 231.3(4), 242.5(4), 237.1(4), 228.6(4), 251.9(3), and 250.6(4) pm, respectively, where two are considerably longer than the others. The ring is also significantly puckered with C–C bond lengths around the ring consistent with distortion toward a 1,3-diene-like coordination mode of the π-bound arene ring. Treatment of the amido-containing complexes [MoNPh-{*o*-(Me$_3$SiN)$_2$C$_6$H$_4$}(CH$_2$CH$_2$)] and [MoNPh{*o*-(Me$_3$SiN)$_2$C$_6$H$_4$}(η^2-PhC$_2$Ph)] with trialkylaluminum reagents induced diamide transfer to aluminum and the formation of a π-bound arene complex (Scheme 45).[537] The solid-state structures again show that the π-bound arene distorts from planarity and tends toward 1,3-diene-like coordination to the molybdenum center.

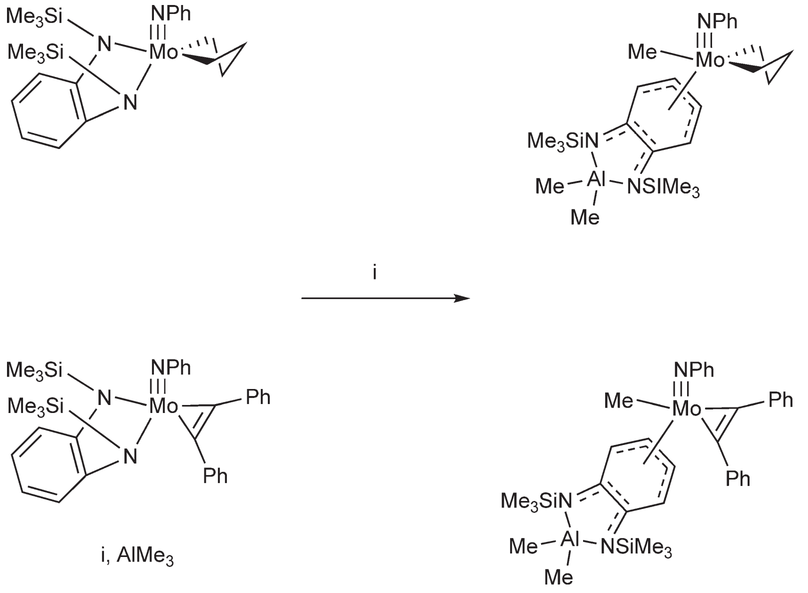


$R^1 = R^2 = R^3 = R^4 = Me$
$R^1 = R^2 = Me; R^3 = R^4 = H$
$R^1 = R^2 = R^3 = H; R^4 = Et$
$R^1 = R^3 = Me; R^2 = R^4 = H$

Ph–R = benzene, toluene, *o*-xylene, *m*-xylene *p*-xylene, diphenylmethane, bibenzyl

i, H$_2$ 15 psi; 15 equiv. arene

Scheme 44



i, AlMe$_3$

Scheme 45

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5.08
Tungsten Compounds with CO or Isocyanides

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5.08.1 Introduction

The field of tungsten compounds containing CO and/or isocyanide ligands is broad and diverse. It is an area of chemistry that has flourished over the past decade. As a consequence of the enormous volumes of materials published during 1993–2004 in this field, this work represents selective coverage of the area, while being as comprehensive as possible. This chapter covers developments over the period 1993–2004 and should be used in conjunction with COMC (1982) (Volume 3; sections 28.1 and 28.2) and COMC (1995) (Volume 5; chapters 3–8). An attempt has been made to avoid any unnecessary duplication of information from earlier editions.

Overall, the chapter is divided into sections based on the nature (donor types) of the non-CO/isocyanide ligands involved in the complexes. There is a significant difference in the set out of this chapter compared to COMC (1995), in particular how cyclopentadienyl complexes are dealt with. In COMC (1995), an entire chapter was devoted to cyclopentadienyl–group 6 metal complexes. The criteria for inclusion in that chapter were based on the sole requirement that the metal center was bound to a cyclopentadienyl ring and, as such, the chapter was further broken down into sections dealing with the presence of additional donor ligands. In general, the subjects in this chapter have been divided based first on non-carbon donor types and then second on the uniqueness of the carbon donor ligands. As a result of the ubiquitous nature of cyclopentadienyl ligands in the chemistry of W–CO complexes, examples are discussed throughout this chapter. Complexes that contain two or more types of ligands (other than CO and CNR) are classified case by case, based on the ligand of most interest or the type of chemistry under discussion. Subsections are based on bonding characteristics (σ-donor; σ-donor/π-acceptor; π-donor) and/or hapticity. In some cases, classifications based on hapticity may follow the number of donor atoms in a particular functional group of interest rather than in the ligand as a whole. Complexes containing metal–metal bonds are categorized based on their ligands and not in a discrete section of their own. Though relevant references are provided throughout this chapter, no in-depth discussion about cluster chemistry is given.

An effort has been made to avoid repetition of information between the chapter sections except where it has been deemed necessary. In general, but particularly for cyclopentadienyl complexes, it is best to regard this chapter in its entirety and not in its parts.

5.08.2 Complexes Containing Only CO and/or Isocyanide Ligands

Many of the fundamental details associated with compounds related to this area, in particular, related to $[W(CO)_6]$, are covered in detail in COMC (1982) and COMC (1995). Every endeavor has been made to cover the latest developments in this area. Where applicable, the subheadings have been chosen to be consistent with earlier editions.

5.08.2.1 Tungsten Hexacarbonyl

5.08.2.1.1 Theoretical and spectroscopic studies of $[W(CO)_6]$

Theoretical studies have examined the W–CO bond and the bond-dissociation energies for the dissociation of one CO from $[W(CO)_6]$ as well as the geometries for $[W(CO)_6]$.[1–14] These studies have used a variety of density functional theory (DFT), Hartree–Fock (HF) theory, Møller–Plesset second-order perturbation theory (MP2) and coupled-clusters (CC) approaches. Force constants and vibrational frequencies for $[W(CO)_6]$ have been calculated using DFT.[10,11,13–16] Comparisons have been made between HF theory, DFT, and MP2 for the calculation of molecular geometries, vibrational frequencies, and bond-dissociation energies for $[W(CO)_6]$.[3] A DFT approach proved superior to HF and MP2 methods in terms of result reliability and computational cost. Theoretical studies have calculated ^{13}C and ^{183}W NMR chemical shifts for $[W(CO)_6]$.[10,17]

Spectroscopic studies have been performed on $[W(CO)_6]$ in the gas phase[18–20] as well as in various liquid, supercritical fluid, and glass matrices. Infrared laser jet spectroscopy has been used to probe the rotational structure and octahedral splitting of the ν_6 fundamental band of $[W(CO)_6]$,[19] and also to investigate the nature of the rare gas-$[W(CO)_6]$ complexes Ar·$[W(CO)_6]$, Kr·$[W(CO)_6]$, and Xe·$[W(CO)_6]$.[18] The vibrational dynamics of $[W(CO)_6]$ in the gas phase has been examined using infrared pump-probe experiments,[20] while infrared photon echo experiments have been used to probe the vibrational dynamics of $[W(CO)_6]$ in 2-methyltetrahydrofuran, 2-methylpentane, and dibutyl phthalate glasses.[21] Vibrational lifetimes and vibrational line positions for the asymmetric CO-stretching mode of $[W(CO)_6]$ in supercritical fluids near the critical point have been investigated using picosecond infrared pump-probe experiments, and a theoretical study indicated that clustering of the solvent around the solute was not required to explain the data.[22,23] The experimental results were also interpreted using a microscopic statistical mechanical theory.[24]

W–C and W–O distances in $[W(CO)_6]$ at room temperature have been determined by extended X-ray fine absorption structure (EXAFS), and the results (W–C 2.05 Å, W–O 3.19 Å) were in good agreement with values obtained previously by X-ray and electron diffraction (W–C 2.026 Å, W–O 3.172 Å).[25]

5.08.2.1.2 Photolysis of $[W(CO)_6]$ and CO dissociation

Photolysis-induced CO dissociation from $[W(CO)_6]$ has been widely studied. Techniques used in the various studies have included picosecond transient absorption spectroscopy,[26] time-resolved IR absorption spectroscopy,[27–29] time-of-flight and quadruprole mass spectrometry,[30–32] and femtosecond-IR and -mid-IR techniques.[33–35] Studies involving ultrafast photodissociation of $[W(CO)_6]$ suggest a mechanism for CO dissociation, more complex than the traditional textbook mechanisms.[36] Studies have included investigations into vibrational relaxation rates of the photoproducts, that is, $[W(CO)_5 \cdot S]$ formed from the association of the original dissociation product $[W(CO)_5]$ with solvent.[26] In solution studies, it has been shown that after excitation of $[W(CO)_6]$, CO and $[W(CO)_5]$ were found to dissociate in <1 ps, and it took ca. 3 ps for the $[W(CO)_5]$ to associate with a molecule of cyclohexane, the solvent in this case.[26] In the gas phase, photolysis of $[W(CO)_6]$ with a 355 nm laser yields the unsaturated $[W(CO)_5]$, which in the presence of benzene forms $[W(CO)_5(\eta^2\text{-}C_6H_6)]$.[29] With a 266 nm pulsed laser, photolysis of $[W(CO)_6]$ leads predominantly to $[W(CO)_4]$ with smaller quantities of $[W(CO)_5]$.[27,29] When $[W(CO)_4]$ is formed, in the presence of benzene $[W(CO)_4(\eta^2\text{-}C_6H_6)]$ is formed;[29] however in the presence of C_2H_4 reaction leads initially to $[W(CO)_4(\eta^2\text{-}C_2H_4)]$ and subsequently $[\textit{cis}\text{-}W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ is formed.[27] In the absence of other ligands both $[W(CO)_5]$ and $[W(CO)_4]$ react with the parent $[W(CO)_6]$ to form polynuclear species.[27,29] In the presence of alkynes, the photolysis of matrix-isolated $[W(CO)_6]$ can lead to a variety of complexes including $[W(CO)_5(\eta^2\text{-}RC{\equiv}CR)]$, and if the alkynes are terminal then vinylidene complexes $[R(H)C{=}C{=}W(CO)_5]$ can also form along with a number of other species.[37] Photolysis of $[W(CO)_6]$ in supercritical Xe, Kr, Ar, and CO_2, in the presence of CO, yields the pentacarbonyl adducts $[W(CO)_5L]$ (L = Xe, Kr, Ar, and CO_2), the formation of which is reversible.[28] The reactivity of the complexes $[W(CO)_5L]$ (L = Xe, Kr, Ar, and CO_2) with CO is in the order: $[W(CO)_5Ar] > [W(CO)_5Kr] > [W(CO)_5Xe] \approx [W(CO)_5(CO_2)]$. For the series $[W(CO)_5Ar]$, $[W(CO)_5Kr]$, and $[W(CO)_5Xe]$, the trend in reactivity is in line with calculated W–L bond energies (L = Xe, Kr, Ar).[38]

Laser photolysis of $[W(CO)_6]$ in cyclohexane (CyH) solution produces $[W(CO)_5(CyH)]$, and displacement of the coordinated CyH by thiophene, tetrahydrothiophene, pyrrole, and pyrrolidine has been investigated by time-resolved infrared spectroscopy.[39,40] The geometries and bonding energies of $[W(CO)_5L]$ (L = $C_{1\text{–}3}$ alkanes and fluoromethanes) have been calculated using *ab initio* methods.[41] In general, the lowest energy geometry found for alkane complexes involved η^2-agostic W/C–H interaction, but the existence of several structures (η^2 or η^3) with just slightly higher energies suggested that the complexes would be fluxional.

Photolysis of $[W(CO)_6]$ in a polyethylene matrix, in the presence of N_2 or H_2, leads to the formation of $[W(CO)_5(N_2)]$ and $[\textit{cis}\text{-}W(CO)_4(N_2)_2]$ or $[W(CO)_5(\eta^2\text{-}H_2)]$ and $[\textit{cis}\text{-}W(CO)_4(\eta^2\text{-}H_2)_2]$.[42] Vacuum UV photoionization/MS studies on $[W(CO)_6]$ have been used to investigate photoionization efficiency spectra for a range of charged ions produced from photodissociation.[31,32] Unsaturated $[W(CO)_n]$ ($n < 6$) species, from the laser pyrolysis of $[W(CO)_6]$ in the gas phase, have been shown to be effective abstractors of O or Cl atoms when such species are formed in the presence of chlorinated or oxygenated organic compounds.[43,44] Using femtosecond IR methods, the photolysis of $[W(CO)_6]$ in neat Et_3SiH has been studied.[34] The coordinatively unsaturated $[W(CO)_5]$, initially generated, is quickly (<2 ps) solvated by the C–H bonds in the solvent. Rearrangement of this solvated species yields a silyl hydride product.[34] It should be noted that laser-ablated W atoms react with CO in excess Ne to give many of the same unsaturated $[W(CO)_n]$ ($n = 3$, 4, and 5) species observed from photodissociation of $[W(CO)_6]$.[45] Photolysis of $[W(CO)_6]$ in CCl_4 or CBr_4 has yielded *in situ* catalytically active species for aldol-type condensations and metathesis polymerizations.[46,47] The photolysis product of $[W(CO)_6]$ in THF, $[W(CO)_5(THF)]$, is active in the Pauson–Khand cyclization reaction.[48]

5.08.2.1.3 Studies of solid-supported $[W(CO)_6]$

$[W(CO)_6]$ has mainly been supported on alumina[49,50] and zeolite materials,[51,52] and the chemistry of $[W(CO)_6]$ in the void spaces of zeolites has been reviewed.[53] $[W(CO)_6]$ has also been immobilized in organosilica-based xerogels[54] and on TiO_2.[55] Deposition methods have included gas-phase techniques, where the supports were exposed to $[W(CO)_6]$ vapor.[49–52,56] Tungsten carbonyl species, containing *mer*-$W(CO)_3$ and *cis*-$W(CO)_2$ structures, immobilized on a silica support, have been prepared by UV photoreduction of silica-supported W(VI) in a CO atmosphere.[57] Thermal decomposition of supported $[W(CO)_6]$ leads initially to $W(CO)_3$(ads) species.[52,56] Further decomposition results in the loss of the remaining CO ligands and yields supported W(0) materials that have catalysis applications in hydrodesulfurization,[58] and have also been used in the synthesis of polymeric and low molecular weight phthalocyanines.[55]

A variety of techniques have been used to study $[W(CO)_6]$ deposited on alumina and zeolite supports. These include diffuse reflectance IR Fourier transform (DRIFT) spectroscopy,[50] attenuated total reflection (ATR) Fourier transform infrared (FTIR), and Raman spectroscopies.[51] Transmission FTIR has also been used to characterize tungsten carbonyl species on silica and zeolite supports.[52,57] The vibrational dynamics of CO stretching in $[W(CO)_6]$-doped xerogels have been examined with a free-electron laser (FEL) source.[54]

Theoretical studies have also examined solid-supported $[W(CO)_6]$. These include Monte Carlo simulations of $[W(CO)_6]$ encapsulated in a zeolite[51] as well as studies into the interactions of $[W(CO)_6]$ with surface sites on alumina.[59]

5.08.2.2 Charged Tungsten Carbonyl Complexes

COMC (1982) and COMC (1995) have comprehensive details on the synthesis and reactions of charged tungsten complexes bearing only carbonyl ligands.

Photolysis of $[W_2(CO)_{10}]^{2-}$ in MeCN or THF results in the formation of the $[W(CO)_5]^{-\cdot}$ radical, and radical–radical recombination yields $[W_2(CO)_{10}]^{2-}$.[60] The radical, which has been studied by transient absorption spectroscopy in the IR and UV-VIS regions, rapidly forms a 19e$^-$ $[(solvent)W(CO)_5]^{-\cdot}$ radical in THF or MeCN.[60] These 19e$^-$ radicals are extremely strong reducing agents.

The electronic structure and geometry of $[W(CO)_n]^+$ ($n = 1$–6) have been studied theoretically at *ab initio* and B3KYP levels, and the results compared with available experimental data.[61] Agreement between experimental and calculated W–CO bond-dissociation energies varied between fair and poor.

5.08.2.3 Tungsten Carbonyl Complexes Containing Isocyanide Ligands

5.08.2.3.1 Synthesis

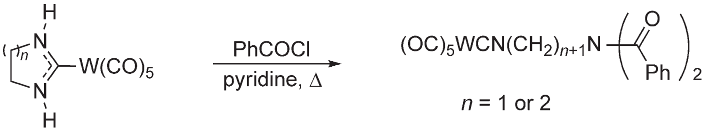
Most complexes of the form $[W(CO)_n(CNR)_{6-n}]$ are prepared by reaction of the appropriate isocyanide with $[W(CO)_6]$, $[W(CO)_5(THF)]$, $[W(CO)_3(TolH)]$, $[W(CO)_3(MeCN)_3]$, etc. Some recent examples are summarized in Table 1 (see COMC(1982) and COMC(1995) for coverage of earlier literature on this and a few other methods).

Reaction of $[W(CO)_6]$ with the phosphinimine $Ph_3P{=}N(CH_2)_3PPh_2$ results in deoxygenation of a CO group and formation of the isocyanide complex $[(CO)_5WCN(CH_2)_3PPh_2]$.[70] Other routes to tungsten isocyanide complexes include reduction of $[W(OAr)_2Cl_4]$ in the presence of an isocyanide (Equation (1)),[71] reaction of $[W(CO)_5CN]^-$ with a cationic carbyne complex (Equation (2)),[72] acylation of diaminocarbene (imidazolinylidene) complexes (Equation (3)),[73,74] and reaction of $[W(CO)_5THF]$ with lithiated benzoxazole followed by Cp_2TiCl_2 (Equation (4)).[75]

$$[W(OAr)_2Cl_4] \xrightarrow[CNR]{4Na/Hg} [W(CNR)_6] + [W(OAr)_2(CNR)_4] \qquad (1)$$

$$ArO = OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5$$
$$CNR = CNC_6H_3Me_2\text{-}2,6$$

(2)



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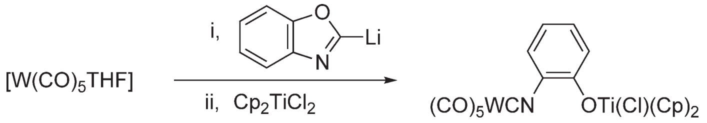

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Table 1 Examples of tungsten isocyanide complexes containing CO ligands

Complexes	*Synthesis*	*Comments*	*References*
$[W(CO)_5CNR]$	$[W(CO)_6] + CNR$	R = alkyl; PdO catalyst	62
$[W(CO)_5CNR]$, $[W(CO)_4(CNR)_2]$	$[W(CO)_6] + CNR$	R = *p*-$C_6H_4NO_2$; $CoCl_2{\cdot}2H_2O$ catalyst	63
$[W(CO)_5CNR]$	$[W(CO)_5THF] + CNR$	R = *o*-C_6H_4–N_3, *o*-C_6H_4–$OSiMe_3$, *o*-C_6H_4–NO_2	64–66
$[W(CO)_5CNR]$	$[W(CO)_5I][NEt_4] + CNR$	R = *o*-C_6H_4–CH_2OSiMe_3	67
mer-$[W(CO)_3(CNC_6F_5)_3]$	$[W(CO)_3(TolH)] + CNR$		68
fac-$[W(CO)_3(CNR)_3]$	$[W(CO)_3(TolH)] + CNR$	R = $C_6H_2Pr^i{}_2$-2,6-X-4; X = I, C≡CH, C≡Cpy-4	69
cis-$[W(CO)_4(CNR)_2]$	$[W(CO)_3(MeCN)_3] + CNR$	R = $C_6H_2Pr^i{}_2$-2,6-C≡Cpy-4 Additional CO presumably from decomposition of some $[W(CO)_3(MeCN)_3]$	69

5.08.2.3.2 Structural and spectroscopic characterization

^{13}C NMR and IR spectra are the most commonly used spectroscopic tools for the characterization of tungsten complexes having CO and/or isocyanide ligands, and a number of complexes have also been characterized by X-ray methods; representative literature data are summarized in Table 2. In the ^{13}C NMR spectrum, the isocyanide W–C signal typically occurs in the region δ145–180, whereas the W–CO signal occurs further downfield, δ190–200. Satellites due to ^{183}W–^{13}C coupling are rarely detected due to the low intensity of the CO and isocyanide signals in the ^{13}C spectrum.

5.08.2.3.3 Applications

The pentacarbonyl isocyanides [W(CO)$_5$(CNR)] (R = *n*-pentyl and 1-methylbutyl) are useful precursors for chemical vapor deposition (CVD) of tungsten oxide films at atmospheric pressure.[62] At room temperature the complexes are liquid and show little reactivity to air and water, but show sufficient volatility and reactivity toward oxygen at 200–300 °C for CVD applications. [W(CO)$_5$(CNR)] (R = *n*-pentyl) has also been used in plasma-assisted CVD of tungsten oxide films.[77]

The monoisocyanide complex [W(CO)$_5$(CNC$_6$H$_4$-*p*-NO$_2$)] is an effective catalyst for the distannation of alkynes[63,78]

When subjected to attack by nucleophiles at the isocyanide carbon, certain tungsten isocyanide complexes are converted into tungsten carbene complexes. See Section 5.08.15.6.1.

5.08.3 Nitrogen Ligands

This section is divided in a manner to be consistent with COMC (1995), the two main divisions being σ-donor ligands and π-acceptor ligands.

Table 2 ^{13}C NMR, IR, and structural properties of representative tungsten isocyanide complexes

Compound	δ_C (WC)(J_{WC})[a]	*IR* (cm^{-1})	*Bond distances* (Å)	*References*
[W(CNR)$_6$] R = 2,6-Me$_2$C$_6$H$_3$	179.9 (CN); (123)	ν_{CN} 1940	W–CN 2.048–2.057	71
[(CO)$_5$WCN-*o*-C$_6$H$_4$NO$_2$]	163.2 (CN); 193.3 (*cis*), 195.4 (*trans*) (CO)	ν_{CN} 2134; ν_{CO} 2044, 1995(sh), 1928	W–CN 2.073 W–CO 2.036–2.073 (*cis*), 2.038 (*trans*)	65
[(CO)$_5$WCN-*o*-C$_6$H$_4$OTi(Cl)Cp$_2$]	178.0 (CN); 194.4 (*cis*), 196.3 (*trans*) (CO)	ν_{CN} 2145; ν_{CO} 2060, 1998, 1947	–	75
[(CO)$_5$WCN–(CH$_2$)$_2$PPh$_2$]	145.6 (CN); 195.8, 194.0 (CO)	ν_{CN} 2174; ν_{CO} 2068, 1948	W–CN 2.08 W–CO 1.93–2.08 (*cis*), 1.97 (*trans*)	73
[(CO)$_5$WCN–(CH$_2$)$_3$-N(COPh)$_2$]	143.0 (CN); 196.1, 194.3 (CO)	ν_{CN} 2175; ν_{CO} 2068, 1956		76
cis-[(CO)$_4$W(CNR)$_2$] R = C$_6$H$_2$Pr$^i{}_2$-2,6-C≡Cpy-4	198.7, 196.0 (CO)	ν_{CN} 2135, 2073; ν_{CO} 2008, 1940, 1929	W–CN 2.113, 2.116 W–CO 2.026, 2.049 (*cis* to both CNR), 2.000, 2.004 (*trans* to one CNR)	69
fac-[(CO)$_3$W(CNR)$_3$] R = C$_6$H$_2$Pr$^i{}_2$-2,6-I-4	165.6 (CN); 201.4 (CO)	ν_{CN} 2131, 2058; ν_{CO} 1942, 1900	–	69
mer-[(CO)$_3$W(CNC$_6$F$_5$)$_3$]	–	–	W–CN 2.064 (×2, mutually *trans*), 2.050 (*trans* to CO) W–CO 2.025 (*trans* to CNR), 2.042 (×2, mutually *trans*); Twofold crystallographic symmetry	68

[a] ^{13}C NMR, δ in ppm; J_{WC} in Hz in parentheses.

5.08.3.1 σ-Donor Nitrogen Ligands

Complexes containing sp^3-nitrogen donor amines, amides, imines (except 1,4-diimines, which will be covered in Section 5.08.3.2), diazenes, nitriles, and inorganic nitrogen-based ligands are reviewed in Section 5.08.3.1.

5.08.3.1.1 Synthesis

The synthetic methods for the preparation of W–CO or W–CNR complexes bearing nitrogen donor ligands have not markedly changed since they were reviewed in COMC (1995).[79] Typical methods include:

(i) thermally or photochemically promoted substitution of $[\mathrm{W(CO)_6}]$;
(ii) ligand exchange with labile W(0) precursors such as $[\mathrm{W(CO)_5(THF)}]$, $[\mathrm{W(CO)_3(NCR)_3}]$ (R = Me, Et, Pr), $[\mathrm{W(CO)_3(chpt)}]$, $[\mathrm{W(CO)_4(pip)_2}]$ (pip = piperidine), or W(II) sources such as $[\mathrm{W(CO)_3(NCMe)_2I_2}]$, or more complex precursors.

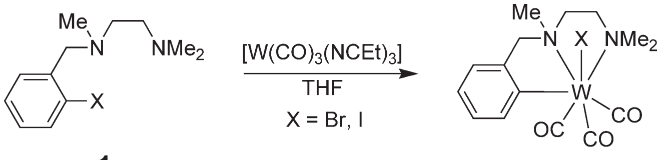
Examples of recently prepared amine, amide, imine, nitrile, and cyanide complexes are listed in Table 3. In addition to the above methods, alternative synthetic procedures include the use of microwaves to prepare complexes such as *cis*-$[\mathrm{W(CO)_4(pip)_2}]$ and $[\mathrm{W(CO)_4(en)}]$,[80,81] and the use of hydroxylamine as an alternative to the commonly used trimethylamine-*N*-oxide in the oxidative decarbonylation of $[\mathrm{W(CO)_6}]$, which forms the labile $[\mathrm{W(CO)_5(NH_3)}]$ and $\mathrm{CO_2}$.[82]

The reaction of the diamine **1** with $[\mathrm{W(CO)_3(NCEt)_3}]$ results in the substitution and oxidative addition product **2** (Equation (5)).[83] The addition of primary amines to the coordinated alkyne of $[\mathrm{W(CO)_2(HC{\equiv}CPh)Tp'}]^+$ [Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate] results in the formation of amido complexes $[\mathrm{W(CO)_2\{N(R)\text{-}CH{=}CHPh\}Tp'}]$ (R = Ph, $\mathrm{Bu^t}$, Bn),[84] while the reaction of primary amines with the coordinatively unsaturated $[\mathrm{W(CO)_2I(Tp')}]$ yields the amido complexes $[\mathrm{W(CO)_2(NHR)Tp'}]$ (R = H, $\mathrm{Bu^n}$, Ph).[85] Reduction of the triamidoamine complex **3** in the presence of CO or CNAr yields the corresponding neutral CO and CNAr complexes (Equation (6)).[86] Hydrazine can displace a weakly bound triflate ligand in $[\mathrm{W(CO)_2(PPh_3)_2(NO)(OTf)}]$ to form a hydrazine complex, and subsequent oxidation of the coordinated hydrazine yields a diazene complex **4** (Equation (7)).[87]

Table 3 Examples of W–CO and W–CNR complexes with σ-donor nitrogen ligands

Complex[a]	*Synthesis*[b]	*Comments*	*W–N*$_{av}$ (Å)	*References*
Amines				
$[\mathrm{W(CO)_5(H\overline{NCH_2C}Me_2)}]$	(i)		2.31	88
$[\mathrm{W(CO)_4(\eta^2\text{-}O_2CCHRNH_2\text{-}}N,O)]^-$	(ii)	R = H, $\mathrm{Bu^t}$	2.32	89,90
$[\mathrm{W(CO)_3(\mathbf{5})}]$	(i) or (ii)	Serves as a labile *fac*-$\mathrm{W(CO)_3}$ source if R = Me	2.33	91–93
$[\mathrm{W(CO)_3(\mathbf{6})}]$	(i)	R = $\mathrm{Pr^i}$		94
$[\mathrm{W(CO)_2({\equiv}CPh)(\mathbf{6})}]^+$	(ii)	R = Me	2.28	95
Amides				
$[\mathrm{W(CO)_3(}o\text{-}\mathrm{NHC_6H_4X\text{-}}N,X)]^{2-}$	(ii)	X = S, O, NH	2.10	96, 97
$[\mathrm{W(CO)_5(\mathbf{7})}]^-$	(ii)		2.28	98
$[\mathrm{W(CO)_5\{N(SiMe_3)_2\}}]^-$				99
Imines				
$[\mathrm{W(CO)_4(}\mu\text{-}\mathbf{8})\mathrm{W(CO)_4}]^{2-}$	(ii)	*N,O* chelate	2.22	100
mer-$[\mathrm{W(CO)_3(\mathbf{9})}]$	(ii)	*P,N,P′* chelate		101
Nitriles				
$[\mathrm{W(CO)_3(NCR)_2I_2}]$	(ii)	R = Et, $\mathrm{Bu^t}$, Bn, Ph, $\mathrm{CH_2}$(3-thiophene)	2.19	102–104
$[\mathrm{W(CO)(\eta^2\text{-}NCR\text{-}}N,C)\mathrm{I(Tp')}]$		R = Me, Et, Ph; 4e$^-$ donor RCN		105
Inorganic cyanide derivatives				
$[\mathrm{W(CO)Cp_2(\mu\text{-}NC)Mo(CO)_5}]^+$		Bridging $\mathrm{CN^-}$	2.10	106
$[\mathrm{W(CO)_3(NCBH_3)_3}]^{3-}$	(i) or (ii)	$[\mathrm{W(CO)_3(NCMe)_3}]$ + $\mathrm{NaBH_3CN}$	2.215	107
$[\mathrm{W(CO)_5(NCX)}]^-$		X = S, O		99

[a] Some ligand structures are shown below.
[b] See text for synthetic method.



1 **2**

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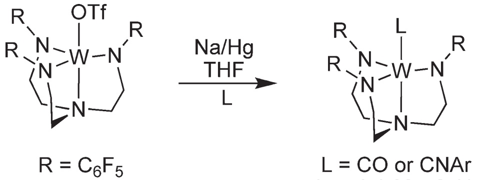

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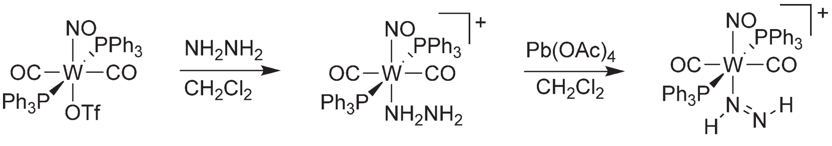

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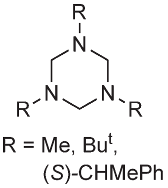

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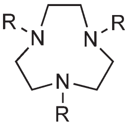

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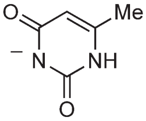

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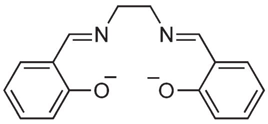

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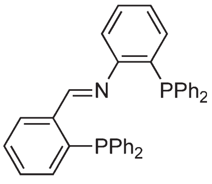

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5.08.3.1.2 Structure and properties

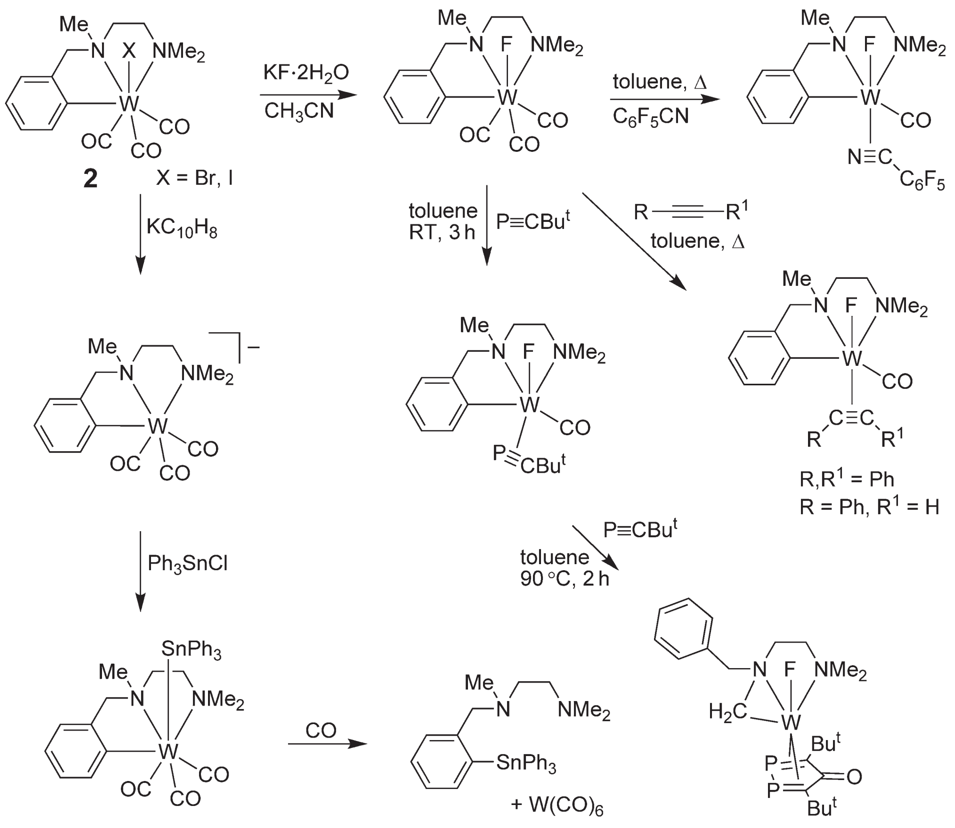
A number of studies examining specific properties, such as IR CO stretching frequencies, ^{13}C NMR chemical shifts, dipole moments and photochemistry, of simple amine–W–CO complexes including *cis*-[W(CO)$_4$(pip)$_2$],[108] [W(CO)$_4$(en)],[109] and [W(CO)$_5$(NMe$_3$)][110] have been undertaken. Examples of W–N$_{av}$ bond distances are listed in Table 3. The modes of complexation of cyclic and linear polyamines with [W(CO)$_6$] have also been investigated.[111,112]

Triazacyclohexane **5** complexes exhibit much smaller N–M–N angles than similar triazacyclononane **6** complexes {59.8° for [W(CO)$_3$(**5**)] (R = Bu^t)[91] versus 76.9° for [Mo(CO)$_3$(**6**) (R = Pr^i)[94]}. The small angles and exposed W(CO)$_3$ fragment in [W(CO)$_3$(**5**)] (R = Me) account for the labile nature of the triazacyclohexane ligand (see reactions in Section 5.08.3.1.1).[91] The complex undergoes rapid solvolysis in dimethyl sulfoxide (DMSO), with displacement of **5**, and is air sensitive. The analogous triazacyclononane complex [W(CO)$_3$(**6**)] (R = Me) is air stable.[113] However, increasing the steric bulk of R on **5**, which shields the W(CO)$_3$ fragment, significantly increases the stability of the complexes; [W(CO)$_3$(**5**)] (R = Bu^t) does not undergo solvolysis in DMSO and is air stable indefinitely.[91] Enthalpies of protonation for a range of [W(CO)$_3$(L-*N*,*X*,*X*)] (*X* = S, P, N) complexes (where L represents a tridentate ligand) including [W(CO)$_3$(**6**)] (R = Me) have been reported.[114] The complex [W(CO)$_3$**6**] {R = CH$_2$C$_6$H$_3$-3,4-(OC$_{10}$H$_{21}$)$_2$} exhibits mesomorphic behavior.[115]

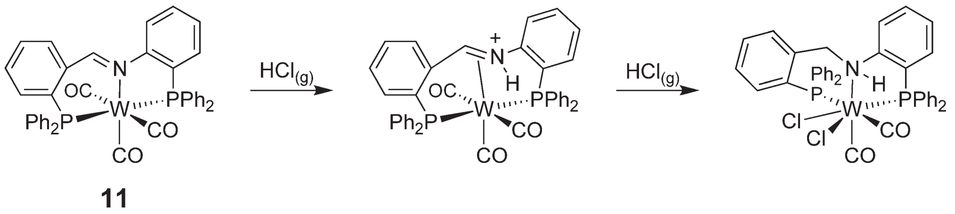
[W(CO)$_3$(NCMe)$_2$I$_2$] exhibits catalytic activity for the polymerization of acetylenes and norbornene.[116,117] Both cyanide-[99,106,118,119] and nitrile-containing species[120,121] are used as bridging ligands in the formation of bimetallic complexes, and in some cases such complexes have been studied for their nonlinear optical (NLO) properties.

5.08.3.1.3 Reactions

Examples of the reactivity of the chelate W(CO)$_3$ complex **2** are summarized in Scheme 1.[83,122,123] The highly fluorinated imine derivative of **2**, **10**, exhibits some similar chemistries; however with electron-deficient alkynes

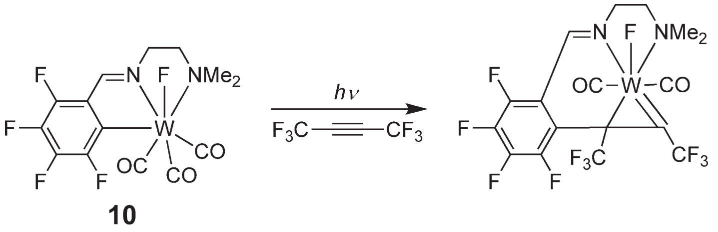


Scheme 1



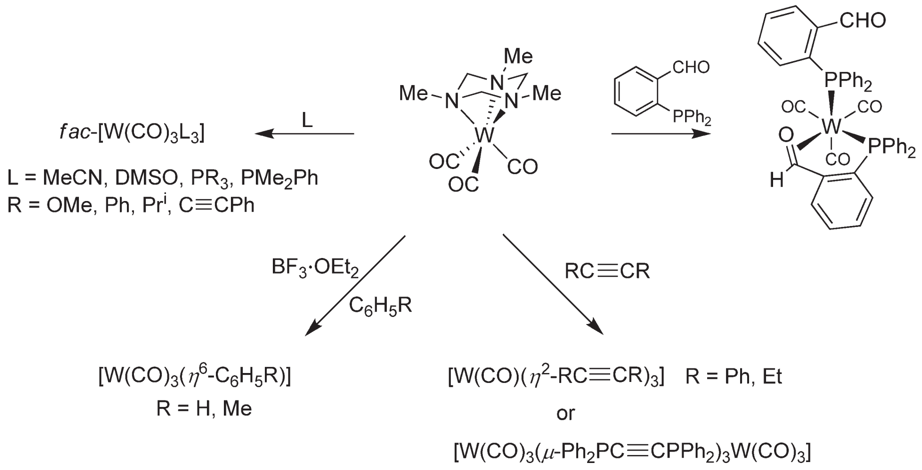
Scheme 2

insertion reactions can occur (Equation (8)).[123–127] Reaction of the imine complex **11** with $HCl_{(g)}$ gives an amine complex, via a stable π-bound iminium intermediate (Scheme 2).[128]

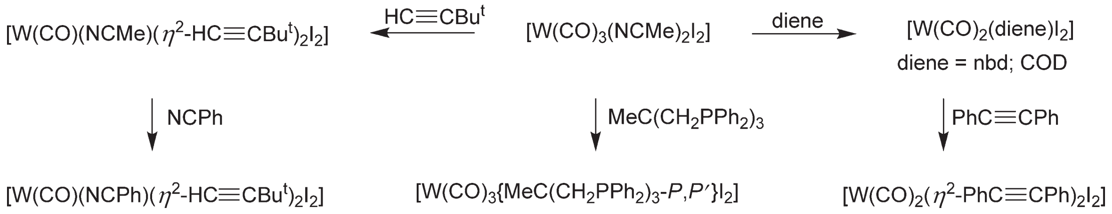


(8)

The oxidation chemistry of the triazacyclohexane complex $[W(CO)_3(\mathbf{5})]$ (R = Bu^t) parallels that of the triazacyclononane complexes $[W(CO)_3(\mathbf{6})]$, which was covered in COMC (1995).[129] Reaction of $[W(CO)_3(\mathbf{5})]$ (R = Bu^t) with Br_2 or I_2, CF_3SO_3H, or H_2O_2 affords $[W(CO)_3(\mathbf{5})X]^+$ (X = Br or I), $[W(CO)_3(\mathbf{5})H]^+$, and $[W(\mathbf{5})O_3]$, respectively.[130] The



Scheme 3



Scheme 4

most significant difference in reactivity between $W(CO)_3$ complexes of triazacyclohexanes and triazacyclononanes is the ease of which the triazacyclohexane ligand can be displaced from $[W(CO)_3(\mathbf{5})]$ when R = Me. As a consequence, $[W(CO)_3(\mathbf{5})]$ (R = Me) is a facile source of the *fac*-$W(CO)_3$ fragment (Scheme 3).[91,92,131–133]

The $W(CO)_3$ fragment can be used as a protecting group in the ω-mono *N*-alkylation of linear polyamines.[134] Amines, amides, and nitriles coordinated to a W–CO center can undergo a range of reactions including protonation, deprotonation, oxidation, reduction, and addition of nucleophiles resulting in the formation of various amine, amido, imine, nitrile, azavinylidene, and imido complexes. In the cases involving complexes with the Tp′W(CO) fragment, these have been recently reviewed (see Section 5.08.3.2.3.(i), Schemes 11 and 12).[135,136] In particular, coordinated acetonitrile can be oxidized to form acylimido complexes, coupled to form diiminobutane complexes or methylated to form iminoacyl complexes.[137–139]

The halocarbonyl complexes $[W(CO)_3(NCMe)_2X_2]$ (X = Br, I), but, in particular, the iodo complex, are extremely versatile starting materials, and have been used to prepare an immense range of W–CO complexes bearing numerous donor types, including arenes and alkynes, nitrogen-, phosphorus-, oxygen-, sulfur-, and arsenic-donor ligands. This area has been reviewed thoroughly;[140–142] recent examples are included in Scheme 4.[143–146]

5.08.3.2 π-Acceptor Nitrogen Ligands

This section includes complexes of *N*-heterocyclic, nitrene (bent) and imido (linear), and dinitrogen and nitrosyl ligands. While some of the ligands detailed in this section may be only weak π-acceptor ligands, for convenience and ease of comparison they are all grouped in this section (see COMC (1995)[147]). Within this class of compounds, complexes of tris(pyrazolyl)borates constitute one of the biggest subsets. Due to the presence of other donor types in many complexes bearing this ligand type, the chemistry of complexes bearing a tris(pyrazolyl)borate ligand is also covered in other sections in this chapter. Relevant and representative examples will be included in this section.

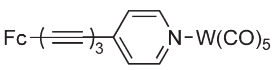
5.08.3.2.1 Synthesis

5.08.3.2.1.(i) 1,4-Diimines and heterocyclic ligands

Complexes of *N*-heterocyclic ligands represent the largest grouping within the N-donor ligands. The synthesis of W–CO complexes within this class invariably involves thermal substitution of [W(CO)$_6$]. Examples of complexes involving more unique ligands, useful synthetic pathways, or representative examples of the field are detailed in Table 4. Recent reviews include the coordination chemistry of oxazoline ligands,[148] complexes with bis(pyrazolyl)-alkane-based ligands,[149,150] and the coordination chemistry of tris(pyrazolyl)methane ligands.[151,152]

Oligomers such as [W(CO)$_5$(μ-4,4′-bipy)Mo(CO)$_4$(μ-4,4′-bipy)Mo(CO)$_4$(μ-4,4′-bipy)W(CO)$_5$] can be prepared by a sequence of photochemical substitution reactions.[153] Reaction of 2,2′-pyridyl diselenide or disulfide (2,2′-pySeSepy or 2,2′-pySSpy) with W(0)–CO sources yields the W(II) pyridyl complexes [W(CO)$_3$(2-Xpy-*N*,*X*)$_2$] (X = Se or S).[154,155] The similar complex [W(CO)$_3$(2-Spym-*N*,*S*)$_2$] (pym = pyrimidine) is prepared by the reaction of K[2-Spym] with the W(II) source [W(CO)$_3$(NCMe)$_2$I$_2$].[156] Reaction of the aminotroponimine **12** with [W(CO)$_3$(NCMe)$_3$] yields a diimine complex where the ligand has tautomerized, and subsequent reaction with KH affords the charged complex **13** (Scheme 5).[157]

The reaction of [W(CO)$_4$(≡CR)Br] (R = *p*-Tol) with elemental sulfur and then K[Tp] yields the dithiocarboxylate complex [W(CO)$_2$Tp(η^2-S$_2$CR)]; however the analogous reaction with K[H$_2$B(pz)$_2$] yields a bis(pyrazolyl)thiolatoborate complex (Scheme 6).[158] Organotin-modified bis(pyrazolyl)methanes react with [W(CO)$_5$(THF)] to produce a range of products, depending on the substituents on the Sn center or the pyrazolyl rings (Scheme 7).[159]



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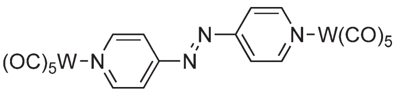

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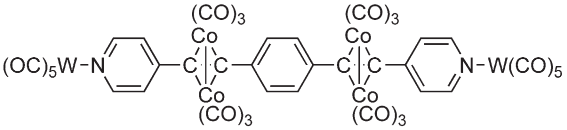

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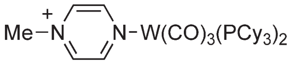

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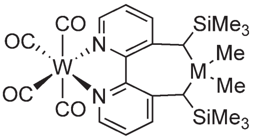

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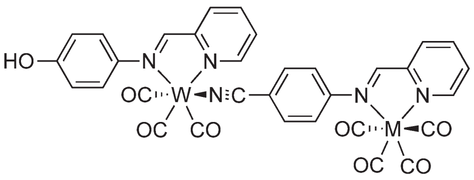

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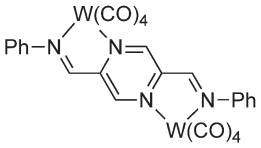

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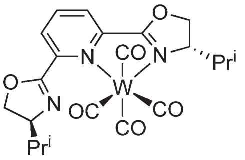

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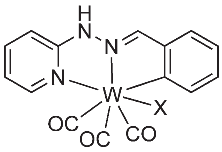

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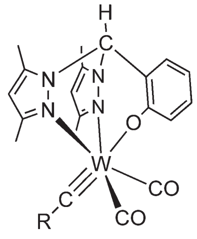


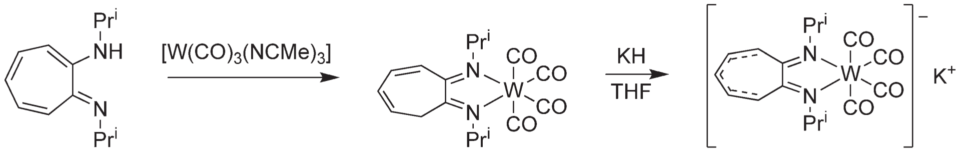
23

5.08.3.2.1.(ii) Nitrene and imido complexes

To be consistent with COMC (1995), the term "nitrene" is used to indicate the bent M═NR species while "imido" indicates the linear M≡NR species. The field of imido metal complexes has been recently reviewed.[186] The zwitterionic amido complex **24** acts as a protected zerovalent imido precursor.[187,188] Oxidation of **24** yields the highly versatile W(IV) imido dimers **25** (Scheme 8).[189–191] A range of substitution reactions on **25** yields additional imido species (Scheme 8). A series of dinuclear complexes linked by bis(imido) ligands has been

Table 4 Examples of W–CO and W–CNR complexes with 1,4-diimines and heterocyclic ligands

Complex	*Comments*	*W–N$_{av}$* (Å)	*References*
Monodentate and bridging ligands			
14		2.277	160
15		2.27	161
16			162
17	Strong π-acceptor; short W–N bond	2.10	163
cis-$[W(CO)_4(4\text{-}NaO_2Cpy\text{-}N)_2]$	Water soluble		164
Chelate and polydentate ligands			
18	M = Ge, Sn	2.22	165
$[W(CO)_2(bipy)(O_2CCF_3)(\equiv C–C\equiv C–SiMe_3)]$			166
19	M = Cr, Mo, W; solid and solution phase synthesis		167,168
20			169
21	Fluxional in solution		170
22	Synthesis involves oxidative addition of Ar–X bond; X = Cl, Br.		171
23	R = Me, Ph; from reaction of L$^-$ with $[W(CO)_4(\equiv CR)Cl]$	2.239	172
$[W(CO)_2(CNR^2)\{H_2B(pz)_2\}(\equiv CR^1)]$	R^1 = Ar; R^2 = Ar, Bu^t; from $[W(CO)_2(CNR^2)_2(\equiv CR^1)Br]$		173
fac-$[W(CO)_3\{X(2\text{-}py)_3\text{-}N,N',N''\}]$	X = P, P=O, SnBu^n		174–176
fac-$[W(CO)_2\{X(2\text{-}py)_3\text{-}N,N',N''\}(\equiv CPh)]^+$	X = CH, P		177
$[W(CO)_3\{HSi(3,5\text{-}Me_2pz)_3\}]$		2.284	178
$[W(CO)_2Tp'(\eta^3\text{-}CH_2CHCHR)]$	R = H, Me, Et, CH$_2$Ph		179
$[W(CO)_2Tp'(\mu\text{-}S)W(CO)_2Tp']$			180
$[W(CO)_2(\eta^4\text{-}C_5H_4O)Tp]^+$			181
$[W(CO)_2Tp'(\equiv CH)]$	Improved synthesis		182
$[W(CO)_2Tp'(\equiv C–C\equiv C\text{-}Ph)$			183
$[W(CO)_3(NCMe)Tp']^+$			184
$[W(CNEt)_2Tp'(\equiv C–NEt_2)]$			185



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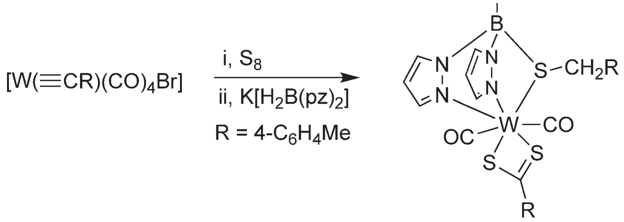
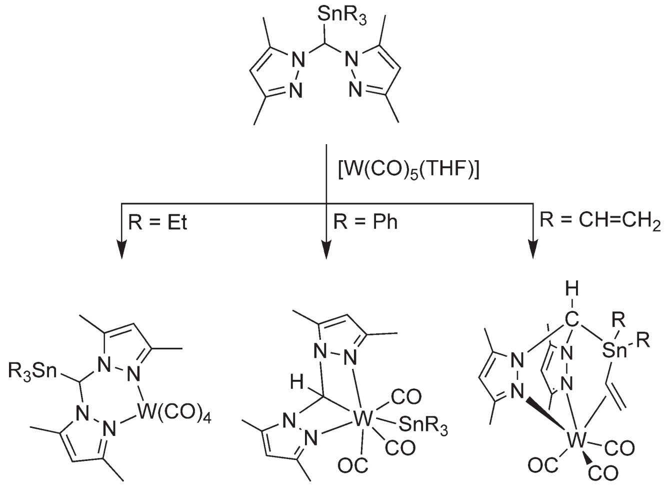
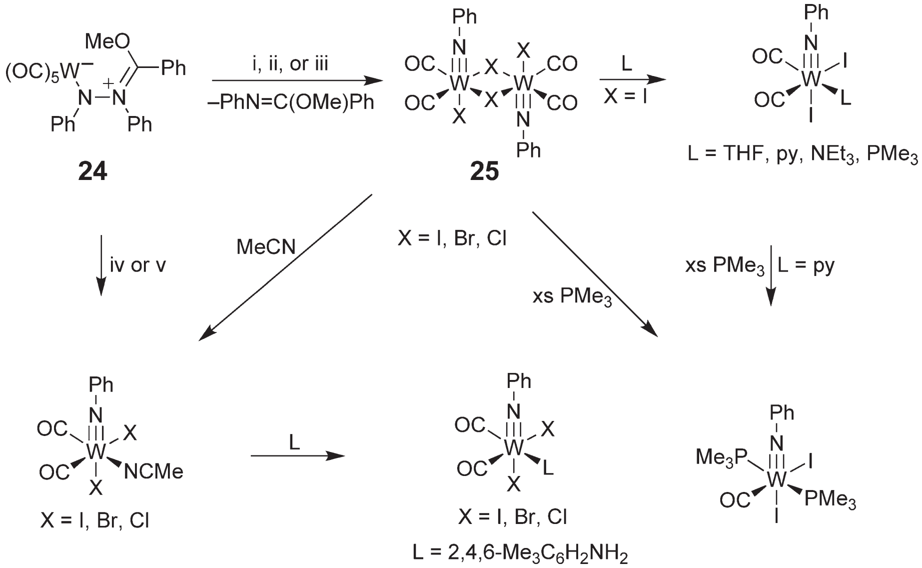
Scheme 5



Scheme 6



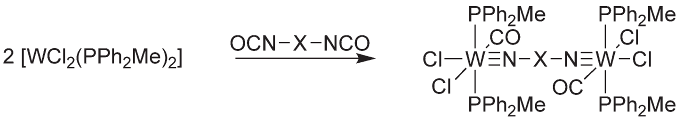
Scheme 7



i, 1 equiv. I_2, Et_2O, RT, 76%; ii, Br_2, CH_2Cl_2/Et_2O, –78 °C, 13%; iii, PCl_5, Et_2O, 0 °C, 63%;
iv, Br_2, $MeCN/Et_2O$, 0 °C, 81%; v, PCl_5, $MeCN/Et_2O$, 0 °C, 88%

Scheme 8

prepared by oxidative addition of diisocyanates with $[W(PPh_2Me)_2Cl_2]$ (Equation (9)).[192,193] The synthesis of imido complexes containing the $Tp'W(CO)_2$ or $Tp'W(CO)(PhC{\equiv}CMe)$ fragments has been recently reviewed (see Scheme 11).[135]



$$2\,[WCl_2(PPh_2Me)_2] \xrightarrow{OCN-X-NCO} Cl_2(OC)(PPh_2Me)_2W{\equiv}N-X-N{\equiv}W(CO)Cl_2(PPh_2Me)_2 \qquad (9)$$

X = p-C_6H_4; p-$C_6H_4C{\equiv}CC_6H_4$; p-$(C_6H_4)_3$

26

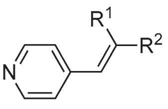
5.08.3.2.1.(iii) Dinitrogen and nitrosyl ligands

The chemistry of nitrosyl metal complexes has been recently reviewed.[198] In general, dinitrogen complexes are very labile, and are often formed and then studied *in situ*. Photolysis of [W(CO)$_3$Cp(Me)] in *n*-heptane under 200 kPa of N$_2$ yields the short-lived species [W(CO)$_2$(N$_2$)Cp(Me)].[199] Photolysis of [W(CO)$_6$], under dinitrogen at high pressure and at low temperature in a novel polyethylene matrix, leads initially to the formation of [W(CO)$_5$(N$_2$)] and on prolonged photolysis *cis*-[W(CO)$_4$(N$_2$)$_2$].[42] Under similar conditions, photolysis of [W(CO)$_5$(CS)] in the presence of dinitrogen leads to *cis*-[W(CO)$_4$(CS)(N$_2$)]. Reaction of the complex [W(CO)$_3$(PPr$^i_3$)$_2$] (which is stabilized by an agostic interaction) with dinitrogen leads to the relatively stable and isolable bridging dinitrogen complex [{W(CO)$_3$(PPr$^i_3$)$_2$}$_2$(μ-N$_2$)].[200] The gas-phase reaction of [W(CO)$_5$] with nitric oxide initially yields [W(CO)$_x$(NO)] (x is probably 4 or 5), which reacts further with nitric oxide to form [W(CO)$_3$(NO)$_2$].[201] Reaction of the *in situ* generated [W(CO)$_3$(Tp$^{\text{Bn,Me}}$)]$^-$ (Tp$^{\text{Bn,Me}}$ = hydrotris(3-benzyl-5-methylpyrazol-1-yl)borate) with *n*-butyl nitrite yielded the nitrosyl complex [W(CO)$_2$(Tp$^{\text{Bn,Me}}$)(NO)].[202] A range of nitrosyl complexes can be prepared from the trispyridyl complex [W(CO)$_3${P(2-py)$_3$-*N*,*N*′,*N*″}]; reaction with 1 equiv. of NOBF$_4$ in CH$_2$Cl$_2$ yields [W(CO)$_2$(NO){P(2-py)$_3$-*N*,*N*′,*N*″}][BF$_4$]; reaction with 2 equiv. of NOBF$_4$ in CH$_3$NO$_2$ yields [W(CO)(NO)$_2${P(2-py)$_3$-*N*,*N*′,*N*″}][BF$_4$]$_2$; and in the presence of MeCN the later reaction yields [W(NCMe)(NO)$_2${P(2-py)$_3$-*N*,*N*,′*N*″}][BF$_4$]$_2$.[174] Reaction of 2 equiv. of PPh$_2$(2-py) with [W(CO)$_2$(NCMe)$_3$(NO)][BF$_4$] yields the mixed donor complex [W(CO)$_2${PPh$_2$(2-py)-*P*}{PPh$_2$(2-py)-*P*,*N*}(NO)][BF$_4$].[203] Reaction of [W(CO)$_2$(phen)(SPh)$_2$] with nitric oxide yields the thiolate-displaced product [W(CO)$_2$(phen)(SPh)(NO)] with simultaneous formation of PhSNO, whereas reaction with the chelating thiolate complex [W(CO)$_2$(phen)(3,4-S$_2$C$_6$H$_3$Me)] yields the CO-displaced product [W(phen)(NO)$_2$(3,4-S$_2$C$_6$H$_3$Me)].[204] Reaction of [W(CO)$_4${CH$_2$(pz)$_2$}] with NOBF$_4$ in methanol yields the solvate [W(CO)$_2$(MeOH){CH$_2$(pz)$_2$}(NO)][BF$_4$].[205]

5.08.3.2.2 Structure and properties

5.08.3.2.2.(i) 1,4-Diimines and heterocyclic ligands

A selection of W–N$_{av}$ bond distances is listed in Table 4. Numerous spectroscopic and photochemical studies have been performed on [W(CO)$_4$(diimine)] (diimine = bipy, phen, 1,4-diazabutadienes) complexes, which have been reviewed.[206] More recent studies in this area have suggested a new interpretation of the electronic excited states.[207] The use of such complexes as luminescent probes for monitoring thermal and photochemical polymerizations has also been reviewed.[208] Spectroscopic and theoretical studies on W–CO complexes of pyridine derivatives can be broadly broken into two types: (i) studies involving monometallic complexes with simple or conjugated pyridine ligands and (ii) studies involving bimetallic complexes, where two metal centers are connected by highly conjugated ligands. Studies of simple [W(CO)$_5$(4-Xpy)] (X = H, CN, Ac, NMe$_2$) complexes have examined excited-state character and dynamics,[209,210] photosolvation,[211,212] CO π-bonding,[213] and polarizability.[214] Similar studies have examined the W–CO complexes of highly conjugated pyridines **29**.[215–218] Numerous examples of conjugated-bimetallic systems (e.g., **30**,[219–221] **31**,[222–224] and **32**,[225–228]) have been investigated for their NLO, electrochemical, and electronic properties.



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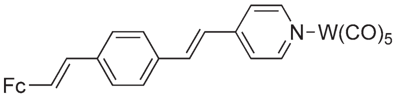
R^1	R^2
H	9-anthryl
CN	CN
CN	CO$_2$Me
H	CH=CHCHO
H	4-C$_6$H$_4$NMe$_2$



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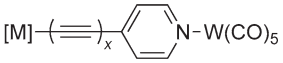
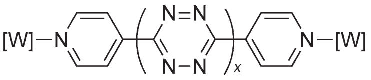


x = 3 [M] = Fc
x = 1 [M] = Ru(PPh$_3$)$_2$Cp
x = 1 [M] = Re(CO)$_3$bipy

31



x = 1 [W] = W(CO)$_3$(PPr$^i_3$)$_2$
x = 1 [W] = W(CO)$_5$
x = 0 [W] = W(CO)$_5$

32

5.08.3.2.2.(ii) Nitrene and imido complexes

Table 5 contains W$\equiv$N bond lengths and W$\equiv$N–R angles for examples of crystallographically characterized imido complexes. The data confirm the assignments as the linear imido complexes, with W$\equiv$N bond lengths ca. 1.75 Å and W$\equiv$N–R angles ca. 171°, which are dramatically different from the structurally characterized nitrene complex [W(CO)$_3$(dppe)(=N–NMe$_2$)] (W=N bond length ca. 2.12 Å and W=N–R angle ca. 139°).[229]

5.08.3.2.2.(iii) Dinitrogen and nitrosyl ligands

The dinitrogen complex [{W(CO)$_3$(PPr$^i_3$)}$_2$(μ-N$_2$)] has been crystallographically characterized (W–N$_{av}$ 2.119 Å; N–N 1.136 Å).[200] The N–N bond length is only marginally longer than the gaseous N$_2$ (1.098 Å). A number of theoretical studies have been conducted on dinitrogen W–CO complexes of the type [W(CO)$_5$(N$_2$)] and [W(CO)$_4$(N$_2$)], examining different coordination modes (side-on vs. end-on) and aspects of structure and bonding.[9,230,231] Theoretical studies have also examined [W(CO)$_5$(NO)]$^+$.[9] The nitrosyl complex [W(CO)(NO)$_2${P(2-py)$_3$-*N,N′,N″*}][BF$_4$]$_2$ is used as a Lewis acid pre-catalyst for Diels–Alder, Friedel–Crafts alkylation and aldehyde cyclotrimerization reactions.[174,232]

5.08.3.2.3 Reactions

5.08.3.2.3.(i) 1,4-Diimines and heterocyclic ligands

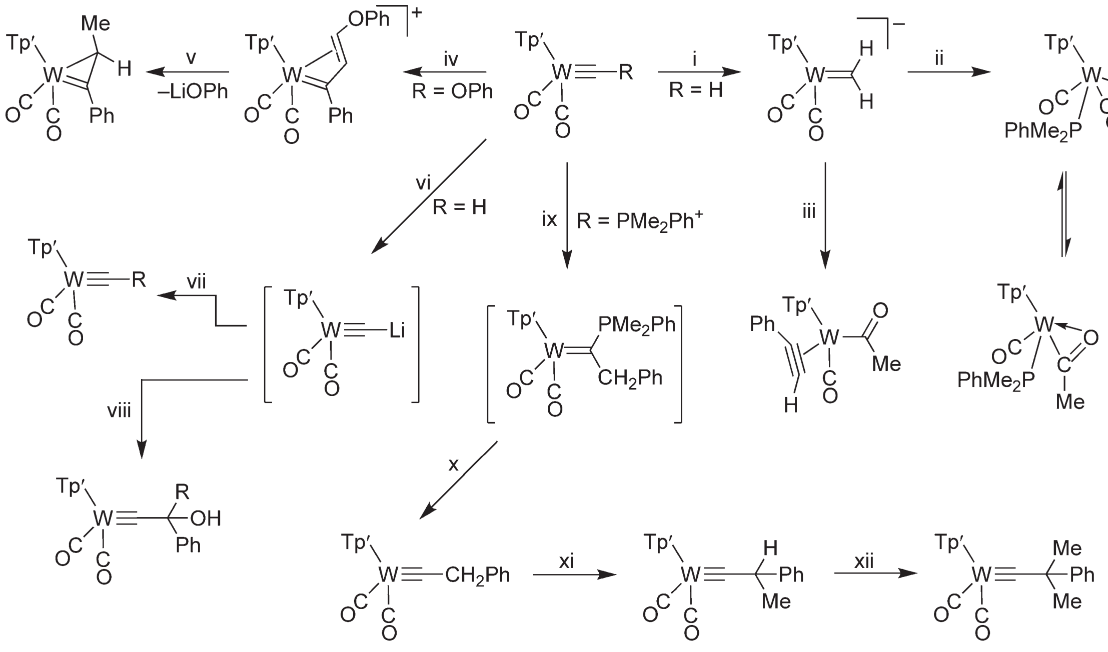
The chemistry of tris(pyrazolyl)borate–W–CO complexes is immense, with much of the chemistry involving ancillary carbon-donor ligands (alkynes, carbenes, etc.), and is also covered in other sections of this chapter; however, recent examples are described here (Schemes 9[182,240–242] and 10[233]). Reaction of [W(CO)(CN)(HC$\equiv$CH)Tp′] with HOTf or MeOTf yields the electrophilic addition products [W(CO)(CNX)(HC$\equiv$CH)Tp′][OTf] (X = H, Me), whereas reaction with HBF$_4$ gives the neutral [W(CO)(CNBF$_3$)(HC$\equiv$CH)Tp′].[234] Oxidation of [Et$_4$N][W(CO)$_3$Tp′] with I$_2$, NBS (*N*-bromosuccinimide), NCS (*N*-chlorosuccinimide), or PhICl$_2$ yields the halocarbonyl complexes [W(CO)$_3$Tp′(X)] (X = I, Br, Cl), whereas oxidation with Br$_2$ yields a mixture of [W(CO)$_3$Tp′Br] and [W(CO)$_3$(Tp^{Br})Br] (Tp^{Br} = hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borate).[235,236] The reaction of [Et$_4$N][W(CO)$_3$Tp′] with S$_8$ at room temperature yields the W(VI) complex [Et$_4$N][WTp′(S)$_3$].[237] Reaction of [W(CO)$_3$Tp′I] with DMSO at 100 °C yields the hydroxodioxo species [WTp′O$_2$(OH)].[238] Deprotonation and then alkylation of the propargylic carbon of the chiral complex [W(CO)(CH$_3$C$\equiv$CCH$_3$)Tp′(I)] is regioselective and stereoselective.[239] Use of a single enantiomer of [W(CO)(CH$_3$C$\equiv$CCH$_3$)Tp′(I)] in a series of deprotonation and alkylation steps, and then a ligand displacement procedure, yields an optically pure alkyne.

One area of particular importance to this section is that of tris(pyrazolyl)borate–W–CO complexes bearing monodentate N-donor ligands (e.g., amine, nitrile, imido, and azavinylidene ligands) and their interconversion, summarized in Schemes 11[135] and 12.[243] This area has been recently reviewed.[135] It is important to note that the interconversion chemistry differs for species involving the two fragments Tp′W(CO)$_2$ and Tp′W(CO)(PhC$\equiv$CMe), a consequence of the ability of the alkyne to behave as a two- or four-electron donor.[135] Hydride addition to an imine complex of the type [W(CO)(PhC$\equiv$CMe)(NH=R^{1}R^2)Tp′] to form an amido complex is diastereoselective if $R^1 \neq R^2$.[135,136,244]

Complexes of the type [W(CO)$_4$(L)] (L = phen, bipy) also exhibit a broad range of reactivities. [W(CO)$_3$(phen)(NCEt)], which can be prepared from [W(CO)$_6$] and phen in EtCN or from the reaction of phen and [W(CO)$_3$(NCEt)$_3$],[245,246] undergoes oxidative addition with disulfides to form the 16e$^-$ complexes [W(CO)$_2$(phen)(SR)$_2$] (R = Ph, Me, Bn, Bu^t).[245] In the reaction of [W(CO)$_3$(phen)(NCEt)] with thiols instead of

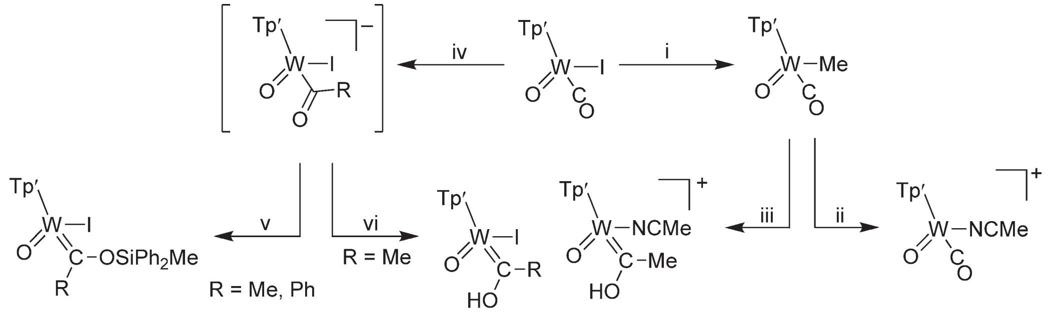
Table 5 Selected examples of W$\equiv$NR complexes

Complex	*Synthesis*	*W$\equiv$N$_{av}$* (Å)	*M–N–R* (°)	*References*
[{W(CO)$_2$I($\equiv$NPh)(μ-I)}$_2$] **25** X = I	See Scheme 8	1.76	177	189
[W(CO)$_2$(pip)I$_2$($\equiv$NPh)]	**25** (X=I) + pip	1.76	165	194
[{W(CO)$_2$I($\equiv$NPh)(μ-OMe)}$_2$]	**25** (X=I) + LiOMe	1.76	169	195
26 X = *p*-C$_6$H$_4$	See Equation (9)	1.74	173	193
[W(CO)$_2$Tp′($\equiv$NPh)]$^+$	[W(CO)$_2$Tp′(NHPh)] + Ph$_3$C$^+$	1.755	172	85
[W(CO)(PhC$\equiv$CMe)Tp′($\equiv$NPh)]$^+$		1.79	174	196
[W(CO)Tp′(SPh){$\equiv$NC(O)Me}]		1.78	167	138
27	See Scheme 14	1.74	170	197
28	See Scheme 14	1.74		197



i, $NaHBEt_3$;[182] ii, PMe_2Ph, HCl;[240] iii, PhC≡CH, HCl;[240] iv, HBF_4, PhC≡CH;[241] v, $LiHBEt_3$;[241] vi, Bu^nLi;[182] vii, I_2 (R = I), MeI (R = Me), TMSOTf (R = TMS) or PhC(O)Br (R = C(O)Ph);[182] viii, PhC(O)R, H_2O (R = H or Ph);[182] ix, $PhCH_2MgCl$;[242] x, MeI;[242] xi, Bu^nLi, MeI;[242] xii, Bu^nLi, MeI[242]

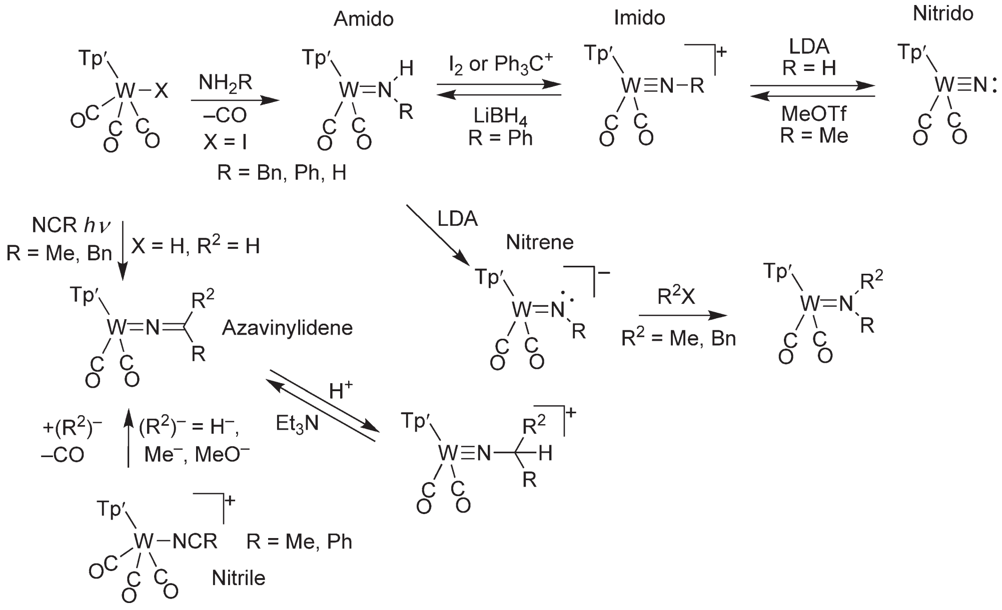
Scheme 9



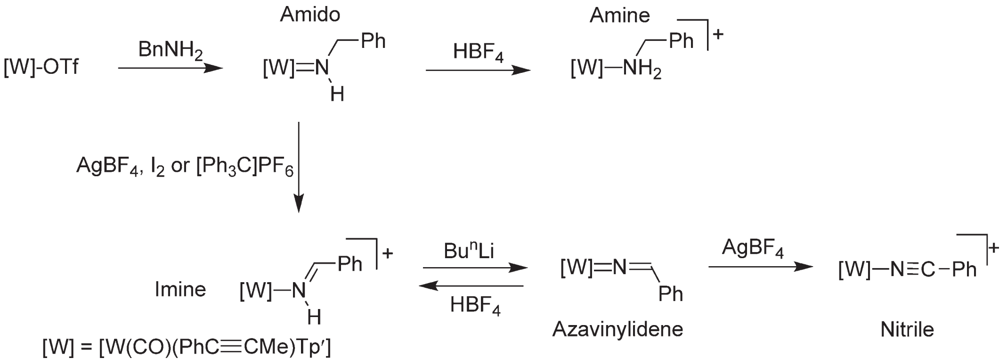
i, $LiCuMe_2$; ii, $HBAr'_4$, CH_2Cl_2, 3 equiv. MeCN; iii, $HBAr'_4$, MeCN; iv, RLi (R = Me, Ph); v, $ClSiPh_2Me$; vi, $PhCO_2H$; Ar′ = $C_6H_3(CF_3)_2$-3,5

Scheme 10

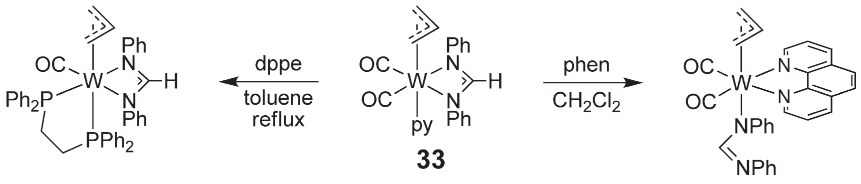
disulfides, alkyl thiols underwent ligand-substitution reactions to form $[W(CO)_3(phen)(HSR)]$ ($R = Bu^n$, Bu^t) while aryl thiols such as thiophenol resulted in oxidative addition products, for example, $[W(CO)_3(phen)(SPh)(H)]$.[247] Reaction of the dithiolate complex $[W(CO)_2(phen)(SPh)_2]$ with nitric oxide yields the nitrosyl complex $[W(CO)_2(phen)(SPh)(NO)]$ and PhSNO.[204] The bimetallic species $[W(CO)_3(phen)(\mu\text{-}Cl)M(CO)_xCl_y)]$ (M = Rh or Ir, $x = 2$, $y = 0$; M = Ru or Os, $x = 3$, $y = 1$), with a W–M bond (M = Rh, Ir, Ru, or Os), are formed by the reaction of $[W(CO)_3(phen)(NCMe)]$ with $[Rh(CO)_2Cl]_2$, $[Ir(CO)_2Cl(pyz)]$ (pyz = pyrazine), or $[M(CO)_3Cl_2]_2$ (M = Ru, Os).[248] The allyl complex $[W(CO)_2(phen)(\eta^3\text{-}C_3H_4)Cl]$ reacts with enolate, alkyl, and acetylide anions to form $[W(CO)_2(phen)(\eta^3\text{-}C_3H_4)R]$ [R = OC(=CH$_2$)Ph, Me, Bn, C≡CPh, C≡CH).[249,250] The mechanism for photosubstitution reactions of $[W(CO)_4(phen)]$ with PR_3 has been studied. Results indicate that the particular mechanism, dissociative, interchange, or associative, can be varied by choice of nucleophile, nucleophile concentration, excitation wavelength, and the pressure in the system.[251,252]



Scheme 11



Scheme 12

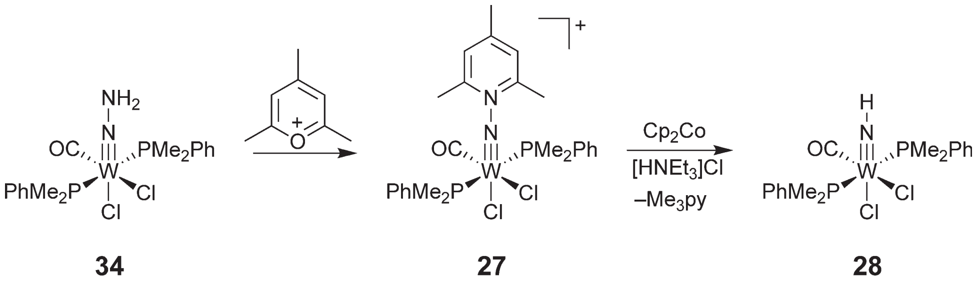


Scheme 13

The amidinato-pyridine complex **33** is a versatile precursor for a range of complexes (Scheme 13).[253]

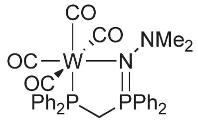
5.08.3.2.3.(ii) Nitrene and imido complexes

In addition to the chemistry summarized in Schemes 11 and 12, further reactions of imido complexes of the Tp′W(CO)$_2$ and Tp′W(CO)(PhC≡CMe) fragments are detailed in the review of Vogeley and Templeton.[135] The hydrazido complex **34** reacts with pyrylium cations to yield pyridinio-imido complexes (e.g., **27**), which can undergo N–N bond cleavage to yield the imido complex **28** and a pyridine species (Scheme 14).[197] Reaction of the nitrene



Scheme 14

complex [W(CO)$_5$=N–NMe$_2$] with dppm yields the phosphinimine complex **35**.[187] In addition to the synthetic pathways summarized in Scheme 8, the imido dimer [{W(CO)$_2$I(≡NPh)(μ-I)}$_2$] [**25** (X = I)] can react with LiOMe to yield [{W(CO)$_2$I(≡NPh)(μ-OMe)}$_2$] and [{W(CO)$_2$(OMe)(≡NPh)(μ-OMe)}$_2$].[195]



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5.08.3.2.3.(iii) Dinitrogen and nitrosyl ligands

The nitrogen ligand in the dinitrogen complex [{W(CO)$_3$(PPr$^i_3$)$_2$}$_2$(μ-N$_2$)] undergoes facile displacement in the presence of a small excess of acetonitrile or under an atmosphere of ethylene to form [W(CO)$_3$(PPr$^i_3$)$_2$L] (L = NCMe, C$_2$H$_4$).[200] However, in the presence of excess THF the dinitrogen complex is stable. Addition of HBF$_4$ to [{W(CO)$_3$(PPr$^i_3$)$_2$}$_2$(μ-N$_2$)] yields the seven-coordinate [W(CO)$_3$(PPr$^i_3$)$_2$(H)(FBF$_3$)].[200] The mixed donor complex [W(CO)$_2${PPh$_2$(2-py)-*P*}{PPh$_2$(2-py)-*P*,*N*}(NO)][BF$_4$] reacts with RedAl [sodium bis(2-methoxyethoxy)aluminum hydride] to form the hydride complex [W(CO)$_2${PPh$_2$(2-py)-*P*}$_2$H(NO)], which reacts with hydroiodic acid, acetic acid, and carbon dioxide to form *trans*,*trans*-[W(CO)$_2${PPh$_2$(2-py)-*P*}$_2$I(NO)], *trans*-[W(CO){PPh$_2$(2-py)-*P*}$_2$(η^2-O$_2$CCH$_3$)(NO)], and *trans*-*trans*-[W(CO)$_2${PPh$_2$(2-py)-*P*}$_2$(η-O$_2$CH)(NO)], respectively.[203]

5.08.4 Phosphorus Ligands

This section contains W–CO and W–CNR complexes bearing phosphorus-donor ligands, concentrating on σ-donor complexes. Phosphorus-donor ligands constitute the largest class of heteroatom-donor complexes in this chapter. Phosphorus-donor ligands, particularly phosphines (PR$_3$), are common ancillary ligands in complexes bearing other donor types, and for this reason examples of complexes bearing phosphorus-donor ligands are prevalent throughout this chapter. This section attempts to summarize important developments in this area since COMC (1995), focusing on examples with unusual structure or reactivity, examples that have been structurally characterized and developments in synthetic or characterization techniques, and expanding on the thorough coverage of core synthetic, structural, and reactivity details provided in COMC (1995).[254] Examples of π-bound phosphaarenes are covered in Section 5.08.16.7 on π-bound arenes.

Recently reviewed areas include the coordination chemistry of phosphinine (phosphabenzene) derivatives,[255,256] cationic phosphenium complexes,[257,258] the chemistry of 2*H*-azaphosphirene metal complexes,[259] terminal phosphinidene complexes,[260–262] and phosphaalkenes, and phosphaalkynes.[260]

5.08.4.1 Monodentate Phosphorus Ligands

Following the conventions of COMC (1995), in this section the symbol R indicates alkyl and aryl functionalities bound to phosphorus while Y is used to represent carbon, hydrogen and heteroatom (O, S, N, P, halogen, main group metal) substituents. In the characterization of synthetically challenging and intricate phosphines, it is common to form the $W(CO)_5$ adduct of the phosphine, using $[W(CO)_5(THF)]$ as the W–CO source, so crystallographic studies can be easily undertaken and the structure of the phosphine confirmed. Such studies are of interest for their synthetic sequences, and unless they involve template synthesis at a tungsten center will, in most cases, not be covered in this section.

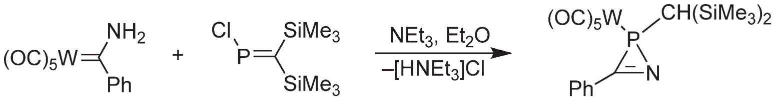
5.08.4.1.1 Synthesis

5.08.4.1.1.(i) PY_3 species

Representative examples of W–CO complexes bearing at least one PY_3 ligand are listed in Table 6. The synthetic procedures used to prepare such complexes include the following.

(i) Substitution of $[W(CO)_6]$ promoted by thermal, chemical, or photochemical methods.
(ii) Substitution of the labile ligand(s) from common W(0)–CO precursors such as $[W(CO)_5(THF)]$, $[W(CO)_3(NCMe)_3]$, *cis*-$[W(CO)_4(TMPDA)]$ $\{TMPDA = Me_2N(CH_2)_3NMe_2\}$, and $[W(CO)_4(py)_2]$. Recently used labile sources include $[W(CO)_5(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$.[263]
(iii) Ligand substitution from labile W(II)–CO precursors such as $[W(CO)_3(NCMe)_2(X)_2]$ and $[W(CO)(NCMe)(\eta^2\text{-}RC{\equiv}CR^1)_2(I)_2]$.[140,141,145,264–266]
(iv) Functionalization of the phosphorus center in an anionic phosphido-W–CO complex,[267,268] for example, Scheme 15.[267]

Additional recent methods include the reaction of chiral or achiral phosphine boranes $R_3P{\cdot}BH_3$ with $[W(CO)_5(pipz)]$ (pipz = piperazine), which afford the phosphine complexes $[W(CO)_5(PR_3)]$ in high yield under mild conditions.[269] The complexes $[W(CO)_2(L)(Cp)I]$ and $[\{W(CO)_2(L)I\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ $\{L = PPhMe_2, PCy_3, PBu^n{}_3$, and $P(OMe)_3\}$ are prepared by substitution of CO in $[W(CO)_3(Cp)I]$ and the fulvalene complex $[\{W(CO)_3I\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ with phosphine ligands. The reactions are rapid, high yielding and occur under mild conditions if the oxidative decarbonylation agent Me_3NO is used.[270] Conventional thermal methods are considerably longer for the Cp complex and in the case of the fulvalene complex do not produce any product. Photolysis of $[\{W(CO)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)](W\text{–}W)$ in the presence of 1 equiv. of PPh_3 affords $[W(CO)_3(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)W(CO)_2(PPh_3)](W\text{–}W)$, and in the presence of excess PPh_3 $[\{W(CO)_2(PPh_3)\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)](W\text{–}W)$ is isolated.[271] *2H*-Azaphosphirene complexes can be prepared by rearrangement of metal carbene complexes (Equation (10));[272–274] the chemistry of these complexes has been reviewed.[259] The W–CO-bound phosphide $Li[W(CO)_5(PPh_2)]$ reacts with $[W(Cp)_2(Cl)_2]$ via substitution on a Cp ring to yield the bimetallic complex **36**, photolysis of which affords the bridging chloride complex **37** (Scheme 16).[268,275,276] COMC(1995) covers additional synthetic methods.[254]



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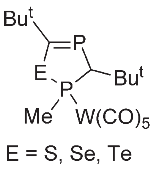

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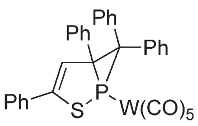

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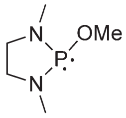

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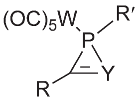

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5.08.4.1.1.(ii) PY_2 species

This section includes phosphaalkenes, η^1-phosphinine (phosphabenzene), and η^1-phosphole derivatives with a –P= fragment, and terminal phosphido and phosphenium complexes. Table 7 details selected examples of W–CO complexes with monodentate PY_2 ligands. Synthetic methodologies include the following.

Table 6 Examples of W–CO complexes with monodentate PY_3 ligands

Complex	*Synthesis*[a]	*Comments*	*W–P$_{av}$* (Å)	δ(WP) (J_{WP})[b]	*References*
Phosphines					
fac-$[W(CO)_3(PPh_{3-n}H_n)_3]$	(i)	$n = 1, 2$; $[W(CO)_6] + PPh_{3-n}H_n + NaBH_4/EtOH$	2.50 ($n = 1$)	4.3 (217) ($n = 1$) −72.0 (209) ($n = 2$)	277
cis-$[W(CO)_4(PPh_{3-n}H_n)_2]$	(ii)	$n = 1, 2$; $[W(CO)_6] + PPh_{3-n}H_n +$ *cis*-$[W(CO)_4(TMPDA)]$	2.49 ($n = 1$)	−4.6 (227) ($n = 1$) −80.9 (200) ($n = 2$)	277
$[W(CO)_5(Bu^t\overline{PCH_2C}H_2)]$	(ii)	$[W(CO)_5(THF)] + PR_3$		−163.5 (244)	278
$[W(CO)_5(PHR_2)]$	(ii)	$R = CF_3, C_6F_5$; $[W(CO)_5(THF)]$	2.48 ($R = C_6F_5$)	−100.1	279
$[W(CO)_4\{PPh_2(2\text{-}py)\}_2]$	(ii)	*cis-trans*-Isomerism pH responsive	2.56 (*cis*)	26 (236) (*cis*)	280
38	(iv)	$R = Bu^t$	2.57	−31.2 (189)	267
$[W(CO)_5(PH_3)]$		$[W(CO)_5(THF)] +$ (i) $P(SiMe_3)_3$, (ii) MeOH	2.49		281
$[W(CO)_5(PY_3)]$		$Y = H, D$; $[W(CO)_5(PCl_3)] + R_3SnY$			282
Phosphites, thiophosphites, and related species					
$[W(CO)(\eta^2\text{-}RC{\equiv}CR^1)\{P(OPr^i)_3\}_2I_2]$	(iii)	$R = R^1 = Et$; $R = Me$, $R^1 = Me$ or Ph	2.54 ($R = R^1 = Et$)	94.7 (228) ($R = R^1 = Et$)	264,265
$[W(CO)_{5-n}\{P(OR)_3\}_nI_2]$	(iii)	$R = Me$, $n = 3$; $R = Pr^i$, $n = 2$	2.45–2.57 ($R = Me$)	117.6, 107.4, 93.8 ($R = Me$)	266
40	(ii)	E = S, Se, Te	2.52 (S), 2.52 (Se)	67.1 (118) (S); 47.5 (126) (Se); 20.3 (130) (Te)	283
41	(ii)	Undergoes thermally induced ring expansion, contrasts to reactivity of free phosphirane	2.48	−55.4 (266)	284

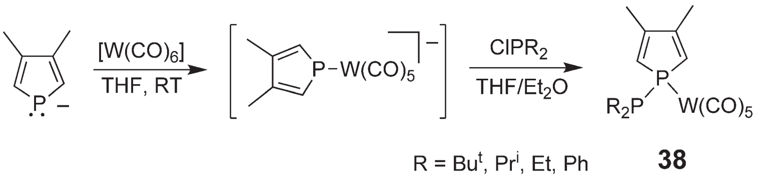
(*Continued*)

Table 6 (Continued)

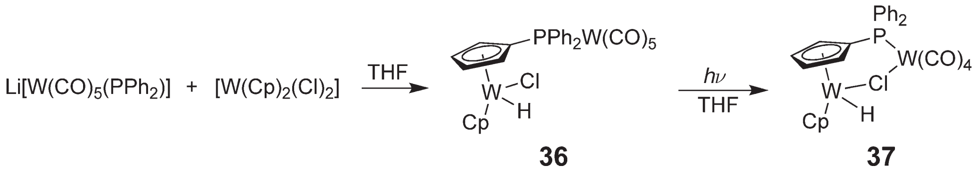
Complex	*Synthesis*[a]	*Comments*	*W–P*$_{av}$ (Å)	δ(WP) (J_{WP})[b]	*References*
Phosphaamines and related species					
trans-[$W(CO)_4\{P(NEt_2)Ph_2\}_2$]	(ii)	*cis*-[$W(CO)_4(pip)_2$] + $P(NEt_2)Ph_2$		85.1 (298)	285
cis-[$W(CO)_4\{P(NHR)Ph_2\}_2$]	(ii)	R = Ph, Cy	2.49	50.7 (253) (Ph)	286
[$W(CO)_5\{P(NEt_2)_2$(2-py)}]	(ii)	[$W(CO)_5$(THF)] + $P(NEt_2)_2$(2-py)	2.54	111 (289)	287
[$W(CO)_2\{Ph_2PN(Ts)CH_2CH_2N(Ts)PPh_2$-*P*,*P*′}(NO)Br]		*trans*-[$W(CO)_4$(NO)Br] + L		77.1 (271)	288
[$W(CO)_3$(bipy)(**42**)]		[$W(CO)_4$(bipy)] + **42**		129.8 (335)	289
39		Equation (10)	2.47	−108.8 (295)	272
43		R = PhX-4, R^1 = Cp*, Y = N	2.47 (X = H)	−167.3 (288)	273
43		R = N(H)Pr^i, R′ = $CH(SiMe_3)_2$, Y = P	2.52	−150.6 (264)	290
Halophosphines					
[$W(CO)_5(PX_3)$]	(ii)	X = Cl, Br	2.38 (Cl)		110, 291
[$W(CO)_5(PF_3)$]		[$W(CO)_5(PCl_3)$] + Bu_3SnF		120.6 (496)	282
Main group metallophosphines					
[$W(CO)_5(PH_2BH_2\cdot NMe_3)$]	(iv)	Li[$W(CO)_5(PH_2)$] + $ClBH_2\cdot NMe_3$	2.54	−184.2 (177)	292
[$W(CO)_5(PH_2EH_2\cdot NMe_3)$]		E = Al, Ga; [$W(CO)_5(PH_3)$] + $EH_3\cdot NMe_3$	2.55 (Al)	−240 (165) (Ga)	293
Mixed and pendant systems					
[$W(CO)_5(\eta^1$-dppm)]			2.52		294
[$W(CO)_2\{Ph_2P(CH_2)_nPPh_2)\}\{P(OR)_3\}I_2$]		R = Ph, *n* = 1; R = Me, Et, Pr^i *n* = 2; [$W(CO)_3\{Ph_2P(CH_2)_nPPh_2)\}I_2$] + $P(OR)_3$	2.49–2.65		295

[a] See text for synthetic methods.

[b] ^{31}P NMR; δ in ppm; ^1JWP in Hz in parentheses.



Scheme 15



Scheme 16

Table 7 Examples of W–CO complexes with monodentate PY_2 ligands

Complex	*Synthesis*[a]	*Comments*	*W–P$_{av}$* (Å)	δ_P (WP)(J_{WP})[b]	*References*
48	(i)		2.53	40 (265)	304
49	(i)	Ar = $C_6H_2R_3$-2,4,6, R = Pr^i, Bu^t;		154.1 (250) (R = Bu^t)	305
50	(i)	R = $NPr^i{}_2$	2.62	41.7 (115)	306, 307
51	(i)	R = Me, H		201.5 (286) (R = H)	308
52	(i)			44.7 (228)	309
53	(i)	E = S, Se, Te; E = S ligand can form a π-bound η^5-complex.	2.48 (S), 2.49 (Se), 2.51 (Te)	208 (247) (S), 221.8 (241) (Se), 216 (231) (Te)	310–312
54		Lithio-phosphole + $[W(CO)_3(Cp)(Cl)]$		−102.4 (50)	313, 314
55		Phosphole + $[W(CO)_5(cyclooctene)]$		70.6 (259)	315
56	(i)	E = P, [M] = $FeCp^*$, $CuPPh_3$; E = Sb, [M] = $FeCp^*$, $RuCp^*$			316–318
$[W(CO)_3(Cp)\{P(H)Mes^*\}]$	(ii)	$[W(CO)_3(Cp)(H)]$ + $ClP(H)Mes^*$/Et_3N		−141.0 (51)	296
$[W(CO)_2(Cp)\{{=}P(H)Mes^*\}]$	(iii) or (iv)			211.8 (604)	296
47	(v)	Equation (11)		233.7 (442)	289
57		44 + PPh_3; TfO^- counteranion	2.25	150.0 (598) (PN_2); 24.3 (211) (PPh_3)	303

[a] See text for synthetic methods.

[b] ^{31}P NMR; δ_P in ppm; J_{WP} in Hz in parentheses. Mes* = 2,4,6-tri-*tert*-butylphenyl.

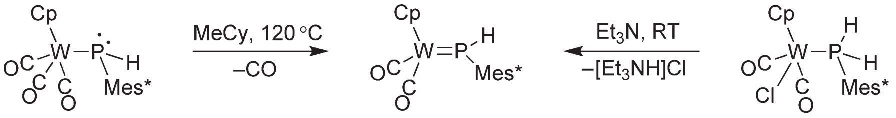
(i) Ligand displacement from labile precursors such as $[W(CO)_5(THF)]$ and $[W(CO)_{6-n}(NCMe)_n]$ (n = 1–3).

(ii) Reaction of a monochlorophosphine with $[W(CO)_3Cp(H)]$ or $[W(CO)_3(Cp)]^-$ to afford phosphido complexes $[W(CO)_3Cp(PR_2)]$.[296,297]

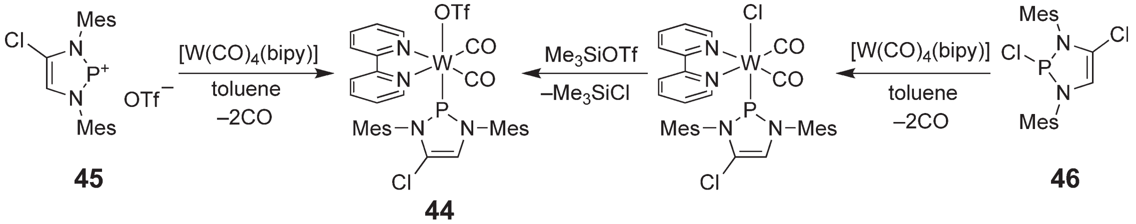
(iii) Loss of CO from a phosphido complex to afford a phosphenium complex (Scheme 17).[296]

(iv) Base-assisted dehydrohalogenation of a halo-W–CO complex bearing a PHY_2 ligand to afford a phosphenium complex (Scheme 17).[296] The P–H-functionalized phosphenium complex, shown in Scheme 17, is only stable because of the sterically demanding supermesitylene substituent ($Mes^* = C_6H_2Bu^t{}_3$-2,4,6).[298]

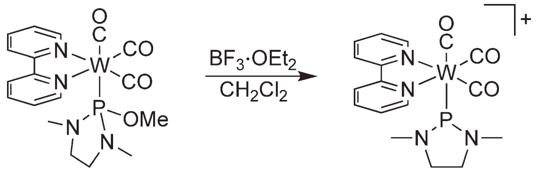
(v) Abstraction of an alkoxide from a coordinated phosphite with a Lewis acid to form cationic phosphenium complexes (Equation (11)).[257,289,299] Phosphenium species can undergo migratory insertion reactions.[300]



Scheme 17



Scheme 18



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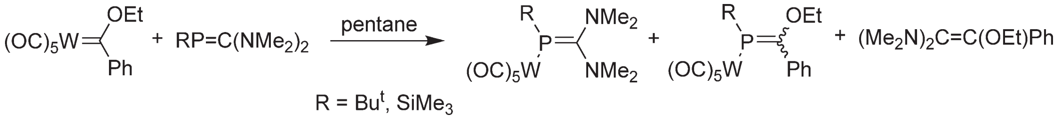
(11)

The reaction of inversely polarized phosphaalkenes with carbene-W–CO complexes affords phosphaalkene complexes as a result of ligand displacement and metathesis processes (Equation (12)).[301,302] The phosphenium complex **44**, bearing a phosphorus analog of an imidazol-2-ylidene, has been prepared via two routes (Scheme 18), starting with a stable phosphenium cation **45** or a *P*-chloro species **46**, which undergoes coordination-induced ionization of the P–Cl bond.[303]



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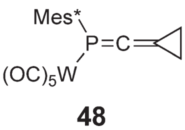

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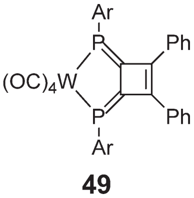

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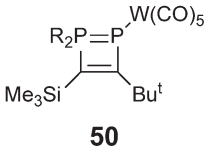

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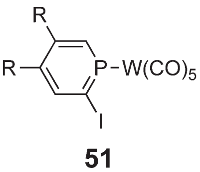

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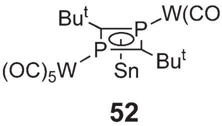

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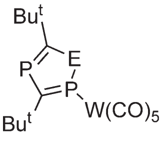

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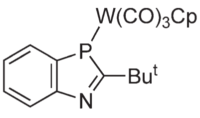

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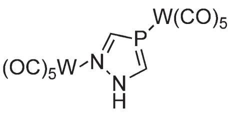

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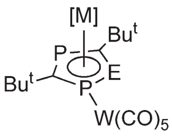

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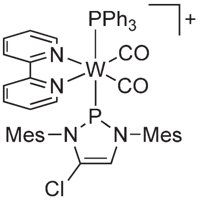

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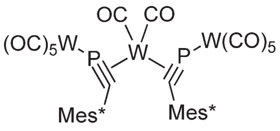
5.08.4.1.1.(iii) PY species

Terminal phosphinidene (phosphanediyl) complexes are typically unstable, and examples of isolated complexes are rare.[319] The most common W–CO species are the transient [W(CO)$_5$(PR)] complexes that are formed from the thermal activation of **58** and **59** (Scheme 19).[261,262] The reactivity of these transient species is discussed in Section 5.08.4.1.3.(ii). An isolable aminophosphinidene-W–CO complex **60**, the structure of which is discussed in Section 5.08.4.1.2.(ii), has been prepared by chloride abstraction from a chloroaminophosphido complex (Equation (13)).[320]

$$[\mathrm{W(CO)_3(Cp^*)\{P(Cl)NPr^i{}_2\}}] \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{AlCl_3}} \underset{\textbf{60}}{[\mathrm{W(CO)_3(Cp^*)(PNPr^i{}_2)][AlCl_4]}} \qquad (13)$$

The σ-bound phosphaalkyne complex [W(CO)$_3$(PCy$_3$)$_2$(P$\equiv$CMes*)] has been prepared by the reaction of P$\equiv$CMes* with [W(CO)$_3$(PCy$_3$)$_2$], and has been structurally characterized {W–P($\equiv$C) 2.39 Å}.[321] However, the reaction of phosphaalkynes with [W(CO)$_5$(THF)] affords a variety of π-bound phosphaalkyne- and phosphorus heterocycle-W–CO complexes, including **61** and **62**.[322]



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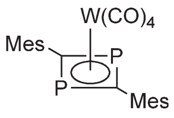

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5.08.4.1.2 Structure and properties

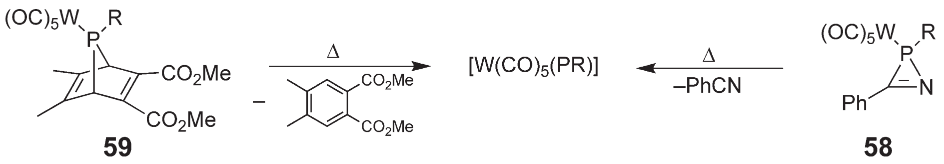
COMC(1982) and COMC(1995) cover, in detail, many of the basic structural aspects and properties of PY$_3$, PY$_2$, and PY complexes.[254,323,324]

5.08.4.1.2.(i) PY$_3$ species

Table 6 contains W–P bond lengths and ^{31}P NMR spectral details for a range of W–CO complexes bearing PY$_3$ ligands.

Kinetic and thermodynamic studies have been conducted on the isomerization of linkage isomers for phosphine–W–CO complexes bearing pendant (dangling) phosphines.[325–327] The pendant complexes [W(CO)$_5${η^1-PPh$_2$CH$_2$CH(PPh$_2$)$_2$}] **63** and [W(CO)$_5${η^1-PPh$_2$CH$_2$CH$_2$P(*p*-Tol)$_2$}] **64** exist in equilibrium with the linkage isomers [W(CO)$_5${η^1-PPh$_2$CH(PPh$_2$)CH$_2$PPh$_2$}] **65** and [W(CO)$_5${η^1-P(*p*-Tol)$_2$CH$_2$CH$_2$PPh$_2$}] **66**, respectively. The rate of exchange between of **63** and **65** is four orders of magnitude faster than the rate of exchange between **64** and **66**; the transition state between **63** and **65** is thought to involve two phosphine–W interactions and one phosphine–CO interaction, which may accelerate the reaction.[326] Calorimetric studies to determine heats of protonation have also been undertaken for a series of pendant phosphine complexes, [M(CO)$_5$(η^1-dppm)] (M = Cr, Mo, W) and [M(CO)$_3$(bipy)(η^1-dppm)] (M = Mo, W).[328] The pendant phosphorus center is more basic than the metal center. Similar studies have examined the simple PR$_3$ complexes *fac*-[W(CO)$_3$(PR$_3$)$_3$] (PR$_3$ = PMe$_3$, PEt$_3$, PMe$_2$Ph, PEt$_2$Ph, PMePh$_2$, and PEtPh$_2$), and found that the heats of protonation of the metal center were influenced by both electronic and steric factors.[329] Solid-state isomerization of *cis*- and *trans*-isomers of [W(CO)$_2$(PR$^2{}_3$)(η^5-C$_5$H$_4$R^1)I] (R^1 = Me, Bu^t; R^2 = Ph, OPr$^i{}_3$) has been studied.[330]

Crystallographic, spectroscopic, electric dipole, and electro-optical studies have examined the metal–ligand bonding, particularly M → P π-backbonding, in [M(CO)$_5$(PY$_3$)] (M = Cr, W; R = Me, Cl, Br).[110,291] High resolution photoelectron spectroscopic studies, with synchrotron radiation, have examined [W(CO)$_{6-n}$(PMe$_3$)$_n$] (n = 0–3).[331]



Scheme 19

Theoretical studies have examined the nature of the M–P bond in $[W(CO)_5(PY_3)]$ (M = Cr, Mo, W; Y = H, Me, F, Cl).[282,332] The studies indicate that there is no correlation between M–P bond lengths or bond energies, and that PCl_3 is a poorer σ-donor and a stronger π-acceptor than the other phosphines. DFT studies have examined the effect of different phosphines on the orientation of coordinated ethylene in $[W(CO)_3(PY_3)_2(\eta^2\text{-}H_2C{=}CH_2)]$ (Y = H, Me, F, Cl, Br, I).[333] Structural properties including bond energies have been calculated for $W(CO)_5$ complexes of azaphosphirenes and azaphosphiranes.[259,334] A range of different computational methods have been examined for the prediction of ^{31}P chemical shift tensors in phosphine, phosphido, and phosphinidene metal complexes.[335]

5.08.4.1.2.(ii) PY_2 and PY species

Table 7 contains W–P bond lengths and ^{31}P NMR spectral details for a range of W–CO complexes bearing PY_2 ligands. Of particular note are the large $^1J_{WP}$ coupling constants for the phosphenium complexes, which may be suggestive of multiple bond character. Theoretical studies of the cationic phosphenium complex **47** (in Equation (11)) have examined the thermodynamic stability of the facial complex and its meridional isomer, rotational behavior about the W–P bond, and the characteristics of the W–phosphenium bond.[336] Results suggest that the phosphenium ligand has strong π-electron-accepting character, stronger than a CO ligand, and that π-donation to the phosphenium center comes predominantly from the metal center and not from the amino substituents on the phosphorus. Strong π-acceptor ability has also been suggested for the unsaturated phosphenium ligand in **44** (Scheme 18), and there is structural and spectroscopic evidence for W–P multiple bond character in such complexes.[303]

A number of studies have examined the nature of bonding in the terminal phosphinidene complexes $[W(CO)_5PR]$.[260,261,337–340] The reactivity of these complexes mimics that of singlet carbenes and they can be considered as phosphorus analogs of electrophilic Fischer-type carbenes. The phosphinidene in $[W(CO)_5PR]$ complexes is a two-electron donor with a bent W–P–Y structure, where the W–P bond can be described as a σ-dative bond with some π-backbonding. Calculated bond lengths in $[W(CO)_5PR]$ are consistent with single bond character.[260,337,338]

The structure of the electrophilic aminophosphinidine complex **60** (in Equation (13)) has been reported, and represents only the second example of a structurally characterized terminal phosphinidene–W–CO complex.[320] The complex exhibits a bent W–P–N structure (W–P–N 118.7°) and a reasonably long W–P bond (2.45 Å), longer than other bent phosphinidene–W complexes (e.g., $[W(Cp)_2\{{=}P(C_6H_2Bu^t_3\text{-}2,4,6)\}]$ W–P 2.35 Å) and considerably longer than the W≡P bond in $[W(CO)(PMe_2Ph)_2Cl_2\{{\equiv}P(C_6H_2Bu^t_3\text{-}2,4,6)\}]$ (W–P 2.17 Å; W–P–C 168°).[319,320,341] The structure of **60**, with a long W–P bond and a bent W–P–Y group, is consistent with the above discussion on the structure of electrophilic terminal phosphinidene complexes.

Theoretical studies have also examined the formation of $M(CO)_5$ (M = Cr, Mo, W) complexes with electron-rich methylenephosphanes (η^1-RP=CHR).[342]

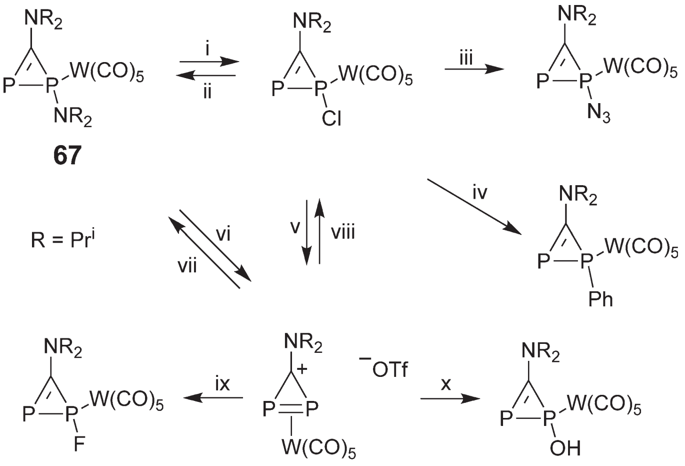
5.08.4.1.3 Reactions

5.08.4.1.3.(i) PY_3 species

In general, reactions involving W–CO complexes of PY_3 can be divided into three groups: reactions involving (i) the metal center, (ii) the P-donor atom, or (iii) substituents on the P-donor ligand. Examples that involve the metal center and donor types other than phosphorus are covered throughout this chapter under the relevant donor-type section.

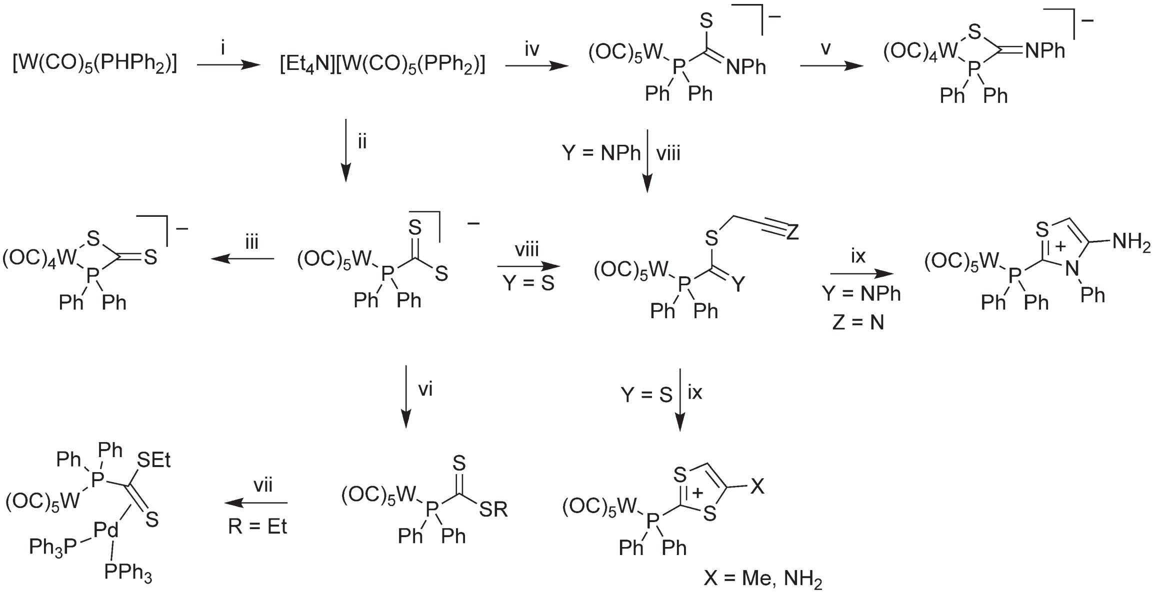
The aminophosphine complex *trans*-$[W(CO)_4\{P(NEt_2)Ph_2\}_2]$ undergoes substitution of the amino functionality on reaction with anhydrous $HCl_{(g)}$ in CH_2Cl_2, anhydrous $HCl_{(g)}$ in alcoholic solutions or with aqueous H_2SO_4 to afford *trans*-$[W(CO)_4\{P(R)Ph_2\}_2]$, where R = Cl, OR^1, or OH, respectively.[285] The amino group on the tungsten-bound phosphorus in the diphosphirene complex **67** can also be replaced by a chloride (Scheme 20). The reactivity of the diphosphirane complex and its derivatives is summarized in Scheme 20.[343] The reaction of CS_2 or PhNCS with $[W(CO)_5(PPh_2)]^-$, formed from $[W(CO)_5(PHPh_2)]$, affords dithio- and thio-/azo-functionalized phosphine complexes that serve as precursors for a range of complexes (Scheme 21).[344–347]

The trifluoromethylphosphine complex $[W(CO)_5\{PH(CF_3)_2\}]$ undergoes a series of reactions with cyanides. The reaction with [18-crown-6-K]CN affords [18-crown-6-K]$[W(CO)_5\{P(CF_3)_2\}]$,[348] reaction with $Hg(CN)_2$ affords $[\{W(CO)_5(\mu\text{-}P(CF_3)_2)\}Hg\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}]$,[349] and the reaction with $[Ag(CN)_2]^-$ affords $[\{W(CO)_5(\mu\text{-}P(CF_3)_2)\}Ag\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}]^-$.[350] Analogous products are formed from the phenyl derivative $[W(CO)_5\{PH(C_6F_5)_2\}]$.



i, HCl, Et$_2$O; ii, R$_2$NH, THF; iii, Me$_3$SiN$_3$, THF; iv, NaBPh$_4$, CH$_2$Cl$_2$; v, AgOTf, CH$_2$Cl$_2$; vi, CF$_3$SO$_3$H, CH$_2$Cl$_2$; vii, R$_2$NH, CH$_2$Cl$_2$; viii, [Ph$_3$PNPPh$_3$]Cl, CH$_2$Cl$_2$; ix, NBu$_4$F, CH$_2$Cl$_2$; x, air/H$_2$O, CH$_2$Cl$_2$, 1 h

Scheme 20

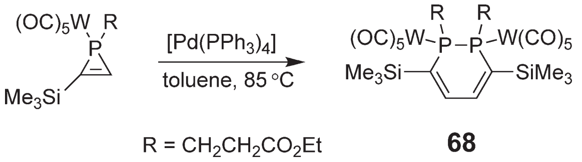


i, NEt$_4$Br, LiBu^n; ii, CS$_2$, THF; iii, refluxing THF, 1 h; iv, PhNCS; v, $h\nu$, benzene; vi, RX, CH$_2$Cl$_2$; vii, [Pd(PPh$_3$)$_4$], CH$_2$Cl$_2$; viii, BrCH$_2$CCH (Z = CH) or ICH$_2$CN (Z=N); ix, HBF$_4$, Et$_2$O

Scheme 21

Phosphirene–W(CO)$_5$ complexes can dimerize in the presence of catalytic [Pd(PPh$_3$)$_4$] to afford 1,2-diphosphirine complexes (Equation (14)).[351,352] A series of transformations can convert 68 (R = CH$_2$CH$_2$CO$_2$Et) into the dibenzyl derivative (R = Bn), thermolysis of which affords a phosphole complex.[352]

The reactivities of the 7-phosphanorbornadiene and azaphosphirene complexes 59 and 58 (in Scheme 19) are covered in the next section on terminal phosphinidene complexes.

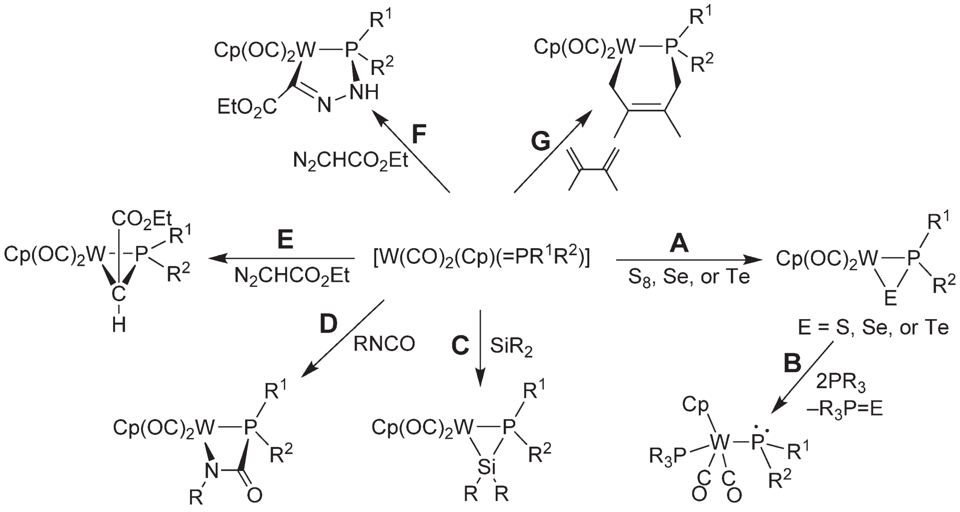


(14)

5.08.4.1.3.(ii) PY_2 and PY species

Phosphenium complexes of the type $[W(CO)_2({=}PR^1R^2)Cp]$ exhibit a range of reactivities based on attack of nucleophiles and cycloaddition reactions, which are summarized in Scheme 22 and Table 8. The phosphenium complex $[W(CO)_2\{{=}P(H)Mes^*\}Cp]$ can be functionalized at the P center; reaction with CCl_4 affords $[W(CO)_2\{{=}P(Cl)Mes^*\}Cp]$, while treatment with $KOBu^t$ then MeI affords $[W(CO)_2\{{=}P(Me)Mes^*\}Cp]$.[296,298] The phosphido complexes $[W(CO)_3Cp(PR^1R^2)]$ ($R^1 = R^2 = Bu^t$, *o*-Tol; $R^1 = Mes$, $R^2 = H$, Me) react with dimethyldioxirane to afford the oxides $[W(CO)_3Cp\{P({=}O)R^1R^2\}]$. The phosphides $[W(CO)_3Cp\{P(X)Bu^t\}]$ (X = H, Cl) convert at room temperature into the three-membered diphosphametallacycles $[\overline{W(CO)_2(Cp)\{P(X)Bu^tPBu^t}\}]$ (X = H, Cl) and $[W(CO)_3Cp(X)]$ (X = H, Cl).[353]

Reactions of complexes bearing a PY ligand are dominated by the reactivity of the transient $[W(CO)_5(PY)]$. The transient $[W(CO)_5(PY)]$ species derived from 7-phosphanorbornadiene complexes **59** have proved to be very versatile for the synthesis of new organophosphorus molecules. The area has been reviewed,[260–262] and selected recent examples are summarized in Scheme 23[354–357] and Scheme 24.[358] The R group in **59** can be chiral, which enables formation of a chiral $[W(CO)_5(PY^*)]$ species and subsequent incorporation of the chiral group into other molecules.[359] The mechanism of the CuCl-catalyzed decomposition of 7-phosphanorbornadiene complexes to the transient

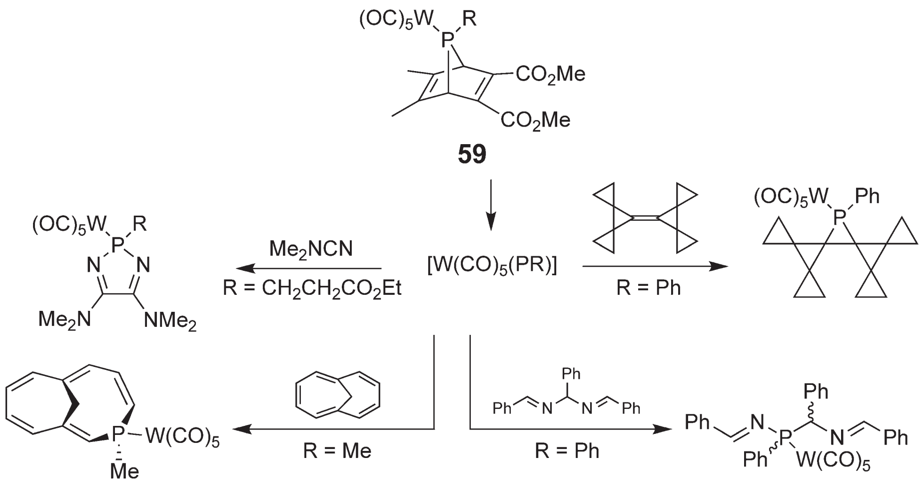


Scheme 22

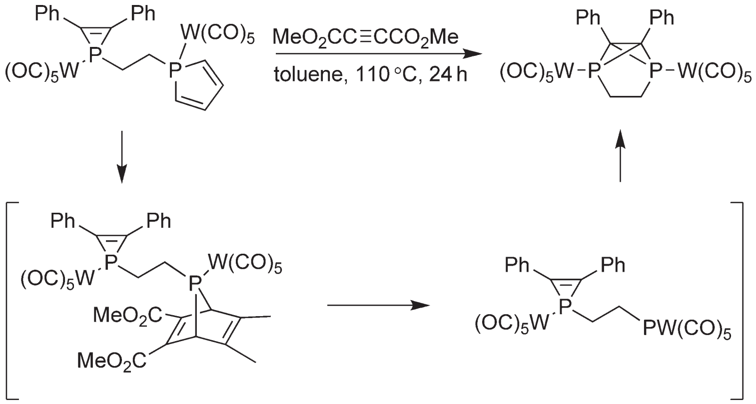
Table 8 Selected reactions of $[W(CO)_2(Cp)({=}PR^1R^2)]$

Cp	*R^1*	*R^2*	*Reaction*[a]	*References*
Cp	Ph	$N(SiMe_3)_2$	**A** (S, Se); **C** (R = Me, Ph)	297, 369
Cp, Cp^*	H	Bu^t	**A** (S, Se, Te)	370
Cp	*o*-Tol	Ph	**A** (Se); **B** (PMe_3, $PPhMe_2$, PPh_2Me); **D** (R = Et, Ph)	371, 372
Cp	Mes	Ph	**E**	373
Cp	Bu^t	Bu^t	**F**; **G**	373, 374
Cp	Ph	Ph	**G**	374

[a] See Scheme 22.

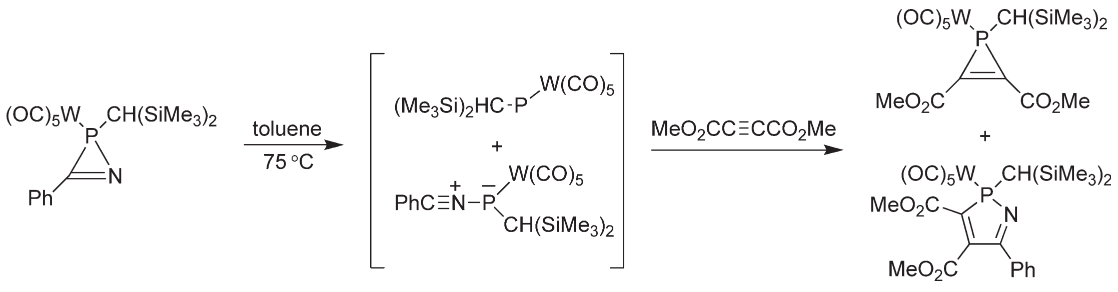


Scheme 23

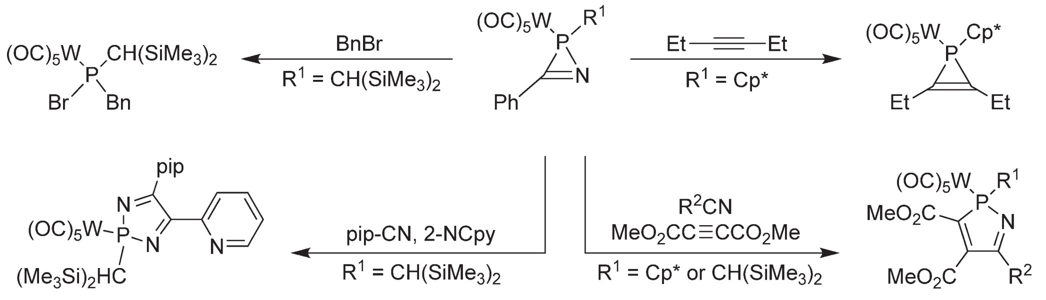


Scheme 24

phosphinidene complex has been studied by DFT methods.[340] The reactivity of the azaphosphirene complexes **58** (in Scheme 19) are similar to that of **59**, however, studies suggest that in addition to the formation of the reactive terminal phosphinidene complex $[W(CO)_5(PY)]$, a nitrilium intermediate contributes to its difference in chemistry compared to that of **59** (Scheme 25).[259] The chemistry of azaphosphirene–$W(CO)_5$ complexes has been reviewed;[259] selected examples are given in Scheme 26.[360–364] Ring-expansion reactions of the azaphosphirene–$W(CO)_5$ complexes can be catalyzed by TCNE and ferrocenium hexafluorophosphate.[365,366] Decomplexation of phosphines from the $W(CO)_5$ fragment has been achieved chemically and electrochemically.[367,368]



Scheme 25



Scheme 26

5.08.4.2 Polydentate Phosphorus Ligands

This section includes polyphosphines, mixed-donor polydentate ligands with at least one phosphorus donor, bridging phosphides (PY_2) and phosphinidenes (PY), phosphenes (YP = PY) as well as unusual phosphorus-rich ligands and "naked" phosphorus species.

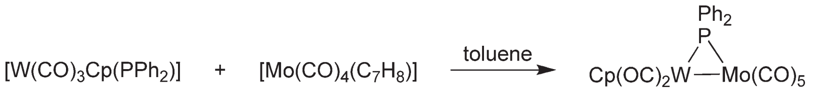
Areas that have been covered by recent reviews include: phosphinine-based bidentate ligands,[255] mixed phosphorus–sulfur-donor ligands,[375] coordination chemistry of 1,1′-bis(diphenylphosphino)ferrocene,[376] coordination chemistry of tridentate and tetradentate polyphosphines and mixed-donor ligands,[377] metal cluster complexes with group-15 elements,[378] P_n species as ligands,[379] and complexes involving M≡P and M≡P–M′ fragments.[380]

5.08.4.2.1 Polydentate phosphines and related species

5.08.4.2.1.(i) Synthesis

Numerous types of polydentate phosphorus-containing ligands, exhibiting mononuclear and dinuclear metal coordination modes, are considered under this heading. The various types are listed in Table 9 along with representative examples in each case. The typical synthetic methodologies used to prepare complexes in this section are similar to the methods used for monodentate complexes (Section 5.08.4.1.1.(i)). Briefly, these are the following.

(i) Substitution reactions of $[W(CO)_6]$.
(ii) Substitution of labile ligands(s) from W(0)–CO precursors such as $[W(CO)_3(NCR)_3]$, $[W(CO)_4(pip)_2]$, $[W(CO)_5(THF)]$, and $[W(CO)_4(nbd)]$.
(iii) Substitution of labile ligands(s) from W(II)–CO precursors such as $[W(CO)_3(NCMe)_2(X)_2]$ or $[W(CO)(NCMe)(\eta^2\text{-RC}{\equiv}\text{CR})_2I_2]$.[140,141]
(iv) Reaction of a phosphido-metal complex with a second metal source, a method used to prepare PY_2-bridged bimetallic complexes, both homo- and hetero-nuclear, for example, Equation (15).[381–384] Additional synthetic methods are also detailed in Table 9.



$$[W(CO)_3Cp(PPh_2)] + [Mo(CO)_4(C_7H_8)] \xrightarrow{\text{toluene}} Cp(OC)_2W(\mu\text{-}PPh_2)Mo(CO)_5 \quad (15)$$

The thermal reaction of $[\{W(CO)_2Cp\}_2](W{\equiv}W)$ with HPR_2 (R = Cy, Et, Ph) affords the monophosphido complexes $[\{W(CO)_2Cp\}_2(\mu\text{-H})(\mu\text{-PR}_2)](W\text{–}W)$.[385] However, photolysis of a mixture of $[\{W(CO)_3Cp\}_2](W\text{–}W)$ and HPR_2 afforded the bis-phosphido complexes $[\{WCp\}_2(\mu\text{-CO})(\mu\text{-PR}_2)_2](W{\equiv}W)$.[385] Combining these methods allows the preparation of mixed bis-phosphido complexes. Treatment of the P_2 complex $[\{W(CO)_2Cp\}_2(\mu\text{-}\eta^2:\eta^2\text{-P}_2)](W\text{–}W)$ with hydroxide in an aqueous THF mixture followed by protonation with HBF_4 affords the phosphido complex $[\{W(CO)_2Cp\}_2(\mu\text{-H})(\mu\text{-PH}_2)]$.[386]

Microwave-assisted synthetic methods have been reported for $[M(CO)_4(L_2)]$ (M = Cr, Mo, W; L_2 = dppm, dppe).[81] Four different methods have been examined for the preparation of **69** from $[W(CO)_3(\eta^5\text{-C}_5H_4PPh_2)]^-$.[387] The kinetics of thermal substitution of a diene by $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–3) in $[M(CO)_4(\eta^4\text{-diene})]$ (M = Cr, Mo, W; diene = cod, nbd) have been studied by FTIR spectroscopy.[388,389] In addition to the examples in Table 9, a number of W–CO complexes bearing multidentate ligands based on phosphine-functionalized metallocenes have been

Table 9 Examples of W–CO and W–CNR complexes containing polydentate phosphines or related ligands

Complex	*Synthesis*[a]	*Comments*	*W–P$_{av}$* (Å)	δ (WP)($^1J_{\mathrm{WP}}$)[b]	*References*
Diphosphine donors—mononuclear complexes					
[W(CO)$_2$(dppe)(Br)(η^3-cyclohexenyl)]	(iii)	[W(CO)$_2$(NCMe)$_2$(Br)(η^3-cyclohexenyl)] + dppe		30.4 (205)	395
[W(CO)$_4${PhHP(CH$_2$)$_2$PHPh}]	(i)	Improved preparation; *rac*- and *meso*-isomers		2.5 (223) (*meso*); 4.9 (223) (*rac*)	396
[W(CO)$_2$(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$(I)]I	(iii)			37.8 (160)	397
[W(CO)$_4$(*o*-H$_2$PC$_6$H$_4$PH$_2$)]	(ii)		2.47	−62.4 (212)	97
cis-[W(CNC$_6$H$_4$X-4)$_2$(dppe)$_2$]		X = –CN, –NC, CF$_3$, NO$_2$; *trans*-[W(N$_2$)$_2$(dppe)$_2$] + CNC$_6$H$_4$X	2.45 (–NC)	32.3 (190), 47.8 (269) (–NC)	398, 399
trans-[W(CNC$_6$H$_4$X-4)$_2$(dppe)$_2$]		X = F, Me, OMe; *trans*-[W(N$_2$)$_2$(dppe)$_2$] + CNC$_6$H$_4$X			399
[W(CO)$_3$(NCMe)(η^2-dppf)]	(ii)	[W(CO)$_3$(NCMe)$_3$] + dppf	2.56	22.4 (234)	
74	(ii)	[M] = FeCp, TiCl$_2$Cp	2.51 (Fe); 2.53 (Ti)	29.4 (232) (Fe); 33.6 (244) (Ti)	400, 401
[W(CO)(η^2-MeC≡CMe){PhP(CH$_2$CH$_2$PPh$_2$)$_2$-*P,P′*}I$_2$]	(iii)		2.48, 2.56		402
Diphosphine donors—bridging complexes					
[W(CO)$_5$(μ-**75**)W(CO)$_5$]	(ii)	*cis*- and *trans*-isomers synthesized	2.53 (*trans*)	30.4 (166) (*trans*)	403
[W(CO)$_5$(μ-dppm)W(CO)$_5$]	(ii)	2 [W(CO)$_5$(NH$_2$Ph)] + dppm or [W(CO)$_5$(η^1-dppm)] + [W(CO)$_5$(NH$_2$Ph)]	2.54		294
76		[MW(CO)$_4$Cp$_2$] + R$_2$PCH$_2$PR$_2$; M = W, R = Ph, Me; M = Mo, P = Ph			404, 405
77		R = Ph, Me; [W(CO)$_2$Cp(μ-R$_2$PCH$_2$PR$_2$)W(CO)$_2$Cp] + Δ	2.27 (Ph)	27.2 (421)	404
78		[W(CO)$_5$(η^1-Ph$_2$PXPPh$_2$)] + [Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$]; X = CH$_2$, NH	2.50 (X = CH$_2$)	12.2 (X = CH$_2$)	406,407
79		Na[W(CO)$_3$Cp] + [Ru(η^2-dppm)Cp(Cl)]	2.42		408
Other diphosphorus donors					
80		[W$_2$(CO)$_4$Cp$_2$] + (EtO)$_2$POP(OEt)$_2$; mixture of isomers	2.35	134.7 (512); 124.8	409
81	(ii)		2.58	−163	410
[W(CO)$_4$(Ph$_2$PNHPPh$_2$-*P,P′*)]	(i)		2.49	46.1 (208)	411
[W(CO)$_4${R$_2$PN(Me)N(Me)PR$_2$-*P,P′*}]	(ii)	R = Ph, CH$_2$CF$_3$	2.42 (R = Ph)	169.3 (373)	412
[W(CO)$_2$(L^1)(L^2){Ph$_2$PN(R)CH$_2$CH$_2$N(R)PPh$_2$-*P,P′*}]		R = Me, L^1 = L^2 = CO; R = Ts, L^1 = NO, L^2 = Br			288, 413

(*Continued*)

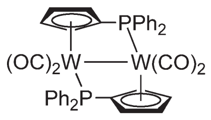
Table 9 (Continued)

Complex	*Synthesis*[a]	*Comments*	*W–P$_{av}$* (Å)	δ (WP)($^1J_{WP}$)[b]	*References*
Bidentate mixed donors					
82		Y = P, R^1 = Mes*, R^2 = Me; Y = N, R^1 = Cy, R^2 = NHCy			414, 415
[W(CO)$_4$(PR$_2$py-2-*P*,*N*)]		Photolysis of [W(CO)$_5$(PR$_2$py-2-*P*)]; R = Ph, NMe$_2$	2.54 (Ph); 2.51 (NMe$_2$)	−11 (196) (Ph); 85 (245)(NMe$_2$)	287
[W(CO)$_4$(Ph$_2$PC$_6$H$_4$R-2-*P*,*X*)]	(i)	R = NH$_2$, NHMe, NMe$_2$ (X = N); SMe (X = S)	2.32 (NH$_2$)	38.3 (240) (NH$_2$)	416, 417
[W(CO)$_2$(NO)(L)(Ph$_2$PC$_6$H$_4$R-2-*P*,*X*)]^z		R = O$^-$ (*X* = *O*, z = 0), L = PMe$_3$, PPhMe$_2$, PPh$_2$Me; R = CO$_2$$^-$ (*X* = *O*, z = 0), L = PMe$_3$, PPhMe$_2$, PPh$_2$Me; R = NH$^-$ (*X* = *N*, z = 0), L = PMe$_3$; R = NMe$_2$ (*X* = *N*, z = +1), L = CO	2.13 (NH)	27.3 (249)(PPh$_2$); −32 (251) (PMe$_3$)	416, 418
[W(CO)$_2${Ph$_2$P(py-2)-*P*}{Ph$_2$P(py-2)-*P*,*N*}NO]$^+$		[W(CO)$_2$(NCMe)$_3$(NO)][BF$_4$] + Ph$_2$P(py-2)			203
83		Photolysis of η^1-P-bound W(CO)$_5$ adduct	2.46	17.8 (248)	419
Polydentate phosphorus donors					
fac-[W(CO)$_3$(**84**-*P*,*P*′,*P*″)]	(ii)	P–W–P 83.75, 84.9, 85.5°	2.39–2.40	247 (237)	420
fac-[W(CO)$_3$(**85**-*P*,*P*′,*P*″)]	(ii)	P–W–P 84.8, 84.6, 88.5°	2.43–2.50	213.1	421
fac-[W(CO)$_3$(**86**-*P*,*P*′,*P*″)]	(ii)	P–W–P 98.2, 98.6, 99.1°	2.55–2.57	211.6 (228)	421
fac-[W(CO)$_3$(**87**-*P*,*P*′,*P*″)]		[W(CO)$_3$(H$_2$PCH$_2$CH=CH$_2$)$_3$] + AIBN; R = H		−80.1 (204)	422
[W(CO)(η^2-MeC≡CMe){PhP(CH$_2$CH$_2$PPh$_2$)$_2$-*P*,*P*′,*P*″}I]$^+$			2.52–2.53	66.8 (263), 32.5 (277)	423
[W(CO)(NCMe){PhP(CH$_2$CH$_2$PPh$_2$)$_2$-*P*,*P*′,*P*″}(≡CTol)]$^+$		PhP(CH$_2$CH$_2$PPh$_2$)$_2$ + [W(CO)$_2$(pyMe-4)$_2$-(≡CTol)Br]	2.48–2.51	80.9 (204), 47.7 (289)	424
Polydentate mixed donors					
mer-[W(CO)$_3$(**88**-*P*,*N*,*P*′)]	(ii)			45, 36.6 (313, 315)	101
fac-[W(CO)$_3$(**89**-*P*,*N*,*N*′)]	(ii)		2.48	31.7 (227)	425
fac-[W(CO)$_3$(**90**-*P*,*N*,*P*′)]	(ii)		2.50, 2.55	48.3 (223), 42.7 (250)	426
Bridging phosphide complexes					
[W(CO)$_5$(μ-PH$_2$)W(CO)$_5$]$^-$	(iv)	W–P–W 127°	2.58	−267.7 (146)	427
[W(CO)$_5$(μ-PPh$_2$)WCl{Me$_2$C(η^5-C$_5$H$_4$)$_2$}]	(iv)			−55.4 (193)	428
[W(CO)$_5$(μ-PPh$_2$)Fe(CO)(PMe$_3$)Cp]		[W(CO)$_5$(μ-PPh$_2$)Fe(CO)$_2$Cp] + PMe$_3$; W–P–Fe 119°	2.63	−4.4 (195)	429

[a] See text for synthetic methods.

[b] ^{31}P NMR; δ in ppm; J_{WP} in Hz in parentheses.

reported (e.g., 70–73), some of them analogous to the well known 1,1′-bis(diphenylphosphino)ferrocene (dppf) ligand.[390–394] These are prepared by reaction of the phosphine-containing ligand with a labile source of $W(CO)_n$.



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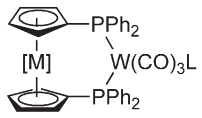

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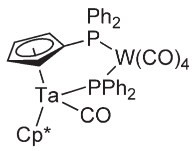
$[M] = Yb(THF)_3, L = CO$

$ZrCl_2, L = CNBu^t$



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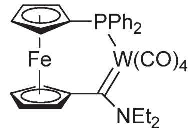

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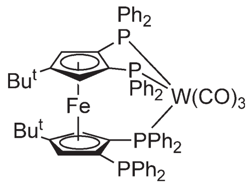

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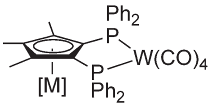

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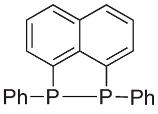

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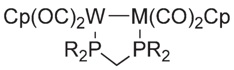

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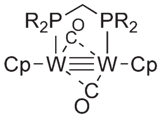

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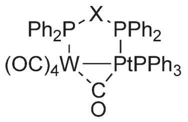

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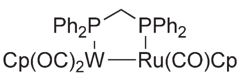

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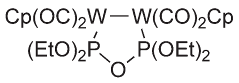

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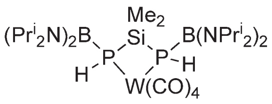

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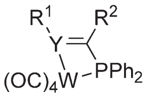

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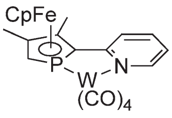

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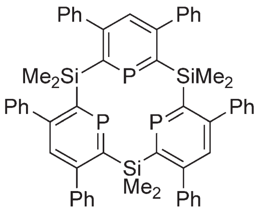

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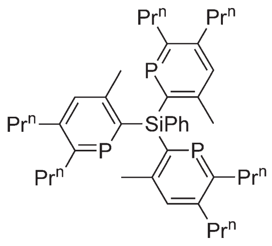

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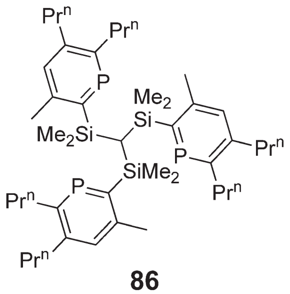

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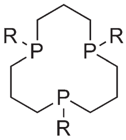

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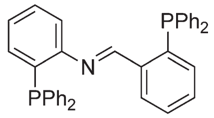

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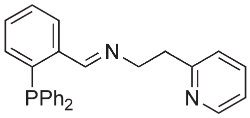

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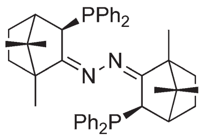

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5.08.4.2.1.(ii) Structure and properties

Table 9 lists W–P bond length information, for crystallographically characterized examples, and ^{31}P NMR chemical shifts for selected W–CO and W–CNR complexes bearing polydentate phosphorus ligands. The representative examples in Table 9 exhibit a range of coordination modes.

The effects of chelate size and substituent type on the donor ability of the diphosphine ligands in the complexes $[W(CO)_4(L_2)]$ {$L_2 = $dppm, dppe, dppp, dppb, dmpe, and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$} have been investigated by synchrotron radiation XPS and DFT calculations.[430] The chelate size has only a minor effect compared to the effects due to the nature of the substituents on the phosphorus center. The isocyanide complexes [W(dppe)$_2$(*p*-CNC$_6$H$_4$R)] can form *cis*- and *trans*-complexes depending on the electronic nature of the R substituent. Strong electron-withdrawing groups lead to the electronically stabilized, but sterically less favored, *cis*-conformation, whereas electron-donating substituents lead to the *trans*-conformation.[398,399] In the *cis*-[W(dppe)$_2$(*p*-CNC$_6$H$_4$R)] complexes the bound isocyanide ligand exhibits significant bending, with average C–N–C$_{\text{phenyl}}$ angles in the range 137–149°, whereas in the *trans*-complexes the isocyanide ligand remains approximately linear, a result of increased electron density on the nitrogen center of the isocyanide ligand in the *cis*-complexes.[399] Electrochemistry has been employed to study the effect on oxidation potentials of dppf-binding modes in the complexes [M(CO)$_5$(η-dppf)], [M(CO)$_4$(η^2-dppf)], and [M(CO)$_5$(μ-dppf)M′(CO)$_5$] (M = W, Mo, Cr; M′ = W, Mo, Cr).[431] Electrochemical studies have also examined the kinetics and thermodynamics of two-electron reduction of [{M(CO)$_4$}$_2$(μ-PPh$_2$)$_2$] (M–M) to [{M(CO)$_4$}$_2$(μ-PPh$_2$)$_2$]$^{2-}$ (M = W or Mo), which occurs with M–M bond cleavage.[432] Comparisons with structurally similar PhS$^-$-bridged analogs suggest that the bridging ligand type has a greater influence on electron-transfer energetics than the metal types.[432]

5.08.4.2.1.(iii) Reactions

Bimetallic complexes bridged by polyphosphine ligands, such as PhP(CH$_2$CH$_2$PPh$_2$)$_2$ and MeC(CH$_2$PPh$_2$)$_3$, can be readily prepared by the reaction of a W–CO complex, bearing a pendant (dangling) phosphine, with a labile metal precursor.[144,402,433–435] For example, the reaction of [W(CO)(η^2-MeC≡CMe){η^2-PhP(CH$_2$CH$_2$PPh$_2$)$_2$-*P*,*P*′}I$_2$] with [Mo(CO)$_3$(NCMe)$_2$I$_2$] affords [W(CO)(η^2-MeC≡CMe)I$_2${μ,η^2:η^1-PhP(CH$_2$CH$_2$PPh$_2$)$_2$-*P*,*P*′,*P*″}Mo(CO)$_3$-(NCMe)I$_2$].[402] The reaction of *fac*-[W(CO)$_3$(NCMe)(*o*-Ph$_2$PC$_6$H$_4$PPh$_2$-*P*,*P*′)] with C$_{60}$ affords only the *mer*-[W(CO)$_3$(η^2-C$_{60}$)(*o*-Ph$_2$PC$_6$H$_4$PPh$_2$-*P*,*P*′)] isomer.[436] The mechanistic processes of the reactions of *fac*-[W(CO)$_3$(NCMe)(η^2-dppf)] with dppm or dppe have been examined and compared with the reactions of dppf with *fac*-[W(CO)$_3$(NCMe)(η^2-dppm)] and *fac*-[W(CO)$_3$(NCMe)(η^2-dppe)].[437] A range of different products have been identified including various meridional and facial isomers. The complex *fac*-[W(CO)$_3$(NCMe)(η^2-dppf)] also reacts with PMe$_3$ or I$_2$ to form the substitution and oxidation products *fac*-[W(CO)$_3$(PMe$_3$)(η^2-dppf)] and [W(CO)$_3$(η^2-dppf)I$_2$], respectively.[438] Further oxidation of the iodide [W(CO)$_3$(η^2-dppf)I$_2$] with H$_2$O$_2$ affords the *P*,*O*-bound monophosphine oxide complex [W(CO)$_3${η^2-{Fe(η^5-C$_5$H$_4$PPh$_2$)(η^5-C$_5$H$_4$P(=O)Ph$_2$)}-*P*,*O*}I$_2$]. The phosphorus centers in the macrocyclic phosphine complex [W(CO)$_3$(**87**-*P*,*P*′,*P*″)] (R = H) can be functionalized to afford the complexes [W(CO)$_3$(**87**-*P*,*P*′,*P*″)] {R = CH$_2$SiMe$_3$, (CH$_2$)$_3$NH$_2$}, and the W(0) center can be oxidized to yield the W(II) complexes [W(CO)$_3$(**87**-*P*,*P*′,*P*″) X]X (X = I, Br; R = H), which can be converted into [W(CO)$_2$(**87**-*P*,*P*′,*P*′)X$_2$].[422,439]

The reactivity of the dppm-bridged W–W complex [{W(CO)$_2$Cp}$_2$(μ-dppm)] (W–W) is summarized in Scheme 27.[404,443–446] Similar reactivities are observed for dmpm complexes. In the case of the mixed Mo–W complex [{W(CO)$_2$Cp}(μ-dppm){Mo(CO)$_2$Cp}] (Mo–W) or the phosphite complex [{W(CO)$_2$Cp}$_2${μ-(EtO)$_2$POP(OEt)$_2$}](W–W), thermal decarbonylation leads to the phosphido complexes [{W(CO)Cp}(μ-Ph$_2$PCH$_2$-*P*,*C*)(μ-PPh$_2$){Mo(CO)Cp}] (Mo = W) and [{W(CO)Cp}$_2${μ-(EtO)$_2$PO-*P*,*O*}{μ-P(OEt)$_2$}] (W=W), respectively.[405,409] The W–Pt complex [{W(CO)$_4$}(μ-dppm)(μ-CO){Pt(PPh$_3$)}] (W–Pt) reacts with isocyanides to yield [{W(CO)$_3$(CNR)}(μ-dppm)-(μ-CO){Pt(PPh$_3$)}](W–Pt) or [{W(CO)$_4$}(μ-dppm)(μ-CNR){Pt(PPh$_3$)}] (W–Pt) depending on the nature of the isocyanide.[406]

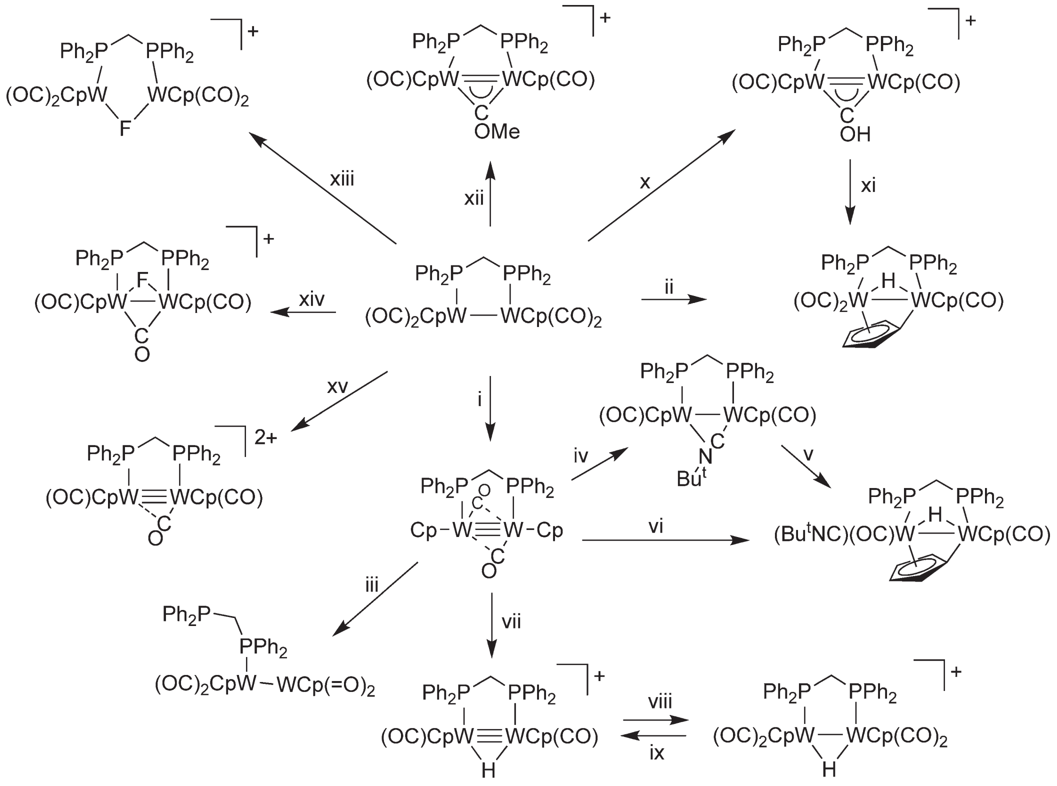
The substitution reactivity of the bridging phosphido complexes [{W(CO)$_2$Cp}(μ-PPh$_2$){M(CO)$_5$}](W–M) (M = W, Mo) is summarized in Scheme 28. Substitution reactions with diphosphines can produce mixtures of products.[381,382,384,440,441] Reaction of the phosphido complex [{W(CO)$_2$Cp}$_2$(μ-PH$_2$)]$^-$ (W–W) with ECl$_3$ (E = P, As, Sb) affords the “naked” PE complexes [{W(CO)$_2$Cp}$_2$(μ-η^2:η^2-PE)](W–W) (E = P, As, Sb). The reaction of these complexes with [W(CO)$_5$(THF)] leads to preferential binding of W(CO)$_5$ to the phosphorus atom of the PE moiety.[442]

5.08.4.2.2 Phosphinidene (bridging) and phosphene ligands

Developments in the area of W–CO complexes bearing bridging phosphinidenes and phosphenes, since COMC (1995), are discussed here. COMC (1982) and COMC (1995) provide important background information.

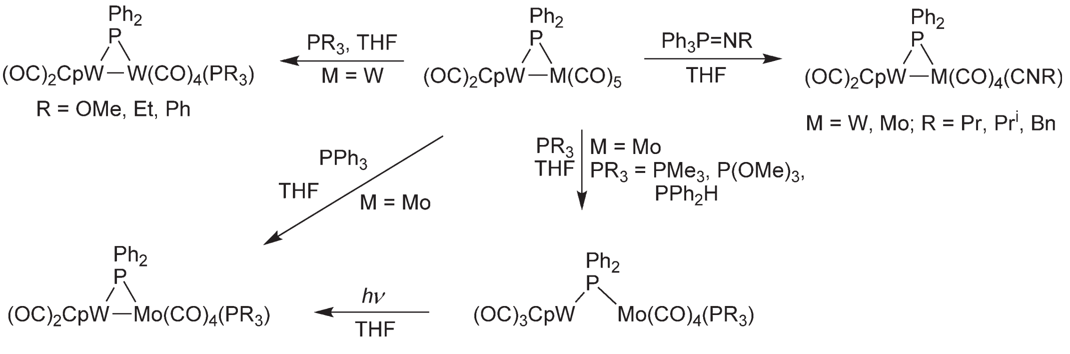
The diphosphene complex **91**, prepared by thermal decomposition of the **59** (R = Ph) in the presence of CuCl, reacts with unsaturated species to form various addition products (Scheme 29).[447,448] The reaction of Na$_2$[W$_2$(CO)$_{10}$] with PCl$_3$ affords, after workup, the dichlorodiphosphene complex **92**.[449]

The bridging phosphinidene complex [{W(CO)$_5$}$_2$(μ-PCp*)] has been structurally characterized (W–P = 2.44, 2.43 Å; W–P–W 125°).[450] Thermolysis or photolysis of [{W(CO)$_5$}$_2$(μ-PCp*)], in the absence or presence of unsaturated compounds (alkynes and nitriles), affords a range of W–CO complexes with different phosphorus-donor ligand

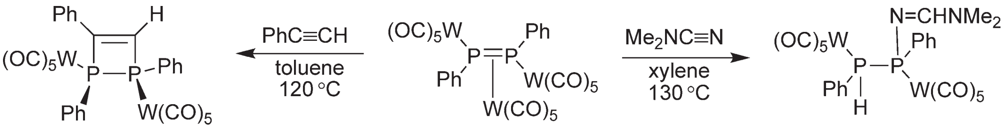


i, *n*-octane, reflux;**404** ii, *hν*, THF, 0 °C;**404** iii, air, THF;**404** iv, CNBu^t, THF, 0 °C;**404** v, RT;**404** vi, CNBu^t, THF, RT;**404** vii, $HBF_4{\cdot}Et_2O$, CH_2Cl_2, –30 °C;**443** viii, CO, CH_2Cl_2;**443** ix, *hν*, THF, –10 °C;**443** x, $HBF_4{\cdot}Et_2O$, CH_2Cl_2, –40 °C;**443** xi, dbu, CH_2Cl_2, –40 °C;**443** xii, $(Me_3O)BF_4$, CH_2Cl_2, RT;**443,444** xiii, $[Fc]BF_4$, CH_2Cl_2, –30 °C;**445** xiv, $[Fc]PF_6$, CH_2Cl_2;**445** xv, $[Fc]BAr'_4$ {Ar′ = $C_6H_3(CF_3)2$-3,5}, CH_2Cl_2**446**

Scheme 27



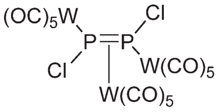
Scheme 28



91

Scheme 29

types including 93–95; postulated intermediates include the W–P–W complex $[W(CO)_5(\mu\text{-}P)\{W(CO)_3Cp^*\}]$ and the W≡P–W complex $[W(CO)_5\{P{\equiv}W(CO)_2Cp^*\}]$.[450–454] The reduction of $[W(CO)_5(PCl_3)]$ with magnesium affords the chlorophosphinidene $[\{W(CO)_5\}_2(\mu\text{-}PCl)]$ and P_4.[455]



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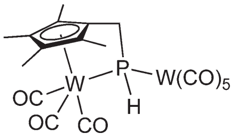

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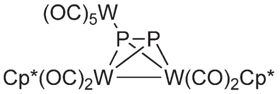

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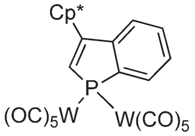

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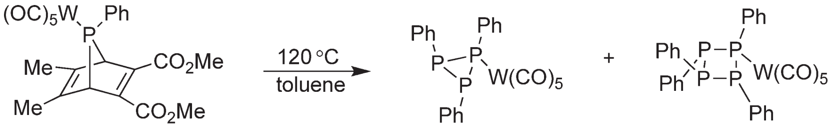
5.08.4.2.3 Complexes with phosphorus rich ligands or "naked" phosphorus ligands

This section contains W–CO complexes bearing ligands with three or more contiguously bound phosphorus atoms, or "naked" phosphorus ligands where P or P_2 species are bound to only metal centers. Representative examples appear in Table 10, along with synthetic details, core-structure information, ^{31}P NMR chemical shifts, and W–P bond length information for crystallographically studied complexes. Selected areas within this section have been reviewed.[378–380,456] Of particular note is the asymmetric linear coordination mode of the naked phosphorus in the W≡P–W complexes (see Table 10).

The thermal decomposition of the phosphanorbornadiene complex 96 over prolonged periods of time can form the P_3 and P_4 complexes 97 and 98 (Equation (16)).[447] Theoretical calculations have been performed on $[W(CO)_5(P_2)]$, which suggest end-on binding of the P_2 fragment is favored over side-on binding.[230] The tetrahedrane complex $[\{W(CO)_2Cp\}_3(\mu^3\text{-}P)]$ can react with O_2 or S_8 to afford the oxidized products $[\{W(CO)_2Cp\}_3(\mu^3\text{-}P{=}O)]$ and $[\{W(CO)_2Cp\}_3(\mu^3\text{-}P{=}S)]$, respectively, the oxidation with sulfur being reversible.[457,458] The electronic structure of the oxide complex has been examined by DFT calculations.[459] The reaction of $[W(CO)_3(\eta^6\text{-}MesH)]$ with P_7^{3-} affords $[W(CO)_3(\eta^4\text{-}P_7)]^{3-}$ (see Table 10 for core structure). The apical phosphorus atom on the complex can be alkylated and protonated.[460–463]



96 **97** **98**

(16)

5.08.5 Arsenic, Antimony, and Bismuth Ligands

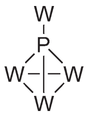
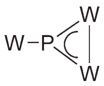
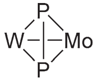
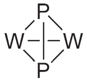
This section contains W–CO and W–CNR complexes bearing arsenic-, antimony-, and bismuth-donor ligands, including ER_3-, ER_2-, ER-ligands (E = As, Sb, Bi) and As-, Sb- or Bi-rich or "naked" ligands. In general, the synthesis, structure, and reactivity of complexes in this section share many similarities with those of their phosphorus analogs. Reviews relevant to this section have covered the areas of coordination complexes with organoantimony and Sb_n ligands,[470] complexes with arsenic– and antimony–metal triple bonds,[380] As_n ligands,[379] and transition metal cluster complexes with group 15 elements.[378]

There are numerous examples of W–CO complexes bearing $AsPh_3$ or $SbPh_3$, particularly, W(II)–CO complexes such as $[W(CO)_3(NCMe)(AsPh_3)I_2]$, which is a versatile precursor for the synthesis of complexes bearing additional donor types.[103,141,471] In addition to their synthesis, complexes such as $[W(CO)_3(NCMe)(EPh_3)X_2]$ (E = P, As, Sb; X = halide) and $[W(CO)_3(NCMe)(AsPh_3)I_2]$ have been explored for their catalytic activity.[116,472] The synthesis and reactivity of these types of complexes will not be covered further in this section.

5.08.5.1 Synthesis

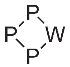
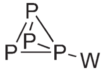
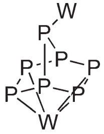
Table 11 details selected examples of W–CO complexes bearing arsenic-, antimony-, and bismuth-donor ligands, along with synthetic details. In general, the synthetic methods for the preparation of ER_3 complexes follow

Table 10 Examples of W–CO complexes with phosphorus-rich or "naked" phosphorus ligands

Complex	*Synthesis*	*Core structure*	$W\text{–}P_{av}$ (Å)	δ (WP)(J_{WP})[a]	*References*
$[\mathrm{W(CO)_5}(\mu^4\text{-P})\{\mathrm{W(CO)_2Cp}\}_3]$			2.59 {P-W(CO)$_5$}; 2.43-2.48 {P–WCp}		457,464
$[\{\mathrm{W(CO)_2}(\eta^5\text{-C}_5\mathrm{H_4Bu^t})\}_2\{\mu\text{-PW(CO)}_3(\eta^5\text{-C}_5\mathrm{H_4Bu^t})\}]$			2.30, 2.49	690 (60, 247)	455
$[\mathrm{W(CO)_4}\{\mathrm{P{\equiv}W}\{\mathrm{N(CH_2CH_2NSiMe_3)_3}\text{-}N,N',N'',N'''\}_2\}]$	$[\mathrm{W(CO)_5(THF)}] + [\mathrm{P{\equiv}W}\{\mathrm{N(CH_2CH_2NSiMe_3)_3}\text{-}N,N',N'',N'''\}]$	W≡P–W–P≡W	2.46 (P–W), 2.20 (P≡W)	679.8 (426, 151)	465
$[\mathrm{W(CO)_5}\{\mathrm{P{\equiv}W(OBu^t)_3}\}]$	$[\mathrm{(Bu^tO)_3W{\equiv}W(OBu^t)_3}] + [\mathrm{W(CO)_5(THF)}] + \mathrm{MesC{\equiv}P}$	W≡P–W	2.48 (P–W), 2.13 (P≡W)	546.0 (553, 163)	466, 467
$[\{\mathrm{W(OAr)_2}\}_2\{\mu\text{-PW(CO)}_5\}_2]$	$[\mathrm{W(CO)_5}\{\mathrm{P{\equiv}W(OAr)_3(THF)}\}]$ + toluene, RT, 4d; $\mathrm{Ar = C_6H_3Me_2}$-2,6		2.49 {P–W(CO)$_5$}; 2.28 {P–W(OAr)$_2$}	558.2	467
$[\mathrm{W(CO)_2Cp}(\mu\text{-}\eta^2{:}\eta^2\text{-P}_2)\mathrm{Mo(CO)_2Cp}]$	$[\{\mathrm{Mo(CO)_3Cp}\}_2] + [\mathrm{W(CO)_2Cp}(\eta^3\text{-P}_3)]$; mixture of products			−244.8	457
$[\{\mathrm{W(CO)_2Cp}\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-P}_2)]$	$[\{\mathrm{W(CO)_3Cp}\}_2] + [\mathrm{W(CO)_2Cp}(\eta^3\text{-P}_3)]$; major product		2.47, 2.56	−299.0	457

(*Continued*)

Table 10 (Continued)

Complex	*Synthesis*	*Core structure*	*W–P$_{av}$* (Å)	δ (WP)(J_{WP})[a]	*References*
$[W(CO)_4\{PBu^t(PHBu^t)_2\}]$	$[W(CO)_5(THF)] + Bu^tP(PHBu^t)_2$		2.512	−67.0	468
$[W(CO)_3(PCy_3)_2(\eta\text{-}P_4)]$	$[W(CO)_3(PCy_3)_2] + P_4$		2.46 (W-P$_4$)	−422 (W–P$_4$)	321
$[W(CO)_3(\mu\text{-}\eta^4{:}\eta\text{-}P_7)W(CO)_3(en)]^{3-}$	$[W(CO)_3(\eta^4\text{-}P_7)]^{3-} + [W(CO)_3(\eta^6\text{-}MesH)]$/en		2.643 (η^1-P-W); 2.60, 2.67 (η^4-P–W)		469

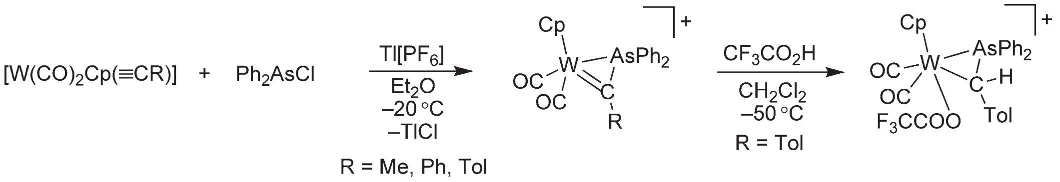
[a] ^{31}P NMR; δ in ppm; J_{WP} in Hz in parentheses.

Table 11 Examples of W–CO complexes with arsenic-, antimony-, and bismuth-donor ligands

Complex	*Synthesis/comments*	*W–E$_{av}$* (Å)	*References*
$[W(CO)_3(NCR)(EPh_3)I_2]$	$[W(CO)_3(NCR)_2I_2] + EPh_3$; E = As, Sb; R = Et, Bu^t, Ph	2.64 (E = As, R = Et)	103
$[W(CO)_5(EPh_3)]$	$[W(CO)_5(THF)] + EPh_3$; E = As, Sb, Bi	2.62 (As), 2.75 (Sb), 2.83 (Bi)	484,485
$[W(CO)_5(\eta\text{-}AsH_2BH_2\cdot NMe_3)]$	$Li[W(CO)_5(AsH_2)] + ClBH_2\cdot NMe_3$	2.64	292
$[W(CO)_4\{\eta^2\text{-}o\text{-}(Me_2SbCH_2)_2C_6H_4\}]$	$[W(CO)_4(pip)_2] + o\text{-}(Me_2SbCH_2)_2C_6H_4$		486
$[\{W(CO)_4\}_2(\mu\text{-}R_2SbCH_2SbR_2)_2]$	$[W(CO)_4\{Me_2N(CH_2)_3NMe_2\}] + R_2SbCH_2SbR_2$; R = Me, Ph	2.75 (Ph)	487
$[W(CO)_3\{\eta^3\text{-}MeCH_2(CH_2SbPh_2)_3\}]$	$W(CO)_6 + MeCH_2(CH_2SbPh_2)_3/NaBH_4/EtOH$		488
$[W(CO)_3Cp^*\{Sb(CF_3)_2\}]$	$[W(CO)_3Cp^*(H)] + Sb(CF_3)_3$	2.81	489
$[\{W(CO)_5\}_2(\mu\text{-}BiPh_2)]^-$	$[W_2(CO)_{10}]^{2-} + Ph_2BiCl$	2.89	490
$[\{W(CO)_5\}_2(\mu\text{-}AsCp^*)]$	$Na_2[W_2(CO)_{10}] + Cp^*AsCl_2$	2.55	475
101	R = CH_2SiMe_3	3.07	479
$[W(CO)_5\{SbH_2CH(SiMe_3)_2\}]$	$[W(CO)_5THF] + SbH_2CH(SiMe_3)_2$	2.76	491
$[\{W(CO)_5\}_2\{\mu\text{-}R(H)SbSb(H)R\}]$	R = $CH(SiMe_3)_2$; *meso*- and DL isomers	2.778 (*meso*)	491
104	$[\{W(CO)_2Cp\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PE)] + [W(CO)_5(THF)]$; E = As, Sb	2.59, 2.69 (As)	442
105	$[Co_2(CO)_6(\mu\text{-}\eta^2{:}\eta^2\text{-}As_2)] + [W(CO)_3Cp\{Co(CO)_4\}]$	2.58, 2.63	492
106	$[W(CO)_5(THF)] + cyclo\text{-}(RSbSe)_n$ (n = 2 and 3 in equilibrium)	2.75	493
107	Pentacoordinate Sb	2.765	494

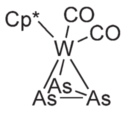
conventional procedures. The arsine complex $[W(CO)_5(AsH_3)]$ has been prepared by the reaction of $[W(CO)_5(THF)]$ with $As(SiMe_3)_3$ followed by alcoholysis in a one-pot procedure, a method that avoids the direct use of gaseous arsine.[281] Reaction of the carbyne complexes $[W(CO)_2Cp(\equiv CR)]$ with Ph_2AsCl affords η^2-arsinocarbene complexes, which can react with CF_3CO_2H (Scheme 30).[473,474]

The reaction of Cp^*AsCl_2 with $Na_2[W_2(CO)_{10}]$ afforded the bridging arsenidene complex $[\{W(CO)_5\}_2(\mu\text{-}AsCp^*)]$, thermolysis and photolysis of which gave a range of structurally characterized species including **99**, the As≡As complex $[\{W(CO)_5\}_3(\mu\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}As_2)]$ as well as two distorted W_4As_4 heterocubanes.[475] Possible intermediates in these reactions include $[W(CO)_5\{As{\equiv}W(CO)_2Cp^*\}]$ and $[\{W(CO)_5\}_2(\mu\text{-}As)]$. The reaction of $CpSbCl_2$ with $Na_2[W_2(CO)_{10}]$ also afforded a range of species including $[\{W(CO)_5\}_2(\mu\text{-}SbCl_2)]^-$, $[\{W(CO)_5\}_3(\mu^3\text{-}SbCl)]$, and $[\{W(CO)_5\}_3(\mu\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}Sb_2)]$.[476] Reaction of $[W(CO)_5(THF)]$ with *cyclo*-$(RBi)_n$ {R = *o*-$C_6H_4(CH_2NMe_2)$; n = 3 and 4 in equilibrium} afforded the intramolecularly stabilized bismuthidene complex **100** (W–Bi$_{av}$ 2.83 Å), the analogous reaction with *cyclo*-$(RSb)_4$ {R = *o*-$C_6H_4(CH_2NMe_2)$} afforded the Sb analog of **100** (W–Sb$_{av}$ 2.75 Å).[477,478] The reaction of *cyclo*-$(RBi)_n$ (R = CH_2SiMe_3 or CH_2CMe_3, n = 3 and 5 in equilibrium) with $[W(CO)_5(THF)]$ afforded **101**, which decomposed to **102**.[479,480] The cyclostibanes, *cyclo*-$\{SbCH(SiMe_3)_2\}_3$ and *cyclo*-$(SbCH_2SiMe_3)_5$, react with $[W(CO)_5(THF)]$ to afford the structurally characterized $[W(CO)_5\{SbCH(SiMe_3)_2\}_3]$ and $[\{W(CO)_5\}_2\{\mu\text{-}(SbCH_2SiMe_3)_5\text{-}Sb^1,Sb^3\}]$, respectively.[481,482] The reaction of E_7^{3-} (E = As, Sb) with $[W(CO)_3(\eta^6\text{-}MesH)]$ afforded



Scheme 30

$[W(CO)_3(\eta^4\text{-}E_7)]^{3-}$ with a norbornadiene-like η^4-E_7 ligand.[460] The reaction of $Na_2[W_2(CO)_{10}]$ with $[Fe(CO)_2(\eta^5\text{-}C_5H_3Bu^t{}_2)(BiCl_2)]$ afforded the W_2Bi_3 cluster **103**.[483]



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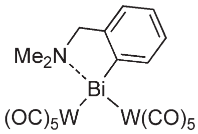

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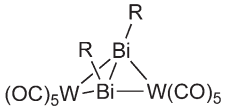

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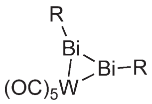

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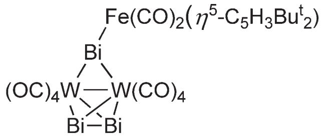

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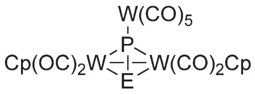

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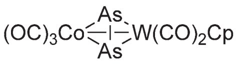

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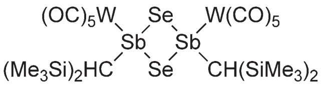

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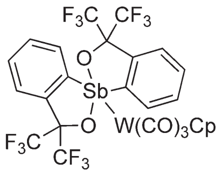

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5.08.5.2 Structure and Properties

Examples of structurally characterized W–CO complexes bearing arsenic-, antimony-, or bismuth-donor ligands are detailed in Table 11. Many of the structural features of the complexes in this section are similar to their phosphorus analogs.

The complete series $[M(CO)_5(EPh_3)]$ (M = Cr, Mo, W; E = P, As, Sb, Bi) has been structurally and spectroscopically (^{13}C NMR and IR) characterized.[484,485] The distibinomethane ligands $R_2SbCH_2SbR_2$ (R = Ph, Me) can form $M(CO)_n$ (M = Cr, Mo, W) complexes with monodentate and bridging binding modes; however, unlike their phosphorus and arsenic analogs, no examples of $M(CO)_n$ complexes exist in which the distibinomethane ligands bind in a chelate manner.[487] Theoretical studies on $[W(CO)_5(E_2)]$ (E = As, Sb, Bi) suggests that side-on binding of the E_2 fragment to the tungsten center is preferred over end-on coordination.[230]

5.08.5.3 Reactions

The arsine complex $[W(CO)_5(AsH_3)]$ undergoes oxidative addition reactions with $[Pt(PPh_3)_2(H_2C{=}CH_2)]$ to afford *cis*- and *trans*-isomers of $[W(CO)_5(\mu\text{-}AsH_2)PtH(PPh_3)_2]$.[281] The arsine complex can also be deprotonated with Bu^{n}Li to afford the isolable $Li[W(CO)_5AsH_2]$, which can be further functionalized at the As center.[292] The antimony complex $[W(CO)_5\{\mu\text{-}R(H)SbSb(H)R\}W(CO)_5]$ (R = $CH(SiMe_3)_2$) can be dehydrogenated to yield $[W(CO)_5(\eta^2\text{-}RSbSbR)]$.[491]

5.08.6 Oxygen Ligands

This section includes a range of neutral and anionic oxygen-donor ligands, including, ethers, ketones, alcohols, phosphine oxides, alkoxides, carboxylates, hydroxides, oxides, carbonates, and nitrites. One of the most commonly used and prepared oxygen-donor complexes is $[W(CO)_5(THF)]$, which is used as a labile source of $W(CO)_5$. Examples of $[W(CO)_5(THF)]$ as a reactive precursor will not be explicitly covered; however there are recent reports on more fundamental studies of W–CO complexes involving THF, including formation and binding modes as well as alkylated and dehydro (e.g., 2-MeTHF, 2,5-dihydrofuran, 2-methylfuran) derivatives.[495–501]

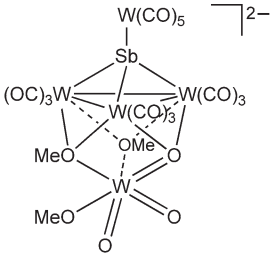
5.08.6.1 Synthesis

Examples of a range of complexes with oxygen-donor ligands in a variety of binding modes are given in Table 12. Typical synthetic methods are also detailed in Table 12.

The reaction of $[W(CO)_6]$ with $NaSbO_3$ in methanol yields the mixed carbonyl–alkoxide–oxide cluster **108**, which contains terminal and bridging alkoxide and oxide ligands.[502] Oxides are also common ligands in heterometallic clusters (e.g., **109**).[503] The synthesis of chelating imidazolidinone/oxazolidinone–carbene complexes **110** has been recently reviewed.[504]

Table 12 Examples of W–CO and W–CNR complexes with oxygen donor ligands

Ligand	*Complex*	*Synthesis/comments*	*W–O$_{av}$* (Å)	*References*
R_2O	$[W(CO)_3(OEt_2)(C_5Me_5)]^+$	$[W(CO)_3Me(C_5Me_5)] + HBAr_4/Et_2O$	2.197	506
ROR^2	$[W(CO)_3\{O(Me)Bn\}Cp]^+$	$[W(CO)_3(H)Cp] + PhCH(OMe)_2/TfOH$	2.206	507
ROH	$[W(CO)_3(HOPr^i)Cp]^+$	$[W(CO)_3(H)Cp] + Me_2CO/TfOH$	2.176	508
OR	$[W(CO)_2(phen)(OMe)(C_3H_5)]$	$[W(CO)_2(phen)Cl(C_3H_5)] + NaOMe$	2.031	509
OR	$[W(CO)_4(o\text{-}O_2C_6H_2Bu^t{}_2\text{-}3,5)]^{2-}$	Coordinatively unsaturated	2.16	510
OR	$[W(CNR)_4(OC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}Me_2)_2]$	$R = 2,6\text{-}C_6H_3Me_2$	2.01	71
μ-OR	$[\{W(CO)_2(\equiv NPh)I\}_2(\mu\text{-}OMe)_2]$		2.093	195
μ-OR	$[W(CO)_3(\mu\text{-}Opy\text{-}3)_3W(CO)_3]^{3-}$	$[W(CO)_3(\mu\text{-}OMe)_3W(CO)_3]^{3-} + 3\text{-}HOpy$	2.22	511
μ^3-OR	$[W(CO)_3(\mu^3\text{-}OMe)]_4{}^{4-}$	$[W(CO)_4(\mu\text{-}OMe)_2W(CO)_4]^{2-} + \Delta$	2.21	512
η-O_2CR	$[W(CO)_4\{NH_2CH(Bu^t)CO_2\text{-}N,O\}]$	$[W(CO)_5(THF)] + [NH_2CH(Bu^t)CO_2]^-$	2.18	90
η^2-O_2CR	$[W(CO)_2(PPh_3)_2Br(\eta^2\text{-}O_2CCF_3)]$	$[W(CO)_2(PPh_3)_2Br_2] + NaO_2CCF_3$		513
μ-C_2O_4	$[\{W(CO)_2(PMe_2Ph)_2Br\}_2(\mu\text{-}C_2O_4)]$	$[W(CO)_2(NCMe)(PMe_2Ph)_2Br_2] + Na_2C_2O_4$	2.19	513
acac	$[W(CO)_2(PEt_3)_2I(acac)]$	$[W(CO)_3(PEt_3)_2I_2] + Na(acac)$	2.14	514
η-HC(=O)R	$[W(CO)_3\{HC(=O)Ph\}Cp]^+$	$[W(CO)_3(H)Cp] + PhCOCl/TfOH$; σ-bound aldehyde	2.179	515
η^2-HC(=O)R	$[W(CO)_2\{o\text{-}HC(=O)C_6H_4PPh_2\text{-}P,C,O\}_2]$	π-Bound aldehyde	2.06	131
η-O=CRR^2	$[W(CO)(MeC\equiv CMe)\{O=C(Me)Et\}Tp]^+$	$[W(CO)(MeC\equiv CMe)(Me)Tp] + HBAr_4/MeCOEt$		516
$O=PR_3$	$[W(CO)_5(O=PPh_3)]$	W–O–P angle 134.3°	2.244	517
η-O_2COH	$[W(CO)_5(O_2COH)]^-$	$[W(CO)_5(acetone)] + HCO_3{}^-$	2.19	518
η-O	$[W(CO)(NCMe)Tp'(=O)]^+$		1.781	139
η-O	$[W(CO)(\eta^1\text{-}S_2PPh_2)Tp'(=O)]$	$[W(CO)_2(\eta^1\text{-}S_2PPh_2)Tp'] +$ pyridine *N*-oxide	1.702	519
μ^3-O	**109**		1.942	503
η^2-NO_2	$[W(CO)_2(PPh_3)_2(O,O\text{-}NO_2)_2]$	$[W(CO)_2(PPh_3)_2Br_2] + NaNO_2$		520



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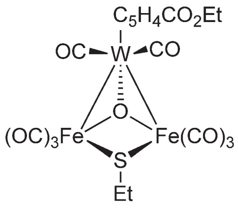

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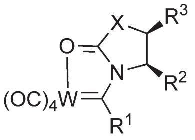

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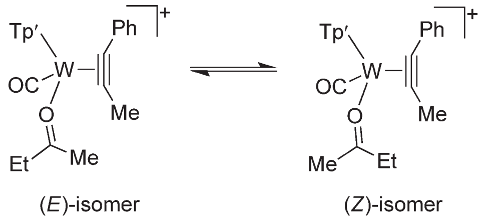
X = O, R^1 = Me, R^2 = R^3 = H
X = O, R^1 = propenyl, R^2 = Me, R^3 = Ph
X = NMe, R^1 = propenyl, R^2 = Ph, R^3 = Ph

Laser-ablated W atoms reacted with CO_2 to give a number of species including W(CO)O and $W(CO)_2O_2$, which have been trapped using matrix isolation and identified by their spectroscopic properties.[505]

5.08.6.2 Structure and Properties

Table 12 details a range of oxygen-donor types with different binding modes, including terminal and bridging ligands and varying hapticity, and lists associated W–O bond distances. Clearly, a diverse range of structures are possible, particularly with alkoxide ligands. Theoretical studies have investigated structure and ligand-dissociation energies for a range of $[W(CO)_5L]$ complexes bearing oxygen-donor ligands, including OH_2, OC (isocarbonyl), OH^-, SO_2, CH_2O, and CO_2.[8,521–523]



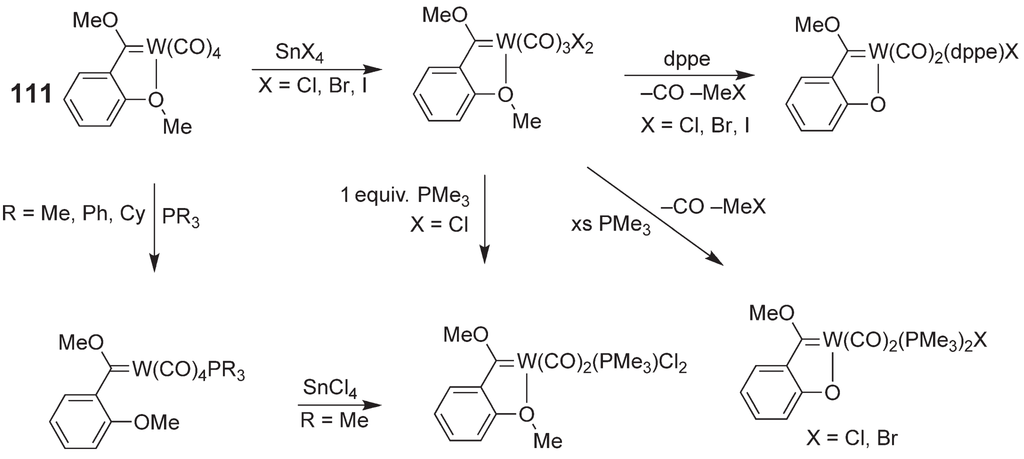
Scheme 31

Complexes of ketones and aldehydes exhibit interesting structural features. The complexes $[\mathrm{W(CO)(PhC{\equiv}CMe)\{O{=}C(Me)Et\}Tp'}]^+$ and $[\mathrm{W(CO)(MeC{\equiv}CMe)\{O{=}C(Me)Et\}Tp}]^+$ display E/Z-isomers for the σ-bound ketones (e.g., Scheme 31).[516] The barrier to E/Z-interconversion is higher for the more sterically demanding Tp′ complexes and are higher for the tungsten complexes compared to their molybdenum analogs. In the case of similar aldehyde complexes, $[\mathrm{W(CO)(PhC{\equiv}CMe)\{\eta\text{-}O{=}C(H)Et\}Tp'}]^+$ and $[\mathrm{W(CO)(MeC{\equiv}CMe)\{\eta^2\text{-}O{=}C(H)Et\}Tp}]^+$, σ-($\eta^1$)- and π-($\eta^2$)-bound aldehyde complexes are observed.[524] It is interesting to note that *p*-anisaldehyde binds to the $[\mathrm{M(CO)(MeC{\equiv}CMe)Tp}]$ (M = Mo, W) fragment as a σ-bound ligand in the case of Mo and as π-bound ligand in the case of W.[525]

The W(II) triflate complex $[\mathrm{W(CO)_5(OTf)}]\mathrm{OTf}$[526] has been used as a Lewis acid catalyst for allylic substitution and intramolecular carbonyl ene cyclization reactions.[527,528] The ketone complex $[\mathrm{W(CO)_2(PPh_3)(O{=}CEt_2)Cp}]^+$ acts as a catalyst precursor for the hydrogenation of $\mathrm{Et_2CO}$ under mild conditions.[529]

5.08.6.3 Reactions

The reactivity of complexes bearing oxygen-donor ligands is diverse. The chelating ether–carbene complex **111** undergoes oxidation and substitution reactions to yield a range of W(0) and W(II) complexes (Scheme 32).[530–532] The carbyne complex $[\mathrm{W(CO)_2L({\equiv}CTol)}]$ ($\mathrm{L = CpCo\{P(OMe)_2{=}O\}_3^-}$), bearing a tripodal oxygen ligand, can be readily oxidized with $\mathrm{PhICl_2}$, $\mathrm{O_2}$, or $\mathrm{S_8}$ to give $[\mathrm{WCl_2L({\equiv}CTol)}]$, $[\mathrm{\{WO_2L\}_2(\mu\text{-}O)}]$, and $[\mathrm{W(CO)_2L(\eta^2\text{-}S_2CPhMe)}]$, respectively, where $\mathrm{L = CpCo\{P(OMe)_2{=}O\}_3}^-$.[533,534] Hydride addition to the aldehyde complex $[\mathrm{W(CO)(O{=}CHBu^t)(PhC{\equiv}CMe)Tp'}]^+$ gives the alkoxide complex $[\mathrm{W(CO)(OCH_2Bu^t)(PhC{\equiv}CMe)Tp'}]$, whereas reaction of hydride with the ketone complex $[\mathrm{W(CO)\{O{=}C(Me)Bu^t\}(PhC{\equiv}CMe)Tp'}]^+$ affords the enolate complex $[\mathrm{W(CO)\{OC({=}CH_2)Bu^t\}(PhC{\equiv}CMe)(Tp')}]$.[535] The hydroxide complex $[\mathrm{W(CO)_5OH}]^-$ inserts $\mathrm{CO_2}$, COS, or $\mathrm{CS_2}$ to afford $[\mathrm{W(CO)_5\{O_2COH\}}]^-$, $[\mathrm{W(CO)_5\{SC(O)OH\}}]^-$, and $[\mathrm{W(CO)_5\{S_2COH\}}]^-$, respectively.[518,536] While the reaction with $\mathrm{CO_2}$ is reversible, the insertion reactions of COS and $\mathrm{CS_2}$ are irreversible. The bridging methoxide complex $[\mathrm{W(CO)_3(\mu\text{-}OMe)_3W(CO)_3}]^{3-}$ undergoes ligand-exchange reactions with alcohols that are more acidic than methanol; thus, reaction with *p*-$\mathrm{HOC_6H_4NH_2}$, *p*-$\mathrm{HOC_6H_4CN}$, or *m*-HOpy affords $[\mathrm{W(CO)_3(\mu\text{-}OR)_3W(CO)_3}]^{3-}$, where OR = *p*-$\mathrm{OC_6H_4NH_2}$, *p*-$\mathrm{OC_6H_4CN}$, and *m*-Opy, respectively.[511]



Scheme 32

5.08.7 Sulfur, Selenium, and Tellurium Ligands

In this section, unless otherwise indicated, E will to refer to sulfur, selenium, or tellurium, since there are many examples of ligands with thio, seleno, and telluro analogs. The chemistry of sulfur, selenium, and tellurium ligands is divided into three sections: neutral, anionic, and elemental ligands. Neutral ligands include thiols, ER_2, E_2R_2, $E{=}CR_2$, and $E{=}PR_3$ species, CS_2, SO_2, and the zwitterionic R_3PCS_2. Anionic ligands include thiolates, thiocarboxylates, thiocarbamates, dithiophosphates, and dithiophosphinates, and their seleno and telluro analogs. Complexes containing "naked" sulfur, selenium, and tellurium ligands are most conveniently treated separately, even though they can be considered as anionic E^{2-} (or the oligomeric E_n^{m-}) ligands in many cases.

