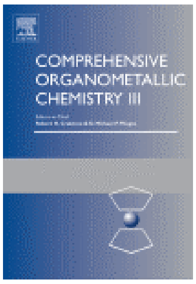

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8.01
Nickel Complexes with Carbonyl, Isocyanide, and Carbene Ligands

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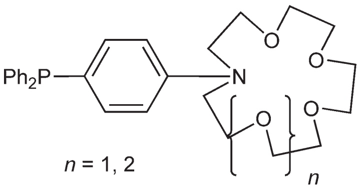
8.01.1 Introduction

The organometallic chemistry of nickel has a long history, dating back to the preparation in 1890 of nickel carbonyl, $Ni(CO)_4$, and its use in the Mond process for refining nickel metal.[1] The presence of π-acceptor ligands such as carbonyls, isocyanides, and carbenes tends to stabilize lower oxidation states and these ligands are often encountered in zero valent nickel chemistry, but they also are frequently found in Ni(II) complexes, and in more recent years in the growing number of stable Ni(I) complexes. This chapter reviews the organometallic chemistry of nickel complexes with carbonyl, isocyanide, and carbene ligands. The chapter covers the literature reported since publication of COMC(1995). As with the organometallic chemistry of the other transition metals and the lanthanides and actinides, the introduction of *N*-heterocyclic Arduengo-type carbenes (NHCs)[2,3] has led to a rapid proliferation in the literature of nickel carbene complexes. Nickel complexes with carbonyl, isocyanide, and carbene ligands are of considerable importance as catalysts for processes, including alkyl and aryl cross-coupling, alkene polymerization, hydrocyanation of alkenes, and alkene isomerization (see Chapters 8.02 and 8.03), where the catalytic applications of these classes of organonickel complexes are discussed in more detail.

8.01.2 Mononuclear Nickel Complexes

8.01.2.1 Complexes with Carbonyl Ligands

The substitution of the carbonyl groups of $Ni(CO)_4$ by other two-electron ligands remains the principal method of preparation of nickel complexes with carbonyl ligands. The 15-crown-5 ether–triarylphosphine hybrid ligands, **1** and **2**, have been used to prepare the corresponding $Ni(CO)_3L$ complexes.[4]



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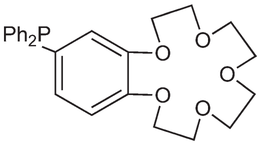

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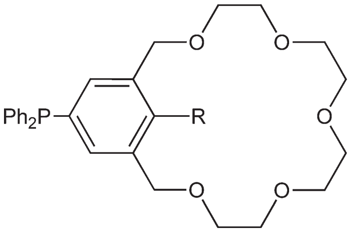
The 18-crown-5–triarylphosphine hybrid ligand **3** has also been prepared, structurally characterized, as phosphine oxide, and used to prepare additional $Ni(CO)_3L$ complexes.[5]



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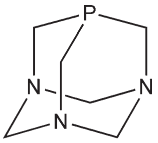
The CO stretching frequency, $\nu(CO)$, of the complexes was used as a proof of the binding of alkali metal ions Na^+, K^+, and Cs^+ to the crown ether sites. In general, the degree of shift in $\nu(CO)$ values upon binding of alkali metal ions to the $Ni(CO)_3L$ complexes, where L = crown ether–triarylphosphine ligands **1–3**, does not follow known formation constants for binding of the alkali metal ions to the free crown ethers.[5]

The first isocarbonyl complex of Ni(0) was reported in 2005.[6] The recent availability of the anionic phosphine borate ligand $[PhB(CH_2PPh_2)_3]^-$[7,8] allows the ability to prepare unusual anionic Ni(0) complexes. In the case of the reaction of $Ni(CO)_4$ with $[Li(TMEDA)][PhB(CH_2PPh_2)_3]$ in THF, the anionic Ni(0) carbonyl complex $[Ni(CO)\{PhB(CH_2PPh_2)_3\}][Li(THF)_3]$ is obtained. The solid-state structure reveals that the Li^+ ion is strongly coordinated to the carbonyl oxygen atom, *d*(Li-O) = 1.924(5) Å, with the isocarbonyl bond angle, Li–O–C, 151.1(2)°.[6] The presence of the isocarbonyl linkage to Li^+ causes a dramatic lowering of the $\nu(CO)$ value to $1812\,cm^{-1}$ in the solid state.

Recent interest in "green" chemical technologies and the replacement of toxic organic solvents with nontoxic solvents such as water has led to research on organometallic catalysts that are soluble in water. This effort has extended to include several water-soluble nickel carbonyl complexes.[9,10] The chelating 1, 2 bis[bis(2-pyridyl)-phosphinoethane] ligand ($py_2P\text{-}CH_2CH_2\text{-}Ppy_2$) was used to displace the two phosphine ligands of the complex $Ni(CO)_2(PPh_3)_2$ to give the complex $Ni(CO)_2(py_2P\text{-}CH_2CH_2\text{-}Ppy_2)$, which dissolves in water to give a pale yellow solution. The precise nature of the complex in water is under investigation.[9] The ligand 1, 3, 5-triaza-7-phosphaadamantane (PTA) **4** has also been investigated for its ability to render metal complexes water-soluble.



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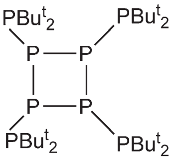
The series of complexes $Ni(CO)_{4-n}(PTA)_n$ ($n = 1 - 3$) was prepared by the addition of CO to $Ni(PTA)_4$ in water.[10] The initial CO substitution step is rapid, but substitution of the first PTA ligand by CO greatly retards the rate of dissociation of the second PTA ligand. The complex $Ni(CO)(PTA)_3$ is quite soluble in water. The disubstituted complex $Ni(CO)_2(PTA)_2$ is sparingly soluble in water, whereas complex $Ni(CO)_3(PTA)$ is insoluble in water. The disubstituted complex $Ni(CO)_2(PTA)_2$ was characterized by X-ray diffraction.

The unusual P-rich cyclotetraphosphane $P_4(PBu^t{}_2)_4$ **5** reacts with $Ni(CO)_4$ to give a nickel carbonyl dimer [{*cyclo*-$P_4(PBu^t)_4$}{$Ni(CO)_2$}$_2$}] in which each $Ni(CO)_2$ unit is coordinated by two adjacent $Bu^t{}_2P$ groups forming two five-membered P_4Ni rings in an overall "chair"-type conformation.[11]



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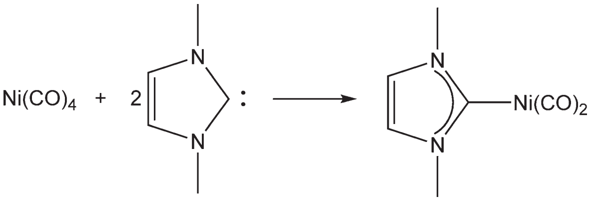
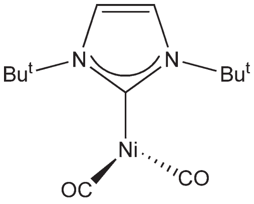
Arsine and stibine ligands are often used to obtain complexes analogous to those formed by phosphine ligands. The coordination chemistry of bis(diphenylphosphino)methane (dppm) has been investigated extensively. The ligands bis(diphenylstibino)methane (dpsm) and bis(dimethylstibino)methane (dmsm) have found much more limited use until a recent report of the syntheses of several new compounds and reinvestigations of others, including several nickel carbonyl complexes.[12] The reaction of $Ni(CO)_4$ with dpsm gave both $Ni(CO)_3(\eta^1\text{-dpsm})$ and the binuclear complex $Ni(CO)_3(\mu_2\text{-dpsm})Ni(CO)_3$. In the case of dmsm, only the binuclear complex $Ni(CO)_3(\mu_2\text{-dmsm})Ni(CO)_3$ was observed. A very unusual arsine ligand is the metalloarsaalkene $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe{=}AsC(NMe_2)_2]$, which reacts with $Ni(CO)_4$ in much the same way as it reacts with the other first-row transition metal carbonyls $Cr(CO)_6$ and $Fe(CO)_5$ to afford complexes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{=}As(M(CO)_n)C(NMe_2)_2$ in which there is a normal coordinate covalent interaction between the arsenic atom of the metalloarsaalkene and the metal carbonyl fragment. This was confirmed in the X-ray crystal structure of the all-iron complex $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe{=}As\{Fe(CO)_4\}C(NMe_2)_2]$.[13]

Nickel complexes with carbene ligands will be discussed later in this section. However, several nickel carbene complexes also contain carbonyl ligands, and they will be considered here. The reaction of *N*-heterocyclic carbene (NHC) reagents with $Ni(CO)_4$ typically results in the simple monosubstitution reaction to give $Ni(CO)_3(NHC)$. However, a 2,5-dimethyl-substituted NHC ligand combines with $Ni(CO)_4$ to give the disubstituted dicarbonyl-dicarbene complex (Equation (1)).[14]



(1)

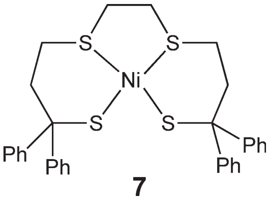
When bulky Bu^t or adamantyl groups are placed in the 2,5 positions of NHC ligands, stable three-coordinate complexes $Ni(CO)_2(NHC)$ are obtained.[15] These are rare examples of three-coordinate nickel carbonyl complexes 6.



6

A related three-coordinate dicarbonyl-carbene complex can be obtained by reaction of $Ni(CO)_4$ with the carbodiphosphorane "double ylide" $Ph_3{=}C{=}PPh_3$.[16] The reaction of $Ni(CO)_4$ with $Ph_3{=}C{=}PPh_3$ in toluene gives the tricarbonyl complex $Ni\{C(PPh_3)_2\}(CO)_3$, but in THF solvent the deep red 16-electron three-coordinate complex $Ni\{C(PPh_3)_2\}(CO)_2$ was obtained. Both the three- and four-coordinate compounds $Ni\{C(PPh_3)_2\}(CO)_n$, ($n = 2$, 3) were structurally characterized by X-ray diffraction.[16]

There has been considerable recent interest in Ni(II) carbonyl complexes because of their role as model complexes for nickel-containing CO dehydrogenase enzymes.[17,18] This has spawned considerable growth in the number of known Ni(II) carbonyl complexes. Tripodal tetradentate ligands of the type $P(CH_2CH_2PPh_2)_3(PP_3)$, $P(CH_2CH_2PEt_2)_3(PP_3E)$, and $N(CH_2CH_2PPh_2)_3(NP_3E)$ have been used in the syntheses of dicationic five-coordinate Ni(II) carbonyl complexes.[19] The crystal and molecular structure of $[Ni(CO)(PP_3E)]^{2+}$ shows that the overall structure is trigonal-bipyramidal with the CO ligand *trans* to the central phosphorus atom of the PP_3E ligand and the three PEt_3 groups in the equatorial plane. The complex $[Ni(CO)\ (NP_3E)]^{2+}$ undergoes two reversible single-electron reductions, as observed by cyclic voltammetry. Both the Ni(0) and Ni(I) complexes $Ni(CO)(NP_3E)$ and $[Ni(CO)(NP_3E)]^+$ are known. The corresponding PP_3 and PP_3E complexes do not exhibit reversible electrochemistry. The sterically hindered tripodal phosphine trithiolate ligand tris(3-phenyl-e-thiophenyl) phosphine ($PS3^*$) as the trilithium salt $Li_3[PS3^*]$ and $Ni(acac)_2$ were combined and exposed to CO to give the anionic trigonal-bipyramidal Ni(II) carbonyl complex $[Ni(PS3^*)(CO)]^-$.[20] In this complex, the coordination of CO to Ni(II) was found to be persistent under vacuum. An extended series of square-planar Ni(II) carbonyl complexes have been reported that incorporate pentafluorophenyl ligands.[21] Both the complex anion $[NiBr(C_6F_5)_2(CO)]^-$ and the neutral *cis*-complex $Ni(C_6F_5)_2(CO)_2$ were characterized by X-ray diffraction. The complex $Ni(C_6F_5)_2(CO)_2$ is unstable with respect to reductive elimination of $C_6F_5{-}C_6F_5$. Square-planar Ni(II) carbonyl complexes that contain thiolate and selenolate ligands have also been reported recently.[22] The distorted square-planar complex anion $[Ni(CO)(2\text{-}SC_4H_3S)_3]^-$, where $2\text{-}SC_4H_3S^-$ is 2-thienylthiolato, was prepared by the reaction of *fac*-$[Fe(2\text{-}SC_4H_3S)_3(CO)_3]^-$, $2,2'\text{-}SC_4H_3S\text{-}SC_4H_3S$, and $[NiCp(CO)]_2$. Mixed chalcogenolate complexes $[Ni(SePh)_n(SPh)_{3-n}(CO)]^-$ were obtained by $PhSe^-/PhS^-$ exchange. The Ni(II) carbonyl-thiolate complexes were found to be more unstable than the corresponding Ni(II) carbonyl-selenolate complexes. The carbonyl ligands in all complexes were found to be readily exchangeable. Naturally occurring hydrogenase enzymes are known to contain mixed sulfur/selenium ligand-binding environments for the nickel atom, and the spectroscopic properties and reactivity with CO of the mixed ligand complexes $[Ni(SePh)_n(SPh)_{3-n}(CO)]^-$ have been discussed as possible models for natural systems.[23] The tetradentate sulfur ligand 2,2,11,11-tetraphenyl-1,5,8,12-tetrathiadodecane (tpttd) was employed to prepare the square-planar Ni(II) complex 7.[24]



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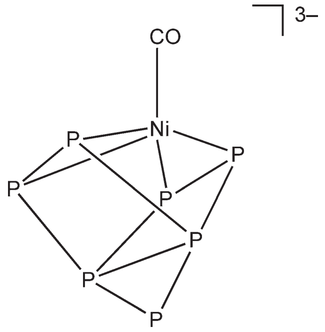
Single-electron reduction of **7** in the presence of CO under electrochemical conditions indicates that an Ni(I) anionic complex is formed that binds CO, $[Ni(CO)(tpttd)]^-$, with a ν(CO) value of 1940 cm^{-1}.

The group 15 Zintl ions, E_7^{3-} (E = P, As, Sb), have been used to form stable complexes with several metal carbonyl complexes, including $Ni(CO)_4$. Ethylenediamine solutions of K_3P_7 react with $Ni(CO)_2(PPh_3)_2$ to give the norbornadiene-like complex $[\eta^4\text{-}P_7Ni(CO)]^{3-}$ **8**.[25]



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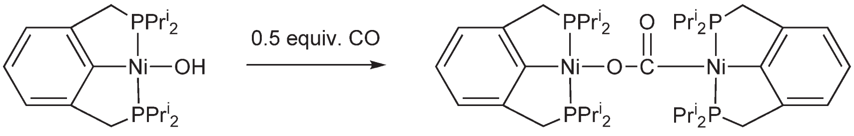
The ν(CO) value measured of a solid-state sample of the [K(2,2,2-crypt)]$[Bu^n_4P]$ salt is exceptionally low at 1785 cm^{-1}. Complex **8** can be protonated with methanol to give the conjugate acid complex, $[\eta^4\text{-}HP_7Ni(CO)]^{2-}$. Group 14 Zintl ions, E_9^{3-} (E = Ge, Sn, Pb), were also used to prepare a nickel carbonyl complex, $[Sn_9Ni_2(CO)]^{3-}$.[26] The $[Sn_9Ni_2(CO)]^{3-}$ anion possesses a fairly regular *closo*-Sn_9Ni unit with an additional interstitial Ni atom.

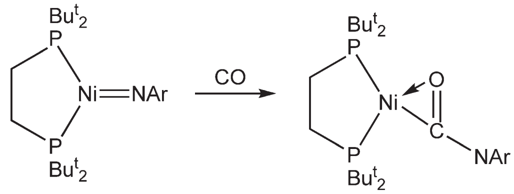
8.01.2.2 Complexes with Carbon Dioxide and Related Ligands

There is now a growing literature of nickel organometallic complexes that contain carbon dioxide or related cumulene ligands that result from reactions with carbon monoxide. The first structurally characterized complex of carbon dioxide was the nickel complex $Ni(CO_2)(PCy_3)_2$ reported in 1975.[27] A more recent study of this complex provides the complete assignments of the vibrational spectra and theoretical calculations of different isomers in support of a mechanism for CO_2 fluxionality that involves end-on coordination.[28] The tridentate "pincer" ligand 2,6-bis((diisopropylphosphino)methyl)phenyl (PCP) has been used to form the square-planar Ni(II) hydroxide complex Ni(OH)(PCP).[29] The complex Ni(OH)(PCP) reacts with CO to give a binuclear μ-CO_2 complex (Equation (2)).



(2)

An isocyanate complex has been prepared by the carbonylation of an unusual tricoordinate imido complex.[30] The 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe) nickel imido complex [Ni=NAr(dtbpe)], where Ar = 2,6-diisopropylphenyl, can be cleanly carbonylated to give an η^2-arylisocyanate complex with overall structure similar to the original Aresta CO_2 complex[27] (Equation (3)).



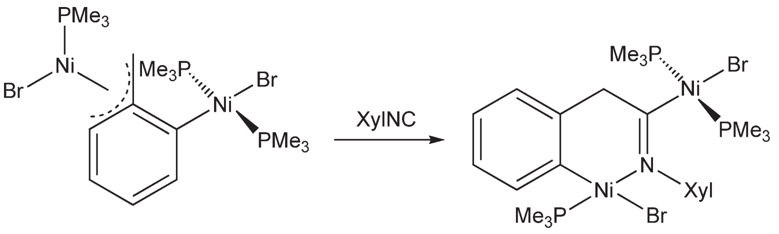
(3)

8.01.2.3 Complexes with Isocyanide Ligands

The series of Ni(0) isocyanide-phosphine complexes Ni(CNR)(PPh_3)$_3$, Ni(CNR)$_2$(PPh_3)$_2$, and Ni(CNR)$_3$(PPh_3) (R = Bu^t, Cy, Bz, *p*-TsCH$_2$) were prepared starting with Ni(cod)$_2$ and different mole ratios of the isocyanide and phosphine ligands. The X-ray structure of the bis(benzylisocyanide) complex, Ni(CNBz)$_2$(PPh_3)$_2$, confirmed the expected overall pseudo-tetrahedral geometry.[31] The tris(triphenylphosphine) isocyanide complexes Ni(CNR)$_3$(PPh_3) (R = Bu^t, Cy, Bz, *p*-TsCH$_2$) were reacted with SO_2 and *p*-TolNSO to afford Ni(CNR)(η^1-SO_2)(PPh_3)$_2$ and Ni(CNR)(η^2-*p*-TolN-S=O)(PPh_3) complexes, respectively. Crystal and molecular structures of Ni(CNCy)(η^1-SO_2)(PPh_3)$_2$ and Ni(CNBu^t)(*p*-TolN-S=O)(PPh_3) were reported.[32]

A series of Ni(II) isocyanide complexes with the phosphine ligands $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), and PPh_3 have been reported. The reaction of NiCl$_2$(dppp) with XylNC in the presence of NH_4PF_6 gave the complexes [NiCl(CNXyl)$_2$(dppp)][PF$_6$] and [Ni(CNXyl)$_3$(dppp)][PF$_6$]$_2$. The complex [NiCl(CNXyl)$_2$(dppp)][PF$_6$] was shown by X-ray diffraction to possess a square-pyramidal structure with an axial chloride ligand, *cis*-XylNC ligands, and *cis*-dppp phosphine coordination. The reaction of NiCl$_2$(dppe) with MesNC in the presence of NH_4PF_6 also gave a mixture of complexes [NiCl(CNMes)$_2$(dppe)][PF$_6$] and [Ni(CNMes)$_3$(dppe)][PF$_6$]$_2$. The complex [Ni(CNMes)$_3$(dppe)][PF$_6$]$_2$ was also shown by X-ray diffraction to possess a square-pyramidal structure, but with an axial MesNC ligand and two *cis*-MesNC ligands and *cis*-dppp phosphine coordination in the equatorial positions. Similar reactions with NiCl$_2$(PPh_3)$_2$ were found to give [NiCl(CNXyl)$_2$(PPh_3)$_2$][PF$_6$] and [Ni(CNXyl)$_3$(PPh_3)$_2$][PF$_6$]$_2$. It was found by X-ray crystallography that when the mono-tertiary phosphine ligand PPh_3 is used in place of the diphosphines, dppe and dppp, the complex [NiCl(CNXyl)$_2$(PPh_3)$_2$][PF$_6$] did have square-pyramidal geometry, but with *trans*- PPh_3 and XylNC ligands.[33] Electrochemical studies indicated that in the presence of isocyanide ligands, the chloro bis(isocyanide) cationic complexes are in equilibrium with the tris(isocyanide) dicationic complexes.

The insertion reactions of isocyanide ligands have not been investigated as thoroughly as those of carbonyl ligands. However, some important differences between CO and CNR insertions have come to light. These include the greater tendency of imidoyl ligands to bond in a η^2 manner, compared to acyl ligands; the tendency of isocyanides to undergo multiple (polymeric) insertions; and the stability of imidoyl ligands to the microscopic reverse deinsertion reaction. The pseudoallyl complex *trans*-[(Me_3P)BrNi-CH$_2$-C$_6$H$_4$NiBr(PMe_3)$_2$] **9** was studied with respect to its insertion of both CO and isocyanides.[34] Complex **9** reacts with XylNC to give insertion into the benzylic Ni–CH$_2$ bond of the pseudoallyl ligand (Equation (4)).



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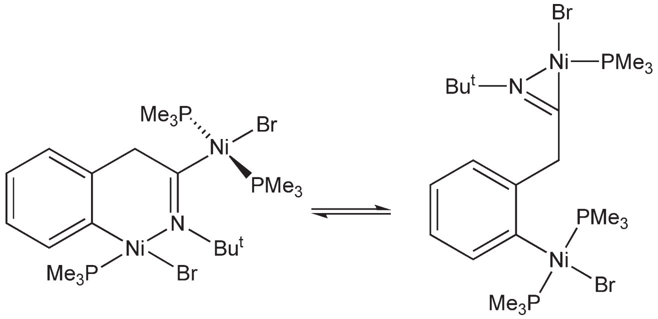
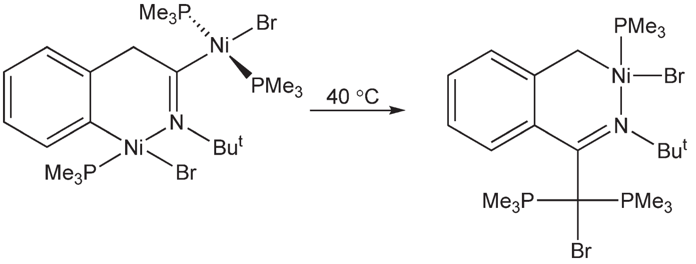
(4)

The insertion of CO was found previously to occur at the aryl carbon of the pseudoallyl ligand.[34] The reaction of Bu^{t}NC with complex **9** also results in insertion into the benzylic Ni–CH$_2$ bond and a μ_2-η^2-imidoyl product with structure similar to the XylNC derivative. However, in solution, the Bu^t μ_2-η^2-imidoyl structure was found by NMR to be in equilibrium with an acyclic η^2-imidoyl structure (Equation (5)).



(5)

At higher temperatures, a formal migration of a Bu^{t}NC ligand in a μ_2-η^2-imidoyl structure bonded to the benzylic carbon occurs to a μ_2-η^2-imidoyl structure bonded to the aryl carbon (Equation (6)).



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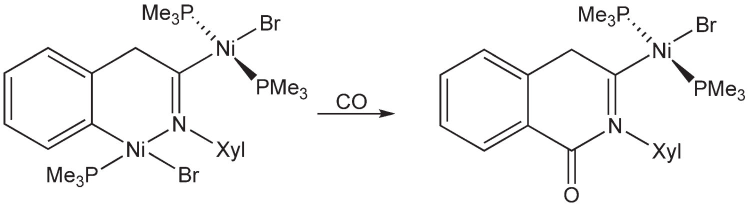
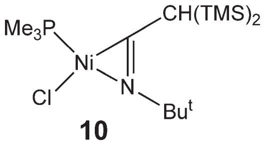
The Xyl μ_2-η^2-imidoyl complex can be carbonylated to give a bicyclic amide nickel complex, whose formation presumably involves the intramolecular coupling of acyl and imidoyl groups (Equation (7)).



(7)

The free *N*-aryl-1-isoquinolone molecule can be obtained by hydrolysis of the carbonylated nickel complex shown in Equation (6).

The alkylation of $NiCl_2(PMe_3)_2$ with Mg{CH(TMS)$_2$}Cl gave the dimeric alkyl complex [Ni(μ-Cl){CH-(TMS)$_2$}PMe$_3$]$_2$, which readily inserts Bu^{t}NC to afford the alkaneimidoyl complex **10**.[35]



10

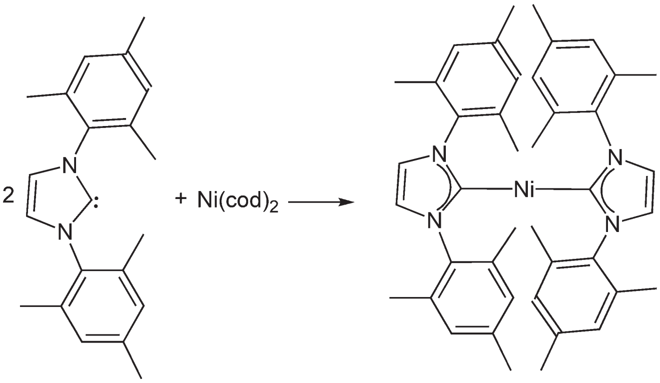
Transition metal C–N bond activation is an important step in several catalytic processes and was recently the subject of a theoretical investigation.[36] Another type of C–N bond activation that has been reported recently is the multiple-bond metathesis between the C≡N bonds of isocyanides and the C=O bonds of carbon dioxide. Reactions of the tetrakis(alkyl) or aryl isocyanide complexes $Ni(CNR)_4$ (R = Me, Xyl) with carbon dioxide in the presence of Li^+ give the corresponding diisocyanide-dicarbonyl complexes $Ni(CNR)_2(CO)_2$ and the alkyl or aryl isocyanate. Isotope labeling studies with both $^{13}CO_2$ and ^{13}CNMe indicate that the carbonyl ligands of the complexes $Ni(CNR)_2(CO)_2$ are produced by multiple bond metathesis between CO_2 and CNR, not by formal deoxygenation of CO_2. A mechanism based on the cycloaddition of CO_2 with a coordinated isocyanide ligand is proposed.[37]

8.01.2.4 Complexes with Carbene Ligands

Since the discovery of stable NHCs,[2] the range of *N*-substituted heterocyclic carbenes containing a stable divalent carbon center has expanded considerably, as has the number and variety of nickel(0) and nickel(II) complexes bearing NHC ligands.

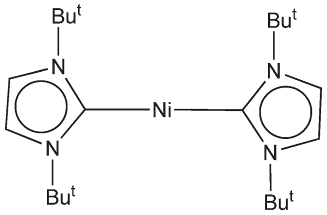
8.01.2.4.1 Nickel(0) complexes stabilized by carbene ligands

Structurally characterized, well-defined Ni(0) NHC complexes are rare. Low-coordinate carbene complexes of nickel(0) are of interest because of their postulated intermediacy in various organometallic transformations. The synthesis and X-ray characterization of the first two-coordinate homoleptic bis(carbene) adduct [NiL_2] was reported by Arduengo *et al.*[3] This 14-electron carbene complex is available from the reaction of the stable, sterically bulky, nucleophilic carbene, 1,3-dimesitylimidazol-2-ylidene, and $Ni(cod)_2$ (Equation (8)).



(8)

The co-condensation, using metal vapor deposition (MVD) techniques, between the vapors of nickel and di-Bu^t NHC ligand 1,3-di-N-Bu^t-imidazol-2-ylidene proved to be a straightforward path for the synthesis of the 14-electron species [NiL_2] **11**.[38] Following Arduengo's synthetic procedure, the zerovalent 14-electron nickel complex $Ni(tmiy)_2$ **12** (tmiy = 1,3,4,5-tetramethylimidazol-2-ylidene) was produced *in situ* from the reaction of $Ni(cod)_2$ with the NHC ligand.[39]



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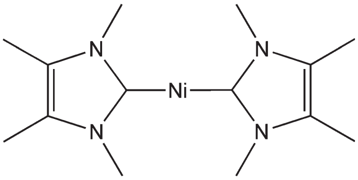
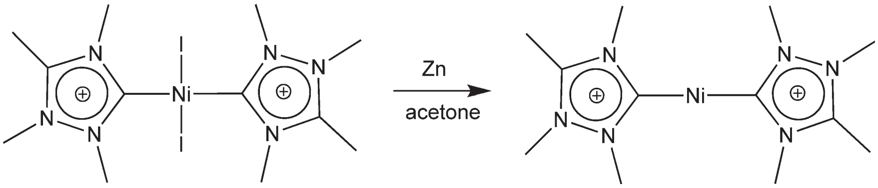


12

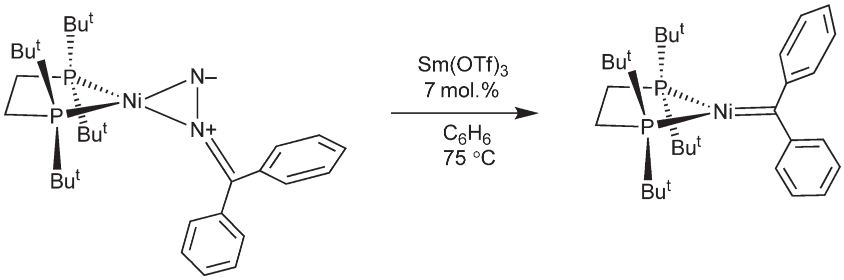
Reduction of $[NiI_2(trz)_2][OTf]_2$ (trz = 1,2-triazol-2-ium-5-ylidene) in acetone solution with zinc leads to hydrophilic cationic complexes of Ni(0) (Equation (9)).[40]



(9)

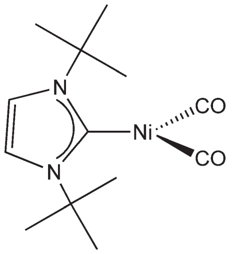
Addition of carbon monoxide to this complex results in the isolation of a tetrahedral cationic dicarbonyl complex $[Ni(CO)_2(trz)_2][OTf]_2$. Due to their ionic character, these nickel NHC complexes are extremely soluble in polar solvents, including water, promising catalytic applications in aqueous media.

The three-coordinate 16-electron nickel complex (dtbpe)Ni═CPh_2 was obtained by N_2 extrusion from the diphenyldiazomethane complex (dtbpe)Ni(N,N′:N_2CPh_2), dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane, in the presence of a catalytic amount of samarium triflate (Equation (10)).[30]



(10)

Other examples of 16-electron complexes come from the substitution reactions involving NHC ligands, carrying bulky R groups like Bu^t **13** and adamantyl **14**, with $Ni(CO)_4$. These substitution reactions afford three-coordinate complexes of the type $Ni(CO)_2(NHC)$, **13** and **14**.[15]



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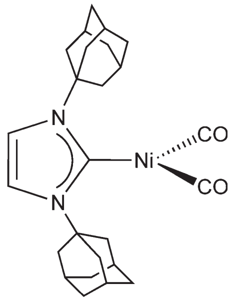
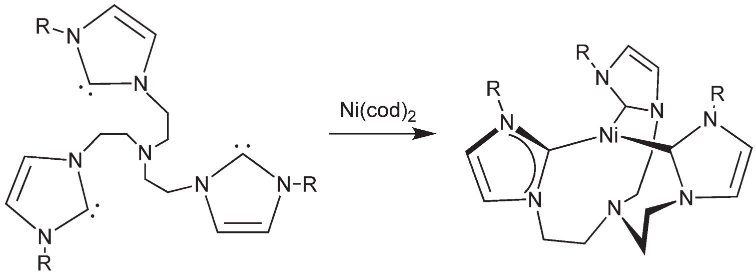


14

The equilibria associated with these NHC substitution reactions were investigated by FT-IR to obtain thermodynamic parameters and allow access to the Ni–NHC bond energies (BDEs). Calculated BDEs were 43 ± 3 kcal mol^{-1} for the adamantyl carbene complex **14** and 39 ± 3 kcal mol^{-1} for the Bu^t derivative **13**.[15] Carbonyl substitution reactions involving NHCs carrying less bulky groups such as methyl lead to tetrahedral 18-electron Ni(0) complexes $Ni(CO)_2(NHC)_2$.[14]

Reaction of $Ni(cod)_2$ with a nitrogen-anchored tripodal NHC ligand TIMEN^R = tris[2-(3-alkylimidazol-2-ylidene)-ethyl]amine, R = Bu^t, leads to an Ni(0) 16-electron tris-carbene complex Ni(TIMEN$^{t\text{-Bu}}$)[41] (Equation (11)).

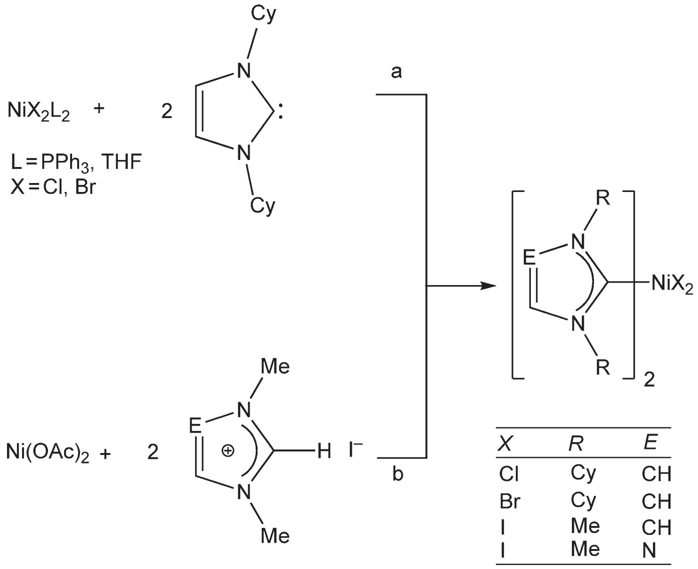


(11)

Agostic interactions Ni···H–C between the electron-rich metal center and alkyl protons were observed in the X-ray structure. A cyclic voltammetric study of the complex Ni(TIMEN$^{t\text{-Bu}}$) shows two quasi-reversible redox couples at −2.5 and −1.09 V versus Fc/Fc$^+$, and these correspond to the Ni(0)/Ni(I) and Ni(I)/Ni(II) couples, respectively. The observed electrochemical reversibility underscores the structural flexibility of the tripodal NHC ligand that makes it capable of stabilizing three different oxidation states of nickel.

8.01.2.4.2 Nickel(II) complexes stabilized by carbene ligands

An expanding body of empirical evidence suggests that an analogy can be drawn between NHC ligands and σ-donating phosphine ligands. While Ni(II) complexes with phosphine ligands are abundant, the first Ni(II) complexes of NHC ligands were not reported until 1997 by Herrmann.[42] The reactions of the free carbene 1,3-dicyclohexylimidazole-2-ylidene with NiX_2L_2 (X = Cl, Br; L = PPh_3, THF) complexes, or by *in situ* deprotonation of the corresponding azolium salts such as 1,3-dimethylimidazolium iodide with $Ni(OAc)_2$, afford bis-complexes, $NiX_2(NHC)_2$, in good yields (Equation (12)).

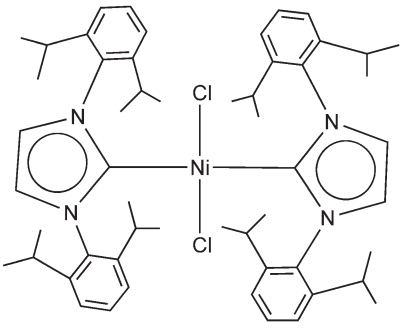


X	*R*	*E*
Cl	Cy	CH
Br	Cy	CH
I	Me	CH
I	Me	N

(12)

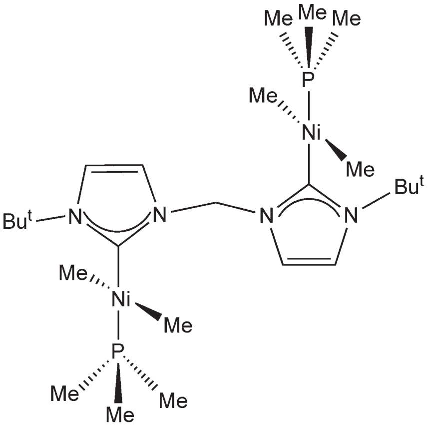
All of these complexes were isolated as violet-red solids which are stable to air and soluble in polar organic solvents such as chloroform, DMSO, and THF. The solids can be heated to 240 °C, without decomposition. The 1,3-dicyclohexylimidazole-2-ylidene complex $NiCl_2(NHC)_2$ was characterized by X-ray diffraction, and revealed a square-planar nickel atom with *trans*-carbene ligands and the imidazole rings twisted away from the square plane. A similar approach by reacting the electron-rich 1,3-diallylimidazolidin-2-ylidene ligand and $NiCl_2(PPh_3)_2$ gave *trans*-$[NiBr_2(L^{allyl})_2]$ and *trans*-$[NiI_2(L^{allyl})_2]$ complexes in good yield.[43] The clean, quantitative substitution of phosphine ligands by NHC ligands clearly reflects the strong σ-donor properties of the nucleophilic imidazol-2-ylidenes.

A key feature of many olefin polymerization catalysts based on square-planar nickel compounds is the presence of ligands, which provide considerable steric hindrance to access the sites of coordinative unsaturation above and below the square plane.[44] The complex *trans*-$NiCl_2$\{1,3-bis(2,6diisopropylphenyl)imidazol-2-ylidene\}$_2$ **15** was synthesized from $NiCl_2(PPh_3)_2$ by a ligand-substitution reaction.[45]



15

Complex **15** was characterized by X-ray diffraction. It was also shown that **15** catalyzes dimerization, but not the oligomerization or polymerization of ethylene. Much experimental evidence supports the notion that complexes that contain chelating bis(phosphine) ligands show improved catalytic properties relative to complexes with monodentate phosphine ligands. The origins of this effect are believed to be: (i) chelating ligands help to stabilize reactive intermediates or transition states; (ii) the chelate effect reduces the dissociation rate of the phosphine; and (iii) chelating ligands influence the activity and selectivity through electronic and steric effects. It is expected that catalysts that contain chelating bis(NHC) ligands will perform better than their singly coordinated NHC counterparts in catalytic processes such as Heck- (Pd) and Suzuki-coupling (Pd, Ni). Alkyl complexes of Ni(II) incorporating di-*N*-heterocyclic carbenes have been prepared by ligand substitution reactions from $NiMe_2(PMe_3)_2$ and $NiMe_2(bipy)$ precursors.[46] The binuclear complex **16** results from the incomplete substitution of PMe_3 from $NiMe_2(PMe_3)_2$ by a methylene-bis(NHC). The use of an ethylene-bis(NHC) to substitute the bipy ligand of $NiMe_2(bipy)$ led to formation of a mononuclear dialkyl complex with a chelating bis(NHC) ligand, **17**.



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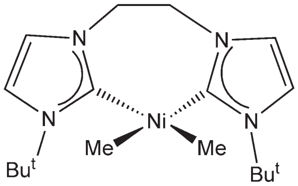
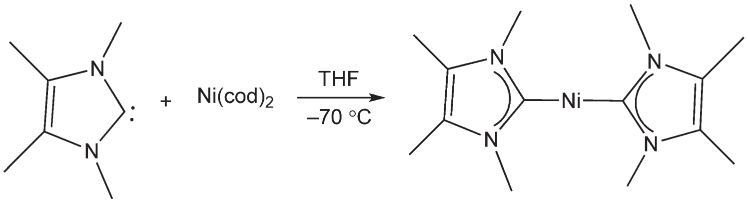
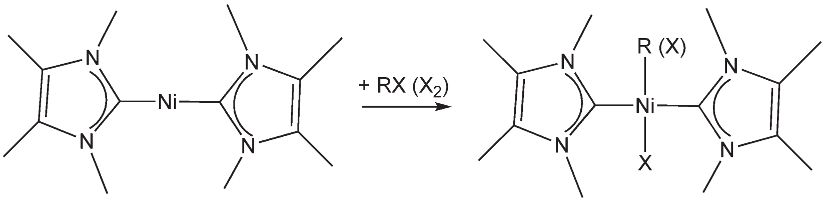


17

Oxidative addition of organic halides or iodine to the nickel(0) complex $Ni(tmiy)_2$ formed *in situ* by the reaction of $Ni(cod)_2$ and tmiy, is a straightforward synthetic pathway to nickel(II) carbene complexes (Equations (13), (14)).[39]



(13)

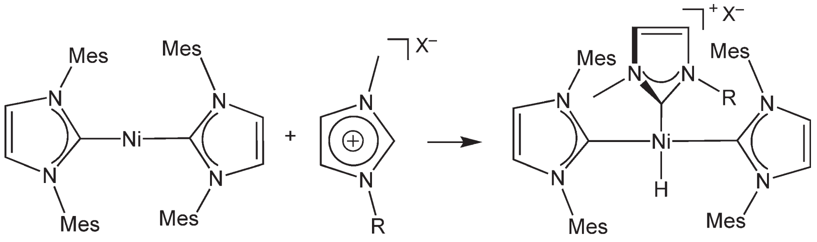


(14)

X = Br, R = *o*-tol
X = I, R = Me
$X_2 = I_2$

Thus, addition of *o*-tolyl bromide to Ni(tmiy)$_2$ and tmiy at room temperature yields the nickel(II) complex NiBr(*o*-Tol)(tmiy)$_2$ in good yield (70%). An X-ray crystal structure of this complex shows the carbene ligands in a *trans*-arrangement with a rather long Ni–C$_{\text{tmiy}}$ bond (1.947(3) Å). The complex NiIMe(tmiy)$_2$ rapidly decomposes in solution via 1,2,3,4,5-pentamethylimidazolium ion elimination and was only characterized by NMR and MS. The other complexes shown (Equation (14)) were characterized by X-ray diffraction.

Oxidative addition reactions of imidazolium salts to electron-rich, coordinatively unsaturated Ni^0(NHC)$_2$ complexes have been used to synthesize Ni(II) tris(carbene)-nickel-hydrido complexes (Equation (15)).[47]

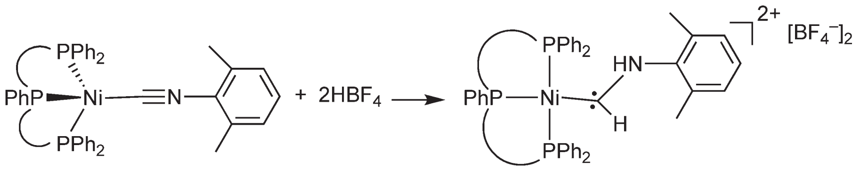


R = Me, Bu
X = BF$_4$, PF$_6$

(15)

The surprising stability of such complexes was rationalized in terms of both steric and electronic effects imparted by the three carbene ligands. From the crystal structure of the Bu^n derivative shown in Equation (15), it was noted that a significant distortion away from square-planar geometry occurs with the bulky mesityl-substituted carbenes bent toward the small hydride group with an angle of 164.22(16)°.

While the advent of NHC ligands brought much new activity to the field of nickel carbene chemistry, important progress was also made with more traditional Fischer-type carbene complexes. The typical route to methoxy(amino) or bis(amino) Fischer-type carbene complexes is the nucleophilic attack of alcohols or amines on coordinated isocyanides.[39,48] A new and efficient route to heteroatom-stabilized carbene nickel(II) complexes was recently reported to occur by a protonation reaction of the nickel(0) complex Ni(CNXyl)(triphos).[49] Addition of 2 equiv. of HBF$_4$ to solution of Ni(CNXyl)(triphos) in THF affords the stable dicationic nickel carbene complex [Ni{C(H)N(H)Xyl}(triphos)]$^{2+}$(BF$_4{}^-$)$_2$ (Equation (16)).



(16)

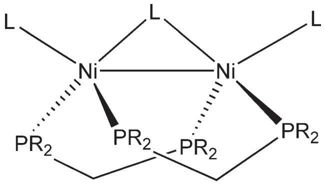
Protonation of Ni(CNXyl)(triphos) to afford the carbene complex results in oxidation of Ni(0) to Ni(II). This is evident in the change of coordination geometry from tetrahedral to square planar. The C(5)–N(1) bond distance in the carbene complex (1.268(5) Å) is shorter than a typical C–N single bond (1.472(5) Å), but longer than the C–N triple bond of isocyanides (1.157(5) Å). The three substituents on the carbene carbon are coplanar, consistent with the sp^2 character of the carbon atom. The nickel–carbon bond distance of the carbene complex *d*(Ni(1)–C(5)), 1.860(4) Å, is 0.07 Å longer than the Ni–C distance of the Ni(0) isocyanide complex. Overall, the metrical parameters fall into a range that reflects essentially no π-carbene character and significant iminium formyl character.

The two basic problems in homogeneous catalysis—separations and recycling of the catalyst—have been elegantly solved by using a water-soluble rhodium complex.[50] This result continues to be a strong motivation for the elaboration of new hydrophilic ligands and their metal complexes.[50] This effort has extended to include several water-soluble nickel carbene complexes.[40,51] One-pot deprotonation of dicationic triazolium salts 1,2,4-triazol-2-ium-5-ylidenes with Ni(OAc)$_2$ in THF solution in the presence of NaI leads to water-soluble nickel(II) carbene complexes. The X-ray crystal structure of NiI$_2$(OTf)$_2$(trz)$_2$ (trz = 1,2,4-triazol-2-ium-5-ylidene) shows a remarkably short nickel–carbon bond length of 1.765(3) Å.

8.01.3 Dinuclear Nickel Complexes

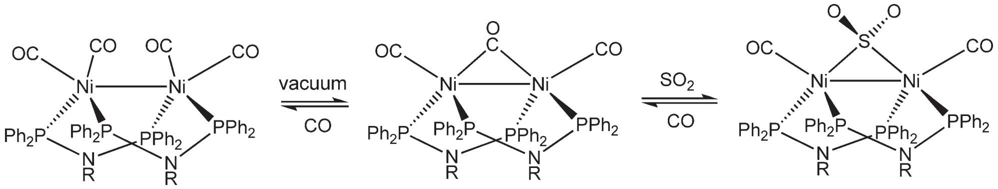
8.01.3.1 Complexes with Carbonyl Ligands

The dinuclear M_2L_7 complexes that have come to be known as "cradle" or "W-frame" complexes, **18**, are now one of the largest classes of dinuclear nickel complexes.



18

The dppm-bridged dinickel complex $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ was first reported to be formed by a fragmentation reaction of a tripodal triphos ligand-supported nickel trimer.[52] Two more straightforward preparative procedures for this complex have been reported since then.[53,54] The CO-dependent equilibria between the dinuclear complexes $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ and $Ni_2(CO)_4(dppm)_2$, and also between the mononuclear complexes $Ni(CO)_2(\eta^1\text{-}dppm)_2$ and $Ni(CO)_3(\eta^1\text{-}dppm)$, have been investigated.[54] At room temperature, the mononuclear complex $Ni(CO)_2(\eta^1\text{-}dppm)_2$ also exists in equilibrium with $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$, CO, and free dppm. The diphosphines, bis(diphenylphosphino)amine (dppa) and bis(diphenylphosphino)methylamine (dppma), have been investigated more recently as bridging ligands in dinuclear complexes, and the properties of complexes bridged by the methylene diphosphine, dppm, and the amine diphosphines, dppa and dppma, have been compared. Nickel carbonyl, $Ni(CO)_4$, reacts with dppa to afford the dinuclear tetracarbonyl complex $Ni_2(CO)_4(dppa)_2$. Under vacuum, this complex loses CO to give $Ni_2(\mu\text{-}CO)(CO)_2(dppa)_2$, which was found to react with SO_2 to give substitution of only the bridging carbonyl to form $Ni_2(\mu\text{-}SO_2)(CO)_2(dppa)_2$ (Equation (17)).[55]

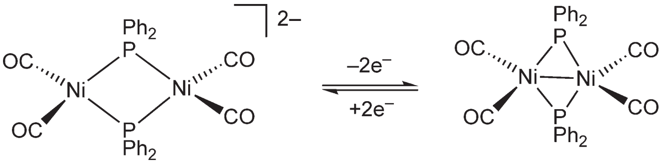


(17)

The complex $Ni_2(\mu\text{-}SO_2)(CO)_2(dppa)_2$ was characterized by X-ray crystallography. The corresponding dppma complexes were also prepared, and they were found to have very similar reactivity to the dppa complexes shown in Equation (17). It was noted that, in general, the dppa and dppma complexes were less reactive than the corresponding dppm complexes. This was ascribed to the lower basicities of dppa and dppma relative to dppm, and the somewhat greater size and flexibility of dppm. The dppa complex $Ni_2(\mu\text{-}CO)(CO)_2(dppa)_2$ was independently prepared and structurally characterized by another research group who also reported electrochemical data and a molecular orbital calculation.[56] The complex $Ni_2(\mu\text{-}CO)(CO)_2(dppa)_2$ undergoes two quasi-reversible single-electron oxidations at +0.24 and +0.50 V versus SCE in THF solution. The HOMO is computed to involve strong $Ni_2(d\pi)$–μ-CO($p\pi$) interactions. The molecular orbital calculation also predicts an Ni–Ni bond order of 0.39 while the X-ray structure of $Ni_2(\mu\text{-}CO)(CO)_2(dppa)_2$ revealed a Ni–Ni separation of 2.5824(7) Å. The dppa complex $Ni_2(\mu\text{-}CO)(CO)_2(dppa)_2$ was also reported to be involved in a CO and temperature-dependent equilibrium with $Ni_2(CO)_4(dppa)_2$ and the mononuclear complex $Ni(CO)_3(\eta^1\text{-}dppa)$.[56] The mononuclear complex $Ni(CO)_2(\eta^1\text{-}dppa)_2$ was obtained in good yield by the reaction of dppa with the complex $Ni(CO)_2(PPh_3)_2$.[57]

Binuclear Ni(I) carbonyl complexes $Ni_2Cl_2(CO)(PMe_3)_3$ have been obtained by the reaction of oxalyl chloride, $(COCl)_2$, with $Ni(cod)(PMe_3)_2$ (Equation (4)).[58] The corresponding binuclear Ni(I) thiocarbonyl complex $Ni_2Cl_2(CS)(PMe_3)_3$ was obtained similarly by the reaction of thiophosgene with $Ni(cod)(PMe_3)_2$. However, the crystal and molecular structure of the thiocarbonyl complex showed that the thiocarbonyl group condensed with one PMe_3 ligand to give a bridging $Me_3P{=}C{=}S$ group.

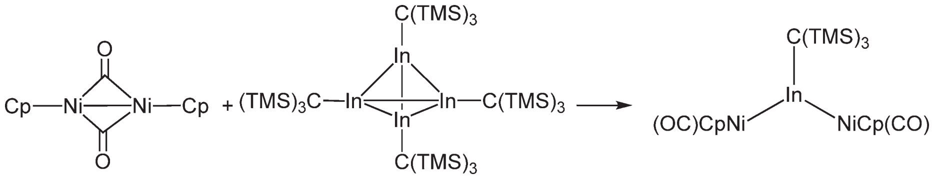
A dinuclear, dianionic, diphenylphosphido-bridged Ni(0) complex, $[Ni_2(\mu\text{-}PPh_2)_2(CO)_4]^{2-}$, was prepared by potassium metal reduction of $Ni(CO)_2(PPh_3)_2$ in toluene.[59] The crystal and molecular structure of the complex dianion shows that each nickel center can achieve an 18-electron configuration without an Ni–Ni bond, *d*(Ni–Ni) = 3.397(1) Å. This compares with an Ni–Ni bond distance of *d*(Ni–Ni) = 2.506 Å in the neutral complex, $Ni_2(\mu\text{-}PPh_2)_2(CO)_4$. The cyclic voltammetry of the dianionic complex $[Ni_2(\mu\text{-}PPh_2)_2(CO)_4]^{2-}$ shows a reversible oxidation at −1.5 V (versus $FeCp_2^{+/0}$) and a quasi-reversible oxidation at −1.1 V. This established a chemically reversible two-electron redox chemistry connecting the dianionic and neutral complexes (Equation (18)).



(18)

It also established the stability of an Ni(0)–Ni(I) mixed valence species. Such a species, $[Ni_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_2(PPh_3)_2]^-$, was prepared as one of the products of the reaction of $Ni(CO)_2(PPh_3)_2$ with Sn_9^{4-}.

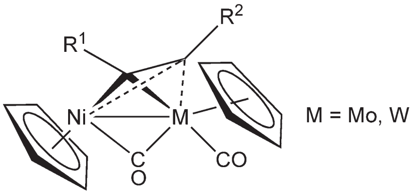
The most studied class of binuclear nickel carbonyl complexes is $[NiCp(CO)]_2$, which may be formed simply by the combination of $NiCp_2$ and $Ni(CO)_4$. The dinuclear structure of this complex is easily cleaved by reaction with most electron-pair donor ligands. The high degree of lability of $[NiCp(CO)]_2$ has been used in the preparation of a wide variety of heterodinuclear complexes. The tetrahedral indium cluster $In_4\{C(TMS)_3\}_4$ reacts with 4 equiv. of $[NiCp(CO)]_2$ with insertion of the $InC(TMS)_3$ fragment into the Ni–Ni bond (Equation (19)).[60]



(19)

Both the indium and gallium clusters $E_4\{C(TMS)_3\}_4$ (E = Ga, In) react with 2 equiv. of $[NiCp(CO)]_2$ to give the bis(μ-$EC(TMS)_3$)-substituted complexes, $[Ni(CO)Cp]_2\{\mu\text{-}EC(TMS)_3\}$ which are isostructural with the starting carbonyl complex. Quantum chemical calculations support the view that there are no In–In or Ga–Ga bonding interactions in the "butterfly structure" complexes, $Ni\{\mu\text{-}EC(TMS)_3\}Cp_2$.

The reactions of $NiCp(CO)MCp(CO)_3$ (M = Mo, W) with alkynes have been studied in detail.[61–63] More recently, the alkyne chemistry of the coordinatively unsaturated $NiCp^*$ complexes $NiCp^*MCp(CO)_3$ (M = Mo, W) has been explored.[61,62] The complexes $NiCp(CO)MCp(CO)_3$ (M = Mo, W) generally react with alkynes to afford the dimetallatetrahedrane type complexes, **19**. Nickelacyclobutenone complexes, **20**, are also obtained, but generally only for the Mo heterometallic dimers.



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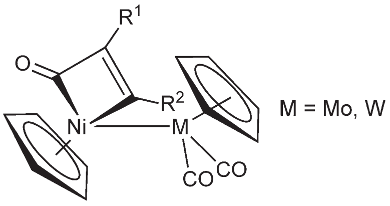
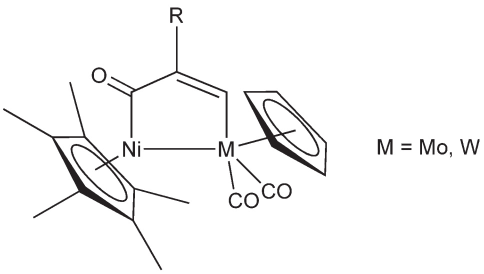


20

The four-membered nickelacyclobutenone results from alkyne–carbonyl ligand coupling.[61] The $NiCp^*$ complexes $NiCp^*MCp(CO)_3$ (M = Mo, W) react with alkynes in a similar fashion to the NiCp analogs. The primary difference is that the nickelacyclobutenone products of general structure **20** appear to be more stable with Cp^* substitution at nickel. The reaction chemistry of both the dimetallatetrahedrane **19** and nickelacyclobutenone complexes, **20**, with a variety of electrophilic and nucleophilic reagents has been examined. Reactions of the nickelacyclobutenone complexes with electrophiles are found to induce an interesting ring flip of the carbocyclic fragment of the metallocycle from nickel to molybdenum or tungsten.[61] A more complex mixture of products is obtained in the reactions of the NiCp* complexes NiCp*MCp(CO)$_3$ (M = Mo, W) with terminal alkynes. The principal products are five-membered dimetallacycles, **21**.



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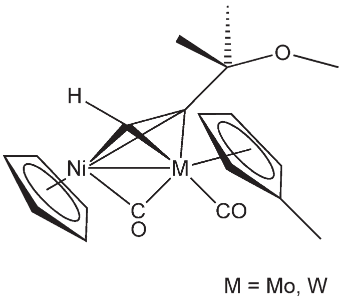
Alkylation or protonation of these dimetallacycles leads to a rearrangement, that is, a four-membered molybdenacycle or tungstenacycle cationic complex, analogous to the reactions of complexes of structure **20** with electrophiles. The complex NiCp(CO)M(MeCp)(CO)$_3$ (M = Mo, W) with 3-methoxy-3-methyl-1-butyne gives enantiomeric μ-alkyne complexes which have chiral dimetalatetrahedrane cores, **22**, and five-membered metallacycles formed by regioselective alkyne–CO coupling, **23**. Protonation of the dimetalatetrahedrane complex **22** gives the μ-propargylic cation **24**.



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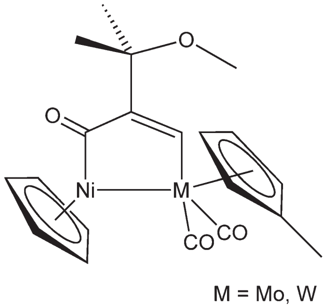

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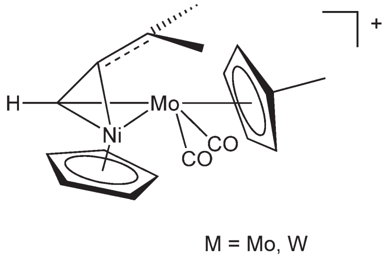

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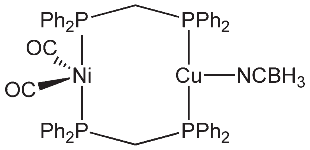
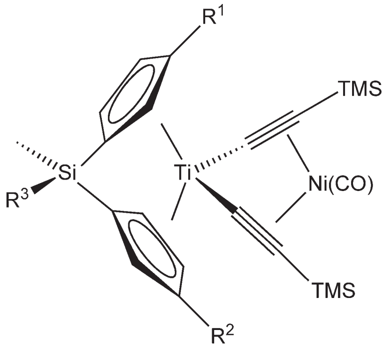
Heterodinuclear complexes that contain nickel carbonyl groups have been prepared by a variety of methods. The heterodinuclear complex [NiCu(μ-dppm)$_2$(CO)$_2$(NCMe)$_2$]X (X = ClO$_4$, BPh$_4$, PF$_6$) and the related neutral complex NiCu(μ-dppm)$_2$(CO)$_2$(NCBH$_3$) were prepared by reactions of Ni(CO)$_2$(η^1-dppm) with Cu(I). The X-ray crystal structure of NiCu(μ-dppm)$_2$(CO)$_2$(NCBH$_3$) shows an approximately tetrahedral coordination geometry about Ni(0) and a slightly distorted trigonal-planar geometry about Cu(I), **25**.



25

The Ni–Cu distance of 3.171(4) Å is too long for significant metal–metal interaction.[64] Main group-metal–nickel heterodinuclear complexes have been prepared by the reactions of aluminum pnictines such as (4-dimethylaminopyridine)Al(Me)$_2$E(TMS)$_2$ (E = P, As, Sb) with Ni(CO)$_4$.[65] Crystal structures reveal open structures with the pnictinogen atom lone pair coordinated to Ni(CO)$_3$ fragments. A series of bis-(trimethylsilyl)ethynyl-*ansa*-titanocenes have been reacted with $Ni(CO)_4$ to give heterodinuclear complexes in which an Ni(CO) fragment is coordinated by the pendant alkynyl groups of the *ansa*-titanocene, **26**.[66]



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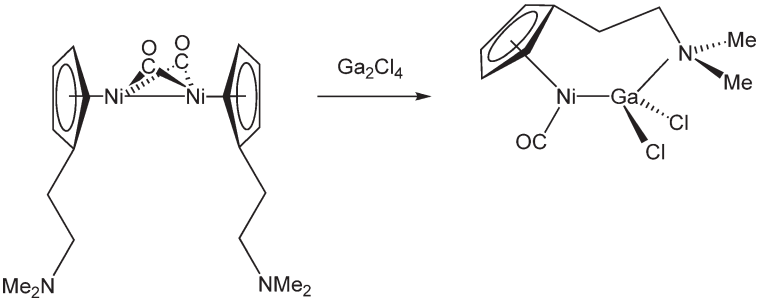
The nickel cyclopentadienyl carbonyl dimer $[NiCp^N(CO)]_2$, where Cp^N is *N*,*N*-(dimethylamino)ethylcyclopentadienyl, was reacted with Ga_2Cl_4 to give a heterodinuclear complex (Equation (20)).

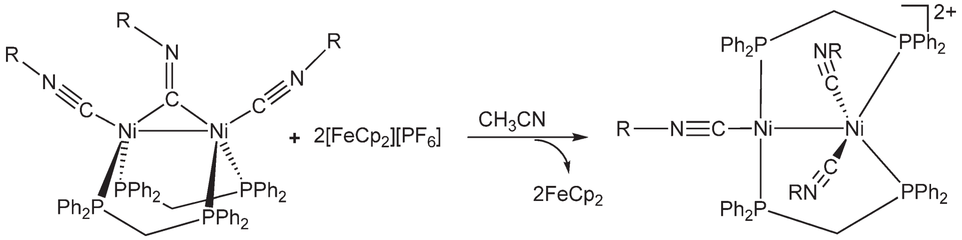


(20)

The X-ray crystal structure shows an exceptionally short Ni–Ga distance of 2.279(7) Å.[67]

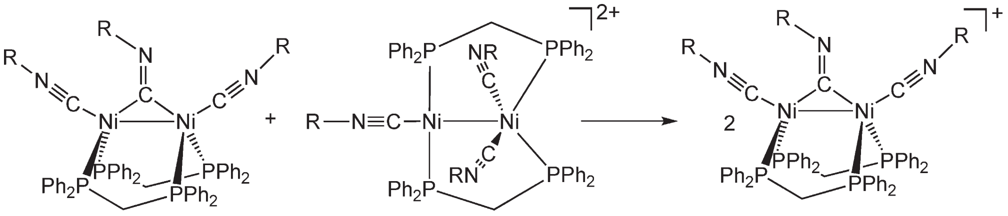
8.01.3.2 Complexes with Isocyanide Ligands

Much of the work on dinuclear nickel complexes with isocyanide ligands during the period covered by COMC III concerned complexes of the "cradle" or "W-frame" type, **18**.[53,68–70] The preparation of the methyl isocyanide complex $[Ni_2(\mu\text{-CNMe})(CNMe)_2(dppm)_2]$ starting from nickelocene has been reported.[53] A systematic study of the structures, comprising spectroscopic and electrochemical studies of a series of differently substituted isocyanide dimers $Ni_2(\mu\text{-CNR})(CNR)_2(dppm)_2$ (R = Me, Bu^n, Bz, Pr^i, Cy, Bu^t, 4-I-Ph, and Xyl) together with their Ni(0)–Ni(I) and Ni(0)–Ni(II) mixed valence states, was recently published.[70] The cyclic voltammograms of the dimers exhibit two reversible and sequential single-electron oxidations to the +1 and +2 forms. Specular reflectance infrared spectroelectrochemical measurements demonstrated reversible interconversions between the neutral Ni(0) dimers and their +1 and +2 forms. Bulk samples of the +2 forms are prepared by chemical oxidation using $[FeCp_2][PF_6]$ (Equation (21)).



(21)

The +2 forms of the complexes with Bu^{t}NC and XylNC ligands were structurally characterized and were found to possess asymmetric structures with one locally square-planar and one locally tetrahedral metal center. The structural data were interpreted in terms of an Ni(II)–Ni(0) mixed valence state. The +1 forms $[Ni_2(\mu\text{-}CNR)(CNR)_2(dppm)_2]^+$ were prepared by the comproportionation of neutral and +2 forms (Equation (22)).



(22)

The X-ray structural characterization of $[Ni_2(\mu\text{-}CNBu^t)(CNBu^t)_2(dppm)_2]^+$ showed a symmetric structure, similar to that of the neutral complex. On the basis of structural, spectroscopic, and electrochemical data, the +1 forms of the complexes were assigned to Robin–Day class III, fully delocalized Ni(+0.5)–Ni(+0.5) mixed-valence complexes.[70] In contrast to the simple comproportionation between Ni(0) and Ni(II) evident in Equation (22), the Ni(0) dppa complexes $Ni_2(\mu\text{-}CNR)(CNR)_2(dppa)_2$ (R = Me, Bu^n, Xyl) were reported to react with Ni(II) to give cleavage of the dppa ligand and μ-diphenylphosphido Ni(I) complexes of the type $[Ni_2(\mu_2\text{-}PPh_2)(CNR)_2(dppa)_2]X$ (R = Me, Bu^n, Xyl, X = Cl, I, BPh_4).[69] The dinuclear dppa complexes $[Ni_2(\mu\text{-}CNR)(CNR)_2(dppa)_2]$ (R = Me, Bu^n) were found to be catalysts for the electrochemical reduction of carbon dioxide.[68] Electrochemical reduction of $[Ni_2(\mu\text{-}CNR)(CNR)_2(dppa)_2]$ (R = Me, Bu^n) at −1.0 V versus $FeCp_2^{+/0}$ gives the radical anion $[Ni_2(\mu\text{-}CNR)(CNR)_2(dppa)_2]^-$ which reacts with CO_2 resulting ultimately in the reductive disproportionation of CO_2 to CO and carbonate.

In Ni(I) dinuclear complexes, the subtle factors that favor the asymmetric internally disproportionated Ni(0)–Ni(II) structure over the symmetric Ni(I)–Ni(I) "A-frame" structure have not been identified completely. Oxidative addition of phenylisocyanide dichloride ($PhNCCl_2$) to $Ni(cod)_2$ in the presence of dppm gave the complex $Ni_2(\mu_2\text{-}CNPh)Cl_2(dppm)_2$ which was found by X-ray diffraction to have an "A-frame" type structure with a long Ni–Ni separation of 2.917(4) Å.[71]

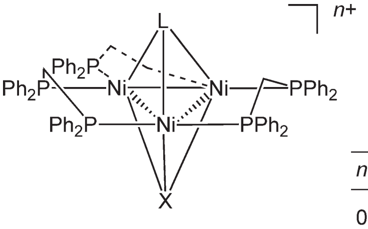
8.01.3.3 Complexes with Carbene Ligands

Other than the dinuclear *N*-heterocyclic carbene Ni(II) complex **16** described in the preceding section on mononuclear nickel carbene complexes, no further examples of dinuclear nickel complexes with carbenes were reported beyond those summarized in COMC(1995).

8.01.4 Higher Cluster Complexes

8.01.4.1 Clusters with Carbonyl Ligands

The class of dppm-bridged trinuclear clusters $[Ni_3(\mu_3\text{-}L)(\mu_3\text{-}X)(\mu_2\text{-}dppm)_3]^{n+}$ **27** has become extensive.



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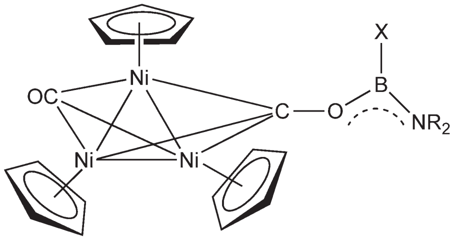
n	*X*	*L*
0	Cl^-, Br^-, I^-	Cl^-, Br^-, I^-, $SnCl_3^-$, $Sn(OH)_3^-$
1	Cl^-, Br^-, I^-	Cl^-, Br^-, I^-, CO, CNR, $SnCl_2$

The first members of this class had capping halide ligands (X = Br^-, I^-) and capping π-acceptor ligands (L = CO, CNR) to give cationic (*n* = 1) 48-electron complexes.[72] Recently, related clusters with capping trichlorostannyl and dichlorostannylene ligands[73] and an unusually structurally characterized cluster with a μ_3-trihydroxyl tin capping ligand have been reported.[74] A study comparing plasma desorption (PD) and fast atom bombardment (FAB) mass spectrometry to characterize clusters of this type has appeared.[75] Strong molecular ion peaks were observed for CO- and CNR-capped clusters, but not for the NO^+-capped cluster.

Carbonyl-capped trinuclear nickel clusters have been prepared by the reaction of K[NiCp(CO)] with chloroboranes $BCl_2(NR_2)$ ($NR_2 = NBu^t(TMS)$, $N(TMS)_2$) or 1, 2-dichlorodiboranes $B_2(NMe_2)_2Cl_2$.[76] The chloroboranes attack one of the carbonyl ligands to give μ_3-boryloxycarbyne bridged clusters, **28**. Heteropolynuclear nickel carbonyl clusters have been prepared by a variety of methods. The novel triphosphaferrocene $FeCp^*(\eta^5\text{-}C_2Bu^t{}_2P_3)$ was reacted with $Ni(CO)_4$ to afford a dinickel diiron cluster, **29**, which was characterized by X-ray crystallography.[77]



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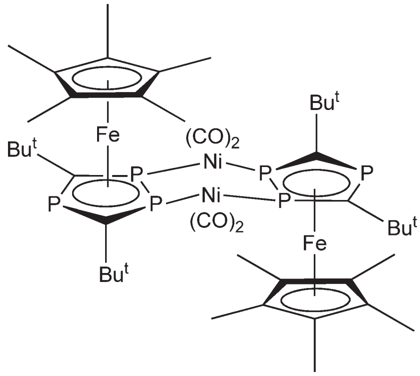

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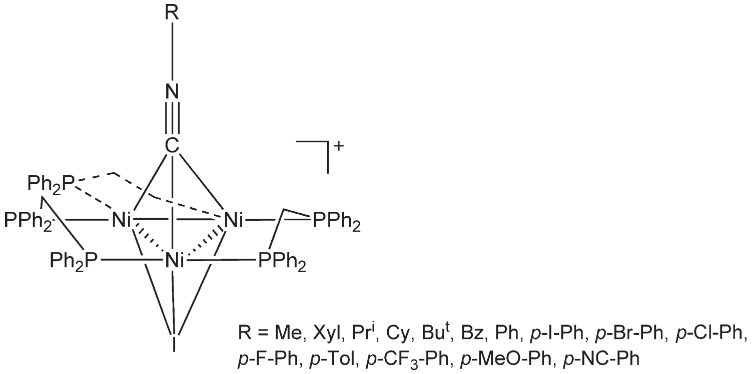
The remarkable preference of nickel for CO and of iron for thiolate ligands is seen in the reaction of the Ni(II) dithiolate complex Ni(dsdm) (H_2dsdm═N,N′-dimethyl-N,N′-bis(2-sulfanyl-ethyl)ethylenediamine) with $K[FeH(CO)_4]$.[78] The product is a linear tetranuclear cluster in which a dinuclear $Fe^{II}{}_2(dsdm)_2$ core is bound by two peripheral $Ni(CO)_3$ fragments each bonded to one thiolate of the iron core, thus demonstrating a complete reshuffling of ligands and oxidation states. The cluster $[NiRu_3(\mu_3\text{-}H)(\mu\text{-}CO)_3(CO)_9]^-$ is prepared by the smooth condensation of $Ni(CO)_4$ with $[Ru_3H(CO)_{11}]^-$. The cluster was characterized by X-ray diffraction and found to possess a distorted tetrahedral $NiRu_3$ core with nine terminal and three edge bridging CO ligands. The cluster $[NiRu_3(\mu_3\text{-}H)(\mu\text{-}CO)_3(CO)_9]^-$ was deprotonated with the strong base $KOBu^t$ to afford the dianion $[NiRu_3(CO)_{12}]^{2-}$. The latter was found by X-ray crystallography to have a tetrahedral $NiRu_3$ core with eight terminal and four edge bridging CO ligands.[79] The $NiCo_3$ cluster $CpNiCo_3(CO)_9$ was reacted with cyclooctatetraene to give a remarkable $NiCo_2$ cluster $NiCo(CO)_6(C_8H_8)$ in which a triangular $NiCo_2(CO)_6$ metal cluster sits atop a facially coordinated, essentially planar cyclooctatetraene ligand.[80] High nuclearity nickel carbonyl clusters with skeletal antimony atoms have been reported to be prepared by the reaction of $[Ni_6(CO)_{12}]^{2-}$ with $SbCl_3$.[81] The cluster $[Ni_{15}(\mu_{12}\text{-}Sb)(CO)_{24}]^{2-}$ was obtained in reasonable yield and found by X-ray crystallography to have a structure based on a distorted iscosahedral $Ni_{12}(\mu_{12}\text{-}Sb)$ core capped by three Ni atoms on three adjacent triangular cores.

8.01.4.2 Clusters with Isocyanide Ligands

The class of dppm-bridged trinuclear cluster cations capped by isocyanide ligands $[Ni_3(\mu_3\text{-}CNR)(\mu_3\text{-}I)(\mu_2\text{-}dppm)_3]^+$ **30** includes derivatives prepared from 15 different isocyanide ligands (R = Me, Xyl, Pr^i, Cy, Bu^t, Bz, Ph, *p*-I-Ph, *p*-Br-Ph, *p*-Cl-Ph, *p*-F-Ph, *p*-Tol, *p*-CF_3-Ph, *p*-MeO-Ph, *p*-NC-Ph).[72] The infrared spectra of the isocyanide ligands in the CN-stretching region were found to be complicated by Fermi resonances. The Fermi resonances appear to involve the interaction between the CN triple bond fundamental, $\nu(C{\equiv}N)$, and the overtone of the CN single bond of the isocyanide, 2 ν(C–N), which can have similar energies.[72]

A study comparing plasma desorption (PD) and fast atom bombardment (FAB) mass spectrometry to characterize clusters of this type found that the isocyanide-capped clusters **30** showed strong molecular ion peaks by both methods.[75] PD and FAB were also used to identify the molecular ions of "dimers of trimers,"

$[Ni_3(\mu_3\text{-}I)(\mu_2\text{-dppm})_3(\mu_3\text{-CN-spacer-}\mu_3\text{-NC})Ni_3(\mu_3\text{-}I)(\mu_2\text{-dppm})_3]$, formed from diisocyanides with *p*-phenyl and 1,6-hexyl group spacers. The isocyanide-capped clusters **30** show a reversible single-electron reduction from a 48-electron to a 49-electron electronic configuration at ca. −1.20 V versus SCE. A study of the electrocatalytic activity of clusters **30** toward the reduction of carbon dioxide has appeared.[82] Electrochemical kinetics indicate that the rates of reaction with CO_2 are first order on [cluster] and first order on $[CO_2]$. The observed products are carbon monoxide and carbonate, corresponding to the reductive disproportionation of CO_2.



R = Me, Xyl, Pr^i, Cy, Bu^t, Bz, Ph, *p*-I-Ph, *p*-Br-Ph, *p*-Cl-Ph, *p*-F-Ph, *p*-Tol, *p*-CF_3-Ph, *p*-MeO-Ph, *p*-NC-Ph

30

8.01.4.3 Clusters with Carbene Ligands

At the time of this writing, no nickel cluster compounds containing carbene ligands were reported beyond those discussed in COMC(1995). Maekawa and co-workers have described the synthesis and structure of the bis(acetylide)-capped cluster, $Ni_3(\mu_3\text{-CCPh})_2(\text{dppm})_3$.[83] A dichlorostannylene-capped cluster $[Ni_3(\mu_3\text{-}I)(\mu_3\text{-SnCl}_2)(\text{dppm})_3][PF_6]$ was reported to be formed by chloride abstraction from a trichlorostannyl-capped cluster, $[Ni_3(\mu_3\text{-}I)(\mu_3\text{-SnCl}_3)(\text{dppm})_3]$.[73]

8.01.5 Theoretical and Physical Studies

8.01.5.1 Theoretical and Physical Studies of Nickel Carbonyls

Several physical and computational studies have added to our fundamental understanding of nickel carbonyl complexes. The bond strengths of the first-row metal carbonyl anions were measured by energy-resolved collision-induced dissociation of the carbonyl anions in the gas phase.[84] This method was used to probe CO dissociation from $[Ni(CO)_n]^-$ ($n = 2$, 3) to obtain bond strengths, $D[(CO)_2Ni\text{–}CO] = 38.5 \pm 2.3$, $D[(CO)Ni\text{–}CO] = 43.4 \pm 5.8$, and $D[Ni\text{–}CO] = 32.4 \pm 5.8\ \text{kcal mol}^{-1}$. The bond energies in the anions were used together with literature electron affinities to give bond energies for the neutral metal carbonyls, $D[(CO)_2Ni\text{–}CO] = 28.3 \pm 2.3$, $D[(CO)Ni\text{–}CO] = 47.1 \pm 5.8$, and $D[Ni\text{–}CO] = 40.5 \pm 5.8$ (kcal mol^{-1}).[85] In a separate study, the bond-dissociation energies of CO from the neutral Ni(0) and cationic Ni(I) carbonyl complexes were reported.[86] The reported values are: $D[(CO)_3Ni\text{–}CO] = 25.4 \pm 2.3$, $D[(CO)_2Ni\text{–}CO] = 18.5 \pm 6.9$, $D[(CO)Ni\text{–}CO] = 53.0 \pm 16$, and $D[Ni\text{–}CO] = 30.0 \pm 16$; $D[(CO)_3Ni^+\text{–}CO] = 12.5$, $D[(CO)_2Ni^+\text{–}CO] = 30.4$, $D[(CO)Ni^+\text{–}CO] = 45.2$, and $D[Ni^+\text{–}CO] = 52.6\ \text{kcal mol}^{-1}$. The dynamics of CO dissociation from $Ni(CO)_4$ were also examined by these authors.[86] Time-resolved nonresonant (800 nm) multiphoton ionization was used to probe relaxation processes that occur on the femtosecond (fs) timescale. Several relaxation processes with timescales of 22–70 fs were assigned to internal conversion between metal-to-ligand charge transfer states in intact, excited $Ni(CO)_4$. The dissociation of CO from $Ni(CO)_4$ occurs with a time constant of 600 fs, longer than most other mononuclear transition metal carbonyl complexes studied. This dissociation product is $Ni(CO)_3$ in its S_1 state which luminesces after intersystem crossing to a triplet state. The photoluminescence of the complex $Ni(CO)_2(PPh_3)_2$ has been examined in the condensed phase.[87] The red ($\lambda_{max} = 650$ nm) photoluminescence is assigned as originating from a Ni(0) to PPh_3 metal-to-ligand charge-excited triplet state. Hybrid density functional molecular orbital calculations have been employed to describe the properties of transition metal monocarbonyls in their first excited state.[88] The excited nickel carbonyl $[Ni\text{–}CO]^*$ is calculated to be a

$^3A'$ state with a bent geometrical structure (149°). The geometry and electronic structure of the dinuclear Ni(I) carbonyl complex cations $[Ni_2(CO)_2]^{2+}$ and $[Ni_2(CO)_6]^{2+}$ were also studied by density functional theory.[89] The $[Ni_2(CO)_2]^{2+}$ ion is predicted to be planar (D_{2h}) with the carbonyl ligands bridging. The ion is predicted to have a D_{2d} structure in which all carbonyl ligands are terminally bound and there is a strong and directional Ni–Ni bond.

8.01.5.2 Theoretical and Physical Studies of Nickel Isocyanides

The electronic structures of peroxonickel(II) bis(isocyanide) complexes have been examined by theoretical studies.[90] The only nickel–dioxygen complex that has been fully characterized is the peroxonickel(II) bis(Bu^t-isocyanide) complex, $Ni(O_2)(CNBu^t)_2$. This complex has a square-planar geometry and is diamagnetic. Several electronic states of the molecule $Ni(O_2)(HNC)_2$ were calculated using various *ab initio* methods to determine the ground state and low-lying excited states. The computed $^1A_1$ ground state is in agreement with the reported dimagnetism of $Ni(O_2)(CNBu^t)_2$ and was shown to be formally represented as $[Ni^{II}–O_2]^{2-}$ with a partial contribution of a superoxo $[Ni^{I}–O_2]^{-}$ formulation to the ground state wave function. The superoxo description dominates the lowest excited state which was computed to be $^3B_1$.

8.01.5.3 Theoretical and Physical Studies of Nickel Carbenes

At the time of this writing, no studies specifically addressing theoretical or physical studies of nickel complexes with carbene ligands were reported.

8.01.6 Catalytic Applications

8.01.6.1 Organic Reactions Mediated by Nickel Carbonyls and Catalytic Applications

Catalytic applications of nickel complexes that contain carbonyl ligands are discussed in detail in sections of COMC III that specifically treat applications of nickel complexes in catalysis.

8.01.6.2 Organic Reactions Mediated by Nickel Isocyanides and Catalytic Applications

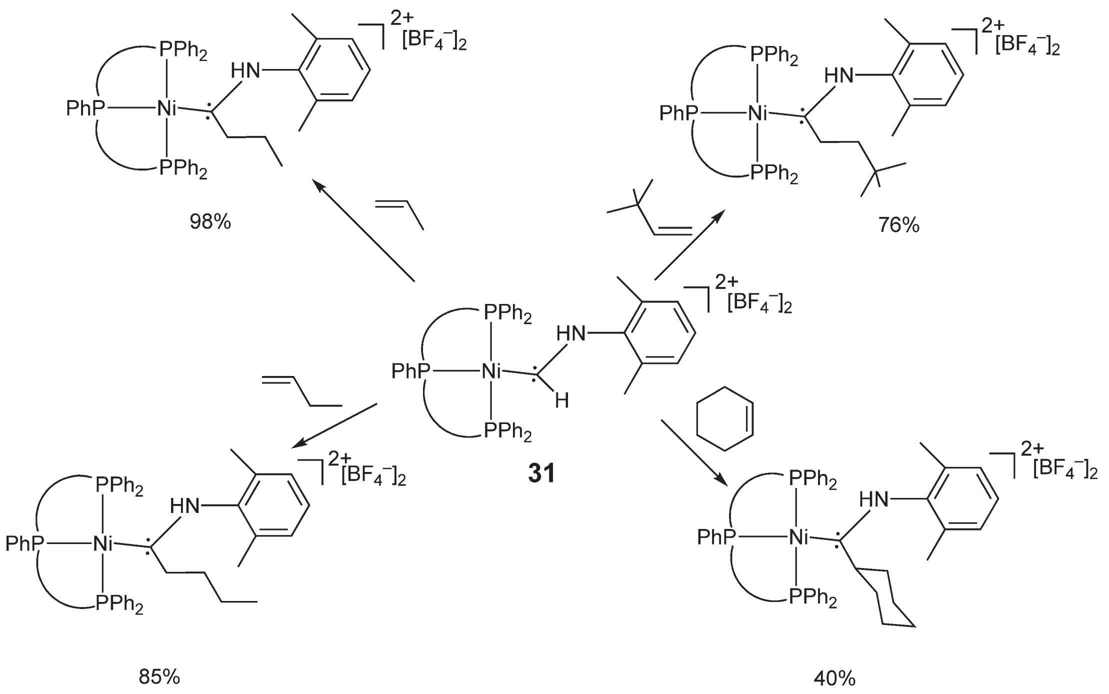
One catalytic application of nickel complexes that contain isocyanide ligands is particularly noteworthy. The nickel allyl complex $[Ni(\eta^3\text{-}C_3H_5)(O_2CCF_3)]_2$ is a catalyst for the living polymerization of aryl isocyanides.[91,92] Isocyanide complexes of nickel, $NiBr_2(CNAr)_2$, were also found to be catalysts for the polymerization of ethylene in the presence of methylaluminoxane (MAO).[93] The most active catalysts are those that bear 2,6–diphenylphenylisocyanide ligands. Catalysts based on 2-phenylphenylisocyanide produce lower molecular weight polyethylene.

8.01.6.3 Organic Reactions Mediated by Nickel Carbenes and Catalytic Applications

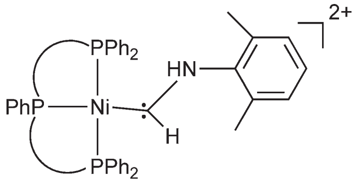
Since Reppe's discovery[94] of the cyclotrimerization of acetylene to benzene in the presence of nickel carbonyl-phosphine complexes, the use of nickel catalysts in many organic transformations has become popular. Transition metal complex catalysis provides many elegant entries to carbon–carbon bond-forming reactions in organic synthesis. One notable example is carbocyclic ring expansion mediated by nickel(0) complexes.[95]

8.01.6.3.1 Carbon–carbon bond formation: hydrocarbation reactions

In 1982, Casey and co-workers reported the first reactions that could be considered "hydrocarbations" because they involved the direct C–H bond addition across the C–C double bond of alkenes.[96] They showed that the cationic bridging iron methylidyne complex undergoes this type of reaction with alkenes with anti-Markovnikov regioselectivity.[97] No other hydrocarbation reactions had been reported until recently, when Kubiak and co-workers reported hydrocarbation reactions of a nickel carbene complex with alkenes. Thus, the dicationic aminocarbene complex **31** reacts with ethylene, resulting in a complete conversion to the ethylcarbene complex (Scheme 1).



Scheme 1



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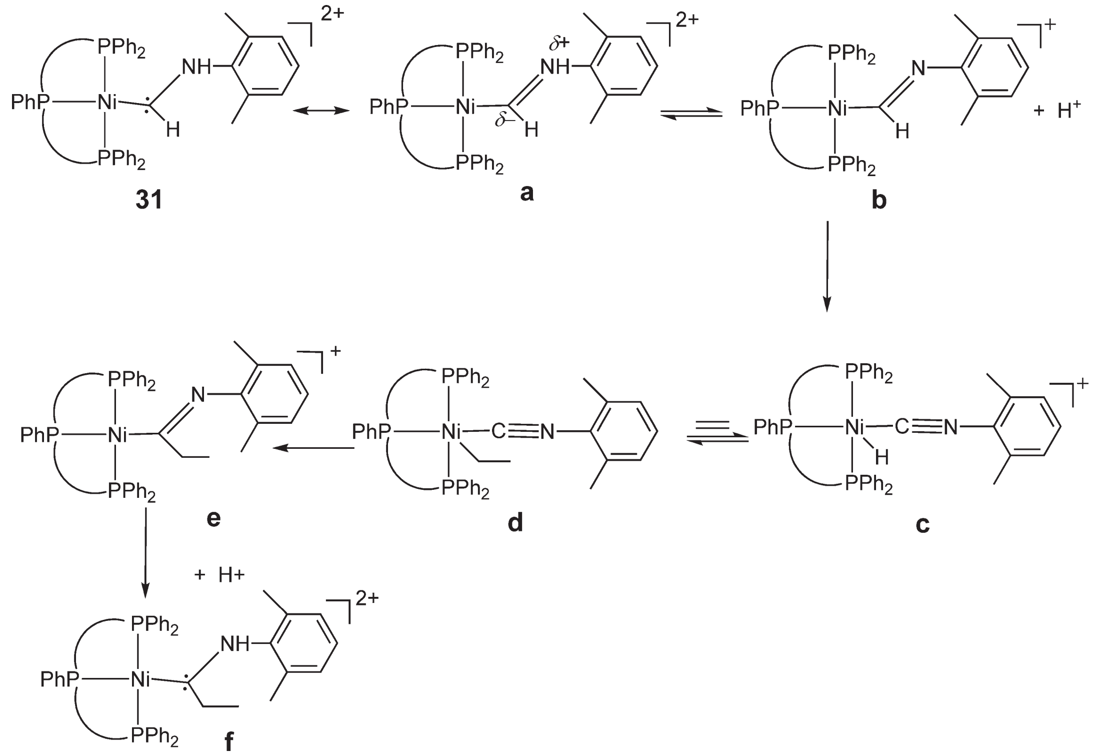
The crystal structure of the ethyl carbene complex shows a short C–N bond distance (1.302(3) Å), intermediate between a single (1.472 (5)) and triple (1.157(5)) bond of isocyanides, providing evidence of significant iminium alkyl character, similar to that observed in parent carbene **31**. Complex **31** reacts similarly with cyclohexene, propene, 1-butene, and 3,3-dimethyl-1-butene quantitatively and regiospecifically to give the anti-Markovnikov hydrocarbation products (Scheme 1). Thus, the regiochemistry is the same as that of hydroboration and hydrocarbation reported earlier by Casey.[97] However, mechanistic studies suggest the importance of a "hydride" pathway over "alkene" (metallocycle formation or carbocation) pathways (Scheme 2).

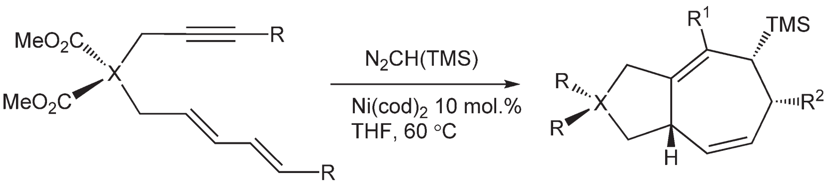
An α-hydrogen elimination is the microscopic reverse of hydride insertion/imino formyl formation and affords the nickel(II) hydride complex (**c**, Scheme 2). Subsequent olefin insertion and isocyanide insertion gives hydrocarbation product (f, Scheme 2). Isotopic labeling experiments by using d_4-ethylene or $[Ni\{C(D)N(D)xylyl\}(triphos)](CF_3SO_3)_2$ showed deuterium at both the methylene group and the methyl group of the α-ethyl carbene (f, Scheme 2), not expected in an alkene pathway.

8.01.6.3.2 Carbon–carbon bond formation: cyclization reactions

The catalytic syntheses of seven-membered rings has long been an elusive goal,[95] achieved only rarely and in poor yields.[98] Significant advances have been made in the last decade through the use of nickel carbene complexes. Thus, using a diazoalkane carbene precursor in the presence of $Ni(cod)_2$, an efficient [4 + 2 + 1]-cycloaddition to a seven-membered ring was reported.[99] (Equation (23)).



Scheme 2

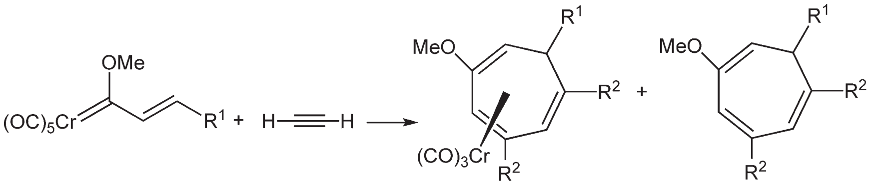


(23)

$X = C; R = MeO_2C; R^1,R^2 = Me$ or H
$X = N; R = Ts, R^1,R^2 = H$
$X = O; R^1,R^2 = Me$

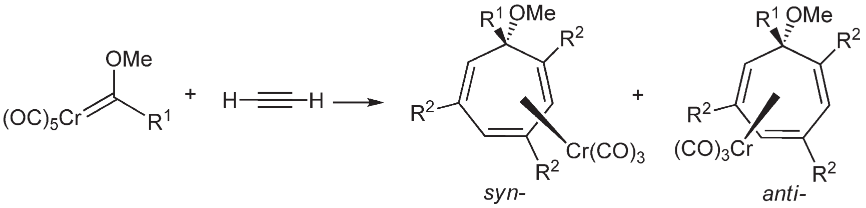
This reaction occurs with a large degree of chemoselectivity over other [4+2], [4+1], [2+1], [2+2+1], [2+2+2], [4+4], [4+2+2] potential cycloadditions, with yields of more than 65% for the [4+2+1]-cycloadduct. The mechanism of this transformation remains unclear, and formation of a nickel carbene intermediate is proposed. Nonetheless, this is an important reaction, preparatively useful by providing a catalytic chemoselective entry to seven-membered rings that allows the incorporation of heteroatoms.

Another synthetic pathway to seven-membered rings is by reacting chromium Fisher carbene complexes with alkynes in the presence of $Ni(cod)_2$ (Equations (24) and (25)).[100]



(24)

$R^1 = Ph, Cp_2Fe, Pr^n$, 2-furyl
$R^2 = Pr^n, TMS, Ph, (CH_2)_3CN, CO_2Me$



(25)

R^1 = Ph, Cp_2Fe, Pr^n, 2-furyl
R^2 = Pr^n, TMS, Ph, $(CH_2)_3CN$, CO_2Me

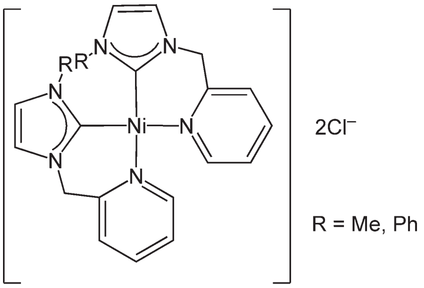
The corresponding [3 + 2 + 2]- and [2 + 2 + 2 + 1]-cyclization reactions between these complexes and alkynes are very efficient in the presence of Ni(0). Transmetallation reactions between chromium Fischer carbene complexes and $Ni(cod)_2$ with formation of nickel carbene intermediates is presumed to be responsible for this transformation. The metal-free cycloadducts are easily obtained by ligand exchange reactions at low CO pressures. A [3 + 2]-cyclization reaction of a chromium Fischer carbene complex and allene building blocks was accomplished, using similar synthetic procedures by Barluenga's group.[101] This transformation was reported to be chemo- and stereoselective and proceeds with very high yields.

8.01.6.3.3 Isomerization, polymerization, other C–C and C–N coupling reactions

In view of the growing importance of nickel complexes as olefin polymerization catalysts,[44] attempts had been made to use nickel carbene complexes as catalysts in these important reactions. The *trans*-$NiCl_2(IPr)_2$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complex was synthesized and crystallographically characterized.[45] Attempts to polymerize ethylene or propylene using this complex failed; however, ethylene dimerization was observed. The complexes $NiI_2(carbene)_2$ (carbene = 1-R^1-3-R^2-imidazolin-2-ylidene, R^1 = Me, Bu, Pr^i; R^2 = Pr, Pr^i, Me) were synthesized and crystallographically characterized[102] to reveal a *trans*-configuration. Catalytic studies in toluene using 1-butene as a substrate showed low catalytic activity toward olefin dimerization. The reaction was performed at −15 °C and only the isopropyl carbene species was active with TON = 50. The use of ionic liquid solvents appears to significantly increase catalytic activity. For example, use of imidazolium-based ionic liquids with these same complexes showed high activities with TONs ranging from 1910 to 3510. These are significantly higher activities than that of the olefin dimerization catalyst $NiCl_2(PCy_3)_2$.

Isomerization of unactivated vinyl cyclopropanes to cyclopentanes using nickel carbene complexes has been accomplished.[103] The nickel carbene catalyst was generated *in situ* from $Ni(cod)_2$, Pr^iBF_4 salt and base. These reactions constitute a simple protocol for the preparation of cyclopentenes by the isomerization of vinyl cyclopropanes. This result, combined with recent developments in the preparation of vinyl cyclopropanes,[104] may provide a powerful new approach to the preparation of five-membered ring structures.

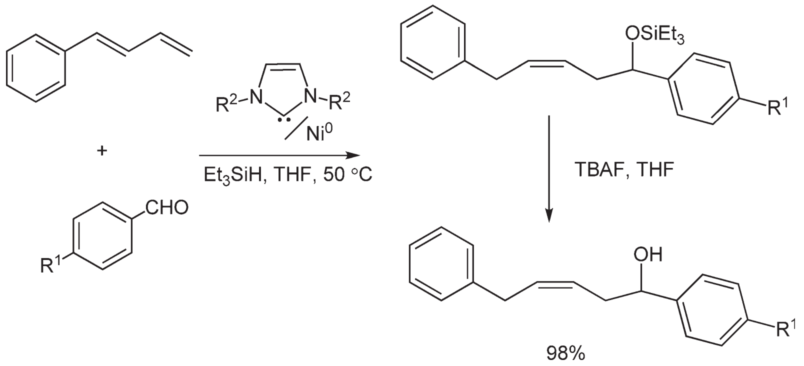
Picolyl-functionalized *N*-heterocyclic carbene complexes $NiCl_2(NHC)_2$ (NHC = 3-R-1-picolylimidazolin-2-ylidene, R = Me, Ph) show high catalytic activities toward polymerization of ethylene or norbornene in the presence of methylaluminoxane (MAO) as co-catalyst.[105] Although the detailed mechanism of the catalytic olefin polymerization is not clear, these cationic nickel complexes contain a hemilabile picolyl carbene ligand that allows the formation of a vacant site for olefin coordination, 32.



R = Me, Ph

32

The coupling of 1,3-dienes and aldehydes can be achieved in good yield stereoselectively (Equation (26)).[106]

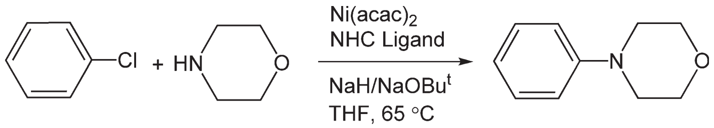


(26)

Although the precise nature of the Ni(0) carbene catalyst has not been rigorously established, the method is experimentally simple and reproducible. This new approach provides synthetic results that are complementary to those of phosphine-based catalysts.

Alkynes and aldehydes were reductively coupled to allylic alcohols by using a nickel 1,3-dimesitylimidazolium catalyst.[107] These reactions proceed regioselectively in a very high yield. A variety of aromatic, alkyl, alcoholic, and allylic R groups on alkynes and aldehydes can be tolerated. A deuterium-labeling crossover experiment was utilized to demonstrate that catalyst formulations that use PBu_3 and the NHC ligands proceed largely by fundamentally different mechanisms.

The Suzuki coupling of 4-bromo-acetophenone with phenylboronic acid was achieved using $NiI_2(tmiy)_2$ with 19 to 58% aryl halide conversion and TONs of 630 to 1930.[39] Amination of aryl chlorides was accomplished by using a nickel hydroimidazoline carbene complex (Equation (27)).[108]



(27)

The only side-product observed was the arene resulting from reduction of the starting aryl chloride. This is in fact the first example of carbon–nitrogen couplings mediated by nickel dihydroimidazolidine carbene complexes.

8.01.6.3.4 Catalytic carbon–halogen bond activation with nickel carbene complexes

The transformation of aryl and alkyl halides into arenes and alkanes represents an important chemical transformation in organic synthesis as well as in industrial applications.[109] The environmental remediation of aryl chlorides because of their deleterious environmental and health impacts has driven efforts to develop practical and effective processes for the reduction of aryl chlorides to arenes.

Dehalogenation of aryl halides was efficiently effected in refluxing THF using a catalytic combination of Ni(0)/NHC/β-hydrogen-containing alkoxide.[110] Catalytic preparations consisting of IMes·HCl (1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride) with either $Ni(acac)_2$ or Ni(0) precursors together with $NaOPr^i$ were found to be the most effective for the dehalogenation of functionalized aryl chlorides, bromides, iodides, and polyhalogenated hydrocarbons. Mechanistic studies, using isotopically labeled isopropoxide, showed that the source of the transferred hydrogen atom is the isopropoxide group. The reactivity of halogens was found to follow the general order $I > Br > Cl$. Partial defluorination (25%) was observed during the reductions of 4-bromo- and 4-chlorofluorobenzenes to fluorobenzene.

Catalytic defluorination of aryl fluorides was efficiently performed with a β-hydrogen-containing alkoxide in the presence of 3 mol.% of [1:1] Ni(0)/IMes·HCl catalyst (IMes = 1,3-dimesitylimidazol-2-ylidene).[111] Oxidative addition of the aryl fluoride to a Ni^0L species, subsequent fluoride ligand displacement by the alkoxide ligand, followed by β-hydrogen elimination were proposed as the key steps in the catalytic cycle.

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8.02
Nickel–Carbon σ-Bonded Complexes

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8.02.1 Introduction

This chapter reviews progress in the chemistry of nickel complexes containing σ-bonded carbon ligands within the period 1993–2004. The first year (1993) overlaps with the coverage of COMC (1995) to ensure the continuity of the series. The account will be limited to compounds containing alkyl, alkenyl, aryl, and alkynyl ligands as well as alkylidene- or alkylidyne-bridged binuclear and polynuclear complexes. Although it is now recognized that heterocyclic carbenes are essentially σ-carbon ligands, nickel complexes with these ligands are described in Chapter 8.01. A strong emphasis is made on synthesis and reactivity, but significant structural or spectroscopic properties are frequently mentioned in the text or displayed in schemes and equations. Lists of compounds (restricted to those that have been isolated in pure form) can be found in the tables, which also indicate the characterization data available for each of them.

The organization of the chapter follows the general lines laid out in COMC (1982) and COMC (1995), although it presents some relevant variations. Thus, the distinction between "monoligand" and "bisligand" complexes has been omitted, but in order to systematize the large body of information relative to the synthesis of mono and bis(organo)-nickel complexes (Section 8.02.3), these have been classified according to the open or cyclic structure of the ligands, distinguishing between "simple" mono and bis(organo)nickel derivatives, monoorganonickel complexes containing a chelating anionic ligand (e. g., acetylacetonate, salicyladiminate, etc.) and cyclometallated complexes, that is, those in which the C-bonded ligand presents a secondary donor interaction with the nickel atom, involving a coordinate bond. The latter compounds have been distinguished from metallacycles, which have been defined as those containing a dianionic chelating ligand with at least one Ni–C bond. Metallacycles are discussed separately in Section 8.02.4.

As in COMC (1982) and COMC (1995), catalysis results are only mentioned in those cases where σ-bonded organometallic complexes have been isolated or characterized. However, since the discovery of the α-diimine nickel catalysts in 1996, the interest in the field has been strongly polarized toward the study of the new olefin polymerization and oligomerization catalysts, many of them σ-organonickel compounds themselves. In order to account for this important aspect of the chemistry of σ-bonded organonickel compounds, the different kinds of catalysts and mechanistic studies are discussed in Section 8.02.3.4.4.

The rapid growth of nickel chemistry is also noticeable in the emergence of new types of compounds. Stable σ-organonickel complexes in oxidation states other than 2 are becoming more common. These compounds are described in Section 8.02.7. The connection of the organometallic chemistry of nickel with important biological processes continues to lead to significant advances, such as the preparation of organometallic compounds with macrocyclic ligands, which are reviewed in Section 8.02.8.

8.02.2 Ligand-Free and Solvated σ-Organonickel Complexes

Base-free complexes of Ni of composition NiR_2 or Ni(R)X, where R is a σ-bound organic fragment and X is a simple anion (halide, pseudohalide, hydroxide) are in general very unstable species, and their isolation remains very rare. However, the chemistry of anionic "ate" complexes $[NiR_{2+n}]^{n-}$ and $[NiR_2(\mu\text{-}X)]_2{}^{-}$ is growing steadily, especially in the case of the perfluoroaryl derivatives (Table 1). This section will cover all these compounds as well as their adducts

Table 1 Ligand-free and solvated compounds

Compound[a]	*Characterization*[b]	*References*
$Ni\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2$, **1**	A, *m/d*, MS, IR, ^1H, ^{19}F	10
$Ni\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2dme$, **5**	A, MS, IR, ^1H, ^{19}F, XR	15
$\{Li(THF)_4\}Ni(Mes)_3$, **13**	XR, EPR, (dec > −10 °C)	23
$[NEt_4]_2[Ni(C{=}C{-}C{=}N)_4]$, **6**	IR, XR	16
$\{Li(THF)\}_2Li_2\{NiMe_4\}_2$, **10**	A, ^{13}C, ^7Li, XR	20
$\{Li(THF)\}_4\{NiMe_4\}_2$, **11**	A, ^{13}C, ^7Li, XR	20
$\{Li(THF)_2\}_2NiPh_4$, **12**	A, ^1H, ^{13}C, ^7Li, XR	21
$\{Li(OEt_2)\}_2Ni(CH_2NMe_2)_4$, **14**	A, ^1H, ^{13}C, XR	24,25
$\{Li(OEt_2)\}_2Ni(CH_2NC_5H_{10})_4$, **14**	A, ^1H, ^{13}C	24
$Li_4\{Ni(CH_2NMe)_2CH_2)_2\}_2$, **15**	A, *m/d*, MS, ^1H, ^{13}C, ^7Li, XR	26
$\{Li(OEt_2)\}_2Ni(CH_2SBu^t)_4$, **16**	^1H, ^{13}C, XR	27
$\{Li(tmda)\}_2\overline{Ni(CH_2CH_2CH_2CH_2C(O)O})_2$	A	19
$\{Li(tmda)\}_2\overline{Ni(CH_2CMe_2CMe_2C}H_2)_2$	A, *m/d*, ^1H, ^{13}C, XR	17
$\{Li(THF)\}_2\overline{Ni(CH_2CMe_2CMe_2C}H_2)_2$	A	17
$[NBu_4]_2[Ni(C_6F_5)_4]$, **17**	A, IR, ^{19}F	32
cis-$[Ni(C_6F_5)_2(THF)_2]$, **18**	IR, ^1H, ^{19}F, XR	32
cis-$[Ni(C_6F_5)_2(CO)_2]$, **21**	IR, ^1H, ^{19}F, XR, (dec > −40 °C)	32
$[NBu_4][Ni(C_6F_5)_3(CO)]$, **23**	A, IR, ^{19}F	32
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}X)_2]$, **20** X = Cl, Br, I	A, IR, ^{19}F	32
cis-$[NBu_4][Ni(C_6F_5)_2X(CO)]$, **22** X = Cl, Br, I	A, IR, ^{19}F	32
$[PPh_4]_2[Ni(C_6F_5)_2(SCN)_2]$	A, *m/d*, Λ_m, UV, ^{31}P, ^{19}F	34

(Continued)

Table 1 (Continued)

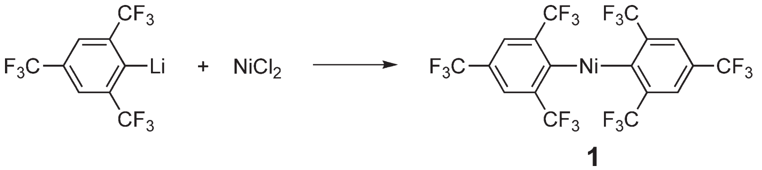
Compound[a]	*Characterization*[b]	*References*
$[PPh_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}X)_2]$, **20**	A, *m/d*, Λ_m, UV, ^{31}P, ^{19}F	34
$X = SCN, OCN, N_3$		
$[PPh_4]_2[Ni(C_6F_5)_2(\mu\text{-}SCN)_2Pd(\mu\text{-}SCN)_2Ni(C_6F_5)_2]$	A, *m/d*, Λ_m, UV, ^{31}P, ^{19}F	34
$[PPh_4]_2[Ni(C_6F_5)_2(\mu\text{-}SCN)_2Pd(SCN)_2]$	A, *m/d*, Λ_m, UV, ^{31}P, ^{19}F	34
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OAr)_2]$, **30**	A, *m/d*, Λ_m, UV, ^{1}H, ^{19}F	35
$Ar = Ph$, *p*-Tol, $C_6H_4NO_2$-4, C_6F_5		
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}NHC_6F_5)_2]$, **30**	A, *m/d*, Λ_m, UV, ^{1}H, ^{19}F	35
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}SR)_2]$, **30**	A, IR, ^{1}H, ^{19}F	36
$R = H$, Me, Et, Pr^i, Ph, *p*-Tol		
$[NBu_4]_2[Ni(C_6F_5)_2(\mu\text{-}SEt)_2Ni(\mu\text{-}SEt)_2Ni(C_6F_5)_2]$	A, IR, ^{1}H, ^{19}F, XR	36
$Ni(C_6F_5)_2(\mu\text{-}SAr)_2M(dppe)$	A, *m/d*, Λ_m, UV, ^{31}P, ^{19}F	34
$M = Ni$, Pd, Pt; $Ar = Ph$, *p*-Tol, $C_6H_4NO_2$-4		
$[NBu_4]_2[Ni(C_6F_5)_2(\mu\text{-}S)_2M(\mu\text{-}S)_2Ni(C_6F_5)_2]$, **27**	A, Λ_m, UV, IR, ^{19}F, (XR, M = Mo)	38
$M = Mo$, W		
$[NBu_4]_2[Ni(C_6F_5)_2(\mu\text{-}S)_2M(X)(Y)]$, **28**		
$M = Mo$; X,Y = S, S; S,O; O,O	A, UV, IR, ^{1}H, ^{19}F	38
$M = W$; X,Y = S, S; S,O	A, UV, IR, ^{1}H, ^{19}F	38
$[NBu_4][Ni(C_6F_5)_2(PS_2(OR)_2\text{-}\kappa^2\text{-}S,S)]$, **26**	A, Λ_m, IR, ^{1}H, ^{13}C, ^{31}P	39
$R = Me$, Et, Pr^i		
$[NBu_4][Ni(C_6F_5)_2(PS_2(OR)(Ar)\text{-}\kappa^2\text{-}S,S)]$, **25**	A, Λ_m, IR, ^{1}H, ^{13}C, ^{31}P	39
$R = Me$, Et, Pr^i; $Ar = C_6H_4OMe$-4	(XR, R = Et; Ar = Ferrocenyl)	
$R = Me$, Et, Pr^i; Ar = Fc		
$[NBu_4][Ni(C_6F_5)_2(P(S)(O)(OR)(Ar)\text{-}\kappa^2\text{-}S,O)]$, **25**	A, Λ_m, IR, ^{1}H, ^{13}C, ^{31}P, XR	39
$R = Pr^i$; Ar = Fc		
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OAr)(\mu\text{-}pz)]$	A, *m/d*, Λ_m, ^{1}H, ^{19}F	37
Ar = *p*-Tol, $C_6H_4NO_2$-4, C_6F_5	(XR, $R = C_6F_5$)	
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}7\text{-}aza\text{-}1H\text{-}indole)]$, **29**	*m/d*, Λ_m, ^{1}H, ^{19}F, XR	37
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}SR)(\mu\text{-}pz)]$	A, IR, ^{1}H, ^{19}F	36
R = H, Ph, *p*-Tol		
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}SR)(\mu\text{-}tz)]$	A, IR, ^{1}H, ^{19}F	36
R = H, Ph, *p*-Tol		
$\overline{Ni\{CH_2CH_2P(N(TMS)_2)N}(TMS)\}(\eta^2\text{-}C_2H_4)$ **31**	XR	41

tz, 1,3,4-triazolate; A, elemental analysis; *m/d*, melting or decomposition point; Λ_m, molar conductivity; MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^{1}H, ^{13}C, ^{31}P, ^{19}F, ^{7}Li, NMR spectra; XR, X-ray diffraction; CV, cyclic voltammetry; dec, decomposition temperature.

with solvent molecules or other weak ligands, which can be considered as base-free complex equivalents for most purposes. Since it is often difficult to be precise about what is understood by a "weak" ligand, we will follow the criterion adopted in COMC (1995) and will consider only ligands that do not contain group 15 donors, such as ethers, olefins, or CO. Isocyanide and heterocyclic carbene ligands will be excluded as well.

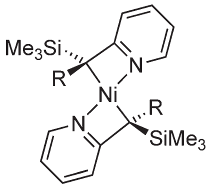
The formation of Ni–C and Ni–H bonds by the interaction of nickel atoms with organic molecules in the gas phase or in surfaces has received a great deal of attention in the past. Reference to a large body of this work can be found in COMC (1982) and COMC (1995). Recent developments in this field have used advanced mass spectrometry techniques, such as Fourier transform cyclotron resonance[1] or time-resolved mass spectrometry[2] to explore the interaction of Ni^+ ions with hydrocarbons. The selectivity of the cleavage of C–C and C–H bonds depends on the electronic state of the Ni atom. Methane activation by Ni atoms has been explored by experimental and theoretical methods. Ground state Ni(0) atoms do not react with CH_4 (although they do with SiH_4 or GeH_4), but on excitation with UV light, oxidative addition of a C–H bond takes place, giving rise to $NiH(CH_3)$, identified by its characteristic ν(Ni–H) IR absorption at $1954\,cm^{-1}$.[3] Several calculations have addressed the mechanism of the $H–CH_3$ oxidative addition to naked Ni atoms. A correct handling of electronic correlation is essential in these studies,[4] and therefore the application of DFT methods has been an important advance in this field.[5–9] In general, it is found that the process is mildly exothermic (ca. −8 to $-10\,kcal\,mol^{-1}$), but the activation energy barrier appears to be higher for ^1D or ^3D ($4s^13d^9$) configurations (ca. $10–18\,kcal\,mol^{-1}$)[6–8] than for the ^1S state ($3d^{10}$) ($0.5–4\,kcal\,mol^{-1}$).[4,5]

Apart from two early examples of homoleptic complexes ($NiMes_2$ and $Ni(CPh_3)_2$, see COMC (1982)), few examples of NiR_2 complexes have been described. The bis-aryl $Ni(C_6H_2(CF_3)_3\text{-}2,4,6)_2$, **1**, was reported by Edelmann and Belay in 1994 (**1**, Equation (1)).[10] Rather surprisingly, this compound is said to be diamagnetic and thermally stable, but unfortunately no structural data are available for it. Three other homoleptic NiR_2 compounds, **2**,[11,12] **3**,[13] and **4**[14] have been reported, but they will not be commented upon here since they are stabilized by strong intramolecular donor interactions (see Sections 8.02.3.1 and 8.02.4.2).



1

(1)



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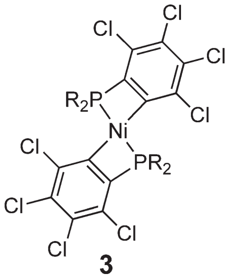

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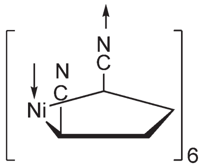
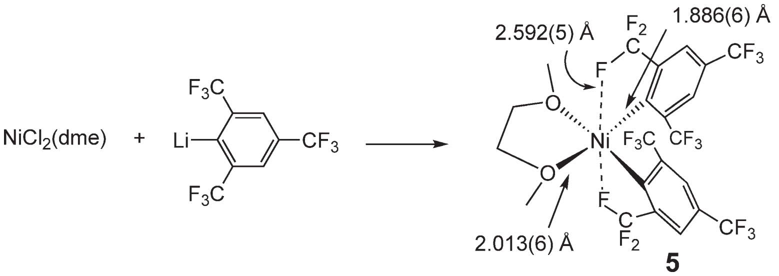


4

An adduct of compound **1** with dimethoxyethane has been prepared and characterized (Equation (2)).[15] In the crystal structure, two fluorine atoms of the *ortho*-CF_3 groups display short contacts with the nickel atom. Variable-temperature ^{19}F NMR spectra confirm the existence of F–Ni bonding interactions which exchange their positions at room temperature with $\Delta G^{\ddagger} = 12.5\,\text{kcal mol}^{-1}$ (Equation (3)).



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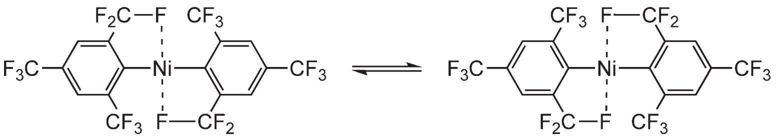
(2)

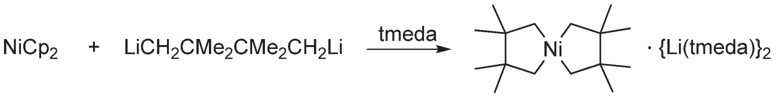


(3)

Nickel "ate" complexes of composition NiR_4^{2-} have been known for a long time, especially the tetraalkynyl derivatives, which are readily preparable compounds. A recent example is shown in Equation (4).[16] Tetraalkyl and tetraaryl nickelate compounds are very air sensitive, but thermally stable. The stability of these compounds is improved when the alkyl moiety forms a metallacyclic structure. Some of these compounds have been prepared by conventional transmetallation routes, although the choice of the starting material ($NiCp_2$, $KNi(NPh_2)_3$) seems to be important for the success of the reaction (Equation (5)).[17,18] As shown in Equations (6)–(8), their stability is further enhanced by avoiding β-H atoms and by stabilizing the alkali metal cation with strongly chelating ligands. The metallacycle **8** inserts 2 equiv. of CO_2 into the two Ni–C bonds giving a metalladilactone.[19]

$$[NEt_4]_2[NiBr_4] + 4Me_3SnC{\equiv}C{-}C{\equiv}N \xrightarrow[-4SnMe_3Br]{} [NEt_4]_2[Ni(C{\equiv}C{-}C{\equiv}N)_4] \quad (4)$$

6



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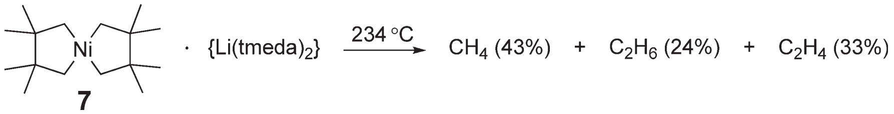
(5)



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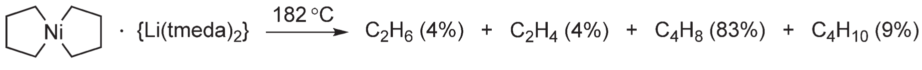
(6)



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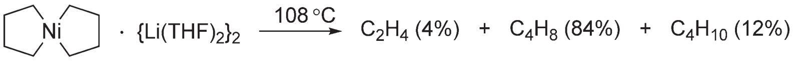
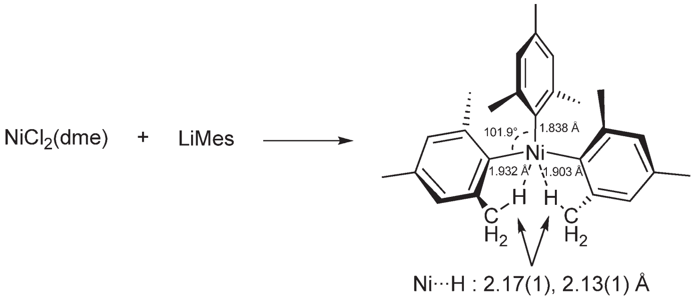
(7)



9

(8)

Binuclear complexes of Ni and Pd containing oxamidinate (OXAM) ligands have been successfully employed in the synthesis of tetramethyl and tetraphenyl metallate complexes (Scheme 1).[20,21] The methyl derivative **10** has a binuclear structure in the solid state (Figure 1) that features two $NiMe_4$ units held together in a parallel fashion by agostic interactions of the Me groups with the four Li atoms located in the intermediate wedge. Complex **10** can add two extra THF molecules to the open Li positions without noticeable changes in the structure (compound **11**). In contrast with the $NiMe_4$ complexes, the phenyl derivative **12** is monomeric and displays π-interactions of the Li atoms with the phenyl rings directed to the *ipso*-carbon atoms. Compounds **11** and **12** may be identical to those reported by Taube and Honymus in 1975.[22] An exceptional member of this kind of compounds is the trismesityl complex **13** (Equation (9)).[23] Although its synthesis follows the same route used for **5**, in this case the dme ligand is not retained. The complex is paramagnetic and decomposes above −10 °C. Its crystal structure shows an unusual tricoordinated Ni center that exhibits a T-shaped geometry, with two agostic interactions occupying vacant coordination positions.



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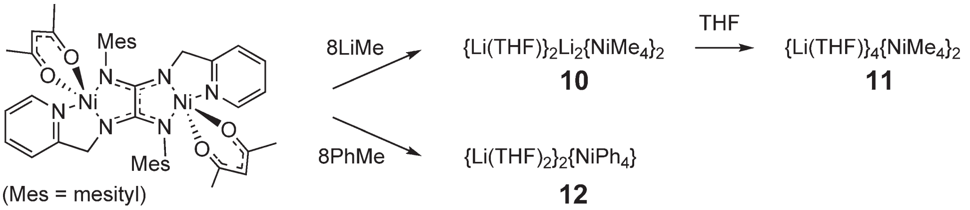
(9)



Scheme 1

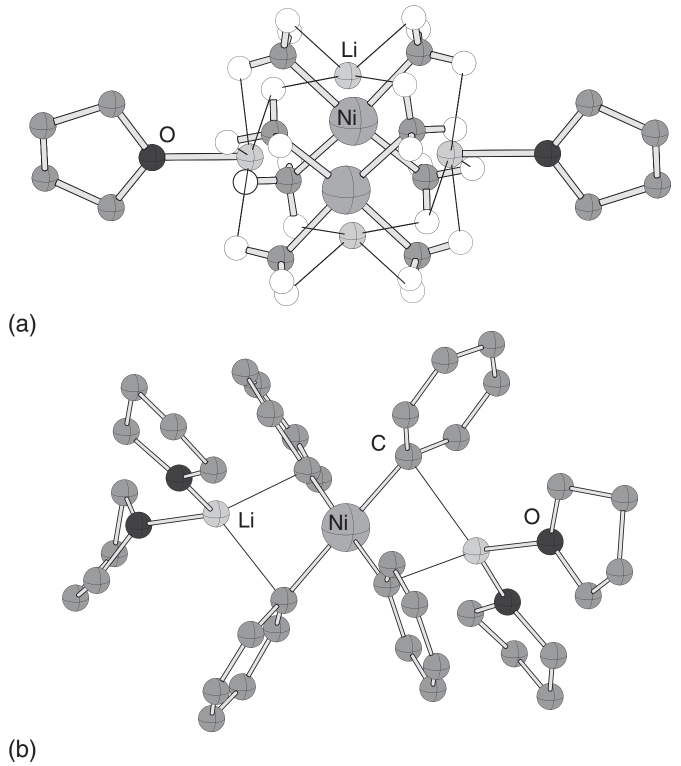
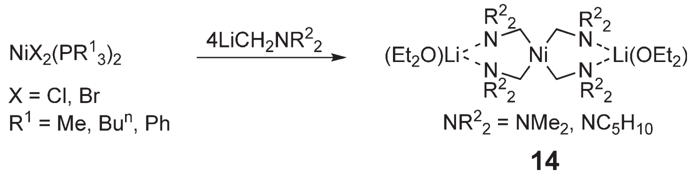
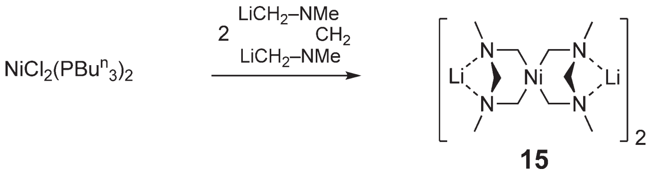


Figure 1 Crystal structures of compounds (a) **10** and (b) **12**.

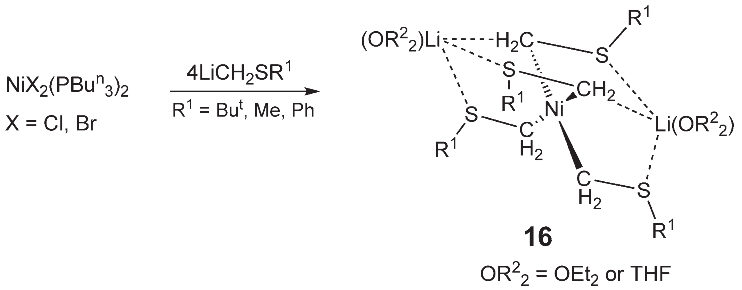
Several tetraalkylnickelate complexes containing aminomethyl[24–26] and thiomethyl[27] ligands have been reported (Equations (10)–(12)). It is remarkable that their structures show no Ni–N or Ni–S interactions. In addition to the expected Li–heteroatom bonds, interactions of Li with the α-C atoms of the functionalized alkyl groups are observed in these compounds. The cyclic compound **15** displays a binuclear structure exhibiting two parallel square-planar units bridged by Li atoms in a manner that is reminiscent of that observed for **10** and **11**.



(10)



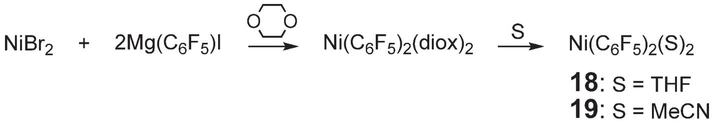
(11)



(12)

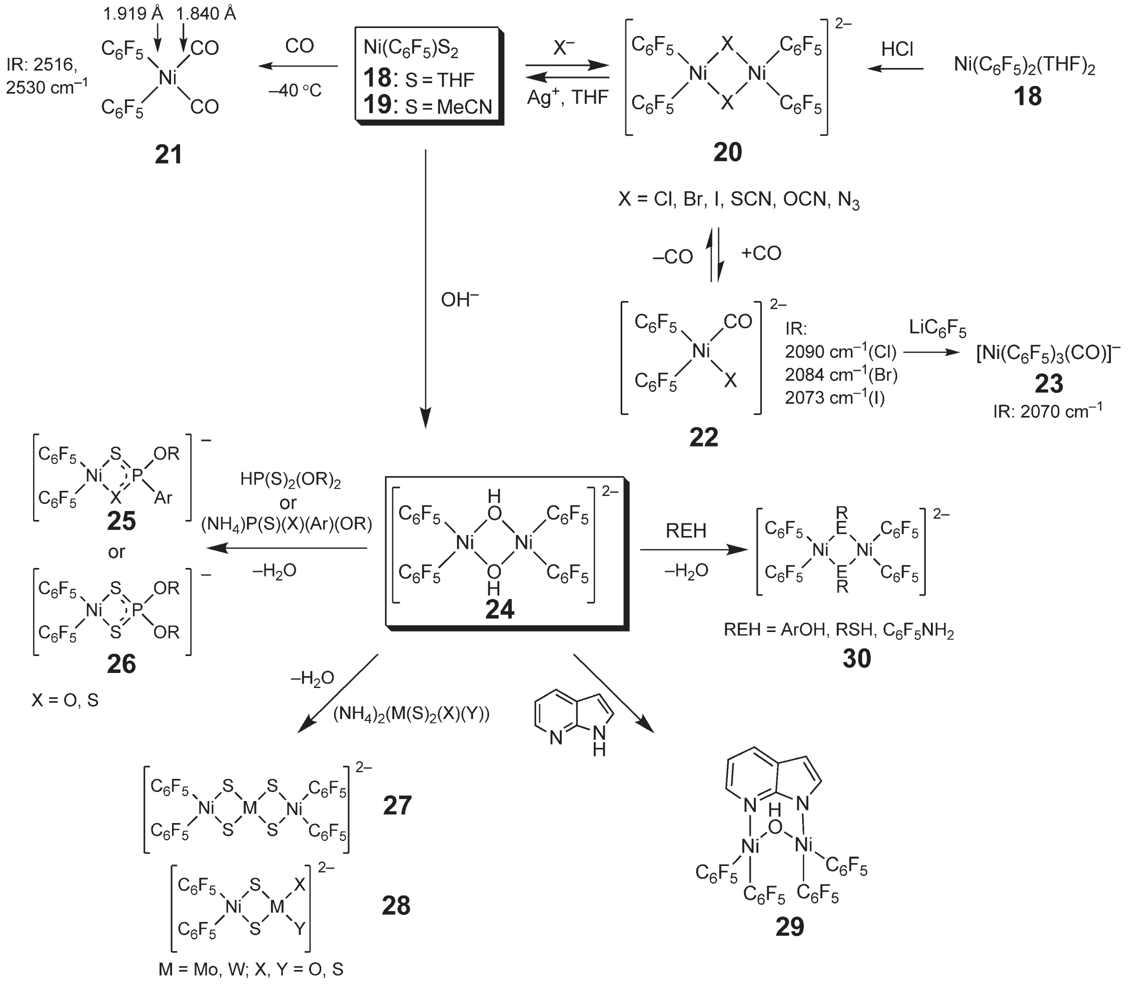
It is well known that perfluorophenyl groups impart improved stability to their organometallic derivatives, and this has allowed the development of an extensive chemistry of their ligand-free Pd and Pt complexes. The preparation and properties of several perfluorophenylnickel complexes has been known for many years (see COMC (1982) and COMC (1995)), but many other ligand-free Ni perfluorophenyl compounds have been reported recently, paralleling the chemistry of the two heavier group 10 elements. Some of these results are summarized in Equations (13) and (14) and in Scheme 2. Some complexes, such as $[NBu_4]_2[Ni(C_6F_5)_4]$ (**17**, Equation (13))[28] and $Ni(C_6F_5)_2(THF)_2$[29] (**18**) have been revisited and their characterization has been completed. The reaction of $NiBr_2$ with $Mg(C_6F_5)I$ followed by treatment with 1,4-dioxane gives the corresponding dioxane solvate,[30] which can be used in turn to obtain the acetonitrile[31] or THF adducts (Equation (14)).[32] However, the latter is best prepared from the halide-bridged anionic derivatives (see below).

$$[NBu_4]_2[NiBr_4] + 4LiC_6F_5 \longrightarrow \underset{\mathbf{17}}{[NBu_4]_2[Ni(C_6F_5)_4]} \tag{13}$$



$$NiBr_2 + 2Mg(C_6F_5)I \longrightarrow Ni(C_6F_5)_2(diox)_2 \xrightarrow{S} Ni(C_6F_5)_2(S)_2 \tag{14}$$

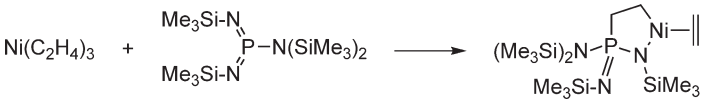
18: S = THF
19: S = MeCN



Scheme 2

The anion $[Ni(C_6F_5)_4]^{2-}$ is oxidized by Cl_2,[33] giving rise to the paramagnetic $[Ni^{III}(C_6F_5)_4]^-$ (see Section 8.02.7). It also reacts with HCl to yield **20** (X = Cl), a chloro-bridged binuclear compound, which serves as a starting material for an improved synthesis of $Ni(C_6F_5)_2(THF)_2$, by chloride abstraction with Ag^+.[32] A number of halogen and pseudohalogen binuclear derivatives **20** can also be prepared from the acetonitrile compound **19**.[34] The high degree of stabilization achieved by perfluorophenyl derivatives is reflected by the isolation and full characterization of a range of perfluoroarylnickel carbonyl complexes,[32] since compounds of this kind are usually unstable. Thus, the THF ligands of **18** can be displaced by CO at −40 °C, giving the dicarbonyl **21**. Although this compound decomposes by reductive elimination above −10 °C, it has been structurally characterized. Carbon monoxide cleaves the halide dimers **20** (X = Cl, Br, I) to the corresponding mononuclear carbonyls **22**, but due to the presence of the potentially bridging halide ligands, the process is easily reversed. Replacement of the halide ligand by a third C_6F_5 group gives the more stable complex **23**. It is interesting to mention that this compound is also formed when $[Ni(C_6F_5)]_4{}^{2-}$ is reacted with HCl in the presence of CO, indicating the preference of the electron-rich Ni center to bind CO over Cl^-. The hydroxide **24**, prepared from the acetonitrile adduct **19**, is a versatile starting material for the synthesis of a wide range of derivatives containing the $Ni(C_6F_5)_2$ unit. This compound reacts with weak acids such as ArOH,[35] RSH,[36] $C_6F_5NH_2$,[37] or heterocycles,[35,37] giving rise to the corresponding ArO, RS, C_6F_5NH, and heterocycle-bridged binuclear compounds. An analogous reaction with ammonium thiomolybdates or thiotungstates provides sulfide-bridged heterobi- and trinuclear complexes.[38] A similar strategy allows the preparation of complexes containing dithiophosphate, thiophosphonate, and dithiophosphonate ligands.[39]

The reaction of Ni(0) compounds with transmetallation reagents provides access to a wide range of alkyl "ate" complexes supported by olefin ligands. These are important due to their connection with catalytic olefin oligomerization reactions ("nickel effect"), but most of them were reviewed in COMC (1982) and COMC (1995). Fewer Ni olefin alkyl compounds are mentioned in the recent literature, probably due to the present interest in Ni(II) polymerization catalysts. Compounds of composition $Ni(R)(AlR_2)(cod)$ are thought to be produced in the reaction of $Ni(cod)_2$ with aluminum alkyls or hydrides.[40] Crystals of a unusual compound, **31**, displaying a metallacyclic moiety and an η^2-ethylene ligand have been isolated from the reaction of $Ni(\eta^2\text{-}C_2H_4)_3$ with an iminophosphorane (Equation (15)).[41] The reaction of $Ni(cod)_2$ with ligands containing an acidic hydrogen is a classical method for the synthesis of Ni(II) alkyl complexes displaying internal η^2-olefin interactions. When acetylacetone-d_2 is used in this reaction (Equation (16)), product **32** incorporates ca. 70% D in the *anti*-position of the carbon β to nickel, indicating that the mechanism involves direct attack of the proton at carbon, rather than protonation at the metal, followed by migratory insertion of the double bond into the nickel hydride.[42] Related complexes with catalytic activity in olefin oligomerization have been generated by reacting $[Ni(acac)_2]_3$ with aluminum alkyls. The structure of one of these catalysts has recently been studied in solution with the aid of UV–visible spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS) at different temperatures (Scheme 3).[43] $[Ni(acac)_2]_3$ reacts reversibly with $Al(Et)_2OEt$ in the presence of 1-hexene giving equilibrium mixtures of an alkyl–olefin complex **33** and unreacted starting materials. The equilibrium favors the latter at low temperature (−70 °C), but the alkylated complex prevails at 0 °C. The EXAFS data for this species indicate the presence of an Ni(acac) unit with three Ni–C bonds, consistent with an alkyl–olefin complex. Addition of a good donor ligand (PEt_3) gives a new product identified as the ethylphosphine complex **34**. Time-resolved EXAFS studies of the transmetallation process allowed the identification of an intermediate species **35** identified as a trinuclear compound derived from $[Ni(acac)_2]_3$ by replacement of two terminal acac groups by alkyl and olefin ligands.



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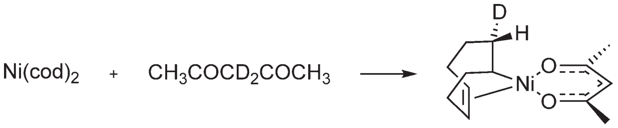
(15)



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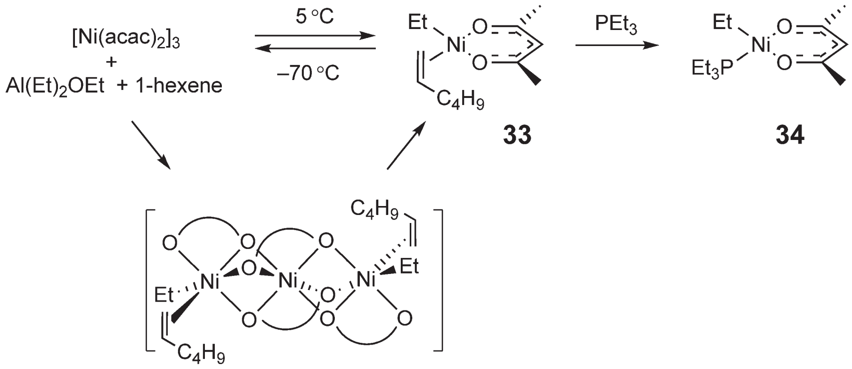


Scheme 3

8.02.3 Ni(R)XL$_n$ and NiR$_2$L$_n$ Compounds

This section covers the synthesis of nickel complexes containing one or two simple σ-organic fragments (alkyl, aryl, or alkynyl), and group 14 or 15-based donor ligands (either mono- or polydentate). A very large number of σ-bound organometallic compounds fall within this description. In order to rationalize the content of this section, a subdivision will be applied, considering first compounds in which the anionic R and X ligands form simple and well-separated fragments, and then related derivatives in which these parts are included in cyclic units: compounds containing chelating anionic ligands and cyclometallated complexes (where one organic ligand posseses a donor atom that coordinates to the metal). Since the reactivity of these compounds shares many common aspects, their chemical reactions will be addressed jointly.

8.02.3.1 Synthesis of Simple Ni(R)XL$_n$ and NiR$_2$L$_n$ Compounds

The general paths for the synthesis of simple alkyl, aryl, and other σ-bonded organometallic compounds are well established, and can be classified in methodologies involving transmetallation, oxidative addition, and electrophilic attack to Ni(0) alkene or alkyne compounds. While not contributing directly to the formation of new Ni–C bonds, electrophilic cleavage of one Ni–C bond and ligand exchange are also important for synthetic purposes. Tables 2 and 3

Table 2 Neutral complexes of composition Ni(R)XL$_n$

R	*X*	*L*	*Characterizatation*	*References*
Me	CN	dippe	XR, ^{1}H, ^{13}C, ^{31}P, A	97
Me, 154	N(Me)(*p*-Tol)	bipy	A, ^{1}H, ^{13}C	126
Me	OC$_6$H$_4$-(*cyclo*-C$_3$H$_5$S$_2$)-2-Me-3-Bu^t-5	(PMe$_3$)$_2$	A, ^{1}H, ^{13}C, IR	125
Me	O(Xyl)	(PMe$_3$)$_2$	A, ^{1}H, ^{13}C, ^{31}P	62
Me	O(Xyl)	dippe	A, ^{1}H, ^{13}C, ^{31}P	62
Me	O(Xyl)	dippp	A, ^{1}H, ^{13}C, ^{31}P	62
Me	Tf	dtbpe	A, *m/d*, ^{1}H, ^{31}P, MS, IR	50
Me	Cl	dtbpm	XR	119
Me	S(*p*-Tol)	bipy	XR, A, H	118
Me	S(Mes)	bipy	A, H	118
Me	S(C$_6$H$_4$Cl$_2$-2,6)	bipy	XR, A, H	118
Me, 49	I	(Imidazol-2-ylidene-1,3,4,5-Me$_4$)$_2$	^{1}H, MS	100
Me	I	dtbpe	A, *m/d*, ^{1}H, ^{31}P, MS, IR	50
CD$_3$	I	dtbpe	^{1}H, ^{31}P, IR	50

(Continued)

Table 2 (Continued)

R	*X*	*L*	*Characterizatation*	*References*
Et, 154	N(Et)(*p*-Tol)	bipy	A, ^{1}H, ^{13}C	125
Et, 155	OEt	bipy	A, ^{1}H, ^{13}C, IR	127,128
Et	S(Mes)	bipy	H	118
Bu^i, 154	$N(Bu^i)(Mes)$	bipy	A	129
CH_2CMe_2Ph	O(Xyl)	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P	62
CH_2CMe_2Ph	O(Xyl)	dippe	A, ^{1}H, ^{13}C, ^{31}P	62
CH_2CMe_2Ph	O(Xyl)	dippp	A, ^{1}H, ^{13}C, ^{31}P	62
$CH_2CMe_2C_6H_4Me\text{-}4$	Cl	$(PMe_3)_2$	^{1}H, ^{13}C, ^{31}P	102
Bz	Br	dippm	XR, A, ^{1}H, ^{31}P	93
Bz	Br	dippe	XR, ^{1}H, ^{31}P	93
$CH_2C_6H_4(CF_3)\text{-}4$, 130	Cl	dippm	A, ^{1}H, ^{13}C, ^{31}P	80
$CH_2C_6H_4(CF_3)\text{-}4$, 130	Cl	dippe	A, ^{1}H, ^{13}C, ^{31}P	80
$CH_2C_6H_4(CF_3)\text{-}4$, 130	Cl	dippp	A, ^{1}H, ^{13}C, ^{31}P	80
$CF_2CF_2C_6H_4I\text{-}2$	Cl	dcpe	^{31}P, ^{19}F	120
$CH(PMe_3{}^+)CMe_2Ph\ OH^-$	Cl	$(PMe_3)_2$	^{1}H, ^{13}C, ^{31}P	130
$CF_2CF_2C_6H_4I\text{-}2$	I	dcpe	^{31}P, ^{19}F, MS	120
CH_2TMS	O(Xyl)	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P	62
CH_2TMS	O(Xyl)	dippe	XR, A, ^{1}H, ^{13}C, ^{31}P	62
CH_2TMS	O(Xyl)	dippp	XR, A, ^{1}H, ^{13}C, ^{31}P	62
$CH(TMS)_2$, 38	Cl	$(PMe_3)_2$	XR, A, ^{1}H, ^{13}C, ^{31}P	45
$CH(TMS)_2$	Cl	dmpe	XR, A, ^{1}H, ^{13}C, ^{31}P	45
1-(2-methylcyclo-hexenyl), 69	I	dcpe	^{1}H, ^{31}P, MS	116
$CF{=}CF_2$	I	$(PEt_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, ^{19}F	101
$CBr{=}CF_2$	Br	$(PEt_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, ^{19}F	101
$\text{-}\overline{C{=}CHCH_2CMe_2\text{-}C}_6H_4\text{-}2$	Br	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P	131
$\text{-}\overline{C{=}C\text{-}C_6H_4\text{-}2\text{-}CH(O)N}(Xyl)$	Br	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	132
$C(C{\equiv}CBu^t){=}C(Bu^t)C{\equiv}CBu^t$	Cl, Br or I	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C(C{\equiv}CTMS){=}C(TMS)\text{-}C{\equiv}CTMS$	Cl, Br or I	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C(C{\equiv}CSiPr^i{}_3){=}C(SiPr^i{}_3)\text{-}C{\equiv}CSiPr^i{}_3$	Cl, Br or I	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C(PMe_3){=}C(Bu^t)C{\equiv}CBu^t$	$(I)_2$	PMe_3	XR, A, ^{1}H, ^{13}C, ^{31}P, MS	133
$C(PMe_3){=}C(TMS)C{\equiv}CTMS$	$(I)_2$	PMe_3	XR, A, ^{1}H, ^{13}C, ^{31}P, MS	133
$C(PPh_2){=}CH(R)$, 70 R = H, Ph	Cl	dcpe	XR, ^{1}H, ^{13}C, ^{31}P, IR, MS	117
$C(PPh_2){=}CH(CO_2Me)$	Cl	dcpe	^{1}H, ^{13}C, ^{31}P, IR, MS	117
$C(Ph){=}CH(PPh_2)$, 71	Cl	dcpe	XR, ^{1}H, ^{13}C, ^{31}P, IR, MS	117
$\text{-}\overline{C{=}CH(O)ON{=}N}Ph$	Cl	$(PEt_3)_2$	A, *m*/*d*, ^{31}P, IR	69
$\text{-}\overline{C{=}CH(O)ON{=}N}Ph$, 57	Br	$(PEt_3)_2$	A, *m*/*d*, ^{31}P, IR	69
$\text{-}\overline{C{=}CH(O)ON{=}N}Ph$	Br	$(PPh_3)_2$	A, *m*/*d*, ^{31}P, IR	69
COMe	$S(C_6H_3Cl_2\text{-}2,6)$	bipy	A, ^{1}H, IR, XR	118
$COBu^t$, 48	Cl	$(PEt_3)_2$	XR	66
$\text{-}C({=}O)\overline{C{=}CH(O)ON{=}N}Ph$,136	Br	$(PEt_3)_2$	A, IR	69
$C({=}NBu^t)Ph$	Br	$(PMe_3)_2$	A, ^{1}H, ^{31}P, IR	134
$\eta^2\text{-}C({=}NBu^t)CH(TMS)_2$, 143	Cl	PMe_3	XR, A, ^{1}H, ^{13}C, ^{31}P, IR	135,45
2-Thienyl, 62	Cl	$(PEt_3)_2$	A, ^{1}H, ^{13}C, ^{31}P	68
$3\text{-Thienyl-}NO_2\text{-}5$, 63	H	$(PEt_3)_2$	A, ^{1}H, IR	68
Ph	CN	bipy	XR, A, IR	95
Ph	CN	dippe	XR, ^{1}H, ^{31}P	94,96
Ph	$\kappa^1\text{-}Bp^{Bu\text{-}t}$	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	102
Ph	$\kappa^1\text{-}Tp^{Bu\text{-}t}$	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	102
Ph, 112	NHPh	$(PMe_3)_2$	^{1}H, ^{31}P	136
Ph	NH(DiPP)	$(PMe_3)_2$	A, ^{1}H, ^{31}P	136

(Continued)

Table 2 (Continued)

R	*X*	*L*	*Characterizatation*	*References*
Ph	Cl	$(PMe_3)_2$	XR	126
Ph	Cl	dippe	A, ^1H, ^{31}P	92
Ph	Cl	dcpe	A, ^1H, ^{31}P	92
Ph	Cl	$(PPh_3)_2$	XR, ^1H, ^{13}C, ^{31}P, A	70
Ph	Br	dcpe	XR	87
Ph, **162**	SH	dippe	A, ^1H, ^{31}P	92
Ph	SH	dcpe	A, ^1H, ^{31}P	92
o-Tol	ArNNNAr ($Ar = C_6H_4F$-4)	$(PEt_3)_2$	XR, A, ^1H, ^{19}F, ^{31}P	137
p-Tol	κ^1-$Bp^{Bu\text{-}t}$	$(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P, IR	102
p-Tol	κ^1-$Tp^{Bu\text{-}t}$	$(PMe_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P, IR	102
o-Tol, **50**	Br	(Imidazol-2-ylidene-1,3,4,5-$Me_4)_2$	XR, A, ^1H, ^{13}C, MS	100
o-Tol	Br	$(PMe_3)_2$	^1H, ^{13}C	102
p-Tol	Br	$(PMe_3)_2$	A, ^1H, ^{13}C	102
Mes	PhNNNPh	$(PMe_2Ph)_2$	A, H	138
Mes, **114**	NHPh	$(PMe_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P	139,136
Mes	NH(DiPP)	$(PMe_3)_2$	A, ^1H, ^{31}P	136
Mes, **123**	$NPhC(O)NHBu^t$	$(PMe_3)_2$	XR, A, ^1H, ^{31}P	136
Mes, **123**	NPhC(O)NHPh	$(PMe_3)_2$	A, ^1H, ^{31}P	136
Mes, **122**	$NPhC(O)CHPh_2$	$(PMe_3)_2$	XR, A, ^1H, ^{31}P	136
Mes, **121**	O_2CNHPh	$(PMe_3)_2$	A, ^1H, ^{31}P	136
Mes, **36**	Br	bis(oxazoline)-4,4,4′,4′-Me_4	XR, A, ^1H, ^{13}C, MS	44
Mes	Br	$(py)_2$	XANES, EXAFS, A, ^1H, ^{13}C	46,140
Mes	Br	bipy	XANES, EXAFS, XR, A, *m*/*p*, ^1H, ^{13}C, UV, CV	99,48, 140,49
Mes	Br	$Pr^iN{=}CHCH{=}NPr^i$	XANES, EXAFS, XR, A, H	140,49
Mes	Br	$(MeO)(pzCH_2)$-$C(CH_2PPh_2)_2$	A, ^1H, ^{13}C	141
Mes	Br	phen-3,3′,4,4′-Me_4	EXAFS, A, ^1H, UV	49
Mes	Br	bipy-4,4′-Me_2	EXAFS, A, ^1H, UV	49
Mes	Br	bipym	EXAFS, A, ^1H, UV	49
Mes	Br	bpz	EXAFS, A, ^1H, UV	49
Mes	Br	bpm	EXAFS, A, ^1H, UV	49
Mes	Br	terpy	EXAFS, A, ^1H, UV	49
Mes	OMe	bipy	XANES, EXAFS, A, ^1H, ^{13}C	140
C_6H_4Ph-4	Br	$(PEt_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P	72
C_6H_4Mes-2, **51**	I	bipy-4,4′-Me_2	XR, A, H	91
nap	Cl	bipy	XR, *m*/*d*, ^1H, ^{13}C	142
nap	Cl	quinolin-PPh_2-8	XR, A, ^1H, IR	143
9-Phenanthrenyl	Br	dcpe	^{31}P	144
$C_6H_4(BC_6H_2O_2)$-2	Br	$(PEt_3)_2$	^1H, ^{13}C, ^{31}P	87
$C_6H_4(BC_6H_2O_2)$-2	Br	$(PCy_3)_2$	^1H, ^{31}P, MS	87
$C_6H_4(BC_6H_2O_2)$-2	Br	$(PPh_3)_2$	XR, ^1H, ^{13}C, ^{31}P, A, MS	87
$C_6H_4(BC_6H_2O_2)$-2	Br	dcpe	^1H, ^{31}P, MS	87
$C_6H_4(BC_6H_2O_2)$-2	Br	dppe	^1H, ^{31}P, ^{13}C, MS	87
$C_6H_4(BC_6H_2O_2)$-2	Br	dppb	^1H, ^{13}C, ^{31}P	87
$C_6H_4(CN)$-3	CN	bipy	^1H, IR	95
$C_6H_4C(O)Me$-2, **192**	Cl	dippe	A, ^1H, ^{13}C, ^{31}P, IR	76
$C_6H_4C(O)Et$-2	Cl	dippe	A, ^1H, ^{13}C, ^{31}P, IR	77
$C_6H_4(OMe)$-4	κ^1-$Bp^{Bu\text{-}t}$	$(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P	102
$C_6H_4(OMe)$-4	κ^1-$Tp^{Bu\text{-}t}$	$(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P	102

(Continued)

Table 2 (Continued)

R	*X*	*L*	*Characterizatation*	*References*
$C_6H_4(OMe)$-4	Br	$(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P	102
$C_6H_2(O_2CMe)$-2-Bu^t-3-Me-5	Cl	$(PMe_3)_2$	A, *m/d*, ^1H, ^{13}C, ^{31}P, IR	126
$C_6H_2(O_2CPh)$-2-Bu^t-3-Me-5	Cl	$(PMe_3)_2$	A, *m/d*, ^1H, ^{13}C, ^{31}P, IR	126
$C_6H_2(O_2CBu^t)$-2-Bu^t-3-Me-5	Cl	$(PMe_3)_2$	A, *m/d*, ^1H, ^{13}C, ^{31}P, IR	126
$C_6H_4(NMe_2)$-4	κ^1-Bp$^{Bu\text{-}t}$	$(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P	102
$C_6H_4(NMe_2)$-4	κ^1-Tp$^{Bu\text{-}t}$	$(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P	102
$C_6H_4(NMe_2)$-4	Br	$(PMe_3)_2$	^1H, ^{13}C, ^{31}P	102
C_6F_5	F	$(PEt_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P, ^{19}F, IR, MS	71
C_6F_5	F	dtbpe	^{31}P, ^{19}F	105
C_6F_5	Cl	$(PEt_3)_2$	^1H, ^{13}C, ^{31}P, ^{19}F	71
C_6F_5	S(*o*-Tol)	$(PMe_2Ph)_2$ or $(PMePh_2)_2$	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	S(*p*-Tol)	$(PMe_2Ph)_2$ or $(PMePh_2)_2$	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	$S(C_6H_4Cl$-4)	$(PMe_2Ph)_2$ or $(PMePh_2)_2$	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	$S(C_6H_4Cl_2-2,6)$	$(PMe_2Ph)_2$ or $(PMePh_2)_2$	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	$S(C_6H_4NO_2-4)$	$(PMe_2Ph)_2$ or $(PMePh_2)_2$	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	S(*p*-Tol)	dppe	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	$S(C_6H_4Cl$-4)	dppe	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	$S(C_6H_4Cl_2-2,6)$	dppe	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
C_6F_5	$S(C_6H_4NO_2-4)$	dppe	A, *m/d*, ^1H, ^{19}F, ^{31}P	145
1-Naphthyl-Br-9	Br	$(PMe_3)_2$	RX, A, ^1H, ^{13}C, ^{31}P, IR	79
1-Naphthyl-I-9	I	$(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P	79
2-Naphthyl-F_9, **54**	F	$(PMe_3)_2$	^1H, ^{31}P, ^{19}F	82
$C_6Cl_4(C_6Cl_5)$-3, **52**	Cl	$(PEt_3)_2$	XR	74
$C_6Cl_4(C_6Cl_5)$-4, **53**		$(PEt_3)_2$	XR	74
$C_6Cl_4(CH_2NMe_2)$-2	Cl	$(PMe_2Ph)_2$	A, H	107
$C_6Cl_4(PPh_2)$-2	Cl	$(PMe_2Ph)_2$	A, ^{31}P	13
$C_6Cl_4(PPh_2)$-2	Cl	$(PEt_3)_2$	XR, A, ^{31}P	13
$C_6Cl_4(PPh_2)$-2	Cl	$(PBz_3)_2$	A, ^{31}P	13
$C_6Cl_4(PPh_2)$-2	Cl	$(PPh_3)_2$	A, ^{31}P	13
$C_6Cl_4(PEt_2)$-2	Cl	$(PBz_3)_2$	A, ^{31}P	13
C_6H_4Br-4	Br	$(PEt_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P	72
3-Anthracenyl-Br-4	Br	$(PEt_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P	72
2-Py	CN	dippe	A, ^1H, ^{13}C	96
3-Py	CN	dippe	A, ^1H, ^{13}C	96
4-Py	CN	dippe	A, ^1H, ^{13}C	96
2-PyF_3-3,5,6	F	$(PEt_3)_2$	A, ^1H, ^{31}P, ^{19}F, ^{13}C, MS, IR	71
2-$PyF_3(CH{=}CH_2)$-3, **157**	F	$(PEt_3)_2$	^1H, ^{19}F, ^{31}P	111
2-PyF_4, **42**	F	$(PEt_3)_2$	A, ^1H, ^{31}P, ^{19}F, ^{13}C, MS, IR	71,54,110
2-PyF_4, **126**	Cl	$(PEt_3)_2$	A, ^1H, ^{13}C, ^{31}P, ^{19}F, IR	110
2-PyF_4, **127**	OTf	$(PEt_3)_2$	XR, A, ^1H, ^{31}P, ^{19}F, ^{13}C, MS, IR	54
2-PyF_4	OPh	$(PEt_3)_2$	XR, A, ^1H, ^{31}P, ^{19}F, ^{13}C, MS, IR	54
3-PyF_4	Cl	$(PEt_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P, ^{19}F	55
3-PyF_4	Cl	$(PCy_3)_2$	XR, A, ^1H, ^{13}C, ^{31}P, ^{19}F	55
3-PyF_3Cl-5	Cl	$(PEt_3)_2$	A, ^1H, ^{13}C, ^{31}P, ^{19}F, IR, MS	71
2-PyCl-3, **58**	Cl	$(PEt_3)_2$	A, ^1H, ^{13}C, ^{31}P, MS	88
2-PyCl-3	Cl	dcpe	A, ^1H, ^{13}C, ^{31}P, MS	88
4-PyBr-3/3-PyBr-4 (isomeric mixture)	Br	$(PPh_3)_2$	^1H, ^{31}P	88
4-PyBr-3/3-PyBr-4 (isom. mixt.), **61**	Br	dcpe	^1H, ^{31}P, IR, MS	88
6-Pyrimidyl-F_2-3,4	F	$(PEt_3)_2$	A, ^1H, ^{13}C, ^{31}P, ^{19}F, IR	81

(Continued)

Table 2 (Continued)

R	*X*	*L*	*Characterizatation*	*References*
6-Pyrimidyl-F_2-3,4	HF_2	$(PEt_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, ^{19}F, IR	81
5-Pyrimidyl-F_3	Cl	$(PEt_3)_2$	A, ^{19}F, ^{31}P	83
4-Pyrimidyl-F_2-Cl-5, **62**	F	$(PEt_3)_2$	A, ^{19}F, ^{31}P	83
4-Pyrimidyl-F_2-Cl-5, **63**	Cl	$(PEt_3)_2$	A, ^{19}F, ^{31}P	83
2-Quinolyl	CN	dippe	XR, A, ^{1}H, ^{13}C	96
2-Quinolyl	CN	dippe	XR, A, ^{1}H, ^{13}C	96
$C\equiv CMe_3$	Cl or Br	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C\equiv CPh$	Cl or Br	$(PMe_3)_2$	XR, A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C\equiv CTMS$	Br	$(PMe_3)_2$	XR	67
$C\equiv CSiEt_3$	Cl or Br	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C\equiv CSiPh_3$	Cl, Br or I	$(PMe_3)_2$	XR, A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C\equiv CPh$	Br	$(PMe_3)_3$	A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C\equiv CPh$	I	$(PMe_3)_3$	XR, A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C\equiv CSiPh_3$	Br or I	$(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P, IR	67
$C\equiv CCl$	Cl	$(PBu_3)_2$	A, ^{13}C, ^{31}P, IR	89
$C\equiv CCl$, **67**	Cl	$(PPh_3)_2$	A, IR	89
$C\equiv CPMe_3{}^+BPh_4{}^-$	Cl	$(PMe_3)_2$	^{31}P, IR	89
$C\equiv CPMe_3{}^+Cl^-$	Cl	$(PPr_3)_2$	A, ^{31}P, IR	89
$C\equiv CPPr_3{}^+\ BPh_4{}^-$	Cl	$(PPr_3)_2$	A, ^{31}P, ^{13}C, IR	89
$C\equiv CPBu_3{}^+Cl^-$	Cl	$(PBu_3)_2$	A, ^{31}P, ^{13}C, IR	89
$C\equiv CPBu_3{}^+BPh_4{}^-$	Cl	$(PBu_3)_2$	A, ^{31}P, ^{13}C, IR	89
$C\equiv CPBu_3{}^+PF_6{}^-$, **68**	Cl	$(PBu_3)_2$	A, ^{31}P	89
$C\equiv CPBu_3{}^+ClO_4{}^-$	Cl	$(PBu_3)_2$	A, ^{31}P	89
$C\equiv CPBu_3{}^+SbF_6^-$	Cl	$(PBu_3)_2$	A, ^{31}P	89

Xyl, 2,6-dimethylphenyl, DiPP, 2,6-diisopropylphenyl; A, elemental analysis; *m/d*, melting or decomposition point, MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^{1}H, ^{13}C, ^{31}P, ^{19}F, NMR spectra; XR, X-ray diffraction; CV, cyclic voltammetry.

Table 3 Cationic complexes of composition $[NiRL_n]^+X^-$

R	*X^-*	*L_n*	*Characterization*	*References*
Me	PF_6, SbF_6, $BAr^F{}_4$, or Tf	bipy, N(Me)═CH(*p*-Tol)	^{1}H, ^{13}C, IR	146
Me, **150**	PF_6	bipy, N(Pr^i)═CH(*p*-Tol)	^{1}H, ^{13}C, IR	146
Me	PF_6	bipy, N(Bu^t)═CH(*p*-Tol)	^{1}H, ^{13}C, IR	146
Me	PF_6	bipy, N(Bz)═CH(*p*-Tol)	A,^{1}H, ^{13}C, IR	146
Me	PF_6	bipy, N(Ph)═CH(*p*-Tol)	^{1}H, ^{13}C, IR	146
Me, **73**	$BAr^F{}_4$	DiPPN═CHCH═NDiPP, Et_2O	A, ^{1}H, ^{13}C	57
Me, **73**	$BAr^F{}_4$	DiPPN═CMeCMe═NDiPP, Et_2O	A, ^{1}H, ^{13}C	57
Me	$BAr^F{}_4$	$BIAN(Xyl)_2$, H_2O	^{1}H, ^{13}C (dec > 0 °C)	58
Me	$BAr^F{}_4$	$BIAN(Xyl)_2$, Et_2O	^{1}H, ^{13}C (dec > −15 °C)	58
Me	$BAr^F{}_4$	$BIAN(DiPP)_2$, H_2O	^{1}H, ^{13}C (dec > 0 °C)	58
Me	$BAr^F{}_4$	$BIAN(DiPP)_2$, Et_2O	^{1}H, ^{13}C (dec > −15 °C)	58
Me	BPh_4	$PPh_2(CH_2)_2S(CH_2)_3S(CH_2)_2$-$PPh_2$	A, ^{1}H, ^{31}P, IR, CV	147
Me	BPh_4	$(PPh_2(CH_2)_2SEt)_2$	A, ^{1}H, ^{31}P, IR, CV	147
$CHPh_2$	$BAr^F{}_4$	dtbpe	A, ^{1}H, ^{13}C, ^{31}P	148
$COCH_3$	BPh_4	$PPh_2(CH_2)_2S(CH_2)_2$-$S(CH_2)_2PPh_2$	IR	147
$COCH_3$	BPh_4	$(PPh_2(CH_2)_2SEt)_2$	IR	147
η^2-C(═O)NHDiPP, **152**	PF_6	dtbpe	A, ^{1}H, ^{13}C, F, ^{31}P, IR	149
η^2-C(═O)NHDiPP	$BAr^F{}_4$	dtbpe	XR, A	149

(Continued)

Table 3 (Continued)

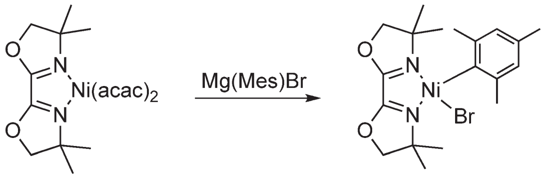
R	X^-	L_n	*Characterization*	*References*
Mes	NO_3	bipy, py	A	140
$C_6H_4(CH_2PPh_2)$-2	BF_4	$(PBz_3)_3$	A, ^{31}P	51
Mes	Br	$(py)_3$	A, ^1H, UV	140
Mes	PF_6	$(MeO)C(PPh_2)(CH_2Pz)_2$-κ^2-*P*, *N*, PPh_3	XR, A	141
2-pyF_4	BF_4	$(PEt_3)_2$, MeCN	A, ^1H, ^{13}C, ^{31}P, F, IR, MS	110
2-pyF_4, **128**	BPh_4	$(PEt_3)_2$, MeCN	A, ^1H, ^{31}P, F, IR	110
$C_6Cl_4(PPh_2)$-2	BF_4	dppe	A, ^1H, ^{31}P	13
$C_6Cl_4(PPh_2)$-2	BF_4	dppe, PMe_2Ph	A, ^1H, ^{31}P	13
$C_6Cl_4(PPh_2)$-2	BF_4	$(\kappa^1$-dppm$)_2$	A, ^1H, ^{31}P	13
$CF{=}CF_2$	$BAr^F{}_4$	$(PEt_3)_2$, MeCN	A, ^1H, ^{13}C, ^{31}P, IR	101
$CF{=}CF_2$, **131**	$BAr^F{}_4$	$(PEt_3)_2$, $CNBu^t$	A, ^1H, ^{13}C, ^{31}P, IR	101
$C{\equiv}CBu^t{}_3$	Br or I	$(PMe_3)_4$	A, ^1H, ^{13}C, ^{31}P, IR, UV	67
$C{\equiv}CPh$	Br or I	$(PMe_3)_4$	A, ^1H, ^{13}C, ^{31}P, IR, UV	67
$C{\equiv}CTMS$	I	$(PMe_3)_4$	A, ^1H, ^{13}C, ^{31}P, IR, UV	67
$C{\equiv}CSiEt_3$	Br or I	$(PMe_3)_4$	A, ^1H, ^{13}C, ^{31}P, IR, UV	67
$C{\equiv}CPr^i{}_3$	Br or I	$(PMe_3)_4$	A, ^1H, ^{13}C, ^{31}P, IR, UV	67

Xyl, 2,6-dimethylphenyl, DiPP, 2,6-diisopropylphenyl; Ar^F, $C_6H_3(CF_3)_2$-3,5, $BIAN(Ar)_2$ = *N,N′*-bisarylacenaphthylene-1,2-diimine; A: elemental analysis; MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^1H, ^{13}C, ^{31}P, NMR spectra, XR, X-ray diffraction; CV, cyclic voltammetry; dec, decomposition temperature.

collect references for simple Ni complexes containing one Ni–C bond (neutral and cationic, respectively), while Table 4 lists non-cyclic complexes that possess two Ni–C bonds. References for binuclear or polynuclear complexes without metal–metal bonds can be found in Tables 5 and 8.

8.02.3.1.1 Synthesis by transmetallation

Transmetallation is widely used for the synthesis of organonickel complexes, especially those containing two Ni–C bonds. Probably because of their ready availability, organomagnesium reagents are the most commonly used by far. In addition, they often allow the introduction of one organic group in a selective manner. Recent examples of selective monoalkylation reactions are shown in Equation (17)[44] and Scheme 4. The sterically crowded derivative **38** reversibly loses one phosphine ligand, giving rise to a chloro-bridged binuclear compound, **37**.[45] Addition of PMe_3 regenerates the *cis*-mononuclear derivative **38**.



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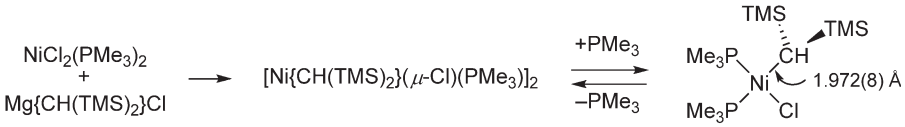
(17)



37 **38**

Scheme 4

Table 4 Complexes of composition NiR_2L_n

R	*L*	*Characterization*	*References*
Me	$(py)_2$	^{1}H, ^{13}C	46
Me	bipy	XR, EXAFS	49,118
Me	Xyl-2,6-N=C(H)C(H)=NXyl-2,6	A, ^{1}H, ^{13}C	46,57
Me	Xyl-2,6-N=C(Me)C(Me)=NXyl-2,6	A, ^{1}H, ^{13}C	46
Me	DiPP-2,6-N=C(H)C(H)=NDiPP-2,6	A, ^{1}H, ^{13}C	46,57
Me	DiPP-2,6-N=C(Me)C(Me)=NDiPP-2,6	A, ^{1}H, ^{13}C	46
Me	BIAN(Ar)$_2$, Ar = Xyl, DiPP	^{1}H, ^{13}C, dec > −10 °C	58
Me, **45**	$(:\overline{CN(Bu^t)CH{=}CHN})CH_2CH_2(\overline{NCH{=}CH(Bu^t)N}C:)$	A, ^{1}H, ^{13}C, XR	64
Me	dippe	A, ^{1}H, ^{13}C, ^{31}P	62
Me	dippp	A, ^{1}H, ^{13}C, ^{31}P	62
Me	dtbpe	A, *m/d*, IR, ^{1}H, ^{13}C, ^{31}P, XR	50
Me	$(C_6H_4OMe\text{-}2)_2PCH_2CH_2P(C_6H_4OMe\text{-}2)_2$	^{1}H, ^{13}C, ^{31}P	127
CD_3	dtbpe	IR, ^{1}H, ^{31}P	50
Et	BIAN(Ar$_2$), Ar = Xyl, DiPP^i	^{1}H, ^{13}C	59
Pr^n, **74**	BIAN(Ar$_2$), Ar = Xyl, DiPP^i	^{1}H, ^{13}C	59
Bu^i	bipy	A, IR, ^{1}H, ^{13}C	128
CH_2CMe_2Ph	$(py)_2$	^{1}H, ^{13}C	46
$C(CN)_3$	(2-Methylimidazole)$_2$	A, UV–Vis, IR	150
$C(CN)_3$	(4-Methylimidazole)$_2$	A, UV–Vis, IR	150
Bz	$(py)_2$	^{1}H, ^{13}C, XR	46
Bz	bipy	^{1}H, ^{13}C	46
Bz	tmda	^{1}H, ^{13}C	46
$CH_2C_6H_4Me$-2	dmpe	A, ^{1}H, ^{13}C, ^{31}P	61
$CH_2C_6H_4Me$-2	depe	A, ^{1}H, ^{13}C, ^{31}P	61
$CH_2C_6H_4Me$-2	dippe	A, ^{1}H, ^{13}C, ^{31}P	61
CH_2CN, **39**	dppe	^{1}H, ^{31}P, dec > −40 °C	47
CH_2SMe, **40**	$(PBu_3)_2$	A, ^{31}P, ^{13}C, XR	27
CH_2SBu^t, **40**	$(PBu_3)_2$	A, ^{31}P, ^{13}C, XR	27
CH_2SPh, **40**	$(PBu_3)_2$	A, ^{31}P, ^{13}C, XR	27
CH_2TMS	$(py)_2$	A, ^{1}H, ^{13}C	46
CH_2TMS	Xyl-2,6-N=C(H)C(H)=NXyl-2,6	A, ^{1}H, ^{13}C	46
CH_2TMS	Xyl-2,6-N=C(Me)C(Me)=NXyl-2,6	A, ^{1}H, ^{13}C	46
CH_2TMS	DiPP-2,6-N=C(H)C(H)=NDiPP-2,6	A, ^{1}H, ^{13}C	46,60
CH_2TMS	DiPP-2,6-N=C(Me)C(Me)=NDiPP-2,6	A, ^{1}H, ^{13}C	46,60
CH_2SiMe_2Ph	dmpe	A, ^{1}H, ^{13}C, ^{31}P	61
CH_2SiMe_2Ph	depe	A, ^{1}H, ^{13}C, ^{31}P	61
CH_2SiMe_2Ph	dippe	A, ^{1}H, ^{13}C, ^{31}P, XR	61
cis-Mes	$(py)_2$	A, ^{1}H, ^{13}C, XR	46
trans-Mes	$(py)_2$	^{1}H, ^{13}C	46
Mes	bipy	A, UV–Vis, ^{1}H, ^{13}C, XR, EXAFS, CV	48,49,99
Mes	2,2′-bispyrazine	A, UV–Vis, ^{1}H, ^{13}C, EXAFS	49
Mes	3,3′,4,4′-Me$_4$Phen	A, UV–Vis, ^{1}H, ^{13}C, EXAFS	49
3-pyrazolyl-1-Me-4-CO_2Me-5-Cl, **55**	bipy	A, ^{1}H, *m/d*, UV–Vis, IR, XR	84,85
3-pyrazolyl-1,4-Me$_2$-5-Cl, **56**	bipy	A, ^{1}H, *m/d*, UV–Vis, IR, XR	84,85
C_6F_5	bipy	A, ^{1}H, ^{19}F, XR	86,90
C_6F_5	$R^1N{=}C(R^2)C(R^2){=}NR^1$ $R^1 = H$, $R^2 = Ph$, *o*-Tol, *p*-Tol $R^1 = Me$, $R^2 = Ph$, *o*-Tol, *p*-Tol	A, IR, ^{1}H, ^{19}F	63
C_6F_5, **47**	Ph_2PCH_2COPh	XR, ^{1}H, ^{13}C, MS	65
$C{\equiv}C$-Fc	$(PBu_3)_2$	A, UV–Vis, IR, ^{1}H, ^{13}C	121
$C{\equiv}C\text{-}PBu_3^+\ SbF_6^-$	$(PBu_3)_2$	A, IR, ^{31}P, XR	89

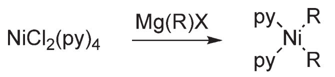
BIAN, = bis(imino)acenaphtene; DiPP, 2,6-diisopropylphenyl; Xyl, 2,6-dimetylphenyl; A, elemental analysis; *m/d*: melting or decomposition point; Λ_m: molar conductivity; MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^{1}H, ^{13}C, ^{31}P, ^{19}F, ^{7}Li, NMR spectra; XR: X-ray diffraction; CV, cyclic voltammetry; dec, decomposition temperature.

Table 5 Mixed bis-alkyl complexes NiR ^{1}R ^{2}L$_n$

R	*R*	*L$_n$*	*Characterization*	*References*
Mes, **41**	C≡C–C(NMe$_2$)═W(CO)$_5$	(PMe$_2$Ph)$_2$	A, *m/d*, MS, IR, ^{1}H, ^{13}C,^{31}P, XR	53
Me, **43**	pyF$_4$-2	(PEt$_3$)$_2$	A, IR, ^{1}H, ^{13}C, ^{31}P, ^{19}F	54
Me	pyF$_4$-3	(PEt$_3$)$_2$	A, ^{1}H, ^{13}C, ^{31}P, ^{19}F, XR	55
Ph, **44**	pyF$_4$-2	(PEt$_3$)$_2$	A, IR, ^{1}H, ^{13}C, ^{31}P, ^{19}F	54
Mes, **151**	C(CO$_2$Me)═C(CO$_2$Me)NHPh	(PEt$_3$)$_2$	A, ^{1}H, ^{31}P	136
Me	C(C≡CR)═C(R)C≡CR R = TMS, Ph, C≡CH, C≡CCH$_3$, C≡CCH$_2$TMS, C≡CC$_6$H$_{11}$, C≡CPh, C≡CSiPh$_3$, C≡CCH$_2$Br	(PMe$_3$)$_2$	^{1}H, ^{31}P	52
Bu^t	C(C≡CR)═C(R)C≡CR R = C≡CC$_6$H$_{11}$, C≡CPh,C≡CC$_6$H$_4$F-4	(PMe$_3$)$_2$	^{1}H, ^{31}P	52
Me	κ^2*C*,*P*-[C(═O)C$_6$H$_4$PPh$_2$-2]	(PMe$_3$)$_2$	A, *m/d*, ^{1}H, ^{13}C, ^{31}P	151

A, elemental analysis; *m/d*, melting or decomposition point; MS, mass spectrum, UV, ultraviolet–visible; IR, infrared; ^{1}H, ^{13}C, ^{31}P, ^{19}F, NMR spectra; XR, X-ray diffraction; CV, cyclic voltammetry.

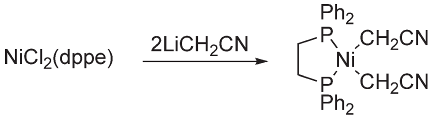
Alkylation of complexes bearing pyridine ligands yields bis(organo)nickel complexes, independently of the reagent ratio (Equation (18)).[46] These compounds are very air sensitive, and display moderate to low thermal stability, but are useful starting materials for ligand exchange reactions (see below). The *cis*-configuration is strongly favored for the dialkyls, but the mesityl derivative is obtained as a separable mixture of *cis*-and *trans*-[Ni(Mes)$_2$py$_2$].



R = Me, CH$_2$TMS, CH$_2$Ph, CH$_2$CMe$_2$Ph, Mes

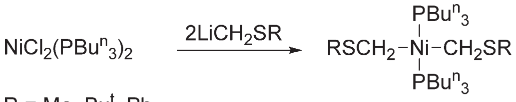
(18)

Owing to their stronger transmetallating power, organolithium compounds are frequently employed in the preparation of dialkylnickel derivatives. These transmetallation reactions are usually fast and take place at low temperature, allowing the generation of thermally unstable dialkyl compounds like **39** (Equation (19)).[47] As discussed in Section 8.02.1, an excess of the organolithium reagent can displace the co-ligands to give tetraorgano-nickelate complexes, but for thiomethyl derivatives, this process can be performed in a stepwise manner, allowing the isolation of compounds **40** (Equation (20)).[27]



39

(19)

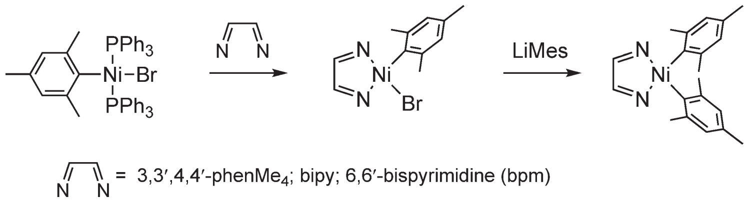


R = Me, Bu^t, Ph

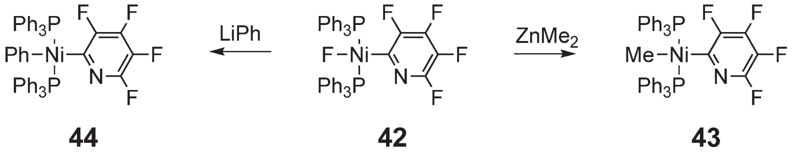
40

(20)

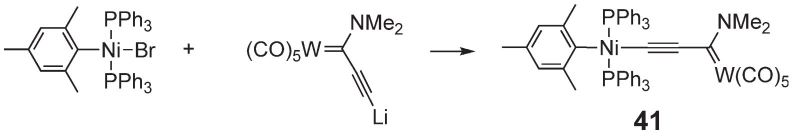
Monoalkylated species serve as starting materials for the synthesis of dialkyl compounds.[48–50] This route facilitates the synthesis of bulky dialkylated compounds (Scheme 5[48,49]), and allows also the synthesis of mixed complexes bearing two different organic groups[51–55] (Equation (21)),[53] Scheme 6.[54] The capability of experiencing double alkylation reactions without undergoing alkyl scrambling is at the basis of the ability of Ni complexes to catalyze cross-coupling reactions.[56]



Scheme 5

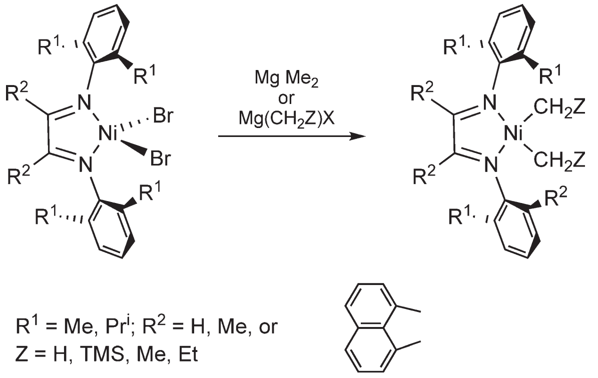


Scheme 6

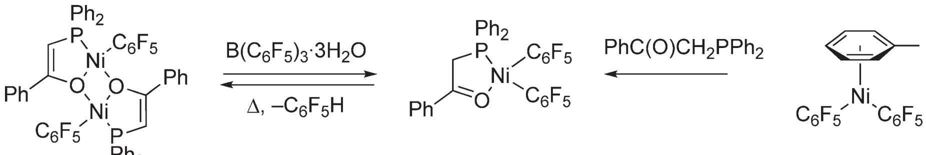


(21)

The synthesis of dialkyl complexes of Ni containing α-diimine ligands (Equation (22)) has been an important milestone in Brookhart's investigation of the Ni-catalyzed olefin polymerization reaction (see below and Section 8.02.3.4.4).[57–59] These dialkyls are extremely air sensitive materials that show only limited thermal stability, so that their isolation in pure form poses a considerable experimental challenge. Even when stabilizing trimethylsilylmethyl groups are used,[60] their synthesis by transmetallation is often plagued with low isolated yields. An alternative method for the synthesis of these compounds employs a ligand exchange reaction, using the corresponding pyridine-ligated dialkyls as precursors (Equation (23)).[23] This procedure facilitates the synthesis of methyl and trimethylsilyl complexes with α-diimine ligands in high yields. The method can also be applied for the preparation of many other derivatives (e. g., tmeda, bipy, or phosphine complexes), and the pyridine precursors can be generated *in situ* and used without isolation.[46,61,62] Bis(perfluorophenyl)nickel compounds bearing α-diimine ligands have also been prepared by a ligand exchange reaction, starting from the acetonitrile solvate $Ni(C_6F_5)_2(NCMe)_2$.[63] Ligand exchange reactions are useful when the precursor dihalo complexes are not available for transmetallation reactions, as in the case of the chelating bis-carbene compounds **45** and **46**.[64] The perfluorophenyl complex **47** has been obtained by arene displacement from labile $Ni(C_6F_5)_2(\eta^6\text{-toluene})$. This compound was originally isolated from the unusual reaction shown in Scheme 7, which involves the protonation of a binuclear ylide with $[B(C_6F_5)_3{\cdot}3H_2O]$ followed by perfluoroaryl transfer.[65] Another uncommon transmetallation reaction, shown in Equation (24), involves an acyl group transfer from Sb to Ni.[66]

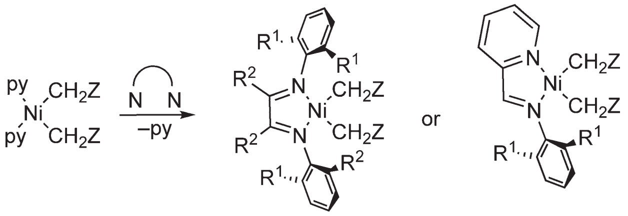


(22)



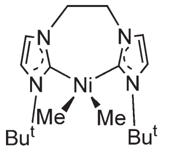
47

Scheme 7

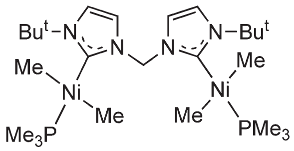


Z = H, TMS
R^1 = Me, Pr^i
R^2 = H, Me

(23)



45



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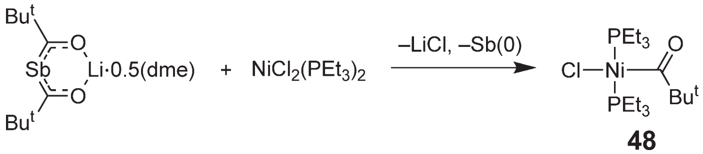


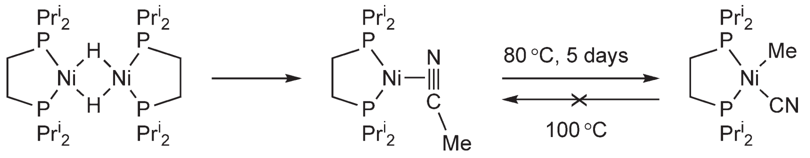
48

(24)

8.02.3.1.2 Synthesis by oxidative addition

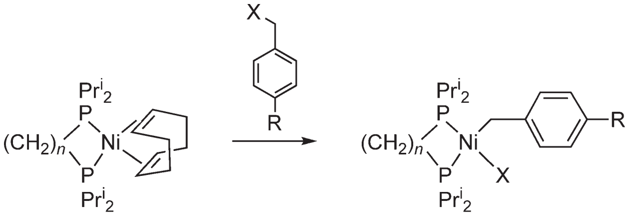
Oxidative addition is a very useful reaction for the synthesis of mono(organo)nickel compounds. The starting Ni(0) compounds used in these reactions are phosphine complexes $Ni(PR_3)_n$ ($n = 3, 4$)[67–71], or more commonly cyclooctadiene complexes of the type NiL_n(cod), which can be generated *in situ* by reacting $Ni(cod)_2$ and the corresponding ligands.[13,55,72–86] Other Ni(0) compounds (e. g., ethylene complexes) are used as well.[50,87] A very useful procedure is to generate reactive Ni(0) species by reduction of Ni(II) halo complexes,[74] often with Zn powder.[88,89] Dialkylnickel compounds such as NiR_2bipy[90,91] readily undergo reductive elimination, and act as Ni(0) precursors. The Ni(I) hydride species $[Ni(\mu\text{-H})(dippe)]_2$ has been used as an Ni(0) equivalent in oxidative addition reactions.[92–97] Electrogenerated compounds are occasionally used for synthetic purposes.[98,99]

The oxidative addition of alkyl halides to Ni(0) is infrequent, with the exception of those displaying β-unsaturated fragments, such as allyl or benzyl halides, which often lead to η^3-coordinated complexes. However, depending on the experimental conditions and the type of secondary ligands present in the Ni(0) precursor, oxidative addition of benzyl halides may afford η^1-benzyl compounds (Equation (25)).[80,93] The reaction of an Ni(0)–bis(carbene) complex with MeI produces traces of the desired methyl compound **49**, while the same reaction with 4-bromotoluene gives the corresponding aryl, **50**, in good yield (Equation (26)).[100] However, methyl complexes have been prepared by oxidative addition of MeI or MeOTf to $Ni(\eta^2\text{-}C_2H_4)$(dippe) (Equation (27)).[50] The η^2-acetonitrile complex shown in Scheme 8 slowly undergoes irreversible oxidative addition of the Me–CN bond at room temperature.[97] Other



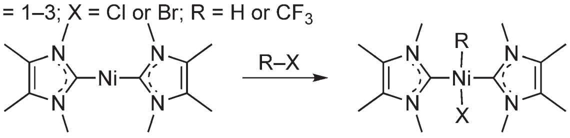
Scheme 8

η^2-nitrile complexes with higher alkyl chains require photochemical activation ($\lambda > 300$ nm) to experience R–CN bond cleavage, and the reaction is followed by β-H elimination, leading to the formation of mixtures of products.[97]



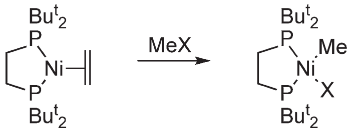
n = 1–3; X = Cl or Br; R = H or CF_3

(25)



49: R = Me
50: R = p-Tol

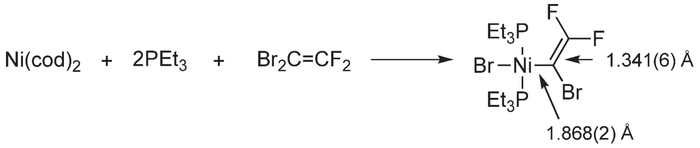
(26)



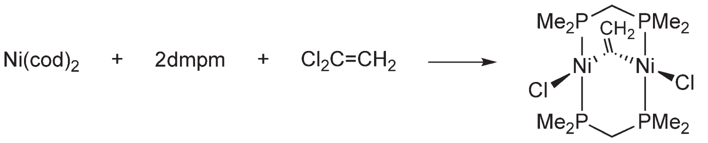
X = I or Tf

(27)

Nickel insertion into C(sp^2)–X bonds is a well-known process. Equation (28) shows an example of oxidative addition of a reactive *gem*-dibromoalkenyl halide to a single Ni(0) center.[101] In contrast, small bite-angle phosphines favor the double oxidative addition of *gem*-dihaloolefins, leading to the formation of A-frame, vinylidene-bridged binuclear compounds (Equation (29)).[73]



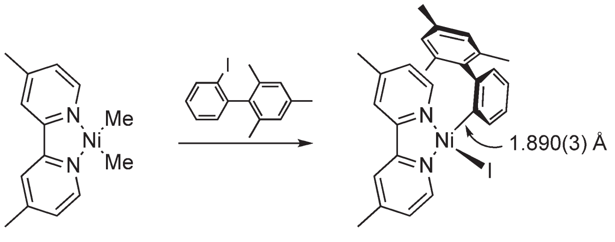
(28)



d(Ni–Ni): 1.898(2) Å
d(C=C): 1.35(2) Å

(29)

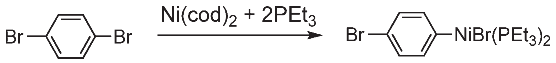
The oxidative addition of aryl halides constitutes a general method for the synthesis of a wide variety of arylnickel complexes. Aryl iodides,[91] bromides,[72,79, 87,102] and \chlorides[70,76–78,92,103] can be employed. The use of expensive aryl iodides is usually unnecessary, but facilitates the success of difficult reactions, such as the incorporation of the very bulky biphenyl fragment shown in Equation (30).[91] The resulting nickel complex, **51**, exhibits one of the largest tetrahedral distortions observed in a square-planar σ-organometallic Ni complex (33.4°). Its NMR spectra in solution are also noteworthy, since they unexpectedly show only three methyl resonances, indicating that a fluxional process (either square-planar/tetrahedral interconversion or iodine dissociation) is exchanging the two sides of this sterically hindered molecule. Oxidative addition allows the preparation of aryl complexes containing a wide range of organic functionalities that are not available by transmetallation reactions, for example, boryl esters[87] and ketones.[76,77]



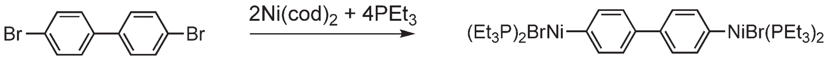
51

(30)

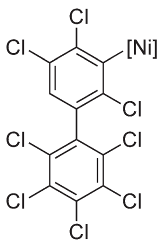
The reactivity of polyhalogenated aromatic molecules toward Ni(0) complexes has been studied due to its relevance for catalytic reductive coupling and dehydrohalogenation processes. Double oxidative addition of dibromoarenes has not been observed for 1,4-dibromobenzene (Equation (31)) or 1,9-dibromoanthracene, but it does take place when two remote centers are involved, as in 4,4′-dibromobiphenyl (Equation (32)). Interestingly, the products arising from the single oxidative addition were not detected in the latter case, independently of the reagent ratio.[72] Two singly metallated derivatives of perchlorobiphenyl, **52** and **53**, have been isolated in low yield from the reaction of this substrate with Ni(0) complexes used for catalytic dehydrohalogenation, and have been structurally characterized.[74]

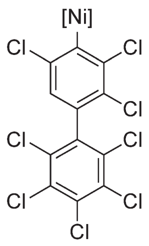


(31)



(32)

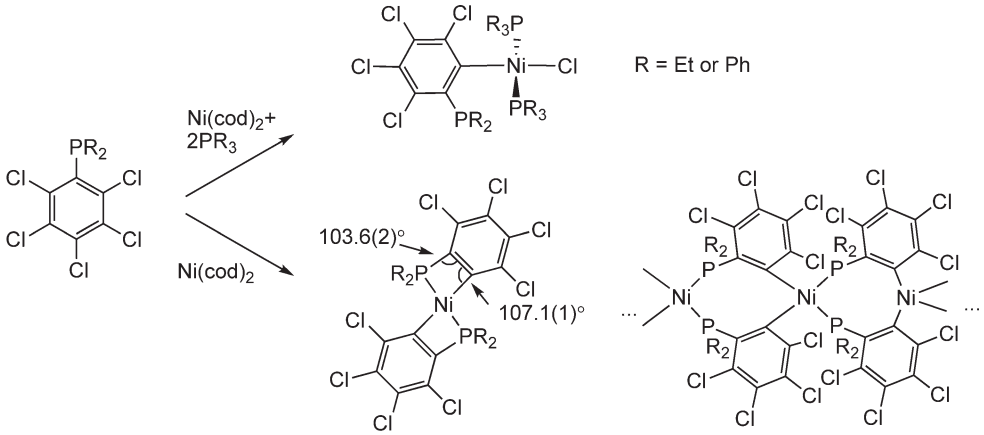




[Ni] = *trans*-NiCl(PMe$_3$)$_2$

52 **53**

Muller *et al.* have studied a group of interesting perchlorophenyl phosphine ligands (Scheme 9).[13] The reaction of these species with Ni(0) in the presence of 2 equiv. of the phosphine leads to the formation of mono aryl derivatives as a result of the selective activation of one *ortho*-chlorine atom. However, in the absence of added ligands, the reaction with Ni(cod)$_2$ takes place with the formation of the homoleptic bis(aryl) compounds **3**. While the crystal structure of the derivative with R = Et **3a** shows a bicyclic, stressed mononuclear structure, the corresponding Ni(C$_6$Cl$_4$PPh$_2$)$_2$ derivative seems to be a coordination polymer **3b**, and exhibits ferromagnetic behavior in the solid state. In solution, complexes **3** take up one extra molecule of PR$_3$ giving rise to pentacoordinated species. If the reaction of the chlorophosphine and Ni(cod)$_2$ is performed in the presence of an intermediate amount of phosphine (i.e., 1 equiv.), a mixture of products is formed.



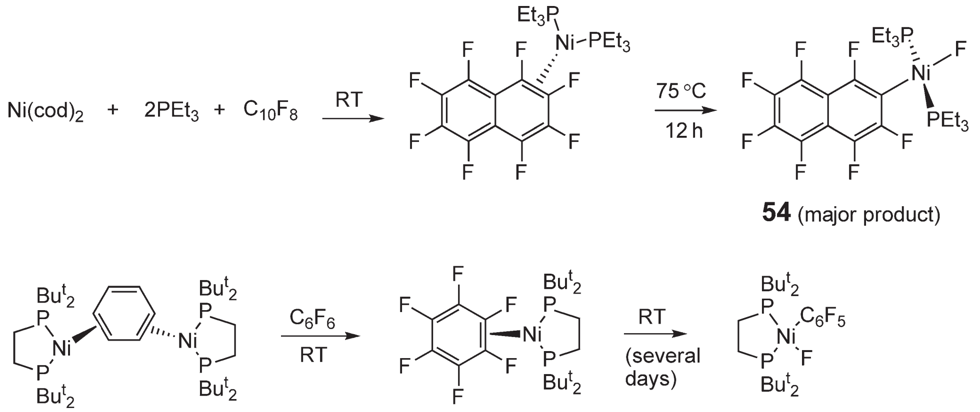
3a: R = Et **3b**: R = Ph

Scheme 9

Oxidative addition reactions of Ar–X to Ni^0(bipy) are often followed by disproportionation of the initially formed Ni(Ar)(X)bipy complex into NiAr$_2$(bipy) and NiX$_2$(bipy). It is believed that the latter process involves the intermediacy of binuclear species with bridging aryl groups, formed by dissociation of X$^-$, and hence is favored by polar solvents, such as dmf.[104] Relatively bulky aryls, such as mesityl[99] or naphthyl,[78] help to prevent disproportionation, while smaller aryl groups tend to favor it. The formation of NiAr$_2$(bipy) can be followed by reductive elimination of biaryl, although the final outcome of the overall process depends markedly on the reaction conditions.[86,104]

Unreactive aryl fluorides or cyanides react with Ni(0) complexes, giving rise to the corresponding organometallic derivatives. These reactions have received much attention in recent years, due to their potential for the activation and functionalization of the otherwise inert C–F and C–CN functionalities. Thus, simple perfluoroarenes such as perfluorobenzene or perfluoronaphthalene react with phosphine Ni(0) complexes to furnish η^2-arene complexes,[82,71,105] which slowly undergo oxidative C–F bond addition to the metal giving the corresponding (fluoro)aryl complexes (Scheme 10). DFT calculations support the involvement of η^2-arene intermediates in the path to the oxidative addition of perfluoroarenes by [Ni^0(H$_2$PCH$_2$CH$_2$PH$_2$)],[106] rather than η^2-C–F σ-complexes, which would be expected with fluoroalkanes.[9] The reaction of bipyridyl–nickel complexes with C$_6$F$_6$ is followed by disproportionation, giving rise to Ni(C$_6$F$_5$)$_2$(bipy).[86,90]

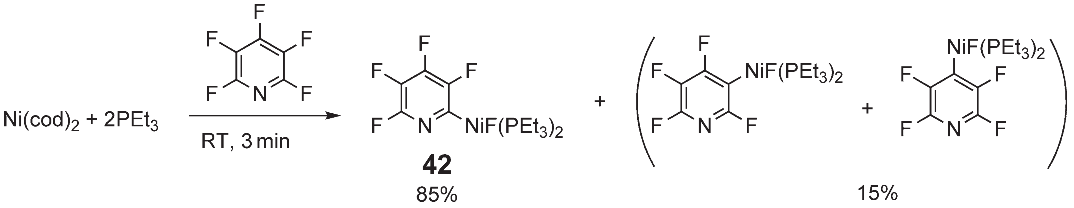
Pentafluoropyridine reacts readily with Ni(0) precursors. The products are formed within minutes, as compared with the longer reaction times (days or weeks) required by the perfluorocarbons (Equation (33)).[71] The reaction



54 (major product)

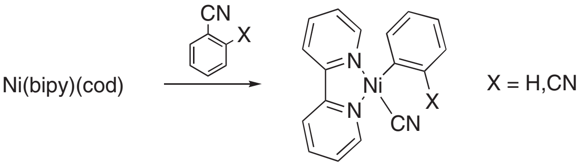
Scheme 10

proceeds with high selectivity (>80%) for the activation of the C–F bond in the 2-position, and 2,3,5,6-tetrafluoropyridine gives ca. 99% of the 2-addition product. Although the role of the N-atom in the enhancement of the rate and selectivity of the oxidative addition of fluorinated pyridines is currently not well understood, it seems likely that coordination to the Ni center could facilitate the cleavage of the neighboring C–F bonds. In agreement with this possibility, the reaction of pentafluorophenyl imines with Ni(0)/phosphine complexes takes place readily (ca. 1 h at RT), yielding cyclic C–F oxidative addition products that retain the N–Ni interaction[107,108] (see Section 8.02.3.3).



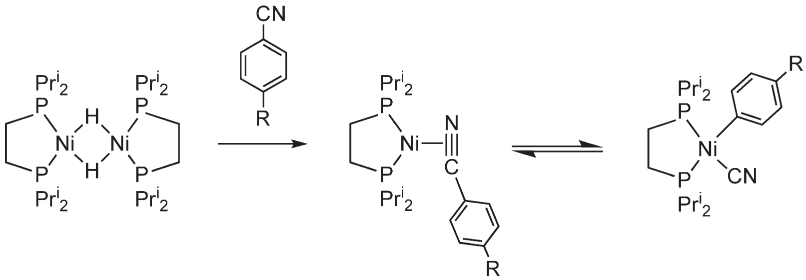
(33)

Like acetonitrile, aryl cyanides react with Ni(μ-H)(dippe) forming η^2-cyanide complexes. These undergo a slow, reversible oxidative addition reaction furnishing equilibrium mixtures of the η^2-nitrile and the (cyano)aryl complexes (Scheme 11).[94] The reaction rates and equilibrium constants measured for various *p*-substituted benzonitrile derivatives give linear Hammett plots with positive slopes, indicating that the process is favored by electron-withdrawing substituents.[96] In the case of electronically poorer heterocyclic cyanides, such as cyanopyridines or cyanoquinolines, the equilibrium strongly favors the oxidative addition product. In the Ni(bipy) system, the oxidative addition of aromatic nitriles is thermodynamically favorable, although the reaction is reversed by the addition of electron-poor olefins (Equation (34)).[95,109]



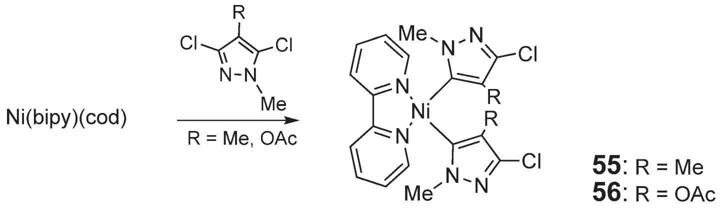
(34)

Several groups have studied the synthesis of heterocyclic derivatives of nickel, as an intermediate stage *en route* to synthetically useful applications. Thus, oxidative addition of substituted 3-chloropyrazoles to Ni^0(bipy) is followed by disproportionation and leads to bis(pyrazolyl) derivatives as stable compounds that do not eliminate the C–C coupled product readily (Equation (35)).[84,85] Nickel complexes containing sydnone fragments have been prepared by oxidative addition of either 1-bromosydnone or the corresponding mercurial derivative (Equation (36)).[69] As observed in the case of pentafluoropyridine (Scheme 6), the oxidative insertion of 2,3-dichloropyridine shows a preference for the metallation at the 2-position (Equation (37)), while 3,4-dibromopyridines give a mixture of two isomers (Equation (38)).[88] The synthesis of organonickel derivatives of fluorinated pyridines and pyrimidines has opened new synthetic pathways leading to heterocyclic compounds that are difficult to prepare by conventional organic methodologies[55,71,81,82,110,111] is given by Braun and Perutz.[112] The selectivity of the metallation at the pyridine ring can



Scheme 11

be directed by taking advantage of the different reactivities of the C–X bonds, as well as by controlling the steric properties of the metal center. Thus, 3-tetrafluoropyridyl complexes can be selectively generated from 3-chlorotetrafluoropyridine, given the much higher reactivity of the C–Cl bond (Equation (39)).[55,71] Interestingly, the preference for C–Cl/C–F activation can be reversed if the bulky PCy_3 is employed instead of PEt_3 (Scheme 12).[83]



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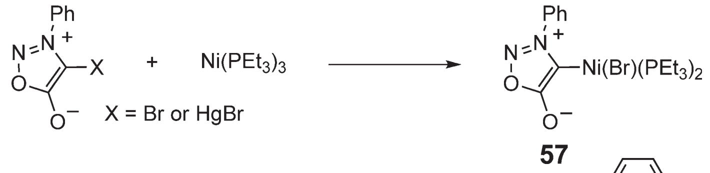

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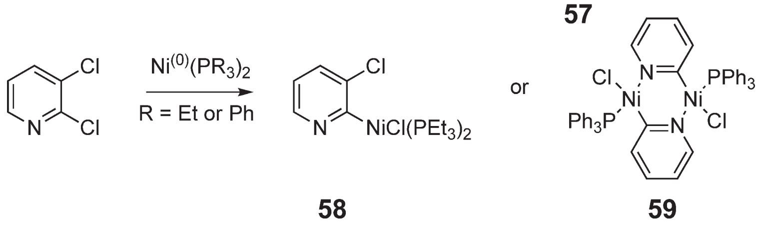

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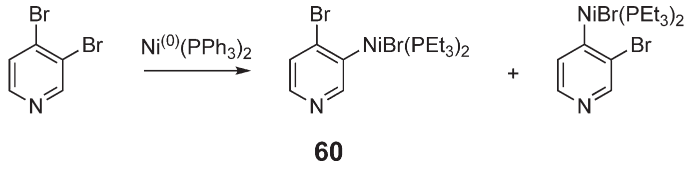

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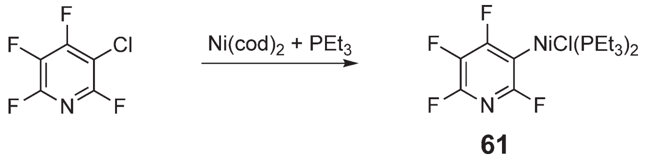

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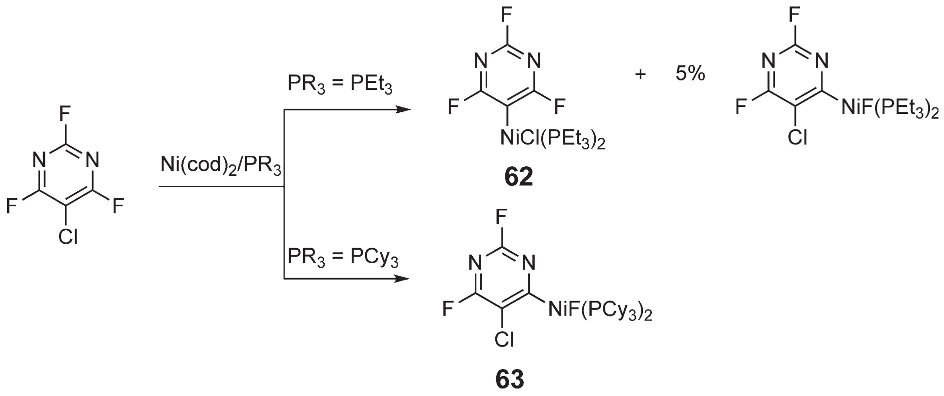
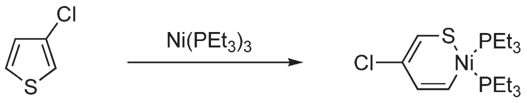


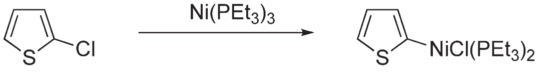
Scheme 12

The reaction of thiophenes and other related sulfur heterocycles with low-valent metal fragments has importance in relation to the catalytic hydrodesulfurization (HDS) process (see Section 8.02.4.1).[113–115] Oxidative addition of halogenated thiophenes can involve C–S bond cleavage (Equation (40)) or oxidative addition of the C–X bond (Equation (41)).[68] The selectivity of the reaction depends on the substitution pattern on the thiophene ring. In the case of 2-nitrothiophene (introduced as a mixture with 3-nitrothiophene), a surprising C–H bond activation takes place to afford **66** (Equation (42)), formulated as a hydride on the basis of its IR spectrum (ν(Ni–H): 2150 cm^{-1}).[68]



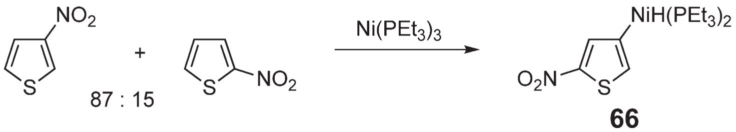
64

(40)



65

(41)



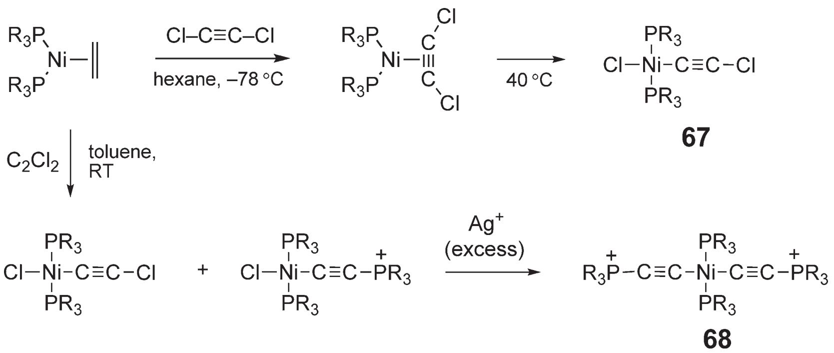
66

(42)

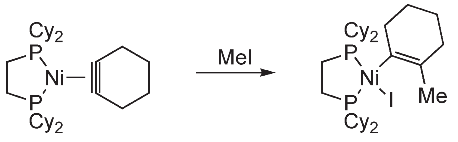
Although alkynylnickel compounds are readily available through facile exchange reactions mediated by base, or by transmetallation reactions, oxidative addition of C(*sp*)–X bonds provides an alternative method for the synthesis of such compounds. Klein has shown that a number of alkynyl chlorides, bromides, and iodides react with $Ni(PMe_3)_4$ giving rise to different kinds of alkynyl compounds: ionic 18-electron species $[Ni(C{\equiv}CR)(PMe_3)_4]^+ I^-$, pentacoordinated $Ni(C{\equiv}CR)(X)(PMe_3)_3$, and neutral, square-planar $Ni(C{\equiv}CR)(X)(PMe_3)_2$ (X = Cl or Br).[67] The reaction of dichloroacetylene with *in situ* generated Ni(0) ethylene complexes leads to the formation of chloroalkynyl or phosphonioalkynyl compounds, depending on the reaction conditions. Treatment of monophosphonioalkynyl complexes with Ag^+ induces the formation of bis(phosphonioalkynyl) complexes (Scheme 13).[89]

8.02.3.1.3 Synthesis by electrophilic attack to Ni(0) and NiR_2 complexes

Electrophilic attack on alkene or alkyne complexes can be a route to σ-organonickel derivatives. One example is the reaction of a cyclohexyne compound with iodomethane shown in Equation (43).[116] The reaction of η^2-phosphinoalkyne complexes with HCl gives a mixture of two isomeric phosphinovinyl compounds with *syn*-stereoselectivity (Equation (44)). The regioselectivity of the protonation depends on the electronic properties of the alkyne substituents, and has been correlated with the chemical shift of the ^{13}C resonances of the two acetylenic carbon atoms.[117]

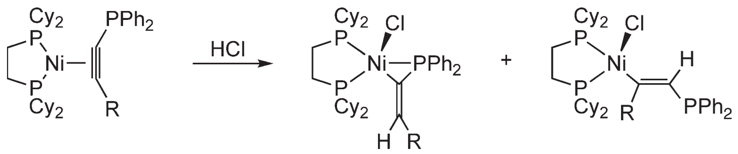


Scheme 13



69

(43)

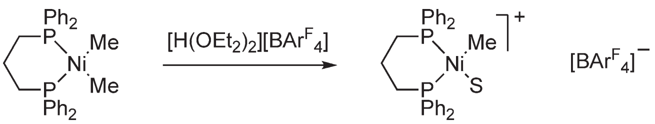


70 **71**

(44)

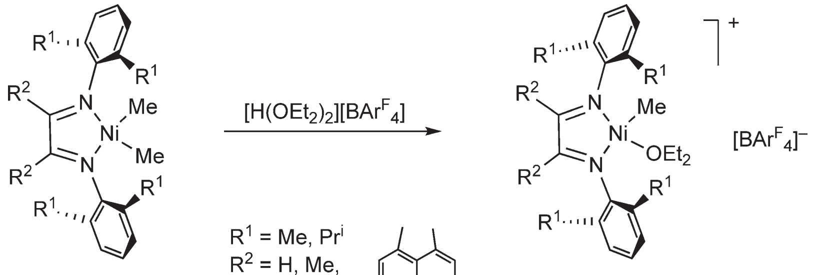
R	**70**		**71**
Me	100	:	0
Ph	92	:	8
CO_2Me	67	:	33

The selective cleavage of one Ni–C bond of a dialkyl or metallacyle with electrophilic reagents bears a formal resemblance to the latter reactions. This reaction has attained great importance in organometallic synthesis. Nickel dialkyls react selectively with many types of electrophilic reagents such as thiols,[118] phenols,[62] and other protic acids[46,50] as well as alkyl halides,[119] and triflates[50] or halogens[120] yielding monoalkylated complexes. Cleavage of Ni–C bonds by terminal acetylenes provides a path for new acetylide derivatives.[20,121] The reaction of dialkyl complexes with acids containing anions of low coordinating capability leads to highly reactive, solvated or coordinatively unsaturated species, which can act as intermediates in different catalytic processes. The synthesis of these cationic species has been reviewed.[122] This is exemplified by Brookhart's investigation of the mechanism of nickel-catalyzed polymerization reactions. The protonation of dimethyl complexes containing chelating diphosphine[123,124] or diimine[57,58,59] ligands with the oxonium acid $[H(OEt_2)_2]^+$ $[BAr^F{}_4]^-$ ($Ar^F = C_6H_3(CF_3)_3$-3,5) at very low temperatures gives rise to cationic complexes where one molecule of solvent occupies the vacant site (Equations (45) and (46)). These compounds can be isolated in the solid state and stored at low temperature. Displacement of the solvent by reactive substrates, (ethylene[57,58] or CO[124,127]) gives rise to catalytic species, whose behavior has been subjected to detailed investigations (see Section 8.02.3.4.4).



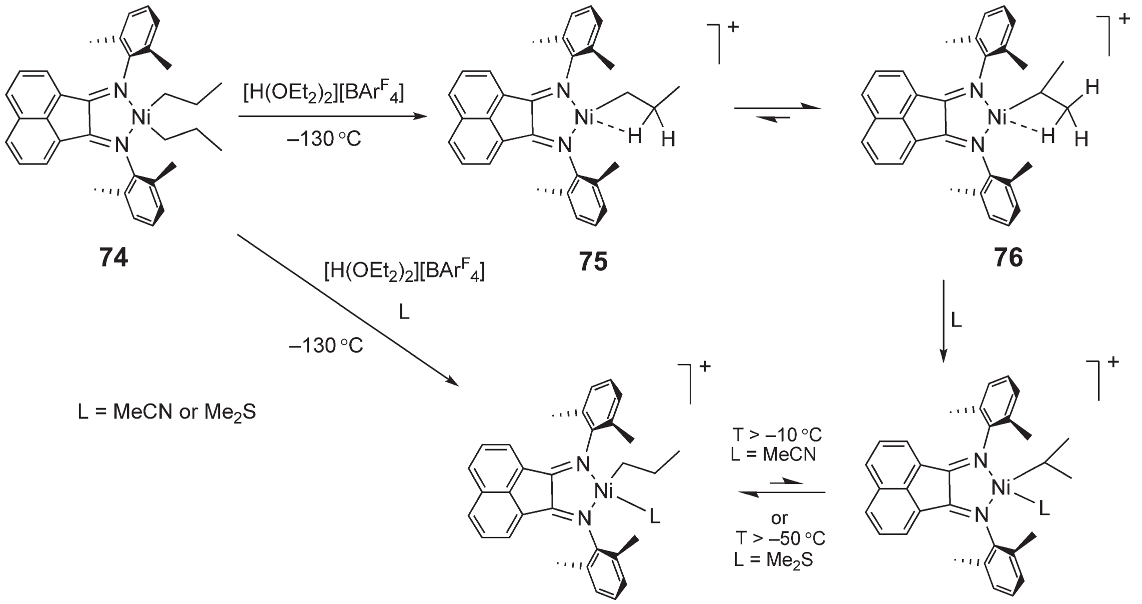
72: S = solvent molecule

(45)



73

(46)



Scheme 14

The protonation of α-diimine bis(*n*-alkyl) complexes (R = ethyl, propyl) at −130 °C gives cationic compounds where a strong β-agostic interaction competes with the solvent for the vacant position.[59] In the case of the ethyl derivatives, the ether adduct is the major product, but β-agostic alkyl complexes are formed quantitatively if the diethyloxonium acid is replaced by $[H(OPr^i{}_2)_2]^+$ $[BAr^F{}_4]^-$ as the proton source. In contrast, the protonation of the bis(*n*-propyl) derivatives with $[H(OEt_2)_2]^+$ $[BAr^F{}_4]^-$ leads to an equilibrium mixture of the *n*-propyl and the *i*-propyl agostic alkyls 75 and 76 (Scheme 14), the latter being thermodynamically favored (75 : 76 ~ 1 : 20). The initially formed *n*-propyl complex can be trapped if the protonation is carried out in the presence of ligands such as acetonitrile, dimethylsulfide, or ethylene. The equilibration of the non-agostic *n*-propyl and *i*-propyl complexes is much slower and takes place at relatively high temperature (>−10 °C for the MeCN complexes). The relative thermodynamic stabilities of the agostic complexes are opposite for agostic and non-agostic compounds, with the *n*-propyl species being strongly favored in the latter case.

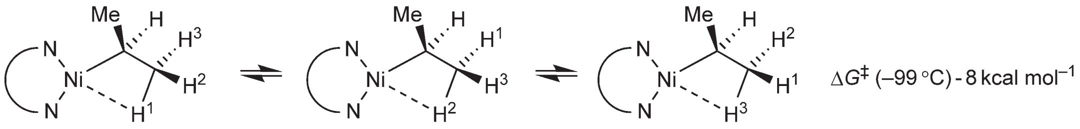
At very low temperatures (below −100 °C), the agostic protons of 75 and 76 give rise to characteristic high field ^1H NMR signals (ca. −12 to −14 ppm), but at higher temperatures rapid exchange ensues, revealing the highly dynamic nature of these compounds. Three fluxional exchange mechanisms have been identified (Scheme 15), and their energy barriers measured. In-place methyl rotation and isopropyl methyl exchange have very low activation barriers (only a few kcal mol^{-1}), and are very rapid at low temperatures (ca. −70 °C). A slower fluxional mechanism involving the exchange of the methyl and the methyne groups becomes evident at ca. −5 °C. This process involves the intermediacy of a hydride–olefin complex generated by a β-hydrogen elimination, and therefore is responsible for the *n*-propyl/*i*-propyl equilibration. The free energy of activation associated with this fluxional process (ca. 14 kcal mol^{-1}) can be taken as a close estimation of the barrier for the β-elimination step.

8.02.3.2 Synthesis of Complexes Containing Anionic Polydentate Ligands, NiR(chelate)L

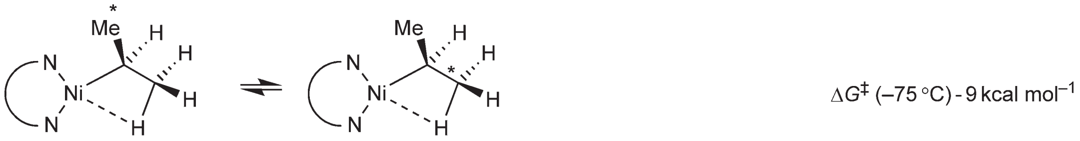
8.02.3.2.1 Synthesis from a σ-organonickel precursor

Nickel organometallic complexes containing bidentate or tridentate anionic ligands have become very common in recent years (Table 6). Interest in these compounds arises largely as a result of the quest for new neutral catalysts for olefin polymerization or oligomerization.[152–154] In most cases, the synthesis of such compounds involves the transfer of the chelate ligand to a suitable organometallic precursor, for example, by metathetical ligand exchange with a salt of the ligand anion. The synthesis of alkyl or aryl complexes containing pyrazolylborate ligands is a good example of this methodology. The success of these reactions often depends on the nature of the organic fragment attached to Ni and the steric features of the pyrazolylborate ligand. Thus, the reaction of Ni(*o*-Tol)Br$(PPh_3)_2$ with a range of

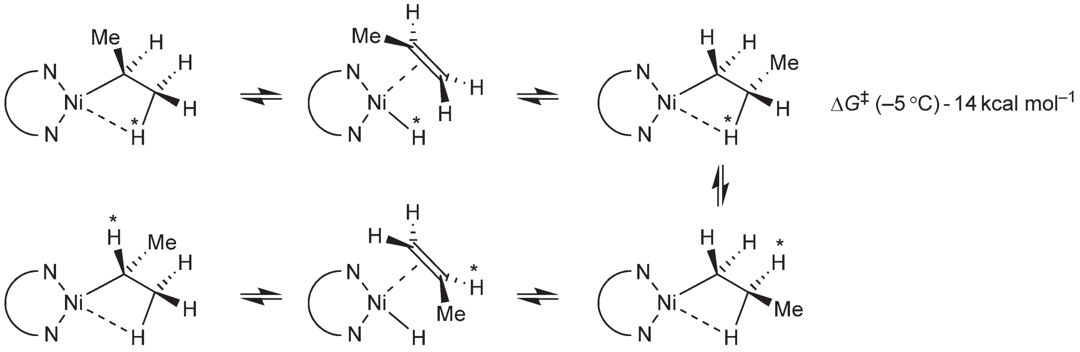
a) In-place methyl rotation:



b) Isopropyl methyl exchange:



c) Methyl–methyne exchange:



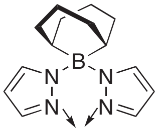
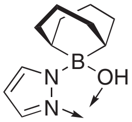
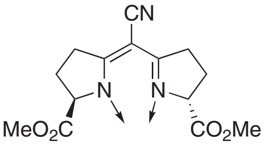
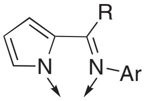
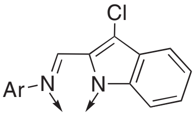
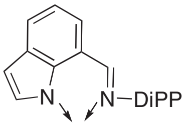
Scheme 15

Table 6 Nickel alkyl and aryl complexes containing anionic chelating ligands, Ni(R)(chelate)(L)

R	*Chelate*	*L*	*Characterization*	*References*
(a) O,O ligand				
Et	acac	PEt_3	EXAFS	43
Et, **90**	acac	PPh_3	^1H, ^{13}C, ^{31}P, IR	200
(b) N,N ligand				
Et, **93**	Xyl-N═C(Me)CHC(Me)═NXyl		XR, A, ^1H, ^{13}C	204
Pr^n, **93**	Xyl-N═C(Me)CHC(Me)═NXyl		XR, A, ^1H, ^{13}C	204
Me, **92**	Xyl-N═C(Me)CHC(Me)═NXyl	2,4-lut	A, ^1H, ^{13}C	202
Et, **92**	Xyl-N═C(Me)CHC(Me)═NXyl	2,4-lut	XR, A, ^1H, ^{13}C	202
Pr^n, **92**	Xyl-N═C(Me)CHC(Me)═NXyl	2,4-lut	XR, A, ^1H, ^{13}C	202
Mes	κ^2-*N,N″*-PhNNNPh	PPh_3	A, ^1H, IR	138
Mes	κ^2-*N,N″*-PhNNNPh	PBz_3	A, IR	138
CH_2Bu^t	Bp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
Bz, **82**	κ^2-*N,N′*-(Ar-NC(═O)C(Me)═NAr) Ar = Ph or DiPP	PMe_3	XR, ^1H, ^{13}C, ^{31}P, A	173
Bz	κ^2-*N,O*-(Ar-NC(═O)C(Me)═NAr) Ar = $C_6H_4Pr^i$-2	PMe_3	XR, ^1H, ^{13}C, ^{31}P, A	173
CH_2TMS	Bp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
Ph	Bp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
$COCH_2Bu^t$	Bp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
$COCH_2TMS$	Bp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
Ph, **137**	Tp	PMe_3	XR, A, ^1H, ^{13}C, ^{31}P, IR	102

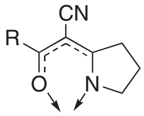
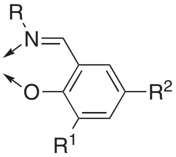
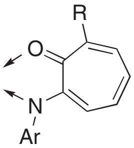
(Continued)

Table 6 (Continued)

R	*Chelate*	*L*	*Characterization*	*References*
o-Tol	Tp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
$C_6H_4Bu^t$-2, **77**	Tp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
$C_6H_3Bu^t$-2-Me-5	Tp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
COPh	Tp	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
Ph	Tp^{Me2}	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
COPh, **138**	Tp^{Me2}	PMe_3	A, ^1H, ^{13}C, ^{31}P, IR	102
o-Tol, **178**	Tp^{Ph}	PPh_3	XR, A, ^1H, ^{13}C, ^{31}P, IR	155
COEt, **139**	Tp^{iPr2}	CO	XR, A, ^1H, ^{13}C, IR	206,207
o-Tol, **78**		PPh_3	XR, A, ^1H, ^{31}P, IR, MS	156
o-Tol		PPh_3	XR, A, ^1H, ^{31}P, IR, MS	156
o-Tol, **180**		PPh_3	^1H, ^{31}P, MS	177
				
Ph	Ar = DiPP; R = H	PPh_3	XR, A, ^1H, ^{13}C	208
Ph	Ar = $C_6H_3R^1,R^2$-2,6, R = H R^1,R^2 = Me, Pr^i; Et, Et; H, Bu^t	PPh_3	A, ^1H, ^{13}C	208
Ph, **177**	Ar = Mes; R = Me	PPh_3	XR, A, ^1H, ^{13}C	169
				
nap	Ar = DiPP; Xyl; $C_6H_3Et_2$-2,6; $C_6H_4NO_2$-4; $C_6H_2F_3$-2,3,4	PPh_3	A, IR	168
nap	Ar = $C_6H_2Me_3$-2,3,6	PPh_3	XR, A, IR	168
Ph, *o*-Tol		PPh_3	XR, A, ^1H, ^{13}C, ^{31}P	171
(c) S,S ligand				
$CH(TMS)_2$	$S_2C(OMe)$	PMe_3	A, ^1H, ^{13}C, ^{31}P	45
C_6F_5, **312**	$S_2C(NR_2)$; R = Et, Pr^i, C_5H_{10}, C_4H_8	$PMePh_2$, PMe_2Ph, PEt_3	A, *m*/*d*, ^1H, ^{13}C, ^{31}P (XR for R = Pr^i)	145
κ^2-*C*,*S*-CH_2SBu^t	$B(Ph)(CH_2SBu^t)_3$		XR, ^1H, UV	209

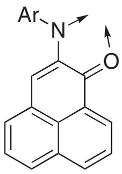
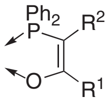
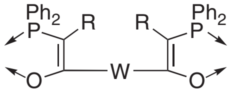
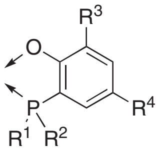
(Continued)

Table 6 (Continued)

R	*Chelate*	*L*	*Characterization*	*References*
(d) N,O ligand				
Ph, **170**	O_2C-2-py	PPh_3	A, ^1H, ^{31}P	167
o-Tol, **170**	O_2C-2-py	PPh_3	XR, A, ^1H, ^{31}P	166,167
o-Tol, **170**	O_2C-2-py	PBz_3, PCy_3	A, ^1H, ^{31}P	167
Mes, **170**	O_2C-2-py	$PMePh_2$, PMe_2Ph	XR, A, ^1H, ^{31}P	167
o-Tol, **170**	O_2C-2-py(OMe)-4	PPh_3	A, ^1H, IR	166
o-Tol, **170**	O_2C-2-pyNO_2-4	PPh_3	XR, A, ^1H, IR	166
o-Tol, **170**	O_2C-2-pyrazyl	PPh_3	A, ^1H, IR, MS	166
o-Tol, **171**	O_2CCH_2-2-py	$PMePh_2$	A, ^1H, ^{31}P	167
Ph	O=C(Me)CHC(Me)=NXyl	PPh_3	A	63
Ph	O=C(Me)CHC(Me)=NDiPP	PPh_3	XR, A	63
Bz	O=C(Ph)C_6H_4N{C(=O)Ph}-2	PMe_3	A, ^1H, ^{13}C, ^{31}P	210
Bz	O=C(Ph)C_6H_4N{C(=O-B$(C_6F_5)_3$)Ph}-2	PMe_3	XR, ^1H, ^{31}P, ^{19}F	210
	O-C_6H_4-2-$\overline{\text{C=NCH}_2\text{CH}_2\text{O}}$			
Ph		PPh_3	XR	178
o-Tol	R = Me, CF_3. C_7F_{17}, Ph	PPh_3	A, ^1H, ^{31}P, MS	177
	R = C_3F_7	PPh_3	XR, A, ^1H, ^{31}P, MS	177
				
Me	R = Ph, Pr^i, Bu^n, Bu^t, $CH_2CH(OMe)_2$, CH_2CF_3; $R^1 = R^2 = H$	PMe_3	A, *m/d*, ^1H, ^{13}C, IR	184
Me, **173**	R = DiPP; R^1 = 9-anthracenyl; R^2 = H	MeCN	XR, A, ^1H, ^{13}C	77,159
Me, **173**	R = DiPP; $R^1 = CPh_3$, 9-phenanthrenyl; R^2 = H	MeCN		159
Me	R = $C_6H_3Ph_2$-2,6, $C_6H_3\{C_6H_3(CF_3)_2\}_2$-2,6; $R^1 = R^2$ = I	py	XR, A, ^1H, ^{13}C	179
Me	R = $C_6H_3\{C_6H_4(OMe)_2\}_2$-2,6, $C_6H_3\{C_6H_4(NO_2)\}_2$-2,6; $R^1 = R^2$ = I	py	A, ^1H, ^{13}C	179
Ph	R = DiPP; $R^1 = Bu^t$; R^2 = H	PPh_3	A, ^1H, ^{13}C, ^{31}P	63,157,159
Ph, **79**	R = DiPP; R^1 = H; R^2 = OMe, NO_2	PPh_3	A, ^1H, ^{13}C, ^{31}P	157
Ph	R = $C_6H_2Pr^i_2$-2,6-allyl-4; R^1, R^2 = H, H; Bu^t, Me	PPh_3	A, ^1H, MS	160,161
Ph	R = $C_6H_2Pr^i_2$-2,6-allyl-4; $R^1 = R^2 = NO_2$, NO_2	PPh_3	XR, A, ^1H, MS	160,161
Ph	R = $C_6H_2Me_2$-2,6-allyl-4; R^1, R^2 = Ph, H	PPh_3	XR, A, ^1H, MS	160,161
Ph	R = C_6H_4-allyl-4; R^1,R^2 = Ph, H	PPh_3	A, ^1H, MS	161
η^1:η^2-cyclo-oct-3-enyl	R = DiPP; R^1, R^2 = NO_2, NO_2; H, NO_2; Ph, H		^1H	211
				
Et, Pr^n, **95**	Ar = DiPP; R = H	2, 4-Lut	A, ^1H, ^{13}C	164
Et, Pr^n, Hex^n	Ar = DiPP; R = H	PPh_3	A, ^1H, ^{13}C, ^{31}P	164

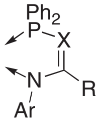
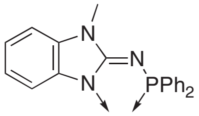
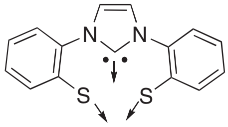
(Continued)

Table 6 (Continued)

R	*Chelate*	*L*	*Characterization*	*References*
Pr^i	Ar = DiPP; R = H	PPh_3	A, ^1H, ^{13}C, ^{31}P (dec > −25 °C)	164
Ph	Ar = DiPP; R = H	PPh_3	XR, A, ^1H, ^{13}C, ^{31}P	162,163,164
Ph	Ar = *o*-Tol, Xyl, $C_6H_4Bu^t$-2, $C_6H_3Bu^t$-2-Me-6, $C_6H_3Ph_2$-2,6, $C_6H_3Cl_2$-2,3, $C_6H_3Br_2$-2,6; R = H	PPh_3	A, ^1H, ^{13}C, ^{31}P	163,164
Ph	Ar = C_6F_5, $C_6H_3(CF_3)_2$-3,5, C_6H_3Me-2-(CF_3)-3, $C_6H_3F_2$-2,6; R = H	PPh_3	A, ^1H, ^{13}C, ^{31}P, ^{19}F	163,164
Ph, **80**	Ar = DiPP, $C_6H_4(OMe)$-4; R = Ph, nap	PPh_3	A, ^1H, ^{13}C, ^{31}P	163,164
Ph	Ar = $C_6H_4(CF_3)$-4; R = Ph, nap	PPh_3	A, ^1H, ^{13}C, ^{31}P	163,164
				
Ph, **81**	Ar = DiPP	PPh_3	A, ^1H, ^{13}C, ^{31}P	165
Ph, **81**	Ar = Xyl	PPh_3	XR, A, ^1H, ^{13}C, ^{31}P	165
(e) O,P ligand				
				
Ph	R^1 = Ph; R^2 = H	py	A, ^1H, ^{31}P	212
Ph	R^1 = Ph; R^2 = H	PMe_3 or PCy_3	A, ^1H, ^{31}P	196,198
Ph, **163**	R^1 = Ph; R^2 = H	PPh_3	A, ^1H, ^{31}P	65,196,198
Ph	R^1 = Ph; R^2 = H	$CH_2{=}PPh_3$	^1H, ^{31}P	212
Ph, **85**	R^1 = $C_6H_4(OH)$-2, $C_6H_4(NHMe)$-2, $C_6H_4(NHPh)$-2, R^2 = H	PPh_3	^1H, ^{13}C, ^{31}P	194
Ph	R^1 = *p*-Tol; R^2 = SO_3^- Na^+, SO_3^- $C_{16}H_{33}NMe_3^+$	PPh_3	^{13}C, ^{31}P	195
				
Ph	R = H; W = 1,4-C_6H_4-	PPh_3	A, ^1H, IR, UV	213
Ph	R = Ph; W = 1,3-C_6H_4-, -$(CH_2)_8$-, -$(CH_2)_4$-, 4,5-bicyclo-C_7H_8, 1, 1′-ferrocenediyl	PPh_3	A, ^1H, IR, UV	213
Ph	R = CO_2Me; W = -$(CH_2)_8$-	PPh_3	A, ^1H, IR, UV	213
				
Me, **83**	R^1 = R^2 = Ph; R^3, R^4 = Bu^t, Bu^t; Me, Bu^t	PMe_3	A, *m/d*, ^1H, ^{13}C, ^{31}P	183
Me, **83**	R^1 = Pr^i; R^2 = Ph; R^3 = R^4 = Bu^t	PMe_3	A, *m/d*, ^1H, ^{13}C, ^{31}P	183
Me, **83**	R^1 = Bu^t; R^2 = Ph; R^3 = R^4 = Bu^t	PMe_3	A, *m/d*, ^1H, ^{13}C, ^{31}P	183
Me, **83**	R^1 = R^2 = Pr^i; R^3, R^4 = Bu^t, Bu^t; H, F	PMe_3	A, *m/d*, ^1H, ^{13}C, ^{31}P	183
Me, **84**	R^1 = R^2 = Ph; R^3 = R^4 = Bu^t	$(PMe_3)_2$	XR, A, *m/d*, ^1H, ^{13}C, ^{31}P	183
Me, **84**	R^1 = Bu^t; R^2 = Ph; R^3 = R^4 = Bu^t	$(PMe_3)_2$	XR, A, *m/d*, ^1H, ^{13}C, ^{31}P	183

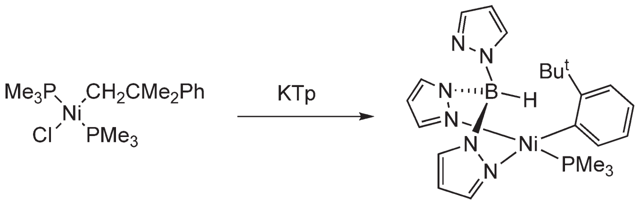
(Continued)

Table 6 (Continued)

R	*Chelate*	*L*	*Characterization*	*References*
Ph, **166**	$R^1 = R^2 = Ph$; $R^3 = R^4 = H$	PMe_3, PMe_2Ph, $PMePh_2$, PCy_3, PPh_3, $P(Tol)_3$	A, ^1H, ^{31}P	198
Ph	$R^1 = R^2 = Ph$; $R^3 = R^4 = H$	$P(OMe)_3$, $P(C_6H_4OMe\text{-}4)_3$	^{31}P	198
(f) N,P ligands				
	$N(DiPP)S(O)_2CH_2PR_2$			
Me	$R = Et$, Cy, Bu^t, Ph, *o*-Tol, *p*-Tol	MeCN	A, ^1H, ^{13}C, ^{31}P	182
Me	$R = Ph$	PPh_3, py	A, ^1H, ^{13}C, ^{31}P	182
	$N(R)C(O)C_6H_4PPh_2\text{-}2$			
Bz	$R = Bu^t$, Ph	PPh_3	XR, A, ^1H, ^{13}C, ^{31}P	177
Ph, **82**	$NHC_6H_4PPh_2\text{-}2$	$P(o\text{-}Tol)_3$	^{31}P	198
				
Ph	$Ar = Ph$; $R = Ph$; $X = CH$	$N(Ph){=}C(Ph)\text{-}CH{=}PPh_3$	^1H, ^{31}P, MS	196
Ph, **86**	$Ar = Ph$; $R = Ph$; $X = CH$	PMe_3, PMe_2Ph, $PMePh_2$	^1H, ^{31}P	196
Ph	$Ar = Ph$; $R = Ph$; $X = N$	$N(Ph){=}C(Ph)\text{-}N{=}PPh_3$	^1H, ^{31}P, MS	197,214
Ph, **86**	$Ar = Ph$; $R = Ph$; $X = N$	PMe_3, PMe_2Ph, $PMePh_2$	A, ^1H, ^{31}P, MS	197,214
Ph		$P(Tol)_3$	^1H, ^{31}P, MS	197,214
(g) Miscellaneous ligands				
Me, Et, Bu^n, Bu^i, Ph, CH_2TMS, **97**	$[N(C_6H_4PPh_2\text{-}2)_2]\text{-}\kappa^3\text{-}P,N,P$		A, ^1H, ^{31}P, ^{13}C	205,215
	 [Li{12C4}$_2$]			
Me, **311**			A, ^1H, ^{13}C	216
COMe			^1H, IR	216
Ph, **88**	$SnPh_2CH_2CH_2PPh_2$			
	$PPh_2(CH_2CH_2SnPh_3)$	A, ^1H, ^{13}C, ^{31}P, ^{119}Sn	199	
Ph, **89**	$SnPh_2CH_2CH_2PPh_2$	PMe_2Ph	^1H, ^{13}C, ^{31}P, ^{119}Sn	199
Ph	$SnPh_2CH_2CH_2PPh_2$	PCy_3	A, *m/d*, ^1H, ^{13}C, ^{31}P, ^{119}Sn	199

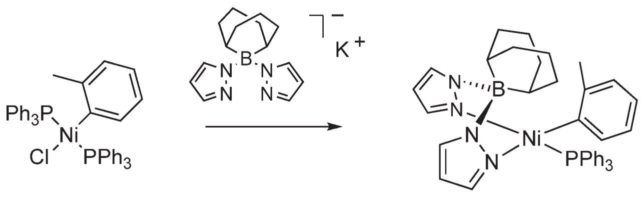
nap, 1-naphtyl; Xyl, 2,6-dimethylphenyl; DiPP, 2,6-diisopropylphenyl; 2,4-lut, 2,4-lutidine; A, Elemental analysis; *m/d*, melting or decomposition point; MS, mass spectroscopy; UV, ultraviolet–visible; IR, Infrared; ^1H, ^{13}C, ^{31}P, ^{19}F, ^{119}Sn, NMR spectra; XR, X-ray diffraction; dec, decomposition temperature.

thallium tris(pyrazolyl)borates leads to the desired organometallic compounds Ni(*o*-Tol)(κ^2-Tp^R)(PPh_3),[155] only for the ligands that contain aryl or tolyl-substituted pyrazole groups (Tp^{Ph}, Tp^{Tol}). Similar Tp complexes containing PMe_3 can be prepared in the same way, if the organic group attached to Ni is phenyl or substituted phenyl, but not when it is an alkyl group.[102] Interestingly, in the case of the 2-arylalkyl derivatives, the introduction of the Tp ligand causes an isomerization process that yields a 2-alkylaryl product (Equation (47)). Organonickel hydro(bispyrazolyl)-borate (Bp)[102] derivatives and the related complex **78** (Equation (48))[156] have been synthesized following an analogous procedure. In the latter case, a byproduct containing a hydroxy(pyrazolyl)borate ligand is produced as well. The reaction of aryl complexes of the type $Ni(aryl)X(PPh_3)_2$ (particularly where aryl = Ph or *o*-Tolyl) with anionic ligands has become a standard procedure for the synthesis of nickel catalysts for olefin oligomerization or polymerization. Examples of these reactions are the preparation of Grubbs' salicylaldiminato[63,157–161] **79** and Brookhart's anilinotropolone[162–164] **80** or anilinoperinaphthenone[165] **81** polymerization catalysts, but many others, including Cavell's pyridinecarboxylate oligomerization catalysts[166,167] as well as different heterocyclic[168–171] and non-heterocyclic[172] ligand-based complexes displaying an aryl group and PPh_3 are prepared in the same manner. A closely related reaction is the preparation of benzyl compounds from the pseudoallylic precursors $Ni(\eta^3\text{-Bz})Cl(PMe_3)$ reported by Bazan[173–175] and others[176] (Equation (49)).



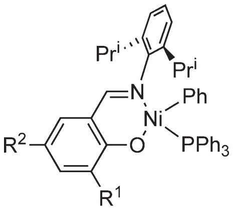
77

(47)

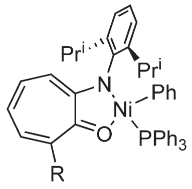


78

(48)



79



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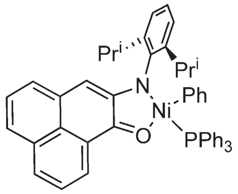

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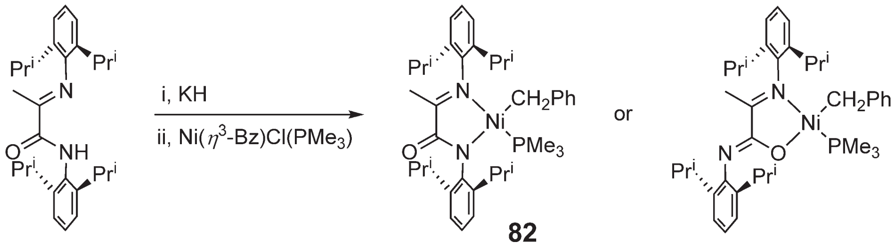
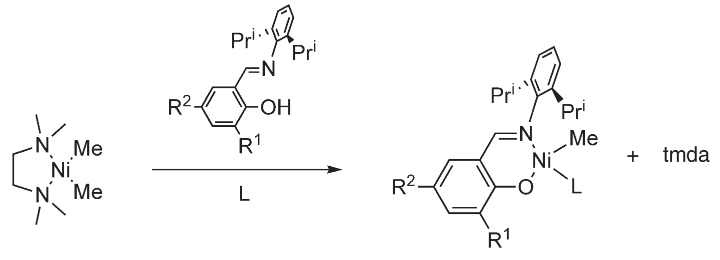


82

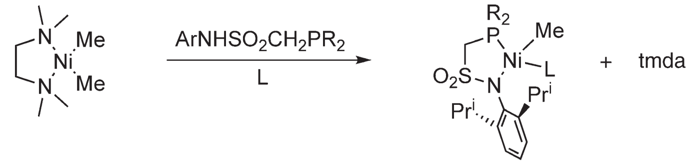
(49)

In some cases, the chelate ligand can be introduced in its neutral, acidic form in the presence of a mild base.[177,178] Furthermore, acidic ligands can react directly with a suitable dialkylnickel compound. The dimethyl complex $NiMe_2$(tmeda) has proved to be a very versatile precursor. The bidentate tmeda is displaced by the incoming ligand, leaving an open coordination site that can be occupied by a two-electron donor molecule (e.g., acetonitrile). This reaction is quite general, and has been applied for the synthesis of salicylaldiminate complexes containing methyl and pyridine[179,180] or acetonitrile[181] co-ligands, which are efficient polymerization catalysts (Equation (50)). A potential difficulty associated with this methodology is the formation of undesired Ni(ligand)$_2$ complexes.[181] For example, this problem prevented the preparation of phenylnickel complexes containing 2-iminopyrrolyl ligands.[169] However, a number of methyl complexes containing phosphinosulfonamide and monodentate ligands (PPh$_3$, pyridine, or acetonitrile) were prepared successfully following the same methodology (Equation (51)).[182]



(50)

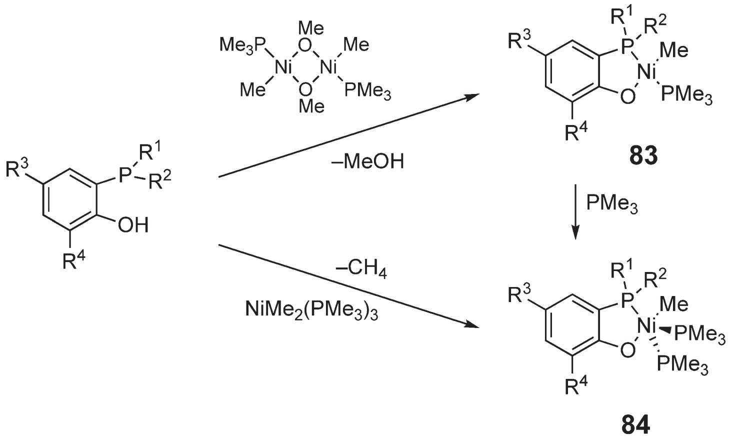
R^1, R^2 = I; L = py
R^1 = 9-anthracenyl; R^2 = H, L = CH$_3$CN



(51)

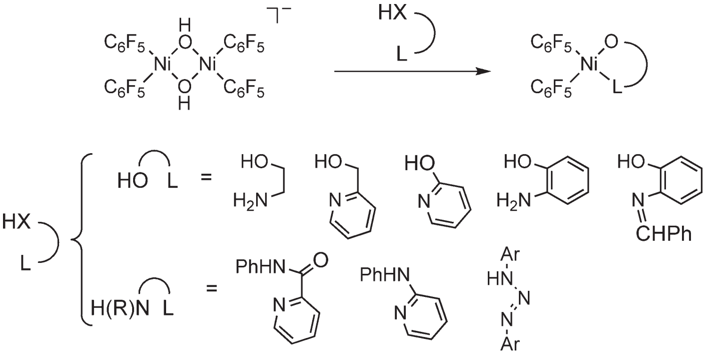
L = CH$_3$CN, PPh$_3$, py; R = Ph
L = CH$_3$CN; R = alkyl or aryl

Organometallic alkoxides and hydroxides are excellent starting materials for acid–base exchange reactions. H. F. Klein has developed a method for the synthesis of 2-phosphinophenolate,[183] salicylaldiminate,[184] and related cyclometallated complexes based on the use of the binuclear methoxide [Ni(Me)(μ-OMe)(PMe$_3$)]$_2$ (see also Section 8.02.3.3). Some 2-phosphinophenols tend to produce large amounts of Ni(phosphinophenolate)$_2$ as a byproduct. Performing the reaction in the presence of added PMe$_3$ minimizes this problem but, under these conditions, five-coordinated complexes **84** containing two phosphine ligands are obtained (Scheme 16). The same compounds are produced in high yield when the 2-phosphinophenol ligands are reacted with NiMe$_2$(PMe$_3$)$_3$. In a similar vein, the



Scheme 16

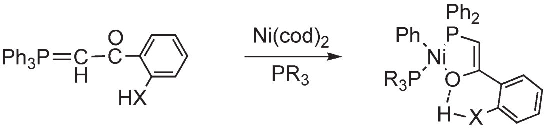
hydroxo dimer $[Ni(C_6F_5)_2(\mu\text{-}OH)]_2$ is the starting material for the preparation of many anionic bis(pentafluorophenyl) derivatives containing bidentate anionic ligands (Equation (52)).[35,37]



(52)

8.02.3.2.2 Preparations not involving a σ-organonickel precursor

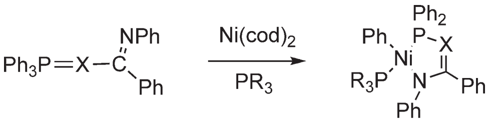
The preparations described in this section can be considered as an extension of two general procedures already described for simple mono- and dialkyl complexes, namely oxidative addition and transmetallation. Oxidative addition to Ni(0) precursors containing anionic ligands are not frequent, but a benzyl complex containing a 2-phosphinobenzoate ligand has been synthesized by reacting benzyl chloride with $Ni(cod)_2$ in the presence of the sodium salt of the ligand.[185] Stabilized phosphonium ylides oxidatively add to Ni(0), giving rise to organometallic phosphinoenolate catalysts used in the Shell Higher Olefin Process (SHOP).[186,187] This reaction is very general and provides access to many related complexes.[188–193] For example, the aryl substituents present in the ligand can bear functional groups that act as a hydrogen bond donor to the enolate oxygen (Equation (53)).[194] Anionic sulfonato groups can be attached to the P–O ligand in order to increase their solubility in water.[195] The oxidative addition of ylides has been extended to the synthesis of the nitrogen analogs of the classic SHOP catalysts (Equation (54))[196,197] and phosphinophenolate compounds (Equation (55)).[198] A formally similar oxidative addition reaction involving a Sn–C bond cleavage takes place when $Ni(cod)_2$ is treated with 2-(triphenylstannyl)ethyl phosphines (Scheme 17).[199] However, the oxidative addition of other stannylphosphines with $SnR_3 = SnMe_3$ or $SnHPh_2$ is followed by the displacement of the Ni–C bond, giving rise to bis(ligand) complexes. A similar product is obtained when the phenylstannyl compound 88 is heated at 70 °C.



XH = OH, NHMe, NHPh

85

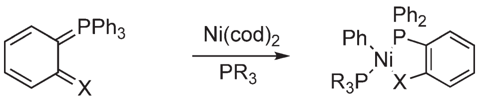
(53)



X = CH or N

86

(54)

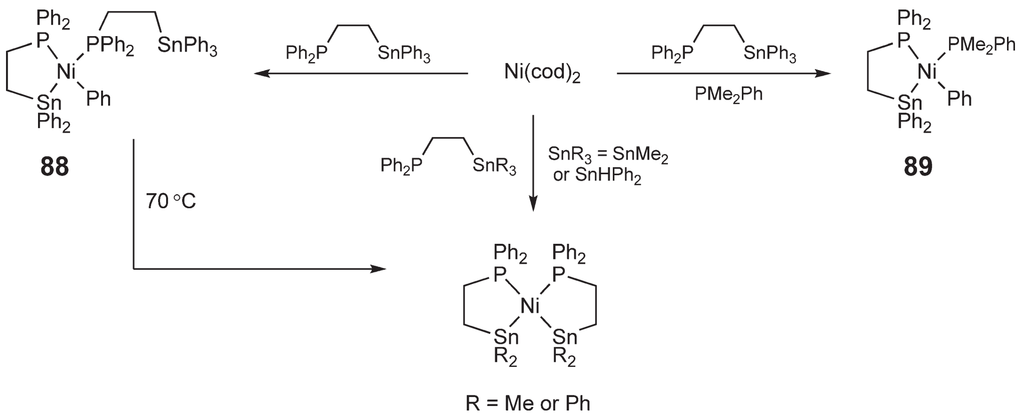


X = O, NH·HBr

X = O, NH

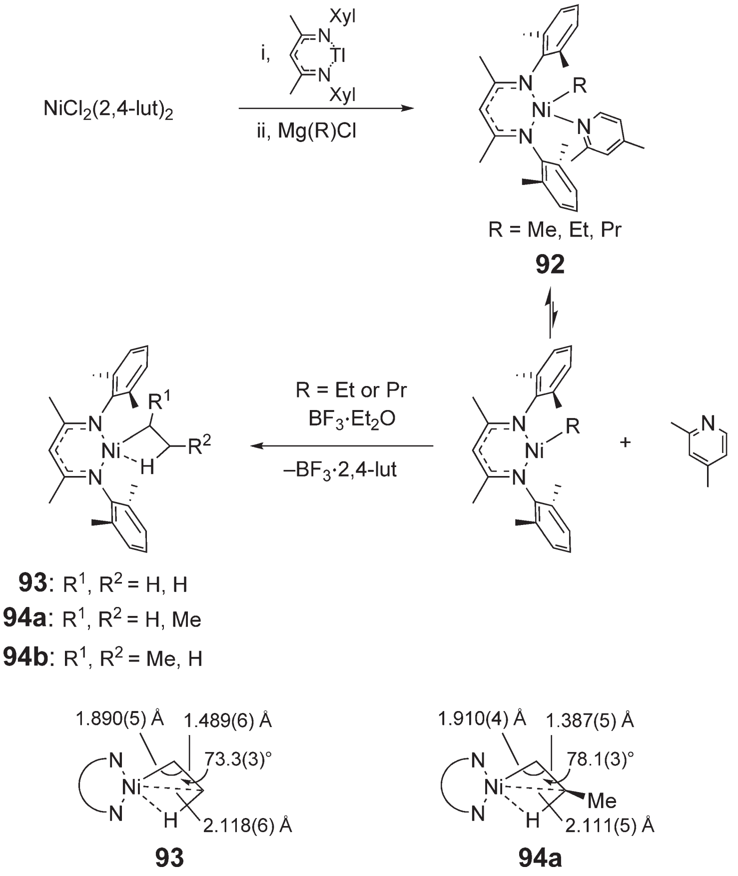
87

(55)



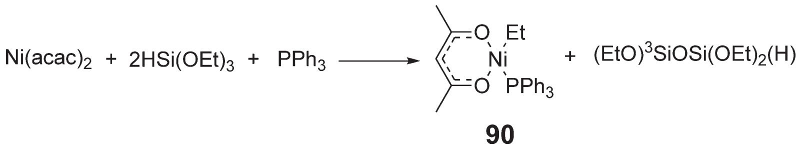
Scheme 17

An unusual but synthetically convenient method for the synthesis of the well-known compound Ni(Et)(acac)(PPh$_3$) has been described, which involves the use of HSi(OEt)$_3$ as a source of the ethyl group (Equation (56)).[200] The alkylation of inorganic nickel chelates with organolithium or Grignard reagents has been recently used in the synthesis of stable alkyls that are resistant to β-elimination reactions. Thus, very stable (up to 180 °C) binuclear butyl and *n*-hexyl compounds bearing an oxalamidinate ligand (OXAM) have been prepared in this way (Equation (57)).[20,201] A similar strategy has been used by Warren for the preparation of Me, Et, and Pr complexes containing β-diketiminate and 2,4-lutidine as a very weak secondary co-ligand (Scheme 18).[202] It is noteworthy that



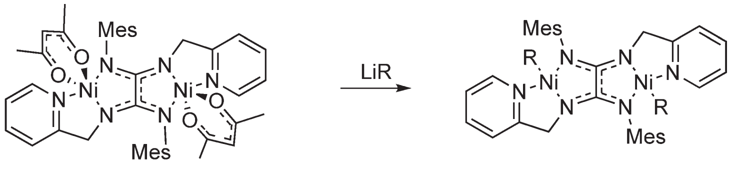
Scheme 18

attempts to synthesize alkyls by direct alkylation of an Ni (β-diketiminate)Br complex with LiMe,[203] or by reacting lithium β-diketiminate with $Ni(Ph)Cl(PPh_3)_2$[63] were unsuccessful, affording the nickel(I) complexes Ni(β-diketiminate)(L) (L = THF or PPh_3, respectively). In solution, the alkyl β-diketiminate complexes **92** reversibly dissociate the heterocyclic base, giving formally three-coordinated complexes that are stabilized by β-agostic interactions.[204] Addition of $BF_3{\cdot}Et_2O$ shifts the equilibrium toward the agostic species, allowing the isolation and structural characterization of compounds **93** and **94**. The propyl derivative **94** exists in solution as a mixture of the secondary and primary isomers, with the latter being favored in the equilibrium. As expected, they exhibit dynamic behavior in solution. Brookhart has applied this synthetic approach for the preparation of ethyl, propyl, and hexyl derivatives supported by anilinotropolone and 2,4-lutidine ligands (Scheme 19).[164] At variance with the diketiminate agostic propyl, the anilinotropolone derivative shows a strong thermodynamic preference for the secondary isomer.



90

(56)

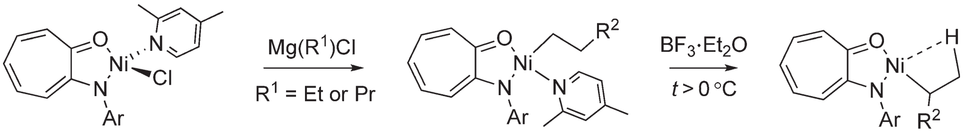


R = Me, Ph, C≡CH, Bu^n, Hex^n

91

(57)

An example of an N–C activation process by Ni(0) has been reported (Scheme 20). The product, **97**, was formed in low yield (1–5%), but was identified by comparison of its spectroscopic properties with those of an authentic sample prepared by alkylation of an Ni(II) precursor with LiMe.[205] It is worth mentioning that the analogous N–H activation reaction leads to the corresponding hydride in high yield.

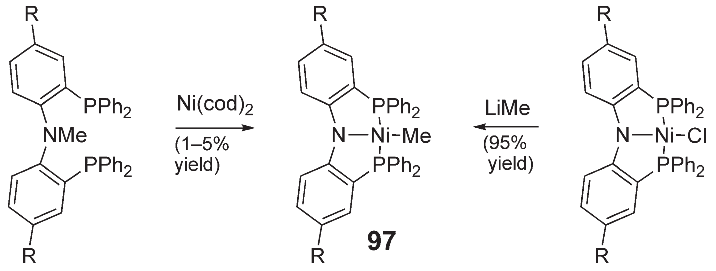


(R^2 = H or Me)

95

96

Scheme 19

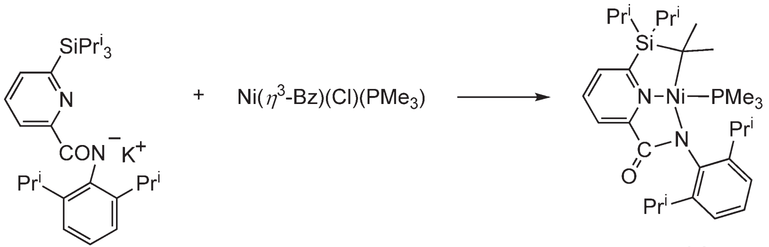


97

Scheme 20

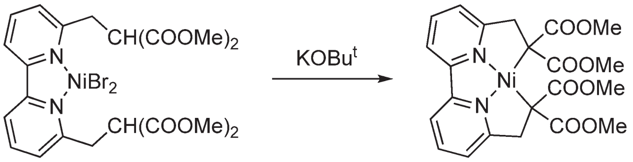
8.02.3.3 Synthesis of Cyclometallated Complexes, Ni(C-chelate)X(L)

Cyclometallation reactions are less common for Ni than for Pd or Pt. However, intramolecular C–H activations can be observed under favorable conditions. For instance, cyclometallation can be favored by very bulky ligands[217] (Equation (58)) or by the presence of acidic C–H bonds in the complex (Equation (59)).[218] The reaction of phosphine ligands containing aldehyde functionalities with a dimethylnickel complex gives cyclometallated products featuring an internal acyl functionality (Equation (60)).[151]



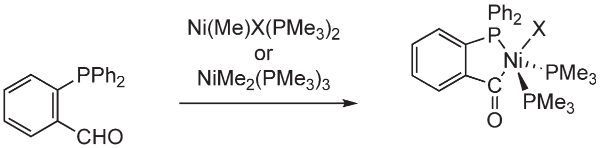
98

(58)



99

(59)



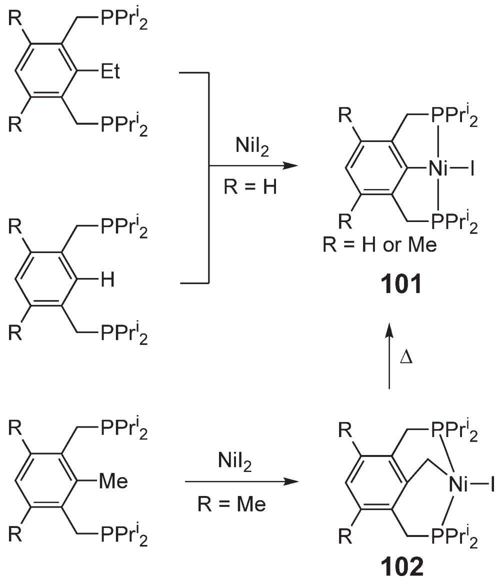
X = Me, Cl, Br, or I

100

(60)

The special configuration of the so-called "pincer" PCP (2,6-bis(phosphinomethyl)phenyl) ligands favors the intramolecular activation of the aromatic C(1)–H bond by many transition metals,[219] and nickel is not an exception.[220–222] The introduction of an alkyl group at the C(1) position allows a comparison of the ability of the metal center to activate C–H and C–C bonds.[223] Thus, the reaction of 3,5-bis(diisopropylphosphino)benzenes with Ni halides can take place with C(sp^2)–H, C(sp^2)–C, or C(sp^3)–H activation, depending on the group attached to C(1). As shown in Scheme 21, the ligand containing an ethyl group at C(1) leads to the same product **101** obtained from the unsubstituted precursor, via activation of the C–ethyl bond. However, methyl substitution at C1 leads to **102**, a benzyl product resulting from CH_2–H activation. Further activation of the C(aryl)–C(alkyl) bond is observed when the latter is thermolyzed at 180 °C. No Ni–C bonds were formed when the ligand precursor bears OMe or OH substituents at C(1), but cyclic phenoxide products, arising from O–CH_3 or O–H bond cleavage, are obtained instead.[223,224]

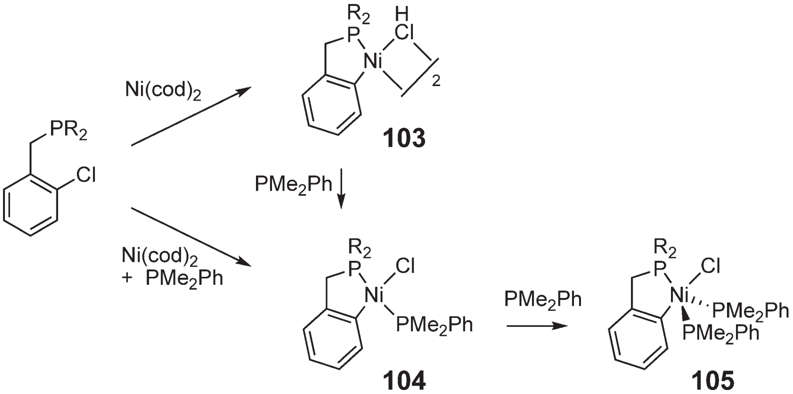
Oxidative addition reactions offer an alternative pathway for the synthesis of nickel cyclometallated complexes. Many derivatives with NCN[225–227] or PCP[228] pincer ligands have been prepared from the corresponding halogenated precursors and $Ni(cod)_2$. These intramolecular oxidative addition reactions take place under very mild conditions and are usually preferred over cyclometallation when the suitable precursors are available. The formation of small amounts of Ni(III) byproducts is not rare in the case of the NCN ligands.[226,229] The synthesis of cyclometallated complexes containing bidentate N,C[13,51,107,108] or C,P[13,230] as well as polydentate[231–233] ligands by oxidative addition reactions has been extensively developed by Muller and Granell. As discussed in Section 8.02.3.1.2 (see Scheme 9), the reaction of perchlorophenyl phosphines with $Ni(cod)_2$ leads to the doubly cyclometallated **3** or to polymeric complexes, while in the presence of monodentate phosphines, cyclic 2-phosphinoaryl compounds are formed.[13] In contrast, the oxidative addition of 2-halogenated benzylphosphines to Ni(0) invariably produces cyclometallated complexes either in the presence or absence of added phosphine (Scheme 22).[230] Although formally analogous, the oxidative addition of halogenated benzylamines affords cyclic products when nitrogen donors (pyridine or pyridine derivatives) are chosen as secondary ligands, while phosphine co-ligands lead to acyclic complexes



101

102

Scheme 21



103

104

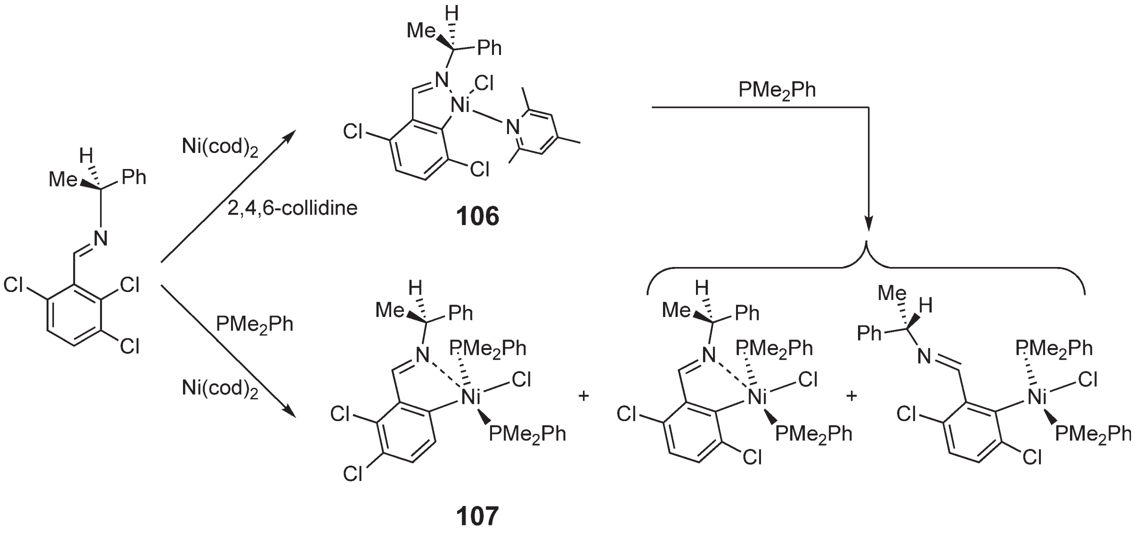
105

Scheme 22

containing two PR_3 units.[107] Halogenated aromatic imines behave similarly, although in this case a secondary N···Ni interaction can be preserved (Scheme 23).[107,108] The nature of the co-ligand influences the selectivity of the oxidative addition when two different C–X bonds are available. As shown in the same scheme, nitrogen co-ligands induce a selective reaction, while in the presence of phosphines, a mixture of products is formed. Interestingly, perfluorophenylimines react with Ni(0) with oxidative addition of the C–F bond (Table 7).[107]

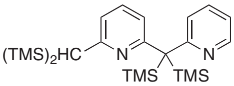
Nickel complexes containing cyclometallated moieties can also be prepared by transmetallation reactions. The successful formation of the stable homoleptic 2-pyridyl complexes **2** is favored by precursors containing relatively weak ligands that are readily displaced (PPh_3, tmeda) (Scheme 24).[11,12] In contrast, the use of a chelating diphosphine leads to the formation of a complex product as a result of nucleophilic attack on the coordinated pyridylmethyl ligand by LiR in an intermediate stage of the reaction.