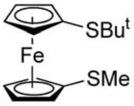
Recently reviewed areas include the chemistry of mixed phosphorus–sulfur-donor ligands,[375] metal carbonyl complexes bridged by S, Se, or Te,[537] S- and Se-bridged cubane-type clusters,[538] coordination chemistry of complexes with EH^- (E = S, Se, Te) or H_2S ligands,[539,540] the coordination chemistry of S_2CPR_3,[541] the coordination chemistry of ER_2 (E = Se, Te),[542] tellurium-based ligands,[543] and dithiolene chemistry.[544]

5.08.7.1 Synthesis

5.08.7.1.1 Complexes with neutral ligands

Selected examples of W–CO complexes bearing neutral S-, Se-, and Te-donor ligands are detailed in Table 13. The synthetic methods employed to prepare these complexes generally follow conventional ligand substitution methods.

(i) CO substitution on $[W(CO)_6]$ using thermal, photolysis or chemical (*N*-oxide mediated CO oxidation) methods.
(ii) Ligand displacement from labile W(0) precursors $[W(CO)_5(THF)]$, $[W(CO)_3(NCMe)_3]$, $[W(CO)_4(nbd)]$, and $[W(CO)_4(pip)_2]$, and related species.
(iii) Ligand displacement from labile W(II) precursors $[W(CO)_3(NCMe)_2X_2]$, $[W(CO)(NCMe)(\eta^2\text{-PhC}{\equiv}\text{CPh})_2X_2]$, $[W(CO)_3(PPh_3)({\equiv}CPh)X]$, $[W(CO)_2(py)_2({\equiv}CPh)Cl]$, and $[W(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)Br]$ and related species. Some alternative methods are detailed in COMC(1995).[545]



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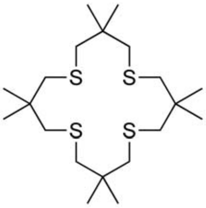

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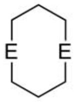

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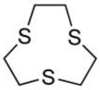

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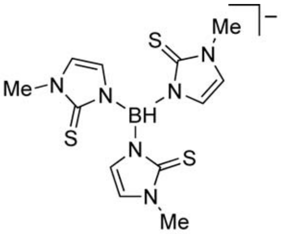

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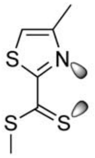

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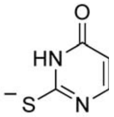

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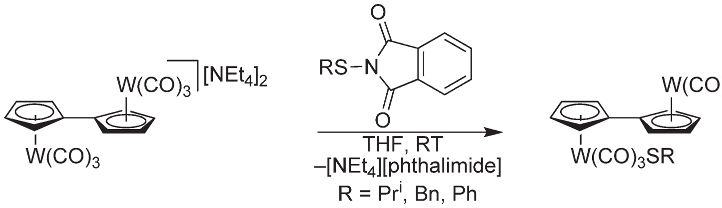
The reaction of $[W(CO)_5(THF)]$ with $S(chpt)_2$ (chpt = 2,4,6-cycloheptatriene) at room temperature yields $[W(CO)_5\{S(chpt)_2\}]$, and at elevated temperatures yields the isomerized product $[W(CO)_5\{S(chpt)(Bn)\}]$.[546]

5.08.7.1.2 Complexes with anionic ligands

Selected examples of W–CO and W–CNR complexes bearing anionic S-, Se-, and Te-donor ligands are detailed in Table 14. The synthetic procedures used for the neutral ligands are commonly used for the anionic ligands, and thus reference to the synthetic methods in Table 14 includes the methods mentioned previously in Section 5.08.7.1.1 (i.e., (i), (ii), and (iii) above). Additional synthetic methods include the following.

(iv) The oxidative addition of disulfides, diselenides, or ditellurides to low-valent W–CO complexes.
(v) Reaction of elemental S or Se with W–H or anionic W species (e.g., Scheme 33[575]).
(vi) Substitution (metathesis) of W-bound halides with –ER or HER.
(vii) Insertion of CS_2 into W–C or W–N bonds to form thiocarboxylates or thiocarbamates.

An alternative to the oxidative addition with disulfides ((iv) above) involves the formal oxidative addition of thiophthalimides to W(0) species to form W(II) thiolate complexes (Equation (17)).[576]



(17)

Table 13 Examples of W–CO complexes of ligands with neutral S, Se, and Te ligands

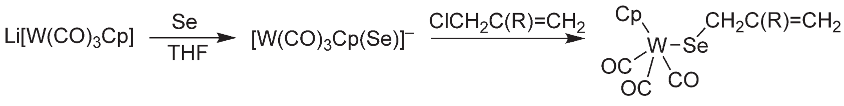
Complex	*Synthesis*[a]	*Comments*	*W–E*$_{av}$ (Å)	*References*
Thioethers and related donors				
$[W(CO)_5\{S(\text{chpt})_2\}]$	(ii)	$[W(CO)_5(\text{THF})] + S(\text{chpt})_2$ at RT	2.573	546
$[W(CO)_5(\text{DBT})\}]$	(i)	DBT = dibenzothiophene	2.580	547
$[W(CO)_5(\mathit{cis}\text{-}\overline{\text{SCHMeC}}\text{HMe})]$	(ii)		2.56	548
$[W(CO)_5(\overline{\text{SSCH}_2\text{CH}{=}\text{CHC}}\text{H}_2)]$		from $[W(CO)_5(\text{NCMe})]$ + vinylthiirane	2.549	549, 550
$[W(CO)_3\{\text{PhS}(CH_2)_2\text{SPh}\text{-}S,S'\}Br_2]$	(iii)		2.557, 2.573	551
$[W(CO)\{\text{MeS}(CH_2)_2S(CH_2)_2\text{SMe}\text{-}S,S'\}(\eta^2\text{-PhC}{\equiv}\text{CPh})I_2]$	(iii)		2.470, 2.574	552
$[W(CO)_4\{\text{RE}(CH_2)_3\text{ER}\text{-}E,E'\}]$	(ii)	E = Te, R = Me, Ph; E = S or Se, R = Me		553
$[W(CO)_4\{o\text{-}C_6H_4(CH_2\text{TeMe})_2\text{-}Te,Te'\}]$	(ii)	Invertomers present in solution	2.791	554
$[W(CO)_4(\mathbf{112}\text{-}S,S')]$	(ii)			555
$[W(CO)_4\{\text{PPh}_2(o\text{-}C_6H_4\text{SMe})\text{-}P,S\}]$	(i)		2.527	417
$[W(CO)_2(\mathbf{113}\text{-}S,S',S'',S''')I]^+$	(ii)	Isolated with $[W(CO)_3(\mathbf{113}\text{-}S,S',S''')I]^+$	2.545-2.618	556
$[W(CO)_4(\mathbf{114}\text{-}E,E')]$	(ii)	E = S, Se	2.650 (Se)	557, 558
$[W(CO)_3(\mathbf{115}\text{-}S,S',S'')I]^+$	(iii)		2.51, 2.55	559
$[W(CO)_2(\mathbf{115}\text{-}S,S',S'')({\equiv}\text{CPh})]^+$	(iii)			177
$[W(CO)_3\{\text{MeC}(CH_2\text{EMe})_3\text{-}E,E',E''\}]$	(ii)	E = S, Se, Te		560
$[W(CO)_3\{\text{MeSi}(CH_2\text{SMe})_3\text{-}S,S',S''\}]$	(ii)	S_3 ligand is displaced in CH_3CN	2.57	561
$[W(CO)_3\{\text{BuSn}(CH_2\text{SMe})_3\text{-}S,S',S'\}]$	(ii)		2.574	176
Thioketones and related donors				
$[W(CO)_3I(\mathbf{116}\text{-}S,S',S'')]$		$I_2 + [W(CO)_3(\mathbf{116})]^-$	2.528–2.597	562
$[W(CO)_2({\equiv}\text{CR})(\mathbf{116}\text{-}S,S',S'')]$	(iii)	R = $\text{NPr}^i{}_2$, C≡C-Bu^t	2.534–2.635	563
$[W(CO)_3(\text{dmpe})(\eta^2\text{-S}{=}\text{CHR})]$		R = H, Et, Bu^i, Ph	2.498	564, 565
$[W(CO)_4(\mathbf{117}\text{-}N,S)]$	(ii)			566
$R_3P{=}E$ donor complexes				
$[W(CO)_5(E{=}\text{PPh}_3)]$		E = S, Se	2.601 (S), 2.718 (Se)	517
$[W(CO)_3\{\text{Ph}_2P(S)CH_2P(S)\text{Ph}_2\text{-}S,S'\}X_2]$	(iii)	X = Br, I		551, 567
$[W(CO)_4\{\text{Ph}_2P(E)N(\text{Ph})\text{PPh}_2\text{-}P,E\}]$	(ii)	E = S, Se		568
SO_2 complexes				
$[W(CO)(\text{phen})(\eta^2\text{-}SO_2\text{-}S,O)(\text{SPh})_2]$		$[W(CO)_2(\text{phen})(\text{SPh})_2] + SO_2$	2.486 (SO_2)	569
$[W(CO)_2(\text{MeCp})(\mu\text{-}SO_2\text{-S})(\mu\text{-CO})\text{Ni}(C_5Me_5)]$		$[W(\text{MeCp})(\mu\text{-CO})_3\text{Ni}(C_5Me_5)] + SO_2$	2.441	570
$\mathit{mer}\text{-}[W(CO)_3(\text{dppe})(\eta\text{-}SO_2\text{-}S)]$	(ii)	$\mathit{fac}\text{-}[W(CO)_3(\text{dppe})(\text{NCMe})] + SO_2$	2.258	571
CS_2 complexes				
$[W(CO)_5(\mu\text{-}\eta^1{:}\eta^2\text{-}CS_2\text{-}S{:}C,S')\text{Fe}(CO)_2(\text{PPh}_3)_2]$	(i)	$[\text{Fe}(CO)_2(\text{PPh}_3)_2(\eta^2\text{-}CS_2)] + [W(CO)_6]$	2.531	572
R_3PCS_2 complexes				
$[W(CO)_2(\eta^3\text{-}C_3H_5)\text{Br}(\eta^2\text{-}S_2\text{CPR}_3)]$	(iii)	R = Cy, Pr^i		573
$[W(CO)_2(\eta^3\text{-}C_3H_5)(\mu\text{-}\eta^2{:}\eta^3\text{-}S_2\text{CPR}_3)\text{Co}(CO)_2]$		$[W(CO)_2(\eta^3\text{-}C_3H_5)\text{Br}(\eta^2\text{-}S_2\text{CPR}_3)] + [\text{Co}_2(CO)_8]$; R = Cy, Pr^i		574

[a] See text for synthetic methods.

Table 14 Examples of W–CO and W–CNR complexes of ligands with anionic S, Se, and Te ligands

Complex	*Synthesis*[a]	*Comments*	*W–E$_{av}$* (Å)	*References*
Monodentate thiolates and related donors				
$[\mathrm{W(CO)_5}(\mathbf{118}\text{-}S)]^-$	(ii)		2.553	577
$[\mathrm{W(CO)_2(phen)(SPh)_2}]$	(iv)		2.361	245
119	(v)	R = H, Me	2.63	575
$[\mathrm{W(CO)_2(Tp')(SBn)}]$	(vi)		2.298	578
$[\mathrm{W(CO)_3(SH)(C_5R_5)}]$	(v)	$[\mathrm{W(CO)_3(H)(C_5R_5)}] + \mathrm{S_8}$ (R = H) or $\mathrm{Ph_3Sb{=}S}$ (R = H, Me)	2.522 (R = Me)	579
cis-$[\mathrm{W(CNMe)_4(SC_6H_2Pr^i_3\text{-}2,4,6)_2}]$		$[\mathrm{W(PMe_2Ph)_2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3}] + \mathrm{CNMe}$	2.395	580
$[\mathrm{W(CNBu^t)(SBu^t)_3(Cp^*)}]$		$[\mathrm{W(SBu^t)_3(Cp^*)}] + \mathrm{CNBu^t}$	2.338–2.458	581
$[\mathrm{W(CNBu^t)_3(SeBu^t)(Cp^*)}]$		$[\mathrm{WCl_4(Cp^*)}] + \mathrm{LiSeBu^t/CNBu^t}$	2.627	582
$[\mathrm{W(CO)Cp(EAr)_3}]$	(vi)	E = Se, Ar = $\mathrm{C_6F_5}$; E = S, Ar = Ph, $\mathrm{C_4H_4Me\text{-}4}$, $\mathrm{C_6F_4H\text{-}4}$		583, 584
Polydentate thiolates and related donors				
$[\mathrm{W(CO)_3(2\text{-}Sepy\text{-}}Se,N)_2]$	(iv)		2.635, 2.658	154
$[\mathrm{W(CO)_4(}o\text{-}\mathrm{S_2C_6H_4}\text{-}S,S')]^{2-}$			2.548	97
$[\mathrm{W(CO)_4}(\mathbf{118}\text{-}S,N)]^-$	(ii)			577
$[\mathrm{W(CO)_2(dppe)(}o\text{-}\mathrm{S_2C_6H_4)}]$	(vi)	$[\mathrm{W(CO)_3(dppe)I_2}] + o\text{-}\mathrm{(HS)_2C_6H_4}$	2.38	585
$[\mathrm{W(CO)_2(PEt_3)_2\{S(CH_2)_3S}\text{-}S,S'\}]$	(vi)	$[\mathrm{W(CO)_3(PEt_3)_2I_2}] + \mathrm{Na_2[S(CH_2)_3S]}$	2.403	586
$[\mathrm{W(CO)_2\{S_2C_2Me_2}\text{-}S,S'\}_2]^z$		$z = 0, 1-, 2-$	2.376 ($z = 0$), 2.452 ($z = 2-$)	587, 588
$[\mathrm{W(CO)Cp({\equiv}CNEt_2)\{S_2C_2(CN)_2}\text{-}S,S'\}]$	(vi)		2.45	589
Bridging thiolates and related donors				
$[\{\mathrm{W(CO)_4}\}_2(\mu\text{-}\mathrm{SPh})_2]$		$[\mathrm{W(CO)_4(}\mu\text{-}\mathrm{SPh)_2W(CO)_4}]^{2-} + \mathrm{I_2}$	2.476	590
$[\{\mathrm{W(CO)_2(C_5H_4R)}\}_2(\mu\text{-}\mathrm{TePh})_2]$	(iv)	$[\mathrm{W(CO)_2(C_5H_4R){\equiv}W(CO)_2(C_5H_4R)}] + \mathrm{PhTeTePh}$; R = $\mathrm{CO_2Et}$	2.806	591
$[\mathrm{W(CO)Cp(}\mu\text{-}\mathrm{SPh)_2(}\mu\text{-}\mathrm{PPh_2)Mo(CO)_3}]$		Thiolate transfer to $[\mathrm{W(CO)_2Cp(}\mu\text{-}\mathrm{PPh_2)Mo(CO)_5}]$	2.469, 5.505	592
$[\mathrm{W(CO)_5(}\mu\text{-}\mathrm{SPh)Fe(CO)_2Cp}]$	(ii)	From $[\mathrm{Fe(CO)_2Cp(SPh)}]$	2.582	593
Thiocarboxylates and thiocarbamates				
$[\mathrm{W(CO)_4(}\eta^2\text{-}\mathrm{S_2CNC_5H_{10})}]^-$	(vii)		2.586	594
$[\mathrm{W(CO)_2(}\eta^2\text{-}\mathrm{S_2CTol\text{-}4)Tp}]$		$[\mathrm{W(CO)_4({\equiv}CTol\text{-}4)Br}] + \mathrm{S_8} + \mathrm{KTp}$		158
Thiophosphates and thiophosphinates				
$[\mathrm{W(CO)_2Tp'\{}\eta\text{-}\mathrm{S_2P(OPr^i)_2\}}]$	(vi)		2.361	595
$[\mathrm{W(CO)_4\{}\eta^2\text{-}\mathrm{S_2P(OEt)_2\}}]^-$	(ii)		2.610	596, 597
$[\mathrm{W(CO)_2(dppe)I\{}\eta^2\text{-}\mathrm{S_2P(OEt)_2\}}]$	(iii)		2.609	598
$[\mathrm{W(CO)_2Tp'(}\eta\text{-}\mathrm{S_2PPh_2)}]$	(vi)			599

[a] See text for synthetic methods.



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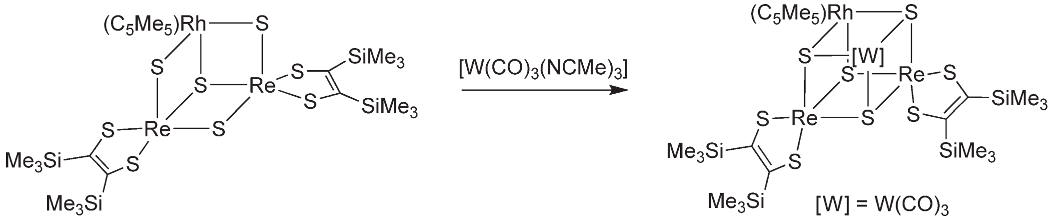
Scheme 33

5.08.7.1.3 Complexes with "naked" sulfur, selenium, and tellurium ligands

Sulfido, selenido, and tellurido (E^{2-}) ligands can bind to metal centers in a number of different ways, for example, terminal-binding (W=E), dinuclear-bridging (μ-E) and trinuclear- and tetranuclear-bridging (μ^3-E and μ^4-E); thus, the synthetic methodologies for such complexes are diverse. Representative examples of sulfido, selenido, and tellurido terminal ligands, dinuclear-bridging and oligomeric ligands $\{(\mathrm{E}_m)^{n-}\}$, including synthetic details, are listed in Table 15. Trinuclear- and tetranuclear-bridging ligands (μ^3-E and μ^4-E) constitute part of the central core for a large range of heterometallic clusters. Some examples of the synthesis of these types of clusters are given in Equations (18)–(21),[600–603] and further examples of the various core structure types are given in Table 16.



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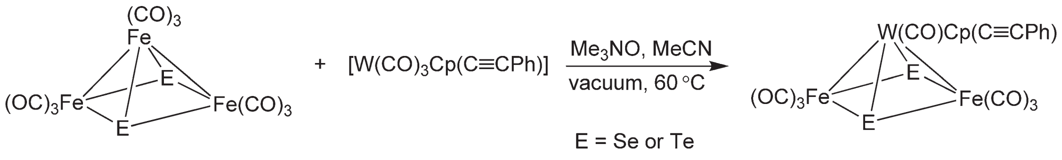

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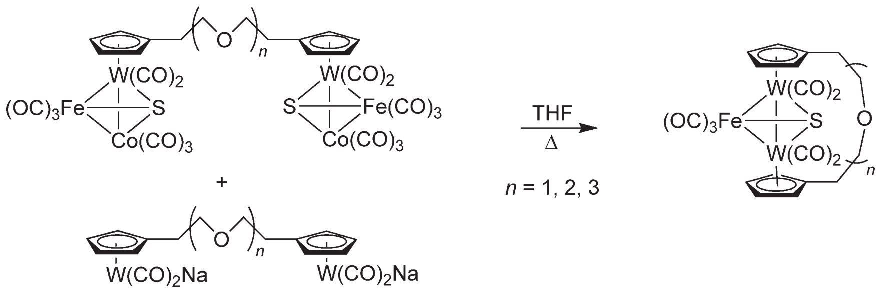

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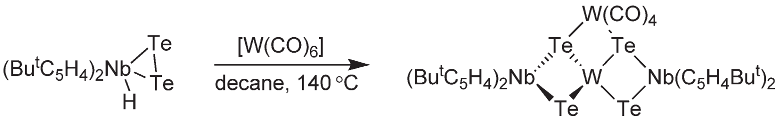


(21)

Table 15 Examples of W–CO and W–CNR complexes with "naked" S, Se, and Te ligands

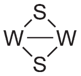
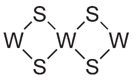
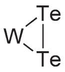
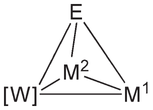
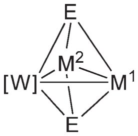
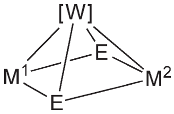
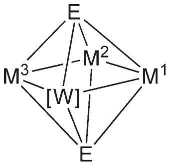
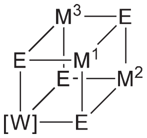
Complex	*Synthesis*	*Core structure*	*W–E$_{av}$* (Å)	*References*
Terminal binding				
[W(CNBu^t)$_2$(PMe$_3$)$_2$(=E)$_2$]	[W(PMe$_3$)$_4$(=E)$_2$] + Bu^{t}NC; E = S, Se	W=E	2.248 (S), 2.375 (Se)	604
[W(CO)(η-S$_2$PPh$_2$)(Tp′)(=S)]	[W(CO)(η^2-NCMe)(η-S$_2$PPh$_2$)(Tp′)] + propylene sulfide	W=S	2.132 (W=S)	519
Dinuclear bridging				
[{W(CO)$_2$Tp′}$_2$(μ-S)]	[W(CO)$_3$XTp′] + propylene sulfide; X=H, Br	W–S–W	2.181	180
[W(CO)$_3$(μ-S)$_2$W(=S)Tp′]$^-$	[W(CO)$_3$(NCMe)$_3$] + [W(=S)$_3$Tp′]		2.408	605
[W(CO)$_4$(μ-S)$_2$W(μ-S)$_2$-W(CO)$_4$]$^{2-}$	[W(CO)$_6$] + Na$_2$S$_2$		2.51 (WS$_2$), 2.21 (WS$_4$)	606
Oligomeric ligands				
[W(CNBu^t)$_4$(PMe$_3$)(η^2-Te$_2$)]	[W(PMe$_3$)$_4$(=Te)$_2$] + Bu^{t}NC		2.868, 2.877	604
[{W(CO)$_3$Cp}$_2$(μ-Se$_n$)]	[W(CO)$_3$CpLi] + Se + SiO$_2$; n = 2, 3, 4	W–(Se)$_n$–W	2.64	607, 608

Table 16 Core structures of selected W–CO clusters with μ^3-E and μ^4-E (E = S, Se, and Te) ligands

Core structure	*Variations*	*References*
	$[W] = W(CO)(\equiv CAr)Cp$; $M^1 = M^2 = Fe(CO)_3$; E = Te	609
	$[W] = W(CO)_2(C_5H_4R)$; $M^1 = Ru(CO)_3$; $M^2 = NiCp$; E = S	610
	$[W] = W(CO)_2(C_5H_4R)$; $M^1 = Ru(CO)_3$; $M^2 = Co(CO)_3$; E = Se	611
	$[W] = W(CO)_2(C_5H_4R)$; $M^1 = Co(CO)_3$; $M^2 = Fe(CO)_3$; E = S	612
	$[W] = W(CO)_4$; $M^1 = W(CO)_3$; $M^2 = Cr(CO)_3$; E = Te	613
	$[W] = W(CO)Cp(C\equiv CPh)$; $M^1 = M^2 = Fe(CO)_3$; E = Se	601
	$[W] = W(CO)_4$; $M^1 = M^2 = Fe(CO)_3$; E = S	614
	$[W] = M^2 = W(CO)_2(\mu\text{-}CO)_2$; $M^1 = M^3 = Ru(CO)PPh_3$; E = Se	615
	$[W] = W(CO)_2(\mu\text{-}CO)_2$; $M^1 = M^3 = Ru(CO)PPh_3$; $M^2 = Ru(CO)_2(\mu\text{-}CO)_2$ E = Se	616
	$[W] = W(CO)_3$; $M^1 = M^2 = M^3 = Fe(SMes)$; E = S	617
	$[W] = W(CO)_3$; $M^1 = M^2 = M^3 = MoCp$; E = S	618
	$[W] = W(CO)_3$; $M^1 = Ir(C_5Me_5)$; $M^2 = M^3 = Re\{SC(SiMe_3){=}C(SiMe_3)S\text{-}S,S'\}$; E = S″	600

5.08.7.2 Structure and Properties

5.08.7.2.1 Complexes with neutral ligands

Table 13 lists selected W–E bond lengths for W–CO complexes bearing neutral S, Se, or Te ligands. The table also reveals that many of the neutral donors can bind in a range of different modes, for example, thioketone-type donors can bind in an end-on or side-on fashion. SO_2 can bind to metals in η^1-*S*, η^2-*S,O* and bridging modes. Reaction of *fac*-$[W(CO)_3(dppe)(NCMe)]$ with SO_2 initially yields *fac*-$[W(CO)_3(dppe)(\eta^2\text{-}SO_2\text{-}S,O)]$, which isomerizes to *mer*-$[W(CO)_3(dppe)(\eta\text{-}SO_2\text{-}S)]$.[571] Likewise, CS_2 can bind to metal centers in a variety of ways. Theoretical studies have examined the equilibrium geometries of CS_2 binding to the $W(CO)_5$ fragment, and suggest an end-on binding mode that is favored in this case.[522] The zwitterionic ligands R_3PCS_2 can bind to a single metal center in an η^2-*S,S′* or η^3-*C,S,S′* fashion but can also bridge two metal centers in an η^2-*S,S′* : η^3-C,*S,S′* fashion.[573,574,619] Combined structural, spectroscopic, and theoretical studies of W–CO complexes bearing neutral O-, S-, Se-, and Te-donor ligands indicate that σ-donor bonding to low-valent metals increases in the order O < S < Se < Te.[517,553] In complexes bearing bidentate ligands of the type RE–R^1–ER, slow pyramidal inversion of the atom E can lead to invertomer mixtures that are identifiable by NMR.[553] For example, in a solution of the complex $[W(CO)_4\{o\text{-}(MeTeCH_2)_2C_6H_4\}]$, DL and *meso*-isomers were identified.[554] Other NMR solution studies have examined the dynamics of chair/boat conformational changes in W–CO complexes of 1,5-dithiacyclooctane.[557]

The $W(CO)_5$ complexes of cyclic thioethers exhibit catalytic activity involving ring-opening chemistry, for example, $[W(CO)_5(\overline{SCH_2C}H_2)]$ and $[W(CO)_5(\overline{SCH_2CHMeC}H_2)]$ catalyze the formation of macrocyclic polydisulfides from thiirane (ethylene sulfide) and macrocyclic polythioethers from 3-methylthietane, respectively.[548,550,620] A study of the enthalpies of protonation of $[W(CO)_3(L_3)]$ complexes, where L_3 represents tridentate ligands with N-, P-, or S-donor atoms, suggests that thioether groups can behave as donors that are nearly as strong as phosphine groups, a result that may be due to the additional lone pair of electrons on the sulfur atom.[114]

5.08.7.2.2 Complexes with anionic ligands

Table 14 lists W–E bond lengths for W–CO and W–CNR complexes bearing anionic S, Se, and Te ligands. Of particular note from Table 14, thiolates, and their selenate and tellurate analogs, can adopt terminal and bridging binding modes similar to those of alkoxides, and thiophosphinates and thiophosphates can bind in η^1- or η^2-modes.

Coordinatively unsaturated, $16e^-$ $W(CO)_3$ complexes bearing thiolate ligands have been studied experimentally and theoretically.[97,231] Theoretical studies of $[W(CO)_3(S_2C_2H_2)]^{2-}$ suggest that the stability of the $16e^-$ species is due to a combination of $L \rightarrow W$ π-donation and the ability of the anionic ligand to increase the bond strength of the three W–CO bonds.[231] Experimental and theoretical studies into the $16e^-$ complexes $[W(CO)_3(o\text{-}XYC_6H_4\text{–}X,Y)]^{2-}$ (X,Y = NH,NH; NH,O; O,O; NH,S; O,S; S,S) conclude that, as the π-donation ability of the ligands decreases (N > O > S), the energy difference between the saturated $18e^-$ complexes $[W(CO)_4(o\text{-}XYC_6H_4\text{–}X,Y)]^{2-}$ and the unsaturated $16e^-$ species increases. More forceful conditions were required to remove CO from the $18e^-$ $[W(CO)_4(o\text{-}XSC_6H_4\text{–}X,S)]^{2-}$ (X = N, O, S) to form unsaturated $16e^-$ species than in the case of non-thiolate-bearing complexes.[97]

The enthalpies of insertion of sulfur from $Ph_3Sb{=}S$ and S_8 into the W–H bond of $[W(CO)_3(C_5R_5)H]$ (R = H, Me) have been determined by solution calorimetry.[579] Desulfurization of the resulting $[W(CO)_3(C_5R_5)SH]$ (R = H, Me) with PCy_3 occurred only when R = H. The M–SH bond strength estimates for $[M(CO)_3(C_5Me_5)SH]$ increase in the order Cr < Mo < W.[579]

The isostructural bis(dithiolene) series $[W(CO)_2\{S_2C_2Me_2\}_2]^z$ ($z = 0, 1-, 2-$) have been isolated.[588] Geometric and electronic properties over the three oxidation states have been examined by structural, spectroscopic, and DFT studies. The studies indicate that electron-transfer reactions in the series are mainly ligand-based processes. In the case of $[W(CO)_2\{S_2C_2Me_2\}_2]^{2-}$, bond distances indicate that the dithiolene ligand approaches an ene-dithiolate structure and the metal oxidation state can be assigned as W(II).

5.08.7.2.3 Complexes with "naked" sulfur, selenium, and tellurium ligands

As mentioned above "naked" sulfido, selenido, and tellurido (E^{2-}) ligands can bind to W–CO and W–CNR species in a diverse manner. In particular, there are numerous examples of different cluster cores containing μ^3-E and μ^4-E moieties. Selected examples of the different binding modes are given in Tables 15 and 16. Table 15 also details selected W–E bond distances for the different binding modes.

5.08.7.3 Reactions

5.08.7.3.1 Complexes with neutral ligands

Complexes with coordinated SO_2 and R_3PCS_2 display interesting reactivities. The SO_2 complex $[W(CO)(phen)(SO_2)(SPh)_2]$ extrudes sulfur with concomitant loss of CO to produce $[W(phen)(SPh)_2(O)_2]$.[569] The reaction of diazomethane with *fac*-$[W(CO)_3(dppe)(\eta^2\text{-}SO_2)]$ or *mer*-$[W(CO)_3(dppe)(\eta\text{-}SO_2)]$ yields the sulfene (thioformaldehyde *S,S*-dioxide) complex *mer*-$[W(CO)_3(dppe)(\eta^2\text{-}CH_2SO_2\text{-}C,S)]$.[571] The complex $[W(CO)_2(\eta^2\text{-}S_2CPCy_3\text{-}S,S')(C_3H_5)Br]$ bearing a bidentate S_2CPR_3 ligand can react with $Co_2(CO)_8$ or $[M(CO)_3(NCR)_3]$ (M = W, R = Et; M = Mo, R = Me) to form $[W(CO)_2(C_3H_5)(\mu\text{-}\eta^2{:}\eta^3\text{-}S_2CPCy_3\text{-}S,S'{:}C,S,S')Co(CO)_2]$ and $[W(CO)_2(C_3H_5)(\mu\text{-}\eta^2{:}\eta^3\text{-}S_2CPCy_3\text{-}S,S'{:}C,S,S')(\mu\text{-}Br)M(CO)_3]$ (M = W, Mo), respectively. In each product, the S_2CPR_3 acts as a bridging ligand between the two metal centers.[573,574]

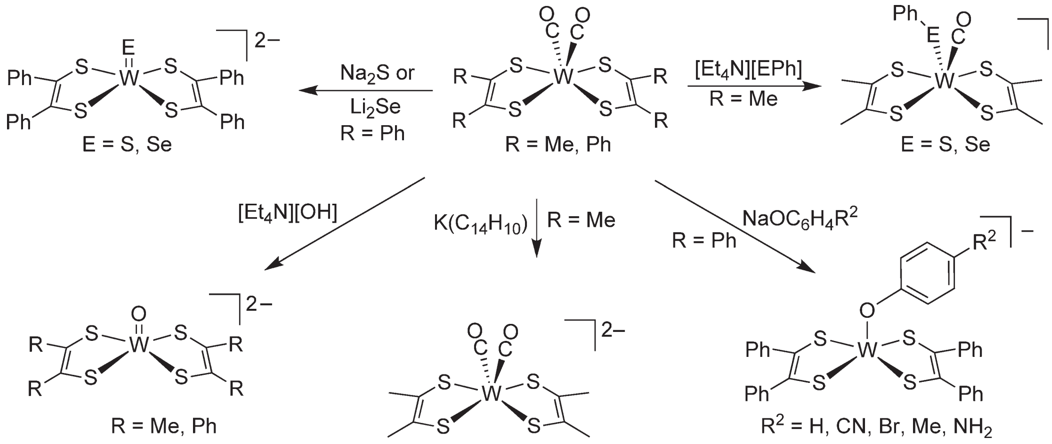
5.08.7.3.2 Complexes with anionic ligands

Complexes bearing anionic ligands undergo a wide range of reactions, both at the metal centers and on the coordinated E atom.

Complexes bearing thiolate ligands can be subjected to thiol-/thiolate-exchange reactions. The thiolate complex $[W(CO)_2(phen)(SBu^t)_2]$ reacts with 2 equiv. of thiophenol to form $[W(CO)_2(phen)(SPh)_2]$, which can react with 1 equiv. of 3,4-toluenedithiol to form $[W(CO)_2(phen)(o\text{-}S_2C_6H_3Me\text{-}4)]$.[245,247]

Hydrosulfide complexes, for example, $[W(CO)_3(dmpe)SH]^-$, can react with formaldehyde and aromatic and aliphatic aldehydes to form η^2-thioaldehyde complexes $[W(CO)_3(dmpe)(\eta^2\text{-}S{=}CHR)]$.[564,565] The thioaldehyde complexes can be methylated to form $[W(CO)_3(dmpe)(\eta^2\text{-}MeS\text{–}CHR\text{–}S,C)]^+$, and subsequent hydride addition yields the thioether complexes $[W(CO)_3(dmpe)(MeSCH_2R)]$.[565]

The fulvalene thiolate complexes $[\{W(CO)_3(SR)\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (R = Pr^i, Bn, Ph) react with CS_2 to yield the thioxanthate complex $[\{W(CO)_3(S_2CSR)\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$.[576] The bis(dithiolene) complexes $[W(CO)_2(S_2C_2R_2)_2]$ (R = Me, Ph) can react to produce a diverse range of species; typical reactions are summarized in Scheme 34.[587,588,621–623]

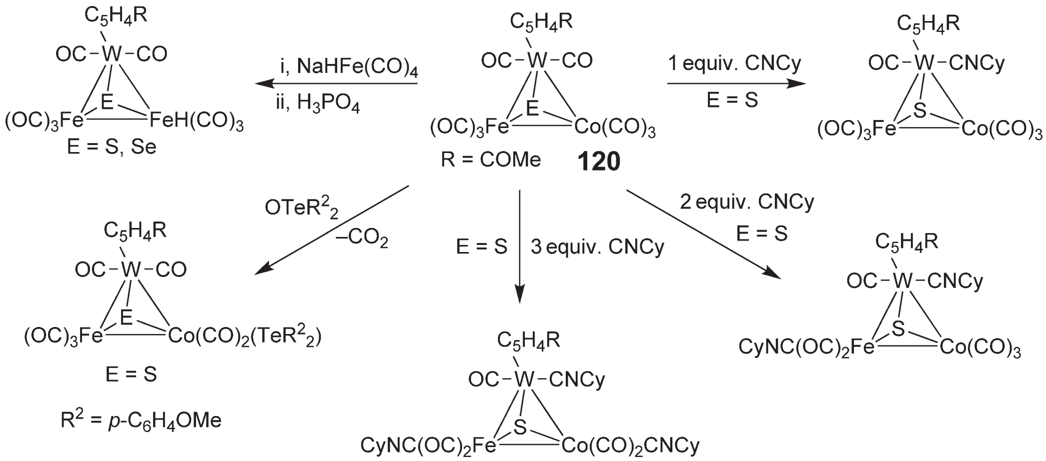


Scheme 34

Thiophosphinate, thiophosphate, and thiocarbamate carbonyl complexes of W(II) can undergo oxidation chemistry to produce W(IV) and W(VI) complexes; $[W(CO)_2Tp'(S_2PPh_2)]$ reacts with pyridine *N*-oxide to produce $[W(CO)Tp'(S_2PPh_2)({=}O)]$, or $[WTp'(S_2PPh_2)({=}O)_2]$ when pyridine *N*-oxide is used in excess.[519,599] The η^2-MeCN complex $[W(CO)(\eta^2\text{-NCMe})Tp'(S_2PPh_2)]$ reacts with propylene sulfide to yield $[W(CO)Tp'(S_2PPh_2)({=}S)]$, which can subsequently react with pyridine *N*-oxide to form $[WTp'(S_2PPh_2)({=}S)({=}O)]$.[519,624,625] Using a similar methodology, $[W(CO)_2Tp'(S_2CNEt_2)]$ and $[W(CO)Tp'\{S_2P(OEt)_2\}({=}S)]$ react with pyridine *N*-oxide to form $[WTp'(\eta^2\text{-}S_2CNEt_2)({=}O)]$ and $[WTp'\{S_2P(OEt)_2\}({=}S)({=}O)]$, respectively.[625,626] A CO ligand in $[W(CO)_2Tp'(S_2CNEt_2)]$ can be displaced by phenylacetylene to yield $[W(CO)(\eta^2\text{-PhC{\equiv}CH})Tp'(\eta\text{-}S_2CNEt_2)]$, the reaction occurring in refluxing 1,2-dichloroethane. The analogous reaction with 2-butyne-1,4-diol produces $[W(CO)(\eta^2\text{-HOCH}_2C{\equiv}CCH_2OH)Tp'(Cl)]$, while the reaction with dimethyl acetylenedicarboxylate produces a more complicated product.[627] Amino acids and peptides bearing terminal alkynes readily react with $[W(CO)_3(S_2CNMe_2)_2]$ to yield the coordinated alkyne complexes $[W(HC{\equiv}CR)_2(S_2CNMe_2)_2]$.[628,629]

5.08.7.3.3 Complexes with "naked" sulfur, selenium, and tellurium ligands

A broad range of different reactivities is available within this area given the diversity of structural types and as such only a few selected examples are presented. The tetrahedral clusters **120** (E = S, Se) undergo a range of reactions, including site-selective CO substitution with CyNC,[630] site-selective oxidation with a telluroxide,[631] and metal-fragment-exchange reactions (Scheme 35).[632] Functional group transformations, such as ketone reductions and etherifications of alcohols, can be employed on appropriately substituted cyclopentadienyl fragments of similar tetrahedral clusters.[633,634]



Scheme 35

5.08.8 Halo Complexes

Complexes containing at least one W–X (X = F, Cl, Br, I) bond are considered in this section. However, the ubiquitous nature of halo complexes means the synthesis of halo-tungsten complexes, and the reactivity of the W–X bond is also covered in other sections of this chapter, particularly where, in addition to a halide ligand, complexes bear less common ligands or where a halo-tungsten complex is used as a synthetic precursor to complexes with other donor ligands.

5.08.8.1 Synthesis

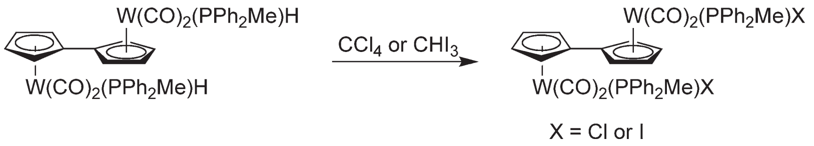
Table 17 contains selected examples of halocarbonyl–tungsten complexes, with reference to their syntheses. Halocarbonyl–tungsten complexes can be prepared using a number of different methodologies. The most common of these methods include the following.

(i) CO displacement from W–CO species in the presence of $[NR_4]X$ or alkali metal halides with chelating ethers, commonly used to prepare the M(0) species $[M(CO)_5X]^-$. Attempts to prepare $[W(CO)_5F]^-$ from $[W(CO)_5(THF)]$ and $[NEt_4]F$ yielded the dinuclear complex $[\{W(CO)_3\}_2(\mu\text{-}F)_3]^{3-}$. Treatment of this complex with CO yielded the unstable $[W(CO)_5F]^-$, which readily reverted back to the dinuclear species in the absence of CO, a consequence of the labilizing ability of the F^- ligand.[635]
(ii) Oxidative addition of a halide source to a W(0)–CO or W(II)–CO species. For example, $[W(CO)_3Tp'][NEt_4]$ reacts with $PhICl_2$ to form $[W(CO)_3Tp'(Cl)]$.[235] The range of halide sources used in this procedure has increased significantly and includes not only the commonly used Br_2 and I_2 but also $PhICl_2$,[235,636] $SnCl_4$,[637,638] $GeCl_4$,[639] $SbCl_5$,[640] the *N*-halosuccinimides (chloro, bromo, and iodo),[235,236,641] PCl_3 and PBr_3,[642] PCl_5,[191] and I_2Cl_6.[643]
(iii) Exchange of one halide with another.[83,644]
(iv) Reaction of a W–H species with a halide source, typically CCl_4, I_2, $CHBr_3$, or CHI_3 (e.g., Equation (22)).[645,646]
(v) Oxidative addition of an alkyl or aryl halide to a W(0)–CO or W(II)–CO species (e.g., Equation (23)).[83,171,647]
(vi) Displacement of labile ligands from a halocarbonyl-W(II) precursor.

Table 17 Examples of halocarbonyl tungsten complexes

Complex	*Synthesis*[a]	*Comments*	*W–X*$_{av}$ (Å)	*References*
W(0) complexes				
$[W(CO)_5I]^-$	(i)	$[Li(diglyme)_2]^+$ countercation	2.871	655
$[W(CO)_5Br]^-$	(i)		2.736	656
$[\{W(CO)_3\}_2(\mu\text{-}F)_3]^{3-}$	(i)	$[W(CO)_5(THF)] + [NEt_4]F$	2.178	635
W(II) complexes				
$[W(CO)(\eta^2\text{-}MeC{\equiv}CMe)Tp'(X)]$	(i)	X = F, Cl, Br, I	2.595 (Br)	657
$[W(CO)(NCR)(\eta^2\text{-}HC{\equiv}CBu^t)_2I_2]$	(vi)	R = Me, Et, Ph	2.89 (Ph)	145
$[W(CO)_2\{P(OMe)_3\}_3I_2]$	(iv)	Capped trigonal prism; P cap	2.924, 2.871	266
$[W(CO)_3(NCMe)_2Cl(SnCl_3)]$	(ii)	Capped octahedron; Sn cap	2.511	637
$[W(CO)_3(NCR)_2Cl(GeCl_3)]$	(ii)	R = Me, Et, Ph;	2.423 (Et)	639
$[W(CO)_3\{HB(3\text{-}Pr^ipz)_3\}I]$	(ii)	CO capped octahedron	2.849	235
$[W(CO)_3(NCEt)_2I_2]$	(vi)	Distorted CO capped octahedron	2.828, 2.864	104
$[W(CO)_2(NCMe)_2(\eta^3\text{-}C_5H_5O)Br]$ **121**	(v)	See Scheme 36		181
$[W(CO)_2(\eta^3\text{-}C_3H_4\text{-}2\text{-}Me)(\mu\text{-}Cl)_3Rh(\eta^5\text{-}C_5Me_5)]$		$[W(CO)_2(\eta^3\text{-}C_3H_4\text{-}2\text{-}Me)Cl] + [\{RhCl(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}Cl)_2]$	2.544, 2.590	658
$[W(CO)_3(NCEt)_2(SnRCl_2)Cl]$	(ii)	R = Bu, Ph		659
W(IV) complexes				
$[W(CO)_2(NCMe)({\equiv}NPh)Cl_2]$	(ii)	See Section 5.08.3.2.1.(ii)		191
$[\{W(CO)_2({\equiv}NPh)Br\}_2(\mu\text{-}Br)_2]$	(ii)	See Section 5.08.3.2.1.(ii)	2.673, 2.726(μ-Br)	191
$[W(CO)(PMe_3)(Cp)(Cl)_3]$	(ii)	Distorted octahedron	2.461, 2.476, 2.498	636

[a] See text for details.



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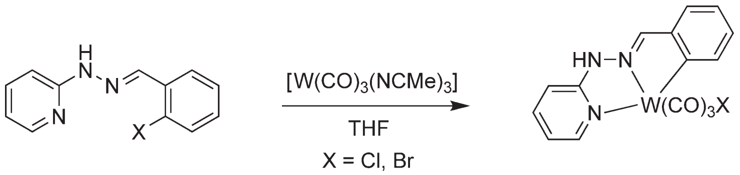


(23)

Further examples of the synthesis of halocarbonyl–tungsten complexes involving ligand exchange with halocarbonyl–tungsten precursors are detailed in Section 5.08.8.3. The labile precursors $[W(CO)_3(NCMe)_2X_2]$ $(X = Br, I)$ have proved to be highly versatile starting materials for the synthesis of carbonyl-W(II) complexes. The reactivity of these precursors has been reviewed thoroughly,[140–142] with more recent examples detailed in Section 5.08.3.1.3.

There are a number of less common methods for the preparation of halocarbonyl–tungsten complexes. Reaction of the aminocarbyne complex $[W(CO)_2Cp(\equiv CNEt_2)]$ with hydrochloric acid yields the chloro-aminomethylene complex $[W(CO)_2(=CHNEt_2)(Cp)Cl]$ (W–Cl 2.508 Å), whereas oxidation with $PhICl_2$ yields the chloro-aminocarbyne complex $[W(CO)Cp(\equiv CNEt_2)Cl_2]$.[648,649] Oxidation of $[W(CO)_6]$ with SbF_5 in HF–SbF_5 under a CO atmosphere yielded the structurally characterized $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ (W–F 2.109 Å), the $2e^-$ oxidation occurring without loss of CO.[650] The reaction of $[W(CO)(Cp)_2]$ with CCl_4 yields the electrophilic addition product $[W(CO)(Cp)(\eta^4\text{-}C_5H_5\text{-}exo\text{-}CCl_3)Cl]$ (W–Cl 2.474 Å),[651] and similarly $[W(CO)(Cp)\{\eta^4\text{-}C_5H_5\text{-}exo\text{-}CF(CF_3)_2\}I]$ (W–I 2.854 Å) is isolated from the reaction of $[W(CO)(Cp)_2]$ with $ICF(CF_3)_2$.[652] Reaction of TsCl with the nitrido complex $[W(CO)_2(Tp')(\equiv N)]$ yields the chloro–imido complex $[W(CO)(Cl)(Tp')(\equiv NTs)]$ (W–Cl 2.33 Å).[85] Oxidation of the sterically crowded $[W(CO)_3(PPr^i_3)_2]$ with I_2 yields the $17e^-$ $[W(CO)_3(PPr^i_3)_2I]$ (W–I 2.794 Å), whereas the reaction with HI yields the $18e^-$ $[W(CO)_3(PPr^i_3)_2(H)I]$ (W–I 2.841 Å), from which the strength of the W–H bond has been determined.[653,654]

5.08.8.2 Structure and Properties

Table 17 lists W–X_{av} bond lengths for selected halocarbonyl–tungsten complexes, bearing both terminal and bridging halide ligands. Seven-coordinate halocarbonyl complexes exhibit a range of structures in the solid state, including distorted and almost-idealized capped octahedra, and capped trigonal prisms. The cap in these cases can be either CO or another ligand, and ^{13}C NMR studies can be used to determine if the capping species is a CO ligand.[639,660] In many cases, NMR studies indicate that at room temperature the solution structure of seven-coordinate halocarbonyl complexes is fluxional on the NMR timescale. These fluxional processes can sometimes be “frozen out” in low-temperature studies.[104,130]

Structures of the anionic series $[W(CO)_5X]^-$ $(X = Cl, Br, I)$ have now been reported. The W–X bond lengths increase down the period 2.560 Å (Cl),[661] 2.736 Å (Br),[656] and 2.871 Å (I),[655] as would be expected, due to an increase in atomic radii. The *trans*-W–C (CO) bonds [1.96 Å (Cl), 1.93 Å (Br), 1.97 Å (I)] are consistently shorter than the *cis*-W–C (CO) bond lengths [1.99–2.03 Å (Cl), 2.03 Å (Br), 2.04–2.10 Å (I)], which suggests greater $W \rightarrow CO$ π-back-donation into the *trans*-bond. Theoretical studies of the series $[M(CO)_5X]^-$ $(M = Cr, Mo, W; X = NH_2, OH, F, Cl, Br, I, CH_3, H)$ have reinforced experimental evidence that loss of CO *cis* to the X ligand is most facile and that M–CO-dissociation energies increase in the order $NH_2 < OH < F < Cl < Br < I < CH_3 < H$.[521] Strong π-donation from X induces σ-antibonding interactions between *cis*-CO ligands and the metal center.[521]

Halocarbonyl–tungsten complexes have been studied electrochemically. The reduction of $[W(CO)_3(Cp)X]$ $(X = Cl, Br, I)$ to $[W(CO)_3(Cp)]^-$ becomes easier with the decreasing electronegativity and increasing size of the halide.[662] The oxidation of $[W(CO)_3(Cp)X]$ to $[W(CO)_3(Cp)X]^+$, which is unstable and readily decomposes, is more difficult moving down the period. This order is opposite to what would be expected based on only halide electronegativity since decreasing electronegativity would involve increased electron density on the metal atom.[662] This so-called “inverse halide order” is also seen in the first oxidation step of the series $[W(CO)_2(MeC\equiv CMe)(Tp')X]$

(X = F, Cl, Br, I), whose potential becomes more positive moving down the period; thus, the complex with the most electronegative halogen has the most electron-rich metal center.[657]

Halocarbonyl–tungsten complexes exhibit catalytic activity in a range of reactions, including oxidative carbonylation of amines,[663] allylic substitution,[527] intramolecular carbonyl ene reactions,[528] and olefin metathesis and polymerization reactions.[116,644,664,665]

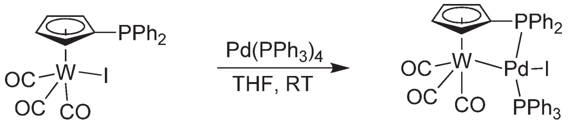
5.08.8.3 Reactions

Numerous examples of ligand-displacement reactions involving halocarbonyl–tungsten complexes exist and involve displacement of halides, CO ligands, or ancillary ligands, such as MeCN, from the metal center. As mentioned earlier in this section, reactions of $[W(CO)_3(NCMe)_2X_2]$ (X = Br, I), which exemplify the range of displacement reactions, are covered in Section 5.08.3.1. Additional examples are summarized below.

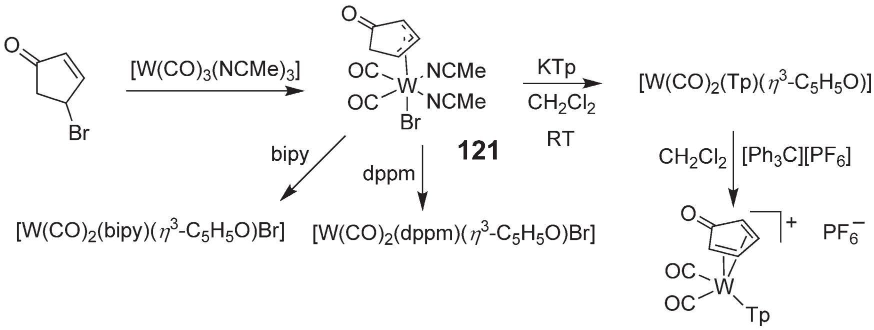
The reaction of $[W(CO)_3(NCMe)_2Cl_2]$ (prepared from $[W(CO)_3(NCMe)_2I_2]$ and NaCl) with excess 3-hexyne yields $[W(CO)(NCMe)(\eta^2\text{-EtC}{\equiv}\text{CEt})_2Cl_2]$, which can react with PPh_3, $Ph_2P(CH_2)_3PPh_2$, or bipy to yield $[W(CO)(PPh_3)(\eta^2\text{-EtC}{\equiv}\text{CEt})_2Cl_2]$, $[W(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-EtC}{\equiv}\text{CEt})Cl_2]$, and $[W(CO)(bipy)(\eta^2\text{-EtC}{\equiv}\text{CEt})_2Cl]Cl$, respectively.[666] The tin complex $[W(CO)_3(NCMe)_2(SnCl_3)Cl]$ reacts with nitriles RCN (R = Et, Pr, Ph) to give the exchange products $[W(CO)_3(NCR)_2(SnCl_3)Cl]$.[637] Reaction of $[W(CO)_3(NCEt)_2(SnBuCl_2)Cl]$ with $P(OMe)_3$ yields $[W(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$.[659] The allyl complex $[W(CO)_2(NCMe)_2(\eta^3\text{-}C_5H_5O)Br]$ **121** undergoes Br^-- and MeCN-displacement reactions, which are summarized in Scheme 36.[181]

The anion of the salt $[Li(diglyme)_2][W(CO)_5I]$ reacts with various nucleophilic reagents, such as $NaPPh_2$, $LiSiMe_2Ph$, $LiN(SiMe_3)_2$, and $PhCH_2MgCl$, to yield the iodide-substituted products $[Li(diglyme)_2][W(CO)_5R]$ $\{R = PPh_2, SiMe_2Ph, N(SiMe_3)_2, CH_2Ph\}$.[99] Attempts to substitute Cl^- with OTf^- in $[W(CO)_5Cl]^-$ to form $[W(CO)_5OTf]^-$ using AgOTf gave oxidation products.[526]

The reaction of the chloro complexes $[W(CO)(PMe_3)_2(Cp)Cl]$ and $[W(CO)_2({=}CHNEt_2)Cl]$ with $GeCl_2$ yields the insertion products $[W(CO)(PMe_3)_2(Cp)(GeCl_3)]$ and $[W(CO)_2({=}CHNEt_2)(GeCl_3)]$, respectively.[636,648] The chloro phosphine complex $[W(CO)_2(PH_2Bu^t)(Cp)Cl]$ can be dehydrochlorinated with base to yield the phosphenium complex $[W(CO)_2({=}PHBu^t)(Cp)]$.[298] Palladium(0) complexes can add to W–I bonds to form complexes with W–Pd bonds (Equation (24)).[641,667,668] Such complexes provide insights to the mechanism of Pd(0)-catalyzed M–C bond formation in the catalyzed reaction of $[M(CO)_n(Cp)I]$ with $Me_3SnC{\equiv}CR$ to from $[M(CO)_n(Cp)(C{\equiv}CR)]$.



(24)



Scheme 36

5.08.9 Hydride Complexes

In COMC (1982) and COMC (1995), hydride complexes have been split into two sections, complexes related to [W(CO)$_3$(Cp)H] as a subset of Cp complexes and complexes not bearing a Cp ligand in a section dedicated to hydrides. In this edition, these sections have been merged under Section 5.08.9. However, as with other areas of chemistry in this chapter, hydride complexes also appear in other sections where relevant.

5.08.9.1 Synthesis

Selected examples of the synthesis of hydride complexes are presented in Table 18. There are a number of general synthetic pathways that have not significantly changed since COMC (1995),[669] including the following.

(i) *Protonation of a metal center*. Anionic and neutral complexes can be protonated with H$^+$, the strength of the acid required being dependent on the electron density of the metal center. Typical acids include TfOH, HBF$_4$, and CF$_3$CO$_2$H. Hydride complexes can be protonated with strong acids to form dihydride complexes.[670] The dihydrides [W(CO)$_3$Cp(H)$_2$] and [W(CO)$_3$Cp*(H)$_2$] are extremely acidic, the phosphine-substituted analog [W(CO)$_2$(PMe$_3$)Cp(H)$_2$] is less acidic.[670] An experimental investigation into the protonation of [W(CO)$_2$(PMe$_3$)Cp(H)] suggests that the kinetic site of protonation is at the hydride rather than at the metal center, initially forming a dihydrogen intermediate which can then form the dihydride complex as the thermodynamic product.[671] Titration calorimetry studies have determined enthalpies of protonation for the reaction of [W(CO)$_3$(L)] (where L is tridentate ligands bearing N, S, and P donors) with CF$_3$CO$_2$H to form [W(CO)$_3$(L)(H)]$^+$.[114] A correlation between the enthalpy of protonation and ν(CO) was obtained.

(ii) Reaction of a transition metal hydride or a main group hydride with a W–CO species, involving attack at the metal center or replacement of a coordinated halide or labile solvent molecule.

(iii) Oxidative addition of H$_2$, silanes, HI, and thiols[654] to low-valent metal centers, not only W(0) but also W(ii) (e.g., Scheme 37).[672] Photolysis of *cis*-[W(CO)$_4$(PMe$_3$)$_2$] followed by treatment with H$_2$ afforded the unstable dihydride [W(CO)$_3$(PMe$_3$)$_2$(H)$_2$]. This result is in stark contrast to the formation of the dihydrogen complex [W(CO)$_3$(PCy$_3$)$_2$(η^2-H$_2$)], which, while existing in equilibrium with the dihydride form, is the predominant form in solution.[673] Dihydrogen can react photochemically with the bimetallic complex [{W(CO)$_3$Cp}$_2$] to form [W(CO)$_3$Cp(H)], however substantial hydride formation only occurs if the photolysis wavelengths are of high enough energy to cause CO loss.[674] Theoretical studies have examined why the dihydride [W(CO)$_3$Cp(H)$_2$]$^+$ forms in the reaction of [W(CO)$_3$Cp]$^+$ with dihydrogen, instead of the dihydrogen complex [W(CO)$_3$Cp(η^2-H$_2$)]$^+$.[675]

Photolysis of [W(CO)$_6$] in the presence of BH$_3$·L (L = PMe$_3$, PPh$_3$, or NMe$_3$) adducts yields the H-bound borane complexes [W(CO)$_5$(η-HBH$_2$·L)], but prolonged photolysis did not form the bidentate complex.[676] Using a similar method the H-bound gallane complex [W(CO)$_5$(η-HGaH$_2$·quinuclidine)] has been isolated.[677] The bidentate borohydride complexes [W(CO)(PR$_3$)$_2$($\equiv$CMes)(η^2-H$_2$BH$_2$)] have been prepared by the reaction of [W(CO)(PR$_3$)$_2$($\equiv$CMes)Cl] with NaBH$_4$, and subsequent reaction with quinuclidine and additional PR$_3$ afforded the hydride complexes [W(CO)(PR$_3$)$_2$($\equiv$CMes)(H)].[678] Similarly, the borohydride complex *mer*-[W(CO)(PMe$_3$)$_3$(NO)(η-HBH$_3$)], which can be prepared form [W(CO)$_3$(PMe$_3$)$_2$(NO)][BF$_4$], PMe$_3$, and NaBH$_4$, reacts with excess PMe$_3$ to form *mer*-[W(CO)(PMe$_3$)$_3$(NO)(H)].[679]

5.08.9.2 Structure and Properties

Table 18 lists ^{1}H NMR chemical shifts, including J_{WH}, and W–H bond lengths for selected hydride complexes. It is common in crystallographic studies of hydride complexes for the position of the hydride not to be determined and as such only a few examples of W–H bond lengths are listed in Table 18. The high field ^{1}H NMR chemical shifts of the hydride signals, commonly up-field of δ0 are diagnostic of hydride complexes. For hydrides bridging multiple transition metal centers, the ^{1}H chemical shift of the hydride is extremely up-field. Hydride complexes can exhibit fluxional behavior in terms of binding geometries, and in some cases this dynamic behavior can be “frozen out” in low-temperature NMR studies, while in other cases an average chemical shift is reported when the dynamic behavior cannot be sufficiently slowed down.[670] In many instances the hydride chemical shift is reported at low temperature. Borane and diborane complexes [W(CO)$_5$(η-HBH$_2$·PMe$_3$)] and [W(CO)$_5$(η^1-HB$_2$H$_3$·2PMe$_3$)] exhibit rapid exchange

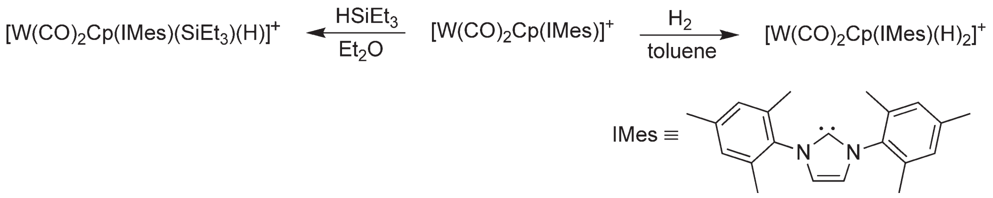
Table 18 Synthetic details, W–H bond lengths and ^1H NMR chemical shifts for selected W–CO and W–CNR hydride complexes (grouped by "formal" oxidation states)

Complex	*Synthesis*[a]	*Comments/H source*	δ (WH) $[J_{WH}]$[b]	$W\text{–}H_{av}$ (Å)	*References*
W(0)					
trans,trans-$[W(CO)_2\{Ph_2P(2\text{-}py)\}_2(NO)(H)]$	(ii)	$[(MeOCH_2CH_2O)_2AlH_2]Na$	0.62 (31)		203
mer-$[W(CO)(PMe_3)_3(NO)(H)]$	(ii)	*mer*-$[W(CO)(PMe_3)_3(NO)(NCMe)] + BH_4^-$	−0.20	1.80	679
$[\{W(CO)_4\}_2(\mu\text{-}H)_2]^{2-}$	(ii)	$[W(CO)_4(TMEDA)] + [Et_4N][BH_4]$			692
W(II)					
$[W(CO)_3(PMe_3)_2(H)_2]$	(iii)	$[W(CO)_3(PMe_3)_2] + H_2$	−5.37 (18)		673
$[W(CO)_3(PPr^i_3)_2I(H)]$	(iii)	$[W(CO)_3(PPr^i_3)_2] + HI$	−7.49		654
$[W(CO)_2(PMe_3)_3Cl(H)]$	(ii)	$[W(CO)_2(PMe_3)_3Cl_2] + LiBEt_3H$	−5.78 (19)	1.78	693
$[W(CO)_2Cp(IMes)(H)]$			−6.43 (45)		694
$[W(CO)_3(PCy_3)_2(SiH_2Ph)(H)]$	(iii)	$PhSiH_3$	−4.51 (28)		200
$[\{W(CO)_3(H)\}_2(\mu\text{-}Fv)]$	(i)	$[\{W(CO)_3\}_2(\mu\text{-}Fv)]^{2-} + CF_3CO_2H$	−6.98 (38)		646
cis-$[W(CO)_4(PPh_3)(H)]^-$				1.682	695
$[\{W(CO)_3(H)\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)]$	(i)	$KHSO_4$	−7.11 (37)		696
$[W(CO)_4(o\text{-}Ph_2PC_6H_4NH_2\text{-}N,P)H]^+$	(i)	$[H(OEt_2)][BAr'_4]$			416
W(IV)					
$[W(CO)_2Cp(IMes)(SiEt_3)(H)]^+$	(iii)	$[W(CO)_2Cp(IMes)]^+ + HSiEt_3$	−2.60 (36)		672
$[W(CO)_2(PMe_3)(Cp)(H)_2]^+$	(i)	$[W(CO)_2(PMe_3)(Cp)(H)] + [H(OEt_2)][BAr'_4]$	−2.48 (av)	1.62, 1.83	670
$[W(CNBu^t)(Cp)_2(H)]^+$		$[W(Cp)_2(H)_2] + CF_3SO_3Me/CNBu^t$	−11.4 (68)		697
Bridging hydrides					
$[W(CO)(PMe_3)_2(\equiv CMes)(\eta^2\text{-}H_2BH_2)]$			−2.0, −4.1		678
$[W(CO)_5(\eta\text{-}HBH_2{\cdot}PMe_3)]$			−2.1 (av)	2.01	676
$[W(CO)_5(\eta\text{-}HGaH_2{\cdot}quinuclidine)]$			−7.32	1.80	677
$[W(CO)_4(\mu\text{-}dppm)(\mu\text{-}H)Fe(CO)(\eta^5\text{-}MeC_5H_4)]$			−16.9 (37)	1.812	698
$[W(CO)_2(Cp)(\mu\text{-}dppm)(\mu\text{-}H)\text{-}Ru(CO)(Cp)]^+$			−17.7 (47)	1.70	408
$[\{W(CO)_3\}_2(\mu\text{-}H)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)]$	(i)	CF_3CO_2H	−22.7		696
$[\{W(CO)_2(Cp)\}_2(\mu\text{-}H)\text{-}(\mu\text{-}PCy_2)]$		$[\{W(CO)_3(Cp)\}_2] + HPCy_2$	−16.4 (40)		385
$[\{W(CO)_2(Cp)\}_2(\mu\text{-}dppm)(\mu\text{-}H)]^+$			−20.8 (47)		443

[a] See text for synthetic method.

[b] δ in ppm; in parentheses J_{WH} in Hz; Spectra recorded at various temperatures.

$BAr'_4 = B\{3,5\text{-}C_6H_3(CF_3)_2\}_4$. IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene. Fv = fulvalene.



Scheme 37

of the coordinated hydrogen atom with the non-coordinated geminal hydrogen atom(s).[676,680] In the case of the diborane complexes, exchange between the vicinal hydrogen atoms is slow.

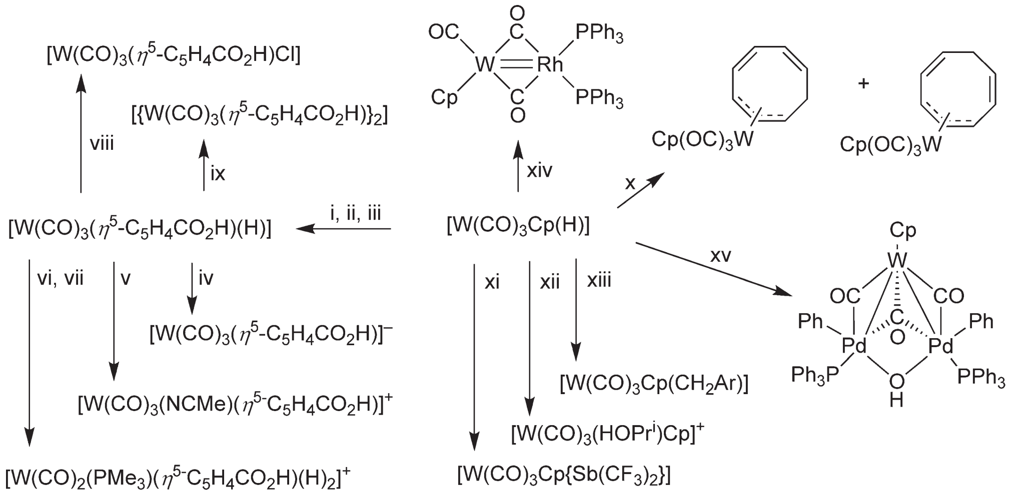
Studies of ^{2}H NMR T_1 relaxation times on $[W(CO)_2(PR_3)_2(NO)(D)]$ (R = Me, Ph) have been used to determine deuterium quadrupole coupling constants and the ionic contributions to the W–D bond.[681] Intermolecular W–H···H–OR hydrogen bonding of acidic alcohols to the hydride ligand of $[W(CO)_2(PR_3)_2(NO)(H)]$ has been characterized by NMR and IR spectroscopy.[682] Theoretical studies have also examined similar intermolecular W–H···HR bonding.[683]

A W–H bond length of 1.79 Å for $[W(CO)_3Cp(H)]$ has been determined from high resolution rotational spectral studies.[684] Homolytic M–H bond-dissociation energies and pK_a values for the two series $[M(CO)_3Tp(H)]$ and $[M(CO)_3Tp'(H)]$ (M = Cr, Mo, W), and their cation radicals, have been determined and compared to data on $[M(CO)_3Cp(H)]$.[685] Both BDEs and pK_a values for the hydrides decrease in the order $[M(CO)_3Cp(H)] > [M(CO)_3Tp(H)] > [M(CO)_3Tp'(H)]$, for acetonitrile solutions. The homolytic W–H BDEs have also been estimated for $[W(CO)_3(PR_3)_3(H)]^+$ ($PR_3 = PMe_3$, PEt_3, PEt_2Ph, PEt_2Ph, $PMePh_2$), $[W(CO)_2(dppm)_2(H)]^+$, and $[W(CO)_3\{PhP(CH_2CH_2PPh_2)_2\}(H)]^+$.[686] One-electron reduction and hydrogen atom-transfer reactions, in aqueous solutions, of $[W(CO)_2(L)(\eta^5\text{-}C_5H_4CO_2H)H]$ (L = PMe_3, CO) have been studied with pulse radiolysis.[687] Electrochemical studies have examined the oxidation and reduction chemistry of the two cationic hydride series $[M(CO)_2(L\text{-}P,P')_2H]^+$ (M = Cr, Mo, W; L = dppe, dppm).[688] The oxidized species $[M(CO)_2(L\text{-}P,P')_2H]^{2+}$ can be considered extremely strong acids.

Tungsten–hydride species, such as $[W(CO)_3Cp(H)]$, $[W(CO)_2(PPh_3)Cp(H)]$, and $[W(CO)_2(IMes)Cp(H)]$ {IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene}, are catalyst precursors and/or catalytic intermediates in the hydrosilylation and hydrogenation of ketones.[529,672,689] The hydrogenation of alkenes and alkynes is also facilitated by $[W(CO)_3(Cp)(H)]$ in the presence of TfOH.[690,691]

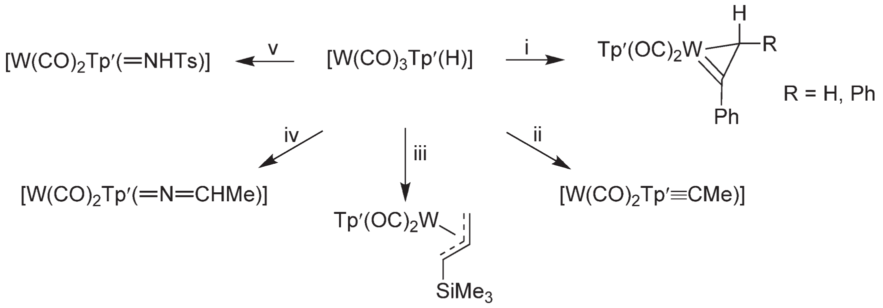
5.08.9.3 Reactions

This section is dominated by the reactivity of hydride complexes bearing the facially coordinating Cp or Tp ligands. Examples of the reactivity of hydride complexes with and without such ligands are discussed. Typical reactions include non-hydride ligand exchange/displacement (e.g., CO, labile solvents, coordinated halides), hydride insertion reactions, hydride transfer, protonation, and deprotonation. Examples of the diverse range of reactivity for $[W(CO)_3Cp(H)]$, $[W(CO)_3Tp'(H)]$, and related complexes are given in Schemes 38[489,508,529,701–705] and 39.[179,706–708]



i, 2 equiv. *n*-BuLi, THF; ii, $CO_{2(g)}$; iii, H_3PO_4;[701] iv, 1 equiv. KH, THF;[701] v, Ph_3CBF_4, MeCN;[701] vi, PMe_3, toluene; vii, TfOH;[701] viii, CCl_4;[701] ix $(Ph_3C)_2$, toluene;[701] x, cot, photolysis;[702] xi, $Sb(CF_3)_3$, toluene;[489] xii, acetone, TfOH, CH_2Cl_2;[508,529] xiii, $[W(CO)_5({=}CHAr)]$, CH_2Cl_2, −40 °C;[703] xiv, $1/2[\{Rh(PPh_3)_2\}_2(\mu\text{-}OH)_2]$;[704] xv, $[\{Pd(PPh_3)Ph\}_2(\mu\text{-}OH)_2]$[705]

Scheme 38



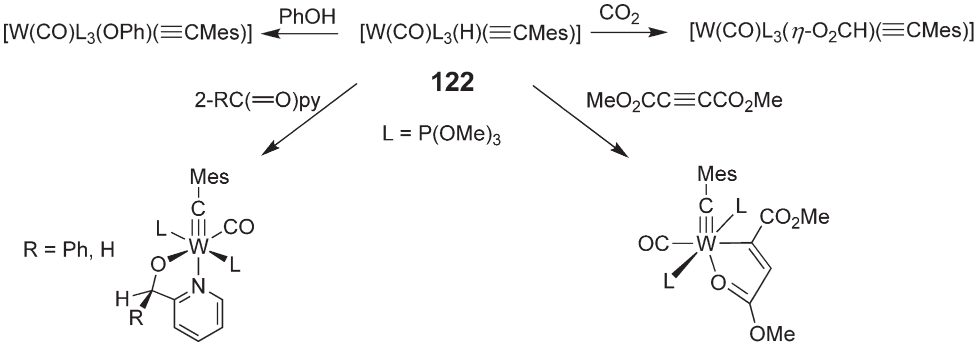
i, PhC≡CR, THF, hν;[179,706] ii, HC≡CH, THF, hν;[179,706] iii, MeC≡CSiMe$_3$, THF, hν;[179,706] iv, NCMe, THF, hν;[707] v, TsN$_3$, THF[708]

Scheme 39

For the hydride/chloro complex [W(CO)$_2$(PMe$_3$)$_3$Cl(H)], which is prepared by the reaction of [W(CO)$_2$(PMe$_3$)$_3$Cl$_2$] and LiBEt$_3$H, the second chloride cannot be displaced by the addition of more hydride, but the chloride ligand undergoes facile metathesis with bidentate ligands to form [W(CO)$_2$(PMe$_3$)$_2$(H)(L)] (L = *S,S′*-S$_2$CNMe$_2$, *S,S′*-S$_2$COMe, acac).[693] The hydride complex **122** reacts with a range of oxygen-containing species to give a variety of oxygen-donor complexes (Scheme 40).[678] The W–W complex [W(CO)$_5$(μ-H)W(CO)$_4$(NO)] undergoes CO displacement with CNR and THF to yield [W(CO)$_5$(μ-H)W(CO)$_2$(L)$_2$(NO)] (L = CNR or THF). In addition, [W(CO)$_5$(μ-H)W(CO)$_4$(NO)] undergoes nucleophilic attack at CO by Ph$_3$P═NR to give [W(CO)$_5$(μ-H)W(CO)$_{4-n}$(CNR)$_n$-(NO)], where *n* depends on the nature and quantity of Ph$_3$P═NR.[699,700] The hydride complex [W(CO)(PMe$_3$)$_3$(NO)(H)] reacts readily with CO$_2$, ketones and aldehydes, and metal carbonyls such as Fe(CO)$_5$ to yield [W(CO)(PMe$_3$)$_3$(NO){OC(O)H-*O*}], [W(CO)(PMe$_3$)$_3$(NO)(OCHRR^1-*O*)] (R = H, Me, Ph; R^1 = Ph, Et, Me), and [W(CO)(PMe$_3$)$_3$(NO)(μ-OCH-*O:C*)Fe(CO)$_4$], respectively.[679] In comparison with the limited insertion reactivity of [W(CO)$_2$(PMe$_3$)$_2$(NO)(H)], the additional PMe$_3$ significantly enhances the reactivity of [W(CO)(PMe$_3$)$_3$(NO)(H)].

Displacement of the phosphine in [W(CO)$_2$(PR$_3$)Cp(H)] (R = Me, Ph) with the *N*-heterocyclic carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) yields the carbene complex [W(CO)$_2$(IMes)Cp(H)].[694]

Hydride-transfer reactions have been intensely studied, particularly to determine the hydride-donor abilities, or hydricity, of different hydride complexes. These studies have included thermodynamic, free energies of hydride donation, kinetics and isotope effects on kinetics.[695,709–712] The various hydride complexes studied include [W(CO)$_3$Cp(H)], [W(CO)$_3$Cp*(H)], [W(CO)$_3$(η^5-C$_5$H$_4$CO$_2$Me)(H)], [W(CO)$_3$(indenyl)(H)], [W(CO)$_3$(η^5-C$_5$H$_4$Me)(H)], and [W(CO)$_4$(L)(H)]$^-$ {L = PPh$_3$, P(OMe)$_3$, CO}.[695,709–712] The anionic complexes [W(CO)$_4$(L)(H)]$^-$ {L = PPh$_3$, P(OMe)$_3$, CO} are relatively strong hydride donors, considerably stronger than [W(CO)$_3$Cp(H)].[695]



Scheme 40

5.08.10 Dihydrogen Complexes

The field of W–CO complexes bearing coordinated dihydrogen is dominated by studies of the complexes originally reported by Kubas and co-workers, namely $[W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]$ ($R = Cy, Pr^i$) and their derivatives.[713,714] Also of great interest is the simple adduct $[W(CO)_5(\eta^2\text{-}H_2)]$, which has been the focus of numerous studies. Recent attempts to prepare $[W(CO)_3(PMe_3)_2(\eta^2\text{-}H_2)]$ and $[W(CO)_5(\eta^2\text{-}H_2)]$, by treatment of H_2 with the products from the photolysis of *cis*-$[W(CO)_4(PMe_3)_2]$ and $[W(CO)_6]$ in toluene-d_8, afforded only the dihydrides $[W(CO)_3(PMe_3)(H)_2]$ and $[W(CO)_5(H)_2]$ respectively, neither of which were isolated.[673]

Photolysis of $[W(CO)_6]$ in the presence of H_2 using low-temperature and high-pressure matrix-isolation methods with a novel polyethylene matrix leads to the successive formation of $[W(CO)_5(\eta^2\text{-}H_2)]$ and *cis*-$[W(CO)_4(\eta^2\text{-}H_2)_2]$, which were identified by spectroscopic techniques.[42] Similarly, photolysis of $[W(CO)_5(CS)]$ in the presence of H_2 affords *cis*-$[W(CO)_4(CS)(\eta^2\text{-}H_2)]$, which isomerizes to *trans*-$[W(CO)_4(CS)(\eta^2\text{-}H_2)]$ with visible light photolysis ($\lambda > 400$ nm). Reaction of $[W(CO)_5(\eta^2\text{-}H_2)]$ with N_2 leads to the exchange product $[W(CO)_5(\eta^2\text{-}N_2)]$; the reverse reaction is much slower.[42]

Spectroscopic techniques, especially NMR spectroscopy, are particularly important in the study and identification of dihydrogen and dihydride complexes.[714] Solid-state ^2H NMR studies on $[W(CO)_3(PCy_3)_2(\eta^2\text{-}D_2)]$ have examined the hydrogen–deuterium isotope effect on exchange rates.[715] These studies included an examination of spin lattice relaxation and spectral line widths. Study of T_1 and T_2 relaxation of H_2 in $[W(CO)_3(PPr^i{}_3)_2(\eta^2\text{-}H_2)]$ at various temperatures has been reported.[716] A resolution-enhanced ^1H NMR spectrum of $[W(CO)_3(PPr^i{}_3)_2(\eta^2\text{-}HD)]$ at $-20\,^\circ C$ reveals fine splitting, from which $^1J_{H,D}$ (34 Hz), $^1J_{H,W}$ (34 Hz), and $^2J_{H,P}$ (3 Hz) coupling constants could be determined.[716] Line shape analysis of inelastic neutron scattering (INS) spectra for $[W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)]$ has been conducted in a study of coherent and incoherent dihydrogen exchange.[717] IR, Raman, and INS vibrational data for $[W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)]$, $[W(CO)_3(PCy_3)_2(\eta^2\text{-}HD)]$, and $[W(CO)_3(PCy_3)_2(\eta^2\text{-}D_2)]$ have been reported.[718] Electrochemical studies have been conducted on a range of complexes with the fragment "$W(CO)_3(PCy_3)_2$" including $[W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)]$, which exhibits an irreversible oxidation. It was assumed that due to the high acidity of oxidized dihydrogen- and polyhydride-metal complexes, the oxidized complex readily loses a proton to the solvent.[228]

Numerous theoretical studies have been conducted on dihydrogen complexes. These can be broadly broken into two groups: examinations of (i) $[W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]$[718–726] and (ii) $[W(CO)_5(\eta^2\text{-}H_2)]$.[7,722,727–731] Theoretical studies involving $[W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]$ have included the equilibrium isotope effect on the binding of H_2,[718,725] electron density analysis of H–H and W–H bonds,[721] and the nature of the M-η^2-H_2 bond in $[W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]$ versus $[W(CO)_5(\eta^2\text{-}H_2)]$ which indicated that the M-η^2-H_2 interaction is stronger in the phosphine complex due to increased $W \rightarrow \sigma^*(H)$ π-backdonation.[720,722] Other studies have examined the $[W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]$/$[W(CO)_3(PR_3)_2(H)_2]$ equilibrium, including isotope effects,[726] the structure of the dihydrogen and dihydride complexes, and the process of oxidative addition that converts the dihydrogen complex into the dihydride.[723,724] Studies of $[W(CO)_5(\eta^2\text{-}H_2)]$ have focused on the structure and bond-dissociation energies in the complex with comparisons to the Cr and Mo analogs, though one study[729] has also included calculations on $[M(CO)_{6-x}(\eta^2\text{-}H_2)_x]$ ($M = Cr, Mo, W$; $x = 2$ and 3).[7,727–729] Another study has included isotope effects for the coordination and oxidative addition of dihydrogen to $[W(CO)_5]$ and for the interconversion of $[W(CO)_5(\eta^2\text{-}H_2)]$ and $[W(CO)_5(H)_2]$.[730]

5.08.11 Boron Ligands

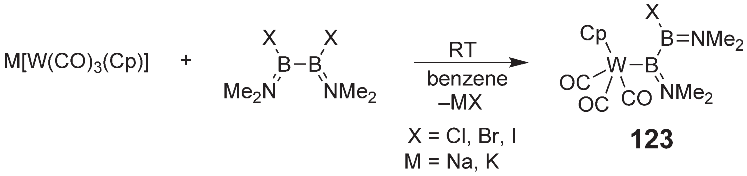
This section covers W–CO and W–CNR complexes bearing boron-donor ligands, for which there is a predominance of carboranes, and can be broadly split into two sections, complexes bearing either (i) ligands that bind to a tungsten center via only one boron donor (monodentate or bridging boron-donor ligands), or (ii) ligands that bind to a tungsten center via multiple boron donors (polydentate boron donor-ligands). Recent reviews have examined synthesis, reactivity, structure, and bonding aspects of borane-, boryl- and borylene-transition metal complexes.[332,719,732–737]

5.08.11.1 Synthesis

5.08.11.1.1 Monodentate or bridging boron-donor ligands

A variety of different methods are available for the preparation of W–CO complexes bearing boron-donor ligands. The most common method involves reaction of a W–CO anion with a haloborane. An interesting example involves the reaction of the 1,2-dihalodiboranes $B_2(NMe_2)_2X_2$ ($X = Cl, Br, I$) with $M[W(CO)_3Cp]$ (Equation (25)).[738–741] In the case of the chloride and bromide only the monosubstituted product was identified in the reaction mixture.

However, in the case of the iodide, the dinuclear boryloxycarbyne complexes **124** and **125** could be isolated, depending on the reaction conditions, both of which could be converted into the mononuclear **123** (X = I) by reaction with $B_2(NMe_2)_2I_2$.[741]



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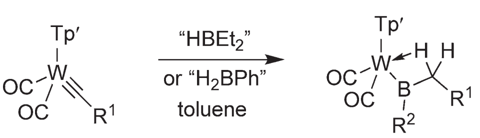
(25)

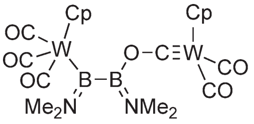
Additional synthetic methods include: B–H bond activation by a transition metal complex (the photolysis of $[W(CO)_3(Cp^*)(Me)]$ in the presence of $BH_3{\cdot}PMe_3$ yields $[W(CO)_3Cp^*(BH_2{\cdot}PMe_3)]$)[742] and hydroboration of the Fischer carbyne complex $[W(CO)_2Tp'(\equiv CR)]$ (Equation (26)) (the analogous reaction with $[W(CO)_2Cp(\equiv CR)]$ yields products without W–B bonds).[743,744]



R^1	R^2
Me	Et **126**
Me	Ph
4-MePh	Et
4-MePh	Ph

(26)

Table 19 contains selected examples of W–CO complexes bearing monodentate boron-donor ligands and their synthetic pathways.



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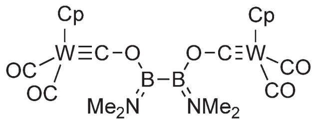

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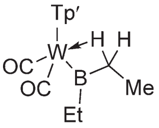

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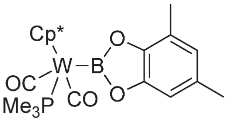

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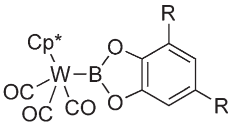

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5.08.11.1.2 Polydentate boron-donor ligands

Tungsten–CO complexes bearing polydentate boron-donor ligands, particularly carborane complexes, are commonly prepared by the reaction of a preformed boron-containing ligand with a labile metal complex such as $[W(CO)_3(NCR)_3]$,[747–749] $[W(CO)_2(NCMe)_2Br(\eta^3\text{-}C_3H_5)]$,[747,750,751] or $[W(CO)_4Br(\equiv CR)]$.[752] Examples of some

Table 19 Examples of W–CO complexes with monodentate boron-donor ligands

Complex	*Synthesis/comments*	*W–B$_{av}$* (Å)	δ (W–B)[b]	*References*
127	$[W(CO)_2(PMe_3)Cp^*]^- + ClBR_2$		58	745
128	$[W(CO)_3Cp^*]^- + ClBR_2$; R = H		52.4	745
123	See text; R = Cl;	2.37	62.7	738
$[W(CO)_5\{{=}B{=}N(SiMe_3)_2\}]$	$[W(CO)_5]^{2-} + Br_2BN(SiMe_3)_2$; W–B–N 178°	2.15	86.6	746
$[W(CO)_3Cp^*(BH_2{\cdot}PMe_3)]$	See text	2.48	−27.6	742
126	Agostic W···H interaction 2.22 Å	2.06	77	743

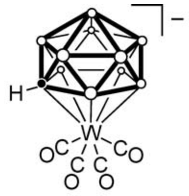
[a] See text for synthesis.

[b] ^{11}B NMR chemical shift in ppm.

Table 20 Examples of W–CO complexes with polydentate boron-donor ligands

Complex	*Synthesis/comments*	*W–B$_{av}$* (Å)	*References*
129	Na_3[*nido*-7-$CB_{10}H_{11}$] + (i) [$W(CO)_3(NCEt)_3$], (ii) CO + $HBF_4 \cdot Et_2O$		748
130	7-NH_2Bu^t-*nido*-7-$CB_{10}H_{12}$ + (i) $LiBu^n$, (ii) [$WCO)_6$] + EtCN	2.37	754
131	$Na_2[7,8\text{-}C_2B_9H_{11}]$ + [$W(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)(Br)$]		750
132	Multiple syntheses	2.38	748
133	See 5.08.11.3 reactions	2.43	751
134	[$W(CO)_3(NCEt)_3$] + $[Et_2C_2B_4H_4]^{2-}$		755
135	[$Co(Et_2C_2B_3H_5)(Cp^*)$] + (i) $LiBu^n$, (ii) [$\{W(CO)_4(Br)\}_2(\mu\text{-}Br)_2$]	2.33	755
136	[$W(CO)_4(\equiv CR)(Br)$] + $[B_3H_8]^-$	2.54	752

selected polydentate boron-donor W–CO complexes, including synthetic information, are detailed in Table 20. The area of metal complexes bearing monocarbon carboranes with amino substituents has been recently reviewed.[753]



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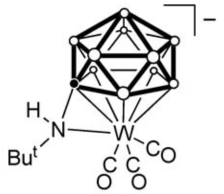

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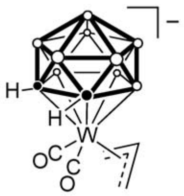

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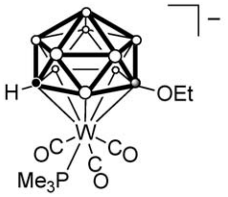

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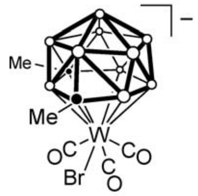

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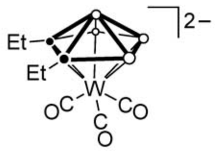

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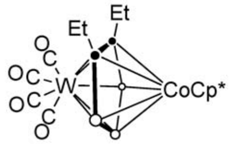

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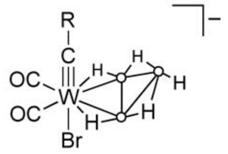


R = 2,6-$C_6H_3Me_2$

136

○ = BH ◉ = C ● = B

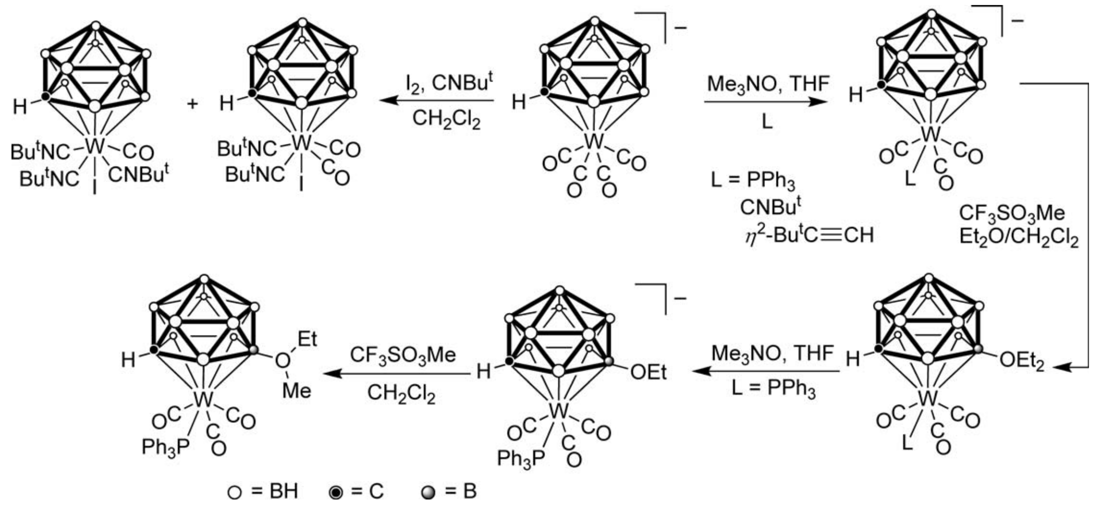
5.08.11.2 Structure and Properties

Tables 19 and 20 contain W–B$_{av}$ bond lengths and ^{11}B NMR chemical shift data (W–B) for a variety of selected W–CO complexes bearing boron-donor ligands. In addition to the various structural motifs displayed in Tables 19 and 20, boron fragments, including B, BH, BH_2, and BH_3, constitute part of a number of homo- and hetero-multinuclear complexes.[756–758]

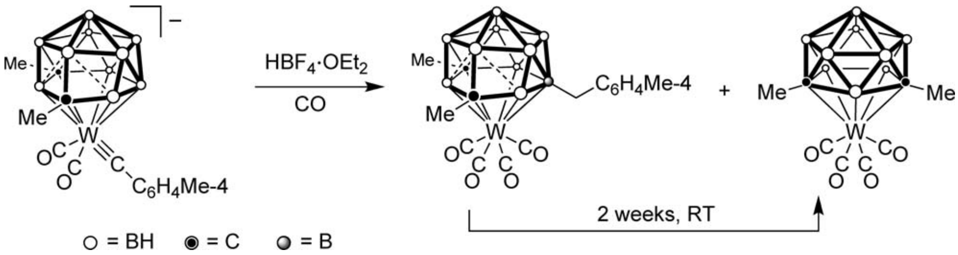
The dioxyboryl complexes **127**(see Table 19) and **128** (R = Me) can terminally functionalize unreactive alkanes and can functionalize arenes at C–H bonds.[745] For example, the photolysis of **128** (R = Me) in pentane yields a 1-pentylboronate ester; the initial metal-containing product formed was identified as [$W(CO)_3Cp^*(H)$]. The mechanistic pathway for this reaction has been examined by experimental and theoretical techniques.[759,760] Theoretical studies on the borylene complex [$W(CO)_5\{BN(SiMe_3)_2\}$], and its Al, Ga, In, and Tl analogs, have examined equilibrium geometries and W–E bond-dissociation energies as well as the nature of the W–E bond (E = B, Al, Ga, In, Tl).[761]

5.08.11.3 Reactions

The reactivity of W–CO complexes with boron-donor ligands is dominated by examples of carborane chemistry;[747–751,755,762–765] selected examples of the reactivity of carborane complexes are summarized in Schemes 41[748,762] and 42.[763] The carborane complex $[W(CO)_3(C_2B_9H_{11})]^{2-}$ reacts with excess PhSSPh to afford



Scheme 41



Scheme 42

the bridged $[\{W(C_2B_9H_{11})\}_2(\mu\text{-SPh})_4]^{2-}$.[766] The B_3H_8 complex **136** (see Table 20) reacted rapidly with Bu^{n}Li to afford the polyhedral $[B_{12}H_{12}]^{2-}$, which was readily isolated as the NBu_4^+ salt in high yield.[752] There are a few examples of note of the reactivity of non-carborane boron complexes, besides the C–H activation chemistry mentioned in Section 5.08.11.2. The borylene complex $[W(CO)_5\{{=}B{=}N(SiMe_3)_2\}]$ acts as a source of the borylene $BN(SiMe_3)_2$; reaction of the complex with $[Cr(CO)_5(NMe_2)]$ afforded $[Cr(CO)_5\{{=}B{=}N(SiMe_3)_2\}]$, while reaction with $[Re(CO)_3(Cp)]$ afforded $[\{Re(CO)_2Cp\}_2\{\mu\text{-}BN(SiMe_3)_2\}]$.[767] The borane complex $[W(CO)_3Cp^*(BH_2{\cdot}PMe)]$ is susceptible to W–B cleavage; reaction with $HCl_{(g)}$, MeI, or $PPhMe_2$ yields $[W(CO)_3Cp^*(H)]$ and $BH_2Cl{\cdot}PMe$, $[W(CO)_3Cp^*(Me)]$ and $BH_2I{\cdot}PMe$, and the salt $[BH_2(PMe_3)(PPhMe_2)][W(CO)_3Cp^*]$, respectively.[742]

5.08.12 Aluminum, Gallium, Indium, and Thallium Ligands

This section covers W–CO and W–CNR complexes bearing aluminum-, gallium-, indium-, and thallium-donor ligands, though there have been no significant developments in the chemistry of W–CO complexes bearing thallium-donor ligand. Recent reviews have covered the coordination chemistry as well as the nature of bonding of group 13-donor ligands to transition metals.[332,719,768,769] There are comparatively few examples in this field. Selected examples are listed in Table 21, along with synthetic details and $W\text{–}E_{av}$ (E = Al, Ga, In) bond lengths for complexes that have been crystallographically characterized. The most common synthetic methodology involves the reaction of an anionic W–CO species and an aluminum, gallium, or indium halide species with concomitant salt elimination.[770,771] However, there are alternative synthetic methods: reaction of $GaCp^*$ with *fac*-$[W(CO)_3(NCEt)_3]$ or $[\{W(CO)_2Cp\}_2]$ affords *fac*-$[W(CO)_3\{Ga(\eta^5\text{-}Cp^*)\}_3]$ and $[\{W(CO)_2Cp\}_2\{\mu\text{-}Ga(\eta^1\text{-}Cp^*)\}_2]$, respectively.[772]

Table 21 Examples of W–CO complexes with aluminum-, gallium-, and indium-donor ligands

Complex	*Synthesis*	*W–E$_{av}$* (Å)	*References*
$[W(CO)_5\{AlBu^t(TMPDA\text{-}N,N')\}]$	$K_2[W(CO)_5]$ + (i) Cl_2AlBu^t, (ii) TMPDA = $Me_2N(CH_2)_3NMe_2$	2.74	776
$[W(CO)_5\{AlCl(TMPDA\text{-}N,N')\}]$	$K_2[W(CO)_5]$ + (i) $AlCl_3$, (ii) TMPDA	2.645	774
$[W(CO)_5\{AlEt(TMEDA\text{-}N,N')\}]$	$K_2[W(CO)_5]$ + (i) Cl_2AlEt, (ii) TMEDA	2.67	774
$[W(CO)_5\{GaCl(TMEDA\text{-}N,N')\}]$	$K_2[W(CO)_5]$ + (i) $GaCl_3$, (ii) TMEDA		774
$[W(CO)_5\{In(Tp'\text{-}N,N',N'')\}]$	$K_2[W(CO)_5] + Tp'InCl_2{\cdot}THF$	2.78	775
$[W(CO)_5\{Ga(\eta^5\text{-}Cp^*)\}]$	$Na_2[W_2(CO)_{10}] + Cl_2GaCp^*$ or $ClGaCp^*{}_2$	2.57	777
$[\{W(CO)_3Cp\}_3(\mu^3\text{-}In)]$	$K[W(CO)_3Cp] + Cl_2InCp^*$; trigonal planar In	2.88	777
fac-$[W(CO)_3\{Ga(\eta^5\text{-}Cp^*)\}_3]$	$[W(CO)_3(NCEt)_3] + GaCp^*$	2.52	772
$[\{W(CO)_2Cp\}_2\{\mu\text{-}Ga(\eta^1\text{-}Cp^*)\}_2]$	$[\{W(CO)_2Cp\}_2] + GaCp^*$	2.75	772
$[\{W(CO)_2Cp\}_2\{\mu\text{-}\overline{In(CH_2)_3N}Me_2\}]$	$Na[W(CO)_3Cp] + BrIn\{\overline{(CH_2)_3N}Me_2\}_2$; $In\{\overline{(CH_2)_3N}Me_2\}_3$ byproduct		771
$[W(CO)_5(InCl_3)]^{2-}$	$K_2[W(CO)_5]$ + (i) $InCl_3$, (ii) Ph_4PCl; via $[W(CO)_5\{InCl{\cdot}THF\}]$		778

Some points of interest include the following.

(i) The W–Al complexes $[W(CO)_5\{AlR(TMPDA)]$ (R = Cl, Bu^i; TMPDA = $Me_2N(CH_2)_3NMe_2$) exhibit luminescence in the visible spectral region.[773]

(ii) The W–E bond length in complexes in this area tends to become shorter if alkyl substituents on E are replaced by halides.[774]

(iii) The W–In bonding in $[W(CO)_5\{In(Tp'\text{-}N,N',N'')\}]$ can be considered as a dative bond from the In center to the $W(CO)_5$ fragment.[775]

(iv) Theoretical studies have examined the bonding in a range of $W(CO)_5$ complexes bearing a group 13-donor ligand (B, Al, Ga, In, and Tl); the group 13 ligands generally behave as strong σ-donors with significant acceptor abilities.[761,774]

5.08.13 Silicon Ligands

There has been increasing interest in this field, particularly with regard to silylene complexes and the nature of the W–Si bond. Recent reviews have covered stable silylenes and their metal coordination chemistry, bridged silylene complexes, the reactivity of silylene complexes, and the reactions of hydrosilanes with transition metals to form silyl–metal complexes.[779–783]

5.08.13.1 Synthesis

The nature of different silicon-donor ligands and their various binding modes suggest a significant variation in the synthetic methods used to prepare such complexes. Table 22 details selected examples of W–CO complexes bearing silicon-donor ligands and their synthetic pathways. The more common synthetic methods include:

(i) Reaction of an anionic W–CO species with a halo-[784,785] or triflate-functionalized silane,[786] for example, the reaction of $Li[W(CO)_2(PMe_3)Cp]$ with $HSiCl_3$, affords $[W(CO)_2(PMe_3)Cp(SiHCl_2)]$.[787] This method can be used to prepare complexes with multiple W–CO centers linked by oligosilanes.[784,786]

(ii) Oxidative addition of an SiH species to a low-valent W center, for example, reaction of $[W(CO)_3(PCy_3)_2]$ with $PhSiH_3$, affords the unstable $[W(CO)_3(PCy_3)_2(SiH_2Ph)(H)]$.[200]

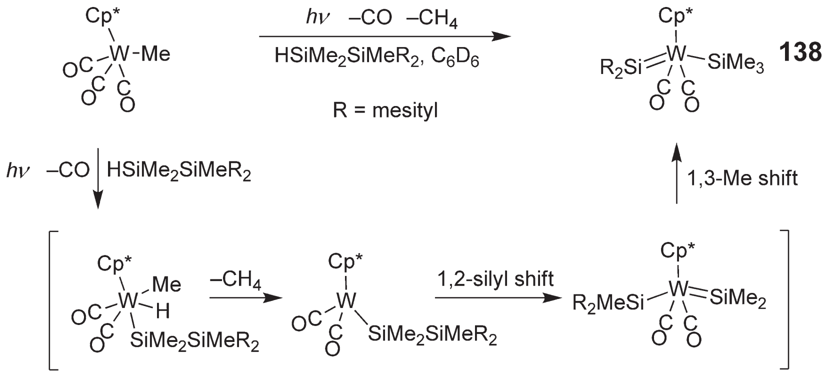
The initial products from the oxidative addition of an SiH species to a tungsten center often undergo reductive elimination involving the hydride before yielding the isolable product. For example, the process summarized in Equation (27) is thought to involve an oxidative addition/reductive elimination sequence.[788] The two-step process is common in the reaction of SiH species with methyl–W–CO complexes in which CH_4 results from the reductive

Table 22 Examples of W–CO complexes with silicon-donor ligands

Complex	*Synthesis*[a]	*Comments*	*W–Si$_{av}$* (Å)	δ *(W–Si)* [J_{WSi}][b]	*References*
$[W(CO)_2(PMe_3)Cp(SiHCl_2)]$	(i)			52.6 (21)	787
$[W(CO)_2(PMe_3)Cp^*(SiH_2Me)]$		$[W(CO)_2(PMe_3)Cp^*(SiCl_2Me)] + LiAlH_4$	2.56	10.4 (46)	785
$[W(CO)_2(PMe_3)Cp^*(SiH_3)]$		$[W(CO)_2(PMe_3)Cp^*(SiCl_3)] + LiAlH_4$	2.53	−43.2 (50)	785
$[W(CO)_2(PPh_3)Cp(SiHMe_2)]$	(i)			7.4 (42)	794
$[W(CO)_2(PMe_3)Cp(SiCl_2OSiCl_3)]$	(i)			26.4	795
137	(ii)	Reductive elimination step; μ-silylene	2.58	211.3 (55)	788
$[W(CO)_2(IMes)Cp(H)(SiEt_3)]^+$	(ii)	IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene		43.2	672
$[W(CO)_2Cp^*(\eta^3\text{-}Me_2SiCHCMe_2)]$	(ii)	$[W(CO)_2(NCMe)Cp^*(Me)] + HSiMe_2(CHCMe_2)$; η^3-silaallyl species	2.57	8.8	796
$[W(CO)_2(SiPh_2{\cdot}py)Cp^*(H)]$	(ii)	$[W(CO)_2(py)Cp^*(Me)] + H_2SiPh_2$; donor stabilized silylene	2.445	94.0 (111)	797
$[W(CO)_2\{SiHC(SiMe_3)_3\}\text{-}(\eta^5\text{-}C_5Me_4Et)(H)]$ **142**	(ii)	$[W(CO)_3(\eta^5\text{-}C_5Me_4Et)(Me)] + H_3SiC(SiMe_3)_3$; silylene···hydrido interaction	2.370	275.1 (110)	798
$[W(CO)_2(SiMes_2)Cp^*(SiMe_3)]$ **138**	(ii)	Donor-free silylene	2.385 (W–Si); 2.65 (W–Si)	380.9 (155) (W–Si); 22.1 (30) (W–Si)	789
$[W(CO)_2(SiMe_2{\cdot}HMPA)Cp(SiMe_3)]$		$[W(CO)_3(SiMe_2SiMe_3)Cp] + h\nu$/HMPA $\{OP(NMe_2)_3\}$; donor-stabilized silylene	2.48 (SiMe$_2$); 2.55 (SiMe$_3$)	92.5 (121) (SiMe$_2$); 18.6 (59) (SiMe$_3$)	790
$[\overline{W(CO)_2Cp\{SiMe_2O(Me)Si}Me_2\}]$	(ii)	$[W(CO)_3Cp(Me)] + HSiMe_2SiMe_2OMe$; donor-stabilized silylene	2.50	99.3 (99.3)	791
139	(ii)	Donor-stabilized silylene	2.49	115 (103)	792
141			2.47	97.8	793
$[W(CO)_5\{\overline{SiMe(Si}Me_2)_5\}]^-$		$[W(CO)_5I]^- + \{\overline{SiMe(Si}Me_2)_5\}^-$	2.67		99
$[\overline{W(CO)_2Cp\{SiMe_2O(Me)Si}Me_2\}]$		$[W(CO)_6] + Ph_2PCH_2CH_2SiHPh_2 + h\nu$, three-center W, H, Si bond		11.4	799

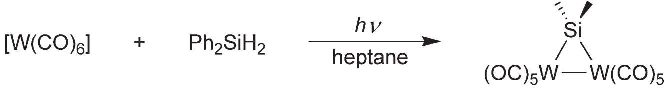
[a] See text for synthesis.

[b] ^{29}Si NMR chemical shift in ppm; in parentheses J_{WSi} in Hz.



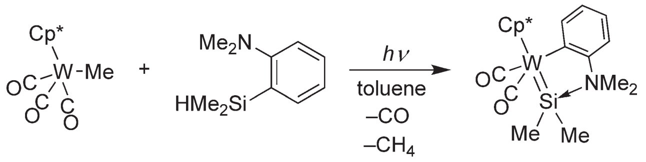
Scheme 43

elimination of the generated hydride and the methyl group. In cases where the reaction of a methyl–W–CO complex with an SiH species involves an oligosilane, the oxidative addition/reductive elimination sequence can be followed by a 1,2-silyl shift to yield a silyl-silylene–tungsten complex (Scheme 43).[789–791] The example in Scheme 43 is a special case because, first, it also involves a 1,3-methyl migration presumably to reduce steric congestion, and, second, **138** is an example of a donor-free silylene–tungsten complex.[789] A similar 1,2-shift, involving an aryl group, occurs in the formation of the donor-stabilized silylene **139** (Equation (28)).[792]



137

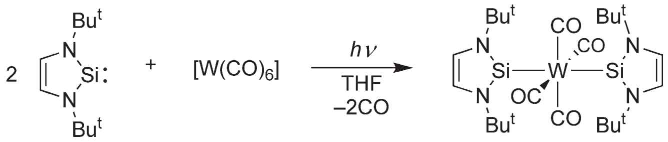
(27)



139

(28)

The stabilized *N*-heterocyclic silylene **140** reacts with $[W(CO)_6]$ under photolysis conditions to form the silylene complex **141** (Equation (29)).[780,793]



140 **141**

(29)

5.08.13.2 Structure and Properties

Selected examples of W–CO complexes bearing an Si-donor ligand are listed in Table 22 along with ^{29}Si NMR chemical shifts and $J_{\text{W–Si}}$ coupling constants, and W–Si bond length information for structurally characterized complexes. Recent developments in the coordination of silicon-donor ligands to tungsten–CO centers include the characterization of complexes containing μ-silylene, η^3-silaallyl and donor-free silyl/silylene species.[788,789,796,798] Recent attention has also focused on silylene complexes and the nature of the W–Si bond. Structural and spectroscopic information provides a useful comparison of silylene versus donor-stabilized silylene versus silyl complexes and helps to clarify the double bond versus partial double bond versus single bond distinction. For example, the donor-free silylene complexes **138** and **142** (in Table 22) exhibit short W–Si bond lengths (2.385 and 2.37 Å) and significantly downfield signals in ^{29}Si NMR spectra (δ380.9 and 275.1) with large W–Si coupling constants,[789,798] whereas donor-stabilized silylene complexes exhibit longer W–Si bonds and less downfield ^{29}Si NMR signals (see Table 22). Silyl complexes generally exhibit much longer W–Si bond lengths, upfield ^{29}Si NMR signals and smaller W–Si coupling constants.

Theoretical studies have examined the nature of the bond in Si–W–CO species.[800,801]

5.08.13.3 Reactions

Reactions on W–CO complexes bearing silicon-donor ligands can involve the metal center, for example, the 1,2-shifts mentioned earlier or the substituents on the silicon-donor ligands. The donor-stabilized silylene complex $[W(CO)_2(SiEt_2{\cdot}py)Cp^*(H)]$ reacts with excess $MePhSiH_2$ to form the silylene exchange product $[W(CO)_2(SiMePh{\cdot}py)Cp^*(H)]$ and Et_2SiH_2.[797] Examples of the reactions involving the substituents on the silicon center are summarized in Scheme 44.[785,787,802] The hydrolysis of silanes to silanols (second step in Scheme 44) can also be performed with urea–hydrogen peroxide and catalytic $MeReO_3$.[794]

5.08.14 Germanium, Tin, and Lead Ligands

This section deals with W–CO and W–CNR complexes bearing germanium-, tin-, and lead-donor ligands. As with silicon chemistry, interest in this area has continued to grow over the last decade. There is a large number of W–CO complexes bearing germanium- and tin-donor ligands, and comparatively very few complexes bearing lead-donor ligands.

5.08.14.1 Synthesis

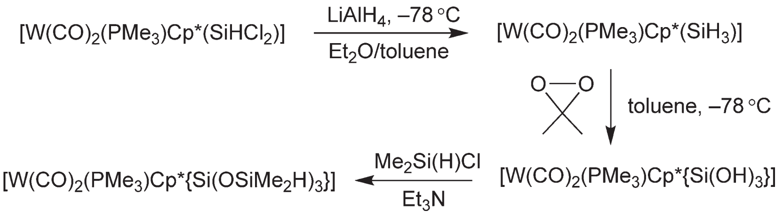
The synthetic methods vary quite significantly for germanium- and tin-donor complexes. Table 23 lists selected examples of W–CO complexes with germanium-, tin-, and lead-donor ligands and makes reference to their synthetic pathways. The more common synthetic methods include the following.

(i) Reaction of $SnCl_4$,[637,638,803–806] $RSnCl_3$,[659,803–805] R_2SnX_2,[807] R_3SnCl,[808,809] or $GeCl_4$[639,810] with a low-valent neutral or anionic W–CO species, often involving photolysis of the reaction mixture. This method is particularly common for the preparation of complexes bearing a tin-donor ligand. Reaction of a neutral complex generally affords the addition product with the formation of W–X and W–E (E = Sn, Ge) bonds, whereas reaction with an anionic complex generally affords the salt-elimination product with formation of only a W–E bond, analogous to method (i) in the synthesis of silicon-donor ligands.[807,808]

(ii) Insertion of $GeCl_2$[636,648,811,812] or Cp^*GeCl[813] into W–Cl bonds, for example, Scheme 45.[812,813]

(iii) Ligand substitution of $[W(CO)_5(THF)]$ by a germanium, tin, or lead donor ligand. A diverse range of complexes, including donor-stabilized and donor-free germylene and stannylene complexes, can be prepared by this method, for example, **143**,[814] **144**,[815] **145**,[816,817] **146**,[818] **147**,[819] and **148**.[820,821] In an attempt to prepare a plumbylene–$W(CO)_5$ complex, the bridging complex **149** was isolated in low yield.[822]

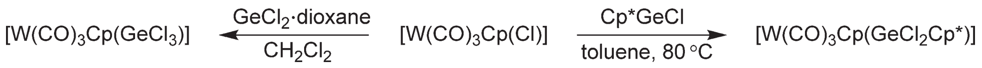
The alkyl–W–CO complexes $[W(CO)_3Cp(CH_2GeMe_2SiMe_3)]$ and $[W(CO)_3Cp(CH_2SiMe_2GeMe_3)]$ undergo a photochemical reaction to afford $[W(CO)_3Cp(GeMe_2CH_2SiMe_3)]$ and $[W(CO)_3Cp(GeMe_3)]$, respectively.[823]



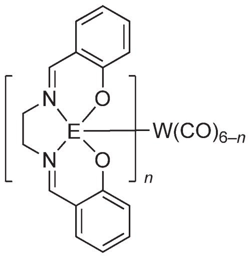
Scheme 44

Table 23 Examples of W–CO complexes with germanium- tin-, and lead-donor ligands

Complex	*Synthesis*[a]	*Comments*	*W–E$_{av}$* (Å)	*References*
Ge-donor ligands				
$[W(CO)_3(\eta^4\text{-nbd})Cl(GeCl_3)]$	(i)	$[W(CO)_4(\eta^4\text{-nbd})] + GeCl_4$	2.64	810
$[W(CO)_3(NCMe)_2Cl(GeCl_3)]$	(i)	$[W(CO)_4(NCMe)_2] + GeCl_4$		639
$[W(CO)_3(NCEt)_2Cl(GeCl_3)]$		$[W(CO)_3(NCMe)_2Cl(GeCl_3)] + EtCN$	2.57	639
$[W(CO)_2(PMe_3)Cp^*(GeCl_3)]$	(ii)	Solid-state *cis* → *trans* isomerization	2.56 (*cis*); 2.52 (*trans*)	811
cis-$[W(CO)_2(NCEt)Cp^*(GeCl_3)]$	(ii)	*cis*-$[W(CO)_2(NCEt)Cp^*(Cl)] + GeCl_2\cdot$dioxane	2.54	812
$[W(CO)(\equiv CNEt_2)Cp^*(Cl)(GeCl_3)]$	(ii)	$[W(CO)(\equiv CNEt_2)Cp^*(Cl)_2] + GeCl_2\cdot$dioxane	2.58	648
$[\{W(CO)_3Cp\}_2(\mu\text{-}GeCl_2)]$		$[W(CO)_3Cp(GeCl_3)] + Li[W(CO)_3Cp]$	2.66	824
145 (E = Ge; X = Cl)	(iii)		2.57	817
146			2.595	818
148	(iii)		2.59	820
$[W(CO)_2(GeMe_2)Cp^*(GeMe_3)]$		$[W(CO)_3Cp^*(GeMe_2GeMe_3)] + h\nu$, 1,2-$GeMe_3$ shift	2.46 ($GeMe_2$); 2.67 ($GeMe_3$)	825
$[W(CO)_2(GeMe_2\cdot py)Cp^*(GeMe_3)]$		Donor-stabilized germylene	2.53 ($GeMe_2$); 2.63 ($GeMe_3$)	825
$[W(CO)_3Cp(GeR)]$ **150**	(i)	R = C_6H_3-2,6-($C_6H_2Pr^i_3$-2,4,6); W–Ge–C = 115°	2.681	826
$[W(CO)_2Cp(\equiv GeR)]$ **151**		photolysis of **150**; W-Ge-C = 171°; R = C_6H_3-2,6-($C_6H_2Pr^i_3$-2,4,6)	2.278	826
Sn-donor ligands				
$[W(CO)_3\{CH_2(3,5\text{-}Me_2pz)_2\}Cl(SnCl_3)]$	(i)	$[W(CO)_4\{CH_2(3,5\text{-}Me_2pz)_2\text{-}N,N'\}] + SnCl_4$	2.74	803
$[W(CO)_4(\mu\text{-}Cl)_3W(CO)_3(SnCl_3)]$	(i)	$[W(CO)_6] + SnCl_4 + h\nu$	2.73	827
$[W(CO)_3(NCMe)_2(Cl)(SnCl_3)]$	(i)	$[W(CO)_4(NCMe)_2] + SnCl_4$	2.71	637, 806
$[W(CO)_3(NCEt)_2Cl(SnRCl_2)]$	(i)	$[W(CO)_3(NCEt)_3] + SnCl_3R$; R = Bu, Ph		659
$[W(CO)_3(\eta^4\text{-nbd})Cl(SnCl_3)]$		$[W(CO)_3(NCMe)_2Cl(SnCl_3)] +$ nbd	2.76	828
$[\{W(CO)_3(Cp)\}_2\{\mu\text{-}Sn(OSiMe_3)_2\}]$			2.81	829
cis-**143** (E = Sn; *n* = 2)	(iii)		2.71	814
147	(iii)		2.75	819
Pb-donor ligands				
149			2.75	822
$[W(CO)_3Cp\{Pb\text{-}C_6H_3(C_6H_2Pr^i_3\text{-}2,4,6)_2\text{-}2,6\}]$		$Li[W(CO)_3Cp] + BrPb\text{–}C_6H_3(C_6H_2Pr^i_3\text{-}2,4,6)_2\text{-}2,6$	3.00	830

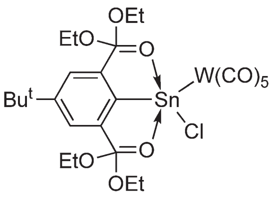


Scheme 45



E = Ge, Sn, Pb; *n* = 1, 2

143



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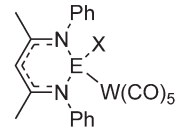
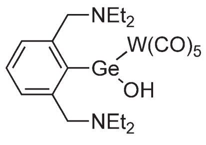


X = Cl, E = Ge, Sn
X = I, E = Ge

145



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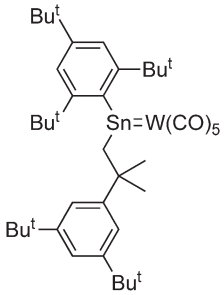

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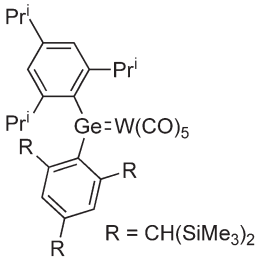
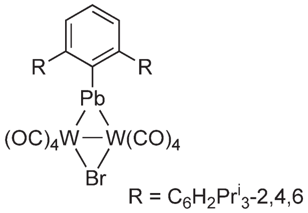


R = CH(SiMe$_3$)$_2$

148



R = C$_6$H$_2$Pr^i$_3$-2,4,6

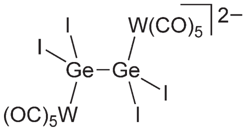
149

5.08.14.2 Structure and Properties

Selected examples of structurally characterized W–CO complexes bearing germanium-, tin-, and lead-donor ligands, along with the associated W–E$_{av}$ bond lengths, are listed in Table 23. Of particular note is the W≡Ge complex **151** (in Table 23). In the W≡Ge complex **151**, the W–Ge–C moiety is almost linear (ca. 171° cf. 115° for **150**) and the W≡Ge bond (ca. 2.28 Å) is considerably shorter than the W–Ge bond (ca. 2.68 Å) in **150**.[826] In addition to the complexes discussed above, bearing ligands with a single germanium-, tin-, or lead-donor atom, a variety of W–CO complexes containing E–E or E-based cluster species as ligands (where E = Ge, Sn, and Pb) have been synthesized and structurally characterized, including the anions **152–154** and $[W(CO)_3(E_9)]^{4-}$ (E = Sn, Pb).[831–836]

Theoretical studies have examined binding modes, bond energies, and the nature of bonding in model compounds such as $[W(CO)_5(E_2)]^{2-}$, $[W(CO)_5\{E(OH)_2\}]$, and $[W(CO)_4Cl(EH)]$ (where E = Si, Ge, Sn, and Pb) and *trans*-$[W(CO)_4Cl(\equiv GeCp)]$.[230,801,837]

Germanium- and tin-donor complexes of W–CO species exhibit catalytic activity or act as pre-catalysts for alkyne polymerization,[639,838] allylic substitution,[839] and ring-opening metathesis polymerization (ROMP).[840–842]



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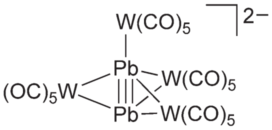

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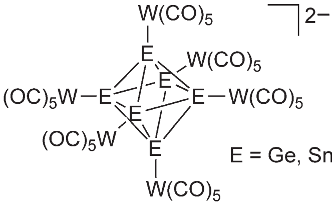

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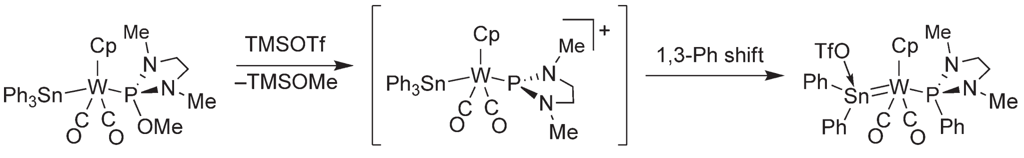
5.08.14.3 Reactions

Reactions involving W–CO complexes bearing germanium- or tin-donor ligands can be broadly broken into three groups:

(i) Reactions involving the E–X bonds and not the W center. Examples include reaction of $[W(CO)_3Cp(GeCl_3)]$ with $Li[W(CO)_3Cp]$ to afford $[\{W(CO)_3Cp\}_2(\mu\text{-}GeCl_2)]$,[824] and the substitution of the chlorides in $[W(CO)(PMe_3)_2Cp(GeCl_3)]$ with N_3^- to afford $[W(CO)(PMe_3)_2Cp\{Ge(N_3)_3\}]$.[843] Halides can also be replaced by alkyl groups, sulfides, and heterocyclic nitrogen donors such as bipy and phen.[807,817,844] The E–X bonds can undergo hydrolysis or alcoholysis reactions to give E–OH and E–OR species bound to a W–CO center.[818,829,845,846]

(ii) Substitution reactions at the W center not involving the W–E bonds. The labile precursors $[W(CO)_3(NCMe)_2Cl(SnCl_2R)]$ (R = Cl, Bu, Ph) can undergo CO and MeCN substitution reactions with nitrile-, phosphorus-, sulfur-, and alkenyl-donor ligands.[637,659,828]

(iii) Reactions involving the W–E bond. Tungsten–CO complexes bearing Cp and tin-donor ligands can undergo base-induced migration of the SnR_x group from the W center to the Cp ring,[847,848] for example, the sequential reaction of $[W(CO)_2\{{=}C(Ph)OEt\}Cp(SnPh_3)]$ with LDA ($LiNPr^i{}_2$) and then benzoyl chloride affords the



155 **156**

Scheme 46

carbyne complex $[\mathrm{W(CO)_2(\equiv CPh)}(\eta^5\text{-}\mathrm{C_5H_4SnPh_3})]$, presumably via $[\mathrm{W(CO)_2\{=C(Ph)OEt\}}(\eta^5\text{-}\mathrm{C_5H_4SnPh_3})]^-$.[848] The stannyl complex **155** can be converted into the donor-stabilized stannylene complex **156** by the action of a Lewis acid followed by a 1,3-migration of a phenyl group (Scheme 46).[809]

5.08.15 σ-Bonded Carbon-Donor Ligands

This section contains W–CO and W–CNR complexes bearing σ-bonded carbon-donor ligands, including alkyl, acyl, alkynides, σ-bound aryl ligands, thiocarbonyl and selenocarbonyl ligands, carbenes, and carbynes. Carbene complexes are divided into three sections: (i) carbenes with no heteroatom (stabilizing) substituents, including vinylidenes and related species, (ii) oxacarbenes, stabilized by an oxygen or related heteroatom, and (iii) azacarbenes stabilized by a nitrogen substituent, which include *N*-heterocyclic carbenes. Some complexes and their relevant chemistries that fall within this category have been covered in earlier sections of this chapter. In general, examples that have appeared earlier in this chapter will not be repeated in the carbon-donor sections. In particular, the use of $[\mathrm{W(CO)_3Cp(Me)}]$ for the preparation of complexes with other donor types will not be repeated. The chemistry of complexes which contain the Tp and Tp′ ligands in addition to σ-bonded carbon-donor ligands are covered in Section 5.08.3.2; additional examples are included here. The use of carbene– and alkynide–W(CO) complexes in the synthesis of elaborate organic molecules, which is extensive, is, in general, not covered in this chapter (see *Volumes 10* and *11* in this series). The use of propargyl, alkynide, or Fischer carbene complexes of the types $[\mathrm{W(CO)_3Cp(CH_2C\equiv CR)}]$, $[\mathrm{W(CO)_3Cp(C\equiv CR)}]$, and $[\mathrm{W(CO)_5\{=C(X)R\}}]$ ($\mathrm{X = OR^1, NR^1_2}$) for the preparation of heterocyclic and carbocyclic compounds has been reviewed.[849–852]

5.08.15.1 σ-Donor Ligands

This section includes alkyl, aryl, vinyl, acyl, and iminoacyl ligands. Selected examples of crystallographically studied complexes are detailed in Table 24.

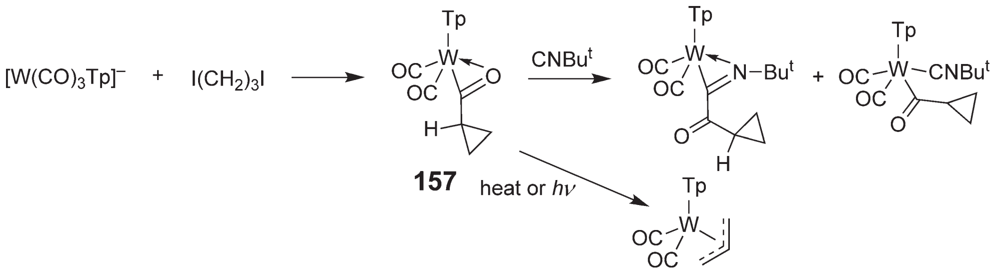
σ-Bound aryl complexes can be prepared by oxidative addition of an aryl halide species to a low-valent metal complex. A number of examples involving nitrogen-donor complexes are discussed in Section 5.08.3. Acyl complexes are typically used in the preparation of oxacarbene complexes (see Section 5.08.15.5).

Long-chain alkyl and acyl complexes $[\mathrm{W(CO)_3Cp(R)}]$ ($\mathrm{R} = n\text{-}\mathrm{C_6H_{13}}$, $n\text{-}\mathrm{C_7H_{15}}$, and $n\text{-}\mathrm{C_{10}H_{21}}$) and $[\mathrm{W(CO)_3Cp\{C(O)C_{11}H_{23}\}}]$ have been prepared from $\mathrm{Na[W(CO)_3Cp]}$ and the appropriate alkyl iodide or acyl chloride.[853] Treatment of $\mathrm{Na[W(CO)_3Cp]}$ with excess $\mathrm{Br(CH_2)}_n\mathrm{Br}$ ($n = 3-7$) affords the ω-bromoalkyl complexes $[\mathrm{W(CO)_3Cp\{(CH_2)}_n\mathrm{Br\}}]$, and subsequent reaction with NaI affords $[\mathrm{W(CO)_3Cp\{(CH_2)}_n\mathrm{I\}}]$.[854,855] Reaction of $[\mathrm{W(CO)_3Cp\{(CH_2)}_n\mathrm{I\}}]$ with $\mathrm{Na[Mo(CO)_3Cp]}$, $\mathrm{Na[Mo(CO)_2(PPh}_m\mathrm{Me}_{3-m}\mathrm{)Cp]}$ ($m = 0-3$), or $[\mathrm{Pt(bipy)Me_2}]$ affords the polymethylene-bridged heterobimetallic complexes $[\mathrm{W(CO)_3Cp\{}\mu\text{-}\mathrm{(CH_2)}_n\mathrm{\}Mo(CO)_3Cp}]$, $[\mathrm{W(CO)_3Cp\{}\mu\text{-}\mathrm{(CH_2)}_n\mathrm{\}Mo(CO)_2(PPh}_m\mathrm{Me}_{3-m}\mathrm{)Cp}]$ ($m = 0-3$), and $[\mathrm{W(CO)_3Cp\{}\mu\text{-}\mathrm{(CH_2)}_n\mathrm{\}Pt(bipy)(I)Me_2}]$, respectively.[856,857] The reaction of $\mathrm{Na[W(CO)_3Cp^*]}$ with *o*-, *m*- and *p*-α,α'-dichloroxylenes affords the *o*-, *m*-, and *p*-xylyl-linked dinuclear complexes $[\mathrm{W(CO)_3Cp^*}(\mu\text{-}\mathrm{CH_2C_6H_4CH_2)W(CO)_3Cp^*}]$.[858] Reaction of $[\mathrm{W(CO)_3Tp}]^-$ with $\mathrm{I(CH_2)_3I}$ affords the η^2-acyl cyclopropanation product **157**, which can subsequently react with $\mathrm{CNBu^t}$ to afford an η^2-iminoacyl complex or undergo decarbonylation to yield an η^3-allyl complex (Scheme 47).[859] The sequential reaction of $[\mathrm{W(CO)_6}]$ with LDA, iodine, and $\mathrm{PPh_3}$ gives the η^2-carbamoyl (acyl-like) complex *fac*-$[\mathrm{W(CO)_3(PPh_3)I\{}\eta^2\text{-}\mathrm{C(=O)NPr^i_2}\text{-}O,C\}]$, which can act as a precursor of other carbamoyl complexes.[860] Reaction of $[\mathrm{W(CO)_2(L)(NO)]PF_6}$ (L = 1,4,7-triisopropyl-1,4,7-triazacyclononane) with $\mathrm{LiAlH_4}$ affords the methyl complex $[\mathrm{W(CO)(L)(NO)Me}]$.[861] The structure of $[\mathrm{W(CO)_5\{C(O)Ph\}\{Li(diglyme)\}}]$ has been reported recently.[862] The reaction of $[\mathrm{W(CO)_3(NCMe)_3}]$ with *spiro*-[2.4]hepta-4,6-diene affords the chelating complex **158** (Equation (30)).[863]

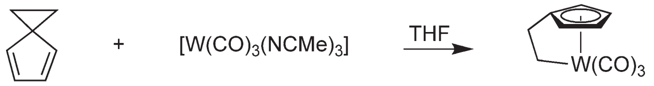
Table 24 Selected structurally characterized examples of W–CO and W–CNR complexes with σ-donor carbon ligands

Complex	*Comments*	*W–C$_{av}$* (Å)	δ (WC)[a]	*References*
Alkyl				
$[W(CO)_3Cp\{(CH_2)_5I\}]$		2.35 (CH_2)	−10.9 (CH_2)	854, 855
$[W(CO)_3Cp\{\mu\text{-}(CH_2)_3\}Mo(CO)_2(PPh_3)Cp]$		2.32 (CH_2)	−3.7 (CH_2)	856
$[W(CO)_2(CNBu^t)(\eta^5\text{-}C_9H_7)Me]$	*cis*- and *trans*-isomers	2.26 (Me, *cis*)	−20.4 (Me, *cis*)	867
158		2.36	−61.7 (CH_2)	863
$[W(CO)_3Cp^*(\mu\text{-}CH_2C_6H_4CH_2)W(CO)_3Cp^*]$	*o*-, *m*-, and *p*-xylyl isomers	2.36		858
Aryl				
161		2.17 (aryl C)	124.3 (aryl C)	866
Acyl				
160	*cis*- and *trans*-isomers	2.29 (acyl), 2.36 (CH_2) (*trans*)	253.3 (acyl), 25.3 (CH_2) (*trans*)	876
$[W(CO)(PMe_3)\{\eta^2\text{-}C(O)Me\}Tp']$	W–O 2.21 Å	1.98 (acyl)	267.1 (acyl)	240
157	W–O 2.22 Å	2.02 (acyl)		
Ketenyl				
162	η^1-ketenyl complex; In equilibrium with $[W(CO)_2(Cp^*)(\equiv CSiPh_3)]$ in solution; η^2-NCMe	2.17 (ketenyl)	20.7 (ketenyl)	879
Iminoacyl				
$[W(CO)_2\{\eta^2\text{-}C(Me){=}NBu^t\text{-}C,N\}(\eta^5\text{-}C_9H_7)]$	W–N 2.14 Å	2.10 (C=N)	188.4 (C=N)	867

[a] ^{13}C NMR, δ in ppm.



Scheme 47

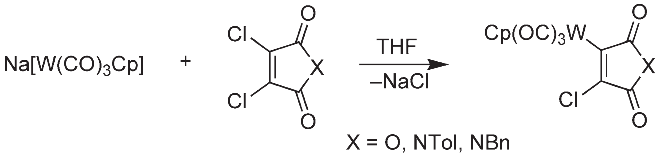


158 (30)

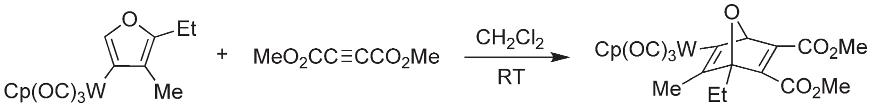
The reaction of $[W(CO)_3Cp(Me)]$ with PPh_3 or $P(C_6H_4F\text{-}4)_3$, which afforded the migratory insertion product $[W(CO)_2(PR_3)Cp(COMe)]$, has been studied in the absence of solvent.[864,865] The reaction of $[W(CO)_3Cp(Me)]$ with $B(C_6F_5)_3$ afforded $[W(CO)_2Cp\{\eta^2\text{-}C_6F_4C(O)Me\text{-}2\text{-}C,O\}]$ **161**.[866] Thermolysis of the isocyanide complexes $[W(CO)_2(CNR)(\eta^5\text{-}L)(Me)]$ ($L = Cp$, Cp^*, indenyl) affords mixtures of the isomeric η^2-iminoacyl and η^3-azaallyl complexes $[W(CO)_2\{\eta^2\text{-}C(Me){=}NR\text{-}C,N\}(\eta^5\text{-}L)]$ and $[W(CO)_2\{\eta^3\text{-}H_2CC(H)NR\}(\eta^5\text{-}L)]$, respectively.[867,868] The proportions of each isomer formed are dependent on ring type (Cp, Cp^*, C_9H_7) and the solvent used in the reaction. If the thermolysis is performed in acetone, then the metallacyclic product $[W(CO)_2(\eta^5\text{-}L)\{\eta^2\text{-}C(Me){=}N(R)C(Me)_2O\text{-}C,O\}]$ is isolated.

The propargyl complex $[W(CO)_3Cp(CH_2C{\equiv}CH)]$ reacts with aniline to afford the allyl complex $[W(CO)_2Cp\{\eta^3\text{-}CH_2C(CONHPh)CH_2\}]$, or with $AlCl_3$ in the presence of fumaric acid to give the acid chloride $[W(CO)_2Cp\{\eta^3\text{-}CH_2C(COCl)CH_2\}]$, which can hydrolyze to the carboxylic acid or can react with $[W(CO)_3Cp]^-$ to afford the bridged bimetallic complex $[W(CO)_2Cp\{\mu\text{-}\eta^3\text{:}\eta\text{-}CH_2C(CH_2)C({=}O)\}W(CO)_3Cp]$.[869] Mild thermolysis of $[W(CO)_3Cp(\eta\text{-}CH_2C{\equiv}CH)]$ affords the allenyl complex $[W(CO)_3Cp(\eta\text{-}CH{=}C{=}CH_2)]$, which reacts with RNH_2 to form the azatungstacyclobutane complex $[W(CO)_2Cp\{\eta^2\text{-}CH(CONHR)CH(Me)NHR\}]$.[870] Reaction of the allenyl complex with MeOH affords $[W(CO)_2Cp\{\eta^3\text{-}CH_2CHCH(CO_2Me)\}]$ or $[W(CO)_2Cp\{\eta^2\text{-}C(Me){=}CHC(O)OMe\text{-}C,O\}]$ depending on the reaction solvent. Treatment of the propargyl complexes $[W(CO)_3Cp(CH_2C{\equiv}CR)]$ (R = Me, Ph) with TfOH followed by quenching with water or primary amines (R^2NH_2) affords carbonylation products, including $[W(CO)_2Cp\{\eta^3\text{-}C(O)OCH(R)CH{=}CH_2\}]$ and $[W(CO)_2Cp\{\eta^3\text{-}C(O)N(R^2)CH(R)CH{=}CH_2\}]$.[871]

Nucleophilic substitution of chloride in dichloroalkenes by $[W(CO)_3Cp]^-$ affords vinyl complexes (Equation (31)).[872] The vinyl complex $[W(CO)_3Cp(\eta\text{-}CH{=}CHC(O)Me)]$ undergoes facile carbonylation and cyclization to afford a γ-lactone complex; further carbonylation in the presence of acid yields a cyclic anhydride complex.[873] η^1-Furyl–W–CO complexes undergo cycloaddition reactions with alkynes and alkenes to afford η^1-bicyclic alkene–W–CO complexes (e.g., Equation (32)).[874]



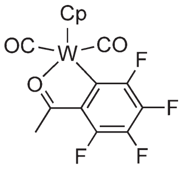
(31)



(32)

Reactivity of the bridging ketene complex $[W(CO)_3Cp\{\mu\text{-}\eta{:}\eta^2\text{-}CH_2C(O)\}W(CO)_2Cp]$ **159** is summarized in Scheme 48.[875,876] Protonation of the carbene complex $[W(CO)_2({=}CH_2)Tp']$ in the presence of PR_3 affords the methyl complex $[W(CO)_2(PR_3)Me(Tp')]$, which exists in equilibrium with the η^2-acyl complex $[W(CO)(PR_3)\{\eta^2\text{-}C(O)Me\}Tp']$.[240] Protonation of the carbene in the presence of $PhC{\equiv}CH$ affords the η^1-acyl complex $[W(CO)(\eta^2\text{-}PhC{\equiv}CH)\{\eta^1\text{-}C(O)Me\}Tp']$.

Photolysis of $[W(CO)_3Cp(Me)]$ in *n*-heptane and subsequent reaction of $[W(CO)_2Cp(Me)]\cdot$*n*-heptane with CO, PPh_3, and N_2 has been studied by time-resolved IR.[199] $[W(CO)_3Cp(Et)]$ and various derivatives with partially deuterated ethyl groups have been studied by FTIR to determine C–H bond properties of the ethyl substituent.[877] Theoretical studies have examined the electronic structure and CO ligand-dissociation energies of $[M(CO)_5Me]^-$ (M = Cr, Mo, W).[521] The mechanism for carbene formation by methane elimination from $[W(L)Cp(Me)_2]^-$ (L = CO, NO) has also been studied by DFT calculations.[878] The results suggest that the CO complex favors a two-step oxidative addition–reductive elimination mechanism, whereas the NO complexes prefers a one-step mechanism.



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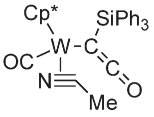

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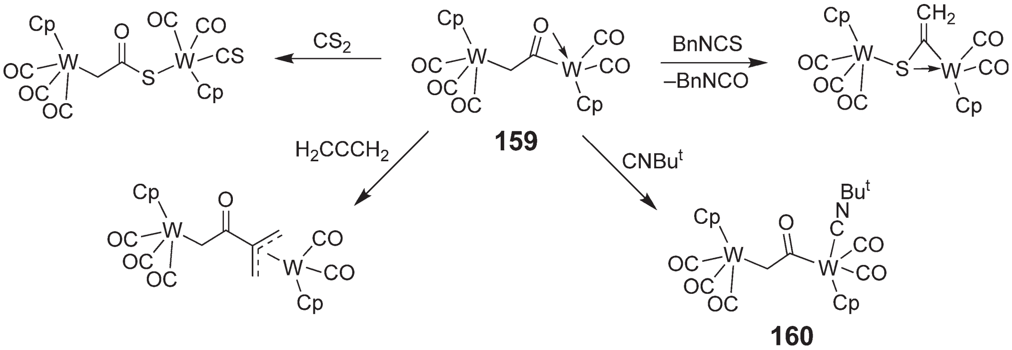


Scheme 48

5.08.15.2 Alkynide Complexes

The majority of the chemistry in this field still focuses on derivatives of $[W(CO)_3Cp(C\equiv CR)]$. Polyyne complexes $\{M–(C\equiv C)_n–\}$, in particular, have seen significant development and have been the subject of recent reviews covering synthesis, structure and properties, and reactivity.[880,881] There is significant interest in the preparation of bimetallic complexes linked by polyyne units as well as the use of alkynide complexes in the preparation of complex mixed metal clusters.

5.08.15.2.1 Synthesis

In general, the synthesis of alkynide complexes has not significantly changed since COMC (1995),[882] though new developments are covered here. The palladium-catalyzed coupling of $[W(CO)_3Cp(I)]$ and $Bu_3SnC\equiv CR$ ($R = H$, Pr, Ph) affords the alkynide complexes $[W(CO)_3Cp(C\equiv CR)]$.[883] The methods used to prepare the ferrocenyl-capped polyyne complexes $[W(CO)_3Cp\{(C\equiv C)_nFc\}]$ ($n = 1 - 4$) demonstrate some of the various synthetic methodologies available.[884] The reaction of $[W(CO)_3Cp(Cl)]$ with $Fc(C\equiv C)_2H$ in the presence of $CuI/NHEt_2$ affords $[W(CO)_3Cp\{(C\equiv C)_2Fc\}]$, the Pd(0)/Cu(I)-catalyzed coupling of $[W(CO)_3Cp\{(C\equiv C)_2H\}]$ with $FcC\equiv CI$ affords $[W(CO)_3Cp\{(C\equiv C)_3Fc\}]$, and the oxidative coupling reaction of $[W(CO)_3Cp\{(C\equiv C)_2H\}]$ and $Fc(C\equiv C)_2H$ with $CuCl/TMEDA/O_2$ in acetone affords $[W(CO)_3Cp\{(C\equiv C)_4Fc\}]$.[884] Reaction of *cis*-$[W(CO)_2(\eta^2\text{-dmpm})(\eta^3\text{-}C_3H_5)Cl]$ with $LiC\equiv CPh$ affords *cis*-$[W(CO)_2(\eta^2\text{-dmpm})(\eta^3\text{-}C_3H_5)(C\equiv CPh)]$, which rapidly isomerizes to the isomer with the CO ligands mutually *trans*, and then slowly decomposes in solution liberating $PhC\equiv CCH_2CH{=}CH_2$.[885]

5.08.15.2.2 Reactions

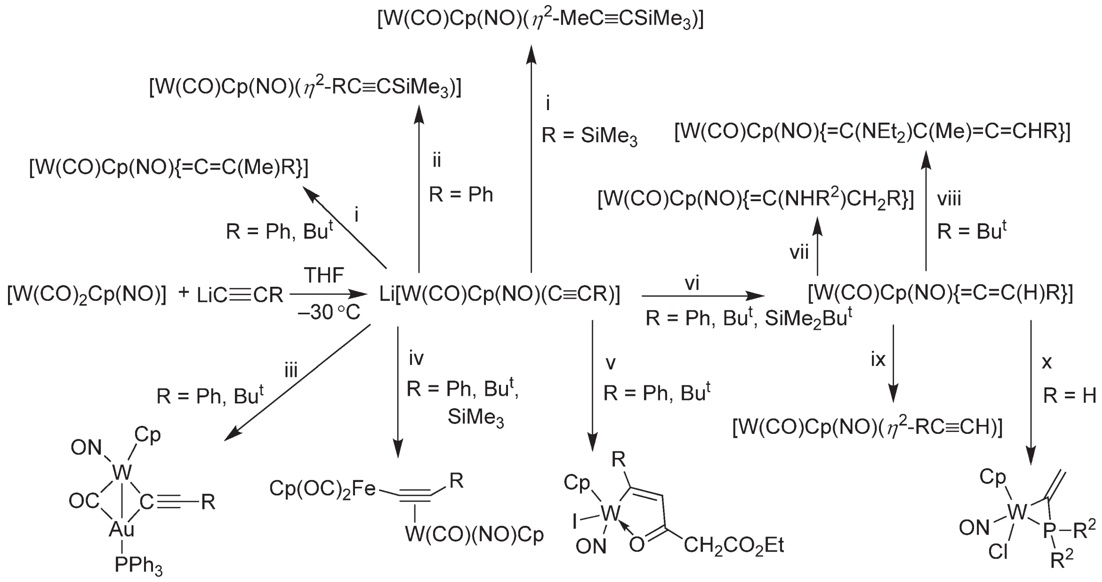
Treatment of $[W(CO)_3Cp(C\equiv CCH_2C_6H_4OMe\text{-}4)]$ with excess TfOH at −78 °C followed by quenching with water yields the acyl complex $[W(CO)_3Cp\{C(O)CH_2CH_2C_6H_4OMe\text{-}4\}]$, but if the reaction mixture is slowly warmed over a prolonged period, then the oxidative carbonylation product $[W(CO)(OTf)_2Cp\{\eta^2\text{-}C(O)C(CH_2)CH_2C_6H_4OMe\text{-}4\}]$ is isolated.[886]

The reaction of $[W(CO)_3Cp^*(C\equiv CPh)]$ with $[Re(CO)_5X]$ ($X = Br$, I) yields the alkynide-bridged $[W(CO)_2Cp^*(\mu\text{-}\eta{:}\eta^2\text{-}C\equiv CPh)(\mu\text{-}X)Re(CO)_3]$ (W–Re), and the bridging halide can be exchanged with PhS^- or AcO^- by reaction with PhSH or AcOH, respectively.[887] The reaction of $[W(CO)_3Cp(C\equiv CPh)]$ with the rhenium dioxo dimer $[ReCp^*(O)(\mu\text{-}O)]_2$ affords the bridging alkynide complex $[W(CO)_2Cp(\mu\text{-}\eta{:}\eta^2\text{-}C\equiv CPh)Re(O)Cp^*]$ (W–Re), whose thermolysis affords the isomeric complex $[W(O)Cp(\mu\text{-}\eta^2{:}\eta\text{-}PhC\equiv C)(\mu\text{-}CO)Re(CO)Cp^*]$, a result of an oxygen atom transfer between the metal centers.[888] The bridged alkynide complex $[W(CO)_2Cp(\mu\text{-}\eta{:}\eta^2\text{-}C\equiv CPh)W(CO)_2Cp]^-$ (W–W), generated *in situ* by reaction of $LiC\equiv CPh$ with $[W_2(CO)_4Cp_2]$, reacts with $ClAuPR_3$ ($R = Me$, Ph) to afford the μ-alkyne complex $[W(CO)_2Cp(\mu\text{-}\eta^2{:}\eta^2\text{-}R_3PAuC\equiv CPh)W(CO)_2Cp]$ (W–W).[889]

The terminal alkyne of the diynyl complex $[W(CO)_3Cp(C\equiv CC\equiv CH)]$ can be readily functionalized by conventional lithiation procedures, Cu(I)/Pd(0)-catalyzed coupling methods, or oxidative coupling reactions to afford $[W(CO)_3Cp(C\equiv CC\equiv CR)]$ $\{R = Ph$, Tol, $C_6H_4CO_2Me\text{-}4$, $SiMe_3$, $P(O)Ph_2\}$, $[W(CO)_3Cp\{\mu\text{-}(C\equiv C)_2\text{-}C_6H_4(C\equiv C)_2\}W(CO)_3Cp]$, and $[W(CO)_3Cp\{\mu\text{-}(C\equiv C)_4\}W(CO)_3Cp]$.[890,891] The diynyl complex $[W(CO)_3Cp(C\equiv CC\equiv CH)]$ can also be functionalized with a diverse range of metal species to form the C_4-bridging bimetallic complexes $[W(CO)_3Cp(\mu\text{-}C\equiv CC\equiv C)ML_n]$ $\{ML_n = Mo(CO)_3Cp$, $W(CO)_3Cp$, $Fe(CO)_2Cp$, $Ru(CO)_2Cp$, $Rh(CO)(PPh_3)_2$, $Ir(CO)(PPh_3)_2$, $Mn(CO)_5$, and $Au(PPh_3)\}$ and trimetallic complexes $[W(CO)_3Cp(\mu\text{-}C\equiv CC\equiv C)(ML_n)(\mu\text{-}C\equiv CC\equiv C)W(CO)_3Cp]^z$ $\{ML_n = Hg$, *cis*-Pt(dppe), *cis*-$Pt(PEt_3)_2$, $z = 0$; $ML_n = Au$, $z = -1\}$.[892–894] Oxidation of $[W(CO)_3Cp^*\{\mu\text{-}(C\equiv C)_2\}W(CO)_3Cp^*]$ with H_2O_2 affords the bis-dioxo complex $[W(O)_2Cp^*\{\mu\text{-}(C\equiv C)_2\}W(O)_2Cp^*]$.[895] Reaction of $[W(CO)_3Cp\{\mu\text{-}(C\equiv C)_2\}Au(PPh_3)]$ with the cluster $[Co_3(\mu^3\text{-}CBr)(\mu\text{-dppm})(CO)_7]$ results in the elimination of $(Ph_3P)AuBr$ and formation of the complex $[W(CO)_3Cp\{\mu\text{-}(C\equiv C)_2C\}\{Co_3(\mu\text{-dppm})(CO)_7\}]$ with a C_5-chain.[896]

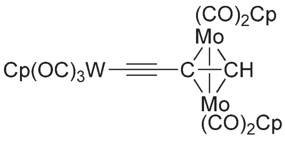
Alkynide and polyyne complexes $[W(CO)_3Cp(C\equiv CR)]$ and $[W(CO)_3Cp\{(C\equiv C)_nR\}]$ can react with $[Co_2(CO)_8]$, $[Co_2(\mu\text{-dppm})(CO)_6]$, and $[\{Mo(CO)_2Cp\}_2]$ to afford π-bound alkyne complexes such as the structurally characterized **163** and **164**.[884,890,897,898] Interestingly, the reaction of $[W(CO)_3Cp(C\equiv CSiMe_3)]$ with $[\{W(CO)_3Cp\}_2]$ yielded the π-bound diyne complex **165**.[898] Alkynide complexes $[W(CO)_3L(C\equiv CR)]$ and $[W(CO)_3L(C\equiv CC\equiv CR)]$ ($L = Cp$ or Cp^*) react with $[Ru_3(CO)_{10}(NCMe)_2]$,[899] $[Os_3(CO)_{10}(NCMe)_2]$,[900–902] $[Ru_4(CO)_{13}(\mu^3\text{-}PPh)]$,[903] $[Ru_5(CO)_{15}(\mu^5\text{-}C)]$,[904] $[Ir_2W_2Cp_2(CO)_{10}]$,[905] $[Fe_3(CO)_9(\mu^3\text{-}E)_2]$ ($E = S$, Se, Te),[601,906–910] $[Fe_2Ru(CO)_9(\mu^3\text{-}E)_2]$ ($E = S$, Se),[911] $[Fe_2W(CO)_{10}(\mu^3\text{-}S)_2]$,[912] and $[Fe_2Mo(CO)_{10}(\mu^3\text{-}E)_2]$ ($E = S$, Se)[913] to afford a variety of mixed metal-cluster complexes.

The *in situ* formation of the alkynide $[W(CO)Cp(C\equiv CR)(NO)]^-$ is thought to occur in the reaction of $[W(CO)_2Cp(NO)]$ with $LiC\equiv CR$.[914] Reaction of the *in situ*-formed alkynide complex with various electrophiles leads to the formation of a variety of species including vinylidene and η^2-alkyne complexes (Scheme 49).[914–922]



i, TfOMe; ii, Me$_3$SiCl; iii, AuCl(PPh$_3$); iv, [Fe(CO)$_2$(THF)Cp]$^+$; v, (a) ICH$_2$CO$_2$Et, (b) H$_2$O; vi HCl$_{(aq)}$; vii, NHR^2 (R^2 = Bu^n, Bu^t); viii, MeC≡CNEt$_2$; ix, Δ, toluene; x, ClPR$^2_2$ (R^2 = Ph, Bu^t)

Scheme 49



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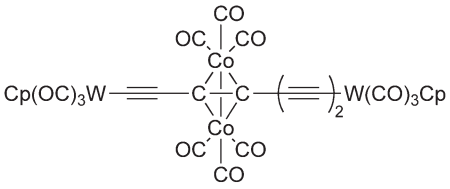

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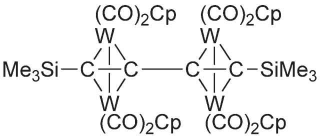

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5.08.15.3 Thiocarbonyl and Selenocarbonyl Complexes

There has been little development in the area of W–CS or W–CSe complexes; reports in the area have focused on theoretical studies of the complexes [W(CO)$_5$(CS)], [W(CO)$_5$(CSe)], and [W(CO)$_4$(CS)(H$_2$)].[7,9,15,727] Matrix-isolation studies have examined the photolysis of [W(CO)$_5$(CS)] in the presence of H$_2$ or N$_2$ to form *cis*-[W(CO)$_4$(CS)(H$_2$)] and *cis*-[W(CO)$_4$(CS)(N$_2$)], respectively, which isomerize to the *trans*-isomers upon photolysis with visible light.[42] The reaction, in Scheme 48, of **159** with CS$_2$ affords a W–CS complex, which has been structurally characterized; the CS ligand is not displaced under 1 atm of CO.[875]

5.08.15.4 Carbene Complexes with No Heteroatom-stabilizing Substituents

This section contains carbene complexes without heteroatom-stabilizing substituents bonded directly to the carbene carbon, including vinylidene and related complexes. η^2-Vinyl complexes will also be considered in this section, since they exhibit W=C double bond metallocyclopropene structure, as will η^2-ketenyl complexes. The synthesis, structure and properties, and reactivity of η^2-vinyl complexes of transition metals have been recently reviewed.[923]

5.08.15.4.1 Synthesis, structure, and properties

Table 25 contains structural details on selected examples of W–CO complexes bearing carbenes with no heteroatom-stabilizing substituents. Synthetic procedures have not significantly changed since COMC (1995).[924]

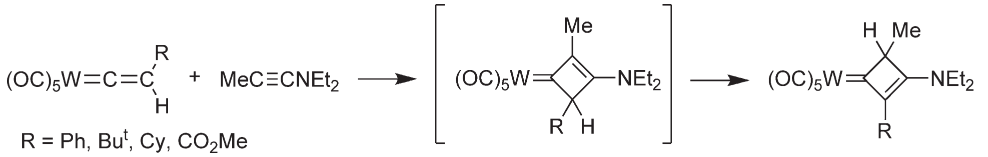
Table 25 Selected examples of W–CO complexes with carbene ligands with no heteroatom stabilizing substituents

Complex	*Comments*	*W═C$_{av}$* (Å)	δ(WC) (J_{WC})[a]	*References*
[W(CO)(η-PhC≡CMe)(═CH$_2$)-Tp′][BAr′$_4$]	Ar′ = C$_6$H$_3$(CF$_3$)$_2$-3,5	2.02	307.3 (109) (W═C)	925
166	Ar = Ph, BAr′$_4$ counteranion	1.97	238.1 (W═C)	241
170	L = NC$_5$H$_4$Me-4	1.98	240.3 (W═C)	929
171	W–H 1.92 Å; W═C–Me 167°; W═C–H 75°; δ_H (W–H) −2.36	1.86	224.0 (W═C)	930
172	W–H 1.88 Å; W═C–Ph 168°; W═C–H 72°; δ_H (W-H) −2.57; BF$_4^-$ counter anion	1.88	230.4 (W═C)	930
167 R = Ph	W–C 2.26 Å (W–C(H)Ph)	1.99	241.0, 255.7 (W═C, two isomers)	706, 940
168	W–C 2.16 Å (W–C═O); η^2-ketenyl complex	1.98	207.8 (W═C)	932
169		2.24	136.7	936

[a] ^{13}C NMR, δ in ppm; *J*WC in Hz in parentheses.

Reaction of [W(CO)$_5${C(H)(OMe)R}]$^-$ with HBF$_4$·OEt$_2$ affords the carbenes [W(CO)$_5$(═CHR)] (R = Ph, Tol, C$_6$H$_4$OMe-4).[703]

The cationic methylene complex [W(CO)(η^2-PhC≡CMe)(═CH$_2$)Tp′]$^+$ has been prepared by hydride abstraction from the methyl complex [W(CO)(η^2-PhC≡CMe)(Me)Tp′] using Ph$_3$C$^+$, and isolated and structurally characterized as the BAr′$_4^-$ salt {Ar′ = C$_6$H$_3$(CF$_3$)$_2$-3,5}.[925,926] The BAr′$_4^-$ salt proved to be more stable than the PF$_6^-$ analog. The air-stable anionic carbene complex [W(CO)$_2${═C(CN)$_2$}Tp′]$^-$ has been prepared and isolated by the reaction of [W(CO)$_2$(≡CCl)Tp′] with CN$^-$. A high-field ^{13}C NMR chemical shift for the carbene carbon (δ_C 167.8) is attributed to the electron-withdrawing effect of the cyano groups.[927] Reaction of *in situ*-generated vinylidenes of the type [W(CO)$_5${═C═C(R)H}] with electron-rich alkynes afford cyclobutenylidene complexes after tautomerization of the [2 + 2]-cycloadditon product (Equation (33)).[928] The reaction of the carbyne complex [W(CO)$_2$(pyMe-4)$_2$Br(≡CPh)] with allyl bromide affords the η^3-allylidene complex **170**.[929] The reaction of [W(CO)$_2$(≡COAr)Tp′] with [(Et$_2$O)$_2$H][BAr′$_4$] and phenylacetylene affords the η^3-vinylcarbene complex **166** (Equation (34)).[241] The intermediate in the reaction, a carbene with an agostic W–H interaction, was characterized by spectroscopic techniques. The cationic methylene complex [W(CO)$_2$(═CH$_2$)Tp′]$^+$, prepared by protonation of the carbyne [W(CO)$_2$(≡CH)Tp′] and isolated as the BAr′$_4^-$ salt, exhibits a similar agostic interaction.[182] The agostic interaction in [W(CO)$_2$(═CH$_2$)Tp′]$^+$ is revealed by ^{1}H NMR spectroscopy; one of the methylene protons resonates at δ9.05, while the proton with the agostic interaction resonates at δ1.38, and the methylene carbon exhibits two distinct $^1J_{HC}$ coupling constants in the ^{13}C NMR spectrum. The *in situ*-generated anionic complex [W(CO)$_2$-(═CH$_2$)Tp′]$^-$, prepared by addition of hydride to the carbyne [W(CO)$_2$(≡CH)Tp′], does not display an agostic interaction.[182] Protonation of [W(CO)(PMe$_3$)$_2$(py)(≡CMe)Cl] with HCl and of [W(CO)(PMe$_3$)$_2$(CNBu^t)(≡CPh)Cl] with HBF$_4$ affords the neutral [W(CO)(PMe$_3$)$_2${═C(H)Me}Cl$_2$] **171** and cationic [W(CO) (PMe$_3$)$_2$-{═C(H)Ph}Cl][BF$_4$] **172** carbenes, respectively.[930] Both these carbenes have been isolated and structurally characterized, **171** by a neutron diffraction study, and both exhibit an η^2-carbene with an agostic W–H interaction. The W═C and W–H bond lengths in each case are very similar and the C–H bond lengths (1.18 and 1.17 Å) of the alkylidene moieties are longer than a normal C(sp^2)–H bond. The alkylidene protons are significantly upfield (δ−2.36 and −2.57) in the ^{1}H NMR spectrum. Additional structural details are listed in Table 25.



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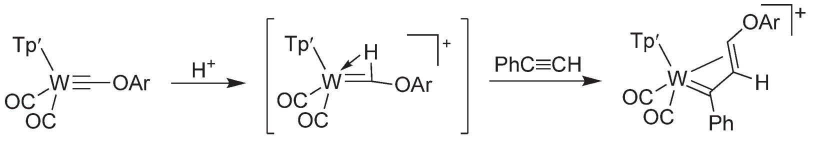
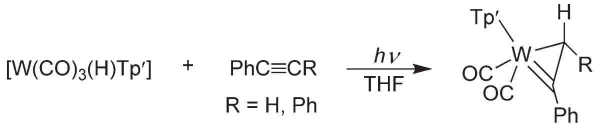


Ar = Ph, Tol, C_6H_4OMe-4

166

(34)

The reaction of the hydride complex $[W(CO)_3(H)Tp']$ with PhC≡CR (R = H, Ph) affords η^2-vinyl complexes (Equation (35)).[706] Alternatively, η^2-vinyl complexes can be prepared by reaction of the alkyne complexes $[W(CO)_3(\eta^2\text{-}RCH_2C{\equiv}CH)Tp']^+$ (R = H, Pr^n, Ph) with Li[HBEt$_3$].[931] The vinyl moiety of the η^2-vinyl complex **167** (R = Ph) has one short W–C distance (1.99 Å), characteristic of a W=C double bond, and one longer W–C bond (2.26 Å). The C–C bond length (1.405 Å) in the metallacyclopropene is between what is expected for a C–C single bond and a C=C double bond, and the C(H)Ph unit (for R = Ph) is twisted out of the plane of the three-membered ring, while the phenyl group bound to the carbene carbon is in the plane. η^2-Ketenyl complexes have been isolated by the reaction of carbyne complexes, for example, $[W(CO)_2(PR_3)_2(\equiv CAr)X]$ (X = Cl, Br), with additional donor ligands, which causes a coupling of the carbyne with a carbonyl ligand (e.g., Scheme 50).[173,932–935] Again, one of the ketenyl W–C bonds is much shorter than the other, 1.98 (W–CAr) versus 2.16 Å (W–C=O). Interestingly, the reaction of Tp$^-$ with *cis*-$[W(CO)_2(PPh_3)_2(\equiv CAr)Br]$ affords the carbyne complex $[W(CO)_2(\equiv CAr)Tp]$.[932]

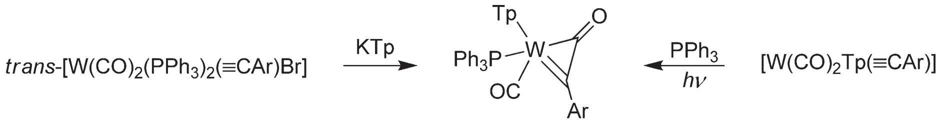


167

(35)

Reaction of a stable cyclopropenylidene with $[W(CO)_5(THF)]$ affords the carbene complex **169** (Equation (36)).[936] The NMR and structural data for **169** are consistent with its assignment as a nucleophilic carbene, with σ-donor/π-acceptor abilities similar to those of heteroatom-stabilized heterocyclic carbenes. Structural features such as a long W–C (carbene) bond (2.24 Å) as well as near-identical C–C bond lengths in the cyclopropenylidiene ring and short C–NPr$^i_2$ bonds suggest contributions from various resonance forms (Scheme 51). The carbene center is stabilized by π-bonding from the nitrogen substituents, and thus more closely resembles an azacarbene than a non-stabilized carbenes.

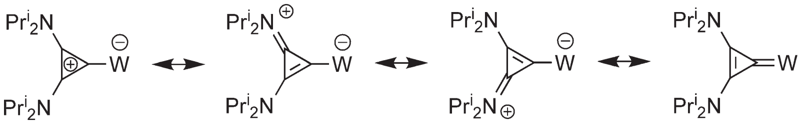
A number of theoretical studies have examined structure and bonding in the model carbene complexes $[W(CO)_5(CH_2)]$, $[W(CO)_5(CHF)]$, and $[W(CO)_5(CF_2)]$.[7,719,801,937–939] Studies suggest that the bond strengths for the M=C double bond in group 6 complexes are in the order W=C > Cr=C > Mo=C.



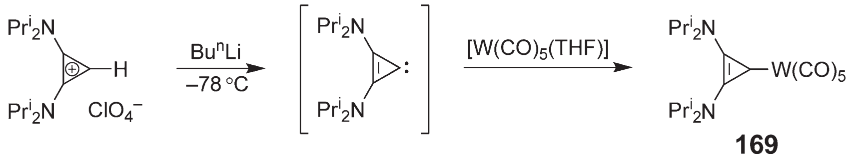
168

Ar = C_6H_4Me-4

Scheme 50



Scheme 51



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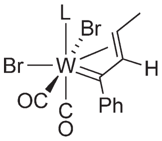

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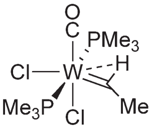

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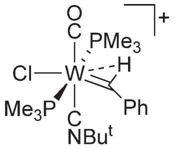
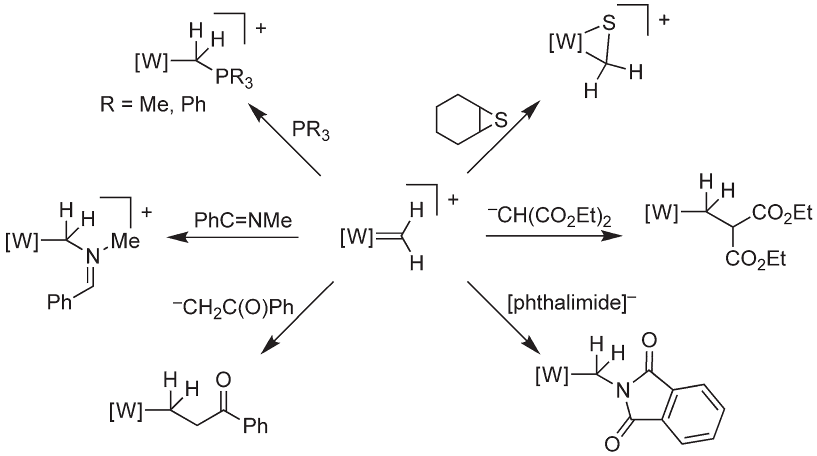


172

5.08.15.4.2 Reactions

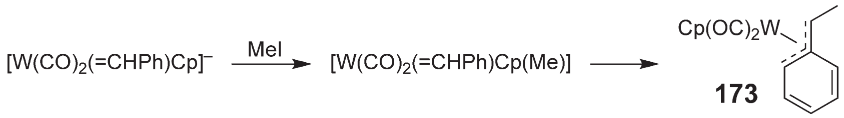
COMC (1995) summarizes the reactivity of the carbene complexes [W(CO)$_5$(=CPh$_2$)] and [W(CO)$_5${=C(H)Ph}].[924] The electrophilic behavior of the methylene complex [W(CO)(η^2-PhC≡CMe)(=CH$_2$)Tp′]$^+$ is summarized in Scheme 52.[925,926,941] The methylene complex can also transfer the methylene fragment to olefins to form cyclopropanes and acts as a catalyst for aziridine formation from imines and ethyl diazoacetate. The reaction of [W(CO)(η^2-PhC≡CMe)(=CH$_2$)Tp′]$^+$ with base {NaOH$_{(aq)}$ or KH} in CH$_2$Cl$_2$ affords the C$_3$H$_5$-bridged dimer [W(CO)(η^2-PhC≡CMe)Tp′{μ-C$_3$H$_5$}W(CO)(η^2-PhC≡CMe)Tp′]$^+$, the unusual binding of the C$_3$H$_5$ unit is discussed.[942] Interestingly, the additional carbon atom is not derived from the solvent.

Reaction of the anionic carbene complexes [W(CO)$_2$(=CHPh)Cp]$^-$ with MeI affords the isolable *trans*-[W(CO)$_2$(=CHPh)Cp(Me)], which isomerizes in solution, by intramolecular methyl to carbene migration, to afford the η^3-benzyl complex **173** (Scheme 53).[943] The reaction of [W(CO)(=CHPh)Cp(I)] with MeLi affords **173** directly. The reaction of [W(CO)$_5$(=CHPh)] with Me$_2$NC≡CNMe$_2$ affords a binuclear complex [W(CO)$_5${=C(NMe$_2$)C(NMe$_2$)=}W(CO)$_5$] and the insertion product [W(CO)$_5${=C(NMe$_2$)C(NMe$_2$)=CHPh}]. The reaction of [W(CO)$_5${=C(H)R}] (R = Ph, Tol, C$_6$H$_4$OMe-4) with the hydrides [W(CO)$_3$Cp(H)] and [Mn(CO)$_5$H] affords the benzyl complexes [W(CO)$_3$Cp(CH$_2$R)] and [Mn(CO)$_5$(CH$_2$R)] (R = Ph, Tol, C$_6$H$_4$OMe-4), respectively, by formal transfer and insertion of the carbene.[703]

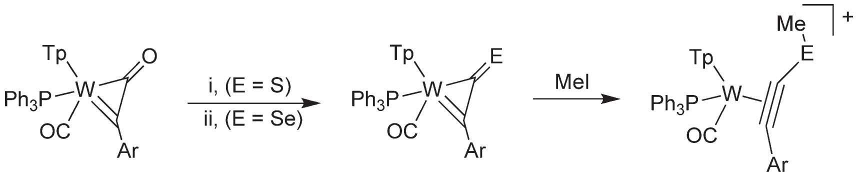


[W] = [W(CO)(η^2-PhC≡CMe)Tp′]

Scheme 52



Scheme 53



168 **174**

Ar = *p*-Tol i, E = S, $(S_2PC_6H_4OMe)_2$; ii, E = Se, $4(PPh_3)/5Se_8$.

Scheme 54

The η^2-ketenyl complexes **168** can be converted into the η^2-thioketenyl and η^2-selenoketenyl analogs **174** (Scheme 54), which can then be alkylated with MeI to form the thio- and selenoalkyne complexes.[933,944]

5.08.15.4.3 Vinylidenes and related species

Vinylidene ($M{=}C{=}CR_2$), allenylidene ($M{=}C{=}C{=}CR_2$), and higher-order cumulenylidene $\{M{=}C({=}C)_n{=}CR_2, n>1\}$ metal complexes have been the subject of a number of recent reviews covering synthesis, structure and properties, and reactivity.[881,945–950] Specific reviews have focused on the areas of π-donor-substituted allenylidene and cumulenylidene complexes,[946] redox-induced reactions of vinylidene complexes,[949] and the tautomerization mechanism that converts alkyne and vinylidene complexes.[950] Due to the recent and comprehensive nature of these reviews, this area will not be discussed further, except where it is covered in other sections. Examples of the reactivity of $[W(CO)Cp(NO)\{{=}C{=}C(H)R\}]$ are detailed in Scheme 49 in Section 5.08.15.2.2. The complexes $[W(CO)_5\{{=}C({=}C)_n{=}CH_2\}]$ ($n = 2$, 3) have been the subject of a recent computational study.[951]

5.08.15.5 Oxacarbene Complexes

In addition to oxacarbenes, this section includes η-thiocarbenes and η^2-thiocarbenes (η^2-thioacyl, tungstathiacyclopropenes). The area of bi- and polymetallic complexes containing at least one oxa- or azacarbene fragment has been reviewed.[952]

5.08.15.5.1 Synthesis

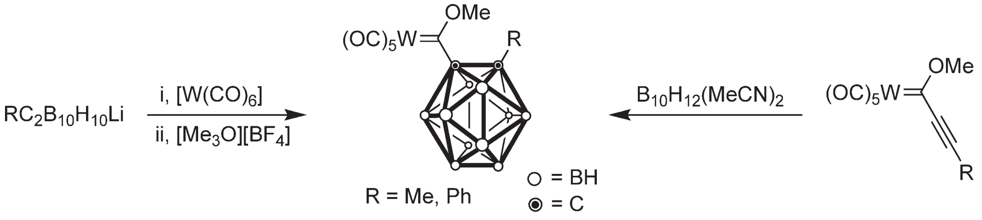
As with the carbene complexes discussed above, the synthetic methodologies used to prepare oxacarbene complexes have not significantly changed since COMC (1995).[924] Table 26 includes selected oxacarbene and thiocarbene complexes with structural and synthetic details. The examples in Table 26 and those given below cover some of the various synthetic methods available.

Alkylation of the acylate complexes $[NMe_4][W(CO)_5\{{=}C(O)Me\}]$ (formed from $[W(CO)_6]$ and MeLi followed by salt metathesis) with the alkyldiphenylsulfonium salts $[Ph_2SR]BF_4$ $\{R = Me, Pr^i, (CH_2)_2OEt, (CH_2)_3X\ (X = Cl, CN, OH, CH{=}CH_2), (CH_2)_5CO_2Me\}$ affords the carbene complexes $[W(CO)_5\{{=}C(OR)Me\}]$ in good yield. In contrast to the typically used alkylating agents $[R_3O]BF_4$, this method readily allows for a large variety of functionalized alkyl groups.[953] The reaction of $[W(CO)_2Tp'(NO)]$ with MeLi followed by MeOTf affords the carbene complex $[W(CO)\{{=}C(OMe)Me\}Tp'(NO)]$.[954] Photolysis of MeOH/THF solutions of $[W(CO)_6]$, in the presence of prop-2-yn-1-ol derivatives, affords alkenyl-functionalized carbene complexes $[W(CO)_5\{{=}C(OMe)CH{=}CR^1R^2\}]$ (Equation (37)).[955,956] The method is suitable for a large variety of alkenyl-functionalized prop-2-yn-1-ol derivatives,[955] as well as dialkynyl derivatives, such as p-$\{HC{\equiv}CCH(OH)\}_2C_6H_4$, which has been used to prepare mixed bis(carbene) complexes.[956] The carborane-functionalized carbenes **175** have been prepared from $[W(CO)_6]$

Table 26 Selected examples of W–CO complexes with oxacarbene or thiocarbene ligands

Complex	*Synthesis/comments*	*W=C$_{av}$* (Å)	δ(WC)(J_{WC})^a	*References*
Oxacarbenes				
$[W(CO)(\eta^2\text{-PhC}{\equiv}\text{CMe})\{{=}C(OMe)Bu^n\}Tp']^+$	$[W(CO)(\eta^2\text{-PhC}{\equiv}\text{CMe})\{C({=}O)Bu^n\}Tp'] + MeOTf$	2.09	333.5 (133) (W=C)	963
180	X = Cl, I; see 5.08.6.3 for synthesis and reactivity of this class of compounds	2.13 (Cl), 2.13 (I)	285.2 (W=C, Cl), 293.2 (W=C, I)	530, 964
181	2-lithio-1-methyl-1,3-benzazaphosphole + $[W(CO)_6]$	2.21	298.6 (W=C)	965
175	R = Ph	2.14	321.5 (W=C)	957
178	R = CO_2Et; **178** {R = C(OEt)=W(CO)$_5$} + O_2	2.19	288.6 (W=C)	960
182	4-methylthiazole + (i) Bu^{n}Li, (ii) $[W(CO)_6]$, (iii) $[Cr(THF)_3Cl_3]$	2.16		966
$[W(CO)_5\{{=}C(R)OSi(Pr^i)_2C({=}N_2)CO_2Me\}]$	$[W(CO)_6]$ + (i) RLi, (ii) $TfOSi(Pr^i)_2C({=}N_2)CO_2Me$; R = Me, Ph		322.9 (W=C)	967
179	See Equation (38)	2.19		962
Thiocarbenes				
183	$[W(CO)_3L]^- + Me_2NC({=}S)Cl$; L = Cp, Tp′	2.10 (Cp)	234.6 (W=C, Tp′)	968
184	$[W(CO)_2(\eta^2\text{-BnSC}{\equiv}\text{CSBn})Tp'][PF_6] + [CoCp_2]$; W–C 2.14 Å (W–C=S); two isomers	2.01	232.7, 237.6 (W=C)	969

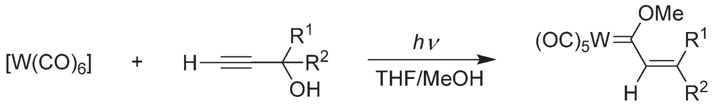
^{a} ^{13}C NMR, δ in ppm; J_{WC} in Hz in parentheses.



175

Scheme 55

and $[W(CO)_5\{{=}C(OMe)C{\equiv}CR\}]$ (Scheme 55).[957] Lithiation of a ring system followed by sequential treatment with $[W(CO)_6]$ and then $[Et_3O]^+$ affords the carbene complexes **176–178**; in two cases (**176** and **177**), the ring system is already π-bound to an addition metal center prior to lithiation.[958–961] The reaction of a sterically crowded germacyclopropabenzene with $[W(CO)_6]$ affords the germoxycarbene **179** (Equation (38)).[962]



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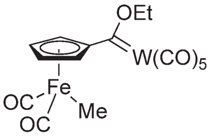

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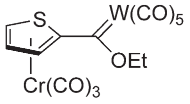

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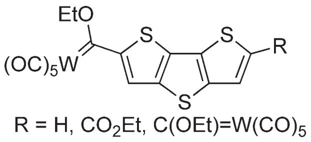

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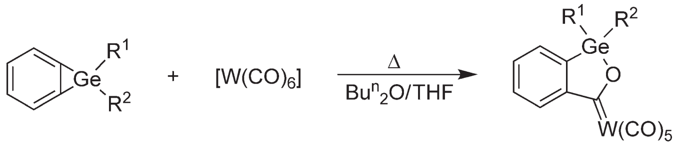
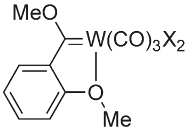


$R^1 = C_6H_2\{CH(SiMe_3)_2\}_3$-2,4,6
$R^2 = C_6H_3Pr^i_2$-2,6

179

(38)



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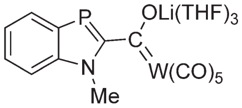

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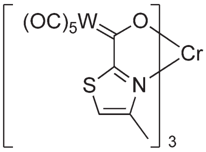

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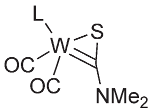

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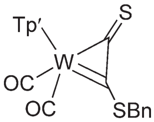

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5.08.15.5.2 Structure and properties

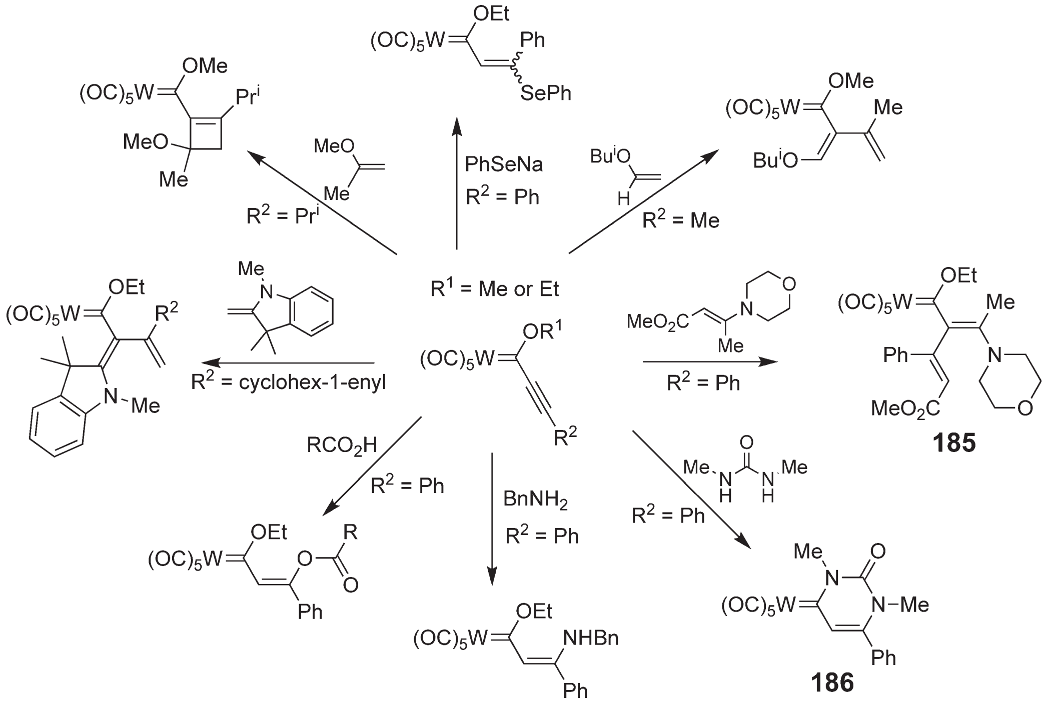
Table 26 lists tungsten–carbene bond lengths and carbene carbon ^{13}C NMR chemical shifts for a selection of oxa- and thiocarbene complexes. What is immediately obvious is the general increase in W═C bond lengths of the oxacarbene complexes compared to the carbene complexes with no heteroatom-stabilizing substituents (see Table 25). See COMC (1995) for discussion on metal–carbene bonds showing single-bond character with significant double-bond structure between the carbene carbon and the substituent oxygen atom (for carbene complexes with π-donor substituents).[924] Recent theoretical studies indicate that the carbene bond in $[W(CO)_5(CH_2)]$ is shorter and stronger than in oxacarbene derivatives such as $[W(CO)_5(CHOH)]$.[719,801,938] Due to the partial double-bond character between the carbene carbon and the oxygen substituent atom in $[W(CO)_5\{{=}C(OR)R\}]$, restricted rotation around the C–O bond has been identified and results in *anti*- and *syn*-isomers. Photolysis studies of $[W(CO)_5\{{=}C(OR)R\}]$ using laser flash photolysis and time-resolved Raman, IR, and UV–VIS spectroscopy have examined the *anti* ↔ *syn*-isomerization. In addition to the photoisomerization processes, CO loss can occur as an independent single-photon process.[970,971] The quantum yield for the isomerization process is 10 times higher than the process for CO elimination.[970] A DFT study has examined the bias for *anti*-isomers over *syn*-isomers.[972] Studies on the chiral $[M(CO)\{{=}C(OMe)R\}Tp'(NO)]$ (M = Mo, W) suggest two different processes that have different barriers of rotation: rotation about the M═C bond and rotation about the C–O bond.[954] The barrier for rotation about the M═C bond was higher than the barrier for rotation about the C–O bond.