Bis(iminophosphoranyl)methyl complexes of Ni, prepared by a transmetallation procedure, display an unusual structure with a central Ni–C bond and therefore can be formally regarded as cyclometallated complexes (Equation (61)). The crystal structure of one derivative (Ar = 2,6-diisopropylphenyl) exhibits a planar PCP unit, approximately perpendicular to the coordination plane, and relatively short P–C bonds. These features have been interpreted in terms of resonance between sigma and η-ylidic canonic forms.[234]



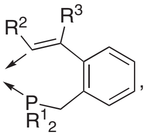
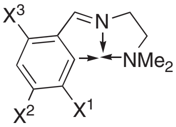
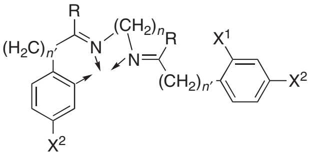
Scheme 23

Table 7 Cyclometallated compounds, Ni(C-Chelate)X(L)

C-Chelate	*X*	*L*	*Characterization*	*References*
C(TMS)$_2$-2-py, 108	Cl		XR, *m/d*, MS	12
$C_6H_4(CH_2NMe_2)$-2	Br	2,4-lut	A, ^{1}H	107
$C_6H_4(CH_2NMe_2)$-2	Br	2,4,6-col	A, ^{1}H	107
$C_6Cl_4(CH_2NMe_2)$-2	Cl	2-pic	A, ^{1}H	107
$C_6Cl_4(CH_2NMe_2)$-2	Cl	2,4-lut	A, ^{1}H	107
C_6H_4(CH=NBz)-2	Br	2-pic	A, ^{1}H, MS	107
C_6H_4(CH=NBz)-2	Br	2,4,6-Col	XR, A, ^{1}H, MS	107
C_6H_4(CH=NBz)-2	Br	$(PMe_2Ph)_2$	A, ^{1}H, ^{13}C, ^{31}P, MS	107
C_6H_4\{CH=NC(H)(Me)Ph\}-2	Br	2,4,6-col	A, ^{1}H	108
C_6H_4\{CH=NC(H)(Me)Ph\}-2	Br	$(PMe_3)_2$	A, ^{1}H, ^{31}P	108
C_6H_4(CH=NPh)-2	Br	$(PMe_2Ph)_2$	A, ^{1}H, ^{13}C, ^{31}P, MS, IR	107
C_6H_3Cl-3-(CH=NBz)-2	Cl	2,4-lut	A, ^{1}H, MS	107
C_6H_3Cl-3-(CH=NPh)-2	Cl	2,4-lut	A, ^{1}H	107
C_6H_3Cl-3-(CH=NBz)-2	Cl	$(PMe_2Ph)_2$	A, ^{1}H, ^{13}C, ^{31}P, MS, IR	107
C_6H_3Cl-3-\{CH=NC(H)(Me)Ph\}-2	Cl	2,4-lut	A, ^{1}H, MS	108
C_6H_3Cl-3-\{CH=NC(H)(Me)Ph\}-2	Cl	2,4,6-col	A, ^{1}H, MS	108
C_6H_3Cl-3-\{CH=NC(H)(Me)Ph\}-2	Cl	$(PMe_2Ph)_2$	A, ^{1}H, ^{31}P	108
$C_6H_2Cl_2$-3,6-\{CH=NC(H)(Me)Ph\}-2, 106	Cl	2,4,6-col	^{1}H	108
$C_6H_2Cl_2$-3,4-\{CH=NC(H)(Me)Ph\}-2, 107	Cl	$(PMe_2Ph)_2$	A, ^{1}H, ^{31}P	108
$C_6H_2Cl_2$\{CH=NBz\}-2 (*isomeric mixture*)	Br	$(PMe_2Ph)_2$	^{1}H, ^{31}P, MS	108
$C_6H_2Cl_2$\{CH=NC(H)(Me)Ph\}-2 (*isomeric mixture*)	Br	$(PMe_2Ph)_2$	^{1}H, ^{31}P, MS	108
C_6F_4(CH=NBz)-2	Br	$(PMe_2Ph)_2$	A, ^{1}H, ^{13}C, ^{31}P, ^{19}F, MS, IR	107
C_6F_4\{CH=NC(H)(Me)Ph\}-2	Br	2,4,6-col	A, ^{1}H, ^{31}P, ^{19}F	108
C_6F_4\{CH=NC(H)(Me)Ph\}-2	Br	$(PMe_2Ph)_2$	A, ^{1}H, ^{31}P, ^{19}F	108
$C_6Cl_4(CH_2NMe_2)$-2	Cl	2-pic	A, ^{1}H	107
$C_6Cl_4(CH_2NMe_2)$-2	Cl	2,4-lut	A, ^{1}H	107
$C_6Cl_4(CH_2NMe_2)$-2	Br	2,4-lut	A, ^{1}H	107
$C_6Cl_4(CH_2NMe_2)$-2	Br	2,4,6-col	A, ^{1}H, MS	107

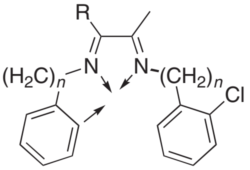
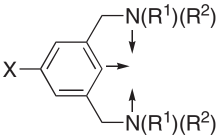
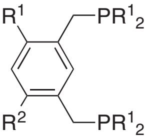
(Continued)

Table 7 (Continued)

C-Chelate	*X*	*L*	*Characterization*	*References*
$C_6H_4(CH_2PEt_2)$-2	Cl	PBz_3	A, ^{31}P	230
$C_6H_4(CH_2PPh_2)$-2	Cl	PEt_3	A, ^{1}H, ^{31}P	51
$C_6H_4(CH_2PPh_2)$-2	Cl	PBz_3	XR, A, ^{1}H, ^{31}P	51
$C_6H_4(CH_2PPh_2)$-2, **104**	Cl	PMe_2Ph	A, ^{1}H, ^{31}P	51
$C_6H_4(CH_2PPh_2)$-2	Cl	PPh_3	^{31}P	51
$C_6H_4(CH_2PPh_2)$-2	Br	PEt_3	^{1}H, ^{13}C, ^{31}P	237
$C_6H_4(CH_2PPh_2)$-2	Br	PBz_3	^{1}H, ^{13}C, ^{31}P, MS	237
$C_6H_4(CH_2PPh_2)$-2	SCN	PBz_3	^{31}P	51
$C_6H_4(CH_2PPh_2)$-2	Mes	PBz_3	A, ^{1}H, ^{31}P	51
				
$R^1 = Et$; $R^2 \equiv R^3 = Ph$	Cl	PBz_3	A, ^{1}H, ^{31}P	230
$R^1 = Et$; $R^2 = Ph$; $R^3 = CO_2Et$	Cl	PBz_3	A, ^{1}H, ^{31}P	230
$R^1 = Ph$; R^2, $R^3 = Et$, Ph (*isomeric mixture*)	Br	PBz_2Ph	^{1}H, ^{13}C, ^{31}P, MS	237
$R^1 = Ph$; $R^2 = R^3 = Ph$	Cl	PEt_3	A, ^{1}H, ^{31}P	51
$R^1 = Ph$; $R^2 = R^3 = Ph$	Cl	PMe_2Ph	A, ^{1}H, ^{31}P	51
$R^1 = Ph$; $R^2 = R^3 = Ph$	Cl	PBz_3	XR, A, ^{1}H, ^{31}P	51,230
$R^1 = Ph$; R^2, $R^3 = CO_2Me$, H (*isomeric mixture*)	Br	PEt_3	^{1}H, ^{13}C, ^{31}P	237
$R^1 = Ph$; $R^2 = H$; $R^3 = CF_3$	Br	PBz_2Ph	XR	238
$R^1 = Ph$; $R^2 = H$; $R^3 = CO_2Me$	Br	PBz_2Ph	XR, IR, ^{1}H, ^{13}C, ^{31}P, A	237
$R^1 = Ph$; $R^2 = Me$; $R^3 = CO_2Me$	Br	PEt_3	^{1}H, ^{13}C, ^{31}P, MS	237
$R^1 = Ph$; $R^2 = Me$; $R^3 = CO_2Me$	Br	PBz_2Ph	XR, ^{1}H, ^{13}C, ^{31}P, A	237
$R^1 = Ph$; $R^2 = Ph$; $R^3 = CO_2Et$	Br	PEt_3	^{1}H, ^{13}C, ^{31}P	237
$R^1 = Ph$; $R^2 = Ph$; $R^3 = CO_2Et$	Cl	PMe_2Ph	A, ^{1}H, ^{31}P	230
$R^1 = Ph$; $R^2 = Ph$; $R^3 = CO_2Et$	Cl	PBz_3	XR, A, ^{1}H, ^{31}P	51
$R^1 = Ph$; $R^2 = Ph$; $R^3 = CO_2Et$	Cl	PPh_3	A, ^{1}H, ^{31}P	230
$R^1 = Ph$; $R^2 = CO_2Et$; $R^3 = CF_3$	Br	PBz_2Ph	^{1}H, ^{13}C, ^{31}P, IR, MS	237
$R^1 = Ph$; $R^2 = R^3 = CO_2Me$	Cl	PBz_3	A, ^{1}H, ^{31}P	230
$C(=O)C_6H_4PPh_2$-2, **100**	Cl, Br, I	$(PMe_3)_2$	A, *m*/*d*, A, ^{1}H, ^{13}C, ^{31}P, IR	151
$C(=O)C_6H_4(CH_2PPh_2)$-2	Cl	PEt_3	A, ^{1}H, ^{31}P, IR	51
$C(=O)C_6H_4(CH_2PPh_2)$-2, **135**	Cl	PMe_2Ph	A, ^{1}H, ^{31}P, IR	51
$C(=O)C_6H_4(CH_2PPh_2)$-2	Cl	PBz_3	A, ^{1}H, ^{31}P, IR	51
$C_6Cl_4PPh_2$-2	Cl	PBz_3	A, ^{31}P	13
$C_6Cl_4PPh_2$-2	Cl	dppe	A, ^{1}H, ^{31}P	13
$C_6Cl_4PPh_2$-2	Cl	dppp	A, ^{31}P	13
				
$X^1 = X^2 = X^3 = H$	Br		A, ^{1}H, MS	231
$X^1 = Cl$; $X^2 = X^3 = H$	Cl		XR, A, ^{1}H, MS	231
$X^1 = X^2 = Cl$; $X^3 = H$	Cl		A, ^{1}H	231
$X^1 = H$; $X^2 = X^3 = Cl$	Cl		A, ^{1}H	231
				

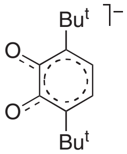
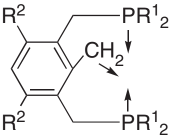
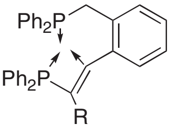
(Continued)

Table 7 (Continued)

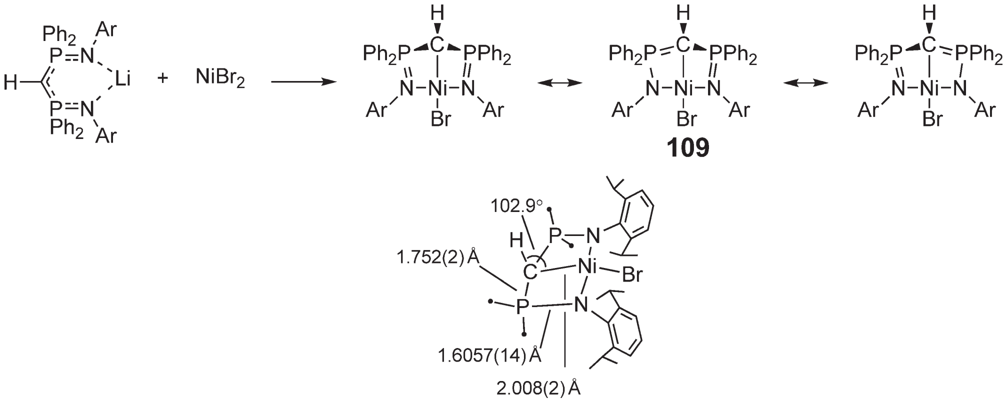
C-Chelate	*X*	*L*	*Characterization*	*References*
$n=2$; $n'=0$; $X^1=Br$ or Cl; $X^2=H$; $R=H$	Cl		A, ^1H	232
$n=2$; $n'=0$; $X^1=Cl$; $X^2=Cl$; $R=H$	Cl		A, ^1H	232
$n=3$; $n'=0$; $X^1=Cl$; $X^2=Cl$; $R=H$	Cl		A, ^1H	232
$n=4$; $n'=0$; $X^1=Cl$; $X^2=Cl$; $R=H$	Cl		A, ^1H	232
$n=2$; $n'=1$; $X^1=Cl$; $X^2=H$; $R=Ph$	Cl		A, ^1H	232
				
$n=1$; $R=H$	Cl		A, ^1H	233
$n=1$; $R=Me$	Cl		A, ^1H	233
$n=2$; $R=Me$	Cl		A, ^1H	233
κ^3-*C,N,N'*-[-C_6H_4-{$CH_2N{=}C(Me)$-2-py}-2]	Cl		A, ^1H	233
κ^3-*C,N,N'*-[-C_6H_4-{$(CH_2)_2N{=}C(Me)$-2-py}-2]	Cl		A, ^1H	233
κ^3-*N,N',C*-[-N(DiPP)CO-2-py-6-$Si(Pr^i)_2C(Me)_2$-], **98**		PMe_3	XR, A, ^1H, ^{13}C, ^{31}P	217
				
$R^1=R^2=Et$	Br		XR, A, ^1H, UV	225
$R^1=R^2=Me$; $X=H$, Cl, NH_2, Ph_2N, MeCONH, MeCO	Br		A, ^1H, ^{13}C, MS, CV, UV	225, 226
$R^1=R^2=Et$; $X=H$	Cl, I		A, ^1H, UV	225
$R^1=R^2=Pr^i$; $X=H$	Br		A, ^1H, UV	225
$R^1=Me$; $R^2=Cy$; $X=H$	Br		A, ^1H, UV	225
$R^1=R^2=Me$; $X=SiMe_2(CH_2)_2C_nF_{2n+1}$ ($n=6$, 10)	Cl		XR, A, ^1H, ^{19}F	235
$N(R^1)(R^2)=$ pyrrolidyl; $X=H$	Br		A, ^1H, UV	225
$N(R^1)(R^2)=$ piperidyl; $X=H$	Br		A, ^1H, UV	225
$N(R^1)(R^2)=$ pyrrolidyl-2-Me, $X=H$	Br		XR, A, ^1H, ^{13}C, UV	227
N $N(R^1)(R^2)=$ pyrrolidyl-2,5-Me_2, $X=H$	Br		XR, A, ^1H, ^{13}C, UV	227
N $N(R^1)(R^2)=$ pyrrolidyl-2,5-$(CO_2Me)_2$, $X=H$	Br		XR, A, ^1H, ^{13}C, UV	227
				
$R^1=Pr^i$; $R^2=H$, **115**	Br		A, ^1H, ^{13}C, ^{31}P	228
$R^1=Pr^i$; $R^2=H$, **101**	I		XR, A, ^1H, ^{13}C, ^{31}P, MS	223
$R^1=Pr^i$; $R^2=H$, **117**	OH		XR, A, ^1H, ^{13}C, ^{31}P, IR, MW	228
$R^1=Pr^i$; $R^2=H$, **124**	OMe		XR, A, ^1H, ^{13}C, ^{31}P, IR	228
$R^1=Pr^i$; $R^2=H$, **116**	NH_2		XR, A, ^1H, ^{13}C, ^{31}P, IR	239
$R^1=Pr^i$; $R^2=H$, **125**	N=C(H)Ph		A, ^1H, ^{13}C, ^{31}P, IR	238
$R^1=Pr^i$; $R^2=Me$, **101**	I		A, ^1H, ^{13}C, ^{31}P, MS	223
$R^1=Ph$; $R^2=H$	Br		XR, A, ^1H, IR	240,241

(Continued)

Table 7 (Continued)

C-Chelate	*X*	*L*	*Characterization*	*References*
$R^1 = Ph$; $R^2 = H$, **119**			XR, EPR	241
				
$R^1 = Pr^i$; $R^2 = CH_3$, **102**	I		XR, ^1H, ^{13}C, ^{31}P, MS	223
				
R = Ph, **149**	Br		XR, ^1H, ^{13}C, ^{31}P, MS	237
κ^3-*P,C,P′*-[-CH(C=PXyl)$_2$]	Br		XR, A, ^1H, ^{13}C, ^{31}P	234
κ^3-*P,C,P′*-[-CH(C=PDiPP)$_2$], **109**	Br		A, ^1H, ^{13}C, ^{31}P	234
κ^3-*C,S,S′*-[-$CH_2CMe_2CH_2SC_6H_4$-2-S-]		py	XR, A, ^1H	242
κ^3-*C,S,S′*-[-$CH_2CMe_2CH_2SC_6H_4$-2-S-], **313**		PMe_3	^1H, ^{13}C	242
κ^3-*C,S,S′*-[-$COCH_2CMe_2CH_2SC_6H_4$-2-S-], **314**		PMe_3	XR, A, ^1H, ^{13}C, IR	242
Doubly cylcometallated compounds				
$C(TMS)_2$-2-py, **2**	$C(SiMe_3)_2$-2-py		XR, A, ^1H, ^{13}C, IR, MS	11,12
C(TMS)(Ph)-2-py, **2**	$C(SiMe_3)(Ph)$-2-py		XR, A, ^1H, ^{13}C, MS	12
$C_6Cl_4PEt_2$-2	$C_6Cl_4PEt_2$-2		XR, A, ^{31}P	13
$C_6Cl_4PPh_2$-2	$C_6Cl_4PPh_2$-2		A, ^{31}P	13
$C_6Cl_4PPh_2$-2	$C_6Cl_4PPh_2$-2	PEt_3	A, ^1H, ^{31}P	13
$C_6Cl_4PPh_2$-2	$C_6Cl_4PPh_2$-2	PBu_3	XR, A, ^{31}P, UV	13
bipy($CH_2C(CO_2Me)_2$)-3,3′, **99**			A, ^1H, ^{13}C	218

lut, lutidine; col, collidine; pic, picoline; DiPP, 2,6-diisopropylphenyl; Xyl, 2,6-dimethylphenyl; A, Elemental analysis; *m/d*: melting or decomposition point; MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^1H, ^{13}C, ^{31}P, ^{19}F, NMR spectra; XR, X-ray diffraction; CV, cyclic voltammetry.



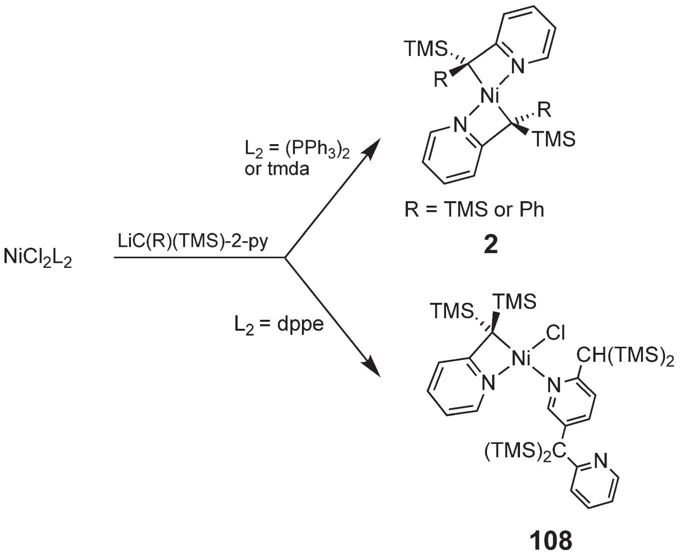
(61)

Table 8 Binuclear and polynuclear complexes without metal–metal bonds

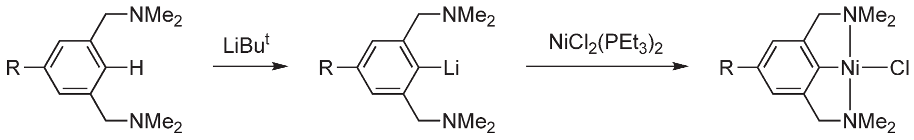
Compound	*Characterization*	*References*
$\{NiMe_2(PMe_3)\}_2$-$\{[5\text{-}Bu^t imidazolyl\text{-}2\text{-}ylidene\text{-}2]_2CH_2\}$, **46**	XR, A, ^{1}H, ^{13}C, ^{31}P	64
$[Ni(Me)(\mu\text{-}OC_6H_4(CHO)\text{-}2)(PMe_3)]_2$	^{1}H, ^{13}C, IR	243
$[Ni(Me)(\mu\text{-}OC_6H_2(CHO)\text{-}2\text{-}Bu^t\text{-}6\text{-}Me\text{-}4)(PMe_3)]_2$	A, ^{1}H, ^{13}C, IR	243
$[Ni(Me)(\mu\text{-}OC_6H_2(CHO)\text{-}2\text{-}Bu^t{}_2\text{-}4,6)(PMe_3)]_2$	A, ^{1}H, ^{13}C, IR	243
$[Ni(Me)(\mu\text{-}O\text{-}1\text{-}naphtyl\text{-}(CHO)\text{-}2)(PMe_3)]_2$	A, ^{1}H, ^{13}C, IR	243
$\{NiMe\}_2(OXAM)$, **91**	XR, A, ^{1}H, ^{13}C, MS	20
$[Ni(CH_2SiMe_3)(\mu\text{-}Cl)(PMe_3)]_2$, **37**	A, ^{1}H, ^{13}C, ^{31}P, M_w	45
$[NiBz(\mu\text{-}O_2CC_6H_4PPh_2\text{-}2)]_2$	A, IR	185
$\{NiBu^n\}_2(OXAM)$, **91**	XR, *m/d*, A, ^{1}H, ^{13}C, MS, CV	201
$\{Ni(Hex)\}_2(OXAM)$, **91**	XR, *m/d*, A, ^{1}H, ^{13}C, MS, CV	201
$\{NiPh\}_2(OXAM)$, **91**	A, ^{1}H, ^{13}C, MS	20
$[Ni\{C(Ph){=}C(Ph)C_6H_4(CH_2PPh_2)\text{-}2\}(\mu\text{-}Cl)]_2$	A, ^{1}H	230
$[Ni\text{-}\kappa^2\text{-}C,P\text{-}\kappa\text{-}P'\text{-}\{C(PPh_2){=}C(CO_2Me)C_6H_4(CH_2PPh_2)\text{-}2\}(Br)]_2$, **148**	XR, ^{31}P	237
$[NiPh(\mu\text{-}NHPh)(PMe_3)]_2$, **113**	A, ^{1}H, ^{31}P	136
$[Ni(Ph)\text{-}\kappa^2\text{-}O,P\text{-}(\mu\text{-}OC(Ph){=}CHPPh_2)]_2$	A, ^{1}H, ^{19}F, MS	65
$\{Ni(Ph)(PPh_3)\}_2\{1,4\text{-}BQI\text{-}[N(Xyl)]_2\text{-}2,5\}$, **176**	A, MS	172
$\{Ni(Ph)(PPh_3)\}_2\{1,4\text{-}BQI\text{-}[N(DiPP)]_2\text{-}2,5\}$, **176**	A, ^{1}H, MS	172
$\{Ni(Ph)(PPh_3)\}_2\{1,4\text{-}BQI\text{-}[N(nap)]_2\text{-}2,5\}$, **176**	A, MS	172
$\{Ni(Ph)(PPh_3)\}_2\{1,4\text{-}BQI\text{-}(NPh)_2\text{-}2,5\}$, **176**	A, MS	172
$\{Ni(Ph)(PPh_3)\}_2\{1,4\text{-}BQI\text{-}(NCy)_2\text{-}2,5\}$, **176**	A, MS	172
$[Ni(Mes)(\mu\text{-}OH)(PMe_3)]_2$, **120**	A, ^{1}H, ^{31}P	136
$[Ni(C_6F_5)(\mu\text{-}SC_6H_4NO_2\text{-}4)(PMe_2Ph)]_2$	XR, A, ^{1}H, ^{13}C, ^{31}P, ^{19}F	145
$[Ni(C_6F_5)\text{-}\kappa^2\text{-}O,P\text{-}(\mu\text{-}OC(Ph){=}CHPPh_2)]_2$	A, ^{1}H, ^{19}F, MS	65
$\{Ni(C{\equiv}CH)\}_2(OXAM)$	A, ^{1}H, ^{13}C, MS	20
$\{Ni(C{\equiv}CPh)\}_2(OXAM)$	A, ^{1}H, ^{13}C, MS	20
$(PCP)NiCOONi(PCP)$ $(PCP = C_6H_3(CH_2PPr^i{}_2)\text{-}2,6)$, **153**	A, ^{1}H, ^{13}C, ^{31}P, IR	228
$Ni(\mu\text{-}py\text{-}2)(Cl)(PEt_3)$, **59**	XR, A, ^{1}H, ^{31}P	88
$Ni(\mu\text{-}pyF_4\text{-}2)(Cl)(PEt_3)$, **129**	A, ^{1}H, ^{13}C, ^{31}P, ^{19}F, IR	110
$Ni_2(\mu\text{-}C{=}CH_2)(\mu\text{-}dmpm)_2(Cl)_2$	XR, A, ^{1}H, ^{31}P, UV	73
$Ni_2(\mu\text{-}C{=}CH_2)(\mu\text{-}dmpm)_2(X)_2$; $X = Br$ or I	A, ^{1}H, ^{31}P, UV	73
$Ni_2(\mu\text{-}C{=}CH_2)(\mu\text{-}dppm)_2(X)_2$; $X = Cl$, Br, I, NCS, or OCS	A, ^{1}H, ^{31}P, UV	73
$(Br)(PEt_3)_2Ni\text{-}4\text{-}C_6H_4\text{-}4\text{-}C_6H_4Ni(Br)(PEt_3)_2$	XR, A, ^{1}H, ^{13}C, ^{31}P	72
$\overline{NiBr(PMe_3)\text{-}2\text{-}C_6H_4CH_2C(=N}Bu^t)Ni(Br)(PMe_3)_2$, **144**	XR, A, ^{1}H, ^{13}C, ^{31}P, IR	132
$\overline{NiBr(PMe_3)\text{-}2\text{-}C_6H_4CH_2C(=N}Xyl)Ni(Br)(PMe_3)_2$, **145**	XR, A, ^{1}H, ^{13}C, ^{31}P, IR	132
$\overline{NiBr(PMe_3)CH_2\text{-}2\text{-}C_6H_4C(=N}Bu^t)Ni(Br)(PMe_3)_2$, **146**	A, ^{1}H, ^{13}C, ^{31}P, IR	132
$Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pz)(Br)(PMe_3)_2$, **111**	XR, A, ^{1}H, ^{13}C, ^{31}P	244
$Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pz)(N_3)(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P	244
$Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pz)(PyrrolMe_2\text{-}2,5)(PMe_3)_2$	A, ^{1}H, ^{13}C, ^{31}P	244
$[Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pz)(PMe_3)_3]BPh_4$	A, ^{1}H, ^{13}C, ^{31}P	244
$[Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pz)(PMe_3)(dmpe)]BPh_4$	A, ^{1}H, ^{13}C, ^{31}P	244
$Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pzR\text{-}3)(Br)(PMe_3)_2$ $R = Me, Bu^t$	A, ^{1}H, ^{13}C, ^{31}P	244
$[Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pzMe\text{-}3)(PMe_3)_3]BPh_4$	A, ^{1}H, ^{13}C, ^{31}P	243
$Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pzR_2\text{-}3,5)(PzR^1{}_2\text{-}3,5)(PMe_3)_2$; $R, R^1 = Me, Bu^t$	XR, A, ^{1}H, ^{13}C, ^{31}P	244
$[Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pzR_2\text{-}3,5)(pzH)(PMe_3)_2]Br$	XR, A, ^{1}H, ^{13}C, ^{31}P, Λ_μ	245
$[Ni_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_6H_4CH_2\text{-}2)(\mu\text{-}pzR_2\text{-}3,5)(pzH)(PMe_3)_2]BPh_4$	A, ^{1}H, ^{13}C, ^{31}P, Λ_μ	245

OXAM, *N,N′*-dimesityloxalamidinate; Xyl, 2,6-dimethylphenyl; DiPP, 2,6-diisopropylphenyl; BQI, benzoquinone imine; pzR, 3-alkylpyrazolate; PzR_2, 3,5-dialkylpyrazolate; A, elemental analysis; *m/d*, melting or decomposition point; MS: mass spectrum; UV, ultraviolet–visible; IR: infrared; ^{1}H, ^{13}C, ^{31}P, ^{19}F, NMR spectra; XR: X-ray diffraction; CV, cyclic voltammetry.

Transmetallation reactions are useful for the synthesis of NCN pincer derivatives, since the free ligand is readily metallated with $LiBu^t$ (Scheme 25).[235] This method is best suited for the synthesis of dendrimeric molecules capped with NCN–Ni units, as multiple oxidative addition processes compete with the one-electron oxidation of the Ni(II) centers. Dendrimers containing from 4 to 36 NCN coordination sites have been prepared and metallation levels of up



Scheme 24



Scheme 25

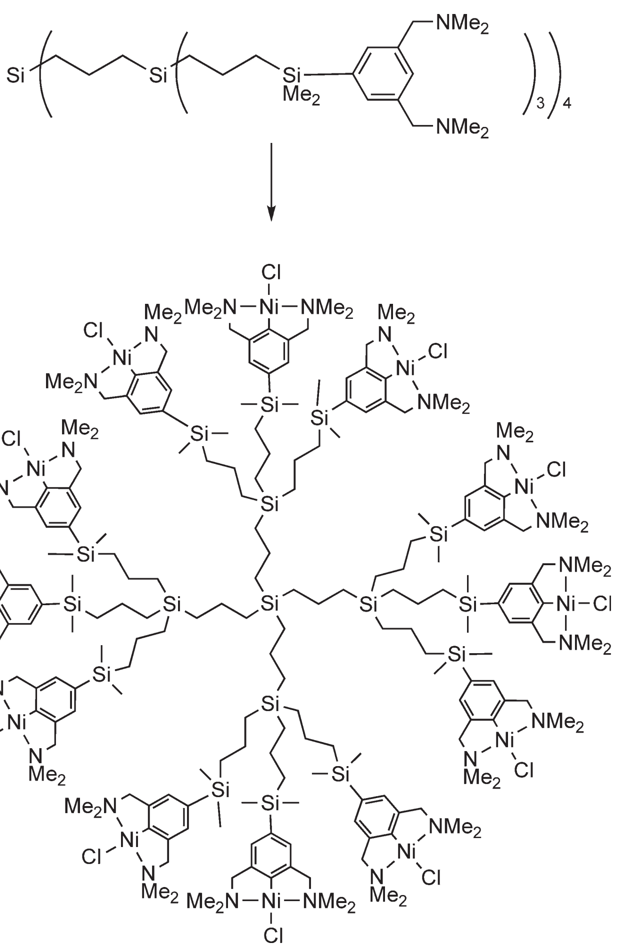
to 90% have been achieved (Scheme 26). The procedure allows the synthesis of dendrimeric complexes with different morphologies, which display catalytic activity in the Kharsch addition of polyhalogenated molecules to olefins.[236]

8.02.3.4 Reactions

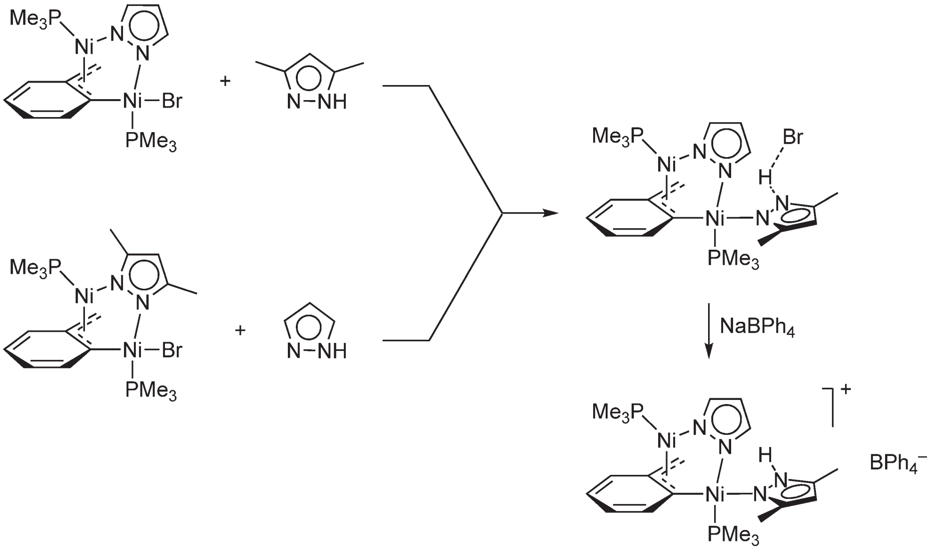
This section will cover the main aspects of the reactivity of the σ-organonickel complexes described in the three preceding ones. Following the organization of COMC (1982) and COMC (1995), this section has been futher subdivided in three parts, devoted to reactions which do not involve the Ni–C bonds, those in which new Ni–C bonds are formed and reactions in which the alkyl or aryl groups are displaced.

8.02.3.4.1 Reactions in which the Ni–C bond is not involved

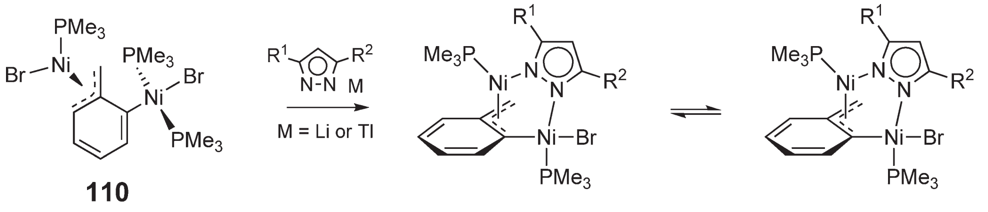
Ligand exchange reactions leading to chelated complexes have been described in Section 8.02.3.1. In general, halide and pseudohalide exchange reactions are facile processes. The kinetics and the thermodynamics of the displacement of halide by SCN have been investigated in binuclear A-frame complexes by two-dimensional $^{31}P\{^{1}H\}$ EXSY spectroscopy.[246] Halide ligands are also readily displaced by heterocyclic groups. Attempts to displace halide and PR_3 with very bulky hydrotris(3-*t*-butylpyrazolyl)borate ligands lead to the formation of products that contain monodentate Tp′ ligands.[102] In contrast, the reaction of the binuclear complex **110** with lithium or thallium pyrazolates causes the displacement of one halide and one phosphine ligand with the formation of pyrazolate-bridged compounds (Equation (62)). The relatively short Ni–Ni distance (2.710 Å) found in the parent pyrazolate derivative **111** ($R^1 = R^2 = H$) may suggest the existence of a weak M–M interaction. Pyrazoles containing a substituent in the 3-position give an equilibrium mixture of the two geometric isomers.[244] The remaining halide ligand can be exchanged by pseudohalide, pyrrolyl, or a second pyrazolate group.[244,245] The monopyrazolyl derivatives feature interesting reactivity toward free pyrazoles, summarized in Scheme 27.[245]



Scheme 26



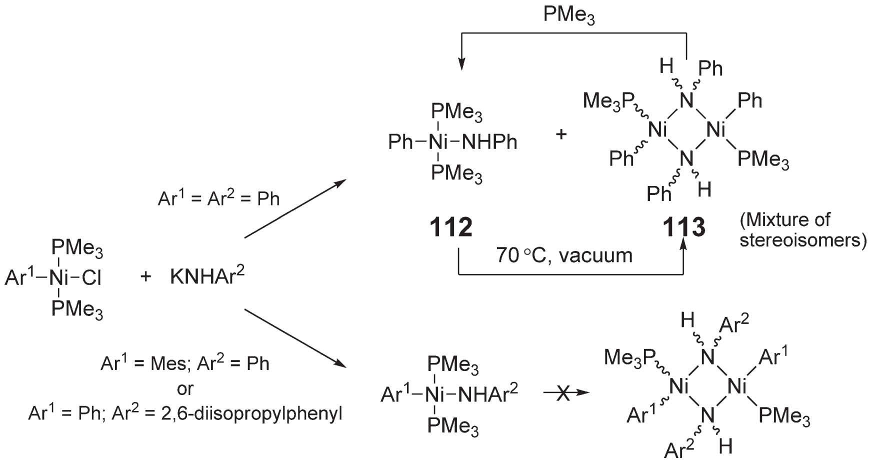
Scheme 27



111: R^1, R^2 = H, H; Me, H; Me, Me; Bu^t, H; Bu^t, Bu^t

(62)

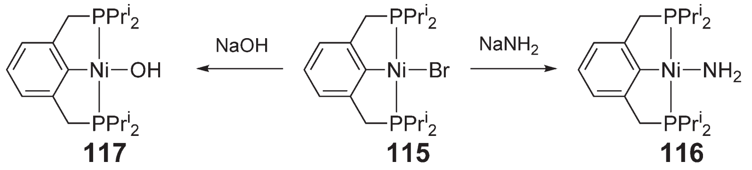
Mononuclear nickel complexes containing hard hydroxo, alkoxo, or amido ligands can be prepared by methathetical exchange of halide. Boncella has reported several arylnickel compounds containing terminal anilido groups.[136,139] The introduction of steric hindrance proves to be an efficient strategy to avoid the formation of anilido-bridged complexes. Thus, while the phenyl–anilido derivative **112** reversibly loses PMe_3, the analogous mesityl–anilido **114** and phenyl-2,6-diisopropylanilido complexes are stable in the mononuclear form (Scheme 28). An efficient approach to avoid dimerization is the use of tridentate pincer ligands. Thus, stable complexes containing terminal OH **117**[228] and NH_2 **116**[239] ligands can be prepared by direct halide exchange with sodium hydroxide and amide, respectively (Scheme 29). A mononuclear Ni(II) semiquinone complex, **119**, has been prepared by the same route (Equation (63)). The EPR spectrum of this compound shows that the unpaired electron is localized at the semiquinone ligand.[241]



d (Ni–N) = 1.932(3) Å

114: Ar^1 = Mes; Ar^2 = Ph

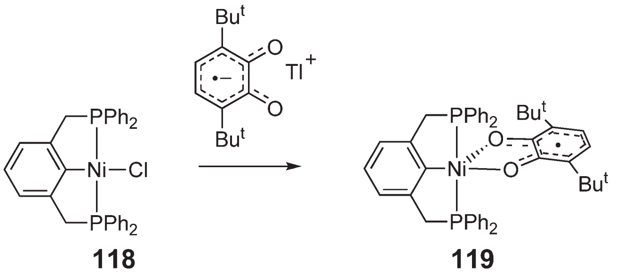
Scheme 28



d(Ni–O): 1.865(2) Å

d(Ni–N): 1.872(2) Å

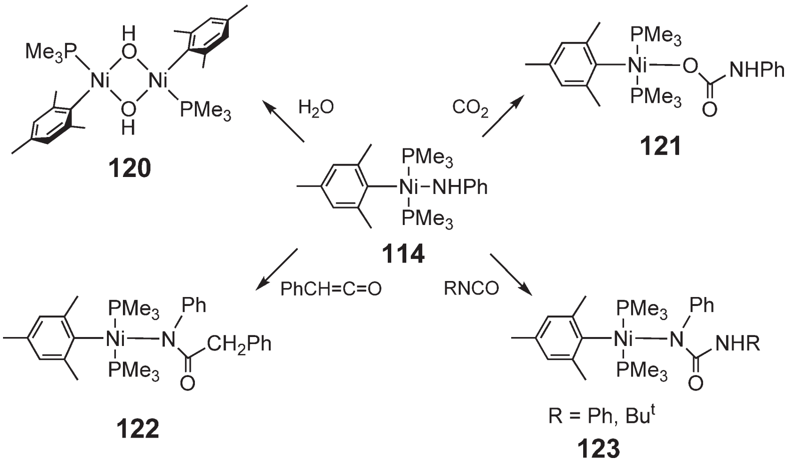
Scheme 29



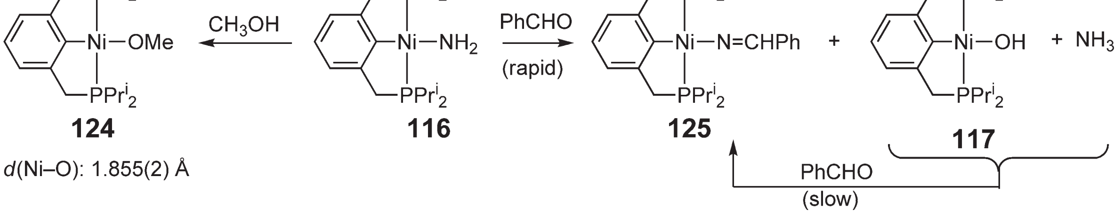
(63)

Nickel alkoxo and amide complexes exhibit high reactivity toward a variety of electrophilic reagents. Thus, the Ni–anilido complex **114** is readily hydrolyzed, and undergoes the insertion of CO_2 into the Ni–N bond (Scheme 30).[136] Other heterocumulenes, such as isocyanates and diphenylketene, give products that are formally described as the result of insertion into the N–H bond of the amido complex.[247] Electrophilic unsaturated molecules such as CO[136,228] or dimethyl acetylenedicarboxylate[136] can also insert into Ni–O or Ni–N bonds giving rise to new Ni–C bonds (see also Section 8.02.3.4.2). The reactivity of the parent amido compound **116** evinces its strongly basic and nucleophilic character (Scheme 31).[239] Thus, water or MeOH readily displace the NH_2 ligand, forming the corresponding hydroxide or methoxide **124**. It also reacts instantaneously with PhCHO, giving the aldiminate complex **125**. Note that the hydroxide **117** and the ammonia generated in the process react slowly with PhCHO giving the same product. The reaction of perfluorophenyl hydroxide dimer $[Ni(\mu\text{-}OH)(C_6F_5)_2]_2^{2-}$ with ligands that incorporate a nitrile functionality gives products that result from the intramolecular addition of the OH ligand to the C≡N bond.[37]

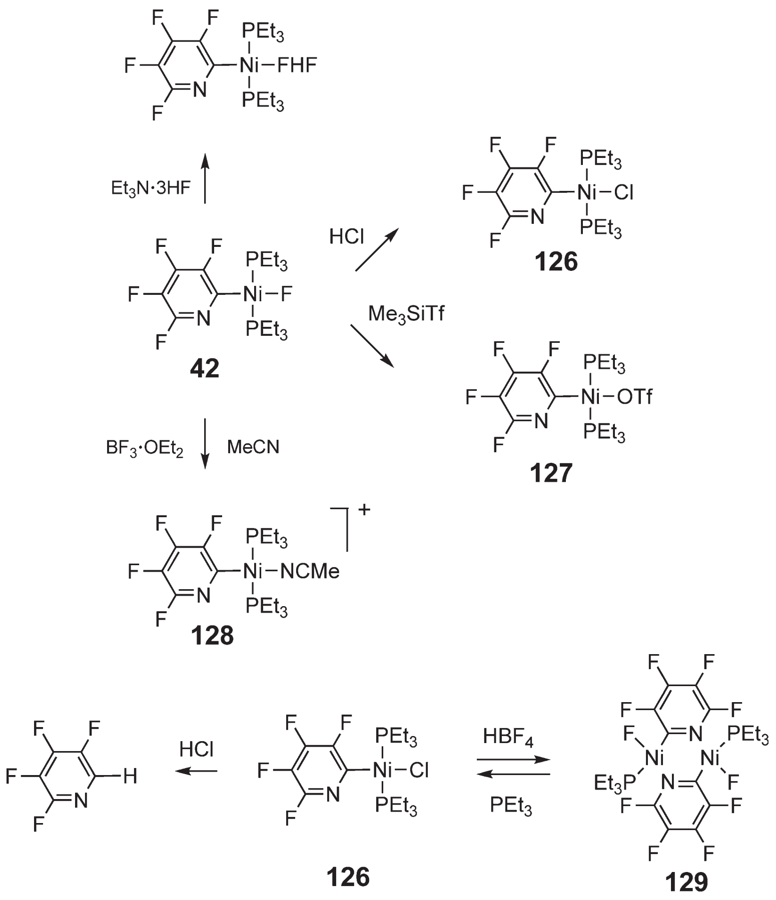
Although to a lesser extent, terminally bound fluoride ligands also exhibit basic character. As shown in Scheme 32, fluoride complexes undergo a variety of reactions with different types of protic and Lewis acids. This reactivity may



Scheme 30



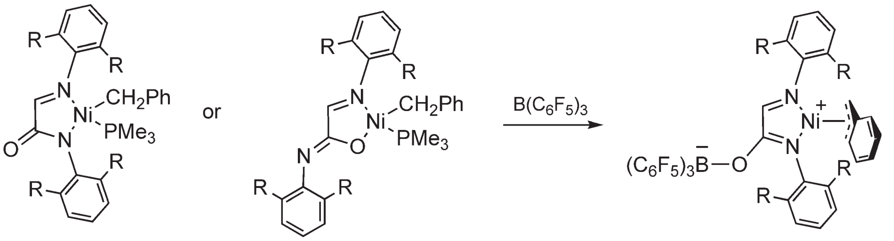
Scheme 31



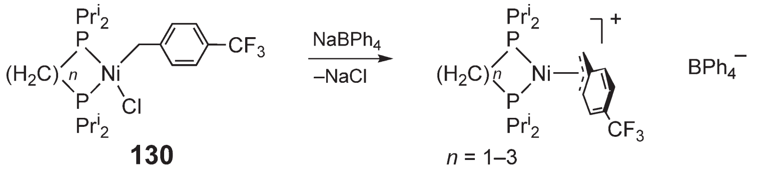
Scheme 32

be compared with that of the analogous chloro derivative (same scheme, below), which undergoes protonation either at the aryl or phosphine ligands.[110]

Lewis acids such as $B(C_6F_5)_3$ can abstract anionic or neutral ligands, leaving a coordination vacancy that can be compensated by different mechanisms. As discussed in Section 8.02.3.2.2, this reaction was used to prepare agostic alkyl complexes. Benzyl ligands can compensate the electronic deficiency by adopting an η^3-coordination mode (Equation (64)).[173,174,210] The facile $\eta^1 \rightarrow \eta^3$ benzyl rearrangement can be induced by milder Lewis acids such as BF_3[248] or $ZnBr_2$.[93] Halide abstraction with precipitating salts induces this process too (Equation (65)).[80]

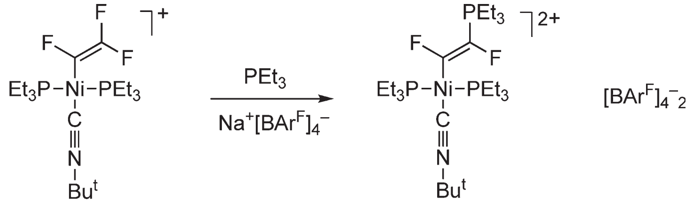


(64)



(65)

Nucleophilic attack at remote positions of coordinated ligands is observed when these are activated by strongly electron-withdrawing groups. For instance, PEt_3 displaces a fluoride atom from complex **131** affording a phosphoniovinyl complex (Equation (66)).[101] A related reaction is the hydrolysis of coordinated 2,4,6-trifluoropyrimidine, to afford a 4,6-difluoropyrimidin-2-one complex.[81] An unusual reaction is the formal insertion (probably electrophilic attack) of heterocumulenes (CS_2 or CO_2) into a coordinate Ni–P bond of **70** (Equation (67)).[117]

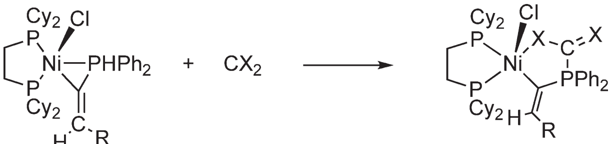


131

$Ar^F = C_6H_3(CF_3)_2$-3,5

132

(66)



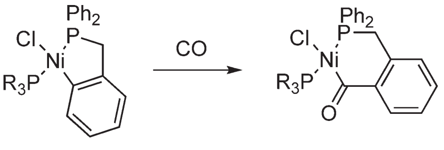
X = S, O

70 **133**

(67)

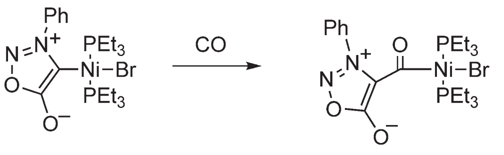
8.02.3.4.2 Reactions in which new Ni–C bonds are formed

Migratory insertion reactions allow the generation of different kinds of Ni–C bonds. CO insertion is a classic example that has received much attention due to its involvement in catalytic and stoichiometric C–C bond formation processes.[112,249] Although the carbonylation of σ-organonickel complexes is often followed by reductive elimination processes, many stable Ni–acyl complexes have been isolated. Recent examples of such reactions are shown in Equations (68)[51] and (69).[64] Their formation is usually reversible, as demonstrated by the equilibrium shown in Equation (70), which indicates that the insertion of CO into Ni–aryl bonds is thermodynamically favored over the insertion into Ni–alkyl bonds.[250] Acyl complexes containing Bp or Tp ligands have been prepared by carbonylation of the corresponding alkyl or aryl precursors.[102,206,207] The ready carbonylation of the Tp derivative **137** (Equation (71)) contrasts with the lack of reactivity of the formally isoelectronic 18-electron $NiCp(R)(PR'_3)$ compounds.[102] The reaction of the tetrahedral complex $NiCl(Tp^{Pr-i})$ with Mg(Et)Cl under a CO atmosphere allows trapping of an unstable tetrahedral alkyl intermediate as the pentacoordinated acyl **139** (Equation (72)).[206,207] Brookhart has studied related acyl–carbonyl species that are formed in solution when cationic, coordinatively unsaturated alkyl complexes stabilized by diphosphine ligands are exposed to CO at low temperature (Scheme 33).[124,127] A pentacoordinated alkyl–dicarbonyl complex, **140**, detected at −130 °C, experiences CO insertion at a slightly higher temperature. The resulting acyl–dicarbonyl complexes undergo stepwise decarbonylation when CO is removed with an Ar stream. In the case of the dppp derivative, this process affords a mixture of two species, identified as the alkyl–carbonyl **141** and a purported η^2-acyl, **142**. Stable η^2-acyl complexes of Ni have not been reported so far. The observation of alkyl–carbonyl complexes with coordination numbers 4 and 5 indicates that CO insertion in nickel alkyls proceeds either through tetracoordinate or pentacoordinate intermediates. DFT calculations show that both processes are feasible, but the latter is usually kinetically favored.[251,252]



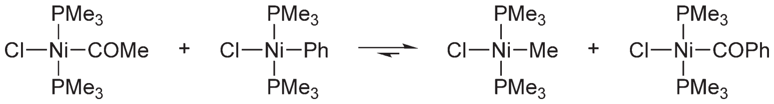
104 **135**

(68)



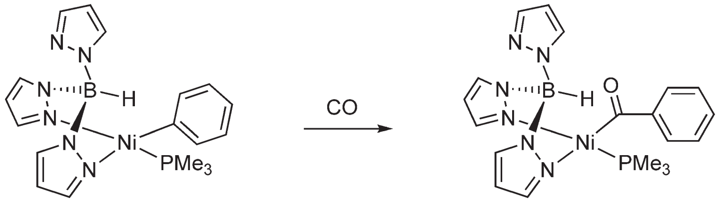
(69)

57 **136**



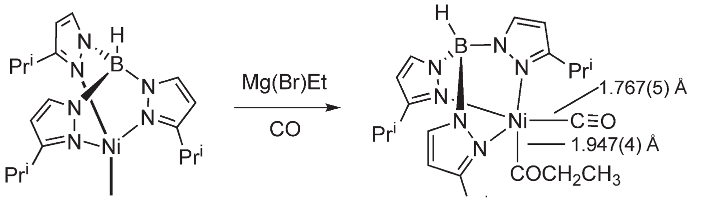
$$\underset{\textstyle PMe_3}{\overset{\textstyle PMe_3}{Cl{-}Ni{-}COMe}} + \underset{\textstyle PMe_3}{\overset{\textstyle PMe_3}{Cl{-}Ni{-}Ph}} \rightleftharpoons \underset{\textstyle PMe_3}{\overset{\textstyle PMe_3}{Cl{-}Ni{-}Me}} + \underset{\textstyle PMe_3}{\overset{\textstyle PMe_3}{Cl{-}Ni{-}COPh}}$$

(70)



(71)

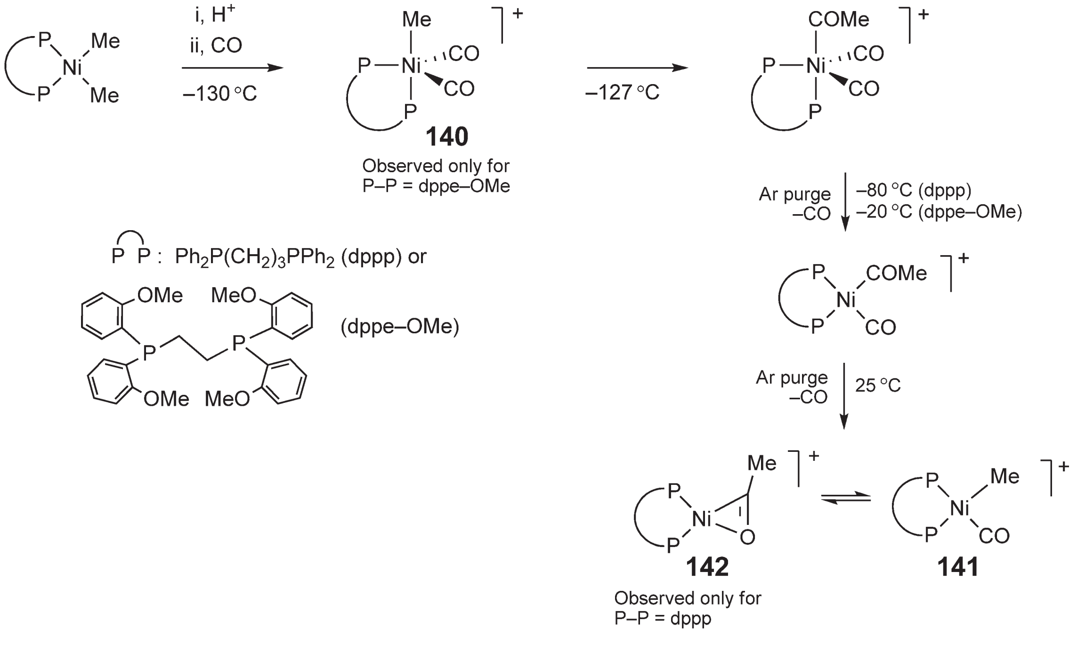
137 **138**



(72)

139

ν(CO): 2009, cm^{-1}; 1680 cm^{-1}
δ ^{13}C: 187.4 ppm (CO); 225.9 ppm (COR)



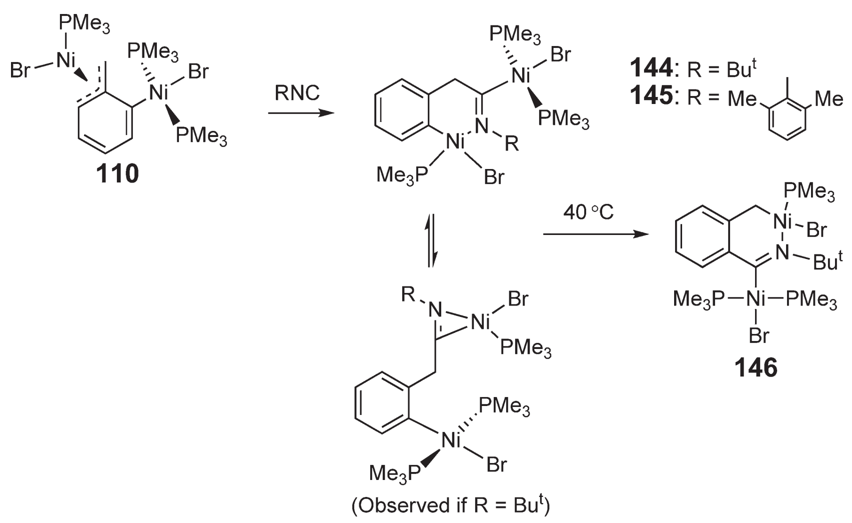
140
Observed only for
P–P = dppe–OMe

142
Observed only for
P–P = dppp

(δ ^{13}C: 187.4 ppm)

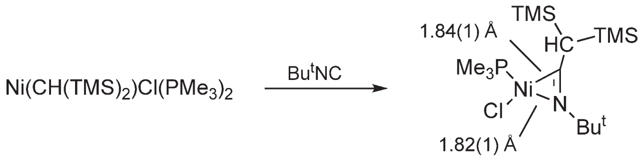
141

Scheme 33



Scheme 34

Isocyanide insertion into σ-Ni–C bonds is also a facile reaction, and many examples have been reported, as described in the previous COMC editions. In contrast to acyls, iminoacyl ligands show some tendency to coordinate to Ni in an η^2-fashion (Equation (73)).[45,135] Isocyanides ($\mathrm{Bu^tNC}$ or XylNC) insert selectively into the Ni–CH_2 bond of the binuclear complex **110**, affording the cyclic products **144 and 145** that contain a bridging iminoacyl functionality (Scheme 34).[132] In solution, the $\mathrm{Bu^t}$ derivative **144** is in equilibrium with an isomer displaying an open structure. At 40 °C, this complex rearranges to **146**, an unusual process that implies the migration of the inserted isocyanide unit from one Ni center to the other.



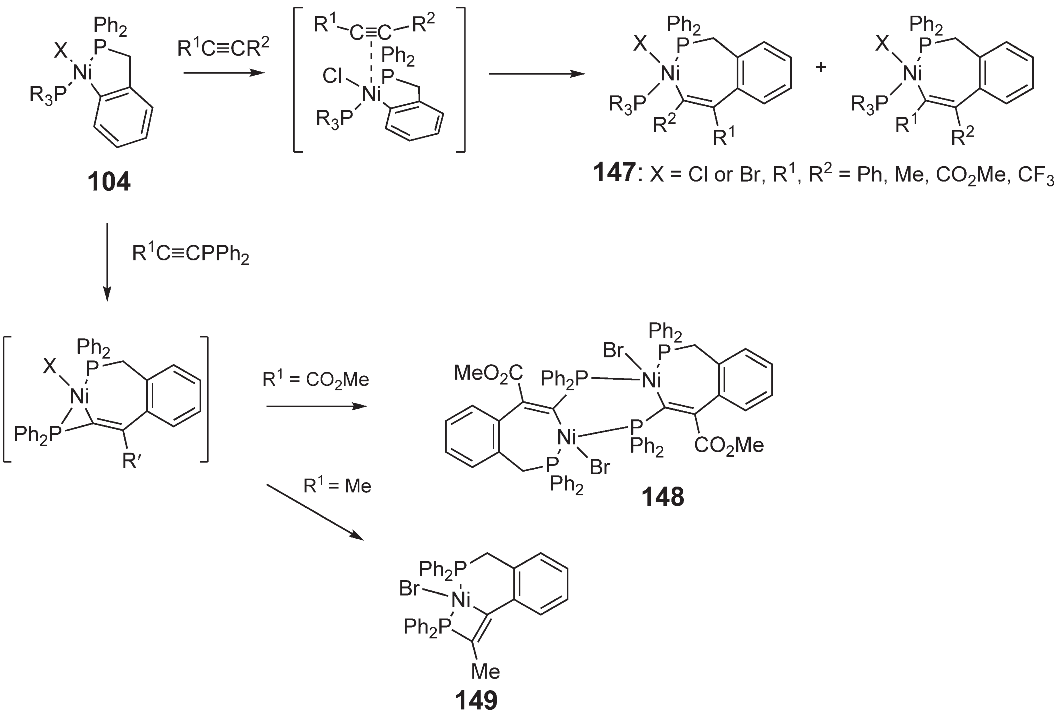
143

(73)

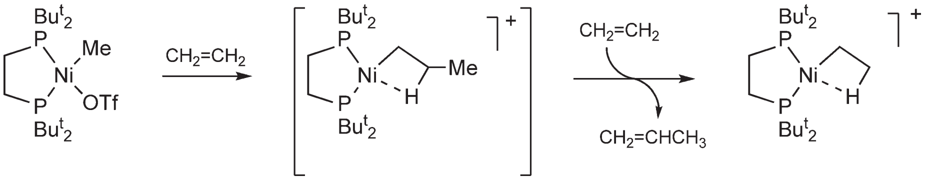
Alkynes insert into the Ni–C bond of the cyclometallated complexes **104**, affording seven-membered cyclic products (Scheme 35).[51,230] The reaction rate is independent of added phosphine, and $\Delta S^{\ddagger} \ll 0$, suggesting an associative mechanism involving a pentacoordinate intermediate. The regioselectivity of the insertion of nonsymmetric alkynes ($R^1C{\equiv}CR^2$) has been studied in detail.[237,238] Electronic factors play an important role in this reaction, favoring the product that displays the least electron-withdrawing substituent next to the metal center. Alkynyl phosphines $RC{\equiv}CPPh_2$ insert regiospecifically, affording products with the PPh_2 in the position adjacent to the metal, allowing P–Ni coordination. These compounds are unstable and dimerize subsequently or rearrange to bicyclic compounds with six-**148** and four-**149** member rings (Scheme 35, below).[237]

Olefin insertion into Ni–C bonds is a key step in olefin oligomerization or polymerization processes, but it seldom leads to stable organometallic compounds. One such example is provided by the reaction of NiMe(Tf)(dtbpe) with ethylene to give an agostic ethyl complex (Scheme 36).[50] The cationic methyl–imine complexes **150** shown in Scheme 37 undergo C=N insertion only after the Ni–C bond is carbonylated to the corresponding acyl. It seems that the formation of a strong amide bond provides the driving force for this reaction.[146] The compound NiPh(Br)(bipy) reacts with CO_2 in DMF affording carboxylated products that have not been characterized.[253]

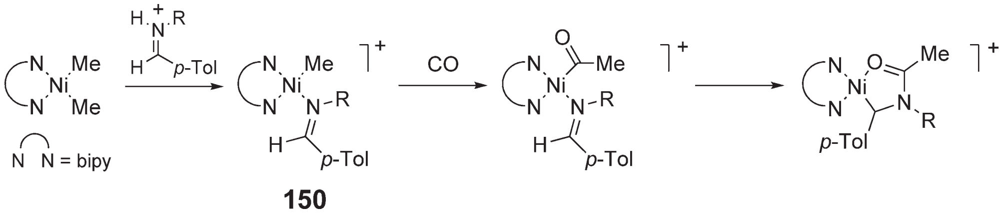
As already mentioned, reactive nickel amide, hydroxo, or alkoxo complexes can experience insertion reactions giving rise to new Ni–C bonds. The mononuclear anilido complex **114** reacts with dimethyl acetylenedicarboxylate, resulting in the formation of the alkenyl complex **151** (Equation (74)).[137] The insertion of CO into the Ni–N bond of an unusual tricoordinated Ni(II) amido complex yields a carbamoyl ligand that features an unprecedented η^2-*C,O*



Scheme 35



Scheme 36



Scheme 37

coordination mode (Equation (75)).[149] The reaction of the mononuclear hydroxide **117** with CO affords a binuclear CO_2-bridged product, **153** (Equation (76)).[228] The insertion of CO into M–OR bonds (M = Ni, Pd, Pt) has been examined theoretically.[252,254] For the model compounds *cis*-[M(OMe)(CH_3)(PH_3)$_2$], CO insertion into the M–OMe bond is favored thermodynamically and kinetically over insertion into the M–CH_3 bond, and it is assisted by the lone pairs of the alkoxide ligand (see Figure 2). However, in a similar Ni–OAr model, the acyl product is strongly favored, both thermodynamically and kinetically.[252]

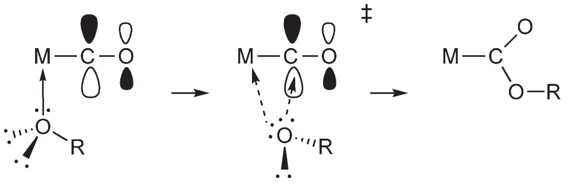
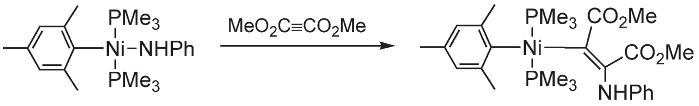
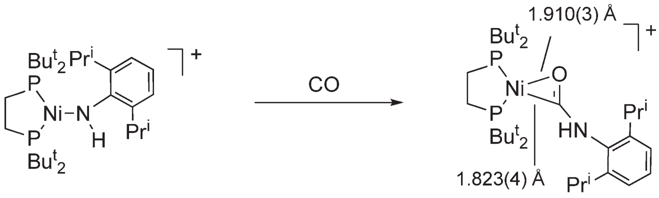


Figure 2 Migratory insertion of CO into M–OR bonds.



114 **151**

(74)

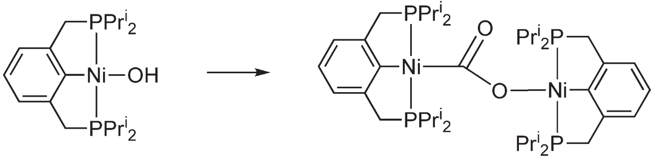


ν(CO): 1577 cm^{-1}

δ ^{13}C: 183.2 ppm

152

(75)

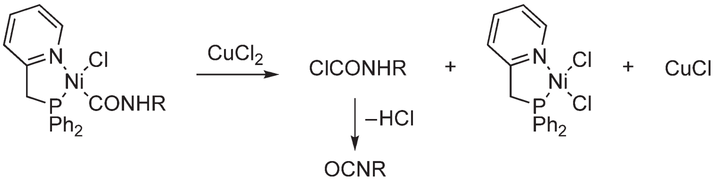


117 **153**

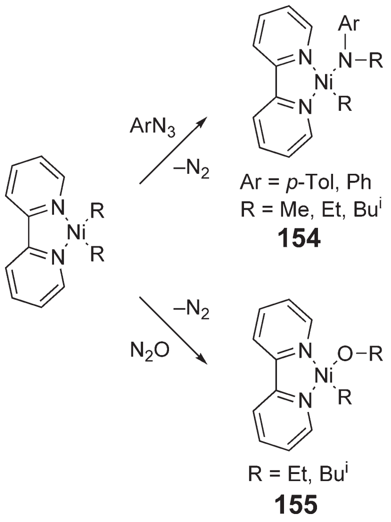
(76)

8.02.3.4.3 Reactions in which the Ni–C bonds are displaced

The reaction of σ-organonickel complexes with protic acids or halogens causes the rupture of the Ni–C bonds and the release of the corresponding organic C–H or C–X functionalities. The cleavage of Ni–C bonds by different types of coordinating and non-coordinating acids has already been addressed in Sections 8.02.3.1.3 and 8.02.3.2.1. The mechanism of the reaction of $[NiMe\{PPh(CH_2CH_2\ PPh_2)_2\}]^+$ with anhydrous HCl in MeCN has been investigated by stopped-flow kinetics. Although it involves the initial protonation of the Ni center, a subsequent protonation of the methyl group is required before methane can be released.[255] Some examples of Ni–C bond cleavage by electrophilic reagents are shown below. Transition metal salts can be used as mild halogen sources (Scheme 38).[256] The electrophile may undergo formal insertion into the Ni–C bond; this is the case of the well-known insertion of SO_2 (e.g., Equation (77)).[51] An example of NO insertion has been recently reported to give an

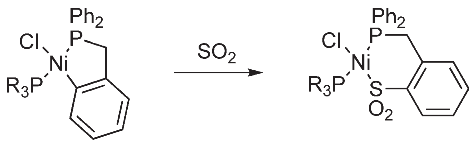


Scheme 38

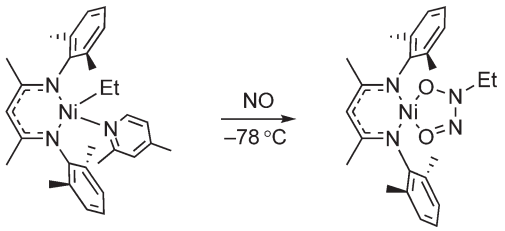


Scheme 39

N-alkyl-N-nitroxohydroxylaminate complex (Equation (78)).[257] Hillhouse has shown that the reactions of nickel dialkyls with organic azides[125,129] or nitrous oxide[128] takes place with selective insertion of an NR or O unit into one of the two Ni–C bonds (Scheme 39).

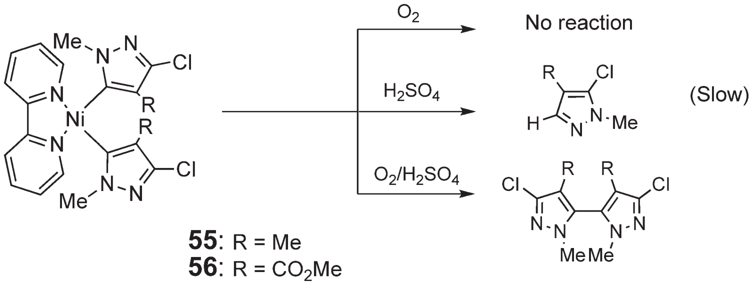


(77)



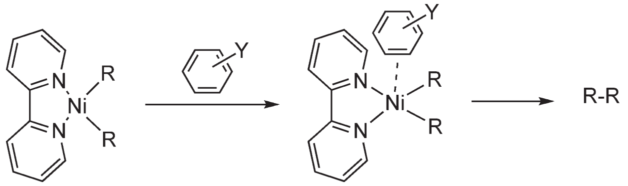
(78)

The bis(3-pyrazolyl)nickel complexes 55 and 56 are reported to be very stable to air. Under inert atmosphere, they are only slowly attacked by H_2SO_4, releasing the corresponding pyrazoles. However, the reaction with the acid in the presence of air induces reductive elimination, affording the corresponding coupling products (Scheme 40).[84,85,86] A similar situation was observed for $Ni(C_6F_5)_2(bipy)$, which releases perfluorobiphenyl upon treatment with

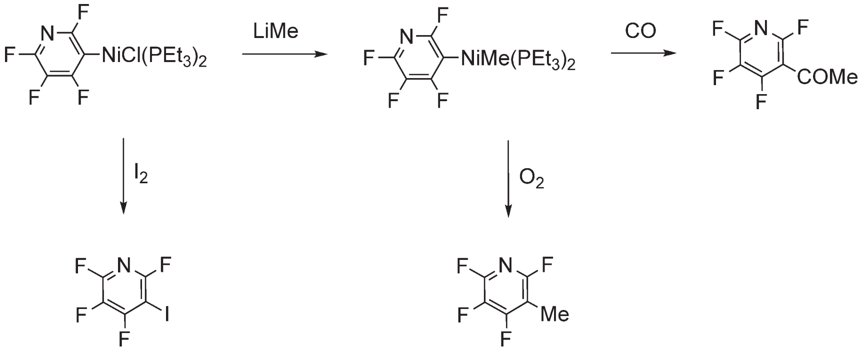


Scheme 40

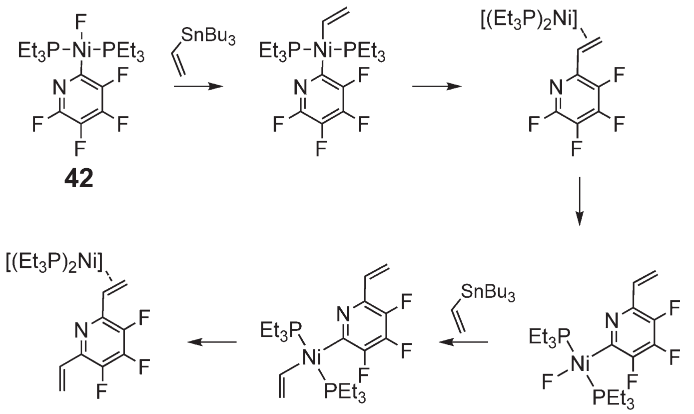
trifluoroacetic acid under air. UV–VIS monitoring of these reactions suggests that the protonation of the metal center precedes the O_2-induced coupling. The reductive elimination of related dialkyl complexes NiR_2(bipy) is more facile and can be induced by electron-poor aromatic molecules (Scheme 41).[86] In contrast with its stable Pd analog, the bis(cyanomethyl) compound $Ni(CH_2CN)_2$(dppe) decomposes at room temperature into a complex mixture of products. However, introduction of oxygen at low temperature induces the selective coupling of the organic fragments, yielding succinonitrile.[47] Oxygen also induces the reductive elimination of alkyl–fluoropyridyl compounds, shown in Scheme 42. Other coupling reactions shown in this scheme involve reductive carbonylation and iodination.[54,55] Reductive elimination of vinyl and fluoropyridyl groups occurs during the reaction of complex **42** with a vinylstannane, which affords a mixture of the Ni(II) and Ni(0) complexes **156 and 157** (Scheme 43).[111] The process can be performed catalytically to afford 2-vinylfluoropyridines, although only a few turnovers were achieved. The application of these and related reactions in the synthesis of various types of fluoroheterocyclic derivatives has been discussed in a review article.[258]



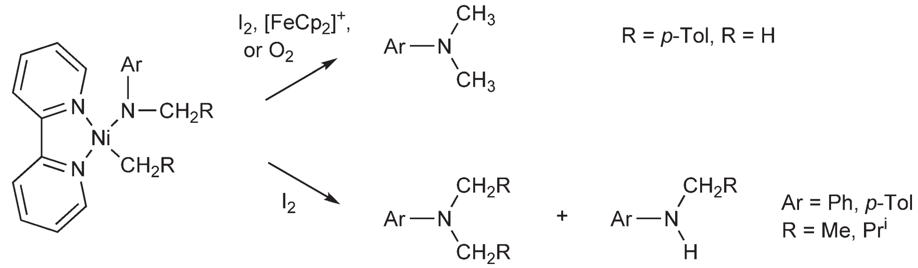
Scheme 41



Scheme 42



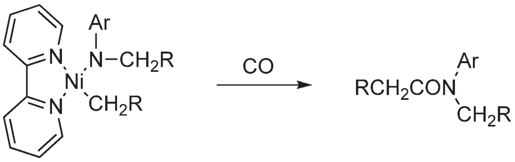
Scheme 43



Scheme 44

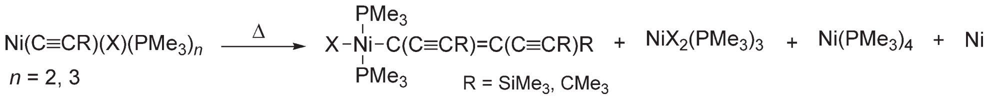
The study of C–X (X = O, N, S) coupling reactions is attracting much interest, especially in view of their potential incorporation in catalytic processes that have found ample application in organic synthesis, such as the synthesis of aromatic amines.[259,260] Most nickel alkyl–alkoxo or alkyl–amido complexes are reluctant to undergo thermal C–N or C–O coupling, but this can be induced by oxidation with O_2, $[FeCp_2]^+$, or I_2.[128,129] In the case of complexes carrying alkyl groups with β-hydrogen atoms, the coupling reaction competes with β-elimination, which leads to the formation of secondary amines (Scheme 44).[129] A theoretical paper concludes that the exothermicity of the reductive elimination of CH_3–X from *cis*-$[M(CH_3)X(PH_3)_2]$ (X = OH, NH_2, CH_3; M = Ni, Pd, Pt) decreases in the same order as the homolytic M–X bond energies, that is, $OH < NH_2 < CH_3$. Two reaction channels, involving four- and three-coordinate intermediates, were identified. For Ni, the dissociative path is somewhat more favorable for X = OH and NH_2, while reductive elimination from a square-planar intermediate is preferred for $X = CH_3$.[261]

Insertion of carbon monoxide followed by reductive coupling is an old reaction that continues to be studied and developed. Examples of this reaction are the carbonylation of nickel dialkyl complexes to give ketones,[224] alkyl–alkoxides to yield esters,[62,128] and alkyl–amides to give organic amides (Equation (79)).[129] The carbonylation of the binuclear complex **145** leads to the formation of an isoquinolone ring with the elimination of one of the two Ni atoms, but no CO insertion occurs at the second metal moiety. Hydrolytic cleavage of the remaining Ni–C bond provides the free heterocyclic base (Scheme 45).[132]

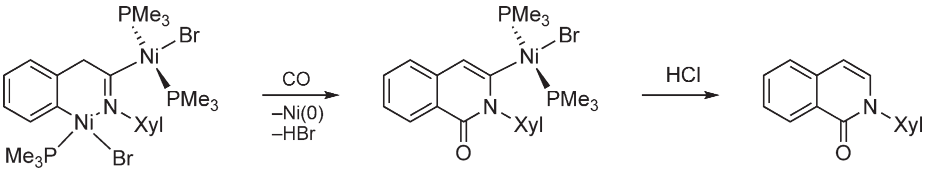


(79)

An unusual elimination reaction described as a linear alkyne trimerization takes place when solid samples of nickel (halo)acetylide complexes containing PMe_3 are heated (Equation (80)).[52,67] These compounds have been used in the synthesis of complex polyunsaturated hydrocarbon molecules (Scheme 46).[52]

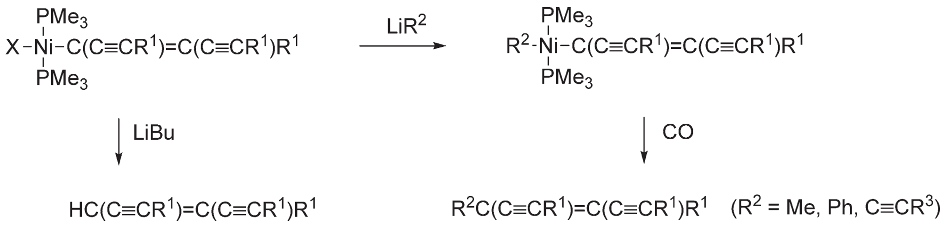


$$\underset{n = 2,\,3}{Ni(C{\equiv}CR)(X)(PMe_3)_n} \xrightarrow{\Delta} X\text{-}\overset{PMe_3}{\underset{PMe_3}{Ni}}\text{-}C(C{\equiv}CR){=}C(C{\equiv}CR)R + NiX_2(PMe_3)_3 + Ni(PMe_3)_4 + Ni \quad R = SiMe_3,\ CMe_3 \tag{80}$$



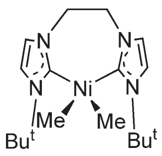
145 **158**

Scheme 45



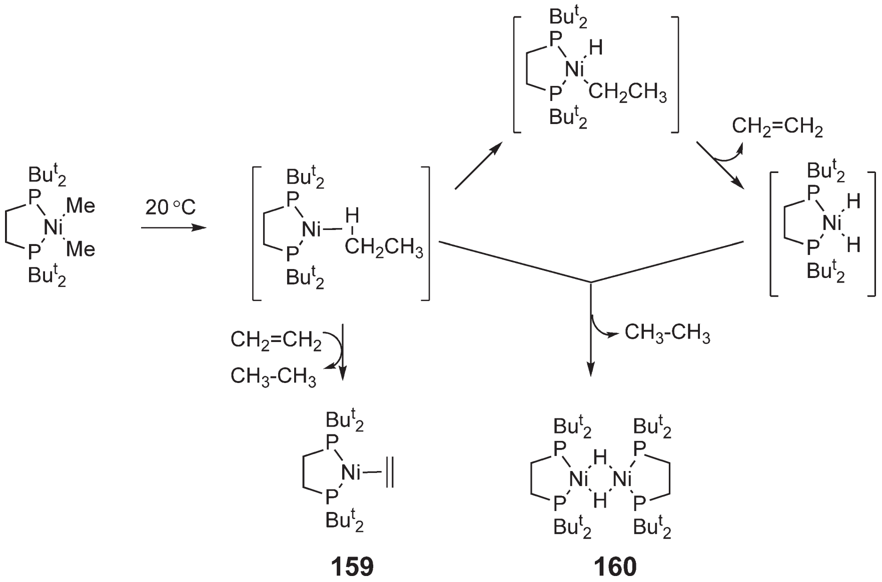
Scheme 46

Nickel dimethyl complexes $NiMe_2(PR_3)_2$ decompose readily in solution, either thermally or photochemically, providing an efficient method for the generation of Ni(0) complexes.[262] The complex $NiMe_2$(dtbpe) undergoes reductive elimination in benzene at 50–60 °C, giving rise to a binuclear Ni(0) π-arene complex.[105] Careful thermolysis in THF-d_8 over several days at 20 °C affords a 1 : 2 : 1 mixture of the ethylene complex **159**, the hydride **160**, and ethane (Scheme 47). If the reaction is carried out in the presence of ethylene, equimolecular amounts of **159** and ethane are formed. These results can be explained by assuming that the decomposition process involves the formation of a σ-C_2H_6 complex. In contrast with this behavior, the bis(carbene) dimethyl complex **45** decomposes giving methane as the only organic product.[62] The reaction follows first-order kinetics, and the rate is independent of the concentration of added bis(carbene) ligand, suggesting a unimolecular process. Reexamination of the decomposition of $NiMe_2$(dppe)[263] showed that it produces a 1 : 1 mixture of ethane and methane, although the ethane : methane ratio increases to 9 : 1 in the presence of added phosphine.[62]

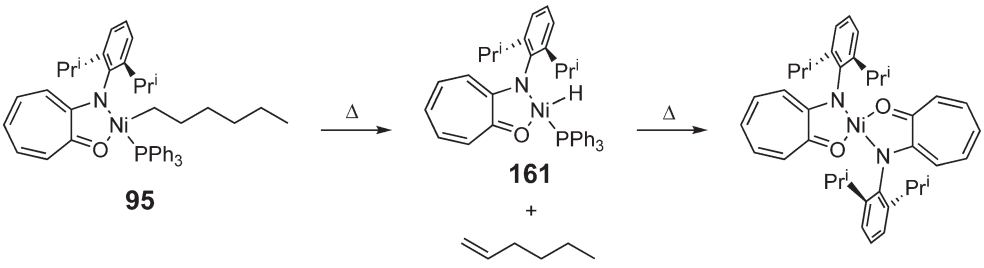


45

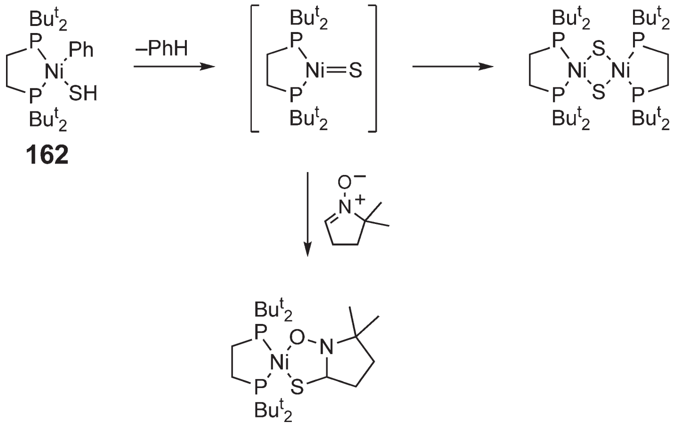
Although β-elimination is a very common process in nickel alkyl chemistry, the direct observation of this reaction and the characterization of the metal-containing products are rare, since both the starting alkyl and the resulting hydride are usually unstable species. The decomposition of the 1-hexyl anilinotropolone compound shown in Scheme 48 takes place



Scheme 47



Scheme 48



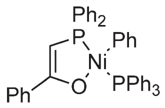
Scheme 49

in C_6D_6 at 50 °C, producing hexene together with the stable hydride **161**. Prolonged heating of the solution causes the transformation of the hydride into the bis(anilinotropolone) complex. It is suggested that the latter process involves the reductive elimination of free anilinotropolone, which reacts with the hydride to afford the final product.[164]

The terminal hydrosulfide complex **162** loses benzene in solution giving a binuclear sulfido-bridged dimer. A terminal sulfido intermediate can be trapped if the reaction is carried out in the presence of nitrones (Scheme 49).[92,264]

8.02.3.4.4 Nickel alkyl and aryl complexes in olefin polymerization and oligomerization catalysis

The investigation of nickel-catalyzed olefin oligomerization and polymerization reactions has contributed very significantly to the advance of the organometallic chemistry of this element. The identification of the species involved in the so-called "Nickel effect" first, and later the development of the SHOP oligomerization catalysts **163**, have constituted, for a long time, an important stimulus for the study of organonickel chemistry. Excellent accounts of the early investigations in this field can be found in COMC (1982) (Volume 6, Chapter 37.4.; Volume 8, Chapter 52). Although some reports by Fink,[265] and Klabunde[266–268] showed in the 1980s that nickel catalysts can be turned to olefin polymerization activity, the discovery of highly active nickel and palladium α-diimine catalysts **164** in 1995 triggered an intense wave of interest for a new kind of nickel polymerization catalysts, Ni(II) complexes incorporating nitrogen- and oxygen-based ligands. Much of this work does not involve explicitly the synthesis or the identification of σ-alkyl organonickel compounds, and it is beyond the scope of this account, but several reviews and books have extensively covered these aspects.[122,152,153,269–271] However, the use of organonickel complexes as catalyst precursors has important advantages,[186] such as a better knowledge of the nature of the active species, which allows detailed studies of the mechanism of the polymerization reaction (as shown by Brookhart's seminal investigation using the cationic alkyls **165**, see below), as well as the development of aluminum-free catalysts exhibiting tolerance to polar substances. Apart from Brookhart's work, there have been several reports on the use of cationic[232,233] or zwitterionic η^3-benzylnickel compounds[173,185,217,248] as oligomerization or polymerization catalyst precursors.



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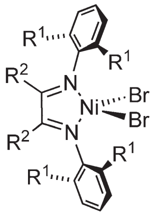
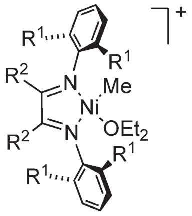
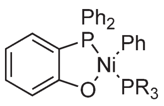


164



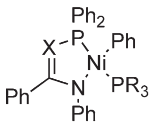
165

Neutral aryl and alkyl complexes have proved a very fertile ground for new catalytic developments. In spite of the attention devoted to new catalysts based on hard donor ligands, phosphinoenolate complexes (SHOP catalysts)[189,190, 193,194,212] 163 and the related phosphinophenolates 166[183,198] continue to attract much attention. These complexes provide considerable tolerance to polar substances and can even be used in aqueous media.[189,272,273]



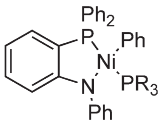
166

Somewhat disappointingly, replacement of the oxygen atom by nitrogen in the SHOP-type and phosphinoenolate complexes provides the analogous, although, inactive complexes 167[196,197,214] and 168.[198] However, a group of active catalysts containing PN phosphinosulfonamide ligands, 169, have been described recently.[182]



X = CH or N

167



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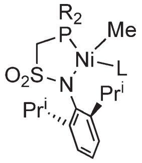
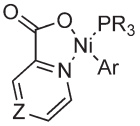


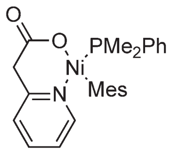
169

Anionic N,O ligands have been particularly successful in the search for new oligomerization/polymerization nickel catalysts. Pioneering work by Cavell showed that nickel aryls containing pyridinecarboxylate ligands 170 and 171 are low to moderately active ethylene oligomerization catalysts.[166,167] These complexes also catalyze the alternating co-polymerization of CO and ethylene.[166] Grubbs has achieved high molecular weight polyethylene and high catalytic activity with the neutral nickel salicylaldiminate catalysts 172.[157] Bulky R groups such as Ph, 9-phenanthrenyl, or 9-anthracenyl are important to obtain high activity in the absence of the co-catalyst.[159] It is believed that the role of bulky substituents is to improve catalyst stability[181] as well as promote the dissociation of the PPh_3 ligand. The substitution of the latter for the labile acetonitrile ligand gives more active catalysts 173.[181,179] The salicylaldiminate catalysts display a remarkable tolerance to polar substances, and can co-polymerize ethylene with functionalized norbornenes,[159,274] and find use in emulsion polymerization in water.[180,273,275] However, chlorinated monomers cause the deactivation of the catalyst through a β-chloride abstraction process.[276] Allyl substitution in the N-bound aromatic group causes the molecule of catalyst to become self-inmobilized into the growing polyethylene chain.[160,161] Ligand-free salicylaldiminate $\eta^1:\eta^2$-4-cyclooctenyl complexes have been used as polymerization precursors.[277,278]



Z = C(OMe), N, C(NO_2)

170



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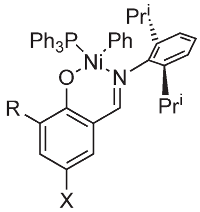
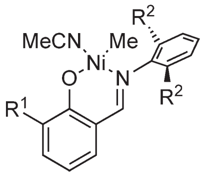
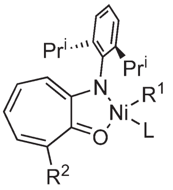


172



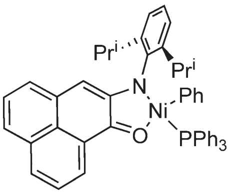
173

Other nickel complexes displaying N–O anionic ligands have been found to be active as ethylene polymerization catalysts, displaying activity levels comparable to those of the salicylaldiminate complexes. The structures of some of these complexes **174–176**, are truly remarkable. Like the salicylaldiminate complexes, anilinotropolone **174**[162–164] and anilinoperinaphthenone derivatives **175**,[165] display electron delocalization in a five-membered chelate, giving rise to highly active ethylene polymerization catalysts, although they display limited lifetimes under the polymerization conditions. The binuclear catalyst **176** is another example of a catalytically active complex featuring a five-membered N–O chelate.[172]



L = PPh_3 or 2,4-Lut

174



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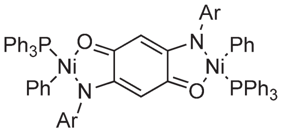
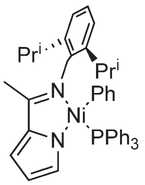


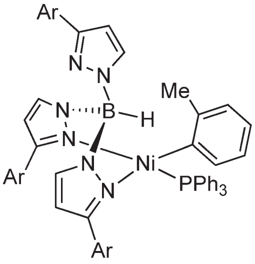
Ar = 2,6-$C_6H_3Pr^i_2$, Xyl, nap

176

Many Ni alkyl or aryl complexes containing bidentate nitrogen donors, among them compound **177**, have been used as moderately active catalysts for olefin polymerization.[168,169,171,208] The pyrazolylborate complexes **178**[155] and **179**[156] catalyze the co-polymerization of ethylene and CO, and, in contrast to other Ni catalysts, do not require preactivation with ethylene. The N–N- and N–O-ligated complexes **180 and 181** are even more efficient and the latter can be used in supercritical CO_2.[177]

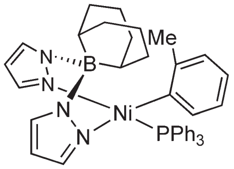


177



Ar = Ph, *p*-Tol

178



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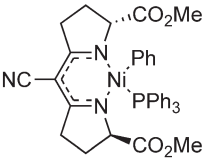
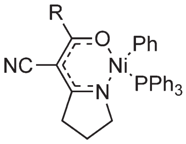
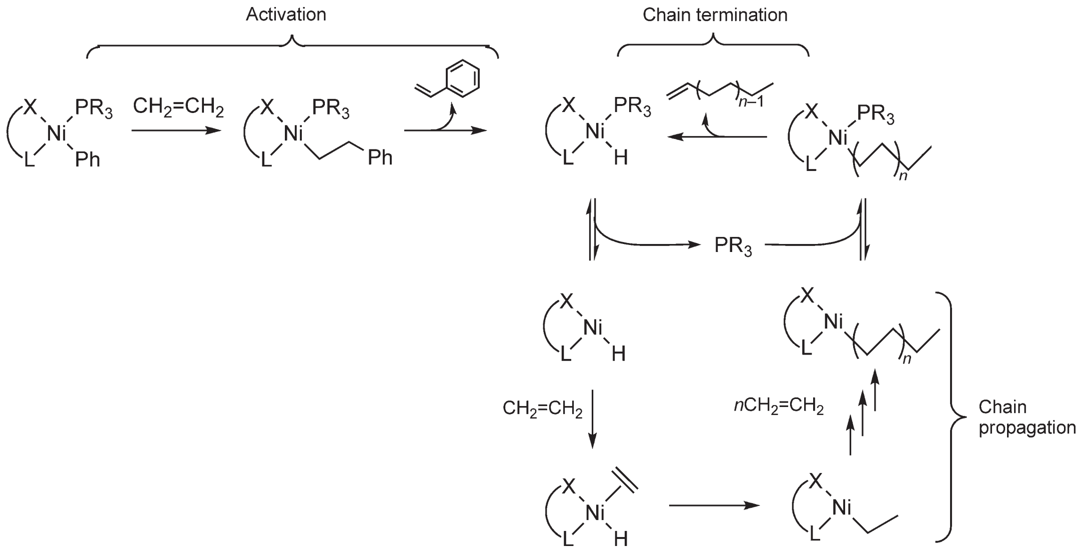


180



181

The mechanism of ethylene oligomerization by SHOP and related catalysts, such as phosphinophenolate complexes, has been the subject of intense investigation (see COMC (1982), Chapter 52, references cited by Heinicke *et al.*[183] and Pietsch *et al.*[198] It is generally agreed that the actual catalytic species are nickel hydride complexes, generated by ethylene insertion into the Ni–aryl bond of the precursor followed by β-H elimination reaction (Scheme 50). Styrene or styrene derivatives can be detected in the reaction medium as a product of this activation process.[196,197,212] In the case of the salicylaldiminate and anilinotropolone catalysts, styrene elimination is not required, but chain propagation starts directly from the phenyl complex.[159,164] While the activation stage might involve either a pentacoordinate, 18-electron intermediate (associative mechanism) or displacement of the PR_3 ligand by ethylene,[166,167] it is widely accepted that the chain propagation step requires phosphine dissociation. Coordination of the PR_3 ligand to the propagating species generates an electron-rich 16-electron species that is much less reactive toward ethylene, but readily undergoes β-elimination, regenerating the hydride. Therefore, the equilibrium between free and coordinated phosphine plays an important role, modulating the activity of the catalyst and the molecular weight of the products. In accordance with this mechanism, SHOP catalysts are strongly inhibited by added

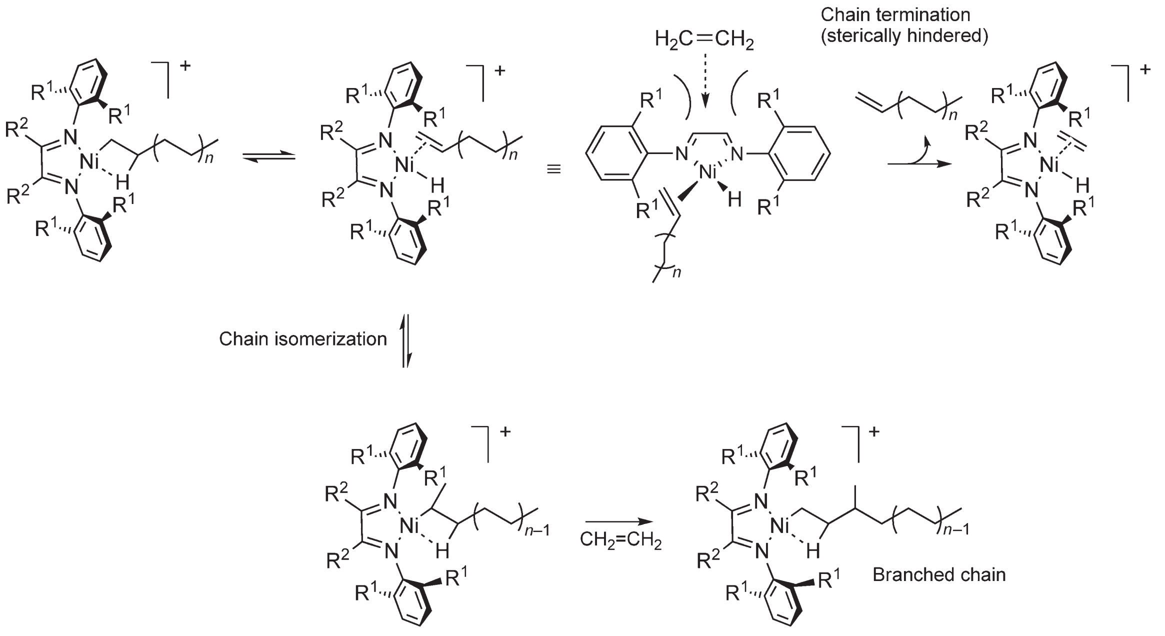


Scheme 50

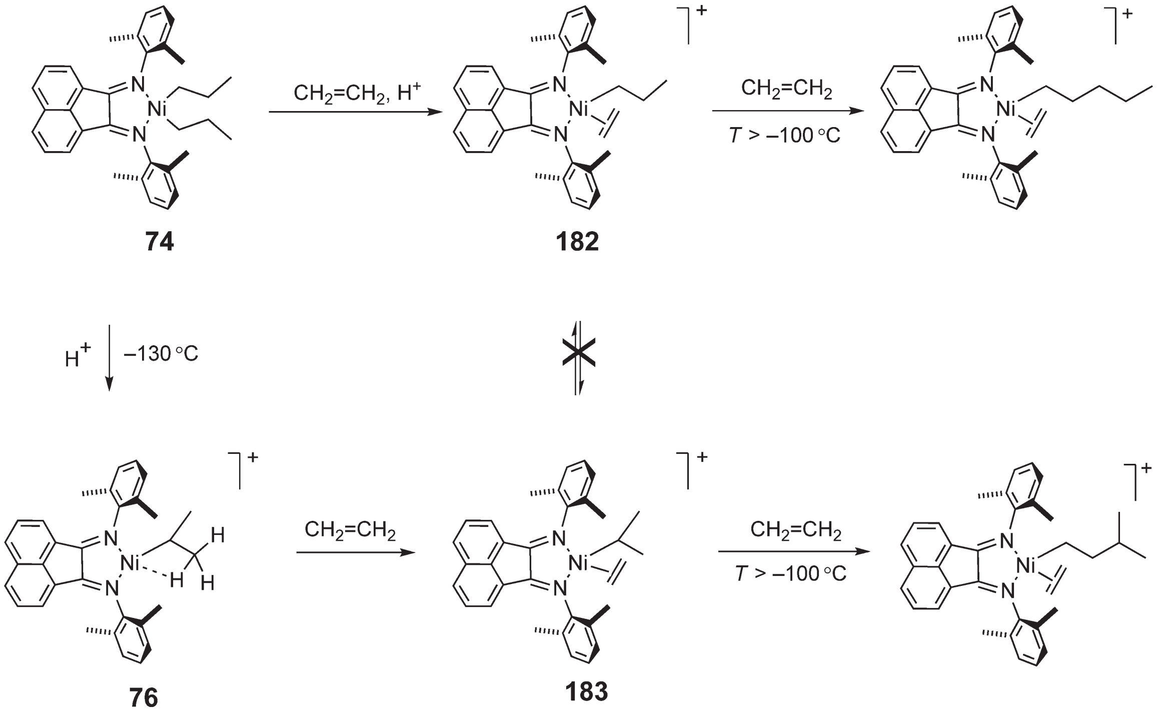
phosphine, since the ligand decreases the concentration of the propagating species. Other neutral catalysts such as salicylaldiminates **172**[159] or phosphinosulphonamide complexes **169**[182] are inhibited by added ligand (PPh_3 or CH_3CN, respectively), indicating that a dissociative path is operating in these neutral catalysts as well. NMR experiments have suggested that the resting state of these catalysts is a 16-electron ligand-coordinated alkyl or hydride complex. In contrast, anilinotropolone catalysts **174** are less sensitive to added phosphine.[163] It has been suggested that in this case, the catalyst rests as an equilibrium mixture of the alkyl–phosphine and alkyl–ethylene complexes, with the latter being predominant at high ethylene concentration.[164] In spite of the negative influence of the ligand on the rate of the catalytic process, it is often observed that it has a beneficial influence on the stability of the catalyst. Thus, salicylaldiminate catalysts are indefinitely stable if the co-ligand (PPh_3) is not removed by phosphine scavengers.[159,181] Neutral catalysts decay over time to catalytically inert bis(ligand) $Ni(Lig)_2$ nickel complexes.[273] Studies on the anilinotropolone system showed that $Ni(Lig)_2$ is formed by decomposition of the intermediate hydride species (Scheme 46, Section 8.02.3.4.3), a process inhibited by free PPh_3.

Although the neutral SHOP catalysts can be induced to produce low molecular weight polyethylene, the production of high molecular weight polymer requires an efficient mechanism to limit the speed of the chain termination process. The introduction of the α-diimine catalysts has been of enormous importance in this respect, illustrating how steric effects can efficiently reduce the rate of chain transfer. As shown in Scheme 51, the axial disposition of the *ortho*-aryl substituents effectively blocks the axial positions of the nickel complex, preventing the displacement of the growing chain, even when the β-elimination process is still operative.[57,153] This important mechanistic concept has received support from a number of theoretical investigations.[279–282] While steric hindrance prevents chain displacement by the monomer, it allows the isomerization of the growing alkyl chain, causing the appearance of methyl branches. Eventually, the repetition of this process may lead to longer branches, a process termed "chain walking."[57,153]

As the resting state of many nickel catalysts is a 16-electron alkyl stabilized by an additional co-ligand (PPh_3, MeCN, etc.), direct observation of the chain propagation step is often difficult or impossible. This is true even for the extremely labile cationic etherate complexes **165** since, in contrast with their Pd analogues,[57] displacement of the Et_2O ligand by the monomer and insertion of the latter proceed at comparable rates.[59] Fortunately, the synthesis and isolation of agostic ethyl and propyl complexes (Scheme 15, Section 8.02.3.1.3) allowed the detection of the corresponding alkyl–ethylene complexes and the precise measurement of the rates of chain propagation and isomerization (Scheme 52).[59] Exposure of the agostic *i*-propyl complex **76** to ethylene or protonation of the bis-*n*-propyl complex **74** under an ethylene atmosphere leads to the *i*-propyl and *n*-propyl ethylene complexes **183** and **182**, respectively. At variance with analogous Pd complexes,[283] which equilibrate to an *i*/*n* mixture prior to insertion, **183** and **182** undergo ethylene insertion without chain isomerization. This observation is consistent with the fact that nickel catalysts produce less-branched polyethylene than their Pd analogs. The isomerization of the alkyl complexes



Scheme 51

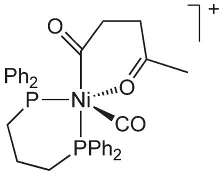


Scheme 52

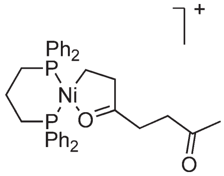
requires the dissociation of the ethylene ligand and the restoration of the formally 14-electron agostic species, which is favored at higher temperatures and low ethylene concentration. This is in good agreement with bulk polymerization experiments, which demonstrated that high temperatures and low pressures favor the formation of more branched polymers.[284]

A very precise picture of the intimate steps of these processes has emerged from DFT calculations, covering aspects such as the binding of the monomer to group 10 metal centers,[285,286] the mechanism of the propagation, chain-transfer and termination steps,[285,287–290] the influence of different types of ligands on the monomer insertion barrier,[291,292] the effect of bulky ligands (by combined MM-DFT methods),[279,280,282,293,294] and the insertion of functionalized monomers.[286,295,296] The salicylaldiminate[297] and anilinotropolone[298] catalysts have been investigated as well.

The basic steps of the alternating ethylene–CO polymerization with nickel complexes containing chelating diphosphines have been investigated using the acyl–carbonyl complexes depicted in Scheme 31 (Section 8.02.3.4.2). Using the dppe derivative, several intermediates of this process, such as the pentacoordinated acyl **184** and the "second-generation" acyl **185**, have been identified.[124] This is in contrast with the analogous Pd system where pentacoordinated species have not been observed. The barrier for the CO/ethylene co-polymerization propagation was estimated to be less than 10 kcal mol^{-1}, and hence the lower efficiency of Ni catalysts (as compared to Pd) was attributed to the formation of very stable pentacoordinated resting states of type **184**.



184



185

8.02.4 Metallacycles

Although in a strict sense the term metallacycle applies to cyclic complexes containing two Ni–C σ-bonds,[299] in this section we use a broader definition of the term, to comprise also those compounds that contain an Ni–C and an Ni–heteroatom bond where the heteroatom has a formal negative charge. The two types of metallacycles can be distinguished by the terms "carbometallacycles" and "heterometallacycles," but their synthesis and reactivity are closely related, and will be treated together (Table 9). Those complexes displaying cyclic structures closed by one

Table 9 Metallacycles

Compound	*Characterization*	*References*
(a) Carbometallacycles		
$\mathrm{Ni(CH_2CH_2CH_2CH_2)(phen)}$	A, ^{1}H, ^{13}C, IR	128
$\mathrm{Ni(CH_2CH(Me)CH(Me)CH_2)(bipy)}$	A, ^{1}H, ^{13}C, IR	128
$\mathrm{Ni(CH(Me)CH_2CH_2CH_2)(bipy)}$	A, ^{1}H, ^{13}C, IR	128
$\mathrm{Ni(CH_2C({=}CH_2)C({=}CH_2)CH_2)(bipy)}$	A, ^{1}H, ^{13}C, IR	128
$\mathrm{Ni(CH_2\text{-}2\text{-}C_6H_4CH_2)(bipy)}$	A, ^{1}H, ^{13}C, IR	128
$\mathrm{Ni(CH_2\text{-}2\text{-}C_6H_4\text{-}2\text{-}C_6H_4CH_2)(bipy)}$, **188**	^{1}H, ^{13}C	304
$\mathrm{[Ni(CH(CN)CH_2CH_2CH(CN))]6}$, **4**	XR	14
$\mathrm{Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4)(py)2}$, **189**	A, ^{1}H, ^{13}C	46
$\mathrm{Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4)(bipy)}$	A, ^{1}H, ^{13}C	250
$\mathrm{Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4)(N(DiPP){=}CH\text{-}2\text{-}py)}$	A, ^{1}H, ^{13}C, IR	46

(Continued)

Table 9 (Continued)

Compound	*Characterization*	*References*
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4)(PMe_3)(CNBu^t)$	A, ^1H, ^{13}C, ^{31}P	46
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4)(PMe_2Ph)_2$	^1H, ^{13}C, ^{31}P	337
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4)(dippe)$, **190**	A, ^1H, ^{13}C, ^{31}P	62
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4)(dippp)$	A, ^1H, ^{13}C, ^{31}P	62
$[Ni(CH(PMe_3)CMe_2\text{-}2\text{-}C_6H_4)(\mu\text{-}Cl)]_2$	A, ^1H, ^{13}C, ^{31}P	130
$Ni(CH(PMe_3)CMe_2\text{-}2\text{-}C_6H_4)(Cl)(PMe_3)$, **266**	XR, A, ^1H, ^{13}C, ^{31}P	130
$Ni(CH(PMe_3)CMe_2\text{-}2\text{-}C_6H_4)(Cl)(CNBu^t)$	A, ^1H, ^{13}C, IR	130
$Ni(CF_2CF_2\text{-}2\text{-}C_6H_4)(dcpe)$, **229**	A, ^1H, ^{13}C, ^{31}P, ^{19}F, IR, MS	120
$Ni(CF_2CF_2\text{-}2\text{-}C_6H_4)(PEt_3)_2$	^1H, ^{13}C, ^{31}P, ^{19}F	120
$Ni(CF_2CF_2\text{-}2\text{-}C_{10}H_6\text{-}3)(dcpe)$	XR, A, ^{13}C, ^{31}P, ^{19}F	327
$Ni(CF_2CF_2\text{-}2\text{-}C_{10}H_6\text{-}3\text{-}CO)(dcpe)$	XR, ^1H, ^{13}C, ^{31}P, ^{19}F, IR, MS	120
$Ni(CF_2CF_2\text{-}2\text{-}C_{10}H_6\text{-}3\text{-}C(CO_2Me){=}C(CO_2Me))(dcpe)$	^{31}P	120
$Ni(CF_2CF_2\text{-}2\text{-}C_6H_4C(CO_2Me){=}C(CO_2Me))(dcpe)$, **230**	XR, ^1H, ^{13}C, IR, MS	327
$Ni(2\text{-}C_6H_4\text{-}2\text{-}C_6H_4)(dippe)$, **186**	A, ^1H, ^{13}C, ^{31}P	301, 313
$Ni(2\text{-}C_6H_4\text{-}2\text{-}C_6H_4)(dcpe)$	A, ^1H, ^{13}C, ^{31}P, MS	144
$Ni(C(Ph){=}C(Ph)C(Ph){=}C(Ph))(dppe)$, **187**	IR, MS	302
$[Ni(2\text{-}C_6H_4\text{-}2\text{-}C_6H_4)(\mu_3\text{-}S)_2\{Ni(dippe)\}_2]$, **228**	XR, A, ^1H, ^{13}C, ^{31}P	301, 313
$[Ni(2\text{-}C_6H_4\text{-}2\text{-}C_6H_4Me\text{-}4)(\mu_3\text{-}S)_2\{Ni(dippe)\}_2]$	XR, ^1H, ^{31}P	313
(b) Heterometallacycles		
$Ni(CH_2CH_2CH_2CH_2O)(bipy)$, **223**	XR, A, ^1H, ^{13}C, IR	127, 128
$Ni(CH_2CH_2CH_2CH_2O)(phen)$	A, ^1H, ^{13}C, IR	128
$Ni(CH(Me)CH_2CH_2CH_2O)(bipy)$	A, ^1H, ^{13}C, IR	128
$Ni(CH_2CH(Me)CH(Me)CH_2O)(bipy)$	A, ^1H, ^{13}C, IR	128
Ni(3-(*exo-trans-endo*-2,2′-binorborn enyl)-O-3′)(bipy)	A, ^1H, ^{13}C	337
$[Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4\text{-}\mu_2\text{-}O)(PMe_3)]_2$	A, ^1H, ^{13}C, ^{31}P	338
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4\text{-}\mu_2\text{-}O)(bipy)$	A, ^1H, ^{13}C	338
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4\text{-}\mu_2\text{-}O)(phen)$	A, ^1H, ^{13}C	338
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4\text{-}\mu_2\text{-}O)(dmpe)$	XR, ^1H, ^{13}C, ^{31}P	338
$Ni(CPh_2C({=}CPh_2)O)(dtbpe)$, **216**	XR, A, ^1H, ^{13}C, ^{31}P, IR	148
$[Ni(CF_2CF_2\text{-}2\text{-}C_6H_4\text{-}\mu\text{-}O)(PEt_3)]_2$	^{31}P, ^{19}F	120
$[Ni(CF_2CF_2\text{-}2\text{-}C_{10}H_6\text{-}\mu\text{-}O\text{-}3)(PEt_3)]_2$	XR, A, ^1H, ^{13}C, ^{31}P, ^{19}F, IR	120

(Continued)

Table 9 (Continued)

Compound	*Characterization*	*References*
$[Ni(C(CF_3)_2CH{=}C(Ph){-}\mu{-}O)(CNBu^t)]_2$, **217**	XR, A, ^1H, ^{19}F	336
$[Ni(C(SiMe_3)(SiMe_2{-}\mu{-}O)(SiMe_2{-}2{-}py))]_2$, **288**	XR	340
$Ni(CPh{=}CCH_2CH_2CH_2CHCH{=}CHO)(tmeda)$, **211**	XR, A, ^1H, ^{13}C, IR	164
$Ni({-}2{-}C_6H_4C({=}CH_2)O)(dippe)$, **193**	XR, A, ^1H, ^{13}C, ^{31}P, IR	76
$Ni({-}2{-}C_6H_4C({=}CHMe)O)(dippe)$	A, ^1H, ^{13}C, ^{31}P, IR	77
$Ni({-}2{-}C_6H_4C({=}CHCHMeOH)O)(dippe)$	^1H, ^{13}C	76
$Ni({-}2{-}C_6H_4C({=}CHCHPhOH)O)(dippe)$	A, ^1H, ^{13}C, IR	76
$Ni({-}2{-}C_6H_4C({=}CHCHMeCH_2COMe)O)(dippe)$	A, ^1H, ^{13}C, ^{31}P, IR	77
$Ni({-}2{-}C_6H_4C(CHMeCH_2CH{=}CMeO)O)(dippe)$	XR, A, ^1H, ^{13}C, ^{31}P, IR	77
$Ni({-}2{-}C_6H_4CMe_2CH_2CH_2{-}O)(bipy)$	A, ^1H, ^{13}C	339
$[Ni(C({=}O){-}2{-}C_6H_4{-}\mu{-}O)(PMe_3)]_2$	A, ^1H, ^{13}C, ^{31}P, IR	243
$Ni(C({=}O){-}2{-}C_6H_4{-}O)(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P, IR	243
$Ni(C({=}O){-}2{-}C_6H_4{-}O)(PMe_3)_3$, **191**	A, ^1H, ^{13}C, ^{31}P, IR	243
$Ni(C({=}O)C_6H_2Bu^t{-}3{-}Me{-}5{-}O{-}2)(PMe_3)_3$	XR, A, ^1H, ^{13}C, ^{31}P, IR	243
$Ni(C({=}O)C_6H_2Bu^t{}_2{-}3{,}5{-}O{-}2)(PMe_3)_3$	XR, A, ^1H, ^{13}C, ^{31}P, IR	243
$Ni(C({=}O){-}2{-}C_{10}H_6{-}O{-}1)(PMe_3)_3$	A, ^1H, ^{13}C, ^{31}P, IR	243
$Ni(C({=}O)C{=}C(CH_2CH_2CH_2CH_2){-}O)(PMe_3)_3$	A, *m/d*, ^1H, IR	126, 305
$Ni(C({=}O)C{=}C(C_6H_4CH_2CH_2){-}O)(PMe_3)_3$	A, *m/d*, ^1H, IR	126
$Ni(C({=}O)C{=}C(CHPhCH_2CH_2CH_2){-}O)(PMe_3)_3$	A, *m/d*, ^1H, IR	305
$Ni(C({=}O)C{=}C(CHBu^tCH_2CH_2CH_2){-}O)(PMe_3)_3$	A, *m/d*, ^1H, IR	305
$Ni(C({=}O)C(Ph){=}C(Ph)O)(PMe_3)_3$	XR, A, *m/d*, ^1H, ^{13}C, ^{31}P, IR	305
$Ni(CH_2CH_2COO)(py)_2$	XR, A, ^1H, ^{13}C, IR	341
$Ni(CH_2CH_2COO)(bipy)$	XR	126
$Ni(CH_2CH_2COO)(Me_2Si(py{-}2)_2)_2$	XR, A, ^1H, ^{13}C, IR	341
$Ni(CH_2CH_2COO)(RCH{=}NCH_2CH_2N{=}CHR)$	A, IR	310
$Ni(CH_2CH_2COO)(PPh_2CH_2P({=}O)Ph_2)$	XR, A, ^1H, ^{31}P, IR	126
$Ni(CH_2CH_2COO)(PPh_2C({=}NMes)C({=}NMes)PPh_2)$, **220**	XR, ^1H, ^{31}P	342
$Ni(CH_2CH_2COO)(PPh_2C{=}C(N(p{-}Tol)C_6H_3Me{-}3{-}NH{-}2)$, **221**	XR, A, ^1H, ^{13}C, ^{31}P	342
$Ni(CH_2CH_2COO)(PPh_2C{=}CPPh_2(N(C_6H_4Bu^t{-}4)C_6H_3Bu^t{-}3{-}NH{-}2)$	^{31}P	342

(Continued)

Table 9 (Continued)

Compound	*Characterization*	*References*
Ni(CH$_2$CH$_2$CH$_2$COO)(RCH=NCH$_2$CH$_2$N=CHR)	A, IR	310
Ni(CH$_2$CH(*N*-phtalimido)COO)(Me$_2$phen)	IR	308
Ni(CH$_2$CH(*N*-phtalimido)COO)(dppe)	A, ^{1}H, ^{13}C, ^{31}P, IR	308
Ni(CHMeCH(*N*-phtalimido)COO)(dppe), **197**	^{1}H. ^{13}C, ^{31}P, IR	307
Ni(CH$_2$C(=CH$_2$)COO)(bipy)	A, IR	309
Ni(CF$_2$CF$_2$C$_6$H$_4$-2-COO)(dcpe)	XR, ^{13}C, ^{1}H, ^{31}P, ^{19}F, MS	120
Ni(C(Et)=C(Et)COO)(py)$_2$	XR, A, ^{1}H, ^{13}C, IR	341
Ni(CH$_2$C(=CH$_2$)COO)(tmeda)	A, IR	309
Ni(CHCH(CH$_2$CH=CHCH$_2$)COO)(tmeda)	XR	306
Ni(C=C(CH$_2$CH$_2$CH$_2$CH$_2$)COO)(dcpe)	*m/d* ^{13}C, ^{31}P, IR, MS	116
Ni(C(CO$_2$Me)=C(CO$_2$Me)C=C((CH$_2$)$_3$CH$_2$)COO)(dcpe)	^{1}H, ^{13}C, ^{31}P, IR, MS	116
Ni(-2-C$_6$H$_4$-2-C$_6$H$_4$COO)(bipy), **196**	A, IR	309
Ni(-2-C$_6$H$_4$-2-C$_6$H$_4$COO)(tmeda), **196**	XR, A, ^{1}H, ^{13}C, IR	309
Ni(2-C$_{10}$H$_6$-COO)(dcpe)	XR, A, ^{1}H, ^{13}C, ^{31}P, MS	327
Ni(C(=O)CHCH(CH$_2$CH=CHCH$_2$)COO)(bipy), **195**	A, ^{1}H, DTA/TG	306
Ni(C(=O)CHCH(CH$_2$CH=CHCH$_2$)COO)(tmeda), **195**	A, ^{1}H, DTA/TG	306
[Ni(C(Ph)HN(furfuryl)COO(N(furfuryl)=CHPh)]$_6$·(1,4-dioxane)$_4$	XR, A, IR	319
[Ni(C(Ph)HN(furfuryl)COO(N(furfuryl)=CHPh)]$_6$·(THF)$_{4,}$ **207**	XR, A, ^{13}C, IR, MS	319
[Ni(C(Ar)HN(furfuryl)COO)(N(furfuryl)=CH–Ar)]$_n$ Ar = *p*-Tol,C$_6$H$_4$(OMe)-4, Fc, 2-Furyl	A, IR	320
[Ni(C(Ph)HN(furfuryl)COO)(PMe$_3$)]$_6$·(THF)$_4$	A, IR, MS	319
Ni(C(Ph)HN(furfuryl)COO)(bipy), **210**	A, IR, MS	319
Ni(C(Ph)HN(furfuryl)COO)(pmedta), **210**	A, IR	319
[Ni(C(Ph)HN(furfuryl)COO)(N(furfuryl)=CHPh)]$_2$	XR, A, ^{1}H, ^{31}P, IR, MS	319
Ni(C(Ph)HN(furfuryl)COO)(N(furfuryl)=CHPh)$_2$	XR, A, ^{1}H, ^{13}C, IR	320
Ni(C(Ph)HN(furfuryl)COO)(N(furfuryl)=CHPh)(PMe$_3$)	XR, A, ^{1}H, ^{31}P, IR, MS	319
[Ni(C(Ph)HN(furfuryl)COO)(Ni(η^2-N(furfuryl)=CHPh))(PMe$_3$)]$_2$, **208**	XR, A, IR, MS	320
[Ni(C(Ph)HN(furfuryl)COO)-, **209**-(Ni(η^2-N(furfuryl)═CHPh)(η^1-N(furfuryl)═CHPh))]$_2$	RX, A, IR	319
Ni(CH$_2$CH$_2$CH$_2$CH$_2$N(*p*-Tol))(bipy), **224**	A, ^{1}H, ^{13}C	125,343
Ni(CH$_2$CH$_2$N(SO$_2$-*p*-Tol))(bipy), **198**	XR, A, ^{1}H, ^{13}C	312

(Continued)

Table 9 (Continued)

Compound	*Characterization*	*References*
$Ni(CH_2CHRN(SO_2\text{-}p\text{-}Tol))(bipy)(R = Me,Bu^n,Pr^i)$	A, ^1H, ^{13}C	312
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4CON(Ph))(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P, IR	250
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4C(=N\text{-}p\text{-}Tol)N(\text{-}p\text{-}Tol))(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P, IR	250
$Ni(C(=NBu^t)CH_2CMe_2\text{-}2\text{-}C_6H_4C(O)NPh)(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P, IR	250
$Ni(C(=NBu^t)CH_2CMe_2\text{-}2\text{-}C_6H_4C(N\text{-}Tol)N\text{-}Tol)(PMe_3)_2$	A, ^1H, ^{13}C, ^{31}P, IR	250
$Ni(CH_2CMe_2C_6H_4\text{-}2\text{-}N(p\text{-}Tol)(bipy)$, **225**	^1H, ^{13}C, MS	343
$Ni(C(CF_3)_2N=CHN(Mes))(CNBu^t)_2$, **218**	XR, A, ^1H, ^{19}F, IR	336
$Ni(CH_2CH_2S)(bipy)$, **206**	A, ^1H, ^{13}C, MW	314
$Ni(CH_2CHMeS)(bipy)$	A, ^1H, ^{13}C, MW	314
$Ni(CH_2CH_2CH_2S)(bipy)$	A, ^1H, ^{13}C, MW	314
$[Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4\text{-}S)(PMe_3)]_2$, **237**	A, ^1H, ^{13}C, ^{31}P	344
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4\text{-}S)(bipy)$	^1H, ^{13}C	344
$Ni(CH_2CMe_2\text{-}2C_6H_4\text{-}S)(dmpe)$	A, ^1H, ^{13}C, ^{31}P	344
$Ni(CH_2CMe_2\text{-}2\text{-}C_6H_4C(=NPh)S)(PMe_3)_2$	^1H, ^{13}C, ^{31}P, dec $> -10°$ C	250
$Ni(CH=CHCH=CHS)(dippe)$,**199**	XR, A, ^1H, ^{13}C, ^{31}P	301,313
$Ni\text{-}\mu\text{-}(CH=CHCH=CH\text{-}S)(dippe)Ni(dippe)$, **226**	A, ^1H, ^{31}P	313
$Ni(CH=CH\text{-}2\text{-}C_6H_4\text{-}S)(dippe)$, **200**	XR, A, ^{13}C, ^{31}P	301,313
$Ni\text{-}\mu\text{-}(CH=CH\text{-}2\text{-}C_6H_4\text{-}S)(dippe)Ni(dippe)$, **227**	XR, A, ^1H, ^{31}P	313
$Ni(CH=CHC(Cl)=CHS)(dippe)$,**64**	A, ^1H, ^{13}C, ^{31}P	68
$Ni(2\text{-}C_6H_4\text{-}2\text{-}C_6H_4\text{-}S)(dippe)$, **201**	XR, A, ^1H, ^{13}C, ^{31}P	301
$Ni(2\text{-}C_6H_4CH_2\text{-}2\text{-}C_6H_4S)(dippe)$, **205**	XR, A, ^1H, ^{31}P	313
$Ni(2\text{-}C_6H_4S\text{-}2\text{-}C_6H_4S)(dippe)$, **204**	XR, A, ^1H, ^{31}P	313

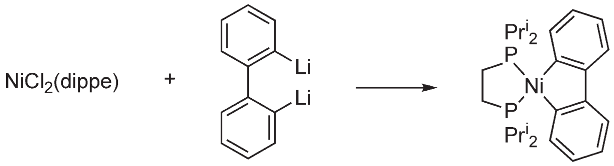
DiPP, 2,6-diisopropylphenyl; A, elemental analysis; *m/d*, melting or decomposition point; MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^1H, ^{13}C, ^{31}P, ^{19}F, NMR spectra; XR, X-ray diffraction; dec, decomposition temperature; MW, molecular weight; DTA/TG, differential thermal analysis, thermal gravimmetry.

dative L–Ni bond, where the donor atom is formally neutral (cyclometallated complexes), have already been discussed in Sections 8.02.3.3 and 8.02.3.4.

During the past decade, the chemistry of nickel metallacycles has experienced a remarkable growth,[300] which justifies a specific treatment. This view was already adopted in COMC (1995).

8.02.4.1 Synthesis

Transmetallation reactions have been used for the preparation of relatively simple metallacycles, but the method is limited by the availability of suitable transmetallation reagents. Some examples involving the preparation of ligand-free, anionic nickelabicycles are presented in Section 8.02.2. Transmetallation reactions shown in Equations (81)–(83) provide examples involving Li[301], Zr,[302,303] and Mg[304] reagents.



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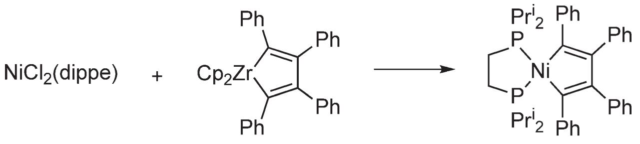
(81)



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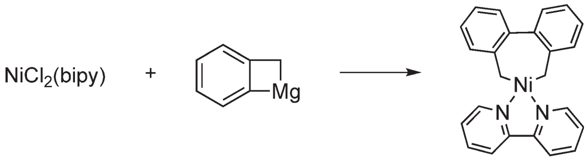
(82)



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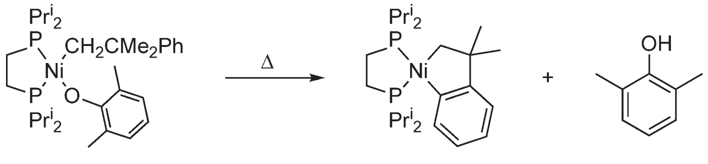
(83)

There are relatively few examples of the formation of nickel metallacycles by intramolecular C–H activation processes. A well-known example is the thermal decomposition of bis-neophyl (-CH_2CMe_2Ph) complexes.[300] This process is observed only for complexes that contain monodentate PR_3 ligands. Thus, reductive elimination is the dominant decomposition pathway for the bispyridine complex (Scheme 53), but the addition of a catalytic amount of PMe_3 leads to the selective formation of the corresponding pyridine-containing metallacycle, **189**. The latter compound serves as a starting material for the preparation of metallacyclic derivatives containing other nitrogen ligands by facile ligand exchange reactions.[46] A related cyclometallation reaction is observed for neophyl–aryloxide derivatives containing chelating diphosphines (Equation (84)).[62] The inverse selectivity (i.e., aryloxide cyclometallation) is ascertained in the case of methylnickel aryloxides that bear an aldehyde functionality (Scheme 54).[126,243,305] The same procedure allows for the synthesis of related cyclic acyl–enolate complexes from 1,3-ketoaldehydes.[126,305] Deprotonation of 2-acylarylnickel derivatives with potassium *t*-butoxide leads to *O*-bound cyclic enolate complexes (Scheme 55).[76,77] When the enolic carbon bears no substituent, the *O*- and *C*-bonded tautomers **193 and 194** display comparable thermodynamic stabilities and equilibrate upon gentle heating.[76]



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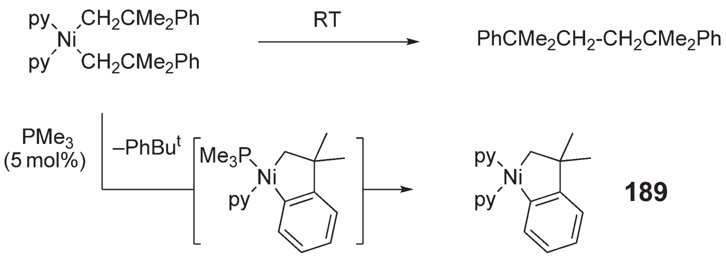
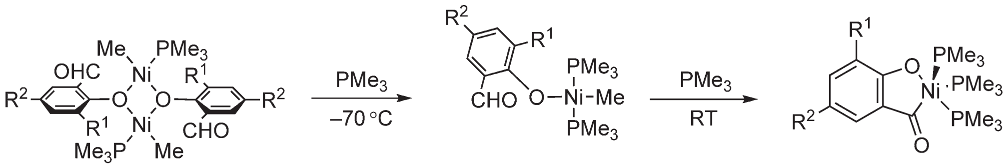
(84)



Scheme 53



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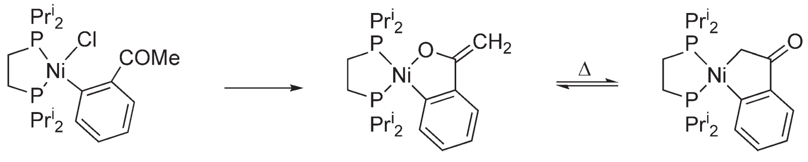
Scheme 54

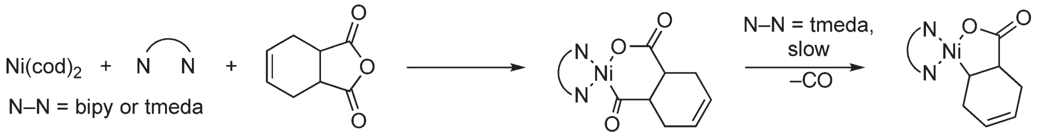


192 **193** **194**

Scheme 55

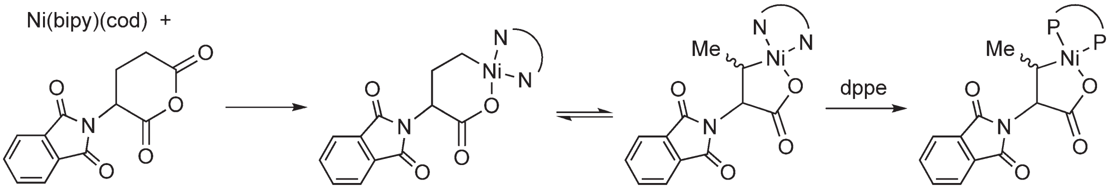
Cleavage of C–X bonds of reactive heterocyclic compounds by Ni(0) complexes has been used for the preparation of a number of nickel metallacycles[299] (see COMC (1995)). A well known example is the oxidative addition of cyclic anhydrides of dicarboxylic acids.[306–311] The initial product of the reaction is a cyclic acylcarboxylate, which can be isolated in some cases (Scheme 56),[306] but more frequently it decarbonylates to give the corresponding nickelalactone. The cycle formed in the oxidative addition of *N*-phthaloylglutamic anhydride undergoes a reversible ring contraction. Exchange of bipy by the diphosphine dppe shifts this equilibrium, allowing the isolation of the five-membered nickelalactone **197** (Scheme 57).[307] Aziridines add to Ni(bipy)(cod) giving four-membered nickelacycles. Isotopic-labeling studies show that this process takes place with inversion of the stereochemistry of the Ni-bonded carbon atom, indicating that in this case the oxidative addition involves an S_N2 nucleophilic attack of Ni to the aziridine carbon atom. (Scheme 58).[312]

Oxidative addition of thiophene and other sulfur-containing heterocycles to low-valent metal centers is a key step in the catalytic HDS process, carried out by the petrochemical industry on a multimillion ton scale to remove sulfur compounds from petroleum oil derivatives.[113–115] These heterocycles react with [NiH(dippe)]$_2$ (a source of the Ni^{0}dippe fragment) under mild reaction conditions to give thianickelacycle complexes (Scheme 59 and Equation (85)).[301,313] Alkylated dibenzothiophenes are among the least reactive components of the crude oil distillate;



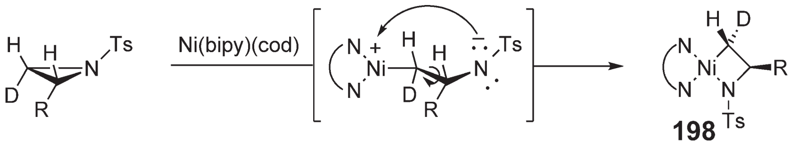
195 (stable if N–N = bipy) **196**

Scheme 56

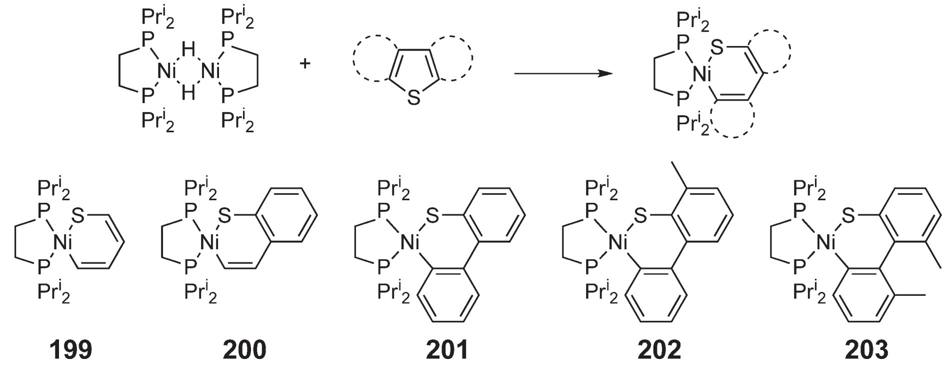


197

Scheme 57

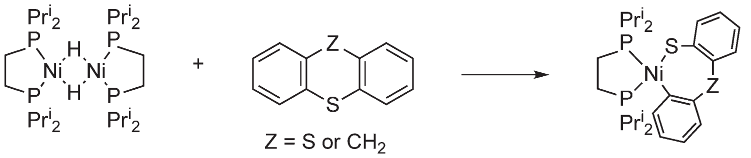


Scheme 58



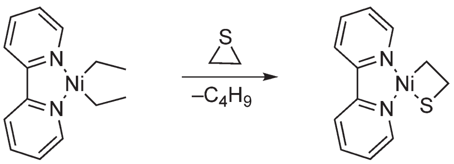
Scheme 59

however, they react similarly. The C–S oxidative addition is reversible, and in solution the thiametallacycles exchange the organic fragment with free heterocycles, giving rise to equilibrium mixtures of metallacyclic products (Scheme 60). Thiiranes and thiethane add to NiEt$_2$(bipy) affording the corresponding nickelathioheterocycles (Equation (86)).[314]



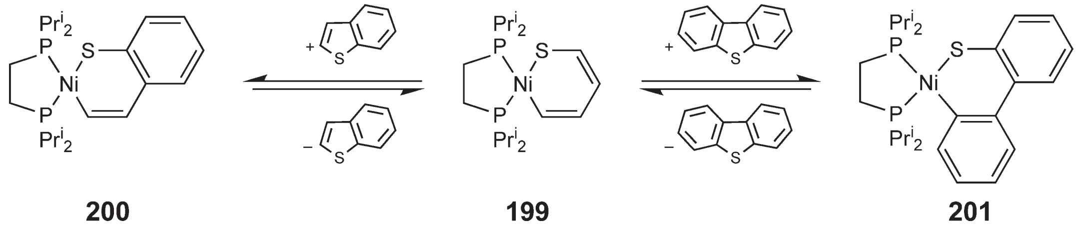
(85)

204: Z = S
205: Z = CH$_2$



(86)

206

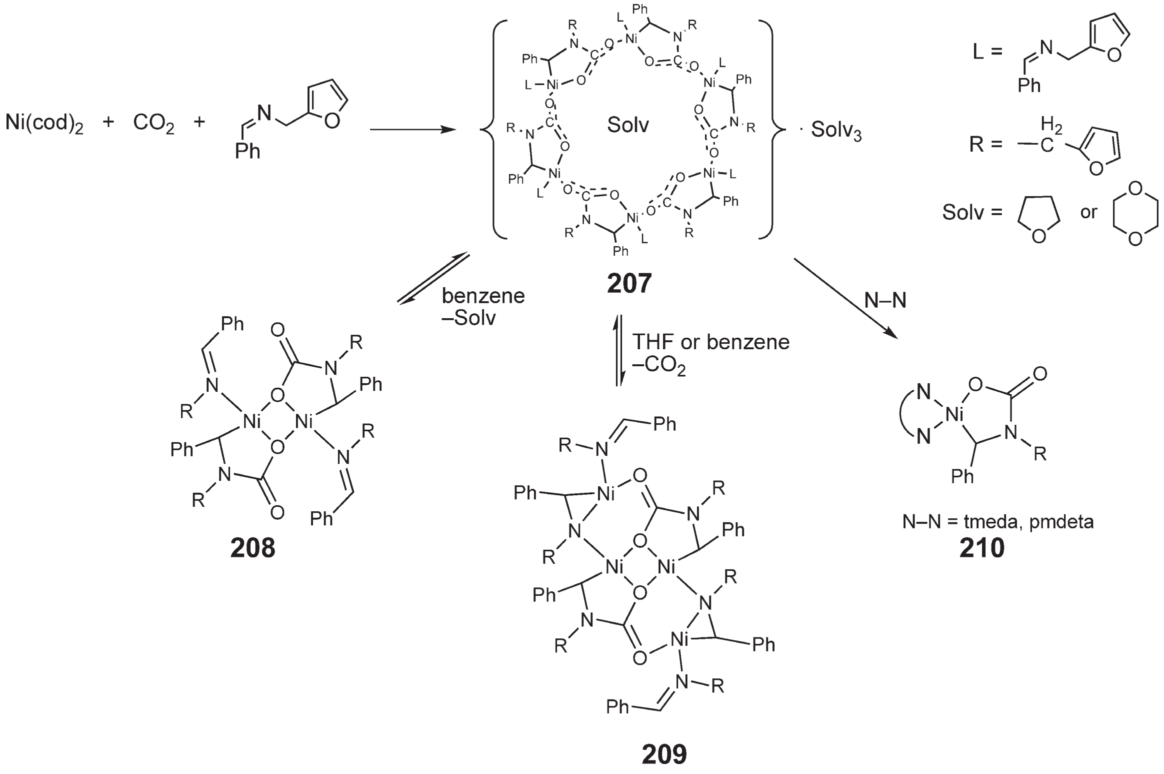


Scheme 60

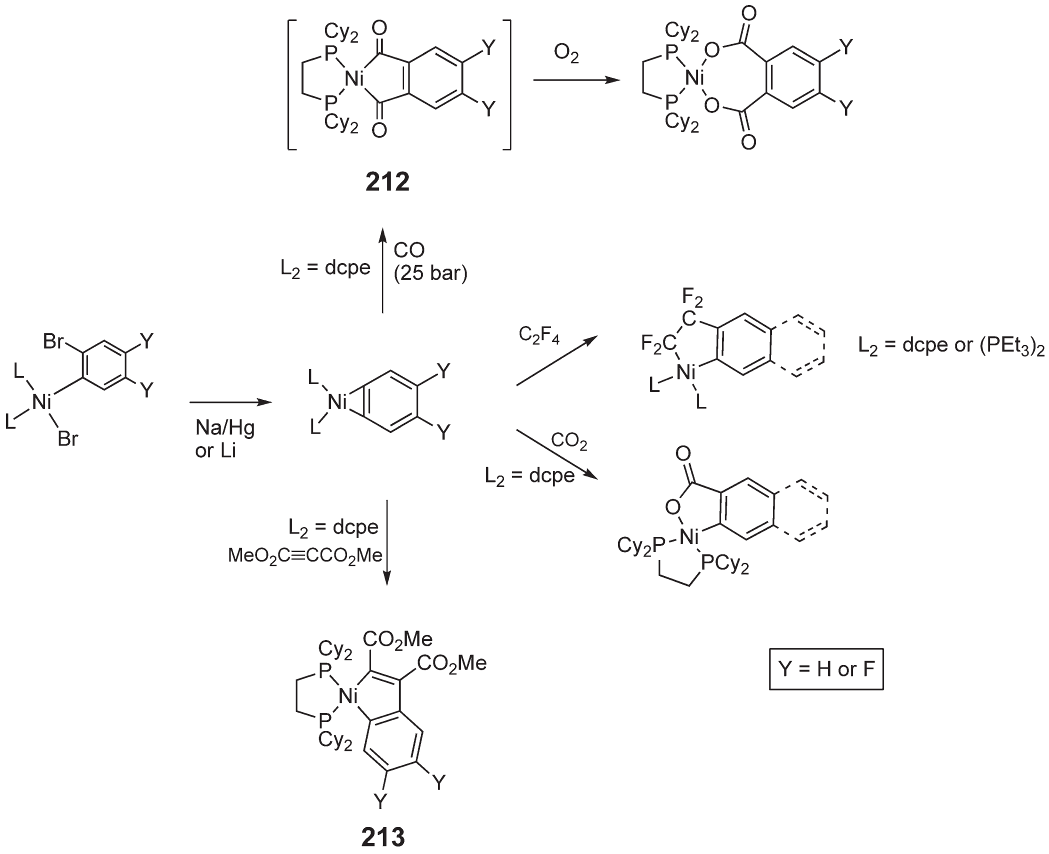
The cycloaddition of unsaturated fragments at the coordination sphere of the metal center is one of the most characteristic pathways to metallacyclic compounds. These processes have found wide application in both stoichiometric and catalytic synthesis.[300,315] Reduction of the dihalocomplexes $NiBr_2L_2$ (L = tertiary phosphine) with sodium hydride in MeCN in the presence of tetrafluoroethylene gives products containing five-membered NiC_4F_4 rings.[316] Carbon dioxide couples with olefin and alkynes at Ni(0) centers affording nickelalactones.[317,318] The reaction of $Ni(cod)_2$ with CO_2 and imines in THF or dioxane gives rise to oligomeric metallacycles containing imine as the only stabilizing co-ligand (Scheme 61).[319,320] The product formed with *N*-furfurylbenzylidene imine displays the macrocyclic structure **207** composed of six metallacyclic units, associated through bridging carboxylate interactions. Interestingly, the hexamer appears to be stabilized by four solvent molecules located both inside and outside of the molecular cavity. When these are removed (by dissolving the compound in benzene), the structure collapses to the dimer **208**. In solution, complexes **207** release CO_2 reversibly, giving a tetranuclear Ni(0)/Ni(II) complex, **209**. As expected, chelating ligands such as pmdeta or bipy cleave the metallacyclic oligomers yielding mononuclear complexes.

An SD-CI calculation shows that the coupling of acetylene and CO_2 proceeds with initial formation of the alkyne complex, followed by addition of the CO_2 molecule.[321] When the alkyne is HC≡COH, the formation of the product with the OH group in the β-position is favored both kinetically and thermodynamically.[322]

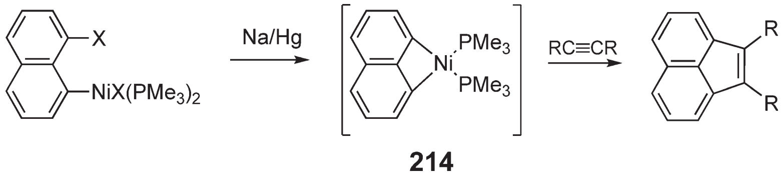
Montgomery has developed recently a methodology for the synthesis of complex organic molecules from alkynyl enones or alkynyl enals, based on the intramolecular coupling of C═C and C═O at an Ni(0) center.[323] The key intermediates are metallacyclic enolates like **211**, which has been structurally characterized (Equation (87)).[324,325] Nickel complexes of benzynes and other strained alkynes[87,88,326,327] are versatile starting materials for the preparation of different types of nickel metallacycles.[328] As shown in Scheme 62, benzyne and naphthalyne complexes react with unsaturated molecules such as CO_2 or tetrafluoroethylene, affording the corresponding five-membered metallacycles.[327,329] Cyclohexyne complexes react similarly with CO_2 or CS_2.[116] Carbonylation of the benzyne complexes under high CO pressure gives rise to highly reactive bis-acyl metallacycles **212** which become readily oxidized by traces of O_2 to the corresponding phthalates.[330,331] The reaction of benzyne or naphthalyne complexes with acetylenes is difficult to control, as it is normally followed by the insertion of a second alkyne, followed by reductive elimination.[326,332–334] Only in the case of dimethyl acetylenedicarboxylate can the primary metallacyclic



Scheme 61

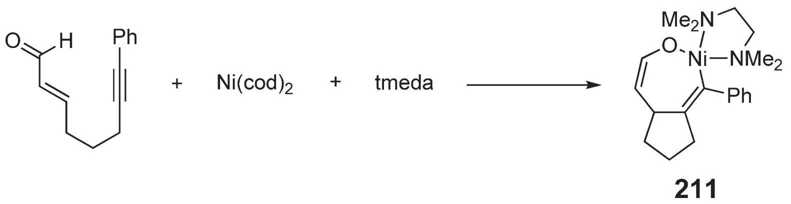


Scheme 62



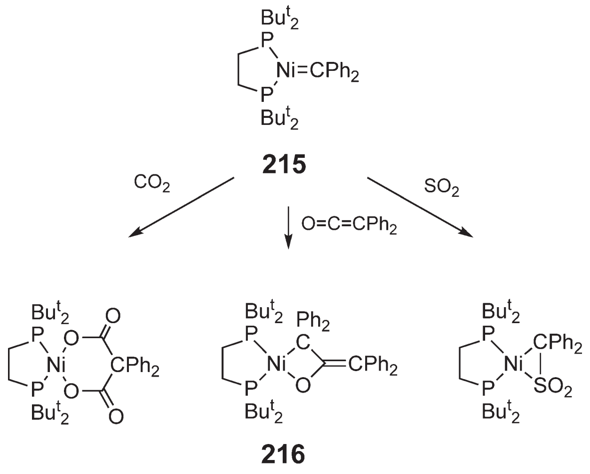
Scheme 63

complex **213**[326] be detected. A related reaction is the reduction of 8-halo-1-naphthyl nickel complexes (Scheme 63), which leads to the formation of a strained three-membered metallacycle, **214**, which is trapped with alkynes to give acenaphthenes.[79,335]

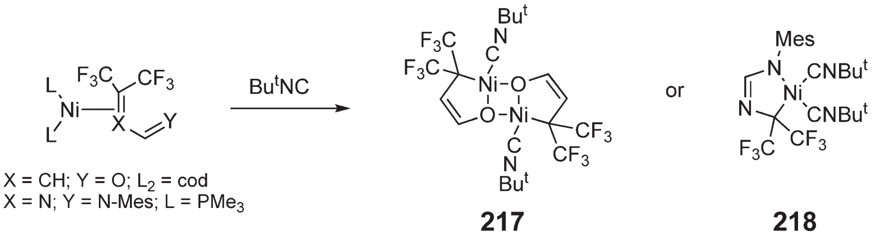


(87)

The unusual Ni carbene complex **215** reacts with unsaturated molecules producing different cyclic structures (Scheme 64).[148] Equation (88) summarizes examples of isomerization of η-heterodienes to σ-metallacycles, induced by ligand exchange.[336]



Scheme 64

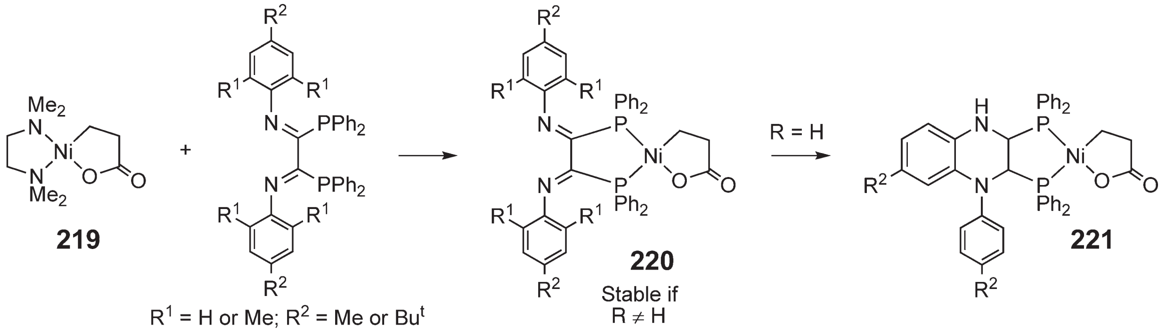


(88)

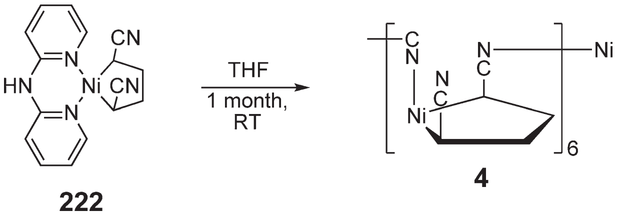
8.02.4.2 Reactivity

Nickel metallacycles display a very rich reactivity. Complex processes consisting of several consecutive elemental steps are frequently found.

Metallacyclic complexes containing labile pyridine or tmeda ligands are useful starting materials that readily undergo many ligand exchange reactions.[46,341] The displacement of tmeda from a nickelalactone by 2,3-bis(diarylphosphanyl)-1,4-diazadienes is accompanied by a cyclization of the diazadiene moiety (Scheme 65).[342] An unusual example of ligand displacement is the loss of dipyridylamine from the metallacycle 222 on prolonged standing in THF solution to afford the hexameric complex 4, stabilized by intermolecular C=N–Ni interactions (Equation (89)).[14]

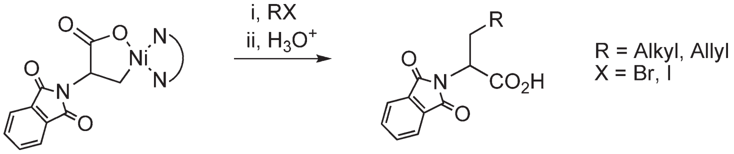


Scheme 65

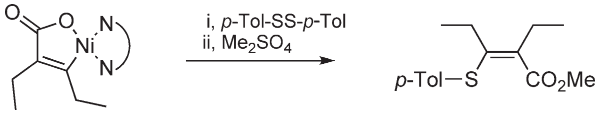


(89)

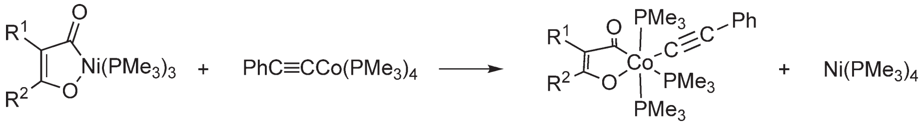
Cleavage of metallacycles by electrophilic reagents such as protic acids[19,127,128,307,308,338] or alkyl halides[304,306,308,341] constitute direct forms of releasing the organic fragment from the transition metal, and therefore these processes find some synthetic utility. The latter reaction constitutes a method for the selective formation of new C–C bonds. Equations (90) and (91) provide some selected examples.[308,311] The metallacyclic unit can also be cleaved by redox transmetallation reactions, as shown in Equation (92).[305]



(90)

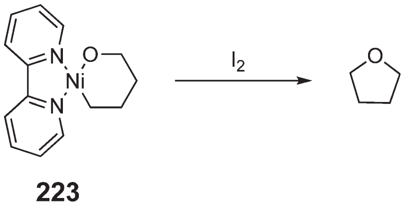


(91)

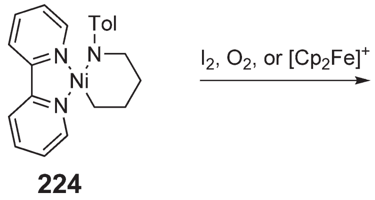


(92)

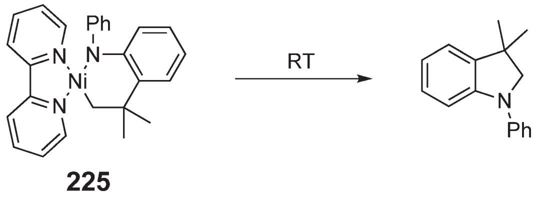
Metallacycles can undergo reductive C–C or C–X coupling to afford the corresponding carbocyclic or heterocyclic organic products. The capability of π-acids such as maleic anhydride to induce the decomposition of carbometallacycles compounds is well known.[304,128] Heterometallacycles are less prone to experience reductive elimination processes. Although the reaction of nickel metallacycles with iodine can cleave Ni–C bonds with formation of Ni–I and C–I bonds,[55,329] this reagent can also promote C–X coupling in heterometallacycles. Thus, Hillhouse has used I_2 or other oxidizing reagents to achieve the formation of cyclic ethers or thioethers from nickel metallacycles containing Ni–O[127,128,337,339] (Equation (93)) or Ni–S[345] linkages, which do not undergo thermal reductive elimination. Although the reductive elimination of azanickelacycloalkanes can also be induced with oxidizing reagents (Equation (94)),[129] thermal N–C reductive elimination has also been observed (Equation (95)).[129,343] The decomposition of metallacycles containing Ni–C(sp^2) and Ni–S bonds is often a facile process. On standing in solution at room temperature, the metallacycles **199** or **200** spontaneously lose thiophene or benzothiophene, giving binuclear complexes bridged by the cyclic thiolate fragment (Equation (96)). The same compounds can be prepeared by the addition of $[NiH(dippe)]_2$ to **199** or **200**.[313] The decomposition of the metallacycle **201** constitutes an example of a homogenous HDS process, leading to 2,2′-biphenylnickel metallacycles, together with sulfur-containing nickel complexes (Equation (97)).[301,313]



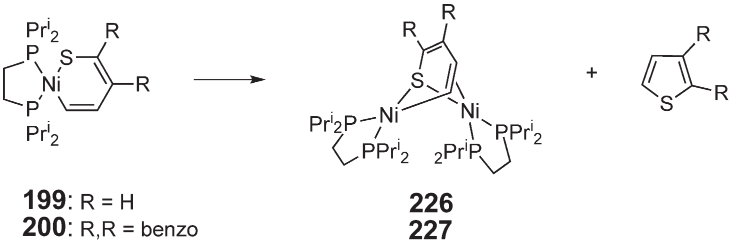
(93)



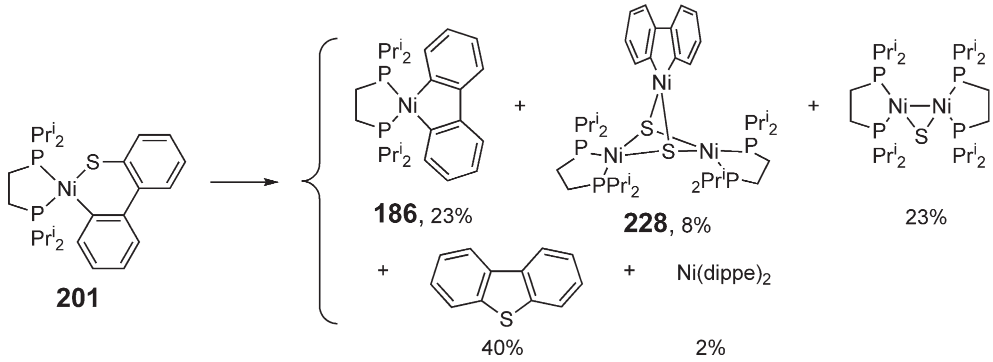
(94)



(95)

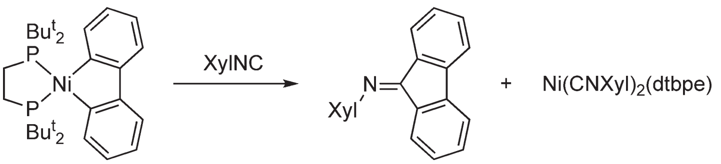


(96)

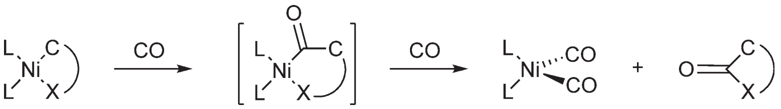


(97)

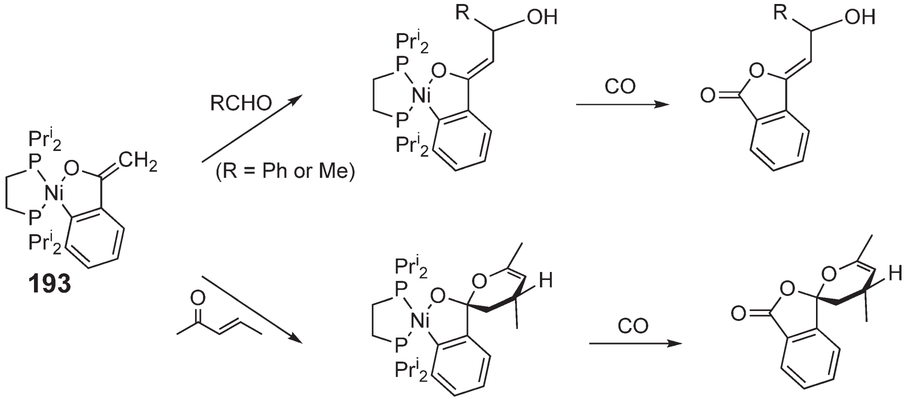
In general, nickel metallacycles react readily with carbon monoxide. In most cases, this reaction is almost immediately followed by metal reduction (Scheme 66) and formation of a cyclic carbonylated organic compound (ketone,[250,314,329,346] lactone,[76,127,128,130,307,320,338] lactam,[125,129] thiolactone,[314,345] or related heterocycles[250]) usually in high yield and with an excellent selectivity. The intermediate acyl species is generally unstable, but sometimes it can be detected spectroscopically.[346,329] The reaction of nickelacycles with isocyanides can follow a similar path to afford cyclic imine (Equation (98)),[346] but formation of stable isocyanide adducts has also been observed.[250]



(98)



Scheme 66

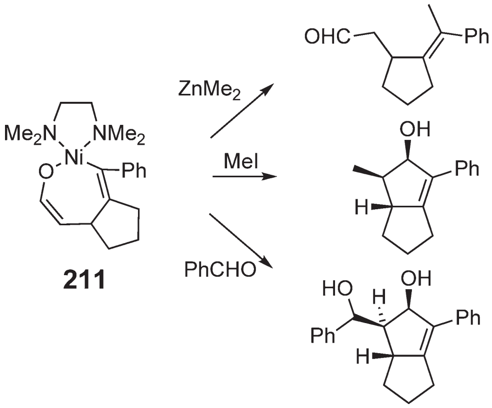


193

Scheme 67

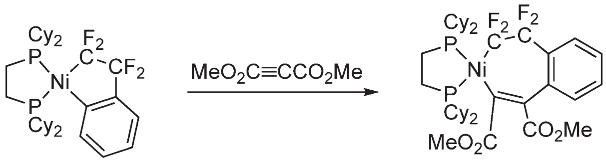
In the example shown in Scheme 67, the characteristic reactivity of the organic fragment of the metallacycle **193** (which contains an enolate functionality), such as addition to aldehydes[76] or to α,β-unsaturated ketones,[77] is combined with carbonylation reactions to afford lactones in a highly selective manner. In a similar fashion, the cyclic enolate **211** experiences the nucleophilic attack of $ZnMe_2$ at the Ni–O bond or selective addition of PhCHO or MeI to the enolate carbon (Scheme 68).[324] In the latter two cases, the flexible seven-membered ring allows the coupling reaction to proceed, giving rise to bicyclic organic products.

As in the case of carbonylation, the reaction of alkynes with nickel metallacycles is often followed by reductive elimination. In some cases, the insertion product is stable and can be isolated (e.g., alkyne insertion in nickelalactones[116] or fluorinated metallacycles,[327,329] Equation (99)), but more frequently it is unstable and decomposes rapidly to afford substituted benzenes,[302] dihydronaphthalenes,[131,329] naphthalenes,[332] or phenanthrenes.[346] The reaction of Ni(0) dippe complexes with biphenylene and alkynes in the presence of traces of O_2 catalytically produces phenanthrenes, in a process that involves the intermediacy of a carbonickelacycle.[346]



211

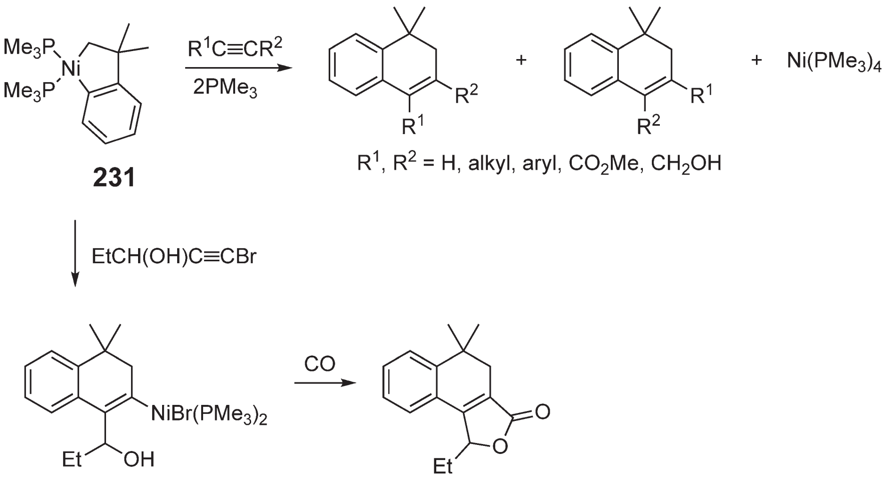
Scheme 68



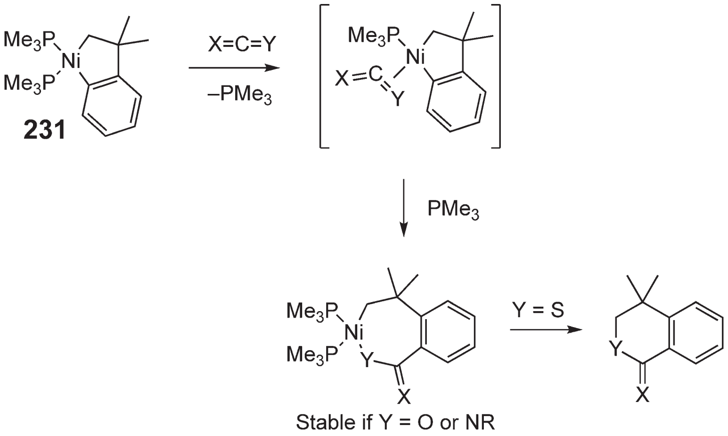
229 **230** (99)

Alkynes bearing two different alkyl groups attached to the triple bond react with the nickelacycle **231** to afford a mixture of two isomeric products can be produced (Scheme 69), but frequently one of the products is strongly favored.[131] The selectivity of this reaction is controlled by a combination of electronic and steric factors.[326,332] The tolerance of Ni to polar groups allows the incorporation of many different functionalities (e.g., OH, CO_2R, PR_2, SR, etc).[131,333,334] In the case of halogenated alkynes, the reductive elimination step is followed by oxidative addition of the C–X bond, and the resulting organonickel compound may undergo further transformations (Scheme 69, below).[131]

The reaction of the metallacycle **231** with hetererocumulenes of the type X═C═Y (X, Y = O, S, NR) has been studied in detail.[250,347,348] These molecules insert selectively in the Ni–C(aryl) bond of **231** (Scheme 70).[250] It has been proposed that the selectivity is controlled by the facile displacement of the PMe_3 ligand located *cis* to the aryl,



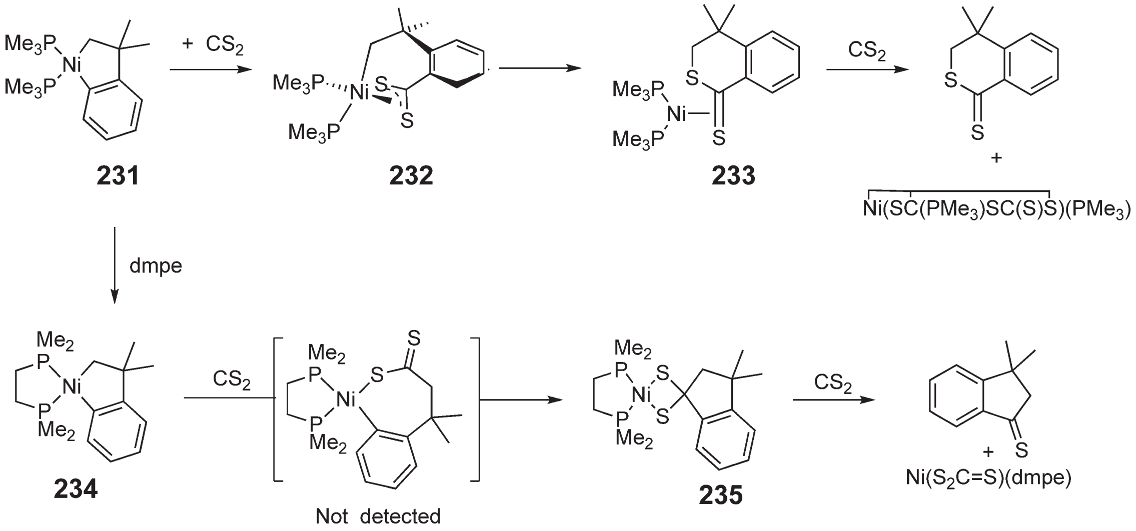
Scheme 69



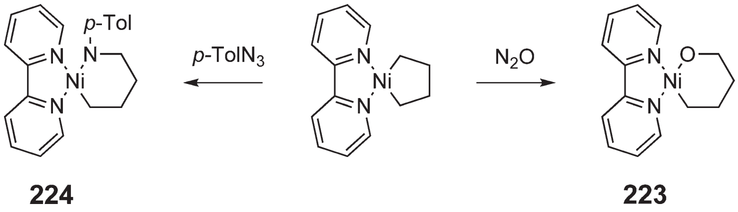
Scheme 70

which is labilized by the strong *trans*-effect of the alkyl group. The reactivity of the heterocumulenes toward **231** decreases in the order $CS_2 \sim COS$ (fast reaction at −90 °C) > PhNCS > PhNCO > TolNCNTol > CO_2 (reacts at room temperature over several days). The regioselectivity of the heterocumulene insertion is also very high, and favors the insertion of C═S bonds over C═N, and of these over C═O, which are the least reactive. The stability of the insertion products depends on the nature of the heteroatom bonded to Ni. The products containing Ni–O or Ni–N bonds are stable at room temperature, but those containing Ni–S bonds decompose readily. The primary product of CS_2 insertion, **232**, displays an η^3-coordinated dithiocarboxylate moiety, and rearranges above −60 °C to the Ni(0) complex **233** (Scheme 71). An excess of CS_2 readily displaces the η^2-dithiolactone ligand contained in the latter. Interestingly, the related metallacycle **234**, where PMe_3 has been replaced by the chelating diphosphine dmpe, also reacts with CS_2, giving rise to a different type of product, the *gem*-dithiolate **235** without any detectable intermediates. As observed in the PMe_3 system, **235** reacts with excess of CS_2, which formally displaces the organic fragment from the NiS_2CR_2 linkage yielding thioketone and a trithiocarbonate complex. Mechanistic studies show that in the case of the dmpe nickelacycle **234**, the initial insertion of CS_2 probably takes place into the Ni–CH_2 bond. The sequential reaction of the metallacycle **231** with different heterocumulenes (CS_2, COS, PhNCO, PhNCS, or TolN═C═NTol) and CO or Bu^{t}NC leads to eight-membered metallacycles, which undergo a facile reductive elimination process, a reaction that allows the synthesis of seven-membered heterocycles displaying unusual functional groups.[250]

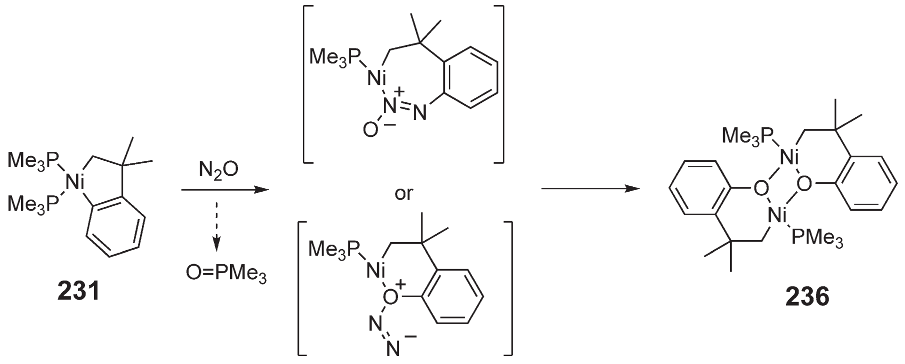
As discussed in Section 8.02.3.4.3, nitrous oxide (N═N═O) and aryl azides (N═N═NAr) react with nickel alkyls giving alkoxo and amido complexes as the result of the insertion of oxo or nitrene units in the Ni–C bond. Nickelacyclopentanes react in the same fashion, affording cyclic alkoxo[127,128,337] and amido[125] derivatives, respectively (Scheme 72). Note that the reaction of the metallacycle **231** with N_2O results in selective transfer of O to the Ni–C_{aryl} bond, suggesting that this reaction could involve a mechanism analogous to that proposed for



Scheme 71

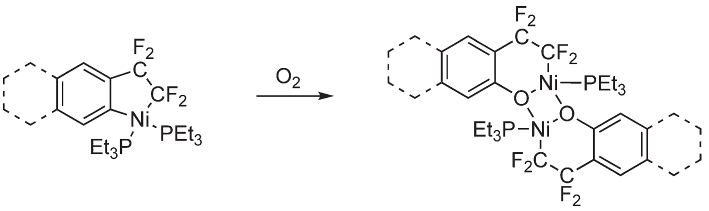


Scheme 72

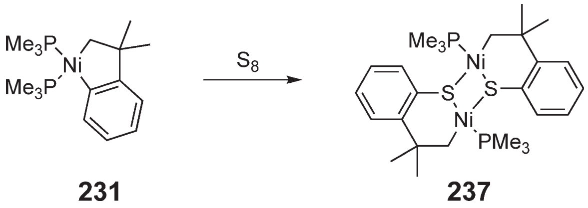


Scheme 73

X═C═Y heterocumulenes, followed by loss of N_2 (Scheme 73).[338] This reaction is accompanied by the oxidation of one of the two PMe_3 ligands to phosphine oxide, and formation of the oxygen-bridged dimer **236**. The reaction of **231** with aryl azides leads to no stable insertion products, since both PMe_3 ligands are removed as ArN═PMe_3;[129,343] however, a stable product displaying the NPh group inserted into the Ni–C(aryl) bond is formed when PMe_3 is replaced by bipy. The insertion of elemental oxygen (Equation (100))[329] and sulfur (Equation (101))[345] into nickel metallacycles has also been observed. Also in this case the insertion of the chalcogen occurs in the Ni–C(sp^2) bond.



(100)

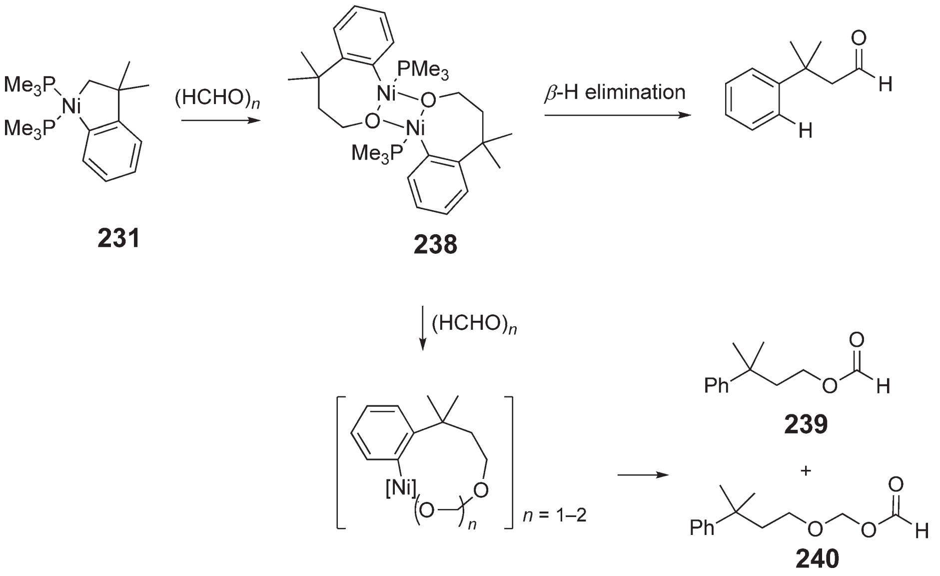


(101)

The reaction of the metallacycle **231** with formaldehyde to give the oxanickelacycle **238**, reported by Carmona in 1986, represents an unusual case of heteroolefin insertion into an Ni–C bond.[347,349] More recently, Hillhouse has found that this product decomposes by β-hydrogen elimination of the alkoxide functionality, and not by reductive C–O coupling (although the latter can be induced by oxidation with O_2). Upon prolonged exposure to an excess of paraformaldeyde, **231** is converted into a mixture of the organic compounds **239** and **240**, as a result of the consecutive insertion of two or three CH_2═O units into the Ni–C_{aryl} bond (Scheme 74).[339]

8.02.5 η³-Allyl-, η⁵-Cyclopentadienyl-, and η-Indenylnickel Complexes with σ-Bonded Carbon Ligands

Most η^3-allyl- and η^5-cyclopentadienylnickel complexes exhibit 16-electron and 18-electron counts, respectively, differing considerably in structure and properties. For this reason, the two groups of compounds have received separate treatment in COMC (1985) and COMC (1995). Few examples of allyl derivatives bearing σ-carbon bonded ligands have appeared in recent years, but a number of η-indenylnickel complexes, whose structure and properties can be considered somehow intermediate between those of allyl and cyclopentadienyls, have been reported by

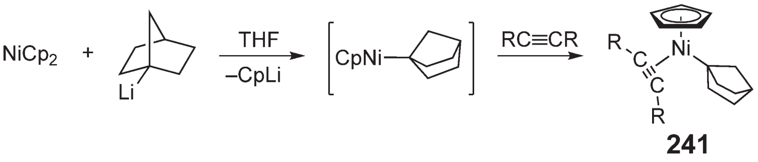


Scheme 74

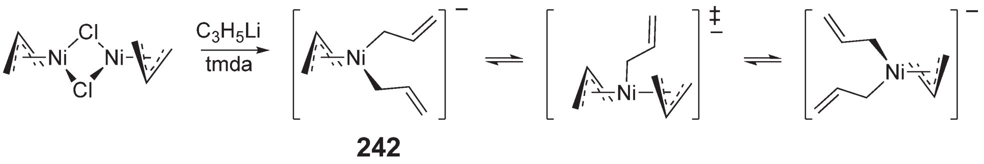
Zargarian.[350] This situation and the similarity of the synthetic methodologies available for the synthesis of all these compounds suggest a joint treatment in this occasion.

Apart from the σ- and the π-bound carbon ligands, most compounds in this section exhibit one additional donor ligand, in order to achieve stable 16- or 18-electron configurations. An attempt to generate the 14-electron species ($(\eta^3\text{-}C_3H_5)Ni$(1-norbornyl) by reacting $[(\eta^3\text{-}C_3H_5)Ni(\mu\text{-}Cl)]_2$ with 1-norbornyllithium at −78 °C gives a highly unstable species which decomposes under the reaction conditions, but stable $(\eta^3\text{-}C_3H_5)Ni$(1-norbornyl)(PPh_3) was isolated from $(\eta^3\text{-}C_3H_5)Ni(Cl)(PPh_3)$.[351] The 16-electron (η-Cp)Ni(1-norbornyl), generated from $NiCp_2$ and 1-norbornyllithium, is stable in THF solution up to −30 °C, when it reacts with alkynes giving rise to stable adducts (Scheme 75).[352] Ligand-free, anionic η^3-allylnickel species can be prepared by the reaction of $(\eta^3\text{-}C_3H_5)_2Ni$ with alkyllithiums.[353] The reaction with allyllithium provides the homoleptic trisallyl derivative **242** (Scheme 76). The crystal structure of this compound displays discrete $[(\eta^3\text{-}C_3H_5)Ni(\eta^1\text{-}C_3H_5)_2]^-$ anions, which do not interact with the lithium cation. Solid-state CP-MAS $^{13}C\{^1H\}$ spectroscopy shows that the π- and σ-allyl ligands undergo a fluxional exchange in the solid state. The related metallacyclopentane complex $[(\eta^3\text{-}C_3H_5)Ni(CH_2CH_2CH_2CH_2)]^-$ was formed when 1,4-dilithiobutane was reacted with $(\eta^3\text{-}C_3H_5)_2Ni$ (Table 10).

The displacement of one Cp group of nickelocene by various organolithium or organomagnesium reagents leads to transient (η-Cp)Ni(R) species, which have been extensively studied by Pasynkiewicz.[354,355] In the presence of



Scheme 75



Scheme 76

Table 10 η^3-Allyl, η^5-Cyclopentadienyl and η-Indenylnickel Complexes

Compound	*Characterization*	*References*
(*a*) η^3-*Allylnickel complexes*		
$(\eta^3\text{-}C_3H_5)Ni(1\text{-norbornyl})(PPh_3)$	A, ^{11}H, ^{13}C, P	351
$[(\eta^3\text{-}C_3H_5)Ni(\eta^1\text{-allyl})_2][Li(tmeda)]_2$, **242**	XR, *m*/*d*, A, ^{11}H, ^{13}C	353
$[(\eta^3\text{-}C_3H_5)\overline{Ni(CH_2CH_2CH_2CH_2})][Li(tmeda)_2]$	XR, *m*/*d*, A, ^{11}H, ^{13}C	353
(*b*) η^5-*Cyclopentadienylnickel complexes*		
$(\eta^5\text{-}Cp)Ni(Me)(\eta^2\text{-}CH_2{=}CHBu^n)$, **269**	A, ^1H, ^{13}C, MS	356
$(\eta^5\text{-}Cp)Ni(Me)(\overline{CN(Ar)CH{=}CHN}(Ar))$ $(Ar = C_6H_4Me_2\text{-}2,6\text{-}Br\text{-}4)$	*m*/*d*, A, ^1H, ^{13}C, MS	364
$(\eta^5\text{-}C_5Me_5)Ni(Me)(PEt_3)$	XR, *m*/*d*, A, ^1H, IR, MS	360
$[(\eta^5:\mu\text{–}C_5H_4PPh_2)Ni(Me)]_2$	XR, A, *m*/*d*, ^1H, ^{31}P	363
$(\eta^5\text{-}Cp)Ni(\eta^1:\eta^2\text{-}CH(Me)CH_2CH_2CH{=}CH_2)$, **246**	^1H, ^{13}C, MS	359
$(\eta^5\text{-}Cp)Ni(1\text{-norbornyl})(\eta^2\text{-}RC{\equiv}CR)$ (R = Me, Ph, TMS, CH_2OMe, CH_2NMe_2, CH_2OTMS), **241**	A, ^1H, ^{13}C, MS	352
$(\eta^5\text{-}Cp)Ni(PMe_3)(\mu\text{-}CH_2C_6H_4\text{-}2\text{-})Ni(PMe_3)(\eta^5\text{-}C_5Me_5)$	A, ^1H, ^{13}C, ^{31}P	244
$(\eta^5\text{-}Cp)Ni(CH(TMS)_2)(PMe_3)$	^1H, ^{13}C, ^{31}P	23
$(\eta^5\text{-}Cp)Ni(\mu\text{-}CH(SiMe_3)\text{-}2\text{-}py)_2$, **245**	XR, *m*/*d*, ^1H, ^{13}C, MS	12,358
$(\eta^5\text{-}Cp)Ni(\eta^1\text{-}Cp)(\overline{CN(Ar)CH{=}CHN}(Ar))$ $Ar = C_6H_4Me_2\text{-}2,6\text{-}Br\text{-}4$, **252**	XR, A, ^1H, ^{13}C, MS	373
$(\eta^5\text{-}Cp)Ni(\kappa^2\text{-}(C(TMS)_2py\text{-}2)\text{-}C,N)$, **244**	XR, ^1H, ^{13}C, MS	358
$(\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}3,5)Ni(\kappa^2\text{-}C(TMS)_2py\text{-}2)\text{-}C,N$	^1H, ^{13}C, MS	358
$[(\eta^5\text{-}Cp)Ni(\eta^1:\mu_2\text{-}C(Me){=}CMe_2)]_4$, **243**	^1H, ^{13}C, MS	357
$(\eta^5\text{-}C_5Me_5)Ni(\eta^1:\eta^2\text{-}C(Ph){=}C(Ph)C(Ph){=}CHPh)$, **247**	A, ^1H, ^{13}C, MS	361
$(\eta^5\text{-}Cp)\overline{Ni((C{=}N(Ar)C(C{\equiv}CPh)C{=}N}(Ar))$, **253** $(Ar = C_6H_4CONHBz\text{-}3, C_6H_4COO(menthyl\text{-}2)\text{-}3, p\text{-}Tol)$	A, IR, ^1H, ^{13}C, ^{3131}P, MS	371
$(\eta^5\text{-}C_5Me_5)Ni(C(O)NH\text{-}p\text{-}Tol)(CO)$, **254**	A, ^1H, IR	374
$(\eta^5\text{-}C_5Me_5)Ni(C(NBu^t)NH\text{-}p\text{-}Tol)(CNBu^t)$, **255**	A, *m*/*d*, ^1H, ^{13}C, MS, IR	374
$(\eta^5\text{-}Cp)Ni(Ph)(PMe_3)$	^1H, ^{13}C, ^{31}P	102
$(\eta^5:\eta^1\text{–}Cp,N\text{–}C_5H_4CH_2CH_2NMe_2)Ni(Mes)$	XR, A, ^1H, ^{13}C, MS	365
$(\eta^5\text{-}C_5RMe_4)\overline{Ni(C_6H_4N{=}N}Ph)(R{=}Me,Et)$, **249**	A, ^1H, ^{13}C, IR, UV	335
$(\eta^5\text{-}C_5EtMe_4)\overline{Ni(\text{-}Fc\text{-}CH_2N}Me_2)$, **251**	XR, A, ^1H, ^{13}C, MS	362
$(\eta^5\text{-}Cp)Ni(C{\equiv}CH)(PPh_3)$	A, *m*/*d*, ^1H, IR	371
$(\eta^5\text{-}Cp)Ni(C{\equiv}CH)(PPh_3)$	XR, A, *m*/*d*, ^1H, ^{13}C, ^{31}P, IR, MS	366,369,371
$(\eta^5\text{-}Cp)Ni(C{\equiv}CCH{=}NHAr)(PPh_3)$ $(Ar = Ph, C_6H_4NO_2\text{-}4)$	A, *m*/*d*, IR, UV, ^1H, ^{13}C	372
$(\eta^5\text{-}Cp)Ni(C{\equiv}CCH{=}C(CN)_2)(PPh_3)$	A, *m*/*d*, IR, UV, ^1H, ^{13}C	372
$(\eta^5\text{-}Cp)Ni(C{\equiv}CCH{=}\overline{CC(O)ON{=}C}Ph)(PPh_3)$	XR, A, *m*/*d*, IR, UV, ^1H, ^{13}C	372
$(\eta^5\text{-}Cp)Ni(C{\equiv}CCH(OEt)_2)(PPh_3)$	A, *m*/*d*, ^1H, ^{13}C, IR, UV	370
$(\eta^5\text{-}Cp)Ni(C{\equiv}CCHO)(PPh_3)$	XR, A, *m*/*d*, ^1H, ^{13}C, IR, UV	370,372
$(\eta^5\text{-}Cp)Ni(C{\equiv}CC_6H_4NO_2\text{-}4)(PPh_3)$	XR, A, ^1H, ^{13}C, ^{31}P, IR, MS	366,369
$(\eta^5\text{-}Cp)Ni(C{\equiv}Cpy)(PPh_3)$	A, ^1H, ^{13}C, ^{31}P, UV, ^{13}CV	367
$(\eta^5\text{-}Cp)Ni(C{\equiv}C\text{-}2\text{-}pyNO_2\text{-}4)(PPh_3)$	XR, A, ^1H, ^{13}C, ^{31}P, UV, ^{13}CV	367
$(\eta^5\text{-}Cp)Ni(C{\equiv}C\text{-}4\text{-}C_6H_4C_6H_4NO_2\text{-}4)(PPh_3)$	XR, A, ^1H, ^{13}C, ^{31}P, IR, MS	366,369
$(\eta^5\text{-}Cp)Ni(C{\equiv}C\text{-}4\text{-}C_6H_4CH{=}CH\text{-}C_6H_4NO_2\text{-}4)(PPh_3)$	XR, A, ^1H, ^{13}C, ^{31}P, IR, ^{13}CV, MS	366,369
$(\eta^5\text{-}Cp)Ni(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}C\text{-}C_6H_4NO_2\text{-}4)(PPh_3)$	XR, A, ^1H, ^{13}C, ^{31}P, IR, MS	366,369
$(\eta^5\text{-}Cp)Ni(C{\equiv}CC{\equiv}CH)(PPh_3)$	XR, A, ^1H, ^{13}C, IR	368
$(\eta^5\text{-}Cp)Ni(C{\equiv}CC{\equiv}CCO_2Me)(PPh_3)$	A, *m*/*d*, ^1H, IR	371
$(\eta^5\text{-}Cp)Ni(C{\equiv}CC(NMe_2){=}Cr(CO)_5)(PPh_3)$	A, *m*/*d*, ^1H, ^{13}C, ^{31}P, IR	53
$(\eta^5\text{-}Cp)Ni(C{\equiv}CC(NMe_2){=}W(CO)_5)(PPh_3)$	XR, A, *m*/*d*, ^1H, ^{13}C, ^{31}P, IR	53
$(\eta^5\text{-}Cp)Ni(C{\equiv}CCH(OEt_2)(Co_2(CO)_6))(PPh_3)$	A, *m*/*d*, ^1H, ^{13}C, IR, UV	370
$(\eta^5\text{-}Cp)Ni(C{\equiv}CCHO(Co_2(CO)_6)(PPh_3)$	XR, A, *m*/*d*, ^1H, ^{13}C, IR, UV	370,372

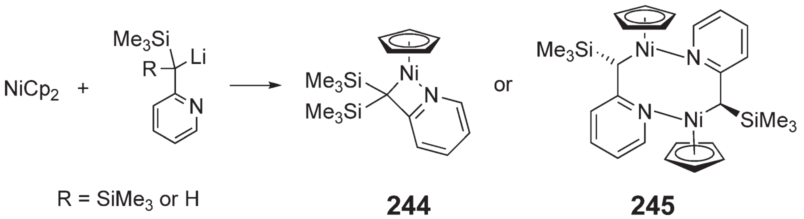
(Continued)

Table 10 (Continued)

Compound	*Characterization*	*References*
(*c*) *η-Indenylnickel complexes*		
(η-Indenyl-Me-1)Ni(Me)(PMe_3)	XR, ^1H, ^{13}C, ^{31}P, A	376
(η-Indenyl-Me-1)Ni(Me)(PCy_3)	XR, ^1H, ^{13}C, ^{31}P, A	376
(η-Indenyl-Me-1)Ni(Me)(PPh_3), **259**	XR, ^1H, ^{13}C, ^{31}P, A	375
(η-Indenyl-($CH_2CH_2NMe_2$)-2)Ni(Me)(PMe_3)	A, ^1H, ^{13}C, ^{31}P	377
(η-Indenyl-($CH_2CH_2NMe_2$)-2)Ni(Me)(PPh_3)	A, ^1H, ^{13}C, ^{31}P	377
(η-Indenyl-Me-2)Ni(thienyl)(PPh_3)	XR, A, ^1H, ^{13}C, ^{31}P	378
(η-Indenyl-Et-2)Ni(thienyl)(PPh_3)	XR, A, ^1H, ^{13}C, ^{31}P	378
(η-Indenyl-Pr^i-2)Ni(thienyl)(PPh_3)]	A, ^1H, ^{13}C, ^{31}P	378
(η-Indenyl-CH_2Ph-2)Ni(thienyl)(PPh_3)	A, ^1H, ^{13}C, ^{31}P	378
(η-Indenyl-Ph-1-Me-2)Ni(thienyl)(PPh_3)	XR, A, ^1H, ^{13}C, ^{31}P	378
(η-Indenyl)Ni(C$\equiv$CPh)(PCy_3)	XR, A, ^1H, ^{13}C, ^{31}P, IR	379
(η-Indenyl)Ni(C$\equiv$CPh)(PPh_3)	XR, A, ^1H, ^{13}C, ^{31}P, IR	379
(η-Indenyl-$CH_2CH_2NMe_2$-2)Ni(C$\equiv$CPh)(PPh_3)	A, ^1H, ^{13}C, ^{31}P, IR	377

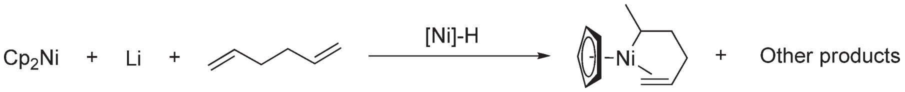
A, elemental analysis; *m/d*, melting or decomposition point; MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^1H, ^{13}C, ^{31}P, NMR spectra; XRD, X-ray diffraction; CV, cyclic voltammetry; dec, decomposition temperature.

alkenes or alkynes, these intermediates form relatively stable adducts, which can be isolated in favorable cases. For example, a stable methyl complex (η^5-Cp)Ni(Me)(η^2-hexene) could be isolated when Cp_2Ni was reacted with LiMe in the presence of hexene at low temperature.[356] Most often however, they undergo subsequent transformations that lead to different types of mononuclear and cluster organometallic compounds (see Scheme 77[357] and Equations (102)[358] and (103)[359]) (Table 10).



244 **245**

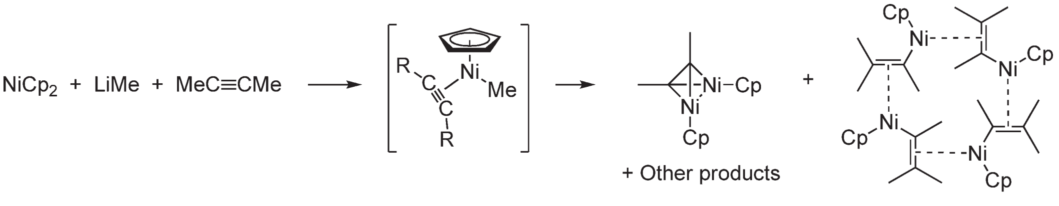
(102)



246

(103)

Pentamethylcyclopentadienyl derivatives are obtained by reaction of alkyllithiums with (η^5-Cp^*)Ni(acac). In the presence of PMe_3, LiMe leads to the complex (η^5-Cp^*)Ni(Me)(PMe_3),[360] and with 2,4-dilithio-1,2,3,4-tetraphenylbutadiene the internally stabilized alkenyl complex **247** is formed. The latter rearranges at 60 °C to give a mixture of isomeric allyl complexes (Scheme 78).[361] The binuclear decacyclene complex **248** readily undergoes the



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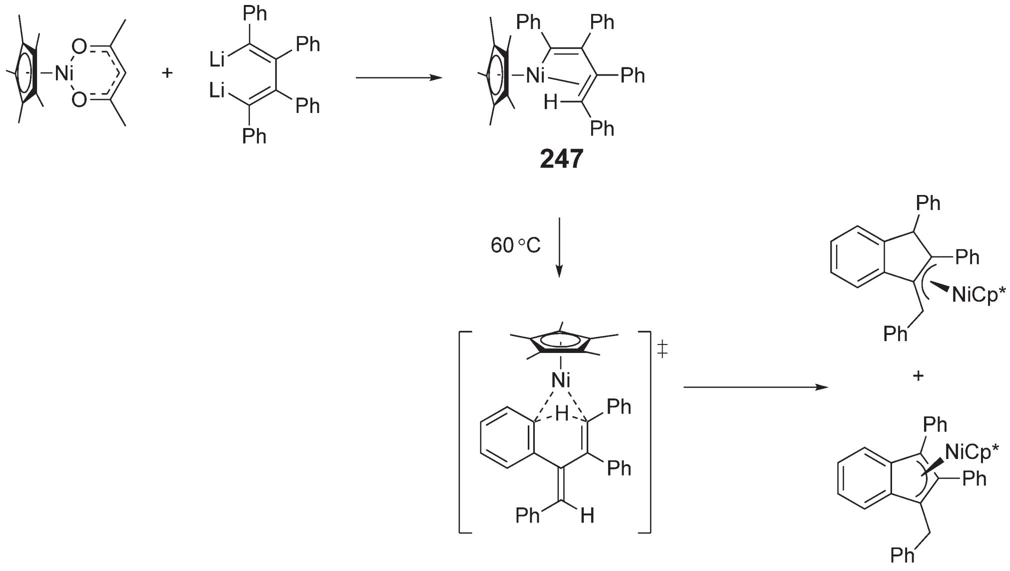
Scheme 77

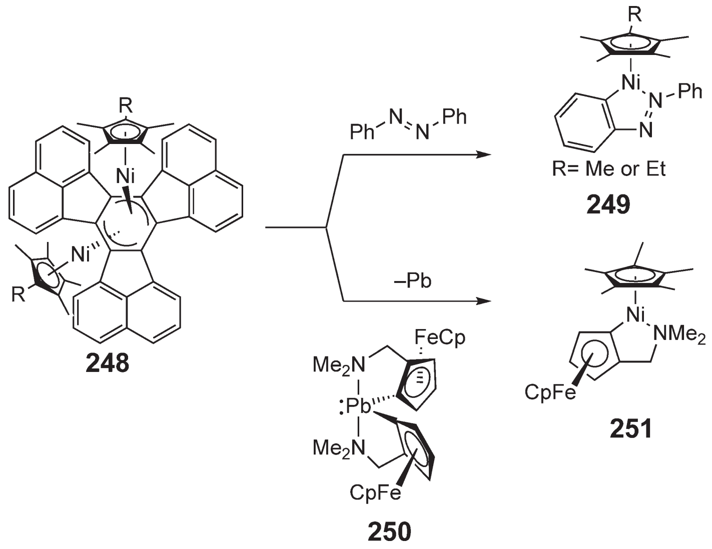


Scheme 78

displacement of the arene ligand, and therefore acts as a source of the 15-electron fragment Cp*Ni. This reactive species reacts readily with azobenzene at room temperature giving **249** (the synthesis of the analogous Cp complex from nickelocene requires prolonged heating under reflux), and with the plumbylene **250** yields the cyclometallated ferrocene derivative **251** (Scheme 79).[362]

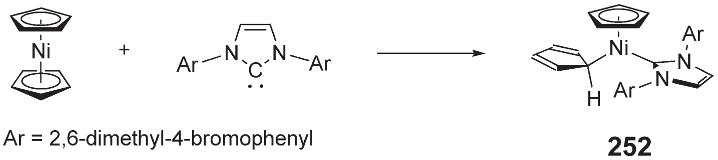
Transmetallation reactions with cyclopentadienyl complexes of the type (η^5-Cp)NiX(L) (L = phosphine,[45,363] heterocyclic carbene,[364] amine[365]) to give σ-organonickel complexes are usually straightforward. The same starting materials serve for the preparation of alkynylnickel complexes by mild dehydrohalogenation reactions in the presence of NEt_3 and CuI.[366–372] Interest in this type of alkynyl compounds stems from their potential to display non-linear optical properties.

Cyclopentadienylnickel complexes have also been prepared from suitable alkyl complexes by ligand exchange reactions with NaCp or other Cp salts.[244,332] Although most synthetic routes toward these compounds involve the metathetical introduction of the σ-organic ligand, there are some examples in which the σ-Ni–C bond is generated by other means. An interesting case is the reaction of Cp_2Ni with *N,N′*-bis(2,5-dimethyl-4-bromophenyl)imidazole-2-ylidene, which



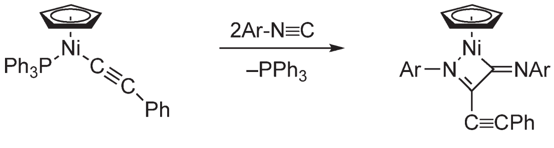
Scheme 79

causes the shift of one of the two Cp rings from η^5- to the η^1-coordination mode (Equation (104)).[373] Insertion reactions can also lead to the formation of new Ni–C bonds, although these are not frequent for 18-electron (η^5-Cp)Ni complexes (Equation (105)).[371] Andersen and Bergman have reported that the dimeric amide [(η^5-C_5Me_5)Ni(μ-NH-*p*-Tol)]$_2$ reacts with CO or Bu^{t}NC, affording carbamoyl and amidinyl complexes (Scheme 80).[374]



252

(104)

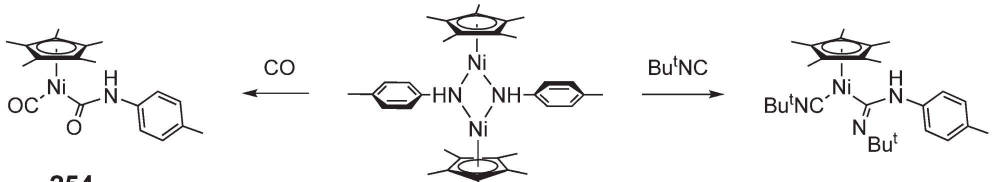


253

(105)

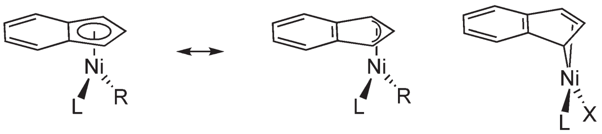
The alkylation of halogenated precursors is the preferred route for the synthesis of alkyl,[375–377] thienyl,[378] and alkynyl[377,379] η-indenylnickel compounds. Although the indenyl ligand is formally isoelectronic with cyclopentadienyl, structural and ^{13}C NMR data indicate that its coordination to the transition metal center is usually intermediate between η^5 and η^3 (Figure 3, **256**, **257**). As a consequence of the comparable *trans*-influence of the alkyl and the phosphine ligands, the bonding of the allyl fragment is very symmetrical, in contrast with the (η-indenyl)NiX(PR_3) complexes, where the π-ligand shows a significant alkyl–ene distortion (Figure 3, **258**).[350,380] This effect is also noticed in the rotation barriers of the indenyl ligand, which are lower in the alkyl than in the halo complexes.[375]

η-Indenylnickel complex catalyzes the polymerization of silanes,[376,381] olefins,[377,382] and alkynes.[378,379,383] An aluminum alkyl activator is generally needed, although the η-indenylnickel alkyls oligomerize silanes on their own. It is believed that the aluminum co-catalyst alkylates the Ni center and then activates the Ni–C bond, though the catalytic species are neutral. The catalytic activity of the methyl derivative **259** in $PhSiH_3$ oligomerization is strongly increased (ca. 50 times) in the presence of stoichiometric amounts of ($Me_2PCH_2AlMe_2$)$_2$, although the NMR spectra of these mixtures show no evidence for the formation of a new compound.[384] The catalytic activity is further enhanced by the addition of a Lewis base such as NEt_3, which cleaves the phosphinoalane dimer. Under these



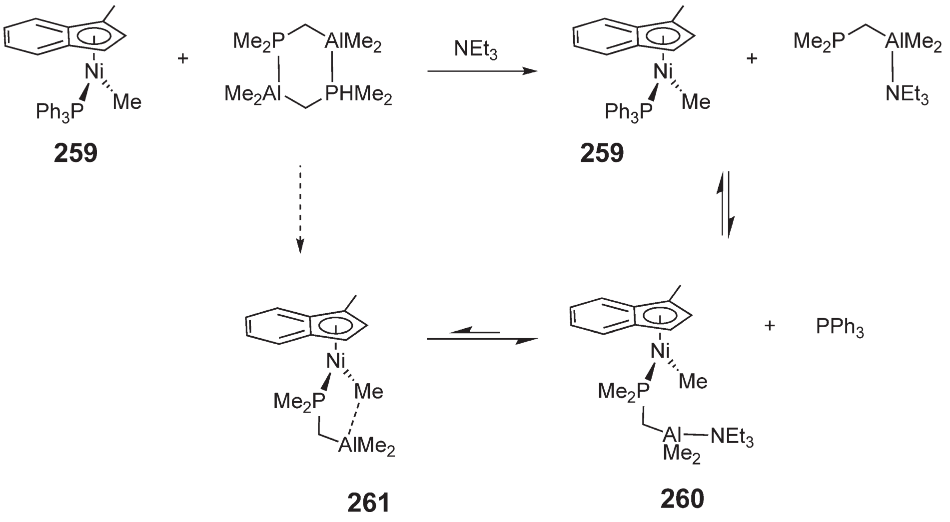
254 **255**

Scheme 80



256 **257** **258**

Figure 3 Coordination modes of the indenyl ligand.



Scheme 81

conditions, the reversible formation of a new complex, **260**, arising from the displacement of the PPh_3 ligand (Scheme 81) is observed. The increased catalytic activity of **260** could be due to the intramolecular activation of the Ni bond by the $AlMe_2$ group, as shown in **261**.

8.02.6 Binuclear and Polynuclear Complexes Containing Nickel–Metal and Nickel–C σ Bonds

This section summarizes the synthesis and properties of cluster complexes, including binuclear or heterobinuclear compounds displaying nickel–metal bonds. For the purposes of this survey, the discussion will be restricted to those compounds exhibiting terminal or bridging Ni–C σ-bonds, including alkylidene and alkylidyne ligands. Compounds containing bridging carbonyl, isocyanide, alkene, or alkyne have been discussed in Chapter 8.01 (Table 11).

8.02.6.1 Homometallic Clusters

The η^3-xylyl complex (η^3-CH_2-*o*-C_6H_4Me)NiCl(PMe_3) abstracts one α-hydrogen atom and one phosphine ligand from the metallacycle **231**, affording the tetranuclear product **262**. A similar reaction takes place between **231** and (η^3-C_3H_5)CpNi, to afford the related compound **263**, also formed when **262** is treated with NaCp (Scheme 82).[385] These compounds exhibit Ni–Ni distances of 2.384(3) and 2.353(1) Å, respectively, which indicate a substantial Ni–Ni bonding interaction. Trimethylphosphine, and chelating P and N ligands, cleave the chloro bridges of **262**, yielding binuclear products. An excess of PMe_3 leads to the mononuclear ylide **266**, probably through the intermediacy of the mononuclear alkylidene **265** (Scheme 83).[130]

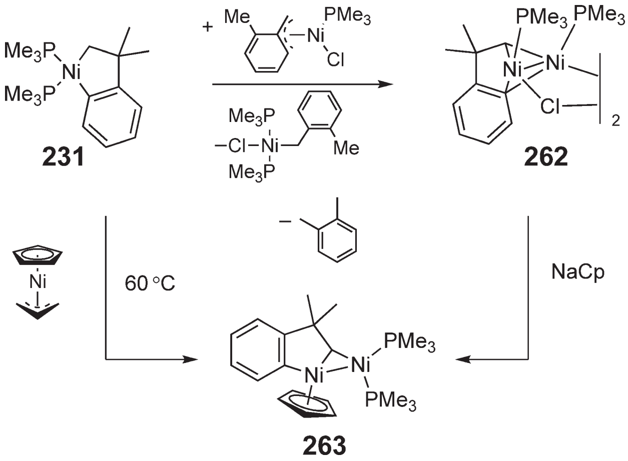
An Ni(I) dimetallacycle **267** displaying an Ni–Ni bond results from the reaction of 1,2-dilithiotriphenyl with $NiCl_2(PEt_3)_2$. This compound exhibits an interesting metallacycle-like reactivity, inserting CO and alkynes to afford carbocyclic compounds. In the latter case, the insertion is accompanied by C–C bond cleavage to give pyrene derivatives (Scheme 84).[386]

A large number of organometallic compounds, including nickel clusters containing bridging alkylidyne ligands or metallacyclic fragments, have been isolated from the mixtures generated in the reaction of nickelocene with organolithium or organomagnesium compounds.[354,355] The reaction of $NiCp_2$ with LiMe gives rise to a complex mixture that includes the ethylidyne cluster **268** (Equation (106)),[387] probably through the intermediacy of the analogous methylidyne complex, **270**. The latter compound has been recently prepared by the controlled decomposition of the alkene complex **269** (Equation (107)).[356] The open trinickel clusters **271** and **272** were isolated from the mixture generated in the reaction of Cp_2Ni and LiMe in the presence of alkynes (diphenyl acetylene[388] or 2-butyne[389,390]).

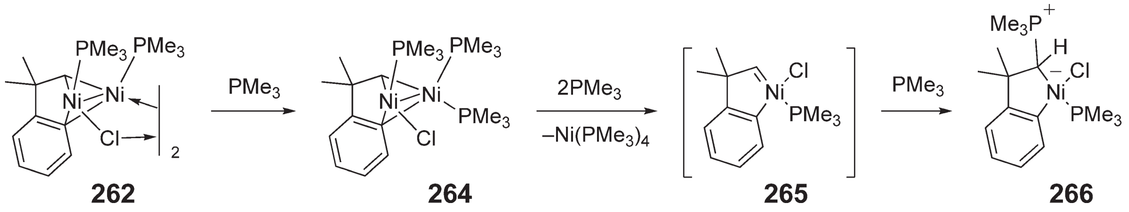
Table 11 Binuclear and polynuclear compounds with metal–metal and Ni–C σ-bonds

Compound	*Characterization*[1]	*References*
(a) Homonuclear compounds		
[{Ni(PMe$_3$)}$_2$(μ_2:μ_2-CHCMe$_2$-2-C$_6$H$_4$-)}$_2$(μ_2-Cl)]$_2$, **262**	XR, A, ^{1}H, ^{13}C, ^{31}P	385
{Ni(PMe$_3$)$_2$}(μ_2:μ_2-CHCMe$_2$-2-C$_6$H$_4$-){Ni(PMe$_3$)(Cl)}, **264**	XR, A, ^{1}H, ^{13}C, ^{31}P	385
[{Ni(dmpe)}$_2$(μ_2:μ_2-CHCMe$_2$-2-C$_6$H$_4$-)]$^+$Cl$^-$	A, ^{1}H, ^{13}C, ^{31}P	385
(η^5-Cp)Ni(μ_2-CHCMe$_2$-2-C$_6$H$_4$)Ni(PMe$_3$)$_2$, **263**	XR, A, ^{1}H, ^{13}C, ^{31}P	385
(η^5-C$_5$H$_4$Me)Ni(μ_2-CHCMe$_2$-2-C$_6$H$_4$)Ni(PMe$_3$)$_2$	A, ^{1}H, ^{13}C, ^{31}P	385
(η^5-C$_5$H$_4$Pr^i)Ni(μ_2-CHCMe$_2$-2-C$_6$H$_4$)Ni(PMe$_3$)$_2$	A, ^{1}H, ^{13}C, ^{31}P	385
{Ni(PMe$_3$)}$_2$(μ_2:μ_2-CHCMe$_2$-2-C$_6$H$_4$-)(μ_2-κ^1-*N*:κ^1-*N′*-tp)	A, ^{1}H, ^{13}C, ^{31}P	385
{Ni(PMe$_3$)}$_2$(μ_2:μ_2-CHCMe$_2$-2-C$_6$H$_4$-)(μ_2-κ^1-N:κ^1-N′-tp$^{\mathrm{Bu^t}}$)	A, ^{1}H, ^{13}C, ^{31}P	385
{Ni(PEt$_3$)}$_2$-μ-2,2′-(1,1′-biterphenylyl), **267**	XR, A, ^{1}H, ^{13}C, ^{31}P	386
{(η^5-Cp)Ni}$_3$(μ_3-CH), **270**	^{1}H, ^{13}C, MS	356
{(η^5-Cp)Ni}$_3$(μ_3-C-Me), **268**	^{1}H, ^{13}C, MS	356,387
{(η^5-Cp)Ni}$_3$(μ_3-C-Bu^n)	A, ^{1}H, ^{13}C, MS	394
{(η^5-Cp)Ni}$_3$(μ_3-C-Pent^n)	XR, A, ^{1}H, ^{13}C, MS	393,394
{(η^5-Cp)Ni}$_3$(μ_3-C-Hex^n)	^{1}H, ^{13}C, MS	359
{(η^5-Cp)Ni}$_3$(μ_3-C-C$_9$H$_{19}$)	^{1}H, ^{13}C, MS	393
{(η^5-Cp)Ni}$_3$(μ_3-C-(CH$_2$)$_3$CH═CH$_2$)	^{1}H, ^{13}C	359
{(η^5-Cp)Ni}$_3$(μ_3-C-CH(Me)CHMe$_2$)	^{1}H, MS	359
{(η^5-Cp)Ni}$_3$(μ_3-C-CH(Me)CH$_2$CMe$_3$)	^{1}H, MS	393
{(η^5-Cp)Ni}$_3$(μ_3-C-CH(Me)(Ph))	XR, ^{1}H, ^{13}C, MS	391
{(η^5-Cp)Ni}$_3$(μ_3-C-Bz), **273**	^{1}H, ^{13}C, MS	392
{(η^5-Cp)Ni}$_3$(μ_3-C-Bu^n)(μ_3-H)	XR, A, IR, MS	394
{(η^5-Cp)Ni}$_3$(μ_3-C-Hex^n(μ_3-H)	A,IR, MS	394
{(η^5-C$_5$Me$_5$)Ni}$_3$(μ_3-CH)(μ_3-H), **274**	XR, EPR, μ_{eff}, MS	396
Ni$_3$(μ_2-dppm)$_3$(μ_3-C═CPh)$_2$, **275**	XR	397
(η^5-Cp)Ni(μ_2,η^2(1,4):η^4-CPh=CPhCPh=CPh)-Ni(μ_2-PhC≡CPh)Ni(η^5-Cp), **271**	XR, ^{1}H, MS	388
(η^5-Cp)Ni(μ_2,η^2(1,4):η^4-CMe=CMeCMe=CMe)-Ni(μ_2-MeC≡CMe)Ni(μ^5-Cp), **271**	^{1}H, MS	389
(η^5-Cp)Ni(μ_2,η^2(1,4):η^4-CMe=CMeCMe=CMe)-Ni(μ_3-MeC≡CMe){Ni(η^5-Cp)}$_2$, **272**	XR, A, MS, EPR	390
(b) Heteronuclear compounds		
(η^5-C$_5$Me$_5$)Ni{μ-η^2(1,3-*Ni*),η^2(1,2–*Mo*)-C(Me)═C(Me)CO)}-Mo(CO)$_2$(η^5-Cp), **277**	^{1}H, ^{13}C, IR, MS	399
(η^5-C$_5$Me$_5$)Ni{μ-η^2(1,3-*Ni*),η^2(1,2–*W*)-C(Me)═C(Me)CO)}-W(CO)$_2$(η^5-C$_5$H$_4$Me), **277**	^{1}H, ^{13}C, IR	399
(η^5-C$_5$Me$_5$)Ni{μ-η^2(1,3-*Ni*),η^2(1,2–*W*)-C(Ph)═C(Me)CO)}-W(CO)$_2$(η^5-Cp), **277**	^{1}H, ^{13}C, IR	399
(η^5-C$_5$Me$_5$)Ni{μ-η^2(1,3-*Ni*),η^2(1,2–*W*-C(Ph)═C(H)CO)}-W(CO)$_2$(η^5-C$_5$H$_4$Me), **277**	^{1}H, ^{13}C, IR	398
(η^5-Cp)Ni{μ-η^3(*Ni*),η^1(*M*)–CO–C(CMe$_2$OMe)═CH}-M(CO)$_2$(η^5-C$_5$H$_4$Me) (M = Mo, W), **276**	A, ^{1}H, ^{13}C, IR, MS	400
(η^5-C$_5$Me$_5$)Ni{μ-η^3(*Ni*),η^1(*M*)–CO–C(Ph)═CH}-M(CO)$_2$(η^5-C$_5$H$_4$R) (M = Mo, W, R = H; M = W, R = Me), **276**	^{1}H, ^{13}C, IR	398
(η^5-C$_5$Me$_5$)Ni{μ-η^3(*Ni*),η^1(*Mo*)–CO–C(H)═CH}-Mo(CO)$_2$(η^5-C$_5$H$_4$R) (M = Mo, W, R = H; M = W, R = Me), **276**	A, ^{1}H, IR	398
{(η^5-Cp)Ni}$_2${Mo(CO)$_2$(η^5-Cp)}-μ_3-C–C(Ph)═C$_5$H$_4$, **279**	XR, IR	402
(η^5-C$_5$Me$_5$)Ni{Mo(CO)$_2$(η^5-Cp)}$_2$-μ_3-CCH$_2$CO$_2$Me, **278**	XR	401
Ni(Me)(μ-dppm){(μ–Si(OMe)$_2$(-OMe)-κ(*O*,*Ni*),κ(*Si*,*Fe*))}Fe(CO)$_3$, **282**	XR, A, ^{1}H, ^{31}P, IR	403
{Ni(HB(3-bromopyrazolyl)$_3$)}(μ-C═CHPh)(μ-CO)Ru(CO)$_2$(η^5-Cp), **283**	XR, IR, ^{1}H, ^{13}C	404
{(η^5-Cp)Ni}{μ_2,η^2:η^1-C(H)PPh$_2$-C=C(PPh$_2$)COOCO}-Co$_2$(CO)$_4$(μ-CO), **286**	XR, A, ^{31}P, IR	405
{(η^5-Cp)Ni}{μ_2,η^2:η^1-C(H)-C=C(PPh$_2$)COOCO}-Co$_2$(CO)$_4$(η-PPh$_2$), **287**	XR, A, ^{31}P, IR	405

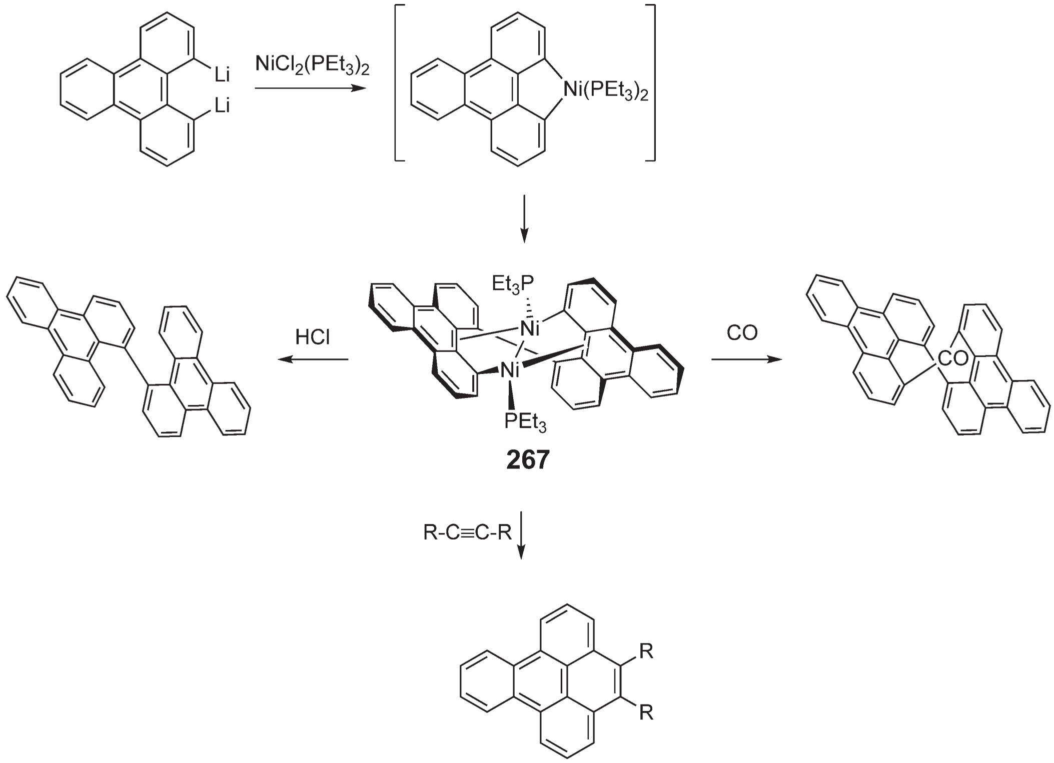
A, elemental analysis; MS, mass spectrum; IR, infrared; ^{1}H, ^{13}C, ^{31}P, NMR spectra; XR, X-ray diffraction.



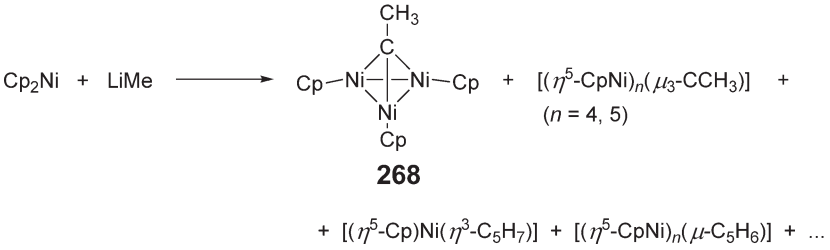
Scheme 82



Scheme 83



Scheme 84



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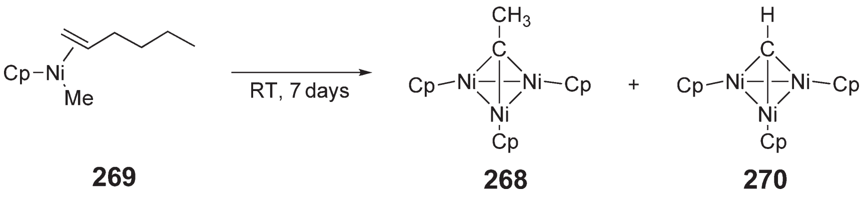

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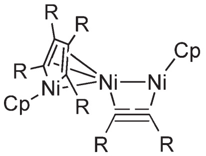
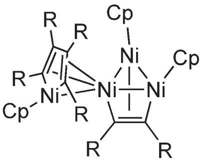


R = Ph, Me

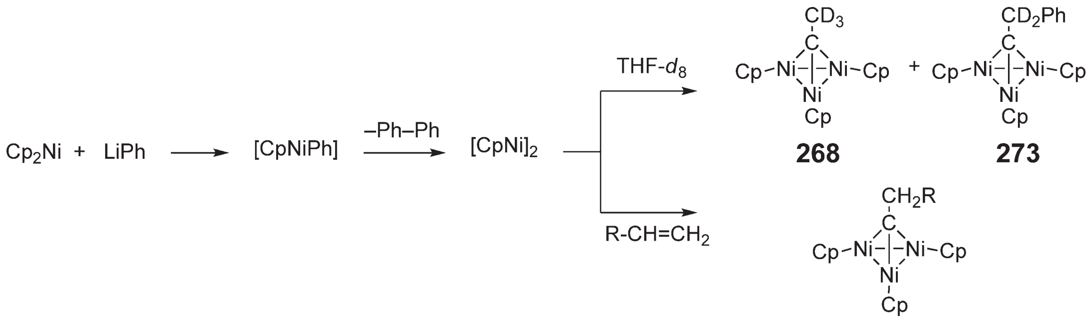
271



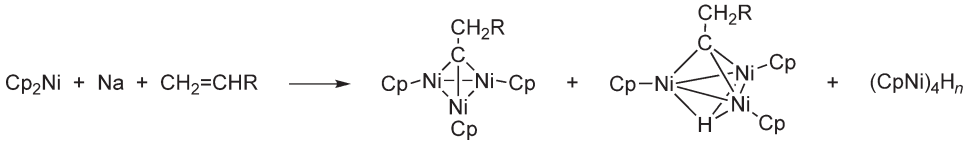
R = Me

272

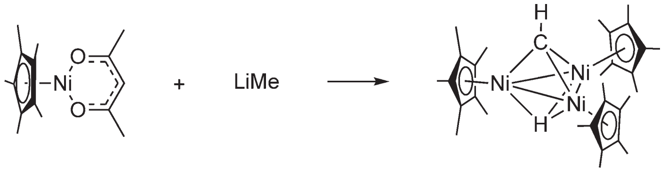
It has been known for many years that whereas organolithium or organomagnesium reagents containing M–CH_2R (R = Ph, CMe_3, $SiMe_3$) units react with nickelocene to give alkylidyne-capped clusters, these are not formed when the reagent has β-hydrogen atoms. However, the cluster $((\eta^5\text{-Cp})Ni)_3(\mu_3\text{-CCHMePh})$ has been recently prepared from Cp_2Ni and $Mg(CH_2CH(Me)Ph)Br$.[391] The products formed in the reaction of Cp_2Ni with LiPh have been interpreted on the basis of the formation of the Cp_2Ni_2 intermediate (Scheme 85). Thus, deuterated ethylidyne **268** and the related benzylidyne **273** are formed when the reaction is carried out in THF-d_8, as a result of the cleavage of the solvent by Ni_2Cp_2.[392] When the reaction is performed in the presence of olefins, these are incorporated in the final products as alkylidyne ligands.[393] The reaction of $NiCp_2$ with alkaline metals (Li or Na) in the presence of different internal or terminal olefins affords similar alkylidynes, together with doubly capped alkylidyne–hydride 49-electron clusters (Equation (108)).[394,395] A trinuclear compound of the latter type, **274**, is produced in high yield in the reaction of $(\eta^5\text{-}C_5Me_5)Ni(acac)$ with LiMe (Equation (109)). As expected, the latter compound is paramagnetic, with one unpaired electron.[396] On the other hand, the Cp-free 44-electron triangular cluster **275**, bicapped by two acetylide bridges, is formed when 1,4-diphenylbutadiyne reacts with $Ni(cod)_2$ and dppm (Equation (110)).[397]



Scheme 85

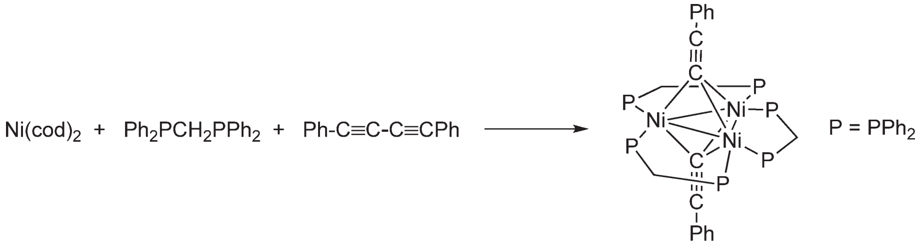


(108)



274

(109)

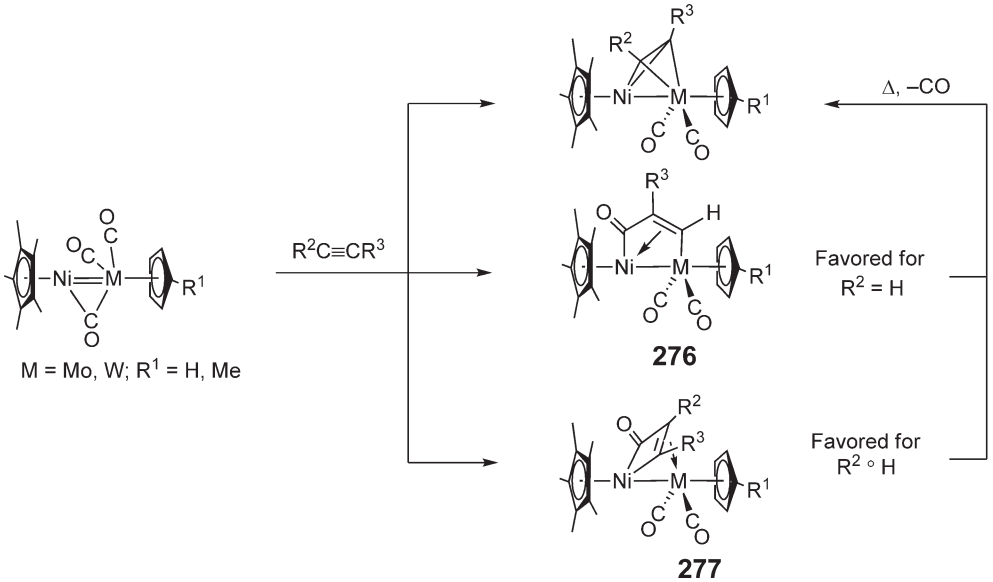


275

(110)

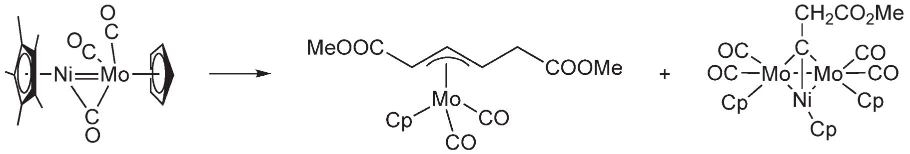
8.02.6.2 Heterometallic Clusters

The metal–metal bonded compounds $(C_5Me_5)Ni–M(CO)_3Cp'$ (M = Mo, W) react with alkynes giving rise to two types of isomeric metallacyclic compounds. Terminal alkynes favor the formation of five-membered bimetallacyclic structures **276**,[398] while internal alkynes give rise to compounds displaying a four-membered nickelacyclobutenone fragment **277**, which loses CO readily to give alkyne-bridged binuclear compounds[399,400] (Scheme 86). The binuclear carbonyl $(C_5Me_5)NiMo(CO)_3Cp$ reacts with methyl acrylate to give a mixture of an Mo allyl complex and the alkylidyne-capped $NiMo_2$ triangular cluster **278** (Equation (111)).[401] It is interesting to note that the



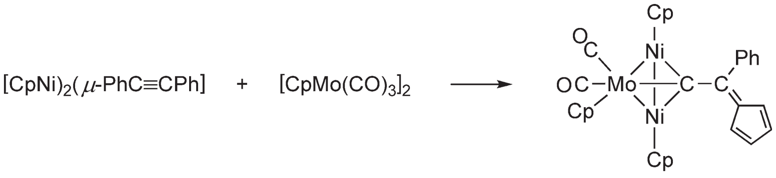
Scheme 86

formation of **278** is formally related to the reaction of the transient species Cp_2Ni_2 (isoelectronic with the hypothetical fragment $[(C_5Me_5)Ni–Mo(CO)_2Cp]$) with olefins to give trinickel alkylidines (Scheme 85). An Ni_2Mo alkylidyne triangular cluster **279** has been synthesized by reacting the Cp_2Ni_2-diphenylacetylene complex with $[CpMo(CO_3)]_2$ in hot xylene (Equation (112)).[402]



278

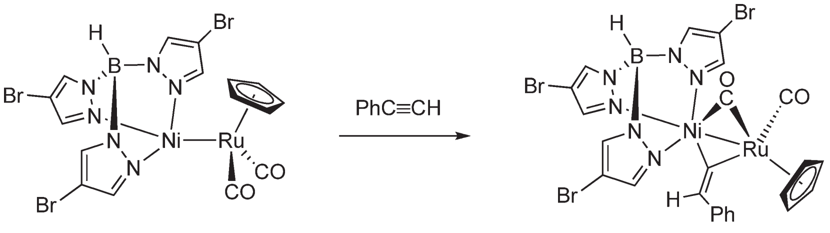
(111)



279

(112)

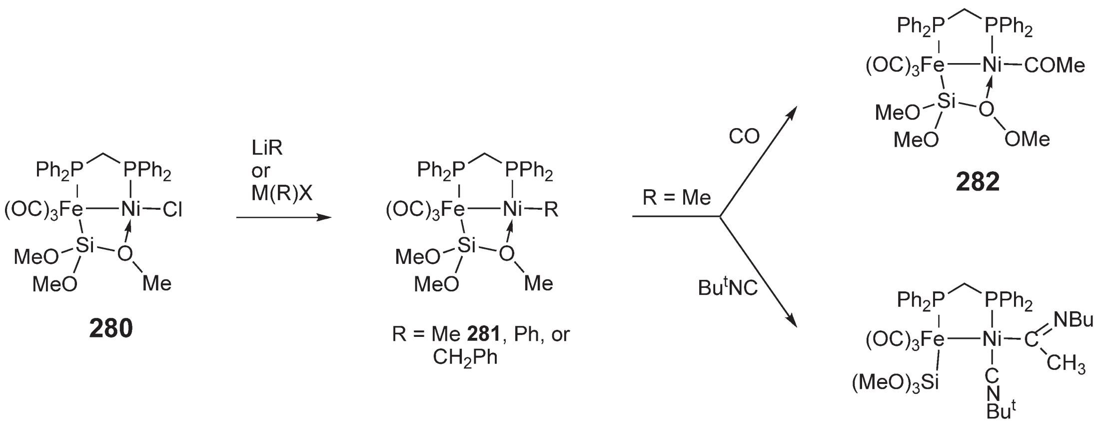
Alkylation of the bimetallic Fe–Ni compound **280** with LiMe, LiPh, or Mg(Bz)Cl leads to the formation of heterobinuclear complexes displaying Ni–R bonds, although only the methyl derivative **281** was isolated in pure form.[403] Compound **281** reacts with CO or *t*-BuNC, giving acetyl **282** or iminoacyl **283** complexes that were characterized in solution (Scheme 87). A second example of Ni–group-8 element heterobimetallic complex is the alkenylidene **285**, prepared as shown in Equation (113).[404]



284
High spin Ni(II)

285
Low spin Ni(II)

(113)



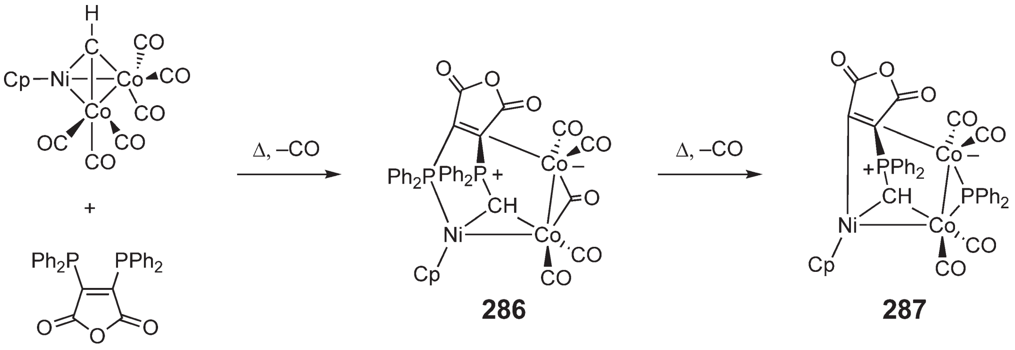
280

R = Me **281**, Ph, or CH$_2$Ph

282

283

Scheme 87



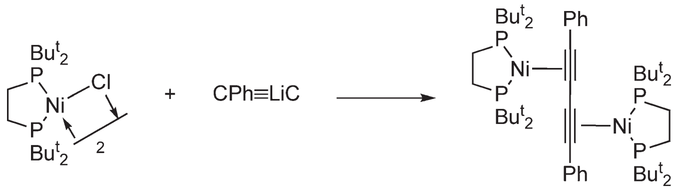
Scheme 88

The diphosphine 2,3-bis(diphenylphosphino)maleic anhydride reacts with the methylidyne-capped triangular cluster $CpNiCo_2(CO)_6$ with the opening of the tetrahedral framework and formation of a zwitterionic product containing a bridging phosphoniomethylidene, **286**. Under the reaction conditions, **286** converts into **287**, by oxidative addition of one P–C bond to the $NiCo_2$ unit with the formation of a new Ni–C σ-bond and displacement of the bridging CO ligand by the PPh_2 fragment. Kinetics of the reaction indicate that the release of CO is the rate-limiting step in this process (Scheme 88).[405]

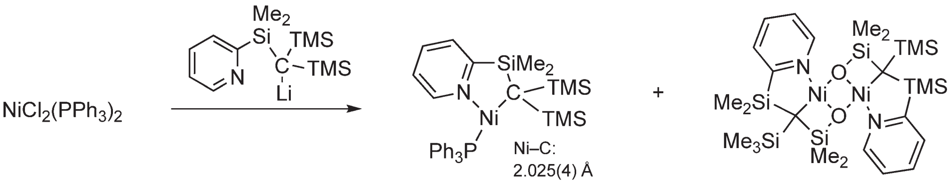
8.02.7 Nickel Alkyl and Aryl Complexes in Oxidation States I, III, and IV

The coordination chemistry of nickel in oxidation states different from 0 or II has experienced a considerable growth in recent years, due in part to the involvement of nickel in biological processes, where the oxidation states I and III may play an important role (see next section). Organometallic nickel(I) and nickel(III) species have been postulated as intermediates in important organometallic reactions, such as oxidative addition and reductive elimination.[98,406] More recently, Hillhouse has pointed out the importance of the oxidation of Ni(II) alkyl–alkoxo and alkyl–amido complexes to achieve C–O and C–N reductive elimination, presumably through the intermediacy of Ni(III) species.[129,337,339] Although stable organometallic Ni(I) and Ni(III) compounds continue to be rare, several examples have been reported.

Nickel(I) halide and hydride complexes have been known for many years, and some amido and phosphido complexes have been described recently.[407,408] Attempts to transfer σ-organic ligands to Ni(I) centers may lead to reduction to Ni(0), as exemplified in Equation (114).[409] Sometimes, attempts to prepare organometallic Ni(II) compounds are frustrated by the formation of undesired reduction to Ni(I),[63,203] but formation of organometallic species is very unusual. In one case, shown in Equation (115), a transmetallation reaction was unexpectedly accompanied by reduction of the Ni center, to afford the only example known of a stable Ni(I) σ-organometallic complex, **288**.[340] The formation of a small amount of the Ni(II) metallacycle **289** was attributed to the presence of impurities in the starting material. The tricoordinated Ni(I) center is planar and exhibits a T-shaped geometry, with a very wide P–Ni–C angle (155.67(11)°). As expected for a monomeric d^9-complex, it is paramagnetic with a single unpaired electron.



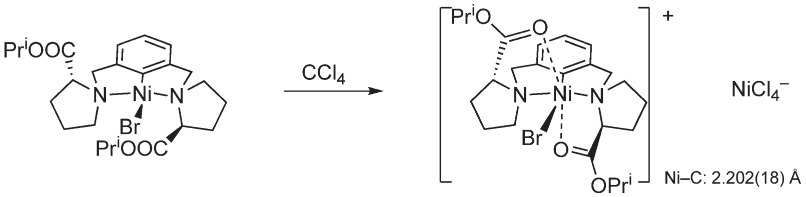
(114)



288 **289**

(115)

Chelating pincer "NCN" ligands are known to stabilize Ni(III) complexes,[410,411] which play a key role in the nickel-catalyzed Kharasch addition of CCl_4 and other halogeno compounds to olefinic double bonds.[412] The Ni(II) pincer complexes display very low oxidation potentials and are readily oxidized by mild reagents such as CCl_4 (Equation (116)).[229] Complex **290** features a six-coordinate octahedral geometry, but other reported examples of Ni(III) pincer compounds are five coordinate, square pyramidal.[236] A four-coordinated, square-planar homoleptic Ni(III) complex, **291**, has been prepared by oxidation of the corresponding Ni(II) precursor with Cl_2 at low temperature (Equation (117)).[33] This complex has low thermal stability and slowly decomposes at room temperature, with the production of perchlorobiphenyl. Organometallic Ni(III) compounds have low spin electronic configurations, and display well-resolved EPR spectra (Table 12).



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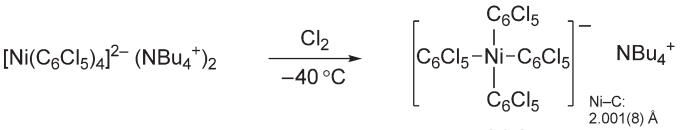
(116)

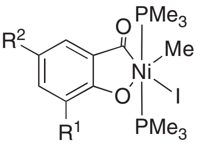
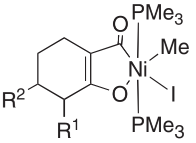


$$[Ni(C_6Cl_5)_4]^{2-}\ (NBu_4^+)_2 \xrightarrow[-40\,°C]{Cl_2} \left[C_6Cl_5\text{–}\overset{\displaystyle C_6Cl_5}{\underset{\displaystyle C_6Cl_5}{Ni}}\text{–}C_6Cl_5 \right]^- NBu_4^+ \quad \text{Ni–C: } 2.001(8)\ Å$$

291

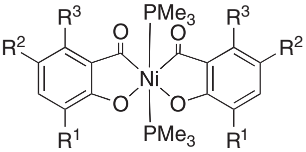
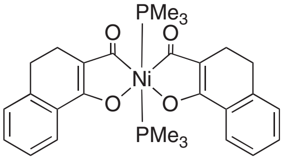
(117)

Table 12 Alkyl and aryl complexes in the oxidation states I, III, and IV

Compound	*Oxidation State*	*Characterization*	*References*
$\overline{\mathrm{Ni(C(SiMe_3)_2SiMe_2\text{-}2\text{-}py}}\mathrm{)(PPh_3)}$, **289**	I	XR, EPR, μ_{eff}	340
$[NBu^n{}_4][Ni(C_6Cl_5)_4]$, **291**	III	XR, EPR, IR, CV	33
$Ni\{C_6H_4(CH_2NMe_2)_2\text{-}2,6\}Cl_2$	III	A, XR, EPR, MS	236
$[Ni\{C_6H_4(CH_2\text{-}N\text{-pyrrolidyl}(CO_2Pr^i)\text{-}2)_2\text{-}2,6\}(Cl)]^+[CuBr_4]^-$	III	A, XR, EPR, IR	229
$[Ni\{C_6H_4(CH_2\text{-}N\text{-pyrrolidyl}(CO_2Pr^i)\text{-}2)_2\text{-}2,6\}(Cl)]^+[NiCl_4]^-$, **290**	III	A, EPR, IR	229
$Ni(1\text{-norbornyl})_3(Br)$, **296**	IV	A, *m/d*, ^{13}C, XR	415
 **292**			
$R^1 = Bu^t$; $R^2 = Me$	IV	XR, A, ^1H, ^{13}C, ^{31}P, IR	413
$R^1 = Bu^t$; $R^2 = Bu^t$	IV	A, ^1H, ^{13}C, ^{31}P, IR	413
			
$R^1 = H$; $R^2 = H$	IV	A, ^1H, IR	126

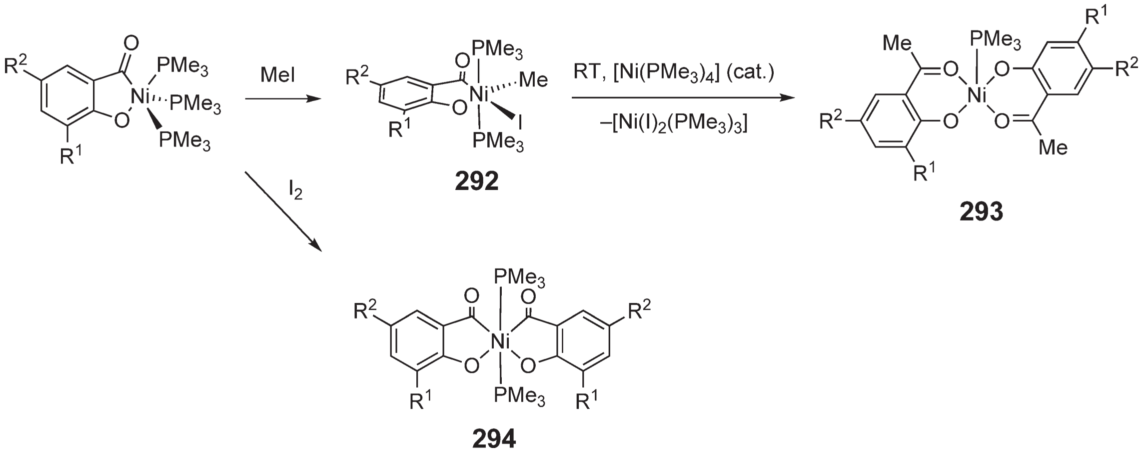
(Continued)

Table 12 (Continued)

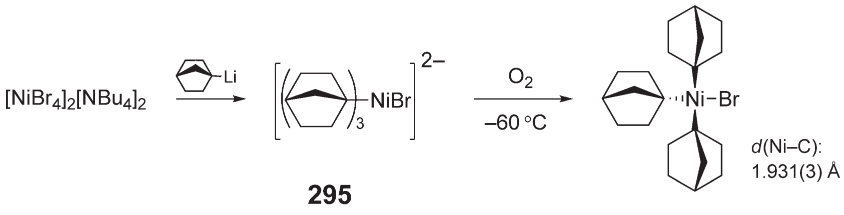
Compound	*Oxidation State*	*Characterization*	*References*
R^1, R^2 = benzo	IV	IR	126
 **294**			
R^1 = H; R^2 = H; R^3 = H	IV	^{1}H, ^{13}C, ^{31}P, MS, IR	414
R^1 = Bu^t; R^2 = Me; R^3 = H	IV	XR, A, ^{1}H, ^{13}C, ^{31}P MS, IR	126,414
R^1 = Bu^t; R^2 = Bu^t; R^3 = H	IV	*m/d*, ^{1}H, ^{13}C, ^{31}P, MS	126,414
R^1 = OMe; R^2 = H; R^3 = H	IV	^{1}H, IR	126,414
R^1 = H; R^2, R^3 = benzo	IV		414
	IV	A, *m/d*, ^{1}H, ^{31}P	126

A, elemental analysis; *m/d*, melting or decomposition point; MS, mass spectrum; UV, ultraviolet–visible; IR, infrared; ^{1}H, ^{13}C, ^{31}P, NMR spectra; XR, X-ray diffraction; CV, cyclic voltammetry.

Although oxidation states above III are much rarer for nickel than for its heavier congeners Pd and Pt, several examples of surprisingly stable Ni(IV) organometallic complexes have been reported. Klein has shown that, under carefully controlled conditions, metallacyclic acylphenolato[126,413,414] complexes undergo oxidative addition of MeI to yield isolable low spin, 18-electron octahedral Ni(IV) compounds (Scheme 89). In solution, the Ni(IV) 2-acylphenolates **292** undergo acyl-CH_3 coupling above 0 °C, giving rise to the Ni(II) complex **293**. This transformation is catalyzed by $Ni(PMe_3)_4$. Attempts to generate similar Ni(IV) complexes from higher iodoalkanes afforded C–C coupling products, while acyl chlorides gave rise to products resulting from acylation of the O atom.[126] Oxidation of the acylphenolato complexes with I_2 or I_2 surrogates (CH_2I_2, $C_2H_4I_2$) give the more robust bis-chelated Ni(IV) acyls **294**, which are stable in solution. Some of these derivatives can be sublimed *in vacuo* at 130 °C. Upon oxidation with MeI or I_2, nickel(II) acylenolate complexes give rise to anologous products, although these are considerably less stable than their phenolate counterparts.[126] A second type of Ni(IV) complex is the norbornyl derivative **296**, obtained by



Scheme 89

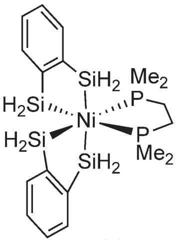


295

296

Scheme 90

oxidation of the unstable Ni(II) trisnorbornyl anion **295** with oxygen at low temperature (Scheme 90).[415] This compound decomposes readily in solution by reductive elimination, but its stability in the solid state is astonishingly high for an unsaturated 14-electron Ni(IV) compound (dec > 130 °C). In spite of its pseudotetrahedral geometry, confirmed by X-ray diffraction, **296** is diamagnetic. This is probably due to significant rupture of orbital degeneracy due to the actual C_{3v} symmetry of the molecule, which permits the spin pairing. Although not strictly organometallic, it is worth mentioning here the stable Ni(IV) silyl complex **297**, prepared by the reaction of Ni(dmpe)$_2$ with 1,2-disilylbenzene.[416]



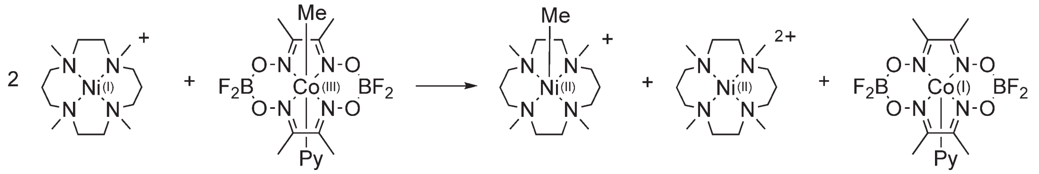
297

8.02.8 Nickel Organometallic Complexes of Biological Significance

Nickel is an essential trace element for all living beings. Although its role in animals or plants is not known in many cases, its involvement in bacterial biochemistry is better understood.[417] Nickel forms part of the active center of metalloenzymes with three different functions, namely methyl-*S*-co-enzyme M reductase (MCR), carbon monoxide dehydrogenase (COD), and acetylco-enzyme A synthase (ACS), which are found in archeobacteria with methanogenic, acetogenic, and sulfate-reducing activity. These proteins are involved in methyl transfer processes connected with the formation of methane, and the synthesis of acetate from CO$_2$, which are thought to involve organometallic species. Compared to the organometallic complexes of nickel commonly found in the laboratory, the coordination environment of nickel in these metalloenzymes is rather exotic, and belongs to two main groups. The prosthetic group of MCR is a porphyrinoid complex called F430 because its UV–VIS absorption band occurs at 430 nm,[418] while a bifunctional enzyme bearing an Ni atom in a sulfur/nitrogen donor set carries out the COD and ACS activities.[419,420] The study of the functional metalloproteins also indicates that the activity of the Ni center could involve the oxidation states I, II, and III. The elucidation of the mechanisms has attracted many research groups to investigate nickel organometallic systems that could mimic the natural processes.

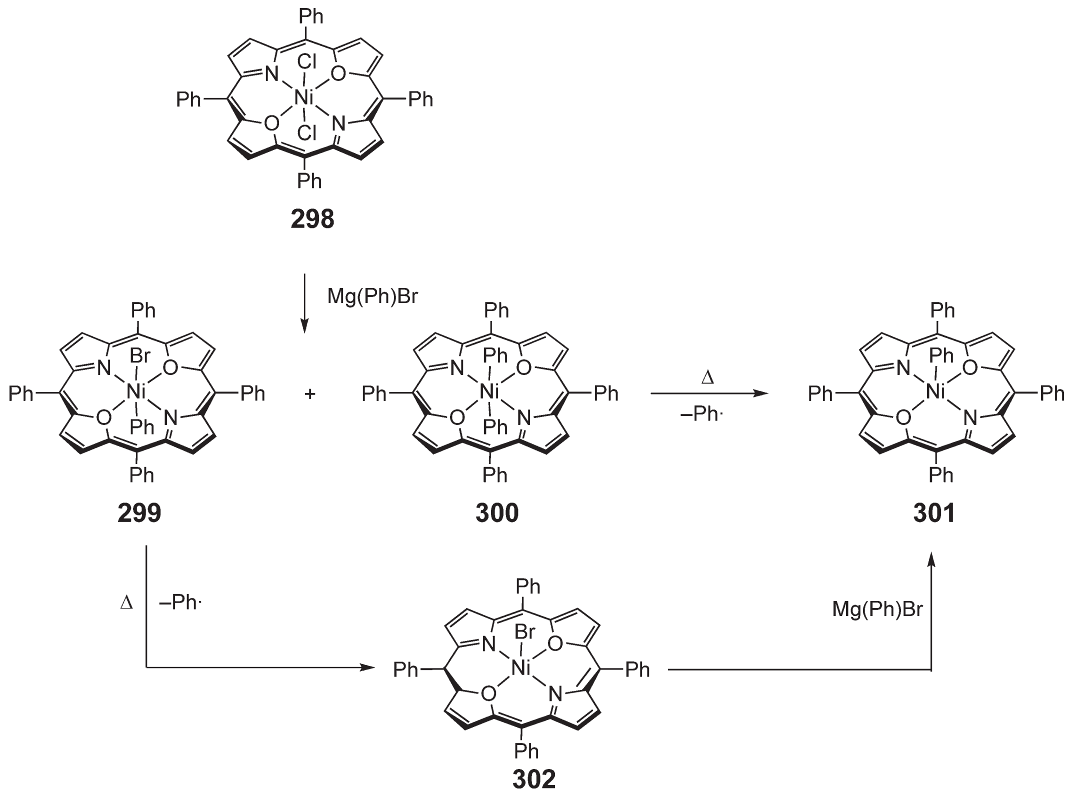
8.02.8.1 Nickel Organometallic Complexes with Macrocyclic Ligands

The enzyme MCR catalyzes the final step of the methane synthesis in archeobacteria. Several mechanisms have been suggested for this process, some of them involving methyl transfer to the Ni center in the porphyrinoid prosthetic group F430, although a recent theoretical paper favors the intermediacy of short-lived methyl radicals rather than genuine organometallic species.[418] There is also evidence regarding the implication of the F430 complex in the bacterial degradation of perchlorohydrocarbons.[74] Because of its biological significance, the organometallic chemistry of Ni in macrocyclic environments has received much attention. Among the first examples of such organometallic complexes are those containing the macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc). It has been found that Co(III) alkyl complexes can transfer an alkyl group to the Ni species [Ni(tmc)]$^+$ (Equation (118)), mimicking the alkylation of the carbon monoxide dehydrogenase Ni site by methylcobalamin.[421] Detailed mechanistic studies have demonstrated that the alkyl transfer involves electron transfer from Ni to Co, followed by Co–C bond homolysis and capture of the free radical by Ni.[422] It is interesting to recall here that an example of the inverse process, that is, alkyl transfer from Ni(II) to Co(I), has been observed as well (see Equation (92), Section 8.02.4.2).[305] The kinetics of the homolytic decomposition of Ni(tmc) benzyl complexes in solution have been measured.[423]



(118)

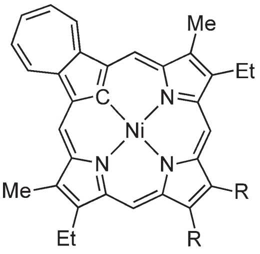
Porphyrin-like ligands offer a close similarity to the active center of enzymes such as MCR. The organometallic chemistry of Ni with this type of ligands has received a strong impetus from several groups, especially that of Latos–Grazynski.[424] Substitution of one or two of the pyrrolyl nitrogen atoms of porphyrin by oxygen or selenium leads to related monoanionic or neutral ligands featuring different cavity sizes capable of producing penta- or hexacoordinated Ni(II) complexes with metal-bound halide ligands. The reaction of these complexes with arylmagnesium reagents (e.g., Mg(Ph)Cl) gives rise to unusually high spin Ni(II) organometallic complexes, which have been characterized *in situ* by ^{1}H and ^{2}H NMR as well as EPR spectroscopies.[425,426] These compounds are thermally unstable and decompose above −10 °C by Ni–C bond homolysis, giving Ni(I) complexes. The titration of the NiCl$_2$ complex **298** with Mg(Ph)Cl displaces only one chloro ligand, while Mg(Ph)Br leads to a mixture of the mono- and diphenyl derivatives **299 and 300** (Scheme 91). The homolytic decomposition of the mixture of the two complexes gives a



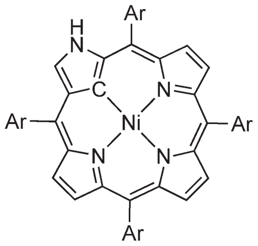
Scheme 91

single product, the Ni(I) phenyl **301**, since the Ni(I) halide **302** that results from the homolytic decomposition of **299** is rapidly arylated by the excess of Grignard reagent.[426]

A second approach to the generation of organometallic nickel complexes with macrocyclic porphyrin-type ligands is to replace one of the pyrrole groups by a carbocyclic fragment, in order to generate an Ni–C bond in the equatorial plane. Some examples have been reported where the macrocycle incorporates an azulene unit **303**[427] or a benzene ring (**309**, see below).[428] However, a more simple and very successful approach is the use of the so-called "*N*-confused porphyrins" **304**,[429] an isomeric form of the porphyrin ligand where one pyrrole has inverted its position, offering a carbon atom to the metal center. The Ni(II) ion readily inserts into the C–H bond of these ligands under mild conditions. Following the synthesis of the first examples of *N*-confused Ni(II) porphyrin complexes in 1993,[430] various compounds of the same kind displaying C-metallated macrocyclic ligands have been reported.[431–435]



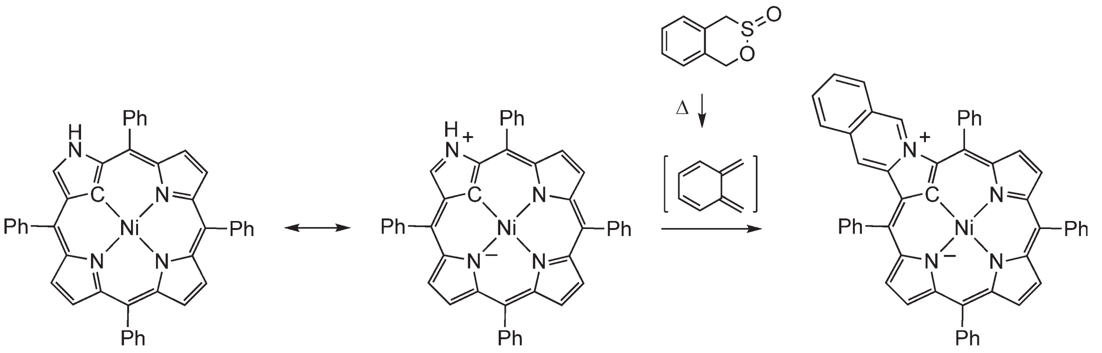
303



304

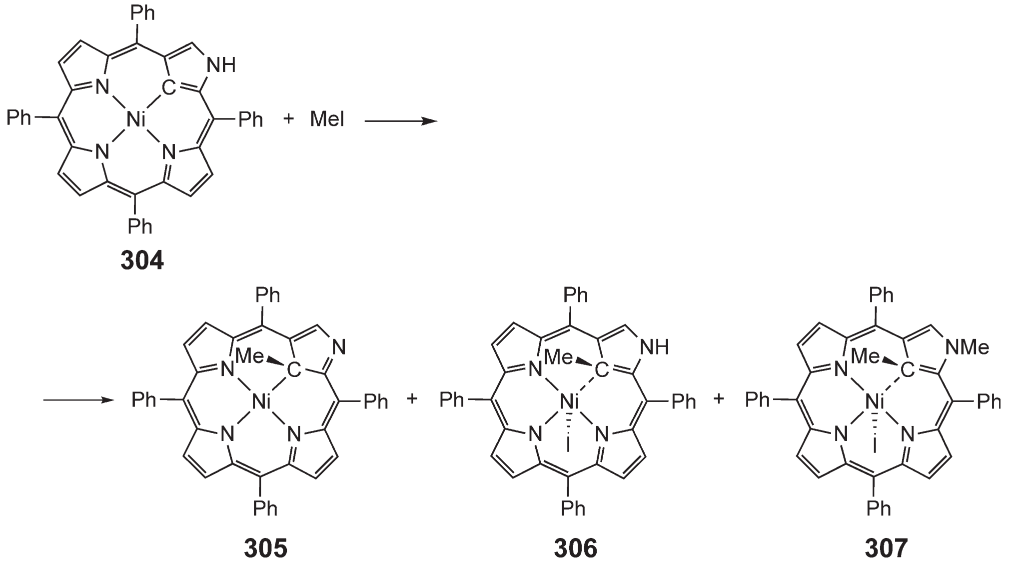
The Ni–C bond is strongly stabilized by its inclusion within the macrocyclic framework, and the complexes can undergo different transformations without Ni–C dissociation. For example, a range of chemical oxidizing reagents (Br_2, Ce(IV), Ag^+, etc.,) react with **304** giving pentacoordinated $\mathrm{Ni^{III}}$(*N*-confused porphyrin)(X) complexes (X = Br, NO_3, OH) which have been characterized in solution.[436] Interestingly, **304** behaves as a dienophile in Diels–Alder reactions, evidencing some iminium character of the *N*-confused pyrrole ring (Scheme 92).[437] The "iminium" proton of **304** is acidic and can be removed by sodium methoxide, giving rise to highly reactive anionic species that are trapped by the electrophilic reagent dichloro dicyano quinone (DDQ).[438]

The reaction of complex **304** (Ar = Ph) with methyl iodide (Equation (119)) is of special interest because it provides an insight into the mechanism of alkyl transfer to Ni in porphyrinic systems.[439] In the diamagnetic product **305**, the alkylated carbon becomes tetrahedral (sp^3), and the Ni–C distance (2.005(6) Å) is typical of a single σ-bond. Compounds **306** and **307** are paramagnetic, and differ only in the substituent at the confused pyrrole nitrogen atom (H or Me). Like **304**, complexes **306** and **307** display a methylated inner carbon atom, but this atom shows a planar sp^2 configuration, suggesting a weak π-C–Ni donor interaction. This is confirmed by the long Ni–C distance (2.406(11) Å in **306**), and the relatively acute angle formed by the pyrrole ring and the Ni–C bond (70.1°), as compared with the flatter structure displayed by **305** (Figure 4). As suggested in Scheme 93, the mechanism of this reaction may involve either concerted addition of MeI to the Ni–C bond or initial alkylation of the Ni atom followed by methyl migration from the metal to the carbon atom, to give **306**, which reversibly loses HX producing the diamagnetic **305**. Compound **307** is formed by subsequent methylation of **305** at the external N atom.



304

Scheme 92



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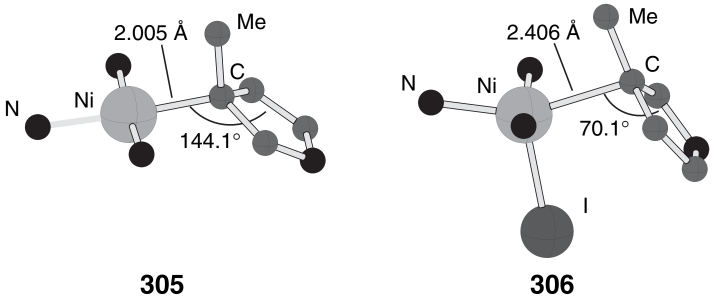
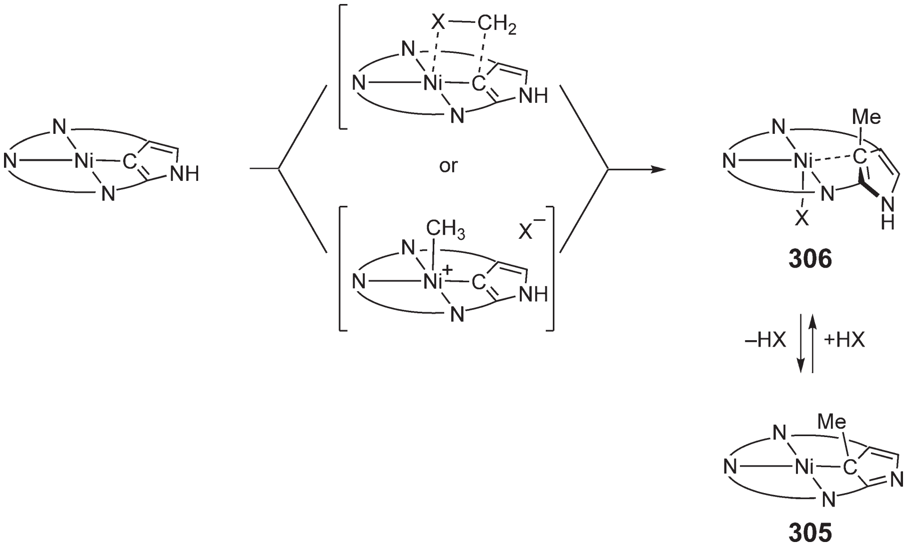


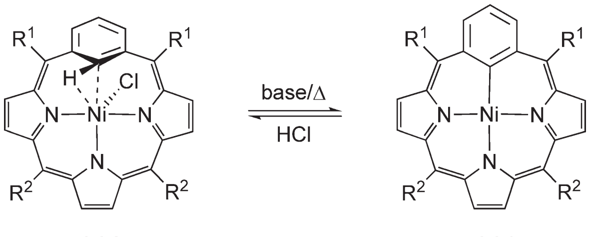
Figure 4



Scheme 93

The alkylated complexes **305–307** exhibit an interesting reactivity. Thus, the external nitrogen atom of **305** has basic character and can be bound by metal centers such as Pt to form large bimetallic assemblies.[440] The chloride analog of the N-methylated complex **307** undergoes halogen exchange with PhLi and LiBu^n, to give thermally unstable, high spin paramagnetic species that have been characterized in solution.[441]

It is interesting to point out the relationship between the structure of compound **306** and that of other π-arene complexes of Pd and Pt involved in M–C bond formation or cleavage processes.[442,443] The ability of macrocyclic ligands to stabilize previously undetected nickel π-arene reactive complexes is further evidenced by the isolation and characterization of compound **308**, which readily undergoes σ-Ni–C bond formation to give **309** (Equation (120)).[428]



308 **309**

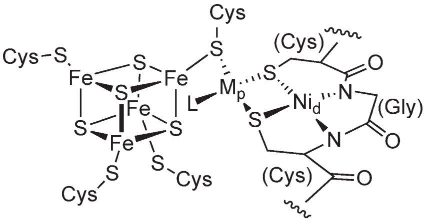
(120)

8.02.8.2 Models of the Carbon Monoxide Dehydrogenase – AcetylCoA Synthase (COD/ACS)

Carbon monoxide dehydrogenase – acetylCoA synthase is an enzyme involved in the fixation of carbon dioxide by anaerobic autotrophic bacteria and archeobacteria.[419,420] The enzyme catalyzes two processes, the reduction of CO_2 to CO, and the synthesis of acetylCoA from CO, coenzyme A, and a methyl group furnished by an iron–sulfur protein (CFeSP) (Equations (121) and (122)). The structure of the active center **310** has been deduced from a combination of spectroscopic results, and was recently confirmed by the resolution of the crystal structure of the enzyme from *Morella Thermoacetica*.[420] It contains three active centers, an Fe_4S_4 cluster and two metal atom sites, called "distal" (M_d) and "proximal" (M_p), respectively. While the distal atom has been identified as nickel, the identity of the proximal has been the subject of some controversy since the site can be occupied by Cu, Zn, or Ni. In spite of this progress, the details of the mechanism of the acetylCoA synthesis are still unknown, although it probably involves the formation of an Ni–CH_3 bond, followed by carbonylation of this entity and the coupling of the resulting acetyl group to the thiol group of CoASH. Recent theoretical work has modeled the active site, and has studied the feasibility of different mechanistic proposals.[444]

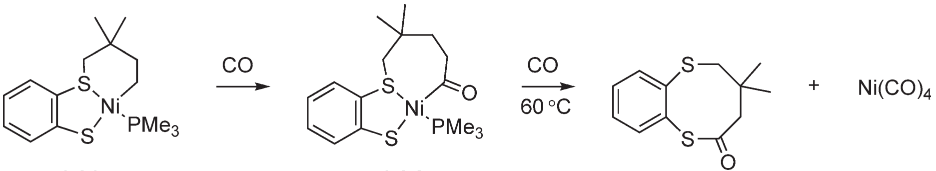
$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \qquad (121)$$

$$CO + CH_3\text{–CFeSP} + CoA \rightleftharpoons CH_3CO\text{–CoA} + CFeSP \qquad (122)$$



310

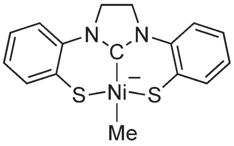
The connection of the COD/ACS with the organometallic chemistry of nickel has prompted the search for model complexes in order to mimic the activity of the enzyme. One of the difficulties associated with this task is that organometallic complexes of Ni supported by sulfur donor ligands are scarce. Two interesting examples of this type of compounds, **311**[216] and **312**,[99] have been reported recently. The final step in the synthesis of acetylCoA has been



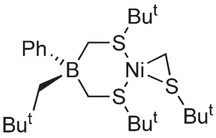
313 **314**

Scheme 94

investigated in different types of model complexes.[147,242] The compounds NiMe(SR)(bipy) readily undergo SR exchange with free thiols and react with CO to give acyl complexes Ni(COMe)(SR), which reductively eliminate the corresponding thioester in the presence of an excess of CO.[118] The metallacyclic thiolate complex **313** illustrates the same process in a sulfur-ligated environment more akin to the active center of the enzyme (Scheme 94).[242]



311



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8.03
Nickel–Carbon π-Bonded Complexes

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8.03.1 Introduction

This chapter reviews reports on organometallic complexes of nickel involving π-bound ligands, that is, complexes featuring carbon-based ligands bonded to one or more nickel atoms through π-bonds. The main theme of the present discussion is synthesis, characterization, and bonding aspects of the compounds, but brief references have been provided in many instances for more extensive physical studies carried out on some complexes or their applications in organic synthesis and catalysis.

The review covers the literature in the period between 1993 and 2005. A number of recently published reviews provide a partial treatment of some of the themes discussed here, including the following topics: benzyne, aryne, and cycloalkyne complexes,[1–6] the use of alkynes in the preparation of tetrathiafulvalenes,[7] nucleophilic attacks involving Ni–allyl complexes,[8,9] organonickel complexes derived from nickelocene,[10] high-spin NiCp complexes[11] and NiCp complexes based on functionalized Cp ligands,[12–15] indenyl complexes of group 10 metals,[16] metal complexes of C_2B_4 carboranes,[17] and metallacarboranes.[18–20]

The chapter is divided into various sections according to the nature and hapticity of the main ligands involved in the complex. Thus, the discussion begins with dihapto ligands and continues through to trihapto, pentahapto, and hexahapto ligands. Each of these sections is further divided into subsections according to specific families of compounds being discussed. In cases where more than one type of π-bound ligand is present in the complex under discussion, priority has been given to the main ancillary ligand, usually the one with the higher hapticity (e.g., Cp vs. olefin or alkyne). By the same rationale, η^4-diene complexes involving conjugated dienes are discussed separately from alkene complexes, but complexes involving non-conjugated dienes are considered as bis(η^2-alkene) complexes and discussed in the section on Ni–alkene complexes. On the other hand, if the alkene or diene moiety is part of an arene ring, the discussion is included in the arene section regardless of hapticity. Similarly, complexes featuring Cp or Ind complexes of various hapticities are still discussed along with the complexes of pentahapto-bound ligands; this is meant to emphasize the existence of variable Ni–ligand bonding modes within this class of complexes. Finally, in most sections, multimetallic complexes have been discussed separately from their monometallic counterparts, but in some instances species bearing more than one metal center have been discussed in the context of monometallic compounds if inclusion of these species flows from or facilitates the discussion.

8.03.2 Nickel Complexes With η^2-Ligands

8.03.2.1 η^2-Alkene Complexes

8.03.2.1.1 General comments

Alkene complexes of nickel have played a central role in the development of organometallic chemistry over the past 50 years. Beginning with the discoveries of olefin oligo- and polymerization reactions, the desire to understand the nature of Ni–olefin interactions and the impact of structural features, characteristics, and bonding modes on these reactions have prompted many investigations on the synthesis, characterization, and reactivities of a large variety of Ni–olefin complexes. A number of mechanistic studies have also addressed the possible formation of Ni–olefin intermediates and their reactivities. These include a recent study on the so-called Ziegler nickel effect in the Ni-catalyzed hydro- and carboalumination reactions,[21] as well as experimental[22,23] and computational[24,25] studies of ethylene polymerization catalyzed by bis(imine)Ni or (aldimine)Ni complexes. Most of these studies have shown that the Ni–olefin bonds are, in general, fairly labile, which helps explain why there are relatively few simple Ni–olefin complexes.

A number of Ni–olefin complexes have also been used as pre-catalysts for organic transformations. Perhaps the Ni–olefin complex most extensively used for this purpose is $Ni(cod)_2$ (cod = 1,5-cyclooctadiene). Some of the most challenging applications of $Ni(cod)_2$ and other analogous complexes in reductive cyclizations have been described in a recent review.[26]

8.03.2.1.2 Theoretical and physical studies

A number of computational studies using the hybrid density functional theory (DFT) methods at the B3LYP level of theory have been used to investigate the energetics of M–ethylene bonds (M = Pt, Pd, Ni) in the complexes $[MCl_n(\text{ethylene})(NH_3)_{3-n}]^{2-n}$ ($n = 1-3$)[27] and $[MR_3(\text{ethylene})]^-$ (R = Cl, C_6F_5).[28] These studies have shown that, in general, the coordinating ability order is: Pt > Pd > Ni. The Ni–ethylene bond strength in the unknown anionic species $[NiCl_3(\text{ethylene})]^-$ is estimated at ca. 6 kcal mol^{-1} compared to ca. 30–45 kcal mol^{-1} for the analogous

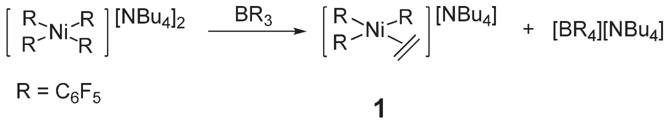
Pt complexes. On the other hand, the strength of the corresponding bond in the unknown complex $[(\text{ethylene})Ni(NH_3)_3]^{+2}$ was found to be much higher (ca. 25 kcal mol^{-1}). As expected, Ni has the weakest π-backbonding interaction of group 10 metals. It is interesting, however, to note that these studies indicate little or no dependence of π-backbonding interaction on the net charge of the complex; indeed, the more stable Ni–ethylene bond is in the cationic tris(ammino) species as opposed to the anionic trichloro one. Finally, the Cl^- ligand was found to exert a stronger *trans*-influence on ethylene than NH_3.

For the complexes $[MR_3(\text{ethylene})]^-$ ($R = Cl, C_6F_5$), a combination of the better π-donor properties of Cl^- and the better π-acceptor properties of $[C_6F_5]^-$ results in a greater degree of π-backbonding in the chloro analogs. More specifically, the π-acceptor ability of the coordinated ethylene follows the trends $Pt > Ni > Pd$ in the C_6F_5 series, and $Pt > Pd > Ni$ in the chloro complexes. Similarly, the σ-acceptor ability of the $[MR_3]^-$ fragment follows the trends $Pt > Ni > Pd$ for the C_6F_5 series, and $Pt > Pd > Ni$ for the chloro complexes. The approximate M–ethylene binding energies (in kcal mol^{-1}) estimated by these studies are 11 (C_6F_5) and 8 (Cl) for Ni, 12 (C_6F_5) and 16 (Cl) for Pd, and 19 (C_6F_5) and 34 (Cl) for Pt. Interestingly, the overall stabilities of these complexes are predicted to follow the trend $Pt >> Ni > Pd$ for both series of complexes; in some cases, however, the experimental studies have indicated that the Pd complexes have greater thermal stabilities.

8.03.2.1.3 Synthetic and reactivity studies

8.03.2.1.3.(i) Nickel–ethylene complexes

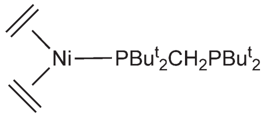
As mentioned above, computational studies have confirmed the generally accepted notion that Ni^{II}–alkene bonds are weaker than the corresponding Pt^{II}–alkene bonds; on the other hand, the energetics of the Pd^{II}–alkene bonds differ only slightly from those of Ni analogs, being stronger or weaker in different compounds. Consistent with these notions, Zeise's salt, $[PtCl_3(C_2H_4)]^-$, has been known for over 150 years (it was the first reported organometallic species isolated in analytically pure form), whereas the Ni analog of this compound has not been prepared and is likely unstable. The Pd analog has been detected as a transient intermediate in solution, but not isolated. A recent report has shown that *all*-organometallic analogs of Zeise's salt can be prepared by replacing the Cl ligands by C_6F_5 ligands.[28] The Pt and Pd derivatives have been prepared, via different routes, isolated, and characterized fully. In contrast, the Ni analog has proved to be more difficult to prepare and isolate. Thus, abstraction of a C_6F_5 ligand from $[Ni(C_6F_5)_4]^{2-}$ under 1 atm of ethylene generates the ethylene complex **1** at −78 °C (Equation (1)); this species is unstable above −50 °C, which limited its characterization to solution NMR spectra (^1H and ^{19}F) recorded at −80 °C.



1

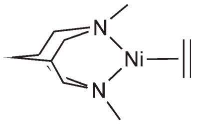
(1)

Ni(0)–ethylene complexes are also quite rare, presumably because of the relatively weak π-accepting nature of ethylene. The lability of Ni(0)–ethylene complexes is still greater when the remaining auxiliary ligands are strongly donor, weak π-acceptor bases such as amines. Moreover, the mismatch between the soft Ni(0)–olefin moiety and the hard amines must result in unfavorable interactions. Nevertheless, trigonal-planar complexes of the type $Ni(\eta^2{-}C_2H_4)_2(L)$ (L = monodentate amines or phosphines) can be prepared by judicious choice of the ligand L and careful control of reaction conditions. Thus, the reaction of $Ni(C_2H_4)_3$ with $Bu^t{}_2PCH_2PBu^t{}_2$ at low temperatures gives a yellow solid identified as $Ni(C_2H_4)_2(\eta^1{-}Bu^t{}_2PCH_2PBu^t{}_2)$, **2**, that has been characterized by crystallography.[29,29a] The NMR spectra of this compound indicate that the rotation of the ethylene ligands about the Ni–ethylene axis is restricted at ca. −80 °C becoming free above −30 °C; the exchange of the P atoms is not fast at −30 °C. The solid-state structure of **2** confirms the monodentate coordination of the phosphine despite the electronic unsaturation of the Ni center, presumably because of the conformational strain of the bidentate mode of bonding.



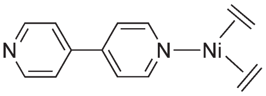
2

The analogous complex Ni(C_2H_4)$_2$(quinuclidine) has also been prepared, and its low-temperature crystal structure shows a long Ni–N bond distance (207 pm).[30] Even lower stabilities are found for complexes having one ethylene and two amine ligands. Thus, although computational studies have suggested that the simplest homolog Ni(η^2-C_2H_4)(NH_3)$_2$ should be thermodynamically stable,[31] many attempts to prepare such compounds with monodentate amines have failed. The situation is similar for complexes incorporating acyclic or monocyclic diamines, but a recent report has shown that the bicyclic diamine *N,N*-dimethyl-3,7-diazabicyclo[3.3.1]nonane (DABN, $C_9H_{18}N_2$) can form Ni(0)–ethylene complexes. Thus, the reaction of this base with Ni(η^2-C_2H_4)$_3$ at low temperatures gives Ni(η^2-C_2H_4)(η^2-DABN) **3**. This complex has been isolated and characterized spectroscopically, but its tendency to decompose above 0 °C has prevented detailed structural characterization.[32] Reactions of this species with CO or cod give Ni(CO)$_4$ or Ni(cod)$_2$, respectively, underlining the lability of both DABN and ethylene. NMR and IR spectra of complex **3** indicate that DABN is a very strong donor: ν(C=C) ~ 1,510 cm^{-1} versus 1,623 cm^{-1} in free ethylene; δ(H of ethylene) ~ 0.27 ppm versus 5.30 ppm in free ethylene. The unique ability of DABN to form Ni(0)–ethylene adducts is attributed to the special arrangement of the donor N atoms that appear to be pre-positioned for coordination to metals.



3

Novel Ni(0)–ethylene compounds featuring a bridging 4,4′-bipyridine ligand have been prepared by reacting this ligand with (cod)$_2$Ni in a reaction mixture saturated with ethylene at −40 °C.[33] The resulting red solid is very susceptible to aerobic oxidation and is thermally unstable unless kept under ethylene at low temperatures. The mono- and dinuclear Ni(0)–ethylene species **4 and 5** co-crystallize in the unit cell of the product. The Ni centers are coordinated by two ethylene molecules and a pyridine moiety in a trigonal-planar arrangement. The average C=C distance of 137 pm in these complexes is only slightly longer than that of free ethylene (134 pm), implying that most of the Ni → ligand π-backbonding is directed at the bipyridine moiety.



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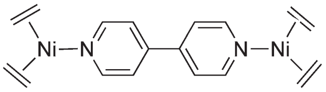
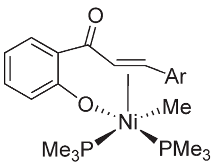


5

8.03.2.1.3.(ii) Monometallic nickel–alkene complexes

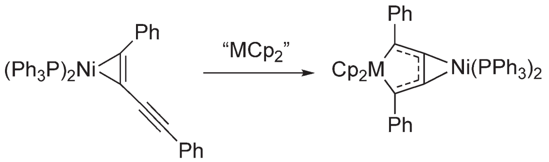
The complex Ni(cod)(dppf) can be prepared by reacting Ni(cod)$_2$ and dppf (dppf = 1,1′-bis(diphenylphosphino)-ferrocene);[34] the preparation of this versatile compound has been the subject of a patent.[35] The recently reported complexes **6** and **7** represent rare examples of electronically saturated, five-coordinate Ni^{II}–olefin species.[36] The solid-state structure of **6** has shown that the Ni(II) center adopts a trigonal-bipyramidal geometry, in which the methyl and phenolato ligands are in the axial positions and the olefin and PMe$_3$ ligands are held at relatively long distances in the equatorial plane (Ni–P ~ 225 ppm; Ni center of C=C moiety ~ 198 ppm). Significantly, the C=C bond is somewhat shorter in this Ni complex relative to the analogous Co complex (139 vs. 145 pm), implying weaker π-backbonding in Ni(II).



6: Ar = Ph
7: Ar = 3,4,5-(OMe)$_3$C$_6$H$_2$

The reaction of $Ni(cod)_2$ with methacrylates in the presence of PCy_3 has provided a route for the formation of Ni{η^2-$CH_2{=}C(Me)COOR\}(PCy_3)_2$, **8**, and Ni{$\eta^2$-$CH_2{=}C(Me)COOR\}_2(PCy_3)$, **9**, the first structurally characterized Ni–methacrylate complexes.[37] Like many Ni(0)–olefin compounds, **8** and **9** are yellow and highly air and moisture sensitive. The crystal structure of **8–Me** showed a significantly lengthened C=C bond (141 pm) and no bonding interaction between the carbonyl moiety and the Ni center. The crystal structure of **9–Me** also showed relatively long C=C distances (ca. 140 pm), no Ni–O interactions, and a head-to-head orientation of the two acrylate ligands with the carbonyl moieties placed close to each other. The presence of two prochiral, geminally substituted methacrylates in **9** leads to the formation of diastereomeric mixtures with the *meso*-isomer being the major component, as determined by NMR.

Heterobimetallic complexes involving group 4 metallocene and Ni(0)–cycloolefin moieties have been prepared from Ni–alkyne complexes. For instance, reacting the butadiyne–Ni(0) complex Ni(η^2-Ph–C≡C–C≡C–Ph)$(PPh_3)_2$, **10**, with MCp_2 precursors (M = Ti and Zr) leads to the species **11**, in which metallacyclopentadienes are coordinated in η^2-fashion to the Ni center (Equation (2)).[38] It is important to note that these complexes are stable with Ph substituents only.

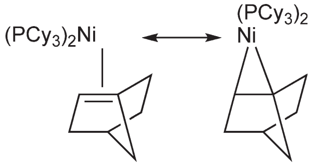


10 **11**

(2)

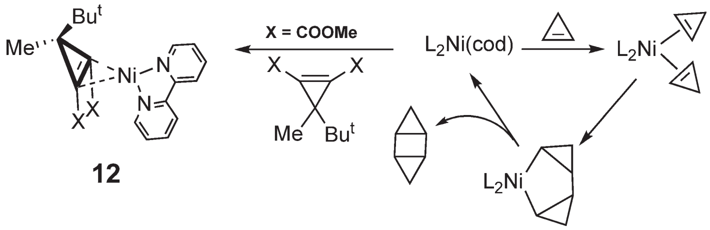
A number of nickel(0) complexes containing a cyclopropene ligand have been prepared and shown to catalyze the oxidative coupling of cyclopropene derivatives to compounds with a cyclobutane core. A recent study of the kinetics of these reactions has led to the isolation of a putative intermediate **12** (Scheme 1), which crystallizes in a trigonal-planar structure.[39] It is interesting to note that the carboxylate substituents are bent out of the coordination plane, while the *t*-Bu group is *endo* with respect to the Ni center; this orientation is presumably favored over the alternative *cis*-disposition of the *t*-Bu and carboxylate substituents, which would engender greater steric repulsions.

An interesting example of a complex featuring an unusual η^2-bound 1-norbornene ligand has been prepared, but electrochemical measurements and solid-state structural data indicate that the Ni–olefin interaction in **13** is more aptly described as metallacyclopropane rather than the Dewar–Chatt extreme of the bonding continuum.[40] For instance, the C–C bond distance for the coordinating moiety is much longer than the theoretical bond length of the double bond located at the bridgehead (145 vs. 136 pm); this is presumably caused by a combination of the ring strain caused by the bridgehead double bond and the strongly π-basic Ni center.



13

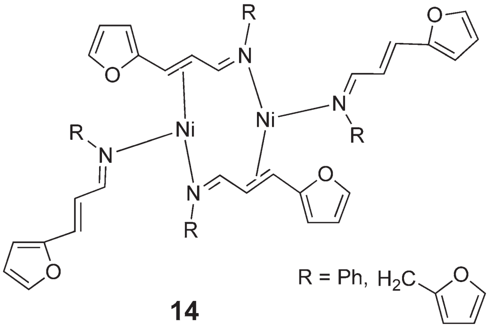
A novel series of Ni–alkene complexes **14–17** has been prepared with 1-aza-1,3-dienes acting as terminal or bridging ligands that coordinate Ni(0) centers in η^2(C,C):η^1(N) fashion.[41] Complexes **14** are very air sensitive, thermally unstable, deep blue compounds that react with PPh_3 to produce the dimeric species **15** (deep red). In contrast, reactions



12

Scheme 1

with propargylic alcohols give 16 and 17 (dark green) that are less sensitive to air and moisture. Solid-state studies have shown that the inner part of these complexes can be described as eight-membered, dinickela–diazaoctadiene rings existing in two conformations; the Ni(0) centers do not interact with each other. These compounds represent unusual species featuring Ni(0) centers surrounded by olefinic, azomethine, and alkyne or phosphine moieties.



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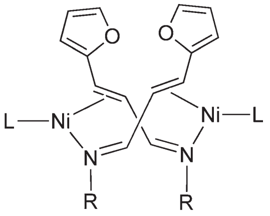
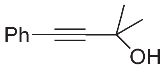


15: L = PPh_3



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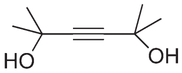
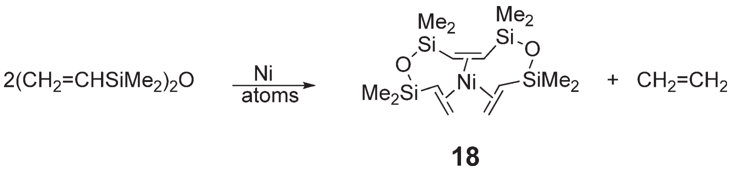


17

Reaction of 2,6-dimethylpyridine with the tris(alkene) dinickel species $[(\eta^2,\eta^2\text{-(1,6-heptadiene)Ni})]_2(\mu,\eta^2,\eta^2\text{-(1,6-heptadiene)})$ gives the intense yellow compound $Ni(\eta^2,\eta^2$-(1,6-heptadiene)(2,6-dimethylpyridine).[42] The solid-state structure of this complex showed that the pyridine is oriented perpendicular to the plane of $Ni(olefin)_2$, implying significant π-backbonding from Ni into the pyridine π^* orbitals. The reaction of this bis(alkene) species with alkynes gives the corresponding bis(alkyne) complexes (*vide infra*).

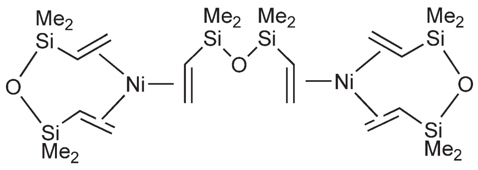
The uncommon Ni(0)–triene compound $Ni^0\{\eta^2,\eta^2,\eta^2\text{-}(CH_2{=}CHSiMe_2OSiMe_2)_2(CH{=}CH)\}$, 18, has been synthesized via a metal-vapor synthesis involving the condensation of electron-beam produced Ni vapor onto a liquid-nitrogen cooled matrix of the diene $(CH_2{=}CHSiMe_2)_2O$ (Equation (3)).[43] It should be noted that metal-vapor syntheses have been used for the preparation of other Ni(0)–alkene complexes such as $Ni^0(\eta^2\text{-}CH_2{=}CHR)_3$ (R = H,[44] Ph[45]), but the uniqueness of the reaction under discussion here is that it appears to be a rare example of an Ni-promoted olefin metathesis reaction! The crystal structure of the orange-red, air and moisture sensitive 18 shows that the three alkene units are arranged in a planar fashion around Ni, their midpoints defining a trigonal-planar geometry; the central alkene unit adopts a *cis*-(*Z*)-configuration. Solution NMR studies of 18 have indicated, however, that a slow chemical exchange process involving the dissociation of an alkene ligand leads to the formation of other conformers in which the central alkene unit adopts a *trans*-(*E*)-configuration.[46]



18

(3)

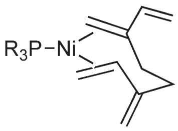
The homoleptic olefin–Ni(0) dimer 19, the Ni analog of Karstedt's catalyst, can be prepared by reacting the bis(alkene) ligand $(CH_2{=}CHSiMe_2)_2O$ with $Ni(cod)_2$[47] or Ni(*t,t,t*-CDT)[48] at ambient temperature (*t,t,t*-CDT = *trans,trans,trans*-cyclodedeca-1,5,9-triene), or by metal-vapor synthesis techniques.[49] Complex 19 is an efficient catalyst for the addition of $SiH(OEt)_3$ and $SiHMe_2Ph$ to terminal alkenes such as styrene, vinylsilanes, and vinylsiloxanes, and for alkene coupling reactions.[47] The catalytic reactivities of 19 likely arise from the lability of the vinyl moieties. The fluxional processes arising from this phenomenon have been studied and seem to indicate that intramolecular dissociation/re-association processes are at work.[46] The lability of the vinyl moieties also allows the preparation of the monomeric phosphine derivatives $Ni\{\eta^2,\eta^2\text{-}(CH_2{=}CHSiMe_2)_2O\}(PR_3)$, **20**, of which the PPh_3 and PCy_3 derivatives have been characterized by X-ray diffraction studies.[50]



19

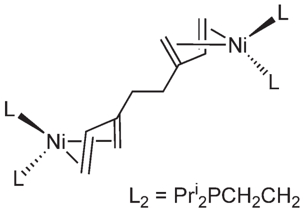
8.03.2.1.3.(iii) Monometallic nickel–diene complexes

A series of Ni(0)–diene compounds has been prepared by reacting Ni(cod)$_2$ or Ni(*t*,*t*,*t*-CDT) with the tetraene ligand 2,6-dimethylene-1,7-octadiene (DMOD). These homoleptic Ni^0(diene)$_2$ species are thermally unstable, but derivatives bearing one or two *P*-donor ligands have been prepared and isolated as yellow solids.[51] Among the 16-electron species **21**, the phosphite derivative displays greater thermal stability relative to its trialkylphosphine analogs, whereas the 18-electron bis(phosphine) dimer **22** is isolated as a red solid that melts at 140 °C without decomposition. The solid-state structure of the phosphite derivative of **21** was established by X-ray crystallography and shows that the DMOD ligand coordinates the Ni(0) center in an η^2,η^2-manner, thus giving a formally 16-electron species. The Ni(0) center adopts a trigonal geometry, while the coordinated 1,6-heptadiene fragment of the DMOD ligand adopts a chair conformation. NMR experiments have indicated that the solid-state structure is maintained in cold solutions, but the structure is found to be fluxional at room temperature due to the pairwise exchange of the vinyl and methylene groups. Structural analysis of complex **22** has shown it to be a dimer featuring two tetrahedral, 18-electron η^4-DMOD–NiL$_2$ units. As expected, the Ni–olefin distances (measured from the midpoint of the C=C bond) are longer in the four-coordinate species (ca. 199 vs. 190 ppm). Interestingly, changing the length of the chain linking the two *i*-Pr$_2$P moieties from two to three or one appears to result in the formation of monomeric (deep violet, **23**) or dimeric (yellow, **24**) tricoordinate species, respectively, but the latter structures have not been confirmed by X-ray diffraction studies.



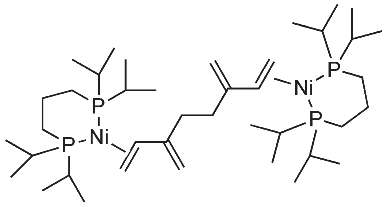
$\mathrm{R = Pr^i, Cy, OC_6H_4}$-*o*-Ph

21

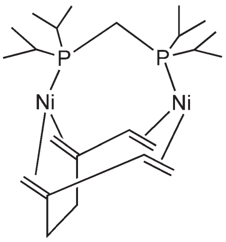


$\mathrm{L_2 = Pr^i{}_2PCH_2CH_2PPr^i{}_2}$

22



23



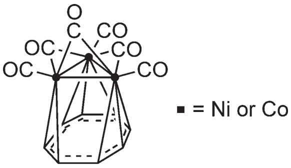
24

A number of complexes bearing diene-type arene ligands have been reported and will be discussed in the Ni–arene complexes section.

8.03.2.1.3.(iv) Polymetallic (cluster) Ni–alkene complexes

The Ni^0(ethylene)(η^2-DABN) complex **3** discussed above can serve as a precursor for the 1,3-butadiene complexes Ni(η^2-butadiene)$_2$(η^2-DABN) and [Ni(η^2-butadiene)(η^2-DABN)]$_2$(μ,η^2,η^2-butadiene) that have been characterized by NMR and mass spectroscopy;[32] the latter compound is analogous to the bipyridine complex [Ni(η^2-butadiene)(bipy)]$_2$(μ,η^2,η^2-butadiene).

Given the involvement of Ni species in heterogeneously catalyzed hydrocarbon re-forming processes, the study of Ni clusters incorporating well-characterized unsaturated, cyclic hydrocarbons can shed light on the manner in which hydrocarbon substrates can adsorb onto an array of metal atoms arranged on a single crystal surface. One such study has shown that refluxing the tetranuclear cluster $NiCo_3(CO)_9Cp$ and cyclooctatetraene (cot, C_8H_8) in toluene gives the new cluster **25**, which is isoelectronic with the anionic tricobalt analog $[Co_3(CO)_6(\mu_3\text{-cot})]^-$.[52] The solid-state structure of this diamagnetic cluster compound was established in a single crystal X-ray diffraction study, and showed that a non-planar cot ligand coordinates a Co_2Ni triangle facially in an η^2:η^3:η^3-fashion; unfortunately, however, the diffraction data did not allow an unambiguous identification of the individual metal atoms (Ni or Co). In contrast, the analogous reaction with the bis(silyl) derivative of cot gave the corresponding product, for which the positions of the Ni and Co atoms could be assigned.[53] In solution, all of the CO ligands and cot display a fluxional behavior, resulting in only one ^{13}C signal for the six CO ligands (at ca. 185 ppm) plus one ^{13}C signal (at ca. 72 ppm) and one ^{1}H signal (at ca. 3.4 ppm) for the cot.



25

8.03.2.2 Nickel–Allene Complexes

Very few Ni–allene complexes have been isolated and characterized, but many such species have been postulated as key intermediates in organic transformations catalyzed by Ni precursors. Notable examples of such applications include the cyclization of two arynes and one allene to give 10-methylene-9,1-dihydrophenanthrenes,[54] the one-pot coupling of allenes with aldehydes and silanes to give allyl silyl ethers,[55] selective [3+2]-cyclization of allenes and Fischer carbenes,[56] regio- and stereoselective, three-component assembly of allenes with aryl iodides and alkenylzirconium reagents,[57] and regio- and chemoselective [2+2+2]-cycloaddition of electron-deficient diynes with allenes to polysubstituted benzene derivatives.[58]

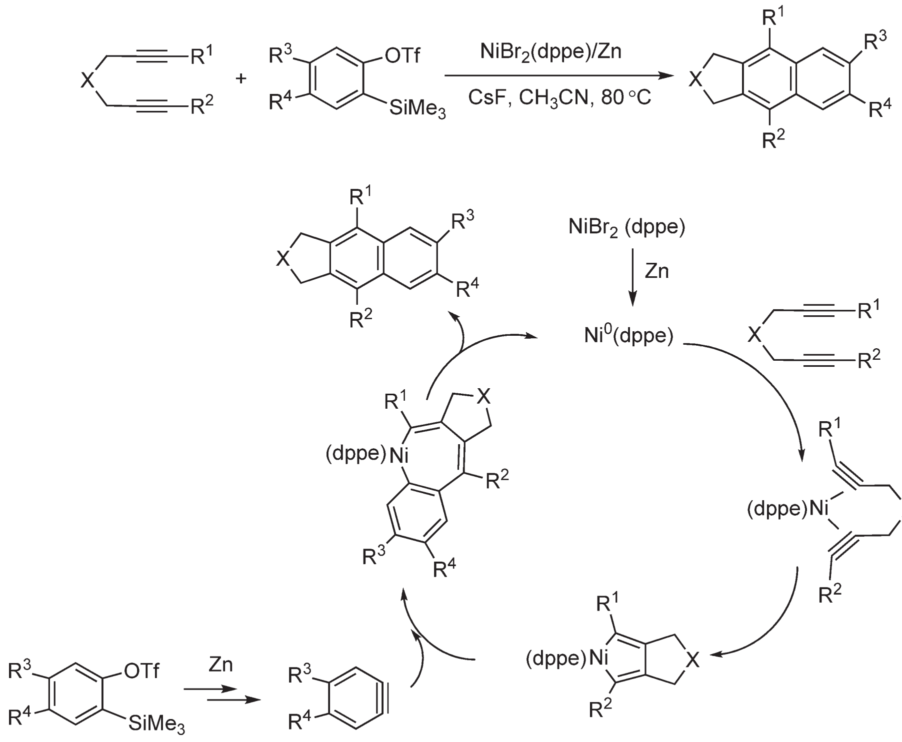
8.03.2.3 Nickel–Alkyne Complexes

8.03.2.3.1 General comments

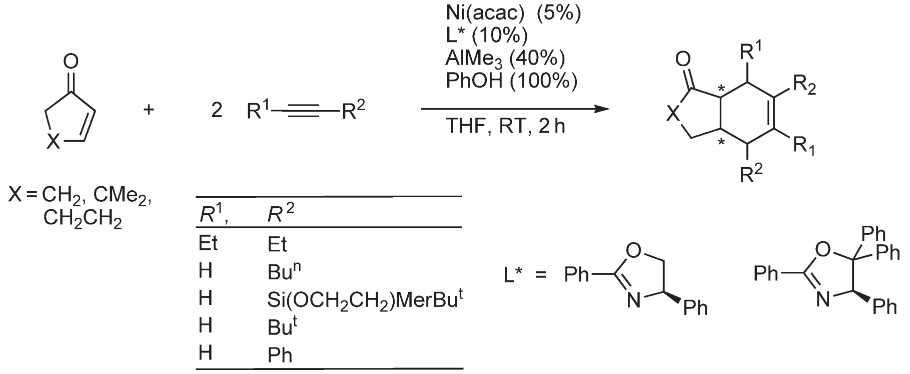
Ni–alkyne bonding consists of contributions from both the η^2,π- and σ,diyl tautomers. This bonding picture helps visualize the insertion reactions with alkynes, alkenes, and CO that result in the formation of metallacycles. Thanks to such insertion reactions, Ni–alkyne species are active intermediates in a number of catalytic applications such as alkyne oligomerization, carbonylation, and insertion of heterocumulenes such as CS_2 and CO_2. For example, a recent example of a CO_2-fixation reaction involved the stoichiometric, alkylative or arylative carboxylation of alkynes to give α,β- and β,β'-unsaturated carboxylic acids.[59] Ni(0)–alkyne complexes have also been used as pre-catalysts in the addition of hydrosilanes to alkynes. In most cases, monoalkynes react to give the products of *cis*-addition, whereas diynes produce enynes (1,2-addition), allenes (1,4-addition), or 1,3-butadienes (1,2,3,4-addition).[60]

Cyclization of alkynes also involves nickel–alkyne intermediates, and bis(alkyne)nickel species have been proposed as intermediates in the catalytic cyclization of diynes with *in situ* generated benzynes to give naphthalene derivatives, as shown in Scheme 2.[61] A related, intermolecular [2+2+2]-cycloaddition of an alkene and two alkynes is also catalyzed by *in situ* generated Ni(0) species; the use of chiral, monodentate oxazoline ligands renders this process enantioselective (Scheme 3).[62]

In situ generated, Ni(0)–alkyne complexes are also involved in Ni-catalyzed head-to-head dimerization of terminal alkynes (Equation (4)).[63] In these reactions, the *in situ* generated Ni–(terminal alkyne) intermediates are thought to react by oxidative addition of the C_{sp}–H bond to produce Ni^{II}(hydrido)(σ-alkynyl) species; the latter then insert a free alkyne into the Ni–H moiety to produce an (alkenyl)(alkynyl) intermediate, which reductively eliminates to give enynes and regenerate the Ni(0) catalyst.

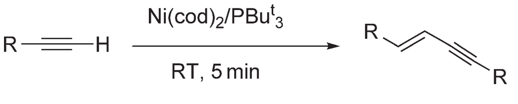


Scheme 2



R^1,	R^2
Et	Et
H	Bu^n
H	$Si(OCH_2CH_2)MerBu^t$
H	Bu^t
H	Ph

Scheme 3



(4)

8.03.2.3.2 Theoretical and physical studies

A computational study has been carried out on the model complexes $Ni_2(HC{\equiv}CH)_2(NH_3)_2$, $Ni_2(HC{\equiv}CH)_3$, $Ni_3(HC{\equiv}CH)_4$, and $(CpNi)_2(\mu\text{-}HC{\equiv}CH)$ in an effort to describe the Ni–alkyne bonding in homoleptic $Ni_n(alkyne)_{n+1}$ complexes.[64] The natural bond order population analysis carried out by DFT methods has shown that dinuclear Ni(0)–alkyne complexes are stabilized by the delocalization of electron density from the filled 3*d*-orbitals of one Ni into empty 4*s*-orbitals of the other. The strength of this $Ni(d^{10})$–$Ni(d^{10})$ interaction varies among the models studied (ca. 26–66 kJ mol^{-1}) becoming weaker upon formation of additional bridging alkynes.

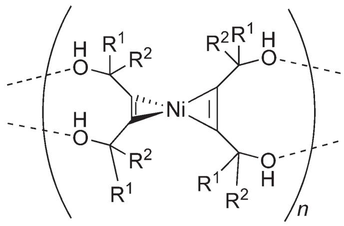
8.03.2.3.3 Synthetic and reactivity studies

8.03.2.3.3.(i) Nickel–ethyne (acetylene) complexes

Very few Ni–ethyne complexes have been reported. One such compound has been prepared by reacting the $Ni^0(C_2H_4)(\eta^2\text{-DABN})$ (complex **3** discussed above) with ethyne to give $Ni^0(\eta^2\text{-}C_2H_2)(\eta^2\text{-DABN})$, which decomposes above −30 °C in solid and above −60 °C in solution.[32] The strongly donor character of DABN is reflected in the unusually weak $\nu(C{\equiv}C)$ peak in this compound (1,560 cm^{-1}) relative to free acetylene (1,974 cm^{-1}) or in $Ni(\eta^2\text{-}C_2H_2)(PPh_3)_2$ (1,630 cm^{-1}), as well as the unusually downfield shifts of the acetylenic H and C nuclei, respectively, relative to acetylene: 4.65 ppm versus 2.40ppm; ca. 119 ppm versus 72 ppm.

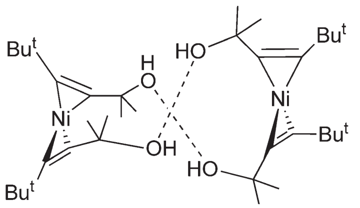
8.03.2.3.3.(ii) Monometallic nickel–alkyne complexes

A number of homoleptic π-alkyne complexes have been prepared from the reaction of a variety of propargylic alcohols with Ni(*t,t,t*-CDT) or $[Ni(cot)]_2$. Thus, the reactions of Ni(*t,t,t*-CDT) with propargylic diols lead to a number of yellow, extremely air sensitive bis(alkyne) complexes **26** in which the Ni(0) center adopts a tetrahedral geometry.[65] The $\nu(C{\equiv}C)$ values are in the range 1,880–1904 cm^{-1}, indicating a substantial degree of π-backbonding. X-ray diffraction analysis of one of the derivatives (**26**; R^1, R^2 = Et, Et) has shown that intermolecular hydrogen bonds between the OH moieties of adjacent molecules form a polymeric supramolecular structure; the $Ni–C_{sp}$ and $C_{sp}–C_{sp}$ bond lengths are ca. 187 and 126 pm, respectively. The analogous reaction with a propargylic alcohol gives the complex **27** that exists as a dimer in the solid state, thanks to intermolecular (but not intramolecular) hydrogen bonds. That the solid-state structures of this class of compounds are governed by the crystallization conditions is indicated by the observation that when the crystallization is carried out at −78 °C, the trimeric $Ni_3(alkyne)_4$, **28**, is obtained.[66] The central Ni atom in **28** is coordinated by two bridging alkyne moieties, whereas each terminal Ni atom binds one bridging and one terminal alkyne moiety. As expected, the terminal C≡C moieties show greater bond order relative to their bridging counterparts, this difference being reflected both in the respective bond lengths (125 vs. 132 pm) and IR frequencies (1,887 vs. 1,638 cm^{-1}). Altogether, there are 12 Ni–C bonds (ca. 188–197 pm), two Ni–Ni bonds (256 pm; Ni–Ni–Ni angle is 118°), and three intramolecular hydrogen bonds in each molecule. In addition, two intermolecular hydrogen bonds lead to a rope-like polymeric superstructure. Another derivative of **28** (R^1 = $SiMe_3$) has been shown to have a similar structure.[67]

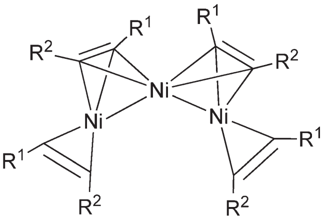


R^1, R^2 = Et, Et;
Me, Et; Me, Pr; c-$(CH_2)_5$; Me, Bu^i

26



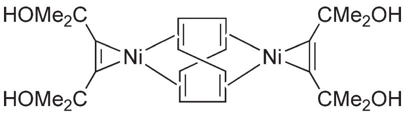
27



R^1 = Bu^t, $SiMe_3$
R^2 = CMe_2OH

28

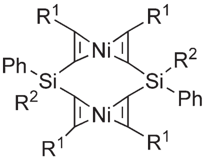
The reaction of $[Ni(cot)]_2$ with 2,5-dimethylhex-3-yne-2,5-diol gave the mixed ligand species **29** in which the cot ligand bridges the two Ni(alkyne) fragments.[67] The Ni–C bonds in this orange-red compound are much shorter with the alkyne moieties relative to the alkene ligands (188 vs. 209 pm), implying more effective $Ni–C_{sp}$ versus $Ni–C_{sp^2}$ interactions. The crystal lattice in **29** is dominated by exclusively intermolecular hydrogen bonds between the alkyne moieties (two from each alkyne, eight from each molecule) leading to a polymeric supramolecular structure. For other complexes bearing propargylic ligands, see 16 and 17.



29

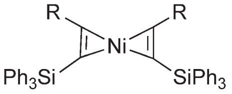
Reacting 26 with the bidentate ligands TMEDA and cod leads to the formation of the binuclear species [(η^2-alkyne)Ni(μ-alkyne)Ni(η^2,*N*,*N'*-TMEDA)], **30**, and the mononuclear compound [Ni(η^2-alkyne)(η^2-cod)], **31**, respectively (alkyne = (μ-(OH)$Me_2C{\equiv}CMe_2$(OH))).[68] These compounds crystallize in a double-stranded form **30** or a polymeric chain **31**. Reaction of 26 with PPh_3 has allowed the preparation of the mononuclear species [Ni(η^2-alkyne)$(PPh_3)_2$], **32**, which forms a dimeric crystal structure, thanks to the hydrogen bonds between the OH moieties and an acetonitrile solvate.

Similar reactions between Ni(CDT) and the silyl-substituted di- or trialkynes $SiPh_2(C{\equiv}C–R)_2$ (R = Bu^t or $SiMe_3$) and $SiPh(C{\equiv}C–Bu^t)_3$ have led to the preparation of the homoleptic Ni(0)–alkyne dimers whose solid-state structures are not influenced by the intermolecular O–H interactions, as shown in 33.[69] The analogous reactions between $Ph_3Si–C{\equiv}C–Bu^t$ and $Ni(cod)_2$ or Ni(CDT) give the monomeric compounds 34 and 35.



R^1 = Bu^t, $SiMe_3$; R^2 = Ph
R^1 = R^2 = CC–Bu^t

33



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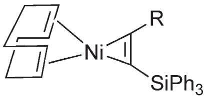
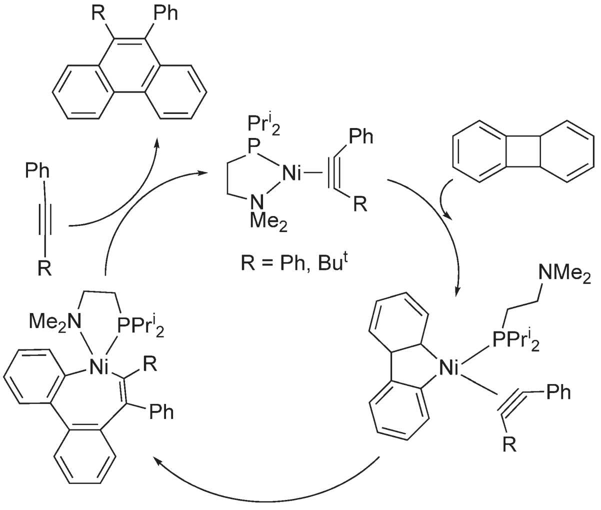


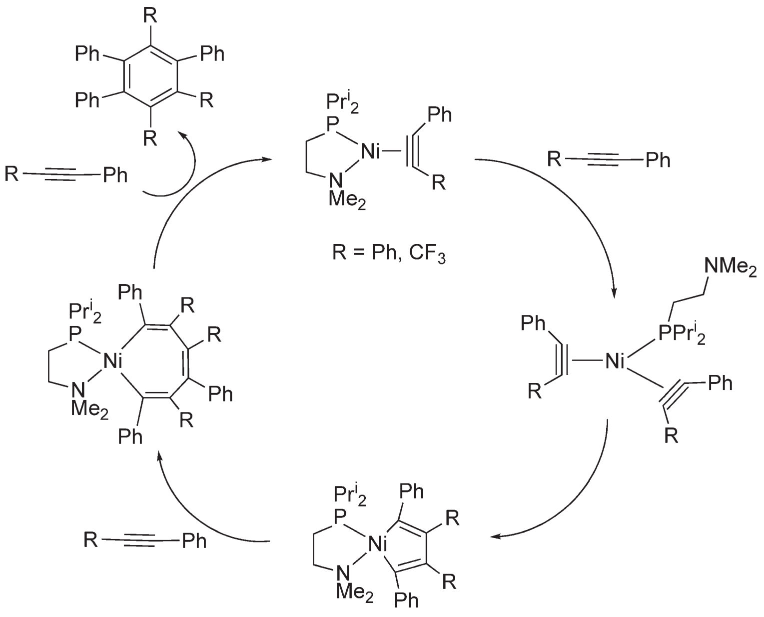
35

The reactions of $Ni(cod)_2$ with R–C≡C–Ph in the presence of the hemilabile ligand $Pr^i_2P(CH_2)_2NMe_2$ lead to the 18-electron, (π-alkyne)–Ni(0) complexes Ni(η^2-R–C≡C–Ph)(κ^P, κ^N-$Pr^i_2P(CH_2)_2NMe_2$), **36** (R = Ph) and *cis*- and *trans*-**37** (R = Bu^t, CF_3).[70] The analogous reaction with the diyne Ph–C≡C–C≡C–Ph gave the dimeric species $[(Pr^i_2P(CH_2)_2NMe_2)Ni]_2$($\mu$,$\eta^2$,$\eta^2$-Ph–C≡C–C≡C–Ph), **38**. The solid-state structures of **36** and *cis*-**37** (R = CF_3) showed that the alkyne moiety is in the P/Ni/N plane. The Ni–C bonds are somewhat non-symmetrical in **36** (ca. 185 vs. 190 pm), presumably because of the unequal *trans*-influences of the phosphine and amine moieties ($PR_3 > NR_3$). On the other hand, fairly symmetrical Ni–C bonds were observed in the CF_3 derivative (ca. 186 and 187 pm). The alkyne substituents are bent back significantly (C_{sp}–C_{sp}–Ph angles ca. 142–145°, C_{sp}–C_{sp}–CF_3 angle of ca. 139°) and the C_{sp}–C_{sp} distances of ca. 129 pm are much longer than the corresponding distance of ca. 120 pm in the free alkynes.

Complexes **36** and **37** (R = Bu^t) are active catalysts for the insertion of R–C≡C–Ph into biphenylene to form 9,10-disubstituted phenanthrenes (Scheme 4). Significantly, no cyclotrimerization of the alkyne was observed as long as biphenylene was present, but in its absence hexaphenylbenzene was produced from PhC≡CPh at a slow rate (ca. 0.4 turnover/day). On the other hand, the CF_3 derivative did not promote the formation of phenanthrenes, leading instead to the formation of cyclic trimers (Scheme 5). The proposed mechanism for the insertion of alkynes into biphenylene involves the dissociation of the Ni–NMe_2 moiety to allow the coordination of the incoming biphenylene



Scheme 4



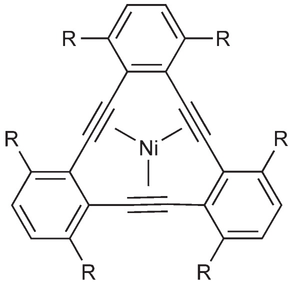
Scheme 5

substrate; consistent with this picture, the catalytic insertion reaction is much more sluggish with the diphosphine analogs of **36** in which the dissociation is slower.[71]

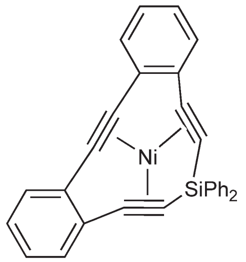
A study on the insertion reactivities of similar π-alkyne complexes bearing $Me_3Si–C{\equiv}C–SiMe_3$ and the diphosphine bis(di-*iso*-propylphosphino)ethane (dippe) has led to unexpected products, thus underlining the important role of the alkyne substituents and the nature of the auxiliary ligand.[72] The products and proposed mechanistic details for their formation are shown in Scheme 6.

Reaction of some alkynes with Ni(η^2,η^2-(1,6-heptadiene)(2,6-dimethylpyridine) leads to the displacement of the olefin ligands and the formation of the red bis(alkyne) complexes, of which Ni(η^2-Ph–C≡C–SiMe$_3$)$_2$(2,6-dimethylpyridine) **39** and [(2,6-dimethylpyridine)Ni]$_2$(μ,η^2,η^2-Me$_3$Si–C≡C–SiMe$_3$)$_2$ **40** have been isolated and characterized.[42] In contrast, the corresponding reaction with acetylene led to the formation of polyacetylene. Unlike many of their homologs that are unstable above −20 °C, these complexes are relatively stable solids up to 49 and 124 °C, respectively. The ν(C≡C) values for the alkyne moieties in both the monomer (1,810 cm^{-1} vs. 2,160 cm^{-1} for free Ph–C≡C–SiMe$_3$) and the dimer (1,850 and 1,890 cm^{-1} vs. 2,068 cm^{-1} for free Me$_3$Si–C≡C–SiMe$_3$) indicate significant π-backbonding into alkyne π^* orbitals. The C≡C distance is ca. 126 pm in the monomeric complex. The diyne complexes Ni(η^2,η^2-(HC≡C(CH$_2$)$_3$C≡CH)(PR$_3$) **41** have been prepared by reacting 1,6-heptadiyne with the bis(olefin) compound Ni(η^2,η^2-(CH$_2$=CHCH$_2$)$_2$O)(PR$_3$).[73]

A series of Ni(0) complexes bearing cyclic triynes 42, and 43 have been reported.[74,75] The planar conformation of the triyne allows an efficient Ni–alkyne interaction. Interestingly, the alkyne moieties bearing the silyl substituents adopt a *trans*-geometry rather than the usual *cis*-geometry dictated by the Dewar–Chatt–Duncanson model for σ-bonding/π-backbonding.



42: R = H, OMe



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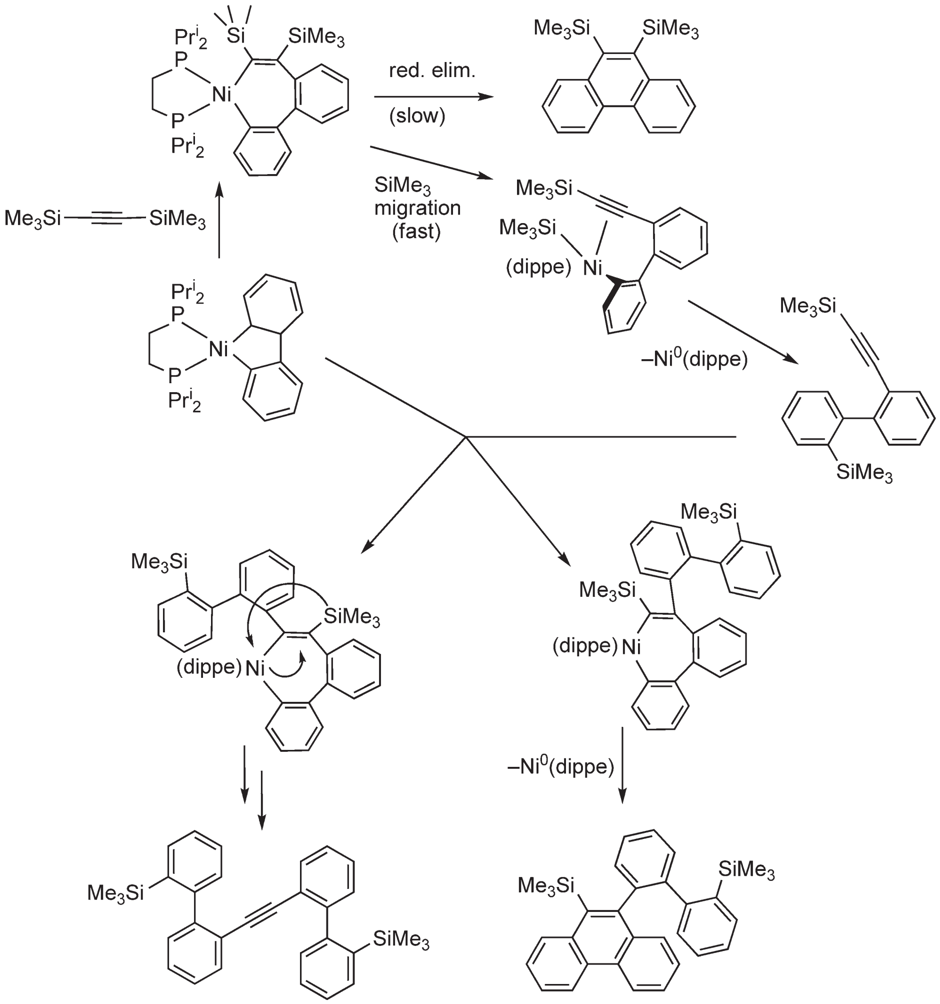
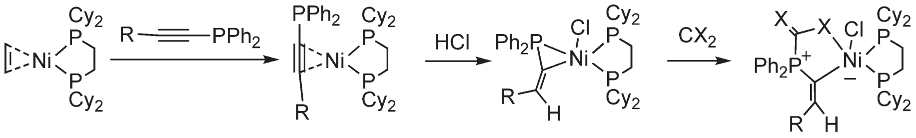


Scheme 6



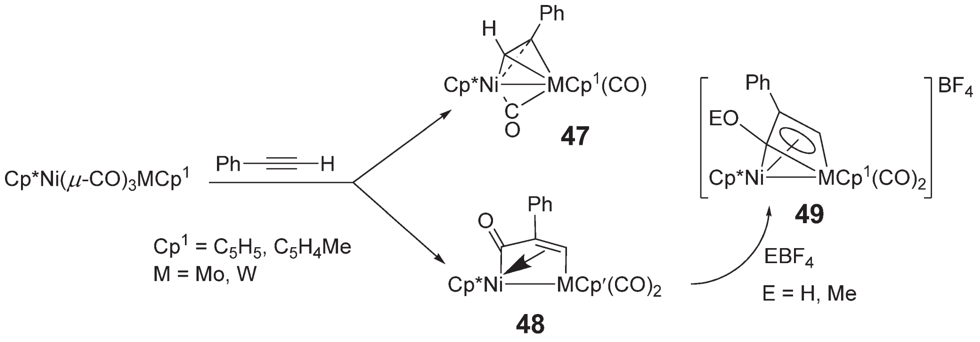
44 **45** **46**

Scheme 7

The Ni(0)–alkynylphosphine complexes **44** featuring the unusual coordination of the alkyne moiety in preference over the phosphine moiety have been reported recently (Scheme 7).[76] A rare opportunity to study alkyne insertion reactions was presented by the reaction of **44** with HCl, which gives the Ni^{II} η^2-vinyl complexes **45**. The Ni–P bond in **45** undergoes another insertion by CO_2 or CS_2 to give five-coordinate, zwitterionic complexes **46**.

8.03.2.3.3.(iii) Multimetallic Ni–alkyne complexes

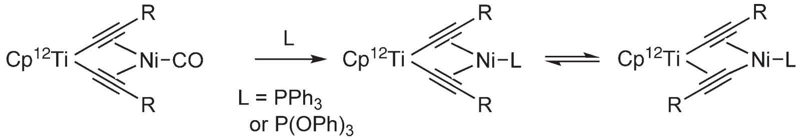
A series of dimetallic species featuring μ-η^2:η^2-alkyne moieties have been prepared by reacting $Cp^*Ni(\mu\text{-}CO)_3MCp$ ($M = Mo, W$) with phenylacetylene to produce the compounds **47** and the dimetallacyclopentenones **48**. The latter reacts with electrophiles to generate **49**, featuring a metallacyclobutadiene that is η^4-coordinated to the Ni center, as shown in Scheme 8.[77]



Scheme 8

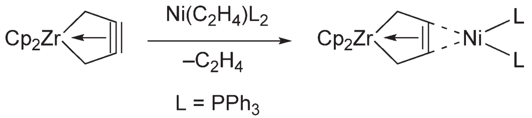
A number of heterobimetallic complexes have been prepared in which one or more metal–alkynyl moieties, $L_nM–C{\equiv}C–R$, serve as π-alkyne ligands to nickel. This family of complexes is often referred to as π-tweezer compounds. Thus, reacting $Ni(CO)_4$ with $Ti(Cp^1)_2(CC–R)_2$ (Cp^1 = C_5H_5 or $C_5H_4(SiMe_3)$; R = Ph, Bu^t) gives $Ti(Cp^1)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C–R)_2Ni(CO)$, **50**; the bis(alkynyl)Ti moiety in **50** acts as a chelating, bis(alkyne) ligand for Ni, as shown in Scheme 9.[78–80] Despite the greater Ni → CO backbonding in **50** (ν(CO) = 1,990–1,995 cm^{-1}) relative to $Ni(CO)_4$ (ν(CO) = 2,052 cm^{-1}), the CO moiety in **50** is displaced readily by phosphites or PPh_3 to give **51**.[81] Closely related Hf complexes have also been reported.[82] Structural characterization of two derivatives of **51** revealed that the coordination geometry around Ti and Ni is pseudo-tetrahedral (C_α–Ti–$C_{\alpha'}$ = 89°) and trigonal planar, respectively. The Ni–C distances in the solid state are non-symmetric, Ni–C_α being shorter than Ni–C_β. Some derivatives of **51** appear to undergo a dynamic exchange process in solution that transfers one of the alkynyl groups from Ti to Ni, giving $(C_p{}^1)_2Ti(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C–R)Ni(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C–R)(L)$, **52**. Similar complexes have also been obtained from the reaction of the metallocenes $TiCp_2(\eta^2\text{-}SiMe_3–C{\equiv}C–SiMe_3)$ and $ZrCp_2(\eta^2\text{-}SiMe_3–C{\equiv}C–SiMe_3)(THF)$ with $Ni(\eta^2\text{-}SiMe_3–C{\equiv}C–C{\equiv}C–SiMe_3)(PPh_3)_2$. Cleavage of the C_{sp}–C_{sp} single bond in the latter species gives $(\eta^5\text{-}C_5H_5)_2M(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C–R)Ni(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C–R)(PPh_3)$ (M = Ti, Zr). In contrast, the reaction with $Ni(\eta^2\text{-}Ph–C{\equiv}C–C{\equiv}C–SiMe_3)(PPh_3)_2$ did not result in C–C bond cleavage and transferred the diyne to the metallocene to give a "zigzag" butadiyne complex.[83,38]

Heterobimetallic complexes involving zirconocene and Ni(0)–alkyne moieties have been prepared by reacting the zirconacyclopentyne precursor with $Ni(ethylene)L_2$, as shown in Scheme 10.[84] The reduced triple-bond character of the cycloalkyne moiety in $Cp_2Zr[\mu\text{-}(\eta^4\text{-}H_2CCCCH_2)]NiL_2$, **53**, is evident from the following spectroscopic and structural data: (i) the ν(C≡C) IR absorption frequencies in **53** (1,655 and 1,626 cm^{-1} for PPh_3 and PCy_3 derivatives, respectively) are significantly weaker than the corresponding value of 2,018 cm^{-1} in the zirconacyclopentyne precursor, (ii) the ^{13}C NMR chemical shifts for the alkyne carbon nuclei move downfield upon complexation (ca. 114 and 117 ppm vs. 103 ppm), (iii) the C–C distance for the alkyne moiety lengthens upon coordination to Ni (ca. 130 pm in **53** vs. ca. 124 pm).



50 **51** **52**

Scheme 9



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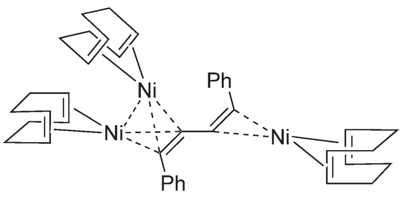
Scheme 10

A series of tri- and tetranickel diyne complexes have been prepared by reacting 1,4-diphenyl-1,3-butadiyne and 1,4-bis(trimethylsilyl)-1,3-butadiyne with Ni(cod)$_2$. The trinickel complexes $[\mathrm{Ni(cod)}]_3(\eta^2{:}\mu,\eta^2,\eta^2\text{-RC}{\equiv}\text{C–C}{\equiv}\text{CR})$, **54**, were obtained when these reactions were carried out for 2–4 h only.[85,86] One of the Ni centers has a distorted trigonal geometry with three π-bound ligands, whereas the other two Ni centers adopt a distorted tetrahedral geometry with three π-bound ligands and a weak Ni–Ni bond (ca. 266 pm). The C_{sp}–C_{sp} acetylenic bond distance is longer in the μ,η^2,η^2-bound alkyne moiety (ca. 134 vs. 126 pm), indicating much greater π-backbonding from the two Ni centers to the bridging alkyne moiety. When the reaction between Ni(cod)$_2$ and 1,4-diphenyl-1,3-butadiyne was allowed to proceed for 18 h, the tetranickel species $\mathrm{Ni_4(cod)_4}(\mu{:}\eta^2,\eta^2;\mu{:}\eta^2,\eta^2\text{-PhC}{\equiv}\text{C–C}{\equiv}\text{CPh})$, **55**, was obtained in which each alkyne moiety bridges two Ni(cod) fragments fairly symmetrically, and all diyne *sp*-carbons are co-planar.[87] The relatively long C_{sp}–C_{sp} distances of ca. 135 pm and the very weak ν(C≡C) frequencies of ca. 1,780 and 1,590 cm^{-1} indicate strong π-backbonding from Ni to the alkyne moieties. In contrast, the C_{sp^2}–C_{sp^2} distances in the cod ligands are quite unchanged relative to free cod. All four Ni centers adopt a distorted tetrahedral geometry with three coordination sites occupied by the three π-bound ligands and one site involving a weak Ni–Ni bond (ca. 266 pm). Interestingly, the reaction of **55** with 1,1′-bis(diphenylphosphinomethane) (dppm) led to the cleavage of the central C_{sp}–C_{sp} single bond and formed the mixed-valence trinickel complex $\mathrm{Ni_3(C{\equiv}C\text{–}Ph)_2(\mu\text{-dppm})_3}$, **56**.[88] The dimeric complex $[(\mathrm{Pr^i{}_2P(CH_2)_2NMe_2})\mathrm{Ni}]_2(\mu,\eta^2,\eta^2\text{-Ph–C}{\equiv}\text{C–C}{\equiv}\text{C–Ph})$, **57**, was obtained by the reaction of Ni(cod)$_2$ with the diyne Ph–C≡C–C≡C–Ph in the presence of $\mathrm{Pr^i{}_2P(CH_2)_2NMe_2}$.[89]



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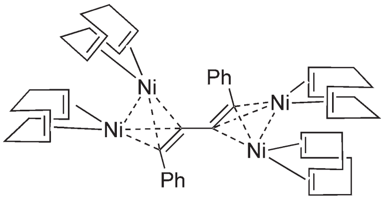

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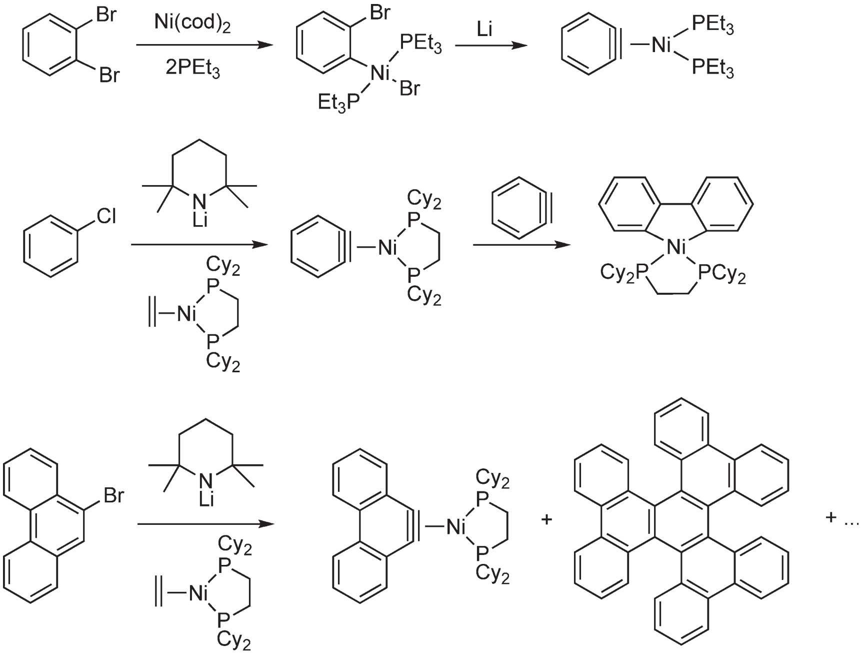
8.03.2.3.3.(iv) Ni–cycloalkyne complexes

By far, the most commonly studied species among Ni–cycloalkynes are the complexes of benzynes or arynes. The synthesis of Ni–benzyne complexes is typified by the reaction of *ortho*-dibromobenzene with Ni(cod)$_2$/PEt$_3$, followed by reaction of the resulting *ortho*-halophenyl moiety with Li, as shown in Scheme 11.[90] The 2,3-naphthalyne

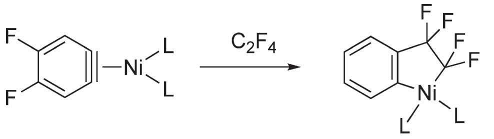


Scheme 11

complexes have also been prepared similarly by reacting $Ni^{II}Br(3\text{-bromonaphthyl})L_2$ with Na/Hg.[91] Another synthetic method involves the dehydrohalogenation of haloarenes in the presence of Ni(0) sources bearing labile ligands such as ethylene; the reaction is carried out at low temperatures to avoid the competing oxidative addition to give the Ni–aryl species (Scheme 11).[92] One side-reaction encountered frequently in this approach is the single or double insertion of *in situ* generated arynes into the initial Ni–aryne species. In an interesting example of this type of side-reaction, hexabenzotriphenylene was produced from 9-bromophenanthrene (Scheme 11). This side-reaction appears to be avoided when the synthesis is carried out with *o*-bromophenyl (pinacolato)boronic ester instead of *ortho*-dibromobenzene. Thus, reacting this halide with Ni(0) species generated *in situ* from the Zn reduction of $NiBr_2(PPh_3)_2$ gives $NiBr\{o\text{-}C_6H_4B(\text{pinacolato})\}(PPh_3)_2$; the subsequent reaction of this intermediate with KO^tBu gave the η^2-benzyne complex.[93]

Nickel(0)–aryne complexes readily undergo insertion reactions with unsaturated substrates such as CO, CO_2, olefins, and alkynes.[1,94–96] The latter often undergo double insertions. For instance, the complex $Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2$ undergoes double insertion of alkynes to form substituted naphthalenes (Scheme 12),[97] while double insertion of thioalkynes gives various 2,3-thioether naphthalenes, as shown in Scheme 13.[98] A recent report has also demonstrated the application of this insertion reaction to various diynes such as dialkynyl naphthalenes.[99] The factors that determine the regiochemistry of these insertions have been reviewed.[100]

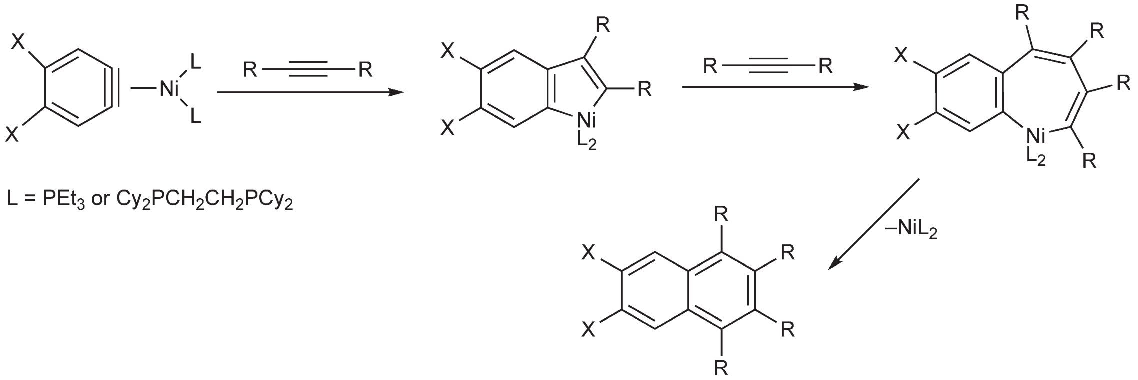
The reactivities of Ni–arynes with CO appear to depend on the concentration of CO in the reaction solution: at low [CO], created by controlled diffusion of CO into the reaction medium, a monoinsertion occurs to produce fluorenones, whereas at higher [CO], created by rapid bubbling of CO through the reaction medium, a double insertion occurs to produce nickelacyclic anhydrides that can be oxidized to bis(acetyl) complexes and the corresponding free benzanhydrides (Scheme 14).[101] Some Ni–arynes react with tetrafluoroethylene (C_2F_4) to give a nickelaindane product **56**, as shown in Equation (5).[102]



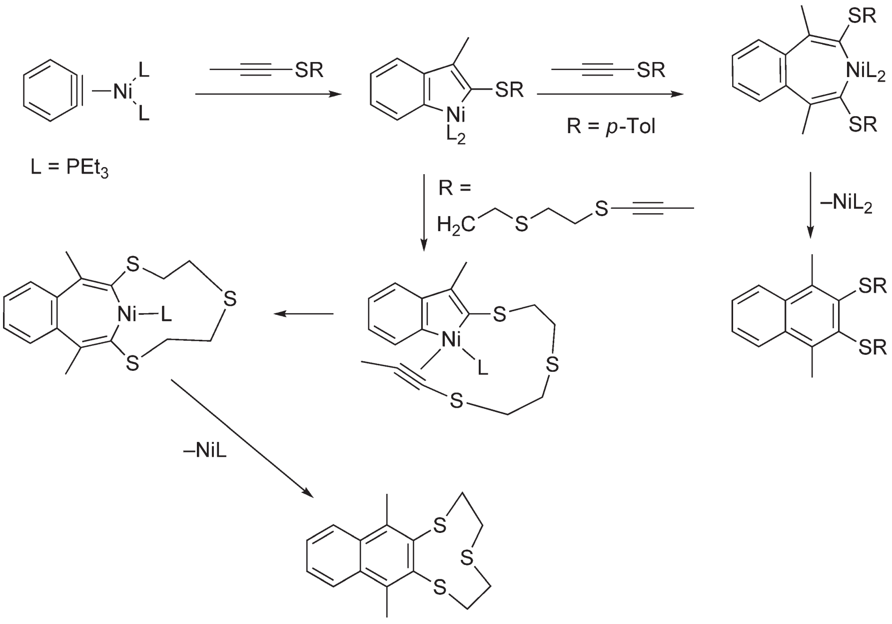
56

(5)

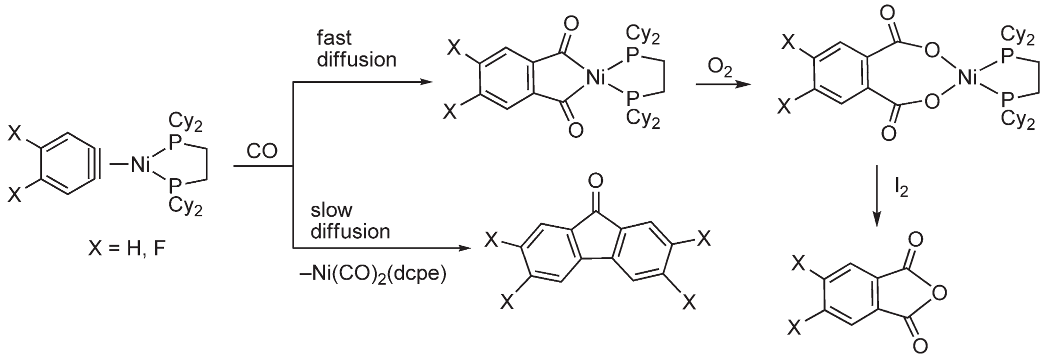
Complex **58** represents an interesting case of a dinuclear species featuring an unprecedented $\mu,\eta^2{:}\eta^2$-aryne moiety. This compound, an orange solid, comes about from the reaction of the mononuclear precursor **57** with *in situ* generated $Ni^0(PEt_3)_2$.[103] The symmetric structure of this compound is indicated by the solution NMR data (e.g., one signal each for the aromatic hydrogens at ca. 7.3 ppm, the fluorines at ca. −74 ppm, and the phosphorus nuclei at ca. 15 ppm). The solid-state structure of **58** shows slightly shorter C–C bonds for the carbon atoms not bonded to Ni, in addition to a very long Ni–Ni distance (ca. 272 pm). This compound was shown to catalyze the rearrangement of the initial aryne species **57** to the isomer **59**, an unusual process reminiscent of the well-known chain-walking process occurring in many alkene complexes (Scheme 15).



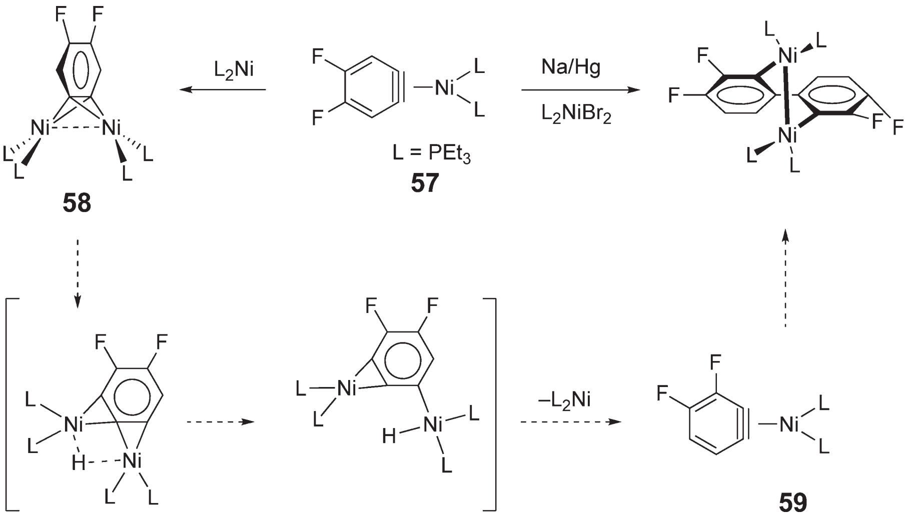
Scheme 12



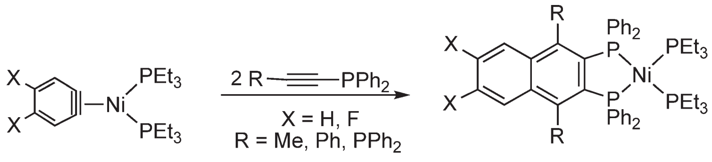
Scheme 13



Scheme 14



Scheme 15



60 **61**

Scheme 16

Alkynylphosphines have also been shown to undergo an interesting double insertion with Ni(0)–benzyne complexes. Thus, 2 equiv. of $Ph_2P–C{\equiv}C–R$ insert into the Ni–benzyne bond in **60** to form a series of novel naphthalene-based bis(phosphine) ligands coordinated to the Ni center (**61**, Scheme 16).[104]

8.03.2.4 Nickel–Nitrile (Ni-(η^2-N≡CR)) Complexes

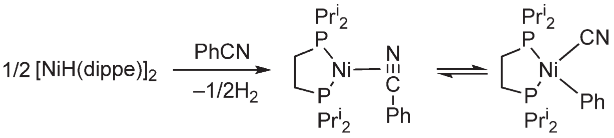
Reaction of the wine-red Ni(I) dimer $[NiH(dippe)]_2$ with benzonitrile gives the yellow η^2-nitrile complex Ni(η^2-N≡CPh)(dippe), **62**, which is in a slow equilibrium ($K_{eq} \sim 1$ at 91 °C) with Ni(CN)(Ph)(dippe), **63** (Scheme 17).[105] The solid-state structures of both compounds have been elucidated by X-ray diffraction studies. The nominally three-coordinate complex **62** is essentially planar, and the elongated C–N bond distance (ca. 123 pm) and N–C–C angle (ca. 151°) indicate significant π-backbonding. The $^{13}C\{^1H\}$ NMR spectra show a significant downfield shift of the *C*-N signal from ca. δ119 in free benzonitrile to ca. 169 in **62** and ca. 138 in **63**. In addition, the IR spectrum of **62** showed a ν(C≡N) band at 1,745 cm^{-1}, which signals a significant reduction in the C–N bond order when compared to the corresponding frequency of 2,235 cm^{-1} in free benzonitrile. The ν(C≡N) band in **63** appeared at 2,108 cm^{-1}, consistent with a σ-bonded cyano group.

8.03.3 Nickel Complexes of η^3-Ligands

8.03.3.1 η^3-Allyl Complexes

8.03.3.1.1 General comments

Allyl complexes have contributed significantly to the development of the organometallic chemistry of nickel and the applications of nickel complexes in organic synthesis, for example, nucleophilic attack on coordinated allyl ligands.[8,106,107] In addition, allylnickel complexes have been identified as key intermediates in the oligomerization and cyclization of olefins and dienes. For example, the Ni(0)-catalyzed hydrocyanation of butadiene to adiponitrile, the main component of a major commercial process for the production of nylon, involves Ni^{II}(π-allyl) intermediates.[108] Moreover, the η^3/η^1-rearrangements of allylnickel species have helped explain the facile isomerization of olefins in the presence of nickel complexes. The Ni-catalyzed homoallylation of carbonyl compounds with 1,3-dienes also involves Ni(π-allyl) complexes; this subject has been reviewed recently.[9] New applications include the cleavage of C–C bonds in the deallylation of malonates,[109] the preparation of cyclopentenones by carbonylative cycloadditions,[110] and asymmetric hydrovinylation of olefins and vinylarenes.[111] The vast majority of allylnickel complexes are four-coordinate, 16-electron complexes of the type $Ni(allyl)_2$, $[Ni(\mu\text{-}X)(allyl)]_2$, NiX(allyl)L, or $[Ni(allyl)LL']^+$ (L and X are neutral and anionic two-electron donor ligands, respectively).



62 **63**

Scheme 17

8.03.3.1.2 Theoretical and physical studies

Theoretical studies of varying sophistication have been carried out to probe the energetics, structures, and reactivities of Ni(allyl)$_2$.[112–114] A computational study has also been carried out on the oxidative addition of allyl ammonium salts to the model species Ni^0(PH$_3$)$_2$.[115] This study proposes an associative mechanism for the uptake of the allyl ammonium substrate, followed by C–N bond activation, and addition of the allyl to form the cationic intermediate [Ni(η^3-allyl)(PH$_3$)$_2$]$^+$; the latter species undergoes an associative displacement of PH$_3$ by NH$_3$ to give the products [Ni(η^3-allyl)(PH$_3$)(NH$_3$)]$^+$. These conclusions are consistent with the results of the experimental studies to be discussed below.

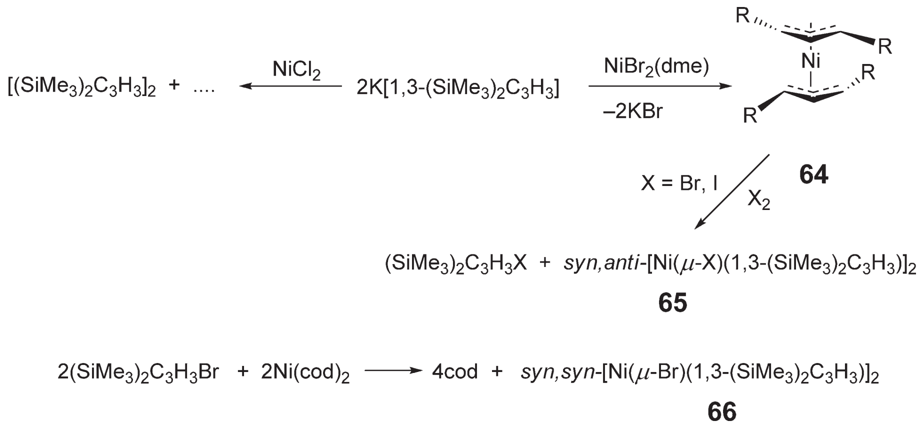
Another computational study has examined the mechanism of the stereoregular 1,4-polymerization of butadiene according to the π-allyl insertion scenario.[116] This study has elucidated the detailed chain-propagation steps and put forth mechanisms for the $\pi \rightarrow \sigma$ and *syn-anti*-isomerizations that lead to stereoregular polymers. Finally, a theoretical investigation of the carbonylation of allyl bromide catalyzed by Ni(CO)$_4$ has found that the allyl ligand coordinated to the intermediates of the catalysis undergoes $\eta^3 \rightarrow \eta^1$ isomerization, and the carbonylation step is more facile with the η^1-allyl species.[117]

Protonation of organometallic complexes, L$_n$M–R, is a reaction of fundamental importance both in the industrial applications of organometallic complexes and also in bioinorganic chemistry.[118–120] Aside from the numerous stoichiometric and catalytic reactions reported for Ni–allyl compounds, a number of recent studies have examined the protonation kinetics for a series of [(triphos)Ni(η^3-allyl)]$^+$ complexes. These studies have shown that the Ni center in these derivatives is ca. 10^6 times more basic relative to the analogous Ni–Me complexes;[121,122] this is presumably due to the electronically saturated configuration of the Ni-η^3-allyl species (18 electron).

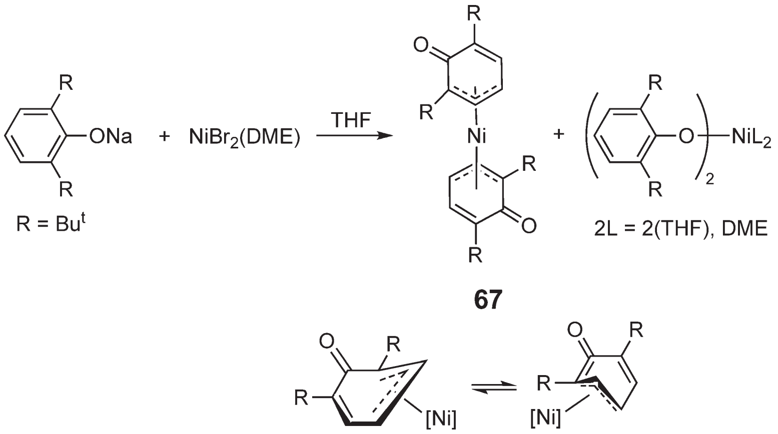
8.03.3.1.3 Synthetic and reactivity studies

Homoleptic allyl complexes have played an important role in the historical development of the organometallic chemistry of nickel. The parent compound, Ni(η^3-C$_3$H$_5$)$_2$, which was first prepared more than 40 years ago,[123] has served as a precursor for the preparation of many other heteroleptic allyl derivatives of Ni and is used as a pre-catalyst for numerous organic transformations.[124–127]

Given the importance of Ni(η^3-C$_3$H$_5$)$_2$ in a wide range of applications and in view of its pyrophoric nature and limited oxidative and thermal stability at ambient temperatures, it is rather surprising that only a few substituted derivatives of this compound have been prepared.[128] A recent report has described the preparation of one such derivative, Ni{η^3-1,3-(SiMe$_3$)$_2$C$_3$H$_3$}$_2$, **64**, as shown in Scheme 18.[129] This complex crystallizes as orange needles that are soluble in a range of solvents, can be sublimed under vacuum, melts at 64 °C, and decomposes only above 100 °C. The greater thermal stability and reduced air and moisture sensitivity of **64** compared to its parent complex is remarkable: solid samples of **64** are stable in the air for several hours, and hexane solutions can be layered on top of water without observable decomposition for several hours. NMR spectra of this diamagnetic solid have indicated the existence of eclipsed (*cis*) and staggered (*trans*) forms in solution; the latter form is more stable at higher temperatures. Both forms have been studied by crystallography and show that the SiMe$_3$ substituents are *syn*/*anti* with respect to



Scheme 18



67

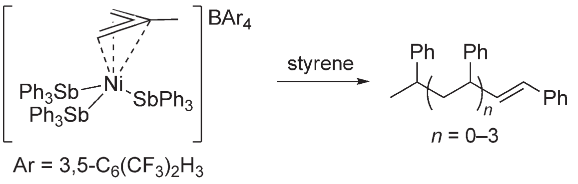
Scheme 19

each other. The reaction of **64** with I_2 gives $Ni_2(\mu\text{-}I)_2\{\eta^3\text{-}1,3\text{-}(SiMe_3)_2C_3H_3\}_2$, **65**, as a purple-red solid, which decomposes above 130 °C, giving off purple vapors of I_2. The Br analog of **65** can be prepared in the same way, or by oxidative addition of $1,3\text{-}(SiMe_3)_2C_3H_3Br$ to $Ni(cod)_2$ (Scheme 18). The arrangement of the $SiMe_3$ groups in the solid state of these complexes is *syn/syn* **66** and *syn/anti* **65**.

Reaction of $NiBr_2(DME)$ with $Na[2,6\text{-}Bu^t{}_2\text{-}C_6H_3O]$ in THF has given another homoleptic allyl complex (**67**, Scheme 19).[130] The allyl moieties in this diamagnetic, purple solid are defined by the *ortho*-, *meta*-, and *para*-carbon atoms of each aryloxide ligand. The unusual enone character of the aryloxide ligand is reflected in strong C–O interactions observed in solution IR and solid-state studies: $\nu(CO) \sim 1{,}600\ cm^{-1}$; C–O ~ 124 pm. The C–C distances in the aryl ring and its puckering indicate significant disruption of aromaticity: C=C ~ 137 pm; $C\text{–}C_{allyl} \sim$ 139–142 pm; C–C ~ 142–149 pm; the angle between the enone and allyl moieties ~ 17°. The simple NMR spectra of **67** are attributed to an averaging of the signals resulting from the fast metal exchange between the two possible allyl moieties (Scheme 19).

Dinuclear allyl complexes have played a great role in the development of the stoichiometric and catalytic chemistry of Ni–allyl complexes. A recent report has described the preparation of the trifluoroacetate-bridged derivatives $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}OC(=O)CF_3)]_2$.[131]

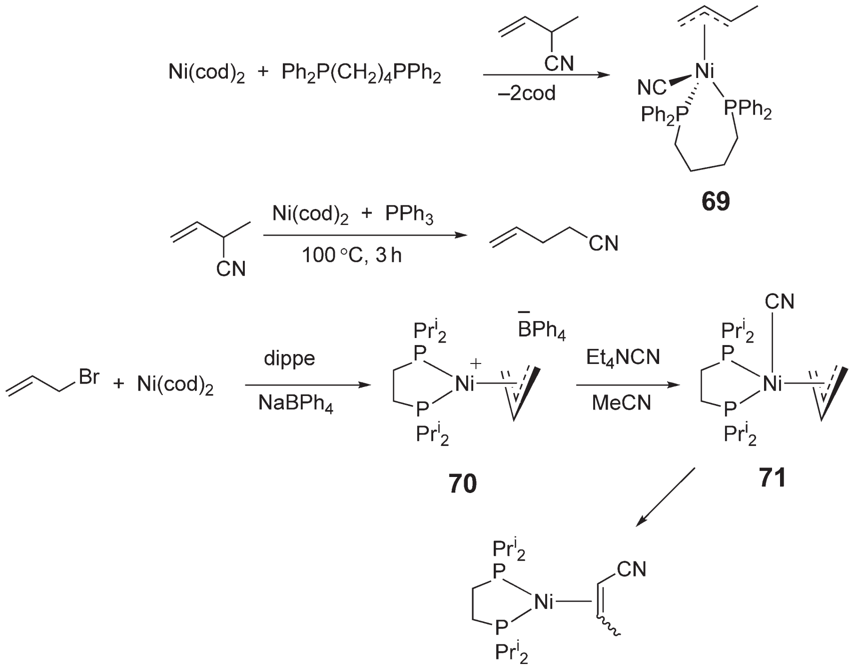
As stated above, most Ni–allyl complexes are four-coordinate, 16-electron species, but a few 18-electron species that are formally five-coordinate have been reported recently (Equation (6)). These include the cationic compound **68**, which is a thermally stable but highly reactive catalyst for the oligomerization of styrene (turnover frequency of up to 2,000 min^{-1}).[132] The unusual coordination of three $SbPh_3$ ligands and their great lability are presumably due to the longer, less robust Ni–Sb bonds. Another example is $NiBr(\eta^3\text{-allyl})(dmpe)$, which gives the cationic, four-coordinate, 16-electron species $[Ni(\eta^3\text{-allyl})(dmpe)][B(C_6F_5)_4]$ upon reaction with $Tl[B(C_6F_5)_4]$.[133]



68

(6)

Oxidative addition of allylic compounds to Ni(0) precursors is a reliable route to Ni–allyl complexes, with allyl halides being the most commonly used substrates for this purpose. For example, addition of $BrCH_2C(R)=CH_2$ (R = Me or H) to $Ni(cod)_2$, followed by reaction with $NaBPh_4$ and dippe, has given the cationic species $[Ni(\eta^3\text{-}CH_2C(R)=CH_2)(dippe)]BPh_4$.[134] Other substrates such as allylic nitriles can also be versatile precursors for the formation of interesting allyl species. Thus, the reaction of $Ni(cod)_2$ with 2-methyl-3-butenenitrile has been reported to proceed by the oxidative activation of the allyl–CN bond to form an allyl intermediate, which has been trapped as the cyano complex **69** in the presence of 1,4-bis(diphenylphosphino)butane (dppb), as shown in Scheme 20.[135] The closely related complex of dippe, **71**, has been prepared by the reaction of the cationic species **70**[134] with various sources of cyanide ion.[136]



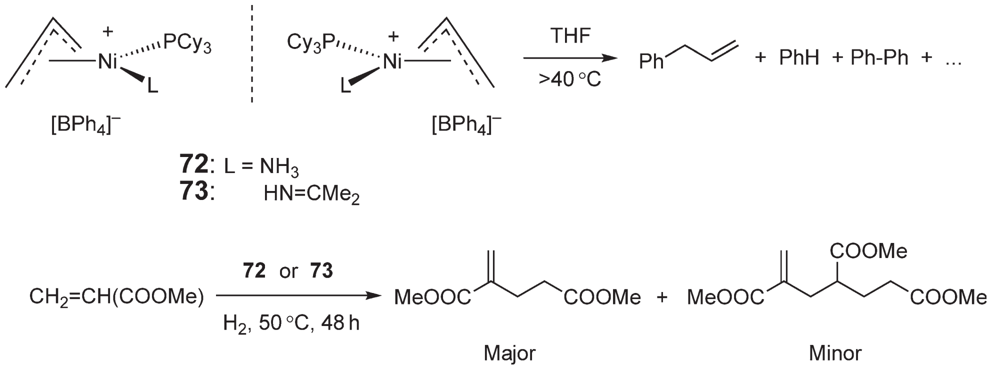
Scheme 20

Structural characterization of these species has revealed that complex **69** adopts a trigonal-bipyramidal geometry in which the methylallyl moiety occupies the apical position (Ni–CN ~ 189 pm), whereas complex **71** adopts a square-pyramidal structure with the cyanide ligand at the apical position at a relatively long distance from the Ni center (Ni–CN ~ 199 pm). The latter structure is similar to the bromo analog NiBr(allyl)(dippe), prepared from the reaction of the nickel(I) hydrido dimer $[NiH(dippe)]_2$[137] and allyl bromide. The involvement of allyl cyano species such as **69** and **71** in the catalytic hydrocyanation of butadiene is supported by the following observations: (i) complex **69** catalyzes the isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile (ca. 100 turnovers at 100 °C), (ii) complex **71** decomposes slowly to give Ni(0) complexes of *cis*- and *trans*-crotonitrile (Scheme 20).

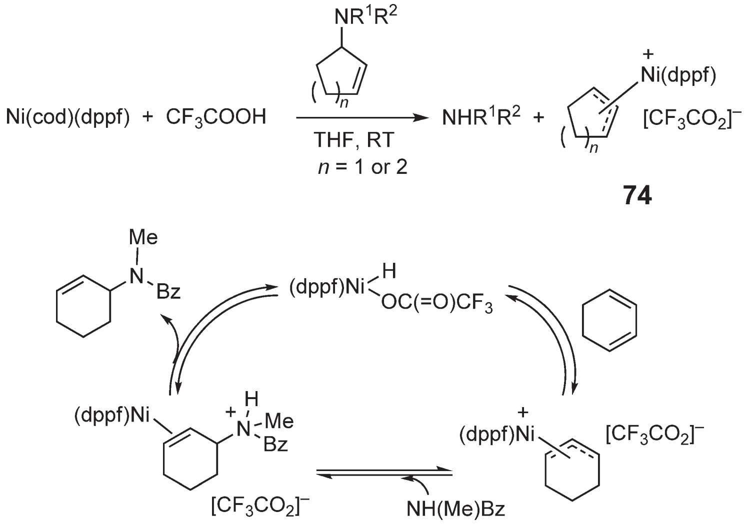
The low-temperature reaction of allyl cyanide with the Ni^I hydrido dimer $[NiH(dippe)]_2$ gives the Ni(0) complex $Ni(\eta^2\text{-}CH_2{=}CHCH_2CN)(dippe)$, which rearranges to the nickel(II) allyl(cyano) complex **71** (via C–CN bond activation) and the olefin-isomerization product $Ni(\eta^2\text{-}CH_3CH{=}CHCN)(dippe)$ (via C–H bond activation).[138] The kinetics of these bond-activation processes has been studied and the role of Lewis acids in these competitive reactions has been clarified.

Allyl–Ni complexes have also been prepared via direct oxidative addition of ammonium tetraphenylborate salts $[(allyl)NH_3][BPh_4]$ or $[(allyl)HN({=}CMe_2)][BPh_4]$ to the Ni(0) species $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ and $[Ni(PCy_3)_2]_2(\mu\text{-}N_2)$; this approach furnishes the dissymmetrical (chiral) cations $[Ni(allyl)(PCy_3)(NH_3)]^+$, **72**, or $[Ni(allyl)(PCy_3)(\eta^1(N)\text{–}HN{=}CMe_2)]^+$, **73** (Scheme 21).[139] The solid-state structure of complex **72** has been studied.[140] In solution, the allyl ligand is fluxional in the NH_3 derivative **72** but quite rigidly bound in the imine derivative **73**. Studies on the thermal stability of complex **72** have shown a relatively facile Ni-promoted phenyl transfer from the BPh_4 anion to the allyl ligand, yielding allylbenzene; other products of this decomposition are benzene and biphenyl (Scheme 21). Such phenyl transfers have precedents,[141–143] and have been reviewed recently.[144] In the presence of H_2, complex **72** catalyzes the head-to-tail oligomerization of methylacrylate to dimethyl methyleneglutarate and 2,4,6-tri(carbomethoxy)-1-hexene.

Oxidative addition of allylic amines to Ni(0) precursors in the presence of acid has been shown to lead to cationic (allyl)Ni complexes. Thus, Ni(cod)(dppf) reacts with a range of cyclic allylic amines in the presence of trifluoroacetic acid (TFA) to generate complexes **74**, as shown in Scheme 22.[34] This process can proceed by protonation of the amine and the oxidative addition of the resulting ammonium salts, as above. The same system or a mixture of $Ni(cod)_2$ and dppf catalyzes the hydroamination of dienes. In this case, the catalysis is thought to proceed via the initial protonation of Ni(0) precursor to give an Ni–H species that undergoes insertion of the diene to generate an allyl



Scheme 21

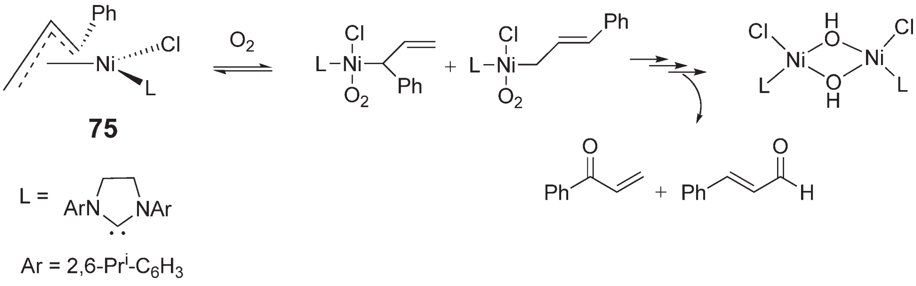


Scheme 22

complex. The latter can then undergo a nucleophilic attack by the amine to give the product, an allylic amine, and regenerate the Ni–H intermediate (Scheme 22). Since the nucleophilic attack of the amine on the allyl–Ni intermediate and the oxidative addition of the ammonium salt are in equilibrium, this system can also catalyze the exchange of secondary amines with allylic amines.

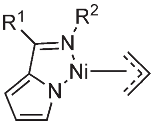
Another route to allyl complexes involves (formal) protonation of a diene. A recent report has described the addition of the O–H bond in 2-phosphinophenolates to the cod moiety in Ni(cod)$_2$.[145] The allyl complexes thus formed display interesting catalytic activities in the polymerization of ethylene.[146] The formation of the allyl complexes was also accompanied by the formation of the unusual Ni(0) compound Ni(cod){$R_2P(2\text{-}OH\text{–}C_6H_4)$} featuring agostic interactions between the Ni center and an allylic hydrogen of cod.

A large number of charge-neutral complexes of the type NiX(η^3-allyl) (L) (L = tertiary phosphines) are known and have served as catalysts or precursors for other derivatives, and an interesting example bearing a chiral azaphosphole ligand has been reported recently.[147] On the other hand, simple compounds have been derivatized to give more unusual complexes. For example, the reaction of NiCl(allyl)(PPh$_3$) with Li[1-norbornyl] gives the corresponding norbornyl complex, which has been isolated and characterized by NMR.[148] The analogous complexes NiCl(allyl)(NHC) (**75**, NHC = *N*-heterocyclic carbene) have been prepared in very high yields from the reaction of [Ni(μ-Cl)(η^3-allyl)]$_2$ with various NHC (Scheme 23); the solid structure of one derivative has been described.[149] These complexes bind oxygen reversibly and with a fairly high equilibrium constant ($K_{eq} \sim 2{,}100 \pm 100\ \mathrm{l\ mol^{-1}}$). The resulting Ni–O$_2$ adduct decomposes to a hydroxyl-bridged species with the loss of the oxidized allyl moiety ($K_2 \sim 4 \times 10^{-3} \pm 0.2 \times 10^{-3}\ \mathrm{s^{-1}}$); the half-life of this process is ~7 s. The interesting ability of the Ni center in **75** to split oxygen and form C–O bonds is of potential value for Ni-catalyzed aerobic oxidations.



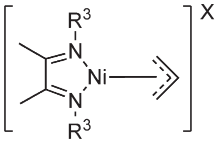
Scheme 23

Complex 76 is a charge-neutral complex of the type Ni(LX)(η^3-allyl) with LX representing an iminopyrrolyl ligand. The preparation and modest activities of these complexes for the oligomerization of ethylene have been described.[150] The related allyl–Ni complexes 77 featuring a positive charge and extensively substituted α-diimine ligands have also shown activities in the polymerization of ethylene.[151,152] In contrast, the cationic complexes 78 based on chelating 2-phosphinophenol ligands promote oligomerization of ethylene to butenes and hexenes;[153] the latter species is fairly unstable in solution, decomposing to the tetranuclear complexes 79. Cationic allyl–$\mathrm{Ni^{II}}$ complexes have also been reported with the neutral form of β-diimine ligands (β-iminoamine or NacNacH); the diamagnetic, yellow-brown complexes [Ni(η^3-2-methylallyl)(*N*,*N'*-(ArN=CMe(CH$_2$)$_3$CMe=NAr))]PF$_6$ have been prepared and characterized.[154]



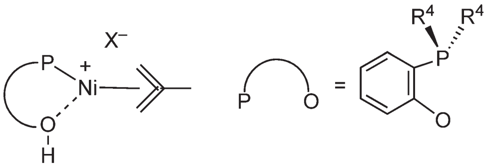
R^1 = H, Me
R^2 = 1,3,6-$Me_3C_6H_2$

76



77

R^3 = 2,6-(4-$SiMe_3$-C_6H_4)$_2C_6H_3$) 2,6-(3-$SiMe_3$-C_6H_4)$_2C_6H_3$),
2,6-(5-Me-furanyl)$_2$-4-phenyl-C_6H_2, 2,6-(2-benzofuranyl)$_2$-C_6H_3
X = SbF_6, B(3,5-(CF_3)$_2C_6H_3$)$_4$



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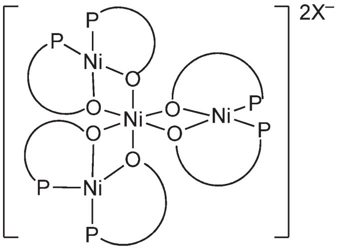
R^4 = Ph, Cy
X = SbF_6



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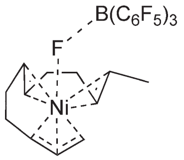
The cationic π-benzyl complexes [Ni(η^3-benzyl)(diphosphine)][ZnBr$_3$(THF)] (diphosphine = dippe, bis(di-*iso*-propylphosphino)methane (dippm)) have been prepared by the abstraction of Br$^-$ from NiBr(η^3-benzyl)(diphosphine) by ZnBr$_2$ or the reaction of ZnBr(PhCH$_2$) and NiBr$_2$(diphosphine).[155] Such halide abstractions are thought to be involved in the Ni/Zn-catalyzed cross-coupling reactions (Negishi coupling), since the cationic Ni–R intermediates are expected to be more reactive toward the incoming nucleophiles.

A number of allyl–Ni complexes have been prepared via the protolysis of Ni–dodecatriene. Solid-state and solution NMR studies of a few derivatives (e.g., 80) have been carried out to complement the computational studies alluded to above on the mechanism of Ni-catalyzed 1,4-*cis*-polymerization of butadiene.[156–158]



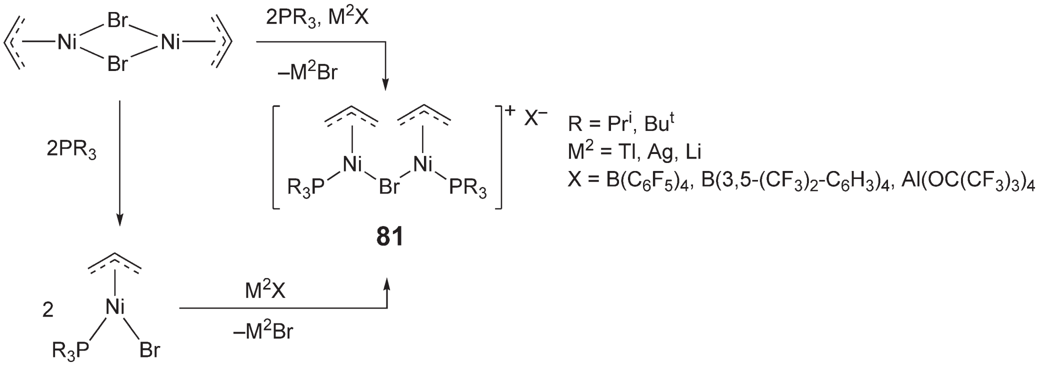
80

Although charge-neutral (π-allyl)Ni dimers featuring symmetrical halide bridges have been known for a long time, a recent report has introduced an interesting family of cationic dinuclear complexes in which only one halide bridges two Ni(π-allyl)(L) moieties, as in complexes 81 (Scheme 24).[159] The thermal stabilities of these complexes are influenced by both the steric bulk of the PR_3 ligands ($Pr^i > Bu^t \gg Me$) and the anions ($[B(C_6F_5)_4]^- \sim [Al(OC(CF_3)_3)_4]^- > [OSO_2CF_3]^-$); the analogous Pd complexes are also more stable. The solid-state characterization of one derivative, $[\{Ni(allyl)(PPr^i_3)\}_2(\mu\text{-}Br)][Al\{OC(CF_3)_3\}_4]$, has shown fairly symmetrical Ni–Br (ca. 235 pm) and Ni–P (ca. 222 pm) bonds, a relatively narrow range of Ni–C bonds (ca. 197–205 pm), and an Ni–Br–Ni angle of ca. 118°.

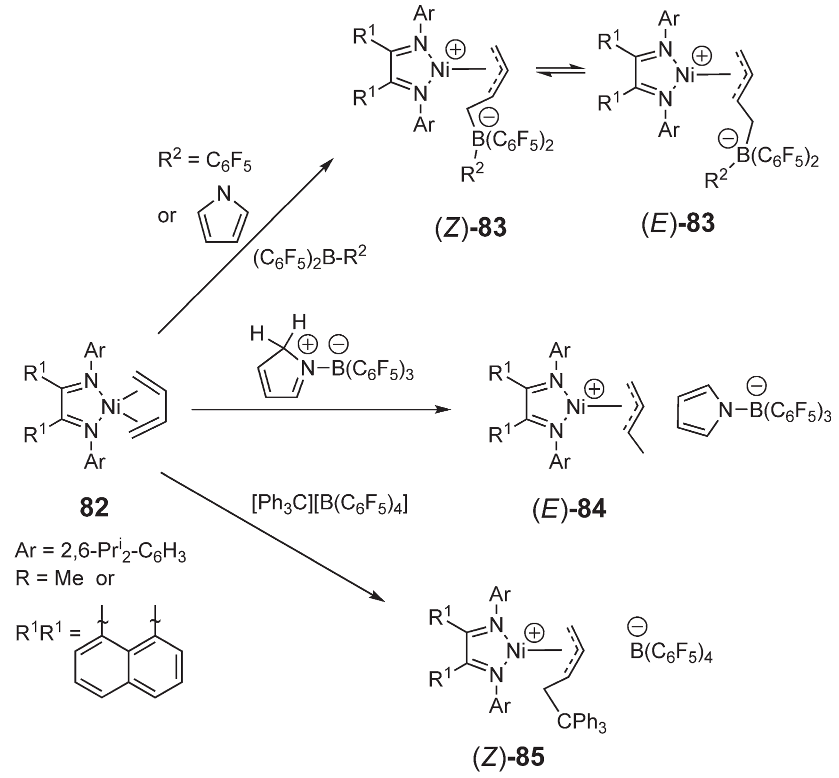
Two rare examples of anionic (allyl)nickelate(II) complexes have been reported recently.[160] Thus, reaction of Ni(η^3-allyl)$_2$ with allyllithium gives the homoleptic allyl complex $[Li(TMEDA)_2][Ni(\eta^3\text{-allyl})(\eta^1\text{-allyl})_2]$ as a thermally labile (dec. 55 °C) red solid. In the solid state, this nickelate species adopts a square-planar structure, whereas in solution, it is totally fluxional. The analogous reaction with Li_2[butane-1,4-diyl] gave $[Li(TMEDA)_2][Ni(\eta^3\text{-allyl})(\eta^1,\eta^1\text{-}(CH_2)_4]$ as an orange solid (dec. 20 °C); this compound displays a temperature-independent ^{1}H NMR spectrum featuring sharp signals. The structural and NMR features of these complexes indicate that the negative charge is mostly delocalized over the π-allyl ligand such that little or no electrostatic interaction is present between Ni and Li metals. This lack of contact of ion pairs is, in turn, proposed to explain the limited stabilities of these complexes in comparison to analogous nickelate compounds bearing σ-organyl ligands such as $[Li(TMEDA)]_2[Ni(\eta^1,\eta^1\text{-}(CH_2)_4)_2]$ (dec. 186 °C) that involve intimate Li–Ni and Li–CH_2 interactions.[161–166]

In addition to the cationic, neutral, and anionic (allyl)Ni^{II} complexes discussed above, another family of zwitterionic (or betaine) (allyl)Ni^{II} compounds have been reported to exhibit interesting reactivities in the polymerization of ethylene. Thus, the butadiene complexes 82 were allowed to react with Lewis acids such as $B(C_6F_5)_3$ or B(pyrrolyl)$(C_6F_5)_2$ to form the allyl compounds 83 shown in Scheme 25. Alternatively, addition of the Bronsted acid 2H–pyrrolyl/$B(C_6F_5)_3$ or the electrophile $[Ph_3C][B(C_6F_5)_4]$ to 82 gave the cationic allyl complexes 84 and 85, respectively.[167,167a,168] In general, the addition of the Lewis acid or the electrophile is always at the terminal carbon, thereby rendering the products chiral. In most cases, the initially observed (*Z*)-allyl form equilibrates with the thermodynamically more stable (*E*)-allyl form; this rearrangement is more facile with the less bulky allyl ligands.

Similar zwitterionic complexes have also been prepared by reacting $B(C_6F_5)_3$ with Ni(η^3-benzyl)(α-iminocarboxamidato) 86; addition of the Lewis acid to the O atom of the α-iminocarboxamidato moiety furnishes the product.[169,170] Analogous zwitterionic Ni-(η^3-2-methylallyl) 87 and Ni-(η^3-benzyl) 88 complexes supported by α-iminoenamido ligands have been prepared by a similar approach, using as Lewis acid either $B(C_6F_5)_3$ or $Al(C_6F_5)_3$.[171] Similarly, addition of $B(C_6F_5)_3$ to allyl complexes bearing *o*-diphenylphosphine(benzoate) ligands gave the analogous zwitterionic complexes 89.[172,173] Structural studies seem to indicate that the Ni center in these

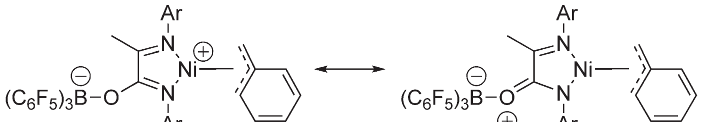


Scheme 24



Scheme 25

complexes bears a substantial positive charge. Moreover, solid-state structures of two derivatives have shown that the Ar substituent bound to the N atom adjacent to the $MR(C_6F_5)_3$ moiety is closer to the 2-methylallyl ligand, presumably because of the shorter M–C bond in the borate versus aluminate derivative.



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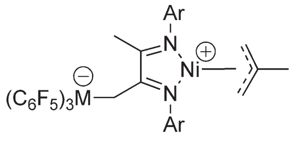
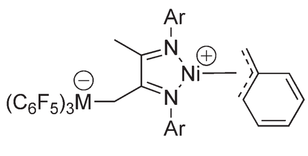
(M = B or Al)



87: Ar = 2,6-Pr^i_2-C_6H_3



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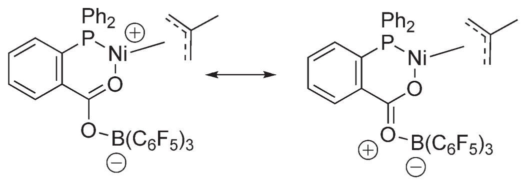

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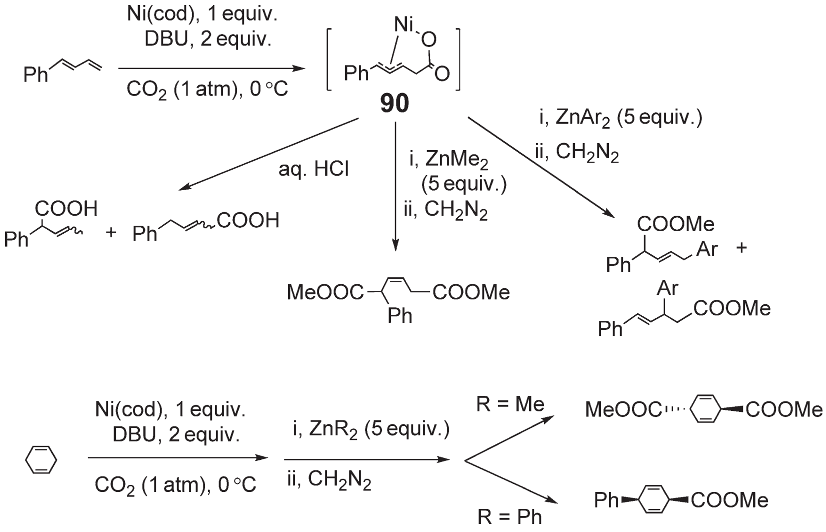
Polymerization studies have revealed interesting observations on the structure–activity relationships of this family of complexes. For example, the 2-methylallyl derivative is completely inert in contrast to the benzyl analog, implying that the more tightly bound allyl ligand does not provide the requisite open site around the Ni center. In addition, the α-iminoenamido derivatives require the presence of additional $M(C_6F_5)_3$ (M = B or Al; 2.5 equiv. with respect to Ni) to sustain polymerization, in contrast to the α-iminocarboxamidato derivatives that are single-component catalysts. On the other hand, the poly(ethylene) (PE) obtained from the latter systems have lower M_w values.

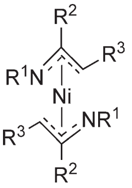


Scheme 26

A large number of Ni–allyl species are presumed to act as intermediates in Ni-promoted organic transformations. One such case involves the oxidative cycloaddition of CO_2 to conjugated dienes as an efficient method for preparing a number of mono- and dicarboxylic acid derivatives, illustrated in Scheme 26.[174] Thus, the reaction of $Ni(cod)_2$ (in stoichiometric amounts) with the diene and CO_2 (1 atm) is believed to produce the oxo-π-allyl nickel intermediates **90** that can be hydrolyzed or transmetallated with zinc reagents. The presence of 2 equiv. of 1,8-diazabicylco-[5.4.0]undec-7-ene (DBU) is essential for the success of this transformation. It is not known why $ZnMe_2$ leads to dicarboxylation whereas $ZnAr_2$ gives arylative carboxylation.

8.03.3.2 η^3-1-Azaallyl Complexes

A series of novel (η^3-1-azaallyl)-Ni^{II} complexes **91** and **92** has been reported recently.[175,176] The solid-state structures of these complexes confirm the η^3-coordination of the azaallyl ligands (Ni–C ~ 203–206 pm; Ni–N ~ 188–192 pm). Variable-temperature NMR studies have shown that **91** and **92** undergo a dynamic process in solution that generates three different isomers, presumably via η^3/η^1-slippage processes.



91	**92**
$R^1 = SiMe_3$	$R^1 = SiMe_3$
$R^2 = Bu^t$	$R^2 = Ph$
R^3 = *p*-Tol	$R^3 = SiMe_3$

8.03.4 Nickel Complexes of η^5-Ligands

8.03.4.1 General Comments

The most frequently reported Ni-(η^5-ligand) complexes are those of the Cp ligand and its many substituted derivatives, some of which feature functionalized moieties poised for chelation. The most well-known complex is $NiCp_2$, which has been used both as reagent for promoting various reactions (e.g., as a convenient precursor to $Ni(PR_3)_4$ in catalytic carbon–carbon bond formations)[177] and as a precursor to other Ni–Cp derivatives. Until very recently, the chemistry of Ni–Cp complexes was dominated by that of nickelocene and its derivatives,[10] but this is no longer true as there has been a resurgence of interest during the 1990s in the preparation and structural/

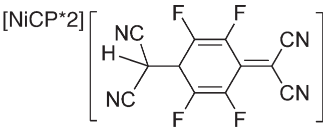
reactivity studies of non-nickelocene-type Ni–Cp complexes. This section will discuss the syntheses and characterization of a variety of Ni–Cp complexes and will outline their reactivities; the discussion will include complexes based on functionalized Cp ligands, an emerging class of compounds whose chemistry has been reviewed.[12–15]

The chemistry of the analogous indenyl (Ind) complexes has also experienced a significant resurgence, and dozens of new compounds have been prepared and subjected to structural and reactivity studies. Some of the major developments in this area have been reviewed[16] and outlined in the following sections. The chemistry of complexes featuring other η^5-bound ligands such as cyclohexadienyl and carborane complexes have been discussed in subsequent sections.

8.03.4.2 Theoretical and Physical Studies

The nickelocenium cation, the Ni(III) analog of nickelocene, was prepared as its BF_4^- salt almost three decades ago,[178,179] but the solid-state structures of the cation as salts of various anions were reported quite recently. Thus, the selective reducing property of $NiCp^*_2$ ($E_{1/2}{}^{+/0}$ = –0.65 V vs. SCE)[180] makes it suitable for producing the C_{60} anion ($E_{1/2}{}^{0/1-}$ ~ –0.45 V and $E_{1/2}{}^{1-/2-}$ ~ –0.9 V vs. SCE)[181] such that the crystalline 1 : 1 salt $[NiCp^*_2]^+[C_{60}]^-\cdot CS_2$ can be isolated from an equimolar CS_2 solution of these compounds.[182] In the solid state, the $[NiCp^*_2]^+$ is found directly over a pentagonal ring of the $[C_{60}]^-$, with Cp* rings being parallel to the Cp rings of the anion and at an average interplanar distance of 317 pm.

Another structurally characterized $[NiCp^*_2]^+$ salt has been prepared by reacting $NiCp^*_2$ with the strong electron-acceptor perfluoro-7,7,8,8-tetracyano-*p*-quinodimethane (F_4TCNQ); the donor–acceptor salt $[NiCp^*_2]^+\cdot[HF_4\text{-}TCNQ]^-$, **93**, was isolated and studied by X-ray diffraction studies.[183] The nickelocenium cation in **93** adopts an approximate D_{5d}-symmetry with Ni–$C_{average}$ bond distances of 215 pm; the anion forms a polymeric structure via H bonds. This compound forms a one-dimensional chain in which the C_6 ring of the anion is parallel to the Cp* plane.



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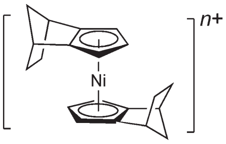
A recent report has described the low-temperature electrochemical generation of highly oxidized and reduced derivatives of nickelocene by the use of ultramicroelectrode techniques and appropriate solvents (SO_2 for oxidations and THF for reductions).[184] The redox states $[NiCp_2]^{2+/+/0/-/2-}$ were identified at –80 °C with the following $E°$ values (in V): 0.81 for $[NiCp_2]^{2+/+}$, 0.01 for $[NiCp_2]^{+/0}$, –1.84 for $[NiCp_2]^{0/-}$, and –3.13 for $[NiCp_2]^{-/2-}$. These results confirm the existence of a linear relationship between redox potentials and ionization potentials of Ni and imply that, as in most metallocenes, the frontier molecular orbitals of nickelocene are primarily metal based.

An interesting derivative of nickelocene has been prepared using the isodicyclopentadienyl ligand.[185] Curiously, only one of the three possible isomers, *exo,exo*-**94** was obtained for Ni, whereas the corresponding Fe and Co derivatives formed the *exo,endo*- and *endo,endo*-isomers as well. Detailed analyses of the NMR spectra of **94** (n = 0) and its paramagnetic Ni(III) cation (n = 1) have allowed a probe of the spin densities in these compounds.



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Magnetic susceptibility measurements have shown that the dimers $[Ni(\mu\text{-}X)(R_nCp)]_2$ (R = Pr^i, Bu^t) are paramagnetic[186] and Ni(acac)Cp* exhibits a low-spin–high-spin equilibrium between a diamagnetic ground state and a low-lying triplet excited state (K_{eq} ~ 0.47 at 303 K).[187] The dimer $[Ni(Pr^i_4C_5H)(\mu\text{-}CO)]_2$ has been studied by electron impact (EI) and nanosecond multiphoton ionization (MPI) spectrometry to obtain information on gas-phase formation enthalpies for these complexes and some of their fragments.[188] EI ionization allowed the detection of molecular ions and revealed that the decomposition process proceeds by successive losses of the CO and the $\mathrm{Pr^i{}_4C_5H}$ ligands, whereas no molecular ions were detected by MPI studies at 193 nm, the highest observed mass being that of the ion $\mathrm{[Ni_2(Pr^i{}_4C_5H)_2]^+}$.

A series of alkynyl complexes of the type $\mathrm{NiCp(C{\equiv}C{-}X)(PPh_3)}$ has been prepared, and the alkyne bond order has been probed by IR, NMR, and UV spectroscopy, X-ray crystallography, and in terms of reactivities with $\mathrm{Co_2(CO)_8}$ to form the complex $\mathrm{[NiCp(PPh_3)]\{\mu{-}\eta^1(Ni),\eta^2{:}\eta^2(Co,Co){-}C{\equiv}C{-}CH({=}O)\}[Co_2(CO)_6]}$ in which the triple bond moiety bridges the Co atoms.[189] These studies demonstrate that the $\mathrm{NiCp(PPh_3)}$ moiety is a net donor when the X group is a strong acceptor. Accordingly, the increasing electron-withdrawing nature of X increases the charge separation resulting from the greater contribution of cumulenic mesomers such as $\mathrm{Ni^+{=}C{=}C{=}X^-}$; this, in turn, reduces the alkyne bond order. Thus, the spectral data have been used to estimate the relative electron-withdrawing ability for X: $\mathrm{CH(OEt)_2 < CH{=}NNHPh < CH{=}NNH(2,4\text{-}(NO_2)_2Ph) < CH{=}C(CN)_2}$. A closely related series of complexes of the type $\mathrm{NiCp(C{\equiv}C{-}R{-}NO_2)(PPh_3)}$ (**95**, R = 4-$\mathrm{C_6H_4NO_2}$, 4,4′-$\mathrm{C_6H_4C_6H_4NO_2}$, (*E*)- or (*Z*)-4,4′-$\mathrm{C_6H_4{-}CH{=}CHC_6H_4NO_2}$, 4,4′-$\mathrm{C_6H_4C{\equiv}CC_6H_4NO_2}$, 4,4′-$\mathrm{C_6H_4N{=}CHC_6H_4NO_2}$,) has been prepared and subjected to electrochemical studies to elucidate the influence of the extent of conjugation in R on the oxidation potential of the complex.[190]

Computational studies have been carried out to map the reaction mechanisms involved in the polymerization of butadiene catalyzed by complexes of the type NiCp(η^1-phenyl)(η^2-butadiene).[191] This study has probed the crucial steps of insertion, allylic isomerization, and $\eta^1(\sigma) \rightarrow \eta^3(\pi)$ rearrangement. Variable-energy photoelectron spectroscopy has been used to study and assign the molecular orbitals of NiCp(allyl), and comparison to computational studies has indicated that the lowest binding energy peak is associated with the HOMO which has mainly Ni 3*d*–Cp π_2 bonding character.[192]

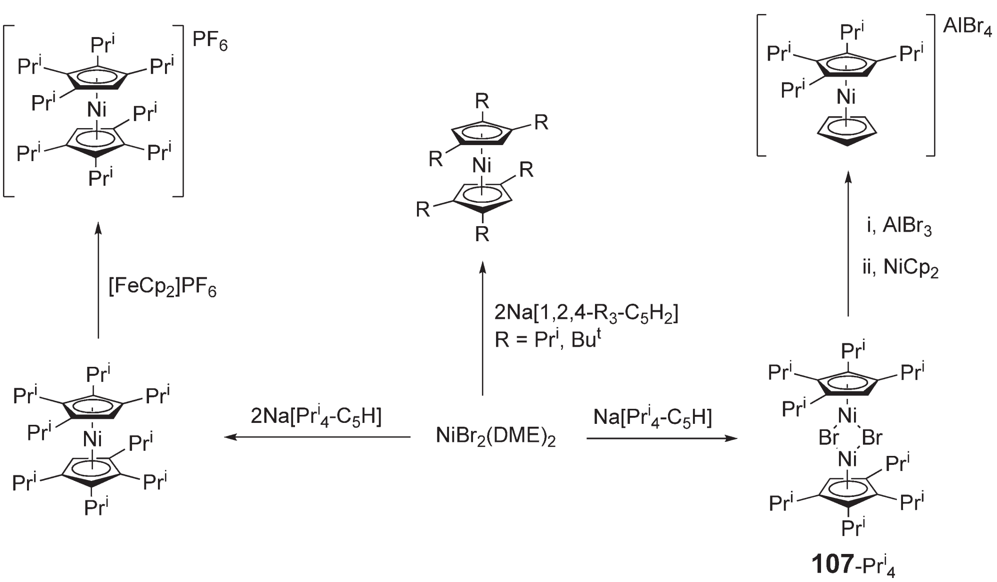
The metastable excited states of the complex NiCp(NO) have been probed by IR spectroscopy, which shows significant red shifts in the values of ν(NO) (as much as 460 cm^{-1}).[193] Although the origins of this observation are not well understood, a reasonable explanation is the Ni → NO charge transfer in the photoexcited complex with the resulting bending of the Ni–N–O moiety. Structural and computational studies with NiCp*(NO) have proved to be consistent with this phenomenon.[194] Since the latter is a solid at room temperature, as opposed to NiCp(NO) that is a liquid, the crystalline structure of the complex could be studied at low temperature (25 K) with and without irradiation (excited and ground states, respectively). Structural comparisons for the ground and metastable states showed that the Ni–N bond is somewhat longer (170 vs. 162 pm) while the Ni–O distance is much shorter in the metastable state, consistent with a significant bending of the Ni–N–O angle (93° in the metastable structure). DFT studies indicate that the energy difference between NiCp*(NO) and NiCp*(η^2-NO) is about 1 eV.

A detailed study combining spectroscopic work (NMR, IR, UV–VIS, MS), cyclic voltammetry and variable-temperature magnetic susceptibility measurements, single crystal X-ray diffraction analysis, and computational work (Fenske–Hall MO analysis) has been reported on the trimetallic complexes $\mathrm{[Ni_3(\mu^3\text{-}S)_2Cp_3]}^n$ (n = 1+ or 0).[195] The bonding picture that emerges from this study indicates that the three Ni centers in the 52-electron monocation are involved in two formal Ni–Ni bonds totaling a bond order of 1; consistent with this picture, the metal centers form an isosceles triangle with a non-bonding edge (ca. 315 pm) and two bonding edges (ca. 254 pm). The latter Ni–Ni bonds are slightly longer in the 53-electron neutral species (ca. 274 pm). These results appear to endorse the valence-bond-based prediction that trimetal clusters having more than 48 valence electrons experience weakened metal–metal interactions because the extra electrons populate the antibonding HOMO orbitals.

8.03.4.3 Synthetic and Reactivity Studies

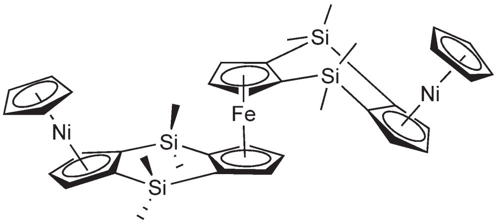
8.03.4.3.1 Substituted nickelocenes and related mixed-sandwich complexes

The substituted nickelocene analogs $\mathrm{Ni(1,2,4\text{-}R_3\text{-}C_5H_2)_2}$ (R = Pr^i, Bu^t) and $\mathrm{Ni(Pr^i{}_4C_5H)_2}$ have been prepared (Scheme 27).[186,196] The dark green $\mathrm{Ni(Pr^i{}_4C_5H)_2}$ reacts with $\mathrm{[FeCp_2][PF_6]}$ to give the cherry-red nickelocenium ion $\mathrm{[Ni(Pr^i_4C_5H)_2]^+}$ (Scheme 27). X-ray diffraction studies of this product have shown a slightly bent $\mathrm{Cp'_{center}Ni{-}Cp'_{center}}$ axis (ca. 174.5°). The novel, mixed-ligand nickelocenium $\mathrm{NiCp(Pr^i_4C_5H)]^+}$ was prepared by reacting nickelocene with $\mathrm{[Ni(\mu\text{-}Br)(Pr^i_4C_5H)]_2/AlBr_3}$ (Scheme 27); unfortunately, the solid-state structure of this compound could not be elucidated due to the low quality of the crystals obtained.[186]



Scheme 27

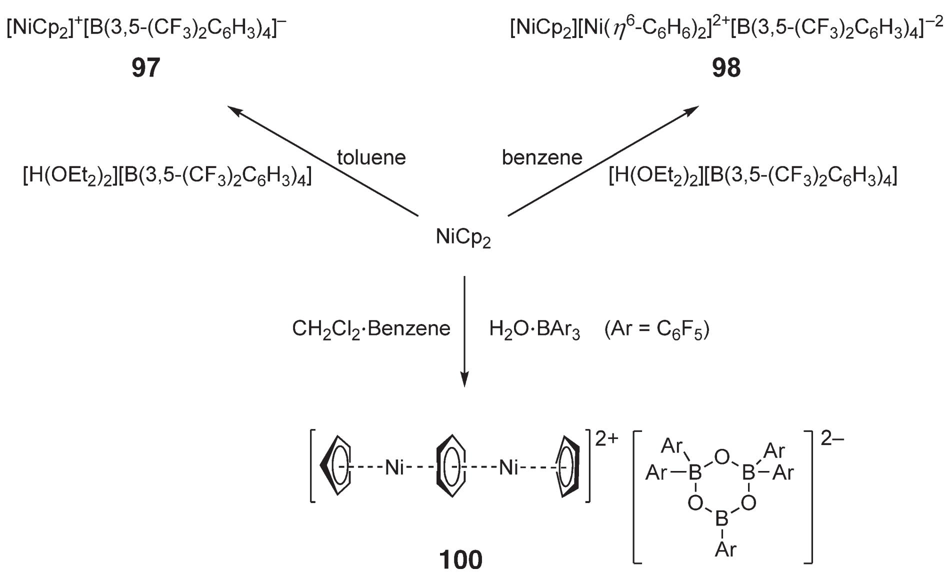
An interesting nickelocene derivative has been prepared by using a ferrocene-based bridge to connect two nickelocene units.[197] The three metallocene moieties in this trinuclear NiFeNi compound **96** adopt a *trans*,*cis*-arrangement of the Ni and Fe atoms relative to the bridging ligand. The solid-state structure shows that the bending about the Si—Si vector is smaller for the *cis*- than the *trans*-moiety; this means that the Me groups on the *trans* side are axial and equatorial, whereas those on the *cis* side are *syn* and *anti* with respect to the adjacent nickelocene. NMR spectroscopy has been used to study the structural distortions in solution and to examine the delocalization of spin density on the ferrocene and nickelocene units. The spin transfer from one metallocene to the next and to the Me groups has also been analyzed by MO studies.



96

An unsubstituted nickelocenium salt has been prepared by protonating nickelocene with Brookhart's acid, $[H(OEt_2)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$, in toluene, giving the green-blue nickelocenium **97** as the $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ salt (Scheme 28).[198] The magnetic moment of **97** is 1.69 μ_B, corresponding to only one unpaired electron. The Cp rings in **97** are eclipsed, as in nickelocene, but the average Ni–C distance is shorter in the cation (ca. 207 vs. 218 pm). When the protonation was carried out in benzene, the red-brown crystals contained the salt $[Ni(\eta^6\text{-}C_6H_6)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]_2$, **98**, and a molecule of neutral nickelocene as solvate (Scheme 28). On the other hand, protonation of nickelocene with $HBF_4{\cdot}Et_2O$ or $H_2O\text{–}B(C_6F_5)_3$ gave the triple-decker sandwich complexes **99** and **100**, respectively. Interestingly, the average Ni–C distance in the dication portion of **98** is very similar to that in nickelocenium (ca. 208 pm). The structure of **100** will be discussed later.

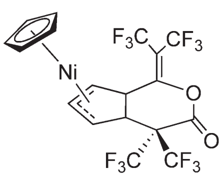
Mixed-sandwich derivatives of nickelocene have been prepared by substituting one of the Cp ligands by a hydrotris(pyrazolyl)borate anion (Tp⁻), an isoelectronic analog of Cp. For instance, golden-brown NiTpCp*, **101**, was obtained by reacting Ni(acac)Cp* with KTp, but the Cp analog was more difficult to generate reproducibly.[199] NiTpCp* can be oxidized by reaction with the ferrocenium cation, but the resulting dark



Scheme 28

brown cation is thermally unstable in solution. The solid-state structure of **101** showed that all three pyrazolyl moieties are coordinated to Ni with average Ni–N bond lengths of 209 pm that are similar to the corresponding distance in $NiTp_2$.[200] Interestingly, the average Ni–C bond length is much longer in **101** relative to nickelocene (225 vs. 216 pm), but similar to the average Ni–C bond length in $Ni(C_5Ph_4H)_2$.[201] The oxidation potential of **101** is only slightly different from that of nickelocene but it is significantly more difficult to oxidize this species relative to $Cp^*{}_2Ni$, indicating that Tp is a poorer electron donor compared to Cp^*.

The labile nature of the Cp ligands in nickelocene is manifested in various insertion and cycloaddition reactions with unsaturated moieties. One such reaction between nickelocene and 2 equiv. of bis(trifluoromethyl)-ketene has generated the cycloadduct **102** featuring a new allyl moiety. The solid-state structure of this compound has been elucidated. It is noteworthy that an earlier report had shown that the analogous reaction between nickelocene and dimethyl ketene leads to a very different species **103**, illustrating how the electronic nature of the incoming substrate can determine the reaction outcome. A recent report has shown that nickelocene undergoes a Diels–Alder-type reaction with an *o*-quinone that acts as a heterodiene. Thus, one of the Cp rings of $NiCp_2$ reacts with 3,6-di-*tert*-butyl-*o*-benzoquinone to form a π-allyl-type ligand that interacts with the Ni center in a trihapto fashion as in **104**.[202]



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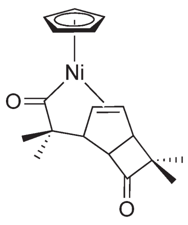

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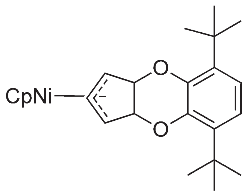
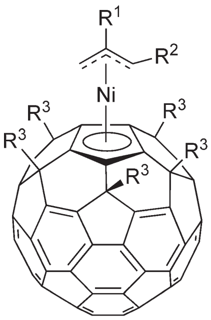


104

8.03.4.3.2 Monometallic complexes of Cp and its substituted derivatives

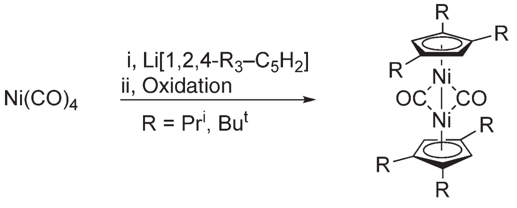
An interesting compound in which the Cp moiety is part of a substituted C_{60} derivative has been prepared by reacting the allyl dimers $[NiBr(R^1,R^2\text{-allyl})]_2$ with $K[C_{60}R^3{}_5]$.[203] The compounds $Ni(\eta^5\text{-}C_{60}R^3{}_5)(\eta^3\text{-}R^1,R^2\text{–allyl})$, **105**, and, in particular, the $C_{60}Ph_5$ derivative, are significantly more stable than the parent complex $NiCp(\eta^3\text{-allyl})$, underlining the importance of bulky substituents for kinetic stability of these compounds.



R^1, R^3 = Me; R^2= H
R^1, R^2 = H; R^3= Ph
R^2 = Me; R^2 = H; R^3 = Ph

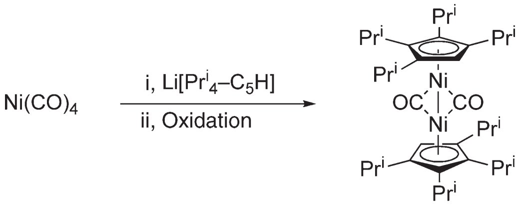
105

Highly substituted Cp ligands have also been used to prepare new analogs of previously studied CpNi complexes. For instance, the complexes $[Ni(R_nC_5H_{5-n})(\mu\text{-}CO)]_2$, **106**–$R_n$, new derivatives of the known $[NiCp(\mu\text{-}CO)]_2$, have been prepared by reacting $Ni(CO)_4$ with $M[R_nC_5H_{5-n}]$ followed by oxidation (Equations (7)–(9); M = Li, Na; R = Bu^t, $n = 3$; R = Pr^i, $n = 3, 4, 5$).[204] The analogous bromide-bridged dimers $[Ni(\mu\text{-}Br)(R_nCp)]_2$, **107**, have also been reported (Equation (10) and Scheme 27),[186] whereas the Cp or $\{(SiMe_3)_3C_5H_2\}$ analogs of these species are thermally unstable.[11] It is interesting to note that the 18-electron species **107**–R_3 and **107**–Pr^i_4 are paramagnetic, their magnetic moments corresponding to two unpaired electrons; as a result, their ^1H NMR spectra show very broad signals in the spectral region of 10–40 ppm. The reaction of **107**–Pr^i_4 with NaN_3 gives the analogous μ-azide dimer **108**, which can be converted into the monomeric diamagnetic PPh_3 adduct (Scheme 29). Reacting **107**–Pr^i_4 with phosphines or KPF_6/MeCN also gives diamagnetic, monomeric derivatives (Scheme 29). Moreover, reaction of the halide dimers with bulky aryloxides leads to 16-electron monomers or 18-electron dimers, depending on the steric bulk of the aryl group,[11,205] whereas reaction with disodium dichalcogenides gives the dinuclear dichalcogenides $[Ni(R_nC_5H_{5-n})]_2(\mu(\eta^2{:}\ \eta^2\text{-}E_2)$ (**109**, E = S, Se, Te; Scheme 29).[206] The solid-state structural studies of the latter have shown that the four-membered Ni_2E_2 rings allow significant interactions between the chalcogenide atoms, while electrochemical studies have shown both ligand- and Ni-based reductions that give mixed-valent Ni^{II}/Ni^{III} species.



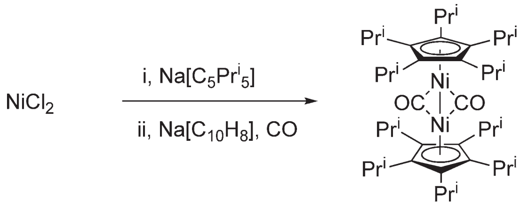
106-R_3

(7)



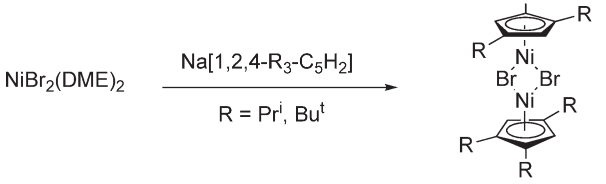
106-Pr^i_4

(8)



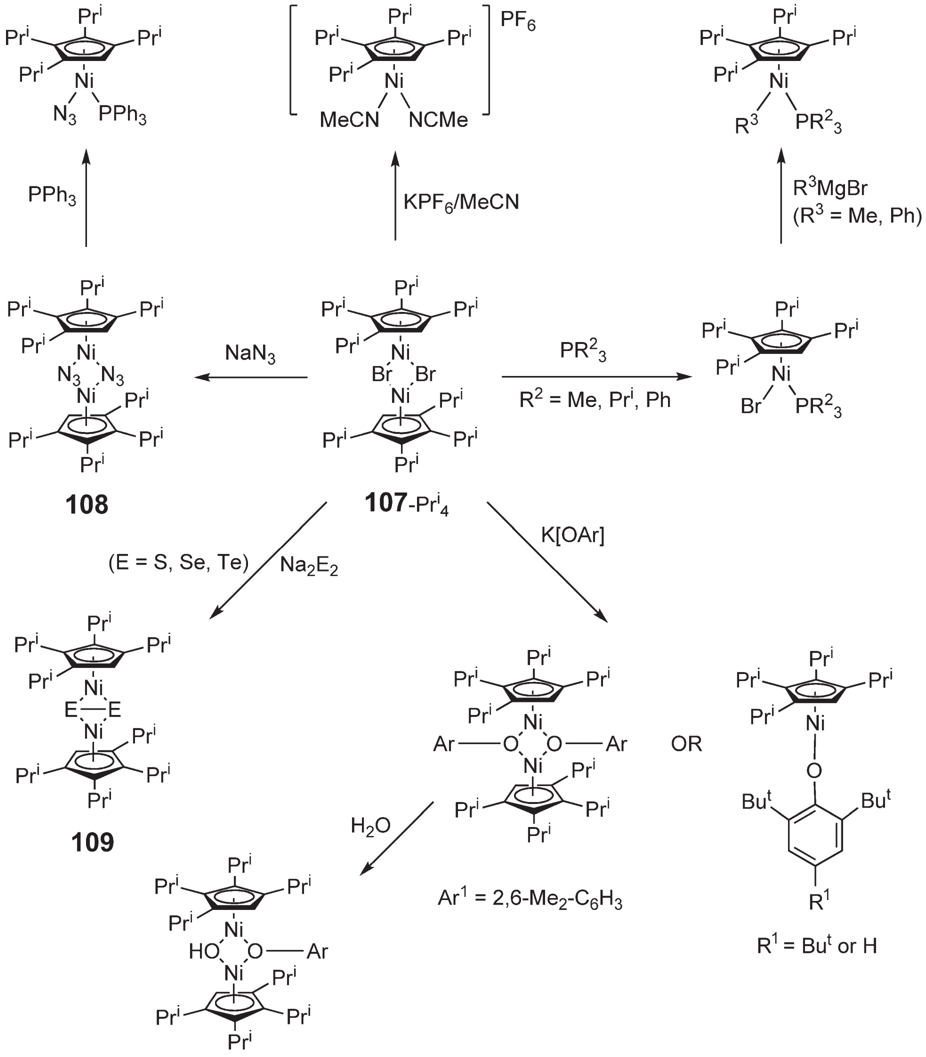
106-Pr$^i_5$

(9)

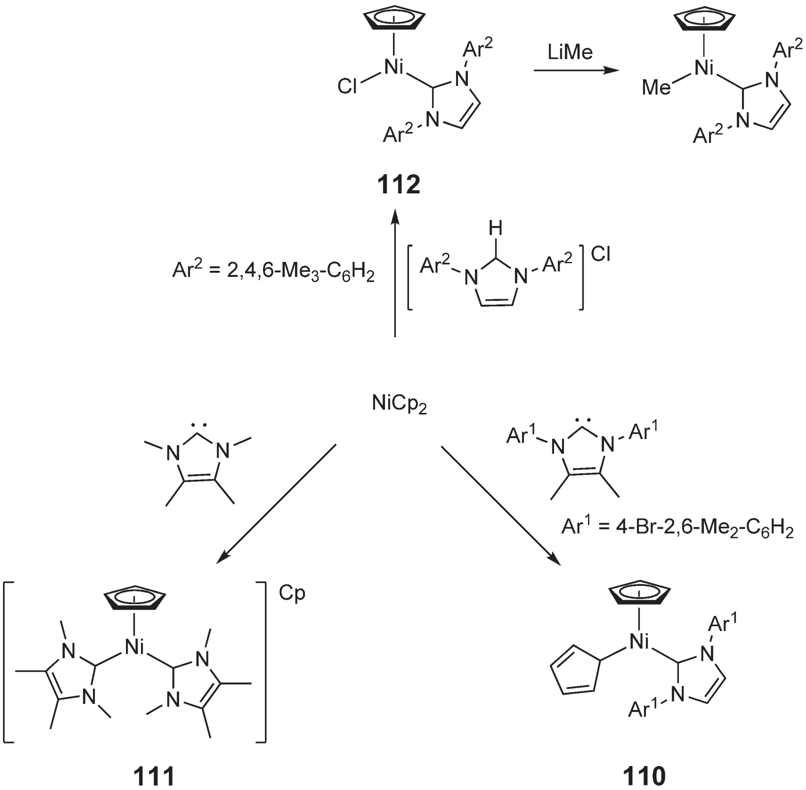


107-R$_3$

(10)



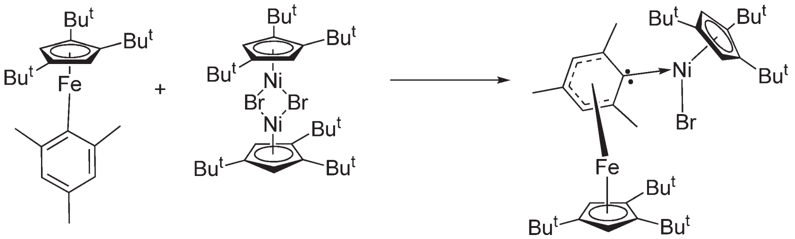
Scheme 29



Scheme 30

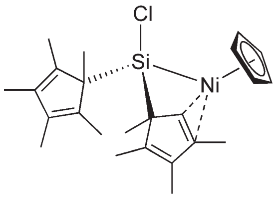
A new series of mono-Cp complexes featuring *N*-heterocarbenes have been reported. For instance, reacting nickelocene with 1 equiv. of the carbene 1,3-bis(4-bromo-2,6-dimethyl–phenyl)imidazol-2-ylidene gives Ni(η^5-Cp)-(η^1-Cp)(carbene), **110**, whereas using 2 equiv. of the less bulky carbene tetramethylimidazol-2-ylidene results in displacement of one of the Cp ligands altogether to give the bis(carbene) cation [NiCp(carbene)$_2$]$^+$, **111**, a complex featuring only Ni–C bonds (Scheme 30).[207] Alternatively, using imidazolium chlorides to protonate a Cp ligand gave the corresponding Ni–Cl derivatives, **112**, which was converted into the Ni–Me derivative, another complex featuring only Ni–C bonds.[208] Structural studies on **110–112** have shown that the Ni–C$_{\text{carbene}}$ bonds are shorter than the Ni–C$_{sp^3}$ bonds (ca. 189 vs. 202 pm).

Ni(Cl)Cp(carbene) complexes with the carbenes 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro imidazol-2-ylidene, 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydorimidazol-2-ylidene, and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene have also been prepared, structurally characterized, and shown to have catalytic activities in the aryl amination and aryl halide dehalogenation reactions.[209] Structurally similar carbene complexes have also been reported with the novel carbene formed by aryl → cyclohexadienyl–ylidene rearrangement, as shown in Equation (11); the solid-state structure of this complex has shown an Ni–C$_{\text{carben}}$ bond of ca. 189 pm.[210]



(11)

A cyclopentadienyl nickel complex featuring a rare Si–Ni linkage has been prepared by reacting SiCp$^*_2$ with Ni(Cl)Cp(PPh$_3$); the solution spectra and solid-state studies have identified the product as [CpNi{μ:η^2(Ni),η^1(Si)–(Cp*}-Si(Cl)(η^1–Cp*)], **113**.[211] The solid-state structure of **113** shows an Ni–Si bond length of 220 pm and a fairly symmetrical interaction between Ni and the η^2-Cp* (ca. 204 pm).

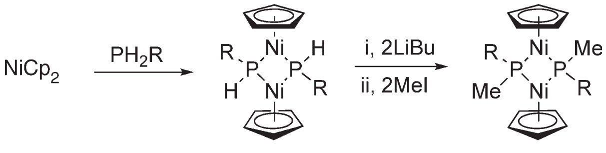


113

The reaction of nickelocene with primary phosphines has allowed the preparation of the phosphido-bridged dimers **114**; deprotonation and methylation of the phosphido moiety results in the formation of the methylated derivatives **115** (Scheme 31).[212] Analogous reactions with 2-phosphinophenolates give Ni(2-phosphinophenolato)Cp complexes.[213] Reaction of nickelocene with 1-norbornyl lithium and alkynes leads to NiCp(1-norbornyl)(η^2-RC≡CR) (R = Me, $SiMe_3$, Ph, CH_2OMe, CH_2NMe_2, CH_2OH). These complexes have been characterized by ^1H and ^{13}C NMR and mass spectroscopy.[214]

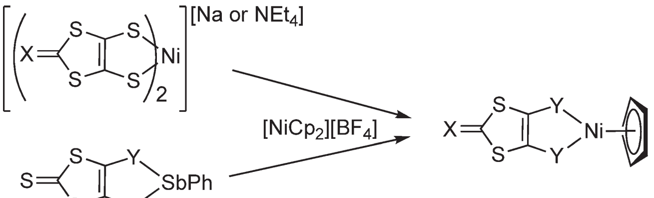
An unexpected reaction between nickelocenium and $Na[Ni^{III}(C_3S_5)_2]$ gave the Ni^{III} dithiolene species $Ni(C_3S_5)Cp$ (**116**, Scheme 32).[215] This reaction demonstrated that nickelocenium salts can be suitable sources of the $[NiCp_2]^+$ fragment. A close variant of this methodology has been employed recently to prepare an analogous series of compounds bearing related dithiolene ligands.[216] A combination of structural, spectroscopic, and computational studies has revealed that the unpaired electron in **116–118** (Scheme 32) is primarily delocalized on the dithiolene ligand. The solid-state structure of **116** shows symmetrical Ni–S distances (ca. 213 pm); moreover, these compounds show interesting three-dimensional intermolecular interactions that promote promising magnetic properties.

A large series of pentamethylcyclopentadienyl (Cp*) derivatives have been prepared by reacting Ni(acac)Cp*, which was shown to be a paramagnetic, 18-electron, spin-equilibrium molecule (*vide supra*),[217] with PEt_3 followed by addition of a variety of reagents such as LiMe, LiBr, PR_3, NaOMe.[218,219] Systematic structural studies of these complexes have led to interesting generalizations about the haptotropic distortions observed in the Cp* ring; these distortions range from a symmetrical allyl–ene to dienyl-type distortions (Scheme 33). In addition, the impact on the



114 **115**

Scheme 31



116: X, Y = S
117: X = O; Y = S
118: X = S; Y = Se

Scheme 32

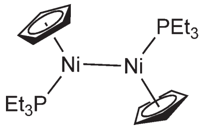
X = H, Me, Bz, Br, OMe, OAr, SAr, NHAr

Scheme 33

Ni–Cp interactions of the ligand *trans*-influence exerted by the other auxiliary ligands has been discussed and the following approximate *trans*-influence order has been suggested: alkyl, hydride > phosphine, methoxide > arylamide, aryloxide, arylthiolate, bromide. A study of the Ni–amido derivatives with Bronsted acids HX has led to the observation that the Ni–X bonds have a significant electrostatic component.

The unusual Ni(I) dimer $[Ni(\eta^5\text{-}Cp)(PEt_3)]_2$ **119** has been synthesized by reacting $NiCl(\eta^5\text{-}Cp)(PEt_3)$ with activated magnesium.[220] It is noteworthy that the related Pd(I) dimer **120** adopts a different structure featuring bridging Cp ligands.[221] The Ni–Ni bond distance in **119** (241 pm) is within the normal range expected for Ni^I–Ni^I species. The NMR spectra have indicated that the rotation around the Ni–Ni axis is hindered, presumably because of the steric hindrance caused by the PEt_3 ligands; the importance of the sterics is also suggested by the unsuccessful attempts to prepare the Cp^* or PPh_3 analogs of this compound.

The Ni–Ni bond in **119** is very reactive toward insertion reactions with group 16 elements, giving Ni^{II} thiolato, selenolato, and tellurolato complexes. For example, reaction with elemental sulfur or selenium yields the trinuclear species $\{Ni(\eta^5\text{-}Cp)\}_2(\mu_3\text{-}S)\{Ni(PEt_3)_2\}$ **121** and $[\{Ni(\eta^5\text{-}Cp)(PEt_3)\}(\mu^3\text{-}E)\{Ni(\eta^5\text{-}Cp)\}]_2$ (**122**; E = S or Se). On the other hand, the analogous reaction with Te gives $[Ni(\eta^5\text{-}Cp)(PEt_3)]_2(\mu\text{-}Te)$ **123**, whereas reaction with $(TeMes)_2$ at 80 °C has given the tellurolato complex $NiCp(TeMes)(PEt_3)$ **124**.[222] The insertion of $SnCl_2$ into the Ni^I–Ni^I bond of **119** gives $[Ni(\eta^5\text{-}Cp)(PEt_3)]_2SnCl_2$ **125**. The latter dimer reacts with alkyllithium to give compounds of the type $[Ni(\eta^5\text{-}Cp)(PEt_3)]_2SnR_2$, whereas reaction with activated magnesium yields $[Ni(\eta^5\text{-}Cp)(PEt_3)]_3SnCl$ **126**. These complexes have been characterized spectroscopically and by X-ray diffraction studies. A related series of Ni–chalcogenides of the type $Ni\{E\text{-}(p\text{-}X\text{-}Ph)\}(R^1\text{-}Cp)(PR^2{}_3)$ (R^1 = H or Me; R^2 = Ph, Bu, OPh, OEt, or OMe; E = S or Se; X = Cl or Br) has been prepared and characterized.[223] The chalcogen-based ligand in these complexes can use a lone pair on S or Se to bind SO_2 reversibly.



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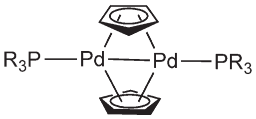

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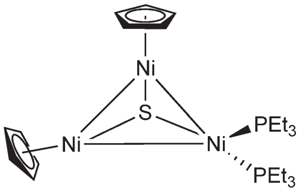

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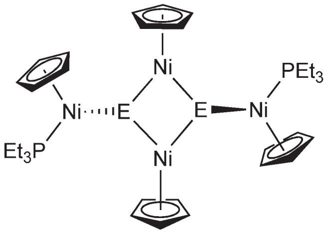
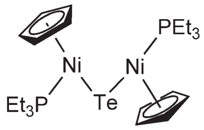


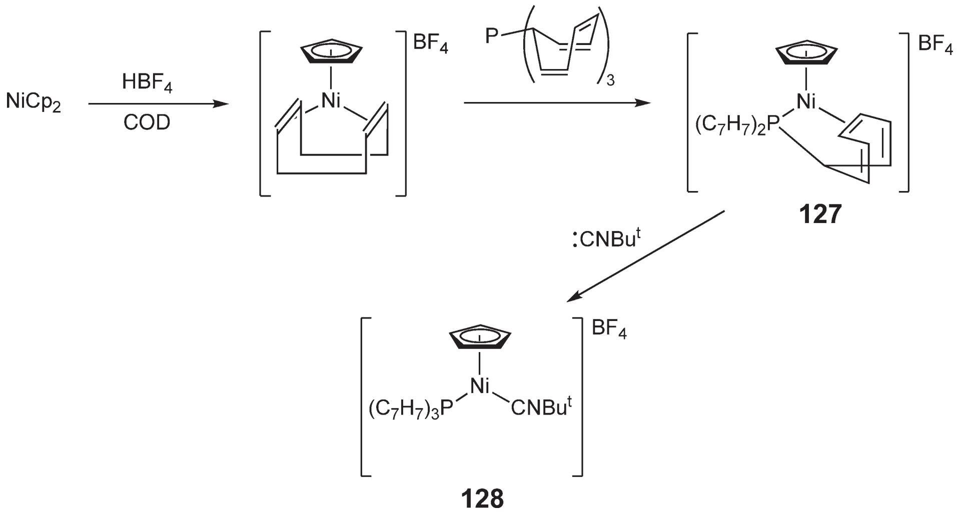
122: E = S or Se



123

8.03.4.3.3 Cationic complexes of the type $[CpNiLL']^+$

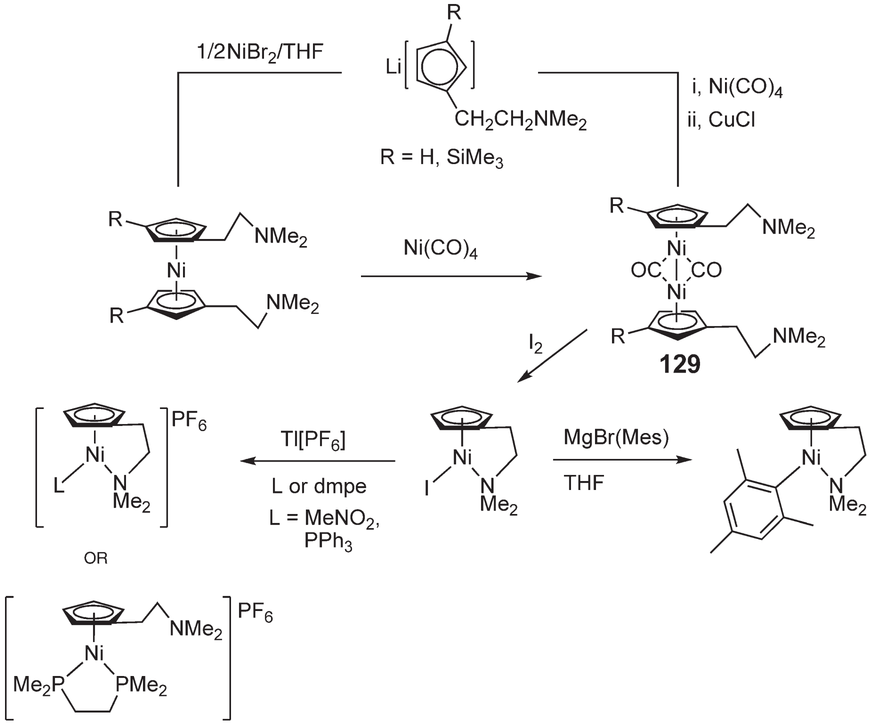
An interesting compound has been prepared via a two-step synthesis that converts $NiCp_2$ first into $[NiCp(cod)]^+$ and then into the corresponding cation in which the relatively labile cod ligand has been displaced by the multidentate ligand tris(1-cyclohepta-2,4,6-trienyl)phosphine, as shown in Scheme 34.[224] The solid-state structure of complex **127** (dark green) indicates that the Ni–C_{Cp} distance opposite from the olefin moiety is shorter than that opposite to the phosphine moiety (204 vs. 212 pm), implying a stronger *trans*-influence for the phosphine ligand. The chelate ring in **127** is fairly strong, since it does not open in the presence of excess PPh_3 or $P(OMe)_3$, but reaction with Bu^tNC: gives **128** as a dark red solid. The cationic complex $[NiCp^*(dippe)]BPh_4$ has been prepared. Structural characterization of this complex shows that the Cp^* ligand displays an allyl–ene interaction with the Ni center.[134]



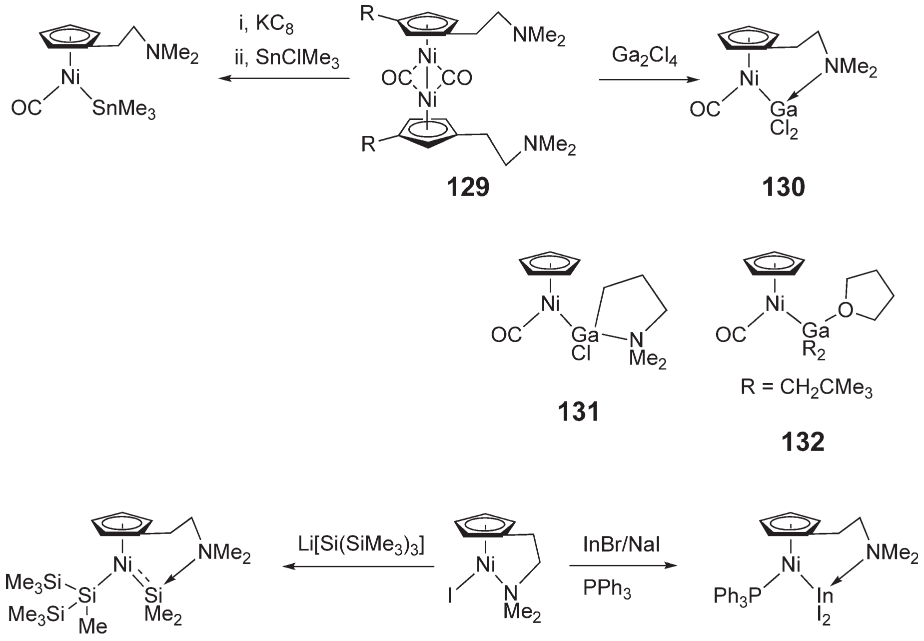
Scheme 34

8.03.4.3.4 Donor-functionalized Cp^L complexes

Functionalized cyclopentadienyl ligands Cp^L (^ = the tethering group linking L to Cp) have been used in diverse applications ranging from catalysis to materials chemistry and the preparation of electronic materials. A number of interesting Ni complexes bearing hemilabile (dimethylamino)ethyl–Cp have been reported (Schemes 35 and 36), whereas the analogous Ni–Cp^PR_2 complexes have not been reported, even though many such complexes are known for other metals. As is discussed later, the analogous Ni–Ind^PR_2 complexes are also difficult to isolate (*vide infra*).



Scheme 35



Scheme 36

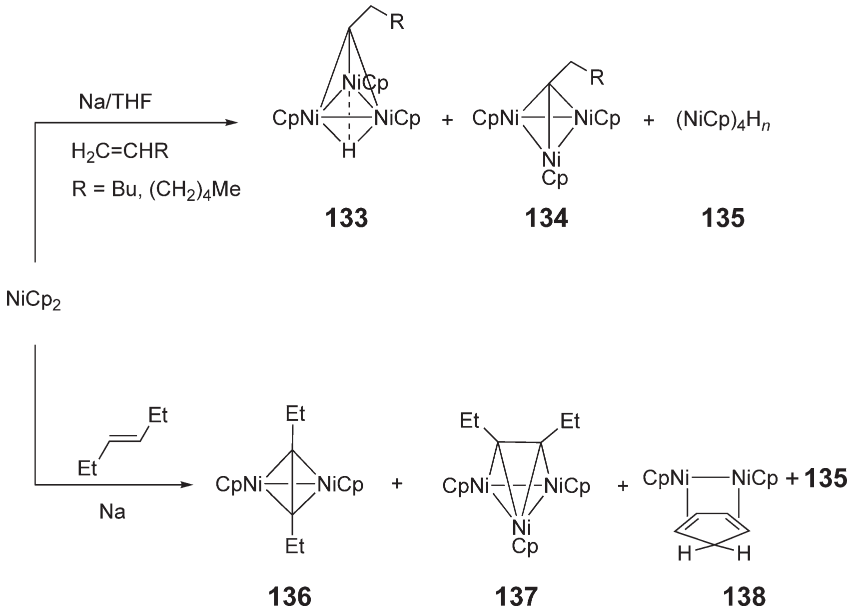
Synthetic routes have been reported for a series of Cp^NMe$_2$ complexes in which the tethered amino moiety coordinates to the Ni center, but the hemilabile character of this moiety allows the formation of species in which the Ni center is coordinatively saturated by other ligands, thus forcing the amino moiety into a dangling position (Schemes 35).[225] Compounds featuring Ni–MX$_n$ moieties (M = main group metals such as Ga, In, etc.) that are stabilized by the *N*-donor-functionalized Cp ligand have also been reported (Scheme 36).[226,227] For instance, reacting the dimeric Ni(I) species [Ni(CO){η^5(Cp),η^1(N)–Cp^NMe$_2$}]$_2$ (Cp^NMe$_2$ = $C_5H_4CH_2CH_2NMe_2$; **129**) with Ga_2Cl_4 gives the monomeric complex Ni(CO){η^5(Cp),η^1(Ga)–Cp^NMe$_2$·GaCl$_2$} (**130**, Scheme 36). Analogous complexes **131** and **132** in which the Ga moiety is stabilized differently have also been prepared, as shown in Scheme 36.[228] Structural characterization of **130** revealed a rather short Ni–Ga bond (228 pm) compared to **132** (241 pm)[229] and (NiGaCp*)$_4$(CO)$_6$ (244 pm).[230]

8.03.4.3.5 Polymetallic complexes of Cp and its substituted derivatives

8.03.4.3.5.(i) Products arising from reactions of nickelocene

A series of recent reports have shown that reacting nickelocene with various hydrocarbons in a reducing environment results in the formation of a family of novel complexes, as shown in Scheme 37. For instance, the reaction of nickelocene with 1-pentene or 1-hexene in the presence of metallic sodium gave the red, paramagnetic alkylidyne–hydrido clusters (NiCp)$_3$(μ_3-CR)(μ_3-H), **133** (R = Bu, (CH$_2$)$_4$Me) in addition to the known (NiCp)$_3$(μ_3-CR), **134**, and (NiCp)$_4$(μ-H)$_n$ (**135**, Scheme 37).[231] The solid-state structure of **133** shows that the bridging hydride ligand caps one face of the Ni$_3$ moiety. The solid-state structure of **135** has also been described.[239] Closely related trinickel μ_3-alkylidynes have been obtained from very different routes, by reaction of Ni(acac)Cp* or NiCp$_2$ with LiMe (*vide infra*).

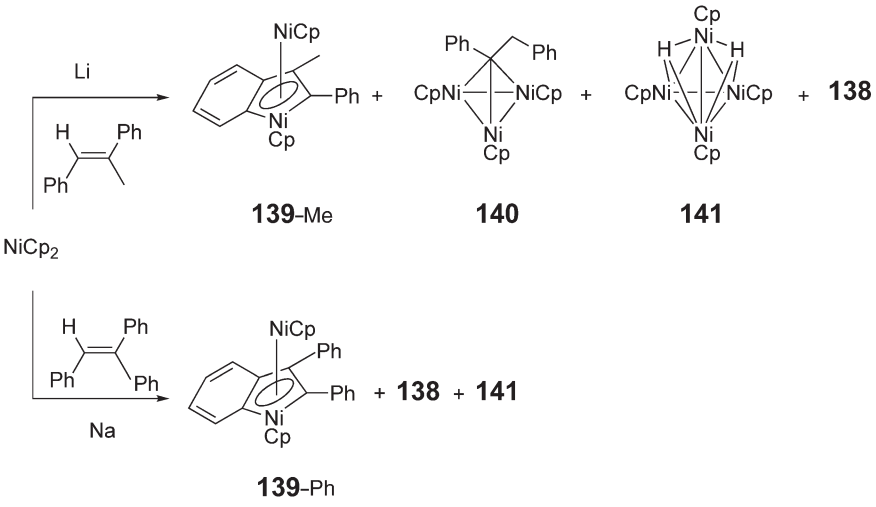
The analogous reactions with some internal alkenes have led to the formation of species bearing coordinated alkynes that arise from a net dehydrogenation of the alkene moiety. For instance, reacting nickelocene with Na and *trans*-3-hexene led to the formation of the 3-hexyne-coordinated species (NiCp)$_2$(μ,η^2-Et–C≡C–Et), **136**, and (NiCp)$_3$(μ_3,η^2)-Et–C≡C–Et), **137**, in addition to the known species **138** and **135** (Scheme 37).[232] The solid-state structure of complex **136** was not of sufficiently high quality to provide the main features precisely, but the structure of complex **137** showed that the bridging alkyne moiety is closer to two of the three Ni centers (ca. 189 ppm vs. 200 pm) even though the three Ni–Ni distances are fairly uniform (237–242 pm). The C_{sp}–C_{sp} distance is fairly long (137 pm), reflecting the extensive $2\sigma + \pi$ interactions with the Ni$_3$ moiety.



Scheme 37

A new set of products have been obtained from analogous reactions involving Ph-substituted internal alkenes. Thus, the reaction of nickelocene with Li in the presence of (*E*)-PhC(H)═C(Me)Ph has led to the following four species: the nickelanickelocene-type compound (η^5-Cp)(η^5-(1-(η^5-Cp)-2-phenyl-3-methyl-1-nickela-indenyl)nickel, 139–Me, the μ_3-alkylidyne species 140, the dinickel compound $(NiCp)_2(\mu\text{-}CpH)$, 138, and the tetrameric cluster $(NiCp)_4(\mu\text{-}H)_2$, 141 (Scheme 38).[233–235]

Compound 139–Me is obtained as brown solids in 1–2% yields; like its analogous nickelocene, this compound is paramagnetic. The solid-state structure of 139–Me showed that the nickelaindenyl moiety has unsymmetrical interactions with the CpNi, with unequal bonds to the benzo (221 and 225 pm) and vinylic (212 and 219 pm) carbon atoms; the Ni–Ni distance is 242 pm. The analogous reaction with Na and PhC(H)═CPh_2 gave the Ph derivative 139–Ph, in addition to 138 and 141 (Scheme 38). Paramagnetic 139–Ph has been identified by its EIMS spectrum (m/e = 500).



Scheme 38

The μ_3-alkylidyne species **140** displayed a characteristically downfield ^{13}C signal at 294 ppm. The solid-state structure of this complex has shown that the Ni–Ni distance is 241 pm, the average Ni–C_{Cp} distances are 212 pm, and the Ni–C distances for the ligating C atoms of the bridging cyclopentadiene are fairly unsymmetrical (192 and 202 pm); the μ-CpH ring is puckered, with the sp^3-C pointing away from the Ni–Ni axis.

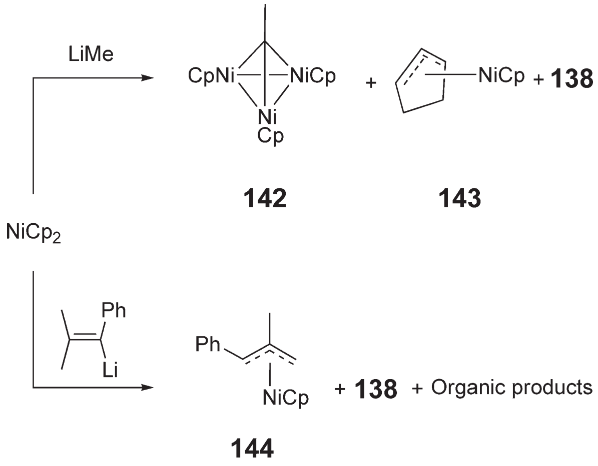
The cluster **141** is diamagnetic and displays informative NMR spectra. For example, its ^{1}NMR spectrum showed a sharp singlet at ca. 5.3 ppm for the Cp protons and a fairly broad signal at ca. –20 ppm (linewidth ~ 5 Hz) for the hydrido ligands, whereas the $^{13}C\{^1H\}$ NMR spectrum shows only one signal at ca. 83 ppm for the Cp carbon nuclei. The Ni–Ni distances in the cluster range from 238 to 242 pm.

Novel products have also been isolated from the reactions of nickelocene with organolithium or Grignard reagents in the absence or presence of alkenes or alkynes. For example, reaction of nickelocene with LiMe gave $(NiCp)_3$-$(\mu_3$-CMe), **142**,[236,237] along with the previously known complex NiCp(η^3-C_5H_7), **143**,[238] and the blue dinickel compound $(NiCp)_2(\mu$-CpH), **138**,[239] (Scheme 39). Reacting $NiCp_2$ with 2-methyl-1-phenyl-propenyl-lithium also gave **138**, along with NiCp(η^3-$CH_2C(Me)CH(Ph)$), **144**, and a range of organic products, including $(Me_2C{=}CPh)_2$ (Scheme 39). It is noteworthy that the analogous reaction of Ni(acac)Cp* with LiMe gives only $(NiCp^*)_3(\mu_3$-CH)-$(\mu_3$-H), **145**.[187] This 49-electron cluster has one unpaired electron ($\mu = 1.77\mu_B$ in solution) in its SOMO and shows a relatively low $\nu(Ni_3(\mu_3$-H) frequency at 981 cm^{-1} (682 for μ_3-D).

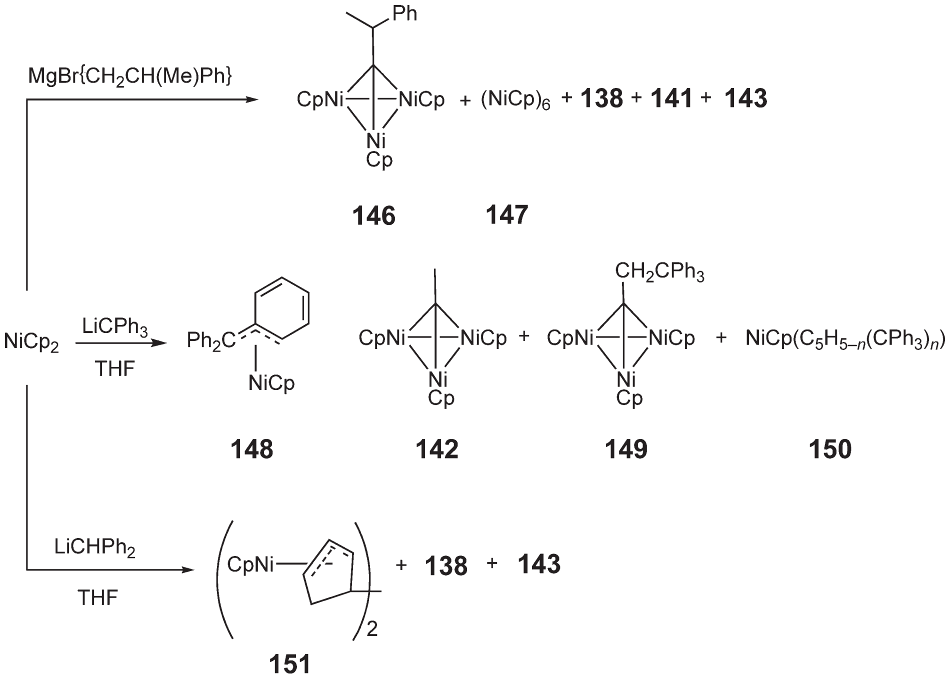
The reactions of nickelocene with MgBrR (R = Et, Pr, $(CH_2)_7$Me, and $CH_2CH(Me)Ph$) have shown that μ-alkylidyne trinickel species can be formed in the presence of β-hydrogens in the R group.[240] The reaction with MgBr{$CH_2CH(Me)Ph$} was particularly informative on the involvement of α- and β-H eliminations in such transformations and illustrated some of the multitude of mechanistic steps involved in these reactions. This reaction resulted in the formation of the cluster $(NiCp)_3\{\mu_3$-CCH(Me)Ph}, **146**, in addition to the above discussed species **138,141,143**, and the previously reported $(NiCp)_6$[241] (**147**, Scheme 40). The solid-state structure of complex **146** shows relatively short Ni–$C_{alkylidyne}$ bonds (184–188 pm), Ni–Ni–Ni angles of ca. 60°, and Ni–C–Ni angles of ca. 78°.

Formation of complex **146** implies that the presence of α-hydrogens is responsible for the formation of alkylidyne species. Indeed, reactions of nickelocene with $LiPh_2CH$ and $LiCPh_3$ have shown that new products arise if two α-hydrogens are not present, as follows.[242] Reacting nickelocene with $LiCPh_3$ in THF gives the allyl derivative NiCp(η^3-CPh_3) **148** as the main product; small amounts of the alkylidyne species $(NiCp)_3(\mu_3$-CR) (R = Me **142**, CH_2CPh_3 **149**) as well as mono- and dialkylated nickelocenes NiCp{η^5-$C_5H_{5-n}(CPh_3)_n$} (**150**; n = 1, 2) also formed (Scheme 40). The analogous reaction with $LiCHPh_2$ also leads to the formation of allyl species, but in this case, the allyl moiety consists of two Cp fragments coupled to each other and forming a bridging diallyl ligand. Other products included alkylated nickelocenes and the above discussed $(NiCp)_2(\mu,\eta^2,\eta^2$-$C_5H_6)$, **138**, and NiCp($\eta^3$-Cp), **143** (Scheme 40). The dimeric species **151** was characterized by X-ray crystallography and showed standard Ni–C distances for the Cp and allyl moieties.

Reacting nickelocene with organolithium reagents in the presence of alkenes or alkynes generates a number of unusual species. For instance, the reaction of nickelocene with LiPh in the presence of 1-decene in THF gave



Scheme 39



Scheme 40

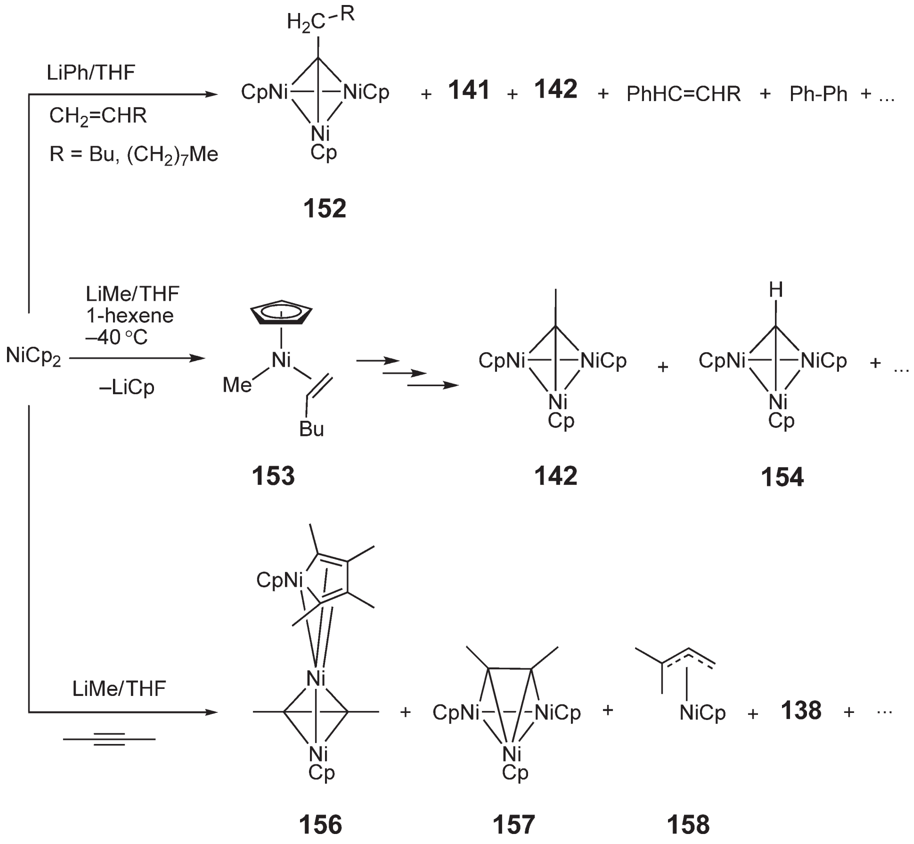
$(NiCp)_3(\mu_3\text{-}CR)$ (R = Me **142**, $(CH_2)_7CH_3$ **152**) along with the tetranickel cluster **141** and a mixture of organic products (Scheme 41).[243,244] It is noteworthy that the closely related complexes $(NiCp)_4(\mu\text{-}H)_n$ ($n = 1$ or 3; **135**) have also been obtained from the reaction of nickelocene with sodium naphthalide in THF[241] or by reacting Ni(NO)Cp with $AlCl_3$ and $LiAlH_4$.[245–247] In contrast to **141** (*vide supra*), **135** are paramagnetic.

The reaction of nickelocene with LiMe in the presence of 1-hexene gives NiCp(Me)(η^2-1-hexene), **153**, which was identified on the basis of ^{1}H NMR. Subjecting this species to chromatography on alumina produced a number of compounds, including the two trinickel μ-alkylidyne clusters **142** and **154** featuring face-capping ethylidyne and methylidyne ligands, respectively (Scheme 41).[248] It is noteworthy that the methylidyne proton in **154** resonates at ca. 12.9 ppm! Analysis of **154** by X-ray diffraction has located the methylidyne hydrogen, showing a $C_{methylidyne}$–H distance of ca. 90 pm. Most other structural features of this complex are similar to those of analogous alkylidyne clusters discussed above.

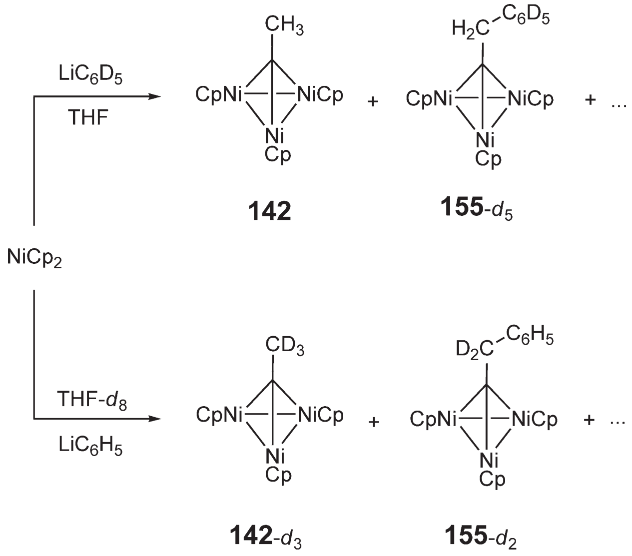
The unexpected formation of alkylidyne species in the above reactions hints at the possible involvement of the solvent in these reactions. An interesting D-labeling study has substantiated this possibility, as follows. Thus, reacting nickelocene with LiC_6D_5 in THF and with LiC_6H_5 in d_8-THF gave $(NiCp)_3(\mu_3\text{-}CR)$ with R being CH_3 (**142**) and $CH_2C_6D_5$ (**155**)-d_5 for the first reaction, and CD_3 (**142**)-d_3 and $CD_2C_6H_5$ (**155**)-d_2 for the second reaction (Scheme 42).[249] The cleavage of THF has been invoked to rationalize these observations.

Reactivities of nickelocene with alkynes have also been probed. For example, reaction of nickelocene with 2-butyne and LiMe produces the novel, 65-electron, paramagnetic tetranickel cluster $(NiCp)(\mu,\eta^2,\eta^2\text{-Me–C}{\equiv}\text{C–Me})Ni\{\eta^5\text{-}(Ni(Cp)C_4Me_4)\}$, **156**, in addition to the new μ^3-alkyne cluster $(NiCp)_3(\mu_3\text{-Me–C}{\equiv}\text{C–Me})$, **157**, the allyl species Ni(Cp)(η^3-1,1-dimethylallyl), **158**, and the known **138** (Scheme 41).[250–252] Examination of the solid-state structure of **156** has revealed that the nickelacyclopentadiene ring is nearly planar, with fairly normal C_{vinyl}–Ni bonds of 186 and 190 pm. Once the four Ni–Ni bonds are taken into account, the formal electron count reveals three 18-electronic CpNi moieties and a 19-electron NiL_2 moiety.

When nickelocene is reacted with phenyl- or methyllithium in the presence of bis(trimethylsilyl)acetylene instead of 2-butyne, a number of interesting species are formed. For example, the reaction with phenyllithium gives the μ-alkyne dimers $(NiCp)_2(\mu,\eta^2,(\eta^2\text{-}Me_3Si\text{–C}{\equiv}\text{C–}SiMe_3)$, **159**, and $(NiCp)_2(\mu,\eta^2,\eta^2\text{-}Me_3SiC{\equiv}CPh)$, **160**, and the μ-1,3-butadiyne tetramer $(NiCp)_4(\mu,\mu,\eta^2,\eta^2,\eta^2,\eta^2\text{-}Me_3Si\text{–C}{\equiv}\text{C–C}{\equiv}\text{C–}SiMe_3)$, **161**, whereas the methyllithium reaction gives **159**, **161**, and the butadiyne-coordinated dimer $(NiCp)_2(\mu,\eta^2,\eta^2\text{-}Me_3Si\text{–C}{\equiv}\text{C–C}{\equiv}\text{C–}SiMe_3)$, **162**.[253] The formally Ni(I) centers in compounds **159** and **161** are within 190–200 pm of the alkyne carbons, 170–180 pm of the

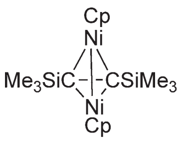


Scheme 41



Scheme 42

center of the Cp ligand they are coordinated to, and 230–240 pm of the Ni center they are bonded to directly. The alkyne C_{sp}–C_{sp} distance in 159 is fairly long (141 pm) and the Si–C_{sp}–C_{sp} angle is ca. 146°. In the diyne complex 161, the two C_{sp}–C_{sp} distances in the multiply bonded moieties are ca. 135 pm and the distance between the two alkyne moieties is ca. 146 pm.



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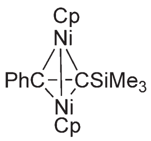

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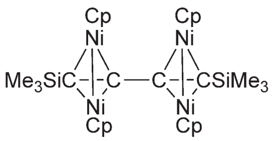

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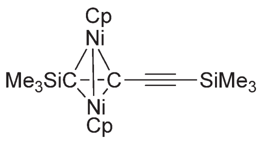
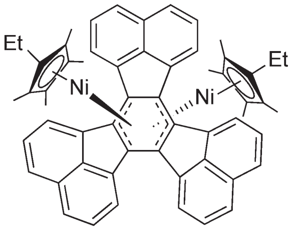


162

8.03.4.3.5.(ii) Multimetallic derivatives from non-nickelocene sources

The reaction of Ni(acac)(η^5-C_5Me_4R) with variously substituted azulenyl anions yields a series of paramagnetic dinickel complexes **163** in which the azulenyl ligand bridges the two Ni(η^5-C_5Me_4R) moieties via its five-membered ring and the pentadienyl moiety of the seven-membered ring, as shown in Scheme 43.[254] Cyclic voltammetry studies of **163** have shown that one-electron reduction brings about ring slippage at the Cp moiety of the azulenyl ligand in the anionic **164**. The related compounds **165–172** were also prepared by the analogous reaction of Ni(acac)(η^5-C_5Me_5) with magnesium anthracene or dianions of pyrene and perylene (Scheme 43).[255]

Analogously to the above syntheses, the reaction of Ni(acac)(η^5-Me_4EtC_5) with the decacyclide dianion $[C_{36}H_{18}]^{2-}$ gave black crystals that were identified as the triple-decker complex $[Ni(\eta^5\text{-}Me_4EtC_5)]_2(\mu\text{-}C_{36}H_{18})$, **173**, on the basis of NMR spectra and X-ray analysis.[256] The Ni centers are equally displaced by 172 pm on opposite faces of the central benzene ring of the bridging decacyclene moiety. The η^3-enyl bonding interaction between the Ni centers and the benzene ring distorts this otherwise planar ring into a chair conformation with ca. 25° hinge angles between the planes of the trihapto-coordinated C_3 moieties and the central C_4 plane. The Cp^* analog of **173** has also been reported.[257] The bridging decacyclene ligand in these complexes is quite labile and the possibility of its facile displacement makes these complexes suitable sources of the 15-electron CpNi fragments. Thus, reaction of **173** with RE–ER (E = chalcogenides) gives the dimers $[Ni(\mu\text{-}ER)(\eta^5\text{-}Me_4EtC_5)]_2$ (ER = SPh **174**, SeMes **175**, TeMes **176**, Te(naphthyl) **177**). The analogous reaction of **173** or its Cp^* homolog with azobenzene gives the products of an orthometallation reaction as intense, bright blue solids Ni(*o*-C_6H_4-N_2Ph)(η^5-$Me_4(CH_2R)C_5$), **178**, which were analyzed by NMR, UV–VIS, and photoelectron spectroscopy. The reaction of **173** with an intramolecular donor-stabilized plumbylene gave the (*R*,*S*)-Ni(η^5-Me_4EtC_5)[η^1,η^1- ((dimethylamino)methyl)ferrocenyl], **179**, as a racemic mixture. The solid-state structure of **179** has been studied by X-ray analysis.



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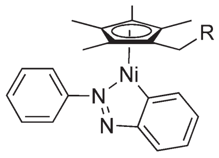
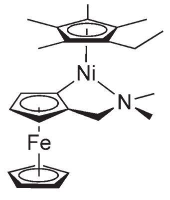


178: R = H, Me

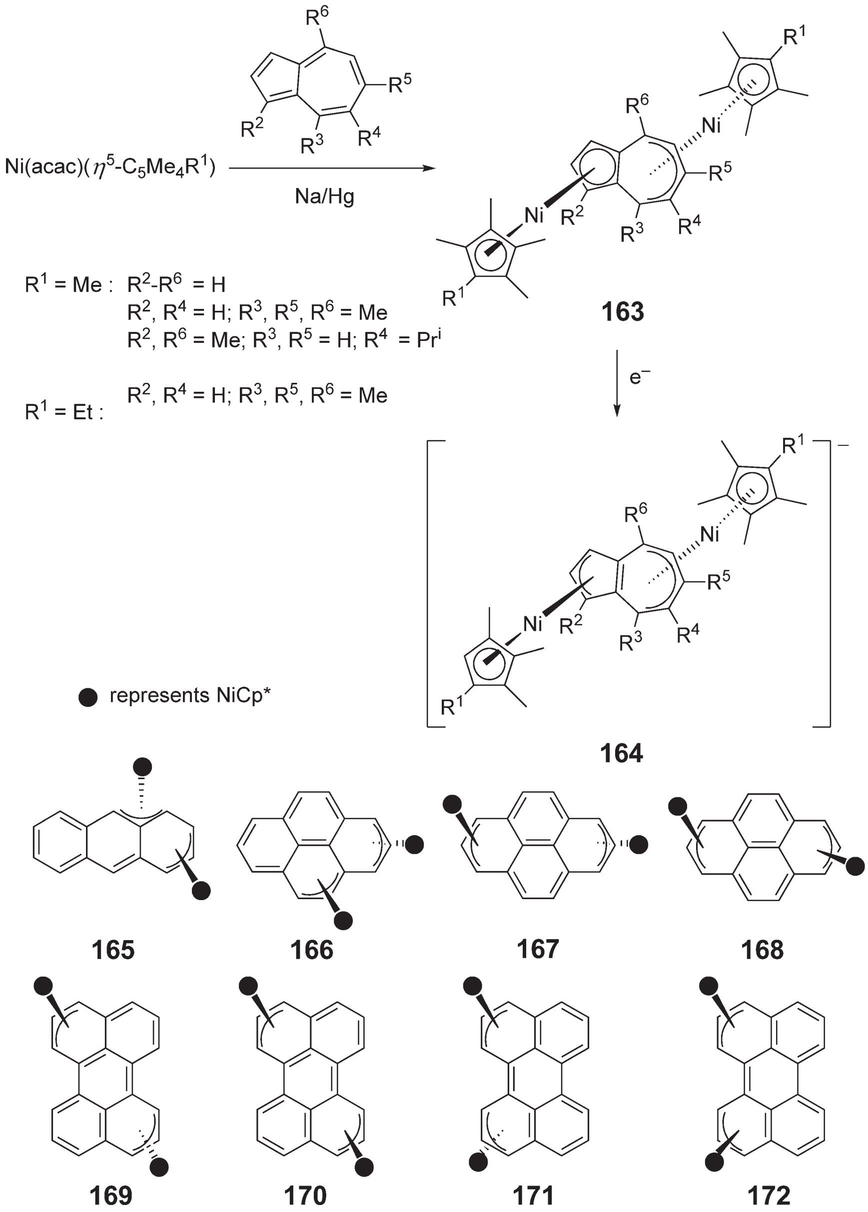


179

The dinuclear dications $[\{Ni(PPh_3)_2\}_2\{\mu\text{-}CMe_2(\eta^5\text{-}C_5H_4)_2\}][PF_6]_2$, **180**,[258] and $[\{Ni(CNR)(PPh_3)\}_2\{\mu\text{-}CMe_2(\eta^5\text{–}C_5H_4)_2\}][PF_6]_2$, **181**,[259] have been prepared and structurally characterized. The latter complexes catalyze the non-living polymerization of the isocyanide *S*-(–)-C≡NCH(Ph)Me to materials possessing M_n values of ca. 50×10^3 Da; the proposed mechanism of the polymerization reaction involves migratory insertion of the isocyanide into the Ni-(η^1-Cp) moiety. The compounds $[(NiCp^*)_2(\mu,\eta,\eta\text{-indacenyl})]^{n+}$ (**182**; $n = 0, 2$)[260] have been structurally characterized.

A series of Ni–Mn cluster compounds have been prepared by reacting $[NiCp(CO)_2]_2$ with various sources of Mn and chalcogenides, as shown in Scheme 44.[261] The clusters 183 and 187 are paramagnetic species with one unpaired electron that occupies a low-lying antibonding orbital delocalized unequally across the Ni_2Mn moiety.

A series of bimetallic complexes of the type $NiCp^1(\mu,\eta^2,\eta^2\text{-}HC{\equiv}CCMe_2OMe)M(CO)_2(Cp^2)$ (M = Cr, Mo, Cr; Cp^1 = Cp or Cp^*; Cp^2 = Cp or 1-Me-Cp) have been prepared and used as scaffolding for transforming alkyne ligands.[262–267] Thus, reacting $NiCp(CO)M(CO)_3$(1-Me–Cp), 188, with the propargyl ether HC≡CCMe$_2$(OMe) gave the complexes $NiCp[\mu,\eta^2,\eta^2\text{-}HC{\equiv}CCMe_2(OMe)]M(CO)_2$(1-Me–Cp), 189, and $NiCp[\mu\text{-}C(O)C(CMe_2\text{-}(OMe)){=}CH]M(CO)_2$(1-Me–Cp), 190, (M = Mo, W; Scheme 45).[268] Reaction of 189–Mo and 190–Mo with HBF_4 converted the bridging moieties into a μ-allenyl by loss of methanol; the analogous reaction with



Scheme 43

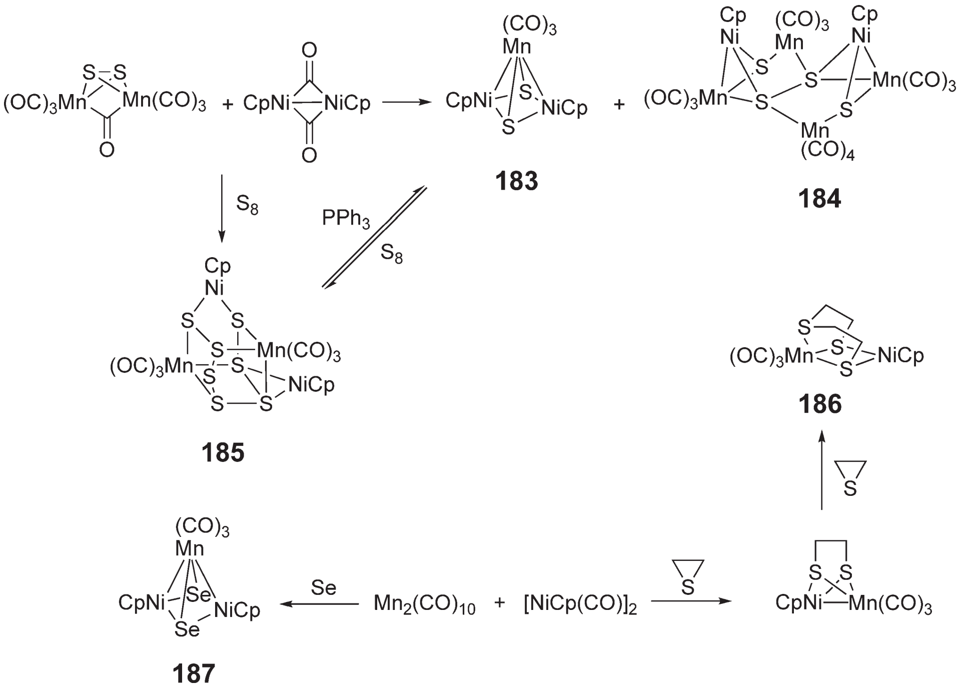
189–W did not give an isolable product, while that of **190**–W resulted in an unusual protonation of the carbonyl moiety and subsequent formation of a novel cationic tungstacylce that acts as an η^3-allyl to Ni (**192**; Scheme 45).

A number of multimetallic compounds bearing various CpNi and carborane fragments have been reported and are discussed in the section dedicated to carborane compounds (*vide infra*).

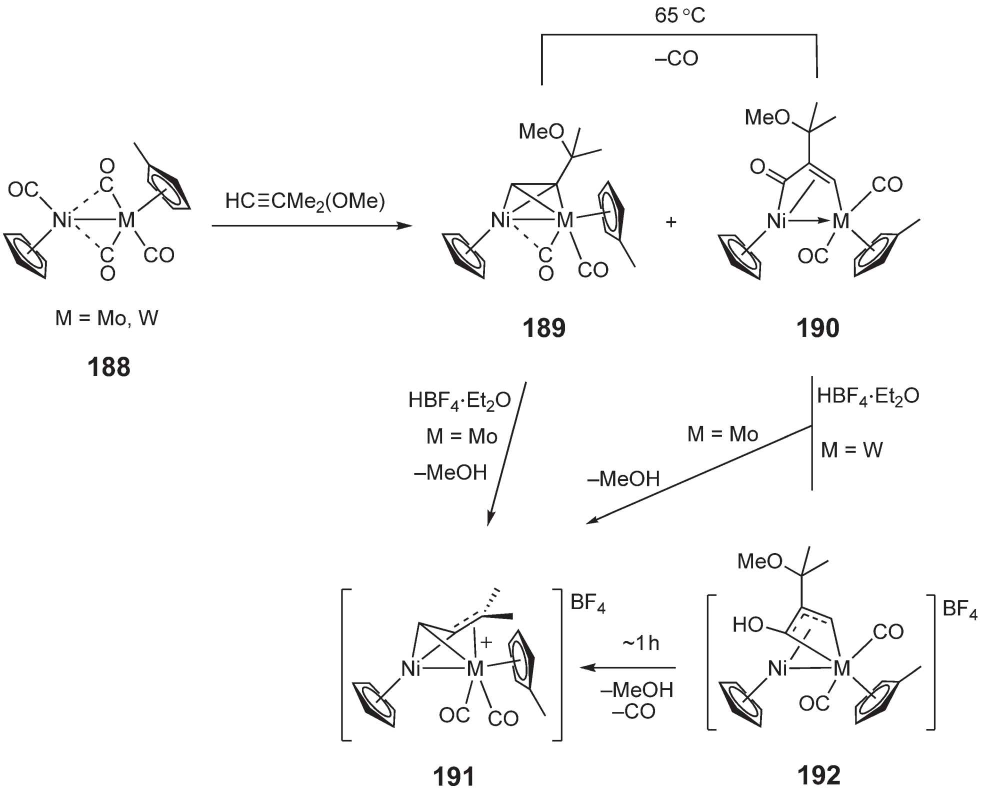
8.03.4.4 Ni–Indenyl Complexes

8.03.4.4.1 General comments

Ind complexes of transition metals have been studied since the 1960s, and it has been shown that in some cases these complexes possess greater reactivities in comparison to their closely related Cp counterparts. This phenomenon, the so-called indenyl effect, is believed to arise from the flexible and responsive nature of M–Ind bonding, which



Scheme 44



Scheme 45

facilitates a number of interesting stoichiometric and catalytic reactions. The bonding mode adopted by the Ind ligand in a given complex depends strongly on the electronic configuration of the metal (d^n) and its formal electron count. Therefore, electronically saturated compounds, and, in particular, those of electron-rich late transition metals, would be expected to display various degrees of slip-fold distortions π^{1-5}-Ind).

Curiously, very few IndNi complexes were studied prior to the 1990s, and little was known on the structures and reactivities of these complexes beyond a few sporadic reports on $NiInd_2$. This situation has changed over the past decade with the publication of dozens of reports on the structures and reactivities of Ni^{II}Ind complexes Ni(X)Ind(L) and $[NiInd(L)L']^+$. Some of these complexes have also been shown to be competent pre-catalysts for a number of reactions. These developments have been reviewed recently[16] and are discussed below.

8.03.4.4.2 Theoretical and physical studies

The electronic and structural properties of $NiInd_2$ have been studied to probe the relationship between the number of valence electrons on the Ni center and the extent of slip-fold distortions in the hapticity of Ind. For instance, MO analyses reported in a theoretical treatment of bonding in Ind complexes indicate that going from $FeInd_2$ to $NiInd_2$ is tantamount to adding two extra electrons to the high-lying LUMO of $FeInd_2$.[269] Since this LUMO has metal–indenyl antibonding character, the Ind ligands bend (or fold) to minimize destabilizing interactions, and the Ni–Ind bonding is weakened as a result. The formal electron count for the Ni center in $NiInd_2$ can thus be considered to be between 16 and 18 electrons; in other words, the flexible hapticity of the Ind ligands allows this complex to avoid the formal electron count of 20. This is in contrast to the situation in the analogous $NiCp_2$ where the extra pair of electrons (relative to ferrocene) are localized in the degenerate, antibonding ligand orbitals, leading to a nearly uniform lengthening of the Ni–C distances and rendering this compound paramagnetic.[270]

In addition to the differences in the ground-state structures of nickelocene and $NiInd_2$, there is some preliminary evidence suggesting that the excited states of these complexes are also different. For instance, the UV–VIS spectrum of $NiInd_2$ shows an intense, broad absorption band (with a bandwidth of ca. 5,000 cm^{-1}) in the green spectral region with its maximum at 20,200 cm^{-1} (ca. 500 nm) and a molar absorptivity of 3,180 M^{-1} cm^{-1}.[271] In comparison, the lowest energy absorption band for nickelocene is in the red spectral region, with a maximum at 14,500 cm^{-1} (ca. 700 nm) and a molar absorptivity of 60 M^{-1} cm^{-1}.[272–274] Moreover, no luminescence is observed for $NiInd_2$ at temperatures greater than 5 K, whereas nickelocene shows weak, near-infrared luminescence under the same conditions.

The UV–VIS spectra of the neutral complexes Ni(X)Ind(L) have shown that their electronic structures are typical of other d^8-compounds in that they possess two absorption bands in the visible region of the spectrum (ca. 600–400 nm). EHMO calculations on $Ni(Cl)(1\text{-}Me\text{-}Ind)(PPh_3)$ and $Ni(1\text{-}Me\text{–}Ind)Me(PPh_3)$ point to HOMO–LUMO gaps of ca. 20,000 cm^{-1} (2.5 eV) and 22,000 cm^{-1} (2.7 eV), respectively.[271]

Variable-temperature NMR studies have shown that some [Ni(X)Ind(L)] and $[NiIndLL']^+$ complexes display significant energy barriers to the rotation of the Ind ligand about the Ni–Ind axis: $Ni(Cl)(1,3\text{-}Me_2\text{-}2\text{-}Ph\text{-}Ind)(PPh_3)$ (>16.9 kcal mol^{-1}), $Ni(Cl)(2\text{-}Ph\text{-}Ind)(PPh_3)$ (16.5 kcal mol^{-1}), $Ni(Cl)Ind(PPh_3)$ (ca. 16 kcal mol^{-1}), $Ni(Cl)(1,3\text{-}Me_2\text{-}Ind)(PPh_3)$ (15.6 kcal mol^{-1}), $[Ni(1\text{-}Me\text{-}Ind)(PPh_3)_2]^+$ (ca. 14 kcal mol^{-1}), and $NiInd(Me)(PPh_3)$ (ca. 10 kcal mol^{-1}).[16] A series of NiInd complexes have been studied by cyclic voltammetry and shown to undergo irreversible reductions at potentials ranging from –1.16 to –2.33 V (vs. SCE). These electrochemical measurements are in fairly good agreement with the results of solution NMR and X-ray crystallographic data that signal a correlation between the apparent electron richness of the Ni center and the Ind–Ni and Ind–phosphine interactions; an empirical correlation was also noted between the Ind hapticities (ΔM–C), Ni–P distances, reduction potentials, and ^{31}P NMR chemical shifts. These observations have been interpreted in terms of the hard–soft acid–base theory.[275]

8.03.4.4.3 Synthetic and reactivity studies

8.03.4.4.3.(i) $NiInd_2$ and Its derivatives

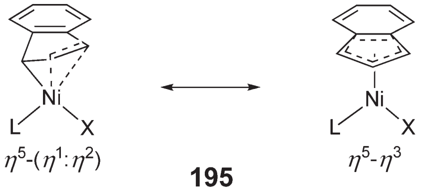
$NiInd_2$ was first reported in 1969 by Köhler who described its preparation from $Ni(acac)_2$ and MgBrInd, and discussed its ^1H NMR and mass spectra as well as its magnetic moment ($\mu = 1.05$ D).[276] The solid-state structure of $NiInd_2$ features two equally slipped Ind ligands;[277] this is in contrast to the presence of differently slipped Ind ligands, one almost fully η^3 and another almost fully η^5, in the complexes $M(CO)_2Ind_2$ (M = V,[278] W)[279].

Very little is known about the structures and reactivities of $NiInd_2$ derivatives bearing substituted Ind ligands. Recently, Schumann *et al.* have reported that all three possible diastereomers of the complex $Ni\{1\text{-}((–)\text{-}3\text{-}menthyl)\text{-}4,7\text{-}Me_2\text{-}Ind\}_2$, **193**, can be obtained upon reacting $NiCl_2(DME)$ with the lithium salt of the corresponding indenyl ligand;[280] the separation and isolation of the individual diastereomers have not been achieved. The attempted syntheses of Ni(1-R-Ind)$_2$ bearing achiral substituents (e.g., Ni(1-Me–Ind)$_2$) have also given complex mixtures of products.[281] As a result, no structural information is available to date for NiInd$_2$ compounds bearing unsymmetrically substituted Ind ligands. On the other hand, the complex Ni(2-Ph-Ind)$_2$ has been structurally characterized.[282]

In contrast to the relatively well-studied reactivities of nickelocene,[177,283] the chemistry of NiInd$_2$ has not been studied much; it is reasonable to expect, however, that the reactivities of these species should be similar. For example, analogously to nickelocene, NiInd$_2$ can react with SiHCl$_3$ and PPh$_3$ to give Ni(SiCl$_3$)Ind(PPh$_3$) **194**.[284]

8.03.4.4.3.(ii) NiX(Ind)L complexes

The metathetic reaction of MInd (M = Li, Na) with Ni–halide precursors NiX$_2$(PR$_3$)$_n$ has been the most common synthetic route to the neutral complexes Ni(X)Ind(PR$_3$), **195**.[285,286] Although this approach yields the desired products in most cases, some syntheses are complicated by a side-reaction arising from the homocoupling of the indenyl anions.[287] A potentially interesting alternative to the metathetic route involves the oxidative addition of 1-bromoindene to Ni(0) precursors, but the successful application of this approach has been applied to only one complex so far, namely: NiBr(indenyl)(PPh$_3$) (**195**–Br, Scheme 46).[288]



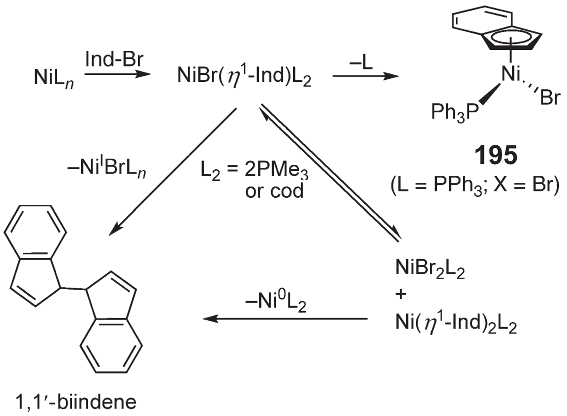
195

L = PR$_3$, carbene
X = halide, imidate, triflate, thiolate

L = PR$_3$
X = Me, Et, *i*-Pr, thienyl, alkynyl

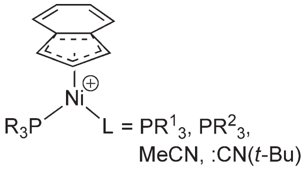
A number of closely related derivatives of **195** have been prepared via similar routes. For instance, the complex NiInd(η^3-allyl), **196**, where both L and X are incorporated in one ligand, has been prepared from LiInd and [NiCl-(η^3-allyl)]$_2$.[289] Moreover, analogous complexes have also been prepared via substitution of the phosphine or X ligand in **195**. For instance, complexes featuring *N*-heterocarbene ligands have been prepared by substitution of PPh$_3$ in NiX(1-Me–Ind)(PPh$_3$) by the carbene ligands (1,3-dimesityl)imidazol-2-ylidene (IMes), (1,3-dimesityl)-4,5-dichloro-imidazol-2-ylidene (IMesCl$_2$), (1,3-di-*t*-butyl)imidazol-2-ylidene (IBut), (1,3-di-*i*-propyl)imidazol-2-ylidene (IPr).[290] An alternative route involves reacting NiInd$_2$ with the protonated carbenes, that is, 1,3-diisopropylimidazolium halides.[291] A number of derivatives have been prepared through a metathetic exchange of X in Ni(X)Ind(L) by other anionic ligands such as alkenyl, alkynyl, imidates, etc.[292–295]

The neutral complexes can be converted into the cationic Ind complexes of the type [NiInd(PR$^1{}_3$)L]$^+$ (**197**; L = PR$^1{}_3$, PR$^2{}_3$, MeCN, CNBu^t) by halide abstraction, protonation of organic ligands, or simple displacement of the triflate moiety.[296] This strategy has been employed for the preparation of an extensive series of cationic complexes, including the monometallic species [Ni(2-Me–Ind)(dippe)]BPh$_4$, **198**,[134] and the bimetallic Ni complexes bearing



Scheme 46

two Ind or mixed Ind/Cp ligands $CpCMe_2Ind$, 199, or $IndCMe_2Ind$, 200.[258] The structural and reactivity features of these compounds have been studied in depth.[16]



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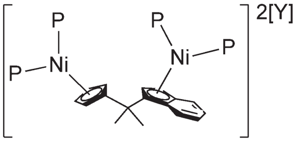
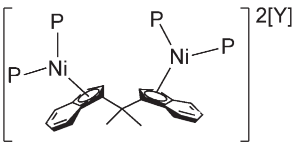


P = PPh$_3$; Y = PF$_6$

199



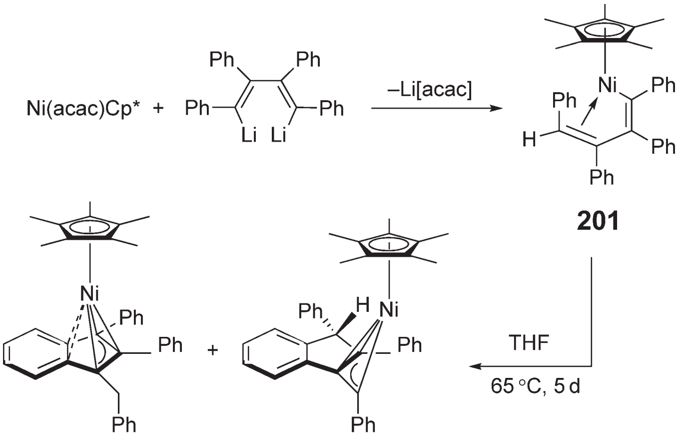
200

An unusual indenyl compound has been prepared through a rearrangement thought to proceed via a cyclometallation step and a subsequent ring closing, as shown in Scheme 47.[297] Complexes 201 (brown), 202 (red), and 203 (green) have been studied by X-ray crystallography. The NiCp* fragment interacts with a nearly trihapto Ind moiety in 202 (ΔM–C = 0.50 Å), whereas in 203, the interaction is with the exocyclic allyl moiety of the 1,2-Ph_2-3-$PhCH_2$-indenyl ligand.

8.03.4.4.4 Structural features

The detailed characterization, in solution and solid state, of various derivatives of complexes Ni(X)Ind(L) and $[NiIndLL']^+$ has provided a relatively large selection of bonding parameters.[134,271,286] These parameters, and, in particular, the ΔM–C values (ΔM–C = 1/2{Ni–C3a + Ni–C7a} – 1/2{Ni–C1 + Ni–C3}), are useful for developing a sense of the bonding picture in these complexes. A detailed analysis of Ni–Ind bonding modes as a function of the many factors that influence the Ni–Ind interactions (e.g., nature of ligands L and X, Ind substituents, overall charge, etc.) has been provided recently.[16] As was seen for the Cp* complexes discussed earlier, the *trans*-influence differences of the ligands L and X has a major influence on the Ind–Ni bonding mode: ligands of widely different *trans*-influence values (e.g., PPh_3 and Cl) lead to a non-symmetric hapticity approaching (η^5-(η^1:η^2))-Ind, whereas ligands of similar *trans*-influence values (e.g., PPh_3 and Me) give symmetrically slipped interactions described as (η^5/η^3)-Ind.[287] Interestingly, the more strongly donor and covalent ligands such as Me and PPh_3 result in stronger Ni–Ind interaction (less slip-folded, shorter Ni–C bonds), whereas weaker and more ionic ligands such as halides result in weaker Ni–Ind interactions (large slip-fold distortions, longer Ni–C bonds).[292]

More specifically, in the neutral complexes $Ni(X)Ind(PPh_3)$, the least slippage is found for X that are carbon-based ligands such as alkyl, alkenyl, and alkynyl possessing effective σ-donor properties and strong *trans*-influences (ΔM–C < 0.21 Å). In contrast, heteroatom-based X ligands such as Cl, SAr, OTf, phthalimide that are potentially π-donating



202 **203**

Scheme 47

and relatively poor σ-donors possessing weak *trans*-influences cause greater slippage (ΔM–C $\sim$ 0.25 Å). Furthermore, for a given X (e.g., Cl or Me), the more basic the L ligand, the higher the ΔM–C value: *N*-heterocarbenes > PMe_3 $\sim$ PCy_3 > PPh_3. Solution NMR studies have established that the bonding features observed in the solid-state structures of these complexes are maintained in solution for the most part. Overall, less pronounced slip-fold distortions have been found in Ni(X)Ind(L) (e.g., ΔM–C $\sim$ 0.17–0.35 Å) and $[NiIndLL']^+$ (ΔM–C $\sim$ 0.18–0.30 Å) compared to $NiInd_2$ (ΔM–C $\sim$ 0.49 Å).

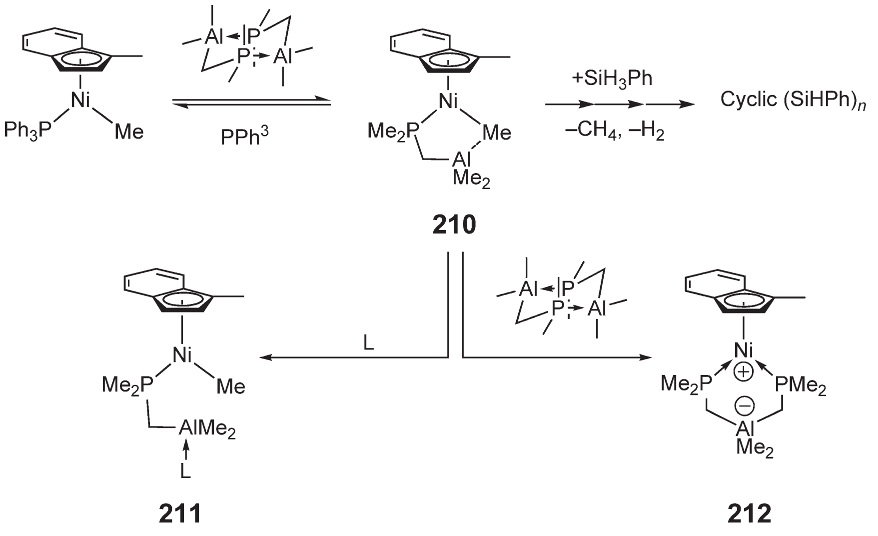
Smaller distortions have also been found for cationic versus neutral complexes. In general, the positive charge on cationic complexes would be expected to increase the electrophilicity of the metal center and results in a stronger M–Ind interaction (i.e., less pronounced slippage). This appears to be the case for some of the complexes having ΔM–C values of 0.15–0.20 Å, but in some other complexes the slippage parameters are similar to those found for the neutral complexes (ΔM–C ca. 0.23–0.27 Å). Another important factor that affects the extent of slippage in these complexes appears to be the steric environment around the metal. This is evident from a comparison of the ΔM–C values for $[Ni(1\text{-}Me\text{–}Ind)(PPh_3)_2]^+$ (**204**, 0.27 Å), $[Ni(1\text{-}Me\text{–}Ind)(PPh_3)(PMe_3)]^+$ (**205**, 0.18 Å), and $[Ni(1\text{-}Me\text{–}Ind)(PMe_3)_2]^+$ (**206**, 0.15 Å). These observations seem to suggest that the larger steric bulk of the PPh_3 ligand might be the cause of the larger slippage in **204**; if the donor power of the phosphines were crucial, we would anticipate the opposite order of slip-fold distortions, because the more basic PMe_3 would be expected to cause more slippage. In addition, the smaller slippage in the complex $[Ni(1\text{-}Me\text{–}Ind)(dppp)]^+$ (**207**, 0.21 Å) compared to **204** is consistent with the smaller cone angle of dppp due to chelation. It should be noted, however, that in some cases the influence of the steric factors is not as important as the electronic factors. This can be seen from a comparison of the slippage values in the complexes $[Ni(1\text{-}Pr^i\text{–}Ind)(PPh_3)(CNBu^t)]^+$ (**208**, 0.17 Å) and $[Ni(1\text{-}Pr^i\text{–}Ind)(PPh_3)(NCMe)]^+$ (**209**, 0.23 Å); the greater π-accepting nature of the isocyanide ligand in **208** versus that of the nitrile ligand in **209** is presumably the cause of the unusually small slippage in **208**.

8.03.4.4.5 Reactivities

In general, Ind complexes appear to be less stable and more reactive than the corresponding Cp^* analogs. As expected on the basis of their d^8-configurations, compounds Ni(X)Ind(L) undergo associative ligand-substitution reactions. For example, the rate of exchange of PPh_3 in $Ni(Cl)(1\text{-}Me\text{–}Ind)(PPh_3)$ by PCy_3 shows a clear dependence on $[PCy_3]$, and the reaction possesses the following activation parameters: $\Delta H^\ddagger = 6.40 \pm 0.07\ \text{kcal mol}^{-1}$ and $\Delta S^\ddagger = -40 \pm 4$ eu.[298] The steric bulk of the Ind ligand also exerts a great influence on the rate of this ligand-exchange reaction (1-Me-2-Ph-Ind < 1-Me-Ind < Cp).

The complexes $Ni(X)Ind(PR_3)$ (X = Cl, Me, OTf) react with SiH_2PhR (R = Me, H) to catalyze silane oligomerization and hydrosilylation reactions. The direct reaction of the Ni–Me precursors with SiH_3Ph (in the absence of initiators or co-catalysts) results in the formation of oligosilanes $(SiHPh)n$. The initial step of the reaction of $Ni(1\text{-}Me\text{–}Ind)\text{-}Me(PMe_3)$ with SiH_3Ph is believed to go through a concerted σ-bond metathesis ($K_H/K_D \sim 10$, at 313 K).[299] On the other hand, combining the Ni precursors with MAO gives a mixture of species which react with a large excess of SiH_3Ph to produce linear and cyclic polysilanes $(SiHPh)_n$.[300] The linear portion of these polymers has M_w in the range of $2\text{–}7 \times 10^3$ and relatively narrow polydispersities ($M_w/M_n \sim 2$). Many of these Ni–Ind complexes are also efficient pre-catalysts for the hydrosilylation of olefins, alkynes, and ketones.[301] These reactions are believed to involve a hydrido intermediate, which can be generated by a direct reaction between silanes and the neutral or cationic complexes. Studying the reactivities of $1\text{-}R^1$–Ind and $1,3\text{-}R^2{}_2$–Ind derivatives (R^1 = Me, CH_2Ph, $SiMe_3$; R^2 = CH_2Ph, $SiMe_3$) in the hydrosilylation of styrene has shown that 1,3-disubstituted precursors facilitate the catalysis (up to 500 catalytic turnovers).[284,302]

Combining $Ni(X)Ind(PR_3)$ with MAO also generates intermediates that polymerize ethylene to high MW PE[303] and phenylacetylene to *cis*,*transoid*-poly(alkynes).[293–295,304] Cationic intermediates are also formed in these reactions and lead to efficient dimerization of ethylene (*vide infra*); some of the 1-butene thus produced is then incorporated into the growing polymer chain to give PE which is mostly linear but contains a small number of ethyl branches. The independently prepared cationic bis(phosphine) complexes $[NiInd(PR_3)_2]^+$ and the highly electrophilic, *in situ* generated cations $[NiInd(PR_3)]^+$ catalyze the dimerization of ethylene[296] and oligo- and polymerization of other olefins such as styrene and norbornene.[305,306] The cationic species $[Ni(2\text{-}Me\text{–}Ind)L_2]^+$ (L_2 = 2 $PMePr^i{}_2$, $PPhPr^i{}_2$, $Pr^i{}_2PCH_2CH_2PPr^i{}_2$) also catalyze the non-living polymerization of styrene to fairly high MW, atactic poly(styrene) in the absence of initiators or co-catalysts.[306] As mentioned above, the cations $[Ni(1\text{-}R\text{–}Ind)(PPh_3)L]^+$ can be prepared conveniently from the complexes $Ni(OTf)(1\text{-}R\text{–}Ind)(PPh_3)$; the latter also promote the dimerization of ethylene, polymerization of styrene, and isomerization of 1-hexene.[294] The key element in these reactions is the facile displacement of the triflate moiety by L or substrate molecules. In the

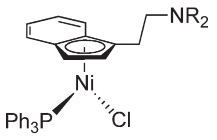


Scheme 48

dimerization of ethylene, the final mixture contained the vinyl-substituted indenes (e.g., 1-CH_2=CH-3-Pr^i-IndH), whereas the corresponding reaction of the Ni–OTf derivative with 1-hexene gives the 1-hexenyl-substituted indene 1-(1-hexenyl)-3-*i*-Pr-IndH.

An interesting approach involving the use of a bifunctional ligand has been applied to probing the mechanism of silane oligomerization with these NiInd complexes. Thus, reaction of Ni(1-Me-Ind)Me(PPh_3) with the dimeric compound $[AlMe_2CH_2PMe_2]_2$ results in the formation of a new species **210** that converts $PhSiH_3$ into cyclic oligomers very efficiently.[307] Reaction of this species with bases gives the base-stabilized complexes **211** (Scheme 48), whereas reaction with excess $[AlMe_2CH_2PMe_2]_2$ gives the zwitterionic compound **212**.

A number of complexes bearing functionalized Ind ligands have been prepared. It is noteworthy that the derivatives bearing amine (**213–215**) [308–312,275] and alkene (**216–218**)[313] functionalities can be isolated both in the "dangling" and chelating modes, those bearing an ether functionality (**219**) could not be induced to chelate,[314] while the phosphine derivatives could be isolated only if the tethered phosphine moiety was protected **220**.[315] The hemilabile nature of the amine and alkene moieties in **215** and **218** facilitates a number of interesting catalytic reactions (Scheme 49).



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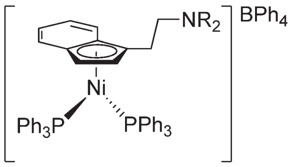

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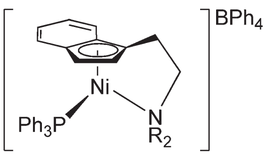

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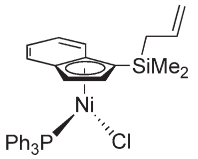

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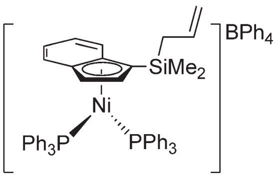

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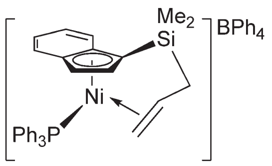

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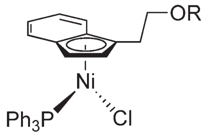

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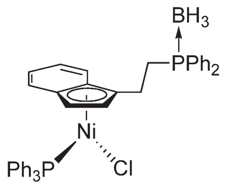

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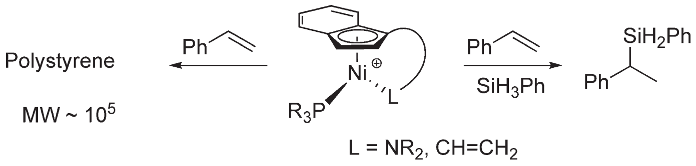
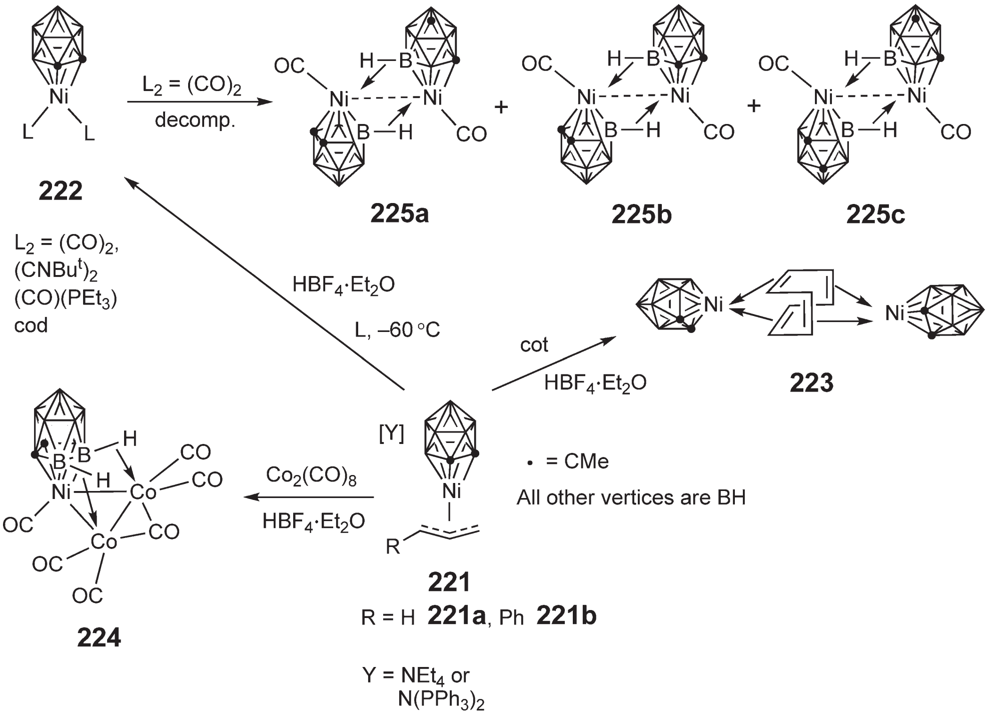


Scheme 49

8.03.4.5 Complexes of η^5-Carborane Ligands

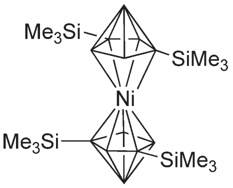
The isolobal relationship between the Cp anion and the open face of various dicarbollide dianions [*nido*-$C_2B_9H_{11}$]$^{2-}$ has allowed the preparation of a variety of carborane–transition metal complexes that are often configurationally analogous to Cp derivatives, with the main difference being the dianionic character of carboranes. Although relatively few nickelacarboranes have been reported to date,[20,316–318] a number of recent reports have shown that such derivatives are accessible via simple routes.[319,320] For example, reacting Na_2[*nido*-7,9-$C_2B_9H_{11}$] with [Ni(μ-Br)-(R–allyl)]$_2$ gives the complexes **221** that are anionic analogs of half-sandwich-type NiCp(allyl) species.[321] Displacement of the allyl moiety by various charge-neutral ligands gives a range of neutral derivatives **222**, including the novel system **223** featuring a bridging cot ligand (Scheme 50).[322,323] The solid-state structure of **221b** (R = Ph) has revealed that the B_3C_2 face of the carborane is puckered and the Ni–C bonds are longer than the Ni–B bonds (ca. 215 vs. 209 pm). Significantly longer Ni–$C_{\text{carborane}}$ distances of ca. 218–220 pm were noted in the solid-state structure of complex **223**. Protonation of complex **221** in the presence of $Co_2(CO)_8$ gives the $NiCo_2$ cluster **224** in which the NiC_2B_9 metallacarborane cage forms two exopolyhedral B–H → Co "agostic" interactions. The bis(carbonyl) derivative of **222** loses a CO ligand in CH_2Cl_2 to form a mixture of the isomeric dinickel species **225** in which the carborane CMe groups of both cages occupy vertices in different layers of the η^5-C_2B_9 *nido*-cages, and the ligating CB_4 ring shows pronounced non-planarity. In addition, the Ni–Ni vector is spanned by two three-center, two-electron B–H → Ni "agostic" interactions.

The full- and half-sandwich complexes **226** and **227** have been prepared from the smaller "carbons-apart" carborane precursors *nido*-[$(CR)_2(BH)_4$]$^{2-}$.[324,325] It is interesting to note that complex **226** is obtained via a disproportionation reaction that generates an Ni(IV) species and an Ni(0) byproduct. These studies have shown



Scheme 50

that the “carbons-apart” carboranes lead to more stable complexes in comparison to their structurally analogous “carbons-adjacent” carboranes. Solid-state structures of complexes 226 and 227 have shown a symmetrical Ni–(C_2B_3) bonding.



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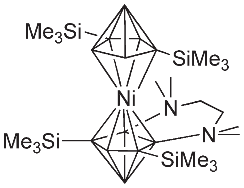

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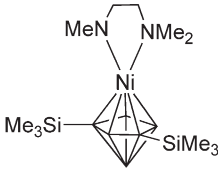
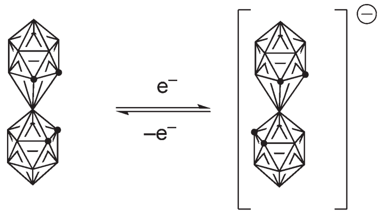


228

Vertices bearing $SiMe_3$ groups are C, those ligated by N are B, all others are BH

A recent report has demonstrated that an electron-transfer or photoexcitation process can induce controlled, rotational, oscillatory motion in the formally Ni(IV) “sandwich”-type complex *commo*-bis(7,8-dicarbollylcarborane) Ni, 229.[326] Thus, converting the initial Ni(IV) species into the Ni(III) species 230 changes the initial *cisoid*-configuration to a *transoid* one in which the Ni(III) center is the center of symmetry reflecting the two pairs of carbon vertices in the carbollide cages; this change results in a controlled 4π/5 rotation of the dicarbollide ligands (Equation (11)). Since the redox process is reversible, it is plausible that such a strategy can lead to unidirectional rotation of ancillary structures that can be attached to the dicarbollide moiety, thus creating a molecular machine. Photoexcitation (i.e., transfer of an electron from the HOMO to the LUMO orbital) can also prompt such rotational motion, since it induces geometrical changes similar to those brought about by electrochemical reduction.

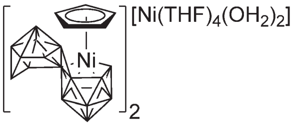


(12)

229 **230**

• = CH, all other vertices are BH

Half-sandwich complexes have also been reported with macropolyhedral boranes, but the Ni–borane bonding in these complexes does not involve π-interactions. For instance, reacting nickelocene with *anti*-$B_{18}H_{22}$ results in the elimination of CpH and formation of the 19-vertex *conjuncto*-structure anions $[B_{18}H_{20}NiCp]^-$, 231; subtle differences in the reaction conditions lead to the oxidation of 231 to give 232.[327] Structural studies of these compounds have shown that their overall structures consist of two edge-fused cluster subunits (a *nido*-10-vertex and a *nido*-10-vertex) featuring four Ni–B bonds ranging from 203 to 220 pm. According to electron-counting schemes for such *conjuncto*-cluster systems,[328,329] the polyhedral borane units in these compounds have 23 electron pairs, of which 1.5 (three electrons) are engaged with the CpNi fragment.



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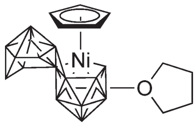
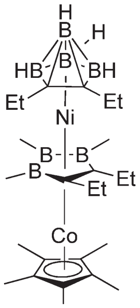


232

All vertices in the macropolyhedral borane ligand represent BH

A series of novel triple-, tetra-, penta-, and hexadecker complexes featuring Cp and various carborane ligands have been prepared. For example, the reaction of $NiBr_2$ with the dianions $[Co(\eta^5\text{-}\{(BMe)_3(CEt)_2\})Cp^*]^{2-}$ and the pyramidal $[\{(BH)_3(CEt)_2\}(\mu^5\text{-}BH)]^{2-}$, followed by air oxidation, gives a diamagnetic red-brown solid characterized by NMR, UV, and mass spectroscopy as the triple-decker Co^{III}/Ni^{IV} species [Co(η^5-{(BMe)$_3$(CEt)$_2$})Cp*Ni(η^5-{(BH)$_3$-(μ^5-BH)(CEt)$_2$})] 233.[330] A similar approach using the dianionic Co(III) sandwich compound [Co^{III}(η^5-{(BH)$_3$-(μ^5-BH)(CEt)$_2$})(η^5-{(BH)(HB(μ-H)BMe)(CEt)$_2$})]$^{2-}$ gave the novel carborane-bicapped tetradecker nickel(III) hydrido species NiH{(η^5-{(BH)$_2$(BMe)(CEt)$_2$})CoH(η^5-{(BH)$_3$(μ^5-BH)(CEt)$_2$})}$_2$ 234 that was characterized by elemental analysis, UV–VIS, and mass spectroscopy. A related Cp*/carborane-capped diamagnetic, 42-electron tetradecker species of Ni(IV) was prepared by reacting NiBr$_2$ with the dianion [Co(η^5-{(BH)$_2$BMe(CEt)$_2$})Cp*]$^{2-}$ and the trianion [Co^{III}(η^5-{(BH)$_3$(μ^5-BH)(CEt)$_2$})(η^5-{(BH)$_2$BMe(CEt)$_2$})]$^{3-}$ and identified as [Co(μ,η^5,η^5-{(BH)$_2$BMe(CEt)$_2$})-Cp*]Ni^{IV}[(μ,η^5,η^5-{(BH)$_2$BMe(CEt)$_2$})Co^{III}H(η^5-{(BH)$_3$(μ^5-BH)(CEt)$_2$})] 235 on the basis of NMR spectra. Analogous reactions have led to the preparation of a novel heterometallic pentadecker Ni(IV) complex. Thus, reacting NiBr$_2$ with the tripledecker dianion [Co(μ,η^5,η^5-{(BH)$_2$BMe(CEt)$_2$})Cp*Co(η^5-{(BH)$_3$(CEt)$_2$})]$^{2-}$ and the sandwich dianion [Co^{III}(η^5-{(BH)$_2$BMe(CEt)$_2$})Cp*]$^{2-}$ followed by workup in air gave the black solid [Co^{III}(μ,η^5,η^5-{(BH)$_2$-BMe(CEt)$_2$})Cp*Co^{III}H(η^5-{(BH)$_3$(CEt)$_2$})]$_2$Ni^{IV} (μ,η^5,η^5-{(BH)$_3$(CEt)$_2$})Co^{III}H 236.[331] The ^{1}H NMR of this compound displays the characteristic broad features of a paramagnetic species, and its X-band ESR spectrum has $g_\perp = 2.07$ and no resolved $g_\parallel$ or hyperfine structure. The paramagnetism of this compound is surprising since its 54 valence electrons correspond to the "magic number" for a filled-shell pentadecker sandwich complex having five six-electron donor ligands and four d^6 metal centers.



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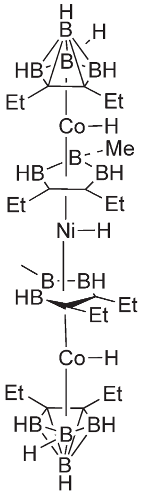

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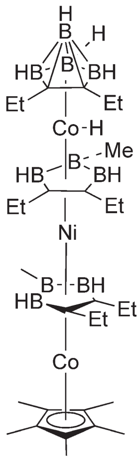

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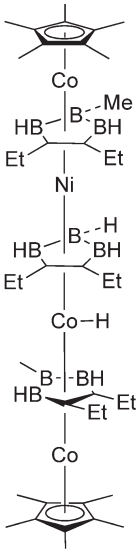
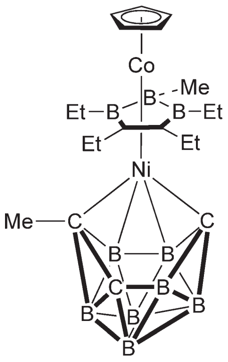


236

A series of hybrid Cp/diborolyl/tricarbadecaboranyl triple-decker complexes of the general formula Co(μ,η^5,η^5-(MeEt$_4$B$_2$C$_3$})(η^5–Cp)M(B$_7$H$_9$MeC$_3$) (M = Fe, Co, Ni) has been prepared by reacting the [Co(μ,η^5,η^5-(MeEt$_4$B$_2$C$_3$})-Cp]$^{-1}$ and *nido*-[6-Me-5,6,9-B$_7$H$_9$C$_3$]$^{-1}$ anions with MX$_2$.[332] Structural characterization and electrochemical measurements have shown that the MC$_3$B$_7$ moieties in these complexes adopt a *closo*-geometry for the Fe derivative, a *nido*-geometry for the Ni derivative, and an intermediate geometry for the Co derivative. Thus, the 24-skeletal-electron *closo*-tricarbadecaboranyl ligand in the Fe complex functions as an η^6-bound ligand and contributes five electrons for a total of 30 valence electrons, whereas the *nido*-tricarbadecaboranyl ligand in the Ni derivative functions as an η^4-bound ligand and contributes three electrons for a total of 30 valence electrons (complex 237). These observations suggest that the tricarbadecaboranyl ligand possesses a variable electron-donating ability that can respond to the electronic needs of the metal center it is coordinated to, much like Cp and Ind ligands. Thus, the lower hapticity of the C$_3$B$_7$ moiety in the Ni derivative 237 avoids forming a 32-electron paramagnetic system. The preparation and structural characterization of the 18-electron, double-decker complexes Ni(η^6-2-Me-2,3,5-B$_7$H$_9$C$_3$)(η^3-allyl) 238 and Ni(η^4-8-Me-7,8,10-B$_7$H$_9$C$_3$)((η^5–Cp) 239 have provided further support for the flexible hapticity of tricarbadecaboranyl ligands. It is worth noting that the "essentially non-bonding" Ni–C and Ni–B distances in 237 and 239 are significantly longer than the "normal" bond distances (ca. 284–288 pm vs. 199–214 pm).



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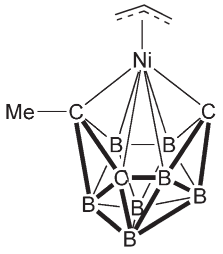

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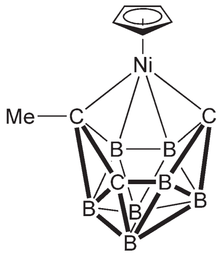
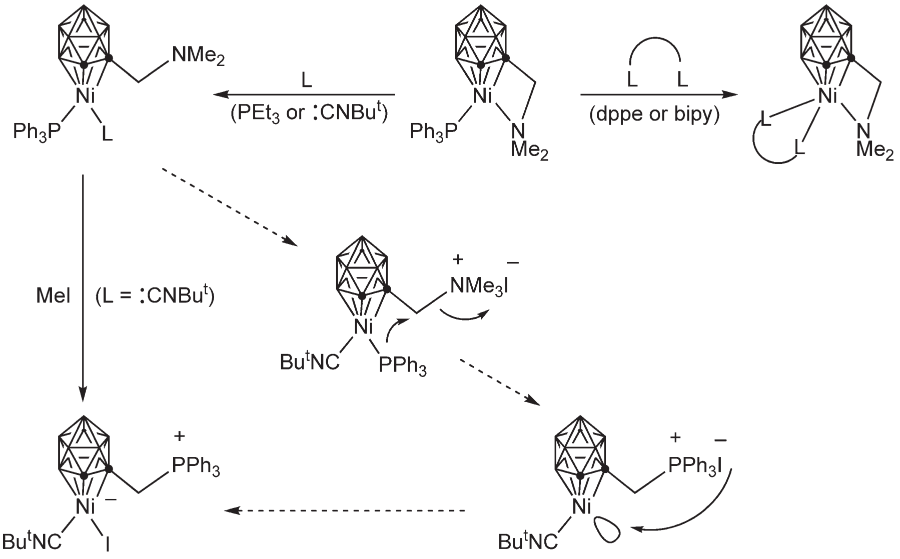


239

All unsubstituted boron atoms bear a hydrogen each

A new series of Ni complexes featuring bifunctional dicarbollyl ligands has been reported (Scheme 51).[333] The structural and spectroscopic traits of the neutral PPh_3 adduct featuring an NMe_2 moiety tethered to the dicarbollyl ligand are similar to those of the analogous cationic Cp and Ind complexes discussed above. Reaction of the PPh_3 adduct with the monodentate ligands PEt_3 and :$CNBu^t$ leads to the displacement of the chelating amine moiety, whereas the bidentate ligands dppe and bipy displace PPh_3 to give the unusual, formally 20-electron, species shown in Scheme 51. X-ray analysis of the bipy adduct showed that the excess electron density arising from the coordination of the bidentate ligand serves to weaken all Ni–ligand bonds. Thus, the distances from the Ni center to the NMe_2 moiety and the B_3C_2 ring are longer in the bipy compound relative to the corresponding distances in the PPh_3 adduct: 226 vs. 206 pm; 168 vs. 150 pm. An unexpected zwitterionic derivative has been obtained from the reaction of the :$CNBu^t$ adduct with MeI. The proposed mechanism of this transformation is shown in Scheme 51.

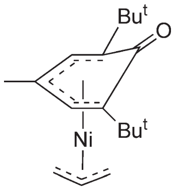
• represents CH or CR moieties; all other vertices are BH



Scheme 51

8.03.4.6 η^5-Cyclohexadienyl Complexes

As was discussed above (allyl complexes), the metathetic reaction of $NiBr_2(DME)$ with sterically hindered aryloxides leads to the generation of the anticipated *O*-bound aryloxide species $Ni(aryloxide)_2(DME)$, in addition to unexpected species in which two aryloxide ligands are bound to Ni thorugh an allylic moiety (**67** in Scheme 19). A related study has shown that the analogous reaction involving a different Ni precursor results in the formation of new compounds featuring *O*-bound aryloxides or a pentahapto-arylato ligand. Thus, reacting 2 equiv. of the aryloxide with the $[Ni(\mu\text{-}Cl)(allyl)]_2$ (Ni : aryloxide ratio 1 : 1), gave the complex **240** in which the aryloxide ligand is η^5-bound like a cyclohexadienyl ligand.[334] Interestingly, under the same reaction conditions, the analogous Pd precursor $[Pd(\mu\text{-}Cl)(allyl)]_2$ gave dimeric complexes featuring *O*-bound bridging aryloxides. The ratio of starting materials plays a crucial role in the outcome of the reaction: using 3 or 4 equiv. of the aryloxide resulted in the formation of the ate complexes **241** or **242**, respectively. It is noteworthy that mixing equimolar quantities of **240** and **242** generates complex **241** and free THF. Complex **240** has been characterized by the upfield shifted NMR signals for the arylato protons and carbon nuclei; for example, *C*-Me resonates at ca. 85 ppm, while C-*H* resonates at ca. 6 ppm. In addition, the carbonyl moiety displays IR absorptions at 1,565 and 1,541 cm^{-1}. The NMR spectra of complex **241** showed two different allyl- and aryloxide moieties, the latter in a 2 : 1 ratio.



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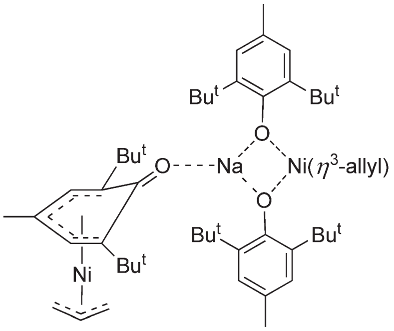

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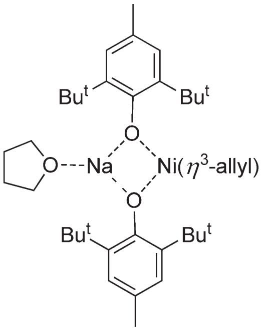


242

8.03.5 Nickel Complexes of η^6-Ligands

8.03.5.1 π-Arene Complexes

8.03.5.1.1 General comments

Although π-arene complexes of nickel are still relatively rare, an increasing number of such compounds featuring a variety of Ni–arene interactions have been reported.[335] Of these, most Ni(0) compounds are prepared by the generation of an unsaturated Ni(0) species in the presence of aromatic solvents. Given the relative electron richness of Ni(0), the Ni–arene interaction in most of these complexes is η^2 or η^4, and rarely η^6; exceptions are $Ni(\eta^6\text{-}benzene)(\eta^1\text{-}Bu^t{}_2\,PCH_2CH_2PBu^t{}_2)$ [29,29a] (*vide infra*).

The reactivities of Ni–arene complexes have not been studied extensively, but the arene ligand in most Ni(0) compounds is usually quite labile and often easily displaced by other arenes or more strongly donor ligands. Some reports have also shown their involvement in catalytic processes including the dimerization and isomerization of terminal olefins.[335]

8.03.5.1.2 Theoretical and physical studies

Gas-phase studies using laser vaporization techniques have provided evidence for Ni–benzene compounds displaying so-called "rice-ball" structures in which one or more Ni center is completely surrounded by benzene molecules.[336] On the other hand, η^6-interactions predominate in (π-arene)–Ni^{II} compounds, which are often prepared by metal-vapor techniques or in liquid nitrogen matrices. In a few cases, more conventional synthetic routes have been used for the preparation of (π-arene)–Ni^{II} compounds. For instance, the reaction of Ni(II) salts with various sources of aryl ligands C_6X_5 (X = F zor Cl) in the presence of arene sources (usually an aromatic solvent) gives $Ni(C_6X_5)_2(\eta^6\text{-}arene)$.[335]

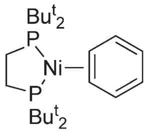
NMR spectra, both solution and solid state, are quite useful for the characterization of arene complexes. The ^1H and $^{13}C\{^1H\}$ NMR signals for the coordinating arene ligands resonate fairly upfield of the corresponding signals in the free arene; this is presumably due to the greater *sp*^{3}-character of the coordinating C atoms. The upfield shifts are especially evident in the solid-state ^{13}C CP/MAS NMR spectra in which the signals for individual nuclei are often resolved. The normally large difference between the chemical shifts of the coordinating and non-coordinating C atoms can thus help determine the hapticity of the arene ligand. In some cases, molecular ions can be detected in FAB-MS spectra.[337] Gas-phase, laser vaporization techniques coupled with mass spectroscopy have been used for preparing and analyzing Ni–benzene complexes,[336] while the electronic structures and properties of such species have been studied by computational techniques.[338]

8.03.5.1.3 Synthetic and reactivity studies

A very simple and most interesting Ni(0)–benzene compound has been generated by reacting $Ni(C_2H_4)_2(\eta^1\text{-}Bu^t{}_2PCH_2PBu^t{}_2)$, 2, with acetylene at –78 °C; the precipitation of flakes of red-colored polyacetylene and the formation of $Ni(\eta^6\text{-}C_6H_6)(\eta^1\text{-}Bu^t{}_2PCH_2PBu^t{}_2)$, **243**, confirms the involvement of Ni(0)–alkyne species in the polymerization and cyclooligomerization of alkynes.[29,29a] This complex has good thermal stability in the solid state (m.p. 83 °C), and has been analyzed by mass spectrometry; in solution, however, it decomposes above –30 °C by dissociation of the benzene ligand. Its low-temperature NMR spectra show sharp singlets at $\delta(H) = 5.95$ and $\delta(C) = 92.0$ ($J_{C\text{–}H} = 168$ Hz); these data are comparable to other benzene complexes (e.g., $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ gives $\delta(H) = 5.67$ and $\delta(C) = 95.5$ ($J_{C\text{–}H} = 175$ Hz) and represent upfield shifts and stronger coupling constants compared to free benzene (7.15–7.35 ppm, 128.0–129.0 ppm, and 159 Hz, respectively). The solid-state structure of **243** confirms the pseudo-linear geometry of the Ni center. The benzene ligand is virtually planar and the C–C and Ni–C bond distances are quite uniform at 141 and 214 pm, respectively. The distance from the center of the benzene ring to the Ni atom is ca. 161 pm, which is considerably shorter than the corresponding distance of ca. 169 pm in the Ni(II) species $Ni(C_6F_5)_2(\eta^6\text{-arene})$ (arene = toluene[339] or mesitylene[340].

As discussed earlier, protonation of nickelocene in benzene gave red-brown crystals containing the salt $[Ni(\eta^6\text{-}C_6H_6)_2][B(3,5\text{-}(CF_3)_2C_6H_3))_4]_2$, 98, and a molecule of neutral nickelocene as solvate (Scheme 28).[198] The magnetic moment of 98 is $4.26\mu_B$, corresponding to four unpaired electrons, two for $NiCp_2$ and two for the bis(benzene) dication. The protonation of nickelocene with $HBF_4{\cdot}Et_2O$ or $H_2O{\cdot}B(C_6F_5)_3$ gives the known triple-decker cation $[Ni_2Cp_3]^+$, 99, and the novel triple-decker dication $[(NiCp)_2(\mu\text{-}C_6H_6)]^{2+}$, **100**, respectively (Scheme 28).[198] The average $Ni\text{–}C_{benzene}$ and $Ni\text{–}C_{Cp}$ bond lengths in the latter are ca. 212 and 217 pm, respectively; the Cp rings are eclipsed. The dianion in **100** consists of a six-membered B_3O_3 ring in which one of the boron atoms bears a single aryl substituent, thus forming a neutral moiety, whereas the other two boron atoms are anionic, tetrahedral moieties bearing two aryl groups each. The way in which this novel dianion forms from $H_2O{\cdot}B(C_6F_5)_3$ is not known.

Thermal reductive elimination of ethane from $NiMe_2L_2$ ($L_2 = Bu^t{}_2PCH_2CH_2PBu^t{}_2$) or reduction of the corresponding dichloro species $NiCl_2L_2$ in benzene leads to the complex $Ni(\eta^2\text{-benzene})L_2$, 244, which dimerizes readily to the $\mu\text{-}\eta^2(1,2){:}\eta^2(3,4)\text{-}C_6H_6$ species 245.[337] The dimeric complex 245 is thermally stable in toluene and enters a slow equilibrium that exchanges the benzene moiety with other arenes, indicating that the Ni–arene interactions are labile. On the other hand, a gradual decomposition takes place in non-aromatic solvents to produce $(NiL_2)_2(\mu\text{-}H)_2$. The μ-benzene in complex 245 is not displaced by a sterically hindered arene such as mesitylene, whereas the electron-poor arene C_6F_6 displaces it to give $Ni(\eta^2\text{-}C_6F_6)L_2$; this complex was isolated in its monomeric form 246 and shown to undergo a slow decomposition in THF to give the Ni(II) species $Ni(F)(C_6F_5)L_2$, **247**. That 246 undergoes an oxidative addition of a C–F bond might implicate such (η^2-arene) species as intermediates in the arylation of Ni(0) species, such as the oxidative addition of Ph–Cl to $Ni^0(PPh_3)_4$ or $C_6F_5\text{–}F$ to $Ni(cod)(PEt_3)_2$.[341] The complex **247** appears to react further to give NiF_2 and $C_6F_5\text{–}C_6F_5$.



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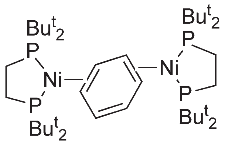

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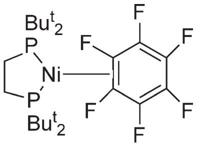
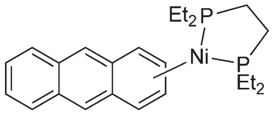


246

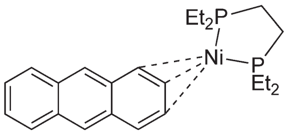
The solid-state structural studies of complexes 245 and 246 have established interesting bonding patterns, as follows. The symmetry-related Ni centers in 245 are coordinated to adjacent C=C bonds of the bridging benzene ring in an antifacial manner. Although the benzene ligand is planar, the bonding within the ring appears to be quite localized: the C–C distance in the two moieties interacting with the Ni centers is ca. 142 pm, which is significantly longer than the distance of ca. 134 pm between the two non-coordinating C atoms farthest from the Ni centers and significantly shorter than the corresponding distances of ca. 145–147 pm in the remaining non-coordinating C–C moieties. Consistent with these observations, the chemical shifts of the coordinating C nuclei in the solid-state ^{13}C CP/MAS spectrum of **245** are at ca. 58–59 ppm (four carbons) and at ca. 121 ppm (two carbons); the arithmetic mean of these values is very close to the average chemical shift observed in the solution spectrum (ca. 80 ppm). Thus, the bridging benzene ligand can be described as a μ-η^2:η^2-cyclohexatriene.

The solid-state structure of complex **246** establishes unequivocally the dihapto coordination of the arene ligand. Interestingly, the Ni–P and Ni–C bonds in this complex are more similar to those in the Ni(II) precursor $NiMe_2L_2$ than the corresponding Ni(0) complex **245**, implying that the Ni–C_6F_6 bonding involves significant contributions from the nickela-cyclopropane canonical form. This is consistent with a fairly long C–C bond length of ca. 149 pm for the coordinated C=C moiety, whereas the remaining C–C distances are much shorter (alternating at 142 and 132 pm). Moreover, the C–F bonds at the coordinating C atoms are significantly bent away from the Ni center (44°). Despite the apparent localization of bonding within the C_6F_6 ring, the arene ligand remains planar and makes an angle of 114° with the C–Ni–C plane.

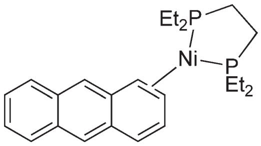
The preparation and structural characterization of a series of Ni(0)–anthracene compounds has shown an interesting range of η^2–η^4-modes of interactions between the aromatic moiety and the Ni center.[342,343] For instance, in the complexes **248–250**, the Ni–(C1–C4) distances define an η^2-anthracene for **248** (201, 196, 270, and 338 pm), an η^3-anthracene for **249** (206, 196, 234, and 282 pm), and an η^4-anthracene for **250** (218, 201, 207, and 230 pm). The hinge angles ϕ, the angle between the planes defining the C1–C4, on the one hand, and the rest of the anthracene molecule, are in accord with the proposed hapticities for each species: ca. 12°, 17°, and 26° for the η^2-, η^3-, and η^4-compounds, respectively. The η^3-species is thought to be a diradical. This series of structures represents a rare model for the haptotropic $\eta^2 \leftrightarrow \eta^3 \leftrightarrow \eta^4 \leftrightarrow \eta^3 \leftrightarrow \eta^2$ processes that such complexes undergo in solution.



248



249



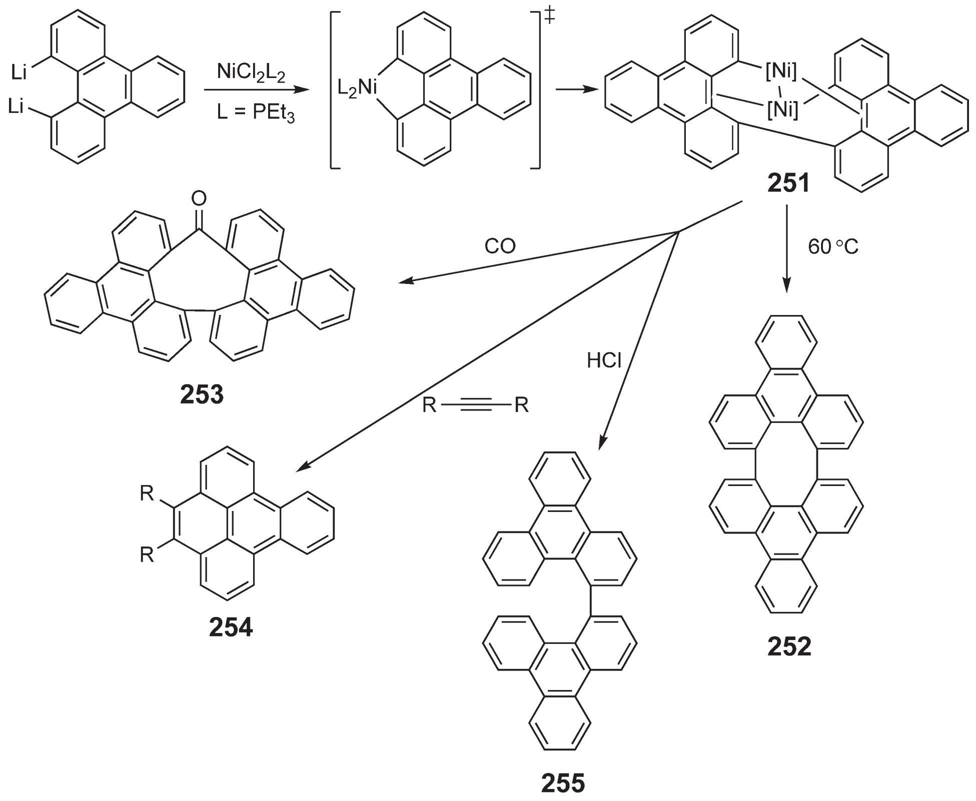
250

When polyaromatic ligands are σ-bonded to unsaturated Ni centers, a π-interaction is often possible between one of the arene moieties and the Ni center. One such species was isolated and characterized during the Ni-promoted coupling of triphenylenediyl moieties, as shown in Scheme 52.[344] Thus, addition of 1,12-dilithiotriphenylenediyl to $Ni^{II}Cl_2(PEt_3)_2$ gives the dimeric Ni^I–Ni^I species **251** featuring both σ- and π-Ni–carbon bonds. X-ray crystallographic characterization of **251** has confirmed the Ni–(η^2-arene) interaction (Ni–C_{arene} ~ 212 and 223 pm; C_{arene}–C_{arene} ~ 144 pm), the Ni–C σ-bonds (ca. 193 pm), and the short Ni–Ni distance (ca. 235 pm).

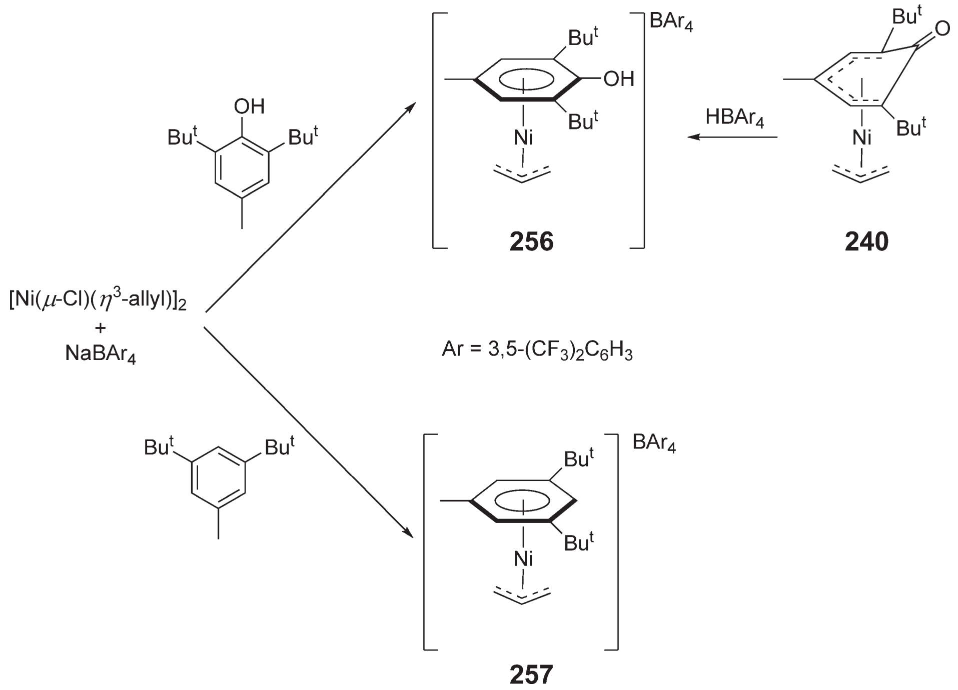
Evidently, the dimer **251** is obtained from a dimetallic (and bimolecular) reductive elimination of two Ni–C_{aryl} moieties. A second dimetallic reductive elimination (this one, a unimolecular one) can be induced by heating **251** to 60 °C, giving both enantiomers of a chiral tetraphenylene derivative **252**. On the other hand, reaction of **251** with CO gives the diarylketone **253** via insertion followed by reductive elimination. Compound **251** displays another intriguing reactivity, namely, a C–C bond cleavage induced by reaction with internal alkynes to give substituted benzo[e]pyrenes **254**. Finally, protonation of **251** gives bi-(triphenylene) **255** (Scheme 52).

A straightforward synthesis of Ni^{II}–arene complexes bearing an allyl ligand involves Cl abstraction from [Ni-(μ-Cl)(allyl)]$_2$ in the presence of aromatic solvents, as shown in Scheme 53. It should be noted that complex **256** can also be obtained by protonation of its (η^5-cyclohexadienyl-one) precursor **240**.[345] Complexes **256** and **257** are very active catalysts for the polymerization of 1,3-butadiene, giving stereoregular and high molecular weight polymers ($M_n \sim 16$–53×10^3); **256** also polymerizes styrene to low molecular weight ($M_n \sim (1$–$2) \times 10^3$), primarily atactic, head-to-tail polystyrene. The solid-state characterization of complex **256** has shown that the arene ring is virtually planar and nearly parallel to the plane defined by the allyl carbons. The short distance between the Ni center and the center of the arene ligand (ca. 166 pm) indicates strong Ni–arene interactions, while the fairly uniform C_{arene}–C_{arene} and Ni–C_{arene} bonds imply η^6-coordination.

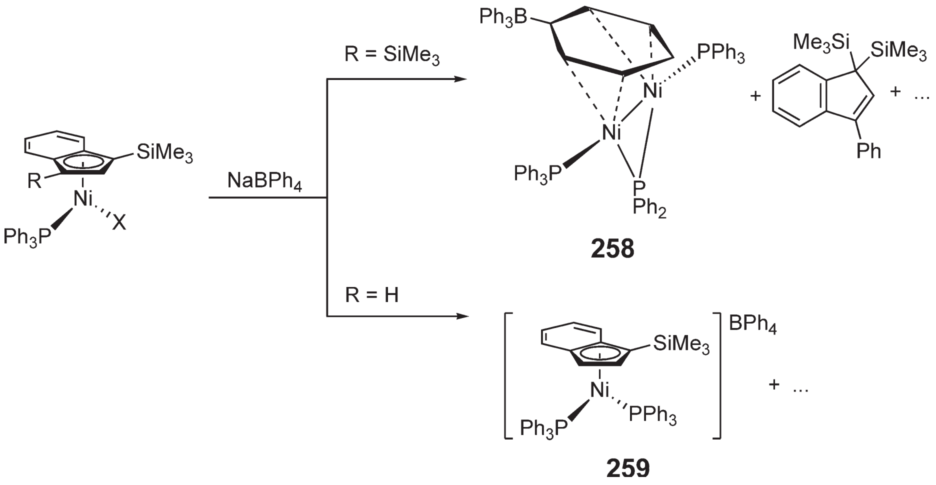
A recent report has shown that Cl^- abstraction from NiCl{1,3-$(SiMe_3)_2$-Ind}(PPh_3) by $NaBPh_4$ furnishes the dimeric complex **258** that is composed of two $[Ni^I(PPh_3)]^+$ fragments bridged by a $[PPh_2]^-$ and a $[PhBPh_3]^-$ moiety (Scheme 54).[346,346a] The analogous reaction with the less bulky NiCl(1-$SiMe_3$-Ind)(PPh_3) leads to the thermally



Scheme 52



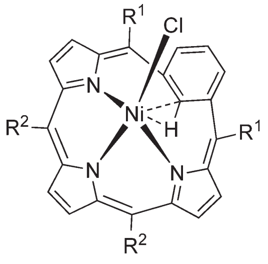
Scheme 53



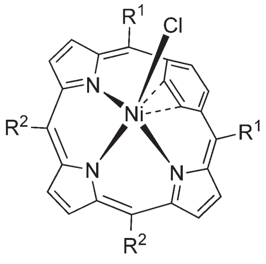
Scheme 54

unstable bis(PPh$_3$) cation **259**. It is interesting to note that the synfacially coordinated μ-[PhBPh$_3$]$^-$ moiety interacts with the Ni(I) centers in complex **258** through two non-adjacent double bonds from opposite edges of the μ-arene ring. This unusual configuration serves, presumably, to minimize steric interactions between the Ph groups on PPh$_3$ ligands and the borate moiety. The bonding between the borate moiety and the Ni centers in complex **258** is reinforced by the electrostatic attractions within the zwitterionic dimer. Complex **258** is the first Ni compound bearing a coordinated tetraphenyl borate moiety, and the first compound in which one of the Ph rings of this moiety is coordinated to more than one metal center.