5.08.15.5.3 Reactions

As mentioned at the start of this section, the reactivity of carbene complexes including the oxacarbene complexes $[W(CO)_5\{{=}C(OR')R\}]$ is dominated by their use in organic synthesis, particularly alkenyl- ($R = CR{=}CR_2$) and alkynyl- ($R = C{\equiv}CR$) substituted carbene complexes. Readers are directed to the reviews mentioned at the start of Section 5.08.15 as well as Volumes 10 and 11 in this series. In many cases, the synthetic transformations described in the reviews involve only the organic fragments, and thus afford new carbene complexes. COMC (1995) also covers a broad range of oxacarbene reactions.[924] Only selected examples will be covered here.

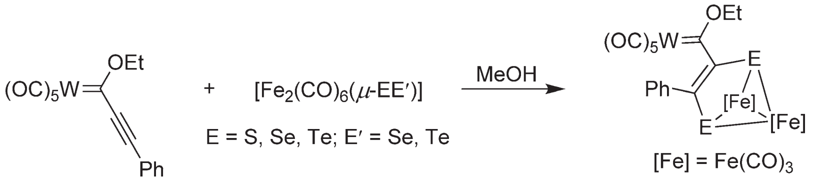
A series of studies have examined kinetic and thermodynamic aspects of simple reactions of various carbene complexes of the type $[W(CO)_5\{{=}C(XR^1)R^2\}]$ (X = O, S). Earlier studies in this area have been reviewed.[973] Recent studies have examined kinetic and thermodynamic aspects of acidities,[974,975] reactions with nucleophiles {RS^-,[976,977] RO^-,[978] $CH(CN)_2^-$,[979] RNH_2,[980] R_2NH[981]}, hydrolysis,[982] and intramolecular cyclizations.[983,984]

Substitution of the alkoxy functionality in $[W(CO)_5\{{=}C(OR^1)R^2\}]$ (where R^1 is typically methyl or ethyl) with more complex alcohols or amines is a common reaction, and in the case of amines is the standard procedure for the preparation of azacarbene complexes. The condensation of bis-alkoxycarbenes of the type $[W(CO)_5\{{=}C(OMe)C_6H_4CMe_2C_6H_4C(OMe){=}\}W(CO)_5]$ with diamines has been used to prepare polymers with azacarbene–$W(CO)_5$ moieties in the polymeric backbone.[985]



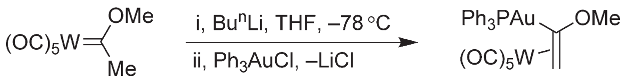
Scheme 56

The alkynyl–carbene complexes $[W(CO)_5\{=C(OR^1)C\equiv CR^2\}]$ undergo a range of addition and cyclization reactions involving the alkynyl fragment; examples are given in Scheme 56.[986–993] In solution, **185** undergoes mutual exchange of the ethoxy and morpholino functionalities.[991] Formation of the uracil derivative **186** involves addition at the alkyne and substitution of the alkoxy substituent. The reaction was performed with microwave irradiation, which results in a drastic reduction in reaction times compared to conventional procedures.[992] The reaction is suitable for a range of 1,3-dinitrogen systems.[994] The reaction of $[W(CO)_5\{=C(OEt)C\equiv CPh\}]$ with various diamines affords a range of monocarbene and bis-carbene complexes as a result of the addition of the amine to the alkynyl functionality or substitution of the alkoxy group.[995] Reaction of $[W(CO)_5\{=C(OEt)C\equiv CPh\}]$ with $Fe_2(CO)_6(\mu\text{-}EE')$ (E = S, Se, Te; E′ = Se, Te) affords cluster complexes as a result of addition to the alkynyl functionality (Equation (39)).[996,997]



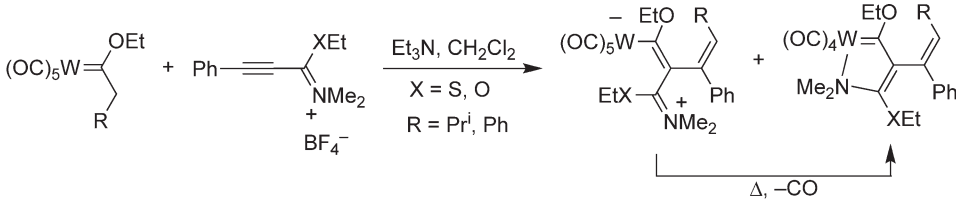
(39)

Under phase-transfer conditions, $[W(CO)_5\{=C(OR)Me\}]$ (R = Me, Et, Bn) can be readily dialkylated with methyl iodide or allyl halide derivatives to afford $[W(CO)_5\{=C(OR)CHR^2{}_2\}]$.[998] The condensation of $[W(CO)_5\{=C(OMe)Me\}]$ with the ferrocene-functionalized aldehydes $[Fc(CH=CH)_nCHO]$ ($n = 0$–3) affords the conjugated bimetallic complexes $[W(CO)_5\{=C(OMe)(CH=CH)_{n+1}Fc\}]$.[999] Lithiation of $[W(CO)_5\{=C(OMe)Me\}]$ followed by reaction with the allenylidene complex $[Ru(PPh_3)_2(\eta^5\text{-}C_9H_7)(=C=C=CPh)_2]$ affords the bimetallic carbene/alkynide complex $[W(CO)_5\{=C(OMe)CH_2CPh_2C\equiv C\}Ru(PPh_3)_2(\eta^5\text{-}C_9H_7)]$.[120] Treatment of the lithio species $[W(CO)_5\{=C(OMe)CH_2Li\}]$ with pyrylium salts affords methylenepyran carbene complexes,[1000] while reaction with Ph_3PAuCl affords a π-bound vinyl complex (Equation (40)).[1001] Reaction of $[W(CO)_5\{=C(OMe)Ph\}]$ with metal carbonyl anions such as $[CpFe(CO)_2]^-$, $[Re(CO)_5]^-$, $[Fe(CO)_4]^{2-}$, and $[Mo(CO)_3Cp]^-$ results in demethylation of the carbene complex.[1002] Reaction of the metallophosphaalkene complex $[Fe(CO)_2Cp^*\{P=C(NMe_2)_2\}]$ with $[W(CO)_5\{=C(OEt)Me\}]$ affords $[W(CO)_5\{\mu\text{-}\eta\text{:}\eta\text{-}P=C(OEt)Me\text{-}P,P\}Fe(CO)_2Cp^*]$.[1003]



(40)

Dinuclear complexes bearing an alkenyloxacarbene–W(CO)$_5$ fragment and an alkenylazacarbene–W(CO)$_5$ fragment can undergo selective Diels–Alder reactions with 1,3-dienes at the alkene moiety of only the oxacarbene fragment.[1004] Recent studies have shown that electron-deficient alkynes can insert into the C–C single bond between the carbene carbon atom and the α-carbon atom in [W(CO)$_5${=C(OEt)CH$_2$R}] (R = Pr^n, Ph) (Equation (41)).[1005] Reaction of [W(CO)$_5${=C(OMe)Ph}] with SmI$_2$ and methanol in THF at −78 °C afforded *trans*-stilbene (PhCH=CHPh), and in the presence of excess ethyl acrylate, PhCH=CHCH$_2$CO$_2$Et and PhCH(OMe)CH$_2$CH$_2$CO$_2$Et were isolated.[1006] The coupling of alkenylcarbene complexes using SmI$_2$ and MeOH affords biscarbene complexes, which can also be produced by the reaction of the alkenylcarbene complexes and C$_8$K (Equation (42)).[1006,1007] Bis-carbene complexes, as well as monocarbene complexes, can undergo palladium-catalyzed carbene ligand dimerization to afford alkenes species (Equation (42)).[1007,1008] The reaction of alkoxycarbene complexes with dihydropyridines affords pyridinium complexes, a number of which have been structurally characterized (W–C, 2.32–2.38 Å; δ_C52–57) (Equation (43)).[1009–1012] These complexes react with C=C double bonds to form cyclopropane species.



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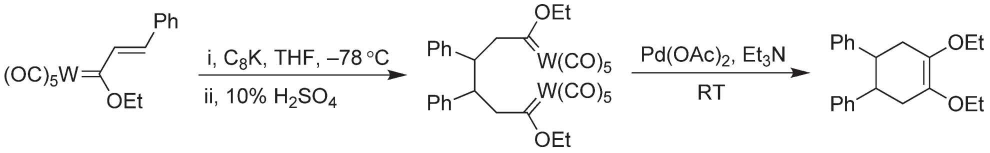
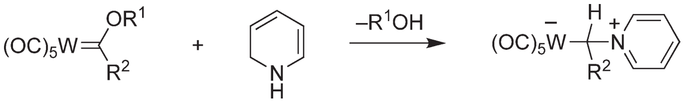


(42)



(43)

5.08.15.6 Azacarbene Complexes

In addition to azacarbenes, this section also includes phosphinocarbene derivatives, including η^2-phosphinocarbenes (tungstaphosphinocyclopropenes). One area that has seen significant development is the field of heterocyclic carbenes, particularly the diamino *N*-heterocyclic carbenes based on the imidazol-2-ylidenes. Diagrammatic representation of these types of carbenes in the literature is varied, and is discussed briefly in Section 5.08.15.6.2. Carbenes bearing two heteroatom donors, and, in particular, diamino carbenes and imidazol-2-ylidenes, and their metal complexes, have been the subject of a number of recent reviews.[1013–1020]

5.08.15.6.1 Synthesis

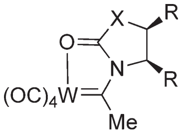
Representative examples of azacarbene and phosphinocarbene complexes, including synthetic details, are summarized in Table 27. The common method for the preparation of azacarbene complexes of the type [W(CO)$_5${=C(NR$^1_2$)R^2}] is the reaction of oxacarbene complexes [W(CO)$_5${ =C(OR^1)R^2}] with the appropriate amine. Reaction of [W(CO)$_5${=C(OMe)Me}] with amino acid esters affords the azacarbene complexes [W(CO)$_5${=C(NHCHR^{1}CO$_2$R^2)Me}] as a mixture of (*E*)- and (*Z*)-isomers.[1021] The vinylidene complex [W(CO)(=C=CHBu^t)Cp(NO)] reacts with excess primary or secondary amines to yield azacarbene complexes

Table 27 Selected examples of W–CO complexes with azacarbene and phosphinocarbene ligands

Complex	*Synthesis/comments*	*W═C$_{av}$* (Å)	δ (WC) (J_{WC})[a]	*References*
Azacarbenes				
$[W(CO)_5\{=C(NMe_2)CH=C(SPh)Ph\}]$	$[W(CO)_5\{=C(OEt)CH=C(SPh)Ph\}]$ (*E*/*Z*-isomers) + $HNMe_2$; only (*Z*)-isomer isolated	2.247	249.8 (W═C)	993
191	$[W(CO)_5\{=C(OMe)Ph\}]$ + (i) 2-H_2Npy; (ii) I_2	2.135	258.5 (W═C)	964
$[W(CO)\{=C(NEt_2)C(Me)=C=CHBu^t)Cp(NO)]$	$[W(CO)(=C=CHBu^t)Cp(NO)]$ + $MeC\equiv CNEt_2$; ynamine insertion; two rotamers observed at low temperature	2.118	250.9, 251.6 (W═C)	921
$[W(CO)_4(PPh_3)\{=C(NH_2)Tol\}]$	$[W(CO)_4(PPh_3)\{=C(OEt)Tol\}]$ + NH_3	2.217	269.0 (W═C)	1032
192	$[W(CO)_5\{=C(NMe_2)SiPh_2CMe=CHMe\}]$ + *hν*	2.204	291.4 (82) (W═C)	1033
193	Agostic W–H interaction; $[W(CO)_5\{=C(NMe_2)SiHMes_2\}]$ + *hν*; W–H 2.10 Å, Si–H 1.50 Å; δ_H −2.40 (SiH, J_{HW} 34 Hz)	2.14		1034
$[W(CO)_5\{=C(NMe_2)OTi(NMe_2)_2Cp^*\}]$	$[W(CO)_6]$ + $[Cp^*Ti(NMe_2)_3]$; CO insertion into Ti–N bond	2.271	229.6	1035
189	See Scheme 57; weak interaction between W and Mes unit	2.188	179.6 (W–CN_2)	694
194	R = *S*-CHMePh, *R*-CHMe(Nap), Cy, $(CH_2)OEt$; Free-carbene method (i)	2.282 (Cy)	176.4 (99) (Cy) (W–CN_2)	1036–1038
195	R = CH_2Bu^t, Method (i), non-planar carbene ring; R = $CH_2CH=CH_2$, H, Method (ii)	2.28 (CH_2Bu^t)	196.86 (W–CN_2) (R = CH_2Bu^t)	64, 1039
196	L = CO, py, PPh_3	2.24 (PPh_3)	188.9 (L = CO) (W–CN_2)	1026
197	R^1 = H, R^2 = OH; R^1 = Me, R^2 = OH; R^1 = Me, R^2 = OMe; R^1 = $CH_2CH=CH_2$, R^2 = H; Method (ii)	2.198 (R^1 = $CH_2CH=CH_2$)	215.5 (W-CN) (R^1 = $CH_2CH=CH_2$)	1023, 1024
198	L^1 = L^2 = CO (see Scheme 59); L^1 = CO, L^2 = PPh_3; L^1L^2 = dppe; **190** (R = Bn) + phosphine	2.2786–2.290	209.1 (95.1) (W–CN_2) (L^1 = L^2 = CO)	70, 1025
Phosphinocarbenes				
199	$[W(CO)_2Cp(\equiv CTol)]$ + $Me_2PCl/TlPF_6$	2.032	243.9 (W═C)	1030
200	$[W(CO)_2Tp'\{\equiv C{-}P=C(NEt_2)_2\}]$ + TfOH	1.980	242.0 (W═C)	1040
201	Ar = $C_6H_4NO_2$-4, R = Me, W–C 2.21 Å (W–C═O)	2.00		1031

[a] ^{13}C NMR, δ in ppm; J_{WC} in Hz in parentheses.

$[W(CO)\{{=}C(NR^1R^2)CH_2Bu^t\}Cp(NO)]$. After short reaction times, less stable η^2-carbamoyl–vinyl complexes $[WCp\{\eta^2\text{-}C(O)NR^1R^2\}(CH{=}CHBu^t)(NO)]$ can be isolated.[919] The preparation and reactivity of the chelating azacarbene complexes of the type 187 have been reviewed.[504]



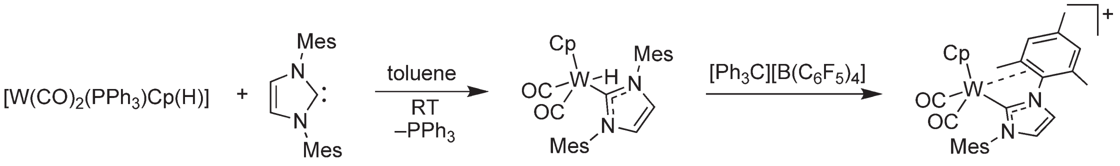
X = O, NMe

187

The syntheses of heterocyclic carbene complexes are different to conventional Fischer azacarbenes. Many free heterocyclic carbenes are relatively stable species and in some cases may be isolated, and, as such, the free carbene species can be prepared and then added to the appropriate metal source. *N*-Heterocyclic complexes of tungsten can be prepared by a number of methods, including the following.

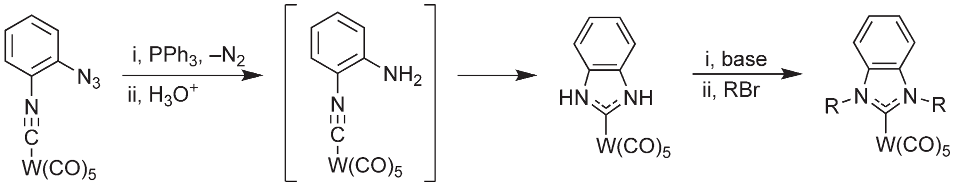
(i) The free carbene method, where an *N*-Heterocyclic carbene is prepared (though not often isolated) and then reacted with a metal source, such as $[W(CO)_6]$ or $[W(CO)_5(THF)]$, and more recently, W(II) sources (e.g., Scheme 57).[694] This method is generally suited to stable *N*-Heterocyclic carbenes.

(ii) Intramolecular nucleophilic addition to an isocyanide ligand bound to a $W(CO)_5$ fragment (e.g., Scheme 58),[64,65,1022–1024] a method that has been recently reviewed.[1017] The reaction of $H_2N(CH_2)_nN{=}PPh_3$ ($n = 2$, 3) with $[W(CO)_6]$ initially forms the isocyanide complex $[W(CO)_5\{CN(CH_2)_nNH_2\}]$, which cyclizes to afford complexes of five- and six-membered cyclic diaminocarbenes (Scheme 59).[70,1025]

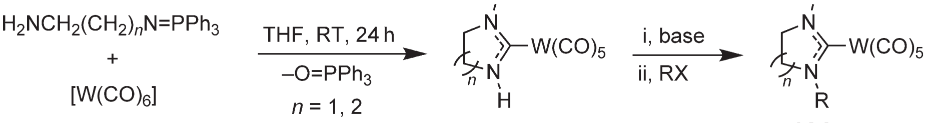


188 **189**

Scheme 57



Scheme 58



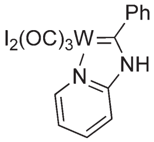
190

R = Et, $CH_2CH{=}CH_2$, $n = 1$, 2
R = Bn, $n = 1$

Scheme 59

Imidazol-2-ylidene carbene complexes can also be prepared by reaction of the appropriate imidazolium salt with the carbonyl metallate $K_4[W_4(\mu\text{-OMe})_4(CO)_{12}]$.[1026] The reaction of lithiated azoles (1-methylimidazol-2-yllithium, benzothiazol-2-yllithium) with $[W(CO)_6]$, followed by *N*-methylation, affords *N*-heterocyclic carbene–$W(CO)_5$ complexes.[1018,1027] The one-pot condensation of $[NEt_4][W(CO)_5(CN)]$, Bu^tNC, PhCHO, and amino acid ester hydrochlorides affords 4-aminoimidazolin-2-ylidene-$W(CO)_5$ complexes.[1028]

η^2-Phosphinocarbene complexes can be prepared from carbyne complexes. The reaction of $[W(CO)_2(L)(\equiv CR)]$ (L = Cp, R = Me, Ph, Tol; L = Tp, R = Tol) with $PR^2{}_2Cl$ in the presence of $TlPF_6$ or $NaBPh_4$ affords the η^2-phosphinocarbene complexes $[W(CO)_2(L)\{{=}C(PR^2{}_2)R\text{-}C,P\}]^+$.[1029,1030] Treatment of the phosphonium–carbyne complexes $[W(CO)_2(\equiv CPR_2Ph)Tp']^+$ (R = Me, Ph) with KOAr (Ar = C_6H_4X-4; X = NO_2, CN, Cl) affords the η^2-ketenyl complexes **201**.[1031]



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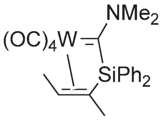

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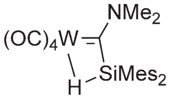

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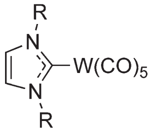

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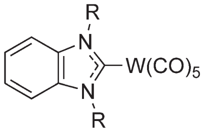

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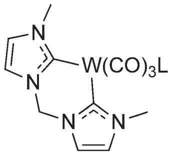

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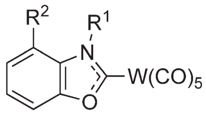

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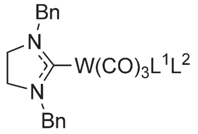

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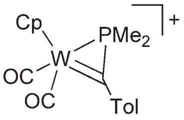

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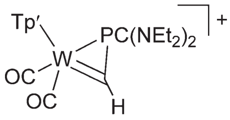

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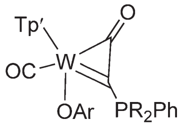

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5.08.15.6.2 Structure and properties

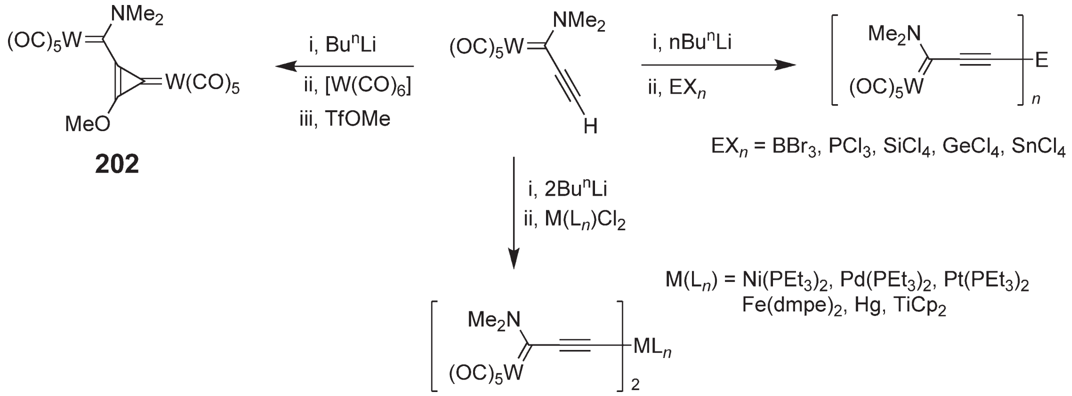
Table 27 contains W–C(carbene) bond length and ^{13}C NMR chemical shift details for a range of azacarbene and phosphinocarbene W–CO complexes. As with oxacarbenes, π-donation from the nitrogen substituent to the carbene carbon results in partial double-bond structure in the C–N bond. A consequence is the formation of (*E*)- and –(*Z*)-isomers about the C–N bond when the groups on the nitrogen center are different, as in $[W(CO)_5\{{=}C(NR^1R^2)R^3\}]$. The bonding in *N*-heterocyclic carbene–metal complexes is a special case, and has been the subject of recent interest.[1013,1016,1019,1020,1041] These types of carbenes are strong σ-donating ligands that show no, or very little, M → C π-backbonding, and are thus more like phosphine ligands than classical Fischer-type or Schrock-type carbenes. Diagrammatic representations involving a W=C metal bond in these types of complexes is somewhat misleading. The W–carbene bonds in *N*-heterocyclic carbene–metal complexes are typically longer than those involving classical carbenes and are much less reactive.

The W(II)–imidazol-2-ylidene complex **189** (in Scheme 57) is an effective recyclable catalyst for the hydrosilylation of carbonyl compounds.[672] Calculations on models of the chelate complexes **192** and **193** suggest that the agostic W···H–Si interaction in **193** transfers as much electron density to the W center as the interaction of the π-bound alkene with the W center in **192**.[1033] The agostic interaction in **193** significantly increases the stability of the complex to thermal degradation. Isomerism in the chelate complexes formed from *N*-allyl-functionalized azacarbenes has been investigated.[1042] A comparison of structural aspects of cyclic and acyclic phosphinocarbenes and aminocarbenes, and their $W(CO)_5$ complexes, has been the subject of a recent computational study.[1041]

5.08.15.6.3 Reactions

As discussed earlier, azacarbene complexes of the type $[W(CO)_5\{{=}C(NR^1{}_2)R^2\}]$ are used in organic synthesis. Reactivities of complexes related to organic synthesis will, in general, not be covered here, and readers are directed to the reviews mentioned at the start of this section.

Functionalization of the azacarbene $[W(CO)_5\{{=}C(NMe_2)C{\equiv}CH\}]$ affords a range of conjugated bimetallic and polymetallic complexes, including the unexpected **202**, the synthesis of which is dependent on solvent type (Scheme 60).[1043–1046] Coupling of $[W(CO)_5\{{=}C(NMe_2)C{\equiv}CH\}]$ with $IC{\equiv}CC{\equiv}CSiMe_3$ affords $[W(CO)_5\{{=}C(NMe_2)(C{\equiv}C)_3SiMe_3\}]$, which can be desilylated to afford $[W(CO)_5\{{=}C(NMe_2)(C{\equiv}C)_3H\}]$.[1047] Reaction of the triyne $[W(CO)_5\{{=}C(NMe_2)(C{\equiv}C)_3H\}]$ with Bu^nLi and then $HgCl_2$ affords the trimetallic complex



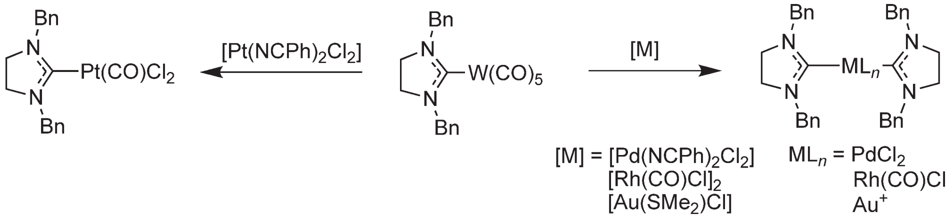
Scheme 60

$[W(CO)_5\{{=}C(NMe_2)(C{\equiv}C)_3\}Hg\{(C{\equiv}C)_3C(NH_2){=}\}W(CO)_5]$.[1047] Alternatively, the triyne can be converted into $[W(CO)_5\{{=}C(NMe_2)(C{\equiv}C)_3I\}]$ and $[W(CO)_5\{{=}C(NMe_2)(C{\equiv}C)_3SnBu^n{}_3\}]$, which can be coupled to afford $[W(CO)_5\{{=}C(NMe_2)(C{\equiv}C)_6C(NH_2){=}\}W(CO)_5]$.[1043] The azacarbene $[W(CO)_5\{{=}C(NH_2)C{\equiv}CH\}]$ can be difunctionalized to afford the trimetallic complexes $[W(CO)_5\{{=}C(NHM)C{\equiv}CM\}]$ $\{M = Fe(CO)_2Cp, Ni(PMe_2Ph)_2Mes$.[1048] The lithiated azacarbene $[W(CO)_5\{{=}C(NMe_2)CH_2Li\}]$ undergoes nucleophilic addition to the π-bound arene of $[Mn(CO)_3(\eta^6\text{-}C_6H_6)][PF_6]$ to afford the η^5-cyclohexadienyl complex $[W(CO)_5\{\mu\text{-}\eta{:}\eta^5\text{-}{=}C(NMe_2)CH_2C_6H_6\}Mn(CO)_3]$.[1049]

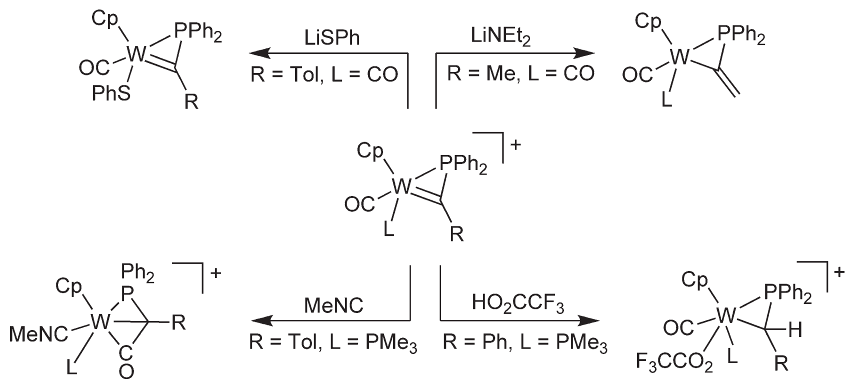
The 2*H*–azaphosphirene complexes, which are discussed in detail in Section 5.08.4.1, are prepared by the reaction of $[W(CO)_5\{{=}C(NH_2)Ar]$ with $RPCl_2$ or $R_2C{=}PCl$.[365,1032,1050] The azacarbene complex, $[W(CO)_5\{{=}C(NH_2)\text{-}CH{=}CHC_6H_4CH(OH)C{\equiv}CH\}]$ (with a terminal propynol unit), reacts with $[Cr(CO)_5(THF)]$ to afford the bridged heterobimetallic complex $[W(CO)_5\{{=}C(NH_2)CH{=}CHC_6H_4CH{=}CHC(OMe){=}\}Cr(CO)_5]$.[1051] Thermolysis of $[W(CO)_5\{{=}C(NMe_2)CH{=}C(SPh)Ph\}]$ affords the chelate complex $[W(CO)_4\{\eta^2{=}C(NMe_2)\text{-}CH{=}C(SPh)Ph\text{-}C,S\}]$.[993] Chelate complexes are also formed when $[W(CO)_5\{{=}C(R)NMe(CH_2CH{=}CHCH_2OH)\}]$ (R = Me, Ph) are photolyzed; the pendant alkene coordinates to the W center with associated loss of CO.[1052] Both the terminal OH and the methyl substituent on the carbene carbon can be further functionalized. Dialdehydes can condense with $[W(CO)_5\{{=}C(NMe_2)CH_2SiMe_3\}]$, after pre-treatment with Bu^nLi, to afford bis-azacarbene complexes.[1053] Suitable dialdehydes include 1,1′-ferrocene dialdehydes and carotenoid polyene dialdehydes, in which case, long conjugated systems are produced.

The *N*-heterocyclic carbene–$W(CO)_5$ complexes can act as carbene sources and readily transfer the carbene ligand when reacted with various metal sources to form new carbene complexes (e.g., Scheme 61).[1025] Cleavage of *N*-heterocyclic carbene–$W(CO)_5$ complexes **190** (in Scheme 59) to afford the cyclic iminium salts occurs readily with aqueous HBF_4/THF mixtures with catalytic Cu(I) in the absence of air or by the reaction with iodine.[1025,1054] Reaction of the non-alkylated complexes in Scheme 59, or monoalkylated species, with acylating agent affords ring-opened isocyanide complexes of the type $[W(CO)_5\{CN(CH_2)_nNC(O)Ph\}]$ ($n = 2$, 3).[73,74] Osmium tetraoxide can add to the C=C double bond of the imidazol-2-ylidine ligand of 1,3-dimethylimidazol-2-ylidine–$W(CO)_5$.[1055]

The reactivity of η^2-phosphinocarbene complexes is summarized in Scheme 62.[474,1056,1057]



Scheme 61



Scheme 62

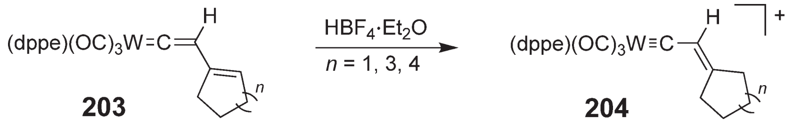
5.08.15.7 Carbyne Complexes

In general, carbyne–W–CO and W–CNR complexes can be divided into two categories: $[W(CO)_4(\equiv CR)X]$ and derivatives, or $[W(CO)_2(\equiv CR)L]$ (L = Cp, Tp, or related ligands) and related derivatives. Carbyne complexes feature throughout this entire chapter, in particular in the sections dealing with nitrogen, phosphorus, oxygen and sulfur donor ligands. Carbyne complexes bearing the Tp and Tp′ ligands are covered in Section 5.08.3.2 as well as here, though repetition of information is minimized.

5.08.15.7.1 Synthesis

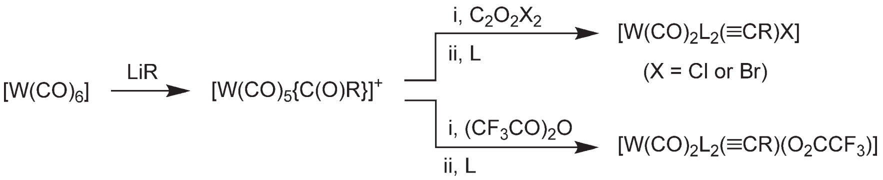
Selected examples of carbyne complexes, with associated synthetic details, are listed in Table 28. The carbyne complexes $[W(CO)_2L_2(\equiv CR)X]$ (X = halide or CF_3CO_2; L = CO, py, CNR; L_2 = TMEDA) and $[W(CO)_3(PPh_3)(\equiv CR)X]$ are common precursors for carbyne complexes bearing a range of donor ligands. Selected examples of the reactivity of these precursors appear throughout this chapter.

One of the most common procedures for the preparation of carbyne complexes involves the treatment of $[W(CO)_6]$ with lithium reagents to afford acyl complexes, which can be isolated as their NMe_4^+ salts. Reaction of these salts with oxalyl halide (chloride or bromide) or trifluoroacetic anhydride generates carbyne complexes $[W(CO)_4(\equiv CR)X]$, which in turn react with suitable donor ligands to give the readily isolated $[W(CO)_2L_2(\equiv CR)X]$ (L = py; L_2 = bipy, TMEDA) (Scheme 63). The procedure is suited to the preparation of a wide range of substituted carbynes {R = C_6H_4X-4 (X = I, Br, Me, NMe_2, OMe),[172,930,1058] Fc,[1059] $C{\equiv}CR$ (R = $SiMe_3$, Bu^t, Ar),[166,183] alkyl (including cyclopropyl[1060]), and aryl groups[930,1061]}. The procedure can also be performed with the lithiated species $[(\eta^6\text{-}LiC_6H_4Me)Cr(CO)_3]$.[172] If $LiC_6H_4N(SiMe_3)_2$ is used, then the carbyne complex with a free amino group $[W(CO)_2L_2(\equiv CC_6H_4NH_2\text{-}4)X]$ is isolated without a specific desilylation procedure.[1062] Treatment of $[W(CO)_6]$ with the lithium amide LDA followed by $C_2O_2X_2$ (X = Cl, Br) affords the aminocarbyne complexes $[W(CO)_4(\equiv CNPr^i_2)X]$, which act as versatile aminocarbyne precursors.[1063] The sequential treatment of $[W(CO)_6]$ with LDA·LiI, $(CF_3CO)_2O$, and PPh_3 affords $[W(CO)_3(PPh_3)(\equiv CNPr^i_2)I]$.[860] The reaction of the vinylidene complexes **203** with HBF_4 in Et_2O affords the carbyne complexes **204** (Equation (44)).[1064]



203 **204**

(44)



Scheme 63

Carbyne complexes of the type $[W(CO)_2(\equiv CR)L]$ (L = Cp, Tp, or related ligands) are generally prepared from the carbyne precursors mentioned above; Table 28 contains examples. The reaction of $[W(CO)_4(\equiv CR)Cl]$ (R = cyclopropyl) and $[W(CO)\{P(OMe)_3\}_3(\equiv CR)Cl]$ with NaCp affords $[W(CO)_2(\equiv CR)Cp]$ and $[W(CO)\{P(OMe)_3\}(\equiv CR)Cp]$, respectively.[1060] Reaction of $[W(CO)_2(pyMe\text{-}4)_2(\equiv CNR_2)X]$ (R = Pr^i, X = Br; R = Cy, X = Cl) with NaCp gives $[W(CO)_2(\equiv CNR_2)Cp]$ (R = Pr^i, Cy).[1063] The reduction of $[W(Tp')I_2\{\equiv CN(R)Et\}]$ (R = Me, Et) with Na/Hg in the presence of EtNC leads to $[W(CNEt)_2(Tp')\{\equiv CN(R)Et\}]$, which can further react with $[Et_3O]BF_4$ to yield the bis-aminocarbyne complexes $[W(CNEt)(Tp')(CNEt_2)\{CN(R)Et\}][BF_4]$.[185] The reaction of $[W(CO)_2Tp'(\equiv CCl)]$, PPh_3, and KPF_6 affords $[W(CO)_2Tp'(\equiv CPPh_3)]PF_6$ in excellent yield, which can then react with $NaHBEt_3$ to give $[W(CO)_2Tp'(\equiv CH)]$ also in good yield.[182]

Heterodinuclear bridging carbyne complexes have been prepared by the reaction of a tungsten carbyne complex and an additional metal species. The reaction of $[W(CO)_2\{\equiv CN(Et)Me\}Cp]$ with $[Au(tht)(C_6F_5)]$ (tht = tetrahydrothiophene) affords $[W(CO)_2Cp\{\mu\text{-}CN(Et)Me\}Au(C_6F_5)]$ (W–Au);[1065] reaction of $[W(CO)_2(\equiv CC_6H_5)Cp]$ with $[M(CO)_4(\eta^2\text{-}HC{\equiv}CH)]$ (M = Fe, Os) affords $[W(CO)_2Cp(\mu\text{-}CC_6H_5)M(CO)_4]$ (W–M);[1066] reaction of $[W(CO)_2(\equiv CTol\text{-}4)L]$ (L = Cp, Tp′ with $[Ru(CO)_2(THF)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ affords $[W(CO)_2L(\mu\text{-}CTol\text{-}4)Ru(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ (W···Ru);[1067] and the reaction of $[W(CO)_2(\equiv CTol\text{-}4)Cp]$ with the cyclometallated palladium complex $[Pd(\eta^2\text{-bhq-}N,C)Cl]_2$ (bhqH = benzo(*h*)quinoline) affords $[W(CO)_2Cp(\mu\text{-}CTol\text{-}4)PdCl(\eta^2\text{-bhq-}N,C)]$.[1068] Selected structural details of these complexes are listed in Table 28, and further discussion of these complexes is given in Section 5.08.15.7.2. Trimetallic WAu_2 complexes with a μ^3-bridging carbyne have been obtained by reaction of $[W(CO)_2(\equiv CTol\text{-}4)Cp]$ with 2 equiv. of a gold carborane complex.[1069] A range of heteronuclear cluster compounds contain a μ^2- or μ^3-bridging carbyne fragment, and in some cases, μ^3-carbyne and carbido fragments are formed by scission of acetylide species.[1070–1076]

5.08.15.7.2 Structure and properties

Table 28 contains W–C$_{carbyne}$ bond length and ^{13}C NMR chemical shift information for a variety of alkylidyne, μ-alkylidyne, and heteroatom-substituted carbyne complexes. Additional structural features are detailed for the μ-alkylidyne and μ-aminocarbyne complexes.

Theoretical studies covering structure and bonding have been performed on model complexes of the type *trans*-$[W(CO)_4(CH)X]$ (X = F, Cl, Br, I, Me), and comparisons have been made to high-valent Schrock-type carbyne complexes of the type $[WX_3(CR)]$ (X = F, Cl, Me, OH).[719,801,1081] The studies predict that W–C$_{carbyne}$ bond lengths of Fischer-type carbyne complexes *trans*-$[W(CO)_4(CH)X]$ are approximately 0.2 Å shorter than the W–C$_{carbene}$ bond lengths in model Fischer carbene complexes, and about 0.1 Å longer than the W–C$_{carbyne}$ bond lengths in the model Schrock-type carbyne complexes. The nature of the W–C$_{carbyne}$ bond in the Fischer- and Schrock-type carbyne complexes is also discussed. Density functional methods have been used to study the interconversion reactions of $[W(CO)(PH_3)_3(\equiv CH)H]$ and $[W(CO)_2(PH_3)_2(\equiv CH)H]$ to the five-coordinate carbene complexes $[W(CO)(PH_3)_3(=CH_2)]$ and $[W(CO)_2(PH_3)_2(=CH_2)]$, respectively.[1082]

Laser flash photolysis techniques have been used to examine the lowest excited states of the aryl–carbyne complexes $[W(CO)\{P(OMe)_3\}Cp(\equiv CAr)]$ (Ar = Ph, *o*-Tol, 2-naphthyl).[1083] A number of complexes of the type $[\{W(CO)_2(TMEDA)Cl(\equiv CC_6H_4NC)\}_2ML_n]$ (ML_n = *fac*-$Re(CO)_3Cl$, *cis*-$PdCl_2$, *trans*-PdI_2, *trans*-PtI_2) and $[\{W(CO)_2(TMEDA)Cl(\equiv CC_6H_4C{\equiv}CC_6H_4NC)\}_2ML_n]$ (ML_n = *fac*-$Re(CO)_3Cl$, *trans*-PdI_2, *trans*-PtI_2) have been examined by spectroscopic techniques to determine the possibility of electronic communication between the metal centers.[1084] The Raman, IR, and pressure-tuning Raman and IR spectra of similar complexes have been studied.[1085] Electronic coupling in the bis-carbyne complexes $[W(CO)_2Tp'\{\equiv CCH_2C\equiv\}W(CO)_2Tp']$, $[W(CO)_2Tp'\{\equiv CCH_2CH_2C\equiv\}W(CO)_2Tp']$, $[W(CO)_2Tp'\{\equiv CCH{=}CHC\equiv\}W(CO)_2Tp']$, and $[W(CO)_2Tp'(\equiv CC{\equiv}CC\equiv)W(CO)_2Tp']$ has been examined by electrochemical studies.[1086] The degree of coupling in the bis-carbyne complexes is smaller than in dimers, where the bridge is connected to the metal center via single bonds. It is suggested that the lower coupling is mainly due to a highest occupied molecular orbital (HOMO) that is oriented orthogonal to the bis-carbyne bridge.

The bonding in heteroatom carbyne complexes is of interest. For instance, the methoxycarbyne complex $[W(CO)_2(\equiv COMe)Tp']$ exhibits a short C$_{carbyne}$–O bond (1.27 Å), significantly shorter than that expected for a C–O single bond (1.43 Å).[1077] The shorter C$_{carbyne}$–O bond indicates a contribution from the oxonium resonance form $[W(CO)_2(=C{=}OMe)Tp']$. A similar observation has been made previously for aminocarbyne complexes. Restricted rotation about the C$_{carbyne}$–N bond in $[W(CO)(\equiv CNR_2)(Cl)_2Cp]$ (R = Pr^i, Cy) has been identified in variable-temperature ^{1}H NMR studies.[1063] It is suggested that the stability of the bis-aminocarbyne complex $[W(CNEt)(Tp')(CNEt_2)\{CN(R)Et\}][BF_4]$ results from the strong interaction of a lone pair at the amino nitrogen atom with a vacant *p*-orbital at the carbyne carbon.[185] IR studies support the conclusion for this π-interaction with two

Table 28 Selected examples of W–CO and W–CNR complexes with carbyne ligands

Complex	*Synthesis/comments*	*W≡C$_{av}$* (Å)	δ_C(W≡C) (J_{WC})[a]	*References*
[W(CO)$_2$(TMEDA)(≡CC$_6$H$_4$I-4)Cl]	[W(CO)$_2$(pyMe-4)$_2$(≡CC$_6$H$_4$I-4)Cl] + TMEDA	1.807	259.5	1058
[W(CO)$_2$(dppe)(≡CC$_6$H$_4$NH$_2$-4)Cl]	[W(CO)$_2$(pyMe-4)$_2$(≡CC$_6$H$_4$NH$_2$-4)Cl] + dppe	1.812	270.1	1062
[W(CO)(PMe$_3$)$_2$(CNBu^t)(≡CPh)Cl]	[W(CO)(PMe$_3$)$_2$(py)(≡CPh)Cl] + CNBu^t	1.82	263.2	930
[W(CO)$_2$(dppf)(≡CR)Cl]	[W(CO)$_2$(py)$_2$(≡CR)Cl] + dppf; R = Me, Ph, Fc	1.82 (Ph)	267.2 (Ph)	1059
[W(CO)$_2$(TMEDA)(≡CC≡CR)Cl]	R = SiMe$_3$, Ph; Scheme 63 LiR = LiC≡CR	1.834 (R = Ph)	230.4 (R = Ph)	183
[W(CO)$_2$(bipy)(≡CC≡CR)(O$_2$CCF$_3$)]	R = SiMe$_3$, Ph; Scheme 63 LiR = LiC≡CR		244.1 (R = Ph)	166
[W(CO)$_2${η^3-P(2-py)$_3$}(≡CPh)]BPh$_4$	[W(CO)$_2$(py)$_2$(≡CPh)Cl] + (i) P(2-py)$_3$, (ii) NaBPh$_4$	1.811	286.3	177
[W(CO)$_2$(η^3-L)(≡CPh)]BPh$_4$	[W(CO)$_2$(py)$_2$(≡CPh)Cl] + (i) L, (ii) NaBPh$_4$; L = 1,4,7-trimethyl-1,4,7-triazacyclononane	1.800	288.4	95
[W(CO)$_2$(pyMe-4)(≡CR){η^2-H$_2$B(pz)$_2$}]	[W(CO)$_2$(pyMe-4)$_2$(≡CR)Br] + K[H$_2$B(pz)$_2$]; R = C$_6$H$_3$Me$_2$-2,6	1.810	294.5	173
[W(CO)$_2$(≡CTol-2){η^3-L-*N*,*N*,*O*}]	[W(CO)$_4$(≡CTol-2)Cl] + K[L]; L = HC(Me$_2$pz)$_2$(C$_6$H$_4$O$^-$-2)	1.7551	275.2	172
[W(CO)$_2$(≡CNPr$^i{}_2$)Cp*]	[W(CO)$_2$(pyMe-4)$_2$(≡CNPr$^i{}_2$)Br] + NaCp*		265.3	1063
[W(CO)$_2$(≡COMe)Tp′]	[W(CO)$_2$(≡CPPh$_3$)Tp′]$^+$ + NaOMe	1.86	228.2	1077
[W(CO)$_2$(≡CC$_6$H$_2$Me$_3$-2,4,6)Tp]	[W(CO)$_2$(pyMe-4)$_2$(≡CC$_6$H$_2$Me$_3$-2,4,6)Br] + K[Tp]	1.826	288.5 (193)	1078
[W(CO)$_2${≡CP=C(NEt$_2$)$_2$}Tp′]	[W(CO)$_2$(≡CCl)Tp′] + Me$_3$SiP=C(NEt$_2$)$_2$	1.838	319.0	1079
[W(CO)$_2${≡CAs=C(NMe$_2$)$_2$}Tp′]	[W(CO)$_2$(≡CCl)Tp′] + Me$_3$SiAs=C(NEt$_2$)$_2$	1.825	329.1	1080
[W(CO)$_2$(≡CTol-4)L]	[W(CO)$_5${=C(O)Tol-4}] + NaL + (CF$_3$CO)$_2$O; L = CpCo{P(OMe)$_2$=O}$_3{}^-$		279.1	534
[W(CO)$_2$Cp(μ-CC$_6$H$_5$)M(CO)$_4$]-(W–M)	M = Fe, Os; W-M$_{av}$ 2.844 (Fe), 2.9141 (Os) Å; C$_{carbyne}$–M$_{av}$ 2.016 (Fe), 2.120 (Os) Å	1.913 (Fe), 1.955 (Os)	332.4 (Fe), 332.0 (Os)	1066
[W(CO)$_2$Cp{μ-CN(Et)Me}Au(C$_6$F$_5$)]-(W–Au)	W–Au$_{av}$ 2.727 Å; C$_{carbyne}$–Au$_{av}$ 2.13 Å; C$_{carbyne}$–N multiple-bond character.	1.90	259.6	1065
[W(CO)$_2$L(μ-CTol-4)Ru(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_{11}$)]-(W···Ru)	L = Cp, Tp; W···Ru$_{av}$ 2.949 (Cp), 3.0472 (Tp) Å; C$_{carbyne}$–Ru$_{av}$ 2.19 (Cp), 2.213 (Tp) Å	1.92 (Cp), 1.921 (Tp)	301.9 (Cp), 287.4 (Tp)	1067
[W(CO)$_2$Cp(μ-CTol-4)PdCl(η^2-bhq-*N*,*C*)]	W···Pd$_{av}$ 2.8001 Å; C$_{carbyne}$–Pd$_{av}$ 2.084 Å; bhqH = benzo(*h*)quinoline; No W–Pd bond	1.897	303.3	1068

[a] ^{13}C NMR, δ in ppm; *J*WC in Hz in parentheses.

low frequency ν($C_{carbyne}$–N) absorptions identified in the spectra. Carbyne complexes of the type shown in Scheme 66, with a conjugated alkenylcarbyne ligand, have been examined by electrochemical and theoretical studies, which indicate the alkenylcarbyne ligand behaves as an especially strong π-electron acceptor.[1087–1089] NMR spectroscopic studies suggest a high *trans*-influence of the alkenylcarbyne, with a sequence for the *trans*-influence in the order alkenylcarbyne > alkenylvinylidene > CO.[1064]

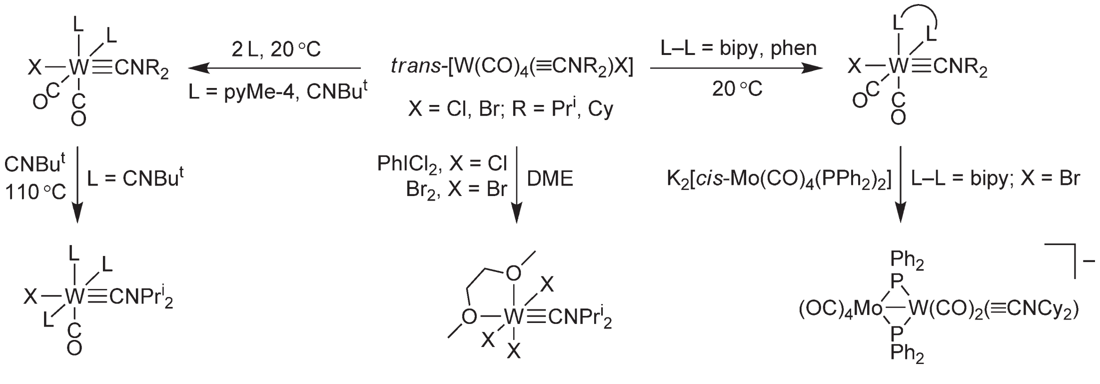
5.08.15.7.3 Reactions

Carbyne complexes undergo a wide range of reactions. These include substitution at the tungsten center that does not effect the carbyne fragment, reactions that change the substituent on the carbyne carbon but which retain the formal carbyne structure, and reactions that result in non-carbyne products. In the case of complexes of the type *trans*-[$W(CO)_4(\equiv CR)X$] and its CO-substituted derivatives, substitution at the tungsten center can occur at the *trans*- or the *cis*-positions selectively depending on the reacting donor ligand. Many of these reactions plus others are covered in COMC (1995);[1090] more recent reactions that typify this diverse chemistry are given below.

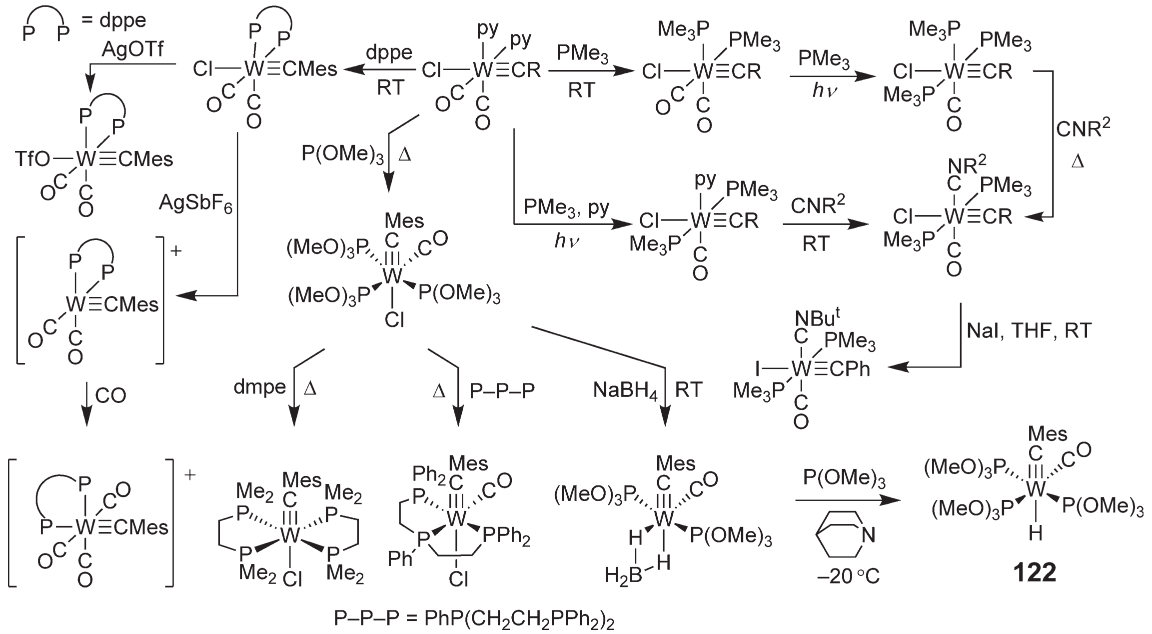
The selective substitution chemistry of *trans*-[$W(CO)_4(\equiv CR)X$] and *trans*-[$W(CO)_4(\equiv CNR_2)X$] and their CO-substituted derivatives is exemplified by the examples given in Schemes 64,[1063] 65[424,678,930,1061,1091] and 66.[935,1064,1087–1089] Of particular note is the selectivity of donor types binding in the *trans*- and *cis*-positions, especially when a donor group migrates from one position to another to allow for the binding of a different donor type. In general, halides or pseudohalides bind at the *trans*-position with respect to the carbyne, and CO and CNR bind at the *cis*-positions. The reactivity of the hydride complex **122** (in Scheme 65) is covered in Section 5.08.9.3.

The amino carbyne complex [$W(CO)_2(\equiv CNEt_2)Cp^*$] reacts with nitrilium salts {[$MeC\equiv NMe]BF_4$} by a formal [2 + 2]-cycloadditon to afford the carbene complex [$W(CO)_2\{\eta^2$-$=C(NEt_2)CMe=NMe\}Cp^*$] having a chelating imine group.[1092] Oxidation of [$W(CO)_2(\equiv CNEt_2)Cp^*$] with $PhICl_2$ affords the 18-electron complex [$W(CO)Cl_2(\equiv CNEt_2)Cp^*$],[649,1063] which can undergo CO substitution with $CNBu^t$ to afford [$W(CNBu^t)Cl_2(\equiv CNEt_2)Cp^*$].[649] Subsequent protonation of the CNR complex with HCl yields the alkyne complex [$W\{\eta^2$-$Et_2NC\equiv CNHBu^t)(Cl)_3Cp^*$]. The dichloride [$W(CO)Cl_2(\equiv CNEt_2)Cp^*$] reacts with 1,2-dithiolates to form [W(CO)(L-*S*,*S*′)($\equiv CNEt_2)Cp^*$], where L is a 1,2-dithiolate.[589] In the case of [$W(CO)(o$-$S_2C_6H_4)(\equiv CNEt_2)Cp^*$], protonation with HCl affords the carbene complex [$W(CO)(=CHNEt_2)(o$-$S_2C_6H_4)(Cl)Cp^*$], which loses CO upon heating to afford the 16-electron complex [$W(=CHNEt_2)(o$-$S_2C_6H_4)(Cl)Cp^*$].[589] Unlike the Cp^* analog discussed above, oxidation of [$W(CO)_2(\equiv CNEt_2)Tp'$] with 1 equiv. of Br_2 or I_2 affords the 16-electron dihalide complexes [$W(\equiv CNEt_2)(X)_2Tp'$] (X = Br, I).[185] Similarly, oxidation of the alkylidyne complex [$W(CO)_2(\equiv CPh)Tp$] with Br_2 yields [$W(\equiv CPh)\ (Br)_2Tp$].[1093] Oxidation of the alkylidyne complex [$W(CO)_2(\equiv CC_6H_3Me_2$-2,6)Tp] with thionyl chloride affords [$W(\equiv CC_6H_3Me_2$-2,6)$(Cl)_2Tp$], but the analogous reaction of [$W(CO)_2(\equiv CC_6H_3Me_2$-2,6)Cp] with $SOCl_2$ affords the carbene chelate complex [W{=C(R)SC(S)R-*C*,*S*}$(Cl)_3Cp$] (R = $C_6H_3Me_2$-2,6).[1078]

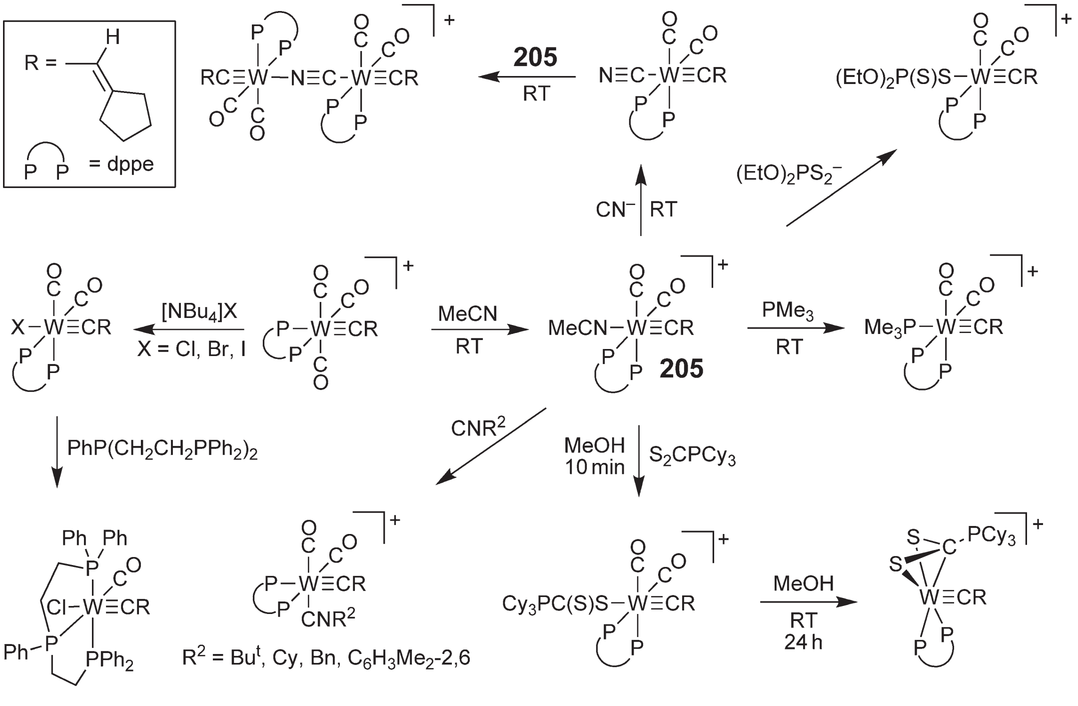
Examples of the functionalization of the carbyne carbon in [$W(CO)_2(\equiv CH)Tp'$] and the benzylic carbon in [$W(CO)_2(\equiv CCH_2Ph)Tp'$] are described in Section 5.08.3.2.3. Chloride displacement from [$W(CO)_2(\equiv CCl)Tp'$] with $LiMe_2Cu$ affords the methylcarbyne complex [$W(CO)_2(\equiv CMe)Tp'$], deprotonation of which affords the nucleophilic vinylidene anion [$W(CO)_2(=C=CH_2)Tp'$]$^-$ that can react with a range of electrophiles such as MeI, PhC(O)R (R = H, Me), and PhC(O)Cl to give [$W(CO)_2(\equiv CEt)Tp'$], [$W(CO)_2\{\equiv CCH_2C(R)(OH)Ph\}Tp'$] (R = H, Me), and [$W(CO)_2\{\equiv CCH_2C(O)Ph\}Tp'$], respectively.[1094] In the presence of base, [$W(CO)_2\{\equiv CCH_2CH(OH)Ph\}Tp'$]



Scheme 64



Scheme 65



Scheme 66

eliminates H_2O to form the conjugated $[W(CO)_2(\equiv CCH{=}CHPh)Tp']$. Oxidation of the vinylidene anions $[W(CO)_2({=}C{=}CHR)Tp']^-$ ($R = H$, Me, Bn) with nitrobenzene yields the bridging bis-carbyne complexes $[W(CO)_2Tp'\{\equiv CCH(R)CH(R)C\equiv\}W(CO)_2Tp']$.[1095] Treatment of these bis-carbyne complexes with 2 equiv. of base and then oxidation of the dianions with nitrobenzene yields the conjugated bis-carbyne complexes $[W(CO)_2Tp'\{\equiv CC(R){=}C(R)C\equiv\}W(CO)_2Tp']$. Repetition of the deprotonation/oxidation process with the complex where $R = H$ gives $[W(CO)_2Tp'(\equiv CC\equiv CC\equiv)W(CO)_2Tp']$. Reaction of $[W(CO)_2({=}C{=}CH_2)Tp']^-$ with

$[W(CO)(\eta^2\text{-}PhC\equiv CPh)(I)Tp']$ affords $[W(CO)_2Tp'\{\mu\text{-}\equiv CCH_2\}W(CO)(\eta^2\text{-}PhC\equiv CPh)Tp']$, and subsequent deprotonation with $KOBu^t$ and then oxidation of the anion with I_2, affords the bis-carbyne complex $[W(CO)_2\text{-}Tp'\{\equiv CC\equiv\}W(CO)(\eta^2\text{-}PhC\equiv CPh)Tp']$.[1096] Reaction of $[W(CO)_2(=C=CH_2)Tp']^-$ with $[Mo(CO)_2(\equiv CCl)Tp']$ yields the heterobimetallic bis-carbyne complex $[W(CO)_2Tp'(\equiv CCH_2C\equiv)Mo(CO)_2Tp']$.[1097] Treatment of $[W(CO)_2Tp'(\equiv CC\equiv CSiMe_3)]$ with $[BNu_4]F$ and metal sources leads to a range of bimetallic and trimetallic complexes such as $[W(CO)_2Tp'(\equiv CC\equiv C)\{Rh(CO)(PPh_3)_2\}]$, $[\{W(CO)_2Tp'(\equiv CC\equiv C)\}_2\{Ir(CO)\ (PPh_3)_2H\}]$, and $[\{W(CO)_2Tp'\text{-}(\equiv CC\equiv C)\}_2Hg]$.[1098–1101]

Treatment of $[W(CO)_2(\equiv CCl)Tp']$ with $Me_3SiE=C(NMe_2)_2$ ($E = P$, As) affords $[W(CO)_2\{\equiv C\text{–}E=C\text{-}(NMe_2)_2\}Tp']$,[1079,1080] which can be subsequently methylated with MeOTf to give $[W(CO)_2\{\equiv C\text{–}E(Me)\text{-}C(NMe_2)_2\}Tp'][OTf]$.[1040,1080] Oxidation of $[W(CO)_2\{\equiv C\text{–}P=C(NMe_2)_2\}Tp']$ gives the zwitterionic $[W(CO)_2\{\equiv C\text{–}P(O)_2C(NMe_2)_2\}Tp']$.[1102] The reactions of $[W(CO)_2\{\equiv C\text{–}P=C(NMe_2)_2\}Tp']$ with $[Au(CO)Cl]$ affords $[W(CO)_2\{\equiv C\text{–}P(AuCl)_2C(NMe_2)_2\}Tp']$; however, reaction of the arsenic analog with $[AuC(CO)Cl]$ results in As=C cleavage and formation of a cyclotriarsane complex $[\{W(CO)_2Tp'(\equiv C\text{–}As)\}_3]$ (*cyclo*-As_3).[1103] The reaction of the μ-alkylidyne complex $[W(CO)_2Cp(\mu\text{-}CTol\text{-}4)Fe(CO)_4]$ with tellurium powder affords the "WFeTeC" tetrahedral complex $[W(CO)_2Cp(\mu^2\text{-}\eta^2{:}\eta^2\text{-}TeCTol\text{-}4\text{-}Te,C)Fe(CO)_3]$ (W–Fe).[609]

The reaction of carbyne complexes with S_8 or methylthiirane can afford η^2-thioacyl (thiocarbene) and η^2-dithiocarboxylate complexes, while the reaction of $[W(CO)_2(pipy)(\equiv CC_6H_4OMe\text{-}4)Br]$ with methylthiirane affords $[W(CO)_2(bipy)\{\eta^2\text{-}C(S)C_6H_4OMe\text{-}4\text{-}C,S\}Br]$ and $[W(CO)_2(bipy)\{\eta^2\text{-}S_2CC_6H_4OMe\text{-}4\text{-}S,S'\}Br]$.[158,1104] Carbyne complexes of the type $[W(CO)_2(L\text{–}L)(\equiv CC_6H_4R\text{-}4)X]$ (L–L = dppe, TMEDA), where R is an iodo or amino functionality, can undergo additional functionalization based on conventional palladium-catalyzed coupling reactions (when R = I) or nitrogen-group transformations (when $R = NH_2$).[1058,1062]

The protonation of carbynes to form η^2-carbenes having agostic W–H interactions is discussed in Section 5.08.15.4.[182,424,678,930] The addition of a donor ligand to a carbyne–W–CO complex can induce coupling of the carbyne fragment with a carbonyl ligand to form η^2-ketenyl complexes.[173,879,933–935,1031,1105,1106] See also the carbene complexes (Sections 5.08.15.4 and 5.08.15.6).

5.08.16 π-Carbon-donor Ligands

This section deals with W–CO and W–CNR complexes bearing carbon-donor π-bonding ligands. The material is mostly organized according to the number of donor atoms, but with complexes of alkynes, cyclopentadienyl complexes, and π-arene complexes treated under separate subheadings.

5.08.16.1 η^2-Complexes

5.08.16.1.1 Complexes of alkenes

Simple alkene complexes $[W(CO)_{6-n}(\eta^2\text{-alkene})_n]$ ($n = 1, 2$) have been known for many years and are discussed extensively in COMC (1982) (Section 28.2)[1107] and COMC (1995) (Section 6.2);[1108] nevertheless, there has been considerable recent research in the field. These complexes are typically prepared photochemically, from $[W(CO)_6]$ and the appropriate alkene.[1109–1114]

The mono(alkene) complexes $[W(CO)_5(\eta^2\text{-alkene})]$ are usually of limited stability and rarely isolated, but $[W(CO)_5(\eta^2\text{-vinylferrocene})]$[1112] and $[W(CO)_5(\eta^2\text{-norbornene})]$[1111] are relatively stable in the solid state and the latter has been structurally characterized.[1111] $[W(CO)_5(\eta^2\text{-norbornene})]$ promotes ROMP of norbornene.[1111]

The bis(alkene) complexes $[W(CO)_4(\eta^2\text{-alkene})_2]$ are much more stable than the mono(alkene) adducts. In the synthesis of *trans*-$[W(CO)_4(\eta^2\text{-(E)-cyclooctene})_2]$ from $[W(CO)_6]$ and (*E*)-cyclooctene under photochemical conditions, $[W(CO)_5(\eta^2\text{-}(E)\text{-cyclooctene})]$ and *cis*-$[W(CO)_4(\eta^2\text{-}(E)\text{-cyclooctene})_2]$ were formed as intermediates.[1109] Isolation of $[W(CO)_5(\eta^2\text{-}(E)\text{-cyclooctene})]$ and *cis*-$[W(CO)_4(\eta^2\text{-}(E)\text{-cyclooctene})_2]$ from photochemical reaction mixtures was difficult, and these complexes were more easily prepared by thermal reactions of (*E*)-cyclooctene with $[W(CO)_5(\eta^2\text{-(Z)-cyclooctene})]$ and $[W(CO)_5(\eta^2\text{-}Me_3SiC\equiv CSiMe_3)]$, respectively.[1109] The bis(alkene) adduct *trans*-$[W(CO)_4(\eta^2\text{-}(E)\text{-cyclooctene})_2]$ (formed from racemic (*E*)-cyclooctene) exists as two diastereomers, and the fact that these diastereomers can be separated by fractional crystallization[1109] is an indication of the stability of the bis(alkene) complexes. In various matrix isolation and solution studies of the reaction of ethylene with $[W(CO)_6]$ under photochemical conditions, $[W(CO)_5(\eta^2\text{-}C_2H_4)]$, *cis*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$, *trans*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$, *fac*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$, and *mer*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ were detected.[1110]

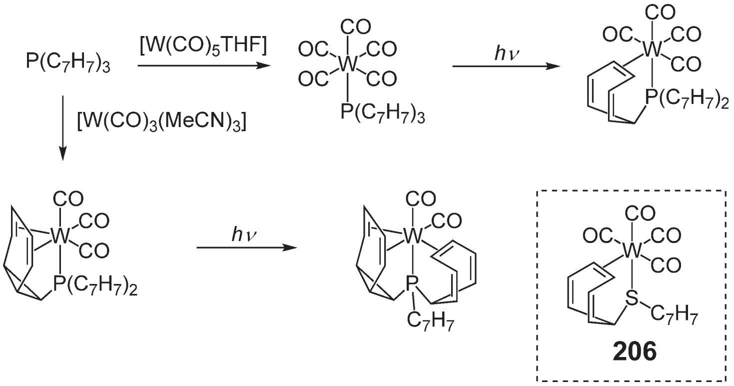
In an interesting study, polymer-bound complexes $[W(CO)_5(\eta^2\text{-alkene})_{PE}]$ (PE = polyethylene) were formed by photochemical reaction of $[W(CO)_6]$ with residual alkene groups in samples of polyethylene.[1115] The complexes were identified by their IR spectra. Upon extended photolysis, complexes involving terminal alkene units isomerized to complexes involving *trans*-internal alkene units.

Tri(1-cyclohepta-2,4,6-trienyl)phosphine $P(C_7H_7)_3$ exhibits interesting reactivity with tungsten carbonyl sources, yielding products that contain cycloheptatrienyl groups acting as η^2- and/or η^4-donors (Scheme 67).[1116] Addition of di(1-cyclohepta-2,4,6-trienyl)sulfide $S(C_7H_7)_2$ to a mixture containing $[W(CO)_5(MeCN)]$, $[W(CO)_4(MeCN)_2]$, and $[W(CO)_3(MeCN)_3]$ afforded the tetracarbonyl complex (**206**) which also contains an η^2-cycloheptatrienyl group.[546]

Both *trans*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$[1110] and *trans*-$[W(CO)_4(\eta^2\text{-(E)-cyclooctene})_2]$[1109] have been structurally characterized. In both cases, the C═C bonds of the alkenes are staggered with respect to each other and eclipse two W–CO bonds. For a range of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ complexes, ^1H NMR studies have been used to study restricted rotation of the alkene about the axis defined by the metal and the midpoint of the C═C group,[1113,1114] and for *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)_2]$, the barrier to rotation was measured as $46\,kJ\,mol^{-1}$.[1114] The preferred alignment of the C═C group with respect to P–W–P and C–W–C axes in *trans*-$[W(CO)_3(PX_3)_2(C_2H_4)]$ (X = H, Me, F, Cl, Br, I) has been explored by DFT studies,[333] which suggested that while electronic effects of the PX_3 groups were most important, steric effects were also significant for X = Br, I.

The nature of the metal–ethylene bonding in $[W(CO)_5(\eta^2\text{-}C_2H_4)]$ has also been studied by DFT[231,1117] and HF and MP2 methods.[522] The results of energy partition analysis suggest that the covalent character of the W–(η^2-C_2H_4) bond is dominated by ligand to metal σ-donation.[1117]

Properties of selected η^2-alkene complexes are summarized in Table 29.



Scheme 67

Table 29 Structural and spectroscopic properties of selected tungsten carbonyl complexes with η^2-alkene ligands

Complex	*IR* (cm^{-1})	*NMR* (ppm)	*Bond distances* (Å)	*References*
trans-$[W(CO)_4(\eta^2\text{-}C_2H_4)]$	ν_{CO} (hexane) 2059, 1997, 1966, 1936	δ_H 2.12, δ_C 198.0 (CO), 31.2 (C═C)	W–CO 2.033, 2.045; W–C_{alkene} 2.299, 2.315; C═C 1.413	1110
trans-$[W(CO)_4(\eta^2\text{-}CH_2CHCH_3)]$	ν_{CO} (hexane) 2058, 1990, 1954, 1928, 1917	δ_H 2.12, δ_C 200.0 (CO), 50.2 (═CH–), 37.4 (H_2C═)	–	1114
$[W(CO)_5(\eta^2\text{-(norbornene)})]$	ν_{CO} (heptane) 2078, 1951; ν_{CO} (KBr) 2077, 1998, 1923	δ_C 200.6 (CO_{ax}), 197.5 (CO_{eq}) 88.6 (C═C)	W–CO_{ax} 2.011; W–CO_{eq} 2.031–2.047; W–C_{alkene} 2.425, 2.451; C═C 1.384	1111
$[W(CO)_5(\eta^2\text{-(E)-cyclooctene})]$	ν_{CO} (hexane) 2080, 1999, 1966, 1954, 1947	δ_C 201.7 (CO_{ax}), 196.9 (CO_{eq}) 83.9 (C═C)	W–CO_{ax} 1.983; W–CO_{eq} 2.042–2.077; W–C_{alkene} 2.497, 2.510; C═C 1.37	1109
trans-$[W(CO)_4(\eta^2\text{-(E)-cyclooctene})_2]$	ν_{CO} (hexane) 1984, 1950	δ_C (C_7D_8) 200.9 (CO), 57.8 (C═C)	W–CO 2.026, 2.049; W–C_{alkene} 2.327, 2.328; C═C 1.412, 1.424	1109
206	ν_{CO} (pentane) 2032, 1942, 1927, 1896	δ_C ($CDCl_3$) 198.8–203.8 (4 × CO), 76.0, 76.8 (η^2-C═C)	W-CO 1.957, 1.991, 2.021, 2.028; W–C_{alkene} 2.460, 2.470; η^2-C═C 1.386	546

5.08.16.1.2 Fullerene complexes

A number of tungsten carbonyl complexes with fullerenes serving as η^2-ligands are known, and early studies in this area have been reviewed.[1118] These surprisingly robust complexes can be formed under thermal or photochemical conditions (Table 30). For those that have been structurally characterized to date, the fullerene is attached to W via a 6:6 ring junction, with the C–C distance at this 6:6 junction being substantially lengthened and the C–C unit "pulled away" from the rest of the fullerene cage upon coordination.[436,1119–1121] These complexes exhibit a rich electrochemistry, C_{60} adducts typically displaying three fullerene-centered reversible one-electron reductions at potentials 0.1–0.2 V more negative than for the free fullerene.[1120] The nature of the paramagnetic radicals formed on electrochemical reduction of *mer*-[W(CO)$_3$(diphosphine)C$_{60}$] has been investigated by ESR studies, the results of which suggest that the paramagnetic species possess significant metallic character.[1122,1123]

Table 30 Tungsten carbonyl complexes with η^2-fullerene ligands

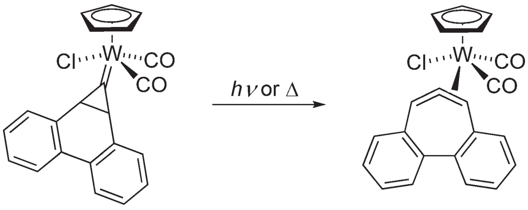
Complex	*Synthesis*	*Comments*[a]	*References*
mer-[W(CO)$_3$(dppe)(η^2-C$_{60}$)]	[W(CO)$_4$(dppe)] + C$_{60}$ + *hν*	Forest green: yield 21%; ν_{CO} (CH$_2$Cl$_2$) 2002, 1937, 1884 cm^{-1}; W–C1/C2 2.291, 2.296; C1-C2 1.497; W–CO 2.009, 2.026, 2.037 Å	1119, 1124
mer-[W(CO)$_3$(dppf)(η^2-C$_{60}$)]	[W(CO)$_4$(dppf)] + C$_{60}$ + *hν*	ν_{CO} (KBr) 1998, 1936, 1868 cm^{-1}; δ_{CO} (CDCl$_3$) 206.0, 204.6, 204.0; W–C1/C2 2.316, 2.338; C1-C2 1.489; W–CO 2.008, 2.014, 2.036 Å CV: three reversible C$_{60}$-centered reductions, E°′ −0.78, −1.17, −1.74 V	1120
[*mer*-{W(CO)$_3$(dppf)}$_2$(η^2:η^2-C$_{60}$)]	[W(CO)$_4$(dppf)] + C$_{60}$ + *hν*	Byproduct in synthesis of *mer*-[W(CO)$_3$(dppf)(η^2-C$_{60}$)]: ν_{CO} (KBr) 1995, 1929, 1870 cm^{-1}	1120
mer-[W(CO)$_3$(dppf)(η^2-C$_{70}$)]	[W(CO)$_4$(dppf)] + C$_{70}$ + *hν*	ν_{CO} (KBr) 1999, 1937, 1870 cm^{-1} CV: two reversible C$_{70}$-centered reductions, E°′ −0.73, −1.04 V; loss of C$_{70}^{3-}$ at −1.54 V	1120
[{*mer*-W(CO)$_3$(dppf)}$_2$(η^2:η^2-C$_{70}$)]	[W(CO)$_4$(dppf)] + C$_{70}$ + *hν*	Byproduct in synthesis of *mer*-[W(CO)$_3$(dppf)(η^2-C$_{70}$)]: ν_{CO} (KBr) 1998, 1935, 1870 cm^{-1}	1120
mer-[W(CO)$_3${*o*-C$_6$H$_4$(PPh$_2$)$_2$}(η^2-C$_{60}$)]	*fac*-[W(CO)$_3${*o*-C$_6$H$_4$(PPh$_2$)$_2$}(MeCN)] + C$_{60}$ at 80 °C in PhCl	ν_{CO} (KBr) 2006, 1942, 1885 cm^{-1}; W–C1/C2 2.291, 2.295; C1-C2 1.501; W–CO 1.990, 2.003, 2.007 Å CV: three reversible C$_{60}$-centered reductions, E°′ −0.80, −1.14, −1.64 V	436, 1122
mer-[W(CO)$_3${*o*-C$_6$H$_4$(PPh$_2$)$_2$}(η^2-C$_{70}$)]	*fac*-[W(CO)$_3${*o*-C$_6$H$_4$(PPh$_2$)$_2$}(MeCN)] + C$_{70}$ at 80 °C in PhCl	ν_{CO} (KBr) 2009, 1943, 1886 cm^{-1}	1125
mer-[W(CO)$_3${(−)-diop}(η^2-C$_{60}$)]	[W(CO)$_6$] + (−)-diop + C$_{60}$ + *hν*	ν_{CO} (KBr) 2000, 1938, 1870 cm^{-1} CV: three reversible C$_{60}$-centered reductions, E°′ −0.78, −1.15, −1.65 V	1123
[W(CO)$_2$(phen)(dbm)(C$_{60}$)] (dbm = dibutyl maleate)	[W(CO)$_2$(phen)(dbm)$_2$] + C$_{60}$ in refluxing toluene	ν_{CO} (KBr) 1963, 1895 cm^{-1}; W–C1/C2 2.300, 2.304; C1-C2 1.429; W–CO 1.974, 2.010 Å CV: three reversible C$_{60}$-centered reductions, E°′ −0.76, −1.17, −1.60 V	1126, 1127
[W(CO)$_2${4,4′-(Bu^{n}OCO)$_2$-2,2′-bipy}(C$_{60}$)$_2$]	[W(CO)$_4${4,4′-(Bu^{n}OCO)$_2$-2,2′-bipy}] + C$_{60}$ in refluxing xylene	CO groups mutually *cis*, C$_{60}$ groups mutually *trans* ν_{CO} (KBr) 1962, 1898 cm^{-1};W–C1/C2 2.28 Å (average); C1–C2 1.483 Å (average)	1121

[a] C1, C2 are the fullerene atoms bonded to W. Cyclic voltammetry (CV) E°′ values are relative to SCE.

5.08.16.1.3 Complexes of η^2-allenes

The cationic tricarbonyl η^2-allene complex **208** (Scheme 68) was obtained by reaction of the propargyl tungsten complex **207** with Ph_3CPF_6 in CH_2Cl_2.[1128] In MeCN, **208** decomposes to $[CpW(CO)_3(MeCN)]^+$ and two 1,1-diphenyldihydronaphthalenes, a process which is believed to involve an intramolecular [3 + 3]-cycloaddition to form the intermediate **209** (Scheme 68).[1128] The neutral dicarbonyl η^2-allene complex **210**, prepared in two steps from the cationic complex **208** (Scheme 68), has been structurally characterized.[1129]

The η^2-dibenzoheptatetraene complex **212** is the major product (up to 67% yield) of decomposition of the cyclopropylidene complex **211** (Equation (45)).[1130] The interesting heterobimetallic complex **213** containing an η^2:η^2-allene ligand has also been prepared (Scheme 69).[1131] Both **212** and **213** have been structurally characterized.[1130,1131]

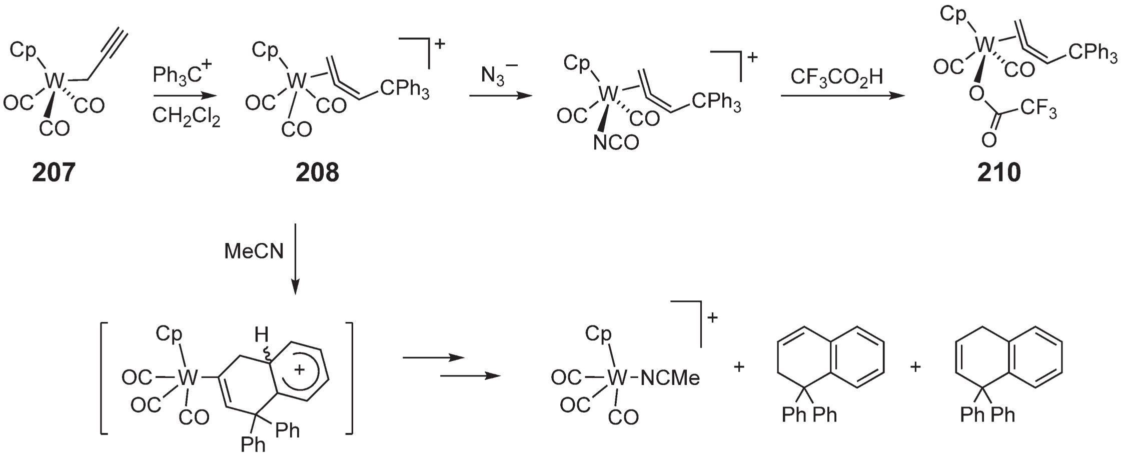


211 **212**

(45)

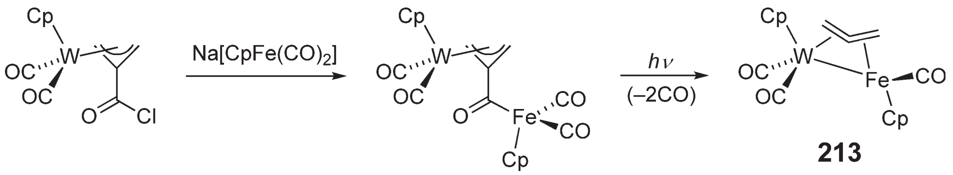
5.08.16.2 η^3-Complexes

η^3-Allyl tungsten chemistry is a well-established field and standard routes to allyl tungsten compounds are discussed in COMC (1982) and COMC (1995). Recent syntheses of tungsten complexes containing η^3-allyl and related η^3-groups include: (i) reaction of $[W(CO)_3Cp\{\mu\text{-}\eta\text{:}\eta^2\text{-}CH_2C(O)\}W(CO)_2Cp]$ **159** with allene to give



207 **208** **210** **209**

Scheme 68



213

Scheme 69

[W(CO)$_3$Cp{μ-η:η^3-CH$_2$C(O)C$_3$H$_4$}W(CO)$_2$Cp][875] (see Scheme 48, Section 5.08.15.1); (ii) oxidative addition of 4-bromo-2-cyclopentenone to [W(CO)$_3$(MeCN)$_3$] to give [W(CO)$_2$(MeCN)$_2$(Br)(η^3-C$_5$H$_5$O)];[181] (iii) oxidative addition of allyl chloride to [(W(CO)$_3$(EtCN)$_3$], followed by addition of KTp′, to give [Tp′W(CO)$_2$(η^3-C$_3$H$_5$)];[179] (iv) isomerization of the (cyclopropylcarbonyl)tungsten complex [TpW(CO)$_2${η^2-C(O)-c-C$_3$H$_5$}] to [TpW(CO)$_2$(η^3-C$_3$H$_5$)][859] (see Scheme 47, Section 5.08.15.1); and (v) photochemical addition of MeC$\equiv$CSiMe$_3$ to [Tp′W(CO)$_3$H] to give [Tp′W(CO)$_2$(η^3-C$_3$H$_4$SiMe$_3$)][706] (see Scheme 39, Section 5.08.9.3). Additional examples are summarized in Table 31.

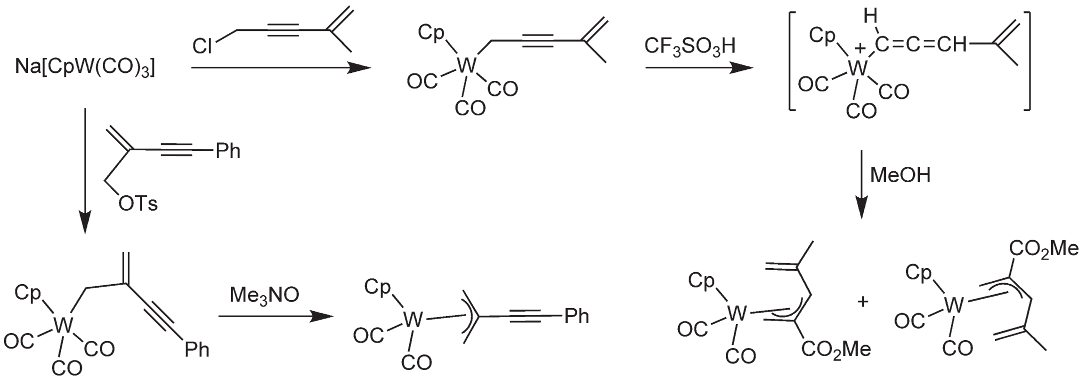
Compounds containing η^3-allyl-like groups have also be prepared by reaction of strong acid with tungsten complexes containing η^1-propargyl groups[1132] or by decarbonylation of complexes containing an η^1-allyl group[1133] (e.g., Scheme 70).

The ease with which the MeCN ligands can be displaced from the 2-methallyl complex [W(CO)$_3$(MeCN)$_2$(η^3-2-Me-C$_3$H$_4$)] allows this compound to be used[658] as a starting material for synthesis of bimetallic halo-bridged complexes [(1,3,5-C$_6$H$_3$Pr$^i_3$)Ru(μ-Cl)$_3$W(CO)$_2$(η^3-2-Me-C$_3$H$_4$)] (by reaction with [{(1,3,5-C$_6$H$_3$Pr$^i_3$)RuCl$_2$}$_2$]), [Cp*Rh(μ-Cl)$_3$W(CO)$_2$(η^3-2-Me–C$_3$H$_4$)] (by reaction with [{Cp*RhCl$_2$}$_2$]), [(CO)$_3$Ru(μ-Cl)$_3$W(CO)$_2$(η^3-2-Me–C$_3$H$_4$)] (by reaction with [{(CO)$_3$RuCl$_2$}$_2$]), and [(CO)(dCypb)Ru(μ-Cl)$_3$W(CO)$_2$(η^3-2-Me–C$_3$H$_4$)] (by reaction with [{(CO)(dCypb)RuCl$_2$}$_2$], dCypb = 1,4-bis(dicyclohexylphosphino)butane). These reactions are facile and high yielding, and thus suitable for combinatorial synthesis.[658]

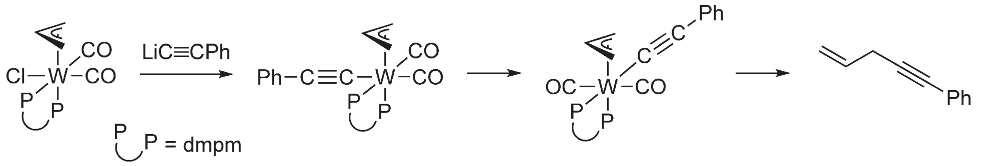
The η^3-1,3-butadienyl complexes [W(CO)$_2$L(η^3-CH$_2$C(COCl)C=CH$_2$)Cl] (L = phen, bipy) have been synthesized in good yields by reaction of 1,4-dichloro-2-butyne and PPh$_4$[WCl(CO)$_3$L] in chlorinated solvents.[1134] The acid chloride substituent on the butadienyl group reacts with MeOH, BuSH, or Et$_2$NH to yield the methyl ester [W(CO)$_2$L(η^3-CH$_2$C(CO$_2$Me)C=CH$_2$)Cl], the butanethiolate ester [W(CO)$_2$L(η^3-CH$_2$C(COSBu)C=CH$_2$)Cl], and the diethyl amide [W(CO)$_2$L(η^3-CH$_2$C(CONEt$_2$)C=CH$_2$)Cl], respectively.[1134]

Table 31 Selected tungsten complexes with π-donor η^3-ligands

Compound	*Synthesis*	*Comments*	*References*
[W(CO)$_2$(OMe)(phen)(η^3-C$_3$H$_5$)]	[W(CO)$_2$(Cl)(phen)(η^3-C$_3$H$_5$)] + NaOMe	X-ray structure reported	509
217	See Scheme 9, Section 5.08.3.2.3.(i)	X-ray structure reported	241
131	Na$_2$[7,8-C$_2$B$_9$H$_{11}$] + [W(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_5$)(Br)]		750
218	[W(CO)(η^2-MeC$\equiv$CMe)$_2$(η^5–7,8-C$_2$B$_9$H$_{11}$)] + Bu^{t}NC	X-ray structure reported	750
[W(CO)$_2$(MeCN)$_3$(η^3-C$_7$H$_9$)][BF$_4$]	[WI(CO)$_3$(η^5-C$_7$H$_9$)] + AgBF$_4$ in MeCN + Et$_3$N (see Scheme 73, Section 5.08.16.4)		1137
[WI(CO)$_2$(Bu^{t}NC)$_2$(η^3-C$_7$H$_7$)]	[WI(CO)$_2$(η^7-C$_7$H$_7$)] + Bu^{t}NC (see Section 5.08.16.4)	X-ray structure reported	1138
[W(η^5-indenyl)(CO)$_2$(η^3-cyclooctatrienyl)]	[W(η^5-indenyl)(CO)$_3$H] + cot + $h\nu$	Two isomers; X-ray structure reported	702

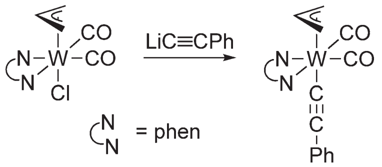


Scheme 70



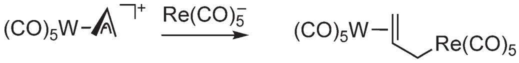
Scheme 71

Insight into the mechanism of W-catalyzed allylation has been gained through studies of the reaction of carbanions with $[W(CO)_2(phen)(\eta^3\text{-allyl})Cl]$ and $[W(CO)_2(dmpm)(\eta^3\text{-allyl})Cl]$. $[W(CO)_2(dmpm)(\eta^3\text{-allyl})Cl]$, in which Cl is *cis* to the allyl group, reacts with carbanions (e.g., $PhC{\equiv}C^-$) to give allylated products (e.g., $CH_2{=}CHCH_2C{\equiv}CPh$), Scheme 71).[885] In contrast to this result, $[W(CO)_2(phen)(\eta^3\text{-allyl})Cl]$, in which Cl is *trans* to the allyl group, reacts with carbanions to form products that are stable with respect to elimination of an allylation product even on prolonged refluxing in THF (e.g., Equation (46)).[250]



(46)

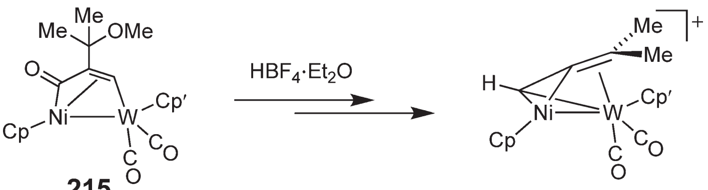
Nucleophilic attack on an η^3-allyl ligand has been used as a route to the heterobimetallic complex **214** (Equation (47)).[1135]



214

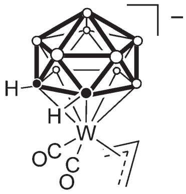
(47)

The η^3-allylidene complex $[WCO)_2(NC_5H_4Me\text{-}4)(\eta^3\text{-}C(Ph)CHCHMe)(Br)_2]$ (**170**, Section 5.08.15.4.1) was formed by reaction of allyl bromide with the alkylidyne complex $[W(CO)_2Br(NC_5H_4Me\text{-}4)_2(CPh)]$.[929] A complex assigned on the basis of spectroscopic data as the cation **216** (Equation (48)), which contains an allenylic (propargylic) cation stabilized by coordination η^3 to W and η^2 to Ni, was formed by treatment of the metallacyclic complex **215** (see also Equation (55) in Section 5.08.16.5) with $HBF_4{\cdot}Et_2O$.[1136]



215 **216**

(48)



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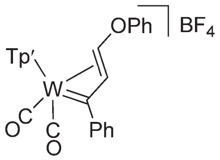

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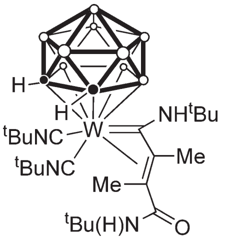


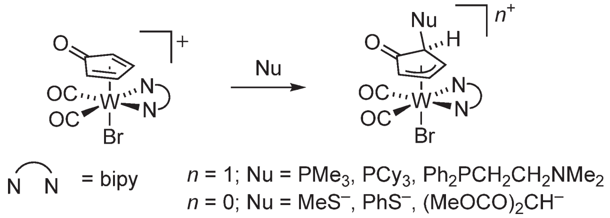
218

5.08.16.3 η^4-Complexes

η^4-Norbornadiene complexes have been conveniently synthesized by reaction of norbornadiene (nbd) with $[WXY(CO)_3(MeCN)_2]$. Reaction of $[W(I)_2(CO)_3(MeCN)_2]$ with nbd in refluxing toluene gave the 16-electron complex $[W(I)_2(CO)_2(\eta^4\text{-nbd})]$,[143] whereas reaction of $[WCl(SnCl_3)(CO)_3(MeCN)_2]$ with nbd in CH_2Cl_2 at room temperature gave the 18-electron complex $[WCl(SnCl_3)(CO)_3(\eta^4\text{-nbd})]$.[828]

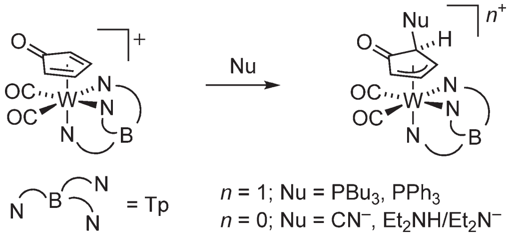
η^4-Cyclobutadiene complexes $[WL(\eta^2\text{-ArC}{\equiv}\text{CAr})(\eta^4\text{-Ar}_4C_4)]$ (L = MeCN, Ar = Ph, 4-MeC$_6$H$_4$; L = CO, Ar = Ph) have been formed by reaction of $[WL(\eta^2\text{-Ar–C}{\equiv}\text{CAr})_3]$ with ArC≡CAr.[1139,1140] The reaction proceeds more readily when L = MeCN, and, in studies using PhC≡CPh under forcing conditions, product mixtures included complexes **229** and **230** (Section 5.08.16.5) that contain an η^4-pentaphenylcyclopentadienyl fragment.[1140]

Hydride abstraction from the η^3-cyclopentenoyl complexes $[TpW(CO)_2(\eta^3\text{-}C_5H_5O)]$, $[W(bipy)(CO)_2(\eta^3\text{-}C_5H_5O)Br]$, and $[W(dppm)(CO)_2(\eta^3\text{-}C_5H_5O)Br]$ gives the η^4-cyclopentadienone derivatives $[TpW(CO)_2(\eta^4\text{-}C_5H_4O)]PF_6$, $[W(bipy)(CO)_2(\eta^4\text{-}C_5H_4O)Br]PF_6$, and $[W(dppm)(CO)_2(\eta^4\text{-}C_5H_4O)Br]PF_6$ in excellent yields.[181] The cations $[TpW(CO)_2(\eta^4\text{-}C_5H_4O)]^+$ and $[W(bipy)(CO)_2(\eta^4\text{-}C_5H_4O)Br]^+$ have been shown to react with a variety of nucleophiles to form η^3-cyclopentenoyl complexes (Equations (49) and (50)) in good to excellent yields.[1141]



n = 1; Nu = PMe$_3$, PCy$_3$, Ph$_2$PCH$_2$CH$_2$NMe$_2$
n = 0; Nu = MeS$^-$, PhS$^-$, (MeOCO)$_2$CH$^-$

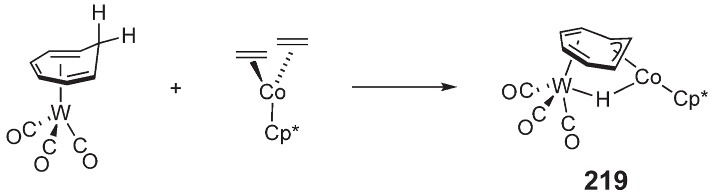
(49)



n = 1; Nu = PBu$_3$, PPh$_3$
n = 0; Nu = CN$^-$, Et$_2$NH/Et$_2$N$^-$

(50)

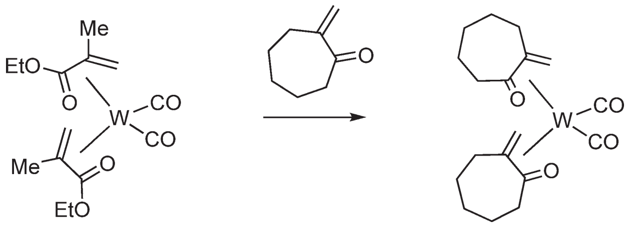
The interesting heterobimetallic complex **219** containing an η^3:η^4-cycloheptatrienyl bridging group has been reported (Equation (51)).[1142] This complex was formed in 63% yield, considerably higher than for the analogous Cr and Mo complexes.



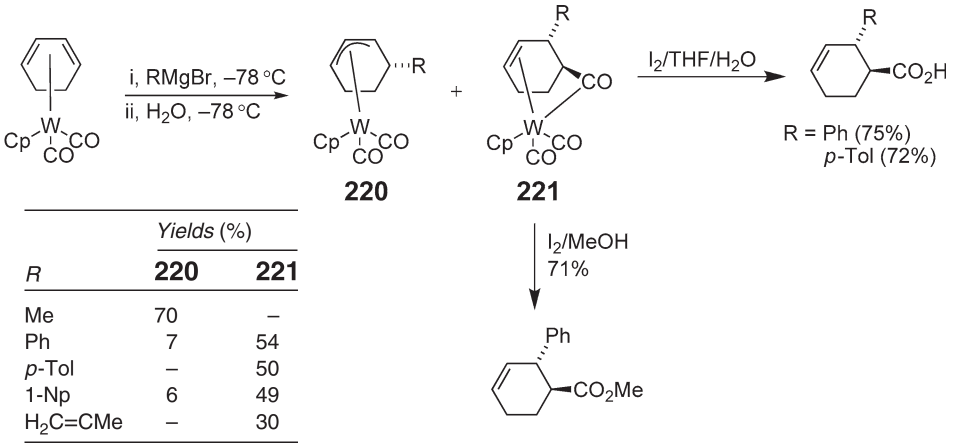
219

(51)

Complexes $[W(CO)_2(\eta^4\text{-}H_2C{=}C(Me)CO_2R)_2]$ (R = Me, Et), containing η^4-methacrylate ester groups, have been synthesized by reaction of the appropriate methacrylate ester with $[W(CO)_3(EtCN)_3]$ in hydrocarbon solvents at elevated temperatures. The coordinated methacrylate ester groups are readily displaced by α,β-unsaturated ketones at room temperature (e.g., Equation (52)) to give η^4-oxa-1,3-diene complexes.[1143]



(52)



R	Yields (%) 220	Yields (%) 221
Me	70	–
Ph	7	54
p-Tol	–	50
1-Np	6	49
$H_2C{=}CMe$	–	30

Scheme 72

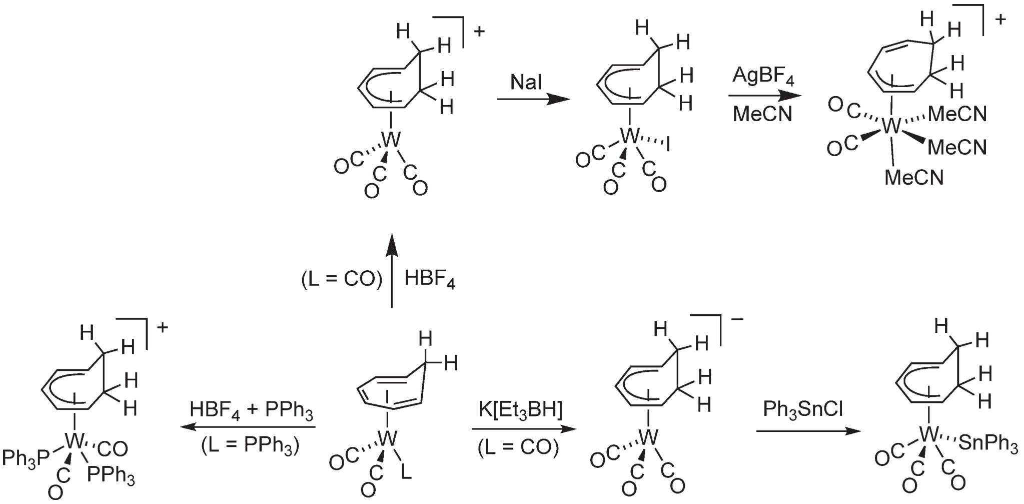
Coordinated η^4-buta-1,3-diene units usually undergo nucleophilic attack exclusively at a terminal carbon. The well-known cation $[CpW(CO)_2(\eta^4\text{-cyclohexadiene})]^+$ has been found to undergo nucleophilic attack by sp^2-centered carbanions primarily at an internal carbon to give σ,π products, from which cyclohexene-4-carboxylate derivatives can be obtained by treatment with I_2 and MeOH or H_2O (Scheme 72).[1144]

5.08.16.4 η^5-, η^6-, and η^7-Complexes, Excluding Cp and π-arene Complexes

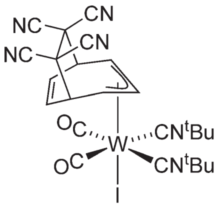
The majority of recent work relevant to this section concerns the chemistry of the well-known cycloheptatriene and cycloheptatrienyl complexes $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ and $[W(CO)_3(\eta^7\text{-}C_7H_7)]^+$ and their derivatives.

Attack of either H^- (in the form of Et_3BH^-)[808] or H^+ (as HBF_4)[1137] on the η^6-cycloheptatriene ring in $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ provides routes to η^3-cycloheptadienyl and η^5-cycloheptadienyl complexes (Scheme 73).

$\eta^7 \rightarrow \eta^3$ Hapticity interconversion in cycloheptatrienyl Mo and W complexes $[MX(CO)_2(\eta^7\text{-}C_7H_7)]$ has been studied systematically.[1145] $[WX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = NCO, Br) react with MeCN to form η^3 complexes $[WX(CO)_2(MeCN)_2(\eta^3\text{-}C_7H_7)]$,[1145] and $[WI(CO)_2(\eta^7\text{-}C_7H_7)]$ reacts with Bu^{t}NC to form $[WI(CO)(Bu^tNC)_2(\eta^3\text{-}C_7H_7)]$.[1138] The diene portion of $[WI(CO)(Bu^tNC)_2(\eta^3\text{-}C_7H_7)]$ undergoes an interesting [4 + 2]-cycloaddition reaction with tetracyanoethylene to give 222.[1138]



Scheme 73



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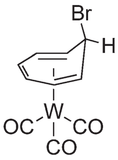

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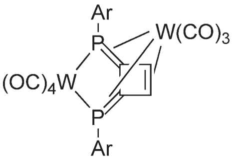
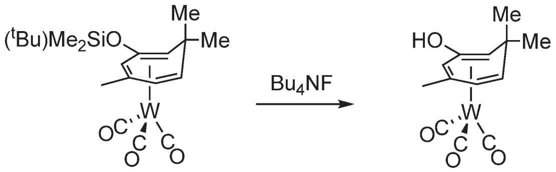


224

Attack of nucleophiles on the η^7-cycloheptatrienyl group in $[W(CO)_3(\eta^7\text{-}C_7H_7)]^+$ is a versatile route to η^6-cycloheptatriene–tungsten complexes (Scheme 74).[1148–1151] The factors influencing the regio- and stereochemical courses of the reactions involving attack of phosphines and phosphites on $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$ (M = Cr, Mo, W) have been examined by experimental and computational methods.[1146] The dimer **225** (Scheme 74) can also be formed by reductive dimerization of $[W(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ using potassium naphthalenide, while reduction of $[W(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ using potassium naphthalenide in the presence of CBr_4 gives the bromide **223**.[1147]

The η^6-cycloheptatriene complex **226**, which contains a stable metal–enol structure, was obtained by fluoride-induced cleavage of the corresponding silyl ether (Equation (53)).[1152] Curiously, this procedure is high yielding for both the W and Cr analogs, but fails for the Mo analog. The metallaheteroborane complex $[7\text{-}\{W(CO)_2(\eta^7\text{-}C_7H_7)\}(\textit{nido}\text{-}7,8\text{-}As_2B_9H_{10})]$ has been synthesized by reaction of $[W(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ with $[Me_4N][\textit{nido}\text{-}7,8\text{-}As_2B_9H_{10}]$.[1153]

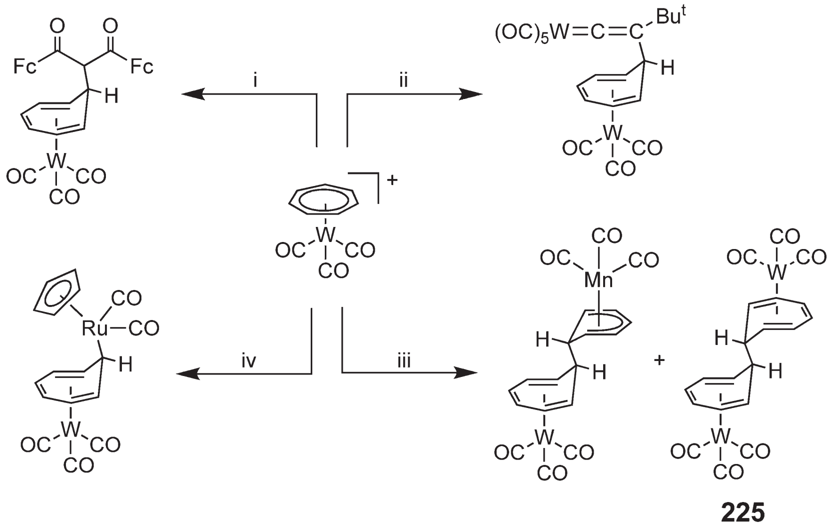


226

(53)

The dinuclear complex **224**, which contains an η^6-bis(phosphinidene)cyclobutene unit, has been synthesized by the reaction of 3,4-bis(2,4,6-triisopropylphenylphosphinidene)cyclobutene with $[W(CO)_4(MeCN)_2]$.[305]

Theoretical studies of 1,2,4-triphosphole $HP_3C_2H_2$ and its hypothetical complex $[Mo(CO)_3(\eta^5\text{-}HP_3C_2H_2)]$ suggest that 1,2,4-triphosphole has aromatic character, and its η^5-complex should be considered as a close relative to $[Mo(CO)_3(\eta^6\text{-arene})]$ complexes.[1154] Consistent with these studies, reaction of $[W(CO)_5(THF)]$ with 1-dimethylsilyl-3,5-di-(t-butyl)-1,2,4-triphosphole gave $[W(CO)_3(\eta^5\text{-}\{P_3C_2(Bu^t)_2CH(SiMe_3)_2\}]$.[1154]



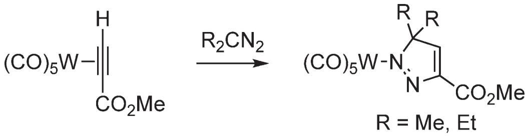
i, $(FcCO)_2CH_2$, KH;[1148] ii, $[Et_4N][W(CO)_5(C{\equiv}C\text{-}Bu^t)]$;[1149] iii, $[Mn(CO)_3(\eta^4\text{-}C_6H_6)]^-$ (from $[Mn(CO)_3(\eta^6\text{-}C_6H_6)]PF_6$ + Na naphthalenide);[1150] iv, $Na[CpRu(CO)_2]$[1151]

Scheme 74

5.08.16.5 Alkyne Complexes

The photochemical behavior of $[W(CO)_6]$ in the presence of acetylene, propyne, and 2-butyne has been examined under matrix-isolation conditions.[37] Photolysis experiments in CH_4 or Ar matrices at 20 K using wavelengths near 313 nm resulted in formation of $[W(CO)_5(\eta^2\text{-}RC{\equiv}CR^1)]$ ($R, R^1 = H, H; H, Me; Me, Me$). For the terminal alkynes, however, the dominant product of photolysis was not the η^2-alkyne complex but a product assigned as a vinylidene species, $[W(CO)_5({=}C{=}CHR)]$ ($R = H$, Me). In experiments involving acetylene, prolonged irradiation resulted in formation of tetracarbonyl species assigned as $[W(CO)_4(HC{\equiv}CH)]$ (in which the acetylene ligand is acting as a 4-electron donor), and $[W(CO)_4({=}C{=}CH_2)(\eta^2\text{-}HC{\equiv}CH)]$. Identification of products in these matrix-isolation experiments was based solely on characterization by infrared spectroscopy.[37] Recently, similar photolysis experiments using acetylene, propyne, and *t*-butylacetylene have been undertaken in $CDCl_3$ and toluene-d_8 solution at 200 K (with characterization of photolysis products by NMR at 200–300 K) and in hexane at 270 K (with characterization of photolysis products by IR at ambient temperature).[1155] NMR studies, in particular, provided convincing evidence for the formation of $[W(CO)_5(\eta^2\text{-}HC{\equiv}CR)]$ and $[W(CO)_5({=}C{=}CHR)]$ ($R = H$, Me, Bu^t). In these solution experiments, NMR results also indicated the presence of $[W(CO)_4(\eta^2\text{-alkyne})]$, $[W(CO)(\eta^2\text{-alkyne})_3]$, and $[W(CO)_3(\eta^6\text{-arene})]$ complexes.

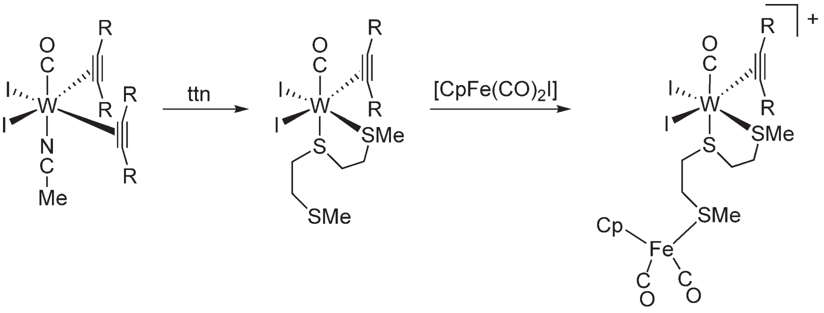
The coordinated terminal alkyne in $[W(CO)_5(\eta^2\text{-}HC{\equiv}CCO_2Me)]$ undergoes a cycloaddition reaction with diazoalkanes to form 3*H*-pyrazole complexes (Equation (54)).[1156] Tungsten–pentacarbonyl adducts of terminal alkynes, $[W(CO)_5(HC{\equiv}CR)]$, exist in rapid equilibrium with their vinylidene tautomers $[W(CO)_5({=}C{=}CHR)]$, the latter usually being present in amounts too small to be detected spectroscopically. The vinylidene tautomer can be trapped with *N*,*N*-dimethylaminopropyne to form cyclobutenylidene complexes via a [2 + 2]-cycloaddition process (see Equation (33) in Section 5.08.15.4.1).[928]



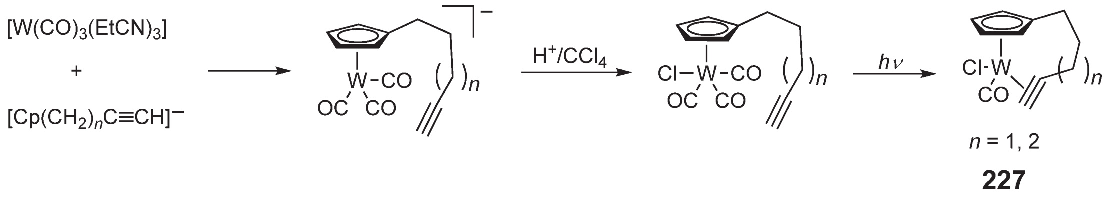
(54)

Tungsten–halocarbonyl complexes of form $[WXY(CO)_3(MeCN)_2]$ (X, Y = halide, pseudohalide) are versatile starting materials that have spawned a branch of tungsten chemistry that includes numerous alkyne complexes, and has been the subject of reviews.[140,141] Recent work in this area includes: (i) the synthesis of $[WCl_2(CO)(MeCN)(\eta^2\text{-}EtC{\equiv}CEt)_2]$ by reaction of $[WCl_2(CO)_3(MeCN)_2]$ with excess 3-hexyne, and subsequent conversion of $[WCl_2(CO)(MeCN)(\eta^2\text{-}EtC{\equiv}CEt)_2]$ into $[WCl_2(CO)L(\eta^2\text{-}EtC{\equiv}CEt)_2]$ ($L = NPh_3$, PPh_3), $[WCl_2(CO)L_2(\eta^2\text{-}EtC{\equiv}CEt)]$ ($L_2 = Ph_2P(CH_2)_nPPh_2$, $n = 1,3,4,6$; $L_2 = 2P(OR)_3$, R = Et, ^{i}Pr), and $[WCl(CO)(bipy)(\eta^2\text{-}EtC{\equiv}CEt)_2]Cl$;[666] (ii) conversion of $[WI_2(CO)(MeCN)(\eta^2\text{-}EtC{\equiv}CEt)_2]$ into $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC{\equiv}CEt)_2]$ (R = Me, ^{i}Pr, Ph);[264] (iii) conversion of $[WI_2(CO)(MeCN)(\eta^2\text{-}RC{\equiv}CR)_2]$ into $[WI(CO)(terpy)(\eta^2\text{-}RC{\equiv}CR)]I$ (R = Me) and $[WI(terpy)(\eta^2\text{-}RC{\equiv}CR)_2]I$ (R = Ph);[1157] (iv) reaction of $[WI_2(CO)_3(MeCN)_2]$ with $HC{\equiv}CCO_2H$ to form $[WI_2(CO)(MeCN)(\eta^2\text{-}HC{\equiv}CCO_2H)]_2$, the sodium salt of which is water soluble;[1158] and (v) the synthesis of bimetallic complexes[552] (Scheme 75) and larger polymetallic aggregates.[144,434,435]

Both $[WCl(SnCl_3)(CO)_3(MeCN)_2]$[637] and $[WCl(GeCl_3)(CO)_3(MeCN)_2]$[639] catalyze cyclotrimerization and polymerization of $PhC{\equiv}CH$. The alkyne complexes $[WCl_2(CO)(MeCN)(PhC{\equiv}CR)_2]$ and $[WCl_2(MeCN)_2(PhC{\equiv}CR)_2]$ (R = H, Ph), identified on the basis of NMR and IR data, but not isolated, were formed when $[WCl(SnCl_3)(CO)_3(MeCN)_2]$ was treated with the appropriate alkyne in CH_2Cl_2.[637] Similar experiments with



Scheme 75

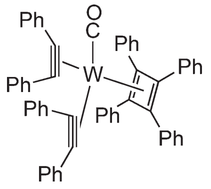


Scheme 76

$[WCl(GeCl_3)(CO)_3(MeCN)_2]$ and PhC≡CPh gave mixtures containing $[WCl_2(MeCN_2)(PhC{\equiv}CPh)_2]$ and $[WCl_2(CO)_2(GeCl_2)(PhC{\equiv}CPh)]$, the products again being identified by IR and NMR data, but not isolated.[639]

Tungsten complexes having pendant alkynyl groups are rare, presumably because of the high reactivity of tungsten with respect to alkynes. One of the few examples of such systems, $[W(CO)_3Cl\{Cp(CH_2)_2(CH_2)_nC{\equiv}CH\}]$ ($n = 1, 2$) undergoes intramolecular displacement of 2 × CO to form the chelated alkyne complex **227** (Scheme 76).[1159] The ^{1}H NMR chemical shift of the alkynyl proton in **277** (ca. $\delta 12$) is indicative of the alkyne behaving as a four-electron donor.

Heating $[W(CO)(\eta^2\text{-}PhC{\equiv}CPh)_3]$ with PhC≡CPh in a sealed tube resulted in formation of various alkyne–alkyne coupling products, including the tetraphenylcyclobutadiene adduct **228** (40%), **229** (13%), **230** (6%), and, interestingly, a tungstenocene oligomer $[W(C_5Ph_5)_2]_x$ (32% yield).[1140] The mechanisms for formation of **229**, **230**, and $[W(C_5Ph_5)_2]_x$ are not known, but these products do not arise from the tetraphenylcyclobutadiene adduct **228**.



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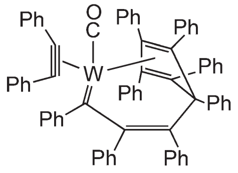

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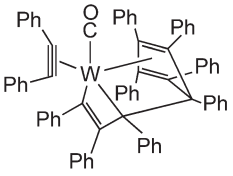

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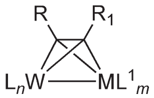
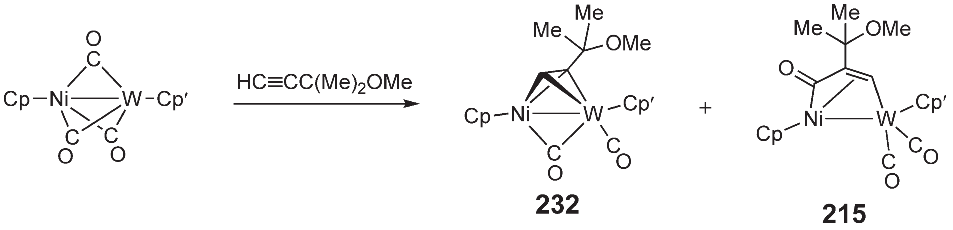


231

Bimetallic and heterobimetallic tungsten complexes **231** having η^2,η^2-alkynes as bridging π-donor ligands are well known. These complexes are susceptible to attack by H^+ (to form complexes containing $\eta^1{:}\eta^2$-vinyl groups[1160]), phosphinoalkynes (to form complexes containing $\eta^1{:}\eta^2$-vinyl groups or alkenylphosphine groups[1161]), and Ph_2PCl (to form complexes with bridging Ph_2P and/or bridging $\eta^1{:}\eta^2$-vinyl groups[1162]). Heterobimetallic complexes having bridging $\eta^2{:}\eta^2$-alkyne groups (e.g., **232** and **233**), along with isomeric metallacyclic products (e.g., **215** and **234**), have been synthesized by reaction of $[CpNi(\mu\text{-}CO)_3WCp']$ (Ni–W) or $[Cp^*Ni(\mu\text{-}CO)_3WCp]$ (Ni–W) with alkynes (e.g., Equations (55) and (56)).[1136,1163,1164] The structures of the metallacyclic complexes **215** and **234** were inferred from spectroscopic data, but definitive structural evidence from X-ray studies is yet to be obtained.



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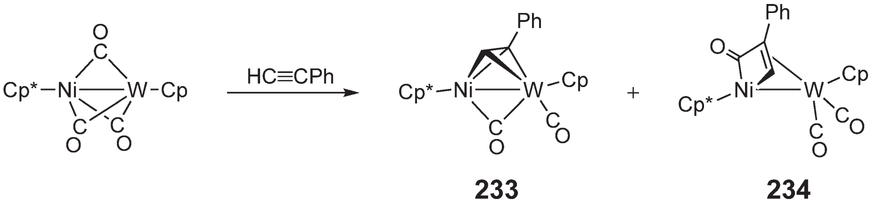


(56)

Syntheses of selected tungsten alkyne complexes are summarized in Table 32.

Table 32 Selected tungsten alkyne complexes having CO or CNR ligands

Compound	*Synthesis*	*Comments*	*References*
$[\mathrm{W(CO)I_2(PMe_3)_2}(\eta^2\text{-}\mathrm{PhC{\equiv}CSH}\text{-}C,C)]$	$[\mathrm{W(CO)I_2(PMe_3)_2({=}CHPh)}] + \mathrm{CS_2/PPh_3}$		1165
$[\mathrm{W(CO)_2(L_2)}(\eta^2\text{-}\mathrm{RC{\equiv}CR'})_2]$	$[\mathrm{W(CO)_3(MeCN)_3}] + (\mathrm{L_2}) + \mathrm{RC{\equiv}CR'}$	$\mathrm{L_2} = \mathrm{en}$, $\mathrm{R/R'} = \mathrm{Ph/CO_2Et}$ or $\mathrm{CO_2Me/CO_2Me}$; $\mathrm{L_2} = \mathrm{bipy}$ or phen, $\mathrm{R/R'} = \mathrm{CO_2Me/CO_2Me}$, $\mathrm{Ph/CO_2Et}$, $\mathrm{H/CO_2Me}$, $\mathrm{H/CO_2Et}$	246
$[\mathrm{W(CO)(PPh_3)}\{\eta^2\text{-}(p\text{-}\mathrm{Tol})\mathrm{C{\equiv}CSeMe}\text{-}C,C\}\mathrm{(Tp)}]\mathrm{I}$	$[\mathrm{W(Tp)(CO)(PPh_3)}\{\eta^2\text{-}(p\text{-}\mathrm{Tol})\mathrm{CC{=}Se}\text{-}C,C\}]$ **174** + MeI; See Scheme 54 in Section 5.08.15.4.2		944
$[\mathrm{W(CO)}\{\eta^2\text{-}(p\text{-}\mathrm{Tol})\mathrm{C{\equiv}CCl}\text{-}C,C\}\mathrm{(Tp)Cl}]$	$[\mathrm{W(Tp)(CO)(PPh_3)}\{\eta^2\text{-}(p\text{-}\mathrm{Tol})\mathrm{CC{=}O}\}]$ (**168** in Scheme 50 in Section 5.08.15.4.2) + $\mathrm{Ph_3PCl_2}$		932
$[\mathrm{W(CO)}\{\eta^2\text{-}\mathrm{HOCH_2C{\equiv}CCH_2OH}\}\mathrm{(Tp')Cl}]$	$[\mathrm{W(CO)_2(S_2CNEt_2)Tp'}] + \mathrm{HOCH_2C{\equiv}CCH_2OH} + \mathrm{ClCH_2CH_2Cl}$		627
$[\mathrm{W(CO)}(\eta^2\text{-}\mathrm{MeOC{\equiv}CPMe_2Ph})(\mathrm{OC_6H_4NO_2}\text{-}4)\mathrm{Tp'}]\mathrm{OTf}$	$[\mathrm{W(CO)}(\mathrm{OC_6H_4NO_2}\text{-}4)(\eta^2\text{-}\mathrm{C(O)CPMe_2Ph}\text{-}C,C)\mathrm{Tp'}]$ (**201**; in Section 5.08.15.6.1) + MeOTf		1031
$[\mathrm{W(CO)}\{\eta^2\text{-}\mathrm{PhC{\equiv}CCH{=}C(Me)Fc}\}\mathrm{Tp'(I)}]$	$[\mathrm{W(CO)}(\eta^2\text{-}\mathrm{PhC{\equiv}CMe})\mathrm{(Tp')I}] + \mathrm{Bu^nLi}$ followed by $\mathrm{FcCHO{\cdot}BF_3}$		1166
$(-)$-$[\mathrm{W(CO)}\{\eta^2\text{-}\mathrm{MeC{\equiv}CCH(Me)Bn}\}\mathrm{Tp'(I)}]$	$(-)$-$[\mathrm{W(CO)}(\eta^2\text{-}\mathrm{MeC{\equiv}CEt})\mathrm{(Tp')I}] + \mathrm{BuLi}$ followed by $\mathrm{PhCH_2Br}$	The optically active alkyne is liberated by photolysis of the complex in solution under air	239
$[\mathrm{W(CO)({=}CH_2)}(\eta^2\text{-}\mathrm{PhC{\equiv}CMe})\mathrm{Tp'}][\mathrm{PF_6}]$	$[\mathrm{W(CO)}(\eta^2\text{-}\mathrm{MeC{\equiv}CPh})\mathrm{Tp'(Me)}] + [\mathrm{Ph_3C}][\mathrm{PF_6}]$		926
$[\mathrm{W(CO)}(\eta^2\text{-}\mathrm{MeC{\equiv}CPh})\{\eta^1\text{-}\mathrm{C(O)R}\}\mathrm{Tp'}]$	$[\mathrm{W(CO)_2}(\eta^2\text{-}\mathrm{MeC{\equiv}CPh})\mathrm{Tp'}][\mathrm{BF_4}] + \mathrm{LiCuR_2}$, $\mathrm{R} = \mathrm{Me}$, Ph		963
$[\mathrm{W(CO)(OEt_2)}(\eta^2\text{-}\mathrm{MeC{\equiv}CPh})\mathrm{Tp'}][\mathrm{BAr_4}]$	$[\mathrm{W(Tp')(CO)(Me)}(\eta^2\text{-}\mathrm{MeC{\equiv}CPh})] + \mathrm{HBAr_4}$ in $\mathrm{Et_2O/CH_2Cl_2}$ $(\mathrm{Ar} = 3,5\text{-}(\mathrm{CF_3})_2\mathrm{C_6H_3})$		1167
$[\mathrm{W(CO)}(\eta^2\text{-}\mathrm{RC{\equiv}CSiMe_3})\mathrm{Cp(NO)}]$	$[\mathrm{W(CO)_2Cp(NO)}] + \mathrm{RC{\equiv}CLi}$ followed by $\mathrm{Me_3SiCl}$, $\mathrm{R} = \mathrm{Me}$, Ph, $\mathrm{CMe_3}$, $\mathrm{SiMe_3}$, $\mathrm{CH_2OCH_2CH{=}CH_2}$, $\mathrm{(CH_2)_2OSiMe_2Bu^t}$		914

5.08.16.6 Cyclopentadienyl Complexes

In COMC (1982) and COMC (1995), an entire chapter was devoted to cyclopentadienyl–group 6 metal complexes, which was broken into sections based on additional donor ligands, for example, nitrosyl, hydrides, halides, group 13, 14, 15, and 16 elements, etc. In this chapter subjects are divided based on non-carbon donor types and then the uniqueness of carbon donor ligands. For example, the hydride complexes of the type $[W(CO)_3Cp(H)]$ are discussed in Section 5.08.9 and not in Section 5.08.16.6, like COMC (1995). As a result of the ubiquitous nature of cyclopentadienyl ligands in the chemistry of W–CO complexes, examples are discussed throughout this chapter. This section focuses more specifically on the chemistry of cyclopentadienyl complexes not involved with other donor types, and covers complexes with bridged cyclopentadienyl rings, including complexes with multiple cyclopentadienyl rings directly connected by a C–C single bond (e.g., fulvalene complexes), complexes with interesting substituents on the cyclopentadienyl rings, as well as radical species of the type $\{W(CO)_3Cp\}$ and the dimeric complexes $[W_2(CO)_nCp_2]$ with W–W bonds.

As discussed previously, efforts have been made to avoid repetition of information. Particularly for cyclopentadienyl complexes it is best to regard the chapter in its entirety and not in its parts. The reactivity of species associated with this section that produce complexes with additional donor types, in general, are covered in other sections in this chapter based on the additional donor type. Standard synthetic techniques and structural details of complexes in this section have not significantly changed since COMC (1995).[1168]

5.08.16.6.1 $[W_2(CO)_nCp_2]$ and $\{W(CO)_3Cp\}$ radical complexes and their derivatives

The mechanisms and intermediates in the photochemistry of $[W_2(CO)_6Cp_2]$, and their ring-coupled analogs, have been recently reviewed.[1169] Facile carbonyl exchange between the metal centers in $[WMo(CO)_6Cp_2]$ via $[W(CO)_2Cp(\mu\text{-}CO)_2Mo(CO)_2Cp]$ has been observed in ^{13}C NMR studies.[1170] The immobilization of $[W_2(CO)_6Cp_2]$ and $[W_2(CO)_4Cp_2]$ on silica followed by oxidation affords CO-free surface-bound W(IV)–W(IV) species, which have been used for the coupling of acetaldehyde or acetone.[1171] Isolated W(IV) species do not exhibit the same reactivity. EXAFS spectra suggest the W–W bond length in the dimeric species is 2.96 Å. The substituted Cp complexes $[W_2(CO)_6(\eta^5\text{-}L)_2]$ ($L = 1,2,4\text{-}C_5H_2Pr^i{}_3$, $1,2\text{-}C_5H_3Bu^t{}_2$) have been prepared from the appropriate cyclopentadienide and $[W(CO)_6]$, followed by acidification and oxidation with aqueous acetic acid/$Fe_2(SO_4)_3$.[1172,1173]

Reaction of $[W_2(CO)_4(\eta^5\text{-}C_5H_4R)_2]$ $\{R = C(O)Me, CO_2Me, CO_2Et\}$ with BnSeSeBn affords $[W(\eta^5\text{-}C_5H_4R)(\mu\text{-}Se)_2(\mu\text{-}SeBn)_2W(\eta^5\text{-}C_5H_4R)]$ (W═W), as a mixture of *trans/anti*- and *trans/syn*-isomers.[1174] The reaction of $[W_2(CO)_6Cp_2]$ with $[TiCp_2(OBu^t)]$ affords $[W(CO)_2Cp(\mu\text{-}CO\text{-}C,O)TiCp_2(OBu^t)]$, where the carbon atom of the bridging carbonyl binds to the W center and the oxygen atom binds to the Ti center.[1175] Photolysis of a mixture of $[W_2(CO)_6Cp_2]$ with $[WCp_2(H)_2]$ afforded the $\mu\text{-}\eta^1{:}\eta^5$-cyclopentadienyl complex $[W(CO)_2Cp\{\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4\}W(CO)Cp]$ (W–W)(as a result of C–H activation of the Cp ring) and $[W(CO)_3Cp(H)]$.[1176] Using this procedure, mixed W/Mo complexes were readily prepared from the appropriate precursors. The Mo–W bond length in the structurally characterized $[Mo(CO)_2Cp\{\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4\}W(CO)Cp]$ (Mo–W) is 3.069 Å.

A recent review has covered thermodynamic and kinetic aspects of the generation and reactions of low-valent transition metal radical complexes, including $\{W(CO)_3Cp\}^{\cdot}$ derivatives.[1177] Investigation of ultrafast photochemical disproportionation reactions of $[W_2(CO)_6Cp_2]$ in CH_2Cl_2 solutions containing $P(OMe)_3$, using femtosecond IR spectroscopy, suggests that one of the two initially formed 17-electron radicals, $\{W(CO)_3Cp\}^{\cdot}$, can react with $P(OMe)_3$ (within ca. 300 ps) from the solvent cage to form the 19-electron radical $\{W(CO)_3\{P(OMe)_3\}Cp\}^{\cdot}$.[1178] Rapid electron transfer (within ca. 130 ps) between $\{W(CO)_3Cp\}^{\cdot}$ and $\{W(CO)_3\{P(OMe)_3\}Cp\}^{\cdot}$, which are held in close proximity by the solvent cage, results in the formation of $[W(CO)_3Cp]^-$ and $[W(CO)_3\{P(OMe)_3\}Cp]^+$. A study of the effect of radical size and mass on the recombination efficiency of photochemically generated radical pairs, held in a solvent cage, included comparisons of $[W_2(CO)_6(\eta^5\text{-}C_5H_4Me)_2]$, $[Mo_2(CO)_6(\eta^5\text{-}C_5H_4Me)_2]$, and $[Mo_2(CO)_6(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3)_2]$ (which is similar in molecular mass to the tungsten complex).[1179] The study suggested that the differences in the W–W bond compared to Mo–Mo bond, including bond-energy differences, have a greater influence on recombination efficiency than mass or sterics. Using photomodulated voltammetry, direct electrochemical measurements have been made on the photogenerated 17-electron radicals $\{M(CO)_3(\eta^5\text{-}C_5H_4R)\}^{\cdot}$ (M = Cr, Mo, W; R = H, Me).[1180] The $[W(CO)_3(\eta^5\text{-}C_5H_5)]^{\cdot/-}$ one-electron reduction potential was measured as +0.04 V (vs. SCE in DMF), a value that is higher than previously reported values. Radical lifetimes could also be estimated using photomodulated voltammetry. Laser flash photolysis of $[W_2(CO)_6(\eta^5\text{-}C_5H_4CO_2{}^-)_2]$ in aqueous solutions results in the formation of $\{W(CO)_3(\eta^5\text{-}C_5H_4CO_2{}^-)\}^{\cdot}$, and the reactivity of the 17-electron radical toward dimerization, electron transfer, and reactions with halo compounds, Bu^tOOH, and phosphines has been investigated.[1181]

5.08.16.6.2 Cyclopentadienyl and indenyl complexes without substituents on the rings

A detailed study based on Raman and IR spectral data, of intra-ring and inter-ring (ring-metal) vibrational modes of the M-(η^5-C_5H_5) unit in a range of complexes, including $[W_2(CO)_6Cp_2]$ (W–W), has been reported.[1182] A theoretical study has investigated the energetics related to the dissociation of CO from $[M(CO)(\eta^5\text{-}C_5H_5)_2]$ (M = Cr, Mo, W).[1183] The dissociation energy increases in the order Cr ⩽ Mo < W, and it is suggested that the increased thermal stability down the period is a result of an inability of Mo and W to form a low-energy metallocene product. The reaction of $[W(CO)(\eta^5\text{-}C_5H_5)_2]$ with $ICF(CF_3)_2$ affords the *exo*-fluoroalkylated η^4-cyclopentadiene complex $[W(\eta^5\text{-}C_5H_5)\{\eta^4\text{-}C_5H_5CF(CF_3)_2\}(CO)I]$, which has been structurally characterized. A mechanistic pathway involving nucleophilic attack at the iodine atom by the tungsten center has been proposed. The reactivity of $[W(CO)(\eta^5\text{-}C_5H_5)_2]$ toward $ICF(CF_3)_2$ differs to that of $[W(C_2H_2)(\eta^5\text{-}C_5H_5)_2]$.[652] The cationic complex $[W(\eta^5\text{-}C_5H_5)_2(H)(CNBu^t)]^+$ has been prepared by reaction of $[W(\eta^5\text{-}C_5H_5)_2(H)_2]$ with MeOTf in the presence of $CNBu^t$.[697]

The reaction of $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)]BF_4$[1184] with NEt_3 affords $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)]$. The details of the experimental procedure are very important, since decomposition of the product into $[W(CO)(H)(\eta^5\text{-}C_5H_5)_2]BF_4$ can be facile, depending on the reaction workup method.[1185] Oxidation of $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)]$ with $[NBu_4]Br_3$ followed by anion metathesis afforded $[W(CO)_2(\eta^5\text{-}C_5H_5)_2][BF_4]_2$ in high yield. Alternatively, hydride abstraction from $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)]^+$ also afforded $[W(CO)_2(\eta^5\text{-}C_5H_5)_2]^{2+}$.[1184,1186] Photolysis of $[W(CO)_2(\eta^5\text{-}C_5H_5)_2][BF_4]_2$ in MeCN afforded $[W(CO)(NCMe)(\eta^5\text{-}C_5H_5)_2][BF_4]_2$, which can react with I^- at room temperature to form $[W(CO)I(\eta^5\text{-}C_5H_5)_2][BF_4]$ or under thermal and photolytic conditions to afford $[WI_2(\eta^5\text{-}C_5H_5)_2]$. The formation of $[W(CO)(H)(\eta^5\text{-}C_5H_5)_2]BF_4$ by photolysis of $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)]BF_4$ was unsuccessful, but photolysis of $[W(CO)_2(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_5H_6)]BF_4$[1184] afforded $[W(CO)(H)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]BF_4$ in good yield.[1186] $[W(CO)_2(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_5H_6)]BF_4$ and $[W(CO)(H)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]BF_4$ have been structurally characterized.[1186] The reaction of $[W(CO)_2(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_3H_5)]$ with $HCl_{(g)}$ in CH_2Cl_2 affords $[W(CO)_2(\eta^5\text{-}C_9H_7)Cl_3]$, which in turn can react with K[indenide] or NaCp to give $[W(CO)_2(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_9H_7)]$ or $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_9H_7)]$, respectively. Reaction of these η^3-indenyl complexes with 2 equiv. of $[Ph_3C]BF_4$ affords the η^5-indenyl complexes $[W(CO)_2(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)][BF_4]_2$ and $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)][BF_4]_2$, which can be converted into diiodide complexes by a combined thermal and photolytic treatment of the dicarbonyl complexes in the presence of I^-.[1186] A DFT study has examined bis-indenyl complexes, including $[W(CO)_2(C_9H_7)_2]$, which suggests the preferred conformation is with staggered indenyl rings with one η^5-indenyl ring and one η^3-indenyl ring.[1187] The calculated structures were in very good agreement with experimental results.

5.08.16.6.3 Complexes of substituted cyclopentadienyl ligands

The highly ring-substituted complexes $[W(CO)_3Me(\eta^5\text{-}L)]$ ($L = C_5HPr^i_4$, C_5Et_5, C_5Bn_5) have been prepared by the reaction of the appropriate lithium cyclopentadienide with $[W(CO)_6]$ followed by treatment with MeI.[1188,1189] The complexes $[W(CO)_3Me(\eta^5\text{-}C_5HPr^i_4)]$ and $[W(CO)_3Me(\eta^5\text{-}C_5Bn_5)]$ have been structurally characterized. Oxidation of the complexes with $PhICl_2$ or PCl_5 afforded $[W(Cl)_4(\eta^5\text{-}L)]$ ($L = C_5HPr^i_4$, C_5Et_5, C_5Bn_5). The *in situ* treatment of $Li[W(CO)_3(\eta^5\text{-}C_5Ph_5)]$, formed by the reaction of C_5Ph_5Li with $[W(CO)_6]$, with PCl_3, PBr_3, or I_2 afforded $[W(CO)_3(\eta^5\text{-}C_5Ph_5)X]$ (X = Cl, Br, I).[642] Bulk electrochemical reduction of $[W(CO)_3(\eta^5\text{-}C_5Ph_4R)Br]$ $\{R = C_6H_3(OMe)_2\text{-}2,5\}$ afforded $[W(CO)_3(\eta^5\text{-}C_5Ph_4R)]^-$.[1190] The complexes $[W(CO)_3(\eta^5\text{-}L)Me]$ (L = 1,2,3-trimethyl-4,5,6,7-tetrahydroindenide) and $[W(CO)_3(\eta^5\text{-}L)X]$ (L = *cis*-1-methyl-3-phenyl-bicyclo[3.3.0]octadienide; X = H, Cl) (bearing a partially saturated ring fused to a Cp) have been prepared.[1191,1192]

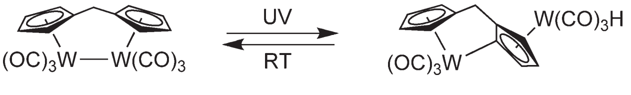
Reaction of the chiral cyclopentadienide $Li[C_5Me_4R]$ (R = pinanyl), derived from (+)-pinanaldehyde, with $[W(CO)_6]$ generates $[W(CO)_3(\eta^5\text{-}C_5Me_4R)]$, which was reacted with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) to afford the chiral complex $[W(CO)_2(\eta^5\text{-}C_5Me_4R)(NO)]$ (R = pinanyl).[1193] The crown ether-substituted complex $[W(CO)_3(\eta^5\text{-}C_5H_2Me_2CH_2CH_2R)Me]$ (R = aza-12-crown-4) has been prepared.[1194] Palladium-catalyzed Stille coupling of $[W(CO)_3(\eta^5\text{-}C_5H_4I)Me]$ with organotin alkynides $Me_3SnC{\equiv}CXC{\equiv}CSiMe_3$, where X is a conjugated spacer, affords $[W(CO)_3(\eta^5\text{-}C_5H_4C{\equiv}CXC{\equiv}CSiMe_3)Me]$. The procedure allows for the preparation of complex conjugated systems through functional group conversions of the terminal alkyne (e.g., $\text{–}SiMe_3 \rightarrow \text{–}H \rightarrow \text{–}SnMe_3 \rightarrow$ –[M], where [M] is a metal center or metal complex).[1195] Lithiation of $[W(CO)_3Cp(Me)]$ followed by treatment with a 2,6-diphenylpyrylium salt gives a pyran-substituted cyclopentadienyl complex $[W(CO)_3(\eta^5\text{-}C_5H_4R)(Me)]$, which reacts with $[Ph_3C][BF_4]$ to yield a pyrylium complex $[W(CO)_3(\eta^5\text{-}C_5H_4R)(Me)]BF_4$ (R = 2,6-diphenylpyrylium).[1196] Treatment of $[W(CO)_3Cp(H)]$ with 2 equiv. of Bu^nLi followed by reaction with CO_2, and then acidification, affords the structurally characterized water-soluble $[W(CO)_3(\eta^5\text{-}C_5H_4CO_2H)H]$.[701] In water, the CO_2H site is more acidic than the W–H proton, but this order is reversed in organic solvents. Treatment of [W(CO)$_3$(η^5-C$_5$H$_4$CO$_2$H)H] with (Ph$_3$C)$_2$ or of K[W(CO)$_3$(η^5-C$_5$H$_4$CO$_2$H)] with [Ph$_3$C][BF$_4$] afforded the water-soluble bimetallic complex [W$_2$(CO)$_6$(η^5-C$_5$H$_4$CO$_2$H)$_2$]. Similarly, the successive treatment of [W(CO)$_3$Cp(Me)] with Bu^{n}Li, CO$_2$, and acid affords [W(CO)$_3$(η^5-C$_5$H$_4$CO$_2$H)Me].[1197] Reaction of the carboxylic acids [W(CO)$_3$(η^5-C$_5$H$_4$CO$_2$H)X] (X = I, Me) with succinimide and 1,3-dicyclohexylcarbodiimide affords the *N*-succinimidyl esters, both of which have been structurally characterized. The reaction of these active esters with amines, amino acids, and proteins form amide-functionalized complexes. The active esters allow for heavy metal protein labeling.

Reaction of *cyclo*-[(Bu^{t}P)$_3$As]$^-$ with [W(CO)$_3$Cp(Cl)] affords the structurally characterized [W(CO)$_3$(η^5-C$_5$H$_4${*cyclo*-As(PBu^t)$_3$})Cl], the unexpected result of addition of the arsenic species to the Cp ring; substitution of the chloride was the expected outcome.[1198] The ring-substituted silyl-cyclopentadienyl complexes [W(CO)$_3$(η^5-C$_5$H$_4$SiMe$_2$Cl)X] (X = H, Cl) have been prepared from the silyl-substituted cyclopentadiene.[1199] Transition metal complexes with silyl-functionalized cyclopentadienyl ligands have been reviewed.[1200] Deprotonation of siloxycyclopentadienes followed by treatment with [W(CO)$_3$(NCMe)$_3$] and then MeI afforded [W(CO)$_3$(η^5-C$_5$H$_2$R$_2$OSiMe$_2$Bu^t)Me] (R = H, Me).[1201] Cleavage of the silyl ethers with [NBu$_4$]F yielded the alcohol complexes [W(CO)$_3$(η^5-C$_5$H$_2$R$_2$OH)Me] (R = H, Me).

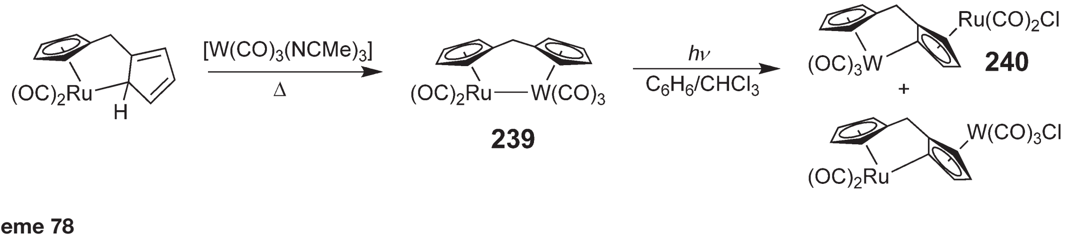
The reaction of the complex [Cr(CO)$_3$(η^6-C$_6$H$_5$-C$_5$H$_5$)] (bearing a pendant cyclopentadiene ring) with NaH, and then [W(CO)$_3$(NCEt)$_3$], afforded Na[Cr(CO)$_3${μ-(η^6-C$_6$H$_5$)(η^5-C$_5$H$_4$)}W(CO)$_3$], which was subsequently reacted with MeI, Br$_2$, or Diazald to afford [Cr(CO)$_3${μ-(η^6-C$_6$H$_5$)(η^5-C$_5$H$_4$)}W(CO)$_3$X] (W = Me, Br) or [Cr(CO)$_3${μ-(η^6-C$_6$H$_5$)(η^5-C$_5$H$_4$)}W(CO)$_2$(NO)], respectively.[1202,1203] Similarly, treatment of the cyclopentadiene C$_5$H$_3$R$_2$ {R = (η^5-C$_6$H$_6$)Mn(CO)$_3$} with Bu^{n}Li, and then [W(CO)$_3$(NCMe)$_3$] and either MeI or Diazald, afforded trimetallic complexes, of which the methyl complex has been structurally characterized.[1204]

5.08.16.6.4 Complexes of coupled cyclopentadienyl rings, including heterometallic species

Reaction of the dianion [C$_5$H$_4$CMe$_2$C$_5$H$_4$]$^{2-}$ with [W(CO)$_3$(NCMe)$_3$], followed by oxidation, gave [{W(CO)$_3$}$_2${μ-(η^5-C$_5$H$_4$)CMe$_2$(η^5-C$_5$H$_4$)}] (W–W) in low yield.[1205] Protonation of [{W(CO)$_3$}$_2${μ-(η^5-C$_5$H$_4$)CH$_2$(η^5-C$_5$H$_4$)}] (W–W) with TfOH affords the bridging hydride complex [{W(CO)$_3$}$_2$(μ-H){μ-(η^5-C$_5$H$_4$)CH$_2$(η^5-C$_5$H$_4$)}] {δ_H −22.74 (μ-H)}, whereas reduction with Na/K followed by acidification affords [{W(CO)$_3$(H)}$_2${μ-(η^5-C$_5$H$_4$)CH$_2$(η^5-C$_5$H$_4$)}].[696] Under visible light, the dihydride complex reverts to [{W(CO)$_3$}$_2${μ-(η^5-C$_5$H$_4$)CH$_2$(η^5-C$_5$H$_4$)}] (W–W), photolysis of which results in the thermally unstable "twist"-rearranged species [W(CO)$_3${μ-(η^5-C$_5$H$_4$)CH$_2$(η^1:η^5-C$_5$H$_3$)}-W(CO)$_3$H] (Scheme 77). The "twist" rearrangement only occurs with photolysis in the high-energy band. Reaction of dilithiated 1,2-bis(3-indenyl)ethane with [W(CO)$_5$(THF)], followed by oxidation with [Fc]BF$_4$, afforded the structurally characterized [{W(CO)$_3$}$_2${μ-(η^5-C$_9$H$_6$)CH$_2$CH$_2$(η^5-C$_9$H$_6$)}] (W–W) as a mixture of *meso*- and *rac*-isomers.[1206] Photolysis in chlorinated solvents yielded the structurally characterized "twist"-rearranged product **235**. The structurally characterized *ansa*-metallocene [W(CNC$_6$H$_3$Me$_2$-2,6){(η^5-C$_5$H$_4$)CMe$_2$(η^5-C$_5$H$_4$)}Cl] has been reported.[1207] The reaction of the chelate complex [Ru(CO)$_2${(η^5-C$_5$H$_4$)CH$_2$(η^1-C$_5$H$_4$)}] with [W(CO)$_3$(NCMe)$_3$] afforded the heteronuclear ring-coupled complex **239**, photolysis of which in the presence of halogenated solvents afforded two rearrangement products in low yield, one of which, **240**, has been structurally characterized (Scheme 78).[1208]

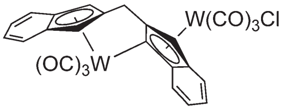


Scheme 77



Scheme 78

Treatment of $[W(CO)_3(\eta^5\text{-}C_5H_4CO_2Me)Me]$ with $Li[C_5Me_4H]$ and then Me_3SiCl afforded $[W(CO)_3\{\eta^5\text{-}C_5H_4C(OSiMe_3)C_5Me_4\}]$, which can be hydrolyzed to $[W(CO)_3\{\eta^5\text{-}C_5H_4C(O)C_5Me_4H\}]$ **241**, the coordination chemistry of which is summarized in Scheme 79.[1209–1211] The W–Ru bond lengths in **242** and **243** are both 2.978 Å. The reaction of $[W(CO)_3(\eta^5\text{-}C_5H_4Li)Me]$ with $[M(CO)_3(\eta^5\text{-}C_5H_4CHO)]$ (M = Mn, Re) followed by acidification affords $[W(CO)_3Me\{\mu\text{-}(\eta^5\text{-}C_5H_4)CH(OH)(\eta^5\text{-}C_5H_4)\}M(CO)_3]$.[1212] The anionic complexes $Na_2[W(CO)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)X(\eta^5\text{-}C_5H_4)\}W(CO)_3]$ with extended linkages between the two cyclopentadienyl rings $\{X = C(O)CH_2CH_2C(O),\ C(O)C_6H_4C(O),\ CH_2(CH_2OCH_2)_3CH_2\}$ have been used as precursors to bridged polycluster species (e.g., **236**) as well as macrocyclic complexes (e.g., **237** and **238**).[807,1213–1215]



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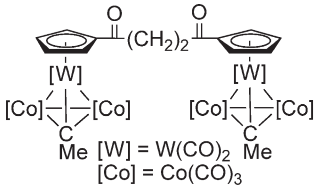

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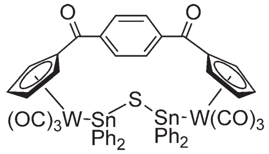

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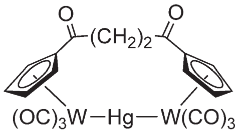
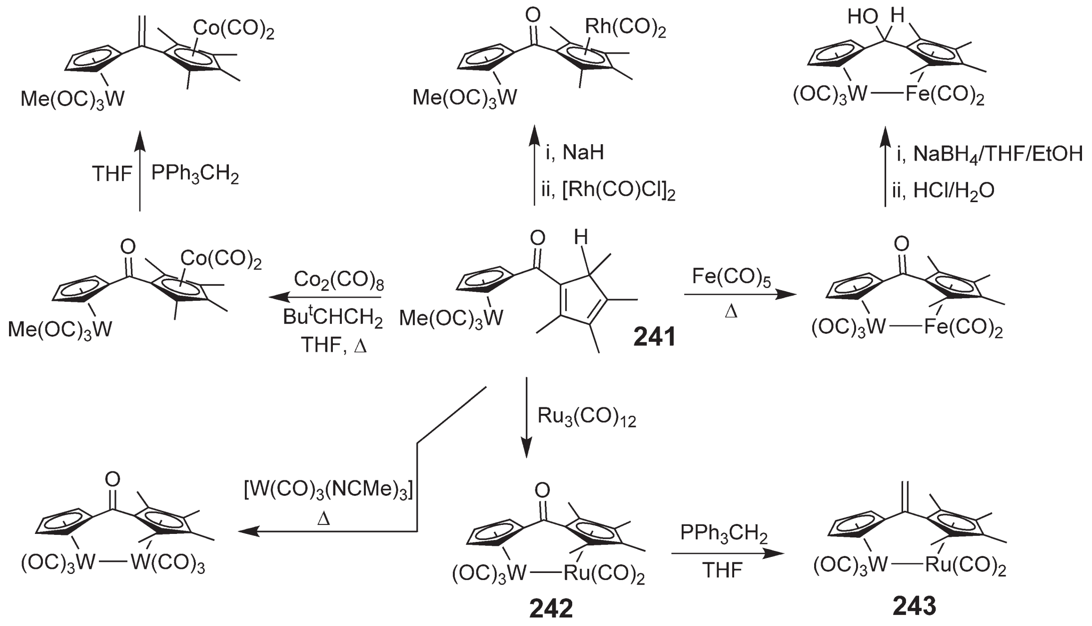


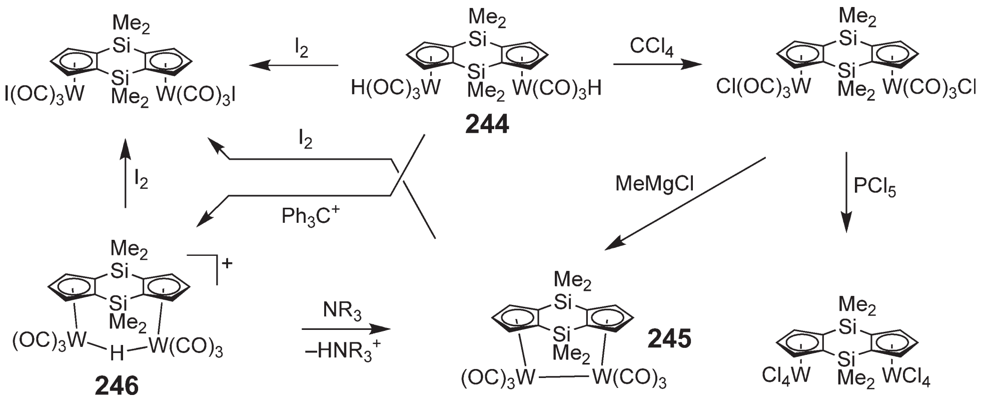
238

The reaction of the silyl dibridged bis-cyclopentadiene $(C_5H_4)_2(SiMe_2)_2$ with $[W(CO)_3(NCR)_3]$ (R = Me, Et) afforded *cis*- and *trans*-$[W(CO)_3H\{\mu\text{-}(\eta^5\text{-}C_5H_3)(SiMe_2)_2(\eta^5\text{-}C_5H_3)\}W(CO)_3H]$, which can be separated (the *cis*-isomer **244** is shown in Scheme 80).[1216,1217] The reactivity of the hydride complexes is similar to other Cp and coupled Cp complexes, and examples are shown in Scheme 80.[1216–1218] The W–W bond length in **245** is 3.260 Å and the $Cp_{centroid}$–W–W–$Cp_{centroid}$ dihedral angle is 28.7°, much smaller than in singly ring-coupled analogs.[1216] It is suggested that there is a relationship between the small dihedral angle and the relatively long W–W bond in terms of steric repulsion of opposing carbonyl groups. The crystal structure of the bridging hydride **246** shows very little twist in the molecule with the carbonyl groups essentially eclipsed ($Cp_{centroid}$–W–W–$Cp_{centroid}$ dihedral angle is 1.9°).[1216] The heterometallic complex $[W(CO)_3H\{\mu\text{-}(\eta^5\text{-}C_5H_3)(SiMe_2)_2(\eta^5\text{-}C_5H_3)\}\{TiCl_2Cp^*\}]$ has been reported and structurally characterized.[1219] Reaction of the mixed dibridged bis-cyclopentadienes $(C_5H_3)_2(X)(Y)$ $\{X = CMe_2,\ C(CH_2)_5;\ Y = SiMe_2,\ GeMe_2\}$ with $[W(CO)_6]$ afforded, in low yield, a range of ditungsten products including desilylation and degermylation species, as well as species with W–Si and W–Ge bonds and $\eta^5{:}\eta$-Cp ligands.[1220]

Examples of complexes with the fulvalene ligand ($\eta^5{:}\eta^5$-C_5H_4–C_5H_4; $C_{10}H_8$) appear in other sections of this chapter, including sections dealing with halogens, phosphines and sulfur donor ligands. Additional examples are covered here. In many cases, fulvalene W–CO complexes exhibit many of the typical properties displayed by other



Scheme 79



Scheme 80

Cp complexes; however, in a number of cases, there are important reactivity differences. It has been suggested that differences in reactivity are caused by a combination of strain effects and electronic effects, since electronic communication can occur through the fulvalene ring system.[646] Reduction of $[W_2(CO)_6(\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ (W–W) with Na/K or $LiHBEt_3$ affords the dianion $[\{W(CO)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]^{2-}$, which has been structurally characterized as the NEt_4^+ salt.[646] An alternative preparation of the NEt_4^+ salt has been reported.[576] In the solid state, the fulvalene ring system of the dianion is planar, and the two tungsten centers are in an *anti*-conformation.[646] The dianion readily reacts with electrophiles to afford $[\{W(CO)_3X\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ $\{X = Me, Et, (CH_2)_3I, CH_2OMe, CH_2CH{=}CH_2, Bn\}$, and the reactivity of the dialkyl derivatives has been investigated.[646] Treatment of the dianion with TfOH afforded the isolable dihydride $[\{W(CO)_3H\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$, whereas the molybdenum analog decomposes at room temperature. The dihydride reacts with CCl_4, $CHBr_3$, and I_2 to afford the expected halide complexes $[\{W(CO)_3X\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ (X = Cl, Br, I).[646] The structure of the iodo complex has been reported.[270] The first pK_a of the dihydride was estimated to be 14.0 and the second 16.6, which compares to a pK_a of 16.1 for $[W(CO)_3Cp(H)]$.[646] Thermolysis of the dihydride afforded $[W_2(CO)_6(\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ (W–W) and dihydrogen. The dihydride complex readily reacts with phosphines to afford $[\{W(CO)_2(PR_3)H\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ as a mixture of isomers; however, $[W_2(CO)_6(\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ (W–W) does not react with PPh_3, dppm, or dppe upon thermolysis or photolysis. Reaction with the strongly donating phosphines PMe_3 and dmpm, afforded the zwitterionic complexes $[\{W(CO)_3\}(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)\{W(CO)_2(L_2)\}]$ $\{L_2 = (PMe_3)_2$, dmpm$\}$.[646] A more efficient synthesis of $[\{W(CO)_3\}(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)\{W(CO)_2(PMe_3)_2\}]$ has been reported using Me_3NO as an oxidative decarbonylation agent.[1221] In addition to $[\{W(CO)_3\}(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)\{W(CO)_2(PMe_3)_2\}]$, heterobimetallic zwitterionic complexes such as $[\{W(CO)_3\}(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)\{M(CO)(PR_3)_2\}]$ (M = Fe, R = Me, OMe; M = Ru, R = Me) have been prepared using Fe(I) catalysts.[1222] Protonation of $[W_2(CO)_6(\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ (W–W) with $HBF_4{\cdot}Et_2O$ in MeCN afforded the highly acidic bridging hydride species $[\{W(CO)_3\}_2(\mu\text{-}H)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$, but under similar conditions, $[W_2(CO)_6Cp_2]$ did not produce a bridging hydride complex.[646] Unlike the case for the molybdenum analog or $[W(CO)_3Cp(I)]$, no reaction occurred between $[\{W(CO)_3I\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ and $PPhMe_2$, PPh_2Me, or PCy_3 under thermal conditions.[270] The phosphine-substituted products $[\{W(CO)_2(PR_3)I\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ were obtained quickly and cleanly when 2 equiv. of Me_3NO were used. The ratio of *cis*- and *trans*-isomers is dependent on the nature of the phosphorus ligand.[270,646] The dihydride $[\{W(CO)_3H\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ reacts with S_8 to afford the hydrosulfide complex $[\{W(CO)_3(SH)\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$, treatment of which with PhN=NPh gave the bridging disulfide complex $[\{W(CO)_3\}_2(\mu\text{-}S_2)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$.[1223] The reaction of sulfur with the hydride complex was studied by solution calorimetry. Along with the hydrosulfide and bridging disulfide complexes, the bridging monosulfide complex $[\{W(CO)_3\}_2(\mu\text{-}S)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$ has also been structurally characterized.[1223] Complexes of the type $[\{W(CO)_2(X)(Y)\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)]$, where X and Y are different donors, exist as a mixture of isomers in equilibrium. NMR spectroscopic techniques have been used to identify and quantify the mixtures.[270,576,645] Indenyl derivatives of fulvalene complexes, for example, $[W_2(CO)_6(\mu\text{-}\eta^5{:}\eta^5\text{-dibenzo[a,d]fulvalene})]$ (W–W) have been reported.[1224,1225] Electron transfer along tercyclopentadienyl trimetallic complexes of the type $[WM^1(CO)_6\{\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_3R\}]^-$ $\{R = (\eta^5\text{-}C_5H_4)M^2(CO)_3$; $M^1 = W, Mo$; $M^2 = W, Mo\}$ has been studied, including kinetic and thermodynamic measurements of electron- and ligand-exchange reactions.[1226] The heterobimetallic complex $[\{W(CO)_3Me\}(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{–}C_5H_4)\{Fe(CO)_2(PPh_3)\}]PF_6$ has been prepared from $[Fe(CO)_2(PPh_3)Cp]I$ by the sequential treatment with NaCp (which adds to the Fe-bound Cp ring), Bu^nLi, $[W(CO)_3(NCEt)_3]$, MeI, and then, $[Ph_3C]PF_6$.[1227] The Fe-bound Cp ring can be further functionalized using similar methods.

5.08.16.6.5 Heterometallic complexes with W–M bonds

A diverse range of heterometallic complexes containing a Cp–W–CO fragment exists. In general, examples containing additional donor types bound to a tungsten center are covered elsewhere in this chapter. This section details examples where a tungsten complex contains a W–M bond and only η^5-Cp and carbonyl ancillary ligands bound to the tungsten center.

The reaction of [Pd(dppe)Me(Cl)] with $AgNO_3$ and then $Na[W(CO)_3Cp]$ affords $[W(CO)_3Cp\{Pd(dppe)Me\}]$ (W–Pd).[1228] The W–Pt complexes $[W(CO)_3Cp\{Pt(cod)R\}]$ (W–Pt) (R = alkyl, aryl) have been prepared by a similar metathesis method, except without the need for Ag^+.[1229] Thermolysis of $[W(CO)_3Cp\{Pt(cod)R\}]$ results in migration of the R groups to the tungsten center, effectively a reductive elimination to give $[W(CO)_3Cp(R)]$. Migration is accelerated with the addition of CO, PPh_3, $P(OPh)_3$, or acrylonitrile. For $[W(CO)_3Cp\{Pt(cod)Me\}]$ in the presence of PMe_3, however, methyl migration did not occur, and instead, the salt $[Pt(PMe_3)_3Me][W(CO)_3Cp]$ was isolated. The reaction of $[W(CO)_3Cp]^-$ with $[\{Pt(PPh_3)I\}_2(\mu\text{-}H)(\mu\text{-}PPh_2)]$ (Pt–Pt) affords a WPt_2 cluster $[Pt_2W(\mu\text{-}CO)_3(\mu\text{-}PPh_2)Cp(PPh_3)_2]$.[1230]

The reaction of $Na[W(CO)_3Cp]$ with $[Ru(CO)_2Cp(I)]$ afforded $[W(CO)_3Cp\{Ru(CO)_2Cp\}]$ (W–Ru), which was isolated from a mixture that also contained $[W(CO)_3Cp(H)]$, $[\{W(CO)_3Cp\}_2]$, and $[\{Ru(CO)_2Cp\}_2]$.[1231] The W–Ru bond length is 2.9974 Å and the Cp ligands are *trans* to each other in the solid state. The reaction of $Li[W(CO)_3Cp^*]$ with $[Rh(PPh_3)_3Cl]$ afforded $[\{W(CO)Cp^*\}(\mu\text{-}CO)_2\{Rh(PPh_3)_2\}]$ (W–Rh), the W–Rh bond length is 2.5820 Å. The complex is fluxional in solution and undergoes intramolecular interchange of the inequivalent PPh_3 groups.[1232] The reaction of $Li[W(CO)_3(\eta^5\text{-}C_5Me_4Et)]$ with $[Ru(NCMe)_3Cp^*]BF_4$ gave the W≡Ru complex $[\{W(\eta^5\text{-}C_5Me_4Et)\}(\mu\text{-}CO)_3(RuCp^*)]$ (W≡Ru).[1233] The short W–Ru bond length of 2.41 Å is suggestive of a triple bond structure.

The reaction of anionic species such as $[W(CO)_3(\eta^5\text{-}C_5Bn_5)]^-$ with PhHgCl afforded the Hg-linked complex $[\{W(CO)_3(\eta^5\text{-}C_5Bn_5)\}_2(\mu\text{-}Hg)]$ (W–Hg–W) with a linear W–Hg–W fragment and W–Hg bond lengths of 2.7532 Å.[1234] There are a range of cluster complexes that have been reported that contain a $Cp(OC)_3W$–Hg fragment where the Hg center links the $W(CO)_3Cp$ fragment to the cluster core, some of which have been structurally characterized and investigated by electrochemical methods.[1235–1238]

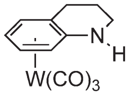
Numerous heteropolymetallic cluster complexes contain a CpW(CO) fragment, in which the tungsten center comprises part of the cluster core. Examples include Fe_2W,[1239] Os_3W,[1240] Ru_3W_2, and Ru_3W,[1241–1243] Ru_6W,[1244] and Ir_3W and Ir_2W_2[1245–1250] species. Typical tungsten sources in the preparation of the cluster cores include $Na[W(CO)_3Cp]$, $[W(CO)_3Cp(H)]$, and $[W_2(CO)_4Cp_2]$.

5.08.16.7 π-Arene Complexes

The synthesis and reactivity of $[W(CO)_3(\eta^6\text{-arene})]$ complexes is well known and the key reactivity patterns have been covered in COMC (1982) and COMC (1995). The major use of $[W(CO)_3(\eta^6\text{-arene})]$ complexes is as labile sources of "$W(CO)_3$" for organometallic synthesis, and recent applications include the use of these materials as catalysts for polymerization reactions.[1251,1252] New tungsten π-arene complexes are summarized in Table 33.

Table 33 Tungsten π-arene complexes with CO ligands

Complex	*Synthesis*	*Comments*	*References*
247	$[W(CO)_6]$ + 1,2,3,4-tetrahydroquinoline		1256
248	$[W(CO)_6] + PhSi(OCH_2CH_2)_3N$	Treatment with Bu^nLi leads to metallation at *meta*- or *para*-positions on the Ph group	1257
249	$[W(CO)_3(\eta^6\text{-}PhMe)] + (Bu^t)_3C_3P_3$	Photoelectron spectra reported, DFT studies	1258,1259
250	$[W(CO)_3(MeCN)_3]$ + **251**	ν_{CO} Values suggest that the iridathiabenzene group is more strongly donating than toluene	1260,1261
252	**250** + PEt_3	X-ray structure reported	1261
253	$[W(CO)_5\{{=}C(OR)Ph\}] + PhC{\equiv}CMe$; R = (−)-menthyl	X-ray structure reported. The $W(CO)_3$ group is easily removed (MeCN, air, light) to leave the free optically active indene (2:1 enantiomeric ratio)	1262



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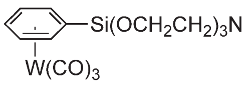

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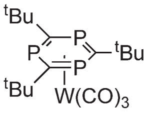

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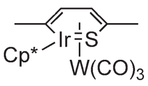

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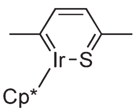

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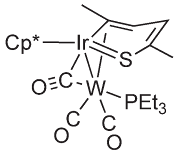

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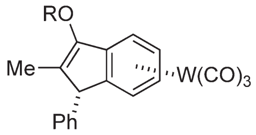

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Theoretical studies have considered the possibility of fullerenes behaving as η^6-ligands in [W(CO)$_3$(η^6-C$_{60}$)] and [W(CO)$_3$(η^6-C$_{70}$)],[1253] but to date, all structurally characterized examples of fullerene–metal complexes have η^2-fullerene coordination (see Section 5.08.16.1.2). DFT has been used to examine how formation of [M(CO)$_3$(η^6-arene)] complexes (M = Cr, Mo, W) affects aromaticity of the arene ring.[1254] [W(CO)$_3$(η^6-mesitylene)] has been characterized by EXAFS.[25]

The reaction of benzene with [W(CO)$_4$] and [W(CO)$_5$] in the gas phase has been examined by time-resolved IR spectroscopy. The products are believed to be [W(CO)$_4$(η^2-benzene)] and [W(CO)$_5$(η^2-benzene)].[29] The ability of TpW(L)(NO) (L = various CO and various N donors) to disrupt aromaticity in benzene by formation of [W(L)(η^2-benzene)Tp(NO)] has been investigated by DFT.[1255]

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5.09
Tungsten Compounds without CO or Isocyanides

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5.09.1 Introduction

This chapter focuses on non-carbonyl-bearing organometallic complexes of tungsten, with key starting materials classified according to the nature of the primary carbon donor ligands and then according to ancillary *N*-donor ligands. It is inevitable that when multiple ligands of interest occur in the same complex, some cross-referencing to other sections will occur. Discussion will be mainly limited to those systems with tungsten–carbon bonding.

5.09.2 Alkyl Complexes

This facet of tungsten organometallic chemistry has been well studied, but one particular structural report bears special mention, that of one of the earliest homoleptic alkyl complexes, $[WMe_6]$. Other alkyl complexes will be discussed later in the context of their presence as co-ligands in alkylidene and alkylidyne complexes.

5.09.2.1 Structure and Properties

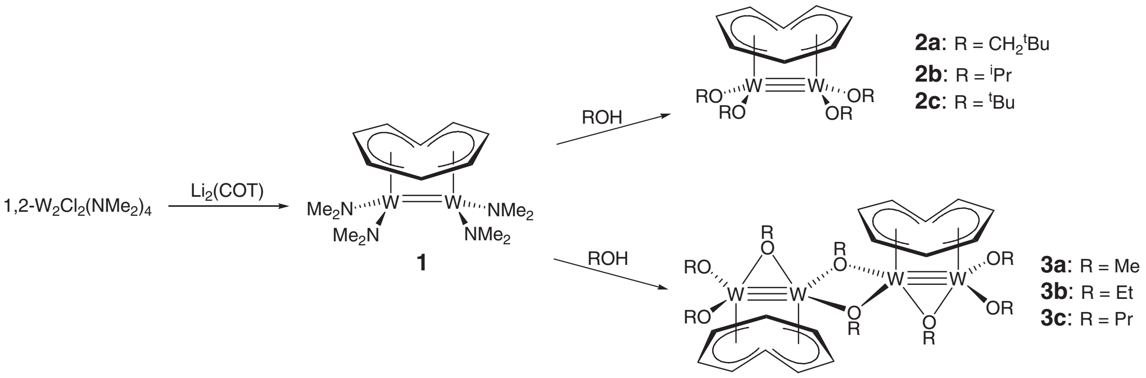
It is striking that the X-ray structure determination of $[WMe_6]$ should not be reported until some 30 years after its synthesis was first reported by Wilkinson,[1] but not surprising given the highly unstable, explosive nature of this complex. Thus, X-ray crystallography of a single crystal of $[WMe_6]$, grown from acetone solution at $-90\,^\circ C$, was carried out at $-163\,^\circ C$ and revealed a strongly distorted trigonal-prismatic structure with C_{3v} symmetry.[2] This was actually at odds with previous electron diffraction experiments, which predicted D_{3h} symmetry, although readily understood in terms of the expansion of one triplet of C–W–C angles to 93.3–96.9°, while the opposite triplet of corresponding angles closed down to 75.4–78.2°. This in turn was rationalized using qualitative molecular orbital analysis, which predicted that a 12-valence electron d^0-ML_6 complex should indeed possess C_{3v} symmetry.

5.09.3 Alkene Complexes

This arena has been traditionally dominated by carbonyl-containing complexes, rendering it mostly beyond the scope of this work. However, reports by Chisholm *et al.* of W_2 dimer complexes of COT (1,3,5,7-cylcooctatetraene) are of note. The W≡W bond has provided a versatile scaffold for this ligand leading to interesting dynamics in solution.

5.09.3.1 Synthesis

Although the starting materials and resulting complexes in this area are either amido or alkoxido complexes (Scheme 1), the COT ligand is clearly the main feature of interest. Thus, treatment of $[1,2\text{-}W_2Cl_2(NMe_2)_4]$ with $Li_2(COT)$ afforded the bridged complex $[W_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_8H_8)(NMe_2)_4]$ **1** (Table 1).[3] A note of caution is that an excess of the Li reagent should be avoided in order to prevent the formation of the previously reported complex $[W_2(COT)_3]$. Complex **1** may also be used as a precursor to the alkoxido complexes $[W_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_8H_8)(OR)_4]$ (**2a**, $R = CH_2{}^tBu$; **2b**, $R = {}^iPr$; **2c**, $R = {}^tBu$) by treatment with the corresponding alcohols ROH.[4] The syntheses of further alkoxido complexes



Scheme 1

Table 1 Synthesis of COT W_2 complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[1,2\text{-}W_2Cl_2(NMe_2)_4] + Li_2(COT)$ in THF (0 °C)	$[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(NMe_2)_4]$ **1**	60	Green	X-ray: $W{=}W$ 2.4297(5) Å	3
1 + ^{t}BuCH$_2$OH in toluene (25 °C)	$[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(OCH_2{}^tBu)_4]$ **2a**	75	Purple		4
1 + ^{i}PrOH in *n*-pentane (−78 °C)	$[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(O^iPr)_4]$ **2b**	92	Purple		4
1 + ^{t}BuOH in *n*-pentane (25 °C)	$[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(O^tBu)_4]$ **2c**	73	Purple	X-ray: $W{\equiv}W$ 2.3887(1) Å; heat sensitive	4
1 + ROH in *n*-pentane (25 °C)	$[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(\mu\text{-}OMe)_2(OMe)_2]_2$ **3a**	82	Aqua		5
	$[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(\mu\text{-}OEt)_2(OEt)_2]_2$ **3b**	90	Aqua		5
	$[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(\mu\text{-}OPr)_2(OPr)_2]_2$ **3c**	74	Aqua	X-ray: $W{\equiv}W$ 2.3917(2) Å	5

$[W_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_8H_8)(\mu\text{-}OR)_2(OR)_2]_2$ (**3a**, R = Me; **3b**, R = Et; **3c**, R = Pr) of the same empirical formula using unbranched alcohols were later reported.[5] With the exception of complex **2b**, the synthetic procedures for complexes **2** and **3** were all carried out at ambient temperatures, usually in *n*-pentane, by simple addition of the alcohol to the reagent **1**.

5.09.3.2 Structure and Properties

The parent complex **1** bears a bridging "tub-shaped" $\mu\text{-}\eta^5,\eta^5$-COT ligand spanning a $W{=}W$ connectivity, as determined in the solid-state X-ray structure analysis.[3] The tungsten–tungsten distance of 2.4297(5) Å is commensurate with that of a $W{=}W$ double bond and this assertion is supported by Fenske–Hall MO calculations. The molecule is nevertheless fluxional in toluene-d_8 at room temperature with facile mobility of the COT ligand leading to the observation of two isomers. Although the second isomer was not formally structurally identified, it was postulated from the NMR data to retain a mirror plane of symmetry orthogonal to the $W{=}W$ bond, with a $\mu\text{-}\eta^2,\eta^2$-slipped ligand configuration likely. The alkoxido species **3** are essentially similar in both structure and function to the amido complex **1**, in terms of molecular architecture with a symmetrical bridging $\mu\text{-}\eta^5$, η^5-COT ligand resulting in pseudo C_{2v} molecular symmetry.[4] One notable difference is the inference from the tungsten–tungsten bond length in the X-ray structure determination of **2c** that the slightly shorter bond should be classified as a $W{\equiv}W$ triple bond.

Dynamic behavior was probed using VT EXSY ^{1}H NMR spectroscopy, revealing exchange involving a 1,2-allyl shift of the COT ligand. Density functional theory (DFT) analysis of a simplified analog $[W_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_8H_8)(OH)_4]$ predicted that an *anti*-facial structure for the COT ligand should be some 13.7 kcal mol^{-1} more stable than the *syn*-facial conformer. The complexes **3** crystallized as tetranuclear complexes comprising centrosymmetric $[W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(\mu\text{-}OR)(OR)_2]$ fragments tethered by symmetrically bridging alkoxido ligands. In solution, the complexes were not fluxional in contrast to the congeners **2**, and this was attributed to increased W_2–COT backbonding.[5]

5.09.3.3 Reactions

The complexes **3** were decidedly inert, with the inter-W_2-bridging alkoxido ligands proving to be extremely resistant to cleavage by σ-donor molecules such as THF and pyridine and π-acceptors such as 2-butyne (Equation (1)).

$$1/2\ [W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(\mu\text{-}OR)_2(OR)_2]_2\ \mathbf{1} + B \nrightarrow [W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(\mu\text{-}OR)(OR)_2(B)] \tag{1}$$

B = pyridine, THF, 2-butyne

5.09.4 Alkyne Complexes

Once again, non-carbonyl-containing alkyne adducts are dominated by Chisholm's work with alkoxido tungsten dimers, but as with the above discussion of COT complexes, the focus is the reactivity of the alkyne functionality.

5.09.4.1 Synthesis

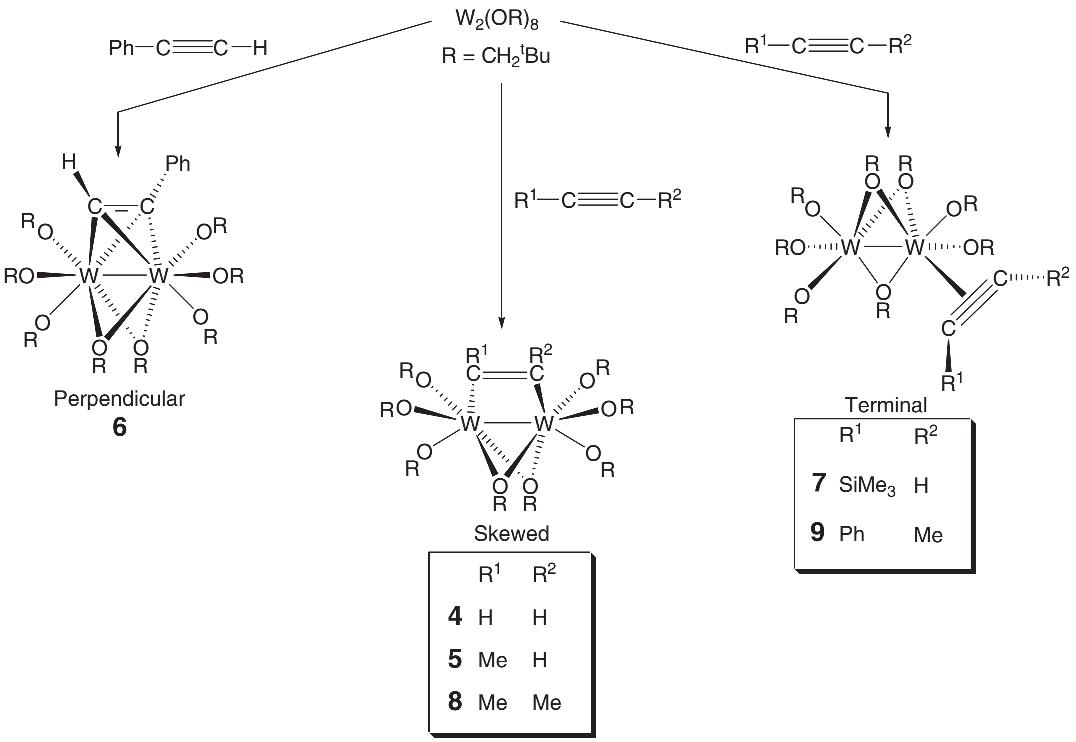
The alkoxido dimer complex $[W_2(OCH_2{}^tBu)_8]$ has proved to be a valuable precursor to a number of adducts, some of which will be mentioned later. One of these is the bridging ethyne complex $[W_2(\mu\text{-}C_2H_2)(\mu\text{-}OCH_2{}^tBu)_2(OCH_2{}^tBu)_6]$ **4**, with further alkyne adducts later isolated and characterized using the terminal alkynes $MeC{\equiv}CH$, $PhC{\equiv}CH$, and $Me_3SiC{\equiv}CH$ as well as the internal alkynes $MeC{\equiv}CMe$ and $PhC{\equiv}CMe$ yielding complexes **5–9**, respectively (Scheme 2).[6–9]

The methodology was simple, involving addition of the alkyne to suspensions of the purple $[W_2(OCH_2{}^tBu)_8]$ starting material (Table 2). A similarly skewed alkyne complex $[W_2(\mu\text{-}PhC{\equiv}CPh)(\mu\text{-}SC_6H_4Me\text{-}2)_2(SC_6H_4Me\text{-}2)_4]$ **10** was isolated from the metathetical reaction between the alkylidyne complex $[W({\equiv}CPh)(O^tBu)_3]$ and the thiol 2-MeC_6H_4SH in toluene.[10]

The adducts $[W_2(\mu\text{-}RC{\equiv}CR)_2(\kappa^2\text{-}O_2C^tBu)_4]$ (**11a**, R = Me; **11b**, R = Et; **11c**, R = Ph; **11d**, $RC{\equiv}CR = PhC{\equiv}CMe$) with two bridging alkyne ligands have also been reported using the ditungsten tetrapivalate synthon $[W_2(\kappa^2\text{-}O_2C^tBu)_4]$, formed by treatment with internal alkynes $RC{\equiv}CR$ (R = Me, Et, Ph) and $PhC{\equiv}CMe$ in benzene or toluene at room temperature.[11] These reactions exploit the uniquely reactive nature of the tungsten–tungsten quadruple bond in the $[W_2(\kappa^2\text{-}O_2C^tBu)_4]$ starting material. Reactions with ethyne, propyne, or $Me_3SiC{\equiv}CSiMe_3$ produced intractable products or simply did not proceed, as was the case with the latter alkyne, an outcome attributed to its steric bulk. No monoalkyne products were observed, irrespective of starting material mole ratios.

5.09.4.2 Structure and Properties

The prototypical complex in this group, complex **4**, comprises a highly unusual non-perpendicular/non-parallel bridging alkyne, which was confirmed by X-ray structural analysis and computational work.[6,7] This alkyne skewing phenomenon was attributed to second-order Jahn–Teller distortion stabilization.[5] Despite solid-state structural confirmation, NMR analysis in toluene-d_8 of the $^{13}C_2H_2$-enriched isotopomer did not permit the authors to distinguish between a rapid interconversion of perpendicular/parallel μ-alkyne isomers and a dynamic process where the twisted μ-alkyne oscillates

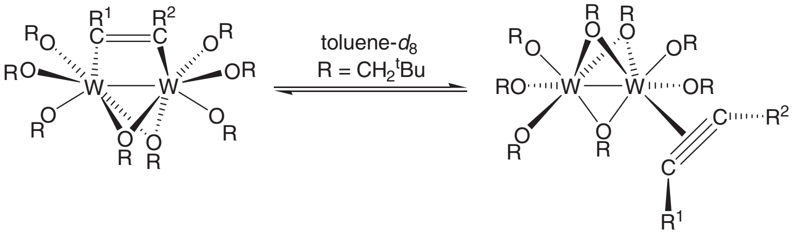


Scheme 2

Table 2 Synthesis of alkoxido and tetrapivalate alkyne W_2 complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W_2(OCH_2{}^tBu)_8] + HC{\equiv}CH$ in toluene (−196 °C)	$[W_2(\mu\text{-}\eta^2,\eta^2\text{-}C_2H_2)(\mu\text{-}OCH_2{}^tBu)_2(OCH_2{}^tBu)_6]$ **4**	86	Red	X-ray: W–W 2.6228(3) Å, skewed μ-alkyne	6,7
$[W_2(OCH_2{}^tBu)_8] + MeC{\equiv}CH$ in hexanes (−196 °C)	$[W_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC{\equiv}CH)(\mu\text{-}OCH_2{}^tBu)_2(OCH_2{}^tBu)_6]$ **5**	–	Red-brown	X-ray: W–W 2.6295(2) Å, skewed μ-alkyne; NMR: isomeric mixture	8,9
$[W_2(OCH_2{}^tBu)_8] + PhC{\equiv}CH$ in hexanes (25 °C)	$[W_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC{\equiv}CH)(\mu\text{-}OCH_2{}^tBu)_2(OCH_2{}^tBu)_6]$ **6**	95	Green	X-ray: W–W 2.5957(2) Å, perpendicular μ-alkyne	8,9
$[W_2(OCH_2{}^tBu)_8] + Me_3SiC{\equiv}CH$ in hexanes (45 °C)	$[W_2(\eta^2\text{-}Me_3SiC{\equiv}CH)(\mu\text{-}OCH_2{}^tBu)_3(OCH_2{}^tBu)_5]$ **7**	95	Green	NMR: non-bridging alkyne	8,9
$[W_2(OCH_2{}^tBu)_8] + MeC{\equiv}CMe$ in hexanes (25 °C)	$[W_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC{\equiv}CMe)(\mu\text{-}OCH_2{}^tBu)_3(OCH_2{}^tBu)_5]$ **8**	–	Green	X-ray: W–W 2.6361(2) Å, skewed μ-alkyne; NMR: isomeric mixture	8,9
$[W_2(OCH_2{}^tBu)_8] + PhC{\equiv}CMe$ in hexanes (25 °C)	$[W_2(\eta^2\text{-}PhC{\equiv}CMe)(\mu\text{-}OCH_2{}^tBu)_3(OCH_2{}^tBu)_5]$ **9**	–	Green	X-ray: W–W 2.6536(5) Å, terminal alkyne; NMR: isomeric mixture	8,9
$[W({\equiv}CPh)(O^tBu)_3] + >3$ mol equiv. 2-MeC_6H_4SH in toluene (25 °C)	$[W_2(\mu\text{-}PhC{\equiv}CPh)(\mu\text{-}SC_6H_4Me\text{-}2)_2(SC_6H_4Me\text{-}2)_4]$ **10**	60	Green	X-ray: skewed μ-alkyne	10
$[W_2(\kappa^2\text{-}O_2C^tBu)_4] + RC{\equiv}CR$ in benzene (70 °C)	$[W_2(\mu\text{-}MeC{\equiv}CMe)_2(\kappa^2\text{-}O_2C^tBu)_4]$ **11a**	40	Orange	X-ray: W=W 2.4888(2) Å	11
	$[W_2(\mu\text{-}EtC{\equiv}CEt)_2(\kappa^2\text{-}O_2C^tBu)_4]$ **11b**	39	Orange		11
	$[W_2(\mu\text{-}PhC{\equiv}CPh)_2(\kappa^2\text{-}O_2C^tBu)_4]$ **11c**	35	Purple		11
	$[W_2(\mu\text{-}PhC{\equiv}CMe)_2(\kappa^2\text{-}O_2C^tBu)_4]$ **11d**	34	Red	X-ray: W=W 2.4925(2) Å	11

about a symmetric perpendicular position. A similarly skewed bonding mode for the alkyne was elucidated in the X-ray structures of complexes **4**, **5**, and **8**, whereas the asymmetric PhC≡CH alkyne in complex **6** demonstrated a purely perpendicular bridging mode.[8,9] Complexes **7** and **9**, on the other hand, were shown to comprise non-bridging alkyne modes in the solid state. Despite these X-ray structural characterizations, NMR analysis provided clear evidence for dynamic isomeric exchange for several of the complexes (Equation (2)). Thus equilibria between skewed μ-alkyne and terminal η^2-alkyne isomers of complexes **5**, **8**, and **9** were established, with the major isomers corresponding to the observed solid-state structure for complexes **5** and **9**. Curiously for complex **8**, the terminal η^2-isomer dominates in toluene-d_8 solution in contrast to its solid-state structure with the twisted μ-alkyne conformation.

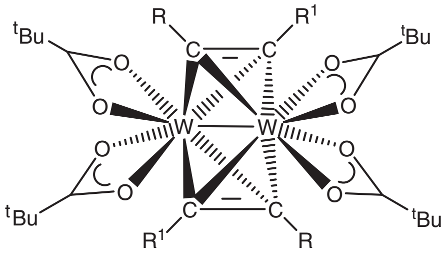


	R^1	R^2	ratio
5	Me	H	3 : 1
8	Me	Me	1 : 9
9	Ph	Me	1 : 3

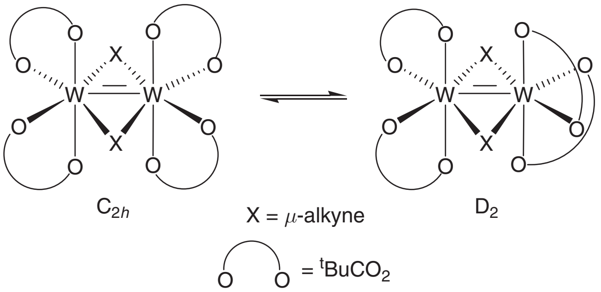
(2)

Complex **10** was isolated as part of a study to investigate Schrock "chop-chop" metathetical reactions between W≡W and C≡C or C≡N systems.[10] Quantitative isolation of complex **10** verified computational predictions that the tetrahedral W_2C_2 adduct formed by the initial coupling of the reactants would be more stable than the final detached metathesis W≡C products.

The X-ray diffraction studies of complexes **11a** and **11d** established the general architectural motif for this class of complex as doubly bridged moieties with the alkynes perpendicularly spanning W=W bonds.[11] In solution, the complexes underwent solvent-assisted intramolecular isomerization from pseudo-C_{2h} to D_2 symmetrical structures (Equation (3)). This process may be catalyzed by the presence of the free acid, ${}^tBuCO_2H$, in solution.



	R^1	R^2
11a	Me	Me
11b	Et	Et
11c	Ph	Ph
11d	Ph	Me



(3)

5.09.4.3 Reactions

There were no subsequent reactions to report for these alkyne adducts, although it was noted that when the complexes **11** were tested for further reaction with excess alkyne, the results were negative.

5.09.5 Alkynyl Complexes

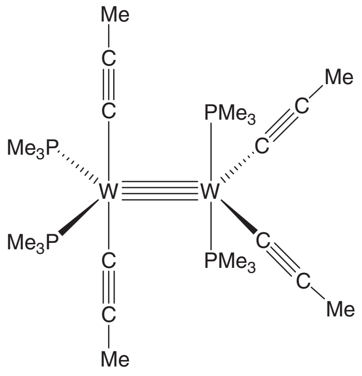
This is another field of organometallic tungsten chemistry that is typically dominated by carbonyl-bearing metal centers. There has, however, been one report of note that comes under the purview of this work.

5.09.5.1 Synthesis

Typically the source of alkynyl ligands can either be via introduction of a main group metal acetylide salt (i.e., simple metathesis), or by rearrangement of a predisposed alkyne moiety. The former is exemplified by treatment in dimethoxymethane (DME) of the quadruply bonded tungsten–phosphine complex $[W_2Cl_4(PMe_3)_4]$ with $LiC{\equiv}CR$ to afford the complexes $[W_2(C{\equiv}CR)_4(PMe_3)_4]$ (**12a**, $R = {}^tBu$; **12b**, R = Me), noting that the *tert*-hexynyl complex **12a** is produced in considerably superior yield compared with the corresponding propynyl analog **12b** (Table 3).[12,13] Synthetic procedures were carried out carefully in a bid to avoid contamination by chloride-containing impurities, and DME was specifically used as other common solvents (Et_2O, THF) resulted in poorer yields.

Table 3 Synthesis of alkynyl W_2 complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W_2Cl_4(PMe_3)_4] + LiC{\equiv}CR$ in DME (0 °C)	$[W_2(C{\equiv}C^tBu)_4(PMe_3)_4]$ **12a**	83	Aqua-blue		12
	$[W_2(C{\equiv}CMe)_4(PMe_3)_4]$ **12b**	39	Aqua-blue	X-ray: W≡W 2.2742(9) Å	12,13



12b

5.09.5.2 Structure and Properties

Single crystal X-ray diffraction analysis of complex **12b** confirmed a D_{2d} symmetry with the *transoid* alkynyl ligands on one metal mutually orthogonal to those on the adjacent metal center.[13] Interestingly, from comparison with the structures of $[1,1,2',2'\text{-}W_2(C{\equiv}CMe)_2Cl_2(PMe_3)_4]$ and $[W_2Cl_4(PMe_3)_4]$, it was suggested that the alkynyl units impart an additive contribution to the W≡W bond length, with the former's W≡W bond length approaching the average value of those of **12b** and $[W_2Cl_4(PMe_3)_4]$. Furthermore, while the alkynyl units were internally linear ($\angle(C{\equiv}C\text{–}Me) = 175(3)\text{–}177.9(4)°$), the ligands were somewhat bent back ($\angle(M\text{–}C{\equiv}C) = 165(2)\text{–}172.4(5)°$) owing to steric interactions with the PMe_3 groups from across the W≡W bond. Further comparisons with analogous molybdenum complexes were hampered by poor crystal quality.

5.09.6 Alkylidene Complexes

The synthesis and characterization of alkylidene complexes have provided remarkable insight into the fundamental concepts of multiple bonding between carbon and transition metals, perhaps more for tungsten than any other member of the *d*-block. The ramifications with regard to investigations of their subsequent catalytic activity have been enormously important, though the following discussion will be essentially limited to synthesis and structural properties. Any subsequent reactivity will not focus on their function in the catalysis of organic reactions, as this facet has been dealt with elsewhere in this set of volumes. Once again, it is inevitable that further alkylidene complexes will be met with later in this particular work, making categorization difficult. Indeed this moiety is prevalent in non-carbonyl tungsten complexes with amido and imido ligands (Sections 5.09.8 and 5.09.9, respectively). One subclass of alkylidenes that has proved to be particularly intriguing is the bis(alkylidene) tungsten complexes. Early reports of bis(alkylidene) complexes had been limited to proposed reactive intermediates in high oxidation state alkyl–alkylidyne complex rearrangements. As an example, the transformation in Equation (4) has been cited, without isolation of the purported bis(alkylidene) intermediate.[14] Because alkylidene chemistry is often intimately associated with alkylidyne chemistry, examples of the latter will also be introduced here as a prelude to Section 5.09.7.

$$[W({\equiv}CSiMe_3)(CH_2{}^tBu)_3] \rightleftharpoons [W({=}CHSiMe_3)({=}CH^tBu)(CH_2{}^tBu)_2] \rightleftharpoons [W({\equiv}C^tBu)(CH_2SiMe_3)(CH_2{}^tBu)_2] \qquad (4)$$

5.09.6.1 Synthesis

The first isolated tungsten bis(alkylidene) complex $[W({=}CH^tBu)_2(Si^tBuPh_2)(CH_2{}^tBu)]$ **13a** was synthesized in moderate yield by reaction of $Li(THF)_3(Si^tBuPh_2)$ with the alkylidyne complex $[W({\equiv}CBu^t)Cl(CH_2{}^tBu)_2]$ (Table 4).[15] The compound is formed as an equilibrium mixture with its alkyl–alkylidyne isomer (*vide infra*) and is stable in the solid state, but slowly decomposes in solution at room temperature, yielding SiH^tBuPh_2 and

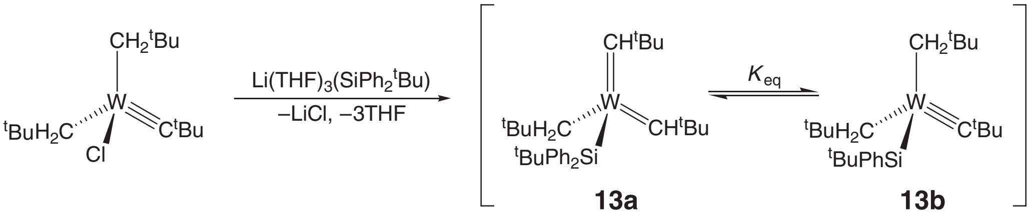
Table 4 Synthesis of bis(alkylidene) W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W(\equiv CBu^t)Cl(CH_2{}^tBu)_2] + Li(THF)_3(Si^tBuPh_2)$ in Et_2O ($-40\,°C$)	$[W(=CH^tBu)_2(Si^tBuPh_2)(CH_2{}^tBu)]$ **13a**	58	Yellow-orange	^{13}C NMR: W=C δ 272.30	15, 16
$[W(\equiv CSiMe_3)(CH_2SiMe_3)_3] + PMe_3$ in toluene-d_8, crystallized from an equilibrium mixture at $-30\,°C$	$[W(=CHSiMe_3)_2(CH_2SiMe_3)_2(PMe_3)]$ **14a**	–	–	^{13}C NMR: W=C δ 256.43, 254.71	17

some unknown species. The phosphine-stabilized bis(alkylidene) complex $[W(=CHSiMe_3)_2(CH_2SiMe_3)_2(PMe_3)]$ **14a** has also been observed, formed by addition of PMe_3 to toluene-d_8 solutions of $[W(\equiv CSiMe_3)(CH_2SiMe_3)_3]$.[16]

5.09.6.2 Structure and Properties

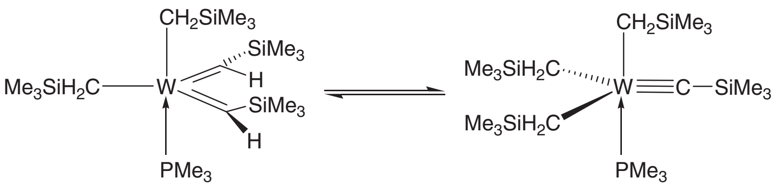
Complex **13a** was, strictly speaking, not isolated but observed to be in equilibrium with its alkyl–alkylidyne variant **13b**, owing to α-H migration (Equation (5)).



(5)

Due to decomposition, comprehensive solid-state characterization was not possible, with the exception of solid-state CPMAS $^{13}C\{^1H\}$ NMR spectroscopy, which showed both isomers to be present. NMR studies on solutions of **13** revealed both the alkylidene– and alkylidyne–carbon resonances for **13a** (δ272.30) and **13b** (δ318.38), respectively. VT ^1H NMR spectroscopy confirmed the equivalence of the alkylidene moieties in **13a** with one resonance (δ6.03) for the $=CH^tBu$ proton, ruling out W=C bond rotation as an equivalencing mechanism. The alkylidene ligands thus necessarily adopted an *anti,anti*-configuration. A VT NMR study of the mixture **13** revealed the alkylidene isomer **13a** to be dominant from 287 K ($K_{eq} = 3.34$) to 237 K ($K_{eq} = 4.590$).

At ambient temperatures an equilibrium between the bis(alkylidene) **14a** and alkyl–alkylidyne **14b** complexes was also observed, favoring the former by ca. 10 : 1 (Equation (6)).[17] It was noted that in the absence of the PMe_3, the complex $[W(\equiv CSiMe_3)(CH_2SiMe_3)_3]$ was observed to exist only in the alkylidyne form.



14a **14b**

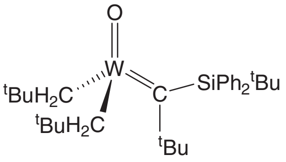
(6)

Although the expected single resonance was observed for the alkylidyne **14b** (W≡C δ358.81), two resonances appeared due to inequivalent alkylidene ligands in **14a** (W=C δ256.43 and 254.71), which along with ^1H NMR data ($=CHSiMe_3$ δ7.985 and 7.192) supported an *anti,syn*-configuration for these ligands, again without rapid rotation of the W=C bonds. The unique properties of the silyl system were demonstrated by comparison with a neopentyl analog, $[W{\equiv}(C^tBu)(CH_2{}^tBu)_3]$, which reacted with PMe_3 in benzene-d_6 at 25 °C affording $[W({\equiv}C^tBu)({=}C^tBu)(CH_2{}^tBu)(PMe_3)_2]$, resulting from a combination of α-H abstraction followed by CMe_4 elimination. Computational analysis of the two systems $[W({\equiv}CSiMe_3)(CH_2SiMe_3)_3]$ and **14** indicated that the phosphine binding reversed the stability of the alkylidyne isomer in the former complex with the bis(alkylidene) isomer in **14**, resulting in the observed predominance of **14a**.

A more detailed DFT computational analysis of the alkyl–alkylidyne/bis(alkylidene) systems $[W({\equiv}CH)(X)(Me)_2]/[W({=}CH_2)_2(X)(Me)]$ ($X = Cl$, Me, CF_3, SiH_3, SiF_3) showed that the relative stability of the bis(alkylidyne) tautomer increased with increasing π-accepting ability of the substituted ligand X.[18] This was in turn attributed to the increasing electrophilic interaction between X and the more electron-rich metal–alkylidene π-bonds. Interestingly, when $X = SiH_3$, the alkyl-alkylidyne/bis(alkylidene) tautomeric pairs were found to have similar stabilities.

5.09.6.3 Reactions

Exposure of benzene-d_6 solutions of complex **13** to 1 mol equiv. O_2 resulted in a rapid reaction to afford red crystals of the oxo complex $[W\{{=}C(^tBu)(Si^tBuPh_2)\}({=}O)(CH_2{}^tBu)_2]$ **15** in 32 % yield.[15]



15

The mechanism of the formation of complex **15** involved the migration of the silyl ligand to the alkylidyne in tautomer **13a**, thus producing the alkylidene moiety ${=}C(^tBu)(Si^tBuPh_2)$, the first reported example of such a silyl migration. The structure of complex **15** was confirmed by X-ray crystallography, which revealed a W=C bond distance of 1.920(7) Å, consistent with other structurally characterized d^0-W–alkylidene complexes. Further reactions with O_2 were observed, but identification of the products has not yet been reported.

5.09.7 Alkylidyne Complexes

The interplay between organic molecules/fragments and transition metal centers is nowhere more exemplified than in the metal–alkylidyne arena, a facet that has been put to good use in countless organic synthetic methodologies, thanks to the exhaustive work of Schrock and Grubbs (2005 co-Nobel laureates, along with Chauvin) among others. Tungsten alkylidyne complexes have played a vital role in this continually evolving field. They are also proving to be potentially useful for applications in materials chemistry, particularly when isolated as polymers.

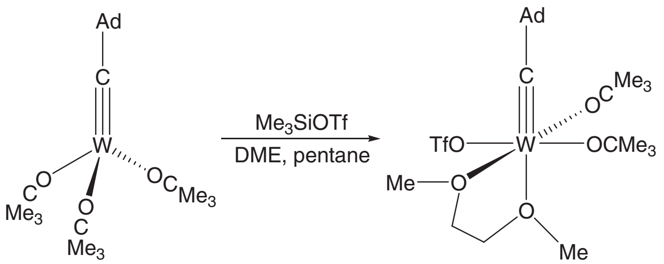
5.09.7.1 Synthesis

The first tungsten silyl–alkylidyne complex has been reported with the synthesis of $[W({\equiv}C^tBu)\{Si(SiMe_3)_3\}(CH_2{}^tBu)_2]$ **16** from the neopentyl–alkylidyne $[W({\equiv}C^tBu)(CH_2{}^tBu)_3]$ by reaction of the latter with HCl in Et_2O, followed by addition of $LiSi(SiMe_3)_3$.[19]

A series of reactions have been described by Schrock, detailing the synthesis and reactivity of cyclopentadienide (Cp) tungsten alkylidyne complexes. The critical precursor, $[W({\equiv}CAd)(OTf)(O^tBu)_2(DME)]$ **18**, was synthesized from a simple alkoxido–alkylidyne $[W({\equiv}CAd)(O^tBu)_3]$ **17** by addition of Me_3SiOTf in DME (Table 5) (Equation (7)). The starting reagent **17** was itself produced by treatment of $[W_2(O^tBu)_6]$ with 1-adamantanecarbonitrile in pentane.[20]

Table 5 Synthesis of cyclopentadienide alkylidyne W complexes

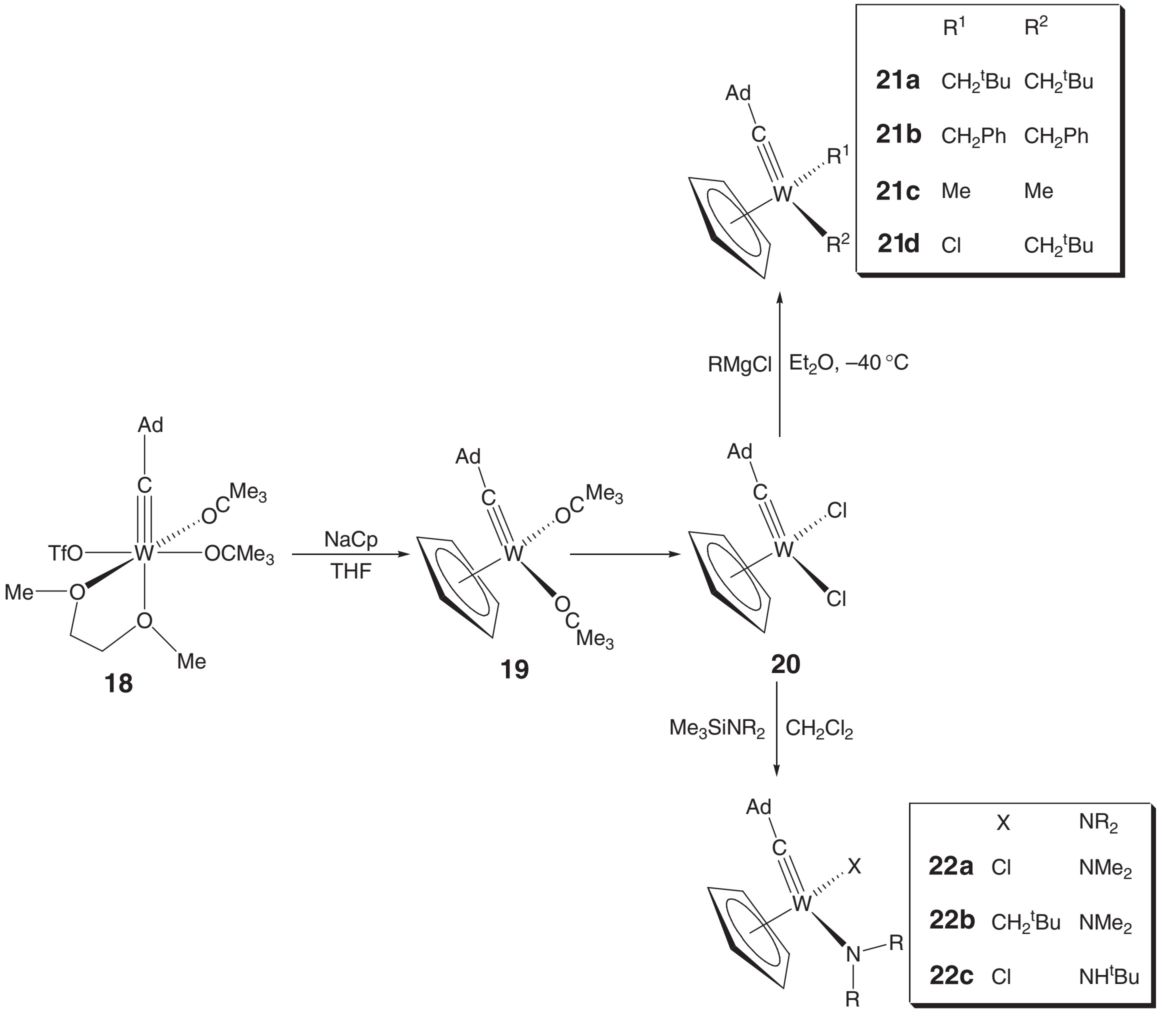
Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W_2(O^tBu)_6]$ + AdCN in pentane (25 °C)	$[W(\equiv CAd)(O^tBu)_3]$ **17**	80	Colorless	Ad = adamantyl; ^{13}C NMR: W≡C δ 272.1	20
17 + Me_3SiOTf in DME/pentane (−40 °C)	$[W(\equiv CAd)(OTf)(O^tBu)_2(DME)]$ **18**	96	Yellow	^{13}C NMR: W≡C δ 288.1	20
18 + NaCp in THF (−40 °C)	$[W(\equiv CAd)(O^tBu)_2Cp]$ **19**	99	Yellow	^{13}C NMR: W≡C δ 285.2	20
19 + excess Me_3SiCl in CH_2Cl_2 (25 °C), 2,6-lutidinium hydrochloride (cat.)	$[W(\equiv CAd)Cl_2Cp]$ **20**	81	Purple	^{13}C NMR: W≡C δ 328.6	20
20 + 1 mol equiv. RMgCl in Et_2O (−40 °C)	$[W(\equiv CAd)Cl(CH_2{}^tBu)Cp]$ **21a**	76	Red	^{13}C NMR: W≡C δ 313.6	20
20 + 2 mol equiv. RMgCl in Et_2O (−40 °C)	$[W(\equiv CAd)(CH_2{}^tBu)_2Cp]$ **21b**	71	Red	X-ray: W≡C 1.746(9) Å; ^{13}C NMR: W≡C δ 300.4	20
	$[W(\equiv CAd)(CH_2Ph)_2Cp]$ **21c**	79	Yellow	^{13}C NMR: W≡C δ 294.5	20
	$[W(\equiv CAd)Me_2Cp]$ **21d**	72	Red	^{13}C NMR: W≡C δ 300.4	20
20 + 1 mol equiv. Me_3SiNMe_2 in CH_2Cl_2 (−40 °C)	$[W(\equiv CAd)Cl(NMe_2)Cp]$ **22a**	87	Yellow	^{13}C NMR: W≡C δ 302.3	20
22a + 1 mol equiv. $^tBuCH_2MgCl$ in Et_2O (−40 °C)	$[W(\equiv CAd)(CH_2{}^tBu)(NMe_2)Cp]$ **22b**	70	Orange	^{13}C NMR: W≡C δ 291.7	20
20 + 1.5 mol equiv. Me_3SiNH^tBu in CH_2Cl_2 (25 °C)	$[W(\equiv CAd)Cl(NH^tBu)Cp]$ **22c**	88	Yellow	^{13}C NMR: W≡C δ 303.54	20



17 **18** (7)

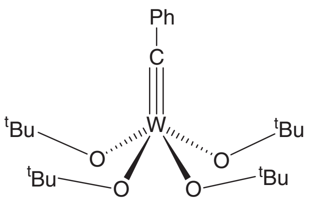
The introduction of the η^5-Cp ligand to give $[W(\equiv CAd)(O^tBu)_2Cp]$ **19** was achieved through conventional metathesis procedures by reaction of **18** with NaCp in THF, with direct substitution of a ^tBuO group in **17** directly by NaCp proving to be unsuccessful. Conversion to the dichloro species **20** was readily accomplished by subsequent reaction with Me_3SiCl in the presence of an acidic ammonium salt catalyst in CH_2Cl_2. The dichloro complex **20** proved to be an excellent precursor to a number of alkylidyne complexes with alkyl and amido groups **21–22**, listed in Table 5 (Scheme 3).

A convenient synthetic methodology for the formation of complexes of the type $[W(\equiv CR)X_3(DME)]$ (**23**, R = ^tBu, ^nPr, Ph, X = Cl, Br) has been developed.[21] Given the importance of these alkylidyne complexes in the fields of high- and low-valent metal–alkylidyne synthesis, metallacycle formation, olefin metathesis, and other polymerization catalysis processes, this was a welcomed step forward in their efficient production. Previous procedures were not particularly adaptable to variation in the alkylidyne moiety in addition to being expensive and time-consuming. Thus the syntheses of $[W(\equiv CR)Cl_3(DME)]$ (**23a**, R = Ph; **23b**, R = ^tBu; **23c**, R = ^nPr), for example, were achieved in good yield (78–87%) by reaction of $[W(\equiv CR)(O^tBu)_3]$ with BCl_3 in a pentane/DME (40 : 1) mixture of solvents (Table 6). Although stoichiometries could be altered to produce unidentified complex products, a minimum of 3 mol equiv. BX_3 to alkylidyne was suggested in an on-going effort to optimize the procedure.

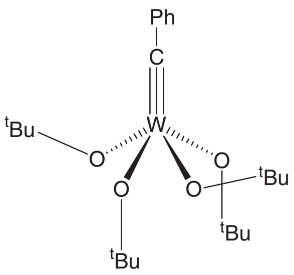


Scheme 3

In effort to probe cation–anion interactions with anionic d^0-W–benzylidyne complexes, the compounds [Na(L)][W(≡CPh)(O^{t}Bu)$_4$] (**24a**, L = blank; **24b**, L = 15-crown-5; **24c**, L = crypt-2,2,2) have been synthesized.[22] The primary complex **24a** was formed by simple addition of NaO^{t}Bu to the precursor [W(≡CR)(O^{t}Bu)$_3$] in pentane. The sodium counterion could then be readily encapsulated by addition of either 15-crown-5 or crypt-2,2,2 in THF to afford **24b** or **24c**, respectively (Table 6).



24c-α
λ_{em} (solid) = 640 nm



24c-β
λ_{em} (solid) = 714 nm

Table 6 Synthesis of other high-valent alkylidyne W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W(\equiv CR)(O^tBu)_3]$ + 3 mol equiv. BCl_3 in pentane/DME (40 : 1) (−78 °C)	$[W(\equiv CPh)Cl_3(DME)]$ **23a**	84	Purple		21
	$[W(\equiv C^tBu)Cl_3(DME)]$ **23b**	87	Purple		21
	$[W(\equiv C^nPr)Cl_3(DME)]$ **23c**	78	Purple		21
$[W(\equiv CR)(O^tBu)_3]$ + 3 mol equiv. BBr_3 in pentane/DME (40 : 1) (−78 °C)	$[W(\equiv CPh)Br_3(DME)]$ **23d**	77	Green		21
$[W(\equiv CR)(O^tBu)_3]$ + NaO^tBu in pentane (25 °C)	$Na[W(\equiv CPh)(O^tBu)_4]$ **24a**	95	Yellow	X-ray: W≡C 1.755(1) Å; ^{13}C NMR: W≡C δ 258.7; λ_{em}(solid) 612 nm	22
24a + 15-crown-5 in THF, crystals grown at −35 °C	[Na(15-crown-5)]-$[W(\equiv CPh)(O^tBu)_4]$ **24b**	82	Yellow	X-ray: W≡C 1.780(4) Å; ^{13}C NMR: W≡C δ 260.2; λ_{em}(solid) 631 nm	22
24a + crypt-2,2,2 in THF, crystals grown at −80 °C	[Na(crypt-2,2,2)] $[W(\equiv CPh)(O^tBu)_4]$ 24c	82	Orange	X-ray: 2 polymorphs W≡C 1.772(3) and 1.756(9) Å; ^{13}C NMR: W≡C δ 257.1; λ_{em}(solid) 640 or 714 nm	22

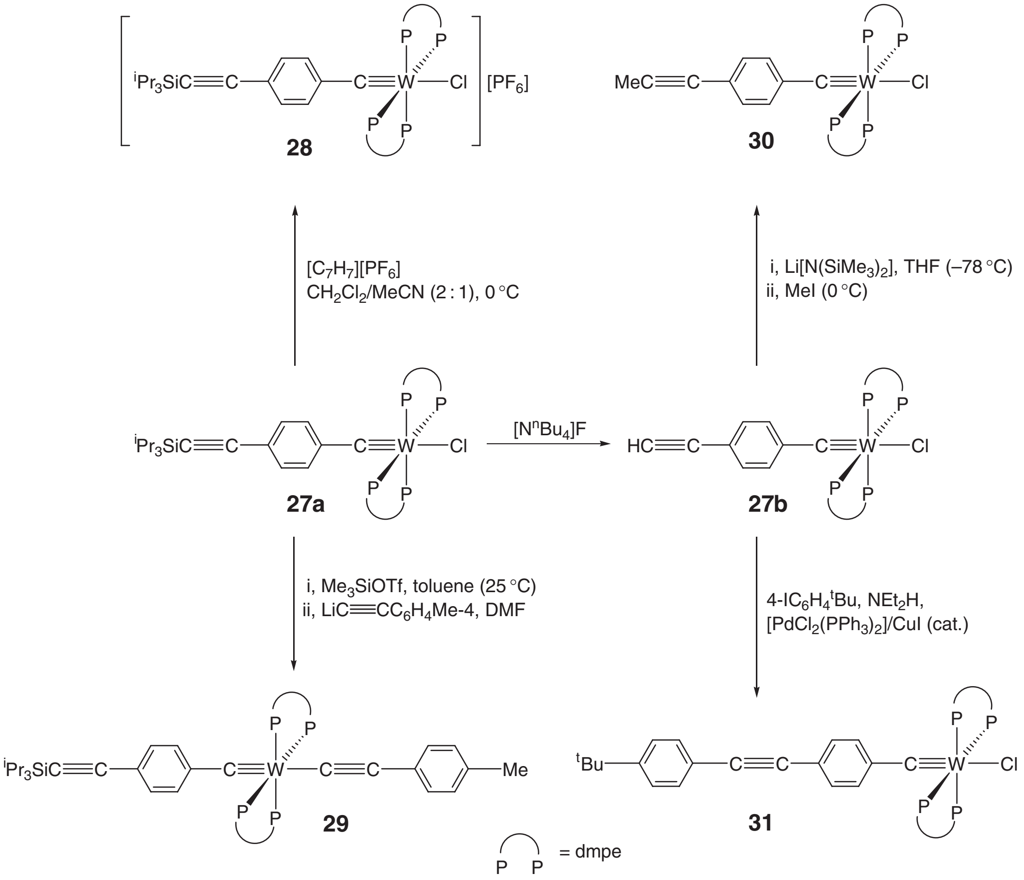
The reaction between $[W(\equiv CH)(OTf)(\kappa^2\text{-dmpe})_2]$ and ^nBuLi has afforded the alkyl–methylidyne complex $[W(\equiv CH)^nBu(\kappa^2\text{-dmpe})_2]$ (**25**, dmpe = bis(dimethylphosphino)ethane)) (Table 7), the subject of a revealing X-ray structural study (*vide infra*).[23] A related complex $[W(\equiv CH)Br(\kappa^2\text{-dmpe-}d_{12})_2]$ **26** has also been synthesized by addition of LiBr to a solution of $[W(\equiv CH)(OTf)(\kappa^2\text{-dmpe-}d_{12})_2]$ in THF.[24] Incorporating the Hopkins

Table 7 Synthesis of phosphine alkylidyne W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W(\equiv CH)(OTf)(\kappa^2\text{-dmpe})]$ + ^nBuLi in pentane/toluene (25 °C)	$[W(\equiv CH)^nBu(\kappa^2\text{-dmpe})_2]$ **25**	45	Yellow	X-ray: W≡C 1.827(5) Å, ∠(W≡C–H) = 162.3(39)°; ^{13}C NMR: W≡C δ 244.9	23
$[W(\equiv CH)(OTf)(\kappa^2\text{-dmpe-}d_{12})]$ + LiBr in THF (25 °C)	$[W(\equiv CH)Br(\kappa^2\text{-dmpe-}d_{12})_2]$ **26**	92	Yellow	Neutron diff.: W≡C 1.750(12) Å (100 K), 1.786(8) Å (213 K), ∠(W≡C–H) = 178.0(7)° (100 K), 164(6)° (213 K)	24
$[W_2(O^tBu)_6]$ + (i) $^iPr_3SiC\equiv CC_6H_4C\equiv C^nPr$, (ii) BCl_3 in DME, (iii) dmpe, 2 Na/Hg	$[W(\equiv CC_6H_4C\equiv CSi^iPr_3\text{-}4)\text{-}Cl(\kappa^2\text{-dmpe})_2]$ 27a	–	–	^{13}C NMR: W≡C δ 252	25
27a + $[N^nBu_4]F$	$[W(\equiv CC_6H_4C\equiv CH\text{-}4)\text{-}Cl(\kappa^2\text{-dmpe})_2]$ 27b	–	–	^{13}C NMR: W≡C δ 252	25
27a + $[C_7H_7][PF_6]$ in CH_2Cl_2/MeCN (2 : 1) (0 °C)	$[W(\equiv CC_6H_4C\equiv CSi^iPr_3\text{-}4)\text{-}Cl(\kappa^2\text{-dmpe})_2][PF_6]$ 28	–	–	17-electron complex	25
27a + (i) Me_3SiOTf in toluene (25 °C), (ii) $LiC\equiv CC_6H_4Me\text{-}4$ in DME (0 °C)	$[W(\equiv CC_6H_4C\equiv CSi^iPr_3\text{-}4)\text{-}(C\equiv CC_6H_4Me\text{-}4)(\kappa^2\text{-dmpe})_2]$ 29	–	–	X-ray: W≡C 1.93(3) Å; ^{13}C NMR: W≡C δ 255	25
27b + (i) $Li[N(SiMe_3)_2]$ in THF (−78 °C), (ii) MeI (0 °C)	$[W(\equiv CC_6H_4C\equiv CMe\text{-}4)\text{-}Cl(\kappa^2\text{-dmpe})_2]$ 30	–	–	^{13}C NMR: W≡C δ 252	25
27b + $4\text{-}IC_6H_4{}^tBu$ in NEt_2H, $[PdCl_2(PPh_3)_2]$/CuI (cat.) (25 °C)	$[W\{\equiv CC_6H_4(C\equiv CC_6H_4{}^tBu\text{-}4)\text{-}4\}Cl(\kappa^2\text{-dmpe})_2]$ 31	–	–	^{13}C NMR: W≡C δ 253	25

alkylidyne/BX$_3$ methodology described above, phosphine–alkylidyne precursors to building blocks for redox-active poly(phenyleneethynylene)s have been synthesized. Thus, metathesis reaction of $[\mathrm{W_2(O^tBu)_6}]$ with $\mathrm{^iPr_3SiC{\equiv}CC_6H_4C{\equiv}C^nPr}$, followed by treatment with BCl$_3$ in DME and then reduction in the presence of dmpe, gives $[\mathrm{W({\equiv}CC_6H_4C{\equiv}CSi^iPr_3\text{-}4)Cl(\kappa^2\text{-dmpe})_2}]$ **27a**.[25] The ^{i}Pr$_3$Si group was easily removed by routine desilylation with $[\mathrm{N^nBu_4}]$F to yield $[\mathrm{W({\equiv}CC_6H_4C{\equiv}CH\text{-}4)Cl(\kappa^2\text{-dmpe})_2}]$ **27b**. Further alkylidyne derivatives have been produced from both complexes **27a** and **27b**. These include complexes **28–31** listed in Table 7 and shown in Scheme 4, with the most intriguing being the 17-electron complex $[\mathrm{W({\equiv}CC_6H_4C{\equiv}CH\text{-}4)Cl(\kappa^2\text{-dmpe})_2}][\mathrm{PF_6}]$ **28**, which was synthesized by one-electron oxidation of complex **27a** with $[\mathrm{C_7H_7}][\mathrm{PF_6}]$.[25] The syntheses of complexes **29** and **31** also represent ways of readily forming extended hyperconjugated metal–alkylidynes, using non-aggressive coupling methods, through M–C and Sonogashira-catalyzed C–C bond formation, respectively.

High-valent monomeric tungsten alkylidyne complexes have emerged as candidates for important polymeric materials. In particular, treatment of either $[\mathrm{W({\equiv}CEt)(O^tBu)_3}]$ or $[\mathrm{W_2(O^tBu)_6}]$ with the alkynyl–pyridines $\mathrm{NC_5H_2Me_2\text{-}3,5\text{-}C{\equiv}C^nPr\text{-}4}$ or $\mathrm{NC_5H_4C{\equiv}C^nBu\text{-}3}$ has afforded the products $[\mathrm{W\{{\equiv}C(4\text{-}NC_5H_2Me_2)\}(O^tBu)_3}]_\infty$ **32a** and $[\mathrm{W\{{\equiv}C(3\text{-}NC_5H_4)\}(O^tBu)_3}]_\infty$ **32b**, respectively (Table 8).[26] In benzene they precipitate out readily, the low solubility suggesting the formation of polymeric products, given the high solubility of the simple monomeric complexes $[\mathrm{W({\equiv}CR)(OR^1)_3}]$ ($\mathrm{R} \neq$ pyridyl) in organic solvents. Similar results using non-pyridyl donor substituents on the alkylidyne–aryl group have afforded the complexes $[\mathrm{W({\equiv}CC_6H_4X\text{-}4)(O^tBu)_3}]_\infty$ (**33a**, $\mathrm{X = NMe_2}$; **33b**, $\mathrm{X = SMe}$).[27] This time the products were formed via metathesis of the dimeric complex $[\mathrm{W_2(O^tBu)_6}]$ with $\mathrm{4\text{-}XC_6H_4CN}$ ($\mathrm{X = NMe_2}$, SMe, respectively). The immediate precipitation, however, is that of the white polymeric byproduct $[\mathrm{WN(O^tBu)_3}]_\infty$. The desired alkylidyne polymers are recovered by filtration of the reaction suspension and then recrystallization from pentane solution at −35 °C.



Scheme 4

Table 8 Synthesis of polymeric alkylidyne W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W(\equiv CEt)(O^tBu)_3]$ or $[W_2(O^tBu)_6] + NC_5H_2\text{-}3,5\text{-}Me_2\text{-}4\text{-}C\equiv C^nPr$ in benzene (25 °C)	$[W\{\equiv C(4\text{-}NC_5H_2Me_2)\}(O^tBu)_3]_\infty$ **32a**	–	Yellow-orange	X-ray: W≡C 1.766(13) Å, 1.770(15) Å, pseudo square-pyramidal W	26
$[W(\equiv CEt)(O^tBu)_3]$ or $[W_2(O^tBu)_6] + NC_5H_4\text{-}3\text{-}C\equiv C^nBu$ in benzene (25 °C)	$[W\{\equiv C(3\text{-}NC_5H_4)\}(O^tBu)_3]_\infty$ **32b**	–	Yellow-orange	X-ray: W≡C 1.775(9) Å, 1.789(8) Å, pseudo-trigonal-bipyramidal W	26
$[W_2(O^tBu)_6] + 4\text{-}XC_6H_4CN$ in pentane (25 °C), crystallized from pentane (−35 °C)	$[W(\equiv CC_6H_4NMe_2\text{-}4)(O^tBu)_3]_\infty$ **33a**	73	Yellow-orange	X-ray: W≡C 1.754(7) Å	27
	$[W(\equiv CC_6H_4SMe\text{-}4)(O^tBu)_3]_\infty$ **33b**	74	Yellow-orange	X-ray: W≡C 1.757(6) Å	27

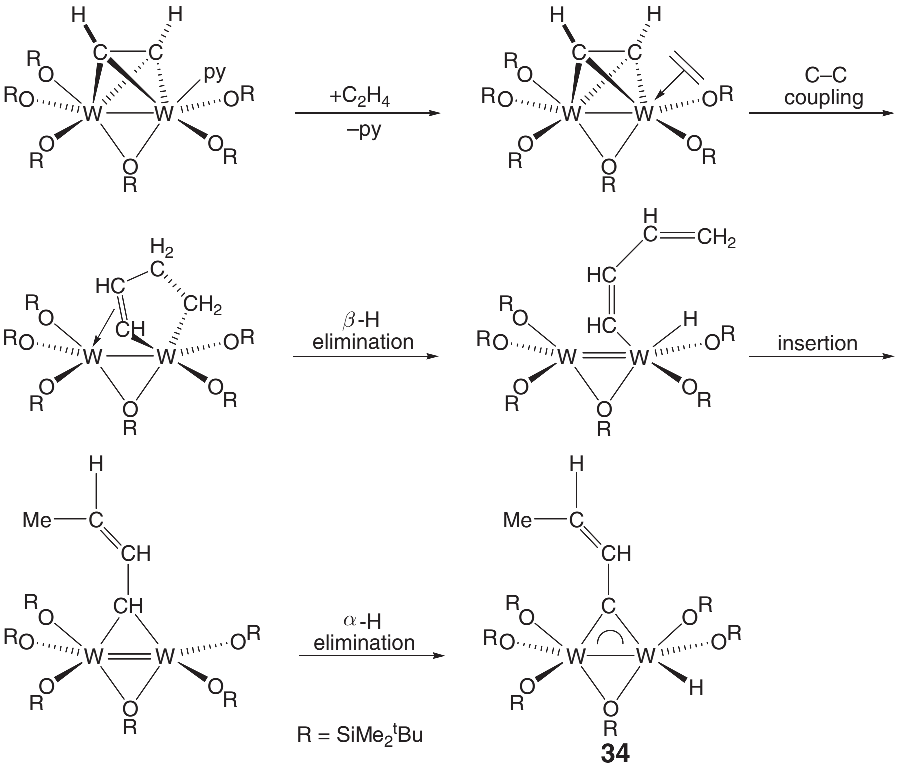
Table 9 Synthesis of bridging alkylidyne W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[W_2(\mu\text{-}C_2H_2)(OSiMe_2{}^tBu)_6(py)]$ + ethane in toluene or hexanes (−20 °C)	$[W_2(\mu\text{-}CCH{=}CHMe)H(OSiMe_2{}^tBu)_6]$ **34**	45	Blue-black	X-ray W–W 2.658(1) Å; ^{13}C NMR: W–μ-C–W δ 313.8	28
$[W_2(\mu\text{-}C_2H_2)(OSiMe_2{}^tBu)_6(py)]$ + allene in toluene (−20 °C)	$[W_2\{\mu\text{-}CC({=}CH_2)(CH{=}CH_2)\}H(OSiMe_2{}^tBu)_6]$ **35**	27	Red	X-ray W–W 2.561(1) Å	28

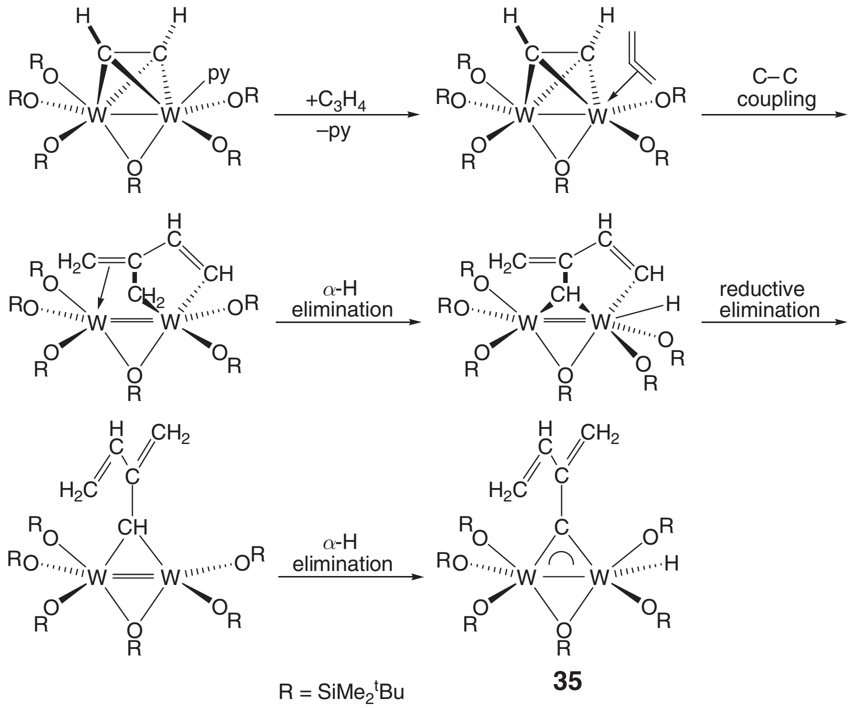
Bridging alkylidyne ligands in non-carbonyl-containing tungsten polynuclear systems appear to be considerably less ubiquitous than their monomeric congeners. Nevertheless two such complexes of interest have been synthesized via ene–yne coupling reactions using the bridging ethyne complex $[W_2(\mu\text{-}C_2H_2)(OSiMe_2{}^tBu)_6(py)]$ with ethene and allene to afford $[W_2(\mu\text{-}CCH{=}CHMe)H(OSiMe_2{}^tBu)_6]$ **34** and $[W_2\{\mu\text{-}CC({=}CH_2)(CH{=}CH_2)\}H(OSiMe_2{}^tBu)_6]$ **35**, respectively (Table 9).[28] Following ethyne coordination, the initial stages of the mechanism for the formation of these bridging alkylidyne complexes is believed to occur via C–C coupling followed by either β-H or α-H migration for **34** and **35**, respectively. In the former case, insertion, then α-H migration produces the product **34** (Scheme 5), while for the latter, complex **35** is formed through reductive elimination and then α-H elimination (Scheme 6).

5.09.7.2 Structure and Properties

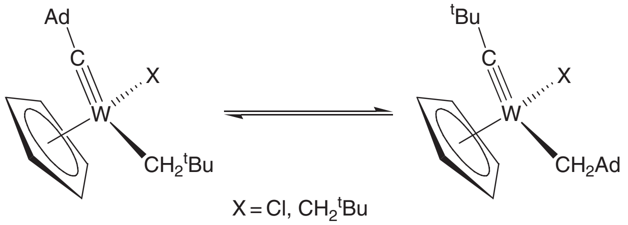
Of the cyclopentadienide tungsten complexes **19**–**22**, X-ray structural characterization of only **21b** was reported, revealing restricted rotation of the neopentyl groups in the crowded metal coordination sphere, as well as a tentative α-agostic linkage from these neopentyl CH_2 groups.[20] This was supported by the observation of upfield α-CH chemical shifts in the ^1H NMR spectra of complexes **21a** and **21b** along with diminished $^1J_{CH}$ couplings. The tungsten–alkylidyne in the structure of **21b** deviates only slightly from linearity ($\angle(W\equiv C\text{–}C) = 166.2(6)^\circ$) owing to the bulk of the adamantyl group. Slight slippage of the η^5-Cp ring was also noted with W–C distances ranging from 2.328(7) to 2.512(10) Å. Both complexes **21a** and **21b** tautomerized in benzene-d_6 solution at room temperature, the former more slowly than the latter (Equation (8)).



Scheme 5



Scheme 6



(8)

X = Cl, $CH_2{}^tBu$

21a: $K_{eq} = 1.05$ (1–2 weeks)

21b: $K_{eq} = 2.1$ (24 h)

The amido complex **22b** does not indicate any such tautomerization and also lacks any vestige of an α-CH agostic linkage, this being attributed to donation of the amido nitrogen lone pair into the empty orbital used for agostic bonding in complexes **21a** and **21b**. The complex **22c**, on the other hand, does isomerize to the *syn*- and *anti*-rotamers of an alkylidene–imido complex **36** (Equation (9)).

$$[W(\equiv CAd)Cl(NH^tBu)Cp]\ \mathbf{22c} \rightarrow [W(\equiv N^tBu)(=CHAd)ClCp]\ \mathbf{36} \qquad (9)$$

Systematic X-ray structure determinations of the complex salts **24a**–**24c** revealed a great deal about the interactions of these alkylidynes with their counterions.[22] Basic square-pyramidal W complexes with short W≡C bonds were common to all three structures. Differences occur in the interaction between the counterion and the ^{t}BuO oxygen atoms as well as the configuration of the ^{t}BuO groups in the solid state, which may lie *cisoid* or *transoid* to the alkylidyne ligand. Ambient temperature phosphorescence ($\tau \geq 1\ \mu s$) was directly impacted by these differing interactions, decreasing in energy in both solution and in the solid state in the order **24a** > **24b** > **24c** (Table 6). The solid-state structure of **24c** was particularly noteworthy given its propensity to produce two polymorphs (α or β), depending on whether crystallization occurs above or below −35 °C.

The X-ray structure of the phosphine–methylidyne complex **25** highlighted the potentially strong perturbation by the *trans*-ancillary ligand in these complexes.[23] Bending of the alkylidyne unit ($\angle(W\equiv C{-}H) = 162.3(39)^\circ$) was unexpected, given the absence of any kind of electrophilic acceptor group interacting with the W≡C bond. Although so-called crystal packing forces could account for the distortion, it was also suggested that the asymmetric binding of the dmpe groups caused the lifting of the degeneracy of W≡C π-orbitals leading in turn to the tilting of the alkylidyne-bound group. Other electronic effects were also considered such as the impact of the *trans*-^{t}Bu group. Subsequently, however, the reliability of X-ray measurements was called into question when a neutron diffraction experiment on compound **26** revealed no significant bending of the methylidyne group, and in the end these spurious X-ray data have been attributed to experimental artifacts.[24]

The complex **25** was synthesized subsequent to other phosphine–alkylidyne–tungsten complexes such as $[W(\equiv CH)Cl(PMe_3)_4]$ **37**, primarily as part of a study of the nature of M≡C–H bonds and M≡C vibrational behavior. The nature of the M≡C triple bond was re-evaluated through W≡C stretching frequency and force constant analysis using complex **37** and its deuterated W≡C–D and PMe_3-d_9 analogs as the primary models.[29,30] Raman vibrational measurements revealed a much lower stretching frequency (and hence force constant) for the W≡C–H system than related M≡C–R moieties with bulkier R groups. With negligible coupling between the W≡C and C–H stretches of the methylidyne ligand, a pseudodiatomic-oscillator approximation could be reliably employed in comparison of measured data with calculated values.

Complexes **27**–**31** were characterized by UV-VIS spectroscopy in addition to routine NMR/vibrational analysis.[25] As expected, n–π^* electronic transitions from the non-bonding $(d_{xy})^2$ orbital of the formally W(II) metal center shifted to lower energy as the hyperconjugated π-system was extended. Specifically, such red shifts were attributed to the lowering of the π^* LUMO energy, as the d_{xy} δ-symmetry orbital must necessarily be non-bonding with respect to the extended σ- and π-frameworks.

Alkylidyne complexes have presented a unique opportunity to produce one-dimensional polymeric materials with alternating organic and transition metal subunits. The structures of compounds **32a** and **32b** verified this as an exciting opening into optoelectronically active polymeric organometallics.[26] Both structures were composed of

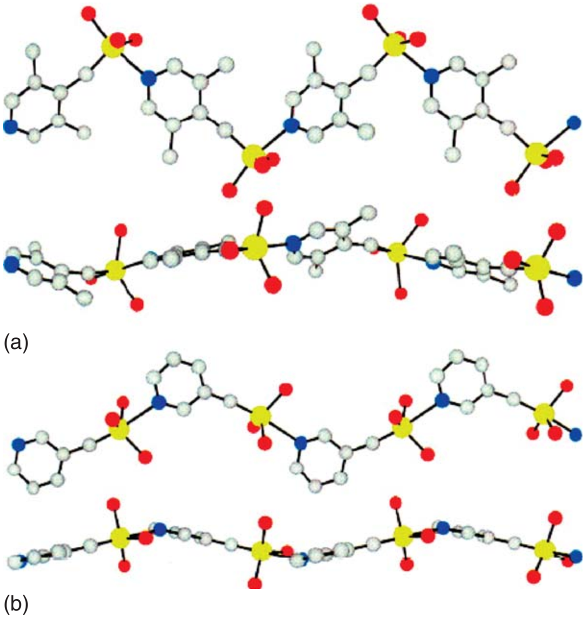


Figure 1 Face and edge views of tetrameric sections of (a) **32a** (b) one of the strands of **32b**·(1/2C_6H_6). Hydrogen atoms, *tert*-butyl groups, and interstitial C_6H_6 molecules have been omitted for clarity. Reprinted with permission from Pollagi, T. P.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 6051. © 1994 American Chemical Society.

approximately planar, zigzag W(≡Cpy)(O^tBu)$_3$ (py = pyridyl) units, joined head-to-tail by W←N(py) bonds (Figure 1). There is nevertheless a notable difference between these two materials in that **32a** is composed of a single type of polymer strand with a monomer composed of two crystallographically distinct W(≡Cpy)(O^tBu)$_3$ units within it, while **32b** also contains two types of W(≡Cpy)(O^tBu)$_3$ unit, but each within its own chain, that is, there are two distinct polymer strands. Furthermore, there is a significant variation in metal geometry with pseudo-square planar in **32a** and pseudo-trigonal bipyramidal in **32b** (Figure 2). Both materials are luminescent in the solid state (λ_{em} = 635 **32a** and 640 nm (**32b**)) and in solution at ambient temperatures, a surprising consequence of polymerization given the monomer complexes show no comparable optical properties. The emissions were attributed to LMCT states, which are rare in the solution phase for such organometallic complexes. Similarly zigzag-linked alkylidyne

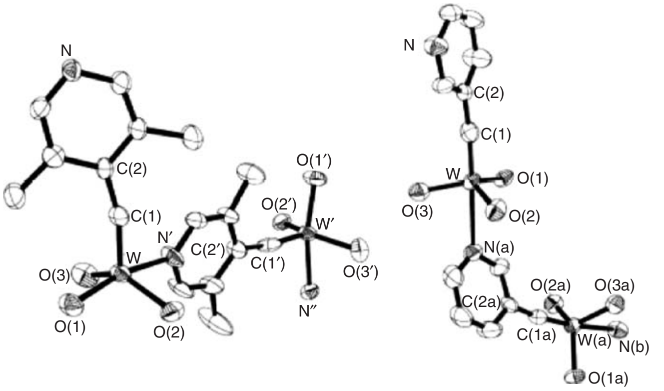


Figure 2 Structural skeletons of the asymmetric unit of **32a** (left) and a dimer unit of **32b**·(1/2C_6H_6) (right); an additional nitrogen atom is shown ligated to the tungsten terminus of each dimer. Reprinted with permission from Pollagi, T. P.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 6051. Copyright 1994 American Chemical Society.

complexes **33a** and **33b** have also been structurally characterized by X-ray crystallography, although the interalkylidyne W–N and W–S donor bonds appear to be weak (W–N 2.767(4) Å **33a**, W–S 3.079(2) Å (**33b**)) resulting in little distortion of the pyramidal W coordination geometry from the monomer structure.[27] In the case of complex **33a**, π-conjugation of the amino lone pair is disrupted by this solid-state interaction, although this appears to be not so much the case for the sulfide lone pair in **33b**.

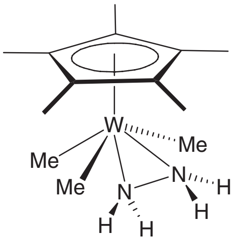
The dinuclear complexes **34** and **35** have been characterized by X-ray crystallography, although neither structure determination was of sufficient quality to confidently locate the hydrido ligands.[28] It was, however, firmly established that the alkylidyne ligand symmetrically bridged (W–μ-C–W 1.93(1) and 1.98(1) Å) the W–W single bond (2.658(1) Å) in **34**. The W–W single bond in complex **35** is somewhat more asymmetric (W–μ-C–W 1.72(4) and 2.01(2) Å).

5.09.8 Amino Complexes

The are few examples of amines as ligands in high oxidation state tungsten chemistry. One publication of note concerns the employment of hydrazine as a ligand in pentamethylcyclopentadienide complexes.

5.09.8.1 Synthesis

The synthesis of a series of paramagnetic hydrazine complexes [WMe$_3$(η^2-L$_2$)Cp*][OTf] (**38a**, L$_2$ = NH$_2$NH$_2$; **38b**, L$_2$ = NHMeNHMe; **38c**, L$_2$ = NH$_2$NHMe; **38d**, L$_2$ = NH$_2$NMe$_2$) was achieved by treatment of the complex [WMe$_3$(OTf)Cp*] directly with hydrazine or its *N*-methylated derivatives in Et$_2$O (Table 10).[31]



38a

5.09.8.2 Structure and Properties

An X-ray crystallographic study of single crystals of complex **38a** confirmed the η^2-nature of the hydrazine ligand bonding with very similar W–N bond lengths (2.131(7) and 2.174(7) Å).[31] One nitrogen lies in a roughly equatorial

Table 10 Synthesis of hydrazine W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
[WMe$_3$(OTf)Cp*] + NH$_2$NH$_2$ in Et$_2$O (25 °C)	[WMe$_3$(η^2-NH$_2$NH$_2$)Cp*] [OTf] **38a**	85	Orange	X-ray: W–N 2.131(7) Å and 2.174(7) Å, N–N 1.43(1) Å; ESR: ⟨*g*⟩ = 2.012	31
[WMe$_3$(OTf)Cp*] + NHMeNH-Me in Et$_2$O (25 °C)	[WMe$_3$(η^2-NHMeNHMe)Cp*] [OTf] **38b**	96	Orange	ESR: ⟨*g*⟩ = 2.004	31
[WMe$_3$(OTf)Cp*] + NH$_2$NHMe in Et$_2$O (25 °C)	[WMe$_3$(η^2-NH$_2$NHMe)Cp*] [OTf] **38c**	92	Orange-red	ESR: ⟨*g*⟩ = 2.009	31
[WMe$_3$(OTf)Cp*] + NH$_2$NMe$_2$ in Et$_2$O (−40 °C)	[WMe$_3$(η^2-NH$_2$NMe$_2$)Cp*] [OTf] **38d**	77	Orange	ESR: ⟨*g*⟩ = 1.992	31

plane with the methyl groups, while the other has an axial disposition. The single N–N bond order was confirmed from the N–N distance of 1.43(1) Å.

All the reported hydrazine complexes 38a–**d** were paramagnetic with an isotropic *g*-value close to that for the free electron, and all the salts were confirmed to be 1 : 1 electrolytes from conductivity measurements.

5.09.8.3 Reactions

Most notable for the complexes **38** was their deprotonation in THF or CH_2Cl_2 with bases such as NEt_3 or DBU. Citing complex 38a as the chief example, the initial product of deprotonation was believed to be $[WMe_3(\eta^2\text{-}NHNH_2)Cp^*][OTf]$ **39a**, which was not stable and underwent disproportionation affording $[WMe_3(\eta^1\text{-}NNH_2)Cp^*]$ **40**, $[W(\equiv NH)Me_3Cp^*]$ **41**, and free NH_3.[31] The same products may be produced, although not as cleanly, by reduction with Na/Hg in THF at −40 °C. Complex 38b, on the other hand, yielded the diazene complex $[WMe_3(\eta^2\text{-}NMeNMe)Cp^*]$ 42 along with $[WMe_3(\equiv NMe)Cp^*]$ 43 and methylamine upon deprotonation. An intermediate 39b similar to **39a** was nevertheless invoked in the mechanism (Scheme 7).

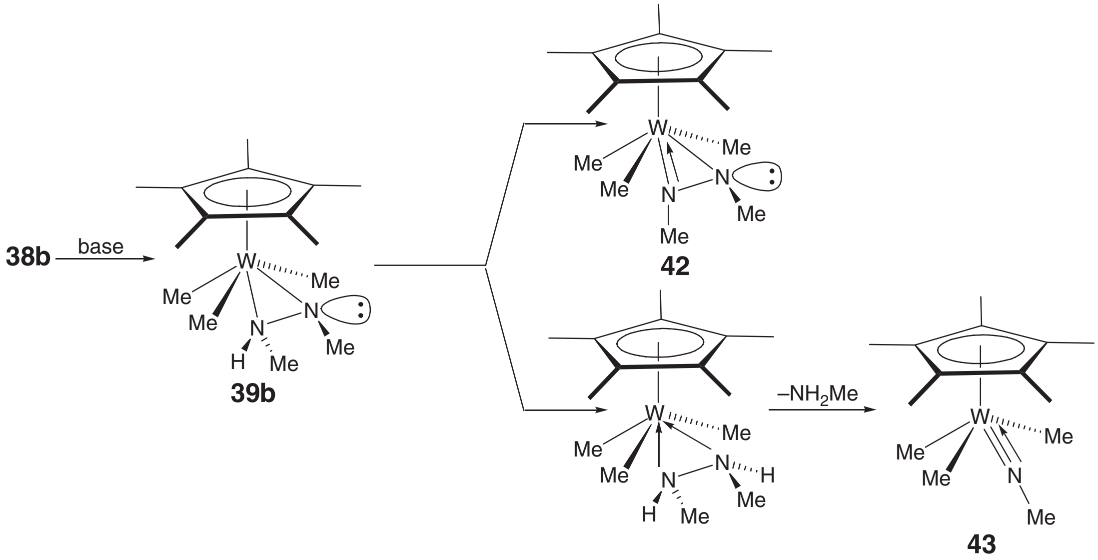
5.09.9 Amido Complexes

This area is dominated by the work of Schrock who has exploited the properties of chelating multidentate amido species. In particular, triamido–amine ligands have proved to be especially profitable. These complexes may be broadly divided into three classes depending on whether the terminal amido groups carry perfluoroalkyl, alkyl/aryl, or silyl groups.

5.09.9.1 Synthesis

Most of the amido complexes discussed here do not bear cyclopentadienide ligands, but we begin with one exception. The complex $[WCl(\kappa^3\text{-}2\text{-}NHC_6H_4NC_6H_4O\text{-}2')Cp^*]$ 44a was formed by reaction of $[WCl_4Cp^*]$ with 2-amino-2′-hydroxydiphenylamine ($2\text{-}NH_2C_6H_4NHC_6H_4OH\text{-}2'$).[32] Reaction was carried out in THF at −40 °C in the presence of 3 mol equiv. of NEt_3 to give the product as a green solid in good yield (85 %). A similar *all*-nitrogen donor version, $[WCl(\kappa^3\text{-}2\text{-}NHC_6H_4NC_6H_4NH\text{-}2')Cp^*]$ 44b was also synthesized in 76% yield as red crystals using the same procedure but with the ligand 2,2′-diaminodiphenylamine.

The chloro and iodo tungsten complexes $[WX(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)]$ (45a, X = Cl; 45b, X = I) comprising the *tris*(perfluorophenyl)triamido–amine ligand may be synthesized by treatment of $[WCl_4(SEt_2)_2]$ with

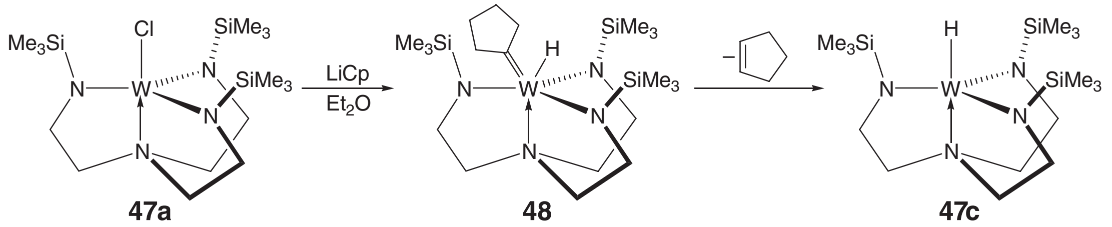


Scheme 7

$N\{(CH_2)_2NHC_6F_5\}_3$ to yield **45a**, which may be converted easily into **45b** by reaction with Me_3SiI (Table 11).[33,34] Aryl derivatives $[WX(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)]$ (**45c**, X = Ph; **45d**, X = C_6H_3Me-3,5) may be synthesized by reaction of **45b** with the appropriate LiAr reagent.[34] Complexes comprising the triamido–amine ligand, but with the amido nitrogens bearing simple aryl rather than perfluoroaryl groups, were reported sometime later. Thus the complexes $[WCl(\kappa^4\text{-}N\{(CH_2)_2NAr\}_3)]$ (**46a**, Ar = Ph; **46b**, Ar = C_6H_4F-4; **46c**, Ar = $C_6H_4{}^tBu$-4; **46d**, Ar = $C_6H_3Me_2$-3,5; **46e**, Ar = $C_6H_3Ph_2$-3,5) may be synthesized by reaction of the basic starting complex $[WCl_4(DME)]$ with the tetraamine ligands $N\{(CH_2)_2NHAr\}_3$ followed by addition of 3 mol equiv. of the Grignard reagent, MeMgCl.[35] In the synthesis of complex **46c**, if 4 mol equiv. of MeMgCl are used, then the metal chloro ligand is also substituted to give the methyl complex $[WMe(\kappa^4\text{-}N\{(CH_2)_2NC_6H_4{}^tBu\text{-}4\}_3)]$ **46f**, albeit in poor yield. Silyl versions of these complexes have also been reported, synthesized from the same basic starting materials ($[WCl_4(THF)_2]$ or $[WCl_4(DME)]$) and the trilithium salts of the ligands. Most notably, the complex $[WCl(\kappa^4\text{-}N\{(CH_2)_2NSiMe_3\}_3)]$ **47a** has exemplified these compounds and has been most heavily studied in terms of its reactivity.[36] From **47a**, the methyl complex **47b** may be readily isolated by reaction with LiMe.[36] Through a somewhat indirect route, the hydrido complex **47c** may be isolated by treatment of **47a** with LiCp, which produces the alkylidene complex $[WH({=}CC_4H_8)(\kappa^4\text{-}N\{(CH_2)_2NSiMe_3\}_3)]$ **48**.[37] Decomposition of complex **48** in C_6D_6 at 45 °C yielded complex **47c** quantitatively, purportedly via β-elimination from a cyclopentyl intermediate (Scheme 8).

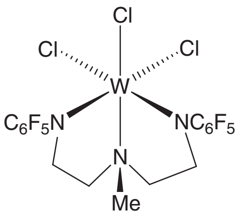
Table 11 Synthesis of triamido–amine W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[WCl_4(SEt_2)_2] + N\{(CH_2)_2NHC_6F_5\}_3$ + 3 mol equiv. NEt_3 in THF (25 °C)	$[WCl(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)]$ **45a**	63	Orange	$E_{red} = -2.39$ V (irrev.) versus Fc, $E_{ox} = -0.04$ V versus Fc (quasi rev.)	33
45a + Me_3SiI in CH_2Cl_2 (25 °C)	$[WI(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)]$ **45b**	97	Orange		34
45b + LiPh in toluene/THF (25 °C)	$[WPh(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)]$ **45c**	59	Orange		34
45b + LiC_6H_3Me-3,5 in toluene/THF (25 °C)	$[W(C_6H_3Me\text{-}3,5)(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)]$ **45d**	81	Burgundy		34
$[WCl_4(DME)]$ + (i) $N\{(CH_2)_2NHAr\}_3$ in THF (65 °C), (ii) + 3MeMgCl in THF (−35 °C)	$[WCl(\kappa^4\text{-}N\{(CH_2)_2NPh\}_3)]$ **46a**	24	Orange		35
	$[WCl(\kappa^4\text{-}N\{(CH_2)_2NC_6H_4F\text{-}4\}_3)]$ **46b**	28	Red		35
	$[WCl(\kappa^4\text{-}N\{(CH_2)_2NC_6H_4{}^tBu\text{-}4\}_3)]$ **46c**	43			35
	$[WCl(\kappa^4\text{-}N\{(CH_2)_2NC_6H_3Me_2\text{-}3,5\}_3)]$ **46d**	41			35
	$[WCl(\kappa^4\text{-}N\{(CH_2)_2NC_6H_3Ph_2\text{-}3,5\}_3)]$ **46e**	35			35
$[WCl_4(DME)]$ + (i) $N\{(CH_2)_2NHAr\}_3$ in THF (65 °C), (ii) + 4MeMgCl in THF (−35 °C)	$[WMe(\kappa^4\text{-}N\{(CH_2)_2NC_6H_4{}^tBu\text{-}4\}_3)]$ **46f**	22	Orange		35
$[WCl_4(THF)_2]$ or $[WCl_4(DME)] + Li_3N\{(CH_2)_2NSiMe_3\}_3$ in THF (25 °C)	$[WCl(\kappa^4\text{-}N\{(CH_2)_2NSiMe_3\}_3)]$ **47a**	18	Yellow		36
47a + LiMe in Et_2O (25 °C)	$[WMe(\kappa^4\text{-}N\{(CH_2)_2NSiMe_3\}_3)]$ **47b**	86	Orange	$\mu = 2.5\mu_B$	36
48 in C_6D_6 (45 °C)	$[WH(\kappa^4\text{-}N\{(CH_2)_2NSiMe_3\}_3)]$ **47c**	87	Orange		37
47a + LiCp in Et_2O (25 °C)	$[WH({=}CC_4H_8)(\kappa^4\text{-}N\{(CH_2)_2NSiMe_3\}_3)]$ **48**	99	Yellow	X-ray: W=C 1.97(1) Å; ^1H NMR: δ19.4 (WH)	37



Scheme 8

A related diamido–amine complex salt $[NHEt_3][WCl_3(\kappa^3\text{-}NMe\{(CH_2)_2NC_6F_5\}_2)]$ **49** has been isolated in 60% yield using the ligand $[NMe\{(CH_2)_2NC_6F_5\}_2]^{2-}$.[38]



49

In dinuclear tungsten amido systems, a useful synthon has been the complex $[1,2\text{-}W_2Cl_2(NMe_2)_4]$. In work valuable from the perspective of hydrodesulfurization of fuels, the complexes $[1,2\text{-}W_2(\sigma\text{-}2\text{-}X)_2(NMe_2)_4]$ (**50a**, X = thienyl; **51**, X = furyl) have been isolated by reaction of $[1,2\text{-}W_2Cl_2(NMe_2)_4]$ with the thienyl reagent $2\text{-}LiC_4H_3S$ or with the analogous furyl reagent $2\text{-}LiC_4H_3O$ (Equation (10)).[39]

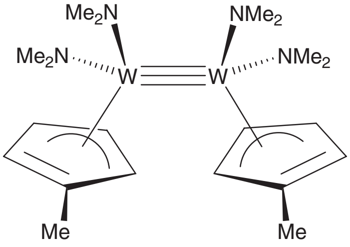
$$[1,2\text{-}W_2Cl_2(NMe_2)_4] + 2[2\text{-}LiX] \xrightarrow[\text{toluene/THF or } Et_2O]{22\,°C} [1,2\text{-}W_2(\sigma\text{-}2\text{-}X)_2(NMe_2)_4] \qquad (10)$$
$$(X = 2\text{-}C_4H_3S,\ 2\text{-}C_4H_3O)$$

Further thienyl systems have been isolated using this method based on the reagents 2-lithiobenzothiophene, 3-lithiothiophene, 2-lithio-5-methylthiophene, all yielding orange crystalline complexes **50b–d** (Table 12).

Table 12 Synthesis of amido–thienyl, –furyl, and –cyclopentadienide W_2 complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[1,2\text{-}W_2Cl_2(NMe_2)_4] + 2\text{-}LiC_4H_3S$ in toluene/THF (25 °C)	$[1,2\text{-}W(\sigma\text{-}2\text{-}C_4H_3S)_2(NMe_2)_4]$ **50a**	71	Orange-red	X-ray: W≡W 2.2895(4) Å, W–C 2.138(15) Å	39
	$[1,2\text{-}W(\sigma\text{-}2\text{-}C_8H_7S)_2(NMe_2)_4]$ **50b**	53	Orange-yellow		39
	$[1,2\text{-}W(\sigma\text{-}3\text{-}C_4H_3S)_2(NMe_2)_4]$ **50c**	42	Orange-yellow		39
	$[1,2\text{-}W\{\sigma\text{-}2,5\text{-}C_4H_2(Me)S\}_2(NMe_2)_4]$ **50d**	75	Orange-yellow		39
$[1,2\text{-}W_2Cl_2(NMe_2)_4] + 2\text{-}LiC_4H_3O$ in toluene/Et_2O (25 °C)	$[1,2\text{-}W(\sigma\text{-}2\text{-}C_4H_3O)_2(NMe_2)_4]$ **51**	64	Orange-yellow		39
$[1,2\text{-}W_2Cl_2(NMe_2)_4] + LiMeCp$ in Et_2O (25 °C)	$[W_2(\eta^3\text{-}MeCp)_2(NMe_2)_4]$ **52a**	55	Yellow	X-ray: W≡W 2.345(1) Å	40
$[1,2\text{-}W_2Cl_2(NMe_2)_4] + Li_2[Me_2Si(\eta^3\text{-}C_5H_4)_2]$ in THF (25 °C)	$[W_2\{Me_2Si(\eta^3\text{-}C_5H_4)_2\}(NMe_2)_4]$ **52b**	54	Orange		40

Reactions of [1,2-$W_2Cl_2(NMe_2)_4$] have also been carried out with lithium salts of the anions $MeCp^-$ and $Me_2Si(C_5H_4)_2^{2-}$ to afford the complexes [$W_2(\eta^3\text{-}X)_2(NMe_2)_4$] (**52a**, X = MeCp; **52b**, $(\eta^3\text{-}X)_2 = Me_2Si(C_5H_4)_2$), where two η^3-C_5 rings coordinate each metal center (Table 12).[40]



52a

5.09.9.2 Structure and Properties

The Cp* complex **44a** was not characterized by X-ray crystallography, but being paramagnetic, gave rise to an ESR signal ($\langle g \rangle = 1.93$), confirming the presence of a single unpaired electron.[32] This was consistent with a d^1-W(V) center. Complex **44b** was surprisingly air stable with an ESR signal at $\langle g \rangle = 1.94$, again confirming the single unpaired electron.

The structures of the triamido–amine complexes **45–47** are, almost without exception, trigonal bipyramidal complexes. They are usually paramagnetic owing to the degeneracy of d_{xy} and d_{yz} orbitals and result from a high-spin d^2-ground state.[33–37] All measured NMR spectra showed prominent broadening of resonances with large paramagnetic shifts. Solid-state susceptibility measurements on complexes **45a** and **47a–47c** revealed an expected decrease in magnetic moment from 300 K to 5 K, thanks to pronounced heavy metal spin–orbit coupling.[34,41] Cyclic voltammetry measurements for complexes **45** revealed an irreversible reduction at $E_p = -2.39$ to -2.62 V and quasi-reversible oxidations at $E_{1/2} \approx -0.1$ V. An X-ray structure determination for complex **48** revealed the nature of the cyclopentylidene ligand (W=C 1.97(1) Å) and although the hydrido position was located in difference Fourier synthesis maps, it did not survive refinement.[37] An NMR resonance for the latter was, however, detected at δ 19.4.

An X-ray structure determination for the diamido–amine complex **49** verified the *fac*-Cl_3 nature of the approximately octahedral complex.[38]

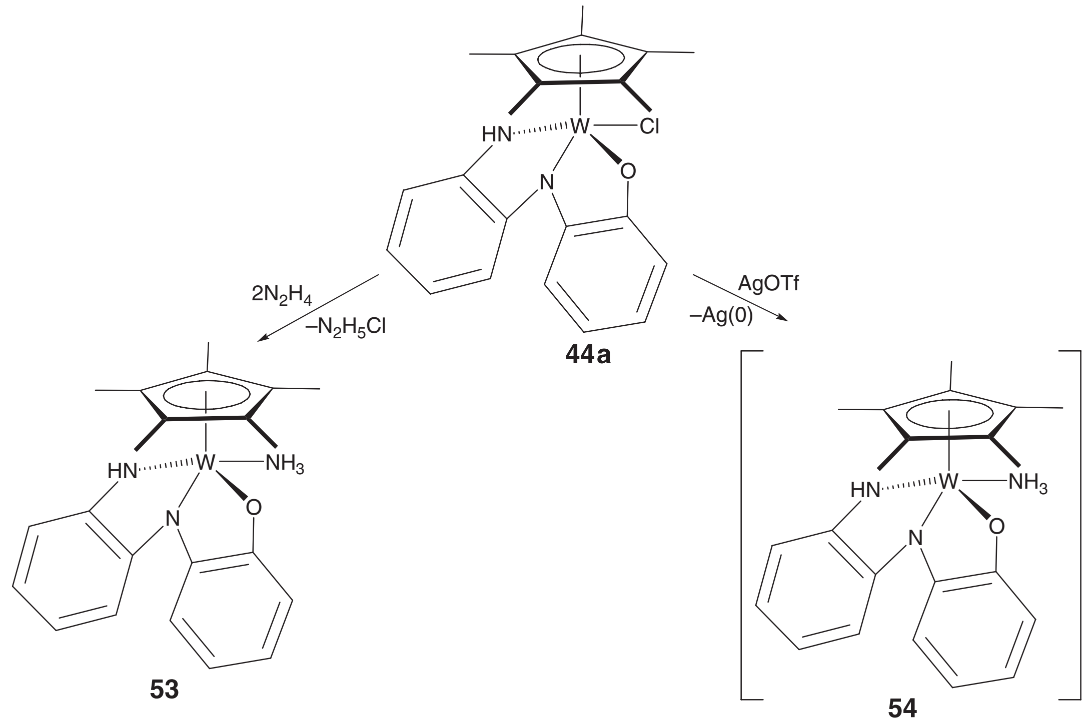
The structure of complex **50a** was determined by X-ray crystallography, and the bonding of the thienyl 2-C carbon atoms to each metal center (W–C 2.138(15) Å) in the centrosymmetric structure was clearly revealed, with no evidence of tungsten–sulfur contacts (W···S 3.3 Å).[39] In solution, these complexes exist as a mixture of *anti*- and *gauche*-rotamers with rapid rotation on the NMR timescale about the W–C bonds bound to the ethane-like $CN_2W{\equiv}WN_2C$ core. The η^3-binding of the MeCp rings in complex **52a** was confirmed by X-ray structure determination, which showed the positioning of the MeCp methyl groups distal to the W≡W bond, and resulting in a virtual C_2-molecular symmetry in the solid state.[40]

5.09.9.3 Reactions

Complex **44a** could be derivatized in a number of ways including reduction with hydrazine to replace the chloro with an ammine ligand to give complex **53**, and oxidation to give a cationic complex **54** (Scheme 9).[32]

Complex **44b** has somewhat more extensive chemistry giving complexes **55–61**, illustrated in Scheme 10.

The perfluoro–triamido–amine complexes have been demonstrated to have a rich chemistry. In particular, the complexes **45a** and **45b** react with primary lithium alkyl reagents, $LiCH_2R$, to afford alkylidyne products [$W({\equiv}CR)(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)$] (**62a**, R = Me; **62b**, R = ^{n}Pr; **62c**, R = $SiMe_3$; **62d**, R = ^{t}Bu; **62e**, R = Ph) (Scheme 11).[34] Complex **45a** also reacts with cyclopropyllithium to afford the basic methylidyne complex [$W({\equiv}CH)(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)$] **62f**, with reaction presumably taking place via ethylene loss (Scheme 11). Reaction of **45a** or **45b** with pyridine-*N*-oxide afforded the octahedral oxo complex [$WX({=}O)(\kappa^4\text{-}N\{(CH_2)_2NC_6F_5\}_3)$] **63**.

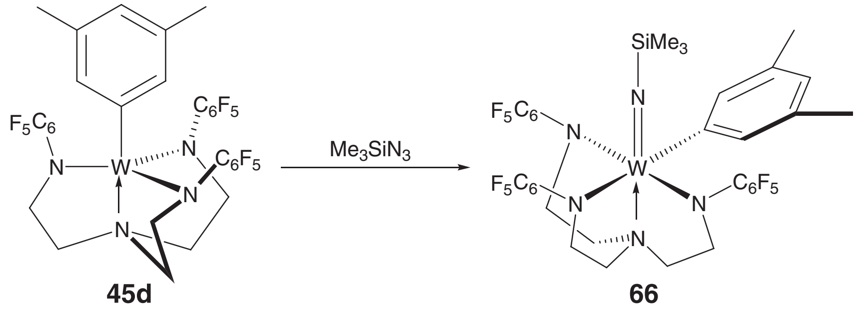


Scheme 9

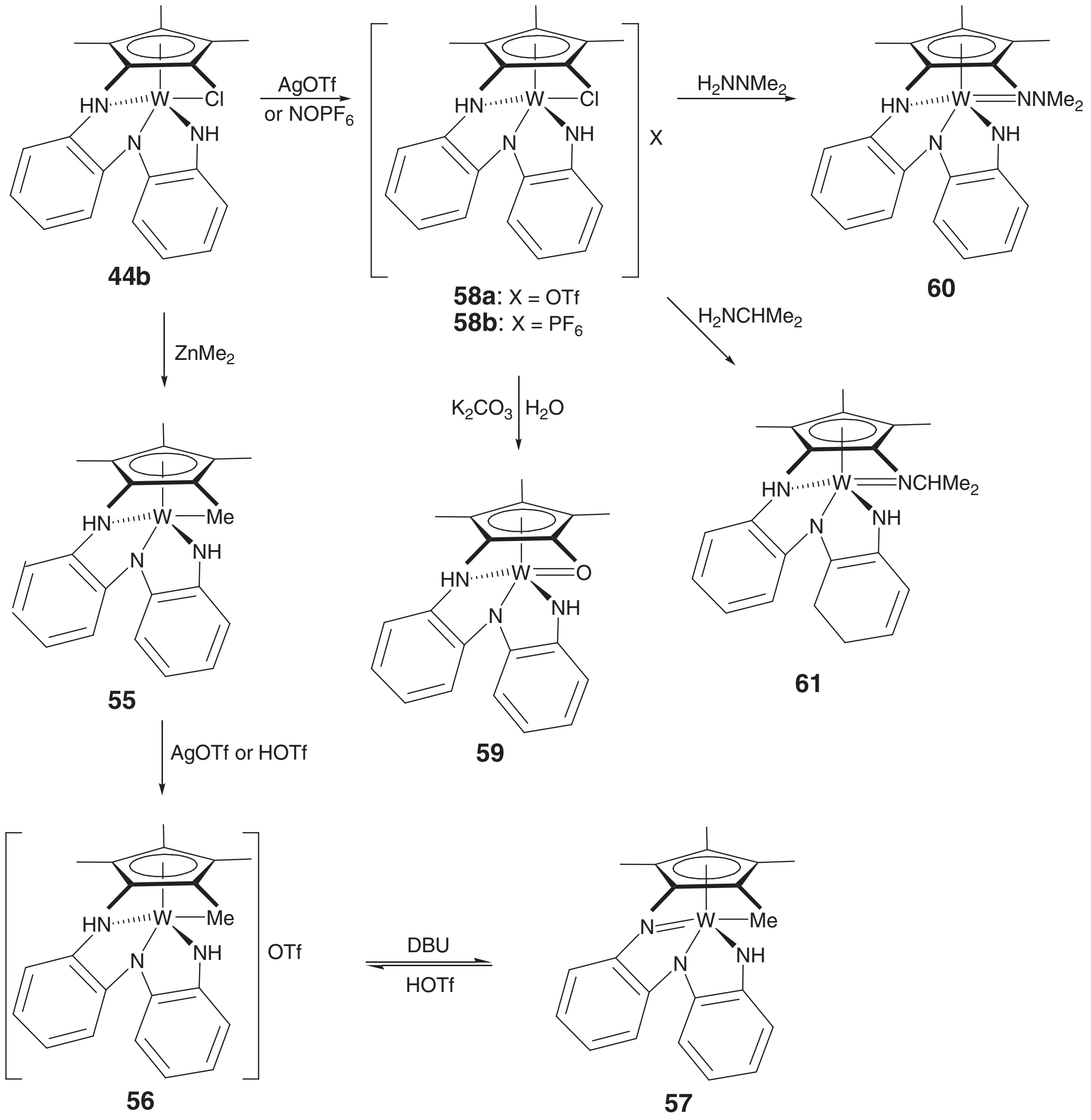
The derivative aryl complexes **45c** and **45d** have reacted with hydrogen to yield the trihydrido complex $[\mathrm{WH_3}(\kappa^4\text{-N}\{(\mathrm{CH_2})_2\mathrm{NC_6F_5}\}_3)]$ **64** (Equation (11)).[34]

$$[\mathrm{WAr}(\kappa^4\text{-N}\{(\mathrm{CH_2})_2\mathrm{NC_6F_5}\}_3)]\ \mathbf{45c}\text{ and }\mathbf{45d} \xrightarrow[\text{toulene, 40 °C}]{3.0\text{ atm H}_2} [\mathrm{WH_3}(\kappa^4\text{-N}\{(\mathrm{CH_2})_2\mathrm{NC_6F_5}\}_3)]\ \mathbf{64} \tag{11}$$

The ^{1}H NMR spectrum of **64** displayed an expected resonance at $\delta 11.1$ with strong coupling to tungsten ($J_{\mathrm{HW}} = 25$ Hz) and most importantly, the classical hydride nature of the complex was indicated by relaxation time measurements ($T_1 = 344 \pm 5$ min). These two aryl complexes also reacted with CO to give the η^2-acyl complexes $[\mathrm{W}\{\eta^2\text{-C(O)Ar}\}(\kappa^4\text{-N}\{(\mathrm{CH_2})_2\mathrm{NC_6F_5}\}_3)]$ (**65a**, Ar = Ph; **65b**, Ar = $\mathrm{C_6H_3Me}$-3,5).[42] Complex **45d** also reacted with trimethylsilyl azide to afford the C_s-octahedral imido complex $[\mathrm{W}({=}\mathrm{NSiMe_3})(\mathrm{C_6H_3Me}\text{-3,5})(\kappa^4\text{-N}\{(\mathrm{CH_2})_2\mathrm{NC_6F_5}\}_3)]$ **66**, the product of nitrogen atom transfer (Equation (12)).[34]



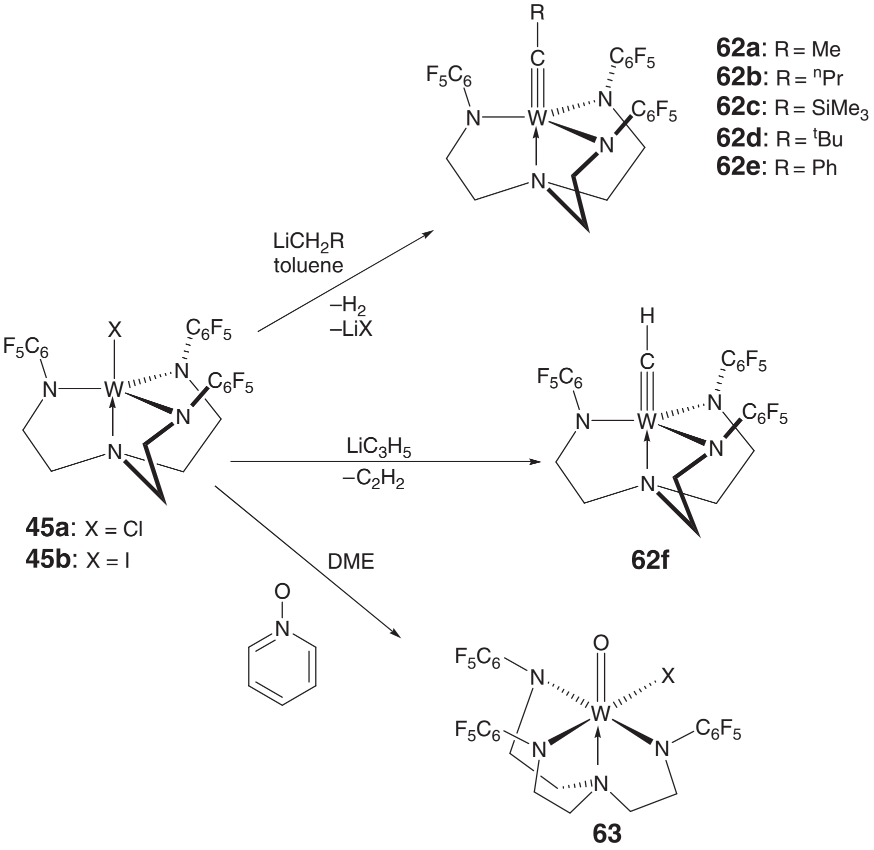
(12)



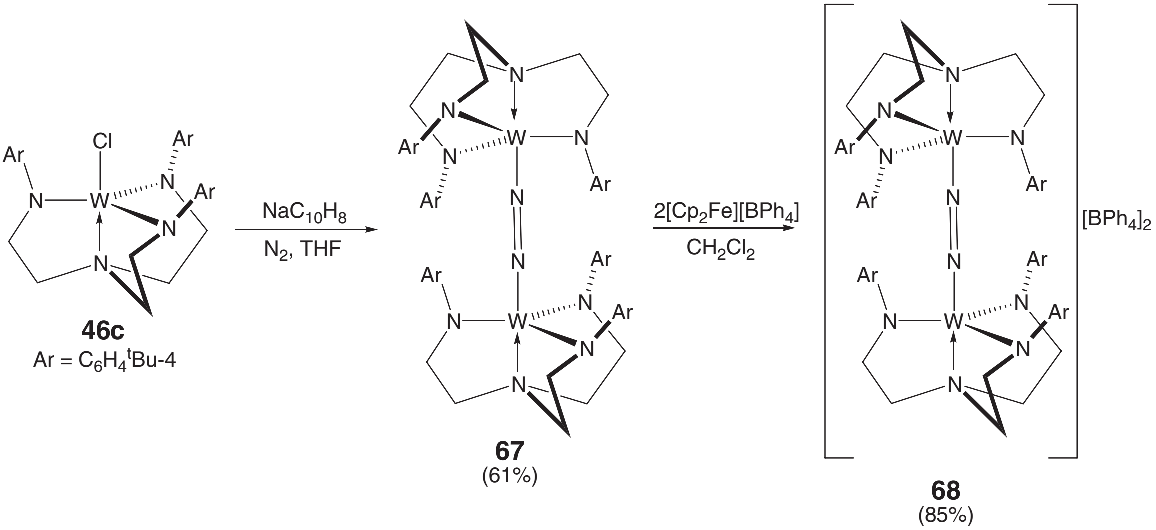
Scheme 10

The second class of triamido–amino complex, the non-perfluoro systems **46**, have also had their chemistry exploited. Most interesting is the reduction of complex **46c** with sodium naphthalenide under an N_2 atmosphere in THF to afford the bridged dinitrogen complex **67**, which may itself be oxidized to the tune of two electrons to yield the complex salt **68** (Scheme 12).[43] The latter complex may also be observed electrochemically by sequential one-electron oxidations of **67** at $E_{1/2} = -0.75$ and -1.63 V. Complex **67** also shows a reversible reduction at $E_{1/2} = -3.09$ V, demonstrating that the W–N bonds of the dinitrogen bridge are stable toward reduction even at this most negative potential.

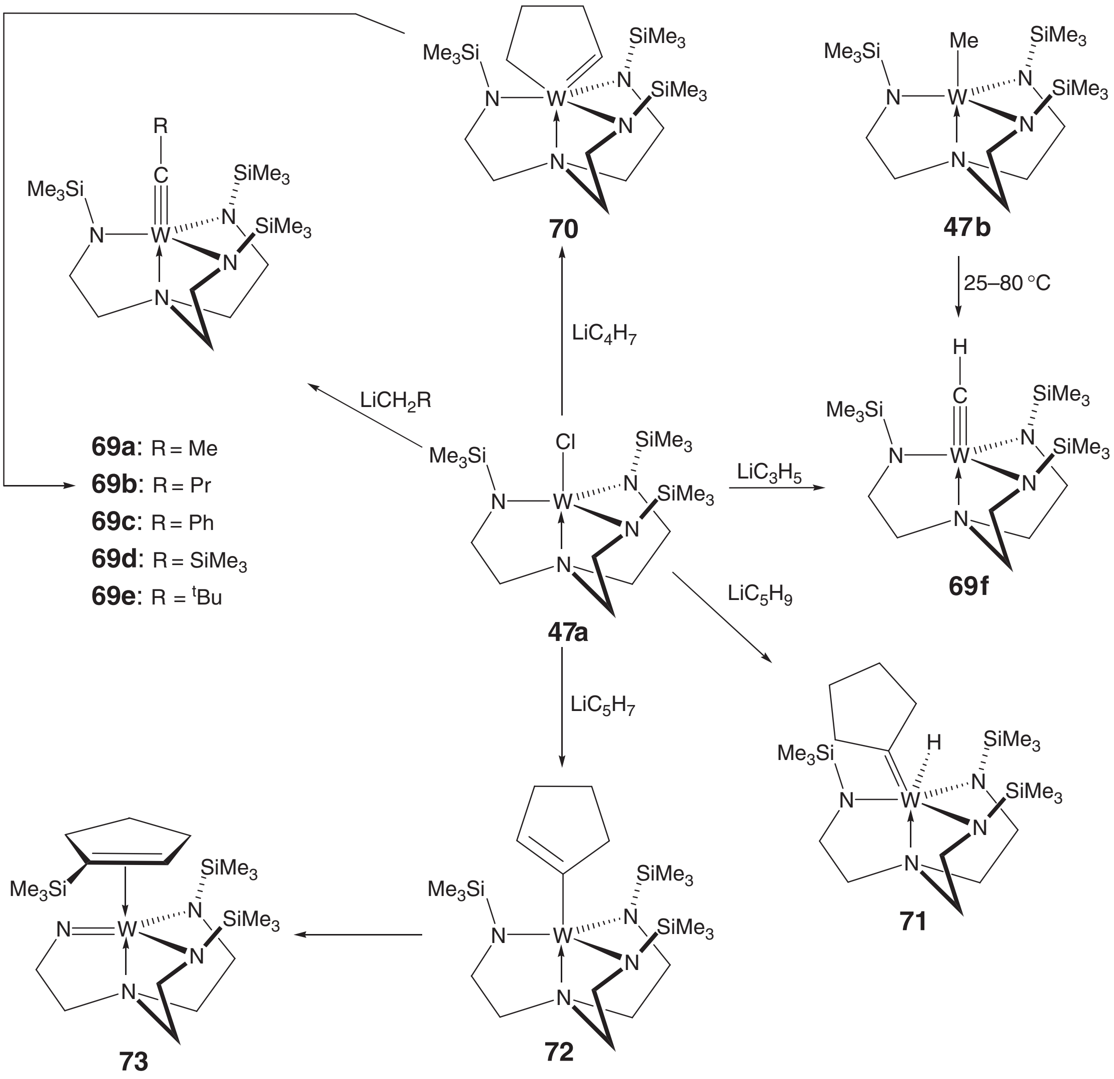
Many of the reactions of the silyl systems **47** mirror those of their perfluoro counterparts, **45**, giving compounds **69**–**73** (Scheme 13). Normally the integrity of the triamido–amine ligand is maintained, although, interestingly, the complex **72** decomposes at room temperature via N–Si bond cleavage, transferring the $SiMe_3$ group to the cyclopentene moiety to give complex **73**.[41] Reactions of complex **47c** have also been described.[44] In particular, insertions of alkynes have been observed to afford metallacyclopropene complexes **74** (Equation (13)).



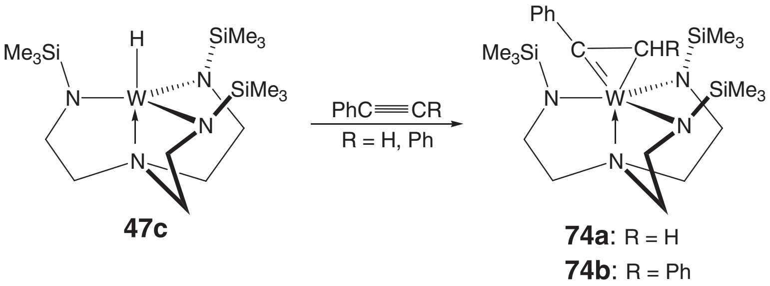
Scheme 11



Scheme 12

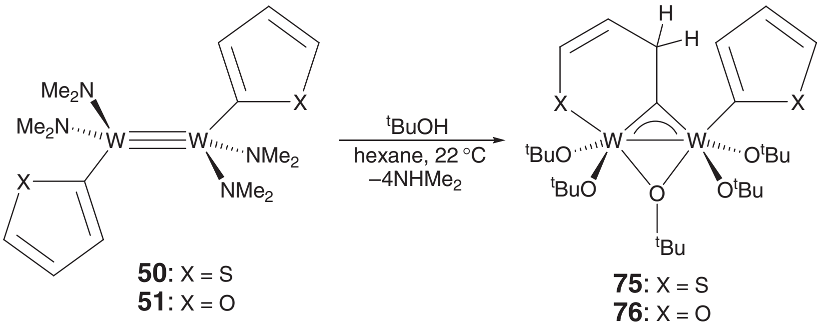


Scheme 13



(13)

The most pertinent reactions of the ditungsten complexes **50a** and **51** include ring opening of the thienyl and furyl ligands as a consequence of reaction with ᵗBuOH. Thus the complexes [$W_2(\mu\text{-}CCH_2CHCHX)(\sigma\text{-}2\text{-}C_4H_3S)(O^tBu)_5$] (**75**, X = S; **76**, X = O), where all the amido ligands are ultimately expelled, have been isolated and structurally characterized (Equation (14)).[39] Interestingly, no ring opening was observed to occur under similar conditions with the related complexes **50b–50c**.



50: X = S
51: X = O

75: X = S
76: X = O

(14)

5.09.10 Imido Complexes

Imido complexes have proved to be rather useful tools to the organic synthetic chemist, and in combination with alkylidene ligands their utility in all manner of catalyzed processes from metathesis to polymerization has been a hallmark of applied organometallic chemistry. Aspects of organic synthesis using these complexes have been dealt with elsewhere in this collection, so this section focuses on the most important selection of original reports of imido and imido–alkylidene species.

5.09.10.1 Synthesis

The phosphine–imido complexes $[WCl_2({=}NAr)(PR_3)_3]$ (**77a**, $PR_3 = PEt_2Ph$, $Ar = C_6H_3Me_2$-2,6; **78a**, $PR_3 = P(OMe)_3$, Ar = Ph; **78b**, $Ar = C_6H_3Me_2$-2,6; **78c**, $Ar = C_6H_3{}^iPr_2$-2,6) have been isolated by reduction with sodium amalgam of the starting tetrachloro–imido tungsten complexes $[WCl_4({=}NAr)]$ in the presence of the respective phosphine or phosphite (Table 13).[45] Complex **77a**, in particular, offered the advantage of stability over a previously synthesized system $[WCl_2({=}NPh)(PMePh_2)_3]$ **77b** and its $={NC_6H_3R_2}$-2,6 (R = Me, ^{i}Pr) derivatives, which comprise a somewhat bulkier, less powerful donor phosphine.

Using a similar methodology, bis(imido) species have also been reported with the tetrahedral complexes $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)_2(PR_3)_2]$ (**79a**, $PR_3 = PMe_2Ph$; **79b**, $PR_3 = PMePh_2$) being produced by reduction of $[WCl_2({=}NC_6H_3{}^iPr_2\text{-}2,6)_2(DME)]$ by sodium amalgam, again in the presence of the appropriate phosphine (Table 14).[46] Further related tetrahedral silyl and germyl bis(imido) complexes have been reported by Tilley and co-workers, with the formation of $[WCl({=}NC_6H_3{}^iPr_2\text{-}2,6)_2\{X(SiMe_3)_3\}]$ (**80a**, X = Si; **80b**, X = Ge) using the same starting material.[47] The principal group 14 reagent is the lithium salt of the $[X(SiMe_3)]^-$ anion.

The synthesis of valuable precursors to alkylidene-imido complexes, $[WCl_2({=}NAr)\{OCMe(CF_3)_2\}_2(THF)]$ (**81a**, Ar = Ph; **81b**, $Ar = C_6H_3Me_2$-2,6; **81c**, $Ar = C_6H_3{}^iPr_2$-2,6) (Table 15) have been described by reaction of the starting material $[WCl_4({=}NAr)]$ with an alkoxide (Equation (15)).[48] This work was driven by the lack of suitability of the complex $[WCl_4({=}NAr)]$ itself as such a starting material in reactions with phosphoranes (*vide infra*).

Table 13 Synthesis of phosphine–imido W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[WCl_4({=}NAr)] + Na(Hg) + PR_3$ in benzene (25 °C)	$[WCl_2({=}NC_6H_3Me_2\text{-}2,6)(PEt_2Ph)_3]$ **77a**	53	Tan		45
	$[WCl_2({=}NPh)\{P(OMe)_3\}_3]$ **78a**	80	Purple		45
	$[WCl_2({=}NC_6H_3Me_2\text{-}2,6)\text{-}\{P(OMe)_3\}_3]$ **78b**	80	Grey		45
	$[WCl_2({=}NC_6H_3{}^iPr_2\text{-}2,6)\text{-}\{P(OMe)_3\}_3]$ **78c**	78	Purple-grey	X-ray: W=N 1.767(3) Å, ∠(W=N–C) = 173.5(2)°	45

Table 14 Synthesis of bis(imido) W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[WCl_2({=}NC_6H_3{}^iPr_2\text{-}2,6)_2(DME)] + Na(Hg) + PR_3$ in THF (25 °C)	$[W({=}NC_6H_3{}^iPr_2\text{-}2,6)_2(PMe_2Ph)_2]$ **79a**	48	Purple		46
	$[W({=}NC_6H_3{}^iPr_2\text{-}2,6)_2(PMePh_2)_2]$ **79b**	45	Red	X-ray: W═N 1.805(5) Å and 1.793(5) Å, ∠(W═N–C) = 166.0(5)° and 172.8(5)°, ∠(N═W═N) = 128.8(2)°	46
$[WCl_2({=}NC_6H_3{}^iPr_2\text{-}2,6)_2(DME)] + [Li(THF)_3][X(SiMe_3)]$ in Et_2O (−78 °C)	$[WCl({=}NC_6H_3{}^iPr_2\text{-}2,6)_2\{Si(SiMe_3)_3\}]$ **80a**	–	Orange	Not crystallized; ^{29}Si NMR: δ −2.0, −22.9	47
	$[WCl({=}NC_6H_3{}^iPr_2\text{-}2,6)_2\{Ge(SiMe_3)_3\}]$ **80b**	–	Orange	Not crystallized; ^{29}Si NMR: δ4.43	47

Table 15 Synthesis of alkoxido–imido W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
$[WCl_4({=}NAr)] + 2LiOCMe(CF_3)_2$ in THF (0 °C)	$[WCl_2({=}NPh)\{OCMe(CF_3)_2\}_2(THF)]$ **81a**	94	Orange		48
	$[WCl_2({=}NC_6H_3Me_2\text{-}2,6)\{OCMe(CF_3)_2\}_2(THF)]$ **81b**	93	Red		48
	$[WCl_2({=}NC_6H_3{}^iPr_2\text{-}2,6)\{OCMe(CF_3)_2\}_2(THF)]$ **81c**	83	Red		48
$[WCl_4({=}NC_6H_3Me_2\text{-}2,6)] + 2LiOCMe_2CF_3$ in THF/Et_2O (−40 °C)	$[WCl_2({=}NC_6H_3Me_2\text{-}2,6)(OCMe_2CF_3)_2]$ **81d**	90	Orange	Precursor to dimer **94**	49

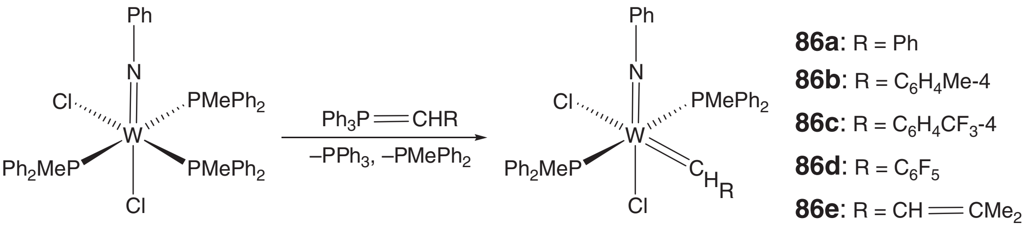
$$[WCl_4({=}NAr)] + 2LiOCMe(CF_3)_2 \xrightarrow[-2LiCl]{THF} [WCl_2({=}NAr)\{OCMe(CF_3)_2\}_2(THF)]\ \mathbf{81} \tag{15}$$

$$Ar = Ph,\ C_6H_3Me_2\text{-}2,6,\ C_6H_3{}^iPr_2\text{-}2,6$$

A related dialkoxido species can be produced by reaction of $[WCl_4({=}NC_6H_3Me_2\text{-}2,6)]$ with 2 mol equiv. of the alkoxido reagent $LiOCMe_2CF_3$ to afford the complex $[WCl_2({=}NC_6H_3Me_2\text{-}2,6)(OCMe_2CF_3)_2]$ **81d**.[49]

Some of these basic imido complexes have been employed as precursors to alkylidene–imido complexes. Thus the complexes **77a** and **78** react with 3,3-diphenylcyclopropene or 4,8-dioxaspiro[2.5]oct-1-ene to form the alkylidene ligand in complexes **82–85** (Table 16) with loss of one or two of the phosphine/phosphite ligands (Scheme 14).[45] In some cases, the intermediate alkene complexes were also isolated and characterized.

Complex **77b** has also been successfully employed as a precursor to the alkylidene–imido complexes through reaction with phosphoranes $Ph_3P{=}CHR$ to afford a range of products, a selection of which includes $[WCl_2({=}NPh)({=}CHR)(PMePh_2)_2]$ (**86a**, R = Ph; **86b**, R = C_6H_4Me-4; **86c**, R = $C_6H_4CF_3$-4; **86d**, R = C_6F_5; **86e**, R = CH═CMe$_2$) (Equation (16)).[48]

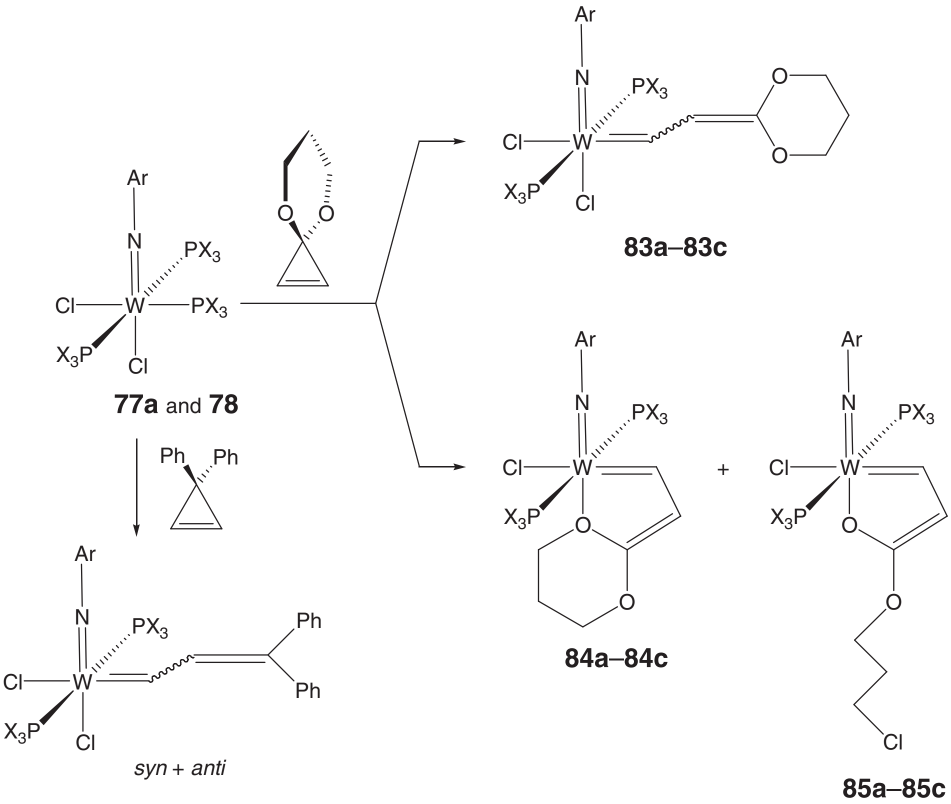


77b

(16)

Table 16 Synthesis of alkylidene–imido W complexes

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
77a + $\mathrm{C_3H_2Ph_2}$-3,3 in $\mathrm{Et_2O}$ (25 °C)	$[\mathrm{WCl_2({=}NC_6H_3Me_2\text{-}2,6)({=}CHCH{=}CPh_2)(PEt_2Ph)_2}]$ **82a**	80	Yellow	^{13}C NMR: W=C δ 271.7	45
78b + $\mathrm{C_3H_2Ph_2}$-3,3 in (i) $\mathrm{Et_2O}$, (ii) $\mathrm{CD_2Cl_2}$ (25 °C)	$[\mathrm{WCl_2({=}NC_6H_3Me_2\text{-}2,6)({=}CHCH{=}CPh_2)\{P(OMe)_3\}_2}]$ **82b**	–	–	^{13}C NMR: W=C δ 276.6 (major rotamer), 283.7 (minor)	45
78c + $\mathrm{C_3H_2Ph_2}$-3,3 in benzene (80 °C)	$[\mathrm{WCl_2({=}NC_6H_3{}^iPr_2\text{-}2,6)({=}CHCH{=}CPh_2)\{P(OMe)_3\}_2}]$ **82c**	72	Orange	^{13}C NMR: W=C δ 276.8	45
77b + $\mathrm{Ph_3P{=}CHR}$ in benzene (25 °C)	$[\mathrm{WCl_2({=}NPh)({=}CHPh)(PMePh_2)_2}]$ **86a**	61	Yellow-brown	^{13}C NMR: W=C δ 290.9	48
	$[\mathrm{WCl_2({=}NPh)({=}CHC_6H_4Me\text{-}4)(PMePh_2)_2}]$ **86b**	58	Brown-orange	X-ray: W=N 1.752(3) Å, W=C 1.975(3) Å, ∠(W=N–C) = 168.8(2)°, ∠(N=W=C) = 99.1(1)°; ^{13}C NMR: W=C δ 290.7	48
	$[\mathrm{WCl_2({=}NPh)({=}CHC_6H_4CF_3\text{-}4)(PMePh_2)_2}]$ **86c**	42	Gold	^{13}C NMR: W=C δ 288.3	48
	$[\mathrm{WCl_2({=}NPh)({=}CHC_6F_5)(PMePh_2)_2}]$ **86d**	57	Yellow	^{13}C NMR: W=C δ 261.5	48
	$[\mathrm{WCl_2({=}NPh)({=}CHCH{=}CMe_2)(PMePh_2)_2}]$ **86e**	82	Golden-yellow	^{13}C NMR: W=C δ 284.0 (major rotamer), 274.2 (minor)	48
77b + $\mathrm{Ph_3P{=}CH(C_6H_4)_2CH{=}PPh_3}$ in benzene (25 °C)	$[\mathrm{WCl_2({=}NPh)({=}CHC_6H_4)\text{-}(PMePh_2)_2]_2}$ **87**	80	Yellow	^{13}C NMR: W=C δ 288.83	48
81 + $\mathrm{Ph_3P{=}CHC_6H_4OMe\text{-}2}$ + (i) Na/Hg in THF, (ii) CuCl in benzene	$[\mathrm{W({=}NPh)\{\kappa^2\text{-}({=}CHC_6H_4OMe\text{-}2)\}\text{-}\{OCMe(CF_3)_2\}_2(THF)}]$ **89a**	64	Burnt-orange	^{13}C NMR: W=C δ 246.4	48
	$[\mathrm{W({=}NC_6H_3Me_2\text{-}2,6)\{\kappa^2\text{-}({=}CHC_6H_4OMe\text{-}2)\}\{OCMe(CF_3)_2\}_2(THF)}]$ **89b**	71	Olive-yellow	X-ray: W=N 1.737(4) Å, W=C 1.943(5) Å, ∠(W=N–C) = 174.6(4)°, ∠(N=W=C) = 99.2(2)°; ^{13}C NMR: W=C δ 240.2	48
	$[\mathrm{W({=}NC_6H_3{}^iPr_2\text{-}2,6)\{\kappa^2\text{-}({=}CHC_6H_4OMe\text{-}2)\}\{OCMe(CF_3)_2\}_2(THF)}]$ **89c**	46	Gold	^{13}C NMR: W=C δ 248.1	48



77a and **78**

82a–82c

83a–83c

84a–84c

85a–85c

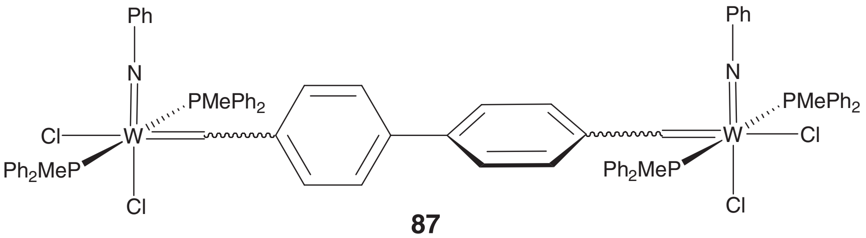
a: Ar = $C_6H_3Me_2$-2,6; PX_3 = PEt_2Ph

b: Ar = $C_6H_3Me_2$-2,6; PX_3 = $P(OMe)_3$

c: Ar = $C_6H_3{}^iPr_2$-2,6; PX_3 = $P(OMe)_3$

Scheme 14

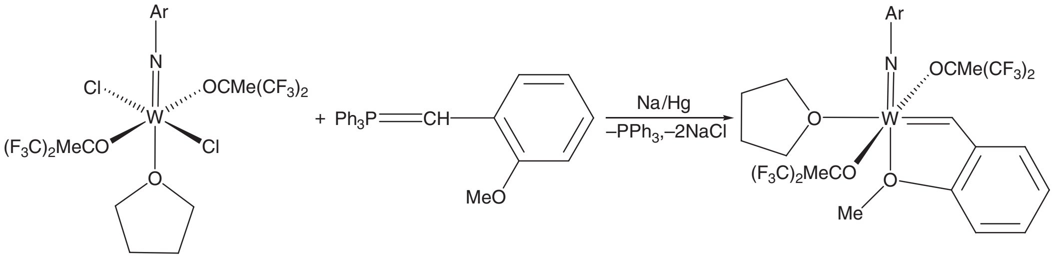
This methodology was successfully extended to *bis*(ylide) species to afford the bridged bimetallic complex 87 in very good yield.[48]



87

The alkoxido–imido precursor 81b has been treated with phosphoranes $Ph_3P{=}CHR$ under reductive conditions (sodium amalgam) to give the trigonal-bipyramidal alkoxido–alkylidene–imido complexes $[W({=}NC_6H_3Me_2\text{-}2,6)({=}CHR)\{OCMe(CF_3)_2\}_2(PPh_3)]$ 88 in NMR sample scale reactions.[48] Although corresponding reactions with $Ph_3P{=}CHCH{=}CMe_2$, $Ph_3P{=}CH_2$, and $Ph_3P{=}CHC_6H_4CF_3$-4 were unsuccessful, the phosphorane

$Ph_3P{=}CHC_6H_4OMe$-2 with complexes **81** yielded the octahedral species $[W({=}NAr)\{\kappa^2\text{-}({=}CHC_6H_4OMe\text{-}2)\}\{OCMe(CF_3)_2\}_2(THF)]$ (**89a**, Ar = Ph; **89b**, Ar = $C_6H_3Me_2$-2,6; **89c**, Ar = $C_6H_3{}^iPr_2$-2,6) (Table 16) (Equation (17)).



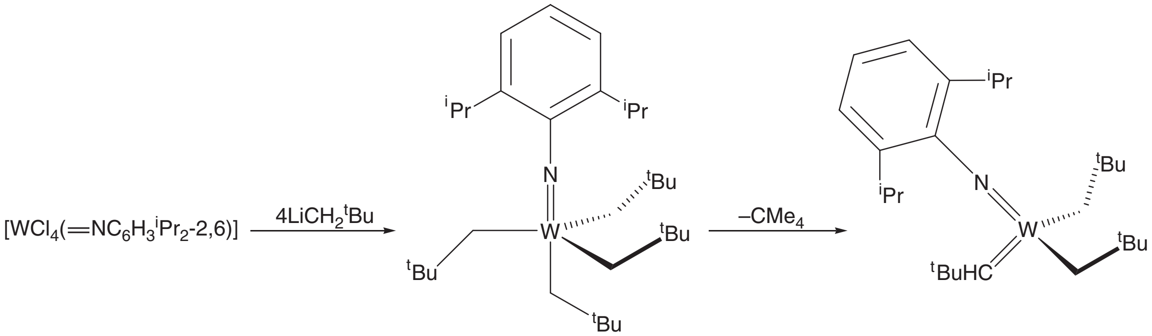
(17)

81a–81c

89a: Ar = Ph
89b: Ar = $C_6H_3Me_2$-2,6
89c: Ar = $C_6H_3{}^iPr_2$-2,6

An improved synthesis of the complex $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)({=}CH^tBu)(CH_2{}^tBu)_2]$ **91** has been described.[50] The starting reagent $[WCl_4({=}NC_6H_3{}^iPr_2\text{-}2,6)]$ is combined with 4 mol equiv. of $LiCH_2{}^tBu$, and reaction proceeded through the intermediacy of the complex $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)(CH_2{}^tBu)_5]$ **90**, which then underwent α-hydride abstraction to afford **91** (Scheme 15).

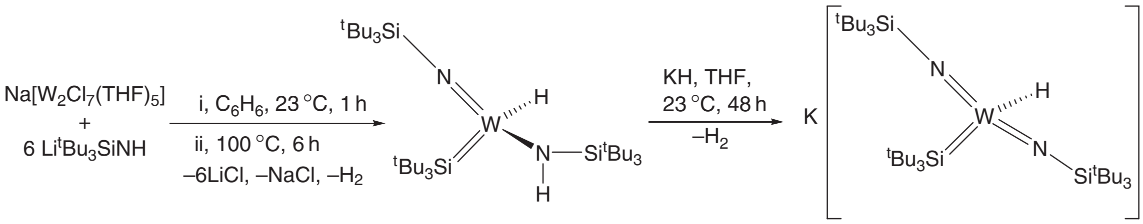
A triimido species $K[WH({=}NSi^tBu_3)_3]$ **93** has been synthesized by reaction of $Na[W_2Cl_7(THF)_5]$ with Li^tBu_3SiNH, which initially afforded the complex $[WH({=}NSi^tBu_3)_2(NHSi^tBu_3)]$ **92**.[51] Deprotonation of the latter with KH then produced compound **93** as its potassium salt (Scheme 16).



90

91

Scheme 15



92

93

Scheme 16

Table 17 Products leading to the dimer complex $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)(CH_2{}^tBu)(OC_6F_5)]_2$ **94**

Synthesis	*Complex*	*Yield (%)*	*Colour*	*Comments*	*References*
88 + ROH in C_6D_6 (25 °C)	$[W({=}NC_6H_3{}^iPr_2\text{-}2,6)(CH_2{}^tBu)_3(OC_6F_5)]$ **95a**	82	Yellow		50
	$[W({=}NC_6H_3{}^iPr_2\text{-}2,6)(CH_2{}^tBu)_3\{OC(CF_3)_3\}]$ **95b**	97	Yellow		50
92 in toluene-d_8 (80 °C)	$[W({=}NC_6H_3{}^iPr_2\text{-}2,6)({=}CH{}^tBu)(CH_2{}^tBu)\text{-}(OC_6F_5)]$ **96a**	–	Not isolated	dec. to **97**	50
	$[W({=}NC_6H_3{}^iPr_2\text{-}2,6)({=}CH{}^tBu)(CH_2{}^tBu)\text{-}\{OC(CF_3)_3\}]$ **96b**	98	Red-brown Oil	^{13}C NMR: W=C δ 263.3	50
96a in toluene-d_8 (80 °C)	$[W({=}NC_6H_3{}^iPr_2\text{-}2,6)(CH_2{}^tBu)(OC_6F_5)]_2$ **97**	70	Red	X-ray: W=W 2.4445(3) Å, W=N 1.749(3) Å, ∠(N=W=W) = 90.38(10)°, ∠(W=N–C) = 165.5(3)°	50

While mononuclear imido complexes are by far and away the dominant species in this class, some interesting results with regard to dinuclear species have been discovered. Reduction of complex **81d** with either sodium amalgam or KC_8 led to dimerization yielding the product **94** (Equation (18)).[49]

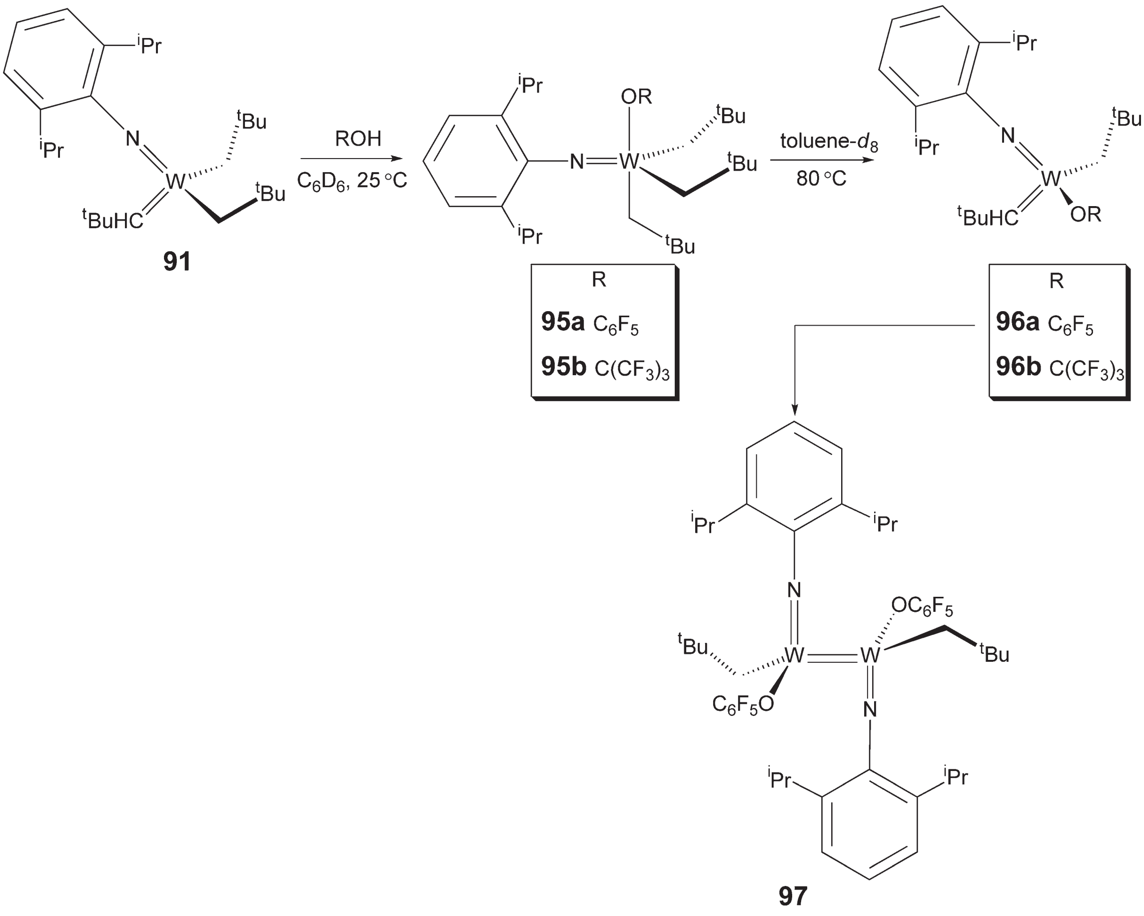
$$\underset{\textbf{81d}}{[WCl_2({=}NC_6H_3Me_2\text{-}2,6)(OCMe_2CF_3)_2]} \xrightarrow{\text{Na/Hg or KC}_8} \underset{\textbf{94}}{[W({=}NC_6H_3Me_2\text{-}2,6)(OCMe_2CF_3)_2]_2} \tag{18}$$

This important dimeric product type has been implicated in the decomposition of a number of alkylidene complexes.

A critical comparison (*vide infra*) may be drawn between the structure of **94** and that of $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)(CH_2{}^tBu)(OC_6F_5)]_2$ **97** (Table 17). The latter dinuclear species may be synthesized by heating the complex $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)(CH_2{}^tBu)_3(OC_6F_5)]$ **95a** in toluene-d_8, itself formed by treatment of complex **91** with C_6F_5OH (Scheme 17). This is a thermal reaction which proceeds via the intermediacy of the regenerated alkylidene–imido complex $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)({=}CH{}^tBu)(CH_2{}^tBu)(OC_6F_5)]$ **96a** and also produces the alkene *trans*-$^tBuCH{=}CH^tBu$ as a byproduct.[50] Interestingly, the monomeric congener **96b** is thermally stable at 80 °C and does not decompose to the analogous dimeric product.

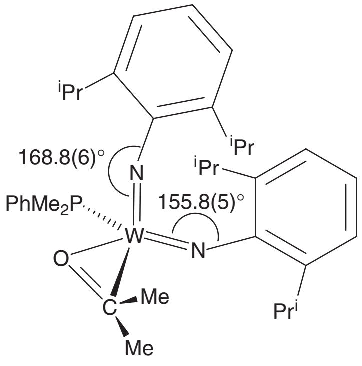
5.09.10.2 Structure and Properties

The basic architecture of the phosphine–imido complexes **77** and **78** was determined specifically by an X-ray structure analysis of complex **78c**, which revealed the meridional configuration of the phosphite groups.[45] This was confirmed by the ^{31}P NMR for all these complexes which showed two signals: doublet and triplet resonances in a ratio of 2 : 1. The imido ligand is near-linear (∠(W=N–C) = 173.5(2)°), which was also the case for both imido ligands in the X-ray crystallographic study of the tetrahedral phosphine–bis(imido) complex **79b** (∠(W=N–C) = 166.0(5)° and 172.8(5)°).[46] Of the other tetrahedral bis(imido) complexes **80**, no solid-state characterization was carried out, although the analogous molybdenum complexes did afford tractable crystals for X-ray crystallography.[47] Solution NMR measurements on the alkoxido–imido complexes **81a–81c** indicated that with equivalent CF_3 groups the two $OCM(CF_3)_2$ ligands must have a mutually *trans*-arrangement.[48] Of the alkylidene–imido complexes, **86b** and **89b** both comprise *cis*-alkylidene/imido ligands and *trans*-phosphine and *trans*-alkoxido groups for the former and latter, respectively.[48] All of the X-ray structure determinations discussed here revealed near-linear imido ligands. However, simple treatment of complex **79b** with acetone (among other aldehydes and ketones) afforded the phosphine-substituted η^2-$OCMe_2$ complex $[W({=}NC_6H_3{}^iPr_2\text{-}2,6)_2(\eta^2\text{-}OCMe_2)(PMePh_2)]$ **98**, single-crystal X-ray diffractomeric



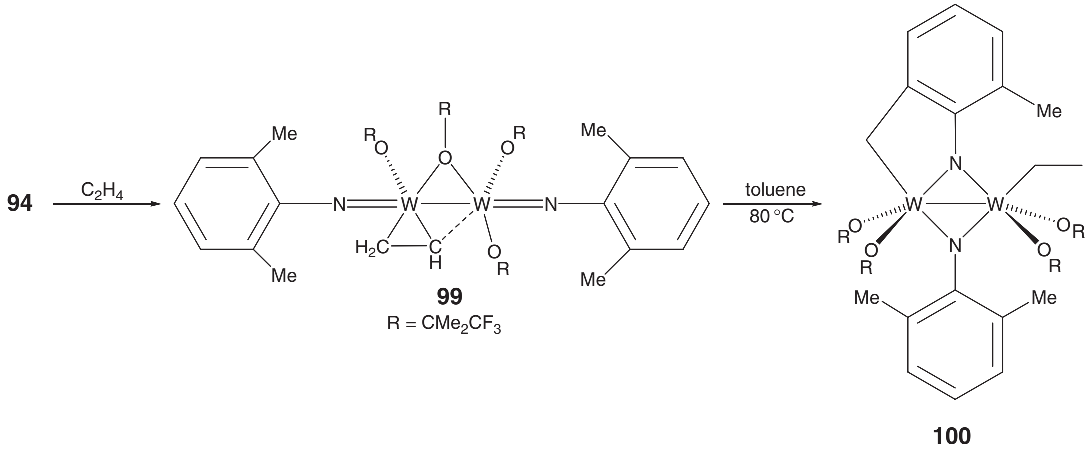
Scheme 17

analysis of which revealed significant bending of one of the imido ligands (∠(W═N–C) = 155.8(5)°).[46] The C–O bond length (1.39(1) Å) and the absence of an IR stretching frequency above 1,400 cm^{-1} suggested that the structure of 98 be best described as an oxametallacyclopropane.



98

The dimeric system 94 was not subjected to a single crystal X-ray study, but a monoadduct with the simple two-electron donor ethylene [$W_2(\mu\text{-}C_2H_4)(\mu\text{-}OCMe_2CF_3)({=}NC_6H_3Me_2\text{-}2,6)_2(OCMe_2CF_3)_3$] 99 was synthesized and its



Scheme 18

structure determined by X-ray crystallography.[49] This displayed the bridging and semi-bridging nature of one of the alkoxido ligands and the ethylene ligand, respectively, while the W–W bond length (2.6429(4) Å) was consistent with a single bond. Although each metal center is bound by terminal imido ligands, the dimer may be isomerized by heating in toluene at 80 °C to afford the complex $[W_2(\mu\text{-}NC_6H_3(Me)CH_2\text{-}2,6)(\mu\text{-}NC_6H_3Me_2\text{-}2,6)(CH_2Me)(OCMe_2CF_3)_4]$ **100** (Scheme 18). An X-ray structure determination verified that the imido groups switched to a symmetrical bridging mode (the alkoxido groups becoming all-terminal), and that one of the imido lutidyl methyl groups was activated, undergoing a C–H oxidative addition with one of the metal centers and ultimately protonating the ethylene group, converting it into a terminal ethyl ligand. Reformation of **94** was also observed in this process.

The structure of the dimeric complex **97** is perhaps most remarkable of all, in that by comparison with **94** and its derivatives, it contains an unusual, unbridged W(IV)═W(IV) double bond (2.4445(3) Å) (Figure 3).[50] The linear imido groups on each metal center are necessarily terminal, but disposed almost perfectly *trans* in a centrosymmetric structure (∠(N═W═W) = 90.38(10)°).

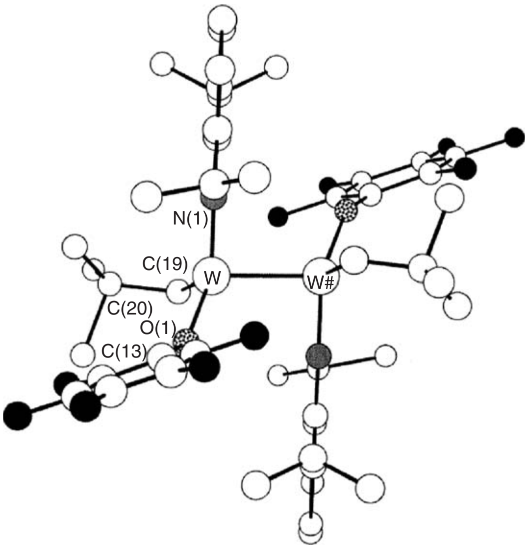


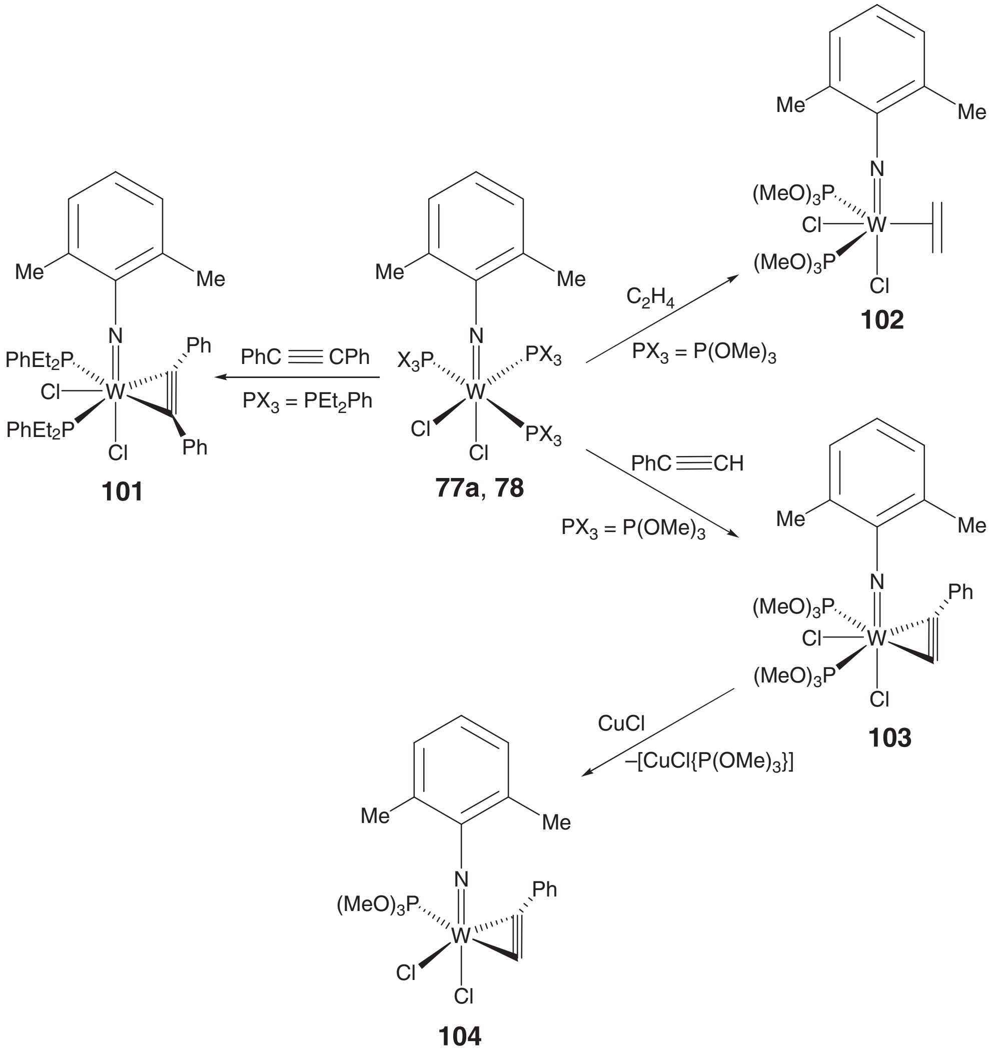
Figure 3 Structure of complex **97**. Reprinted with permission from Lopez, L. P.; Schrock, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 9526. © 2004 American Chemical Society.

5.09.10.3 Reactions

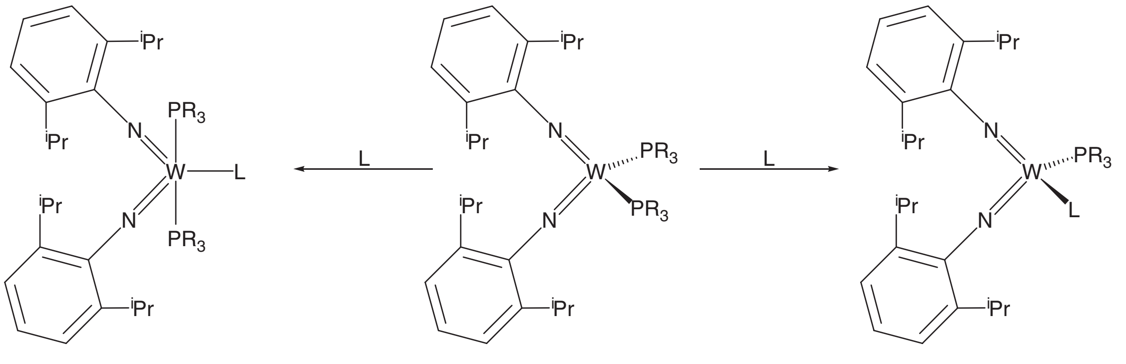
The lability of complexes **77** and **78** was established in part by their reaction with strained cyclopropenes to produce the alkylidene–imido species discussed above. This reactivity was also supported by other substitution reactions. Thus, complex **77a** afforded the η^2-alkyne adduct **101**, while phosphite lability proved to be even greater, with adducts of weakly π-acidic ethylene such as **102** being formed (Scheme 19). Reaction of **78b** with the terminal alkyne PhC≡CH afforded the single substitution product **103**, but in the presence of the phosphite scavenger, CuCl, released a second $P(OMe)_3$ ligand to yield complex **104**.[45]

The tetrahedral phosphine-bis(imido) complexes **79** also formed η^2-alkene and -alkyne adducts. With small donors, such as ethylene and ethyne, a five-coordinate trigonal-bipyramidal complex **105** with *trans*-apical phosphines resulted, while for more sterically encumbered donors, such as norbornene, $Me_3SiC{\equiv}CH$, aldehydes, and ketones, phosphine substitution occurred to give tetrahedral complexes such as **98** and **106** (Scheme 20).[46]

Ligand lability has also been investigated with the alkylidene–imido complexes **89**.[48] With PMe_3, the THF is readily displaced to give complexes **107**, where the alkoxido ligands switch from a *trans*- to a *cis*-configuration. Heating complexes **89** in toluene also resulted in THF loss to give pentacoordinate complexes **108** (Scheme 21).



Scheme 19

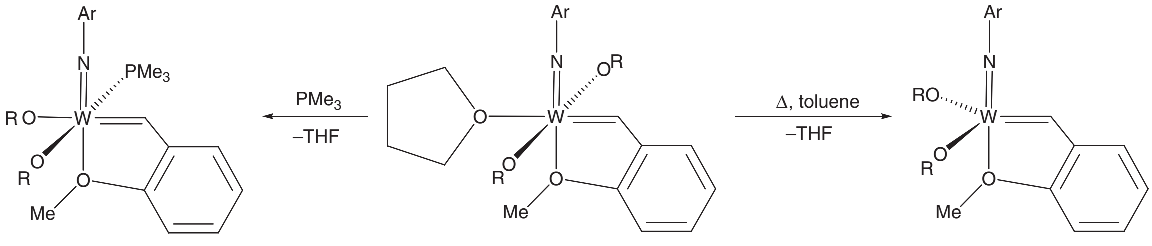


L = C_2H_4, C_2H_2
105

79

L = $Me_3SiC{\equiv}CH$, norbornene
106

Scheme 20



107

89

108

Ar = Ph, $C_6H_3Me_2$-2,6, $C_6H_3{}^iPr_2$-2,6
R = $OCMe(CF_3)_2$

Scheme 21

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5.10
Manganese Compounds with CO Ligands

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5.10.1 Introduction

Ever since the characterization of $Mn_2(CO)_{10}$ in 1954, manganese has played an important role in the development of organometallic chemistry. The low cost of the metal, its many accessible oxidation states, the versatility of its many reaction pathways, and the general ease of carrying out transformations involving coordinated ligands suggest that manganese will assume an increasingly important role in organometallic chemistry and will be a vehicle for important technological advances in synthetic, biomedical, and materials science. This review summarizes advances in the organometallic chemistry of manganese over the period 1994–2004. Especially noteworthy are significant applications of organomanganese complexes to the organic chemistry of coordinated arenes, acyls, alkynes, carbenes, vinylidenes, and other π-hydrocarbons. Other significant advances involve C–H bond activation and C–C bond formation reactions, the activation of strong covalent bonds in organic heterocycles, and the synthesis of multidimensional supramolecular coordination networks featuring a high degree of structural control.

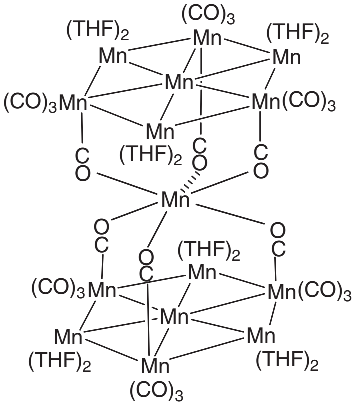
5.10.2 Manganese Carbonyl Complexes and Isonitrile Complexes

5.10.2.1 Carbonyl Complexes

Dimanganesedecacarbonyl continues to be the subject of considerable research, both experimental and theoretical. Experimental values for the Mn–Mn bond dissociation enthalpy determined over the years span the large range of 79 to 176 kJ mol^{-1}. Density functional calculations for $Mn_2(CO)_{10}$ with a large variety of STO basis sets and with correction for basis set superposition error have been applied to this problem and it was found that convergence occurs with the Mn–Mn dissociation energy in the range 112–114 kJ mol^{-1}.[1] DFT calculations for $Mn_2(CO)_x$ ($x = 7$–10) suggest[2] that the transient species $Mn_2(CO)_9$ contains a four-electron bridging carbonyl and that transient[3] $Mn_2(CO)_8$ has either a symmetrical unbridged or unsymmetrical unbridged[4] $(OC)_3Mn–Mn(CO)_5$ structure. The computed Mn–Mn distance ranges from 3.01 Å for $Mn_2(CO)_{10}$ to 2.14 Å for a monobridged $Mn_2(CO)_7$ species, which is calculated to have a metal–metal quadruple bond.[2] Time-dependent DFT calculations of the electronic spectrum of $Mn_2(CO)_{10}$ have been found[5] to support the assignment of the two lowest energy bands made years ago.[6] A multipole analysis of low temperature X-ray diffraction data obtained for $Mn_2(CO)_{10}$ has permitted an accurate description of the charge density in the Mn–Mn bond.[7,8]

The photochemistry of $Mn_2(CO)_{10}$ has long been a subject of interest.[9,10] UV irradiation leads to CO loss and Mn–Mn bond scission to afford $Mn_2(CO)_9$ and $Mn(CO)_5$ species. Longer wavelength excitation (400 nm) was reported to yield predominantly the monometal product, $Mn(CO)_5$, with a branching ratio of ≥ 2.5 in cyclohexane or isopropanol solvent.[10] The vibrational energy relaxation decay time of $Mn(CO)_5$ is on the 60 ps timescale in both solvents. Brown and Zhang[11] found that flash photolysis of $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ with a xenon lamp at 93 K in 3-methylpentane glass leads to loss of CO and initial formation of $Mn_2(CO)_9(S)$ and $MnRe(CO)_9(S)$ (S = solvent), respectively. The former intermediate readily loses solvent at 93 K to form the semibridged $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$. In contrast, $MnRe(CO)_9(S)$ is stable at 93 K and upon warming recombines with CO without formation of the semibridged form. However, $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ does form upon irradiation of $MnRe(CO)_9(S)$ at 93 K with visible light. Once formed, the semibridged form is more stable than the solvent form in both cases. An analogous study with $Mn_2(CO)_9(PR_3)$ showed that the semibridged $Mn_2(CO)_7(PR_3)(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ recombines with CO at a rate that reflects steric hindrance by the phosphine ligand, for example, $PMe_3 > P(i\text{-}Pr)_3$.[12]

Dimanganese decacarbonyl anchored to an insoluble aminated poly(siloxane) surface functions as an effective heterogeneous catalyst for the hydrosilation of terminal olefins.[13] FT-IR spectra indicate that the supported catalyst remains dimeric, with each manganese center bound via $\text{-}Si(CH_2)_3NH_2$ links. In comparison to a homogeneous $Mn_2(CO)_{10}$ catalyst, the supported complex is just as reactive and displays better selectivity for hydrosilation over unwanted olefin isomerization. $Mn_2(CO)_{10}$ reacts with trimethylaluminum in hexane/THF to give the stable $Mn[Mn_7(THF)_6(CO)_{12}]_2$ **1** along with the less stable $Mn_3(THF)_2(CO)_{10}$ **2** and $[Mn(THF)_6][Mn(CO)_5]_2$ **3**.[14] Complex **1** is a fascinating compound consisting of two $[Mn_7(THF)_6(CO)_{12}]^-$ anions, each coordinated to an Mn^{2+} cation via three carbonyl oxygens in an octahedral fashion. Each of the anions contains a six-membered ring of manganese atoms, all of which are bound to a seventh manganese located at the center, resulting in a planar Mn_7 unit. The six-membered ring contains alternating $Mn(THF)_2$ and $Mn(CO)_4$ fragments. The paramagnetic **2** has Mn–Mn bond lengths and an Mn–Mn–Mn bond angle very similar to that found in **1**. It is proposed[14] that **1** and **2** form from stepwise interactions of the $Mn(THF)_6{}^{2+}$ cation and $Mn(CO)_5{}^-$ anion in **3**.



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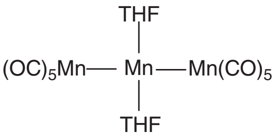
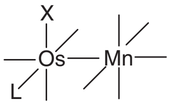


$$(OC)_5Mn\text{—}\overset{THF}{\underset{THF}{Mn}}\text{—}Mn(CO)_5$$

2

From microcalorimetric measurements of the enthalpies of sublimation, bromination, and iodation reactions, the enthalpy contribution to the strength of the heterometallic M–M′ bond in $(OC)_5Mn\text{–}Co(CO)_4$ and $(OC)_5Mn\text{–}Re(CO)_5$ has been estimated as 114 ± 23 and $145 \pm 29\,\text{kJ mol}^{-1}$, respectively.[15] $Mn(CO)_5X$ (X = Cl, Br, I) and $Os(CO)_4(L)$ ($L = CNBu^t$) react to give the heterobimetallic $(OC)_3(L)(X)OsMn(CO)_5$ **4**, the formation of which requires X migration from Mn to Os and CO migration from Os to Mn.[16] Further CO substitution in **4** occurs upon treatment with additional $Os(CO)_4(L)$ to afford trinuclear and tetranuclear products **5** and **6**. Complexes **4–6** are thought to evolve from the initially formed donor–acceptor complex **7**.[16] A number of other interesting heterometallic complexes containing manganese have been reported, including $(t\text{-}BuO)_3TiMn(CO)_5$,[17] the bridged species **8**,[18] and the ruthenium-centered **9** ($X = Mn(CO)_5$, $SnPH_3$, Br).[19,20] The electrochemical oxidation or reduction of the tetranuclear $[Rh_2(TM4)_4Mn(CO)_5]_2{}^{2+}$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane), which contains an Mn–Rh–Rh–Mn linkage, results in eventual Rh–Mn bond cleavage.[21] The initially formed one-electron oxidized transient can be observed via fast scan cyclic voltammetry in MeCN. Photochemical studies of homolytic metal–metal′ bond cleavage and/or CO dissociation have been reported for $(OC)_5MnRu(Me)(CO)_2(\alpha\text{-diimine})$,[22] $(OC)_5ReMn(CO)_3(\alpha\text{-diimine})$,[23] and $(OC)_5MnRe(CO)_3(L)$ (L = 2,2′-bipyrimidine, 2,3-bis(2-pyridyl)pyrazine).[24]



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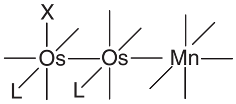

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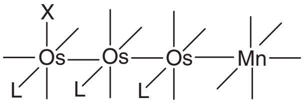

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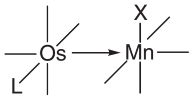

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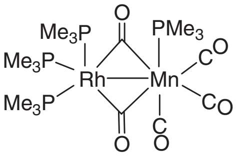

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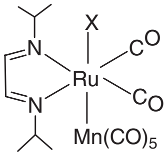
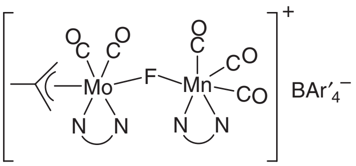


9

DFT calculations were utilized to study the dissociation energies, vibrational frequencies, and ^{13}C NMR chemical shifts for a series of 18-electon species $[M(CO)_6]^{z}$.[25] The calculated dissociation energy (in $kJ\,mol^{-1}$) for the first CO in the manganese triad series follows the order $Re(CO)_6^+$ (213) > $Mn(CO)_6^+$ (187) > $Tc(CO)_6^+$ (176), which is a similar trend found for the triads of $M(CO)_6$ (M = Cr, Mo, W) and $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os) in that the 4*d* metal has the lowest dissociation energy and the 5*d* metal the highest. The latter fact is ascribed to an important contribution of relativistic effects in the 5*d* systems. DFT calculations for $Mn(CO)_5^-$ indicate, as expected, a very small energy difference between D_{3h} and C_{4v} structures.[26,27] In comparison to $Mn(CO)_5^-$, the isoelectronic $Cr(CO)_4NO^-$ is a considerably poorer S_N2 nucleophile, which has been ascribed to the calculated lack of an accessible C_{4v} structure for the chromium complex.[27] Cobaltocene reacts readily with $Mn_2(CO)_{10}$ in THF or MeCN to afford the moderately stable salt $[Cp_2Co][Mn(CO)_5]$.[28] The interesting aspect of this electron-transfer reaction is that it does occur, given the lower (more negative) reduction potential of $Mn_2(CO)_{10}$ compared to Cp_2Co. The key to this is the chemically irreversible nature of the reduction of the former, which results in an overall two-electron process with cleavage of the Mn–Mn bond.

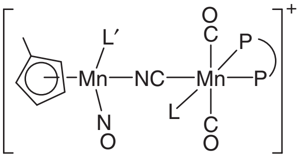
Manganese carbonyl halides are stable compounds often used as precursors in synthetic procedures. High resolution variable-energy photoelectron spectra of $Mn(CO)_5X$ (X = Cl, Br, I) provide firm assignments of the molecular orbital structures of these compounds.[29] The occupied valence orbitals in C_{4v} symmetry are in the ionization energy order a_1(Mn–X) > *e*(X) > b_2(Mn) > *e*(Mn) for the chloride and bromide, but in the order a_1(Mn–I) > *e*(Mn) > b_2(Mn) > *e*(I) for $Mn(CO)_5I$. In order to understand the observed photochemistries, density functional calculations were performed on the ground and excited states of $Mn(CO)_5Cl$ and $Mn_2(CO)_{10}$.[30,31] For $Mn(CO)_5Cl$, potential energy curves show that the lowest excited states, which involve transitions to the Mn–Cl σ^*-orbital at equilibrium geometry, are dissociative for CO loss. It is concluded that Mn–Cl bond homolysis cannot occur out of the lowest excited state even though the associated energy excitation is to the Mn–Cl σ^*-orbital. EPR data for the radical produced by γ-irradiation of $Mn(CO)_5Cl$ in a single crystal or in a $Cr(CO)_6$ matrix at low temperature could not distinguish between the 19-electron $[Mn(CO)_5Cl]^-$ **10** and the 17-electron $[Mn(CO)_4Cl]^-$ **11**, the latter being the product of simple CO dissociation.[32,33] To address this question, DFT calculations were applied to both **10** and **11**.[34] The Mn–CO (axial) bond dissociation energy in **10** was calculated to be $79\,kJ\,mol^{-1}$. This result, and the agreement between the experimental and calculated anisotropic hyperfine coupling constants for **10**, led to the conclusion that the 19-electron $[Mn(CO)_5Cl]^-$ is thermodynamically stable with respect to loss of axial CO and is the species responsible for the reported EPR spectra.

In other work involving manganese carbonyl halides, the thermal reactivity of $Mn(CO)_5Br$ on zeolite surfaces was investigated by FTIR and Raman spectroscopies.[35] The obvious motivation for such studies is an understanding of species relevant to heterogeneous catalysis. It was found that $Mn(CO)_5Br$ on zeolite Y reacts thermally by disproportionation to afford $MnBr_2$ and $Mn_2(CO)_{10}$, with the latter being trapped in the zeolite supercages. The reagent Me_3NO is often used to labilize a CO ligand in metal carbonyls. In the case of $Mn(CO)_5Cl$, it was found[36] that reaction with Me_3NO in CH_2Cl_2 affords the series of products $[Mn(CO)_4Cl_2]^-$, $[Mn(CO)_3Cl_3]^{2-}$, and $[Mn_2(CO)_6(\mu\text{-}Cl)_3]^-$. The source of "extra" chloride in these products is the solvent CH_2Cl_2. Further reaction of these intermediate complexes with $PPNNO_2$ in CH_2Cl_2 leads to $[Mn(CO)_3Cl_2(\mathit{N}O_2)]^{2-}$, $[Mn(CO)_3Cl(\mathit{N}O_2)_2]^{2-}$, and $[Mn(CO)_3(\mathit{N}O_2)_2(\mathit{O}NO)]^{2-}$. In an interesting reaction, the allylic molybdenum fluoro complex $MoF(\eta^3\text{-}C_3H_4Me)(CO)_2(phen)$ was found to function as an "organometalloligand" by replacing triflate from $Mn(CO)_3(bipy)(OTf)$ in the presence of $NaBAr'_4$ to produce the fluoride-bridged **12**.[37]



12

Cyanide-bridged multimetallic complexes have long been a topic of interest due to potential or actual magnetic, photophysical, and electron-transfer properties. The manganese cyanide complex $[Mn(CN)(CO)_2P(OEt)_3(dppm)]$ **13** serves as an organometalloligand by binding through the cyanide nitrogen to $SbCl_5$ to afford the paramagnetic low spin Mn(II) complex $[Mn(CNSbCl_5)(CO)_2P(OEt)_3(dppm)]^+$.[38] It appears from structural data that **13** has a ligand donor strength similar to common O- and N-donors. Complex **13** and analogs react similarly with transition metal dichlorides MCl_2 (M = Mn, Fe, Co, Ni) to give paramagnetic redox-active bi- and polynuclear species, for example, $[Cl_2Co\{(\mu\text{-}NC)Mn(CO)_2(P(OEt)_3)(dppm)\}_2]$.[39] Analogous products are obtained with the main group salts MX_2 (M = Zn, Cd, Hg; X = Br, I, NO_3).[40] For example, $ZnBr_2$ in acetone reacts with **13**, abbreviated "$NCMnL_x$", to yield tetrahedral **14**, **15**, or **16**, depending on the reactant ratio (Scheme 1). In related work, it was shown that $[Mn(CN)(L)(NO)Cp']$ (L = PPh_3, $P(OPh)_3$) reacts with $[Mn(CO)(L)(NO)Cp']^+$ in the presence of Me_3NO to give the green homobimetallic $[Cp'(L)(NO)Mn(\mu\text{-}CN)Mn(L)(NO)Cp']^+$.[41] In an interesting variation on this theme, the reaction of $[Mn(CN)(CO)_2(L)(dppm)]$ with $[MnI(NO)(L')Cp']$ and $[MnBr(CO)_2(L)(ppm)]$ with $[Mn(CN)(NO)(L')Cp']$ in the presence of $TlPF_6$ affords the linkage isomers **17** and **18**.[42] Electrochemical measurements show that the order of oxidation of the two Mn(I) sites in **17** and **18** depends on the orientation of the CN bridge, on the geometry at the octahedral Mn(I) site, and on the ancillary ligands (L) at the metal centers. In this way, the direction and energetics of metal-to-metal charge transfer in the mixed valence Mn(I)–Mn(II) dications can be controlled.



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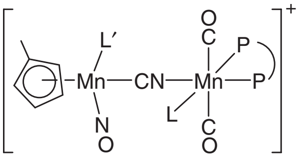
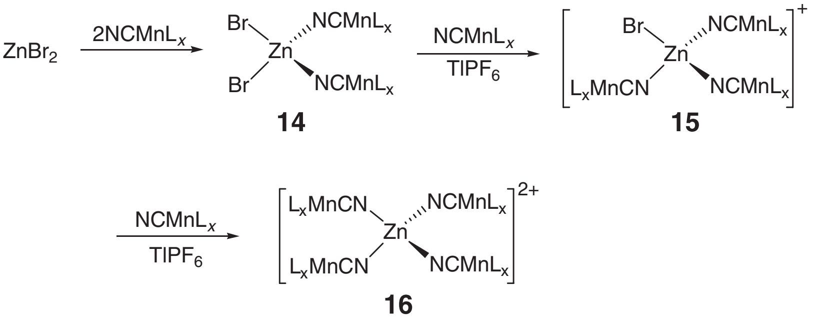


18

L = $P(OEt)_3$; L′ = $CNBu^t$

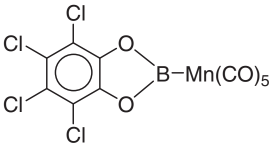
Perchlorocatecholborane reacts with $NaMn(CO)_5$ to give the boryl complex **19**.[43] A number of complexes containing a manganese–gallium bond have been reported. The alkyl gallium cluster Ga_4R_4 dissociates in solution to monomeric fragments GaR, which are isolobal to carbon monoxide and able to replace CO ligands in $Mn_2(CO)_{10}$ to afford **20**.[44] Transition metal substituted gallanes such as **21** are obtained from nucleophilic attack of $Mn(CO)_5^-$ on organogallium chlorides, $ClGaR_2(L)$ (L = amine).[45,46] The trichlorosilyl complex $(OC)_5Mn–SiCl_3$ was synthesized according to Equation (1) and examined by He I photoelectron spectroscopy and by DFT calculations in order to



14 **15** **16**

Scheme 1

better understand the nature of the transition metal–silicon bond.[47] The most interesting conclusion is that there is very little π-backbonding from the metal to the silicon. Rather detailed structural and spectroscopic studies have been reported for *para*-substituted $(OC)_5Mn–SnAr_3$ complexes and for $[(OC)_5Mn]_2EPh_2$ (E = Sn, Pb).[48,49]



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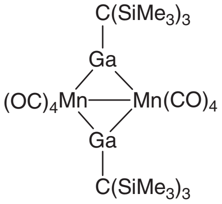

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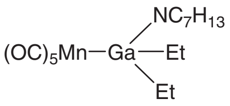
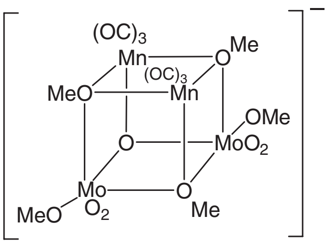


21

$$Mn_2(CO)_{10} + 2SiHCl_3 \longrightarrow 2(OC)_5MnSiCl_3 + H_2 \tag{1}$$

A number of interesting manganese carbonyls containing an Mn–O bond have been reported. The oxidation of $Mn_2(CO)_{10}$ with $Xe(OEF_5)_2$ affords $(OC)_5MnOEF_5$ (E = Se, Te).[50] The sodium salt of tetraphenylimidodiphosphinic acid reacts with $Mn(CO)_5Br$ to give the oxygen-bridging bimetallic chelate $[Mn_2(CO)_3(Ph_2P(O)NP(O)Ph_2)_3]$.[51,52] The reaction of $Mn(CO)_5Br$ with the polyoxomolybdate $Mo_2O_7{}^{2-}$ in methanol affords mixed organometallic clusters, of which the cubane **22** is one example.[53] The manganese complexes $[Mn(CO)_{4-n}(L)_n(DBSQ)]$ containing the radial anion ligand 3,5-di-*tert*-butyl-1,2-benzosemiquinone, along with a variety of ordinary co-ligands (L), have been subjected to extensive spectroscopic and electrochemical studies.[54] The five-coordinate $[Mn(CO)_3(DBCat)]^-$ **23** undergoes facile CO substitution with PEt_3 and $P(OEt)_3$, while pyridine and bulky phosphines such as PPh_3 form six-coordinate adducts.[55] Complex **23** undergoes a one-electron oxidation localized at the catechol ring and a one-electron reduction localized at the metal. The oxidation is accompanied by the uptake of a Lewis base, which may be solvent, to produce six-coordinate semiquinone complexes $[Mn(CO)_3(L)(DBSQ)]$ which upon further oxidation yield the quinone species $[Mn(CO)_3(L)(DBQ)]^+$.



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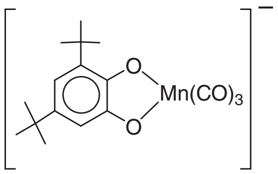
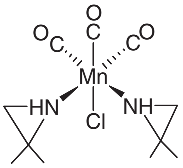


23

By hydrolysis of $[(OC)_3Mn(acetone)_3]^+$, the organometallic aqua complex *fac*-$[(OC)_3Mn(OH_2)_3]^+$ **24** was prepared.[56] Potentiometric titrations established that trinuclear $[(OC)_3Mn_3(OH)_4]^-$ is the principal condensation product at pH > 6 prior to slow conversion to the stable tetramer $[(OC)_3Mn(OH)]_4$. NMR line broadening indicated that water exchange in **24** is four orders of magnitude faster than with the rhenium analog, $[(OC)_3Re(OH_2)_3]^+$. The aqua complex *fac*-$[Mn(CO)_3(dppe)OH_2]^+$ (dppe = bis-diphenylphosphinoethane) contains a fairly labile water that can be conveniently replaced by OMe^-, CN^-, RCN, and RNC type ligands.[57] An attempt to prepare the fluoro complex led to the isolation of $[(OC)_3Mn(dppe)OH_2 \cdots\cdots FMn(CO)_3(dppe)]BF_4$, which is held together by a very strong hydrogen bond ($O \cdots\cdots F = 2.46$ Å).[58] The manganese formato complex *fac*-$[(OC)_3(dppp)MnOC(O)H]$ (dppp = 1,3-bis(diphenylphosphino)propane), prepared from *fac*-$[(OC)_3(dppp)MnH]$ and formic acid, is unusual in that the formato ligand is bound in a terminal monodentate fashion.[59] $Mn_2(CO)_{10}$ reacts with dppp and primary alcohols RCH_2OH in the presence of CO_2 to give equal moles of *fac*-$[(OC)_3(dppp)MnH]$ and 1 equiv. of the alkylcarbonato complex *fac*-$[(OC)_3(dppp)MnOC(O)OCH_2R]$.[60] Treatment of dirhenium heptoxide, Re_2O_7, with *fac*-$[(OC)_3(dppp)MnX]$ (X = H, OR, OC(O)OMe, CH_2OMe) yields the perrhenato complex *fac*-$[(OC)_3(dppp)MnOReO_3]$.[61]

A large number of manganese carbonyls exist that contain an Mn–N bond. The complex $[(OC)_3(\mathrm{phen})\mathrm{MnL}]^z$, where L is an imidazole, is stable as the *fac*-isomer when the charge z is +1, but conversion to the *mer*-isomer occurs upon oxidation ($z=+2$).[62] Sodium azide reacts very rapidly to displace the aquo ligand from *fac*-$[(OC)_3(\mathrm{dppe})\mathrm{MnOH_2}]^+$.[63] The resulting azido complex undergoes a 1,3-dipolar addition with CF_3CN to afford coordinated tetrazoles. Bis-aziridine and benzoylhydrazine complexes 25 and 26 have been reported.[64,65] Acetone adds intramolecularly to coordinated diazabutadiene in *fac*-$[(OC)_3\mathrm{Mn}(^t\mathrm{BuN{=}CHCH{=}NBut})(\mathrm{Me_2CO})]^+$ to yield *fac*-$[(OC)_3\mathrm{Mn}\{^t\mathrm{BuN{=}CHCH(CH_2COMe)N(H)}^t\mathrm{Bu}\}]^+$, which is a bicyclic complex containing a ketone–amino–imino ligand.[66] Aryldiazene complexes such as $[(OC)_3\{\mathrm{PPh(OEt)_2}\}_2\mathrm{Mn(ArN{=}NH)}]^+$ can be obtained by treating the appropriate aryldiazonium salt with $\mathrm{MnH(CO)_3(P)_2}$ at −80 °C.[67,68] Analogous bimetallic complexes with a bis(aryldiazene) bridge are made similarly (e.g., 27). Deprotonation of the aryldiazene complexes occurs readily to afford the neutral aryldiazenido analogs.



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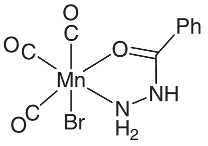

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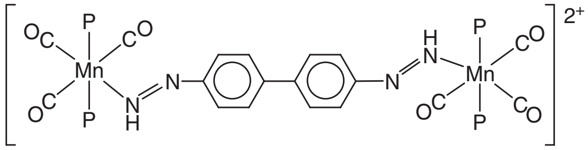
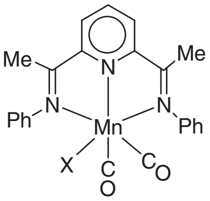


P = PPh(OEt)$_2$, PPh$_2$OEt

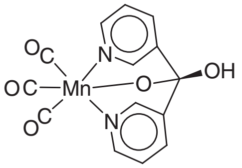
27

Other recently reported manganese carbonyls containing an Mn–N bond include $[\mathrm{Mn(CO)_2(X)(dapa)}]$ 28[69] and the pyridylketone derived 29.[70] The ferrocenyl bimetallic 30 may have useful non-linear optical properties.[71] The hexafunctionalized cyclotriphosphazene $N_3P_3(p\text{-}OC_5H_4N)_6$ reacts with *fac*-$[\mathrm{Mn(CO)_3(bipy)OClO_3}]$ to give the interesting hexametallic complex 31.[72] Analogous manganese complexes coordinated to polyphosphazenes through nitrile ligands are known as well.[73]



X = Br, Re(CO)$_5$

28



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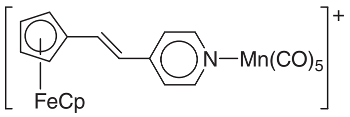

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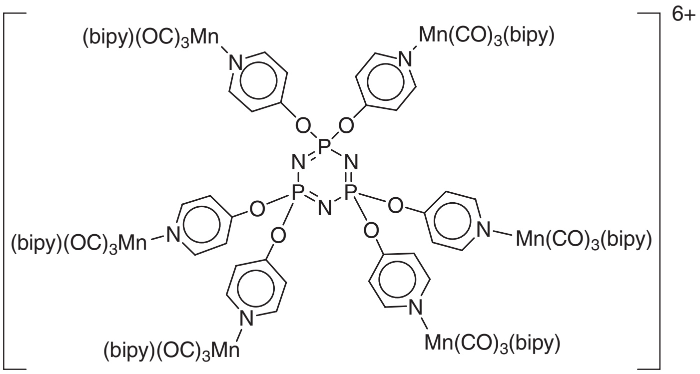
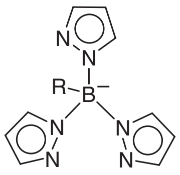


31

Tris(pyrazolyl)borate tripodal ligands 32 are widely recognized as one of the most important classes of ligands in transition metal chemistry. The parent $\mathrm{HB(pz)_3}^-$ or "Tp" ligand (R = H) readily coordinates to manganese carbonyl to form $(\mathrm{Tp})\mathrm{Mn(CO)_3}$. Placing one or two electron-withdrawing CF_3 substituents on the pyrazole rings was found to have a very substantial effect on the electron density at the metal center, as judged from IR and X-ray data, and theoretical calculations.[74] A wide variety of Tp ligands and associated metal complexes having substituents on the pyrazole rings is known. Variation of the "R" group attached to boron is much less common, being generally restricted to hydride, simple alkyls, or phenyl due to synthetic difficulties. There were no examples of Tp ligands with a chiral R group bound to the boron until the recent report of a tris(pyrazolyl)borate bearing a chiral isopinocampheyl (lpc) group.[75] Complexation to afford [(lpc)B(pz)$_3$Mn(CO)$_3$] was found to be facile. In an interesting variation on the borate systems, bis(pyrazolyl)acetate ("bpza") **33** was found to also act as a tripodal "scorpionate" ligand, readily forming [(bpza)Mn(CO)$_3$].[76] Spectroscopic data indicate, however, that **33** is less electron donating than Tp, Cp*, and even Cp.



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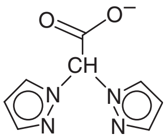

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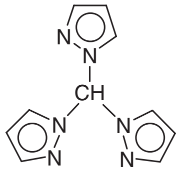
Replacement of the boron in **32** with carbon affords tris(pyrazolyl)methane **34**, which acts as a neutral tridentate donor in the complex [**34**Mn(CO)$_3$]$^+$.[77] Elaboration of **34** to include multiple metal receptor sites as in **35** has permitted the synthesis of complexes such as [**35**{Mn(CO)$_3$}$_4$][BF$_4$]$_4$, which form supramolecular 3D structures dictated by π-π stacking and C–H·····F interactions.[78,79] Heteroscorpionate ligands based on di(pyrazolyl)(2-pyridyl)methane units have been reported, with **36** as an example of one that binds to one or two [Mn(CO)$_3$]$^+$ moieties.[80]



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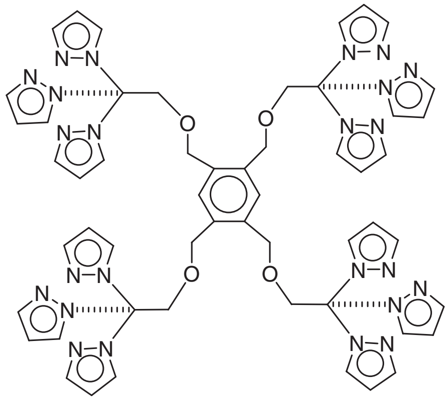

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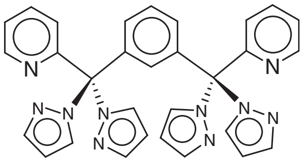
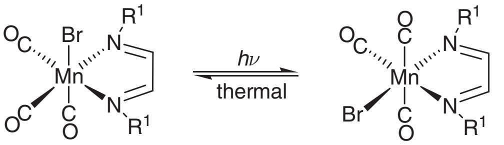


36

The photochemistry of the α-diimine complexes [Mn(R)(CO)$_3$(R^1-DAB)] **37**, where R = methyl or benzyl, is determined by the nature of R group.[81,82] The methyl complex loses CO upon irradiation into the MLCT bands. With the benzyl analog, visible excitation leads to efficient bond homolysis of the Mn–CH$_2$Ph bond. The contrasting behavior of the methyl and benzyl complexes is attributed to the difference in the relative energies of the two excited states. Experiment and theory indicate that *fac*-[Mn(Cl)(CO)$_3$(H-DAB)] has low energy MLCT excited states which are not by themselves Mn–CO dissociative.[83,84] The observed loss of equatorial CO upon MLCT excitation is explained by a radiationless transition from the MLCT states to the dissociative continuum of the electronic ground state. The photoisomerization of *fac*-[Mn(Br)(CO)$_3$(R^1-DAB)] to the *mer*-isomer **38** as shown in Scheme 2 has been

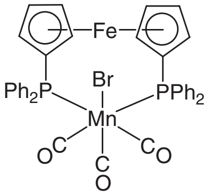


37 **38**

Scheme 2

studied mechanistically, as has the thermal back reaction *mer*→*fac*.[85,86] Electrochemical reduction of [Mn(Br)$(CO)_3$(*i*-Pr-DAB)] occurs via an overall two-electron ECE mechanism in which the chemical step is the dissociation of bromide after the first electron addition.[87] The intermediate radical [Mn$(CO)_3$(*i*-Pr-DAB)] is then spontaneously reduced to the anion $[Mn(CO)_3(i\text{-Pr-DAB})]^-$.

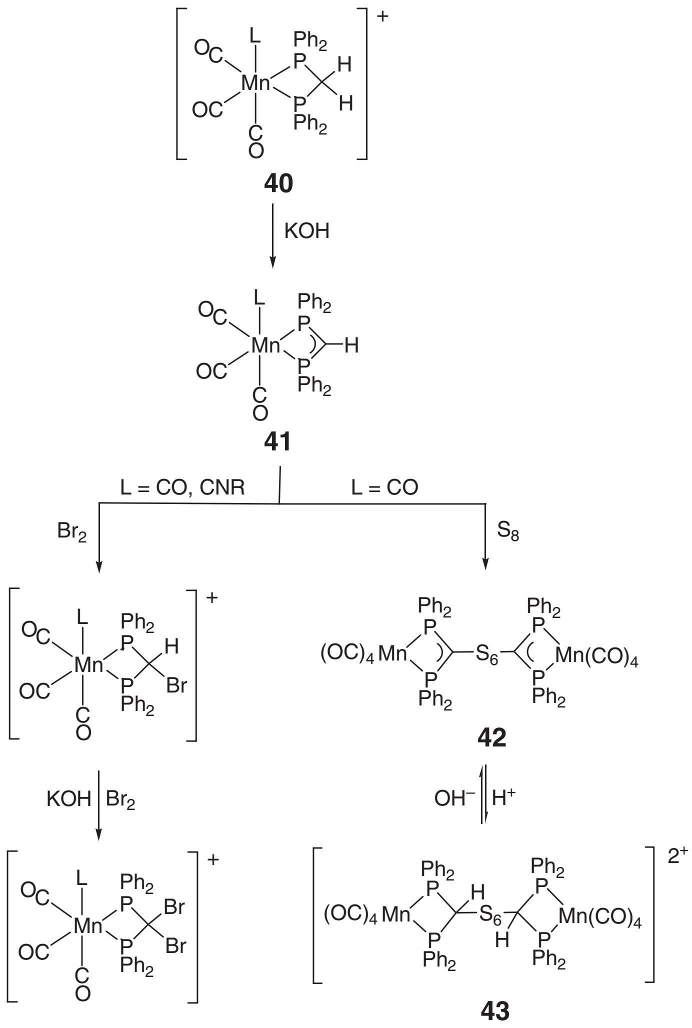
Manganese carbonyls with an Mn–P bond constitute a very large class of known compounds. It has been shown that in some cases carbonyl substitution can be effected by a solid–solid reaction with no solvent needed.[88] For example, a physical mixture of $Mn(CO)_4(PPh_3)Br$ and PPh_3 reacts upon mild heating to give $Mn(CO)_3(PPh_3)_2Br$. A large number of *fac*-tricarbonyl manganese complexes of the types $Mn(CO)_3$(P–P)X (X = anionic ligand; P–P = bidentate phosphine such as depe, dppe, dppp) and $[Mn(CO)_3(P\text{–}P)(L)]^+$ (L = neutral ligand) have been characterized by IR and theoretical calculations.[89,90] A new series of $Mn(CO)_3(L_2)Br$ complexes have been reported that includes the ferrocenyl bimetallic **39**.[91] Multinuclear NMR and redox studies have appeared for the series of phosphine, arsine, and stibine carbonyls *fac*-[Mn$(CO)_3$(L–L)X] (X = Cl, Br; L–L = dppm, dppe, dppp, *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PH_2)_2$, *o*-$C_6H_4(AsMe_2)_2$, $Ph_2AsCH_2CH_2AsPh_2$, $Ph_2SbCH_2CH_2CH_2SbPh_2$, $Me_2SbCH_2CH_2CH_2SbMe_2$).[92] The reaction of $Mn_2(CO)_{10}$ with bis(dicyclohexylphosphino)methane (dcpm) yields the simple substitution products $Mn_2(CO)_8$(dcpm) and $Mn_2(CO)_6(dcpm)_2$ in which the dcpm ligands bridge the dimanganese core.[93] The bidentate phosphite ligand $Ph_2POCH_2H_2OPPh_2$ reacts with $Mn(CO)_5Br$ to give $Mn(CO)_3$(L–L)Br, which further reacts with unidentate phosphates, phosphonites, and phosphinites (L′) to produce $Mn(CO)_2$(L–L)(L′)Br.[94] The *arachno*-2-metallatetraboranes $Mn(CO)_2L_2(B_3H_8)$ (L = phosphine ligand) have been synthesized from the reaction of $[NBu_4][B_3H_8]$ with $Mn(CO)_3L_2Br$ under photolytic conditions.[95]



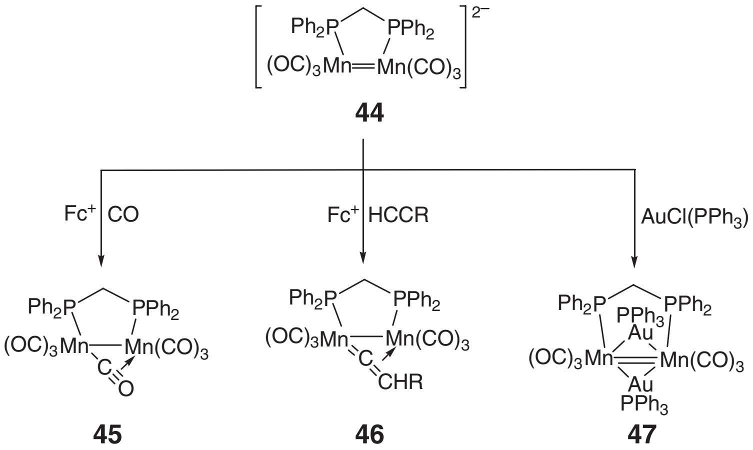
39

The ligand $Ph_2PCH_2PPh_2$ (dppm), when coordinated, is readily deprotonated to diphosphinomethanide, and this allows for functionalization of the CH carbon as illustrated in Scheme 3.[96,97] Deprotonation of **40** (L = CO, CNR) gives the nucleophilic methanide **41**, which reacts with halogens and pseudohalogens as shown. Reaction of **41** (L = CO) with elemental sulfur gives the intriguing dimeric hexasulfur-bridged **42**, concomitant with the formation of $[Mn(CO)_4(dppm)]^+$.[98] As would be anticipated, **42** is reversibly protonated to **43**. The deep green dianionic $[Mn_2(CO)_6(\mu\text{-dppm})]^{2-}$ **44** is formed quantitatively by the sodium amalgam reduction of $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-dppm})]$ in THF.[99–102] As shown in Scheme 4, oxidation of **44** with ferrocenium affords the CO-bridged species **45** or, in the presence of alkynes, the vinylidene complex **46**. The reaction of **44** with a variety of organic electrophiles has been reported. The interesting multimetallic **47** results from the substitution of chloride in the "inorganic" electrophile $AuCl(PPh_3)$.