Weak Ni–arene interactions have been observed in the benziporphyrin complexes **260** and **261**.[347] The crystal structure of the *m*-benziporphyrin compound **260** shows quite short distances between the Ni center and the CH moiety of the arene ring that is incorporated into the porphyrinic macrocycle (Ni–C = 255 pm, Ni–H = 240 pm). Moreover, the C–H bond is not co-planar with the phenylene ring, which confirms the presence of an agostic interaction. In the *p*-benziporphyrin compound **261**, on the other hand, the Ni–arene interaction is between the Ni center and the C═C moiety facing it, as opposed to the C–H moiety. Thus, the Ni–C distances in this complex are fairly similar to that in **260** (ca. 259 vs. 255 pm), whereas the Ni–H interactions are 40 pm longer. That these solid-state interactions persist in the solution has been confirmed by analyzing the paramagnetic shifts for the arene protons in these paramagnetic complexes ($S = 1$).



260



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8.04
Palladium Complexes with Carbonyl, Isocyanide, and Carbene Ligands

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8.04.1 Carbonyl Complexes

8.04.1.1 Homoleptic Carbonyls

The binding of CO to Pd has been quite extensively studied both experimentally and particularly theoretically since COMC (1995) was published.[1] This has partly been due to the desire to understand the differences in stability of the group 10 carbonyls. While $Ni(CO)_4$ is stable at ambient temperature, the Pd and Pt analogs have been observed only at low temperature in matrix isolation, as have $Pd(CO)_{1-3}$.[1] Palladium carbonyls also feature in a number of studies due to the use of metal carbonyls as reference complexes in the development of methods for estimating M–L bond energies and bond distances. The importance of Pd–CO interactions in both homogeneous and heterogeneous

Table 1 Bonding properties of homoleptic palladium carbonyls

Species	*Expt. v(CO)* (cm^{-1})	*r(Pd–C)* (Å)	D_0 (kJ mol^{-1})	*References*
Pd(CO)	2,056	1.843(3) (expt)	154–164	11,18,4
$Pd(CO)_2$	2,066	1.965	124	11
$Pd(CO)_3$	2,063	2.020	48	11
$Pd(CO)_4$	2,075	2.070	20	11
$[Pd(CO)]^-$	1,909	1.873		11
$[Pd(CO)_2]^-$	1,834	1.935	137	11
$[Pd(CO)_3]^-$	1,872	1.976	81	11
$[Pd(CO)]^+$	2,206	1.996		11
$[Pd(CO)_2]^+$	2,210	2.061	136	11
$[Pd(CO)_3]^+$		2.088	64	11
$[Pd(CO)_4]^+$		2.174	44	11
$[Pd(CO)]^{2+}$		1.904	546	16
$[Pd(CO)_2]^{2+}$		1.945	300	16
$[Pd(CO)_3]^{2+}$		1.947, 2.044	245	16
$[Pd(CO)_4]^{2+}$	2,259	2.036	226	16,20

catalysis has also stimulated studies that examine the fundamental aspects of CO binding to Pd complexes and surfaces. Bonding properties of homoleptic carbonyls are summarized in Table 1.

The theoretical treatment of Pd carbonyl bonding has been refined over the last decade as a result of the advances in theoretical chemistry, such as the development of density functional techniques, methods of decomposing wave functions into various bonding elements, and the ability to carry out calculations at increasingly higher levels of theory. Despite the apparent simplicity of the linear PdCO molecule, very high levels of theory have been required to afford an accurate description of the bonding. It was previously recognized that relativistic contributions are important in such calculations.[1] More recent studies have confirmed this, and as a result, the predicted Pd–C distance in PdCO has decreased to the range 1.81–1.88 Å.[2,3] With this relativistic shortening of the Pd–CO bond comes an increase in the predicted binding energy.[3] The most recent high-level calculations on PdCO probably represent the most accurate estimates for both Pd–C bond length (1.838–1.846 Å) and bond-dissociation energy (154–164 kJ mol^{-1}).[4] In particular, the bond distance is in close agreement with recent experimental results (1.843(3) Å, see below).

The mode of coordination of CO has long been described by the Pauling model of σ-donation and π $M \rightarrow L$ backdonation. Theoretical studies are in agreement with this, and quantitatively show that backdonation contributes significantly to the bonding in PdCO. However, while σ-donation contributions in NiCO and PdCO are of the same magnitude, the degree of backdonation in PdCO is significantly reduced relative to Ni. This may be the main reason for weaker CO bonding with Pd than with Ni.[5,6]

Theoretical studies on $Pd(CO)_4$ again highlight the importance of relativistic effects, and the same outcome on bond length and energy are observed as for PdCO. $Pd(CO)_4$ is predicted to have the longest and weakest bonds of the Ni triad. The first bond-dissociation energy [$Pd(CO)_4 \rightarrow Pd(CO)_3 + CO + \Delta H^0$] predictions range from 20 to 69 kJ mol^{-1}. The Pd–CO distance is calculated to be 2.0–2.1 Å, while that for $Pd(CO)_3$ is 1.98–2.02 Å and $Pd(CO)_2$ 1.942 Å.[7–15] The bonding situation in $Pd(CO)_4$, as studied by charge decomposition analysis, reveals that π-back-bonding is still significant, although $CO \rightarrow Pd$ donation is now the dominant bonding element.[14] This analysis seems to fit well with predictions that bond length increases as the number of carbonyl ligands in $Pd(CO)_n$ increases, due to a decrease in the degree of metal → ligand backbonding.

Theoretical studies on dicationic Pd carbonyls, $[Pd(CO)_n]^{2+}$, predict much higher bond-dissociation energies relative to the neutral analogs (Table 1). This is consistent with the observation that dicationic carbonyls are experimentally more stable (see below), and it is thought that coulombic interactions dominate the bonding in these species. Theoretically predicted geometries are linear for $[Pd(CO)]^{2+}$, linear or bent for $[Pd(CO)_2]^{2+}$ (with bent more stable), T-shaped for $[Pd(CO)_3]^{2+}$, and square planar for $[Pd(CO)_4]^{2+}$.[16]

Compared to the number of theoretical studies on homoleptic Pd carbonyls, there have been relatively fewer experimental studies carried out. The infrared spectrum of PdCO in solid argon has been reinvestigated, and the spectrum of 20 isotopic species of PdCO allowed assignment of all fundamental vibrations.[17] Reinterpretation of the spectrum assigns the bands at 2,044 cm^{-1} and 2,050 cm^{-1} to CO stretching of PdCO in two different sites of the argon matrix. This study confirms the geometry as linear, or very close to it. Comparison of this work with theoretical studies shows that earlier IR predictions on Pd carbonyls are, in general, unreliable. The first gas-phase study of PdCO has been carried out by microwave spectroscopy, in which the molecule was prepared by laser ablation of Pd in the presence of CO.[18] This study again confirms a linear structure, and the Pd–CO distance was determined to be 1.843(3) Å.

The charged carbonyls have also been examined, and it is observed that the anions have enhanced Pd → CO backdonation, while the cations have much reduced π-backbonding. A photoelectron spectroscopic study of the $PdCO/[PdCO]^-$ couple estimates that the bond energy of the anion is $0.046 \pm 0.013\,eV$ larger than in the neutral species for this reason.[19] The matrix infrared spectra of the Pd monoanions $[PdCO]^-$, $[Pd(CO)_2]^-$, and $[Pd(CO)_3]^-$, and the monocations $[PdCO]^+$ and $[Pd(CO)_2]^+$, have been measured, along with the neutral species $Pd(CO)_2$, $Pd(CO)_3$, and $Pd(CO)_4$.[11] The CO stretching modes of these species are summarized in Table 1. The reduced backbonding in $[Pd(CO)]^+$ and $[Pd(CO)_2]^+$ results in CO stretching frequencies that appear at higher wave numbers than free CO ($2{,}143\,cm^{-1}$). The cationic species thus belong to the “non-classical” class of transition metal carbonyls. On moving to dicationic palladium, the stability of the carbonyls increases to such an extent that it has proved to be possible to isolate $[Pd(CO)_4]^{2+}$.[20,21] Solvolytic carbonylation of palladium precursors in superacidic media, for example, Equation (1), generates the dication along with the non-coordinating anion $[Sb_2F_{11}]^-$. The average CO stretching frequency of $[Pd(CO)_4]^{2+}$ is $2{,}259\,cm^{-1}$. Such a high value is indicative of insignificant backbonding from CO, and is consistent with the theoretical description of bonding as predominantly coulombic. The single crystal X-ray structure of $[Pd(CO)_4][Sb_2F_{11}]_2$ has recently been determined and confirms a square-planar geometry with average Pd–C distances of 1.992(6) Å.[22]

$$PdCl_2 + 4CO + 6SbF_5 \xrightarrow{80\,^{\circ}C} [Pd(CO)_4][Sb_2F_{11}]_2 + SbF_4Cl \tag{1}$$

8.04.1.2 Bonding of CO to Palladium Surfaces

The role of CO interactions with Pd surfaces in heterogeneous catalysis, particularly in the field of automobile exhaust catalysts, has meant that CO adsorption on palladium surfaces has been studied by a broad range of surface science methods. These studies reveal that CO adsorbs to Pd surfaces in different configurations, depending both upon the degree of CO coverage on the surface and the nature of the palladium substrate. As a result, CO binding to a single palladium atom (“on-top” configuration) by twofold bridging and by higher coordination has been detected.[23] Since COMC (1995), photoelectron spectroscopy has been employed to unravel the complicated picture of CO adsorption on palladium surfaces.[23,24,25] The transition between molecular palladium carbonyls and extended adsorption systems has been studied by this method, with both CO adsorbed on palladium islands on an alumina film, and palladium deposition in a CO atmosphere, leading to growth of $Pd_x(CO)_y$.[24] The resultant electronic properties that are observed are strongly dependent on island size and CO coverage. More recent work has focused on the interaction of CO with single palladium atoms on various supports, using vibrational spectroscopy.[26–29] Here again, the species observed is dependent upon conditions. For instance, on MgO surfaces PdCO and $Pd(CO)_2$ are observed at low temperature, whereas at higher temperatures palladium aggregates form in which bridging CO is detected.[28] The development of IR–VIS sum frequency generation (SFG) spectroscopy and its recent application to palladium crystals and nanoparticles has also led to advances in the understanding. This technique allows experiments to be conducted at higher CO pressures than traditional surface science techniques, and hence can be more representative of actual catalytic conditions. At low pressure and on well-ordered palladium particles, it has been found that CO preferentially adsorbs at bridge sites, whereas on-top coordination becomes significant on less-ordered particles. However, at higher pressure (200–1,000 mbar), the site occupancy is nearly independent of the palladium particle surface structure.[30–33]

The kinetics of CO oxidation to CO_2 on palladium surfaces has in recent years been studied by molecular beam techniques, which confirm that CO undergoes chemisorption on the palladium surface prior to oxidation.[34,35] Infrared spectroscopic studies on the palladium-catalyzed NO–CO reaction ($NO + CO \rightarrow N_2 + CO_2$) show that both PdCO and bridged PdC(O)Pd surface species are formed during the reaction; however, only the linear PdCO adsorbate leads to CO_2 production.[36]

Given the complicated and variable nature of CO binding to palladium surfaces, it is not surprising that, until fairly recently, theoretical studies have struggled to adequately model palladium surface chemistry. The molecules PdCO and Pd_2CO (bridging CO coordination) have been evaluated as models for CO on a palladium surface in a number of studies. The core ionization spectra of these complexes have been calculated and compared to experimental data for

CO on a palladium surface, and it is concluded that Pd_2CO is an inadequate model for CO on palladium, and in fact is less accurate than PdCO.[37] Similarly, the calculated CO dissociation energy of Pd_2CO ($313\,kJ\,mol^{-1}$), considered an approximation of the CO chemisorption energy, is overestimated relative to the experimental chemisorption energy of ca. $150\,kJ\,mol^{-1}$.[38,39] It seems that qualitative features of CO binding to surfaces may be represented by Pd_2, but quantitative predictions require higher level treatments. Even by moving to Pd_3CO, the calculated core ionization spectrum is in better agreement with palladium surface experimental data.[40] In recent years, it has proved to be possible to start modeling much larger systems, such as palladium carbonyls on zeolites[41] and on MgO support.[42] Certainly, some of the CO dissociation energies calculated for PdCO at various sites of MgO are closer to the experimental value of a palladium surface. This work also shows that the CO dissociation energy is probably higher than the MgO–Pd binding energy, and therefore predicts that at elevated temperature, diffusion of palladium carbonyls on the support could occur before CO desorption does. The most recent theoretical studies related to palladium surfaces utilize the density functional method to study Pd and Pd/Zn nanoclusters and their CO complexes.[43,44] Here, an impressive agreement between the theoretically predicted CO bond energies and the experimental surface value is found. For instance, the binding energy is calculated to be $151\,kJ\,mol^{-1}$ in $Pd_{28}CO$ and $142–169\,kJ\,mol^{-1}$ in $Pd_{140}(CO)_8$ (μ_3-CO binding). This demonstrates that it is already possible for theoretical methods to accurately reproduce palladium surface–CO bonding properties. It is likely that advances in computational chemistry will mean that it will, in the near future, become a powerful tool for modeling not only CO binding to palladium surfaces, but also reaction chemistry of the CO molecule adsorbed on these surfaces.

8.04.1.3 Insertion of CO in Pd(II) Alkyl, Aryl, Alkoxide, and Aryloxide Complexes

Migratory insertion of CO into the Pd–R bond (R = H, alkyl, aryl, alkoxy) represents an important elementary step in many types of palladium-catalyzed processes, and as such this reaction has been widely studied. Such reactions include carbonylation of aryl halides (Heck carbonylation)[45–47] and alcohols,[48] alkoxycarbonylation of olefins, and the alternating co-polymerization of CO and olefins. It is beyond the scope of this section to cover in detail the complete mechanism of these reactions, suffice to say that CO insertion into a Pd–R bond can be implicated in most cases, and it is this particular fundamental step that is covered here. The co-polymerization of alkenes with CO,[49–52] and the production of low molecular weight oxygenates from CO/alkene/ROH,[53] have been recently reviewed. Due to the large number of studies where products of CO insertion into Pd–R have been observed, it is impossible to detail each example here. Thus, it is the case in which Pd–carbonyl intermediates have been isolated or observed prior to insertion that will be concentrated on. Studies, which have investigated the energetics, kinetics, and ancillary ligand effects on CO migratory insertion, will also be covered, as will the theoretical studies be.

It is now widely known that "insertion" reactions involve "migration" of the R group onto the coordinated CO ligand, which then becomes a formally anionic acyl group.[54] Thus, the term insertion is misleading, but is widely used. The descriptions insertion, migratory insertion, and migration of the R group onto CO will be used synonymously in this section. Studies prior to 1996 concerning fundamental aspects of migratory insertion of CO have been reviewed.[55] Migration invariably occurs from a palladium intermediate in which the migrating group and the carbon ligand are in mutually *cis*-positions. The reaction is facilitated by orbital overlap between the σ-orbital of the migrating group and the poorly occupied π^*-orbital of CO (Figure 1(a)). Computational studies on $[PdEt(CO)(H_2PCH{=}CHPH_2)]^+$ illustrate this, and show that in the transition structure of ethyl migration, the ethyl group α-carbon orientates its sp^3 σ-orbital toward the π^*-orbital on CO.[56] As such, a low π^*-occupation (low Pd → CO backbonding) favors this interaction, and is thought to favor CO migratory insertion. In the context of this chapter, direct comparisons can be made here with the isoelectronic NHCs. Such an interaction between a palladium *d*-orbital, an sp^3-σ-orbital, and the formally empty *p*-π-orbital of the carbene facilitates either reductive elimination of an imidazolium cation or alkyl migration onto the carbene (Figure 1(b)).

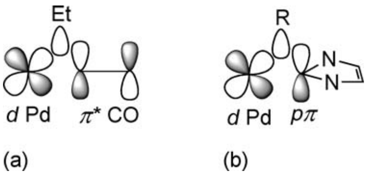
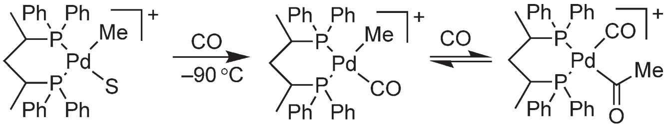


Figure 1 Orbital interactions during (a) alkyl migration to CO, and (b) alkyl-carbene reductive elimination.

The insertion of CO into alkylpalladium(II) complexes chelated with bidentate ligands has been extensively studied over the last decade. Such complexes, particularly monocationic, are efficient catalysts for ethylene/CO co-polymerization, which has stimulated this interest. Insertion of CO into a Pd–alkyl bond in such complexes is a key step in this transformation. In particular, complexes of diphosphine and diimine chelates have been studied in this respect. Square-planar *cis*-methyl(carbonyl)(diphosphine)palladium complexes have been prepared via CO displacement of a weakly coordinating ligand, such as MeOH, H_2O, or Et_2O. The first example of this observation is shown in Equation (2).[57] While ligand substitution was found to be accelerated by an increase in CO pressure, the rate of insertion was independent of CO pressure, and as such the reaction occurs via trapping of CO followed by a rate-determining migration. The reversibility of this migration step is a general feature of these complexes, as is the independence of rate on CO pressure, which shows that a five-coordinate insertion intermediate is not present.[58–60]



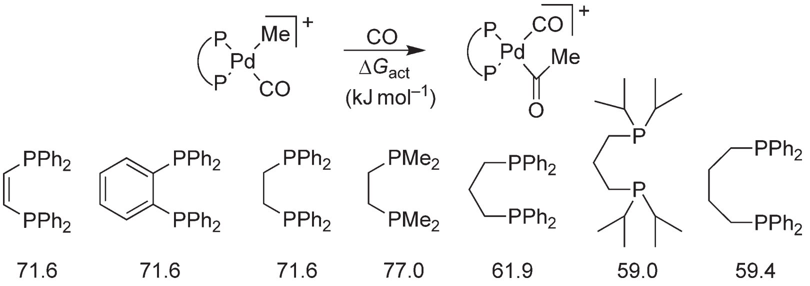
(2)

The activation parameters have been determined for a series of $[PdMe(CO)(P\wedge P)]^+$ complexes,[59] and confirm that as the chelate bite angle increases, the activation barrier is reduced (Scheme 1). Greater steric bulk on the phosphine substituents also lowers the barrier. Both effects can be related back to the mode of methyl migration, in which the angle between the two reacting groups decreases in the transition state, and the chelate angle of the diphosphine concomitantly increases. The $\Delta S^{\neq}$ values for these reactions are close to zero, which is consistent with the intermolecular nature of the reaction and the fact that there is no additional ligand (CO) assistance in the transition state. However, additional CO is required to stabilize the otherwise three-coordinate product, and in the absence of excess CO, the *cis*-methyl(carbonyl)palladium complexes are stable against migration. The migratory insertion reaction of CO in a microcrystalline diphosphine methylpalladium complex has recently been followed by IR spectroscopy for a heterogeneous polyketone catalyst.[61]

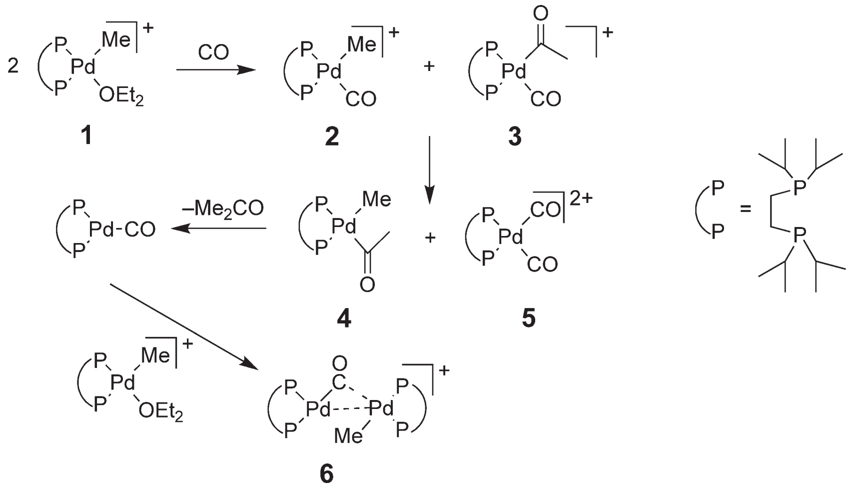
Theoretical studies on a model diphosphine complex $[PdEt(CO)(H_2PCH_2CH_2PH_2)Pd]^+$ underestimate the activation energy for insertion somewhat ($48\,kJ\,mol^{-1}$).[56,62] The product of CO insertion is predicted to adopt an η^2-acyl conformation following insertion, on account of its three-coordinate nature, although experimentally a further ligand coordinates as discussed above. The activation barrier for a second CO insertion into the palladium–acyl complex is calculated to be $109\,kJ\,mol^{-1}$, and the reaction is strongly endothermic by $80\,kJ\,mol^{-1}$. This provides an explanation for the lack of observable double CO insertion in palladium catalyzed CO/ethylene co-polymerization.

Further reactions following insertion have been observed for a cationic 1,2-bis(diisopropylphosphino)ethane complex (Scheme 2).[63] Reaction of the precursor **1** with CO generates both the methyl–carbonyl **2** and acyl–carbonyl **3** complexes, which react together to give the neutral acyl–methyl complex **4** and the dicationic bis(carbonyl) **5**. Reductive elimination of acetone then generates the Pd^0–monocarbonyl complex which forms an adduct with the Lewis-acidic methylpalladium complex to give dimer **6**.

Similar insertion chemistry occurs with alkylpalladium diimine complexes as for diphosphine complexes. Square-planar *cis*-methyl(carbonyl) palladium complexes are formed by CO displacement of weakly coordinating ligands, such as diethyl ether,[64,65] acetonitrile,[66,67] or a β-agostic alkyl interaction.[68] The insertion barrier for phenanthroline-ligated *cis*-methyl(carbonyl) palladium has been determined to be $64.5\,kJ\,mol^{-1}$ (Equation (3)).[64,65] This barrier is lower than that required for insertion of ethylene into the alkyl bond, and as such is a contributing factor in perfectly alternating olefin/CO co-polymerizations. Like the diphosphine complexes, an incoming ligand (usually CO) is

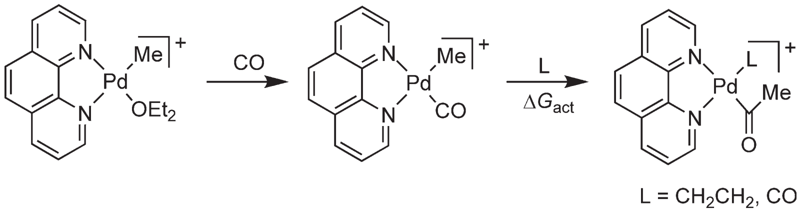


Scheme 1



Scheme 2

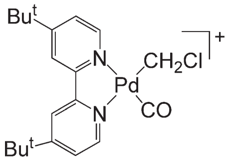
required to stabilize the product, and without this, insertion does not occur.[69] This ligand is not involved in the transition state, however, as the activation free energy is not affected by the incoming ligand in Equation (3). The insertion is reversible, and upon removal of the ligand (evacuation, purging), the *cis*-methyl(carbonyl) complex is regenerated.[69,70,71] Molecular modeling of a model cationic diimine complex $[PdMe(CO)(H_2NCHCHNH_2)Pd]^+$ gives an insertion barrier of $62.3\,kJ\,mol^{-1}$,[72] in close agreement with the experimental value of the phenanthroline complex. The activation energy for subsequent insertion into the Pd–acyl bond is calculated to be $56\,kJ\,mol^{-1}$ higher and the reaction is endothermic, as was found for diphosphine model complexes.



(3)

The effect that electron-withdrawing groups on the migrating alkyl group have on the rate of insertion has been evaluated.[73,74] Electron-withdrawing substituents on the alkyl group disfavor the CO insertion reaction. For instance, diimine complex 7 with a $–CH_2Cl$ alkyl group is stable up to 20 °C under a CO atmosphere, after which insertion occurs, whereas complex 8 with $–CHCl_2$ does not undergo insertion up to 70 °C, after which it decomposes. In contrast, analogous diimine complexes with a methyl group react under a CO atmosphere at −78 °C.

In general, the insertion reaction from *cis*-alkyl(carbonyl)palladium complexes of unsymmetrical P ∧ N chelate ligands occurs slower than from the symmetrical N ∧ N or P ∧ P complexes. For instance, P ∧ N complex 9 undergoes insertion only slowly at room temperature, giving complete conversion in ca. 17 h.[75] This effect has been put down to the requirement for a pre- or post-insertion isomerization, in which the initial carbonyl intermediate must isomerize to give the preferred pre-insertion intermediate (P *trans*-alkyl), or the final acyl product must isomerize to give the thermodynamically preferred product (N *trans*-acyl).[55] More recent studies on P ∧ N[76] and P ∧ OP[77] palladium complexes seem to confirm that pre- or post-insertion isomerizations are taking place.



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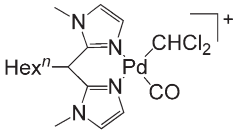

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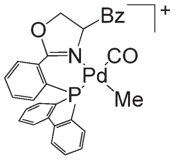
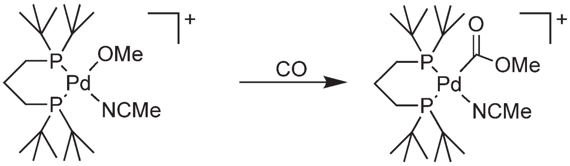


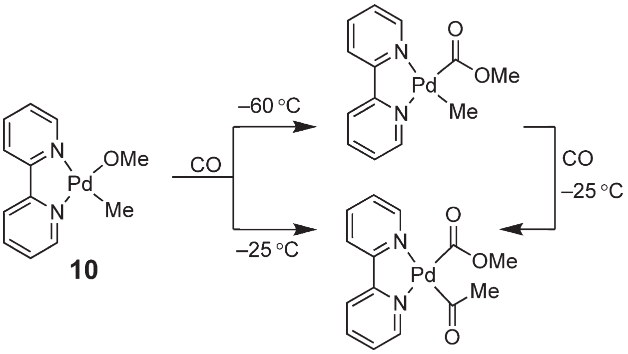
9

Although it has not received the same attention as migration of alkyl groups to coordinated CO, the migration of alkoxide groups on palladium(II) carbonyls is of interest as a key step in one of the two proposed mechanisms for alkoxycarbonylation of alkenes.[53] Both the hydride cycle (alkene insertion into Pd–H)[78–80] and the carbomethoxy cycle (CO insertion into Pd–OMe)[81] have now been conclusively demonstrated. The intermediate *cis*-methoxy (carbonyl) complex was not detected, which is probably a result of the lower barrier for alkoxide migration compared to alkyl migration (see below). This reaction (Equation (4)) was found to be irreversible, in contrast to the migration of an alkyl group. Several studies have shown that carbonyl-bridged palladium(I) dimers are present during methoxycarbonylation of alkenes, although these species were not thought to be part of the catalytic cycle.[82,83]



(4)

The relative rates of insertion into Pd–alkoxide and Pd–alkyl bonds has been inferred by reacting *cis*(alkoxide)alkylpalladium diimine complexes with CO.[84] Insertion is thought to take place into either the Pd–OR bond or Pd–Me bond, depending upon the identity of R, and the relative rates of insertion follow the order Pd–Ome > Pd–Me > Pd–OAr. As an example, *cis*(methoxy)methylpalladium phenanthroline complex **10** reacts with CO first through insertion into the Pd–OMe bond (−60 °C), followed by CO insertion into the Pd–Me bond (−25 °C) (Equation (5)).



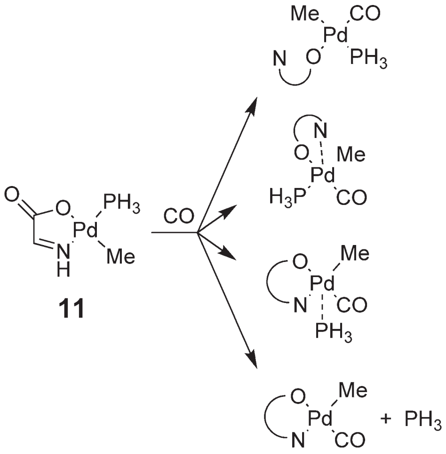
(5)

Theoretical studies on four- and five-coordinate palladium(II) model complexes containing a methyl, carbonyl, and methoxide ligand have been carried out,[85] and the results obtained are in agreement with the above experimental observations. A kinetic and thermodynamic preference for insertion into the Pd–OMe bond over Pd–Me is found. The activation energy for methoxide migration was calculated to be between 33 and 42 kJ mol^{-1}, compared to 62 and 73 kJ mol^{-1} for methyl migration in the same complexes.

8.04.1.4 Insertion of CO from Five-coordinate Intermediates

As detailed above, in the majority of cases, CO insertion occurs from a four-coordinate square-planar palladium complex, in which coordination of CO and subsequent alkyl migration can be considered as two distinct stepwise processes. However, insertion from transient five-coordinate intermediates has been implicated under conditions of coordinative saturation at the palladium center. The description as purely dissociative (four coordinate) and purely associative (five coordinate) represents limiting cases, and it is likely that the actual situation occurs somewhere between these. That is, CO substitution for a ligand leads to a long and weak fifth bond to palladium, which is maintained during the migration, and recoordinates more fully as the migration takes place. The situation is further complicated by the fact that ligand substitution by CO probably occurs via an associative route, even if insertion does not.

These considerations are illustrated by an *ab initio* study of cationic palladium amine complexes.[86] Experimentally, it is found that methylpalladium complexes of chelating terdentate nitrogen ligands insert CO readily. Calculations of the model reaction $[PdMe(NH_3)_3]^+ + CO \rightarrow [Pd(COMe)(NH_3)_3]^+$ showed that a purely five-coordinate pathway (with five ligands firmly coordinated to palladium) could be ruled out. Similarly, a purely dissociative route in which an NH_3 ligand dissociates completely was high in energy. The most favorable route was found to be a hydrid pathway in which a five-coordinate intermediate is a transition state, first to partial NH_3 dissociation. In the subsequent



Scheme 3

transition state of methyl migration, the weak fifth bond to NH_3 is maintained, and in fact stabilizes the transition state. In the four-coordinate product, the amine ligand has fully recoordinated. Subsequent modeling studies with actual terdentate *NNN* ligands led to the same mechanism.[87]

Similar conclusions can be drawn from theoretical studies of the carbonylation of neutral N ∧ O-chelated complex **11**, in which insertion from four possible intermediates was studied (Scheme 3).[88,89] Again, ligand substitution (PH_3 or O ∧ N) occurs via an associative pathway. A purely four-coordinate mechanism has an activation energy at least 29 kJ mol^{-1} higher than the five-coordinate pathway, and the preferred mechanism overall was that in which the nitrogen donor arm forms a weak fifth bond that re-establishes a normal coordination mode concomitantly with methyl migration. A related study on cationic palladium complexes (neutral N ∧ O chelate ligand) revealed a similar situation, but in this case, it is the neutral *O*-donor bond which undergoes elongation.[90] In this instance, a five-coordinate palladium complex with a weak apical bond to the *O*-donor arm ($d_{\text{Pd–O}} = 2.78(1)$ Å) was actually structurally characterized, lending support to the theoretical studies.

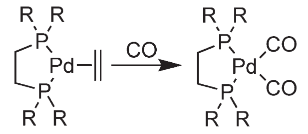
The exact pathway followed, whether four coordinate or five coordinate, depends on the nature of the ligands present, probably and most importantly the coordinating strength of these. Theoretical studies on $[PdMe(CO)(PH_3)_2(Me)]^+$ showed that insertion occurs with a barrier of 28 kJ mol^{-1}, but attempts to optimize the five-coordinate precursor, $[PdMe(CO)_2(PH_3)_2(Me)]^+$, did not lead to a stable structure.[91] This is in accord with the experimental results that show an independence of rate of insertion to the CO pressure. Another theoretical study looking at CO insertion into Pd–Me and Pd–OMe bonds from four-coordinate $Pd(OMe)(Me)(CO)(PH_3)$ and five-coordinate $Pd(OMe)(Me)(CO)(PH_3)_2$ complexes found little difference between the activation barriers from either complex.[85]

8.04.1.5 Mononuclear Carbonyls

Isolated mononuclear palladium(0) carbonyl complexes are relatively rare, although more examples have been identified in solution. This appears to be due to facile loss of CO from the palladium center. Those identified or isolated recently are based almost exclusively on monodentate or bidentate phosphine ligands, and result from studies of the alkoxycarbonylation reaction. The stability depends on the nature of the phosphine ligand, with bidentate chelating phosphines containing sterically demanding substitution affording the most stable complexes.

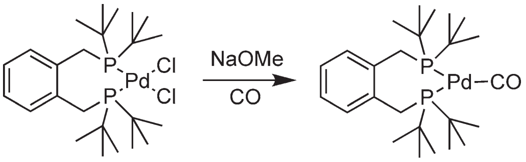
The carbonyl complexes are generated either by reduction of palladium(II) salts under the conditions of catalysis, or by displacement of neutral ligands from palladium(0) precursors. For instance, when $Pd(OAc)_2$ is treated with excess PPh_3, TsOH, and CO in methanol, a number of palladium(0) carbonyls are detected by NMR spectroscopy as shown in Equation (6). When 10 equiv. of TsOH is present, the highly unstable Pd(II) hydride $[PdH(CO)(PPh_3)_2][OTs]$ predominates.[92] Reaction of $Pd(dba)_2$ with CO and 10–30 equiv. of PPh_3 also generates $Pd(CO)(PPh_3)_2$ in equilibrium with $Pd(CO)_2(PPh_3)_2$.[93] $Pd(CO)(PPh_3)_2$ has also been generated by electroreduction of $PdCl_2(PPh_3)_2$ under CO.[94] Treatment of $Pd(dippp)(PEt_3)$ (dippp = bis(diisopropylphosphino)propane) with CO gives in the first instance the dicarbonyl $Pd(dippp)(CO)_2$, which can be transformed into the three-coordinate monocarbonyl Pd(dippp)(CO) by purging with nitrogen. Neither complex could be isolated, however, due to facile loss of CO. NMR spectroscopy indicated rapid exchange of coordinated and dissolved CO.[95] An analogous reaction with palladium(0) complexes of bis(diisopropylphosphino)ethane and bis(di-*tert*-butylphosphino)ethane generates the dicarbonyls **12** and **13** (Equation (7)), which could be isolated.[96] The isopropyl-substituted complex decomposes at 42 °C, whereas the more bulky *tert*-butyl-substituted complex is stable up to 125 °C. The molecular structure of **13** has been determined by X-ray crystallography and reveals a tetrahedral geometry with an average Pd–CO distance of 1.946(8) Å. Most recently, the first example of an isolable three-coordinate monocarbonyl **14** has been prepared by reductive carbonylation of a palladium(II) complex coordinated with a bulky bidentate phosphine ligand (Equation (8)). The complex has been structurally characterized and was found to be trigonal planar, with a Pd–C distance of 1.872(7) Å.[97]

$$\mathrm{Pd(OAc)_2 + 4PPh_3 + 2TsOH \xrightarrow[\text{MeOH}]{\text{CO}} Pd(CO)(PPh_3)_3 \rightleftharpoons Pd(CO)(PPh_3)_2 \rightleftharpoons [Pd(CO)(PPh_3)]_{\mathit{n}}} \qquad (6)$$



(7)

12: R = Pr^i
13: R = Bu^t



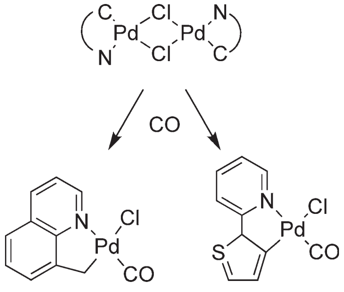
(8)

14

Mononuclear palladium(II) carbonyls are similarly normally prepared via weak ligand displacement with CO. These complexes have mainly been isolated in CO insertion studies, and as such most examples of mononuclear palladium(II) carbonyls are to be found in Section 8.04.1.3. As found in palladium(0) carbonyls, the CO ligand in palladium(II) complexes is labile. The rate of exchange of CO in $[PdCl_3(CO)]^-$ with free CO has been determined, and the activation parameters obtained.[98] The rate is first order in both $[PdCl_3(CO)]^-$ and CO, with an enthalpy of activation of $60 \pm 8\ \mathrm{kJ\ mol^{-1}}$ and an entropy of activation of $-47 \pm 30\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The negative entropy of activation is suggestive of an associative five-coordinate exchange mechanism. The first thermally stable bis(carbonyl) palladium(II) complexes, *cis*-$[Pd(SO3F)_2(CO)_2]$ (Equation (9)), has been isolated and structurally characterized.[99,100] Reductive carbonylation of mixed valence $Pd^{II}Pd^{IV}(SO_3F)_6$ which contains very weakly nucleophilic anionic ligands occurs in the solid state to give the *cis*-complex, which is stable up to 117 °C. The X-ray structure shows the expected square-planar geometry with Pd–C distances of 1.945(5) and 1.919(5) Å.

$$\mathrm{Pd^{II}Pd^{IV}(SO_3F)_6 + 5CO \longrightarrow 2Pd(SO_3F)_2(CO)_2 + CO_2 + S_2O_5F_2} \qquad (9)$$

Palladium(II) carbonyls can also be prepared via bridge-splitting coordination of CO to halide-bridged dimers, such as shown in Scheme 4, to prepare cyclometallated palladium carbonyls **15** and **16**.[101,102]



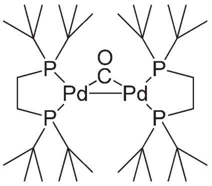
15 **16**

Scheme 4

8.04.1.6 Homonuclear Carbonyl Dimers

Like mononuclear palladium(0) carbonyls, dinuclear palladium(0) carbonyls are rare, with most palladium(0) carbonyls taking the form of higher nuclearity clusters, which are abundant (Section 8.04.1.7). One example is known, prepared by concentration under vacuum of $Pd(CO)(d^{t}bpe)$ **13** to yield structure **17**.[96] This complex has been structurally characterized and contains a Pd–Pd bond of 2.714(1) Å and a Pd–C length of 1.98(4) Å. Complex **17** is the lowest member of the series of clusters of general formula $L_nPd_x(\mu\text{-}CO)_y$.

In contrast, palladium(I) carbonyl dimers are well known, most of which involve a μ_2-bridging mode of CO bonding. Palladium(I) carbonyl dimers, along with higher oligomers, have been reviewed.[103] The majority of these complexes also contain formal Pd–Pd single bonds. The reductive carbonylation of $Pd^{II}/Pd^{IV}(SO_3F)_6$ (Equation (9)) also produces the byproduct *cyclo*-$Pd_2(SO_3F)_2(\mu\text{-}CO)_2$.[104] The molecular structure shows planar, cyclic $Pd_2(\mu\text{-}CO)_2$ units **18** linked by bidentate SO_3F^- groups to give a polymeric sheet. The CO groups bridge the two palladium centers symmetrically with an average Pd–C distance of 1.975 Å and the Pd–Pd distance (2.6929(6) Å) is indicative of a single bond. When $PdSO_4$ is reduced by CO in concentrated H_2SO_4 cation, **18** is also detected by infrared spectroscopy ($\nu(CO) = 1{,}972\ cm^{-1}$). This solution was active for the carbonylation of alcohol/olefin mixtures to give tertiary carboxylic acids.[105,106] This dication has also been analyzed by theoretical methods, and the bonding and electronic structure compared with the nickel and platinum homologs.[107]



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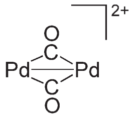
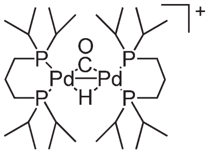


18

A number of palladium(I) dimers of general formula $[L_2Pd(\mu\text{-}H)(\mu\text{-}CO)PdL_2]X$ have been isolated or detected in solution. These complexes are normally formed under conditions of alkoxycarbonylation, and result from reduction of palladium(II) precursors with CO/ROH.[92,95] In most instances, the complexes probably form via a combination of $Pd(CO)_{1-2}L_2$ and $PdX(H)L_2$, and may be in equilibrium with palladium(0) carbonyls. Although no recent structural data are available, earlier work shows there is a Pd–Pd single bond in these dimers.[1] Derivatives prepared recently include structures **19** ($\nu(CO) = 1{,}789\ cm^{-1}$),[95,108] **20** ($\nu(CO) = 1{,}835\ cm^{-1}$),[109] and **21**.[110] These complexes are not thought to be active species in the alkoxycarbonylation of olefins, but rather represent a form of catalyst resting state. The neutral carbonyl-bridged dimer **22** has also been prepared and was found to be active in the alkoxycarbonylation reaction.[111]



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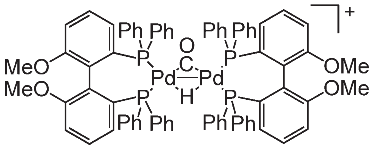

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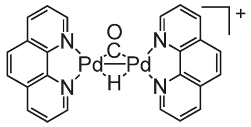

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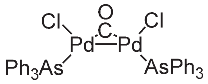
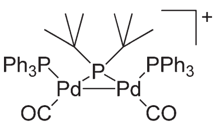


22

While most palladium(I) dimers involve carbonyl bridging, a number of them have been prepared in which the CO ligand is bound in a terminal position. These appear to result from carbonylation of precursors in which the bridging coordination mode of another ligand is already established. Carbonylation of $[Pd_2(\mu\text{-}PBu^{t}_2)(PPh_3)_2(py)_2]^+$ yields isomeric structures **23** and **24** ($\nu(CO) = 2{,}064$ and $2{,}091\ cm^{-1}$).[112] A variety of derivatives of structure **25** have also been prepared.[113,114] The carbonyl ligand in these complexes is labile, and is easily removed by purging or under vacuum.



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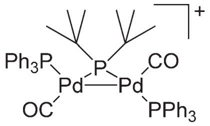

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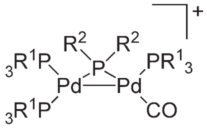
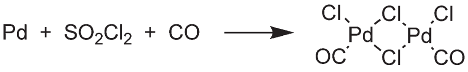


25

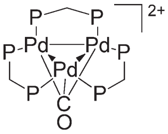
Very little work dealing with palladium(II) carbonyl dimers has appeared since COMC (1995). The previously known dimer $Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2$ has been reinvestigated, including a new synthesis via oxidation of either poorly defined $[Pd_2CO]_n$ or palladium metal with SO_2Cl_2 under CO (Equation (10)).[115] The molecular structure has now been obtained, and reveals a *cis*-arrangement of the ligands. This is in contrast to its previous formulation as the *trans*-isomer, and also to the platinum analog, which is *trans*. The Pd–Pd distance is non-bonding at 3.624 Å and the two terminal Pd–CO distances are 1.891(13) and 1.879(15) Å.[116]



(10)

8.04.1.7 Higher Nuclearity Homopalladium Clusters

The most extensively studied palladium cluster is $[Pd_3(\mu\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ **26**, prepared by reduction of palladium(II) acetate with CO/CF_3CO_2H in the presence of bis(diphenyphosphino)methane (dppm).[1] The structure is composed of a triangular array of palladium atoms located at the bottom of a cavity formed by six phenyl groups of the dppm ligands, with the μ_3-CO ligand binding to palladium on the other side. The palladium array in this cavity is accessible to small ligands, which leads to interesting host–guest chemistry. It is this chemistry, as well as related photochemical and electrochemical properties of this cluster, that have been studied since 1994. A very recent review covers most of this work,[117] and related group 10 triangulo clusters have also been reviewed.[118]



26

A number of combined theoretical and experimental studies have been carried out on the photochemistry of **26** and the geometry of its excited states.[119,120] The absorption energies of the lowest energy singlet and triplet excited states were calculated, giving good agreement with experimental values. The lowest energy excited state is the triplet $^3A_2$ state. Analysis of the HOMO shows that it is mostly composed of Pd *d*-orbitals with some p_z and some σ-CO character, and there is Pd–Pd bonding in the Pd_3-plane. The LUMO is mainly composed of metal in-plane *d*-orbitals, and is Pd–Pd antibonding. This raises the expectation that in the excited state, Pd–Pd bond elongation should occur. In an earlier study,[119] the Pd–Pd excited state distortion (ΔQ) was estimated to be 0.7 Å, and the geometry of this excited state was approximated by optimization with the Pd–Pd bond distances set to 3.3 Å. The result was a noticeable increase in the size of the host cavity, and it was concluded that larger molecules may penetrate into the excited state than is possible in the ground state. In a later study,[120] the ground state and excited triplet state structures of $[Pd_3(CO)(PH_3)_6]^{2+}$ were calculated as a model for **26**. In this work, ΔQ was calculated to be much less (~0.186 Å), and probably represents a more accurate value. Experimentally, the phosphorescence spectrum of **26** was analyzed to give an approximation of ΔQ, which was in close agreement with the theoretically derived value. Such an elongation in the Pd–Pd bonds in the excited states (Pd–Pd = 2.778–2.881 Å) suggests weak bonding in the excited states. It is thought that the binding of μ_3-CO may hold the palladium atoms together to some extent.

The binding constants of various small ligands with **26** have been determined and are used to support the host–guest model where cavity and guest ligand size affect the binding ability.[121,122] The binding properties can be tuned via a change in the cavity size that results when bis(diphenylarsino)methane (dpam) is employed to prepare $[Pd_3(CO)(dpam)_3][X]_2$, $X = CF_3CO_2^-$ and PF_6^-. The molecular structure of this complex has been determined, and reveals that longer Pd–L bonds in the arsine analog lead to a cavity of 5.9–7.3 Å across, compared to 5.5–6.5 Å in **26**. While the PF_6^- anion cannot fit into the cavity of **26**, the structure of the arsine analog shows PF_6^- inside the cavity, and binding constants of various small molecules are always larger for the dpam cluster than for **26**.[122]

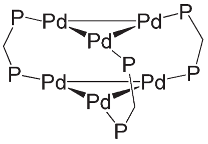
The chemical reduction of **26** has not been successful, but electrochemical studies reveal that **26** undergoes a two-electron reduction to yield $Pd_3(CO)(dppm)_3$, $\nu(CO) = 1{,}761\ cm^{-1}$. Density functional calculations on $[Pd_3(CO)(PH_3)_6]^+$ and $Pd_3(CO)(PH_3)_6$ as models for the products of one-electron and two-electron reduction show increases in the Pd–Pd distances in both cases, as expected due to occupation of the LUMO by reduction. For $Pd_3(CO)(PH_3)_6{}^0$, the Pd–Pd distances are predicted to be ~3 Å, indicative of homolytic cleavage of the Pd–Pd bonds.[123] The fact that the cluster does not break up upon reduction reflects the role dppm and CO play in holding the palladium atoms together. $Pd_3(CO)(dppm)_3$ can also be prepared by electrochemical reduction of $Pd_2Cl_2(dppm)_2$ under CO_2.[124] The high affinity of **26** for halide anions leads to pronounced effects on its electrochemistry. For instance, in the presence of I^-, $[Pd_3I(dppm)_3(CO)]^+$ results, which increases the reduction potential due to an increase in electron density at palladium.[125]

The high affinity of **26** for halide ligands also leads to a number of organic halide activation reactions. These can be of two types. They can be photoinduced, in which case **26** undergoes oxidative degradation (Equation (11)), which is a complex sequence thought to start from a host–guest pre-assembly of **26** with the chorocarbon substrate.[126] When electrochemically induced (one-electron reduction), the cluster remains intact (Equation (12)).[127] The mechanism is thought to involve reduction to $Pd_3(O_2CCF_3)(dppm)_3(CO)$, which leads to faster release of $CF_3CO_2^-$ such that the organohalide can bind and react. When acid chlorides are used, no electrochemical induction is required, and the generated RCO^+ cation can be employed in reactions with a variety of nucleophiles. A number of methods have been developed to make these reactions catalytic, and therefore of use in organic synthesis.[128–130]

$$[Pd_3(CO)(dppm)_3]^{2+} \xrightarrow[h\nu]{R\text{–}Cl} PdCl_2(dppm) + R\text{–}R \qquad (11)$$

$$[Pd_3(CF_3CO_2)(dppm)_3(CO)]^+ + RX \rightleftharpoons [Pd_3X(CO)(dppm)_3]^+ + R^+ + CF_3CO_2^- \qquad (12)$$

A number of palladium(0) carbonyl complexes containing the dppm ligand have also been prepared. Reduction of K_2PdCl_6 or $Pd(OAc)_2$ with $NaBH_4$ in the presence of CO and dppm led to a mixture of **26**, $Pd_2Cl_2(\mu\text{-}CO)$ (μ-dppm)$_2$, $Pd_2(\mu\text{-}dppm)_3$, and $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-}dppm)_3$ **27** (for clarity, carbonyls are omitted in the structure shown), along with a fluxional Pd/dppm/CO complex.[131,132] Complex **27** has been structurally characterized and found to be a new type of palladium hexamer in which two planar triangulo $Pd_3(\mu_2\text{-}CO)_3$ units are bridged together by dppm ligands (Pd–CO = 1.96(2)–2.13(2); Pd–Pd = 2.658(2)–2.724(2) Å). The fluxional complex is thought to be $[Pd_3(\mu_2\text{-}CO)_3(dppm)_2]_n$, most likely $n = 1$, in which the dppm ligands migrate around the $Pd_3(\mu_2\text{-}CO)_3$ core.



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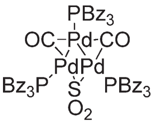
The majority of palladium carbonyl clusters that do not contain dppm instead contain monodentate phosphines, and most are based on palladium(0) in which the carbonyl ligand is either doubly or triply bridging. The usual means of characterization of the higher nuclearity carbonyls is via single crystal X-ray diffraction, and in all the succeeding cases, molecular structures have been obtained. They are normally prepared by reactions involving smaller palladium(0) clusters with CO; however, in some cases, other reagents have been employed as a source of CO. For instance, $Pd_2(\mu\text{-}SO_2)(\mu\text{-}dba)(PBz_3)_2$ reacts with CO to yield the 42-valence-electron triangulo cluster $Pd_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PBz_3)_3$ **28**.[133] Two edges of this complex are bridged by CO (ν(CO) = 1,911, 1,857 cm^{-1}) and one by SO_2. The bonding parameters of this and higher $Pd_x(CO)_yL_n$ clusters, including Pd–CO and Pd–Pd bond ranges, are summarized in Table 2. When the same starting material, $Pd_2(\mu\text{-}dba)(\mu\text{-}SO_2)(PBz_3)_2$, is reacted with COS, cleavage of the OC–S bond occurs to give tetrahedral $Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4$ **29**.[134] The CO ligand is terminal in this complex (ν(CO) = 2,030 cm^{-1}, Pd–C = 1.938(6) Å), and is bound to a palladium that is bridged to two other palladiums with a μ_3-S ligand. The Pd–Pd distances lie between 2.7416(6) and 2.9404(6) Å. The valence electron count of 58 is normally associated with butterfly (one edge of the tetrahedron opened) group 10 M_4 clusters,[1] while a tetrahedral M_4 core geometry normally results from 60 valence electrons.



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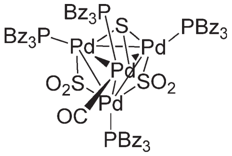

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Table 2 Summary of bonding in $Pd_x(CO)_y(PR_3)_n$ clusters

Cluster	*No (μ_2-CO)*	*No (μ_3-CO)*	*r (Pd–μ_2-CO) (Å)*	*r (Pd–μ_3-CO) (Å)*	*r(Pd–Pd) (Å)*
$Pd_3(CO)_2(SO_2)(PBz_3)_3$	2	0	2.048(6)–2.086(6)		2.6850(6)–2.7192(6)
$Pd_{10}(CO)_8(CNXyl)_2(PEt_3)_6$	6	2			2.707(8)–3.34(1)
$Pd_{12}(CO)_{12}(PBu^n{}_3)_6$	6	6			2.740–3.362
$Pd_{16}(CO)_{13}(PMe_3)_9$	6	7	1.995(11)–2.074(10)	2.086(9)–2.186(11)	2.687(1)–3.053(1)
$Pd_{35}(CO)_{23}(PMe_3)_{15}$	15	8	1.89(4)–2.15(4)	1.98(4)–2.39(4)	2.597(4)–3.551(4)
$Pd_{39}(CO)_{23}(PMe_3)_{16}$	15	8	1.83(4)–2.14(7)	1.87(6)–2.48(6)	2.556(3)–3.278(4)
$Pd_{59}(CO)_{32}(PMe_3)_{21}$	18	14	1.904(15)–2.069(14)	1.977(16)–2.216(18)	2.661(1)–3.101(2)
$Pd_{30}(CO)_{26}(PEt_3)_{10}$	22	4			2.77 (mean)
$Pd_{54}(CO)_{40}(PEt_3)_{14}$	32	8			2.76 (mean)
$Pd_{69}(CO)_{36}(PEt_3)_{18}$	18	18			2.657(1)–3.127(2)

The synthetic routes followed for larger clusters typically involve oxidative elimination of ligands (phosphines, CO) from smaller clusters resulting in aggregation. These preparations invariably lead to a mixture of clusters that are separated by crystallization. The construction of these can conceptually be thought of as a condensation ("twinning") of smaller cluster building blocks, followed by capping of some of the external faces with $(\mu_{2,3}\text{-CO})_n Pd(PR_3)$ groups. This conceptual construction becomes increasingly complicated as the size of the cluster grows, and a complete treatment for all of the compounds discussed below is beyond the scope of this chapter. Most $Pd_x(CO)_y(PR_3)_n$ clusters are composed of octahedral, cuboctahedral, and icosahedral (20-sided) units in various combinations. Large variations in the Pd–Pd distances are often found in high-nuclearity palladium carbonyl clusters (Table 2). Despite this, the mean bond distances between interior and surface Pd–Pd interactions are very similar, and normally within 0.1 Å of that in cubic close packed palladium metal (2.751 Å). This has been taken as evidence for delocalized Pd–Pd bonding in the larger clusters.

When the tetranuclear cluster $Pd_4(CO)_5(PBu^n{}_3)_4$ was treated with Me_3NO in acidic solution, the 156-valence-electron cluster $Pd_{12}(CO)_{12}(PBu^n{}_3)_6$ was crystallized from solution.[135] The structure is formed by two $Pd_6(\mu_3\text{-CO})_3(PBu^n{}_3)_3$ units linked together by six μ_2-edge-bridging CO ligands, resulting in a distorted hexacapped octahedron (an octahedral central Pd_6 core, capped by six palladium atoms). The cluster $Pd_{10}(CO)_{12}(PEt_3)_6$ is also based on an octahedral Pd_6 core, this time tetracapped.[136] Interestingly, when reacted with 2,6-xylyl isocyanide, this cluster gave $Pd_{10}(\mu_2\text{-CO})_6(\mu_3\text{-CO})(\mu\text{-CNXy})_2(PEt_3)_6$ in which the core is now based on a Pd_8 tetracapped tetrahedral unit along with two further palladium caps. The steric influence of the bulky isocyanide ligand in this cluster therefore leads to a geometry change, and an exception from the normal octahedral core geometry of palladium clusters of this size.

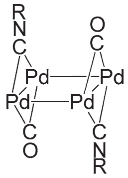
The reaction of a Pd–Ni carbonyl cluster with PMe_3 under acidic conditions did not give the expected phosphine-substituted Pd–Ni cluster, but rather by a series of extractions, a range of homopalladium clusters of formulas $Pd_{16}(CO)_{13}(PMe_3)_9$, $Pd_{35}(CO)_{23}(PMe_3)_{15}$, $Pd_{39}(CO)_{23}(PMe_3)_{16}$, and $Pd_{59}(CO)_{32}(PMe_3)_{21}$ (a cluster of formula $Pd_{29}Ni_3(CO)_{22}(PMe_3)_{13}$ was isolated as a minor product).[137,138] The 204-electron complex $Pd_{16}(CO)_{13}(PMe_3)_9$ is made up of a centered-icosahedral Pd_{13} core plus three exopolyhedral μ_2-$Pd(\mu_2\text{-CO})_2(PMe_3)$ fragments. Face condensation of two of the same Pd_{13} centered icosahedra leads to a symmetrical Pd_{23} biicosahedron with 12-face condensed palladium caps in $Pd_{35}(CO)_{23}(PMe_3)_{15}$ (426 electrons). The 468-electron cluster $Pd_{39}(CO)_{23}(PMe_3)_{16}$ is similarly based on a face-fused Pd_{23} biicosahedral core, but much less symmetrical than in $Pd_{35}(CO)_{23}(PMe_3)_{15}$. The final member of the series, 696-electron $Pd_{59}(CO)_{32}(PMe_3)_{21}$, is formed of two outer-centered icosahedra, which are connected together via an inner face-shared bioctahedron. Icosahedral packing of the metal atoms is also found in the cluster $Pd_{34}(CO)_{24}(PEt_3)_{12}$.[139]

In a similar manner, reaction of the triethylphosphine-substituted cluster $Pd_{10}(CO)_{12}(PEt_3)_6$ with Me_3NO gave $Pd_{69}(CO)_{36}(PEt_3)_{18}$, which is again based on icosahedral units.[140] This time, a conceptual face condensation of three centered icosahedra gives a linear Pd_{33} triicosahedron, which then lies inside a hexagonal Pd_{30} tube, completed by six capping palladium groups. The products obtained in these reactions depend very much upon the conditions employed. When the same precursor, $Pd_{10}(CO)_{12}(PEt_3)_6$, was deligated with trifluoroacetic acid under CO, the two clusters $Pd_{30}(CO)_{26}(PEt_3)_{10}$ and $Pd_{54}(CO)_{40}(PEt_3)_{14}$ were isolated.[141] This time, the structures are not based on icosahedra, but rather cubooctahedra. The 372-electron $Pd_{30}(CO)_{26}(PEt_3)_{10}$ cluster is made up of interpenetrating Pd_{13} centered cuboctahedra, giving what is termed a twinned Pd_{20} centered bicuboctahedron core, that is completed by six face-capping palladium atoms and four edge-bridged palladium atoms. The 648-electron complex

$Pd_{54}(CO)_{40}(PEt_3)_{14}$ is similarly composed of a multi-twinned geometry of cuboctahedral building blocks. The bonding parameters of all of the above $Pd_x(CO)_y(PR_3)_n$ clusters are summarized in Table 2.

The largest homopalladium carbonyl cluster prepared to date is $Pd_{145}(CO)_x(PEt_3)_{30}$, $x \approx 60$, prepared by reduction of $PdCl_2(PEt_3)_2$.[142] The cluster is composed of three shells of palladium atoms, the largest of which is stoichiometrically capped. The first icosahedral shell is composed of a central palladium surrounded by 12 palladium atoms. This is encapsulated by 42 palladium atoms of icosahedral shell two, which in turn is encapsulated by 60 palladium atoms of the third shell. The 30 square polygons of the third shell are capped by 30 palladium atoms. The CO groups ($\nu(CO) = 1{,}870\,cm^{-1}$) are disordered, but it is thought that 60 CO ligands edge bridge the 30 capping palladiums with half of the square basal palladium atoms of the faces. The Pd_{115} kernel is spherical with a diameter of 1.27 nm, and with capping atoms, the total diameter is 1.65 nm.

In terms of palladium(I) carbonyl cluster compounds, several publications on previously known $Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CR)_4$ have appeared.[143] Some reactions of these compounds were covered in COMC (1995), and this work has been continued. The bridging CO ligands in $Pd_4(O_2CMe_3)_4(CO)_4$ can be replaced with isocyanide ligands.[144] The parent cluster is made up of a rectangular arrangement of palladium atoms, with the short Pd–Pd contacts bridged by CO and the long contacts by $\mu\text{-}O_2CCH_3$, and this geometry is retained in the products. When 2 equiv. of 2,6-dimethylphenylisocyanide is employed, the cluster $Pd_4(\mu\text{-}O_2CMe)_4(\mu\text{-}CO)_2(\mu\text{-}CNXy)_2$ results, while 4 equiv. leads to complete substitution of the carbonyl ligands. Infrared spectroscopy ($\nu(CO) = 1{,}897\,cm^{-1}$) suggests the structural isomer **30** (excluding acetate ligands).



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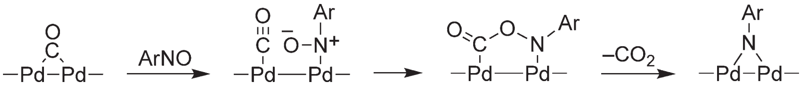
These clusters react with amine oxides, nitroso compounds, and hydroxylamines to give CO_2 and reduction of the NO group.[145,146] The reaction of carbonyls with amine oxides is well known, and reaction of nitrosobenzene or phenylhydroxylamine is thought to proceed in a similar fashion. The mechanism is thought to involve coordination of the nitrogen-containing compound to the cluster, followed by nucleophilic attack of the NO group on the carbonyl. This is illustrated for *o*-nitrosobenzene in Scheme 5. The supposed unstable palladium nitrene intermediate disproportionates to palladium(0) and palladium(II) species with elimination of nitrene, which reacts to yield a variety of organic products.

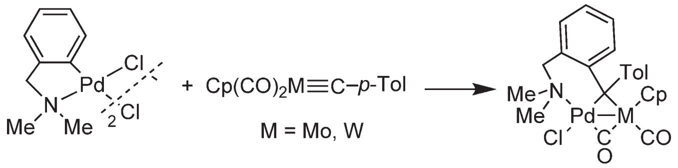
8.04.1.8 Heterometallic Dimers and Clusters

Dimers in which palladium is bridged to another transition metal both through bridging carbonyl and bridging carbene coordination have been prepared, predominantly in which the other center is an early transition metal. A wide range of Pd–Mo and Pd–W dimers are known, prepared by reacting cyclopalladated complexes with metallacarbynes of molybdenum and tungsten, for example, Equation (13).[147] The μ-alkylidene, μ-carbonyl dimers result from formal insertion of the metallacarbyne into the palladium–carbon bond, in direct analogy to the insertion of alkynes. When the reaction was attempted with chromium, different but unidentified products were obtained. By starting with different cyclopalladated ligands along with different substituents on the metallacarbyne, numerous complexes were prepared. One example for which the molecular structure has been obtained is **31**. This shows the carbonyl ligand to be semi-bridging (Pd–CO = 2.235(5) Å) and the Pd–$C_{alkylidene}$ distance to be 2.024(4) Å. The geometry around palladium is approximately square planar, with the carbene, sulfur, and chloride in a normal square-planar arrangement, with the tungsten and bridging carbonyl together making up the fourth coordination site. NMR



Scheme 5

studies on these complexes have been carried out and discussed in terms of whether the alkylidene ligand is better described as either an sp^3-dianion or a neutral carbene.[148] The conclusion was that the actual bonding situation lies somewhere between these two extremes. In terms of reactivity, treatment of these complexes with Me_3NO results in oxidation of both the carbonyl and carbene ligands, to CO_2 and ketone, respectively.[149]



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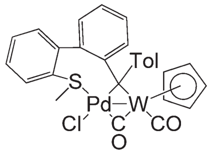

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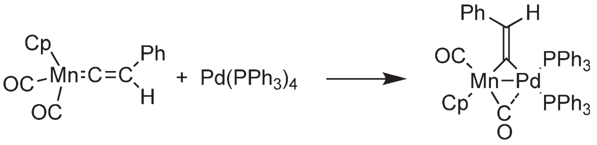
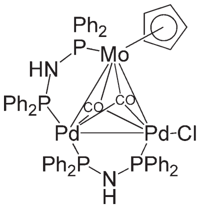
The insertion of metallacarbynes of molybdenum into the palladium–methyl bond (non-cyclopalladated) has also been carried out, similarly giving μ-alkylidene, μ-carbonyl dimers.[150] The resultant complexes seem to display similar bonding characteristics to the cyclopalladated complexes, although are less stable in solution.

Related palladium–manganese dimers can be prepared simply by reacting manganese vinylidenes with $Pd(PPh_3)_4$ (Equation (14)).[151] Further modification is possible by displacing the triphenylphosphine ligands with chelating phosphines, such as dppe. Again the carbonyl is best described as semi-bridging, and the actual degree of interaction between the palladium and the carbonyl ligands has been studied by infrared spectroscopy, and depends on the nature of the phosphine ligands.[152] More strongly donating ligands, such as dppe, promote electron density from palladium to the π^*-carbonyl orbital, resulting in a stronger semi-bridging interaction.



(14)

Just as $[Pd_3(CO)(dppm)_3]^+$ chemistry has been further developed over the last decade, related clusters containing other metal centers have been investigated in more detail. COMC (1995) covered such complexes in which the dppm moiety was used as an assembly ligand to prepare clusters such as $CoPd_2Cl(\mu_3\text{-}CO)_2(\mu\text{-dppm})_2$. Following on from this, PNP assembling ligands, mostly bis(diphenylphosphino)amine (dppa), have been employed for this purpose. The complexes are normally formed by the action of carbonyl metallates on palladium chloride complexes; for instance, the reaction between $Pd_2Cl_2(\mu\text{-dppa})_2$ and $Na[MoCp(CO)_3]$ gives $CpMoPd_2Cl(\mu_3\text{-}CO)_2(\mu\text{-dppa})_2$ **32**.[153] Such complexes are based on a planar-triangular M_3 array with either one or two μ_3-CO capping ligands, and as such the analogies between these and $[Pd_3(\mu_3\text{-}CO)(dppm)_3]^+$ and derivatives (Section 8.04.1.7) can easily be seen. A further example is $Co_2Pd_2(\mu_3\text{-}CO)_2(CO)_5(\mu\text{-dppa})_2$, **33**, prepared from $Pd_2Cl_2(\mu\text{-dppa})_2$ and 2 equiv. of $Na[Co(CO)_4]$.[154] The main difference between the dppa clusters as compared to dppm analogs is that the active NH proton of dppa opens up possibilities for functionalization. Treatment of the clusters with bases, such as KH or DBU, followed by addition of alkylating agents (RX) leads to a variety of derivatives in which the nitrogen is substituted. An example which results from methylation is $[CoPd_2(\mu_3\text{-}CO)_2(\mu\text{-dppaMe})_3]PF_6$ **34**, for which the molecular structure has been obtained. This shows that the μ_3-carbonyl ligands are not symmetrically bound, but rather have two shorter bonds to cobalt and palladium, and one longer bond to the other palladium center.



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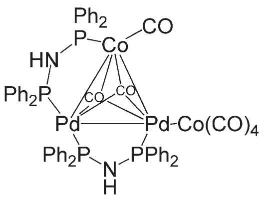

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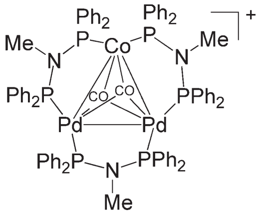

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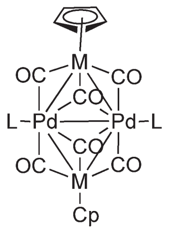
A family of palladium–iron dimers have been prepared, which contain either a dppm or dppa ligand, along with semi-bridging carbonyls located predominantly on iron.[155] The general structure of these is as shown for **35**, prepared as shown in Scheme 6. The structures of these dimers reveal the semi-bridging Pd–CO distances to be ca. 2.5–2.6 Å, suggesting only weak interaction of CO with palladium. When an alkyl group is coordinated to the palladium atom in these dimers, addition of further CO leads to insertion and palladium acyl complex **36** results. Addition of another ligand, such as PEt_3, then leads to coupling of the acyl and silyl groups, and a bridging carbene ligand forms (**36a**, Scheme 6).

Carbonylmetallates, such as $[MCp(CO)_3]^-$ (M = Cr, Mo, W), have long been employed to prepare mixed metal carbonyl clusters. As detailed in COMC (1995), when these are reacted with palladium(II) complexes, clusters such as that shown in general structure **37** result. The HOMO of $[MCp(CO)_3]^-$ is mostly *d*-orbital in character, and thus forms Pd–M bonds readily. This methodology has now been extended to include metal carbonyl fragments which are isolobal with $[MCp(CO)_3]^-$. For instance, the borole-containing rhenate **38**, which is isolobal with $[WCp(CO)_3]^-$ but has a more delocalized negative charge, reacts with $PdCl_2(NCPh)_2$ to yield $[PdRe(\eta^5\text{-}C_4H_4BPh)(CO)_3]_2$ **39**.[156] The Pd_2Re_2 core consists of a planar, triangulated rhombus with a Pd–Pd distance of 2.899(2) Å, in which two carbonyl ligands edge-bridge each of the short Pd–Re bonds. The palladium centers also interact with the boron and *ipso*-carbon atom of the phenyl ring, giving what is a two-electron three-center B–C_{ipso}–Pd bond.



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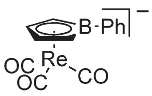

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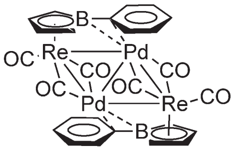

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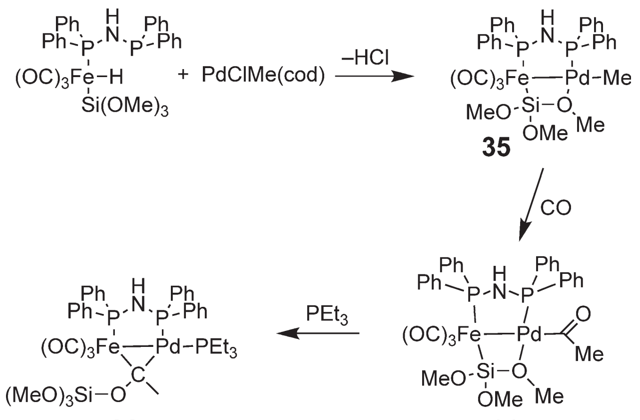
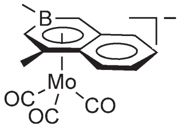


Scheme 6

A fragment isolobal with $[\mathrm{MoCp(CO)_3}]^-$ results when a 2-boratanaphthalene ligand (MeBn) is used to prepare $[\mathrm{Mo(MeBn)(CO)_3}]^-$ **40**, which reacts with $\mathrm{PdCl_2(PEt_3)_2}$ to yield $\mathrm{Pd_2Mo_2(MeBn)_2(CO)_6(PEt_3)_2}$ **41**.[157] This cluster has the same structure as the Cp analogs, **37**, composed of a linear L–Pd^{I}–Pd^{I}–L moiety bridged by $[\mathrm{Mo(MeBn)(CO)_3}]^-$ fragments. It has a short Pd–Pd bond (2.5955(4) Å) and Pd–CO distances of 2.331(3)–2.442(4) Å.

An alternative but related approach that has been used is the "neutralization" of palladium hydroxides with W, Mo, and Cr hydrides $\mathrm{MHCp(CO)_3}$.[158] When $\mathrm{Pd_2(\mu\text{-}OH)_2Ph_2(PR_3)_2}$ dimers are reacted with 1 equiv. of $\mathrm{MHCp(CO)_3}$, water is expelled and one bridging hydroxyl group is replaced with the $[\mathrm{MCp(CO)_3}]^-$ group to give **42**. An interesting feature of this cluster is that it contains a phenyl, carbonyl, and a hydroxide ligand, but does not undergo aryl migration reactions. This can be attributed to the rigidity of the cluster, and the fact that the semi-bridging carbonyls are located mainly on Cr, Mo, or W, whereas the hydroxide and phenyl ligands are solely on palladium. The molecular structure of the Cr cluster has been determined, and shows Pd–μ_2-CO and Pd–μ_3-CO distances of 2.305(9) and 2.234(8) Å, respectively. When an excess of $\mathrm{MHCp(CO)_3}$ is used, the tetranuclear clusters $\mathrm{(R_3P)_2Pd_2M_2Cp_2(\mu\text{-}CO)_4(\mu_3\text{-}CO)_2}$ of structure **37** result. It is also possible to prepare mixed metal clusters, such as $\mathrm{Pd_2MoW}$, of the same structure, and the mechanism by which these are formed has been studied.



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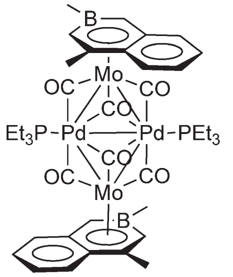

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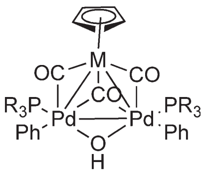
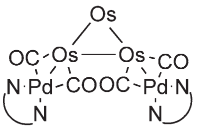


42

Numerous palladium–osmium clusters have been prepared and characterized through the reaction of osmium carbonyl clusters with palladium(0) and palladium(II) complexes. The simplest of these is probably $\mathrm{\{(bipy)Pd\}_2Os_3(CO)_{12}}$, which is prepared from $\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}$ and $\mathrm{Pd(OAc)_2(bipy)}$.[159] This cluster is made up of a triangular arrangement of $\mathrm{Os_3(CO)_8}$, with two $\mathrm{(\mu\text{-}CO)_2Pd(bipy)}$ units attached to two of the osmium atoms (**43**, terminal osmium carbonyls omitted for clarity). Each palladium atom has one symmetrically bound and one semi-bridging carbonyl ligand associated with it (Pd–CO = 1.98(2) and 2.34(2) Å).

A totally different range of products is formed when the same cluster, $\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}$, is reacted with $\mathrm{Pd_2Cl_2(\mu\text{-}dppm)_2}$. In this instance, $\mathrm{Os_5Pd_6(\mu\text{-}H)_2(CO)_{13}(\mu\text{-}CO)_5(\mu\text{-}dppm)}$, $\mathrm{Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_6(\mu\text{-}dppm)}$, and $\mathrm{Os_4Pd_6(\mu\text{-}CO)_8(\mu\text{-}dppm)_2}$ result in low yields.[160] The central core in each of these clusters is composed of a $\mathrm{Pd_6}$ bicapped tetrahedron, along with capping of some of the triangular faces with osmium (Pd–Os = 2.716(1)–3.180(2) Å). The bridging carbonyls on these complexes bridge Os–Pd bonds, while the other carbonyls are terminal and located on the osmium centers. While these clusters are composed of palladium cores, the more common arrangement for Os–Pd carbonyl clusters is an $\mathrm{Os_5(\mu_5\text{-}C)}$ core with capping $\mathrm{(\mu\text{-}CO)PdL}$ groups. These are prepared by reaction of $\mathrm{Os_5C(CO)_{15}}$ or $[\mathrm{Os_5C(CO)_{14}}]^{2-}$ with palladium(0) or palladium(II) complexes. An example is the reaction of $\mathrm{Os_5(\mu_5\text{-}C)(CO)_{15}}$ with $\mathrm{Pd(PPh_3)_4}$, which yields $\mathrm{Os_5Pd(\mu_5\text{-}C)(CO)_{12}(\mu\text{-}CO)_2(PPh_3)_2}$ **44** (terminal osmium carbonyls omitted for clarity).[161] The structure of these clusters is based on a square-based pyramidal $\mathrm{Os_5}$ core with a central carbide carbon in the basal plane. In **44**, one face is capped with a $\mathrm{(\mu\text{-}CO)_2Pd(PPh_3)}$ moiety, along with phosphine coordination to an osmium atom on the opposite side of the base. Other clusters based on this structure include $\mathrm{Os_5Pd_4(\mu_6\text{-}C)(CO)_{12}(\mu\text{-}CO)_3(\mu\text{-}dppm)_2}$, which is made up of an $\mathrm{Os_5Pd}$ octahedron with three additional edge-bridging palladium atoms,[162] $\mathrm{Os_5Pd(\mu_6\text{-}C)(CO)_{13}(\mu\text{-}CO)(\mu\text{-}dppf)}$,[163] and $\mathrm{Os_5PdCl^{I}(\mu_5\text{-}C)(CO)_{12}(\mu\text{-}PPh_2py)}$.[164]



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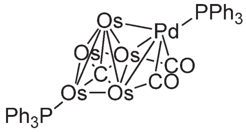
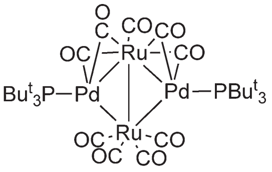


44

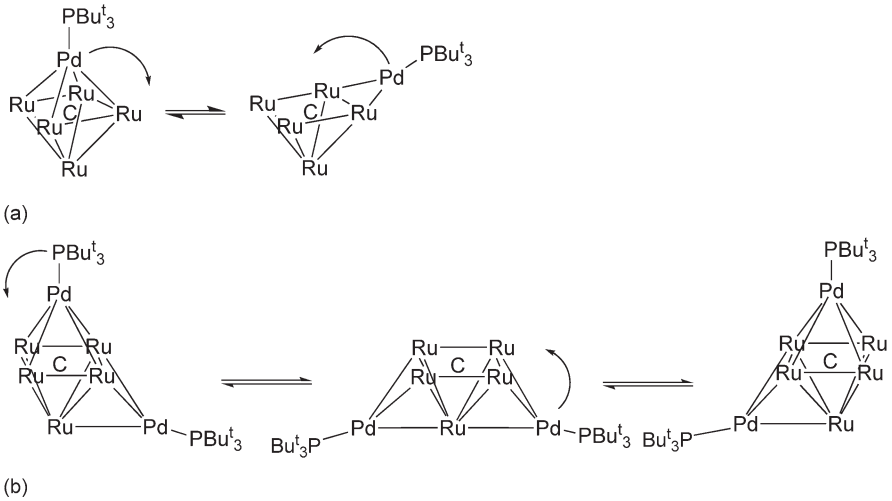
Very recently, the synthesis of palladium–group 8 carbonyl clusters has focused on ruthenium, which to a certain extent mirrors Os–Pd cluster chemistry. Most of this work has utilized the reaction of $Pd(PBu^t{}_3)_2$ with Ru carbonyl clusters of various sizes, in which loss of one phosphine ligand leads to a $Pd(PBu^t{}_3)$ fragment bridging an Ru–Ru bond. The reaction of $Ru_3(CO)_{12}$ with $Pd(PBu^t{}_3)_2$ yields $Ru_3Pd_3(CO)_{12}(PBu^t{}_3)_3$, which is made up of a triangular Ru_3 array with bridging (μ-CO)$Pd(PBu^t{}_3)$ on each edge.[165] With $Ru(CO)_5$ the resultant cluster is $Ru_2Pd_2(CO)_9(PBu^t{}_3)_2$ **45**, which contains an Ru–Ru bond bridged by palladium on each side. One of the ruthenium atoms undergoes bridging carbonyl coordination with the palladium atoms, which results in shorter Pd–Ru distances (2.7863(7), 2.7694(6) Å) as compared to those with the other ruthenium (2.8009(6), 2.8207(7) Å). The bonding situation in this complex has been assessed with molecular orbital calculations.[166]



45

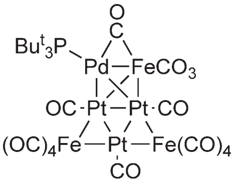
As for osmium, most work has focused on clusters that contain the $Ru_5(\mu_5\text{-}C)(CO)_x$ square-pyramidal core, the octahedral $Ru_6(\mu_6\text{-}C)(CO)_x$ core, or derivatives. Reacting $Pd(PBu^t{}_3)_2$ with $Ru_6(\mu_6\text{-}C)(CO)_{17}$ gave two isomers of $Ru_6Pd_2(\mu_6\text{-}C)(CO)_{17}(PBu^t{}_3)_2$, one in which the palladium bridges two edges of the octahedron with four bridging carbonyl ligands, and another in which one palladium is edge bridging and the other is face capping, with a total of three bridging carbonyl ligands.[165] When the palladium phosphine complex is reacted with $Ru_5(\mu_5\text{-}C)(CO)_{15}$, capping of the square base takes place to give octahedral $Ru_5Pd(\mu_6\text{-}C)(CO)_{15}(PBu^t{}_3)$.[167] One carbonyl ligand bridges a Pd–Ru edge, which results in this being the shortest Pd–Ru bond in the cluster (2.7997(3) Å). Based on NMR spectroscopic studies, the fluxional process shown in Scheme 7(a) is proposed for this cluster in solution, in which the palladium phosphine fragment flips between capping and edge bridging. The cluster $Ru_5Pd_2(\mu_6\text{-}C)(CO)_{15}(PBu^t{}_3)_2$ was also isolated in which the octahedral Ru_5Pd core is capped by an additional palladium phosphine fragment. This cluster contains two bridging carbonyl ligands (one per palladium), and similarly undergoes a fluxional process in solution as shown in Scheme 7(b).

A number of derivatives that maintain the octahedral M_6 core have been prepared. The mixed metal clusters $PtRu_5(\mu_6\text{-}C)(CO)_{16}Pd_n(PBu^t{}_3)_n$, $n = 1$ or 2, are derived from $PtRu_5(\mu_6\text{-}C)(CO)_{15}$, in which palladium bridging of either an Ru–Ru edge, or both an Ru–Ru and Pt–Ru edge, takes place.[168] In the former there are two Pd–μ-CO–Ru carbonyl ligands, whereas in the latter there are a total of three (μ-CO)Pd–Ru carbonyls. Similarly, the benzene-coordinated clusters $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-}C_6H_6)Pd_n(PBu^t{}_3)_n$, $n = 1$ or 2, are derived from $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-}C_6H_6)$.[169]



Scheme 7

Two Pd–Fe–Pt clusters have recently been prepared by reacting $Pd(PBu^t{}_3)_2$ with $Fe_3Pt_3(CO)_{15}$, yielding a mixture of $Pt_3Fe_3Pd(CO)_{15}(PBu^t{}_3)$, **46**, and $Pt_3Fe_2Pd_2(CO)_{12}(PBu^t{}_3)_2$, **47**.[170] Only **46** has a bridging carbonyl between a palladium and iron atom, while **47** contains a single Pd–Pd bridging carbonyl ligand.



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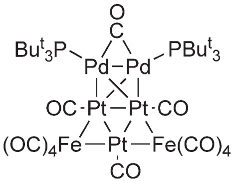
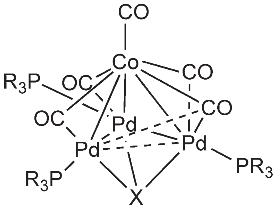


47

A number of Pd–Co carbonyl dimers and clusters have been prepared, either by reacting neutral cobalt carbonyl clusters or by anionic cobalt carbonyl metallates with palladium complexes. Treatment of either $Pd_4(\mu\text{-}Cl)_3(\mu_3\text{-}CH)(PBu^t{}_3)_4$ or $Pd_2(\mu\text{-}X)_2(PBu^t{}_3)_2$ with $Co_2(CO)_8$ gives the tetranuclear cluster $CoPd_3(\mu_3\text{-}X)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3$ **48** (X = Cl, Br, I).[171] The M_4 core is intermediate between a distorted tetrahedron and a butterfly arrangement. The Pd–Co distances range between 2.5847(7) and 2.6506(7) Å, and all three bonds are bridged by carbonyl groups. One Pd_2Co face is asymmetrically capped by CO and the Pd_3 face is capped by the chloride ligand. A range of clusters have also been prepared by reacting palladium complexes with cobalt carbonyl clusters containing the bridging 1,2-bis(diphenylphosphino)acetylene ligand.[172] An example is shown in Equation (15). In these clusters, the Co–Pd bond is bridged by the phosphine ligand, along with one or two semi-bridging carbonyls located predominantly on cobalt. In **49**, for example, the palladium carbonyl distances are 2.434(3) and 2.556(3) Å.



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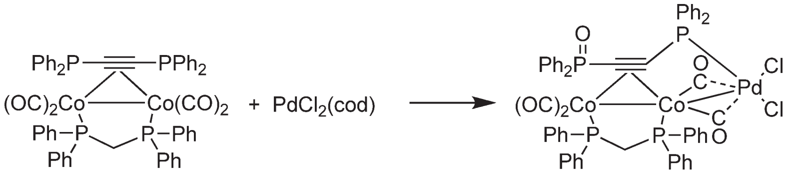
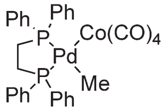


49

(15)

Heterometallic clusters are often studied for possible cooperative effects between the different metal centers, and for some Co–Pd carbonyl dimers, this has been found to be the case. The complex $Pd\{Co(CO)_4\}Me(dppe)$, **50**, results when $Pd(NO_3)Me(dppe)$ is reacted with $[Co(CO)_4]^-$, and the molecular structure reveals two semi-bridging carbonyls on cobalt (Pd–CO = 2.49(6), 2.67(8) Å).[173] When treated with CO, the acylpalladium dimer results, $Pd\{Co(CO)_4\}(COMe)(dppe)$, and it is found that the insertion rate is 80 times higher than CO insertion into PdClMe(dppe). Theoretical studies on this system indicate that the reaction occurs via a sequence of methyl migration to cobalt, insertion of CO into the Co–Me bond, followed by acyl migration back to palladium.[174] A related Pd–Co carbonyl dimer has also been employed as a catalyst for co-polymerization of aziridine with CO.[175]

Carbonyl metallates have also been used to prepare Rh–Pd clusters. The cluster $Rh_4(\mu\text{-}p\text{-}TolN)_2(CO)_7(cod)$ can be viewed as a synthon for the anionic fragment $[Rh_3(\mu\text{-}p\text{-}TolN)_2(CO)_6]^-$, and reacts with $PdCl_2(NCPh)_2$ to afford $\{Rh_3(\mu\text{-}p\text{-}TolN)_2(CO)_6\}_2Pd(CO)(NCPh)$, **51**.[176] The molecular structure reveals a planar arrangement of the seven metal atoms, in which the pseudo-octahedral palladium atoms are bound to two Rh_3 fragments through four unbridged Rh–Pd bonds. As such, the only palladium carbonyl interaction is the terminal Pd–CO bond.



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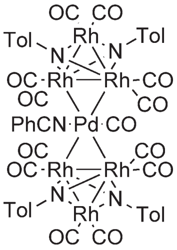


51

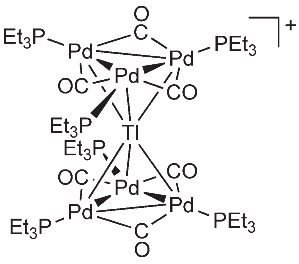
Much work seems to have gone into preparing large palladium carbonyl clusters with nickel, platinum, and gold, and some of this work is closely analogous to the larger homopalladium cluster systems covered in Section 8.04.1.7. When the simple mononuclear complexes $PtCl_2(PMe_3)_2$ and $PdCl_2(PPh_3)_2$ are reduced with $[Ni_6(CO)_{12}]^{2-}$ (in this case, simply as a reductant), the cluster $Pd_{28}H_{12}(PtPMe_3)(PtPPh_3)_{12}(CO)_{27}$ was isolated, which contains 12 hydrido atoms.[177] The cluster is composed of a $Pd_{28}Pt$ core capped by $PtPPh_3$ fragments and contains 18 μ_2-carbonyls and nine μ_3-carbonyls. The 12 hydrido atoms are thought to occupy the 12 available octahedral Pd_5Pt sites, and the cluster is described as a molecular hydrogen-storage model for palladium metal. The source of the hydrido atoms is unknown.

When the same nickel carbonyl reductant was reacted with $PdCl_2(PPh_3)_2$, the 518-valence-electron cluster $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$ was isolated.[178] The metal core of this cluster is made up of five stacked triangular layers in which the bottom, middle, and top layers are Pd_7Ni_3, and the second and fourth layer Pd_6. It contains five terminal carbonyls, two of which are on palladium, 24 edge bridging, and 12 face capping.

The first large gold–palladium carbonyl cluster characterized was $[Au_2Pd_{14}(CO)_9(PMe_3)_{11}]^{2-}$, prepared from $Pd_8(CO)_8(PMe_3)_7$, $AuCl(PCy_3)$, and $TlPF_6$.[179] The cluster consists of an Au_2Pd_{11} centered icosahedron, capped by a $Pd_3(PMe_3)_3$ triangle. The two gold centers are unexpectedly naked, in that they only interact with palladium without additional carbonyl or phosphine ligation. There are seven μ_3-carbonyl ligands, capping exposed Pd_3 faces ($Pd–C = 1.98(5)–2.22(4)$ Å), and two μ_2-bridging carbonyl ligands. Following this, the family of clusters $Au_2Pd_{21}(CO)_{20}(PEt_3)_{10}$, $Au_2Pd_{21}(CO)_{20}(PMe_3)_{10}$, and $[AuPd_{22}(CO)_{20}(PPh_3)_4(PMe_3)_6]^-$ were prepared through reduction of mixtures of $PdCl_2(PR_3)_2$ and $AuCl(PPh_3)$ with sodium hydroxide and CO.[180] All three are structurally very close to the homopalladium analog $Pd_{23}(CO)_{20}(PEt_3)_{10}$,[1] and contain 16 bridging carbonyls and four μ_3-capping carbonyl ligands. They all have a valence electron count of 290, as does $Pd_{23}(CO)_{20}(PEt_3)_{10}$.

A trimetallic Pd/Ni/Au cluster has been prepared of composition $[Au_6Pd_6(Pd_{6-x}Ni_x)Ni_{20}(CO)_{44}]^{6-}$, again through the use of $[Ni_6(CO)_{12}]^{2-}$ as a reductant with $Pd(OAc)_2$ and $AuCl(PPh_3)$.[181] The 480-valence-electron cluster is composed of two inner triangular $Au_3M_3Ni_6$ layers ($M = Pd$, Ni), along with two outer Pd_3 layers, completed by eight capping nickel atoms. Substitutional Pd/Ni disorder is found at six metal sites within the inner layers, and structural determinations of seven different crystals showed the value of x to range between 2.1 and 5.5. Of the 44 carbonyl ligands in this cluster, eight are terminal on nickel, 30 are edge bridging, and six are μ_3 capping.

Two examples of Pd–Tl carbonyl clusters have been reported. Efforts to prepare Pd–Au clusters from $Pd_{10}(CO)_{12}(PEt_3)_6$, $AuCl(PPh_3)$, and $TlPF_6$ resulted instead in the isolation of $[Tl_2Pd_{12}(CO)_9(PEt_3)_9]^{2+}$, which was initially mistakenly formulated as the Au_2Pd_{12} cluster.[182] The two thallium atoms sit at the center of this cluster, which contains six Pd–Pd edge-bridging carbonyls and three Pd_3 capping carbonyl ligands. A thallium sandwich cluster, $[(\mu_6\text{-Tl})Pd_6(\mu_2\text{-CO})_6(PEt_3)_6]^+$ **52**, can be prepared by reacting $Pd_4(\mu\text{-CO})_5(PEt_3)_4$ with $TlPF_6$.[183] The cluster is made up of two unconnected triangular $Pd_3(\mu\text{-CO})_3(PEt_3)_3$ units with a single thallium cation between them. While platinum sandwich complexes such as this are well known, this is the first example of a structurally characterized Pd_3—M–Pd_3 sandwich cluster. The bridging Pd–CO distances are quite closely ranged at 2.056(5)–2.096(5) Å and the average Pd–Tl distance is 2.91 Å. The cluster is unstable in solution, and slowly converts to the above discussed cluster, $[Tl_2Pd_{12}(CO)_9(PEt_3)_9]^{2+}$.



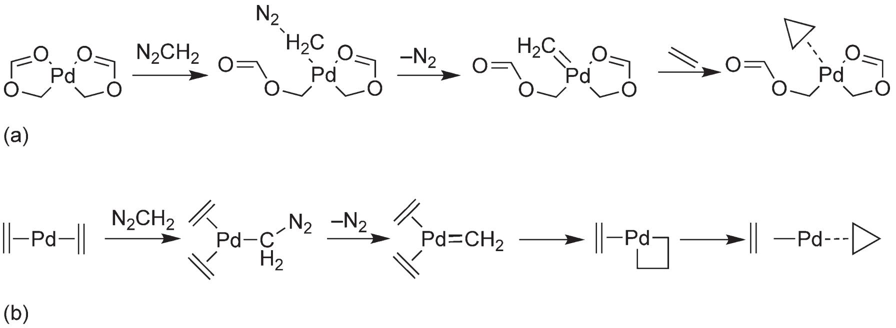
52

8.04.2 Carbene Complexes

8.04.2.1 Non-heteroatom Carbene Complexes

Until recently, monometallic palladium complexes ligated by non-heteroatom-stabilized carbene ligands were unknown; all examples contained Fischer-type or diheteroatom carbenes. Despite this, such carbene complexes have long been postulated as intermediates in several palladium-catalyzed processes. Evidence for palladium(0) alkylidene intermediates in the Stille coupling of olefinic stannanes has been reported,[184] and the palladium-catalyzed cyclopropanation of olefins has been studied by theoretical methods.[185–188] A possible mechanism for the cyclopropanation of ethylene with diazomethane has been calculated in which diazomethane reacts with a palladium(II) complex to yield a palladium methylidene in two steps (Scheme 8(a)).[185] The $\Delta G^{\ddagger}$ barrier for the second step, loss of nitrogen and generation of the palladium carbene, was calculated to be 59.8 kJ mol^{-1}. Following this, a barrierless attack of ethylene on the carbene yields a weak cyclopropane complex, which can release cyclopropane and regenerate the active palladium species. The latest theoretical studies argue for a palladium(0) carbene intermediate.[188] Again looking at the cyclopropanation of ethylene with diazomethane, a catalytic pathway with a lower overall barrier than the palladium(II) mechanism was found. This mechanism begins with coordination of diazomethane to a palladium(0) complex, also giving a Pd–CH_2–N_2 complex, which leads to a palladium(0) carbene through loss of N_2 (Scheme 8(b)). As such, the initial stages of the reaction are the same as for the palladium(II) mechanism. However, the next step involves an oxidative cyclization of the carbene with coordinated ethylene to yield a palladacyclobutane. Reductive elimination of cyclopropane regenerates the active palladium(0) complex.

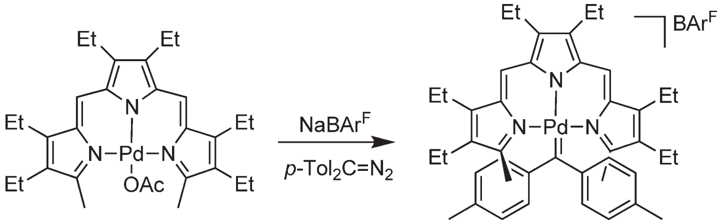
The generation and reactions of CH_2 on palladium surfaces has been studied both experimentally and theoretically. Adsorbed CH_2 on palladium is produced by photolysis of CH_2I_2 at 90 K.[189] This was analyzed by photoelectron spectroscopy, and it was found that CH_2 dimerizes to adsorbed ethylene at low temperature. At higher temperature, ethylene formation is accompanied by some methane formation. The stepwise dissociation of CH_4 to C and H on a palladium surface has been studied by DFT methods as a first step in the conversion of methane to CO/H_2.[190] It was found that CH_3 adsorbed "on top" can undergo dehydrogenation to CH_2 with a barrier of 0.52 eV. In the transition state, one C–H bond is elongated and the CH_2 fragment moves from the on-top coodination site to a bridge site. The bridged CH_2 is in turn dehydrogentated to CH with a barrier of only 0.20 eV, whereby the CH fragment moves to a hollow (μ_3-CH) site.



Scheme 8

Apart from these reactivity studies, the bonding in $[Pd{=}CH_2]^+$ has been studied by theoretical methods.[191] As has been done for the palladium carbonyls (Section 8.04.1.1), relativistic effects were evaluated and found to lead to a small contraction in the Pd–CH_2 bond length (1.856 Å with relativistic effects) and a bond strengthening of $63\,kJ\,mol^{-1}$. The bond dissociation energy for $[Pd{=}CH_2]^+$ was estimated to be $348\,kJ\,mol^{-1}$.

The first monometallic non-heteroatom-stabilized palladium carbene complex to be isolated contains the ditolylcarbene ligand, derived from ditolyldiazomethane (Equation (16)).[192] The carbene carbon in this complex resonates at 313.4 ppm in the ^{13}C NMR spectrum. A molecular structure has been obtained, and reveals a Pd–C bond length of 1.978(7) Å, which is similar to that found in the heterocyclic carbenes and is indicative of little M → L π-back-donation. This fact, together with the stability of this complex, probably results from a degree of $p(\pi)$-donation from the tolyl groups to the empty $p(\pi)$-orbital on the carbene. As such, the ligand probably has more similarities to the heteroatom-stabilized carbenes than might initially be thought. A further example of a non-heteroatom-stabilized palladium carbene has recently been prepared (Equation (17)).[193] The ^{13}C NMR shift of the carbene carbon (207.8 ppm), along with the Pd–C bond length (1.986(3) Å), are both similar to those observed in heteroatom-stabilized carbenes, and little backbonding is suggested. Here again, donation from the π-system (and the γ-heteroatoms) to the $p(\pi)$-carbene orbitals can be envisaged.



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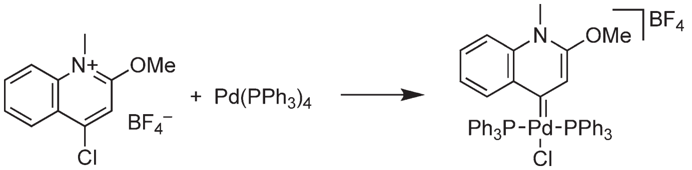
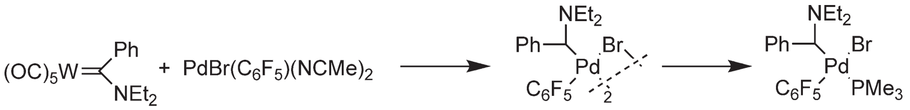


(17)

A number of bimetallic complexes which contain bridging alkylidene and vinylidene ligands semi-bonded to palladium are known, and as these also contain bridging carbonyl ligands, they are discussed in Section 8.04.1.8. In these dimers, the carbene ligand is more closely associated with the early transition metal, for which Schrock-type carbene complexes are well known.

8.04.2.2 Complexes Stabilized by One Heteroatom (Fisher-type Carbenes)

Complexes in which the carbene ligand is stabilized by one heteroatom, traditionally known as Fischer carbenes, are still relatively rare for palladium, certainly when compared to the heterocyclic carbene complexes of the following section which contain two heteroatoms. No examples of such palladium complexes were reported in COMC (1995). These complexes have been proposed as intermediates in a number of palladium-catalyzed reactions, including carbene transfer from chromium and tungsten Fischer carbene complexes,[194] and carbene insertion into benzyl halides.[195] Evidence that Fischer carbenes transfer from early transition metals to palladium has recently been provided by the isolation of palladium(II) complexes in which the carbene ligand is derived from tungsten complexes, for example, Equation (18).[196,197] The crystal structure of **53** has been obtained and shows a Pd–$C_{carbene}$ bond distance of 2.030(5) Å, which is indicative of a single bond containing little Pd → L backbonding, and is consistent with those found in palladium complexes of the heterocyclic carbenes. As shown in Equation (19), these amino carbene complexes undergo reductive elimination with the aryl group to yield iminium cations and palladium(0).



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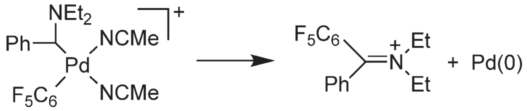
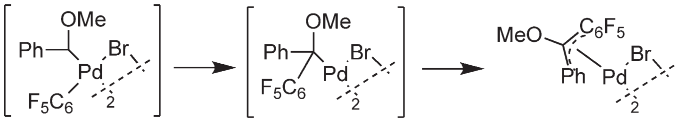
(18)



(19)

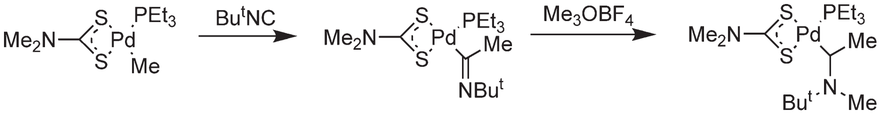
The analogous methoxy carbene complexes could not be isolated by following this carbene transfer route, and instead products of carbene insertion into the palladium–aryl bond **54** are observed, for example, Equation (20). These reactions are directly analogous with those observed for alkyl- and arylpalladium heterocyclic carbene complexes, in which both reductive elimination and carbene insertion reactions have been observed (Section 8.04.2.3.4).



(20)

54

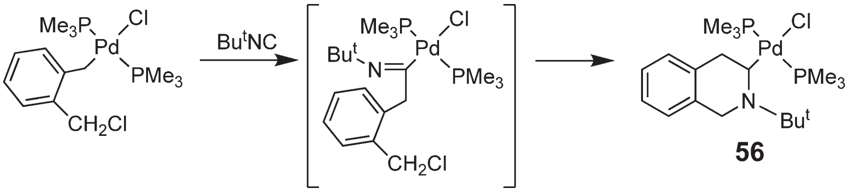
Apart from carbene transfer from early transition metals, insertion of isocyanides into a palladium alkyl bond, followed by alkylation, has been found to lead to palladium(II) amino carbene complexes (Equation (21)).[198,199] Isocyanide insertion first leads to an iminoacyl complex, from which the carbene is generated by alkylation or protonation of the nitrogen. The molecular structure of **55** has been determined and a Pd–C bond length of 1.97(1) Å observed.



(21)

55

An example of this reaction has been reported in which the alkylpalladium group is functionalized with a chlorobenzyl moiety, in which case intramolecular attack on the aminoacyl leads to a cyclic carbene ligand (Equation (22)).[200] The structure of **56** has also been obtained and a Pd–C bond length of 2.01(2) Å found. In both of the above cases, deprotonation of the carbon α to the carbene atom can be carried out, leading to formally anionic vinyl ligands.



(22)

56

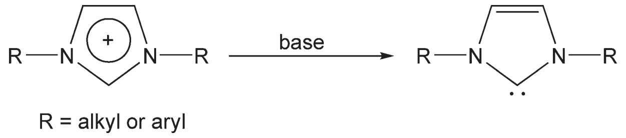
8.04.2.3 Complexes of *N*-heterocyclic and Related Carbenes

8.04.2.3.1 Introduction

In the past 10–12 years, the chemistry of palladium has seen a strong growth in interest in complexes of NHCs and their derivatives. The main focus has been in the use of NHCs as ligands, and the resulting palladium complexes as catalysts in various coupling reactions. Despite having its beginnings as far back as the 1960s, the escalation of interest in NHC chemistry resulted from the synthesis of free imidazole-based NHCs in 1991.[201,201a] To illustrate this point, there has been an almost exponential increase in publications on Pd–carbene chemistry: from one publication in 1993 to over 50 publications on Pd–carbene complexes in 2004, and rising. The isolation of free carbenes allowed researchers to apply NHCs as ligands in much the same way as phosphines and other neutral two-electron donor ligands are utilized. Comparisons to free phosphines are frequently made and the view has some validity; however, NHCs with their very high basicity, poor π-acidity, and unusual distribution of steric bulk, display unique properties. The early literature on NHC chemistry has been extensively reviewed in a variety of excellent publications.[202,202a–202h] The reviews include discussions of carbene synthesis, their electronic structure and stability, and carbene complexation; hence, these earlier accounts will not be discussed further here. This chapter will deal primarily with literature appearing since COMC (1995)[1] up until the end of 2004.

8.04.2.3.1.(i) Formation of complexes via free carbene

The proton in the 2-position of azolium salts is quite acidic and can be removed under a variety of conditions yielding the carbene ligand; the first free NHCs were generated by the deprotonation of imidazolium salts using strong bases (Equation (23)).[201,201a] This has now become a common route to preparing a wide range of carbene complexes, and the prior generation of free carbene ligand probably provides the best route to forming Pd(0) and simple hydrocarbylpalladium(II) complexes of carbenes. The initial base of choice was NaH with catalytic amounts of KOBu^{t}, and this is still the base most commonly used.[201,201a] The first Pd^{II}Me(carbene) complexes were prepared by this route.[203,204] The treatment of PdClMe(cod) with 1 equiv. of free 1,3-dimethylimidazolin–2-ylidene or 1,3,4,5-tetramethylimidazolin–2-ylidene gave a dinuclear chloro-bridged dimer, which reacted with neutral and anionic ligands, in the presence of Ag^{+}, to give a range of PdMe(carbene)L_2 complexes in high yield. These included the interesting but unstable complex, [PdMe(1,3-dimethylimidazolin–2-ylidene)(cod)]BF_4 **57**, in which the palladium is bound to carbon only, and which decomposes to give 1,2,3-trimethylimidazolium salt and Pd(0) (Equation (24)).[204] Bis-carbene complexes, PdClMe(carbene)$_2$, were prepared by the addition of 2 to 3 equiv. of free carbene to PdClMe(cod).[204]



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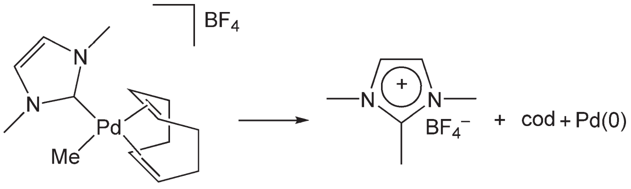

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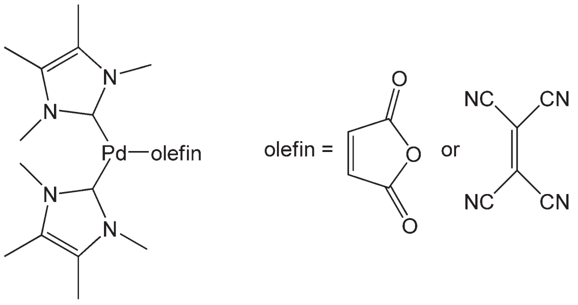
(24)

Alternative bases have also been successfully applied to generate free carbene. A liquid ammonia route in which the azolium salt is dissolved or suspended in a mixture of liquid ammonia and a polar aprotic solvent and treated with NaH at very low temperatures has been developed.[205,206] Butyllithium[207,208] has been used as an alternative base, and milder bases such as $\text{K[N(SiMe}_3)_2]$ and $\text{Li[NPr}^{\text{i}}{}_2]$ in combination with low temperatures have also been applied in the deprotonation of base-sensitive functionalized imidazolium salts.[209,210]

Zero-valent palladium complexes are readily prepared by the addition of free carbene to appropriate palladium(0) starting compounds. Pd^0(carbene)$_2$ complexes with activated olefins, **58**, were prepared by the addition of free carbene to Pd(cod)(olefin) complexes.[211] IR and NMR studies on the complexes demonstrated the very powerful σ-donor and poor π-acceptor characteristics of the carbene ligands. Very large shifts to lower energy for the $\text{C}{\equiv}\text{N}$ and $\text{C}{=}\text{O}$ stretches in tetracyanoethylene and maleic anhydride ligands, and significant upfield shifts in the ^{1}H NMR for the olefinic protons, reflect the large movement of electron density from the carbene through the metal center to the olefin. Homoleptic palladium(0) carbene complexes, **60**, have been conveniently prepared by the reaction of free carbene with palladium(0) (tri-*ortho*-tolylphosphine)$_2$ by ligand exchange (Equation (25)).[207] The exchange process occurs in a stepwise manner via the mixed phosphine–NHC complex **59**, which (where $\text{R} = \text{Bu}^{\text{t}}$) showed high activity in Suzuki coupling between phenylboronic acid and *p*-chlorotoluene, whereas the other complexes gave poor conversions.



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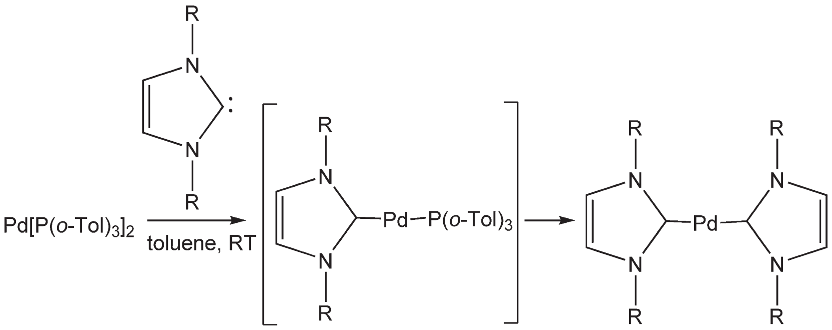
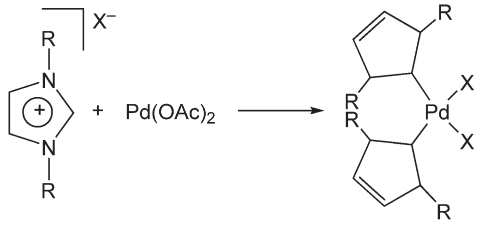


59 **60**

(25)

8.04.2.3.1.(ii) *In situ* deprotonation of azolium salts in the presence of a suitable metal fragment

In situ deprotonation of an azolium salt by a basic ligand on the precursor metal complex can be used to generate the metal–carbene complex.[202a] The formation of a strong M–carbene bond is presumably an important factor in driving this reaction, even in the presence of a weak base. This approach has been used effectively to synthesize many metal–carbene complexes and has been particularly widely employed for the preparation of NHC complexes. For example, mono- and bidentate imidazol–2-ylidene, and triazol–5-ylidene palladium(II) complexes have been prepared by the direct reaction of $Pd(OAc)_2$ with the appropriate precursor azolium salt,[212,205,213] as illustrated in Equations (26) and (27). A modified approach, using high temperatures and DMSO as the solvent, was developed to give an improved yield of the chelating dicarbene complex **62**.[214] The resulting complex was used to catalyze various coupling reactions (Suzuki, Heck, and alkyne). Subsequent studies by the same group led to further improvements in the synthesis of chelating di-NHC complexes using a stepped heating regimen and DMSO as solvent.[215–217] Dicationic homoleptic and heteroleptic di{bis(NHC)} complexes of palladium were also successfully prepared.[216] Complexes of type **62** (R = Me, Mes; X = Br, I) were converted to mono- and dicationic palladium complexes by treatment with $K[PF_6]$, $Na[PF_6]$, or $Ag[BF_4]$. A molecular structure of the dicationic complex $[Pd\{1,1'\text{-dimethyl–}3,3'\text{-methylenediimidazolin–}2,2'\text{-diylidene}\}(NCMe)_2][BF_4]_2$ was obtained.[215] The Pd–C distances are short (av. 1.969(3) Å] and the C–Pd–C bite angle quite small [84.1(1)°]. These studies on dicarbene complexes were summarized in a further report describing an improved synthesis of sterically demanding 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolin-2,2′-diylidene complexes.[217] Stable PdX_2(di-carbene) complexes (X = anionic fluorocarboxylate ligands) have been synthesized by treatment of a complex of type **62** with $Ag[O_2CR]$.[218] A palladium complex of chelating dicarbene with 4-methoxybenzyl substituents on the nitrogens has been synthesized and an X-ray structure provided.[219] Other examples of di-*tert*-butyldiimidazolin–2,2′-diylidene Pd(II) complexes have been prepared, which include $Pd^{II}Me_2$ complexes of chelating carbenes containing methylene and ethylene bridges.[220]



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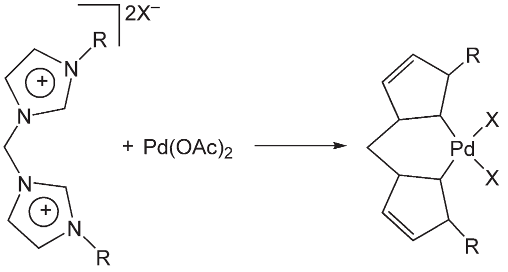
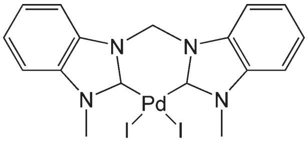


(27)

62

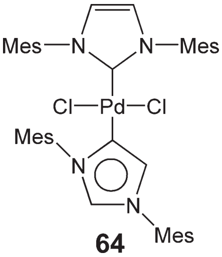
Palladium complexes of monodentate and chelating bidentate benzimidazolin-2-ylidene ligands have been prepared in moderate to good yield, via *in situ* deprotonation, with $Pd(OAc)_2$ in THF.[221] To effect formation of the chelated 1,1′-methylene–bis(benzimidazolin–2-ylidene)palladium complex 63, it was necessary to reflux for 8 h and then stir for a further 24 h in THF. A complex of the bidentate ligand, 1,3-bis-(3-neopentylbenzimidazol-2-ylidene)-2,2-dimethylpropane, has been prepared and structurally characterized.[222] The same group has also synthesized the dicarbene palladium complex *trans*-$[PdBr_2L_2]$ ($L_2 = $ 1,3-di-(2-propenyl)-benzimidazol-2-ylidene), and an X-ray structure was obtained.[223]



63

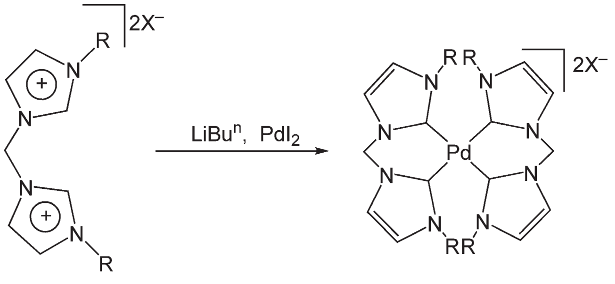
Fluoroalkylated NHC complexes and complexes of NHCs with long chain alkyl groups may be synthesized by the reaction of the appropriate imidazolium salt with $Pd(OAc)_2$.[224] These complexes, which are formed via the well-established bridged, binuclear intermediates, are soluble in $scCO_2$. However, preliminary coupling reactions carried out in $scCO_2$ were disappointing.

Reaction of imidazolium salt, *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolium chloride, with $Pd(OAc)_2$ in dioxane at 80 °C, gave the first example of a palladium complex 64 with a carbene bound through the C5 carbon.[225] Whether 64 forms or not is sensitive to reaction conditions, which may explain why a complex of this type had not been reported before. Surprisingly, complex 64 gave rise to a substantially better cross-coupling catalyst than a complex with two normally bound carbenes.



64

The synthesis of carbene complexes by *in situ* deprotonation may be further extended by the addition of base to the reaction mixture to assist deprotonation of the azolium salt.[208,226] For example, 1,1′-methylene-3,3′-dialkyldiimidazolium salts were deprotonated with *n*-butyllithium in the presence of PdI_2 to yield bis-dicarbene complexes **65**, containing two bidentate dialkyldiimidazolin-2,2′-diylidene chelate ligands (Equation (28)). *In situ* deprotonation of imidazolium salts has also been successfully applied to the synthesis of a palladium complex of the functionalized carbene 1,3-di-(ethoxycarbonylmethyl)imidazolin-2-ylidene **66**, containing ester groups in the 1- and 3-positions, using $Pd(OAc)_2$ and NaOEt.[227] The synthesis of mixed ligand $PdI_2(carbene)(PR_3)$ complexes was achieved by a similar method, via iodo-bridged dinuclear $[PdI(\mu\text{-}I)(carbene)_2]_2$.[228] An *in situ* method using $KOBu^t$ to deprotonate the imidazolium salt in the presence of $PdCl_2$ has been exploited to prepare [1-(9-anthracenylmethyl)–3-alkylimidazol–2-ylidene] complexes,[229] which were found to be fluorescent.[230] Interestingly, the *CN*- ligands generated during the formation of these complexes come from the cleavage of the acetonitrile solvent.



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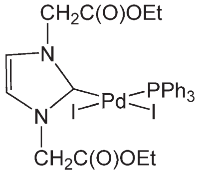
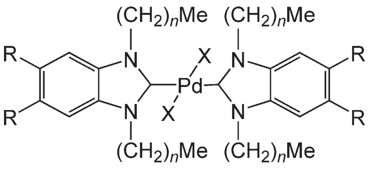
65



66

8.04.2.3.1.(iii) Carbene-transfer reactions

Carbene-transfer reactions are particularly valuable in the formation of Pd–carbene complexes in which the free carbene is not readily accessible, or where a functionalized imidazolium salt, which contains acidic protons other that the C2 proton, is used. Therefore, an important development in the synthesis of carbene complexes was the use of Ag–carbene compounds to transfer the carbene to other metal centers. The complex $PdCl_2$(*N*,*N*′-diethylbenzimidazol-2-ylidene) was prepared by this route.[231] The Ag–carbenes are prepared by the reaction of imidazolium salts with the weakly basic Ag_2O. Thermally stable liquid crystalline Pd(ii)–carbene complexes **67** and **68** were also prepared by this method.[232] In this case, the Ag–carbene compounds were generated and used *in situ* to form the palladium complexes. The unsymmetrical complex $PdCl_2$(1-ethyl-3-methylimidazol-2-ylidene)$_2$ complex, with different *N*-alkyl substituents, has also been synthesized via the Ag transfer route and the complex has been structurally characterized.[233]



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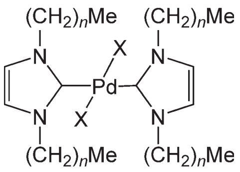


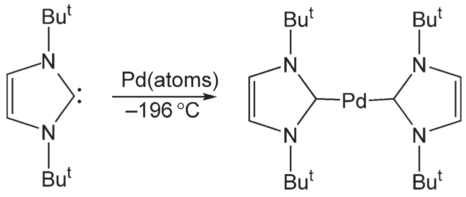
68

R = H, Me; *n* = 9, 11, 13, 15; X = Cl, Br

Other transition metal carbene complexes may also be used to transfer carbenes to palladium. The complexes M(carbene)$(CO)_5$, where M = W, Mo, and Cr, have been employed to transfer saturated NHC ligands to a range of metals, including Pd, in good yield.[234,235] The presence of other ligands on the group 5 metal can dramatically affect the reaction behavior. Reacting W(carbene)$(CO)_4PPh_3$, as the transfer agent, with $PdCl_2(NCPh)_2$ gave a mixture of Pd products, which could not be purified, and attempts to use W(carbene)$(CO)_3$(dppe) gave only $PdCl_2$(dppe) and free imidazolium salt. It would appear that the chelating bis(phosphine) has been preferentially transferred to the Pd, and the imidazolium salt is generated from the decomposition of the remaining W entity.

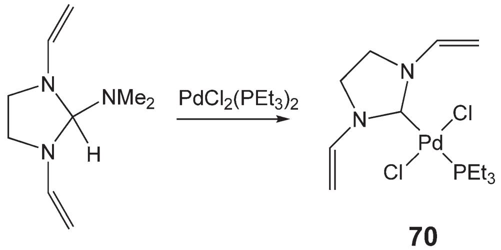
8.04.2.3.1.(iv) Miscellaneous methods

Co-condensation of palladium vapor with 1,3-di-*N*-*tert*-butylimidazol-2-ylidene provided an alternative synthetic route to a two-coordinate, homoleptic, zero-valent palladium–carbene complex shown in Equation (29).[236]



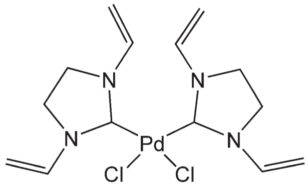
(29)

The aminal **69** has been used to synthesize Pd(carbene) complexes with saturated carbene ligands in which allyl groups are attached to the nitrogens (Equation (30)).[237,238] This method provides a potentially useful synthetic route to carbenes which are prone to alkyl group rearrangements. By adding increasing amounts of aminal to the palladium(II) starting complex, mono-, bis-, and tris-carbene complexes were synthesized. Monocarbene **70** and bis-carbene complexes **71** have been prepared and the interconversion of *cis*- and *trans*-complexes of type **71** has been studied.[238]



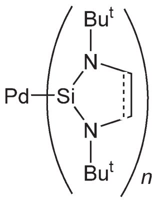
69 **70**

(30)



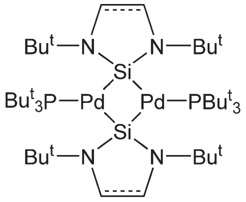
71

The synthesis of the first homoleptic palladium complexes of saturated and unsaturated *N*-heterocyclic silylenes, **72**, has been reported.[239] Reaction of $Pd(PBu^t)_3$ with excess saturated silylene gave the tetrakis-silylene, and reaction with excess unsaturated carbene gave the tris-silylene. The complexes were identified in solution by NMR. On working up the solutions in the presence of displaced phosphine, the dinuclear complex **73** was obtained and identified by X-ray crystallography. The two silylene ligands bridge the two palladiums. Complex **74** was also identified in solution but could not be isolated.



n = 4 (for saturated silylene)
3 (for unsaturated silylene)

72



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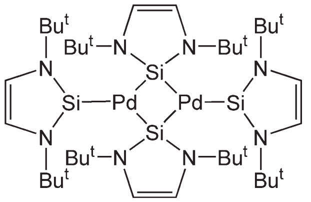

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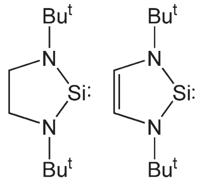


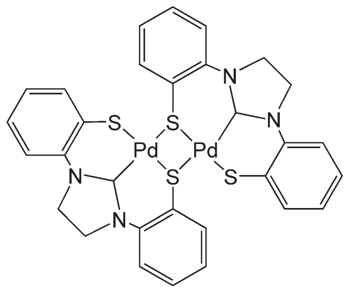
silylene reagent

A common method for the *in situ* synthesis of carbene complexes has been via isocyanide complexes, although this method is used less frequently now that free carbenes have been isolated. An example of this approach is the reaction of the (1,1-ethylenedithiolato)(isocyanide)palladium(II) complexes with $NHEt_2$ and NH_3.[240] Reaction of $M\{\eta^2\text{-}S_2C{=}C[C(O)Me]_2\}(CNR)_2$ (M = Pd, Pt; R = Bu^t, Xy) with $NHEt_2$ gave the complexes $M\{\eta^2\text{-}S_2C{=}C[C(O)Me]_2\}(CNR)\{C(NEt_2)(NHR)\}$, in which one isocyanide ligand was converted into an acyclic carbene. However, reaction with ammonia, where CNR = CNXy, both isocyanide ligands reacted and a bis-acyclic carbene complex resulted. Other examples of isocyanides being converted into carbenes are mentioned in the following section on isocyanide chemistry.

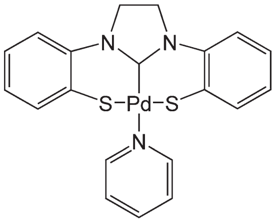
Carbene ligands have also been synthesized via a thermal process which eliminates pentafluorobenzene from the 2-position of the heterocyclic ring; a palladium complex was prepared by reaction of the carbene precursor with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ to give a 95% yield in air and without prior solvent purification.[241]

8.04.2.3.2 Functionalized carbenes

A variety of palladium complexes with functionalized carbenes have been synthesized and a range of synthetic methods have been employed. A dinuclear Pd(II) complex containing the carbene–dithiolate ligand, 1,3-imidazolidinyl–*N*,*N*′-bis(2-benzenethiolate) **75**, was prepared in a one-pot reaction between $PdCl_2(cod)$ with [1,2-ethanediamine-*N*,*N*′-bis(2-benzenethiolate)]$^{2-}$ and $CH(OEt)_3$.[242,243] Treatment with pyridine split the dimer to give the mononuclear complex **76**. An interesting *in situ* metal template synthesis of a chelating phosphine-functionalized carbene complex **77** has been reported (Equation (31)).[244]



75



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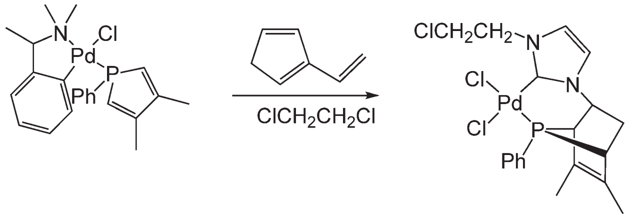
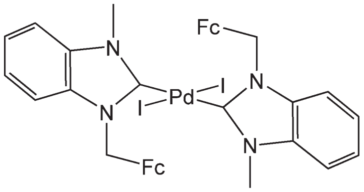


(31)

77

Palladium(II) complexes of imidazoline-2-ylidenes with pendant 1- and 1,3-di-methylferrocenyl substituents, 78 and 79, were prepared by the reaction of the relevant benzimidazolium salt with Pd(OAc)$_2$ and a crystal structure of 79 obtained.[245] In common with other related carbene complexes, the plane of the benzimidazole rings are twisted with respect to the palladium coordination plane; the dihedral angle is 85.17(23)°. The closely related 1-ferrocenyl-3-methyl-benzimidazolin-2-ylidene complex (in which there is no methyl linker between the N and the ferrocenyl group) has also been prepared by a similar route.[246] 1-Ferrocenylmethyl-3-benzylimidazolidinium and 1-ferrocenyl-methyl-3-(2,4,6-trimethylbenzyl)imidazolidinium iodide salts were prepared and complexed to Pd by an *in situ* deprotonation route.[247] Cyclic voltammetry studies on the salts and the Pd complex show a number of redox processes, indicating that the ferrocenyl substituents are electronically isolated from the remaining molecular framework.



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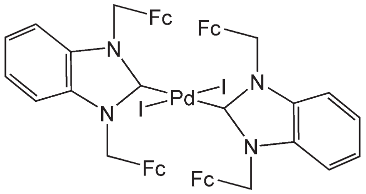
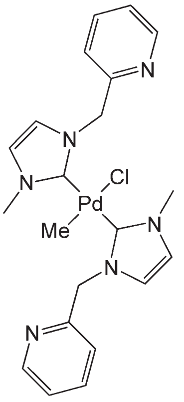


79

Strong bases are often incompatible with functionalized imidazolium salts due to the reactivity of protons other than the C2 proton of the ring; consequently, synthetic routes avoiding the use of such bases may be necessary. Pd^{II}Me complexes of a chelating carbene–picolyl ligand and other functionalized carbenes 80–82 were first prepared via a silver-transfer route, and this method is now a common route to such complexes.[248] These complexes were found to provide very efficient catalysts for coupling reactions. Subsequent studies on the synthesis of closely related Pd^{II}Me complexes of chelating carbene–pyridine ligands showed that it is possible to prepare such complexes by deprotonation using a milder base, for example, LiNPr$^{i}_{2}$, at low temperatures, and then trapping the *in situ*-formed free carbene with the appropriate metal complex.[209] Reaction of the imidazolium salt 1,3-bis(2-pyridyl)imidazol-2-ylidene (pyimypy) with Pd(OAc)$_2$ affords complex 83, in which the potentially tridentate ligand is coordinated in a bidentate manner.[249] The ligand was shown to be hemilabile and treatment with diverse reagents led to complexes in which the ligand was variously monodentate or bidentate. Structures were obtained for a number of new complexes.



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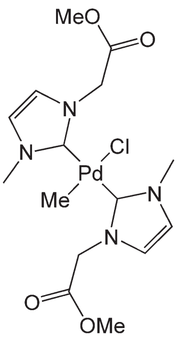

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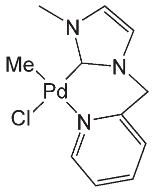

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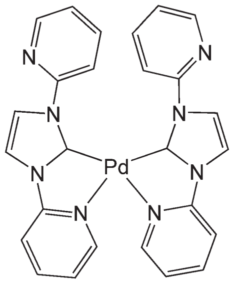
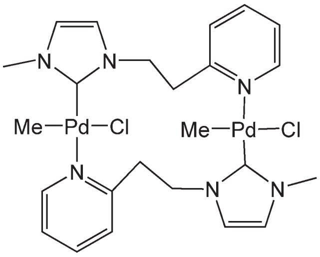


83

Methylpalladium(II) complexes of bidentate carbene–pyridine (ethyl spacer between the carbene and pyridine **84**) and picolyl–carbene–picolyl **85** ligands were prepared via Ag transfer.[250] The ligand with the ethyl spacer gives rise to a dimeric complex **84** rather than the expected mononuclear species. Related complexes, **86** , of the tridentate 1,3-bis(diisopropyl–2-ethylamino)-imidazol–2-ylidene ligand were also prepared.[250] The complex **86**, where X = Me, was found to be very unstable and rapidly decomposed at room temperature to give 1,3-bis(diisopropyl-2-ethylamino)-2-methylimidazolium salt. Carbene–cyclophane, **87**, and half-cyclophane-type complexes, **88** and **89**, of Pd were synthesized from Pd(OAc)$_2$.[250] The complexes were tested in Heck and Suzuki coupling and showed good reactivity for coupling aryl bromides. A comprehensive study of the synthesis of imidazolium-linked cyclophanes, their coordination to Pd, and catalytic testing in Heck and Suzuki coupling has been reported.[251] A large range of different ligand types were synthesized and reacted with Pd(OAc)$_2$ or other Pd salts in the presence of base to give tetrakiscarbene (bis-cyclophane) and dicarbene complexes such as **87**, **90**, and **91**.[251] A number of X-ray structures were obtained. Complex **87** showed the best catalytic performance in Heck and Suzuki coupling between iodo- and bromoaryls and acrylates or phenylboronic acid, respectively.



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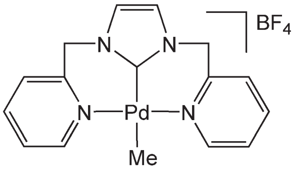

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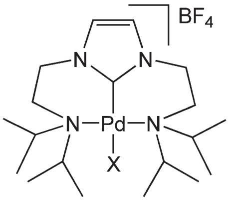
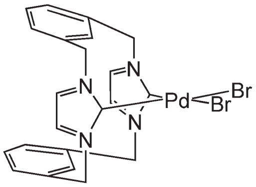


X = Me, Cl

86



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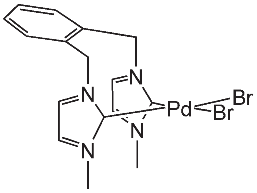

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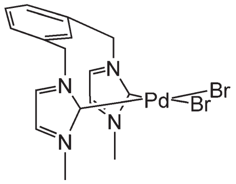

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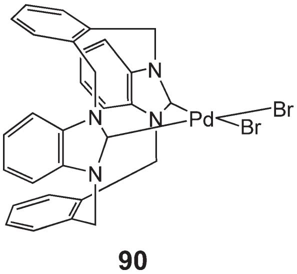

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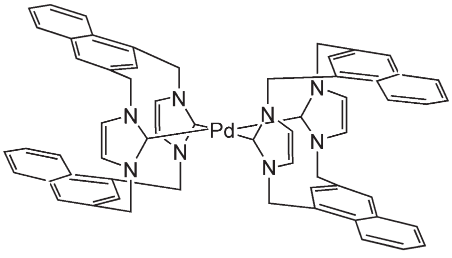
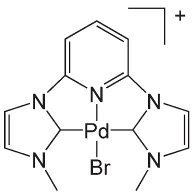


91

Further examples of palladium picolyl- and pyridyl-functionalized carbene complexes, and also a methoxy ether-functionalized complex have been reported.[252–255] The synthesis of *C–N* chelating and *N–C–N* pincer carbene complexes of palladium have been described.[252–254] Complexes were generally prepared by a silver-transfer route, although several were prepared via the free carbene method. Structural studies were undertaken on a number of the complexes. Air and thermally stable tridentate carbene *C–N–C* **92**, **93** and *C–C–C* **94** palladium pincer complexes have been prepared.[256,257] Complex **94** is formed by the reaction of the appropriate aryl-bridged precursor with

$Pd_2(dba)_3$; 92 and 93 are generated by the reaction of $Pd(OAc)_2$ with the ligand precursor. Aspects of their structure, fluxional behavior, and catalytic reactivity have been reported. The conformer interconversion for the cationic carbene–pyridine–carbene (*C–N–C*) pincer **93** and the neutral *C–C–C* dicarbene Pd pincer **94** complexes were investigated, and it was found that, for cationic complexes, the choice of anion can affect the mechanism for interconversion.[258]



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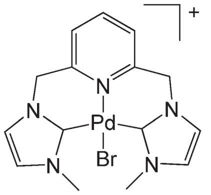

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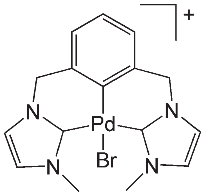
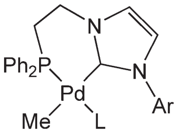


94

(Diphenylphosphino)alkyl-functionalized carbenes have also been extensively investigated and a number of palladium complexes have been synthesized by trapping free carbene, generated *in situ* with $K[N(SiMe_3)_2]$ in THF or NaOAc in DMSO, by an appropriate metal precursor (examples include complexes of type 95).[259–261] Several complexes were structurally characterized, and several were tested in Heck coupling.[259] Complex 95, where L = Me and Ar = 2,6-$Pr^i_2C_6H_3$, was also tested in CO/ethylene co-polymerization.[259] The unusual complex 96 was isolated from the reaction of MeI with 95 (L = Me).[259] A mechanism for its formation was proposed, which involved successive Pd(II)–Pd(IV) oxidative addition (of MeI) and reductive elimination (of CH_3CH_3) cycles, terminating with the reductive elimination of methylimidazolium.



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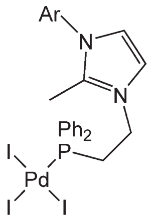
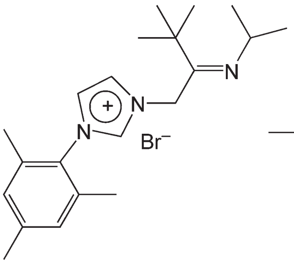


96

L = CH_3, pyridine, MeCN, PhCN, PMe_3; Ar = Mes, 2,6-$Pr_2^iC_6H_3$

Several examples of imino-functionalized carbene complexes of palladium have been described.[262–264] The imidazolium salt 97 was prepared and coordinated to Pd by an Ag-transfer reaction.[262] Tautomerization of the carbene–imine bond occurs during the transfer reaction to give the the enamine complex 98. Neutral and cationic Pd complexes of a second closely related chelating iminocarbene ligand, 99, were also prepared via an Ag-transfer route.[264] In this case, no tautomerization was reported. However, evidence of solvent-dependent hemilability was observed.



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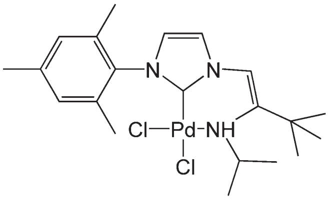

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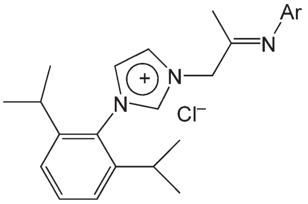
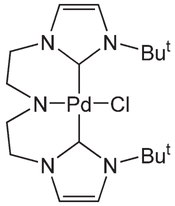


99

New approaches to interesting functionalized carbenes and their Pd complexes remain an area of considerable interest. A chelating imido–dicarbene has been prepared and a Pd complex 100 obtained by an Ag-transfer route.[265]

A benzimidazole-type NHC derived from phen has been prepared, and its Pd complex **101** was synthesized from $Pd(OAc)_2$.[266] Preliminary catalytic testing in Suzuki coupling was undertaken. Palladium complexes of phenolate-functionalized saturated carbenes have also been synthesised **102**.[267] Allylpalladium dimer reacts with keto-functionalized imidazolium salt in the presence of base to generate an anionic NHC–enolate ligand on complexation **103**; the complex has been structurally characterized.[268] Sterically demanding, bioxazoline-derived NHC ligands have been synthesised and complexed to Pd **104**.[269] The complexes have been successfully tested in Suzuki coupling of sterically hindered aryl chlorides and boronic acids to give tetra-*ortho*-substituted biaryls in good yield. There is a clear correlation between catalyst performance and the size of the oxazoline side ring.



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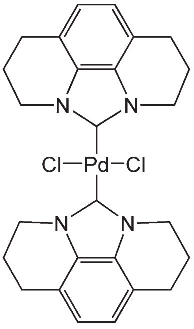

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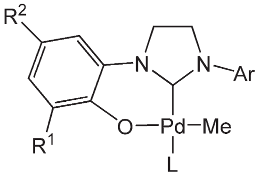

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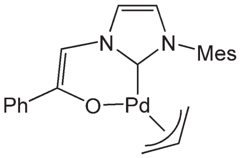

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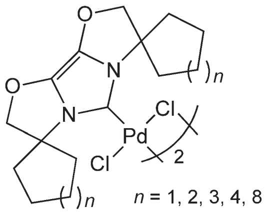
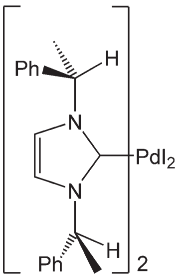


104

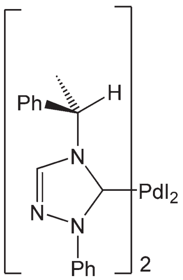
8.04.2.3.3 Chiral carbenes

A comprehensive review focused on chiral carbene-based catalysts, with a range of transition metal centers, and their catalytic performance has been recently published.[202h] The first chiral carbenes were synthesized some years ago and recently, there has been a great interest in the area. The synthesis of chiral (imidazolinylidene)- and (triazolinylylidene)palladium complexes, **105 and 106**, as potential catalysts for enantioselective catalysis, was achieved in high yields by the reaction of chiral imidazolium or triazolium salts with $Pd(OAc)_2$, NaI, and base ($KOBu^t$).[226] Excess (3 equiv.) of imidazol- or triazolium salt gives mononuclear complexes $PdI_2(carbene)_2$. Addition of 1 equiv. of salt is thought to generate dinuclear, iodo-bridged palladium carbene complexes, in which there is only one carbene per palladium atom. Addition of a Lewis base ligand L to the dinuclear species leads to mononuclear $PdI_2(carbene)L$ complexes.[226] By using a chiral amine as the Lewis base, further chiral information can be introduced. Preliminary enantioselective Heck coupling experiments gave low asymmetric inductions; however, the catalysts appear to very stable and can be recycled. Enantiomerically pure oxazoline/imidazoline-2-ylidine ligands were synthesized via the reaction of *N*-imidoester imidazolium salts, formed from the cyanomethyl imidazolium chloride, with 2-aminoalcohols. Palladium complexes were synthesized by treatment of the imidazolium salts with $Pd(OAc)_2$ in the presence of lithium *tert*-butoxide and sodium iodide. Only dimeric palladium complexes of type **107** were isolated, and no asymmetric catalysis was reported.[270]



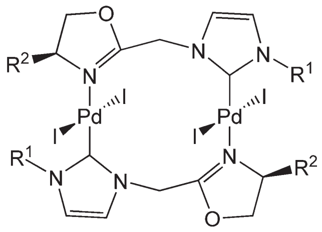
cis- and *trans*-isomers

105



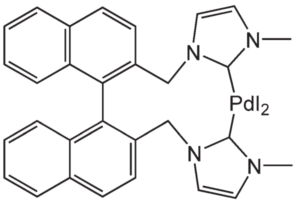
trans-*syn*- and *trans*-*anti*-isomers

106



107

Chiral bidentate bis-carbene complexes of Pd(II), **108**, have been prepared from bisimidazolium salt [(*S*)-2,2′-bromomethyl–1,1′-binaphthyl] and $Pd(OAc)_2$.[271] Preliminary Heck coupling was undertaken, and no enantioselective catalysis was reported. Palladium complexes of carbenes functionalized with cyclohexanol and its acylated derivative **109** have been synthesized.[272] The ligands are chiral and offer a route into enantiomerically pure complexes. Enantiomerically pure imidazolium triflates, **110 and 111**, have been prepared. The salt **111** was deprotonated with $KOBu^t$ and KH in the presence of a Pd precursor to give complex **112**.[273] The complex was tested in the catalytic enantioselective arylation of amides, ee's were generally in the region of 30%. The bis-imidazolium salts **113** were prepared and coordinated to Pd by an Ag-transfer reaction to give *trans*-chelating bidentate-carbene complexes **114**.[274] Attempts to use the complexes as catalysts for intramolecular Heck reactions gave poor yields and enantioselectivities. This was put down largely to the *trans*-coordination, and it was suggested that octahedral metals might provide more effective catalyst systems.



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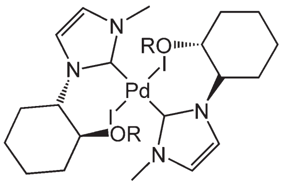
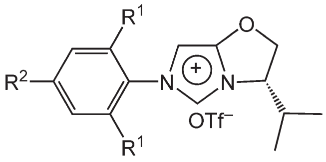


R = H, Me

109



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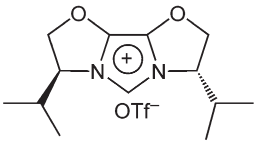

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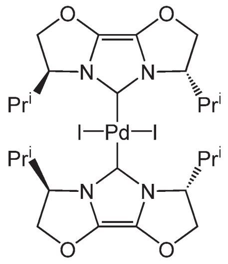

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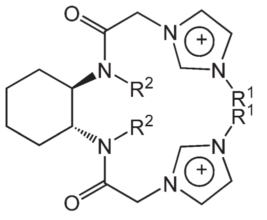
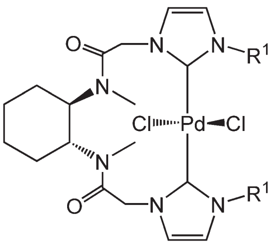


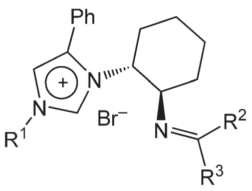
$R^1 = (Pr^i)_2Ar, Bu^t, Me, Cy, Pr^i, CHPh_2$
R^2 = H, Me

113



114

The synthesis of chiral NHC–imine ligands of type **115** and their Pd complexes have been reported.[275] When coordinated to Pd, the imino function of ligand **115**, where $R^3 = H$, may be hydrolyzed in triethylammonium chloride and water to give the chiral amino complex **116**.[276] Extensive structural studies on these systems were undertaken. The complexes were applied in asymmetric allylic alkylation and, in general, reaction rates and ee's for catalysts were disappointing compared with many known chiral phosphine-based systems. The chiral chelating carbene ligand precusors **117** have been synthesized and coordinated to Pd via the Ag-transfer route—no asymmetric catalysis using these complexes is reported.[277] Chiral bis(imidazolin-2-ylidene) complexes **118** have been prepared by a silver-transfer route, and a mixed carbene/phosphine complex **119** obtained by reaction with $Pd(OAc)_2$ and base.[278] The complexes were tested in Heck coupling with modest success. The reduction of the Pd(II) complexes to Pd(0) was examined using electrochemical methods and using chemical reductants. Mixed ligand phosphine/carbene Pd(II) complexes were found to undergo reduction more readily that the bis(carbene) complexes. However, the electron-rich bis(carbene)Pd(0) complexes were found to undergo oxidative addition more readily. Palladium complexes of monodentate carbenes with chiral substituents on the nitrogens[279] **120** and/or on the backbone **121** have been synthesized.[280] NMR and X-ray analysis demonstrated the stereogenic nature of the Pd center.



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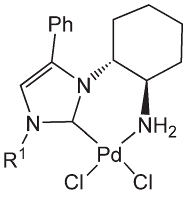
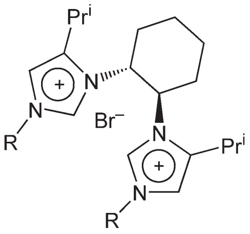


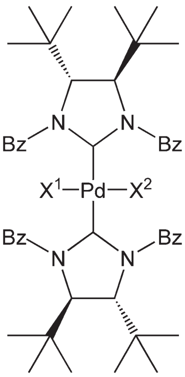
$R^1 = Pr^n, CHPh_2$

116



$R = Pr^n, Pr^i, CHPh_2$

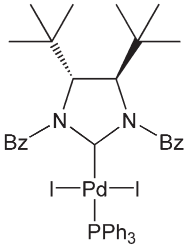
117



Bz = benzyl

$X^1 = X^2 = Cl, I; X^1 = Cl, X^2 = Br$

118



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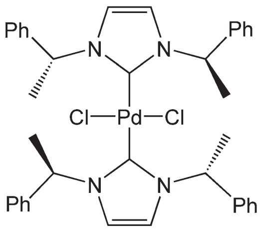

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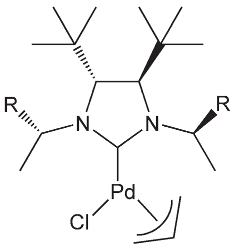
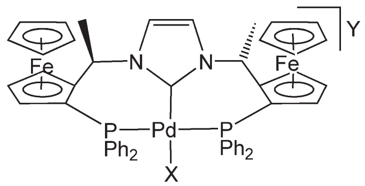


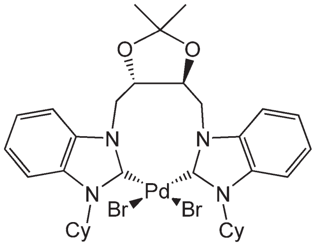
121

$Pd(OAc)_2$ was reacted with an imidazolium salt with two ferrocenyl phosphine substituents to give a complex **122** with a chiral tridentate PCP ligand.[281] Treatment with $[Et_3O]PF_6$ gave a dicationic complex, $[Pd(PCP)(NCMe)](PF_6)_2$, which was an effective catalyst for the enantioselective addition of morpholine to methacrylonitrile in high yield and 37% ee. A C_2-symmetric benzimidazol–2-ylidene, containing a *trans*-2,2-dimethyl–1,3-dioxalane backbone, has been complexed to Pd(II) **123** and an X-ray structure obtained.[282] Both *cis*- and *trans*-isomers were obtained. A strategy of synthesizing chiral Pd(II)–carbene complexes by oxidative addition of enantiopure 2-chloro–1, 3-disubstituted imidazolium salts to Pd(0) complexes has been developed.[283] As an example of the method, the complex **124** has been synthesized by oxidative addition of the imidazolium salt to $Pd(PPh_3)_4$.



Y = PF_6, OAc
X = Cl, I

122



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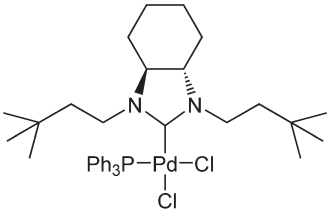
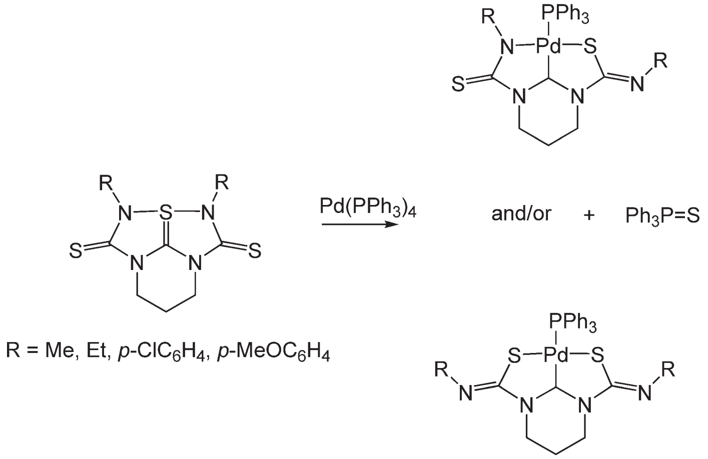


124

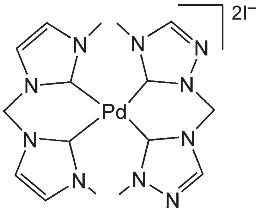
8.04.2.3.4 Complexes of NHCs with a non-imidazole core

A number of investigations have been undertaken on Pd complexes of NHCs, which do not have the usual imidazole ring system. These include five-membered rings with a triazoline core, and ring systems containing other heteroatoms such as those based on the thiazole and benzothiazole structures. Complexes of six-membered ring systems based on a tetrahydropyrimidine core have also been synthesized. Studies on these less common carbene systems are limited. In an early example of more unusual carbene ligand systems, palladium complexes of tridentate, functionalized tetrahydropyrimidine-based carbenes have been synthesized (Equation (32)).[284] The reaction of 10-*S*-3-tetraazapentalene derivatives, 2,3-disubstituted 6,7-dihydro–5*H*-2*a*-thia(2*a*-S^{IV})–2,3,4*a*,7*a*-tetraazacyclopent[*cd*]indene–1,4(2*H*,3*H*)-dithiones, with $Pd(PPh_3)_4$ gives Pd(II) carbene complexes in low to modest yield. A driving force in the generation of the carbene complexes is the extraction of sulfur from the 2-position of the ring via formation of $Ph_3P{=}S$ in stoichiometric amounts. The resulting carbenes are six-membered ring systems functionalized with *N* and/or *S* donors (Equation (32)). The structure of the complex was determined by X-ray crystallography and shows the tridentate ligand coordinated through the two sulfurs and the carbene carbon. Analogous tridentate selenium donor systems were also prepared by a similar route.[285]



(32)

1,3-Diisopropyl- and 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene ligands and complexes of Pd(II) have been synthesized.[286] The complexes were obtained via an Ag–carbene transfer reaction with $PdCl_2(NCMe)_2$ and X-ray structures determined. The complexes were found to be extremely effective in Heck coupling reactions with aryl bromides but much less so with aryl chlorides. Palladium complexes of the triazole-based carbenes, 1,4-dimethyl-1,2,4-triazolin-2-ylidene, and chelating 1,1′-methylenebis(4-alkyl-1,2,4-triazolin-2-ylidene) have been synthesized by reaction with $Pd(OAc)_2$ under generally mild conditions.[287–289] It was found that, for the chelating dicarbene where the *N*-substituent was a methyl group, an acetate complex was formed, but in all other cases, diiodo complexes were formed (Equation (33)).[288] Heating the diiodo complexes to 160 °C gave dinuclear carbene-bridged complexes (Equation (33)). Solid-state structures for the two types of complexes were obtained. Dicationic palladium complexes consisting of two different chelating carbene ligands, one of which is the 1,1′-methylenebis(4-alkyl-1,2,4-triazolin-2-ylidene) dicarbene **125**, have been synthesized.[289] A dendrimer-like trinuclear palladium complex chelated by the dicarbene 1,1′-methylenebis(4-butyl-1,2,4-triazolin-2-ylidene) has also been reported.[290] Interesting water-soluble dicationic Pd complexes **126** have been prepared by the reaction of $Pd(OAc)_2$ with dicationic 1,2,4-triazolium salts.[291] The dicationic salts are synthesized by treatment of the initial triazolium salts with excess MeOTf to give a salt in which all three nitrogens have hydrocarbyl substituents. A molecular structure has been determined.



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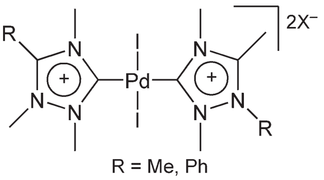

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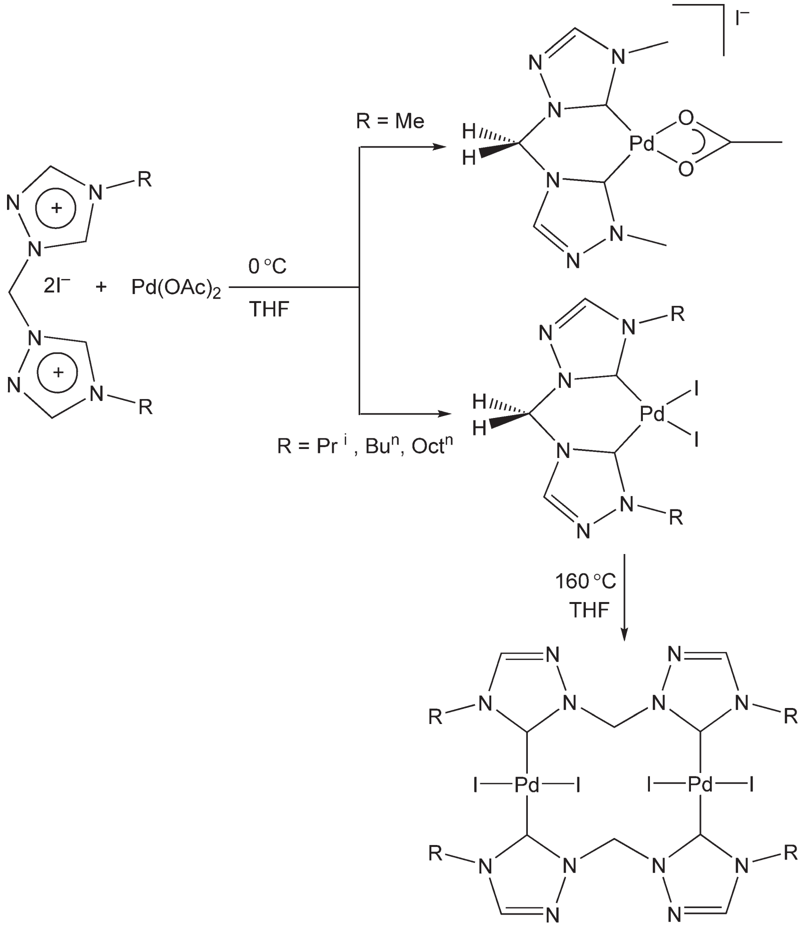
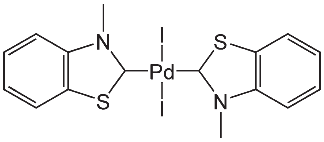


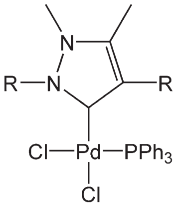
(33)

A number of early reports on thiazolin-2-ylidene and benzothiazolin-2-ylidene have appeared and spectroscopic studies carried out.[292–294] These were prepared either from preformed heterocyclic rings[292,293] or from the reaction of Pd isocyanides with thiirane to generate the heterocyclic ring on the metal *in situ*.[294] More recently, a number of publications reporting the synthesis of a Pd complex of benzothiazole **127** and its application in coupling reactions have appeared. Synthesis has been via the reaction of a benzothiazolium salt with Pd(OAc)$_2$.[295] Heck coupling of α- and β-substituted acrylates with aryl halides has been investigated using THF, molten tetraalkylammonium bromide, or tetraphenylphosphonium salts as solvent.[295–299] The carbonylation of aryl halides, and the arylation of allylic alcohols, have also been investigated in tetrabutylammonium bromide melt as solvent.[300,301] Palladium nanoparticles have been detected and hence implicated in Heck reactions using the (benzothiazolin-2-ylidene)Pd complex, **127**, and tetrabutylammonium acetate in tetrabutylammonium bromide melt as solvent.[302]



127

Novel pyrazolin-3-ylidene type carbene complexes, in which pyrazolium salts have been oxidatively added to Pd(PPh$_3$)$_4$, have been synthesized **128**.[303] A molecular structure has been obtained and the preformed complexes tested in Heck coupling.



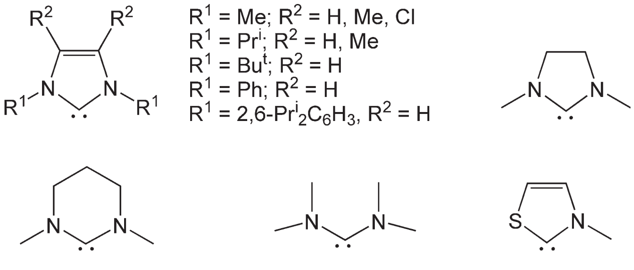
R = Ph, Me

128

8.04.2.3.5 Fundamental studies on properties and reactivity of NHC complexes and related species

Photoelectron spectroscopy and DFT calculations have been applied to an investigation of the electronic structure of Pd(0)(carbene)$_2$ complexes. It was found that bonding occurs predominantly through σ-donation from the nucleophilic carbene carbon into a metal (sd_{z^2}) hybrid orbital with little evidence of π-interactions.[304] In contrast, a comprehensive DFT investigation of Pd(0)(1,3-di-*tert*-butylimidazol–2ylidene)$_2$, along with several group 11 carbene complexes, concluded that the π-acceptor ability of carbenes is arguably not "negligible," and for electron-rich metal centers, π backbonding may be as significant as 20–30% of the orbital interaction energy of a metal–NHC complex.[305]

High-level theoretical methods have been applied to the calculation of pK_a's for a range of NHCs (Scheme 9) in several solvents.[306] Carbenes investigated include saturated, unsaturated, and six-membered ring systems and thiazole-based carbenes. The pK_a values indicate free carbenes are highly basic. In the few examples where experimental data exists, agreement between theoretical and experimental pK_a's are excellent. A comparison of

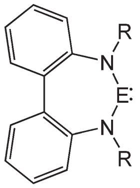


Scheme 9

carbene basicity in water with that of phosphines indicates that even the least basic carbene (thiazol-2-ylidene; $pK_a = 21.2 \pm 0.2$) has a pK_a value approximately twice that of the most basic phosphine noted ($PBu^t{}_3$; $pK_a = 11.40$).

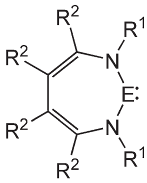
The planar structure of NHCs makes Tolman's classical cone angle concept inappropriate for the determination of steric bulk. In response to this problem, the steric influence of a range of carbene complexes generated from the reaction of $[PdCl(allyl)]_2$ with free carbene has been assessed by introducing the concept of "buried volume."[307] Here, the steric requirement of an NHC was conceptualized as a sphere of imposed radius centered around the Pd atom and the volume occupied by the ligand. The trend in reactivity in the cross-coupling of amines with aryl halides was discussed in terms of the steric properties of the ligands.

An *ab initio* computational study has predicted that 8π-homologs (**129** and **130**) of planar aromatic carbenes and silylenes will form twisted C_2-geometries, providing palladium complexes with Möbius-aromatic chiral character, and present an opportunity to design potentially chiral monodentate metal coordination.[308]



E = C, Si

129



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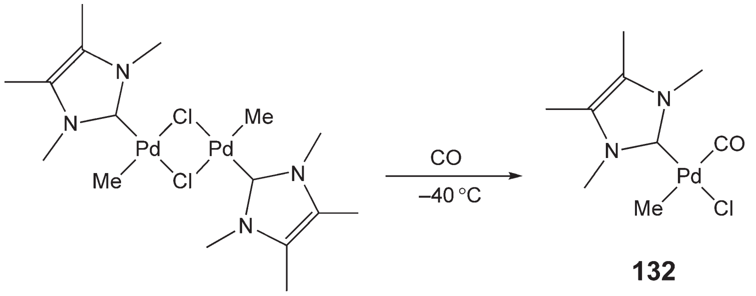
A digital functional approach has been employed to investigate important steps in the Heck reaction catalyzed by a bis(carbene)Pd complex and one in which the Pd is coordinated by a bidentate carbene–phosphine ligand.[309] The crucial steps of olefin insertion into the palladium–aryl bond and β-hydride elimination were investigated. For the bis(carbene)Pd catalyst, a mechanism was proposed, which proceeds via halide abstraction, to give a cationic species, prior to olefin coordination and insertion. The total insertion/elimination process was found to be exothermic ($-8.9\,\mathrm{kcal\,mol^{-1}}$). For the carbene–phosphine ligated system, the vacant site for olefin coordination was provided by phosphine dissociation. The energetics for the total insertion/elimination process was very similar to that of the bis-carbene system.

In early studies on PdMe(carbene) complexes, the unstable complex [PdMe(1,3,-dimethylimidazolin-2-ylidene)(cod)]BF_4 was found to decompose, yielding 1,2,3-trimethylimidazolium salt and Pd(0).[204] It was subsequently noted by the same group that this decomposition route was a common and often facile process for PdMe(carbene) complexes. The same reductive coupling process has since been found to occur for carbene–hydride, –aryl[211] and –acyl[310] complexes. For example, in carbonylation studies on the palladium dimer **131** (Equation (34)), treatment of **131** at −40 °C with CO gives the complex **132**, which decomposes, giving predominantly 1,2,3,4,5-pentamethylimidazolium salt as the organic product; traces of the 2-acyl-1,3,4,5-tetramethylimidazolium salt were also detected.[310] Repeating the reaction in the presence of Ag^+, to abstract the halide, 2-acyl-1,3,4,5-tetramethylimidazolium salt was obtained as the main product with minor amounts of 1,2,3,4,5-pentamethylimidazolium salt. Thus, it was concluded that Pd(acyl)(carbene) complexes are prone to the same mode of decomposition as Pd(hydrocarbyl)(carbene) compounds and it was proposed that the reaction provides a likely route to catalyst decomposition for CO/ethylene co-polymerization catalysts based on Pd–carbene complexes.

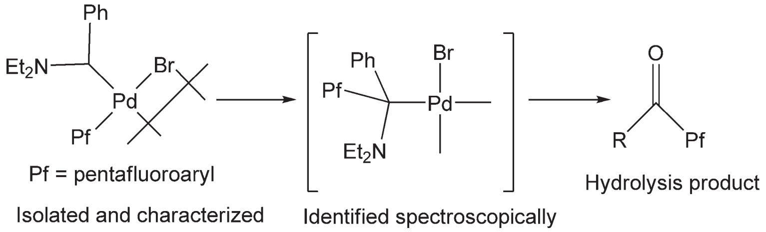


131 **132** (34)

From a systematic study of mixed ligand (carbene)Pd–phosphine complexes, a detailed mechanism for the decomposition process and decomposition pathway has been presented based on a combination of kinetic and density functional theory (DFT).[311] The decomposition is thought to proceed via a concerted reductive elimination of the methyl and carbene ligands and represents a low-energy pathway to catalyst deactivation for catalysts with NHCs as ligands. Reductive elimination from methylpalladium complexes of tridentate CNC pincer carbene complexes was also shown to occur, although the process seems less facile and high temperatures are required for decomposition.[312] Theoretical studies have shown that the formally empty C_2 p-orbital perpendicular to the plane of the carbene ($p(\pi)$-orbital) is appreciably occupied due to donation from the $p(\pi)$ lone pairs on the nitrogens.[313–315] It is believed that this C_2 p-orbital is intimately involved in the reductive elimination process.[311]

It has been observed that reductive elimination can also occur for aryl–Pd–carbene complexes. Such complexes were investigated in mechanistic studies on Heck coupling and catalyst decomposition routes.[316] Reductive elimination products with direct imidazolium–aryl coupling were observed and in one case fully characterized. Such products provide direct evidence of the Heck coupling mechanism and of intermediates in the catalytic cycle. Important mechanistic studies on the oxidative addition of aryl chlorides to a 14-electron $\mathrm{Pd(0)(carbene)_2}$ complex have demonstrated that oxidative addition occurs via a dissociative process and this step is probably the rate-determining step in the amination of aryl chlorides.[317] Aryl–carbene reductive coupling was observed in this study of the amination reaction, and directly coupled aryl-imidazolium compounds were isolated.[317] A further study on an (aryl)Pd(carbene) complex has also demonstrated that such complexes undergo facile reductive elimination to form aryl-imidazolium salt.[318]

Evidence for an alternative reaction pathway to reductive elimination, that is, migratory insertion, has been provided. Studies on palladium pentafluoroaryl complexes of highly electrophilic acyclic carbenes have allowed the direct (spectroscopic) observation of the migratory insertion of the carbene into the aryl–Pd bond.[319] The process was monitored by NMR and a likely pathway has been proposed (Equation (35)). A second experimental study indicating the possibility of migratory insertion as a reaction pathway for coordinated NHCs has been reported.[320] Reaction of the ligand, **133**, with $\mathrm{PdMe_2(tmeda)}$ gave, as the only carbene-containing product, complex **134** in good yield, demonstrating migratory insertion of the methyl group onto a coordinated carbene to give a σ-alkyl complex.



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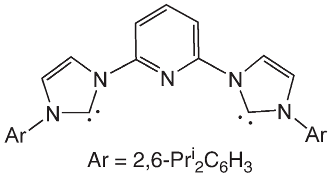

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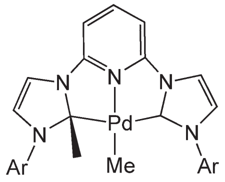
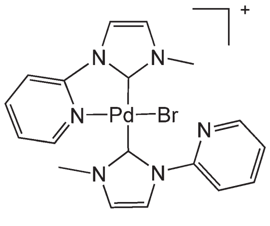


134

DFT calculations on $\mathrm{Pd^{II}}$Me complexes of NHC, silylene, and germylenes have shown that the activation barrier for methyl migration to the "carbene" follows the order Si < Ge < C. With Si and Ge, the initial products from the coupling step have short, relatively strong Pd–E bonds (comparable with those for anionic sp^3 silyl and germyl bonds to Pd(II)) and the geometry about Si and Ge is approaching tetrahedral.[321] Hence it is considered that the reaction is best described as alkyl migration to give an anionic ligand, rather than the reductive elimination more typical for carbene/imidazolium salts.

It had been observed that imidazolium salts may oxidatively add to low-valent palladium centers to generate carbene complexes.[322,323] It was noted that even in the absence of base, imidazolium salt reacted with Pd(0) to give a detectable Pd–H complex.[322] It was also demonstrated that reaction of $\mathrm{Pd_2(dba)_3}$ with *N*-(2-pyridyl)imidazolium salts gave bis-carbene complexes **135**, and **136**, apparently resulting from double oxidative addition of the imidazolium salt.[323] In this case, no hydride was observed; however, a mechanism for the reaction was proposed. Unambiguous evidence that oxidative addition occurs was provided in studies combining experimental methods and DFT calculations.[324–326] The complex Pt(PCy$_3$)$_2$ was reacted with 1,3-dimethylimidazolium tetrafluoroborate to give PtH(dmiy)(PCy$_3$)$_2$, and a similar reaction with 3,4-dimethylthiazolium tetrafluoroborate afforded the complex PtH(dmty)(PCy$_3$)$_2$. Theoretical studies showed that under appropriate reaction conditions, all group 10 metal complexes would undergo oxidative addition of imidazolium salts with virtually no energy barrier to the reaction.[324,325] In subsequent studies, stable hydrido complexes of Pd and Ni were generated from the reaction of imidazolium salt (of the type used as ionic liquid (IL) solvents) with electron-rich low-valent metal complexes (Equation (36)).[327] Molecular structures were obtained for the hydrido complexes. The surprising stability of the complexes (M = Ni, Pd) was explained as being due to the steric protection afforded the hydride by the carbene ligands.[327]



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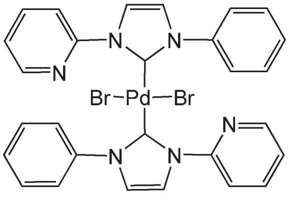

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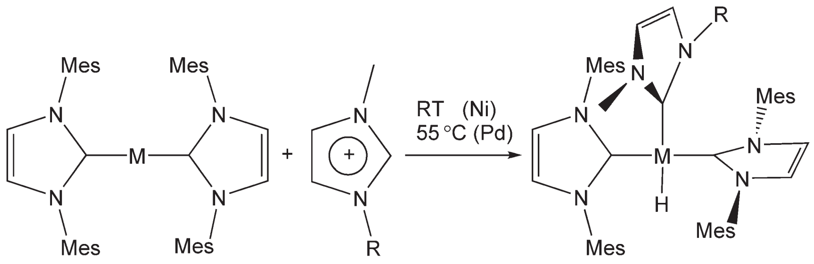
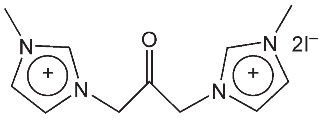


(36)

R = Me, Bu^n
M = Ni, Pd

In an interesting reaction, the treatment of functionalized bis(imidazolium) salt, **137**, with Pd(OAc)$_2$ gave the complex **138** as the only product.[328] The formation of this product is indicative of the acidity of the protons in the bridging –CH$_2$ groups. Single crystal X-ray crystallography and IR spectroscopy revealed a highly puckered pallada-cyclobutan-3-one ring with a significant η^3-allylic contribution to the interaction between the ligand and the Pd. The lengthening of the C═O bond, the shortening of the C–O bond, and the IR spectra of the complex suggest a significant charge delocalization across the C$_3$O$^-$ fragment.



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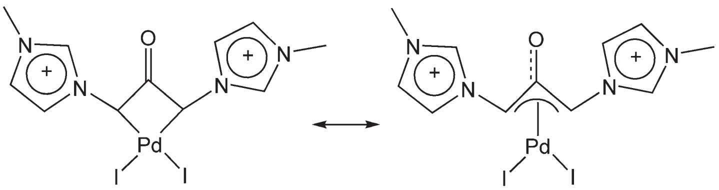

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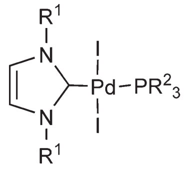
8.04.2.3.6 Catalysis by palladium–carbene complexes

A major focus in studies using NHCs as ligands has been targeted at their use in homogeneous catalysis. It was recognised very early on that the highly basic NHCs are capable of stabilizing metals in both high and low oxidation states, and to date, the most effective use of carbenes has been to promote catalytic reactions in which the Pd center undergoes a redox change during the course of the reaction. Early examples of the use of carbene complexes as catalysts were reported in the 1970s and 1980s.[329–331] However, the main developments in the application of carbenes took place after the successful isolation of free carbenes.

8.04.2.3.6.(i) Cross-coupling reactions

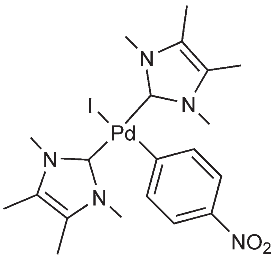
Following initial patents reporting the application of carbene complexes in hydroformylation and C–C coupling reactions,[332,332a,332b,333,333a,202c] the application of Pd(II) bis-monodentate and bridged bidentate imidazolin–2-ylidene complexes **61 and 62** in Heck coupling was reported.[212] The catalysts showed good activity, were long-lived, but exhibited a long induction phase unless a suitable reducing agent, such as hydrazine, was added to the system. The reducing agent was thought to be necessary to convert the Pd(II) complex to the catalytically active Pd(0) species. When Pd(0) complexes were used to initiate catalysis, no induction period was observed. A related diodo–palladium complex with a chelating bis(carbene) ligand was tested in Heck, Suzuki, and alkyne coupling reactions.[214] High product yields were obtained with both aryl bromides and aryl chlorides. However, higher temperatures were required and no mention was made of an induction period. Mixed ligand phosphine/carbene complexes of Pd(II) **139** were synthesized and tested in aryl coupling reactions (Heck, Suzuki, and Stille coupling) and Sonogashira coupling.[228,334] The philosophy was to fine-tune the catalysts by gaining the benefits of a combination of these two classes of ligand: using the tightly bound NHC as the resting ligand and the phosphine as the labile ligand. However, in CD_2Cl_2, a ligand-exchange reaction was evident, indicating that both the carbene and the phosphine exhibit lability. The complexes showed promising performance for the conversion of both aryl bromides and aryl chlorides in the Suzuki reaction, but were less effective with aryl chlorides in the Stille reaction.



R^1 = Me, Bu^t, CHMePh
R^2 = Ph, *o*-Tol, Cy, Bu^t

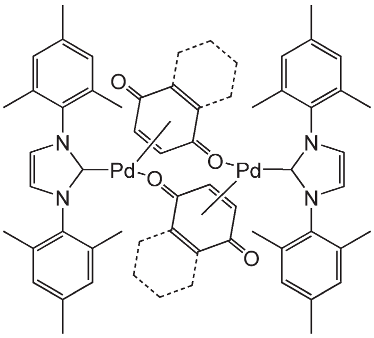
139

The application of $Pd^{II}Me$(carbene) complexes as catalysts resulted in significantly improved Heck coupling catalysis.[204] The presence of the methyl group gives rise to highly active catalysts with no discernible induction period, thus removing the need for a reducing agent to generate the active Pd(0) species. It was suggested that the active species was a 14-electron $Pd^0(\text{carbene})_2$ complex. A pathway for the formation of the active species was proposed, involving alkene insertion into the Pd–Me bond, β-elimination, then reductive elimination of HBr in the presence of base to give the Pd(0)(carbene) catalyst. An alternative activation process for $Pd(0)(\text{carbene})_2$ complexes could be envisaged, in which reductive elimination of the methyl and carbene moieties occurs to give the mono-carbene species. The Pd(II) complex **140** and the Pd(0) complex (**58**, where olefin = tetracyanoethylene) have been tested in Heck and Suzuki coupling of 4-bromoacetophenone and *n*-butyl acrylate.[211] Very high turnover numbers (TONs) were obtained with low catalyst loadings. For the Pd(II) complex, it was felt that the presence of the aryl ligand on the Pd provided a facile route to the active Pd(0) species; cf. the methylpalladium system discussed above. For the Suzuki coupling reaction, the Pd(0) complex gave markedly higher TONs than the Pd(II) system, **140**. Mechanistic studies of olefin insertion into $Pd^{II}Ph$(carbene) complexes provided information on the Heck coupling and on catalyst decomposition routes.



140

Monocarbenepalladium(0) complexes with bridging benzoquinone and naphthoquinone ligands, **141**, have also been prepared and found to be very effective in catalytic cross-coupling reactions between aryldiazonium salts with olefins and arylboronic acids.[335] The application of well-defined Pd(0)(carbene) complexes in the Heck catalyzed coupling of aryl chlorides with styrene and 2-ethylhexyl acrylate has also been reported.[336] Tetrabutylammonium bromide was found to be an excellent high-temperature solvent for the reaction. In a further example, well-defined Pd(0)carbene complexes were applied as catalysts in cross-coupling reactions.[337] The synthesis of the Pd(0)(carbene)$_2$ complex **142** and its application in the Suzuki cross-coupling of aryl chlorides is described. The complex is able to cross-couple sterically unhindered aryl chlorides at room temperature in high yields and with very high TOFs and TONs. The possibility of Pd clusters acting as the active catalyst is raised.



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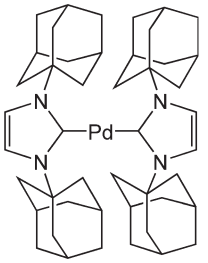
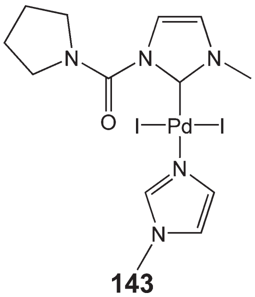


142

Addition of sodium dimethylmalonate to the dimer [PdCl(η^3-C_4H_7)]$_2$ in the presence of the carbene 1,3-di-*tert*-butylimidazol–2-ylidene gave the 14-electron bis-carbene palladium(0) complex in good yield in a one-pot reaction.[338] The bis-carbene complex was found to be effective in both Sonogashira-type coupling and amination of chloroarenes. Preformed Pd(II) carbene complex **143**, in which the carbene is functionalized with an *N*-carbamoyl substituent, was formed by refluxing Pd(OAc)$_2$ and 2 equiv. of carbamoyl imidazolium salt in THF.[339] The complex was found to be very effective in Sonogashira cross-coupling of aryl iodides and bromides with alkynes. The addition of PPh$_3$ to the catalyst mixture increased catalyst activity, and subsequently complex **144** was prepared.



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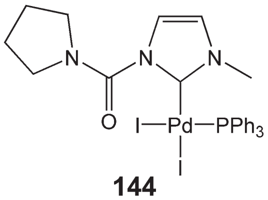
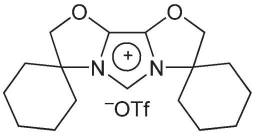


144

Well-defined air- and moisture-stable mononuclear Pd(allyl)(carbene) complexes have been synthesized and tested in a number of cross-coupling reactions (amination, Suzuki–Miyaura, and coupling of ketones and aryl chlorides).[340] Treatment of the complex with a base, such as NaOBu^t, generated the active catalyst in a process thought to proceed via an intermediate of the type Pd(OBu^t)(allyl)(NHC), which then undergoes reductive elimination to form the active Pd(0)(NHC) species. Other examples of well-defined and stable monocarbene–Pd complexes have been prepared and tested in cross-coupling reactions.[341,342] These included halide-bridged dimeric complexes, which were prepared by the reaction of 1 equiv. of free carbene with a suitable Pd(II) source.[341,203] Aryl amination reactions with aryl chlorides and bromides were carried out under mild conditions under aerobic conditions with good yields and activities. Several PdCl(allyl)(NHC) complexes were also prepared and found to be active catalysts for the arylation of ketones.[342] Preformed PdCl(allyl)(NHC) complexes were efficient catalysts in Suzuki coupling, dehalogenation of aryl chlorides, and aryl amination.[343] The preferred base in each case is NaOBu^t and reactions proceed in short reaction times and under mild conditions. In a further study, a Pd(allyl)(NHC) complex was applied to the catalytic intramolecular amination reaction for the generation of alkaloid structures.[344] Aryl chlorides and triflates were converted in generally high yields in 1 h with low catalyst loadings. A palladium complex of the carbene 2-(4,4-dimethyl)oxazolinylimidazol–2-ylidene has been prepared via the silver-transfer route and tested in Heck and Suzuki coupling reactions with aryl bromides and chlorides with moderate activity.[345] Reaction of 4-chlorotoluene with Pd(0)(1,3-di-*tert*-butylimidazol–2-ylidene)$_2$ has allowed the isolation of the oxidative addition product, which was identified by X-ray crystallography.[346] Reaction of this complex with morpholine and KOBu^t afforded the arylated amine in >95% yield.

The first Kumada cross-coupling reactions with alkyl chlorides were undertaken using both preformed Pd(0)(carbene)(olefin) complexes, and *in situ* systems with Pd(OAc)$_2$ and imidazolium salts; in general, these systems were found to be effective catalysts for coupling alkyl chlorides with aryl Grignard reagents.[347] In each case, the carbene with mesitylene substituents on the nitrogens gave the best results. A valuable comparison of Pd–carbene- and Pd–phosphine-based catalyst systems for cross-coupling reactions has been undertaken; a range of preformed and *in situ*-generated catalysts was investigated in Suzuki, Kumada, and amination reactions.[348] Both carbene and phosphine catalyst systems proved effective, and *in situ*-formed systems often performed better than preformed catalysts. Overall, it was concluded that phosphine-based catalysts performed better in amination and Suzuki reactions of aryl chlorides, whereas carbene-based systems were more efficient in Kumada coupling of aryl chlorides. NHC–palladacycle complexes have been prepared and successfully applied as a pre-catalyst in Heck, Suzuki, amination reaction, and α-arylation of ketones with aryl halides.[349,350] High yields were achieved with low catalyst loadings and short reaction times.

A number of publications on room-temperature Suzuki cross-coupling of sterically hindered aryl chlorides have appeared, using palladium–carbene complexes as catalysts.[351,352] In one example, the imidazolium salt **145**, which utilizes the concept of flexible steric bulk, was used *in situ* with Pd(OAc)$_2$ to cross-couple di-*ortho*-substituted aryl chlorides in high yield.[351] In the second case, the preformed pre-catalyst **146** was used to cross-couple di-*ortho*-substituted aryl chlorides with various boronic acids in high yields with isopropanol as solvent.[352] An activation pathway, involving loss of the chelate ligand via reductive elimination, to generate the Pd(0) carbene catalyst was proposed. Flexible, ethylene-bridged chelating dicarbene complexes of Pd have been prepared and tested in Suzuki and Heck coupling.[353] Performance is moderate and comparable to that observed for the more common methylene-bridged dicarbene ligands. A calix[4]arene-bridged dicarbene ligand has been attached to Pd and the resultant complex used in Suzuki cross-coupling with modest performance.[354] The application of technical-grade 2-propanol as solvent in Pd–carbene-based Suzuki cross-coupling between electron-rich aryl chlorides and sterically hindered aryl boronic acids under mild conditions has been reported.[355] It is concluded that the solvent is not innocent in these systems.



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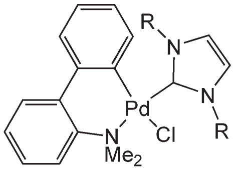


R = 2,6-Pr$^i{}_2$C$_6$H$_3$

146

An important development in Pd-catalyzed cross-coupling reactions, such as the Suzuki[356] and Kumada[357] reactions, has been the demonstration that reproducible and efficient catalysts could be produced by mixing Pd(OAc)$_2$ or Pd$_2$(dba)$_3$, imidazolium salt, and base to generate *in situ* the active catalytic species. Some examples have been discussed above, and much of this work has been reviewed.[358] These *in situ* catalyst systems were very efficient for the cross-coupling of aryl chlorides with arylboronic acids (Suzuki coupling) or aryl Grignard reagents (Kumada coupling).[356,357] Tolerance to a range of functional groups on the aryl substrate was demonstrated, and high conversions were achieved in a few hours with 1–1.5 mol% catalyst. The Kumada coupling reaction was particularly interesting as separate base was not required; the aryl Grignard reagent acted as the base to form the carbene ligand from the imidazolium salt. In this reaction, the carbene ligand 1,3-bis(2,6-diisopropylphenyl)imidazol–2-ylidene (IPr^i) proved to be particularly efficacious.

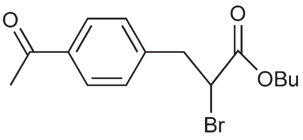
A comprehensive study on Suzuki–Miyaura cross-coupling has further demonstrated the power of an *in situ* approach.[359] Starting from either Pd(0), $[Pd_2(dba)_3]$ or Pd(II), $[Pd(OAc)_2]$ with a Pd : imidazolium salt ratio of 1 : 2, highly efficient catalysts for the coupling of aryl chlorides or aryl triflates with arylboronic acids were generated. The effects of imidazolium salt, added base, and Pd/imidazolium salt ratio were studied, and the functional group tolerance of the catalyst system was also investigated. Catalytic systems were also successfully tested in the synthesis of two pharmaceutical targets, Fenbufen and the sartan intermediate, 2-cyano–4′-methylbiphenyl. Similar *in situ* studies investigating the amination of aryl chlorides, bromides, and iodides have demonstrated the versatility and effectiveness of this methodology.[360,361] A comprehensive study of amination-type reactions found that *in situ* palladium/imidazolium salt catalyst systems were very efficient in aminations involving aryl chlorides and bromides.[362] The $Pd(0)/IPr^i/HCl/KOBu^t$ system was the most effective with a large range of substrates, including electron-neutral and electron-poor aryl chlorides and a variety of sterically demanding amines. Mechanistic considerations support an active species consisting of a single carbene ligand per Pd. Preformed, two-coordinate Pd(0) complexes of NHCs and mixed phosphine/NHC were found to be very effective catalysts for amination of aryl chlorides. But it was found that both saturated and unsaturated carbenes readily dissociate from the Pd(0) center to generate the proposed monoligated, Pd–L, active species to which oxidative addition of the aryl chloride may occur.

An interesting reaction catalyzed by the palladium(0)/imidazolium salt systems is the catalytic dehalogenation of aryl chlorides.[322] The preferred *in situ* catalyst system was the ligand precursor (2,4,6-trimethylphenyl)dihydroimidazolium chloride in conjunction with $Pd(dba)_2$. A mechanism for the reaction is proposed. An important observation made during the course of these studies was that even in the absence of base it appeared that imidazolium salt could add to Pd(0) to form a $Pd^{II}H$(carbene) complex. Although no metal–hydride complex was isolated or fully characterized, this was the first time such a possibility had been noted. *In situ* $Pd(OAc)_2$/imidazolium chloride catalyst systems have also been successfully applied to the Sonogashira cross-coupling reaction of aryl bromides with various alkynylsilanes.[363] It was found that a catalytic system consisting of 3 mol% $Pd(OAc)_2$, 6 mol% IMes·HCl, and Cs_2CO_3 proved to be an efficient system for coupling aryl bromides with alkynylsilanes.

A further valuable development has been the establishment of an *in situ* protocol for the efficient low-temperature Suzuki coupling of electron-rich and electron-deficient aryl chlorides.[364] The catalyst system consisted of Pd(0)/1,3-bis(2,6-di-*iso*-propylphenyl)imidazolium chloride (1 : 1 Pd/ligand ratio) plus KOMe as the base and tetra-*n*-butylammonium bromide additive. The first examples of Suzuki alkyl–alkyl cross-couplings using similar catalyst protocols were also described.[364] Reaction of free NHC with purified $Pd(OAc)_2$ or $Pd(O_2CCF_3)_2$ in toluene generates $Pd(carboxylate)_2$(carbene) complexes in good yield; reaction of the acetate complexes with strong acids leads to the replacement of the acetate ligands with the corresponding counteranions, preserving the stable carbene–Pd core.[365] The acetate complexes are effective catalysts for the hydroarylation of alkynes with good selectivity.

8.04.2.3.6.(ii) Functionalized carbenes in catalysis

A number of donor-functionalized Pd–carbene complexes, including **80–82**, have been tested in various coupling reactions (Heck, Suzuki, Sonogashira, and Stille) with generally noteworthy results.[248] The $Pd^{II}Me$ complexes were tested at very low loadings and showed excellent stabilities and high activities. As noted previously, the methyl group provides a facile route to the catalytically active Pd(0) species with no induction period. In Heck coupling of 4-bromoacetophenone with butyl acrylate, with complexes **80 and 81**, total turnovers of up to 1.7 million over 120 h were obtained (average TOF of 14,200 turnovers h^{-1}) with high selectivity to *n*-butyl (*E*)-4-acetylcinnamate. The bis(carbene) complexes performed better than the monocarbene complex **82**. Coupling with 4-chlorobenzaldehyde (0.2 mol% catalyst) resulted in a TON of ~350 in 24 h. Suzuki coupling of 4-bromoacetophenone with phenylboronic acid showed similar performances, with TONs > 100,000. In subsequent studies, closely related $Pd^{II}Me$(picolylimidazolin–2-ylidene) complexes demonstrated similarly high TONs for the coupling of phenyl iodide with methylacrylate.[209] Palladium complexes **84–88** of bidentate and tridentate carbene-functionalized ligands, and of carbene–cyclophane and half-cyclophane ligands for the Heck and Suzuki coupling of 4-bromoacetophenone showed excellent catalytic performances at low catalyst loadings.[250] A brominated coupling product, **147**, was also obtained (5–10%) with complex **85**. It was suggested that the pyridyl arms of the ligand interfered with the β-elimination step and led to alkyl/halide reductive elimination to give **147**.



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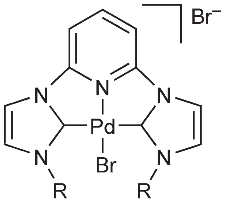
The Pd complex of the tridentate pincer (CNC) bis-carbene, **92**, proved to be a very robust catalyst for Heck coupling.[256] The complex is thermally very stable (it may be heated to >180 °C in air), and coupling reactions carried out in air gave good yields and turnover frequencies for the reaction of phenyl bromide and phenyl iodide with styrene. Palladium complexes of pincer ligands based on a 2,6-lutidine core, that is, 2,6-bis[(3-methylimidazol–2-ylidine)methyl]pyridine, have also been prepared.[366] In the solid state, the complexes exhibit C_2-symmetry. The racemate was tested in Heck coupling with modest effect. Similar studies were undertaken on Pd$^{\text{II}}$Me complexes of the 2,6-bis[(3-methylimidazol–2-ylidine)methyl]pyridine ligand.[367] The complexes were prepared by an *in situ* reaction using Ag_2O as a transfer reagent. Similar catalytic behavior was observed.

Thermally and air stable Pd(II) complexes of a 2,6-lutidine type CNC ligand, and the first CCC bis-carbene pincer ligand, **94**, have also been synthesized and used in Heck catalysis with activated aryl chlorides.[257] A complex of type **148**, where R = Bu^n, was used in Heck olefination reactions to generate first-generation dendrimers with high efficiency and selectivity.[368] The catalyst system consisted of complex **148**, $Bu^n{}_4NBr$, NaOAc, and DMA at 130 °C. A description of the preparation and detailed catalytic properties of complex **148** was reported separately.[269] The X-ray structure shows a rigid and planar ligand system. A related Pd complex with a bidentate carbene–pyridyl ligand was also prepared for comparison. The catalysts were tested in a range of coupling reactions (Heck, Suzuki, and Sonogashira). The pincer complex is an effective catalyst for the C–C coupling; in particular, the catalyst shows high turnovers in the Heck reaction with activated aryl chlorides, and maintains good activity on reuse.



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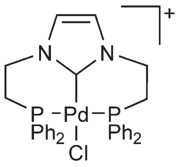
A functionalized imidazolium salt containing a phosphine donor, 1-ethylenediphenylphosphino–3-(mesityl)imidazol–2-ylidene, was used in the *in situ* palladium-catalyzed Heck coupling of aryl bromides.[370] The catalyst system proved efficient, giving high yields of product in short reaction times. Both *in situ* catalyst systems[371] and preformed catalysts[260] utilizing (diphenylphosphino)alkyl-functionalized ligands have been applied in Suzuki coupling. A pincer PCP NHC ligand and variety of mono- **149** and di- **150** cationic Pd complexes have been reported[372] and investigated in Suzuki and Heck coupling. For Heck coupling, the dicationic complexes are more efficient than the monocationic.



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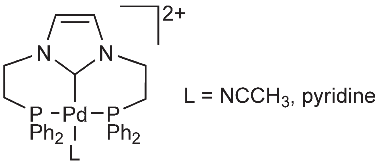

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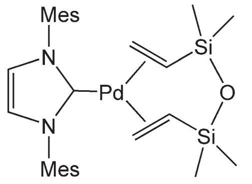
8.04.2.3.6.(iii) CO/ethylene co-polymerization

Dicationic NHC chelate complexes of Pd have been employed in the catalytic co-polymerization of ethylene and CO with modest activity under mild conditions of temperature and pressure.[215] It was concluded that only a very small percentage of the palladium pre-catalyst is active in the co-polymerization reaction, although no suggestion of what the actual active species might be was provided. This is an interesting report; chain-growth reactions (oligomerization and polymerization) catalyzed by group 10 metal–carbene complexes, in which the metal center remains in a single oxidation state throughout the cycle, are still rare.

8.04.2.3.6.(iv) Telomerization

The first publication of the application of palladium carbene complexes as catalysts in telomerization appeared in 2002.[373] Treatment of the Pd(0)(diallylether) complex of 1,3-dimesitylimidazol–2-ylidene carbine (dmi) in 1,1,3,3-tetramethyl–1,3-divinyl–disiloxane (dvds) at low temperature gave the complex Pd(0)(dmi)(dvds) **151**. The use of the preformed complex as a catalyst in the telomerization of butadiene with methanol at 90 °C showed considerably enhanced activity and selectivity over previously known catalyst systems. Extremely high TONs were achieved. Other alcohols and phenol were also tested, and in general, the monocarbene catalyst was found to be more active and selective than other catalyst systems. A second report describing *in situ* generation of Pd(0) carbene complexes from imidazolium salts for the telomerization of butadiene with alcohols was published soon after.[374] A number of different imidazolium salts, including examples functionalized with ferrocenyl moieties, were tested. The catalyst systems, almost universally, showed exceptional catalyst productivities and regioselectivities for a number of different alcohol feedstocks. In a further study, a range of preformed Pd(carbene)(diene) (diene = dvds) complexes have been used to generate industrially viable catalysts for the telomerization of butadiene with alcohols.[375] Catalysts with extremely high efficiencies, high TONs and TOFs were generated. A number of *in situ*-generated carbene catalyst systems were also investigated. *N*,*N*-dialkyl-substituted imidazol–2-ylidine ligands showed significantly lower activity. Electronic and steric effects on the performance of the catalysts were discussed, based on DFT. Preformed cationic Pd(allyl)(NHC) complexes **152** have been successfully applied in the telomerization of butadiene with amines as the nucleophile.[376]



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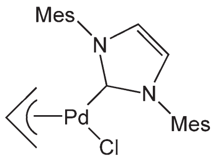

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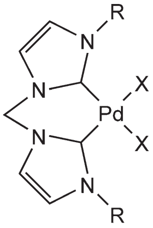
8.04.2.3.6.(v) C–H activation of methane

Palladium–carbene-based catalyst systems have also been applied to a number of novel catalytic reactions. One fascinating report that has appeared is the catalytic C–H activation of methane using a preformed catalyst system based on chelating Pd(II)(carbene)$_2$ complexes of type **153** (where X = Br).[377] To generate the active catalyst, complex **153** was dissolved in trifluoroacetic acid/trifluoroacetic acid anhydride, and potassium peroxodisulphate was added. The system was pressurized with methane and heated to 80/90 °C for 24 h. The conversion reached TON = 30 in 14 h. The resistance of the NHC complexes to strongly acidic conditions plus strong oxidants is extraordinary. Neither reprotonation of the carbene ligand, nor any appearance of Pd black was observed. In later studies, Pd complexes of type **153** (where R = Me) have been synthesized and the effect of the co-ligands (X) on the catalytic conversion of methane to methanol compared.[378] The catalysis was carried out at 90 °C in trifluoroacetic acid/trifluoroacetic acid anhydride as solvent and $K_2S_2O_8$ as oxidant. The influence of the co-ligand is small and TONs were consistently around 24.



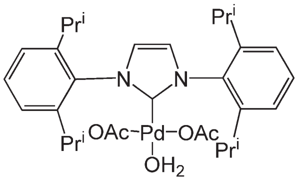
R = Bu^t, Me
X = Cl, Br, I, O_2CCF_3

153

8.04.2.3.6.(vi) Novel catalytic applications

The borylation of aryldiazonium ions, oxidative carbonylation of bisphenol A, and the aerobic oxidation of alcohols are examples of other catalytic reactions that have been studied using Pd–carbene catalysts.[379,380,381] Catalysts generated *in situ* from saturated and unsaturated imidazolium salts and Pd(OAc)$_2$ were found to be efficient systems for borylation of aryldiazonium ions. No base was added to the system; the OAc$^-$ ion is basic enough to generate the active catalyst.[379] The pre-catalyst **153**, with a bulky bis-carbene ligand (R = Bu^t), was found to be efficient for the synthesis of polycarbonate from CO and bisphenol A.[380] Relatively high molecular weights polymers were produced in high yield.

A potentially important development is the application of a well-defined Pd–carbene complex for the oxidation of alcohols; the complex Pd(OAc)$_2$(IPr^i)(OH$_2$) **154** has been synthesized and found to be an extremely effective and robust catalyst for the aerobic oxidation of alcohols.[381,382] Nearly quantitative conversion was achieved with 5 mol% catalyst in less than 2 h.[381] A rational mechanism is proposed for the catalytic reaction and studies have indicated that β-hydride elimination is the rate-limiting step; calculations using DFT confirm that view.[382] An extension of these studies has led to oxidative kinetic resolution of secondary alcohols using dimeric Pd complexes of the type shown as **155**.[383] Achiral and chiral carbene ligands used in conjunction with the chiral base (−)-sparteine provide enantiodiscrimination of the alcohol. Further studies investigating aerial oxidation with the Pd(0) complex Pd(IMes)$_2$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol–2-ylidene) led to the isolation of an η^2-peroxo complex (IMes)$_2$Pd(O$_2$), **156**.[384] Treatment of this complex with acetic acid gives the hydroperoxopalladium complex **157**; further protonolysis proceeds slowly to give H$_2$O$_2$ and the Pd(OAc)$_2$(IMes) complex.



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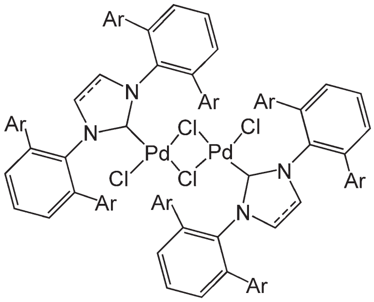

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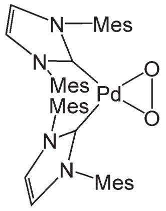

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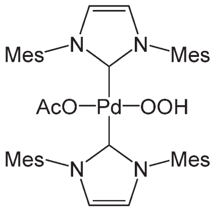

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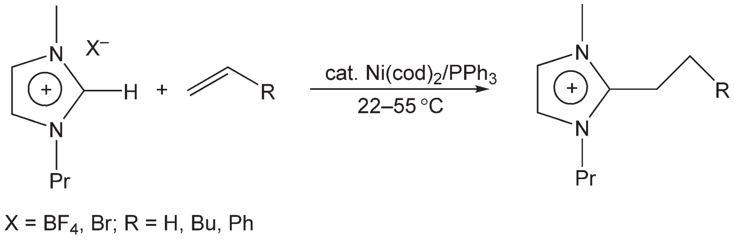
Novel, one-pot, multicatalytic, or cascade reactions have been developed and successfully applied for the conversion of alcohols into alkenes and for the conversion of an alcohol into a cyclic ether.[385] In the first, two-step, cascade process, two different catalysts were used: a Pd–carbene complex for aerobic oxidation of alcohols and an Rh complex for methylenation of the resultant carbonyl compound. In the second three-step process, an Ru-catalyzed ring-closing metathesis reaction was included. It has been demonstrated that monodentate, achiral NHC ligands are capable of demonstrating a regioselective “memory effect” (where the original site of attachment of the leaving group plays a significant role in determining the regiochemistry of the product) in allylic alkylation.[386]

A novel catalytic C–C bond coupling reaction, in which imidazolium salts act as substrate, that proceeds through a redox process involving an M–carbene intermediate has been reported.[387] By combining the individual steps of oxidative addition of imidazolium salts to low-valent group 10 metals,[325,327] with reductive elimination from M(alkyl)(carbene) complexes,[311] 2-substituted imidazolium salts are generated (Equation (37)). These results demonstrate a unusual reactivity for the imidazolium/NHC pair, and have significance for the use of imidazolium-based ILs as solvents, and indicate that such solvents may be used to generate M(hydride)(carbene) complexes *in situ* for use as catalysts.



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8.04.2.3.6.(vii) Supported/two-phase catalysis

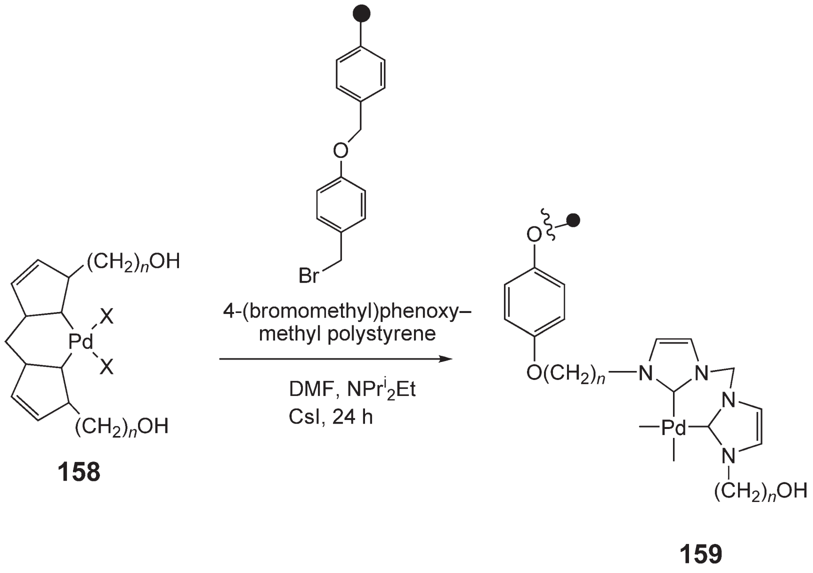
Of significance is the early report that during the Pd-catalyzed Heck reaction, undertaken in IL solvent, there was a considerable enhancement in catalytic activity when an imidazolium-based, instead of a pyridinium-based, IL solvent was used.[388] The suggestion was that under the basic conditions of the Heck reaction, the imidazolium IL might be deprotonated and Pd–carbene complexes generated *in situ*. This proposal was supported by the further observation that insoluble palladium black redissolves in hot imidazolium IL even in the absence of other ligands. Consistent with these studies, it was found that carbene complexes could be isolated from the Heck coupling reaction using $Pd(OAc)_2$ in imidazolium-based IL solvents.[389] Other studies purporting the non-innocence of imidazolium-based IL solvents have demonstrated the formation of Pd–carbene complexes during reactions carried out in the IL.[390,391,392] Similar observations have been made when the cross-coupling reactions are carried out in ILs promoted by ultrasound[393] or microwave heating.[394] In each case, either base-promoted coupling reactions were studied or $Pd(OAc)_2$ was used as a source of Pd. Under such conditions, deprotonation of the imidazolium salt is known to occur. This behavior is consistent with the known facile conversion of imidazolium salts to carbenes in the presence of base.

Using ILs as co-solvents in the telomerization of butadiene and methanol, with a catalyst system consisting of $Pd(OAc)_2$ plus phosphine ligand, leads to complete deactivation of the catalyst.[395] It was suspected that stable carbene complexes were formed, thus deactivating the catalyst; hence, 1,2,3-trialkylimidazolium salts were used as the IL co-solvent, that is, the reactive proton in the 2-position of the salt was replaced by an alkyl group. Consistent with this view, highly active and selective catalysts for the telomerization reaction were then obtained.[395] The *in situ* formation of Pd–carbene complexes has been demonstrated for Pd-catalyzed Suzuki coupling reactions carried out in a range of IL solvents.[396] It was noted that 2-arylimidazolium salts were generated in the reaction. However, it was shown that these salts could also act as a source of arene for the coupling reaction. Thus, both reductive elimination and oxidative addition of 1,3-dialkyl–2-arylimidazolium salts appeared to be occurring.

Typical $PdCl_2(carbene)_2$ complexes have been synthesized from the azolium salt and $Pd(OAc)_2$ and then applied in the amination of aryl chlorides using ILs as solvent.[397] The IL/catalyst system could be recycled several times without significant loss of performance. Similarly, mixed ligand carbene/phosphine Pd complexes have been used in low-viscosity IL solvent as catalysts for cross-coupling reactions.[398] A continuous microflow system, using the same low-viscosity IL as the reaction medium, and a mixed ligand carbene/phosphine Pd catalyst, has been developed for Heck cross-coupling.[399] The system allowed efficient catalyst recycling. In a variation on the two-phase approach to catalysis, a fluorous ether was used as the sole solvent and a fluorous complex was used as a catalyst in Heck coupling.[400] The fluorous phase containing the catalyst could be recycled several times without loss in activity.

Polymer-supported carbene complexes, **159**, have been developed and their application in Heck coupling studied.[401] Complex **158** was attached to the support through an ether linkage (Equation (38)). Solid-state ^{13}C NMR confirmed the presence of the supported palladium complex. IR spectra indicated that about 50% of the –OH moieties remained unreacted, suggesting that the supported Pd complex exists as the mono-ether species.

Relatively low loadings (~1%) of complex were achieved. The resulting system was tested in Heck coupling with modest success. With aryl bromides, the catalytic performance, in terms of selectivity and TON, was similar to that observed for the equivalent homogeneous systems. However, the supported catalyst was ineffective with aryl chlorides. The heterogeneous catalysts are not sensitive to air or moisture and could be used a number of times without detectable loss in performance, although, at odds with this statement, significant initial leaching of the catalyst was observed.



(38)

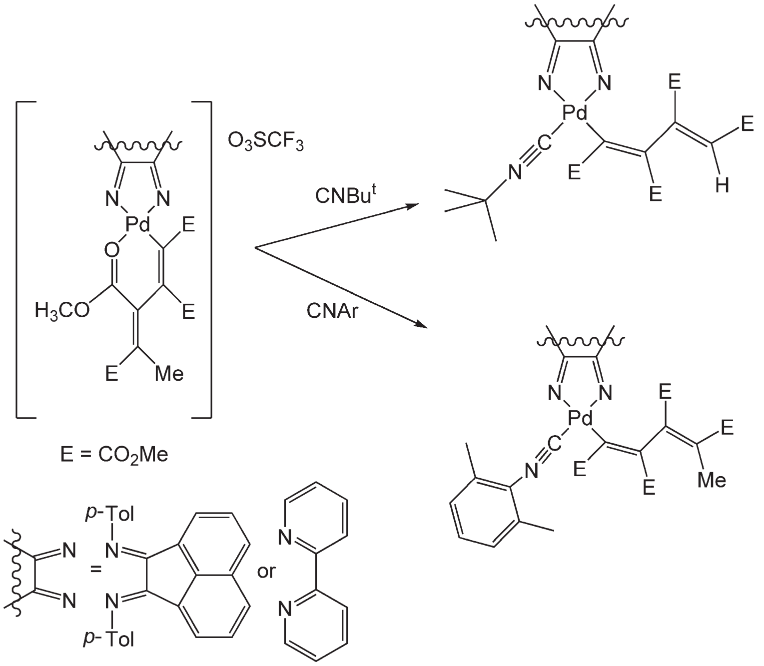
Clay (montmorillonite K-10) -supported Pd complexes containing tridentate pincer bis-carbene ligands have been synthesized and applied as catalysts in Heck and Sonogashira cross-coupling reactions.[402,403] The catalyst systems were found to be at least as efficient as related homogeneous catalysts and they could be recycled without significant loss of activity. Polymer-supported carbene complexes have also been synthesized and tested as catalysts in cross-coupling reactions.[404,405] A monodentate carbene complex, supported on polystyrene, was investigated for Suzuki cross-coupling.[404] In the second study, a CNC dicarbene pincer system was investigated in Heck and Suzuki coupling; it was found that this very stable system could be recycled at least 14 times without significant loss in activity.[405]

8.04.3 Isocyanide Complexes

Isocyanides have been used extensively as ligands in palladium complexes; they are frequently used as supplementary or spectator ligands to stabilize a range of complex types. Their bonding properties are often compared to those of carbon monoxide. Some mention will be made of isocyanides as support or ancillary ligands; however, the main focus of this chapter will be on those systems where the isocyanide is either an important constituent in the formation of new complexes, or acts as a substrate and is converted to a new organic moiety—a common example of this is the migratory insertion of the unsaturated isocyanide into Pd–E bonds.

8.04.3.1 Synthesis of Complexes

A large number of studies have been reported in which the isocyanide ligand acts as a simple ancillary ligand for stabilization of palladium complexes. For example, isocyanide–Pd complexes containing such ligand systems as (arylsulphonyl)alkyl-,[406] arylamido-[407] and (diphenylphosphino)pyridine[408,409] have been reported. Benzene–1,2-dithiolate complexes of the type $Pd(S_2C_6H_4)L_2$ (where L = PEt_3 and CNXy),[410] and ferrocene-based dinuclear thiolato-bridged Pd(II) complexes with ancillary isocyanide ligands (CNR; R = Bu^t, $–CH_2CO_2Me$), have been reported.[411] $\mathrm{CNBu^t}$ has been used as a stabilizing ligand in the synthesis of complexes of the chelating diolefins diallyl ether and 1,3-divinyl–1,1,3,3-tetramethyldisiloxane.[412,413] Similarly, $\mathrm{CNBu^t}$ was used to form palladium complexes of the ligands py{SCHC(O)R}-2 (py-2 = 2-pyridyl; R = Ph, Me, OMe), in which the ligand is cyclometallated through the thioether carbon.[414] The *o*- and *m*-bromotetrafluorophenyl complexes, *cis*- and *trans*-$[\mathrm{Pd(C_6BrF_4)_2L_2}]$ (L = CNMe as one of the ancillary ligands), have been prepared, and atropisomerism studied by $^{19}\mathrm{F}$ NMR.[415] $\mathrm{Bu^tNC}$ has been used as a supporting ligand for a complex which contains the fluorinated ligand 2,4,6-tris(trifluoromethyl)phenyl.[416] The isocyanide ligands $\mathrm{Bu^tNC}$ and $\mathrm{2,4\text{-}Me_2ArNC}$ have been used to form stable cationic complexes of σ-dienyl ligands, which have been generated from palladacyclopentadiene complexes (Equation (39)).[417] The second-order non-linear optical properties have been measured for a range of Pd(II) and Pt(II) Schiff-base complexes, including complexes of the type $\mathrm{PdCl(R^1C_6H_3CH{=}NC_6H_4R^2)(CNC_6H_4R^3)}$ (where $\mathrm{R^1}$, $\mathrm{R^2 = NO_2}$ and $\mathrm{OC_8H_{17}}$, or $\mathrm{N(C_4H_9)_2}$; $n = 4$ or 8, and $\mathrm{R^3 = NO_2}$, $\mathrm{OC}_n\mathrm{H}_{2n+1}$, $\mathrm{N(C}_m\mathrm{H}_{2m+1})_2$; $n = 4$ or 8; $m = 1$ or 4), and the influence of the ligands on the optical behavior observed.[418]



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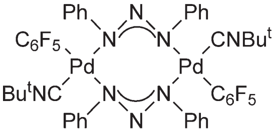
Mixed metal Fe–Pd complexes, bridged by dppm, have been synthesized, and in one example, XyNC has been used as an auxiliary ligand.[419] Isocyanides have been used as ancillary ligands in the formation of palladium complexes of a triazenide ligand (μ-ArNNNAr), **160**;[420] a phosphinoterthiophene ligand, **161**;[421] the ligand 1,8-bis[(diphenylphosphino)methyl]naphthalene, **162**;[422] β-iminophosphines, **163** and **164**;[423] and a bridging tetrakis(1-pyrazolyl)borate ligand, **165**.[424] Isocyanides have also been employed as ancillary ligands in palladium complexes of cyclometallated ligands. The cyclometallated complexes **166–168**[425,426,427] have been synthesized. Reaction of $\mathrm{CNBu^t}$ or 2,6-dimethylisocyanide with metallated Pd–diazabutadiene complexes gave new isocyanide complexes.[428] Reaction of the metallated dimer **169** with various ligands, including $\mathrm{CNBu^t}$, gives the monomeric square-planar complexes **170**, which are unstable in solution to give chloro-bridged dimers and propargyl amines.[429] A number of fluoromesityl complexes with isocyanides as ancillary ligands have been prepared by displacement of less strongly bound ligands.[430,431] Displacement of cod in PdCl(FMes)(cod), FMes = 2,4,6-tris(trifluoromethyl)phenyl, by $\mathrm{CNBu^t}$ gives the new complex $\mathrm{PdCl(FMes)(CNBu^t)_2}$.[430] Similarly, displacement of $\mathrm{SMe_2}$ in *trans*-$[\mathrm{Pd(FMes)_2(SMe_2)_2}]$ with $\mathrm{CNBu^t}$ or CNTol-*p* yields the bis-isocyanide complex *trans*-$[\mathrm{Pd(FMes)_2(CNR)_2}]$.[431]



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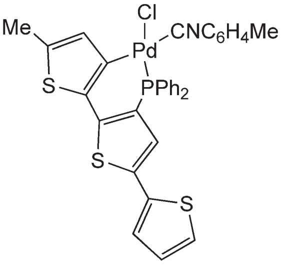

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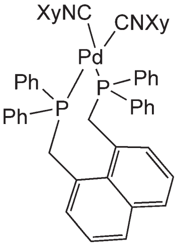

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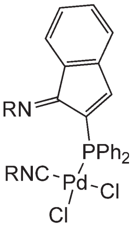
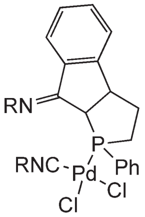


R = Xy

163



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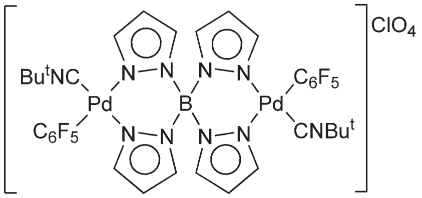

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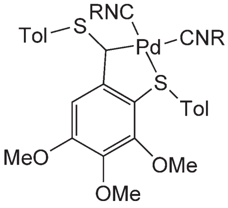
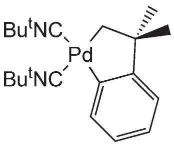


R = Xy, Bu^t

166



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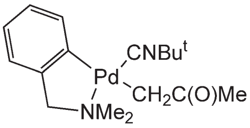

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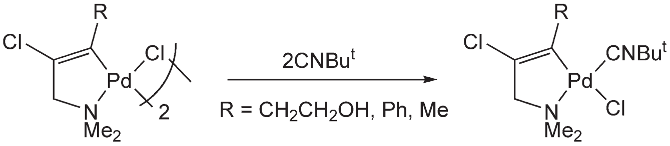
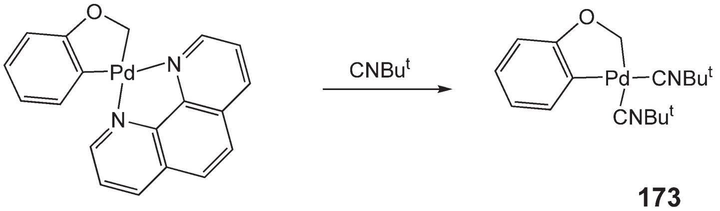


169 **170**

Cationic palladatelluraborane complexes, [2-L–2-(PPh$_2$)–*closo*-2,1-PdTeB$_{10}$H$_9$(PPh$_3$)][BF$_4$], where L = CO, CNBu^t, and CNCy, have been prepared and characterized by X-ray crystallography.[432] In related studies, a complex containing a 12-vertex (PdAs$_2$B$_9$) cage with the Pd η^5-bonded to an As$_2$B$_3$ ring, and with a Bu^t–isocyanide ligand attached to a cage boron, has been prepared and a structure obtained.[433] Palladium metallaheteroborane complexes have been synthesized as a mixture, from which the minor product (<1% yield) was characterized by X-ray crystallography and found to be the complex *A*-[2-1-2-(CNBu^t)–3-(Bu^{t}NHCH)–*closo*-2,1-PdTeB$_{10}$H$_9$] in which the CNBu^t is coordinated to the Pd and a secondary carbene ligand (Bu^{t}NHCH) is attached to the PdTeB$_{10}$-cage at B(3).[434] Oxapalladacycles of type 171 and 172 undergo ligand-exchange reactions with CNR to give the oxapalladacycle isocyanide complexes 173 and 174.[435,436] Complex 173 is a rare example of an organopalladium complex with only Pd–C bonds. Ligand-exchange methods were utilized to synthesize a number of complexes of the tridentate ligand [2,6-bis(thiocarboxylate)]$^{2-}$ of type 175, which included several isocyanide derivatives.[437] The cationic complex [Pd(CNBu^t)$_2$(dppe)][SO$_3$CF$_3$] was prepared by a simple ligand-exchange process from the triflate precursor.[438]



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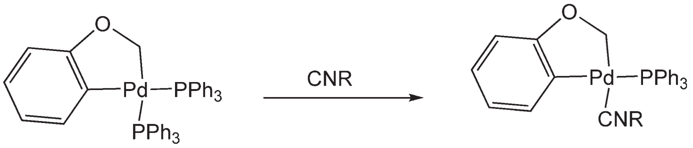
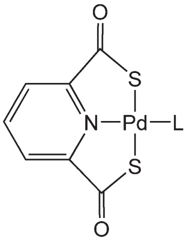


172

R = Bu^t, Xy

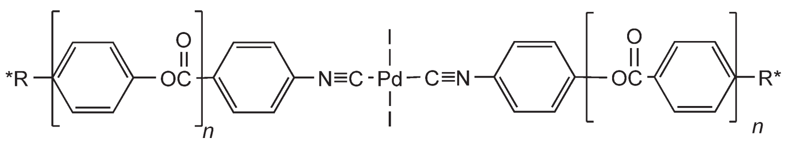
174



L = CNBu^t, CNC$_8$H$_{17}$, CNC$_6$H$_4$OC$_8$H$_{17}$

175

Mesogenic isonitrile ligands, and their Pd complexes (PdX$_2$(CNR)$_2$, where R = –C$_6$H$_4$–OC(O)–C$_6$H$_4$-OC$_n$H$_{2n+1}$; –C$_6$H$_4$–C(O)O–C$_6$H$_4$-OC$_n$H$_{2n+1}$; –C$_6$H$_4$–C$_6$H$_4$–OC$_n$H$_{2n+1}$ have been prepared, providing examples of liquid crystalline materials.[439] The thermal behavior of the complexes was investigated and phase-transition temperatures recorded. Palladium– (and platinum–) diiodo complexes of a series of 4-isocyanobenzilidene–4-alkoxyphenylimines, 4-CN–3,5-R$_2$C$_6$H$_2$CHNCC$_6$H$_4$–4-OC$_n$H$_{2n+1}$ (R = Me, ^{i}Pr) were prepared, and where R = Me the complexes exhibit mesomorphic behavior.[440] The complexes MX$_2$[CNC$_6$H$_2$(3,4,5-OC$_n$H$_{2n+1}$)$_3$]$_2$ (M = Pd, Pt; X = Cl, Br, I; *n* = 4, 6, 8, 10, 12) show hexagonal columnar phases, and in the mesophase, the complexes seem to be *cis* for X = Cl and Br but *trans* for X = I.[441] Chiral isocyanide ligands have been employed to synthesize palladium complexes of type **176**, creating helical SmC* and Ch mesophases.[442] *S*,*N*,*S* and *O*,*N*,*O* pincer ligands have been synthesized and coordinated to palladium; where the fourth coordination site is occupied by isonitrile ligands (4-CN–C$_6$H$_4$–R, 4-CN–C$_6$H$_4$–C$_6$H$_4$–R-4′), only the *S*,*N*,*S* pincer gave rise to stable isolable complexes, **177**.[443] In most cases, the *S*,*N*,*S* pincer complexes give rise to mesomorphic materials (S$_c$). Nickel and palladium complexes of similar 4-substituted *S*,*N*,*S* pincer ligands form mesogenic complexes when coordinated to 4-substituted biphenyl isocyanides of the type 4-CN–C$_6$H$_4$–C$_6$H$_4$–R^1-4′ (R^1 = OC$_{10}$H$_{21}$, OC$_4{}^*$H$_9$) and 4-CN–C$_6$H$_4$–O$_2$C–C$_6$H$_4$–R^2-4′ (R^2 = OC$_8{}^*$H$_{17}$).[444] The isostructural complexes [Pt(CNMe)$_4$](PF$_6$)$_2$ and [Pd(CNMe)$_4$](PF$_6$)$_2$ have been prepared and their crystal structures determined.[445] The reaction of 1 equiv. of RNC with the acetonitrile-palladium complex **178** gave the complex **179**; however, addition of excess isocyanide leads to displacement of the tridentate n-donor ligand, forming the complex [Pd(CNR)$_4$](BF$_4$)$_2$.[446] In contrast, when excess isocyanide ligand was added to complex **180**, only **181**, in which the ferrocene bis-phosphine ligand remained coordinated, was formed. This ligand-exchange behavior was provided as an explanation for the observed ineffectiveness of complex **180** in enantioselective catalysis in the presence of excess isocyanide ligand.



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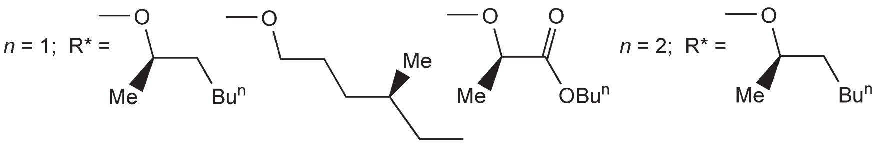

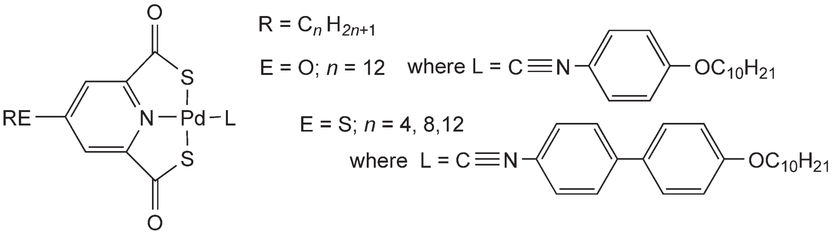

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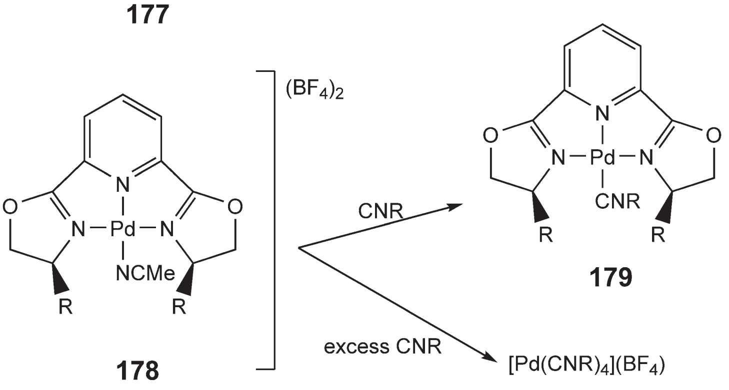
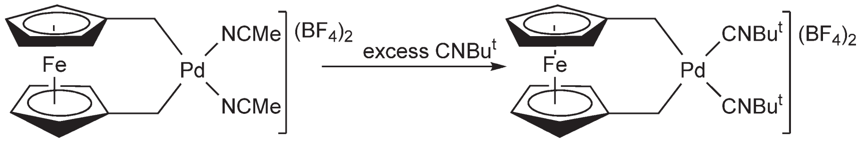


178 **179**



180 **181**

The isonitrile ligand, $CNBu^t$, has been used as an ancillary ligand in the synthesis of carborane palladium complexes.[447] The complex $Pd(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$ was synthesized and fully characterized. Reaction of complexes of the type $1,1\text{-}(PMe_2Ph)_2$–*closo*-1,2,3-$PdAs_2B_9H_9$ and $1,1\text{-}(PMe_2Ph)_2$–*closo*-1,2,3-$PdC_2B_9H_{11}$ with $CNBu^t$ and $PdCl_2(CNBu^t)_2$ leads to complexes in which the isonitrile has been dealkylated, forming complexes in which the CN is coordinated to a ring boron.[448]

A series of complexes of pyridyl-functionalized isocyanides, *trans*-$[PdI_2(CNR)_2]$, where R = 2-, 3-, and 4- pyridine, 3- and 5- quinoline, 4-quinaldine, and 5-isoquinoline, have been prepared and the molecular structure of *trans*-$[PdI_2$(CN–3-quinolyl)$_2]$ determined. The molecular units are packed to form two-dimensional sheets, which are held together by π–stacking of the quinolyl units.[449] In a related study, the synthesis of an alkylbenzoate-functionalized isocyanide complex, *trans*-$[PdI_2(CNC_6H_4CO_2Me\text{-}4)_2]$, has also been reported and the molecular structure determined.[450] Functionalized isocyanide ligands, which allow formation of extended molecular networks, have been developed. Cyanoisocyanoarene complexes $PdI_2(CNR)_2$ (CNR = 3-CN–C_6H_4–CN, 4-CN–3-C_2H_5–C_6H_3–CN, 4-CN–3-Cl–C_6H_3–CN, 4-CN–1,2-(NC_2)–C_6H_3, 4-CN–C_6H_4–CH_2CN) and alkynyl- and cyano-substituted diisopropylphenylisocyanide complexes of Pd and Pt (*trans*-$[MI_2(CNR)_2]$, where M = Pd, Pt; and CNR = $CNC_6H_2R_2$–*i*-Pr_2-2,6–X-4

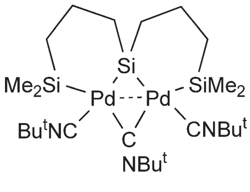
(X = Br, I, $-C{\equiv}CSiMe_3$, $-C{\equiv}C-C_6H_4-C{\equiv}CH$-4, CN) have been synthesized.[451,452] Examples of these complexes were shown to form coordination polymers.

The isocyanides, L = $CNC_6H_2R_2$-2,6–CHNOH-4, $CNC_6H_2R_2$-2,6–CHNNH(2-C_5H_4N)-4, and $CNC_6H_2R_2$-2,6–CHNNHCHO-4 (R = Me, R = $CHMe_2$), and their Pd complexes, *trans*-$[PdI_2L_2]$, were synthesized. The molecular structure of *trans*-$[PdI_2L_2]$ (L = $CNC_6H_2R_2$-2,6–CHNOH-4; R = $CHMe_2$) demonstrated the formation of extended hydrogen-bonded networks.[453] The complexes *trans*-$[PdI_2CNR]$ (CNR = 3-(4-pyridylethynyl)phenylisocyanide, 4-(4-pyridylethynyl)phenylisocyanide, 2,6-diisopropyl–4-(4-pyridylethynyl)phenylisocyanide, and 2,6-diisopropyl–4-(4-pyridyl)phenylisocyanide) were prepared as building blocks for coordination polymers and supramolecular assemblies.[454] For example, the complexes *trans*-$[MI_2\{CNC_6H_2-(i\text{-}Pr)_2\text{-}2,6-(C_5H_4N\text{-}4)\text{-}4\}_2]$ (M = Pd, Pt) react with $Pd(SO_3CF_3)_2(dppp)$ to form molecular squares, Pd(dppp){*trans*-$[MI_2(CNC_6H_2\text{-}(i\text{-}Pr)_2\text{-}2,6\text{-}(C_5H_4N\text{-}4)\text{-}4)_2]_4$-$(SO_3CF_3)_8$. Isocyanoalkylidynes and their heteronuclear complexes, $\{WCl(CO)_2L_2[{\equiv}C-C_6H_4-(C{\equiv}C-C_6H_4)_n-NC\}]\}_2-ML_m$ (L_2 = TMEDA, dppe; ML_m = PdX_2 (X = Cl, I)), have been synthesized and employed in the formation of extended α,ω-dimetalla-π-systems, and in some cases, photoinduced electron-transfer processes can be observed.[455] The ligand 1,8-diisocyano–*p*-menthane (dmb) has been employed as a linker ligand to form organometallic oligomers and polymers.[456,457] Amorphous oligomers of the type $\{[Pd_2(dmb)(diphos)_2](ClO_4)_2\}_n$ were formed and characterized by thermal methods.[456] Polymers had the general formula $\{Pd_2(dmb)_2(diphos)^{2+}\}_n$.[457]

A number of dinuclear, polynuclear, and mixed metal complexes of Pd with isocyanide ligands have been synthesized. The bimetallic complexes $(OC)_2(\mu\text{-}C_5H_4Me)Mn(\mu\text{-dppm})PdCl_2(CNR)$ (where R = Bu^t, 2,6-Xy), in which there is no metal–metal interaction, have been prepared.[458] Treatment of the complex $Pd_2Cl_2(dpmf)_2$ {where dpmf = 1,1′-bis[(diphenylphosphino)methyl]ferrocene} with $Pd_2(CNXy)_6$ in the presence of NH_4PF_6 and excess isocyanide gave the macrocyclic polynuclear complex $[Pd_4(CNXy)_8(dpmf)_2]^{4+}$.[459]

The dinuclear Pd(I) complex, $[Pd_2(CNR)_6](PF_6)_2$ (R = 2,6-xylyl, mesityl), reacts with 1,1′-bis(diphenylphosphino)-ferrocene (dppf) to give the complexes $[Pd_2(CNR)_2(dppf)_2](PF_6)_2$, which are extremely photosensitive, undergoing homolytic cleavage in room light.[460] Reaction of dinuclear $[Pd_2(CNR)_6]^{2+}$ with the ligand $(Ph_2PCH_2)_2PPh$ (dpmp) gave the complex $[Pd_2(CNR)_2(dpmp)_2]^{2+}$, in which the potentially tridentate phosphine ligand both bridges the Pd–Pd centers and chelates to a single Pd; the complex rearranges on heating.[461] In a related study, treatment of $[Pd_2(CNR)_6]^{2+}$ (R = Xy) with the monodentate phosphines $PPh_2[C_6H_3(OMe)_2]$, $PPh[C_6H_3(OMe)_2]_2$, and $P[C_6H_3(OMe)_2]_3$ led to displacement of the axial isocyanide ligands and formation of $[Pd_2(CNR)_4(phosphine)_2]^{2+}$, and reaction of the neutral dimer $Pd_2Cl_2(CNR)_4$ with $P[C_6H_3(OMe)_2]_3$ gave the ionic complex $[Pd_2(CNR)_4\{P[C_6H_3(OMe)_2]_3\}_2]Cl_2$.[462] The synthesis of a dimeric azavinylidene-bridged complex $[Pd\text{-}(\mu\text{-}N{=}CPh_2)(C_6F_5)(CNBu^t)]_2$ has been described and the molecular structure of the complex determined.[463] The complex $[Pd(\mu\text{-}Cl)(\eta^3\text{-Ind})]_2$ reacts with $CNBu^t$ to give the dimeric complex $[Pd(\mu\text{-}Cl)(\eta^1\text{-Ind})(CNBu^t)]_2$ (Ind = indenyl), which represents the first example of an isolated and fully characterized Pd(II) complex of an η^1-Ind ligand. A molecular structure of the dimer was obtained.[464]

Reaction of 1,1,6,6-tetramethyl–1,5,6-trisilaspiro[4,4]-nonane with $Pd^0(CNBu^t)_2$ gives the dinuclear Pd complex **182**, in which one of the isocyanide ligands bridges the two palladium atoms.[465] The dimeric complex Pd_2-$(\mu\text{-}X)_2(PBu^t_3)_2$ (X = Br, I), where X = Br, polymerizes phenylacetylene. With disubstituted alkynes, trimeric palladium complexes are formed; however, with CNR (R = Xy), the phosphine ligands are displaced and the simple non-bridged dimers $Pd_2X_2(CNXy)_4$ are formed.[466] The interaction of phosphide-bridged dinuclear palladium complexes with the isonitrile $CN-C_6H_4-Me$-4 gave the complex **183** and excess isonitrile led to formation of the trinuclear complex **184**.[467] A dipalladium complex $[Pd_2Na(CNXyl)_2(\mu\text{-dpnapy})_3](PF_6)$ [dpnapy = 2,7-bis(diphenylphosphino)–1,8-naphthyridine] was prepared by the reaction of $Pd_3(CNXy)_6$ with dpnapy and $NaPF_6$.[468] The terminal isocyanide ligands in the dipalladium complex are readily replaced by CO.



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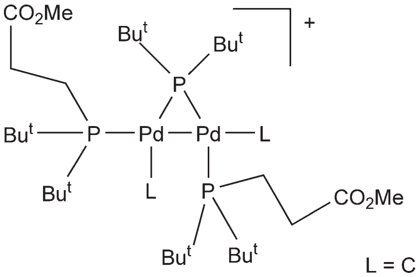

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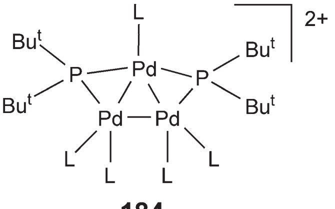

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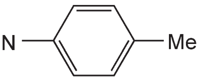
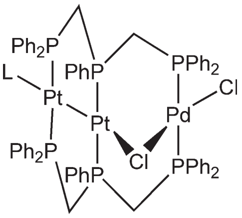
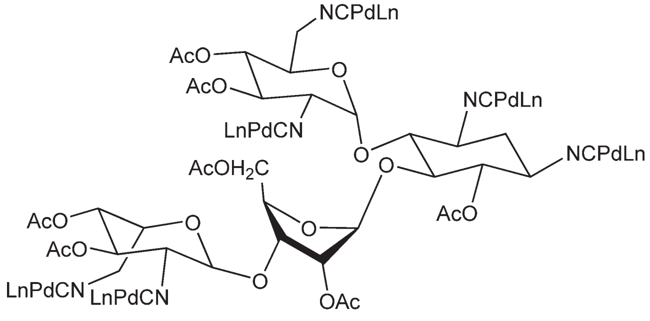


Trinuclear, palladium complexes, $[Pd_3(CNR)_6L_2]^{2+}$ ($L = PPh_2[C_6H_3(OMe)_2]$, $PPh[C_6H_3(OMe)_2]_2$) could be obtained by the reaction of $[Pd_3(CNR)_8]^{2+}$ with the appropriate phosphine. The synthesis and structures of dinuclear Pd(I) isocyanide complexes with *N*-donor bidentate ligands (bipy, phen, and 2,9-dimethyl–phen) was also investigated.[469] The mixed metal trinuclear cluster **185** has been prepared by the reaction of $PdCl_2(cod)$ with the cationic dimer $[Pt_2(CNR)_2(\mu\text{-dpmp})_2]^{2+}$ (dpmp = bis{(diphenylphosphino)methyl}phenylphosphine; R = Xy).[470] Similar A-frame trinuclear complexes were synthesized by reaction of $[Pt_2(CNR)_2(\mu\text{-dpmp})_2]^{2+}$ with $Pd_3(CNR)_6$, R = Mes.[471] The reaction proceeds via insertion of the Pd(0) fragment $Pd(CNR)_2$ into the Pt–Pt bond. A-frame tripalladium complexes $[Pd_3(CNR)_2(\mu\text{-dpmp})_2](PF_6)_2$, where R = Xy and Mes, were also prepared, by the reaction of $[Pd_3(CNR)_8](PF_6)_2$ with dpmp. Further examples of di- and trinuclear complexes of palladium, bridged by dpmp, and with isocyanide ligands, were synthesized by the same group.[472] Treatment of *syn*-$[Pt_2(CNR)_2(\mu\text{-dpmp})_2](PF_6)_2$ with $M_3(CNXy)_6$ (M = Pd, Pt) gave the linear trinuclear cluster *linear*-$[Pt_2M(CNXy)_2(\mu\text{-dpmp})_2](PF_6)_2$ with the additional metal center in the terminal position of the trinuclear aggregate; undertaking the same reaction with *anti*-$[Pt_2(CNR)_2(\mu\text{-dpmp})_2](PF_6)_2$ gave an A-frame trinuclear cluster A-*frame*-$[Pt_2M(CNXy)_2(\mu\text{-dpmp})_2](PF_6)_2$ in which the three metal centers are joined by two metal–metal bonds and bridged by two dpmp ligands.[473] Reaction of the trinuclear, linear Pt_2Pd mixed ligand complex, *linear*-$[Pt_2Pd(CNXy)_2(\mu\text{-dpmp})_2](PF_6)_2$ with electron-deficient alkynes, $R^1C{\equiv}CR^2$ ($R^1 = R^2 = CO_2Me$, CO_2Et; $R^1 = H$, $R^2 = CO_2Me$; $R^1 = H$, $R^2 = CO_2Et$; $R^1 = Me$, $R^2 = CO_2Et$) led to the formation of unsymmetrical A-frame clusters $[Pt_2Pd(CNXy)_2(\mu\text{-dpmp})(\mu\text{- }Ph_2PCH_2P(Ph)CH_2P(Ph)_2CR^1CR^2)](PF_6)_2$.[474] Linear hexametallic clusters containing the redox-active $Pt_2M_2Pt_2$ grouping have been prepared, linked by the tridentate phosphine ligand dpmp and with terminal CNXy ligands.[475]



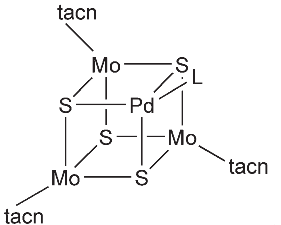
185

The Pd(I) dimer, $Pd_2(\mu\text{-}X)_2(PBu^t_3)_2$ (X = Br, I), reacts with CNXy to give the new dimer $Pd_2X_2(CNXy)_4$.[476] Trinuclear complexes of the type $[Pt_2Pd(CNR)_2(dpmp)_2]^{2+}$ were also prepared. The trinuclear cluster cation $[Pd_3(\mu^3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ reacts with excess xylylisocanide to give the binuclear Pd(I) complex cation $[Pd_2(CNXy)_2(\mu\text{-dppm})_2]^{2+}$; subsequent reaction with Pd(0) isocyanide species gives the trinuclear A-frame cluster complex $[Pd_2(CNXy)_2\{\mu\text{-}Pd(CNXy)_2\}(\mu\text{-dppm})_2]^{2+}$, thus reforming a trinuclear cluster.[477] Isostructural clusters, $Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CNR)(PBz_3)_4$ ($R = Bu^t$, Cy, Xy, Me), have been prepared by reacting the dimer $Pd_2(\mu\text{-}SO_2)(\mu\text{-dba})(PBz_3)_2$ with COS and CNR.[478] Hexanuclear Pd isocyanide complexes have been synthesized from acetate-protected neomycin B, **186**, and fully characterized by spectroscopic methods.[479] The isocyanide $CNBu^t$ has been used as an auxiliary ligand in the synthesis of the SO_2-bridged palladium trimer, $Pd_3(\mu\text{-}SO_2)_2(CNBu^t)_2(PBz_3)_3$, which was crystallographically characterized.[480] Experimental and theoretical studies have been undertaken on the tetranuclear palladium complex $[Pd_4(dmb)_4(PPh_3)_2]Cl_2$ and its organometallic polymer $\{[Pd_4(dmb)_5](O_2CMe)_2\}_n$ representing the first examples of 58-electron linear Pd_4 clusters.[481]



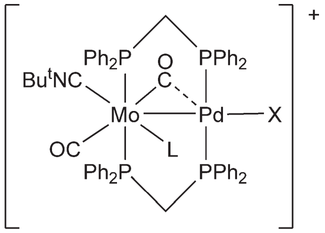
186

The cluster $[PdMo_3S_4(tacn)_3Cl]Cl_3$ (tacn = 1,4,7-triazacyclononane) reacts with species such as alkenes, CO, and $CNBu^t$ to give single cubane-type clusters $[PdMo_3S_4(tacn)_3L]^{4+}$, **187**.[482] A trinuclear mixed metal PdPtCo cluster containing an isocyanide ligand has been synthesized and its halide-binding ability has been investigated.[483] The use of *p*-cyanoisocyanoarenes as ligands has allowed the construction of one-, two-, and three-dimensional polynuclear molecular solids to be synthesized; for example, the complex *trans*-$[PdI_2(CNC_6H_4–CN\text{-}4)_2]$ was prepared, from which a crystalline, one-dimensional solid was obtained by reaction with $Cu(hfacac)_2$ in a 1 : 1 ratio.[484] Electrochemical methods have been used to synthesize binuclear and trinuclear complexes containing chelating diphosphine ligands.[485,486] Isocyanide complexes of binuclear palladium(I) with a bridging μ^3-indenyl ligand have been reported.[487] Treatment with acetic acid converted the dinuclear species to a Pd(I) tetranuclear cluster, $Pd_4(\mu\text{-}OAc)_4(\mu\text{-}CNBu^t)_4$ with bridging acetate and isocyanide ligands; and $PdCl_2(CNBu^t)_2$ has been reacted with *mer*-$[Mo(CO)_3(dpm\text{-}P,P')(dpm\text{-}P)]$ to give dinuclear complexes of the type **188** in which there is an Mo → Pd dative bond, and in which an isocyanide ligand has been transferred to the molybdenum.[488] The mixed metal organometallic polymer, $\{[Pd_2Cl_2(CNR)_4][Mo_2(O_2CCF_3)_4]\}_n$ (R = Xy), where metal–metal-bonded dinuclear Pd–Pd and Mo–Mo units are bridged by chloro atoms, has been prepared by treatment of $Pd_2Cl_2(CNR)_4$ with $Mo_2(O_2CCF_3)_4$ in dichloromethane.[489] A mixed metal Au_6Pd cluster with isocyanide ligands, $[Pd(CNXy)_2(AuPPh_3)_6](NO_3)_2$, has been synthesized.[490]



L = alkene; CO; $CNBu^t$

187



X = Cl, I
L = Cl, CO

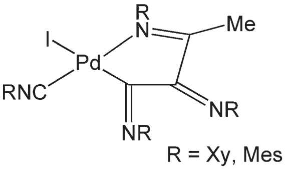
188

8.04.3.2 Reactions of Complexes

Rate constants for the carbonylation of *trans*-$[PdMe(L)(PMe_3)_2]$ complexes (L = solvent (acetonitrile, acetone, dichloromethane), NO_3^-, Cl^-, $CNBu^t$, etc.), have been determined, and it was found that the rate was dependent on the availability of a suitable site for reaction to proceed; strongly bound ligands such as $CNBu^t$ retarded the reaction.[491] Electron transfers to and from photogenerated organometallic radicals based on Pd and Pt isocyanide complexes have been studied by laser flash photolysis. The radicals were found to be stronger reductants and oxidants compared to their parent ground-state dimers.[492]

8.04.3.2.1 Isocyanide-insertion reactions

Insertion reactions involving small molecules, such as alkenes, CO, and isocyanides into M–C bonds is an important reaction in organometallic chemistry and catalysis, and insertion is a common reaction undergone by isocyanide ligands. Many examples have been reported. Reaction of *trans*-$[PdIMe(PPh_3)_2]$ with CNXy led to the multiple insertion of the isocyanide into the Pd–Me bond to give the tris-imino insertion product **188**.[493] Similar results were obtained with CNMes, and where the Me group on the Pd was replaced by Ph. Reaction of **189** with copper(II) chloride gave the dinuclear complex **190**. Multiple insertions of CNXy were observed when $PdCl_2(PPh_3)_2$ was treated with excess isocyanide and SiH_2MePh in refluxing toluene.[494] The presence of SiH_2MePh leads to the *in situ* generation of a hydride complex, into which the isocyanide inserts. A mononuclear complex, **191**, of a polyimino ligand, and a novel heterobicyclic compound, **192**, were obtained. Reaction of the polyimino Pd complex with phenylacetylene gave a pyrrol compound, **193**. The complex *trans*-$[PdCl\{CH_2S(O)Ph\}(PPh_3)_2]$ **194** underwent a double insertion reaction with $CNBu^t$ to give the complex **195**.[495] A systematic study, investigating the influence of chelating phosphines, in complexes of the type PdClMe(P–P) (P–P = dppe, dppp, dppf), on the insertion of CNR (R = Xy, $\mathrm{Bu^t}$) into the Pd–Me bond has been undertaken.[496] For dppe, the reaction is slower and only single insertion is observed; for dppp and dppf, single, double, and multiple insertions are observed. Reaction of PdIPh(dppe) with CNXy gave the imidoyl complex, PdI{C(Ph)═NXy}(dppe), and further reaction of this complex with isocyanates and isothiocyanates, RNCE (R = Ph, E = O; R = Ph, Me, E = S), gave rise to a range of novel insertion products.[497]



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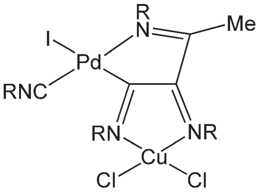

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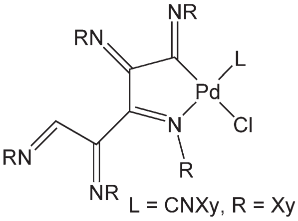

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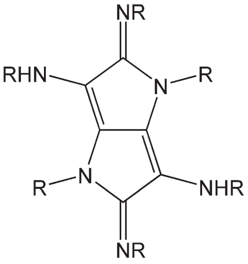

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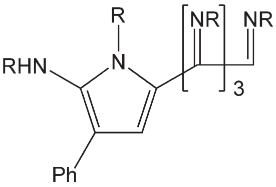

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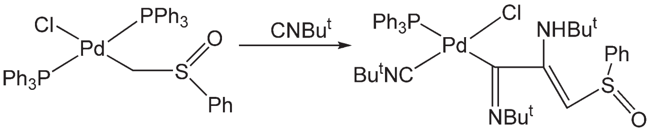
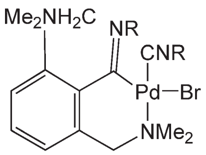


194

195

The insertion of isocyanides into Pd–C bonds was observed in reactions of PdBr[$C_6H_3(CH_2NMe_2)_2$-2,6] with isocyanides to give complexes of type 196.[498] Diphenylphosphinomethane-bridged bimetallic Fe–Pd–Me complexes were found to undergo isocyanide insertions into the Pd–Me bond generating new C–C bonds; multiple insertions were observed.[499] A comprehensive structural and mechanistic study of isocyanide insertion into the Pd–C bond of complexes stabilized by chelating nitrogen ligands has been undertaken.[500] Insertion of CNXy, $\mathrm{CNBu^t}$, and $\mathrm{CNCH_2Ts}$ into the Pd–Me bond of PdClMe(N∼N) (N∼N = bipy, phen, 2,2′-bipyrimidine) gave the complexes PdCl{C(═NR)Me}(N∼N) (R = Xy, $\mathrm{Bu^t}$, and $\mathrm{CH_2Ts}$) in quantitative yield. Kinetic studies demonstrated that the rate of migration of the methyl group to precoordinated isocyanide (in complexes, PdClMe(CNR)(N∼N), formed as intermediates in the reaction) increases with increasing electrophilicity of the isocyanide. Complexes of the type 197 and 198, have been synthesized and their reactions with alkynes and isocyanides studied.[501] Reaction of 197 (R = $\mathrm{NHBu^t}$) with CNXy gave the isocyanide-insertion product 199; where R = H, the heterocyclic compound 200 was obtained.



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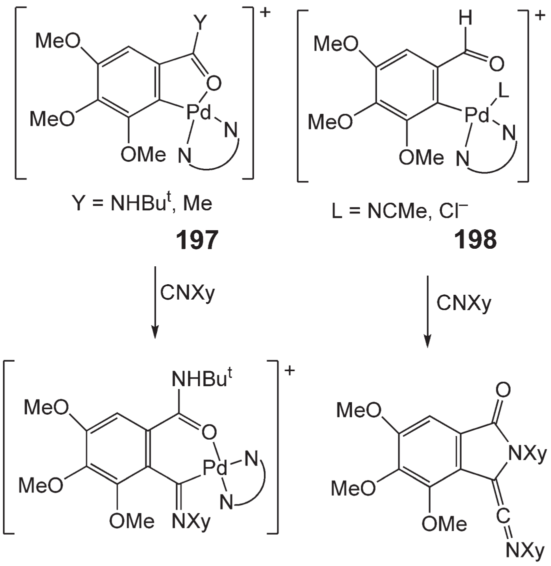


Y = NHBu^t, Me

197

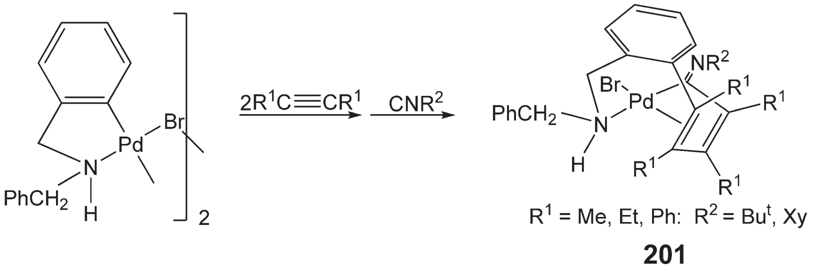
L = NCMe, Cl$^-$

198

199

200

Stepwise insertion of alkynes ($R^1C{\equiv}CR^1$; $R^1 = Me$, Et, Ph) and isocyanides (CNR^2; $R^2 = Bu^t$, Xy) into the Pd–carbon bond of arylated complexes gave rise to complexes of type **201** (Equation (40)).[502] A comparison of the insertion of CO, isocyanides, and olefins into the Pd–C bond of neutral and cationic organopalladium complexes ($[PdR(solvent)L_2]A$; $PdXR(L)_2$; $[PdMe(Y)(L)_2]A$, where R = organo group; L = tertiary phosphine; $A = BF_4$, PF_6, triflate; X = halide; Y = tertiary phosphine, pyridine, isocyanide) has been reported.[503] Successive insertions of isocyanide and CO into the Pd–Me bond were also studied. Stepwise reaction/insertion of $CNBu^t$ and Cp^- with $[Pd(\mu\text{-}Cl)\{CH(SiMe_3)_2\}(PMe)_3]_2$ afforded fulvene complexes of the type $Pd\{C(NHBu^t){=}C(C_4H_3R)\}\text{-}\{CH(SiMe_3)_2\}(CNBu^t)(PMe_3)$, **202**.[504] A molecular structure was obtained for the complex where R = Me. These studies were continued, and the stepwise reaction of $[Pd(\mu\text{-}Cl)\{CH(SiMe_3)_2\}(PMe_3)]_2$ with $CNBu^t$ and Cp^- or Ind to give metal-substituted fulvenes was investigated.[505] A study has been made on the insertion of CO, isocyanides, alkenes, and alkynes into *ortho*-palladated phenol derivatives, and consecutive insertions have also been investigated.[506] For example, reaction of **203** with an alkyne affords the complex **204**, which when reacted with CNXy gives the product **205** (Equation (41)).



201

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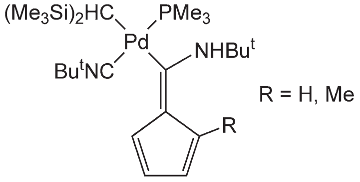

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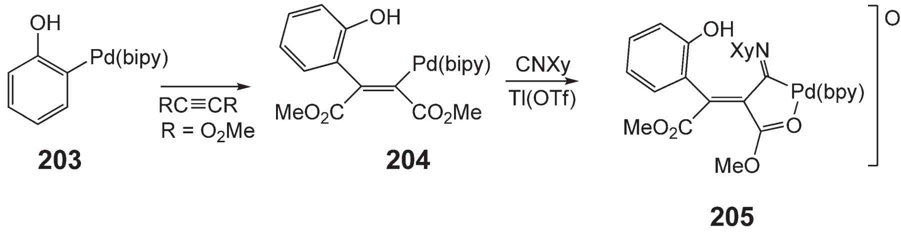
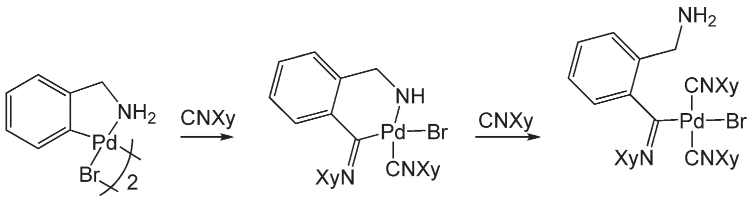


(41)

Several studies on isocyanide insertion into orthopalladated complexes have been reported. The reaction of 2-ROC$_6$H$_5$I with Pd(dba)$_2$ and isonitriles gives rise to the complexes *trans*-[PdI{C(=NR^1)C$_6$H$_4$OR-2}(CNR^1)$_2$] (R = H, R^1 = Xy, Bu^t; R = C(O)Me, R^1 = Xy); complexes with bipy as an ancillary ligand were also prepared.[507] In a related study, the reaction of 2-iodoanaline with Pd(dba)$_2$ and isonitriles (CNXy, CNBu^t) gives rise to the complexes PdI{κ^2C,N-C(=NXy)C$_6$H$_4$NH$_2$-2}-(CNXy) and *trans*-[PdI{C(=NBu^t)C$_6$H$_4$NH$_2$-2}(CNBu^t)$_2$]. The complex, *trans*-[PdI{C(=NXy)C$_6$H$_4$NH$_2$-2}(CNXy)$_2$], reacts with Tl(OTf) to give the cyclopalladated product *cis*-[Pd{κ^2C,N-C(=NXy)C$_6$H$_4$NH$_2$-2}(CNXy)$_2$]OTf.[508] A further study consisted of an investigation of insertion of isocyanides into the Pd–C bond of orthopalladated primary amines.[509] The reaction pathway followed is described in Equation (42). The reaction of a series of 2-substituted arylpalladium(II) complexes with CNXy has been investigated in detail; depending on the ring substituent, mono- or triinsertion of the isocyanide is observed.[510] Iminoacyl- and 2-acetylarylpalladium (II) complexes, formed by the reaction of isocyanide with PdBrRL$_2$ (L$_2$ = bipy; R = C$_6$H$_4$(C(O)Me)-2, C$_6$H(OMe)$_3$-2,3,4–(C(O)Me)-6; L = PPh$_3$, R = C$_6$H$_4$(CH=CH$_2$)-2), react with Tl(OTf) leading to depalladation.[511] Orthopalladated aryl-carbodiimide complexes **206, and 207**, of palladium react with isocyanides CNR^2 (R^2 = Xy, Bu^t) to generate palladated quinazoline complexes **208** and **209**, via an isocyanide-insertion process (Equation (43)).[512] Iminophosphoranes, Ph$_3$P=NC$_6$H$_4$R-4 (R = Me, OMe) react with Pd(OAc)$_2$ to give complex **210**; further reaction with CNBu^t affords complex **211**.[513] Reaction of the iminophosphorane Ph$_3$P=NC$_6$H$_4$I-2 with Pd(dba)$_2$, TMEDA, and then CNXy gives rise to the insertion products **212** and **213**.[513] In related studies by the same group, complexes of orthopalladated aryldithioacetals react with the isocyanides, CNBu^t and CNXy, to yield complexes in which the isocyanide acts as a simple spectator ligand, and also where insertion takes place (e.g., complex **214**).[514]



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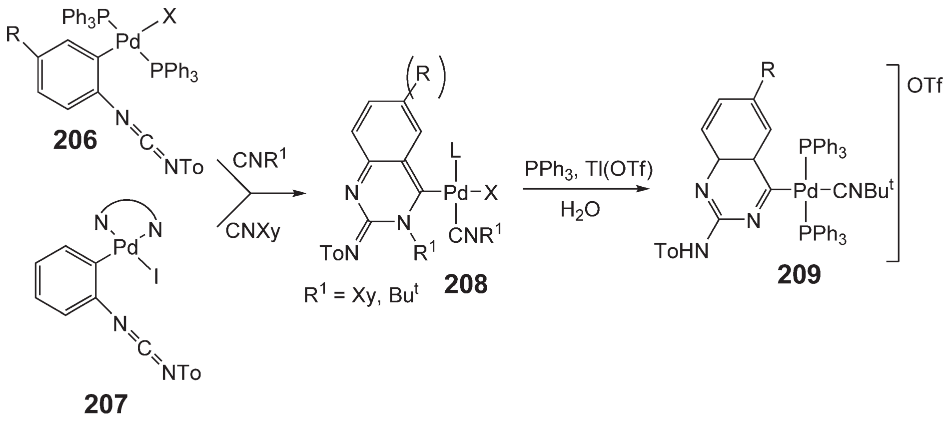

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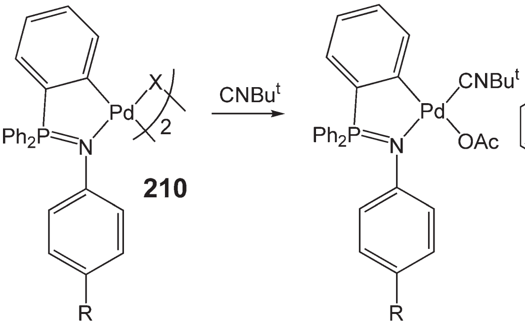
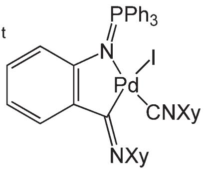


210

R = Me, OMe
X = OAc

211



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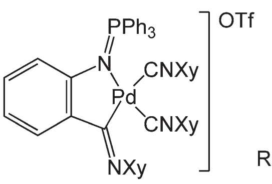

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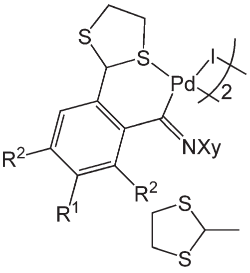
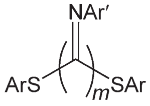


R^1 = OMe,
R^2 = H, OMe

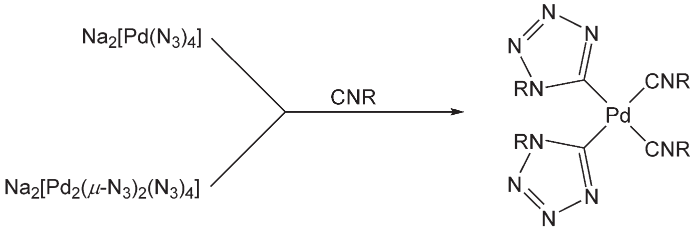
214

The first evidence of isocyanide insertion into an M–S bond was demonstrated by reacting $(ArS)_2$ with the isocyanide, CNC_4H_4–4Me, using $Pd(PPh_3)_4$ as a catalyst, to produce $(ArS)(C{=}NAr)_m(SAr)$, **215**.[515] A mechanistic study revealed that the complex $Pd(SAr)_2(CNAr)(PPh_3)$ is the likely resting state in the first step of the reaction. A similar catalytic process, involving the palladium-catalyzed reaction of diselenide $(ArSe)_2$ with isocyanide, CNC_4H_4–4Me, to give the compounds $(ArSe)(C{=}NAr)_m(SeAr)$ ($m = 2, 3$) was also reported.[516] The palladium azido complexes $Na_2[Pd(N_3)_4]$ and $Na_2[Pd_2\text{-}(\mu\text{-}N_3)_2(N_3)_4]$ react with aliphatic isocyanides to give metal–carbon-bonded tetrazolato complexes as described in Equation (44).[517] In further studies on insertion of isocyanides into arylated complexes, reaction of the complex **216** with mesityl isocyanide led to replacement of Cl and insertion of isocyanide to produce complex **217**, for example, Equation (45).[518]



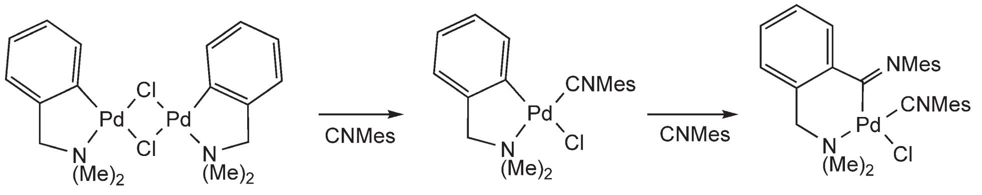
m = 1–9

215



(44)

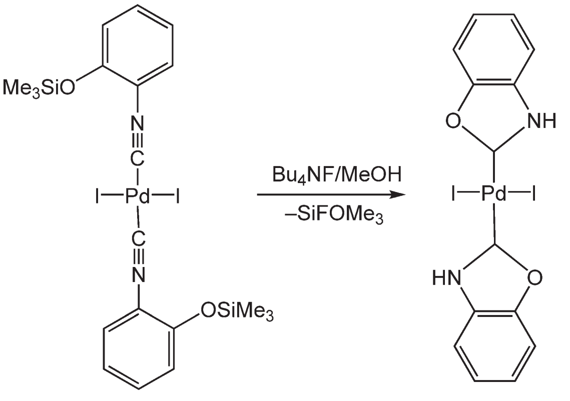
R = Bu^t, Cy, $(CH_2)_3CH_2Cl$, $CH_2CH{=}CH_2$



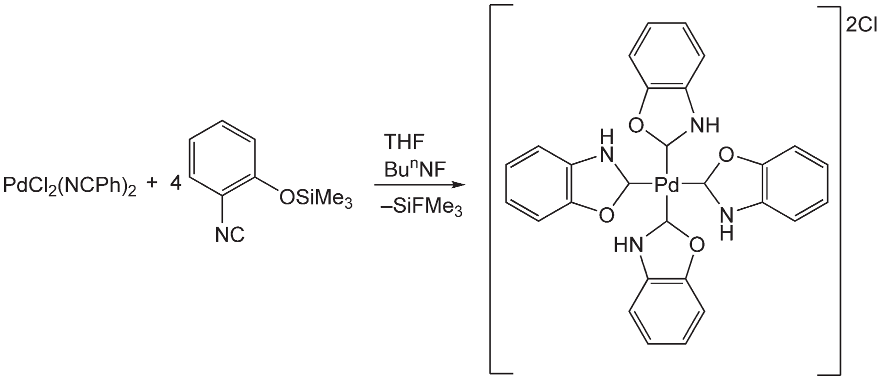
216 **217** (45)

8.04.3.2.2 *N*-heterocyclic and acyclic carbene formation

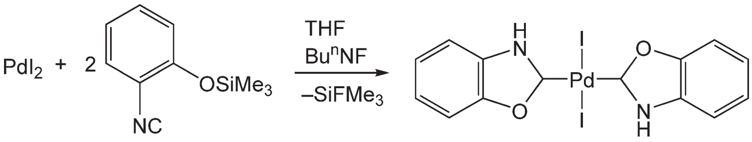
Reaction of 2-(trimethylsiloxy)phenylisocyanide with PdI_2 gives square-planar $PdI_2(CNR)_2$, **218**. Interestingly, cleavage of the Si–O bond, followed by ligand rearrangement, gives rise to the NHC complex **219** (Equation (46)).[519] 2-Trimethylsiloxyphenylisocyanide reacts with the complexes $MCl_2(NCPh)_2$ (M = Pd, Pt) and PdI_2 to form M(II) isocyanide complexes, which undergo hydrolysis of the Si–O bond leading to intramolecular attack at the isocyanide carbon, forming complexes of the NHC, 1,2-dihydrobenzoxazol-2-ylidene (Equations (47) and (48)).[520] Isocyanide complexes *cis*-$[MCl_2(CNC_6H_4\text{–}2\text{-}CH_2OSiMe_3)_2]$ (M = Pd, Pt) and *cis*-$[PdCl_2(CNC_6H_4\text{–}2\text{-}CH_2OSiMe_3)(PPh_3)]$ are converted into the corresponding NHC complexes, via an intramolecular insertion process, in the presence of catalytic amounts of F^- ions in MeOH.[521] 1,1-Ethylenedithiolato complexes of Pd and Pt, containing isocyanide ligands, react with diethylamine and with ammonia to form complexes of acylic carbenes (Equation (49)).[522] The unusual six-membered ring NHC complex, **220**, has been formed via the intramolecular reaction of 2-(azidomethyl)phenyl isocyanide ligand according to Equation (50).[523] A mechanism for the reaction is proposed.



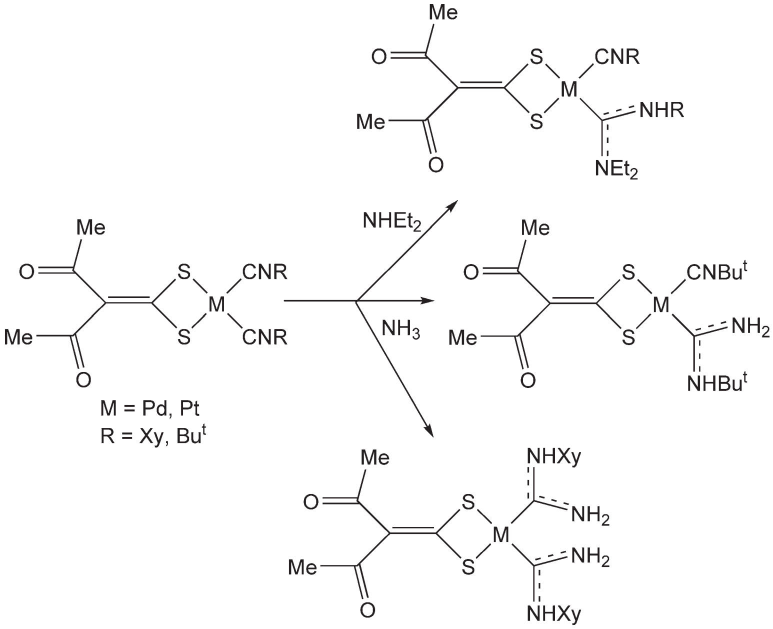
218 **219** (46)



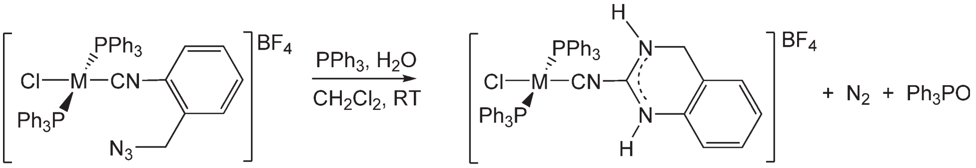
(47)



(48)



(49)



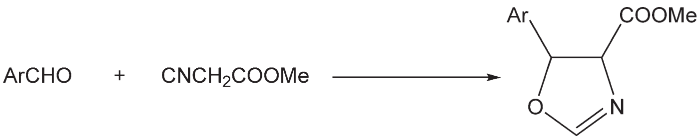
M = Pd, Pt

220

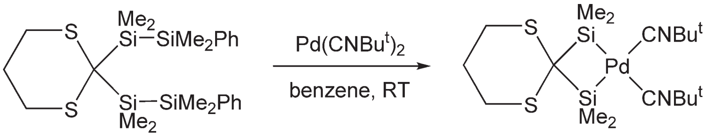
(50)

8.04.3.3 Isocyanide Complexes in Catalysis

Acetonitrile complexes of palladium have been shown to be effective catalysts for aldol-type condensation of methyl isocyanoacetate with benzaldehyde (Equation (51)).[524] Mono- and diisonitrile Pd complexes were prepared and, as the latter complex is an effective catalyst, it is possible that it is a catalytic intermediate. The complexes (*tert*-alkylNC)$_2$Pd react with Si–Si σ-bonds in bis(disilanyl)alkanes to give cyclic Pd(silyl)$_2$(*tert*-alkylNC)$_2$ complexes (Equation (52)), for example, **221**, which was isolated and an X-ray structure obtained.[525] Similarly, Pd(CNBu^t)$_2$ reacts with Ge–Si σ-bonds in bis(silylgermyl)dithiane to give the cyclic Pd(organogermyl)$_2$(*tert*-alkylNC)$_2$ complex.[526] Reaction of the bis(disilanyl)alkanes with phenylacetylene or electron-deficient olefins, in the presence of catalytic amounts of Pd(OAc)$_2$ and isocyanide ligand, led to bis-silylations of the unsaturated species giving cyclic organic silicon compounds in good yields.[525]



(51)



221

(52)

A co-polymer of *cis*-$PdCl_2(IPA)_2$ (IPA = 3-isocyanidopropylacrylate) with dimethylacrylamide and methylenebis-acrylamide (as cross-linking agent) was dispersed within an IOPN (interpenetrating organometallic polymer network) material and applied as a catalyst in the mild and selective hydrogenation of *p*-nitrotoluene to *p*-toluidine.[527] Ring-enlargement oligomerization of cyclic disilanes via Si–Si σ-bond metathesis, catalyzed by $Pd(CNBu^t)_2$, has been reported.[528] The palladium isonitrile complex, $PdCl_2(CNBu^t)_2$, has been applied as a catalyst for the bis(stannylation) of terminal alkynes with hexaalkylditin as the stannyl group transfer agent.[529] The reaction is atom-efficient, operates under mild conditions, and is functional group tolerant. An *in situ* catalyst system consisting of $Pd(OAc)_2$ and CNOct has been applied to the distannylation of a range of arynes with moderate efficiency.[530] It was assumed that the reaction is initiated by oxidative addition of the Sn–Sn bond of the distannane to a Pd(0) complex, and thus the complex $Pd(SnBu_3)_2(CNOct)_2$ was synthesized, from the reaction of $Pd(CNOct)_2$ with distannane, and found to be highly reactive for the insertion of benzyne to form the distannylated product.

8.04.3.4 Theoretical Studies

The ground and lowest energy triplet excited-state geometries of the model compounds $Pd_2Cl_2(CNMe)_4$, $Pd_2Cl_2\{CN(CH_2)_4NC\}_2Cl_2$, and $[Pd_3(CO)(PH_3)_6]^{2+}$ have been determined using DFT; computed ground-state structures were found to be in excellent agreement with X-ray data.[120]

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8.05
Palladium–Carbon σ-Bonded Complexes

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8.05.1 Introduction

In this chapter, the following aspects of the chemistry of organopalladium σ-bonded complexes is discussed; Pd(0)- and Pd(I)-hydrocarbyl complexes, Pd(II)-alkynyl, Pd(II)-alkenyl, Pd(II)-metallacyclic, and Pd(IV)-hydrocarbyl compounds. Reference to the corresponding chapters in COMC (1982)[1] and COMC (1995)[2] is assumed throughout. In some cases, selected references to the early literature and some of the late references in COMC (1995) have also been given. Examples of classes of complexes and reaction system are discussed.

The topics covered and references to the original literature appearing from 1994 to 2004 are intended to be comprehensive.

The subchapters pertaining to Pd(II)-alkyl and Pd(II)-aryl compounds have not been included in the printed text; these will appear in the electronic version only.

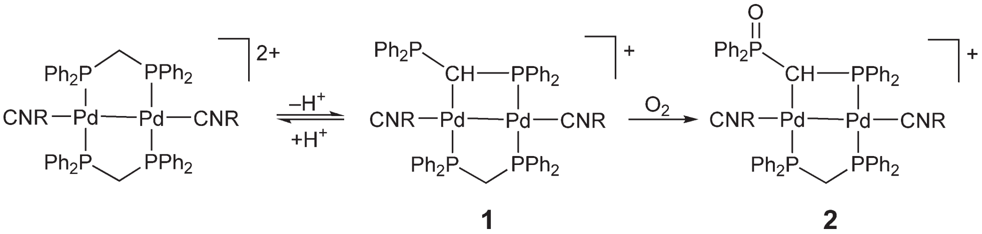
8.05.2 Hydrocarbylpalladium(0) and Palladium(I) Complexes

Only a small number of new hydrocarbyl compounds of palladium(0) or Pd(I) have been found in the literature of the period 1994–2005. Most of the known Pd(0) and Pd(I) compounds are halide, carbonyl, nitrile, isonitrile, carbene (including NHC), and suchlike compounds, or they contain only π-bonded ligands, which are treated in other chapters. Several of the Pd(0)- and Pd(I)-carbon σ-bonded compounds published were already known and have been collected in COMC (1995).

However, new facts and use of $[Pd^0Ph(PPh_3)_2]^-$[3] were reported and the existence of a similar thienyl derivative $[Pd^0(C_4H_3S)(PPh_3)_2]^-$ has been established electrochemically.[4] A catalytic cycle involving $[Pd^0Ar(PPh_3)_2]^-$ (Ar = Ph, thienyl) and five-coordinate $[Pd^{II}X(Ar)(Ar')(PPh_3)_2]^-$ accounting for the palladium-catalyzed homo-coupling of aryl halides has been proposed on the basis of these and previous results. The exact nature of the five-coordinate intermediate remains uncertain, as it could only be inferred from kinetic results. Finally, it was verified and concluded that hetero-coupling of aryl fragments only took place in batch procedures with stoichiometric amounts of a palladium complex.[4]

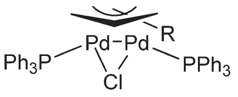
The palladium(0) carbide compounds Na_2PdC_2 and K_2PdC_2, and the X-ray crystal structure of Na_2PdC_2 have been reported.[5] The characteristic feature is that $[Pd(C_2)]^{2-}$ chains run along one of the crystallographic axes. These chains are separated by the alkali metal ions, which show interactions with three carbon atoms at short and with three at longer distances, resulting in a local distorted trigonal prism. In the chains, each palladium atom is linearly coordinated end-on by two $C_2{}^{2-}$ units and vice versa. The C–C distance is 0.1263(3) nm, which is distinctly longer than for a C–C triple bond, but it is 0.0026(3) nm shorter than that of the platinum analog. The elongation is consistent with the weak side-on interaction of the carbide with the main group ions.

Palladium(I) compounds generally occur as Pd–Pd bonded dimers; this topic has been reviewed for the subclass of their organopalladium compounds.[6] Most of these were already known, or contain π-bonded ligands. Palladation of the methylene of a dppm ligand in $[Pd_2(\mu\text{-dppm})_2(CNR)_2]^{2+}$ (R = 2,6-$Me_2C_6H_3$) led to the formation of **1**, which was oxidized to **2** (Scheme 1).[7] Several novel μ-η^3-allyl compounds **3** (analogs of known parent compounds) and their properties were studied. Theoretical calculations indicated that the strong back-donation in dipalladium complexes causes a remarkable change of the allyl coordination geometry compared to that in mononuclear compounds.[8,9]

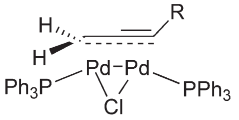


Scheme 1

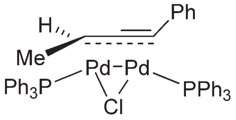
The new μ,η^3-allenyl compounds **4** have been obtained,[10–12] and the intermediacy of **5** in reactions involving propargyl–allenyl transpositions and racemization of chiral allenes have been discussed.[13] The $\mu,\eta^1{:}\eta^3$-ethynyl, μ-η^3-allyldipalladium complex **6** was obtained from [Pd(η^3-allyl)(ethynyl)(PPr^i_3)] and [Pd(PPr^i_3)].[14,15]



3: R = 2-OCH$_2$Ph, 2-Me, 2-Cl, 2-CN, 2-CO$_2$Me, 2-SO$_2$Ph



4: R = H, Ph, *o*-C$_6$H$_4$CH$_2$Cl



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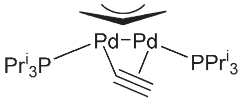

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8.05.3 Alkynylpalladium(II) Complexes

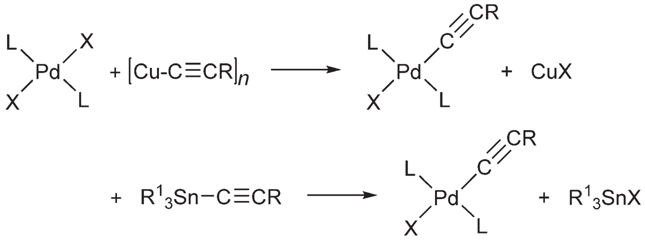
8.05.3.1 Synthesis of Alkynylpalladium(II) Complexes

The synthesis of alkynylpalladium(II) complexes usually proceeds through oxidative addition of a halo-alkyne or of a terminal alkyne to palladium(0) compounds, or by transmetallation employing main group alkynyl compounds and palladium(II) halide precursors. Especially, the dialkynylpalladium complexes are of much interest as molecular inorganic materials because of their remarkable phase behavior and nonlinear optical properties. Several accounts and reviews have appeared.[16–20]

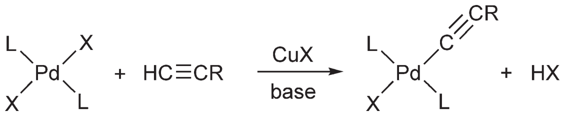
The synthesis of [PdX(C≡CPh)(PPh$_3$)$_2$] (X = Cl, I) by oxidative addition of XC≡CPh to [Pd(PPh$_3$)$_4$] has been revisited; X-ray crystal structures were obtained and the yields improved.[21] The side products *trans*-[PdX$_2$(PPh$_3$)$_2$] and PhC≡C–C≡CPh amount to about 10%, whereas previously, in the case of IC≡CPh, *trans*-[PdI$_2$(PPh$_3$)$_2$] and diphenylbutadiyne had been obtained exclusively.

The most frequently encountered and generally robust methods for the synthesis of alkynylpalladium(II) complexes are copper(I)-catalyzed dehydrohalogenation and transmetallation involving isolated organotin(IV) compounds or well-defined alkynylcopper(I) species (Scheme 2).

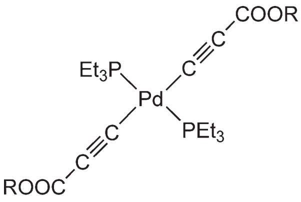
Defined alkynylcopper(I) reagents have been obtained and used for transfer of one or more alkynyl groups to palladium,[16,22] which led to good yields of pure **7–12**.[16,22] Phenylethynyl- and similar alkynylcopper(I) reagents prepared *in situ* from terminal alkynes, CuX and amines (generally NEt$_2$H) also provide alkynylpalladium(II) complexes with satisfactory results (Scheme 3), for instance in the synthesis of **13**,[23] **14** and **15**.[24] Palladium–copper catalyzed cross-coupling of terminal acetylenes with C(sp^2) halides dates back to Sonogashira,[25] who recently discussed recent advances and future challenges of this ubiquitous method to generate alkynylpalladium(II) complexes.[18,26] In order to obtain differential reactivity, trialkylsilyl–alkynyl compounds have also been used, for instance, for the synthesis of pallada-dehydrobenzo[19]annulene, relying on stannylation via fluoride followed by trimethyltin dimethylamide and transmetallation with [PdCl$_2$(PEt$_3$)$_2$] to give the product.[27]



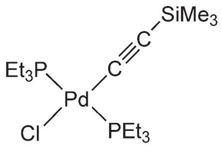
Scheme 2



Scheme 3



7: R = Me, Et, Bu^t



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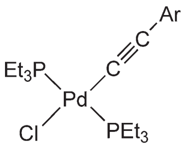
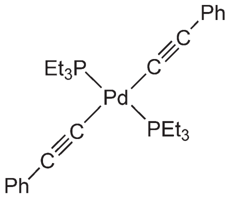
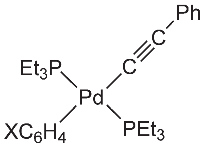


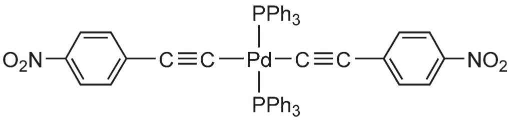
9: Ar = Ph
10: Ar = Tol



11: R = Me, Et, Bu^t



12: X = Me, F, OMe



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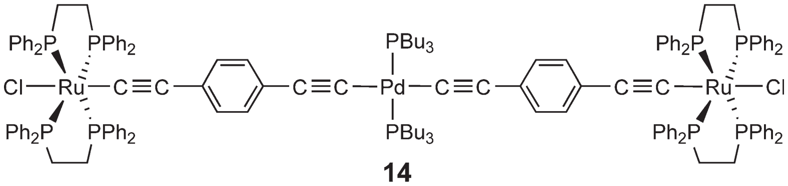

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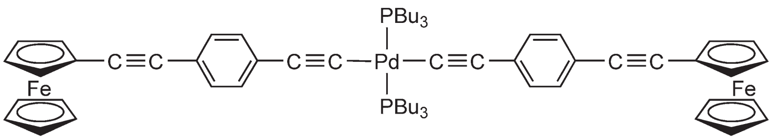
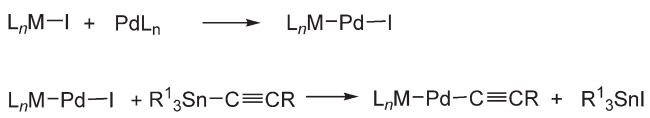


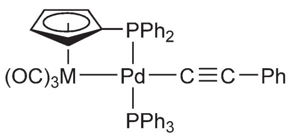
15

A special case of the transmetallation methodology using organotin(IV) reagents has been developed. This protocol takes advantage of the ready oxidative addition of transition metal iodides, especially of group 6, to zerovalent palladium species to give intermediate $[\mathrm{PdI(ML}_n)(\mathrm{PR}_3)_2]$ complexes that subsequently react with the organotin(IV) reagents (Scheme 4).[28,29] A range of heterodimetallic alkynylpalladium(II) complexes like 16 and 17 have been isolated and characterized.[28] This protocol has also been used to synthesize organometallic copolymers consisting of alkynylpalladium(II) units.[29] Mechanistic details of these reactions have recently been elucidated by NMR.[30–32]

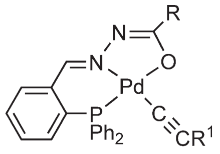


Scheme 4

Alkynylpalladium complexes $[Pd(C{\equiv}CPh)(\kappa^3\text{-}PP_2)][BF_4]$ and $[Pd(C{\equiv}CPh)(\kappa^3\text{-}PP_2)][OAc]$ with the tridentate phosphine ligand ($PPh_2 = PhP(CH_2CH_2PPh_2)_2$) were obtained from $[Pd(PP_2)][O_3SCF_3]_2$ and from $[Pd(OAc)_2]$ and PP_2 with phenyl acetylene, respectively.[33] Several stable alkynylpalladium complexes $[Pd(PNO)(C{\equiv}CR)]$ ($R = Ph$, Bu^t) **18–22** have been obtained. NMR and an X-ray crystal structure of **19** confirmed the κ^3 coordination of the PNO ligand and the position of the alkynyl group *trans* to the imine nitrogen.[34]



16: M = Mo
17: M = W



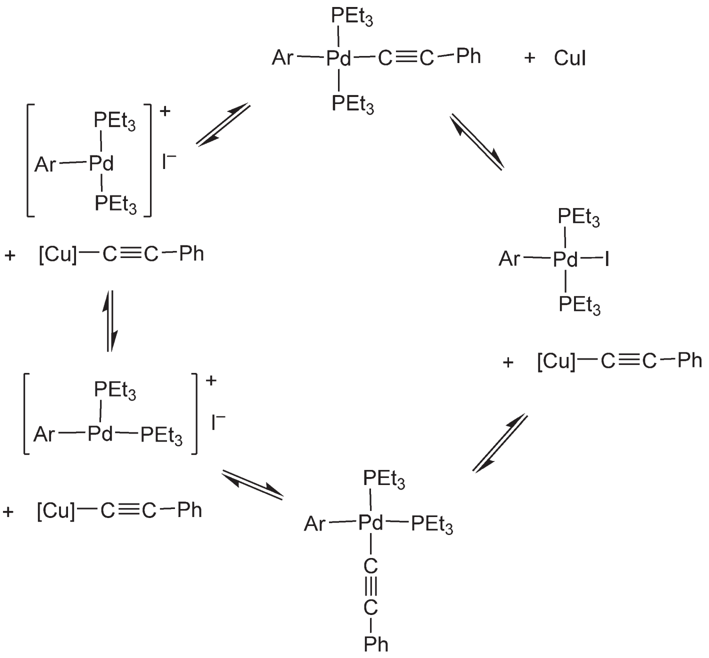
18: $R = Me$; $R^1 = Ph$
19: $R = Ph$; $R^1 = Bu^t$
20: $R = C_6H_4\text{-}Me$; $R^1 = Ph$
21: $R = C_6H_4\text{-}Br$; $R^1 = Ph$
22: $R = C_6H_4\text{-}NO_2$; $R^1 = Ph$

A number of palladacyclic compounds with an η^1-metallacarbyne have been reported. Theoretical calculations showed that the bonding is best described by Lewis acid–Lewis base interaction together with a strong electrostatic component.[35]

8.05.3.2 Reactions and Mechanism Involving Alkynylpalladium(II) Complexes

Yamamoto *et al.* have studied the mechanism of the reactions of group-10 alkynyl complexes in detail. They reported that alkynyl transfer from $[PdR(C{\equiv}CPh)(PEt_3)_2]$ to $[PtI(R')(PEt_3)_2]$ was enhanced to a large extent by addition of CuI, indicating reversible ligand transfer between Pd(II) and Cu(I) complexes.[36] Such transfers have also been observed between dialkynylpalladium and diodoplatinum species, leading to comproportionation of the Pd complexes or to ligand transfer from Pd to Pt, depending on the nature of the alkynyl ligand and the reaction conditions.[37] Two mechanisms are proposed to explain the formation of coupling products: (i) removal of a phosphine from Pd by CuX, which induces dissociative reductive elimination of alkynyl and aryl groups from $[Pd(C{\equiv}CPh)Ar(PEt_3)]$ and (ii) alkynyl ligand transfer between Pd and Cu to give a mixture of *trans*- and *cis*-$[Pd(C{\equiv}CPh)Ar(PEt_3)_2]$ (Scheme 5) where the *cis* complex seems to undergo rapid reductive elimination of the product.

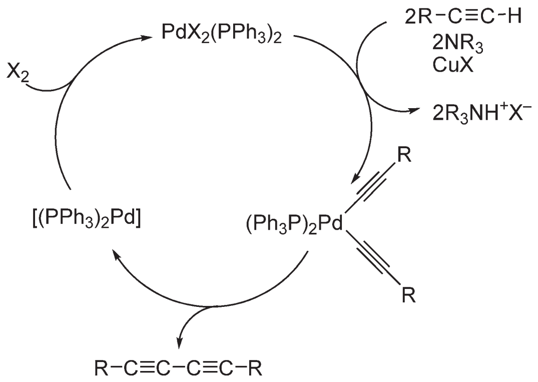
The standard Sonogashira–Hagihara protocol[25] for the palladium–copper-catalyzed cross-coupling of aryl and vinyl halides with terminal alkynes is very reliable for the synthesis of a host of conjugated acetylenic compounds. The relatively high temperature causes side-reactions and the catalyst loading is somewhat high. Novel variants that work at room temperature and allow the use of aryl bromides instead of iodides have been devised.[38] The active catalyst has been considered to be metallic Pd^0, $[Pd^0(PR_3)_2]$ or anionic $[PdX(PR_3)_2]^-$. It has been shown that, in the case of $P(o\text{-}C_6H_4Me)_3$ and large phosphines, palladium-monophosphine species $[Pd(PR_3)]$ are the active catalysts.[39] A very active and air-stable pre-catalyst *trans*-$[PdCl_2(PBu^t{}_3)_2]$ has been claimed.[18] Other active precatalysts are monomeric and dimeric palladacycles (see Section 8.05.4) that give high turnover numbers in the absence of CuI in NEt_3.[40,41] Addition of bases dramatically slows down the reaction. The orthopalladated dimer $[Pd(OAc)(CH_2\text{-}o\text{-}C_6H_4P(o\text{-}C_6H_4Me)_2)]_2$ is in fact closely related to the known $[Pd^0P(o\text{-}C_6H_4Me)_3]$ system;[39] the dimer constitutes merely a thermally stable reservoir for the active species.



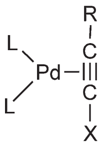
Scheme 5

Intermolecular palladium-catalyzed homo- and hetero-coupling of terminal alkynes is well documented, but rigorous mechanistic investigations of this oxidative coupling have not been reported. The proposed mechanisms revolve about (isomerization of) intermediate dialkynylpalladium(II) complexes and subsequent reductive elimination.[17,42] The catalytic cycle in the presence of iodine is shown in Scheme 6.

The mechanism of the palladium-catalyzed non-oxidative heterocoupling of alkynes was examined recently.[43] NMR studies revealed oxidative addition of haloalkynes to $[\mathrm{Pd}^0\mathrm{L}_2]$ via a $[\mathrm{Pd}(\eta^2\text{-}\mathrm{XC{\equiv}CPh})\mathrm{L}_2]$ complex **23**. The observed drastic acceleration of the oxidative addition by added CuX and the *cis*-configuration of the resulting $[\mathrm{PdX}(\mathrm{C{\equiv}CPh})\mathrm{L}_2]$ **24** led to the suggestion of intermediate heterobimetallic complexes **25**. Intermediates underway to a dialkynylpalladium species from **24** were not supported by NMR; it could proceed through transmetallation by alkynylcopper(I) species, or via complex **26**.[43] An alternative mechanism involves transmetallation between two alkynylpalladium complexes *cis*-$[\mathrm{PdH}(\mathrm{C{\equiv}CR}^1)\mathrm{L}_2]$ and *cis*-$[\mathrm{PdX}(\mathrm{C{\equiv}CR}^2)\mathrm{L}_2]$, to provide the dialkynylpalladium complex $[\mathrm{Pd}(\mathrm{C{\equiv}CR}^1)(\mathrm{C{\equiv}CR}^2)\mathrm{L}_2]$ from which reductive elimination takes place.[44]



Scheme 6



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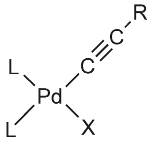

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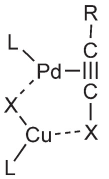

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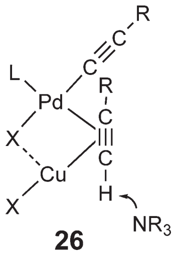


26

Intermolecular addition of terminal alkynes to alkynoates has resulted in some unusual regioselectivity, up to exclusive formation of the C–C bond at the α-carbon.[45] Intramolecular dimerization of a sterically constrained trialkyne proceeding through alkynylpalladium(II) and yn-enylpalladium(II) was reported.[46] Interestingly, one of the tolyl groups of the ancillary phosphine ligand was transferred to the remaining alkynyl moiety.

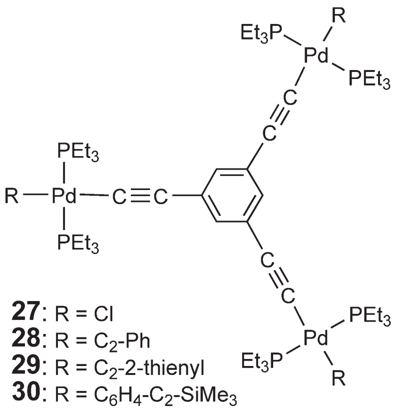
The mechanisms of the Stille reaction have been reviewed in the broad and comprehensive sense, including those involving alkynyl compounds.[47] Stille-type couplings of alkynyltin(IV) and other organotin(IV) reagents with alkynes and similar reactions with organic halides and triflates have been reviewed.[48] Coupling reactions of terminal alkynes leading to diynes have been extended to couplings of propargylic substrates with other alkynes in water using water-soluble [Pd(OAc)$_2$(Tppts)].[44]

Insertion reactions of alkynylpalladium complexes with carbon monoxide and isonitriles have been reported. With CO, simple insertions take place, but with the parent acetylene in the presence of oxygen, oxygenates are formed and with alcohols alkynoates result.[49] Insertion of isonitriles in [L$_2$ClPdC$\equiv$CPdClL$_2$] (L = PR$_3$) leads to known single and double insertion products and at higher temperatures to living polymerization to give dipallada-polyisonitrile oligomers and polymers.[50–52] An X-ray structure determination of [(Et$_3$P)$_2$(PhNC)PdC$\equiv$CPdCl(CNPh)(PEt$_3$)$_2$] was carried out.[51] This polymerization of isonitriles has been extended to include chiral Ar*NC (Ar* = C$_6$H$_4$CO$_2$-menthyl), which gave substrate-induced “screw-sense-selective” polymerization to give a preferred handedness to the helical enantiomorphism of the polymer.[53,54] Palladium(II) acetylides [Pd(C$\equiv$CR)$_2$L$_2$] were also used as initiators for polymerization of dimethylaminoethyl methacrylate (R = Ph, CH$_2$OH; L = PPh$_3$, PBu$^n{}_3$)[55] and for polymerization of propargyl alcohol (R = H, Ph, CH$_2$OH, C$_6$H$_4$C$\equiv$CH; C$\equiv$CCH$_2$OCOCH$_3$, C$\equiv$CCH$_2$OCOPh, C$\equiv$CCH$_2$OCO-C$_6$H$_4$OH; L = PPh$_3$).[56–59]

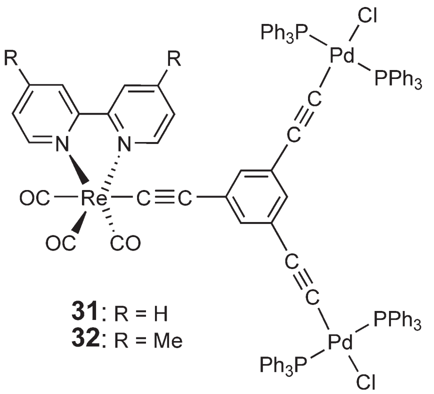
Other reactions that presumably involve alkynylpalladium complexes are insertions of alkynes into the Si–Si bond of 3,4-benzo-1,2-disilacyclobut-3-ene to give 5,6-benzo-1,4-disilahexa-2,5-dienes,[60] and activation of unstrained C–C bonds by β-alkynyl elimination in the palladium-catalyzed reaction of propargylic alcohols with ethyl acrylate to give enynes.[61]

8.05.3.3 Metallodendrimers and Polymers Involving Alkynylpalladium Complexes

Cascade procedures and Sonogashira conditions have been used to obtain dendrimer building blocks like **27–30**[62,63] and metallodendrimers. Luminescent heterodimetallic rhenium-alkynylpalladium complexes **31** and **32** were obtained through the use of *in situ* prepared alkynylsilver(I) species that reacted with common palladium precursors with CuCl/Et$_3$N as the co-catalyst. Complex **31** was authenticated by an X-ray crystal structure.[64]



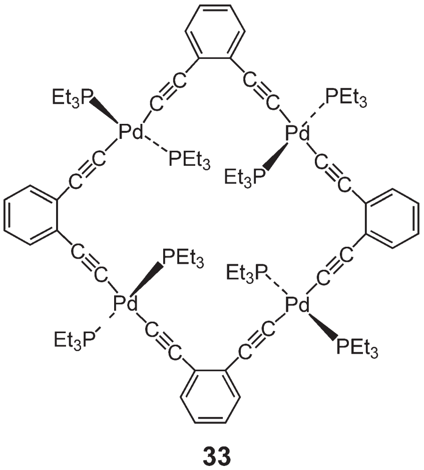
27: R = Cl
28: R = C$_2$-Ph
29: R = C$_2$-2-thienyl
30: R = C$_6$H$_4$-C$_2$-SiMe$_3$



31: R = H
32: R = Me

The synthesis of alkynylpalladium complexes with terminal alkynes requires a large excess of the alkyne to prevent further reaction, leading to oligomers or polymers. After the synthesis of the first polymers in 1975,[65] many have been developed based on dehydrohalogenation, oxidative coupling, and alkynyl ligand exchange. These methods allow the easy control of the degree of polymerization, tailoring the electronic properties of the polymer by the attachment of various end groups on the monomers, simple access to heterodimetallic systems, and variation of the distance between metal centers.[19]

Also, macrocyclic organopalladium complexes are accessible by using the methodologies mentioned above. An esthetically appealing tetranuclear palladium acetylide **33** has been synthesized in one step from *o*-diethynylbenzene and an equimolar amount of $[PdCl_2(PEt_3)_2]$ in the presence of CuCl in diethylamine.[66] The monoaryl dipalladium complexes **34** and **35** were obtained when 2.5 equiv. of $[PdCl_2(PR_3)_2]$ were employed. X-ray crystal structures of **34** and **35** were determined, showing that in **34** the $Pd(PEt_3)_2$ moieties point alternatingly in and out of the macrocycle, leaving little space inside. Hence, the 1 : 1 reaction with $[PdCl_2(PBu^n{}_3)_2]$ gave a mixture of linear oligomers instead, due to the larger steric bulk of the phosphine.



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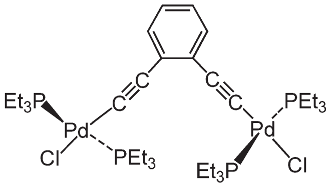

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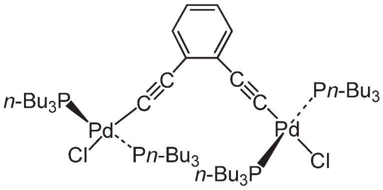
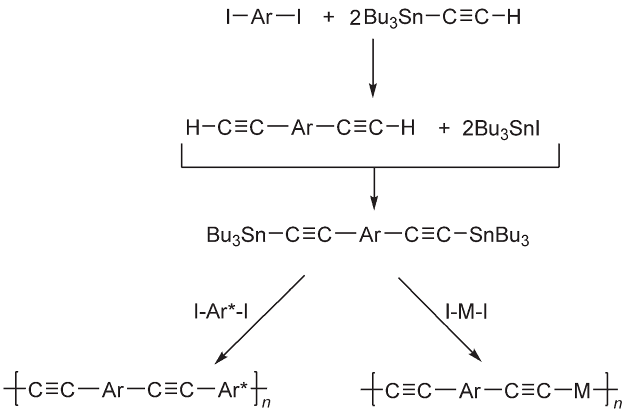


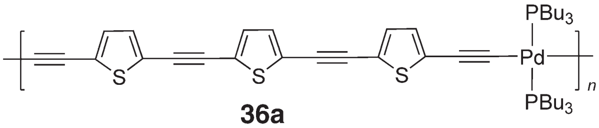
35

Novel routes to oligomeric alkynylpalladium complexes have also been devised according to Scheme 7.[67] In this instance, the procedure has been particularly followed for the synthesis of oligomers like **36a** based on diethynylthiophene. The novel route gives less of the bimetallic byproduct **36b** compared to the dehydrohalogenation

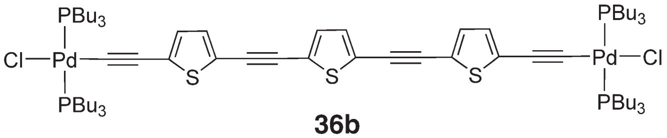


Scheme 7

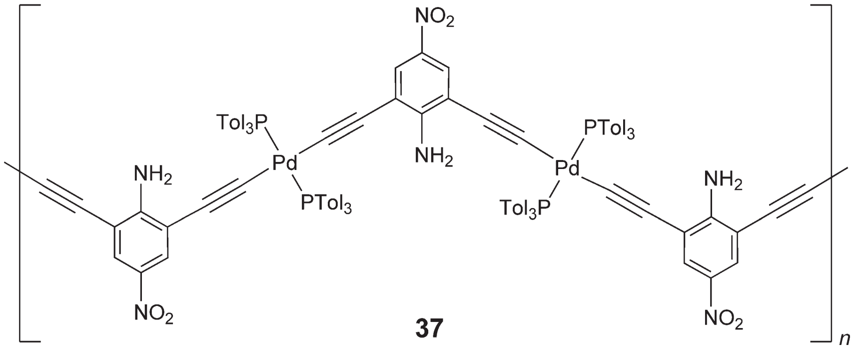
methodology and molar weights are somewhat higher, between 3 and 4×10^3. Traditional methods have resulted in polymers **37** that adopt a helical conformation.[68]



36a



36b

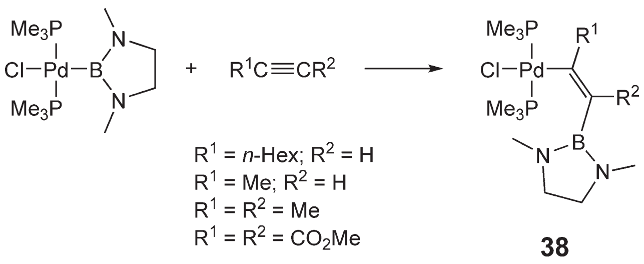


37

8.05.4 Alkenylpalladium(II) Complexes

8.05.4.1 Synthesis of Alkenylpalladium(II) Complexes

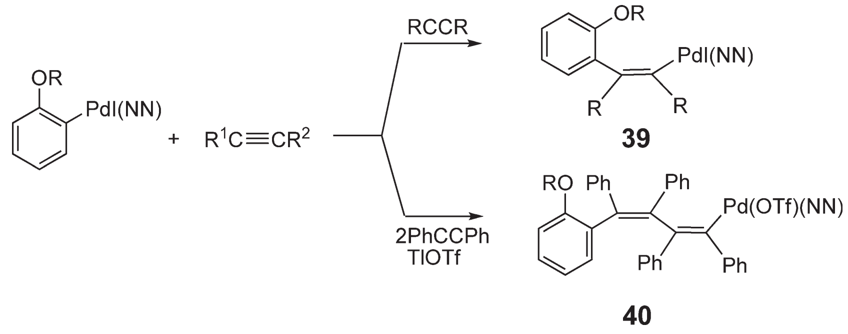
Insertion reactions of alkynes into palladium–element bonds is an important route to palladium(II)–alkenyl complexes. Insertion of alkynes into palladium–boron bonds arising from oxidative addition of boron halides gives complexes **38** (Scheme 8). An X-ray structure was reported for $R^1 = R^2 = CO_2Bu^t$.[69] Alkenyl- and dienylpalladium(II) compounds **39** and **40** (Scheme 9) have been obtained in good yields from arylpalladium complexes by mono- and di-insertion, respectively, and X-ray crystal structures of **39** were determined.[70] The mechanism of this type of reactions and especially the unusual *Z*/*E*-isomerization of the Pd-{C(CO$_2$R) = CPhH} moiety of the inserted complexes has been the subject of investigation.[71] Insertions into Pd–C bonds of palladoles [Pd(CE = CE-CE = CE)R(NN)] by addition of organic halides RX lead to palladium(II)–dienyl complexes [PdX(CE = CE-CE = CE-R)(NN)] (E = CO$_2$Me; NN = bpy, phen, bian, bip; RX = MeI, PhCH$_2$Br, PhI).[72] These compounds are intermediates in three-component cross-coupling reactions.[73] Similar compounds were obtained as intermediates in three-component carbostannylation[74] and the subject has also gained attention for C–S bond formation.[75]



R^1 = *n*-Hex; R^2 = H
R^1 = Me; R^2 = H
$R^1 = R^2$ = Me
$R^1 = R^2 = CO_2Me$

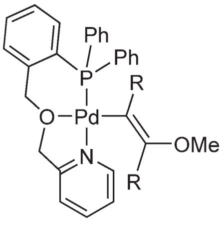
38

Scheme 8



Scheme 9

Insertion of alkynes into palladium–oxygen bonds of incipient palladium–methoxides from $[\mathrm{PdCl_2(L_2)}]$ ($\mathrm{L_2}$ = *o*-$\mathrm{Ph_2PC_6H_4CH_2O(CH_2)}_n$-2-$\mathrm{C_5H_4N}$-*P*,*N* = PON) has been reported to provide [Pd{η^1-(*E*)-PhC=C(OMe)Ph}-(κ^3-PON)] 41 with an X-ray structure for R = $\mathrm{CO_2Et}$.[76] Electrochemical activation of an alkyne coordinated to a $\mathrm{Pd(P_2N_2)}$ fragment has resulted in [Pd{(*E*)-C($\mathrm{CO_2Me}$)=CH($\mathrm{CO_2Me}$)}(PPN)] of which an X-ray structure is given.[77] The reduction seems to be localized at the alkyne, whereupon the generated Pd–C=C$^-$ species deprotonates a methylene group of the $\mathrm{P_2N_2}$ ligand. The alkyne to alkenyl conversion is accompanied by its movement from in-plane to perpendicular to the coordination plane, thereby increasing the contribution of the metal to the HOMO, which is possibly the driving force.



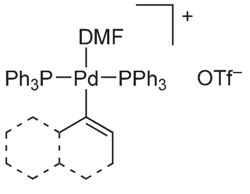
41

Nucleophilic attack of coordinated alkynes is another synthetic approach toward alkenylpalladium compounds. This step plays a role in several palladium-catalyzed addition reactions. The palladium-catalyzed cyclization of 6-aminohex-1-yne gives rise to putative ammonium–alkenylpalladium(II) complexes.[78]

The transmetallation of oxidative addition products of alkenyl halides and zerovalent palladium species by organotin reagents is an important step in Stille type reactions and its mechanism depends on many variables. A recent review on this topic accounts for transmetallation of alkenylpalladium(II) species.[47] The involvement of 14-electron T-shaped species [PdX(R)(L)] in Stille reactions involving alkenyl and other substrates has been refuted as unrealistic. Instead, associative ligand substitution at palladium is advocated, which has been corroborated by full and quantitative evaluation of kinetic data as well as MO considerations.[79]

The need of halides, especially chloride ions, in the Stille coupling of alkenyl triflates with organostannanes has been underscored recently by a mechanistic study, including kinetics, of the oxidative addition of alkenyl triflates and bromides to $[\mathrm{Pd(PPh_3)_4}]$ in DMF.[80] Several complexes *trans*-[Pd(η^1-alkenyl)$\mathrm{(PPh_3)_2}$(DMF)][OTf] 42 (alkenyl = hexen-2-yl, 4-Bu$^\mathrm{t}$-cylohexenyl, benzo[5,6]-cyclohexenyl) have been characterized by NMR and ESMS. Evidence for the generation of vinylphosphonium salts from $\mathrm{PPh_3}$ and alkenyl triflates has been obtained. The study revealed that the positive effect of chloride ions on catalytic Stille reactions does not originate in the oxidative addition, but rather from bypassing the decomposition of [Pd(η^1-alkenyl)$\mathrm{(PPh_3)_2}$(DMF)]$^+$ to vinylphosphonium salts by formation of neutral complexes [PdCl(η^1-alkenyl)$\mathrm{(PPh_3)_2}$].[80–82]

Oxidative addition of allenyl and propargyl halides $\mathrm{R^1R^2C{=}C{=}CHX}$ or $\mathrm{R^1R^2CH{-}C{\equiv}CH}$ to $[\mathrm{Pd(PPh_3)_4}]$ in THF has been extended to give *trans*-[PdX(η^1–CH=C=C$\mathrm{R^1R^2}$)$\mathrm{(PPh_3)_2}$] 43. An unusual thermal *trans–cis* isomerization has been observed, which proceeds diastereoselectively when the steric demands of $\mathrm{R^1}$ and $\mathrm{R^2}$ are large and different, for example, *cis*-[PdBr(η^1–CH=C=CBu$^\mathrm{t}$Me)$\mathrm{(PPh_3)_2}$].[83] Racemization of enantiomerically enriched *trans*-[PdCl{η^1–C(Ph)=C=C(R)H}$\mathrm{(PPh_3)_2}$] is slow in benzene or chloroform and is caused by inadvertent oxygen that leads to decomposition to Ph_3PO, organic material, and $[Pd(PPh_3)_n]$; the latter with 43 forms a π-allenyl-dipalladium complex like 3, which does not racemize itself, but rather via a non-chiral μ-η¹:η¹-vinylpalladium intermediate.[13]



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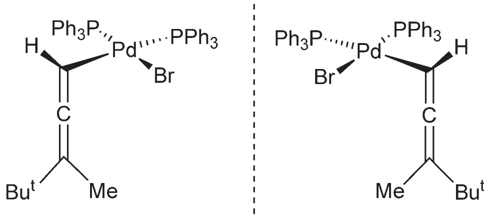


(*M*,*M*) *cis*-**43** (*P*,*P*)

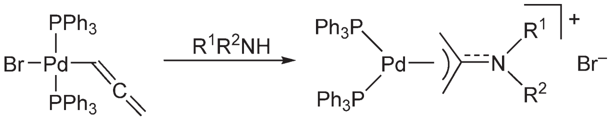
8.05.4.2 Reactions Involving Intermediate Alkenylpalladium(II) Complexes

Palladium-catalyzed hydroboration, haloboration, and similar reactions involving addition of organoboron compounds to alkynes have been reviewed.[84] Alkylborane addition to alkynes followed by intra- or intermolecular cross-coupling with a vinyl halide or triflates according to the Suzuki–Miyaura protocol constitutes a very powerful synthetic route for the generation of two carbon–carbon bonds in cascade. This subject and its applications in synthesis have been reviewed.[85]

Catalytic carbopalladation is a ubiquitous process and alkynes are viable substrates. Alkenyl tellurides couple efficiently with alkynes with retention of the double bond geometry. Relatively large amounts of palladium catalyst are required.[86] Oxidative dimerization of monoterpenes has been assumed to involve alkenylpalladium(II) intermediates.[87] Alkenylpalladium(II) and di(alkenyl)palladium(IV) complexes have been put forward as intermediates in a similar reaction of halogenoterpenes.[88] The subject has been reviewed concerning the formation of heterocycles by intramolecular cyclization of intermediate alkenylpalladium intermediates.[89]

Regioselective addition of ammonia, primary or secondary amines and aniline to neutral η¹-allenylpalladium(II) complexes *trans*-$[PdX(\eta^1\text{–}CH{=}C{=}CH_2)(PPh_3)_2]$ gives the respective η³-azatrimethylenemethane complexes *trans*-$[PdX\{\eta^3\text{-}CH_2C(NR^1R^2)CH_2\}(PPh_3)_2)]X$, 44 (Scheme 10). These η³-*N*-TMM palladium complexes have structural characteristics between those of η³-aminoallyl and metallacyclobutanimine complexes, as evidenced by several X-ray crystal structures.[90]

Insertions of alkynes into palladium–hydride complexes have been reported to take place as part of catalytic cycles, resulting in circumstantial yet credible evidence for the occurrence of alkenylpalladium complexes. The first example of palladium-catalyzed hydroarylation of alkynes with organoboronic acids $B(OH)_2R$ has been given. The mechanistic interpretation based on labeling studies involves hydropalladation of the alkyne to give an intermediate alkenylpalladium(II) species that reacts with the organoboronic acid (Scheme 11).[91] Similar direct coupling reactions



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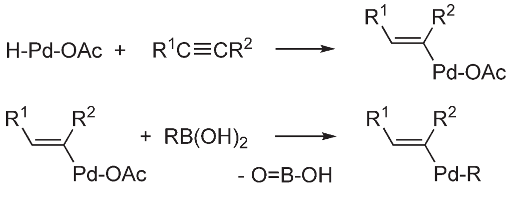
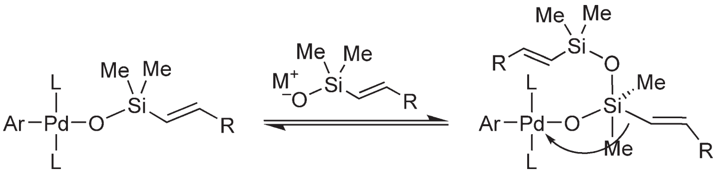
Scheme 10



Scheme 11



45 **46**

Scheme 12

between propargyl alcohols and arylboronic acids have been effected and these are deemed to undergo activation of the OH group by the boronic acid and formation of an η^1-allenylpalladium(II) complex by S_N2'; reaction by $[Pd^0(PPh_3)_n]$, which is transmetallated by the arylboronic acid followed by reductive elimination.[92] Other reactions with propargyl formates and carbonate involve hydrogenolysis of η^1-allenylpalladium(II) complexes.[93] The amount of palladium is very high (10%), suggesting that most of the palladium is in an inactive state.

Addition of element–element compounds to alkynes has been reviewed.[94] Other insertions of alkynes into palladium–hydride bonds have been identified in Drent's palladium-catalyzed alkoxycarbonylation of alkynes; palladium(II)–alkenyl complexes have been invoked to account for the observed H/D exchange when conducted in CH_3OD and to identify the pathway (i.e., through migratory insertion into Pd–H and formation of acyl species by carbonylation) of the overall reaction.[95]

Alkoxycarbonylation of alkenyl halides has been studied and compared to that of iodobenzene. In the case of methoxycarbonylation of PhCH=CHBr, methyl cinnamate was the exclusive product. Model reactions suggest that the high rate of alcoholysis of *trans*-$[PdBr\{(E)\text{-}CH{=}CHPh\}(PPh_3)_2]$ is responsible for the lack of double carbonylation, even at elevated pressure.[96]

Oxidative addition of alkenyl halides, triflates, and other esters to zerovalent palladium compounds has been long known as a viable route to palladium(II)–alkenyl complexes. Stereospecific coupling reactions involving mono- and (*E*)- or (*Z*)-dihalo-alkenes with palladium–copper catalysis under modified Sonogashira conditions are quite versatile and useful. These proceed through oxidative addition of the alkenyl halide via palladium(II) alkenyl complexes, followed by coupling with a nucleophile (usually an alkynylcopper reagent obtained *in situ* with co-catalytic copper(I) from terminal alkynes in the presence of, in this case, a base like piperidine instead of diethylamine).[97]

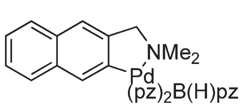
The mechanism of cross-coupling of alkenylsilanolates with 2-iodothiophene has been elucidated by kinetic measurements and involves interesting key intermediates (Scheme 12). After formation of a siloxypalladium(II)aryl complex **45** by transmetallation with $[PdX(Ar)L_n]$, a second silanolate acts as a nucleophilic activator and generates a pentacoordinate siliconate **46**, from which transmetallation to Pd occurs. This generates the alkenylpalladium(II) complex that reductively eliminates the product.[98]

8.05.5 Cyclometallated Palladium(II) Complexes

The field of palladacycles has received much attention since 1994 and has grown exponentially since then. The attractiveness of palladacycles lies often in their ease of synthesis as well as their many applications, that is, in materials science (liquid crystals, photoluminescent materials for example), bioorganometallic chemistry, enantioselective synthesis, ligand resolution, and homogeneous catalysis. A large number of reviews,[99–115] accounts,[116] concepts,[117–119] highlights,[120] and perspectives[121,122] have appeared in this time span.

8.05.5.1 Palladacycles Derived from Amines or Pyridines

The cyclopalladation of 2-[(dimethylamino)aminomethyl]-substituted naphthalenes was investigated.[123,124] Van Koten *et al.* found for 2-[(dimethylamino)aminomethyl]naphthalene that direct palladation occurred selectively at the 3-position versus the 1-position. This was confirmed by the crystal structure of **47**. Acetonyl bridged palladium(II) complexes such as **48** and **49** were obtained from the reaction of the palladium-hydroxo complex $[\{(o\text{-}C_6H_4CH_2NMe_2)Pd\}_2(\mu\text{-}OH)_2]$ with acetone.[125]



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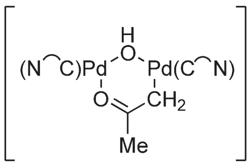

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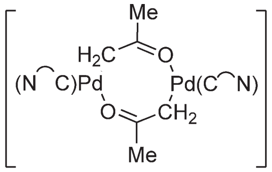

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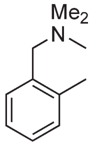
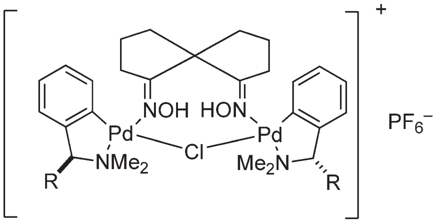


C⌒N

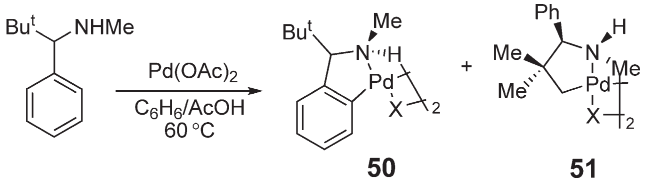
Cyclopalladation of the racemic secondary amine $C_6H_4NHBu^tMe$ with $Pd(OAc)_2$ in a mixture of benzene and glacial AcOH on heating gives a 3 : 1 mixture of regioisomeric complexes **50 and 51** (Scheme 13).[126] Addition of excess acetic acid to this mixture led to the formation of a cyclopalladated imine complex. A related study with regard to the competition between *sp*^{3} and *sp*^{2} C–H bonds in cyclopalladation of *N*-$C_6H_4NHBu^tMe$ was published in 2000.[127]

Cyclopalladated $[Pd(\mu\text{-}Cl)(o\text{-}C_6H_4CH(R)NMe_2)]_2$ (R = H, Me) was reacted with (±)1,6-bisoximo[4,4]nonane in the presence of KPF_6 to give monocationic dimeric complexes **52 and 53** of which the crystal structures were determined.[128] A palladacycle precursor **54** was reacted with a chelating (carboxy)phosphanoalkyl ligand (Scheme 14) giving only one diastereomer, **55**, as evidenced by NMR.[129]



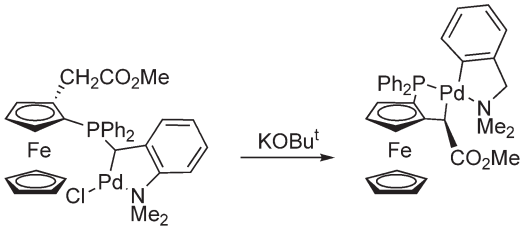
52: R = H
53: R = Me

Heteroleptic heterodinuclear *cis*-$Pd^{II}(C^\wedge N)_2$ complexes such as **56** are obtained from the reaction of *ortho*-mercurated 2-[(η^6-phenyl)tricarbonylchromium]pyridine with μ-chloro cyclopalladated aromatic compounds in the presence of large amounts of $[NMe_4]Cl$.[130,131] The products are valuable precursors of planar chiral cyclopalladated Cr(η^6-arene)$(CO)_3$ complexes, for example, **57**. A series of *ortho*-palladated binuclear Cr(η^6-arene)$(CO)_3$ complexes was reported earlier.[132]



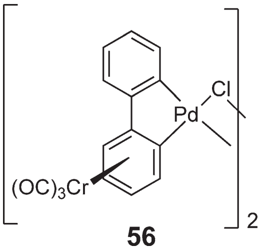
50 **51**

Scheme 13



54 **55**

Scheme 14



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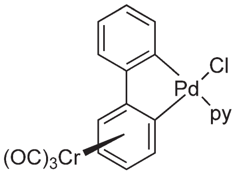


57

The complex $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}C^2,N)]_2$ reacts with diphosphines (dppf, dpmf, dppm, dppe, and dppp) to give $[Pd(C_6H_4CH_2NMe_2\text{-}C^2,N)(\mu\text{-diphosphine})]_2$.[133] The reaction of the dppm complex with $NaPF_6$ gave a six-membered ring complex, which upon addition of $[NEt_3(CH_2Ph)]Cl$ regenerated the original complex.

Benzylamines with electron-withdrawing substituents can be orthometallated and (2-phenyl)ethylamine can be orthometallated to form six-membered rings.[134] The reaction mechanisms going via dimeric species have been evaluated. A series of benzylamines gave chloro-bridged cyclopalladated dimers with Li_2PdCl_4.[135] The reactivities of these complexes with a series of other ligands, that is, 4,4′-bipyridine, 1,1,2,2-tetraacetylethane, α,α,α′,α′-tetraacetyl-*p*-xylene, *N,N*′-bis(2-hydroxybenzylidene)-1,4-diaminobutane, *N,N*′-bis(2-hydroxy-3-t-butyl-5-methylbenzylidene)-1,4-diaminobutadiene and 2-hydroxybenzalazine) were studied, giving cyclopalladated binuclear products.

A facile synthesis of chiral cyclopalladated compounds, that is, the methoxy-palladation of allylamines, has been reported via the reaction of *N,N*-dimethylamino-3-but-1-ene and *N,N*-dimethylamino-1-cyclohexene-2-ene with Li_2PdCl_4 in MeOH.[136]

Secondary benzylamines have been cyclopalladated and reactions of the chloro-bridged complexes with various ligands such as PPh_3, acac, 1,1,2,2-tetraacetylethane, 1-phenylazo-2-naphthol, and 2-hydroxy-3-*t*-butyl-5-methylbenzylidene-*p*-chloroaniline have been carried out.[137] Secondary and primary benzylamines were cyclopalladated in benzene using $Pd(OAc)_2$.[138] Bridge-splitting reactions with, for example, 3,5-lutidine, PPh_3, and thallium acetylacetonate have been carried out.

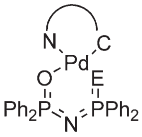
The carbonylation of $[Pd(8\text{-mq})(OCMe_2)_x]ClO_4$ (8-mq = 8-quinolylmethyl-*C,N*) has been carried out giving $[Pd(OClO_3)(8\text{-mq})(CO)]$.[139] This was reacted with anionic or neutral nucleophiles resulting in the displacement of $OClO_3^-$ group and the formation of the corresponding [Pd(8-mq)L(CO)] complexes. The structure of $[Pd(8\text{-mq})(SPPh_3)(CO)]$ is reported.

Ligands $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S or Se) react with NC-palladacycles giving complexes of the type **58**.[140] A study comprising NC-palladacyclic complexes with ligands such as $Ph_2PNHP(O)Ph_2$, $[Ph_2PNP(O)Ph_2]^-$, or $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S or Se) was published in 2000.[141]

Mechanistic studies in Stille coupling led to the synthesis of **59**.[142,143]

A series of *cis*-configured homoleptic and heteroleptic palladium(II) complexes bearing aromatic C,N ligands have been prepared, $Pd(C,N)_2$ with (C,N) being benzo(h)quinoline, 2-phenylpyridine, 2-(2′-benzothienyl)pyridine, 2-(2′-thienyl)quinoline and 2-(2′-thienyl)pyridine, Pd(C,N)(C′,N′), $Pd(bhq)_2$, $Pd(phpy)_2$, $Pd(bthpy)_2$, $Pd(thpy)_2$, Pd(thpy)(phpy), Pd(thpy)(bhq), Pd(bhq)(phpy).[144]

A convenient facile method for heterobimetallic chlorobridged complexes has been developed giving **60** from a binuclear complex and and CN-palladacycle.[145]



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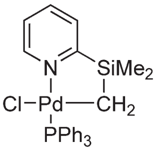

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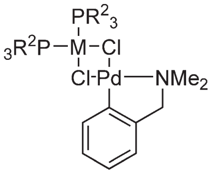


60

Unusual liquid crystalline behavior was observed with a π-stacked *ortho*-palladated bipyridine complex **61**.[146] In the DSC thermogram two sharp peaks were observed at 131 and 168 °C indicative of reversible first-order transitions.

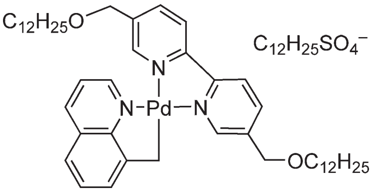
The synthetic utility of palladacycles was investigated by preparing stable racemic azapalladacycles and converting them into racemic 1,2-dihydroquinolines via insertion of alkynes. The same was achieved for oxapalladacycles where insertion of an alkyne gave 2H-1-benzopyrans.[147]

The complex $[\{PdCl(C_6H_4CH_2NMe\text{-}o)\}_2]$ reacts with $Ph_3P{=}CHC(O)CH_3PPh_2$ giving **62** ($X = Cl^-$ or BF_4^-).[148] Primary amines such as 2-phenylaniline and (*R*)-α-methylbenzylamine were cyclopalladated with $Pd(OAc)_2$ and LiBr to give the respective dimers.[149] Bridge-splitting reactions with pyridine and PPh_3 were carried out.

A cyclopalladated complex of 1-(2-diphenylphosphino-1-naphthyl)isoquinoline was used as a tool in the mechanistic study of allylic alkylation.[150] The crystal structure was obtained and distortion from the ideal bond angles was observed as well as some non-planar distortion of the biaryl linkage.

Solid-state thermolysis of 1′-alkyl-2,4′-bipyridinium palladium complexes gave cyclometallated complexes $[PdCl_2(2,4'\text{-R-bipy-H})]$ (R = H, Me, Bu, C_6H_{13}, C_8H_{17} or $C_{10}H_{21}$) in quantitative yield.[151,152]

Propargyl amines $R^1{-}C{\equiv}CCH(R^2)NMe(R^3)$ and thioethers $R^1C{\equiv}CCH{-}(R^2)SR^4$ (R^1 = Me, *n*-Bu, Ph; R^2 = H, Me; R^3 = Me, Bn; and R^4 = Me, *i*-Pr, Ph) were reacted with Li_2PdCl_4 in methanol affording air-stable five-membered palladacyclic compounds **63** and **64**, respectively, resulting formally from the *trans*-nucleophilic addition of the chlorine anion onto the C≡C bond.[153] Sterically more demanding alkynes with groups $R^1{=}Bu^t$ or $SiMe_3$ only form adducts of the type $PdCl_2(alkyne)_2$. Under the same reaction conditions, the terminal alkynes ($R^1{=}H$) afford analogous five-membered palladacyclic compounds in very low yields and an ill-defined mixture of organic/organometallic products.



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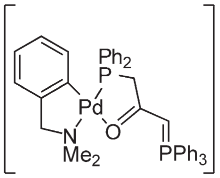

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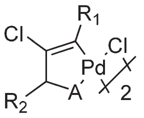
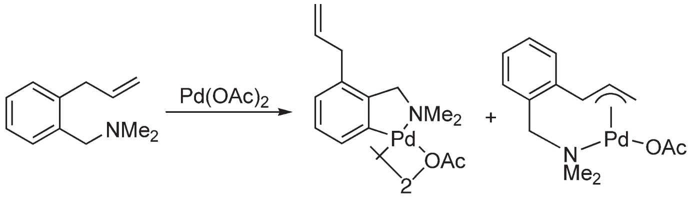


63: A = $NMeR^3$
64: A = SR^4

Competitive allyl versus aryl C–H activation in the presence of stoichiometric amounts of $Pd(OAc)_2$ to give **65** and **66** has been investigated (Scheme 15).[154]

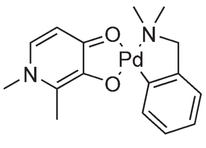
Orthopalladation of (*S*)-α-methyl-4-nitrobenzylamine has been reported.[155] The reaction of $[PdCl(C_6H_4CH_2\text{-}NMe_2)]_2$ with the anion of *N*-methyl-3-hydroxy-2-methyl-4-pyridone afforded **67**.[156] The first six-membered palladacycles such as **68** (X = Br, Cl, OAc; Y = Cl, F, NO_2) synthesized from primary phenethylamines with electron-withdrawing substituents on the aryl ring were reported by Vicente *et al.*[157]

The cyclometallation of (*R*)-(−)-8-(α-deuterioethyl)quinoline with palladium(II) salts results in the formation of the palladium–carbon bond in **69** with a net retention of the configuration at carbon.[158]



65 **66**

Scheme 15



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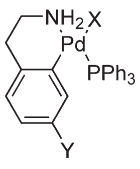

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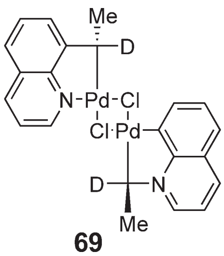
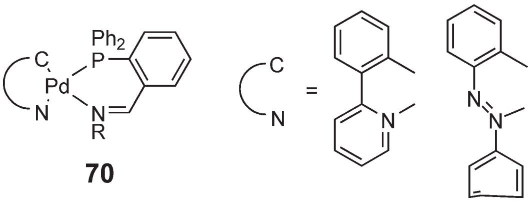


69

Chloro-bridged dipalladium(II) resolving agents (*R*,*R*)- and (*S*,*S*)-*cis*-di-*μ*-chlorobis[l-[1-(dimethylamino)-ethyl]-2-naphthalenyl-*C*,*N*]dipalladium, undergo facile rearrangements into unequal mixtures of *cis*- and *trans*-diastereomers upon dissolution in chloroform or dichloromethane.[159] Concentration of the solution in each case affords in high yield the pure *cis*-diastereomer of the dinuclear metal complex as the corresponding mono-solvate in a typical second-order asymmetric transformation.

The cyclopalladated complex (*S*)-(1)-bis(*μ*-chloro)bis[*N*,*N*-dimethyl-*α*-(2-naphthyl)ethylamine-*C*,*N*]-dipalladium has been used as a chiral template to promote the intramolecular [4 + 2] Diels–Alder reaction between diphenylvinylphosphine and 1-phenyl-3,4-dimethylphosphole.[160] Halide-bridged palladium(II) dimers of orthopalladated (*S*)-(+)-*N*,*N*-dimethyl-*α*-methylbenzylamine and (*S*)-(+)-*N*,*N*-dimethyl[1-(2-naphthyl)ethyl]amine were reported by the same authors.[161] Solution and solid-state structures were determined as well as reactions with 3,4-dimethyl-1-phenylphosphole and allyldiphenylphosphine carried out.

Cyclometallated complexes bearing iminophosphines such as **70** (R = Alk, Ph, MeNH) were reported by Sánchez *et al.*[162]



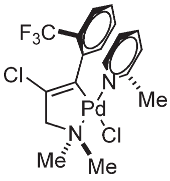
70

2-Benzoylpyridine was successfully cyclopalladated by Aiello *et al.* and the crystal structure of the complex was determined.[163]

Geest and Steel synthesized N,C palladacycles of the two isomeric ligands 2,2′-diphenyl-4,4′bipyridine and 3,3′-di(2-pyridyl)biphenyl.[164]

The complex [{Pd(*μ*-O_2CMe)($C_6H_4CH_2NMe_2$)}$_2$] ($C_6H_4CH_2NMe_2$ = 2-[(dimethylamino)methyl]phenyl) was converted to [{Pd(*μ*-Br)(*μ*-OH)($C_6H_4CH_2NMe_2$)}$_2$] via the addition of 1 equiv. of NBu_4OH to the starting material complex in acetone–water solution, followed by addition of 1 equiv. of LiBr. The product complex reacts with arylamines or thiols in 1 : 1 mole ratio to yield the corresponding amido- or thiolato–bromo complexes. Proton NMR data indicate a *cis*-arrangement of the $C_6H_4CH_2NMe_2$ ligands in the binuclear complexes.[165]

Zanini *et al.* studied the atropisomerism in palladacycles derived from the chloropalladation of heterosubstituted alkynes, for example, **71**.[166]



71

The acetate bridges in a cyclopalladated dinuclear complex containing 3,8-dinitro-6-phenylphenanthridine as ligand can be substituted by the deprotonated model nucleobase 1-methylcytosine to give a doubly bridged 1-methylcytosinato complex.[167]

Narayan *et al.* prepared cyclopalladated dithiolate complexes of the type [Pd(E^C)(S^S)] (E^C = *N*,*N*-dimethylbenzylamine, azobenzene, 4-MeOC_6H_4CH═NC_6H_4Me-4, 2-phenylpyridine or tris-*o*-tolylphosphine; S^S = S_2CNEt_2 or $S_2P(OR)_2$, R = Et, Pr^n, Pr^i, Bu^n, or Bu^s).[168] The reaction of a complex with PPh_3 where R = Bu^n afforded a dynamic equilibrium between [Pd{$S_2P(OPr^n)_2$}(N^C)] and [Pd{$S_2P(OPr^n)_2$}(η^1-C-N)PPh_3].

Iodo-bridged or cationic cyclopalladated complexes derived from *N*-phenyl-2-pyridylamine or phenyl-2-pyridylketone were reacted with internal alkynes giving five-membered heterocyclic and carbocyclic products with high chemoselectivity.[169] The synthesis of [Pt(NCN)(*μ*-PPh_2)-Pd($C_6H_4CH_2NMe_2$-2)(OH_2)][BF_4] was also described.[170] Indoles were obtained regioselectively suggesting electronic and steric control. Indenol derivatives were obtained as stable bis(O,N)-palladated chelates which resulted from the insertion of the alkyne into the Pd–C bond of the palladacycle followed by attack of the palladated vinyl carbon atom on the electrophilic carbonyl function.

The mono-sulfide of (*R*,*R*)-MeDUPHOS was reacted with $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2)]_2$ to give the respective mononuclear cyclopalladated complex of which the crystal structure was determined.[171]

Pseudo-halide bridged complexes $[Pd(\mu\text{-}X)(C_6H_4CH_2NMe_2)]_2$ (X = SCN, NCO) were cleaved with diphosphines.[172] Conductivity measurements were carried out. Compounds with distinctly different structures in the solid state and solution were observed. An earlier study researched the thermal behavior of $[Pd(\mu\text{-}X)(C_6H_4CH_2NMe_2)]_2$ complexes where X = Cl, SCN, NCO, and CN with PdO as the final decomposition product.[173]

Cyclometallated Pd(II) complexes with bridging or terminal imidato ligands were studied by Serrano *et al.*[174] The crystal structures of [{Pd(μ-succinimide)(phpy)}$_2$] (phpy = 2-phenylpyridine) and $[Pd(azb)(succinimide)(PPh_3)]$ (azb = azobenzene) were determined.

The reagent $Ph_2Si(CH_2Li)(CH_2NC_5H_{10})$, with $(CH_2NC_5H_{10})$ being piperidinomethyl, reacts with *trans*-$[PdCl_2(SMe_2)_2]$ giving dimeric $[Pd(\mu\text{-}Cl)\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2\text{-}C,N\}]_2$, where the $[CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2\text{-}C,N]$ ligand forms a palladacycle.[175]

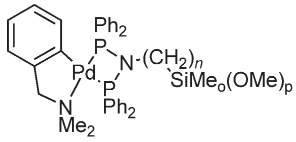
Activation of a C(sp^3)–H bond was observed in the cyclopalladation of [py{$SCH_2C(O)R$]-2] (py-2 = 2-pyridyl, R = Ph, Me, OMe).

An unusual zwitterionic dinuclear Pd(II) complex **73** was obtained with a phosphino-oxazoline ligand.[176] A binuclear N,C-palladium(II) complex bearing a phosphinoenolate as bridging ligand in addition to a mononuclear N,C-Pd(II) complex being ligated by a phosphino-iminolate ligand has also been reported.

A trinuclear complex **74** derived from 2-phenyl-5(4H)-oxazolone is reported by Bauer *et al.*[177]

A cyclopalladated benzylamine complex ligated by an *N*-pyrolyl phosphine bearing a CN group can be converted into a cationic cyclopalladated complex bearing a phosphinopyrolyl oxazoline ligand.[178]

Asymmetric palladacyclizations resulting in six-membered rings, for example, **75**, were carried out by Burke and Overman.[179] A series of reactions of $[Pd(\mu\text{-}Cl)(C_6H_4NMe_2)]_2$ with *rac*-{2-(diphenylphosphino)ferrocenyl}acetic acid and related compounds were carried out.[180]



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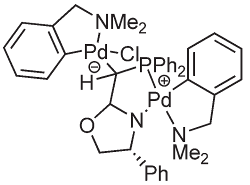

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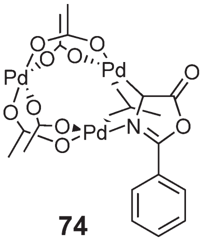

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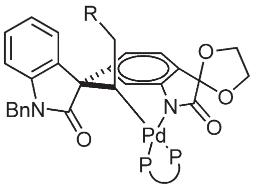


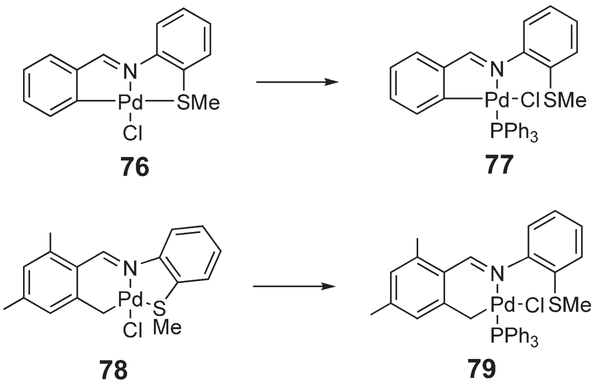
75

Ordered binary crystals were obtained via cocrystallization of quasi-racemic cyclopalladated complexes in a borderline regime between inertness and lability.[181] Braunstein *et al.* devised routes for anchoring a cyclopalladated complex **72** inside a nanoporous alumina membrane.[182]

8.05.5.2 Imine- and Oxime-based Palladacycles

A pentacoordinated cyclometallated palladium(II) complex was reported and characterized by elemental analysis and (solid-state) NMR and X-ray crystallography.[183] A number of new palladium(II) complexes **76–79** of [C_{sp2},*N*,*S*]- and [C_{sp3},*N*,*S*]-ligands were prepared.[184] Thioimines act as [C_{sp2},phenyl,*N*,*S*]$^-$ or [C_{sp^3},*N*,*S*]$^-$ and as a terdentate group. Reactions with PPh_3 have also been reported (Scheme 16). $[Pd\{C_6H_4\text{-}CH{=}N\text{-}(C_6H_4\text{-}2\text{-}O)\}]_4\cdot 2CHCl_3$ is formed from the reaction of a Schiff base with $Pd(OAc)_2$ with a central non-planar "Pd_4O_4" ring by self-assembly.[185] Further reactions with phosphines PPh_3 and dppf were carried out.

A dinuclear cyclometallated complex was obtained from the reaction of a Schiff base ligand with palladium acetate.[186] A series of reactions were carried out, that is, metathesis with chloride, bridge splitting with PPh_3, formation of dinuclear complexes with dppp and dppb, and the formation of a cationic complex with silver triflate. A *syn*-acetato-bridged dinuclear palladacycle of $[Pd(\mu\text{-}OAc)\{2,3,4\text{-}(MeO)_3C_6HC(H){=}NCH_2CH_2OH\}]_2$ was also reported.[187] Comparable cyclopalladated complexes exist for $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH{=}N\text{-}CH_2\text{-}CH_2\text{-}OH\}]$.[188] A mass spectrometric study of a reaction mixture showed signals of nine-membered imine-based palladacycles.[189] The influence of the phenyl ring substituents on cyclometalation has been evaluated.[190]



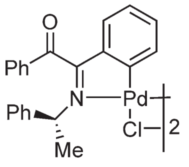
Scheme 16

Complex 80 has been studied, also because of its anticancer activity.[191] Cyclometallated palladium(II) complexes of *N*-(4-chlorophenyl)-α-benzoylbenzylideneamine $[PdX\{4\text{-}ClC_6H_4N{=}C(COC_6H_5)C_6H_4\}]_2$ showed no covalent interaction with DNA when tested for DNA metallation.[192]

Dinuclear cyclometallated palladium(II) complexes 81 have been obtained from Schiff base ligands.[193] Cyclopalladated complexes of oximes 82 and 83 and their ligand-exchange reactions have been studied.[137] Ketoximes form palladacycle dimers such as 84.[194]

A series of five cyclopalladated ferrocenylketimines $[PdCl\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}NC_6H_4R)\}(PPh_3)]$ were synthesized and found to be mixture of *syn*- and *anti*-isomers.[195] Several cyclometallated semicarbazones were reported.[196,197]

A doubly cyclometallated palladium(II) complex 85 was prepared with *N*-(benzylidene)xylylendiamine, and various ligand substitution reactions were carried out.[198] A doubly cyclopalladated complex of 1,3-$[2,3,4\text{-}(MeO)_3C_6H_2C(H){=}NCH_2]_2C_6H_4$ has also been made.[199] Reaction of another Schiff base ligand with $Pd(OAc)_2$ giving two endocyclic cyclometallated compounds $[Pd(\mu\text{-}O_2CMe)\{3,4\text{-}(OCH_2O)C_6H_2C(H){=}NCH_2[3,4\text{-}(OCH_2O)\text{-}C_6H_3]\text{-}C^2,N\}]_2$ and $[Pd(\mu\text{-}O_2CMe)\{3,4\text{-}(OCH_2O)C_6H_2C(H){=}NCH_2[3,4\text{-}(OCH_2O)C_6H_3]\text{-}C^6,N\}]_2$ which can be separated by fractional crystallization.[200] The dimers undergo various metathesis and bridge splitting reactions. Some double cyclopalladated complexes of Schiff base ligands give insoluble halide-bridged polymeric complexes.[201] Bridge-splitting was carried out with a series of compounds and cyclopalladated complexes of azine ligands were also reported (*see* section 8.05.5.3). Five-membered endo-palladacycles were obtained from imines of the formula 3,4-$(MeO)_2C_6H_3CH{=}N(CH_2)_nC_6H_4R$.[202] Steric factors were found to be important in the endocyclic ring formation. A bridged endo-palladacyclic dimer of a benzyl-benzylidene amine was also reported.[203]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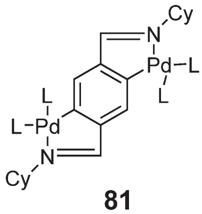
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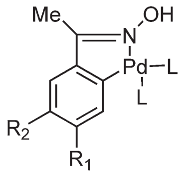
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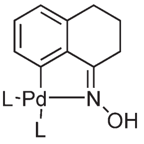
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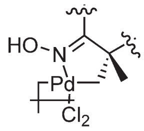
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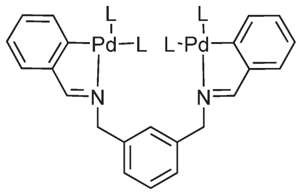
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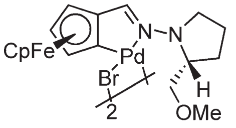
Imine-derived dinuclear palladacycles being ligated by amido or dialkyldithiocarbamato ligands show liquid crystal behavior and nematic smectic A and smectic C phases.[204] Other derivatives being OH-, hydroxo–amido-, amido–thiolato, or amido–carbxylato-bridged have also been prepared. The solution behavior, kinetics and mechanism of the acid-catalyzed cyclopalladation of imines, that is, *N*-benzylidenebenzylamines, -anilines, and -propylamine with $Pd(OAc)_2$ in acetic acid has been studied.[205] C–H electrophilic bond activation occurs to produce different types of metallacycles.

Planar chiral cyclopalladated ferrocenylhydrazones and di-μ-bromo-bridged dimers such as **86** have been synthesized in enantiomerically pure form with a high level of diastereoselectivity and X-ray structures have been obtained.[206] Optically active cyclopalladated compounds derived from chiral arylimines have been obtained.[207]

Three new orthopalladated chromophores **87** ($A,B = NO_2, NR_2; A \neq B$) based on push–pull π-conjugated ligands have been prepared and characterized.[208] Second-order molecular NLO activity has been determined by EFISH measurements. A related study with OH-functionalized orthopalladated Schiff bases was also published by the same group in 2004.[209]



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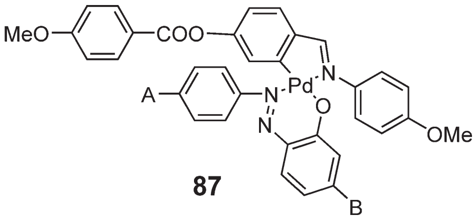


87

Palladacycles of Schiff bases of homoveratrylamine and tryptamine have been synthesized and the insertion of CO has been investigated.[210]

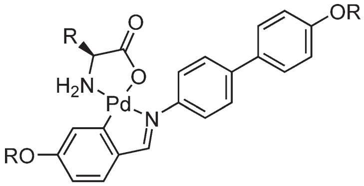
Cyclopalladation of 2,6-dimethyl-*N*-(2′,4′,6′-trimethyl-benzylidene)aniline in refluxing acetic acid and reaction with excess LiX gives the dinuclear complexes $[Pd(1\text{-}CH_2\text{-}2\text{-}\{HC{=}N[2',6'\text{-}(CH_3)_2C_6H_3]\}\text{-}3,5\text{-}(CH_3)_2C_6H_2)X]_2$ ($X = Br, I$), which contain six-membered palladacycles.[211] Folded acetate-bridged *ortho*-palladated complexes of benzoylbenzylideneamines react with DCM to afford unfolded chlorobridged *ortho*-palladated complexes.[212]

Orthopalladated complex $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2{=}NPh\text{-}\kappa\text{-}C,N)]_2$ and related complexes have been obtained by the reaction of $Pd(OAc)_2$ with iminophosphoranes.[213]

Many other palladacycles derived from imines have been reported, and their reactions with diphosphines have been treated extensively;[214–219] their hydrolysis in the presence of bromide and bipy or PPh_3 giving *ortho*-formylaryl complexes has also received attention.[220]

N-Heterocycles were synthesized via insertion of 1,1-dimethylallene into Pd–C bonds of cyclopalladated α-tetralone ketimines.[221] Insertion reactions of alkynes into the Pd–C bond of cyclopalladated ferrocenylimines have also been described.[222] Biomimetic hydrolysis of benzoates has been carried out with a water-soluble cyclopalladated aryl oxime, which was proposed as a potential ‘green’ catalyst.[223] Chiral cyclopalladated liquid crystals **88** were obtained from amino acids and could possibly serve as enantioselective catalysts.[224] Palladacycle **89** has been derived from an anthracene-based Schiff base.

New palladium(II) cyclometallated compounds **90** have been derived from *trans*-cinnamalylideneimines via C–H activation of an sp^2-aliphatic carbon atom.[225] Palladacycles of *N,N*-isophthalylidenebis(cyclohexylamine) were inadvertently obtained.[226] Palladacycles were also obtained from *N,N*-(2,5-dichloro)terephthalylidenebis(cyclohexylamine) by oxidative addition.[227] The X-ray structure of palladacycle $[Pd\{4\text{-}(CHO)C_6H_3C(H){=}NCy\text{-}C,N\}(acac)]$ was reported.[228]



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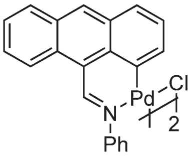

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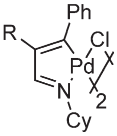


90

Binuclear cyclopalladated imine complexes derived from $C_6H_5CH{=}NAlk$, $4\text{-}MeC_6H_4CH{=}NBu^n$, $4\text{-}CH_3OC_6H_4\text{-}CH{=}NBu^n$, $3,4\text{-}(MeO)_2C_6H_3CH{=}NBu^n$, and $3,4\text{-}(MeO)_2C_6H_3CH{=}NBu^n$ have been detected.[229] A bridged endo-palladacyclic dimer of a benzyl-benzylidene amine,[203] and cyclopalladation of aliphatic compounds together with the X-ray crystal structure of $[Pd(\mu\text{-}Br)(1\text{-}CH\text{-}2\text{-}\{HC{=}N[2',6'\text{-}(CH_3)_2C_6H_3]\}\text{-}3,5\text{-}(CH_3)_2C_6H_2)]_2$ have been reported.[211]

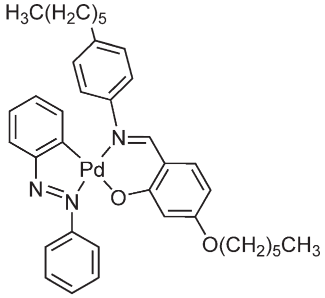
A mass spectrometric study of a reaction mixture showed signals of nine-membered imine-based palladacycles.[189] The *trans*-influence in mononuclear cyclopalladated ferrocenylimine compounds was studied.[230]

Metallomesogens arise from some mono- and dicyclopalladated Schiff base liquid crystals.[231–233] Subsequent reaction of the former with a β-diketone gave new compounds; the alkyl-substituted diketones influence both the melting and clearing point.[232] Disk-like chiral palladacycles were derived from benzalimines.[234] A study of their mesomorphic properties was undertaken.

8.05.5.3 Palladacycles Containing N–N or N═N Bonds

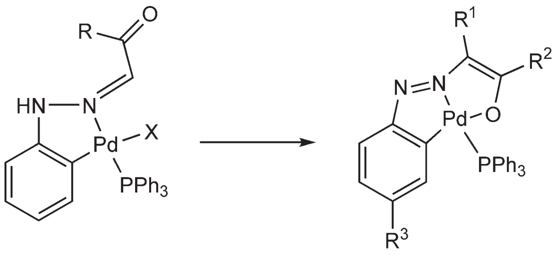
A structurally characterized dimeric acetanilido palladium(II) complex $[\{Pd(\mu\text{-}PhNCOMe)(C_6H_4N{=}NC_6H_5)\}_2]$ was reported; the selectivity between five possible isomers was evaluated.[235] Dimeric cyclopalladated azobenzenes were reacted with either 2-hydroxy- or 2-mercaptobenzenes and the structural differences of the products were studied.[236] A report concerning palladacycles derived from aromatic azo compounds ligated by iminophosphoranes has also appeared.[237]

A cyclometallated azobenzene complex **91** was identified as a new class of highly efficient photorefractive materials.[238] Cyclopalladated azobenzenes with N,O chelating ligands and cyclic voltammetric studies were reported.[239] Mesomorphic materials exhibiting a nematic phase were derived from a cyclopalladated azo compound.[240] Mesogenic cyclopentadienyl cyclopalladated azobenzene complexes were also made.[241] Reactions of cyclopalladated azobenzenes were studied with xanthates and dithiocarbamates yielding ternary complexes.[242] The products were studied electrochemically.



91

Phenylhydrazones derived from 2-oxopropionaldehyde, benzoylformaldehyde, and butane-2,3-dione led to dinuclear metallacycles.[243] The addition of NaOMe in MeOH afforded deep violet compounds which do not contain chlorine atoms. Deprotonation takes place by means of a hydrazo-keto azo-enol tautomerization involving **92** and **93** (Scheme 17).

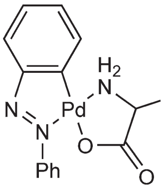


92 **93**

Scheme 17

Palladation of the ketone function of *N*,*N*-dimethylhydrazones,[244] rearrangement of palladacycles derived from 2-oxopropionaldehyde phenylhydrazones,[245] orthopalladation of acetophenonephenylhydrazone,[246] and cyclopalladated compounds derived from pinacolone-*N*,*N*-dimethylhydrazone were reported.[247]

New α-amino carboxylate complexes **94** of palladium(II) have been reported.[248] Cyclopalladated aminoazobenzenes were the subject of dynamic ^{1}H NMR studies;[249] cyclopalladation of *N*-(benzoyl)-*N*′-(2,4-dimethoxybenzylidene)hydrazine[250] and of photochromic 4-methoxyazobenzene[251]were reported.



94

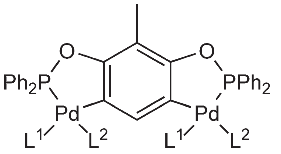
An asymmetrically folded dinuclear phenylhydrazonato anionic complex containing two different hydrazonato ligands of palladium containing a Pd–C(aryl) bond *cis* to a Pd–N(amido) bond was described.[252] Interesting dinuclear cyclopalladated 1,2- and 1,3-bridged squarato complexes containing cyclopalladated 2,6-dimethylazobenzene have appeared.[253]

8.05.5.4 Palladacycles Containing Pd–P Bonds

An example of a doubly orthopalladated aryl bis(phosphinite) ligand **95** has been reported.[254] Aryloxopalladium(II) complexes were synthesized using the Herrmann–Beller palladacycle.[255] Coordination of the 2-acylphenolates to palladium results in a significant perturbation of the delocalization within the aromatic ring. Another example involves a doubly orthometallated complex from *o*-$C_6H_4(PBu^t)_2$ and $Pd(OAc)_2$.[256]

N-Carbazolyl phosphines $PPh_{3-n}(NC_{12}H_8)_n$ react with palladium(II) precursors giving $[Pd(\mu\text{-X})\{P(NC_{12}H_8)_2\text{-}(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2$ (X = Cl, OAc) and $[Pd(\mu\text{-Cl})\{PPh(NC_{12}H_8)(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2$.[257]

The complex $[PdH(d^tbpx)(solv)]^+$ in a solution containing 1–7 equiv. of benzquinone forms a species to which the structure **96** has been assigned.[258] A dimeric bromide-bridged palladacycle $[Pd(Bu_2{}^tPCMe_2CH_2)(\mu\text{-Br})]_2$ has been found as a byproduct.[259]



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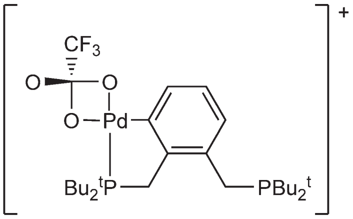


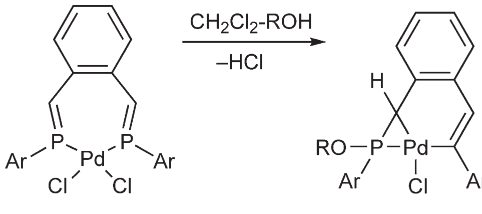
96

A cyclometallated chiral complex **97** arose from the reaction of alcohols (MeOH, EtOH) with a seven-membered ring complex (Scheme 18).[260]

The binding modes and charge distribution of Pd–(MOP) complexes **98** were studied.[261] The coordination chemistry of the MAP ligand with Pd(II) complexes **99** has been investigated.[262]

Enantiopure ferrocene-based phosphapalladacycle **100** with planar chirality have been synthesized,[263,264] and optically active phosphapalladacycles were obtained via asymmetric exchange of cyclopalladated ligands.[265,266]

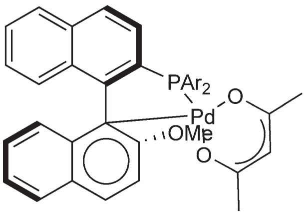
The photo-assisted formation of a chelating diphos ligand from PPh_3 and a cyclopalladated $[P(C_6H_4)(C_6H_5)_2]^-$ ligand was reported.[267] New P,C-chelated Pd(II) complexes were formed via phosphine-assisted oxidative addition of an aliphatic C–Cl bond.[268]



97

Scheme 18

Small ring P,C palladacycles were synthesized and characterized,[269,270] and the synthesis of an atropisomeric phosphapalladacycle **101** has been described.[271]



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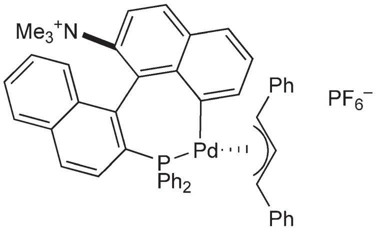

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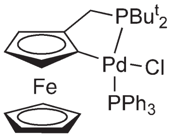

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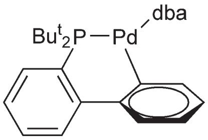


101

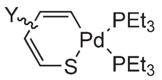
8.05.5.5 Palladacycles Containing Pd–S Bonds

Palladated aryldithioacetals show unexpected rearrangements involving C–S and C–Pd bonds.[272] A related study was published by Vicente *et al.* in 2002[273] and 2004.[274]

Substituted thiophenes react with $[Pd(PEt_3)_3]$ to give thiapalladacycles of the general structure **102** (Y = Cl, NO_2, OMe).[275]

Orthopalladation of (1-*t*-butylsulfanylethyl)benzene, (1-methylulfanylethyl)benzene, and 2-(1-t-butylsulfanylethyl)naphthalene yields the respective racemic sulfur chloro-bridged palladacycles. Single isomers as well as a mixture of two diastereomers have been isolated.[276] Variable-temperature ^{1}H NMR shows that the S-*t*-Bu palladacycle is configurationally stable, whereas the 2-Me palladacycle readily undergoes pyramidal inversion at the sulfur atom.

López reported the binuclear complex **103** containing two five-membered thiopalladacyclic rings.[277]



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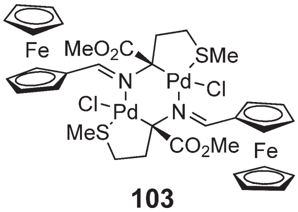


103

The cyclopalladation of *N*,*N*-dimethyl-2-bromothiobenzamide and related thioamides was carried out by Nonoyama *et al.*[278] Another study by the same group was directed toward the cyclopalladation of *N*-(*p*-thiotoluoyl)-pyrrolidine and –piperidine.[279] Depending on the reaction conditions either *ortho*-C–H activation or α-CH_2 activation occurs.

Propargyl thioethers result readily in five-membered cyclopalladated compounds of the formula $[Pd(\mu\text{-}Cl)\{C(Ph){=}C(Cl)CHR_1SR\}]_2$ according to a procedure by Dupont *et al.*[280]

Palladacycles derived from arylsulfides and sulfoxides react with *m*-chloroperbenzoic acid giving regioselective aromatic metaloxylation (Pd–Ar → Pd–O–Ar).[281] No oxidation of the sulfur atoms was observed.

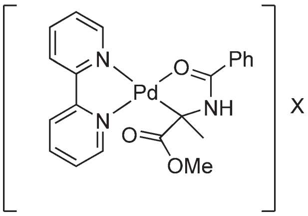
The complex [Pd(η^1-OAc)(η^2-MeSCHCO$_2$Et-*C,S*)(PPh$_3$)] was synthesized as part of a study of the early steps of the Heck reaction.[282] It was found to be remarkably stable.

A series of mono-, di-, and trinuclear cyclopalladated complexes of α-substituted thioethers were reported by Basato *et al.* in 2000.[283] Three-membered C,S palladacycles containing a W(CO)$_5$ group and their reactions in one of the side-chains were reported by Yih *et al.* in 2000.[284]

8.05.5.6 Palladacycles Containing Pd–O Bonds

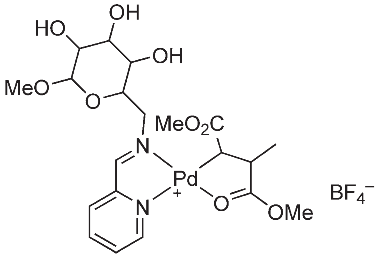
Cationic bipyridine-ligated palladacycles of α-metallated glycine esters **104** were reported by Beck *et al.*[285] The effect of halide ligands on the reaction of **105** and **106** with acrolein was investigated by Lu *et al.*[286]

The reaction of a [Pd(N,N-chelate)(olefin)] complex (in which one of the is substituted by a carbohydrate) with [OMe$_3$]BF$_4$ affords **107**.[287] The synthesis of a tetrameric complex of the formula [Pd{κ^2-(C,O)-μ^2(O)-C(=NXy)C$_6$H$_4$O-2}(CNXy)]$_4$ was documented by Vicente *et al.*[288] The cyclopalladation of indole-3-acetate results in the formation of a unique spiro-compound **108**.[289] A large number of oxapalladacycles were reported by the research group of Echavarren.[290]



104

105: Y = Cl
106: Y = OAc



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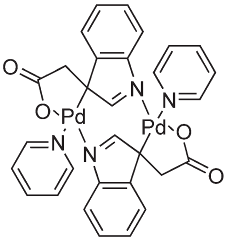


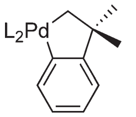
108

8.05.5.7 *C,C*-Chelating Ligands

Palladacycles **109** were prepared starting from [PdCl(CH$_2$CMe$_2$C$_6$H$_5$)L$_2$] (L$_2$ = (PMe$_3$)$_2$, cod) by treatment with base or ligand exchange reaction.[291] Reactions of these metallacycles with alkynes and SO$_2$ were carried out.

The synthesis and structure of [Pd(PEt$_3$)$_2$(2,2′biphenyl)] was reported by Edelbach *et al.*[292,293]

Bidentate phosphorus complexes of [Pd(CHRCOCHR)L$_2$] were obtained from the reaction of [Pd$_2$(dba)$_3$]·CHCl$_3$, L$_2$, O$_2$ with esters of 3-oxopentanedioic acid in diethylether.[294] New members of a little studied class of alkyl(aryl)palladium(II) complexes **110** and **111** have been synthesized.[295]



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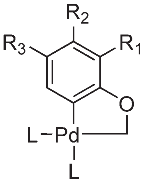

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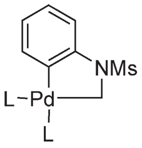
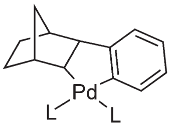


111

The reaction of **112** with alkynes has been studied by Catellani *et al.*[296] The intramolecular η^2-arene complexes Pd[C$_7$H$_8$(η^2-Ar)](PPh$_3$)I were reacted in CH$_2$Cl$_2$ with aqueous sodium hydroxide in the presence of PPh$_3$ giving, for example, **113**.[297] Complex **113** can be reacted with MeI to give the *o*-methyl product. Ligand exchange with CO has been observed.

Oligomeric palladacyclopentadiene complexes **114** are useful in [2 + 2 + 2]alkyne cyclotrimerizations.[298] An X-ray crystal structure of **114** was obtained.[299] Palladacyclopentadienes have also been employed as precatalysts.[300] A series of palladacyclopentadiene complexes being ligated with an N,P-donor ligand or pyridazine were studied by Sánchez *et al.*[301] A palladacyclopentadiene complex was obtained from the reaction of Pd(dba)$_2$ with Ar-BIAN and dimethyl butynedioate giving **115**.[302] A synthetic and computational study concerning the reactivity of palladacyclopentadienes **115** containing bidentate nitrogen ligands toward dihalogens has been described.[303]



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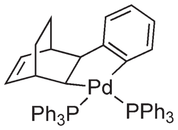

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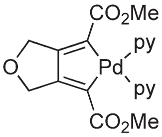

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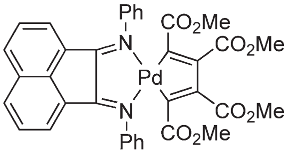
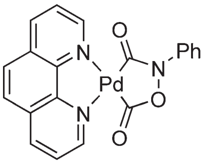


115

Metallacyclic complexes **116** and **117** have been obtained starting from nitro- and nitrosobenzene[304] and an intermediate of the type **118** was detected.[305] Novel olefin palladium(II) complexes **119** containing poly(pyrazol-1-yl)borate and -methane ligands were obtained.[306]



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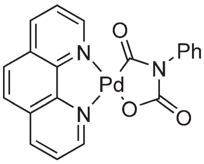

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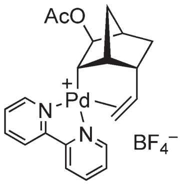

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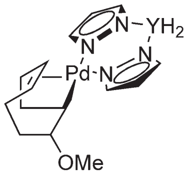
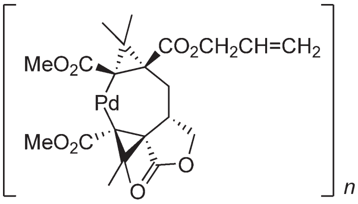


119

Enantiomerically pure 5-palladatricyclo[4.1.0.0^{2,4}]heptanes have been prepared and been converted into enantiomerically pure complexes with helical chirality at palladium.[307] The reaction of an excess of dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate with $[Pd_2(dba)_3]\cdot CHCl_3$ gave diastereoselectively as side-product a new palladacycle **122**.[308] Furthermore, a highly diastereoselective synthesis of palladepanes **120** and **121** has been achieved.[309]



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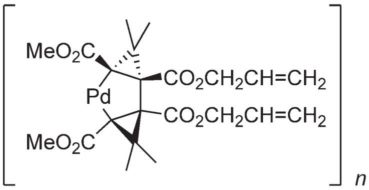

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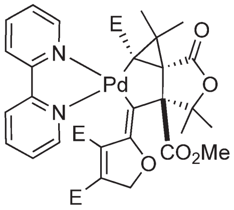


122: E = CO_2Me

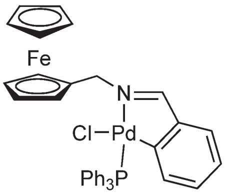
The synthesis of palladacyclobutanes gave insight into the reaction mechanism of cyclopropanation.[310] The cleavage of palladium metallacycles by acids has been found to be a probe for the cyclometalation reaction.[311] Orthopalladated complexes of the *C,C*-chelating ligand C_6H_4-2-PPh_2*C*(H)$COCH_2PPh_3$ and their reactivity toward deprotonating reagents was studied.[312]

8.05.5.8 Ferrocene-based Palladacycles

Hydroxyferrocene was converted into a phosphite ester with chiral (racemic) butane-1,3-diol which then yielded a cyclopalladated complex when reacted with $PdCl_2$; planar chirality has been observed but no diastereoselectivity.[313] Chiral ferrocenylimines were reacted with Na_2PdCl_4 and NaOAc to give a mixture of diastereomeric cyclopalladated products.[314] Enantiopure compounds were isolated via column-layer chromatography.

The reactivity of a ferrocene-based palladacycle $[\mathrm{PdCl}\{[(\eta^5\text{-}\mathrm{C_5H_3})\text{-}\mathrm{CH{=}N}\text{-}(\mathrm{CH_2})_2\text{-}\mathrm{NMe_2}]\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\}]$ with diphosphines was studied giving monomeric and dimeric complexes.[315]

Schiff bases derived from aminomethylferrocene were used to prepare a series of palladacycles 123 and 124.[316] Four diastereoisomers of bis(cyclopalladated) $[\{\mathrm{PdCl}[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{CMe{=}N}](\mathrm{PPh_3})\}_2]$ in solution have been revealed by ^{1}H and ^{31}P NMR spectra; the meso form has been examined by X-ray crystallography.[317] Cyclic voltammetry and Mössbauer spectra are also reported.



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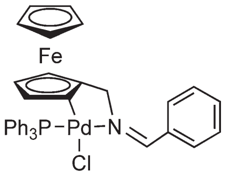


124

The effects of the nature of the nitrogen donor atom (sp^2 vs. sp^3) upon the properties and chemistry of palladated complexes with σ(Pd-C(sp^2)), ferrocene) bonds were studied by López *et al.*[318] Mössbauer spectra show that palladium(II) acts as electron withdrawing, and in the derivatives of ferrocenyl Schiff bases most electron density is withdrawn from the imine.

Ferrocenylimines derived from benzoylferrocene were synthesized and cyclopalladated by Bosque *et al.*[319] The σ(CH) bonds in ferrocenyl- and bis(ferrocenyl)imines were activated in cyclopalladation reactions.[320] Depending on the imine, five- and six-membered palladacycles were obtained. Bosque and López also studied the cyclopalladation of mono- and bidentate primary ferrocenylimines.[321,322] Mak *et al.* studied the cyclopalladation of ferrocenylimines in which the nitrogen of the imine is also substituted with a cyclic ether.[323] Enantiopure bis(μ-acetato)-bridged dimers were obtained. The insertion of diphenylacetylene was also investigated.

The lability of the Pd–N bond in cyclopalladated Schiff base complexes was evaluated.[324] The substituent on the nitrogen plays an important role determining the ease with which the Pd–N bond is being cleaved. López *et al.* reported the synthesis of optically active cyclopalladated complexes of (*S*)-(–)-*N*,*N*-dimethyl-1-ferrocenylethylamine.[325] Ligand exchange and insertion reactions were carried out with the bridged dimers.

Transmetallation reactions in order to obtain mercurated ferrocenes were carried out with a series of planar chiral cyclopalladated ferrocenylimines.[326]

The crystal structures of alkyne insertion products into Pd–C bonds of planar chiral cyclopalladated Schiff base complexes were published in 1998 by Mak *et al.*[327] A similar study including electrochemical studies was published in the same year.[328]

8.05.5.9 Palladacycles Derived from Heterocycles

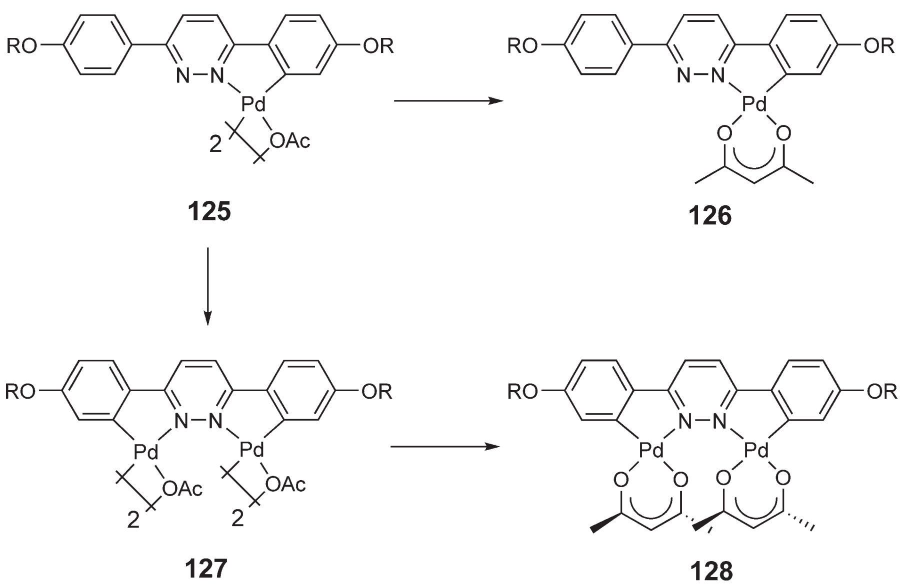
The cyclometallation of pyridazines, pyrimidines, pyrazines, and tetrazines has been studied.[329,330] It was found that pyridazines formed singly and doubly cyclometallated compounds and pyrazines only metallated once. Tetrazines and pyrimidines metallate once while doubly metallated species were identified in solution. Transmetallation reactions were carried out with cyclopalladated benzylamine complexes.

Mono- and dicyclopalladation of mesogenic pyridazines was achieved and the subsequent reaction with β-diketones gave metallomesogens 125–128 (Scheme 19).[331] Monometallated derivatives have a flat central core, dimetallated derivatives have a sterically induced twist in the molecule rendering them chiral. Smectic A phases are exhibited, with transition temperatures in the region of 100/300 °C.

Nonoyama *et al.* described the cyclopalladation of 3-phenyl-6-p-toluidinopyridazine and the X-ray structure of the respective complex.[332]

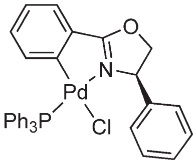
(4*R*)-phenyl-2-oxazoline-derived palladacycles bearing endo- or exo-C=N bonds form dimeric as well as mononuclear coumpounds 129 from $\mathrm{PPh_3}$ bridge-splitting reactions.[333]

1,4-Bis(benzothiazol-2-yl)benzene was doubly cyclopalladated to give a nonpolymeric acetate-bridged counterhinged molecular box[334] and dimeric six-membered cyclopalladated complexes of 2-benzylbenzothiazole were investigated as well.[335]



Scheme 19

The first report of C–H activation in the arylsydnone system **130** was reported by Lin *et al.*[336]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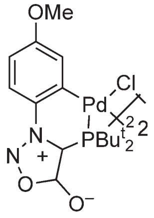


130

Dibenzo[a,c]phenazine and dibenzo[f,h]quinoxaline can be cyclopalladated and studied spectrophotometrically and electrochemically.[337]

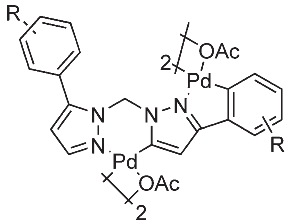
Unique spiro-rings were formed by the cyclopalladation of indole-3-acetate.[289]

Zamora *et al.* were able to show how the protection of the NH group of unsubstituted derivatives of 2-phenylimidazole aids in the palladation.[338]

1,3-Bis-(benzimidazol-2-yl)-benzene reacts with $Pd(OAc)_2$ giving the mono-palladated complex which can undergo self-assembly to a molecular tricorn.[339,340] However, the heterocyclic compound may also undergo a second cyclometallation. Benzimidazole, -oxazole, and -thiazole compounds were orthopalladated and studied by NMR and X-ray.[341] The structures of two polymorphic crystals are discussed. The synthesis and extensive NMR study of the cyclopalladated complex of 2-phenylimidazoline was undertaken.[342] 1-Methyl-2-phenylimidazole was cyclopalladated and reacted with tertiary diphosphines.[343]

Unusual double palladation of diarylbis(N-pyrazolyl)methanes was reported by Alonso *et al.*[344] The complexes contain two different five- and six-membered palladacycles as well as an aromatic metal–carbon bond and a pyrazole metal–carbon bond, for example, **131**.

Cyclopalladation of *N*,*N*-dimethylbenzo[h]furan-2-carbothio (and seleno) amides takes place readily.[345] and a cyclopalladated nitro palladium(II) complex was formed unexpectedly from the metallation of 2-(2-pyridyl)benzo[b]-furan and 1-(2-pyridyl)- and 1-(2-pyrimidyl)indole **132–134**.[346]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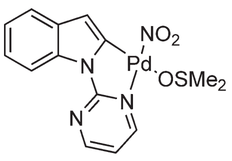
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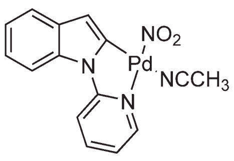
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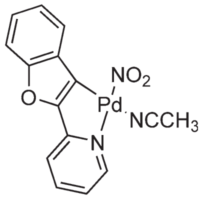
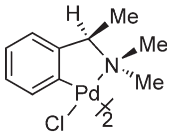

134

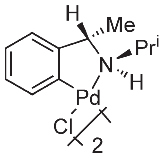
8.05.5.10 Resolution and Determination of Enantiomeric Purity of Compounds Using Palladacycles

The enantiomeric purity of 2,2′-bis(dicyclohexylphosphino)-1,1′-bibenzimidazole was determined by ^{31}P NMR using the respective complexes with enantiopure **135**.[347] Complex **135** was used for resolving a P–N chelating ligand (*R*)- and (*S*)-6-(2′-diphenylphosphino-1′-naphthyl)phenanthridine.[348] Atropisomerically pure (*S*)-4-phenyl-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]phosphepine was also obtained by resolution of the racemic mixture with **135**.[349] Complex **135** and (*S*)-(+)-di-*μ*-chlorobis{2-[1-(dimethylamino)ethyl]phenyl-C,N}dipalladium were applied in the resolution of electron-poor biphenyl-based ligands,[350] 2-(2-diphenylphosphinyl-naphthalen-1-yl)-1-isopropyl-1H-benzoimidazole[351] and 2,2′-bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (BINASb).[352]

The anion *rac*-7-diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate was resolved using **135** by Brunner *et al.*[353] An enantiopure 2,2′-bisphospholene was also obtained via resolution with **135**.[354]


135

A novel racemic palladacyclic dimeric complex **136** was resolved via recrystallization of its diastereomeric (*S*)-prolinate derivatives **137** and **138** (Scheme 20).[355] The chemistry and resolution of chiral PMeBu^{t}Ph was studied using **139** and **140**.[356] Complex **139** was also used in the resolution of stilbenediamine.[357] The P-chiral phosphine PBu^{t}Ph(4-BrC$_6$H$_4$) was resolved using **141**.[358]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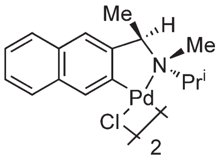
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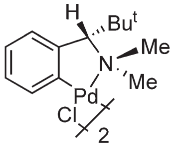
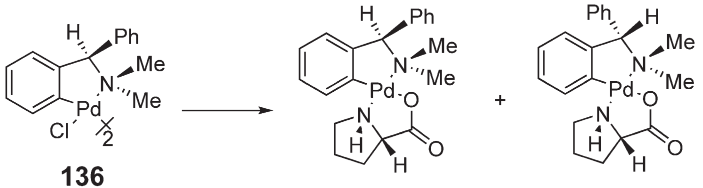
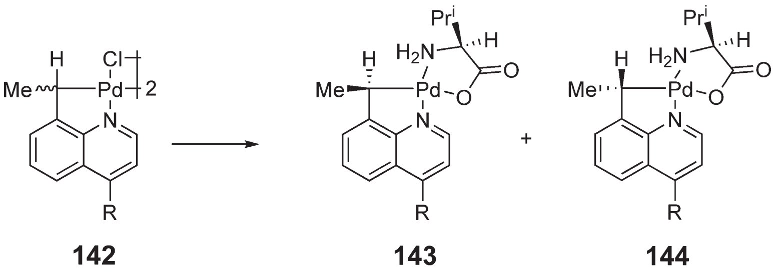

141

The ligand S_P-(+)-(2-methoxyphenyl)-P-phenyl-P-(2′-diphenylphosphino)ethylphosphine (70% ee) was reacted with bis-(*R*)-dimethyl(1-(1-naphthyl)ethylaminato-*C*^{2},*N*)dipalladium dichloride giving four possible diastereomers of which, via successive recrystallizations, the more soluble pair of diastereomers was removed leaving a second pair in a


136 **137** **138**

Scheme 20



Scheme 21

10 : 1 ratio.[359] The X-ray structure of one of the diastereomers was determined. McCarthy *et al.* used the same palladacycle to resolve the atropisomeric 2-phenyl-quinazolinap ligand.[360] A related naphthalene-based palladacycle was applied to the resolution of benzylisopropylphenylphosphine.[361] Other new palladacycles containing imines as resolving agents were also designed by the same group.[362] Benzylmesitylphenylphosphine was resolved using two different naphthalene derived N,C palladacycles.[270]

The enantiomerically enriched palladacycle **142** was resolved using (*S*)-leucine as chiral auxiliary (Scheme 21; **142–144**).[363]

^{19}F NMR spectroscopy was applied in the enantiomeric excess determination of (*N*,*N*-dimethyl-(2,2,2-trifluoro-1-phenylethyl)amine-*C*,*N*)palladium complexes of α-amino acids.[364] Dunina *et al.* used ^{31}P NMR spectroscopy and a P*-chiral phosphapalladacycle for the enantiomeric purity determination of α-amino acids.[365] ^{31}P NMR spectroscopy was also used in the enantiomeric excess determination of *N*,*C ortho*-palladated complexes of P-chiral phosphines.[366]

A ferrocene-based reagent (R_P,S_C,S_C,R_P)-(+)-$[Pd(\mu\text{-}Cl)\{[(\eta^5\text{-}C_5H_3)CHMeNMe_2]Fe(\eta^5\text{-}C_5H_5)\}]_2$ was successfully designed for the chiral recognition of β-hydroxyphosphines and the discrimination of (±)-bis(diphenylphosphino)-1,1′-binaphthyl.[367]

8.05.5.11 Enantioselective Synthesis

P-chiral phosphines were obtained from the reactions of ligated phosphole ligands with dienophiles.[368–372] The phosphole ligands were bonded to N,C-palladacycles. Similar reactions of dienes were carried out with diphenylvinylphosphine and 2-diphenylphosphinofuran bonded to N,C-palladacycles.[373–375]

The synthesis of homochiral cyclopalladated complexes of (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline has been described.[376]

8.05.5.12 Insertion Reactions into Palladacycles

Lu and Malinkova researched the regio- and diastereoselective insertion of allenes into stable oxapalladacycles giving 3,4-dihydro-2H-1-benzopyrans.[377] The insertion of allenes into Pd–C bonds of cyclopalladated pyridine derivatives was studied giving novel cationic heterocycles (berberinium derivatives).[378]

An orthometallated complex was obtained from dibenzylamine and $Pd(OAc)_2$, subsequent reaction with NaBr gives a bridged dimer $[Pd(\mu\text{-}OAc)\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}]_2$ [379]Insertion reactions with alkynes were carried out. It is noted that double insertion can occur. Furthermore, reactions with Tl(acac), $PPh_3NH(CH_2Ph)_2$, and AgX were studied. Internal acetylenes can be inserted into orthopalladated α-methylbenzylamine.[380] Double and tri-insertion may occur depending on the alkyne.

The regioselectivity of insertion reactions of unsymmetrical ester-activated alkynes with *o*-benzylamine palladacycles was examined resulting in seven-membered palladacycles where the carboxylate group is preferentially located next to the phenyl group.[381] This substitution pattern can be reversed by using electron-deficient and/or coordinatively unsaturated palladium centers.

Diphenylacetylene can be inserted into the Pd–C bond of planar chiral cyclopalladated derivatives of ferrocene.[382] The use of stoichiometric amounts of diphenylacetylene leads to monoinsertion, whereas an excess results in double insertion. A [2.3.3] cyclazine was obtained from the reaction of dimethyl acetylenedicarboxylate into the Pd–C bond of an enantiomerically enriched cyclopalladated 8-ethylquinoline complex.[383] Concerted alkyne insertion takes place. Double insertion of diphenylacetylene into the Pd–C bond of a cyclometallated ferrocene-imine complex provides an *endo*-type nine-membered metallacycle.[384]

Insertion of carbenes (dichlorocarbene or diazoalkanes) into the Pd–C bond of four-membered azapalladacycles derived from *N*,*N*′-dialkyl-2-iodoanilines gives the respective 5-membered palladacycles.[385]

8.05.5.13 Catalysis with Palladacycles

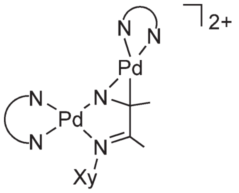
A large number of palladacycles have been applied as (pre)catalysts in C–C coupling reactions such as Heck and Suzuki reactions.[386–423] The subject has been recently reviewed.[424]

Evidence has been obtained for palladacycles being catalyst precursors for soluble Pd(0) species and/or Pd nanoparticles.[425–436] Palladacycles have been successfully employed as catalysts for alternating CO/alkene copolymerization.[437,438] They have been amenable to allylic substitution,[392] to oxygenation of unactivated sp^3 C–H bonds,[439] to allylic imidate rearrangement,[440,441] and to oxidation of alcohols to aldehydes and ketones.[442]

8.05.5.14 Three-membered Palladacycles

A novel dipalladium complex **145** containing a three-membered NC-palladacycle was synthesized by Owen *et al.*[443]

Three-membered thiopalladacycles **146** with X = Br, Cl were synthesized via insertion of alkenyl sulfides into a Pd–aryl bond.[444] Subsequent reaction with Br_2 and PPh_3 were studied as well as the decomposition of these complexes at elevated temperatures.



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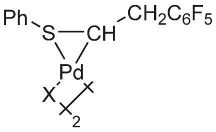
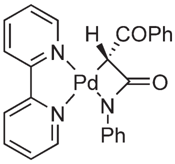


146

Lu and Peters studied the amine activation process mediated at a zwitterionic Pd(II) center which included the synthesis of a series of three-membered N,C-palladacycles.[445]

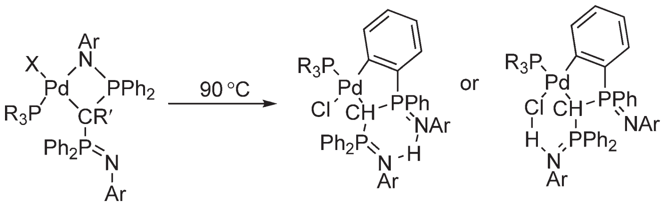
8.05.5.15 Four-membered Palladacycles

The cyclometalation of 2-benzoylacetanilide results in the formation of a four-membered palladalactam **147**.[446] The ring of the bipy palladium complex is almost planar.



147

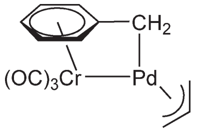
Metal-induced tautomerization and orthopalladation was found to occur in the reaction of bis(iminophosphoranes) with palladium(II) dichloride.[447] Four-membered Pd-N-P-C palladacycles, for example, **148**, were obtained from the reaction of sodium bis(*n*-aryliminophosphoranyl)alkanides with $[Pd_2X_4(PR_3)_2]$. At elevated temperatures, **148** converts into rare *C*,*C*′-palladacycles **149** and **150** (Scheme 22).[448] Although strictly speaking not a four-membered



148 **149** **150**

Scheme 22

metallacycle, α-palladated (η^6-alkylarene) tricarbonylchromium complex **151** containing a palladium–chromium bond has been included here,[449] its structure, dynamic behavior in solution, and cross-coupling reactions were studied by Moiseev *et al.*



151

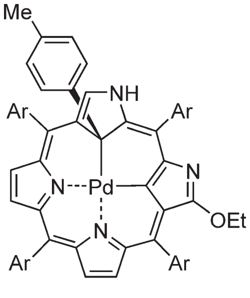
The lithium salt Li(thf){($C_6H_3Pr^i{}_2$)NC(Me)CHPPh_2($NC_6H_3Pr^i{}_2$)} reacts with [PdCl$_2$(NCPh)$_2$] giving [PdCl{($C_6H_3Pr^i{}_2$)-NC(Me)CHPPh$_2$($NC_6H_3Pr^i{}_2$)}(PPh$_3$)] in which the phosphinimine is *N,C*-bound.[450] A structural study is reported and the implications of the ligand in olefin-polymerization catalysts is discussed.

Four-membered azapalladacycles were described by Solé *et al.*[451]

8.05.5.16 Palladacycles Derived from Porphyrin Analogs

Pd(OAc)$_2$ and an "inverted porphyrin" (meaning one of the pyrrolic rings being inverted) yield an inner C-tolyl substituted Pd^{2+} complex **152** in toluene.[452] The X-ray structure was obtained. The possibility of a Pd^{3+} intermediate has been suggested in the formation of this compound.

The organometallic chemistry of carbaporphyrinoids or azuliporphyrins has been studied by Lash *et al.* resulting in complexes such as **153** and **154**.[453–455] The electrochemistry of these complexes was studied, and UV–VIS, X-Ray, and NMR spectroscopic studies were undertaken.



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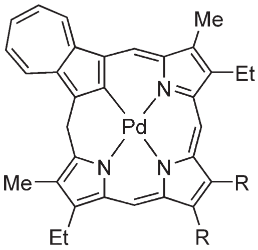
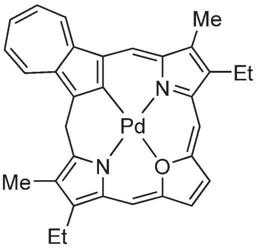


153



154

8.05.6 Palladium(IV) Complexes

The existence of organopalladium(IV) complexes, in particular triorganopalladium(IV) species, has been invoked as intermediates in carbon–carbon bond-formation reactions involving dimethyldiphosphinepalladium(II) compounds and iodomethane by Milstein and Stille as early as 1979.[456]

Stable triorganopalladium(IV) compounds containing exclusively phosphines as the ancillary ligands have still not been isolated, although several such species have been proposed.[457] Apart from a few cases, these mostly relied on speculations; several cases of organopalladium(IV)-phosphine compounds initially claimed, proved later to have been erroneously interpreted. However, complexes with one phosphine ligand in the presence of other ancillary ligands are currently known.[458–460]

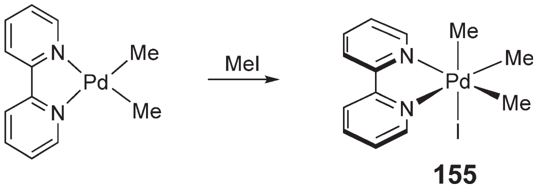
The field of (tri)organopalladium(IV) compounds has been opened by Canty and co-workers in 1986 with the synthesis, isolation, and characterization of $[PdIMe_3(bpy)]$.[461] After this finding, many other (similar) di- and triorganopalladium(IV) compounds have followed, several of which have already been described in the previous edition of this series.[2]

8.05.6.1 Palladium(IV) Complexes with Bidentate Nitrogen Ligands

The archetypical triorganopalladium(IV) compound [*fac*-$PdIMe_3$(bpy)] **155**, obtained from oxidative addition of MeI to $[PdMe_2(bpy)]$ (Scheme 23), has been known for two decades.[461] Similar compounds $[PdXR_3(N_2)]$, based on simple and more sophisticated bidentate N-ligands, have been characterized and isolated since. Such triorganopalladium(IV) compounds are generally obtained by oxidative addition of an organic halide to a dialkyl- or methyl(aryl)palladium(II) complex containing the specific bidentate *N*-ligand $[PdR^1R^2(N_2)]$. Early work has been reviewed.[462] The mechanism of the formation of **155** has been investigated in detail by high-pressure stopped-flow UV–VIS studies.[463] The observed negative activation volume for this reaction supports the validity of the S_N2 mechanism proposed earlier and the numerical values for the obtained second-order rate constants are in close agreement.[464] The reductive elimination of ethane from **155** was also studied by high pressure;[463] the positive activation volumes obtained both in the presence and absence of added NaI show a large volume increase, pointing to a considerable bond cleavage in the transition state. The methyl group transfer from Pd(IV) to Pd(II) centers was discussed in a review on mechanisms of d^8 organometallic compounds involving electrophiles and intramolecular assistance.[465]

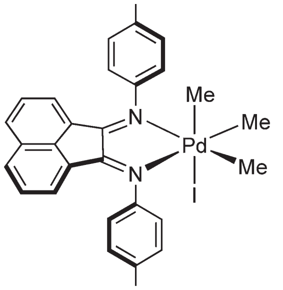
Triorganopalladium(IV) complexes [*fac*-$PdIMe_3$(*p*-Tol-bian)] **156**, [$PdBrMe_2(CH_2Ph)$(*p*-Tol-bian)] **157**, and [*fac*-$PdXMe_3$(Ph-bic)] **158** with the rigid bidentate N-ligands Ar-bian and Ph-bic ligands, respectively, have been isolated and characterized.[466] Complexes **157** and **158** were isolated as mixtures of two isomers. Especially, the Pd(IV) complexes of Ar-bian are rather stable.

Oxidative addition of diiodine to $[PdMe_2(NN)]$ gave [*cis,trans*-PdI_2Me_2(NN)] **159** for *p*Tol-bian and Ph-bic (the latter contained a small amount of the *cis,cis*-isomer), which could not be isolated.[466] Oxidative adition of $PhCH_2Br$ to [$PdMe_2$(*o,o′*-$Pr^i_2C_6H_3$-bian)] was much slower and gave [PdBrMe(*o,o′*-$Pr^i_2C_6H_3$-bian)]. Compounds **156–158** are quite stable in $CDCl_3$ solution; reductive eliminations obey first-order kinetics with rates between 10^{-5} and 10^{-4} s^{-1} at 20 °C. Reductive elimination from [*fac*-$PdIMe_3$(*p*-Tol-bian)] **156** took place to some extent by addition of chloroform to resulting [$PdMe_2$(*p*-Tol-bian)]. Compounds **157a, 157b** are more stable than **156**, and after a week at 20 °C a mixture of [$PdBrMe_2(CH_2Ph)$(*p*-Tol-bian)], [PdBrMe(*p*-Tol-bian)], and [$PdBr(CH_2Ph)$(*p*-Tol-bian)] in the ratio 40 : 35 : 25 was obtained.[466] The interplay between the (*ortho*)-substituents on the *N*-aryl substituent and the groups perpendicular to the plane decisively influences the addition–elimination equilibria, hence the relative stabilities of the Pd(II) relative to the Pd(IV) compounds. The rate of elimination was 7×10^{-5} s^{-1} at 50 °C leading to elimination of ethane and ethyl benzene in a ratio of 60 : 40, whereas there is a pronounced preference for ethane elimination in all other reported cases.[464]

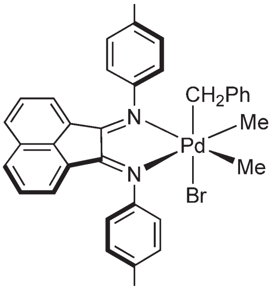


155

Scheme 23

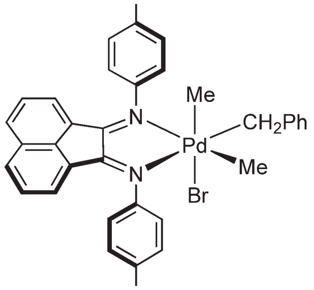


156

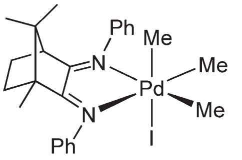


157a: 77%

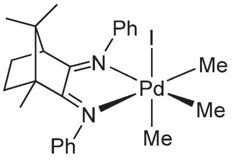
+



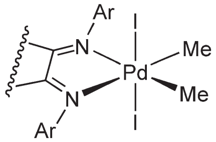
157b: 23%



158a: 54%

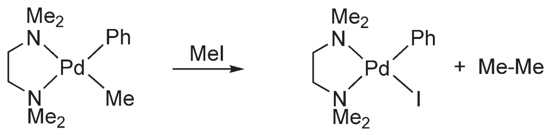


158b: 46%

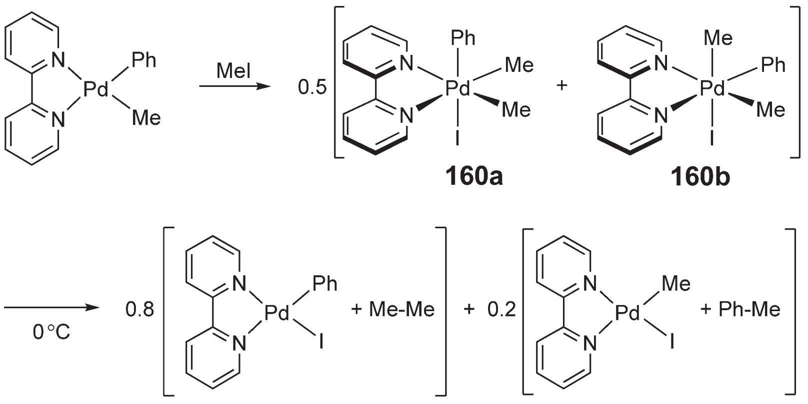


159

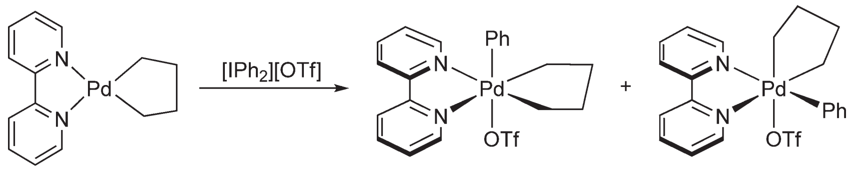
Phenyl- and arylpalladium(IV) complexes have been elusive. An excellent entry into this area has been attempted by adding MeI to [PdMe(Ph)(NN)]. In the case of NN = tmeda, only [PdI(Ph)(tmeda)] and ethane were obtained (Scheme 24); palladium(IV) intermediates were not observed.[467] However, for NN = bpy at 0 °C in acetone, two isomers of [PdIMe$_2$(Ph)(bpy)] were detected by NMR. At this temperature, reductive elimination to form ethane, toluene, and [PdI(R)(bpy)] (R = Ph, Me) is rapid (Scheme 25). [PdIMe$_2$(Ph)(bpy)] **160** and [PdIMe$_2$(CH$_2$Ph)(bpy)] (**161** and **162** X = I, Br) could be isolated by addition of pentane after cooling the reaction mixture to −60 °C.



Scheme 24

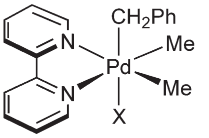


Scheme 25

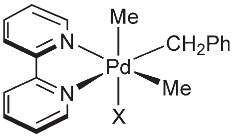


163a **163b**

Scheme 26



161a: X = Br
162a: X = I



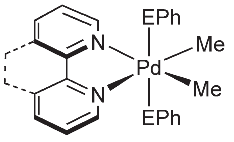
161b: X = Br
162b: X = I

Similar complexes have been attached to carbosilane dendrimers, by addition of organic halides to various generations of such dendrimers in which aryl groups at the periphery of the dendrimer (D_{Si}) have first been covalently C–Pd linked to a number of $Pd^{II}Me(bpy)$ fragments. This resulted, after oxidative addition of RX, in oligo- and polypalladium(IV)-functionalized carbosilane dendrimers D_{Si}-[Ar-$Pd^{IV}X(R)Me(bpy)]_n$ that have been analyzed by NMR.[468]

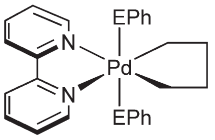
Transfer of aryl groups to palladium(II) centers with the formation of arylpalladium(IV) complexes has been established.[469,470] The first identified transfer of Ph^+ from diphenyliodonium(III) triflate (Scheme 26) to the metallacyclic complex $[Pd(C_4H_8)(bpy)]$ led to the formation of a new phenylpalladium(IV) bond, providing easy access to species such as $[Pd(OTf)C_4H_8(Ph)(bpy)]$ **163**. This elegant procedure features a model reaction for suggested reactions of C(sp^2)–X bonds with Pd(II) substrates.[389,471–473]

Pallada(IV)cyclopentane complexes can be obtained from oxidative addition of organic halides to known pallada(II)cyclopentanes at −20 °C in acetone. In this way, $[PdX(R)(C_4H_8)(bpy)]$ for R = Me, Et, $PhCH_2$, $CH_2{=}CH{-}CH_2$ **164–167** have been isolated and were fully characterized. For all cases reported, stereospecific *trans*-addition took place, except for MeI; **164a** and **164b** were obtained in a 1 : 4 ratio. Complexes **166** and **167** are stable at 20 °C, but **164** and **165** are unstable; these may be stored at −20 °C for a few days. A similar complex with R = CF_3 **168** was too unstable to permit isolation, but was identified by NMR.[474] Decomposition of the compounds gives a complicated mixture of products, depending on the group R (Scheme 27).

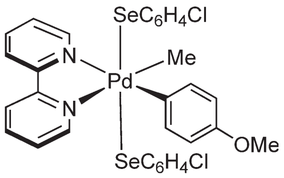
Diorganopalladium(IV) dichalcogenides have been synthesized by oxidative addition of $(PhE)_2$ (E = S, Se) to $[PdR_2(bpy)]$ and similar compounds, providing **169–171**.[475–478] The sulfur compounds were unstable and were observed by NMR. Complex **171** was in equilibrium with $[PdMe(C_6H_4OMe)(bpy)]$ and $(SeC_6H_4Cl)_2$; it is the major compound at low temperatures and can be isolated. An X-ray structure of **170** (E = Se) has been obtained.



169: E = Se, S



170: E = Se, S

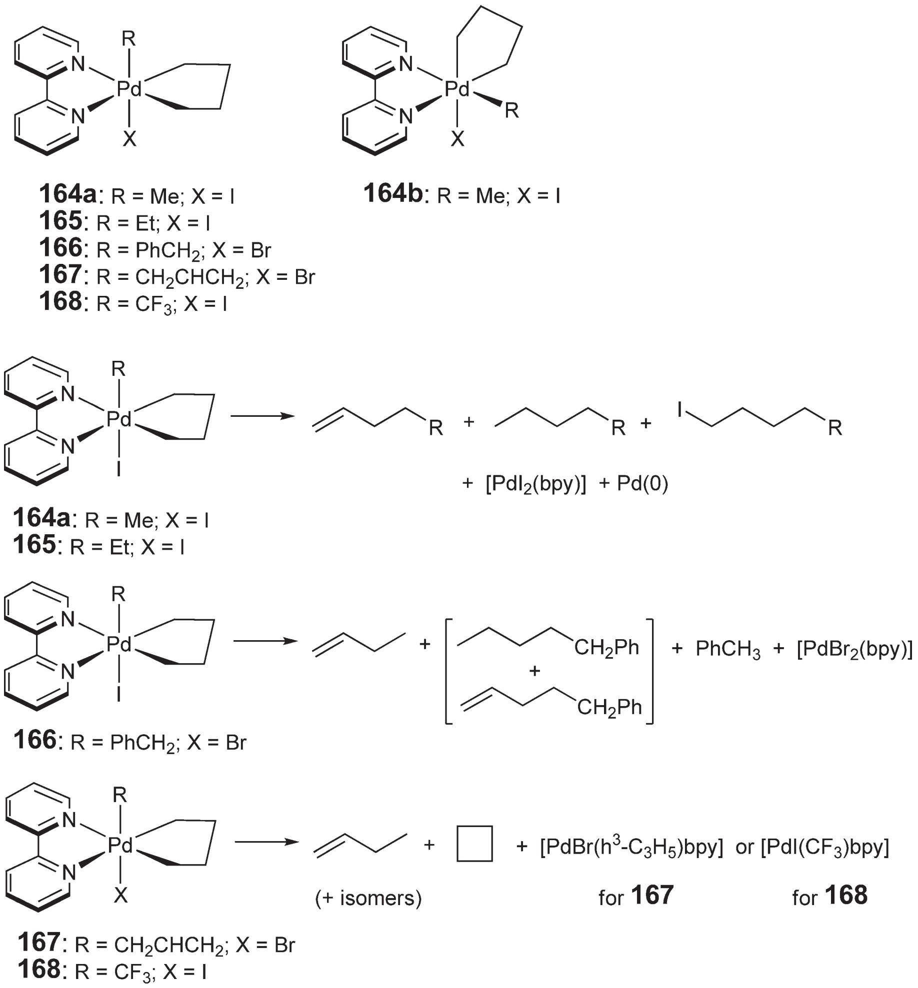


171

8.05.6.2 Palladium(IV) Complexes with Tridentate Nitrogen Ligands

Some complexes of bidentate N-ligands are also treated here because of their similar synthesis or direct connection with chemistry of palladium(IV) complexes with tridentate ligands.

Organopalladium(IV) complexes with tridentate N-ligands like tris(pyrazolyl)borate (pz_3BH^-, Tp) and tris(pyrazolyl)methane (pz_3CH) are ubiquitous and are often thermally quite stable. Reaction of $[PdMe_2(tmeda)]$,



164a: R = Me; X = I
165: R = Et; X = I
166: R = PhCH$_2$; X = Br
167: R = CH$_2$CHCH$_2$; X = Br
168: R = CF$_3$; X = I

164b: R = Me; X = I

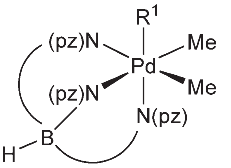
164a: R = Me; X = I
165: R = Et; X = I

166: R = PhCH$_2$; X = Br

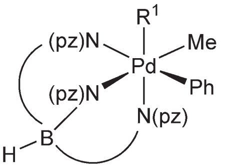
167: R = CH$_2$CHCH$_2$; X = Br
168: R = CF$_3$; X = I

Scheme 27

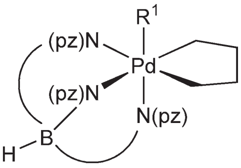
[PdMe(Ph)(tmeda)], and [Pd(C_4H_8)(tmeda)] with potassium tris(pyrazolyl)borate and organic halides in acetone leads to palladium(IV) compounds of the type *fac*-[PdMeRR′(Tp)] (R = Me, Ph; R′ = Me, Et, CH_2Ph, $H_2C–CH=CH_2$) **172–179** and similar *fac*-[Pd(C_4H_8)R′(Tp)] **180–183**.[479,480] Notably, these include triorganopalladium(IV) compounds with palladacyclopentane and/or an ethyl group that are at least as stable as ethylpalladium(II) complexes reported before. X-ray crystal structures of **172, 173** and of *fac*-[PdMe$_3$(pz$_4$B)] were obtained.[479,480] The X-ray crystal structure of the related *fac*-[PdMe$_3$(ind$_3$BH)] (ind = indazol-1-yl) was also obtained and theoretical studies of palladium and platinum analogs were carried out.[481]



172: R^1 = Me
173: R^1 = Et
174: R^1 = CH$_2$Ph
175: R^1 = CH$_2$CHCH$_2$



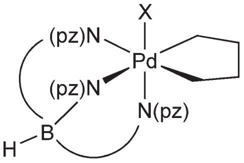
176: R^1 = Me
177: R^1 = Et
178: R^1 = CH$_2$Ph
179: R^1 = CH$_2$CHCH$_2$



180: R^1 = Me
181: R^1 = Et
182: R^1 = CH$_2$Ph
183: R^1 = CH$_2$CHCH$_2$

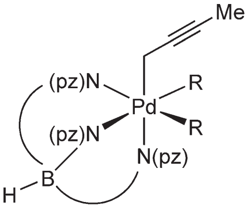
The first isolated palladium(IV) complexes with intramolecularly coordinated carbon ligands have been obtained from reaction of [PdMe(R)(bpy)] (R = Me, Ph) and K[PdMe(R)(pz_2BH_2)] (pz_2BH_2 = bis(pyrazolyl)borate) with 8-(bromomethyl)quinoline (mqBr). The complexes [PdMe(R)(mq)(bpy)]Br (R = Me, Ph), [PdMe(Ph)(mq)(pz_2BH_2)], [PdMe(Ph)(mq)(bpy)]BF_4,[482] [PdMe(CH_2CMe_3)(mq)(bpy)]Br, and [PdMe(CH_2SiMe_3)(mq)(bpy)]Br[483] contain a C,N bidentate coordinating 8-quinolylmethyl anion. The X-ray crystal structure of the latter has been described. The pallada(IV)cyclic complex [Pd(C_4H_8)(mq)(bpy)] has also been isolated. X-ray crystal structure analyses were reported for the phenylpalladium(IV) complex [PdMe(Ph)(mq)(pz_2BH_2)] which has *fac*-PdC_3 configuration with Ph *trans* to the quinolyl N-atom, and for [$PdMe_2$(mq)(pz_2BH_2)].[482] Similar neutral complexes [$PdMe_3$(pz_2BH_2)(L)] (L = py, PMe_2Ph) have been synthesized as well.[484]

Oxidation of a solution of K[Pd(C_4H_8)(Tp)], obtained from KTp and [Pd(C_4H_8)(tmeda)], with phenyliodonium dichloride, dibromine, or diiodine gave the relevant halo-diorganopalladium(IV) complexes *fac*-[PdX(C_4H_8)(Tp)] (X = Cl, Br, I) **184–186**.[485,486] Oxidation of [Pd] by water yielding organopalladium(IV) complexes has been observed for the first time.[479,485–487] Other oxidants like hydrogen peroxide also perform this oxidation. Hydroxo complex **187** forms adducts with aryl alcohols and the water complex **188** is also known. X-ray crystal structures have been obtained.[485,487]

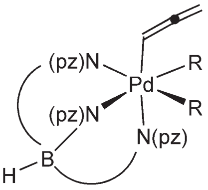


184: X = Cl
185: X = Br
186: X = I
187: X = OH
188: X = OH_2^+

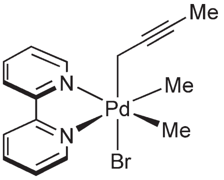
Triorganopalladium(IV) complexes [$PdBrMe_2$($CH_2C{\equiv}CR'$)(bpy)], [$PdBrMe_2$($CH{=}C{=}CH_2$)(bpy)], [PdR_2($CH_2C{\equiv}CR'$)(Tp)], [PdR_2($CH{=}C{=}CH_2$)(Tp)] **189–193** with a propargyl or allenyl moiety as well as two alkyl groups have been obtained in a series featuring the bidentate and tridentate N-ligands bpy and tris(pyrazolyl)borate as the ancillary ligand.[488] Generally, single structural isomers were obtained, but in the case of [$PdBrMe_2$($CH_2C{\equiv}CH$)(bpy)], a mixture of structural isomers was obtained. In most cases, the propargyl tautomer is favored in the case of the substituted alkyne terminus, whereas the parent system prefers the allenyl form,[488] although this may also be a function of whether the starting material is a propargyl rather than an allenyl halide.[83,489,490]



189: R = Me
190: R-R = C_4H_8



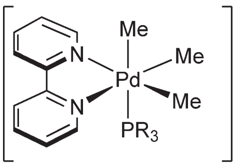
191: R = Me
192: R-R = C_4H_8



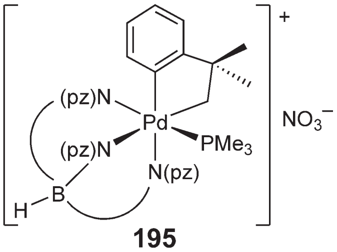
193

8.05.6.3 Palladium(IV) Complexes with Phosphine Ligands

The first triorganopalladium(IV) phosphine complexes have been obtained.[459] Addition of triphenylphosphine to [$PdIMe_3$(bpy)] in dichloromethane at −40 °C resulted in detection of about 10% of [$PdMe_3$(bpy)(PPh_3)]I. Stronger donor phosphines $PPh_{3-n}Me_n$ ($n = 1, 2$) led to 66% and 100% conversion. Avoiding presence of iodide as a competing ligand, reactions of methyl triflate with [$PdMe_2$(bpy)] followed by addition of $PPh_{3-n}Me_n$ gave pure [$PdMe_3$(bpy)($PPh_{3-n}Me_n$)]OTf **194**, one of which ($n = 1$) was authenticated by an X-ray crystal structure determination. Similar compounds have been obtained with PCy_3 and $P(OMe)_3$ and for PMe_2Ph with phen and tmeda as the bidentate N-ligands.[458] In an attempt at formation of *fac*-[$PdMe_3(P)_3$], the potentially *fac*-coordinating tridentate phosphine 1,5,9-triethyltriphosphacylododecane (Et_3[12]ane-P_3) was employed. This did not lead to substitution of the bidentate N-ligand, but gave stable phosphine [$PdMe_3$(bpy)(Et_3[12]ane-P_3)]OTf and [{$PdMe_3$(bpy)}$_2$(μ:κ^2-Et_3[12]ane-P_3)][OTf]$_2$ instead.[458] The diorganopallada(IV)cyclic phosphine complex **195** has recently been obtained by substitution of nitrate for PMe_3 in [Pd(ONO_2)($CH_2CMe_2C_6H_4$-*o*)(Tp)].[460]



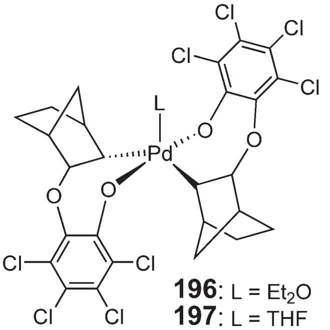
194



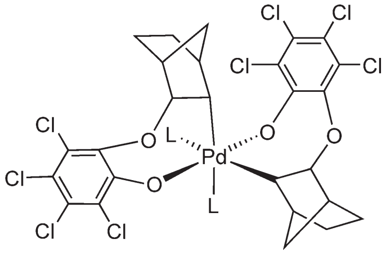
195

8.05.6.4 Other Palladium(IV) Complexes

In contrast to the synthetic approach to all known organopalladium(IV) complexes through (isolated) palladium(II) complexes, the dialkyl-dialkoxy-palladium(IV) compound **196** was formed in a single step from [$Pd_2(dba)_3$], norbornene, and *o*-chloranil.[491] Complexes **197** and **198** were obtained from **196** by treatment with THF or pyridine, respectively. The coordination number seems to depend on the basicity of the monodentate donor molecules; **196** and **197** are five-coordinate but **198** is distorted octahedral, as confirmed by X-ray structures of the latter two. The palladaspirocycle fragments have C_2 symmetry.

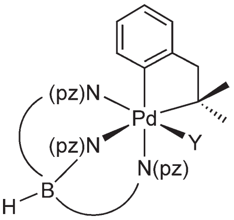


196: L = Et_2O
197: L = THF



198: L = py

The first silylpalladium(IV) compound [Pd{*o*,*o*′-$(SiH_2)_2C_6H_4$}$_2$(dmpe)] has been obtained from [$PdMe_2$(dmpe)] and *o*,*o*′-$(H_3Si)_2C_6H_4$, presumably through [$PdHMe_2$(HL)(dmpe)] and [PdHMe(L)(dmpe)] (H_2L = *o*,*o*′-$(H_3Si)_2C_6H_4$) and the X-ray crystal structure of [Pd(*o*,*o*′-$(SiH_2)_2C_6H_4)_2$(dmpe)] has been reported.[492] Nitrosyl-, nitro-, and nitrato-pallada(IV)cyclic complexes [Pd(CH_2CMe_2-C_6H_4-*o*)(κ^3-Tp)Y] (Y = NO, NO_2, ONO_2) **199–201** have been obtained from [Pd(CH_2CMe_2-C_6H_4-*o*)(κ^2-Tp)].[460] Spectroscopic analysis led to assignment of the bent Pd–NO geometry to the NO complex **199**, hence formulation as a Pd(IV) complex. Reaction of **201** with PMe_3 gave substitution of the nitrate to give [Pd(CH_2CMe_2-C_6H_4-*o*)(κ^3-Tp)(PMe_3)]NO_3.

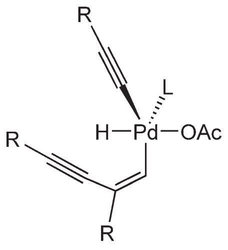


199: Y = NO
200: Y = NO_2
201: Y = ONO_2

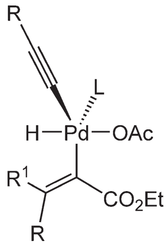
8.05.6.5 Palladium(IV) Complexes as Intermediates in Synthesis and Catalysis

Many reactions have been reported in which undetected palladium(IV) species are discussed as possible intermediates.[45,88,96,122,389,471–473,493–495] Organopalladium(IV) intermediates probably occur in a range of (catalytic) synthetic reactions involving oxidative addition-reductive elimination sequences.[496–503] In several cases, intermediates have been well characterized, for example, by NMR and with reference to authenticated structures of organopalladium(IV) compounds with similar spectroscopic data.

Palladium-catalyzed trimerization of alkynes has been developed,[504] but simple terminal alkynes undergo dimerization to form enynes.[505,506] A mechanism for the formation of head-o-tail enynes has been proposed that proceeds through palladium(IV) complexes 202 or 203.[45,494] Probably, however, the acidic terminal alkyne will cleave the palladium–alkenyl bond to give the enyne product and an alkynylpalladium(II) species that can enter a new catalytic cycle instead.[46]

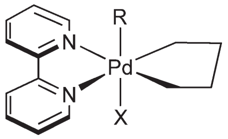


202

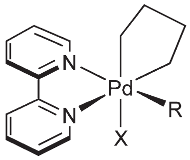


203

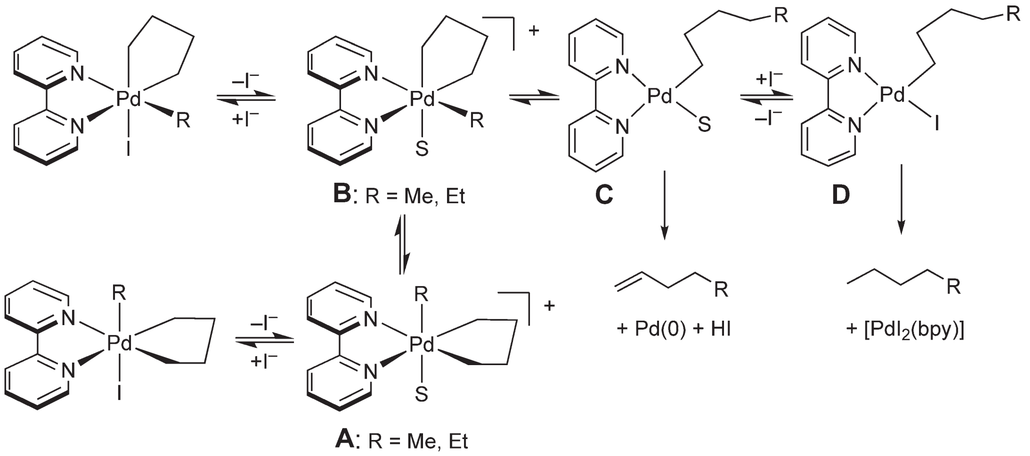
Decomposition of palladacyclopentane complexes 204–208 in CD_2Cl_2 involves initial halide dissociation to give unstable five-coordinated (or solvated six-coordinated) complex cations. The solvento isomers A and B (Scheme 28) are expected to be in equilibrium since similar complexes show fluxional behavior at low temperatures. Reductive elimination is expected to occur from B preferentially to give C, from which formation of all products is readily explained.[474]



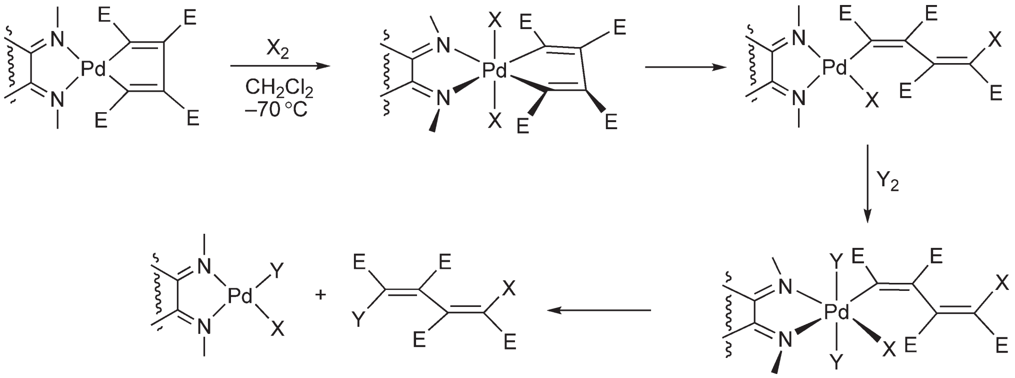
204a: R = Me; X = I
205: R = Et; X = I
206: R = $PhCH_2$; X = Br
207: R = CH_2CHCH_2; X = Br
208: R = CF_3; X = I



204b: R = Me; X = I

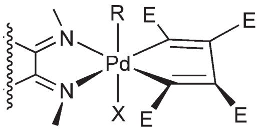


Scheme 28

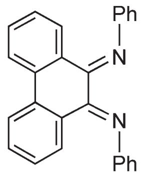


Scheme 29

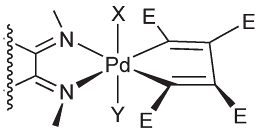
The palladium-catalyzed three-component synthesis of conjugated dienes from electron-poor alkynes, an organic halide, and organotin reagent most probably proceeds through organopalladium(IV) intermediates like **209–211**, with the ligand as **212**.[72,73,122] Stereospecific reactions of dihalogens with palladacyclopentadiene complexes lead to 1,4-dihalo-1,3-dienes via [PdX$_2$(CE=CE-CE=CE)(NN)] **213–215**. Several of the intermediate Pd(IV) complexes have been observed by NMR at −90 °C. DFT calculations at the B3LYP level carried out on model systems have shown the energetic feasibility of a sequence of oxidative addition of dihalogens to a Pd(II) cycle, generating an organopalladium(IV) species, followed by stereospecific reductive elimination.[507] This is then followed by a similar sequence on the resulting [PdX(CE=CE-CE=CE-X)(NN)] complex according to Scheme 29.



209: NN = bpy
210: NN = Ar-bian
211: NN = Ph-bip **212**
E = CO$_2$Me, CF$_3$
R = PhCH$_2$; X = Br
R = Me; X = I



212



213: NN = bpy
214: NN = Ar-bian
215: NN = Ph-bip
E = CO$_2$Me, CF$_3$
X = Y = Cl, Br, I
X = Cl; Y = Br, I

The possible involvement of Pd(IV) intermediates in catalytic Heck reactions has been put forward by several authors and a considerable debate has developed.[386,388,394,431,472,508–514] All experimental evidence obtained so far seems to speak against a Pd(II)/Pd(IV) mechanism and for a sequence involving only Pd(0) and Pd(II). The subject has been very well reviewed recently.[424]

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8.06
Palladium–Carbon π-Bonded Complexes

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8.06.1 Introduction

This chapter collects developments in the chemistry of palladium complexes with carbon π-bonded ligands since the publication of COMC (1995). It is organized in sections according to the type of ligand, and subheadings vary through the chapter to ensure the most convenient presentation of the contents of each section. The readers are referred to the previous works, COMC (1982) and COMC (1995), for essential information about the chemistry of palladium with carbon π-bonded ligands preceding the research reported here.

Palladium chemistry with alkene, alkyne, and enyl ligands has deep implications for palladium-catalyzed organic syntheses and in polymer chemistry. The importance of these catalytic reactions is enormous, and new developments and applications appear every year. In recent years, a great impulse has been given to the fields of alkene polymerization,[1] co-polymerization of alkenes with CO,[2] and the Heck reaction.[3] New improvements in the application of Pd catalysis to organic synthesis have been achieved. Recent reviews have appeared on the synthesis of heterocycles,[4,5] functionalization of allenes,[6] and enantioselective transformations.[7] In most of these processes, palladium complexes with carbon π-bonded ligands are generated as intermediates and transformed to the target compounds. However, these will not be included in this chapter, and only isolated or well-characterized complexes and their reactivity will be discussed here. Palladium-catalyzed reactions and their mechanisms are dealt with in other volumes of this work (Volumes 10 and 11).

Ligands that contain carbon and other heteroatoms π-bonded to palladium are few, and are not included in this chapter. However, it is worth mentioning the first palladium complex with π-bonded CO_2, $Pd(\eta^2\text{–}CO_2)(PMePh_2)_2$, which was synthesized recently.[8] Palladium complexes with π-bonded carbaboranes have also been reported but will not be treated here. Their structures show that the metal is always slipped away from carbon and closer to boron.[9,10]

8.06.2 π-Complexes of Alkenes

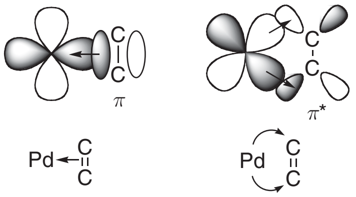
8.06.2.1 General Comments

It is well known that the interaction M–alkene, described by the Dewar–Chatt–Duncanson model (see COMC (1982)), consists of a donation of electron density from an olefin π-orbital to the metal and a backdonation from the metal to an empty π^*-orbital of the alkene (Scheme 1).

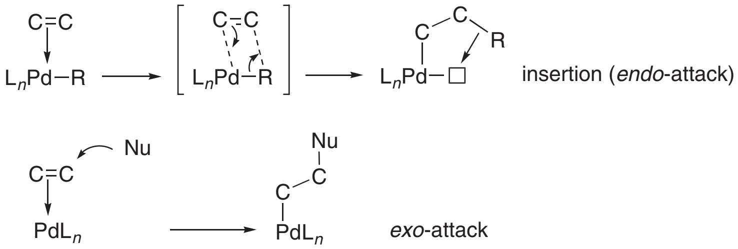
Metals in low oxidation states such as palladium(0) will enhance the backdonation component of the bond, and this is particularly important in the case of olefins with electron-withdrawing groups. The chemistry of stable palladium(0) alkene complexes is thus dominated by this type of olefin and a fairly large number of them have been synthesized in the last 12 years. In addition, the chelate effect favors coordination of chelating alkenes over similar monodentate systems, because of the stabilizing entropy contribution.

In the case of palladium(II), the stabilization of the filled 4*d*-orbitals is high, and the importance of backdonation to the olefin is very much diminished. It is the donation of the π-orbitals of the olefin to the metal, the chelate effect (for chelating ligands), and the strain release for strained alkenes, that are the factors mainly responsible for the stabilization of the palladium–olefin bond. In other words, the dominant character of the metallic center, when coordinated to olefins, changes from π-nucleophilic palladium(0) to σ-electrophilic palladium(II). This does not mean, however, that backdonation to the π^*-orbital of the olefin does not play any role. On the contrary, as discussed in Section 8.06.2.3, it is considered an important factor for the stabilization of five-coordinated palladium (and platinum) complexes.

In the donor–acceptor interplay, the Pd(II)-coordinated olefin becomes activated toward attack by nucleophiles (*exo*-attack). Moreover, the olefin can insert into Pd–C and some other Pd–X bonds (*endo*-attack) (Scheme 2). These



Scheme 1



Scheme 2

two types of olefin activation are the basis of many stoichiometric and catalytic reactions and their fundamental aspects have been discussed in detail.[11,12] The immediate product of these attacks is a σ-bonded Pd–C compound, which can either be stable as a coordinated alkyl, or be stabilized in the form of enyl compounds (η^3-allyl or σ,η^2-enyl), or further transformed to organic products. Examples of these reactions can be found in Sections 8.06.6.2 and 8.06.6.5 in this chapter or Chapter 00103 of this work. The activation that palladium(II) exerts on the alkene toward further reactions implies that the number of palladium(II) alkene complexes stable enough to be completely characterized are few. In consequence, it should be kept in mind that the number of reported palladium(II) alkene complexes is not a good measure of the importance of this type of compound in the chemistry of palladium, particularly in catalysis.

8.06.2.2 Alkene Complexes of Pd(0)

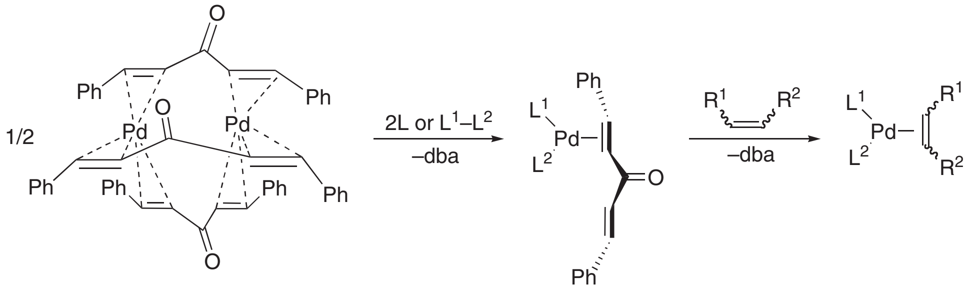
Modern crystallographic facilities and the higher rate of data acquisition, which reduces the problem of compound decomposition, are reflected in a large number of structural studies of Pd(0)–alkene complexes in the period 1993–2004. The dominance of the factors affecting stability, commented upon in Section 8.06.2.1, is particularly evident in looking at the new reports on isolated or detected Pd(0)–olefin complexes, and at the structural determinations carried out. For the same reason of stabilizing higher the complexes, mechanistic studies often use acceptor olefins. We will see later that the use of chelating olefins becomes dominant in the chemistry of palladium(II).

The most frequently encountered kind of complex is Pd(chelate)(olefin), with *P*,*P*- or *P*,*N*-chelates and a strongly π-acceptor olefin such as fumarodinitrile, tetracyanoethylene, maleic anhydride, 1,4-benzoquinone, etc. There are many cases where the olefin is dibenzylideneacetone (dba), and this is for three good reasons.

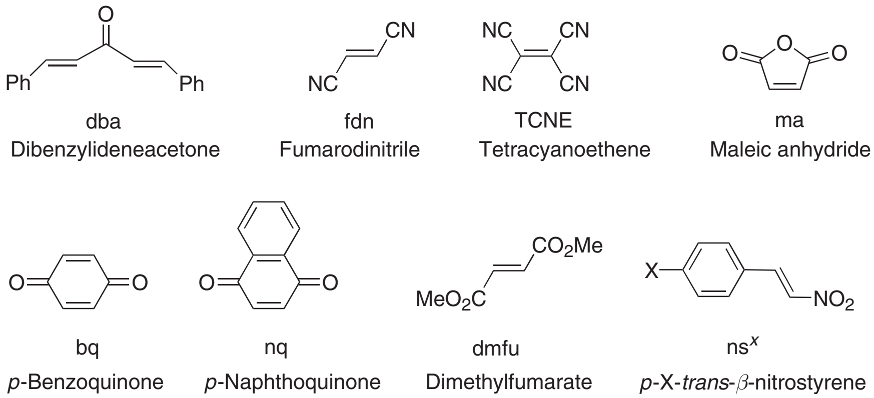
(i) The palladium(0) complex $Pd_2(dba)_3$ is the most used precursor to other Pd(0) complexes.
(ii) Pd(chelate)(dba) complexes are good precursors to other olefin complexes because, as a ligand, dba is bulkier and a weaker acceptor than other olefins used in this chemistry, and behaves as a comparatively labile ligand for Pd(0) in substitution reactions.
(iii) In catalytic applications of Pd(chelate)(olefin) complexes, it is convenient to have one labile ligand on Pd, while the others (often a *P*,*P*- or *P*,*N*-chelate) stabilize species throughout the catalytic cycle. The structure of $Pd_2(dba)_3.CH_2Cl_2$ has been determined again in this period, with better experimental data than for previous determinations, and discussed in close detail.[13]

The preparation of Pd(L^1–L^2)(olefin) (L^1–L^2 = 2L or L^1–L^2 = chelate ligand) complexes is commonly carried out starting from $Pd_2(dba)_3$ by the sequence of reactions drawn in Scheme 3 (particular cases will be presented later).

All complexes share some common features. The coordination geometry of palladium in these complexes is basically trigonal planar, with usually small deviations from the ideal structure (<10° dihedral angle for the C–Pd–C and the L^1–Pd–L^2 planes) due to packing forces, or imposed by crowding with the chelating ligands. The C–Pd–C angles are necessarily small (about 40°) in spite of the elongation of the C–C bond upon coordination, and the L^1–Pd–L^2 angles are those naturally determined by the chelating ligand or by the space requirements of the two monodentate ligands. These are often close to 90°. These data are consistent with an important backdonation from Pd to π^*-(empty) orbitals of the olefin. In other words, participation of the pallada(II)cyclopropane resonance form has



Scheme 3



Scheme 4

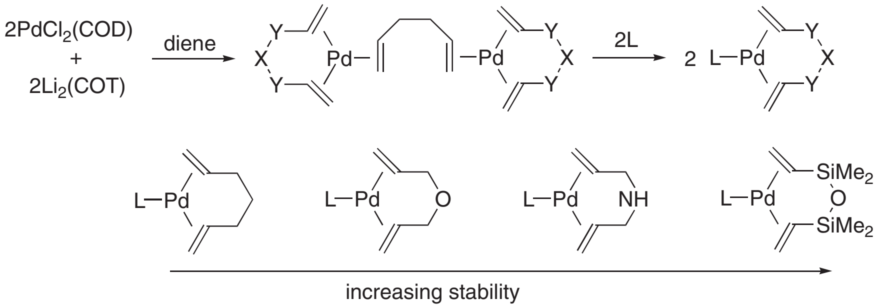
to be taken into account to explain the structure and properties of these complexes with electron-withdrawing substituted olefins. For extremely sterically demanding ligands, the olefin can be lost to afford formally, or actually, dicoordinated palladium(0) complexes PdL_2 or $PdL(\eta^2\text{-olefin})$.

The structures and abbreviations of the most used olefins are given in Scheme 4.

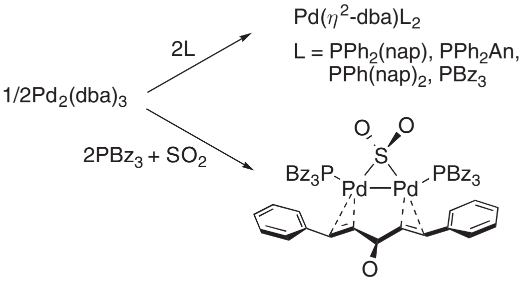
It should be noted that the method of synthesis in Scheme 3 is not universal as the reactivity of $Pd_2(dba)_3$ is moderate. For the use of Pd as catalyst, it is very common to work with mixtures of $Pd_2(dba)_3$ with monodentate or bidentate ligands to prepare the catalyst *in situ*, but for some purposes, alternative methods are needed. Complexes where dba is substituted by weaker acceptor diolefins have been introduced, although not much exploited so far. These complexes, utilizing 1,6-diene ligands (see ligands in Scheme 5), are more difficult to prepare and less stable, but much more reactive than the classical $Pd_2(dba)_3$,[14,15] and more stable and easy to handle than $Pd(COD)_2$ or $Pd(C_2H_4)_3$. They are prepared according to the procedure sketched in Scheme 5 and offer a gradation in stability and (in the reverse order) reactivity as a function of the diene ligands. The molecular structure of the molecule Pd(diallyl ether)(PPh_3) shows a chelate diallyl ether, and the $C{=}C$ distances (mean 1.38 Å) are only slightly lengthened as compared with an uncoordinated double bond (1.34 Å). This indicates poor backdonation, which produces a weak bond responsible for the high reactivity of the molecules.

The latter precursors fail, however, in the preparation of palladium(0) complexes with monodentate ligands of strong donor character such as pyridine or an amine. These can be stabilized only when associated with an acceptor olefin such as ma. Starting with Pd(nbd)(ma),[16] complexes of the type $PdL_2(\eta^2\text{-ma})$ (L = pyridyl (py), $EtNH_2$, $PhNH_2$, NH_3, SMe_2; L_2 = 1,6-heptadiene, TMEDA) can be prepared (nbd = norbornadiene).[17] The structure of the complex with L = py has been determined by X-ray diffraction methods.

The reduction of palladium(II) complexes (often with $Li_2(COT)$) in the absence of other ligands is an experimentally demanding but convenient and fairly general method for the preparation of palladium(0) complexes with olefins, and was used to prepare a complex with methylacrylate (MA), $Pd(dppf)(\eta^2\text{-MA})$, from $PdCl_2(dppf)$, $Li_2(COT)$, and MA.[18]



Scheme 5

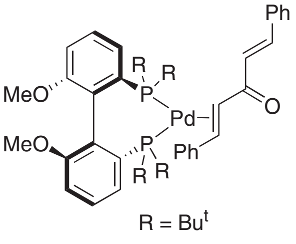


Scheme 6

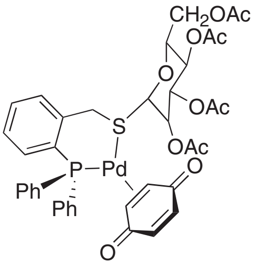
Using the protocol in Scheme 3, complexes Pd(P–P)(η^2-dba) (P–P = dppe, 1,3-diphenylphosphinopropane(dppp), *o*,*o*′-bis(CH_2PPh_2)-binaphthyl) and $Pd(PR_3)_2(\eta^2$-dba) (R = Ph, Cy) are prepared easily. The complex with dppe has been characterized by X-ray analysis. As a typical case, some structural parameters are: C═C distance (coordinated double bond) = 1.407 Å; Pd–C distances (to coordinated double bond) = 2.143 and 2.135 Å; C–Pd–C angle = 38.4°; P–Pd–P angle = 87.19°. The complexes showed high reactivity and underwent oxidative addition of CHX_3 (X = Cl, Br) with cleavage of one C–X bond to give palladium(II) complexes.[19] Similar complexes Pd{$(R_2PCH_2)_2$NMe–*P*,*P*}(dba) (R = Cy, Ph) have been prepared and the X-ray structure for R = Ph has been determined.[20]

The method can be applied to bulky monodentate phosphines (Scheme 6: L = PPh_2Np, PPh_2An, $PPhNp_2$, PBz_3; nap = 1-naphthyl; An = anthracenyl; Bz = benzyl).[21] The structure of the complex for L = PPh_2(nap) was determined, confirming the formulation (a correction of the space group assignment of this structure has been recently published).[22] When the reaction was carried out for L = PBz_3 in the presence of SO_2, a dinuclear complex $Pd_2(\mu$-dba)(μ-SO_2)$(PBz_3)_2$ having the two palladium atoms bridged by one SO_2 and one dba molecule was crystallized. The Pd–Pd distance is 2.885 Å, suggesting bonding interaction.[21]

Complexes with a chiral *P*,*N*-(oxazoline) ligand and olefins (L–L′ = (*S*,*R*)-2–[4-(isopropyl)oxazol–2-yl]–2′-diphenylphosphino–1,1′-binaphthyl; olefin = η^2-dba, fumaronitrile, maleic anhydride) have been prepared. The dynamic behavior of the complexes in solution and their catalytic performance in enantioselective allylic amination/alkylation have been studied.[13] Other chiral ligands used were the P–P and P–S ligands shown in structures 1 and 2. The X-ray structures were determined for the *P*,*P*/dba 1 and for the *P*,*S*/benzoquinone 2 complexes. The latter shows the benzoquinone bonded clearly as an η^2-ligand, with equal distances of the two carbons to the Pd atom (3.138 Å) and a clear elongation of the coordinated C–C double bond (1.411 vs. 1.33 Å for the uncoordinated double bond). The complexes display interesting solution dynamics, studied by exchange spectroscopy.[23] A structure of an ma complex with a chiral phosphito thioether ligand, (*R*)-2-ethylthio-1-(phenylethyl)-(*R*)-binaphthyl phosphite, has been solved, and its solution behavior has been thoroughly studied, as well as for the homolog with pentenedione and fumaronitrile.[24]



1



2

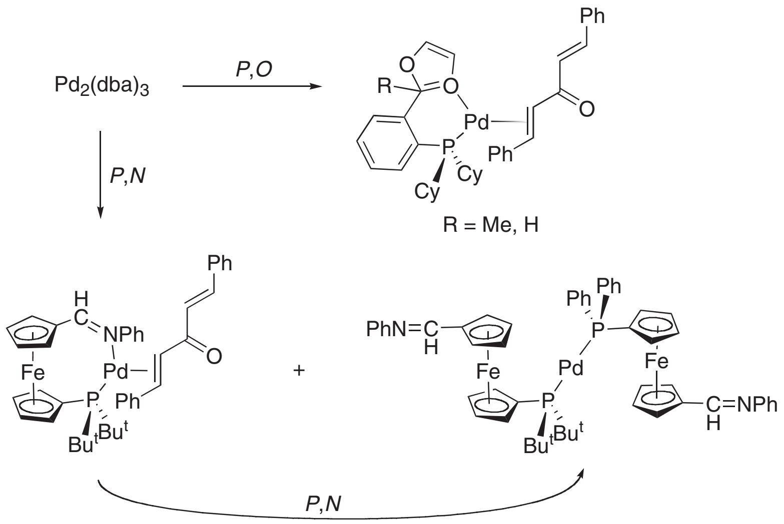
In the Pd(P–P)(η^2-dba) (P–P = $Pr^i{}_2PCH_2CH_2PPr^i{}_2$, $Cy_2PCH_2CH_2PCy_2$) complexes, the η^2-dba ligand adopts an *s-trans*,*s-trans*-conformation, confirmed by the crystal structure of the two complexes;[25] the crystal structure of the complex with $Cy_2PCH_2CH_2PCy_2$ has been solved again recently.[26] ^{1}H and ^{31}P NMR studies suggest facile intramolecular exchange of coordinated and uncoordinated C–C double bond and, at higher temperatures, facile interconversion between the predominant *s-trans*,*s-trans*-conformer and the minor *s-trans*,*s-cis*- and *s-cis*,*s-cis*-conformers. At variance with these observations on preferred conformation of dba, in the Pd(L–L)(η^2-dba) complexes obtained by coordination of *P*,*N*- or *P*,*P*-chiral chelating ligands derived from ferrocene, structural and NMR studies indicate that the dba ligand adopts preferentially an *s-cis*,*trans*-conformation, with the *s-trans*-double bond coordinated to Pd. This is the case in the crystal structure of the complex with L–L = 2-[1-(dimethylamino)ethyl]–1-(diphenylphosphino)ferrocene. The complexes showed a complicated fluxional behavior for which several dynamic processes were identified, including fast rotation around the alkene–Pd bond, Pd–N bond rupture, and, at elevated temperatures, intramolecular diastereoisomer interconversion involving alkene face exchange associated with interchange of coordinated and non-coordinated bonds of the dba ligand.[27]

The chiral (aminoferrocenyl)phosphine ligands derived from ferrocene (2-(1-(dimethylamino)ethyl)–1-(diphenylphosphino)–ferrocene and [η^5-cyclopentadienyl][η^5-4-(*endo*-dimethylamino)–3-(diphenylphosphino)–4,5,6,7-tetrahydro–1*H*-indenyl]iron(II) gave palladium(0) complexes with the electron-withdrawing olefins ma and dmf as a mixture of two diastereoisomers.[28] This is the case commonly encountered in closely related complexes.[29] On the other hand, a racemic mixture of the ligand *N*,*N*-dimethyl–1-[2,1′-bis(diphenylphosphino)–ferrocenyl]ethylamine (BPPFA), which could act as a *P*,*P*- or *P*,*N*-chelate, reacts with $Pd_2(dba)_3$ and dmf or ma to give the complexes Pd(BPPFA-*P*,*P*)(olefin) as a mixture of two diastereoisomers, which do not interconvert at room temperature on the NMR timescale. The structures were assigned by NMR and by X-ray diffraction for the major isomer of the complex with dimethyl fumarate. Variable-temperature studies suggested rearrangements via κ^3-*N*,*P*,*P*-BPPFA intermediates.[30]

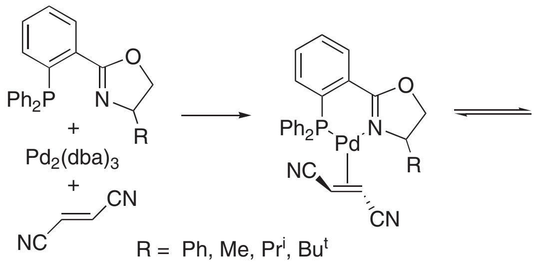
Two Pd(0) complexes have been identified as active catalysts in the efficient Suzuki–Miyaura coupling with aryl chlorides and characterized by X-ray diffraction. One is a dba complex with a *P*,*N*-chelate derived from ferrocene. The other is a 14-electron dicoordinated complex obtained in the presence of excess *P*,*N*-ligand (Scheme 7).[31] Also active in the same type of reaction is a *P*,*O*-ligand, which gives the complexes shown in the upper part of the scheme. A notable superiority as catalyst is found for R = Me, probably because it better stabilizes the catalyst.[32]

The unusually stable hydride complex [PdH(dtbpx)(MeOH)]Tf (dtbpx = 1,2-$(CH_2PBu^t{}_2)_2C_6H_4$) is a key intermediate in an industrial, highly selective methoxycarbonylation of ethene to methyl propanoate catalyzed by [Pd(dtbpx)(dba)]. In the course of the investigation of the mechanism of this transformation, an interesting cationic $[Pd(dtbpx)(dbaH)]^+$compound, involving protonation of dba, was obtained. Its homolog with Cy in place of Bu^t could be crystallized in the form $[Pd(dcpx)(dbaH)][MeSO_3][MeSO_3H][THF]_2$, and the crystal structure studied by X-ray diffraction. An elongation of the C═O bond of the dba from 1.244 to 1.348 Å is produced on protonation of the oxygen. The C═C distances are 1.426 to 1.342 Å for the coordinated and uncoordinated bonds, respectively.[33]

Fumarodinitrile, having C_2-symmetry, has been employed to study the diastereoselectivity of its coordination to complexes containing (dihydrophosphanylphenyl)oxazole ligands (Scheme 8), using X-ray diffraction (four structures were determined), NMR, and DFT methods, in order to understand selectivity in allylic substitution reactions.[34] It was found that the diastereomeric ratio depends on the bulk of the R group, trying to avoid repulsions of this group with the fdn ligand. The coordinated fdn is not planar, due to backdonation, and the C═C distances for the double



Scheme 7

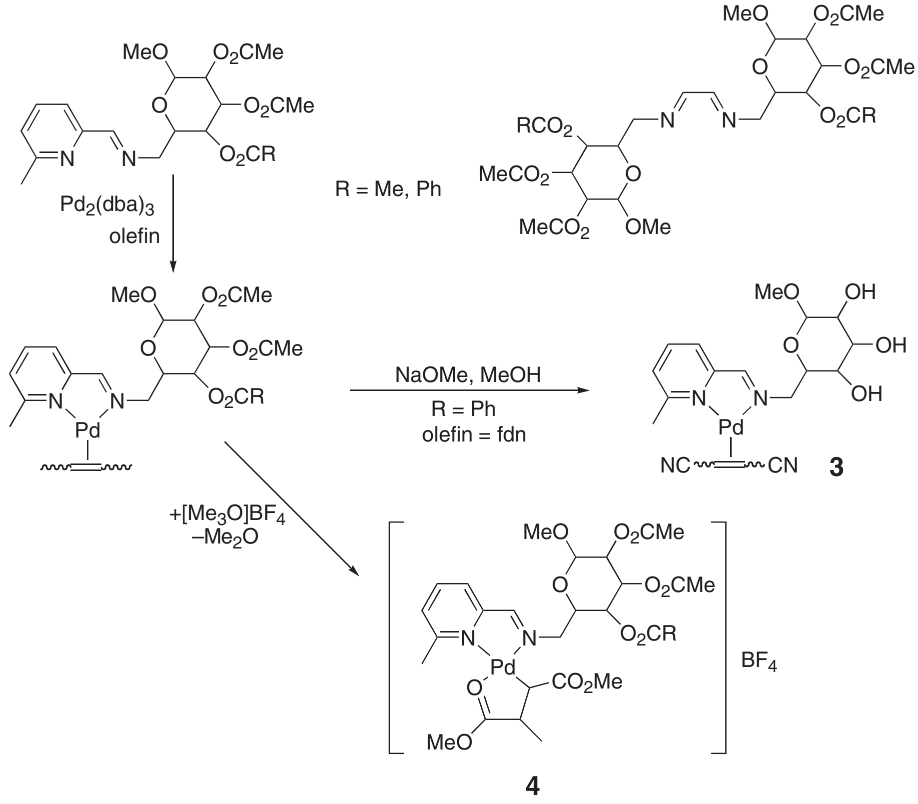


Scheme 8

bond lie in the range 1.438–1.450 Å. Similar compounds with dmfu in place of fdn have been studied,[35] as well as complexes with iminophosphine ligands $Ph_2PC_6H_4CH{=}NR$ ($R = C_6H_4OMe$-*p*, Bu^t, Me, bornyl).[36,37]

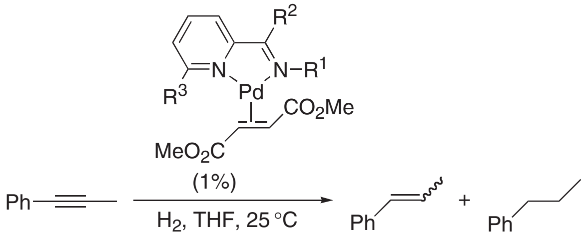
A related study of the enantioselectivity of coordination of the prochiral alkenes dmfu, fdn, and ma has been made with the chiral *N*,*N*-chelate ligands shown in the upper part of Scheme 9, derived from sugar residues. The symmetrical diazabutadiene ligand induces higher enantioselectivity than the pyridylimino ligand. An interesting water-soluble palladium(0) complex **3** was prepared by deprotection of the alcoholic functions of the sugar residue. It formed, as its parent derivative, as a 55 : 45 mixture of two diastereoisomers. The coordinated fdn in this complex showed a C–C bond distance of 1.38 Å and Pd–C distances of 2.05 and 2.04 Å.[38] Similar to a previous report on Pd(phen)(DMF),[39] $[Me_3O]BF_4$ reacts with the DMF complex in a process that produces a cyclometallated compound **4** through initial electrophilic attack of Me^+ to Pd(0) followed by insertion of DMF in the Pd(II)–Me bond formed. This reaction exhibited significant stereoselectivity, producing two diastereoisomers in a 75 : 25 ratio.

Zerovalent palladium complexes with the unsymmetric *N*,*N*-ligands 8-(2-pyridyl)quinoline, 8-(6-methyl–2-pyridyl)-quinoline, or *trans*-4,5-bis(2-pyridyl)norbornane and ma or fn have been obtained from $Pd_2(dba)_3$, the chelating ligand,



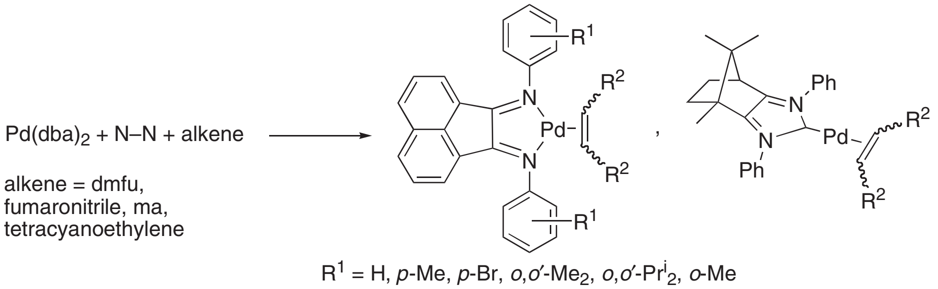
Scheme 9

and the olefin.[40,41] Complexes with ligands of the type pyridine-2-carbaldimine with dmfu have been synthesized and employed in the stereoselective hydrogenation of 1-phenyl-1-propyne (Equation (1)). The stability of the Pd(0) complexes for catalysis increases with the donor ability of the substituents and decreases with the steric bulk of the ligand.[42] The structure of the complex with $R^1 = Et$, $R^2 = Me$, and $R^3 = H$ was determined and showed a long C–C (double bond) distance (1.422 Å). A detailed discussion of this structure was made in comparison with other analogous complexes with aldimine and fumaronitrile.[38]



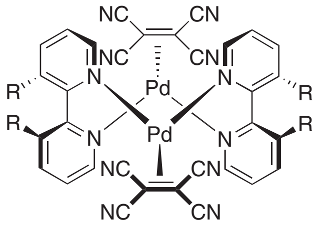
(1)

Complexes Pd(N–N)(η^2-alkene) (N–N = bis(arylimino)acenaphthene, Ar–BIAN; bisphenyliminocamphane, Ph–BIC;[43] *N*,*N*′-diphenyl–1,7,7,-trimethylbicyclo[2.2.1]-heptane–2,3-diimine;[44] see Equation (2)) are easily obtained by reaction of $Pd(dba)_2$ with the corresponding N–N chelate and alkene ligands. Two crystal structures were determined, both with similar features. For instance, the crystal structure of the Ar–BIAN complex with Ar = *o*,*o*′-$Pr^i{}_2C_6H_3$ and olefin = ma shows a long C═C distance (1.408 Å) of the coordinated double bond of ma, which suggests a Pd(II) metallacyclopropane structure. However, the reactivity supports better a Pd(0)–alkene complex. Mechanistic studies of olefin substitutions in zerovalent palladium complexes have been carried out on these complexes. The results support the conclusion that substitution occurs via a fast associative mechanism for the less hindered complexes with Ar–BIAN (Ar = Ph, *p*-Tol), but via a slower dissociative mechanism for Ar = *o*,*o*′-$Pr^i{}_2C_6H_3$. Substitution of the less hindered by the more hindered N–N ligand can also be induced, and occurs with initial dissociation of the alkene. The barriers for rotation of the olefin around the alkene–Pd bond were in the range 50–69 kJ mol^{-1}.



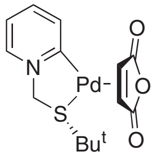
(2)

For N–N = 3,3′-dicarbomethoxy-2,2′bipyridine, the steric hindrance of the substituents hinders the pyridine from being coplanar, and the ligand cannot behave as bidentate chelate. A dimeric palladium(0) compound **5** with TCNE and the bipyridine ligand bridging the two Pd centers has been studied.[45]



5

For the olefin substitution in complexes Pd(N–N)(η^2-alkene) (N–N = 2-$NC_5H_4CH{=}NC_6H_4{=}Me$-4)[46] and Pd(N–S)(η^2-alkene) (N–S = 1-(CH_2SR^1)–5-R^2–pyridine; R^1 = Me, Et, Pr^i, Bu^t, Ph; R^2 = H, Me; olefin = nq, fn, tetramethyl ethylenetetracarboxylate, ma, TCNE),[47] the kinetic parameters indicate an essentially associative mechanism. Two crystal structures studied for the latter 6 and 7 are a good example of the modes of coordination of ma and TCNE. In complex 6, the ma ligand is virtually planar and makes a dihedral angle of 78.5° with the mean coordination plane of Pd. The C═C double bond distance is 1.413 Å. For Pd(N–S)(η^2-TCNE), the C═C bond lies in the coordination plane, and the TCNE is not planar, as the CN substituents are bent away from Pd. The two NC–C–CN planes make a dihedral angle of 127.7° and the C–C double bond distance is 1.48 Å, longer than the distance in the uncoordinated olefin (1.34 Å) by 0.14 Å as a reflection of very significant backdonation into π^*-TCNE orbitals.



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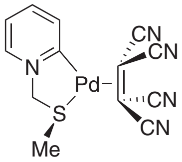
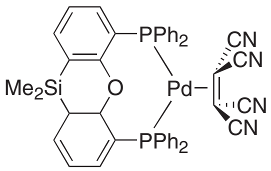


7

Other structures that have been studied with the fragment Pd^0(TCNE) are Pd(PPh_3)$_2$(η^2-TCNE),[48] a Pd(*S*,*S*)(η^2-TCNE) (*S*,*S* = 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene),[49] and three structures with diphosphines and dipyridine with large bite angles 8, 9, and 10.[50] It is interesting that the largest P–Pd–P angle found was 104.6°, and a further increase in the natural angle of the ligand (calculated by MM2) results in elongation of the Pd–P length rather than in an increase of the angle. The ligand 10 (calculated natural angle of 117° by MNDO) assumed a bite angle of 99.5°. The alkene bond distances are 1.508 Å in 8, 1.485 Å in 9, and 1.475 Å in 10.



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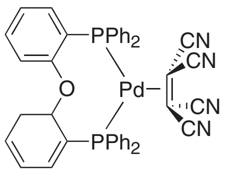

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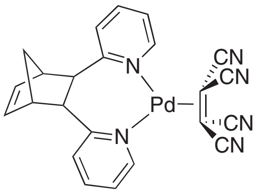


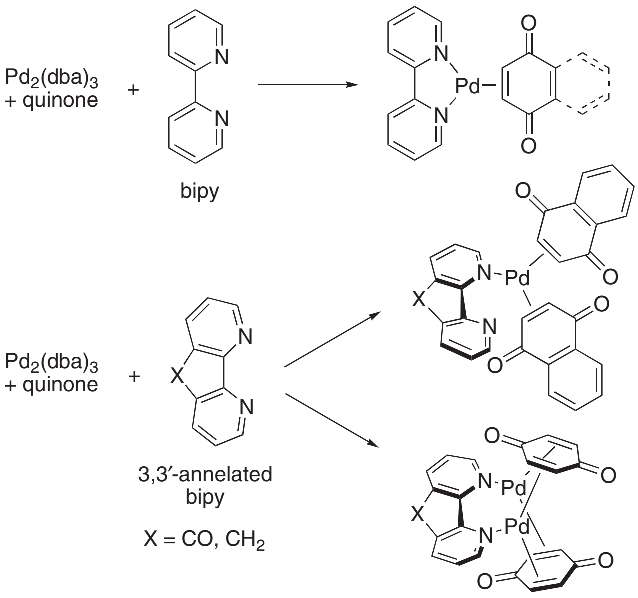
10

The acceptor olefins *p*-benzoquinone and naphthoquinone have a rich coordination behavior when combined with 3,3′-annelated and non-annelated 2,2′-bipyridines as chelating ligands. Annelation disfavors the tendency to bond as chelates for the N–N ligands, because it alters the maximum overlapping direction of the nitrogen atoms, and other structures arise, as shown in the examples of Scheme 10. Non-annelated bipy, bq, and nq behave similarly. For annelated bipy, the ability of bq to act as a bidentate produces dinuclear Pd complexes bridged by one annelated bipy and two bq ligands. The ligand aq cannot act as bidentate, and a structure with one palladium coordinated by one monodentate annelated bipy and two monodentate bq ligands is formed.[51] One crystal structure of each type was studied.

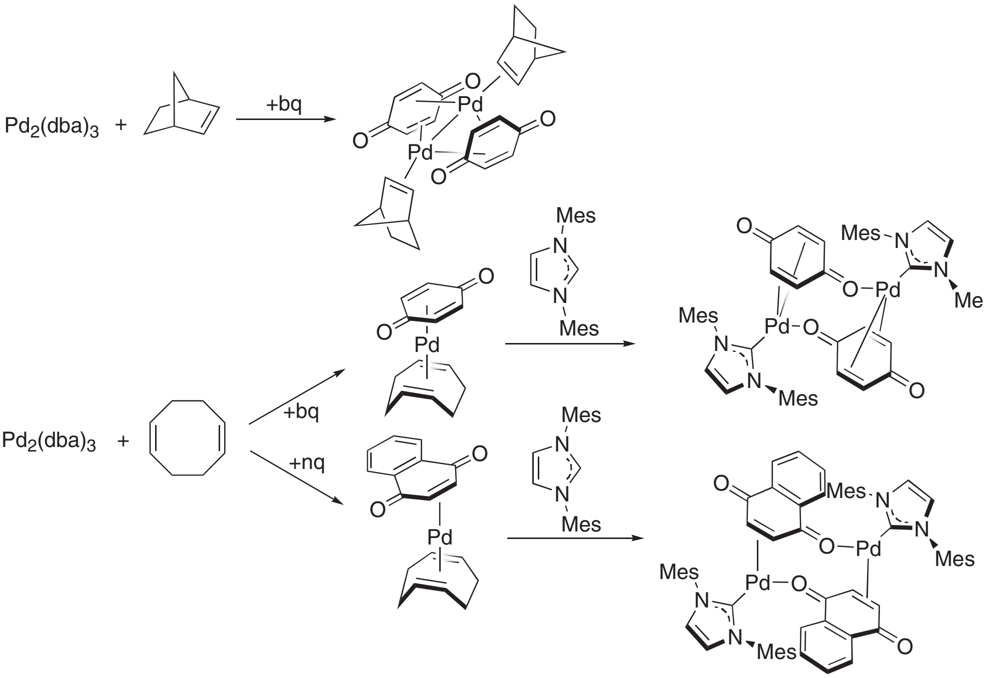
Other remarkable complexes derived from these quinones, which are catalyst precursors for the linear co-trimerization of 1-octene and dimethyl acetylenedicarboxylate, have been made in the group of Yamamoto and Itoh using norbornene (nb) or 1,5-COD as ancillary ligands (Scheme 11). The structure changes with the combination of ligands used. The monomeric complexes illustrate the different coordination behavior of bq and nq.[52] Beller has studied the displacement of the 1,5-COD ligand with a sterically demanding carbene ligand, which leads to the formation of dimeric complexes where the oxygen atoms of the quinones participate in the formation of the bridges.[53] These carbene–quinone complexes are efficient catalysts in the Heck and Suzuki–Miyaura cross-coupling reactions of aryldiazonium salts with olefins or arylboronic acids, respectively, in good to excellent yields.

Starting from the very reactive Pd_2(dae)$_3$ (dae = diallyl ether),[14,15] an alternative route to other carbene complexes of palladium(0) has been reported recently.[54] These are of the type Pd(carbene)(η^4-dae), with differently substituted imidazol-2-ylidene molecules. Theoretical calculations and five X-ray diffraction structures were undertaken to analyze the electronic and steric factors responsible for the unprecedented catalytic efficiency of these compounds in the telomerization reaction of 1,3-butadiene with alcohols to give alkyl octadienyl ethers.

Closely related to some of the complexes in Scheme 11 are the structures of Pd(dtbpx)(η^2-qn),[33] [Pd(PPh_3)$_2$-(η^2-qn)]·2H_2qn,[55] Pd_2(η^2,η^2-qn)$_2$(PPh_3)$_2$,[55] Pd(bipy)(η^2-qn),[56] and Pd{1,2-bis(*N*-(4-methylphenyl)imino)acenaphtene}-(η^2-ma).[57] Also closely related is complex 11, involving a cyclohexenone, which was prepared by two methods in the course of a mechanistic study of the palladium-catalyzed intramolecular cyclization of alkadienyl-substituted 1,3-diketones (Scheme 12).[58]

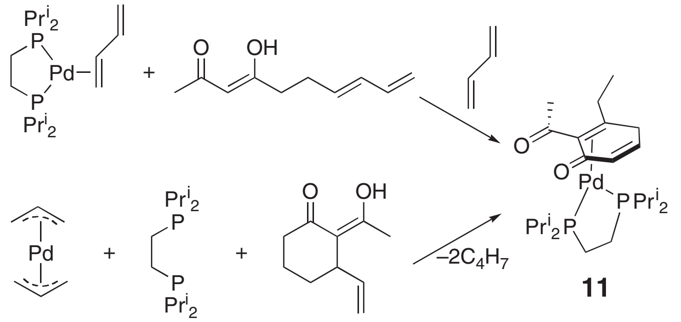


Scheme 10

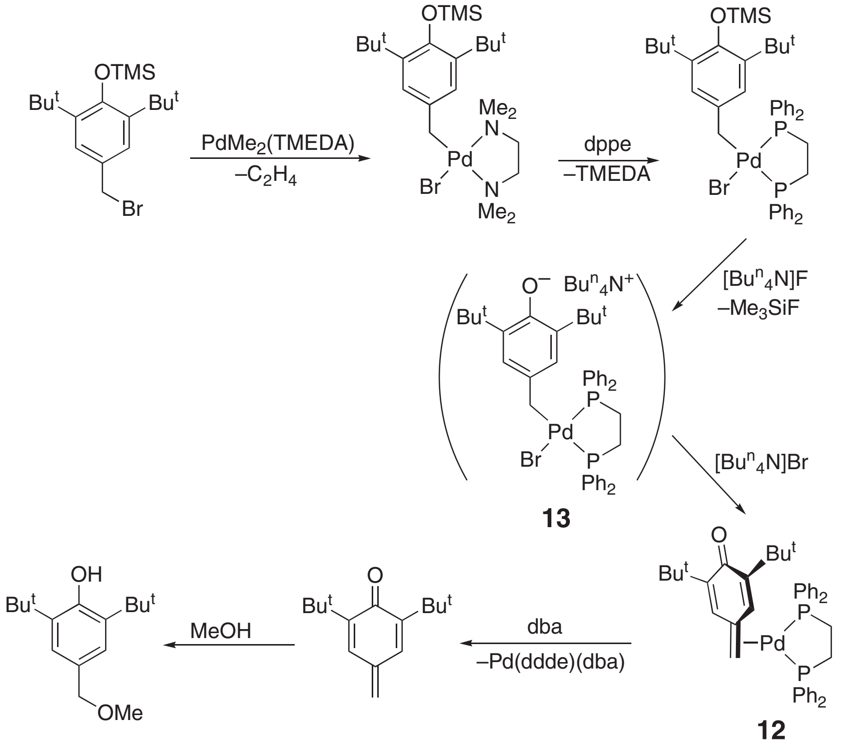


Scheme 11

An elaborate strategy was needed for the synthesis of a palladium(0) complex with a quinonemethide ligand coordinated by the exocyclic double bond (complex **12** in Scheme 13),[59,60] which involves aiming at the synthesis of the unstable palladium(II) complex of the zwitterionic form of the molecule **13**. This non-observed intermediate spontaneously affords the desired complex. Treatment with dba produces the unstable free quinonemethide, which is a biologically relevant metabolite. The crystal structure of **12** was solved and showed a notably elongated exocyclic double bond (1.437 Å) and a displacement of this bond out of the ring plane by 10.78° away from the palladium atom.



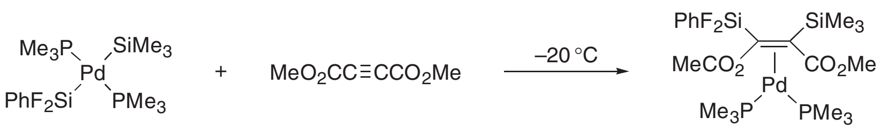
Scheme 12



Scheme 13

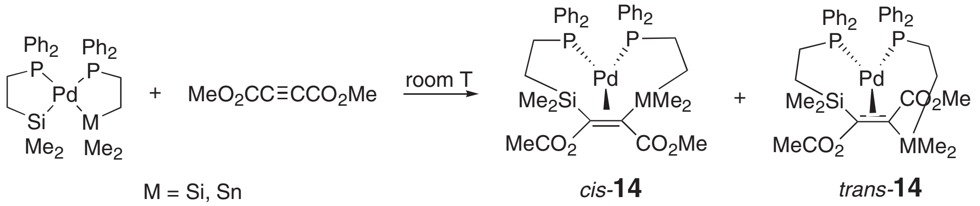
A related structure is the complex Pd(dppf)(η^2-$CH_2{=}C_5Ph_3$); the triphenylfulvalene ligand arises, in this case, from phenylacetylene cyclotrimerization in the presence of $PdCl_2$(dppf).[61] These molecules are reminiscent of the complex $Pd(PPh_3)_2$(η^2-$CH_2{=}C_5HMe_4$), also synthesized by a sophisticated protocol, for which the structure is similar with 1.424 Å and 10.81° for the same structural parameters.[62]

The isolation in stoichiometric conditions of the olefin complex shown in Equation (3), presumed to be formed from a non-observed bis(silylated) palladium(II) intermediate complex, is relevant to the understanding of the palladium-catalyzed bis-silylation of acetylenes and olefins. The crystal structure of the compound showed important distortion of the olefin carbons toward *sp*^{3}, and a C–C distance of 1.461 Å.[63]



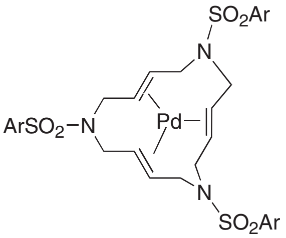
(3)

There are a number of systems where the complex finds extra stabilization by formation of bis-chelate, tris-chelate, or macrocyclic compounds. Some of them are found as intermediates or as byproducts in palladium-catalyzed reactions. Examples very similar to the previous reaction are shown in Equation (4). In this case, the systems can be handled at room temperature, although isomerization from *cis*-**14** to *trans*-**14** occurs.[64]



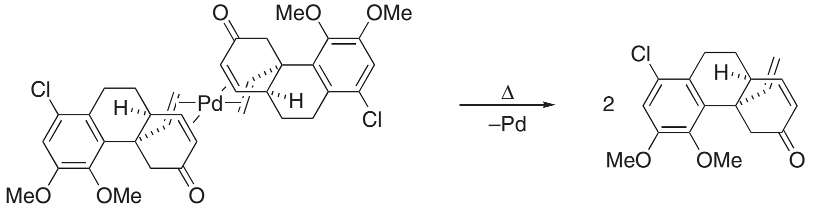
(4)

A further example is the first complex of a series of triazacyclopentadecatriene molecules represented by the general structure **15**, which was first serendipitously found in a Tsuji–Trost allylation of arenesulfonamides with *cis*-2-butene–1,4-diol dicarbonate.[65] A family of derivatives with many different SO_2Ar groups (identical or different) has been prepared later on purpose, and characterized crystallographically for Ar = *p*-Tol.[66] Modification of these molecules to introduce ferrocenyl or 4-pyrrol-1-ylphenyl as Ar groups has been made and they have been studied electrochemically. The complexes containing the pyrrole group (one was studied by X-ray diffraction) polymerize electrochemically generating modified electrodes, which are efficient and selective heterogeneous catalysts in Suzuki cross-couplings.[67]



15

The first case of a tetrahedral palladium(0) tetraolefin complex (more exactly, $Pd(diolefin)_2$) has been isolated in the course of the Saegusa oxidation of a silyl enol ether, aimed at the synthesis of alkaloids. Palladium acetate was used as oxidant in this reaction, and a brown compound separated from the solution, which was characterized by X-ray diffraction as **16** (Equation (5)). It decomposed upon heating to give the expected product of oxidation. This supports the accepted mechanism of Saegusa oxidation.[68]

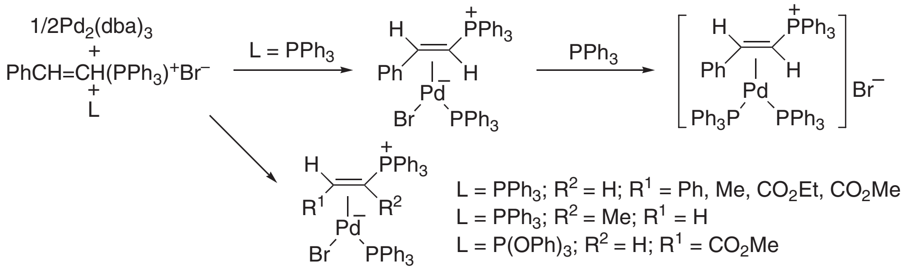


16

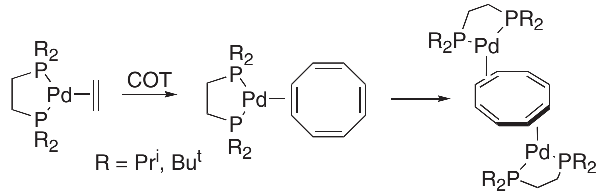
(5)

Zwitterionic complexes containing the cationic ligand $[PhCH{=}CHPPh_3]^+$ are easily formed according to Scheme 14. The styrylphosphonium ligand seems to be strongly bonded and is not displaced by further addition of PPh_3. In fact, the P–C(olefin) distance in both structures is short, suggesting a partial ylide character of the coordinated fragment.[69] The zwitterionic structure can be extended successfully to a number of other ligands and olefins.[70]

In complexes with η^2-COT bonded to palladium(0) (Scheme 15), the COT ligand is semiaromatic; it is planar with alternating long and short C–C bonds. The complex with COT acting as a μ-$\eta^2:\eta^2$-ligand can also be generated, but the COT ligand is very labile and is easily lost to produce the homoleptic $Pd_2(\mu\text{-}R_2PCH_2CH_2PR_2)_2$ complexes. It is



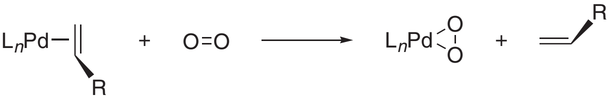
Scheme 14



Scheme 15

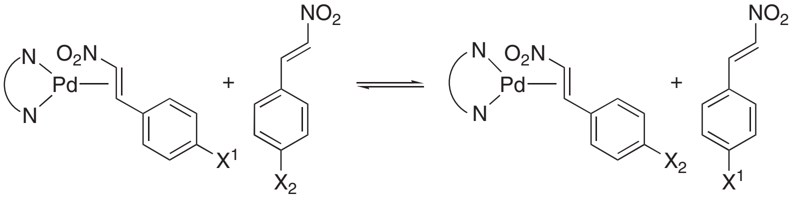
suggested that aromaticity making the coordinated COT ligand electronically equivalent to the monoanion $[C_8H_8]^-$ is to be expected in systems with strong backdonation.[71]

Palladium(0) complexes are catalysts for dioxygen-coupled oxidation reactions.[72] The palladium(0) complex Pd(bc)(dba) (bc = 2,9-dimethyl–4,7-diphenyl–1,10-phenanthroline or bathocuproine) has been prepared, and its structure studied by X-ray diffraction, showing, as expected, an η^2-dba ligand.[73] The complex has been used for mechanistic studies of the reaction between molecular oxygen and palladium(0) species (Equation (6)).[73,74] These studies indicate that the reaction proceeds by an associative mechanism, similar to the associative mechanism reported for olefin substitution at palladium(0). This similarity is interesting since olefins have well-defined donor (filled π-) and acceptor (empty π^*-) orbitals, whereas dioxygen has two singly occupied π^*-orbitals in the ground state.

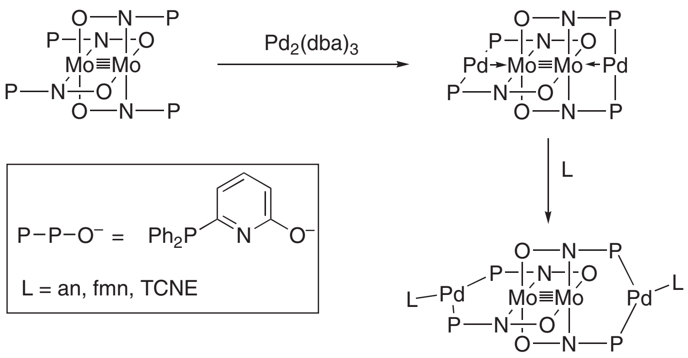


(6)

Although the complexes Pd(bc)(ns^X) (ns^X = *trans*-O_2N-CH=CH-C_6H_4-X-*p*) are rigid in solution at room temperature, they undergo exchange with free olefins. Studies on the associative olefin substitution of Pd(bc)(ns^X) with free ns^X olefins having different X substituents (MeO, Me, H, Br, CF_3) permitted a Hammett analysis of the forward rate constants, which revealed that the rates are faster with the less nucleophilic incoming olefins (Equation (7)).[75] This means that in the substitution reaction, the incoming olefin is acting as the electrophile and the palladium center as the nucleophile, similar to the role played in oxidative addition reactions, but contrary to the dominant idea in substitution reactions in Pd(0) where the incoming olefin was thought to be the nucleophile (as it is in Pd(ii)). For this reason, the case has been called "inverse-electron-demand" ligand substitution. This view has been supported with DFT calculations.[76] The X-ray diffraction structures of three complexes (X = Ph, *p*-Tol, Br) were determined.[75]



(7)



Scheme 16

The case of "inverse-electron-demand" can, perhaps, be recognized in the reaction of Scheme 16, where dative Pd(0)–Mo(II) bonds exist, which are replaced by Pd(0)–olefin bonds.[77] The first step of the reaction is quantitative and, formally, the weaker acceptor dba olefin is replaced by the stronger acceptor Mo in the dinuclear complex to form the tetranuclear cluster. In the second step (moderate yields), stronger acceptor olefins displace the Mo as acceptor group and coordinate to Pd(0).

Mechanistic studies of ligand substitution on $Pd_2(dba)_3$ and oxidative addition reactions of $Pd(dba)L_2$ complexes are worth mentioning in view of their extensive use in catalysis. Complexes $[Pd_2(dba)_3 \cdot L]$ (L = dba or solvent molecule) are used for *in situ* preparation of catalysts in palladium-catalyzed reactions upon addition of other ligands. Apparently, the dba ligands are not completely substituted by the added ligands. Phosphines and diphosphines lead to equilibria which have been studied in detail.[78–82] Upon mixing of $Pd_2(dba)_3$ and PPh_3, $Pd(dba)(PPh_3)_2$ is formed in equilibrium with $Pd(PPh_3)_3$ (Equation (8)).[81,83] The equilibrium constant, $K_0 = 0.14$ in THF, indicates that dba is a better ligand for $Pd(PPh_3)_2$ than PPh_3. Similar equilibria were found for tri-2-furylphosphine (TFP) and triphenylarsine.[84,85,21]

$$\mathrm{Pd(dba)(PPh_3)_2} \quad + \quad \mathrm{PPh_3} \quad \rightleftharpoons \quad \mathrm{Pd(PPh_3)_3} \quad + \quad \mathrm{dba} \tag{8}$$

The rates of oxidative addition of halides, triflates, or acetates to various combinations of dba and other monodentate[85,86] or chelate[18,80,87] ligands on palladium have been studied. All the systems using a bidentate ligand are less reactive than $Pd_2(dba)_3 + 2PPh_3$. The oxidative addition of PhI to $Pd(PPh_3)_4$ or to the anionic complex $[Pd(OAc)(PPh_3)_3]^-$ in the presence of an alkene (styrene, MA) is also slowed down.[18] In general, it is believed that the active complex is PdL_2 or PdL_2(solvent).

8.06.2.3 Alkene Complexes of Pd(II)

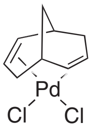
8.06.2.3.1 General comments

The use of palladium(II) complexes with chelating olefins such as COD or nbd, whether in catalysis or in other reactivity studies, where the diene ligand is accessory, or the complex is just the precursor for the *in situ* preparation of the actual catalyst by adding another ligand, is extremely frequent but is not dealt with in this section. For all these reasons, in spite of the importance of palladium(II) complexes in the chemistry of palladium, the size of this section is not proportional to its importance. Here, we will concentrate mostly on new isolated palladium complexes.

8.06.2.3.2 Complexes of Pd(II) with chelating dienes

Crystallographic determinations or corrections have been reported on the simple complexes with chelating diolefins $PdCl_2$(COD),[88] $PdBr_2$(COD),[89] $PdCl_2$(1,5-dimethylbicyclo[3.3.0]octa-2,6-diene),[90] $[PdCl_2$(1-TMS-1,5-COD)],[91] and $PdCl_2$(1,2-divinylcyclohexane).[92] Indirectly, other crystallographic determinations of $PdCl_2$(COD) have been made associated with the co-crystallization of $[PdCl_2(P–N)][PdCl_2(COD)]$ (P–N = 1-diphenyl–phosphino-1′-[6-2,2′-bipyridyl)ferrocene][93] and $[PdCl_2(P–P)][PdCl_2(COD)]$ (P–P = $Ph_2PN(Et)C(O)N(Et)PPh_2$].[94] Less conventional is the structure of $PdCl_2(\eta^4\text{-}C_9H_{12})$ (C_9H_{12} = bicyclo[3.3.1]-nona–2,6-diene) **17**. The molecular structure in solution has been studied by two-dimensional NMR spectroscopy, and the crystal structure has been determined.

The spectroscopic results in solution show clearly that the Pd–diene interactions involve non-equivalent carbon atoms at each of the equivalent double bonds. This is confirmed in the crystal structure where the Pd–C distances, for each C=C, to the two carbons are significantly different.[95]



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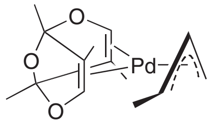
Complexes of the type [Pd(η^3-$R^1R^2CCHCH_2$)(TOND)](BF_4) (TOND = *R*,*R*-(−)-1,3,5,7-tetramethyl–2,6,9-trioxo–bicyclo[3,3,1]-nona–3,7-diene; R^1 = H, Me; R^2 = H, Me) have been prepared. The labile chiral ligand TOND coordinates as chelate and the crystal structure of the crotyl derivative has been determined **18**. The two C=C distances (1.370 and 1.372 Å) are identical within the range of experimental error. A study of the equilibria in solution between diastereomers has been reported.[96]



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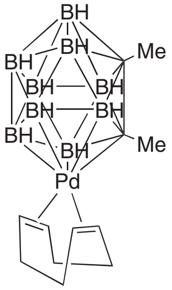
The presence of COD seems to help the preparation of crystals suitable for X-ray diffraction studies. For this reason, it is not unusual that the fragment Pd(COD), providing two *cis*-sites for coordination of other ligands, is chosen in the synthesis of Pd complexes. It is found in the structures of some metallaborane compounds, for instance **19**;[9,10,97] in studies on the coordination chemistry of the *P*-functional organotin chloride $Ph_2PCH_2CH_2SnCl_3$, which reacts with $PdCl_2$(COD) in a ratio 1 : 1 to give the zwitterionic complex PdCl(COD)($PPh_2CH_2CH_2SnCl_4$) **20**;[98] in a trinuclear $PdRh_2$ complex **21**;[99] in the structure of a cyclopalladated primary amine **22**;[100] in a σ-benzyl derivative **23**;[101] and in the preparation of a family of $[PdMeL(COD)]^{n+}$ complexes ($n = 0$, L = OH, alkoxides; $n = 1$, L = OH_2 and other neutral ligands), including a dimeric species $[(\mu\text{-OH})\{PdMe(COD)\}_2]^+$ **24** and a collidine complex **25**,[102] which where characterized crystallographically.



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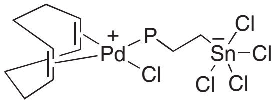

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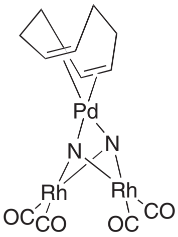

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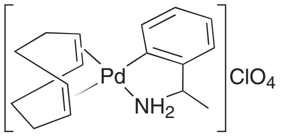

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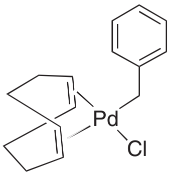

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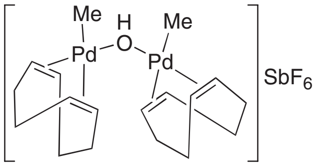

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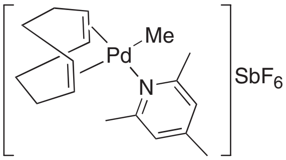
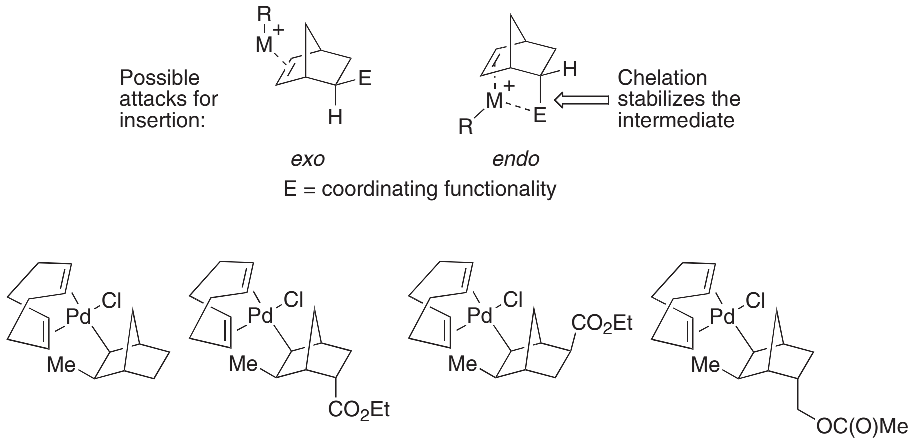


25

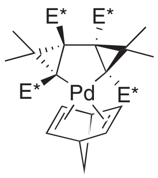
The polymerization of *endo*-functionalized norbornenes with groups containing heteroatoms is slower than for *exo*-functionalized ones or for nb with the conventional cationic catalysts. This is thought to be due to the stabilization of intermediates by coordination of the heteroatom, E, which is only feasible for the *endo*-functionalized molecule (Scheme 17). The insertion into the Pd–Me bond of PdMeCl(COD) of several nb derivatives functionalized either in the *exo*- or in the *endo*-face has been studied in order to check whether this neutral less-electrophilic palladium center



Scheme 17

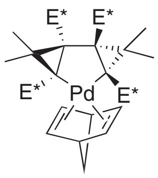
would circumvent the problem. In effect, it was found that nb derivatives with pendant *endo*-ester functionalities insert into the Pd–Me bond through the *exo*-face with rates similar to those found with nb. Moreover, addition of ethyl acetate did not inhibit nb polymerization with this catalyst. This is in stark contrast with the behavior of cationic catalysts. However, rates were too slow for practical use. In this research, the structures of the four complexes of stoichiometric insertion (having COD as ancillary ligand) shown in Scheme 17 were solved to assess the *exo*-stereochemistry of the insertion.[103]

Less common is the use of nbd, but it has been utilized to obtain crystals for the determination of the absolute configuration of chiral palladium(II) complexes of the type palladatricycloheptane produced by regioselective oxidative cyclization of C_2-symmetrical chiral alkenes. The structures of **26** and **27** were determined.[104] Previously, complexes of the racemic equivalent with $E = CO_2Me$ with nbd and with COD were crystallized, and their X-ray structures solved.[105]



E* = CO$_2$-(*R*)-CH(Me)CO$_2$Et

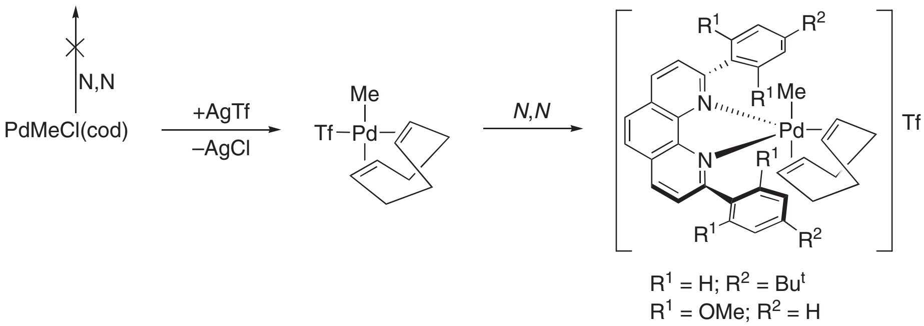
26



E* = CO$_2$-(*S*)-CH(Me)CO$_2$Me

27

The topic of pentacoordinated palladium(II) complexes has been reviewed, and conclusions about the factors stabilizing such structures have summarized the accumulated experience.[106] These complexes require the participation of an acceptor ligand, which is frequently an olefin. *Ab initio* computational studies on the stability of MXY-(N–N)(C_2H_4) (N–N = bidentate donor ligand; X, Y = monodentate ligands) toward the loss of ethylene have been carried out.[107] Occasionally in the period covered in this work, new olefin-containing pentacoordinated complexes (mostly of platinum but also some of palladium) have been reported.[39,108–111] The complex in Scheme 18 is a good example of how a bulky phenanthroline can be better accommodated in a pentacoordinated geometry (where the specific spatial demands of the 2,9-diaryl substituents find no obstacles) than it would be in a four-coordinated square-planar geometry. In fact, the 2,9-diaryl-substituted 1,10-phenanthroline does not give the usual COD substitution on the neutral PdMeCl(COD) complex.[112] In the square-planar compound, the C=C bond distances are 1.368 Å for the double bond *trans* to Tf, and 1.344 Å for the double bond *trans* to the Me group. The C=C bond distances in the pentacoordinated compound are 1.361 Å for the double bond *trans* to Me, and 1.401 Å for the double bond in the equatorial position. In both cases, the longer distances are found in front of the more-donating Me group, which facilitates backdonation to the olefin. These phenanthroline ligands are reminiscent of the diimine ligands used by Brookhart in the palladium-catalyzed olefin polymerization.[113]



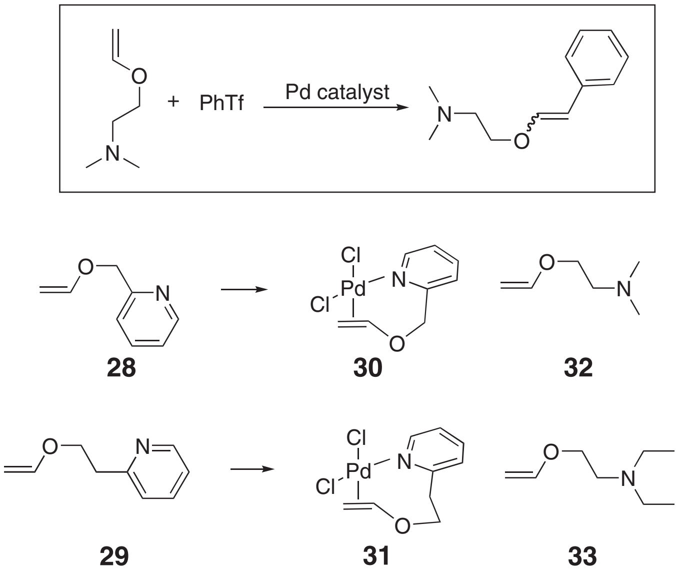
Scheme 18

8.06.2.3.3 Complexes of Pd(II) with monoenes involved in chelate coordination

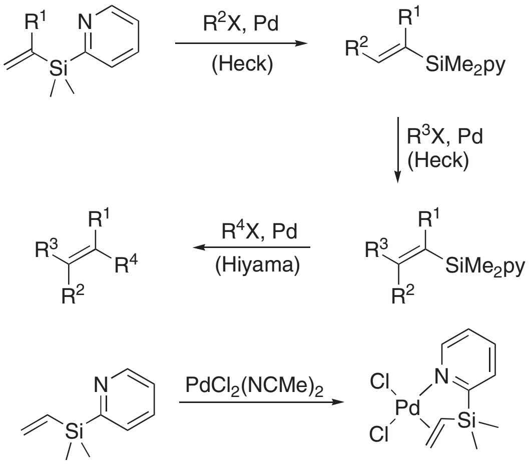
Geometrically, the heteroatom olefin moieties that close 4.5- or 5.5-membered palladacycles are particularly suited to stabilize complexes. This feature dominates all the oxidation states, including palladium(II). This is seen, for instance, in the aminophosphine complex $PdCl_2\{\eta^2\text{-}PPh_2(N(C_3H_5)_2)\}$, which has one pendant allyl group of the allyl amine fragment, and one coordinated.[114]

The sequential integration of palladium-catalyzed cross-coupling reactions is a good illustration of the improvement in synthetic methods using palladium. It can be achieved by intramolecular presentation of the oxidative addition complex, this case having the advantage of making the reaction highly regioselective and rendering substituted olefins more reactive. In this way, multiple arylations can be successfully achieved. One example of this approach is the palladium-catalyzed arylation of vinyl ethers carrying a coordinating amino auxiliary that accelerates and controls the regioselectivity (Scheme 19) to obtain β-aryl vinyl ethers. The procedure was developed from the observation that compounds **28 and 29** undergo fast regioselective arylation, almost exclusively terminal, suggesting that a chelation-controlled insertion is taking place.[115,116] The preparation and X-ray characterization of complexes **30** and **31** support the proposal of similar chelated intermediates acting as intermediates. The method operates very efficiently for the arylation of compounds **32** and **33**.

A more sophisticated case is the series of reactions using 2-pyridyldimethyl(vinyl)silane as platform for the synthesis of multisubstituted olefins. The general approach is sketched in Scheme 20, although different combinations of the methods can be used. The purpose of the $SiMe_2py$ group is to benefit from the so-called



Scheme 19



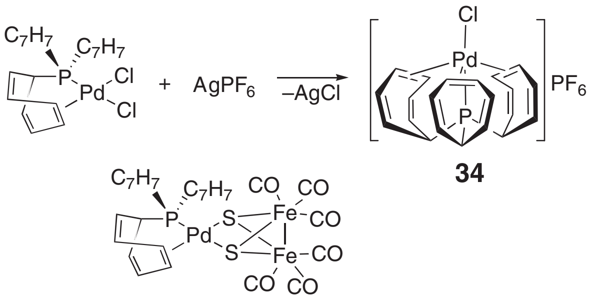
Scheme 20

complex-induced proximity effect (CIPE) to direct the regioselectivity in the Heck reactions, while this group can be removed in a creative Hiyama reaction producing one additional C–C bond. The method works extremely well and the feasibility of the directing mechanism is supported by the synthesis and X-ray characterization of the model ligand shown in the scheme, which contains the pyridine/olefin ligand coordinated as a chelate. In the catalytic process, the group *trans* to py should be an aryl group, and should undergo fast insertion/β-hydride elimination.[117]

Tris-cycloheptatrienyl phosphine is perfectly suited to chelate palladium with the P atom and one double bond. Reaction of [PdCp(COD)]BF_4 with $P(C_7H_7)_3$ (C_7H_7 = cyclohepta-2,4,6-trienyl) affords the symmetrically η^2-coordinated complex [PdCp{$P(C_7H_7)_2(\eta^2$-$C_7H_7)$}]BF_4.[118] Moreover, when a second position is made available on the palladium, a beautiful five-coordinate complex **34** is formed with the ligand coordinated as tripodal tetradentate with the phosphorus and the three double bonds (Scheme 21). The compound is highly symmetric, according to the structure determined for the platinum analog.[119] The ligand has been used also to stabilize dichalcogenato ligands, as in complex **35**.[120]

8.06.2.3.4 Complexes of Pd(II) with monoenes

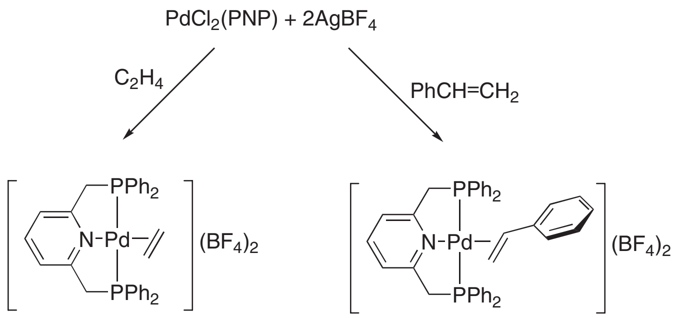
Few reports deal with complexes of palladium(II) monoolefin complexes not participating in the formation of a palladacycle, but the dicationic complexes depicted in Scheme 22, with ethene or with styrene, have been prepared fairly easily, although they are only moderately stable in solution in the presence of excess of free olefin. The crystal structure of the styrene complex could be determined, and the C=C bond distance of the coordinated double bond is only 1.292 Å, the shortest ever reported for Pd(II) or Pt(II) styrene complexes. This supports the idea that in this dicationic compound there is very little (if any) palladium-to-olefin π-backdonation.[110]



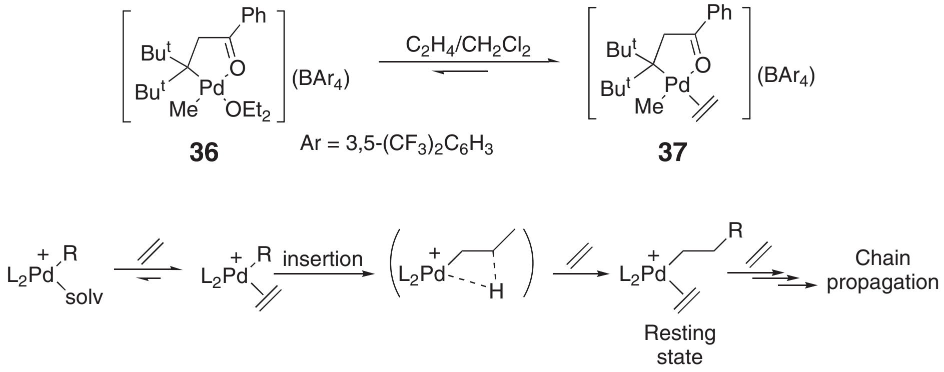
34

35

Scheme 21



Scheme 22


36

37

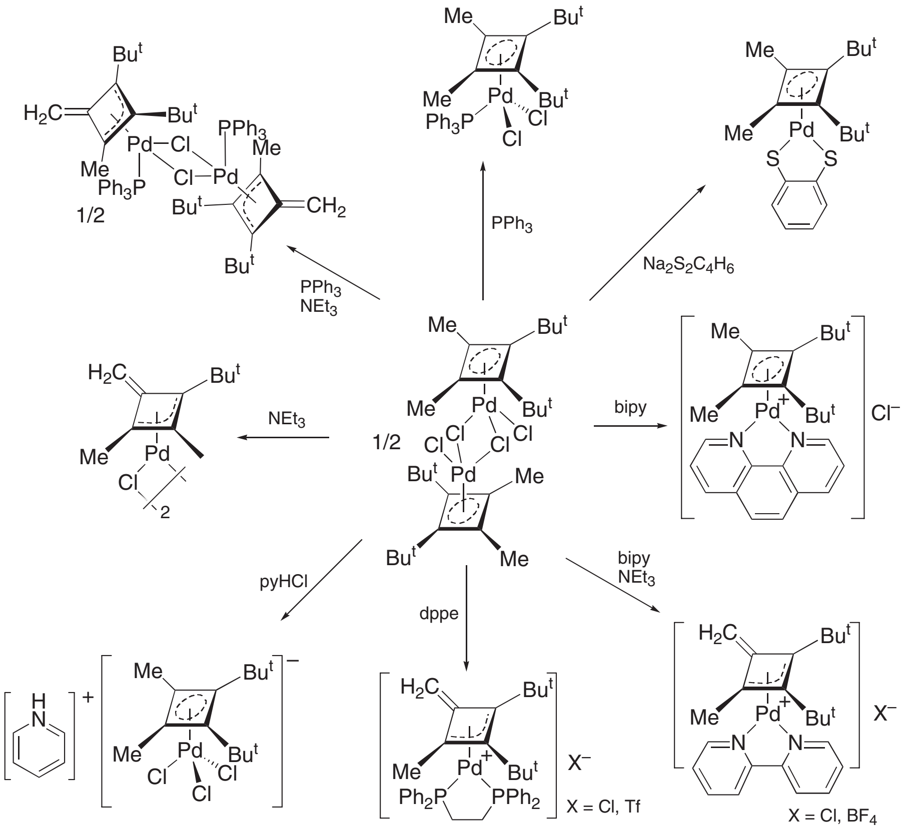
Scheme 23

Another important crystallographic characterization of a monoolefin complex is that of **37** in Scheme 23.[121] The complex is obtained from **36** by treatment with a large excess of ethylene in dichloromethane at −30 °C and precipitation into stirring pentane at −78 °C. It is considered a model for the catalyst resting state for ethylene polymerization by the mechanism shown in the lower part of Scheme 23. Compound **36** actually catalyzes the polymerization of ethylene. Compound **37** can be stabilized in dichloromethane solution in the presence of excess ethylene, and NMR experiments show that the exchange of free for coordinated ethylene is very fast even at −90 °C. The C═C distance in the ethylene, which is coordinated orthogonal to the coordination plane, as expected, is 1.346 Å (very similar to free ethylene) indicating little π-backdonation. The kinetics of insertion of ethylene into the Pd–Me bond was measured, affording $k_{obs} = 5.2 \times 10^{-15}\ s^{-1}$ at 0 °C, corresponding to $\Delta G^{\ddagger} = 21.3\ kcal\ mol^{-1}$.

Norbornene can stabilize cationic complexes containing a P–C–P pincer tridentate ligand derived from metallation of diphosphine xylene ligands. The complexes are of the type $[Pd(dppx)(nb)](BF_4)$ and $[Pd(dappx)(nb)](BF_4)$ (dppxH = 1,3-bis(diphenylphosphino)xylene; dappxH = 1,3-bis(bis(*p*-dimethylaniline)phosphino)xylene) and are well characterized spectroscopically. However, the nb ligand is only weakly bound and can be easily displaced by nucleophiles.[122]

8.06.2.4 Cyclobutadiene Complexes of Pd and Derivatives

The activity in developing cyclobutadiene complexes was extraordinary in the period covered by COMC (1982) and much more limited in COMC (1995), with the last report in 1982. In the period 1993–2004, the activity remained low, but some chemistry has been derived from $[PdCl_2(\eta^4\text{-}C_4Me_2Bu^t{}_2)]_2$,[123] which is gathered in Scheme 24.[124–126] The most interesting result is the ring-methyl deprotonation observed in some cases to give *exo*-methylene–η^3-cyclobutenyl palladium complexes. This methyl activation had been reported before for η^5-pentamethylcyclopentadienyl and for C_6Me_6 complexes, but these are the first reports for cyclobutenyl complexes. As shown in Scheme 24, the deprotonation can be induced by NEt_3 as base, in the presence or in the absence of monodentate or neutral bidentate ligands. Monodentate ligands such as PPh_3 or Cl^- simply split the bridges in $[PdCl_2(\eta^4\text{-}C_4Me_2Bu^t{}_2)]_2$, but bidentate



Scheme 24

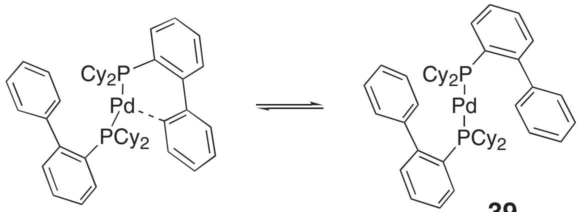
ligands (dppe, bipy) displace, in addition, a Cl$^-$ ligand, making the complex cationic. This can induce spontaneous deprotonation of the resulting cation, as for dppe. Metathesis of two Cl$^-$ ligands by a dithiolato ligand gives a neutral stable complex. The use of py as a base leads to a mixture of the deprotonated complex [Pd(μ-Cl)-{η^3-C$_4$(=CH$_2$)Me$_2$Bu$^t{}_2$}]$_2$, plus the anion [PdCl$_3$(η^4-C$_4$Me$_2$Bu$^t{}_2$)]$^-$ arising from reaction with the [HPy]Cl formed in the deprotonation reaction. The complexes Pd(S$_2$C$_6$H$_4$)(η^4-C$_4$Me$_2$Bu$^t{}_2$),[124] [Pd{η^3-C$_4$(=CH$_2$)Me$_2$Bu$^t{}_2$}(bipy)]-(BF$_4$),[125] and [Pd{η^3-C$_4$(=CH$_2$)Me$_2$Bu$^t{}_2$}(dppe)]Cl[126] were studied by X-ray diffraction methods. As expected, in the two cyclobutenyl complexes, the cycle is not planar (it is folded about 15°), and the ring methylene carbon is bent away from the metal, showing that it is not interacting with Pd.

8.06.3 Complexes of Arenes and Extended Conjugated Alkene Systems

Reports on arene complexes and interactions of Pd with aryl π-electron or, in general, conjugated π-electron density appear only occasionally. The reports in the period 1993–2004, although scarce, have representation of the formal oxidation states 0, I, and II for palladium, and hapticities from η^1- to η^6-arene. It should be noted, however, that the assignment of oxidation state or hapticity is not clear-cut in some systems. Many of the interactions reported are with pendant aryl groups of ligands already coordinated to Pd. The interactions in the form η^3-benzyl are dealt with in the section on allyl complexes.

An unusual intramolecular η^1-arene coordination has been found in the Pd(0) complex [Pd(dcpBiph)$_2$] shown in Equation (9), which is obtained on ligand displacement and reductive elimination of ethane from PdMe$_2$(TMEDA).[127] The X-ray structure of the compound shows a highly congested coordination sphere with the biphenyl substituents shielding almost one hemisphere around the Pd atom, and the Cy substituents shielding the rest. The P–Pd–P angle is only 154.82°, far from linearity. There is apparently an interaction (Pd–C$_{ortho}$ = 2.676 Å) with only one biphenyl carbon atom (the *ortho*-carbon of the unsubstituted ring, structure 38) that is reported as

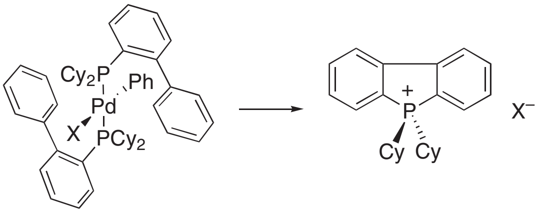
π,η^1-arene coordination and partially satisfies the electron deficiency at palladium. Note, however, that this is a long distance compared to other reported interactions. The aryl ring involved in this interaction remains planar. Variable-temperature ^{31}P NMR experiments revealed an equilibrium between **38** and an uncoordinated conformer **39** with $\Delta H = 2.04\,\mathrm{kcal\,mol^{-1}}$ and $\Delta S = 2.04\,\mathrm{cal\,mol^{-1}\,K^{-1}}$.



38 **39**

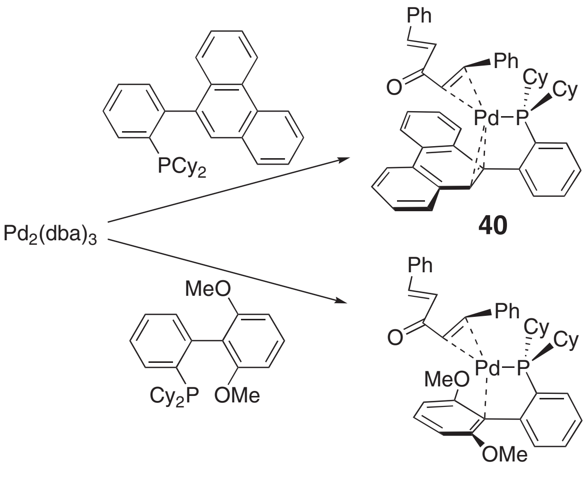
(9)

Oxidation of Pd(dcpBiph)$_2$ by PhX (X = Cl, Br, I) affords the palladium(II) complex PdPhI(dcpBiph)$_2$, which (for X = I) quickly releases one neutral ligand to reduce steric congestion, affording [PdPh(μ-I)(dcpBiph)]$_2$. Interestingly, for X = Br, I, minor decomposition products observed (5%) are the phosphonium salts shown in Equation (10). They probably arise from the metallation of an *ortho*-carbon of the biphenyl ring followed by reductive P–C elimination. This implies that a palladium–arene interaction in Pd(II) similar to that observed in Pd(0) may exist during arene metallation.



(10)

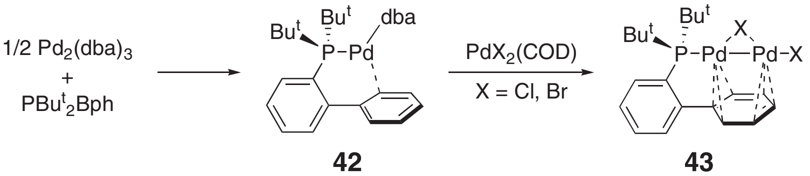
Buchwald *et al.* have reported a number of bulky phosphine ligand $PR^1{}_2R^2$ which give high activity in Suzuki–Miyaura catalysis for the synthesis of sterically hindered biaryls.[128] The conditions used in the catalysis involved the *in situ* preparation of the Pd(0) catalyst from Pd$_2$(dba)$_3$ and the phosphine. Two ligands which proved superior to the others had in common the same polyaromatic R^2 (R^1 = Cy, Ph) as a difference from the rest. A Pd(0) complex could be prepared by mixing Pd$_2$(dba)$_3$ and $PR^1{}_2R^2$ in toluene, which has the X-ray structure **40** sketched in the upper reaction of Scheme 25. The key structural feature of the complex is the short distance of Pd to one double bond of the phenanthrene moiety (distances to the two carbons are 2.298 and 2.323 Å) supporting an η^2-phenanthrene



40

41

Scheme 25



42 **43**

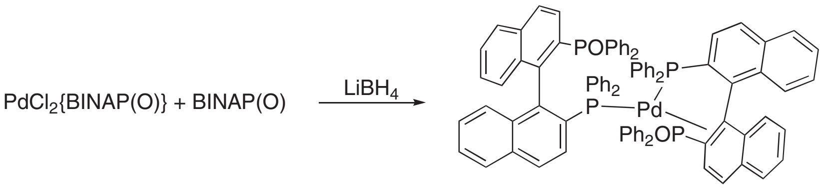
Scheme 26

coordination through the strongest donor double bond of the less aromatized ring. This chelating coordination of the phosphine bearing the anthracenyl moiety describes a 5.5-membered palladacycle. In addition, there is a η^2-coordinated dba ligand. The formation of 5.5-membered palladacycles (counting half C═C bond distance as 0.5) when a biphenyl fragment is involved seems, in general, particularly favorable.

Further elaboration of the phosphine ligand, looking for a rationally designed Suzuki–Miyaura catalyst, led to the Pd(0) catalyst **41**, drawn in the lower reaction of Scheme 25, with methoxy substituents in the *ortho*-positions of the outer ring of the phosphine, in order to prevent cyclometallation and increase the active life of the catalyst. The compound is in fact a very active catalyst and the crystal structure of the complex revealed a Pd(0) π,η^1-arene interaction, in this case to the C_{ipso}.[129] The palladium–carbon distance is much shorter ($Pd–C_{ipso} = 2.374$ Å) than in the case of $Pd(dcpBiph)_2$ ($Pd–C_{ortho} = 2.676$ Å).[127]

The case is very similar in Scheme 26, where the crystal structures suggest interaction of Pd(0) to one *ortho*-carbon of the external ring of the biphenyl in the first complex of the sequence **42**, and a μ_2-$\eta^3:\eta^3$ bridging mode in the palladium(I) complexes **43** obtained by comproportionation with $PdCl_2(COD)$ (see below for more examples of this strategy).[130]

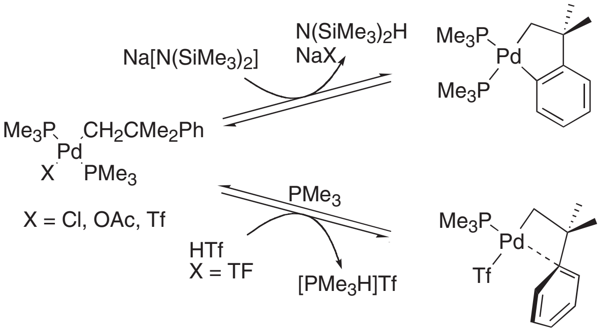
Another closely related palladium(0) structure is found in the complex Pd{BINAP(O)}$_2$, where BINAP(O) is the monoxide of the diphosphine BINAP. The complex is produced by reduction of $PdCl_2${BINAP(O)} in the presence of BINAP(O), Equation (11). Its X-ray structure shows that one of the ligands is only *P*-coordinated, and the second is a chelate with the P atom and an η^2-arene coordination to the naphthalene ring adjacent to the uncoordinated phosphynyl group.[131] This closes again a 5.5-membered palladacycle. The P–Pd–P angle is 117.6°, and the Pd–C distances are 2.228 and 2.160 Å.



(11)

Arene coordination to Pd is invoked in the arene C–H bond activation and arene oxidative coupling by cationic Pd(II) complexes.[132]

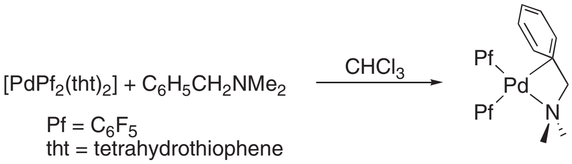
In palladium(II) complexes, the η^2-arene coordination participation in chelating structures closing 4.5-membered and 5.5-membered palladacycles is well represented. The first type is found in the complex obtained by protonation of neophyl derivatives *trans*-$Pd(CH_2CMe_2Ph)X(PMe_3)_2$ (Scheme 27), and it is important as a probe for the study of the metallation reaction. The structure is reported as having π,η^1-coordination of the arene ring in view of the shorter



Scheme 27

distance to the C_{ipso} (2.38 Å) compared to the distances to the C_{ortho} atoms (2.53 and 2.61 Å).[133] Other complexes characterized in this research include the structural characterization of the cyclopalladated complex $Pd(CH_2CMe_2C_6H_4)(COD)$.[134]

This bonding mode is similar to that communicated before for the complex $Pd(C_6F_5)_2(BzNH_2)$ (Equation (12)),[135] and fully reported in a later paper ($Pd–C_{ipso} = 2.335$ Å; $Pd–C_{ortho} = 2{,}663, 2.706$ Å).[136] This interaction is easily broken by weak ligands such as acetone, acetonitrile, dimethyl sulfoxide, or CO.



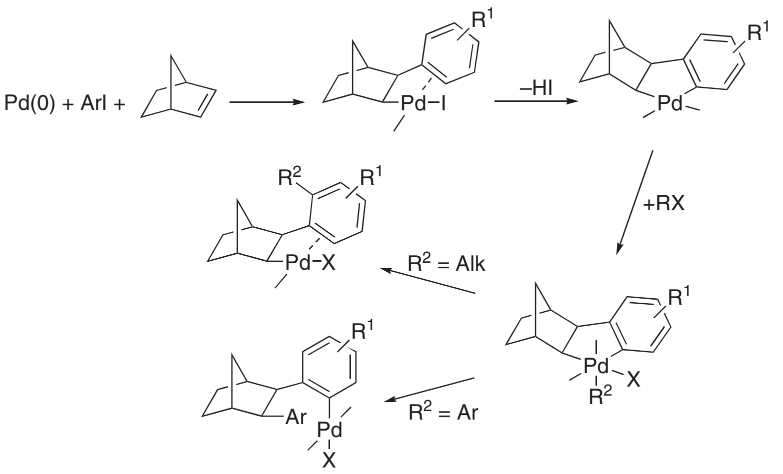
(12)

Some palladium(II) complexes with Pd–arene interactions studied and characterized are catalytic intermediates involved in the systems arising from nbd or nb insertion into Pd–aryl bonds, represented in Scheme 28. These have been extensively studied by the groups of Catellani and Milstein (for nb),[137–145] and Cheng (for nbd).[146–148]

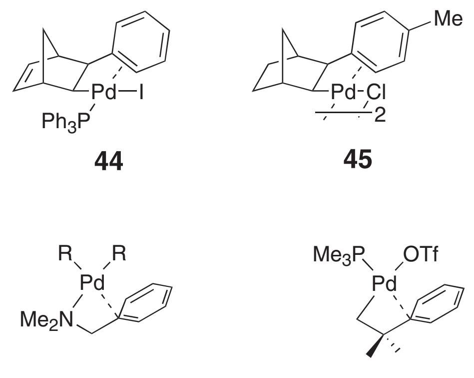
In all palladium(II) complexes discussed here, the arene is not altered upon coordination. On the other hand, a detailed analysis of these structures and others reported in the literature for structurally related systems making 4- to 4.5-membered palladacycles (Scheme 29, structures 44–48)[149] shows that the Pd distances to the *ipso*- and *ortho*-carbons of the arene fluctuate subtly, and can suggest either η^1- or η^2-coordination (or even η^3-coordination), depending on the distance accepted as indicating interaction. DFT-B3LYP calculations using an optimized model $Pd(C_7H_8Ph)Cl(PH_3)$ indicate that the potential energy surface for the oscillation of an unsubstituted phenyl ring between η^1- and η^2-coordination is very flat ($\Delta E \leq 1\,\mathrm{kcal\,mol^{-1}}$), and such an arrangement must be very easy in solution. Calculations were also carried out on several methyl-substituted derivatives of the model, producing, in some cases, a slipped η^2-coordination. The general conclusion was that the unsaturated metal center receives π-electron density of the arene, which comes mainly through its *ipso*-carbon. The interaction may be slightly improved when the *ortho*-carbon comes closer to the metal (slipped η^2-coordination), but in no case does this contribution seem crucial for the stability of the system.[137]

The formation of 5.5-membered palladacycles becomes preferred again when a biphenyl or a phenyl vinyl fragment (that is two sp^2-bonds instead of two sp^3-bonds) are involved in the cycle. At variance with palladium(0), which prefers to coordinate the arene as η^2, the higher preference of palladium(II) for η^1-coordination gives rise also to five-membered palladacycles.

Thus, double insertion of diphenylacetylene into a phenyl–palladium bond (Equation (13)) produces a compound where the arene seems to be coordinated as η^2, considering the similarity of distances of palladium to the two carbon atoms involved in the bonding ($Pd–C_{ipso} = 2.418$ Å; $Pd–C_{ortho} = 2.461$ Å).[150] There are many similar structural examples with an η^2-olefin double bond in place of the η^2-arene (see Section 8.06.6.5).

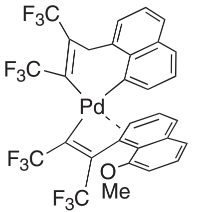


Scheme 28



44 **45**

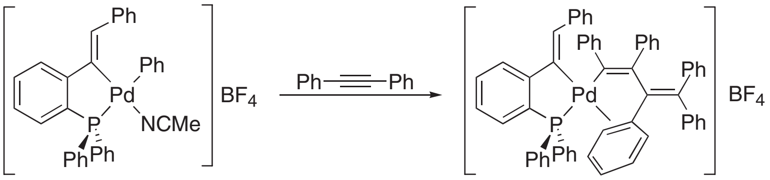
46 **47**



48

Compound	*Pd–C*$_{ipso}$ (Å)	*Pd–C*$_{ortho}$ (Å)
44	2.430	2.591/3.191
45	2.22	2.54/2.79
46	2.39	2.57/3.03
47	2.34	2.66/2.71
48	2.433	2.571/3.21

Scheme 29

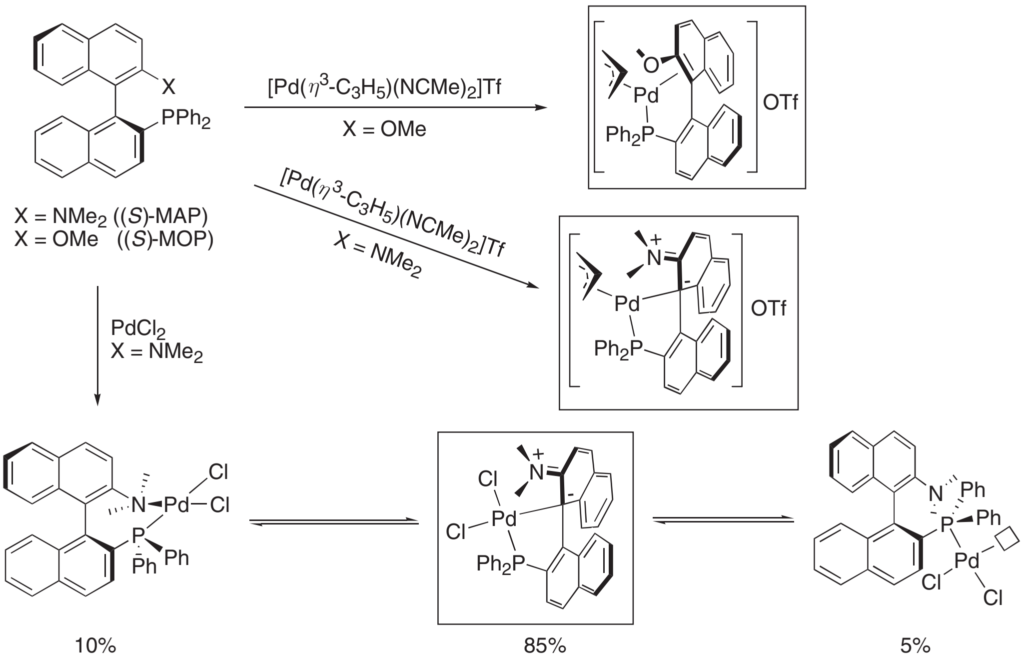


(13)

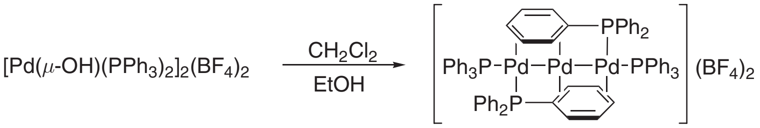
Very interesting examples of arene coordination to palladium(II) were found in the study of the complexes formed by the chiral bidentate ligands MAP and MOP (Scheme 30).[151] The three structures under discussion are highlighted in the scheme. The MOP ligand chelates an allylpalladium fragment by the P atom and one η^2-arene, as suggested by two fairly short and comparable Pd–C distances (Pd–C$_{ipso}$ = 2.34 Å; Pd–C$_{ortho}$ = 2,47 Å; we take C$_{ipso}$ as the C atom bonded to the other binaphthyl), making a 5.5-palladacycle. The MAP ligand, however, clearly prefers η^1-arene coordination, both to PdCl$_2$ or to [Pd(allyl)]$^+$ fragments. The X-ray crystallographic analysis reveals that this is the case, and sheds light on the reason for this remarkably different preference: in both MAP complexes the bond distances and angles at C$_{ipso}$ are closer to those expected for sp^3- than for sp^2-geometry. This is due to an enamine-like character of the ligand, which is enhanced by η^1-C$_{ipso}$ coordination to Pd(II).

The MAP complex with PdCl$_2$ shows the presence of three isomers in solution (85 : 10 : 5) by ^{13}C NMR spectroscopy. The most abundant complex is the chelate with P and η^1-C$_{ipso}$ as donors. The second, but much less abundant, is the *P*,*N*-chelate. Finally, the least abundant species was suggested to be a three-coordinated Pd structure, with the ligand acting as *P*-monodentate. The presence of the latter electron-deficient species has been deemed responsible for the higher catalytic activity found for MAP in Hartwig–Buchwald amination and, more dramatically, in Suzuki coupling. Thus, phenylation of 4-Cl–C$_6$H$_4$CHO with BP(OH)$_2$ in the presence of 3% Pd(OAc)$_2$, MAP, and CsI or Cs$_2$CO$_3$ occurred in less than 20 h at room temperature.

An unprecedented coordination mode has been reported for triphenylphosphine in the complex [Pd$_3$(PPh$_3$)$_4$](BF$_4$)$_2$, which was unexpectedly obtained by reduction of [Pd(μ-OH)(PPh$_3$)$_2$]$_2$(BF$_4$)$_2$ when it was dissolved in dichloromethane in the presence of ethanol or isopropanol as reducing agents (Equation (14)).[152] The X-ray structure of the compound reveals that the cation consists of a Ph$_3$P–Pd–Pd–Pd–PPh$_3$ linear chain sandwiched by two head-to-tail Ph$_2$P–C$_6$H$_5$ groups. The aryl bridging rings act as μ-η^2–η^2-diene units.

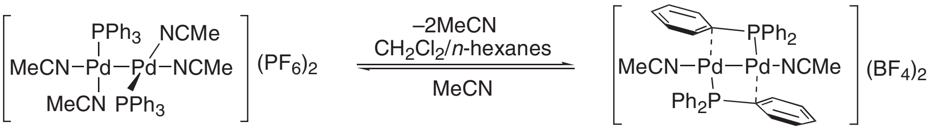


Scheme 30



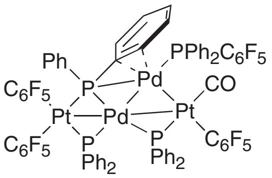
(14)

A closely related system was found starting from a variation of classical palladium(I) dimers but containing labile ligands (Equation (15)).[153] The easy displacement of the MeCN ligands generates two vacant sites that are occupied by an η^2-aryl ring of PPh_3, as shown by the bond distances ($Pd–C_{ipso} = 2.336$ Å and $Pd–C_{ortho} = 2.703$, 2.976 Å). Previously, a structurally identical compound with dppp taking the coordination positions of the nitrile and the phosphine had been reported.[154]



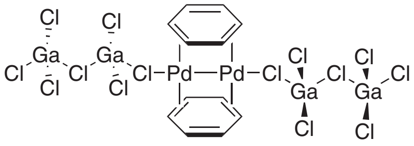
(15)

Related to the previous example, an η^2-interaction is found in one arene ring from a μ_3-bridging diphenylphosphido group of the polynuclear heterometallic compound $Pd_2Pt_2(\mu_2\text{-}PPh_2)_2\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}(C_6F_5)_3(CO)(PPh_2C_6F_5)]$ **49**.[155] The distances from the palladium to the aryl carbons are $Pd–C_{ipso} = 2.425$ and $Pd–C_{ortho} = 2.649$ Å.

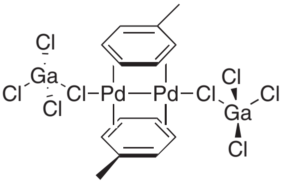


49

Among the older arene complexes of Pd reported are the Pd(I) dimeric compounds having the Pd–Pd bond sandwiched by two arenes, $[\text{Pd}(\eta\text{-arene})\text{X}]_2$ ($\text{X}=\text{AlCl}_4$, Al_2Cl_7).[156,157] The similar compounds **50** and **51** with GaCl_4 or Ga_2Cl_7 have been reported for benzene and toluene, and their structures have been X-ray characterized.[158]



50

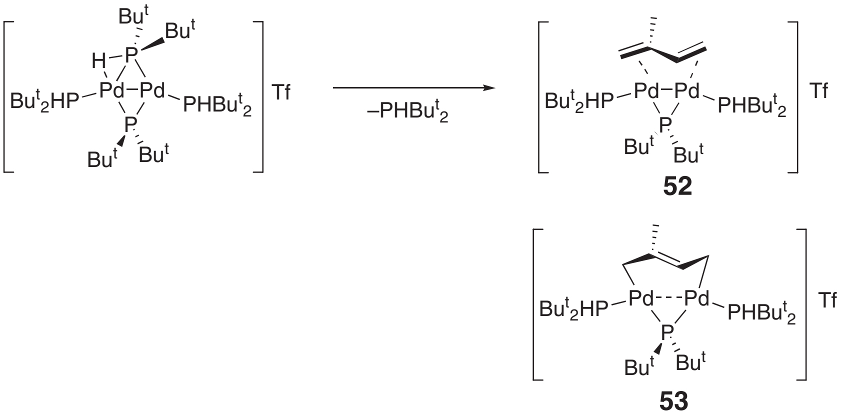


51

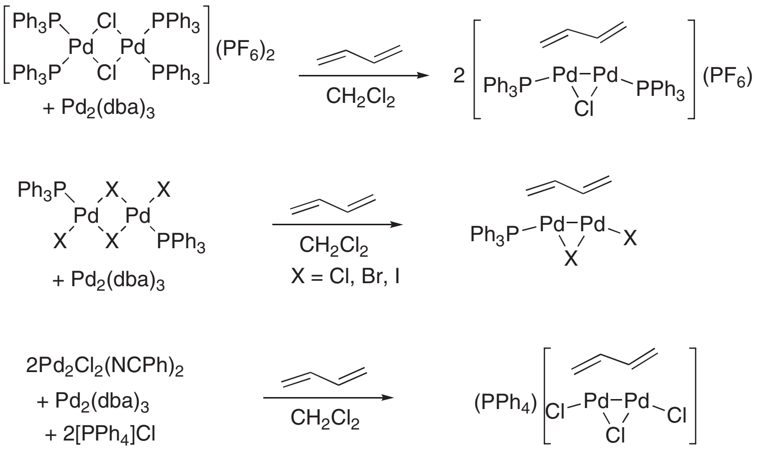
Polyene molecules have a high tendency to attach to systems containing Pd–Pd bonds. Many reactions have been reported. It is interesting to note that the oxidation state of palladium in all these molecules is not clear-cut. Depending on the importance of backdonation to the polyene, oxidative addition of one double bond and, consequently, oxidation of the metal should be considered. In such cases, an elongation of the Pd–Pd distance, yet in the range of a metal–metal bond, is usually observed in the crystal structure of the complexes. For instance, a bridging bulky phosphine is replaced by isoprene in the system represented in Scheme 31. The isoprene molecule has a *trans*-configuration and makes a zigzag above the line of the Pd–Pd bond. The Pd–Pd distance is fairly long (2.751 Å), and the Pd–C distances of the diene carbons to the closest Pd atom are very similar (Pd–C1 = 2.22; Pd–C2 = 2.30; Pd–C3 = 2.28; Pd–C4 = 2.21 Å).[159] Interestingly, the C–C distances are profoundly altered compared to the free isoprene in such a way that the central bond distance becomes shorter than the extremes (C1–C2 = 1.30; C2–C3 = 1.26; C3–C4 = 1.37 Å; cf. 1.34 and 1.48 Å for butadiene). This suggests that, in addition to the resonance form **52** chosen in the original paper, a form **53** depicting a 3-butene-1,2-diyl ligand bridging two palladium atoms in what is formally a Pd(II) dimer might need to be considered.

This uncertainty of oxidation state for palladium and bond-type representation, common in much of the interesting chemistry by Kurosawa and Murahashi, is summarized below, and has been discussed by them in some of their papers. They have developed the rational synthesis of extended arrays of Pd atoms supported by Pd–Pd bonds and π-coordinated extended aromatic and conjugated double bonds. These compounds are accessible, in general, by reaction of polyenes with homologs of the classic palladium(I) complexes $[\text{L}_3\text{Pd–PdL}_3](\text{BF}_4)_2$ containing two or more labile L ligands,[160] or by the use of a combination of Pd(II) and Pd(0) complexes. The early chemistry of these systems has been reviewed.[161]

The rational synthesis of anionic, neutral, and cationic dinuclear palladium complexes containing bridging conjugated dienes is shown in Scheme 32 for butadiene, and consists of the formal redox condensation of Pd(0) and Pd(II) complexes in the presence of the conjugated diene to give Pd(I) dimers.[162] In addition, some complexes with isoprene and with 1,3-cyclohexadiene were made. The isoprene complexes consisted of the expected pair of regioisomers in the case of the less symmetric neutral molecules. The crystal structures of one neutral complex



Scheme 31

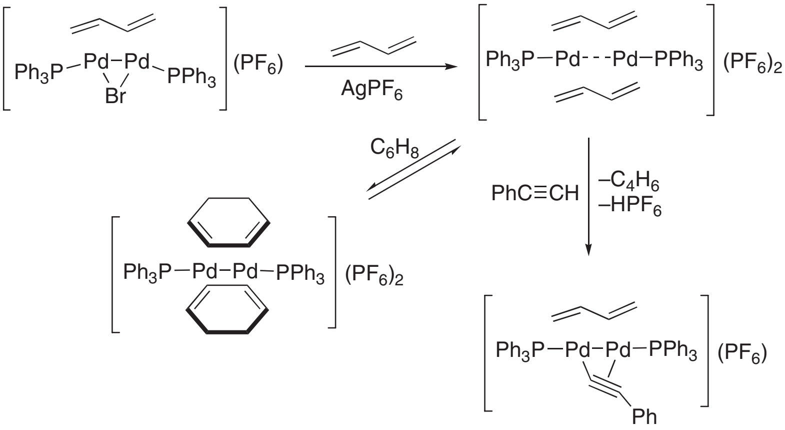


Scheme 32

(X = Br; diene = butadiene) and one anionic complex (X = Cl; diene = isoprene) were determined. The diene had a zigzag structure in both cases and two enantiomers were found in the complexes, corresponding to the two arrangements of the zigzag chain. The coordination of the diene in the compounds was described as μ_2-$\eta^2:\eta^2$-*s-trans*. Some structural parameters are: Pd–Pd = 2.662, Pd–C = 2.12–2.25 for the neutral molecule, Pd–C = 2.332–2.389 Å for the anionic molecule.