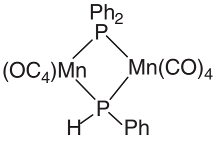
The reaction of $Mn_2(CO)_{10}$ with PPh_2H followed by $PPhH_2$ affords the μ-phosphido complex **48**.[103] Deprotonation of **48** with *n*-BuLi and reaction with the electrophiles MeI or $Mn(CO)_5Br$ gives **49** and **50**, respectively. Binuclear $[Mn_2(CO)_8(\mu\text{-PR}_2)_2]$ complexes have been made from $Mn_2(CO)_{10}$ and the diphosphine disulfide $R_2P(S)P(S)R_2$.[104] Heterobimetallic complexes containing manganese and μ-phosphido **51** and μ-phosphinidene **52** ligands have been reported.[105–108] The coordination of heterocyclic benzo- and dibenzophospholyl ligands (BP, DBP) to manganese affords the π-bonded **53**, its isomeric analoge **54**, and the σ-bonded **55**.[109–111] The reaction of tetramethyl-2,2′-biphosphinine (tmbp) with $Mn_2(CO)_{10}$ affords **56**, in which the tmbp acts as an eight-electron donor.[112] Stepwise electrochemical reduction of *fac*-[Mn$(CO)_3$(tmbp)Br] **57** produces the dimer $[Mn(CO)_3(tmbp)]_2$ and the five-coordinate $[Mn(CO)_3(tmbp)]^-$.[113] The zwitterionic 1-triphenylphosphonio-3-diphenylphosphanyl-benzo[c]phospholide reacts with $Mn_2(CO)_{10}$ to form **58**.[114]



Scheme 3



Scheme 4



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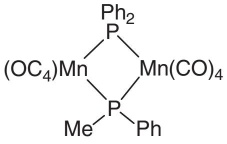

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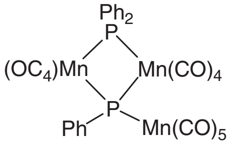

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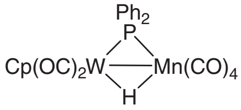

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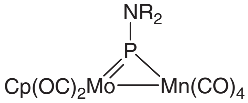

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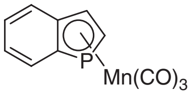

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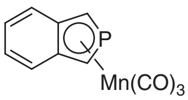

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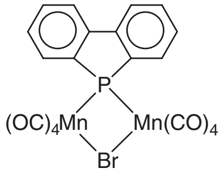

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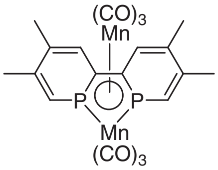

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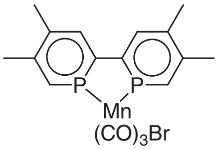

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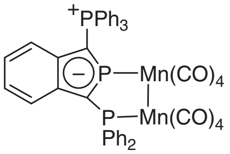
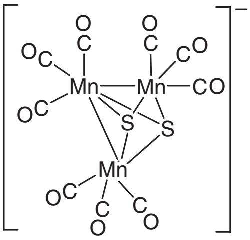


58

The stable monodentate triphenylstilbine complexes $Mn_2(CO)_{10-x}(SbPh_3)_x$ ($x = 1, 2$), $[Mn(CO)_5SbPh_3]^+$, $Mn(CO)_4(SbPh_3)Cl$, and $Mn(CO)_3(SbPh_3)_2Cl$ have been reported.[115] Similarly, the bidentate stibine ligands $Ph_2SbCH_2SbPh_2$ and $Me_2SbCH_2SbMe_2$ react to form $Mn_2(CO)_8(L\text{–}L)$.[116,117]

Electrochemical studies have been reported for a number of manganese carbonyl systems.[118–125] Typical complexes investigated include *cis,mer*-$[Mn(CO)_2\{\kappa^3\text{-}Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2\}X]$, *cis,fac*-$[Mn(CO)_2(\kappa^3\text{-}\{Ph_2PCH_2\}_3CCH_3)X]$, *cis,mer*-$[Mn(CO)_2(\kappa^3\text{-}\{Ph_2P(CH_2)_2\}_3P)X]$ (X = Cl, Br), and *cis,mer*-$[Mn(CO)_2(\kappa^1\text{-dpm})(\kappa^2\text{-dpm})Br]$ (dpm = $Ph_2PCH_2PPh_2$).[118–121] The results yielded an understanding of redox-induced isomerization reactions. The usual solvent for these electrochemical studies was dichloromethane or acetone. The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate was used as the solvent for the cyclic voltammetry of *trans*-$[Mn(CO)_2\{P(OPh)_3\}(Ph_2PCH_2PPh_2)(CN)]$ **59**.[122] "Solid-state" voltammetric studies of **59** and other manganese carbonyls, in which microcrystals of the complex are mechanically attached to a graphite electrode, have been reported.[123,124] The electrochemical oxidation of *fac*-$[Mn(CO)_3(dpm)Cl]$ is extensively photocatalyzed when a microcrystal/electrode/aqueous interface is irradiated with light of wavelength corresponding to the 385 nm charge-transfer band.[125]

A great variety of organomanganese complexes containing an Mn–E (E = S, Se, Te) bond have been reported. For $Mn_2(CO)_8(SEt)_2$, the Mn–S bond enthalpy has been estimated as $162 \pm 5\,kJ\,mol^{-1}$ from calorimetric measurements.[126] A favorite starting material for the synthesis of manganese complexes containing S, Se, and Te is $Mn_2(CO)_{10}$. Reaction of $Mn_2(CO)_{10}$ with $(F_3C)_2EE'R$ (E = P, As; E′ = S, Se, Te) leads to complexes $Mn_2(CO)_8E(CF_3)_2E'R$, in which $E(CF_3)_2$ and E′R act as bridging ligands.[127] Photolysis of $Mn_2(CO)_{10}$ and $Me_2P(S)P(S)Me_2$ affords the chelating dithiophosphinate complex $Mn(CO)_4(S_2PMe_2)$.[128] Photolysis with dicycloheptatriene sulfide gives the thio-bridged dimer $[Mn(CO)_4(\mu\text{-}SC_7H_7)]_2$.[129] The reaction of $Mn_2(CO)_{10}$ with KOH and elemental sulfur produces the cluster $[Mn_3(CO)_9(\mu_3\text{-}S)_2]^-$ **60**, which exhibits a D_{3h} equilateral triangular frame with three $Mn(CO)_3$ moieties apically bicapped by two μ-sulfur atoms.[130] The selenium analog of **60** is obtained by replacing the sulfur with selenium.[131] The interesting tellurium cluster **61** is produced from $Mn_2(CO)_{10}$ and K_2TeO_3.[132] The reaction of $Mn_2(CO)_{10}$ with Ph_3PSe leads to the cluster $Mn_4(CO)_{14}(PPh_3)_2(\mu\text{-}CO)(\mu_3\text{-}Se)$, which contains a butterfly Mn_2Se_2 core, along with minor amounts of $Mn_2(CO)_5(PPh_3)_2(\mu_2\text{-}Se_2)$, which contains a tetrahedral Mn_2Se_2 core.[133] Pyridine-2-thiol and $Mn_2(CO)_{10}$ produce dimeric **62**, which reacts with $[CpMo(CO)_3]_2$ to afford the heterobimetallic **63**.[134,135] $Mn_2(CO)_{10}$ reacts with $[Cp_2Mo(SPh)_2]$ to give the incomplete cubane structure **64**,[136] while photolysis with $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ affords the antiferromagnetic $[Cp'Cr(\mu\text{-}SPh)]_2(\mu_4\text{-}Se)Mn_2(CO)_8$ at room temperature and the paramagnetic **65** at higher temperatures.[137]



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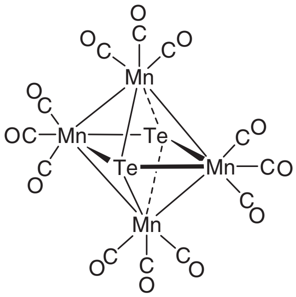

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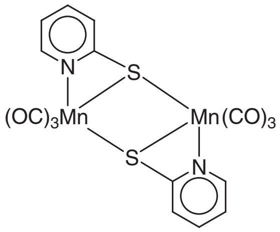

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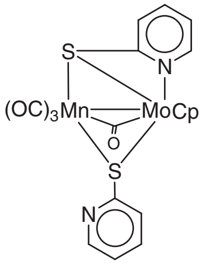

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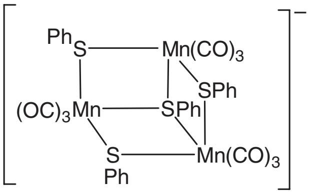

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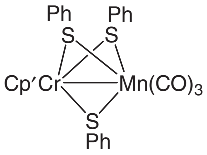
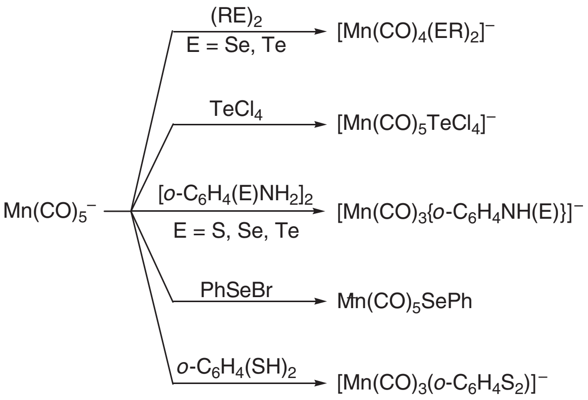
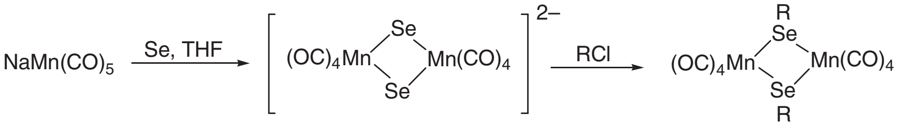


65

Another common starting material for the synthesis of bonds between manganese and group 16 elements is $[Mn(CO)_5]^-$. Some examples of the types of compounds that can be accessed from $[Mn(CO)_5]^-$ are provided in Scheme 5.[138–143] Oxidative addition of organic diselenides and ditellurides affords *cis*-$[Mn(CO)_4(ER)_2]^-$. Reaction of $[Mn(CO)_4(SePh)_2]^-$ and $[Mn(CO)_4(TePh)_2]^-$ with $(SePh)_2$ and Co^{2+} yields the heterotrimetallic $[(OC)_4Mn(\mu\text{-}TePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3]$ **66**.[139] The analogous all-tellurium analog $[(OC)_4Mn(\mu\text{-}TePh)_2Co(CO)(\mu\text{-}TePh)_3Mn(CO)_3]$ is similarly obtained.[140]. In similar chemistry, $[Mn(CO)_4(SeR)_2]^-$ reacts with Ni^{2+} to give $[(OC)_4Mn(\mu\text{-}SeR)_2Ni(\mu\text{-}SeR)_2Mn(CO)_4]$ (R = Me, Ph).[141] Oxidative addition of $[o\text{-}C_6H_4(E)NH_2]_2$ (E = S, Se, Te) followed by deprotonation of the amino group produces **67**.[142,143] Interestingly, $TeCl_4$ reacts with $Mn(CO)_5^-$ not by Te–Cl bond cleavage, but rather forms the simple addition compound $[(OC)_5Mn–TeCl_4]^-$.[144] Reaction of $Te_2Fe_3(CO)_9$ with $[Mn(CO)_5]^-$ gives the $Mn(CO)_4$ bridging butterfly $[Te_2Fe_2Mn(CO)_{10}]^-$, while treatment of $Se_2Fe_3(CO)_9$ with $[Mn(CO)_5]^-$ produces the square-pyramidal $[Se_2Fe_2Mn(CO)_9]^-$.[145] The one-pot synthesis of the selenolato-bridged bimetallic **68** follows the chemistry shown in Scheme 6.[146]



Scheme 5



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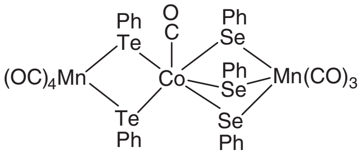
Scheme 6



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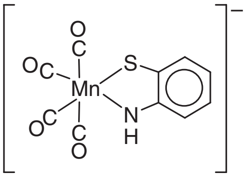

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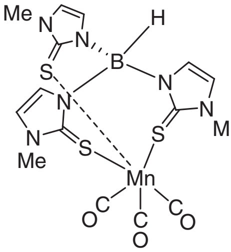
In addition to $Mn_2(CO)_{10}$ and $NaMn(CO)_5$, $Mn(CO)_5X$ (X = halide) is also a common starting material in organomanganese chemistry. The reaction of $Mn(CO)_5X$ with $RS(CH_2)_nSR$ ($n = 2$, 3) or o-$C_6H_4(SMe)_2$ yields the neutral complexes $[Mn(CO)_3\{RS(CH_2)_nSR\}X]$ or $[Mn(CO)_3\{o\text{-}C_6H_4(SMe)_2\}X]$.[147] A closely analogous chemistry obtains for the corresponding selenium and tellurium ethers.[148,149] The xylyl-backboned ditelluroether o-$C_6H_4(CH_2TeMe)_2$ (xyte) reacts with $Mn(CO)_5Cl$ to give the expected $Mn(CO)_3(xyte)Cl$.[150] Manganese carbonyls with dithio- and diselenoimidodiphosphinato ligands, $[N(EPPh_2)_2]^-$ (E = S, Se), have been described.[151,152] The mixed donor pyridine ligand 2-$(MeECH_2)C_5H_4N$ (N–E; E = S, Se) readily forms $Mn(CO)_3$(N–E)Br.[153]

A labile cationic species such as $[Mn(CO)_3(Me_2CO)_3]^+$ can be a useful precursor. For example, the complexes *fac*-$[Mn(CO)_3(L_3)]^+$ ($L_3 = MeS(CH_2)_2S(CH_2)_2SMe$), $MeSe(CH_2)_3Se(CH_2)_3SeMe$, $MeC(CH_2SMe)_3$, $MeC(CH_2SeMe)_3$, $MeC(CH_2TeMe)_3$, $MeC(CH_2TePh)_3$) are readily obtained by mixing the reactants in acetone at room temperature.[154,155] The tris(methimazoyl)hydroborate ligand (Tm) is a soft analog of the well-established tris(pyrazolyl)hydroborate ligand (Tp). NaTm reacts with $[Mn(CO)_3(NCMe)_3]^+$ to give $(Tm)Mn(CO)_3$ **69** as a stable yellow solid.[156] The dianionic sulfide cluster $[Ru_3(CO)_9(\mu_3\text{-}S)]^{2-}$ reacts with $[Mn(CO)_3(NCMe)_3]^+$ to afford the mixed metal sulfide cluster $[HRu_3(CO)_9(\mu_4\text{-}S)Mn(CO)_3(NCMe_3)_2]^+$, which contains a pseudo-tetrahedral μ_4-sulfido atom.[157] The sodium amalgam reduction of $MnRe(CO)_6(\mu\text{-}S_2CPR_3)$ (R = Cy, *i*-Pr) gives, after protonation with ammonium ion, $MnRe(CO)_6(\mu\text{-}SH)\{\mu\text{-}SC(H)PR_3\}(NH_3)$ **70**, which is unstable and rapidly isomerizes at room temperature to **71**.[158] The dianion $[MnRe(CO)_6(\mu_2\text{-}SCPR_3)]^{2-}$ reacts with $PtCl_2(COD)$ to yield a very interesting cymantrene analog that contains a dimetalladithiacyclopentadienyl ring **72**.[159]



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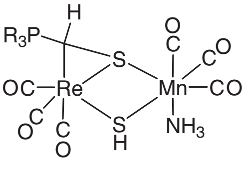

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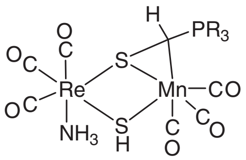

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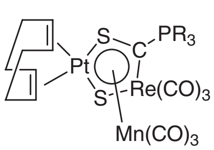

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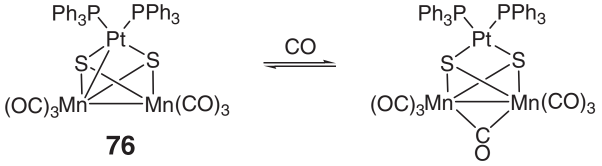
The simplest disulfide of manganese carbonyl, $Mn_2(CO)_6(\mu\text{-}CO)(\mu\text{-}S_2)$ **73**, was synthesized in 2001 from the reaction of $Mn_2(CO)_9(NCMe)$ and thiirane.[160] The behavior of **73** toward phosphines, arsines, thioethers, and electrons has been studied.[161–163] With the thioethers SMe_2, thietane, and 1,5,9-trithiacyclododecane, the products consist of two main types: (i) a dimanganese complex **74** in which the bridging CO in **73** is replaced and the thioether sulfur inserted into the Mn–Mn bond and (ii) a tetramanganese complex $Mn_4(CO)_{14}(SR_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$.[162] The reduction of **73** with sodium amalgam affords the anion **75**, which reacts with $[CpFe(CO)_2(Me_2CO)]^+$ to yield the neutral mixed metal complex $CpFeMn_3(CO)_{12}(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$.[163] The reaction of **73** with organometallic reagents has also been explored.[164–168] With $Pt(PPh_3)_2(PhC_2Ph)$, the process involves PhC_2Ph loss from the platinum and the insertion of a $Pt(PPh_3)_2$ fragment into the S–S bond, along with loss of a CO and formation of an Mn–Pt bond.[165] The product, 76, reversibly adds CO with concomitant Mn–Pt bond cleavage; Equation (2). Insertion of other metal fragments, for example, CpCo and Cp*Rh, into the S–S bond in 73 has been accomplished.[166] Reaction of 73 with $[CpNi(CO)]_2$ follows a more complicated course to yield the paramagnetic 77.[167] The mixed metal disulfide complex 78 is obtained from the reaction of 73 and $[CpMo(CO)_3]_2$.[168] A variety of small molecules such as CO, *t*-butyl isocyanide, ethylene, dimethylacetylene dicarboxylate, and allene insert into the S–S bond in 78. Complex 79 illustrates the product with butyl isocyanide. $CpCo(CO)_2$ also reacts with 78 by insertion into the S–S bond to give complex 80.[169] The reaction of $CpMoMn(CO)_8$ with elemental Se and Me_3NO gives the selenium analog of 78, namely, complex 81.[170] Insertion of small molecules into the Se–Se bond of 81 follows a chemistry similar to that found with the disulfide 78.



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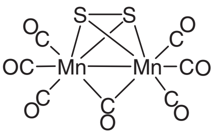

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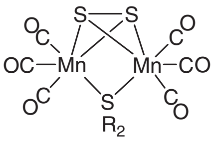

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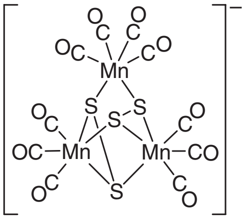

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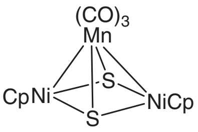

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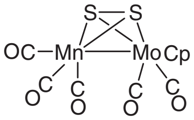

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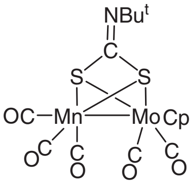

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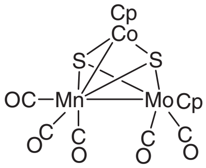

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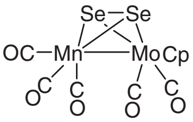

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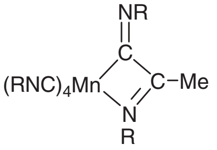
5.10.2.2 Nitrosyl and Isonitrile Complexes

The nitrosyl complex $Mn(NO)(CO)_4$ undergoes CO substitution in the presence of Me_3NO and Ph_2PH to give the trigonal-pyramidal $Mn(NO)(CO)_2(PPh_2H)_2$.[171] Reduction of $Mn(NO)(CO)_3PPh_3$ by sodium amalgam or by potassium tri-*sec*-butylborohydride affords high yields of the air sensitive $[Mn(NO)(CO)_3]^{2-}$ **82**, which is the only known mixed carbonylnitrosylmetallate dianion.[172] Complex **82** reacts with Ph_3SnCl, $Mn(NO)(CO)_4$, and $Fe(CO)_5$ to give chloride or CO substitution products $[Mn(NO)(CO)_3SnPh_3]^-$, $[Mn_2(NO)_2(CO)_6]^{2-}$, and $[MnFe(NO)(CO)_7]^{2-}$, respectively. Laser-ablated manganese atoms react with CO and NO mixtures in solid argon to yield a series of unsaturated species that include Mn(NO(CO), $Mn(NO)_2(CO)$, and $Mn(NO)(CO)_2$.[173] The Mn(NO)(CO) complex isomerizes upon photolysis with visible light to Mn(η^2-NO)(CO), which rearranges upon UV photolysis to the isocyanate molecule OMn(NCO). In frozen ionic matrices at ca. 90 K, visible light initiates the transformation of the nitrosyl ligand in $[CpMn(NO)(CO)_2]^+$ from the standard η^1-NO bonding mode to η^1-ON (isonitrosyl) and η^2-NO species.[174] Continued irradiation in the UV results in eventual CO loss.

The homoleptic manganese isonitrilate $[Mn(CNXyl)_5]^-$ (Xyl $= 2,6\text{-}Me_2C_6H_3$) was prepared by naphthalenide reduction of $Mn(CNXyl)_5Cl$ in THF.[175,176] The [K(18-crown-6)(dme)]$^+$ salt has a trigonal-bipyramidal geometry. Reaction of the nucleophilic isonitrilate with Ph_3SnCl affords $Mn(CNXyl)_5SnPh_3$. The fluorinated isonitrile

CF_3CH_2NC displaces the THF from Cp*Mn(CO)$_2$THF to yield Cp*Mn(CO)$_2$(CNCH$_2$CF$_3$).[177] Isonitriles RNC (R = *p*-MeOC$_6$H$_4$, *t*-butyl, *n*-butyl, 2,6-xylyl) react with the dimer (OC)$_5$MnCo(CO)$_4$ to give CO substitution at equatorial positions at the manganese center, affording (OC)$_4$(CNR)MnCo(CO)$_4$ and (OC)$_3$(CNR)$_2$MnCo(CO)$_4$.[178] It has been shown that phosphoramidates can be used to convert metal carbonyls into metal isonitriles.[179] For example, Et(H)NP(O)(OEt)$_2$, deprotonated with BuLi, converts MeC(O)Mn(CO)$_5$ to MeC(O)Mn(CO)$_4$(CNEt). The use of phosphoramidates to prepare metal isonitriles is convenient in that it avoids the use of volatile and toxic free isonitriles and provides facile access to non-racemic chiral isonitrile ligands.

Organomanganese isonitrile complexes often react with small molecules such as alkyl halides or alkynes by coupling of isonitrile ligands. For example, alkylation of [Mn(CNXyl)$_5$]$^-$ with MeI gives the 1,4-diazabutadien-2-yl complex 83.[180] It is proposed that the first step in the formation of 83 is alkylation at the manganese, followed by insertion to give an iminoacyl intermediate that inserts a second isonitrile to give the product. When activated by Me$_3$NO in the presence of MeNC, Mn$_2$(CO)$_9$(CNMe) reacts with MeO$_2$CC≡CCO$_2$Me by coupling of the alkyne to the isonitrile ligand to afford the cyclometallated enimine 84.[181] Under UV irradiation, 84 undergoes a 1,4-cycloaddition of acetylene to the enimine moiety. Coupling of isonitriles occurs when [Mn(CO)$_4$(CNC$_6$H$_4$-*p*-OMe)(C(O)CH$_2$Ph)] is heated with diphenylacetylene to give the η^5-azacyclohexadienyl complex 85.[182] This reaction likely involves the *in situ* formation of an iminoacyl complex that is trapped by two molecules of the acetylene. Stirring a solution of [Mn(CO)$_5$CH$_2$C$_6$H$_4$-*p*-Cl] with 2,6-xylyl isonitrile in toluene in the presence of a catalytic amount of PdO yields the iminoacyl complexes 86 and 87.[183]



R = 2,6-Me$_2$C$_6$H$_3$

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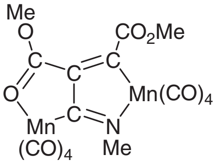

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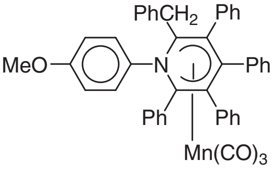

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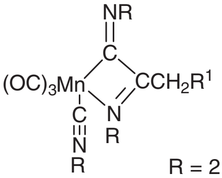

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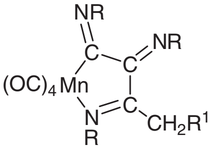


R = 2,6-Me$_2$C$_6$H$_3$
R^1 = 4-ClC$_6$H$_4$

87

The reaction rates for the methylation of Mn(CO)(dppm)$_2$CN, Mn(CO)$_2$(tripod)CN, and (η^6-C$_6$Me$_6$)Mn(CO)$_2$CN (dppm = Ph$_2$PCH$_2$PPh$_2$; tripod = (Ph$_2$PCH$_2$)$_3$CH$_3$) with methyl 4-nitrobenzenesulfonate (MeONs) to produce the isonitrile [L$_n$Mn–CNMe]$^+$ suggest that the mechanism involves nucleophilic attack of the cyanide nitrogen on the methyl of MeONs.[184] The rate constants correlate with IR ν_{CN} frequencies in the reactants and in the products. In addition, there is a correlation between the rate constants and the calculated ν_{CO} of the analogous [L$_n$Mn–CO]$^+$ complex. These correlations may be useful for predicting the nucleophilic character of metal cyanide complexes having a range of metals and ligands, and steric and electronic properties.

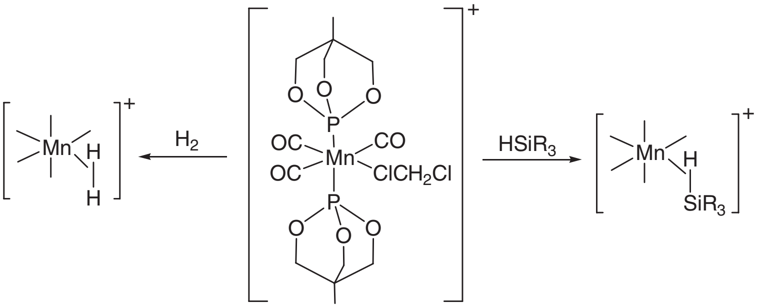
5.10.3 Manganese η^2-Sigma Complexes

It is now well established that single two-electron covalent bonds between main group elements, of which at least one is generally hydrogen (e.g., H–H, C–H, Si–H, B–H, etc.), can in some circumstances "coordinate" to a metal without bond cleavage (oxidative addition) to give "η^2-sigma" complexes. A substantial number of organomanganese complexes of this type are known. Protonation of MnH(CO){P(OEt)$_3$}$_4$ with HBF$_4$ gives the isolable dihydrogen complex [Mn(η^2-H$_2$)(CO){P(OEt)$_3$}$_4$]$^+$ 88.[185] The analogous but less stable [Mn(η^2-H$_2$)(CO)$_2${P(OEt)$_3$}$_3$]$^+$ 89 has also been characterized. Evolution of hydrogen from 88 and 89 gives unsaturated species that react with PhC≡CLi to yield the acetylides Mn(CO){P(OEt)$_3$}$_4$C$_2$Ph and Mn(CO)$_2${P(OEt)$_3$}$_3$C$_2$Ph. The unsaturated dark green

16-electron cation $[Mn(CO)_3(PCy_3)_2]^+$ **90** has an agostic interaction between a cyclohexyl C–H and the metal.[186] Under hydrogen, the yellow $[Mn(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2]^+$ readily forms at room temperature. In comparison to the neutral 16-electron chromium analog, it appears that H_2 binding is stronger to **90**, in spite of the expected decrease in backbonding ability from the cationic manganese center. Apparently, increased σ-donation to manganese more than compensates for decreased backbonding to H_2. Surprisingly, N_2, ethylene, and silanes were not observed to bind to **90**, even at low temperature, from which it is concluded that H_2 becomes an increasingly better ligand compared to N_2 as the electrophilicity of the metal increases. The 16-electron complexes $[Mn(CO)(dppe)_2]^+$ and $[Mn(CO)(depe)_2]^+$ also display agostic C–H interactions and form η^2-H_2 complexes.[187,188] UV irradiation of $Cp^*Mn(CO)_3$ in liquid xenon in the presence of H_2 yields $Cp^*Mn(\eta^2\text{-}H_2)(CO)_2$, which can also be synthesized by the reaction of H_2 with $Cp^*Mn(CO)_2(\eta^2\text{-}CH_2{=}CHOEt)$ or $Cp^*Mn(CO)_2(\eta^2\text{-}HSiEt_3)$ in supercritical CO_2.[189,190] Photolysis of CpMn(CO)(dfepe), where dfepe is the perfluoroalkylphosphine $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, under H_2 at 0 °C in hexane gives a 6:1 mixture of the dihydride and the η^2-dihydrogen complexes, $CpMn(H)_2(dfepe)_2$ and $CpMn(\eta^2\text{-}H_2)(dfepe)_2$, respectively.[191]

The solvent-coordinated Mn(I) carbonyl **91** containing a tied-back phosphite ligand is formed by treating the methyl analog of **91** with trityl cation in CH_2Cl_2.[192,193] Complex **91** is highly electrophilic and readily forms η^2-complexes with H_2 and $HSiR_3$ according to Scheme 7. The "tied-back" nature of the phosphite ligands prevents intramolecular agostic bonding, which would hinder external ligand binding. The dissociation energy of the η^2-silane complexes $CpM(CO)_2(\eta^2\text{-}HSiH_{3-n}Cl_n)$ has been examined theoretically as a function of n and M (Mn, Tc, Re).[194]

The boryl complex $Mn(CO)_4(PR_3)(BH_2PMe_3)$ is protonated to give the borane analog, which contains a sigma bond B–H ligand ($H\text{–}BH_2PMe_3$).[195]. In a similar vein, the σ-borane complex $CpMn(CO)_2(H\text{–}BH_2PMe_3)$ has been characterized, with the conclusion that the bonding consists primarily of σ-donation from the B–H bond with little *d*-orbital backdonation into the B–H σ^* orbital.[196] An upper limit of 100 kJ has been estimated for the η^2-bond energy in the σ-borane complex **92** shown in Scheme 8.[197] The borane ligand in **92** is readily replaced by CO, PhC≡CPh, $HSiMePh_2$, and $HSnPh_3$, with the latter two ligands forming H–Si and H–Sn σ-bond complexes, as indicated in Scheme 8.



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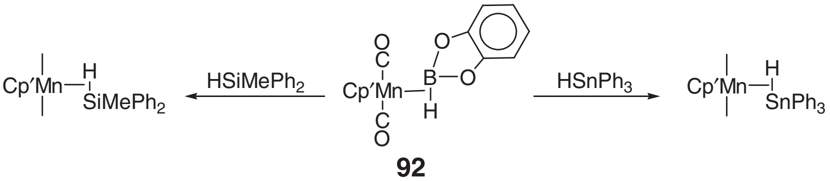
Scheme 7



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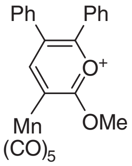
Scheme 8

5.10.4 Manganese Carbonyl Complexes with Hydrocarbon Ligands

5.10.4.1 η^1–η^4 Complexes

The simplest η^1-bonded ligand is hydride. Although not a "hydrocarbon", the hydride ligand is considered in this section along with alkyl, aryl, acyl, and related η^1-ligands. $HMn(CO)_5$ displays a dimeric H$\cdots$H interaction (separation 2.29 Å) in the solid state, the nature of which has been examined by HF and MP2 calculations.[198] The stabilization is computed to be ca. 21 kJ mol^{-1}. $HMn(CO)_5$ is a venerable carbonyl hydride that has been employed in chemical reactions for many years. A recent example is the use of $HMn(CO)_5$ to promote $Rh_4(CO)_{12}$-catalyzed hydroformylation of olefins.[199,200] Mechanistic experiments suggest that the observed synergism is due to bimetallic catalytic binuclear elimination in which $HMn(CO)_5$ is a vehicle for hydride attack on a rhodium-coordinated acyl species. A DFT study of $HMn(CO)_5$ and $HMn(CO)_4$ is in good agreement with experiment.[201] Two isomers (C_s, C_{4v}) are predicted for $HMn(CO)_4$ and this, along with the calculated vibrational spectrum, correlates well with a matrix isolation study.[202] The structure and bonding in *cis*-$HMn(CO)_4PPh_3$ has been studied by low-temperature neutron and high-resolution X-ray diffraction.[203] The Mn–H bond length is 1.573(2) Å and the hydride ligand is nucleophilic (hydridic) in nature with an effective atomic charge of −0.4e. The hydridic hydrogen makes a short contact (2.101(3) Å) with an electrophilic *ortho*-phenyl hydrogen. Calculations suggest that spin–orbit interactions between the low-lying singlet and triplet states in $HMn(CO)_3$(1,4-diaza-1,3-butadiene) are relatively weak.[204] Correspondingly, the influence of spin–orbit interactions on Mn–H bond homolysis occurring via ^{1}MLCT → ^{3}sigma-bond-to-ligand-charge-transfer (SBLCT) intersystem crossing is calculated to be modest. Heating $Mn_2(CO)_6(P–P)_2$ or $Mn_2(CO)_{10}$ plus chelating diphosphine (P–P) in an alcohol solvent produces the hydride $HMn(CO)_3(P–P)$ along with an aldehyde oxidation product.[205] The phosphines P–P include $Ph_2P(CH_2)_nPPh_2$ ($n = 2–5$) and $Cy_2P(CH_2)_2PCy_2$. The X-ray structure of *fac*-$HMn(CO)_3\{(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2\}$ reveals an Mn–H bond length of 1.57(3) Å. The anionic hydride $[Cp'Mn(CO)_2H]^-$ **93** is conveniently made on a large scale from the reaction of $Cp'Mn(CO)_2(H)(SiMePh_2)$ and $K[BEt_3H]$.[206] The X-ray structure of **93** as a potassium crown ether salt features two independent $[Cp'Mn(CO)_2H]^-$ units with Mn–H bond distances of 1.56(2) and 1.54(2) Å.[207] Complex **93** serves as a starting material for an improved synthesis of the borylene complex $[Cp'Mn(CO)_2]_2BR$ ($R = Me_2N$, Me_3C).[206] Dimerization of **93** occurs readily to give the bridged hydride $[Cp'Mn(CO)_2–H–Mn(CO)_2Cp']^-$, whose X-ray structure has been reported.[206] Photolysis of $CpMn(CO)(Me_2PCH_2CH_2PMe_2)$ and similar complexes with other phosphorus donor ligands (P–P) react with phenylsilanes via oxidative addition to yield fluxional silyl hydrides, for example, $CpMn(P–P)(H)(SiPhH_2)$.[208]

Proton spin-lattice relaxation times and ^{13}C chemical shift anisotropy measurements on crystalline $CH_3Mn(CO)_5$ indicate that the barrier to rotation of the methyl group is ca. 22 kJ mol^{-1}.[209] The manganese iodomethyl complex *fac*-$Mn(CO)_3(dppp)CH_2I$ ($dppp = Ph_2P(CH_2)_3PPh_2$) can be prepared from *fac*-$Mn(CO)_3(dppp)CH_2OMe$ by treatment with trifluoroacetic acid and Me_3SiI.[210] The cation *fac*-$[Mn(CO)_4(dppp)]^+$ reacts with $NaBH_4$ by attack on CO to afford the η^1-bonded formyl *fac*-$Mn(CO)_3(C(O)H)(dppp)$, which in solution undergoes spontaneous loss of CO to give the hydride $Mn(CO)_3(dppp)H$.[211] Long-chain alkoxycarbonyl complexes $Mn(CO)_5(C(O)OR)$ with R ranging up to n-$C_{16}H_{33}$ have been synthesized by the reaction of synthesis gas with $Mn(CO)_5(C(O)R^1)$.[212] The pyrylium complex **94** was found to be surprisingly resistant to protolytic Mn–C bond cleavage and CO insertion reactions.[213] It undergoes electrocatalytic CO substitution upon reduction in the presence of PPh_3.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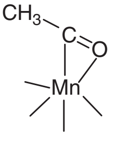
The dimeric complex $[Mn(CO)_4Br]_2$ was found to be a catalyst precursor for the alcoholysis of silanes.[214] The acetyl complex $Mn(CO)_5C(O)Me$ reacts with monohydrosilanes $HSiR_3$ to give mixtures of siloxy ethyl and siloxy vinyl products, $Mn(CO)_5CH(OSiR_3)(Me)$ and $Mn(CO)_5MnC(OSiR_3){=}CH_2$.[215] It was found that carbonylation of $Mn(CO)_5MnC(OSiR_3){=}CHR$, followed by protonolysis, afforded the α-ketoacyl derivatives $Mn(CO)_5C(O)C(O)CH_2R$, which correspond to a net double carbonylation of the precursor $Mn(CO)_5CH_2R$.[216] Manganese acyl complexes, for example, $Mn(CO)_4(PPh_3)C(O)Me$, are very effective catalysts for the hydrosilylation of ketones and esters.[217,218] The carbonylation and decarbonylation of an extensive series of manganese pentacarbonyl alkyl and acyl complexes, $Mn(CO)_5R$ and $Mn(CO)_5C(O)R$, have been reported.[219]

Migratory insertion of an alkyl group into an M–CO bond to give an acyl species is a key step in many catalytic processes. Starting with, for example, $MeMn(CO)_5$, migration is often induced by the presence of a nucleophile L to give the acyl complex MeC(O)Mn(CO)$_4$L. It has been thought for many years that methyl migration to a *cis*-CO ligand occurs to give an intermediate that is trapped by the incoming ligand L. The nature of the intermediate has been addressed in experimental and theoretical studies. Intermediates most commonly discussed include structures **95–97**. In **95**, the acetyl group is η^2-bonded, whereas in **96** there is an agostic interaction between a methyl C–H and the metal. Structure **97** has an η^1-acetyl with solvent occupying the vacated coordination site. Time-resolved infrared and optical kinetics studies of the transient species MeC(O)Mn(CO)$_4$ generated by flash photolysis of MeC(O)Mn(CO)$_5$ in cyclohexane and THF indicate that the intermediate has different compositions in these two media.[219] Based on an analysis of the activation energy data, it is suggested that **95** is the mechanistically relevant intermediate in a weakly coordinating solvent (cyclohexane) and that **97** obtains in coordinating solvents (THF). DFT calculations of the reaction pathway(s) and intermediate structures for methyl migration in MeMn(CO)$_5$ are in partial agreement with experiment.[220–222]



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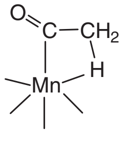

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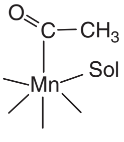
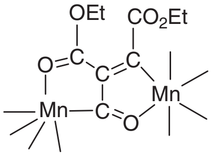


97

The reaction of MeMn(CO)$_5$ with the imine (*p*-tolyl)CH═NMe results in a cyclometallated product, as shown in Scheme 9.[223] The intermediate **98** was observed experimentally, and found to undergo decarbonylation and C–H bond activation to give **99** in preference to imine insertion into the Mn–acyl bond. However, when the reaction is performed in the presence of AlCl$_3$, the product of sequential CO and imine insertion **100** is formed. Most likely, the AlCl$_3$ functions by binding to the acyl oxygen in **98**, thereby increasing the electrophilic nature of the acyl carbon and facilitating attack by the imine. UV photolysis of Mn$_2$(CO)$_{10}$ in the presence of EtO$_2$CC≡CCO$_2$Et proceeds by alkyne insertion into the Mn–Mn bond and coupling to CO to yield **101**.[224] Further treatment of **101** with alkynes and HCl/CO provides a route to carboxylate-substituted pyrans. SO$_2$ and S$_2$O insertion into the η^1-allyl complex **102** to yield **103** has been reported.[225]



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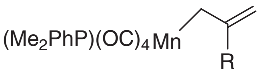

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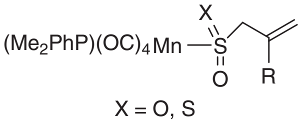
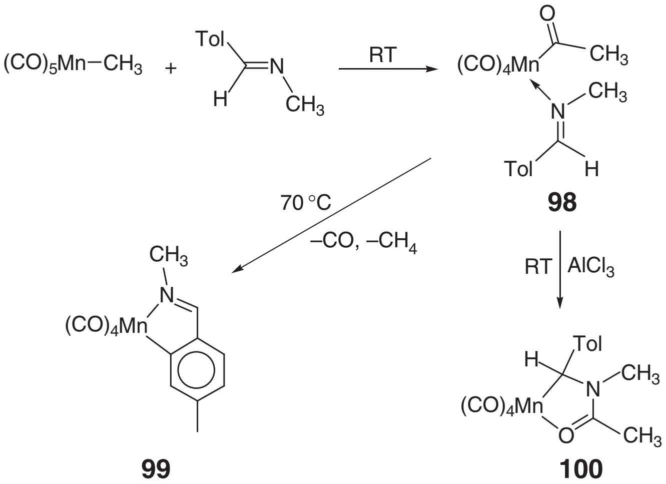


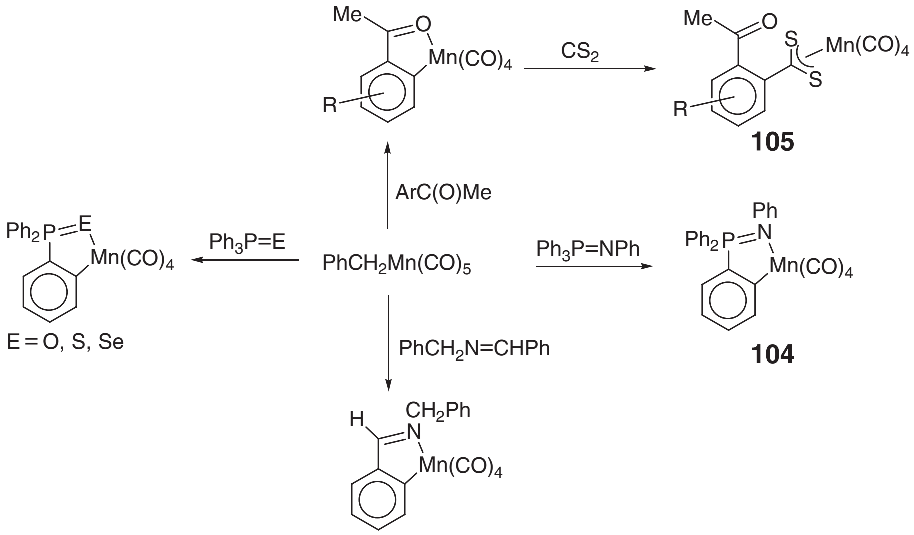
X = O, S

103

Cyclomanganation reactions have been studied for many years. Scheme 10 provides a sample of the types of cyclometallated products that have been characterized.[226–235] Complex **104** is especially interesting because it is thermochromic in solution, changing abruptly from ambient yellow to intense purple as the solution is heated to

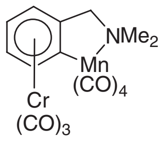


Scheme 9



Scheme 10

100 °C.[227] Cyclomanganated species frequently undergo insertion reactions with a variety of reagents. Scheme 11 provides typical examples of alkyne insertions.[236,237] In other reactions, sulfones and sulfoxides have been inserted into cyclomanganated diterpenoid complexes.[238] Carbon disulfide reacts with cyclomanganated aryl ketones to give η^2-dithiocarboxylato-Mn(CO)$_4$ compounds **105** (Scheme 10).[239] Cyclomanganation of aromatic η^6-arene complexes of chromium with PhCH$_2$Mn(CO)$_5$ has been used to synthesize a variety of interesting multimetallic complexes, for example, structures **106–109**.[240–247] Nucleophilic addition of organolithium reagents to cyclomanganated 2-phenylpyridine derivatives and to cyclomanganated η^6-arene chromium complexes has been reported.[243–245] Other synthetic applications have also appeared.[246,247]



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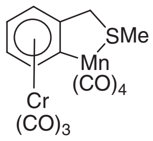

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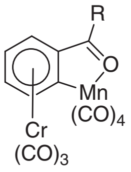

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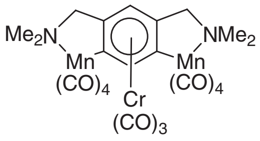
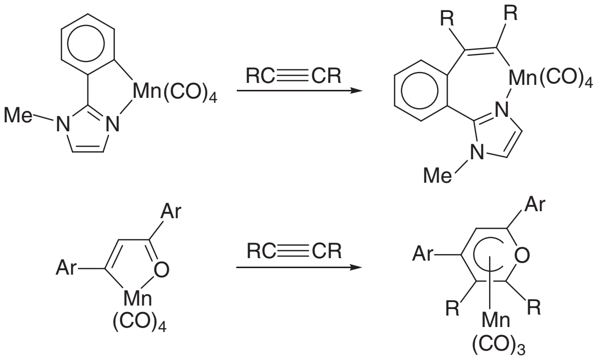


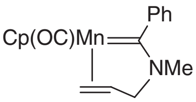
109

A DFT study of the simple carbonyl carbene $[(OC)_5Mn{=}CH_2]^+$ is available.[248] Fischer-type carbene complexes containing manganese are fairly common. Chiral-at-the-metal Fischer carbene complexes are formed when the



Scheme 11

16-electron fragment $[CpMn(NO)(PPh_3)]^+$ is treated with hydroxyalkynes.[249] The likely mechanism of this reaction is given in Scheme 12. Abstraction of iodide from precursor **110** allows coordination of the alkyne, which rearranges to the vinylidene **111**. The latter undergoes intramolecular nucleophilic attack of the alcohol at the α-carbon to generate the chiral carbene **112**. The carbene complex $Cp(CO)_2Mn{=}C(OAc)(Ph)$ reacts with chiral amino alcohols (R^*OH) to afford $Cp(CO)_2Mn{=}C(OR^*)(Ph)$ complexes, which are converted diastereoselectively to $Cp(CO)(PR_3)Mn{=}C(OR^*)(Ph)$ when photolyzed in the presence of PR_3 ligands.[250] The synthesis of chiral carbohydratocarbene complexes by alcoholysis of $CpMn(CO)_2{=}C(OAc)Ar$ with protected carbohydrates and chiral alcohols has been described.[251] The coordination of an independent $CpMn(CO)_2$ fragment to the alkyne in the carbene complex $Cp(CO)_2Mn{=}C(R)C{\equiv}CR^1$ yields a highly fluxional bimetallic species in which the η^1-carbene and η^2-alkyne moieties rapidly exchange as pictured in Scheme 13.[252] A somewhat closely related complex is the η^2-alkene carbene complex **113**.[253] Also of interest is the heterocyclic carbene **114**, as well as the diazomethylsilyl-functionalized carbene $Cp'(OC)Mn{=}C(OEt)CH_2Si(i\text{-}Pr)_2C(N_2)CO_2Me$ and the 2-azoniaallenylidene complex $[Cp(OC)_2Mn{=}C{=}N{=}CR_2]^+$.[254–256] A new class of Fischer-type manganese carbene complexes containing an *o*-carboranyl substituent as in **115** has been reported.[257] Easily generated and reactive manganese trifluoroacetoxy carbene complexes have been applied as convenient intermediates in the synthesis of cyclic enediynes.[258] The reaction of manganese carbene anions $[Cp'(OC)_2Mn{=}C(OEt)(CHR)]^-$ with α,β-unsaturated ketones constitutes a route to 2-cyclohexenones.[259]



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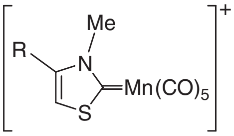

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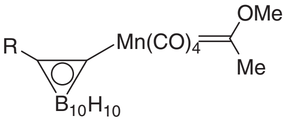

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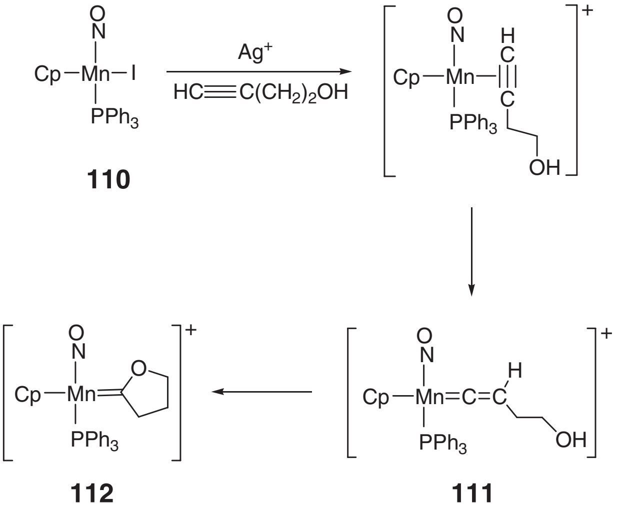
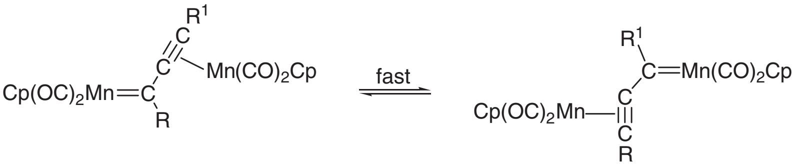
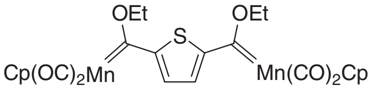


Scheme 12



Scheme 13

A number of bis(carbene) complexes of manganese have been synthesized. The thienylene-bridged **116** is one example.[260] *In situ* deprotonation of Fischer-type manganese carbenes followed by oxidative coupling in the presence of copper or iron salts has been used to synthesize the μ-bis(carbene) complexes **117** and **118**.[261,262]



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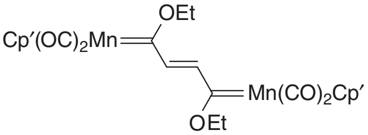

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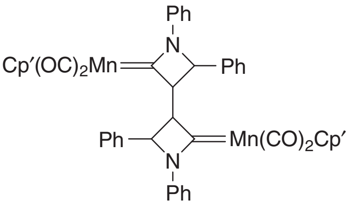
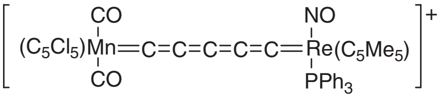


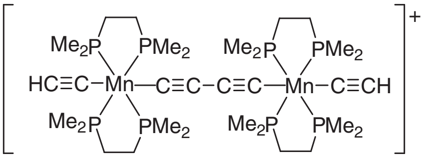
118

Manganese vinylidene complexes may be obtained by treating $Cp'Mn(CO)_3$ with organolithium reagents to form acyl anions $[Cp'Mn(CO)_2C(O)CH_2R]^-$ that react with electrophiles such as acetyl chloride to afford the carbenes $Cp'(OC)_2Mn{=}C(OC(O)Me)(CH_2R)$. The latter complexes eliminate acetic acid and convert to the vinylidenes $Cp'(CO)_2Mn{=}C{=}CHR$.[263] The alkynyl complex $Cp^*(CO)_2FeC{\equiv}CH$ combines with $Cp'Mn(CO)_2(THF)$ to afford the bimetallic vinylidene $Cp'(OC)_2Mn{=}C{=}C(H)(Fp^*)$, where Fp^* stands for the $Cp^*Fe(CO)_2$ fragment.[264] The paramagnetic 17-electron alkynyl complex $Cp'Mn(dmpe)(C{\equiv}CPh)$ reacts with hydride donors to give the vinylidene $Cp'(dmpe)Mn{=}C{=}CHPh$, or with itself to generate the bimetallic bis(vinylidene) $[Cp'(dmpe)Mn{=}C{=}C(Ph)]_2$.[265] The analogous $[Cp(CO)_2Mn{=}C{=}C(Ph)]_2$ complex has been made by an oxidative dehydrodimerization process.[266,267] The oxidative activation of $[Cp(OC)_2Mn{=}C{=}C(Ph)]_2$ toward the addition of nucleophiles has been described.[268] The vinylidene $Cp'Mn(dmpe){=}C{=}CH_2$ can be reversibly coupled by an oxidation/reduction cycle to afford the dimeric $[Cp'Mn(dmpe){\equiv}CCH_2]_2{}^{2+}$ complex.[269] Extended chains containing unsaturated carbon networks that are truncated by metal fragments are models for "molecular wires."[270–273] Structures **119** and **120** illustrate two examples of these. In **119**, the cumulenic chain is capped by different metals. In **120**, the unsaturation is provided by acetylide linkages.



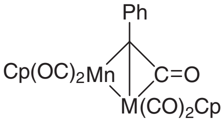
$$\left[(C_5Cl_5)\overset{CO}{\underset{CO}{Mn}}{=}C{=}C{=}C{=}C{=}C{=}\overset{NO}{\underset{PPh_3}{Re}}(C_5Me_5)\right]^+$$

119



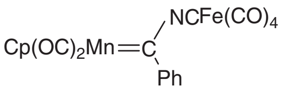
120

The chemistry of carbyne (alkylidyne) complexes containing the $Mn{\equiv}CR$ moiety has been reviewed.[274] The reactions of the electrophilic cationic carbyne $[CpMn(CO)_2{\equiv}CPh]^+$ with a wide range of organometallic anions have been studied.[274–285] Structures **121–125** are examples of the products obtained from reactions with $[CpM(CO)_3]^-$ ($M = Mo$, W), $[Fe(CO)_4CN]^-$, $[Mn(CO)_5]^-$, $[W(CO)_5]^{2-}$ and $[Rh(CO)_4]^-$. The electrophilic nature of the carbyne in the cationic $[Cp(CO)_2Mn{\equiv}CTol]^+$ has been exploited in the synthesis of the alkynylcarbene complex **126** by the copper(I)-catalyzed reaction with (p-Tol)$C{\equiv}CH$.[286,287] The alkynylcarbenes such as **126** dimerize to manganese enediyne complexes, from which free enediynes can be generated by photolysis, copper-catalyzed air oxidation, or stoichiometric oxidation with Cu(II). The alkylidyne complexes $[Cp(OC)_2Mn{\equiv}CCH_2R]^+$ ($R = H$, Me, Ph) undergo facile deprotonation to afford intermediate vinylidene complexes $Cp(OC)_2Mn{=}C{=}CCHR$ that react with imines such as $PhN{=}CHPh$ by $[2+2]$ cycloaddition to give cyclic carbene products **127**.[288] An isonitrile product **128** results from the reaction of $[Cp(OC)_2Mn{\equiv}CMe]^+$ with ${}^tBuN{=}C{=}NBu^t$ and Et_3N. With benzalazine, $Ph(H)C{=}NN{=}C(H)Ph$, $[Cp(OC)_2Mn{\equiv}CMe]^+$ gives the bimetallic bis(carbene) complex **129**, which results from consecutive $[3+2]$ cycloaddition reactions of the azine with two molecules of the organometallic.[288] The mechanism of alkyl migration from oxygen to the iron in the iron–manganese ethoxycarbyne complex **130** has been studied.[289]



M = Mo, W

121



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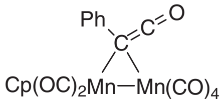

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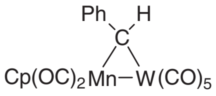

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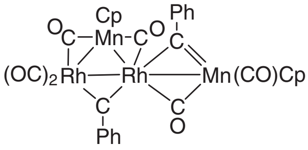

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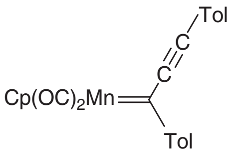

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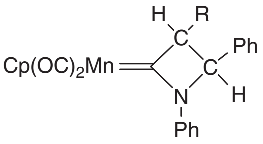
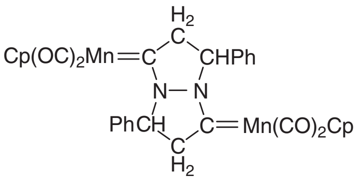


127

$Cp(OC)_2Mn—C{\equiv}NBu^t$

128



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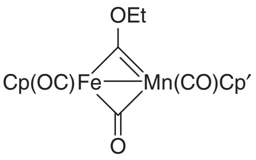
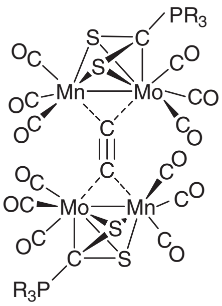


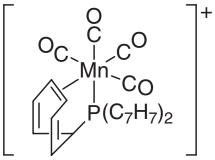
130

The metallocenylacetylide complexes $(OC)_5MnC{\equiv}CC_5H_4MCp$ (M = Fe, Ru) have been reported.[290] Paramagnetic d^5-half-sandwich alkynyl complexes (RCp)(dmpe)MnC≡CR^1 (R = H, Me) have been prepared from the reaction of the manganocene $(RCp)_2Mn$ with terminal or $SnMe_3$-substituted acetylenes and dmpe.[265] As noted above, Cp′(dmpe)MnC≡CPh slowly dimerizes to the binuclear bis(vinylidene) Cp′(dmpe)Mn═C═CPh–CPh═C═Mn(dmpe)Cp′ **131**, which can be reversibly oxidized to the bis(carbyne) dication [Cp′(dmpe)Mn≡C–CPh═CPh–C≡Mn(dmpe)Cp′]$^{2+}$. Cyclic voltammetry of **131** shows two 1-electron chemically reversible oxidations, with a separation of 0.21 V. DFT calculations indicate that the potential separation is due largely to solvation effects and does not signal a significant metal–metal interaction. The synthesis of the first bridging acetylide with two metals at each carbon site, complex **132**, has been reported.[291]



132

The reaction of the η^2-ethylene complex $[Mn(CO)_5(C_2H_4)]^+$ with $[Re(CO)_5]^-$ involves both ligand and electron transfer to produce initially $[Re(CO)_5(C_2H_4)]^+$ and $[Mn(CO)_5]^-$.[292] In addition to binding through the phosphorus, the ligand tris(cycloheptatrienyl)phosphine is able to donate one or more of its double bonds to a metal.[293] Complex **133** is an example illustrating η^2-coordination from one of the triene rings, along with the usual coordination from the phosphorus. The photochemical or thermal reaction of $[Mn(CO)_5]^-$ with C_{60} affords the manganese fullerene complex $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$, in which the metal is attached to a six-membered ring.[294,295] Spectroscopic data suggest that much of the negative charge in **134** is delocalized onto the fullerene ligand. The Mn-η^2-C_{60} bond appears to be unusually strong and **134** exhibits little of the chemistry associated with neutral η^2-C_{60} complexes or with the analogous $[Mn(CO)_5]^-$ ion.



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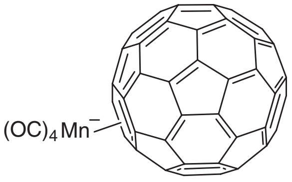
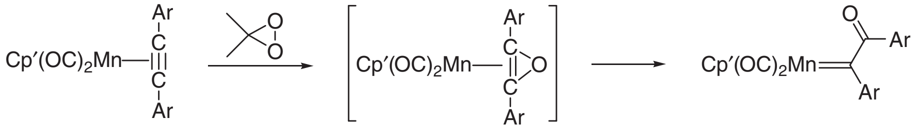


134

A DFT study of the η^2-alkyne to η^1-vinylidene isomerization $CpMn(CO)_2(\eta^2\text{-}HC{\equiv}CH) \rightarrow CpMn(CO)_2{=}C{=}CH_2$ has been published.[296] The vinylidene was calculated to be 37 kJ mol^{-1} more stable than the acetylene complex. A direct 1,2-hydrogen shift pathway, proceeding via an agostic intermediate, is the energetically most favorable, having a barrier of 114 kJ mol^{-1}. A pathway involving C–H oxidative addition to give an alkynylhydrido intermediate is ruled out due to a higher computed barrier (146 kJ mol^{-1}). The alkyne ligand in complexes such as $Cp'Mn(CO)_2(\eta^2\text{-}ArC{\equiv}CAr)$ **135** undergoes oxidation with dimethyldioxirane (DMDO) as shown in Scheme 14.[297] The observed product is the α-keto carbene complex **137**, and it is suggested that the reaction pathway likely involves an initial epoxidation of the coordinated alkyne to give an intermediate with a coordinated oxirene ligand **136**. Evidence for an oxirene is significant because this simple 4π-antiaromatic ring system is predicted to be highly unstable with respect to ring opening and subsequent reaction. Under the correct circumstances, the *in situ* generation of a coordinated oxirene may provide a route to their synthesis and study, similar to the celebrated case of cyclobutadiene.

A theoretical study of two fluxional processes observed on the NMR timescale for the η^3-butenyl complex $(\eta^3\text{-}CH_3CHCHCH_2)Mn(CO)_3$ indicates that the lower-energy one averages the agostically bonded methyl hydrogens.[298] The higher energy process averages the two halves of the *syn*-butadiene fragment and involves oxidative addition of the agostic C–H to give an $(\eta^4\text{-butadiene})Mn(CO)_3H$ intermediate. Microcalorimetric measurements have been reported that pertain to the alkenyl isomerization $Mn(CO)_5(\eta^1\text{-}C_3H_5) \rightarrow Mn(CO)_4(\eta^3\text{-}C_3H_5)$.[299] Irradiation of the bimetallic $(OC)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3$ in a low temperature argon matrix leads to CO dissociation from the manganese but not the chromium center.[300] However, in a dinitrogen matrix, photosubstitution occurs at both metals to yield a variety of dinitrogen complexes, for example, $(OC)_3(N_2)Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3$.

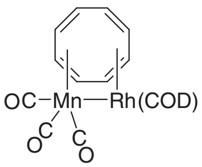
An improved synthesis has been reported for the perchlorate (perchlorates are classified as class A explosives; all experiments with perchlorates must be treated as potentially hazardous) $Mn(CO)_5OClO_3$, which is an excellent precursor for η^4-complexes such as $[(\eta^4\text{-cyclooctadiene})Mn(CO)_4]ClO_4$ and $[(\eta^4\text{-norbornadiene})Mn(CO)_4]ClO_4$.[301] The η^5-cyclooctatrienyl complex $(\eta^5\text{-}C_8H_9)Mn(CO)_3$ can be deprotonated to give the anion $[(\eta^4\text{-COT})Mn(CO)_3]^-$, which functions as a building block for the synthesis of *syn*- and *anti*-facial heterobimetallic complexes such as $(OC)_3Mn(\mu\text{-COT})Rh(COD)$ **138** and $(OC)_3Mn(\mu\text{-COT})Ir(COD)$ **139**.[302] A facile synthesis of η^4-oxapentadienyl



135 **136** **137**

Scheme 14

complexes such as **140** has been reported.[303] $PhCH_2Mn(CO)_5$ reacts with 1,4-diaryl-1-aza-1,3-butadienes to give pyrrolinonyl rings η^4-coordinated to manganese **141**.[304] It is proposed that **141** forms by intramolecular CO insertion into a cyclomanganated intermediate, followed by cyclization.



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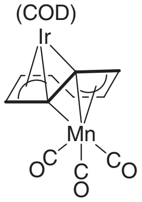

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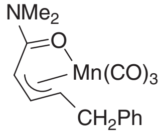

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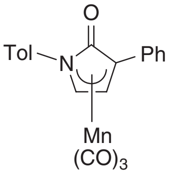


141

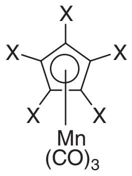
5.10.4.2 Cyclopentadienyl and Related Complexes

Cymantrene, (η^5-Cp)$Mn(CO)_3$, is a robust molecule whose chemistry has been extensively developed. The methyl-substituted analog, (η^5-MeCp)$Mn(CO)_3$ or "MMT", is especially well known because it has replaced alkylleads as an antiknock agent and octane enhancer in gasoline in Canada. Combustion of MMT leads to the emission of manganese oxides into the atmosphere and soil. Additionally, MMT itself is introduced to the environment through evaporation, spillage, or incomplete combustion. MMT is known to photolyze at a substantial rate, but is stable for years in the absence of light. The atmospheric fate of MMT has been studied using laboratory smog chamber simulators.[305] Reaction of MMT with available ozone is rapid. During daytime, atmospheric loss of MMT occurs almost entirely by photolysis, and at nighttime, reaction with ozone becomes significant. Plant absorption of manganese from MMT combustion products and subsequent metabolic effects have been reported.[306] Ultra trace levels of MMT (pg L^{-1}) in water can be determined by a combination of solid phase microextraction techniques and gas chromatography–plasma atomic emission detection.[307] MMT and its inorganic combustion products have been analyzed by the combination of HPLC and diode laser atomic absorption spectrometry.[308] The chemical nature of the manganese-containing particulates from MMT combustion has been examined by X-ray absorption fine-structure spectroscopy (XAFS).[309]

The Penning ionization electron spectrum of $CpMn(CO)_3$ and the negative-ion photoelectron spectrum of $[Cp'Mn(CO)_3]^-$ have been published.[310,311] A vibrational and force field analysis of $CpMn(CO)_3$ has also appeared, as has a study of FTIR spectra in the first and second overtone region.[312,313] Threshold photoelectron–photoion coincidence spectroscopy has been used to investigate the dissociation kinetics of $[CpMn(CO)_3]^+$, which occurs by sequential loss of three CO molecules.[314] The first and third CO loss is slow (microsecond range for lifetimes), accordingly with the successive Mn–CO bond energies in $[CpMn(CO)_3]^+$ of 107, 60, and 104 kJ mol^{-1}, respectively. These energies may be compared with estimates for neutral $CpMn(CO)_3$ of 180, 106, and 99 kJ mol^{-1}. Ultrafast photodissociation of $[CpMn(CO)_3]^+$ using femtosecond laser pulses has been reported.[315]

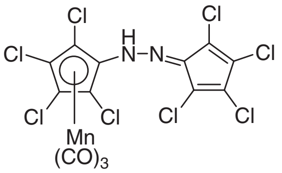
UV photolysis of $CpMn(CO)_3$ in heptane/toluene produces $CpMn(CO)_2$(toluene), which has a metal–toluene bond strength of ca. 60 kJ mol^{-1} and which reacts with THF by a dissociative pathway to afford $CpMn(CO)_2THF$.[316] Photosubstitution of CO in $Cp'Mn(CO)_3$ by phosphite ligands has been studied by photomicrocalorimetry.[317] Ultrafast laser-induced photodissociation dynamics of $CpMn(CO)_3$ has been reported.[318] The photochemical generation of $CpMn(CO)_2(\eta^2\text{-}H_2)$ from $CpMn(CO)_3$ and H_2 in supercritical CO_2 using a flow reactor and using *in situ* high pressure NMR has been described.[319,320] The mechanism of gas phase pyrolysis of (RCp)$Mn(CO)_3$ ($R = H$, Me) has been investigated using a combination of IR laser-powered pyrolysis, flow reactor kinetic measurements, and matrix isolation ESR spectroscopy.[321] The results suggest initial stepwise loss of CO, followed ultimately by release of C_5H_5 or MeC_5H_4 radicals which abstract hydrogen from unreacted starting material.

Cymantrenes bearing a wide variety of substituents on the Cp ring have been synthesized. Complexes with one, two, and three electron-withdrawing pentafluorophenyl groups show the anticipated increase in ν_{CO} frequencies.[322] Pentamercuration of cymantrene has been reported, affording $[\eta^5\text{-}C_5(HgOAc)_5]Mn(CO)_3$, from which the pentahalo derivatives **142** can be obtained.[323] The repeated stepwise treatment of $(C_5Br_5)Mn(CO)_3$ with ^nBuLi and PMe_2Cl yields a mixture of products, from which the pentakisphosphanyl complex $[C_5(PMe_2)_5]Mn(CO)_3$ can be obtained.[324] Lithiation of perhalogenated cymantrenes followed by reaction with a variety of electrophilic reagents has been used to prepare complexes such as **143** and **144**.[325–327] Cymantrenes with ester-disubstituted Cp rings have been reported.[328] The methyl imidate derivative of cymantrene **145** is water soluble and has been used as a redox label for proteins.[329] In particular, **145** attaches to the protein bovine serum albumin through interaction of lysine residues with the imidate substituent. Facile electron transfer at the cymantrene center provides for the redox labeling of proteins with a sensitivity significantly higher than that obtained by FTIR measurements on bio-labeled metal carbonyls.[330] In a similar vein, it has been proposed that pyrylium and pyridinium salts containing a cymantrene substituent attached through the Cp ring can be used to label proteins and thereby aid in the detection and characterization of receptor sites.[331] A biotin tracer, formed by reacting cymantrene with biotin hydrazide, displays good bioactivity toward streptavidin.[332] Manganese tricarbonyl analogs of the PCP (phenylcyclidine) receptor site ligand have been reported.[333]



X = Cl, Br, I

142



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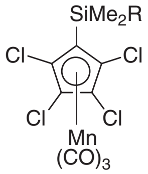

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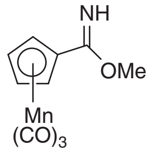
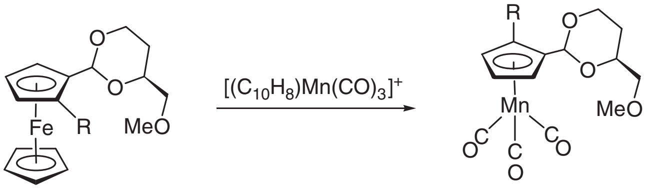


145

The reaction of $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+$ with ferrocene results in ring exchange and formation of $CpMn(CO)_3$ along with $[(\eta^6\text{-napthalene})FeCp]^+$.[334] In a significant application of this chemistry, it was shown that the use of planar chiral ferrocenes in the reaction results in transfer of planar chirality to the manganese complex, as illustrated in Equation (3).[335] The cymantrene complex **146** forms with "100% inversion". Chiral cymantrene complexes such as **146** may be generally useful as auxiliaries in asymmetric reactions and their utility has been demonstrated in high yield asymmetric allylic alkylations with enantioselectivities close to existing benchmarks.[335,336] In chemistry directly related to the synthesis of cymantrenes by ring exchange between $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+$ and ferrocene, it was found that refluxing equimolar amounts of $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+$ and $Cp^*{}_2M$ (M = Fe, Ru, Os) in methylene chloride leads to the air stable "capped" metallocenes **147** as BF_4^- salts.[337] Complexes **147** can be viewed as resulting from the ring transfer in Equation (3) being arrested at an intermediate stage, which appears to be the thermodynamic product for the electron-rich metallocene reactants $Cp^*{}_2M$. Complexes **147** are the first metal carbonyl capped metallocenes with a strictly carbocyclic bridging ligand. The X-ray structure of [**147**]PF_6 (M = Ru) shows that the highly planar Cp* rings adopt a staggered conformation, in contrast to the eclipsed rings found in solid $Cp^*{}_2Ru$. The capped metallocenes are remarkably stable in methylene chloride and do not react with $P(OEt)_3$ over 30 min. A solution of **147** (M = Ru) in the presence of excess naphthalene was found to be unchanged after refluxing in methylene chloride overnight. Acetonitrile at room temperature slowly attacks the Mn center in **147** (M = Fe) to generate $FeCp^*{}_2$ and $[(MeCN)_3Mn(CO)_3]^+$, whereas **147** (M = Ru) is slowly attacked at the Ru center to give $[Cp^*Ru(MeCN)_3]^+$ and $Cp^*Mn(CO)_3$. This difference in reaction pathway is likely due to easier nucleophilic attack by MeCN at the larger ruthenium center, with concomitant Cp* displacement. All three complexes **147** (M = Fe, Ru, Os) undergo "reversible" one-electron reductions to afford 31-electron radicals.[337]



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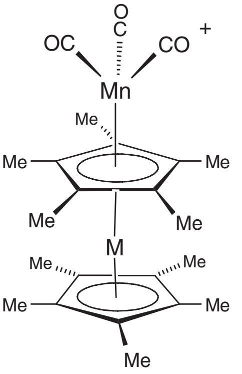

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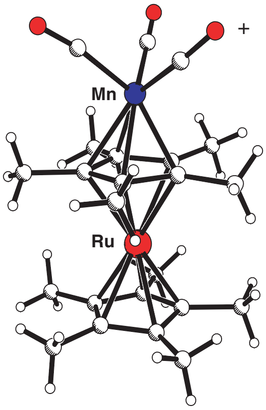
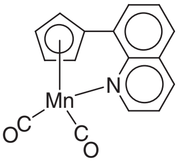


(M = Ru)

Cymantrene readily undergoes photosubstitution of a CO to form new complexes containing aziridine, sulfonylphosphine, thiophene, and 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione ligands.[338–341] Intramolecular photosubstitution of CO by an incipient ligand substituent on the Cp ring has also been reported.[342–345] Examples of products from the latter reaction type include structures **148–150**. β-Cyclodextrin functionalized with thiolate or amino groups on the upper rim give an inclusion complex with cymantrene that undergoes photosubstitution of CO by a rim substituent.[346,347] The water soluble complex $[Cp'Mn(NO)(CN)_2]^-$ is an effective redox mediator for glucose oxidase (GOx).[348] Aqueous electrochemistry pertaining to GOx mediation by neutral manganese half-sandwich complexes was found to be possible by solubilizing neutral complexes such as $Cp'Mn(NO)(S_2CNMe_2)$ via formation of an inclusion compound with β-cyclodextrin **151**. Addition of GOx and glucose to a phosphate buffer solution of **151** leads to a catalytic voltammetric oxidation wave. Consideration of the enzyme active site dimensions and the size of β-cyclodextrin led to the conclusion that there exists an equilibrium between free and included $Cp'Mn(NO)(S_2CNMe_2)$ and that the former is the actual mediator.[348]



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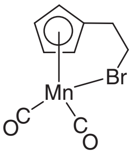

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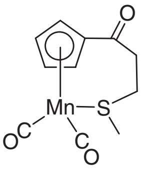

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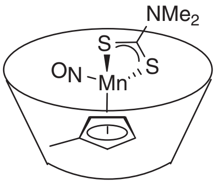
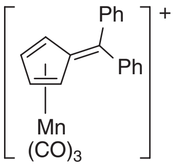


151

The structure and bonding in the η^5-diphenylfulvene (or carbenium ion) complex **152** has been studied.[349] Cymantrenyl carbenium ions stabilized by cobalt–molybdenum clusters attached to a side-chain have been synthesized.[350] Fulvalene complex **153** and analogs have been prepared as candidates for NLO applications.[351,352]



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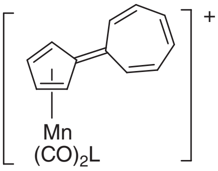
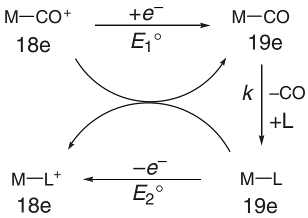


153

An electrochemical investigation of the reduction of a series of $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ complexes (R = H, Me, Cl, CO_2Me) has been reported.[353] The electro- and spectroelectrochemistry of mono- and dinuclear manganese complexes containing the moiety $(\eta^5\text{-}C_5H_4R)Mn(CO)_2(L)$ (L = CO, PR_3) shows reversible oxidations at sub-ambient temperatures for $L = PR_3$.[354] The dinuclear complexes feature two reversible oxidation waves. IR and the electrochemical results indicate that the mixed valent monocations of the dimanganese complexes are valence trapped. A detailed electrochemical study of the reduction of $[Cp'Mn(CO)_2NO]^+$, in the presence or the absence of PR_3

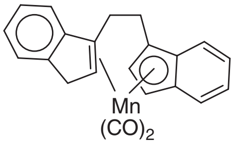


Scheme 15

nucleophiles shows that the CO substitution affording $[Cp'Mn(CO)(NO)PR_3]^+$ is electron-transfer catalyzed (ETC).[355,356] In this reaction, the initially formed 19-electron radical $Cp'Mn(CO)_2NO$ reacts with PR_3 via a strictly dissociative pathway to give $(Cp')Mn(CO)(NO)PR_3$, which is then spontaneously oxidized to product $[Cp'Mn(CO)(NO)PR_3]^+$. The ETC pathway is illustrated in Scheme 15 ($L = PR_3$). It was found that variation of the CO pressure or the PR_3 concentration has no effect on the rate constant k, which, in addition, is the same for all phosphine nucleophiles. Thus, the mechanism is dissociative, in accord with the observed activation parameters: $\Delta H^{\ddagger} = 60\,kJ$; $\Delta S^{\ddagger} = +40\,J\ K^{-1}$. An extension of the work with $[Cp'Mn(CO)_2NO]^+$ to the indenyl analog, $[(\eta^5\text{-indenyl})Mn(CO)_2NO]^+$, produced the superficially surprising result that the radical $(indenyl)Mn(CO)_2NO$ follows the same ETC dissociative mechanism for CO substitution with about the same rate as that seen with $Cp'Mn(CO)_2NO$.[356] The observation of a dissociative mechanism for both Cp′ and indenyl systems suggests that the radicals do not have slipped (η^3-) bonding. Furthermore, there is no "indenyl effect" seen in the CO substitutions at these 19-electron centers. A conclusion from this work is that rapid catalytic substitution via 19-electron intermediates formed due to adventitious impurities may provide a viable alternative pathway for normally slow substitutions at 18-electron centers. A good example of this effect is provided by the observation that normally slow CO substitution in $[Cp'Mn(CO)_2NO]^+$ becomes rapid in the presence of a trace amount of reducing agent NEt_3.[357]

The electrochemical oxidation of $Cp'Mn(CO)_3$ in the presence of $P(OEt)_3$ leads to rapid single and double CO substitution in the 17-electron radical cation.[358] The difference in reactivity between the thermally inert $Cp'Mn(CO)_3$ and the corresponding cation is enormous: the 18-electron complex requires days or longer to substitute a CO, while the 17-electron analog reacts in microseconds by an associative mechanism with a second-order rate constant of $10^8\,M^{-1}s^{-1}$ at room temperature. As might be expected, the placement of bulky substituents on the cyclopentadienyl ring to give $(\eta^5\text{-}C_5MeH_{4-n}R_n)Mn(CO)_3$ (R = Me, Ph, Bu, etc.) inhibits associative CO substitution in the radical cations.[358]

The electrochemical reduction of $(indenyl)Mn(CO)_3$ occurs in two reversible one-electron steps.[359] It is suggested that the dianion contains a slipped η^3-bonded indenyl ligand. Heating $Mn_2(CO)_{10}$ with 1,2-bis(indenyl)ethane affords both monometallated $[C_9H_7C_2H_4(\eta^5\text{-}C_9H_6)]Mn(CO)_3$ and $(OC)_3Mn[\mu\text{-}(\eta^5\text{-}C_9H_6)C_2H_4(\eta^5\text{-}C_9H_6)]Mn(CO)_3$.[360] Photolysis of either product yields complex **154**, in which a CO ligand is replaced by η^2-coordination from a pendant indene group. Lithium fluorenide ($LiC_{13}H_9$) reacts with $Mn(CO)_5Br$ to give an η^1-complex, which slowly dissociates CO and rearranges to the η^5-analog **155**.[361]



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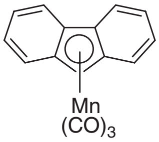
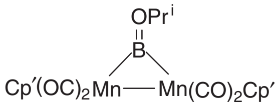


155

The cymantrene dimer $[(C_5H_4)Mn(CO)_3]_2$ can be metallated and then oxidatively coupled to yield $[(C_5H_4)Mn(CO)_3]_n$ ($n = 3, 4$).[362] The $(C_5H_4R)Mn(CO)_2$ fragment has been attached to a variety of monodentate as well as bridging units. Examples with group 14 elements include $(Cp)(OC)_2Mn{=}E(salen)$ and $[(Cp')(OC)_2Mn]_2E(phen)$ (E = Ge, Sn, Pb).[363,364] Examples with group 15 elements include pyrazolate-bridged dimers and $[(Cp')(OC)_2Mn]_2Sb[CH(SiMe_3)_2]$.[365,366] Pyrazolate bridges have also been used to prepare heteronuclear MnZn dimers.[367] The reaction of the borylene complex $[Cp'Mn(CO)_2]_2(\mu\text{-}BCl)$ toward protic reagents has been reported.[368,369] Reaction with i-PrOH gives **156**, while reaction with pyridine in the presence of HBF_4 yields the aminoborylene complex **157**. The latter complex corresponds to formal 1,4-hydroboration of pyridine. Also noteworthy is the In(I) complex $(Cp)(OC)_2Mn\text{-}InC_6H_3\text{-}2,6\text{-}trip_2$ (trip = $\text{-}C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3$).[370] PR_2-substituted derivatives of $(benzene)_2Cr$ have been used as spacers to connect $Cp'Mn(CO)_2$ units as in complex **158**.[371] The tetranuclear complexes $[Cp^*(OC)_2Mn]_4(\mu\text{-}TCNX)$ (TCNX = TCNE, TCNQ, TCNB) are paramagnetic in spite of having an even-electron count.[372] Coordination of the $CpMn(CO)_2$ unit to the strained phosphorus-bridged [1]ferrocenophane ligand gives a monomeric complex that undergoes ring-opening polymerization upon UV irradiation to generate the polymer **159**.[373]



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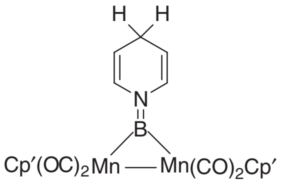

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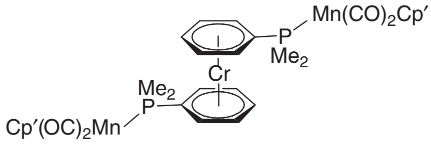

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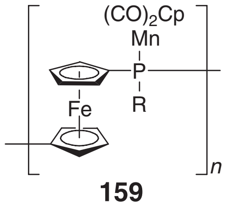
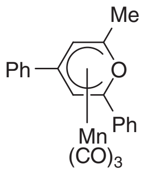


159

Five- or six-membered heterocyclic rings that function as η^5-ligands to a manganese fragment are well known. The rather bizarre dimetalladithiacyclopentadienyl complex **72** was noted previously (*vide supra*).[159] Oxidation of the manganese pyranyl complex **160** causes the $Mn(CO)_3^+$ unit to undergo migration from the pyranyl ring to a phenyl ring.[374] $[Mn(CO)_3(\eta^5\text{-}nido\text{-}7,8\text{-}C_2B_9H_{11})]^-$, the anionic dicarbollide analog of cymantrene, interacts with cationic metal fragments $[M(PPh_3)]^+$ (M = Cu, Ag, Au) to give bimetallic compounds. In contrast, electrophiles such as H^+ and Me^+ abstract hydride from carborane boron vertices.[375,376] Dimethylphosphacymantrene reacts with ^{t}BuLi to give the corresponding η^4-dimethyl-1-*t*-butylphosphole derivative **161**, which acts as a ligand by reacting with $(COD)PdCl_2$ to yield a complex with a Pd_2Cl_2 dimeric core **162**.[377] The triphospholyl complex $(\eta^5\text{-}P_3C^t_2Bu_2)Mn(CO)_3$ has been studied by He I and He II photoelectron spectroscopy and by DFT calculations.[378]



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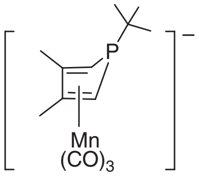

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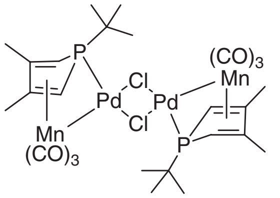
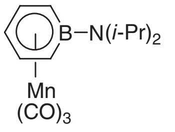


162

5.10.4.3 η^6-Arene and Related Complexes

Transition metal complexes containing an arene ligand bonded in an η^6-manner have been studied for many years and constitute an important class of organometallic compounds. The most thoroughly investigated member of this class is $(arene)Cr(CO)_3$, for which there exists an extensive body of chemical information. The $Cr(CO)_3$ moiety is electron withdrawing, resulting in an electrophilically activated arene. The complex $[(\eta^6\text{-}arene)Mn(CO)_3]^+$ is isoelectronic with $(arene)Cr(CO)_3$ and, as with the chromium complex, can be synthesized with a wide variety of arenes (*vide infra*). The positive charge on the latter complex results in the coordinated arene ring having a greatly enhanced electrophilic character. Correspondingly, the most interesting and useful reactions of $[(\eta^6\text{-}arene)Mn(CO)_3]^+$ are those involving the interaction of the coordinated arene with electron-rich species. In particular, nucleophilic addition, ring deprotonation, and reduction reactions are the most relevant, and some of these have provided useful new synthetic methodologies in organic chemistry. While certain other complexes such as $[(\text{arene})\text{M}(\text{Cp})]^+$ (M = Fe, Ru) also possess highly electrophilic arene ligands, the manganese systems seem to be particularly amenable for synthetic applications.[379–381] The arene ligand in $[(\eta^6\text{-arene})\text{Mn(CO)}_3]^+$ can be (i) monocyclic with a wide range of substituents or (ii) conjugated polycyclic such as naphthalene. The chemistry of these two classes is strikingly different due to facile ring slippage in the latter. For this reason, the two types of complexes are treated separately.

Before discussing manganese arene complexes, it should be noted that other manganese η^6-systems have been reported. The hydrocarbon ring in $[(\eta^6\text{-cycloheptatriene})\text{Mn(CO)}_3]^+$ is extremely electrophilic and the phosphorus ylides such as $\text{CH}_2{=}\text{PPh}_3$ add to the triene ring to give adducts that undergo Wittig-type reactions.[382] Lithium N,N-diisopropyl-1-aminoboratabenzene reacts with $[(\text{MeNC})_3\text{Mn(CO)}_3]^+$ to yield the η^6-complex **163**.[383] In an interesting variation on this reaction, lithium 1-(3-(dimethylamino)propyl)boratabenzene was found to yield a dynamic equilibrium between neutral **164** and zwitterionic **165**.[384]



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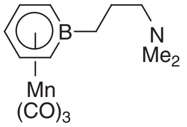

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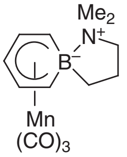
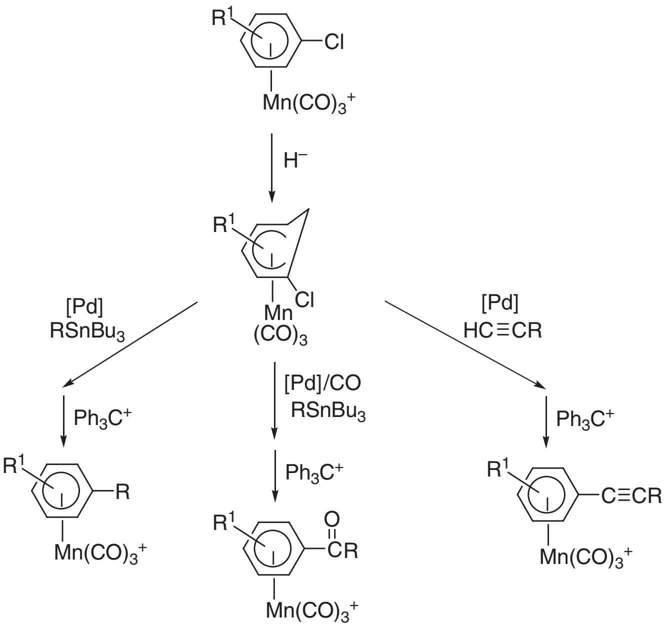


165

Metals coordinated to polycyclic conjugated hydrocarbons that contain both five- and six-membered rings frequently display inter-ring haptotropic rearrangements.[385] The kinetics of the $\eta^6 \rightarrow \eta^5$ haptotropic shift in the fluorenyl complex $(\text{C}_{13}\text{H}_9)\text{Mn(CO)}_2\text{L}$ ($\text{L} = \text{PR}_3$) has been measured.[386] The favored pathway for the $\eta^6 \rightarrow \eta^5$ shift in $(\text{cpp})\text{Mn(CO)}_3$ (cppH = 4H-cyclopenta[def]phenanthrene) has been examined by extended Hückel calculations and suggested to involve the intermediacy of an exocyclic $(\eta^3\text{-cpp})\text{Mn(CO)}_3$ species.[387] In the presence of a donor ligand, $[(\eta^6\text{-trindane})\text{Mn(CO)}_3]^+$ reacts with Bu^tOK to generate $(\eta^5\text{-C}_{15}\text{H}_{15})\text{Mn(CO)}_2\text{L}$, in which the metal has migrated from the central ring onto a peripheral ring that has lost three hydrogens.[388] It is proposed that the mechanism involves three successive C–H insertions, following butoxide addition to a coordinated CO with concomitant loss of CO_2 and formation of an Mn–H bond.

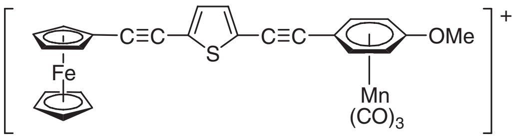
A large number of $[(\eta^6\text{-arene})\text{Mn(CO)}_3]^+$ complexes containing non-conjugated monocyclic arenes have been synthesized. A number of synthetic routes are available to prepare these complexes.[389] The original method involves the reaction of $\text{Mn(CO)}_5\text{Br}$ with the desired arene in the presence of the Lewis acid promoter AlCl_3.[390] The solvent can be the arene itself, or an inert hydrocarbon such as cyclohexane.[389,391] Normally, the reaction mixture is refluxed for several hours. Alternatively, microwave heating can be used to reduce the time required.[392] This method is satisfactory for arenes with substitutents that can withstand the harsh Lewis-acid conditions. In 1981, Pauson proposed a milder method, in which the $\text{Mn(CO)}_5\text{Br}$ is replaced with $\text{Mn(CO)}_5\text{ClO}_4$.[393] In the presence of arenes at room temperature, the latter readily dissociates perchlorate to initiate the generation of $[(\eta^6\text{-arene})\text{Mn(CO)}_3]^+$. The perchlorate, $\text{Mn(CO)}_5\text{ClO}_4$, can be obtained by treatment of $\text{Mn(CO)}_5\text{Br}$ with AgClO_4, or by reacting $\text{Mn}_2(\text{CO})_{10}$ with HClO_4.[301] As an alternative, it is often convenient to utilize AgBF_4 instead, so that $\text{Mn(CO)}_5{}^+\text{BF}_4{}^-$ functions as the starting material. A third method for synthesizing $[(\eta^6\text{-arene})\text{Mn(CO)}_3]^+$ involves heating $\text{Mn}_2(\text{CO})_{10}$ and the arene in trifluoroacetic anhydride containing aqueous HBF_4.[394] A fourth and particularly mild method utilizes the fact that the naphthalene ligand in $[(\eta^6\text{-C}_{10}\text{H}_8)\text{Mn(CO)}_3]^+$ is easily replaced by free arenes (*vide infra*).[395] The four methods mentioned work quite well for many arenes, but are not generally useful when the arene contains strongly electron-withdrawing substituents that exert both a minus-inductive and a minus-resonance influence, such as -C(O)R, -C(O)OR, -CN, -NO_2, etc.

Simple chloroarene complexes such as $[(\eta^6\text{-4-RC}_6\text{H}_4\text{Cl})\text{Mn(CO)}_3]^+$ readily undergo oxidative addition of $\text{Pd(PPh}_3)_4$ into the C–Cl bond to afford the metallated products $[\{\eta^6\text{-4-RC}_6\text{H}_4\text{-PdCl(PPh}_3)_2\}\text{Mn(CO)}_3]^+$.[396] Unfortunately, this reaction is of limited interest because the products are not active under normal catalytic coupling conditions. However, in a new and highly significant advance, the same research group has shown that easily obtained chlorocyclohexadienyl manganese tricarbonyl complexes undergo palladium-catalyzed coupling reactions with a variety of carbon nucleophiles to afford products from which hydride may be abstracted with trityl cation, thus generating new $[(\eta^6\text{-arene})\text{Mn(CO)}_3]^+$ complexes containing substituents that cannot be introduced in any other manner.[397–402] This is particularly true of electron-withdrawing substituents. Scheme 16 illustrates the chemistry involved. Analogous palladium-catalyzed coupling reactions have been used to synthesize multimetallic complexes **166** and **167**.[403,404] As a corollary to the new synthetic methodology, it may be noted that in some cases it constitutes



Scheme 16

a route to cyclohexadienyl manganese complexes possessing a regiochemistry not available via conventional nucleophilic addition to η^6-arene precursors.[402,405] For example, when X in $[(\eta^6\text{-}C_6H_5X)Mn(CO)_3]^+$ is electron donating (e.g., $\text{-}NR^1_2$, $\text{-}OR^1$, $\text{-}SR^1$), nucleophilic addition of R^- yields **168** with high regioselectivity. Starting with **169**, which is the normal product of nucleophilic addition to the chlorobenzene complex, and using a palladium-catalyzed substitution, it is possible to generate **170**, which is the otherwise unavailable *ortho*-isomer of **168**.



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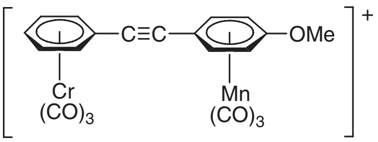

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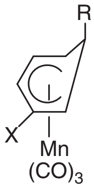

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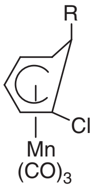

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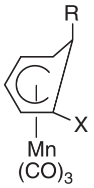
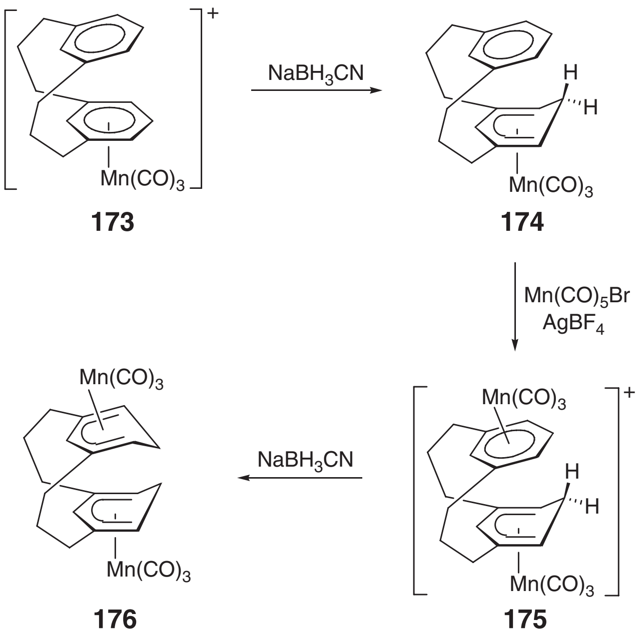


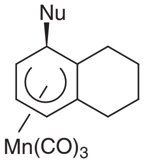
170

The most useful reaction of $[(\eta^6\text{-arene})Mn(CO)_3]^+$ is the very facile addition of a wide range of nucleophiles to afford stable cyclohexadienyl complexes. The electronic structure of the cations and the factors that influence the regio- and stereochemical pathways followed in the reaction with nucleophiles has been examined theoretically.[406,407] The nucleophiles utilized include Grignard reagents, benzylic zinc reagents, alkylmercury chlorides, stabilized enolates, borohydride, aryllithium reagents, phosphinates, anionic metal complexes, etc.[408–417] The stereoselectivity of these addition reactions is almost always exclusively *exo* to the metal and the regioselectivity is often large and strongly dependent on the arene substituents. Ring strain can influence the result in some cases. Thus, $[(\eta^6\text{-tetralin})Mn(CO)_3]^+$ adds nucleophiles α to the bridgehead to give **171**, while $[(\eta^6\text{-biphenylene})Mn(CO)_3]^+$ prefers to be attacked at the bridgehead to yield **172**, with concomitant release of ring strain.[418,419] As shown in Scheme 17, the manganese cyclophane complex $[(\eta^6\text{-}[3_2](1,3)\text{cyclophane}Mn(CO)_3]^+$ **173**



Scheme 17

reacts with a hydride donor to yield the expected cyclohexadienyl product **174**.[420] Subsequent attachment of a second manganese tricarbonyl unit yields **175** and permits the addition of a second hydride to give as the final product the neutral bis-cyclohexadienyl bimetallic **176**. The first synthesis of planar chiral [(1,3-disubstituted-arene)Mn(CO)$_3$]$^+$ cations **177** starting from the readily available achiral [(*p*-cresol)Mn(CO)$_3$]$^+$ and performing sequential deprotonation/nucleophilic addition/electrophilic quenching has been reported.[421] The key to obtaining a chiral product with reasonable ee is the presence of a suitable chiral ligand such as (*S*)-binaphthol in the nucleophilic addition step. The enantiomeric purity of chiral complexes of substituted anisoles and toluenes analogous to **177** is conveniently carried out by ^{1}H NMR analysis after anion exchange with the chiral anion tris(tetrachlorobenzenediolato)phosphate(V) (TRISPHAT).[422] The silatrane complex **178** reacts with MeMgBr to afford a neutral cyclohexadienyl complex that can be "reactivated" by treatment with NOBF$_4$ to the electrophilic **179**.[423] Subsequent hydride addition to **179** and demetallation affords disubstituted cyclohexadiene silatranes.



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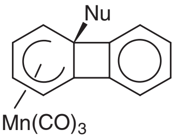

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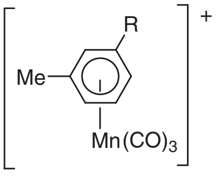
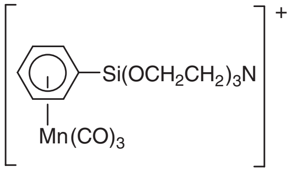


R = Ph, 2-thienyl
177



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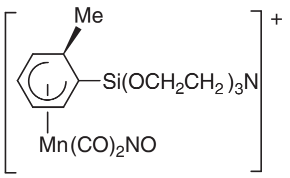
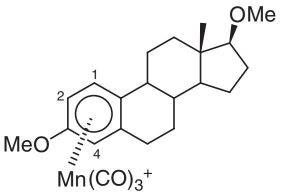


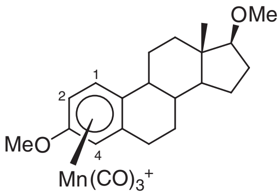
179

It has been demonstrated that coordination of manganese tricarbonyl makes it possible to functionalize aromatic steroids and related natural products. Thus, 3-methoxyestrone and 3,17-dimethoxyestradiol coordinate to form nearly equal amounts of α- and β-isomers, as in 180 and 181.[424,425] Nucleophilic addition to the β-isomer is regiospecifically *meta* (C1), but addition to the α-isomer occurs at sites C1, C2, and C4. This difference in selectivity is due to tripodal carbonyl interactions with the steroidal backbone. An example of the utility of this chemistry is the facile conversion of the steroid estrone to 1-methylestrone **182** in an overall isolated yield of 42%. The synthesis involves (i) protection of the ketone group in estrone, (ii) complexation of $Mn(CO)_3^+$, (iii) addition of MeMgCl to the C1 site, and (iv) deprotection of the ketone and demetallation. This procedure for converting the inexpensive estrone to the very expensive 1-methylestrone is an attractive alternative to purchasing the product. Manganese-mediated functionalization has been applied to the methylated derivative of podocarpic acid **183**, an abundant diterpenoid resin acid found in New Zealand rimy and kahikatea trees and of substantial interest as a precursor to C-ring aromatic steroids.[426,427] Coordination of $Mn(CO)_3^+$ to **183** occurs nearly equally to the α- and β-faces, and activates the aromatic ring to a range of nucleophiles. The α-isomer is attacked regiospecifically at the *meta*-position (C14), but the β-isomer displays the regioselectivity order *ortho* (C13) > *meta* (C14) ≫ *ortho* (C11). Normally, nucleophilic attack at a site *ortho* to an OMe substituent is not seen in manganese arene complexes unless steric factors intervene. In the case of the β-isomer of $[(\eta^6\text{-dimethylpodocarpic acid})Mn(CO)_3]^+$, X-ray structures clearly indicate that the steric interaction of relevance is between Me-17 and a carbonyl ligand. In effect, with the β-isomer there is a balance between electronic factors (favoring *meta*-addition) and steric factors (favoring *ortho*). The α-isomer does not impose steric constraints at either site and, accordingly, the position *meta* to OMe is strongly favored.



α-Isomer

180



β-Isomer

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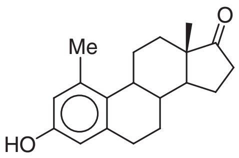

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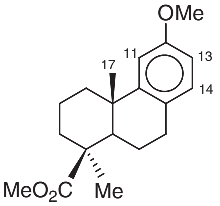
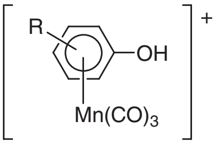


183

The acidity of phenol and cresol complexes **184** is greatly enhanced by the $Mn(CO)_3^+$ moiety and they readily undergo deprotonation to oxocyclohexadienyl complexes **185**. Subsequent nucleophilic addition gives **186**, from which *ortho*-disubstituted phenols **187** are obtained after demetallation.[428,429]



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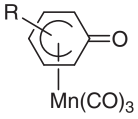

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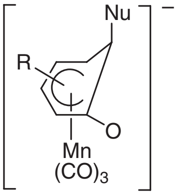

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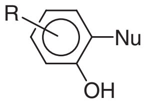
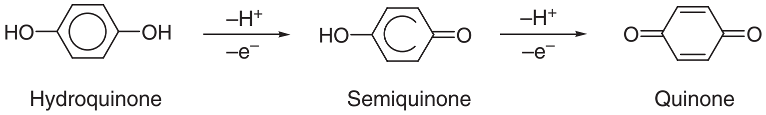


187

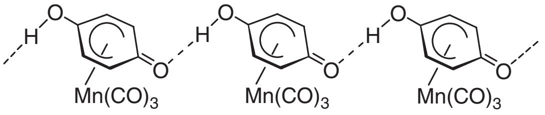
Dihydroxybenzenes or hydroquinones are important in mediating reversible electron and proton transfers in biological systems, as shown in Scheme 18. It would be anticipated that the attachment of a metal fragment to the hydroquinone π-system would significantly influence both proton and electron transfers that result in the formation of semiquinone and quinone oxidation products. It is known that the members of this series generally σ-bond to transition metals through the oxygen atoms rather than through the carbocyclic π-system and, correspondingly,



Scheme 18

there are few examples of π-bonded hydroquinone complexes. It was found, however, that ligand exchange with $[(\eta^6\text{-napthalene})Mn(CO)_3]^+$ affords a facile high yield route to the "thermally stable" π-complex $[(\eta^6\text{-hydroquinone})Mn(CO)_3]^+$ **188**, as well as the *o*-hydroquinone (catechol) and *m*-hydroquinone (resorcinol) analogs.[430] Crystals of the highly insoluble SiF_6^{2-} salt of **188** were obtained from an acetone solution of [**188**]BF_4 in a Pyrex vessel containing a small amount of HBF_4 to suppress proton dissociation (*vide infra*). X-ray analysis verified the expected η^6-bonding and showed that four of the six F atoms in each SiF_6^{2-} are strongly hydrogen bonded to the hydroquinone -OH groups, thus accounting for the insolubility.

The electrophilic activation provided by the metal fragment in **188** results in facile reversible deprotonation of the -OH groups to afford the η^5-semiquinone and η^4-quinone complexes according to Scheme 19. Although the sequence **188** ↔ **189** ↔ **190** in Scheme 19 can be viewed as a series of simple deprotonations, the analogy to the proton and electron transfers occurring with free quinones is evident if it is considered that each proton loss is accompanied by electron transfer to the metal, which acts as an internal oxidizing agent or electron sink. Similar reasoning holds for the catechol analogs shown in Scheme 20. The neutral η^5-semiquinone complex **189** was found to exist in linear polymeric arrays with the structure dictated by strong intermolecular hydrogen bonding.[431,432] By comparison, the catechol analog **192** exists as discrete hydrogen-bonded dimers. The hydrogen-bonding interactions in **189** and **192** are strong and, as judged from ^1H and ^{13}C NMR spectra, also dynamic so that, for example, all four ring hydrogens in **189** are equivalent on the NMR timescale.



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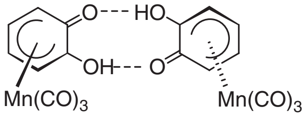
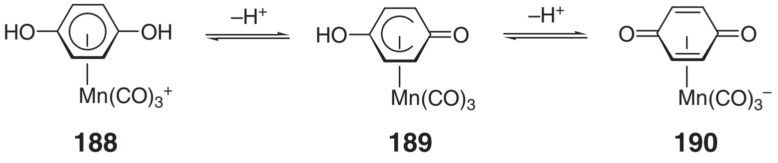
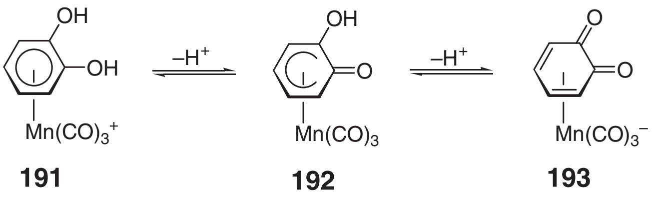


192

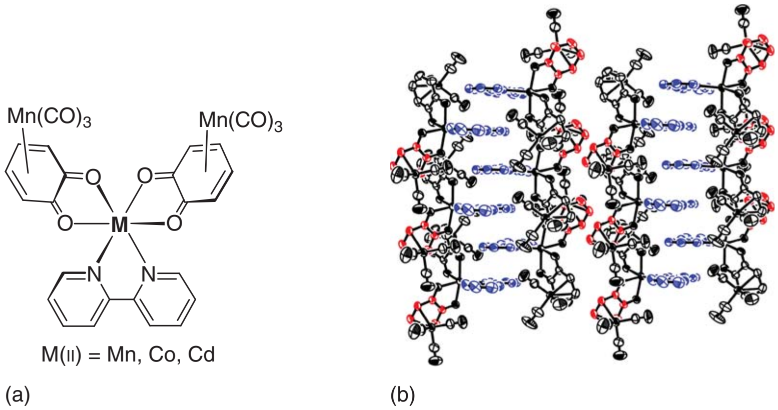
The *o*-quinone organometalloligand **193**, termed "*o*-QMTC" (*o*-quinone manganese tricarbonyl) readily reacts with divalent metal ions by coordinating through the oxygen atoms to afford monomeric neutral complexes M(*o*-QMTC)$_2$(L–L) (M = Mn, Cd, Co; L–L = neutral ligand).[433] X-ray structural studies with 2,2′-bipyridine as the "L–L" ligand reveal complexes that self-assemble into two-dimensional supramolecular networks, the structure of which is determined by π–π stacking and interdigitation of the bipyridine ligands and by a pairwise π–π stacking of one of the two *o*-benzoquinone ligands in each monomeric unit to generate the arrays shown in Figure 1. One-dimensional coordination networks **194** containing M(*o*-QMTC)$_2$(L–L) formula units result when 4,4′-bipyridine is used as a bridging ligand.[434]



Scheme 19

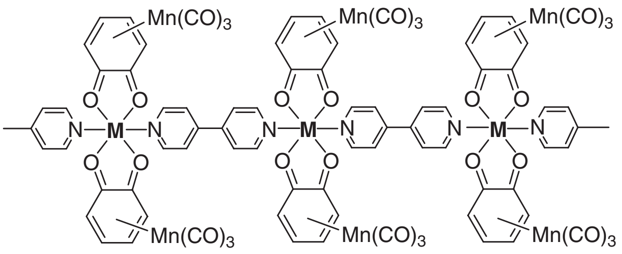


Scheme 20



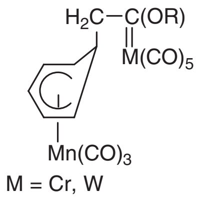
(a) (b)

Figure 1 Structure of (a) M(o-QMTC)$_2$(bipyridine) and (b) π–π stacking in the solid.



194

Nucleophilic addition to $[(\eta^6\text{-arene})\text{Mn(CO)}_3]^+$ has been used to synthesize a variety of heteropolymetallic complexes. Addition of the α-anionic Fischer carbene $[(\text{OC})_5\text{M}{=}\text{C(OR)CH}_2\text{Li}]$ (M = Cr, W) affords the bimetallic cyclohexadienyl complex **195**.[415] The metallophosphide anions $[\text{Cr(CO)}_5\text{PPh}_2]^-$ and $[\text{Fe(CO)}_4\text{PPh}_2]^-$ react similarly to yield **196**.[435] Treatment of lithiated (2,3-dimethoxybenzene)Cr(CO)$_3$ with $[(\eta^6\text{-arene})\text{Mn(CO)}_2\text{L}]^+$ (L = P(OEt)$_3$) gives rise to di-, tri-, and tetranuclear complexes such as **197**.[417] The benzylic carbanion derived from $[\eta^6\text{-C}_6\text{H}_5\text{CHMe(OMe)}]\text{Cr(CO)}_3$ reacts to give dinuclear **198**.[436] The addition of NaCp to $[(\eta^6\text{-C}_6\text{H}_6)\text{Mn(CO)}_3]^+$ gives a cyclohexadienyl product with an *exo*-cyclopentadiene substituent that can be deprotonated and metallated to give heterometallic complexes, of which **199** is an example.[437]



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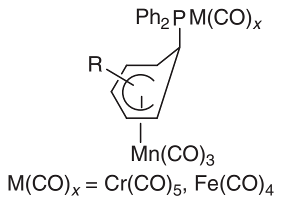

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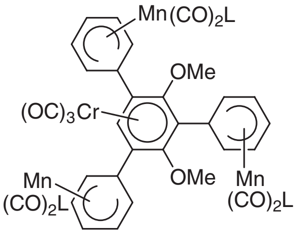

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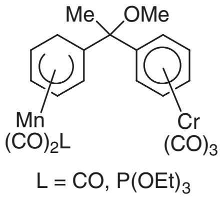

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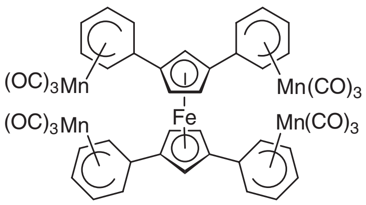
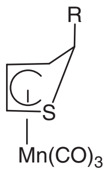
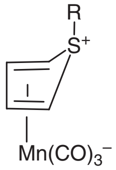


199

Thiophene (T) is a six-electron donor that is analogous to an arene in terms of coordinating to manganese to form $[(\eta^5\text{-T})Mn(CO)_3]^+$. Variously substituted thiophene complexes of manganese have been examined for their non-linear optical properties.[438] When the thiophene contains an aryl-containing side-chain, the metal can bond to either of the two sites and theoretical calculations indicate that the energy difference between the two possibilities is rather small.[439] In the case of dibenzothiophene, as well as dibenzofuran and xanthene, the $Mn(CO)_3{}^+$ moiety prefers the carbocyclic ring.[440,441] The product of nucleophilic addition to $[(\eta^5\text{-T})Mn(CO)_3]^+$ depends on the nature of the nucleophile.[442,443] Hydride, PR_3, and CN^- add to carbon to give **200**, but cuprates and Grignard reagents add to the sulfur, affording zwitterionic thiophenium products **201**. As with thiophene, hydride and cyanide addition to the selenium analog $[(\eta^5\text{-}C_4H_4Se)Mn(CO)_3]^+$ occurs at a carbon adjacent to the heteroatom.[444]



200



201

Curiously, manganese has come to play a significant role in the selective activation of normally robust chemical bonds, which is a research field with major implications in both synthesis and catalysis. In general, selective cleavage of covalent bonds has been accomplished with varying degrees of success by employing high temperature/pressure conditions and/or highly nucleophilic or electrophilic metal species to attack the bond in question. Being able to conduct the chemistry under mild conditions with fairly stable reagents and in a catalytic manner is a highly desirable goal (as the biological world can attest). Within the context of organometallic chemistry this means finding a way to suitably activate the desired bond to cleavage by a mild metal reagent. This "preactivation" methodology is an alternative to using highly reactive, but perhaps not very selective, unsaturated metal fragments to attack the targeted bond. The preactivation of a bond by coordination of a transition metal fragment to a part of the molecule remote from the bond to be broken is termed "remote activation", and the $Mn(CO)_3{}^+$ fragment has been quite successful in this regard.[445] The chief advantage of this approach is that it permits the use of mild and conveniently synthesized reagents to break the required bond, usually in a regioselective manner. Figure 2 illustrates bonds that have been activated by coordination of $Mn(CO)_3{}^+$ to adjacent or nearby carbocyclic rings. The arrows indicate the covalent bond that was found to be cleaved by appropriate metal nucleophiles. With the use of manganese tricarbonyl, remarkable, and in some cases unprecedented, levels of C–C, C–O, C–S, C–Se, and N–H bond activation has been achieved in these systems.[445]

Cleavage of the strained C–C bond in the four-membered ring in biphenylene (BP) is greatly facilitated by coordination of $Mn(CO)_3{}^+$ to one of the aromatic rings. Free BP undergoes no reaction with the mild nucleophiles $M(PPh_3)_2(C_2H_4)$ (M = Pt, Pd). However, these nucleophiles react in minutes at room temperature with $[(\eta^6\text{-BP})Mn(CO)_3]^+$ to give **202**, the product of insertion into the C–C bond.[446] By way of comparison, the far more nucleophilic $Pt(PEt_3)_3$ requires days at 80 °C to break the C–C bond in BP.[447]

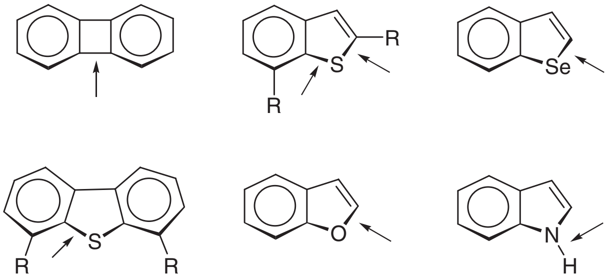
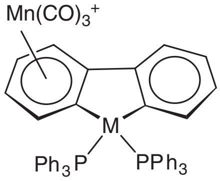


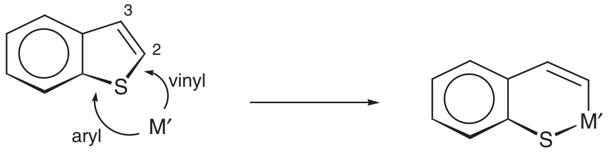
Figure 2 The bonds identified by arrows are activated by coordination of $Mn(CO)_3{}^+$ to the carbocyclic ring.



M = Pt, Pd

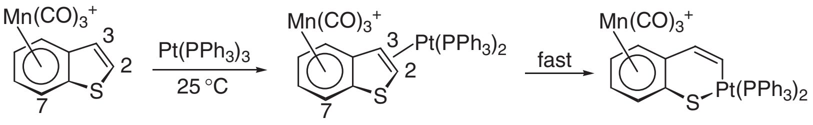
202

The activation of C–S bonds in thiophenes (T), benzothiophenes (BT), and dibenzothiophenes (DBT) is especially important because these and other stable conjugated heterocyclic molecules constitute major pollutants in crude petroleum. The combustion of fuels containing these species contributes significantly to environmental pollution through the release of sulfur oxides. For this and other reasons, crude petroleum is treated with hydrogen to remove sulfur as H_2S (and nitrogen as NH_3), generally with a heterogeneous Mo/Co sulfide on alumina catalyst, in what constitutes the largest volume industrial chemical reaction in the world (30 million barrels/day worldwide). Thiophenic molecules such as BT and DBT are of special concern because their alkylated derivatives are difficult to desulfurize by present technology and, as a consequence, much of the fossil fuel sulfur contamination can be traced to these species. Proposed US government regulations to take effect require deep cuts in sulfur content in gasoline and diesel fuels and this, in turn, requires substantial improvements in "deep" hydrodesulfurization (HDS) technology. In effect, this means finding better ways to desulfurize alkylated thiophenes. Homogeneous organometallic models for HDS have contributed substantially to our understanding of the relevant chemistry. Taking benzothiophene as an example, most model studies have utilized highly reactive and coordinatively unsaturated nucleophilic transition metal fragments (M′) generated photolytically or otherwise, which generally insert into the C(vinyl)–S bond in the case of free BT **203** to give the metallathiacycle **204** according to Equation (4).[448–450]



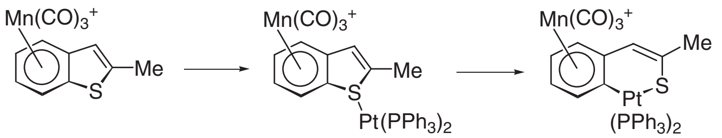
203 **204** (4)

It has been reported that precoordination of $Mn(CO)_3^+$ to a carbocyclic ring in BT or DBT (or to the thiophene ring itself in T) promotes the remote activation of the C–S bonds in the adjacent thiophenic ring to facile C–S bond cleavage by mild nucleophiles or by electrons.[451–461] Scheme 21 illustrates the room temperature reaction of $[(\eta^6\text{-BT})Mn(CO)_3]^+$ with the weak nucleophile $Pt(PPh_3)_3$.[451–454] There is no reaction with free BT. Detailed kinetic studies using $Pt(PPh_3)_2(C_2H_4)$ as the nucleophile established that the first step in Scheme 21 is the very rapid (50 msec) coordination to the thiophenic double bond to give **206** as an intermediate which inserts into the C(vinyl)–S bond within a few seconds to afford **207**.[453] The C–S bond cleavage in **205** can be made regioselective by placement of a methyl substituent at position 2 **208**. As indicated in Scheme 22, this blocks the formation of the η^2-complex, and the η^1-S intermediate **209** forms instead, which then undergoes insertion into the C(aryl)–S bond to afford metallacycle **210**. This η^1-S mechanism is also followed by DBTs, which always undergo cleavage of the C–S bond nearer the coordinated ring, as shown in Scheme 23. It is remarkable that one of the most refractory sulfur contaminants in



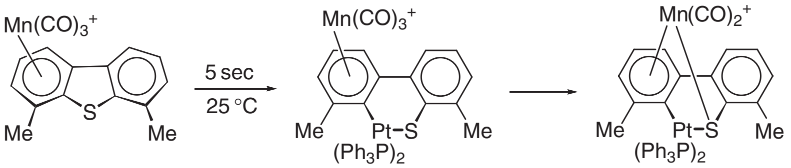
205 **206** **207**

Scheme 21



208 **209** **210**

Scheme 22



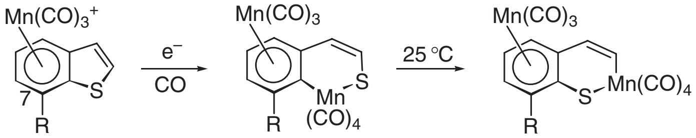
211 **212** **213**

Scheme 23

petroleum, 4,6-dimethyldibenzothiophene, undergoes C–S bond fission within seconds at room temperature when precoordinated in the form of complex **211**. The initial product in this reaction, **212**, contains a nucleophilic sulfur that slowly displaces a CO ligand to afford **213**.[452,453] The C–S activation chemistry described above for BTs was found to apply just as well to the selenium analog, benzoselenophene.[453]

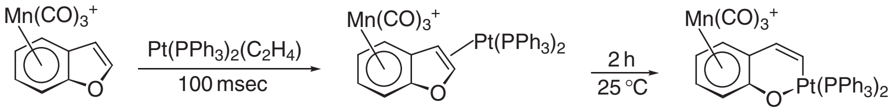
T, BT, and DBT complexes of manganese tricarbonyl are also activated to rapid reductive C–S bond cleavage, as illustrated in Scheme 24 for coordinated BTs.[455–462] Interestingly, the initial product **215**, which is thermodynamically stable if R = H, derives from insertion into the C(aryl)–S bond in BT. A radical mechanism is suggested for the insertion reaction. The isomerization **215** → **216** occurs over several hours for R = Me via reductive elimination to η^1-S bonded Mn(CO)$_4$ followed by oxidative addition. The fact that a substituent at C7 in **214** induces isomerization of the C(aryl)–Mn–S to the C(vinyl)–Mn–S metallathiacycle suggests that precoordination of a metal to the carbocyclic ring in BTs results in regioselective kinetic activation favoring C(aryl)–S over C(vinyl)–S scission, even when the latter is the thermodynamic product. The sulfur atom in **215** is easily protonated and subsequent hydrogenation affords desulfurized organic products along with [Mn(CO)$_4$SH]$_2$ and H$_2$S. DFT calculations concerning the role of precoordination in C–S bond activation accord well with the observed regioselectivity in the C–S cleavage reactions and confirm that an η^1-S–Mn(CO)$_4$$^-$ species is a viable precursor to C–S insertion.[461]

The remote activation methodology was found to work for the ostensibly more difficult problem of C–O activation.[463] As indicated in Scheme 25, the coordinated benzofuran **217** reacts with a mechanism identical to that found with coordinated benzothiophene (Scheme 21), with the significant difference that the rapidly formed η^2-(C═C)



214 **215** **216**

Scheme 24

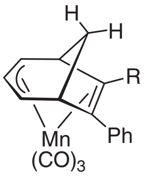


217 **218** **219**

Scheme 25

intermediate **218** slowly converts at room temperature to insertion product **219**. The rate difference is certainly due to the stronger C–O bond in benzofuran compared to the C–S bond in BT. In related work, the reaction of $Pt(PPh_3)_2(C_2H_4)$ with $[(\eta^6\text{-indole})Mn(CO)_3]^+$ did not lead to the expected C–N activation, but rather to platinum insertion into the N–H bond.[445]

There have been a number of studies dealing with cyclohexadienyl manganese tricarbonyl complexes. When the unsaturated part of the cyclohexadienyl unit contains a potential leaving group (X = F, Cl, OMe, OPh, NR_2), treatment with hydride, followed by a proton source, results in loss of HX and generation of new cyclohexadienyl complexes.[464,465] The overall reaction involves the formation of cyclohexenyl intermediates that eliminate an agostic hydrogen along with the X^- group. Nucleophilic attack on a CO ligand in $(\eta^5\text{-}C_6H_6R)Mn(CO)_3$ [R = *exo*-$(C_5H_4)Mn(CO)_3$] affords acylmetallates that can be alkylated to alkoxycarbenes $(\eta^5\text{-}C_6H_6R)Mn(CO)_2{=}C(OEt)R^1$.[466] $(\eta^5\text{-}C_6H_7)Mn(CO)_2(THF)$, generated by photolysis of the tricarbonyl in THF, reacts with allenes to give four types of cycloaddition products.[467] UV irradiation of $(\eta^5\text{-}C_6H_7)Mn(CO)_3$ with alkynes $PhC{\equiv}CR$ gives adducts resulting from metal-mediated cycloadditions, first across the η^5-dienyl ligand and then across the resulting olefin–allyl complex, resulting in **220** and **221**.[468]



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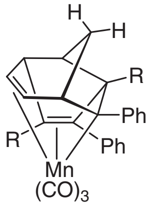
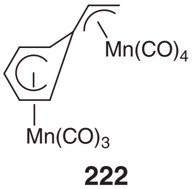


221

Chemical reduction of $[(\eta^6\text{-styrene})Mn(CO)_3]^+$ with cobaltocene yields the bimetallic **222**.[469] Three products are obtained from the reduction of the α-phenylstyrene complex, the analog of **222** along with **223** and **224**. Almost certainly, these reactions involve the formation of radical intermediates. The anionic $[(\eta^4\text{-benzene})Mn(CO)_3]^-$ **225** results from the low temperature two-electron reduction of $[(\eta^6\text{-benzene})Mn(CO)_3]^+$ by potassium naphthalenide.[470–477] Complex **225** survives long enough to react with a variety of electrophiles, some of which are shown in Scheme 26.[470–473] Other reported reactions of **225** include [3 + 2] cycloaddition of N-α-diphenyl nitrone, electrophilic addition of the iron carbene $[CpFe(CO)_2{=}CMe(OMe)]^+$, and acylation with the enoliminium ester $[Me_2CHC(OSO_2CF_3){=}NMe]^+$.[474–476] Reduction of the cyclohexadienyl complex $(\eta^5\text{-}C_6H_7)Mn(CO)_3$ with naphthalenide at −78 °C gives different products depending on the rate of addition of the reductant, as shown in Scheme 27.[477] The interpretation of these observations is that the radical anion $[(\eta^5\text{-}C_6H_7)Mn(CO)_3]^-$ merely couples to give **226** when no other electrophile is present (fast addition). However, under slow addition conditions, the radical anion, once formed, attacks unreacted starting material to give an intermediate that further reduces to **227**.



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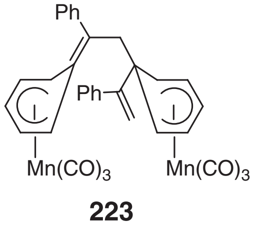

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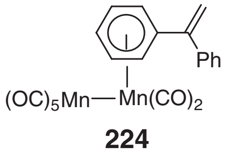
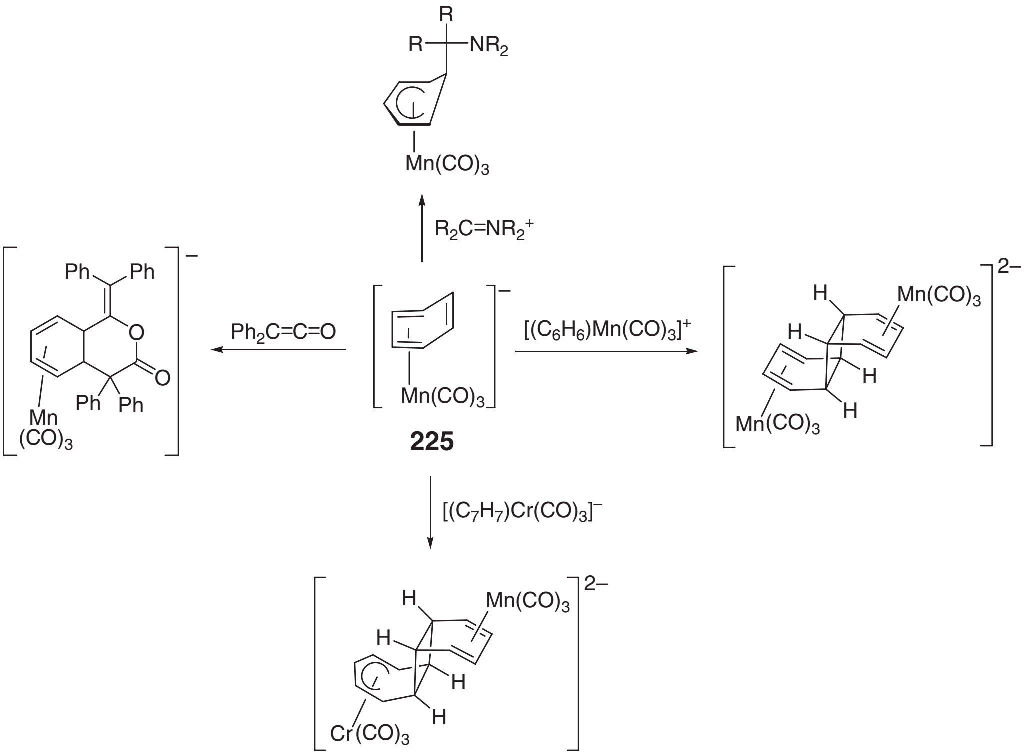
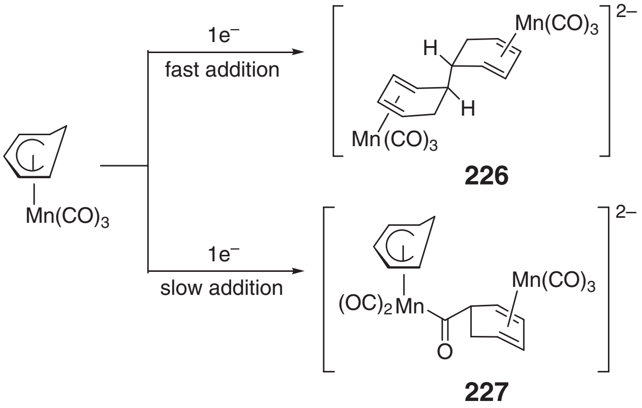


224

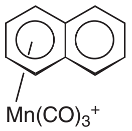
One of the most interesting developments in organomanganese chemistry involves the synthesis of naphthalene and related complexes.[395] The synthesis of $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+$ **228** by heating $Mn(CO)_5Br$ and naphthalene in the presence of $AlCl_3$ was first reported in 1961.[390] It was later determined, however, that the complex actually obtained was the partially hydrogenated tetralin analog **229**.[478] The source of the hydrogen in the formation of **229** was likely adventitious water. It was subsequently demonstrated that **228** and its substituted analogs can be readily synthesized in high yield by adding $Mn(CO)_5{}^+BF_4{}^-$ (prepared *in situ*) to the naphthalene in methylene chloride under rigorously anhydrous conditions.[395]



Scheme 26



Scheme 27



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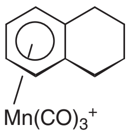


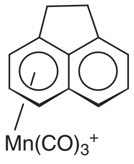
229

Transition metal complexes containing an η^6-naphthalene-type ligand are particularly interesting in comparison to η^6-monocyclic arene complexes because the former often display enhanced reactivity while, at the same time, being thermodynamically stable. For example, (η^6-naphthalene)$Cr(CO)_3$ and $[(\eta^6\text{-naphthalene})RuCp]^+$ are known to undergo associative nucleophilic substitution of the naphthalene at rates orders of magnitude greater than those found for the η^6-benzene analogs.[479–482] It is thought that the naphthalene undergoes ring slippage from η^6 to η^4 as the nucleophile initially binds, and that the most important contributor to the (relative) activation energy is the change in resonance energy concomitant with this slippage. In this context, the naphthalene complexes react faster simply because the loss in resonance energy in forming the η^4-intermediate is much less than that occurring with the monocyclic arenes. Although the η^4-intermediates are generally not observed directly, strong evidence for their viability comes from the existence of structurally characterized η^4-naphthalene chromium and ruthenium complexes obtained by two-electron reduction of η^6-precursors.[482–484]

In the case of manganese systems, it was found that **228** and related polycyclic manganese complexes react within minutes or less with donor solvents, such as that indicated by Equation (5). This great sensitivity to potential nucleophiles explains in part the historical difficulty in synthesizing **228**. The dominant role of $\eta^6 \rightarrow \eta^4$ ring slippage in Equation (5) is evident when comparing the half-lives of the η^6-benzene and η^6-naphthalene complexes: 2 years and ca. 10 s, respectively! This rate difference expressed as an activation energy is quite close to the anticipated 40 kJ greater resonance energy loss for slippage in the benzene complex.[395]

$$[(\eta^6\text{-naphthalene})\mathrm{Mn(CO)_3}]^+ \;+\; 3\mathrm{MeCN} \longrightarrow [(\mathrm{MeCN})_3\mathrm{Mn(CO)_3}]^+ \;+\; \text{Naphthalene} \qquad (5)$$

The most important property of the naphthalene complex **228** is its thermal stability (as a solid salt) coupled with its ready loss of the naphthalene in the presence of an appropriate nucleophile. Thus, **228** can be viewed as a reagent that can transfer the $\mathrm{Mn(CO)_3}^+$ moiety – a manganese tricarbonyl transfer (MTT) reagent. It has been found that many (free) arenes react cleanly with **228** and related polycyclic complexes to generate $[(\eta^6\text{-arene})\mathrm{Mn(CO)_3}]^+$.[395] The reaction merely requires heating the reactants in methylene chloride, and thus constitutes a very mild new synthetic procedure. The most convenient MTT reagent in terms of cost, ease of synthesis, and shelf life, is the acenaphthene complex **230**. Scheme 28 provides an overview of the reactions of **230** with nucleophiles. MTT reagents can be used to synthesize $[(\eta^6\text{-arene})\mathrm{Mn(CO)_3}]^+$ complexes with any arene that does not contain a strongly electron-withdrawing group. The tribenzotriquinacene **231** and the fenestrindane **232** are two examples of complexes synthesized with an MTT reagent.[485] Other examples of reactions exploiting the utility of MTT reagents that were mentioned above include the synthesis of planar chiral cymantrenes (Equation (3)) and metal carbonyl-capped metallocenes **147**.[335,337] Transfer of $\mathrm{Mn(CO)_3}^+$ to metal complexes, thus generating multimetallic systems, is also possible.[334,486] Interestingly, attempts to coordinate manganese to the phenyl groups in the polymer poly(methylphenylsilane) by using $\mathrm{Mn(CO)_5Br}$ and $\mathrm{AgBF_4}$ were unsuccessful, but the desired product could be obtained by reaction with an MTT reagent.[487]



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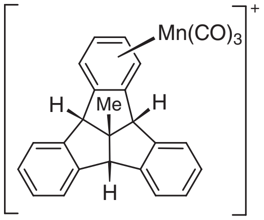

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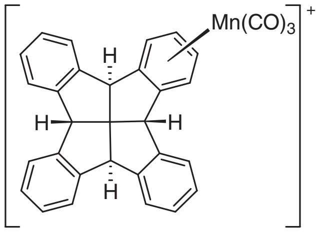

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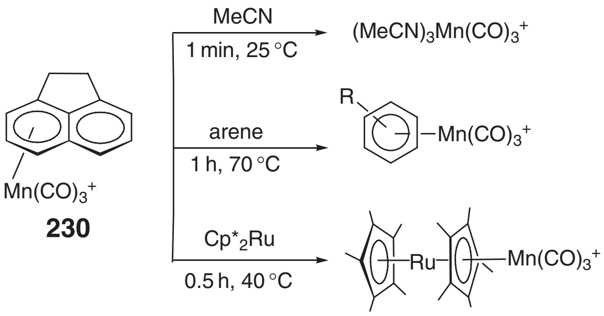
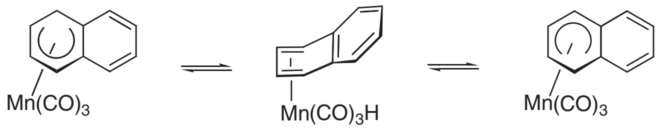


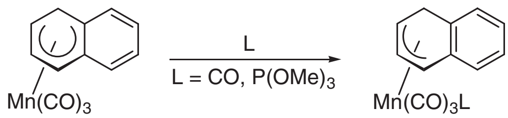
Scheme 28



233 **233**

Scheme 29

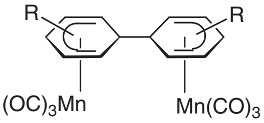
The facile ring slippage in **228** plays a major role in reactions other than nucleophilic substitution for the naphthalene ligand. For example, nucleophilic addition of hydride to **228** generates the η^5-cyclohexadienyl complex **233**, which undergoes a facile 1,4-hydride shift via an intermediate metal hydride, as shown in Scheme 29.[488–492] Equally interesting is the ability of **233** to undergo an $\eta^5 \rightarrow \eta^3$ hapticity change upon the addition of monodentate ligand L according to Equation (6).[489,493,494] Largely due to this rapid and reversible hapticity change, complex **233** is an effective catalyst for the hydrosilylation of ketones.[493,495]



233

(6)

From the above discussion, it is clear that the chemistry of $[(\eta^6\text{-arene})Mn(CO)_3]^+$ is very dependent on whether the arene is monocyclic as in a substituted benzene or is a conjugated polycyclic such as naphthalene. The basis for this reactivity difference is a facile $\eta^6 \rightarrow \eta^4$ hapticity change that occurs with the naphthalene-type complexes in the presence of nucleophiles. Correspondingly, the two classes of arene complexes also behave very differently when chemically or electrochemically reduced.[496] Figure 3 shows typical cyclic voltammograms obtained in CH_2Cl_2 solvent for the non-conjugated (tetralin) and conjugated (naphthalene) complexes. The tetralin complex is reduced irreversibly in a one-electron step while the naphthalene analog undergoes a chemically reversible overall two-electron reduction to $[(\eta^4\text{-naphthalene})Mn(CO)_3]^-$, which is a complex that had been previously prepared by an alternative method and characterized by X-ray diffraction.[497] In general, non-conjugated arene complexes of $Mn(CO)_3{}^+$ undergo one-electron irreversible reductions in CH_2Cl_2, even at relatively fast scan rates (100 V s^{-1}) to afford products of ring coupling **234** or of CO dissociation **235**,[498] although, as noted above, at low temperature, under suitable conditions $[(\eta^6\text{-benzene})Mn(CO)_3]^+$ can be reduced by two electron to $[(\eta^4\text{-benzene})Mn(CO)_3]^-$ **225**.[497]



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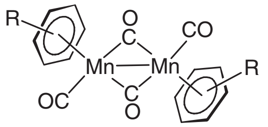

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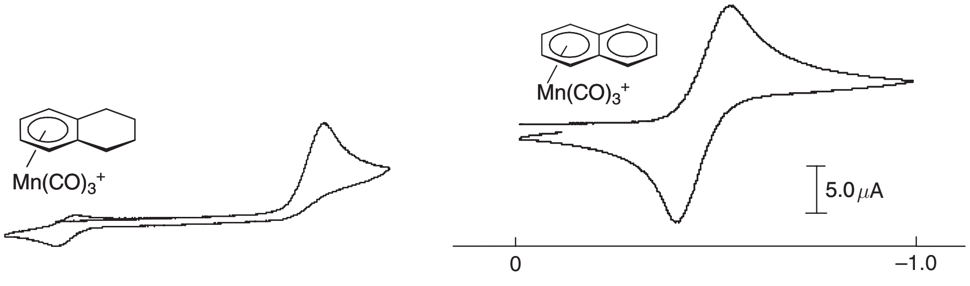


(a) (b)

Figure 3 Cyclic voltammograms of (a) 1.0 mM $[(\eta^6\text{-tetralin})Mn(CO)_3]PF_6$ and (b) 1.0 mM $[(\eta^6\text{-naphthalene})Mn(CO)_3]BF_4$ in CH_2Cl_2–0.10 M Bu_4NPF_6 under N_2 at 25 °C and 0.50 V s^{-1}.

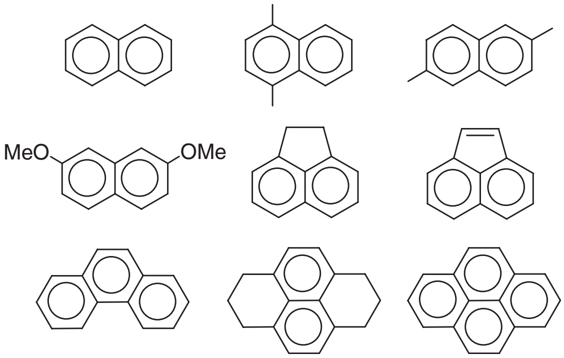
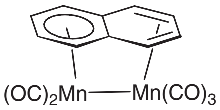


Figure 4 PAHs complexed to manganese tricarbonyl.

Variable-temperature cyclic voltammetric, bulk electrolysis, and chemical reduction techniques have been applied to the manganese tricarbonyl complexes of the polycyclic aromatic hydrocarbons (PAHs) listed in Figure 4.[496] The varying observed behaviors, and associated digital simulations of the voltammetric results, indicate that the second electron addition to $[(\eta^6\text{-PAH})\text{Mn(CO)}_3]^+$ is thermodynamically "easier" but kinetically slower than the first addition for the "unbridged" arenes, that is, $\Delta E = E_{1/2}(2) - E_{1/2}(1)$ is positive. DFT calculations suggest that most of the bending or folding of the naphthalene ring known to accompany the $\eta^6 \rightarrow \eta^4$ hapticity change occurs when the second electron is added. With "bridged" naphthalenes such as acenaphthene and hexahydropyrene, ΔE is slightly negative (by ca. -100 mV) at room temperature and the heterogeneous rate constant for the second electron addition is further decreased from that seen with the unbridged complexes, suggesting, as would be expected, that the bridge hinders both the kinetics and thermodynamics of the folding process. The spontaneous reduction of the 19-electron radical $(\eta^6\text{-PAH})\text{Mn(CO)}_3$ can be short circuited, however, by catalytic CO substitution when phosphite nucleophiles are present.[496]

The facile ring slippage associated with the reduction of $[(\eta^6\text{-PAH})\text{Mn(CO)}_3]^+$ and the demonstrated ease of ring slippage accompanying nucleophilic displacement of the naphthalene from $[(\eta^6\text{-PAH})\text{Mn(CO)}_3]^+$ are related properties that can be exploited simultaneously to produce novel *syn*-facial bimetallic complexes such as **236** and **237**.[496,499] These species are accessed by using 1 equiv. of cobaltocene to reduce $[(\eta^6\text{-PAH})\text{Mn(CO)}_3]^+$. (Excess reducing agent gives the slipped ring $[(\eta^4\text{-PAH})\text{Mn(CO)}_3]^-$ anion.) The Mn–Mn bond length in **236** is 2.9231(7) Å, a value close to that in $\text{Mn}_2(\text{CO})_{10}$. Infrared spectra of **236** give no evidence for bridging carbonyls in solution and ^{1}H NMR spectra down to $-80\,°$C indicate that the manganese atoms are in identical environments on the NMR timescale, suggesting very rapid $\eta^4{:}\eta^6 \leftrightarrow \eta^6{:}\eta^4$ interconversion. Bimetallics such as **236** and **237** undergo partially chemically reversible oxidation at room temperature at a potential close to that of ferrocene. Their intense color and rather low redox potentials suggest that the HOMO is Mn–Mn σ-bonding, as indeed is indicated by ESR spectra at 110 K.[499]



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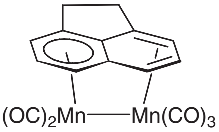
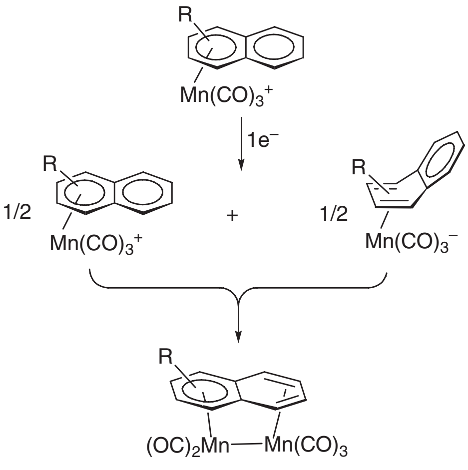


237

The formation of the *syn*-facial naphthalene bimetallics necessarily involves transfer of an $\text{Mn(CO)}_3{}^+$ moiety from one coordinated naphthalene ring to another, and this appears to occur by the pleasingly simple mechanism shown in Scheme (30).[496] The thermodynamic product of the reaction of $[(\eta^6\text{-PAH})\text{Mn(CO)}_3]^+$ with one reducing equivalent is a half-equivalent of η^4-anion and a half-equivalent of unreacted η^6-cation. The η^4-anion then acts as a nucleophile to displace the PAH ligand from the η^6-cation. The co-existence of the η^6-cation and η^4-anion at low temperature was verified by IR spectroscopy, as was their reaction upon warming to give the bimetallic **238**.

In chemistry analogous to that shown in Scheme 30, it was found that cobaltocene addition to a 1 : 1 mixture of $[(\eta^6\text{-naphthalene})\text{Mn(CO)}_3]^+$ and $[(\eta^5\text{-indenyl})\text{Fe(CO)}_3]^+$ led to the *syn*-facial heteronuclear bimetallic **239**.[496,499] Most likely the mechanism involves reduction of the indenyl complex, which then attacks and displaces the naphthalene ligand from the η^6-manganese cation. In this case, as in the reactions giving homonuclear manganese bimetallics **238**,



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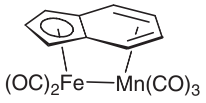
Scheme 30

CO loss from one of the metals allows the formation of a metal–metal bond. When there is no CO (or other ligand) available to dissociate, the formation of a metal–metal-bonded *syn*-facial bimetallic is prevented and an *anti*-facial product is obtained, as illustrated by the zwitterionic *anti*-facial bimetallic **240** as the product of the reduction of a mixture of $[(\eta^6\text{-naphthalene})\text{FeCp}]^+$ and $[(\eta^6\text{-PAH})\text{Mn(CO)}_3]^+$ by cobaltocene. It was established that the naphthalene ring in **240** originates with the iron and not the manganese. The bend in the diene portion of the naphthalene ligand in **240** is 35°.



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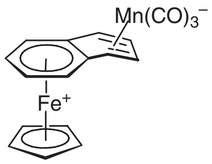
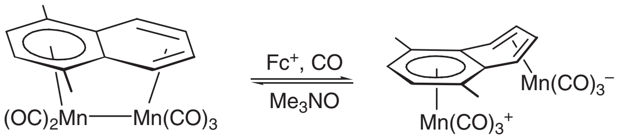


240

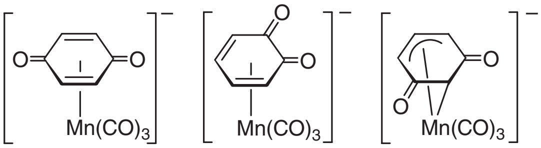
A zwitterionic homonuclear bimetallic of the *syn*-facial variety can be obtained from bimetallic **241** by the chemistry given in Equation (7).[496] Complex **241** under CO at room temperature is rapidly converted to the fascinating zwitterionic **242** by the addition of a catalytic amount of oxidant. The ferrocenium serves to initiate an electrocatalytic process in which **241** is oxidized and reacts to give (**242**$^+$), which then undergoes electron exchange with **241** to propagate the process. Likely, the initial “kick start” by ferrocenium is needed to weaken the Mn–Mn bond so that CO addition can occur and the Mn–Mn bond cleaved. In order to cleave the Mn–Mn bond in **241** upon ligand addition, it is necessary for the naphthalene ring in **242**, which was determined by X-ray diffraction to be 45° to be folded.[496] The transformation **241** + CO → **242** is particularly remarkable because it was found to be reversible. Thus, the addition of Me_3NO to **242** leads to rapid conversion back to **241** (with liberation of CO_2). The neutral but highly polar **242** presents interesting possibilities for bimetallic catalysis because the metals are in close proximity, oppositely charged, and able to convert reversibly to the non-polar Mn–Mn-bonded **241**. Zwitterionic *anti*-facial bimetallics such as **240** do not offer these features.



241 **242** (7)

5.10.5 Metal–Organometallic Coordination Networks

As noted above, MTT reagents have been utilized in the synthesis of stable manganese complexes containing η^6-bonded 1,4-, 1,3-, and 1,2-hydroquinone ligands.[430–432] These are readily deprotonated as shown in Schemes 19 and 20 to the corresponding $[(\eta^4\text{-quinone})Mn(CO)_3]^-$ complexes **190**, **193**, and **243**. These three complexes can function as "organometalloligands" by binding to metals through the oxygen atoms. The *o*-quinone complex **193** or "*o*-QMTC" generally acts as a chelating ligand to form discrete complexes with metal ions.[433] In contrast, the *p*-quinone complex **190** or "*p*-QMTC" is geometrically prevented from chelating a metal ion and instead functions as a bifunctional ligand spacer in the formation of supramolecular coordination networks. The networks consist of metal ions, called nodes, connected by organometalloligand spacers. The whole assembly is termed a metal–organometallic coordination network (MOMN).[434,500–506] Figure 5 illustrates a 1D network built from independent modular units that link by metal–ligand bond formation. Analogous 2D and 3D architectures that contain *p*-QMTC spacers also exist.



p-QMTC **190** *o*-QMTC **193** *m*-QMTC **243**

The coordination-directed self-assembly of supramolecular metal-organic coordination networks (MONs) using transition metals as nodes and simple organic ligands as spacers has been widely studied because of the existence of many potential applications. Typical organic ligand spacers in MONs include multifunctional carboxylates and pyridines. In contrast, MOMNs contain an organometallic "complex" such as **190** as the spacer. Neutral 1D "string" polymers **244** are obtained from the reaction of **190** and divalent metal ions (Mn, Co, Ni, Cd) in DMSO. The axial ligand L is DMSO or pyridine. The 1D strings can be linked together by displacing the axial ligands with a bipyridine spacer to give the 2D structure **245**. With suitable experimental conditions, it is possible to construct 3D analogs of **245** that contain 2D quinonoid planes connected by the bipyridine spacers, as illustrated in Figure 6(a). An alternative 3D diamondoid architecture is found with a metal node preferring a tetrahedral environment, Figure 6(b). Many types of architectures can be constructed with organometallic quinonoid spacer **190**, some of which may be useful in guest–host chemistry, electron-transfer, initiated reactions, nanoparticle self-assembly, and in catalysis. Significantly, it appears that the architectures can be rationally designed based upon the coordination number, oxidation state, and geometrical requirements of the metallic nodes that link the organometalloligands.[500–506]

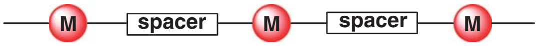


Figure 5 A 1D coordination network with a bifunctional ligand spacer connecting metallic nodes.

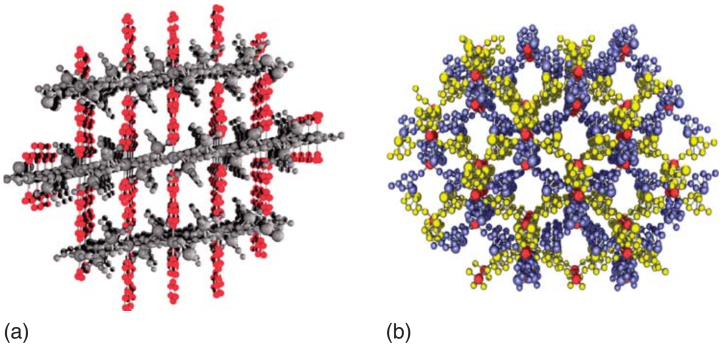
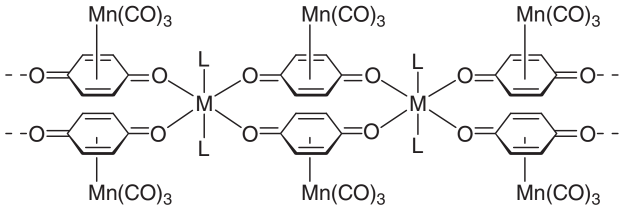


Figure 6 3D MOMNs with *p*-QMTC spacers that consist of (a) 2D quinonoid grids connected by 4,4′-bipyridine via octahedral nodes and (b) a diamondoid structure with tetrahedral Zn(II) nodes.



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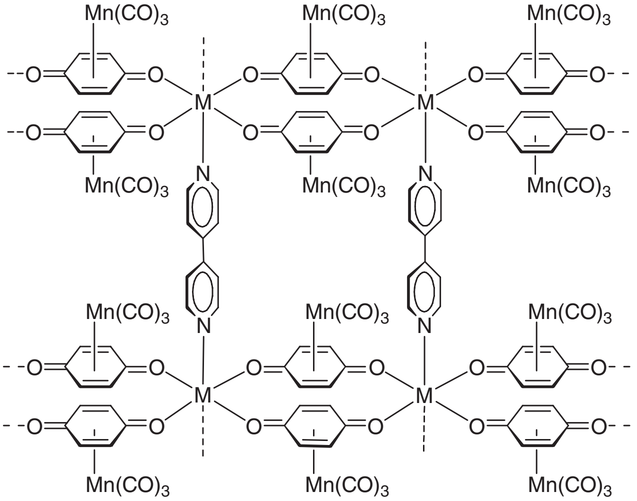


245

By variation of the solvent and the nature of the metallic nodes, it proved possible to synthesize MOMNs based on *p*-QMTC **190** that contain multimetallic clusters or secondary building units (SBUs) as nodes. As an example, Figure 7 shows a 3D "brick" network structure obtained from the reaction of copper acetate with *p*-QMTC linkers. The MOMN consists of bicopper SBUs of formula $Cu_2(\mu\text{-}CH_3CO_2)^{3+}$, which are connected with the square-pyramidal geometry. The resultant structure, which has the molecular formula $[Cu_2(p\text{-QMTC})_3(\mu\text{-}CH_3CO_2)]\infty$, constitutes a previously unknown extended (3D) brick wall architecture. The MOMN pictured in Figure 8 has a particularly interesting structure. It consists of $[Cd_3(OAc)_2]^{4+}$ nodes linked by *p*-QMTC spacers and by one 4,4′-dipyridyldisulfide (DTDP) molecule per node. The DTDP binds through the pyridine nitrogens to the terminal cadmiums in the Cd_3 cluster. The disulfide units, which are not coordinated, aggregate to form channels extending throughout the polymer as shown in Figure 8. The sulfurs are arranged in "rings" of six atoms from three disulfide units. The 4 nm separation of the available sulfur channels in this MOMN suggests their possible use as surface receptor sites in the directed self-assembly of metallic nanoparticles.

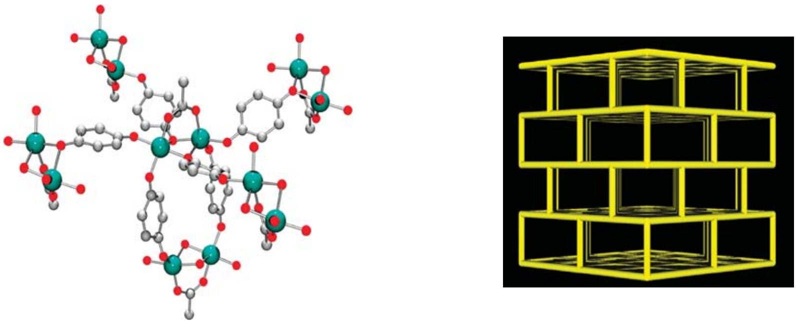


Figure 7 3D brick MOMN consisting of $[Cu_2(OAc)]^{3+}$ nodes connected by *p*-QMTC spacers with a square-pyramidal geometry.

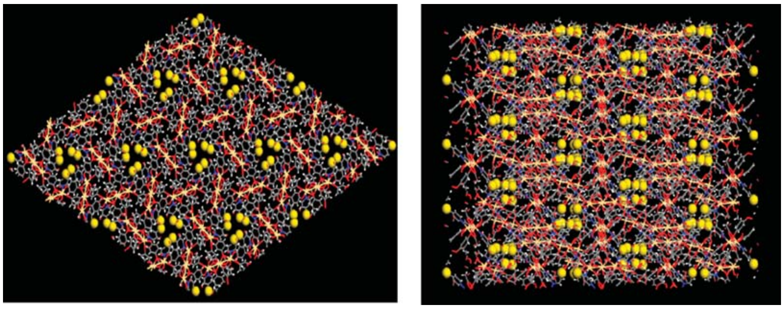
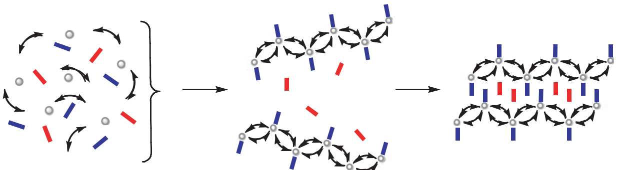


Figure 8 MOMN with formula $[Cd_3(OAc)_2(p\text{-QMTC})_4(DTDP)]_\infty$ that contains channels of sulfur atoms consisting of "rings" of six atoms from three disulfide units. The channels are separated by ca. 40 nm.



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Scheme 31 Cartoon representation of the formation of an interdigitated π-π stacked MOMN from the self-assembly of *p*-QMTC (arrows) and 2,2′-bipyridine (bars).

The reaction of *p*-QMTC and Cd^{2+} or Mn^{2+} in the presence of 2,2′-bipyridine led to the 1D zigzag MOMN **246** by the self-assembly process shown in Scheme 31.[500–507] The individual 1D polymer units in **246** interdigitate via π–π stacking of the 2,2′-bipyridine ligands. Interestingly, two "free" bipyridine molecules were found to be sandwiched between each pair of coordinated bipyridines in **246**, resulting in a continuous π-stacking along the entire length of the polymer. Removal of the "free" bypyridines from **246** could generate "π-pockets" which may be used to accommodate other π-molecules of appropriate size. Applications to PCB remediation and fossil fuel desulfurization via binding of BTs and DBTs are suggested.

Based on the reported use of manganese quinonoid complexes as organometalloligands in the construction of supramolecular MOMNs, it is apparent that organometallics in general has great untapped potential for the design and synthesis of functional materials based on the principle of metal-directed self-assembly via metal–ligand bond formation.

Acknowledgments

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5.11
Manganese Compounds without CO or Isocyanides

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5.11.1 Introduction

The organometallic chemistry of manganese is dominated by complexes containing carbon monoxide ligands, due in part to the availability and stability of complexes like manganese carbonyl, methylcyclopentadienyl manganese tricarbonyl (methylcymantrene), and the arene manganese tricarbonyl cations. Readers of COMC (1982) and COMC (1995) will also note that the chemistry of isonitrile-containing manganese complexes has been widely studied. This review covers the chemistry of manganese compounds without carbonyl or isonitrile ligands from 1993 through 2005, and given that this is a relatively small area of research, emphasis has been made to explain the work in as much detail as possible. Of all the subjects described here, that of manganocene $[Mn(\eta^5\text{-Cp})_2]$ and its derivatives is perhaps the most significant, and it is either a starting point or subject of almost half of the references cited. For example, manganocene is a valuable starting material for the preparation of higher oxidation state complexes (+2 and up) containing imido and amido ligands, which are not necessarily "organometallic" complexes, but which are interesting new catalysts. Another notable area described is that of manganese centers linked by conjugated carbon bridges, with linkages of two, four, and even eight carbons being reported. Interest in these compounds stems from communication between the metal centers through the carbon bridges and the formation of mixed-valence species. The material here is organized by ligand type, and when two or more ligand types are present, the reactions are listed under that with the lower hapticity.

5.11.2 Alkyl and Aryl Complexes

COMC (1995) described many homoleptic alkyl derivatives of manganese; however, few new species have been reported in the period since that review. Nevertheless, one homoleptic metal ate complex, $Li[MnMe_3]$, when combined with magnesium, has been reported to form a catalytic electron-transfer (ET) system. The system was effective for a variety of ET reactions, for example, the desulfonylation of *N*-phenylsulfonyl amides, selective cleavage of *O*-allyl groups, reduction of nitro groups, partial reduction of ketones, and the reductive coupling of diphenyliodinium salts.[1] Organomanganese reagents have also been shown to add to conjugated nitroolefins. The manganese species were generated *in situ* from the appropriate Grignard reagent and $MnCl_4Li_2$ in THF, and in the case of benzylmanganese chloride, 1,4-addition was reported in yields exceeding Grignard and Cu-assisted additions, and the reactions were also reported to be stereoselective.[2]

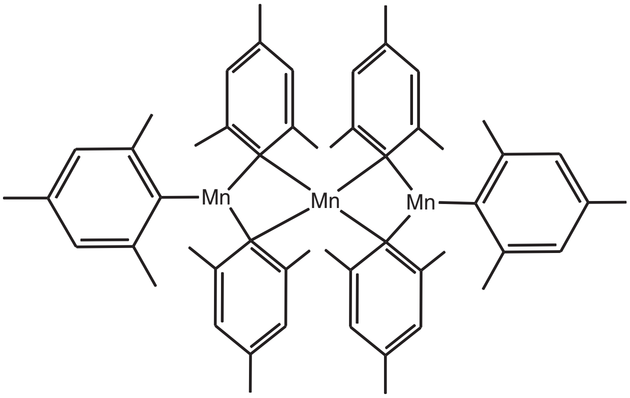


Figure 1 Structure of the trimeric trimesityl complex $Mn_3(mes)_6$ **3**.

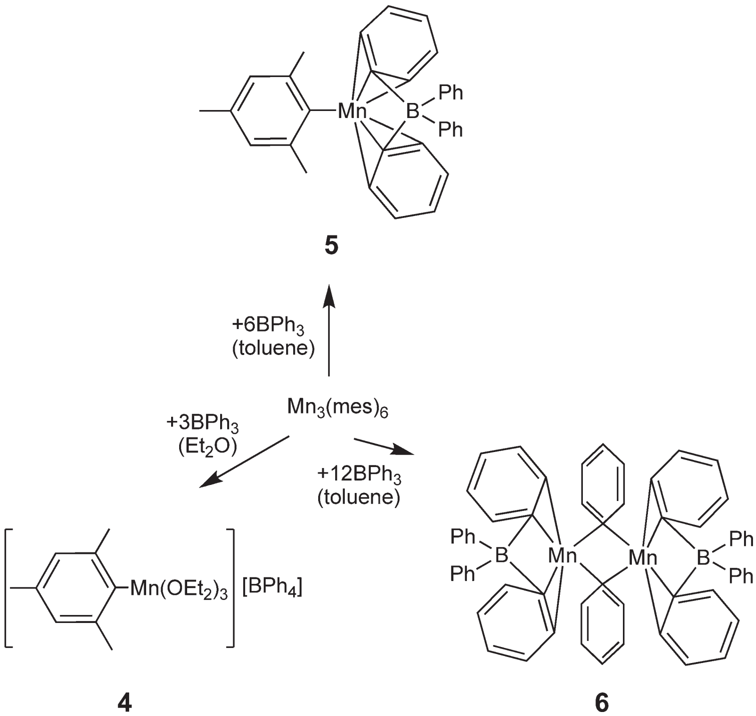
Homoleptic aryl complexes containing sterically demanding ligands have been prepared. The bent complex $Mn(mes^*)_2$ **1** ($mes^* = 2,4,6\text{-}^tBu_3C_6H_2$) can be accessed via treatment of $MnCl_2$ with $Mg(mes^*)_2$ and has an Mn–C bond length of 2.108 Å. The C–Mn–C bond angle is ca. 160° and is thought to be due to a weak interaction between the Mn(II) center and the hydrogens from one of the *ortho-tert*-butyl groups.[3] Reaction of $MnBr_2$ with excess pentafluorophenylmagnesium bromide led to oxidation of the metal and formation of the Mn(III) species $[Mn(C_6F_5)_4]^-$ **2**, which has an approximate square-planar geometry and an Mn–C bond length of 2.068 Å. Anion **2** is the first structurally characterized homoleptic aryl-manganese(III) complex.[4]

Floriani and co-workers reported the detailed preparation and structure of the trimeric mesityl complex $Mn_3(mes)_6$ **3** and a series of unusual Mn(II) aryl species from its reaction with triphenylborane. Trimer **3** (Figure 1) consists of a linear arrangement of manganese centers with two terminal and four bridging mesityl groups. The central manganese atom has distorted tetrahedral geometry and the terminal centers are trigonal. Reaction of **3** with $3BPh_3$ in diethylether gave the monomeric mesityl complex $[(Et_2O)_3Mn(mes)][BPh_4]$ **4**, whereas in toluene with $6BPh_3$ both $[(mes)Mn(\eta^3\text{-}Ph)_2BPh_2]$ **5** and the dimeric $[Ph_2B(\eta^2\text{-}Ph)_2(\mu\text{-}MnPh)_2(\eta^2\text{-}Ph)_2BPh_2]$ **6** were formed. Complex **6** can be prepared exclusively if longer reaction times and 12 equiv. of BPh_3 are used (Scheme 1). The authors reported strong antiferromagnetic coupling between the metal centers in both **3** and **6** of 55.4 and 40.4 cm^{-1}, respectively.[5]

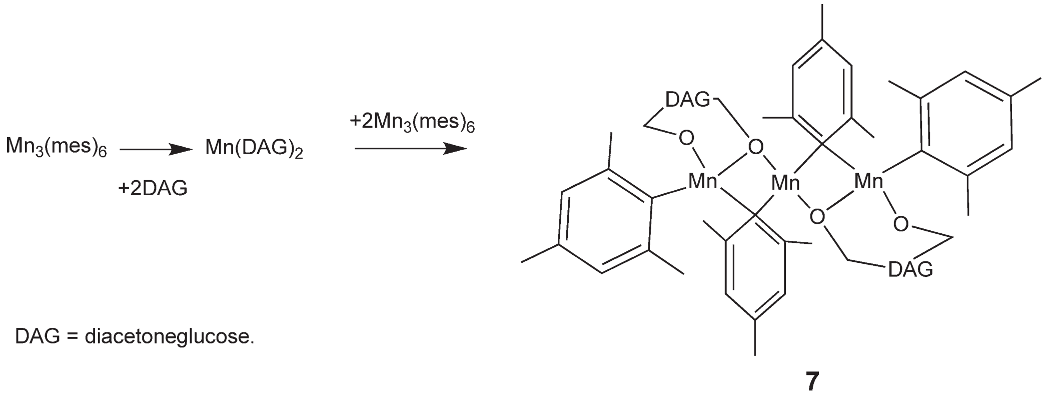
$Mn_3(mes)_6$ was also used to prepare complexes with novel pyrrole-based dinucleating ligands[6] as well as a diacetoneglucose (DAG) complex $[Mn(DAG)_2]$. Reaction of $[Mn(DAG)_2]$ with a further 2 equiv. of $Mn_3(mes)_6$ gave a redistribution reaction and formation of the structurally characterized trimanganese complex **7** (Scheme 2). Complex **7** contains two terminal and two bridging mesityl ligands and is somewhat reminiscent of the $Mn_3(mes)_6$ **3**, with the DAG groups acting as both terminal and bridging ligands. All three Mn(II) metal centers have distorted tetrahedral geometry and show strong antiferromagnetic coupling with spin frustration leading to an overall $S = 5/2$ ground state.[7]

Additionally, $Mn_3(mes)_6$ has proved to be a valuable starting material for the preparation of a number of other novel Mn(II) complexes. Thus, reaction of **3** with a series of tetradentate acac-L-enH_2 derivatives [acac-L-en = *N,N′*-ethylenebis(acetylacetiminato) dianion; L = CH_2CH_2, or a chiral bridge] gave the corresponding Mn(II) Schiff base complexes $[Mn(acac\text{-}L\text{-}en)]_2$. Although these complexes contain no Mn–C bond, they act as carriers for polar organometallics which do possess a metal–carbon bond, and subsequent reaction of $[Mn(acac\text{-}L\text{-}en)]_2$ with organolithiums gave the organometallic complexes [Mn(acac-L-en)R{Li(DME)}] (R = Me, Ph, and mesityl). The X-ray crystal structure of the mesityl and methyl species noted Mn–C bond distances of 2.180 and 2.173 Å, respectively.[8,9]

Alkyl and aryl complexes containing a bulky *β*-diketiminate ligand have been prepared by Roesky and co-workers by reaction of the dimers **8** with organolithiums (Scheme 3). The phenyl derivative **9** had a trigonal-planar mononuclear structure with an Mn–Ph bond distance of 2.077 Å. Surprisingly, the phenyl ring and the chelate were coplanar, and theoretical calculations indicate that this is not due to any Mn–C and Mn–N *d*-*π* conjugation in the complex, but rather the steric repulsion that would occur if the phenyl ring were perpendicular to the chelate. In contrast, the methyl species **10** bridges two distorted tetrahedral manganese(II) centers with Mn–Mn and Mn–Me (av.) distances of 2.809 and 2.273 Å, respectively.[10,11]



Scheme 1



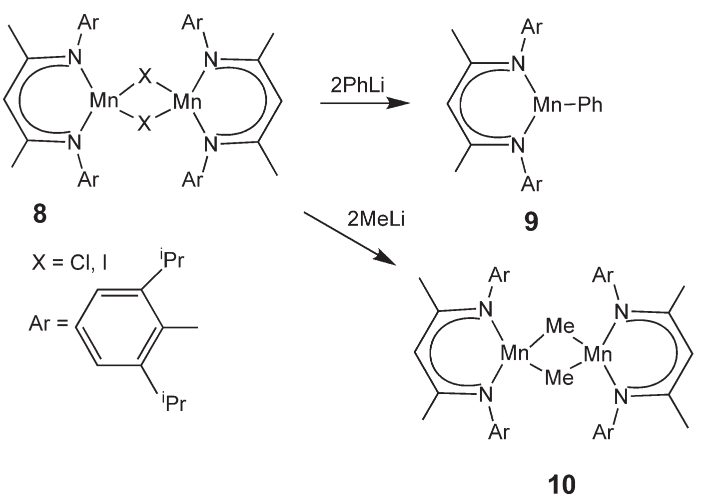
DAG = diacetoneglucose.

Scheme 2

In an earlier work, Power reported the synthesis and structural characterization of a novel dimer with bridging methyl groups in an Mn(II) amido complex from reaction of $AlMe_3$ with $[Mn\{N(SiMe_3)_2\}_2(THF)]$. The product $[\{Mn(\mu\text{-}Me)(N(SiMe_3)_2AlMe_3)\}_2]$ **11** contains a bridging methyl group stabilized by Mn–Me interactions, with a methyl group from $AlMe_3$.[12] The Mn–C bond distances were found to be 2.201 and 2.285 Å for the methyl groups bridging the two Mn atoms, and 2.323 Å for the methyl group bridging Mn and Al. The Mn–Mn distance was reported as 2.712 Å.

Dehnicke and co-workers have reported organomanganese(II) complexes with heterocubane structures from the reaction of $[MnBr(NPEt_3)]_4$ with either ${}^nBuLi$ or MeLi. The terminal alkyl ligands do not form part of the cubane core, which consists of four Mn atoms and four nitrogen atoms from the $NPEt_3$ groups. Mn–C bond distances of 2.168 and 2.195 Å were observed for the butyl and methyl complexes, respectively.[13,14]

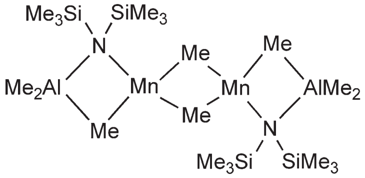
Eaborn and co-workers have demonstrated that alkyl ligands bearing silyl substituents form stable complexes with many metals, including manganese, particularly if the silyl group is also attached to a group that has the ability to form a chelate. Amine and ether chelates were prepared from $MnCl_2$ and the lithium salts



Scheme 3

$Li(THF)_2[C(SiMe_3)_2(SiMe_2NMe_2)]$ and $Li(THF)_2[C(SiMe_3)_2(SiMe_2OMe)]$, respectively.[15] When 0.5 equiv. of $MnCl_2$ was used the mononuclear $[Mn\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2]$ 12 was formed, whereas the 1 : 1 reaction produced the chloride-bridged dimers $[Mn(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ 13 and $[Mn(THF)(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2OMe)\}]_2$ 14. Additionally, the authors reported the X-ray structure of the Mn(III) oxo-bridged species $[Mn(\mu\text{-}O)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ 15, which presumably arises from adventitious admission of air to the reaction. These novel complexes are manganese analogs of Grignard reagents. In an earlier report, the pyridine-based chelate $[Li(THF)_3(\mu\text{-}Cl)MnCl\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}]$ was also reported from reaction of $MnCl_2$ with $Li[C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)]$.[16] The same authors have reported that the bidentate trisiamyl ligand $\{C(SiMe_3)_2SiMe_2CH_2CH_2SiMe_2C(SiMe_3)_2\}^{2-}$ forms a chloride-bridged high-spin lithium manganate(II) complex 16. The high-spin metal center was confirmed by a magnetic moment measurement of 5.4 μ_B, whereas the X-ray structure revealed an Mn–C distance of 2.178 Å.[17]

As noted in the above examples, the requirement of steric bulk and a non-carbon atom in the beta position stabilizes manganese alkyl derivatives. The trimethylsilylmethyl ligand is a particularly good example of such a ligand, and a number of stable species have been prepared. The chiral (−)-sparteine bis(trimethylsilylmethyl)manganese(II) complex 17 was prepared from the (−)-sparteine manganese dibromide by addition of trimethylsilylmethyllithium. The complex is high spin (5.77 μ_B) and has tetrahedral geometry with Mn–C bond distances of 2.158 and 2.165 Å.[18]



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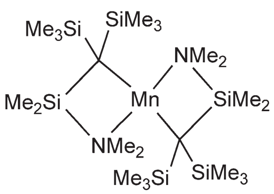

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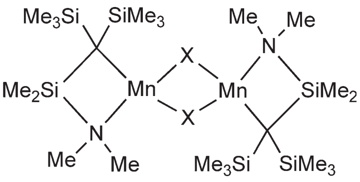
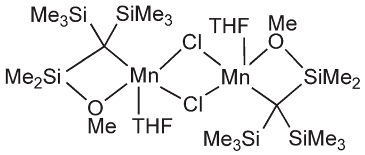


13: X = Cl
15: X = O



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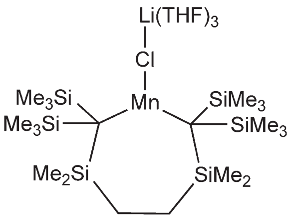

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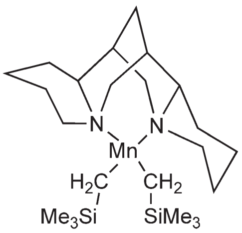


17

The dinuclear species $[(\mu\text{-}CH_2SiMe_3)Mn(CH_2SiMe_3)(THF)]_2$ was reported[19] from reaction of $MnCl_2(THF)_2$ and the lithium reagent, and contrasts with the previously claimed polymer $[(\mu\text{-}CH_2SiMe_3)Mn(CH_2SiMe_3)]_n$ prepared from the Grignard reagent.[20] The new species was structurally characterized and found to have an Mn–Mn distance of 2.788 Å, considered within the bonding range, and bridging Mn–C distances of 2.214 and 2.360 Å compared to the terminal Mn–C bond of 2.129 Å. The complex was used to prepare pyrrolide complexes by reaction with 1,1-dipyrrolylcyclohexane. In THF, an N-bridged dimer resulted, whereas in toluene an unusual octanuclear complex with μ-η^1,η^5-pyrrolide bridging ligands was formed.[19]

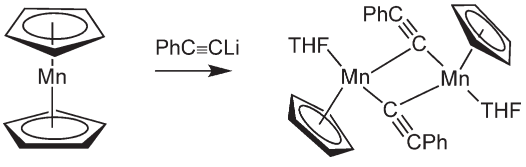
5.11.3 Alkynyl Complexes

In addition to the heterocubane alkyl derivatives described in Section 5.11.2,[13] the alkynyl complexes $[Mn(C{\equiv}CR)(NPEt_3)]_4$ (R = Ph, Tol, CMe_3, $SiMe_3$) have been prepared and have the same Mn_4N_4 heterocubane core structure. The Mn–alkynyl bond lengths were found to be between 2.073 and 2.080 Å and are somewhat longer than those in other alkynyl manganese species.[14]

The dimeric alkynyl-bridged cyclopentadienyl complex **18** was reported from reaction of manganocene with lithium phenylacetylide (PhC≡CLi) (Scheme 4). The complex was characterized by X-ray crystallography and has Mn–C bond distances of 2.162 and 2.249 Å to the bridging carbons, but the long Mn–α-C distance (av. 2.96 Å) suggests little π-interaction of the triple bond.[21] Another quite similar dimeric alkynyl complex **19**, in this case containing the β-diketiminate ligand (Ar = 2,6-diisopropylphenyl), was made by reaction of the trimanganese species **20** with PhC≡CLi (Scheme 5). The alkynyl ligands in **19** symmetrically bridge the two metal centers via a σ-bond (Mn–C, 2.133 Å) and a π-interaction between the triple bond the second metal center (Mn–C, 2.298 Å). The structure of the novel parent complex **20** was also reported and shows that it has a planar Mn_3Cl_4 core with a linear arrangement of manganese atoms.[22]

Bis(alkynyl) complexes of manganese with bis(dimethylphosphino)ethane (dmpe) ligands and related alkynyl-bridged species have been extensively studied by Berke and co-workers, following the preparation of [*trans*-$(RC{\equiv}C)_2Mn(dmpe)_2$] **21** (R = Ph, $SiMe_3$) in 1996 from $MnBr_2$, dmpe, and RC≡CLi (Scheme 6).[23] The complexes were subsequently prepared from [*trans*-$Br_2Mn(dmpe)_2$] and the respective alkynyllithium reagent and were shown to be general for a variety of alkynyl ligands, with R = $SiEt_3$, Si^iPr_3, $Si(Me)_2{}^tBu$, $SiPh_3$.[24,25]

Oxidation of the neutral complexes with ferrocenium ion gave [*trans*-$(RC{\equiv}C)_2Mn(dmpe)_2]^+$ **21**$^+$, and subsequent treatment of the silyl-substituted species **21**$^+$ (R = $SiMe_3$) with tetrabutylammonium fluoride (TBAF) gave the novel mixed-valent C_4-bridged rigid-rod complexes $[\{(HC{\equiv}C)(dmpe)_2Mn\}_2(\mu\text{-}C_4)]^{n+}$ **22**$^{n+}$ (n = 0, 1, 2). The violet



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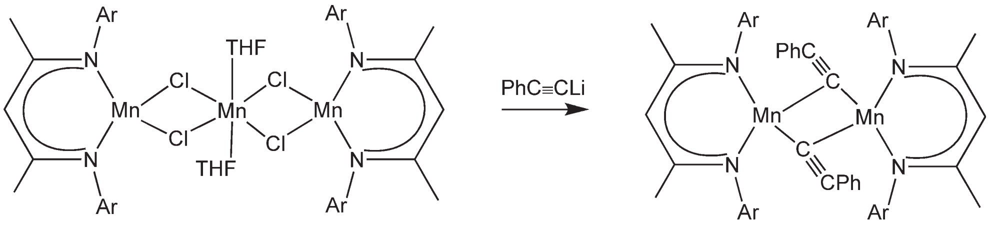
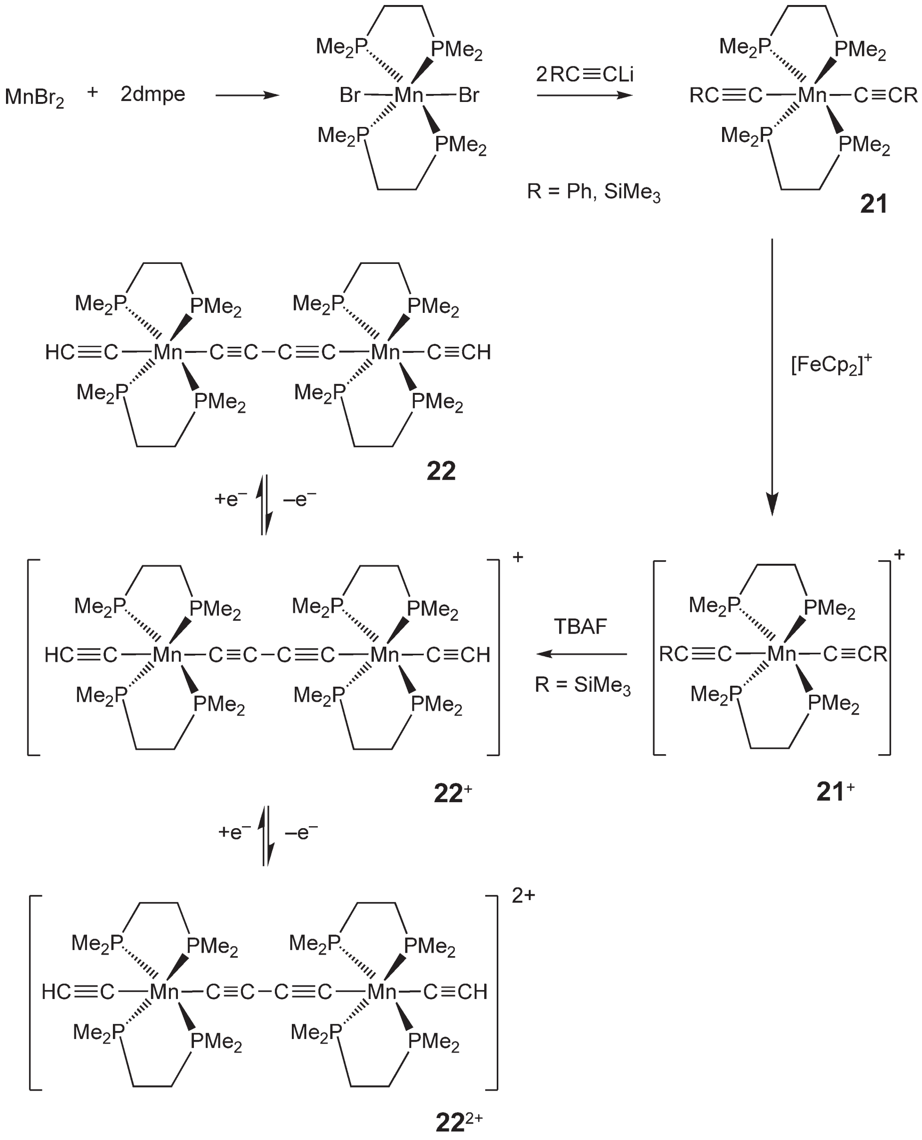
Scheme 4



20 **19**

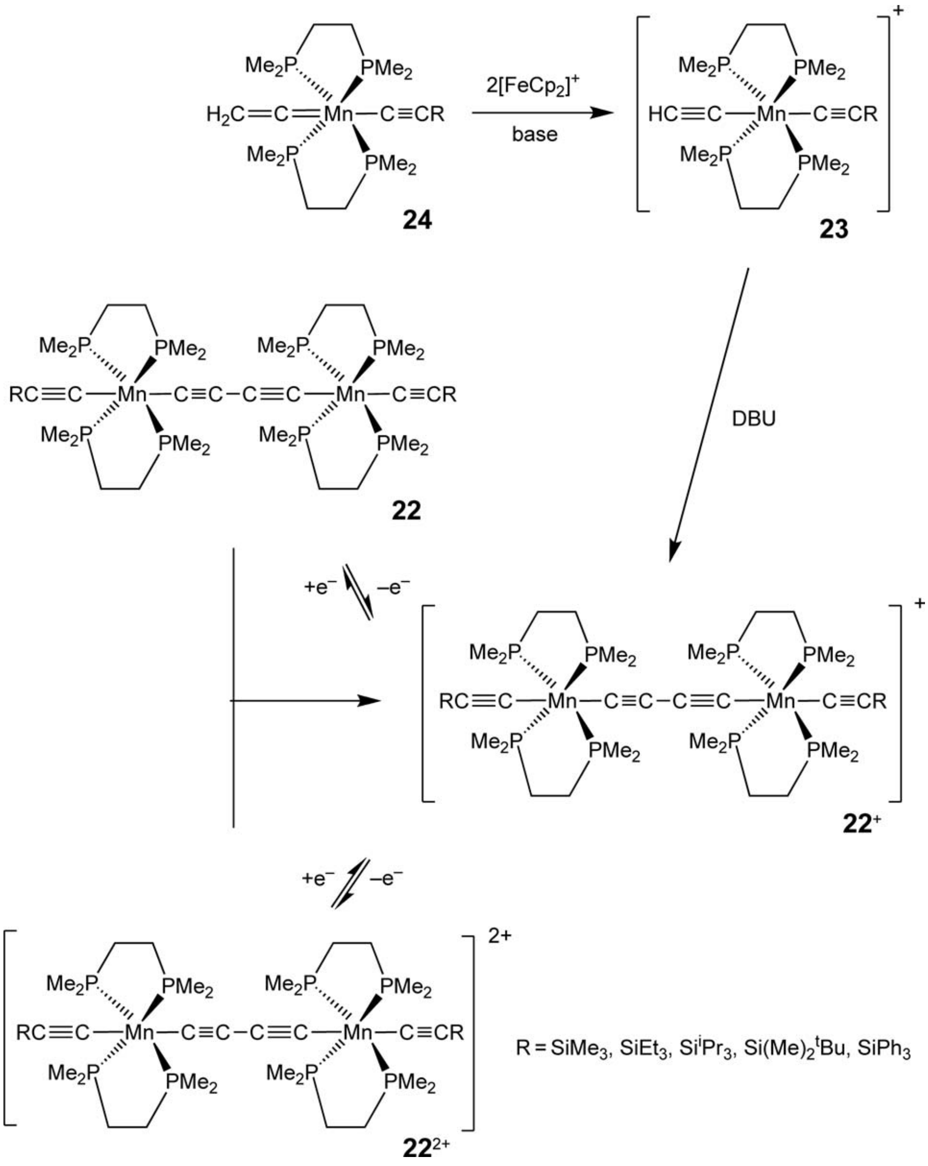
Scheme 5



Scheme 6

monocation was structurally characterized, and density functional theory (DFT) calculations show it to have a triplet ground state that is 90 kJ mol.$^{-1}$ more stable than the singlet state. Magnetic measurements of 2.53 μ_B (250 K) and 1.95 μ_B (100 K) indicate a strong intramolecular antiferromagnetic interaction between the metal centers. The cation **22**$^+$ can be oxidized to the dark brown dication **22**$^{2+}$ with $[FeCp_2]^+$ or reduced to the dark green neutral species **22** by CpFe(η^6-C_6Me_6) (Scheme 6). Cyclic voltammetry of this species showed two fully reversible waves associated with the Mn(III)–Mn(III)/Mn(III)–Mn(II) and Mn(III)–Mn(II)/Mn(II)–Mn(II) couples, as well as an irreversible wave for the Mn(II)–Mn(II)/Mn(II)–Mn(I) reduction.[26]

The novel coupling reaction that generates the bridging C_4 ligand above involves (HC≡C)(dmpe)$_2$Mn(C≡C)$^{\cdot}$ radicals, which could be trapped by TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) as the Mn(I) complex [(HC≡C)(dmpe)$_2$Mn≡C–CO$_2$].[25] The use of TBAF for the coupling reactions precluded the isolation of bridged complexes with silyl substituents on the terminal alkynyl ligands. The authors have reported an elegant alternative approach to the silyl-capped species via the coupling of non-symmetric bis(alkynyl) cations [(HC≡C)(dmpe)$_2$MnC≡CR]$^+$ **23** using the base DBU giving [{(RC≡C)(dmpe)$_2$Mn}$_2$(μ-C$_4$)]$^{n+}$ **22**$^{n+}$ (R = SiMe$_3$, SiEt$_3$, Si^{i}Pr$_3$, Si(Me)$_2{}^t$Bu, SiPh$_3$; $n = 0, 1, 2$). The monocationic complex **22**$^+$ (R = SiR$_3$) was also accessible via a comproportionation of the neutral and dicationic species (Scheme 7).[25] The non-symmetric complexes

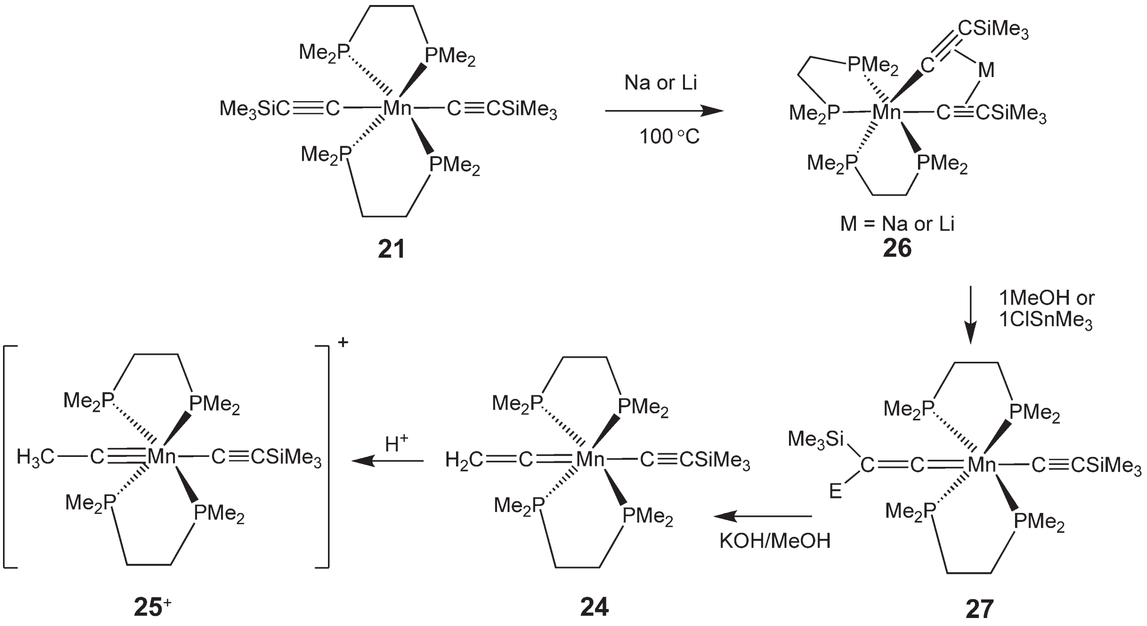


Scheme 7

$[(HC{\equiv}C)(dmpe)_2MnC{\equiv}CR]^+$ **23** were prepared from the alkynyl(vinylidene) species $[(H_2C{=}C{=}Mn(dmpe)_2$-$(C{\equiv}CR)]$ **24** by reaction with 2 equiv. of $[FeCp_2]^+$ and 1 equiv. of base.[25]

Other reactions of the bis(alkynyl) complex **21** ($R = SiMe_3$) were investigated, and addition of $[Bu_4N][Ph_3MH_2]$ ($M = Si$, Sn) gave the expected metathesis products **21** ($R = MPh_3$). Reaction of **21** with HF pyridine gave cations [*trans*-$(Me_3SiC{\equiv}C)_2Mn(dmpe)_2][H_2F_3]$ **21**$^+$ and $[MeC{\equiv}Mn(dmpe)_2(C{\equiv}CSiMe_3)][H_2F_3]$ **25**$^+$, whereas addition of $NaBF_4$ in methanol gave the mixture of cations **21**$^+$, **25**$^+$, and the vinylidene species **24** ($R = SiMe_3$). Reduction of **21** ($R = SiMe_3$) with lithium or sodium at 100 °C gave the anion **26** with *cis*-alkynyl ligands coordinated to the alkali metal cation. Addition of stoichiometric amounts of $ClSnMe_3$ or methanol to these anions gave the substituted vinylidene species $[(Me_3Si)EC{=}C{=}Mn(dmpe)_2(C{\equiv}CSiMe_3)]$ **27** ($E = SnMe_3$ or H), which can be transformed into $[(H_2C{=}C{=}Mn(dmpe)_2(C{\equiv}CSiMe_3)]$ **24** by treatment with methanol and KOH, and ultimately to the carbyne complex $[MeC{\equiv}Mn(dmpe)_2(C{\equiv}CSiMe_3)]^+$ **25**$^+$, by subsequent addition of HBF_4 to **24** (Scheme 8).[27]

A series of dinuclear complexes $[\{I(dmpe)_2Mn\}_2(\mu\text{-}C_4)]^{n+}$ **28** ($n = 0$, 1, 2) have been prepared from bis(trimethylstannyl)acetylene, $[(\eta^5\text{-}C_5H_4Me)(dmpe)MnI]$ **29**, and dmpe, followed by oxidation. X-ray crystallographic studies



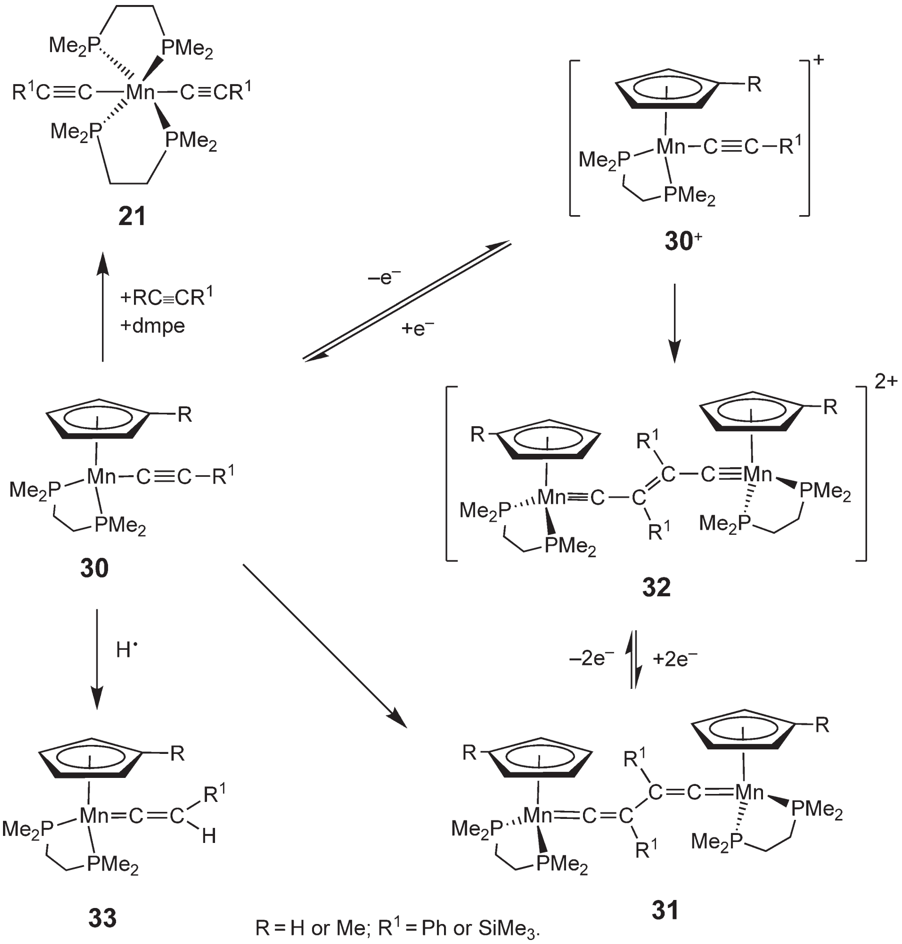
Scheme 8

showed that the dication has a cumulene-like structure of virtually equal length C═C bonds (ca. 1.29 Å), and calculations indicate that in the ground state, two electrons occupy degenerate orthogonal molecular orbitals over the C_4 chain.[28] The preparation of mixed complexes of the type $[Mn(dmpe)_2(C{\equiv}CSiMe_3)I]$ was attempted via reaction of $[(\eta^5\text{-}C_5H_4Me)(dmpe)MnI]$ **29** with $Me_3SnC{\equiv}CSiMe_3$; however, the products obtained were disproportionate to [*trans*-$I_2Mn(dmpe)_2$] and [*trans*-$(Me_3SiC{\equiv}C)_2Mn(dmpe)_2$] **21**.[25]

Berke and co-workers have also studied alkynyl and μ-C_4-bridged complexes of the related $(\eta^5\text{-}C_5H_4R)(dmpe)Mn$ manifold. The simple alkynyl complexes $[(\eta^5\text{-}C_5H_4R)(dmpe)MnC{\equiv}CR^1]$ **30** (R = H or Me; R^1 = Ph or $SiMe_3$) could be isolated from mixtures formed via sequential addition of dmpe to the appropriate manganocene and the alkyne in a 1 : 1 : 1 ratio. The stoichiometry of the reaction is crucial such that a 1 : 2 : 2 ratio of reactants gave the previously reported complex **21**. This arises because **30** converts to **21** in the presence of excess alkyne and phosphine. Complex **30** (R^1 = Ph) can be reversibly oxidized to the monocations $\mathbf{30}^+$. Both the neutral and cationic complexes are highly labile, and can undergo carbon-centered radical reactions including dimerization to bis(vinylidene) **31** and bis(carbyne) **32** species and hydride abstraction to produce mononuclear vinylidene complexes **33**, (Scheme 9).[29]

Novel alkynyl complexes containing methylcyclopentadienyl and tetramethylethylenediamine (TMEDA) ligands have been reported. Reaction of the bis(η^1-methylcyclopentadienyl)(TMEDA)manganese complex **34** with 1 equiv. of terminal or trimethylstannyl-substituted alkynes gave simple alkynyl complexes $[(\eta^5\text{-}C_5H_4Me)(TMEDA)Mn–C{\equiv}CR]$ **35** (R = Ph, $SiMe_3$, $C{\equiv}CSiMe_3$, $C{\equiv}CPh$). Excess of the butadiyne $HC{\equiv}CC{\equiv}CSiMe_3$ gave dimer **36** with an Mn–Mn bond, whereas excess $^tBuC{\equiv}CH$ gave an alkynyl and TMEDA-bridged dimer. Dinuclear species were also accessible from reaction of bis(trimethylstannylethynyl)benzenes and **34**, in which two MeCp(TMEDA)Mn centers are bridged by the diethynylaryl group.[30]

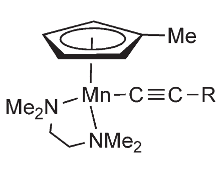
The Berke group has reported C_2-bridged complexes from 1,1′-dimethylmanganocene, dmpe, and bis(trimethylstannyl)acetylene via the $[(\eta^5\text{-}C_5H_4Me)(\eta^2\text{-}C_5H_4Me)Mn(dmpe)]$ intermediate species.[31] This latter complex had previously been reported to have both cyclopentadienyl rings coordinated in an η^5-mode,[32] and the η^2,η^5-bonding contrasts with other related bis(cyclopentadienyl)manganese-chelate complexes. Interestingly, the initial C_2-bridged product is a salt, $[\{(\eta^5\text{-}C_5H_4Me)(dmpe)Mn\}_2(\mu\text{-}C{\equiv}C)][(\eta^2\text{-}C_5H_4Me)_3Mn]$, containing the oxidized mixed-valent cation with the tris(methylcylopentadienyl)manganate(II) anion (see Section 5.11.7).[33] Metathesis of this salt with KPF_6 or $Na[BPh_4]$ gave the PF_6 and $[BPh_4]$ salts that could be reduced with Na/Hg to give the neutral complex $[\{(\eta^5\text{-}C_5H_4Me)(dmpe)Mn\}_2(\mu\text{-}C{\equiv}C)]$ **37**. This species possessed a triplet/singlet spin equilibrium and underwent two fully reversible oxidations to the bis(carbyne) dicationic species.[31] Density functional theory calculations on complexes with bridging C_2 ligands like **37** have been performed to study the changes in the interaction mode of the bridging unit as a



R = H or Me; R^1 = Ph or $SiMe_3$.

Scheme 9

function of the metal parameters. The authors reported that the three limiting structures, namely M–C≡C–M, M═C═C═M, and M≡C–C≡M, depend upon the d^n configuration, the oxidation state of the metals, and the ancillary ligands, but that for manganese systems, the M–C≡C–M mode was preferred irrespective of the d^n configuration.[34]



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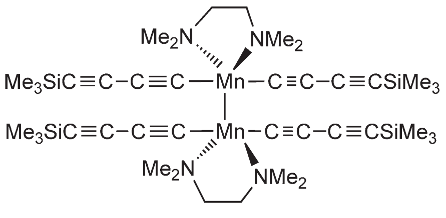

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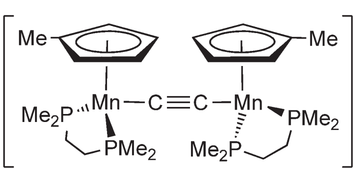


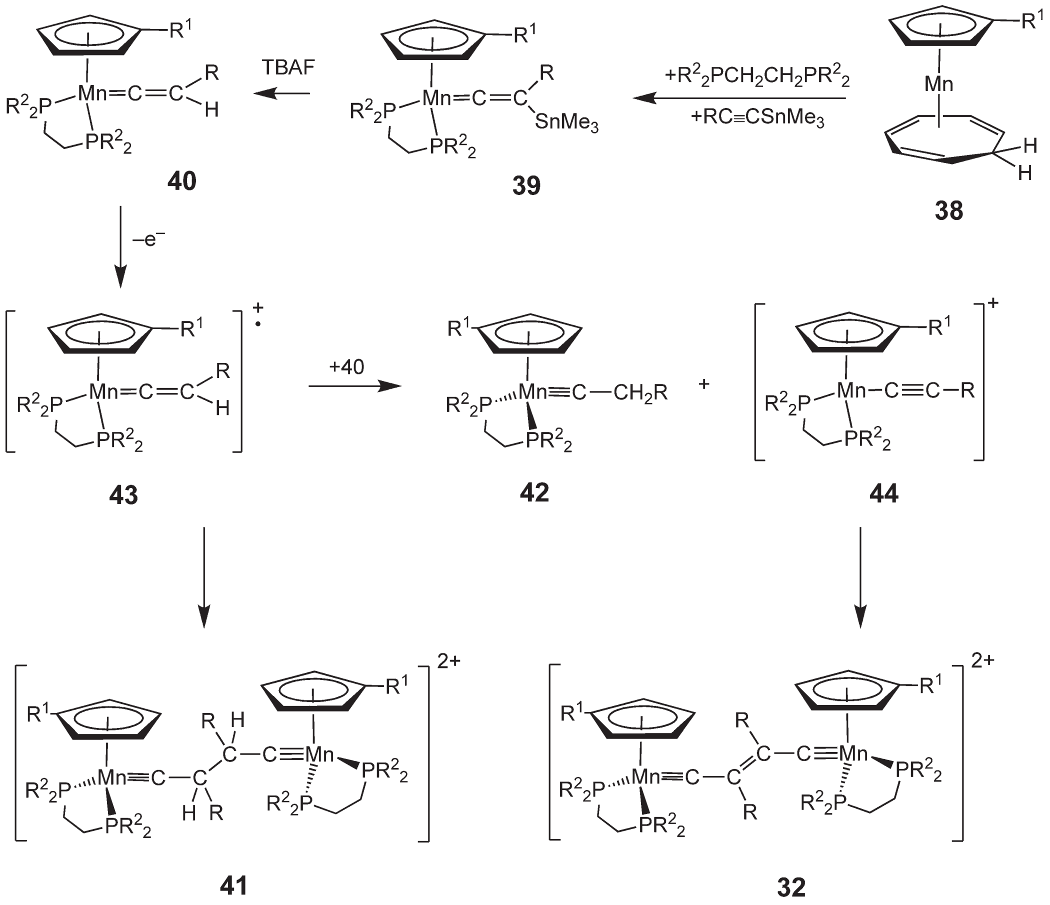
n = 0, +1, +2

37

5.11.4 Vinylidene Complexes

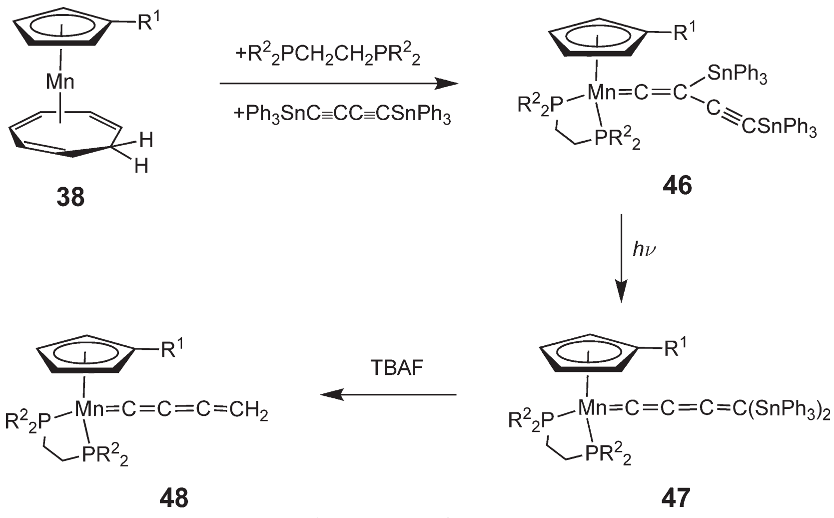
Vinylidene complexes of the [(η^5-$C_5H_4R^1$)LMn] (R^1 = H, Me; L = dmpe, depe) manifold are readily accessible from reaction of stannyl-substituted alkynes with [(η^5-$C_5H_4R^1$)(η^6-cycloheptatriene)Mn] **38** and dmpe or depe, and Berke and co-workers have prepared a range of mononuclear and dinuclear vinylidene complexes in this way (Scheme 10).[35–38] The mononuclear complexes [(η^5-$C_5H_4R^1$)LMn=C=C($SnMe_3$)R] **39** (R = Ph, Tol, $SnMe_3$, C_4H_3S; R^1 = H, Me; L = dmpe, depe), all prepared from RC≡C$SnMe_3$, were treated with Bu_4NF to yield the corresponding vinylidene species [(η^5-$C_5H_4R^1$)LMn=C=CHR] **40**. Oxidation of **40** with ferrocenium ion either gave the bis(carbyne) dimers **41** or a mixture of the dimer **32** and a mononuclear carbyne complex **42**, depending upon the substituents at the C_β carbon. The latter species were proposed to arise from proton transfer from an intermediate radical cation **43** to the starting complex **40**, with dimerization and oxidation of the accompanying alkynyl species **44** giving the conjugated dimers **32**.[35] The X-ray structures of the parent complex [(η^5-C_5H_4Me)(dmpe)Mn=C=CH_2] **40** (R = H) and its oxidized dimer [(η^5-C_5H_4Me)(dmpe)Mn≡CCH_2 CH_2C≡Mn(η^5-C_5H_4Me)(dmpe)]$^{2+}$ **41** (R = H) were reported, the Mn=C and Mn≡C bond distances being 1.755 and 1.655 Å, respectively.[37]

Dinuclear vinylidene complexes, [(η^5-C_5H_4Me)(dmpe)Mn=C=C($SnMe_3$)Ar($SnMe_3$)C=C=Mn(η^5-C_5H_4Me)(dmpe)] **45** (Ar = 1,4-C_6H_4, 1,3-C_6H_4, 4,4′-$C_6H_4C_6H_4$, 1,4-C_4H_2S), with conjugated bridges between the metal centers were prepared from aryl-bridged dialkynes **38** and dmpe.[36] The dimers could be destannylated with excess methanol and the X-ray structures were reported. Reaction of **38** with 1,4-bis(triphenylstannyl)butadiyne gave **46** which contains an alkynyl-substituted vinylidene ligand. Photolysis of **46** gave the



R = Ph, Tol, $SnMe_3$, C_4H_3S; R^1 = H or Me; R^2 = Me or Et.

Scheme 10



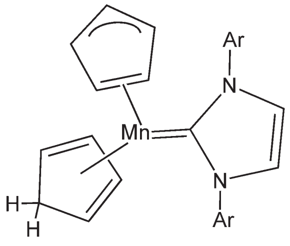
R^1 = H or Me; R^2 = Me or Et.

Scheme 11

butatrienylidene complex $[(\eta^5\text{-}C_5H_4Me)(dmpe)Mn{=}C{=}C{=}C{=}C(SnPh_3)_2]$ **47**, which can be destannylated to the parent cumulene species $[(\eta^5\text{-}C_5H_4Me)(dmpe)Mn{=}C{=}C{=}C{=}CH_2]$ **48** (Scheme 11).[39] The stannyl complex showed increased thermodynamic stability, which was traced to electron donation from the high-lying σ-orbitals of the $SnPh_3$ groups. The related trimethylstannyl complexes were also prepared, and these react with methanol to give novel C_8-bridged dimers containing an MeOC═COMe linkage in the middle of the cumulenic chain.[38]

5.11.5 Carbene Complexes

Stable carbene complexes of manganese(II) have been prepared from the sterically demanding nucleophilic *N*-heterocylic carbenes 1,3-bis(aryl)imidazol-2-ylidene and tetramethylimidazol-2-ylidene by direct reaction with manganocene.[40] The more sterically crowded bis(mesityl) and bis(2,6-dimethyl-4-bromophenyl) carbenes gave stable paramagnetic 15-electron complexes with one carbene ligand, **49** (Mn═C, 2.227Å), and η^2- and η^4-cyclopentadienyl groups. On the other hand, the smaller tetramethyl species gave a bis(carbene) complex **50** (Mn═C, av. 2.218Å) with η^1- and η^2-Cp ligands. Roesky and co-workers also reported *N*-heterocyclic carbene complexes of a bulky β-diketiminate-manganese manifold by reaction of the THF complex **51** or the μ-iodo species **8** with the free carbene. Interestingly, the initial carbene-containing product **52** formed an amido species **53** after reduction or by treatment with LiNHAr. The Mn═C bond distance in this latter complex was found to be 2.270 Å.[41]



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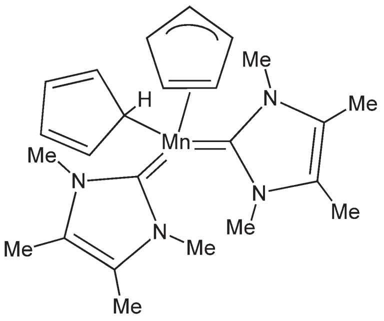

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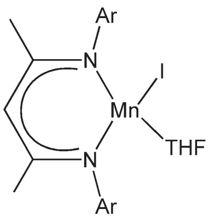

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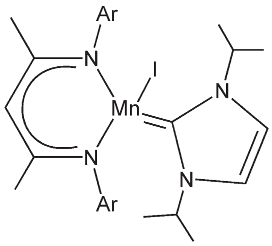

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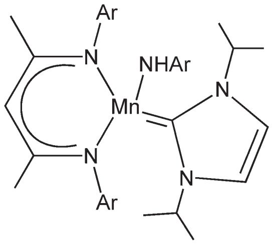
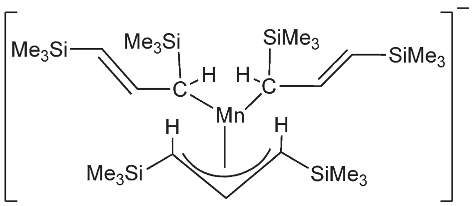


53

The same authors reported the formation of a series of bis(carbene) complexes from 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene and either of the manganese(II) species, $MnCl_2(THF)_2$, MnI_2, or $Mn(MeCO_2)_2$. The dihalide products had distorted tetrrahedral geometry with M═C bond distances between 2.204 and 2.219 Å, whereas the distorted octahedral bis(acetate)bis(carbene)Mn(II) complex had *cis*-carbene ligands with slightly longer Mn═C bond lengths of 2.254 Å. In contrast to the tetrahedral complexes, the acetate derivative had no in-plane or out-of-plane bending of the *N*-heterocyclic carbene.[42]

5.11.6 Allyl Complexes

A homoleptic allyl complex of Mn(II) has been prepared from reaction of $MnCl_2$ with 3 equiv. of $Li\{(Me_3Si)_2C_3H_3\}$. The product **54**, which was isolated as its $[Li(THF)_4]^+$ salt, was structurally characterized and its magnetic properties investigated. The complex contains two η^1-allyl ligands (Mn–C σ-bond 2.184, 2.187 Å) and one η^3-allyl group with Mn–C distances of 2.470, 2.348, and 2.398 Å. The complex displays a low-spin/high-spin equilibrium between $S = 1/2$ and $S = 5/2$ states and behaves as a Curie paramagnet between 5 and 300 K with a magnetic moment of 2.92 to 4.03 μ_B.[43] A β-diketiminate allyl complex **55** ($Ar = 2,6\text{-}^iPrC_6H_3$) has also been reported by Roesky from the trimanganese species **20** and allylmagnesium chloride. The product has distorted tetrahedral geometry and a rare η^1-allyl ligand with an Mn–C σ-bond of 2.132 Å.[22]



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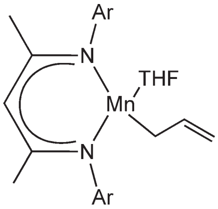

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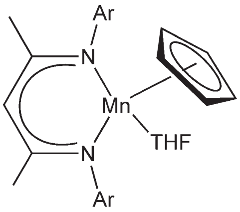
5.11.7 Non-Manganocene Cyclopentadienyl Complexes

The tris(η^2-cyclopentadienyl)manganate(II) anion **56** and its methyl-substituted derivative have been reported by two groups.[33,44] Wright *et al.* reported that reaction of manganocene **57** with either CpK or Cp_2Mg gave $[(\eta^2\text{-}Cp)_3Mn]K.1.5THF$ and $[(\eta^2\text{-}Cp)_3Mn]_2[Mg(THF)_2]$ respectively with the potassium species having a honeycomb sheet structure with Mn–C distances of 2.351–2.392 Å and layer separations of 9.53 Å.[44] The cesium complexes

Cs[(η^2-Cp)$_3$Mn] and Cs[(η^2- C$_5$H$_4$Me)$_3$Mn] were reported by Berke and co-workers, and can be prepared from either MnCp$_2$ or Mn(C$_5$H$_4$Me)$_2$ and the appropriate cyclopentadienylcesium reagent. The X-ray structure of the Cp complex proved to be a rare example of a (10,3) recemic interpenetrating network. Detailed magnetic studies indicated that the complexes are high spin (6.20 and 5.83 μ_B at 300K) and DFT calculations showed that the coordination mode is characteristic of the sextet electronic ground state.[33] Anions containing a mixture of cyclopentadienyl and methylcyclopentadienyl lignds could not be prepared in pure form and isolated, with mixtures of all the possible isomers presumably being formed. Similar cyclopentadienyl ring metathesis has been reported between [Ca(C$_5$Me$_5$)$_2$(THF)$_x$] and manganocene to form decamethylmanganocene [Mn(C$_5$Me$_5$)$_2$].[45]

The β-diketiminate η^5-cyclopentadienyl complex **58** has been prepared from the chloride-bridged dimer **8** (X = Cl) and sodium cyclopentadienide in THF and has a pseudo-tetrahedral geometry with Mn–C distances of 2.42–2.58 Å.[11]



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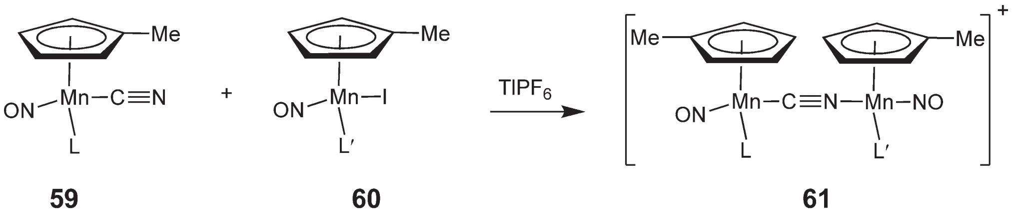
Connelly and co-workers have studied complexes of the type [(η^5-C$_5$H$_4$Me)(NO)(L$_1$)(L$_2$)Mn], where L$_1$ and L$_2$ are MeCN, I$^-$, PPh$_3$, P(OPh)$_3$, ^{t}BuNC, and XylNC (Xyl = 2,6-Me$_2$C$_6$H$_3$).[46] The μ-cyano-bridged linkage isomers [(η^5-C$_5$H$_4$Me)(NO)(L)Mn(μ-CN)Mn(NO)(L′)(η^5-C$_5$H$_4$Me)]$^+$ **61** were formed from reaction of equimolar amounts of [(η^5-C$_5$H$_4$Me)(NO)(L)MnCN] **59** (L = PPh$_3$, ^{t}BuNC, XylNC) and [(η^5-C$_5$H$_4$Me)(NO)(L′)MnI] **60** (L′ = PPh$_3$, ^{t}BuNC, XylNC) with TlPF$_6$ (Scheme 12). Improved synthetic procedures for the Mn(I) mononuclear species **59** and **60** were also reported and their electrochemistry studied. The μ-cyano dinuclear monocations were green and red complexes, and possess two reversible oxidations to the di- and trications as observed by cyclic voltammetry, although isolation of stable di- or tricationic species via chemical oxidation was not possible. The authors concluded that the N-bound manganese centers in these bridged cations were oxidized first. Novel pentametallic trigonal-bipyramidal [Mn{(μ-NC)Mn(η^5-C$_5$H$_4$Me)(NO)(XylNC)}$_4$(OH$_2$)][PF$_6$]$_2$ and octahedral [Mn{(μ-NC)Mn(η^5-C$_5$H$_4$Me)(NO)(XylNC)}$_4$(NO$_3$)][PF$_6$] complexes were also formed from MnI$_2$ and 4 equiv. of the organometallic ligand [(η^5-C$_5$H$_4$Me)(NO)(L)MnCN] in the presence of TlPF$_6$, or by slow decomposition of the dinuclear cations.[46]

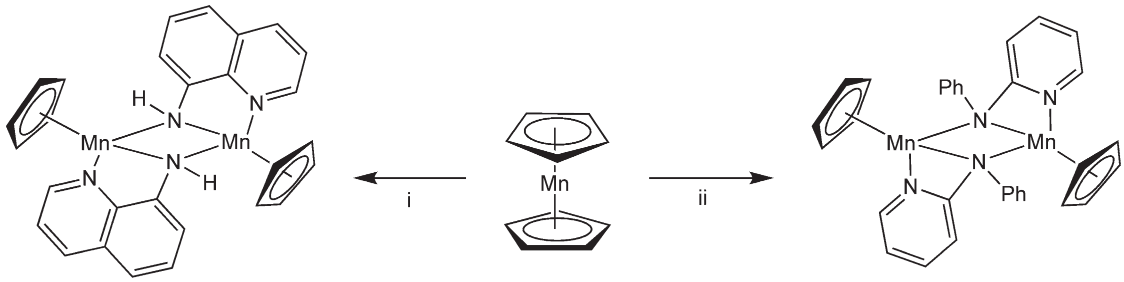
Cyclopentadienyl-substituted heterobimetallic cubanes with manganese and either arsenic and antimony have been prepared by nucleophilic substitution of one cyclopentadienyl ligand of manganocene by [{E$_2$(Ncy)$_4$}$_2$M$_4$] (E = Sb, M = Na; E = Sb, M = Li) and elimination of MCp. The products [{E$_2$(Ncy)$_4$}(MnCp)$_2$] have Mn(II) centers at opposite corners of one face of the cubane core connected to three cyclohexylimido bridging groups. The arsenic or antimony atoms occupy the other corners of the opposite face. The manganese atoms are within bonding distance (2.934 Å, E = As; 3.041 Å, E = Sb), the former being comparable to that in Mn$_2$(CO)$_{10}$. The magnetic properties were investigated and preliminary measurements suggest a high-spin/low-spin equilibrium; however, the Mn–Cp bond distances appear typical of high-spin species (2.389–2.615 Å).[47]

Cyclopentadienyl phenoxide complexes have been prepared by reaction of manganocene with phenols in THF, and the type of product depends on the steric environment of the phenoxide ligand. Thus, phenol gave a white



L or L′ = PPh$_3$, ^{t}BuNC, XylNC.

Scheme 12



62 **57** **63**

i, 8-$NH_2C_9H_6N$; ii, N(Ph)H(C_5H_4N).

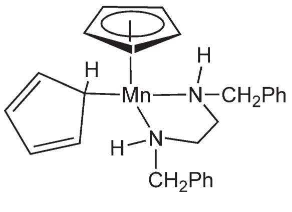
Scheme 13

complex that is a dimer with two oxygen-bound bridging OPh groups, [Cp(THF)Mn(μ-OPh)]$_2$, whereas the bulky phenoxide ligands derived from 2,6-^{t}Bu$_2$C$_6$H$_3$OH or 2,6-Me$_2$C$_6$H$_3$OH coordinate to the metal through an η^5-π-interaction with the phenyl ring to give [CpMn{η^5-2,6-R$_2$C$_6$(=O)H$_3$}] (R = Me or ^{t}Bu). The latter complexes were not structurally characterized but are proposed on the basis of their reaction with CO$_2$, which gives the corresponding 4-hydroxy-3,5-disubstituted benzoic acids.[48]

Alvarez and co-workers have used manganocene to prepare a host of imide and amide cyclopentadienyl derivatives, many of which possess complex cage structures, by reaction with aminopyridines and aminopyrimidine complexes. The simplest of these are dimers **62** and **63** formed from MnCp$_2$ **57** and 8-aminoquinoline and 2-N-anilinopyridine, respectively, in which the pyridine coordinates as a terminal group and the former amino group is doubly deprotonated to form a bridging imido moiety (Scheme 13).[21] Variable temperature magnetic measurements were made to assess the degree of the communication between Mn centers in the dimers as a function of the bridging group, with the N-bridge affording less communication than the more covalent C-bridge in the related alkynyl species **18**.[21]

In contrast to the above reactions, reaction of 2-aminopyridine (L) with manganocene gave hexanuclear [Cp$_2$Mn$_3$(L)$_4$]$_2$ and octanuclear [Mn $_8$(L)$_{12}$(μ_4-O)$_2$] clusters, the latter containing oxygen atoms derived from water in the amine solvate. The hexanuclear cluster contains two Cp$_2$Mn$_2$(L)$_4$ units, which dimerize via doubly deprotonated pyridyl-N–Mn linkages, and has three chemically distinct antiferromagnetically coupled manganese(II) centers. The octanuclear complex has S_6 symmetry and contains a core of two Mn$_4$(μ_4-O) units linked by bridging amido and imido ligands.[49]

In further contrast, the reaction of manganocene with 2-aminopyrimidines gave cage complexes containing eight manganese centers. Thus the 4,6-dimethyl- and 4,6-dimethoxy-2-aminopyrimidines gave novel heteroleptic imido/amido Mn(II) cages with distorted Mn$_4$N$_4$ cubane cages. The Mn centers had distorted tetrahedral geometry and were coordinated to cyclopentadienyl ligands with Mn–C distances of 2.408–2.616 Å, typical of high-spin 17-electron Mn(II).[50,51] On the other hand, the reaction of *N,N′*-dibenzylethylenediamine with manganocene gave the simple adduct [(η^1-Cp)(η^5-Cp)Mn(BnNHCH$_2$)$_2$] **64**, in which no deprotonation of the organic ligand occurred,[51] as did reaction with 1,1,3,3-tetramethylguanidine which gave [(η^1-Cp)(η^2-Cp)Mn{(HN = C(NMe$_2$)$_2$}$_2$] **65**.[21]



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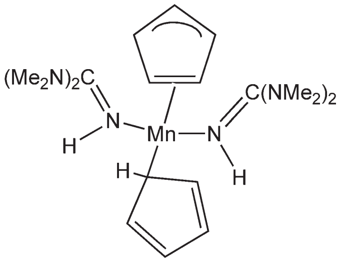

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5.11.8 Manganocenes

Manganocene $[Mn(\eta^5\text{-}C_5H_5)_2]$ **57** is a valuable starting material for the preparation of Mn(II)-containing catalysts. Thus, highly selective epoxidation of styrene has been reported using Mn(II) catalysts derived from $MnCp_2$ and tripodal N-donor ligands. The complexes $[Mn(RNCH_2CH_2)_3N]$ **66** and $[\eta^3\text{-}HB(3\text{-}^tBuPz)_3MnCl]$ ($R = SiMe_3$, Pz = pyrazolyl) were prepared from manganocene and the appropriate anions, and show selective epoxidation of styrene and norbornene using iodosobenzene and oxygen as O atom sources.[52] Similarly, Alvarez and co-workers reacted $MnCp_2$ with the tridentate Al-containing ligand $[MeAl(2\text{-py})_3Li{\cdot}THF]$ (py = pyridyl) to give $[\{MeAl(2\text{-py})_3\}_2Mn]$ **67**, which selectively oxidizes the styrene in air (Scheme 14).[53]

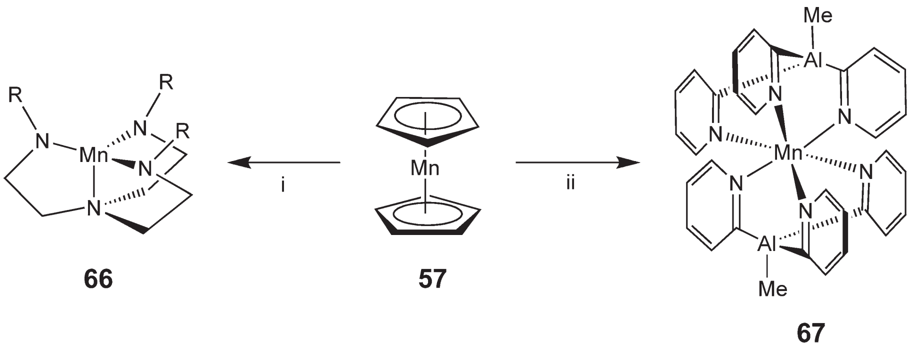
Manganocene itself has been reported to be an olefin polymerization catalyst when methylaluminoxane is used as co-catalyst,[54] and the thermal homo- and co-polymerization of acrylic and methacrylic acids using an $MnCp_2/CCl_4$ initiator combination has been reported although these polymerizations were not living.[55]

The synthesis of manganocenes with sterically demanding alkyl groups attached to the five-membered ring has been reported, and the increase in steric bulk was shown to supersede the electronic influence of the alkyl substituents and give high-spin Mn(II) centers. The substituted manganocenes were prepared from the appropriate sodium salts and $MnCl_2$. 1,1′,2,2′,3,3′4,4′-octaisopropylmanganocene and 1,1′,2,2′,4,4′-hexa-*tert*-butylmanganocene were high spin,[56] whereas less sterically demanding ligands (e.g., 1,2,4-triisopropyl-,[57] 1,2,4-triisopropyl-3,5-dimethyl-,[56] or 1,2,3-trimethyl-4,5-diisopropyl-[58]) gave manganocenes with low-spin/high-spin equilibria, in which spin crossover was observed at lower temperatures for smaller substituents. The X-ray structure of these latter complexes indicates average Mn–C distances of 2.130 Å consistent with low-spin Mn(II). The high-spin complexes showed greater Mn–C distances of ca. 2.42 Å. The high-spin species were also pale yellow in color compared to the orange-red low-spin compounds. Surprisingly, the octaisopropyl complex reacts with tetracyanoethylene to give a tricyanovinylation product $C_5{}^iPr_4HC(CN){=}C(CN)_2$, whereas the hexaisopropylmanganocene gives the simple charge transfer salt.[57]

A manganocene with pendant dimethylphosphinomethyl groups has been prepared from $MnCl_2$ and $Na(C_5Me_4CH_2PMe_2)$. The red-orange product $[Mn(\eta^5\text{-}C_5Me_4CH_2PMe_2)_2]$ has staggered rings with Mn–C distances of 2.092–2.127 Å, and is predominantly low spin with some contribution from the high-spin configuration giving a magnetic moment of 2.64 μ_B, although impurities were not ruled out as the source of the high spin. Reaction of the complex with $B(C_6F_5)_3$ and $Pt(cod)I_2$ gave the expected bis-adduct $[Mn\{\eta^5\text{-}C_5Me_4CH_2PMe_2B(C_6F_5)_3\}_2]$ and chelate $[Mn(\eta^5\text{-}C_5Me_4CH_2PMe_2)_2PtI_2]$, respectively.[59]

The decamethylmanganocenium ion $[Mn(\eta^5\text{-}C_5Me_5)_2]^+$ has been studied in charge transfer-based molecular ferrimagnets with a variety of anions. Thus, salts from methyl tricyanoethylenecarboxylate[60] and dialkyldicyanofumarate[61] have been prepared by addition of $[Mn(\eta^5\text{-}C_5Me_5)_2]$ to the organic compounds, and their magnetic properties studied. Salts that behave as molecular ferrimagnets that have metal-containing anions have also been reported; for example, $[Mn(\eta^5\text{-}C_5Me_5)_2][Ni(dmit)_2]$ (dmit = $C_3S_5{}^{2-}$, 2-thioxo-1,3-dithiole-4,5-dithiolato) and its gold analog were prepared from $[Mn(\eta^5\text{-}C_5Me_5)_2][PF_6]$ and the corresponding tetrabutylammonium salts of the nickel- or gold-based anions.[62] Interestingly, the anionic decamethylmanganocene complex $K[Mn(\eta^5\text{-}C_5Me_5)_2]$ was used as a reducing agent to prepare superconducting metal alkali fullerides, $K_3C_{60}{\cdot}x THF$, in high yields.[63]

Manganocene has continued to be the subject of theoretical studies, with DFT being of recent interest. Such studies have led to more accurate predictions of the binding energy of manganese-cyclopentadienyl

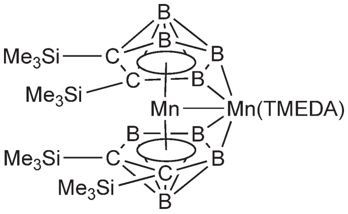


i, $Li_3(RNCH_2CH_2)_3N(THF)_2$, $R = C_6F_5$ or $SiMe_3$; ii, $[MeAl(2\text{-py})_3Li](THF)$.

Scheme 14

(584 kcal mol^{-1}, experimental = +572 kcal mol^{-1}),[64] and determination of the second-order hyperpolarizabilities of both the eclipsed and staggered conformations.[65] The use of unrestricted DFT calculations allowed the reassignment of the photoelectron spectrum of manganocene. The authors found that the ordering of the occupied spin orbitals is inverted with respect to the normal metallocene orbital ordering, with the metal orbitals lying below the ligand e_1 π orbitals.[66] In another study, the Raman and infrared vibrational modes of $MnCp_2$ have been collected and the assignments have been revised.[67] The gas-phase free energies of ionization of $[Mn(\eta^5\text{-}C_5Me_5)_2]$ have been measured using the electron-transfer equilibrium technique and Fourier-transform ion cyclotron resonance mass spectroscopy with the $\Delta G_i°$ found to be 121.6 kcal mol^{-1} and the $E_{1/2}$ being −0.56 V in acetonitrile and −0.64 V in the gas phase.[68]

A carborane complex related to manganocene has been prepared from the gadolinium complex of 2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$. The product **68** contains two pentahapto ligands forming a sandwich structure and a second manganese center coordinated to the boranes in η^2-mode and bonded to the first Mn atom (Mn–Mn = 2.665 Å) and a TMEDA ligand. The Mn–C distances for the two ligands in the sandwich were found to be 2.090–2.227 Å.[69]



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5.11.9 Arene Complexes

The condensation of manganese atoms with toluene at 77 K in the presence of iodine gave the salt $[Mn(\eta^6\text{-}C_6H_5Me)_2]I$. The yield was low but the product was cystallographically characterized, and showed an Mn–ring centroid distance of 1.569 Å.[70] The electronic absorption spectrum of $[Mn(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_6)]$ in pentane and the gas phase has been reported,[71] as well as the ^{55}Mn NMR data for $[Mn(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_6)]$ and a host of other manganese sandwich complexes. The ^{55}Mn chemical shifts were over a large range and were dependent on the ring substituents rather than the oxidation state at the metal center.[72] The thermochemistry of bis(benzene) complexes of the first-row metals including manganese has been investigated by collision-induced dissociation with Xe in a guided ion-beam tandem mass spectrometer.[73]

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5.12

Technetium Organometallics

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5.12.1 Introduction

Technetium was the first man-made element, and was obtained as the isotopes ^{95}Tc and ^{97}Tc by Perrier and Segré in 1937 by bombarding molybdenum with deuterons.[1,1a] Today, 34 isotopes of element Tc are known with mass numbers ranging from 85 to 118, and all are radioactive. The longest-lived isotope is ^{98}Tc ($t_{1/2} = 4.2 \times 10^6$ years), but the most readily available isotope is ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ years). The latter is isolated in large quantities from spent nuclear fuel, where it constitutes approximately 6% of the fission product yield (via ^{99}Mo).[2] In the recovery process, the pertechnetate anion, $[^{99}\mathrm{TcO}_4]^-$, is extracted with pyridine from aqueous solution and ultimately isolated as $[\mathrm{NH}_4][^{99}\mathrm{TcO}_4]$ with a purity of better than 99%. The ammonium salt is readily available at a reasonable cost per gram from Oak Ridge National Laboratory.[3] All other starting materials, including technetium metal, trace their origins to ammonium pertechnetate.

The ^{99}Tc isotope is a weak β-emitter ($E_{\max} = 0.292$ MeV) and decays to stable ^{99}Ru (Equation (1)).

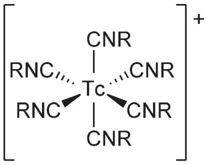
$$ {}_{43}\mathrm{Tc}^{99} \longrightarrow {}_{44}\mathrm{Ru}^{99} + {}_{-1}\mathrm{e}^{0} \tag{1} $$

The decay properties of ^{99}Tc allow handling of the isotope during normal chemical operations in quantities up to ca. 1 g. With this mass limitation, special shielding precautions are not necessary since the low-energy β-radiation is absorbed by ordinary glassware. Larger quantities of ^{99}Tc may produce secondary X-rays (“bremsstrahlung”). It is prudent to remember that ^{99}Tc, like all radionuclides, is a potential health hazard, and protective gloves, lab coats, and safety glasses are essential at all times when working with ^{99}Tc compounds. Special care must be exercised with volatile compounds such as Tc_2O_7, $HTcO_4$, $MeTcO_3$, $Me_3SiOTcO_3$, and $Tc_2(CO)_{10}$ to avoid inhalation and the unwanted spread of radioactivity. The authors have carried out numerous synthetic reactions, spectroscopic measurements, and X-ray structure determinations in laboratories designed for low-level radioactivity using high-efficiency particulate air (HEPA)-filtered fume hoods, Schlenk and glove box techniques, and double or triple containment of samples. Researchers contemplating work with ^{99}Tc should consult local, state, and federal safety regulations dealing with ionizing radiation.

Because technetium bears a close electronic relationship to rhenium, the occurrence of analogous compounds, including organometallics, is to be expected, but the radioactive nature of technetium has served to retard the development of its chemistry relative to its heavier congener. As one dramatic contrast, 13 binary halides have been reported for rhenium, but only three are known and well characterized for technetium, that is, TcF_6, TcF_5, and $TcCl_4$.[4] Other binary halides, new coordination compounds, and organometallics will surely be discovered in the future, but the pace of discovery is limited by the small number of operational technetium laboratories. Technetium organometallic compounds in which the formal oxidation state of the metal center ranges between -1 and $+7$ are known to exist.

Much of the technetium research reported in the literature is coupled to applications. The most important of these is surely nuclear medicine. Compounds containing the isotope ^{99m}Tc, which decays to ^{99}Tc with a 6 h half-life, are used millions of times each year to γ-image various organs of the human body. In the late 1950s, a team of scientists at Brookhaven National Laboratory developed the ^{99}Mo/^{99m}Tc generator.[5] Molybdenum-99 which has a 67 h half-life is loaded onto an alumina column in the form of the molybdate ion, $[^{99}MoO_4]^{2-}$. The daughter product, $[^{99m}TcO_4]^-$, is continuously eluted with dilute saline solution and is then chemically transformed into specific radiopharmaceuticals. The generators are readily available at a reasonable cost, which, together with favorable nuclear properties, account for the popularity of ^{99m}Tc as an imaging agent. In addition, γ-imaging is considered far safer to patients than exploratory surgery or other invasive techniques. Not all of the body's organs are accessible by commercial ^{99m}Tc agents currently available, and many existing agents could be substantially improved if their degree of localization in the target organ (bio-distribution) could be increased. As a consequence, there is considerable medical and industrial interest in developing, testing, and marketing new ^{99m}Tc imaging agents.

There is also considerable interest in the environmental chemistry of technetium, including the behavior and distribution of technetium in nuclear waste processing schemes, and the best long-term storage form for repositories. Nuclear reactors with a nominal power of 100 MW produce over 2 g of ^{99}Tc per day. The first gram of technetium was isolated in the 1950s. Due to the aforementioned safety considerations as well as the expense associated with setting up and maintaining radiation laboratories (including radioactive waste disposal), research into fundamental technetium chemistry has generally been a luxury few could afford. Organotechnetium chemistry has been particularly slow to develop, and the chemistry is not as sophisticated as that developed for neighboring elements in the periodic table. On average, only four organotechnetium references per year appeared in the literature from 1980 to 1987. Since then, the average has increased to roughly nine per year. This is due, at least in part, to the discovery by Professor Davison's group at the Massachusetts Institute of Technology that hexakis(isocyanide)technetium(I) cations **1** are good heart-imaging agents.[6]



1

One derivative (R = methoxyisobutyl), marketed by E. I. duPont under the trade name Cardiolite®, is now commonly used by radiopharmacies around the world. This organometallic compound is surely the most successful radiopharmaceutical ever marketed. Originally, the *t*-butylisocyanide complex was prepared by heating an aqueous solution of pertechnetate in the presence of the isonitrile ligand with dithionite ($S_2O_4^{2-}$) as a reducing agent.[7] The reaction is quantitative and the complex is stable in air over a wide pH range and at elevated temperatures. The kinetic stability (low-spin d^6) is also something of a drawback since the octahedral cation cannot be easily substituted. Since the discovery of Cardiolite®, a number of other organotechnetium compounds have been patented as imaging agents.

Our review was facilitated by a number of excellent review articles published since COMC (1995).[8–20] Many of these focused on nuclear medicine applications or specific aspects of technetium coordination chemistry, although a few provide a general overview of technetium chemistry. A definitive text on technetium was published in 2000 by Schwochau.[22] The latter text should be consulted for additional details and references to the primary literature. The present review of organotechnetium chemistry covers the years 1994 to approximately mid-2005. However, for clarity of presentation, we have included some of the older material presented in COMC (1995).[23]

5.12.2 Technetium Carbonyls and their Halide and Hydride Derivatives

5.12.2.1 Binary and Mixed Metal Carbonyls

Homoleptic ditechnetium decacarbonyl has been synthesized at elevated temperatures and CO pressures from a variety of technetium starting materials (e.g., TcO_2, Tc_2O_7, NH_4TcO_4, $NaTcO_4$) in stainless steel autoclaves.[23–27] These reactions work quite well, but due to safety regulations as well as the cost of the high-pressure autoclaves, it seems unlikely that these syntheses will be reproduced anytime soon. The senior author and Roger Alberto, currently professor of chemistry at the University of Zurich, once prepared several grams of $Tc_2(CO)_{10}$ using a variant of Heinekey and co-workers' preparation of $Re_2(CO)_{10}$ (Equation (2)).[26,28] A small amount of copper powder seems to be crucial to the success of these group 7 carbonylation reactions and was used in the large-scale synthesis of $Tc_2(CO)_{10}$.[26]

$$\mathrm{NaTcO_4} + \mathrm{CO}\ (190\,\mathrm{atm}) \xrightarrow[\mathrm{Cu},\ 230\,^\circ\mathrm{C}]{\mathrm{MeOH}} \mathrm{Tc_2(CO)_{10}} \qquad (2)$$

An interesting alternative to the traditional autoclave techniques was briefly described in a 1997 French patent by Jaouen and co-workers.[29] Reduction of $NH_4[MO_4]$ (M = Tc, Re) suspended in toluene saturated with carbon monoxide at ca. 75 °C with diisobutyl aluminum hydride (DIBAL) provides $M_2(CO)_{10}$ in respectable yields, that is, ca. 60% (Equation (3)). The examples in the patent are all rhenium syntheses, and we are unaware of any publications in the primary literature referencing $Tc_2(CO)_{10}$ prepared in this manner. However, the observation is very encouraging, the preparation should be repeated, and the result offers hope that even more atom-efficient, low pressure routes to this important starting material can be developed.

$$\mathrm{NH_4TcO_4} + \text{excess } (i\text{-}\mathrm{Bu})_2\mathrm{AlH} + \mathrm{CO}\ (1\,\mathrm{atm}) \xrightarrow[75\,^\circ\mathrm{C}]{\mathrm{PhCH_3}} \mathrm{Tc_2(CO)_{10}} \qquad (3)$$

The carbonyl dimer is moderately stable in air and is readily purified by sublimation *in vacuo*. In the solid state, $Tc_2(CO)_{10}$ adopts a staggered D_{4d} geometry similar to that found for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, and the Tc–Tc single bond distance is 3.036(6) Å (Figure 1).[30] The mixed metal Mn–Tc and Tc–Re compounds are also known.[31] The infrared spectrum of $Tc_2(CO)_{10}$ measured in cyclohexane solution exhibits three strong carbonyl stretching vibrations at 2064, 2017, and 1984 cm^{-1}.[32]

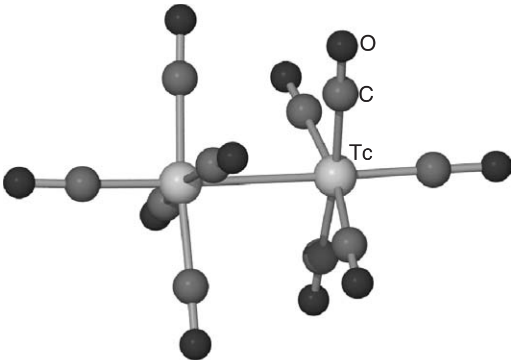


Figure 1 The structure of $Tc_2(CO)_{10}$. The equatorial Tc–C distances average 2.00[1] Å; the axial Tc–C distance is 1.90(1) Å.

A fair amount of technetium organometallic chemistry starts with $\mathrm{Tc_2(CO)_{10}}$. The anion $[\mathrm{Tc(CO)_5}]^-$ is easily prepared via reductive cleavage of the carbonyl dimer with sodium amalgam in THF (Equation (4)), but is less stable than its manganese and rhenium analogs.[32] The super-reduced anion, $[\mathrm{Tc(CO)_4}]^{3-}$, has not been reported but its synthesis should be straightforward. The Tc(I) hexacarbonyl cation, $[\mathrm{Tc(CO)_6}]^+$, can be prepared in one of two ways, that is, treatment of $\mathrm{TcCl(CO)_5}$ with carbon monoxide (300 atm) in an autoclave in the presence of aluminum chloride (Equation (5))[33] or treatment of the aquo-carbonyl $[\mathrm{Tc(CO)_3(H_2O)_3}]^+$ with CO (Equation (6)) in acidic aqueous solution.[34] The latter is obviously the preferred method.

$$\mathrm{Tc_2(CO)_{10}} + 2\mathrm{Na/Hg} \xrightarrow{\mathrm{THF}} 2\mathrm{Na[Tc(CO)_5]} \tag{4}$$

$$\mathrm{TcCl(CO)_5} + \mathrm{CO}\ (300\ \mathrm{atm}) \xrightarrow[\mathrm{AlCl_3},\ 20\,^\circ\mathrm{C}]{\mathrm{C_6H_6}} [\mathrm{Tc(CO)_6}]\mathrm{AlCl_4} \tag{5}$$

$$[\mathrm{Tc(CO)_3(H_2O)_3}]^+ + \mathrm{CO}\ (40\ \mathrm{atm}) \xrightarrow[2\mathrm{M\ HClO_4}]{\mathrm{H_2O}} [\mathrm{Tc(CO)_6}]\mathrm{ClO_4} \tag{6}$$

5.12.2.2 Halo and Hydrido Technetium Carbonyls

The halo derivatives, $\mathrm{TcX(CO)_5}$, can be produced by direct oxidation of the carbonyl with $\mathrm{X_2}$ in carbon tetrachloride or carbon disulfide.[32] The reaction rate follows the order $\mathrm{Cl} > \mathrm{Br} >> \mathrm{I}$. The IR spectra of these compounds are fully consistent with complexes possessing C_{4v} symmetry. The pentacarbonyl halides are decarbonylated in a stepwise manner by heating in non-coordinating solvents or by vacuum sublimation. Decarbonylation initially results in the formation of halide-bridged dimers and, ultimately, tetrameric technetium(I) complexes (Equation (7)). The facility of these reactions decreases in the order $\mathrm{Cl} > \mathrm{Br} > \mathrm{I}$.

$$\mathrm{TcX(CO)_5} \xrightarrow[-\mathrm{CO}]{\Delta} [\mathrm{TcX(CO)_4}]_2 \xrightarrow[-\mathrm{CO}]{\Delta} [\mathrm{TcX(CO)_3}]_4 \tag{7}$$

The edge-shared bioctahedral structure of $[\mathrm{TcI(CO)_4}]_2$ has been reported[35] (Figure 2), as have the cubane-type structures of $[\mathrm{TcCl(CO)_3}]_4$ (Figure 3) and $[\mathrm{TcI(CO)_3}]_4$.[36,37] Crystals of $[\mathrm{TcCl(CO)_3}]_4$ belong to the cubic system I$\bar{4}$3m, and the cluster has T_d-symmetry. A similar cubane structure was suggested (and later verified; see below) for the hydroxide derivative, $[\mathrm{Tc(OH)(CO)_3}]_4$,[38] which was first prepared by heating $\mathrm{KTcO_4}$ with an excess of formic acid in an autoclave. The bromo cubane cluster reacts with excess ethylenediamine (en) to provide *fac*-$[\mathrm{Tc(CO)_3Br(en)}]$, whose structure has been determined.[39] The Tc–Br distance is 2.640(1) Å and the Tc–N distances are 2.211(7) and 2.233(6) Å.

Treatment of $[\mathrm{TcO_4}]^-$ with $\mathrm{BH_3{\cdot}THF}$ in THF under CO provides the novel hydrido carbonyl cluster compound $\mathrm{Tc_3(CO)_{12}}(\mu\text{-H})_3$, whose structure is depicted in Figure 4.[40] The Tc–Tc separations in this cluster average 3.28 Å, while the Tc–H bond lengths average 1.84 Å. The cluster obeys the 18-electron rule.

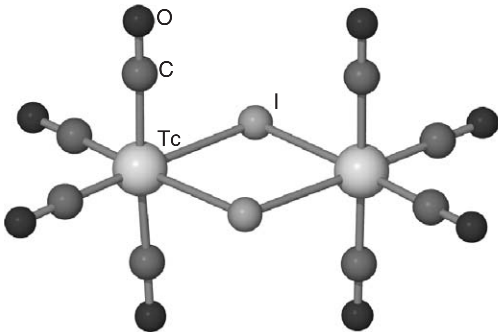


Figure 2 The (non-crystallographic) D_{2h} structure of $[\mathrm{TcI(CO)_4}]_2$. The average Tc–I distance is 2.815[2] Å, and the Tc–I–Tc angles average 95.8[2]°.

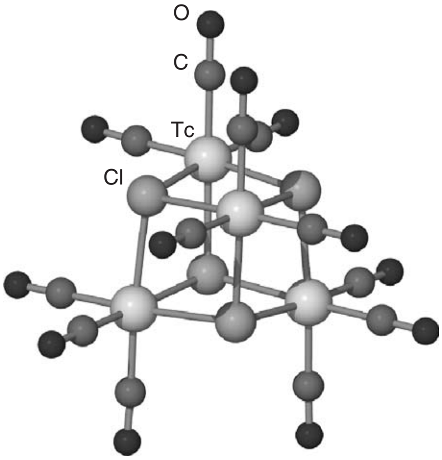


Figure 3 The cubane structure of $[TcCl(CO)_3]_4$. The Tc···Tc separation is 3.840(1) Å and the Tc–Cl distance is 2.559(1) Å. The Cl–Tc–Cl′ and Tc–Cl–Tc′ angles are 82.28(2)° and 97.23(2)°, respectively.

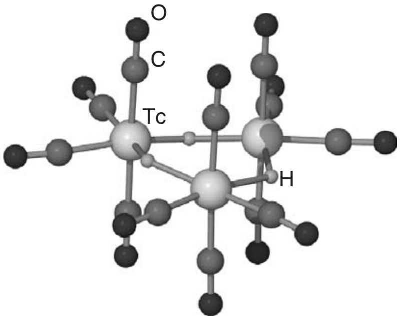


Figure 4 Triangular structure of $Tc_3(CO)_{12}(\mu\text{-}H)_3$. The Tc–Tc–Tc angles are very nearly 60°.

Curiously, the simple hydrido pentacarbonyl complex, $HTc(CO)_5$, is not readily isolated,[32,41] although the corresponding Mn and Re hydrido carbonyls are well known and reasonably stable.[42,42a] In retrospect, it is clear that $HTc(CO)_5$ is more prone to CO loss than its lighter and heavier congeners and oligomerizes in solution to $Tc_3(CO)_{12}(\mu\text{-}H)_3$ or, alternatively, $[HTc(CO)_4]_3$ (Equation (8)).[43]

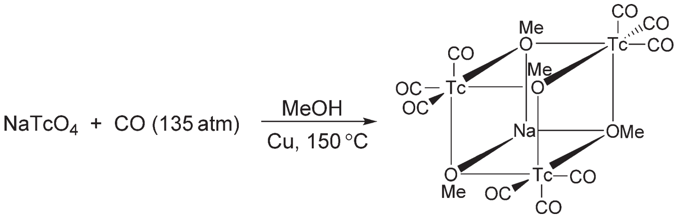
$$Na[Tc(CO)_5] + H^+ \longrightarrow HTc(CO)_5 \xrightarrow{-CO} [TcH(CO)_4]_3 \tag{8}$$

No further chemistry of $Tc_3(CO)_{12}(\mu\text{-}H)_3$ has been reported since 1996, but it is obviously an attractive starting material for further exploration of technetium(I) carbonyl cluster chemistry.

5.12.3 Other Technetium Carbonyl Derivatives

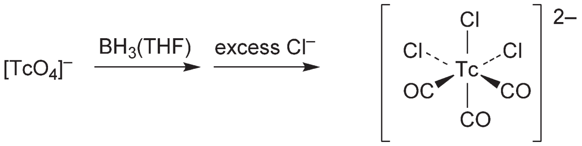
5.12.3.1 Oxygen and Sulfur

When sodium pertechnetate is carbonylated in methanol under conditions that are too mild (135 atm CO, 150 °C, 2 h) to produce $Tc_2(CO)_{10}$, a novel trinuclear technetium(I) carbonyl cluster, $Na[Tc_3(OMe)_4(CO)_9]$, is formed (Equation (9)).[26] Subsequent carbonylation of the cluster, under more forcing conditions (190 atm CO, 230 °C, 2 days), does provide $Tc_2(CO)_{10}$. The trinuclear Tc(I) cluster is a useful starting material for compounds containing the $Tc(CO)_3$ fragment, as it is easily broken up even by weak proton sources such as HC_5H_5 and HC_5Me_5 (see below).[26]

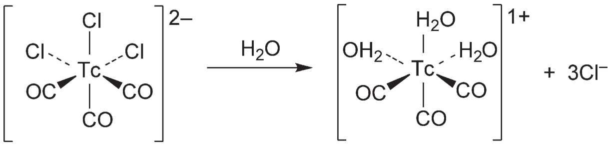


(9)

A remarkable series of tricarbonyl technetium(I) complexes has been prepared by Alberto and co-workers.[8] The key compounds are $[Tc(CO)_3X_3]^{2-}$ (X = Cl, Br) and $[Tc(CO)_3(H_2O)_3]^+$. Starting from $[NBu_4][TcO_4]$, a convenient synthesis of $(NEt_4)_2[MX_3(CO)_3]$ was developed and refined in the mid-1990s.[44–48] The reduction of pertechnetate is performed at slightly elevated temperatures in THF under 1 atm of carbon monoxide with $BH_3 \cdot THF$ as the reducing agent. Evaporation of the solvent followed by treatment of the residue with ethanolic Et_4NX gives the salts in good yield (Equation (10)). The exact reaction mechanism is unclear. It is a six-electron reduction (!) accompanied by the coordination of three CO ligands. One intermediate, dinuclear $[Tc_2Cl_3(CO)_6]^{1-}$, was detected, but it too is a Tc(I) complex.[47] The structure of $[Tc_2Cl_3(CO)_6]^{1-}$ is shown below (Figure 5). Substitution of $[Tc(CO)_3X_3]^{2-}$ with water rapidly yields $[Tc(CO)_3(H_2O)_3]^+$ and free halide (Equation (11)).



(10)



(11)

Aqueous solutions of the aquo-carbonyl cation are stable over most of the pH range. At very high pH, reversible, hydrolytic oligomerization takes place (Equation (12)).[49–50] The aquo complex $[Tc(CO)_3(H_2O)_3]^+$ can be prepared in a more direct and elegant fashion from pertechnetate using the compound boranocarbonate, $[H_3BCO_2H]^-$, which

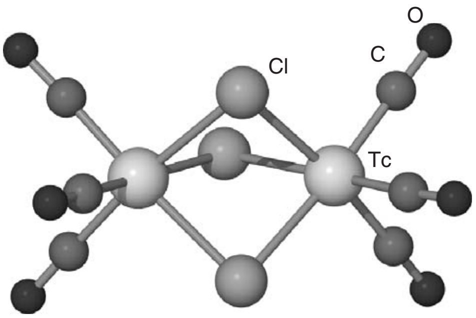
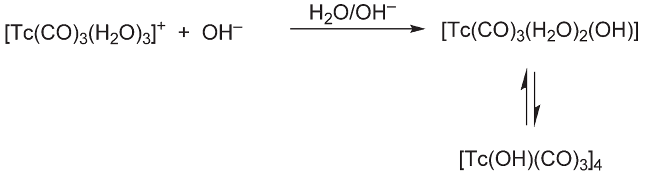
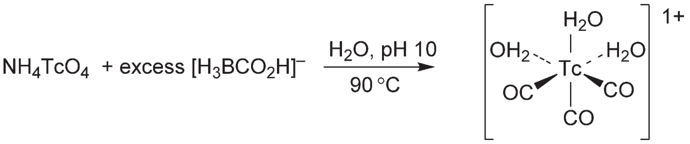


Figure 5 Structure of $[Tc_2Cl_3(CO)_6]^{1-}$. The Tc–Cl distances range from 2.50 to 2.56 Å. The Tc–Cl–Tc′ angles are in the order of 82°.

acts both as reducing agent and source of CO (Equation (13)).[51–52] The latter reaction is quite remarkable. The low concentrations of CO in solution would appear to exclude any stepwise mechanism of reduction followed by CO coordination to yield hypothetical $[Tc(CO)_6]^+$.



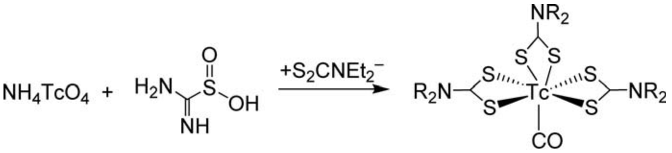
$$[Tc(CO)_3(H_2O)_3]^+ + OH^- \xrightarrow{H_2O/OH^-} [Tc(CO)_3(H_2O)_2(OH)] \rightleftharpoons [Tc(OH)(CO)_3]_4 \tag{12}$$



(13)

$[Tc(CO)_3(H_2O)_3]^+$ is a precursor to a wide variety of compounds containing the *fac*-$[Tc(CO)_3]^+$ moiety under ambient conditions. Substitutions are possible with monodentate, bidentate, and tridentate ligands. One of the first reactions reported was that with the protic ligand 2-mercaptoethanol $HSCH_2CH_2OH$. Two intermediates were observed via IR spectroscopic techniques. The final product was the dinuclear $(NEt_4)[Tc_2(\mu\text{-}SCH_2CH_2OH)_3(CO)_6]$, the structure of which was determined by X-ray diffraction.[47] The cyclic thio-crown ethers, tridentate 1,4,7-trithiacyclononane (9-ane-S_3), and hexadentate 1,4,7,10,13,16-hexathiacyclooctadecane (18-ane-S_6) react with $[Tc(CO)_3(H_2O)_3]^+$ in methanol to provide $[Tc(9\text{-ane-}S_3)(CO)_3]^+$ (Figure 6) and $[Tc_2(18\text{-ane-}S_6)(CO)_6]^{2+}$, both of which have been structurally characterized.[52]

A novel reaction in which the carbon monoxide source is not free CO was reported over 20 years ago by Baldas and co-workers.[53] Reduction of ammonium pertechnetate with formamidene–sulfinic acid in the presence of sodium diethyldithiocarbamate and aqueous base provides the seven-coordinate technetium(III) complex $[Tc(CO)(S_2CNEt_2)_3]$ (Equation (14)) in good yield. In the solid state, $[Tc(CO)(S_2CNEt_2)_3]$ adopts a distorted pentagonal-bipyramidal geometry. The authors suggest that the formation of CO and its binding to the technetium center are mediated at the metal center. Alberto has commented that the mechanistic picture proposed by Baldas is likely also valid for the formation of the *fac*-$[Tc(CO)_3]^+$ moiety.[19] Further studies of reaction (14) are clearly warranted.



(14)

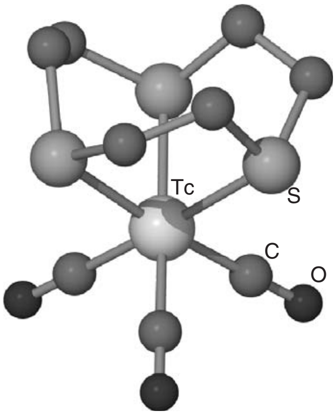
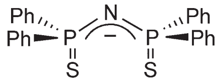


Figure 6 Structure of $[Tc(9\text{-ane-}S_3)(CO)_3]^+$. The Tc–S distances average 2.453[3] Å.

Technetium(I) dithiocarbamate carbonyl complexes can be prepared by metathesis of the halide ligands of $[TcBr(CO)_5]$ or $[TcCl(CO)_3(PPh_3)_2]$ and provide complexes of the type $[Tc(S_2CNR_2)(CO)_4]$ and $[Tc(S_2CNR_2)(CO)_2(PPh_3)_2]$.[23] Bis(diphenylthiophosphoryl)–amide **2** reacts with $(Et_4N)_2[Tc(CO)_3Cl_3]$ in acetonitrile to provide colorless crystals of the neutral complex *fac*-$\{Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$. The X-ray structure of this complex reveals Tc–S distances of 2.546(3) and 2.526(3) Å to *cis*-chelating **2** and 2.155(6) Å to the nitrogen atom of the coordinated acetonitrile ligand.[54]

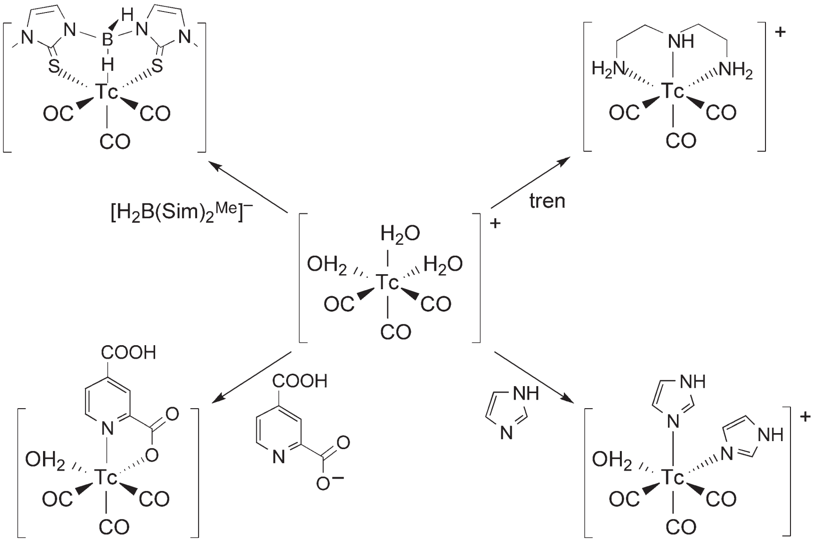


2

5.12.3.2 Nitrogen and Phosphorus

As noted above, $[Tc(CO)_3(H_2O)_3]^+$ can be substituted with a variety of Lewis bases. Because the complexes resulting from water substitution are kinetically stable, almost any type of σ-donor ligand forms coordination complexes with the *fac*-$[Tc(CO)_3]^+$ fragment. Some selected reactions with various monodentate, bidentate, and tridentate ligands are shown in Scheme 1. We have included the unusual dihydridobis(2-mercapto-1-methylimidazolyl)borate ligand, $[H_2B(Sim)_2Me]^-$, in Scheme 1. It acts as a tridentate ligand toward the $[Tc(CO)_3]^+$ fragment, and the product contains a B–H–Tc linkage. The X-ray structure of this complex has been determined and the Tc–S distances are on the order of 2.5 Å.[55] Most of the substitutions depicted in Scheme 1 are rapid in aqueous solution at or slightly above room temperature. When the reactions with monodentate ligands are performed in aqueous saline solution, it is often found that the reaction is fast for the first two incoming ligands and much slower for the third. This is because the excess chloride ion competes favorably for the sixth coordination site. These simple substitution reactions are key to recent developments in ^{99m}Tc radiopharmaceuticals, and the reader is encouraged to consult the excellent 2005 review by Alberto.[19]

Numerous mixed carbonyl-phosphine technetium(0) and technetium(I) complexes are known. The photolytic (hexane solution) or thermal (neat, 110 °C) substitution reactions of $Tc_2(CO)_{10}$ with PF_3 have been studied (Equation (15)). Twenty four different isomers of the type $Tc_2(CO)_{10-x}(PF_3)_x$, where $x = 1$–8 were observed by GC-MS or GC-IR spectroscopy.[56] Under thermal conditions, substitution at the axial sites is preferred. Substitution of both axial and equatorial sites occurs during photolysis. The authors note that the rates of the technetium-substitution reactions are faster than those of either manganese or rhenium. The homoleptic trifluorophosphine complex, $Tc_2(PF_3)_{10}$, is also known.[56a] It is prepared by condensing technetium metal vapor with PF_3 at 77 K. An axially substituted bis-triphenylphosphine derivative,



Scheme 1

[$Tc_2(CO)_8(PPh_3)_2$], has also been reported from the reaction of $Tc_2(CO)_{10}$ with PPh_3 in decalin at 100–150 °C.[57] The intermediate monosubstituted phosphine complex, [$Tc_2(CO)_9(PPh_3)$], can be detected by infrared spectroscopy.

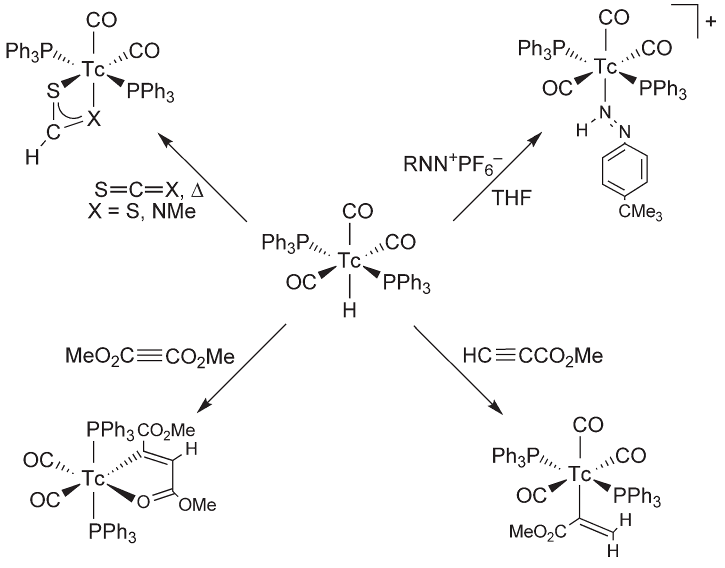
$$Tc_2(CO)_{10} + \text{excess } PF_3 \longrightarrow Tc_2(CO)_{10-x}(PF_3)_x \ (x = 1\text{–}8) \tag{15}$$

Amongst the suite of known technetium(I) carbonyl-phosphine complexes, *mer*-$TcCl(CO)_3(PPh_3)_2$, *trans*-$HTc(CO)(dppe)_2$ and *mer*-$TcH(CO)_3(PPh_3)_2$ are representative examples. The first compound is prepared in essentially quantitative yield from $(Bu_4N)TcOCl_4$ and PPh_3 in refluxing toluene/acetonitrile under one atmosphere of carbon monoxide (Equation (16)).[58] The starting material $(Bu_4N)TcOCl_4$ is easily synthesized by stirring $(Bu_4N)TcO_4$ in concentrated aqueous hydrochloric acid in air.[59] The first hydride complex *trans*-$HTc(CO)(dppe)_2$ was synthesized from the corresponding dinitrogen derivative, $HTc(N_2)(dppe)_2$, and CO in benzene solution.[60] The dinitrogen compound can be prepared in good yield from [$TcCl_4(PPh_3)_2$], dppe, and sodium amalgam in THF under N_2.[61] The use of $TcCl_4(PR_3)_2$ (R = alkyl, aryl) complexes as starting materials for technetium organometallic chemistry merits further study. These materials are easy to prepare and are soluble in organic media.[18] They might, for example, offer a route to alkyl or alkylidene complexes.

$$[TcOCl_4]^- + 2PPh_3 \xrightarrow[\text{CO, 110 °C}]{PhCH_3/CH_3CN} TcCl(CO)_3(PPh_3)_2 \tag{16}$$

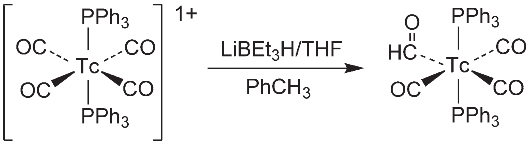
The bis-triphenyl phosphine derivative of $HTc(CO)_5$, viz, $HTc(CO)_3(PPh_3)_2$, is prepared in good yield, not from the hydrido carbonyl, but rather from $H_3Tc(PPh_3)_4$ and CO in benzene.[62] The yellow trihydride is synthesized in quantitative yield from $TcCl_4(PPh_3)_2$, excess phosphine, and sodium borohydride in ethanol.[62] The insertion chemistry of $TcH(CO)_3(PPh_3)_2$ has been studied in some detail.[63] It reacts with a variety of unsaturated substrates, including heterocumulenes, electron-deficient acetylenes, and diazonium salts (Scheme 2).

$TcH(CO)_3(PPh_3)_2$ is a precursor to white *trans*-[$Tc(CO)_4(PPh_3)_2$]BF_4. Stirring the monohydride in benzene under CO, followed by treatment with HBF_4/ether, gives the cationic carbonyl phosphine complex in good yield.[62] The latter is susceptible to nucleophilic attack.[64] It reacts with lithium triethylborohydride in toluene to afford the yellow Tc(I) formyl complex [$Tc(CO)_3(C(O)H)(PPh_3)_2$] in good yield (Equation (17)). The latter complex is unstable in solution and slowly decomposes to $TcH(CO)_3(PPh_3)_2$. Reaction of the formyl complex with 1 equiv. of methyl triflate in toluene produces the Fischer carbene complex [$Tc(CO)_3({=}C(OMe)H)$-$(PPh_3)_2$]SO_3CF_3 in ca. 40% isolated yield.[64] Technetium complexes containing technetium carbon double bonds are quite rare and limited to the vinylidene complexes, $Tc({=}C{=}CCHR)Cl(dppe)_2$ (R = Me, ^{t}Bu, Ph)[65] and $(C_5Me_5)Tc(CO)_2({=}C(OEt)Ph)$[66] (see below). Aqueous sodium hydroxide reacts with *trans*-[$Tc(CO)_4(PPh_3)_2$]$^+$ in



Scheme 2

acetonitrile to give the neutral hydroxy–carbonyl complex $Tc(CO)_3(C(O)OH)(PPh_3)_2$. If this reaction is carried out in the presence of methanol or ethanol, the corresponding alkoxycarbonyl complexes $Tc(CO)_3(C(O)OR)(PPh_3)_2$ (R = Me, Et) are obtained. Finally, the treatment of *trans*-$[Tc(CO)_4(PPh_3)_2]^+$ with NaN_3 in methanol provides the isocyanate complex $Tc(CO)_3(NCO)(PPh_3)_2$. The latter reaction is believed to occur via an acyl–azide intermediate, which quickly loses N_2.[64]



(17)

5.12.4 Technetium Isocyanides and Their Derivatives

5.12.4.1 Binary Technetium Isocyanides

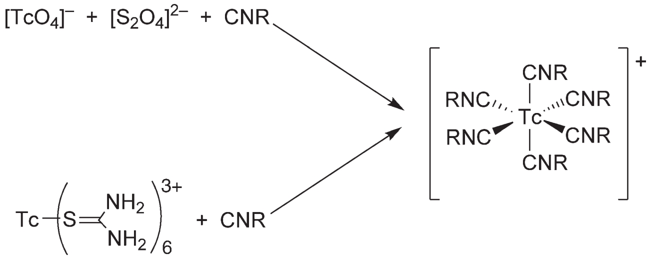
As mentioned in Section X.1, the surge of work in organotechnetium chemistry is due, at least in part, to the discovery that hexakis(isocyanide)technetium(I) compounds are excellent heart-imaging agents.[6] Much of the work published on these systems appears in nuclear medicine journals, and is not covered by the present review.[12,19]

The first time a hexakis(isocyanide)technetium(I) compound was mentioned was in a review article by Jones and Davison.[67] Two major synthetic routes to $[Tc(CNR)_6]^+$ have since been published for a wide variety of R groups, as illustrated in Scheme 3: (i) dithionate reduction of pertechnetate in the presence of isocyanide[68–69] and (ii) reductive substitution of the hexakis(thiourea)technetium(III) cation by isocyanides.[69–70] A minor and more involved variation on the first route involves bulk electrolysis of $[TcO_4]^-$ in the presence of acetate or formate.[71] The resulting "technetium–carboxylate" complex is then reacted with isocyanide to form the hexakis (isocyanide) cation. In the case of the dithionite reduction, it is quite remarkable that a low-valent organometallic compound is the thermodynamic product and, in addition, that it is stable over such a wide pH and temperature range.

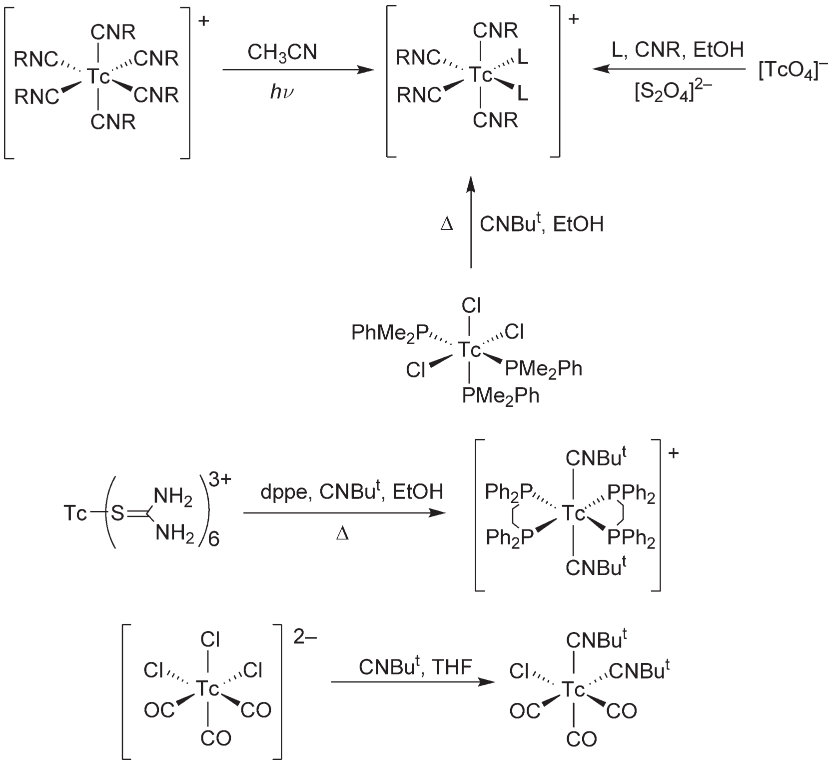
The hexakis(isocyanide)technetium(I) cations are inert toward substitution by other isocyanides. Reaction of the hexakis(thiourea) derivative with mixtures of isocyanides results in statistical distribution of the isocyanides on the metal center.[72]

5.12.4.2 Technetium Isocyanide Derivatives

Attempts to substitute neutral phosphine or nitrogen donor ligands into $[Tc(CNR)_6]^+$ generally result in poor product yields. The "best" routes involve reduction of pertechnetate salts in the presence of the appropriate ligand mixture or substitution of the hexakis(thiourea) technetium(III) complex mentioned above. Even then, yields range from 10% to 25%, and separation from other products (often the homoleptic cation) is difficult. Despite these problems, complexes of the type $[Tc(CNR)_4L_2]^+$ (L = PPh_3, 1/2 dppe, or 1/2 bidentate aromatic amine such as bipy, phen, or their derivatives) and $[Tc(CNBu^t)_5(PPh_3)]^+$ have been isolated (Scheme 4).[73–75] The X-ray crystal structure of $[Tc(bipy)(CNBu^t)_4]^+$ reveals a bent isocyanide ligand (∠C–N–C = 148°) with a shortened Tc–C bond length of 1.90(2) Å.



Scheme 3



Scheme 4

Additionally, spectroscopic data suggest that this compound may have undergone "internal oxidation", resulting in the formation of a technetium(III) carbene.[73]

The structure of *trans*-$[Tc(CNBu^t)_2(dppe)_2]^+$ has also been reported.[74] The complex is prepared from the hexakis(thiourea) technetium(III) complex and the two ligands in refluxing ethanol (Scheme 4). Here, the Tc–C bond distance is 2.03 Å, identical to the value found in $[Tc(CNBu^t)_6]^+$.[76] The Tc–C–N angle at 178.0(5)° is essentially linear, in contrast to the bent coordination found in the aforementioned mixed-ligand complex, $[Tc(bipy)(CNBu^t)_4]^+$. *trans*-$[Tc(CNR)_2(dppe)_2]^+$ undergoes a reversible one-electron oxidation at 0.91 V versus SCE, but the technetium(II) product was not isolated.

Another strategy for the synthesis of mixed phosphine–isocyanide complexes has been advanced by Rochon and co-workers.[77] Refluxing a mixture of *mer*-$TcCl_3(PMe_2Ph)_3$[78] and excess *t*-butyl isocyanide in ethanol, followed by metathesis with NH_4PF_6, provides an ~50% yield of *trans*-$[Tc(PMe_2Ph)_2(CNBu^t)_4]PF_6$ (Scheme 4). The structure of the latter complex has been determined. The Tc–C and Tc–P distances are 2.03 and 2.40 Å, respectively, and the Tc–C–N angles are 175°.[77]

The reaction of $[Et_4N][TcCl_3(CO)_3]$ with excess ${}^tBuNC$ in THF at room temperature provides *fac*-$[TcCl(CNBu^t)_2(CO)_3]$ (Scheme 4).[46] If $[Et_4N][TcCl_3(CO)_3]$ is treated with silver nitrate in water to remove chloride ion and then treated with a solution of ${}^tBuNC$ in ethanol, the trisubstituted cation *fac*-$[Tc(CNBu^t)_3(CO)_3]^+$ is isolated as the nitrate salt.[48] The X-ray structures of pseudo-octahedral $[TcCl(CNBu^t)_2(CO)_3]$ and $[Tc(CNBu^t)_3(CO)_3]$ have been determined, and are quite similar. In the former complex, the Tc–C (isocyanide) distances average 2.10 Å and the Tc–C–N angles are 174.2(5)°. In $[Tc(CNBu^t)_3(CO)_3]$, the Tc–C (isocyanide) bond lengths also average 2.10 Å and the Tc–C–N angles average 174(2)°.

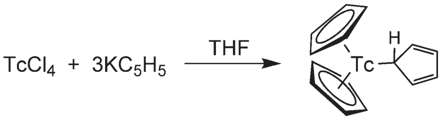
Davison and co-workers have prepared two examples of nitrosyl isocyanide complexes. Refluxing a mixture of $(Bu_4N)[Tc(NO)Cl_4]$ with triphenylphosphine in acetonitrile gives the yellow-orange complex $[Tc(NO)Cl_2(PPh_3)_2(NCMe)]$ in reasonable yield (~70%). The acetonitrile ligand is labile and can be replaced with either CO or ${}^tBuNC$.[79] If the nitrile adduct is refluxed with excess isonitrile in methylene chloride, it is possible to isolate the bis-complex, $[Tc(NO)Cl_2(PPh_3)(CNBu^t)_2]$. In refluxing benzene, it is possible to substitute the coordinated acetonitrile and both phosphine ligands, and isolate *mer,cis*-$[Tc(NO)Cl_2(CNBu^t)_3]$.[79]

5.12.5 Technetium Cyclopentadienyl and Other π-Complexes

5.12.5.1 Cyclopentadienyl Complexes

Although the first cyclopentadienyl complexes of technetium, namely $(\eta^5\text{-}C_5H_5)Tc(CO)_3$ and $(\eta^5\text{-}C_5H_5)_2TcH$, were prepared in the 1960s,[80–82] it was not until the 1980s that the area gained momentum. As an aside, we note that the vapor pressure of the unsubstituted cyclopentadienyl compound $(\eta^5\text{-}C_5H_5)Tc(CO)_3$ at room temperature was determined to be about 1 Pa.[83] Researchers investigating $(\eta^5\text{-}C_5H_5)Tc(CO)_3$ and related compounds should take note and exercise due caution!

Anhydrous technetium tetrachloride reacts with KC_5H_5 in THF to form the red-brown bent-sandwich complex $(\eta^5\text{-}C_5H_5)_2TcCl$ or Cp_2TcCl. With an excess of KC_5H_5, the dark red tris(cyclopentadienyl) complex $Cp_2Tc(\eta^1\text{-}C_5H_5)$ is formed (Equation (18)). The dimeric complex, Cp_4Tc_2, is produced by reduction of the chloride with potassium naphthalide, or by thermolysis of the tris-Cp complex, which also produces the golden yellow hydride Cp_2TcH as a side-product.[84] The structure of Cp_4Tc_2 has not been reported but would be of considerable interest. The hydride complex Cp_2TcH can be prepared directly from the Cp_2TcCl and sodium borohydride in THF.[82] The X-ray structure of Cp_2TcCl is shown below (Figure 7). The Tc–Cp ring centroid distance is 1.87 Å and the Tc–Cl distance is 2.450(3) Å. The Cp–Tc–Cp′ centroid angle is 143.8°.[84] Red-brown $Cp_2Tc(\eta^1\text{-}C_5H_5)$ has also been structurally characterized.[85] The Tc–C_σ distance is 2.30(1) Å. There are no reports of analogs to Cp_2TcCl with substituted cyclopentadienide ligands, and alkyl complexes of the type Cp_2TcR are unknown.



(18)

Numerous substituted η^5-cyclopentadienyl and one η^5-indenyl technetium carbonyl complexes have been reported.[26–27,48,86–89] A key compound is $[(C_5Me_5)Tc(CO)_3]$. It can be prepared by several different routes (Scheme 5). Two of these require the preparation of $Tc_2(CO)_{10}$, which, as we noted earlier, is problematic. A clever route that avoids the synthesis of $Tc_2(CO)_{10}$ was developed by Alberto and co-workers and starts with the hydroxy cubane cluster $[Tc(\mu_3\text{-}OH)(CO)_3]_4$,[48] which, in turn, is easily prepared from $[Tc(CO)_3(H_2O)_3]^+$ and aqueous base (see above). The cluster reacts with neat C_5Me_5H at 150 °C to give the desired compound in quantitative yield. The structure of $[(C_5Me_5)Tc(CO)_3]$ has been determined (Figure 8).[86] It is a familiar three-legged piano stool, and the Tc–CO distances average 1.91 Å. Two closely related complexes, $[(C_5Me_4Et)Tc(CO)_3]$ and $[(C_9H_7)Tc(CO)_3]$, have also been prepared and structurally characterized.[86] A ball and stick drawing of indenyl complex is shown below (Figure 9).

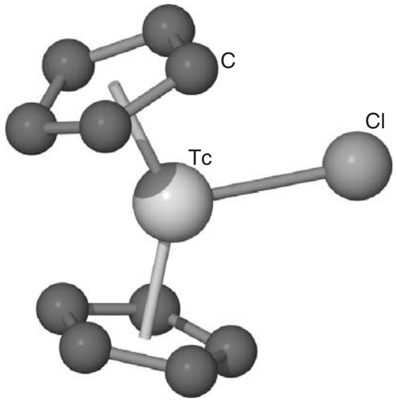
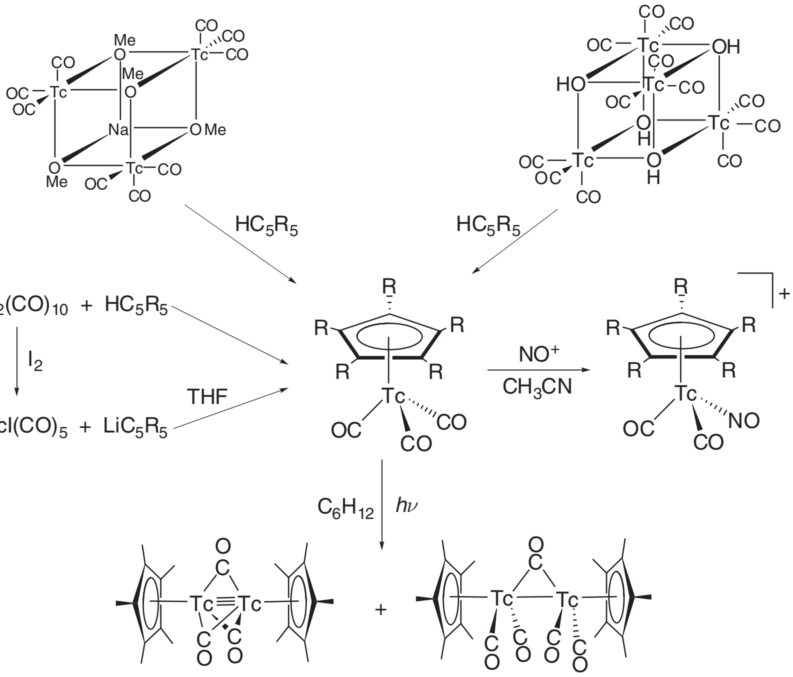


Figure 7 Structure of $(C_5H_5)_2TcCl$.



Scheme 5

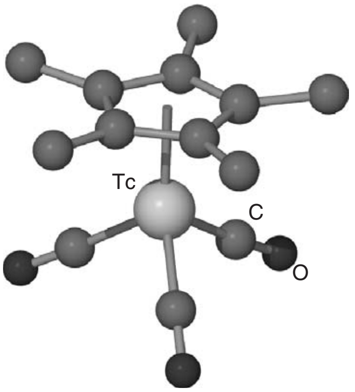


Figure 8 Structure of [$(C_5Me_5)Tc(CO)_3$]. The distance from the metal to the carbons of the C_5Me_5 ring is 2.292(6) Å, and to the ring centroid it is 1.944(6) Å. The Tc–C distance to the carbonyl carbons is 1.907(6) Å.

Under UV irradiation, compound [$(C_5Me_5)Tc(CO)_3$] loses CO in cyclohexane solution. In the presence of triphenylphosphine, $(C_5Me_5)Tc(CO)_2(PPh_3)$ is formed. Its X-ray structure has also been determined; the Tc–P distance is 2.34(1) Å.[89] In the absence of donor ligands, two interesting dinuclear compounds are formed that can be separated by column chromatography (Scheme 5). The deep red triply CO-bridged compound, [$(C_5Me_5)Tc(\mu\text{-}CO)_3Tc(C_5Me_5)$] contains a metal–metal triple bond (2.413(3) Å).[87] The structure of yellow [$(C_5Me_5)(CO)_2Tc(\mu\text{-}CO)Tc(CO)_2(C_5Me_5)$] (Figure 10) is inferred from spectroscopic data and analogy to the known rhenium analog.

[$(C_5Me_5)Tc(CO)_3$] reacts with NO[PF_6] in acetonitrile to provide the nitrosyl complex [$(C_5Me_5)Tc(CO)_2(NO)$](PF_6) in high yield.[27] This was the first example of a dicarbonyl–nitrosyl complex. Other examples of complexes containing the $[Tc(CO)_2(NO)]^{2+}$ core were reported over a decade later.[90–93] $[Tc(CO)_3X_3]^{2-}$ (X = Cl, Br) or $[Tc(CO)_3(H_2O)_3]^{+}$ will react with a number of nitrosylating agents such as

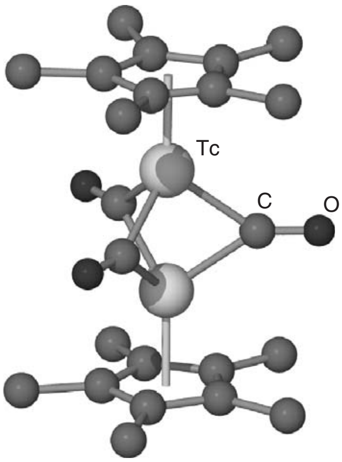


Figure 9 Structure of $[(C_9H_7)Tc(CO)_3]$. The distances to the C_5 ring of the indenyl ligand range from 2.27 to 2.35 Å.

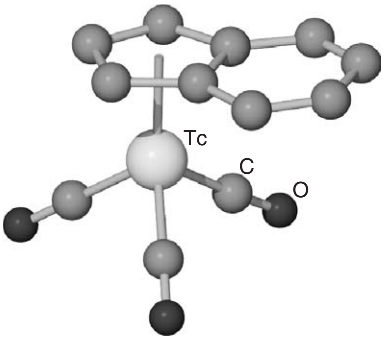
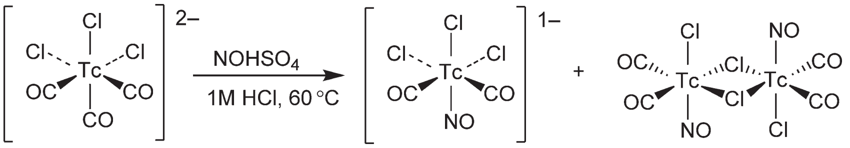


Figure 10 Structure of triply M–M-bonded $[(C_5Me_5)Tc(\mu\text{-}CO)_3Tc(C_5Me_5)]$. The metal to bridging carbonyl distance is 2.09(1) Å.

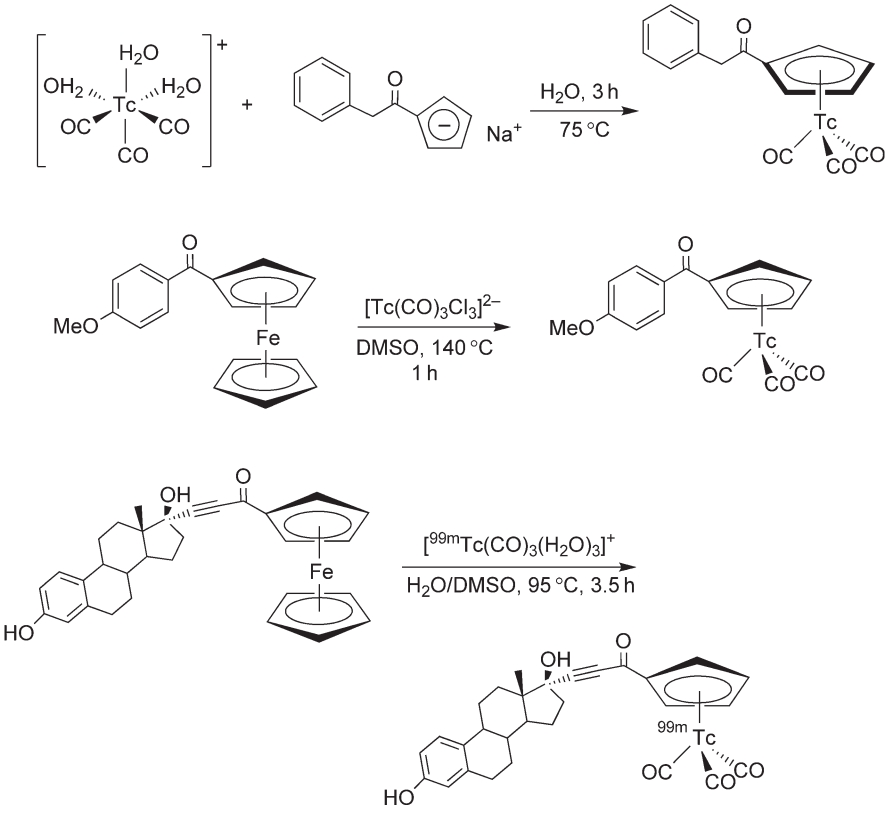
$NO[HSO_4]$, $NaNO_2$, or $NO[BF_4]$ to form complexes of the type $[TcX_3(CO)_2(NO)]^-$ and $[TcCl(CO)_2(NO)]_2$-$(\mu\text{-}Cl)_2$ (Equation (19)).[93] The halogen ligands in the monomers can be substituted with various monodentate, bidentate, and tridentate Lewis bases, and the $[^{99m}Tc(CO)_2(NO)]^{2+}$ core would appear to have a promising future in nuclear medicine applications.[19]



(19)

Cyclopentadienyl complexes of the type $[(RCOCp)Tc(CO)_3]$ can be prepared in aqueous solution from $[Tc(CO)_3(H_2O)_3]^+$ and sodium benzoylCp or sodium phenylacetylCp (Scheme 6). The presence of electron-withdrawing substituents allows the Cp ring to be deprotonated to a reasonable extent at physiological pH values.[94,95] The impact of this work is significant and lies in the possibility of linking the small, robust, highly lipophilic $[RCOCp^{99m}Tc(CO)_3]$ unit onto a wide variety of small receptor-binding biomolecules. The structure of the pale yellow phenyl acetyl derivative has been determined. The average Tc–Cp carbon bond lengths are 2.30 Å and the Tc–CO carbon bond lengths are 1.14 Å.

An aqueous alternative to derivatized sodium Cp salts is provided by ketoferrocene-transfer reagents.[96] The *para*-methoxy phenyl acetyl derivative shown in Scheme 6 is a model for the type of linker that could be tethered to

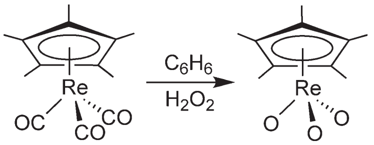


Scheme 6

ethynylestradiols. Technetium-99 radio-labeled estrogen derivatives are candidates for the imaging of breast tumors. In fact, a novel 17α-ethynyl estradiol derivate labeled with ^{99m}Tc has been synthesized (Scheme 6).[96]

Two interesting Tc(III) carbonyl complexes are formed by the oxidation of $[(C_5Me_5)Tc(CO)_3]$ with elemental bromine.[27,48] The products of this reaction are solvent dependent. In trifluoroacetic acid, neutral $[(C_5Me_5)Tc(CO)_2Br_2]$ is formed as a mixture of *cis*- and *trans*-isomers.[27] If the oxidation reaction is performed in methylene chloride, the product is the complex salt $[(C_5Me_5)Tc(CO)_3Br][(CO)_3Tc(\mu\text{-}Br)_3Tc(CO)_3]$ containing a Tc(III) cation and a binuclear Tc(I) anion.[48] At this point in the development of technetium organometallic chemistry, Tc(III) is the highest-known oxidation state capable of binding CO.

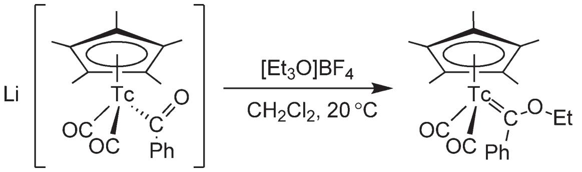
The oxidation of $[(C_5Me_5)Re(CO)_3]$ with hydrogen peroxide provides a facile route to novel and catalytically active rhenium(VII) oxo compound $[(C_5Me_5)ReO_3]$ (Equation (20)).



(20)

Several attempts have been made to synthesize the trioxo technetium analog from $[(C_5Me_5)Tc(CO)_3]$.[28,48,97] In one case, an intriguing polynuclear compound of formula $[(C_5Me_5)Tc_2O_3]_n$ was claimed.[97] Its supershort Tc–Tc bond length of 1.867(4) Å created some controversy in the metal–metal bonding community. Subsequent work by Cotton and co-workers suggests that the purported $[(C_5Me_5)Tc_2O_3]_n$ is most likely $[(C_5Me_5)ReO_3]$, whose complicated and disordered structure was misinterpreted as that of $[(C_5Me_5)TcO_3]_n$.[98] $[(C_5Me_5)TcO_3]$ remains an elusive target.[48] An *ab initio* SCF study predicts that it and other "$[RTcO_3]$" complexes should be stable, although the M–Cp π-bonding is predicted to be relatively weak.[99] The closest analog of $[(C_5Me_5)TcO_3]$ is the imido compound $[Tc(NAr)_3(\eta^1\text{-}C_5H_5)]$ (Ar = 2,6 diisopropylphenyl).[100] As indicated, this compound prefers a σ-bonded cyclopentadienyl ring.

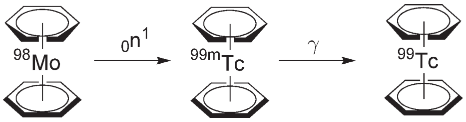
Aside from the photochemical carbonyl-substitution chemistry of $[(C_5Me_5)Tc(CO)_3]$ mentioned earlier, there is a report on the conversion of this complex to a Fischer carbene.[66] Addition of phenyl lithium to an ether solution of $[(C_5Me_5)Tc(CO)_3]$ provides the acyl derivative $Li[(C_5Me_5)(CO)_2TcC(O)Ph]\cdot Et_2O$. The latter reacts readily with triethyloxonium tetrafluoroborate to afford the neutral carbene complex, $[(C_5Me_5)(CO)_2Tc{=}C(OEt)Ph]$ (Equation (21)). The Tc=C distance in the latter compound is 1.977(1) Å, which is considerably longer than the Tc=C distance of 1.861(9) Å in the only other structurally characterized carbene complex $[Tc({=}C{=}CHPh)\text{-}Cl(dppe)_2]$.[65] The most striking feature of $[(C_5Me_5)(CO)_2Tc{=}C(OEt)Ph]$ is the nearly perpendicular orientation of the carbene ligand relative to the C_5Me_5 ring.



(21)

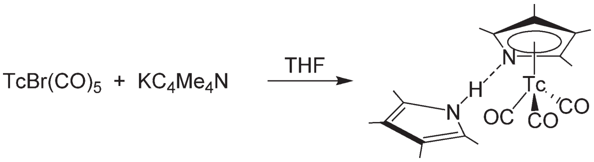
5.12.5.2 Arene and Other π-complexes

The first technetium arene complex, $[Tc(\eta^6\text{-}C_6H_6)_2]^+$, was prepared by irradiating $[Mo(\eta^6\text{-}C_6H_6)_2]$ with thermal neutrons.[101] The ^{98}Mo (24.13% abundance) in the sample of $[Mo(\eta^6\text{-}C_6H_6)_2]$ is converted into ^{99}Mo, which subsequently decomposes to ^{99}Tc via ^{99m}Tc, and generates the technetium cation (Equation (22)). The complex was characterized using radiochemistry techniques. Yellow-green $[Tc(\eta^6\text{-}C_6H_6)_2]^+$ can also be prepared by the more familiar reducing Friedel–Crafts technique, that is, reduction of $TcCl_4$ with aluminum powder in benzene/$AlCl_3$.[102] More recently, Wester and co-workers have shown that the reduction of sodium pertechnetate with Zn/HCl or Al/$AlCl_3$/ultrasound in the presence of a wide variety of arenes in cyclohexane provides the $[Tc(\eta^6\text{-arene})_2]^+$ cations in high yield.[103] Reaction of the cubane cluster $[Tc_3(OMe)_4(CO)_9]^-$ with HCl and benzene yields the arene tricarbonyl complex, $[Tc(CO)_3(\eta^6\text{-}C_6H_6)]^+$, as the chloride salt.[26]



(22)

A heterocyclic half-sandwich complex of tetramethylazacyclopentadiene, viz, $[(C_4Me_4N)Tc(CO)_3]\cdot C_4Me_4NH$ was prepared via the reaction of KC_4Me_4N with $BrTc(CO)_5$ in THF (Equation (23)). The tetramethylpyrrolyl ring is η^5-coordinated to the Tc(I) center, and a free tetramethylpyrrole is hydrogen bonded to nitrogen atom of the coordinated ring.[104]



(23)

Valliant and co-workers investigated the feasibility of using *nido*-7,8-$(C_2B_9H_{11})^{2-}$, isolobal to $[C_5H_5]^-$, as an η<ρχ>^{5}-ligand for Re(I) and Tc(I).[105] The dicarbollide dianion reacts readily with $[Tc(CO)_3Br_3]^{-1}$ to give beige

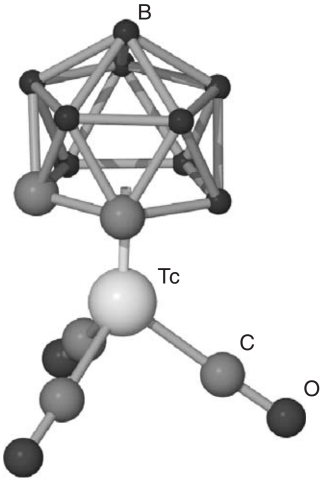
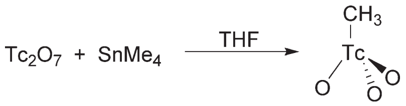


Figure 11 Structure of $[Tc(CO)_3(C_2B_9H_{11})]^{-1}$ in the tetraethylammonium salt.

$[Tc(CO)_3(C_2B_9H_{11})]^{-1}$, which can be isolated as its tetraethylammonium salt. The X-ray structure of dicarbollide complex, the first reported structure of a Tc carborane complex, is shown in Figure 11. It is nearly isostructural with its rhenium analog,[106] and the average distance from the Tc center to an atom of the bonding face of the carborane is 2.32 Å.

5.12.6 Derivatives Containing Single- or Multiple-Bonded η^1-Carbon Groups

Remarkably, the first well-characterized examples of technetium alkyl complexes were reported as late as 1990 by Herrmann and co-workers.[88,107] Technetium heptoxide, Tc_2O_7, reacts with tetramethyltin at 0 °C to form colorless $MeTcO_3$ (Equation (24)). Exceptional care must be exercised in preparing and handling this tetrahedral monomer, as it is extremely volatile (it sublimes at room temperature and atmospheric pressure). If the reaction is carried out at or above room temperature, mixtures of the colorless stannylester $[TcO_3(OSnMe_3)]$ and a remarkable orange paramagnetic technetium(VI) dimer $[Tc(O)Me_2]_2(\mu\text{-}O)_2$ are formed (Figure 12). $MeTcO_3$ will catalytically oxidize alkenes to *cis*-diols in the presence of hydrogen peroxide. Regrettably, no further chemistry of these complexes has been reported in the past 15 years. We have wondered whether the Tc(VI) dimer might provide a route to the elusive technetium(VI) trioxide, TcO_3,[22] via controlled hydrolysis of two of its methyl groups followed by α-elimination of methane (Equation (25)).



(24)

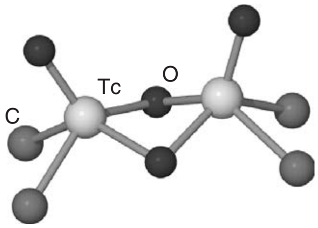
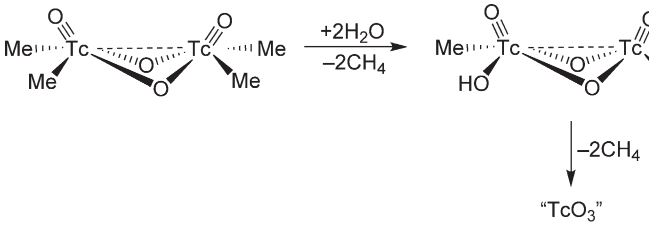
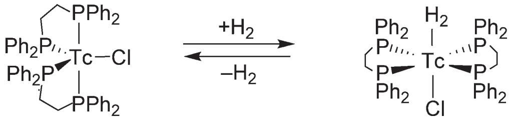


Figure 12 Structure of $[TcOMe_2]_2(\mu\text{-}O)_2$. The terminal Tc–O distances are 1.65 Å (Tc≡O?), the bridging Tc–O distances are 1.90 Å, and the Tc–Me distances are 2.13 Å.



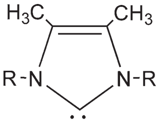
(25)

Compounds containing technetium–carbon multiple bonds are exceedingly rare. Several Fischer carbene complexes have already been mentioned. The green 16-electron technetium(I) bis(diphenylphosphino)ethane complex, [TcCl(dppe)$_2$], reacts with terminal acetylenes to form the neutral orange vinylidene complexes, *trans*-[Tc(=C=CHR)Cl(dppe)$_2$] (R = Me, ^{t}Bu, Ph). Protonation of the β-carbon of the vinylidene yields the colorless carbyne cations [Tc(≡CCH$_2$R)Cl(dppe)$_2$]$^+$. (R = ^{t}Bu, Ph).[65] The ^{t}Bu derivative was isolated as the tetraphenylborate salt and characterized by X-ray crystallography. The Tc≡C distance is 1.724(7) Å. The only other technetium carbyne complex that we are aware of is [(C$_5$Me$_5$)(CO)$_2$Tc≡CPh]BCl$_4$, prepared by the action of BCl$_3$ on [(C$_5$Me$_5$)(CO)$_2$Tc=C(OEt)Ph] at −20 °C in pentane.[66] It has not been structurally characterized. There is another important compound derived from the green 16-electron complex [TcCl(dppe)$_2$]. Treatment of the latter with hydrogen results in an instant color change to the yellow color of [Tc(η^2-H$_2$)Cl(dppe)$_2$]. This is the first and still the only molecular hydrogen complex of technetium. The reaction is completely reversible (Equation (26)).[108]



(26)

N-heterocyclic carbenes of the type shown below **3** react with either [TcOCl$_4$]$^-$ or [TcNCl$_2$(PMe$_2$Ph)$_3$] in THF to provide the technetium(V) cations [TcO$_2$(L$^{i\text{-Pr}}$)$_4$]$^+$ and [TcN(L$^{\text{Et}}$)$_4$]$^{2+}$, which are isolated as the pertechnetate and chloride salts, respectively.[109–110] The Tc–C distances are considerably longer than those found in either the Fischer carbene or vinylidene complexes mentioned earlier and are in the 2.2 Å range.



3

The paucity of technetium carbene and carbyne complexes is surprising given the large number of rhenium complexes containing these functional groups.[111] There is every reason to believe that analogs of the rhenium complexes can be prepared. The challenge is for someone to go in the lab and make them.

5.12.7 Structural Data and ^{99}Tc NMR Studies

5.12.7.1 Structural Data

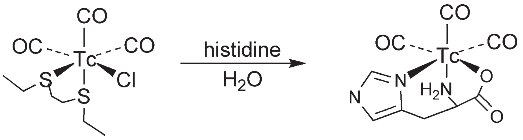
There are two excellent reviews of technetium X-ray crystal structures covering the periods from 1993 to 1999[112] (196 structures) and from 2000 to 2004 (80 structures).[113] The reviews cover both coordination and organometallic compounds, and include some 28 complexes containing the *fac*-[Tc(CO)$_3$]$^+$ moiety.

Technetium–alkyl, technetium–carbene, and technetium–carbyne bond lengths are presented individually in Table 1. They represent a significant class of organotechnetium structures. The Tc–C$_{\text{alkyl}}$ single bond lengths listed in Table 1 agree reasonably well with the range of 2.00–2.13 Å predicted by *ab initio* SCF calculations before any of these compounds were prepared.[114] The technetium–carbon multiple bonds listed in Table 1 are significantly shorter than the technetium–carbon single bonds.

Table 1 Technetium–carbon bond lengths (Å) for selected alkyl, carbene, and carbyne complexes

Formula	*Tc–C*	*Tc=C*	*Tc≡C*	*References*
$[\mathrm{TcOMe_2}]_2(\mu\text{-O})_2$	2.133(2), 2.129(3) 2.128(3), 2.086(3)			107
$[\mathrm{Tc(NAr)_3Me}]$	2.136(17)			115
$[\mathrm{Tc(NAr)Me_2}]_2(\mu\text{-NAr})_2$	2.134(2), 2.149(2), 2.153(2), 2.159(2)			116
$[\mathrm{Tc(bipy)(CNBu^t)_4}]^+$		1.90(2)		73
$[\mathrm{Tc({=}C{=}CHPh)Cl(dppe)_2}]$		1.861(9)		65
$[\mathrm{(C_5Me_5)(CO)_2Tc{=}C(OEt)Ph}]$		1.977(1)		66
$[\mathrm{Tc({\equiv}CH_2Bu^t)Cl(dppe)_2}]^+$			1.724(7)	65

Extended X-ray absorption fine structure spectroscopy (EXAFS) has been used in a few instances to characterize technetium organometallic complexes in solution. One of the first studies was carried out by Edelstein, and co-workers on $Tc_2(CO)_{10}$.[117] A satisfactory fit of the experimental spectrum was possible only with theoretically determined phase and amplitude functions for multiple scattering along the Tc–C–O vector. The structural parameters were in reasonable agreement with the single crystal X-ray data.[30] More recently, Seifert and co-workers have used EXAFS to determine the structure of thioether complexes such as $[Tc(CO)_3Cl(S\text{–}S)]$ (S–S = bidentate dithioether) and $[Tc(CO)_3(S\text{–}S\text{–}O)]$ (S–S–O = tridentate carboxylato dithioether) in aqueous solution and investigate their reactivity toward histidine (His).[118–119] These reactions provide $[Tc(CO)_3(His)]$ (Equation (27)). Structural parameters for the various complexes are reported. The Tc–S distances are on the order of 2.50 ± 0.2 Å in the thioether complexes and the Tc–N distance is 2.20 ± 0.2 Å in the histidine complex. It is possible that reactions similar to Equation (24) lead to the strong protein binding of Tc(I) thioether complexes *in vitro* as well as *in vivo*.



(27)

There is one additional EXAFS study of note with an environmental twist. For a number of years, the identity of the soluble non-pertechnetate species in the Hanford site high-level nuclear waste tanks containing high concentrations of organic complexants (tanks 101-SY and 102-SY) has eluded investigators. The Tc K-edge X-ray absorption near-edge structure (XANES) spectra of samples from these tanks were reported by Blanchard *et al.*, but could not be assigned to a known Tc complex.[120] Lukens and co-workers have re-examined this data and concluded that the XANES spectra are most likely those of the Tc(I) carbonyl species *fac*-$[Tc(CO)_3(\text{gluconate})]^{2-}$. This hypothesis is supported by EXAFS and ^{99}Tc NMR studies of simulants.[121]

5.12.7.2 ^{99}Tc NMR

The ^{99}Tc nucleus (I = 9/2) has a high sensitivity (0.275 vs. the proton), which allows for rapid NMR data acquisition. Unfortunately, it also has a significant electric quadrupole moment [$Q = -0.19(5) \times 10^{-28}\,m^2$], which limits the collection and processing of ^{99}Tc NMR data to molecules of reasonably high symmetry. This limitation can also be used as an advantage for qualitatively assessing the degree of symmetry about technetium in a molecule of unknown structure. ^{99}Tc also exhibits a very broad chemical shift range of over 9000 ppm. An analysis of a ^{99}Tc NMR data for a wide range of Tc complexes in which the formal oxidation state varies from +5 to +3 to +1 to 0 (the "diamagnetic complexes") shows a regular increase in shielding with decreasing oxidation state.[21] Technetium(VII) complexes do not follow this trend. This is likely due to the absence of *d*-electrons and varying degrees of ligand-to-metal charge transfer.

The previous limitations notwithstanding, ^{99}Tc NMR can be quite useful for studying acid–base and substitution reactions. Suglobov and co-workers have examined the reaction of $[Tc(CO)_3(H_2O)_3]^+$ with hydroxide ion.[35] At the ratio OH/Tc < 1, the $[Tc(CO)_3(H_2O)_2(OH)]$ monomer is formed, which polymerizes over time to give the dimeric complex, $[Tc(CO)_3(H_2O)(\mu\text{-}OH)]_2$, and ultimately the tetramer $[Tc(CO)_3(\mu\text{-}OH)]_4$. The fate of each of these species can be followed by ^{99}Tc NMR.

Alberto and co-workers[34] have studied the exchange of carbonyl ligands (using ^{13}CO) in *fac*-$[Tc(CO)_3(H_2O)_3]^+$, and developed a kinetic model to describe the exchange. Mechanistically, an incoming CO ligand replaces a water molecule to generate *cis*-$[Tc(CO)_4(H_2O)_2]^+$. Because of the strong *trans*-effect, one of the two *trans* COs is displaced, and either the original compound $[Tc(CO)_3(H_2O)_3]^+$ or the isotopically labeled analog, $[Tc(^{13}CO)(CO)_2(H_2O)_3]^+$ is formed. At 4 °C, $k_{co} = 0.82 \pm 0.01 \times 10^{-4}\,kg^{-1}\,mol^{-1}$ and at 37 °C, $k_{co} = 10.0 \pm 0.02 \times 10^{-4}\,kg^{-1}\,mol^{-1}$. The intermediates, $[Tc(CO)_4(H_2O)_2]^+$ and $[Tc(CO)_5(H_2O)]^+$, can be observed in solution under steady state conditions. Moreover, the full carbonylation of *fac*-$[Tc(CO)_3(H_2O)_3]^+$ to $[Tc(CO)_6]^+$ was unambiguously demonstrated by ^{99}Tc and ^{13}C NMR spectroscopy, and the first ^{99}Tc–^{13}C coupling constant (354 Hz) was obtained.

Acknowledgments

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5.13
Rhenium Compounds

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5.13.1 Introduction

Rhenium organometallic chemistry expanded swiftly during the last decade. This is mainly due to potential practical applications of several Re organometallics, namely: the luminescent $Re(CO)_3$ derivatives applicable in new materials, molecular sensors and optically responsive materials as well as in radiopharmaceuticals, medical imaging, biological assaying and biomarking; the organometallic Re oxides, like $ReMeO_3$ (MTO), with an unsuspected activity and versatility in oxidation catalysis; sterochemical control of reactions on prochiral ligands bound to chiral-at-metal fragments, for example, $[ReCp'(NO)(PPh_3)]^+$, and a new type of arene activation on $Re^I(k^3\text{-N–N–N})$ complexes. Since the mid-1990s, these activities account for ca. 50% increase in published work in this area.

Fundamental advances have been made in stabilizing a number of elusive “primeval” molecules like HNO, H_2CNH, H_2N_2, linear carbon allotropes as well as pinpointing mechanistic details of the chemistry of unsaturated hydrocarbon ligands, namely, acetylenes and carbenes.

This chapter describes the organometallic chemistry of Re organized by oxidation states within two major sections: the compounds with CO and CNR as the only C ligands and the compounds containing these and/or other C ligands, in which case subsections are organized by hapticity in ascending order. The Re polyhydrides are presented in a separate section. With the exception of Re–CO clusters, the bewildering variety of Re heteropolynuclear complexes has not been covered but several selected examples and review articles are mentioned along the text. Excepting two review articles, no work of 2005 is reviewed.

5.13.2 Complexes Containing CO or CNR as the only Carbon Ligands

5.13.2.1 Re Complexes in Formal Negative Oxidation States

The central species under this heading is the well-known anion $[Re(CO)_5]^-$ **1** obtained by reduction of $Re_2(CO)_{10}$. Several other highly reduced Re carbonyls have been prepared in earlier days.[1,2] However, in recent times this chemistry has not witnessed important advances except in what regards the follow-up chemistry of highly reduced Re carbonyls: Re carbonyl clusters. In fact, the high reactivity of these complexes toward electrophiles, namely H^+, results in the formation of $[Re_n(CO)_xH_y]^z$ species with nuclearities (n) variying from 1 to 6 or higher for carbido clusters $[Re_nC(CO)_x]^z$. One recent example is given by the reaction of $[Sm(Tp')_2]$ with $Re_2(CO)_{10}$. Heating the initiallly formed product $\{Sm(Tp')_2\}Re(CO)_5$ gives moderate yields of the cluster anion $[Sm(Tp')_2]_2[Re_4(CO)_{17}]$. Crystallization from toluene yields the Re carbonyl cluster $[Sm(Tp')_2][HRe_4(CO)_{17}]$.[3] Since the assignment of oxidation states to the Re in many of these clusters does not make much sense as a classifier for their descriptive chemistry, it was decided to present the $[Re_n(CO)_xH_y]^z$ species in one separate section placed below between the Re(0) and the Re(I)complexes.

Due to its good nucleophilicity, **1** has been widely used to add or substitute at electrophilic positions on other organometallic complexes thereby producing a wealth of polynuclear species and clusters with Re–C, Re–Re, and Re–M′ bonds. Binuclear homo- and heterobimetallic complexes bridged by hydrocarbons are among such species.[4] However, this simple picture of nucleophilic substitution may be misleading because electron-transfer processes are often involved due to the reducing power of **1**.[5] Exemplifying such complexity, reaction of **1** with one molar equivalent of PPh_2Cl at −70 °C yielded, as major products, three dinuclear complexes: $Re_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(CO)_8$, $Re_2(CO)_9(PPh_2H)$, and $Re_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_8$. When PPh_2Cl was present in twofold excess, only $Re_2(CO)_9(PPh_2H)$ and $ReCl(CO)_4(PPh_2H)$ were isolated.[6]

5.13.2.2 Re(0) Complexes

5.13.2.2.1 $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$

$Re_2(CO)_{10}$ **2** is the most important starting material in organorhenium chemistry. Two new methods have been introduced for its preparation: the high pressure reduction of K_2ReCl_6,[7] and the simple mild reduction of cheap $[NH_4][ReO_4]$ at atmospheric CO pressure described in Equation (1).[8]

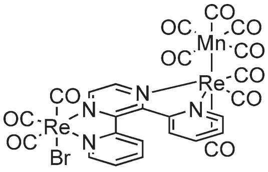
$$[NH_4][ReO_4] \xrightarrow[\substack{\text{DIBAL-H} \\ \text{toluene, 80 °C}}]{\text{CO (1 atm)}} Re_2(CO)_{10} \qquad (1)$$

A modification to the synthesis of $MnRe(CO)_{10}$ was also reported.[9] Recent detailed computational and spectroscopic studies on $MnRe(CO)_{10}$ favor the staggered conformation.[10]

Laser-ablated Re atoms and electrons react with CO upon co-condensation in excess argon and neon to produce subcarbonyls where $Re(CO)_2$ is the major product. Annealing in solid argon in the presence of CO produces higher carbonyls including **2**.[11]

The photoactivation of **2** proceeds along two pathways: Re–Re bond disruption to form $^{\cdot}Re(CO)_5$ and Re–CO bond cleavage to give *eq*-$Re_2(CO)_9$(Solvent). The quantum yields of both processes were re-measured and corrected and shown to be dependent on the wavelength of the irradiation in a manner different to that found for $Mn_2(CO)_{10}$.[12] Donor solvents stabilize $Re_2(CO)_9$ but not the $^{\cdot}Re(CO)_5$ radical that dimerizes back to $Re_2(CO)_{10}$.[13] $MnRe(CO)_{10}$ flash-photolyzed in a 3-methylpentane matrix at 93 K forms $MnRe(CO)_9$(Solvent). Upon irradiation with visible light, the bridged CO species $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$ is formed in which CO is presumed to be η^1-bound to Re and η^2-bound to Mn. Such a bridged species is prevalent for $Mn_2(CO)_9$ but is not observed for $Re_2(CO)_9$.[14]

The dinuclear $(CO)_5MnRe(CO)_3(L)$ and trinuclear $(CO)_5MnRe(CO)_3(L)Re(Br)(CO)_3$ and $(CO)_5MnRe(CO)_3(bpym)W(CO)_4$ complexes (L = 2,2′-bipyrimidine(bpym), (2,3-bis(2-pyridyl)pyrazine (DPP)) undergo photochemical homolysis of the Mn–Re bond upon excitation into their metal-to-ligand charge transfer (MLCT) absorption band(s) in the visible spectral region. The emission properties of the dinuclear species are deeply modified by the introduction of the third metal center, namely in the DPP complex **3**.[15]



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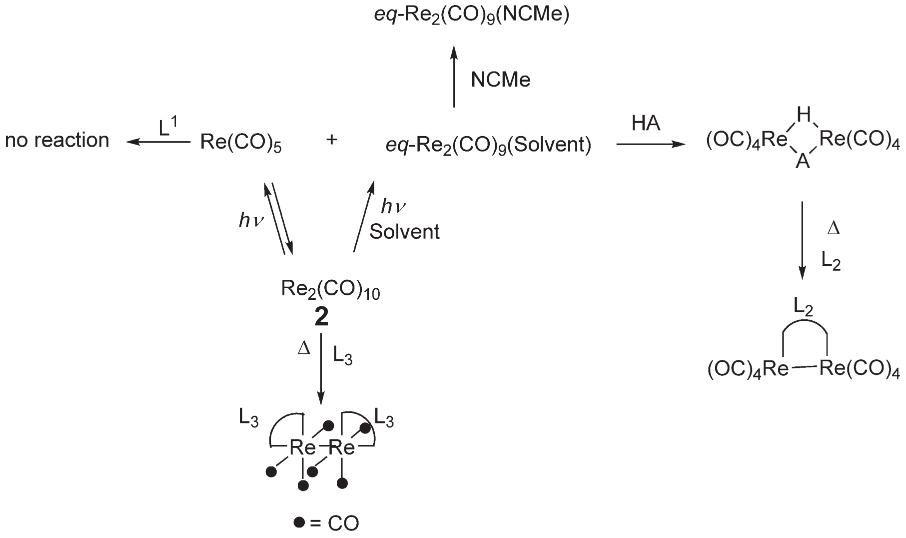
These results should be seen in the light of the extensive photophysics or $[Re(CO)_3(\alpha\text{-diimine})L]^{0/+}$ complexes outlined in Section 5.13.2.3.8.(ii).

5.13.2.2.2 Photo and thermal reactions of $Re_2(CO)_{10}$

Substitution of CO at **2** can take place photochemically, as discussed above, or thermally. Although photoinitiated reactions of **2** proceed with a substantial degree of homolytic Re–Re bond scission, metal–metal bond homolysis is not the primary step for thermally initiated substitution of **2**. Under strictly thermal conditions, substitution proceeds by a dissociative pathway with CO loss, without any Re–Re bond breaking. The outcome of the reactions, however, depends on the nature of the ligand (Scheme 1).

While some ligands produce the Re(0) species of general formula $Re_2(CO)_nL_{10-n}$ keeping the Re–Re bond intact, others undergo formal oxidative addition processes resulting in, usually dimeric, Re(I) compounds. Many of these reactions cleave C–H bonds like in alkenes that afford $Re_2(CO)_8(\mu\text{-H})(\mu\text{-alkenyl})$ complexes that originate from *eq*-$Re_2(CO)_9$ in photochemical substitution of **2**. Indeed, $Re(CO)_5$ concomitantly formed, does not react with alkenes, NCMe, or 2-MeTHF that block the reaction by scavenging $Re_2(CO)_9$.[13] Under photochemical conditions, $Re_2(CO)_{10}$ acts as an efficient and very advantageous catalyst for the transformation of silanes into silyl ethers. The mechanism proposed by Barton considers $Re_2(CO)_9$ the catalytic species able to coordinate an $R_3Si–H$ bond. R^1OH then attacks the Si atom of $Re_2(CO)_9(H–SiR)$ generating $[Re_2(CO)_9H]^-$ and $[R_3SiOR^1H]^+$. H_2 evolution forms the product and reforms the catalyst.[16] A similar initial photodissociation of CO is proposed in the photocatalyzed polymerization of cyclohexene oxide by **2** that takes place without any co-catalyst or promoter.[17] It is also the basis for the catalytic activity of **2** in the mono- and dialkylation of arenes from alkyl halides under mild conditions.[18]



CO substitution reactions of $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$.
L^1 = olefin, NCMe; HA = $HRC{=}CR_2$, HCCR
L_2 = Z-$Ph_2PCH{=}CHPPh_2$
L_3 = 2-NC_5H_4-N=N-C_6H_4(R)

Scheme 1

In spite of being Re(I) species, the $Re_2(CO)_8(\mu\text{-H})(\mu\text{-alkenyl})$ complexes are synthons of the $Re_2(CO)_8$ fragment which they readily generate via facile thermal elimination of the alkene (see Table 1). Therefore, these complexes are described in this section rather than in Section 5.13.3.1 in spite of them having Re–C bonds besides Re–CO bonds. Also useful starting materials for substituted $Re_2(CO)_nL_{10-n}$ complexes are species such as $Re_2(CO)_9(NCMe)$ **4**, $Re_2(CO)_8(NCMe)_2$, and the recently available highly reactive *eq-eq*-$[Re_2(CO)_8(THF)_2]$ **5**. Besides producing $Re_2(CO)_8L_2$ complexes, **4** is a strong activator of H–H and C–H bonds to form dimeric Re(I) complexes of type $Re_2(CO)_8(\mu\text{-H})(\mu\text{-CR}_3)$.[19] Other methods used for the activation of the substitution reactions of **2** are oxidative decarbonylation with Me_3NO or PdO. The latter is a particularly important method for the preparation of Re(0) isonitrile derivatives.[2] Some complexes of general formula $MM'(CO)_nL_{10-n}$ (M = Re, M′ = Mn, Re) containing an M–M′ bond are given in Table 1 together with their synthesis.

Table 1 Complexes of general formula $MM'(CO)_nL_{10-n}$ (M = Re; M′ = Mn, Re)

Compound	*Synthetic method*	*References*
$(CO)_5MnRe(CO)_4(NCBu^t)$	$(CO)_5MnRe(CO)_4(PHR_2) + NCBu^tRe_2(CO)_{10} + Me_3NO + NCBu^t$	625
$Re_2(CO)_9(\kappa^1\text{-}R_2SbCH_2SbR_2)$ (R = Me, Ph)	$Re_2(CO)_{10} + h\nu$ + ligand	626
$Re_2(CO)_9(\kappa^1\text{-}Ph_2P(CH_2)_nPPh_2)$ ($n = 1$–6)	$Re_2(CO)_{10} + Me_3NO$ + ligand	21
$Re_2(CO)_8[(Z)\text{-}Ph_2PCH{=}CHPPh_2]$[a]	$Re_2(CO)_8(\mu\text{-H})(\mu\text{-}\eta^1,\eta^2\text{-CH{=}CHBu})Re_2(CO)_8(NCMe)_2$ + ligand	627
1,2-*eq*,*eq*-$[Re_2(CO)_8(THF)_2]$	$Re_2(CO)_8(\mu\text{-H})(\mu\text{-CH}_3)$ + THF (253 K)	19
1,2-*eq*,*eq*-$[Re_2(CO)_8(THF)(H_2O)]$	1,2-*eq*,*eq*-$[Re_2(CO)_8(THF)_2]$ in wet THF	19
1,2-*eq*,*eq*-$[Re_2(CO)_8(H_2O)_2]$	1,2-*eq*,*eq*-$[Re_2(CO)_8(THF)_2]$ in wet THF	19
$L(CO)_3Re\text{–}Re(CO)_3L$ L = 2-NC_5H_4–N=N-C_6H_4R; R = H, *o*-Me/Cl, *m*-Me/Cl	$Re_2(CO)_{10}$ + ligand in THF/reflux	628
$Re_2(CO)_8(\mu\text{-}S_2CPCy_3)$[b]	$Re_2(CO)_8(\mu\text{-H})(\mu\text{-}\eta^1,\eta^2\text{-CH{=}CHBu}) + S_2CPR_3[Re(CO)_5]^- +$ *fac*-$[Re(CO)_3(S_2CPCy_3)Br]$	629
$Re_2(CO)_6\{\mu\text{-}\eta^2,\eta^3\text{-}S_2CPCy_3\}$[c]	$Re_2(CO)_8(\mu\text{-}S_2CPCy_3)$ reflux in toluene	629
$Re_2(CO)_9(S{=}C(NEt_2)\{NH(p\text{-Tol})\})$	$Re_2(CO)_9(NCMe)$ + ligand	24

[a] One P ligand on each Re atom.
[b] One S ligand on each Re atom.
[c] The bridging ligand is a formal 8e donor.

Rates for the reactions of $Re_2(CO)_9L$ (L = PPh_3, $PMePh_2$, PMe_2Ph, py) with L in the presence of Me_3NO in $CHCl_3$ decrease in the order $PPh_3 > PMePh_2 > PMe_2Ph >$ py by an associative pathway (k_2).[20]

The dangling P atom in the complexes $Re_2(CO)_9(\kappa^1\text{-P–P})$ (P–P = $Ph_2P(CH_2)_nPPh_2$; n = 1–6) can be oxidized by Me_3NO to give $Re_2(CO)_9(\kappa^1\text{-P–P=O})$ together with $[Re_2(CO)_8(\kappa^2\text{-P–P})]$ (see Table 1). Shorter chains form 1,2-*eq-eq* complexes but longer chains form 1,2-*ax-eq* isomers.The steric pressure on the Re–Re bond for $n = 6$ results in the formation of the monomeric $[Re(CO)_4Cl]_2(\mu\text{-P–P})$ upon easy chlorination in CH_2Cl_2.[21]

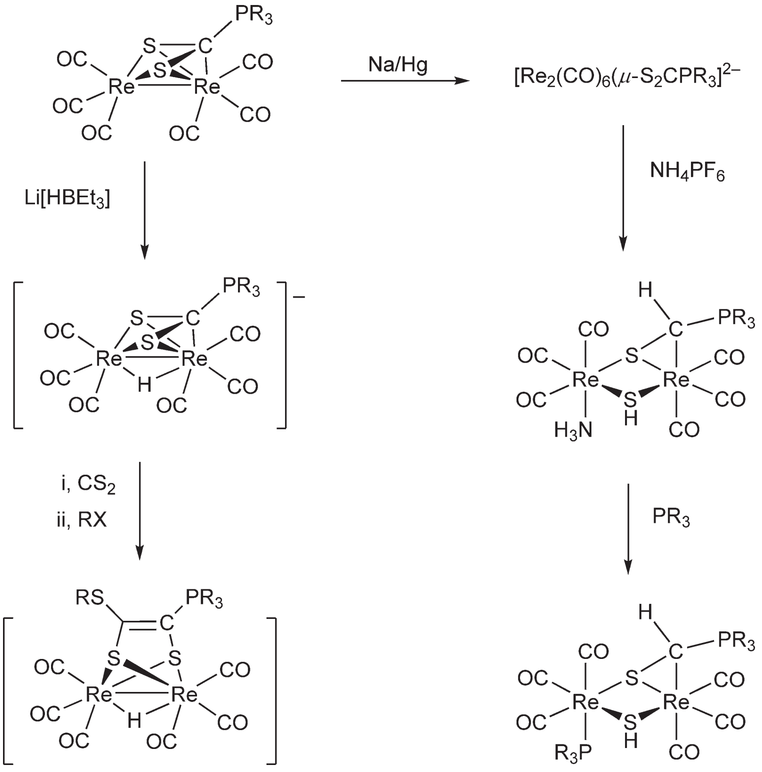
Thioethers (SR_2), like trimethylene sulfide (C_3H_6S; thiethane) and 1,5,9-trithiacyclododecane, 12S3, easily displace NCMe from **4** to form *eq*-$Re_2(CO)_9(SR_2)$. Interestingly, the thiethane complex catalyzes the cyclooligomerization of thiethanes to sulfur macrocycles like 12S3 and 24S6.[22,23]

Reactions of **2** or **4** with tetraalkylthioureas can lead either to simple substitution products[24] or to cleavage of the C–S bonds as in the cluster product with a diamino carbene ligand $[Re_5(CO)_{17}(\mu\text{-R})(\mu_4\text{-S})\{C(NMe_2)_2\}_2]$ (R = SH, OH).[25]

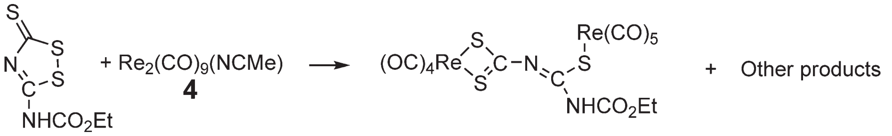
The phosphoniodithioformates R_3PCS_2 are versatile ligands with different bonding modes and donor capabilities.[26] Upon loss of one CO per Re atom, $Re_2(CO)_8(\mu\text{-}S_2CPCy_3)$ transforms into $Re_2(CO)_6\{\mu\text{-}\eta^2,\eta^3\text{-}S_2CPCy_3\}$, where the bridging ligand binds in an η^2(S,S′), η^3(S,C,S′) mode contributing a total of eight electrons. It can be reduced with Na/Hg to the dianion $[Re_2(CO)_6\{\mu\text{-}\eta^2,\eta^3\text{-}S_2CPCy_3\}]^{2-}$ of unknown structure. Protonation with NH_4PF_6 leads to cleavage of and formal hydrogenolysis of one C–S bond as well as cleavage of the Re–Re bond, as in Scheme 2.[27] The NH_3 ligand can be replaced by phosphine. The analog $MnRe(CO)_6\{\mu\text{-}\eta^2,\eta^3\text{-}S_2CPCy_3\}$ complex undergoes a similar chemistry with the interesting observation that the C atom of the $SC(H)PR_3$ ligand can migrate between the metals in an irreversible manner depending on the nature of the ligand (NH_3, PR_3, or $CNBu^t$).[28]

Like its Mn_2 and MnRe analogs $Re_2(CO)_6\{\mu\text{-}\eta^2,\eta^3\text{-}S_2CPCy_3\}$ is reduced with $Li[HBEt_3]$ to form $[Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}S_2CPR_3)]Li$ with the hydride bridging the M–M bond. Reaction with CS_2 is accompanied by extrusion of one S atom and C=C bond formation. The resulting anion can be alkylated and metallated at the S atom generating a family of binuclear complexes that bear the trithiolate ligand $S(SR)C{=}CPR_3$ (Scheme 2).[29,30]

The S–S bond of the 1,2,4-dithiazole-3-thione ring cleaves the Re–Re bond of **4** to give a series of binuclear and mononuclear complexes as in Equation (2).[31]



Scheme 2

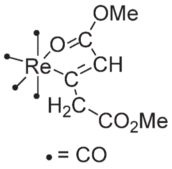


(2)

The cleavage of a P–C bond takes place from **2** under photolytic conditions as in Scheme 3.[32]

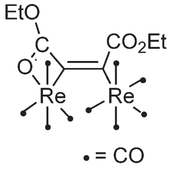
The reaction of Ph_3PSe with $[Re_2(CO)_8(NCMe)_2]$ affords two new clusters, $[Re_4(\mu_3\text{-}Se)_2(CO)_{16}(PPh_3)_2]$ and $[Re_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2]$. Their structures exhibit a nearly square-planar Re_2Se_2 and a butterfly Re_2Se_2 core, respectively. These air stable clusters display a reversible loss/addition of a CO molecule, which is accompanied by the formation/cleavage of an Re–Re bond and the consequent rearrangement of the Re_2Se_2 core, from square to butterfly and vice versa (Scheme 4).[33] A very similar Te derivative has been prepared from **2** and PEt_3Te.[34]

The reactions of $Re_2(CO)_{10}$ **2** with unsaturated hydrocarbons that were widely studied in earlier days[1,2] have provided new examples of the rich chemistry involved. The photochemical reaction of **2** with branched and unbranched allenes gives a bewildering variety of products that can be explained either by initial Re–Re bond homolysis and further radical reactions ensuing from $Re(CO)_5$ or by CO loss followed by coordination of the allene and rearrangements thereof. η^1-, η^2- and η^3-carbon–Re bonds are formed.[35,36] In the case of the allene $MeO_2C(H)C{=}C{=}C(H)CO_2Me$, the complex **6** is formed.[37]



6

Labeling experiments assigned the origin of the extra proton to adventitious water. Alkyne insertion across the Re–Re bond in **2** and other M–M bonds has been studied intensively, among others by Adams and co-workers, and gives rise to a variety of processes and rearrangements mostly reviewed.[2,38] Structure **7** provides a simple example of the result of the thermal reaction of **4** with the electrophilic alkyne $EtO_2CC{\equiv}CCO_2Et$.[39] Insertion of aryl isothiocyanates, CS_2, ethylene sulfide, and $N_2CH(CO_2Et)$ at the Re–C bonds of this kind of bridging acetylenes has been also studied (Scheme 5).[9,40]



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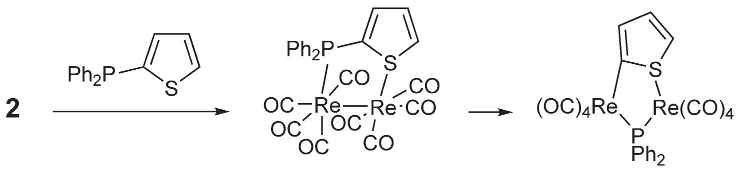
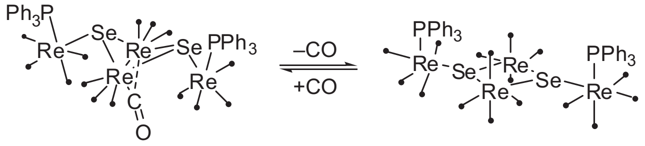
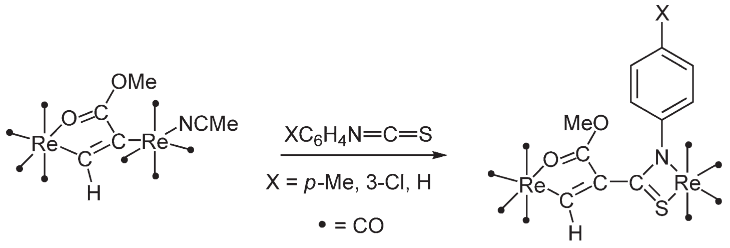


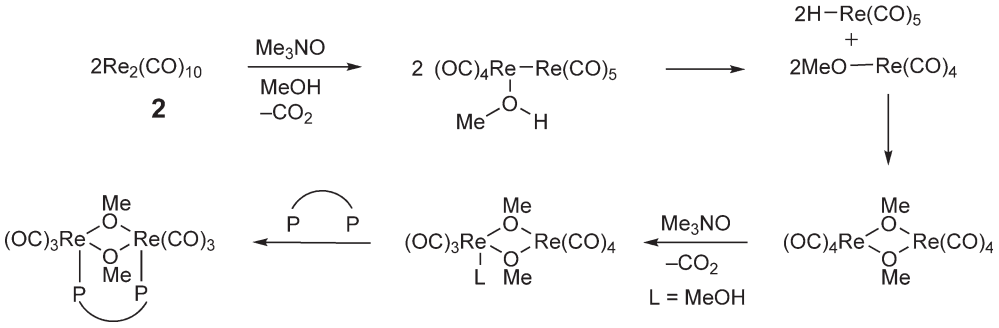
Scheme 3



Scheme 4



Scheme 5



Scheme 6

The easy methoxylation of 2 with rupture of the Re–Re bond that occurs in the presence of Me_3NO has been mechanistically reinterpreted (Scheme 6) on the basis of the study of the analogous reaction of $MnRe(CO)_{10}$ in the presence of a diphosphine yielding mononuclear $[Mn(CO)_3H(\kappa^2\text{-P–P})]$ and the bridged dimer $[Re_2(\mu\text{-OMe})_2(\mu\text{-P–P})(CO)_6]$.[41]

These results also explain those observed in the analogous reaction with phenol that forms *inter alia*, $[Re(CO)_5(\mu\text{-H})\{Re_2(CO)_9\}]$ and $[Re_2(\mu\text{-OPh})_3(CO)_6]^-$. Such alcoholyses are synthetically useful. For instance, alcoholysis with long-chain aliphatic primary alcohols in the presence of bridging ligands like 4,4′-bipy leads, in a one-pot synthesis, to highly luminescent molecular rectangles to be discussed in Section 2.3.8.5.[42,43]

There is a large variety of clusters and polynuclear species derived from $Re_2(CO)_{10}$ and $Re_2(CO)_nL_{10-n}$, the description of which cannot be included in the present work. However, a few leading references to several synthetic methods and specific examples are given.[44–47]

5.13.2.2.3 Surface reactions of $Re_2(CO)_{10}$

Due to the interest in heterogenous reactions with Re metals or unsaturated Re subcarbonyls, a number of studies have been devoted to the understanding of the species resulting from chemisorption of $Re_2(CO)_{10}$ on several inorganic supports.

Vapour phase deposition of 2 onto high surface area $MgAl_2O_4$ (spinel) leads to O-bonded surface adducts, where an axial CO ligand of the Re carbonyl is coordinated to a coordinatively unsaturated Al^{3+} ion at the metal oxide surface. Vacuum heating of the surface adducts at 770 K leads to a surface-bound mononuclear $Re(CO)_3$. Further heating at 820 K led to spinel-supported rhenium metal.[48]

Stable rhenium tricarbonyls bonded to the surface of MgO powder, prepared from a variety of precursors including 2, have been characterized by extended X-ray absorption fine structure (EXAFS) spectroscopy. The surface species are precise analogs of molecular rhenium carbonyls, of general formula $[Re(CO)_3\{OMg\}_x\{HOMg\}_{3-x}]$ (where the braces denote groups terminating the MgO bulk).[49] Similar stepwise decarbonylation is found by IR and temperature-programmed desorption of 2 adsorbed on MgO(111) films.[50] In the opposite sense, carbonylation of K_2ReCl_6 on MgO leads to $[Re(CO)_3\{HOMg\}_x\{OMg\}_{3-x}]$ which is the easiest way of preparing supported $Re(CO)_3$ fragments.[51] Structure 2 is physically adsorbed on almost fully dehydroxylated MgO powder, but it is chemisorbed on hydroxylated MgO, forming $[Re_2(CO)_9]^{2-}$ strongly ion paired with the MgO surface. The chemisorption is inferred to involve nucleophilic attack of surface OH groups on CO ligands of **2** to give $[HRe_2(CO)_9]^-$, which is deprotonated on the basic surface to give $[Re_2(CO)_9]^{2-}$.[52]

The stepwise decarbonylation of **2** on an alumina cluster model was studied by DFT methods. The interaction energetics of rhenium subcarbonyls ($Re_2(CO)_9$, $Re(CO)_4$, and $Re(CO)_3$) on the alumina surface correlate with calculated interaction energies and earlier experimental desorption studies.[53] Rhenium carbonyls bonded to dealuminated zeolite Y calcined at 300 and 500 °C were tested as catalysts for hydrogenation of ethylene and of propylene. The initially formed rhenium tricarbonyls bonded to the zeolite were converted into rhenium dicarbonyls during catalysis, as shown by IR and EXAFS spectra, and the coordination of Re to the support changed, as shown by EXAFS results. Consequently, there were bonding positions on the Re centers for reactive ligands, including those identified by IR spectroscopy as alkyls and π-bonded alkenes. The catalysis is suggested to proceed via reaction of alkyl and hydride ligands on rhenium centers incorporating two CO ligands.[54] The interaction between **2** and a silica surface has been modeled from the reaction of $Re_2(CO)_8(THF)_2$ with silanols, R_2R^1SiOH, and shown to form hydrides like $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiR}_2R^1)]$ that revert to $Re_2(CO)_{10}$ at 150 °C under 1 atm CO.[44]

Electron beam induced chemical vapor deposition (CVD) of $Re_2(CO)_{10}$ has allowed the fabrication of nanostructured wires and rods of Re consisting of only one phase of metallic Re useful for the construction of nanoelectronic devices.[55]

5.13.2.2.4 $Re(CO)_{5-n}L_n$ radicals

The $^{\cdot}Re(CO)_5$ radical generated photolytically from **2** is only weakly solvated in alkane or chlorinated alkane solvents. This weak interaction allows facile recombination with another $^{\cdot}Re(CO)_5$ radical to form the parent $Re_2(CO)_{10}$ without much energy cost in displacing the solvent molecule. Even NCMe is unable to stabilize $[Re(CO)_5(NCMe)]$ and recombination takes place in this solvent with a rate constant, $k_{\mathrm{dim}} = (1.0 \pm 0.2) \times 10^{10}$ $M^{-1}s^{-1}$, a value close to that found in cyclohexane.[56] A study of the ultrafast events following excitation of **2** in the reactive CCl_4 solution at 295 nm reveals that 55% of the excited **2** formed (**2***) reverts to the parent $Re_2(CO)_{10}$ molecule via internal relaxation or geminate radical pair ($^{\cdot}Re(CO)_5$) recombination. A further 20% leads to *eq*-$Re_2(CO)_9(CCl_4)$ stable up to 2.5 μs. 22.5% of formed **2*** dissociates to $^{\cdot}Re(CO)_5$ radicals that escape cage recombination and abstract $Cl^{\cdot}$ to give $Re(CO)_5Cl$. Finally, 2.5% of $^{\cdot}Re(CO)_5$ radicals formed from **2*** dissociation abstract $Cl^{\cdot}$ from the solvent on a timescale faster than vibration cooling. The competing geminate recombination and $Cl^{\cdot}$ atom abstraction processes are regulated by solvent caging.[57]

$^{\cdot}Re(CO)_5$ radicals do not react with cationic macrocyclic tetraazacomplexes $[M(14\text{-N4})]^{2+}$ (M = Cu(II) Ni(II) unless halide ions (Cl, Br) are present, either as $Re_2(CO)_{10}$ stoichiometric counterions or in excess. In this case, the final products are $Re(CO)_5X$ and $[M(14\text{-N4})]^{+}$.[56] In other words, $^{\cdot}Re(CO)_5$ requires coordination of the halide to the $[M(14\text{-N4})]^{2+}$ complexes, to form $[M(14\text{-N4})X]^{+}$, with which it reacts via a bimolecular intermediate $[(CO)_5ReXCu(14N4)]^{+\cdot}$ that undergoes the electron transfer step by an inner-sphere mechanism to produce the final Re(I) and Cu(I) products. Stressing the importance of Re–X bond making in the reactions of $^{\cdot}Re(CO)_5$ is the observation that it only reduces $[Co(bipy)_3]^{3+}$ in the presence of excess halide, via an ion pair $[Co(bipy)^{3+}, X^-]$.[56]

A rather large number of radicals of type $[Re(CO)_3(\alpha\text{-diimine})X]^{\cdot-}$ and $[Re(CO)_3(\alpha\text{-diimine})L]^{\cdot}$ have been characterized and many isolated from photo- and electrochemical reduction of the respective Re(I) complexes, as discussed in Sections 5.13.2.3.8.(ii) to 5.13.2.3.8.(iv). It must be noted, however, that these radicals differ considerably from the $^{\cdot}Re(CO)_5$ radical because the unpaired electron resides essentially on the π-cloud of the α-diimine ligands and dimerization is much less favorable.

5.13.2.3 Re(I) Complexes

5.13.2.3.1 Mononuclear rhenium carbonyl hydrides and dihydrogen complexes

The simplest Re carbonyl hydride, $Re(CO)_5H$ **8**, was first prepared in 1961 by protonation of $[Re(CO)_5]^-$ but other easier routes were later developed that avoid contamination by polynuclear species and clusters.[1,2]

Only few unsaturated molecules (e.g., CO_2, alkynes) insert into the Re–H bond of $Re(CO)_5H$ which is a relatively inert molecule whereas $Re(PR_3)_5H$ complexes are able to activate C–H bonds.[1,2] Since the hydridic character of the Re–H bond can be modulated by the ancillary ligands,[58] the recent interest raised by the discovery of H···H interactions between M–H and X–H bonds, called dihydrogen bonds, as well as the chemistry of η^2-H_2 complexes, led to a series of studies on the monohydrides of the general formula $Re(CO)_xL_{5-x}H$ (L = PR_3 and $P(OR)_3$), which allow a detailed study of such interactions. An improved synthesis for the preparation of hydrides of type $[Re(CO)_3(PR_3)_2H$ has been developed from $Re_2(CO)_{10}$, 1-pentanol, and PR_3.[59] Heating **8** with PR_3 in toluene at 110–130 °C gives high yields of *trans-mer*-$[Re(CO)_3(PR_3)_2H]$ (R = PPh_3, PPh_2Pr^i).[60]

The insertion chemistry of a series of $[Re(CO)_{5-n}(PMe_3)_nH]$ toward aldehydes, CO_2, and alkynes revealed that the hydridic character of the complex, and its reactivity, increase with the number of PMe_3 ligands.[61]

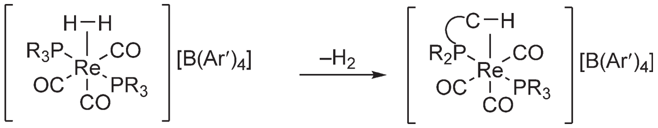
The complex $[(triphos)Re(CO)_2H]$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) has been used as a convenient model for the study of H···H interaction with Re hydrides (dihydrogen bonds). Its interaction with a series of proton donors (PhOH, $(CF_3)_2CHOH$, $(CF_3)_3COH$, $H_2ClCCOOH$, HBF_4) has been studied in CH_2Cl_2 solution by IR and NMR spectroscopies. The $[(triphos)Re(CO)_2H\cdots HOR]$ adducts were detected with rather strong H···H interactions ($-\Delta H = 4.4$–$6.0\ \mathrm{kcal\,mol^{-1}}$; H···H ca. 1.83 Å). The adducts are in equilibrium with the H_2 complex $[(triphos)Re(CO)_2(H_2)]^+$.[62] The effect of replacing CO by the stronger π-acid NO^+ has been studied by Berke and Burger, for instance, on the factors affecting the Re–H···HOR_f interaction in a series of $Re(CO)(NO)(PR_3)_2H_2$ complexes with fluorinated alcohols.[63] Interestingly, this interaction occurs preferably with the hydride *trans* to NO. This increase of the hydric character of *trans*-ON–M–H systems is called the nitrosyl effect.[64] Another study carried out with $Re(CO)(NO)(PR_3)_2HX$ (X = H, R = Me, Et, Pr^i; X = Cl, R = Me) and a series of proton donors (indole, phenols, R_fOH, CF_3CO_2H) showed that hydrogen bonding with the hydride atom precedes proton transfer and the formation of a H_2 complex. A short (1.79(5) Å) H···H interaction with indole was characterized in the solid state.[65]

Protonation of most ReL_5H complexes affords H_2 complexes $[ReL_5(\eta^2\text{-}H_2)]^+$.[66] $[(triphos)Re(CO)_2H]$ is protonated to form $[(triphos)Re(CO)_2(\eta^2\text{-}H_2)]^+$.[62] Protonation of *trans-mer* $Re(CO)_3(PR_3)_2R^1$ (R^1 = H, Me; $R_3 = Ph_3$, Ph_2Pr^i) with $[H(Et_2O)][BArF]$ in CH_2Cl_2 under H_2 atmosphere gives the cationic dihydrogen complexes *mer*-$[Re(CO)_3(PR_3)_3(H_2)][BArF]$ stabilized by large non-coordinating $[BArF]^-$ anions.[60] These are readily deprotonated in CH_2Cl_2 by N bases to give the hydride *mer*-$[Re(CO)_3(PR_3)_2H]$. When the protonation is done in the absence of H_2, or when H_2 is removed from *mer*-$[Re(CO)_3(PR_3)_2(H_2)][BArF]$ under vacuum, a C–H bond from the PR_3 ligands coordinates to the Re in an agostic interaction according to Scheme 7.[60]

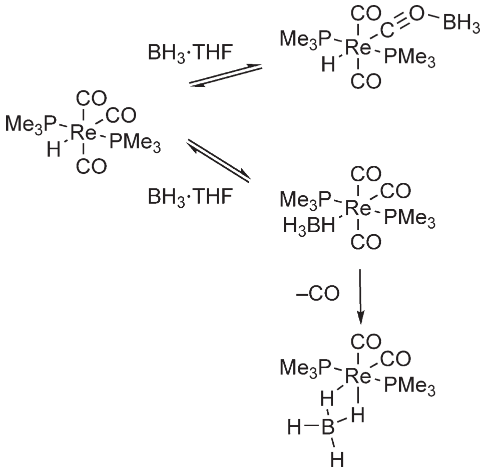
This agostic bond is stable in CH_2Cl_2 solution and a similar one is present in $[(triphos)Re(CO)_2]^+$. In contrast, CH_2Cl_2 is displaced from *cis*-$[Re(CO)_4(PR_3)(CH_2Cl_2)][BArF]$ under 3 atm of H_2 gas affording *cis*-$[Re(CO)_4(PR_3)(\eta^2\text{-}H_2)][BArF]$. Remarkably, as a result of the high electrophilicity of the $[Re(CO)_4(PPh_3)]^+$ core, *cis*-$[Re(CO)_4(PR_3)(\eta^2\text{-}H_2)][BArF]$ is capable of protonating OPr^i_2 to form $^iPr_2OH^+$ and the hydride-bridged dimers $\{[cis\text{-}Re(CO)_4(PR_3)]_2\text{-}(\mu\text{-}H)\}[BArF]$.[67] This strong ability to effect heterolytic activation of H_2 is much higher than that of $[Re(CO)_3(PCy_3)_2(H_2)]^+$ which is moderately acidic but does not protonate ethers.[60] $Re(CNBu^t)_5Cl$ reacts with NaBArF under H_2 to give the very labile cationic H_2 complex $[Re(CNBu^t)_5(\eta^2\text{-}H_2)][BArF]$, which is much less stable that its isoelectronic analog $[Re(PMe_3)_5(\eta^2\text{-}H_2)]OTf$. Increasing the electronic density of the Re center by partial phosphine replacement as in $Re(CNBu^t)_3(PR_3)_2Cl$ (R = Cy, Ph) leads to the extraordinary (reversible) replacement of Cl^- by H_2 in chlorinated solvents to form $[Re(CNBu^t)_3(PCy_3)_2(\eta^2\text{-}H_2)]Cl$.[68] This affinity for H_2 is even superior to that observed for N_2 and is rather unusual in the presence of a coordination anion like Cl^-. This H_2 cation can only be deprotonated by strong bases like alkoxides. In fact, $Re(CNBu^t)_3(PCy_3)_2H$ is so basic that it is protonated by $[HNEt_3]Cl$ in CH_2Cl_2. This is in contrast to the moderate acidity of $[Re(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)]^+$ discussed above.[68] Hydride abstraction with $[Ph_3C][BAr^F]$ from some of the complexes $Re(CO)_x(PMe_3)_{5-x}H$ led to solvento complexes $[Re(CO)_x(PMe_3)_{5-x}(S)][BAr^F]$ (S = PhCl, THF). Under H_2 atmosphere, these cations are able to hydrogenate imines. The equilibrium between $[Re(CO)_x(PMe_3)_{5-x}(\eta^2\text{-}H_2)]^+$ and the dihydride cation $[Re(CO)_x(PMe_3)_{5-x}(H)_2]^+$ allows sequential insertion of the imine across the two Re–H bonds.[69]

The interaction of the complexes $Re(CO)_x(PMe_3)_{5-x}H$ (x = 1, 2, 3) with the boron Lewis acids BH_3 and 9-borabicyclo[3,3,1]nonane (BBNH) gives products of formulas $Re(CO)_{x-1}(PMe_3)_{5-x}(\eta^2\text{-}BH_4)$ and $Re(CO)_{x-1}(PMe_3)_{5-x}(\eta^2\text{-}H_2BBN)$. The intermediacy of $\eta^1\text{-}BH_4$ adducts was established. Interestingly, it was also shown that BBNH and BH_3 interact initially with the O atom of a CO ligand (with a bent C–O–B bond), evolving then to the final product via the $\eta^1\text{-}HBR_3$ intermediate (Scheme 8).[70] Incidentally, this work also showed that $Re(CO)_3(PMe_3)_2H$ is a stronger Lewis base than THF. Indeed, **8** also behaves as a ligand useful in the synthesis of homo- and heteronuclear clusters as discussed in the next subsection.

Structure **8** reacts with dealuminated Y zeolite (DAY) forming a nearly unique $Re(CO)_3$ species, with rhenium bonded to three surface oxygen atoms at a T5 site located at an aluminum center in the zeolite.[71]



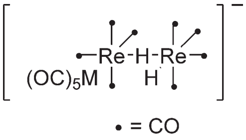
Scheme 7



Scheme 8

5.13.2.3.2 Polynuclear Re carbonyl hydrides and clusters

The next simplest molecule is the dimer [$Re_2(\mu\text{-}H)_2(CO)_8$] **9**, an improved synthesis of which is known.[72] Structure **9** transfers two H atoms to CS_2 resulting in a dinuclear complex bridged by the methanedithiolate ligand [H_2CS_2]$^{2-}$: [{$Re_2(\mu\text{-}H)(CO)_8$}$_2$(μ-S_2CH_2)].[73] N_2CPh_2 inserts into one Re–H–Re bond of **9** to give [$Re_2(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^1\text{-}N(H)NCPh_2)$]. However, $N_2CH(CO_2Et)$ liberates N_2 and forms [$Re_2(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}CH_2CO_2Et)$].[74] With N_2CH_2, [$Re_2(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_8$] is formed. This decomposes at ca. 50 °C to give the very versatile 1,2-*eq*,*eq*-[$Re_2(CO)_8(THF)_2$].[19] Structure **9** is electronically unsaturated; therefore, it adds nucleophiles like [$Re(CO)_5$]$^-$ or [$Re_2H(CO)_9$]$^-$ to give open L-shaped trinuclear, **10**, or tetranuclear anions.



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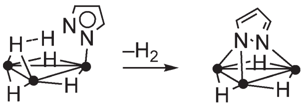
Alternative rational syntheses for open chain clusters and derived species have also been developed for long-chain oligomers [$Re(CO)_5\{ReH(CO)_4\}_{2n}$]$^-$ that can grow up to $n = 4$. Evidently, their stability cannot be compared to that of their isolobal CH_2 chains.[75,76] In fact, $Re(CO)_4H$ is isolobal with singlet methylene, as far as metal–metal bonds are concerned. Therefore, [$Re_2(\mu\text{-}H)_2(CO)_8$] is an analog of ethylene, and [$Re_3(\mu\text{-}H)_3(CO)_{12}$] and [$Re_4(\mu\text{-}H)_4(CO)_{16}$] are analogs of cyclopropane and cyclobutane, respectively. Building upon this concept, D'Alfonso and co-workers assembled the analogs of cyclopentane [$Re_5(\mu\text{-}H)_5(CO)_{20}$] and cyclohexane [$Re_6(\mu\text{-}H)_5(CO)_{20}$]$^-$ which have ring-puckering amplitudes very similar to those of the isolobal cycloalkanes.[77,78]

Following this concept, a series of homo- and heteronuclear clusters have been prepared in a rational way via the reaction of the ethylene-like dimer **9** with organometallic fragments with carbenoid character like $Pt(PPh_3)_2(C_2H_4)$ or (η^5-Ind)Ir(CO)(η^2-C_8H_{14}) in an isolobal mimick of cyclopropanation rather common in cluster chemistry.[79] The study of Re–Pt clusters built in this and other ways is very vast and its interest resides in their catalytic properties in petroleum refining.[80,81] The selective synthesis of the hydridotrirhenium cluster $Re_3(\mu\text{-}H)_3(CO)_{12}$ via direct hydrogenation of $Re_2(CO)_{10}$ by a solvothermal method in excellent yield has been described.[82] The related $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ **11** can be prepared in ca. 90% isolated yield by passing H_2 into a toluene solution of $Re_2(CO)_8(NCMe)_2$ at 80 °C.[83] Structure **11** reacts with C_{60} in refluxing chlorobenzene to give [$Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$] in 50% yield. One CO in **11** can be replaced by PPh_3 or $CNCH_2Ph$ by CO activation with Me_3NO or $PhCH_2N{=}PPh_3$, respectively.[84]

The reactions of **11** with the bidentate ligands HL–L^1 = 2-amino-6-methylpyridine (Hampy) and, 2-mercaptopyridine (Hmerpy) give the binuclear derivatives [$Re_2(\mu\text{-}L\text{-}L^1)_2(CO)_6$]. The unsaturated complex [$Re_4(\mu\text{-}H)_4(CO)_{12}$] reacts with the same HL–L^1 to give the trinuclear anions [$Re_3(\mu\text{-}H)_3(\mu_3\text{-}L\text{-}L^1)(CO)_9$]$^-$.[85]

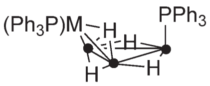
Protonation of $[Re_3(\mu\text{-}H)_3(\mu_3\text{-ampy})(CO)_9]^-$ with $[HOEt_2][BF_4]$ at low temperature liberates H_2 and affords the neutral unsaturated dihydride $[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9]$ unstable above 5 °C. Under CO, $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ is the main product whereas in the presence of PR_3 or alkynes the neutral derivatives $[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(PR_3)(CO)_9]$ (R = Ph; *p*-Tol) or$[Re_3(\mu\text{-}H)_3(\mu_3\text{-ampy})(\mu\text{-}RC{=}CHR^1)(CO)_9]$ ($R = R^1 = Ph$; Et; R = Ph, $R^1 = H$; R = H, $R^1 = Ph$) are the main products. The latter compounds are the first examples of trirhenium clusters containing alkenyl ligands which arise from the insertion of the corresponding alkyne into an Re–H bond.[86] Adducts between $[Re_3(\mu\text{-}H)_3(\mu_3\text{-ampy})(CO)_9]^-$ and the metal electrophile $[Au(PPh_3)]^+$,[87] and quantitative substitution reactions of $Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2$ by thioureas, have been described.[24]

The unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ reacts with neat pyridine, at room temperature, to give the orthometallated derivative $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ and H_2, instead of the expected addition product $[Re_3(\mu\text{-}H)_4(CO)_9(py)]^-$,which, however, is formed when THF is used as reaction solvent.[88] The related pyrazole complex $[Re_3(\mu\text{-}H)_4(CO)_9(Hpz)]^-$ **12** also evolves H_2 forming $[Re_3(\mu\text{-}H)_3(CO)_9(pz)]^-$ **13**, where the pyrazolate ligand adopts a new $\mu_3\text{-}\eta^2$ coordination (Equation (3)). Structure **12** presents an intramolecular dihydrogen bond resulting from the interaction of the N–H proton with the bridging hydride $(\mu\text{-}H)Re_2$. This H···H bond is retained in CH_2Cl_2 solution but replaced by intermolecular dihydrogen bonds in Me_2CO.[89]



12 ● = Re(CO)$_3$ **13** (3)

The reactivity of the related anion $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$ toward the coinage metal electrophiles $[M(PPh_3)]^+$ (M = Cu, Ag, Au) was investigated as part of the general electrophilic reactivity of these cations. The adducts **14** are formed.[90] When treated with PPh_3 in CH_2Cl_2 or by simple dissolution in Me_2CO, the initial complex is restored releasing $[ML(PPh_3)]^+$ (L = PPh_3, Me_2CO).



● = Re(CO)$_3$

14

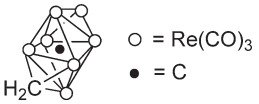
The highly reactive unsaturated cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ opened the way to a series of interesting transformations. It rapidly adds nucleophiles including the weak donor Cl^- to form $[Re_4(\mu\text{-}H)_4Cl(CO)_{12}]^-$ and up to four donor solvent molecules S = MeOH, Me_2CO, NCMe, dimethylformamide (DMF). Py leads to $[Re_3(\mu\text{-}H)_3(CO)_9(py)_3]$.[91] The adduct $[Re_4(\mu_3\text{-}H)_4(CO)_{12}(NCMe)_4]$ (two isomers) decomposes in solution to $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ (see **12** for analogous structure) and $[Re(CO)_3(NCMe)_3]^+$.[92] In the case of MeOH and Me_2CO, a similar intermediate adduct cannot be detected contrary to previous reports, and solvent removal reforms the initial compound according to the equilibrium in Equation (4).[93]

$$[Re_4(\mu\text{-}H)_4(CO)_{12}] \underset{-4\ \text{Solv}}{\overset{+4\ \text{Solv}}{\rightleftharpoons}} [Re_3(\mu\text{-}H)_4(CO)_9(\text{Solv})]^- + [Re(CO)_3(\text{Solv})_3]^+ \qquad (4)$$

In DMF, $[Re_3(\mu\text{-}H)_4(CO)_9][Re(CO)_3(DMF)_3]$ **15** is formed quantitatively. The structure of its 44e anionic cluster has an unsaturation at the Re atom not involved in an Re=Re double bond and readily forms $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ with L = CO, py, PPh_3, NCMe. In solution, VT NMR and IR spectra are consistent with a structure of $[Re_3(\mu_3\text{-}H)(\mu_2\text{-}H)_3(CO)_9]^-$ in which two double bonds are delocalized over the rhenium triangle.[94]

Dissolved in $CHCl_3$/DMF mixtures, **15** transforms into the anions $[Re_5H_7(CO)_{15}]^{2-}$ **16** and $[Re_4H_5(CO)_{12}]^-$ with the counterion $[Re(CO)_3(DMF)_3]^+$. Structure **16** is the first example of a 74-electron square-pyramidal pentatransition-metal cluster without a non-hydride interstitial atom; it undergoes further transformations in CH_2Cl_2/DMF mixtures. Depending on the composition, **15**, $[Re_4H_5(CO)_{12}]^-$, and $[Re_6H_7(CO)_{18}]^{2-}$ are formed.[95]

All the Re carbonyl hydrides $[Re_n(CO)_xH_y]^z$ discussed so far and many others previously known[1,2] span a total of 20 different structural types. The structural data available until 1997 is reviewed and analyzed from several different approaches and Re–Re distances converted into Re–Re bond enthalpies by the group of Wade.[96,97] The synthesis and structure of the novel 64-electron cluster anion $[HRe_4(CO)_{17}]^-$ with $Sm(Tp'_2)^+$ as counterion has only been recently reported.[3] Shapley and co-workers have continued the systematic development of the chemistry of the carbido cluster $[Re_7C(CO)_{21}]^{3-}$. Following two-electron oxidation, the monoanion $[Re_7C(CO)_{21}]^-$ **17** adds two-electron donors forming species like $[Re_7(CO)_{21}P(OPh)_3]^-$ in a process called oxidative substitution. Structure **17** obtained by oxidation with 2 equiv. of $[FeCp_2]^+$ reacts with N_2CH_2 to give anionic 18.

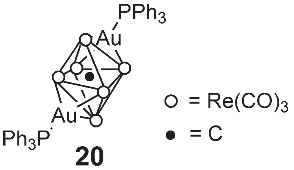


18

The CH_2 bridge occupies a position similar to that occupied by a bridging CO in $[Re_7C(CO)_{21}(\mu\text{-}CO)]^-$. Decapping of an $[Re(CO)_3]^+$ unit in NCMe solution forms $[Re_6C(CO)_{18}(CH_2)]^{2-}$ and $[Re(CO)_3(NCMe)_3]^+$.[98]

Since the anion $[Re_7C(CO)_{21})]^{3-}$ is isolobal with Cp^-, a number of complexes of type $[Re_7C(CO)_{21}(ML_n)]^{x-}$ **19** have been prepared with several ML_n fragments: $[Rh(CO)_2]$,[99] $[IrL(CO)]^+$, $[Ir(H)SiPh_3]^+$,[100] $[HgOH]^+$, $Hg(SC_6H_4Br]^+$,[101] $[HgOAc]^+$,[102] $[Hg_2]^{2+}$,[103] Tl^+, $[AuPPh_3]^+$.[101] Their structure is the same as 18 only replacing CH_2 by ML_n.

The carbido–hexarhenate cluster $[Re_6C(CO)_{19}]^{2-}$ can be capped by $Mo(CO)_4$ and $Re(CO)_3$ fragments in $[Re_6C(CO)_{18}\{Mo(CO)_4\}]^{2-}$ and $[Re_6C(CO)_{18}\{Ru(CO)_3\}]^{2-}$ photogenerated from $Mo(CO)_6$ and $Ru_3(CO)_{12}$, respectively. The $Mo(CO)_4$ fragment, but not the $Ru(CO)_3$, can be replaced by H_2, forming $[Re_6C(CO)_{18}(\eta\text{-}H_2)]^{2-}$. Deprotonation of the acidic H_2 complex with DBU (1 equiv.) affords the trianionic hydride $[Re_6C(CO)_{18}(H)]^{3-}$ which reacts with $AuCl(PPh_3)$ to give $[Re_6C(CO)_{18}(H)\{Au(PPh_3)\}]^{2-}$ with the Au fragment occupying a capping position *trans* to the Re–H–Re site. Excess DBU and 2 equiv. of $AuCl(PPh_3)$ lead to the bicapped $[Re_6C(CO)_{18}\{Au(PPh_3)\}_2]^{2-}$ **20**.[104] Related bicapped Re–Ir–Au and $ReHg_2$ clusters have been reported.[102]



20

5.13.2.3.3 $[Re(CO)]_6^+$

The interest in this rather substitutionally inert complex was recently renewed in connection with the development of new synthetic methods for the synthesis of $^{188}Re(CO)_3$ derivatives for radiopharmaceutical uses. Since radioactive $[Re(CO)_6]^+$ **21** can be obtained by disintegration of $^{188}W(CO)_6$, it can be viewed as an alternative source of the radioactive $[^{188}Re(CO)_3]^+$ fragment so far only available by reduction of $[^{188}ReO_4]^-$ under CO atmosphere. Indeed, Jaouen and co-workers showed that **21** is a useful starting material for the synthesis of $[Re\{C_5H_4C(O)R\}(CO)_3]$ by reaction with $Fe\{C_5H_4C(O)R\}Cp$ in HMPA, DMSO, or DMF solvent at ca. 160 °C. The tricarbonyl complexes $[Re(CO)_3L_3]^+$ (L = hexamethylphosphoramide (HMPA), dimethyl sulfoxide (DMSO), DMF) are intermediates in these reactions.[105,106] The corresponding NCMe derivative is inactive in this reaction but can form $CpRe(CO)_3$ by reaction with TlCp at 160 °C.[107] $Cp'Re(CO)_3$ functionalized for radiopharmaceutical purposes can be prepared from **21** and TlCp′ by the same route in DMF or DMSO in good yields.[107] Section 5.13.2.3.8.(i) presents a discussion on new methods of preparing biologically labeled $Cp'Re(CO)_3$ complexes.