The bridging halides in these complexes can be extracted with silver salts in the presence of conjugated dienes, affording compounds with two bridging dienes. Moreover, exchange reactions between dienes, or with weak labile ligands, can be used to extend the range of these new complexes (Scheme 33).[163] On the other hand, as shown in the same scheme, the reaction with phenylacetylene affords an alkynylpalladium derivative, which presumably has a bridging alkynyl group, μ-1 *K*C1 : 2*K*C1,2-alkynyl.[153]

The dicationic complex with butadiene in Scheme 33 has a strikingly long Pd–Pd distance of 3.1252 Å, near the sum of the van der Waals radii (3.20 Å), due in part to the steric congestion of the diolefins with the PPh$_3$ ligand, which can be better described considering the alternative representations in Scheme 31. Theoretical calculations at HF and MP2 levels on a model compound $[Pd_2(\mu\text{-}C_4H_6)_2(PH_3)_2]^{2+}$, varying the Pd–Pd distance from 2.8 to 3.5 Å,[159] suggest that the Pd–Pd lengthening is produced to reduce congestion, resulting in considerable Pd–Pd weakening, which is compensated by both backdonation and donation interactions between the Pd dinuclear fragment and the diene (Figure 1). The C–C distances observed in the complex (C1–C2 = 1.368; C2–C3 = 1.410; C3–C4 = 1.331 Å) suggest that the participation of an enediyl representation is small, if any, in this case.



Scheme 33

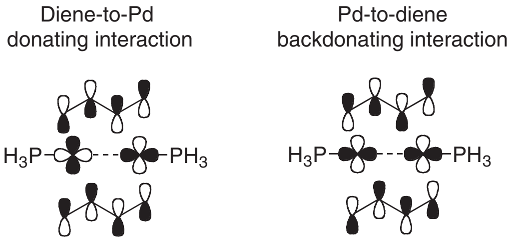
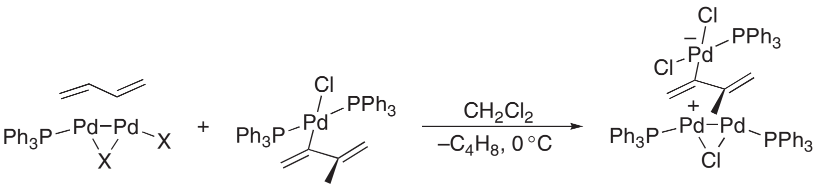


Figure 1

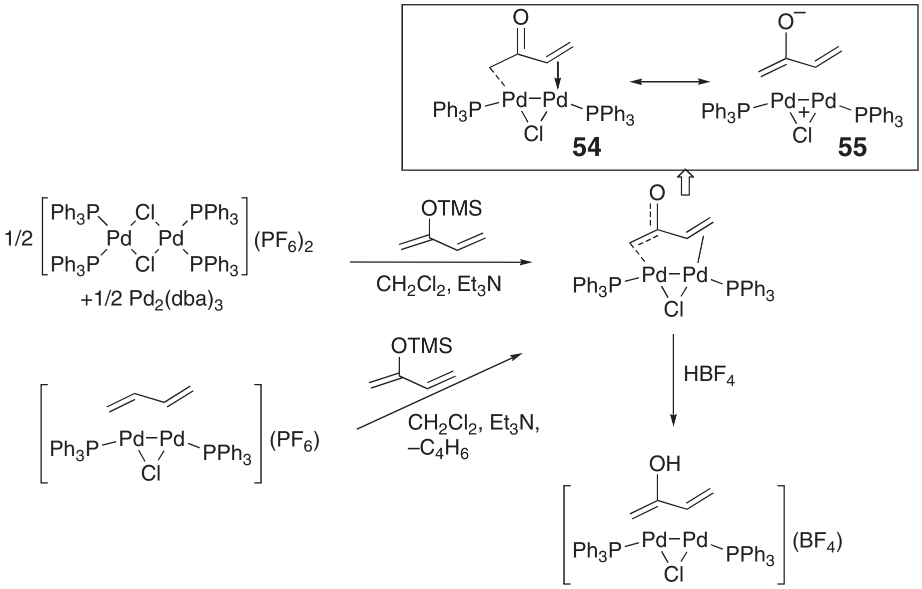
The diene exchange can be also made using a metallated fragment, such as the 2-palladio-3-methyl-1,3-butadienyl palladium complex used in Equation (16). The reaction involves butadiene displacement by the styryl fragment as well as ligand rearrangement to produce 61% yield of a zwitterionic trimetallic species, which was characterized by X-ray diffraction.[164]



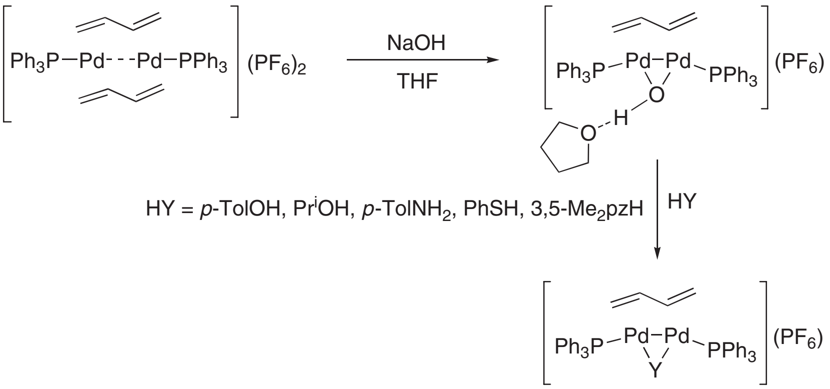
(16)

The Pd–Pd fragment can also coordinate a 2-hydroxy-1,3-butadiene ligand. Initially, the treatment of the starting Pd(0) + Pd(II) mixture (or alternatively the Pd(I)–Pd(I) dimer) with 2-hydroxy-1,3-butadiene, in the presence of NEt_3 as base, gives the desilylated μ_2-$\eta^2:\eta^2$-dienolate dipalladium(I) complex, which can then be protonated to the dienol complex (Scheme 34).[165] Infrared and NMR data support the bonding mode represented in Scheme 34 for the dienolate neutral complex, as a resonance between forms **54** and **55**, supported by the structural parameters found in the X-ray structure determination of the complex.

Further chemistry derived from the dicationic complex in Scheme 33 is summarized in Scheme 35. The use of 1 equiv. of NaOH displaces one diene and affords a μ-hydroxo complex (stabilized with a molecule of THF). This complex reacts with molecules with acidic hydrogens to generate new alkoxy-, aryloxy-, amido-, and thiolato-bridged



Scheme 34



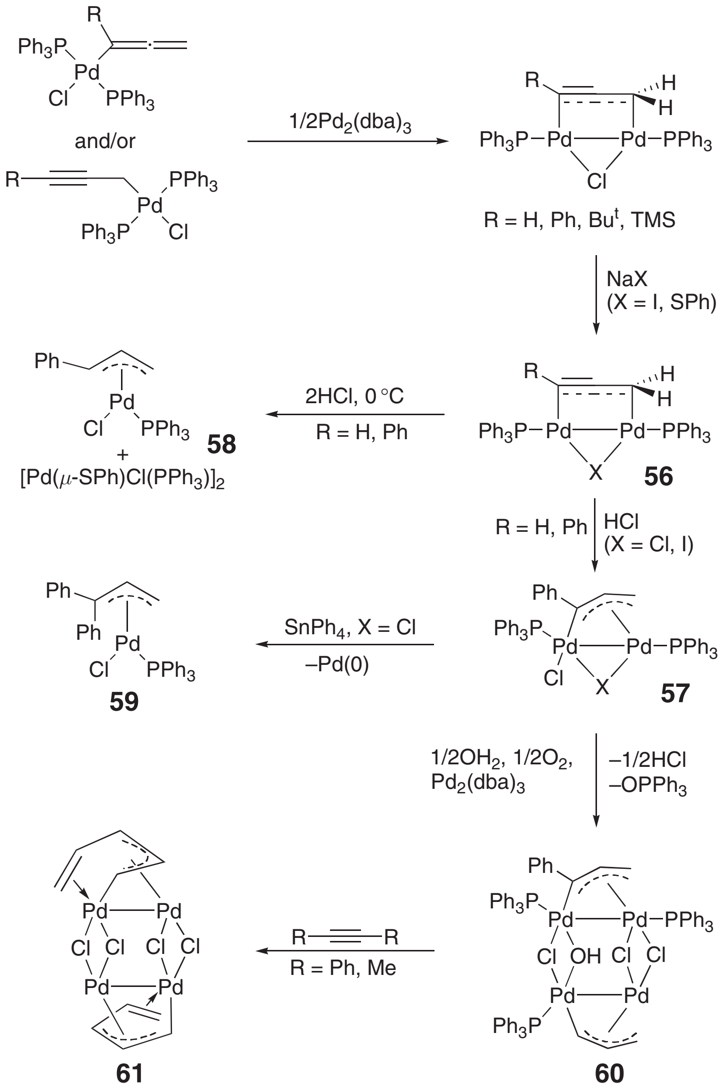
Scheme 35

complexes. The structures of the hydroxo- and amiduro-bridged complexes were determined. Interestingly, as soon as one butadiene is removed, the phosphine ligands can relax the crowding by bending the P–Pd–Pd–P chain, and the Pd–Pd distances recover shorter values in the range of a Pd(I)–Pd(I) bond. These distances are 2.5854 Å for bridging OH, and 2.594 Å for the bridging *p*-tolyl amido.[166]

Structurally related complexes are the η^3-allenyl/propargyl complexes **56** obtained by reaction of η^1-allenyl or η^1-propargyl palladium(II) complexes with $Pd_2(dba)_3$ (Scheme 36).[167] The crystal structures of the complexes with bridging Cl (R = H) and bridging SPh (R = Ph) have been studied, and feature an almost linear μ-η^3-allenyl/propargyl group, and almost equal Pd–Pd (2.642, 2.629 Å) and C1–C3 (2.69, 2.659 Å) distances. The Pd–C short distances are in the range 2.06–2.096 Å. The μ-η^3-allenyl/propargyl complexes **56** (X = Cl, Br; R = Ph) react with 1 equiv. of HCl to give complexes which are formulated (according to the X-ray diffraction structure of the complex with X = Cl) as the first examples of a μ-vinylcarbene (or μ-η^1,η^3-allyl) complex of palladium **57**. Isotopic labeling of the reaction with DCl revealed that it proceeds by unusual electrophilic attack of the proton to the center carbon of the η^3-allenyl/propargyl group. This seems to be due to high electron density at that central carbon atom, and MO (molecular orbital) calculations on the model complex $[Pd(\mu\text{-allyl})(\mu\text{-Cl})(PPh_3)]_2$ suggest that the ligation of the allyl to the metal fragment is largely dependent on the backdonation component, mostly from the Pd–Pd *d*(sigma)-bonding orbital to empty π^*-orbitals of the allyl (which are similar to the empty π^*-orbitals of the allenyl/propargyl ligand).[168] The reaction of the thiolate-bridged complex with 2 equiv. of HCl gave the allyl complex $[Pd(\eta^3\text{-}PhC_3H_4)Cl(PPh_3)]$ **58**, which is formally a hydrogenation product of the starting η^1-allenyl/propargyl palladium(II) complexes (R = Ph). For this reason, it has been suggested that this reaction might be a model for hydrogenation on a metal surface.[167]

The reactivity of the vinylcarbene complexes **57** is also interesting. Phenylation, followed by reductive elimination from the non-observed phenylated intermediate, gives an allyl complex **59**. In the presence of a catalytic amount of dba, **57** reacts with water and O_2 to give **60** (crystallographically characterized), which is transformed into **61** by insertion of alkyne into the Pd–carbene bond to form a new μ-η^3-vinylcarbene moiety.[169]

The rational methods developed for all these syntheses open the possibility to build hybrid organic–inorganic materials consisting of linear chains of palladium atoms sandwiched by conjugated polyenes. Formally, the compounds can be analyzed as having a central spine $-Pd_n^{2+}-$ consisting of $(n-1)$ Pd–Pd bonds with $2(n-1)$ electrons. The metal chain should be supplied by $(n-1)$ Pd(0) and 1 Pd(II) with substitutionally labile ligands, in the presence of the sandwiching polyenes.[170] Bulky ligands, such as PPh_3, should also be avoided at the extremes of the Pd_n chain in order to prevent the elongations of the Pd–Pd bond discussed above, associated with the participation of these ligands. Ligands such as acetonitrile or pyridine are adequate. The method was applied to create chains of three, four, and five palladium atoms, which can take one ligand at the terminal palladium atoms. The complexes with four palladium atoms represented in Scheme 37 were studied by X-ray diffraction methods for $X = 3,5\text{-}(CF_3)_2C_6H_3$ (for better crystallization) and showed highly linear Pd–Pd–Pd–Pd skeletons and planar $-(CH)_8-$ parts. The aryl rings are also coplanar in the complex without terminal ligands, but leaping up from the pyridine ligand in order to avoid congestion in the second case. Two alternative η^3-η^2-η^2-η^3-coordination descriptions can be used to represent bonding in the first case, whereas the second complex can be described just by η^2-η^2-η^2-η^2-coordination. Slippage from one to the other seems to occur easily, as suggested by the broad bands of the complex without additional ligand in the ^{1}H NMR spectra at −90°, which suggests the easy formation of the solvent complexes represented in the scheme.

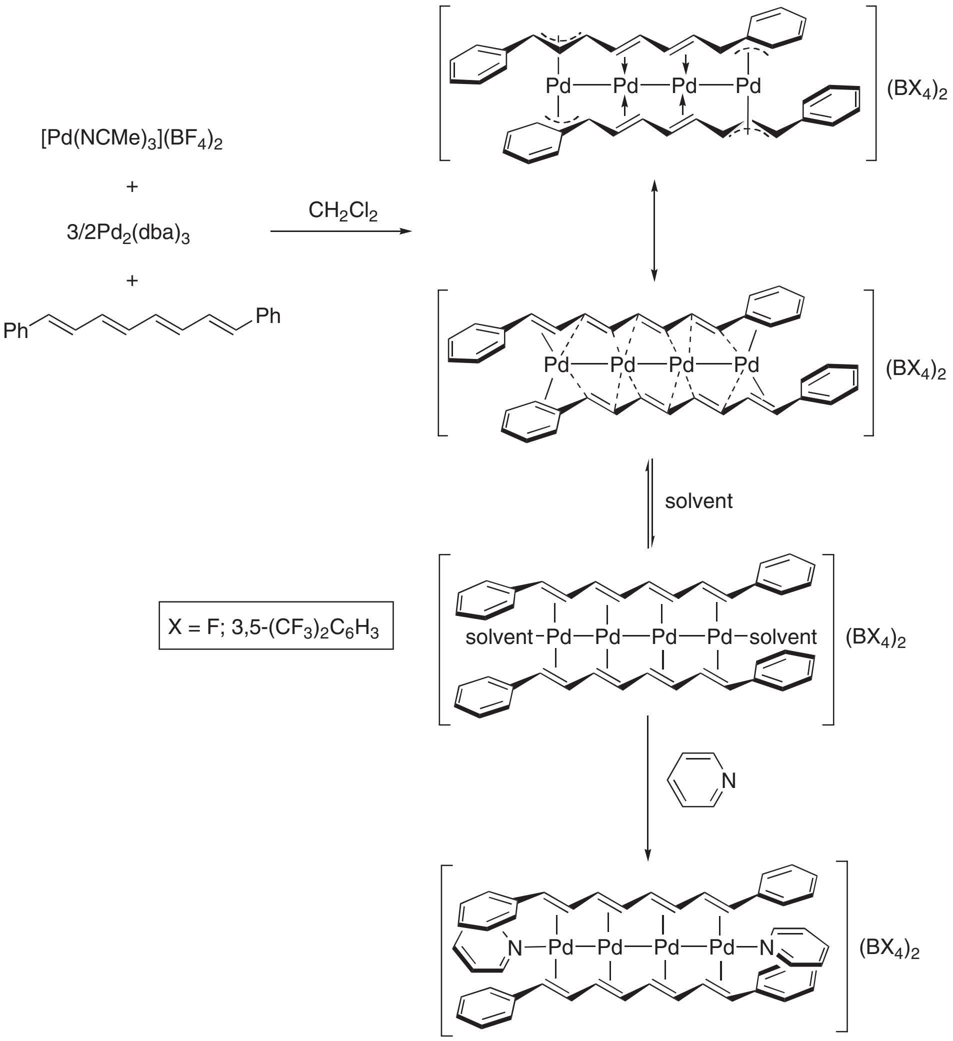


Scheme 36

The Pd(I) complex $[(MeCN)_3Pd–Pd(NCMe)_3](BF_4)_2$ was used in the reactions with *all-trans*-1,6-diphenyl–1,3,5-hexatriene, shown in Scheme 38.[171] The reaction in dichloromethane gives a mixture of the *meso*- and the *rac*-forms of a dinuclear bis-η^3-allyl compound with a Pd–Pd bond where palladium has formally a +III oxidation state as a result of the net addition of one double bond of the triene, which becomes a bis-allyl moiety. The preparations gave different isomer ratios in the range 6 : 4 to 7 : 3, probably due to subtle changes in crystallization conditions. When the solvent was acetonitrile, only one molecule of the triene per palladium was taken, and a mixture of the dimeric *anti*-facial- bis-η^3-allyl complex and the *syn*-facial-isomer (*anti* : *syn* = 78 : 22) was formed. The *meso*- and *synfacial*-complexes were characterized by X-ray diffraction. Treatment of the *synfacial*-isomer with the triene gave the *rac*-isomer as a kinetic product, which slowly converted to the *meso*-form.

The *meso*- and *rac*-isomers derived from polyenes did not interconvert thermally in the absence of free polyene, but it was found that there was a very efficient photoinduced face inversion, which was studied for tetraene ligands on a Pd–Pd–Pd moiety.[172] Starting from a *rac* : *meso* 73 : 27 ratio, irradiation with a xenon lamp (>510 nm) for 7 h leads to a *rac* : *meso* 1 : 99 ratio. Moreover, irradiation with visible light for 38 h lead to a *rac* : *meso* 21 : 79 ratio.

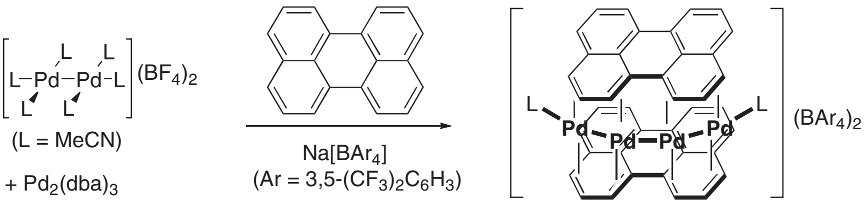
It is interesting that it is possible to grow stepwise the polypalladium chains attached to a polyene. This has been shown for 1,4-diphenyl-1,3-butadiene.[173] Starting with the complex with Pd–Pd, successive additions of $Pd_2(dba)_3$ lead finally to the Pd–Pd–Pd–Pd complex (Scheme 39). The X-ray structures of the three cations shown (the



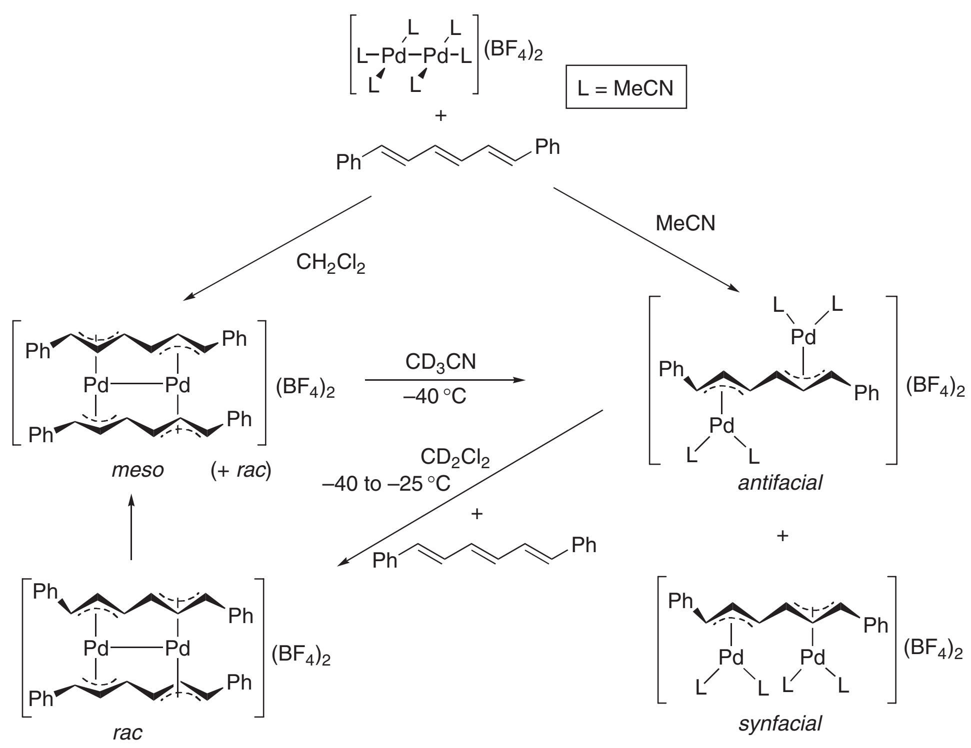
Scheme 37

counterion BF_4^- was changed sometimes for $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ for better crystallization) were determined, supporting the successive change of coordination from μ_2-$\eta^3:\eta^3$ to μ_3-η^3-η^2-η^3, and finally μ_4-$\eta^2:\eta^2:\eta^2:\eta^2$. Whereas the Pd–Pd–Pd chain is linear, the tetrapalladium Pd–Pd–Pd–Pd chain is significantly bent, probably due to the template effect of the bent conjugated sequence of the ligand. In fact, as stated above, the analogous cation $[Pd_4\{Ph(CH{=}CH)_4Ph\}_2(py)_2]^{2+}$ (Scheme 37) is linear.[170]

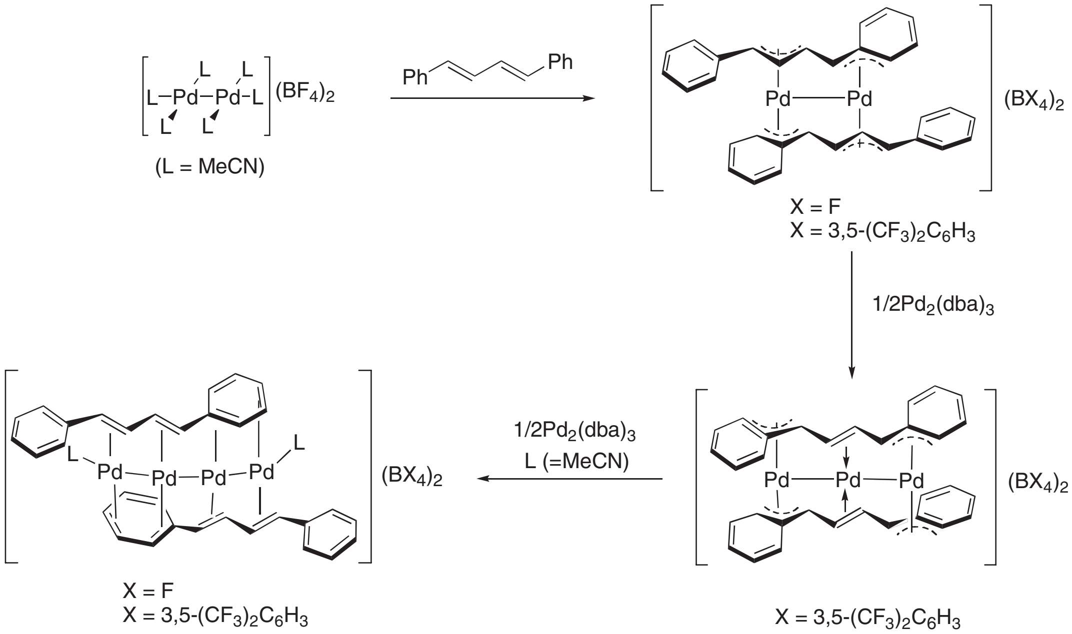
Another Pd–Pd–Pd–Pd bent chain is found in the tetrapalladium sandwich complex with the polycyclic aromatic hydrocarbon perylene shown in Equation (17). The perylene ligand is bonded to the tetrapalladium chain in a μ_4-$\eta^2:\eta^2:\eta^2:\eta^2$ fashion. The acetonitrile ligands can be easily replaced by pyridine ligands, and the perylene ligands in the resulting complex can be replaced with *all-trans*-1,8-diphenyl-octa-1,3,5,7-tetraene, without alteration of the Pd–Pd–Pd–Pd chain.[174]



(17)

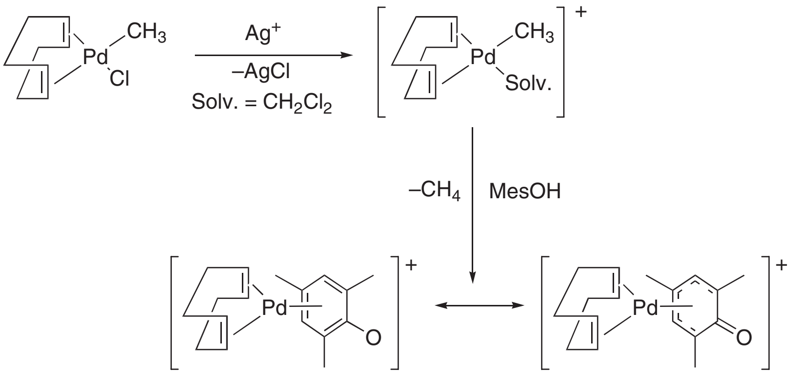


Scheme 38



Scheme 39

Co-crystallization of Pd_6Cl_{12} (the β-polymorph of $PdCl_2$) with benzene, its methylated derivatives, or C_{60} produces binary or ternary compounds where the organic molecules do not seem to play simply the role of filling the crystal, but are ordered in such a way that they seem to interact with the cubic faces of Pd_6Cl_{12}. Presumably, the empty $5e_g$ and $5t_{2u}$ d_{x^2}–y^2-orbitals of Pd_6Cl_{12}, which are contaminated with d_{z^2} and d_{xz} character, respectively, and have large

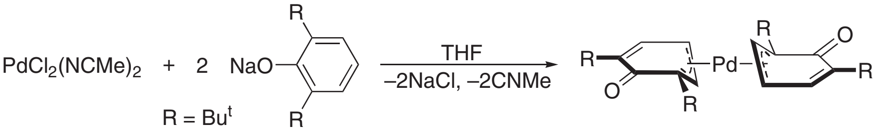


Scheme 40

amplitudes normal to the $PdCl_4$ planes, are involved as acceptors of π-electron density in face-to-face interactions with arenes whose planes are parallel to the $PdCl_4$ face.[175] Related complexes with Pd_6Cl_{12} co-crystallized with *p*-xylene or with (*E*)-stilbene have also been reported.[176]

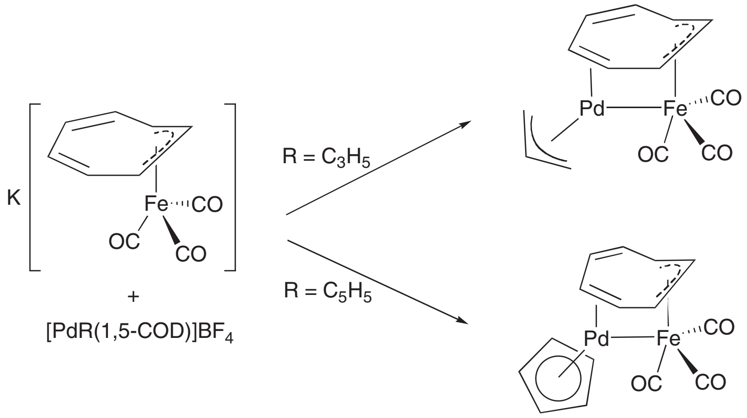
A mesitylato palladium complex, reported as the first structurally characterized η^5-coordinate example, was prepared initially by reaction of PdMe(OMes)(COD) with HBF_4. An improved synthesis is shown in Scheme 40.[177] The crystal structure of the compound (crystallized as its $[SbF_6]^-$ salt) shows what seems a nearly regular η^6-coordination of the aryl ring, with a deviation from the average distance less than 0.19 Å. However, the C–O bond distance (1.23 Å) is markedly shorter than expected for a single bond, and in the same range as C=O in benzoquinone (1.22 Å). This supports the view that the complex should be better regarded as an η^5-oxacyclohexadienyl complex of palladium(II).

A different coordination mode is found for the neutral palladium complex coordinated with two 2,6-di-*tert*-butylphenolate groups, prepared as shown in Equation (18).[178] The crystal stucture of the compound supports, in this case, η^5-allyl coordination of the ring, with the palladium flipping in solution between the two equivalent allyl positions in each ring. The C–O distance observed is 1.234 Å, supporting a double bond, and the ring is not planar.

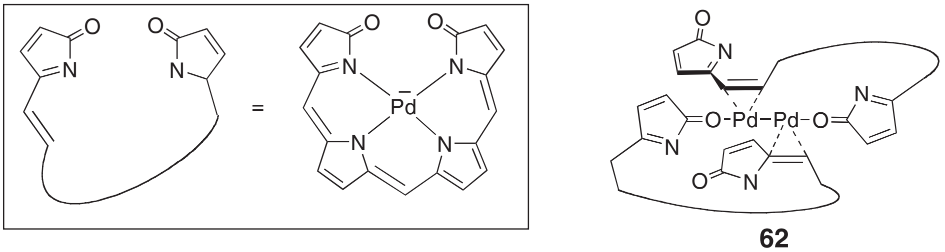


(18)

Two heterobimetallic complexes with a Pd–Fe bond supported by a bridging cycloheptatrienyl group have been reported (Scheme 41). In both cases, the cycloheptatrienyl group binds iron as η^3-allyl. For R = η^5-cyclopentadienyl, the complex formed is $[(OC)_3Fe\{(\mu_2)\eta^3:\eta^2\text{-}C_7H_7\}Pd(\eta^5\text{-}C_5H_5)]$, with Pd–C distances to the two carbons of the



Scheme 41



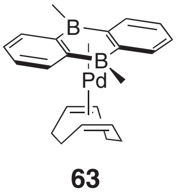
62

Scheme 42

coordinated double bond that are within experimental error (2.153 and 2.150 Å).[179,180] For R $= \eta^3$-allyl, the cycloheptatrienyl group was originally reported to adopt an η^4-coordination,[180,181] but a crystal structure of the compound proved this to be in error. In fact, the complex should be formulated as $[(OC)_3Fe\{(\mu_2)\eta^3:\eta^2\text{-}C_7H_7\}Pd(\eta^5\text{-}C_3H_5)]$, although it is highly fluxional in solution.[182]

A tetrapalladium complex (**62** in Scheme 42) has been reported with tetrapyrrole acting as π-donor in a complex where a Pd(I)–Pd(I) unit is sandwiched between two helical bilindione-palladium(II) moieties. Two oxygens of this moiety are also coordinated to the terminal positions of the Pd(I) atoms.[183]

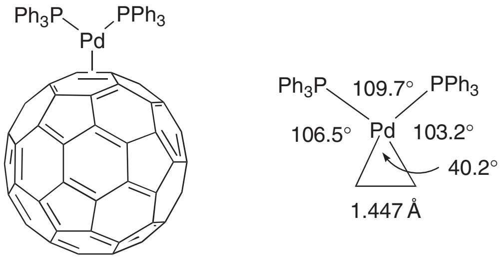
Finally, a palladium complex **63** with a 9,10-dihydro–9,10-dimethyl–9,10-diboraanthracene ligand acting as an "η^6-coordinated" group (taking the B atom as a C atom for the hapticity count) has been reported.[184] It is known that the 1,4-diboracyclohexa–1,5-diene can act as a four-electron donor, and as a two-electron acceptor in the two π- empty orbitals of the two boron atoms to give the corresponding dianion. In the corresponding diboraanthracene compound, the two arenes can formally replace the two double bonds, each acting as an η^2-arene. This, with the two olefin bonds coordinated from the COD ligand, will make an 18-electron Pd(0) complex, approximately tetrahedral as the structure suggests. Alternatively, considering a backdonation of two electrons from Pd, the diboraanthracene ligand can be described as a dianion coordinated to Pd(II). The X-ray structure shows that the central diboraanthracene is not strictly planar in the complex, and the Pd distances to the B atoms (2.349, 2.69 Å) are slightly shorter than to the C atoms (2.414–2.445 Å).



63

8.06.4 π-Complexes of Fullerenes

Fullerenes behave as strongly electron-acceptor polyalkenes, and can bind metal fragments at the (6–6) ring bonds formed at the junctions of two six-membered rings. Coordination of olefins to metal centers able to backdonate electron density into the π^*-antibonding orbitals of the olefin produces a rehybridization of C orbitals toward sp^3. Consequently, the substituents at carbon are bent away from the metal. Fullerenes are made of inherently strained (pyramidalized) carbons with their skeletal bonds forced not to be coplanar due to the ball shape of the molecule. The coordination of electron-rich metal centers, which releases this inherent strain, is then favored. Support for this simple image is provided by theoretical calculations at different levels carried out on $C_{60}Pd(PPh_3)_2$,[185,186] on model complexes such as $C_{60}Pd(PH_3)_2$,[187–190] and on simpler models such as $(C_{14}H_8)Pd(PH_3)_2$ ($C_{14}H_8$ = pyracylene).[191] In all cases, the prediction is that the bonds shared by two six-membered rings ((6–6) ring bonds) give the strongest bonding, and that π-backdonation from 4*d* Pd electron density to carbon–carbon π^*-antibonding orbitals dominates over σ-donation. This means that the metal loses electron density in favor of the fullerene. As acceptor, C_{60} lies halfway between ethylene and electron-deficient olefins such as tetracyanoethylene or tetrafluoroethylene. Calculated bond-dissociation energies are higher than for the corresponding ethylene complexes, but lower than for the complexes with tetracyanoethylene or tetrafluoroethylene.



64

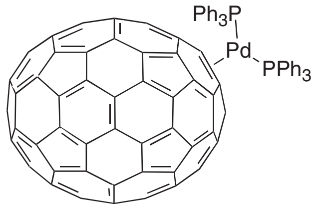
Figure 2

The synthesis of fullerene complexes of Pd was developed following precedents with Pt.[192] Complexes $C_{60}Pd(PR_3)_2$ and $C_{60}\{(Pd(PR_3)_2)_6\}$ (R = Ph, Et, PMe_2Ph, PPh_2Me, or $P(OMe)_3$) were soon prepared,[193,194] and studied with a number of techniques such as electrochemistry[195] and Raman spectooscopy.[193] The Raman spectra demonstrated a reduction in symmetry from I_h in the unsubstituted C_{60}, to C_{2v} in $(\eta^2\text{-}C_{60})Pd(PR_3)_2$, and to T_h in $C_{60}\{(Pd(PR_3)_2)_6\}$. As a consequence, some vibrational modes which are silent in C_{60} become active upon coordination, and some degenerate vibrational modes are split.

$C_{60}Pd(PPh_3)_2$ **64** can be obtained in high yield by reaction of C_{60} with $Pd(PPh_3)_4$. The X-ray molecular structure of the compound (Figure 2) shows the fullerene ligated to palladium in an η^2-fashion, with elongation of the C═C bond, as classically found for coordinated π-acceptor olefins.[196] $C_{60}\{(Pd(PR_3)_2)_6\}$ complexes feature six $Pd(PR_3)_2$ fragments connected to six C_{60} double bonds distributed in octahedral positions at the surface of C_{60}.[192]

The structure found for $(\eta^2\text{-}C_{60})Pd(PR_3)_2$ is systematically reproduced in other $C_{60}PdL_2$ complexes studied by X-ray diffraction methods: L_2 = dppf,[197] 1,1′-diphenylphosphinoruthenocene,[198] 1,1′-diphenylphosphinecobalticinium(PF_6),[198] or $Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2$.[199] Fluxional behavior is detected in ^{13}C NMR studies on $C_{60}PdL_2$ species in solution, where L = PMe_2Ph, PPh_2Me, and $P(OMe)_3$, indicating rotation of C_{60} on the PdL_2 moiety.[194]

In the case of C_{70}, metals bind preferentially at the most curved (and most strained) part of the fullerene, again at the (6–6) ring bonds formed at the junctions of two six-membered rings. This is found in the structure of $(\eta^2\text{-}C_{70})Pd(PR_3)_2$ **65**.[200]



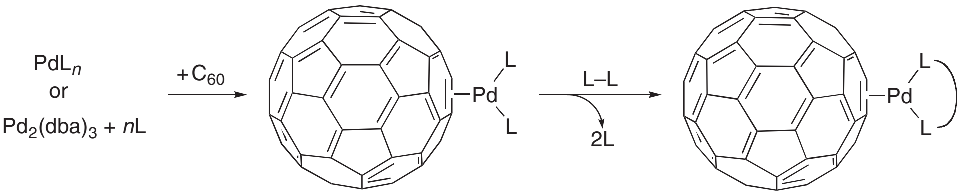
65

Electrochemical studies (by cyclic voltammetry) on $C_{60}Pd(PPh_3)_2$ and on $C_{70}Pd(PPh_3)_2$ in acetonitrile in the presence of excess $Pd(PPh_3)_4$ revealed the disappearance of some reductive waves characteristic of free C_n (n = 60, 70), suggesting the existence of the equilibrium shown in Equation (19).[201]

$$C_nPd(PPh_3)_2 \rightleftharpoons C_n[Pd(PPh_3)_2]_2 + C_n \tag{19}$$

The low oxidation state of Pd(0) and the high π-backbonding acceptor nature of fullerenes contribute to reinforce the Pd–fullerene bond strength. This facilitates the syntheses of these complexes, which can be easily prepared from C_{60} (or C_{70}) and Pd(0) precursors, such as PdL_4, $Pd_2(dba)_3$, or by ligand exchange from $C_{60}PdL_2$ (Scheme 43).[202]

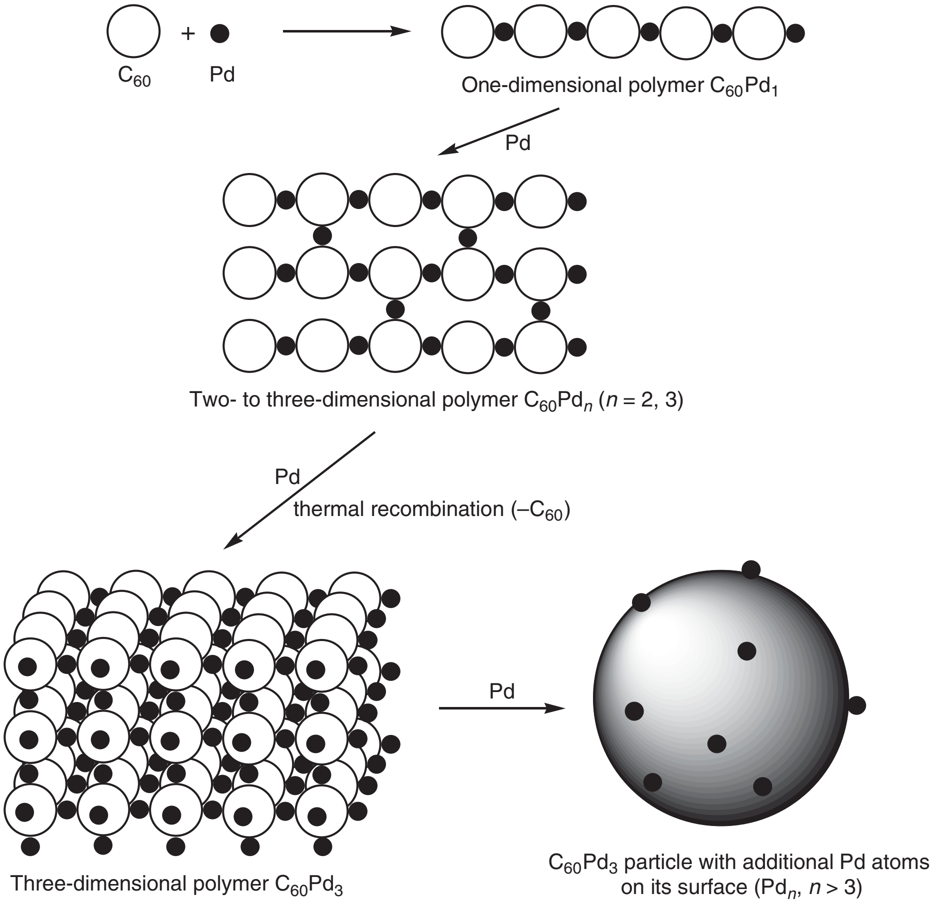
Complexes with monodentate and bidentate ligands have been prepared this way.[197,199,203,204] A palladium complex, $C_{60}Pd\{(+)DIOP\}$, was the first optically active fullerene complex reported.[205] Its circular dichroism spectrum shows many Cotton effects. The C_{70} analog has also been reported and its reactivity to attack by radicals has been studied.[206] A study of the electrochemical properties of the enantiomer $C_{60}Pd\{(-)DIOP\}$ has been reported.[207] It is found often that palladium-containing fullerenyl anion radicals undergo partial or total rupture of the M–C bond,[207,208] because in these monoanions, the added electron pertains to the LUMO involving the metal fragment.



Scheme 43

An interesting consequence of the strong binding of fullerene to metals and the polydentate nature of fullerenes as ligands is that, in the absence of other strong ligands, metal atoms can be used to link fullerenes making what can be considered an organometallic polymer. The system $C_{60}Pd_n$ has been studied in detail. It consists of neutral, amorphous, stable-to-air materials, which can be formed from a Pd(0) precursor and C_{60}. The C_{60} : Pd ratio can be varied by controlling the ratio of reagents in the reaction and by using thermal decomposition. An idealized picture is shown in Scheme 44 (Pd source is $Pd_2(dba)_3 \cdot CHCl_3$).[209] Note, however, that powder X-ray diffraction studies have shown that these polymer-like structures have structures that are more disordered than shown in Scheme 44.[210]

In all compounds, the Pd atom would be linearly coordinated by two olefinic bonds. At lower charges of Pd, a one-dimensional polymer $C_{60}Pd_1$ is formed, with each C_{60} acting as a diolefin toward two different Pd atoms. As C_{60} : Pd ratio is decreased (more Pd), new olefin bonds of C_{60} are used and the newly incorporated Pd atoms create links between polymer chains. The limit ratio for a three-dimensional polymer is $C_{60}Pd_3$, with each C_{60} ball surrounded by six Pd atoms in an octahedral arrangement (as in $C_{60}\{(Pd(PR_3)_2)_6\}$). The $C_{60}Pd_n$ products aggregate and precipitate out



Scheme 44

as particles, which are sized 60–100 nm or higher (by SEM). The material can take more Pd (e.g., $C_{60}Pd_{3.5}$), but these extra Pd atoms are deposited on the surface of $C_{60}Pd_3$ polymer particles. This is indicated by the fact that $C_{60}Pd_n$ ($n > 3$) catalyzes heterogeneous hydrogenation of diphenylacetylene in cyclohexane, whereas $C_{60}Pd_3$ does not.[209]

Under appropriate conditions, $C_{60}Pd_n$ with n ranging from 1 to 7 can be prepared, and there is evidence that, in addition to linear chains made of $\cdots C_{60}Pd\cdots$ units cross-linked by bonds to additional Pd atoms, there are also $C_{60}Pd_6$ subunits within the polymer.[211]

The $C_{60}Pd_n$ polymers can be also prepared by electrochemical reduction of C_{60} in the presence of $PdCl_2(NCPh)_2$, in the form of redox-active, black films that coat the electrode.[212] Addition of PPh_3 to the film dissolves it to produce $C_{60}Pd(PPh_3)_2$. Different kinds of films are produced by varying the Pd compound and the relative concentration of the precursors.[213] The process can be applied successfully to a modified fullerene 2′-ferrocenylpyrrolidinio–[3′,4′;1,2][C_{60}]fullerene.[214] Electrodes modified with these films have been applied in electrochemical studies.[215]

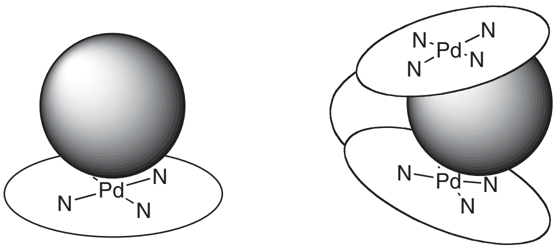
$C_{60}Pd_n$ ($n > 3$) materials[216] and $C_{60}Pd(PPh_3)_2$,[217–219] have been reported as active catalysts for the hydrogenation of olefins and alkynes, whether homogeneous, heterogeneous, or supported. A theoretical model of the adsorption of acetylene molecules on palladium–phosphine fullerene complexes has been developed as a model for the preliminary stage of C≡C scission.[186]

$C_{60}Pd_n$ materials are good precursors for the synthesis of $C_{60}PdL_2$ complexes (L = phosphines, phosphites, isocyanides).[194,220] On the other hand, these materials have been shown to adsorb toluene (a harmful, difficult-to-adsorb molecule) at room temperature and low concentration (1,000 ppb). Theoretical calculations suggest that the π-electrons of toluene adsorb on partially positive atoms of $C_{60}Pd_n$, and the π-electrons of C_{60} and toluene overlap through the *d*-electron orbitals of the Pd atom, producing a stronger interaction than simple physical adsorption.[210]

Fullerenes and porphyrins are spontaneously attracted to each other.[221] Supramolecular compounds involving metalloporphyrin derivatives and fullerene C_{60} have been reported (Figure 3), which include simple planar porphyrins **66**,[222] as well as specially designed jaw-like bismetalloporphyrins offering a cleft to host the fullerene **67**.[223] Interactions with Pd porphyrins are weaker than with free porphyrins or with other metallated porphyrins, but supramolecular compounds and co-crystals have been reported. The long C(porphyrin)–Pd distances (above 3 Å) suggest that there is no important bonding interaction, but a complex contribution of van der Waals forces (π–π interaction), charge transfer, and electrostatic attraction.

The fully aromatic 60π-electron structure of fullerene C_{60} can be degraded by selective lessening of conjugation.[224] For instance, its reaction with a methylcopper reagent formed from MgMeBr and [$CuBr{\cdot}SMe_2$] affords a 50π-electron conjugated bowl plus an isolated pentadiene on the "pole" of the ball (Scheme 45, **68**). After protection of the pentadiene acidic proton in the form **69**, the strategy can be applied again to produce balls with 40π-conjugated electrons plus two isolated pentadiene caps. Compounds **69** possess several isomers arising from the relative arrangement of the two cyclopentadienes and that of the CN and H substituents in the two cyclopentadiene fragments (only one isomer, with the two cyclopentadienes opposite to each other, is represented in Scheme 45 as **70**). The cyclopentadiene can be deprotected by treatment with lithium naphthalenide and subsequent hydrolysis.[225] These compounds have been used as ligands toward palladium and will be dealt with here, although the ligand is no more a fullerene.

The usual method of treatment of C_{60} with $Pd(PPh_3)_4$, but using pentaarylated C_{60} (Scheme 45, **68**, R^1 = Ar), leads to complexes (η^2–$Ar_5C_{60}H$)$Pd(PPh_3)_2$ (Ar = Ph, *m*-Tol, *p*-Tol). In this case, the lower symmetry of pentaarylated C_{60} (C_s) offers 14 kinds of [6 : 6]-double bonds for coordination. Excluding those sterically hindered, 11 isomers (excluding enantiomers) can be formed. *Ab initio* calculations predict that only six of these isomers should have noticeable



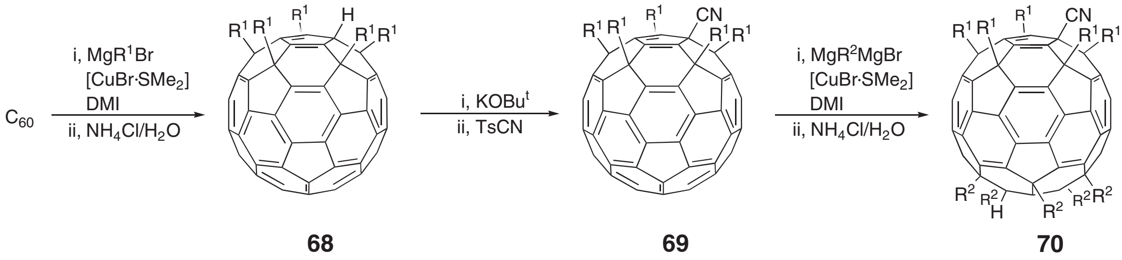
Porphyrin/fullerene

66

Jaw-like porphyrin/fullerene

67

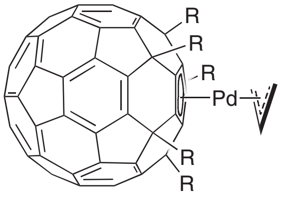
Figure 3



Scheme 45

abundance, and this theoretical result was used to assign the four singlets observed in the ^{1}H spectrum of the complexes for the cyclopentadiene H, at $\delta = 5.1$–5.3 ppm.[226]

On the other hand, treatment of 68 or 70 with base affords a cyclopentadienide anion that can be coordinated to Pd 71 and 72. A number of these cyclopentadienyl derivatives have been prepared by metathetical reactions with allylic complexes of Pd, $[Pd(\mu\text{-}Cl)(allyl)]_2$, and some X-ray structures have been determined.[225,227] In general, enhanced stability of complexes 71 (R = Ph) and 72 is found compared to conventional Cp derivatives, which is due to a kinetic stabilization effect of the five Ph groups surrounding the metal atom in the complex, and a thermodynamic stabilization effect of the electron-withdrawing fullerene moiety.



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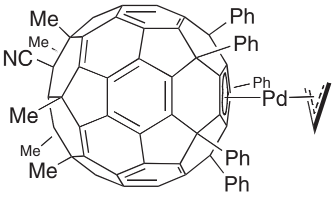

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8.06.5 π-Complexes of Alkynes

8.06.5.1 Structure and Bonding

The bonding of alkynes to palladium continues to attract attention and new theoretical studies have been carried out, often in the context of mechanistic studies on catalytic processes for these substrates. Acetylene is often used as a model alkyne although it is agreed that this may show crucial differences with the substituted alkynes used in most experimental work. The studies have evaluated the importance of the two components of the alkyne metal interaction: donation of the acetylene to the metal and backdonation. Stronger donation than backdonation was calculated for $Pd(CO)_3(C_2H_2)$.[228] The same result was obtained for $Pd(CH_3)Cl(NH_3)(C_2H_2)$, which shows quite long Pd–C distances indicating weak binding of C_2H_2. Two possible conformations of the acetylene were analyzed, that is, "in plane" and perpendicular to the Pd coordination plane. The "in-plane" conformation was found to be more stable by 1–2 kcal mol^{-1}. Such a small energy difference, in agreement with the weak bond calculated, predicts almost free rotation of the acetylene.[229] However, although in real systems with coordination of a different set of ligands and alkyne the energy difference between conformations may be larger, it can be anticipated that steric factors will be very important in determining the arrangement of the alkyne.

Relativistic effects have been analyzed using the $M(PH_3)_2(C_2H_2)$ model for M = Ni, Pd, Pt and shown to be more important for Pt since they produce a destabilization of the 4*d*-orbitals and an increase in backdonation to the alkyne. As a result, when the three metals are compared, the palladium complex shows a minimum in Pd–alkyne bond strength and also the shortest C–C bond length for the coordinated acetylene, consistent with a reduced backdonation for this metal.[230]

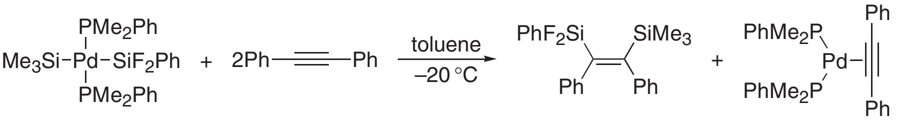
The infrared absorptions of the species formed between laser-ablated Pd atoms and acetylene in excess argon were measured and compared with the values obtained by DFT calculations: $Pd(\eta^2\text{-}C_2H_2)$ and $Pd(\eta^2\text{-}C_2H_2)_2$ species were produced, the latter favored at high acetylene concentrations. The calculations and the IR absorptions (assigned with the aid of isotopic substitution) support a stronger interaction for the species with one molecule of alkyne. The species $Pd_2(\eta^2\text{-}C_2H_2)$, analogous to chemisorbed acetylene, were also detected, and the low values of the C–C stretching vibration (1572.3 and 1565.8 cm^{-1}) indicate that the triple bond is practically reduced to a double bond. The calculations show the same results and predict a lower energy (ca. 5 kcal mol^{-1}) for the "in-plane" isomer versus the perpendicular arrangement of the alkyne and the Pd–Pd unit.[231]

X-ray crystal structures of many new palladium η^2-alkyne complexes have been determined; Pd(0) complexes are mainly trigonal planar showing in-plane coordination of the alkyne. Pd(II) derivatives exhibit out-of-plane η^2-alkynes, rotated to an angle that is much smaller than 90° so that a perpendicular arrangement is never reached; a sum of factors, not only electronic, may play a role in deciding the actual angle adopted, as mentioned above.

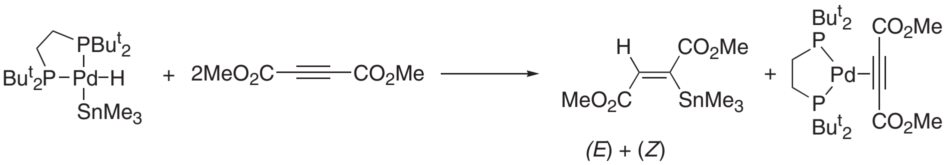
8.06.5.2 Alkyne Complexes of Pd(0)

The general route to the synthesis of palladium(0) complexes with coordinated η^2-alkynes is ligand substitution in a Pd(0) derivative, mainly $Pd_2(dba)_3$ or $Pd(PPh_3)_4$. In some cases, the Pd(0) derivative is generated *in situ* from a Pd(II) complex in the presence of the alkyne. Examples of both preparative methods will be given below.

Complexes of internal alkynes of general formula $Pd(\eta^2\text{-alkyne})(PR_3)_2$ or $Pd(\eta^2\text{-alkyne})(diphos)$ have been reported, often prepared in the course of palladium-catalyzed reactions and other processes. Thus, most of them have been synthesized by decomposition of Pd(II) complexes in the presence of the alkyne as shown in Equations (20)[63] and (21).[232] Insertion into a Pd–E bond and reductive elimination generates the silylated or stannylated alkene and Pd(0), which is trapped by the alkyne in excess.

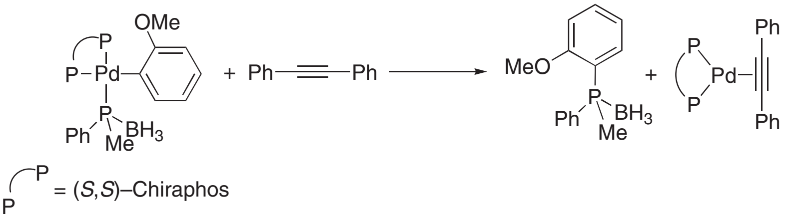


(20)



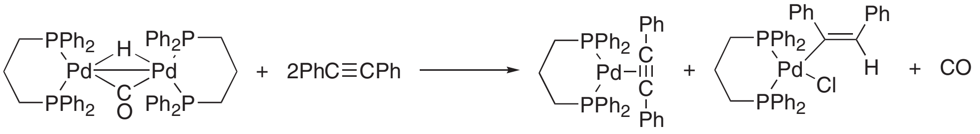
(21)

Other coupling reactions lead to Pd(0), that can be trapped by alkene as represented in Equation (22) for the enantioselective coupling of aryl and a phosphine derivative.[233]



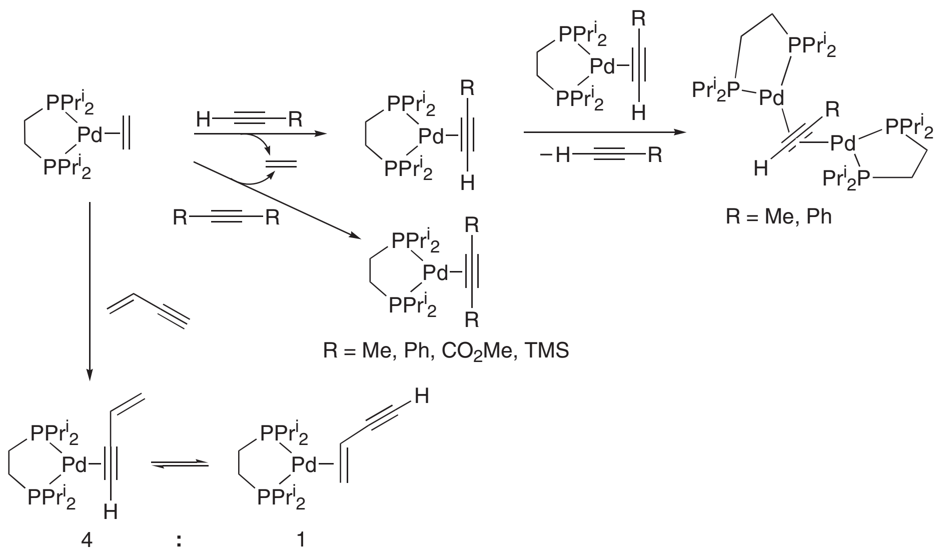
(22)

The Pd(I) dimer depicted in Equation (23) undergoes disproprotionation in the presence of alkyne to give the Pd(0) η^2-alkyne complex and a Pd(II) vinylic derivative.[234]



(23)

A thorough study on the complexation of 1-alkynes and internal alkynes to Pd(0) has been reported.[235] The reaction of alkynes with the Pd(0) complex $Pd(dPr^ipe)(C_2H_4)$ leads to $Pd(dPr^ipe)(\eta^2$–alkyne) derivatives, as shown in Scheme 46. Pd(0) complexes of terminal alkynes were believed to be unstable due to facile oxidative addition of the C–H bond of the alkyne to give an alkynyl(hydrido)palladium(II) complex that could undergo further alkyne



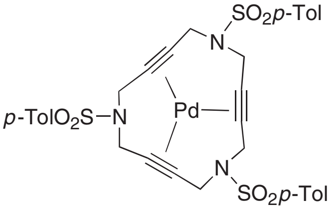
Scheme 46

insertions and lead to oligomerization products. However, complexes of terminal alkynes in Scheme 46 were stable, and only in the presence of excess alkyne they lead to alkyne oligomers. This shows that they are not intrinsically less stable, but more sensitive to the reaction conditions used for their preparation than internal alkynes.

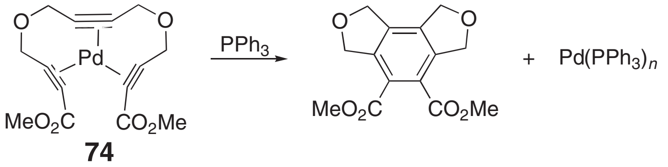
Alkynes with electron-withdrawing substituents are more stable and their complexes do not dissociate alkyne. However, propyne and phenylethyne, or 2-butyne in the case of terminal alkynes, can dissociate in vacuum to form dimeric complexes with a bridging alkyne. IR spectroscopy shows that the shift observed for the C≡C stretching band in these complexes with respect to the value of the free alkyne is much larger in the dimeric complexes than in the monomeric one. The X-ray crystal structure of Pd(dPr^{i}pe)(η^2-CH≡CPh) shows an "in-plane" alkyne and an almost perfect trigonal-planar arrangement. A short C≡C bond (not very different to the free alkyne) was found, and it is less elongated than the C≡C bond in the analogous Pt and Ni complexes, showing a weak backbonding strength for palladium. The same reaction using an enyne as substrate leads to a mixture of isomers, the one with the coordinated triple bond being more stable. Slow intramolecular interconversion between them was observed, probably through a tetrahedral four-coordinated Pd(0) intermediate with both unsaturations bound to the metal.

The complex Pd{$PPh_2CH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPh_2$}{($MeCO_2$)C≡C(CO_2Me)} was synthesized by reaction of the free azine diphosphine with $Pd_2(dba)_3$ in the presence of the alkyne. This complex is converted into a Pd(II) alkenyl with a bound ene–hydrazone diphosphine ligand by controlled potential electrolysis.[236] A complex of the same family, $Pd(PPh_2py)_2${($MeCO_2$)C≡C(CO_2Me)}, was also prepared by ligand substitution from $Pd_2(dba)_3$.[237] Both Pd(0) alkyne complexes were structurally characterized by X–ray diffraction.

Complexation of triynes to Pd(0) has been reported to give homoleptic palladium alkyne complexes that show a trigonal-planar arrangement with all of the alkyne carbons and Pd in the same plane. Complex **73** is a macrocyclic complex synthesized by reaction of the triyne with $Pd(PPh_3)_4$.[238] Due to coordination to the metal, the alkyne carbons are shifted to the center of the cycle and their substituents deviate from linearity by about 22°. Complex **74** undergoes clean intramolecular cyclization at room temperature upon addition of PPh_3 (Equation (24)).[239] No intermediate complexes were detected in the course of this reaction, which is an example of the important cycloisomerization of alkynes and enynes catalyzed, among other transition metal complexes, by Pd(0) derivatives.



73

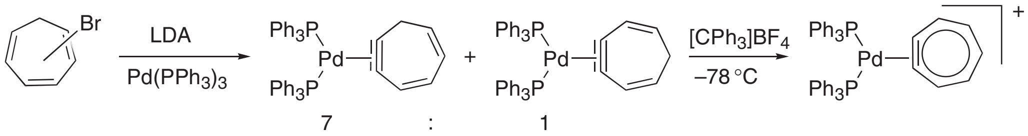


(24)

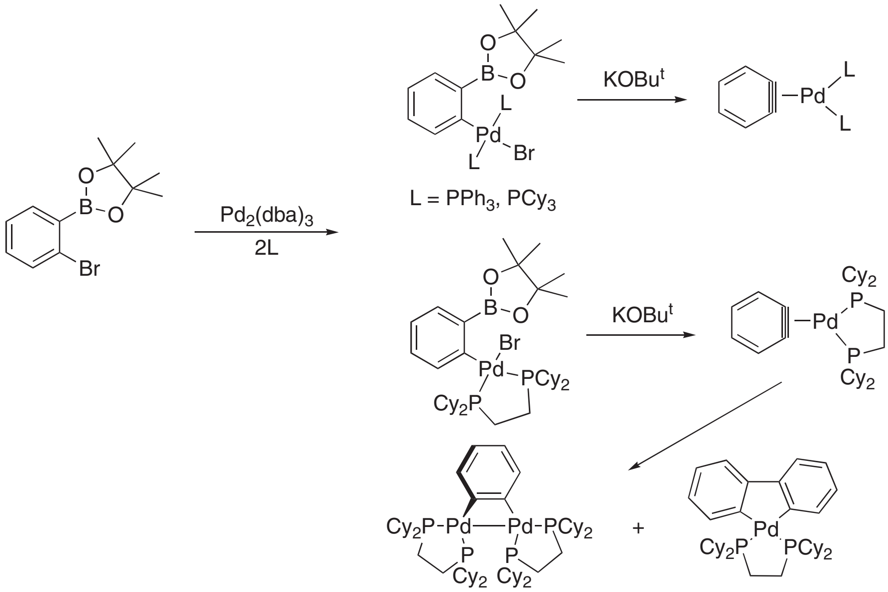
Cycloheptadien-1-yne, generated *in situ* by dehydrobromination of bromocycloheptatriene, coordinates to Pd(0) giving the mixture of isomers depicted in Scheme 47. Treatment of these complexes with the trityl cation affords the tropyne palladium species.[240]

Unusual palladium benzyne complexes can be obtained by an intramolecular Suzuki–Miyaura coupling in a Pd(II) derivative (Scheme 48). The molecular structure of the complex with L = PCy_3 shows a trigonal-planar arrangement, the same as most Pd(0) alkyne complexes, and a C≡C (triple bond) distance of 1.324 Å. The rest of the C–C distances in the ring are all in the range 1.37–1.40 Å, indicating that the ring retains aromatic character.[241] The complex with $L_2 = Cy_2PCH_2CH_2PCy_2$ is unstable, and decomposes producing a novel dinuclear palladium(I) complex with a bridging *o*-C_6H_4 group with a short Pd–Pd distance of 2.645 Å. The molecular core is highly distorted from planarity. *In situ*-generated arynes, by treatment of (2-trimethylsilyl)aryl triflates with CsF, cyclotrimerize to triphenylenes in the presence of a palladium(0) catalyst, and other polyaromatic compounds can be obtained by addition of 1 or 2 equiv. of alkyne.[242–244]

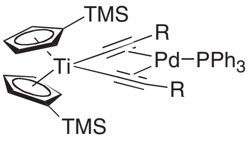
Metal complexes bearing two alkynyl ligands offer two alkyne donor groups that can bind to palladium in a chelating mode. This is the case of the family of titanium metallocenes **75** (R = Ph,[245] TMS,[246] Fc,[247] –C≡CEt, and –$SiMe_2C{\equiv}CTMS$[248]) that gives rise to Pd(0) derivatives by reaction with $Pd(PPh_3)_4$.



Scheme 47



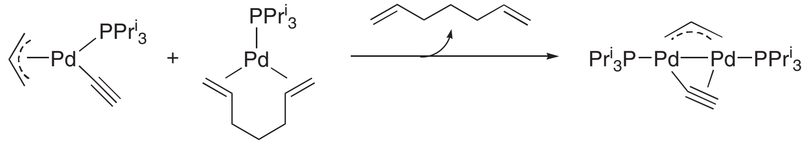
Scheme 48



75

8.06.5.3 Alkyne Complexes of Pd(I)

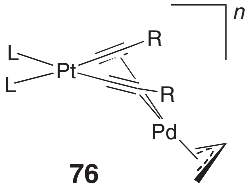
Two analogous dimeric palladium(I) complexes have been reported where an alkynyl moiety binds both palladium atoms, interacting σ-bonded to one of the metals and in an η^2-fashion with the other. Equation (25) shows the preparation by a comproportionation reaction of the allyl, alkynyl-bridged complex.[249] A butadiene alkynyl complex has been prepared from a bis-butadiene Pd(I) dimer and a terminal alkyne.[153]



(25)

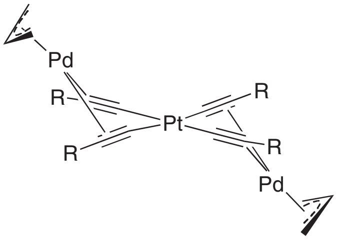
8.06.5.4 Alkyne Complexes of Pd(II)

Very few π-bonded alkyne complexes of palladium(II) have been reported in recent years. Except for two examples of monomeric complexes, most of them are polymetallic derivatives where a metal alkynyl acts as a ligand, as discussed above for some Pd(0) derivatives. These complexes adopt interesting structures that conform to the types shown below. They have been synthesized by reaction of a metal alkynyl with $[PdCl(\eta^3\text{-}C_3H_5)]_2$[250,251] or $Pd(C_6F_5)_2(THF)_2$.[252] Platinum alkynyl complexes are the most common ligand frame used, as shown in structures 76–79, but other metal alkynyls can play the same role, such as the Rh and Ir alkynyls depicted 80 and 81. The η^3-alkyne moieties bound to palladium are rotated out of the Pd-coordination plane. The angles of the C≡C vectors and the normal to the coordination plane have values of 48.6° and 46.7° for complex 78 (R = Ph) as determined by X-ray crystal structure. It is interesting that when alkynyl fragments and phosphinoalkyne are simultaneously bonded to platinum, the alkynyl fragment is always preferred even if it has to be shared with another Pd atom in a bridging arrangement (structure 79).[253]



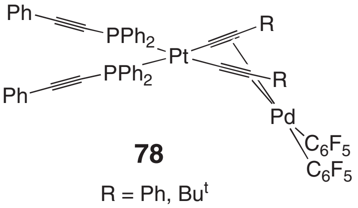
76

L = C_6F_5; $n = -1$
L = PPh_3; $n = +1$
L = C≡CHR; $n = 0$
R = Ph, Bu^t, TMS



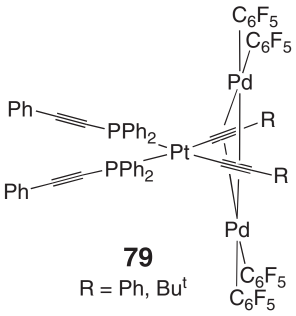
77

R = Ph, Bu^t, TMS



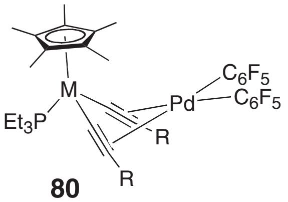
78

R = Ph, Bu^t



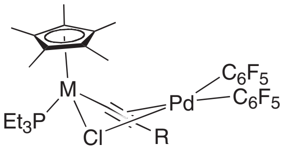
79

R = Ph, Bu^t



80

M = Rh, Ir
R = Ph, Bu^t, TMS

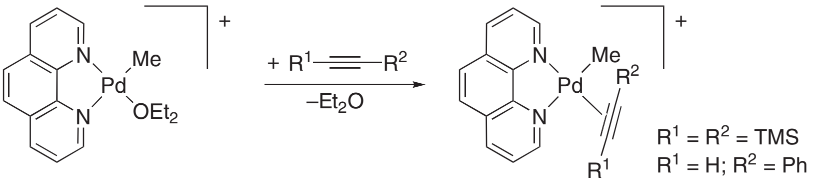


81

M = Rh, Ir
R = Ph, Bu^t, TMS

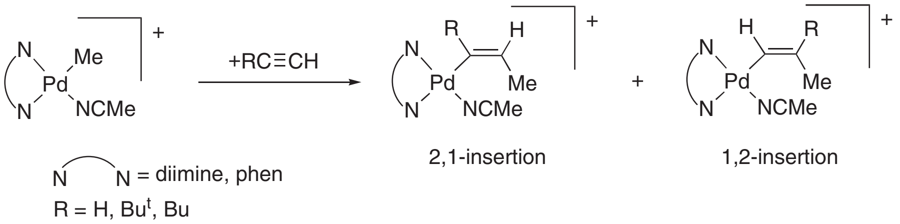
The preparation of $PdCl_2(\eta^2\text{-alkyne})_2$ complexes has been achieved by reaction of $Li_2[PdCl_4]$ and bulky propargyl amines or propargyl thioethers such as $Bu^tC{\equiv}CCHMe(NMe_2)$, $Bu^tC{\equiv}CCHMe(SPr^i)$, and $TMSC{\equiv}CCH_2(SPr^i)$. Less bulky alkynes undergo a chloropalladation reaction to give dimeric complexes with chelating thio or amino vinylic ligands.[254]

The reaction of alkynes with methylpalladium complexes that have *N*-donor chelating ligands bound to the metal is also dependent on the substituents on the alkyne. A fairly stable η^2-alkyne complex was isolated in the reaction with $TMSC{\equiv}CTMS$. $PhC{\equiv}CH$ also coordinates in an η^2-fashion, and the corresponding complex was detected at low temperature in solution by NMR (Equation (26)).



(26)

Other alkynes undergo fast insertion into the Pd–Me bond, so the intermediate compounds with a bound η^2-alkyne could not be detected (Equation (27)). Additional insertion of alkyne into the new Pd–vinyl bond formed also occurs, followed by further insertions and intramolecular cyclization. The regioselectivity of the first insertion for terminal alkynes depends on the bulkiness of the ancillary ligand, and a correlation between the distribution of products for 1-hexyne and the steric bulk of several substituted diimines was found: the more hindered the ligand, the more favored the product of 1,2-insertion.[255]



(27)

The insertion of alkynes into Pd–C or Pd–ER_n bonds ($ER_n = SiR_3$, SnR_3, BR_2, etc.) of palladium(II) derivatives is an important reaction involved in the mechanism of alkyne polymerization and in the numerous Pd-catalyzed additions to alkynes. It must occur by previous coordination of the alkyne to the metal, but the intermediate Pd(η^2-alkyne) complex is usually not detected either in catalytic studies or in examples of stoichiometric reactions reported in recent years,[150,256–258] and those studies will not be collected here. Double insertion of alkynes into Pd–C bonds leads sometimes to σ-η^2-enyl derivatives and some examples will be given in Section 8.06.6.5. Reviews are available dealing with palladium-catalyzed processes of interest where addition of two different groups to alkynes with Pd(II) complexes takes place.[259,260]

8.06.6 Enyl Complexes

8.06.6.1 General Comments

Unsaturated enyl fragments bind the metal in an η^n-coordination where n is an odd number, and may be regarded as neutral n electron donors or, most popularly, anionic $n+1$ electron donors. A trihapto coordination is the most common coordination mode found, either with the three carbon atoms directly linked to each other in a delocalized system (η^3-allyls, η^3-oxodimethylenemethane, η^3-propargyl, etc.), or apart from each other in a σ,η^2-coordination. These types of complexes will be treated separately. Finally, pentahapto enyls, usually cyclopentadienyl complexes, will be discussed.

8.06.6.2 η^3-Allyl Palladium Complexes

8.06.6.2.1 Synthesis

η^3-Allylic palladium complexes can be synthesized through a wide variety of methods that were outlined in COMC (1982) and further illustrated in COMC (1995). Those methods have been profusely used in recent years and more examples will be given below, following, when possible, the same basic scheme used in both the previous editions of COMC, and emphasizing novel findings regarding the scope of the preparations. Although part of the reactivity of η^3-allylic compounds as well, ligand-substitution reactions on palladium that are aimed at synthesis of new η^3-allyls have been included here.

8.06.6.2.1.(i) η^3-Allyl palladium complexes formed by ligand-substitution and metathesis reactions

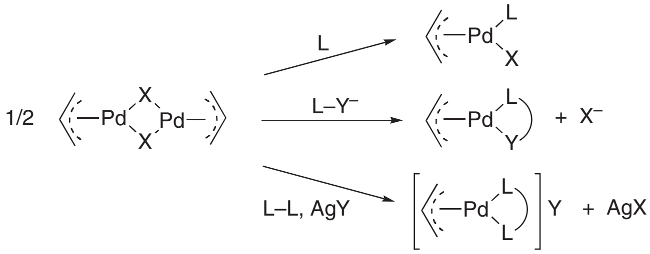
A plethora of new η^3-allylic palladium complexes have been synthesized from preformed palladium allyls by reactions that do not affect the organic moiety but just the ancillary ligands. Many of these derivatives bear chiral ligands and have been synthesized as models to study the mechanism for enantioselective organic transformations of allylic substrates, mainly allylic alkylation.

On the other hand, η^3-allyl Pd complexes are usually quite stable, and the allyl fragment occupies two coordination sites on the metal but exhibits low steric demand (it has a small bite angle). The spectroscopic features of the η^3-allyl fragment are convenient for the study of fluxional processes in the complex that have their origin in the dynamics of the ligand. These features make it an attractive auxiliary ligand to use as a tool in the study of the coordination of other ligands to palladium. Combined with the appropriate ligands, the η^3-allyl Pd fragment has been used in the design of Pd-containing complexes with interesting properties, such as liquid crystals.[261]

Ligand substitution is the most common synthetic route, starting from $[Pd(\mu\text{-}X)(\eta^3\text{-allyl})]_2$ (X = halide, carboxylate). Monodentate ligands split the bridge and give mononuclear neutral complexes. The addition of a twofold amount of monodentate ligand or chelating neutral ligands leads to mononuclear cationic complexes. The reaction is often aided by the use of silver salts to extract halide (X) from the starting complexes (Scheme 49). In some cases, an anionic ligand is generated *in situ* by deprotonation of a precursor in the presence of a palladium complex with a ligand acting as a base, for example, acac in Pd(η^3-allyl)(acac).

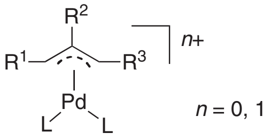
Many types of ligands have been combined with palladium allyls to give new complexes. Table 1 collects the monomeric complexes synthesized by ligand-substitution reactions, organized according to ligand type and ligand fragment.

The synthesis of dimeric or oligomeric η^3-allyl palladium complexes with a variety of bridging ligands has also been accomplished by ligand-substitution or metathesis reactions, starting from preformed η^3-allyl palladium allyls. The most common type is symmetric dimeric complexes with two equal bridging ligands. Metathesis reactions of the halo-bridged



Scheme 49

Table 1 Monomeric η^3-allyl palladium complexes synthesized by ligand-substitution reactions



Donor atoms L,L[a]	*R*^{1}, *R*^{2}, *R*^{3}	*References*
C,C (chiral chelating diene)	H, H, H	262
	H, H, Me	262
	H, H, 3,3-(Me)$_2$	262
C (*N*-heterocyclic carbene),[b] *X* (X = halide)	H, H, H	263–265
	H, Me, H	266
C (*N*-heterocyclic carbene),[b] *L* (L = solvent)	H, H, H	267
C (carbene),[b] *X* (X = O enolate) chelating ligand	H, H, H	268
C (ylide),[c]	H, H, H	269
X (halogen)	H, Me, H	269
N (monodentate chiral ligand), *X* (X = halide)	H, H, H	270,271
N,N (two monodentate ligands)	H, H, H	272,273
N,N (chelating non-chiral ligand)	H, H, H	274–290
	H, H, Me	288,290
	H, H, 3,3-(Me)$_2$	288
	H, Me, H	290–297
	Ph, H, Ph	298
	Me, H, CH(OR)Me (R = Me, C(O)Me)	299
	Cyclohexenyl	300
N,N (chelating chiral ligand)	H, H, H	289,301–316
	H, H, Me	289
	H, H, 3,3-(Me)$_2$	289
	H, Me, H	310
	H, H, Ph	289,310,317
	H, H, 3,3-(Ph)$_2$	289
	Ph, H, Ph	310–320
	H, H, nap	317
	H, H, silylcarbonyl	317
	Cyclohexenyl	289,310
N,P (chelating non-chiral ligand)	H, H, H	37,321–324
N,P (chelating chiral ligand)	H, H, H	325–346
	H, H, Me	347–349
	H, H, 3,3-(Me)$_2$	340,350–352
	Me, H, Me	35,346,353–355
	H, Me, H	28,351,352,356
	H, Me, 3,3-(Me)$_2$	350
	1,1-(Me)$_2$, Me, 3,3-(Me)$_2$	351,352
	Et, H, Et	355
	H, C(O)Me, H	351,352
	H, H, Ph	347–349,357
	H, H, 3,3-(Ph)$_2$	357
	Ph, H, Ph	13,35,341–346,353,354,357–377
	Ph, H, 3,3-(Ph)$_2$	357
	Cyclohexenyl	341,378
N,O (chelating non-chiral ligand)	H, H, H	379
N,O (chelating chiral ligand)	H, H, H	285,380–382
	H, Me, H	382
	Cyclohexenyl	383
N,S (chelating non-chiral ligand)	H, H, H	384
	H, Me, H	385,386
N,S (chelating chiral ligand)	H, H, H	346,387–389

(*Continued*)

Table 1 (Continued)

Donor atoms L,L[a]	*R*^{1}, *R*^{2}, *R*^{3}	*References*
	Me, H, Me	346
	Ph, H, Ph	346,374,390,391
P (monodentate non-chiral ligand), *X* (X = halide)	H, H, H	265,392–394,395[d],396–399
	H, H, Me	265
P (monodentate chiral ligand), *X* (X = halide)	H, H, H	400–407
	H, H, Me	407
	H, H, 3,3-$(Me)_2$	408
	H, Me, H	409,410
	H, H, Ph	407
	Ph, H, Ph	407
	Cyclohexenyl	411
P,*P* (two monodentate chiral ligands)	H, H, H	412,413
	H, Me, H	414
P,*P* (chelating non-chiral ligand)	H, H	415,416
	H, H, 3,3-$(Me)_2$	417
	H, Me, H	418
	Me, H, Me	416,419
	Ph, H, Ph	416
P,*P* (chelating chiral ligand)	H, H, H	420–429,332,430
	H, Me, H	431,432
	Ph, H, Ph	298,332,377,428,429,433–440
	Cyclohexenyl	440,441
	β-pinenyl	430,439,442–444
	Exomethylene–cyclopentene	444
P,*As* (chelating non-chiral ligand)	H, H, H	445
P,*C* (chelating non-chiral ligand)	H, H, H	323[e]
P,*C* (chelating chiral ligand)[f]	H, H, H	151,446
	Ph, Ph	376
P (monodentate non-chiral ligand), *O* (mondentate anionic ligand)[g]	H, Me, H	447,448
P,*O* (chelating non-chiral ligand)	H, H, H	392,393,449,450
	H, Me, H	451
P,*O* (chelating chiral ligand)	H, H, H	452
	Ph, H, Ph	453,454
P,*S* (two monodentate non-chiral ligands)	H, H, H	455
	H, Me, H	414
P,*S* (chelating non-chiral ligand)	H, H, H	416,456,457,458,459
	Me, H, Me	416
	Ph, H, Ph	416,458,459
P,*S* (chelating chiral ligands)	H, H, H	458–461
	Ph, H, Ph	458,459,462,463
O,*O* (chelating non-chiral ligand)	H, H, H	464–466
	H, Me, H	466
S,*S* (chelating non-chiral ligand)	H, H, H	467,416
	Me, H, Me	416,419
	Ph, H, Ph	416
S,*S* (chelating chiral ligand)	Ph, H, Ph	468
Se, Se (chelating non-chiral ligand)	H, H, H	467

[a] Other ligand features given in parentheses.

[b] The carbene ligand is usually generated by deprotonation of the imidazolium salt.

[c] Ilyde introduced by reaction of the allyl dimer with ketenylidenetriphenylphosphorane ($Ph_3P{=}C{=}C{=}O$).

[d] A spin-labeled phosphine was used, and the complex was studied by EPR.

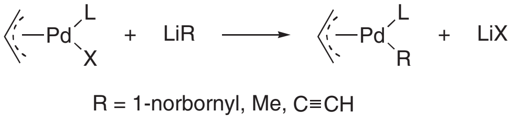
[e] Chelating ligand with a *P*-donor atom and an η^2-coordinated aryl.

[f] Chelating ligands with a *P*-donor atom and a σ-bonded fragment or a *P*-donor atom and an η^2-coordinated alkene.

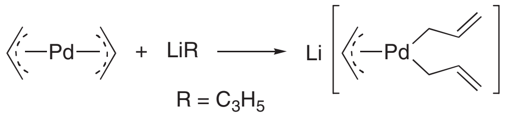
[g] Alkoxide or phosphate derivatives.

η^3-allyl palladium with the corresponding anionic ligand salt lead to dimeric allyl complexes with bridging carboxylates,[469] alkoxides,[447] organothiolates,[455,467,470–474] organoselenolates,[467,473,474] organotellurates,[474] or oxoanions (vanadates,[475] phosphates[476]); *N*,*N*-,[291,292,477–483] *N*,*P*-,[363,484] *N*,*S*-,[316] *P*,*P*-,[427,485,486] and *P*,*O*-donors[392,393,487] can also act as bridges and bind two η^3-allyl palladium units. Dimeric complexes where the Pd atoms are bound by only one donor atom have been reported.[482,488] Asymmetric complexes with two dissimilar bridges,[489] or different coordination environments for each palladium atom (two different η^3-allyls or only a Pd atom bearing an η^3-allyl ligand),[490–493] have also been synthesized. Trimeric[494] and tetrameric[495] η^3-allyl Pd complexes have been reported.

Palladium complexes with an η^3-allyl ligand and other organic groups bound to palladium are generally synthesized by metathesis reactions using a main group organometallic. Organolithium derivatives are commonly used to give alkyl,[496] or alkynyl[249] η^3-allylic Pd complexes (Equation (28)). The reaction of $Li(C_3H_5)$ with $Pd(\eta^3\text{-allyl})_2$ affords the triallylic palladium complex where the incoming allyl coordinates to Pd with concomitant isomerization of one η^3-allyl fragment to σ-allyl and opening of a coordination site (Equation (29)).[497] Other main group organometallics used to introduce an R group have been potassium fulleride,[227] zinc alkyls,[498] and silver *N*-heterocyclic carbenes.[499] Transfer of an aryl group from an anionic η^3-allyl palladium complex to a cationic one leads to the interesting aryl-bridged dimeric complex in Equation (30). The small size and stability of the η^3-allyl moiety allow the stabilization of this unusual bonding situation for palladium.[500]



(28)



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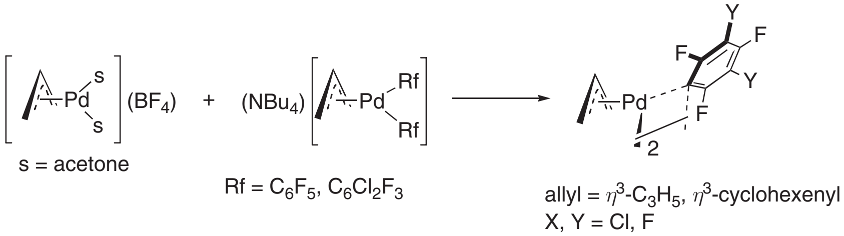
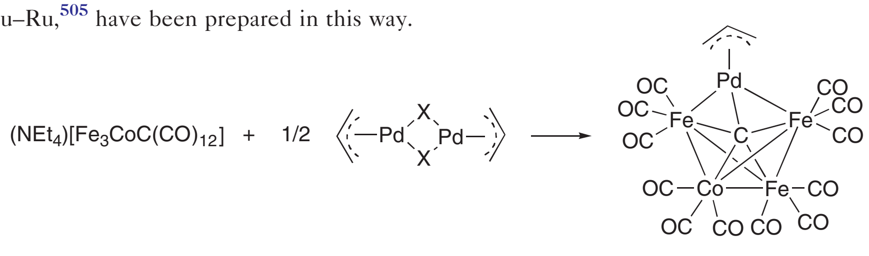


(30)

Heterometallic clusters containing η^3-allylic palladium groups have been generally synthesized by reaction of an anionic cluster with $[Pd(\mu\text{-}X)(\eta^3\text{-allyl})]_2$ (X = halide) in a reaction that resembles a ligand substitution (Equation (31)). The formal oxidation state of Pd in the product cluster is usually different from two, so the reaction can also be considered as a redox transformation; Pd–Fe bimetallic clusters,[182,501–503] and also trimetallic Pd–Fe–Fe–Co[504] **82** and Pd–Fe–Ru–Ru,[505] have been prepared in this way.

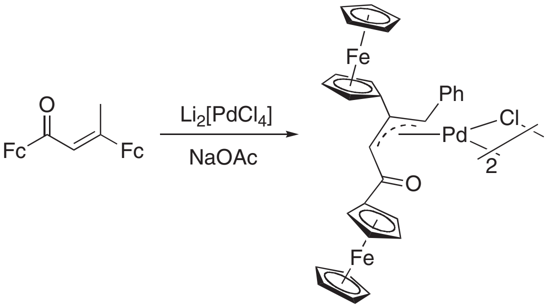


82

(31)

8.06.6.2.1.(ii) Reactions of monoenes

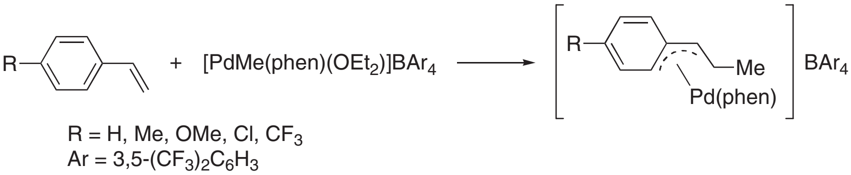
The deprotonation of monoenes leads to allylpalladium complexes. Functionalized alkenes afford substituted η^3-allylic palladium complexes. The structure shown in Equation (32) is an example of a bulky allylic derivative synthesized by deprotonation of 1,3-diferrocenylbut-2-en-1-one with a base in the presence of $Li_2[PdCl_4]$.[506] The reaction of $PdCl_2(NCMe)_2$ with allylsilane and NEt_3 affords $[Pd(\mu\text{-}Cl)(\eta^3\text{-}1\text{-}SiMe_3C_3H_4)]_2$; in the absence of amine, transmetalation of the allyl group occurs to give $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$, and the silyl group is lost.[507] Deprotonation of cyclic alkenes,[508] bicyclic alkenes,[509,510] and steroids[511] has been the route of choice to a variety of allylic complexes.



(32)

Terminal alkenes react with $PdCl_2$ in dichloroethane to give internal palladium allyls. Since deprotonation of these alkenes should lead to terminal 1-3-η^3-allyls, previous isomerization of the terminal alkene to an internal one must occur in the reaction medium. This parallel reaction should be controlled to ensure the regioselectivity and yield of the η^3-allylpalladium product.[512]

Insertion reactions of monoenes into Pd–R bonds also lead to η^3-allylic palladium complexes provided that either the monoene or the R group contain an unsaturated functionality. Thus, the insertion of an alkene into a Pd–vinyl bond leads to η^3-allylic palladium compounds.[513] The insertion of styrene and other vinyl arenes into a Pd–R bond leads to η^3-benzylic palladium complexes. The aryl ring in these derivatives gets involved in bonding, and the η^3-benzylic coordination can be looked at as a particular case of η^3-allyl. Nonetheless, the adoption of σ-coordination is more facile in η^3-benzylic derivatives than in η^3-allyls due to the extra stabilization provided by the aromaticity of the aryl ring in the σ-form. η^3-Benzylic palladium complexes have been prepared by insertion of styrene into Pd–C_6F_5,[514] Pd–Me,[515,516] and Pd–SiR_3[517] bonds, and styrene derivatives into Pd–Me bonds (Equation (33)).[516] Insertion of vinylarenes into a usually non-detected Pd–H bond leads to the synthesis of other η^3-benzylic palladium derivatives.[516,518]



(33)

Other alkene-derived species lead to palladium η^3-allyls by different routes. The unsaturated stabilized ylide $Ph_3P{=}CHC(NMe_2){=}CH_2$ reacts with $PdCl_2(COD)$ to give the palladium complex Pd(1-PPh_3–2-NMe_2–1-3-η^3-propenyl)Cl_2 with an unusual substitution pattern.[519]

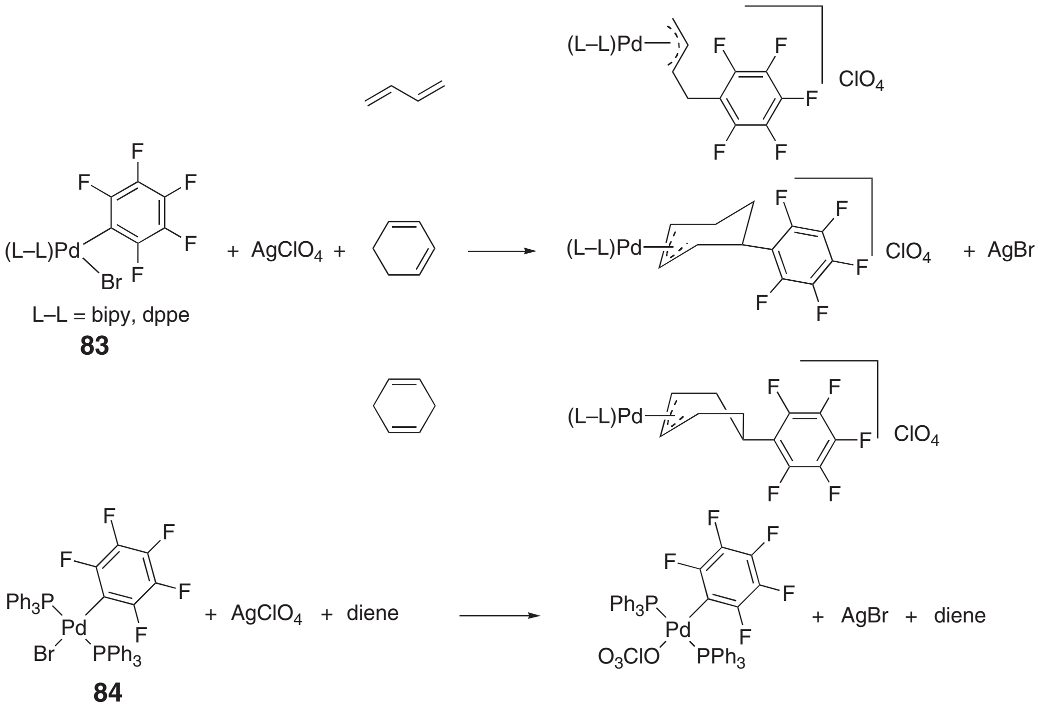
8.06.6.2.1.(iii) Reactions of dienes

Dienes are suitable substrates to prepare η^3-allyl palladium complexes through insertion into Pd–R bonds or by nucleophilic attack on Pd-coordinated dienes.

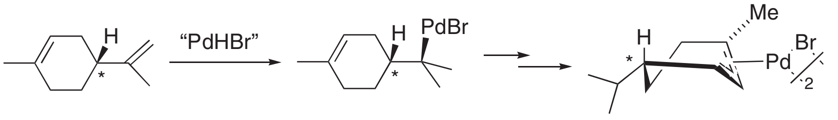
Insertion of a diene into a Pd–R bond leads to η^3-Pd allyls directly for conjugated dienes, or through a subsequent Pd-migration process when a non-conjugated diene is used (see COMC (1995) and Section 8.06.6.5.2 for examples and discussion). This reaction is *cis*-addition of Pd and the R group to the double bond that fixes the stereochemistry of the complex, if, for example, the starting substrate is a cyclic diene. The less-substituted double bond is preferred for insertion when non-equivalent unsaturations are present, usually with 2,1-regiochemistry.[520]

1,3-Dienes react with complexes bearing a metallated dimethylaminomethylferrocene ligand, and insertion into the Pd–C bond leads to η^3-allylic complexes with a coordinated NMe_2 group.[521] Pentafluorophenyl-substituted η^3-allyl Pd complexes have been prepared by insertion of a variety of dienes into a Pd–C_6F_5 bond of $PdBr(C_6F_5)(NCMe)_2$,[520,522,523] or cationic $[Pd(C_6F_5)(L–L)(S)]^+$ (L–L = bipy, dppe; S = solvent) as shown in Scheme 50. Coordination of the diene to palladium is required for insertion, and, in the example shown, this is facilitated by elimination of bromide as insoluble AgBr using a silver salt. A *cis*-arrangement of the diene and the R group on Pd is needed for insertion and this has been experimentally tested using *cis*-precursors **83**, which lead to palladium η^3-allyls, whereas in related *trans*-derivatives **84**, the insertion of the diene does not occur (Scheme 50).[524]

Chiral palladium η^3-allyls have been synthesized taking advantage of the stereoselectivity of palladium migration. Scheme 51 shows an example starting from (*R*)-(+)-limonene. Insertion of the exocyclic double bond into a Pd–H



Scheme 50



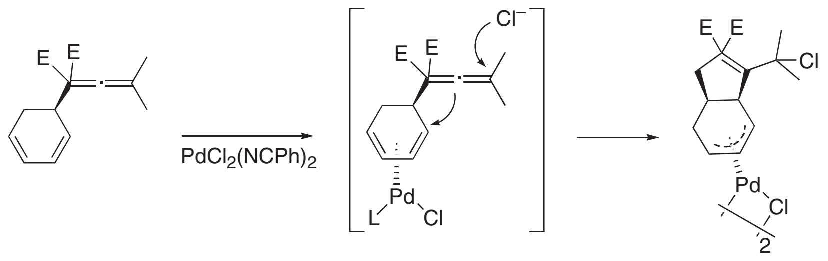
Scheme 51

bond occurs, and it is followed by a stereoselective migration of the metal (sequential *cis*-Pd–H elimination and readdition), creating a chiral allylpalladium fragment. The result is a stereoselective synthesis of the palladium chiral allylic derivative where the chirality at Pd is linked to the chirality at C*.[525]

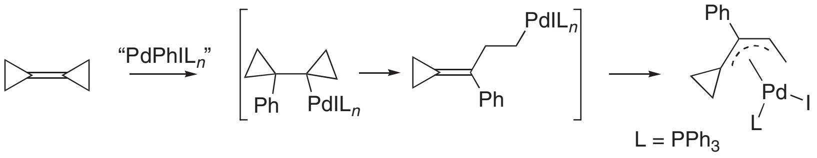
Dienes are activated toward nucleophilic attack upon coordination to palladium. Common nucleophiles such as halides, carboxylates, and alkoxides usually attack the diene without coordinating to palladium, and the arrangement of the metal and the incoming nucleophile in the final η^3-allyl Pd complex is *trans*.[526] Some exceptions to this stereochemical path are known, and have been described in COMC (1982) and COMC (1995). Less common reagents have been shown to attack dienes in a *trans*-fashion resulting in the isolation of palladium η^3-allyls. Thus, cyclohexadienes with a pendant allene moiety lead to a bicyclic η^3-allyl complex by C–C bond formation. The analysis of the stereochemistry of the complex (*trans*-arrangement of Pd and the newly formed C–C bond) rules out *cis*-insertion pathways, and establishes that the complex is formed by nucleophilic *trans*-attack of the central C of the allene to the coordinated cyclohexadiene (*trans*-carbopalladation). Chloride attack on the allene is also produced, and the authors suggest that this could be crucial to activate the allene by generation of a carbanion (Scheme 52).[527] Cyclohexadienes with a pendant allylsilane moiety also lead to related complexes by *trans*-nucleophilic attack of the silane moiety on the diene.[528,529]

8.06.6.2.1.(iv) Reactions of three- and four-membered cycloalkenes involving ring opening

Cyclopropenes, cyclobutenes, and three- and four-membered methylene cycloalkanes have been used as a source of palladium η^3-allyls. The reactions usually involve a Pd-mediated ring opening, but the actual mechanism differs from one reaction to another. Equation (34) shows an example of an η^3-cyclobutenyl palladium complex synthesized from a vinylcyclopropene through a ring-expansion process.[530] Biscyclopropylidene leads to an unusual

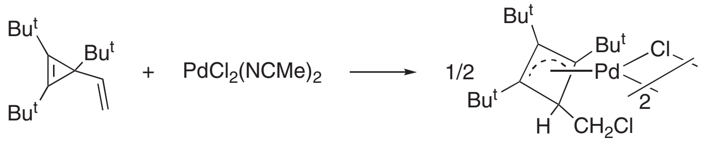


Scheme 52



Scheme 53

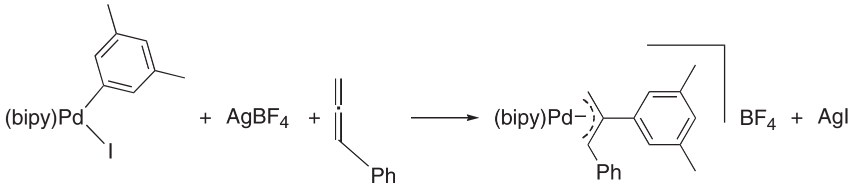
cyclopropyl-substituted Pd η^3-allyl where the opening of just one cyclopropane ring has occurred (Scheme 53). Other examples of linear palladium η^3-allyls from cyclobutenes have been reported.[531]



(34)

8.06.6.2.1.(v) Reactions of allenes

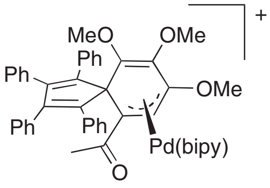
1,2-Dienes (allenes) undergo regioselective 1,2-insertion into Pd–R bonds to give 2-substituted palladium η^3-allylic complexes. Mechanistic studies on PdRX(N–N) systems (N–N = chelating *N*-donor ligand) indicate that insertion of the allene is the rate-determining step, rather than the associative substitution of a ligand by the entering allene.[532] However, substantial mechanistic differences may be found depending on the particular allene and the coordination sphere of the starting palladium complex.[533] Palladium η^3-allyl complexes have been prepared by insertion of allenes into different types of Pd–R bonds, such as Pd–Me,[534] Pd–alkyl and Pd–acyl,[532,533,535,536] Pd–aryl (isolated or being part of a metallated ligand[537]), or Pd–vinyl.[237] Equation (35) shows an example of this general reaction.[258] External nucleophilic attack on coordinated allenes is also a source of palladium allyls, as shown by the *trans*-attack of bromide on the central carbon of allenes.[538]



(35)

8.06.6.2.1.(vi) Reactions involving alkynes, isonitriles, and CO

The syntheses of palladium η^3-allylic complexes from these substrates usually involve the sequential insertion of several of the same or different unsaturated molecules into Pd–R bonds in an often mechanistically complicated process. Some examples have been reported recently. The insertion of two alkyne molecules and subsequent intramolecular insertion (cyclization) leads to a spirocyclic derivative coordinated to Pd in an η^3-allylic form **85**.[539,540] Disubstituted alkynes undergo insertion into a Pd–Me bond followed by reaction with two molecules of CO and cyclization, leading eventually to complex **86** with a γ-lactone-type allylic moiety.[541] Consecutive insertions of a bifunctionalized *ortho*-isocyano alkene arylic derivative, starting with insertion of the RNC moiety into a Pd–Me bond, leads to **87**.[542]



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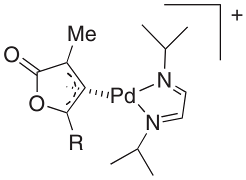
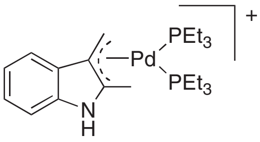


R = Ph, Me

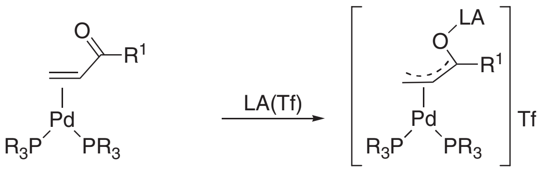
86



87

8.06.6.2.1.(vii) Miscellaneous reactions of alkenyl alcohols, alkoxides, ketones, and other *O*–substituted unsaturated substrates

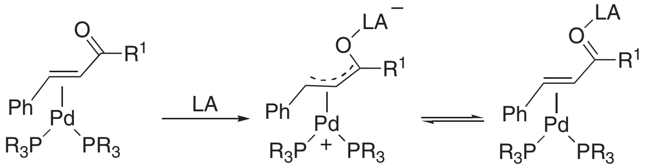
The reaction of zerovalent palladium complexes with α,β-unsaturated aldehydes or ketones, η^2-coordinated through the C–C double bond, with Lewis acids (LAs) produce *O*–substituted η^3-allylic complexes. Protonation of these complexes or reaction with methyl triflate lead to the coordination of the carbonyl carbon to palladium and formation of cationic Pd(II) η^3-allyl complexes (Equation (36)).[543,544]



R^1 = H, Me; LA = H, Me

(36)

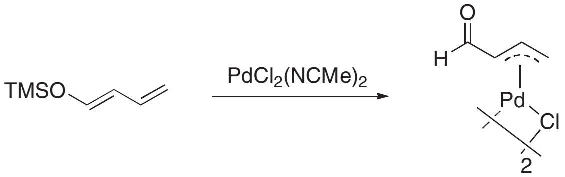
The reaction with trialkylboranes leads to zwitterionic η^3-allylic Pd(II) derivatives when $R^1 = H$, but the η^2-alkene Pd(0) complex is stabilized when $R^1 = Me$ (Equation (37)).[545] A MO calculation of these systems indicates that overlap between Pd and the carbonyl carbon is enhanced upon coordination of the Lewis acid to the oxygen. The degree of overlap varies depending on the complex, and either the η^2-alkene Pd(0) or the η^3-allylic Pd(II) forms predominate as shown by X-ray structural studies. However, contribution of both forms needs to be considered, and the participation of the η^3-allylic coordination mode is proved by spectroscopic NMR data in solution.



LA = H, BF_3, $B(Ar_F)_3$ R^1 = H R^1 = Me

(37)

The reaction of trimethylsilyl dienol ethers with $PdCl_2(NCMe)_2$ affords palladium η^3-allyls with an aldehyde functionality (Equation (38)).[546,547] The actual mechanism of the reaction was not discussed but the rearrangement of a palladium enolate transferred from the siloxane moiety seems plausible. A related rearrangement has been observed in a Pd aryloxide that leads to a bis η^3-allylic Pd complex, as was discussed in Section 8.06.3.[178]



(38)

A palladium 2-amino-substituted η^3-allylic complex $[Pd(\eta^3\text{-}CH_2(NHTol\text{-}p)CH_2)(PPh_3)_2](BF_4)$ has been synthesized from $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4](BF_4)_2$ in acetone in the presence of *p*-toluidine. It is the acetone that provides the building block of the allyl skeleton.[548]

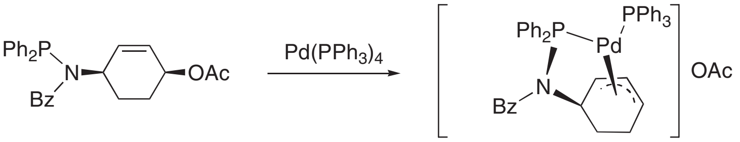
Allylic alcohols have been profusely used in the past in the synthesis of η^3-allylpalladium complexes. Mechanistically different reactions have been reported in recent years that lead to palladium allyls from those derivatives. The insertion of allylic alcohols into intermediate, often not detected, palladium hydrido complexes has been postulated as a plausible mechanism for the formation of palladium η^3-allyls.[549–551] The transformation of allylic alcohols into alkenes has been proposed as a previous step in the formation of palladium allyls from these substrates in acidic medium.[552,553]

8.06.6.2.1.(viii) Oxidative addition to Pd(0) complexes

One of the most important reactions in the synthesis of η^3-allylic palladium complexes is the oxidative addition of allylic substrates, such as allylic halides, carboxylates, carbonates, ammonium or phosphonium salts, to Pd(0) complexes. Besides its preparative value, this reaction is the origin of η^3-allyl palladium intermediates in most Pd-catalyzed transformations of allylic substrates, and the nature of the Pd allyl often determines the outcome of the reaction.

Pd(0) species are believed to coordinate the double bond prior to cleavage of the allyl–X bond and formation of a palladium η^3-allyl. The latter process is usually a S_N2-type reaction, displacing the X group with inversion of configuration. This is the most common pathway observed, although the use of suitable ligands on Pd(0) and a right choice of solvent can afford the allyl complex with retention of configuration. This was discussed in COMC (1995), and Scheme 54 shows a recent application of this synthetic strategy. Interestingly, the doubly functionalized allylic substrate oxidatively adds to Pd(0) with cleavage of the C–Cl bond selectively, evidencing the higher reactivity of allylic halides.

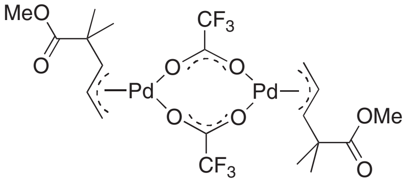
The unusual retention of stereochemistry upon oxidative addition of allylic acetates has been accomplished using allylic substrates bearing a coordinating group such as $-PPh_2$. This group binds to Pd and fixes the orientation of the reactive allylic fragment and the reaction outcome (Equation (39)).[554]



(39)

The mechanism of oxidative addition of allylic carboxylates[87,555,556] and allylic carbonates[557] in the presence of phosphine ligands has been studied by conductivity measurements, and the nature of the starting Pd(0) and final cationic Pd(II) species has been established. These studies confirm the coordination of the double bond to Pd(0) prior to oxidative addition and the reversibility of the process for both substrates. The reverse reaction is a nucleophilic attack of free X^- in solution (X^- = carboxylate, carbonate) to the cationic η^3-allylic Pd(II) complex.

Allyl halides are probably the most common allylic reagents used. Palladium complexes with not only simple η^3-allylic moieties,[558,559] but also cyclic derivatives,[508] η^3-benzyls,[558] η^3-allylic complexes derived from morphine alkaloids,[560] and trialkyltin-subtituted η^3-allyls have been synthesized by oxidative addition of appropriate halides.[561] Allyl carboxylates, especially acetates, are also common. When combined with other functionalities in the substrate, they lead to functionalized η^3-allylic Pd complexes.[562] Examples of ester-substituted η^3-allyls obtained by reaction of the corresponding allylic trifluoroacetates 88 have been reported.[563] Palladium complexes that bear an η^3-allyl with a pendant 2-pySiMe$_2$–, where the py group coordinates to Pd, have been prepared from the corresponding allylic acetates 89.[564] Allyl carbonates are also commonly used both in the stoichiometric preparation of η^3-allylic complexes and in catalytic reactions that proceed through Pd η^3-allylic intermediates.[565]



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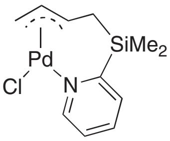

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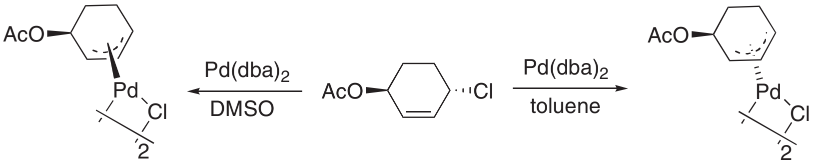
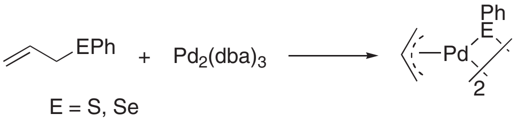


Scheme 54

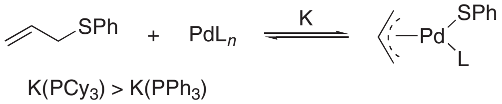
Other allylic substrates have become useful allylic sources to synthesize palladium(II) η^3-allyls by oxidative addition to Pd(0) complexes. Allylic nitrogen derivatives such as ammonium,[566,567] pyridinium,[568,566] iminium salts,[567] and other derivatives[569] have been used. Allyl phosphonium salts[570–572] and allyl phosphates[573] also lead to η^3-allylic palladium(II) complexes. In these examples, a bidentate ligand is present in the reaction medium either coordinated to the Pd(0) precursor or added to the reaction mixture, so the amine, pyridine, imine, or phosphine byproduct does not remain coordinated to the metal in the final η^3-allyl complex.

Oxidative addition of allyl sulfides and selenides to Pd(0) complexes is a reversible process. The equilibrium is shifted to the η^3-allylic dimer when $Pd_2(dba)_3$ is used (Equation (40)).[574]



(40)

Competitive experiments of allyl phenyl sulfide and allyl phenyl selenide with this system indicate that oxidative addition of the organic selenide is faster. The equilibrium displacement between the allylic sulfide and η^3-allylic complex depends on the actual precursor for Pd(0) phosphine complexes (Equation (41)). The stereochemistry of the reverse reaction on η^3-cyclohexenyl palladium thiolate dimers (nucleophilic attack of sulfide) has been determined to be *trans*. According to the principle of microscopic reversibility, the oxidative addition of allylic sulfides must occur with inversion of configuration.



(41)

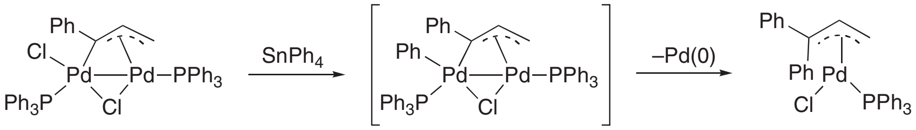
8.06.6.2.1.(ix) Transmetallation of main group allyl derivatives to Pd(II)

Transfer of an organic fragment to palladium from a main group organometallic is a general route to Pd organometallic derivatives, and it has also been applied to allylic fragments to prepare η^3-allylic palladium complexes. The reaction of *o*-Mg(CH_2–*o*-Tol)Cl with $PdCl_2$(COD) and ensuing addition of PMe_3 gives the η^3-benzylic palladium derivative Pd(η^3-*o*-$MeC_6H_4CH_2$)Cl(PMe_3).[575] Allyl silanes have been used to introduce η^3-allylic moieties on palladium,[507,576] and 2-boryl-substituted palladium allyls have been synthesized using the bifunctional 2-boryl allyl silanes.[577] Allylic tin compounds have been the reagents of choice to prepare new Pd η^3-allyls with porphyrin ligands completing the coordination sphere of the metal.[578,579]

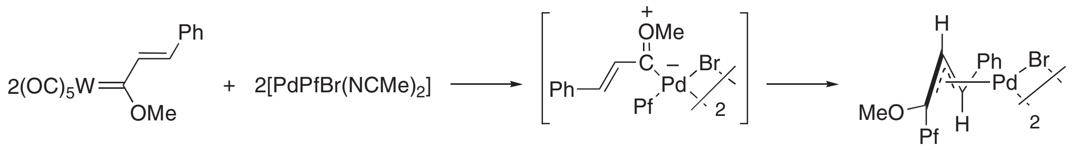
8.06.6.2.1.(x) Migratory insertion in palladium carbenes

Only two examples of this novel type of reaction have been reported. The first involves the reaction of a palladium(I) vinyl carbene with $SnPh_4$. Transmetallation of a phenyl group might form a phenylpalladium carbene, and by coupling of these two moieties, the palladium(II) η^3-allyl and Pd(0) products may be formed (Scheme 55).[169]

The second example is the reaction of a palladium pentafluorophenyl complex with a tungsten methoxy carbene. Transmetallation of the carbene to the Pd atom (a process demonstrated for analogous aminocarbenes) leads to the carbene pentafluorophenyl palladium intermediate and, by migratory insertion, the corresponding η^3-allyl complex (Scheme 56).[580]



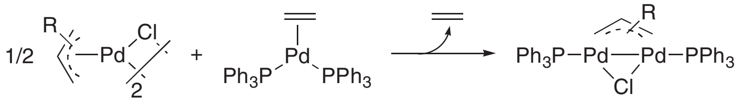
Scheme 55



Scheme 56

8.06.6.2.1.(xi) Synthesis of Pd(I) allyls by reaction of Pd(0) and allylic Pd(II) complexes

The η^3-allylic fragment can act as a bridging ligand in palladium(I) derivatives supporting two palladium atoms linked by a metal–metal bond. The most common preparative route to these derivatives is the reaction of a palladium(II) η^3-allylic complex with a Pd(0) derivative (Equation (42)).[581] The reaction can be interpreted as a comproportionation process but also as a nucleophilic attack of the Pd(0) center on the allylic fragment of the Pd(II) complex in a *cis*- (or *endo*-) fashion, with retention of configuration. Mechanistically equivalent reactions lead to analogous allyl–phosphido[582] and allyl–thiolato[574] Pd(I) dimers.



(42)

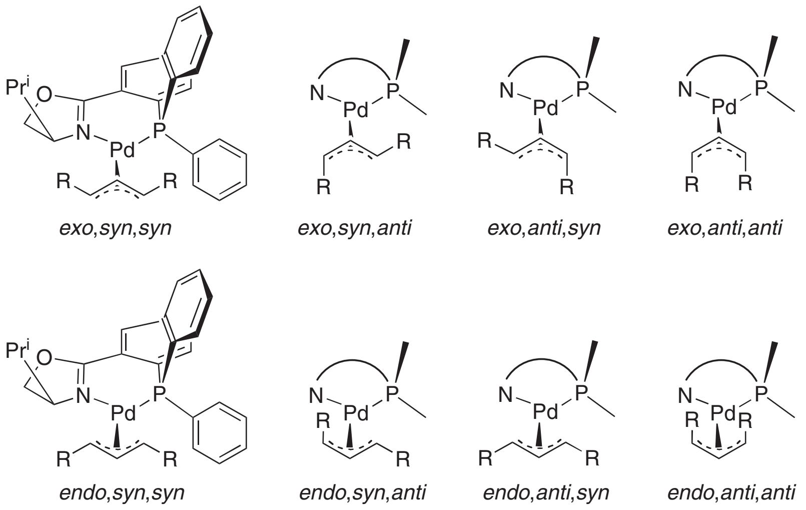
8.06.6.2.2 Structure and bonding

Many X-ray structural determinations of allylic complexes have been carried out in the past 12 years. Most of the complexes collected in the previous section, or at least representative members of a family of compounds, have been studied, and extensive crystallographic information can be found in the Cambridge Crystallographic Data Center (CCDC), Cambridge, UK. The structures found for η^3-allylic Pd(II) complexes show slight differences in distances and angles depending on the substituents of the η^3-allyl fragment, and the auxiliary ligands bound to the metal, in general, conform to the known features for Pd allyls as discussed in COMC (1982) and COMC (1995). The C–C distances are short (commonly 1.36–1.44 Å) and the C1–C2–C3 angle is close to 120° (116°–122° range). Most structures show the distances Pd–C(allyl) in the range 2.08–2.20 Å. The plane of the allyl moiety forms an angle of about 110°–124° with the palladium coordination plane.

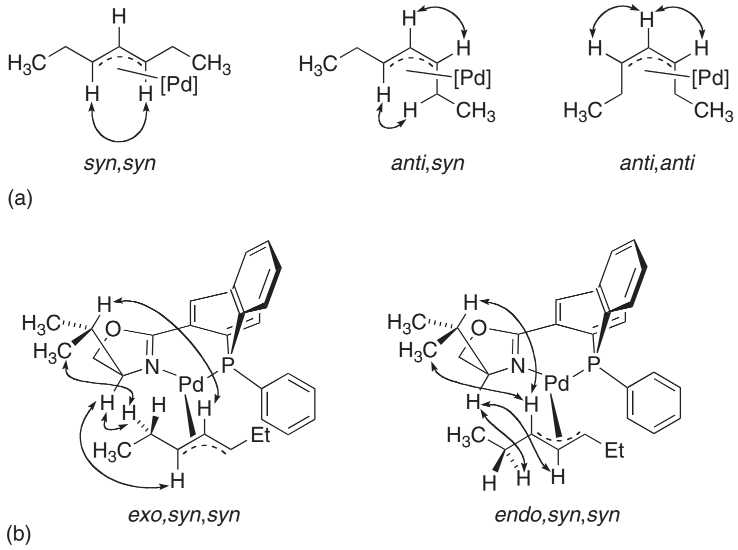
The regio- and stereoselectivity of many catalytic reactions that involve nucleophilic attack on η^3-allyl palladium intermediates are determined by the structure and conformation of these complexes in the reaction medium. For this reason, much effort has been devoted to the determination of the structures of η^3-allylic palladium complexes not only in the solid state but also in solution. X-ray, theoretical, and NMR tools have been developed and used together, so it is now possible to completely characterize a palladium η^3-allylic derivative and explain the factors that control the stability of the preferred structure.[583]

An example that illustrates the procedure usually followed is given in Schemes 57 and 58.[355] The allylic complexes $[Pd(\eta^3\text{-1-R,3-R–}C_3H_3)(PHOX)]SbF_6$ (PHOX = phosphanyldihydrooxazole; R = Me, Et) can adopt different arrangements that result in a maximum of eight isomers (Scheme 57). They arise from the *exo*- or *endo*-configuration of the allyl and the non-planar ligand, and the *syn*- or *anti*-orientation of R (in C1 or C3) with respect to the central hydrogen H2. Four to six isomers are present in solution for each complex. The *anti*,*anti*-isomers, which are less stable, are not observed. The NMR spin system for each complex was identified based on the typical ^{1}H chemical shift and proton coupling values for allylic complexes, already described in COMC (1982) and COMC (1995). Anisotropic shifts due to closed aryl rings in the ligands should be taken into account, and, in some cases, provide useful information. Heteonuclear ^{1}H–^{13}C and ^{1}H–^{31}P correlation experiments were also used to assign the allylic fragment to the corresponding ligand resonances in each isomer.

The *anti*- or *syn*-configuration of the terminal carbons of the allylic moiety were assigned based on the $^3J_{H–H}$ coupling constants, and also the observed NOE effects between protons in the allyl fragment (Scheme 58(**a**), R = Et). Finally, the *exo*- or *endo*-configuration was determined by analysis of the interligand NOE signals between the allyl and the PHOX ligand, that are quite different for both isomers (Scheme 58(**b**)). Interligand NOE interactions are also different for the *syn*- and *anti*-isomers and can be analyzed, but for simplicity are not shown here. Usually, two-dimensional NOESY experiments are carried out that show the complete NOE signal map. Quantum chemical calculations were carried out, and the results realistically reproduce the isomer distribution found in solution.



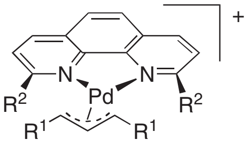
Scheme 57



Scheme 58

Molecular mechanics calculations have also been applied to many systems, and, in spite of the difficulties in developing parameters for η^3-allylic complexes that were discussed in COMC (1995),[584] the approach has been successfully applied to the prediction of complex structures.

Many complexes have been studied by this combination of techniques, especially η^3-allyl derivatives with chiral auxiliary ligands, such as phosphines,[411,446] diphosphines,[298,430,442] *N*,*P*-donors,[358,359,372,439] and *N*,*N*-donors.[303,312,585] These ligands are characterized by their large size that sufficiently intrudes in the allylic coordination area to ensure the observation of interligand NOE effects. For this reason, they "report" about the configuration and conformation of the η^3-allylic fragment. Non-chiral reporter ligands have also been used. The most useful are ligands like bipyridine, phenanthroline, and derivatives where the *ortho*-substituents of the planar ring are directed toward the allyl fragment and can get quite close to it **90**.[289] It is not uncommon that, in order to better fit into the chiral pocket of some bulky asymmetric ligands, the η^3-allyl ligand slightly rotates around the Pd–allyl axis, a distortion that is not observed when small auxiliary ligands are used. Structure **91** shows the orientation of a 1,3-diphenylpropenyl fragment in a palladium derivative with a chiral *N*,*P*-donor with respect to the N–P axis.[360]



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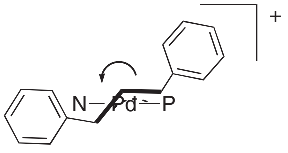

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Structural information regarding the conformation of the η^3-allyl ligand in palladium complexes can be extracted from the analysis of ^{1}H–^{1}H coupling constants from NMR spectra since they are related to the dihedral angles of vicinal protons according to the Karplus equation or improved expressions derived from it. The predominant *boat-* or *chair*-conformation of cyclohexenyl derivatives in solution can be ascertained according to $^2J_{\mathrm{H-H}}$ and $^3J_{\mathrm{H-H}}$ values, which sometimes correspond to the averaged value of both conformations in fast equilibrium;[586] J values have been calculated by application of molecular mechanics and they conform to the experimental values. The analysis of $^3J_{\mathrm{H-H}}$ values has also been used for acyclic 3-substituted η^3-allylic complexes, and gives information about the rotamer distribution and configuration of the allylic moiety.[299,587]

Chemical shifts are sensitive to the electronic features of η^3-allylic complexes, and a comparison with analogous complexes can be useful. For a series of cationic palladium complexes with dppe as auxiliary ligand and 1-(aryl–X-*p*)-substituted η^3-allyls, ^{13}C chemical shifts of the allylic carbon C1 show a good correlation with the Hammett parameter σ for X. ^{31}P chemical shifts for the dppe ligands were also measured and they correlate better with $\sigma+$ than σ, indicating that the positive charge of the complex is mainly concentrated outside the allylic fragment and in the P–Pd–P region.[588]

Most theoretical studies carried out on palladium allyl chemistry are meant to explain certain aspects of the reactivity of allyl complexes, including the prediction of the structure of ground-state diastereomeric mixtures of derivatives as discussed above, and will be mentioned when appropriate in Section 8.06.6.2.4. An excellent review is available that collects an authoritative account of the theoretical studies reported in recent years.[589] It is interesting, however, to compare at this point the bonding of the η^3-allyl fragment in Pd(II) monomeric system and in Pd(I) dimeric complexes, which has been assessed theoretically and experimentally. *Ab initio* MO/MP2-MP4 calculations on both types of allyls lead to the orbital-interaction diagrams shown in Figure 4.[168] Pd allyl bonding in Pd(I) dimeric

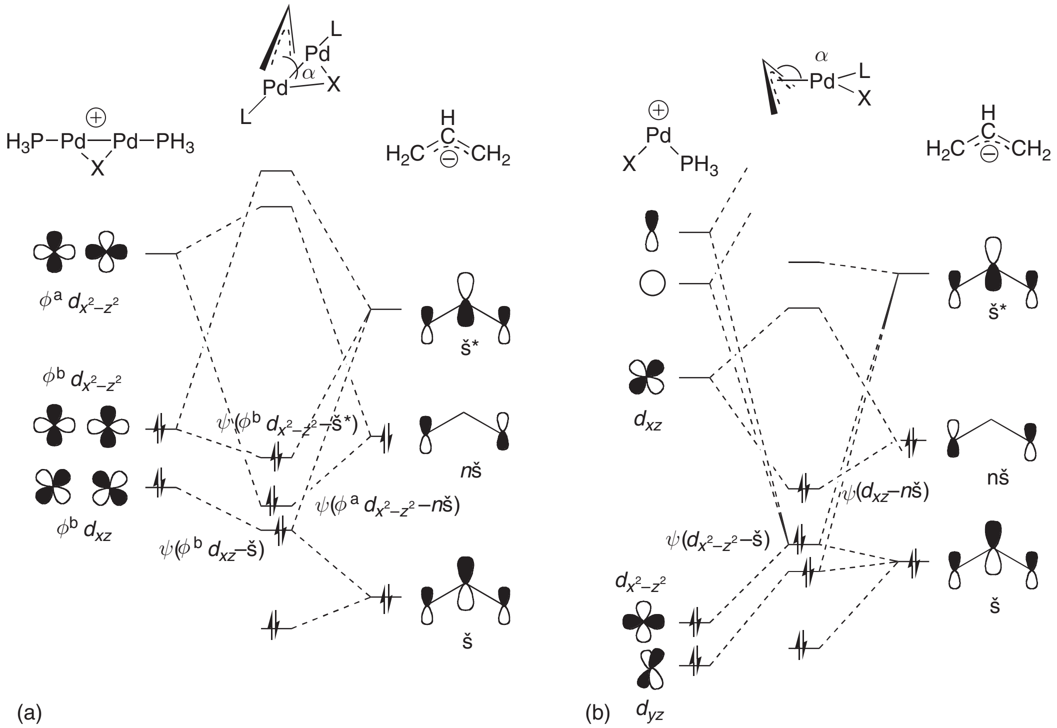
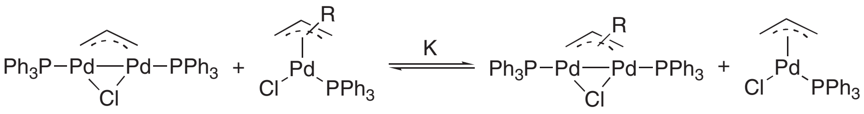


Figure 4



R:	2-OCH$_2$Ph	2-Me	2-Cl	2-CN	2-COOMe	2-SO$_2$Ph
K:	9.2×10^{-3}	1.5×10^{-2}	9.8	1.4×10^{2}	2.5×10^{2}	3.6×10^{2}

Scheme 59

complexes is formed through the donating interaction between the $n\pi$- (allyl) orbital and the empty antibonding $d_{x^2-z^2}$-(Pd–Pd fragment) orbital and the backdonating interaction between the π^*- (allyl) and occupied bonding $d_{x^2-z^2}$-(Pd–Pd) orbitals. Backbonding interaction between the π^*- (allyl) orbital and bonding d_{xz}(Pd–Pd) orbital also occurs (Figure 4(a)). Walsh diagrams show that a decrease of the dihedral angle of the η^3-allyl moiety with the metal coordination plane (α) strengthens the backbonding interactions. This agrees with the experimental results: the angle α found for these complexes is smaller than 90° and the allyl fragment bends so that C2 is closer to the Pd–Pd unit. In contrast, the bonding in Pd(II) allylic complexes is basically a donating interaction between the nπ- (allyl) orbital and the empty d_{xz}- metal orbital. Antibonding mixing of the π^*- (allyl) orbital and the occupied palladium orbitals (also Pd s- and p_z-orbitals) also occurs (Figure 4(b)). This antibonding interaction is reduced (and the donating one reinforced) if the η^3-allyl tilts away from the metal, as found experimentally in the structures of Pd(II) allylic complexes where the allyl plane forms an angle of 110°–124° with the Pd coordination plane. Thus, the allylic bonding in Pd(II) complexes is mainly a donating interaction of the allyl fragment to the metal, whereas in Pd(I) allylic dimers along with the donating interaction, backbonding plays a very important role in the stabilization of the complexes.

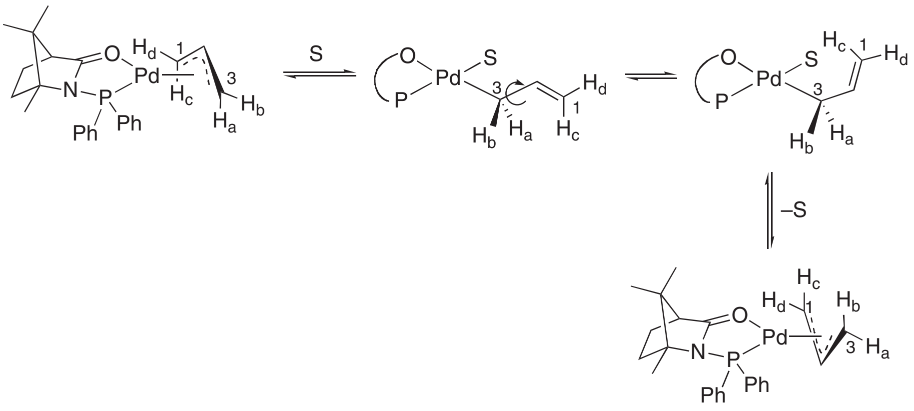
These differences in bonding have been tested experimentally by mixing Pd(I) dimers and Pd(II) monomeric complexes with η^3-allyls bearing different substituents (Scheme 59). Equilibrium constants were evaluated by NMR and show that the Pd(I) dimers are more stable for η^3-allyls with electron-withdrawing substituents, as expected for a higher degree of backdonation in these systems.

Valence orbital energies and composition of *trans*- and *cis*-[M(η^3-allyl)$_2$] (M = Ni, Pd, Pt) were calculated, and the photoelectron spectra for these complexes were assigned by comparison with the theoretical results. The average ionization potential found for the ten *d*-electrons is lower for Ni (8.26 eV) than Pd (9.64 eV) or Pt (9.62 eV). This difference in ground state *d*-orbital energies suggest a better energy match between metal *d*-orbitals and π^*-ligand orbitals (and so an easier backbonding) for Ni.[590] A similar study and spectral assignment was carried out for MCp(η^3-allyl) (M = Ni, Pd).[591]

8.06.6.2.3 Fluxional behaviour

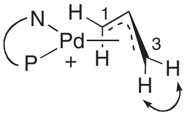
The main dynamic processes that explain the fluxional behavior of η^3-allylic complexes of palladium in solution in the NMR timescale are: (i) syn–anti-Exchange of the substituents on one terminal carbon of the allyl; (ii) apparent rotation of the allyl moiety (or *syn–syn*,*anti–anti*-exchange); and (iii) *cis–trans*-Exchange in dimers. The first process implies a switch in the coordination mode of the allyl between η^3 and σ. The two other phenomena occur by mechanisms that involve the other ligands coordinated to the metal but the allylic fragment remains η^3-coordinated. All these processes have been known for a long time and were discussed in COMC (1982) and COMC (1995). In recent years, many more examples of fluxional η^3-allyls have been reported. Their study is still an important subject since diastereoisomeric Pd η^3-allyls, like those collected in Scheme 57, interconvert through routes discussed in Sections 8.06.6.2.1.(i) and 8.06.6.2.1.(ii). Where these complexes are formed as intermediates, the rates of exchange versus the rate of further reaction control the selectivity of the target transformation. Some recent developments and interesting cases reported will be discussed here.

Selective *syn–anti*-exchange has been observed for many complexes where the interconversion of the substituents on one terminal allylic carbon is faster than the other. Generally, this occurs for complexes with ligands with two different donor atoms completing the coordination sphere of palladium, and the exchange is faster for the allylic carbon *cis* to the donor atom with the highest *trans*-effect. Scheme 60 illustrates this behavior for a *P*,*O*-donor ligand.[452] The phosphorus end of the ligand exerts a higher *trans*-effect and facilitates the decoordination of the allyl moiety from the position *trans* to it. *syn–anti*-Exchange is produced in the carbon atom that remains bound to palladium (C3).



Scheme 60

The same kind of selectivity has been observed for complexes of types **92**[340,355] and **93**[249] (arrows show the site of *syn–anti*-exchange). The solid-state structure of these complexes usually show longer Pd–C bonds *trans* to the phosphine end as it corresponds to the donor group with the highest *trans*-influence. Interestingly, the diphosphino complex **94** selectively exchanges the substituents in C3 showing the sensitivity of this process to changes in the coordination environment.[592] Not only electronic but also steric effects have been deemed responsible for the differences in selective *syn–anti*-exchange observed in complexes **95** and **96**.[458] The different substitution in the allyl moiety produces a pronounced discrimination in exchange rates.[593] For 1- or 3-substituted allyl complexes, this process leads to the interconversion of *syn*- and *anti*-diastereoisomers, and it is slower than *syn–anti*-exchange in the non-substituted carbon **97**;[594] simultaneously, the allyl fragment undergoes an apparent rotation as well (Scheme 60), and this is a route for simultaneous isomerization of *exo*- and *endo*-isomers as well as *syn–anti*-isomers in diastereomeric Pd η^3-allyl mixtures (Scheme 57).



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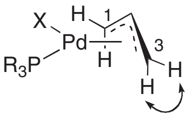

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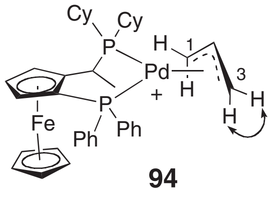

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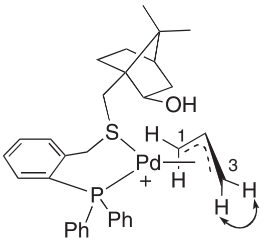

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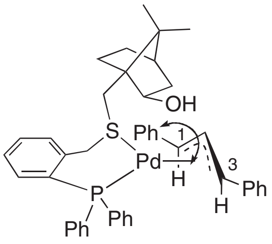

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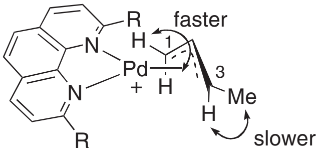

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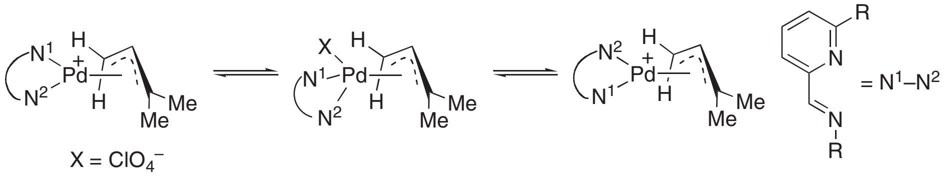
The exchange has been studied by NMR using coalescence, spin saturation transfer, or two-dimensional NOESY experiments. In a detailed study of Pd η^3-allyls with bidentate nitrogen heterocycles, it was found that the addition of chloride accelerated the *syn–anti*-interconversion.[594] A recent theoretical study concluded that the exchange involves four-coordinated intermediates by coordination of solvent or another ancillary ligand, and that an alternative tricoordinated transition state has very high activation energy.[595] Thus, the first step in the exchange must be an associative ligand substitution, the change of an η^3-allyl to a σ-allyl leaving the needed available coordination site.

Apparent rotation of the allyl moiety describes the effect observed in certain dynamic η^3-allylic complexes but, when it is not associated with simultaneous *syn–anti*-exchange, it is usually the result of a change in the auxiliary

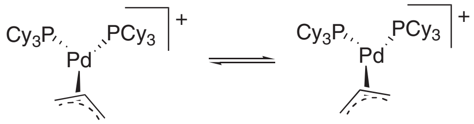


Scheme 61

ligands bound to palladium, not the allyl fragment itself. The process results in equivalence of the two halves of the allyl, and, for non-substituted allyls, exchanges H1(*syn*)–H3(*syn*) and H1(*anti*)–H3(*anti*). Several mechanistic studies have been carried out on palladium complexes with *N*,*N*-chelating ligands that indicate that the attack of a counterion or solvent molecule triggers the process.[296,594] It could be followed by rearrangement in a five-coordinated complex and decoordination of the incoming ancillary ligand (Scheme 61).[596] Decoordination of one of the nitrogen atoms in the chelate has been unmistakably observed in some systems,[597] indicating that other type of intermediates might be involved.

Several examples of *cis–trans*-exchange in palladium η^3-allyl dimers have been reported. Besides the classical exchange in halide-bridged complexes,[508,526] interconversion of *cis*- and *trans*-isomers in aryl-bridged dimeric complexes was studied. The process, followed by NMR, occurs by cleavage of the bridge through associative substitution by a solvent molecule followed by scrambling and dimerization (Scheme 62). The negative entropy of activation, solvent effects, and a crossover experiment with two different allyls support the mechanism.[500]

A fast dynamic process has been detected and studied for the complex $[Pd(\eta^3\text{-}C_3H_5)(PCy_3)_2]BAr_4$ at very low temperatures. The authors described the process as allyl rocking, and derives from the ground-state conformation of the complex where the allyl ligand is slightly rotated around the Pd–allyl bond. At −82 °C, the ^{31}P NMR of the complex exhibits an AB system for two coupled non-equivalent phosphines. Above −50 °C, the signals coalesce because of the fast allyl rocking shown in Equation (43).[598]



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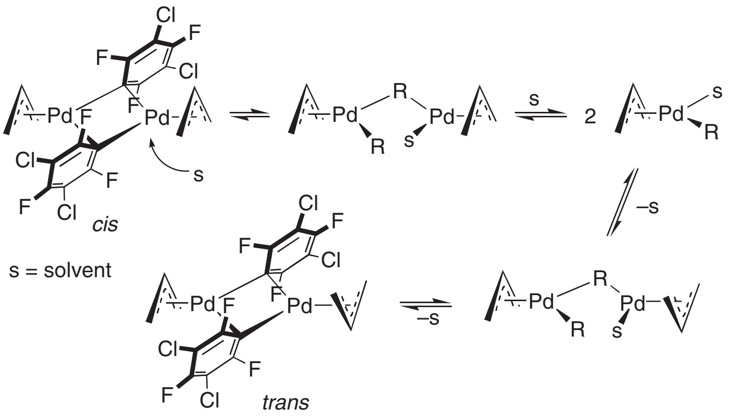
8.06.6.2.4 Reactivity

The reactivity of palladium π-allyl complexes is diverse, and the main processes were already outlined and discussed in COMC (1982) and COMC (1995). Actually, no new reaction types have been discovered for palladium η^3-allylic complexes, although interesting and unexpected examples that fit in one of the reaction types known have been



Scheme 62

described. The mechanisms that explain the reactivity of Pd η^3-allyls are now much better understood, thanks to careful experimental and theoretical work made in recent years.

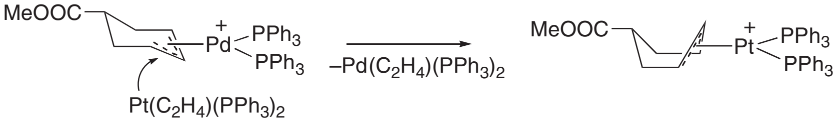
Nucleophilic attack to palladium is one of the important reactions that Pd η^3-allylic complexes undergo. Ligand-substitution reactions and metathesis of the auxiliary ligands lead to new π-allyl complexes, and they are a valuable and common synthetic route for a large number of compounds. These reactions have been collected in Section 8.06.6.2.1. The fluxional behaviour of Pd η^3-allyls often involves nucleophilic attack to palladium, and some examples have been discussed in Section 8.06.6.2.3.

The reactions where the allylic fragment is transformed often imply the decomposition of the palladium complex, and lead to organic derivatives. Most Pd-catalyzed organic transformations of allylic substrates follow mechanisms that involve π-allylpalladium complexes as intermediates, and the transformation of the allylic ligand is a crucial step in the catalytic cycle. The complete mechanism and scope of these transformations are treated in Volumes 10 and 11 of this work. Only the reactions affecting the allylic group of isolated or well-characterized palladium π-allyl derivatives will be collected here. Nonetheless, the study of these reactions is generally aimed at understanding the mechanism of a specific catalytic process.

Some of the reactions collected here may follow mechanisms that involve the transformation of an η^3-allyl into a σ-allyl complex, which is generally not detected. However, specific reactivity of σ-allyl Pd complexes, such as electrophilic attack, is not discussed. β-H and other β-X eliminations that need the isomerization to a σ-allyl (especially facile for η^3-benzylic complexes) are also excluded.

8.06.6.2.4.(i) Transmetallation of the η^3-allyl group to another metal

η^3-Allylic complexes of palladium can be used as a source of the allyl moiety to synthesize other metal η^3-allylic complexes. Redox transmetallation to a Pt(0) complex leads to a platinum η^3-allyl derivative (Equation (44)).[599] The reaction is easier when a cationic palladium allyl is used, and can be viewed as a nucleophilic attack of the Pt(0) complex to the allylic fragment. The transmetallation takes place with inversion of configuration of the allyl group. The same reaction occurs with Pd(0) complexes, a redox exchange with inversion of configuration of the allylic fragment. However, when a neutral palladium(II) η^3-allyl complex is employed, the reaction leads to dimeric palladium(I) derivatives, as discussed before (Equation (41)).



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Redox transmetallation from palladium η^3-allyl complexes to InI to give In(III) allyl derivatives seems to occur in catalytic allylation reactions of aldehydes.[600] η^3-Allyl dicarbonyl(nitrosyl)iron complexes have been synthesized by reaction of $[Pd(\mu\text{-Br})(\eta^3\text{-allyl})]_2$ and $[Fe(CO)_3(NO)]^-$.[601] It has been reported that the mixture of a palladium η^3-allyl alkyl complex and an alkylzinc derivative forms an equilibrium with the corresponding palladium dialkyl and allylzinc compounds.[498]

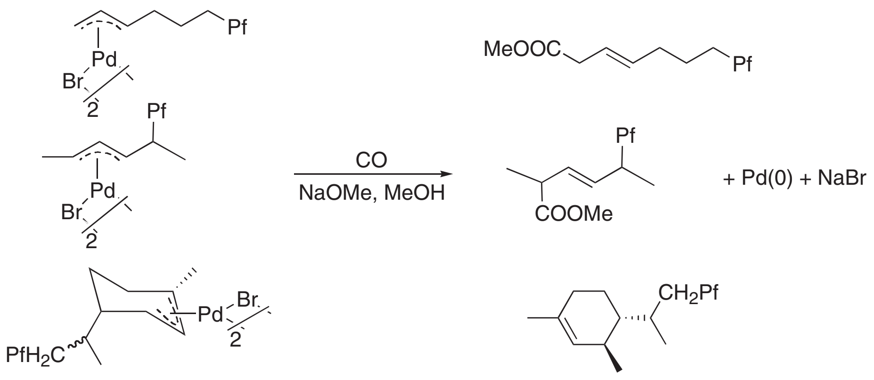
8.06.6.2.4.(ii) Thermal decomposition to give palladium metal

The complexes Pd(η^3-allyl)(η^5-cyclopentadienyl),[602–604] Pd(η^3-allyl)(β-diketonate),[605] and Pd(η^3-allyl)(β-ketiminate)[606] are classical derivatives used to obtain Pd metal surfaces by CVD techniques, and have received some attention in recent years. Thermal or laser-induced[607] decomposition of these complexes has been carried out by different modified techniques, and the resulting surface has been analyzed by spectroscopic techniques and microscopy. The finely dispersed surfaces of the metal have application in catalysis and other fields.

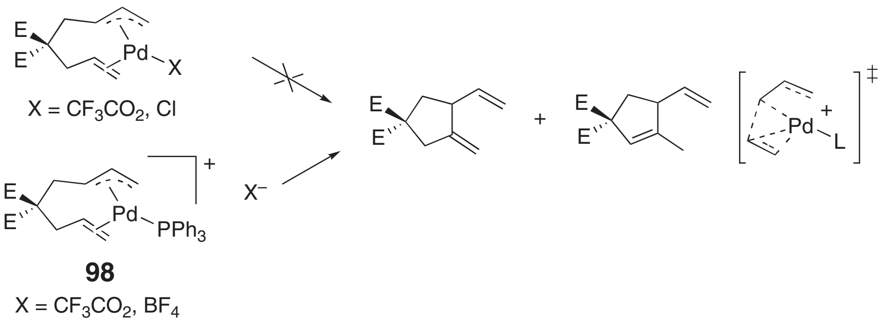
8.06.6.2.4.(iii) Reactions of CO and other unsaturated substrates with Pd η^3-allyl complexes

Reactions of carbon monoxide with η^3-allylic palladium compounds in the presence of an alcohol leads to Pd(0) and the formation of unsaturated alkyl esters. The mechanism of the reaction involves insertion of CO into the Pd–allyl bond and alkoxide attack on the resulting acyl. However, coordination of the CO to palladium and RO^- attack to give a carbalkoxy η^3-allylpalladium derivative and subsequent coupling of both groups is also plausible.[608] The functionalization of the allyl group is regioselective, the ester group binding the less substituted allyl terminal carbon (Scheme 63).[609]

Alkenes insert into Pd–allyl bonds. Examples of intermolecular (Equations (45)[610] and (46)[598]) and intramolecular insertions (Scheme 64) have been reported.[611] The latter leads to the formation of cyclic five- or six-membered rings, and may play a role in catalytic carbocyclization reactions. A cationic phosphine ligated complex **98** undergoes facile

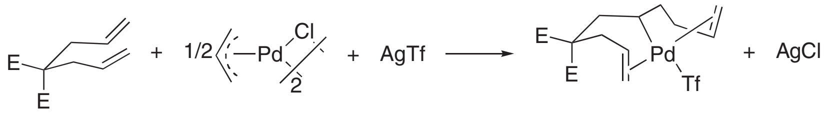


Scheme 63



Scheme 64

insertion in contrast to the analogous species with a chloro or trifluoroacetato ligand. MO calculations favor insertion of the alkene into an η^3-allyl versus formation of an intermediate σ-allyl; the coordination of a donor PR_3 ligand increases backdonation of the metal to the alkene, and favors the adoption of a coplanar arrrangement of the alkene and the η^3-allyl in the transition state.[612]



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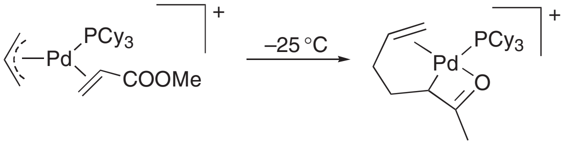


(46)

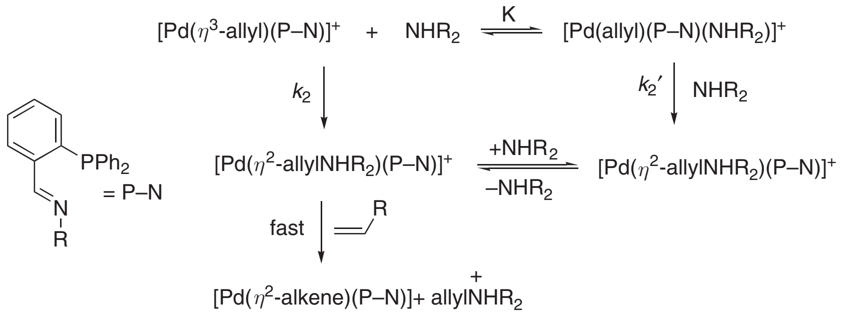
8.06.6.2.4.(iv) Nucleophilic attack at carbon

A large number of Pd-catalyzed reactions of allylic substrates involve the attack of a nucleophile to the η^3-allyl moiety in a Pd complex. C-nucleophiles such as malonates and other stabilized carbanions form the body of the so-called allylic alkylation reactions. Heteroatom-containing nucleophiles are also commonly used. They have been applied in selective allylic trasformations leading to functionalized compounds as well as in total synthesis.

The nucleophiles mentioned above generally attack the allylic fragment from a side opposite to Pd in a *trans-* (or *exo-*) fashion. The reverse sterochemistry, attack from the same side of palladium (*cis-* or *endo*-fashion), implies previous coordination of the nucleophile to the metal. Dual sterochemistry for nucleophilic attack has been found for several reactants and was discussed in COMC (1995). On the other hand, *cis*- (*endo*-) attack is always found for non-stabilized organic groups (alkyls, aryls, etc.), and the C–C coupling in this case can be considered as a reductive elimination reaction; for this reason, these processes will be treated separately.

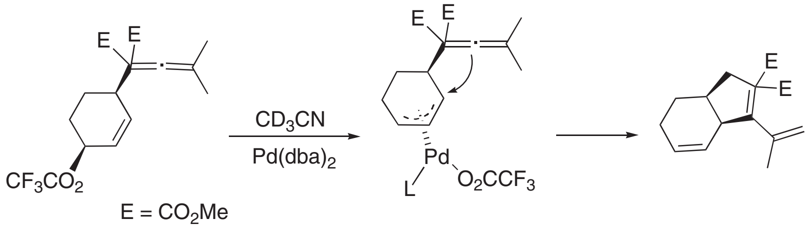
Attempts have been made to quantify the reactivity of cationic Pd(II) η^3-allylic electrophiles by assigning them an electrophilic parameter that, along with nucleophilic parameters for other species, could easily give an estimation of the expected mutual reactivity. Rate constants for the reaction of $[\mathrm{Pd}(\eta^3\text{-1-Ph–propenyl})(\mathrm{PPh_3})_2]^+$ or $[\mathrm{Pd}(\eta^3\text{-1-Ph–propenyl})\{\mathrm{P(OPh)_3}\}_2]^+$ with different nucleophiles were measured and electrophilic parameters derived from them. The triphenylphosphine complex was found to be less electrophilic than the phosphite analog, as expected from the donor properties of the PR_3 ligands, and both are considerably weaker electrophiles than the tropylium or iminium ions. Estimation of the reactivity with a wide range of nucleophiles is, however, limited because of the ambident electrophilic character of palladium complexes, with the allyl fragment and the metal as potential sites of attack.[613] A kinetic study of the reaction of amines with $[\mathrm{Pd}(\eta^3\text{-allyl})(\text{iminophosphine})]^+$ complexes has in fact shown that both Pd and the allyl are simultaneously competing for the nucleophile. Scheme 65 shows the observed rate law and mechanism proposed. Direct external attack of the amine to the η^3-allyl accounts for the first term of k_{obs}. The second term is the result of coordination of the amine to Pd to give an undetected intermediate that undergoes attack by an additional molecule of amine. The basicity of the amine and the steric requirements of the complex and the amine have a high influence in the values of k_2 and the relative weight of the two terms in k_{obs}.[340]

Nucleophilic *trans*- (*exo*-) attack on a palladium allyl is the expected stereochemistry for stabilized carbanions and heteroatom-containing nucleophiles. Some recent studies have confirmed this stereochemistry for the attack of amines on η^3-benzylic palladium complexes,[518] or thiolates on palladium η^3-allyls.[574] Intramolecular attack of allenes to an η^3-allylic palladium complex has been shown to occur with *trans*-sterochemistry as well (Scheme 66). This is unusual for this type of substrate that generally inserts into Pd–allyl bonds, leading to products with opposite stereochemistry. In fact, the addition of chloride to the system depicted in Scheme 66 changes the reaction pathway and reverts the stereochemistry of the final product. The authors suggest that the coordination of chloride to the metal decreases the electrophilicity of the allyl ligand and makes it less prone to external allene attack.[614] Dual steroselectivity has been observed for the attack of acetate or chloride[615] on Pd η^3-allyls; the *exo*- or *endo*-attack of these nucleophiles can be controlled by a suitable choice of reaction conditions to give fused lactones.[616]



$$k_{\mathrm{obs}} = k_2[\mathrm{NHR_2}] + k_3[\mathrm{NHR_2}]^2;\ \ k_3 = k_2'\mathrm{K}$$

Scheme 65



Scheme 66

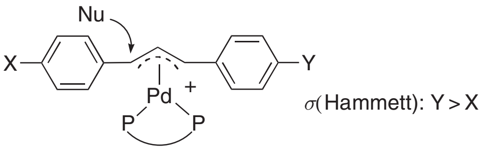
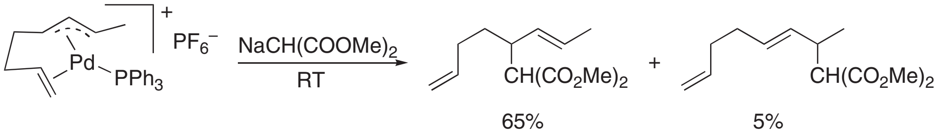


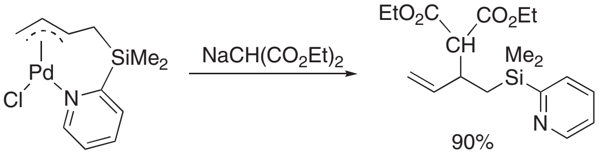
Figure 5

Nucleophilic attack can take place at each of the three C atoms of the allyl fragment. Attack at the central carbon (C2) is uncommon but some examples will be given below. Attack of a nucleophile at the terminal C1 or C3 is the dominant pathway. When the substitution of the allyl is different in C1 and C3, and in the absence of special constraints imposed by the metal environment, attack at the less-substituted carbon is usually observed. More difficult to predict is the site of attack in 1,3-disubstituted asymmetric palladium η^3-allyls. For 1,3-diaryl η^3-allyls having *para*-substituted aryls (Figure 5, **99**), the ^{13}C NMR chemical shifts of C1 and C3 show a good correlation with the Hammett parameters for the substitutents of the aryl.[617] A theoretical study of the system found a shorter Pd–C distance for the allyl C bearing the most electron withdrawing group.[618] Nucleophilic attack takes place at the carbon bearing the least electron withdrawing group, that is, the one with a lower field ^{13}C NMR resonance and less strongly bound to the metal. DFT calculations on 1-silyl, 3-R η^3-allyls (R = alkyl, aryl) to determine the site of nucleophilic attack, taking ammonia as a model nucleophile, have shown that steric and electronic factors play a role, but the balance predicts that the attack of ammonia to the R-substituted allylic carbon (i.e., away from silicon) is preferred.[619]

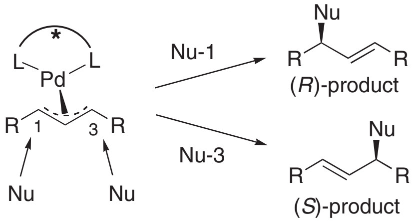
Control of the regiochemistry of the attack has been achieved using specially designed substrates where the presence of a coordinating group induces a configuration of the complex that directs the attack of the nucleophile. For example, an alkene (that coordinates to palladium) induces a ring strain in the complex and directs the attack of the carbanion to C3 in the allylic moiety (Equation (47)).[620]

 (47)

The presence of a py group in the substrate determines the geometry of the complex, and nucleophilic attack to C3 is observed in the example in Equation (48).[564]

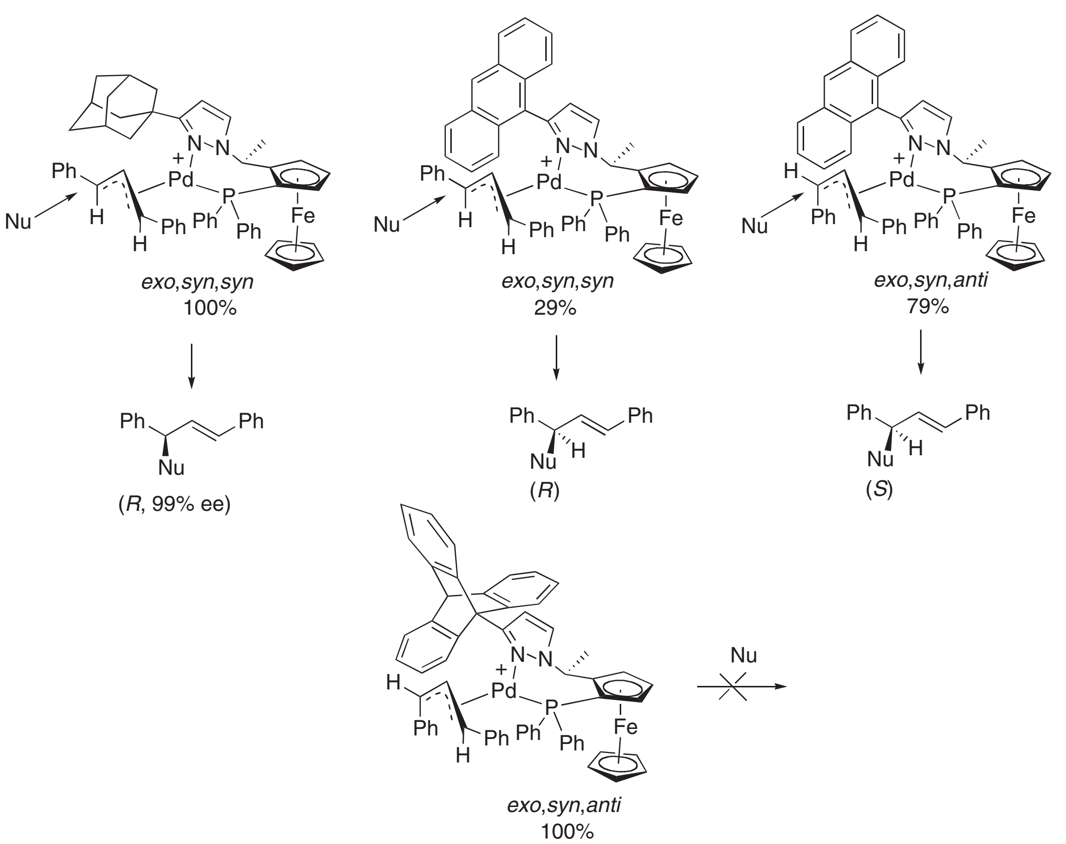
 (48)

Asymmetric Pd-catalyzed allylic alkylations and other allylic transformations can be now performed efficiently with very high enantioselectivity. There are several steps in the catalytic cycle where enantioselection can take place and this is nicely analyzed in a recent review.[621] One of these steps is the nucleophilic attack on a Pd η^3-allyl complex bearing a chiral auxiliary ligand. Considering an equally substituted η^3-allyl and bearing in mind that the stereochemistry of the attack is *trans-* (*exo-*), the regiochemistry (C1 or C3) of the attack controls the configuration of the final product (Scheme 67).



Scheme 67

Several factors influence the actual site of Nu attack and configuration of the final products, including, first, the distribution of diastereoisomers for a given intermediate complex. NMR techniques and quantum mechanical or molecular mechanics calculations have been applied to this task as described above (Section 8.06.6.2.2). Second, it is also necessary to consider the rate of interconversion among them versus the rate of nucleophilic attack: rate of apparent rotation (exchanges *exo*- and *endo*-isomers) and syn–anti exchange. Finally, the reactivity of the diasteroisomers found may be different, the minor isomers being more reactive; so, the final configuration distribution of the products may not parallel the diastereoisomer ratio in solution. The site of nucleophilic attack can be controlled with the chiral auxiliary ligand. Ligands with different donor atoms exert different *trans*-influences on the allyl and it has been found that nucleophilic attack is easier at the allylic carbon less strongly bound to palladium. This is usually the one *trans* to the atom with higher *trans*-influence. Nonetheless, steric effects may be very important to determine a distortion in the complex that may weaken one of the allylic bonds and make that carbon prone to attack by the nucleophile. A study that illustrates these points was carried out on the nucleophilic attack of benzylamine to 1,3-diphenyl–η^3-allylpalladium complexes containing chiral phosphino ferrocenyl pyrazole ligands, a step in asymmetric allylic amination reactions.[360] Several complexes were prepared, their diastereoisomeric composition in solution was analyzed by NMR, and then compared with the configuration of the final allylic amines obtained in the catalytic reaction (Scheme 68). The distribution of isomers changes, depending on the substitution of the pyrazolate ring; the bulkier the group the higher the ratio of *exo*-, *syn*-, *anti*-isomer. According to the final products obtained, nucleophilic attack of the amine occurs selectively on the carbon atom *trans* to the *P*-donor end of the ligand. Even in the case of the bulky triptycyl derivative, where attack to the C atom *trans* to P is severely hindered by steric repulsions, no attack is observed to the other terminal position. This shows the high discrimination that different donor atoms exert on the allylic carbons. This example is a clear-cut one, since interconversion of the isomers shown in solution is slow and the diastereomeric ratio reflects the ratio of final products (mostly R in the case of the adamantyl complex, the same $R:S=29:71$ ratio in the anthryl derivative). Although other examples show that the ratio of products is subjected to dynamics of the complexes or different reactivities of the diasteroisomers, the trend that nucleophilic



Scheme 68

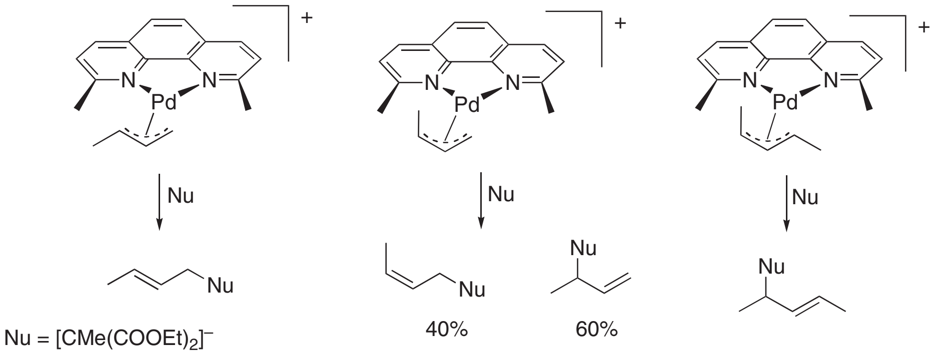
attack is selectively produced on the allylic carbon *trans* to the donor atom exerting the higher *trans*-influence is general.[355,359,374] The same result has been found in MO calculation on model systems.[622,623] For chiral chelating ligands with two equal donor atoms, distortions of the η^3-allyl moiety due to different steric requierements of the ligand usually occur, and a longer Pd–C bond in the ground state is an indicator of the preferred site for attack.[312]

The relative reactivity of *syn*- and *anti*-isomers has been tested in cationic η^3-butenylpalladium complexes of 2,9-dimethyl-1,10-phenanthroline. The *syn*-η^3-butenyl complex is more reactive than the *anti*-η^3-butenyl complex. Nucleophilic attack at the unsubstituted position is observed for the *syn*-isomer, whereas a slight preference for the substituted *anti*-position is shown for the *anti*-isomer. This has been justified taking into account the trajectory of the attacking nucleophile which brings it closer to the *syn*-substituent. When *syn*- and *anti*-geometries are allowed to compete in the same molecule, the *anti*-position is attacked preferentially (Scheme 69).[624]

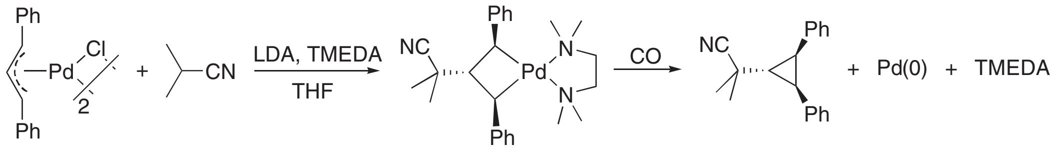
Theoretical studies on η^3-allylic complexes of palladium with substituents in the β-position, that is, [Pd(1-CH$_2$Z–η^3-allyl)L$_n$]$^{x+}$ (Z = Cl, OR, CO$_2$R, etc.), have shown that these substituents interact with palladium stabilizing the complex and inducing slight structural changes (shorter Pd–C1 and C3–C4 distances and longer C4–Z bond length). It has also been found that replacing σ-donor ligands with π-acceptors reduces the effect of the *Z*-substituents. These changes may affect the regioselectivity of nucleophilic attack on the substrates, and the expected effect is to favor the attack at the terminal carbon that does not bear the β-substituent.[625]

Examples of nucleophilic attack of stabilized carbanions to the central carbon of allylic palladium complexes have been reported. The reaction leads to cyclopropanes through the intermediacy of a palladacyclobutane complex (Scheme 70).[626–628]

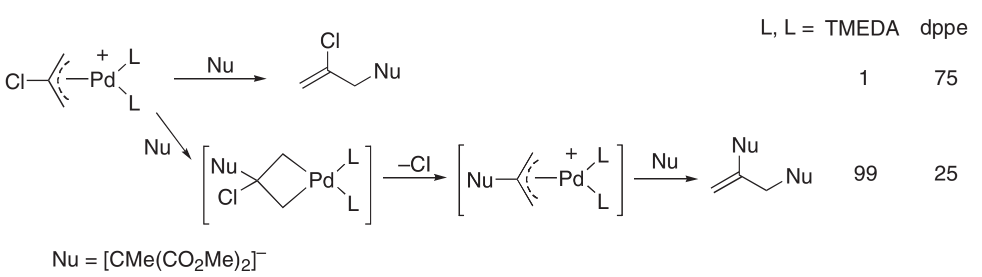
Nucleophilic attack at both the central and terminal carbons of a 2-Cl–η^3-propenyl complex has also been observed with a different outcome (Scheme 71).[629] Experimental and theoretical studies indicate that the choice of auxiliary ligand is crucial to direct the site of nucleophilic attack. Strong σ-donors, such as TMEDA, favor attack to C2. In contrast, weaker σ-donors and π-acceptors direct the nucleophilic attack to the terminal carbons. It seems that the energies of the two lowest unoccupied orbitals of the allyl (with higher coefficients in either the terminal or the central carbon) are rather similar, and vary depending on the ligands bound to palladium, so a change in reaction conditions may lead to a change in regioselectivity.[630]



Scheme 69



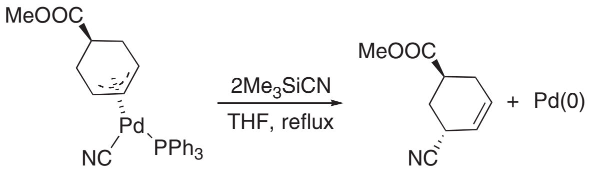
Scheme 70



Scheme 71

8.06.6.2.4.(v) Reductive elimination

Reductive elimination in complexes of the general composition Pd(η^3-allyl)RL lead to the *cis*-coupling of the allyl and R fragments with retention of configuration in the organic product. It often occurs that in many reactions the allyl complex is reacted with a precursor of the R group and the intermediate "Pd(η^3-allyl)R" is not detected. Because of this, the reaction is often termed *cis*- (or *endo*-) nucleophilic attack of R to the allyl group, and the coordination of R to palladium is assumed. The reaction of [Pd(4-methoxy–1,3-η^3-cyclohexenyl)(py–2-CH═NC$_6$H$_4$OMe-4)]$^+$, where the allyl group shows a *trans*-stereochemistry, with [BPh$_4$]$^-$ lead to *trans*-3-methoxy–6-phenylcyclohexene and *trans*-4-methoxy–3-phenyl–cyclohexene in a 1 : 1 ratio. The stereochemistry of the products indicates that transfer of a Ph from tetraphenylborate to palladium and reductive elimination has occurred.[631] Transmetallation of a vinyl group to palladium, using a tin derivative, and reductive elimination is part of the proposed route to explain the transformation of Pd(2-CH$_2$Cl–η^3-propenyl)Cl(PPh$_3$) to Pd(2-CH$_2$(CH═CH$_2$)–η^3-propenyl)Cl(PPh$_3$).[632] The reductive elimination of the palladium cyano derivative **100** in Equation (49) leads to the nitrile compound **101** in the presence of Me$_3$SiCN. Although the role of the trimethylsilyl cyanide is not clear, the stereochemistry of the product undoubtedly points to a reductive elimination pathway.[633]



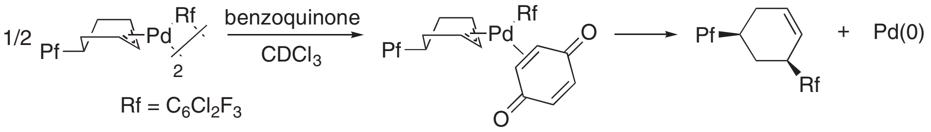
100 **101**

(49)

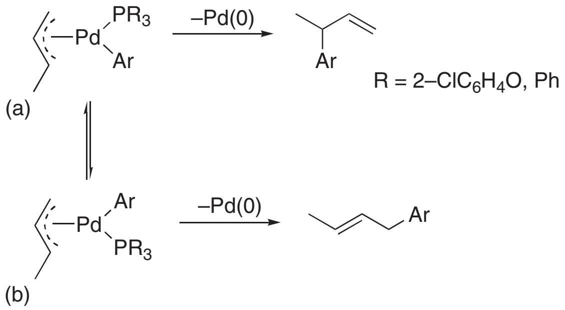
It has been shown earlier that the presence of electron-withdrawing ligands favors the reductive elimination in palladium η^3-allyl complexes. Benzoquinone has been used to perform the clean reductive elimination in η^3-allyl aryl palladium complexes, that otherwise decompose by other competing routes such as β-H elimination. The intermediate complex with a coordinated benzoquinone molecule has been characterized in solution (Scheme 72).[634]

Benzoquinones have also been used to promote the reductive elimination of chloro and an η^3-allyl;[615] Cl$^-$ as a nucleophile toward Pd η^3-allyls usually attacks in a *trans*- (or *exo*-) fashion. A different stereochemistry (*cis*- or *endo*-attack) has been achieved in this work. It was found that the more electron withdrawing the quinone the more favored the *cis*-attack, as supported by theoretical calculations. Allyltin trichloride can be obtained by a reductive elimination reaction from Pd(SnCl$_3$)(η^3-allyl)L. The reaction is accelerated by addition of an electron-withdrawing olefin such as allyl chloride. Tin dichloride also increases the reaction rate.[635]

A new theoretical study has been carried out on the reductive elimination reactions of Pd(η^3-allyl)(XH$_3$)(PH$_3$) (X = C, Si, Ge, Sn). The reaction is more exothermic for CH$_3$ than for the rest of the XH$_3$ groups; the heavier the X



Scheme 72



Scheme 73

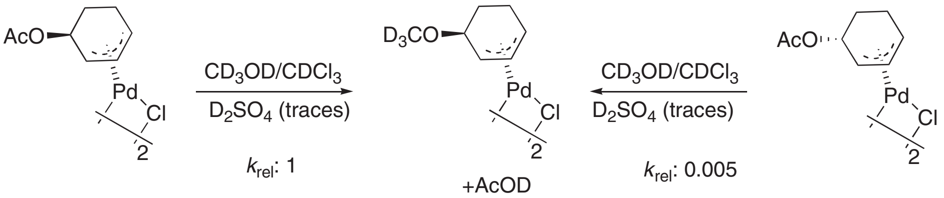
atom the less thermodynamically favored the reaction. However, the activation energy is highest for CH_3. The calculations show that Pd(σ-allyl)(XH_3)(PH_3) does not participate in the reaction course, and thus the reductive elimination takes place from the η^3-allyl species without previous conversion into the σ-allyl. When an additional PH_3 molecule is present, the formation of a σ-allyl and subsequent reductive elimination cannot be excluded, since the activation energy of this process is similar to that needed for reaction from an η^3-allyl.[636] The calculations led to similar results for the reductive elimination of η^3-allyl and hydride in Pd(η^3-allyl)(H)(PH_3).[637]

Some aspects of the regiochemistry of the reductive elimination in palladium η^3-allylic complexes were analyzed using the allylic isomers in Scheme 73. Either regioisomer affords different products, and it was observed that the C–C bond formation in the least substituted carbon is faster. The isomerization of the complexes for the phosphite complex is slow and the ratio of organic products (**a** : **b** = 76 : 24) reproduces the ratio of isomeric complexes (**a** : **b** = 78 : 22). The isomerization seems to be fast for the triphenylphosphine complex, and in this case, the equilibrium ratio of the complexes is mantained during decomposition (**a** : **b** = 85 : 15); the ratio of products (**a** : **b** = 25 : 75) is a consequence of the different rates of reductive elimination.[638,639]

8.06.6.2.4.(vi) Reactivity on the allyl substituents

The coordination to palladium of the η^3-allyl fragment influences the reactivity of the substituents in the β-position with respect to the allylic fragment. The exchanges OCH_3/OCD_3,[640] OAc/OCD_3,[641] and OAc/OAc–D_3[642] in 4-substituted 1,3-η^3-cyclohexenyl palladium complexes have been studied. In the example shown in Scheme 74, the *trans*-complex reacts about 200 times faster than the *cis*-isomer. This has been explained by the lack of conjugative interactions between the Pd atom and the acetoxy substituent (β-substituent effects) in the *cis*-isomer, whereas they are more intense in the *trans*-isomer, producing, among other changes, a lengthening of the C4–OAc bond. This is supported by theoretical calculations. The type of exchange described generally occurs in acidic media, and it is believed to go through dissociation of the β-substituent and formation of a Pd(II) cyclohexadiene complex. Nucleophilic attack of acetate or methoxide on the diene forms the η^3-allyl complex. This implies that a diastereoisomerization occurs when starting from the *cis*-complex (Scheme 74). If decoordination/recoordination of the diene occurs for OAc/OAc exchange, the whole process leads to racemization of the complex.[642]

Substitution reactions of X in Pd(2-CH_2X–1,3-η^3-allyl)LX complexes have been reported. They are believed to occur through palladium trimethylenemethane intermediates and will be treated below.

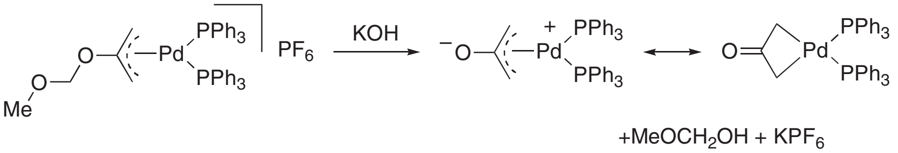


Scheme 74

8.06.6.3 Trimethylenemethane, Oxadimethylenemethane, and Related Complexes

η^3-Oxadimethylenemethane and η^3-azadimethylenemethane palladium complexes have been synthesized. The azadimethylenemethane complexes were synthesized by the reaction of σ-allenylpalladium derivatives with amides (Scheme 75). The same reaction with amines, or the protonation of the azadimethylenemethene complexes, brings about the formation of 2-amino-substituted palladium allyls.[643]

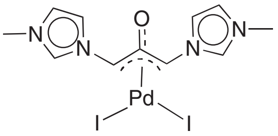
η^3-Allyl complexes with an acetal group bound to C2 afford, upon treatment with a base, η^3-oxadimethylenemethane complexes (Equation (50)).[644,645] It has been found that the starting 2-substituted allyls have a large contribution of an oxonium form, which makes the reaction with bases easier.



(50)

Two resonance forms can be depicted for this type of complex as exemplified in Equation (50), and the contribution of the allylic form is higher than the contribution of the palladacyclobutanone. Interestingly, the reverse situation is found for the analogous platinum complexes.[646] The contribution of the η^3-allyl form can be enhanced in polar media, and its importance is manifest in the facile reactivity of these palladium complexes with electrophiles.[647]

The reaction of a bis-imidazolium salt with $Pd(OAc)_2$ affords another example where a zwitterionic neutral imidazolium fragment is bound to the metal in an η^3-oxatrimethylenemethane form **102**.[648]

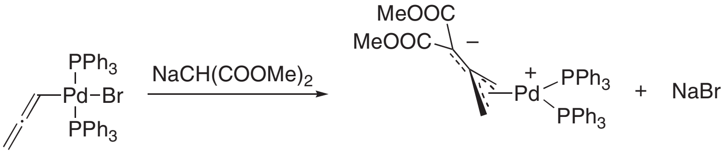


102

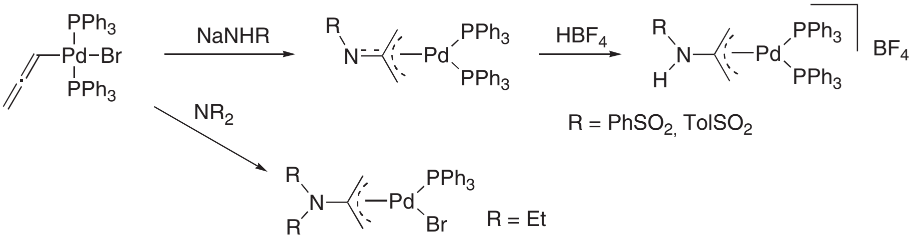
Trimethylenemethane derivatives are more elusive species but they have been proposed as intermediates in reactions of palladium complexes with 2-CH_2X-1,3-η^3-allyl moieties.[649] Scheme 76 shows one of these transformations that was thoroughly studied, where the substitution of a chloro atom in the allyl by a cyclopentadienyl fragment occurs. A second-order rate law for the decay of the starting allylic complex, along with the analysis of the products obtained with other methyl-substituted allyls, led the authors to propose the mechanism shown.[650]

SnR_3 group exchange in a mixture of $[Pd\{2\text{-}(R^1{}_3SnCH_2\text{–}1,3\text{-}\eta^3\text{-allyl}\}L_2]X$ and $ClSnR^2{}_3$ is also believed to occur through trimethylenemethane palladium intermediates, as illustrated in Scheme 77.[651]

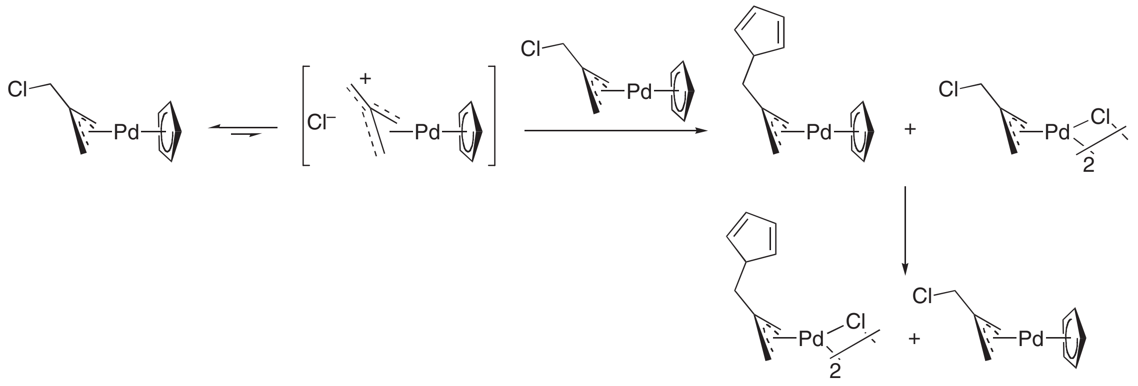
The addition of a carbanion to an allenyl complex leads to a trimethylenemethane derivative that has been isolated, and its structure determined by X-ray crystallography (Equation (51)).[652]



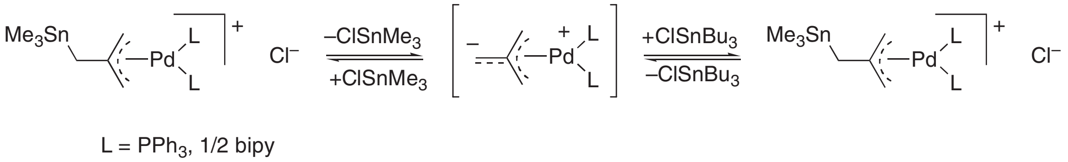
(51)



Scheme 75



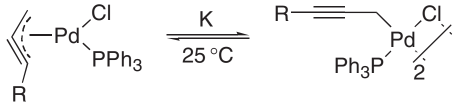
Scheme 76



Scheme 77

8.06.6.4 η^3-Propargyl/Allenyl complexes

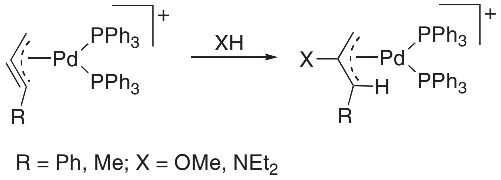
Palladium η^3-propargyl complexes have been found to be more prone to adopt the σ-propargyl or the isomeric σ-allenyl coordination modes than η^3-allylpalladium compounds to be in the σ-allylic form. In fact, it has been found that both propargyl coordination modes can be in equilibrium in solution (Equation (52)).[653]



(52)

Neutral and cationic η^3-propagyl complexes have been obtained, such as $[Pd(\eta^3\text{-}CH_2CCR)(PPh_3)_2]BF_4$[654,655] and $Pd(\eta^3\text{-}CH_2CCBu^t)(C_6F_5)(PPh_3)$.[653] The structures of η^3-propargyl palladium complexes show remarkable differences when compared to η^3-allyls, as shown in Figure 6. The propargyl ligand is bent (C1–C2–C3, about 150°) and is coplanar with the palladium-coordination plane.

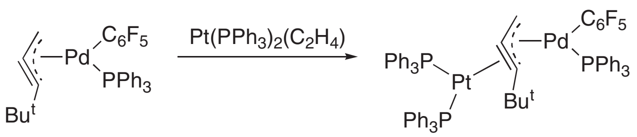
η^3-Propargyl complexes are susceptible to nucleophilic attack at the central carbon to give metallacyclobutenes, or, when NuH addition takes place, the corresponding η^3-allylic palladium complexes (Equation (53)).[656]



(53)

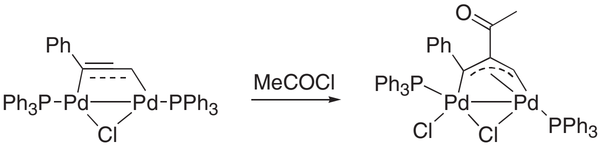
Figure 6

Nucleophilic attack by a Pt(0) complex has also been observed, and leads to a heteronuclear complex with a bridging propargyl ligand (Equation (54)).[653]



(54)

Palladium(I) dimers with a bridging propargyl moiety have been prepared by reaction of a palladium(II) σ-propargyl and a palladium(0) complex. The bridge is linear in these complexes, and the three carbons of the propargyl, the metal, and the two P atoms are all in the same plane.[167,657] As discussed for the η^3-allylic Pd(I) dimers, the organic moiety is expected to be more electron rich in these derivatives than in the Pd(II) monomers. Thus, electrophilic attack at C2 in the propargyl unit has been found to give dimeric vinylcarbene derivatives (Equation (55)). Intramolecular cyclization in this type of complex for conveniently designed substituted propargyls has also been found.[657]



(55)

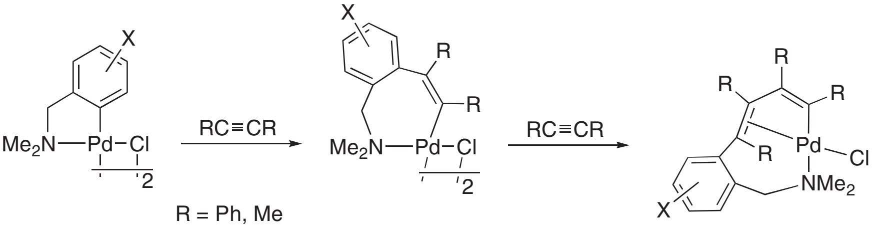
8.06.6.5 σ,η^2-Enylpalladium Complexes

8.06.6.5.1 Synthesis

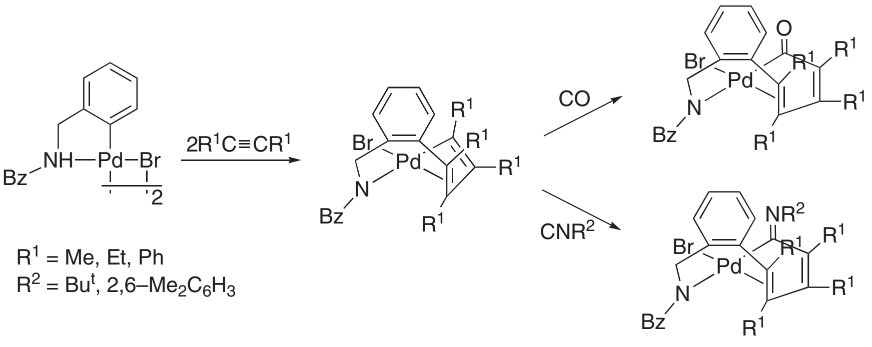
As in the case of allylic complexes, ligand-substitution reactions on preformed σ,η^2-enylpalladium complexes have been used to synthesize new derivatives. Far fewer examples have been reported, and they are restricted to the cyclooctenyl fragment.[108,658] The construction of the σ,η^2-enyl fragment is usually the result of the reaction of dienes or alkynes as substrates, and the description of the examples reported in recent years will be made accordingly.

8.06.6.5.1.(i) Insertion of alkynes into Pd–R bonds

Double insertion of alkynes into Pd–C bonds, usually a Pd–aryl bond of a cyclopalladated ligand, leads to σ,η^2-enyl complexes.[659–661] Palladium is σ-bonded to a vinylic fragment in the resulting complexes, and the enyl system usually forms 4.5-membered palladacycles (the coordinated double bond is counted as half a member of the palladacycle). A detailed study on the mechanism of these reactions was carried out on the cyclometallated benzylic system, shown in Scheme 78. The insertion of the first alkyne is slow, and occurs by previous coordination to the metal accompanied by bridge cleavage in the dimeric complex. The insertion of the second alkyne is faster and, in fact, when preparative experiments were carried out in the presence of excess alkyne, only the σ,η^2-enyl complex was obtained. The monoinserted complex has been isolated when careful reaction conditions are applied, and the reaction of this complex with a different alkyne allows the synthesis of σ,η^2-enyls with a wide range of substitution. Note that the first vinylic moiety undergoes isomerization upon insertion of the second molecule of alkyne, a general feature of this type of reaction.[662]



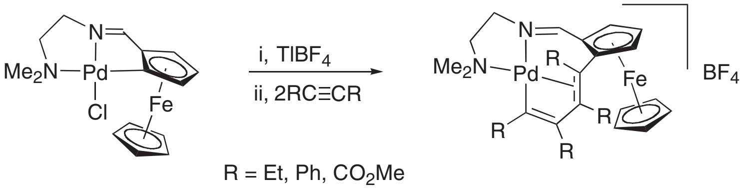
Scheme 78



Scheme 79

Insertion of other unsaturated molecules such as CO or isonitriles in this type of palladacycle affords new types of σ,η^2-enylpalladium complexes where the size of the cycle is increased in one carbon atom (Scheme 79).[663]

Cyclopalladated complexes derived from ferrocene also undergo double insertion of alkynes to give σ,η^2-enyls;[664–671] Equation (56) shows an example.[670] It has been found for these systems that asymmetrically substituted internal alkynes insert in a head-to-tail manner.[671]

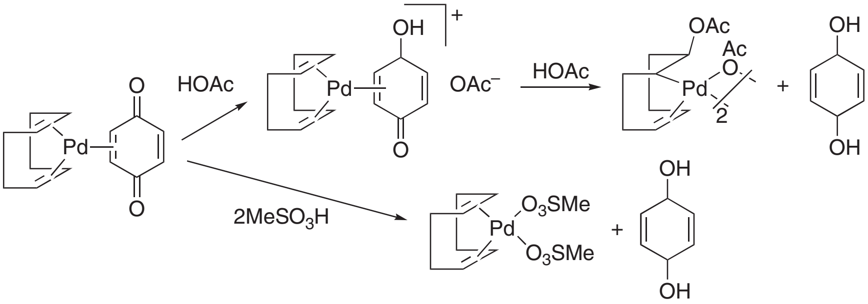


(56)

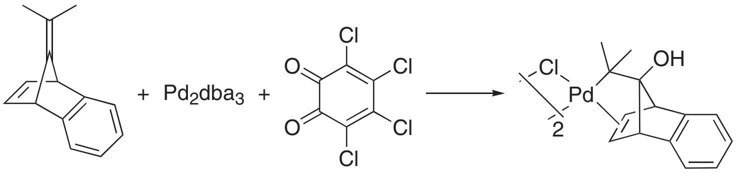
8.06.6.5.1.(ii) Reactions of dienes

Non-conjugated dienes are the source of many palladium σ,η^2-enyl complexes. Nucleophilic attack at one of the double bonds of the coordinated diene has been used most, and many examples can be found in COMC (1982) and COMC (1995). The external attack of the nucleophile leads to an overall *trans*-addition of Pd and the incoming species to the double bond.[672] Oxidation followed by nucleophilic attack on COD affords σ,η^2-enyl derivatives from Pd(1,5-COD)(benzoquinone). In the presence of acid, benzoquinone oxidizes Pd(0) to a Pd(II) diene complex with the concomitant formation of hydroquinone. If a suitable nucleophile is present, such as OAc^- when acetic acid is used, attack on the diene takes place, and a σ,η^2-cyclooctenyl palladium complex is formed (Scheme 80). A weaker nucleophile like $CH_3SO_3^-$ is not capable of adding to the double bond, and the reaction stops at the COD Pd(II) complex. The behavior of other quinones and acids was also studied.[673]

Equation (57) shows another example of the preparation of a Pd(II) σ,η^2-enyl complex by nucleophilic attack of OH^- on a diene, following previous oxidation of a Pd(0) complex by a quinone.

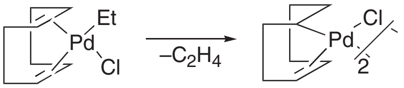


Scheme 80

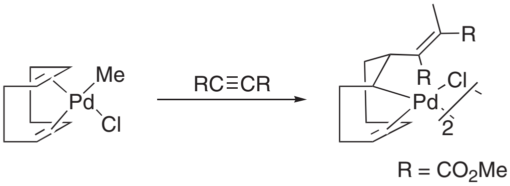


(57)

Insertion of one of the double bonds of a diene into a Pd–C or a Pd–H bond also leads to σ,η^2-enyls. If the diene is not coordinated in the precursor complex, a coordination site needs to be made available to the double bond that undergoes insertion, and this is reflected in the reaction conditions and additives used. The stereochemistry of the attack is *cis*, Pd and the hydrocarbyl (or hydrido) group adding to the double bond on the same side. 1,5-COD is a frequently used olefin that inserts into Pd–R bonds and leads to 8-R–1,4,5-η^3-cyclooctenyl frames. Pd(2-OH–C_6H_4)I(N–N) (N–N = bipy, phen, TMEDA) react with 1,5-COD in the presence of TlTf to give Pd{8-(2-OH–C_6H_4)-1,4,5-η^3-cyclooctenyl}(N–N), obtained by insertion of one of the double bonds into a Pd–(2-hydroxyphenyl) bond.[674] The derivative shown in Equation (58) is another example, formed by insertion of the coordinated COD into a transient Pd–H bond generated by β-H elimination in the precursor ethyl complex.[101] A multistep reaction that implies insertion of an alkyne into the Pd–Me bond and subsequent insertion of a double bond of COD leads to the cyclooctenyl complex depicted in Equation (59).[672]



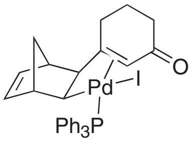
(58)



(59)

The analysis of coupling constants and NOE effects has been applied to the characterization of σ,η^2-cyclooctenyl derivatives.[675]

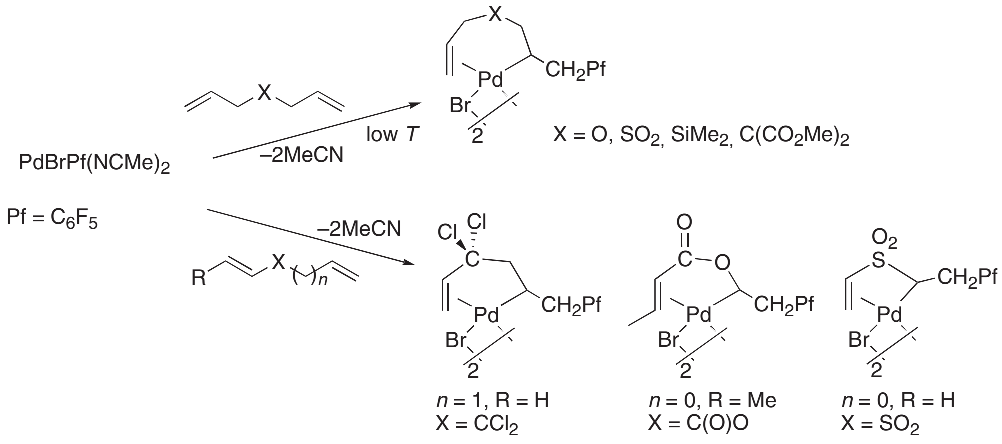
Norbornadiene and its derivatives have been used in the past to form palladium σ,η^2-enyls by insertion of one double bond into Pd–R bonds and coordination of the remaining unsaturation. However, preliminary coordination of the diene through the *endo*-face, usually in a chelating mode, needs to occur. When only one coordination site on palladium is available, nbd binds to the metal through the *exo*-face and, after insertion of one double bond, coordination of the second is not possible. Thus, insertion reactions of nbd into Pd–alkyl, Pd–acyl, and Pd–carboimine complexes that have been reported in recent years do not lead to σ,η^2-enyl derivatives. Only if an additional unsaturation is present in the molecule is an σ,η^2-enyl formed that does not involve the norbornyl double bond, as shown in complex **103**.[147]



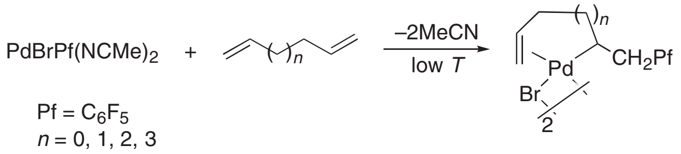
103

Linear dienes lead to σ,η^2-enyls that are generally less stable than the cyclic derivatives, since, in contrast to them, the flexibility of the backbone does not hamper further reactions.

The insertion of $CH_2{=}CH–CH_2–(CH_2)_n–CH{=}CH_2$ ($n = 0, 1, 2, 3$) into a Pd–pentafluorophenyl bond of the complex PdBr(C_6F_5)(NCMe)$_2$ afforded 4-,5-,6-,7- and a half-membered σ,η^2-enyl palladacycles (Equation (60)).[522,523] Their stability strongly depends on the ring size and will be discussed below.



Scheme 81



(60)

The same reaction was carried out with functionalized linear dienes leading to new σ,η^2-enyls (Scheme 81).[678]

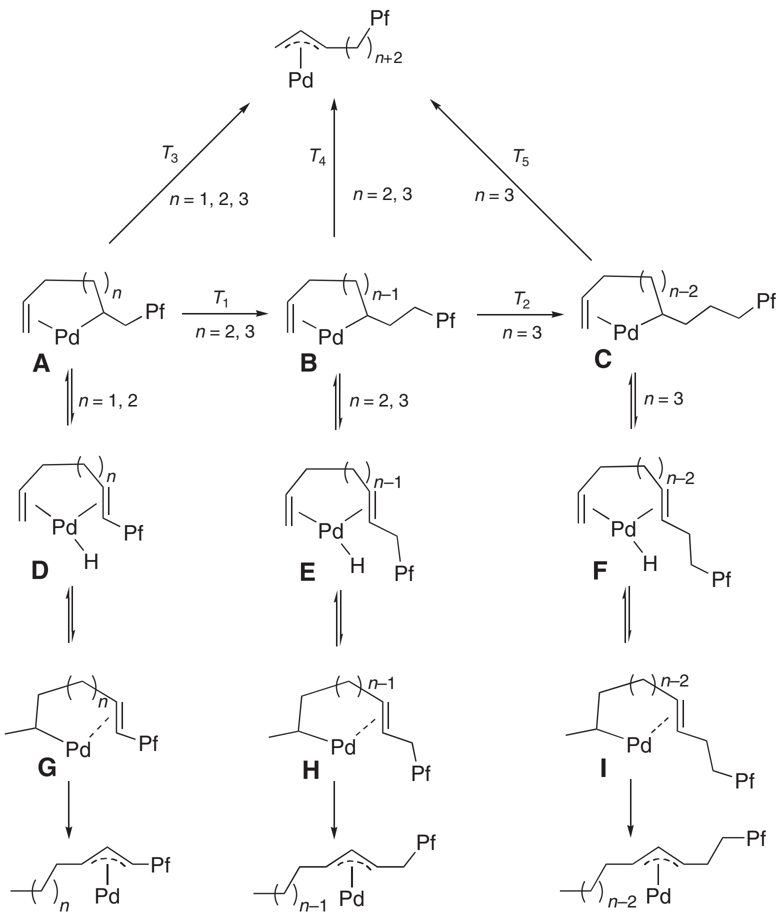
Insertion of dienes or even monoenes into Pd–allyl bonds afford σ,η^2-enyl complexes, and two examples were given in Section 8.06.6.2.4.

8.06.6.5.2 Reactivity

Many reactions of σ,η^2-enylpalladium complexes are just specific examples of the general reactivity of palladium σ-bonded complexes. However, some transformations also involve the coordinated double bond and these processes are discussed in this section.

8.06.6.5.2.(i) Isomerization reactions

σ,η^2-Enylpalladium complexes undergo isomerization to other regioisomeric σ,η^2-enyls or to η^3-allylic complexes. The reaction is a migration of the metal along the hydrocarbyl chain in what is usually called Pd-migration or chain walking. The process involves a series of β-H eliminations and reinsertions of the double bond into the Pd–H bond formed. The stereochemistry of both individual processes is *cis*, so the whole isomerization is also stereoselective. The reaction has been studied in acyclic σ,η^2-enyl complexes derived from insertion of linear dienes into a Pd–pentafluorophenyl bond at low temperature, as was shown in Equation (60). The slow increase of temperature made possible the observation by NMR of different σ,η^2-enyls (**A–C** in Scheme 82), as a result of stepwise Pd-migration to a different carbon of the chain. The migration direction, toward the coordinated double bond, leads eventually to the terminal palladium η^3-allyl complexes. However, several internal palladiumallyls are also observed that do not form a statistical mixture of all possible isomers. They proceed from a change of direction in the migration of palladium only when intermediate 1,5- and 1,6-diene palladium hydrido complexes are formed (**D–F** in Scheme 82). This means that, in the absence of free ligands, the intermediate diene stays coordinated to palladium throughout the whole migration. The situation is different in the presence of certain ligands, and an excess of an added diene, for example, promotes associative substitution of the diene and aborts the migration process.[523] However, carbon monoxide inserts into the Pd–C(σ) bond faster than palladium migration, and σ,η^2-enyls can be regioselectively functionalized to give unsaturated esters. The same substrate can then produce different carbonylated products by just controlling the rate of palladium migration along the chain, CO reacting with the product present in the conditions chosen: σ,η^2-enyl or η^3-allyl.[609]

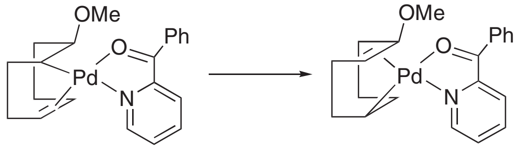


$n = 1$: $T_3 = 293$ K; $n = 2$: $T_1 = T_3 = 263$ K, $T_4 = 293$ K; $n = 3$: $T_1 = T_3 = 243$ K, $T_2 = T_4 = 263$ K, $T_5 = 293$ K

Pf = C_6F_5

Scheme 82

An isomerization that also indicates that insertion of either double bond in a Pd–H moiety may occur in a chelating 1,5-diene is the isomerization of the cyclooctadienyl derivative depicted in Equation (61).[677]



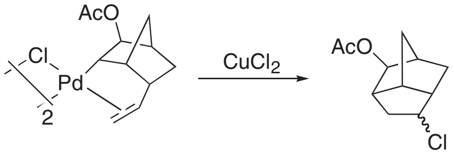
(61)

Decoordination of the double bond is needed for the isomerization when the conformation of the chelating σ,η^2-enyl prevents the attainment of a *cis*-arrangement of Pd and a β-H. Thus, the 5.5-membered palladacycles in Scheme 82 are the most stable, and certain cyclic enyls such as *cis*-σ,η^2-cyclooctenyls require high temperatures for palladium migration along the cycle, since it involves decoordination of the double bond and a conformational change. Diastereoselective isomerization of palladium σ,η^2-enyls to η^3-allyls has been observed as a result of the differences in stability of the palladacycles and their ease to undergo double bond decoordination.[520]

Since the migration of palladium needs CH (or CH_2) links in the chain, the isomerization of acyclic σ,η^2-enyls with a non-hydrogen-containing link may give rise to new processes. The evolution of the enyls depicted in Scheme 81 does not involve palladium η^3-allyls, but mainly organic derivatives brought about by β-X elimination, or dienes by β-H elimination. The ease of C–X bond cleavage found follows the order C–C << C–SO$_2$ < C–Cl < C–O (ether) < C–O (ester) ≈ C–Si.[676]

8.06.6.5.2.(ii) Cyclization processes

Cyclization reactions of σ,η^2-enylpalladium complexes are intramolecular insertions of the coordinated double bond into the Pd–C(σ) bond. These have been much used in organic synthesis (intramolecular Heck reactions) and, when polyene substrates are used, sequential insertions in undetected σ,η^2-enyls lead to polycyclic compounds in a synthetically very efficient process. Examples of this reaction starting from isolated, well characterized σ,η^2-enyls of palladium are, however, scarce. Equation (62) shows the formation of a tricyclic derivative by cyclization of a σ,η^2-enyl derived from *endo*-5-vinyl–2-norbornene promoted by CuCl$_2$.[678]



(62)

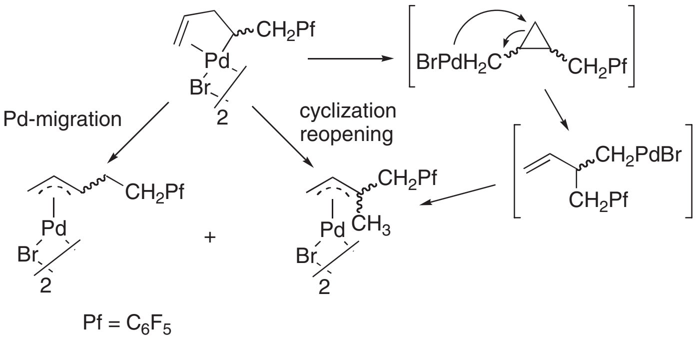
Although five-membered carbocycles are the most common ring size achieved in these reactions, smaller carbocycles (three- and four-membered) can also form. The evolution of the σ,η^2-enyl shown in Scheme 83 occurs by competitive palladium migration (to give the linear η^3-allyl) and cyclization to form a cyclopropane that undergoes further C–C cleavage to form, eventually, an η^3-allyl with a rearranged skeleton.[522]

8.06.6.6 Cyclopentadienyl and Related Palladium Complexes

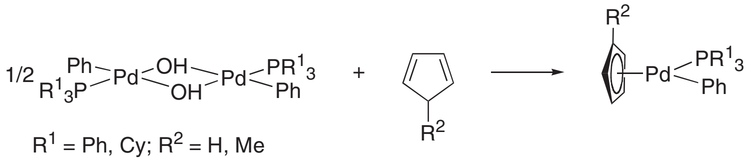
Cyclopentadienyl and other derivatives capable of coordinating in an η^5-mode are not widespread organometallic ligands for palladium. The palladium member of the MCp$_2$ family is still unknown, although a palladocene dication [Pd(C$_5$Me$_5$)$_2$](BF$_4$)$_2$ has been reported. It was obtained by chemical or electrochemical oxidation of [Pd(η^5-C$_5$Me$_5$)(η^4-C$_5$HMe$_5$)]BF$_4$.[679] Fullerenes can coordinate to palladium in a pentahapto fashion and can be considered as Cp analogs. They have been fully discussed in Section 8.06.4.

New η^5-cyclopentadienyl complexes of palladium have been synthesized following common preparative routes already discussed in COMC (1982) and COMC (1995). Many of these complexes just use cyclopentadienyl as an auxiliary ligand to synthesize complexes where the interest is in the other ligands bound to palladium, or in the complete shape of the molecule as in liquid crystal design.[680–683]

Ligand-substitution reactions (or nucleophilic attack at the metal) in cyclopentadienyl complexes of palladium have been used to prepare new derivatives.[118] The classical introduction of a cyclopentadienyl moiety by use of TlCp or NaCp and a cationic or halo palladium complex has been employed in the synthesis of complexes [Pd(η^5-Cp)(dppe)]Tf[684] and PdCp{3-(CHO)C$_6$H$_3$C(H)═NCy}.[685] A novel route has been applied that involves deprotonation of cyclopentadiene by a coordinated hydroxyl group to afford the cyclopentadienyl complexes shown in Equation (63).[686]

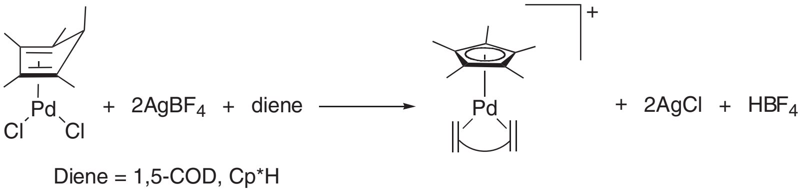


Scheme 83



(63)

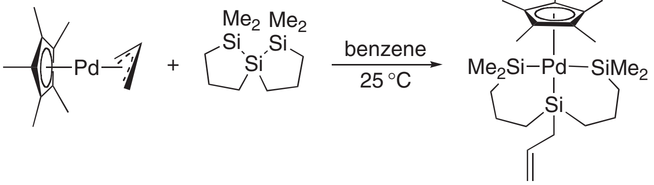
Spontaneous deprotonation of coordinated pentamethylcylopentadiene occurs in the preparation of pentamethylcyclopentadienyl palladium diene derivatives (Equation (64)).[679]



(64)

η^5-Cyclopentadienyl complexes with alkyl groups coordinated to palladium have been synthesized.[687] Interestingly, treatment of PdCp(CH_2Z)(PPh_3) (Z = COPh, COMe, $COCH_2Cl$) with an acid leads to preferential protonation of the alkyl group.[688]

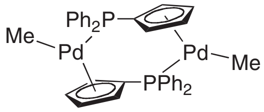
The reaction of Pd(η^5-Me_5Cp)(η^3-allyl) with 1,1,6,6-tetramethyl–1,5,6-trisila-*spiro*-[4.4]-nonane leads to the Pd(IV) derivative schematically shown in Equation (65), where the geometry around the metal is almost tetrahedral.[689]



(65)

The analysis of X-ray crystal structures of η^5-cyclopentadienyl palladium derivatives Pd(η^5-Cp)L_2 has been carried out, and reveals that the Cp ring can adopt a complete range of orientations with respect to the PdL_2 or PdL^1L^2 fragment of the complex. The authors suggest it is not realistic to assign eclipsed or staggered conformations to these types of complexes.[690]

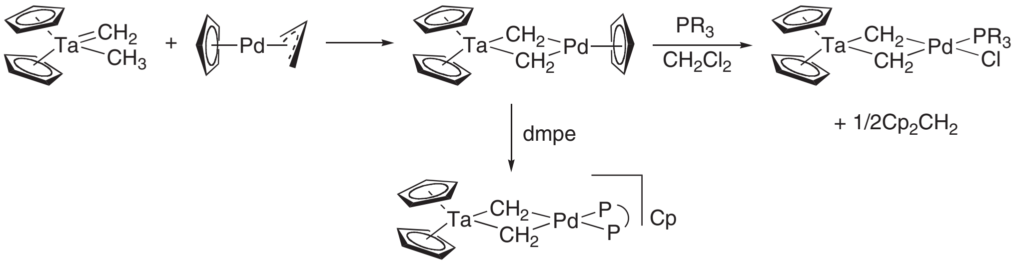
Cyclopentadienyl ligands with a substituent containing an additional donor atom lead to unusual structures when coordinated to palladium. The complex of composition Pd($C_5Me_4CH_2CH_2NMe_2$)(η^3-allyl) has been prepared,[691] and both the Cp ring and phosphorus coordinate to palladium in the dimeric complex shown **104**, whose molecular structure was determined by X-ray diffraction methods. It was synthesized by reaction of Tl(Cp-PPh_2) with PdClMe(COD).[692]



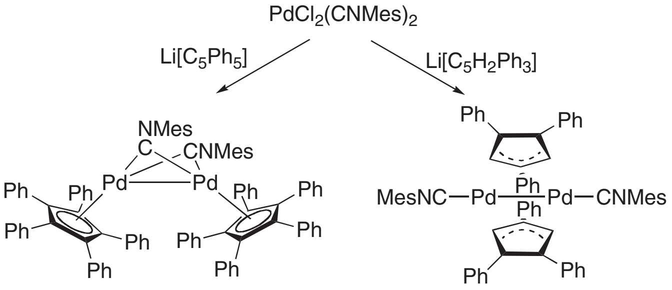
104

An interesting heterometallic Pd–Ta derivative was prepared, as shown in Scheme 84. The reactions of this complex with phosphines lead to substitution of the cyclopentadienyl ring, which decoordinates as a cyclopentadienide anion and then undergoes further reaction with the solvent. The isolation and structural characterization of a bimetallic complex with a Cp^- counterion confirms this mechanistic pathway.[693]

Substitution of the Cp ligand when [Pd(η^5-Cp)(dppe)]Tf is reacted with PEt_3 or PBu_3 in chlorinated solvents has also been observed, [PdCl(PR_3)(dppe)]Tf being obtained as product. Conversely, if chlorinated solvents are avoided, substitution of the diphosphine occurs.[684]



Scheme 84

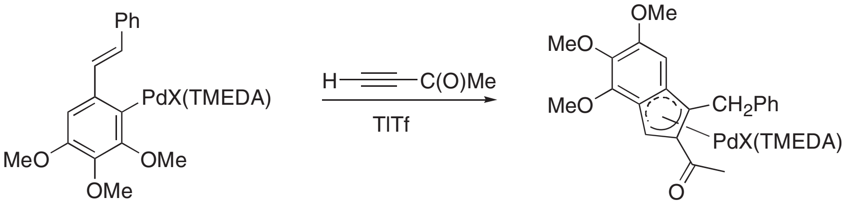


Scheme 85

Other reactions of cyclopentadienyl derivatives include the attack of Cp on intermediate trimethylenemethane species discussed above (Section 8.06.6.3), and the reductive elimination of Pd(η^5-Cp)(η^3-allyl) to give Pd metal by CVD techniques (Section 8.06.6.2.4).

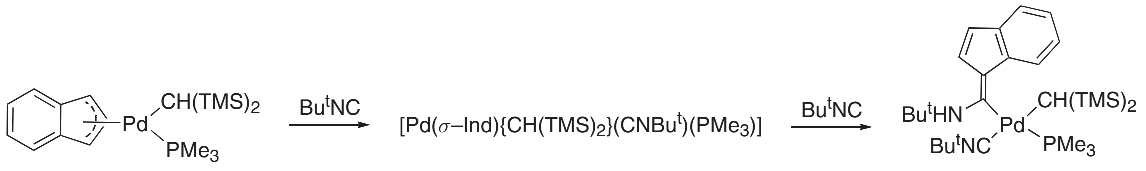
Palladium(I) dimeric complexes bearing cyclopentadienyl terminal or bridging ligands have been reported, and the coordination mode of the Cp derivative strongly depends on the substituents of the ring. Scheme 85 shows the outcome of the reaction of $PdCl_2(CNR)_2$ with different cyclopentadienide salts. The bulky pentaphenylcyclopentadienyl adopts a terminal η^5-arrangement, whereas a less-substituted Cp bridges both Pd atoms in an η^3-fashion giving a complex analogous to the η^3-allyl-bridged Pd(I) dimers.[694]

When coordinated to palladium, the π-indenyl ligand tends to slip from the η^5- to the η^3-coordination mode, and most of the complexes synthesized show severe distortions[695] or clear η^3-indenyl coordination.[695,696] Thus, although being a cyclopentadienyl analog, it is rare to find a true η^5-indenyl coordination to palladium, however common for other transition metals. Metathesis with Li[indenide] and ligand-substitution reactions are common preparative routes for indenyl derivatives. The insertion of an alkyne into Pd–C bonds of vinyl substituted aryls, followed by intramolecular alkene insertion, also leads to highly substituted indenyl palladium complexes. Equation (66) shows one of these examples.[697,698]



(66)

The reaction of palladium indenyl complexes with isonitriles leads to the synthesis of palladium fulvenes (Scheme 86). The reaction seems to occur by decoordination of the indenyl fragment, and the resulting indenide attacks a coordinated isonitrile. An analogous reaction takes place when cyclopentadienyl is used.[699]



Scheme 86

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8.07
Platinum Complexes with Carbonyl, Isocyanide, and Carbene Ligands

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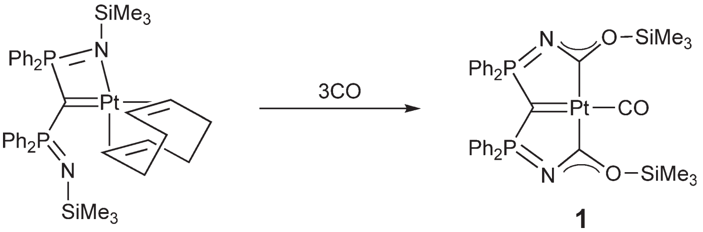
8.07.1 Platinum Carbonyl Complexes

Since the publication of COMC (1995), there have been many new reports of platinum carbonyl complexes. In general, however, the work reported has been incremental and has built on the earlier work. The structure of this section will largely follow that of the previous editions, but with all polynuclear carbonyls considered together.

8.07.1.1 Mononuclear Pt(0) Carbonyls

Neutral homoleptic platinum carbonyls remain unknown under normal laboratory conditions. Platinum monocarbonyl, PtCO, has been prepared by laser ablation of Pt in the presence of CO, and its pure rotational spectrum measured between 6,500 and 20,000 M Hz, using a cavity-pulsed jet Fourier transform microwave spectrometer. A Pt–C bond length of 1.760 and a C–O bond length of 1.148 Å were measured, and may be rationalized in the conventional terms of σ-donation from and π-backbonding to the CO.[1]

A new platinum(0) carbonyl complex has been prepared by the reaction of 3 equiv. of carbon monoxide with a carbene complex (Equation (1)). Not only does the carbon monoxide displace an existing ligand but coordinated CO is also attacked by the ligating nitrogens, with the siloxy group migrating to give the unusual tris-carbene carbonyl complex **1**, where all the donor atoms are carbon.[2] Yields are reported to be quantitative, and an X-ray structure has a short Pt–CO bond of 1.868(6) Å with a CO stretch of 2,038 cm^{-1}. Further aspects of the synthesis of both **1** and its precursor are discussed in Sections 8.07.3.2.2 and 8.07.3.3.



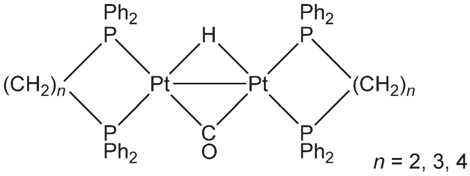
(1)

8.07.1.2 Pt(I) Carbonyls

Platinum(I) chemistry is dominated by dimeric species with a Pt–Pt bond, and the carbonyls are no exception. New reports include the isolation and characterization of the first homoleptic dinuclear platinum(I) carbonyl cation $[(OC)_3Pt–Pt(CO)_3]^{2+}$, which is formed in concentrated sulfuric acid solution via the reductive carbonylation of PtO_2, the reaction taking about 2 weeks at room temperature and atmospheric pressure.[3] NMR studies indicate the molecule to be rigid on the NMR timescale with a Pt–Pt coupling of 551 Hz; Raman spectroscopy gives ν(Pt–Pt) at 165 cm^{-1} and EXAFS shows a Pt–Pt bond of 2.674 Å. Further studies on this compound show that spectroscopic data are consistent with each platinum adopting a square-planar geometry, with B3LYP calculations, suggesting that the two planes should be exactly perpendicular to each other; a revised Pt–Pt distance of 2.718 Å and an average ν(CO) of 2,199 cm^{-1} are given in a later paper.[4]

Fluxional processes in the carbonyl-bridged complex **2** have been studied by variable-temperature NMR with the conclusion that the equilibration of all four phosphorus sites occurs via a rotation about the Pt–Pt bond.[5] In order for this rotation to take place, the bridging ligands have to adopt a terminal arrangement, and the size of the bite angle of the phosphine affects the rate of exchange, with the rate increasing with bite angle.

The reduction of a platinum(II) carbonyl to give platinum(I) carbonyl species **12 and 13** is described in Section 8.07.1.3.



2

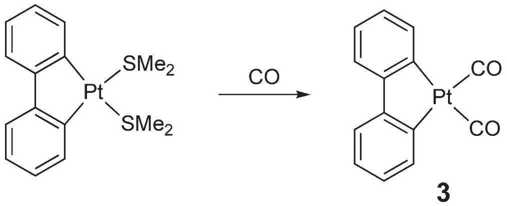
8.07.1.3 Mononuclear Pt(II) Carbonyls

Carbon monoxide continues to be a popular and useful ligand in platinum(II) chemistry, where its π-acceptor properties allow control over the electronic properties of complexes, with the IR stretching frequency of the triple bond providing valuable insight into those properties.[6]

A number of studies of *cis*-[$PtX_2(CO)_2$] have been undertaken with a new synthetic procedure based on the carbonylation of the tetrahaloplatinate ion proceeding in high yield to give both the chloride and the bromide.[10–12] Even though the dichloro compound has been known since 1870, it is only recently that the crystal structure has been published; presumably, technical difficulties associated with its extreme moisture sensitivity hindered earlier study. The Pt–CO distances of 1.901(5) and 1.893(5) Å are among the longest observed, in keeping with the high CO stretching frequencies of 2,170 and 2,128 cm^{-1}. Additional features of the structure include a Pt–Pt interaction at 3.378(1) Å unsupported by any hydrogen bonding contacts.[10] Pt–Pt contacts are not unusual in platinum(II) carbonyls; another report indicates a distance of 3.243(1) Å within "dimers,"[8] and two theoretical studies have been published. In one *ab initio* study of the *cis*-[$PtCl_2(CO)_2$] dimer, Pt–Pt distances of 3.319(5) and 3.249(11) Å were predicted on the basis of metal d_{z^2} interactions.[13] In a later study, the effect of pyramidalization of the metal was studied, and shown to have some bearing on the strength of the Pt–Pt interaction.[14] The complete vibrational analysis of *cis*-[$PtCl_2(CO)_2$] has been reported with 12 of the 15 fundamentals observed experimentally, in both an Ar matrix and in the solid state; significant differences between the two are assigned to secondary intermolecular contacts.[15] The same paper reports the isolation and crystal structure of the *cis*-[$PtX_2(CO)_2$] compound ($X = SO_3F$) and the attempted synthesis of the fluoride ($X = F$). While the fluorosulfate compound can be made in high yield via the reductive carbonylation of the Pt(IV) fluorosulfate,[16] attempts to make the fluoride have yet to succeed. Other new routes into compounds of this type include the oxidation of Pt(0) species with sulfuryl chloride (SO_2Cl_2) in the presence of carbon monoxide[17] and the decarbonylation of DMF by K_2PtCl_4.[18]

The first platinum carbonyl fluoride has been reported: the platinum(II) carbonyl cation $[Pt(CO)_4]^{2+}$ has been synthesized with the platinum(IV) fluoride anion $[PtF_6]^{2-}$ via the reductive carbonylation of the platinum(VI) species PtF_6 in HF. Very high yields were obtained, and a similar synthesis of $[Pt(CO)_4][Sb_2F_{11}]_2$ in anhydrous SbF_5 is also reported.[19,20] Carbonyl stretching bands for both these compounds are reported in the range 2,289–2,233 cm^{-1}, in line with the expectation of minimal π-backbonding to the carbonyl ligand. Further chemical and theoretical studies on these rare homoleptic carbonyl cations have been undertaken.[21] Results indicate that the probable decomposition product of $[Pt(CO)_4][Sb_2F_{11}]_2$ is *cis*-[$Pt(FSbF_5)_2(CO)_2$]; a crystal structure of $[Pt(CO)_4][Sb_2F_{11}]_2$ has Pt–C bond lengths around 1.984 Å, the longest known (the mean Pt(II)–CO bond length is 1.854 Å).

Studies on carbonyl displacement in *cis*-[$PtCl_2(CO)_2$] by an alkene (in particular, cycloheptene) show that the reaction is an equilibrium that can only be driven over to the *cis*-[$PtCl_2$(CO)(alkene)] by removal of the CO;[22] reaction of *trans*-[$Pt_2Br_4(CO)_2$] with alkene yields the *cis*-[$PtBr_2$(CO)(alkene)], with the reaction believed to go via the *trans*-isomer. The synthesis of the analogous compound which has both halides replaced with the biphenyl anion, **3**, is best achieved through the displacement of dimethyl sulfide by carbon monoxide (Equation (2));[23] the Pt–CO bond length is reported to be 1.98(2) Å, with the solid-state structure also containing infinite stacks of molecules (with CO and biphenyls alternating) at a Pt–Pt distance of 3.24 Å.

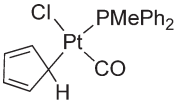


3

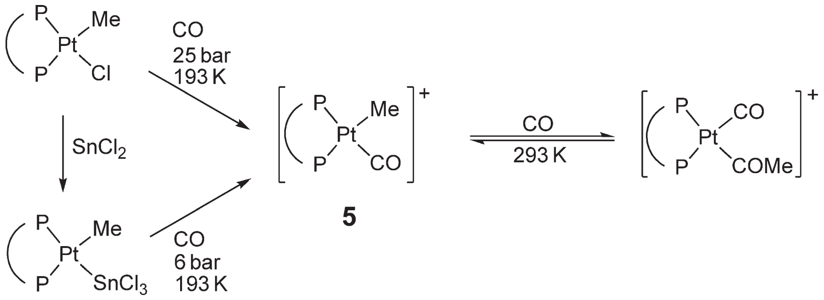
(2)

The kinetics of carbonyl exchange in $[PtX_3(CO)]^-$ has been studied by IR and NMR.[24] The exchange is first order in both CO and complex, with a negative entropy of activation, indicating an associative mechanism. The rates of carbonyl exchange increase as X is changed from Cl to Br to I (approx 1 : 10 : 130), paralleling the increase in *trans*-effect of the halide; a comparison is drawn with the alkene analog, which exchanges alkene at a rate of between 3 and 6 orders of magnitude faster than the carbonyl complex.

The identity of fluxional η^1-cyclopentadienyl groups in $PtCl(C_5H_5)(CO)PR_3$, **4**, previously suggested by NMR has been confirmed via a crystal structure: the Cl and CO are mutually *trans* with the Pt–CO bond at 1.835(6) Å and the Pt–C_5H_5 bond at 2.157(5) Å.[25]



4

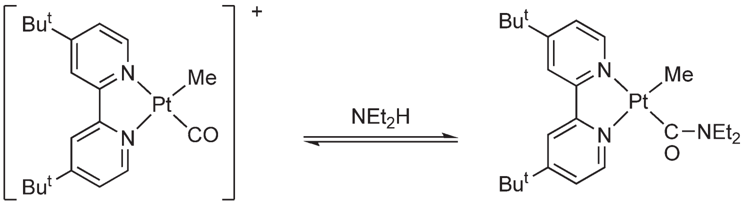


Scheme 1

Cationic carbonylplatinum complexes **5** have been synthesized at low temperatures via the high-pressure carbonylation of a chloro starting material, and also at low pressure in the presence of tin dichloride, where it is believed an $SnCl_3$ group is generated.[26] Once formed, the cationic complexes undergo a reversible alkyl migration in the presence of more carbon monoxide at a higher temperature (Scheme 1). Analogous behavior is observed in other similar complexes at room temperature.[27]

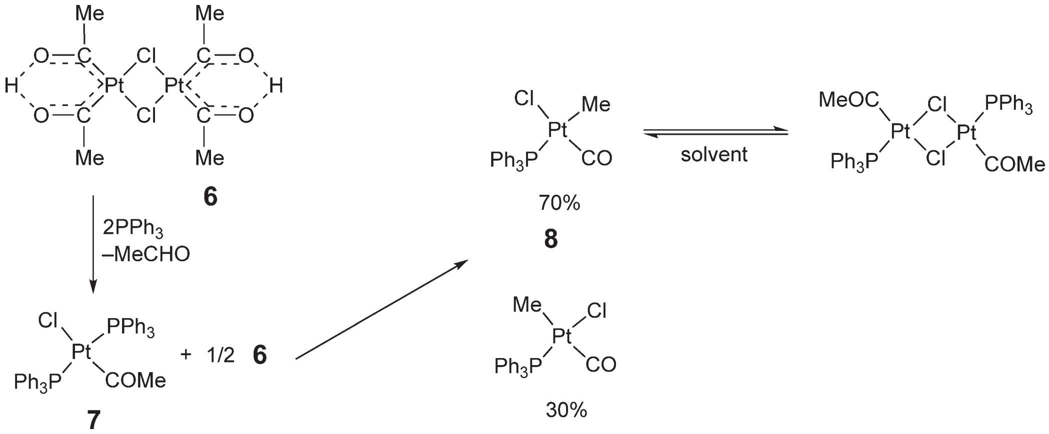
Platina-β-diketone **6** reacts with 2 equiv. of phosphine ligand to give a 50% yield of acyl complex **7**, with half the starting **6** remaining; over time this reaction mixture evolves to give a mixture of *cis*- and *trans*-isomers of methyl carbonyl complexes **8** (Scheme 2). One of the isomers of **8** exhibits a reversible CO insertion/deinsertion, which may be brought about by the simple expedient of solvent removal or addition.

Carbonyl complex **9**, which can be generated by the direct replacement of triflate by carbon monoxide, is, in the presence of diethylamine, in equilibrium with carbamoyl complex **10** (Equation (3)).[28] In the presence of excess amine, in solution, **10** can be formed free from **9**; however, solvent removal always results in partial reversion to **9**.

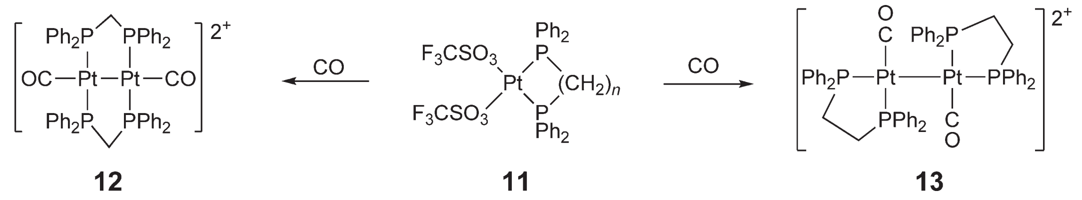


9 **10** (3)

In some similar chelating phosphine complexes, replacement of triflate by carbonyl proceeds with reduction of the platinum(II) centee to a platinum(I) dimer.[29] When the dppm complex **11** ($n = 1$) is reacted with carbon monoxide, the phosphine ends up in a bridging form in the product **12**, whereas when the dppe complex **11** ($n = 2$) is reacted, the



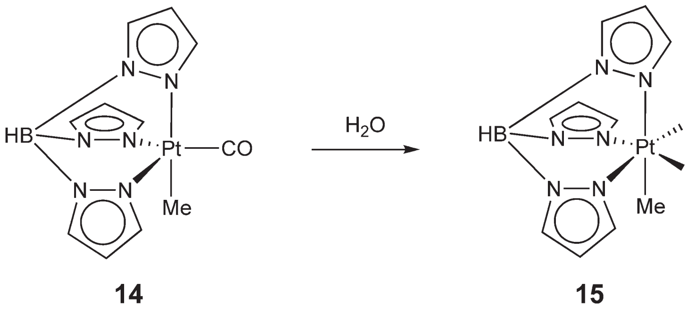
Scheme 2



Scheme 3

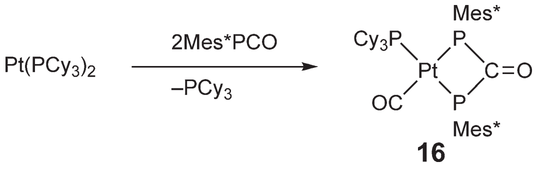
phosphines remain chelating in the product **13** (Scheme 3). The proposed mechanism involves attack on a coordinated carbonyl by water, elimination of carbon dioxide to yield a platinum(0) species, followed by combination of this species with another equivalent of platinum(II) carbonyl to yield the dinuclear platinum(I) compounds.

In the tris(pyrazole)borate complex **14**, attack by water on a coordinated carbonyl also leads to elimination of carbon dioxide, but concomitant protonation of the platinum center leads to the unusual platinum(IV) species **15**, which has two *cis*-hydrides and a methyl group (Equation (4)).[30]



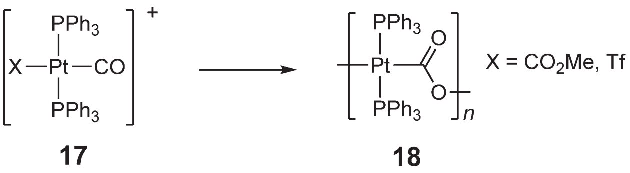
(4)

New platinum carbonyl complexes **16** have been prepared by the decarbonylation of a phosphaketene, though it is unlikely this will be of general utility (Equation (5)).[31]



(5)

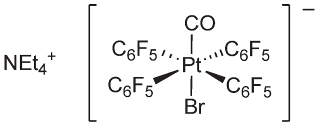
Bifunctional platinum carbonyl complexes such as **17** have been synthesized with a view to producing platina–ester polymers **18** (Equation (6)); however, the steric bulk of the ancillary phosphine ligands prevented the formation of the polymer.[8]



(6)

8.07.1.4 Mononuclear Pt(IV) Carbonyls

The oxidative addition of bromine to a platinum(II) salt, followed by halide extraction in the presence of CO, leads to the isolation of the platinum(IV) carbonyl complex **19**.[32] The authors claim this to be the first example of a structurally characterized platinum(IV) carbonyl, with X-ray data showing a Pt–CO distance of 1.91(3) Å and a CO stretch of 2,166 cm^{-1}. The authors of this paper demonstrate that the compound previously reported as $[NEt_4][PtBr_3H_2(CO)]$ is in fact the platinum(II) species $[NEt_4][PtBr_3(CO)]$.



19

8.07.1.5 Polynuclear Platinum Carbonyls

In this section, we consider polynuclear carbonyl compounds that contain only platinum: we consider polynuclear carbonyls that contain platinum and other metals in Section 8.07.1.6. We further split up the discussion on the platinum only compounds into three groupings: the homoleptic carbonyl anions, the mixed ligand triangular compounds and assorted others.

8.07.1.5.1 Homoleptic platinum carbonyl anions

The so-called Chini complexes $[Pt_3(CO)_6]_n^{2-}$ ($n = 1$–10), which are best considered as stacked platinum triangles, each with three bridging and three terminal carbonyl ligands, dominate the area of platinum carbonyl anions. Since the publication of COMC (1995), a number of papers have reported results in this area, including a synthesis mentioned in passing that relies on the action of CsF on an anhydrous solution of $[Pt(CO)_4][Sb_2F_{11}]_2$ in HF.[15] Of more fundamental interest is a solution X-ray scattering study that was coupled with computational work.[33] Results from this study include the first synthesis and analysis of the structure of the parent $[Pt_3(CO)_6]^{2-}$ ion in solution, and a comparison of it with the $[Pt_3(CO)_6]_2^{2-}$ dimer. The results for the monomer are consistent with a planar arrangement of all atoms needing no additional carbonyls to stabilize it, with the dimer apparently having the two planes staggered at 30° to each other (thus allowing minimal steric interactions between carbonyl ligands), though calculations indicate only a small barrier to rotation of the triangles.

Redox studies of the Chini complexes are of considerable interest, as the change of nuclearity of $[Pt_3(CO)_6]_n^{2-}$ from n to $(n-1)$ corresponds to a reduction. In one paper, the reduction has been studied by time-resolved pulse radiolysis in a water/propan-2-ol solution, where alcohol radicals are generated.[34] The initial step has been demonstrated to be the formation of $[Pt_3(CO)_6]_n^{3-}$, which then immediately splits into $[Pt_3(CO)_6]_4^{2-}$ and $[Pt_3(CO)_6]_{n-4}^{-}$. The fate of the $[Pt_3(CO)_6]_{n-4}^{-}$ ion depends on n: with the smaller values of n (6 or 7), dimerization tends to occur, whereas with larger values (8 or 9), further reduction is more likely. An additional observation was that if small quantities of $[Pt_3(CO)_6]_4^{2-}$ are formed in the presence of excess $[Pt_3(CO)_6]_6^{2-}$, comproportionation results giving 2 equiv. of $[Pt_3(CO)_6]_5^{2-}$.

Another study on the reduction of $[Pt_3(CO)_6]_n^{2-}$ ($n = 3$, 4, 5) by dihydrogen has shown the reaction rate to be independent of the dihydrogen pressure, but second order in complex concentration.[35] The reaction rates were found to be solvent dependent, with reduction being fast in DMF, but slow in solvents such as acetone, THF, or dichloromethane. The reverse reaction (oxidation by acid) is shown to be dependent in a non-trivial fashion on the concentration of H^+, indicating several protonation equilibria; aggregates of clusters are also implicated. Another study by some of the same authors deals with the situation where the counterion is itself redox active.[36] Thus, complexes with methylene blue, safranine O, nicotinamide benzyl chloride, and methylviologen counterions have been studied with selective and total reduction of these ions being observed.

The carbonyl anions $[Pt_3(CO)_6]_n^{2-}$ ($n = 3$, 4, 5), together with the cetyltrimethylammonium counterion, have been used to prepare new platinum-based layered materials.[37] The carbonyl anions are precipitated, and then heat (70 °C) is used to decompose the anions via CO loss to give layered structures with a separation of 19.1 Å; prolonged heating (120 °C) results in the generation of an amorphous powder. In a similar vein, the decarbonylation of some carbonyl anions was studied inside faujasites (X, Y zeolites). In an initial study, the synthesis of the carbonyl anions was performed inside the cavities via the reductive carbonylation of $[Pt(NH_3)_4]^{2+}$ at 90 °C.[38] It was found that the size of the cluster (i.e., the value of n) was strongly dependent on the size and basicity of the cavity in the faujasites—strongly basic high aluminum zeolites giving the best yields of carbonyl anions, with the less basic magnesium and calcium faujasites giving Pt(0) particles. Water was found to be essential to the formation of the carbonyl anions (acting as a source of H^+) and, if the temperature exceeded 90 °C, decomposition to uncharacterized platinum species was observed. A study on the synthesis of the anions in faujasites by FTIR was carried out where similar conclusions were drawn, with the additional insight that too much water retards the carbonylation process, but promotes the formation of smaller clusters.[39] A further study on the oxidation and recarbonylation of carbonyl anions caged in zeolites formed from $[Pt(NH_3)_4]^{2+}$ shows that the formal positive charge on the platinum is maintained even after carbonylation—implying that the negative charge of the cluster is located on the π-systems of the carbonyls.[40] When the $[Pt_3(CO)_6]_2{}^{2-}$ dimer is decomposed by heat, the hexanuclear framework is maintained in an oxide form, which allows a very rapid recarbonylation to give $[Pt_3(CO)_6]_2{}^{2-}$ back.

One report indicates that the $[Pt_3(CO)_6]_n{}^{2-}$ anions have been investigated with a view to increasing the effective quantum yield in silver halide-based photography, and a significant improvement was reported at a relative concentration of 5×10^{-5} Pt atoms per silver ion.[41] Another report describes the use of the protonated ($n = 5$) cluster in synthesizing mixed platinum/tin materials on an alumina support.[42] Finally, a theoretical study of $[Pt_3(CO)_6]^{2-}$ suggests that it is possible to consider each platinum to be a formally 16-electron square-planar entity, with the HOMO being ideally situated to form the intertriangle bonds in the stacked $[Pt_3(CO)_6]_n{}^{2-}$ complexes.[43]

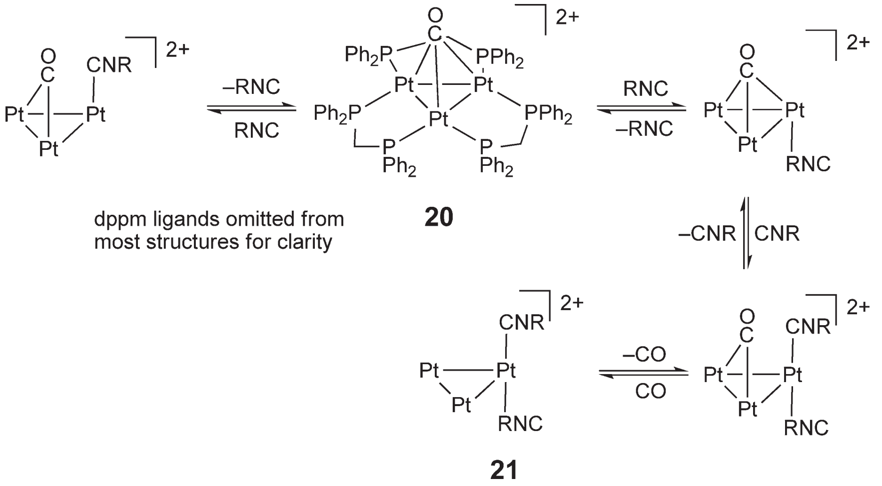
Moving away from the triangular-based $[Pt_3(CO)_6]_n{}^{2-}$ anions, there has been one report on the reactivity of the $[Pt_{19}(CO)_{22}]^{4-}$ anion.[44] This cluster, which is best considered to be three eclipsed pentagonal platinum arrays sandwiching a platinum between each layer, with a further platinum capping the two exposed pentagonal faces, is oxidized by NO^+. The initial product is the $[Pt_{19}(CO)_{21}(NO)]^{3-}$ anion where the NO is terminally bound to one of the two capping platinums, but extended reaction times lead to the previously uncharacterized $[Pt_{38}(CO)_{24}]^{2-}$. The structure of $[Pt_{38}(CO)_{24}]^{2-}$ indicates a ccp Pt_{38} core with Pt–Pt distances in the range 2.749(1)–2.919(1) Å, and those of the central Pt_6 octahedron being in the much narrower range of 2.803(1)–2.818(1) Å.

Reaction of $[Pt_n]^-$ ($n = 3$–7) with carbon monoxide was studied in a flow tube reactor, with bimolecular rate coefficients and the maximum number of CO molecules that bind to each cluster being determined.[45] Subsequently, the collision-induced dissociation of both $[Pt_n]^-$ and $[Pt_n(CO)_m]^-$ was studied using a guided ion beam tandem mass spectrometer.[46,47] The binding energies of CO to the platinum cluster anions was indicative of two different binding sites, that is, terminal (about 80–110 kJ mol^{-1}) and bridged (220–250 kJ mol^{-1}). The thermochemical stabilities of additional neutral and anionic platinum carbonyl species have also been determined.

8.07.1.5.2 Mixed ligand triangular platinum carbonyl clusters

Work with the platinum triangle **20** pioneered by Puddephatt and co-workers has continued.[48] Isocyanide ligands have been used to displace carbonyl ligands, and complex **21** is the first Pt_3 cluster to have been isolated without a bridging atom (Scheme 4). Aspects of the structures of the isocyanide compounds are discussed in Section 8.07.2.6.

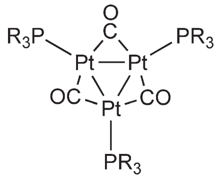
A new synthesis of **20** has been published, simply relying on the reduction of K_2PtCl_4 by $LiBH_4$ under a CO atmosphere, in the presence of dppm: high yields are claimed.[49]



dppm ligands omitted from most structures for clarity

Scheme 4

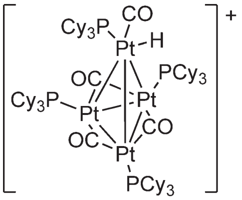
In the neutral carbonyl complexes $Pt_3(\mu\text{-}CO)_3(PR_3)_3$ **22**, the carbonyl ligands may be sequentially replaced giving $Pt_3(\mu\text{-}CO)_{3-n}(\mu\text{-}SO_2)_n(PR_3)_3$ ($n = 0$–3): a complete analysis of the ^{13}C NMR spectra is included.[50]



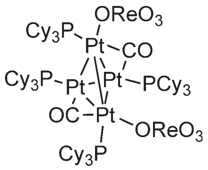
R = Ph, Bz, Cy, ^{i}Pr

22

The oxidation of **22** (R = Cy) by moist Re_2O_7 yields two unusual tetrahedral Pt_4 clusters.[51] In the 56 CVE **23**, the structure is best considered as the neutral triangle **22** donating two electrons to a $[PtH(CO)PR_3]^+$ fragment. In the C_2-symmetric 54 CVE **24**, the structure contains two O-bound ReO_4 fragments.



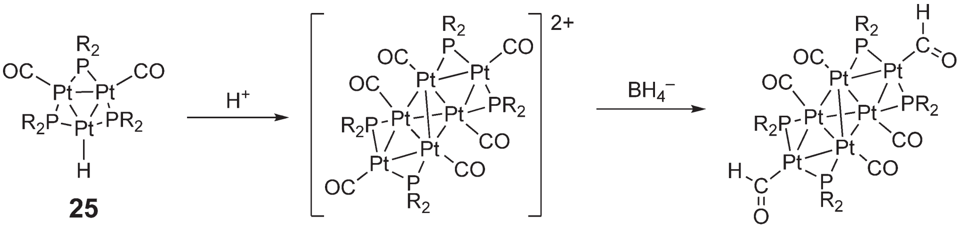
23



24

A similarly unexpected product was formed by the protonation of **25**, which leads to dihydrogen elimination followed by dimerization to **26** (Scheme 5). Cluster **26** can be regarded either as two platinum triangles with perpendicular edges joined, or as a platinum tetrahedron with two opposite edges capped with further platinums.[52] Subsequent reduction of the air stable **26** with borohydride gives the first-ever formyl complex of platinum, with the ^{1}H resonance of the formyl proton at 18.9 ppm showing coupling to two phosphorus nuclei and one platinum being definitive evidence for its existence.

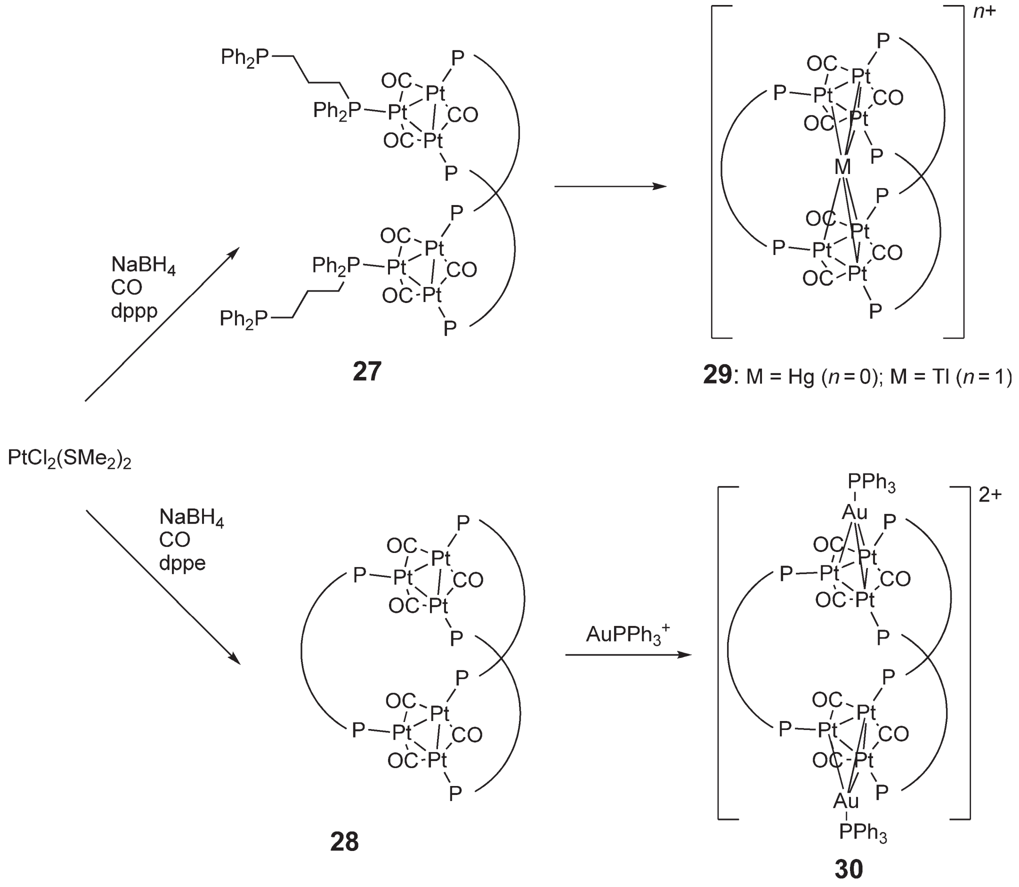
Hexaplatinum cluster complexes that correspond to two linked platinum triangles of the type **22** have been prepared by reduction of $PtCl_2(SMe_2)_2$ with $NaBH_4$ in the presence of CO and the diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (i.e., dppe ($n = 2$), dppp ($n = 3$)); the reaction failed to give isolable products when $n > 3$.[53] The products are the open-cluster $Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppp)_2(dppp)_2$, **27**, and the closed-cluster $Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppe)_3$, **28**, (Scheme 6). The open cluster **27** acts as a cryptand ligand, and will encapsulate mercury(0) or thallium(I) with loss of dppp to give the closed-clusters **29**. An X-ray crystal structure of the thallium derivative shows that the platinum triangles are some 5 Å from each other, with the thallium bonded to all six platinums with Pt–Tl distances in the range 2.86–2.99 Å. The closed-cluster **28** does not encapsulate any other metals (it is thought that the cavity is too small), but it does react with $[AuPPh_3]^+$ to give **30**, whereupon each of the platinum triangles is triply bridged by the gold phosphine moiety. We discuss complexes of this type further in Section 8.07.1.6.2.



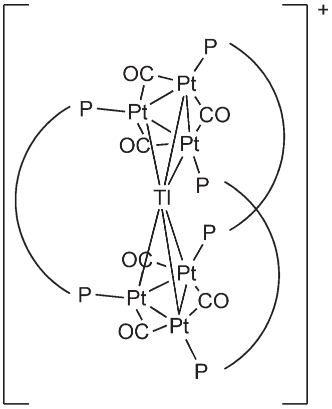
25

26

Scheme 5



Scheme 6



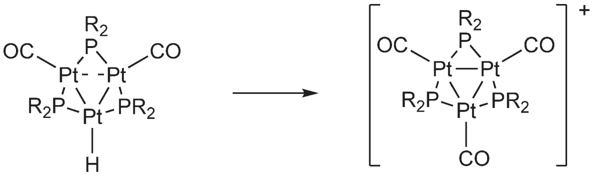
29

In a later communication, the same group reported the dppm-bridged analog of 28, which was observed to add an additional monodentate phosphite. The additional phosphite was seen by NMR to be fluxional over one of the platinum triangles; at room temperature the NMR spectra indicated a triply bridging mode for the phosphite, but the low-temperature spectra indicated it was bound to one platinum only.[54]

Carbon monoxide has been used to reduce the dinuclear Pt(II) derivative $[PtH(\mu\text{-}PBu^t{}_2)_2(PHBu^t{}_2)_2]_2$ into the novel 44-electron platinum triangle 31.[55] The structure of 31 can be treated as having two of the platinum centers in oxidation state +1, and one in the +2 state. The synthesis corresponds to a CO-induced reductive elimination of

$PHBu^t_2$ from the starting complex, yielding the mononuclear Pt(0) carbonyl derivative $Pt(PHBu^t_2)_2(CO)_2$, as an intermediate.

The terminal hydride in **31** may be removed by one-electron oxidants such as ferrocinium, and under carbon monoxide the reaction affords the symmetrical, cationic complex **32**, (Equation (7)).[56] It is possible to replace one of the carbonyl ligands in **32** with other ligands such as ethene. The X-ray structure of this complex, the first platinum cluster to include both a carbonyl and an ethene ligand, is reported: the ethene lies in the plane of the platinum triangle with a C–C distance of 1.25(6) Å.



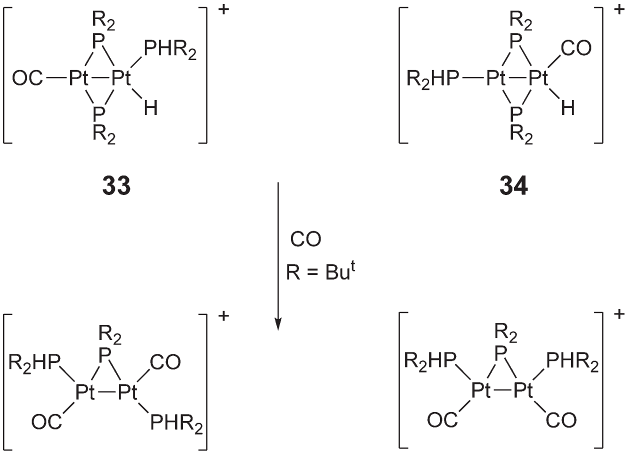
31 **32** (7)

8.07.1.5.3 Assorted other platinum carbonyl clusters

The structure of the dinuclear $Pt_2Cl_4(CO)_2$ complex has been reported: in contrast to the palladium analog, the carbonyl groups are *trans* to each other.[11,12] Pt–C and C–O distances are listed as 1.86(5) Å and 1.08(5) Å. As we noted earlier in Section 8.07.1.3, reaction of *trans*-$[Pt_2Br_4(CO)_2]$ with alkene yields *cis*-$[Pt(CO)Br_2(alkene)]$, with the reaction believed to go via the *trans*-isomer.[22] Phosphido-bridged dimers containing a terminal carbonyl ligand, **33**, are observed to react in a stepwise fashion with terminal alkynes to give stable η^1-alkynyl/alkenyl-bridged derivatives.[57] In these new complexes, the carbonyl is appreciably electrophilic and is attacked by hydride and methoxide to give a formyl species. Both **33** and the isomeric **34** react with further carbon monoxide to give two new species **35** and **36** (Scheme 7).[58] The Pt–Pt bond length in **36** is reported to be 2.6743(5) Å, with Pt–C distances in the range 1.88–1.93 Å.

The synthesis and structural characterization of a new pyrazolato-bridged platinum carbonyl dimer *trans*-$[(OC)ClPt(\mu\text{-pz})(\mu\text{-Cl})PtCl(CO)]$ and its mononuclear precursor *trans*-$[PtCl_2(CO)(Hpz)]$ are reported.[59] The mononuclear precursor contains square-planar platinum centers stacked with a Pt–Pt distance of 3.417(0) Å, whereas the dimeric complex has nearly linear Pt–Pt chains with the shortest Pt–Pt distances being 3.399(5) and 3.427(5) Å.

In a short communication, carbon monoxide is reported to be a useful reagent for the elimination of sulfur as COS from a Pt_2S_2 cluster, giving rise to species containing both bridging and terminal carbonyl ligands.[60] The larger tetraplatinum cluster $Pt_4(\mu\text{-CO})_4(PEt_3)_5$ is reported as a byproduct in the reaction of a platinum dimer containing a



Scheme 7

hydride bridge.[61] The tetranuclear platinum cluster complexes $[Pt_4(\mu\text{-}CO)_3(\mu\text{-dppm})_3(PPh_3)]^{2+}$ and $[Pt_4(\mu\text{-}H)(\mu\text{-}CO)_2(\mu\text{-dppm})_3(PPh_3)]^{+}$ have been prepared by cluster expansion; they have butterfly structures and are fluxional.[62]

8.07.1.6 Heterometallic Polynuclear Platinum Carbonyls

In this section, we consider polynuclear carbonyl compounds containing platinum and one or more other metal. The discussion on these clusters is split into three groupings: heterodinuclear clusters, triangular clusters, and higher nuclearity clusters.

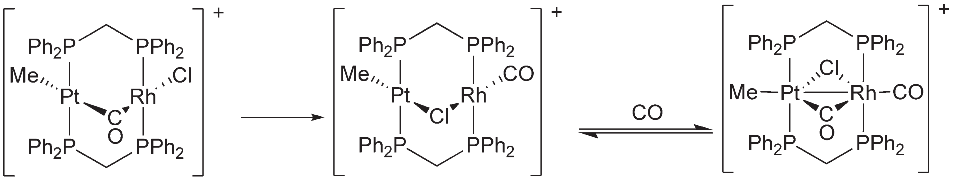
8.07.1.6.1 Heterodinuclear clusters

A series of platinum–tungsten and platinum–molybdenum complexes $(cod)RPt\text{–}MCp(CO)_3$ (R = Me, Et, Ph, and substituted Ph; Cp = C_5H_5, MeC_5H_4, $MeCO_2C_5H_4$) have been prepared.[63] The geometry at platinum is essentially square planar, and the X-ray structure of one molybdenum complex has a Pt–Mo distance of 2.832(1) Å. In the solid state, two of the carbonyl groups are clearly interacting the platinum with Pt–C distances of 2.435(12) and 2.469(15) Å, distances that are longer than would be expected for bridging carbonyls, and substantially longer than the Mo–C distances of 1.996(13) and 1.968(15) Å. Thermolysis of these complexes leads to the migration of the R group from the Pt to Mo or W, eliminating $MCpR(CO)_3$ and a poorly defined Pt(0) species. Subsequent work with complexes where R = Et, and the cod ligand had been replaced by a dppe, showed that a β-hydrogen elimination reaction takes place in high yield with elimination of ethene and retention of the dinuclear structure.[64] A similar unsymmetrical bridging mode for a carbonyl is found in the X-ray structure of **37**.[65] While all spectroscopic evidence points to a terminally bound carbonyl on the rhodium in solution, that is, structure **38**, it is clear that chloride and carbonyl swap roles in the solid state. The Pt–C distance, at 2.32(2) Å, is 0.43 Å longer than the Rh–C distance of 1.89(2) Å and the Pt–Rh distance is reported as 2.801(2) Å. Under a carbon monoxide atmosphere, **38** will add a further equivalent of CO to give **39** (Scheme 8), with spectroscopic evidence clearly indicating both terminal and bridging carbonyls; attempts to solve the solid-state structure of **39** were hampered by its tendency to lose CO. Other examples of semi-bridging carbonyls include a Pt–Fe dinuclear isocyanide complex discussed in Section 8.07.2.7.[66]

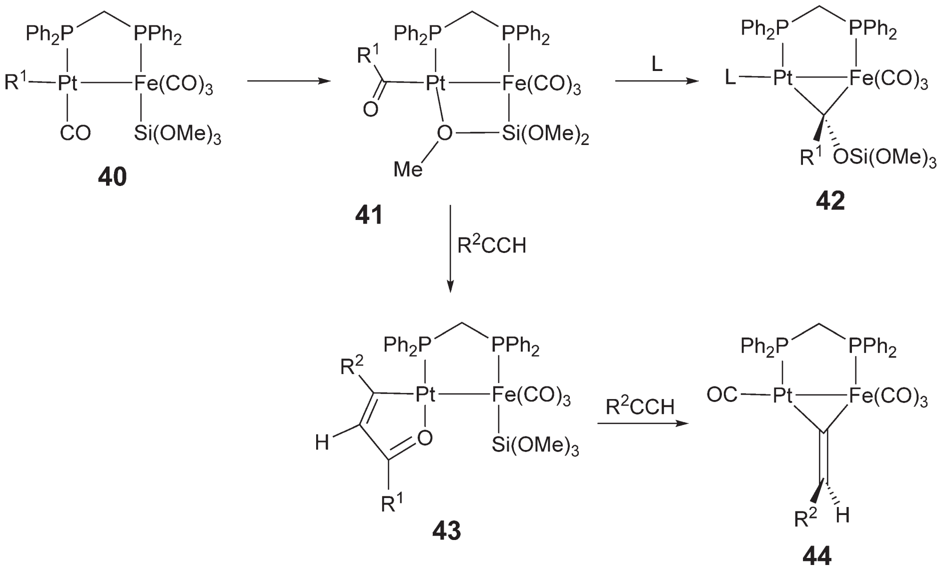
There have been a number of papers concerned with iron–platinum carbonyl clusters bridged by a dppm-type ligand, such as **40**. The facile migration of an alkyl group onto the carbonyl on platinum of **40** yields an acyl complex **41**, which is stabilized by the interaction of a neighboring OMe group; further reaction with a ligand yields a bridging carbene complex **42** (Scheme 9).[67]

Reaction of **41** with terminal alkynes leads to vinyl complexes **43**, with excess alkyne leading to bridging vinylidene **44**, in respectable yield.[68] Reactions similar to the transformation **41** → **43** occur with electron-deficient non-terminal alkynes such as dimethylacetylenedicarboxylate (DMAD) or hexafluorobut-2-yne.

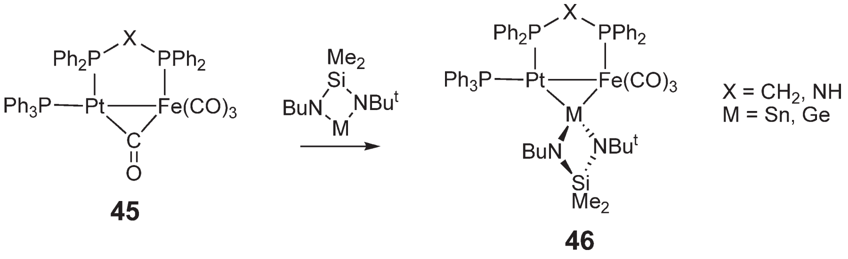
Addition of cyclic tin or germanium diamides to **45** results in displacement of the carbonyl, with the generation of new clusters **46** in high yield (Equation (8)); excess germanium reagent results in displacement of the phosphine on the platinum.[69] Similar carbonyl displacements are observed with isocyanide ligands; the products of these reactions are discussed in Section 8.07.2.7.[70]



Scheme 8

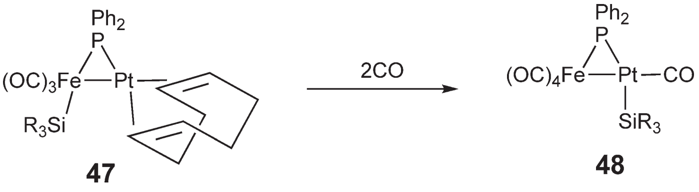


Scheme 9



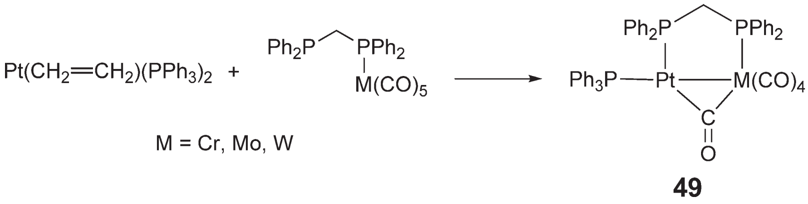
(8)

Phosphido-bridged complexes 47 undergo an unprecedented metal-to-metal silyl group migration to give complexes 48 (Equation (9)).[71] The first stage of the reaction is the displacement of the cod by carbon monoxide, followed by silyl migration with concomitant carbonyl backmigration. The nature of the ligand on the platinum is crucial: while the reaction proceeds when isocyanides are used instead of carbonyls, use of phosphines results in no silyl migration. X-ray structures of two different complexes 48 ($R = Et$, Ph) reveal Fe–Pt distances of 2.7233(7) and 2.7176(9) Å with Pt–CO distances of 1.898(6) and 1.899(7) Å.



(9)

Complexes 49, similar to 45, are synthesized directly in high yields (Equation (10)).[72] The bonding of the bridging carbonyl is asymmetric, with shorter Pt–C distances (1.904(4) Å, $M = Cr$; 1.923(1) Å, $M = W$) than M–C distances (2.389(4) Å, $M = Cr$; 2.418(8) Å, $M = W$). The authors were unable to rationalize the difference in these distances and suggest the need for theoretical calculations.