5.13.2.3.4 $Re(CO)_5$ derivatives

The well-known and readily availabe halides $Re(CO)_5X$[1,2,108] are actually the classical basis for most of the preparative chemistry to be described for Re(I) complexes below. An alternative synthesis for $Re(CO)_5Cl$ from K_2ReCl_6 and CO/Na under pressure is available.[7] The classical method uses the reaction of $Re_2(CO)_{10}$ with X_2 (X = Cl, Br, I).[1,2] Only a few congener complexes with $X = R_2E^-$ (E = P, As) and $X = RA^-$ (A = S, SE, Te) have been made because they tend to decarbonylate easily due to the π-labilization of CO ligands by good π-donors. Indeed, even $Re(CO)_5F$ rapidly decarbonylates to the tetramer $[Re(CO)_3F]_4$.[109] and in spite of several attempts, no alkoxo complex $[Re(CO)_5(OR)]$ was ever isolated due to the facile dimerization of $Re(CO)_3(OR)$ resulting from CO loss induced by the OR ligand (see Scheme 6). However, as already mentioned above, a species formulated as $[Re(CO)_5(OSi{\equiv})]$ has been identified on a silica surface.[110] The unusual high–low oxidation state dinuclear complex $[Re^{I}(CO)_5(ORe^{VII}O_3)]$ has been characterized but is very labile in donor solvents. When dissolved in acetone, it readily forms $[Re(CO)_5(Me_2CO)][ReO_4]$ but upon evaporation reverts to the original formulation.[110] In contrast, $Re(CO)_5OTf$ is stable. The complexes $Re(CO)_5(TePh)$ and $[Re(CO)_5(TeMePh)][BF_4]$ have been reported in a study of the properties of the rare tellurium ligands (see also section $Re(CO)_3$ complexes).[111]

5.13.2.3.5 $Re(CO)_4$ derivatives

Re(I) derivatives of this fragment exist in any of the following general formulations: dimeric $[Re(CO)_4X]_2$, monomeric $Re(CO)_4LX$, and cationic $[Re(CO)_4L_2]^+$ complexes. Some polynuclear species are obtained from multidentate ligands L bridging several $Re(CO)_4$ fragments. A large number of $[Re(CO)_4X]_2$ dimers have been reported in earlier days, generally obtained by room-temperature spontaneous or thermally induced decarbonylation of $Re(CO)_5X$, or by the oxidative additions to $Re_2(CO)_{10}$ described above.[1,2] In the present coverage relatively few advances are done in this chemistry with exception of the compounds prepared for photophysical studies, and the synthesis of the highly reactive $[Re(CO)_4(Et_2O)_2]BF_4$ **22**.

The high electrophilicity of the $[Re(CO)_4]^+$ fragment supports nucleophilic addition to CO with the formation of anionic acyls. The phosphido-bridged complex $[Re_2(\mu\text{-}PPh_2)_2(CO)_8]$ reacts with LiR (R = Me, Bu, Bu^t, Ph) at low temperature forming $Re(CO)_4(\mu\text{-}PPh_2)_2Re(CO)_3\{C(O)RLi\}$. Reaction of this anion with $AuClPPh_3$ ends in an unusual type of acyl rearrangement. Instead of the expected Re–acyl species, the first reported acyl–gold complexes *O*-bound to the $[Re_2(\mu\text{-}PPh_2)(CO)_7]$ complex, $Re(CO)_4(\mu\text{-}PPh_2)_2Re(CO)_3\{O{=}C(R)AuPPh_3\}$ are formed.[112] Not surprising is the synthesis of formyl complexes *fac*-$[Re(CO)_3(P\text{–}P)(CHO)]$ in excellent yields from *fac*-$[Re(CO)_4(P\text{–}P)]^+$ (P–P = 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp)) and $NaBH_4$. Solutions of these formyls undergo spontaneous loss of CO to give the corresponding hydrides, *fac*-$[Re(CO)_3(P\text{–}P)H]$.[113]

cis-$[Re(CO)_4(PPh_3)F]$ made from *cis*-$[Re(CO)_4(PPh_3)Me]$ and anhydrous HF is more stable than $Re(CO)_5F$. The similarly made teflate *cis*-$[Re(CO)_4(PPh_3)(OTeF_5)]$ is significantly less stable than the fluoride as a solid.[109]

A series of complexes of halophosphines and arsines with general formula *cis*-$[Re(CO)_4X(EMe_2X)]$ (E = P, As; X = Cl, Br, I) have been prepared from either $Re(CO)_5X$ or $Re_2(CO)_8X_2$ and the ligand. Their reactions with $[M(CO)]^-$ (M = Mn, Re) give binuclear complexes of type $[ReM(\mu\text{-}EMe_2, \mu\text{-}X)(CO)_8]$ via initial substitution at the E–X bond.[114] The congener selenate complex $Re_2(\mu\text{-}SePh)_2(CO)_8$ has also been reported.[111]

The tetranuclear complexes $\{[Re(CO)_4Cl]_4(\mu\text{-}TCNX)\}$ (TCNX = tetracyanoethylene tetracyanoquinodimethane) are considered as potential central units for divergent dendrimer synthesis with a low-energy acceptor in the center. Indeed, Re(I) to TCNX MLCT absorptions appear in the near-infrared region, an interesting property.[115] $[Re(CO)_4$(8-quinolinolate)] and xanthate $Re(CO)_4(S_2COEt)$ diverge in photophysical properties since the former has green fluorescence and red phosphorescence at room temperature,[116] while the latter is not luminescent.[117] The spectroscopy and redox chemistry of $Re(CO)_4$(daad)Br (daad = 2,6-diazaanthracene-9,10-dione) has also been studied and its ligand-based radical monoanion isolated as the $[CoCp_2]^+$ salt.[118] A similar study was carried out with 3,5-di-Bu^t-1,2-benzosemiquinone (DBSQ) complex, $[Re(CO)_4(DBSQ)]$,[119] and highly luminescent $Re(CO)_4L$ complexes derived from naphthyridyl ligands have recently been reported.[120]

The bis-etherate cation $[Re(CO)_4(Et_2O)_2]^+$ **22** is prepared from $Re(CO)_4(\eta^3\text{-}C_3H_5)$ with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2.[121] It is a versatile starting material for the preparation of derivatives of the $[Re(CO)_4]^+$ unit including $[Re(CO)_4(H_2O)_2]^+$. Somewhat surprisingly, none of the dianions oxalate or squarate replaces the H_2O ligands remaining as counterions. However, nitrile, isonitrile, and thiother complexes are readily prepared from **22**, for example, $[Re(CO)_4(NCR)_2]^+$ (R = Me, CH_2CO_2Et) and $[Re(CO)_4(S\text{–}S)]^+$ (S–S = $PhSCH_2SPh$, $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$).[121] Likewise, protonation of *cis*-$[Re(CO)_4(PR_3)Me]$ **23** (R = Ph, Pr^i, Cy) with $[H(OEt_2)_2][BArF]$ in Et_2O affords *cis*-$[Re(CO)_4(PR_3)(OEt_2)][BArF]$ in very high yields. The Et_2O molecule is strongly bound and is not solvolyzed by CH_2Cl_2. However, *cis*-$[Re(CO)_4(PR_3)(solvent)][BArF]$ (solvent = CH_2Cl_2, Et_2O, NC_5F_5) are obtained in high yields by methyl abstraction from **23** with $[Ph_3C][BArF]$ in CH_2Cl_2 solution. These adducts are moderately air stable in solid and solution. Slow decomposition of their CH_2Cl_2 solutions at room temperature forms chloride-bridged dimers $\{cis\text{-}[Re(CO)_4(PR_3)]_2(\mu\text{-}Cl)\}[BArF]$.[67,122] H_2 gas (3 atm) replaces CH_2Cl_2 affording the highly acidic H_2 complex $[cis\text{-}Re(CO)_4(PR_3)(\eta^2\text{-}H_2)][BArf]$ (see Section 5.13.2.3.1). In the related complexes $[Re(CO)_4L(CH_2Cl_2)][BArF]$, where L is the tied-back phosphite $P(OCH_2)_3CMe)$, CH_2Cl_2 is readily displaced by Et_2O, *cis*-cyclooctene, and Et_3SiH to afford ether-, alkene-, and η^2-H–$SiEt_3$-coordinated complexes less stable than their $[Re(CO)_3(PR_3)_2]^+$ congeners (see $Re(CO)_3$ complexes).[123] H_2 replacement from $[Re(CO)_x\{P(OEt)_3\}_{4-x}(\eta^2\text{-}H_2)]^+$ by hydrazines $RNHNH_2$ (R = H, Me, Ph) is straightforward. Oxidation of the resulting complexes at −40 °C leads to diazene complexes $[Re(RN{=}NH)(CO)_x\{P(OEt)_3\}_{4-x}]BPh_4$. In the case of R = Me, stabilization of the elusive methyleneimine, $HN{=}CH_2$, was achieved in $[Re(\eta^1\text{-}NH{=}CH_2)(CO)_x\{P(OEt)_3\}_{4-x}][BPh_4]$ for the first time.[124]

Schoonover and co-workers have recently re-examined previous data on the excited-state photodynamics of a series of $[Re(CO)_4(\alpha\text{-diimine})]^+$ complexes by means of time-resolved infrared spectroscopy (TRIR). These materials exhibit unique excited-state behavior consistent with a reaction pathway for photodissociation to an $Re(CO)_3$ complex, arising from coupling of the MLCT state to the lowest-lying nominally LC excited state.[125] Similar studies have been performed for a number of substituted bipyridine derivatives of the $[Re(CO)_4]^+$ core assigning the nature of the luminescence properties as a function of the substituents on the rings.[126]

5.13.2.3.6 Re(CO)$_3$ derivatives: mononuclear complexes

The number of complexes in this class has grown extensively in the last decade making it the most populated fragment of Re carbonyl complexes. The three CO ligands in the octahedral d^6 $[Re^I(CO)_3L_3]^z$ complexes may present two stereochemical arrangements: facial or meridional. The former is overwhelmingly dominant due to maximization of π-backbonding to CO. However, a relatively small number of complexes displaying a meridional arrangement of the CO ligands is known,[1,2] and their kinetic formation can depend on the method of preparation as demonstrated by Alberto on the reductive low-pressure carbonylation of Re oxides to be presented below.[127]

The very large number of *fac*-$[Re^I(CO)_3L_3]^z$ complexes results from most of them being prepared having in mind the study of their properties either to understand the fundamental issues underlying photophysical applications or to achieve specific targets within biological areas of application. In fact, relatively few reactivity studies have been reported in the last decade. In contrast, rather innovative synthetic approaches to these complexes have appeared. In order to organize the presentation and facilitate tabulation, the types of compounds available have been divided according to complex charge and ligand denticity as summarized in Figure 1.

The number of anionic complexes of types I–III is rather small for they have no particular applicational value per se except for the use of their common parent species, $[Re(CO)_3X_3]^{2-}$ (X = Cl **24**, Br **25**) as highly versatile starting materials. These trihaloanions had been prepared before by a classical reaction between $Re(CO)_5X$ and E_4NX but became more conveniently accessed by a totally new route: the low-pressure reductive carbonylation, which uses cheap Re precursors $[ReOCl_4]^-$ or $[ReO_4]^-$ at atmospheric CO pressure (Equation (5)).[128]

$$\begin{array}{c}[ReOCl_4]^- \\ \text{or} \\ [ReO_4]^-\end{array} \xrightarrow[\text{ii, } NEt_4X]{\text{i, } BH_3{\cdot}THF/ \text{ CO (1 atm)}} fac\text{-}[Re(CO)_3X_3][NEt_4]_2 \qquad (5)$$

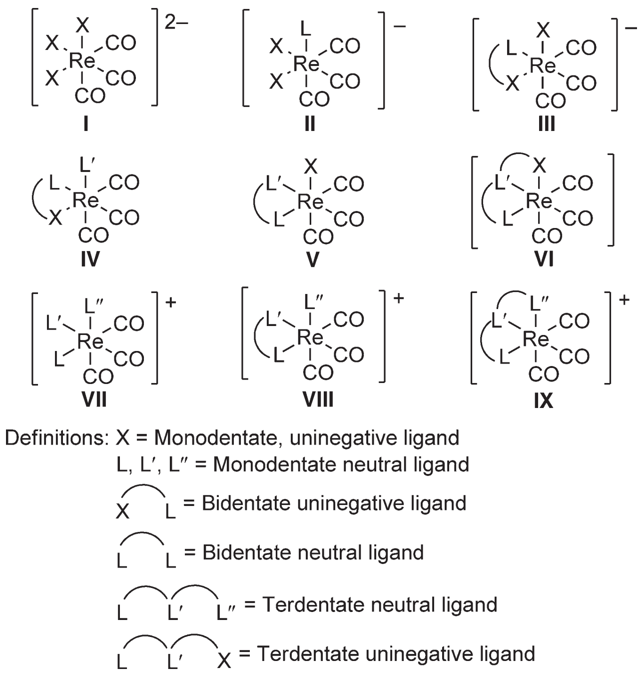


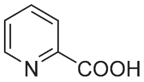
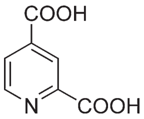
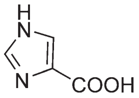
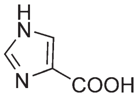
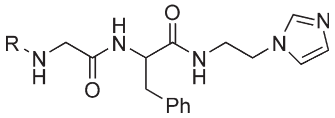
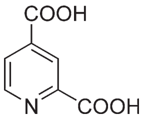
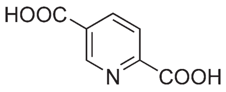
Figure 1 Types of *fac*-$[Re^1(CO)_3L_3]^2$ complexes resulting from different combinations of ancillary ligands.

Reduction of the same oxides with coordinating PR_3 under CO leads to *mer*-$[Re(CO)_3(PR_3)_2X]$ isomers and not to the *fac*-isomers exclusively formed with the weakly coordinating BH_3 reducing agent.

Both **24** and **25** readily hydrolyze in water to give air stable $[Re(CO)_3(H_2O)_3]^+$ **26**, a stabilized strong Lewis acid that readily adds a variety of ligands to produce *fac*-$[Re(CO)_3]^+$ derivatives of almost all other classes considered here. The mild conditions of this synthesis as well as the facile substitution of the Br^- ligands assume exceptional relevance in the field of the synthesis of *fac*-$Re(CO)_3$ derivatives bearing highly functionalized ligands, usually carrying biomolecules, for use in radiopharmaceutical applications (diagnosis or therapy). This chemistry has been developed hand in hand with that of the analogous Tc derivatives that are particularly appropriate for diagnostic and imaging uses. The topic will be discussed in Section 5.13.2.3.8.(i).[127,129] Solvolysis in NCMe and other solvents is slower than in water but can be accelerated by Br^- abstraction to give $[Re(CO)_3(Solv)_3]^+$ complexes, where Solv denotes a donor solvent.[130] $(Et_4N)[Re(CO)_3Br_2(NCMe)]$ crystallizes from a hot acetonitrile solution of **25** despite the fact that in solution only $[Re(CO)_3(NCMe)_3]^+$ can be detected spectroscopically.[130] $[Re(CO)_3(NCS)_3]^{2-}$ is obtained from **25** in high yield and purity using Me_3SiNCS.[131]

The neutral complexes *fac*-$[Re(CO)_3(\kappa^2\text{-L-X}')L^1]$ (type IV) have become important for the development of $Re(CO)_3$ derivatives bearing ligands carrying a pendant biomolecule selected or designed to target the complex to specific biological receptors or tissues. Starting from **26** the reaction of monoanionic bidentate ligands leads to neutral *fac*-$[Re(CO)_3(L–X)(H_2O)]$ complexes that are particularly amenable to substitution of the H_2O ligand by other ligands L^1. The *fac*-$[Re(CO)_3(L\text{-}X')L^1]$ complexes produced in this way possess a wide margin of potential for the attachment of biomolecules and for the tuning of their physicochemical properties. Furthermore, they can be readily prepared in aqueous solution. The biomolecule can be appended either to the $(L–X)'$ ligand or to L^1. In the former case, the tuning of the properties of the biologically active complex can be done by variation of L^1. This is called the [2B + 1]-approach. In the second case, it is L^1 that carries the biological molecule responsible for the targeting properties of the whole complex: the [2+1B]-approach.[132] Some examples of molecules of this type are given in Table 2.

Table 2 Complexes of type *fac*-$[Re(CO)_3(\kappa^2\text{-L-X}')L^1]$ designed for biological application

Bidentate ligand (L–X)	*L^1*	*References*
	H_2O	179
	H_2O	132, 179
	H_2O or imidazole	132
		132
	$CNCH_2Ph$	132
	H_2O or imidazole	132

The dimer $Re_2(CO)_6(OX)_2$, obtained from $Re(CO)_5Cl$ and HOX (HOX = 8-hydroxyquinoline) in boiling toluene, is solvolyzed in polar solvents (Solv) to monomeric [$Re(CO)_3(OX)(Solv)$] which display luminescent properties.[133]

A large number of neutral complexes of formula *fac*-[$Re(CO)_3L_2X$] (X = H, CN, NR_2, PR_2, OR, SR, halide) have been prepared almost invariably by the straightforward halide substitution from $Re(CO)_5X$ with the ligand in refluxing benzene or toluene but solvents like $MeOH/CHCl_3$ have been used. The halides can be replaced by other pseudohalides (CN, NR_2, PR_2,OR, SR) or by weakly binding anions like $[BF_4]^-$ or $[OTf]^-$ (triflate) in the later case by reaction of their Ag^+ salts with the halides $Re(CO)_3L_2X$. A huge variety of bidentate ligands, with group 15 and group 16 ligands as well as mixed ligands have been used. Table 3 lists many reported complexes in this class thus highlighting the variety of the donor functionalities. Since most of the complexes have been designed to meet specific aims, the respective keywords are entered in the table. The majority of the complexes feature α-diimine type ligands, for example, bipyridines, phenanthrolines, 1,4-diazabutadienes (DABs), bipyrimidines, which have useful photophysical and electrochemical properties, the origin of which is already established.[1,2] However, many other *N*-donors are exemplified, like pyrazolyls, pyrazines, or diazo compounds and a wide choice of bifunctional N–L (L = N, P, O, S) ligands has also been used and designed for specific purposes. Recently, several reports investigated the coordination of the *fac*-[$Re(CO)_3Cl$] fragment to a number of biologically relevant molecules such as pteridines (pterins and lumazines),[134,135] riboflavin[136] and characterized their photophysical and electrochemical properties under the general terms described below for $Re(CO)_3$ complexes. The interactions of the group 7 metal carbonyl halides $M(CO)_5X$ (X = Cl, Br, I) with 1 mol equiv. of a variety of diphosphines (P–P) have been investigated extensively and give exclusively *fac*-[$M(CO)_3(\kappa^2$-P–P)X].[1,2] However, when excess P–P is used, binuclear complexes with one bridging P–P ligand or one dangling PR_2 group may be formed depending on the nature of the phosphine and other factors.[137] The new complexes derived from PR_3, $P(OR)_3$, as well as O and S ligands are comparatively few.

Structurally, the *fac*-$[Re(CO)_3]^+$ fragment has a remarkable stereochemical stability. As a result, the *fac*-$Re(CO)_3X$ or *fac*-$[Re(CO)_3L]^+$ moieties provide two coordination positions of *cis*-stereochemistry. The coordination of potentially terdentate ligands to these fragments leaves one of the donor atoms pending out of the coordination sphere. The propensity of this pendant ligand to attach to the metal results in a fluxional mechanism of exchange of both bound and pendant external groups, that is to say, between both possible bidentate environments available to the ligand. The terpy ligand provides the prototypical example first identified by Abel in 1992. This linkage isomerization is a metallotropic 1,4-M–N shift and has been the subject of a number of dynamic NMR studies conducted mainly by Abel, Orrell, Sik, and Heard using a large array of planar, potentially tridentate ligands depicted in Table 4.

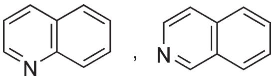
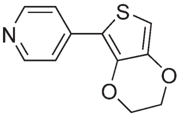
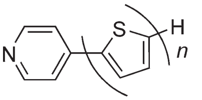
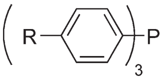
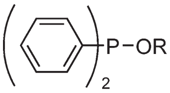
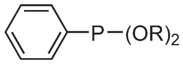
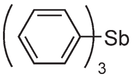
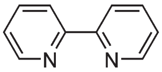
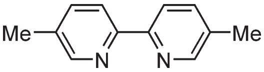
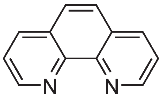
The three mechanisms proposed for this fluxional process are depicted in Scheme 9.

The rotation mechanism involves loosening of the Re–N_3 bond followed by 180° rotation of the $ReX(CO)_3$ moiety via a five-coordinate intermediate to produce the original structure. The tick-tock twist mechanism involves the loosening of both Re–N bonds followed by a twist of the $ReX(CO)_3$ moiety through an angle equal to the N_1–Re–N_2 angle via a seven-coordinate intermediate to produce the enantiomer of the original structure. The mechanism proposed by Rotondo and co-workers for (terpy)MXR_3 (M = Pd, Pt) complexes is dissociative but could be considered as another option. Recently, a closer look at the mechanisms was carried out using chiral centers on the pendant oxazoline ligands (Table 4). These provide an excellent handle to distinguish between otherwise invisible pathways of the movement of the fluxions. Studies using complexes with pendant oxazolines and 1,3-dioxan chiral groups led to the following conclusions that essentially confirmed and wrapped up the whole theme: (i) the rotation and tick-tock twist mechanisms occur simultaneously but the former has $\Delta G^\ddagger \sim 10\,\mathrm{kJ\,mol^{-1}}$ higher presumably because it implies more extensive bond cleavage in the transition state; (ii) the nature of X does not influence $\Delta G^\ddagger$ for the tick-tock pathway but has a large effect on the $\Delta G^\ddagger$ of the rotation mechanism; (iii) the dissociative mechanism cannot be entirely ruled out but the data does not support it in a clear way; (iv) among all ligands reported, the highest values of $\Delta G^\ddagger$ are found for the oxazoline and 1,3-dioxan pendant groups, probably reflecting a very facile and strong coordination of the pendant donors.[138,139] Upon increased reaction temperature, decarbonylation takes place due to coordination of the pendant ligand, for example, $Re(CO)_2(\kappa^3$-terpy)X.

In contrast, potentially tridentate phosphines do not display any similar fluxional behavior. The complexes *fac*-[$Re(CO)_3(\kappa^2$-triphos)X] (X = Cl, Br) adopt a chair or a boat conformation of the ReP2C3 ring. The pendant phosphine can be oxidized,[140] or alkylated with MeI.[141] Compared to the photophysical and electrochemical studies, not much new chemistry was carried out on complexes of this type and most of it came from the group of Riera.

Like in its $Re(CO)_4$ congeners, the CH_2Cl_2 in the complex [$Re(CO)_3L_2(CH_2Cl_2)$][BArF], prepared by reaction of [$Re(CO)_3L_2Me$] with [Ph_3C][BArF] in CH_2Cl_2, is readily displaced by Et_2O, *cis*-cyclooctene, and Et_3SiH. The η^2-(H-$SiEt_3$) complex is stable in solution at RT and is a rare example of an isolable cationic silane complex.[123] [$Re(CO)_4(PR_3)(\eta^2$-H-$SiEt_3$)] is less stable (see Section 5.13.2.3.1).

Table 3 Selected neutral complexes of general formulas $Re(CO)_3L_2X$, $Re(CO)_3(L–L)X$, and $Re(CO)_3(L–L^1)X$

	X	*Keywords*	*References*
Monodentate ligands			
	Cl	Photochemistry and photophysics	630
	Cl	Luminescence	631
 *n* = 1, 2			
 R = H, Me	Cl	Luminescence	632
  R = Me, Et	Br		633
	Cl		634
Bidentate N ligands			
	Cl	Fast time-resolved IR; Emission upon 1 and 2 photon excitation; Excited state transfer	635–637
	NRR^1, PPh_2, OR, SR	Excited state transfer	142
	Cl, CN	Electrochemistry and spectroelectrochemistry	225
	Cl, Br, I	Halide dependence of spectroscopic parameters	638
	Cl	Photo- and electro-catalyzed CO_2 reduction	219 and references therein
	Cl	Excited state transfer	637
	Cl	Excited state transfer	637
	NRR^1, PPh_2, OR, SR	Excited state transfer	142

(*Continued*)

Table 3 (Continued)

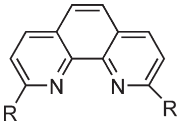
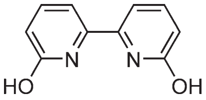
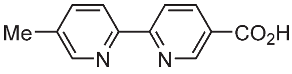
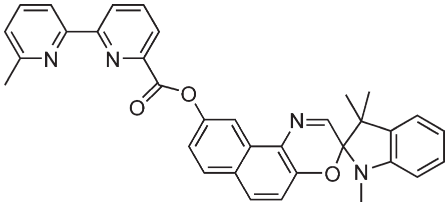
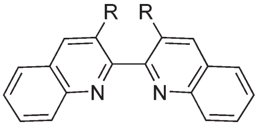
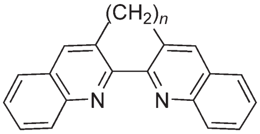
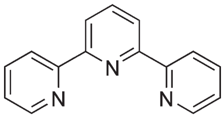
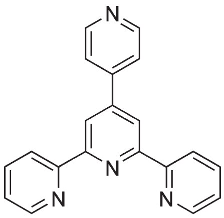
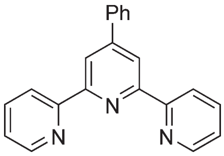
	X	*Keywords*	*References*
	Cl, CN	Electrochemistry and spectroelectrochemistry	225
	btpz	Electroluminescence	249
 R = Me, Ph	Cl	Excited state transfer	637,639
	Cl	Optical properties	640
	Cl	Optical properties and acid–base behavior	641
	Cl	Photochromism, electrochemistry	198
 R = H, Me	Br	Spectroscopical and electrochemical correlations	642–645
 *n* = 2, 3			
			
			
			

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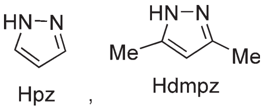
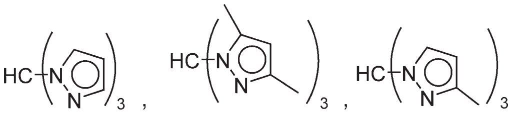
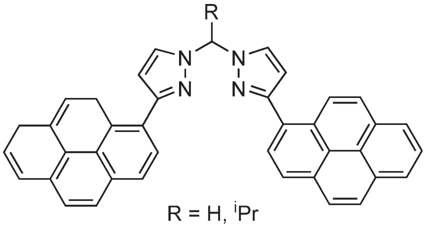
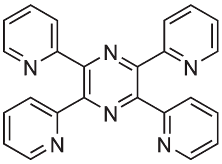
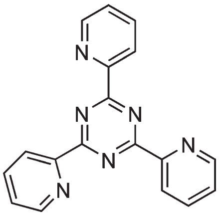
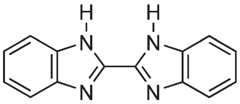
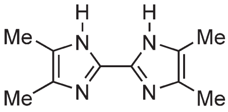
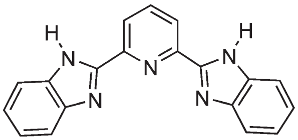
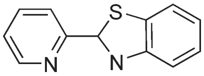
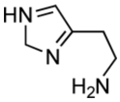
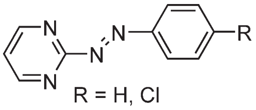
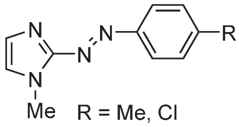
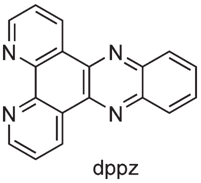
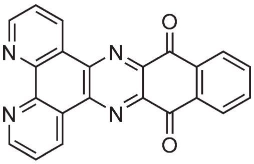
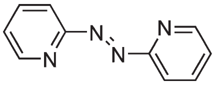
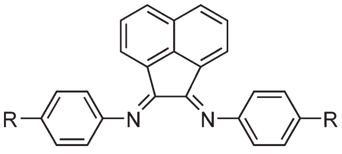
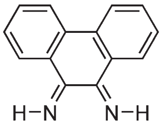
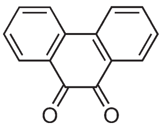
Table 3 (Continued)

	X	*Keywords*	*References*
	Br, pz, Me_2pz	Structure and chemistry	646
	Br	Structure and radiopharma	647
	Br	Interactions between luminescent ligands and metal fragment	648
	Cl, Br	Multiple coordination modes; polynuclear complexes	649
	Cl	Polynuclear complexes	650
  	Cl	Luminescence	651
	Cl, Br, TfO	Radiopharma	652
	Br	Radiopharma	155

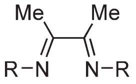
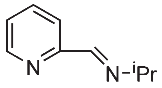
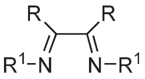
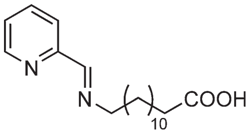
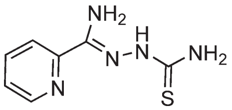
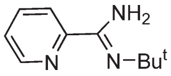
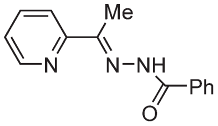
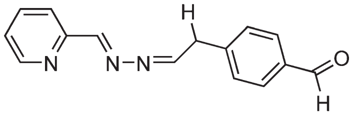
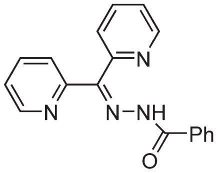
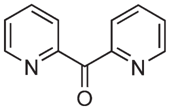
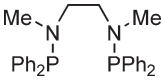
(*Continued*)

Table 3 (Continued)

	X	*Keywords*	*References*
 R = H, Cl	Cl	Isolable radical anions	226
 R = Me, Cl			
 dppz	Cl	Spectroelectrochemistry, resonance Raman	653
 dppn	Cl, TfO	Excited state, charge separated systems	654
	Cl, Br, I	Spectroelectrochemistry, ESR	230,655
 R = H, Me, OMe, Cl	Cl	Non-luminescent	656
 R = H, Me, OMe, Cl	Cl	Non-luminescent	657
	Cl	Spectroscopy, Non-luminescent	658
			
 R = Ph, *p*-Tolyl, anisyl	Br	Photophysics	313

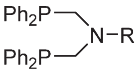
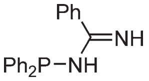
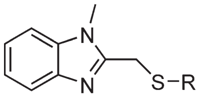
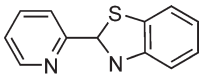
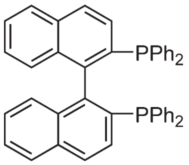
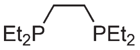
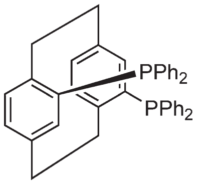
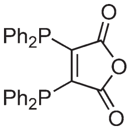
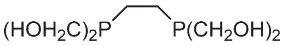
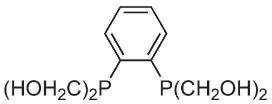
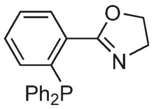
(*Continued*)

Table 3 (Continued)

	X	*Keywords*	*References*
 R = Ph, *p*-Tolyl, *p*-fluorophenyl, anisyl, NPh_2	Br	Photosensitization, photoresponsive polymers	659
 	Cl, Br, I	Halide dependence of spectroscopic parameters	638
 R, R^1 = Me, Ph	Cl	Non-luminescent	660
	Br	Radiopharma	183
	Br	Radiopharma	661
			
	Br	Radiopharma	662
			
			
			
	Br	Structure	663

(*Continued*)

Table 3 (Continued)

	X	*Keywords*	*References*
 R = Ph, CH_2COOH, CH_2CH_2OH, CH_2COOR^1, $CH_2CO\text{-}NHCH_2COOR^1$	Br	Radiopharma (P–P) donor, anti-tumoral	664
	Cl, Br		665
 R = Me, ${}^tBu$	Cl	Electrochemistry	288
	Br, OTf	Radiopharma	666
	Cl	Luminescence	667
	Cl	Luminescence	632
	Cl	Luminescence	668
	Br	Spectroelectro-chemistry	229
 	Br	Radiopharma	669
	Br	Radiopharma (P–N) donor	670
	TfO, BF_4	Weakly binding ligands	671

(*Continued*)

Table 3 (Continued)

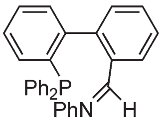
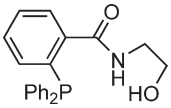
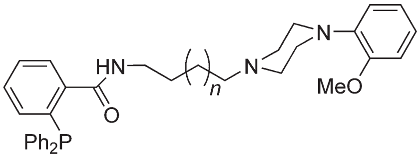
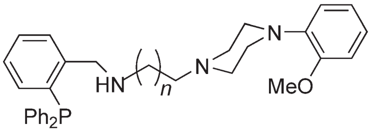
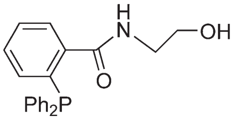
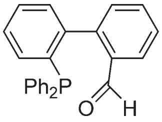
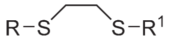
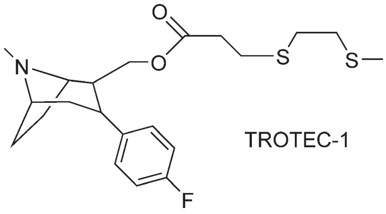
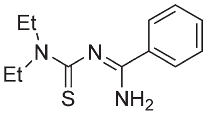
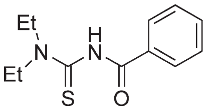
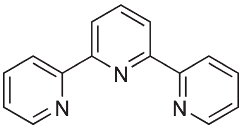
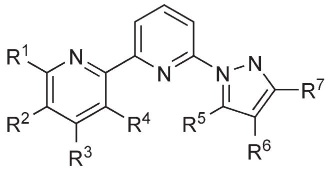
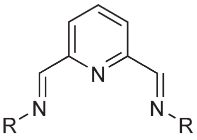
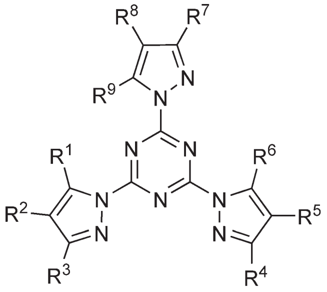
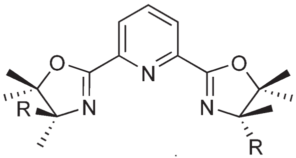
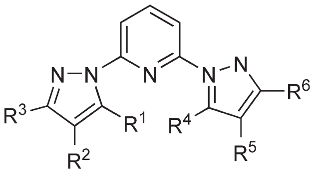
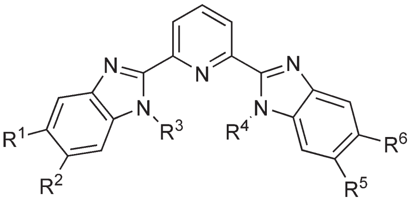
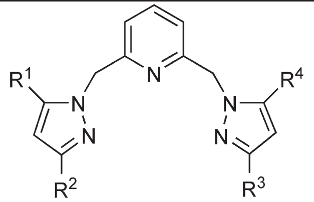
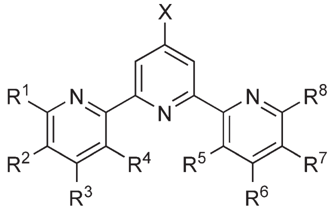
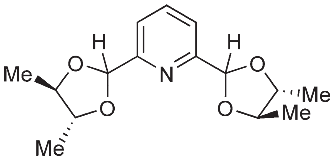
	X	*Keywords*	*References*
	Cl	Radiopharma (P–N) donor	666
	Br	Radiopharma (P–O) donor	670
  	Br	Radiopharma (P–O) donor	672
	Cl	Radiopharma (P–O) donor	666
 R, R^1= CH_2COOH, CH_2CH_2OH, CH_2CCH	Br	Radiopharma	186
 TROTEC-1	S–S	Imaging agent	185
 	Br	Radiopharma	673

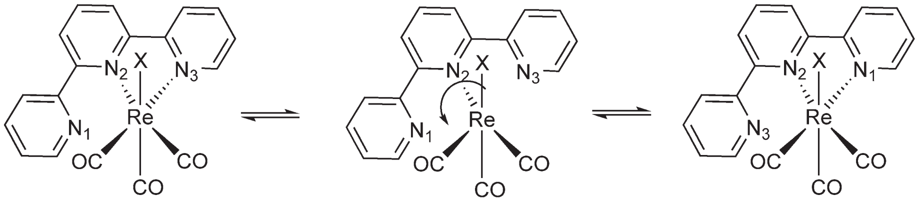
Table 4 Potentially planar tridentate ligands used in fluxionality studies on $Re(CO)_3(\kappa^2\text{-}L\text{–}L\text{–}L)X$ complexes ($X = Cl, Br, I$)

Ligand	*References*
	164
 R^x = H, Me; three substitution patterns	674
 R = Ph, Bn	676
 R^x = H, Me; five substitution patterns	678,679
 R = Me, ^{i}Pr	138,680
 R^x = H, Me; six substitution patterns	163
 R^x = H, Me; four substitution patterns	675

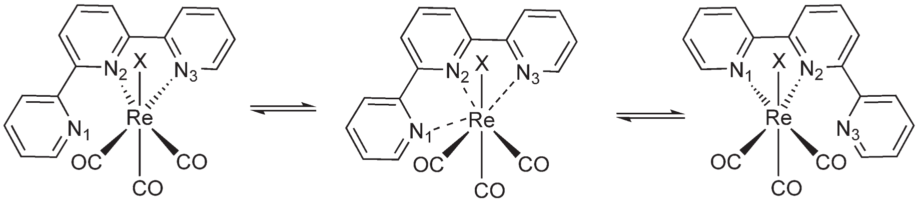
(*Continued*)

Table 4 (Continued)

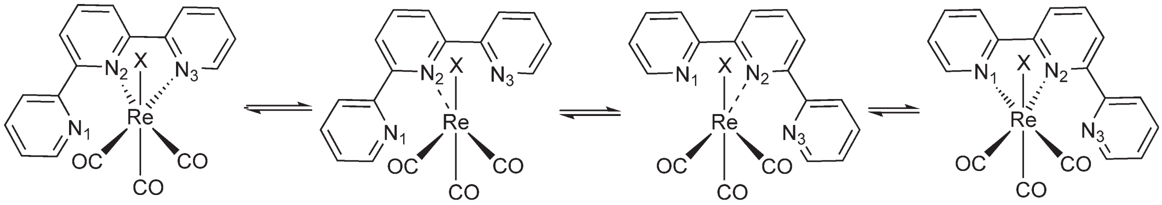
Ligand	*References*
 R^x = H, Me; two substitution patterns	677
 R^x = H, Me, Bu^t; three substitution patterns, X = Cl, SMe	675
	139



Rotation mechanism

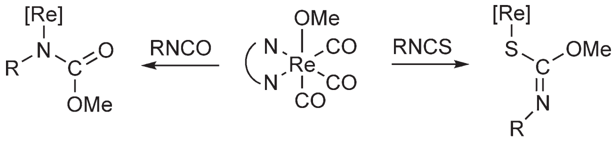


Tick-tock twist mechanism



Rotondo's dissociative mechanism

Scheme 9



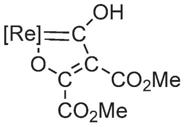
[Re] = Re(CO)$_3$(α-diimine); R = alkyl, aryl

Scheme 10

Reaction of [Re(CO)$_3$(N–N)(OTf)] (N–N = bipy, phen) with KNR$_2$ forms the amido complexes [Re(CO)$_3$-(N–N)](NR$_2$)] (R = H, Ph), which react with PhOH, EtSH, and PPh$_2$H to give [Re(CO)$_3$(N–N)(OPh)], [Re(CO)$_3$-(N–N)(SEt)], and [Re(CO)$_3$(N–N)(PPh$_2$)], respectively. The lone pair of the amido N atom is delocalized over the aromatic ring and the ligand is planar in contrast to the PPh$_2$ ligand that is pyramidal.[142] The alkoxides [Re(CO)$_3$-(N–N)(OR)] (R = Me, Et, Bu^t; N–N = bipy, 4,4′-Me$_2$bipy, phen), are readily made from the triflate. The insertion of unsaturated substrates like RNCO, RNCS (R = alkyl, aryl), CS$_2$, tetracyanoethylene(TCNE), and dimethyl acetylenedicarboxylate(DMAD) into the Re–O and Re–N bonds has been studied and template cyclizations are achieved.[143–146] The insertion mode of RNCO and RNCS (slower) is different (scheme 10).

The insertion of CO$_2$ into the OR bond of Re(CO)$_2$(PR$_3$)$_2$(OR) to form alkylcarbonato complexes is known.[2] Interestingly, reaction of Re$_2$(CO)$_{10}$ with dppp in PrOH/1-pentanol in the presence of air or CO$_2$ gives directly *fac*-[Re(CO)$_3$(dppp){O(O)COPr}] together with *fac*-[Re(CO)$_3$(dppp)H] and CO. The hydride becomes the only product when the reaction is carried out under inert atmosphere. Although attractive, this one-pot reaction that absorbs CO$_2$ from the air, has some restrictions since it does not work when 1-pentanol is the only alcohol used.[147]

The chemistry of the hydroxo complexes [Re(CO)$_3$(N–N)(OH)] (N–N = bipy, Me–2-bipy) prepared in a biphasic H$_2$O/CH$_2$Cl$_2$ medium by reaction of [Re(CO)$_3$(N–N)(OTf)] with KOH has been studied. They can be converted into the dimer [{Re(CO)$_3$(N-N)}$_2$(μ-OH)]OTf by protonation. PhNCO inserts into the O–H bond, alkyl and aryl isothiocyanates insert into the Re–O bond, and DMAD gave **27** in which the metallacycle includes DMAD, OH, and one CO.[148]



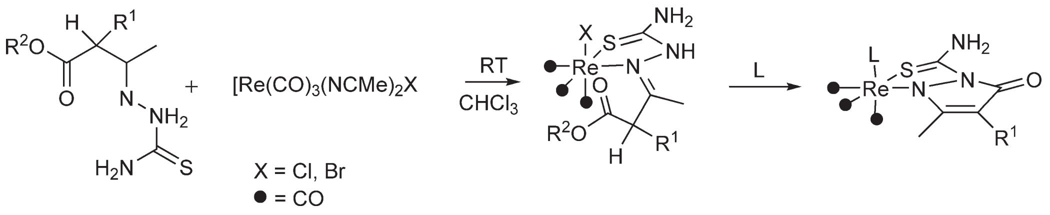
[Re] = Re(CO)$_3$(bipy)

27

The insertion of RCNO into [Re(CO)$_3$(N–N)(NRAr)] takes place across the N–H (R = H) or the Re–N bond (R = Me).[149]

The Lewis acidity of the the Re(CO)$_3$Cl fragment and its rigid *fac*-Re(CO)$_3$ conformation have been used for several purposes. A report presents a templated, controlled, stepwise, cyclization of monothiosemicarbazones derived from β-keto esters to give coordinated pyrazolones a class of compounds with anti-inflammatory properties (Scheme 11).[150]

Also, Re(CO)$_3$Cl was used to compare properties of the family of R$_2$E ligands (E = S, Se, Te) in the derivatives Re(CO)$_3$(L–L)X (X = Cl, Br; L–L = MeTe(CH$_2$)$_3$TeMe, PhTe(CH$_2$)$_3$TePh, *o*-C$_6$H$_4$(TeMe)$_2$). Comparative spectroscopic data for these and analogous thio- and selenoether species show that the telluroether compounds have significantly enhanced σ-donation compared with the lighter S and Se analogs, in accord with theoretical predictions.[111,151]



Scheme 11

The neutral type VI complexes $[Re(CO)_3(\kappa^3\text{-}L\text{–}L^1\text{–}X)]$ featuring a tridentate mononegative ligand have their paradigmatic example in the long-known classical scorpionate complex $TpRe(CO)_3$.[2] This and other Tp′ species have been prepared from $Na[RB(pzR)_3]$ and $Re(CO)_3L_2X$ but cannot be prepared from either **25** or **26** due to decomposition to a number of species with pz ligands.[152,153] In contrast, the soft scorpionate complexes bearing the mercaptoimidazolyl ligand, are readily formed from either **25** or **26** like the complex $[CpCo\{PO(OR)_2\}_3]Re(CO)_3$ resulting from $[CpCo\{PO(OR)_2\}_3]Na$ and $[Re(CO)_3(H_2O)_3]^+$.[154] Further examples have been dictated by the need to obtain biologically compatible complexes with appropriate pharmacokinetic properties. The search for new combinations of donor atoms and the synthesis of the respective ligands has been absorbing most of the energies in this area. A number of ligand types, for example, pyridine hydrazines and thiosemicarbazones, that were essentially absent from the organometallic chemist's lexicon, are now actively explored. Some examples are given in Table 5 most of which were prepared from the tris-aqua complex **26** or its precursor **25**.

The cationic $[Re(CO)_3(L)(L^1)(L^2)]^+$ type VII complexes have been essentially described at the beginning of this section (L = NCMe, DMSO, HMPA, DMF) and by **26**. All of them are used as convenient starting materials. The substitution reactions of **26** show that aliphatic amines, halides, and carboxylates coordinate weakly to the *fac*-$Re(CO)_3$ fragment. Thioethers and thiourea coordinate strongly but under slow kinetic formation. The best ligands both on thermodynamic and kinetic grounds are aromatic amines which are selected as useful anchors for the attachment of biomolecules to this fragment. Studies with imidazole (monodentate), histamine (bidentate), histidine (tridentate), and pyridine hydrazone ligands led the path for the assembling of biomolecules around *fac*-$Re(CO)_3$.[155] The complex $[Re(CO)_3(4\text{-Ph–py})_3]^+$ has shown remarkable energy-transfer properties upon photon excitation.[156]

The large number of cationic complexes $[Re(CO)_3(\kappa^2\text{-}L\text{–}L^1)L^2)]^+$ of type VIII bearing ligands of different groups have been prepared and studied, having in mind either the tuning of the chemical or photophysical properties of the *fac*-$Re(CO)_3$ fragment, or the molecular properties of the complexes in terms of their biocompatibility and biological applications. Many of them can be seen in Table 6 and some have played an important role in this chemistry. As an example, the cationic complexes $[Re(CO)_3(N\text{–}N)(P(OR)_3]^+$ were fundamental to understand the process of photocatalyzed CO_2 reduction as discussed in Section 5.13.2.3.8(iii). Others were fundamental for assembling many supramolecular systems namely those pertaining to charge separation and ion recognition. Triflate removal from $Re(CO)_3(bipy)OTf$ with Na[BArF] in the presence of L^2 allows the synthesis of a wide range of $[Re(CO)_3(bipy)L^2]^+$ cations with very weak ligands under very mild conditions.[157] $[Re(CO)_3(bipy)(THF)]BArF$ is a catalyst for the aziridination of benzylidene–aniline with ethyldiazoacetate(EDA).[157]

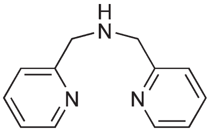
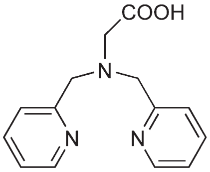
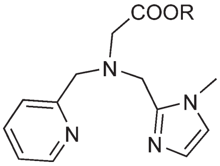
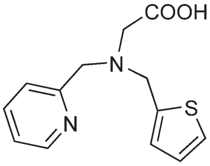
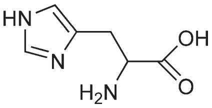
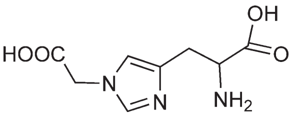
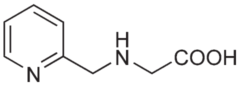
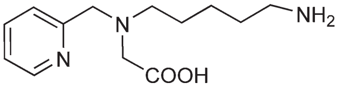
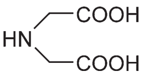
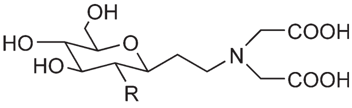
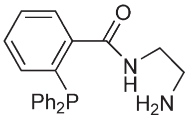
The cationic complexes $[Re(CO)_3(\kappa^3\text{-}L\text{–}L^1\text{–}L^2)]^+$, type IX, are now readily prepared either from **25** or **26**. Previous methods used relatively harsh conditions in order to replace all the other remaining ligands from species like $Re(CO)_5X$. There are few complexes of this type most of them obtained by Br^- abstraction from their bidentate congeners in Table 3 as in the case of the tris-pyrazolyl methane ligands.

A last group of $Re(CO)_3$ derivatives has the general formula $[Re(CO)_3X]_n$ (X = monoanion of groups 15, 16, 17). Many complexes of this type are known from earlier studies, namely, the cubane-like (tetrahedrane) derivatives $[Re(CO)_3X]_4$ (e.g., X = halide, OH, OR, SR) and the dimers $[Re(CO)_3(\mu\text{-}X_3)Re(CO)_3]^-$. $[Re_2(\mu\text{-}X)_2(CO)_6(Solv)_2]$ (X = Cl, Br, I; Solv = THF, NCMe) are easily obtained by refluxing the corresponding $Re(CO)_5X$ in THF. The halide-bridged species are useful precursors of other $Re(CO)_3L_2X$ complexes because the bridges can be cleaved by incoming donors. $[Re_2(\mu\text{-}X)_2(CO)_6(THF)_2]$ (X = Br, I) adds *cyclo*-S_8 and *cyclo*-Se_7.[158] Also useful and easy to obtain are $[Re_2(\mu\text{-}X)_2(CO)_6(NCMe)_2]$ (X = Cl, Br).[159]

Deprotonation of $[Re(CO)_3(H_2O)_3]^+$ with OH^- in aqueous solution leads to the dimer $[(OC)_3Re(\mu\text{-}OH)_3Re(CO)_3]^-$ or the trimer $[Re_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(CO)_9]^-$. The former is isostructural with the MeO-bridged analog and the latter is similar to the tetrahedrane $[Re(CO)_3(OH)]_4$ **28** (not formed in the reaction) with a missing $Re(CO)_3$ corner.[129] $[(OC)_3Re(\mu\text{-}OH)_3Re(CO)_3]^-$ can also be obtained from **28** in H_2O by treatment with base or on a silica surface treated with K_2CO_3. It reacts with Et_3SiOH to give $[Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]^-$.[160] Methanolysis of $Re(\eta^3\text{-}C_3H_5)(CO)_4$ gives propene and $[Re_4(CO)_{12}(\mu\text{-}OH)(\mu\text{-}OMe)_4]$ with a structure similar to those of **28** and $[Re(CO)_3(OMe]_4$. Reaction of $Re(CO)_5Cl$ with acetic acid affords the tetramer $[Re(CO)_3(O_2CCH_3)(THF)]_4$ in which each carboxyate bridges two *fac*-$[Re(CO)_3(THF)]$ fragments through O atoms.[161]

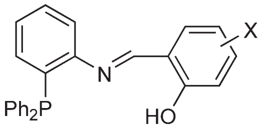
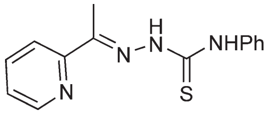
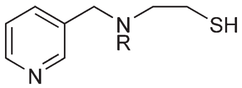
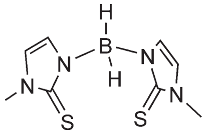
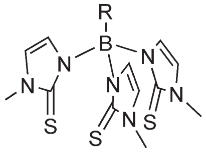
When $Re(\eta^3\text{-}C_3H_5)(CO)_3(CN\text{–}2,5\text{-}Me_2C_6H_3)$ is methanolyzed, the bulk of the isonitrile ligand breaks down the polymeric structure and the dimer $[Re(CO)_2(CN\text{–}2,5\text{-}Me_2C_6H_3)_2(\mu\text{-}OMe)]_2$ is isolated.[162] Compound **28** is easily reduced to $Re_2(CO)_{10}$ under 1 atm CO on a silica surface but not in solution. Evidence points to the role of the intermediate $[Re(CO)_5(OSi{\equiv})]$ formed on the surface.[110]

Table 5 Neutral complexes of formula [Re(CO)$_3$(κ^3-L–L^1–X)] with negative potentially tridentate ligands

L–L^1–X (charge − 1)	*Donors*	*Keywords*	*References*
	N–N–N	Radiopharma	681
			
			
	N–N–O	Radiopharma	681
	N–N–O	Radiopharma	155
	N–N–O	Radiopharma	682
	N–N–O	Radiopharma	179
	N–N–O	Radiopharma	683
	N–O–O	Radiopharma	179
 R = H, OH	N–O–O	Radiopharma	684
	P–N–N	Radiopharma	685

(*Continued*)

Table 5 (Continued)

L–L^1–X (charge – 1)	*Donors*	*Keywords*	*References*
	P–N–O	Radiopharma	686
	N–N–S	Radiopharma	661
 R = H, Et	N–N–S	Radiopharma	687
	S–S–H	Radiopharma	184
	S–S–S	Radiopharma	688

5.13.2.3.7 Re(CO)$_2$ derivatives

Under thermal treatment, the potentially terdentate ligands in complexes [Re(CO)$_3$(κ^2-L–L–L)X] (L = *N*- or *P*-donor) assume full coordination upon CO loss resulting in *cis*-[Re(CO)$_2$(κ^3-L–L–L)X]. Characterized examples include terpy and other similar ligands in table fluxionality, as well as triphos.[163,164] This decarbonylation becomes more favorable for the potentially tetradentate ligand {Ph$_2$P(CH$_2$)$_2$}$_3$P (P3P′).[141]

Tp′Re(CO)$_2$L (L = PMe$_3$,THF) has been generated photolytically from Tp′Re(CO)$_3$ for biological purposes.[165] Many air stable phosphite and phosphinite derivatives of formula *cis,mer*-[ReBr(CO)$_2$L$_3$] (L = PPh$_{3-n}$(OR)$_n$ (R = Me, Et; n = 1–3) or *cis,mer*-[ReBr(CO)$_2$LL^1] [L=Ph$_2$P(O)CH$_2$CH$_2$P(O)Ph$_2$; L^1=P(OMe)$_3$, P(OEt)$_3$, PPh(OMe)$_2$, PPh(OEt)$_2$, PPh$_2$(OMe), PPh$_2$(OEt)] have been described.[166,167]

The moiety [(triphos)Re(CO)$_2$]$^+$ has provided the basis for the development of rather interesting chemistry. The fragment itself stabilizes its unsaturation by means of an agostic interaction of a C–H bond from the ligand (cf. Scheme 7). Its binding affinity for other donors increases in the order: N$_2$ < C–H (agostic) < H$_2$ < HC≡CR < NCMe < CO. Its capacity for activating H$_2$ has been discussed in Section 5.13.2.3.1.

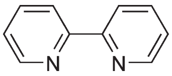
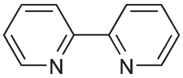
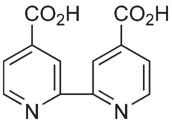
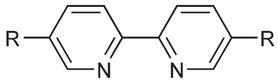
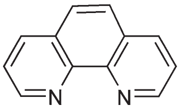
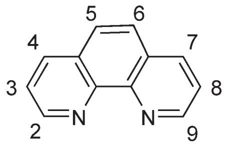
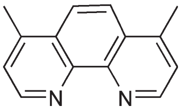
The triflate ligand in [(triphos)Re(CO)$_2$(OTf)] can be easily replaced by different halides and pseudohalides (CN$^-$, N$_3$$^-$, SCN$^-$, SeCN$^-$, OCN$^-$) to give the respective complexes of formula [(triphos)Re(CO)$_2$X]. Selective methylation of [(triphos)Re(CO)$_2$(η^1-E–ECN)] (E = S, Se) affords the complexes [(triphos)Re(CO)$_2${η^1-E-E(Me)(CN)}OTf], which contain the unprecedented methylsulfocyanate and methylselenocyanate ligands.[168]

H$_2$ is displaced from [(triphos)Re(CO)$_2$(η^2-H)$_2$]$^+$ by terminal acetylenes forming the vinylidene cations [(triphos)Re(CO)$_2$(=C=C(H)R)]$^+$ that opened a wide variety of chemistry (see Section 5.13.3.1.1(iii)).[169]

The complexes [(triphos)Re(CO)$_2$X] (X = Cl, Br) have a reversible electrochemistry and its one-electron oxidation product [(triphos)Re$^{\text{II}}$(CO)$_2$X]$^+$ is stable on the synthetic timescale (see Section 5.13.3.2).[141] The triphos analogs with the 12[ane]P3R3 ligand are obtained by reduction of the Re(III) complex ReCl$_3$(12[ane]P3R3) (R = Et, Bu^i) under CO giving [(12[ane]P3R3)Re(CO)$_2$Cl], which reacts with LiAlH$_4$ to yield the corresponding hydride [(12[ane]P3R3)Re(CO)$_2$H].[170] Reaction of these compounds with acetylenes leads to vinylidenes and cumulenes (Section 5.13.3.1.1 (iii)).

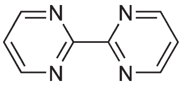
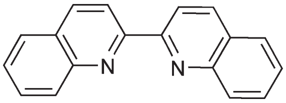
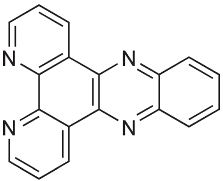
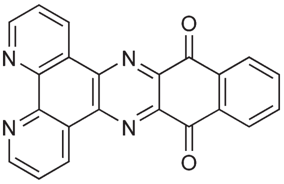
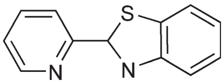
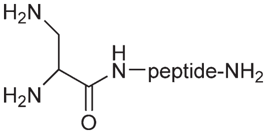
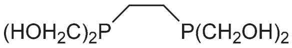
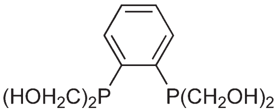
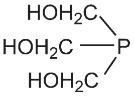
The complexes [(triphos)Re(CO)$_2$(η^1-P$_4$)](OTf) and [{(triphos)Re(CO)$_2$}$_2$(μ,-η^1,η^1-P$_4$)](OTf)$_2$ are the first soluble metal complexes of the tetraphosphorus (P$_4$) molecule where the P$_4$ structure has not undergone any major modification.[171] Derivatives of the *cis*-Re(CO)$_2$ fragment with mixed N and P ligands have been prepared in search of

Table 6 Selected cationic complexes of general formula [Re(CO)$_3$(κ^2-L–L^1)L^2)]X

κ^2-L–L^1	L^2	X^-	*Keywords*	*References*
	NHR_2	TfO	Reactivity studies	142
	NCR, RN=CR$_2$, PR$_3$, OCR$_2$, Et$_2$O, THF, CH$_3$I	TfO	Reactivity studies, aziridination catalysis	157
	PBu$_3$, PEt$_3$, PPh$_3$, P(OMe)Ph$_2$, P(OMe)$_3$, P(OEt)$_3$, P(OPr^i)$_3$, P(OPh)$_3$	SbF$_6$	Photocatalytic CO$_2$ reduction	217, 218, 689
	4-X-py	ClO$_4$ (X = azopy, styryl)	Photoswitches	690
	Histidine	PF$_6$	Luminescence	691
	Pyrazine; 4,4′-bipy		Luminescence, time-resolved spectroscopy, pulse radiolysis, excited-state reactivity	197
	Py-3-NCS	TfO	Fluorescent biomarkers	692
	4-X-py	ClO$_4$	Photophysics	693
	4-X-py	ClO$_4$	Photophysics	693
 R = Me, CF$_3$	Histidine	PF$_6$, CF$_3$CO$_2$	Luminescence	691
	H$_2$O	TfO	Protein binding to surface histidines; charge transfer	245
	NHR_2	TfO	Reactivity studies	142
	py	ClO$_4$	Excited-state properties; charge-transfer emission; intramolecular energy transfer, luminescence	694
	py	ClO$_4$	Excited-state properties; charge-transfer emission; intramolecular energy transfer, luminescence	694
 3,4,7,8 = Me 4,7 = Ph, Me 2,9 = Me, 4,7 = Ph 5,6 = Me 2,9 = Me	py	ClO$_4$	Excited-state properties; charge-transfer emission; intramolecular energy transfer, luminescence	694
	Py-3-NCS, N-(3-pyridyl) maleimide	TfO	Luminescent biomarkers	243, 692
	NCMe, py, MeQ^+	PF$_6$	Spectroscopy and electrochemistry	695
	py	ClO$_4$	Temperature-dependent emission	696
	Py-3-NCS	TfO	Luminescent biomarkers	692

(Continued)

Table 6 (Continued)

κ^2-L–L^1	L^2	X^-	*Keywords*	*References*
	NCMe, py, MeQ$^+$	PF_6	Spectroscopy and electrochemistry	695
	N-(3-pyridyl) maleimide, pz, 4,4′-bipy, 4-XPy (X = OK,Ph, CN)	TfO	Luminescent biomarkers, Luminescence, time-resolved spectroscopy, pulse radiolysis Spectroscopy and Electrochemistry correlations	197, 243, 645, 697
 dppz	py	TfO	Photophysics, time-dependent DFT calculations	202, 697
	4-Mepy	Cl	DNA binding	698
 dppn	py	TfO	Photophysics DNA binding	693
	NCMe	TfO	Radiopharma	652
	H_2O	Br	Radiopharma, prostate cancer	699
	CH_2Cl_2, OH_2,NCMe	BArF	Weakly binding ligands	671
 		Br	Radiopharma peptide labeling	700

enhanced performances in the several uses already discussed for *fac*-Re(CO)$_3$ derivatives. So, [Re(CO)$_2$(2,2′-bipy){P(OEt)$_3$}$_2$]$^+$ was found to be an effective photochemical reductant of CO$_2$,[172] and a new class of luminescent complexes of the type *cis*-[Re(CO)$_2$(N–N)(P–P)]$^+$ (where N–N is a chelate polypyridine ligand and P–P is a chelate diphosphine) has been developed. They possess excited states of extraordinary stability and extremely long lifetimes in CH$_2$Cl$_2$ solution that exhibit red-shifted spectral responses relative to the well-studied *fac*-[Re(bipy)(CO)$_3$L]$^{+/0}$ series.[173]

As mentioned above, the Re(CO)$_3$ fragment is normally photochemically inert. However, some exceptions like *fac*-[Re(X$_2$–bipy)(CO)$_3$(PR$_3$)]$^+$ (X$_2$–bipy = 4,4′-X$_2$–2,2′-bipyridine; X = Me, H, CF$_3$; R = OEt, Ph) undergo photochemical, quantitative, CO substitution to afford *cis,trans*-[Re(X$_2$–bipy)(CO)$_2$(PR$_3$)(MeCN)]$^+$ or *cis,trans*-[Re(X$_2$–bipy)(CO)$_2$(PR$_3$)Y]$^{n+}$ (n = 0, Y = Cl$^-$; n = 1, Y = py, PR$_3$) with four different kinds of ligands.[174]

Relatively, few Re(I) complexes with only one CO ligand are known. Contrary to the previous classes of Re carbonyls that are made by successive stripping of CO from the ultimate $Re(CO)_5$ precursors, this group is accessible by carbonylation of Re compounds devoid of any CO. Reduction of Re_2Cl_{10} or NH_4ReO_4 with $NaBH_4$ and CO in the presence of 1,1-bis(diphenylphosphino)methane(dppm) leads to *trans*-[ReX(CO)(dppm)$_2$] (X = Cl or ReO_4).[175] *cis*-[ReCl(CO)(dppe)$_2$] prepared from *cis*-[ReCl($NCC_6H_4Cl_4$)(dppe)$_2$] slowly isomerizes to the *trans*-isomer in CH_2Cl_2. This isomerization is promoted by oxidation following an electron-transfer chain catalytic process, the origin of which was established by electrochemical methods (see Section 5.13.2.4).[176]

5.13.2.3.8 Special topics on physics and chemistry of the *fac*-[Re(CO)$_3$] fragment

5.13.2.3.8.(i) Bioorganometallic chemistry

The discovery that the derivatives of the *fac*-[Re(CO)$_3$] fragment are stable in water and air, and can be readily prepared in aqueous solutions, led to a rapid expansion of the so-called $Re(CO)_3$ core technology for the development of applications in radioimaging and radiotherapeutic purposes. The wealth of approaches and actual examples is very large due to the variety of the biomolecules that are appended to the ligands presented in simple unfunctionalized form in Tables 2–6. Therefore, the reader is referred to several specialized reviews for more accurate discussion and referencing of the field,[155,177,178] as well as to Chapter 12.08 of this work.

Complexes with tridentate ligands seem to have more favorable pharmacokinetic profiles than those of the type $[Re(CO)_3L_2(H_2O)]^+$ because they show faster clearence *in vivo*, a factor that is important with radioactive substances.[179] The mild synthesis of radioactive $^{188}Re(CO)_3$ derivatives bearing tridentate ligands designed for achieving high specificity in radiopharmaceutical applications has been described in detail from $^{188}[ReO_4]^-$ through *fac*-$[^{188}Re(CO)_3(H_2O)_3]^+$.[180] *N*-functionalized derivatives of the iminodiacetic coordination anchor bearing 5′-aminothymidine have shown inhibition of human thymidine kinase, and may find application in the diagnosis of tumor proliferation.[181] Pyridin-2-yl hydrazine functionalized with estradiol (L^{est}) reacts with *fac*-$[Re(CO)_3Cl_3]^{2-}$ in water to give *fac*-[Re(CO)$_3$(L^{est})Cl]. This complex reveals a higher binding affinity for the estrogen receptor than all other related estradiol derivatives of the $Re(CO)_3$ fragment previously discovered, including the widely cited $Cp^{est}Re(CO)_3$ introduced by Jaouen in 1995 (see Section 5.13.3.1.5(i)(a)).[182] The latter reference presents extensive information on the developments in this area. The Schiff bases derived from pyridine–2-aldehyde functionalized with fatty acid chains were developed for use in myocardial imagiing as surrogates for the ^{99}Tc analogs.[183]

The complexes with the agostic B–H–Re(Tc) bond (see Table 5) are moderately lipophilic and able to cross the blood brain barrier and are, therefore, adequate building blocks for the labeling of CNS-receptor avid molecules. This was further explored by decorating the RBH(mercaptomethylimidazolyl) ring with aryl piperazine fragments able to target the 5-HT1A subclass of serotonergic receptors. The IC_{50} affinity values are in the low nM scale.[152] The agostic B–H–Re bond can be broken by a variety of ligands to give adducts like [Re(κ^2-H_2B(timMe)$_2$}(CO)$_3$L) (L = imidazole, CNR, PPh_3).[184] The CNR (isonitrile) ligands offer an alternative possibility of appending substituents able to target the desired receptors.[152] One of the most important sulfur (thioether) binding complexes is called TROTEC-1, and associates the ligand (see Table 3) with the *fac*-[Re(CO)$_3$Br] fragment to give a complex with exceptional binding affinity to the dopamine transporters (DAT).[185] Other dithioether complexes, mostly bidentate to the *fac*-[Re(CO)$_3$Br] fragment, have shown significant brain intake and do not undergo exchange with glutathione.[186] Derivatization of estradiol with a dithioether-containing moiety allows the synthesis of *fac*-[Re(CO)$_3$BrL$_2$] or *fac*-[Re(CO)$_3$L$_3$] complexes with a moderate to high affinity for the estradiol receptors.[187–189]

5.13.2.3.8.(ii) Photophysical studies and photoactive molecular devices

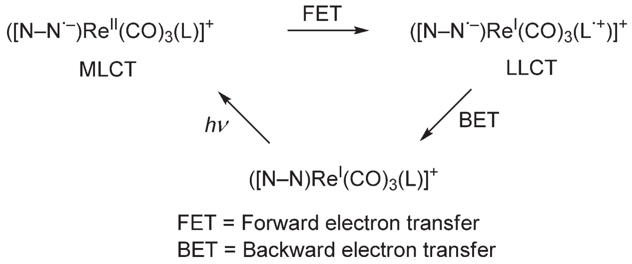
As referred to before and amply verified in Tables 3, 5, and 6 one of the main topics of work on the [Re(CO)$_3$(α-diimine)X] and $[Re(CO)_3(\alpha\text{-diimine})L]^+$ complexes has been the study of their photophysical and photochemical properties by means of spectroscopical and spectroelectrochemical studies.

This interest started in 1974 with Wrighton's discovery of the luminescence of Re(CO)$_3$(bipy)Cl in solution at RT. According to a recent review of the field, this discovery "had a tremendous impact on inorganic and even photochemistry in general."[190] Upon excitation of octahedral low-spin d^6-complexes, higher energy levels become populated as a result of possible electron transitions of the types metal-centered (MC), ligand-centered (LC), metal-to-ligand charge transfer (MLCT), and ligand-to-metal charge transfer (LMCT). Whereas in d^3-metal complexes, MC transitions (absorption and emission) dominate, the Re(I) d^6-complexes exhibit all possibilities with the exception of LMCT processes.[190] As a result of this richness of possibilities, and spurred by the unusual and useful light-emission properties and photoactivity of these excited states, the wealth of photophysical studies ensued cannot be covered here and the reader is referred to specialized review articles.[190–196] Most of the work has been concerned with the luminescence studies, the identification of the emissive states involved, which depends on the nature of the α-diimine ligands that are the best suited for this purpose, and on the energy-transfer processes. Some more recent references are collected,[197–202] and recent computational DFT studies emerged that refer to important aspects of the field.[203–205] Although photochemical CO substitution is commonplace in metal carbonyl chemistry, it does not play an important role in $Re(CO)_3(\alpha\text{-diimine})X$ photochemistry. The MLCT excited states are inert to ligand substitution, because neither the $d\pi$-donor nor the π^*(α-diimine) acceptor are involved in strong M–L bonding or antibonding interactions. It seemed, therefore, that the MC excited states necessary for CO dissociation (^{3}LF) were inaccessible from the emissive ^{3}MCLT state or were unreactive. This “common knowledge” was only interpreted on solid ground in 2002 when it was reported that *fac*-$[Re(CO)_3(X_2\text{–bipy})(PR_3)]^+$ complexes undergo photosubstitution of one CO *trans* to the PR_3 ligand to give *cis,trans*-$[Re(X_2\text{–bipy})(CO)_2(PR_3)(NCMe)]^+$ in NCMe solution.[206] This study established that the substitution occurs from the ^{3}LF state and is possible due to the CO-bond weakening resulting from the *trans*-effect of the PR_3 ligands. In the cases of the photostable *fac*-$[Re(CO)_3(bipy)Cl]$ and *fac*-$[Re(CO)_3(bipy)py]^+$, the opposing *trans*-influence of the Cl^- and py ligands relative to PR_3 prevents substitution, even if, as it seems, the ^{3}LF state is energetically accessible from ^{3}MLCT. Studies on the Re–H bond homolysis in $Re(CO)_3(DAB)H$ led to the conclusion that, in contrast to what was found for the manganese analog, the ^{1}MLCT state is non-reactive and a rather slow (beyond the ps timescale) partial and indirect homolysis of the Re–H bond occurs through $^1\text{MLCT} \rightarrow {}^3\text{SBLCT}$ (sigma-bond-to-ligand charge transfer) intersystem crossing.[207]

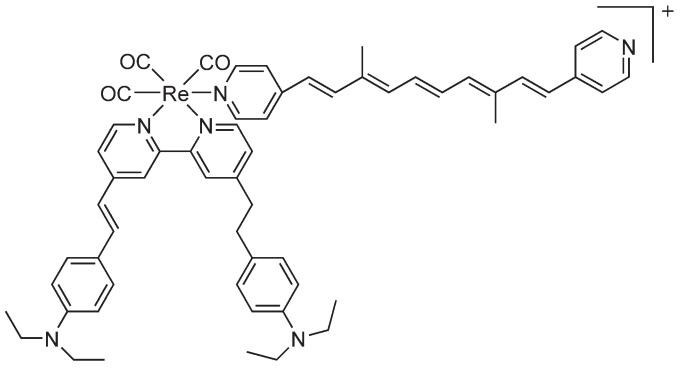
As exemplified in Table 3, not all *fac*-$[Re(CO)_3L_2X]$ complexes are emissive or luminescent. This is due to either a low energy of the MLCT state, or to its inherent reactivity. Emitting MLCT states are also accessible electrochemically and even chemically.[190] Photoswitches that toggle luminescence on–off have also been described, for instance, in the family of complexes $[Re(\alpha\text{-diimine})(CO)_3(dpe)](PF_6)$ (dpe = 1,2-di-(4-pyridyl)ethylene), where the *cis*-dpe form is emissive and the *trans*-dpe form is not. Irradiation of the *trans*-dpe form leads to *trans–cis*-isomerization switching luminescence on.[201]

The emissive ^{3}MLCT state obtained upon excitation is responsive to energy or electron transfer, and these processes may be competing as shown in the case of the complex *fac*-$[Re(dppz)(CO)_3(py\text{-}PTZ)]^+$(dppz = dipyrido [3,2-*a* : 2′,3′-*c*] phenazine). Here, the ^{3}MLCT excited state *fac*-$[Re^{II}(dppz^{\cdot-})(CO)_3(py\text{-}PTZ)]^{+*}$ undergoes intramolecular energy transfer to give the dppz-localized $\pi\pi^*$ excited state $[Re^I(^3dppz)^*(CO)_3(py\text{-}PTZ)]^+$ ($3\pi\pi^*$) in competition with electron transfer to give the redox-separated state (RS) $[Re^I(dppz^{\cdot+})(CO)_3(py\text{-}PTZ^{\cdot+})]^+$. The competition ratio for the formation of the two is $[RS]/[3\pi\pi^*] = 2.4$.[208] In this case, electron transfer is intramolecular between two ligands bound to Re(I). However, it can also take place intermolecularly with an appropriate donor or acceptor in solution that can be either an organic molecule or another metal complex,[195] or intramolecularly to a donor or acceptor located on another ligand,[209–212] or attached to it by means of a spacer.[199,213] In these two last cases, electron transfer may be tuned to produce photoactivated devices such as sensors, switches, or redox agents. These processes are summarized graphically in Scheme 12.

In order to become more effective, they should have efficient formation of the ^{3}MLCT state, followed by fast forward electron transfer (FET) to produce a long-lived charge-separated LLCT state. This means that the back electron-transfer step (BET) should be slow. $[Re(\alpha\text{-diimine})(CO)_3L]^+$ complexes are particularly suitable for these purposes and several examples have contributed to a better identification of the parameters that are crucial for the design of these photoactivated molecular devices, like the nature of the donor–acceptor pairs and the spacers.[199] For instance, the simultaneous coordination of the BPP ligand (with a long conjugated chain) and a modified bipy ligand, DEAS-bipy, on the same metal center, gives rise to a donor–acceptor complex **29**, which forms a long-lived charge-separated state following light excitation.[210]



Scheme 12



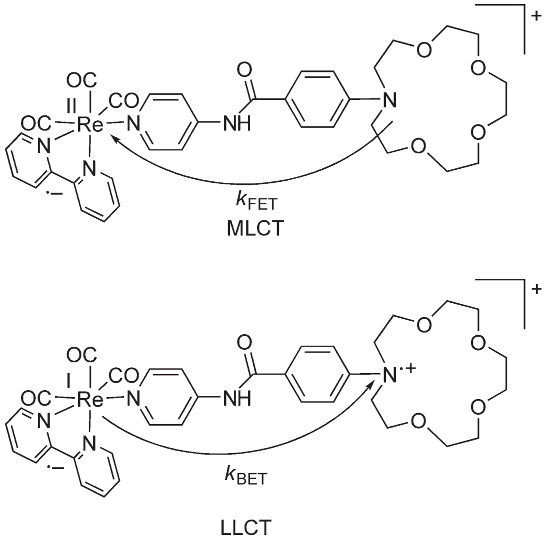
29

Significant interpretation of the nature of the spacer was achieved for the complex in Scheme 13, with a pendant azacrown macrocycle, where k_{FET} (ps timescale) is two orders of magnitude faster than k_{BET} (ns timescale), creating a long-lived LLCT state useful for photodevices.[199]

These properties have recently elicited the use of Re(α-diimine)(CO)$_3$Cl complexes as sensitizers for photovoltaic cells.[214–216]

5.13.2.3.8.(iii) Photo-catalyzed CO$_2$ reduction

Electron transfer leading to redox processes has found application in the photocatalyzed reduction of CO$_2$. The *fac*-[Re(CO)$_3$(bipy)Cl] complex has probably been the most widely studied in this respect. In 1983, Lehn and co-workers reported that *fac*-[Re(CO)$_3$(bipy)Cl] is able to photocatalyze the reduction of CO$_2$ to CO and formate in the presence of an electron acceptor like Et$_3$N (TEA) or triethanolamine (TEOA). In 1984, they reported its use as an electrocatalyst for the same reaction.[2] Photochemically, this system is unique in acting both as a photosensitizer and multi-electron redox catalyst. Subsequent research established the first steps of the CO$_2$ photoactivation reaction as: (i) excitation of [Re(CO)$_3$(bipy)Cl] to the ^{3}MLCT state which is both a strong oxidant and reductant and (ii) electron transfer from the amine donor to the excited complex forming [Re(CO)$_3$(bipy)Cl]$^-$, also called the one-electron reduced (OER) species. This OER complex would then proceed to react with CO$_2$ forming CO. The co-appearance of formate and [Re(CO)$_3$(bipy)(O$_2$CH)] can be suppressed by excess Cl$^-$ but this is not convenient for practical purposes. A host of studies focused on the reaction mechanism following the fate and reactivity of the OER

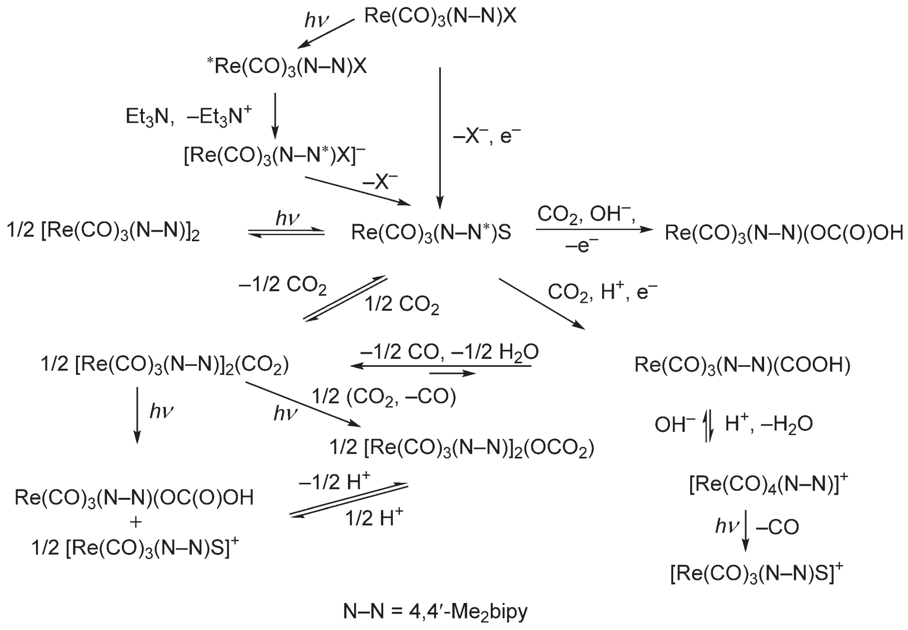


Scheme 13

species but the overall situation remained unclear for a long time, particularly regarding the interaction between the metal species and CO_2. The discovery of the new highly active photocatalysts $[Re(CO)_3(bipy)\{P(OMe)_3\}]^+$,[217] led to the important realization that its high activity is related to its much more stable OER $[Re(CO)_3(bipy^{\cdot})P(OMe)_3]^-$ that is quantitatively produced in a short time and has $\tau_{1/2} = 514$ s much higher than that of $[Re(CO)_3(bipy^{\cdot})Cl]^-$ (6 s).[218] The ensuing studies left clear that the properties of the OER species are highly dependent on the nature of the ligands surrounding the $Re(CO)_3$ fragment, and that important changes are caused upon variation of X, the PR_3 ligand, or even the nature of substituents on the bipy ligand. In the meantime, data from electrochemical and chemical studies on CO_2 complexes of these systems helped identifying some fundamental missing links for the interpretation of the reaction mechanism. All these facts and references are thoroughly discussed, confronted, and reinterpreted in a publication by Fujita *et al*. The reactions observed in the case of N–N = 4,4′-Me_2bipy are shown in Scheme 14.[219]

Some of the central facts in this scheme are: Cl^- loss from the OER species $[Re(CO)_3(N\text{–}N^{\cdot})Cl]^-$ is slow and leads to an octahedral solvent complex $[Re(CO)_3(N\text{–}N^{\cdot})(S)]$ and not to a five-coordinate species; $[Re(CO)_3(N\text{–}N^{\cdot})(S)]$ is a radical with the electron located on the bipy ligand, a fact that prevents the fast Re–Re bond formation expected from a metal-centered radical; $[Re(CO)_3(N\text{–}N^{\cdot})(S)]$ reacts with CO_2 in competition with slow dimerization, in the dark, to form the CO_2-bridged complex $[Re(CO)_3(N\text{–}N)]_2(CO_2)$, which is the key intermediate in the CO formation process upon further irradiation. Another complex, $[Re(CO)_3(N\text{–}N)(COOH)]$, also formed in minor amounts, may become a major player in the liberation of CO via formation of $[Re(CO)_4(N\text{–}N)]^+$ once significant amounts of $TEAH^+$ or $TEOAH^+$ are already formed; the formate complex was formed from $[Re(CO)_3(N\text{–}N)(S)]$ in the absence of added CO_2, under continuous irradiation in DMF solution, and seems to be the result of side decomposition reactions. From a more practical point of view, it was found that under 2.45 MPa CO_2 pressure the catalytic efficiency of *fac*-$[Re(CO)_3(bipy)Cl]$ is highly improved in CO formation.[220]

The electrocatalytic CO_2 reduction with the same catalysts shares some common features but also involves other possible pathways derived from the fact that, under CO_2, the radical species $[Re(CO)_3(N\text{–}N)(S)]$ (S = NCMe, $P(OR)_3$) can undergo a second reduction with rapid formation of CO and CO_3^{2-}. The actual mechanisms are dependent on the solvent and the nature of the diimine N–N, and still have unclear steps in spite of the extensive spectroelectrochemical studies carried out.[221,222] The study of the decomposition of $[Re(CO)_3(dmbpy)(COOH)]$ (dmbpy = 4,4′-Me_2bipy) to $[Re(CO)_3(dmbpy)]_2(CO_2)$ by simple standing in DMSO or DMF solution, as well as its conversion to formato, carbonato, bicarbonato, and formyl derivatives of the $[Re(CO)_3(dmbpy)]^+$ fragment, have been carried out, having in mind the understanding of the CO_2 reduction chemistry.[223]



Scheme 14

5.13.2.3.8.(iv) Electrochemistry

In-depth studies of the electrochemistry of *fac*-[$Re(CO)_3L_2X$] complexes have been able to correlate photophysical and electrochemical properties of *fac*-[$Re(CO)_3$(α-diimine)X] complexes and characterize their redox products. In principle, upon reduction, the added electrons can be accommodated at either the metal or the ligands, namely in the cases where these have empty orbitals of accessible energy. The location of the added electrons is of central importance for the understanding of the reactivity and structure of the reduced states, and the matter has been addressed by means of spectroelectrochemical studies. A fundamental study on the spectroelectrochemical (IR, UV–VIS) determination of the reduction pathways for a series of [$Re(CO)_3$(α-diimine)L^1]$^{0/+}$ (L^1 = halide, TfO^-, THF, NCMe, CCPr, PPh_3, $P(OMe)_3$) complexes was produced by the group of Stufkens,[224] but many others are available from his, Kaim's, and other groups.[225,226] The stability of the reduced [$Re(CO)_3$(α-diimine)L^1]$^{\cdot -/\cdot}$ complexes depends on the ability of the α-diimine radical ligand to accommodate the unpaired electron in its lowest empty π^*-orbital. The higher the energy of this π^*-orbital, the more pronounced the donor character of the α-diimine radical, a fact that is experimentally ascertained by the large frequency shifts of the ν(CO) vibrations to lower frequencies in IR spectra. Concomitant polarization of the radical complex and increased electron density within the Re–(α-diimine) chelate ring labilize the Re–L^1 bond, and may cause dissociation of L^1 and dimerization of the Re radicals, or substitution of L^1 by a better π-acceptor. Therefore, complexes with $L^1 = P(OMe)_3$ are less kinetically labile after reduction. In another study involving a large variety of aromatic and non-aromatic α-diimines, it was found that only the complexes $Re(CO)_3$(1,4-$^tBu_2$-DAB)X and $Re(CO)_3$(1,3-$^tBu_2$-sdi)X (X = Cl, Br; DAB = diazabutadiene; sdi = sulfurdiimine) undergo a reversible oxidation to a Re(II) complex at $E_{1/2} \approx 1$ V. With the exception of $Re(CO)_3$(1,4-$^tBu_2$-DAB)Cl, these are precisely the only complexes studied that do not undergo reversible one-electron reduction to the corresponding Re(0) radicals. This has been interpreted as a result of the capacity of DAB and sdi ligands to donate charge to the metal through their π-orbitals, which, while stabilizing an oxidation, strongly destabilize reduction due to enhanced X^- labilization.[227] The labilizing effect of the strong donating power of the reduced α-diimine ligand on the Re–L^1 bond becomes much more apparent upon the second one-electron reduction step that forms five-coordinated anionic [$Re(CO)_3$(α-diimine)]$^-$ complexes with rather low ν(CO) frequencies. When the α-diimine is a stronger electron acceptor, further reductions can take place.[224] The complexity of the processs can be seen in the fact that the complexes *fac*-[$Re(CO)_3L_2$(MQ)]$^{2+}$ (L_2 = *N*-heterocyclic α-diimines; MQ^+) (MQ^+ = *N*-methyl-4,4′-bipyridinium) undergo four one-electron reduction steps, which could be analyzed using cyclic voltammetry (CV), EPR, IR, and UV–VIS spectroelectrochemistry.[228] The nature of the ligands can vary the detailed processes undergone by the reduced species, as studied under strictly aprotic conditions.[225] A radical anion derived from a redox-active diphosphine ligand (bma = 2,3-bis(diphenylphosphino)maleic anhydride) has been structurally characterized as a derivative of cobaltocinium: *fac*-[$Re(CO)_3Br$(bma)][Cp_2Co].[229] Several stable reduced radical species have been isolated by reaction of the electrogenerated radical anion *fac*-[$Re(CO)_3L_2Cl$]$^-$ (L_2 = 2-(arylazo)-pyrimidine, 2-(arylazo)–1-methylimidazole) with donors like NCMe or PPh_3.[226] This kind of species is central in the understanding of the electrocatalyzed reduction of CO_2 already discussed above. A complete set of $Re(CO)_3X$ complexes (X = F, Cl, Br, I) has been studied in a systematical fashion by example of (abpy)$Re(CO)_3X$ (abpy = 2,2′-azobispyridine). CV, EPR, IR, and UV–VIS spectroelectrochemistry of the reduced forms [(abpy)$Re(CO)_3X$]$^{\cdot -}$ illustrate that the four halide complexes differ only partially in their properties. The strongest deviations are observed for [(abpy)$Re(CO)_3F$]$^{\cdot -}$, which is distinguished by the widest electrochemical potential range but most pronounced chemical lability.[230] A most remarkable result was obtained with the tetranuclear complex {$Re(CO)_3$(bipy)}$_4$(μ-TCNQ)][PF_6]$_4$ (TCNQ = tetracyanoquinodimethane). This the first TCNQ species which exhibits the so-called normal response of metal coordination to a π-acceptor ligand because the fourfold coordination of the Re fragment makes the TCNQ-based reduction easier by 0.74 V relative to free TCNQ due to the strong π-donor capability of [$Re(CO)_3$(bipy)]$^+$. In all other known systems, the extremely strong π-acceptor TCNQ is already essentially reduced when coordinated.[231]

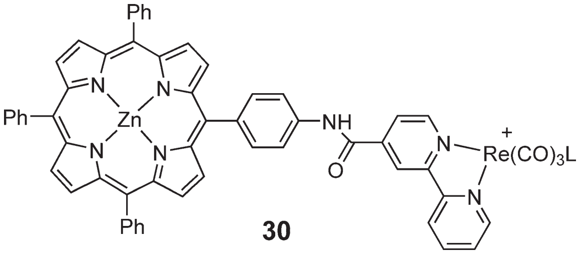
5.13.2.3.8.(v) Polynuclear and supramolecular assemblies, devices, and applications

Due to its high stability and coordination capabilities, the number of binuclear and polynuclear complexes derived from the *fac*-$Re(CO)_3$ unit is very high. Since a full coverage of the subject is not possible, we have been presenting some species of this type throughout the text, whenever properties of the multinuclear assembly are novel or deserve being exemplified. This is the obvious case of the clusters many of which have been used as precursors to catalytic active species (Section 5.13.2.3.2).

Polynuclear transition metal complexes with the properties of the $Re(CO)_3$ core may provide, among other possibilities, multicomponent systems (usually called supramolecular systems) capable of performing useful light- and/or redox-induced functions. This is a very active field of research because such properties may create processes such as energy transfer, electron transfer and exchange, photoinduced charge separation, which can be useful for the assembling of molecular devices for sensors, optical, optoelectronic, and even catalytical applications. Simple polynuclear species, either homo- or heteronuclear, can be assembled via bridging ligands that function as spacers between the metal centers but also as scaffolds that constrain their interaction in geometrical and electronic terms. Much more complex structures can be derived, for instance, from dendrimeric or polymeric arrangements. Polypyridyls offer extensive possibilities to prepare bridging ligands with well-defined lengths and electronic frameworks, but other spacing systems, including hydrogen-bonded ones, have been used.[195] They also offer appropriate means of connecting the $Re(CO)_3$ core to other molecules or ions, tuning or revealing their properties, thereby entering the realm of supramolecular chemistry. Obvious examples are those related to the multidentate pyridine-derived ligands seen in Table 4 and exemplified by **3**. Of a different nature are the unusual high–low oxidation state polynuclear complexes $[Re(CO)_3Cl(WS_4)]^-$ and $[Re(CO)_3X(\mu\text{-}S_2WS_2)Re(CO)_3X]^{2-}$. The latter is electrochemically reducible to a W(V) species in the case $X = CN$.[232]

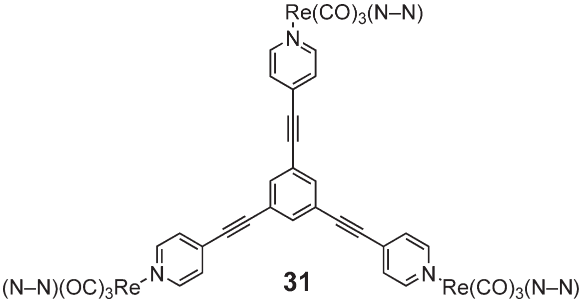
Of course, the number of options is extremely high and, fortunately, an extensive review by Balzani *et al.* covers the earlier literature up to 1996 and retrieves the photophysical and electrochemical data for a awesome number of luminescent and redox-active systems of interest to supramolecular photochemistry, many of which contain the $Re(CO)_3$ fragment.[233]

The scope of the field leads us to just present a few selected examples of striking results obtained in this area of research. Light absorption by the porphyrin ring of complex **30** sensitizes the Re center to electron transfer to Et_3N and induces substitution of L, in accordance with the principles of supramolecular photochemistry.[234]



30

The variation of the nature of the bridges between the chromophore centres in complexes of the general types, **31 and 32**, allows the study of the photoswitching properties of an extensive series of polynuclear *fac*-(α-diimine)$Re(CO)_3$ complexes linked by a *cis–trans* isomerizable stilbene-like bridging ligand.[235]



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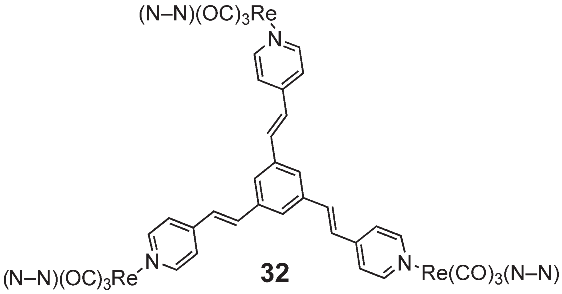
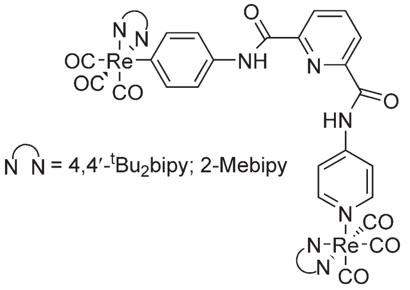


32

Ion sensing is another area of supramolecular chemistry where the $Re(CO)_3$ fragment has been used extensively due to high sensitivity and low detection limit. Two reviews discuss important aspects of the field.[236,237] Just a few recent developments in different areas are briefly presented here.

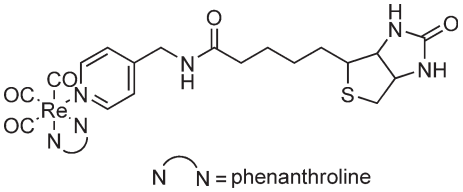
In the area of cation sensing, the energy-transfer process in Scheme 13 has been recently shown to produce a light-controlled ion switch that, upon irradiation, expels Li^+, Na^+, Ca^{2+}, and Ba^{2+} ions on a nanosecond timescale from the azacrown.[238] Hydroxypyridine ligands provide the basis for pH-sensing devices in biomedical and environmental fields due to dramatic changes in emission intensity near pH 7.[239] Several derivatives of 2-pyridylketone hydrazones allow the determination of nM concentrations of acids in aprotic media like DMF.[240]

Successful examples of anion recognition by mononuclear complexes[241] as well as polynuclear complexes have been reported. For instance, the binuclear complexes in Scheme 15 exhibit an outstanding selectivity for a variety of biologically and environmentally important anions with a high binding affinity in the order: $CN^- > F^- > I^- > Cl^- \approx Br^- \approx OAc^- >> H_2PO_4 > NO_3^- > ClO_4^-$.[242]



Scheme 15

The use of $Re(CO)_3$ fragments as biological markers is also growing quickly. Complexes containing dppz and dppn were used for intercalation studies in double-stranded DNA, paving the way for important advances in terms of biological reporter molecules.[200,202] The detection of biotinylated species (DNA, peptides, proteins) has been achieved with molecules like 33.



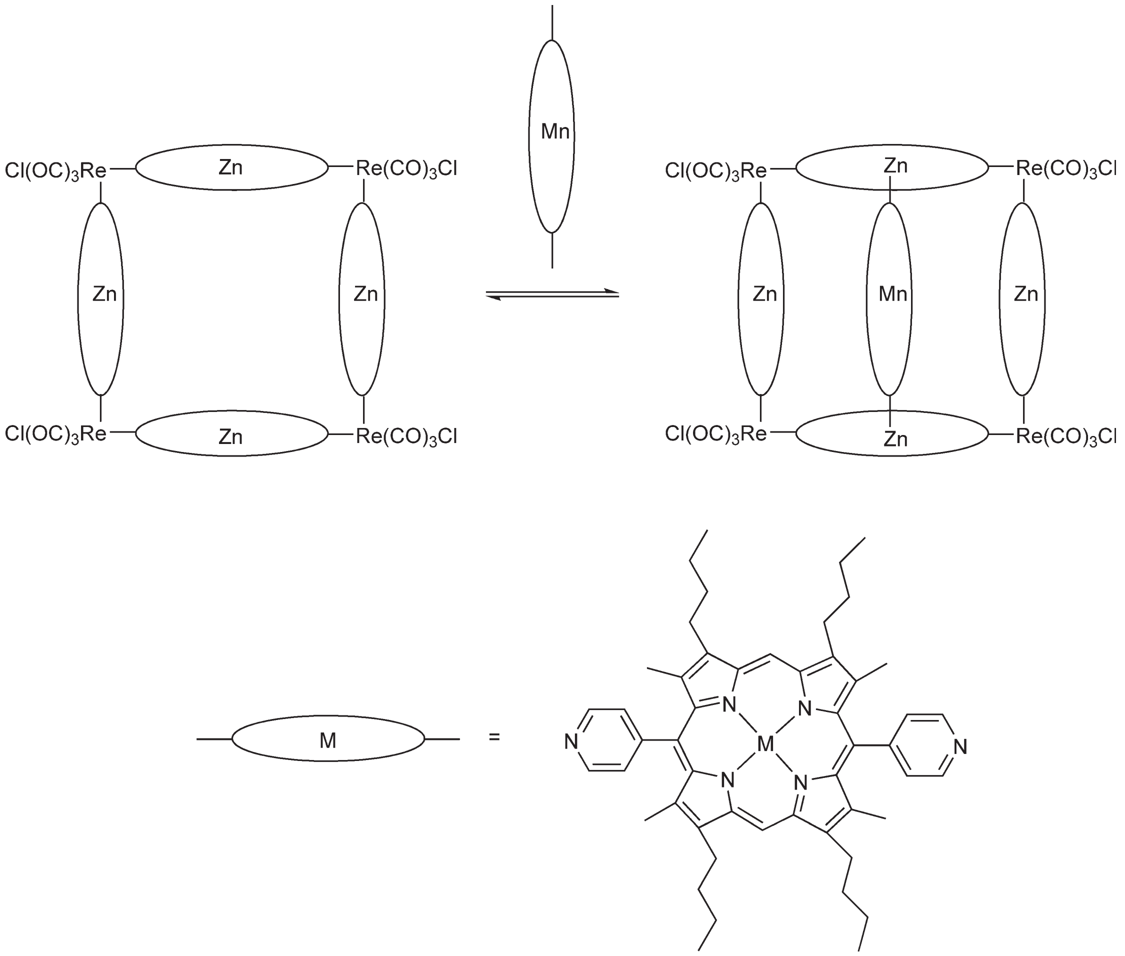
33

Upon binding to avidin, the emission intensity and lifetime actually increase as compared to the isolated complex. This situation overcomes the normal difficulties posed by the severe emission quenching usually observed with classical fluorescent probes designed to bind avidin.[200] Recognition of SH groups in thiolated oligonucleotide, glutathione, and bovine serum albumin and human serum albumin uses the maleimide group in the pyridine ligand in complexes of formula *fac*-$[Re(CO)_3(\alpha\text{-diimine})\{(N\text{-}(3\text{-pyridyl})maleimide\}]^+$,[243] or related ones with iodoacetamide as SH-sensitive group.[244]

The binding of surface histidines on proteins to *fac*-$[Re(CO)_3(phen)]^+$, via H_2O replacement, has been structurally characterized and allowed the study of photogenerated aromatic amino acid radicals in electron-transfer processes between proteins.[245]

Recent works give the latest inputs and summarize the previous achievements and disappointments in areas like photochromic materials,[198] electroluminescent polymers incorporating *fac*-$[Re(CO)_3(bipy)X]$ molecules in the polymer backbone as pendant entities or as dopants,[246–248] light-emitting materials and diodes,[249,250] photovoltaic devices,[214] photoswitches,[201,235] non-linear optics materials,[251–253] liquid crystals,[254,255] and molecular machines.[256] A final topic of relevant interest deals with the assembling of molecules containing the fragment $Re(CO)_3$ into new supramolecular materials called molecular squares, triangles, or rectangles. These types of species result from the availability of two *cis* (90°) coordination positions in the unsaturated *fac*-$[Re(CO)_3X]$ fragment. When bidentate ligands possess their donor atoms on opposite sides at a 180° binding angle, each of the terminal donors will bind a different *fac*-$[Re(CO)_3X]$ group. Instead of oligomerization or polymerization, under 1 : 1 stoichiometric ratios of donor atoms and available coordination positions, highly efficient and thermodynamically driven self-assembly takes place, forming molecular squares or cyclophanes with the bidentate ligands bridging over the $Re(CO)_3X$ centres (see Scheme 16). When the bridging ligands are rather long, molecular triangles are formed instead as the sole product. When the bridging bidentate ligand is bent with a binding angle of ca.120°, dimers are formed. Some purification and characterization problems have been recently solved.[257] Such systems had been previously characterized using the metal fragments, namely square-planar Pd and Pt complexes of type $ML_2(OTf)_2$, and the first $Re(CO)_3$-containing metallocyclophane prepared was actually heterobimetallic containing both two $Re(CO)_3X$ and two Pd(dppp) corners.[258]

The large number of results has been partly condensed in two review articles written by two of the authors that have more decisively contributed to the field with respect to Re luminescent complexes, Hupp[259] and Lees.[260]



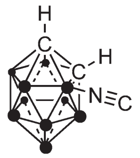
Scheme 16

Molecular rectangles, recently reviewed,[261] elicit access, after reduction, to an unusual category of mixed valence compounds, in which the ligands themselves are the redox centers and interligand electronic communication is controlled by direct ligand-orbital overlap rather than by super-exchange through the metal ions.[262]

The luminescent properties of the $Re(CO)_3X$ fragment together with the potential host–guest chemistry offered by these molecular squares were further developed to build box-like structures where the walls are defined by large planar molecules, such as porphyrins. Depending on the size of the edges, such structures can be constructed with cavities that range from 7 Å × 7 Å to 20 Å × 20 Å and 6 Å × 25 Å. In the solid state, these compounds feature exceptionally large void volumes because of the large cavity sizes and the absence of charge-compensating ions. As such, the molecular solids typically display good mesoporosity and an ability to function as high-capacity hosts for suitably sized guest molecules.[263] Mesoporous solids can complex a variety of molecules and hence can be used as sensors.[256,264,265] A porphyrin walled box has been used to build an artificial enzyme with olefin-epoxidation activity as represented in Scheme 16.[266]

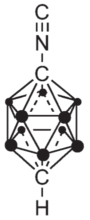
5.13.2.3.9 Re(CNR) derivatives

The majority of Re isonitrile chemistry follows the structural patterns of the isoelectronic carbonyls and, in fact, many of them may be prepared by direct or catalyzed CNR substitution on parent Re carbonyl complexes. The important differences are found mainly in the two different and opposed modes of activation of CNR that depend on the electron density of the metal center as exemplified below. In the wake of the success of $[Tc(CNCH_2C(Me)_2OMe)_6]^+$ as a cardio-imaging agent (Cardiolite),[177] other homoleptic $[Re(CNR)_6]^+$ complexes have been made like the isonitrilecarboranes 34 and 35 designed for boron neutron-capture therapy (BNCT) or boron neutron-capture synovectomy (BNCS).[267]



34

● = BH



35

The bis-isonitrile ligand $L_2 = CN(CH_2)_3O(CH_2)_2O(CH_2)_3NC$ specially designed to impart solubility for blood clearance *in vivo* forms the octahedral complex $[Re(L_2)_3]^+$. The Tc analog has a high binding affinity for the heart.[268]

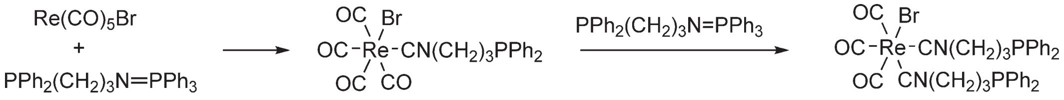
The availability and lability of Re(I) aquo complexes led to exploring new methods of synthesis in aqueous solution. *fac*-$[Re(CO)_3(H_2O)_3]^+$ **26** reacts with $CNBu^t$ in water all the way to *fac*-$[Re(CO)_3(CNBu^t)_3]^+$ even in the presence of excess Cl^-. However, in MeOH or THF, the same complex can only be obtained with weak counter-anions like PF_6^- or NO_3^-. Otherwise, the reaction stops at the disubstitution level forming *fac*-$[Re(CO)_3(CNBu^t)_2Cl]$ even with excess isonitrile.[128] Reaction of **26** with the isonitrile carboranes **34** and **35** readily affords the corresponding *fac*-$[Re(CO)_3(CNcarborane)_3]^+$ and $[Re(CO)_2(CNcarborane)_4]^+$ in good yields and in close parallel to similar chemistry of much smaller isonitriles cited by the authors.[269] $[Re(CO)_4(OH_2)_2]^+$ also reacts with isonitriles to give $[(OC)_4Re(C{=}N{-}R)_2][BF_4]$ ($R = (CH_2)_3Me$, CH_2CO_2Et).[121] The use of these isonitriles functionalized at the terminal opposite to the CN donor allows conjugation with other biomolecules in a more convenient way.[132,184] The chemistry of $Re(CNBu^t)_3(PR_3)_2X$ (X = H, Cl) in the activation of H_2 has been mentioned in Section 5.13.2.3.1.

Alkylation of *trans*-$[Re(CN)_2(dppe)_2][NBu_4]$ affords *trans*-$[Re(CNR)_2(dppe)_2]^+$, whereas *trans*-$[Re(CNH)(CNSiMe_3)(dppe)_2]OTf$ is obtained from the reaction with $Me_3SiO_3SCF_3$.[270] The discovery that phosphinimines react with metal carbonyls to produce OPR_3 and a coordinated isonitrile ligand, led to the synthesis of isonitrile derivatives according to Scheme 17.

The strongly electron-releasing isocyanoborane (Me_3BH_2NC) breaks the bridging halide bridges in $[Re(CO)_4Br]_2$ to give *cis*-$[Re(CO)_4(CNBH_2NMe_3)Br]$ as the major product contaminated by a small amount of the *trans*-isomer. However, there is no equilibration of the isomers in solution.[271] PdO-catalyzed substitution of $ReX(CO)_4(PR_3)$ with $CNBu^t$ leads to the *mer*- and *fac*-isomers of $ReX(CO)_3(PR_3)_2(CNBu^t)$. The *fac*-isomer is favored at higher temperatures.[272] Reaction of $Re(CO)_4(CNR)Br$ with Me_3NO in CH_2Cl_2 leads to $[Re(CO)_3(CNR)(NMe_3)Br]$ for both $R = {}^iPr$, Ph.[273] With primary amines, it is possible to isolate *fac*-$[Re(CO)_3(CNR)(NH_2R)Br]$. In NCMe, the same reaction forms the versatile starting material $[Re(CO)_3(CNR)(NCMe)Br]$. Substitution of NCMe by the isocyanoiminephosphorane $CNNPPh_3$ forms $[ReBr(CO)_3(CNR)(CNNPPh_3)]$. This reacts with ketones to form *fac*-$[ReBr(CO)_3(CNPh)(CNN{=}CR_2)]$ and $OPPh_3$.[274]

Pombeiro and co-workers have developed a thorough study of the chemistry of the $ReCl(L)(dppe)_2$ system, using unsaturated ligand L = CO, CNR, CN^-, carbenes, carbynes, and related species, and pioneered some activation processes of CNR and other ligands on this very electron-rich fragment. Some new methods for preparing CNR complexes of this type have appeared. The coordination chemistry of the simple isonitrile, CNH, has been reviewed, and its complex *trans*-$[ReCl(CNH)(dppe)_2]$ prepared.[275] $CNCH_2SiMe_3$ acts as a reducing species toward $Re(O)Cl_3(PPh_3)_2$ to produce a rare example of a pentacoordinated complex $ReCl(N_2)(PPh_3)(CNCH_2TMS)_2$ under N_2 but not under Ar.[276]

Treatment of $[ReCl(CN)(dppe)_2]^+$ with Me_3SiOTf affords $[ReH(CNMe)(dppe)_2]$, which is also obtained by reaction of $Li[BEt_3H]$ with *trans*-$[ReCl(CNMe)(dppe)_2]$. The latter complex reacts with $[NBu_4]CN$ in the presence of $TlBF_4$ or $[NBu_4]F$ to give *trans*-$[Re(CN)(CNMe)(dppe)_2]$ or *trans*-$[ReF(CNMe)(dppe)_2]$, respectively. CV shows that in aprotic solvents these complexes undergo two successive single-electron reversible oxidations.[277] The structures of several of $[ReX(CNR)(dppe)_2]$ complexes show severe bending of the C–N–R angle, between ca. 140° and 160°, and the $\nu(C{\equiv}N)$ stretching vibrations appear at rather low energies (ca. 1,830 cm^{-1}) compared to normal linear CNR ligands of free CNR (2,150 cm^{-1}). This has an electronic reason but may be overcome by steric hindrance. Recently, a computational study



Scheme 17

reanalyzed these data.[278] This bent geometry assigns an Re$=$C character to the ReCNR bond as well as an electron pair located at the N. As a result, these complexes are activated toward electrophilic attack, producing aminocarbynes. The complex of the simplest aminocarbyne, *trans*-$[ReCl(CNH_2)(dppe)_2]^+$, has been isolated with both BF_4^- and Cl^- anions.[279] The chemistry of Re aminocarbyne species, largely developed by Pombeiro and co-workers, as well as related ones from group 5 and 6 metals, has been reviewed.[280]

Some β-functionalized phenyl isonitriles, CNC_6H_4-2-OR, CNC_6H_4-2,5-$(OR)_2$ (R$=$H, $SiMe_3$), form complexes of the type *trans*-$[ReCl(CNC_6H_4\text{-2-OR})(dppe)_2]$. Due to the strong electron-releasing ability of this Re(I) center, there is no tendency for intramolecular nucleophilic attack of the OH function to the coordinated C atom. This attack, leading to a heterocyclic carbene ligand, is a valuable strategy for preparing new heterocyclic carbene derivatives. On Re, it was only achieved on Re(V) complexes (Scheme 19) where the less electron-rich metal center activates coordinated CNR toward nucleophilic attack. The application of this strategy to Re and several other metals has been reviewed.[281]

The octahedral $[Re(bipy)_2(CNBu^t)_2]^+$ can be obtained by reduction of Re(III) $CNBu^t$ complexes. In more conventional ways, a series of isonitrile complexes of the form *fac*-$[Re(CO)_3(\alpha\text{-diimine})CNR]^+$ (R$=$*n*-alkyl) can have extraordinarily high quantum yields (>0.7) and long excited-state lifetimes (>100 µs) in fluid solutions at RT.[282] The long alkyl chain can be used to form supramolecular aggregates with hydrophobic hosts like cyclodextrins. The complex $Re(CO)_3Cl(CNC_6H_{10}CN)_2$ has been used as building block for the synthesis of trinuclear assemblies (T-joints; 90° angle) by addition of the unsaturated species $[Mo(CO)_3(2,2'\text{-}(Me_3SiC\equiv C)_2\text{–bipy})]$ to each free terminal CN function.[283]

5.13.2.3.10 Re carbonyl nitrosyl complexes

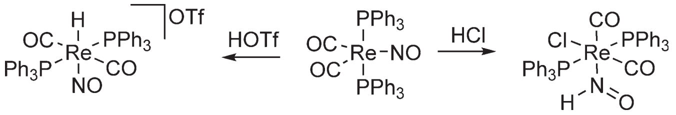
The group of Berke has studied the chemistry of Re nitrosyl complexes under the perspective of comparing their properties with those of the corresponding carbonyls. Different reactivities have been found as the result of the stonger π-acidity of the NO^+ ligand compared to CO. As can be seen in Section 5.13.3.1.5(iv), this substitution may have very important practical consequences. Nitrosylation of the dimer $[Re_2(CO)_6Cl_2(\mu\text{-}Cl)_2]^{2-}$ with $NOBF_4$ gives $[Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}Cl)_2]$ **36**. This is a typical reactivity pattern for low oxidation state Re(I) complexes, for example, in the reaction of $Re(CO)_2(\kappa^3\text{-triphos})X$ with $NOBF_4$, to form $[Re(CO)(NO)(\kappa^3\text{-triphos})X]^+$.[141] Compound **36** reacts with $P(OR)_3$ and PR_3 ligands (R$=$Me, Et, Pr^i, Cy) to give $Re(CO)(NO)L_2Cl_2$. Upon reductive carbonylation with Na/Hg/CO, the latter originate $Re(CO)_2(NO)L_2$, and with Mg/PhC$\equiv$CPh, they produce $Re(CO)(NO)L_2(Ph_2C_2)$. The dimethyls $Re(CO)NO)L_2Me_2$ and dihydrides $Re(CO)(NO)L_2H_2$ are obtained by reaction with LiMe or $Na[AlH_2(OCH_2CH_2OMe)_2]$, respectively.[284]

The nature and reactivity of the Re–OTf bond in these Re(I) complexes was studied from the corresponding $Re(CO)(NO)L_2(OTf)_2$ **37** and $Re(CO)(NO)L_2Cl(OTf)$ complexes. Triflate substitution by NCMe solvent in **37** is a slow process leading to $[Re(CO)(NO)L_2(NCMe)_2](OTf)_2$. The OTf *trans* to CO is replaced faster than the one *trans* to NO. Similarly, reaction of $[Re(CO)(NO)L_2(NCMe)_2](OTf)_2$ with bipy is not a simple substitution, whereas $[Re(CO)_3L_2(bipy)]OTf$ is readily formed from $Re(CO)_3L_2(OTf)$ under similar conditions. This is in accord with a longer Re–OTf bond in $Re(CO)_3L_2(OTf)$ compared with that in $Re(CO)(NO)L_2(OTf)_2$.[285]

Closely related to these complexes are the nitroxyl (NH$=$O) derivatives $[Re(CO)_3(PPh_3)_2(NH{=}O)]OTf$ and $[Re(CO)_2(PPh_3)_2(NH{=}O)Cl]$. The former is obtained by oxidation of the hydroxylamine ligand of $[Re(CO)_3(PPh_3)_2(NH_2OH)]OTf$ with $Pb(OAc)_4$ and the latter by addition of HCl across the Re–N bond of $Re(CO)_2(NO)(PPh_3)_2$ (Scheme 18).

Instead, the stronger protic acid HOTf forms $[Re(CO)_2(NO)(PPh_3)_2H]OTf$ by protonation at the metal.[286] Nitroxyl is a very reactive, elusive species, and these are among the few examples of its stabilization by coordination to a transition metal.

The effect of the NO^+ ligand on the chemistry of Re(I) hydride and H_2 complexes has been described in Section 5.13.2.3.1.



Scheme 18

5.13.2.4 Re(ii) Complexes

5.13.2.4.1 Mononuclear complexes

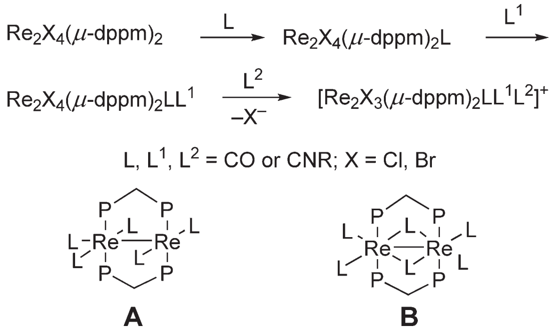
While there are a large number of Re(i) carbonyl halide derivatives known, there has been much less study of the oxidation of these compounds to 17-electron mononuclear Re(ii) species that have abundant, stable Mn counterparts. Since Re(i) complexes are more difficult to oxidize than their Mn analogs, Re(ii) complexes are also likely to be more reactive than their Mn(ii) analogs in a thermodynamic sense. Furthermore, there may be the possibility of overall disproportionation reactions giving stable seven-coordinate Re(iii) derivatives. As mentioned above (see Scheme 12) in the photooxidation of $[Re(CO)_3(\alpha\text{-diimine})X]$, it appears that Re(ii) is short lived and reverts to Re(i) by a variety of mechanisms.[287] However, contrary to most other polypyridyl complexes, $Re(CO)_3(1,4\text{-}^tBu_2\text{-DAB})X$ and $Re(CO)_3(1,3\text{-}^tBu_2\text{-sdi})X$ (X = Cl, Br) undergo a reversible oxidation to an Re(ii) complex at $E_{1/2} \approx 1$ V. This has been interpreted as a result of the capacity of DAB and sdi ligands to donate charge to the metal that stabilizes the oxidized state.[227] CV of the complex $Re(CO)_3(mtb)Cl$ (mtb = 1-methyl(2-^{t}Bu–thiomethyl)–1H–benzimidazole) shows a reversible oxidation but the oxidized complex is very short lived (<1 min) and is ESR silent. Its SMe substituted analog is not even reversibly oxidized in CV.[288]

A systematic electrochemical and spectroelectrochemical study on *cis*- or *trans*-$[Re(CO)_2(P\text{-}P)_2]^+$ and *trans*-$[Re(CO)(P\text{–}P)_2X]$ (P–P = dppm, dppe, *o*-$(Ph_2P)_2(C_6H_4)$(dpbz); X = Cl, Br) has shown that their oxidized Re(ii) species are always stable in solution with these ligand combinations, although the strongest oxidants among the Re(ii) species are reactive to adventitious impurities, or light, and revert back to their 18-electron analogs. As the *trans*-form is dominant in Re(ii), the *cis*-Re(ii) species generated by oxidation isomerize rapidly to the *trans*-isomers.[289] $[Re(CO)_2(\kappa^3\text{-triphos})X]^+$ is stable on the synthetic timescale, and binuclear species with bridging diphosphines show similar behavior.[137] $Re(CNBu^t)_3(PR_3)_2Cl$ is oxidized by chlorinated solvents to give the 17-electron $[Re(CNBu^t)_3(PR_3)_2Cl]Cl$.[68] The complexes $TpRe(CO)(PMe_3)(OTf)$[290] are important starting materials for strong Re(i) complexes capable of coordinating aromatics in an η^2-fashion (Section 5.13.3.1.2).

5.13.2.4.2 Dinuclear complexes $[Re_2(\mu\text{-dppm})_2]^{4+}$

In 1985, Cotton and co-workers discovered that $Re_2Cl_4(\mu\text{-dppm})_2$ readily adds CO at ambient pressure to give $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ and $Re_2Cl_4(\mu\text{-dppm})_2(CO)_2$. Based upon this finding, the group of Walton has continued a thorough investigation of the chemistry of the adducts of the $[Re_2(\mu\text{-dppm})_2]^{4+}$ core in the last two decades. One noteworthy aspect of this chemistry is the ability of $Re_2X_4(\mu\text{-dppm})_2$ to be complexed by π-acceptor ligands, namely, CO and CNR, to afford dinuclear species in which the dppm ligand bridges prevent fragmentation to mononuclear species as readily occurs in the case of the triply bonded complexes $Re_2X_4(PR_3)_4$ which contain monodentate rather than bridging bidentate phosphines. Addition of up to three π-acid ligands L (L = CO, CNR) occurs according to Scheme 19.

In the case of L = CO and $L^1 = L^2$ = CNxylyl, the isomers are based upon the two structural types **A** and **B**. Addition of a fourth CNR was realized in $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNxylyl)_3]^{2+}$, which was isolated in four structurally distinct, non-interconvertible isomers, with reversible redox chemistry. They can be chemically reduced in two steps by Cp_2Co, thereby reducing the Re–Re bond order. Overall, the $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNxylyl)_3]^{2+/+/0}$ span seven different structural variants with bond orders of 3, 2, 1.5, 1, and 0.[291] Three of the neutral isomers react with TlOTf and CNxylyl to produce a complex with five π-acid ligands $[Re_2(\mu\text{-Cl})(\mu\text{-dppm})_2(\mu\text{-CO})(CNxylyl)_4]^+$ of structure type **B**.[292]



Scheme 19

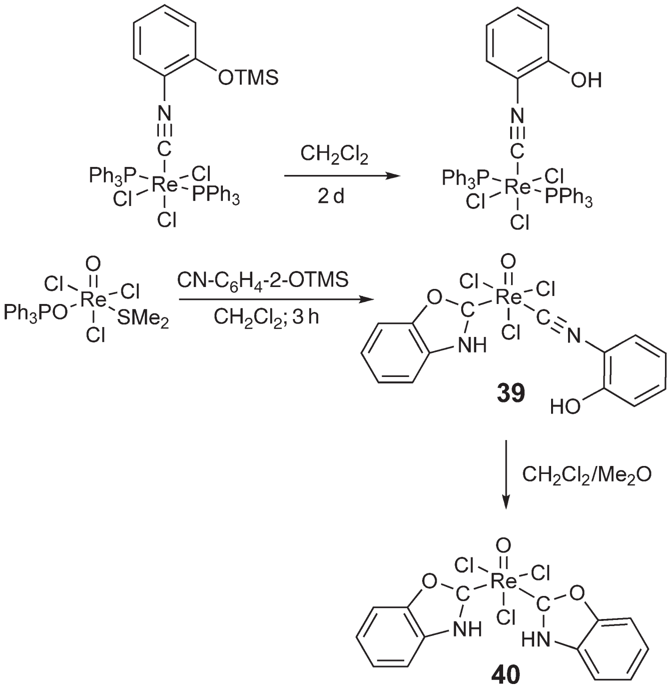
This series of studies on isonitrile derivatives of the $[Re_2(\mu\text{-dppm})_2]^{4+}$ core has reached its 22nd report with the introduction of Cy substituents on the P ligands.[293] Related complexes with CO and NCR ligands have also been studied in terms of their structural features and interconversions.[294]

5.13.2.5 Re(III), Re(IV), and Re(V) Complexes

The reaction of $[Re(CO)_3Br_3]^{2-}$ with Br_2 yields the rhenium(III) anion $[Re(CO)_2Br_4]^-$.[131] The complex $Re\{(C_6F_5NCH_2CH_2)_3N\}Br$ undergoes easy reduction by Mg and the resulting Re(III) fragment readily coordinates wide variety of ligands, including CO in the complex $[Re\{(C_6F_5NCH_2CH_2)_3N\}CO]$.[295] The formation of $[ReBr_3(NNC_6H_4R\text{-}4)(CO)_2]^-$ (R = H, Cl, CO_2Et) from $[ReBr_3(CO)_3]^{2+}$ and $[4\text{-}RC_6H_4N_2]^+$[296] involves net oxidative addition of the diazonium salt to the rhenium with elimination of $[Et_4N][BF_4]$. The diazenide ligand is singly bent, consistent with its formally donating three electrons to the metal.

Re(III) isocyanide derivatives are relatively abundant either as six- or seven-coordinate species (COMC (1982) and COMC (1995)). The cleavage of Re–Re bonds is a common synthetic method as in the case of the complex $[Re(CNCH_2TMS)_5Cl_2]^-$ that was prepared from $Re_2(O_2CCH_3)_4Cl_2$ and the isonitrile ligand in refluxing MeOH.[276] The complex $Re\{N(CH_2CH_2S)_3\}(CNR)$ **38** revealed an unusual chemistry. Indeed, protonation of the CNR ligand in aqueous HCl leads to the unprecedented transformation of CNR into CO producing $Re\{N(CH_2CH_2S)_3\}(CO)$ (R = ^tBu, CH_2COOEt). Again, the CNR ligand in **38** is strongly bent and does not undergo nucleophilic addition at its C atom.[297] The ester function of $Re\{N(CH_2CH_2S)_3\}(CNCH_2COOR)$ can be easily manipulated under basic aqueous conditions. A series of complexes of formula *trans*-$[Re(CNR)(PPh_3)_2Cl_3]$ with functionalized R groups has been prepared either by reduction of *trans*-$[Re(O)Cl_3(PPh_3)_2]$ in the presence of the CNR ligand, or by substitution of the parent acetonitrile derivative.[298] The complex *mer*-$[ReCl_3(CNC_6H_4\text{–}2\text{-}OH)(PPh_3)_2]$ is stable and readily isolated from the parent NCMe analog (Scheme 20). In spite of the higher oxidation state of the metal, no intramolecular cyclization to heterocyclic carbenes is observed like in other Re(I) derivatives of the same ligand.[281,299]

However, the Re(V) complex $Re(O)Cl_3(OPPh_3)(SMe_2)$ reacts with $CN(C_6H_4\text{-}2\text{-}OTMS)$ to give the complexes **39** and **40**.[281,299] Strictly speaking, these complexes have other C ligands and should be mentioned in the next sections. However, since they derive from a very rare intramolecular activation of a CNR ligand on an Re(V) center, they are reported here.



Scheme 20

5.13.3 Complexes with other Carbon Ligands

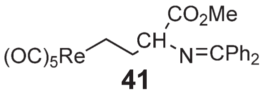
The compounds will be arranged by subsections ordered by increasing hapticity of the C ligands. When more than one C ligand is present, the compound will be filed in the subsection corresponding to the higher hapticity, for example, $CpRe(CO)_2Me$ belongs to the η^5-ligand subsection and η^1-sub-subsection.

5.13.3.1 Re(I) Complexes

5.13.3.1.1 Re complexes with η^1-ligands

5.13.3.1.1.(i) Alkyl derivatives

Nucleophilic addition to the C_2H_4 ligand in $[Re(CO)_5(\eta^2\text{-}C_2H_4)]^+$ has been used to produce unusual functionalized complexes like the one obtained by addtion of $[C_{60}H]^-$,[300] and biologically active molecules labeled with the $Re(CO)_5$ fragment, for example, the α-amino acid Schiff base **41** and barbiturate derivative **42**.[301,302]



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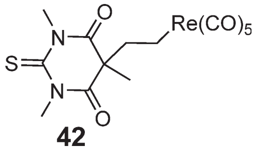


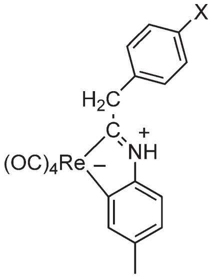
42

Conversely, addition of nucleophilic $[Re(CO)_5]^-$ to a variety of metal-coordinated unsaturated hydrocarbons, carbenes, carbynes, and other electrophilic functions has led to a vast number of polynuclear complexes with $(CO)_5Re(\eta^1\text{-hydrocarbyl})$ bonds. Early examples have been reviewed,[4] and some more recent ones are available, particularly along the series of 48 works on hydrocarbon-bridged metal complexes produced by the group of Beck and others cited therein.[303] $\mu(1,n)$-Alkanediyl complexes $[(OC)_5Re(CH_2)_nRe(CO)_5]$ have been prepared by other methods.[304] Perfluoroorganomanganese and -rhenium compounds $Re(CO)_5Rf$ ($Rf = CF_3$, C_2F_5, C_3F_7, C_4F_9, C_6F_{13}, C_6F_5) are formed in good yields from the reactions of $Re(CO)_5Br$ with $Cd(Rf)_2$ in CH_2Cl_2, either in the presence of stoichiometric amounts of $Ag[BF_4]$ or catalytic amounts of CuI. In the presence of donors like NCMe the mono- or disubstituted complexes $M(CO)_4(NCMe)Rf$ or $M(CO)_3(NCMe)_2Rf$ are formed.[305]

Long-chain alkyls $[Re(CO)_5R]$(R up to $n\text{-}C_{18}H_{37}$) react with PPh_3, to yield *cis*-$[ReR(CO)_4(PPh_3)]$ and not *cis*-$[Re(COR)(CO)_4(PPh_3)]$, as expected.[304] The interchange between the bridged alkyls and the μ-diacyls $[(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5]$ gives rates of carbonylation/decarbonylation dependent on the chain length and different from those of the corresponding mononuclear acyls.[306]

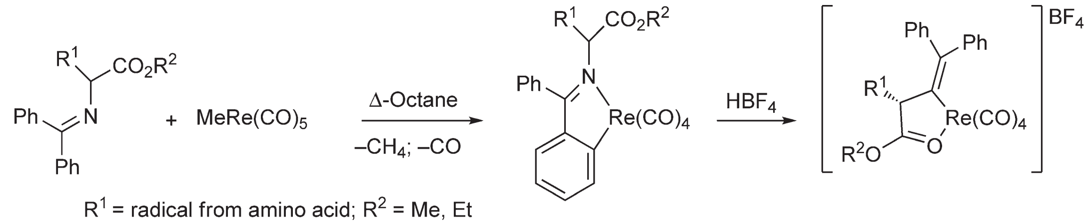
$Re(CO)_5Me$ reacting with a series of phosphines at 110–130 °C for 40–140 h with degassing every 12 h gave *trans-mer*-$[Re(CO)_3(PR_3)_2Me]$ ($R = Cy$, Pr^i, Ph).[60] The PPh_3 complex with a smaller cone angle gives the highest yield. Some isomeric *fac*-$[Re(CO)_3(PR_3)Me]$ complexes were prepared in other ways by Bergman and co-workers.[2]

The benzyl derivatives $Re(CO)_5(CH_2C_6H_4X\text{-}p)$ ($X = Cl$, OMe) undergo smooth substitution by a series of aryl isonitriles (CNAr) forming *cis*-$[Re(CO)_4(CNAr)(CH_2C_6H_4X\text{-}p)$. Upon refluxing in toluene, insertion of the CNAr into the Re–C_2Ar^1 bond takes place followed by *ortho*-metallation and hydride migration to the iminoacyl complex **43**.[307]



43

Although insertions are rare, *ortho*-metallation reactions are widely known for Re(I) carbonyl complexes.[1,2] The *ortho*-metallation of $Re(CO)_5Me$ with Schiff bases derived from amino acids (Scheme 21) has been described within a program for studying organometallic complexes of biologically important ligands.[308]



Scheme 21

A number of alkyl complexes *fac*-[Re(CO)$_3$(α-diimine)R] **44** were prepared by the general procedure in Equation (6) in order to study their photophysics.[309]

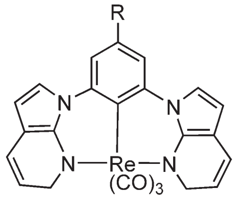
$$\mathrm{Re(CO)_3(N{-}N)X} \xrightarrow[\text{ii, RX}]{\text{i, NaK or Na/Hg in THF}} \mathrm{Re(CO)_3(N{-}N)R} \qquad (6)$$

Upon photolysis, the complexes undergo Re–C bond homolysis, a process that was studied and understood in great detail using the benzyl (Bn) substituent as in Equation (7).[310]

$$\mathrm{Re(CO)_3(N{-}N)Bn} \xrightarrow{h\nu} [\mathrm{Re(CO)_3(N{-}N)(S)}]^{\bullet} + \mathrm{Bn}^{\bullet} \qquad (7)$$

The $\sigma\pi^*$-excited state is populated efficiently and rapidly from the optically excited MLCT state, and is the immediate percursor to the photochemically formed radicals. It may be viewed as a weakly bound biradical $\mathrm{Bn}^{\cdot -}\mathrm{Re(CO)_3(N{-}N^{\cdot -})}$.[310–312]

The reduction of **44** produces radical anionic products in a chemically and electrochemically reversible step.[313] The series of photophysical studies on Re(CO)$_3$L$_2$R complexes includes a study at the femtosecond spectroscopical level.[314–316] What seems to be the first Re(CO)$_3$ derivative of a pincer ligand **45** was recently prepared from the ligand and Re$_2$(CO)$_{10}$ and has green emission.[317]



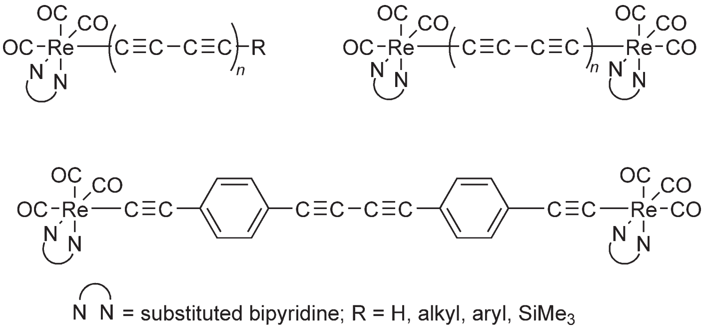
45

Alkylthiomethyl complexes [Re(CO)$_3$(bipy)(CH$_2$SR)] are prepared by reaction of [Re(CO)$_3$(bipy]$^-$ and ClCH$_2$SR (R = Me, Ph). The Re–C bond is readily cleaved by acids like HOTf and Ph$_3$C$^+$. In contrast, MeOTf methylates the S atom to give [Re(CO)$_3$(bipy)(CH$_2$SMeR)](OTf). The latter can be regarded as a stabilized methylidene derivative but only cyclopropanates styrene at 110 °C, forming also [Re(CO)$_3$(bipy)(OTf)] and free SMePh. It does not react with PPh$_3$ or py to exchange SMePh for these nucleophiles, and methylates anions like PPh$_2$$^-$, SEt$^-$, and even I$^-$.[318] This behavior contrasts with that of the [CpRe(PPh$_3$)(NO)(CH$_2$)]$^+$ that reversibly adds SMe$_2$ to the coordinated methylidene.[319]

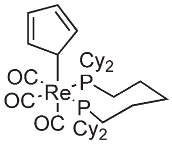
5.13.3.1.1.(ii) Alkenyl, allyl, and alkynyl complexes

The η^1-allyl complexes *fac*-[Re(η^1-C$_3$H$_5$)(CO)$_3$L$_2$] (L$_2$ = bidentate phosphines, bipy, phen), obtained from Re(η^3-C$_3$H$_5$)(CO)$_4$ (Section 5.13.3.1.3), react with CHCl$_3$ to give the corresponding *fac*-[Re(CO)$_3$L$_2$Cl] derivatives. In spite of being potentially tridentate, the triphos ligand remains bidentate in the *fac*-[Re(η^1-C$_3$H$_5$)(CO)$_3$(κ^2-triphos)] complex. In the case of the dppm ligand, the central P–CH$_2$P protons are acidic enough to be abstracted by the η^1-allyl group, releasing propene and yielding a complex with the bidentate diphenylphosphinomethanide ligand (Ph$_2$PCHPPh$_2$) with a planar Re–P–C–P four-membered ring.[162]

The η^1-C$_5$H$_5$ complexes *fac*-[Re(CO)$_3$(PR$_3$)$_2$(η^1-C$_5$H$_5$)] adopt either the usual Re–C(*sp*^{3}) bonding mode in **46** or the less usual Re–C(*sp*^{2}) vinylic bond in **47**, depending on the bulk of the PR$_3$ substituents.[320]



Scheme 22



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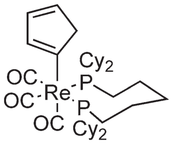


47

Convenient preparations of $(OC)_5ReC{\equiv}CPh$, $(OC)_5ReC{\equiv}CCO_2Me$, and $(OC)_5ReC{\equiv}CSiMe_3$ are reported.[321] The same classical synthesis using $Re(CO)_3$(α-diimine)Cl and $LiC{\equiv}CR$ is limited to few α-diimines, for example, $[Re(CO)_3(4{,}4'\text{-}^tBu_2\text{–}bipy)(C{\equiv}CR)]$.[322] A more general procedure uses $[Re(CO)_3(N\text{–}N)(THF)][BArF]$, the respective terminal alkyne, and an amine base.[157] Based on a one-pot version of this method, a large series of compounds of this type with different α-diimines and terminal R groups has been prepared by the group of Yam, and their luminescence properties characterized and reviewed.[322] These were extended to diynyl, triynyl, and polynyl C chains as represented in Scheme 22.

5.13.3.1.1.(iii) Carbene, vinylidene, allenelydene, and cumulenylidene complexes

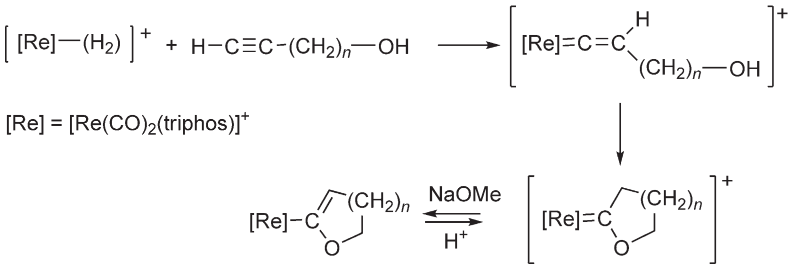
The strong electrophile $[Re(CO)_5FBF_3]$ reacts with 3-butyne-1-oel to give the cyclic oxycarbene complex $[(OC)_5Re{=}\overline{COCH_2CH_2CH_2}][BF_4]$.[323] Following this first example, several other similar species have been developed, primarily by the group of Bianchini, namely those supported by the $[(triphos)Re(CO)_2]^+$ fragment. Vinylidenes $[(triphos)Re(CO)_2({=}C{=}C(H)R)]^+$ are readily formed by the reaction of $[(triphos)Re(CO)_2(H_2)]^+$ with terminal alkynes. In the case of β-, γ-, and δ-alkynols, the final product is the 2-oxacyclocarbene resulting of intramolecular cyclization (Scheme 23). The C_β-proton can be regioselectively (and reversibly) removed with strong base.[324]

Propargylic alcohols, on the other hand, lead to allenylidenes (Scheme 24).

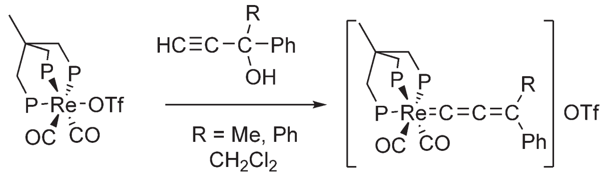
A parallel chemistry is displayed by the related complexes $[Re(CO)_2\{12[ane]P3R3\}Cl]$ and $[Re(CO)_2\{12[ane]\text{-}P3R3\}H]$.[170]

The importance of allenylidene ligands for many innovative synthetic procedures has increased as reviewed.[325,326]

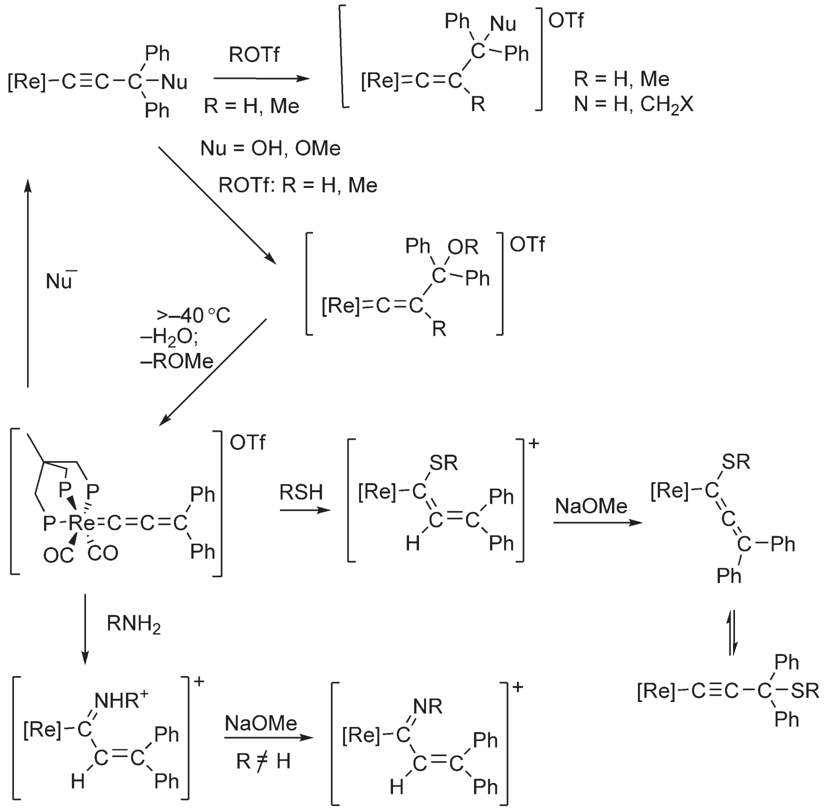
As shown in Scheme 25, the allenylidene does not add water or alcohols but adds HO^- and RO^-.[327] However, it adds thiols, amines, including NH_3,[328] and nucleophilic PR_3.[329]



Scheme 23

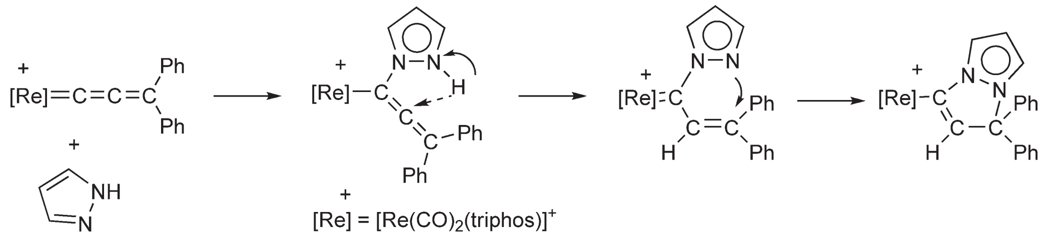


Scheme 24

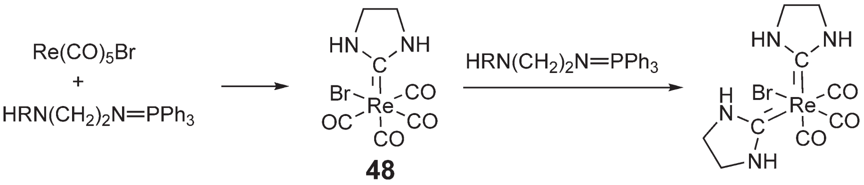


Scheme 25

Several other results involving mechanistic aspects and more sophisticated ligands can be found in[325] or retrieved under the name of Bianchini. Of particular interest, from a synthetic point of view, are the reactions with *N*,*S*- and *N*,*N*-heterocycles that generate heterobicyclic compounds (1,2,3-diheterocyclizations). The different reactivity of the three C atoms allows the reaction sequence of Scheme 26 and other related ones.[325,330]



Scheme 26



Scheme 27

In a modification of the reaction of phosphinimines with coordinated CO, *N*-heterocyclic carbene (NHC) complexes are formed when the dangling PPh_2 group is replaced by an amine group as in Scheme 27.[331]

48 reacts with α-diimines to produce luminescent *fac*-$[Re(CO)_3(N–N)(NHC)]$ complexes.[332]

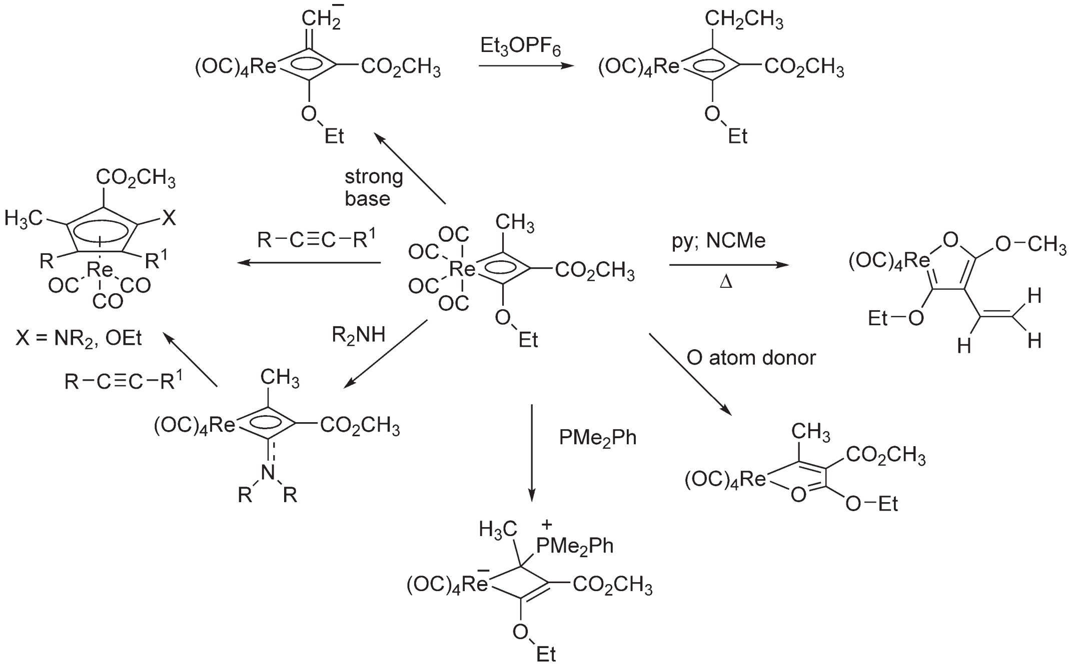
5.13.3.1.1.(iv) Rhenacyclobutadienes

Two joint papers explore the chemistry of rhenacyclobutadienes from the point of view of comparing their reactivity with that of classical Fischer-type carbenes as illustrated in Scheme 28.[333,334]

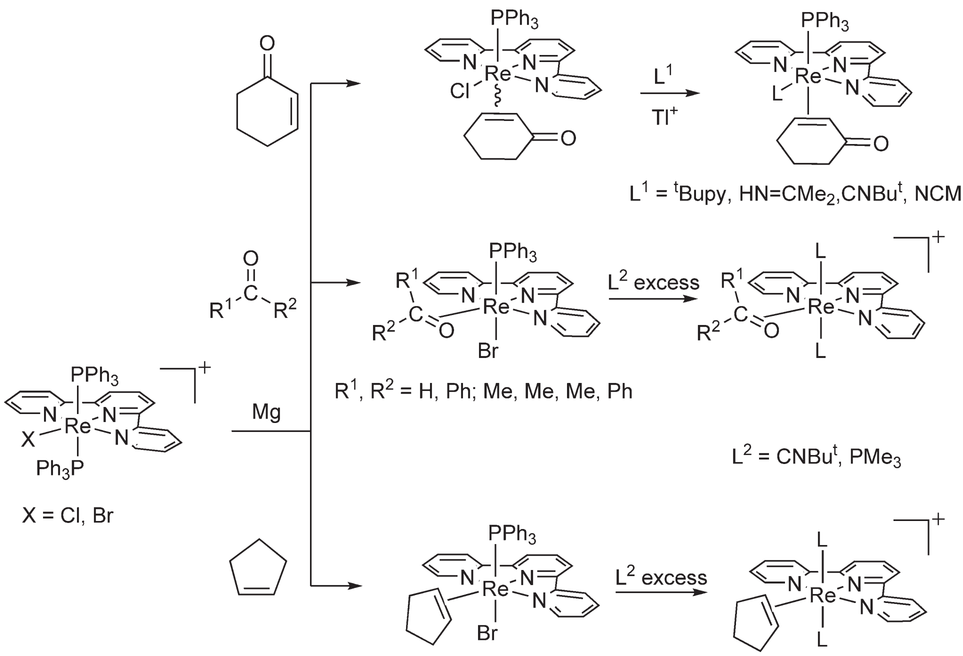
The electrophilicity at both C1 (and its C_α) and C3 is exemplified by deprotonation/alkylation and nucleophilic addition reactions that allow the manipulation of the substituents at these two positions C1 and C3, providing the way to new rhenacyclobutadienes. Addition to C1 is also easy with PR_3 nucleophiles. Acetylenes replace one CO and insert into the Re–C bond forming a rhenabenzene ring that later extrudes $Re(CO)_3$ and results in a highly substituted cyclopentadienyl ring.

5.13.3.1.2 Re complexes with η^2-ligands

Few complexes bearing only alkenes or alkynes as the organic ligand besides CO and other classical ancillary ligands have been reported. In fact, low-valent Re complexes are largely dominated by the presence of strong π-acids like CO, CNR, and NO^+. This fact makes them less useful to bind and activate olefin ligands. However, work from Harman's group led to the finding that the terpyridyl ligand is capable of stabilizing Re(I) to such an extent that more conventional π-acids are no longer required. In fact, reduction of $[Re^{II}(terpy)(PPh_3)_2Cl]OTf$ in the presence of



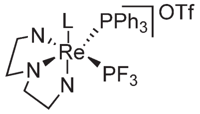
Scheme 28



Scheme 29

cyclohexenone forms Re(terpy)(PPh_3)Cl(η^2-*C*,*C*-cyclohexenone). The Cl ligand is labile and can be replaced by a variety of other ligands L easily affording the cationic derivatives [Re(terpy)(PPh_3)L(η^2-*C*,*C*-cyclohexenone)][PF_6] (L = 4-Bu^{t}py, NH=CMe_2, CNBu^t, NCMe). The double substitution products [Re(terpy)L_2(η^2-*C*,*C*-cyclohexenone)][PF_6] (L = PMe_3, 4-Et–2,6,7-trioxa–1-phosphabicyclo[2.2.2]-octane (ETPB)) are obtained using excess ligand indicating a very stable η^2-C=C–Re bond (Scheme 29).[335]

Reduction of [Re(terpy)(PPh_3)$_2$Br][OTf] with magnesium yields the putative Re(I) complexes of the form [Re(L_π)(terpy)(PPh_3)Br] (L_π = cyclopentene, benzaldehyde, acetone, and acetophenone). These species have been detected by cyclic voltammetry; only the acetone complex could be isolated. The unusual strength of the η^2-C=C and η^2-C=O bonds to this fragments translates into the chemistry of Scheme 29: the *in situ* addition of 2 equiv. of PMe_3 or CNBu^t displaces Br^- and PPh_3 to give isolable olefin, aldehyde, and ketone complexes of the type [Re(L_π)(terpy)L_2][OTf] even with powerful donors such as L = CNBu^t and PMe_3 (Scheme 29).[336] Electrochemical data for several of these terpyridyl complexes reveal two waves Re(II)/Re(I) and Re(I)/Re$^{(0)}$. Many of the terpy–cyclohexenone complexes have d^5/d^6-redox potentials in the expected range for coordination of aromatic molecules but suffer from instability and large steric profiles. The Re(II)/Re(I) reduction potentials are unexpectedly sensitive to the change of a single ligand.[337] The fragment [Re(dien)(PPh_3)(PF_3)]$^+$ readily forms stable η^2-bound complexes with unsaturated organic molecules of the type [Re(dien)(PPh_3)(PF_3)(η^2-L)][OTf] **49** (dien = diethylenetriamine) (L = cyclopentene, *C*,*C*-2-cyclohexen-1-one, ethyl vinyl ether, cyclopentadiene) but fails to form stable η^2-coordinated complexes with arenes or aromatic heterocycles, including furan, naphthalene, *N*-methylpyrrole, and benzene. Steric reasons have been claimed for this behavior, the combination of the bulky PPh_3 and PF_3 ligands most likely compromising the coordinating ability of the rhenium. Indeed, the replacement of PF_3 with CO, a smaller ligand of similar π-acidity, permits isolation of the corresponding [Re(dien)(PPh_3)(CO)(2,3-η^2-furan)][OTf].[338]



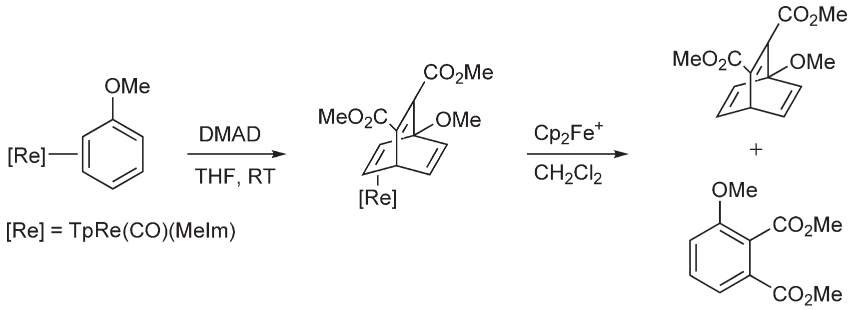
49

The coordination of aromatic molecules (arenes and aromatic heterocycles) to certain strong metal π-bases leads to (η^2-arene)ML_n complexes. This kind of coordination can activate the aromatic molecules toward an electrophilic attack since $d \rightarrow \pi$ backdonation into a π-orbital of the aromatic ligand disrupts their aromaticity. This dearomatization provides important synthetic pathways for the functionalization of aromatic compounds that are complementary to activation toward nucleophilic addition induced by their η^6-coordination to π-acid fragments.[1,2] This has been achieved with the electron-rich metal fragment $[Os(NH_3)_5]^{2+}$ **50**. However, this fragment suffers from several limitations that hamper its wider use, the most serious ones being its lack of chirality, the acidity of the NH_3 ligands, and the reduced solubility due to the high positive charge. The group of Harman has systematically attempted the development of Re(I) surrogates to **50** in order to circumvent these handicaps.[339] Indeed, Re(I) complexes provide the best fragments for η^2-aromatic coordination after **50**. The several $[Cp'Re(L)(L^1)(\eta^2\text{-arene})]^{0,+1}$ ($Cp' = Cp, Cp^*$; L, L^1 = CO, NO, PPh_3; arene = C_6H_5R, thiophene) complexes known are too labile to be of synthetic use. Replacing Cp′ by the better donor Tp from $TpRe(CO)_2(THF)$, stable binuclear complexes $\{TpRe(CO)\}_2)(\mu\text{-}\eta^2\text{-}\eta^2\text{-L})$ are obtained for L = furan, *N*-methylpyrrole, or naphthalene, but still binds thiophene through the S atom.[340] The even stronger π-donor $\{TpRe(CO)(PMe_3)\}$ finally produces a variety of stable η^2-complexes $TpRe(CO)(PMe_3)(\eta^2\text{-L})$ (L = cyclohexene, cyclopentene, naphthalene, phenanthrene, thiophene, 2-methylthiophene, furan, or acetone).[290] They are obtained by reduction of the Re(II) complex $TpRe(CO)(PMe_3)(OTf)$ with Na/Hg in the presence of the unsaturated ligand. The $\{TpRe(CO)(PMe_3)\}$ fragment is isoelectronic with $[CpRe(NO)(PPh_3)]^+$ but considerably more electron rich, as judged by spectroscopic data and by its ability to bind naphthalene in an η^2-coordination mode, to prefer η^2-*C-C*-thiophene over η^1-*S*-thiophene coordination and form stable π-complexes with acetone rather than the more common σ-bonded species like $[CpRe(NO)(PPh_3)(\eta^1\text{-O=CMe}_2)]^+$ (see Section 5.13.3.1.5(iv)). Like the $Cp'Re(NO)(PPh_3)]^+$, $TpRe(CO)(PMe_3)$ is also chiral at metal and is able to discriminate between enantiofaces of the η^2-ligands. For instance, naphthalene binds diastereospecifically. The TpRe(CO)L system was expanded to other ligands of increasing donor ability L = $CNBu^t$, py, PMe_3, MeIm, NH_3. The rates of the propeller-like rotation of ethylene about the ethylene–rhenium bond in the corresponding η^2-ethylene derivatives $TpRe(CO)L(\eta^2\text{-}C_2H_4)$ correlate with both the C≡O stretching frequencies and Re(II/I) reduction potentials for these complexes, indicating that the barrier to rotation is primarily electronic in nature.[341] The coordination stereochemistry and stability of the η^2-bond can be tuned by the nature of L.[342] The complex $TpRe(CO)(MeIm)(\eta^2\text{-}C_6H_6)$ effects dearomatization of the benzene ring allowing its uncoordinated diene system to participate in Diels–Alder and other cycloadditions (Scheme 30), and, therefore, produce a synthetically useful protocol for benzene functionalization.[343]

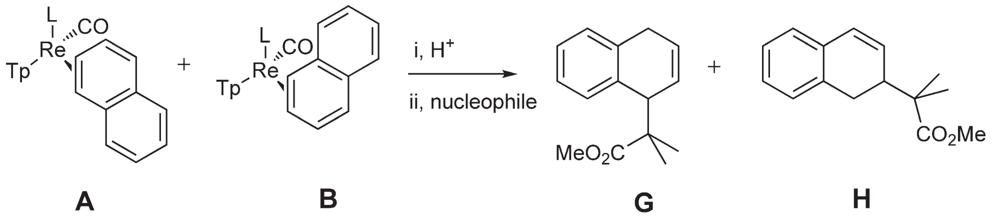
The study includes dipolar cycloadditions,[344] aldehyde addition,[345] as well as unusual sequential electrophilic/nucleophilic additions to η^2-furan complexes as in the acid-catalyzed addition of MeOH to the coordinated η^2-furan ring where the stereochemistry and reactivity are controllable via the nature of L.[346] Tandem electrophilic/nucleophilic addition to coordinated naphthalene (Scheme 31) can also be controlled regio- and stereochemically according to the nature of L.

As seen in Scheme 31, PMe_3 favors 1,4-addition whereas the other ligands favor 1,2-addition. In both cases, the additions take place on the face opposite to the metal and the outcome of the regiochemistry depends on the stereoisomer that is initially attacked by the electrophile H^+. The isomer **A** leads to 1,4-addition whereas **B** leads to 1,2-addition.[347] The 1,4-addition products can be manipulated to form a tricyclic phenanthrene skeleton.[348] The arenium cations resulting from the initial H^+ attack have recently been characterized not only with the TpRe(CO)L fragment but also with the isoelectronic $[TpM(NO)L]^+$ (M = Mo, W).[349] The issues relevant for the stereocontrol of the arene transformations on this fragment and the strategies for engendering chiral dearomatization reagents are critically discussed.[350]

The π-basic metal fragment {TpRe(CO)(MeIm)} forms stable complexes with esters, amides, imides, and anhydrides, offering unusual examples of η^2-coordinated carboxylic acid derivatives unavailable with the fragment



Scheme 30

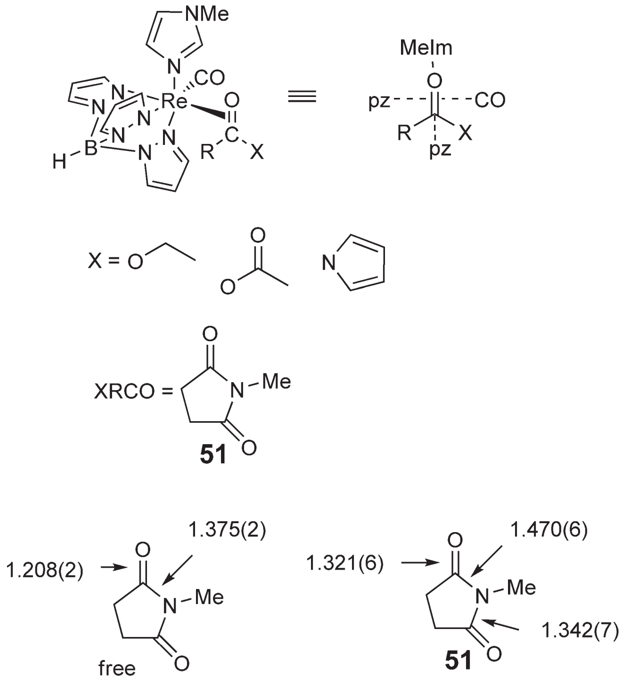


L	*A* : *B*	*G* : *H*
PMe$_3$	10 : 1	12 : 1
py	1 : 3	1 : 7
MeIm	1 : 5	1 : 16

Scheme 31

[Cp′Re(NO)(PPh$_3$)]$^+$ (see Section 5.13.3.1.5(iv)). Coordination is accomplished with a high degree of stereocontrol. In all cases, the bound carbonyl is orthogonal to the Re–CO bond, with the oxygen oriented toward the imidazole ligand and the other heteroatom directed toward the carbonyl (Scheme 32).

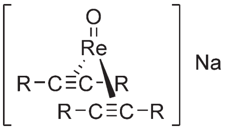
Crystallographic and variable-temperature NMR data indicate that coordination effectively removes the carbonyl from conjugation with the heteroatom. Structural data on **51** show that the coordinated C=O bond of the methyl succinimide ligand lengthens (+0.11 Å), as does the C–N bond adjacent to the metal (+0.10 Å). The latter value indicates a loss of π-interaction between the nitrogen and the bound carbonyl. A shorter bond length (difference of 0.03 Å) for the opposite C–N bond of **51** is observed for the complex, a contraction consistent with an increase in amide character. In the case of amides η^1-bound to Lewis acids, the C=O bond increases only by 0.02 Å, a much smaller effect than detected for this π-basic ligand upon C=O η^2-coordination for the imide produces an increase of more than 0.1 Å. Lewis-acidic coordination of amides leads to a shortening of the adjacent C–N bond, whereas in **51** the opposite effect is much stronger.



(bond distances in Å)

Scheme 32

Furthermore, whereas η^1-bound amide ligands are essentially planar, the bound carbonyl in **51** is bent 40° out of the plane defined by C–N–C (which also contains the methyl carbon and the unbound carbonyl oxygen (1°), consistent with *sp*^{3}-hybridization for the bound amide carbon).[351] The bis-alkyne complex cation $[Re(CO)_4(\eta^2\text{-}C_2Me_2)_2]^+$ was isolated from $[Re(CO)_4(OEt_2)_2]^+$ and 2-butyne in CH_2Cl_2. When exposed in solution to excess Et_2O, other ethers, py, or NEt_3, it rapidly isomerizes to the cyclobutadiene $[Re(\eta^4\text{-}C_4Me_4)(CO)_4]^+$ (see Section 5.13.3.1.4).[352] Another group of acetylene complexes also falls in the category of π-acid-free low oxidation state Re(I) complexes: the oxo-bis(acetylene) anions, $[Re(O)(RC{\equiv}CR)_2]Na$ **52** (R = Me, Et, Ph). These are prepared by reduction of $[Re(O)I(RC{\equiv}CR)_2]$ with a sodium reducing agent. X-ray structures of **1**·crypt and **1**·2NCMe reveal $[Re(O)(RC{\equiv}CR)_2]$ units as isolated anions in the former but, in the latter, connected via Na–O–Na bridges into centrosymmetric dimers. These anions, being highly nucleophilic and strongly reducing, protonate and react with carbon electrophiles such as methyl iodide and acetyl chloride to afford oxo–hydride, oxo–methyl, and oxo–acyl compounds. The anions are also readily oxidized to the dimers $[Re_2O_2(RC{\equiv}CR)_4]$ by dry air, PhI, ^{t}BuI, Cp_2Fe^+, and even Cp_2Co^+, which is telling of their unusual reducing ability.[353]

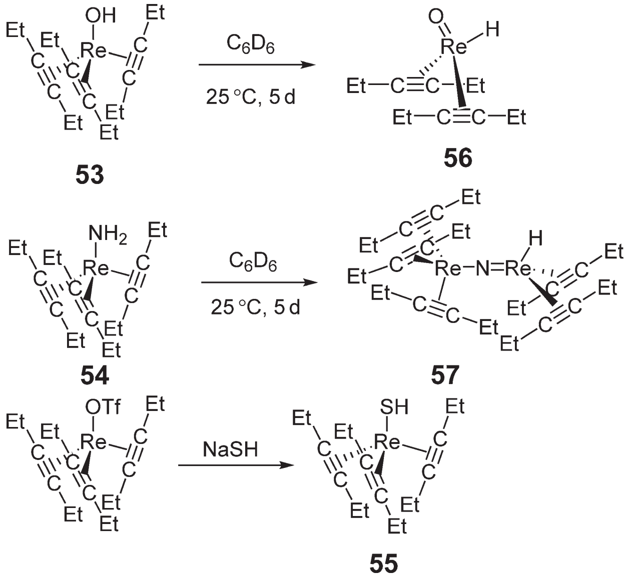


52

The rhenium hydroxide and amide complexes $[Re(OH)(EtC{\equiv}CEt)_3]$ **53**, and $[Re(NH_2)(EtC{\equiv}CEt)_3]$ **54**, have been prepared by deprotonation of $[Re(OH_2)(EtC{\equiv}CEt)_3]^+$ with KOH, and $[Re(NH_3)(EtC{\equiv}CEt)_3]^+$ with $NaNH_2$. The sulfhydryl $[Re(SH)(EtC{\equiv}CEt)_3]$ **55** was prepared as in Scheme 32. Compound **53** spontaneously rearranges to the Re(III) oxo–hydride complex **56** and EtC≡CEt, while compound **54** decays in solution to the unsual μ-nitrido complex **57** (Scheme 33). No rearrangement has been observed for the sulfhydryl **55**, which is indefinitely stable in benzene solutions at RT.[354]

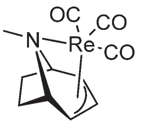
5.13.3.1.3 Re complexes with η^3-ligands

The chemistry of the π-allyl complex $Re(\eta^3\text{-}C_3H_5)(CO)_4$, first reported in 1971, was very little explored. Its most useful application is the synthesis of the reactive cation $[Re(CO)_4(Et_2O)_2]^+$ **58**, made by protonation with $HBF_4{\cdot}Et_2O$. Compound **58** is a convenient entry to many other complexes of the $[Re(CO)_4]^+$ fragment.[121,352,355] A broader reactivity study of this complex was reported recently.[162]



Scheme 33

Under reflux in *n*-octane, the ligands L = PPh_3, py, NCPh, and CNR replace one CO to form complexes of formula [Re(η^3-C_3H_5)$(CO)_3$L]. The first three derivatives are *fac*-isomers but the isonitrile complexes are mixtures of *fac*- and *mer*-isomers. Bidentate diphosphines like dppe, dppp, *SS*-CHIRAPHOS (chiral diphosphine trade mark), bipy, and substituted phenanthrolines force $\eta^3 \rightarrow \eta^1$ slippage forming *fac*-[Re(η^1-C_3H_5)$(CO)_3L_2$] complexes. The synthesis of the tropinidyl complex **59** has been achieved from its tropinidyl–$SnMe_3$ derivative and $Re(CO)_5Br$.[356] This biologically related ligand formally replaces a Cp ring via the η^3-allyl and N two-electron donor set, and has only been used in group 4 metallocenes for olefin polymerization.



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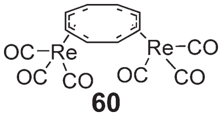
In contrast to the allyl chemistry, Re has contributed to the understanding of the more subtle chemistry of η^3-allenyl and η^3-propargyl complexes that is described in Section 5.13.3.3.3(iii) and recently reviewed.[357,358]

5.13.3.1.4 Re complexes with η^4-ligands

Reaction of $[Re(CO)_3(THF)_2Br]$ with the dianion $[C_8H_8]^{2-}$ leads to the dimer **60** in which each Re atom is bonded to an η^4-C4 fragment of the fluxional C8 ring.[359]



60

The *cis*-bis(alkyne) complex $[Re(CO)_4(\eta^2\text{-MeC}{\equiv}\text{CMe})_2][BF_4]$ isomerizes at RT in the presence of *O*- or *N*-donors to the stable tetramethylcyclobutadiene complex $[Re(CO)_4(\eta^4\text{-}C_4Me_4)][BF_4]$, which forms a distorted trigonal bipyramid with a rectangular, cyclobutadiene ring in the equatorial position, and with remarkably different axial and equatorial Re–C–O bonds.[352] The mechanism proposed for this cyclization, based on molecular orbital calculations, favors a planar rhenacyclopentatriene **61** (Scheme 34).

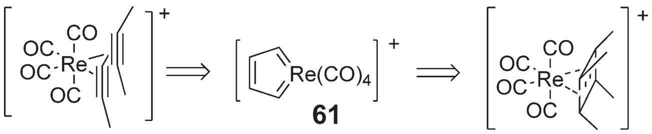
5.13.3.1.5 Re complexes with η^5-ligands

5.13.3.1.5.(i) The cyclic (η^5-Cp′)$Re(CO)_3$ complexes

This is the most important family of complexes in this class. Cp′ represents Cp or any substituted variant or a fused-ring derivative thereof like indenyl. The synthesis of the parent complex $CpRe(CO)_3$ (cyrhetrene) and simple alkyl-substituted analogs, for example, C_5H_4R(CpR), C_5Me_5(Cp^*) is well established.[1,2] However, the need to study more subtle aspects of the chemistry of these molecules and/or to make them suitable for special applications, namely, in catalysis and biology, led to an upsurge of new synthetic approaches to derivatized versions of the cyclopentadienyl ring.

5.13.3.1.5.(i).(a) Synthesis of ring-substituted derivatives Cp′Re(CO)$_3$

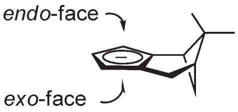
The classical method of deprotonation of the Cp ring with LiBu to form $(C_5H_4Li)Re(CO)_3$ followed by reaction with an electrophile has been used in many instances. The conditions in which this deprotonation actually takes place have been re-examined. In Et_2O, there is no reaction at −78 °C, but at RT, the acyl anion $[CpRe(CO)_2(C(O)Bu^n)]^-$ is formed in 17% yield after conversion into the Fischer carbene $[CpRe(CO)_2({=}C(OMe)Bu^n)]$. However, in THF, at −78 °C, $(C_5H_4Li)Re(CO)_3$ is formed in high yield.[360] This method was used in synthesis of 1,2- and 1,3-disubstituted $(CpR^1R^2)Re(CO)_3$ (R^1 = Me, Bu^t; R^2 = $SiMe_3$),[361] and the synthesis of the hydroxymethyl compounds $(C_5H_4\text{–}CH_2OH)Re(CO)_3$ and $\{C_5H_3(CH_2OH)_2\}Re(CO)_3$ by reaction of $[(C_5H_4Li)Re(CO)_3]$ with paraformaldehyde.[362]



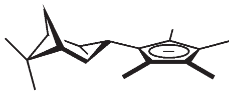
Scheme 34

Several complexes where the Cp ring bears a side chain ended by a donor function have been prepared by similar techniques in order to make tethered complexes with inhibited Cp ring rotation or to carry biologically active functions as seen below.

Still on classical methods, the preparation of more sophisticated examples like the optically active *exo*- and *endo*-isomers of PCpRe(CO)$_3$ (PCp = pinene-fused cyclopentadienyl **62**),[363] or PinCpRe(CO)$_3$,[364] starts from Re(CO)$_3$L$_2$X and a metal salt of the PCp **62**, or PinCp **63**, anions. In the former case, the yield and relative ratio of the two isomers is strongly dependent on solvent, temperature, and the various starting materials Re(CO)$_3$L$_2$X (X = Cl; L = CO, THF, pyridine, NCMe, DME) as well as the derivative MPCp used (M = Li, Tl).

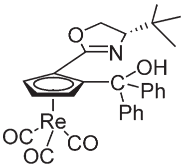


PCp **62**



PinCp **63**

The planar chiral cyrhetrene complexes **64 and 65** and related ones prepared by multisubstitution of the Cp ring in CpRe(CO)$_3$ were successfully used as ligands for catalytic reactions. Very high enantiomeric excesses were obtained in the asymmetric addition of Ph$_2$Zn to aldehydes as well as in asymmetric allylic alkylation, allylic amination, and hydrosilylation.



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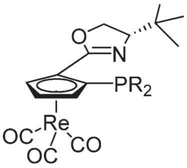
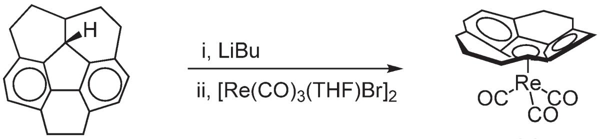


65

In several instances, they compare favorably to more classical planar-chiral ferrocenyl phosphines. The electron-withdrawing power of the Re(CO)$_3$ fragment makes the P atom less nucleophilic than in otherwise similarly substituted ferrocene derivatives.[365,366] Several substituted indenyl complexes have been reported. {η^5-C$_9$H$_6$B-(O$_2$C$_2$Me$_4$)}Re(CO)$_3$,[367] (η^5-C$_9$Me$_7$)Re(CO)$_3$, and [(η^5-C$_9$Me$_7$)Re(CO)$_2$(NO)]$^+$ have been prepared by the classical routes.[368] Likewise, mono- and dimetallated Re(CO)$_3$ derivatives of 1,2-bis-indenylethane are formed from the ligand and Re$_2$(CO)$_{10}$ under reflux.[369] The influence of the electronegative C$_6$F$_5$ substituent on the ν(CO) vibration frequency of {η^5-C$_9$H$_6$(C$_5$F$_5$)}Re(CO)$_3$ and {η^5-C$_9$H$_5$(C$_5$F$_5$)$_2$}Re(CO)$_3$ is marked: ca. 4 cm^{-1} for each C$_6$F$_5$ group.[370] Reaction of diazoindene with Re$_2$(CO)$_8$(NCMe)$_2$ leads to a mixture of mono- and binuclear derivatives of Re(CO)$_3$.[371]

The partially hydrogenated corannulene derivative C$_{20}$H$_{18}$ can be deprotonated and reacted with [Re(CO)$_3$(THF)Br]$_2$ to give [(η^5-C$_{20}$H$_{17}$)Re(CO)$_3$] **66** (Equation (8)).



66

(8)

The η^5-ring of **66** is displaced by PPh$_3$ via an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ ring slippage terminated by a β-H elimination to give Re(CO)$_3$(PPh$_3$)$_2$H and the bowl-shaped C$_{20}$H$_{16}$.[372]

Mercuration of CpRe(CO)$_3$ with Hg(OAc)$_2$ leads to high yields of {C$_5$(HgOAc)$_5$}Re(CO)$_3$ **67**. In contrast to its Mn analog, reaction of the pentamercurated **67** with halogenating agents failed to give perhalo-substituted (C$_5$X$_5$)Re(CO)$_3$.[373]

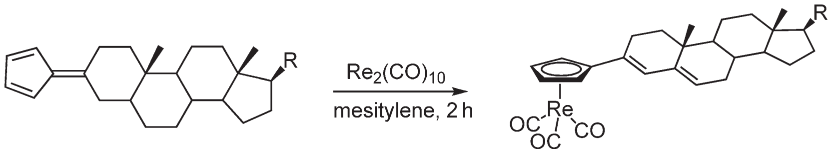
The Cp′Re(CO)$_3$ complexes due to their kinetic and thermodynamic stability became very useful for biomedical imaging and therapy applications. For these purposes, the molecules need to be target specific and possess high affinity for the selected target. This requires complexes of formula (CpR$^{\text{bio}}$)Re(CO)$_3$ complexes where R$^{\text{bio}}$ represents a bioactive molecule, for example, a steroid, a protein, a peptide, bound to the ring with or without a convenient spacer. The synthesis of these complexes poses difficult problems because the traditional methods to introduce delicate functions either in a CpRe(CO)$_3$ complex or in the binding of HCpR$^{\text{bio}}$ to its low-valent precursors like ReX(CO)$_5$ require multistep procedures and/or reaction conditions incompatible with the presence of sensitive bio-groups. The synthetic approach becomes even more demanding when dealing with radioactive isotopes

(^{186}Re and ^{188}Re, $^{99\text{-m}}$Tc) where fast, high-dilution and high-yield methods, and aqueous saline solutions are required. This situation spurred the search for alternative synthetic methods that have opened new avenues in the field of Re (and Tc) organometallic synthesis. The topic has been subject to several reviews and only some of the most innovative methods will be presented here, referring the reader to Chapter 00173 of this work.[374,375]

The approach outlined in Scheme 34 uses the highly stable cymantrene derivatives to assemble the substituent on its Cp ring. The innovation resides on the photolysis in a protic solvent like MeOH that leads to facile liberation of the corresponding substituted cyclopentadiene (CpR$^{\text{bio}}$H) in contrast to oxidation with Ce(IV) or Fe(III) that leads to decomposition. The diene ligand CpR$^{\text{bio}}$H is stable toward dimerization and can be used to form other CpR$^{\text{bio}}$ complexes like the analogs of tamoxifen shown (Scheme 35).[376]

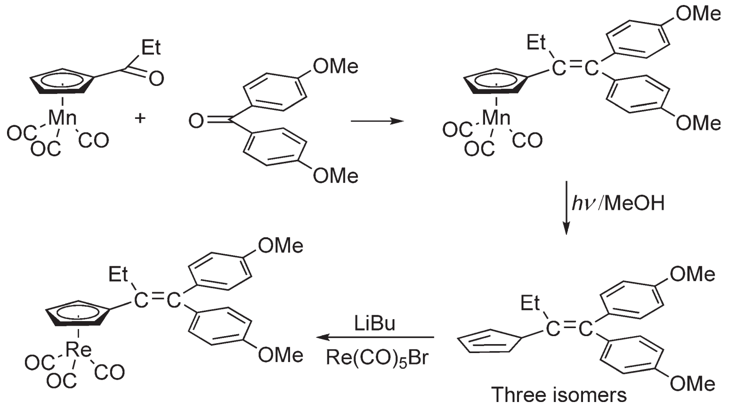
Another strategy developed by Alberto allows the synthesis of (Cp$^{\text{bio}}$)Re(CO)$_3$ derivatives in water (Scheme 36). In fact, acetyl cyclopentadienes have a pK_a of ca. 8 and are partially deprotonated at physiological pH (7.4). They are soluble in water and air stable for a number of hours. Therefore, reaction of [Cp–C(O)R]Na with $[Re(CO)_3(H_2O)_3]^+$ in water was found to give {Cp–C(O)R}Re(CO)$_3$ in fair yields due only to the competing formation of $[Re(CO)_3(OH)]_4$ in basic aqueous solution (see Section 5.13.2.3.6). In the example shown in Scheme 36, the substituent is a ligand for the 5-HT1A subclass of serotonergic receptors but the variety is very large.[377]

Cp-substituted steroids were made by several methods,[375] including reaction of the fulvene derived from cholest-4-en-3-one with $Re_2(CO)_{10}$ in boiling mesitylene according to Equation (9).[378]

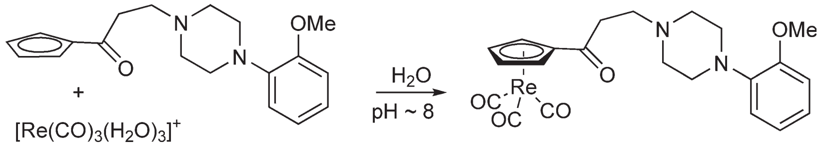


(9)

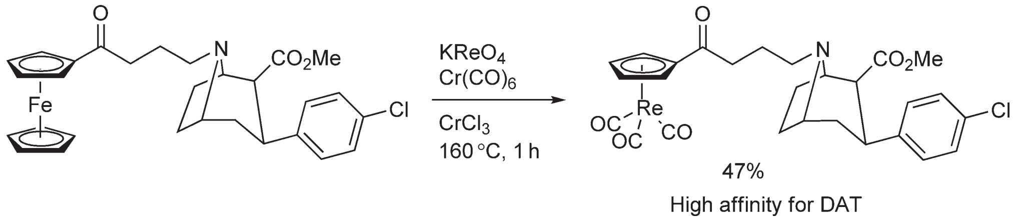
In a process conveniently started from cheap $NaReO_4$, $Re_2(CO)_{10}$ reacts with C_5H_5COOH in refluxing mesitylene to give (CpCOOH)Re(CO)$_3$.[379,380] This is an appropriate reagent to label proteins via its *N*-hydroxysuccinimidyl ester and similar reagents, and also to allow for other simple functionalizations, namely from its acid chloride derivative {$C_5H_4C(O)Cl$}Re(CO)$_3$.[381] Double ligand-transfer reaction was modified and improved by Katzenellenbogen and co-workers.[382] This method has enabled the synthesis of a variety of (CpR$^{\text{bio}}$)Re(CO)$_3$ complexes where R$^{\text{bio}}$ is a tropane derivative aimed at the binding of the complexes to dopamine transporters (DAT) for diagnosis of Parkinson's disease (Scheme 37).[383] This method shows a high tolerance to functional groups.



Scheme 35

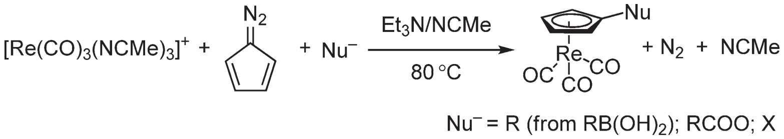


Scheme 36



Scheme 37

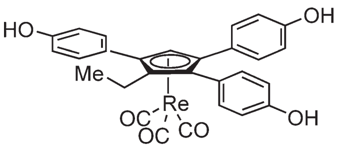
Another versatile method is the three-component synthesis outlined in Equation (10)



(10)

When the nucleophiles are Br^- and I^-, $(CpX)Re(CO)_3$ are formed ($X = Br, I$). These are useful for C–C coupling reactions with Me_3SnR substituents at the Cp ring, catalyzed by $PdCl_2$.[383] When the nucleophile is a carboxylate, $\{C_5H_4O(O)R\}Re(CO)_3$ derivatives are obtained where the R group may contain appropriate functionalities for further conjugation with bioactive molecules. When the nucleophile is a boronic acid, $RB(OH)_2$, the R group bonds to the ring. The mechanism proposed for those reactions is depicted in Scheme 38.[384]

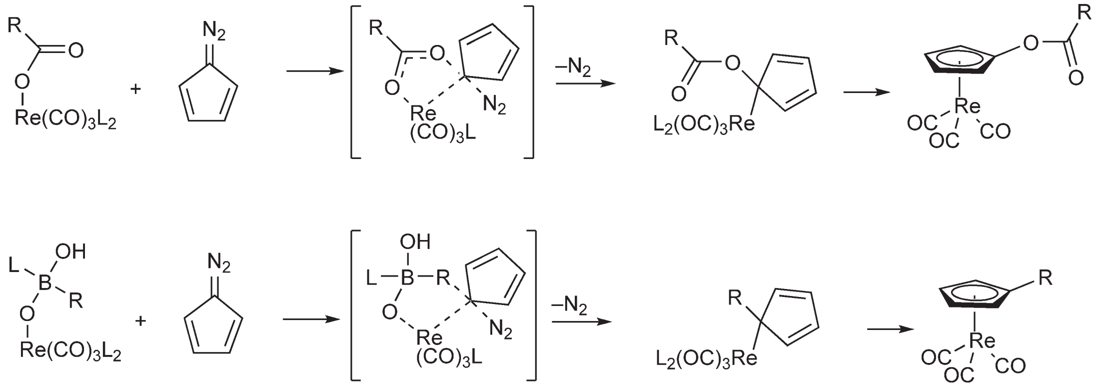
Very conveniently, CpN_2 can be delievered *in situ* from the phosphazine formed with polymer-supported PPh_3 that is cleaved by NCMe.[385] The same group has also recently introduced 68, a new type of integrated organometallic ligand for the estrogen receptor, in which the $Re(CO)_3$ fragment is attached to a cyclopentadiene unit embedded inside the biological ligand framework, which has a high affinity to the estrogen receptor.[386]



68

The use of $[Re(CO)_6]^+$ for the synthesis of steroid-appended $(CpR^{bio})Re(CO)_3$ complexes was mentioned in Section 5.13.2.3.3.[106]

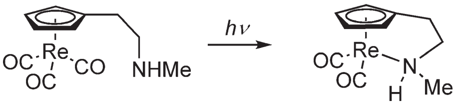
The biological results obtained with many of these complexes are encouraging, and very high affinities have been achieved toward a variety of receptors and immunoassays as reviewed.[177,178,386–389]



Scheme 38

5.13.3.1.5.(i).(b) Substitution and other reactions of $Cp'Re(CO)_nL_{3-n}$ complexes

Thermal substitution of CO is difficult. However, photochemical substitution is easy in THF ($\lambda < 300$ nm), affording $Cp'Re(CO)_2(THF)$, a stabilized form of the very reactive fragment $[Cp'Re(CO)_2]$ and very reactive intermediates thereof.[2] Most of the complexes of the type $Cp'Re(CO)_2L$ are prepared in this mild way, like in the synthesis of the rare type of species CpRe(CO)(dcpe) (dcpe = $Cl_2PCH_2CH_2PCl_2$). Total chloride substitution by F^- or MeO^- is observed upon reaction of CpRe(CO)(dcpe) with these anions.[390] Irradiation is also useful to achieve the preparation of intramolecularly tethered Cp′ complexes as shown in Equation (11).[391]



(11)

Under 100 atm of CO, $(\eta^5\text{-}C_9H_7)Re(CO)_3$ forms $(\eta^1\text{-}C_9H_7)Re(CO)_5$, which is rather stable and decomposes at 90 °C with $t_{1/2} = 10$ min.[392]

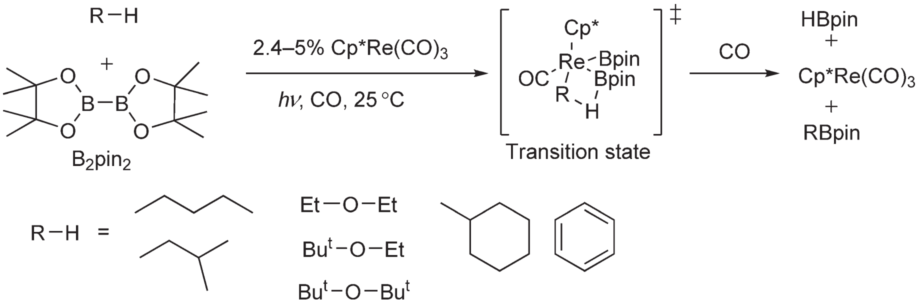
Photolysis of $IndRe(CO)_3$ leads to CO loss with formation of a CO-bridged Re–Re bonded dimer $[IndRe(CO)_2]_2(\mu\text{-}CO)$ that rearranges to $[IndRe(CO)_2\{\mu\text{-}\eta^2,\eta^5\text{-}C_9H_7Re(CO)_3\}]$ with a dihapto bond between $[IndRe(CO)_2]$ and the C6 ring of the other $IndRe(CO)_3$ moiety.[369,393,393] Similarly, photolysis of $(Ind\text{–}CH_2CH_2IndH)Re(CO)_3$ leads to intramolecular coordination of the double bond of the free indene to the metal.[369]

$Cp'Re(CO)_2(H\text{–}MR_n)$ complexes and C–H activation ($M = B, C, Si, Sn$). When saturated hydrocarbons are used in the photolysis, σ-bonded C–H complexes $Cp'Re(CO)_2$(alkane) are formed at low temperature. At RT, the cyclopentane complex $CpRe(CO)_2(C_5H_{10})$ has a rather long lifetime ($\tau = 125$ ms), significantly longer than that of the *n*-heptane analog. Interestingly, the unsubstituted complex $CpRe(CO)_2(C_5H_{10})$ is more stable toward CO substitution than its C_5Me_5 and C_5Ph_5 analogs. It has been studied at low and RT. Both $CpRe(CO)_2(Xe)$ and $CpRe(CO)_2(C_7H_{16})$ complexes have a similar lifetime at a given temperature.[394] Other H–M′ bonds (M′ = B, Si) also coordinate to the $ReCp(CO)_2$ fragment, although photoactivation of $Cp'Re(CO)_3$ in the presence of $HM'R_3$ (M′ = Si, Ge, Sn) leads to oxidative addition $Cp'Re(CO)_2(H)(M'R_3)$ and $CpRe(CO)_2H_2$. In a different way, the complex $Cp^*Re(CO)_2(\eta^2\text{-}HBPin)$ (HBPin = pinacolborane, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) can be prepared by alcoholysis of $ReCp^*(CO)_2(BPin)_2$. Like in its Mn congeners, the σ-B–H bond is stabilized by backdonation from the HOMO of the metal fragment into the free π-orbital at boron. In alkane, silane, or stannane complexes, backdonation occurs into the H–X σ^*-orbital, which is much higher in energy than the borane π-orbital.[395]

The latter studies were carried out in order to shed light on one of the most spectacular examples of C–H activation by transition metals depicted in Scheme 39.

The formation of alkyl boronate esters R–BPin is regiospecific and only terminal C–H bonds are activated with a selectivity >350 : 1 relative to internal C–H activation. Since $ReCp^*(CO)_2(BPin)_2$ catalyzes the reaction in the same way as $Cp^*Re(CO)_3$, it seems likely that this species is formed early in the catalytic cycle leading to the proposal of the depicted transition state. Direct C–H activation by $Cp^*Re(CO)_2$ is less likely in the light of the results mentioned above.

The addition of the Si–H bond of Et_3SiH to the fragment $CpRe(CO)_2$, generated in the singlet state by photolysis in neat silane, has been studied by ultrafast IR spectroscopic methods and compared to the isoelectronic Mn system. The reactions were found to be divided into two pathways of distinct timescales by the initial solvation of the dicarbonyls through the Si–H bond or an ethyl group of the solvent molecule. The timescale for the Si–H



Scheme 39

bond-breaking process was, for the first time, experimentally derived to be 4.4 ps, compared to 230 ns for breaking an alkane C–H bond.[396] Most of the relevant mechanistic data on this Si–H activation is discussed in a DFT and *ab initio* study on the readiness of silane dissociation in η^2-silane complexes $Cp(CO)_2M(\eta^2\text{-}H\text{–}SiH_{3-n}Cl_n)$ (M = Mn, Tc, and Re; $n = 1$–3).[397]

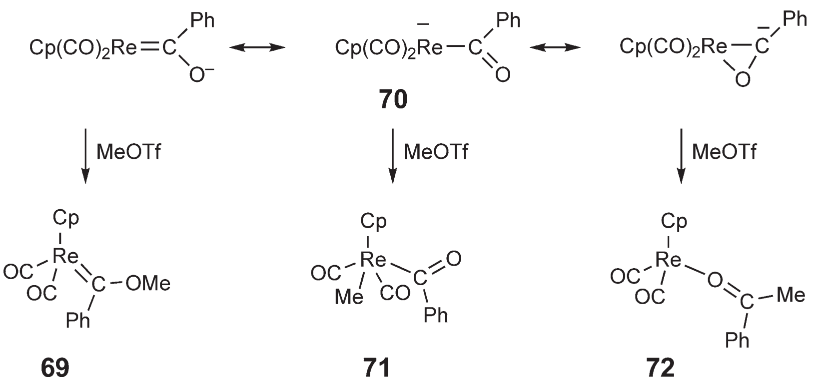
Photolysis of $CpRe(CO)_3$ in benzene initially forms $CpRe(CO)_2(\eta^2\text{-}C_6H_6)$ but the reaction can be taken to $CpRe(\eta^6\text{-}C_6H_6)$.[2] This shows the strong tendency of the $Cp'Re(CO)_2$ to bind olefins and η^2-arenes and its lesser tendency to activate H–C(sp^2) bonds. This tendency, however, is increased in fluorinated arenes. Photolysis of $Cp'Re(CO)_2(N_2)$(Cp' = Cp, Cp^*) with fluorobenzenes $C_6F_nH_{6-n}$($n = 0$–5) gives two classes of products: (i) coordination of the arene in an η^2-fashion like in $Cp^*Re(CO)_2(\eta^2\text{-}C_6H_4F_2)$ and (ii) C–H activation to form a hydrido–aryl complex like $Cp^*Re(CO)_2(H)(C_6H_3F_2)$.[398] Increasing the number of fluorines on the arene ring favors C–H activation. However, a detailed DFT study has shown that this depends on the position of the F substituents relative to the C–H bond being broken: *ortho*-F substituents favor C–H addition, whereas their absence favors η^2-arene coordination. The C–H bonded complex evolves to the *cis*-$[CpRe(CO)_2(C_6H_{5-n}F_n)H]$, which subsequently isomerizes to its *trans*-configuration. Surprisingly, this isomerization is the rate-determining step of the C–H activation of fluoroarenes and not the oxidative addition step.[399]

Chlorinated arenes tend to give oxidative addition of the C–Cl bond (see oxidative addition below). Intramolecular C–H activation under the form of orthometallation is found in the photolytic reactions of $Cp^*Re(CO)(L)(N_2)$ (L = $P(OEt)_3$, $P(OPh)_3$, $P(OCH_2)_3CCH_3$, $P(OMe)_3$, PPh_3) in hydrocarbon solvents. This reaction is only absent in the cases of the tied-back phosphite $P(OCH_2)_3CCH_3$ where an unstable Cp^*Re (CO)L(Ph)H complex is observed when the reaction is performed in benzene, and in $P(OMe)_3$ where a binuclear phosphonate complex $[Cp^*Re(CO)\{PO(OMe)_2\}(CH_3)]_2$ involving methyl migration from a $P(OMe)_3$ ligand to the metal is formed.[400]

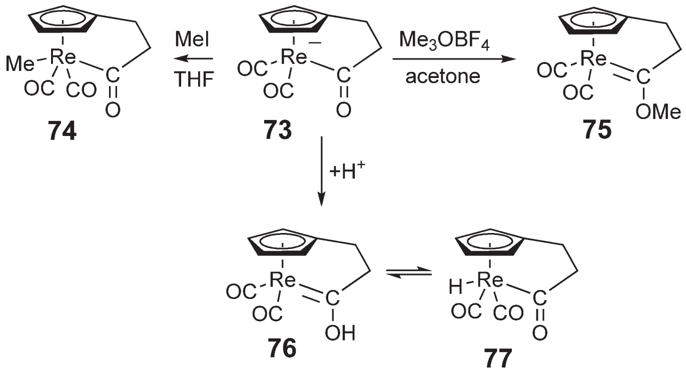
Carbene complexes of Cp′Re(CO)$_n$. The classical synthesis of Fischer carbene derivatives of this system, for example, **69**, is the *O*-alkylation of acyl metallates like **70**, resulting from addition of LiR^1 to $CpRe(CO)_3$, with R^2X.[1,2] Sometimes alkylation occurs at the Re forming alkyl acyls like **71**. Recently, an unexpected third isomer **72** was identified from the reaction of $[CpRe(CO)_2\{C(O)Ph\}]Li$ **70** with the very powerful alkylating agent MeOTf (Scheme 40).[401]

The ketone in **72** is σ-bound in the solid state (X-ray) and fluctuates between σ- and π-coordination in solution (NMR). Also depending on the source of the alkyl cation, **73** can be alkylated either at the metal, **74**, or at the acyl O, **75**.

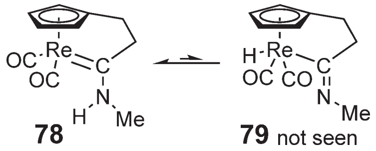
More interestingly, protonation of the acyl anion **73** with aqueous HCl followed by extraction into CH_2Cl_2 led to a mixture of the expected hydroxycarbene complex **76** and the unanticipated metal acyl–hydride complex **77** as a yellow oil in 50% isolated yield exemplifying this type of tautomerization for the first time (Scheme 41). The ratio **76** : **77** showed a strong solvent dependence. Although there is no correlation of the equilibrium constant with solvent polarity, more of the hydroxycarbene is seen in the better hydrogen-bonding solvents, such as, methanol, THF (both 100%), and acetone (91%) than in benzene (50%). The equilibrium between **76** and **77** shifts toward the hydroxycarbene isomer at low temperature. A structural analysis suggests that tethering the side chain destabilizes **76** relative to **77** and provides a rationale for the observation of acyl metal hydrides only in the tethered system since they are not observed in the untethered system first described by Fischer in 1968. This was confirmed by protonation of an acyl anion analog of **73** with a longer tether chain $(CH_2)_3$ that led exclusively to the hydroxycarbene. The possible equilibrium between aminocarbenes **78** and iminoacyl hydrides **79** in Equation (12) was not observed.[360,402]



Scheme 40



Scheme 41

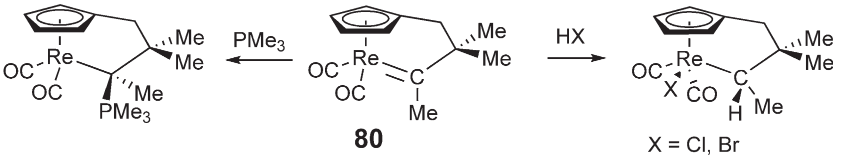


(12)

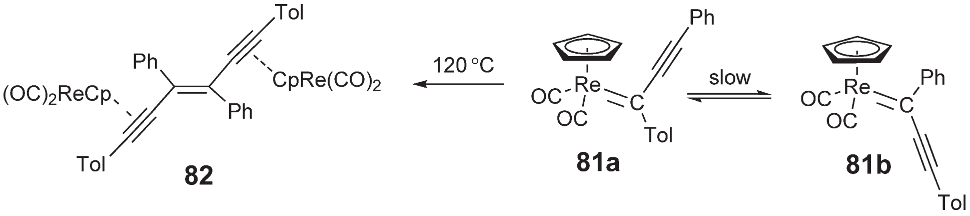
Previous studies by Casey and co-workers had shown that alkylidenes of the type $CpRe(CO)_2({=}CHR)$ displayed a rather unusual amphiphilic behaviour: the carbene carbon undergoes addition of nucleophiles like PMe_3 but can also be protonated with HCl to give the Re(III) complexes $CpRe(CO)_2Cl(CH_2R)$. The stereochemistry of HCl addition, undetermined with a rotating Re═CHR bond, was tested with the tethered alkylidene **80**, and revealed not only the suspected amphiphilic character, but also that HX stereochemistry is *cis*-consistent with a concerted addition of HX across the Re═C bond, as determined by NMR and X-ray crystallography Scheme 42.[403]

Recently, the same group started a systematic study of the reactivity of alkynyl carbenes bound to the $CpRe(CO)_2$ fragment. These black complexes are available through reaction of RC≡CZnBr or BrZnC≡CAr with $[Cp^*(CO)_2Re{\equiv}CPh]BCl_4$. These studies started with the synthesis of the non-donor-substituted alkynyl carbene complex **81a**, its isomerization to **81b** via a virtually unknown [1,3]-Re shift and the dimerization to **82** by coupling of the remote alkynyl carbons (Scheme 43).

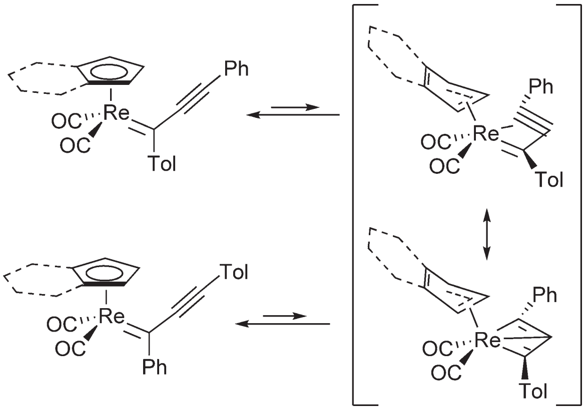
Both the isomerization-equilibrium constant and the rate with which it is attained are dependent on the nature of the substituents on the *para*-position of the Ph group. For X = H **81b**, $K_{eq} = 1.0$ at 120 °C and $k_{obsd} = 4.3 \times 10^{-6}\,s^{-1}$. $X = NMe_2$ decreases this rate but $X = O_2SCF_3$ accelerates it 88-fold, while the use of indenyl instead of Cp leads to a 550-fold rate increase for X = H, without change in the final equilibrium constant. This dramatic rate enhancement was



Scheme 42



Scheme 43



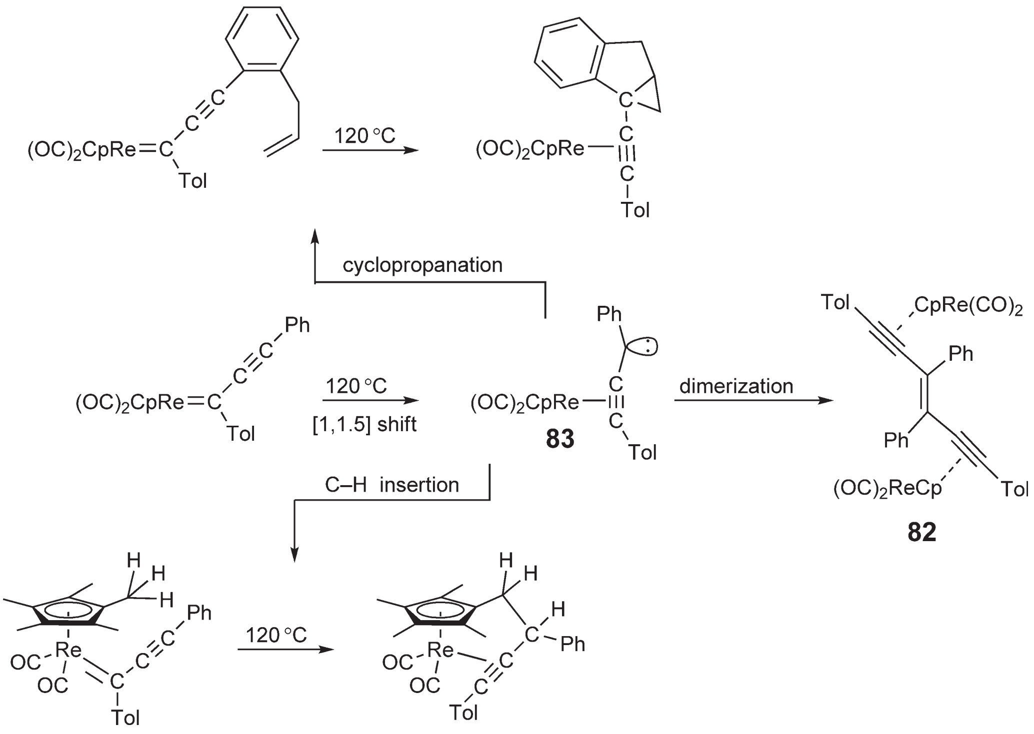
Scheme 44

explained by a ring-slippage effect which IndRe(CO)$_2$ fragments are prone to undergo (Scheme 44).[404] Quite surprisingly, however, the use of Cp* instead of Cp also produces an 84-fold rate acceleration of the same isomerization.[405]

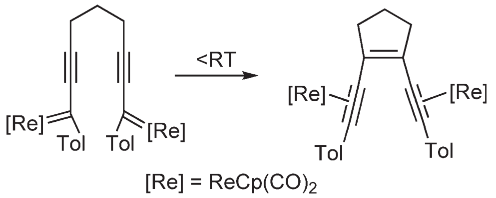
However, in the thermolysis reaction, the dominant process in Scheme 43, the central species is the carbene **83** where the Re has undergone a [1,1.5]-shift (Scheme 45).

The carbene character of the intermediate **83** was ascertained by reactions like the insertion into one Me C–H bond of the analog reaction with Cp*, or the cyclopropanation of a dangling C=C double bond.[405]

The mechanistic study of the dimerization that led to **82** revealed that tethered bis-alkynylcarbenes undergo this process intramolecularly even below RT to produce cyclic *cis*-enediyne complexes as in Equation (13).[406] The limitations to the use of this protocol for the synthesis of these highly biologically active organic compounds are many and led to the search for analog Mn reactions expected to be cheaper and more amenable to decomplexation of the final *cis*-enediyne complex.



Scheme 45



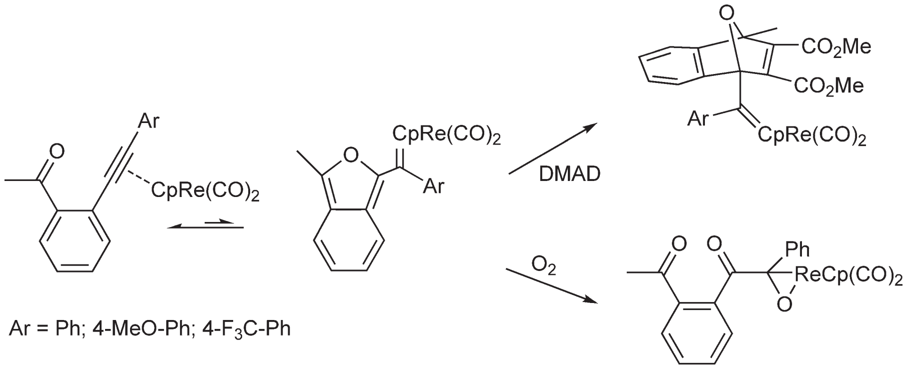
(13)

This [1,1.5]-shift was also used for the synthesis of isobenzofuryl derivatives intercepted *in situ* via Diels–Alder addition to activated acetylenes or O_2 (Scheme 46).[407]

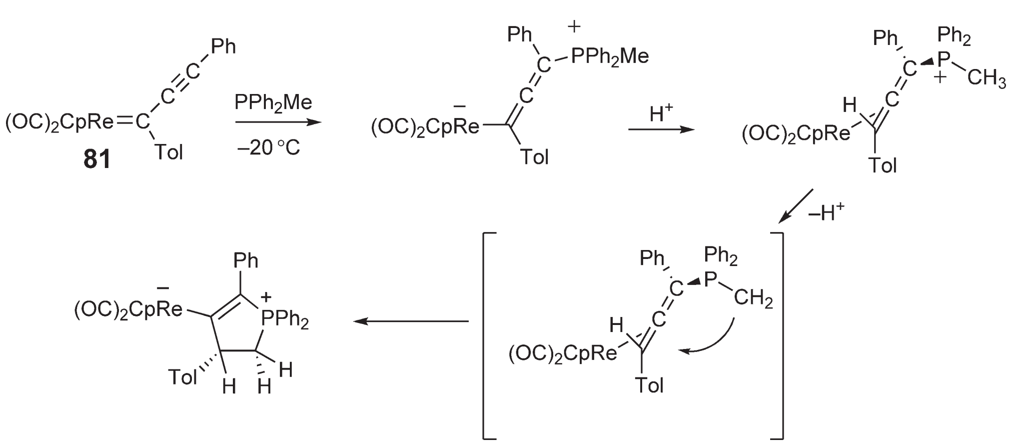
The reaction of **81** with phosphines starts by the formation of a zwitterion. Upon protonation, the reaction follows as in Scheme 47. A mechanism involving a free carbene was disfavored on the basis of inconsistent cyclopropanation data obtained with allyl and vinyl diphenylphosphines.[408]

Reaction of Fischer carbenes, for example, **69**, with Lewis acids A^+ liberates AOR and forms $[Cp'Re(CO)_2(\equiv CR)]^+$. These compounds are treated in Section 3.5.1. In the case of R = Me, decomposition leads to the vinylidene $CpRe(CO)_2({=}C{=}CH_2)$, a very strong dipolarophile producing a variety of reactions with imines and other related unsaturated substrates. One interesting reaction is that of $Cp(CO)_2Re{=}C{=}CH_2$ with carbodiimides (RN=C=NR; R=Pr^i,Bu^t), which proceeds as net metathesis to give the isonitrile complex $CpRe(CO)_2(CNR)$.[409]

$Cp'Re(CO)_n(alkene)_{3-n}$ complexes. The fragment $CpRe(CO)_2$ has a very strong affinity toward alkenes. For this reason, alkyne-hydrogenation catalysts based on the chemistry of the heterobimetallic catalyst $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ are hampered due to stoichiometric formation of stable rhenium alkene products.[410] For example,



Scheme 46

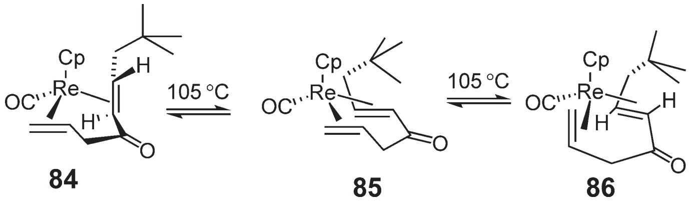


Scheme 47

treatment of a C_6D_6 solution of $Cp(CO)_2Re(\eta^2$-*cis*-MeHC$=$CHMe) with excess 2-butyne at 140 °C for 33 h led to only 31% conversion of a mixture of $Cp(CO)_2Re((\eta^2$-MeC$\equiv$CMe) (16%) and unidentified products (15%). Likewise, the reaction with CO is also very slow.

The labile complex $IndRe(CO)_2(THF)$, obtained by photolysis of $IndRe(CO)_3$ in THF, is a valuable intermediate for the synthesis of complexes $IndRe(CO)_2(L)$ (L = alkene, alkyne, and phosphine).[392] Unexpectedly, replacement of the alkene by alkynes in these indenyl complexes is almost as unfavorable as in the corresponding Cp complexes. However, carbonylation is significantly faster but not as fast as carbonylation of the corresponding $IndRe(CO)_2$(alkyne) complexes. $Cp'Re(CO)_2(\eta^2$-alkenes) undergo H^- abstraction to give $[Cp'Re(CO)_2(\eta^3\text{-allyl})]^+$ complexes. The reverse nucleophilic attack allows the synthesis of a wide range of functionalized alkene complexes of formula $Cp'Re(CO)_2(\eta^2\text{-}C_3H_5Z)$.[411]

The allyl vinyl ketone complex 84 rearranges to diastereomer 86 without the formation of trappable, unsaturated intermediates (Equation (14)).



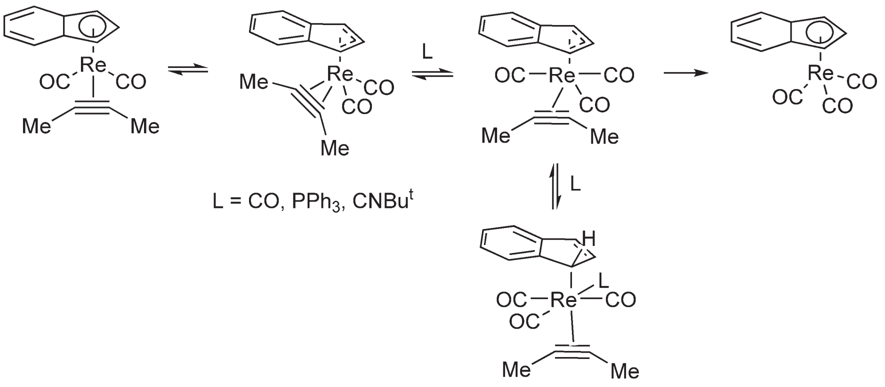
(14)

The reaction takes place with retention of stereochemistry at Re and with enantioface inversion of both complexed alkenes. The kinetically formed parallel–perpendicular isomer 84 rearranges by sequential enantioface inversion of the vinyl π-bond to give parallel–parallel intermediate 85 and then enantioface inversion of the allyl π-bond to form the perpendicular–parallel isomer 86. A mechanism in which Re migrates to the opposite enantiofaces of the alkene ligands via a σ-C–H complexes is proposed.[412]

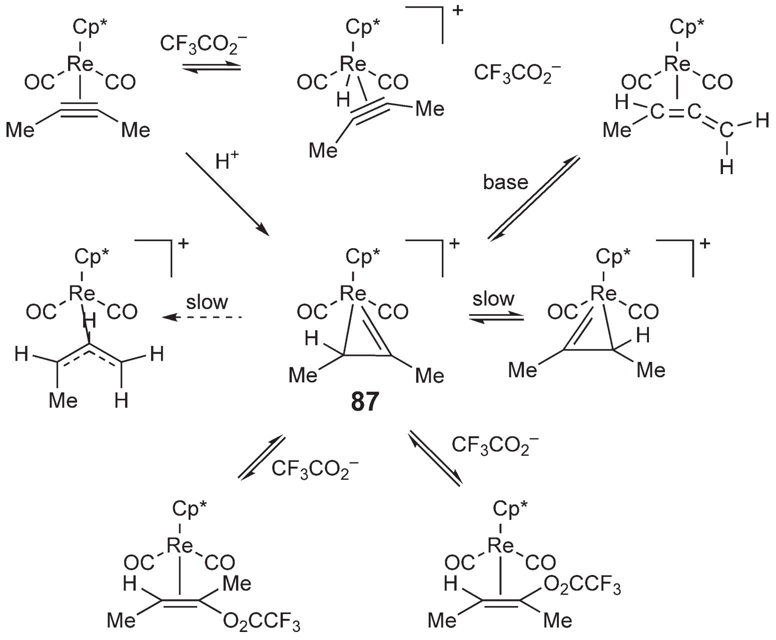
Cp′Re(CO)$_n$(alkyne) complexes. Indenyl and Cp alkyne complexes $Cp'Re(CO)_2(R_2C_2)$ are readily made from the $Cp'Re(CO)_2$(THF precursor) (Cp′ = Cp, Ind).[392] Examination of their rates of reaction with CO indicates an unusually fast reaction as compared to the corresponding alkene complexes. This kinetic acceleration is interpreted as resulting from cooperativity between $\eta^5 \rightarrow \eta^3$ indenyl slippage and shifting of the alkyne ligand from a two- to a four-electron donor as CO associates with the rhenium complex a new aspect of the indenyl effect (Scheme 48).

Still quite unusually, the reaction of $IndRe(CO)_2(Me_2C_2)$ with PPh_3 to form $IndRe(CO)_2(PPh_3)$ is catalyzed by CO. Facilitated ring slippage is also evident due to the isolation of $(\eta^1\text{-}C_9H_7)Re(CO)_4(Me_2C_2)$ and $(\eta^1\text{-}C_9H_7)$-$Re(CO)_2(CN^tBu)_2(Me_2C_2)$ that intercept the $\eta^3\text{-}C_9H_7$ intermediate.[392]

The mechanism of the protonation of $[Cp'Re(CO)_2(\eta^2\text{-}Me_2C_2)]$ (Cp′ = Cp, Cp*) was studied in great detail (Scheme 49). In the first place, it was found that catalytic amounts of H^+ promote the isomerization of the complex to the allene. This counter thermodynamic transformation (free alkynes are more stable than their tautomeric allenes) is favored by the already-mentioned stabilization of π-double bonds to the $Cp'Re(CO)_2$ fragment. An unfavorable interaction between a filled alkyne π-orbital and a filled orbital of the $Cp'Re(CO)_2$ fragment disappears on going to the isomeric coordinated allene complex. This isomerization is mediated by a 1-metallacyclopropene intermediate 87.



Scheme 48



Scheme 49

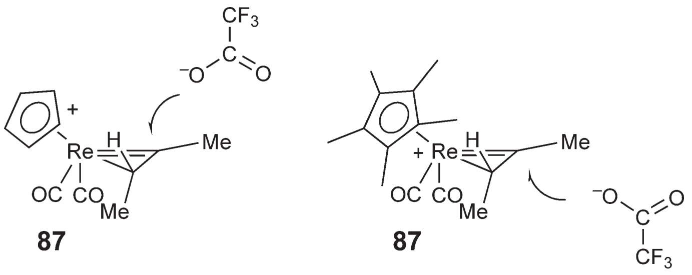
87 is the pivotal species for the understanding of the whole chemistry involving [Cp*Re(CO)$_2$(η^2-Me$_2$C$_2$)] and acids HX (X = Cl, CF$_3$CO$_2$). HCl and HO$_2$CF$_3$ add to the coordinated alkyne to form the (*E*) and (*Z*)-isomers of the vinyl derivatives [Cp′Re(CO)$_2$(η^2-MeHC=CMeX)]. Only one isomer is formed at low temperatures depending on the anion and the size of the Cp ring. Upon warming the (*E*) and (*Z*)-isomer complexes equilibrate. In the case of the CF$_3$CO$_2$$^-$ derivative, this isomerization is explained by dissociation of the anion and readdition onto the more sterically favorable face of the 87 as in Scheme 50.[413]

There are clear stereochemical and structural similarities between this picture and that of H$^-$ attack on the alkynes of [CpReBr(PR$_3$)(η^2-C$_2$R$_2$)]$^+$ (see Section 5.13.3.3.3.(ii)).

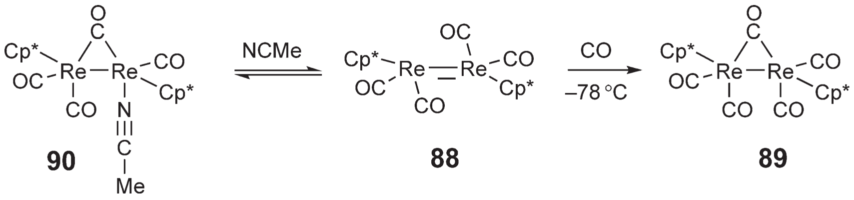
The dimer Cp*(CO)$_2$Re=Re(CO)$_2$Cp*. On standing in the solid form for one week, the yellow Cp*Re(CO)$_2$(THF) transforms in Cp*(CO)$_2$Re=Re(CO)$_2$Cp* 88, the formal dimer of the Cp*Re(CO)$_2$ fragment and a very rare example of a dimer of a 16-electron fragment. This very reactive species adds H$_2$ to give Cp*Re(CO)$_2$(μ-H)$_2$Re(CO)$_2$Cp*. It adds CO and NCMe almost instantaneously at −78 °C to give 89 and 90 (Scheme 51).

89 exhibits only a single CO resonance ^{13}C NMR spectrum at −80 °C implying a rapid fluxional process interchanging the environments of all CO ligands. 90 is stable at RT and structurally characterized. On the contrary, the adducts of both PMe$_3$ and C$_2$H$_4$ collapse at −20 and +25 °C, respectively to give Cp*Re(CO)$_3$ and Cp*Re(CO)$_2$L (L = PMe$_3$, C$_2$H$_4$, THF).[414]

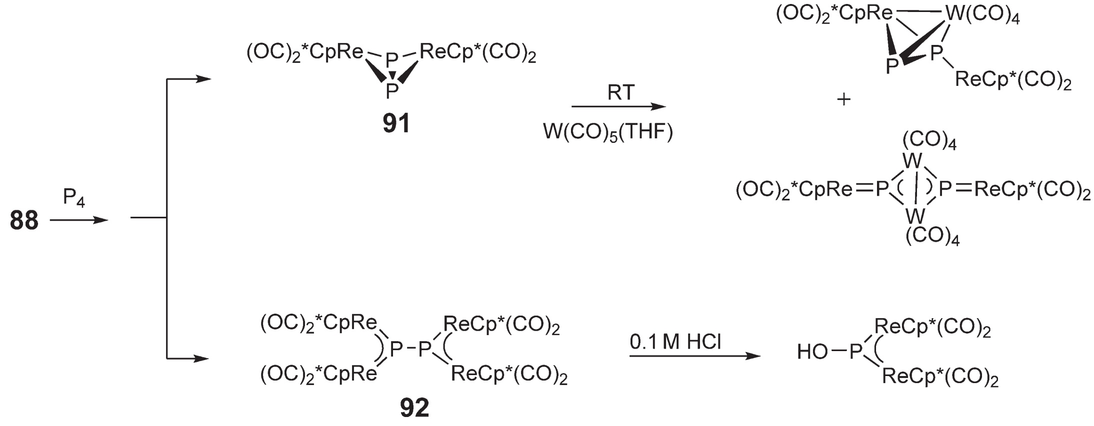
The diphosphinidene complexes 91 and 92 are prepared by reaction of 88 with P$_4$ between −18 °C and RT or at RT, respectively (Scheme 52). When Ph$_2$C$_2$ is used instead of isolobal P$_2$, ReCp*(CO)$_2$(η^2-C$_2$Ph$_2$) and the cyclobutadiene complex ReCp*(CO)(η^4-C$_4$Ph$_4$) are formed.[415–417] Some further transformations of these activated P ligands are also shown.



Scheme 50

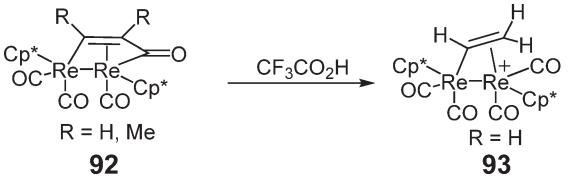


Scheme 51



Scheme 52

88 reacts with various alkynes to give an array of products including (η^2-alkyne) dirhenium complexes, dimetallacyclopentenones, dimetallacyclobutenes, and dimetallabicyclobutanes. Acetylene and 2-butyne gave dimetallacyclopentenones 92, the unsubstituted one being more stable (105 °C, 10 min) and fluxional at 70 °C (Equation (15)).

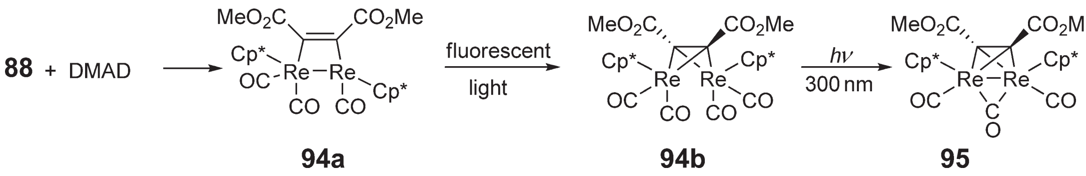


(15)

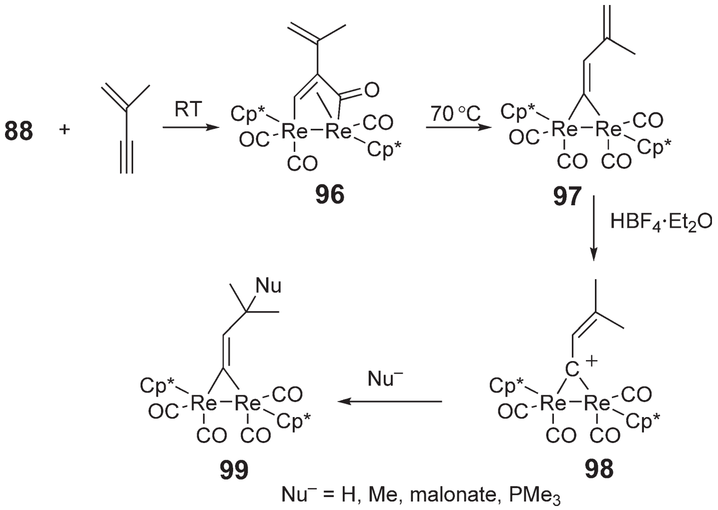
The 2-butyne analog, whose Cp* resonances coalesce at 10 °C, fragments to $Cp^*Re(CO)_3$ and $Cp^*Re(CO)(\eta^2\text{-}Me_2C_2)$.[418] Upon protonation with TFA, μ-vinyl complex cations are formed, for example, 93, completely characterized by NMR. With the electron-deficient alkyne DMAD, the sequence of events in Scheme 53 was characterized.

This is the first case among many related systems with other transition metals where both isomers of the dimetallacylobutene 94a and 94b were observed and crystallographically characterized in spite of their isomerization having been predicted to have a high energy barrier. Further photolysis liberates one CO with formation of a dimetallatetrahedrane 95.[419,420] Overall, it seems that (η^2-alkyne) dirhenium complexes, dirhenacyclobutenes, and dirhenacyclopentenones are all readily interconverted.[421]

Reaction of 88 with the conjugated enyne, 2-methyl-l-buten-3-yne, gave an 81% yield of the 1 : l adduct 96, which decomposes to 97 and $Cp^*Re(CO)_3$ at 70 °C. Protonation of 97 yields the green cationic μ-alkylidyne dirhenium 98, which undergoes attack from a range of nucleophiles at the γ-carbon to form vinylidine complexes (Scheme 54).[422]



Scheme 53



Scheme 54

The reaction of 88 with CH_2Cl_2 gives $[Cp^*ClRe]_2(\mu\text{-}CO)_2$ with a Re=Re bond, $[Cp^*Re(CO)_2]_2(\mu\text{-}CH_2)$ with a Re–Re bond, and the vinylidene $[Cp^*Re(CO)_2]_2(\mu\text{-}C{=}CH_2)$ similar to 99. If the reaction is carried out in THF solvent, $Cp^*Re(CO)_2Cl(CH_2Cl)$ is the product.[423]

5.13.3.1.5.(ii) (η^5-acyclic)Re(CO)$_3$ and (η^5-heterocyclic)Re(CO)$_3$ complexes

The cycloheptadienyl complex $[Re(CO)_3(\eta^5\text{-}C_7H_9)]$ reacts with LiPh to give an acyl metallate $[Re(CO)_2(COPh)(\eta^5\text{-}C_7H_9)]^-$ that is transformed to the carbene complex $[Re(CO)_2\{C(OTMS)Ph\}(\eta^5\text{-}C_7H_9)]$ by reaction with TMSCl.[424]

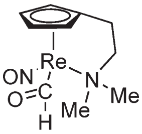
The heterocyclic half-sandwich compounds $(\eta^5\text{-}Me_4C_4N)Re(CO)_3.HNC_4Me_4$ and its Mn and Tc analogs were synthesized by reaction of tetramethylpyrrolyl potassium with $BrM(CO)_5$ in THF. The uncoordinated Me_4C_4NH is bonded to the nitrogen atom of $(\eta^5\text{-}Me_4C_4N)$ by a hydrogen-bridged bond.[425]

5.13.3.1.5.(iii) The $[Cp'ReL_2(N_2Ar)]^+$ complexes

The organometallic chemistry of the diazo ligands has been reviewed by Sutton.[426] Some more advances in this area concerned the characterization of the chemistry of the aryldiazenido ligand, $[N_2Ar]^+$, namely, in complexes of the formula $[ReCp^*L_2(N_2Ar)]^+$. The stereochemical non-rigidity of the slightly bent $[p\text{-}N_2C_6H_4OMe]^+$ ligand has been studied as a function of the bulk of a wide series of $L = PR_3$, $P(OR)_3$ ligands in complexes of the type $[ReCp^*(CO)L(p\text{-}N_2C_6H_4OMe)]^+$ and $[ReCp^*L^1L^2(p\text{-}N_2C_6H_4OMe)]^+$ as well as $[ReCp^*XL(p\text{-}N_2C_6H_4OMe)]^+$ (X = H, Me, Cl). Electronic reasons explain why in the solid-state and solution ground-state structures of these complexes the N_2Ar ligand does not orient symmetrically, that is, with the NNC (aryl) plane bisecting the L^1ReL^2 angle, but lies unsymmetrically with the aryl substituent oriented closer to one of the ligands L^1 or L^2. Interconversion between both possible structures takes place by a conformational isomerization of the aryldiazenido ligand.[427,428] These transformations are related to those of the carbene complexes $ReCp'(CO)_2({=}CRR^1)$ and $[ReCp'(NO)(PPh_3)({=}CRR^1)]^+$. The electrochemical reduction of the same complexes $[ReCp^*LL'\text{-}(p\text{-}N_2C_6H_4OMe)]^+$ with L^1, $L^2 = CO$, PR_3, $P(OR)_3$ results in the formation of the corresponding metal-bound dinitrogen complex ReCp $L^1L^2(N_2)$ and anisole (from the C_6H_4OMe radical).[429] This reduction can also be done chemically with a variety of reducing agents. When the N_2Ar ligand is labeled with $Re{=}^{15}N{=}^{14}NAr$, the reduction product $ReCp'L_2(^{15}N{=}^{14}N)$ retains the Re–^{15}N bond. Further scrambling takes place via an intramolecular, non-dissociative mechanism intermediated by an elusive side-on η^2-N_2 bonded species.[430]

5.13.3.1.5.(iv) The $[Cp'Re(NO)L_2]^+$ and [Cp′Re(NO)LX] complexes

Nitrosylation of $Cp'Re(CO)_3$ with NO^+ salts leads to $[ReCp'(CO)_2(NO)]^+$ **100**. This complex is the starting point as the extensive chemistry of the $[Cp'Re(NO)L_2]^+$ complexes has been outlined before.[2] Reaction of **100** with neutral donors, L, easily forms $[ReCp'(NO)(CO)L]^+$. In the case of $L = PR_3$, reduction of the remaining CO ligand with $NaBH_4$ leads to the corresponding chiral-at-metal methyl complexes $[CpRe(NO)(L)(CH_3)]$. The attempt to apply the same route to a tethered amino derivative of this system stopped at the intermediate acyl complex **101** showing the different reactivity of the amine and phosphine complexes in this rare complete reduction of coordinated CO to methyl.[431]



101

Recently, a new method was introduced to the synthesis of both small and large ring (macrocyclic) ligands which is based on the intramolecular olefin-metatheses reaction catalyzed by the Grubbs catalyst, $[Ru(=CHPh)(PCy_3)_2Cl_2]$ (Scheme 55).[432]

The chemistry of the indenyl analog diverges in some central aspects from that of the Cp congeners mainly because in donor solvents like acetone or NCMe, η^1-Ind complexes $[(\eta^1\text{-Ind})Re(NO)(CO)_2(Solv)_2]^+$ are formed. Therefore, the elaboration of the derivatives of this fragment differs from that used for Cp′ congeners and is described.[433]

5.13.3.1.5.(iv).(a) The metallacarboxylic Cp′Re(NO)L(COOH), metalloester, and acyl complexes

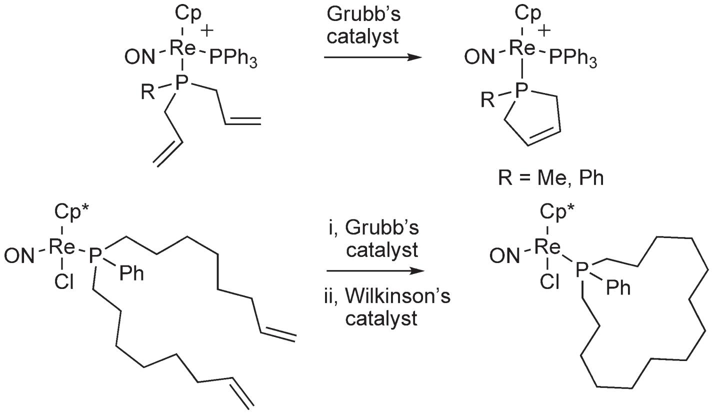
Within the general scenario of CO_2 activation (see also Section 2.3.8(iii)), a number of studies concentrated on the chemistry of the metallocarboxylic acids Cp′Re(NO)(CO)(COOH), mainly conducted by the group of Gibson. Reaction of $Cp^*Re(NO)(CO)COOH$ with Ph_3SnCl and $Re(CO)_4(PPh_3)(F\text{–}BF_3)$ provided the corresponding CO_2-bridged complexes $Cp^*Re(CO)(NO)(CO_2)SnPh_3$ and $Cp^*Re(CO)(NO)(CO_2)Re(CO)_3(PPh_3)$.[434] The structural characteristics of the different bridging modes of CO_2 could be correlated with IR and ^{13}C NMR data. Further studies include other CO_2-bridged complexes, $Cp^*Re(NO)(CO)(CO_2)M$, where M = $Re(CO)_5$, $CpMo(CO)_2$, $CpW(CO)_3$, $CpW(CO)_2$,[435] $Zr(X)Cp_2$ (X = Cl, Me, $SnPh_3$),[436] $SnClMe_2$, $Sn[(O_2C)Re(NO)(CO)Cp^*]Me_2$.[437]

The best yields (ca. 90%) of the rhenium silyl esters $Cp^*Re(NO)(CO)\{C(O)OSiEt_3\}$ and $Cp^*Re(NO)(CO)\{C(O)OSiMe_2Ph\}$ are obtained by treatment of a CH_2Cl_2 solution of $[Cp^*Re(NO)(CO)_2][BF_4]$ with the silanolates $NaOSiEt_3$ and $NaOSiMe_2Ph$. These solids are extremely moisture sensitive: traces of water hydrolyze them to $Cp^*Re(NO)(CO)(CO_2H)$ and the parent silanol. The rhenium CO_2 adducts $[Cp^*Re(NO)(CO)(CO_2)]M$ (M = Li, Na) were generated by deprotonation of $Cp^*Re(NO)(CO)(CO_2H)$ **102** with excess LiH or NaH THF suspensions at 0 °C.[438] **102** reacts with [Rh(COD)(OTf)] and NEt_3 to give a tetranuclear complex **103** that resembles the $[(RCO_2)Rh(\eta^4\text{-diene})]_2$ catalysts. The structure is analogous to that of **104** with CO in place of PPh_3.[439]

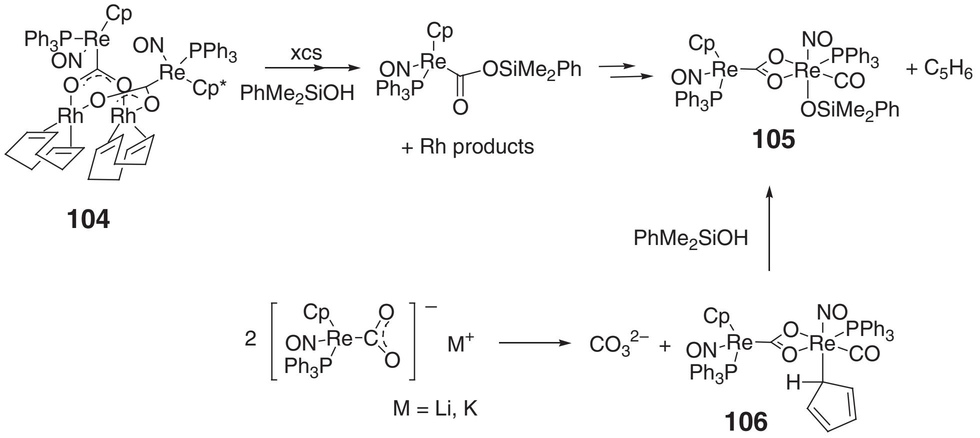
The metallocarboxylic acids $Cp'Re(NO)(PPh_3)(CO_2H)$ also react with several Rh(I)(η^4-diene) complexes to give tetranuclear complexes **104** with the same structure of **103**, only with CO replaced by PPh_3. In the course of studies of these complexes with silanes and silanols, the formation of **105** from degradation of $CpRe(NO)(PPh_3)CO_2SiR_3$ was unexpected (Scheme 56).[440]

The mechanism proposed involves an intermediate with a η^1-C_5H_5 ring that is cleaved by excess R_3SiOH. In fact, later studies showed that **106** has a real existence and is independently obtained from the unusual activation of CO_2 in the lower equation of Scheme 56.[441]

The higher acidity of R_3SiOH relative to MeOH explains that methanolysis of **106** forms $CpRe(NO)(PPh_3)(COOH)$, whereas R_3SiOH forms **105**.[441]



Scheme 55



Scheme 56

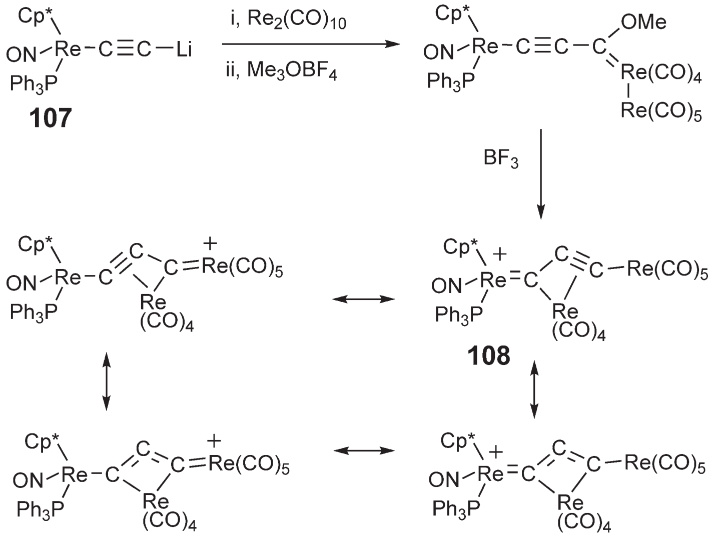
The metalloester IndRe(NO)(PPh$_3$){C(O)OMe} is formed in high yield from [IndRe(NO)(CO)(PPh$_3$)]$^+$ and NaOMe, and reacts with MeMgBr to give the acyl IndRe(NO)(PPh$_3$)(COMe).[433]

5.13.3.1.5.(iv).(b) The Cp′Re(NO)(PPh$_3$)X and [Cp′Re(NO)(PPh$_3$)L]$^+$ complexes

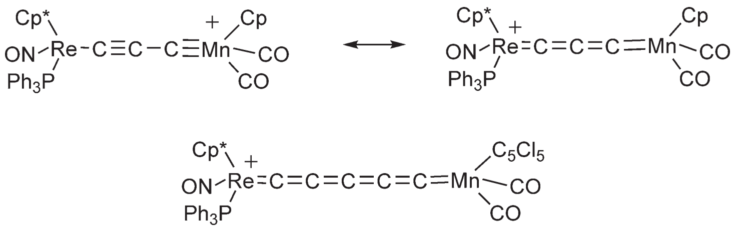
Following the work initiated in the group of Gladysz in the previous decade,[2] the chemistry of these nitrosyl complexes was extensively developed between 1993 and 2004, over and above 120 publications mostly from this group. The central player in this family is the pyramidal Lewis acid fragment [Cp′Re(NO)(PPh$_3$)]$^+$ abbreviated below as {Re}$^+$ or {Re*}$^+$ for Cp and Cp* derivatives, respectively. Functional equivalents of this fragment can easily be made in high enantiomeric purity that bind a variety of chiral and prochiral organic donor ligands in a highly stereoselective manner. The control of the subsequent diastereoselective nucleophilic or electrophilic additions that take place in the [{Re}$^+$–L]$^+$ and [{Re}$^+$–X] complexes is the central goal of this work.

Cp′Re(NO)(PPh$_3$)X. The discovery of the carbon nucleophile [Cp*Re(NO)(PPh$_3$)(C≡CLi)] **107** led to the development of a fascinating series of complexes with long, linear *sp*-carbon chains. The structures and properties of these carbon allotropes of Re and other metals are reviewed.[442,443]

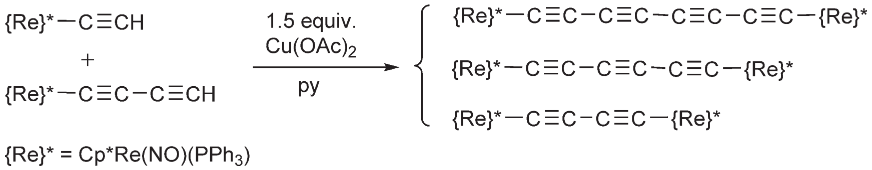
Nucleophilic attack of **107** at the CO of Re$_2$(CO)$_{10}$ and other metal carbonyls[2] produced the first examples of C3 carbon chains connecting two metal centers as in Scheme 57. The trinuclear Re complex has four canonical forms of which structural data (C–C bond lengths) suggests the higher contribution of **108**.[444,445]



Scheme 57



Scheme 58



Scheme 59

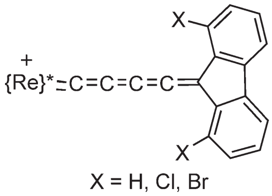
The same methodology soon led to C3 and C5 carbon chains between Re and Mn fragments (Scheme 58).[446,447]

An alkyne coupling methodology led to C4, C6, and C8 chains in Scheme 59.[448]

Termination of the *sp*-carbon chains with other substituents was also achieved, as in the case of {Re}$C_4Os_3(CO)_{10}H$, {Re}$C_3Os_3(CO)_9X$ (X = H, OMe),[449]{Re}C_8SiMe_3,[450]{Re}C_n(Tol) (n = 3, 4, 7, 8).[451]

A new route to heterobimetallic C3 complexes via C≡C metatheses of 1,3-diynyl ligands was developed following the alkyne metathesis reaction in Scheme 60.[452]

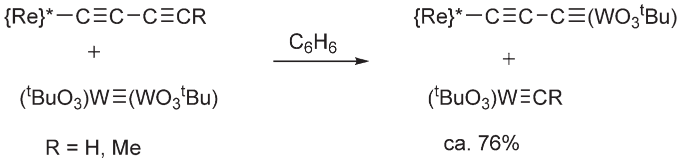
The longest carbon chains in these systems were obtained by desilylation of $ReC_{10}SiR_3$. The resulting labile $\{Re\}^*C_{10}H$ can be coupled *in situ* to give $\{Re\}^*C_{20}\{Re\}^*$ in 34–52% yields.[453] Monometallacumulenes are not stable at long chain lengths but this may also depend on the substitution at the metal center. The pentatetraenylidene complexes **109** are labile at RT, and have been confidently represented as the longest isolable monometallacumulenes that can be derived from the particular end group $Cp^*Re(NO)(PPh_3)$.[454]



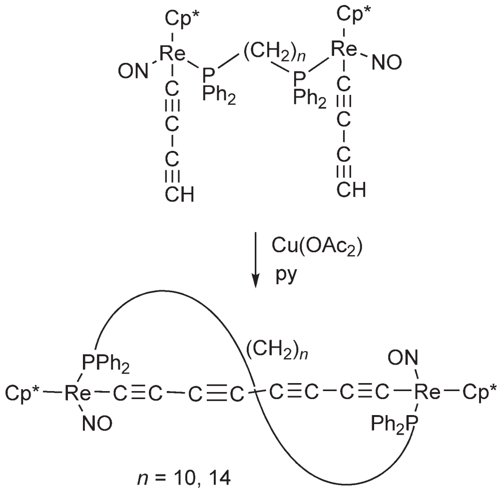
109

The steric shielding of the *sp*-carbon chain has been attempted via intramolecular olefin-metathesis ring closure aiming at enhancing the stabilities of the corresponding radical cations $[\{Re\}C_8\{Re\}]^{\cdot+}$ and dications $[\{Re\}C_8\{Re\}]^{2+}$, since their decomposition seems to involve bimolecular chain/chain or chain/solvent reactions.[455]

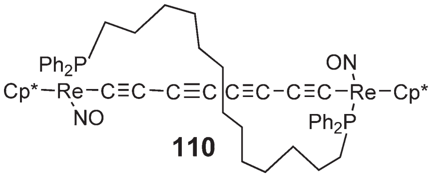
110 was assembled by a sequence of metathesis/hydrogenation reactions similar to Scheme 55, but the final hydrogenation step is not reliable and cannot be scaled up. The circumventing route in Scheme 61 gave the desired compounds in reasonable, reproducible yield.[456]



Scheme 60



Scheme 61



110

Electrochemistry showed that steric protection did not lead, in this case, to an improvement in the stability of mono- or dioxidized species. Indeed, the electrochemical behavior of these *sp*-chains is one of their more interesting properties as materials and one that is clearly chain dependent on chain length and structure. The first such study in this system reported that the UV absorption maxima shifted to longer wavelengths and increased in intensity (ca. 100–150 times compared to MeC_nMe) with the increase in chain length. CV studies revealed two clear oxidations that progressively deviate from reversibility with chain-length increase. Interestingly, the first oxidation becomes thermodynamically more difficult in the same order.[448] $\{Re\}C_4\{Re\}$ is isolable in three oxidation states and crystallographically characterized in the neutral and dicationic forms. The dication is diamagnetic according to NMR, ESR, and magnetic susceptibilty measurements, and its structure is consistent with the description $[\{Re\}^+{=}C{=}C{=}C{=}C{=}\{Re\}]^+$. Its Re–Re distance is shorter than in the neutral complex due to an increase of the π-bonds from four to five. In agreement with the total reversibility of the cyclic voltammogram, comproportionation of the neutral and dicationic complexes gave the monocationic, paramagnetic (one unpaired electron) $[\{Re\}{=}C{=}C{=}C{=}C{=}\{Re\}]^+$.[457] Formally, this d^6/d^5 or Re(I)/Re(II) mixed valence compound can exhibit localized, partially delocalized, or fully delocalized electronic structures. IR, ESR, and UV–VIS–near-IR assigned it as delocalized. Among the possible resonance structures that can accomodate the unpaired electron, the ones with the unpaired electron density residing on Re are favored by ESR data. The ground state of this radical cation is best represented with a half-positive charge and half electron on each {Re} end group, since in the very rapid IR timescale, only one ν(NO) vibration is observed (Equation (16)).

$$\overset{\bullet+}{Re}{-}C{\equiv}C{-}C{\equiv}C{-}Re \longleftrightarrow Re{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\bullet+}{Re} \qquad (16)$$

Bulkier phosphines do not change these properties. The second-generation C6 and C8 complexes in which PPh_3 has been replaced by $P(C_6H_4\text{–}R\text{-}p)_3$ (R = Me, ${}^tBu$, Ph) and PCy_3 undergo electrochemical oxidations at lower potentials than those measured for the PPh_3 analog and with greatly improved reversibilities. However, product isolation remains problematic, indicating a need for new stabilization approaches.[458]

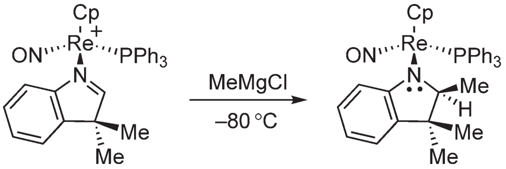
The description of bonding and electronic structure in these systems and in related homo- and heterobimetallic cases, namely, those containing the $Cp^*Fe(dppe)$ fragment, has been addressed by DFT calculations based upon extensive structural data. Important results like the existence of triplet states in the dications have been clarified and helped interpreting magnetic data.[459,460] The methylidene complex $[\{Re\}{=}CH_2][PF_6]$ reacts with diazo compounds N_2CHR (R = H, $Si(CH_3)_3$, COPh, $CO_2C_2H_5$) in CH_2Cl_2 at −80 °C to give alkene complexes $[\{Re\}(\eta^2\text{-}H_2C{=}CHR)][PF_6]$ or

$D_2C{=}CHR$ analogs. The two Re=C geometric isomers of the benzylidene complex $[\{Re\}{=}CHPh]^+$ and CH_2N_2 react to give opposite configurational diastereomers of the styrene complex $[\{Re\}(\eta^2\text{-}H_2C{=}CHPh)]^+$. The stereochemical features of these reactions imply that the diazo compound attacks the Re=C face opposite to the bulky PPh_3. The development of the transition state is also determined by the minimization of the steric interactions with the Cp ligand.[461]

The chiral rhenium–dimethylchlorogermyl complex {Re}–($GeMe_2Cl$) (92%) reacts with $LiAlH_4$ and Me_3SiOTf to yield {Re}–($GeMe_2H$) (74%) and {Re}–($GeMe_2OTf$) (94%), respectively. The latter is in rapid equilibrium with the dimethyl germylene complex $[\{Re\}{=}GeMe_2][TfO]$.[462] Reaction of {Re}OTf with potassium pyrrolyde gives the *N*-pyrrolyl complex **111** (Scheme 62). The pyrrole ring in **111** is more activated toward electrophilic attack than free pyrrole because $\{Re\}^+$ is more electropositive than H^+. Moreover, the sterics of the complex lead to a change in regiochemistry favoring attack at the C_β-atom instead of C_α as found for free pyrrole. This difference in reactivity was proven with both $(CF_3CO_2)_2O$ and DMAD giving the products shown in Scheme 59. Also shown is the protonation with strong acids that takes place at C_α, **112**. However, upon dissolution, **112** isomerizes to the C–Re-bound species (C–pyrrolyl complexes) **113** and **114**. The latter is formed when pyrrole is reacted with {Re}OTf, a most unusual reaction for a transition metal fragment due to higher basicity of the N atom of pyrrolyl. The possible mechanisms are discussed extensively with the aid of MO calculations.[463]

The chemistry of the related indolyl complexes (Scheme 63) was also explored with the aim of creating new stereochemically controlled protocols for the transformation of the indole skeleton of importance in natural products chemistry. Free indole adds electrophiles preferably at C_β-position, but the $\{Re\}^+$ fragment still increases this reactivity as predicted from its pyrrolyl chemistry. For example, the complex **115** reacts with HTOf to give complexes **116** in a 98 : 2 (*RS*,*SR* : *SS*,*RR*) diastereomeric ratio. Alkylation of **115** and related C_α-substituted congeners with ROTf (R = Me, Et) led to new stereocenters at C_β, here exemplified by **117**, the major *SS*,*RR* diastereomer of a 65 : 35 ratio.

The indolenine complexes similar to **117** undergo nucleophilic attack at C_α to create another stereocenter with good to very good diastereoselectivities as exemplified in Equation (17).



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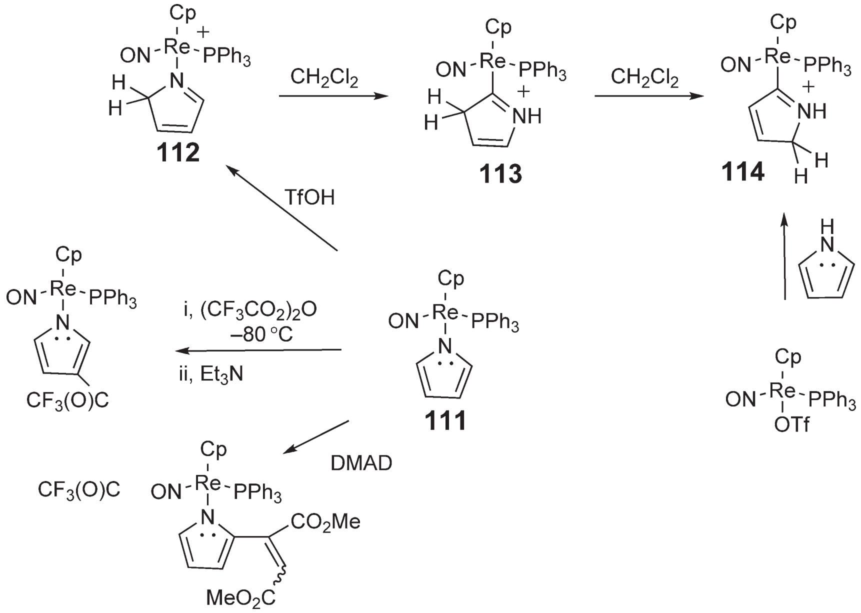
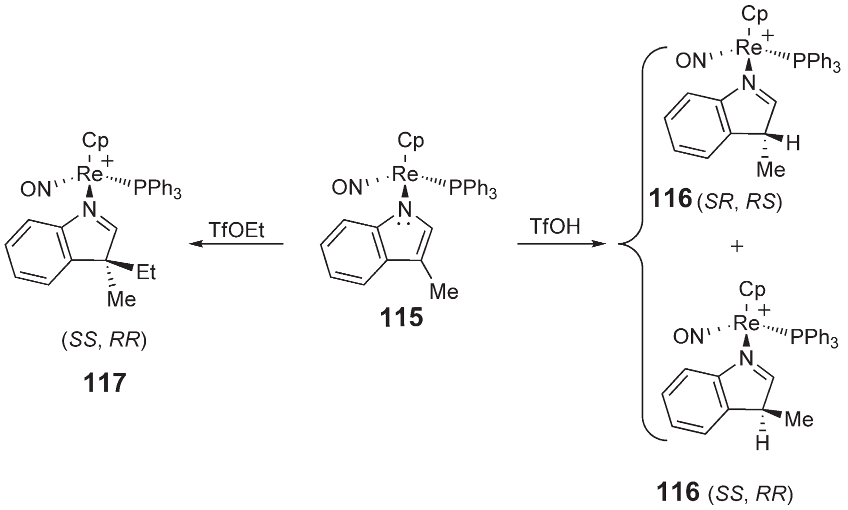


Scheme 62



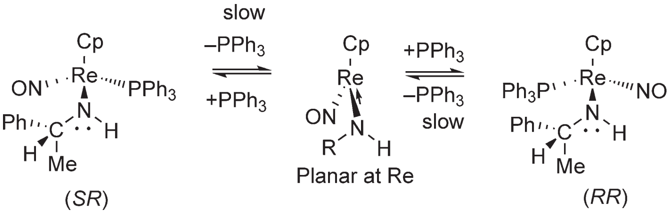
Scheme 63

However, difficulties in resolution of diastereoisomeric mixtures and the diastereoselectivity achieved are not sufficient to establish this as a firm protocol for enantioselective synthesis of indolines.[464]

Adducts of many types of neutral and anionic Lewis bases are easily prepared in enantiomerically pure form. With neutral Lewis bases, remarkable configurational stabilities have been observed. No racemization has ever been detected, including many compounds that have been kept for extended periods at elevated temperatures. Most anionic Lewis bases give adducts of similar configurational stabilities. However, with amido and alkoxide ligands, the rhenium can racemize or epimerize.[2] Depending upon the conditions and ligand, temperatures range from 50 °C to below 20 °C. The mechanism of this racemization was studied in detail with amide complexes derived from enantiomerically pure {Re}OTf and each pure enantiomer of α-MePhHNH$_2$. Treating each of the pure diastereomers with LiBu at −80 °C and warming slowly to 60 °C shows the appearance of the opposite diastereoisomer in each case. Reprotonation and liberation of the amine with CN$^-$ reveals that epimerization took place only at Re in each case without racemization at the C-centre of the amine. The proposed epimerization mechanism at Re (Scheme 64) is essentially similar to the one previously proposed for the rhenium alkoxides {Re}OR that are generally faster and entail epimerization at carbon (via β-hydride elimination), which is not seen in the case of the amido complexes.

PPh$_3$ dissociation is the rate-determining step. The π-donor ability of the X ligand in Cp′Re(NO)(PPh$_3$)X complexes is clearly responsible for the configurational instability at Re. This is evident for X = OR, NR$_2$, Cl but is absent for the weaker π-donors PR$_2$ SR.[465]

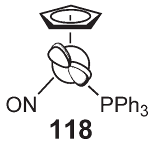
The chemistry of the alkoxide derivatives Cp′Re(NO)(PPh$_3$)(OR) has been described.[2] A large number of chiral racemic thiolato complexes of general formula [CpRe(NO)(PR$_3$)(SR′)] has been prepared either by treating [CpRe(NO)(PR$_3$)(CH$_3$)] with HBF$_4$ followed by HSR^1 and deprotonation, or by treating [CpRe(NO)(PR$_3$)(THF)]$^+$ with NaSR^1. The R^1 groups include: H, Me, Et, CH$_2$CH$_2$Ph, CH$_2$CH$_2$NHAc, CH$_2$CH$_2$CO$_2$H, CH$_2$CH$_2$CO$_2$Me, CH$_2$CHCH$_2$, CH$_2$Ph, CH$_2$(4-C$_6$H$_4$Cl), CH$_2$(4-C$_6$H$_4$OMe), CH$_2$(2-furyl), CH$_2$CO$_2$Et. The bases used may vary according to the basicity of the thiol from NaOEt to Na$_2$CO$_3$, or just chromatographic workup. Optically active thiolates, like that of *N*-acetylcysteine and related molecules, are obtained as pairs of diastereomers.[466–468]



Scheme 64

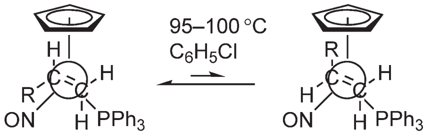
Hydride abstraction with $[Ph_3C]PF_6$ converts the thiolato complexes $\{Re\}SCH_2R$ (R = Ph, 4-C_6H_4Cl, 4-C_6H_4OMe, H, Me) into ionic thioaldehyde complexes $[\{Re\}(\eta^2\text{-S}{=}CHR)]PF_6$, obtained as pure (*RR,SS*) diastereomers, as shown spectroscopically and crystallographically for $[\{Re\}(\eta^2\text{-S}{=}CHPh)]PF_6$.[468]

[Cp′Re(NO)(PPh$_3$)L]$^+$ complexes. The high lability of the complexes $[Cp'Re(NO)(PPh_3)(ClPh)]^+$ and their easy access in enantiomerically pure form led to the synthesis and study of a large number of the title complexes with virtually all kinds of ligands.[2] More important, however, was the possibility of studying the stereochemical control of the chiral $[Cp'Re(NO)(PPh_3)]^+$ fragment on the binding mode and reactions of many of those coordinated ligands. This study was particularly extensive and intensive for the complexes of alkenes, aldehydes, and ketones. Since these are in general prochiral ligands, their binding to the highly configurationally stable chiral-at-Re fragment $[Cp'Re(NO)(PPh_3)]^+$ provides an excellent probe for understanding the steric and electronic factors that control chiral recognition in these π-complexes. **118** sketches the fragment $[Cp'Re(NO)(PPh_3)]^+$ in which the strong π-donor HOMO shown determines the appearance of conformations that maximize π-backdonation to accepting π^*-orbitals of the unsaturated ligands.



118

In stereochemical terms, the order of space congestion in the interstices between the three fragment ligands is PPh_3–NO > Cp–Ph_3 > NO–Cp. Therefore, these factors determine that in a simple case, the thermodynamic binding selectivities of a coordinated monosubstituted alkene lie in the range of ca. **119/120** between 90 : 10 (R = Ph, vinyl) and 99 : 1 (R = ^{i}Pr, ^{t}Bu, C(O)H) (Equation (18)). Most linear alkyls and acyl R groups present selectivities of ca. 96 : 4.



(18)

119 *ac-RS, SR*

120 *sc-RR, SS*

These studies carried out in fine detail over many years and extended to a broad range of prochiral and chiral substrates (alkenes, aldehydes, ketones, allenes, imines) have been reviewed by their author allowing him to develop a general model for enantioface binding selectivities in many other cases of central importance for asymmetric catalysis.[469]

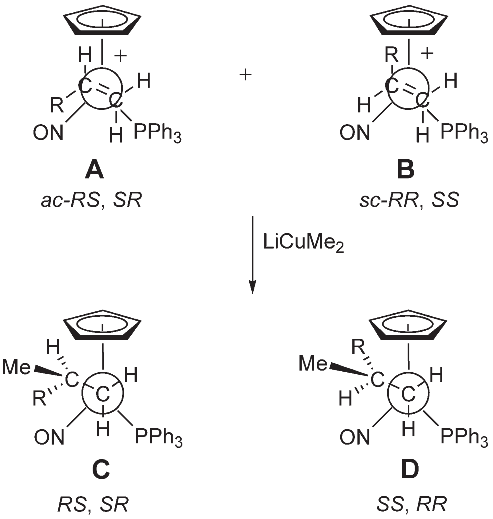
Beyond chiral recognition studies, alkene complexes of $[Cp'Re(NO)(PPh_3)]^+$ also provide access to other interesting transformations. Highly diastereoselective nucleophilic attack at the coordinated alkenes of $[Cp'Re(NO)(PPh_3)]^+$ had been reported.[2] In a closing article on this problem, it is shown that terminal alkenes coordinated to the fragment $\{Re\}^+$ undergo nucleophilic addition from R_2CuLi salts in a regiospecific, enantiospecific, and diastereospecific fashion summarized by the results in Scheme 65.[470]

All alkenes are attacked at the face *anti* to the Re atom, at the substituted carbon, creating C_β-stereocenters, and the enantiomer and diastereomer ratios in the products match those in the enantiomerically pure reactants.

Other transformations include ozonolysis of the free (substituted) double bond of piperylene in $[\{Re\}(\eta^2\text{-}CH_2{=}CH_2CH{=}CHMe)]^+$ to $[\{Re\}(\eta^2\text{-}CH_2{=}CH_2CHO)]^+$ without loss of stereochemistry at the Re and C centers.[471] Likewise, carefully selected reagents enable chemoselective oxidation, reduction, or Wittig reactions to be sequentially performed on propargylic, allylic, and homoallylic alcohol complexes of $\{Re\}^+$,[472] as well as the first example of metal-mediated regio- and stereoselective allylic fluorination.[473]

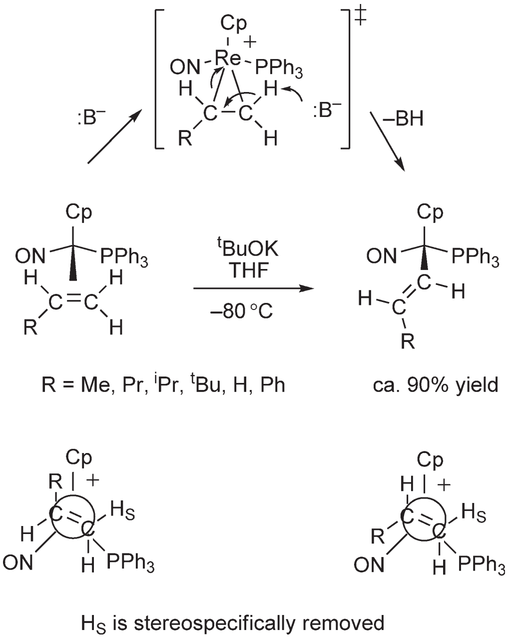
The deprotonation of alkenes coordinated to $\{Re\}^+$ occurs easily to give vinyl derivatives in what was the first example of this kind of C–H activation of coordinated alkenes (Scheme 66). Deprotonation is irreversible and occurs with retention at Re and without PPh_3 dissociation. The deprotonations of styrene complexes (R = Ph) are stereospecific. In each diastereomer, Re replaces the H or D atom in the geminal position closer to the Cp ligand (Hs in Scheme 66).

In this study, no less than seven alternative mechanisms were discarded. Vinylic deprotonation is generally favored over allylic deprotonation which can only be achieved under particular experimental conditions.[474]



R	*A* : *B*	*C* : *D*	*Yield* (%)
CH_2Et	95 : 5	95 : 5	82
CH_2Ph	97 : 3	98 : 2	83
Ph	>99 : 1	>99 : 1	99
Ph	<1 : 99	<1 : 99	>99

Scheme 65



Scheme 66

Although terminal alkynes are sterically less encumbered than monosubstituted alkenes, they are less reactive toward $[CpRe(NO)(PPh_3)(ClR)]^+$ (R = Ph, CH_2Cl) but more stable at higher temperatures. The simplest enyne, vinyl acetylene, slowly forms an alkene adduct at −45 °C that rearranges to its alkyne isomer at RT.[471] The controlled oxidation of propargyl alcohol complexes was also reported.[472]

The chiral recognition and enantioface binding selectivities of π-aldehyde and π-thioaldehyde complexes $[\{Re\}(\eta^2\text{-E}{=}CHR)]^+$ (E = O, S) follow the similar pattern observed for the almost isosteric alkene complexes, and essentially all the work reported in this area has been covered in the same review mentioned above. Enantioface binding selectivities in solution correlate to distances between metal and carbon stereocenters in the solid state.[469] In contrast, nearly all ketones form σ-complexes, except if bearing strongly electron-withdrawing substituents. This fact together with their unsymmetrical geminal disubstitution pattern produces modest binding selectivites.[469,475]

It should be borne in mind that in spite of σ-coordination, σ-methyl ketone complexes $[\{Re\}(\eta^2\text{-O}{=}CMeR)]^+$ undergo hydride addition to give alkoxide complexes of high diastereomeric purities that can be converted to protected alcohols of high enantiomeric purity.[2]

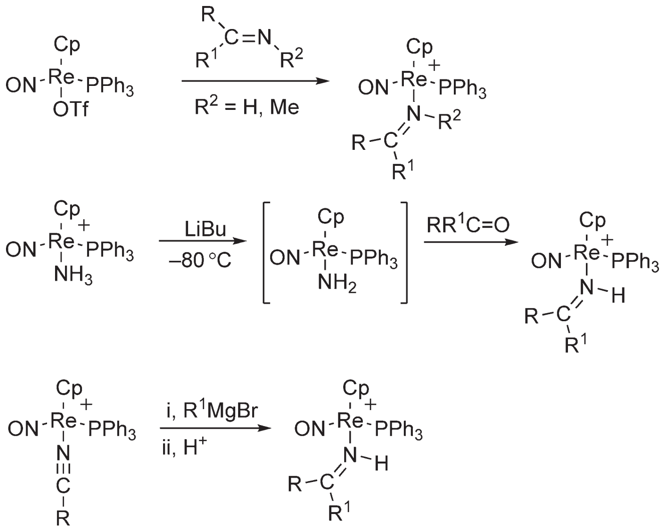
Reaction of $[\{Re\}(ClCH_2Cl)]^+$ with α,β-unsaturated aldehydes and ketones reveals that σ-C=O coordination is kinetically favored at low temperatures. On warming to RT, the complexes rearrange to the generally thermodynamically favored alkene or alkyne Re-bound isomers.[476] The analogous substitutions at the indenyl congener $[IndRe(NO)(PPh_3)(ClCH_2Cl)]^+$ form $[IndRe(NO)(PPh_3)(O{=}CR_2)]^+$: the mechanism is associative but indenyl slippage does not play a role. Instead, a bent nitrosyl intermediate is proposed.[475]

Cyclopentenone and cyclohexenone are the more remarkable exceptions that favor σ-Re–O=C bonding over Re–C=C bonding. This fact enables 1,4-additions with R_2CuLi salts, which, after treatment with HI, yield 3-substituted cycloalkanones. The stereochemical control of the reaction is very dependent on the experimental conditions, but good to excellent enantioselectivities were achieved with several alkyl substituents, at the level of the best known at the time.[477] σ-bound imine complexes $[Cp'Re(NO)(PPh_3)(\eta^1\text{-NR}{=}CR^1R^2)]^+$ have been prepared by the three approaches in Scheme 67.[478]

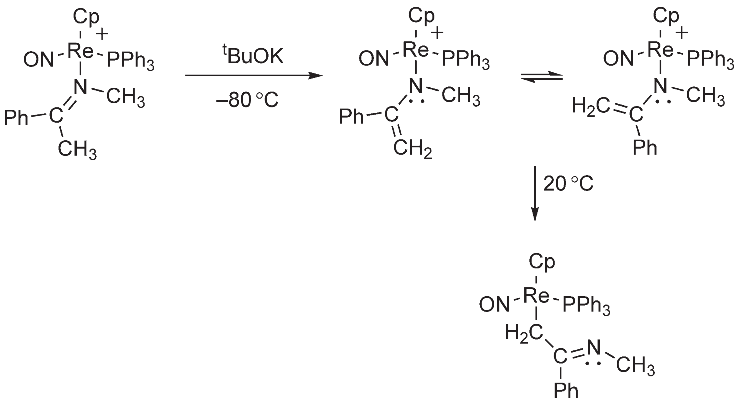
Attempts to prepare π-bound analogs, using strong electron-withdrawing groups, were negative with *N*-protio acetaldimine ($HN{=}CHCH_3$), ($HN{=}C(CF_3)_2$), and ($HN{=}C(CF_3)H$). In contrast, acetaldehyde, 1,3-difluoroacetone, and trifluoroacetaldehyde ligands give only π-isomers. These differences are explained by the better σ-donor capability and lower π-accepting power of the imine nitrogen over the more electronegative *O*-donor in aldehydes and ketones. The three substituents in the imine versus the two in the aldehydes and ketones also destabilize the $[\{Re\}(\pi\text{-imine})]^+$ complex.[479] The latter fact also helps determining the stereochemistry of nucleophilic additions to $[\{Re\}(\eta^1\text{-N(Me)CHPh})]^+$ complexes with RLi (R = Me, $Et_3SiC{\equiv}C$, Me_3SiCH_2). These reactions have several important limitations: (i) complications in obtaining isomerically pure N–C adducts, (ii) often modest diastereoselectivities, (iii) potentially epimerizable addition products, and (iv) competing deprotonations. The first problem is avoided with heterocyclic imines that have a fixed stereochemistry. The deprotonations compete with nucleophilic addition when RLi reagents are used but not with ^{t}BuOK (Scheme 68).[480]

The $\eta^1\text{-HN}{=}CRR^1$ ligands can also be deprotonated with ^{t}BuOK to produce the methylenamido complexes $\{Re\}(\text{–N}{=}CRR^1)$ which can be *N*-methylated with MeOTf.

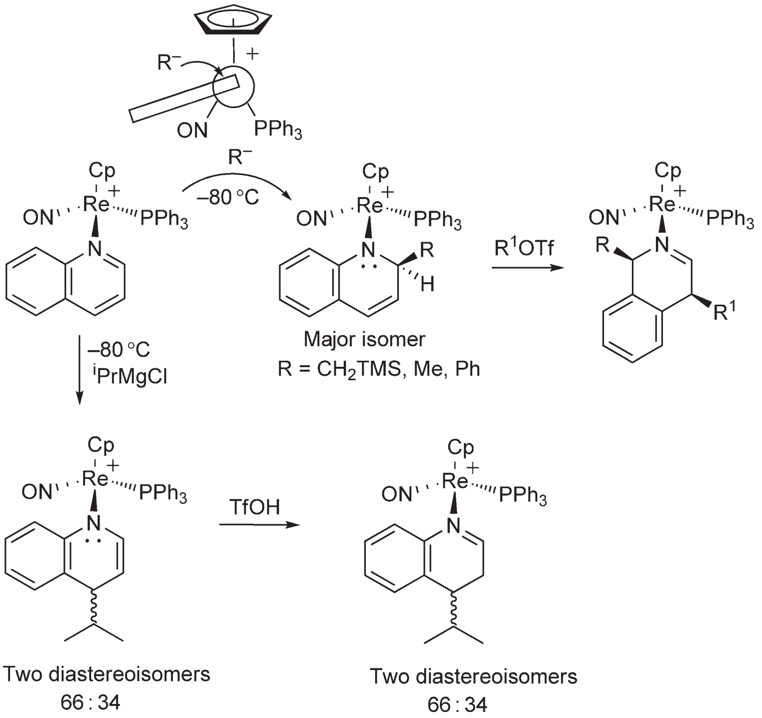
The chiral {Re}complexes of quinoline and isoquinoline (aromatic imines) are activated toward nucleophilic attack. In the case of the isoquinoline complex, the sequential diastereoselective nucleophilic and electrophilic additions allow the synthesis of various alkyl, dialkyl, and trialkyl hydroisoquinoline derivatives of high enantiomeric purity, while the rhenium fragment is easily recycled with retention of configuration.[481] In the case of quinoline, similar sequential reactions give usually 1,2-addition products with diastereoselectivities >92%. Minor isomers are also formed, including eventually products of 1,4-addition, which become dominant with the bulky nucleophile ^{i}PrMgCl (Scheme 69).[482]



Scheme 67



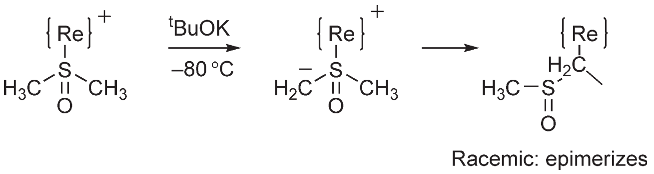
Scheme 68



Scheme 69

Diastereoselective nucleophilic additions to [{Re}L]$^+$ complexes (L = alkene, aldehyde, ketone, imine) do not proceed with weaker nucleophiles such as allylstannanes, because {Re}$^+$, having a high π-basicity, does not strongly activate unsaturated ligands toward nucleophiles unlike many other transition metal Lewis acids. This fact has hampered the development of transformations that would be catalytic in rhenium. This situation remains true even using strong π-acceptor phosphines like $P(4\text{-}C_6H_4CF_3)_3$ or $P(C_6F_5)_3$ instead of PPh_3. Similar reactions are readily catalyzed by Ti, Pd, or Cu Lewis acids. Unexpectedly, however, [{Re}(NO)(CO)($P(C_6F_5)_3$)]$^+$ activates the three *para*-C–F bonds to nucleophilic substitution by MeO$^-$ and MeS$^-$, a relatively rare reaction type.[483] Several studies with transformations of amine ligands coordinated to {Re}$^+$ made in the group of Gladysz are collected in Dewey *et al.*[465] and in the imine-related papers above.

The chiral [{Re}(ClPh)][BF_4] binds sulfoxides O═S(Me)R (R = Me, Et, Pr^i, Bu^t) at −15 °C via the O atom as in [{Re}{O═S(Me)R}][BF_4]. Above 0 °C, they isomerize to the *S*-bound complexes [{Re}{S(═O)(Me)R}][BF_4].



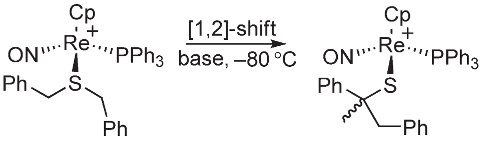
Scheme 70

The thioether complexes [{Re}{S(Me)R}]$^+$ and dimethyldioxirane react (acetone, −20 °C) to give [{Re}{S(=O)(Me)R}]$^+$ with fair to good diastereoselectivities.[484] Deprotonation of the DMSO complex is followed by a [1,2]-shift yielding a ylide complex, which epimerizes through a mechanism involving [{Re}=CH$_2$]$^+$ as intermediate (Scheme 70).[485]

Thioether adducts of the chiral rhenium Lewis acid {Re}$^+$ and symmetrical diallyl or dipropargyl sulfides rapidly react with ^{t}BuOK in THF at −80 °C. Deprotonation at the C$_\alpha$ forms an ylide that undergoes [2,3]-rearrangements to produce air stable thiolate complexes isolated in high yields and diastereomeric purities. Their conformation at the C-stereocenter is controlled by the chiral Re fragment bound to S. These thiolate complexes are easily converted to free, desymmetrized methyl or benzyl sulfides of high enantiomeric purities. The {Re}$^+$ can be conveniently recycled through the cyanide route without loss of configuration (Scheme 71).

This reaction was extended to a large number of substituted S(CH$_2$C=CRR^1)$_2$ (R or R^1 = H, Me, Ph) and S(CH$_2$C≡CMe)$_2$, dibenzyl sulfides, benzyl allyl sulfides, and allyl *β*-keto sulfides. The use of Cp* instead of Cp only gave a marginal increase in stereoselectivities. A mechanism of stereoselection and appropriate transition states are proposed.[486]

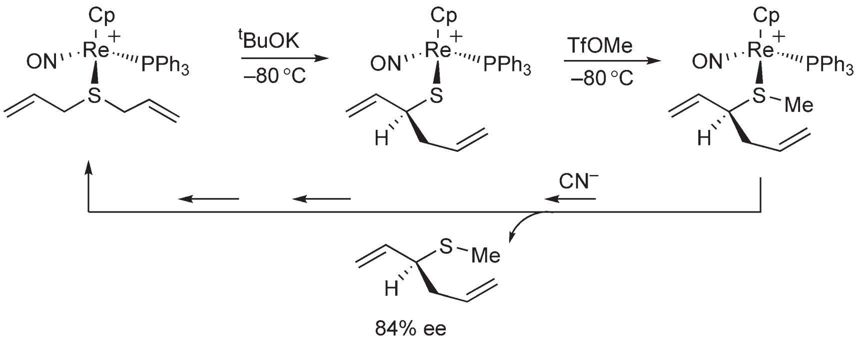
In certain cases (Equation (19)), products derived from other rearrangement pathways, such as the [1,2]-shift, are detected.



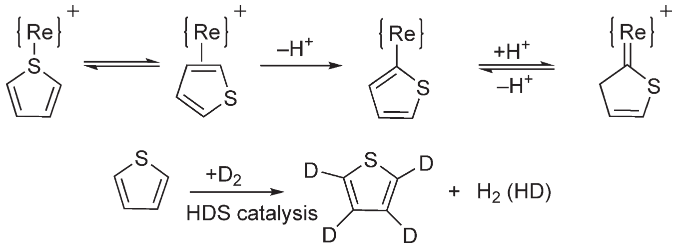
(19)

The deprotonation at C$_\alpha$ of simple dialkylthiothers like [{Re}(SMe$_2$)]$^+$ does not take place.[487] Angelici and co-workers studied the related thiophene and benzothiophene and their Se analog complexes with the long-term purpose of improving the knowledge on the important steps of HDS catalysis. The thiophenes (Th) bind through the S atom, but a fast equilibrium between [{Re}(η^1-*S*-thiophene)]$^+$ and [{Re}(η^2-*C*2,3-thiophene)]$^+$ seems to play a role in the deprotonation reaction leading to the neutral 2 or 3 thienyl [{Re}(η^1-*C*-thienyl)]$^+$ complexes (Scheme 72).

The removal of the *α*-proton from η^1-*S*-thiophene ligands also suggests a mechanism for the exchange of these protons with deuterium during the HDS of thiophenes on heterogeneous catalysts. This series of facile reactions on both thiophenes and benzothiophenes demonstrates that η^1-*S*-thiophene coordination can activate these heterocycles leading to the disruption of the aromaticity of the thiophene ligand upon formation of the thienylcarbene complexes. When the C2 position is substituted, C3 thienyl and benzothienyl species are formed.[488]



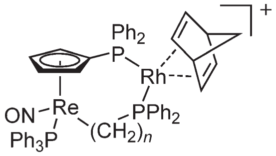
Scheme 71



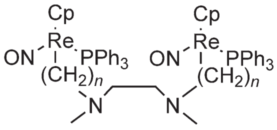
Scheme 72

5.13.3.1.5.(iv).(c) Chiral ligands based on the Cp′Re(NO)(PPh$_3$) fragment

Taking advantage of the extraordinary conformation stability of the {Re}$^+$ fragment, and the variety of methods available for its derivatization, Gladysz introduced new families of chiral organometallic ligands with the {Re}$^+$ stereocenter in the backbone. Some of these phosphine and amine ligands have been successfully used in enantioselective catalytic transformations, for example, Rh-catalyzed hydrogenations and Suzuki couplings. 121 and 122 are two examples. Others can be found in a review.[489]



121 *n* = 0, 1



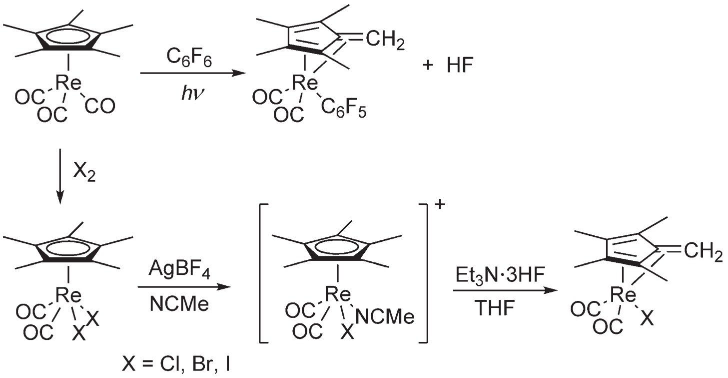
122

5.13.3.1.6 Re complexes with η^6-ligands

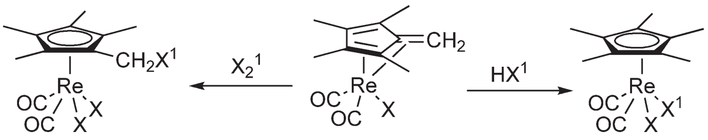
A report on the synthesis and fluxional behavior of a large series of arene-substituted derivatives of formula (η^6-$C_6H_nMe_{6-n}$)Re(CO)$_2$(SiCl$_3$) ($n = 0$–6), prepared from Re(CO)$_5$(SiCl$_3$) and arene at high temperatures, established that the arene exhibits free rotation of the ring until −120 °C.[490] Irradiation of Cp*Re(CO)$_3$ in the presence of C_8H_8 gives Cp*Re(η^6-C_8H_8), the first Re complex structurally characterized with a triolefin ligand.[359]

A series of fulvene complexes of formula (η^6-$C_5Me_4CH_2$)Re(CO)$_2$X (X = halide, haloaryl) have been prepared by the methods in Scheme 73.

The photochemical method is thought to work by intermolecular C–F activation followed by intramolecular H–F elimination from a proton on the Me ring substituent and Re-bound F$^-$.[491] NMR confirms the η^6-triolefin bonding assignment.[492] The second method is based upon the fluorination power of Et$_3$N·3HF followed by HF elimination, as in the previous example. It is more versatile due to the possibility of making mixed halides.[493] The reactivity of these fulvenes with HX and halogens is depicted in Scheme 74 and provides a practical method for halogenation of a Cp* ligand.[493]



Scheme 73



Scheme 74

The fulvene complexes $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2X$ (X = I, C_6F_5) suffer nucleophilic addition at the CH_2 group forming anions of formula $[(\eta^6\text{-}C_5Me_4CH_2Z)Re(CO)_2X]^-$ ($Z^- = CH_2{=}CHCH_2$, 2-thienyl). Alkylation (MeI) or protonation (HCl at low temperature) of these anions takes place at the metal forming $(\eta^5\text{-}C_5Me_4CH_2Z)Re(CO)_2XR$ (R = H, Me). Elimination of C_6F_5H from the corresponding complexes leads to tethering by coordination of the donor function of the dangling CH_2Z (a C=C bond or an S atom) to the metal as in $[(\eta^5\text{-}C_5Me_4CH_2Z)Re(CO)_2]$.[494] Addition of PR_3 (R = Me, Et, Pr^i) to $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2X$ (X = I, C_6F_5) leads to zwitterions $(\eta^5\text{-}C_5Me_4CH_2PR_3)Re(CO)_2X$ or cations $[(\eta^5\text{-}C_5Me_4CH_2PR_3)Re(CO)_2(PR_3)]I$.[495]

5.13.3.2 Re(II) Complexes

5.13.3.2.1 Dinuclear complexes $[Re_2(\mu\text{-dppm})_2]^{4+}$

The first fully alkylated derivative of the $[Re_2(\mu\text{-dppm})_2]^{4+}$ core, namely, $Re_2Me_4(\mu\text{-dppm})_2$, was recently obtained by reaction on LiMe with either $Re_2Cl_4(\mu\text{-dppm})_2$ or $Re_2Cl_6(\mu\text{-dppm})_2$. Reaction of this tetramethyl complex with CO, at RT, leads to CH_4 elimination and formation of the doubly bridged μ-CH_2 complex $Re_2(CO)_4(\mu\text{-}CH_2)_2(\mu\text{-dppm})_2$ with a single Re–Re bond. Reaction of $Re_2X_4(\mu\text{-dppm})_2$ with acetylene neither produces any C–C coupling by itself, as found in other Re(II) complexes,[1,2] nor by reaction with CO. Instead, the acetylene complexes shown in Scheme 75 are formed.

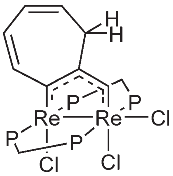
The long C–C bond of the bridging HC≡CH ligand and the long Re–Re bond in the complexes shows that the bridging acetylene behaves as a four-electron donor, whereas the terminal one(s) act as simple two-electron donors and are easily displaced by CO or CNR.[496]

However, reductive coupling has been achieved between CO and alkynes as well as in alkyne cyclization, which results in oxidized derivatives of both Re(III) and Re(IV). These reactions are presented in Sections 5.13.3.3.1 and 5.13.3.4.

5.13.3.3 Re(III) Complexes

5.13.3.3.1 Re complexes with η^1-ligands

The octahedral aryl 16-electron complex $[Re(NO)PhBr_3(PPh_3)]$ was unexpectedly formed in low yield from the reaction of $Re(O)Br_3(PPh_3)_2$ with NO gas. PPh_3 and Ph occupy *trans*-positions.[497] Reductive acetylene coupling was achieved in the reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with 1,7-octadiyne leading to the complex **123** where Re(II) is oxidized to Re(III), and the Re–Re bond becomes quadruple.[498]



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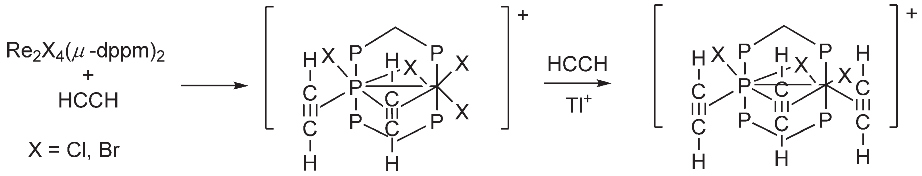
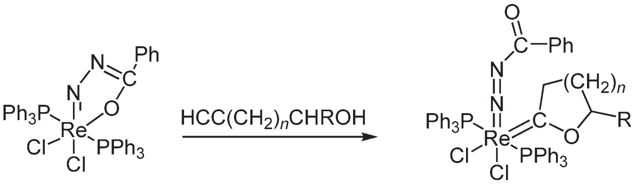


Scheme 75

Extending the carbene chemistry mentioned above for the $[Re(CO)_2(triphos)]^+$ fragment (Section 5.13.3.1.1.(iii)), it was found that the Re(V) benzoylhydrazido complex also reacts with ω-alkynols to form the very stable 2-oxacyclocarbenes of Equation (20). Based upon X-ray structural data and magnetic measurements ($\mu_{eff} = 2.40MB$ for the complex in Equation (20) and $n = 1$, R = Me), the compounds were assigned the oxidation Re(III), in spite of showing NMR spectra typical for diamagnetic complexes.[499]



(20)

5.13.3.3.2 Re complexes with η^2-ligands

The chemistry of Re(III) oxo–bis(acetylene) complexes has been extensively studied by Mayer and co-workers, starting from the iodide derivatives $[Re(O)I(\eta^2\text{-}RC{\equiv}CR)_2]$ **124**. The replacement of the oxo ligand with excess boron sulfide, B_2S_3, in CH_2Cl_2 yields the sulfido complexes $[Re(S)I(\eta^2\text{-}RC{\equiv}CR)_2]$ **125** (R = Et, Me). These are much less stable than their oxo analogs, decomposing at 25 °C over a few days. Reactions ocurring at the sulfido ligand in **125** are quite similar to those involving the oxo ligand in **124**, with the exception of substitution reactions of the iodide which are not successful for the sulfido complex. Reagents that exchange the iodide of **124** for other ligands, such as $NaBH_4$, $NaBH_3CN$, Bu_3SnH, Et_2Zn, TlOEt, TlO_2CH, and $AgSbF_6$/pyridine, cause the decomposition of **125**.

The sulfido–ethyl complex $[Re(S)Et(\eta^2\text{-}MeC{\equiv}CMe)_2]$ is formed at low temperatures from $[Re(O)I(\eta^2\text{-}MeC{\equiv}CMe)_2]$ and B_2S_3 but decomposes within minutes at 25 °C.[500] A series of related oxo complexes, [ReOX(2,7-nonadiyne)] (X = I, Me, Et), have been prepared from 2,7-nonadiyne and $[ReOI_3(PPh_3)_2]$. The reversible protonation of [ReOI(2,7-nonadiyne)] **126** with a variety of acids in NCMe gives $[ReI(NCMe)_3(2,7\text{-nonadiyne})]^{2+}$ through the hydroxo intermediate $[Re(OH)I(2,7\text{-nonadiyne})]^+$, which is further protonated to liberate H_2O (Scheme 76).[501]

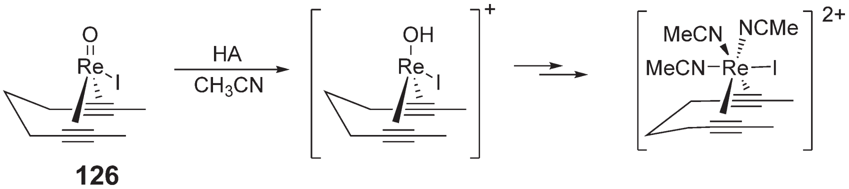
Reduction of the Re(IV) complex $Re\{(C_6F_5NCH_2CH_2)_3N)\}Br$ with the tetradentate trinegative ligand $(C_6F_5NCH_2CH_2)_3N]^{3-}$ with Mg, under ethylene or propylene atmosphere, yields the alkene complexes $Re\{(C_6F_5NCH_2CH_2)_3N)\}(\eta^2\text{-}H_2C{=}CHR)$. The alkene rotates freely at RT but acquires a very particular orientation in the solid state as a result of electronic constraints.[295]

5.13.3.3.3 Re complexes with η^5-ligands

The majority of the complexes in this subsection originates from oxidative additions to the fragment $[Cp'ReL_2]^+$, namely, from the ones where L = CO or its functional equivalents $Cp'Re(CO)_2(THF)$ are easily accessible photochemically from $Cp'Re(CO)_3$. Depending on the nature of the X–Y bond being added, several families of compounds are considered next.

5.13.3.3.3.(i) Halide, hydride, and η^1-hydrocarbyl complexes

Halogenation of $CpRe(CO)_3$ or $(CpR^1R^2)Re(CO)_3$ with Br_2 or I_2 in $CHCl_3$ leads to $Cp'Re(CO)_2X_2$, of which two isomers usually called diagonal (*diag* = *trans*) and lateral (*lat* = *cis*) are formed.[361] Solvent and reaction conditions may play a role in this reaction, since, in CH_2Cl_2, $Cp^*Re(CO)_3$ reacts with Br_2, leading to quantitative isolation of the cation $[Cp^*ReBr(CO)_3]^+$ (M = Re) with the dinuclear complex $[(CO)_3Re(\mu\text{-}Br)_3Re(CO)_3]^-$ as a counterion: $Cp^*Re(CO)_2Br_2$ forms only in trace amounts.[502]



126

HA = CF_3SO_3H, $p\text{-}CH_3C_6H_4SO_3H$, $HBF_4{\cdot}(CH_3)_2O$

Scheme 76

The $Cp^*Re(CO)_2X_2$ complexes are intimately related to the fulvene complexes described in Section 5.13.3.1.6, from which they are formed and, conversely, may be prepared. Substitution of one CO ligand from *diag-* or *lat-*(η^5-C_5H_4R)$Re(CO)_2X_2$ (R = Me, Bu^t, $SiMe_3$; X = Br, I) proceeds rapidly at RT in the presence of Me_3NO and ligands L to afford (η^5-C_5H_4R)$Re(CO)LX_2$ (L = $CNC_6H_3Me_2$, $P(OMe)_3$, $P(OPr^i)_3$, $P(OPh)_3$, PPh_3) in >75%) yields. Typically, the *trans*-isomer is the dominant product (>90%). Upon heating the solid compounds under N_2 below the melting point, the *cis*-isomer is converted into the *trans*-form in excellent yield (>70%). The same isomerization takes place in solution under visible light irradiation at RT.[503] The group of Coville has extensively studied the mechanism of the *diag/lat*-isomerization. These isomerizations are also accelerated by absorption on SiO_2 surfaces and are dependent on the nature of both L and X, the nature of the interaction with the surface, and even the substituents on the Cp′ ring. Themochemical studies established in all studied cases that *diag* → *lat* isomerization is an exothermic process.[504] However, in the case of $CpRe(CO)_2Br_2$, the opposite process, that is, *lat* → *diag* isomerization, is observed in boiling toluene, the first example of a phase-dependent isomerization reaction of an organometallic complex.[505,506]

Treatment of *cis-* or *trans*-$CpRe(CO)_2Br_2$ with Ph_3SnH yields the corresponding dihydride $CpRe(CO)_2H_2$ and Ph_3SnBr in good yields via a radical mechanism.[507] $Cp^*Re(CO)_2H_2$ is best made by reduction of *cis-* or *trans-*$Cp^*Re(CO)_2Br_2$ with Zn in AcOH/MeOH. Its *trans*-to-*cis* photoisomerization was studied in low-temperature matrix and found to be intramolecular and reversed thermally. On reaction with MeI, $Cp^*Re(CO)_2Me_2$ is formed in good yield.[508] Other dialkyl and alkyl/aryl halide complexes $Cp^*Re(CO)_2R_2$ (R = Me, Et) and $Cp^*Re(CO)_2(Ar)I$ were prepared by alkylation of *cis*-$Cp^*Re(CO)_2X_2$ with the corresponding organocopper reagents.[509] Alkylation of $Cp^*Re(CO)_2(Ar)I$ with LiMe gives $Cp^*Re(CO)_2(Ar)Me$.[510] Photolytic reaction of these and similar complexes revealed no reductive elimination reaction. Instead, the products result from Re–C homolysis, and $ReCp^*(CO)_3$ is formed under CO together with alkanes and arenes resulting from the aryl and alkyl radicals formed, abstracting H from the solvent.[511]

A number of haloaryl chlorides $Cp'Re(CO)_2X(Ar^{hal})$ ($Ar^{hal} = C_6H_nCl_{6-n}$) have been prepared upon photolysis of $Cp'Re(CO)_3$ or $Cp^*Re(CO)L(N_2)$ (L = PMe_2Ph; $P(OR)_3$; R = Me, Et) in the presence of Ar^{hal}. In this way, $Cp'Re(CO)_2(C_6H_nCl_{5-n})Cl$ (Cp′ = Cp, Cp*; *n* = 1–5) has been made from $C_6H_nCl_{6-n}$. The *cis*-isomers are favored in polar solvents like NCMe. In the case of $P(OPh)_3$, orthometallation of one Ph ring takes place via C–H activation.[492,512,513]

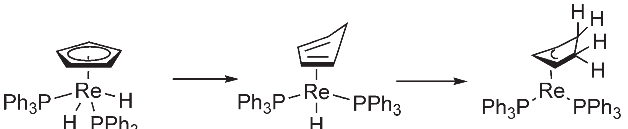
Similar reactions with aryl fluorides also lead to intramolecular C–H activation. In this way, fluoroaryl hydrides $Cp'Re(CO)_2H(Ar^F)$ were prepared (Cp′ = Cp, Cp*; $Ar^F = C_6F_5$ or 2,3,5,6-C_6F_4H).[514] The only example reported of similar Cl–C(sp^3) activation comes from the reaction of [$Cp^*Re(CO)_2(THF)$] with CH_2Cl_2 that affords *cis*-[$Cp^*Re(CO)_2Cl(CH_2Cl)$].[423]

One important observation concerns the reactivity of the compounds resulting from highly fluorinated or chlorinated aryls in which the ring is Cp*. The putative product of the C–F activation of C_6F_6 or $C_6F_5CF_3$ by $Cp^*Re(CO)_2$ would be $Cp^*Re(CO)_2(C_6F_4X)F$ (X = F, CF_3). Instead, the fulvene complexes (η^6-$C_5Me_4CH_2$)$Re(C_6F_4X)$ are formed due to HF elimination. The chloride analog $Cp^*Re(CO)_2(C_6HCl_4)Cl$ also eliminates HCl to form (η^6-$C_5Me_4CH_2$)$Re(CO)_2(C_6HCl_4)$ but only by interaction with silica gel.[492]

$CpRe(PPh_3)_2H_2$ **127** is thermally inert, but undergoes photochemical substitution of one or two PPh_3 ligands. More importantly, **127** photocatalyzes C–H activation in the form of H/D exchange between a deuterated solvent (typically C_6D_6 or THF-d^8) and a variety of arene and alkane substrates, including methane, (Equation (21)). Turnover numbers exceeded 1,000 for THF or Et_2O in C_6D_6.

$$\begin{gathered} C_6D_6 + RH \xrightarrow[h\nu]{CpRe(PPh_3)_2H_2} C_6D_5H + RD \\ RH = C_6H_6,\ CH_4,\ C_2H_6,\ C_3H_8,\ c\text{-}C_3H_6,\ c\text{-}C_5H_{10},\ THF,\ Et_2O \end{gathered} \tag{21}$$

The mechanism originally proposed for this catalytic process, thought to involve PPh_3 dissociation as initial step, was revised. Compelling NMR data showing that both hydrides initially present never exchange with D throughout the reaction led to the proposal of a new activation process depicted in Scheme 77. The active species **128** capable of



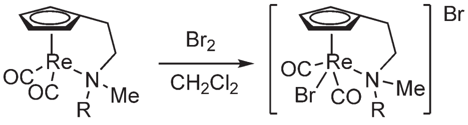
128

Scheme 77

cleaving and exchanging C–H and C–D bonds results from double metal-to-ring H migration, thereby keeping both initial H atoms away from any exchange process.[515]

Oxidation of the Re(I) acyl complexes $[Cp'Re(CO)_2\{\eta^1\text{-}C(O)Ph\}]^-$ ($Cp' = Cp, Cp^*$) with $PhICl_2$, Br_2, I_2 gives the Re(III) complexes *cis*/*trans*-$Cp'Re(CO)_2\{\eta^1\text{-}C(O)Ph\}X$ (X = Cl, Br, I). Excess oxidant cleaves the Re–acyl bond, and $Cp'Re(CO)_2X_2$ are formed.[516]

Similar reactions were carried out on several Re(I) derivatives of the chelating ligand $\eta^5\text{-}Cp(CH_2)_2L$. In contrast to the $Cp'Re(CO)_3$ complexes that add Br_2, the more electron-rich derivatives of $\eta^5\text{-}C_5H_4(CH_2)_2NMeR$ (R = H, Me) form cationic complexes with one Br^- as counterion (Equation (22)).[517,518]



(22)

129

R = H, Me

Alkylation of **129** (R = H) with RX (X = Br, I) takes place exclusively at the metal to give the cations $[(\eta^5\text{-}C_5H_4(CH_2)_2NMeH)Re(CO)_2(R)]X$ (R = Me, $CH_2CH{=}CH_2$, CH_2Ph, $CH_2C{\equiv}CH$, CH_2CO_2Me, CH_2CO_2Me, CH_2CN). In contrast, after *N*-deprotonation of **129** (R = H), the anion $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe)Re(CO)_2]^-$ discriminates between the same RX halides: the last three, bearing CO_2R or CN groups adjacent to CH_2, add exclusively to the metal forming $[(\eta^5\text{-}C_5H_4(CH_2)_2NMeH)Re(CO)_2(R)]X$ after protonation with H_2O; the others add exclusively at the harder *N*-centre forming $(\eta^5\text{-}C_5H_4(CH_2)_2NMeR)Re(CO)_2$.[391]

The amido complexes $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe)Re(CO)_2(R)]$ heated under L = CO, $CNBu^t$, $P(OR)_3$ insert the N–Re bond into one CO and add one extra ligand L via η^2-carbamoyl intermediates **130** (Scheme 78).

Similar reactions take place for the cases where R = Br, PhS, PhSe.[519]

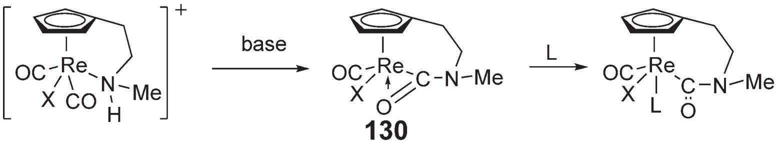
The CO in the cationic complexes $[(\eta^5\text{-}C_5H_4(CH_2)_2NMeR)Re(CO)_2Br]Br$ is readily attacked by nucleophiles. The addition of amines and hydrazine to CO of $[(\eta^5\text{-}C_5H_4(CH_2)_2NMeH)Re(CO)_2Br]Br$ and a variety of products thereof has been described.[520] In the case of $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Re(CO)_2Br]Br$, reaction with NaOH leads to $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Re(CO)(\eta^2\text{-}O{=}C{=}O)]$. Interestingly, this complex is also prepared by oxygen transfer from *m*-$ClC_6H_4C(O)OOH$ to $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)Re(CO)_2$, a rare example of CO_2 remaining coordinated after being oxidized by O transfer.[517]

5.13.3.3.3.(ii) Alkene, alkyne, and η^2-vinyl complexes

Refluxing a mixture of *cis*/*trans*-$Cp^*Re(CO)_2Br_2$ in toluene with $PhC{\equiv}CPh$ or $PhC{\equiv}CMe$ gives $Cp^*ReBr_2(\eta^2\text{-}RC{\equiv}CR)$ where the alkyne acts as a four-electron donor. Forcing the coordination of a second alkyne leads to a cyclobutadiene complex (see below η^4-complexes). Bromide abstraction with $AgBF_4$ in the presence of PR_3 ($R_3 = Ph_3$, $MePh_2$, $(OMe)_3$) or dppe gives the cationic complexes $[Cp^*ReBr(PR_3)(\eta^2\text{-}RC{\equiv}CR)]^+$ or $[Cp^*Re(dppe)(\eta^2\text{-}RC{\equiv}CR)]^{2+}$ (R = Me, Ph) respectively.[521] Nucleophilic H^- attack (from $[^sBu_3BH]^-$) leads to only two diastereoisomers (*S*,*S* and *R*,*R*) of the η^2-(three-electron)vinyl complex $Cp^*Re(PR_3)(\eta^2\text{-}CPhCHPh)$ (only one isomer shown in Scheme 79). These isomers result from stereospecific attack on the acetylene face *cis*- to the PR_3 ligand in the H_{ax} position. With the dppe dication and $[^sBu_3BH]^-$, a monocation is formed from −78 °C to RT. Further reaction at RT ends in the stilbene complex $[CpRe(dppe)(\eta^2\text{-}Z\text{-}CHPh{=}CHPh)]$ (Scheme 79).

When the unsymmetrical acetylene $MeC{\equiv}CPh$ is used, the first step of H^- attack on $CpRe(dppe)(\eta^2\text{-}(MeC{\equiv}CPh)]^{2+}$ also originates the η^2-vinyl derivative, but the second attack, at RT, leads to an allene complex. Protonation with strong acid reverts this step. (Scheme 80).

A theoretical study of the structural preferences of these and many other octahedral η^2-alkenyl complexes has appeared.[522]



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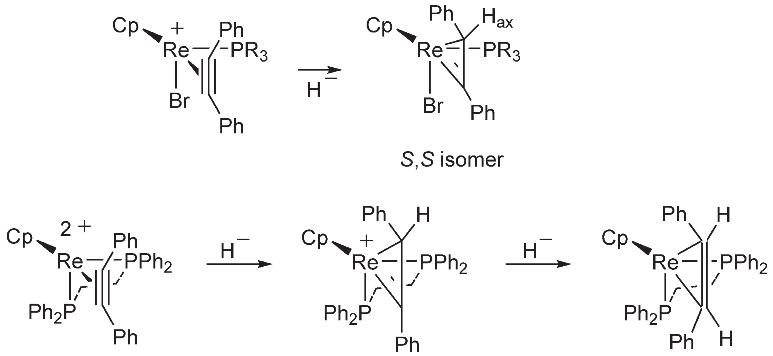
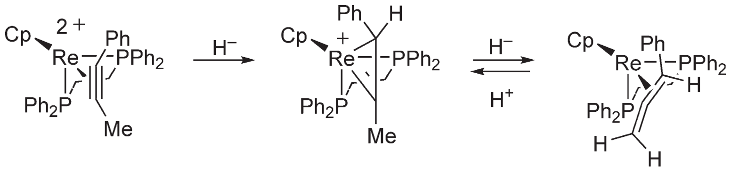
X = alkyl, Br, I, PhS, PhSe; L = CO, $CNBu^t$, $P(OR)_3$

Scheme 78



Scheme 79



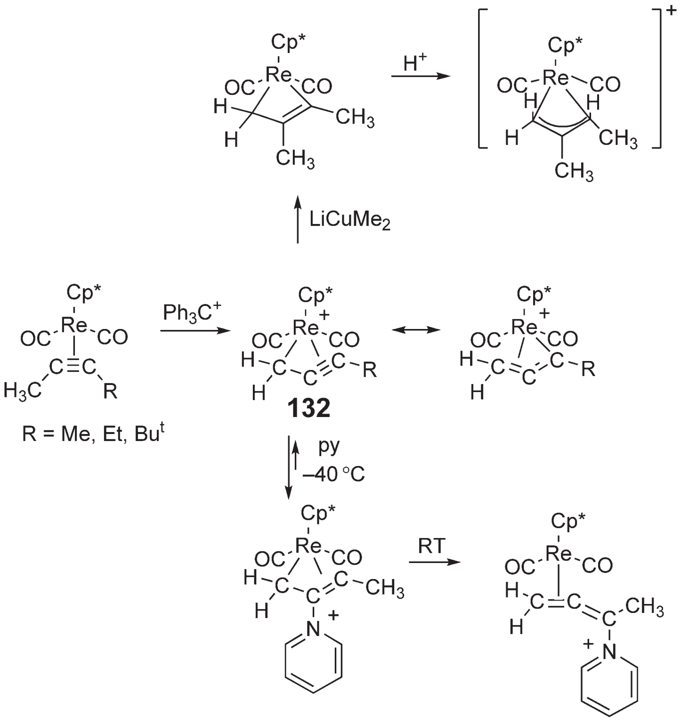
Scheme 80

5.13.3.3.3.(iii) Allyl and propargyl complexes

The chemistry of allylic compexes of Re is relatively limited but a few exploratory studies dealing with quite simple transformations were made, particularly with Re(III) complexes. The cationic complexes $[Cp^*Re(CO)_2(\eta^3\text{-}C_3H_5)]^+$ undergo nucleophilic attack at the CO by PhIO and Me_3NO, in NCMe, to give $[Cp^*Re(NCMe)_2(\eta^3\text{-}C_3H_5)]^+$ and $[Cp^*Re(CO)(NCMe)(\eta^3\text{-}C_3H_5)]^+$ and CO_2.[523] In CH_2Cl_2, in the presence of Me_4NCl, the same reaction yields $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl]$ in very high yield. The NCMe ligands in $[Cp^*Re(\eta^3\text{-}C_3H_5)(NCMe)_2]^+$ are not very labile and suffer attack by $NaBH_4$ to give $[Cp^*Re(\eta^3\text{-}C_3H_5)(NH_2Et)_2]^+$. However, substitution by PMe_3 can be achieved.[524] Nucleophilic attack at CO at low temperature with $Z^- = NH_2$ and Ph gives the acyls $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(COZ)]$. However, a wide range of other nucleophiles, $Z^- =$ Ac, RS, MeO, H, N_3, add to the terminal C atom of the allyl to give $[Cp^*Re(CO)_2(\eta^2\text{-}C_3H_5Z)]$, as expected by the Davies–Green–Mingos rules.[411]

Reaction of $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl]$ with $LiBEt_3H$ gives $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H]$ **131**, and Li alkyls or Grignard reagents give a range of $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)R]$ (R = Me, Et, Bu, $\eta^1\text{-}C_3H_5$, Ph).[524] The hydride **131** is inert toward insertion or substitution reactions with unsaturated ligands (alkenes, alkynes, nitriles, PMe_3) but reacts with several electrophiles. NO^+ and $[p\text{-}N_2C_6H_4OMe]^+$ give $[Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(NO)]^+$ and $[Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(N_2C_6H_4OMe)]^+$, respectively. The reaction is initiated by attack at the metal, followed by reductive elimination from an Re(V) intermediate $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(NO)H]^+$. Strong acids HX form $[Cp^*Re(\eta^2\text{-}C_3H_6)(CO)HX]$ (X = CF_3CO_2, BF_4, CF_3SO_3) from $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H]$. Ph_3C^+ in NCMe abstracts their hydride to give $[Cp^*Re(CO)(NCMe)(\eta^3\text{-}C_3H_5)]^+$.[525] The important progresses achieved in the chemistry of η^3-allenyl and η^3-propargyl complexes of Re and other metals are reviewed.[357,358] Like the $[Cp^*Re(CO)_2(\eta^3\text{-allyls})]^+$ that can be made by H^- abstraction from $[Cp^*Re(CO)_2(\eta^2\text{-alkenes})]$, alkyne complexes may undergo a similar reaction to produce η^3-propargyls as depicted in Scheme 81.

NMR data on **132** indicate that the η^3-propargyl contribution is more important than the possible η^3-allenyl structure in the complex where R = Me, but they seem equally contributing in the case where $R = Bu^t$.[526] H^- abstraction from internal alkynes with Ph_3C^+ was also possible and its regiochemistry follows a highly unusual reactivity order: methylene > methyl >> methine. For instance, $Cp^*Re(CO)_2(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_3)$ gives a 2.5 : 1 mixture of $[Cp^*Re(CO)_2(\eta^3\text{-}CH_3CHC{\equiv}CCH_3)]^+$ over $[Cp^*Re(CO)_2(\eta^3\text{-}CH_3CH_2C{\equiv}CH_2)]^+$. However, methine abstraction from isopropyl proved to be impossible. Most surprisingly, it also failed for the simpler $Cp^*Re(CO)_2(\eta^2\text{-}HC{\equiv}CCH_3)$ and for the unsubstituted Cp derivatives. Protonation of $Cp^*Re(CO)_2(\eta^2\text{-}HC{\equiv}CCH_2OH)$ with $HBF_4{\cdot}Et_2O$ circumvents this synthetic problem, and the unsubstituted propargyl ligand, in complex $[Cp^*Re(CO)_2(\eta^3\text{-}HCC{\equiv}CCH_2)]^+$, is easily prepared. Nevertheless, this method also failed to allow the formation



Scheme 81

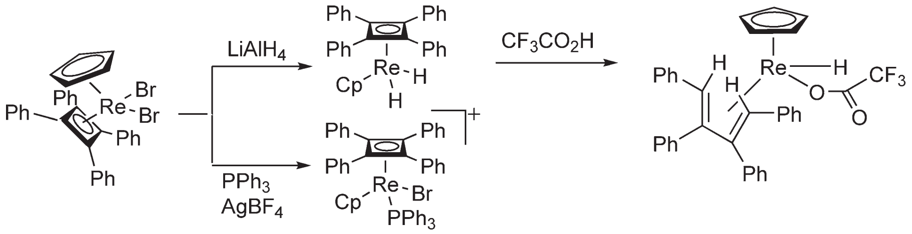
of propargyl ligands derived from the ^{i}Pr group. These facts are explained in terms of the reaction stereochemistry during H^- abstraction or protonation of terminal OH.

Scheme 81 summarizes the chemistry of these complexes. Kinetic addition of a range of nucleophiles (PMe_3, CH_3^-, malonate, $RC{\equiv}C^-$, pyridines, H_2O) to the η^3-propargylic complexes takes place at the central C atom to produce metallacylobutenes. These metallacyclobutene complexes undergo protonation to give $Cp^*Re(CO)_2$-(η^3-allyl) complexes. However, pyridine adducts rearrange to allene complexes or alkyne complexes depending on the bulk of the group bound to the triple bond of the propargyl complex.[526,527]

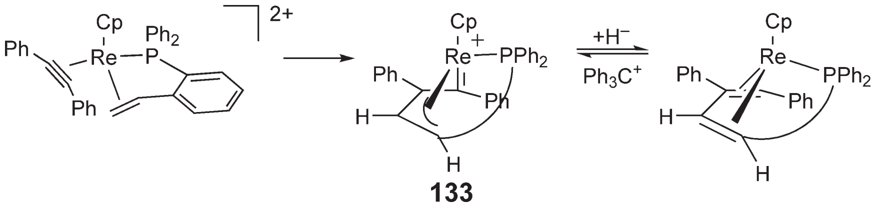
5.13.3.3.3.(iv) Butadiene and cyclobutadiene complexes

Refluxing *cis/trans*-$[CpRe(CO)_2Br_2]$ or $[CpReBr_2(\eta^2\text{-}PhC{\equiv}CPh)]$ with excess Ph_2C_2 in toluene leads to alkyne coupling yielding $[CpRe(\eta^4\text{-}C_4Ph_4)Br_2]$, isoelectronic with the well-known molybdenocene dibromide Cp_2MoBr_2. The similarity of both systems is evident in the formation of $[CpRe(\eta^4\text{-}C_4Ph_4)Br(PPh_3)]^+$ and $[CpRe(\eta^4\text{-}C_4Ph_4)H_2]$. However, protonation of the latter with CF_3CO_2H does not lead to the analog of $[Cp_2MoH_3]^+$ but rather to ring opening, and a butadiene complex is formed (Scheme 82).

The coupling of an alkyne with an alkene takes place intramolecularly during the attempted preparation of cationic $[CpRe(PR_3)_2(\eta^2\text{-alkynes})]^{2+}$, in which one of the R substituents in the phosphine has a dangling double bond



Scheme 82



Scheme 83

(Scheme 83). Formation of **133** also entails a deprotonation reaction and represents a new synthetic pathway to *cisoid*-η^4(five-electron)-butadienyl ligands.

H^- addition and abstraction interconvert the η^4-butadienyl and the η^4-butadiene ligands as shown. This H^+ abstraction from the terminal *anti*-position of the coordinated 1,3-diene is a new type of reaction.[528]

5.13.3.3.3.(v) Rhenocenes

The chemistry of rhenocenes is less developed than that of most other metallocenes. Fortunately, important advances have been reported in this period.

The cationic rhenocene adduct $[Cp_2Re(NCMe)][BF_4]$ **134** is obtained by photolysis of $[Cp_2ReH_2][BF_4]$ in acetonitrile with a medium-pressure mercury lamp. This reaction is considered to proceed through photoinduced reductive elimination of H_2 generating the rhenocene cation $[Cp_2Re]^+$, which is then attacked by a solvent molecule to give **134**. The acetonitrile ligand in **134** is labile and can be replaced by other ligands giving $[Cp_2ReL][BF_4]$ ($L = PPh_3$, $CNBu^t$, $PhC{\equiv}CH$). The first examples of intermolecular C–H bond activation by a rhenocene derivative has been reported for **134** under UV irradiation (Scheme 84) and are not unexpected due to the fact that it is isoelectronic with Cp_2WH_2, which provided the first examples of this type of reaction (Green, 1972).[1] The rhenocene cation $[Cp_2Re]^+$ is electron rich enough to undergo oxidative addition of benzene to give $[Cp_2Re(H)Ph]^+$, and the latter complex is acidic enough for reversible deprotonation.[529]

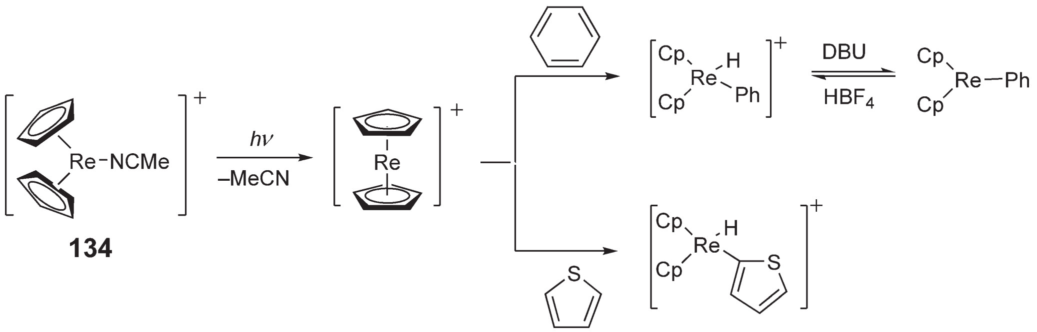
5.13.3.4 Re(IV) Complexes

Historically, Re(IV) is the least populated group of Re organometallic complexes. Since these are really few, there is no need for any subsection.

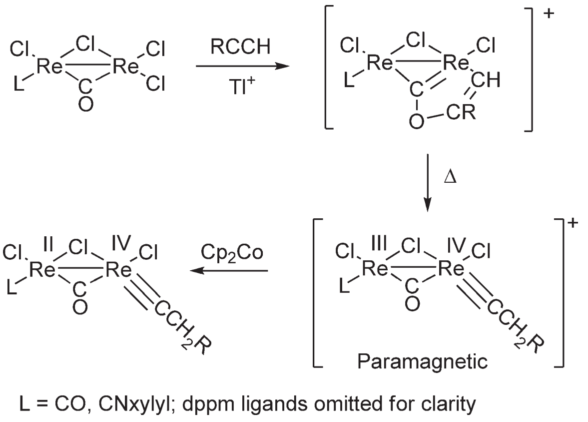
The $Re_2Cl_4(\mu\text{-dppm})_2$ complex is redox active and its Re–Re triple bond is rather electron rich. In fact, this core has already served as a template for nitrile coupling with C–C bond formation.[2] However, CO coupling has not been achieved but CO-to-alkyne coupling has been realized, forming 3-metallafurane derivatives of Scheme 85.[530]

These rearrange upon heating to mixed valence complexes bearing a formal Re(IV) center bound to an alkylidyne ligand and reducible to Re(II)/Re(IV) species.

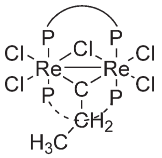
A symmetrically bridging alkylidyne **135** has been structurally characterized and results from a still mechanistically unclear reaction.[531]



Scheme 84



Scheme 85



135

The rhenium(IV) carbyne complex [(PNPcy)Re(H)(≡CMe)($H_2C{=}CH_2$)] **136** is prepared by reaction of the unsaturated [(PNPcy)ReH_4] with ethylene. The four original hydride ligands are abstracted by two molecules of ethylene, effectively a four-electron reduction of Re, which enables reconstruction of ethylene into a hydride and a strongly π-acidic ethylidyne ligand. Ethylene can be removed from **136** by heating at 100 °C under vacuum to afford [(PNPcy)Re(H)(≡CMe)].[532]

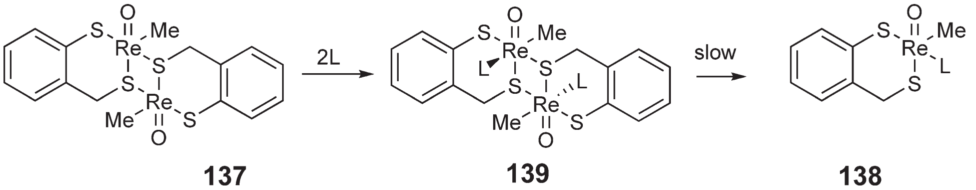
The structure of the labile $OPCl_3$ adduct of $ReCl_4(\eta^2\text{-}C_2Ph_2)$ has been reported. This formally Re(IV) complex has been considered, by magnetic susceptibility measurements, to be better described as a Re(VI) species.[533]

5.13.3.5 Re(v) Complexes

5.13.3.5.1 Re complexes with η^1-ligands

A series of stable thiolato complexes containing the methyloxorhenium(V) core {$MeReO_2$} have been prepared from methyltrioxorhenium, $MeReO_3$, abbreviated as MTO. The great interest in this type of complexes stems from their role in important catalytic oxygen atom-transfer reactions (OAT). Espenson and co-workers have reported extensive and detailed studies of the kinetics and mechanism of the OAT reactions catalyzed by oxorhenium(V) derivatives. MTO reacts with chelating dithiolate ligands, for example, 2-(mercaptomethyl)thiophenol (mtp), 1,2-ethanedithiol (edt), and 1,3-propanedithiol (pdt), to give the sulfur-bridged dimers $[MeReO(dithiolate)]_2$ (dithiolate = mtp **137**, edt, pdt).[534,535]

Compound **137** is monomerized upon reaction with various neutral and anionic monodentate ligands L, giving rise to a new family of rhenium(V) complexes [MeReO(mtp)L] **138** (L = pyridines, PAr_3, DMSO, 4-picoline-*N*-oxide, halide anions,[536] *N*- heterocycles,[537] bipy, phen, and their ring-substituted derivatives).[538] Kinetic observations can readily be interpreted for all ligands by the unified mechanism in Scheme 86. Furthermore, the ligand exchange between the monomeric complexes and free ligand L occurs through an associative pathway according to kinetic studies.[536]

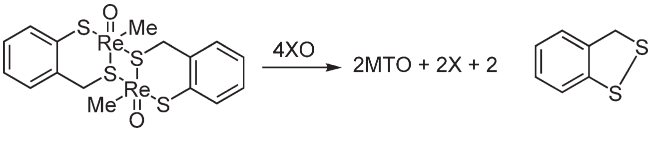


Scheme 86

The monomer [MeReO(mtp)(PPh$_3$)] mimics the OAT reactions catalyzed by the biological Mo and W oxygen transferases containing MO$_2$ fragments of Equation (23).

$$\begin{gathered} \mathrm{XO + Y \longrightarrow YO + X} \\ \mathrm{XO = pyO,\ {}^tBuOOH,\ Me_2SO;\ Y = PPh_3} \end{gathered} \tag{23}$$

The postulated key intermediate [ReMe(O)$_2$(mtp)(XO)] has been modeled from more stable 1,2-hydroxothiolate analogs.[539] Compound [MeReO(mtp)(PR$_3$)] also catalyzes oxidation of R$_2$S and thiophene to sulfoxides and sulfones with Bu^{t}OOH.[540,541] Suitable oxygen-transfer agents convert **137** to MTO; the overall reaction is shown in Equation (24).[542]



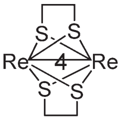
137

(24)

Related [MeReO(A)$_2$] complexes containing monoanionic bidentate ligands (A) with donor atom pairs such as *P,O* (HPO = phosphinocarboxylic acid), *N,O* (HNO = e.g., picolinic acid or 8-hydroxyquinoline), and *N,S* (HNS = 2-mercaptoquinoline) catalyze OAT from milder oxidants, like pyridine *N*-oxides or sulfoxides, to thioethers.[543] The mechanism by which these catalysts function has been the subject of many studies. It has been proved that ligand substitution precedes OAT, being the step that introduces the oxygen atom donor into the coordination shell of rhenium in place of the ligand originally present.[544]

The reaction of [MeReO(mtp)]$_2$ with 1,2-ethanedithiol (H$_2$edt) and 1,2-benzenedithiol (H$_2$bdt) unexpectedly affords the quadruply *S*-bridged rhenium(IV) dimer **140**.

[MeReO(mtp)PPh$_3$] also reacts with H$_2$edt to give [MeReO(edt)PPh$_3$].[545] However, a quite different result is obtained when MTO is treated with H$_2$edt: the complex **141** is obtained by rearrangement of the intermediate [ReMeO(S$_2$C$_2$H$_4$)$_2$]. As Re(VII) was reduced to Re(V), one H$_2$edt molecule was transformed to HS(CH$_2$)$_2$SMe, which remains coordinated to the rhenium(V) center through both sulfur atoms in a κ^2-fashion. This represents the only example of Me transfer from a metal to a thiol ligand other than that of methylcobalamine and Co(II) complexes related to vitamin B12.[543]



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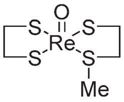
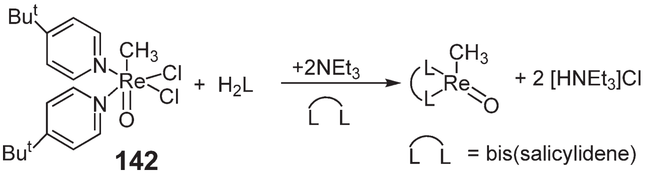


141

[MeReOCl$_2$(4-^{t}Bupy)$_2$] **142** is prepared by reduction of MTO with PPh$_3$ and Me$_3$SiCl in the presence of 2 equiv. of 4-Bu^t–py. Complex **142** exchanges 4-Bu^t–py by chelating N or P donors, such as 4,4′-^{t}Bu$_2$–2,2′-bipyridine and dppe, and reacts with tetradentate Schiff base ligands releasing 4-Bu^t–py and HCl (Equation (25)).[546]

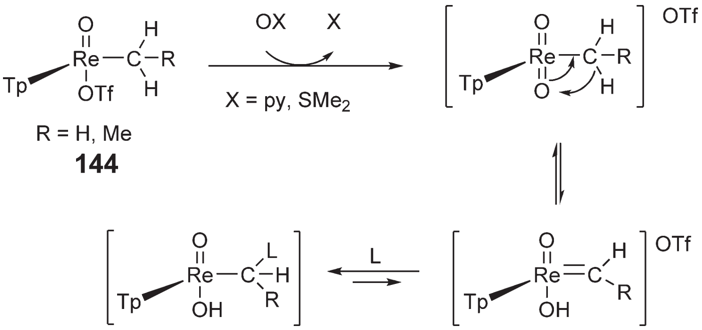


142

(25)

[ReOMe$_2$(bipy)Cl] **143** may also be prepared from [ReOCl$_3$(bipy)] and AlMe$_3$, and it allows the synthesis of mixed trialkyl oxides [Re(O)Me$_2$R^1(bipy)] (R^1 = Me$_3$SiCH$_2$, PhCH$_2$) by reaction with the respective R^{1}MgCl. Halide abstraction from **143** in NCMe affords coordinatively unsaturated cationic species [Re(O)Me$_2$L(bipy)]$^+$ (L = NCMe, PMe$_3$, PMe$_2$Ph, PMePh$_2$, PBu$_3$), which are soluble and stable in water.[547,548]

Mayer and co-workers have reported a series of monooxo rhenium(V) complexes containing the tris-pyrazolylborates Tp and Tp*. On sequential reaction of [Tp′ReOCl$_2$] with dialkyl zinc reagents and AgOTf, [Tp′ReO(R)Cl] (R = Me, Et, Bu^n, Ph), [Tp′(Re)O)R$_2$], and [Tp′ReO(R)(OTf)] **144** (R = Me, Et, Bu^n, Ph) are formed. They have an Re═O stretch at ca. 970–1,000 cm^{-1}.[549,550]

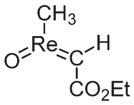


Scheme 87

The triflates **144** are rapidly oxidized by oxygen atom donors like pyridine *N*-oxide and Me_2SO to give $[TpReO_3]$ and the corresponding aldehyde. The oxidation involves initial displacement of TfO with the oxygen atom donor, which generates an Re(VII) dioxo alkyl cation. Subsequent transfer of an α-H from the alkyl group to an oxo ligand generates a carbene, which is trapped by pyridine or SMe_2 to form the ylide complexes $[TpReO(OH)\text{-}\{CH(L)CH_3\}][OTf]$ ($L = py, SMe_2$) (Scheme 87).[549]

The oxidations of the corresponding Tp′Re–oxo complexes are similar but less clean.[550] The isoelectronic *para*-tolylimido complexes of $[TpRe(Ntol)X_2]$ ($X = Cl$ or I) are prepared from $[TpRe(O)X_2]$ and *p*-toluidine. The imido–dihalide compounds are readily converted into the air stable alkyl and aryl derivatives $[TpRe(Ntol)(R)X]$ ($R = Ph$, Me, Et, Pr^i, Bu^n, SPh; $X = Cl$, I) and $[TpRe(Ntol)R_2]$ ($R = Ph$ or Me) using Grignard, organolithium, or organozinc reagents.[551,552] Iodide for triflate metathesis with AgOTf yields $[TpRe(Ntol)(X)OTf]$ [$X = Ph$, Et, Cl]. Reaction of $[TpRe(Ntol)(Et)I]$ with excess rather than stoichiometric AgOTf generates the ethylene hydride cation $[TpRe(Ntol)(\eta^2\text{-}C_2H_4)(H)][OTf]$, which slowly rearranges by ethylene insertion to form $[TpRe(Ntol)(Et)OTf]$. Treatment of $[TpRe(Ntol)(Ph)I]$ with $AgPF_6$ does not give iodide abstraction but rather $[\{TpRe(Ntol)(Ph)I\}_2Ag][PF_6]$, with two Re–I–Ag linkages. TfO substitution by py and other Lewis bases is quite slow for the rhenium–imido compounds $[TpRe(NTol)X(OTf)]$. This contrasts with the rapid substitution observed for related Tp oxo–triflate derivatives.[551,552]

Re(V)-carbene complexes have been proposed as intermediates in several reaction processes, for example, aldehyde olefination using with $N_2CH(CO_2Et)$, PPh_3, and a rhenium–oxo catalyst. The carbene complex **145** that is supposed to be the active intermediate in the catalytic cycle has been identified and characterized spectroscopically.[553] Re–oxo–carbene complexes **146** and **147** have also been identified in the electrospray-ionization mass spectrum of rhenium dioxo precursor complex **148** in Equation (26).[554]



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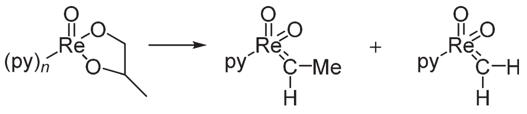
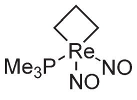


148 **146** **147** (26)

The feasibility of rhenium–carbene-catalyzed alkene polymerization was studied by DFT calculations. The reaction of ethylene with $[(CH_2){=}Re(NO)_2PMe_3]^+$ initially leads to a metallacyclobutane intermediate **149**, which affords a propene π-complex, **150**, via a β-elimination mechanism, as both kinetically and thermodynamically most favorable product.[555]



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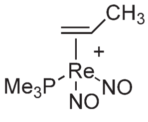
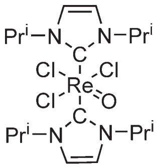


150

A series of rhenium carbyne complexes of the type *trans*-$[ReX(\equiv C–CH_2R)(dppe)_2]^+$ (X = Cl, F; R = alkyl, aryl, ester) have been prepared by protonation of the corresponding vinylidene complexes *trans*-$[ReX(=C=CHR)(dppe)_2]$ with $[NHEt_3][BPh_4]$.[556,557]

The recent boom of metal complexes derived from simple ligand substitution with the stabilized *N*-heterocyclic carbenes has produced only a very limited number of rhenium complexes, exemplified by structures **151 and 152**. Stable Re(V)–oxo and –nitrido derivatives have been prepared by replacement of phosphines.[558–560]



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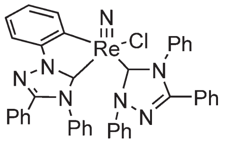


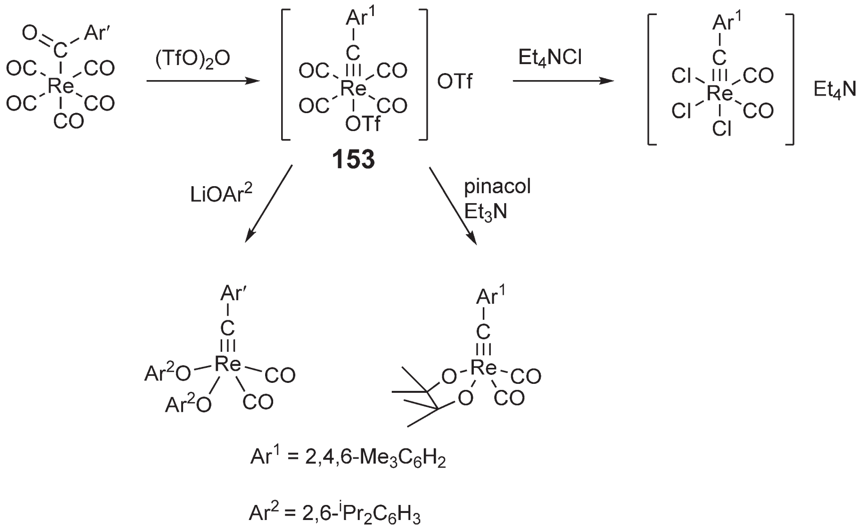
152

There are two synthetic approaches to the synthesis of Re(alkylidyne) complexes. The classical approach uses α-H elimination or abstraction of high oxidation state alkyl complexes and has abundant examples.[2] The oxidation of low-valent Re complexes to high-valent Re(alkylidyne) complexes was first reported by the group of Schrock.[561] According to Scheme 88, O^{2-} is abstracted from an Re(I) acyl complex to give directly an Re(V) carbonyl containing alkylidyne **153** that can be readily derivatized.

Following the same procedure, Che and co-workers prepared a wide range of related alkylidyne complexes bearing phosphine (P), diphosphine (P–P), substituted bipyridyls (N–N), and tris(methylpyrazolyl)borate (Tp′), of formulas like $[ReP_2(CO)(H_2O)(CAr)Cl]^+$, $[Re(P–P)_2(CAr)Cl]^+$, $[Re(CO)_2(P–P)(CAr)Cl]^+$, $[Re(CO)_2(N–N)(CAr)Cl]^+$, $[Re(CO)_2Tp'(CAr)]^+$.[332] The luminescence properties of these complexes were studied. Electrochemistry reveals that no oxidation is observed for all the complexes having two CO ligands, up to 2.3 V, in agreement with earlier reported failure to oxidize this kind of compounds to Re(VII) alkylidynes.[561]

5.13.3.5.2 Re complexes with η^2-ligands

Methyl dioxo rhenium(V) complexes are usually formed by oxygen abstraction from MTO with PPh_3 or H_3PO_2 which forms the elusive $MeReO_2$ that can be trapped with alkynes to give $[MeReO_2(\eta^2\text{-}RC\equiv CR)]$ (R = Ph, Me) **154**. Alkyne rotation in **154** is only observed at ca. 100 °C and isomers exist at RT. The latter are efficient catalysts for the olefination of aldehydes.[553] $[NpReO_2(\eta^2\text{-}RC\equiv CR^1)]$ **155** (R = Me, H; R^1 = Ph) are obtained by acetylene treatment of $[NpReO_2(py)_3]$, which is formed by photolysis of $[Np_3ReO_2]$ in pyridine. On the basis of the spectroscopic data, compounds **154** and **155** are proposed to have tetrahedral-like structures.[562]



Scheme 88

5.13.3.5.3 Re complexes with η^5-ligands

5.13.3.5.3.(i) Re(v) monocyclopentadienyl complexes

Reaction of vicinal diols with [{Cp*ReO}$_2$(μ-O)$_2$], prepared *in situ* from Cp*ReO$_3$ and PPh$_3$, leads to formation of rhenium(V) diolates of the type [Cp*ReO(diolate)] in moderate to good yields.[563] These diolates extrude the alkene reforming Cp*ReO$_3$ in a stepwise mechanism (Scheme 89).[563–566]

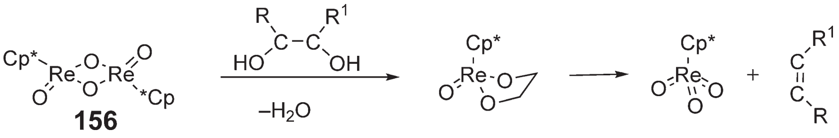
156 [{Cp*ReO}$_2$(μ-O)$_2$] is active in the catalytic deoxygenation of epoxides. Unfortunately, comproportionation between the Re(V) and Re(VII) to form clusters of [{Cp*ReO}$_3$(μ-O)$_6$][ReO$_4$]$_2$ and [{Cp*ReO}$_3$(μ_2-O)$_3$(μ_3-O)$_3$ReO$_3$][ReO$_4$] leads to removal of rhenium from the catalytic cycle and loss of activity.[567]

A number of Cp complexes with polysulfide rings (S3 and S4) and thiolates are known, among them the mononuclear species [Cp*Re(S$_3$)(S$_4$)],[568] [Cp*ReE(S$_4$)] (E = O or NBu^t),[569] [Cp*Re(S$_4$){S$_2$C$_2$(CO$_2$Me)$_2$}],[570] [Cp′Re(S$_3$)Cl$_2$] (Cp′ = Cp*,[569] C$_5$EtMe$_4$[571]), as well as the binuclear [Cp*Re(μ-S$_4$)]$_2$, [Cp$_2$*Re$_2$O$_2$(μ-S)(μ-S$_2$)$_2$],[568] and [(η^5-C$_5$EtMe$_4$)ReCl$_2$(μ-S)]$_2$.[572] An unusual generation of the 5,6-dihydrofulvene-5,6-dithiolato complex [Cp*ReO{(S)(SCH$_2$)C$_5$Me$_4$}] through the migration of a ring ligand to sulfur has been described in the reaction of [Cp*ReOCl$_2$] with H$_2$S.[573]

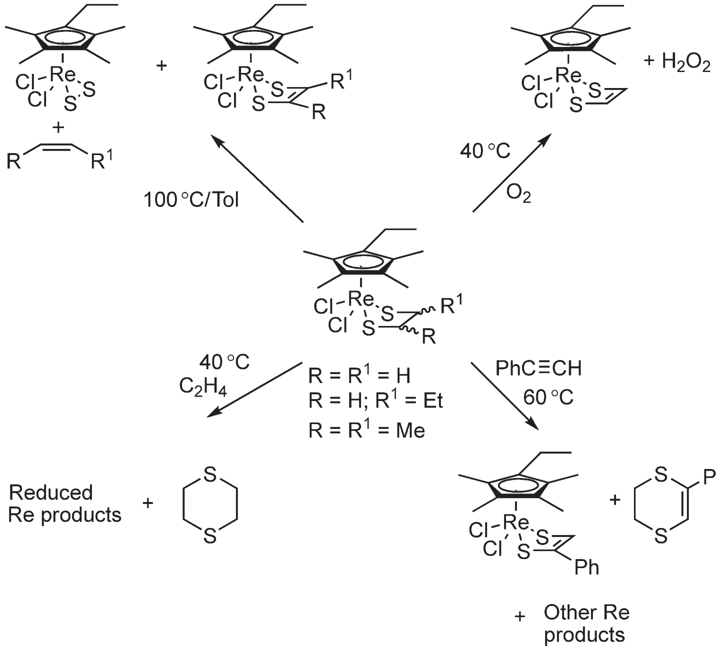
Mononuclear Re(V) dithiolates of the formula [(η^5-C$_5$EtMe$_4$)ReCl$_2$(dithiolate)], [(η^5-C$_5$EtMe$_4$)Re(dithiolate)$_2$] (dithiolate = 1,2-alkanedithiolate) are prepared by reaction of [(η^5-C$_5$EtMe$_4$)ReCl$_4$] and the corresponding dithiols. These complexes undergo a variety of reactions including dithiolate dehydrogenation, alkene elimination, and alkane dithiolate coupling with alkenes and alkynes (Scheme 90).[574,575]

The first complex in this system to present a terminal sulfido Re=S bond, [(η^5-C$_5$EtMe$_4$)ReS(SC$_2$H$_4$S)], has been isolated from the reaction of [(η^5-C$_5$EtMe$_4$)ReCl$_2$(SC$_2$H$_4$S)] with (Me$_3$Si)$_2$S.[571]

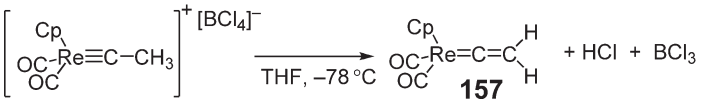
The reaction of the very stable carbene complex Cp*Re(CO)$_2${=CPh(OEt)} with BCl$_3$ or oxalyl bromide is representative of the preparation of the carbyne cations [Cp*Re(CO)$_2$(≡CPh)]$^+$. These complexes are only stable with aryls or SiPh$_3$ because alkyl substituents, for example, CH$_3$, deprotonate spontaneously already at low temperature to give the very reactive vinylidenes **157** according to Equation (27).[409]



Scheme 89

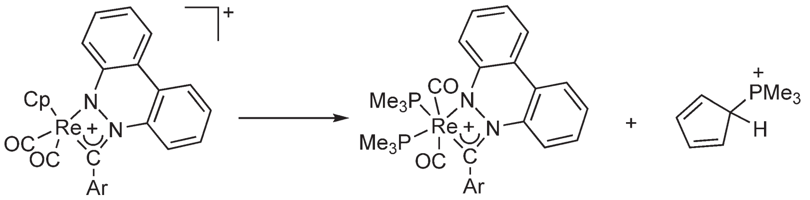


Scheme 90



(27)

$CpRe(CO)_2(\equiv Ctol)]^+$ undergoes [2 + 2]-cycloadditions with ArN=NAr (Ar = Ph, Tol), imines, and $Bu^tN=O$, but not with alkenes or alkynes. Some of the metallacycles formed are very stable and resist nucleophilic addition as in Equation (28).



(28)

The cationic alkylidyne complex $[Cp^*(CO)_2Re\equiv CCH=C(CH_3)_2]^+$ adds nucleophiles including $NaCH(CO_2C_2H_5)_2$, PMe_3, and $NaBH_4$ regioselectively at the γ-carbon of the alkylidyne ligand.[576] The complexes $[CpRe(CO)_2(\equiv CPh)]BBr_4$ undergo nucleophilic attack at the carbyne C atom by a number of carbonyl metallate anions forming a wide variety of polynuclear complexes with bridging carbenes and carbynes that have been reviewd.[577]

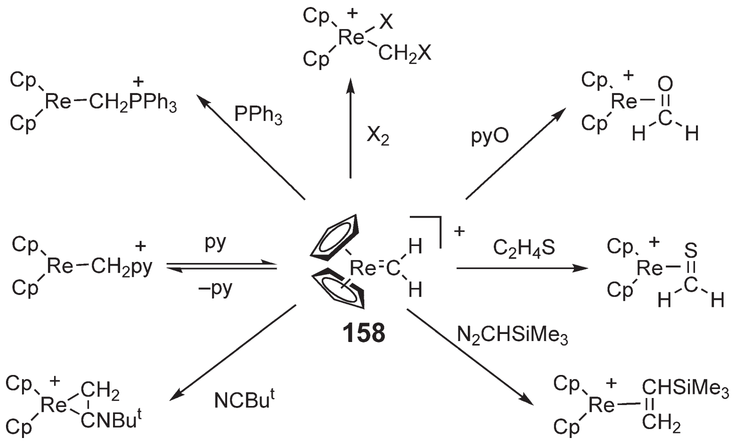
5.13.3.5.3.(ii) Rhenocenes

The air stable rhenocene(V) methylidene complex $[Cp_2Re(CH_2)][BArF]$ **158** is isolated by H^- abstraction from $[Cp_2ReCH_3]$ with $[Ph_3C][BArF]$. Complex **158** is thermally robust and is only observed to decompose to $[Cp_2Re(C_2H_4)]^+$ and $[Cp_2Re(NCCD_3)]^+$ upon prolonged thermolysis in $NCCD_3$ or upon the addition of BF_4^- or PF_6^- salts. In fact, the outstanding stability of **158** depends on the size of the anion being high for $[BArF]^-$ and marginal for BF_4^- and PF_6^-. A tight association between the cation and the $[BArF]^-$ anion is proposed to operate preventing a bimolecular coupling of two $[Cp_2Re(CH_2)]^+$ species that generate $[Cp_2Re(C_2H_4)]^+$ and the solvent-stabilized cation $[Cp_2Re(NCMe)]^+$.[578]

158 adds nucleophiles like py, PR_3, and CNR at the methylene ligand. Other reactions (Scheme 91) include metathesis of the Re=C double bond to other element double bonds by reaction with amine oxides (C=O formation), sulfur (C=S formation), or diazo compounds (C=C formation).

5.13.3.6 Re(VI) Complexes

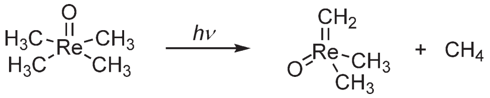
The number of Re(VI) complexes reported since 1993 is much smaller than in the previous decade where a large number of organometallic Re(VI)–oxo complexes were investigated.[2] A reinvestigation of the structure of the only homoleptic Re alkyl, $ReMe_6$, found that it is has a slightly distorted trigonal-prismatic structure that is surprisingly



Scheme 91

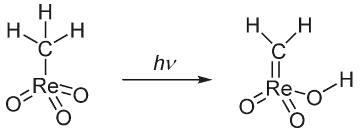
closer to D_{3h}-symmetry than that of WMe_6.[579] Upon reaction with LiMe, the paramagnetic dianion $[ReMe_8]^{2-}$ is formed with an almost-perfect S_8 symmetry axis.[580]

The remaining complexes in this subsection are oxo or imido derivatives. The rhenium methylidene species $ReOMe_2({=}CH_2)$ is generated from low-temperature matrix photolysis of $ReOMe_4$ with the elimination of CH_4 (Equation (29). The methylidene complex is determined to be the primary photoproduct and is assigned on the basis of its infrared spectrum in comparison with the vibrational spectrum calculated by DFT.



(29)

Similar studies of matrix-isolated $Me_3Re(O)_2$ revealed the formation of $[ReO_2Me({=}CH_2)]$ and CH_4.[581] This pathway exists only when the precursor contains two or more alkyl ligands, and in the case of $MeReO_3$, photolysis under similar conditions induces the formation of the long-sought elusive $ReO_2(OH)(CH_2)$, **159**, but by tautomerization rather than elimination (Equation (30)).[582]



162 **159**

(30)

The first examples of emissive d^1-complexes containing a metal–carbon multiple bond $[Re({\equiv}C\text{–}2,3,6\text{-}C_6H_2Me_3)(PPh_3)(H_2O)X_3]$ [X = Cl **160** and Br **161**] are prepared using the Re(V) precursor $[Re({\equiv}C\text{–}2,3,6\text{-}C_6H_2Me_3)(PPh_3)_2(CO)(H_2O)Cl][ClO_4]$ by thermal reaction with HCl in chloroform and by photooxidation in CH_2Br_2, respectively. The paramagnetic nature of **160** and **161** is confirmed by magnetic measurements with μ_{eff} values of 1.96 and 1.90MB, respectively.[583] Compared to the abundant reports on oxo-transfer reactions, few studies have been published on the analogous sulfur-transfer processes. A dimeric rhenium(VI) species, $[\{ReMe(NAr)_2\}_2(\mu\text{-}S)]$, are prepared from the Re(VII) complexes $[\{ReMe(NAr)_2\}_2(\mu\text{-}S)_2]$ by sulfur-transfer reaction to phosphines.[584]

5.13.3.7 Re(VII) Complexes

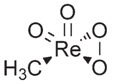
5.13.3.7.1 Re complexes with η^1-ligands

5.13.3.7.1.(i) Oxo and imido hydrocarbyl complexes

The chemistry of $[RReO_3]$ complexes which originated in the group of Herrmann is very extensive, and has been thoroughly reviewed often by the author.[585] $MeReO_3$ (MTO; **162**) is the most prominent member of this family. Initially prepared from Re_2O_7 and $SnMe_4$, it can be now obtained from cheaper $[ReO_4]^-$ salts.[586] MTO is converted to $[ReO_4]^-$ in basic aqueous solution.[587] In water at 70 °C, it forms an electrical conducting polymer of formula $[H_{0.5}\{Re(CH_3)_{0.92}O_3\}]_\infty$. Photolysis homolyzes the Me–Re bond.[588] However, the primary reaction brought about by irradiation into the UV absorption near 260 nm in a solid Ar matrix involves tautomerization of MTO to the methylidene hydroxo derivative $[H_2C{=}ReO_2(OH)]$, **159**.[581] Chemical (thermal) trapping of this tautomer has been achieved by the combined reaction of py and $SnMe_2Cl_2$ to give $[\{(C_5H_5N\text{–}CH_2\text{–}Re(O)\text{–}O)\}_2SnMe_2Cl_2][ReO_4]_2$ where the py adds to the CH_2 ligand of **159**, Equation (30).[589]

MTO readily forms adducts with one or two *N*-donor ligands having trigonal-bipyramidal $MeReO_3L$ (*O*-ligands equatorial) or octahedral structures *fac*-$[MeReO_3L_2]$, respectively. Condensation reactions of MTO with 1,2-phenylenediamine produces $[ReMeO_2\{1,2\text{-}(NH)_2\text{-}C_6H_4\}_2[1,2\text{-}(NH_2)_2C_6H_4]$.[590]

MTO is an astonishingly versatile catalyst, particularly in oxidation and oxygen-transfer reactions. This research, initiated by Herrmann and extended by Espenson in over 70 publications covered here, has been comprehensively reviewed up to 1999 but keeps growing.[591,592] The oxidation of chloride ions by hydrogen peroxide, using MTO as catalyst, has been studied.[593] The rate constants for reaction of these complexes with Cl^- were found to be 10,000 times faster than the rate for the uncatalyzed reaction. The active catalytic species in most of the oxidations are the monoperoxo complex $[ReMeO_2(\eta^2\text{-}O_2)]$ **163** and/or the diperoxo complex $[ReMeO(\eta^2\text{-}O_2)_2(OH_2)]$ **164**. A mechanistic study of the coordination of H_2O_2 to MTO with particular emphasis on the first step of peroxide binding has been reported. Activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$ for the coordination have indicated a mechanism involving nucleophilic attack. Coordination of the H_2O_2 involves its conversion to η^2-O_2 concomitant with loss of protons which are transferred to one oxo ligand which remains on the metal as coordinated H_2O.[594]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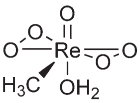

164

The complexes $[ReMeO_3L_2]$ (L_2 = bidentate *N*-donor) are highly selective epoxidation catalysts.[595] However, chiral amines only lead to modest enantiomeric excesses because of rapid decomplexation equilibria in solution.[596] For catalytic purposes, MTO has also been supported on zeolites, niobia, and polymers, a useful means of preparing quinones in high yields.[597] Other useful variations use the urea–H_2O_2 adduct as an oxidant in water-free reactions or ionic liquids as solvents.[598] Instead of *O*-addition to the substrate, the reaction with silanes R_3SiH results in a clean and neat insertion of O into a Si–H bond to give R_3SiOH by a mechanism investigated by DFT calculations.[599,600]

Besides oxidation reactions, MTO supported on Al_2O_3/SiO_2, niobia, or zeolites also catalyzes the metathesis of functionalized alkenes, 1,2 transposition of allylic alcohols, addition of epoxides to ketones, alkoxylation of epoxides, dehydration and amination of alcohols, and Diels–Alder additions in water.[600]

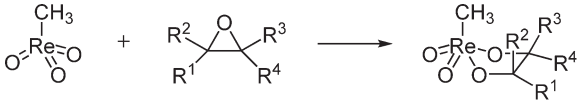
Less studied is the only other methyloxorhenium(vii) compound to be isolated, namely, trimethyldioxorhenium, $[Me_3ReO_2]$ **165**. Isolation of **165** $[Me_3ReO_2]$ in a solid argon matrix at ca. 12 K and exposure to radiation spanning the wavelengths 200–800 nm results in α-hydrogen elimination. In the primary stage, this is achieved through the elimination of CH_4, yielding the novel methylidene–rhenium(vii) compound $[H_2C{=}ReMeO_2]$. IR measurements and DFT calculations confirm that CH_4 elimination is favored thermodynamically over tautomerization to the methylidene hydroxo derivative $[H_2C{=}ReMe_2O(OH)]$. The formation of methylidene derivatives by photodecomposition suggests that **165** like MTO has the potential to catalyze olefin metathesis, although irreversible elimination of CH_4 must impart this function. Moreover, the properties of **165**, which are highly sensitive to attack by air and moisture and thermally fragile, makes it distinctly less attractive than MTO as a viable catalyst.[581]

Analogous compounds are rare but include $[Np_2RReO_2]$ (R = Me, Np, CH_2SiMe_3, and Ph), which have been prepared by ZnR_2 alkylation of oxo halides at low temperatures.

The crystal structure of $[Np_2PhReO_2]$ shows that it has a distorted trigonal-bipyramidal structure with the oxo and Ph ligands in the equatorial plane.[562]

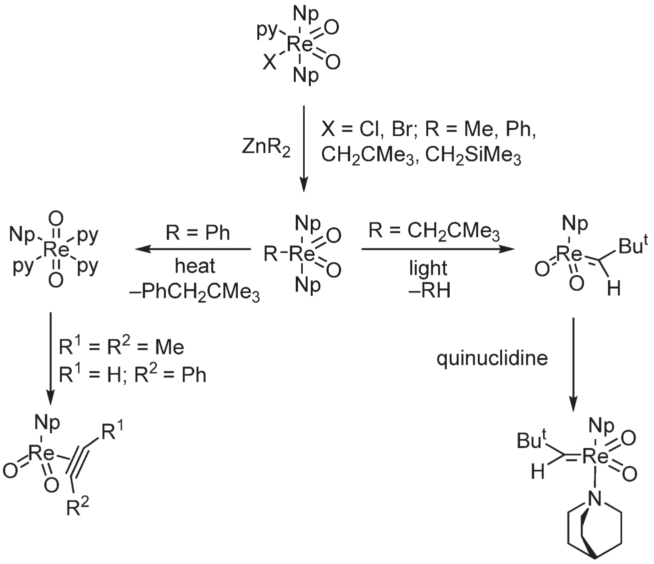
Photolysis of $[Np_3ReO_2]$ in pyridine gives neopentane and $[NpReO_2({=}CHBu^t)]$ that adds L = quinuclidine forming $[NpReO_2({=}CHBu^t)L]$ but does not react with olefins. The reactivity of $[Np_2RReO_2]$ is depicted in Scheme 92.

Rr(vii) dioxo–diolate complexes are generally prepared by condensation of MTO with the corresponding diol. A more convenient method for the synthesis of rhenium complexes containing a chelated bis(diolate) ligand is the reaction of MTO with an epoxide (e.g., 2,3-dimethylbut-2-ene epoxide, styrene epoxide, *cis*-cyclodecane epoxide, and *cis*-stilbene oxide) (see Equation (31)).[601] The bis(alkoxy)Re(vii) complexes react with triphenylphosphine to yield MTO, triphenylphoshine oxide, and olefin. Release of an alkene is strongly enhanced by the phosphine, without phosphine, alkenes are realeased only slowly, if at all, from these Re(vii) derivatives.


(31)

Imido/oxo rhenium(vii) organyl complexes can be easily synthesized by mixing organorhenium(vii) trioxides with organorhenium(vii) tris(imides). Oxo and imido ligand exchange takes place via bridging ligand groups. In solution, there is a temperature-dependent equilibrium between monomers and dimers. In the solid state, compounds with bridging oxygen atoms are isolated. These dimers can formally be regarded as consisting of two very strongly interacting monomeric units, leading to one shorter and one longer Re–O bond in the bridges.[602] The tris(imido)-methylrhenium compound $[MeRe(NAd)_3]$ (Ad = 1-adamantyl) exchanges NAd for O with aldehydes to form imines $RCH{=}NAd$, a metathesis reaction. The reaction occurs in three stages, during which $[MeRe(NAd)_2O]$ and $[MeRe(NAd)O_2]$ are detected. In the third and slowest stage, MTO is formed (Scheme 93). The reactions between $[ReMe(NAd)_3]$ and linear aliphatic aldehydes occur much faster than those of nonlinear aliphatic or aromatic aldehydes, indicating an important steric effect. Analogously, $[ReMe(NAd)_3]$ also exchanges NAd for NR^1 with imines $RCH{=}N^1$ (imine metathesis).[603]

The rhenium(vii) phosphonio–methylidyne complex $[Re(NBu^t)\{{\equiv}C{-}P(NEt_2)_3\}Cl_3]$ **166** is obtained by interaction of an imido ligand in $[Re(NBu^t)_2Cl_3]$ with the phosphorus ylide $(Et_2N)_3P{=}CH_2$. Compound **166** is only stable as a solid; in solution it decomposes into $[Re(NBu^t)_3Cl]$ **167** and $[(Et_2N)_3PCH_3]^+[Re(NBu^t)_2Cl_4]^-$ **168**, via a mechanism



Scheme 92

$$CH_3Re(NAd)_3 + ArCHO \longrightarrow CH_3Re(NAd)_2O + ArCH{=}NAd$$

$$CH_3Re(NAd)O_2 + ArCHO \longrightarrow CH_3Re(NAd)O_2 + ArCH{=}NAd$$

$$CH_3Re(NAd)O_2 + ArCHO \longrightarrow CH_3ReO_3 + ArCH{=}NAd$$

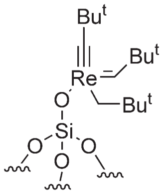
Scheme 93

in which the amine, formally generated from the imido ligand, is trapped by the Lewis acid [Re(NBu^t)$_2$Cl$_3$] with formation of **167** and **168** (Scheme 94).[604]

5.13.3.7.1.(ii) Alkylidyne Complexes

Alkylidyne complexes of the type [Re(≡CBu^t)(CH$_2$Bu^t)$_3$X] (X = OTf, OC$_6$F$_5$, BF$_4$) are prepared by treatment of [Re(≡CBu^t)(=CHBu^t)(CH$_2$Bu^t)$_2$] with a variety of acids HX (X = OTf, OC$_6$F$_5$, BF$_4$, and BArF). When the noncoordinating anion BArF$^-$ is employed, the resulting complex contains 1 equiv. of ether. If traces of water are present, compound [Re(≡CBu^t)(CH$_2$Bu^t)$_3$(CHBu^t)(H$_2$O)][BArF]·Et$_2$O is isolated.

Several coordinating ligands are able to induce α-hydrogen abstraction reactions in [Re(≡CBu^t)(CH$_2$Bu^t)$_3$X] species. [Re(≡CBu^t)(CH$_2$Bu^t)$_3$(OTf)] reacts with py, NCMe, and MeOH in ether to form neopentane and [Re(≡CBu^t)(=CHBu^t)(CH$_2$Bu^t)L$_n$(OTf)] (L = py, $n = 2$; NCMe $n = 1$; CH$_3$OH, $n = 1$–3). α-H abstraction is significantly faster in the systems where cationic intermediates may form. Thus, for a given ligand, α-H abstraction reactions of [Re(≡CBu^t)(CH$_2$Bu^t)$_3$X] are much faster when X = OTf, BArF than when X = Cl, OC$_6$F$_5$. The py adduct [Re(≡CBu^t)(=CHBu^t)(CH$_2$Bu^t)(py)$_2$(OTf)] reacts with L3 = Cp$^-$, Tp$^-$ or 1,4,7-trithiacyclononane (S$_3$C$_6$H$_{12}$) to give [Re(≡CBu^t)(CH$_2$Bu^t)$_3$(L3)]$^{0,+}$. Grafting [Re(≡CBu^t)(=CBu^t)(CH$_2$Bu^t)$_2$] on a silica surface led to well-defined, highly active, heterogeneous olefin-metathesis catalysts **169**, fully characterized by solid-state NMR spectroscopy.[605,606]



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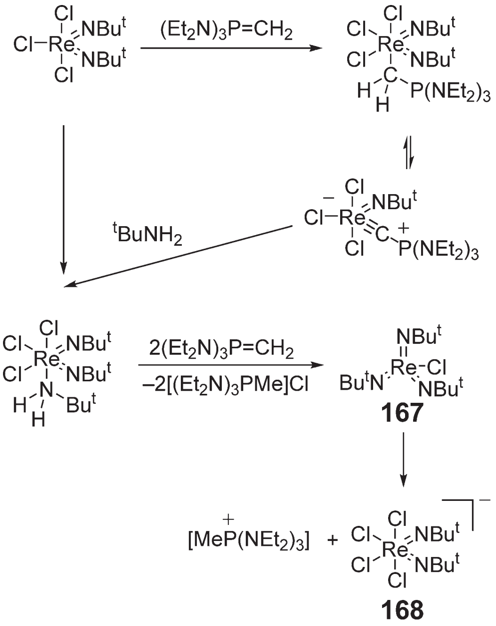


Scheme 94

5.13.4 Polyhydrides

A central compound in this area is [ReH$_7$(PR$_3$)$_2$] (R═Ph, Me, Et) made from [ReOCl$_3$(PR$_3$)$_2$] and LiAlH$_4$.[607] New polyhydride complexes of rhenium of the type [ReH$_7$L] containing diphosphine ligands and phosphite or mixed phosphite species have been prepared by treatment of oxochloro complexes of general formula [ReOCl$_3$L] with NaBH$_4$.[608] Rhenium polyhydrides have also been stabilized by arsine ligands.[609,610] The main characteristic of the reactivity of [ReH$_7$(PPh$_3$)$_2$] **170** and other polyhydrides is their ability to lose H$_2$ upon thermal, photochemical, or oxidative activation giving coordinatively unsaturated species. The resulting intermediates are highly reactive and interact with various substrates to produce new complexes. Alkane dehydrogenation is one main reaction.[611] A new class of chelating bis(silyl) polyhydride complexes, [ReH$_5$(dmsb)(PPh$_3$)$_2$] and [ReH$_5$(dmse)(PPh$_3$)$_2$] (dmsb = 1,2-bis(dimethylsilyl)benzene, dmse = 1,2-bis(dimethylsilyl)ethane) have been prepared by reaction of **170** with excess silane in refluxing THF.[612]

The thermal reactions of [ReH$_7$(L)] with organic acids (HA) [HA = pyridin-2-carboxilic acid (Hpic), 1-isoquinolinecarboxylic acid (Hisoquin), 2-hydroxy-6-methylpyridine (Hmhp), and 2-mercaptoquinoline (Hmq); L = (PPh$_3$)$_2$, dppe] lead to the release of H$_2$, coordination of the anionic organic ligands that are generated, and the formation of seven-coordinate monohydridorhenium(III) complexes [ReH(A)$_2$(L)] (A = pic, isoquin, mhp). With the bulkier anions, 2-hydroxyquinoline (hq) and 2-mercaptoquinoline (mq), the intermediates [ReH$_4$(A)(PPh$_3$)$_2$] (A = hq or mq) can be isolated.[613]

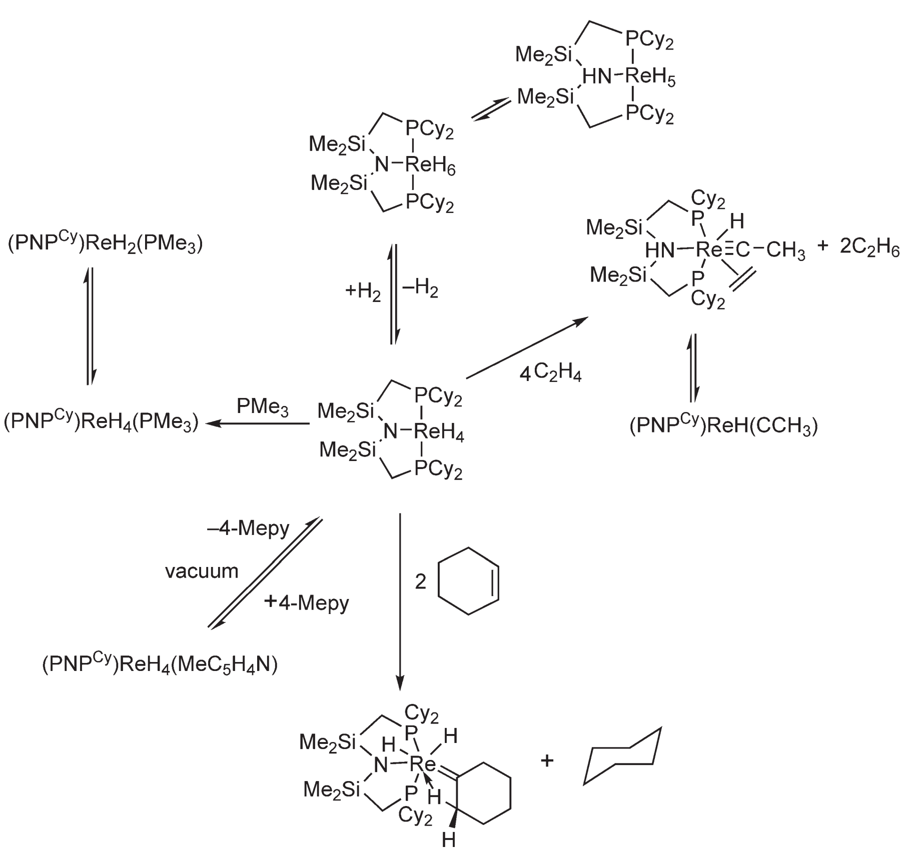
Rhenium(III) complexes of the type [ReH$_2$(A)(PPh$_3$)$_2$(PR$_3$)] (A = hq or mq; PR$_3$ = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$, or PHPh$_2$) are obtained by reaction of [ReH$_4$(A)(PPh$_3$)$_2$] with monodentate phosphines.[614]

The mononuclear Re(V) polyhydride [ReH$_4$(mq)(PPh$_3$)$_2$] **171** provides a new entry into dirhenium polyhydride chemistry. When **171** is treated with the electrophiles, H$^+$ and Ph$_3$C$^+$, abstraction of H$^-$ occurs to afford the 16-electron [ReH$_3$(mq)(PPh$_3$)$_2$]$^+$ cation that dimerizes to [Re$_2$H$_6$(μ-mq)(PPh$_3$)$_4$]$^{2+}$, which opens the access to other polyhydride species that contain the {Re$_2$(μ-mq)$_2$} fragment. These compounds differ from other dirhenium polyhydrides in that they possess no Re–H–Re bridging bonds.[615] A high yield route to a new class of stable alkylidyne complexes of the type [Re(≡CCH$_2$R)H$_2$(mq)(PPh$_3$)$_2$]$^+$ **172** has been developed by treating **171** with an electrophile in the presence of terminal alkynes RC≡CH (R = H, Et, Pr^n, Pr^i, Bu^n, Ph, *p*-Tol, CH$_2$Ph). These complexes are easily deprotonated to neutral monohydrides [Re(≡CCH$_2$R)H(mq)(PPh$_3$)$_2$], which, in turn, can be protonated to reform the dihydrides **172** quantitatively. When these reactions are carried out with internal alkynes with the same carbon skeleton, the same alkylidyne complexes are formed. This observation in conjunction with results from deuterium labeling studies suggests that isomerization of internal to terminal alkynes occurs via η^2-allene intermediates. The structural identity of these alkylidyne complexes has been established by X-ray crystallography on six-coordinate monohydrides of type [Re(≡CCH$_2$R)H(mq)(PPh$_3$)$_2$][PF$_6$] (R = Pr^n, Pr^i, Ph) in which the PPh$_3$ ligands are *trans* to one another and the hydrido and alkylidyne ligands are in a *cis*-arrangement.[616]

A remarkable property of the Re–H bonds in polyhydrides is their ability to establish a new kind of hydrogen bond, hydrogen–hydrogen interaction of the type M–H···H–X (X = O, N, C), called protonic–hydridic or dihydrogen bonds, already mentioned for Re(I) hydrides.[617] The first rhenium complex showing an intermolecular H···H interaction was $[ReH_5(PPh_3)_3]\cdot C_8H_6NH\cdot C_6H_6$. Its X-ray crystal structure shows that the N–H hydrogen atom of indole is close to two of the rhenium hydrides forming a three-center H-type bond.[618] These bonds seem to play a crucial role in catalytic reactions involving M–H and X–H bonds.[619] Most of the Re polyhydrides are stabilized by phosphines. Cp, pyrazolylborates, the tripodal polydentate ligand $N(^iPr_2PCH_2SiMe_2)_2$ (PNP),[620] and the tetradentate ligand $N(CH_2CH_2PPh_2)_3$ (NP3)[621] also stabilize polyhydrides. Most of these complexes are prepared from $[ReH_7(PPh_3)_2]$ or $[Re(O)Cl_2L]$ [$L^- = Cp^*$, Tp, and PNPR] as starting materials. Hydride complexes of Re(III) and Re(V) with (pyrazolyl)borates are also obtained by treating $[Re(O)Cl_3(PPh_3)_2]$ with $Na[H_2B(pz)_2]$ or $Na[H_2B(3,5\text{-}Me_2pz)_2]$ in alcohols. The rhenium polyhydride complex $[ReH_3(\eta^4\text{-}NP3)]$, stabilized by NP3, is prepared using $[ReCl_3(NCMe)(PMe_3)_2]$ as a precursor.[621] An *in situ* IR study of the protonation of $[ReH_3(\eta^4\text{-}NP3)]$ by weak Brønsted acids has shown that the proton selectively attacks the metal atom to give kinetic hydrogen-bonded adducts of the formula $[(\eta^4\text{-}NP3)H_4Re\cdots HOR]$ (ROH = C_2H_5OH, CFH_2CH_2OH, CF_3CH_2OH) that ultimately convert into the thermodynamically stable classical polyhydride $[ReH_4(\eta^4\text{-}NP3)]^+$ with no formation of a transient $\eta^2\text{-}H_2$ species.

The most remarkable consequence of polyhydride reactivity is alkene activation or C–H bond activation with the formation of alkenes or dienes. In the case of C_5H_6, a fast equilibrium between $[ReH_3(\eta^4\text{-}C_5H_6)(PPh_3)_2]$ and $[ReH_2(\eta^3\text{-}C_5H_7)(PPh_3)_2]$ is established. Addition of excess L produces $[ReH(PPh_3)_2L_3]$ or $[ReH(PMe_3)_5]$ and cyclopentene.

Rhenium polyhydrides containing the fragment [(PNPR)Re] have been studied by Caulton and co-workers. The (PNP)Re structures have shown the ability to effect olefin hydrogenation and C–H bond cleavage. $[(NPNCy)ReH_4]$ **173** transforms ethylene[532] and other olefins to hydride carbynes (Scheme 95).[620,622–624] Acyclic alkanes react with **173** to give first $[(NPNCy)ReH_2(olefin)]$, and then $[(NPNCy)ReH_2(carbyne)]$, in equilibrium with its η^2-olefin adduct.



Scheme 95

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