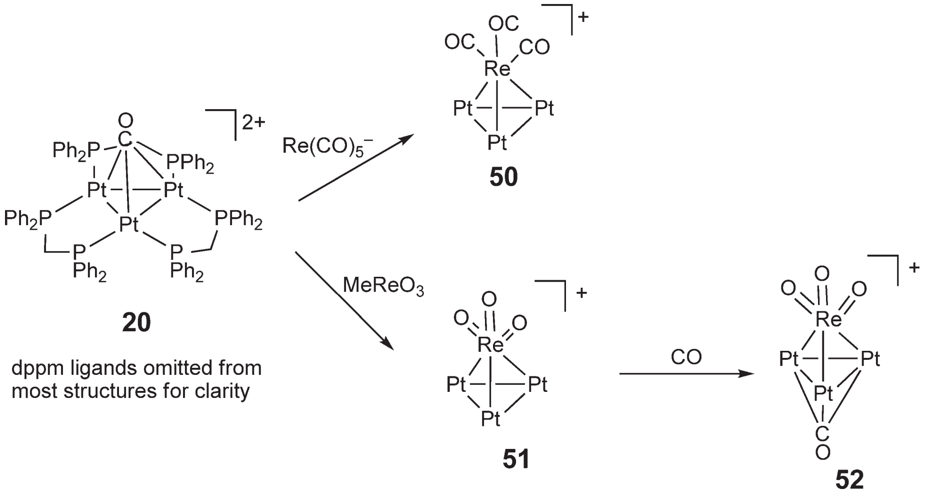
(10)

An IR study of a series of the vinylidene-bridged complexes $Cp(OC)_2MnPt(\mu\text{-}C{=}CHPh)L^1L^2$ (L^1 and $L^2 = CO$, $P(OR)_3$, PPh_3, bridging diphosphines) showed a gradual transformation of one of the terminal CO groups at the Mn atom into a bridging one spanning the Mn–Pt bond, via the intermediate semi-bridging form.[73] Heterodinuclear Pt–Rh complexes have been reported, but the carbonyls are bound to the rhodium, not platinum, and hence they are discussed in Volume 7.[74]

8.07.1.6.2 Triangular clusters and their derivatives

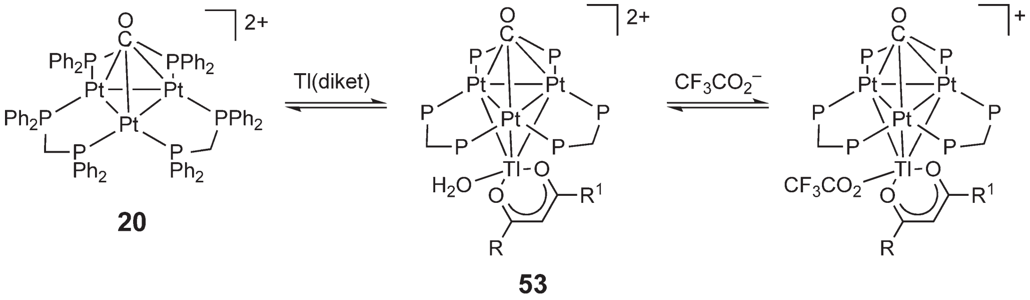
The chemistry of the versatile platinum triangle **20**, pioneered by Puddephatt, was touched upon in Section 8.07.1.5.2, and further aspects of its reactivity are discussed in Section 8.07.2.6; here, we discuss its role in heterometallic clusters. Initial observations centered on the fact that it is possible to replace the triply bridging carbonyl by reaction with $[M(CO)_5]^-$ (M = Mn, Re) to give coordinatively unsaturated clusters **50** (Scheme 10).[75] These clusters have only 54 CVE (compared with the 60 that is usual for saturated tetrahedral complexes); the X-ray structure of the Re complex has short Pt–Pt and Pt–Re bond lengths of 2.5930(9)–2.6114(7) and 2.6488(8)–2.6850(8) Å, respectively. Subsequent work showed that it was possible to replace the formally Re(I) $[Re(CO)_3]^+$ fragment in **50** with the formally Re(VII) $[ReO_3]^+$ fragment to give new clusters **51**.[76] Reaction of these clusters with carbon monoxide gives the triply bridged cluster **52**, from which, it is possible to displace the carbonyl and synthesize other non-carbonyl clusters. It is also possible to displace one or more carbonyls from **50**, giving new clusters.[77]

Some platinum–thallium clusters were touched upon in Section 8.07.1.5.2, here we look at additional examples in more detail. A synthesis of **53** that relies on the reaction of a thallium β-diketonate with **20** has been reported (Scheme 11).[78] The simple procedure gives yields in the range 60–75%, and X-ray structures confirm the triply



dppm ligands omitted from most structures for clarity

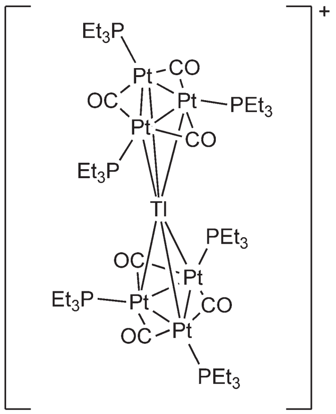
Scheme 10



Scheme 11

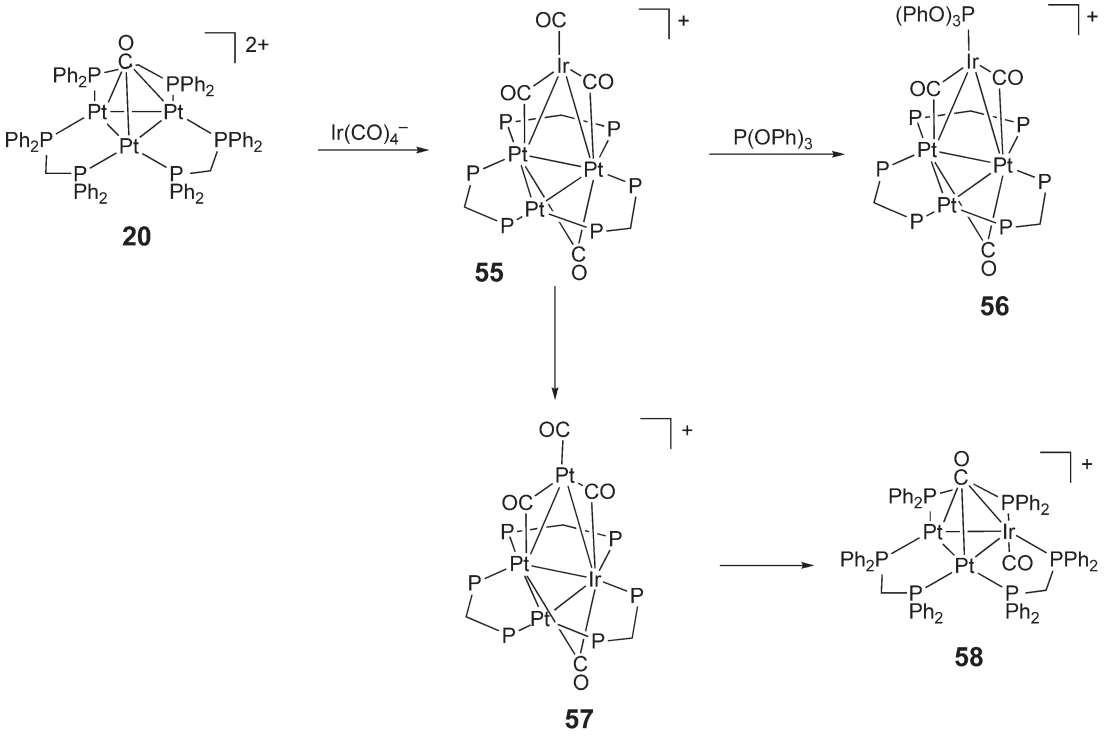
bridging nature of the thallium, and the slightly distorted state of the tetrahedron of metals (Pt–Tl distances are, at about 2.9 Å, about 0.25 Å longer than the Pt–Pt distances).

It might have been thought that platinum–thallium sandwich cluster 29 relied on the bridging ligands to hold it together; however, a new analogous sandwich cluster that does not have bridging ligands has been reported.[79] Complexes 54 were synthesized in 90% yield by the reaction of $Pt_4(\mu\text{-}CO)_5(PEt_3)_4$ with $TlPF_6$. The geometry of the complex was determined by X-ray and found to be a centrosymmetric trigonal-antiprismatic architecture of trigonal D_{3d} symmetry (i.e., the platinum triangles are staggered in relation to each other), and the mean Pt–Tl distance was calculated as 2.96 Å. Intertriangular distances are reported as 5.04 Å, indicating no appreciable Pt–Pt interactions, confirming that it is the strength of the platinum–thallium bonding that is holding the cluster together.



54

At low temperature, platinum clusters 20 react with $[Ir(CO)_4]^-$ to give, via CO loss, butterfly complex 55.[80] One carbonyl ligand in 55 can be displaced by triphenylphosphite giving 56 (Scheme 12), the X-ray structure of which clearly shows a butterfly structure with iridium at a wingtip position. Complex 55 is thermally unstable, and is shown



Scheme 12

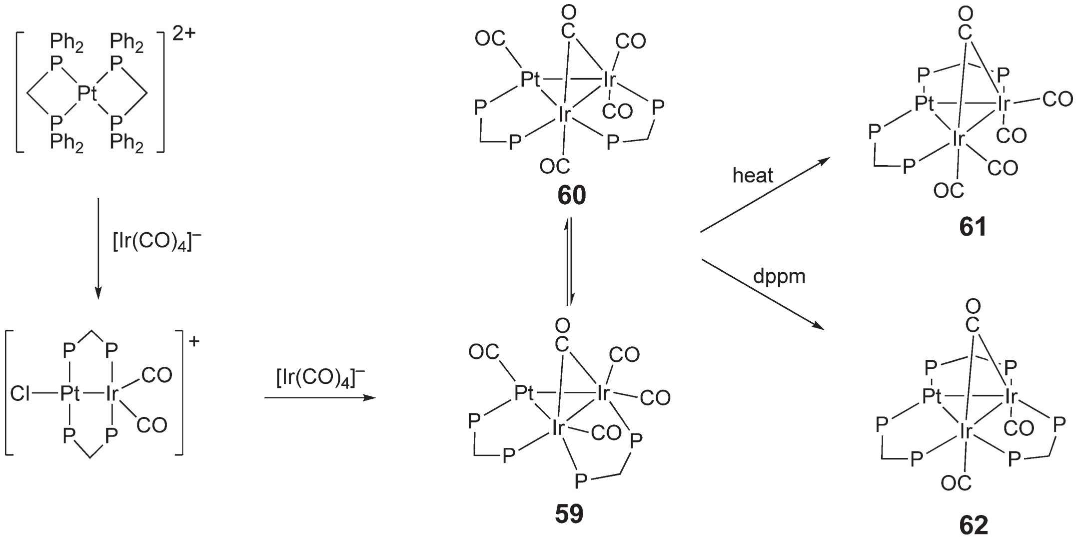
by NMR to rearrange in solution forming the isomeric cluster **57**, in which the iridium atom now occupies a hinge position. The isomerization of **55** to give **57**, via phosphorus migration from platinum to iridium, can be understood, as it results in the iridium adopting an 18-electron hinge position with one of the platinums adopting the 16-electron wingtip position. Under CO, **57** eliminates one platinum atom to form the trimetallic complex **58**. The overall reaction then involves displacement of a platinum atom from the 42-electron cluster cation **20** by IrCO to give the 44-electron cation **58**.

Displacement of a second platinum in **58** by an iridium is not possible via further reaction with $[Ir(CO)_4]^-$; however, the stepwise formation of such a complex from low-nuclearity precursors is possible.[81] Thus, reaction of $[Pt(dppm)_2]Cl_2$ with $[Ir(CO)_4]^-$ gives $PtIr_2$ cluster **59** (Scheme 13). Cluster **59** is shown by NMR to be in equilibrium with its isomer **60**, with roughly equal populations in solution; slow crystallization from this mixture results in pure samples of **60**, which have been used to determine the X-ray structure. The metal triangle in **60** is shown to be nearly equilateral (all metal–metal bonds in the range 2.63–2.68 Å), with both dppm ligands and two of the carbonyls in the same plane. A solution mixture of **59** and **60** rearranges on heating to give new cluster **61**, and, in the presence of a further equivalent of dppm, another new species **62**.

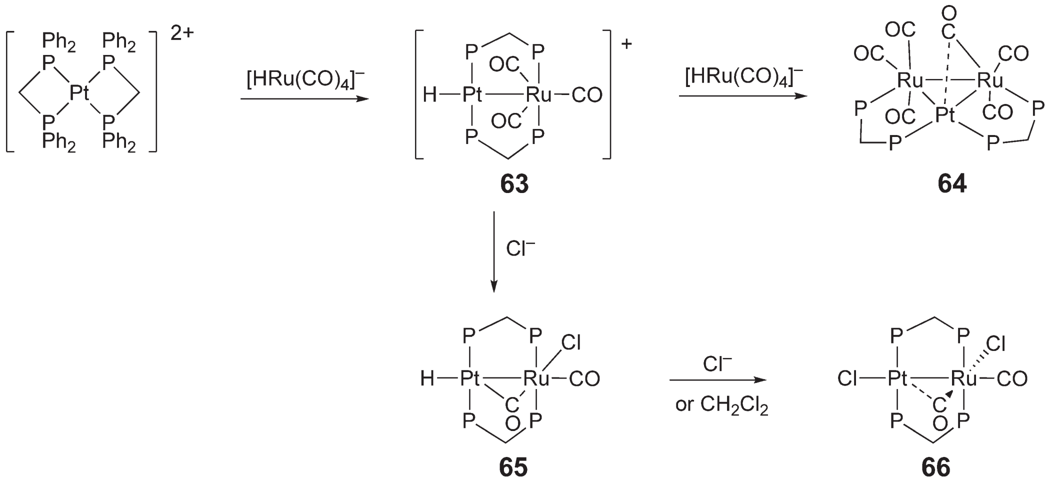
In an analogous reaction platinum–ruthenium clusters have been synthesized.[82] Reaction of $[Pt(dppm)_2]Cl_2$ with 1 equiv. of $[HRu(CO)_4]^-$ gives bimetallic species **63**, and subsequent reaction with a further equivalent gives triangular $PtRu_2$ cluster **64** (Scheme 14). An X-ray structure of **64** confirms the semi-bridging nature of one of the carbonyl ligands in the solid state, though NMR data suggests a fluxional structure in solution with all four possible isomers containing semi-bridging Ru–Pt carbonyls in equilibrium. Bimetallic **63** reacts with its chloride counterion, which displaces a carbonyl ligand, to give neutral species **65**, which reacts with further chloride to give **66**.

Tetranuclear Pt_3Ru cluster **67** is formed when the platinum triangle **20** reacts with $[HRu(CO)_4]^-$.[83] At low temperature **67** is formed cleanly, and can be identified by NMR and IR spectroscopies; however, at room temperature, it isomerizes to **68** in a matter of hours (Scheme 15). Dark purple crystalline samples of **68** can be isolated, and are thermally and air stable. An X-ray structure of **68** shows the metal core to be closer to a butterfly structure than a tetrahedron: the unique Pt–Ru distance is a long 2.9951(6) Å, whereas the other two are 2.7031(6) and 2.7649(6) Å; Pt–Pt distances are in the range 2.61–2.73 Å. Both **67** and **68** are fluxional in solution, with the NMR spectra of **67** showing fast exchange even at −30 °C.

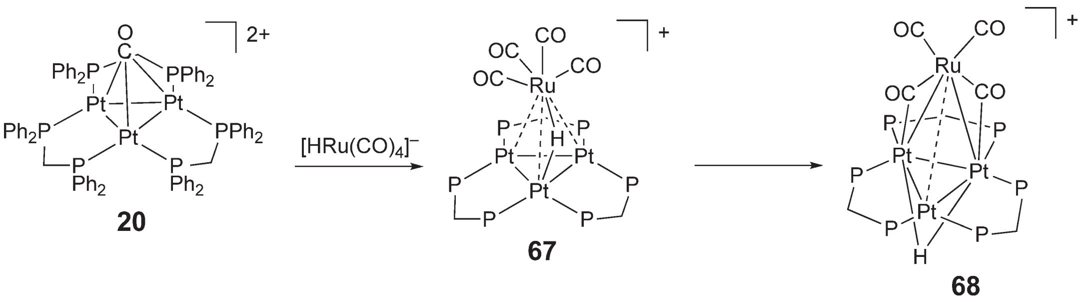
A new Pt_2Co triangular cluster **69** has been reported.[84] Reaction of the precursors at room temperature gave a high yield of crystals of quality suitable for X-ray diffraction (Equation (11)). The diffraction study shows the P–Pt–Pt–P chain to be essentially linear and the Pt–Pt bond to be bridged symmetrically; the Pt–Pt distance is 2.655(1) Å and the Pt–Co distances are 2.547(2) and 2.574(2) Å. An EHMO calculation shows that it is best to treat **69** as two d^9-Pt(I) centers bridged by the 18-electron $[Co(CO)_4]^-$ and the 4-electron $[PPh_2]^-$ fragments.



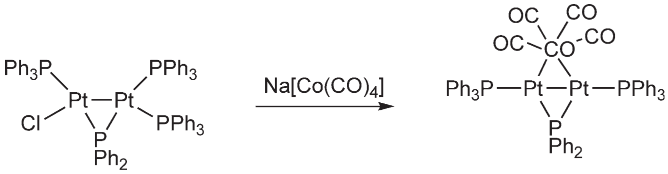
Scheme 13



Scheme 14



Scheme 15

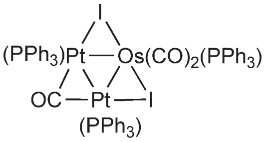


69

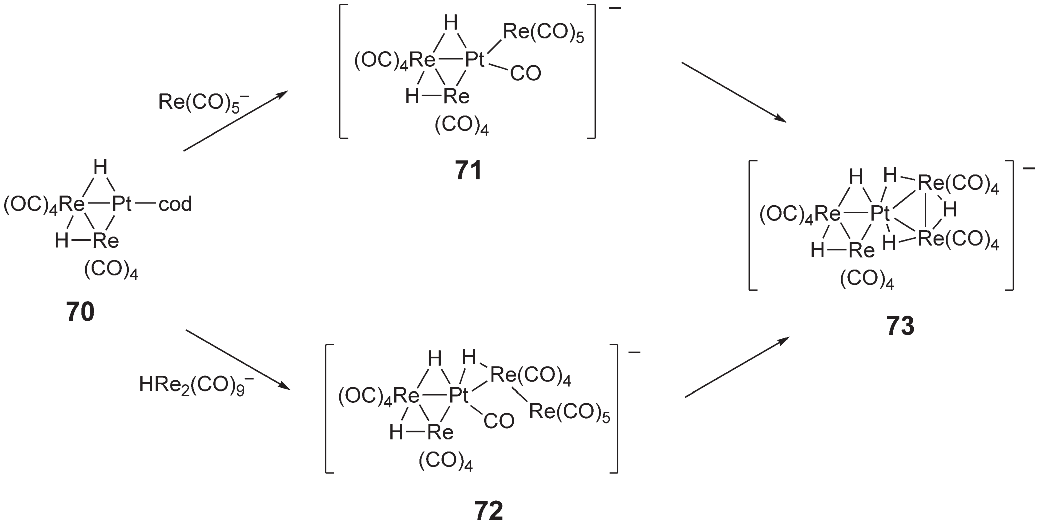
(11)

Triangular Re_2Pt cluster 70 reacts with $[Re(CO)_5]^-$ and $[HRe_2(CO)_9]^-$ in the presence of carbon monoxide to give new clusters 71 and 72 (Scheme 16).[85] Both these new clusters react with rhenium containing impurities to give the known cluster 73. Subsequent work has shown that it is possible to replace the cod in 70 in an analogous reaction with a variety of metal fragments such as $ReH(CO)_4PPh_3$ and $[WCp(CO)_3]^-$.[86]

Triangular $OsPt_2$ cluster 74 can be synthesized by the reaction of $Pt(dba)(PPh_3)_2$ with $Os_2(CO)_6I$ in benzene.[87] The new cluster is symmetrical in solution, with the bridging carbonyl stretching at 1,766 cm^{-1}; the X-ray structure has a Pt–Pt bond of 2.685(2) Å and Pt–Os bonds of 2.796(2) and 2.852(2) Å.



74



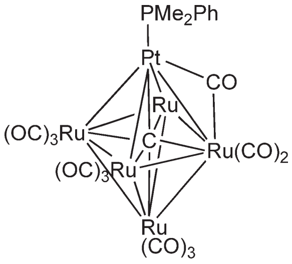
Scheme 16

The reaction of the complexes CpMoMn(CO)$_5$(μ-S$_2$) and Cp*MoMn(CO)$_5$(μ-S$_2$) with Pt(PPh$_3$)$_2$(PhC$_2$Ph) gave new bis-sulfido mixed metal complexes CpMoMn(CO)$_5$Pt(PPh$_3$)$_2$(μ_3-S)$_2$ and Cp*MoMn(CO)$_5$Pt(PPh$_3$)$_2$(μ_3-S)$_2$ by insertion of the platinum into the S–S bond, as well as a small quantity of a monophosphine complex, Cp*MoMn(CO)$_6$Pt(PPh$_3$)(μ_3-S)$_2$; X-ray structure determination confirms the presence of an Mn–Mo bond with the platinums bonded to the core by the triply bridging sulfides.[88]

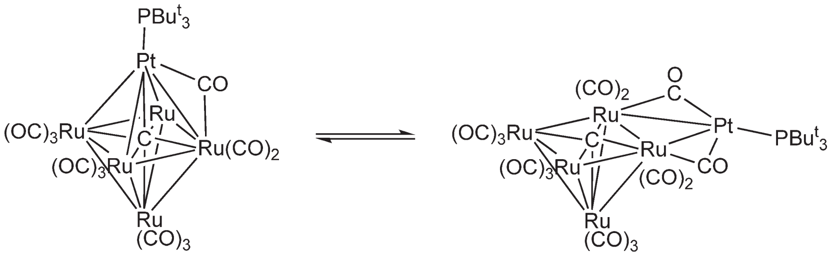
8.07.1.6.3 Higher nuclearity clusters

A mixed platinum–ruthenium carbonyl cluster has been shown to be a selective and versatile catalyst. Pt$_3$Ru$_6$(CO)$_{21}$(μ-H)$_3$(μ_3-H) consists of a triangular (PtCO)$_3$ layer sandwiched between two parallel Ru$_3$(CO)$_9$ layers. The platinum layer is staggered with respect to both ruthenium layers, one of which has an end-capping triply bridging hydride, the other of which has all three Ru–Ru bonds bridged by hydrides: all carbonyls are terminal. Reaction of this cluster with 2 equiv. of diphenylethyne leads to the hydrogenation of one equivalent (giving (*Z*)-stilbene selectively) and the coordination of the second equivalent on one end with loss of a carbonyl to give Pt$_3$Ru$_6$(CO)$_{20}$(μ_3-PhCCPh)(μ-H)(μ_3-H).[89] Subsequent work by the same group demonstrated that the hydrogenation is catalytic under a dihydrogen atmosphere.[90] Analysis of kinetic and spectroscopic data for the hydrogenation reaction suggests that the first step is dissociation of a platinum carbonyl (Pt–CO) ligand followed by oxidative addition of H$_2$ at this vacant site; the rate-determining addition of alkyne is followed by migration of two hydrides to the same face of the alkyne, quickly followed by loss of the (*Z*)-alkene. The same cluster has also been shown to be active in the hydrosilation of diphenylethyne.[91] Once again, carbonyl dissociation is necessary to generate a vacant site before the reaction can proceed, and the reaction is highly selective for *syn*-addition of the silane. Replacement of one the carbonyls in Pt$_3$Ru$_6$(CO)$_{20}$(μ_3-PhCCPh)(μ-H)(μ_3-H) by dimethylsulfide results in a complex that is highly labile, readily exchanging bound dimethylsulfide with free dimethylsulfide in solution.[92] This lability is thought to be behind the enhanced catalytic activity of this complex, compared with the original carbonyl complex, in the hydrogenation of diphenylethyne.

The hexanuclear octahedral complex **75** has been shown to exist in solution as a dynamically exchanging mixture of two isomers: one with the phosphine on the platinum (illustrated), and one with the phosphine on ruthenium.[93] NMR experiments show that the exchange is a unimolecular process, and is only fast on the NMR timescale at 160 °C. A different exchange process takes place with the analogous mixed metal cluster of formula PtRu$_5$(CO)$_{15}$(PBu$^t{}_3$)(C).[94] In solution, this cluster is again a mixture of two interconverting isomers with different core structures, both of which can be separated out by crystallization. Isomer **76** can be isolated by crystallization from benzene/octane solvent and isomer **77** can be isolated by crystallization from diethyl ether (Equation (12)).[95] The exchange between the two isomers is fast on the NMR timescale at 40 °C, with roughly equal proportions of the two at −40 °C. The exchange is thought to be a reversible Pt–Ru bond-breaking process with no dissociation of any fragments. The rate of interconversion between 76 and 77 is faster than between the two isomers of 75, and it is suggested that the additional steric requirements of the bulky *t*-butyl phosphine are responsible for the differential behavior.



75

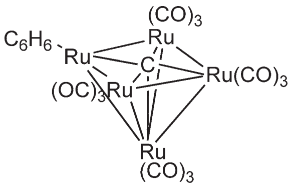


76 **77**

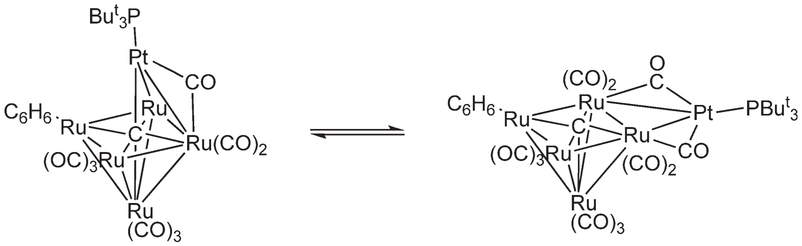
(12)

The bridging carbonyl in cluster 75 is readily replaced by bridging Ph_2Sn and Ph_2Ge groups by the simple expedient of stirring a solution at room temperature with $MHPh_3$; the lead analog can be prepared by reaction with Pb_2Ph_6.[96]

If the $Pt(PR_3)_2$ that is reacted with $Ru_5(CO)_{15}(\mu_5\text{-}C)$ to give clusters 75 and 76 is instead reacted with benzene adduct $Ru_5(CO)_{15}(\eta^6\text{-}C_6H_6)(\mu_5\text{-}C)$, 78, a slightly different exchange process takes place.[97] Now the analog of the octahedral clusters 75 and 76 does not form, but rather, the semi-closed structure 79 does. Cluster 79 is in equilibrium with the more open isomer 80 with exchange rapid on the NMR timescale at 20 °C (Equation (13)), considerably faster than the exchange between 76 and 77. The steric requirements of the benzene ring are invoked to explain the more open nature of cluster 79 compared with 76.



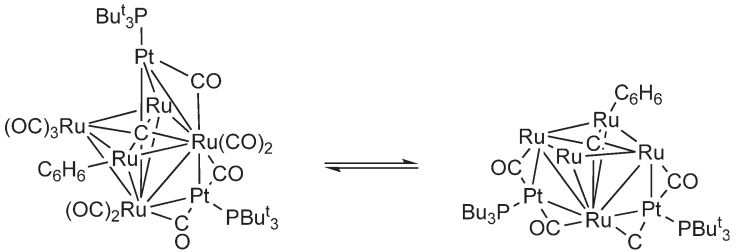
78



79 **80**

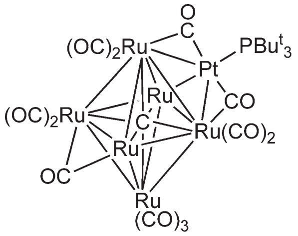
(13)

A further complex **81** is formed in low yield when an excess of the platinum reagent is used; on the NMR timescale both $Pt(PBu^t_3)$ groups are equivalent, with the suggestion that the formation of cluster **82** (terminal carbonyls on Ru omitted for clarity) allows the interchange (Equation (14)).



81 **82** (14)

Further work demonstrated that the addition of $M(PBu^t_3)$ ($M = Pd$, Pt) groups to iron, ruthenium, and rhodium clusters is quite general.[98–100] Thus, clusters of type **83–85** are readily synthesized; all exhibit some degree of fluxionality. An alternative reagent, $Pt(norbornene)_{3-n}(PPr^i_3)_n$ ($n = 1$, 2), has been used to introduce $Pt(PPr^i_3)_n$ fragments to saturated triruthenium clusters.[101]



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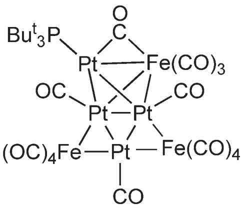

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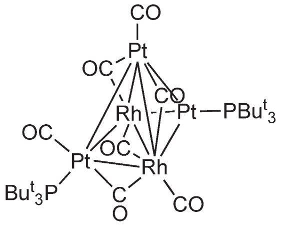
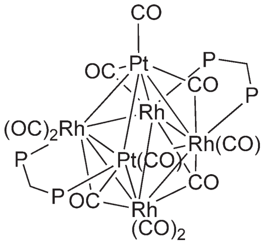
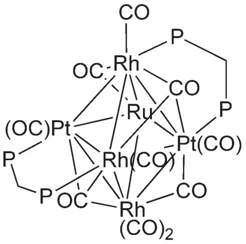


85

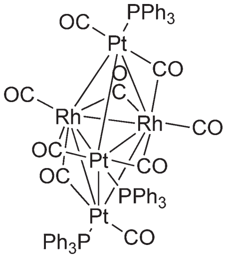
Octahedral clusters **86 and 87**, which do not contain a central carbide, but are bridged by dppm ligands, have been synthesized by the reaction of $Rh_2Pt_2(CO)_6(dppm)_2$ with $Rh_6(CO)_{14}(NCMe)_2$ and $Ru_3(CO)_{12}$, respectively.[102] X-ray structures of both **86 and 87** have been solved, and extensive NMR evidence suggests that the solid-state structures are maintained in solution. Two further mixed platinum rhodium clusters have also been reported: the reaction of $Rh_4(CO)_{12}$ with $Pt(PPh_3)_3$ gives trigonal-bipyramidal cluster **88** and tetranuclear cluster $Rh_2Pt_2(\mu\text{-}CO)_3(CO)_4(PPh_3)_3$.[103] Complex **88** has been characterised by X-ray diffraction, whereas the butterfly structure of the tetranuclear cluster (with the rhodiums occupying the hinge positions) is inferred from various multinuclear NMR techniques.



86



87



88

An octahedral Ru_4Pt cluster with one vertex occupied by a hydroxyphosphinidene has been reported; the appreciable acidity of this, and related clusters, gives rise to a new class of organometallic acids.[104] The reaction of the $Pt_2Ru_4(CO)_{18}$ cluster with 1,8-bis(phenylethynyl)naphthalene results in fragmentation and the low yield of $Ru_2Pt(CO)_6[\mu\text{-}\eta^2\text{-}C_{10}H_6C_4Ph_2]_2$, which has the platinum atom between the two ruthenium atoms.[105] A relativistic Density Functional Theory (DFT) study on the bimetallic $[Pt_3Fe_3(CO)_{15}]^{n-}$ ($n = 0, 1, 2$) clusters has been published, indicating that the HOMO has Pt–Pt antibonding character.[106] A neutral gold–platinum cluster, $Pt_7(\mu\text{-}CO)_8(PPh_3)_4(\mu_4\text{-}AuPPh_3)_2$, has been isolated and characterized; the previously unknown nine-atom metal architecture of the Au_2Pt_7 core may be thought of as a Pt_7 adduct of a Pt_4 butterfly by an edge-opened Pt_3 triangle that is additionally linked by two tetracapping $AuPPh_3$ units.[107] A new example of a carbonyl complex containing a Pt_2Ag_2 tetranuclear structure has been reported, but little data are given.[108]

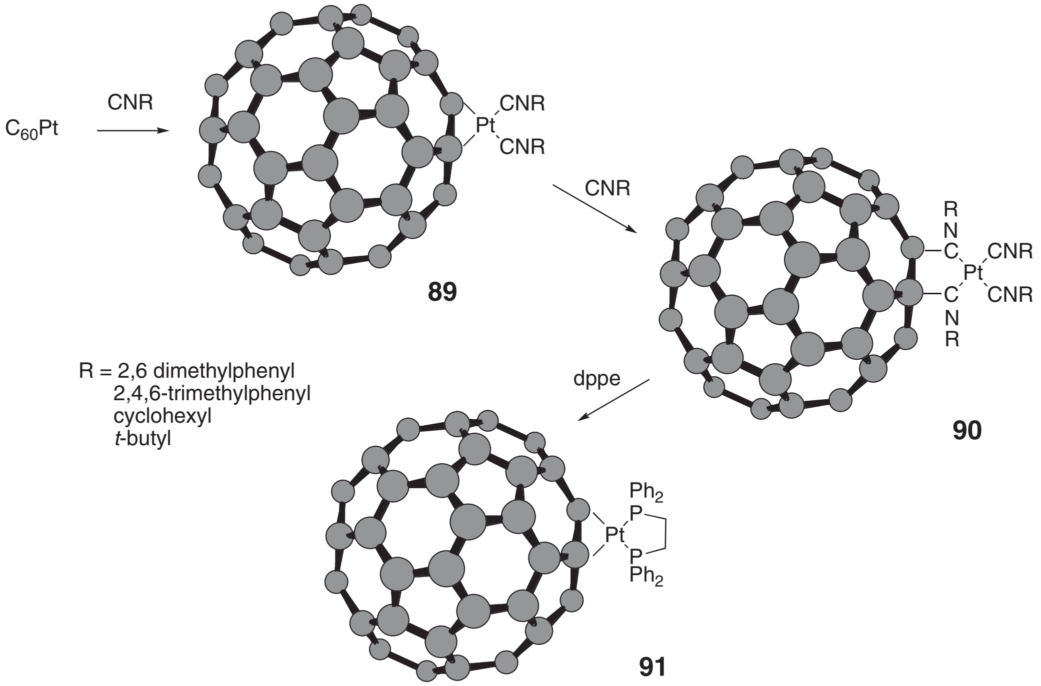
Four reports concern very high nuclearity nickel–platinum clusters. In the first, a tetrahedron of platinum atoms is encased in a distorted and incomplete ν_5 tetrahedron of nickel atoms to give $[Ni_{36}Pt_4(CO)_{45}]^{6-}$ and $[Ni_{37}Pt_4(CO)_{46}]^{6-}$.[109] The new clusters are degraded by carbon monoxide to give $[Ni_9Pt_3(CO)_{21}]^{4-}$ and oxidized by K_2PtCl_4 to give $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 5, 6$). A study of the redox chemistry of these new ions is the subject of the second report, which details the chemical and electrochemical reduction to the minus 7, 8, and 9 charged anions.[110] The third report deals with the reaction of $[Ni_6(CO)_{12}]^{2-}$ with 1.5–2 equiv. of K_2PtCl_4, which leads to formation of the $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ and $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ ($x \approx 2$) tetraanions; the latter cluster has a localized substitutional Ni/Pt disorder and an unprecedented close-packed metal structure.[111] The final report details the synthesis of $[H_{6-n}Ni_{24}Pt_{17}(CO)_{46}]^{n-}$ ($n = 5, 6$) and of the highest nuclearity homoleptic carbonyl cluster anion so far reported: $[Ni_{24}(Ni_8Pt_4)Pt_{20}(CO)_{56}]^{6-}$; both structures are based on a ccp metal lattice fragment.[112]

8.07.2 Platinum Isocyanide Complexes

A significant proportion of all the papers that refer to platinum isocyanide complexes do so in the context of the reactivity of the bound isocyanide, and its conversion into a carbene ligand. All such papers are discussed in Section 8.07.3 where the synthesis of carbene complexes is examined.

8.07.2.1 Mononuclear Pt(0) Isocyanides

Since the publication of COMC (1995), significant reports of new platinum(0) isocyanide complexes are restricted to fullerene derivatives, where direct reaction of (η^2-C_{60})Pt with 2 equiv. of isocyanide leads to (η^2-C_{60})Pt$(CNR)_2$, **89**.[113] Subsequent reaction with 2 further equivalents of isocyanide leads to (η^2-C_{60})Pt$(CNR)_4$, **90**, but only with less bulky isocyanides (i.e., not the *t*-butyl derivative) (Scheme 17). Both new species have 17 ^{13}C resonances for the fullerene, indicating a C_{2v} symmetric complex; the tetrakis(isocyanide) complex has IR bands at 2,217, 2,156, and 1,608 cm^{-1}, indicating both bridging and terminal isocyanides. Subsequent reaction of the tetrakis(isocyanide) complex with dppe yields the known complex (η^2-C-60)Pt(dppe), **91**.



Scheme 17

8.07.2.2 Polynuclear Pt(0) Isocyanides

New reports of polynuclear Pt(0) isocyanides are rare.

Direct reaction of equimolar amounts of $Pt(cod)_2$, PCy_3, and 2,6-dimethylphenylisocyanide (XylCN) gives the trinuclear $Pt_3(PCy_3)_3(CNXyl)_3$ cluster, **92**, in high yield, in contrast to previous attempts to prepare the complex via substitution of carbonyls by isocyanides (Scheme 18).[114] The isocyanides are severely bent at the nitrogen with CNC angles of around 140°, presumably the result of steric interactions with the bulky phosphine groups.

Variation of the ratio of phosphine to isocyanide in the reaction mixture allows all isomers of $Pt_3(PCy_3)_{3-x}(CNXyl)_{3+x}$ ($x = 0, 1, 2, 3$) to be isolated, and direct replacement of the phosphine by isocyanide is also possible. Other ligand exchanges may also be effected. The perisocyanide compound **93** is also obtained when certain pentaplatinum clusters are reacted with excess isocyanide (Scheme 19).

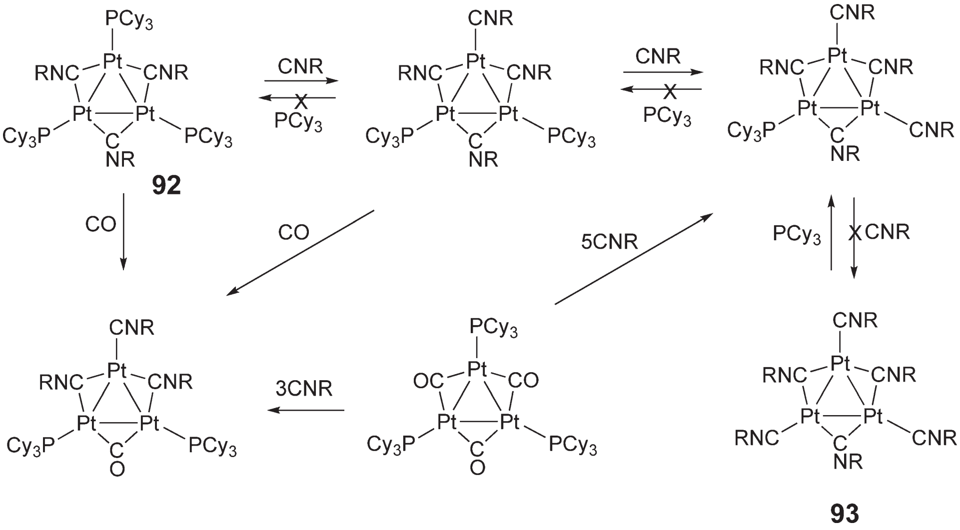
Pentaplatinum cluster **94** can prepared via the reduction of the Pt(II) compound $Pt(CNXyl)_2Cl_2$ with cobaltocene. Spectroscopic data, such as the presence of both terminal and bridging isocyanides, as indicated by IR bands at 2,119, 2,079, 1,652, and 1,585 cm^{-1}, and the three ^{195}Pt resonances observed (−3,445, −4,300, and −4,260 ppm) indicated a structure best described as a platinum tetrahedron with one edge bridged by a further platinum. This structure was confirmed by a single crystal X-ray structure.[115] Replacement of the three bridging isocyanide ligands in **94** by SO_2 proves to be facile, and this cluster will itself react to give other complexes, including the triplatinum perisocyanide complex **93** (Scheme 19). A hexaplatinum cluster can also be obtained from the reaction of two different pentaplatinum clusters, and is identified as having the edge-bridged pentagonal-bipyramidal structure **95**. This compound is only the second hexaplatinum cluster ever to have been reported.

8.07.2.3 Pt(I) Isocyanides

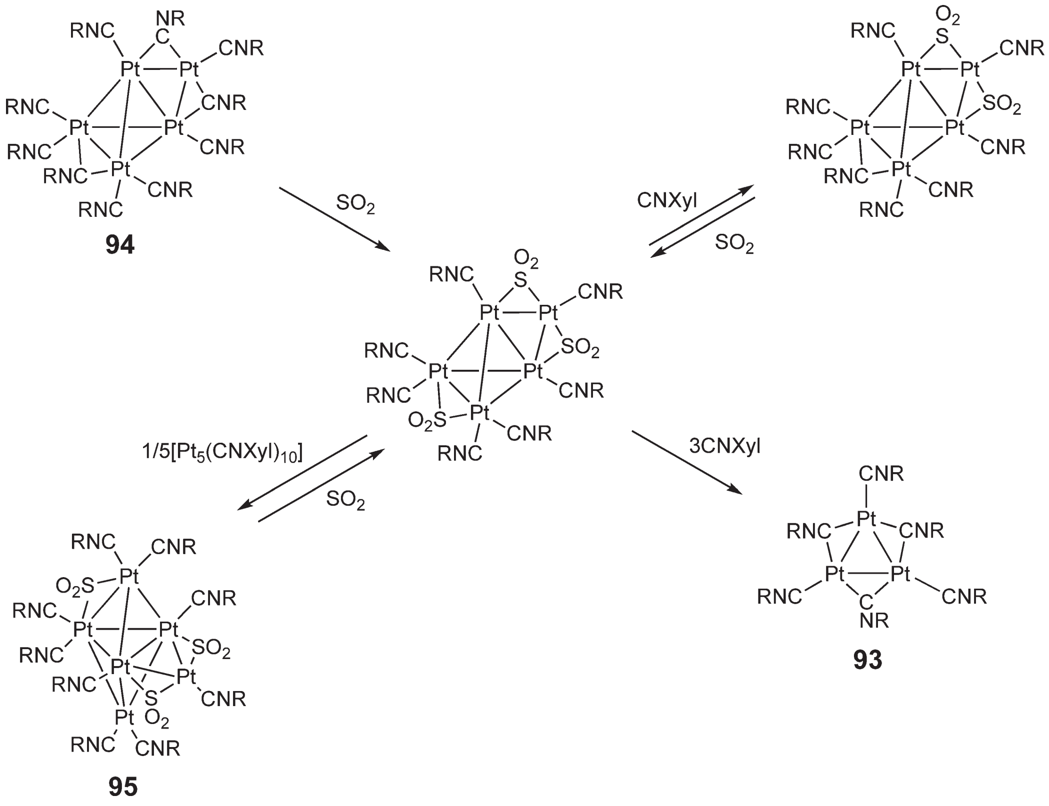
Isocyanides will displace both carbonyl and phosphine ligands in dinuclear phosphide complex **96** leading to mono- and bis(isocyanide) complexes **97** and **98** (Scheme 20).[116] Very low CN-stretching frequencies (1936 cm^{-1} for R = *p*-Tol) in **9** are attributed to the substantial π-basicity of the $Pt_2(\mu\text{-}PBu^t{}_2)_2$ core enhanced by the good σ-donor properties of the $PHBu^t{}_2$ ligand. In agreement with this picture of the bonding, the diisocyanide complex **98** (R = *p*-Tol) has CN-stretching modes at 2,063 and 2,033 cm^{-1}. Reversible insertion of the isocyanide into the Pt–P bond is possible, giving a carbene structure; this is discussed in more detail in Section 8.07.3.

Isocyanides have been used to displace other ligands in complex **99** to ultimately give zwitterionic complexes **100** (Scheme 21).[117] The initial complex **99** can be made by the reductive elimination of ethane from a platinum(II) species.

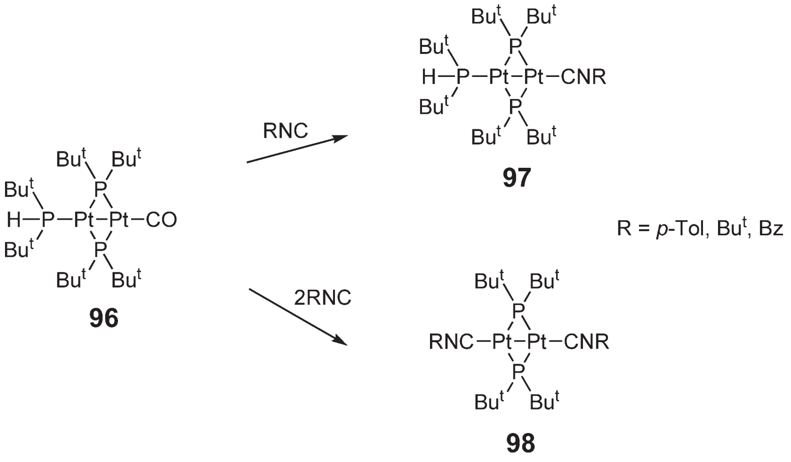
An extensive study on the electrochemical reduction of Pt(II) salts to give dinuclear Pt(I) isocyanides **101** has been carried out.[118] Single crystal and EXAFS studies of 12 such compounds show that the Pt–Pt bond falls in the narrow range 2.625–2.653 Å; NMR and IR data are also reported.



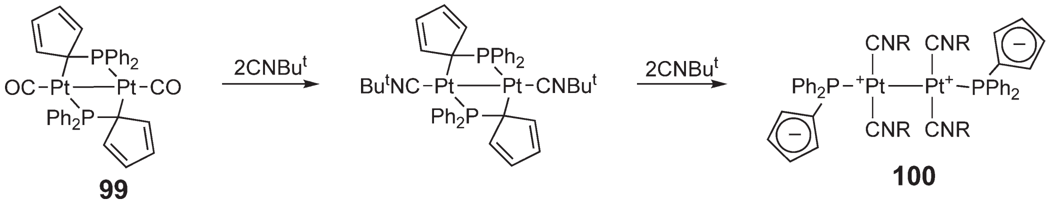
Scheme 18



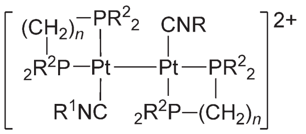
Scheme 19



Scheme 20



Scheme 21

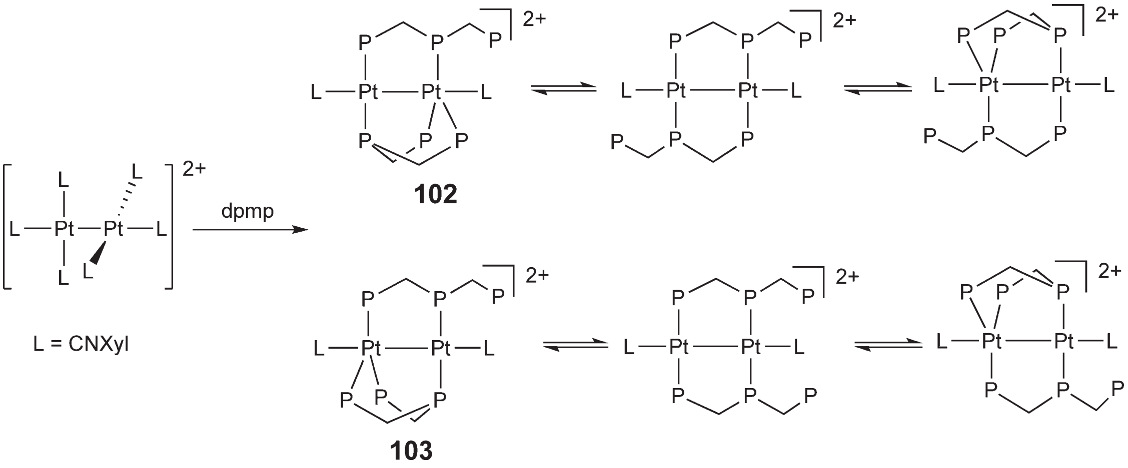


R^1 = Xyl, Mes
R^2 = Ph, Bu^t
n = 2, 3, 4

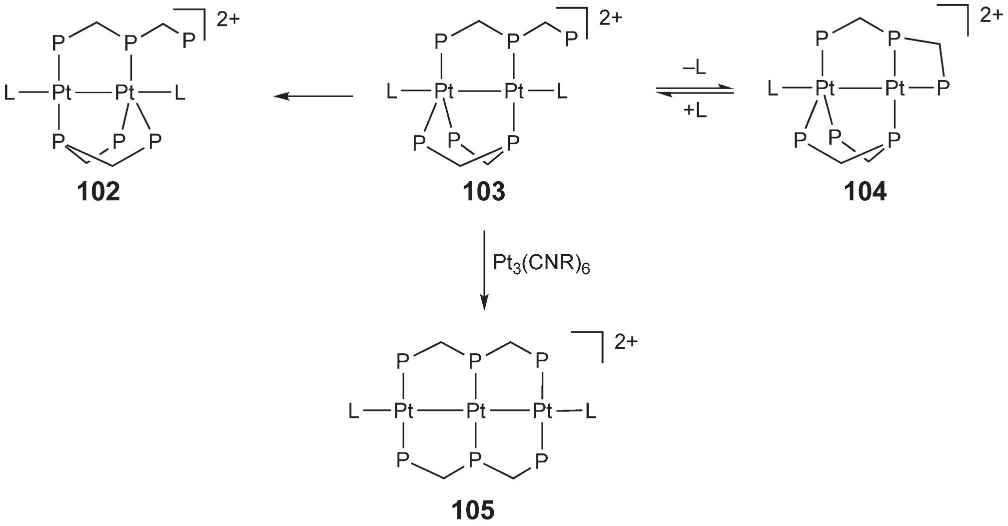
101

Reaction of the dinuclear Pt(I) isocyanide $[Pt_2(CNR)_6][PF_6]_2$, with the tridentate phosphine, bis(diphenylphosphinomethyl)phenylphosphine, dpmp, maintains the Pt–Pt bond and gives two compounds **102** and **103** in 30 and 50% yields, respectively (Scheme 22).[119] The mixed four- and five-coordinate geometry of the platinums is clearly present in the solid state, as evidenced from an X-ray structure. In solution, both compounds **102** and **103** are in dynamic exchange: only one ^1H signal for the isocyanides is observed at ambient temperature, and the ^{31}P resonances are broad. The crystal structure of **102** shows a Pt–Pt distance of 2.7094(8) Å, which is long in comparison with typical Pt(I)–Pt(I) bonds, prompting the speculation that it might be better to consider the five-coordinate platinum to be Pt(0) and the four-coordinate platinum Pt(II), with a dative bond between them.[120]

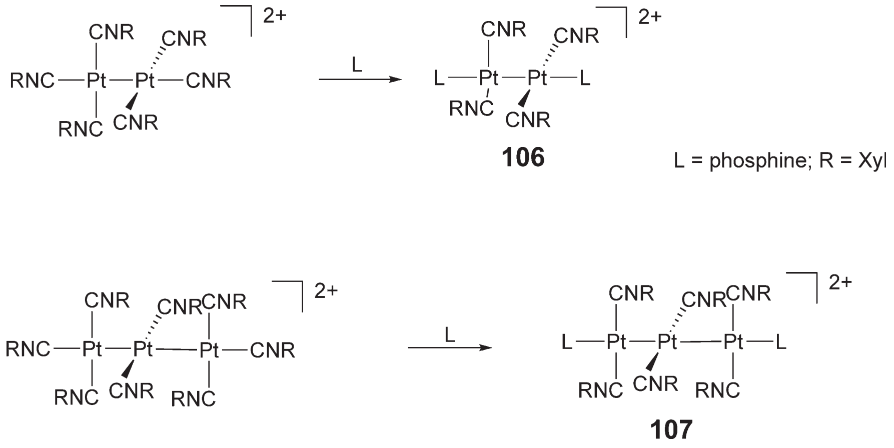
Thermal rearrangement of **103** in refluxing MeCN gives both **102** and a new compound **104** (Scheme 23). Reaction with $Pt_3(CNR)_6$ leads to a new triplatinum compound **105**, subsequent work with these triplatinum compounds[120] and heteronuclear analogs[121] is discussed in Section 8.07.2.7.



Scheme 22



Scheme 23



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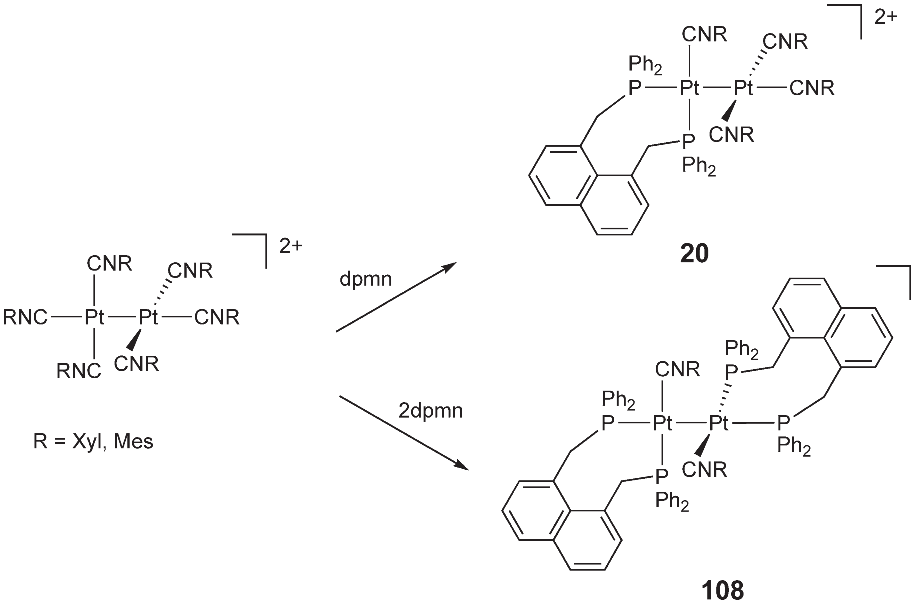
Scheme 24



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108

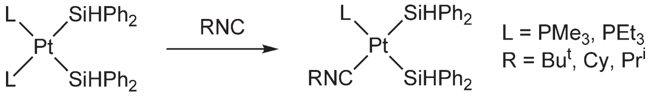
Scheme 25

Reactions of Pt(I) isocyanides with bulky phosphines such as tris(2,6-dimethoxyphenyl)phosphine result in replacement of some of the isocyanides, while maintaining the Pt–Pt bonds (Scheme 24).[122] Spectroscopic evidence suggests that, in solution, the coordination planes of adjacent platinums are perpendicular in both the dinuclear **106** and trinuclear **107** complexes.

Later work with bulky bridging phosphines includes an X-ray structure of **108** that shows the angle between the two platinum planes is 83(1)° in the solid state (Scheme 25).[123]

8.07.2.4 Mononuclear Pt(II) Isocyanides

New silyl platinum isocyanides **109** have been reported (Equation (15))[124] with crystal structures of the Bu^t and Pr^i derivatives confirming the *cis*-structure indicated by NMR spectroscopy. In solution, the NMR spectra of the complexes of the less bulky PMe_3 ligand indicate isomerism between the *cis*- and *trans*-isomers, with the more bulky PEt_3 derivative showing no tendency to isomerize.

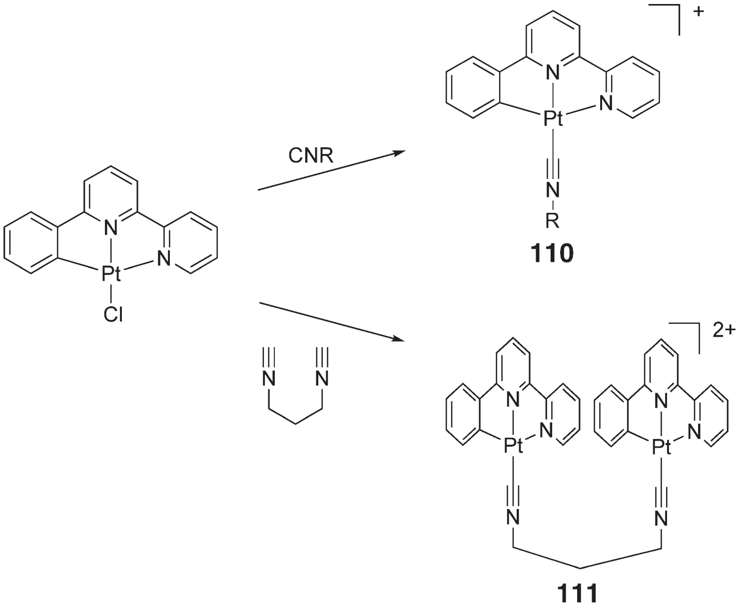


109 (15)

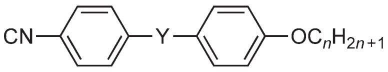
The photophysics of some luminescent platinum isocyanide complexes was studied in detail.[125] Such complexes are of interest as they are air- and moisture-stable, can be readily prepared by reacting a Pt(II) precursor with the appropriate organic ligand, and their photoluminescent properties can be systematically tuned. Crystal structures of two monoplatinum derivatives **110** (R = Bu^t, Xyl) were solved (Scheme 26); major differences between the two include the lack of any significant Pt–Pt interactions with the bulky Bu^t group, whereas the flat 2,6-dimethylphenyl group allows close approach of the platinums. Both structures exhibit π–π interactions between the phenylbipyridine units in the solid state. In solution, however, these complexes show very similar photophysical behavior. Attempts to force a Pt–Pt interaction in solution by using a bridging diisocyanide ligand to give complex **111** did not prove fruitful. The study of the electronic spectra of five monomeric platinum(II) complexes, all containing the same isocyanide-ligated platinum cation $[(C_4H_9N_4\text{-}C,C')Pt(CNMe)_2]^{2+}$, has been reported.[126] The counterion and solvent of crystallization were shown to be crucial in determining whether the solid-state structure contained short Pt–Pt interactions and whether these interactions caused the formation of dimeric or long-chain structures; the aqueous solution spectrum of one of the complexes at high concentration is consistent with dimer formation in solution.

One study reports on the use of a silica-supported platinum catalyst bound through an isocyanide link.[127] A tethered $PtCl_2(CNR)_2$ catalyst was used to study the hydrogenation of cyclohexanone under the mild conditions of 40 °C and 1 atm H_2. Activity was shown to be higher than that of the separate homogeneous complex; even after extended use, catalyst activity remained constant, with no evidence of catalyst leaching.

Isocyanides have also found their way into mesogenic (liquid crystalline) complexes of platinum(II). Rod-like isocyanides **112** that are themselves liquid crystalline continue to exhibit mesophases when coordinated in a *trans*-fashion to platinum, with the additional bonus of an increase in thermal stability.[128] Thus, whereas the uncomplexed isocyanides show smectic A and nematic phases in the range 60–90 °C (with decomposition evident even at these temperatures), the platinum complexes **113** show smectic C and nematic phases in the temperature range 125–275 °C with no decomposition. Both *cis*- and *trans*-geometries were investigated, but the *cis*-complexes exhibited no mesogenic behavior at all.

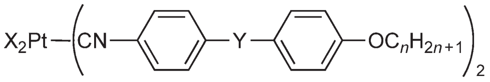


Scheme 26



Y = CO_2, O_2C, nothing

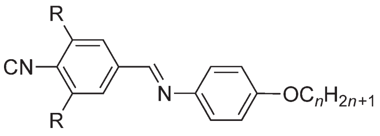
112



X = Cl, Br, I

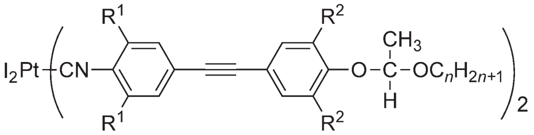
113

Other workers have used different isocyanides and investigated the mesomorphic behavior of the platinum complexes. Thus, non-mesogenic laterally substituted isocyanides **114** show smectic C and nematic phases at temperatures in the range 110–260 °C when coordinated in a *trans*-fashion to platinum diiodide, though only when the lateral group is methyl.[129] Subsequent work by the same group showed how cholesteric (N^*) phases could be induced in complexes **115** with the lateral substitution enhancing the mesogenic properties of the complex.[130]



R = Me, ^{i}Pr

114



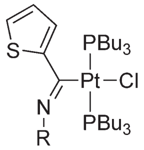
R^1, R^2 = Me, H

115

Columnar mesophases have also been exhibited by isocyanide complexes of Pt. Both *cis*- and *trans*-PtX_2L_2 complexes of $CNC_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$ show hexagonal phases.[131] Typically, the *cis*-dichloro and -dibromo complexes melt into the mesophase around 70 °C and clear into the isotropic at 250 °C. Typically the *trans*-diiodide complexes show a reduced mesogenic range of 30–60 °C. Alternating orientations of metal complexes, giving an extended metal–metal interaction, are invoked to explain the columnar phases in both *cis*- and *trans*-arrangements.

In addition to the papers referenced above, crystallographic studies of a number of platinum isocyanide complexes have been undertaken, with stacking arrangements present in some structures,[132,133] but absent in others.[134]

The coordination of an isocyanide, followed by the migration of an adjacent group to give rise to a coordinated imine, is exemplified by three different examples, giving rise to complexes **116** and [135] **117**[136] and the stanna-*closo*-dodecaborate complex **118**.[137] Platinum-substituted fulvenes can be prepared in a similar manner by attack of a coordinated isocyanide by the cyclopentadienyl anion.[138,139]



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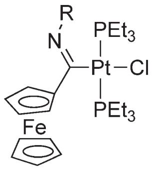

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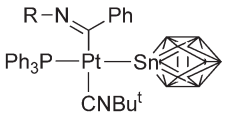
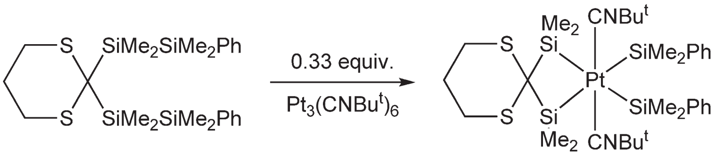


118

8.07.2.5 Pt(IV) Isocyanides

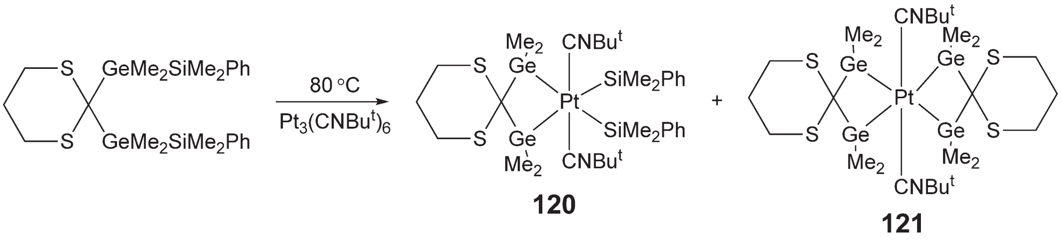
Stoichiometric reaction of the triplatinum(0) isocyanide cluster $Pt_3(CNBu^t)_6$ with a bis(disilanyl)dithiane at 80 °C gives the Pt(IV) complex **119** directly via the double oxidation of Si–Si bonds (Equation (16)).[140] A crystal structure confirmed the proposed formulation.



(16)

119

Reaction of the bis(silylgermyl)dithiane under similar conditions gave the analogous product of oxidative addition of two Si–Ge bonds, **120**, in 30% yield together with a tetrakis(organogermyl) complex **121** in 10% yield (Equation (17)).



(17)

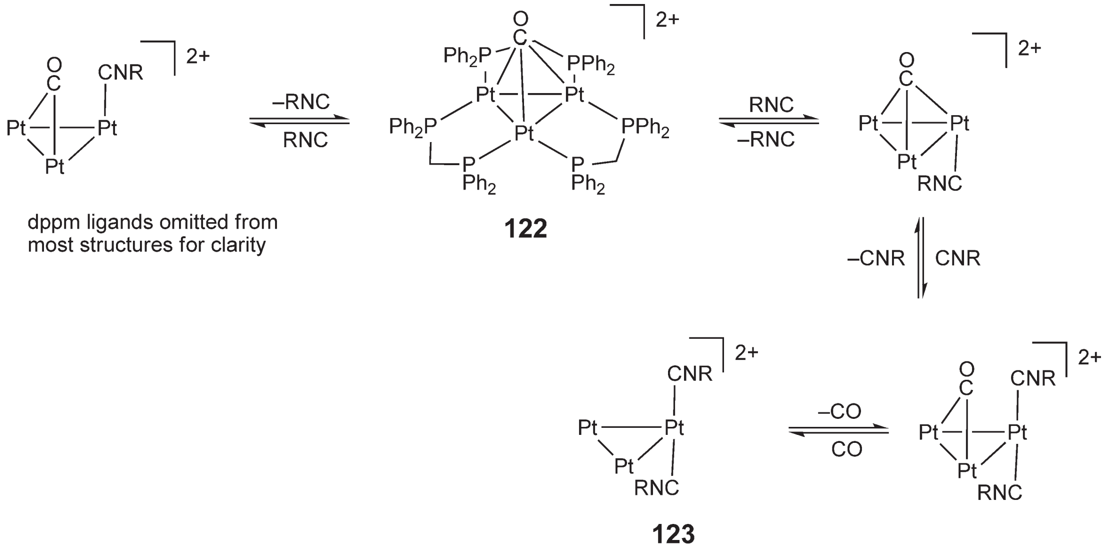
8.07.2.6 Polynuclear Pt Isocyanides

Work with the platinum triangle **122** pioneered by Puddephatt and co-workers has continued.[48] Isocyanide ligands have been used to displace carbonyl ligands, and complex **123** is the first Pt_3 cluster to have been isolated without a bridging atom (Scheme 27). Complex **123** is shown to be fluxional by ^{31}P NMR, which indicates a low barrier to isocyanide migration around the face. A crystal structure shows two longer Pt–Pt bonds at 2.649(1) Å with the unique Pt–Pt bond, significantly shorter at 2.548(1) Å. Linear bridging units have been used to link Pt_3 triangles.

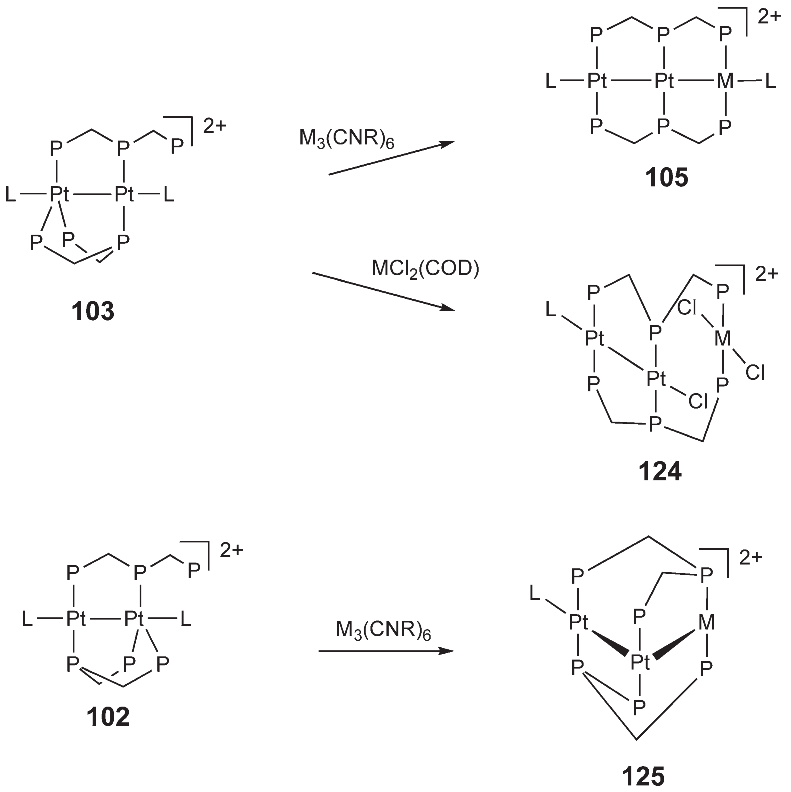
8.07.2.7 Heteronuclear Pt Isocyanides

An extension to work on platinum(I) isocyanides discussed above has been undertaken, showing that it is possible to coordinate metals other than platinum. In the first instance, platinum and palladium compounds were added to the dinuclear Pt(I) compound **103** to give either the linear trinuclear complex **105** (when a d^{10}-M(0) source was used), or a combined dimer–monomer complex **124** (when a d^8-M(II) source was added) (Scheme 28).[121] An A-frame complex **125** results when the d^{10}-source is added to **102**.

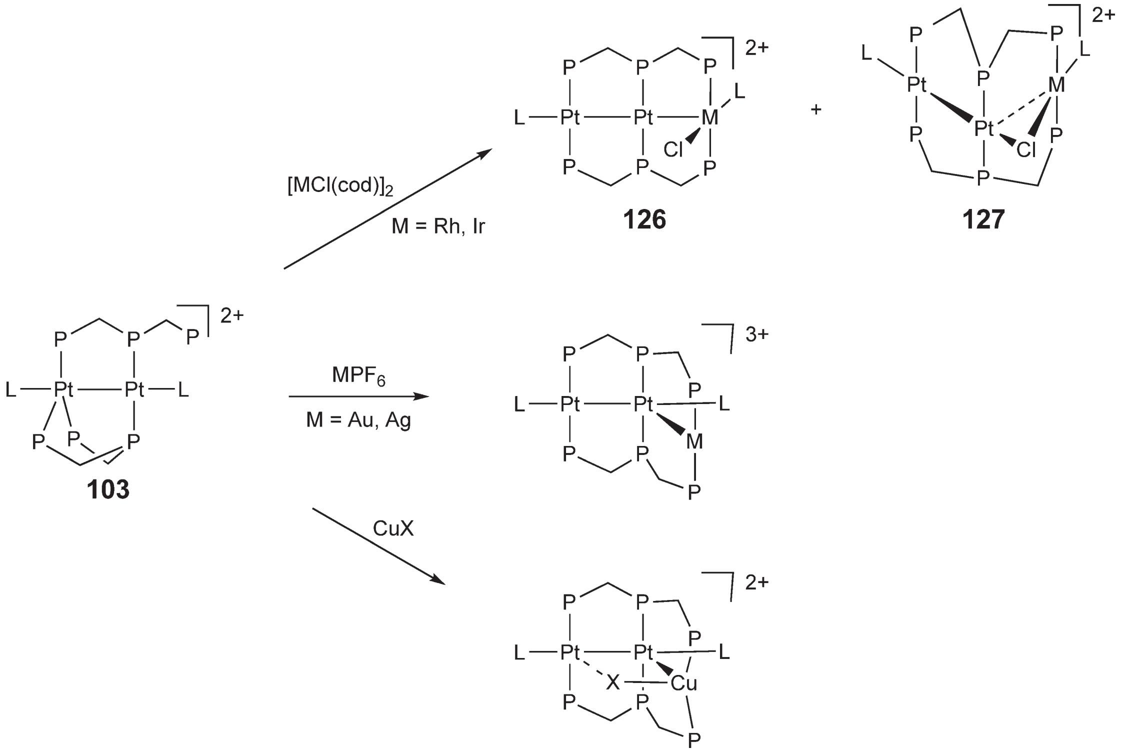
Reaction of **103** with other Rh and Ir d^8-sources gives analogous products **126** and **127** (Scheme 29). Yields were 58 and 32%, respectively, for the Rh complexes, and 36 and 34%, respectively, for Ir. No interconversion in solution between the two products was observed by NMR. In the linear complex **126** (M = Rh), the Pt–Pt–Rh angle is 177.13(1)° with Pt–Pt and Pt–Rh distances of 2.6588(3) Å and 2.7537(5) Å, respectively. In complex **127** (M = Rh), the significant distances are Pt–Pt 2.644(1), Pt–Rh 2.967(2), Pt–Cl 2.563(4), Rh–Cl 2.406(4) Å; the significant angles being



Scheme 27



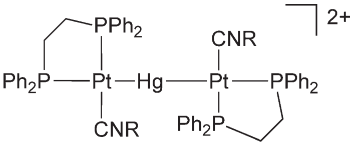
Scheme 28



Scheme 29

Pt–Pt–Rh 125.21(4), Pt–Pt–Cl 174.9(1)°. Copper, silver, and gold complexes are also formed, though no crystallographic data are available.[120]

A previously reported triplatinum cluster, which uniquely had a "naked" central platinum,[118] supported by only two Pt–Pt bonds has now be reformulated as containing a Pt–Hg–Pt core **128**.[141]

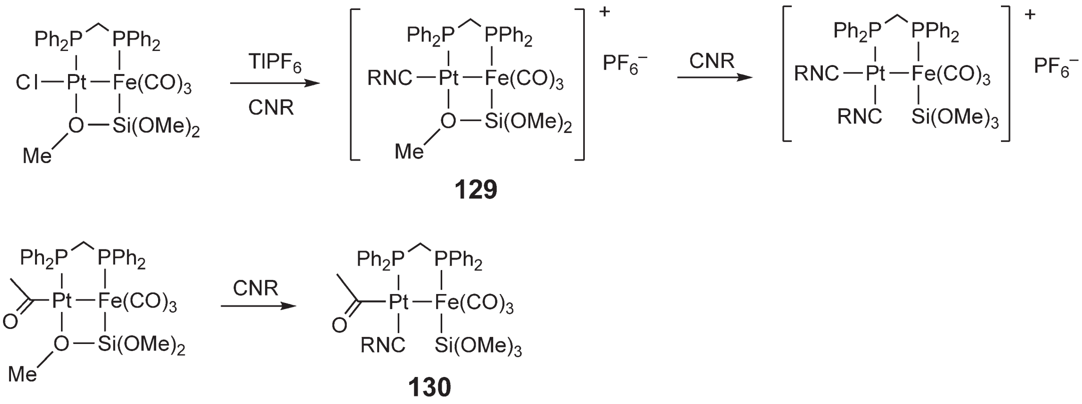


128

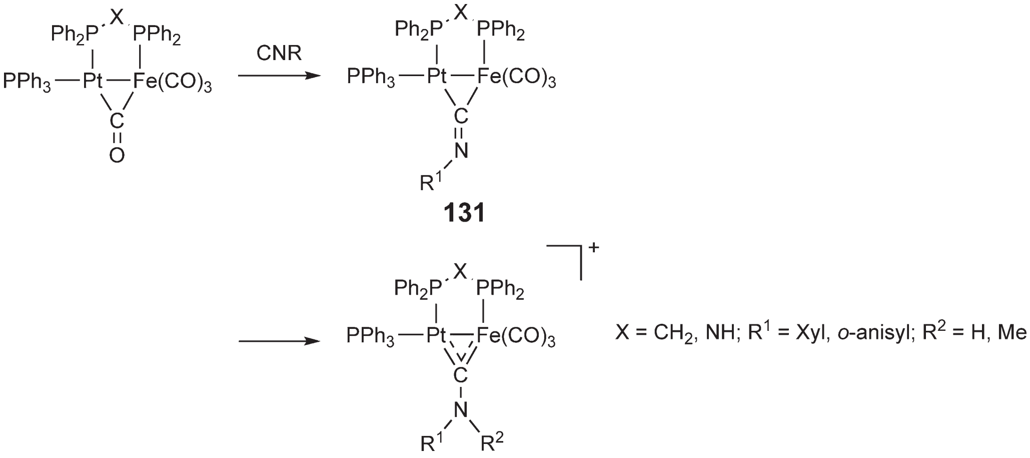
A number of iron–platinum bimetallic clusters with isocyanide ligands have been studied; those, such as **129**, bridged by a dppm ligand have proved to be versatile (Scheme 30).[142] Both charged, **129**, and uncharged, **130**, complexes are possible, depending on the reaction route taken;[68] Fe–Pt bond lengths are typically 2.80 Å.

Heteronuclear dimers **131** bridged by both dppm and other ligands, such as an amino-bridged diphosphine, can be stabilized by bridging isocyanides (Scheme 31), whereupon the Fe–Pt bond length shortens to around 2.53 Å.[66,143,144] In these complexes, the bridging isocyanide is prone to electrophilic attack, and is converted into a bridging carbene.

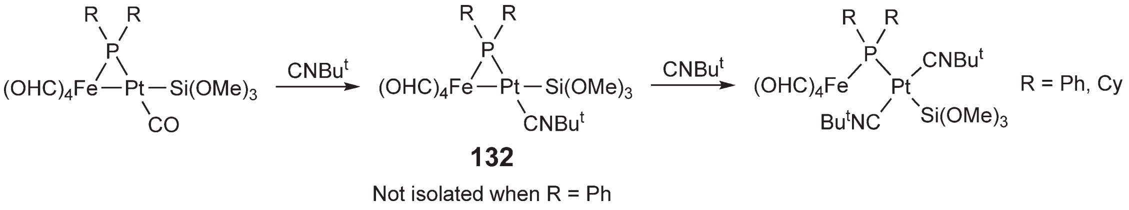
Bridging phosphido ligands are also used (Scheme 32), and here the 2.72 Å Fe–Pt bond present in **132** does not persist in the presence of excess isocyanide.[71]



Scheme 30

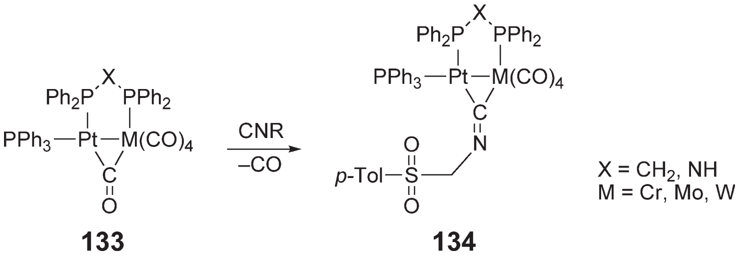


Scheme 31



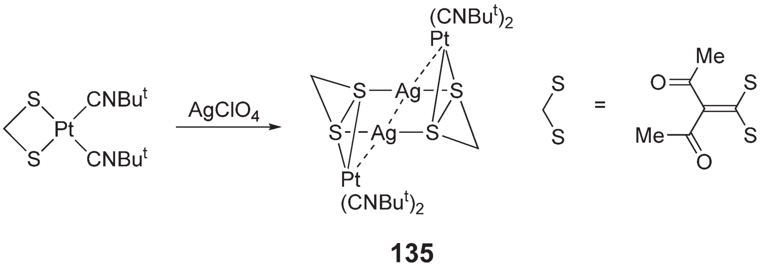
Scheme 32

Bridging carbonyls in **133** are replaced by isocyanides when the *p*-tosylmethyl derivative is used, giving **134** (Equation (18)). If stronger electron-donating isocyanides such as benzyl or 2,6-xylyl isocyanide are used, fragmentation into mononuclear complexes occurs, with no spectroscopic evidence of any compounds containing bridging isocyanide ligands. An X-ray structure of **134** (X = NH, M = W) has a Pt–W bond of 2.810(2) Å, indicative of a single Pt–W bond,[70] whereas one of the analogous dppm-bridged compounds **134** (X = CH_2, M = W) has a slightly shorter Pt–W bond of 2.7907(4) Å.[72] In both cases, the bridging isocyanide is not symmetrically bound, with the Pt–C bond distances at around 1.95 Å, significantly shorter than the Pt–W distances of around 2.28 Å. Protonation of the isocyanide nitrogen leads to aminocarbyne complexes.



(18)

A new example of a Pt_2Ag_2 tetranuclear structure **135** has been reported (Equation (19)), but few data are given.[108]



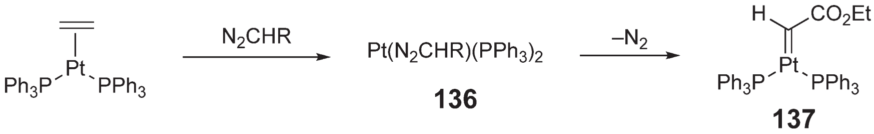
(19)

8.07.3 Platinum Carbene Complexes

The vast majority of platinum carbene complexes are stabilized by one or more adjacent heteroatoms, which allow π-delocalization. However, there have been a few reports of compounds where there is no such stabilization, and we consider these first, before moving on to look at those with heteroatoms.

8.07.3.1 Carbenes without Heteroatom Stabilization

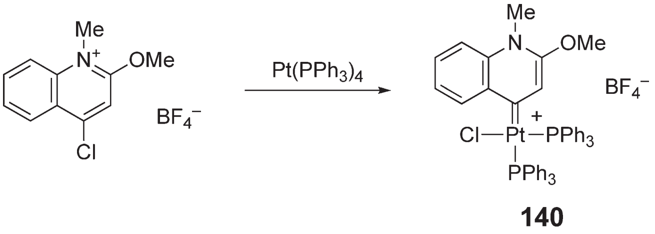
Highly reactive platinum carbene species have been generated in the gas phase via the fast atom bombardment ionization of ethyl diazoethanoate complex **136** (Scheme 33).[145] Elimination of dinitrogen leads to carbene species **137**, which are implicated in the reactivity of the precursor complexes, but had not previously been detected in solution.[146]



Scheme 33

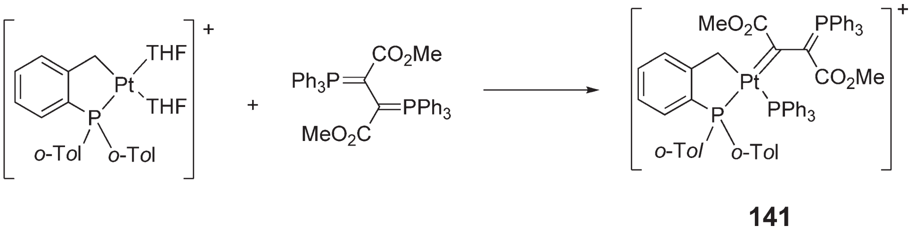
Carbene complex **138** has been isolated under considerably less extreme conditions.[147] The air and water stable complex **138** is isolated from the reaction of potassium tetrachloroplatinate with a free pyridine in ethanoic acid, even though a cyclometallated complex coordinated to the platinum through a nitrogen might have been anticipated. In principle, the carbene structure of **138** could be redrawn as the ionic structure **139** (Scheme 34); however, a short Pt–C distance of 1.952(7) Å in the X-ray structure and a solution ^{13}C chemical shift of 324 ppm for the carbon bonded to platinum confirms that carbene form **138** more accurately represents the molecular form present.

The oxidative addition of a chloroquinolinone to Pt(PPh$_3$)$_4$ yields carbene species **140** (Equation (20)).[148] Like **138**, a non-carbene form could be postulated, but once again a high solution ^{13}C chemical shift of 202 ppm for the carbon bonded to platinum confirms that the carbene form more accurately represents the molecular form present.



(20)

Another example of a non-heteroatom-stabilized carbene is complex **141**, which is derived from a bis-phosphine ylide.[149,150] The reaction can be thought of as the cleavage of a P═C bond generating a free carbene and a phosphine, thus suggesting that the ylide is a true carbene-transfer reagent (Equation (21)). The X-ray structure of **141** gives the Pt–carbene bond length as 2.047(5) and 2.056(5) Å; solution NMR gives a ^{13}C shift of 217 ppm for the carbene carbon.



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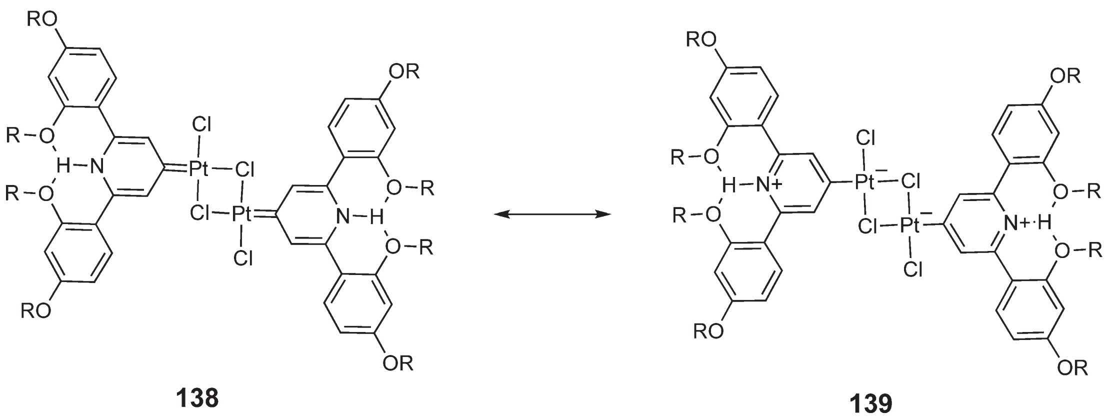
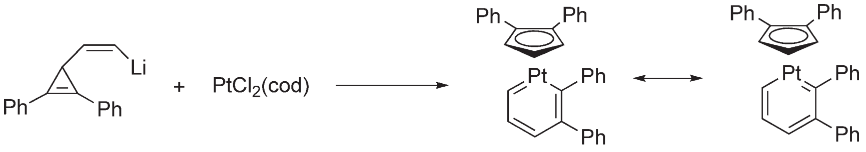


Scheme 34

If metallabenzenes are considered as having localized double bonds, they can be thought of as carbenes. Complex **142**, synthesized as indicated in Equation (22), shows two similar Pt–C distances of 1.959(3) and 1.929(4) Å, indicating a delocalized structure; ^{13}C chemical shifts of 195 and 204 ppm are reported for the carbons bonded to platinum.[151]



142

(22)

8.07.3.2 Synthesis of Heteroatom-stabilized Carbenes

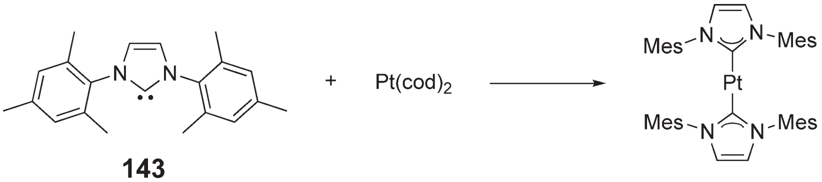
Heteroatom-stabilized carbenes, particularly those where the heteroatoms are part of a ring, have come to the fore since the publication of COMC (1995). Of particular interest are those stabilized by adjacent nitrogen atoms, the so called *N*-heterocyclic carbenes or NHCs. NHCs are now widely used in place of phosphines, and are regarded as being better σ-donors and poorer π-acceptors than the phosphine ligands they replace.

There are a large number of routes into the synthesis of heteroatom-stabilized carbene complexes, and we will consider them under three subsections: the synthesis of NHC complexes, the synthesis of carbenes by attack on a coordinated isocyanide, alkyne, or carbonyl, and other routes.

8.07.3.2.1 NHC complexes from free carbenes or imidazoles

The vast majority of *N*-heterocyclic carbenes contains the carbene in a five-membered ring with two adjacent nitrogen atoms. We consider platinum complexes containing these ligands first, and deal with the cases of those derived from a six-membered ring with one or two nitrogen atoms at the end of this section.

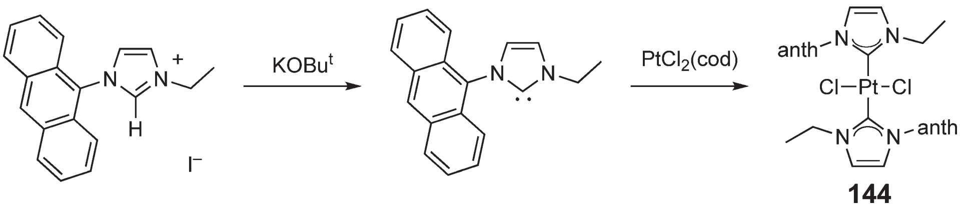
NHC complexes are normally synthesized directly from the free carbene or from the protonated form, the imidazolium salt. Conceptually, the simplest route to carbene complexes is that popularized by Arduengo: reaction of free carbene with a metal complex containing readily displaceable ligands.[152] However, this route is only appropriate when sterically bulky protecting groups are present on the nitrogen atoms, such as the mesityl groups in **143** (Equation (23)). Another simplistic route of little general use is the co-condensation of metal vapor with a free carbene.[153]



143

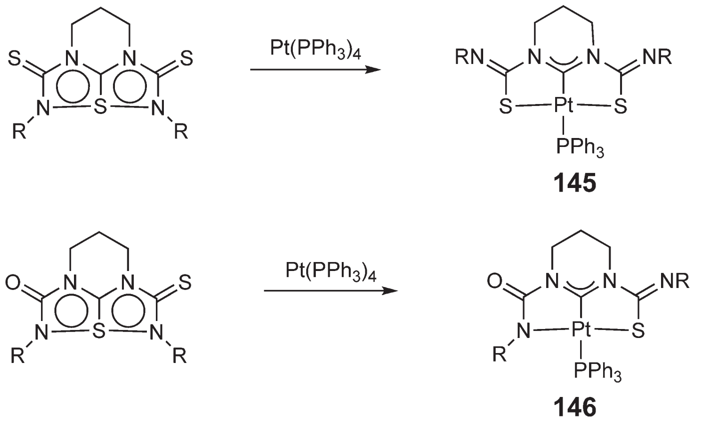
(23)

Reaction of the air and water stable imidazolium salt precursor to an NHC with strong base such as butyl lithium[154] or potassium *tert*-butoxide,[155] often at low temperatures, to generate a free carbene *in situ* is of considerably more use. This method allows the introduction of a wide variety of NHC ligands, as exemplified by the synthesis of **144** (Scheme 35).[155]



144

Scheme 35



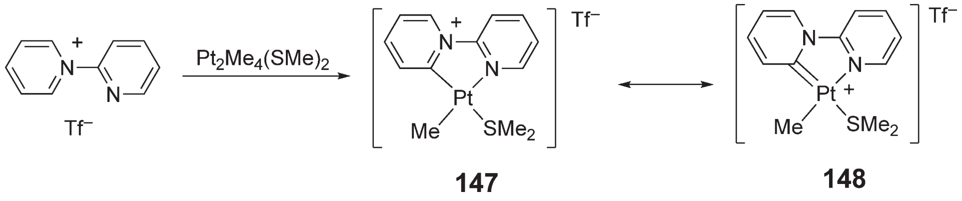
Scheme 36

Other workers have reacted imidazolium salts with metal complexes in the presence of the weak base sodium acetate in a one-pot reaction.[156,157] The advantage of this method is that expensive and air sensitive organometallic reagents are avoided, though higher temperatures may be necessary to drive the reaction to completion. The logical extension of this method, the reaction of imidazolium salt directly with the platinum salt via an oxidative addition reaction, has also been employed.[158–161]

Another common method of introducing NHC ligands has been to isolate silver carbene complexes first, and then react them with a platinum salt. Normally, silver oxide is reacted with an imidazolium salt, before the introduction of the platinum source at ambient or low temperature; insoluble silver byproducts are conveniently filtered off.[162] A conceptually similar approach is the prior formation of a tungsten or molybdenum pentacarbonyl carbene complex, and reaction of this with a platinum precursor. The room-temperature reaction with, for example, $PtCl_2(NCPh)_2$ results in the release of carbon monoxide and the precipitation of an undefined tungsten or molybdenum compound, which may easily be removed by filtration.[163]

An unusual system where the carbene carbon is part of a six-membered ring, but with two adjacent nitrogens, has been the subject of a short series of papers.[164–166] Reactions of hypervalent sulfur-containing precursors with a platinum(0) complex take place under mild conditions, yielding new complexes **145** and **146** (Scheme 36). Little detail is given, but it is believed the displaced sulfur ends up as $Ph_3P{=}S$.

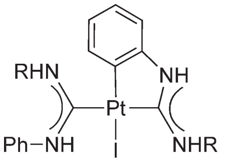
A family of unusual NHC complexes, where the carbene carbon is part of a six-membered ring, has been reported.[167] Cyclometallation of a pyridinium salt leads to complex **147**, which can be drawn as two resonance forms **147** and **148** (Equation (24)). A number of analogs have been synthesized, all showing a short Pt–C bond length (e.g., 1.959(3) Å in **147/148**) in the solid state. Solution ^{13}C chemical shifts of the carbon bonded to platinum are, at 160–174 ppm, significantly downfield from expected, but not as downfield as those in imidazolium-derived carbenes (175–220 ppm). The implication of these results is that both resonance forms contribute significantly to the structure, with the carbene showing significant π-acidity.



(24)

8.07.3.2.2 Heteroatom-stabilized carbene complexes from nucleophilic attack on isocyanides, alkynes, and carbonyls

The synthesis of heteroatom-stabilized carbene complexes via nucleophilic attack on coordinated isocyanides has long been used to introduce carbene moieties into metal complexes, and was discussed extensively in COMC (1982) and COMC (1995). Recent advances in the synthesis of *N*,*N*-stabilized carbenes from isocyanides include the formation of a carbene complex which spontaneously cyclometallates to give **149**,[168–170] the synthesis of unsymmetrical bis(carbene) complexes **150**,[171] and the one-pot synthesis of chelating bis(diaminocarbene) platinum complexes from K_2PtCl_4, excess isocyanide, and 1,2- or 1,3-diamines.[172] Other reports relate to the attack by ammonia[108] or hydrazine[173] on the isocyanide, and the promotion of this attack on the isocyanide by an adjacent pyridyl[174] or pyrazyl[175] ligand.



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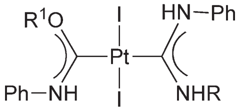
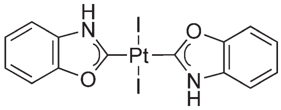


150

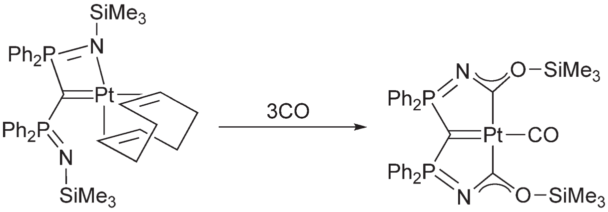
The synthesis of *N*,*O*-stabilized carbenes can be brought about via the attack of a methoxide[176] or an adjacent $OSiMe_3$ group[177] on an isocyanide; in the latter case elimination of the silicon group gives the five-membered heterocyclic carbene present in **151**. More exotic examples include the *N*,*P*-stabilized carbene synthesized by attack of a phosphide on an isocyanide,[116] and a cyclic N,As stabilized carbene synthesized from an isocyanide with a pendant arsonium group.[178]



151

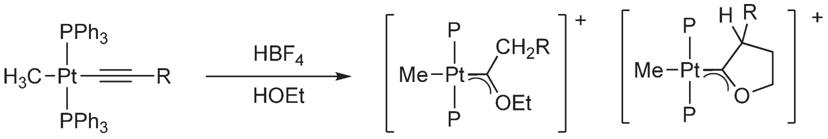
Attack of an η^1-alkynyl group by a nucleophile like ethoxide leads to an oxygen-stabilized carbene such as **152** (Scheme 37).[179,180] Use of oxirane, instead of ethanol, leads simply to cyclic carbenes like **153**.[181] It is not known for certain whether the reactions go either via protonation of the β-carbon followed by attack by the oxygen nucleophile on the α-carbon, or by nucleophilic attack by the β-carbon on the protonated oxygen. Reactions of this type, with carbene intermediates derived from alkynes, are utilized in the synthesis of a number of cyclic organic compounds.[182]

A couple of reports concern the attack on coordinated carbonyl ligands, leading to oxygen-stabilized carbenes. One paper reports the reaction of carbene complex **154**, formed by transmetallation of a lithium carbene with $PtCl_2(cod)$,[183,184] with carbon monoxide (Equation (25)).[2] It is believed that the carbon monoxide displaces the existing cod ligand, whereupon the coordinated CO is attacked by the adjacent nitrogens, with the siloxy group migrating to give the unusual tris-carbene carbonyl complex **155**, where all the donor atoms are carbon. Yields of the formally Pt(0) species are reported to be quantitative, and an X-ray structure has the three platinum–carbene bonds to be 2.002(5), 2.059(6), and 2.048(6) Å.



154 **155** (25)

The synthesis of a heterobimetallic bridging carbene complex **42**,[67] which was formed by attack on a ligated carbonyl was discussed in Section 8.07.1.6.1.

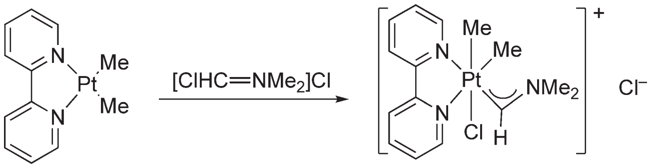


152 **153**

Scheme 37

8.07.3.2.3 Heteroatom-stabilized carbene complexes via other routes

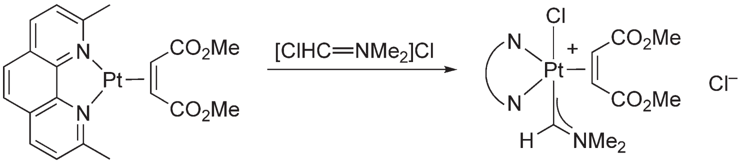
The oxidative addition of a chloroiminium (Vilsmeier) salt to a platinum(II) complex yields platinum(IV) carbene complexes **156** in high yield (Equation (26)); the X-ray structure shows the platinum to carbene carbon bond to be, at 1.991(21) Å, significantly shorter than the Pt–Me distance of 2.129(15) Å.[185]



156

(26)

In an analogous fashion, oxidative addition to a platinum(0) species gives platinum(II) species **157** (Equation (27)).[186] Complex **157** is a rare example of an 18-electron platinum(II) complex, and the platinum–carbene distance is reported as 2.006(6) Å.

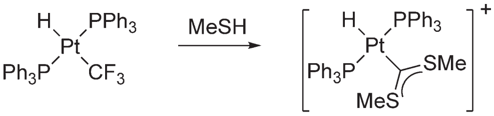


157

(27)

A further example of a nitrogen-stabilized carbene is the dimethyl aminocarbene complex **158**, which derives from a chloromethyl group (Scheme 38).[187] A second, slightly different carbene product, containing a hydrogen-bonded $HNMe_2$ group is obtained when L = Ph_3As.

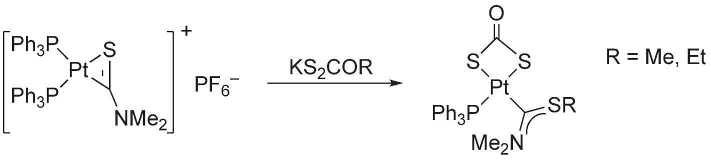
Dithiocarbene **159** is obtained when a trifluoromethyl group is reacted with a thiol (Equation (28)).[188] Yields are high and the solution ^{13}C resonance of the carbon bonded to platinum is reported as 306 ppm. On the NMR timescale, the two SMe groups adopt different orientations relative to the Pt–C bond, indicating that there must be significant π-bonding between the sulfurs and the carbene carbon. This work was expanded to include the synthesis of *S*-heterocylic carbenes with the use of ethane–1,2-dithiol in place of methane thiol.[189]



159

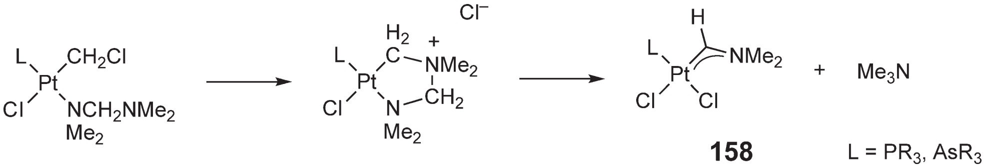
(28)

The migration of an alkyl group from a *O*-alkyldithiocarbonate to a thiocarbamoyl ligand results in the unusual *N*,*S*-stabilized carbenes **160** (Equation (29)).[190] Full characterization data on the platinum compounds **160** are not reported, but data, including an X-ray structure, are given for the palladium analog (R = Me).



160

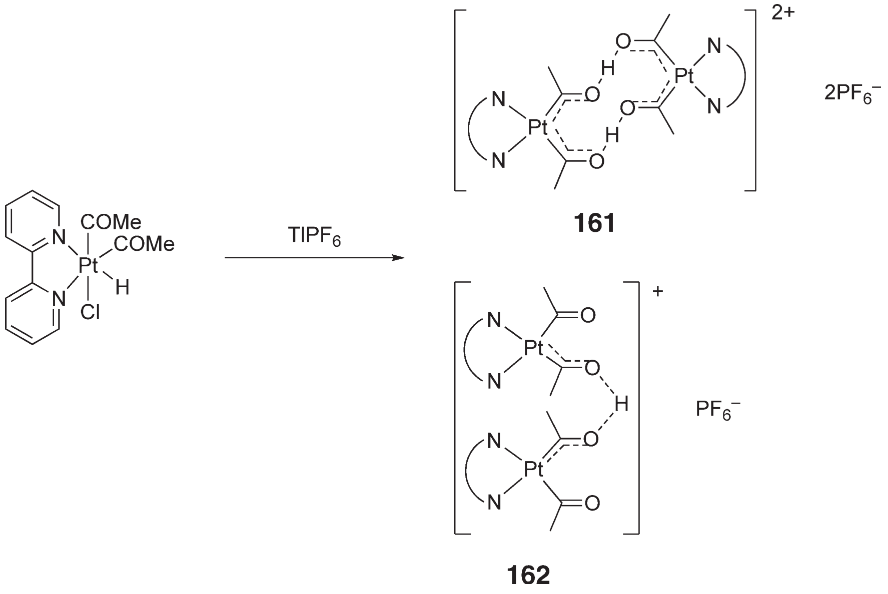
(29)



158

L = PR_3, AsR_3

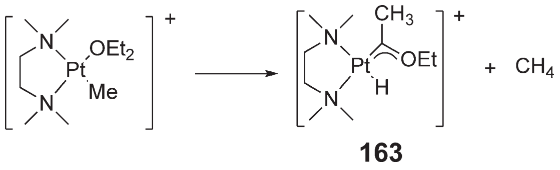
Scheme 38



Scheme 39

Hydroxy carbene complexes **161** and **162**, formed in the same reaction mixture by the abstraction of chloride from an acyl complex, are reported (Scheme 39).[191] X-ray structures of both complexes show crystallographically imposed symmetry, and hence bond lengths that are intermediate between the extremes of Pt–C and Pt═C (and C–O and C═O).

The reaction of electrophilic platinum cations developed to study the oxidative addition of alkanes to platinum center with diethyl ether has been shown to generate carbene complex **163** in high yield;[192] the product is thought to arise from the C–H activation of diethyl ether followed by an α-H elimination reaction (Equation (30)).



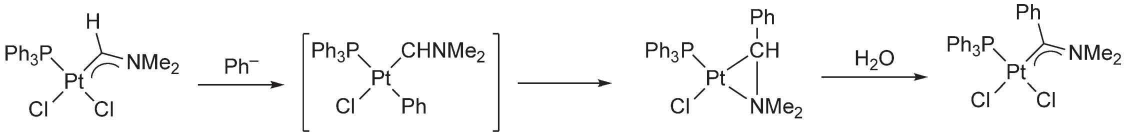
(30)

An oxygen-stabilized rhenium–platinum-bridging carbene has reportedly been synthesized from a mononuclear rhenium carbene.[193]

8.07.3.3 Properties and Reactivity of Platinum Carbene Complexes

One of the recurrent themes in the use of carbene complexes has the advantages that ligands such as the NHCs offer over the more conventional phosphine ligands. Thus, for example, platinum NHC complexes are reported to catalyze the hydrosilation reaction of alkenes with remarkable efficiency and selectivity, avoiding the formation of the platinum colloids that are encountered with other catalytic systems;[194] these catalyst systems are reported to tolerate a wide range of functional and protecting groups, and can be stored for prolonged periods of time.[195] In a similar fashion, the more electron-rich NHC complexes of platinum are more prone to oxidative addition of methyl iodide than their pyridine analogs.[162] The photophysics of some luminescent platinum isocyanide complexes was discussed in Section 8.07.2.4,[125] and the same group have made diaminocarbene analogs of their isocyanide complexes **110** and **111**. They find that, compared with the isocyanide complexes, the emissions from the carbene complexes are red-shifted, in line with expectation of the carbene being a lower-field ligand than the isocyanide.[196]

Strong nucleophiles such as methoxide or hydroxide are observed to attack carbene complex **157** with resulting elimination of the carbene as dimethylformamide and reduction of the platinum to Pt(0), suggesting the formation of an iminium derivative from the attack on the carbene carbon.[186] Carbene complex **164** is observed to react with

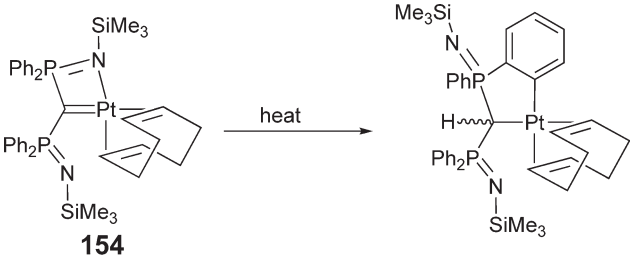


164 **165** **166**

Scheme 40

sources of Ph$^-$ to give **165**, presumably via the undetected intermediate shown (Scheme 40).[197] Complex **165** is stable in the absence of water, but will decompose even if a hint of moisture is present. Decomposition pathways are unclear, but a new carbene species **166** has clearly been identified as a minor product.

Prolonged heating of carbene complex **154** results in a rearrangement, presumably via an orthometallation step to give a platinum(IV) hydride species, in which the hydride migrates onto the carbene carbon to give complex **167** (Equation (31)).[183,184]



154 **167**

(31)

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8.08
Platinum–Carbon σ-Bonded Complexes

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8.08.1 Introduction

Complexes with Pt–C σ-bonds have a long history, and there have been a number of reports on their synthesis, structure, and physical and chemical properties. Advances in this area up to 1994 were reviewed in COMC (1982)[1] and COMC (1995).[2] High thermodynamic and kinetic stability of Pt–C σ-bonds enabled the preparation of a variety of complexes with alkyl, aryl, and alkynyl ligands. The isotopomers having a ^{195}Pt center have assisted characterization of mononuclear and multinuclear complexes by NMR spectroscopy. Before and after 1994, organoplatinum(II) complexes have been the most common among the complexes with Pt(I)–Pt(IV) centers. The number of alkyl- and arylplatinum(IV) complexes has increased significantly during this decade.

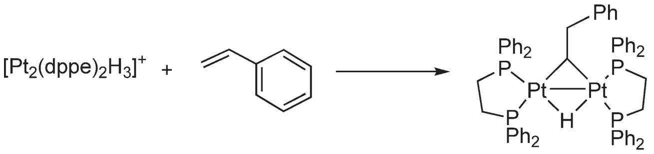
Various supporting ligands, such as dienes, dialkyl sulfides, diamines, bipyridine, and phosphines, stabilize organoplatinum complexes. Newer ligands which are employed for organometallic complexes of other late transition metals have also become important in the preparation of organoplatinum complexes. Planar N–C–N and P–C–P ligands bonded to a transition metal via an M–C σ-bond and two M–N (or M–P) bonds[3] are named as pincer ligands.[4–11] They occupy three coordination sites of square-planar Pt(II) centers or meridional (and occasionally facial) coordination sites of octahedral Pt(IV) centers. Related N–C–C and C–N–C type ligands also form stable complexes. 1,4-Diaza-1,3-butadiene functions as a chelating diimine ligand, similar to 2,2′-bipyridine. Nickel and palladium complexes of these ligands exhibit high catalytic activity for olefin polymerization and co-polymerization of ethylene and acrylic monomers.[12–14] Platinum complexes show higher stability and lower reactivity than the corresponding Ni and Pd complexes. Tris(pyrazolyl)borates,[15] which have played important roles in bioinorganic chemistry,[16,17] are used as the anionic ligands that occupy three facial coordination sites of an octahedral Pt(IV) center. They are able to behave as the bidentate ligand of pentacoordinated Pt(IV) and square-planar Pt(II) complexes.

A recent topic in this area is synthesis of macrocycles and dendrimers containing Pt centers; Pt–C σ-bonds are thermally stable both in the solid state and in solution, and bind the repeating units in these oligomeric molecules.

8.08.2 Pt(I) Complexes

Organoplatinum(I) complexes usually have dinuclear structures with a bond between the d^9-metal centers, similar to non-organometallic Pt(I) complexes. Reports of organoplatinum(I) complexes after 1995 are still limited. They are stabilized by bridging ligands such as dppm and PPh_2 in most cases.

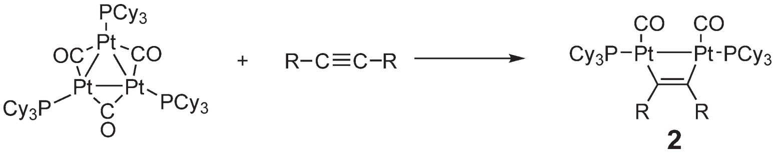
Dinuclear hydridoplatinum(II) complexes with chelating dppe and dppf ligands undergo insertion of styrene into the Pt–H bond to form dinuclear complexes with a bridging 2-phenylethylidene ligand (Equation (1)). A short Pt–Pt distance (273.14(3) pm) in **1** indicates a Pt–Pt bond, and the Pt–C bonds (206.5(7) and 207.6(8) pm) are not elongated significantly compared with those of the Pt–C bonds of mononuclear Pt(II) complexes with phosphine ligands, in spite of an acute Pt–C–Pt angle (82.5(3)°).[18,19]



1

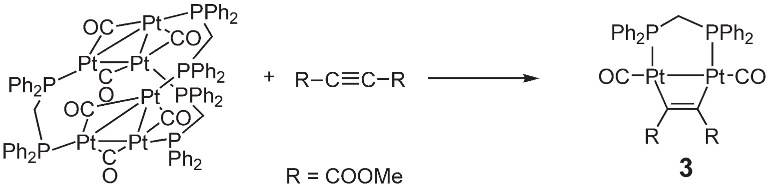
(1)

Reactions of alkynes with a triangular triplatinum(0) complex and with its lantern-type dimer yield dinuclear Pt(I) complexes with a dimetallavinylene ligand **2** and **3** (Equations (2) and (3)). Existence of a Pt(I)–Pt(I) bond is evidenced by X-ray and NMR data.[20] This structure is more reasonable than another possible one having two Pt(0) centers and a bridging alkyne ligand.



2

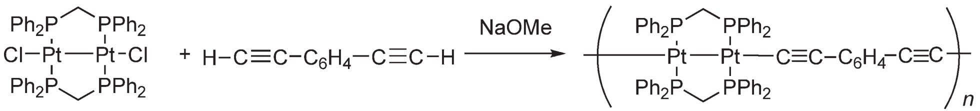
(2)



3

(3)

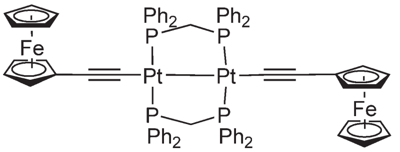
A dinuclear chloroplatinum(I) complex with dppm as ligand reacts with 1,4-diethynylbenzene to produce the alternating co-polymer of diplatinum(I)–dppm groups and π-conjugated organic groups **4** (Equation (4)). Addition of NaOMe to the reaction mixture leads to an insoluble dialkynylplatinum(I) complex having high molecular weights.[21]



4

(4)

A dinuclear Pt(I) complex with bridging dppm ligands and terminal ferrocenyl alkyne **5** shows two reversible redox processes due to mixed valence states of one-electron oxidized species.[22] The adduct of AuCl with the diplatinum complex, having a Pt–Pt–Au three-membered ring, shows a single redox process due to less effective electronic communication between the Pt centers. Conproportionation constants of the two ferrocene units of the complex have been compared with related diferrocene complexes already reported.



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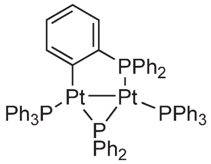

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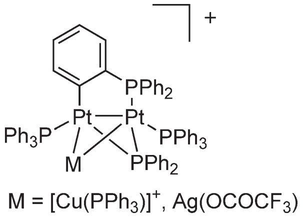
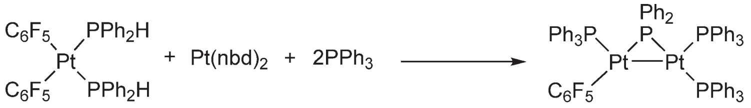


7

The thermal reaction of Pt(ethylene)$(PPh_3)_2$ produces a dinuclear Pt(I) complex having a bridging PPh_2 ligand and an orthometallated PPh_3 ligand **6** as one of the products;[23] Pt–C and Pt–P bonds are 209.4(8) and 267.7(5) pm, respectively. Oxidation by $HgCl_2$ converts the complex to a dinuclear Pt(II) complex. Complexes **7** are obtained by the reaction with Cu(I) and Ag(I) compounds.[24]

A bis(pentafluorophenyl)platinum(II)–PPh_2H complex reacts with a Pt(0) complex and PPh_3 to form the Pt(I) complex with a bridging PPh_2 ligand **8** (Equation (5));[25] Pt–C and Pt–Pt bonds are 209.8(8) and 278.53(7) pm, respectively.



8

(5)

8.08.3 Pt(II) Complexes

8.08.3.1 Alkylplatinum(II) Complexes

8.08.3.1.1 Neutral alkylplatinum(II) complexes – preparation and structure

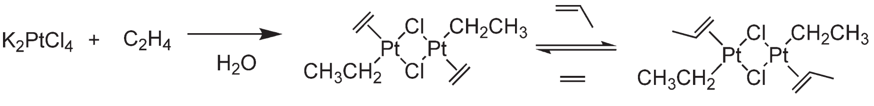
Alkylplatinum(II) complexes mostly have square-planar structures, although trigonal-bipyramidal and octahedral complexes are also known. Preparation reactions of the complexes fall into two categories. One involves Pt–C σ-bond-forming reactions, such as insertion of olefins into a Pt–H bond, oxidative addition of organic halides to Pt(0) complexes, and transmetallation of organomagnesium and lithium compounds with halogeno or pseudohalogeno platinum(II) complexes. In the last decade, there have been fewer numbers of papers on the formation of new Pt–C σ-bonds, affording alkylplatinum(II) complexes, than before.

Introduction of ethylene into an aqueous solution of K_2PtCl_4 affords the dinuclear Pt complex **9** (Scheme 1), whose metal centers are bonded to ethyl and ethylene ligands and are bridged by two chloro ligands.[26]

The mechanism proposed involves a hydridoplatinum intermediate, formed via a Wacker-type reaction, undergoing insertion of ethylene into the Pt–H bond. Ethylene ligands of the complex are easily replaced by propene to form the corresponding ethylplatinum(II)–propene complex.

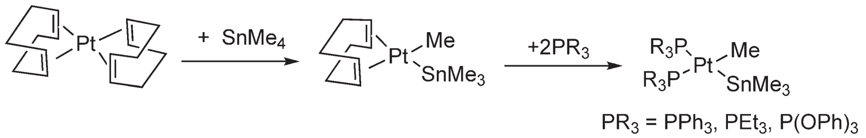
Oxidative addition of tetramethyltin to $Pt(cod)_2$ and exchange of the ligands produces methyl(trimethylstannyl)platinum(II) complexes with cod and phosphine ligands **10** and **11** (Scheme 2).[27]

The thermal reaction of a neopentyl(hydrido)platinum(II) complex with 1,2-bis(dicyclohexylphosphino)ethane in the presence of tris(neopentyl)gallium yields complex **12** (Equation (6)).[28] The starting complex undergoes reductive elimination of neopentane followed by oxidative addition of trialkygallium to the Pt(0) species, affording the complex having alkyl and trialkylgallyl ligands.



9

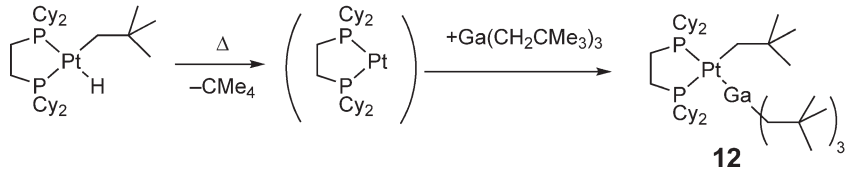
Scheme 1



$PR_3 = PPh_3, PEt_3, P(OPh)_3$

10 **11**

Scheme 2

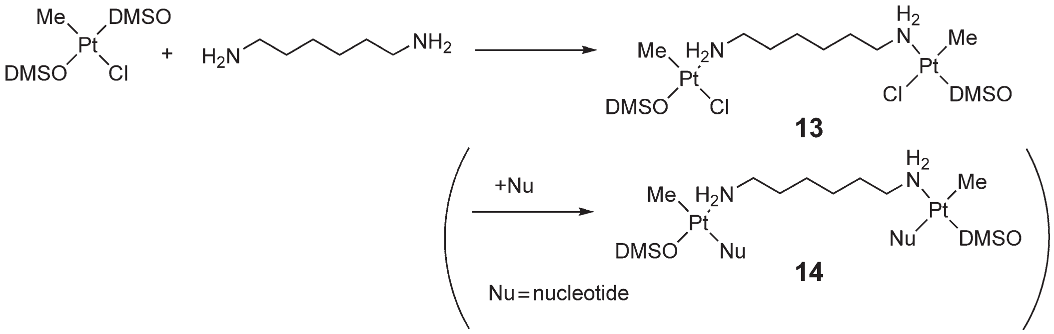


12

(6)

Details of the oxidative addition of C–H bonds to Pt(0) complex are discussed based on the results of a theoretical study.[29]

The other general preparation method for new alkylplatinum(II) complexes is exchange of the auxiliary ligands. Alkylplatinum(II) complexes with cod, SMe_2, and DMSO[30–32] bonded to the metal center exchange these ligands for stronger donors such as diimines and phosphines. Both dimethyl and chloro(methyl)platinum(II) complexes with such weak ligands are employed as common precursors of alkylplatinum(II) complexes with *N*- and *P*-ligands. Addition of alkylenediamine to $PtCl(Me)(DMSO)_2$ yields $[PtCl(Me)(DMSO)]_2\{H_2N(CH_2)_nNH_2\}$ with the bridging alkylenediamine **13** (Equation (7)).[33] Complex **13** reacts with nucleotides to produce complexes such as **14**.

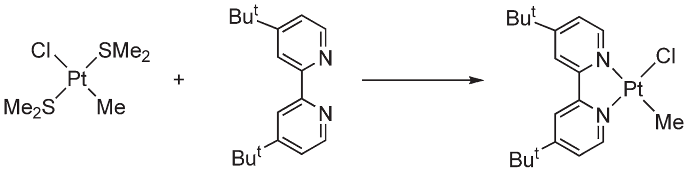


13

14

(7)

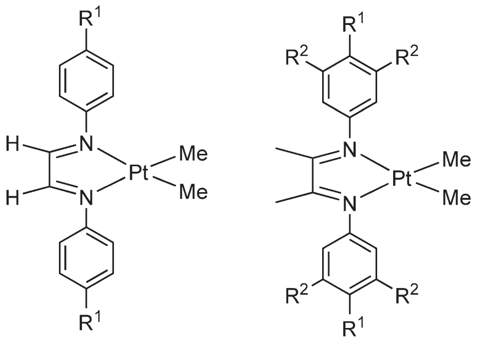
Reaction of 4,4′-$Bu^t{}_2$bipy with *trans*-$PtCl(Me)(SMe_2)_2$ forms the corresponding monomethylplatinum(II) complex **15** (Equation (8)),[34]similar to the preparation of $PtMe_2$(4,4′-$Bu^t{}_2$bipy)[35] and PtCl(Me)(6-Etbipy).[36]



15

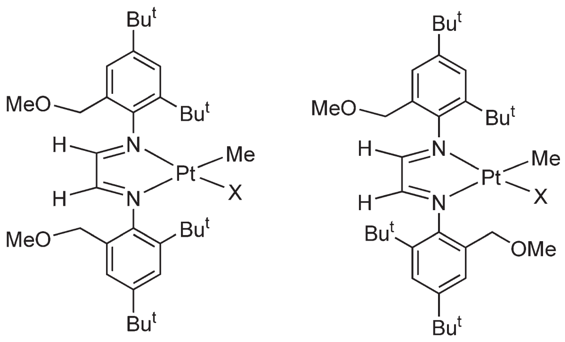
(8)

N,*N*-diaryl–1,4-diaza–1,3-butadienes also form stable dimethyl– and chloro(methyl)–platinum complexes **16** and **17**. Addition of the ligand to $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and $PtMe_2$(cod) yields the dimethylplatinum(II) complexes having chelating diimines.[37–40]



R^1 = Me, OMe; R^2 = CF_3

16

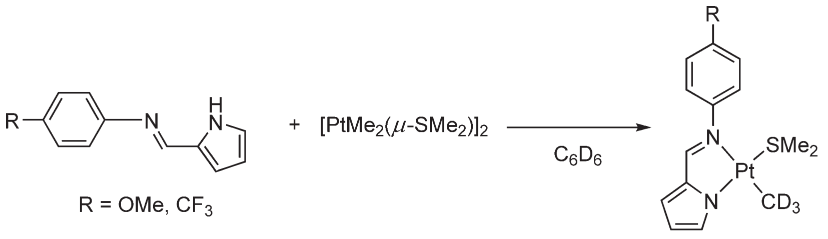


X = Me, Cl

17

Since 2,4-di-*tert*-butyl–(2′-methoxymethyl)phenyl groups at the coordinating nitrogen of the ligand are perpendicular to the coordination plane, dimethyl complexes **17** exist as *syn*- or *anti*-isomers regarding orientation of the substituents of the phenyl groups. Each of the isomers has been isolated and fully characterized, although they are equilibrated by rotation of the C–N bonds in solution above 70 °C. Refluxing the dimethylplatinum complexes in $CHCl_3$ leads to the chloro(methyl)platinum(II) complex with the diimine ligand. The *syn*- and *anti*-isomers of the chloro(methyl)platinum complex undergo mutual exchange more easily than the corresponding dimethylplatinum complex.

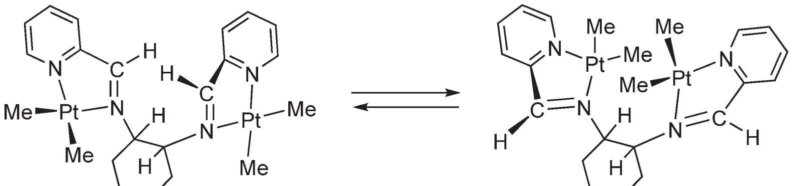
Reaction of 2-iminopyrroles with $[PtMe_2(\mu\text{-}SMe_2)]_2$ in benzene-d_6 causes elimination of methane and formation of a monomethylplatinum complex with the anionic bidentate ligand **18** (Equation (9)).[41] Incorporation of deuterium of the solvent into the methyl group takes place, suggesting scrambling of hydrogen between the methyl ligand and the solvent.



18

(9)

The racemic diimine prepared from 2-picolyl aldehyde and 1,2-*trans*-cyclohexanediamine forms a dinuclear complex with four methyl ligands **19** on reaction with $[PtMe_2(\mu\text{-}SMe_2)]_2$.[42] An NMR study shows conversion between the two isomers, *anti*,*anti* and *syn*,*syn*, in solution, caused by rotation of the C–N single bonds (Equation (10)).

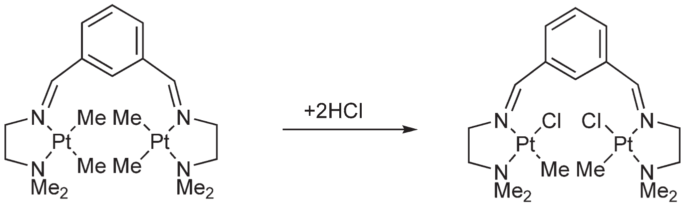


19

anti,*anti* *syn*,*syn*

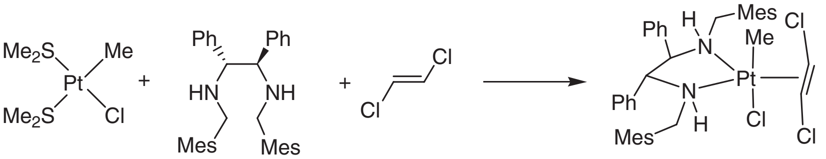
(10)

Dinuclear tetramethyldiplatinum complexes, for example, **20**, are formed by using 1,3- and 1,4-bis(*N*-dimethylaminoethyl)iminobenzene as the ligand. Addition of HCl to the complex with the 1,3-ligand produces the dinuclear complex with two chloro(methyl)platinum(II) centers (**21**, Equation (11)).[43]



20 **21** (11)

Pentacoordinate methylplatinum(II) complexes are obtained by using chelating diamine and diimine ligands. Addition of ethylene or alkenes with electron-withdrawing groups to a mixture of $PtCl(Me)(SMe_2)_2$ and an optically active 1,2-diamine produces complexes with Me and Cl ligands at the apical positions of a trigonal-bipyramidal Pt(II) center 22 (Equation (12)).[44] Extrusion of the olefin ligand forming a square-planar complex does not take place at all. The complex with (*E*)-1,2-dichloroethylene shows stereoselection in coordination of the prochiral olefin.

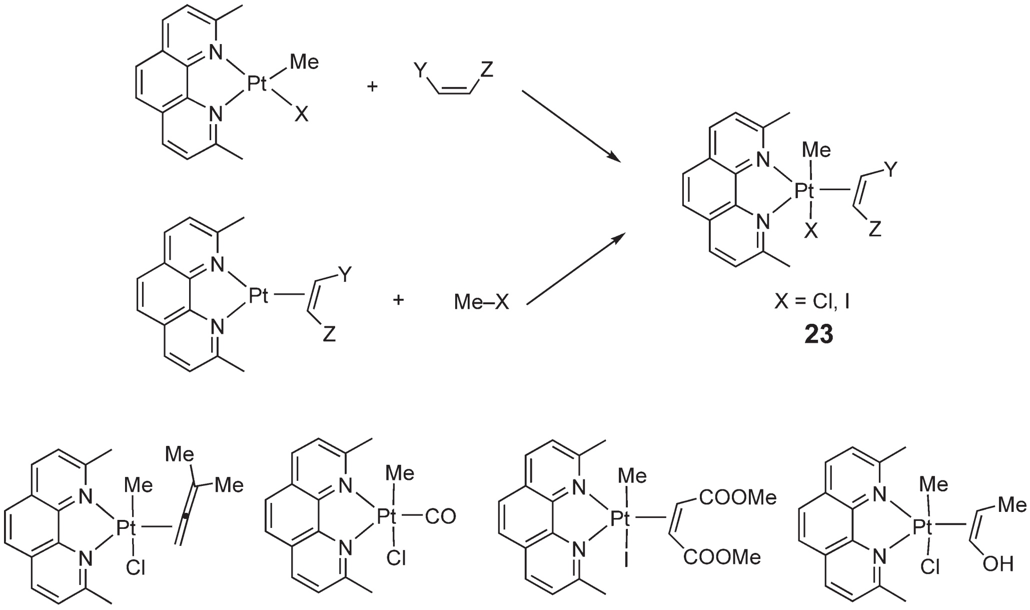


22 (12)

A series of chloro(methyl)platinum complexes having 2,9-dimethyl–1,10- phenanthroline are obtained as the adducts of alkenes, allene, and CO (23–27, Scheme 3).[45–50] Not only does coordination of the unsaturated molecule to the square-planar choro(methyl)platinum(II) complexes occur, but also oxidative addition of alkyl halide to Pt(0) complexes with the olefin ligand to give pentacoordinate complexes.

Polymers having pentacoordinated alkylplatinum complexes as the pendants have been prepared.[51]

Alkylplatinum(II) complexes with chelating *P,N*-ligands, for example, 28, are also obtained by the substitution of diene and SMe_2 ligands (Scheme 4).[52] The Pt–C bond *trans* to the PPh_2 group (206.9(8) pm) of 28 is shorter than that *trans* to the NMe_2 group (221.0(7) pm). The complex reacts with dibutyltin dihydride to form the methylplatinum complex with a dibutylstannyl ligand 29.[53,54]

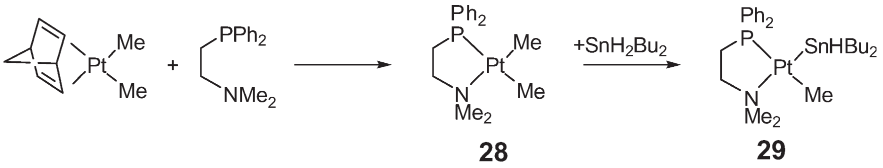


X = Cl, I

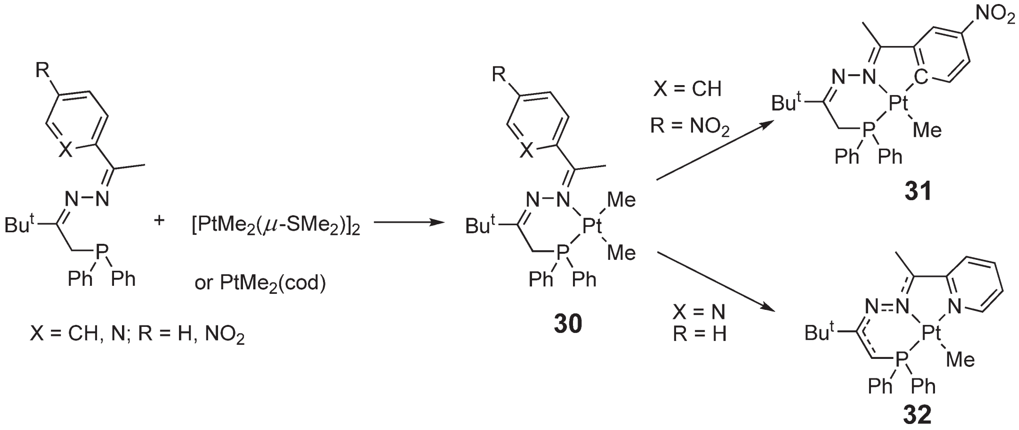
23

24 **25** **26** **27**

Scheme 3



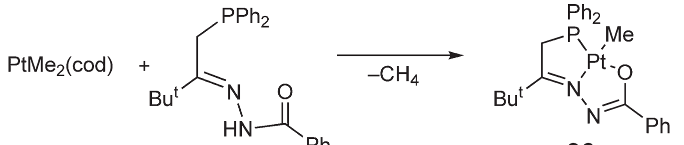
Scheme 4



Scheme 5

Arylated 2,3-diaza-1,3-butadiene derivatives, having a Ph_2P-containing substituent, function as a bidentate *P,N*-ligand and also as a tridentate ligand in methylplatinum complexes. Reaction with $[PtMe_2(\mu\text{-}SMe_2)]_2$ produces the dimethylplatinum complex with the bidentate ligand **30** initially (Scheme 5). The complex undergoes activation of a C–H bond of the aromatic ring to give the complex with a *C,N,P*-tridentate ligand **31** (X = CH), or coordination of the pyridyl group accompanied by abstraction of a hydrogen of the ligand to yield a monomethylplatinum complex with a π-conjugated *N,N,P*-tridentate ligand **32** (X = N).[55,56]

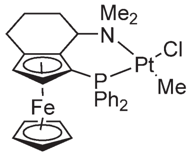
A monomethylplatinum complex with an *O,N,P*-tridentate ligand **33** is also obtained from the reaction of $PtMe_2$(cod) with a compound having imine, amide, and phosphine groups in the molecule (Equation (13)).[57]



33

(13)

Ferrocene-containing *N,P*- and *P,S*-chelating ligands are employed for preparation of chloro(methyl)platinum complexes **34** and **35**.[58,59]



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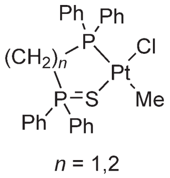

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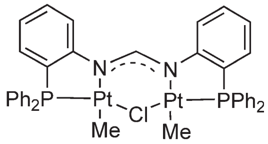
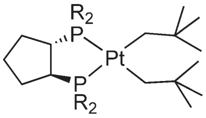
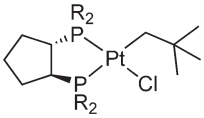


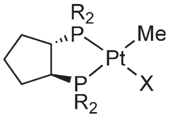
36

A dinuclear complex is formed by using a *P,N,N,P*-ligand composed of an amidinate group and two 2-(diphenylphosphino)phenyl substituents at the nitrogen atoms **36**. The metal centers are bridged both by the amidinate and the chloro ligands.[60,61]

Alkylplatinum(II) complexes with auxiliary phosphine ligands have been often reported. Complexes with optically active diphosphines with a five-membered ring backbone **37–39** are prepared by the reaction of the phosphine ligand with alkylplatinum precursors.[62,63]



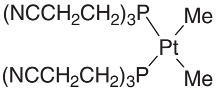




R = OMe, OPh, O–menthyl, etc; X = Cl, Tf

37 **38** **39**

A dimethylplatinum complex with tris(2-cyanoethyl)phosphine has been prepared and fully characterized **40**.[64] Dimethylplatinum(II) complexes with chelating aminophosphine ligands **41–43** are obtained from the reaction of the ligands with $PtMe_2(cod)$.[65–67] A bulky phosphirane ligand also forms a dimethylplatinum(II) complex **44**. Rotation of the P–Pt bonds is restricted by steric hindrance of the ligands, whose energy barrier has been estimated by theoretical calculations.[68] Tri(1-cycloheptatrienyl)phosphine forms a dimethylplatinum complex with the ligand bonded via the P atom and C═C double bond **45**.[69]



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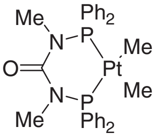

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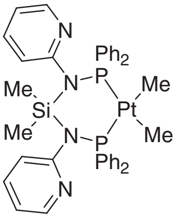

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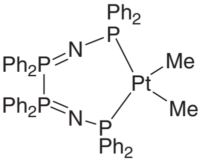

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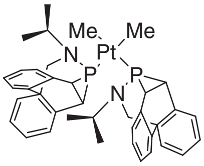

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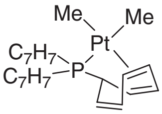
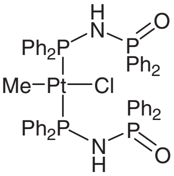


45

Complexes with chloro and methyl ligands **46–49** are prepared by using monodentate and bidentate phosphine ligands.[70–73] Dianionic stanna-*closo*-dodecaborate, $Sn(B_{11}H_{11})$, forms the methyl complex **50**.[74]



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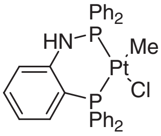

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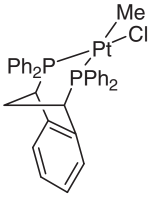

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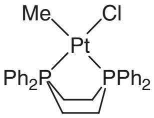

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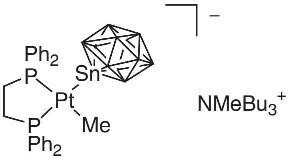
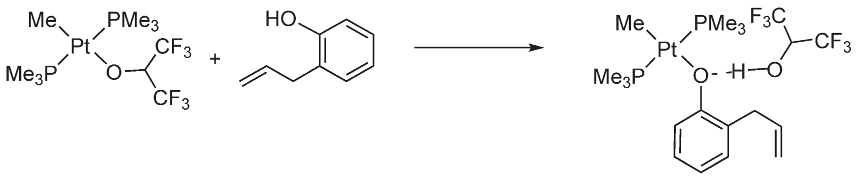


50

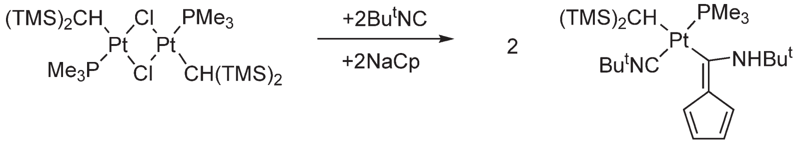
Stable Pt–C σ-bonds enable chemical transformation of the monoalkylplatinum(II) complexes with an anionic ligand by substitution, or reactions of the ligand. Exchange of a fluoroalkoxo ligand on addition of 2-allylphenol forms the aryloxoplatinum complex **51** (Equation (14)). The methyl ligand behaves as a spectator during the reaction.[75]



51

(14)

A methylplatinum complex with a siloxo ligand has been prepared by the metathesis reaction of a chloro(methyl)-platinum complexes with $Na[SiOPh_3]$.[76] A dinuclear Pt complex with bis(trimethylsilyl)methyl ligands and bridging chloro ligands **52** reacts with *t*-butyl isocyanide and then with NaCp to produce the platina(amino)fulvene **53** via addition of Cp to the coordinated isonitrile and migration of the hydrogen atom (Equation (15)).[77]



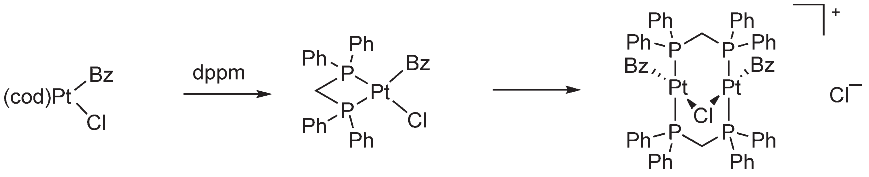
52 **53**

(15)

Addition of dppm to PtCl(Bz)(cod) yields an A-frame type dinuclear benzylplatinum(II) complex with bridging dppm and chloro ligands **54** via an intermediate mononuclear chloro(benzyl)platinum complex with a chelating dppm ligand (Scheme 6).[78]

Structure and bonding aspects of alkylplatinum(II) complexes with phosphine ligands have been investigated systematically by NMR, crystallography, and calorimetric measurements. Calorimetric measurement of the exchange reaction of $PtMe_2(cod)$ with phosphine, forming the dimethylplatinum complex with the phosphine ligands, provides tendencies of thermodynamic stability for the alkylplatinum–phosphine complexes. In general, good σ-donor ligands with small bite angles result in more thermodynamically stable complexes.[79] The dimethylplatinum complexes with chelating diphosphine ligands show negligible difference of the Pt–P bonds from each other, while relative stabilities of the complexes from the calorimetric measurement correlate with donor properties of the diphosphines. The electronic parameter, χ, of the phosphine ligand influences the NMR parameters, $^{31}P\{^1H\}$ NMR peak positions, and ^1J(Pt–C) values.[80] The Pt–C bond energy was compared between $Pt(CH_2CMe_3)_2(PMe_3)_2$ and $Pt(CH_2SiMe_3)_2(PMe_3)_2$ based on the results of calorimetric measurement.[81] A ^{13}C NMR study of the dimethyl-platinum complexes having various supporting ligands in the solid state indicates dependence of chemical shift anisotropy on the kind of ligands.[82] The electron-donating ability of Ar groups in $PtCl(Me)(PAr_3)_2$ has been correlated with ^1J(Pt–P) values.[83]

The chelating bisphosphinidene ligand is a phosphorus analog of 1,4-diaza–1,3-butadienes, and exhibits a strong σ-donor character, while its π-acceptor character is much lower than the phosphine ligands.[84,85] The Pt–C bond distances and $^1J_{C\text{–}Pt}$ values of the dimethylplatinum(II) complexes with phosphinidene ligand **55** are intermediate between the values of dimethylplatinum complexes with 1,4-diaza–1,3-butadiene ligands and with chelating diphosphine ligands.



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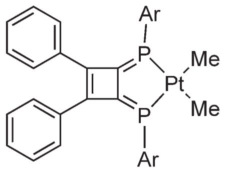
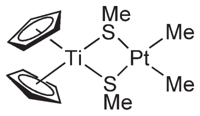
Scheme 6



Ar = C_6H_2-Bu^t_3-2,4,6

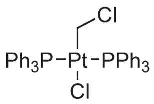
55



56

The dimethylplatinum complex **56** with bis(thiolato)titanocene as the metallaligand is obtained by using $PtMe_2$(nbd) as the precursor.[86]

Platinum complexes having heteroatoms in the alkyl ligands have been reported. Bond parameters for chloro (chloromethyl)platinum complexes **57** and **58** have been compared with the Pd complexes having similar coordination structures,[87,88] and chloro(trifluoromethyl)platinum complexes with chelating ligands **59** and **60** have been prepared.[89]



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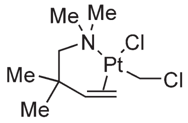

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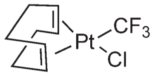

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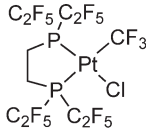

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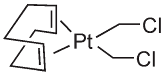

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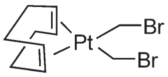

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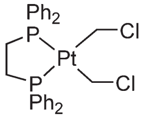
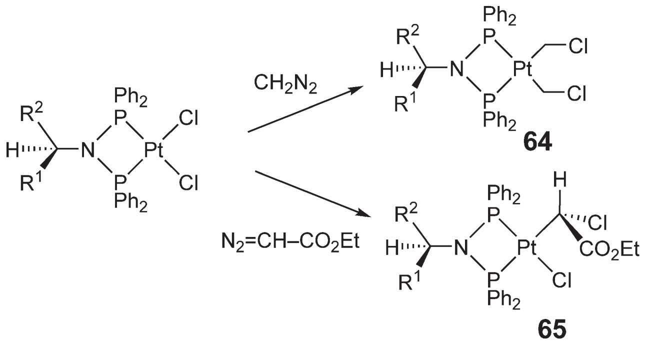


63

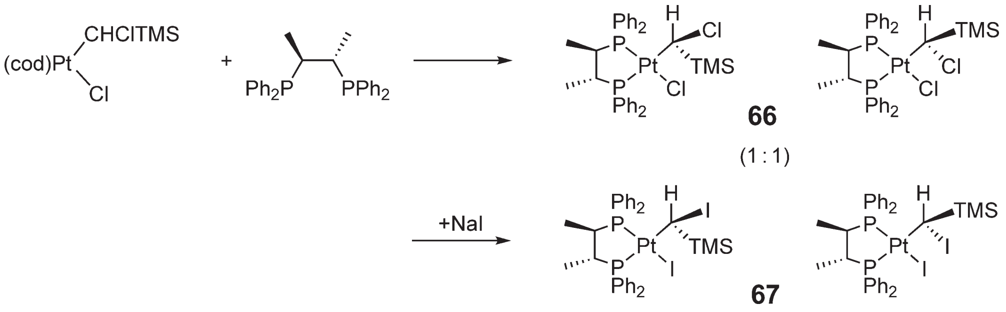
Reaction of Me_3SiHCN_2 with dichloro and dibromo complexes in CH_2Cl_2/acetone/H_2O causes formal insertion of CH_2 groups into the Pt–Cl and Pt–Br bonds, and affords complexes with halomethyl ligands **61–63**.[90] The reaction of diazomethane forms a bis(chloromethyl)platinum complex **64**, while ethyl diazoacetato undergoes insertion into one of the Pt–Cl bonds to yield the complex having a chloro(ethoxycarbonyl)methyl ligand **65** (Scheme 7).[91]

A complex with a chiral alkyl ligand and an optically active diphosphine ligand has been obtained as a mixture of diastereomers **66** (Scheme 8). The chlorine substituent at the α-position of the alkyl ligand can be replaced with I^- to yield **67**.[92,93]

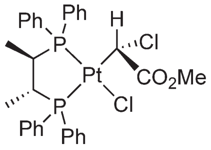
Optically active chelating 2,3-bis(diphenylphosphino)butane forms a Pt complex with a chiral alkyl ligand containing a COOMe group **68**,[94] and a platinum(II) complex with two functionalized methyl ligands **69** has been obtained.



Scheme 7



Scheme 8



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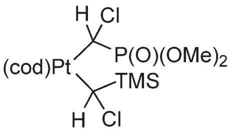
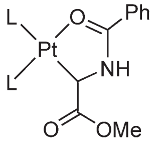


69

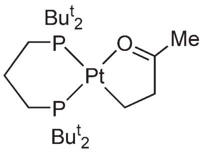
The β-acetylethylplatinum complex **71** has been formed by protonation of a Pt(0) complex having π-coordinated methyl vinyl ketone **70**, using triflic acid, and subsequent isomerization of the hydroxy–η^3-butenyl ligand by addition of Cl^- (Scheme 9).[95]

Alkyl ligands with acyl groups form complexes with cyclic *C,O*-coordinated structures **72** and **73**.[96,97]



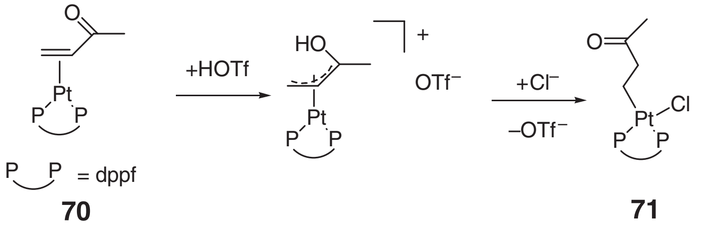
L = PPh_3, 0.5 bpy

72

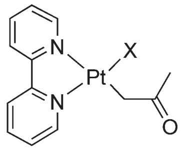


73

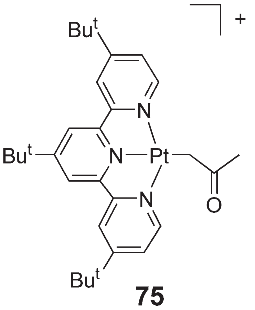
Acetonylplatinum(II) complexes $PtX(CH_2OCH_3)(bipy)$ (X = Cl, CH_2COCH_3) **74** have been prepared by the base-promoted hydrolysis of $PtCl_2(bipy)$ in the presence of acetone.[98,99] Terpy and PPh_3 ligands form complexes with acetonyl and imidomethyl ligands **75** and **76**, respectively.[100,101]

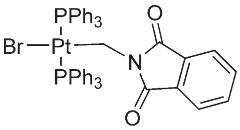


Scheme 9


X = Cl, CH_2COCH_3

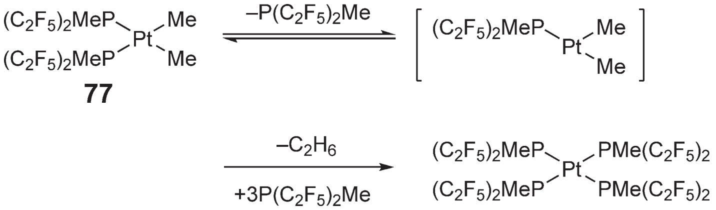
74


75


76

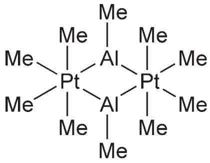
8.08.3.1.2 Neutral alkylplatinum(II) complexes – reactions

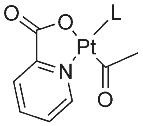
Reactions of alkyl groups bonded to Pt(II) such as reductive elimination, β-hydrogen elimination, and insertion of small molecules into the Pt–C bond are more difficult than those of the corresponding Ni(II) and Pd(II) complexes due to the more stable Pt–C σ-bond. Theoretical results for the stability of metal–carbon bond have been presented.[102] The dimethylplatinum complex having $PMe(C_2F_5)_2$ ligands **77** is converted easily into the Pt(0) complex upon addition of the phosphine (Equation (16)). A mechanism involving initial dissociation of the phosphine ligand has been proposed. Reductive elimination of ethane from a dimethylplatinum(II) complex in a concerted manner has no precedents due to quite stable Pt–Me bonds.[103]


(16)

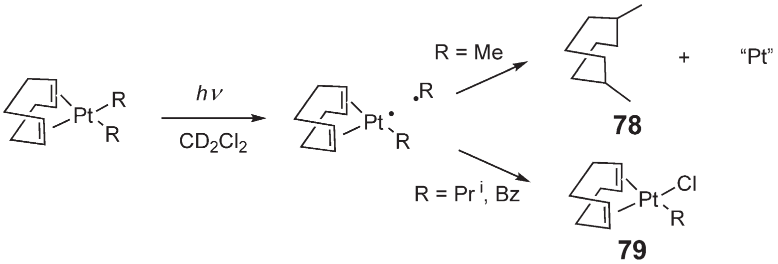
Dialkylplatinum complexes with the cod ligand undergo photolysis at $\lambda_{max} > 320$ nm in CD_2Cl_2 (Scheme 10).[104] The dimethylplatinum complex releases 1,5-dimethylcyclooctane **78** and Pt metal, while the analogs with two isopropyl or benzyl groups produce chloro(alkyl)platinum complexes **79** under the same conditions. Both products are formed via photochemically induced homolytic dissociation of a Pt–C σ-bond.

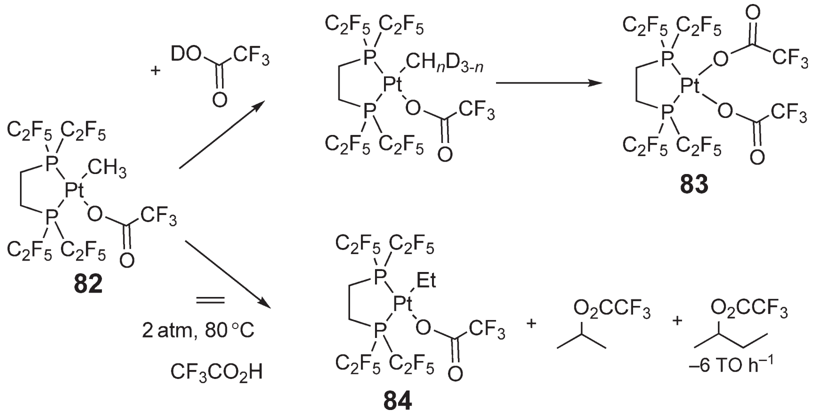
The thermal reaction of binary peralkyl complexes containing two Pt(II) and two Al(III) centers **80** causes decomposition to form Pt as particles with approximately 1.2 nm diameter.[105]


80


L = PPh_3, py, NMe_2Ph

81


Scheme 10

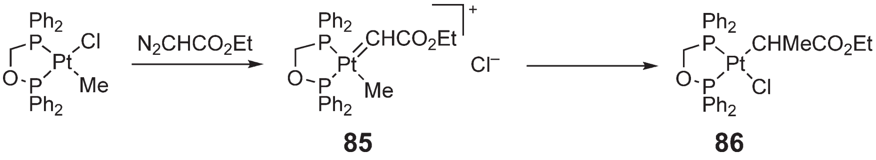


Scheme 11

Insertion of small molecules into the Pt–C bond is an important fundamental reaction of alkyl complexes. The acetylplatinum(II) complex with the 2-picolinate ligand 81 is formed via reaction of CO with the methyl complex.[106] A methylplatinum trifluoroacetato complex with a fluorinated depe ligand 82 undergoes protonation by trifluoroacetic acid to yield a dicarboxylatoplatinum(II) complex 83 (Scheme 11). Kinetic and deuterium labeling studies of the reaction indicate a pathway involving addition of a proton to the Pt–Me bond rather than that involving a Pt(IV) intermediate.[107]

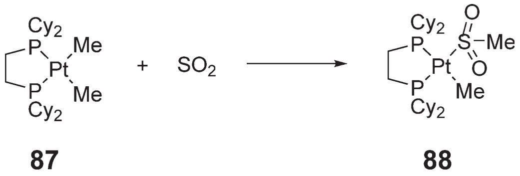
The reaction of ethylene with 82 leads to formation of the ethylplatinum complex with a trifluoroacetate ligand 84 and 2-butyl trifluoroacetate.[108] Conversion of ethylene into a mixture of *cis*- and *trans*-2-butene is promoted by 82.

A methylplatinum(II) complex with a carbene ligand, 85, formed by reaction of ethyl diazoacetate with a chloro(methyl)platinum(II) complex, undergoes insertion of the carbene ligand into the Pt–Me bond to produce the complex with a 1-ethoxycarbonyl ethyl ligand 86 (Equation (17)). A similar reaction of the complex with optically active diphosphine ligands forms the two diastereomers having a chiral center at the carbon bonded to Pt.[109]



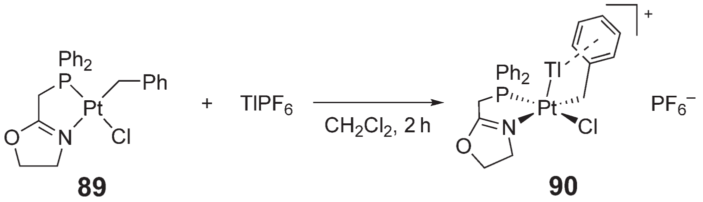
(17)

The chloro(methyl)platinum complex 87, with a chelating 1,2-diphosphine ligand, undergoes insertion of SO_2 into the Pt–C bond to form the methyl sulfonyl complex 88 (Equation (18)).[110]



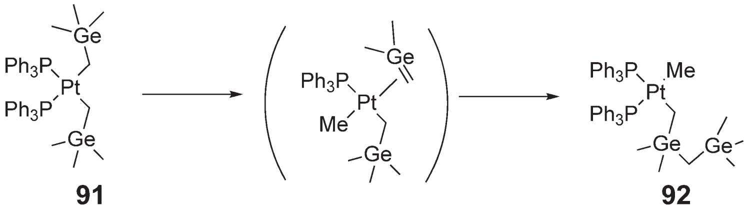
(18)

A chloro(benzyl)platinum complex with an *N*,*P*-ligand having an oxazoline group 89 reacts with thallium hexafluorophosphate to produce complex 90, in which thallium is bonded at the apical position of the Pt center and is weakly bonded to the phenyl ring of the ligand (Equation (19)).[111]



(19)

A bis(trimethylgermylmethyl)platinum complex **91**, formed via transmetallation of the Ge-containing Grignard reagent with a chloroplatinum complex, undergoes thermally induced rearrangement of the ligand (Equation (20)). β-Methyl elimination of a CH_2GeMe_3 ligand and subsequent insertion of a C═Ge bond of the ligand into the Pt–CH_2 bond lead to a complex with the ligand containing two Ge atoms **92**.[112]

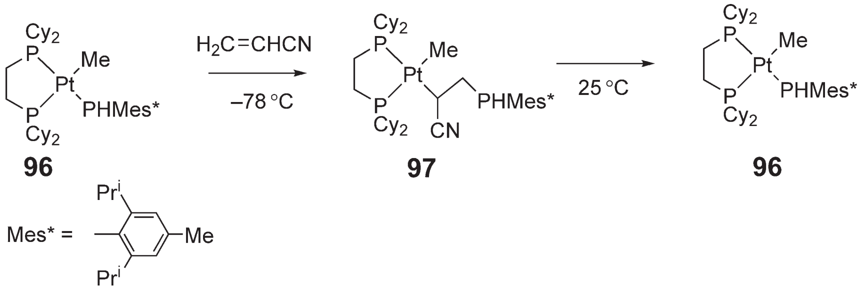


(20)

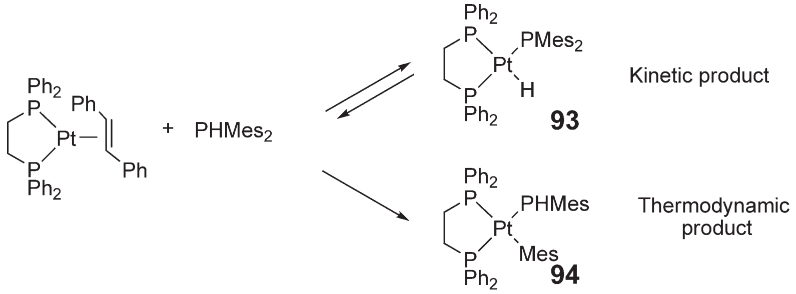
Catalytic addition of a P–H bond to a C═C double bond provides a new method to form functionalized olefins. The Pt(0) complex with dppe and a stilbene ligand promotes the hydrophosphination of acrylonitrile to afford β-phosphino propyonitrile. Model reactions using isolable Pt–dppe complexes suggest that insertion of acrylonitrile into the Pt–P bond occurs to form a Pt complex with a 2-phosphide–1-cyanoethyl ligand.[113] Oxidative addition of secondary arylphosphines to a Pt(0)–stilbene complex with a dppe ligand yields the hydrido(dimesitylphosphino)platinum(II) complex **93** and mesityl(mesitylphosphido)platinum(II) complex **94** as the kinetic and thermodynamic products of the reaction, respectively (Scheme 12).[114,115] NMR spectra of the complexes revealed the electron-donating character of the phosphido ligand.

Acyl(phosphido)platinum complexes with a dppe ligand, **95**, can be prepared in two steps, shown in Scheme 13. NMR studies show rotation of the P–Pt bond and inversion of the P center on the NMR timescale.[116]

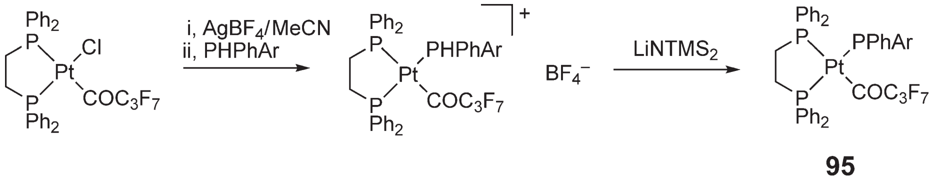
Model compounds of the intermediate for catalytic hydrophosphination have been prepared by using dppe and dcpe as the supporting ligands.[117,118] Methylplatinum phosphido complex **96** undergoes reversible insertion of acrylonitrile into the Pt–P bond to form **97** and its deinsertion from the produced 2-phosphidealkyl ligand to regenerate **96** (Equation (21)). The complex having 2-cyanoethyl and phosphide ligands at *cis*-positions **98** does not yield the product of C–P coupling even at high temperature (Equation (22)).



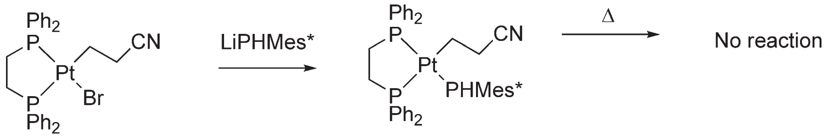
(21)



Scheme 12



Scheme 13



98

(22)

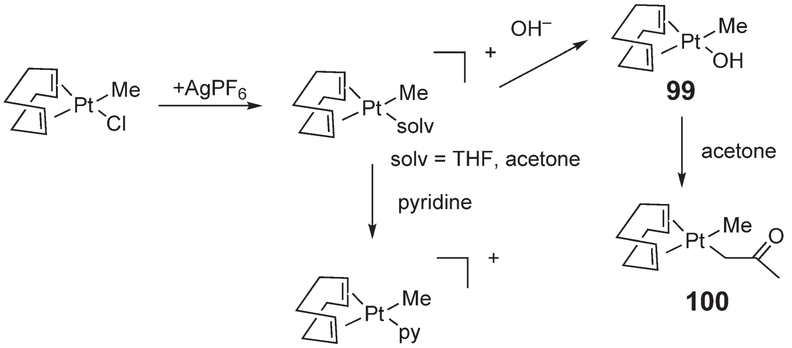
These results suggest that the reaction proceeds via insertion of acrylonitrile into the Pt–P bond and subsequent coupling of the hydrido and 2-phosphide–1-cyanoethyl ligands for the catalytic hydrophosphination, rather than an alternative pathway involving coupling of the alkyl and phosphide ligands bonded to Pt.

8.08.3.1.3 Cationic alkylplatinum(II) complexes

Cationic alkylplatinum(II) complexes have square-planar coordination, similar to most of the neutral complexes. One of the four coordination sites is occupied by labile ligands such as NCMe, ether, CO, alkene, and alkynes in many complexes. Cationic alkylplatinum(II) complexes cause C–H activation of methane and benzene or insertion of alkenes and CO into the Pt–C bond more easily than neutral complexes. One of the reasons for the high reactivity of cationic complexes resides in facile coordination of these small molecules which are inserted into the Pt–C bond. Various counteranions are employed for the cationic Pt complexes. Chloride and OTf are often used as the counter-anions although they are able to coordinate to the Pt center in neutral complexes; BF_4^-, PF_6^-, and BPh_4^- are mostly separated from the Pt center in the solid state and in solution, although these anions show stronger interaction with cationic complexes of early transition metals; $[B(C_6H_3(CF_3)_2\text{-}3,5)_4]^-$ was reported to be effective as a non-coordinating anion for cationic Ni and Pd complexes in 1995, and the cationic Pt complexes having it as the counteranion have also been reported in the last decade. Chemical properties of the cationic complex depend on the kind of labile neutral ligand and counteranions. Several reactions have been reported to form cationic alkylplatinum(II) complexes: abstraction of halogeno and pseudohalogeno ligands from the neutral alkylplatinum(II) complex by metal cations such as Na^+ and Ag^+, abstraction of an alkyl ligand of dialkylplatinum(II) complexes by a strong Lewis acid, and oxidative addition of methyl cation to Pt(0) complexes.

The cationic methylplatinum(II) complex with acetone and cod ligands, $[PtMe(acetone)(cod)]^+$, is obtained as a solution from the reaction of $AgPF_6$ with PtClMe(cod) in acetone (Scheme 14).[119] The acetone ligand is substituted easily by a hydroxo anion to give the corresponding neutral hydroxo complex **99**. The basic hydroxo ligand of the complex deprotonates acetone to form the methylplatinum(II) acetonyl complex **100**. The cationic complex stabilized by pyridine **101** may be isolated as an analytically pure solid.

TMEDA forms cationic methylplatinum complexes with OEt_2 or THF as ligands. Intramolecular activation of a C–H bond of the OEt_2 ligand, accompanied by elimination of methane to produce the cationic complex with a Fischer-type carbene ligand **103**, occurs via an intermediate with hydride and vinyl ethyl ether as the ligands (Equation (23)).[120]

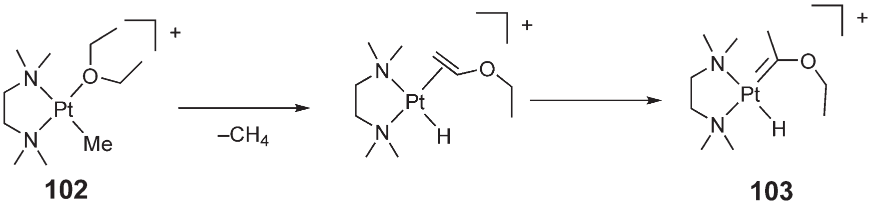


99

100

101

Scheme 14



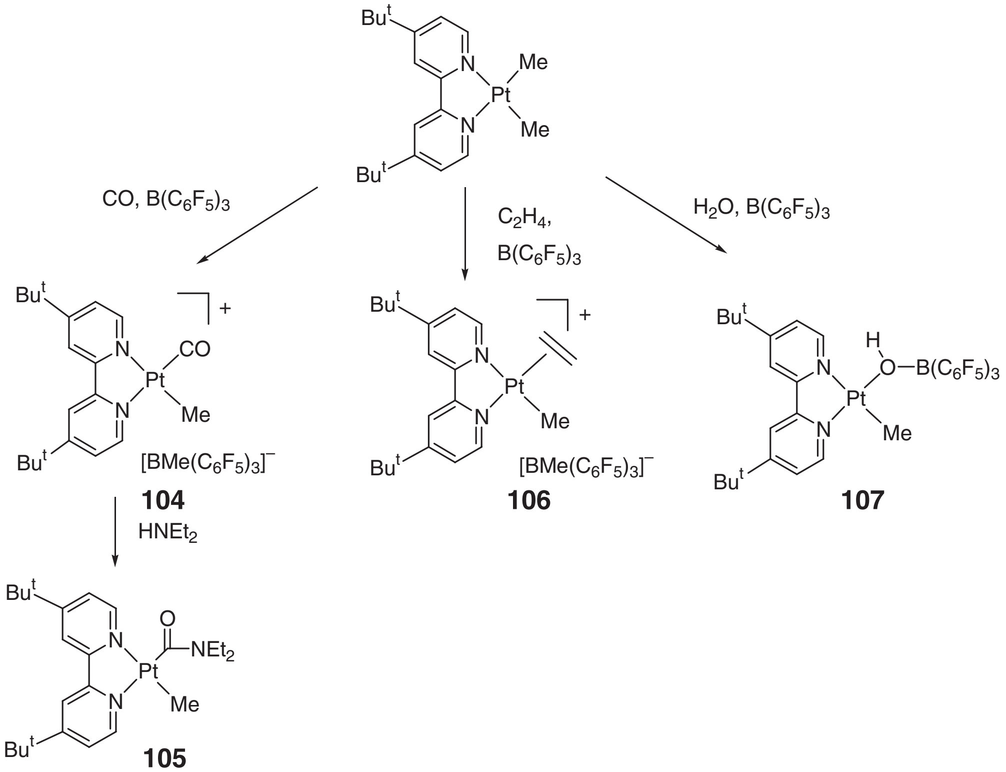
(23)

Combination of highly Lewis-acidic $B(C_6F_5)_3$ and a dimethylplatinum(II)–bipyridine complex in the presence of CO or ethylene affords cationic complexes having $[BMe(C_6F_5)_3]^-$ as the counteranion (**104** and **106**, Scheme 15),[121] and the carbonyl complex **104** reacts with a secondary amine to produce the neutral complex with a carbamoyl ligand **105**. The reaction in the presence of equimolar H_2O leads to an isolable complex with an *O*-bonded hydroxy(triaryl)borato ligand **106**.[122] ^1H NMR studies of the reaction at low temperature suggested initial formation of a hydridoplatinum species (−18.5 ppm) which is converted into the product on warming the reaction mixture.

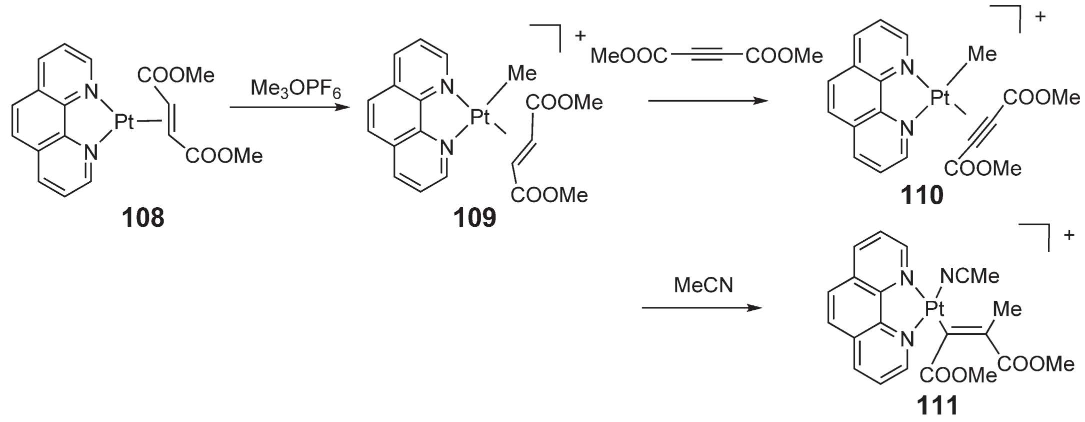
Mechanisms for exchange of the monodentate neutral ligands has been extensively studied by dynamic NMR spectra and kinetic measurement using absorption spectra.[123,124] The cationic methyl complex $[PtMe(PPh_3)(2{,}9\text{-}Me_2phen)]^+$ shows exchange of two sites of Me and PPh_3 ligands via a T-shaped intermediate with monodentate coordination of the phenanthroline ligand.[125]

Oxidative addition of trimethyloxonium tetrafluoroborate to a Pt(0) complex containing dimethylfumarate and phen ligands **108** leads to the corresponding cationic methylplatinum(II) complex **109**,[126,127] and substitution of the coordinated olefin by dimethyl acetylenedicarboxylate **110** leads to insertion of the coordinated alkyne into the Pt–Me bond in MeCN, giving the complex having an alkenyl group and the solvent as ligands **111** (Scheme 16).

Bis(2-pyridyl)amine forms square-planar cationic methylplatinum complexes with a DMSO ligand.[128] A DFT study has been reported for the oxidative addition reaction of methyl imidazolium to $Pt(PH_3)_2$ to give a cationic complex, $[PtMe(CNMeCH{=}CHNMe)(PH_3)_2]^+$, and the geometry of the product optimized.[129]

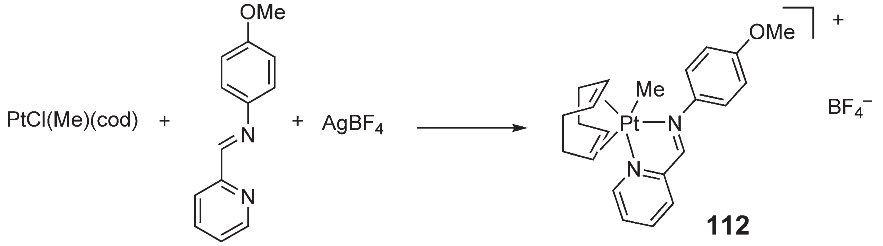


Scheme 15



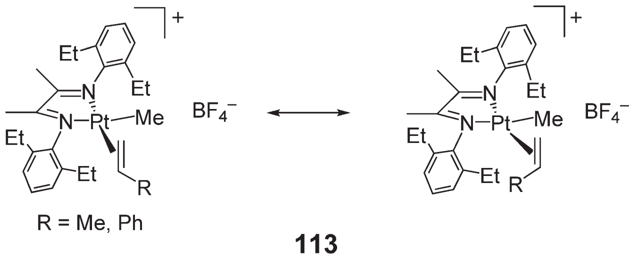
Scheme 16

The pentacoordinated cationic complex **112** has been obtained from the reaction of $AgBF_4$ with PtClMe(cod) in the presence of chelating 2-iminopyridine (Equation (24)).[130] Crystallographic results indicate that the Me ligand and an olefin group of cod occupy the apical coordination sites of a trigonal-bipyramidal complex. The NMR spectra in solution are consistent with the structure in the solid state, while the molecule undergoes site change of the olefin groups of cod on the NMR timescale.



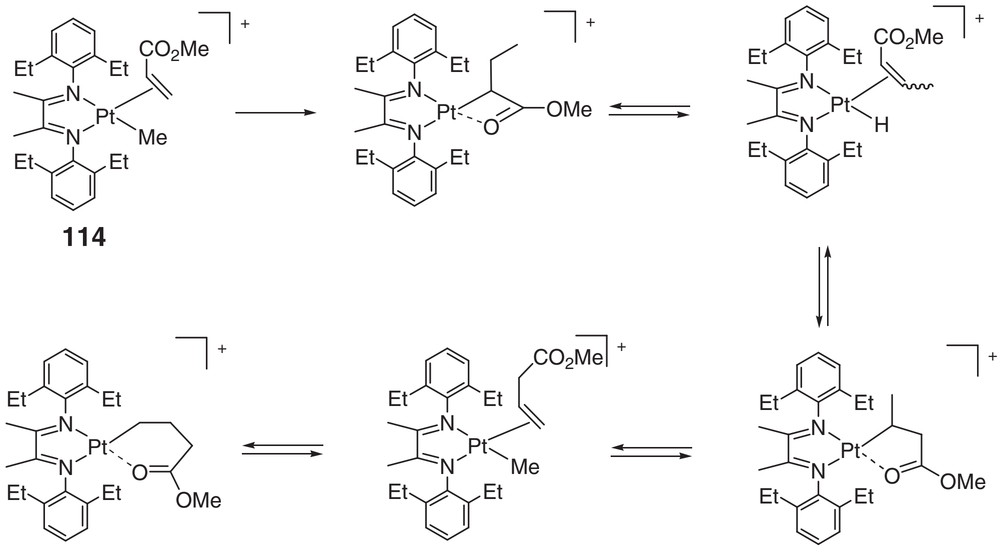
(24)

Several research groups have reported the preparation and chemical properties of cationic alkylplatinum complexes with 1,4-diaza–1,3-butadiene ligands and obtained detailed aspects of the olefin coordination and C–H bond activation of hydrocarbons. The reaction of $AgBF_4$ with chloro(methyl)platinum complexes containing 1,4-diaza–1,3-butadiene, giving cationic complexes, involves dinuclear intermediates which were isolated and fully characterized.[131] Complexes with π-coordinated olefins and 1,4-diaza–1,3-butadiene ligands are stable. Insertion of the ligating olefin into the Pt–C bond is much more difficult than that for Pd and Ni complexes.[132] The complexes having π-coordinated prochiral olefins such as propene and styrene exist as either of the stereoisomers due to orientation of the methyl and phenyl substituents of the ligand (**113**, Equation (25)). These isomers undergo mutual exchange on the ^1H NMR timescale.



(25)

The complex having π-coordinated methyl methacrylate, **114**, undergoes insertion of the olefinic group into the Pt–C bond, affording a cationic alkylplatinum(II) complex with an *O*-coordinated CO_2Me group (Scheme 17).[133] The corresponding Pd(II) complex was reported to undergo a similar reaction of the coordinated methyl methacrylate with the methyl ligand.[134] Insertion of the C=C double bond of the ligand into the Pt–Me bond, and subsequent hydrogen



114

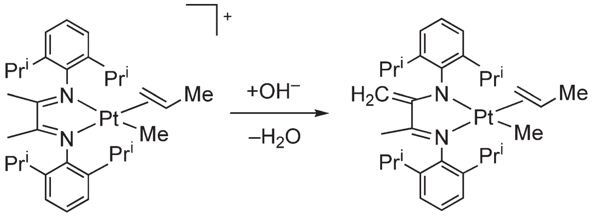
116

115

Scheme 17

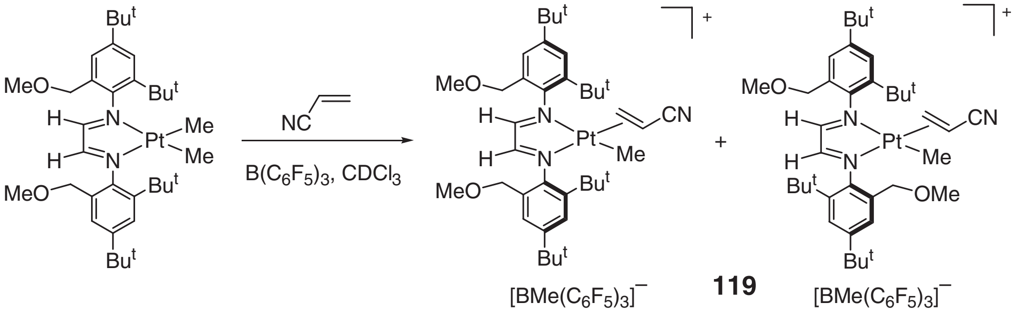
migration within the ligand, caused by repetition of β-hydrogen elimination of the alkyl ligand and reinsertion of the olefin into the Pt–H bond, leads to **115** with a five-membered chelate ring, and then to **116** with a six-membered chelate ring. The ^{1}H NMR spectra of the reaction mixture exhibit signals that are assigned to the intermediates with four- and five-membered cyclic structures.

NMR studies of the methyl(propene)platinum complex having a BF_4^- counterion by the F-H HOESY technique revealed weak interaction between BF_4^- and the diimine group of the ligand or an apical position of the Pt center.[135] The methyl and olefin ligands did not exhibit peaks due to attractive interaction with the counteranion. The complex with 2,3-dimethyl–1,4-diaza–1,3-butadiene ligand **117** undergoes abstraction of a methyl hydrogen from the ligand to produce the neutral imine–imino platinum complex **118** (Equation (26)).[136] The propene ligand of the product is bonded selectively at the position *cis* to the imine group based on the NOESY NMR spectrum.[137]



117 **118** (26)

The complex with π-coordinated acrylonitrile and the diimine with different substituents at 6- and 6′-positions form a pair of diastereomers of **119** (Equation (27)).[39]



119 (27)

The corresponding complexes with *N*-coordinated acrylonitrile or π-coordinated ethylene **120 and 121** are prepared from the reactions of $AgBF_4$ with a chloro(methyl)platinum complex in the presence of the olefins, respectively (Scheme 18).[138,139]

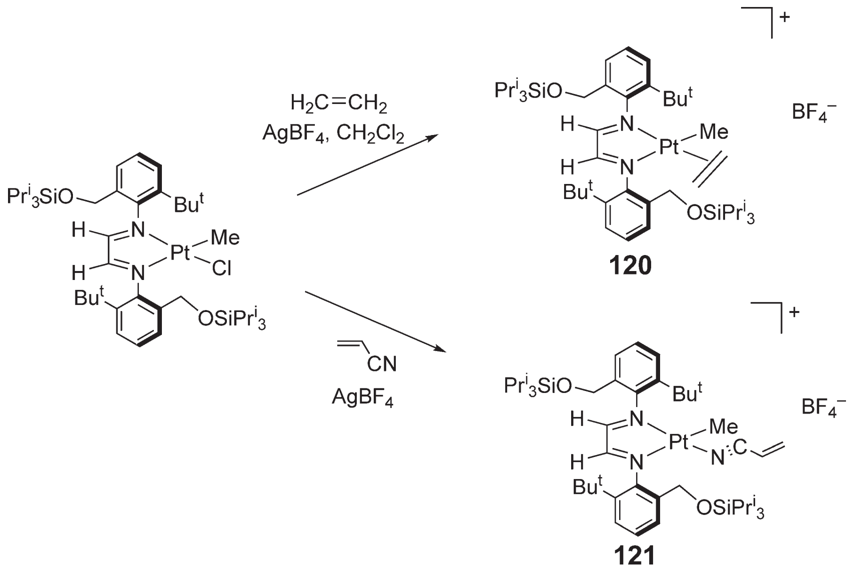
The π-coordinated ethylene is labile and replaced easily by either nitrile, ethylene, CO, or SMe_2 to form the cationic complex having these ligands. The MeCN ligand is also replaced with various σ- and π-donors such as ethylene, CO, and SMe_2. The complex with an MeCN ligand initiates cationic polymerization of vinyl ether, while polymerization of styrene by the complex is much slower than vinyl ether.

The thermodynamic stability of cationic complexes of Ni, Pd, and Pt with methyl, ethylene, and 1,4-diaza–1,3-butadiene ligands, as well as reactivities, have been compared based on the results of theoretical calculations.[140] The bond between ethylene and the metal center decreases in the order, Pt > Pd > Ni, while the energy barrier for insertion of coordinated ethylene into the M–C bond decreases in the same order of the metal center. The cationic methylplatinum complex without ethylene as a ligand is stabilized by an agostic interaction of the β-CH group; β-hydrogen elimination of the alkyl ligand giving a five-coordinated intermediate is unlikely.

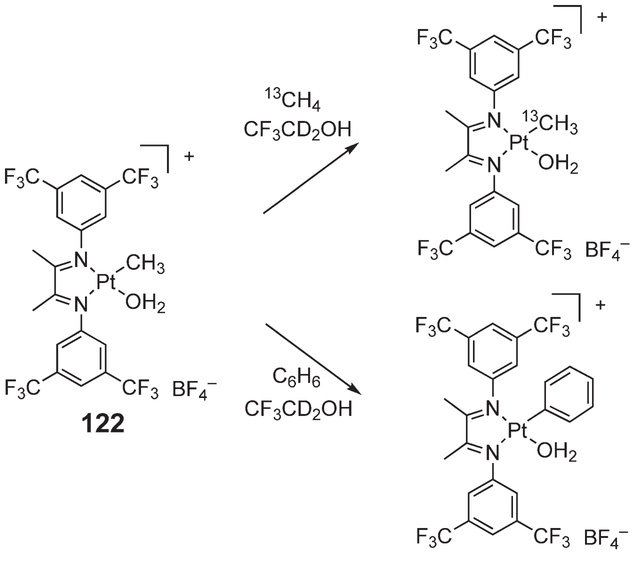
The cationic methylplatinum(II) complexes with 1,4-diaza–1,3-butadiene ligands cause C–H activation of methane and benzene under mild conditions. The complex having a coordinated water molecule and BF_4^- counteranion **122** undergoes exchange of the methyl ligand with isotope-labeled methane at 45 °C in 2,2,2-trifluoroethanol (Scheme 19).[141] The reaction of benzene with the complex yields the cationic phenylplatinum(II) complex **123**.

The reaction using the diimine ligand having 2,6-disubstituted aryl groups at the coordinating nitrogen atoms is retarded by addition of water, and shows a kinetic isotope effect close to unity in the reaction using deuterated benzene, suggesting that the rate-determining step resides at substitution of the aqua ligand by a benzene molecule.[142] ^1H NMR spectra of the reaction mixture at −69 °C exhibit signals assigned to a cationic alkylplatinum(II) intermediate with π-coordinated benzene. The reaction pathway was investigated using DFT calculations, which provided the optimized geometry and relative stability of the Pt(II) and Pt(IV) intermediates formed by C–H bond activation.[38] 2,2,2-Trifluoroethanol, used as the solvent, was proposed to coordinate to the Pt center of a cationic intermediate.

The reactions of toluene and *p*-xylene were conducted in 2,2,2-trifluoroethanol and quenched by addition of acetonitrile whose strong coordination to Pt fixes the structure of the product. Activation of both aromatic C–H and aliphatic C–H bonds takes place.[143] The ratio of the regioisomers of the tolylplatinum complexes formed by the reaction of toluene does not vary significantly depending on the structure of the complex examined (Table 1). The reaction of *p*-xylene is promoted by the complex with a 3,5-bis(trifluoromethyl)phenyl group at the coordinated nitrogen, and that with 2,6-dimethylphenyl groups shows opposite selectivity for the activation of aliphatic and aromatic C–H bonds.



Scheme 18

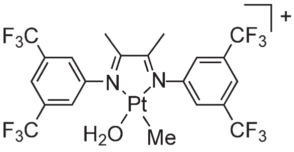
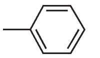
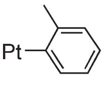
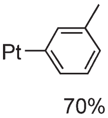
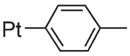
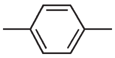
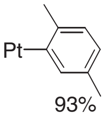
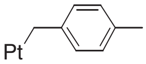
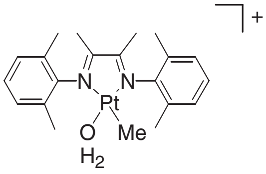
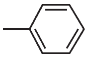
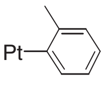
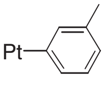
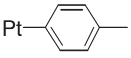
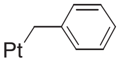
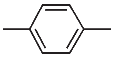
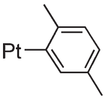
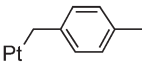


122

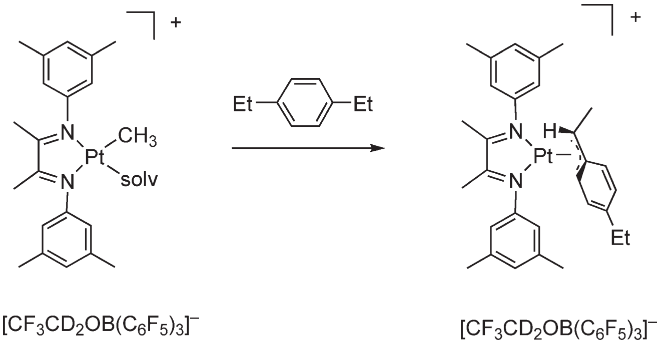
123

Scheme 19

Table 1 Products of C–H activation of aromatic hydrocarbons

Catalyst	*Substrate*	*Products*			
		 9%	 70%	 20%	
		 93%	 7%		
		 4%	 60%	 15%	 21%
		 10%	 90%		

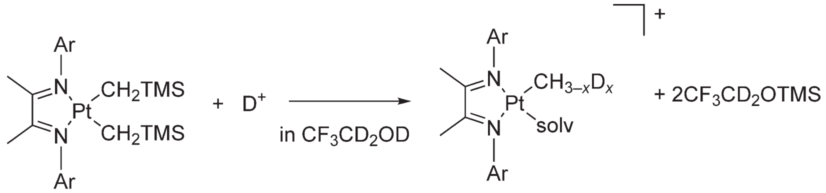
Systematic studies on the reaction of benzene with various complexes indicated that the rate-determining step using the ligands with 3,5-disubstituted aryl groups is the C–H bond activation step, whereas the reaction by the complex with a 2,6-disubstituted aryl group of the diimine ligand involves π-coordination of benzene as the rate-determining step.[144] An associative mechanism for the reaction is supported by the results of activation volume measurement.[145] Total reaction is enhanced by introduction of electron-releasing substituents on the ligand. The reaction of 1,4-diethylbenzene with the cationic Pt complex **124** in anhydrous 2,2,2-trifluoroethanol forms the π-benzoplatinum complex **125** by activation of a benzylic C–H bond (Equation (28)).[146]



124 **125**

(28)

The bis(trimethylsilylmethyl)platinum complex **126** with 1,4-diaza–1,3-butadiene undergoes protonolysis by 2,2,2-trifluoroethanol (Equation (29)).[147]

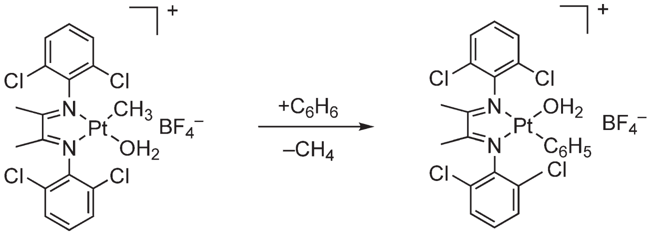


126

(29)

A mixture of tetramethylsilane and trifluoroethanol is converted into the corresponding alkoxysilane catalyzed by the Pt complex. A mechanism involving a Pt(IV) intermediate is proposed to account for the results of stoichiometric reactions of the Pt complexes.

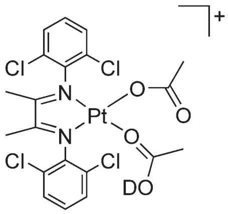
The cationic methylplatinum complex with a 1,3-diaza–1,4-butadiene ligand having 2,6-dichlorophenyl groups **127** promotes C–H bond activation of benzene to afford the cationic phenylplatinum complex **128** (Equation (30)).[148]



127 **128**

(30)

Mass spectrometry of the reaction mixture revealed the presence and distribution of the products and intermediates contained in the mass chamber. The reaction mixture contains the intermediates corresponding to the methyl- and phenylplatinum(II) complexes, which are probably stabilized by intramolecular coordination of a chlorine substituent. The other species detected in the reaction mixture have molecular weights corresponding to the methyl(benzene)platinum(II), phenyl(methane)platinum(II), and hydrido(methyl)phenylplatinum(IV) complexes. The reaction with 2,2,2-trifluoroethanol does not show the mass peaks due to the complex containing trifluoroethanol as the ligand, although it is proposed as the intermediate of C–H bond activation of the hydrocarbons. The reaction using the chlorinated ligand does not involve the intermediate containing the polar solvent as the ligand. The complex catalyzes deuteration of benzene with perdeuterated acetic acid.[149] The following complexes **129–131**, including a coordinatively unsaturated cationic phenylplatinum complex, were observed in the mass spectrum of the reaction mixture.



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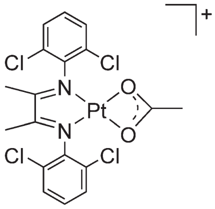

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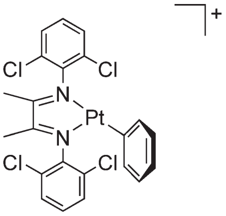
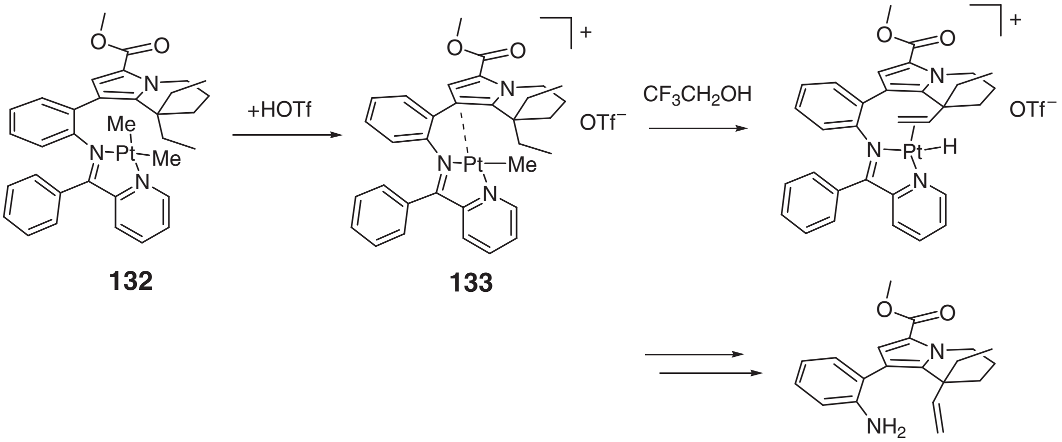


131

The cationic methylplatinum complex with the 1,4-diaza–1,3-butadiene ligand has been applied to the synthesis of a natural product (Scheme 20).[150] The dimethylplatinum complex **132** bonded to an intermediate of the total synthesis of (−)-rhaziniliam is converted into cationic **133** by reaction with HOTf. The Pt complex promotes dehydrogenation of one of the two ethyl groups of the six-membered ring, taking place selectively to form the intermediate with ethyl and vinyl groups at the same carbon. Asymmetric synthesis of the compound is achieved by diastereoselective reaction of the Pt complex with an oxazole-containing diimine ligand.

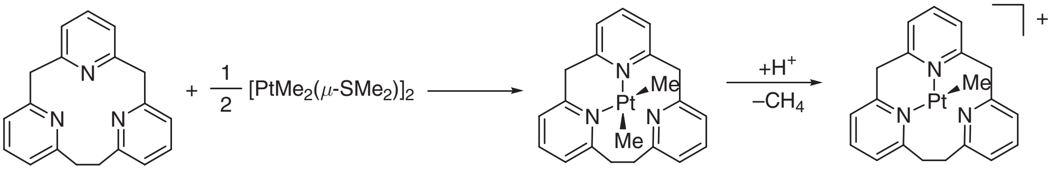
A complex containing four cationic methylplatinum–diimine fragments bridged by 5,10,15,20-tetrakis(4-pyridyl)-dehydroporphyrin forms micellar aggregates of anionic and neutral surfactants.[151,152] [2.1.1]-Pyridinophane forms a dimethylplatinum(II) complex with a bidentate ligand **134** in spite of the presence of three pyridyl groups in the ligand (Scheme 21). Protonation of the complex by $H^+[B(C_6H_3(CF_3)_2\text{-}3,5)_4]^-$ releases methane. DFT calculations for the Pt-containing product indicate formation of a T-shaped 14-electron species **135** rather than a pseudo-tetrahedral four-coordinated species.[153,154]

The dimethylplatinum complex of a 2-pyridylimine having an *N*,*N*-dimethyl–2-aminoethyl group at the imine nitrogen reacts with equimolar HOTf to produce a cationic methylplatinum complex with the tridentate pyridylimine ligand **136** (X = OTf) (Scheme 22).[155] The reaction using HCl causes protonation to form an equilibrated mixture of the cationic complex **136** (X = Cl) and a neutral chloro(methyl)platinum complex with the bidentate pyridylimine ligand **137**. A dimethylplatinum complex with a benzenesulfonate group at the imine nitrogen has also been obtained.[156]



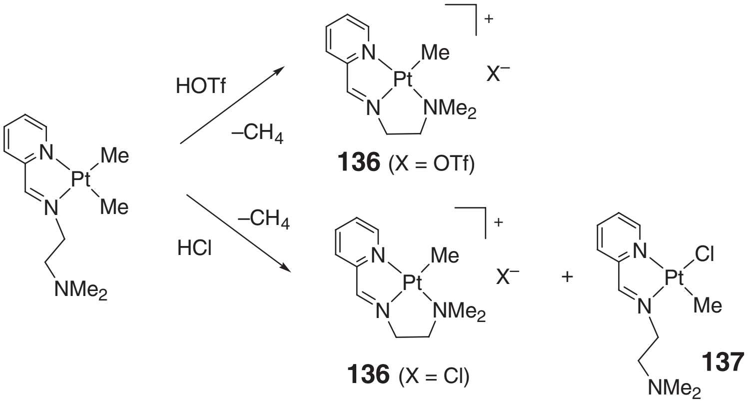
132 **133**

Scheme 20



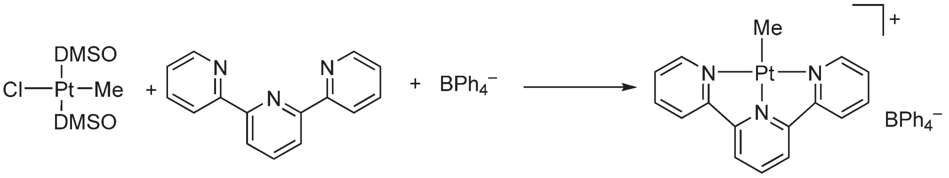
134 **135**

Scheme 21



Scheme 22

The cationic methylplatinum complex with terpy as a ligand **138** is prepared from the neutral chloro(methyl)platinum(II) complex of the ligand in the presence of $NaBPh_4$ (Equation (31)). The crystal structure showed that the coordination planes of the two crystallographically independent molecules are parallel with head-to-tail packing.[157]

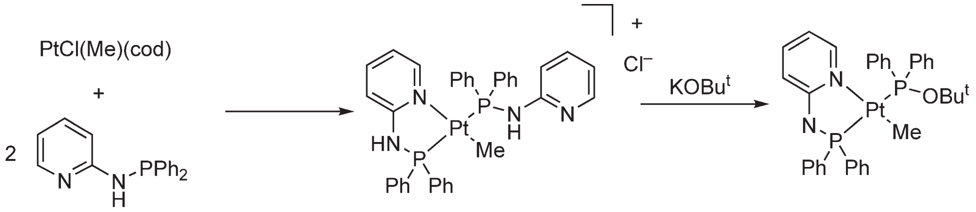


138 (31)

A cationic methylplatinum complex having the two pyridinoaminophosphine ligands in *P*- and *P*,*N*-coordination **139** is obtained from PtClMe(cod) (Scheme 23).[158] It reacts with $KOBu^t$ to cause substitution of the monodentate ligand and NH hydrogen abstraction of the other ligand to form the neutral complex.

An unsymmetrical dinuclear methylplatinum complex with a bridging (2-pyridyl)diphenylphosphine **140** has been prepared (Scheme 24).[159] The preparation procedure involves initial formation of a dinuclear tetramethyl complex with bridging (2-pyridyl)diphenylphosphine and SMe_2. Addition of CF_3COOH to **140** causes protonation of the methyl ligand attached to the Pt coordinated by the pyridine group. Migration of the methyl ligand or change of coordination sites of the *P*,*N*-ligand forms the complex having a trifluoroacetate ligand at the Pt bonded to P **141** selectively. Further addition of the *P*,*N*-ligand provides complex **142**, having an electron donor–acceptor interaction between the neutral and cationic Pt centers.

A cationic alkylplatinum(II) complex with a PNP tridentate ligand **143** has been prepared by nucleophilic attack of the ethylene coordinated to the cationic Pt(II) center by aniline (Equation (32)).[160]



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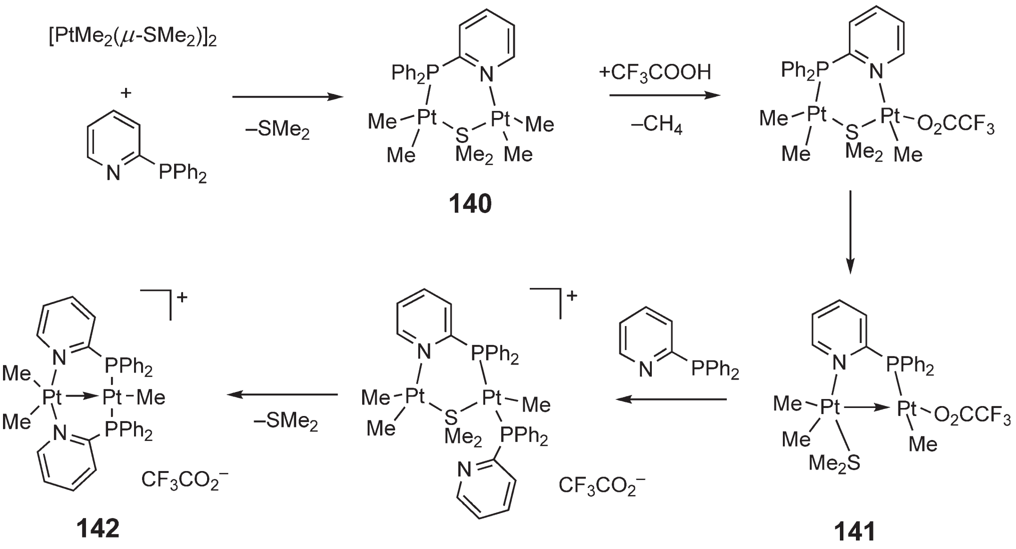
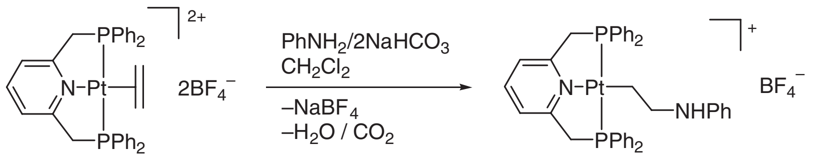
Scheme 23



Scheme 24

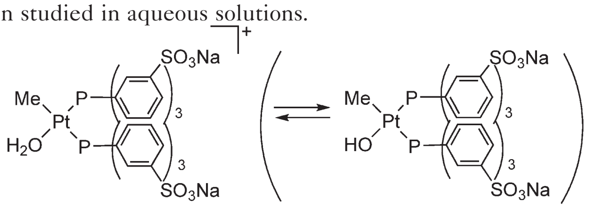


143 (32)

Triphos, $(Ph_2PCH_2CH_2)_2P$, also forms the cationic methylplatinum complex with the tridentate ligand, $[PtMe_2(triphos)]OTf$.[161,162] Optically active *P*,*N*- and *P*,*N*,*S*-chelating ligands have been employed in the preparation of cationic methylplatinum complexes with these ligands.[163,164]

The chloro(methyl)platinum complex with dppe as a ligand reacts with $Ph_3P{=}C{=}C{=}O$ in the presence of $AgBF_4$ to form the cationic complex with the ketenyl ligand, **144** (Scheme 25).[165,166] Addition of alcohol to the C═C double bond of the ligand produces the cationic methylplatinum complex having a phosphoylide ligand **145**.

Cationic methylplatinum(II) complexes with an aqua ligand **146** and **147** are obtained by protonation of the dimethyl complexes having tris(*m*-sulfonatephenyl)phosphine and tris(2-methoxyphenyl)phosphite as the ligands;[167,168] **146** is in equilibrium with a neutral complex having a hydroxo ligand. Protonation of the Pt–Me bond has been studied in aqueous solutions.



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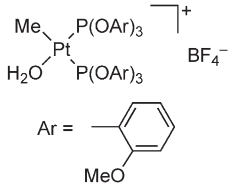

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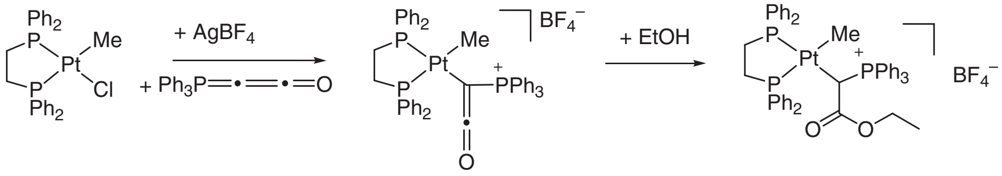
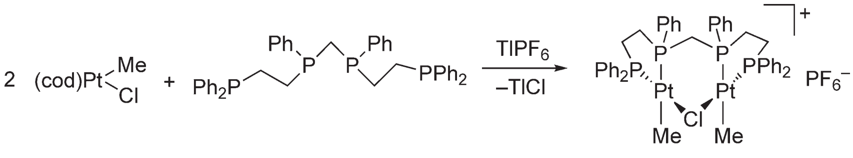


144 **145**

Scheme 25

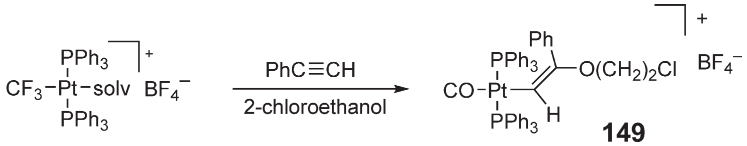
A tetradentate phosphine ligand has been prepared and employed as the chelating ligand in dinuclear platinum complexes (Equation (33)).[169] PtClMe(cod) reacts with the phosphine in the presence of $TlPF_6$ to form the dinuclear complex with a bridging chloro ligand **148**.



148

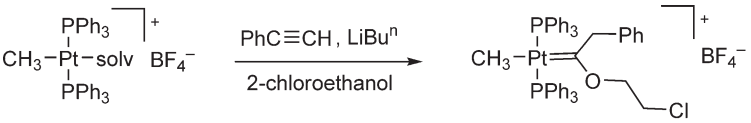
(33)

A cationic trifluoromethylplatinum solvent complex reacts with phenylacetylene and 2-chloroethanol to form a neutral β-alkoxyalkenylplatinum complex **149** via nucleophilic attack of the alcohol to the initially formed alkynyl complex (Equation (34)).[170] The reaction is unique to the complex having an electron-withdrawing CF_3 ligand, and a cationic methylplatinum(II) complex with a similar structure reacts with phenylacetylide to yield the cationic complex with a carbene ligand (**150**, Equation (35)).



149

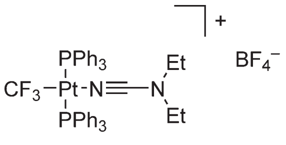
(34)



150

(35)

Cationic trifluoromethylplatinum complexes with cyanoimido and enolate ligands **151–153** have also been prepared.[171–173]



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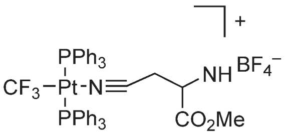

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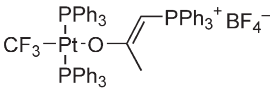
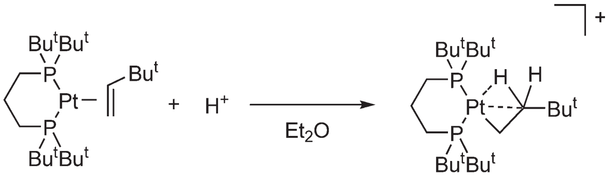


153

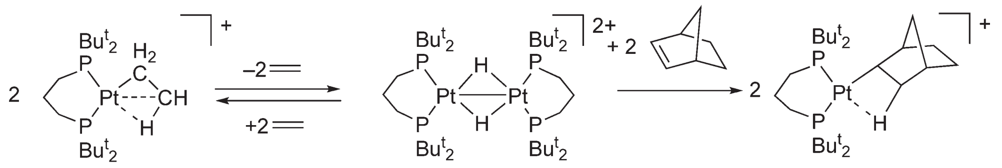
Protonation of the Pt(0)–*t*-butylethylene complex of a bulky six-membered chelating diphosphine leads to the cationic complex having 3,3-dimethyl–butyl ligand **154**, (Equation (36)).[174,175]



154

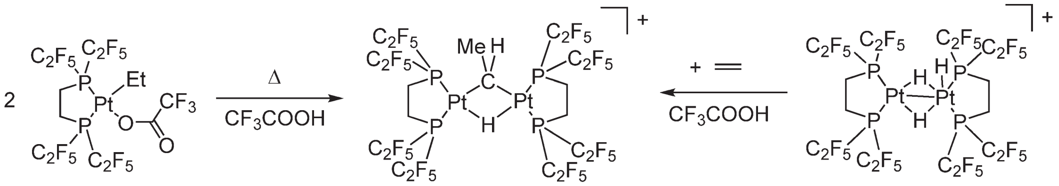
(36)

A β-C–H group of the alkyl ligand has an agostic interaction with the metal center as evidenced by NMR spectroscopy. The ethylplatinum complex **155** undergoes β-hydrogen elimination of the ethyl ligand to produce the dimeric complex having two bridging hydride ligands (**156**, Scheme 26). This β-hydrogen elimination is formally reversible, and the hydrido complex undergoes ethylene insertion into the Pt–H bond to regenerate the ethyl complex. Insertion of norbornene into the Pt–H bond produces a cationic mononuclear Pt complex with the norbornyl ligand having interaction of the β-C–H group with the metal **157**.



155 **156** **157**

Scheme 26

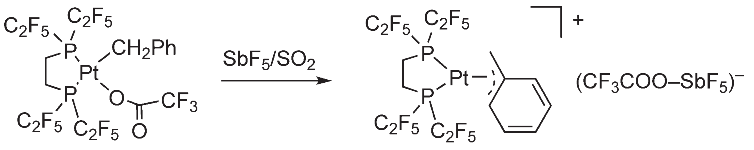


84 **158** **159**

Scheme 27

Heating complex **84** yields a dinuclear complex with bridging hydride and ethylidene ligands (**158**, Scheme 27);[176] **158** is obtained also by reaction of ethylene with the dinuclear trihydride complex **159**, which accompanies catalytic conversion of ethylene into 2-butenyl trifluoroacetate.

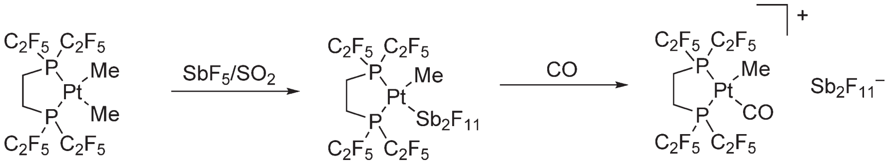
A related benzyl(trifluoroacetato)platinum complex **160** reacts with SbF_5 to produce a cationic η^3-benzyl platinum complex **161** (Equation (37)).



160 **161**

(37)

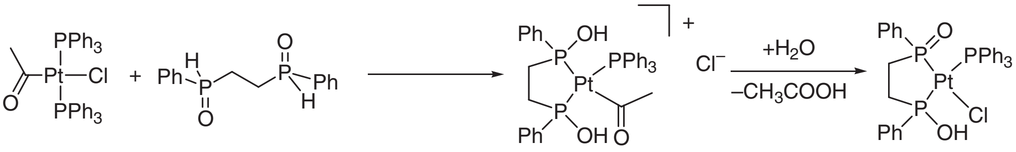
A mononuclear cationic methylplatinum(II) complex with the same diphosphine ligand **162** is formed by the reaction of SbF_5 with the dimethyl complex in SO_2 and introduction of CO to the product (Equation (38)).[177]



162

(38)

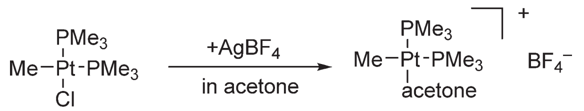
A cationic acetylplatinum complex with a hydroxy group-containing diphosphine **163** is obtained from the reaction of bis(phosphine oxide) with a Pt(II) complex, and this complex is readily hydrolyzed to give neutral chloro complex **164** (Scheme 28).[178]



163 **164**

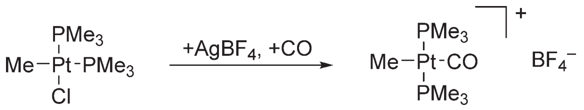
Scheme 28

cis-PtClMe(PMe$_3$)$_2$ reacts with AgBF$_4$ in the absence and presence of CO to produce cationic methylplatinum(II) complexes with *cis*- **165** and *trans*- **166** structures, respectively (Equations (39) and (40)).[179] The *trans*-methylplatinum complex with a carbonyl ligand is formed also by decarbonylation of the acetylplatinum complex. Insertion of CO into the Pt–C bond does not take place, and one reason for this, based on theoretical studies, is the high energy barrier for isomerization of the *trans*-complex to the *cis*-form.



165

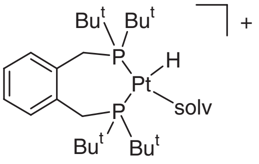
(39)



166

(40)

An NMR study of the reaction mixtures of ethene and CO in the presence of some Pt complexes revealed the presence of hydride, alkyl, and acyl ligands, **167–169**.[180] The complexes are interconverted reversibly by insertion and deinsertion of ethene and CO. They are involved in Pt-complex-catalyzed methoxycarbonylation of ethene.



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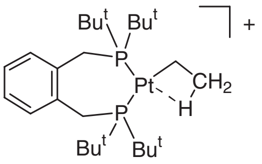

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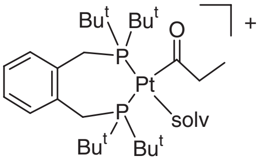
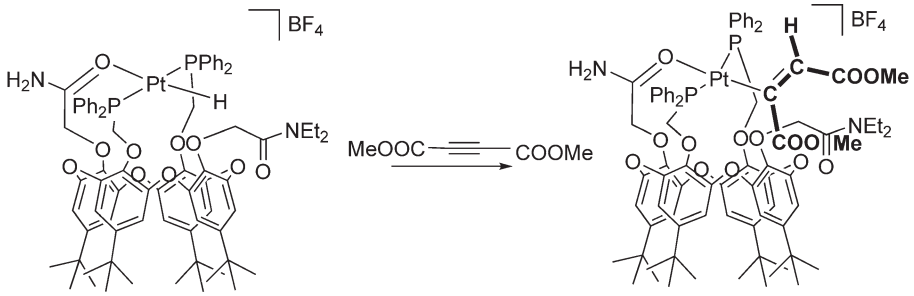


169

8.08.3.2 Alkenylplatinum(II) Complexes

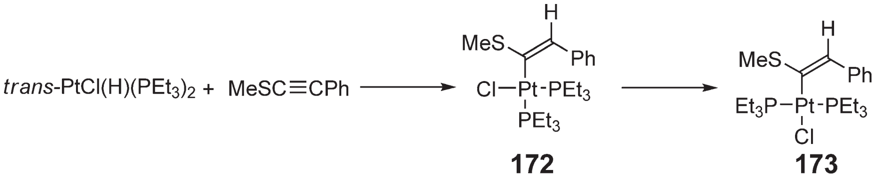
Insertion of an alkyne into a Pt–H bond provides a convenient route to alkenylplatinum(II) complexes. Dimethyl acetylenedicarboxylate reacts with a cationic hydridoplatinum complex with two phosphine donors bonded to a calixarene **170** to produce the alkenyl complex **171** formed via insertion of the C≡C triple bond (Equation (41)).[181] Partial dissociation of a labile amide ligand facilitates *cis–trans*-isomerization of the square-planar intermediate. The intermediate with hydrido and π-coordinated alkyne ligands at *cis*-positions induces facile insertion, giving the alkenylplatinum complex, followed by its isomerization to the *trans*-structure.



170 **171**

(41)

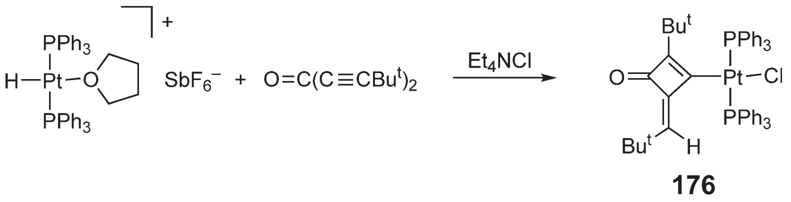
Change of the configuration of the complex is observed during insertion of alkynylthioether into the Pt–H bond of *trans*-PtCl(H)(PEt$_3$)$_2$, giving a 1-methylthiostyrylplatinum complex with a chloro ligand (Equation (42)).[182] The reaction gives the complex with a *cis*-structure **172** initially, and subsequent isomerization occurs to give the thermodynamically more stable *trans*-isomer **173**.



(42)

Structures of the complexes suggested formal *trans*-addition of Pt–H bond to the C≡C bond during the reaction. A detailed study of the reaction of phenylacetylene with *trans*-$PtH(SPh)(PPh_3)_2$ showed formation of the complex with a *cis*-phenylethenyl ligand **174**, although another regioisomer **175** is formed under different conditions (Scheme 29).[183]

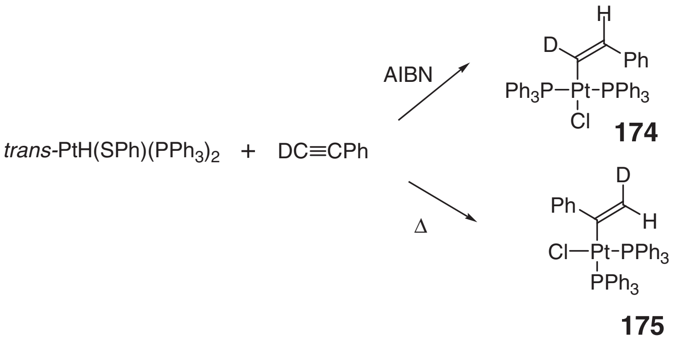
The *trans*-addition occurs without scrambling of hydrogen atoms. It is caused by radical species formed under the reaction conditions. Deprotonation of $[PtCl(\eta^2\text{-}CH_2{=}CHAr)(TMEDA)]ClO_4$ with NEt_3 forms the neutral alkenylplatinum complex $PtCl((E)\text{-}CH{=}CHAr)(TMEDA)$.[184] A dialkynylketone undergoes insertion into the Pt–H bond of a cationic Pt complex, followed by migration within the ligand to form the cyclobutenylplatinum complex **176** (Equation (43)).[185]



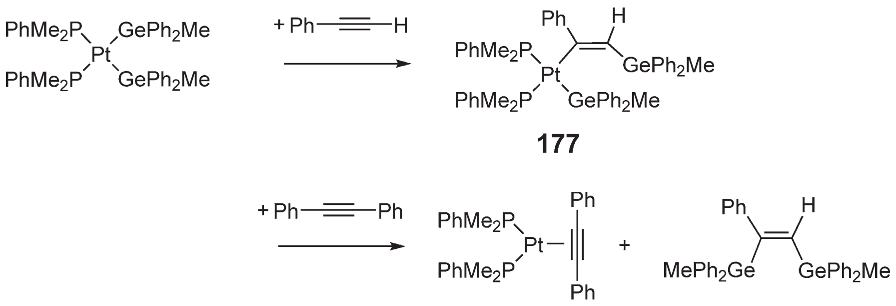
(43)

Insertion of an alkyne into Pt–Ge bonds also produces the alkenyl complex **177** (Scheme 30). The complex formed by normal *cis*-addition undergoes coupling of the alkenyl ligand and germyl ligands to release 1,2-digermylalkene.[186]

A methylplatinum complex having a cyclopropenylvinyl ligand **178** has been obtained by the transmetallation of the corresponding alkenyllithium compound with *trans*-$PtClMe(PEt_3)_2$.[187] Protonation of **178** causes rearrangement

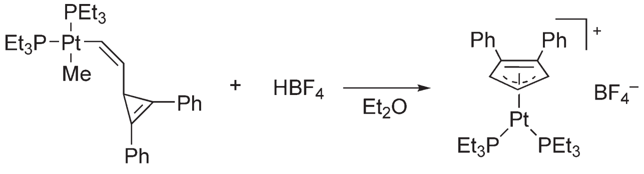


Scheme 29



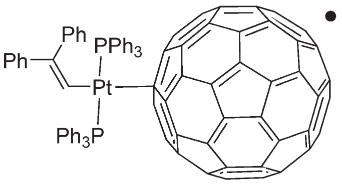
Scheme 30

of the strained ring of the ligand to produce the cationic η^3-cylopentadienylplatinum(II) complex **179** (Equation (44)), although HCl and carboxylic acid induce substitution of the methyl ligand of **178** only.

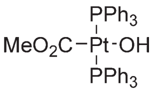


178 **179** (44)

An alkenylplatinum complex, **180**, which is able to support a C_{60} radical as the σ-bonded ligand, has been prepared by transmetallation using an organomercury compound.[188] The complex with carbomethoxy and hydroxy ligands *trans* disposed **181** has been obtained and characterized.[189]

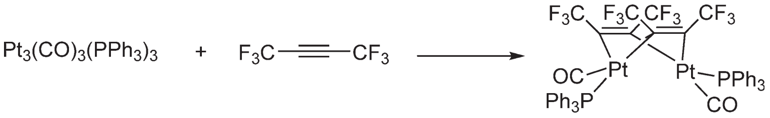


180



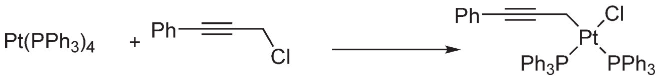
181

Reaction of hexafluoro-2-butyne with $Pt_3(CO)_3(PPh_3)_3$ forms a dinuclear complex with two bridging dialkenyl ligands **182** (Equation (45)), although, depending on the conditions, the reaction is also able to produce a dinuclear complex with alkyne ligands π-bonded to the two Pt centers.[190]

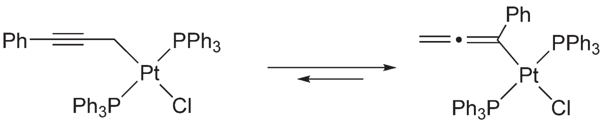


182 (45)

Since a propargyl group can be isomerized into an allenyl group via 1,3-transfer of a CH_2 hydrogen or alkyl group bonded to an unsaturated carbon atom, propargylplatinum complexes exhibit unique reactivities. Oxidative addition of propargyl chloride to $Pt(PPh_3)_n$ ($n = 3, 4$) forms the *cis*-chloro(propargyl)platinum complex with PPh_3 ligands (**183**, Equation (46)).[191] The reaction involves coordination of the C≡C triple bond to the Pt(0) center as the rate-determining step. The *trans*-chloro(propargyl)platinum complex **184** is equilibrated with the allenyl complex **185** (Equation (47)) via a diplatinum intermediate.[192,193]

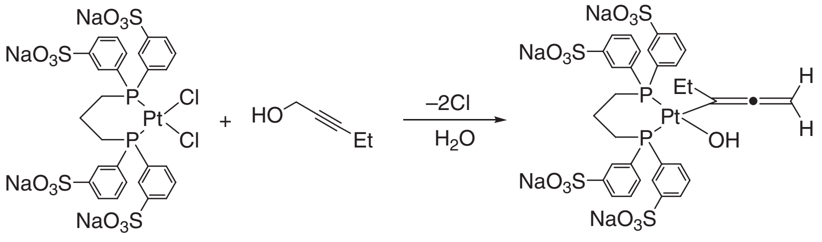


183 (46)



184 **185** (47)

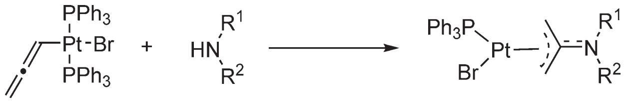
The propargylplatinum complex *trans*-$PtBr(CH_2C{\equiv}CPh)(PPh_3)_2$ reacts with PMe_3 to yield the allenylplatinum complex $[Pt(CPh{=}C{=}CH_2)(PMe_3)_3]^+Br^-$.[194] A water-soluble Pt complex reacts with propargyl alcohol to afford the allenylplatinum complex **186** (Equation (48)).[195] The reaction is related to the mechanism of hydration of propargyl alcohol.



186

(48)

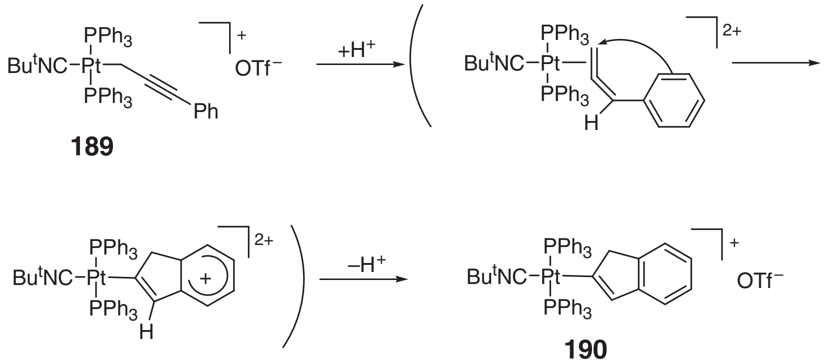
The allenylplatinum complex **187** undergoes nucleophilic reaction of amine at the central carbon of the ligand to form a complex with the azatrimethylenemethane ligand (**188**, Equation (49)).[196]



187 **188**

(49)

Protonation of a propargyl platinum complex **189** causes cyclization of the ligand accompanied by migration of the hydrogen to afford the κ^1-indenylplatinum complex **190** (Equation (50)).[197] The mechanism is proposed to involve initial formation of the intermediate having a π-coordinated allene, cyclization via intramolecular attack by the phenyl group of the ligand, and deprotonation, giving the complex with a π-conjugated ligand.

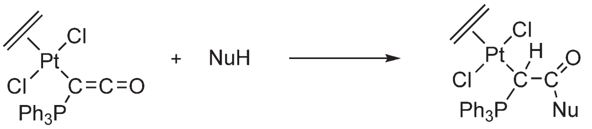


189

190

(50)

A neutral complex with the $Ph_3PC{=}C{=}O$ ligand **191** undergoes addition of secondary amine and alcohols to give **192** (Equation (51)), similar to the cationic methylplatinum complex (Scheme 25). A bis(ketenyl)platinum(II) complex is also formed.[198]

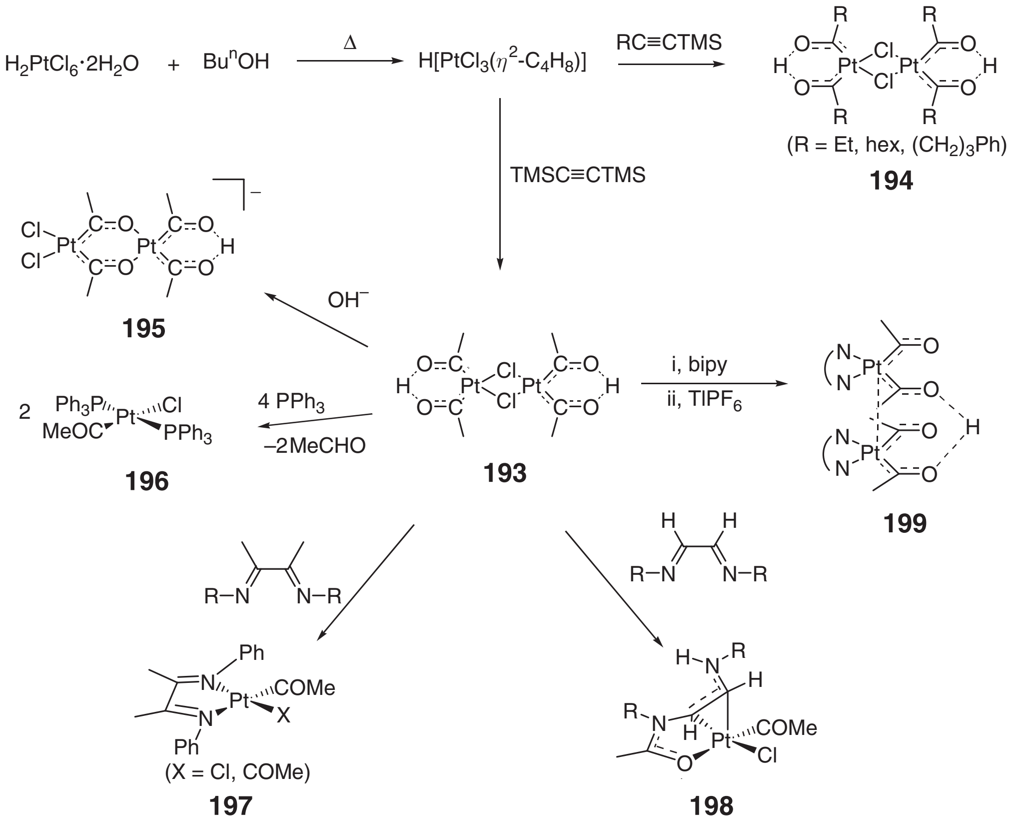


191 Nu = NMe$_2$, MeO, EtO **192**

(51)

Dinuclear platina–β-diketones **193** and **194** are prepared from H_2PtCl_6, trimethylsilylacetylenes, and *n*-BuOH, and the dimeric structure with bridging chloro ligands has been confirmed by X-ray crystallography.[199,200] Scheme 31 summarizes reactions of **193** toward organic reagents.

Reaction of NBu_4OH with **193** forms anionic complex **195** in which two Pt centers are bridged by two acetyl ligands;[201] PPh_3 induces elimination of acetaldehyde from **193** to form the chloro(acyl)platinum complex **196**.[202] Reaction of 1,4-diaza–1,3-butadiene with Me groups at the imine carbon forms chloro(acetyl)platinum(II) and diacetylplatinum complexes **197**, depending on the kind of *N*-substituents.[203] The ligand without an Me group forms **198** with a pentacoordinated Pt center bonded with a chelating ligand, formed via acetylation of one of the imino groups. Reaction of bipy with **193** followed by addition of $TlPF_6$ produces a cationic dimer complex **199** containing O–H···O bond and Pt···Pt interaction between the two platina-β-diketone fragments.[204]



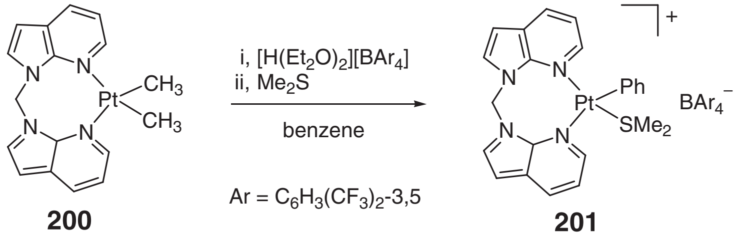
Scheme 31

8.08.3.3 Arylplatinum(II) Complexes

8.08.3.3.1 Preparation and structure

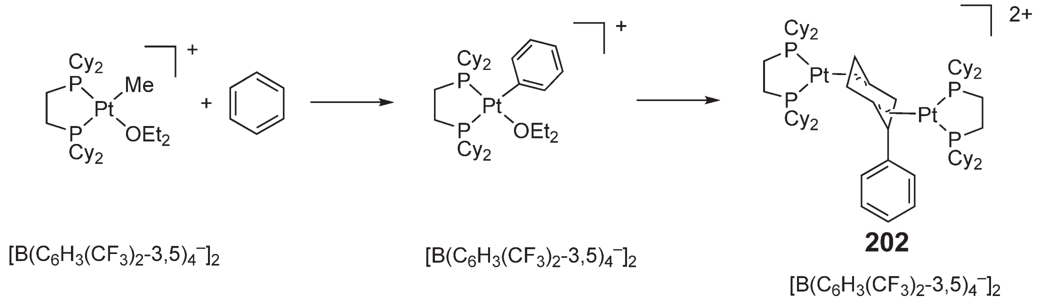
Most of the preparative reactions of arylplatinum complexes, such as oxidative addition of organic halides, transmetallation, and exchange of the auxiliary ligands, are common to those of alkylplatinum complexes. Aromatic C–H bond activation promoted by Pt(0) and Pt(II) complexes is the unique preparation method of arylplatinum complexes. Cationic methylplatinum(II) complexes with *N*-ligands promote C–H activation of aromatic hydrocarbons to form cationic arylplatinum complexes, as mentioned in Section 8.08.3.1.3.

Bis(N^7-azaindolyl)methane-coordinated complexes have been prepared and fully characterized,[205] and addition of $[H(OEt_2)_2]^+$ to the dimethylplatinum(II) complex **200** forms the cationic methylplatinum complex with the ligand, whereas the reaction in benzene forms the cationic phenylplatinum complex **201** via C–H bond activation of the solvent by the cation (Equation (52)).



(52)

Reaction of benzene with the cationic methylplatinum(II) complex of a chelating diphosphine affords the dinuclear cationic complex **202**, which formally contains a dianionic phenyl-substituted benzene ligand bonded to two Pt centers in π-allylic fashion (Equation (53)).

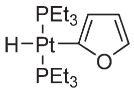


202

(53)

It has been proposed that the reaction involves C–H activation of benzene and intermolecular coupling of the phenyl ligands of the cationic monophenylplatinum(II) intermediate.[206] Protonation of **202** by HCl or oxidation by I_2 releases biphenyl. A monomethylplatinum(II) complex with an anionic diphosphine ligand containing a borate group and a THF ligand **203** also reacts with benzene at 50 °C to produce the cationic phenylplatinum complex **204** via C–H activation of benzene (Scheme 32).[207,208] Gradual disproportionation of **204** yields a mixture of an anionic diphenyl complex and a cationic complex with two THF ligands. A cationic methylplatinum complex **205**, having an $SiPh_2$ group instead of the BPh_2 group of **203**, also reacts with benzene to form the cationic phenylplatinum complex **206**, which is gradually converted into a dinuclear complex with biphenyl as a bridging bis-π-allyl ligand **207**.

Oxidative addition of C–H bonds to Pt(0) is utilized in the preparation of arylplatinum complexes. Furan, benzoxazole, and benzothiazole react with $Pt(PEt_3)_4$ to cause selective oxidative addition of a C–H bond, giving hydrido(aryl)platinum complexes **208–210**.[209]



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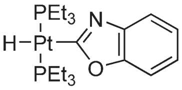

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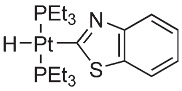

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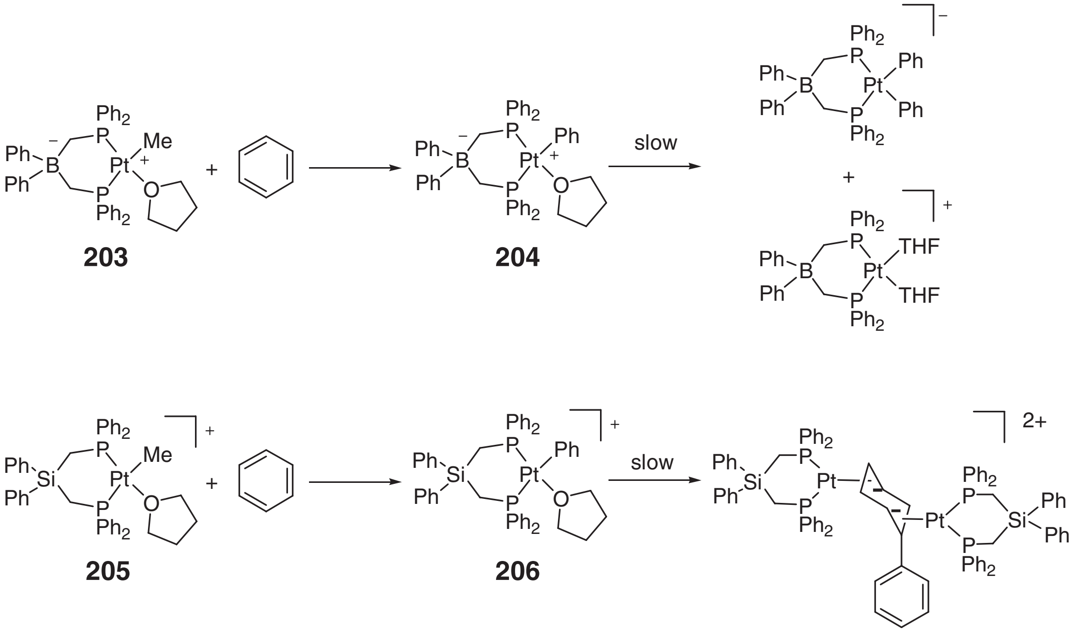
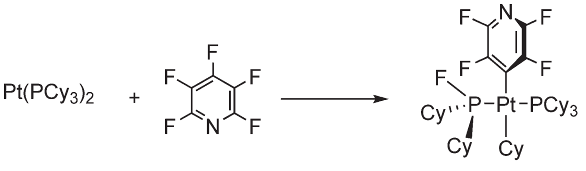


Scheme 32

$Pt(PCy_3)_2$ promotes C–F bond activation of perfluoropyridine in THF to produce a 2,3,5,6-tetrafluoropyridyl-platinum complex with a $PFCy_2$ ligand and a cyclohexyl ligand, **211**, via transfer of the cyclohexyl group from P to Pt (Equation (54)).[210] In hexane, the reactions of perfluoropyridine and of 2,3,5,6-tetrafluoropyridine form a hydrido(tetrafluoropyridyl)platinum(II) complex via C–H bond activation of the substrate or solvent.

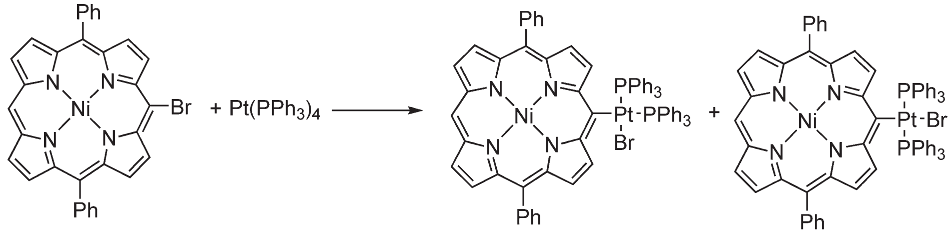


211

(54)

DFT calculations for oxidative addition of pentafluorobenzene to $Pt(H_2PCH_2CH_2PH_2)$ compared two reaction pathways involving cleavage of the C–F or C–H bond.[211] A hydrido(pentafluorophenyl)platinum complex formed via C–H bond activation and a fluoro(tetrafluorophenyl)platinum complex via C–F bond activation are the kinetic and thermodynamic products, respectively. This tendency contrasts with the reaction of $Ni(H_2PCH_2CH_2PH_2)$, which prefers to cleave the C–F bond over the C–H bond.

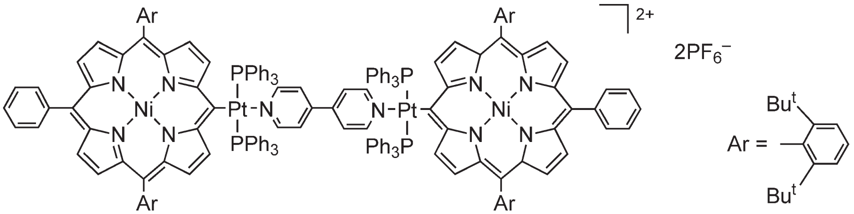
The Pt(II) complexes with an Ni-porphyrin directly bonded to Pt at the 5-position **212**, **213** are obtained from oxidative addition of a bromoporphyrin to $Pt(PPh_3)_4$ (Equation (55)).[212]



212 **213**

(55)

The dinuclear Pt complex with two porphyrin groups **214** is prepared by using 4,4′-bipy as the bridging ligand. Combination of the porphyrin–platinum(II) complex and metal-free porphyrin containing a pyridyl group at the 5-position enables preparation of multinuclear Pt complexes with three **215** and five **216** porphyrin units.[213,214]



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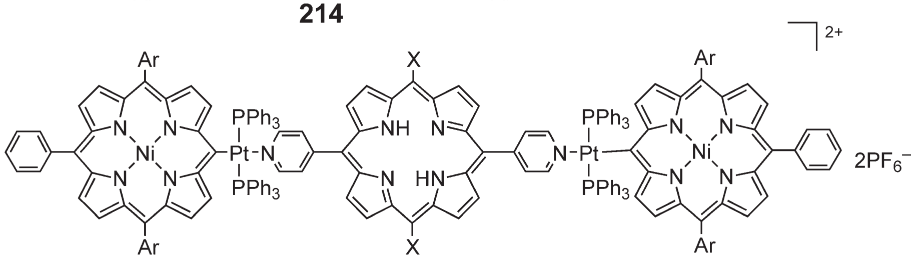
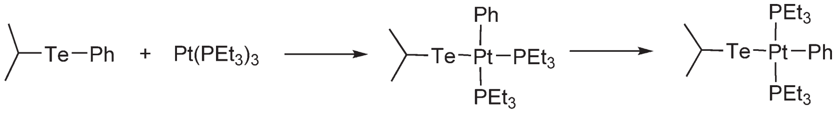


215: X =Tol
216: X = Ni-porphyrin

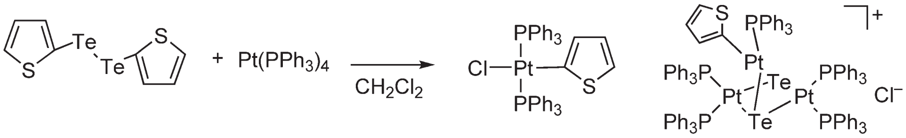
Diaryl telluride reacts with $Pt(PEt_3)_3$ to produce a complex with Pt–C and Pt–Te bonds as the oxidative addition products.[215] Phenyl(isopropyl)telluride forms the *cis*-phenyl(isopropyltellurido)platinum complex **217** as the kinetic product, which is isomerized into the *trans*-complex **218** (Equation (56)). Results of competitive oxidative addition of Ph_2Te and PhI suggest more facile reaction of the former substrate.



217 **218**

(56)

The reaction of dithienyl ditelluride with $Pt(PPh_3)_4$ in CH_2Cl_2 yields the chloro(thienyl)platinum(II) complex **219**, and a trinuclear Pt complex whose metal centers are bridged by two telluride ligands (**220**, Equation (57)).[216] Activation of the Te–Te and C–Te bonds takes place during the reaction.

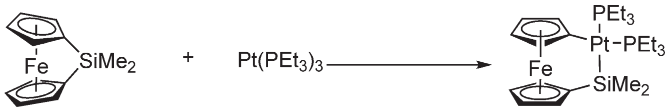


219 **220**

(57)

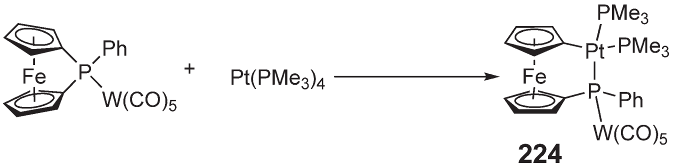
Reaction of chloro(triphenyl)tin with $Pt(cod)_2$ forms the phenylplatinum complex with a chlorodiphenylstannyl ligand **221** via oxidative addition (Scheme 33).[27] It contrasts with the reaction of chloro(trimethyl)tin, which results in cleavage of the Cl–Sn bond to afford the product without a Pt–C σ-bond **222**.

Oxidative addition of small-membered cyclic molecules is enhanced by release of the ring strain caused by the reaction. Sila[1]-ferrocenophane and phospha[1]-ferrocenophane having a $W(CO)_5$ substituent at the P atom react easily with Pt^0–PR_3 complexes to give the product of oxidative addition of the C–Si and C–P bonds accompanied by ring expansion (**223** and **224**, Equations (58) and (59)).[217,218] This type of complex is employed as the initiator of ring-opening polymerization of sila[1]-ferrocenophane.[219]



223

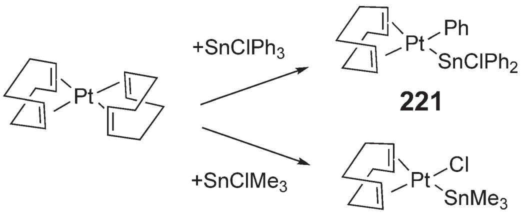
(58)



224

(59)

Transmetallation, involving intermolecular transfer of the aryl ligand, also provides convenient routes for synthesis of arylplatinum(II) complexes. Reactions of 2-methoxyphenyllithium with Pt complexes having optically active diphosphines, DIOP, BINAP, and chiraphos, produce the corresponding diarylplatinum complexes.[220] NMR spectra show the presence of isomers due to restricted rotation around the Pt–C bond of the 2-methoxyphenyl ligand. Anionic

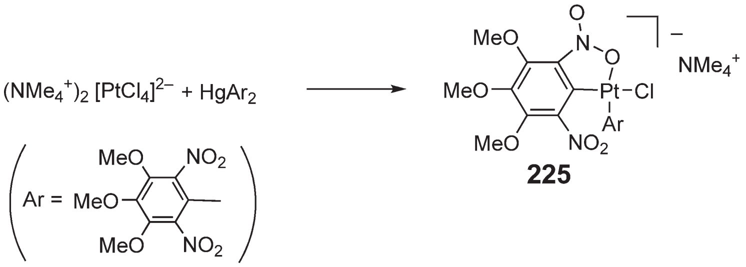


221

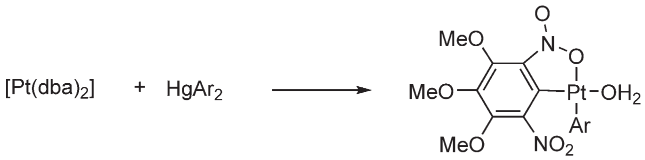
222

Scheme 33

and neutral platinum(II) complexes with 2,6-dinitro–3,4,5-trimethoxyphenyl ligands **225** and **226** have been obtained from the reaction of the diarylmercury with $[PtCl_4]^{2-}$ or with $Pt(dba)_2$ (Equations (60) and (61)).[221,222] One of the aryl ligands of the complex coordinates to the Pt center through a nitro group at the *ortho*-position. Pt–Hg binary complexes with and without a Pt–Hg bond have also been prepared and fully characterized.



(60)

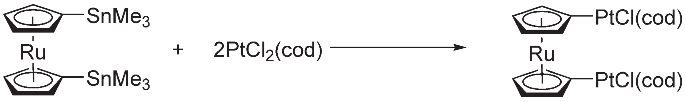


226

(61)

The chloro(phenyl)platinum(II) complex with SMe_2 ligands **227** is obtained by heating the cationic chloroplatinum(II) complex with BPh_4^- counteranion, and by addition of triphenyltin hydride to $PtCl_2(SMe_2)_2$ (Scheme 34).[223] These reactions involve activation of the Ph–B and Ph–Si bonds and formation of a Pt–Ph bond.

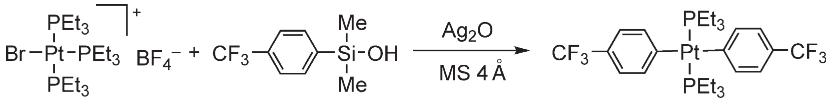
Transmetallation of 1,1′-bis(trimethylstannyl)ruthenocene **228** with PtCl$_2$(cod) has been employed for the preparation of a dinuclear platinum complex with a bridging ruthenocene–diyl ligand (**229**, Equation (62)).[224]



228 **229**

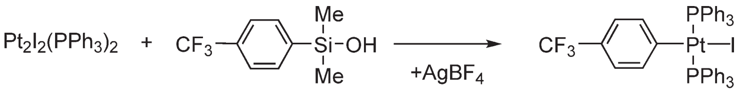
(62)

Transmetallation of arylsilanol with Pt complexes also produces arylplatinum complexes. The cationic bromoplatinum(II) complex with PEt_3 ligands is converted into the diarylplatinum complex **230** by the reaction with arylsilanol in the presence of Ag_2O (Equation (63)),[225] while the reaction of arylsilanol with $PtI_2(PPh_3)_2$ in the presence of $AgBF_4$ leads to the aryl(iodo)platinum complex **231** (Equation (64)).[226] $AgBF_4$ activates the Pt–I bond in the reaction; Ag_2O in the former reaction probably activates both the Pt–Br and B–C bonds.



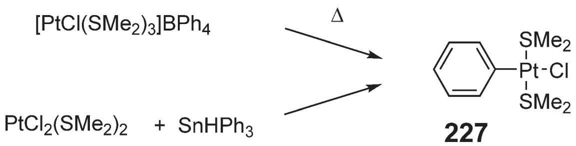
230

(63)



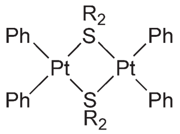
231

(64)



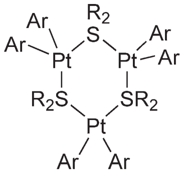
Scheme 34

Ligand exchange is another important method to convert reported arylplatinum(II) complexes into new ones, and $[PtAr_2(\mu\text{-}SMe_2)]_n$ is a convenient precursor of diarylplatinum complexes with various auxiliary ligands.[227,228] A crystallographic study of the complex revealed both dinuclear and trinuclear structures with bridging SMe_2 ligands in the solid state **232** and **233**, although $[PtMe_2(\mu\text{-}SMe_2)]_2$ has a dinuclear structure only **234**.



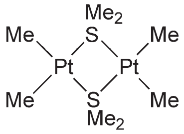
R = Me, Et

232



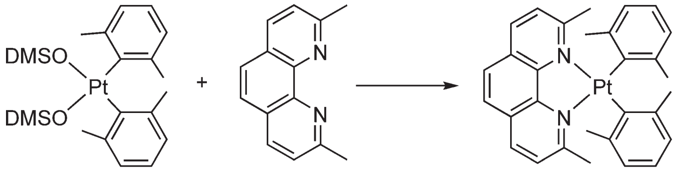
R = Me, Et
Ar = Ph, Tol

233



234

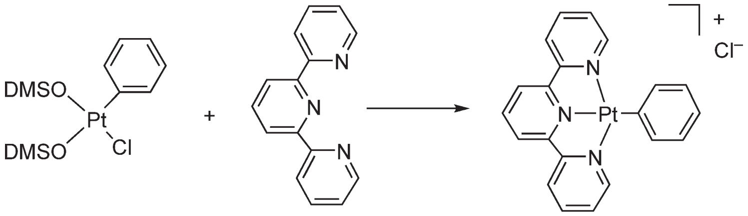
Ligation of the bidentate *N,N*-, *P,P*-, and *P,S*-ligands to *cis*-$PtPh_2(CO)(SEt_2)$ has been studied using kinetic measurements of the reaction.[229,230] Dimesitylplatinum(II) complexes with phenanthroline derivatives, for example, **235**, have been prepared from the reaction of the ligand with $Pt(Mes)_2(DMSO)_2$ (Equation (65)).[231,232]



235

(65)

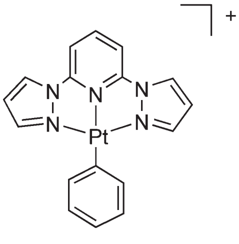
The complexes undergo reversible one-electron reduction to form the radical anion species, which were characterized by absorption spectra and EPR spectra at multi-frequency.[233] Bis(mesityl)platinum complexes with π-conjugated diimine ligands show emission behavior.[234] Substitution of DMSO ligands of $PtClPh(DMSO)_2$ with terpy forms a cationic phenylplatinum complex **236** (Equation (66)).[235]



236

(66)

The cationic complexes with 2,6-bis(*N*-pyrazolyl)pyridine as ligand, **237** and **238**, have been prepared by a similar method.[236] A dinuclear complex with bridging SEt_2 ligands and four biphenyl ligands **239** exists as a mixture of stereochemical atropisomers.[237]



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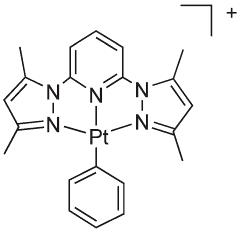

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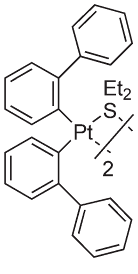
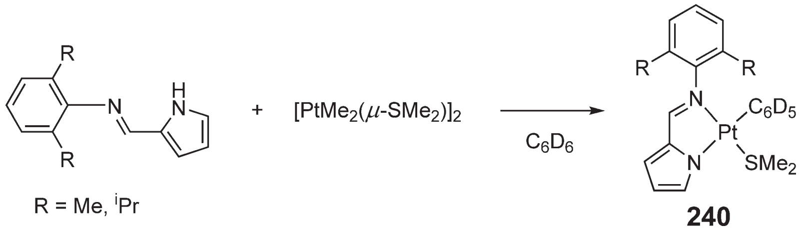


239

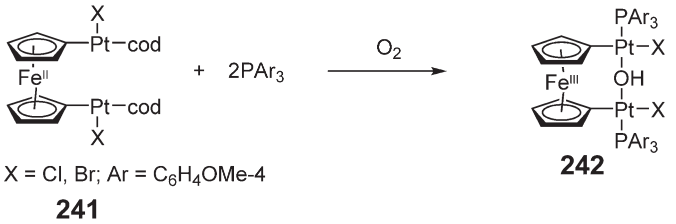
A bidentate ligand with a 2,6-disubstituted aryl group at the imine nitrogen reacts with $[PtMe_2(\mu\text{-}SMe_2)]_2$ in C_6D_6 (Equation (67)).[41] The initially formed methylplatinum(II) complex causes C–D bond activation of the solvent to afford the deuterated phenylplatinum complex **240**. The ligand without the substituents at 2- and 6-positions gives the methylplatinum complex **18**, as mentioned in the previous section.



240

(67)

Addition of tris(*p*-methoxyphenyl)phosphine to the dinuclear Pt(II)–cod complex with a bridging 1,1′-ferrocenylene ligand **241** produces a paramagnetic Pt–phosphine complex with a bridging hydroxo ligand (**242**, Equation (68)).[238] Oxidation of the Fe center by air and coordination of the OH ligand, formed from water impurity, take place during the reaction.

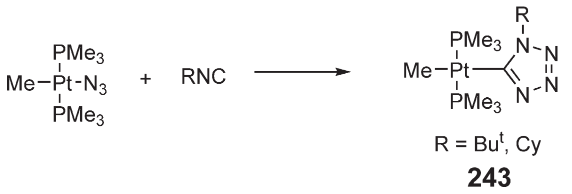


241 **242**

(68)

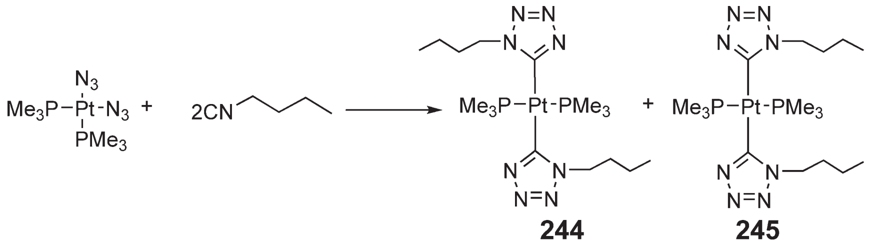
PtPh$_2$(cod) is employed as the precursor of the diphenylplatinum(II) complex with dppf.[239]

The azide ligand of a PMe$_3$ complex reacts with isonitrile to form a complex with *C*-coordinated tetrazolate rings (**243–245**, Equations (69) and (70)).[240,241] Insertion of isonitrile into the Pt–N bond is followed by cyclization via intramolecular nucleophilic attack at the coordinated carbon atom. Since the tetrazolato ring is perpendicular to the square-planar coordination plane, the *trans*-complex with two 5-alkyltetrazolate ligands exists as a mixture of isomers with the alkyl substituents in *syn*- and *anti*-orientations **244** and **245**.



243

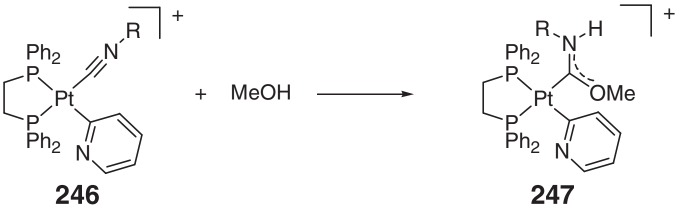
(69)



244 **245**

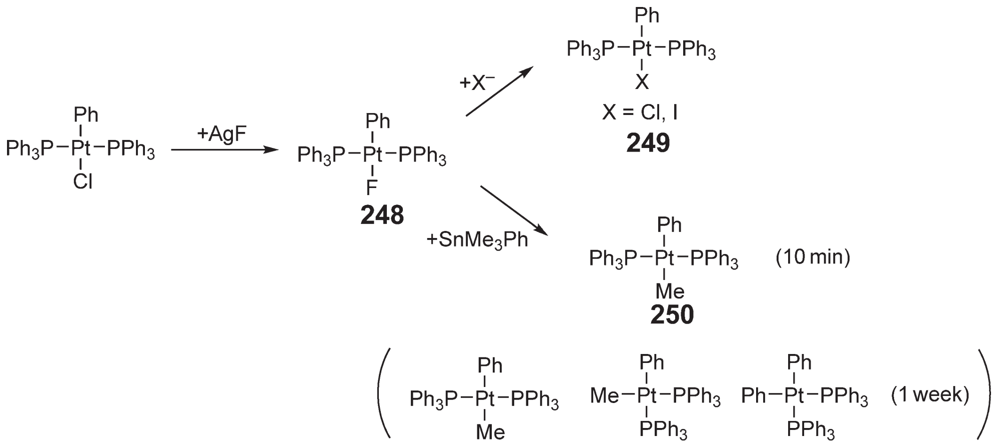
(70)

The cationic 2-pyridylplatinum(II) complex with isonitrile and dppe ligands **246** also undergoes nucleophilic addition of methanol to the coordinated isonitrile, giving a complex with a carbene ligand (**247**, Equation (71)).[242,243]



246 **247**

(71)

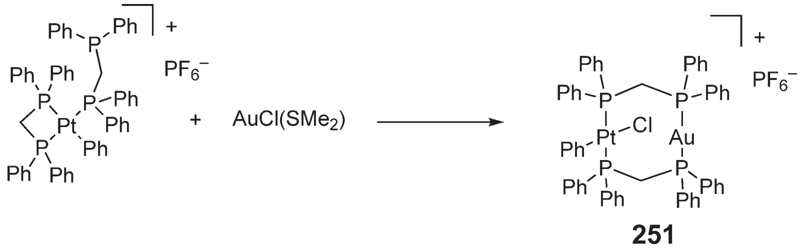


Scheme 35

Protonation of the complexes *cis*-PtAr(Me)(PEt$_3$)$_2$ (Ar = Ph, *p*-Tol) occurs selectively at the methyl ligand to yield cationic aryl complexes. The mechanism of the reaction has been studied kinetically.[244]

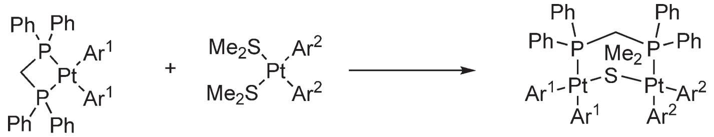
Fluoro(phenyl)platinum(II) complexes with PPh$_3$ and PMe$_2$Ph ligands are obtained from the reaction of AgF with chloro(phenyl)platinum(II) complexes.[245] *trans*-PtF(Ph)(PPh$_3$)$_2$ **248** undergoes exchange of the fluoro ligand on addition of Cl$^-$ and I$^-$ to produce the corresponding halo(phenyl)platinum complex **249** (Scheme 35). Kinetic studies revealed the existence of the associative and dissociative pathways via a cationic intermediate with solvent as ligand for the exchange of the fluoro ligand. Transmetallation of SnMe$_3$Ph with **248** occurs easily, yielding **250**, which is converted gradually into the *cis*-isomer and a diphenyl complex.

The ligand dppm is able to coordinate to a single transition metal and to two metal centers via bridging. A diphenyldiplatinum–dppm complex with an A-frame structure was fully characterized.[246] A cationic phenylplatinum complex with κ^2- and κ^1-bonded dppm ligands reacts with Au(I), Ag(I), and Hg(II) compounds to form the heterodinuclear complexes whose metal centers are bridged by two dppm ligands, for example, **251** (Equation (72)).[247] Rotation of the Ph–Pt bond occurs easily, induced by dissociation of the Cl$^-$ ligand. The reaction of a mononuclear diarylplatinum complex of dppm with diarylplatinum–SMe$_2$ complexes affords dinuclear phenylplatinum complexes with bridging dppm and SMe$_2$ ligands.[248] By choosing starting complexes with different aryl ligands, the dinuclear complex with an unsymmetrical structure **252** has been prepared (Equation (73)).



251

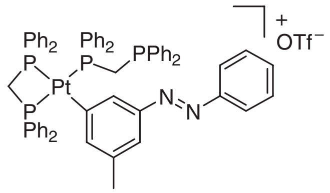
(72)



252

(73)

A mononuclear cationic platinum complex **253** contains two dppm ligands and an azobenzene-containing aryl ligand.[249] Monophenyl complexes with phosphine ligands **254–256** have also been prepared and characterized.[250–252]



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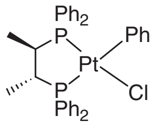

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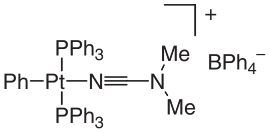

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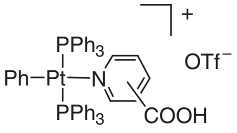
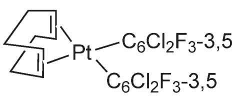


256

8.08.3.3.2 Halogenoaryl complexes

Polyhalogenophenyl ligands form stable coordination bonds with late transition metals, and the pentafluorophenyl group is widely employed as a ligand for platinum complexes. Since the Pt–C_6F_5 bond is stable and inert to coupling and insertion, they are often employed as spectator ligands. The electron-withdrawing ligands stabilize not only neutral complexes but also mono- and dianionic platinate complexes. The anionic part containing these ligands is included in a number of polymetallic complexes. The platinum complexes with 3,5-dichloro–2,4,6-trifluorophenyl ligands and weak auxiliary ligands such as cod, THF, and SMe_2 **257–259** have been prepared and characterized.[253] These complexes are employed as precursors for the synthesis of diarylplatinum complexes with stronger donor ligands.



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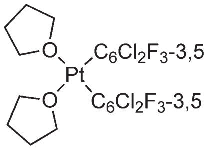

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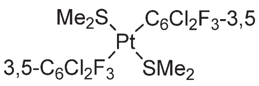
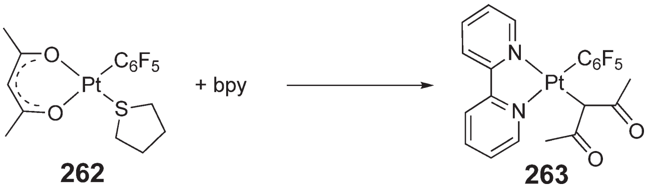


259

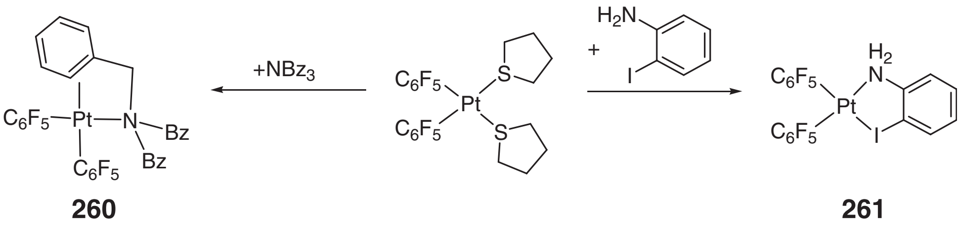
^{19}F NMR of bis(3,5-dichloro–2,4,6-trifluorophenyl)platinum complexes with donor ligands provide a useful tool to study the structure and dynamic behavior of complexes.[254] The bis(pentafluorophenyl)platinum complex with tetrahydrothiophene ligands reacts with tribenzylamine to form the complex whose amine ligand is bonded by a nitrogen atom and by a C=C double bond of a phenyl group (**260**, Scheme 36).[255] Fluxional behavior observed by NMR spectroscopy is attributed to switching of the coordinated C=C bond in the benzyl group. Reaction of 2-iodoaniline forms the complex with the *I,N*-chelating ligand **261**.[256]

A pentafluorophenylplatinum complex with an *O,O′*-chelating acac ligand **262** is converted into *C*-coordinated acac **263** upon reaction with bipy (Equation (74)).[257]

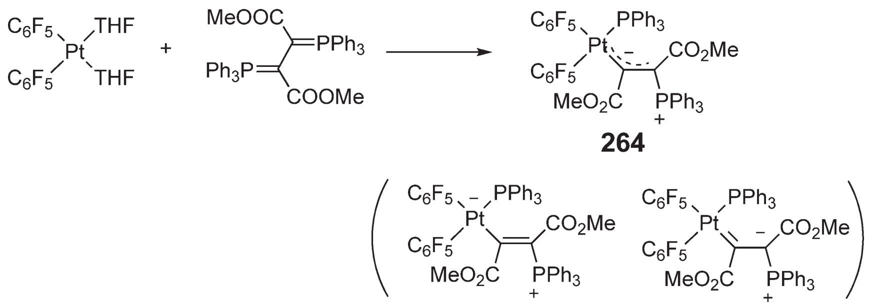


(74)

Reaction of a bis(phosphine)ylide with $Pt(C_6F_5)_2(THF)_2$ leads to formation of a complex with PPh_3 and ylide-carbene ligands **264** via cleavage of the P=C bond by the metal center (Equation (75)).[258]



Scheme 36



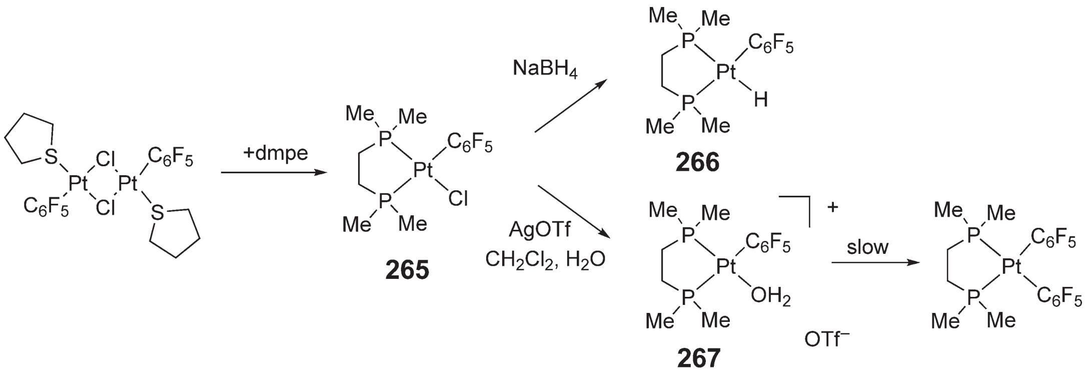
(75)

Platinum complexes with a pentafluorophenyl ligand and dmpe ligand have been prepared from tetrahydrothiophene complexes.[259] Chloro(pentafluorophenyl)platinum complex **265** has been hydrogenated to form the hydrido(pentafluorophenyl)platinum complex **266** (Scheme 37). A cationic monoaryl complex with an aqua ligand **267** is stable in solution, although it slowly changes to the diaryl complex, probably via disproportionation.

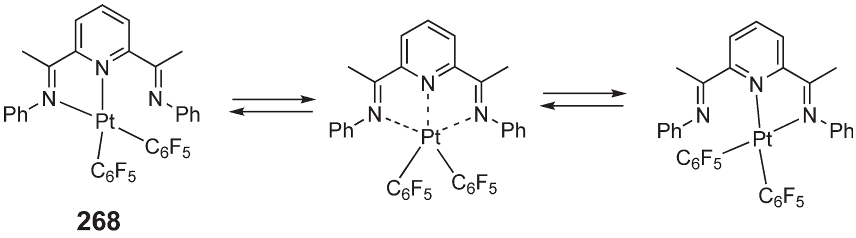
Unsymmetrically substituted terpy and 2,6-diiminopyridine occupy two coordination sites of square-planar Pt complexes with two pentafluorophenyl ligands as a bidentate ligand.[260–262] NMR spectra of **268** indicate fluxional behavior of the complex, which is ascribed to change of the coordination sites via an associative intermediate (Scheme 38).

LDA and LiBu^t promote deprotonation of the PCH_2 group of $Pt(C_6F_5)_2$(dppm) **269** to afford the complex with a carbanion center within the ligand (**270**, Scheme 39).[263] The anionic complex is stabilized by the electron-withdrawing aryl ligands, but reacts with alkyl halides to cause alkylation of the ligand, for example, **271**. The anionic ligand undergoes C–F bond activation of pentafluorobenzonitrile to form **272** and coordination to an Au(I) center, giving a Pt–Au binary complex **273**.

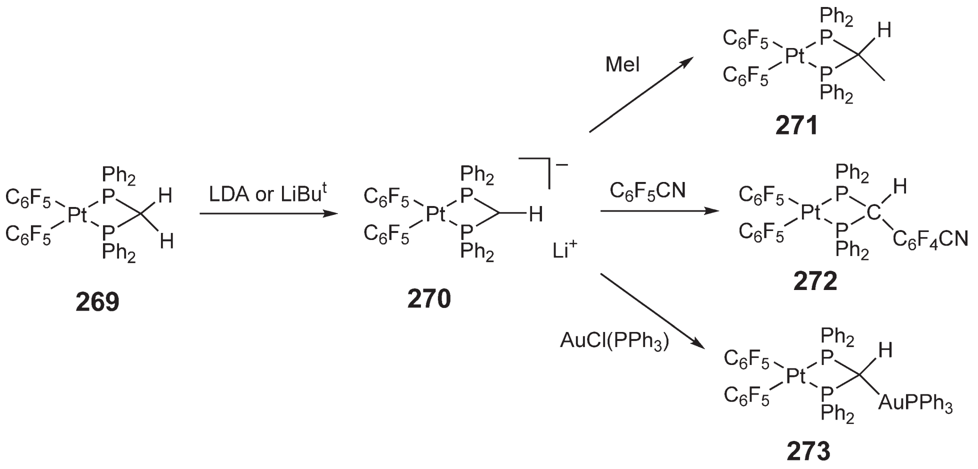
Reaction of bis(pentafluorophenyl)chloroborane with a Pt(0)–PPh_3 complex forms a Pt complex with a pentafluorophenyl ligand **274** via transfer of the aryl group from B to Pt (Equation (76)).[264]



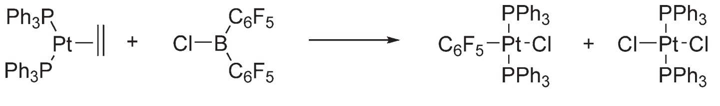
Scheme 37



Scheme 38

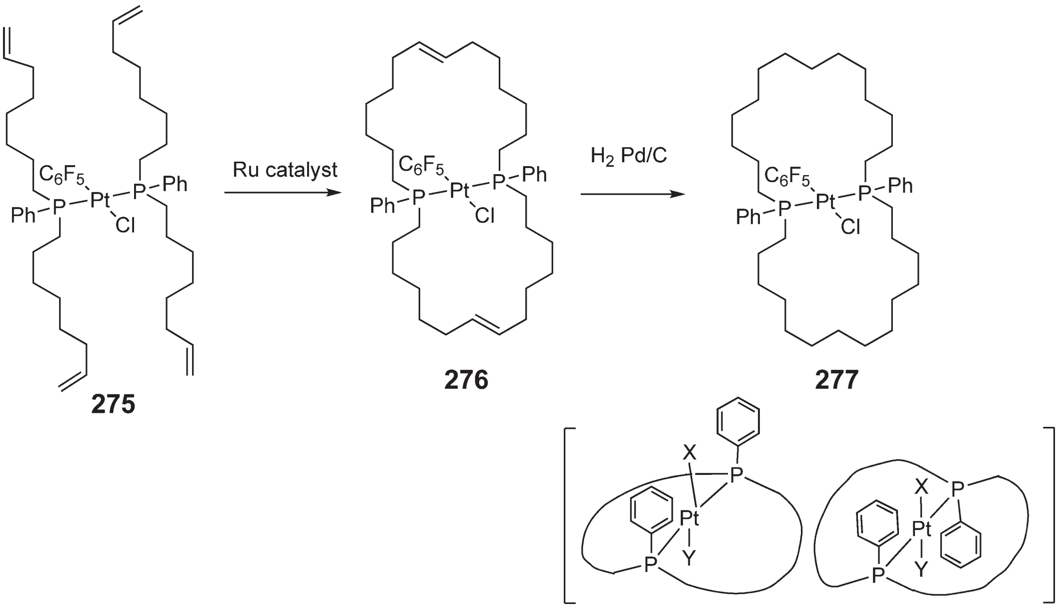


Scheme 39

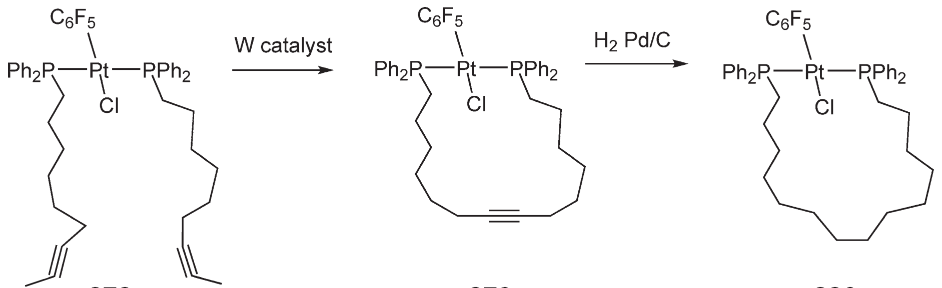


274 (76)

trans-Chloro(pentafluorophenyl)platinum complexes with two phosphine ligands, having long polymethylene linkers, were prepared by bond-forming reactions between the substituents of the two phosphine ligands. A metathesis reaction of the Pt complex **275** with two phenyldi(7-octenyl)phosphines at *trans*-positions catalyzed by Ru–carbene complexes produces **276**. Hydrogenation of the C═C bond of the complex by using a Pd–C catalyst leads to a complex with two macrocyclic rings containing the P–Pt–P linkage (**277**, Scheme 40).[265–267] The metathesis reaction forms mononuclear complexes rather than dinuclear complexes via intermolecular bond formation. Each stereoisomer of the complexes with a saturated ring of the ligands has been isolated and fully characterized.



Scheme 40

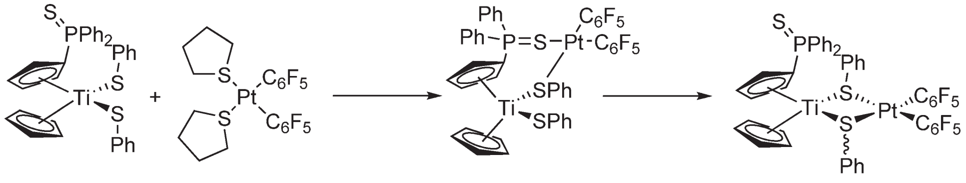


278 **279** **280**

Scheme 41

The chloro(pentafluorophenyl)platinum complex having two *trans*-phosphine ligands with alkyne-containing substituents **278** undergoes cyclization via metathesis of the alkyne by $W(OBu^t)_3(CBu^t)$ to produce a macrocyclic complex with a C≡C bond **279**, which may be hydrogenated to give a complex with a saturated ring, **280** (Scheme 41).[268]

Bis(benzenethiolato)titanocene functions as the metallaligand of a platinum complex with two pentafluorophenyl ligands (**281**, Equation (77)), and the Mo–Ti–Pt ternary complex **282** has been prepared by using a Ti–Mo dinuclear precursor with bridging diphenyl(cyclopentadienyl)phosphine (Equation (78)).[269–272]



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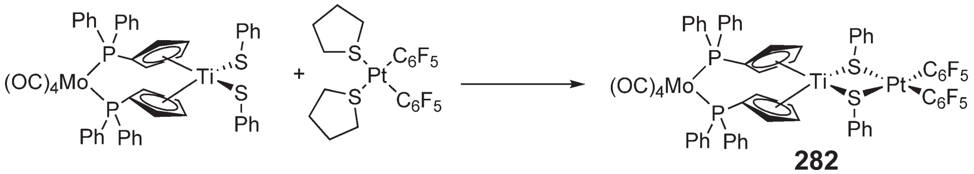
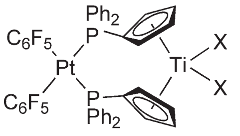


(78)

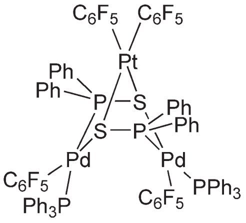
282

A Ti–Pt complex with a bridging diphenyl(cyclopentadienyl)phosphine ligand **283** has also been prepared.[273] The $Pt(C_6F_5)_2$ group is able to bond to the two sulfur atoms of Pd_2 and Pt_2 fragments to form Pd_2Pt and Pt_3 complexes bridged by S atoms **284** and **285**, respectively.[274,275]



X = Cl, SPh

283



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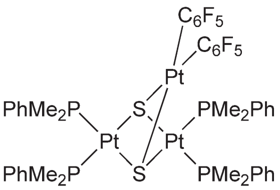
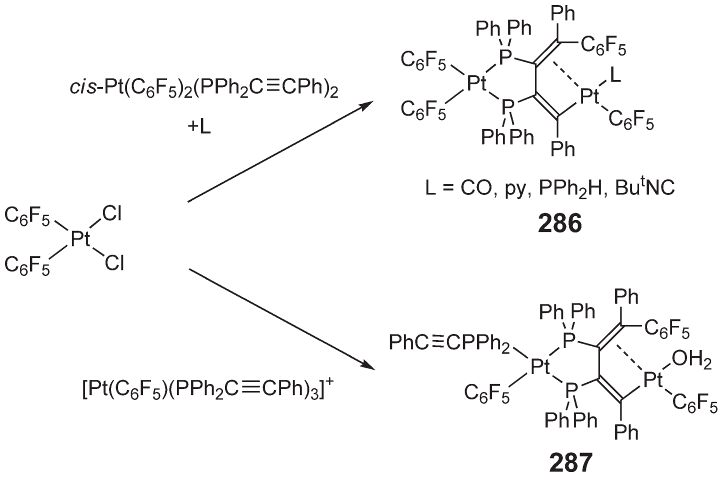


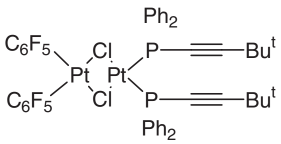
285

Diplatinum complexes **286** and **287**contain a vinylated diphosphine, which coordinates to a $Pt(C_6F_5)_2$ fragment via a chelating diphosphine, and to a $Pt(C_6F_5)(L)$ fragment via a 1,3,4-butadienyl group (Scheme 42).[276,277]

The $Pt(C_6F_5)_2$ fragment is also able to form dinuclear complexes having diphenyl(*t*-butylethynyl)phosphine as monodentate and bridging ligands **288** and **289**.[278]



Scheme 42



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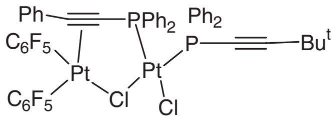
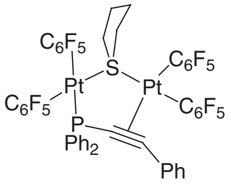


289

Diphenyl(phenylethynyl)phosphine binds the $Pt(C_6F_5)_2$ group to Ru or Pt centers as a σ,π-bifunctional ligand to form Pt–Ru and Pt–Pt complexes. A dinuclear Pt complex containing two tetracoordinate Pt(ii) centers **290**, and one with a Pt(ii) and a tricoordinated Pt(0) center **291**, have been obtained.[279,280] Isomeric Pt–Ru heterobimetallic complexes **292** and **293** have bridging and non-bridging $PPh_2C{\equiv}CPh$ ligands, respectively.[281]



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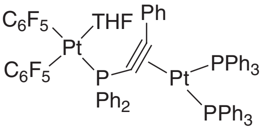

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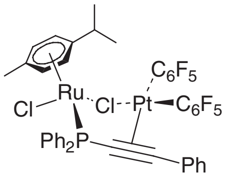

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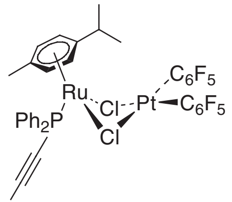
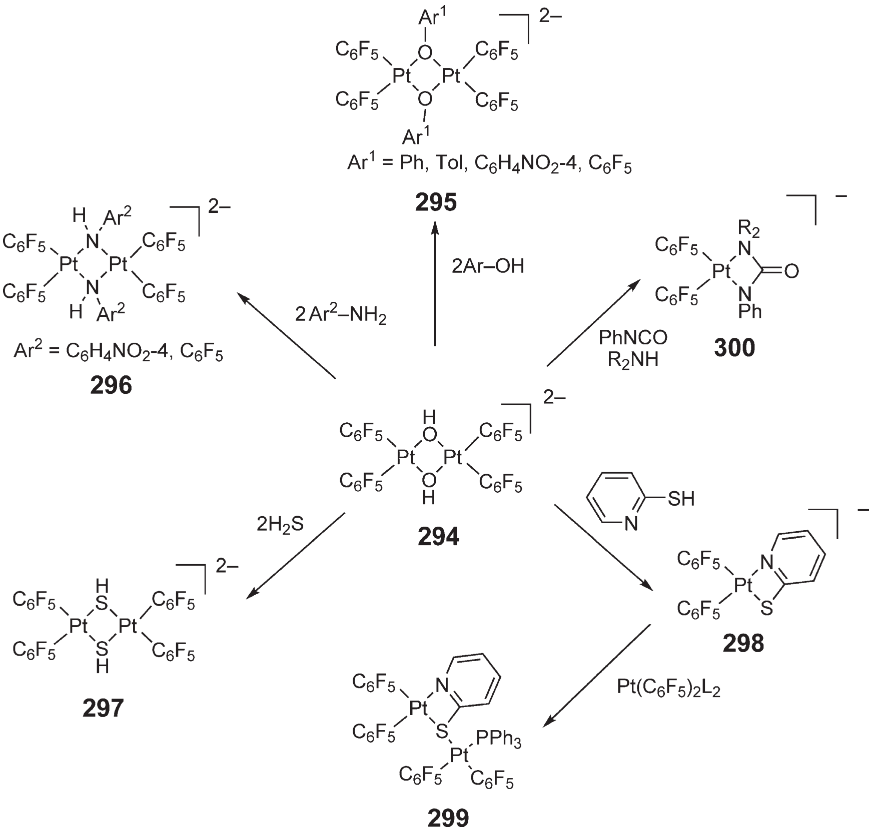


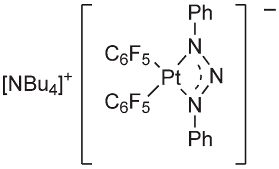
293

Homo- and heterodinuclear Pt complexes containing C_6F_5 ligands show unique reactivity. The complex with a xanthate ligand, $[Pt(C_6F_5)_2(S_2COEt)]^-$, has been prepared from the chloro-bridged dimer $[Pt(\mu\text{-}Cl)_2(C_6F_5)_2]_2^{2-}$.[282] Scheme 43 summarizes reactions of an easily accessible dinuclear Pt complex with bridging hydroxo ligands **294**. Addition of phenol derivatives converts **294** to the dinuclear aryloxo-bridged complex **295**, and then into the mononuclear anionic complexes with PPh_3 or CO as ligand.[283] The bridging hydroxo ligands of the dinuclear complex can be replaced by an arylamide ligand to yield the corresponding amide-briged complexes **296**.[284] The OH ligands are substituted by SH groups on addition of H_2S to form **297**.[285] Reaction of 2-pyridinethiol produces the complex with *N,S*-chelating ligands **298**, which further reacts with $Pt(C_6F_5)_2L_2$ to form dinuclear Pt complex **299**.[286,287] The reaction of a mixture of PhNCO and secondary amines with **294** produces a complex with a chelating urea ligand **300**.[288]

Anionic platinum complexes with pentafluorophenyl ligands have been prepared using various *N*- and *P*-ligands. Diaryl triazenide coordinates to a Pt center in an η^3-fashion to form a bis(pentafluorophenyl)platinum complex **301**.[289] Pentafluorophenyl ligands stabilize the anionic complex of a chelating β-iminoenolate ligand **302**.[290]



Scheme 43



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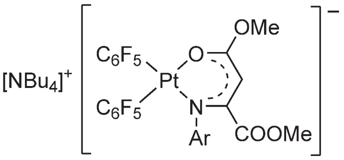
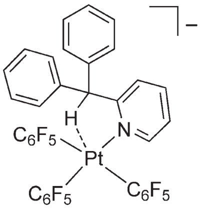


302

Anionic tris(pentafluorophenyl)platinum(II) complexes have been obtained with various amine ligands. Diphenyl(2-pyridyl)methane and 2-isopropylaniline coordinate through the nitrogen atom to the square-planar Pt center of 303 and 304.[291] Crystallographic results for 303 indicate Pt···H interaction of the *N*-ligand (Pt–H 265(7) pm), while the NMR spectra of the complex do not show such interaction in solution. Mono- and dinuclear complexes having non-chelating bipy or phen ligands 305 and 306 have been fully characterized.[292]



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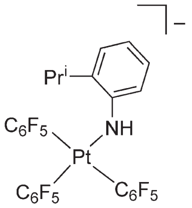

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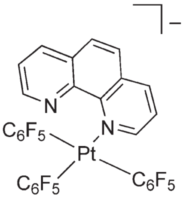

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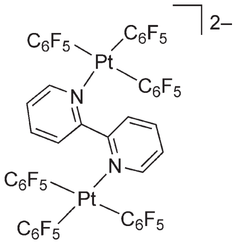
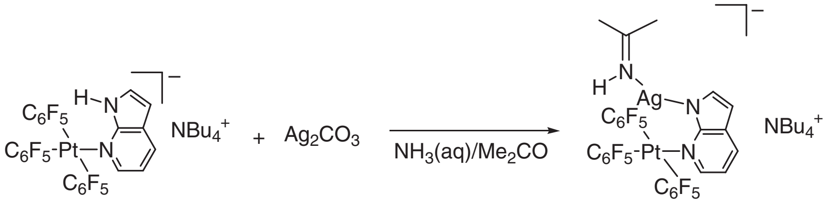


306

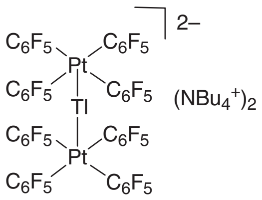
The tris(pentafluorophenyl)platinum complex with a 7-azaindole ligand **307**is converted into a Pt–Ag binary complex **308** in the presence of Ag_2CO_3, acetone, and NH_3 (Equation (79)).[293] Ag(I) is coordinated by a nitrogen of the 7-azaindole ligand and by an acetone imine formed by condensation during the reaction.



307 **308** (79)

Crystallographic studies of complexes $Pt(C_6F_5)_3(L)$ (L = 8-hydroxyquinoline, 8-methylquinoline) revealed Pt···H hydrogen bonding of the OH and CH group of the ligand at apical position of the metal center.[294]

Two C_6F_5-coordinated platinate molecules can be bridged by cationic metal centers to form multinuclear complexes. Thallium(II) binds to apical positions of tetrakis(pentafluorophenyl)platinate to form $Tl[Pt(C_6F_5)_4]_2$ as the first paramagnetic Tl complex **309**.[295] $Pt(C_6F_5)_2(acac)$ reacts with $AgClO_4$ to form a Pt_2Ag_2 complex containing two linear Pt–Ag–O bonds **310**.[296] Addition of tetrahydrothiophene and PPh_3 to the complex causes dissociation of the Ag–O bond to form Pt–Ag dinuclear complexes. Pt_2Ag complex **311** contains two $Pt(C_6F_5)_2$ fragments, which are bridged by OH and dppm ligands and by $Ag(PPh_3)$.[297] Complexes with two $Pt(C_6F_5)_3$ groups **312** and **313** bridged by Pb and by $Tl_2(O_2CMe)_2$ groups have been reported.[298,299] The cyclic triplatinum framework formed by $Pt(C_6F_5)_2$ groups and bridging OH or Cl ligands can be capped by $[HgCl]^+$ or Pb^{2+} ion to form heterobimetallic complexes **314** and **315**.[300,301]



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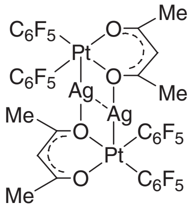

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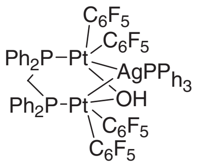

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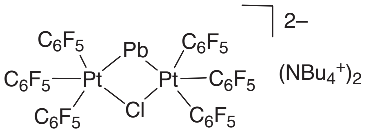

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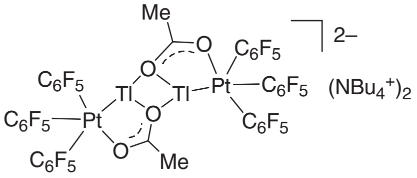

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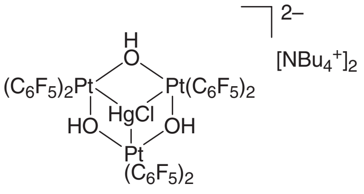

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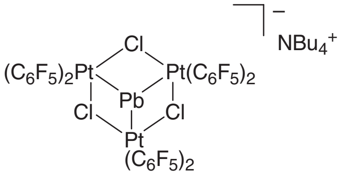
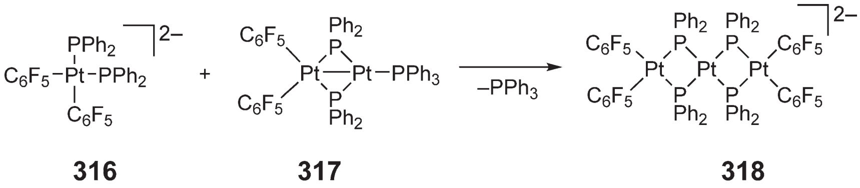


315

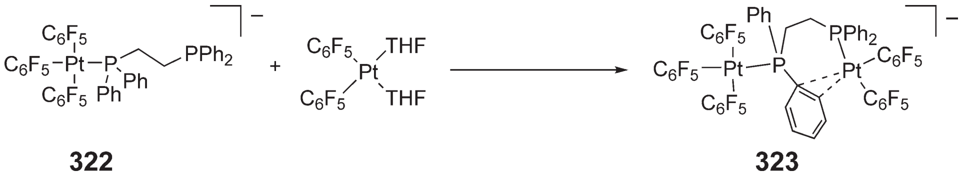
Coupling of a dianionic diarylplatinum(II) complex **316**, prepared *in situ*, with a neutral dinuclear Pt(I) complex with bridging PPh_2 ligands **317** forms a trinuclear anionic complex whose three Pt(II) centers are bridged by PPh_2 ligands (**318**, Equation (80)).[302]



(80)

An anionic dinuclear complex with bridging phosphido ligands **319** reacts with $Pt(C_6F_5)_2(THF)_2$ to form the trinuclear complex **320** (Scheme 44). One of the phosphido ligands coordinates to three Pt centers via σ-bonds.[303,304] A phenyl ring of the ligand shows an interaction of a C═C bond with a Pt center. The reaction of trinuclear complex **318** with $Pt(C_6F_5)_2(THF)_2$ forms the tetranuclear complex **321**. It contains three Pt centers bonded by Pt–Pt bonds and by Pt–P bonds with a PPh_2 ligand, similar to **320**, and the two Pt centers are bridged to the fourth Pt center by two PPh_2 ligands.

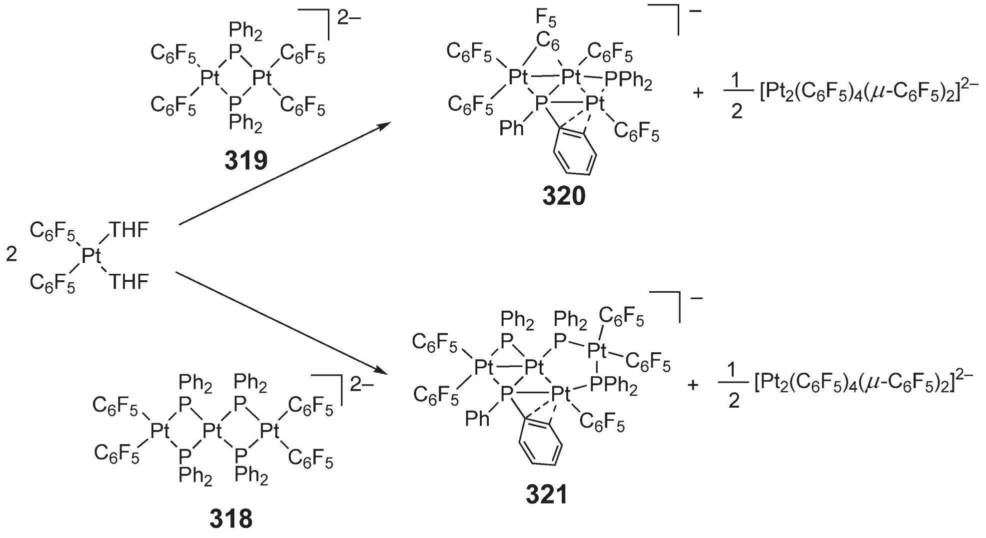
Reaction of the anionic complex with κ^1-bonded dppm, **322**, with $Pt(C_6F_5)_2(THF)_2$ produces a dinuclear complex with bridging dppm, which coordinates to the two Pt centers via P and to a Pt center via π-coordination of the C═C bond of a phenyl ring (**323**, Equation (81)).[305]



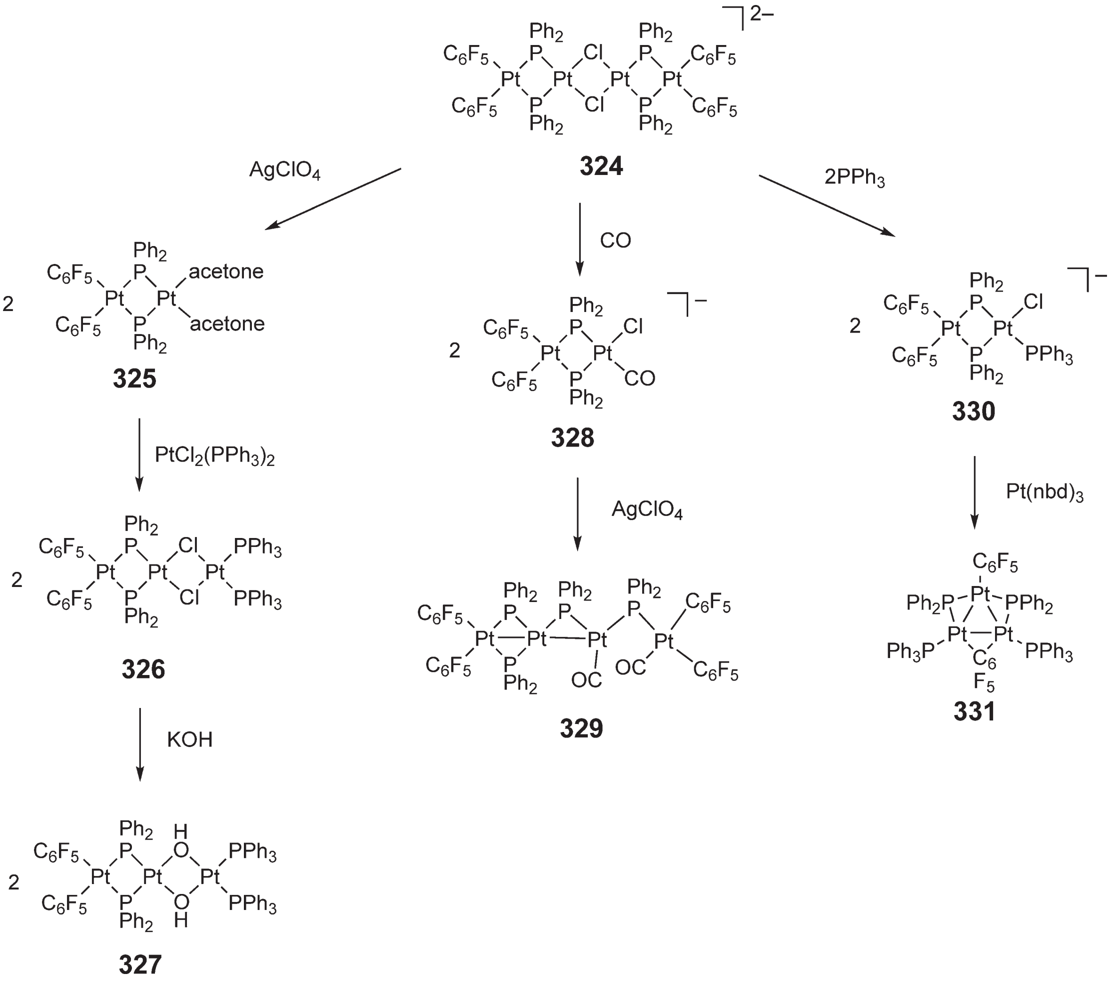
(81)

Scheme 45 summarizes reactions of the dianionic tetranuclear complex **324**, with four C_6F_5 ligands, four bridging PPh_2 ligands, and two bridging chloro ligands. Abstraction of the chloro ligands by $AgClO_4$ and coupling of the produced neutral dinuclear complex **325** with *cis*-$PtCl_2(PPh_3)_2$ yields a trinuclear Pt complex with bridging Cl and PPh_2 ligands **326**.[306] The bridging chloro ligands undergo substitution by OH ligands upon reaction with KOH to form **327**.

Carbonylation of **324** causes cleavage of the two Pt–Cl bonds of the Pt_2Cl_2 four-membered ring to yield a dinuclear chloro(carbonyl)platinum complex **328**.[307,308] Addition of $AgClO_4$ to the complex forms a tetranuclear Pt complex with two Pt–Pt bonds **329**. The four linear Pt centers are bridged by PPh_2 ligands, and two Pt–Pt bonds bind three of them; PPh_3 cleaves the Pt–Cl bonds of **324** to produce the dinuclear complex with a PPh_3 ligand **330**.[309] Further reaction of $Pt(nbd)_3$ with the dinuclear complex results in the cyclic triplatinum complex **331** with bridging PPh_2 and C_6F_5 ligands. Each metal center of **331** has a formal oxidation state of 1.33, similar to a more simple complex $Pt_3Ph(\mu\text{-}PPh_2)_3(PPh_3)_2$, and the three Pt–Pt bonds are in the range 279.1(1)–281.8(1) pm.

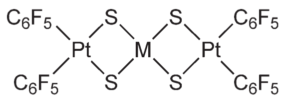


Scheme 44



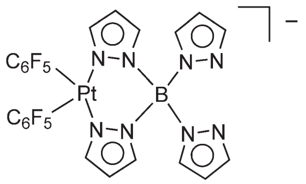
Scheme 45

Trinuclear and dinuclear complexes containing two Pt(C_6F_5)$_2$ fragments and sulfide 332 and (tetrapyrazolyl)borate ligands 333 and 334 have been obtained.[310,311]



M = Mo, W

332



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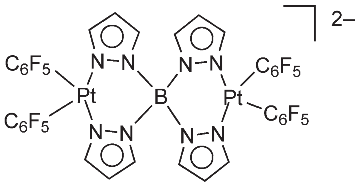
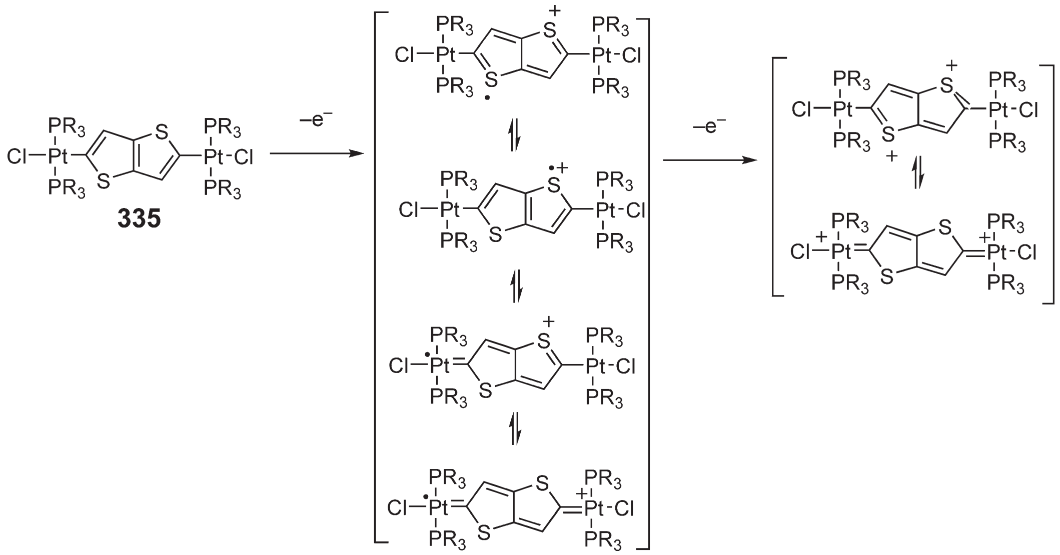


334

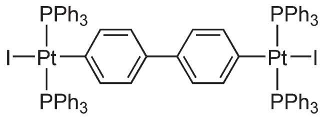
8.08.3.3.3 Complexes with arylene, bisaryl, and macrocycles

Dinuclear Pt complexes whose metal centers are connected by the arylene ligand have been obtained. Complex 335 has a bridging thienothiophene ligand, and exhibits reversible electrochemical oxidation/reduction in two steps at lower potential than the complexes with bridging 2,5-thienylene and 2,2′-bithienylene ligands (Scheme 46).[312] The electrochemical behavior involves electron delocalization within the π-conjugated ligand and involving platinum.



Scheme 46

A dinuclear complex with a bridging biphenylene ligand **336** and that with a triphenylene ligand are prepared by oxidative addition of the diiodoarylenes to a Pt(0) complex.[313] 4,4′-Benzophenonediyl bridges Pt centers of dinuclear complexes **337** and **338**,[313,314] while **339** contains a bridging 2,2′-bithienyl ligand.[315] A dinuclear complex with a bridging *m*-phenylene ligand **340** contains pyridine ligands with stabilized radicals.[316]



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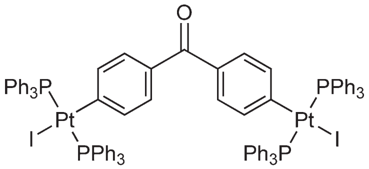

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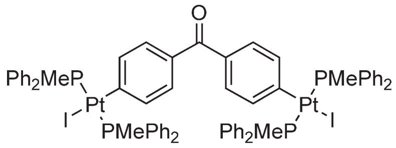

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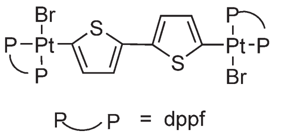

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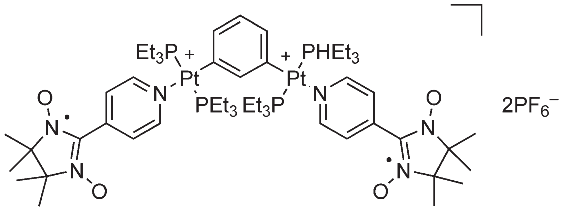
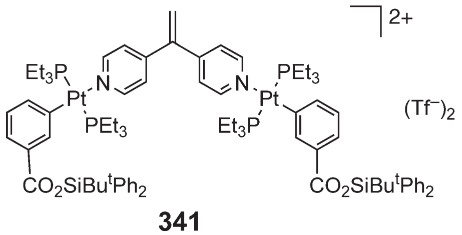


340

Cationic dinuclear complexes **341** and **342** have 1,1-(2-pyridyl)ethene and 4,7-phen as the respective bridging ligands between the two arylplatinum fragments.[317,318]



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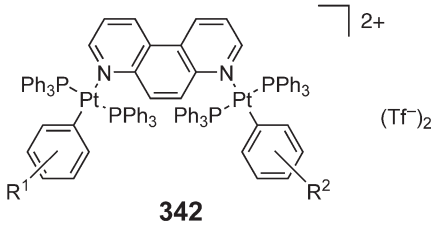
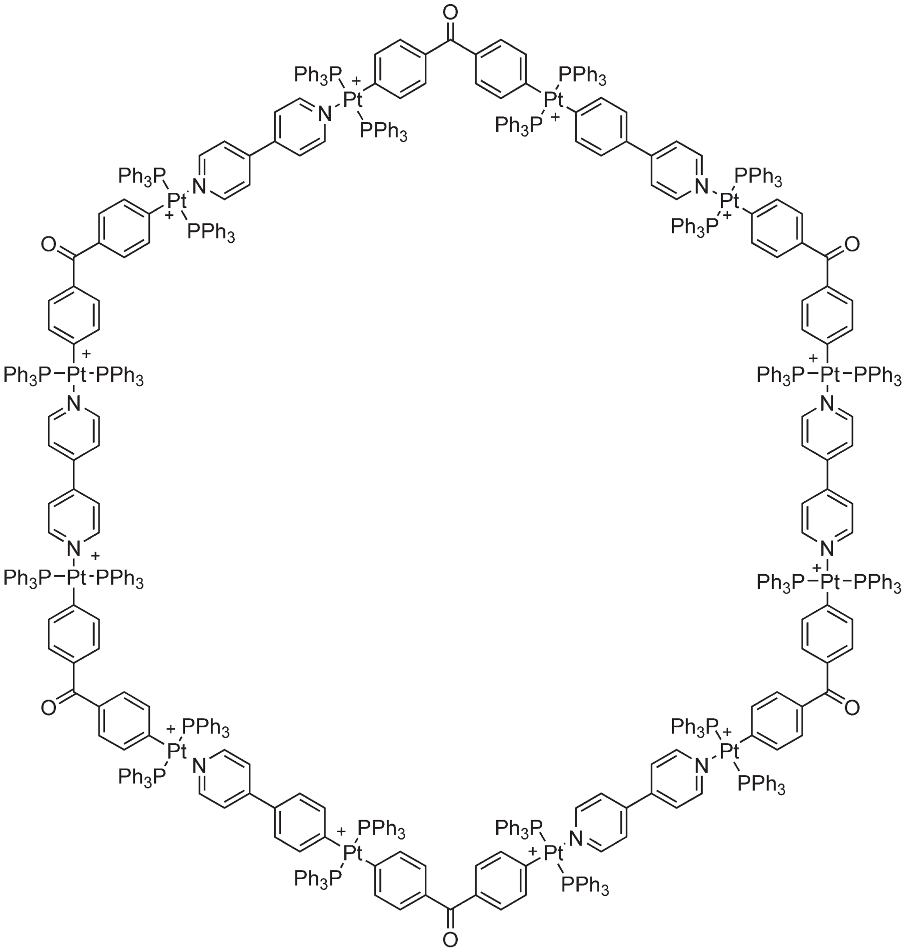


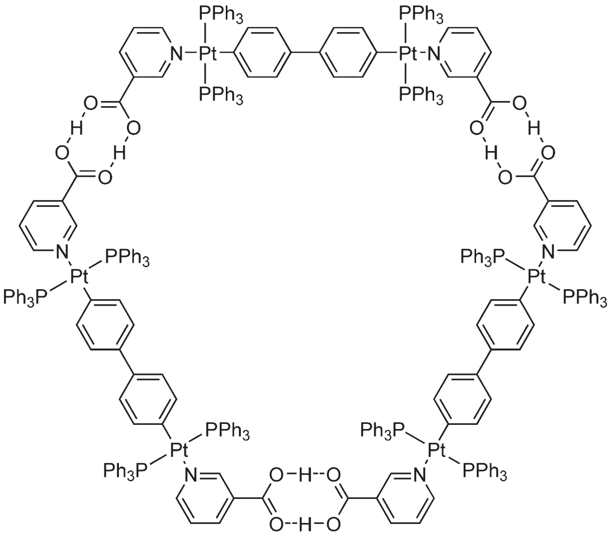
342

The macrocyclic compound **343** contains 12 cyclic units composed of Pt(PPh_3)$_2$, 4,4′-bipy, and 4,4′-benzophenonediyl ligands.[319]



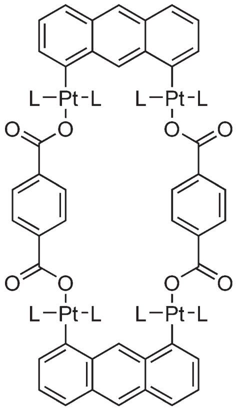
343

A dinuclear complex with bridging 4,4′-biphenylene and two 3-pyridinecarboxylic acid ligands bonded to each of the Pt atoms forms macrocycle **344** by strong intermolecular hydrogen bonding between the carboxylic acids; a linear polymer is also obtained.[320]



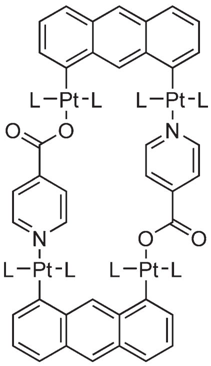
344

Macrocyclic tetraplatinum complexes containing Pt–aryl and Pt–O bonds **345** and **346** have been prepared.[321,322]



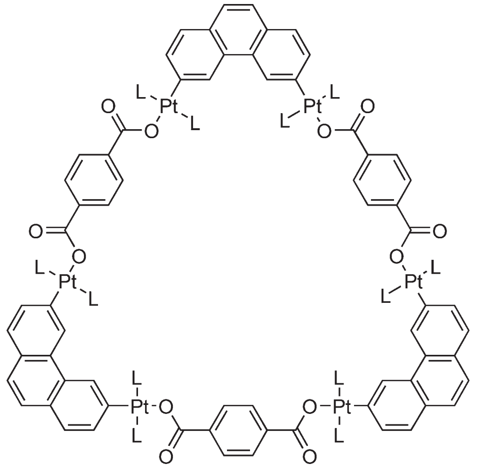
345

L = PEt_3

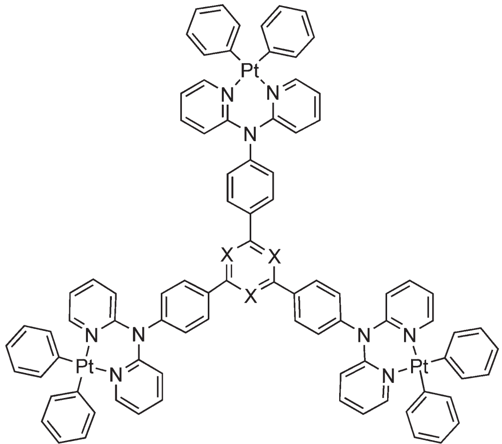


346

Macrocyclic tetra- and hexanuclear complexes containing bifunctional 2,2′-anthracene–diyl and dicarboxylate group, **347**, have been obtained;[323] the hexanuclear complex contains a triangular pore of diameter 19.5 Å.



347



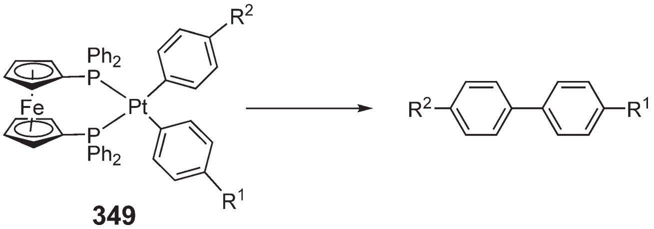
X = CH, N

348

Starburst polymers with diorganoplatinum centers have been prepared by using 2,2′-dipyridylamine-derived ligands, prepared by Suzuki-coupling of boronic acid with aryl bromide.[324] A trinuclear Pt complex **348** may be formed using this ligand, and a related dinuclear complex has been characterized by X-ray crystallography. The branched ligand is fluxional, involving conformers, as studied by crystallography and dynamic NMR spectra.

8.08.3.3.4 Arylplatinum(II) complexes – reactions

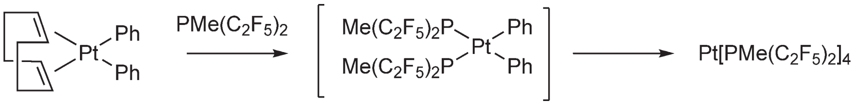
The complex $PtClAr(SMe_2)_2$ undergoes exchange of the chloro ligand with nucleophiles, a process which has been studied by kinetic measurements.[325] Reductive elimination of biaryl from diarylplatinum(II) complexes of phosphines, for example, **349**, has been discussed. Not only electron-donating groups on the aromatic ring but also dissimilarity of the two aryl ligands enhance the reaction (Equation (82)). Retardation of the reductive elimination when two electron-deficient groups are present at the aryl ligand has been ascribed to a ground-state effect.[326]



349

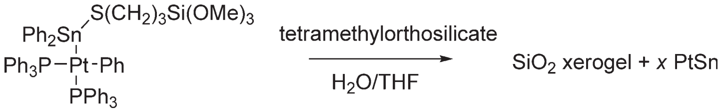
(82)

A diphenylplatinum complex having $PMe(C_2F_5)_2$ as ligands, formed similarly, undergoes reductive elimination of biphenyl at low temperature to form a Pt(0) complex with four phosphine ligands (Equation (83)).[103]



(83)

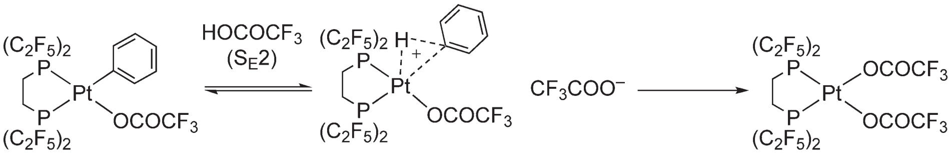
The complex with a stannyl ligand having a trimethoxysilyl group, **350**, has been converted into a silica xerogel and a PtSn composite (Equation (84)).[327,328]



350

(84)

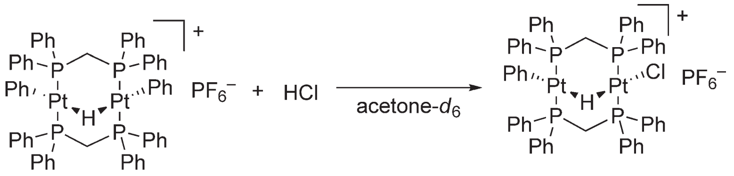
The phenyl(trifluoroacetato)platinum complex with a fluorinated depe ligand, **351**, reacts with trifluoroacetic acid to yield the dicarboxylate complex. An intermediate structure after protonation is proposed (Equation (85)).[329]



351

(85)

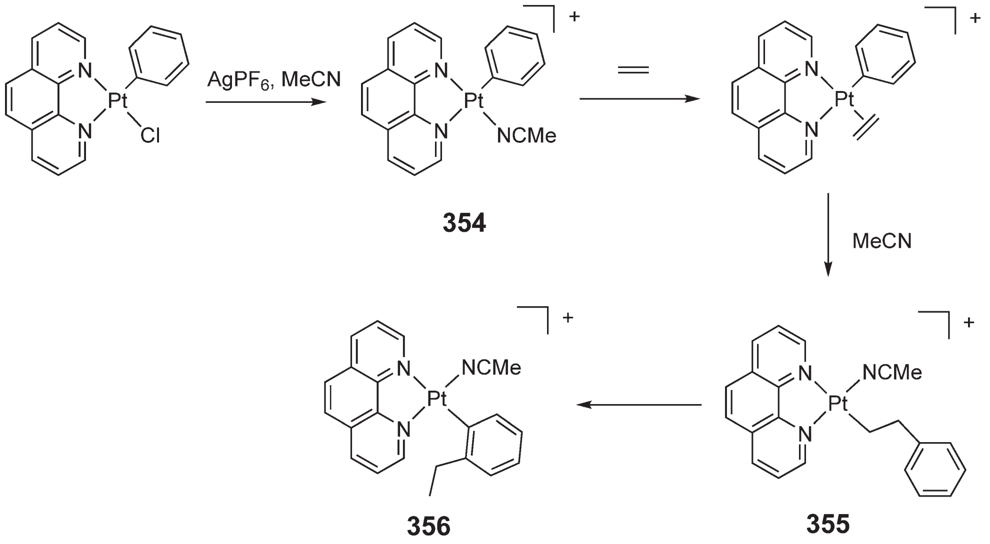
Reaction of HCl with an A-frame dinuclear Pt complex with two Ph ligands, **352**, causes protonation of a phenyl ligand to yield **353** having a Cl ligand at a Pt center (Equation (86)).[330]



352

353

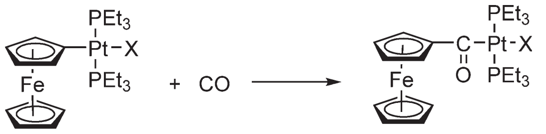
(86)



Scheme 47

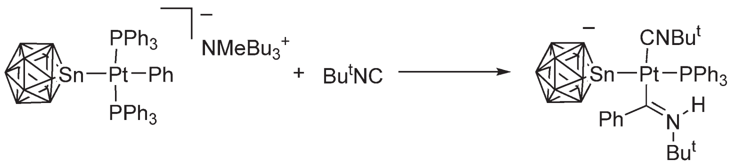
A cationic phenylplatinum(II) complex with a phen ligand, **354**, is formed from the reaction of $AgPF_6$ with PtClPh(phen) in MeCN (Scheme 47).[331] Introduction of ethylene into the solution causes coordination of ethylene and subsequent insertion of ethylene into the Pt–C bond, giving **355**. The 2-phenylethylplatinum ligand formed rearranges to the 2-ethylphenyl ligand via orthometallation of the phenyl group to form **356**.

A σ-ferrocenylplatinum complex **357** undergoes insertion of CO into the Pt–C bond to form the acylplatinum complex **358** (Equation (87)).[332]



357 **358** (87)

A Pt complex with phenyl and stannaborato ligands **359** reacts with isonitrile, resulting in insertion of isonitrile into the Pt–Ph bond to afford the complex with an iminoacyl ligand (**360**, Equation (88)).[333]

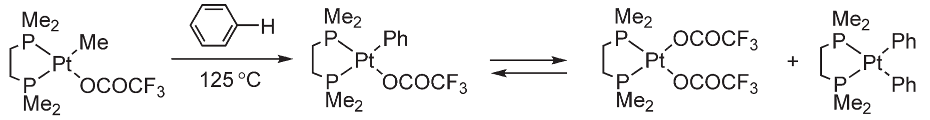


359 **360** (88)

A dinuclear complex with a bridging 2,5-thienylene ligand **361** undergoes insertion of isonitrile into the two Pt–C bonds to give a complex with two iminoacyl–Pt bonds (**362**, Equation (89)).[334]

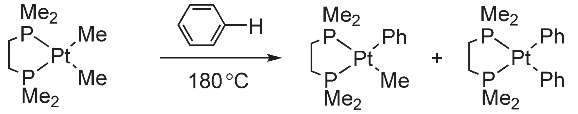
361 **362** (89)

A monophenylplatinum(II) complex with trifluoroacetate and dmpe ligands **364**, formed *in situ* from the reaction of benzene with the corresponding methyl(trifluoroacetate)platinum complex **363**, undergoes disproportionation into a diphenylplatinum(II) complex and a bis(trifluoroacetate)platinum(II) complex (Equation (90)). The disproportionation starting from a 2,3-difluorophenyl(trifluoroacetate)platinum(II) derivative occurs smoothly at 125 °C to produce the three possible complexes in a statistical ratio. Dimethylplatinum(II) complex **365** undergoes C–H bond activation of benzene to form a mixture of methyl(phenyl)platinum and diphenylplatinum complexes (**366** and **367**, Equation (91)).[335]



363 **364**

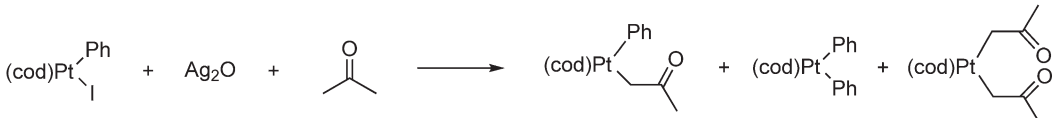
(90)



365 **366** **367**

(91)

A phenyl(acetonyl)platinum complex with cod as a ligand **368** is obtained from the reaction of PtIPh(cod) with acetone in the presence of Ag_2O (Equation (92)). The accompanying formation of diphenyl and diacetonyl complexes **369** and **370** is ascribed to disproportionation of **368** during the reaction.[336]



368 **369** **370**

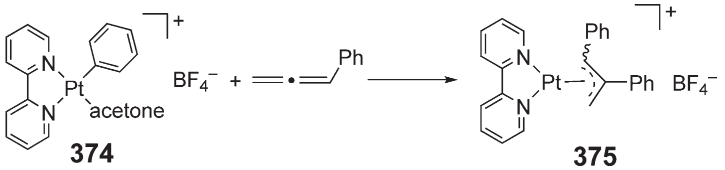
61 : 20 : 19

(92)

Phenyl(iodo)platinum complex with cod ligand **371** reacts with OH^- to form a dinuclear phenylplatinum(II) complex with a bridging OH^- ligand and Ph and cod ligands on each Pt center, **372** which undergoes intermolecular transfer of the phenyl ligand to form **373**, (Scheme 48).[337]

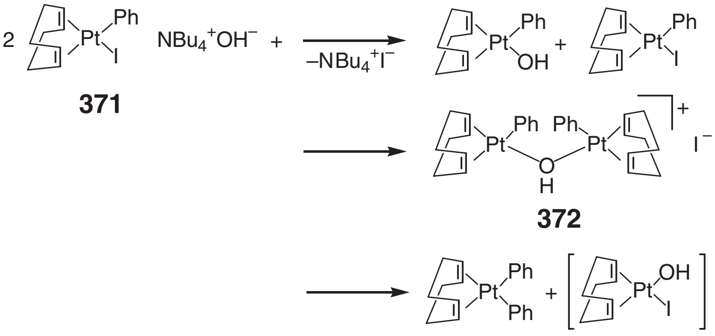
The cationic complex undergoes phenyl group transfer from one metal to the other upon addition of OH^-, although the addition of non-coordinating anions such as PF_6^- does not cause the phenyl group transfer.

Insertion of phenylallene into the Pt–C bond of cationic phenyl complex **374** forms the complex with two Ph substituents in the π-allyl ligand (**375**, Equation (93)).[338]



374 **375**

(93)



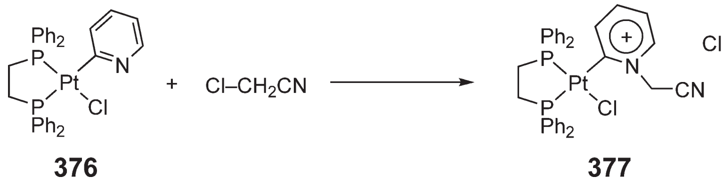
371

372

373

Scheme 48

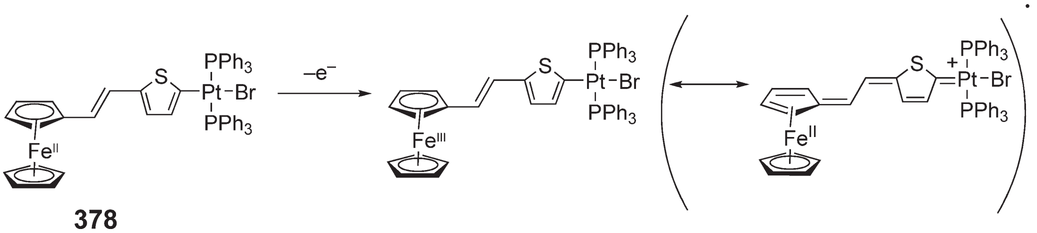
The 2-pyridyl ligand of complex **376** undergoes electrophilic addition of CH_2ClCN to produce **377** containing a pyridinium ligand (Equation (94)).[339]



376 **377**

(94)

A thienylplatinum complex with a ferrocenyl group in the ligand **378** shows an absorption band in the visible region.[340] Reversible two-step electrochemical oxidation reactions of the complex indicate occurrence of electron transfer between Fe and Pt centers of the one-electron oxidized species (Equation (95)).



378

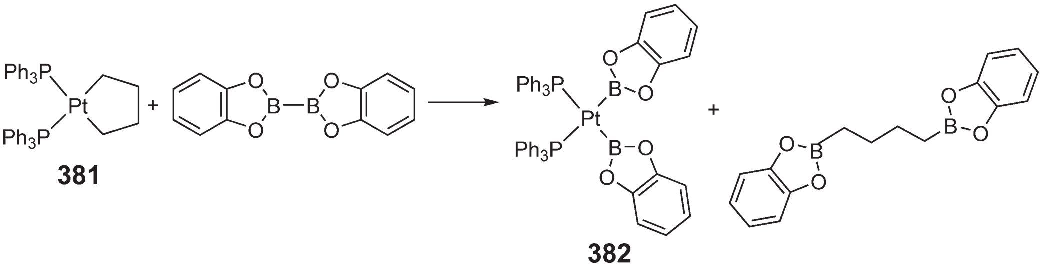
(95)

8.08.3.4 Chelating Alkyl- and Arylplatinum(II) Complex

8.08.3.4.1 Platinacycles with two Pt–C σ-bonds

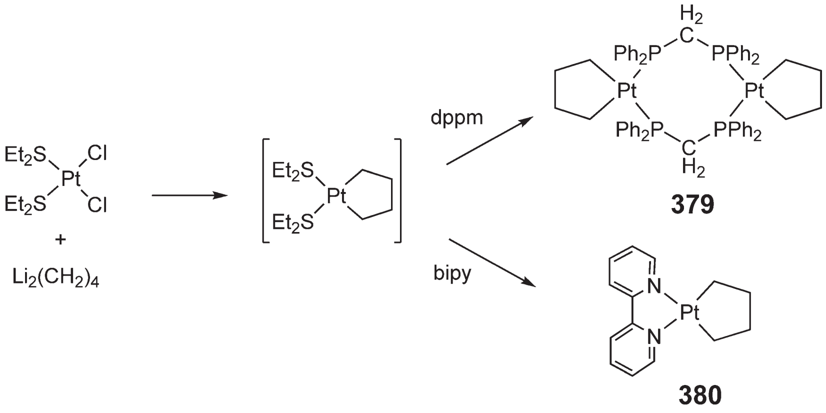
Platinacyclopentanes show both thermodynamic and kinetic stability, and have been isolated using phosphine and diimine auxiliary ligands. The platinacyclopentane with SEt_2 ligands, formed by transmetallation of 1,4-dilithiobutane with a dichloroplatinum complex *in situ*, undergoes ligand exchange with dppm and bipy.[341] The dppm complex has a dinuclear structure with bridging phosphine ligands **379**, while bipy forms a stable mononuclear complex **380** (Scheme 49).

Complex **381** reacts with bis(catechol)borane to produce the diboryl complex **382** (Equation (96)).[342]



381 **382**

(96)

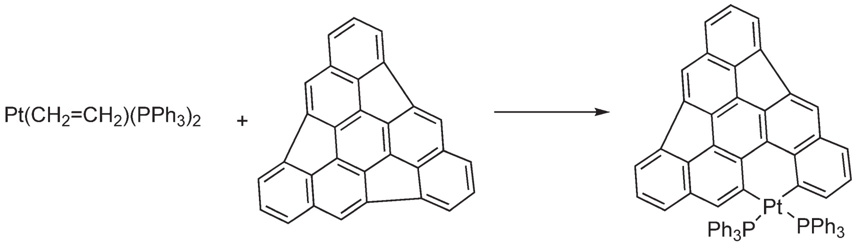


379

380

Scheme 49

Semibuckminsterfullerene ($C_{30}H_{12}$), having a partial structure of C_{60}, undergoes activation of a C–C bond by a Pt(0)–PPh_3 complex to produce a six-membered platinacycle **383** (Equation (97)). The Pt center is folded outward from the mean plane defined by the five carbon atoms of the platinacycle.[343]



383

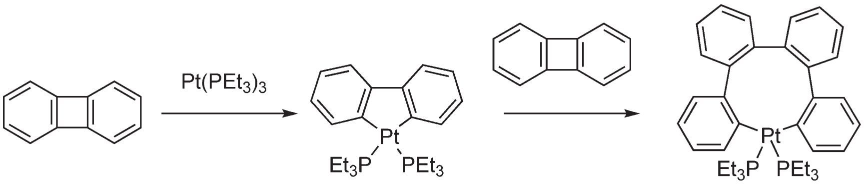
(97)

Carbon–carbon bond activation of biphenylene promoted by $Pt(PEt_3)_3$ at 80 °C affords the five-membered platinacycle **384**, which is formed also by the transmetallation of dilithio biphenylene with $PtCl_2(PEt_3)_2$.[344] Further reaction of biphenyl with the complex at 80 °C produces the platinacycle having a nine-membered ring (**385**, Scheme 50). Cyclodimerization of biphenyl into tetraphenylene occurs at 120 °C, catalyzed by $Pt(PEt_3)_3$, which involves the above platinacycles as the intermediate.

The five-membered platinacycle having diphenyl(*t*-butyl)phosphine as ligands **386** is prepared by transmetallation of the aromatic dilithium reagent with $PtCl_2(SEt_2)_2$ followed by addition of the phosphine ligand to the platinacycle with SEt_2 ligands.[345] Heating the complex at 80 °C yields biphenylplatinum complex **387** by cyclometallation of a phenyl group of the phosphine ligand, and further heating the product with biphenylene at 130 °C forms tetraphenylene (Scheme 51).

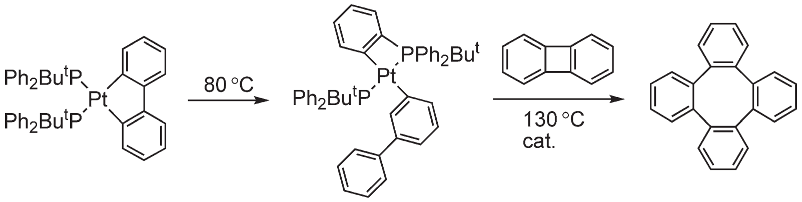
The C–H bond activation of 4,4′-bis(trifluoromethyl)biphenyl by a Pt(0) complex of di(*t*-butyl)phosphinomethane at 40 °C forms the hydrido(aryl)platinum complex **388** (Scheme 52).[346] Heating **388** at 85 °C produces the complex with a biphenylene ligand **390** accompanied by loss of hydrogen. The results indicate that intermediate **389** is formed via reductive elimination of biaryl and its reoxidative addition.

A Pt(0) complex with π-coordinated biaryl, **392**, undergoes thermally induced C–H bond activation of the ligand to give **391**, while **392** is equilibrated with **393**, a regioisomer of **391**, under photoirradiation (Scheme 53).



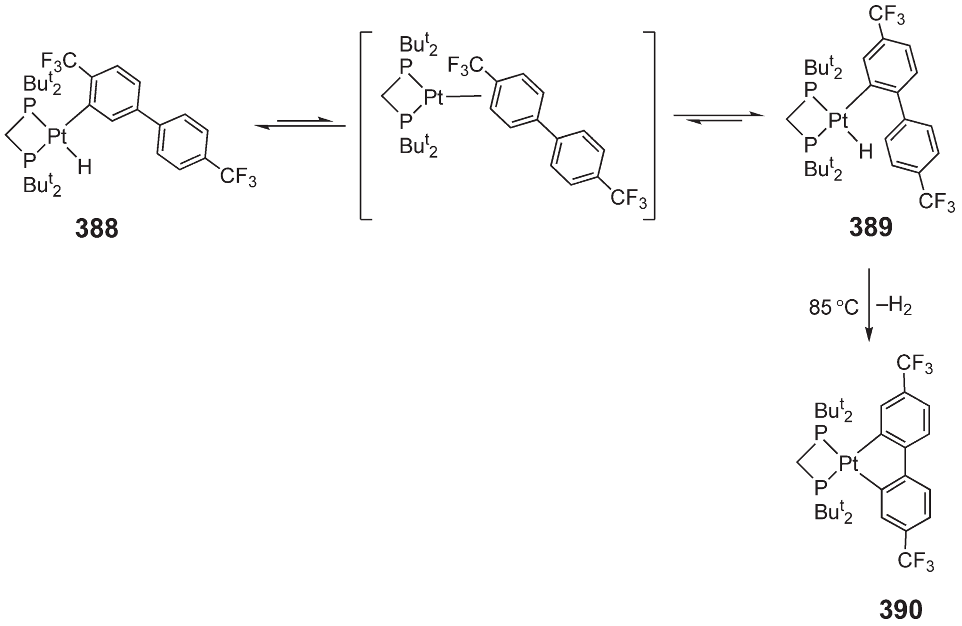
384 **385**

Scheme 50

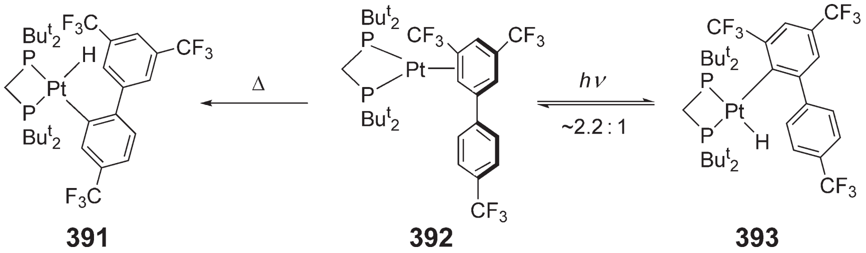


386 **387**

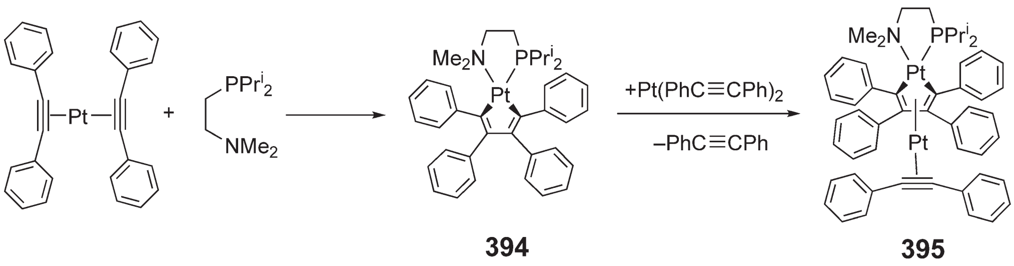
Scheme 51



Scheme 52



Scheme 53

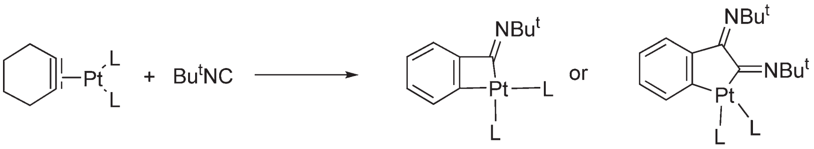


Scheme 54

Pt(PhC≡CPh)$_2$ reacts with a *P*,*N*-chelating ligand to form the platinacyclopentadiene **394** (Scheme 54).[347] Addition of Pt(PhC≡CPh)$_2$ to **394** forms a compound whose five-membered ring coordinates to the Pt(0)–diphenylacetylene fragment in an η^4-fashion **395**.

Electronic spectra and electrochemistry of biphenylene complexes Pt(C$_{12}$H$_8$)(CO)$_2$ and Pt(C$_{12}$H$_8$)(dppf) have been studied.[348,349]

Platinacyclopentanes with heteroatoms or functional groups in the five-membered chelate ring may also be obtained as stable complexes. Single and double insertion of isonitrile into the Pt–C bond of a cyclohexyne–Pt(0) complex[350] produces four- and five-membered platinacycles (396 and 397, Equation (98)).[351] DFT calculations have been applied to a related reaction of CO with a platinacyclobutenone having PPh_3 ligands to produce a five-membered platinacycle via CO insertion into the Pt–C bond.

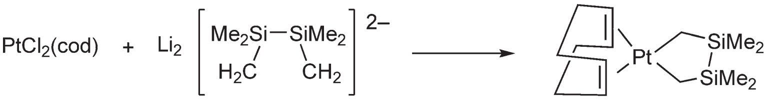


L = PPh_3 L$_2$ = dmpe

396 **397**

(98)

A 3,4-disila–1-platinacyclopentane with a cod ligand **398** has been prepared by the reaction of the dianion of hexamethyldisilane with $PtCl_2$(cod) (Equation (99)).[352]

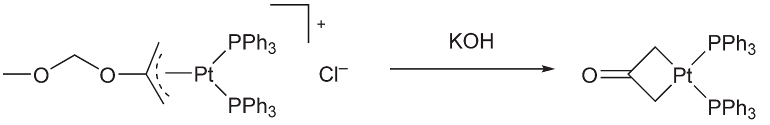


398

(99)

$Pt(PPh_3)_4$ reacts with iodobenzene derivatives having OCH_2SnBu_3 or OCH_2SiMe_3 substituents at the 2-position to form the 3-oxa-platinacycle **399** (Scheme 55).[353] Oxidative addition of a C–I bond to Pt(0) is followed by intramolecular transmetallation via activation of the C–Sn or C–Si bonds. The reactions proceed smoothly without additives, although intermolecular cross-coupling of aryl triflate with vinyl(tributyl)stannane promoted by the Pt complex requires addition of a base such as K_2CO_3.

The reaction of base with a π-allyl Pt complex containing a methoxyethoxy group at the allyl ligand **400** yields a platinacyclobutane containing a C=O group **401**. It has a puckered structure and involves π-allylic character (Equation (100)).[354]

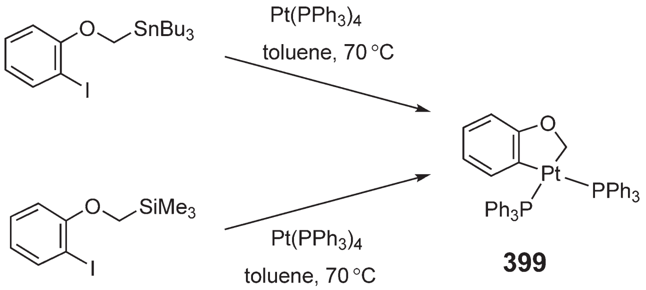


400 **401**

(100)

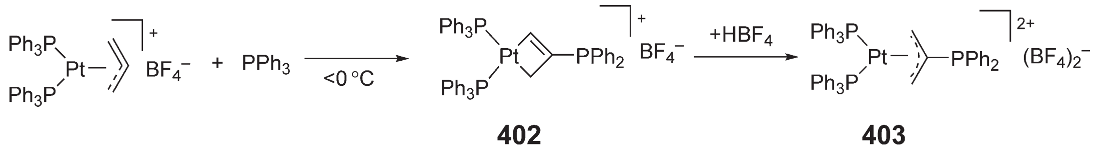
Reaction of PPh_3 with the allenyl complex $Pt(\eta^3\text{-}C_3H_3)(PPh_3)_2$ produces a platinacyclobutene with a β-PPh_2 group **402**, which is isolated below 0 °C. Protonation of **402** leads to an η^3-allyl complex with a PPh_2 substituent (**403**, Scheme 56).[355]

A boron-containing platinacycle **404** has been prepared from the reaction of 1,3,5-trimethyl–2-isopropylidene–4,6-dimethyl–1,3,5-triboracyclohexane with $Pt(cod)_2$ (Equation (101)). The Pt–C distances (211.1(6) and 216.3(6) pm) indicate presence of the four-membered platinacycle structure, although the three boron atoms show interaction with the Pt center (Pt–B = 244.9(7)–265.8(7) pm).[356]

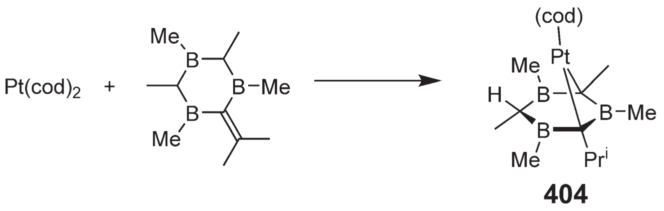


399

Scheme 55

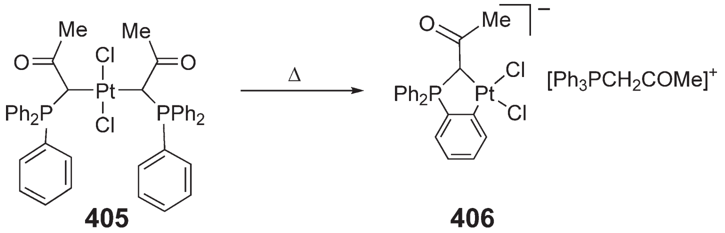


Scheme 56



(101)

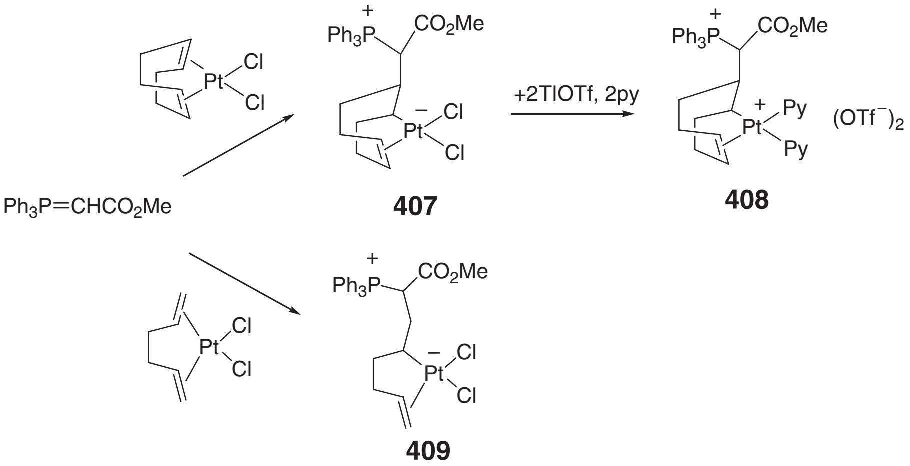
The complex with triphenylphosphonium ylides **405** undergoes orthometallation of the ligand to form the complex with a five-membered platinacyclopentane **406** (Equation (102)).[357]



(102)

8.08.3.4.2 Platinacycles with one Pt–C σ-bond and Pt–C π-bonds

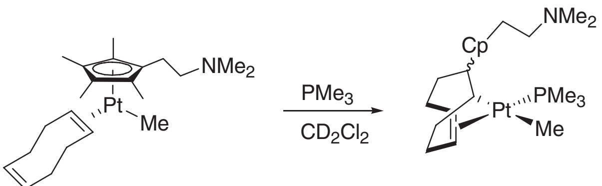
The cod ligand bonded to Pd and Pt is known to undergo facile nucleophilic reaction with bases such as alkoxide and amide to form complexes with the C8 ligand bonded to Pt by a Pt–C σ-bond and by a π-bond between the Pt and C=C double bond of the ligand. Phosphorus ylides also cause the same nucleophilic addition to the 1,5-cyclooctadiene and 1,5-hexadiene ligands bonded to the Pt(II) center, affording complexes having the ligand with σ- and π-coordination bonds (**407**, Scheme 57).[358,359] The complex having an alkylated cod ligand undergoes coordination of pyridine in the presence of Tl(OTf) to form **408**. The reaction is general for the dichloroplatinum(II) complexes



Scheme 57

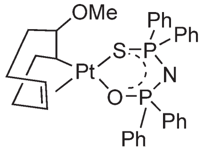
with non-conjugated diene ligands such as cyclopentadiene dimer and 4-vinylcyclohex-1-ene, for example, to form **409** from 1,5-hexadiene.

A PtMe complex with a tetramethylcyclopentadienyl ligand, having a 2-(dimethylamino)ethyl group, and with cod as a monodentate ligand **410**, reacts with PMe_3 to afford a complex whose metal center is bonded to a cyclooctenyl ligand via σ- and π-bonds **411** (Equation (103)).[360]

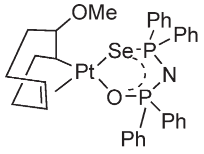


410 **411** (103)

Analogous complexes with *O,S*- and *O,Se*-chelating ligands have also been obtained **412** and **413**.[361]

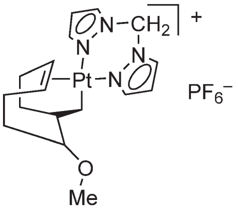


412

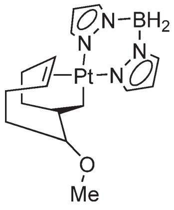


413

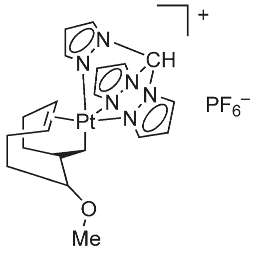
The bidentate bis(pyrazolyl)methane and bis(pyrazolyl)borate ligands, as well as tridentate tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands, also form Pt complexes with the ligand formed by addition of a methoxy group to cod **414–417**.[362]



414



415



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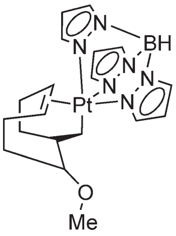
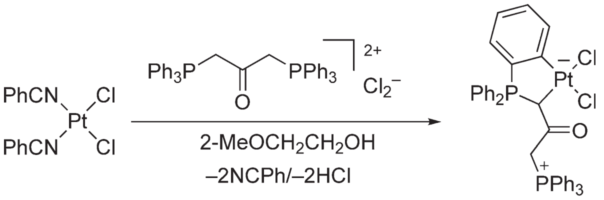
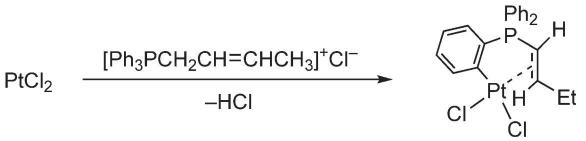


417

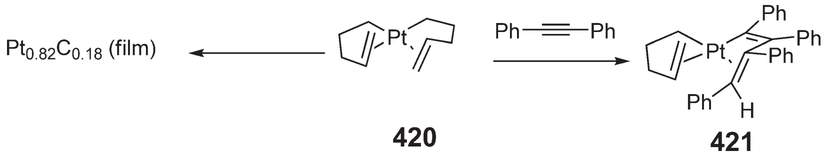
Mono- and diphosphonium salts stabilized by carbonyl or olefinic groups react with dichloroplatinum(II) compounds to afford **418** and **419** (Equations (104) and (105)).[363] Both reactions are induced by C–H bond activation of PPh_3 groups, and the former and latter reactions involve additional C–H activation of a CH_2CO group and isomerization of 2-butenyl to 1-butenyl groups at the P atom, respectively.



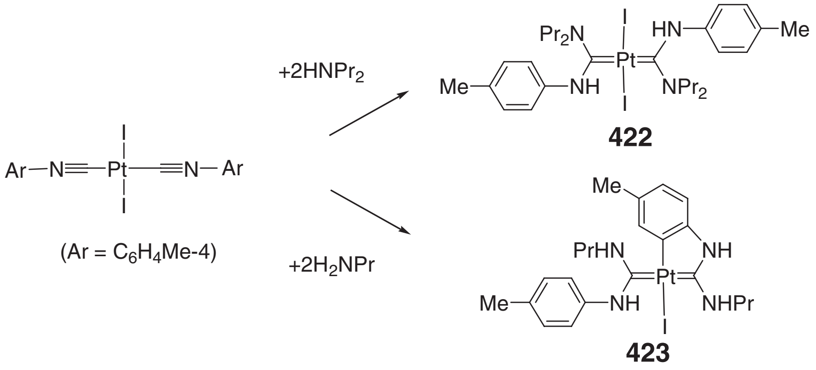
418 (104)



419 (105)



Scheme 58

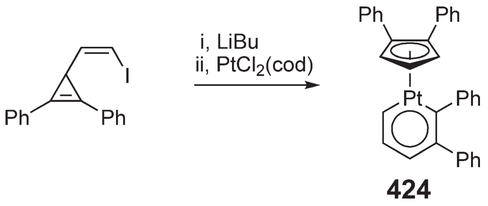


Scheme 59

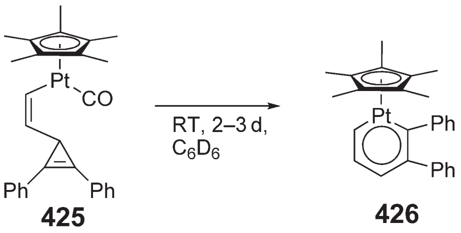
A bis(4-pentenyl)platinum complex **420**, prepared by the reaction of the corresponding bromide with $PtCl_2$(cod) in the presence of Mg, has the ligands bonded to Pt via σ- and π-coordination.[364] The complex undergoes thermolysis on a Cu substrate to form a Pt–C film and is employed as a precursor for chemical-vapor deposition (Scheme 58). The reaction of diphenylacetylene with the bis(4-pentenyl)platinum(II) complex forms a Pt(II) complex containing 4-pentenyl and tetraphenylbutadienyl ligands **421**, formed by β-hydrogen elimination of a pentenyl ligand and insertion of two alkyne molecules into the Pt–H bond.

The diiodoplatinum(II) complex with two aryl isocyanide ligands at the *trans*-positions undergoes nucleophilic addition of a secondary amine to the CN bond to yield a complex having two diaminocarbene ligands (**422**, Scheme 59).[365–367] The reaction using a primary amine causes similar addition of amine and subsequent intramolecular C–H bond activation of the aryl group to yield the complex with a chelating aryl–carbene ligand **423**.

Lithiation of 2-(diphenylcyclopropenyl)vinyl iodide and addition of $PtCl_2$(cod) forms the platinabenzene having a 1,2-diphenylcyclopentadienyl ligand (**424**, Equation (106)).[368] Two diphenylcyclopropenyl ligands formed via transmetallation are isomerized into the diphenylpentacyclodienyl ligand and platinabenzene during the reaction, and three possible intermediates were proposed. A Pt complex with permethylcyclopentadienyl and diphenylcyclopropenyl ligands **425** undergoes slow rearrangement of the small-membered ring-containing ligand into the platinabenzene **426** (Equation (107)).[369]



(106)

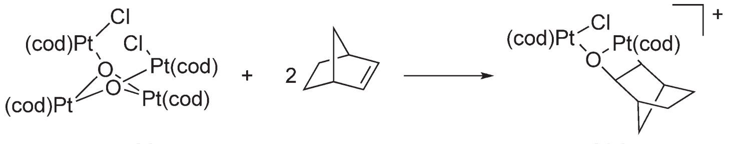


(107)

Transition metallabenzenes including platinabenzene have been investigated by theoretical calculations,[370] and the formation route involving a platinabenzvalene intermediate discussed.

8.08.3.4.3 Platinacycles with one Pt–C σ-bond and Pt–O (or S) bonds

Oxygen or sulfur analogs of platinacycloalkanes have also been prepared. A tetranuclear complex with bridging oxo ligands **427** reacts with norbornene to form a dinuclear complex having a *Pt,O,C,C* four-membered ring **428** via addition of the Pt–O bond to the C=C bond of the substrate (Equation (108)).[371]



427 **428**

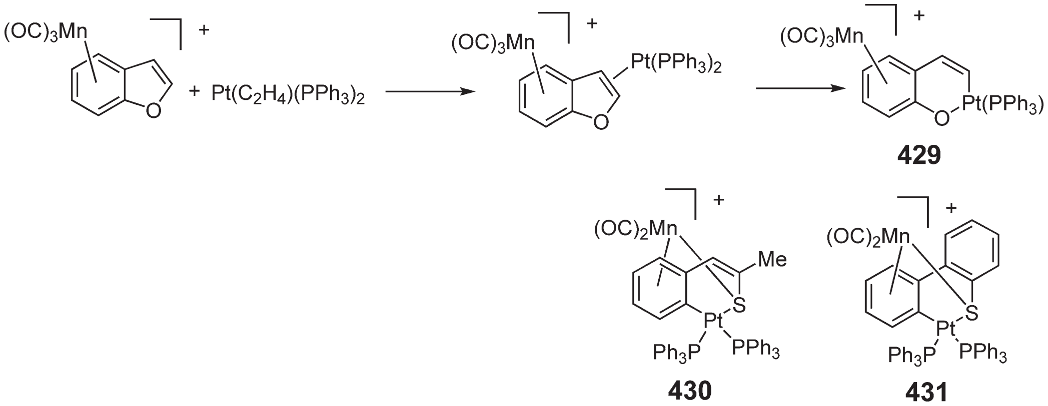
(108)

Benzofuran bonded to an Mn(CO)$_3$ fragment undergoes C–O bond activation by a Pt(0)–PPh$_3$ complex to yield a six-membered 2-oxa-platinacycle **429** (Scheme 60).[372,373] The pathway involving an intermediate Pt(0) complex with π-coordinated benzofuran has been proposed. Analogous complexes with a C–S bond **430** and **431** are prepared from the Mn complex with π-coordinated thiophene derivatives.

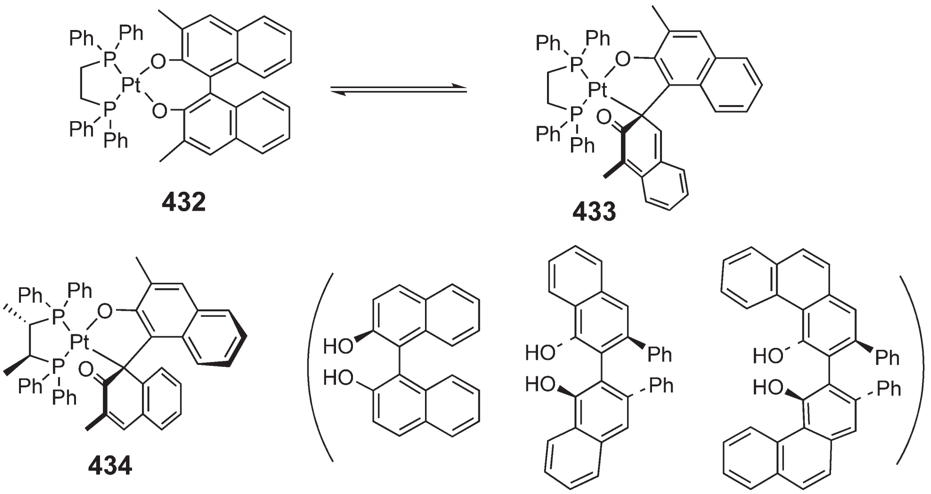
Analogous C–S bond activation of benzothiophene and dibenzothiophene, bonded to Mn(CO)$_3$, leads to metallacyclic compounds with Pt–C and Pt–S bonds **430** and **431**.[374] The reaction of methylbenzothiophene occurs regioselectively to yield a single product, which undergoes slow elimination of a CO ligand and coordination of sulfur to the Mn center.

A complex with dppe and the 3,3′-dimethyl–BINOL ligands **432** undergoes C–H activation of a naphthyl group to form an *O,C*-platinacycle, with coordinating aryl and aryloxy groups (**433**, Scheme 61). The reaction involves tautomeric isomerization between the phenol and the cyclohexadienyl-one.[375] The reaction occurs reversibly, and the equilibrium ratio between the *O,O*- and *O,C*-cyclic forms at room temperature is 24 : 76. The complex with (*S,S*)-chiraphos and optically active diols VANOL and VAPOL are prepared from the reaction of a carbonato Pt(II) complex with the optically active diphosphine.[376] (1*S*)-BINOL is bonded to Pt of **434** as the chelating ligand, while the (1*R*)-BINOL is bonded as the monovalent ligand due to stereochemical mismatching.

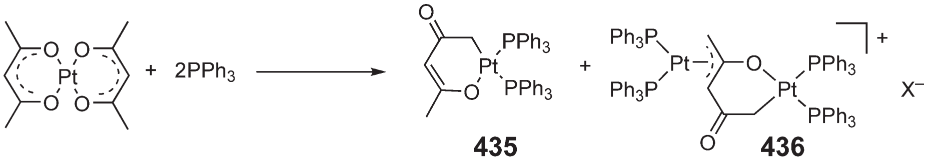
The reaction of PPh$_3$ with Pt(acac)$_2$ produces a mononuclear complex with a *C,O*-chelating acetylacetonato ligand **435** and a dinuclear complex in which the acac ligand bonds to a Pt center via π-allylic coordination and to another as a *C,O*-chelating ligand **436** (Equation (109)).[377]



Scheme 60



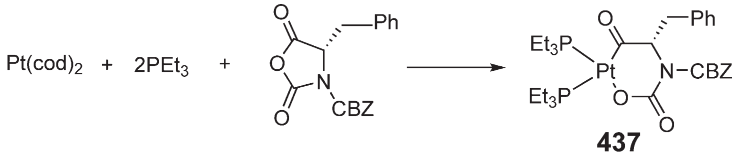
Scheme 61



(109)

X = acac, PF_6

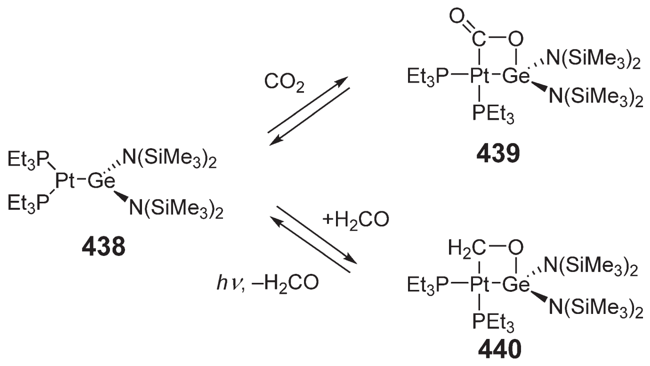
Oxidative addition of α-amino acid–*N*-carboxyanhydrides to a Pt(0) complex leads to a six-membered platinacycle **437** (Equation (110)).[378] The complex initiates ring-opening polymerization of γ-benzyl–L-glutamate–*N*-carboxyanhydride.



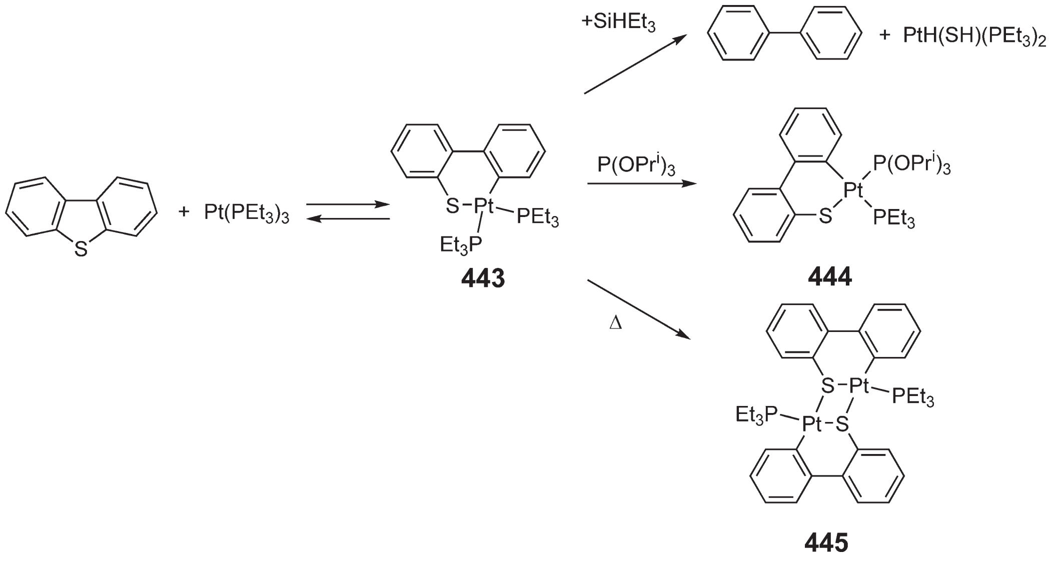
(110)

CBZ = $COCH_2Ph$

A diaminogermylene complex **438** reacts with CO_2 and with formaldehyde to yield the corresponding four-membered platinacycle with Pt–C and Pt–Ge bonds (**439** and **440**, Scheme 62).[379,380] The reaction is reversible and the reverse reaction is facilitated by photoirradiation.

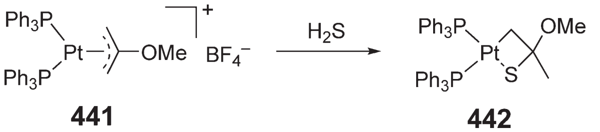


Scheme 62



Scheme 63

A complex with a 2-methoxy–π-allyl ligand **441** reacts with H_2S to form a puckered sulfaplatinacyclobutane with a methoxy substituent (**442**, Equation (111)).[381]

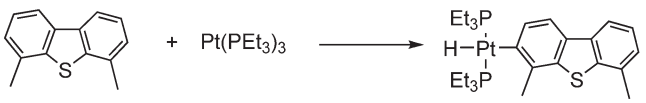


(111)

Various thiophene derivatives cause oxidative addition of a C–S bond to $Pt(PEt_3)_3$ to afford six-membered cyclic compounds. Oxidative addition of dibenzothiophene and benzothiophene causes C–S bond activation of the substrate to $Pt(PEt_3)_3$, affording sulfaplatinacyclohexadiene **443** (Scheme 63).[382] The complex reacts with reducing reagents such as $SiHEt_3$ and $NaBH_4$ to give biphenyl and styrene, respectively, although partial recovery of the thiophene derivatives is also observed. Complex **443** undergoes facile exchange of the ligand with trialkylphosphites to form **444**,[383] and undergoes thermally induced dimerization to form the compound having a Pt_2S_2 core **445**.

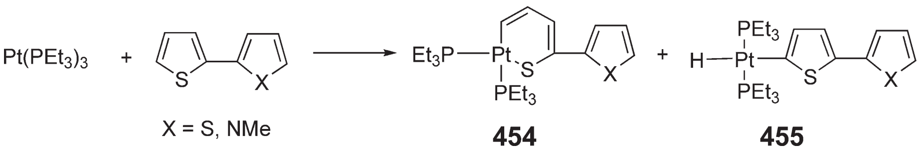
Molecular orbital calculations for the complex formed from benzothiophene indicated that the product of the oxidative addition has a positive charge caused by the reaction.[384] 2-Chloro- and 3-chloro-thiophenes undergo cleavage of less sterically hindered C–S bonds selectively on the reaction with $Pt(PEt_3)_3$, yielding **446** and **447**, respectively (Scheme 64).[385] The reactions of 2-methoxy- and 3-methoxythiophenes produce a mixture of the regioisomers **448–451**, while the dinuclear product **452** is also observed in the latter reaction.

The reaction of 4,6-dimethyldibenzothiophene with $Pt(PEt_3)_3$ results in C–H bond activation of the substrate, rather than C–S bond activation, to form **453** (Equation (112)).[386]

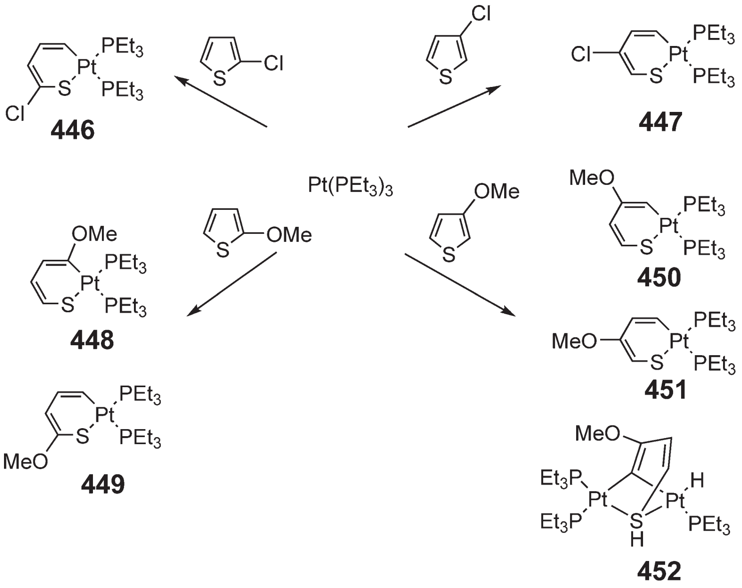


(112)

Bicyclic 2,2′-bithiophene and 1-methyl–2-(2-thienyl)pyrrole also react with $Pt(PEt_3)_3$ to produce a mixture of thiaplatinacyclohexadienes **454** and hydrido(thienyl)platinum(II) complex **455** via competing C–S and C–H bond activation of the substrates (Equation (113)).[387]



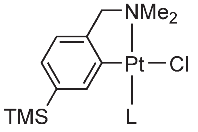
(113)



Scheme 64

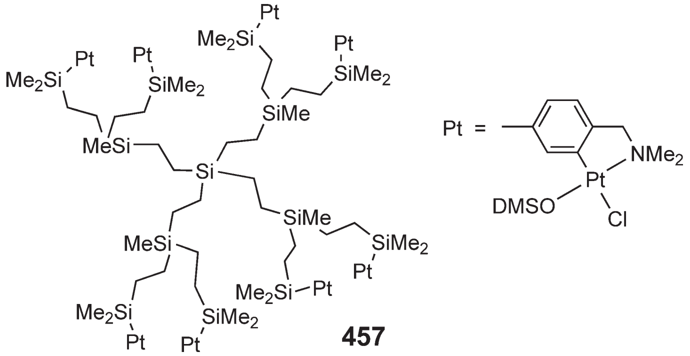
8.08.3.4.4 Platinacycles with one Pt–C σ-bond and Pt–N (or P) bonds

Cyclopatination of benzylamine derivatives produces complexes having a five-membered azaplatinacycle structure. Complex 456 is able to be bonded to dendritic carbosilanes to form the multinuclear complex 457.[388]



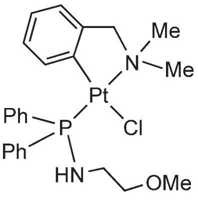
L = DMSO, PPh_3

456



457

Neutral and cationic complexes with cyclometallated *N*,*N*-dimethylbenzylamine and monodentate aminophosphine ligands have been prepared 458–461, where the phosphine ligand occupies the position *trans* to the nitrogen of the cyclometallated ligand.[389]



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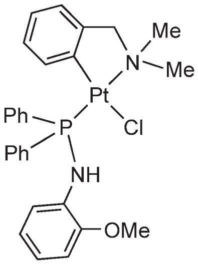

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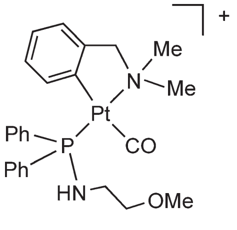

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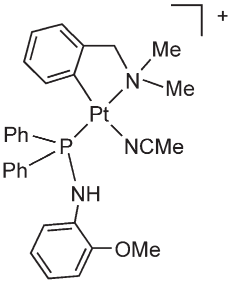
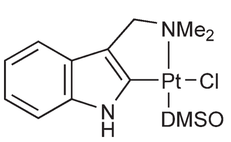


461

Gramine, tryptamine, and (*S*)-tryptamitophan methyl ester undergo metallation to form the five- and six-membered indole-fused platinacycles **462–464**.[390]



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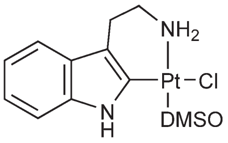
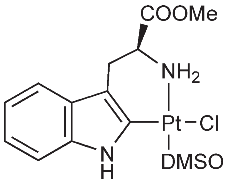
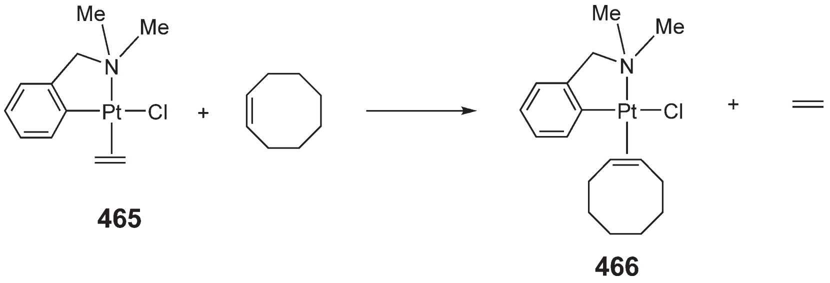


463



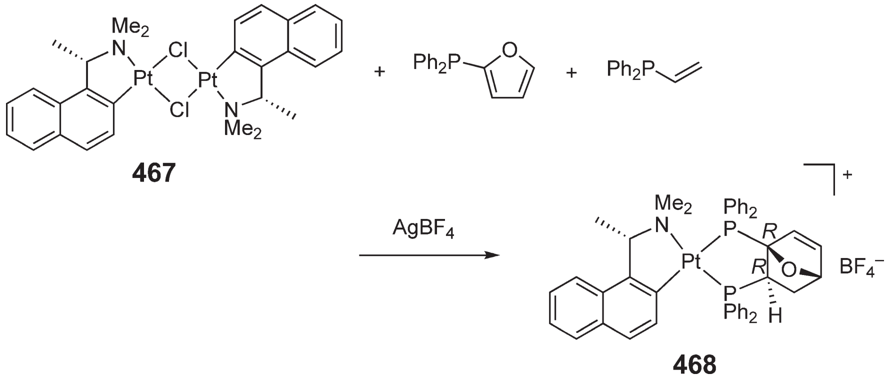
464

The ethylene ligand of the Pt complex with cyclometallated *N*,*N*-dimethylbenzylamine **465** may be substituted by cyclooctene to form the complex with a π-coordinated cyclooctene **466**.[391] The reaction proceeds via an associative pathway (Equation (114)).



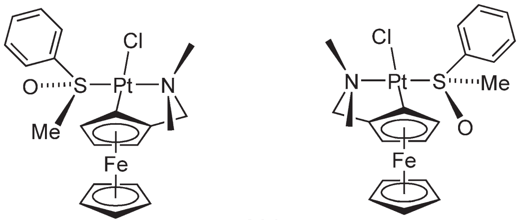
(114)

A chloro-bridged dinuclear complex having cyclometallated optically active amine ligands **467** reacts with diphenyl(furyl)phosphine and vinyl(diphenyl)phosphine in the presence of $AgBF_4$ to produce the complex having a diphosphine formed by Diels–Alder reaction of the two phosphine ligands **468**.[392] The reaction proceeds stereoselectively to afford the product with (*R*,*R*)-configuration. The diphosphine ligand liberated from the Pt center decomposes via a retro-Diels–Alder reaction (Equation (115)).



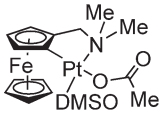
(115)

Ferrocenylmethylamine also functions as a chelating bidentate ligand, and the cyclometallated platinum complex contains a planar chirality. The complex with the cyclometallated (*N*,*N*-dimethylamino)methylferrocene and methyl phenyl sulfoxide ligands **469** is obtained as a mixture of the two diastereomers having the planar chirality and chiral sulfur atom.[393]



469

A series of related complexes with cyclometallated (*N*,*N*-dimethylaminomethyl)ferrocene as the ligands has been prepared **470–475**.[394] The complex with an aqua ligand **472**is oxidized by molecular oxygen to form the corresponding ferrocenium species. Raising the pH of an aqueous solution of **472**, which is stable at pH = 2, causes deprotonation of the aqua ligand to form the complex with an OH ligand **473**.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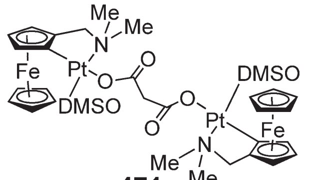
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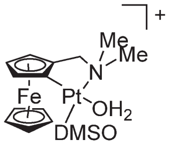
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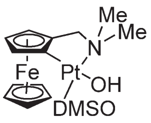
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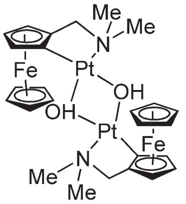
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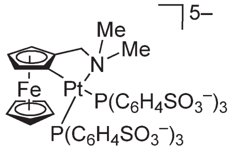
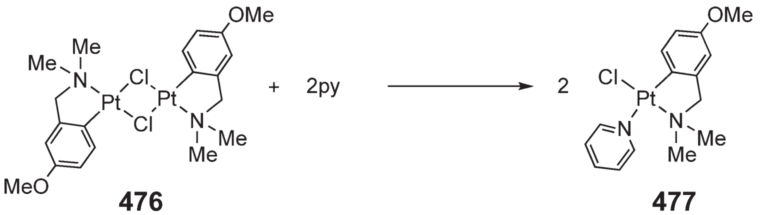
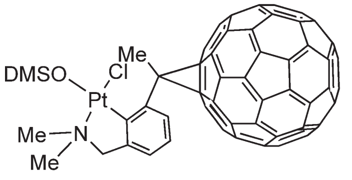

475

Conversion of the dinuclear cyclometallated benzylamine complex with bridging chloro ligands **476** into the mononuclear complex **477** is promoted by pyridine.[395] The reaction proceeds via an associative pathway to form the product with the two ligating nitrogen atoms at *cis*-positions (Equation (116).


476 **477**

(116)

Functionalization of the aromatic ring of the benzylamine ligand enables formation of the cyclometallated complexes with various groups. Dimethylbenzylamine bonded to C_{60} also coordinates to Pt(II) to form complexes containing the C_{60} fragment **478 and 479**.[396] A dinuclear Pt complex with two C_{60}-containing cyclometallated ligands and bridging 4,4′-bipy **480** has also been prepared.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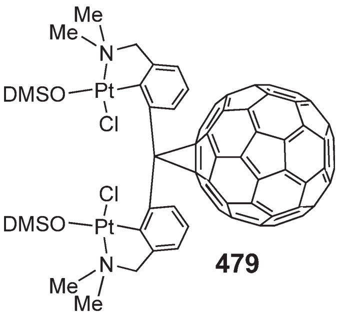
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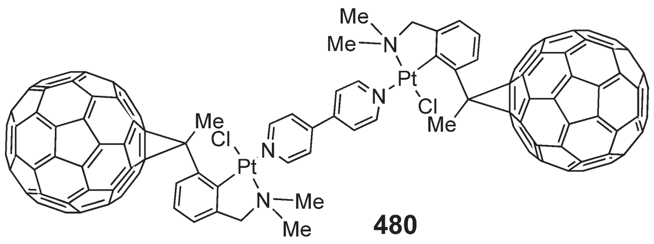
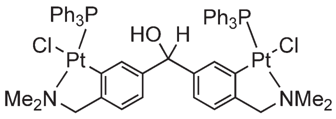

480

Introduction of alkoxymethyl groups to the phenyl ring of the *C*,*N*-chelating ligand leads to the formation of **481** and **482**, and C_{60}-containing dinuclear complex **483**.[397]



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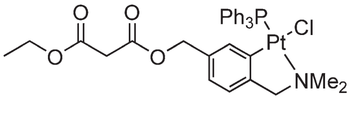

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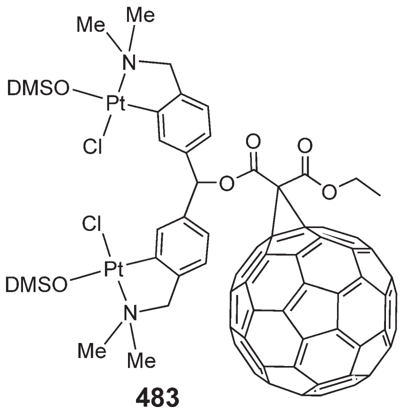
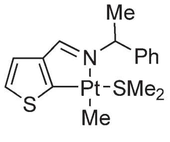


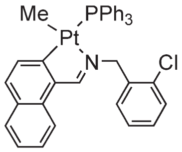
483

2,3,4-Trifluorobenzylidene benzylamine reacts with $[PtMe_2(\mu\text{-}SMe_2)]_2$ to undergo cyclometallation involving C–H bond activation, giving the complex with a five-membered ring **484**;[398] C–F bond activation of the substrate does not occur at all. Addition of PPh_3 to the complex results in substitution of the SMe_2 ligand to form a monophosphine complex **485** or dissociation of the imine ligand to afford a bisphosphine complex **486** depending on the amount of PPh_3 used (Scheme 65).

Complexes with cyclometallated ligands containing thienyl and naphthalenyl groups **487–489** have been obtained.[399–402]



487



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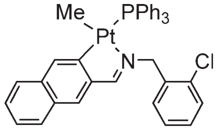
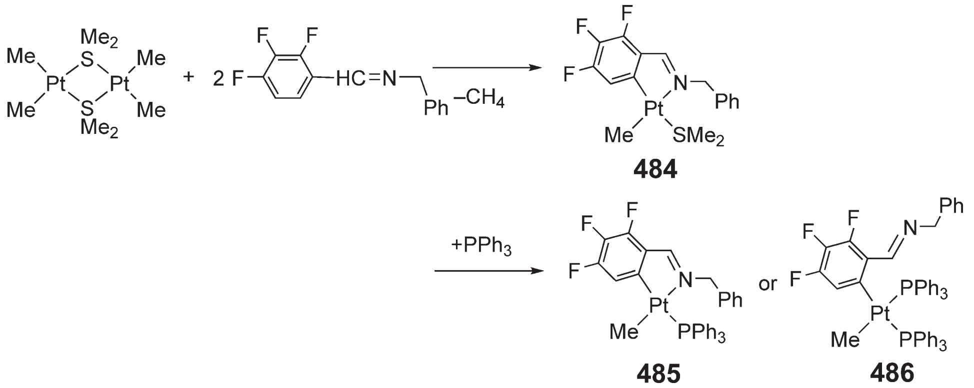
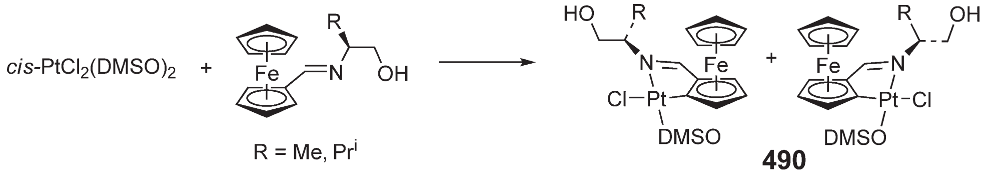


489

Ferrocenylimine also undergoes cyclometallation to produce a platinacycle with planar chirality; the optically active imine forms a pair of diastereomers upon coordination to the Pt complex **490** (Equation (117)).[403]



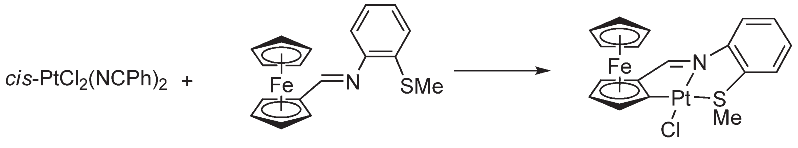
Scheme 65



490

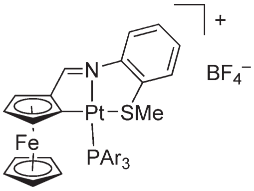
(117)

The reaction of ferrocenylimine having a (2-methylthio)phenyl group at the N atom with $PtCl_2(NCPh)_2$ forms a complex having a *C,N,S*-tridentate ligand (**491**, Equation (118)).[404] Mössbauer, electrochemistry, and molecular orbital calculations were applied to characterize the complexes fully. Related ferrocenylimine-coordinated complexes **492** and **493** have been reported.[405,406]



491

(118)



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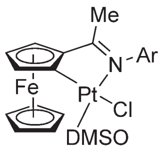
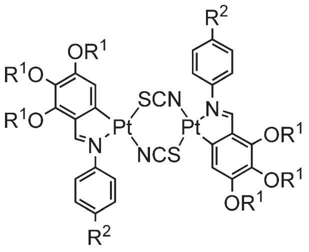


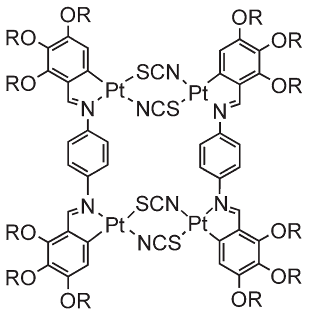
493

Benzylidene anilines having long alkyl and alkoxy groups at the aromatic rings form dinuclear and tetranuclear complexes with bridging SCN ligands **494** and **495**.[407] DSC data for **495** are discussed in relation to its mesomorphic properties. The imines, having electron-donating and electron-withdrawing groups at the two aromatic rings, form dinuclear complexes with bridging Cl, thiolate, and optically active carboxylate ligands **496** and **497**.[408] Dipole moments of the molecules and second-order non-linear optical properties of the compounds have been investigated.



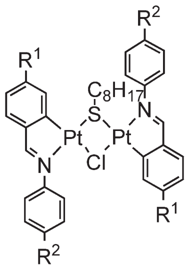
R^1 = Me, C_6H_{13}; R^2 = C_6H_{13}

494

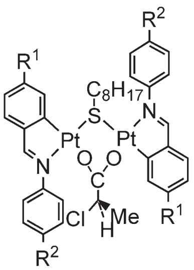


R = C_6H_{13}, $C_{12}H_{25}$

495



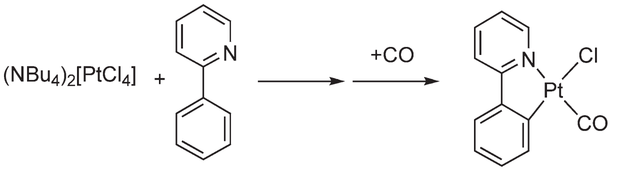
496



R^1 = NO_2; R^2 = OC_8H_{17}
R^1 = OC_8H_{17}; R^2 = NO_2

497

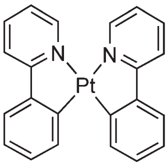
The reaction of 2-phenylpyridine with $(NBu_4)_2PtCl_4$ and introduction of CO into the reaction mixture yield the complex having the *C,N*-chelating ligand (**498**, Equation (119)).[409]



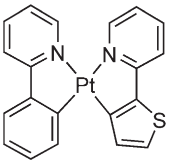
498

(119)

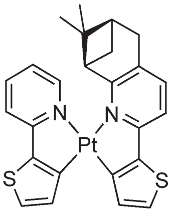
A series of the bis(homoleptic) and heteroleptic complexes with two aromatic *C*,*N*-chelating ligands 499, and 500 has been prepared by exchange of the lithiated ligand with PtCl$_2$(SEt)$_2$.[410] The complex with chiral substituents 501 shows helical distortion of the square-planar geometry.[411]



499



500

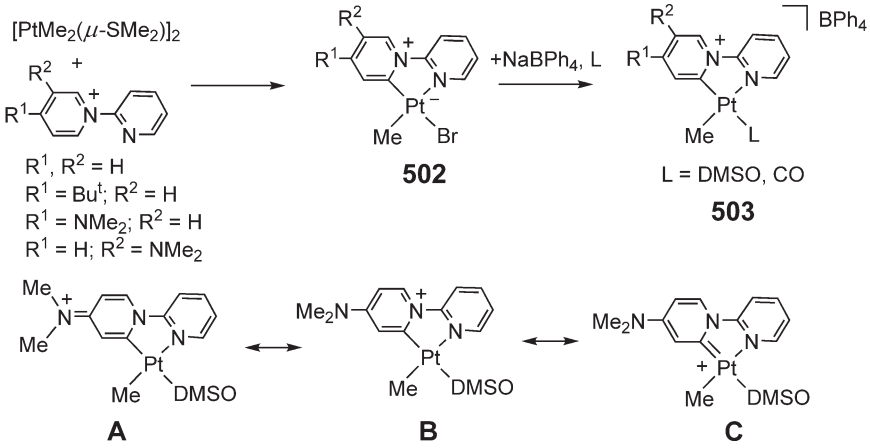


501

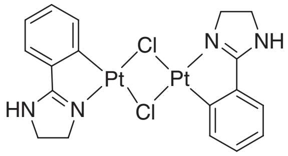
Details of the excited states and emission properties of the complexes with aromatic *C*,*N*-chelating ligands have been investigated by using spectroscopic and theoretical approaches.[412–414] The complexes with a *C*,*N*-chelating ligand and acac ligand show emission which is attributed to a mixed ^{3}LC-MLCT state.[415]

The reagent *N*-pyridyl pyridinium coordinates to Pt(II) as a *C*,*N*-chelating ligand to form neutral and cationic complexes (502 and 503, Scheme 66).[416] NMR studies of the complexes, and IR spectra of the cationic carbonyl–platinum complex (503, L = CO), indicate Pt=C double bond character. The complex with dimethylamino groups at the pyridinium ring can be represented by three stable resonance forms, A, B, and C. Crystal structures of the complexes show localization or delocalization of the π-electrons depending on the position of substituents.

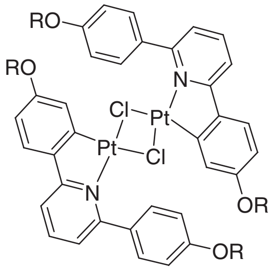
Reactions of 2-phenylimidazoline and of 2,6-bis(4-alkoxyphenyl)pyridine with K$_2$PtCl$_4$ result in cyclometallation of the ligands to form dinuclear complexes with bridging chloro ligands 504 and 505.[417,418] The 2,6-bis(2,4-dialkoxyphenyl)pyridine ligand does not cause cycloplatination but yields a dinuclear complex with a C=Pt bond between Pt and the carbon at the 4-position of the pyridine ring 506; the N–H bond of the ligand is stabilized by hydrogen bonding with alkoxy substituents.



Scheme 66

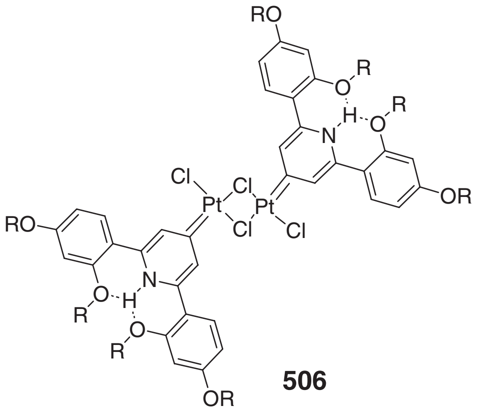


504



505

(R = n-C_6H_{13})

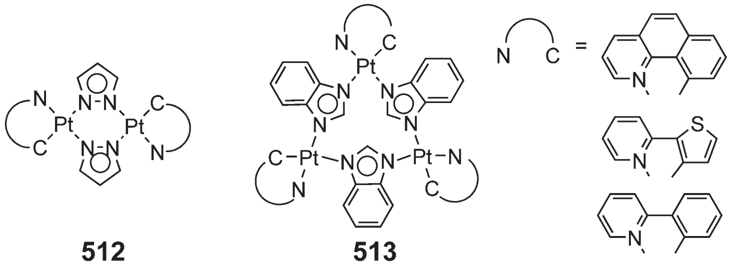


506

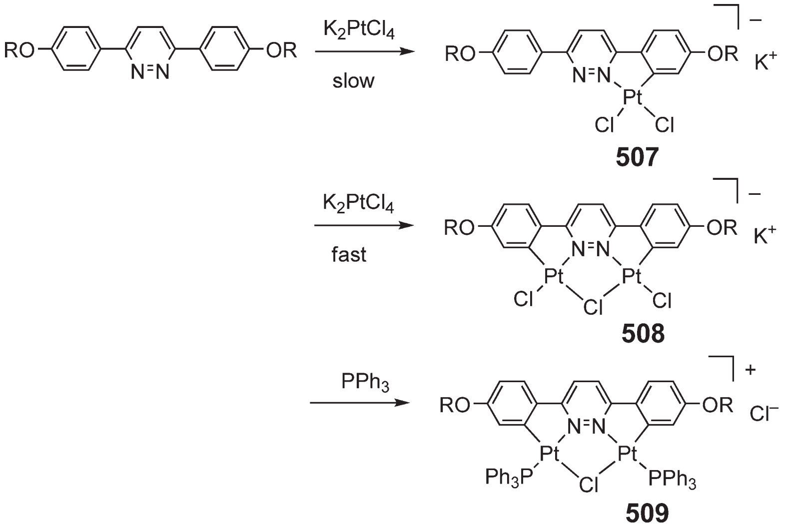
2,5-Diarylpyridazine reacts with K_2PtCl_4 to produce the anionic mononuclear complex **507** (Scheme 67). A further reaction with K_2PtCl_4 yields dinuclear complex **508** whose Pt centers are bridged by a Cl ligand. Non-bridging Cl ligands are replaced by PPh_3 to form cationic complex **509**. The reaction with the pyrazine derivative forms a mononuclear complex exclusively.[419,420]

Azobenzenes with alkyl substituents at the two aromatic rings coordinate to a Pt(II) center, giving complexes with *C,N*-chelating rings (**510** and **511**, Scheme 68).[421] The complexes with a 4-alkoxyphenoxy group at the aryl groups show nematic or smectic liquid crystalline behavior.

A series of dinuclear and cyclic trinuclear Pt(II) complexes is prepared by combining *C,N*-chelating aromatic ligands with pyrazolate and benzimidazolate ligands **512** and **513**.[422] The complexes show a red-shift of the emission peaks compared with the ligand.



512 **513**

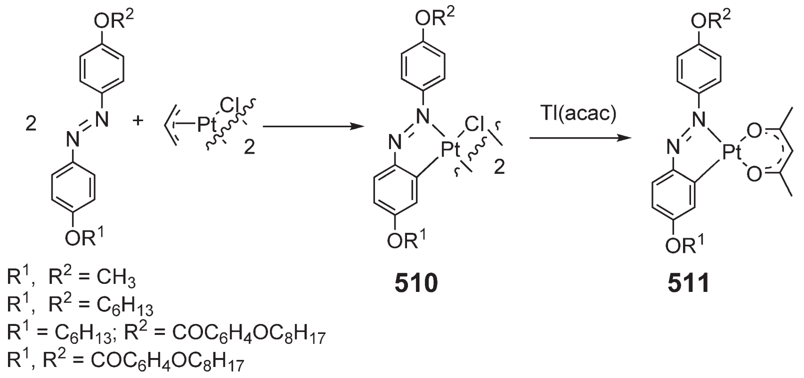


507

508

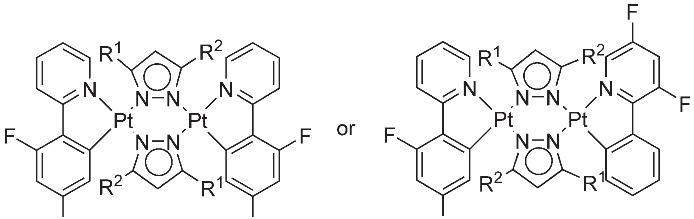
509

Scheme 67



Scheme 68

Table 2 Pt–Pt distances in cyclometallated complexes

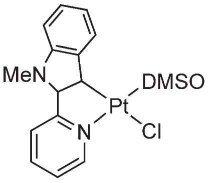


514 **515**

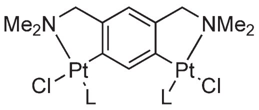
R^1, R^2	*Pt—Pt* (pm)	λ_{max} (nm)
H, H	337.63(7)	458
Me, Me	319.14(9)	462
Me, Bu^t	304.57(7)	515
Bu^t, Bu^t	383.43(6)	570

Dinuclear complexes with cyclometallated pyridyl(difluoro)phenyl ligands 514 and 515 have been obtained by using several pyrazolate detivatives as the bridging ligands.[423] Distances between the Pt centers vary depending on the substituents of the bridging ligands (Table 2). The complexes having longer Pt–Pt distances show longer wavelength for the absorption spectra, and positions of emission are also shifted by changing the bridging ligands.

Pyridyl(*N*-methyl)indole functions as a chelating *C*,*N*-ligand to form a complex with DMSO 516, which reacts with phenylacetylene and alcohol to yield the corresponding complex with a carbene ligand.[424] 1,3-Bis(dimethylamino)benzene reacts with *cis*-$PtCl_2(DMSO)_2$ to form the dinuclear complex 517 (L = DMSO) rather than a mononuclear complex having the ligand with an NCN pincer coordination.[425] Terpy also binds two Pt(II) centers via cycloplatination to form the dinuclear complex 518.[426] Complexes 519 and 520 contain hydroxamate ligands that coordinate to one Pt via *C*,*N*-cyclometallated diimine of benzaldehyde and to another Pt via chelating two oxygen atoms.[427] 2-Pyridyl(diphenyl)phosphine oxide undergoes cycloplatination to form the chloro complex 521.[428]

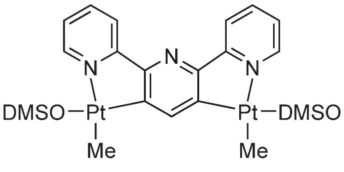


516

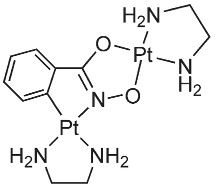


L = DMSO, PPh3

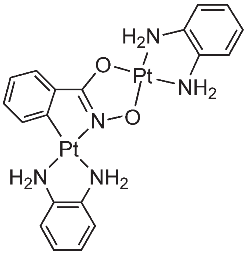
517



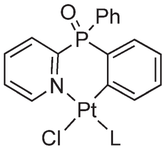
518



519



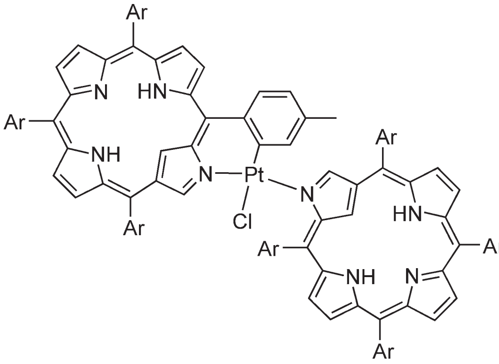
520



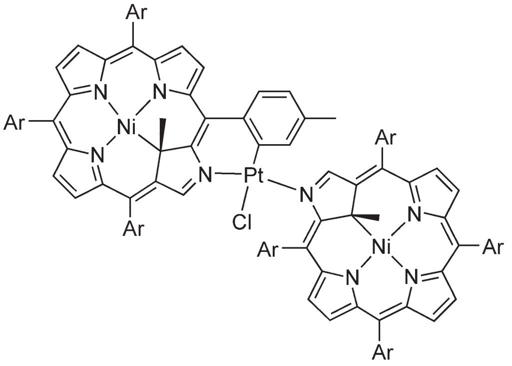
L = CO, SMe_2, PPh_3

521

An *N*-confused porphyrin undergoes cycloplatination upon reaction with $PtCl_2$ to form complex **522**, whose Pt center is bonded to one porphyrin via a metallacycle and to the other porphyrin via a Pt–N single bond.[429] Two nickelaporphyrins having a methyl group at the carbon bonded to Ni coordinate to the Pt center of **523** with a Pt–N σ-bond and *C*,*N*-chelation.[430]

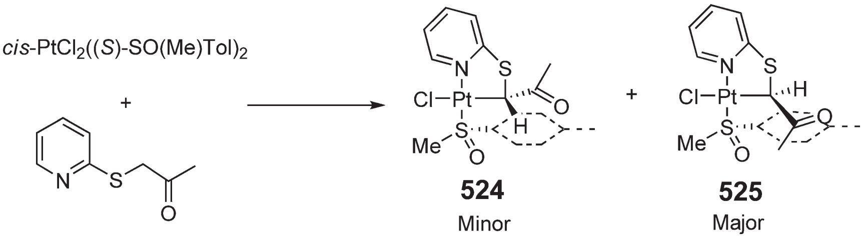


522



523

2-(Acetonylthio)pyridine undergoes cycloplatination involving activation of the C–H bond of the SCH_2 group.[431] The Pt complex with an optically active sulfoxide ligand undergoes stereoselective activation of an enantiotopic C–H bond to form two diastereomeric complexes in different yields **524** and **525** (Equation (120)).

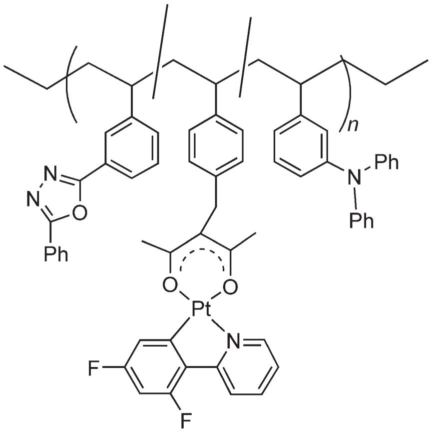


524
Minor

525
Major

(120)

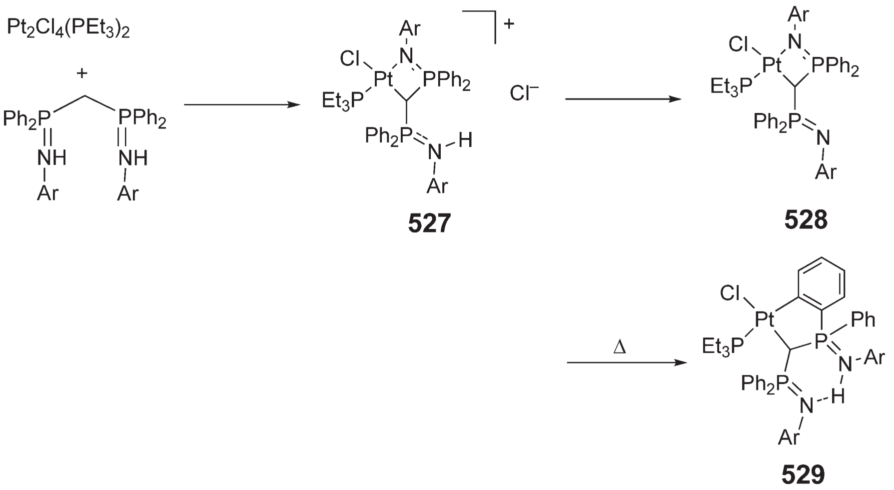
A complex with cyclometallated 2-arylpyridine is employed as the pendant groups of polystyrene functionalized by triphenylamine and isoxazoles **526**.[432] The random co-polymer containing these functional groups in the side chain shows near-white organic light-emitting properties.



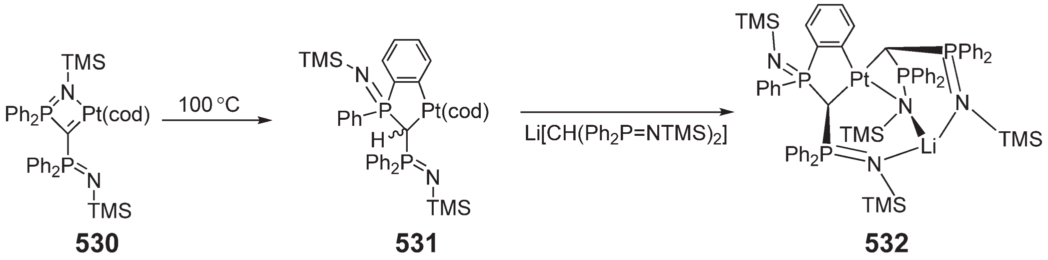
526

Four-membered platinacycles containing a P═N bond are prepared by the reaction of bis(iminophosphoranyl)alkanide with $[PtCl_2(PR_3)]_2$. The reaction of bis(*N*-aryliminophosphoranyl)methane yields cationic and neutral complexes with the –Pt–C–P═N– four-membered ring **527** and **528** (Scheme 69).[433–435] Thermally induced cyclometallation of a phenyl group of the ligand and hydrogen transfer to the coordinating nitrogen atom lead to a five-membered *C*,*C*-platinacycle **529**.

The four-membered platinacycle having P═N and Pt═C double bonds **530** undergoes thermal isomerization into a five-membered cyclic compound **531** via orthometallation of the phenyl group of the ligand; this complex undergoes addition of P═N bond-containing anions to form the multi-cyclic compound **532** (Scheme 70).[436]



Scheme 69



Scheme 70

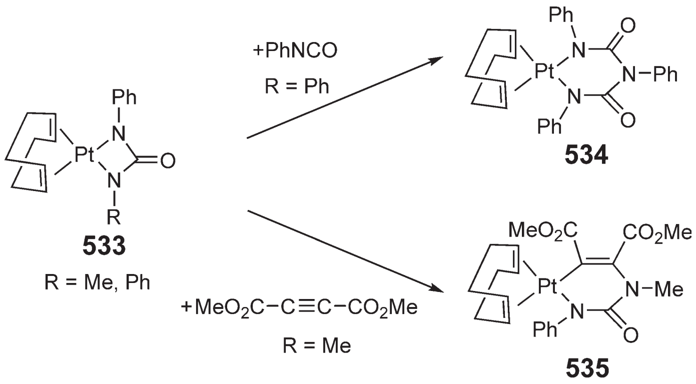
The ureylene Pt complex **533** reacts with phenylisocyanide to form the six-membered cyclic complex **534**, while the reaction of dimethyl acetylenedicarboxylate produces platinacycle **535** via insertion of the alkyne into a Pt–N bond (Scheme 71).[437]

Reactions of benzoylacetoanilide and of cyanoacetylurea with $PtCl_2(PPh_3)_2$ in the presence of base yield the four-membered platinacycles **536** and **537**, respectively (Scheme 72).[438,439]

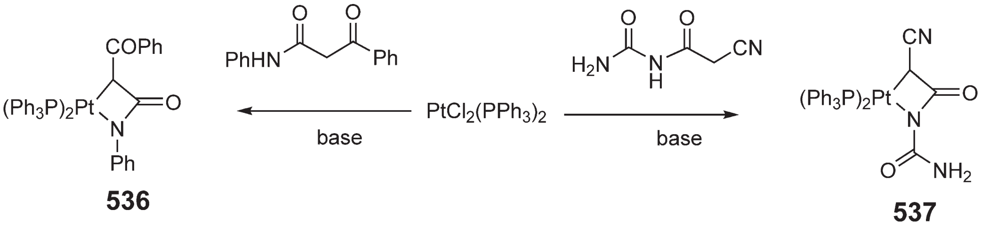
Bis(dimethylamino)methane reacts with $PtCl(CH_2Cl)(cod)$ in the presence of PPh_3 to form a complex having a (dimethylamino)carbene ligand **539** via the isolable intermediate complex with a *C,N*-chelating ligand (**538**, Scheme 73).[439] The reaction using $AsPh_3$ results in isolation of the carbene complex with a protonated dimethylaminomethyl ligand **540**.

A review article summarizes the above reactions involving the insertion of unsaturated molecules and cyclization.[441]

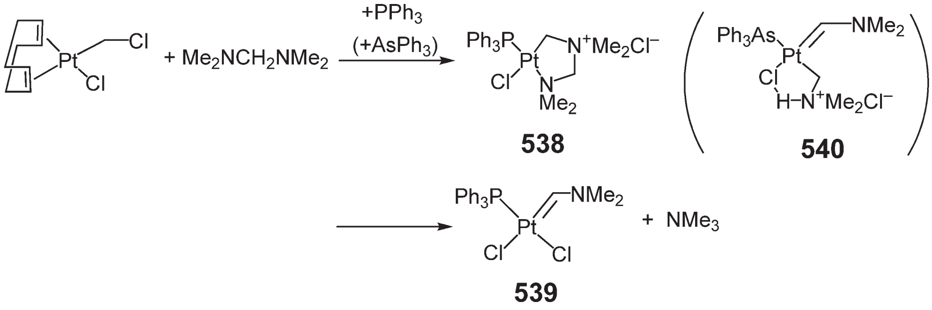
Cycloplatination of phosphine ligands forms complexes with *C,P*-chelating ligands, although it is less common than cycloplatination to give the compounds with a *C,N*-chelating ligand. Hydrolysis of $PtF(PPh_3)_3$ produces



Scheme 71

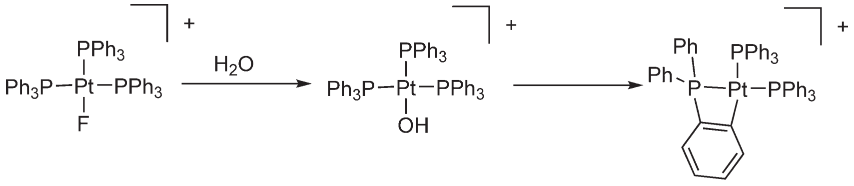


Scheme 72



Scheme 73

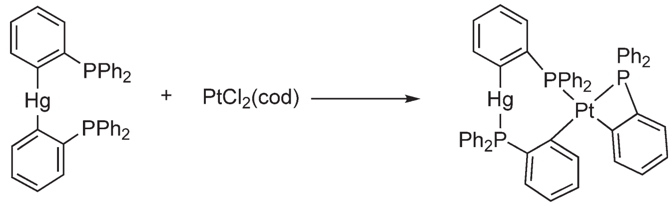
$Pt(OH)(PPh_3)_3$, which is slowly converted to a cationic Pt complex with an orthometallated PPh_3 ligand (**541**, Equation (121)).[442]



541

(121)

Reaction of bis(κ^1,*C*-triphenylphosphine)mercury **542** with $PtCl_2(cod)$ forms the Pt–Hg dinuclear complex having a four-membered phosphaplatinacycle structure **543** (Equation (122)).[443]



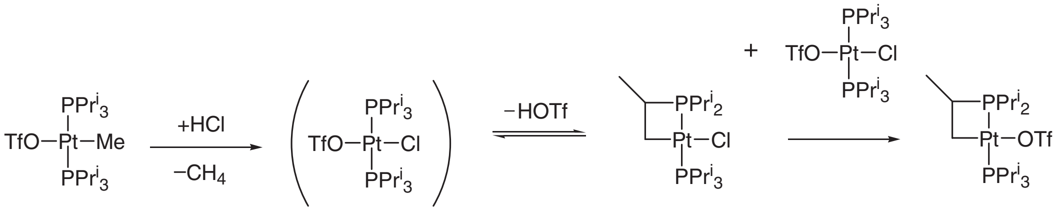
542

543

(122)

A PPr^i_3 ligand bonded to Pt results in metallation of an Me group to form a four-membered cyclic complex. The methyl(triflate)platinum complex is converted into a phosphaplatinacyclobutane with a triflate ligand **545** in the presence of a small amount of HCl (Scheme 74).[444] The reaction involves several steps involving an intermediate phosphaplatinacyclobutane with a Cl ligand **544**.

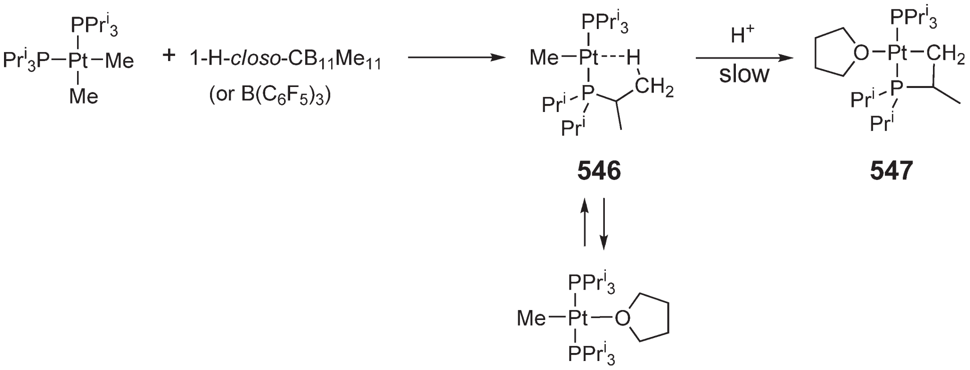
Carborane or $B(C_6F_5)_3$ abstracts a methyl ligand from a dimethylplatinum complex with PPr^i_3 ligands to form the cationic phosphaplatinacyclobutane containing THF ligand **547** (Scheme 75).[445] The T-shaped methylplatinum(II)



544

545

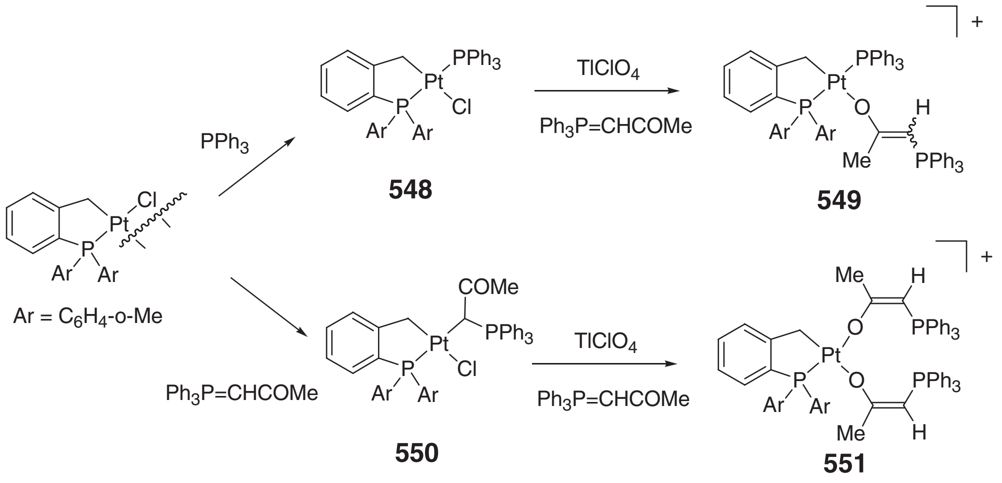
Scheme 74



546

547

Scheme 75

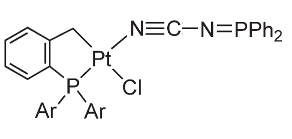


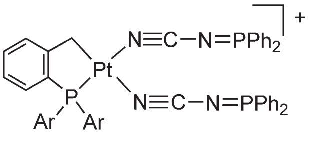
Scheme 76

intermediate having two triisopropylphosphine ligands **546** has been isolated and fully characterized. Crystallographic results show an agostic interaction by the methyl group of a phosphine ligand. Complex **546** in a THF solution is in rapid equilibrium with the methyl complex with a THF ligand and is converted slowly into **547**, a process which is promoted by H^+.

A dinuclear Pt complex with chelating tris(*o*-tolyl)phosphine and bridging chloro ligands has been converted into a neutral PPh_3-coordinated complex **548** and then into cationic complexes containing phosphonium-substituted enolate ligands (**549**, Scheme 76). Reaction with phosphorus ylides produces **550** and **551**.[446]

The *C*,*P*-chelating tris(*o*-tolyl)phosphide ligand supports Pt complexes with one or two iminophosphorane ligands **552** and **553**.[447]



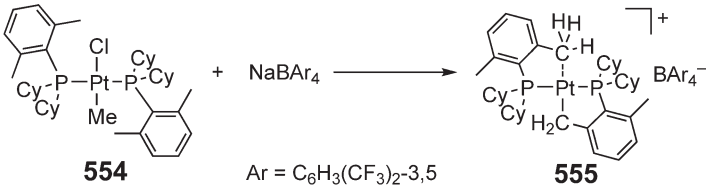


Ar = *o*-Tol

552

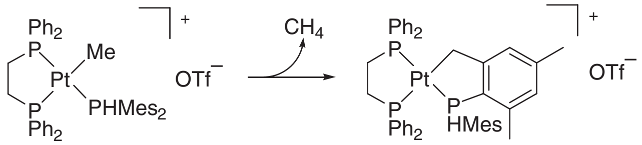
553

The chloro(methyl)platinum complex with two dicyclohexyl(mesityl)phosphine ligands **554** undergoes abstraction of the chloro ligand by $[B(C_6H_3(CF_3)_2\text{-}3,5)_4]^-$, accompanied by cyclometallation of a phosphine ligand to form **555** (Equation (123)).[448] X-ray crystallography indicates that the complex contains a direct interaction between the methyl carbon of the other ligand and the Pt center, rather than a C–H–Pt agostic interaction of the methyl group.



(123)

A cationic complex containing the $PHMes_2$ ligand undergoes cyclometallation of a mesityl group of the phosphine ligands to form a phosphaplatinacyclopentane complex **556** (Equation (124)).[449]

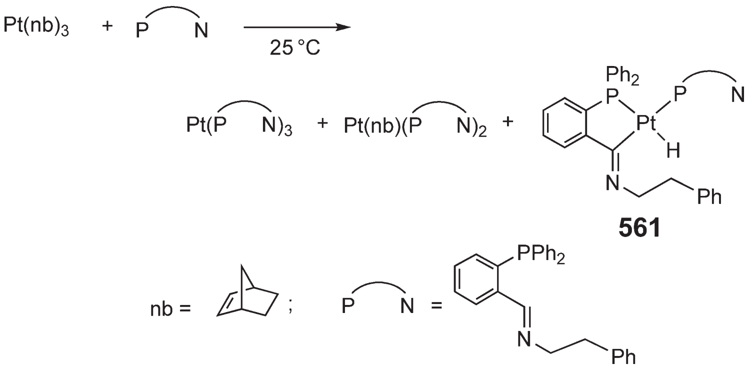


556

(124)

Diisopropyl(mesitylmethyl)phosphine reacts with PtMe$_2$(cod) to form two isomeric methylplatinum complexes with a cyclometallated phosphine **557** and **558** and a complex with two cyclometallated phosphine ligands (**559**, Scheme 77).[450] Complex **557** is obtained as the sole product of the reaction at room temperature and has been fully characterized. The reactions at 100–130 °C produce **558** and **559**, while a geometrical isomer of **559** is not formed at all. Partial dissociation of the Pt–P bond is proposed to explain the isomerization of the complexes and selectivity of the reaction at high temperature. Complex **557** reacts with trialkylsilane to afford a hydridoplatinum complex **560** with phosphorus atom positions changed from *cis* to *trans*, accompanied by elimination of methyl(trialkyl)silane.[451]

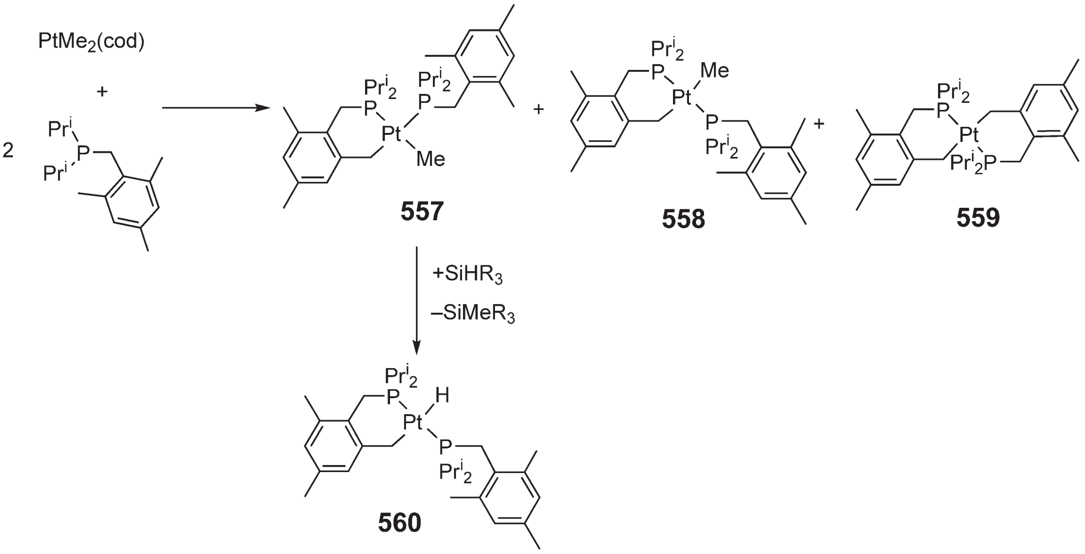
A diphenylphosphine donor as part of an aldimine ligand coordinates to Pt as a *C,P*-ligand via C–H bond activation of the imine carbon to form a hydride complex **561** (Equation (125)). It is equilibrated with the Pt(0) complex Pt(P–N)$_3$.[452]



561

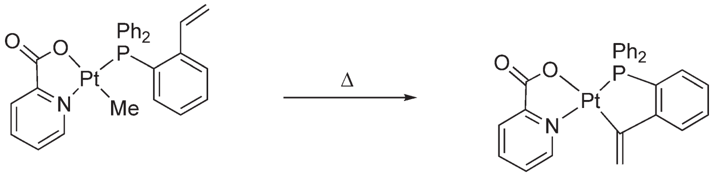
(125)

Diphenyl(*o*-vinylphenyl)phosphine also coordinates to Pt(II) as a chelating *P,C*-ligand to form a five-membered ring (**562**, Equation (126)).[453]



557 **558** **559** **560**

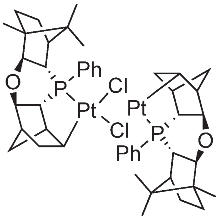
Scheme 77



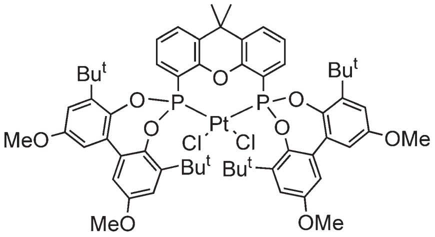
562

(126)

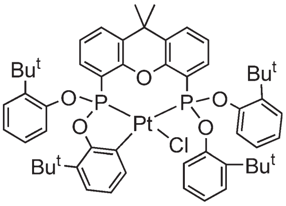
The pentacyclic phosphine containing two norbornyl groups bridged by O and P atoms undergoes cyclometallation of one of the norbornyl groups to give a five-membered phosphaplatinacyclopentane **563**.[454]



563



564

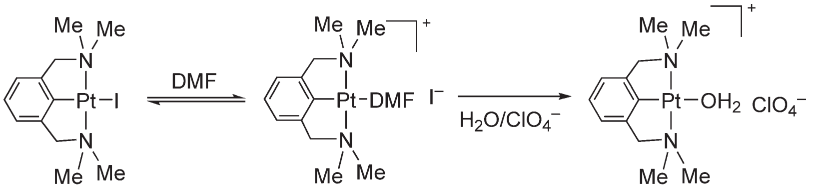


565

Bidentates having two substituted aryloxy substituents and a tricyclic fragment connecting two phosphorus atoms are also able to form a simple $PtCl_2P_2$ type complex **564**, or undergo cyclometallation to give a monochloroplatinum complex with a five-membered ring **565**.[455] The bis(chloromethyl)platinum complex of dppm reacts with PPh_2H to induce formal insertion of a CH_2 group into the Pt–P bond, forming a five-membered platinacycle having two PPh_2 groups within the chelate ring (**566**, Scheme 78);[456] bicyclic complex **567** has also been prepared and fully characterized.

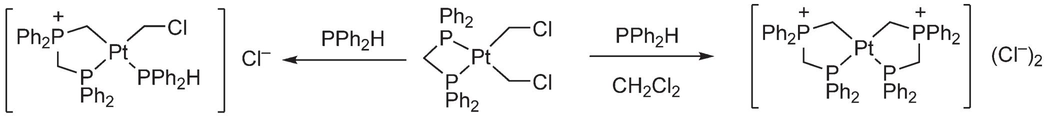
8.08.3.4.5 Platinum(II) complexes with tridentate ligands

Platination of 1,3-bis(*N*,*N*-dimethylaminomethyl)benzene leads to the Pt(II) complex having a 2,6-bis(*N*,*N*-dimethylaminomethyl)phenyl ligand. It is the common and important NCN pincer-type ligand which coordinates not only square-planar Pt(II) and Pd(II) centers but also octahedral Ru(II) centers. The cationic aqua–platinum(II) complex with this pincer ligand **568** is prepared from the corresponding iodoplatinum(II) complex (Equation (127)).[457] The aqua ligand is easily replaced by weak donors such as Cl^-, Br^-, I^-, N_3^-, and NCS^-, and undergoes rapid exchange of the ligand with added water.[458] Kinetic studies have revealed an associative mechanism and enhancement of the ligand exchange by a σ-donating aryl ligand at the *trans*-position.



568

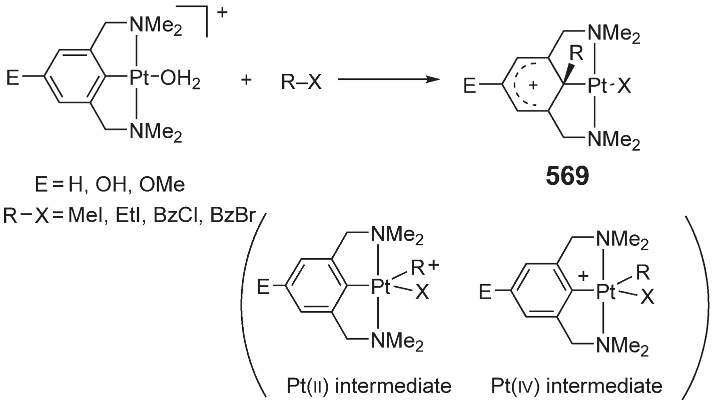
(127)



566 **567**

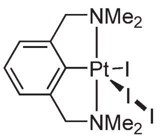
Scheme 78

Cationic platinum(II) complexes with an NCN pincer ligand and an aqua ligand react with MeI, EtI, and BzBr to form a new C–C bond between the aryl and alkyl groups, giving Pt(II) complexes with iodo and alkylarenium ligands (**569**, Equation (128)).[459] The complex with a methyl group at the ligand releases methylated ligand upon reaction with KCN. The C–C bond-forming reaction proceeds via initial formation of a Pt–R bond followed by 1,2-migration of the alkyl group from Pt to the coordinating aryl group. The intermediate complex for R = Bz is spectroscopically evidenced, and is proposed to have Pt(IV) center and a positive charge at the Pt center, rather than a Pt(II) intermediate having a carbocation bonded to Pt.

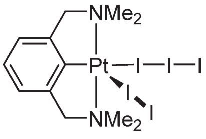


(128)

The iodoplatinum(II) complex with an NCN pincer ligand reacts with I_2 to form the pentacoordinated Pt complex with I and κ^1-I_2 ligands **570** and that with I_3^- and I_2 ligands **571**.[460] They have been fully characterized by crystallography as well as Raman and far IR spectroscopy.



570

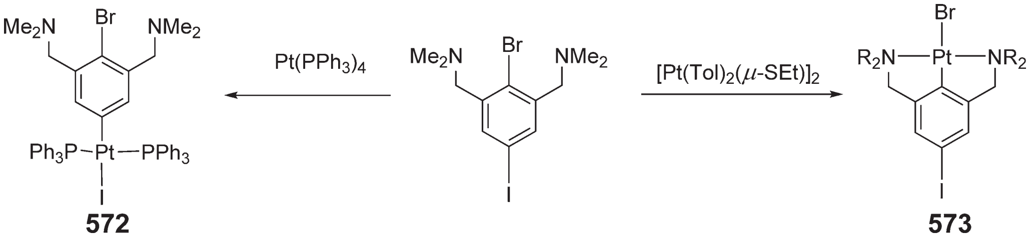


571

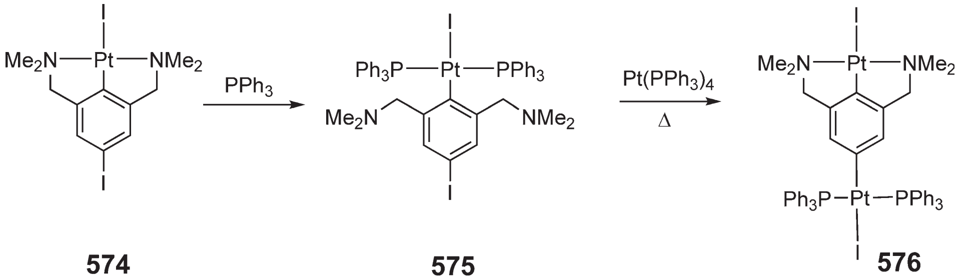
Various functional groups such as formyl, alkoxy, carboxylate, and halogeno groups have been introduced at the *para*-position of the Pt complexes of the pincer ligand.[461] 3,5-Bis(dimethylaminomethyl)–4-bromo–iodobenzene reacts with Pt(PPh$_3$)$_4$ and with Pt(Tol)$_2$(SEt$_2$)$_2$ to produce the complexes having the ligand with κ^1-*C*-coordination **572** and with κ^3-*N,C,N*-coordination **573**, respectively (Scheme 79).

The iodo complex with the 2,6-bis(*N,N*-dimethylaminomethyl)–4-iodophenyl ligand **574** reacts with PPh$_3$ to produce a complex with a κ^1-*C*-ligand and two PPh$_3$ ligands **575** (Scheme 80). Further reaction with Pt(PPh$_3$)$_4$ forms a dinuclear complex whose ligand is bonded to Pt centers via two coordination modes **576**.

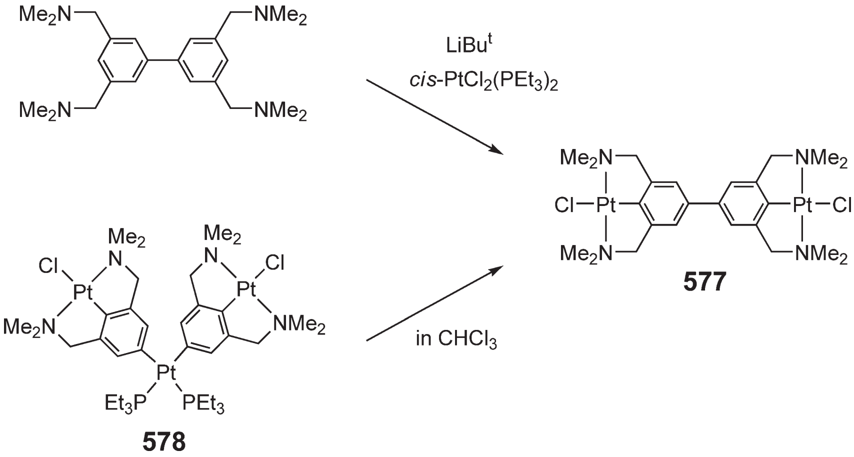
3,3′,5,5′-Tetrakis(dimethylaminomethyl)biphenyl reacts with LiBu^t and *cis*-PtCl$_2$(PEt$_3$)$_2$ to form a dinuclear complex with a bridging dipincer ligand **577**. Reductive elimination from the Pt complex having two pincer ligands *C*-bonded to a Pt center **578** also affords the same dinuclear complex (Scheme 81).[462]



Scheme 79



Scheme 80

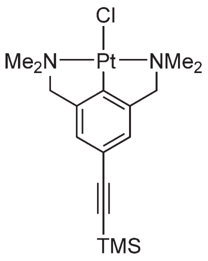


Scheme 81

Cationic dinuclear complex **579** undergoes stepwise methylation by MeI to produce complexes with one or two methylarenium ligands in the molecule depending on the reaction conditions (Scheme 82).

The methylation occurs reversibly, similar to the corresponding mononuclear Pt complexes with a pincer ligand. The dinuclear complex having a phenylene spacer between the Pt centers **580** undergoes monomethylation upon reaction with MeI.[463] A dinuclear Pt–Pd complex with a bridged dipincer ligand **582** has been prepared by stepwise coordination of the bifunctional ligand to the metals (Scheme 83).[464] Lithiation of the ligand precursor having an $SiMe_3$ group occurs at the aromatic C–H bond, followed by introduction of the chloroplatinum group, producing **581**. The $SiMe_3$ group of the ligand is replaced easily by Pd in the presence of LiCl and MeOH to afford **582**.

A complex with an alkynyl group bonded to the phenyl ring **583** may be converted into an Au–Pt complex **584**.[465] A dinuclear Pt complex with the pincer ligand connected by a polyyne spacer **585** has been prepared by metallation of the ligand precursor;[466] electrochemical studies suggested no interaction between the two metal centers of the molecule.



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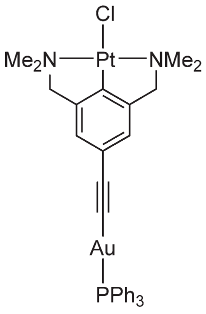

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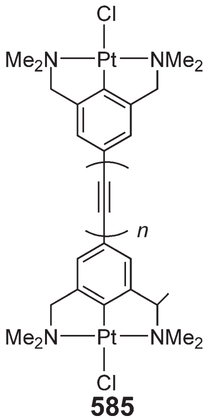

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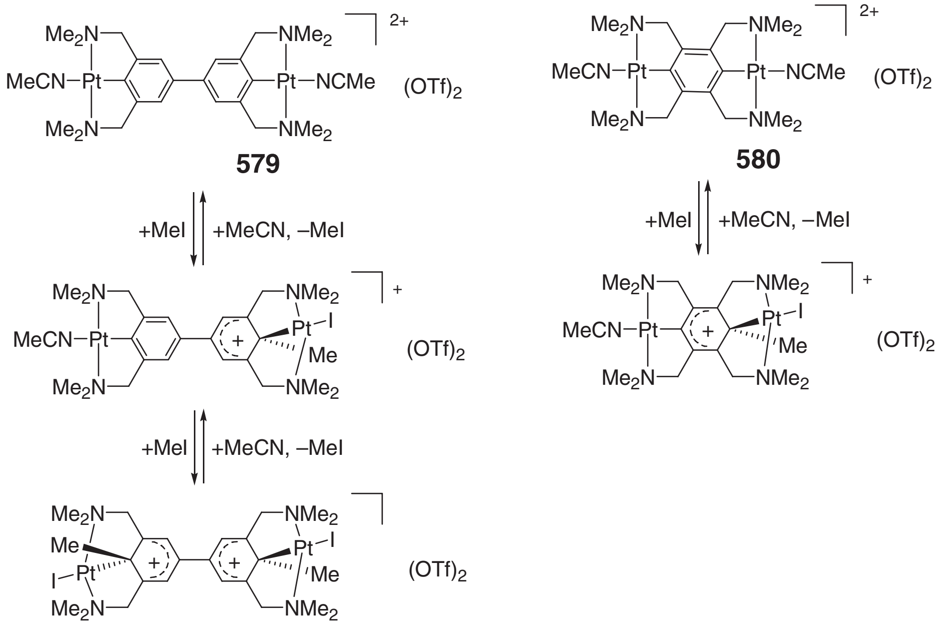
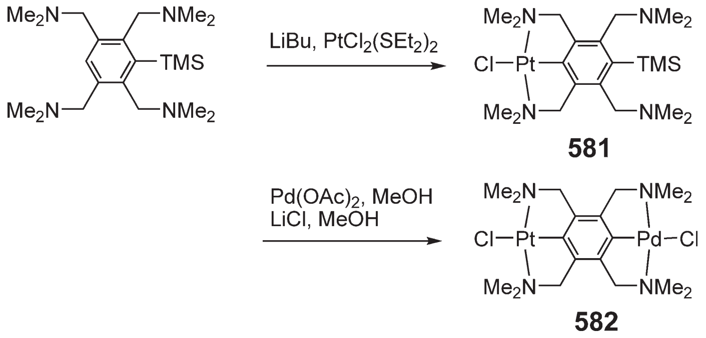
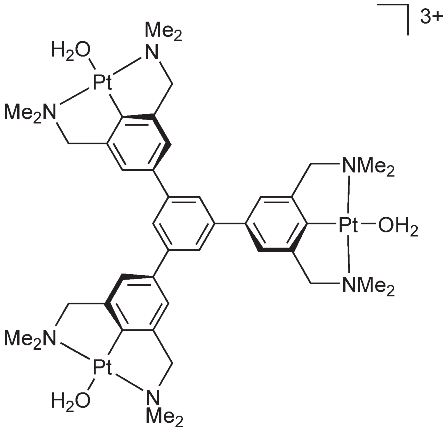


Scheme 82



Scheme 83

Trinuclear **586** and hexanuclear Pt complexes **587** with pincer ligands have been prepared from the corresponding multifunctional pincer ligand.[467,468]



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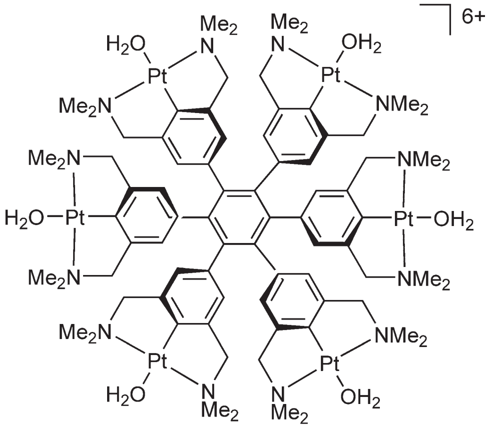
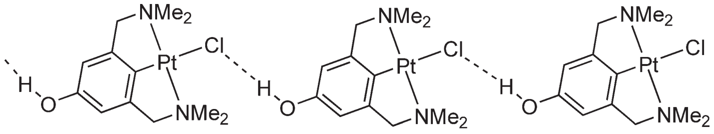


587

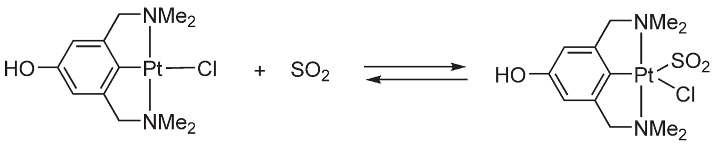
Immobilization of the trinuclear and hexanuclear halogenoplatinum complexes with the pincer ligand on a quartz micromembrane enabled its utilization as the sensor for SO_2 at ppm levels.[469]

Crystallography of the Pt complex with a pincer ligand having an OH group at the 6-position **588** indicated that intermolecular hydrogen bonds between the OH group and the chloro ligand occur to form a one-dimensional hydrogen-bonded polymer structure;[470] relevant structure parameters are Cl···H 230(10) pm and Cl···H–O 161(15)°



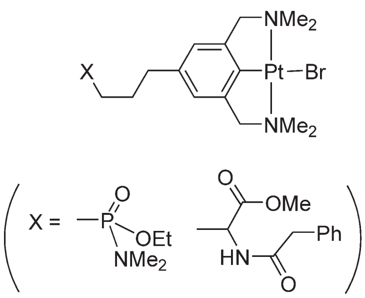
588

The chloroplatinum(II) complex with a 2,6-bis(dimethylaminomethyl)-4-hydroxyphenyl ligand **589** undergoes reversible coordination of SO_2 to form **590** in the solid state (Equation (129)).[471] Both the starting complex and its SO_2 adduct have a strong alignment of the molecules due to intermolecular OH···Cl hydrogen bonding in the solid state. Repetitive expansion and reduction of the crystal lattice is observed without loss of crystallinity during the reversible processes.



589 **590** (129)

Complexes with a functionalized pincer ligand **591**, PPh_2H-coordinated complex **592**, and Pt–Pd dimer with bridging PPh_2 ligand **593** have been reported.[472,473]



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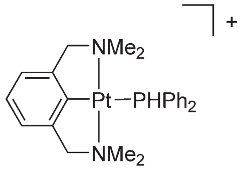

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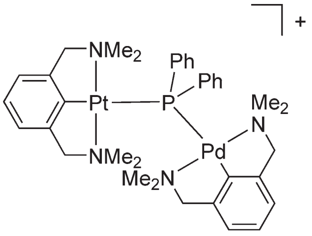
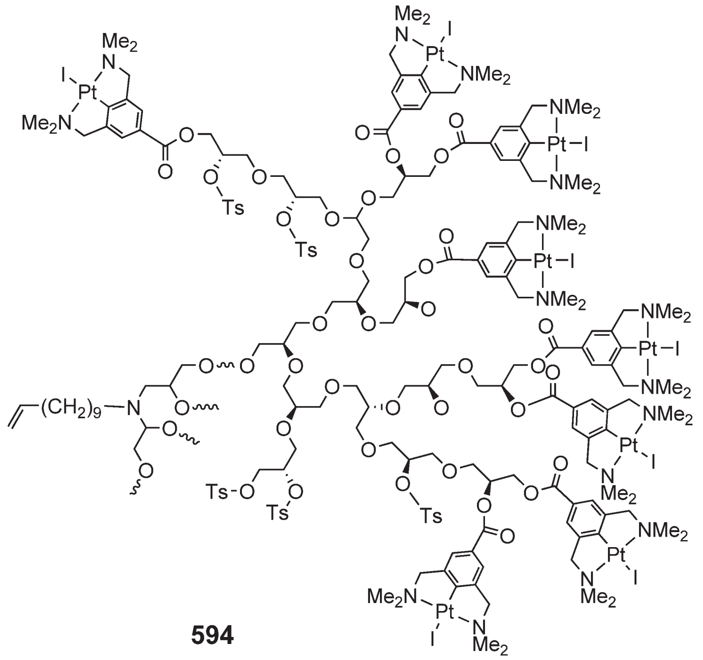


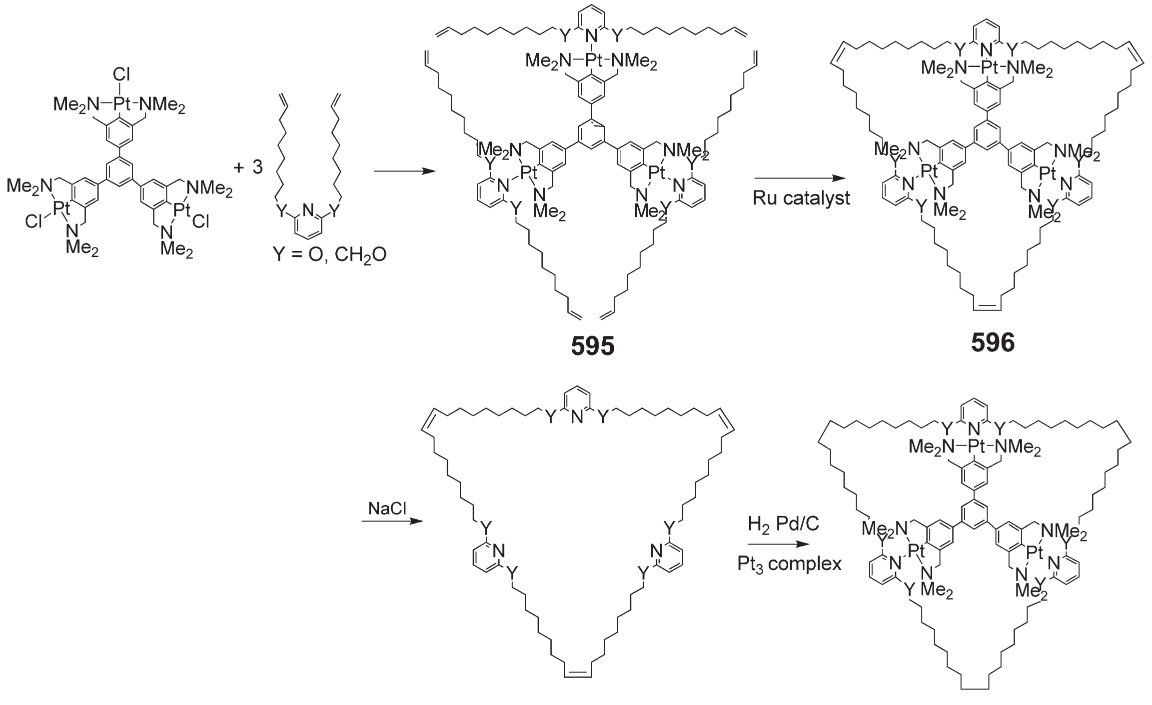
593

A Pt pincer complex is able to be bonded to the optically active hyperbranched polyglycerol as pendant groups **594**. The CD spectra of the polymer complex with different absolute configuration of the monomer units show opposite signs of the peak at 262 nm. The polymer-bonded complex catalyzes asymmetric addition of ethyl α-cyanoacetate to methyl vinyl ketone.[474]



594

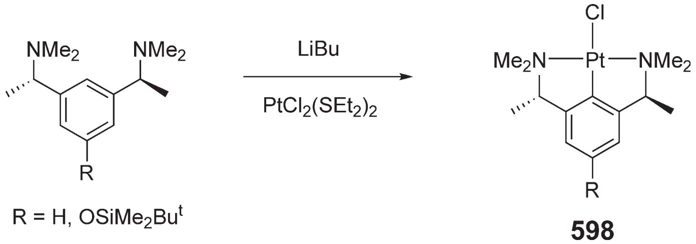
Macrocycles composed of three pyridine rings and polymethylene spacers can be synthesized using the trinuclear Pt–pincer ligand complex **595** as a template (Scheme 84).[475] Metathesis of the vinyl groups of the 2,6-disubstituted pyridine forms the unsaturated macrocycle **596**; demetallation, hydrogenation of the C=C bond, and remetallation of the pyridine groups lead to the trinuclear complex with the tripincer ligand and a pyridine-containing macrocyclic ligand **597**.



595 **596** **597**

Scheme 84

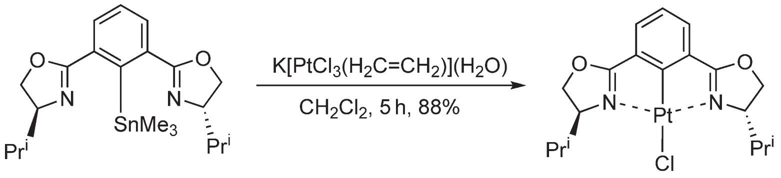
Lithiation of optically active 2,6-bis(1-dimethylaminoethyl)benzene occurs at the aromatic C–H group between the two substituents, and addition of $PtCl_2(SEt_2)_2$ to the lithium salt forms the Pt pincer complex **598** (Equation (130)).[475–478] The complex having an OH group at 4-position is prepared by desilylation of the complex having an $OSiMe_2Bu^t$ group by NBu_4F.



598

(130)

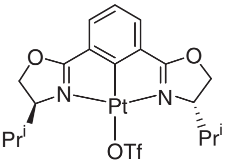
A chloro complex **599** with an optically active NCN pincer-type ligand, having two chiral imidazole groups ((*S*,*S*)-Phebox), has been prepared via the reaction of the stannyl derivative of the ligand with Zeise's complex (Equation (131)).[479]



599

(131)

Complex **599** has been converted to a triflate derivative **600**, to a cationic complex with an aqua ligand **601**, and to a cationic complex with an imine ligand **602**. The complexes catalyze asymmetric addition of alkyllithium to the imine, and aldol-type condensation reactions of aldehyde and isocyanides with active methylene groups.[480] An achiral tridentate ligand with oxazole rings **603** and a diimine having *N*-cyclohexyl groups at the imine groups **604** catalyze Diels–Alder reactions between cyclopentadiene and acrylonitrile.[481,482] Emission properties of the complexes have been studied.[483,484]



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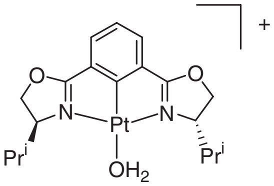

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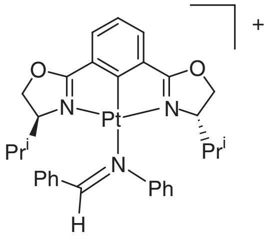

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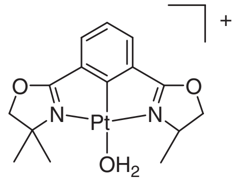

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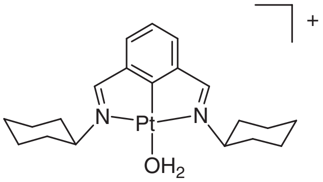
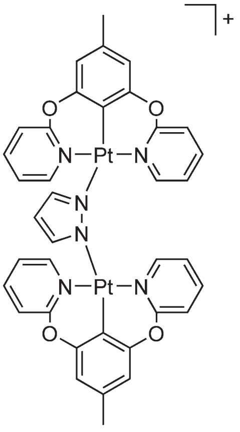


604

The complex having a 2,6-di(2-pyridoxy)phenyl ligand may be formed by cyclometallation, and dinuclear Pt complexes with bridging pyrazole **605** and imidazole ligands **606** have been prepared.[485]



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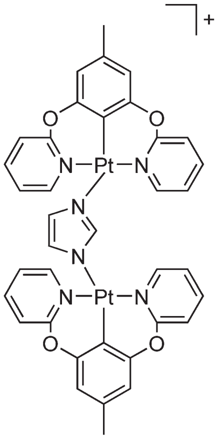

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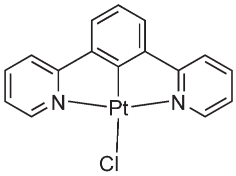

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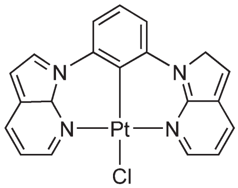
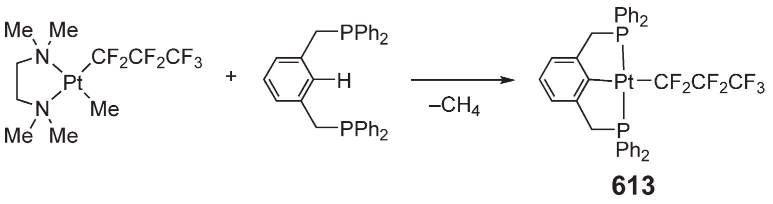


608

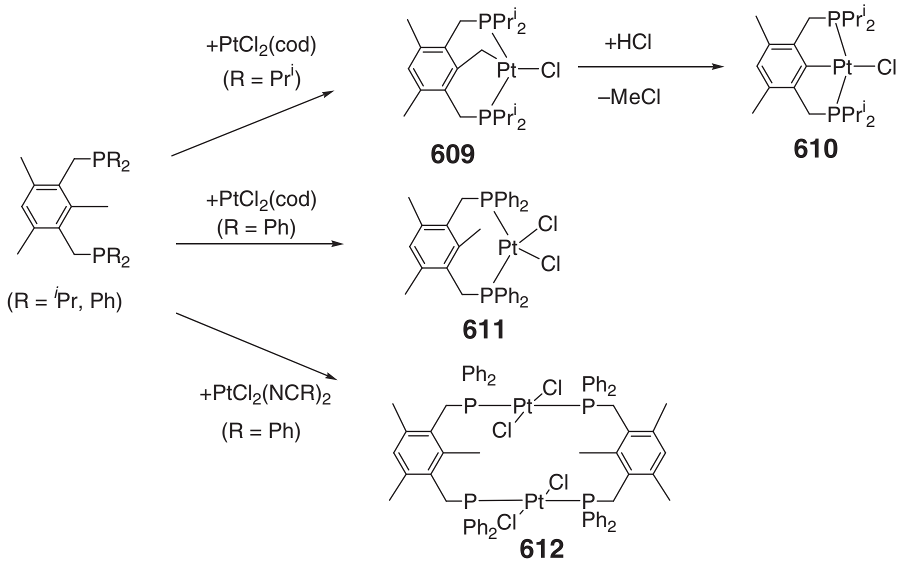
1,3-Bis(2-pyridyl)benzene and 1,3-bis(7-azaindolyl)benzene react with K_2PtCl_4 to form complexes having these compounds present as NCN pincer-type ligands 607 and 608; the direct metallation proceeds with heating in HOAc or MeCN solution.[486–488]

2,4,6-Trimethyl-1,3-bis(diisopropylphosphino)benzene reacts with $PtCl_2$(cod) to produce a benzylic platinum complex 609 via C–H bond activation (Scheme 85).[489,490] Addition of HCl to the isolated complex causes facile C–C bond activation to give the complex with a PCP pincer ligand 610. A similar ligand having diphenylphosphino groups does not cause direct metallation of the Pt(II) complexes, but produces eight- or 16-membered cyclic compounds without a Pt–C bond 611 and 612.[491]

The complex with a PCP pincer ligand and a heptafluoropropyl ligand 613 has been prepared by metallation of 1,3-bis(diphenylphosphinomethyl)benzene by the dialkylplatinum(II) complex of TMEDA (Equation (132)).[492]

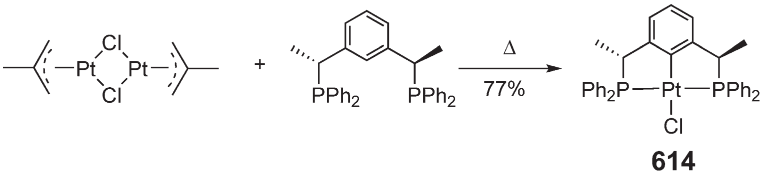


(132)



Scheme 85

The complex with an optically active PCP pincer ligand having C2 chirality **614** is obtained from C–H bond activation of 1,3-disubstituted benzene (Equation (133)), and catalyzes the aldol reaction of methylisocyanoacetate with aldehydes.[493]

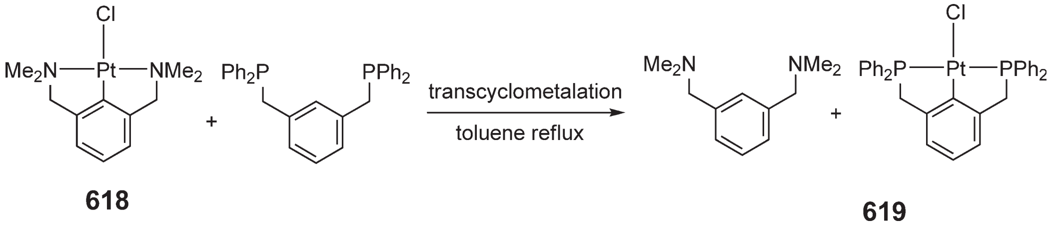


(133)

A 4-methylanilidoplatinum(II) complex with a PCP pincer-type ligand **615** reacts with acrylonitrile to form an alkylplatinum complex **616** via insertion of the C═C bond into the Pt–N bond (Scheme 86). Protonation of the complex releases *N*-(2-cyanoethyl)-4-methylaniline. The Pt complex also catalyzes addition of the aniline to the C═C bond of acrylonitrile.[494]

Protonation of the hydridoplatinum(II) complex with a PCP pincer ligand **617** results in the formation of a cationic dihydrogen-coordinated Pt(II) complex at −80 °C (**617**, Scheme 87).[495] Warming the solution in CD$_2$Cl$_2$ causes evolution of dihydrogen to give the Pt complex with the PCP ligand and the solvent as a ligand.

Transcyclometallation of NCN and PCP pincer ligands, including C–H bond activation of the aryl group, has been investigated.[496] 1,3-Bis(diphenylphosphinomethyl)benzene causes ligand exchange of the Pt complex with the NCN pincer ligand **618** under toluene reflux conditions, giving the complex with the PCP ligand (**619**, Equation (134)). The reactions at room temperature and under benzene reflux form a mononuclear complex with the PCP pincer ligand and κ^1-bonded 2,6-bis(dimethylaminomethyl)phenyl ligand **620** and a cyclic dinuclear complex containing bridging bisphosphine ligands **621**.



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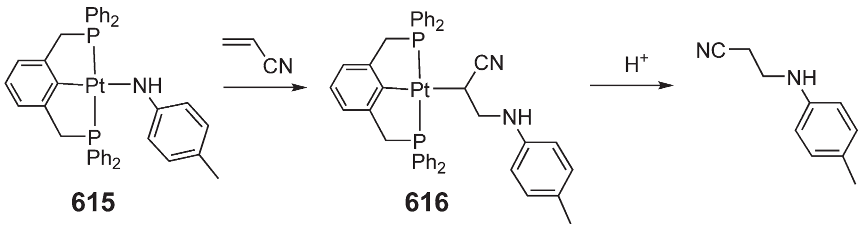
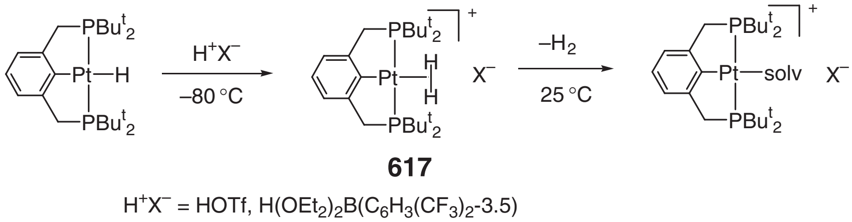
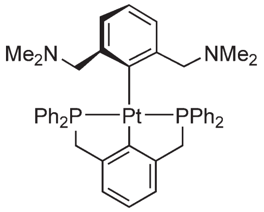


Scheme 86



Scheme 87



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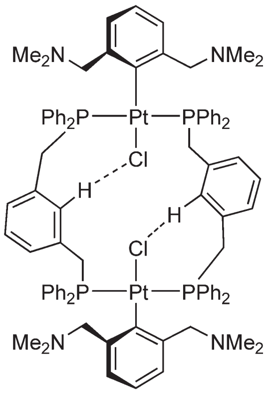
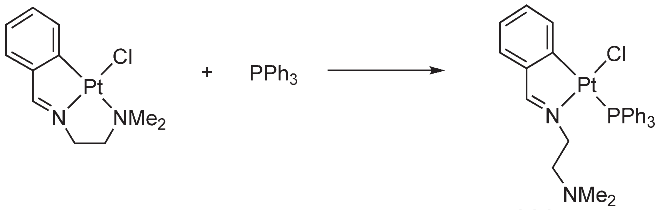


621

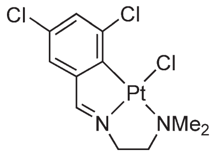
Complexes with *C,N,N*-chelating tridentate ligands have been reported. The 2-(dimethylamino)ethyl imine of benzaldehyde forms methylplatinum(II) and chloroplatinum(II) complexes by cycloplatination of the tridentate ligand. Addition of PPh_3 to the chloroplatinum complex causes decoordination of dimethylamino group to produce the complex with a *C,N*-chelating bidentate ligand (**622**, Equation (135)).[497]



622

(135)

Analogous complexes with chloro and fluoro substituents on the aromatic group have been prepared **623–628**.[498–500] A methylplatinum complex with the CNN ligand formed from furan carboxyaldehyde has been prepared **629**, while the imine of 3-pyridine carboxyaldehyde coordinates as an *N,N*-bidentate chelate and does not undergo cyclometallation **630**.[501]



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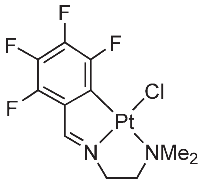

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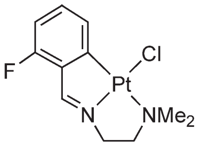

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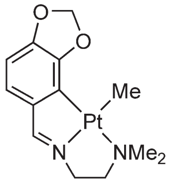

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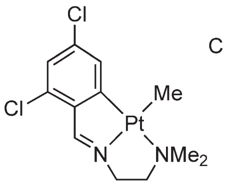

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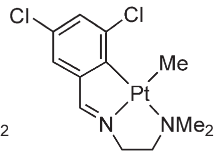

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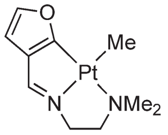

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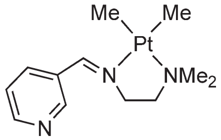
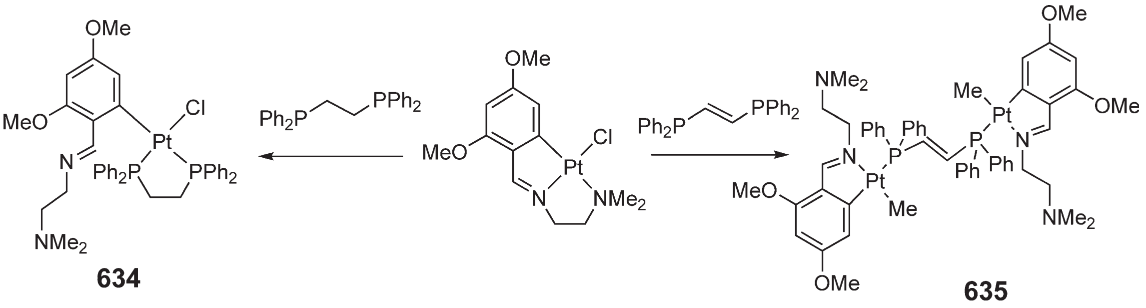
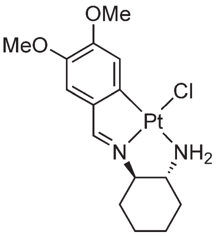


630

Chloroplatinum complexes with *C,N,N*- and *C,N,S*-chelating tridentate ligands **631** and **632** have also been obtained.[502,503] The diimine having a Te-containing pendant also forms a complex with a *C,N,N*-chelating ligand involving coordination of the Te atom **633**.[504]



Scheme 88



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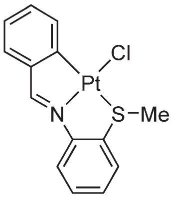

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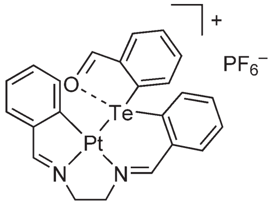
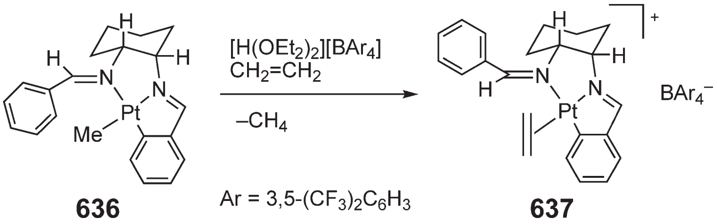


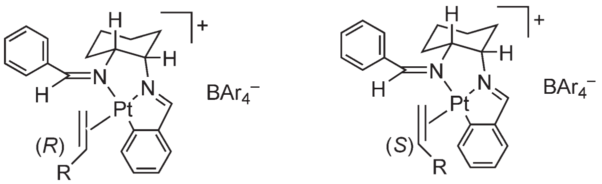
633

Reaction of diphosphines with the complex of a *C,N,N*-tridentate ligand leads to the κ^1C-coordinated arylplatinum complex **634** or the dinuclear complex with the diphosphine ligand that bridges two Pt centers coordinated by bidentate arylimine ligands (**635**, Scheme 88).[505]

The diimine of benzaldehyde with *meso*-1,2-cyclohexanediamine reacts with $[\mathrm{PtMe_2}(\mu\text{-}\mathrm{SMe_2})]_2$ to form a methyl complex with the cyclometallated *C,N,N*-tridentate ligand **636**. The complex exists as a mixture of racemic stereoisomers. Protonation by $[\mathrm{H(OEt)_2}]^+$ in the presence of ethylene produces a cationic complex with π-coordinated ethylene **637** (Equation (136)). Complexes with styrene and with propene **638** exhibit high stereoselectivity toward coordination of enantiofaces of the prochiral olefins.[506,507]



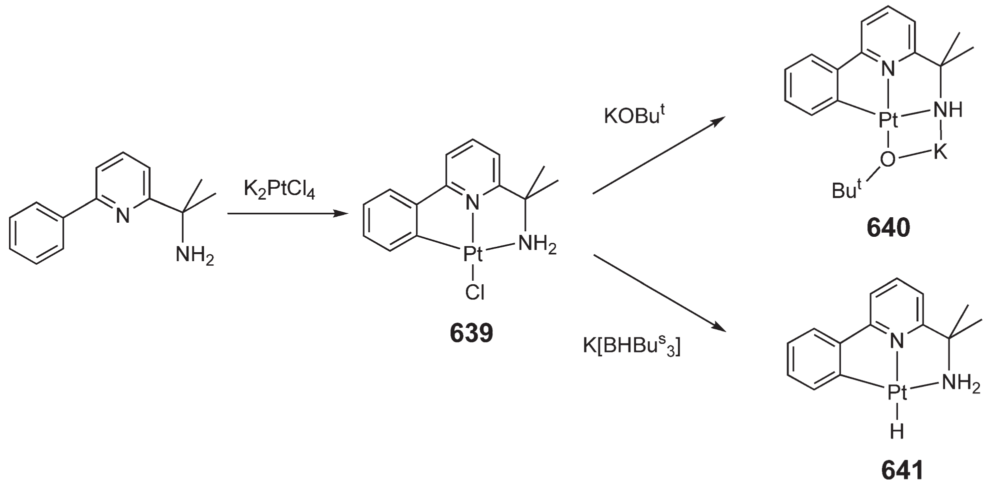
(136)



R = Me, Ph

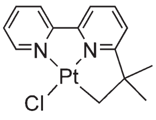
638

2-Phenylpyridine having an aminomethyl pendant at the pyridine ring undergoes platination with K_2PtCl_4 to produce a chloroplatinum(II) complex with the ligand as a *C,N,N*-tridentate **639**, and this complex can be converted into an adduct of KOBu^t **640**, and to the hydrido complex **641** (Scheme 89).[508]



Scheme 89

Chloro complexes having 6-(1,1-dimethylethyl)2,2′-bipyridine and 6-(2,2-dimethylpropyl)-2,2′-bipyridine as the *C,N,N*-tridentate ligands have also been obtained 642 and 643.[509,510] Addition of CO and phosphines to 642 in the presence of $NaBF_4$ forms cationic mononuclear and dinuclear Pt complexes with the phosphine and tridentate ligands 644 and 645.



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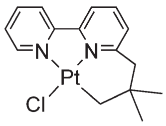

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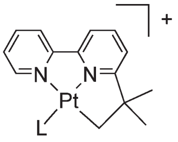
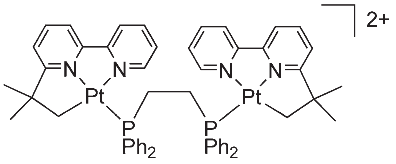


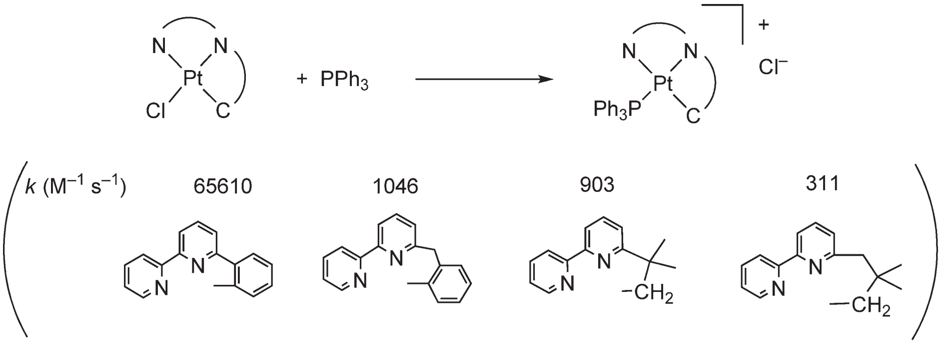
L = CO, PPh_3

644



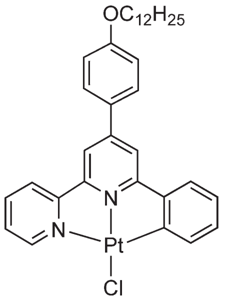
645

The chloro ligand of 642, 643, and the complexes with aromatic *C,N,N*-chelating ligands, is replaced with PPh_3 to form cationic complexes. The reaction rate obeys first-order kinetics with respect to concentration of Pt and also to that of PPh_3, and the second-order rate constants vary significantly for the tridentate ligands listed below (Equation (137)).[511,512]



(137)

Reaction of 6-phenyl–2,2′-bipyridine having a long alkyl chain with $PtCl_2(NCPh)_2$ forms the complex having an aromatic *C,N,N*-tridentate ligand 646.[513] X-ray crystallography has shown formation of a head-to-tail dimer via intermolecular π,π-stacking of the coordination planes. Exchange rates of chloro ligands with external nucleophiles are compared between a neutral complex with the *C,N,N*-tridentate ligand 647 and a cationic complex with terpy as the ligand 648.[514,515]



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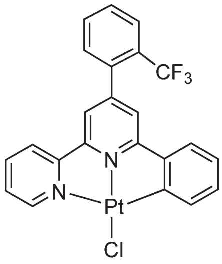

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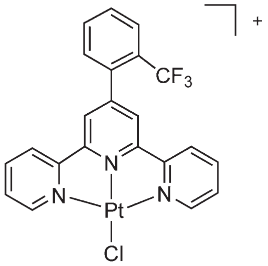
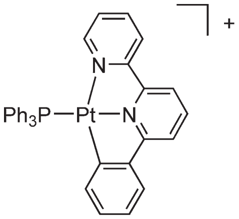
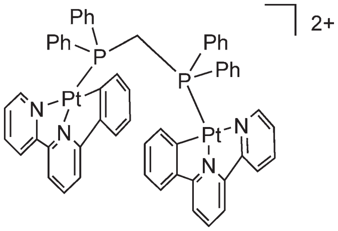


648

Platination of 6-phenyl–2,2′-bipyridine forms mononuclear and dinuclear complexes with the aromatic *C,N,N*-ligand and phosphine ligands **649** and **650**.[516] Coordination of PPh_3 forms the mononuclear complex, while dppm bridges the Pt centers of the dinuclear complex with interaction between the coordination planes including the Pt center (Pt···Pt 327.03(9) pm in the solid state).

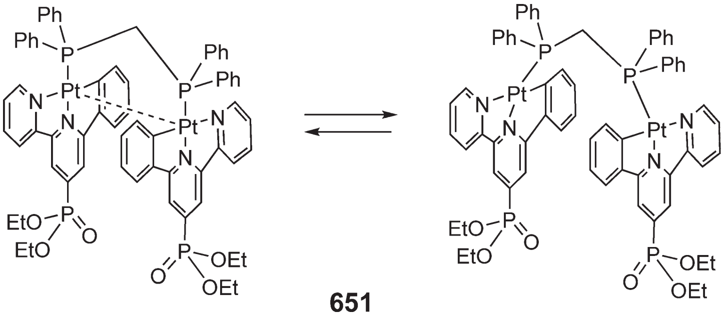


649



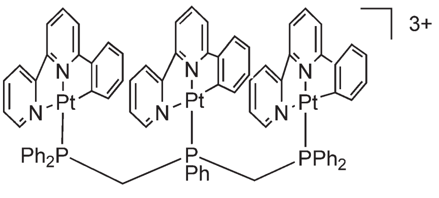
650

Emission behavior of **650** and related complexes has indicated the presence of intramolecular interaction of the two Pt centers, which is stabilized by stacking of the π-conjugated ligands.[517,518] The dinuclear complex with $-P(O)(OEt)_2$ substituents of the ligand **651** shows emission at $\lambda_{max} = 648$ nm in MeCN and at $\lambda_{max} = 530$ nm in SDS micellar solution.[519] The switching behavior is assigned to intramolecular stacking of the two coordination planes in the former solution, and luminesence of a similar complex is enhanced by DNA.[520]

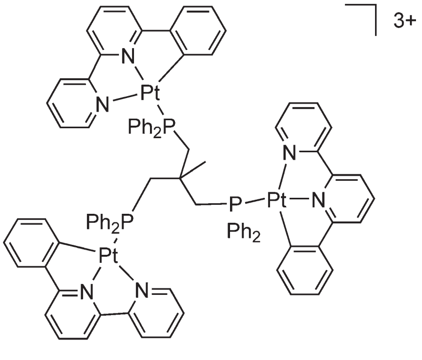


651

A mononuclear complex with PPh_3 and a *C,N,N*-tridentate ligand formed via metallation of 6-phenyl-2,2′-bipyridine, and a dinuclear complex with a bridging dppm ligand have been prepared.[521] Linear and branched triphosphines form trinuclear complexes by binding three Pt–*C,N,N*-tridentate ligand fragments **652** and **653**. Crystallography of the linear Pt_3 complex shows interaction of the Pt centers at the apical position (Pt···Pt 319.4 and 339.9 pm) associated with the π–π-interaction of the coordination planes. An analogous trinuclear complex with the ligand composed of two pyridyl and one thienyl group also shows the alignment of the Pt centers via intramolecular interaction (Pt···Pt 325.4 and 338.9 pm, **654**). The complexes show emission in the visible and near-IR regions, and delicate change of the emission behavior depending on the microenvironment.



652



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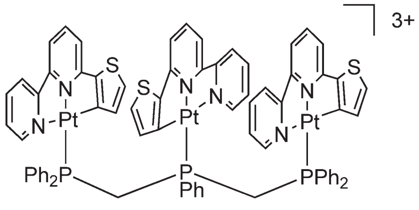
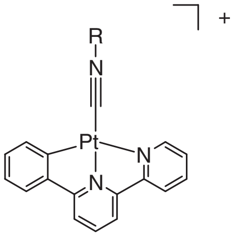


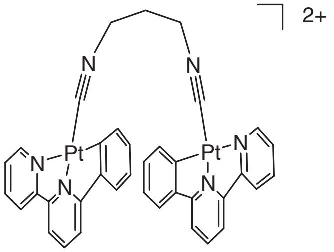
654

Mono- and dinuclear Pt complexes with a *C*,*N*,*N*-tridentate ligand and isonitrile ligands 655 and 656 have also been obtained.[522] Luminescence spectra in the solid state and in solution suggest dynamic behavior of 656 between the structures, with and without significant intramolecular Pt–Pt interaction.



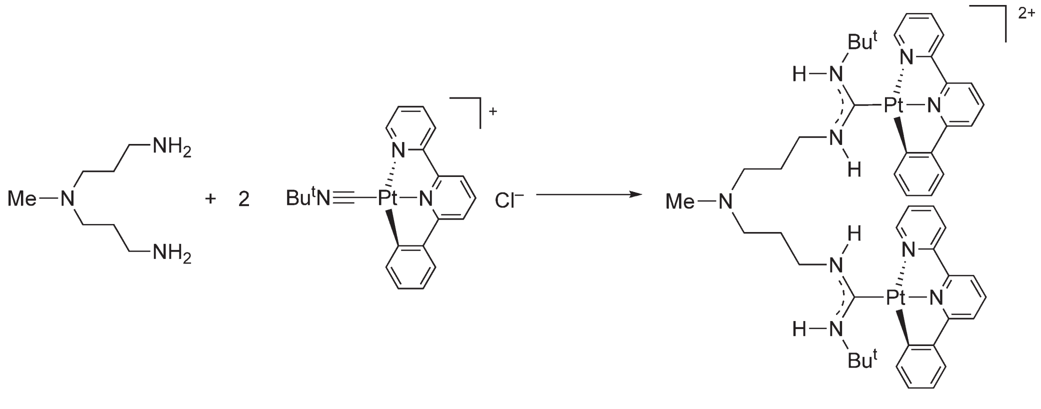
R = Bu^t, Pr^i, Cy, Xyl

655



656

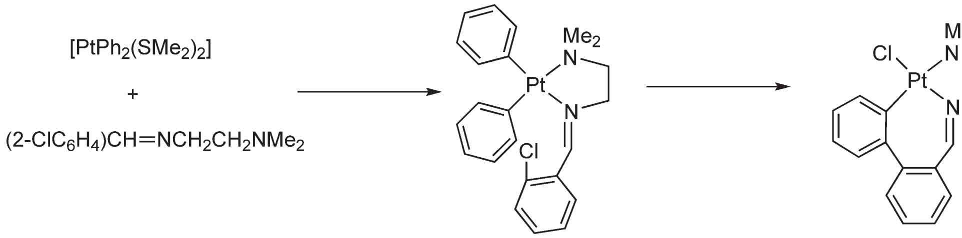
Nucleophilic addition of a linear triamine to the isonitrile ligand of the complex forms dinuclear complex with a bis(diaminocarbene) ligand (657, Equation (138)).[523]



657

(138)

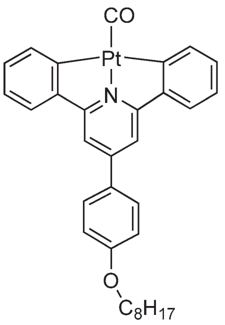
PtPh$_2$(SMe$_2$)$_2$ reacts with (2-ClC$_6$H$_4$)CH=NCH$_2$CH$_2$NMe$_2$ to produce a monophenylplatinum complex having a *C*,*N*,*N*-tridentate ligand (659, Equation (139)).[524] An intermediate diphenyl complex with the bidentate ligand 658 undergoes formation of the new C–C bond between a phenyl ligand and chlorophenyl group of the coordinated imine, accompanied by transfer of the chloro atom from the ligand to Pt and elimination of benzene.



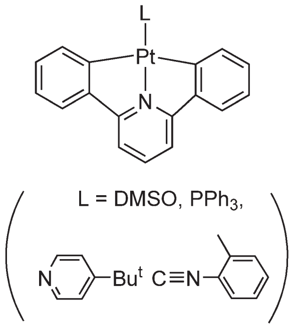
658 **659** (139)

Platination of 2,6-diphenylpyridine results in a *C*,*N*-bonded bidentate **661** and a *C*,*N*,*C*-bonded tridentate ligand **662**, depending on the co-existing ligands and conditions of the reactions (Scheme 90).[525,526] The initial product of the reaction is a dinuclear complex with bridging Cl ligands **660**. Further reaction with DMSO yields the chloro complex of the bidentate ligand, while the reaction in the presence of H_2O results in the complex with the tridentate ligand via a second cyclometallation. The dinuclear complex with a long side chain has also been prepared.

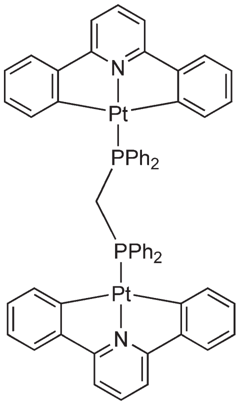
X-ray crystallography of a carbonylplatinum(II) complex having an aromatic *C*,*N*,*C*-terdentate ligand with a long alkyl chain **663** revealed a dimer structure containing a weak Pt–Pt interaction (324.3(3) pm) and stacked coordination planes.[527]



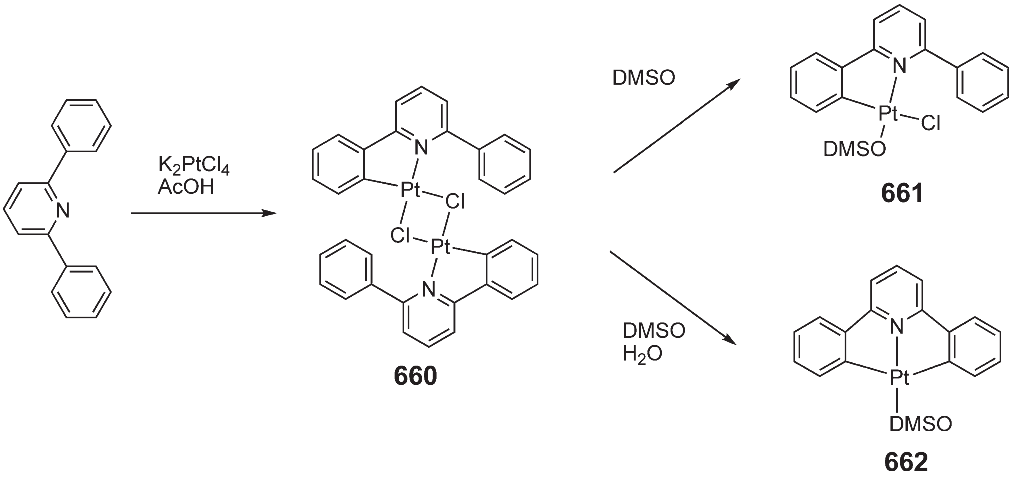
663



664



665

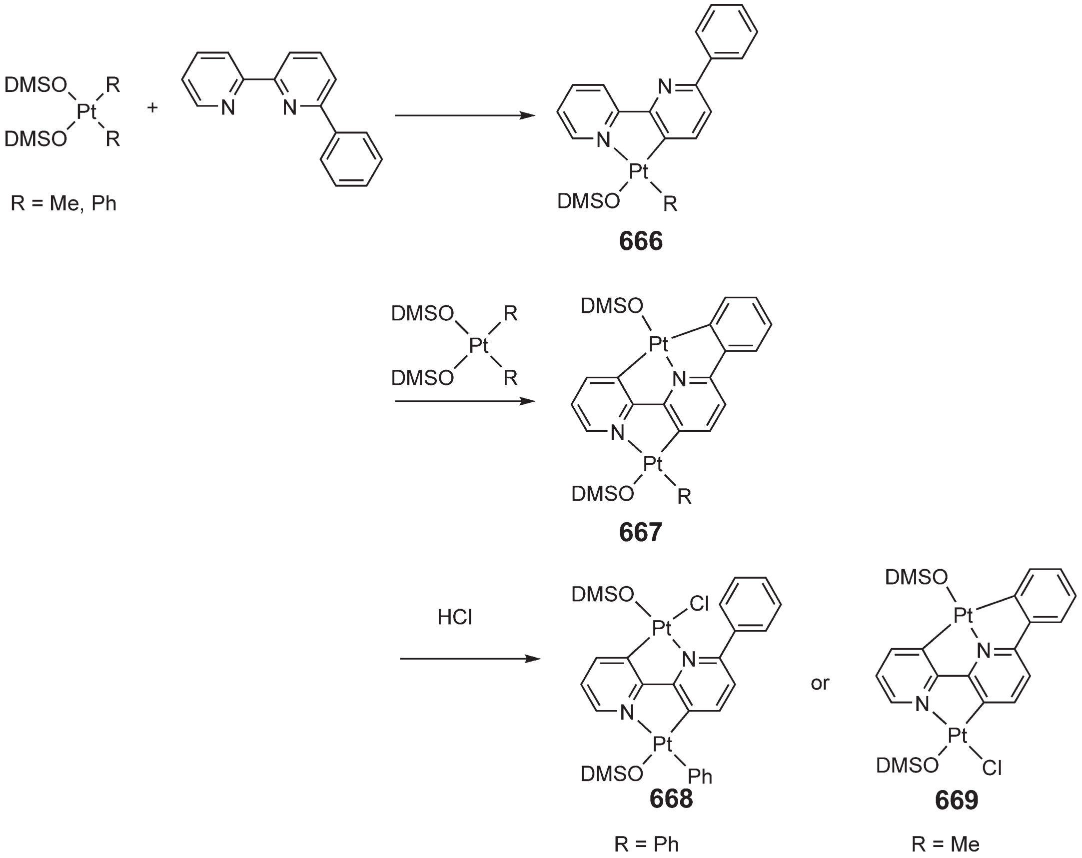


Scheme 90

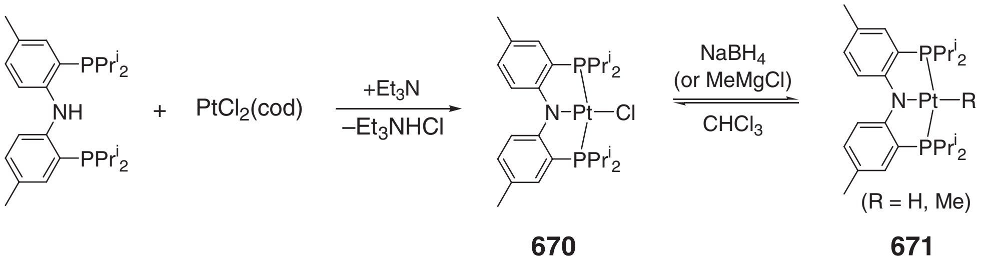
Mononuclear complexes with the aromatic *C*,*N*,*C*-ligand **664** contain intermolecular interaction of the coordination planes to form a head-to-tail dimer in the crystal structure, while the dinuclear complex with bridging dppm **665** shows intramolecular interaction of the Pt centers.[528] Crystals of **665** undergo reversible absorption and desorption of solvents, although it influences the emission behavior of the complex to a small extent.

Reactions of 6-phenyl–2,2′-bipyridine with $PtMe_2(DMSO)_2$ and with $PtPh_2(DMSO)_2$ form monoorganoplatinum complexes with the cyclometallated *N*,*C*-ligand (**666**, Scheme 91).[529] Further reaction with the diorganoplatinum complex yields dinuclear complexes in which the ligand is bonded to the second Pt center as a *C*,*N*,*C*-tridentate ligand **667**. Protonation by HCl occurs at the methyl ligand or the carbon of the tridentate ligand, giving the respective dinuclear complexes **668 and 669**.[530]

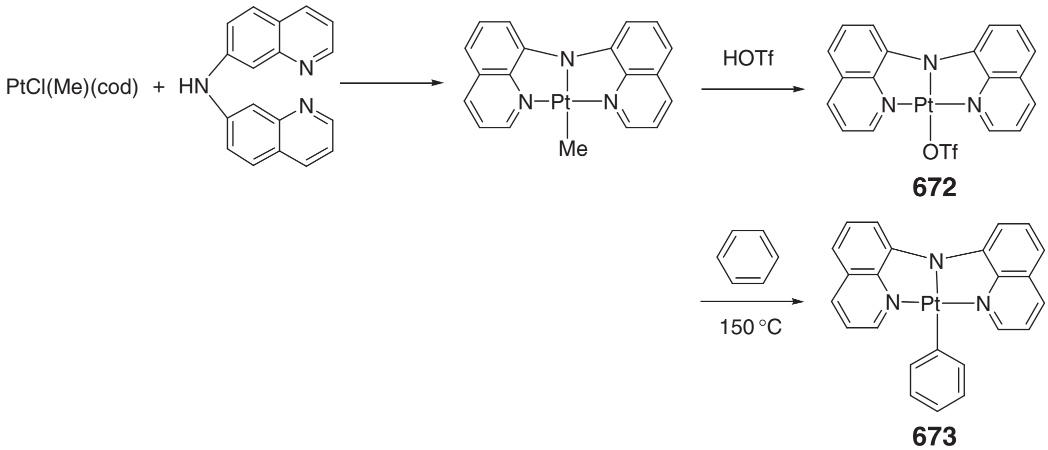
The complex with bis(*ortho*-phosphinoaryl)amine as the *P*,*N*,*P*-tridentate **670** has been prepared by the reaction of the ligand precursor with $PtCl_2(cod)$ (Scheme 92).[531] The complex is converted into hydrido and methyl complexes **671** via treatment with $NaBH_4$ and with MeMgCl, respectively.



Scheme 91



Scheme 92



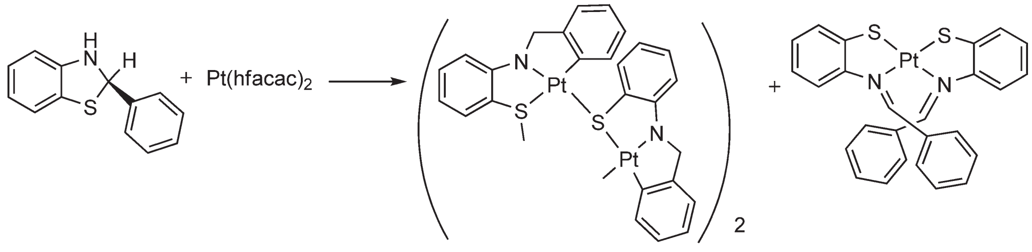
672

673

Scheme 93

Addition of bis(8-quinolinyl)amine to PtClMe(cod) produces a methylplatinum(II) complex with an *N*,*N*,*N*-tridentate ligand (**672**, Scheme 93).[532] The complex is protonated by HOTf to form the corresponding triflato complex, and phenylation of it takes place in benzene at high temperature to give **673**.

Reaction of 2-phenylbenzothiazoline with $Pt(hfacac)_2$ yields a cyclic tetranuclear complex with a *C*,*N*,*S*-tridentate ligand **674** and a mononuclear complex with helical arrangement of two chelating ligands (**675**, Equation (140)).[533]



674 **675**

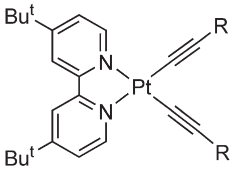
(140)

Other *C*,*N*,*S*-chelating tridentate ligands have also been employed for preparation of the mononuclear and dinuclear complexes containing these ligands.[534,535]

8.08.3.5 Alkynylplatinum(II) Complexes

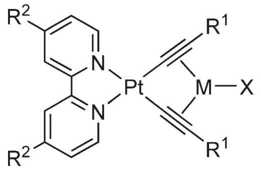
Preparation of alkynylplatinum(II) complexes has been carried out mainly by ligand exchange of haloplatinum(II) complexes with terminal alkynes in the presence of amines.[536] Copper(I) compounds accelerate the reaction significantly, and this approach has been applied for the preparation of alkynylplatinum complexes with various auxiliary ligands as well as of polymers composed of bisalkynyl ligands and platinum centers. Metathesis reactions of acetylides with halogenoplatinum complexes are also used for the preparation of alkynylplatinum complexes. Since alkynylplatinum(II) complexes have a stable Pt–C bond, they are employed as the building block of macrocyclic compounds and dendrimers.

The homoleptic platinate with four cyanoacetylide ligands, $[Pt(C{\equiv}CC{\equiv}N)_4]^{2-}$, has been fully characterized.[537] Di(arylalkynyl)platinum complexes with 4,4′-Bu^t_2bipy **676** have been prepared by the reaction of the alkyne with $PtCl_2$(4,4′-Bu^t_2bipy) in the presence of CuI and Pr^i_2NH.[538] The bis(phenylethynyl)platinum complex undergoes one-electron reduction to give the monoanion, while electrochemical reduction of the bis(4-nitrophenylethynyl)-platinum complex produces the dianion which has been characterized by visible and EPR spectra. The complexes, as well as the alkynylplatinum complexes with bipy and 4,4′-Me_2bipy, form adducts with CuX, AgX, and HgX_2 (X = Cl, Br, NCS; **677** and **678**), in which the d^{10}-metals are π-bonded by the two alkynyl ligands coordinated to the Pt center.[539–541]



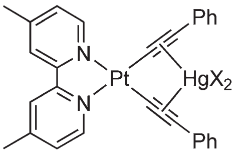
R = TMS, Tol, $C_6H_4NO_2$-4, $C_6H_4Bu^t$-4)

676



(R^1 = C_6H_4-p-Me, $SiMe_3$; R^2 = H, ^tBu; X = Cl, Br, NCS)

677



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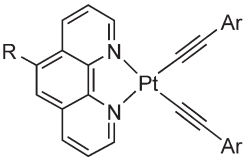
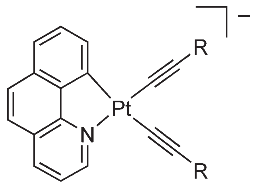


(Ar = C_6H_4CHO-4; R = H, Me, Cl)

679

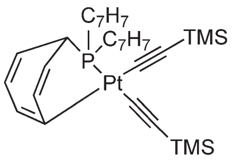
Dialkynyl complexes wtih phenanthroline derivatives as the ligands **679** have also been prepared.[542] The adduct of $AgBF_4$ to the complex with phenylacetylide ligands **680** contains Ag(I), which is coordinated by the alkynyl ligands and by a BF_4^- anion. It reacts with PPh_3 to produce the complex with an $AgPPh_3$ fragment **681** and a cationic complex with alkynyl and PPh_3 ligands (**682**, Scheme 94).[543]

Bisalkynylplatinate complexes with the *C,N*-chelating benzo[*h*]-quinolinate ligand **683** have been prepared by transmetallation of the lithium acetylides with dichloroplatinate.[544] The absorption peaks at 392–405 nm are attributed to ligand (acetylide) to ligand (benzoquinolinate) transition. Tris(cycloheptatrienyl)phosphine and diphenylphosphine oxide form complexes with two alkynyl ligands at *cis*-positions **684** and **685**.[545,546]

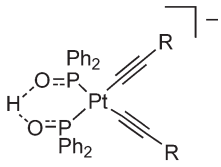


R = Bu^t, TMS, Ph, 2-py

683



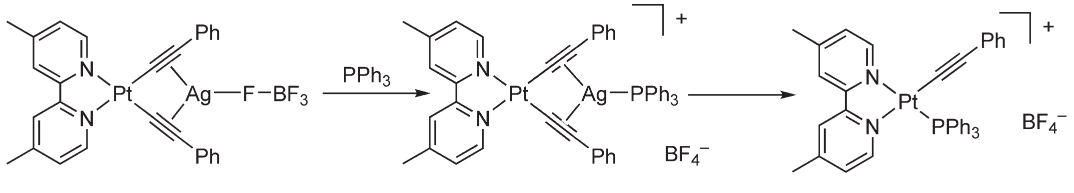
684



R = Ph, Bu^t

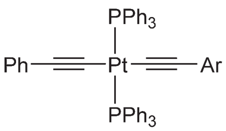
685

Monodentate phosphines tend to form complexes with two alkynyl ligands at *trans*-positions. The complexes having two arylalkynyl ligands with the same or different substituents at the aryl groups **686** and **687** have been prepared.[547,548]



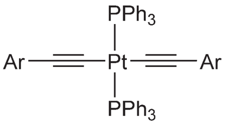
680 **681** **682**

Scheme 94



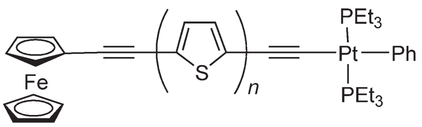
Ar = $C_6H_4NO_2$-4

686

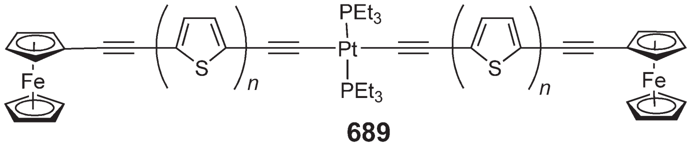


Ar = $C_6H_4NH_2$-4

687



688



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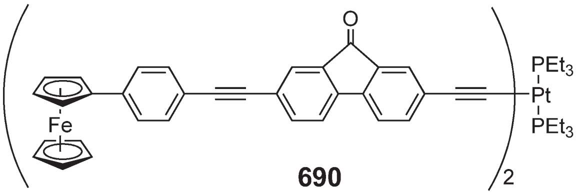

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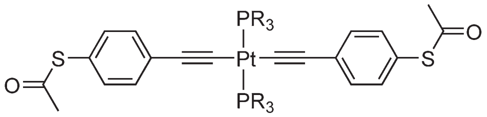
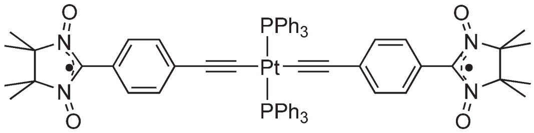


PR_3 = PCy_3, PPh_3, $P(OEt)_3$

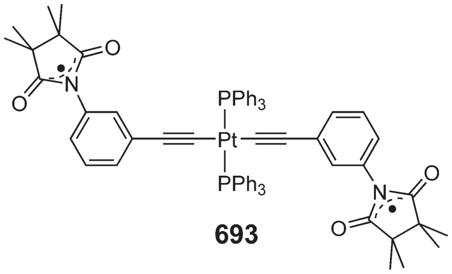
691

Complexes with alkynyl ligands containing an oligothienylene chain and ferrocenyl terminal groups have been prepared 688 and 689.[549] An increase in the length of oligothiophene fragment causes a red-shift of absorption peaks and a decrease of the electrochemical oxidation potential. The alkynylplatinum(II) complex with ferrocenyl groups at the terminal of the alkynyl ligands 690 has been reported.[550] Resonance Raman band and emission have been studied for MLCT transitions of $Pt(C{\equiv}CH)_2(PEt_3)_2$.[551] Dialkynylplatinum complexes with a thioacetate group as the terminal group of the alkynyl ligands 691 have been prepared by platination of the corresponding alkyne using monophosphine ligands.[552] The electrical conductance of the complexes in monolayers, measured by using special Au electrodes, show negligible influence of the phosphine ligands on the current–voltage performance.

Alkynyl complexes having stabilized radicals in the ligands at *trans*-positions 692 and 693 show intramolecular exchange interaction through the metal-containing spacer, as evidenced by ESR data.[553] The dialkynylplatinum complex with triarylamine groups at the ligands 694 undergoes stepwise electrochemical oxidation due to the mixed valence state after one-electron oxidation.[554]



692



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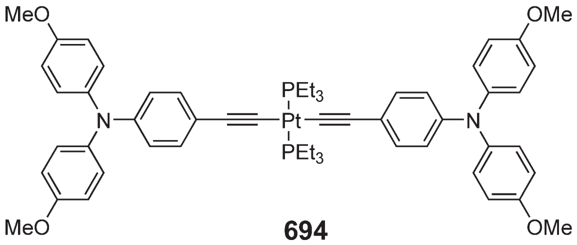
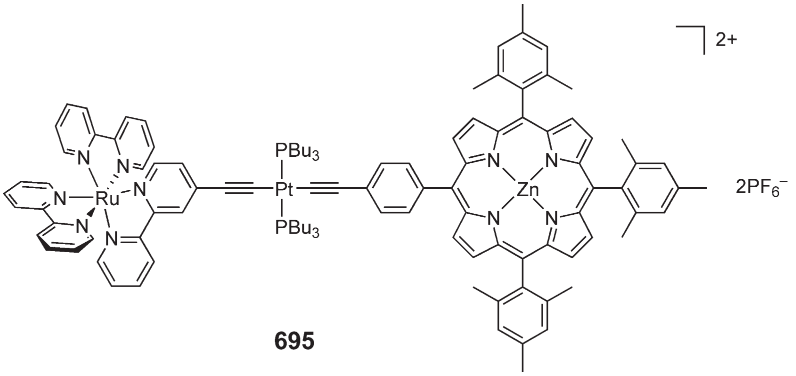


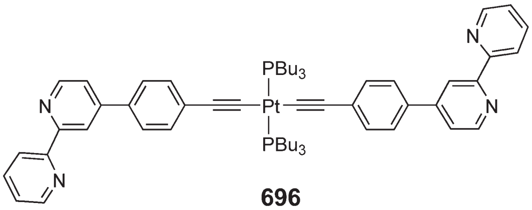
694

A bisalkynylplatinum(II) complex, bonded to Zn–porphyrin and Ru(bipy)$_3$ fragments, has been prepared **695**, as well as the complexes with two Zn–porphyrin groups and with two Ru(bipy)$_3$ groups.[555] Energy transfer between singlet or triplet states occurs smoothly, although the bisalkynylplatinum spacer does not participate in through-bond electron transfer.

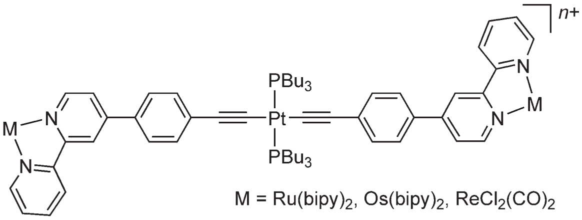


695

The complex with two alkynyl ligands containing two terminal bipy groups **696** forms the complex with up to two photoactive Ru(bipy)$_3$ sites **697**, upon the reaction with an Ru–bipy complex.[556,557] The complex possesses a long-lived triplet excited state derived from the Ru(bipy)$_3$ centers. The dialkylplatinum group does not quench the excited states. Photons collected by the Pt(II) center are transferred to the terminal complexes and the molecule functions as a light-harvesting antenna. Related complexes with the alkynyl ligands at *cis*-positions **698**, and the complex having Fe(bipy)$_3$ unit, which is bonded to three dialkynylplatinum complexes **699**, have been prepared.

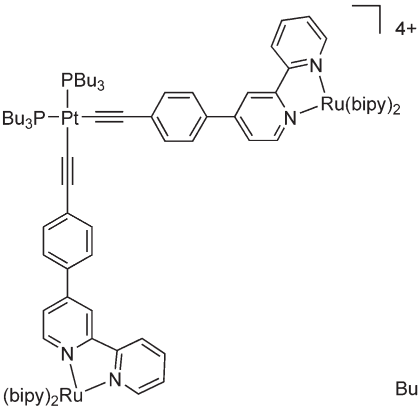


696

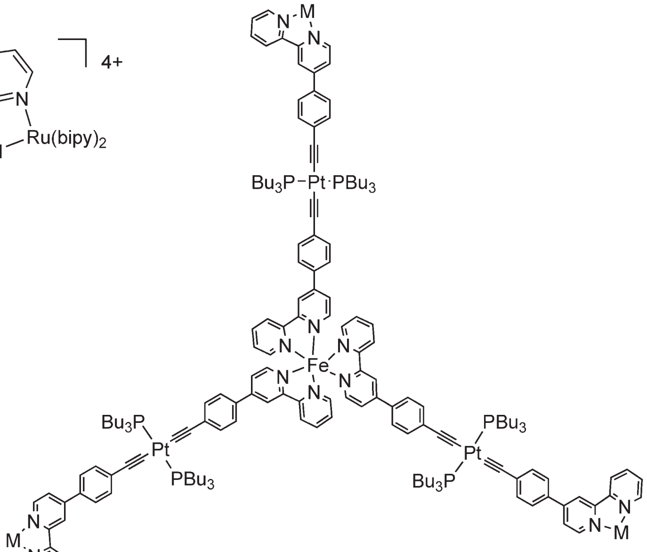


M = Ru(bipy)$_2$, Os(bipy)$_2$, ReCl$_2$(CO)$_2$

697

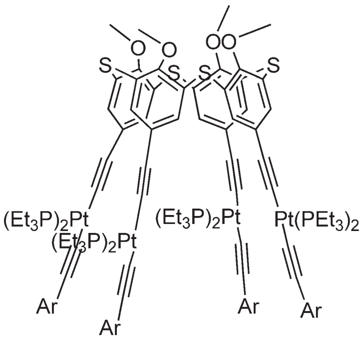


698



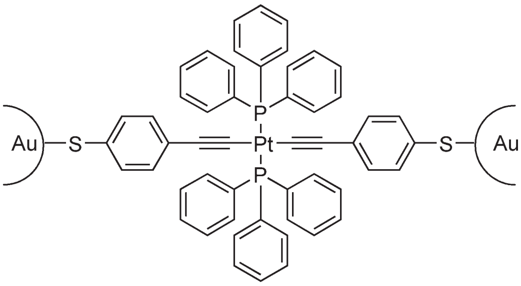
699

Trans-bis(alkynyl)platinum fragments have been introduced into the thiacalix[4]-arene to form **700**.[558] A dialkynylplatinum(II) complex with a *trans*-structure, bonded to Au electrodes **701**, shows a current–voltage curve, which indicates the role of the complex as a molecular insulator between the electrodes.[559]



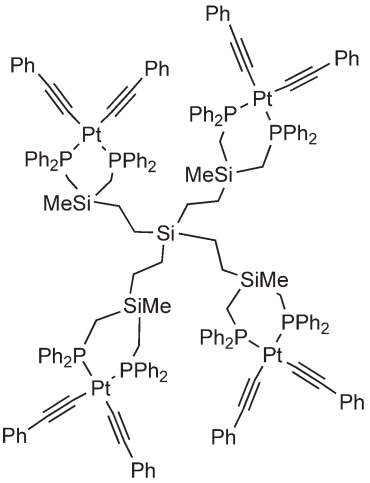
Ar = Ph, C_6H_4-4-C_5H_{11}

700

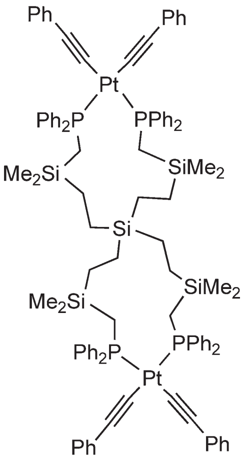


701

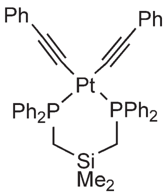
Polydentate phosphine ligands having a carbosilane dendrimer framework form polynuclear alkynyl complexes **702** and **703**.[560] The mononuclear complex with the same six-membered chelating ring **704** has been fully characterized.



702

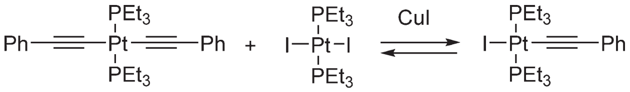


703



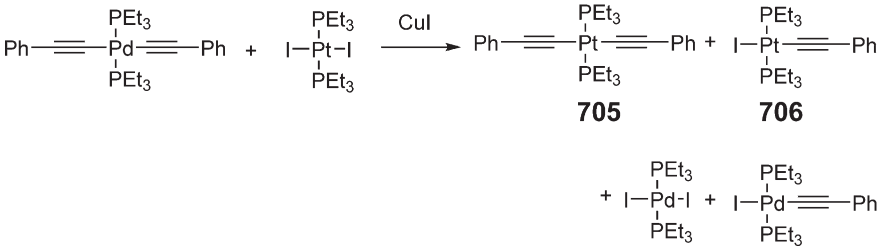
704

Intermolecular exchange of the alkynyl and halide ligands occurs in the presence of CuI, leading to conproportionation of the bisalkynyl complex **705** and dihalogenoplatinum complex, giving halo(alkynyl)platinum complex **706** and disproportionation of the halo(alkynyl)platinum complexes (Equations (141) and (142)).[561] Alkynyl ligand transfer from Pd to Pt complexes takes place to form the alkynyl–platinum bond.



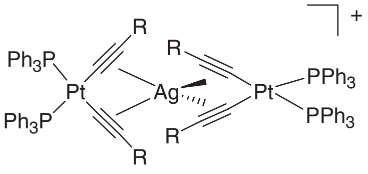
$$\mathrm{Ph{-}C{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}C{-}Ph} + \mathrm{I{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}I} \overset{\mathrm{CuI}}{\rightleftharpoons} \mathrm{I{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}C{-}Ph} \tag{141}$$

705 **706**

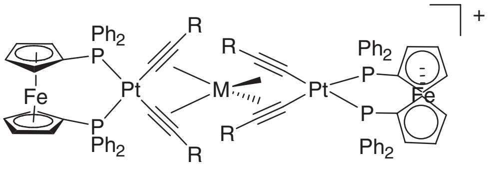


(142)

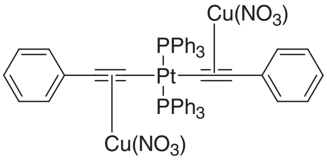
The alkynyl ligand of Pt–phosphine complexes serves as the metallaligand that binds Ag(I) or Cu(I), forming di- or trinuclear complexes. Cationic Ag(I) and Cu(I) centers are bonded with two *cis*-dialkylplatinum complexes to yield the trinuclear complexes with π-coordination of the four alkynyl ligands to a d^{10}-metal center **707** and **708**.[562,563] π-Coordination of alkynyl ligands of the complexes with a *trans*-structure to $Cu(NO_3)$ forms the $PtCu_2$ complex **709**.[564]



707

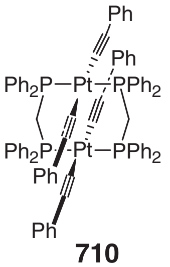


708

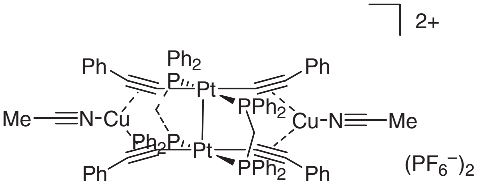


709

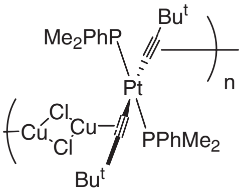
Addition of $[Cu(NCMe)_4]^+$ to a solution of the dinuclear complex having phenylethynyl ligands at each Pt center and a bridging dppm ligand **710** produces the $PtCu_2$ complex containing π-coordination of two alkynyl ligands to a Cu center **711**.[565] The complex obtained exhibits contact of the two Pt centers (Pt–Pt = 301.24(9) pm), although the starting complex does not show such interaction (Pt–Pt = 343.7(1) pm). Emission of the complexes at 460–495 nm (λ_{ex} = 350 nm) has been assigned to phosphorescence of the ligands rather than luminescence derived from a singlet state. Dialkynylplatinum complexes with PMe_2Ph ligands and four-membered cyclic Cu_2Cl_2 core form the alternating co-polymer **712**.[566]



710

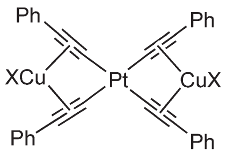


711



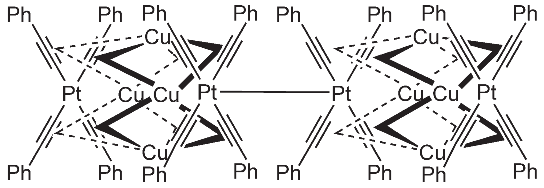
712

The complex $Pt_2Cu_4(C{\equiv}CPh)_8$[567] is converted into anionic $PtCu_2$ complexes **713** upon treatment with NBu_4Cl or NBu_4Br.[568] The alkynyl ligands coordinate to Pt via a σ- bond and to Cu via a π–bond; $Pt_2Cu_4(C{\equiv}CPh)_8$ crystallizes as different polymorphs, and exhibits different colors of the solution depending on the solvent and concentration. In a dilute CH_2Cl_2 solution of the complex, an equilibrium between $Pt_2Cu_4(C{\equiv}CPh)_8$ fragments and its dimer is observed in the absorption spectra, while higher oligomers are formed in concentrated solutions.[569] Crystallography of the dimer **714** that binds two Pt_2Cu_4 units shows interaction of two Pt centers (Pt–Pt = 311.6(2) pm). A violet-green color of the crystal contains the trimer having two Pt–Pt contacts (Pt–Pt = 299.5(1) pm, **715**).[570]

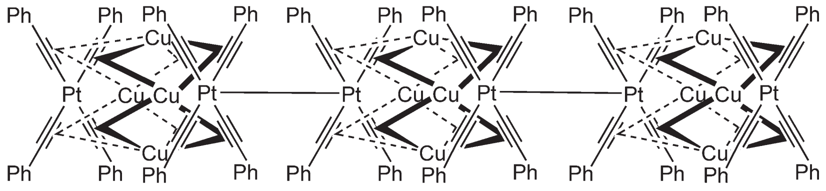


X = Cl, Br

713

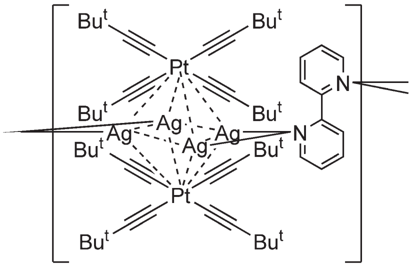


714

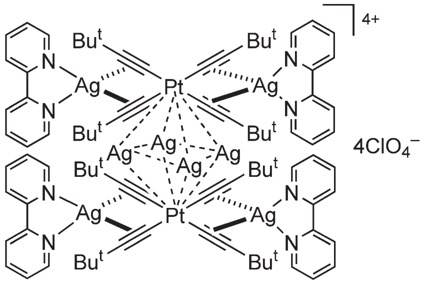


715

The complex $Pt_2Ag_4(C{\equiv}CBu^t)_8$ has no interaction between the Pt_2Ag_4 units in solution and reacts with bipy to form a polymeric complex via coordination of the bipy ligands to Ag^+ cations contained in different monomer units **716**.[571] Addition of $AgClO_4$ and then of bipy to the Pt_2Ag_4 complex forms a cationic Pt_2Ag_8 complex **717**, in which two alkynyl ligands within a coordination plane of the tetraalkynylplatinum complex coordinate to $[Ag(bipy)]^+$. Both the starting Pt_2Ag_4 complex and the Pt_2Ag_8 complex with four bipy ligands exhibit similar emission spectra, indicating that the external Ag^+ cations with bipy ligands show negligible effect on the optical properties of the complexes.

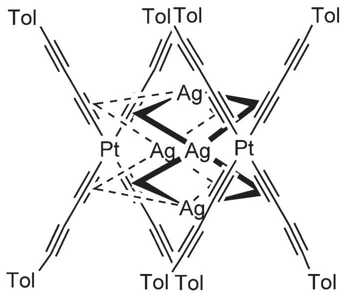


716

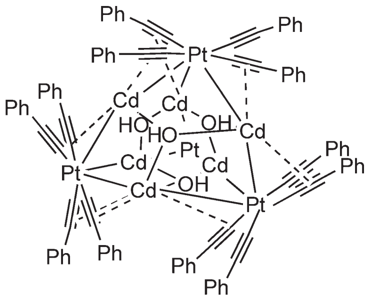


717

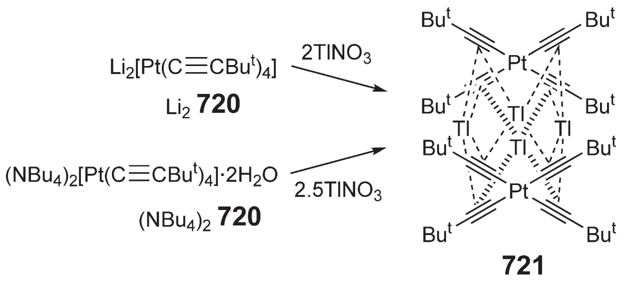
A Pt_2Ag_4 complex having bridging butadiynyl ligands **718** shows intense luminescence due to MLCT transitions.[572] Reaction of $Cd(ClO_4)_2$ with $[Pt(C{\equiv}CPh)_4]^{2-}$ produces the heterobimetallic compound, $Pt_4Cd_6(C{\equiv}CPh)_4(\mu\text{-}C{\equiv}CPh)_{12}(\mu\text{-}OH)_4$ **719**, which contains $[Cd_8(\mu\text{-}OH)_4]^{8+}$ as the core of the cluster.[573]



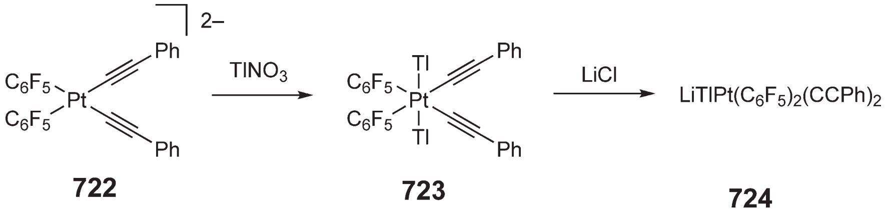
718



719



Scheme 95

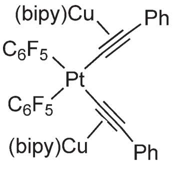


Scheme 96

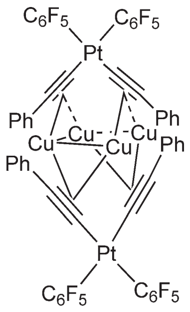
A Pt_2Tl_4 species in which tetraalkynylplatinate **720** interacts with four Tl cations has been prepared by using $TlNO_3$ (**721**, Scheme 95).[574] The emission peak of the Pt_2Tl_4 complex ($\lambda_{max} = 631$ nm) is shifted from the analogous lantern Pt_2Ag_4 complex ($\lambda_{max} = 476$ nm).

The dialkynylplatinate with perfluorophenyl ligands, $[Pt(C_6F_5)_2(C{\equiv}CPh)_2]^{2-}$ **722**, is converted into $Tl_2Pt(C_6F_5)_2(C{\equiv}CPh)_2$ **723** and $TlLiPt(C_6F_5)_2(C{\equiv}CPh)_2$ **724** on treatment with $TlNO_3$ (Scheme 96).[575] The latter product exhibits both ionic electrical conductivity and luminescence.

The platinate **722** forms a complex with two $[Cu(bipy)]^+$ fragments **725**, and a Pt_2Cu_4 cluster compound with the Cu cations π-bonded by the alkynyl ligands **726**.[576]

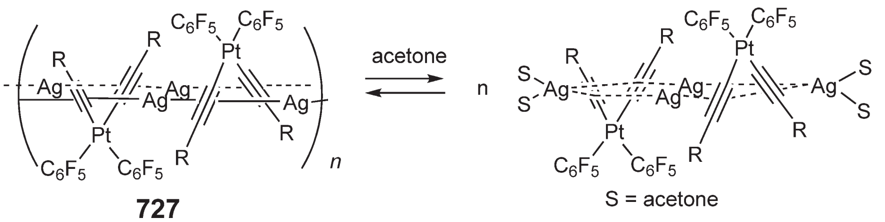


725



726

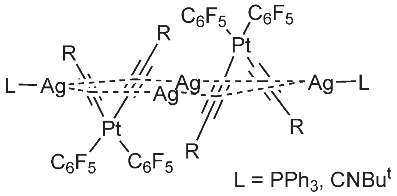
Complex **722** binds Ag^+ cations to form a linear polymer containing the alkynyl ligands and Ag^+ cations along the polymer chain **727**.[577] Addition of acetone to the polymer complex converts it into a Pt_2Ag_4 complex having acetone ligated to Ag **728**. Addition of phosphine and isonitrile to the polymer yields multinuclear complexes having Ag centers coordinated by these added ligands **729** and **730**. NBu_4Br extracts some of the Ag^+ contained in the polymer, affording an anionic Pt_2Ag_2 complex **731**. Pt–Ag multinuclear complexes with bipy ligands have also been prepared.[578] A dialkynylplatinum(II) complex with dppm as ligand forms a stable adduct of the complex in which Ag(I) is π-bonded by the alkynyl ligand and by a P atom of dppm **732**.[579]



727

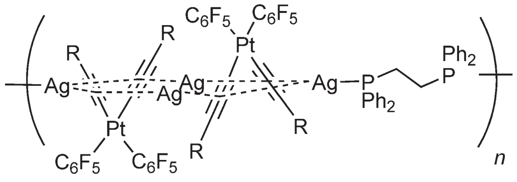
S = acetone

728

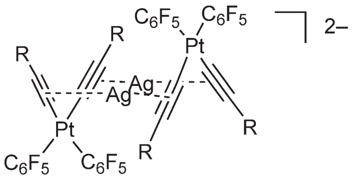


L = PPh_3, $CNBu^t$

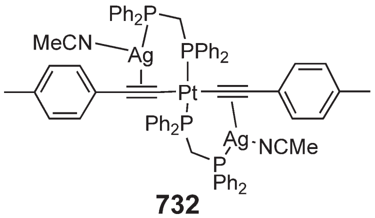
729



730

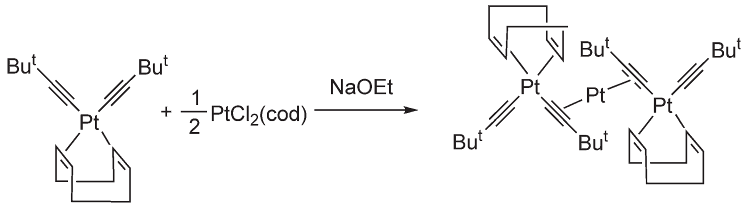


731



732

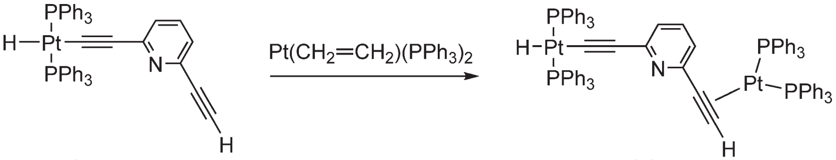
The alkynyl ligand of Pt(II) complexes coordinates to Pt(0) centers in a π-manner to form the complex having the alkynyl ligand bonded to the two metals in a σ,π-fashion. Thus, a 2 : 1 reaction of $Pt(C{\equiv}CBu^t)_2(cod)$ **733** with $PtCl_2(cod)$ in the presence of NaOEt produces a trinuclear $Pt^{II}–Pt^0–Pt^{II}$ complex **734** (Equation (143)).[580]



733 **734**

(143)

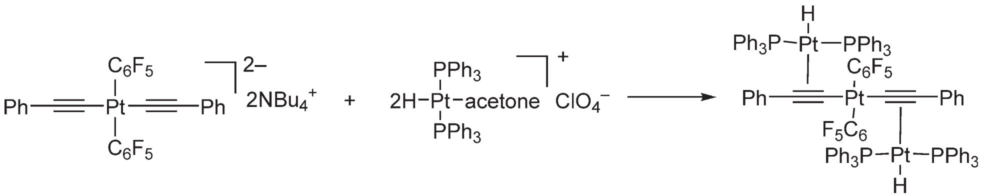
A hydridoplatinum(II) complex with 2-(6-ethynylpyridyl)ethynyl as a ligand **735** coordinates to a Pt(0) complex with PPh_3 ligands (**736**, Equation (144)).[581] The coordination occurs at the uncoordinated alkyne group of the ligand rather than the alkynyl group bonded to the Pt(II) center. Introduction of the second Pt center to the complex shifts the absorption, assigned to MLCT, to longer wavelengths, although the second Pt center has little effect on the emission spectra.



735 **736**

(144)

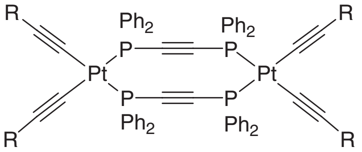
Reaction of dialkynylplatinum complex **737** with the hydridoplatinum complex **738** forms a trinuclear zwitterionic hydrido complex with the alkynyl ligands functioning as bridging σ,π-ligands (**739**, Equation (145)).[582]



737 **738** **739**

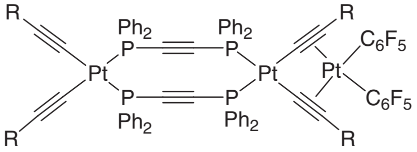
(145)

1,2-Bis(diphenylphosphino)acetylene bridges two bisalkynylplatinum fragments to form dinuclear complexes with two bridging phosphine ligands **740**.[583] Coordination of the two alkynyl ligands at *cis*-positions to $Pt(C_6F_5)_2$ fragments allows formation of trinuclear and tetranuclear Pt complexes **741** and **742**.

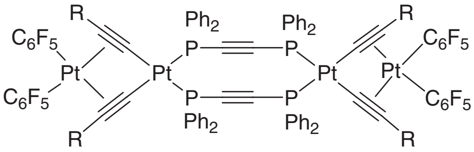


740

(R = Bu^t, Ph)

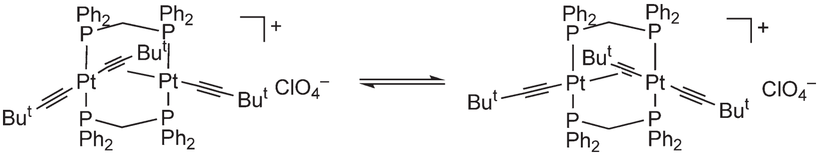


741



742

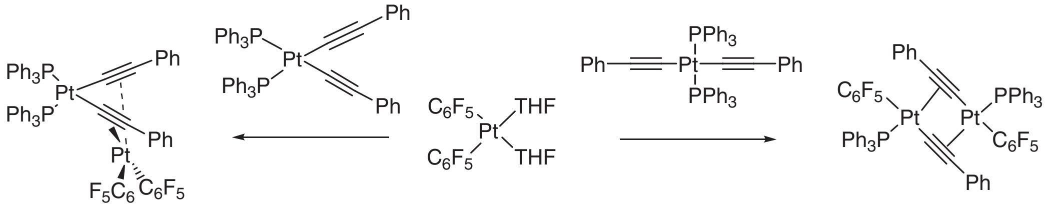
A cationic dinuclear Pt complex whose Pt centers are bridged by two dppm ligands and one alkynyl ligand, bonded in a σ,π-fashion **743**, exhibits coalescence of the NMR signals of the dppm and alkynyl ligands.[584] It is attributed to a switching of the coordination mode between σ,π- and π,σ-structures (Equation (146)). The complexes with arylethynyl ligands with bridging dppm and alkynyl ligands exhibit strong luminescence in the low-energy region.



743

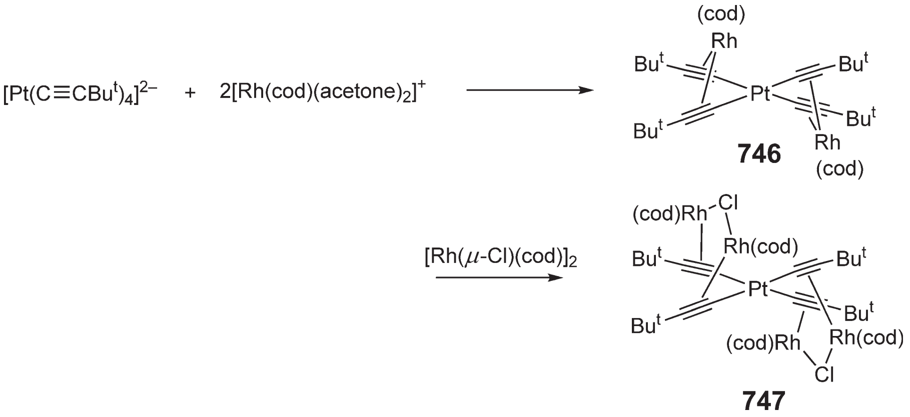
(146)

cis-Pt(C≡CPh)$_2$(PPh$_3$)$_2$ reacts with $Pt(C_6F_5)_2(THF)_2$ smoothly to form a dinuclear complex **744** via π-coordination of the two alkynyl ligands to the Pt(II) center bonded to the aryl ligands accompanied by elimination of THF.[585] The reaction of *trans*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$ yields the dinuclear complex **745** containing two equivalent Pt centers, which are bonded to the alkynyl in a σ,π-fashion (Scheme 97).



744 **745**

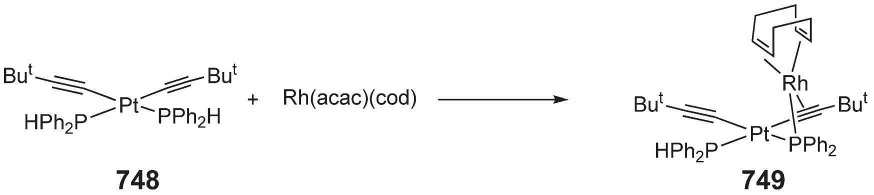
Scheme 97



Scheme 98

Tetrakis(*t*-butylethynyl)platinate reacts with $[Rh(cod)(acetone)_2]^+$ and then with $[Rh(\mu\text{-}Cl)(cod)]_2$ to form $PtRh_2$ **746** and $PtRh_4$ complexes **747**, respectively.[586] The platinum center retains the σ-coordination of the alkynyl ligands during the reaction (Scheme 98).

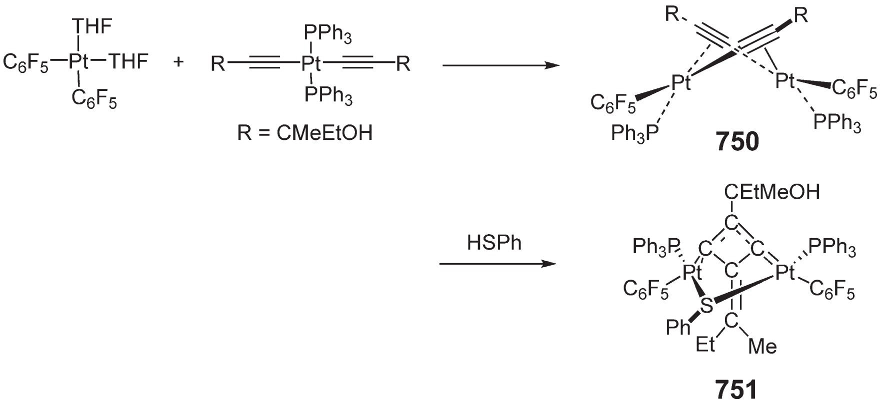
A dialkynyl complex with two PPh_2H ligands **748** reacts with Rh(acac)(cod) to form the Pt–Rh complex in which the alkynyl and PPh_2 ligands bridge the two metal centers (**749**, Equation (147)).[587]



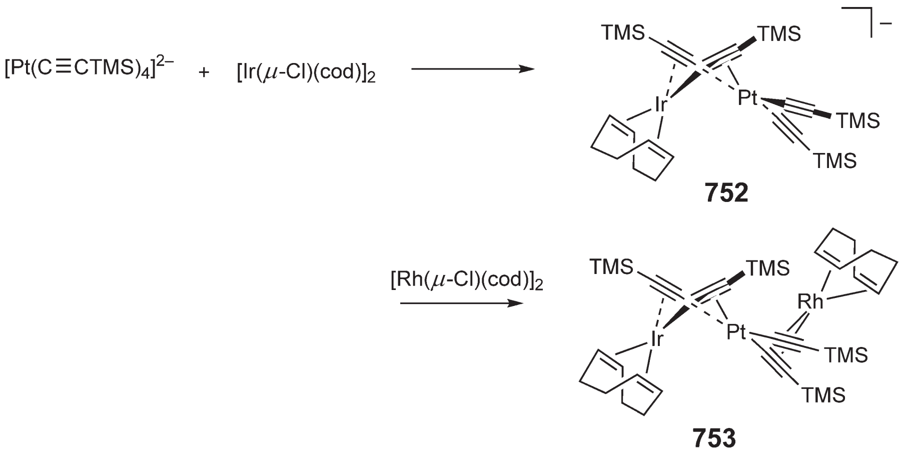
(147)

Reaction of $CoCl_2$ with $[Pt(C{\equiv}CPh)_4]^{2-}$ forms a complex with two $CoCl_2$ fragments that are π-bonded to the alkynyl ligands of the platinate.[588]

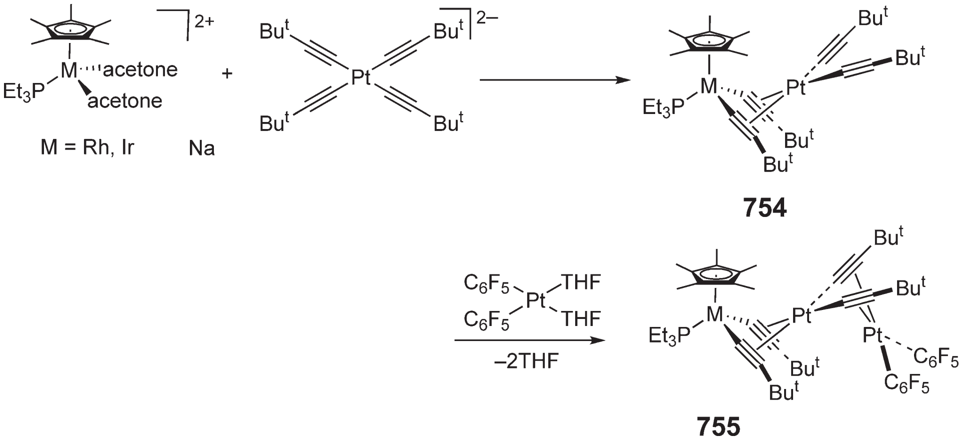
Reaction of *trans*-$[Pt(C{\equiv}C\text{–}CMeEtOH)_2(PPh_3)_2]$ with *cis*-$[Pt(C_6F_5)_2(THF)_2]$ forms a dinuclear Pt complex with two bridging alkynyl ligands (**750**, Scheme 99).[589] Addition of PhSH to the product causes coupling of the two alkynyl ligands to afford the complex with a four-membered cyclic ligand bridging two Pt centers as well as a bridging SPh ligand **751**.



Scheme 99



Scheme 100

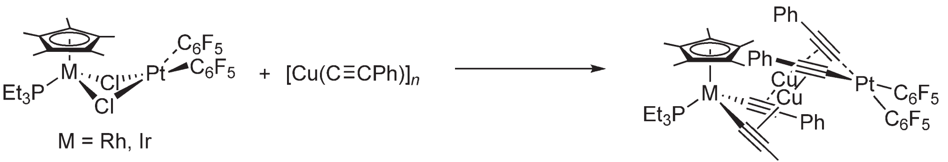


Scheme 101

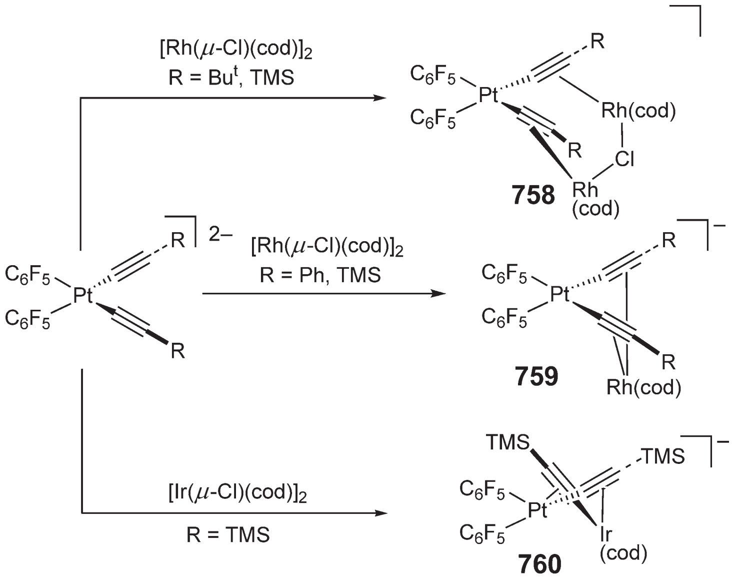
Tetrakis(trimethylsilylethynyl)platinate reacts with [Ir(μ-Cl)(cod)]$_2$ to form the Pt–Ir binary complex **752** (Scheme 100).[590] One of the alkynyl ligands changes its σ-coordination from Pt to Ir during the reaction. Coordination of the remaining two alkynyl ligands to other transition metal complexes form Pt–Ir–Pt and Pt–Ir–Pd complexes. Addition of [Rh(μ-Cl](cod)]$_2$ to **752** results in an Ir–Pt–Rh complex **753**, where switching of the coordination of the alkynyl ligand does not occur during the reaction.

Dicationic RhCp* and IrCp* complexes with labile solvent ligands react with tetraalkynylplatinates to afford heterobimetallic complexes with bridging alkynyl groups (**754**, Scheme 101).[591] The two alkynyl ligands of the platinate complex are turned to become σ-bonded to Rh (or Ir) and π-bonded to Pt, indicated via σ–π–σ-rearrangement of the ligand, and **754** reacts with Pt(C$_6$F$_5$)$_2$(THF)$_2$ to form **755**.

Alkynyl ligand transfer from [Cu(C≡CPh)]$_n$ to Pt–Rh and Pt–Ir complexes with bridging chloro ligands **756** affords the complexes whose metal centers are bridged by two Cu(C≡CPh)$_2$ fragments (**757**, Equation (148)).[592]



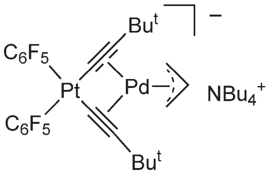
756 **757** (148)



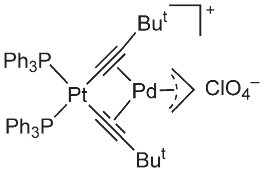
Scheme 102

The platinates with two pentafluorophenyl ligands and two alkynyl ligands also cause π-coordination of the alkynyl ligands to Rh(I) and Ir(I) centers **758–760**.[593] The Ir-containing product **760** has the alkynyl–Ir σ-bond formed via switching of the coordination mode of the ligand (Scheme 102).

A similar reaction of the IrCp* complex forms a new Pt–Ir complex.[594]Dianionic and neutral dialkynylplatinum complexes react with π-allylpalladium species to form Pt–Pd complexes with bridging alkynyl ligands **761** and **762**.[595] Both products contain alkynyl–Pt σ-bonds and π-bonds between the alkynyl groups and Pd.



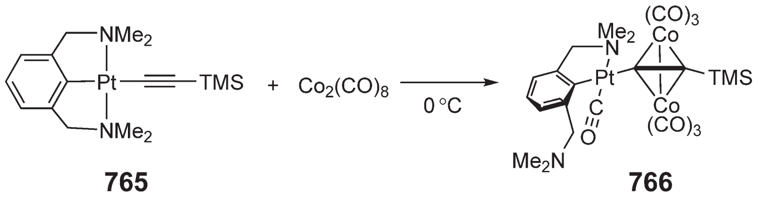
761



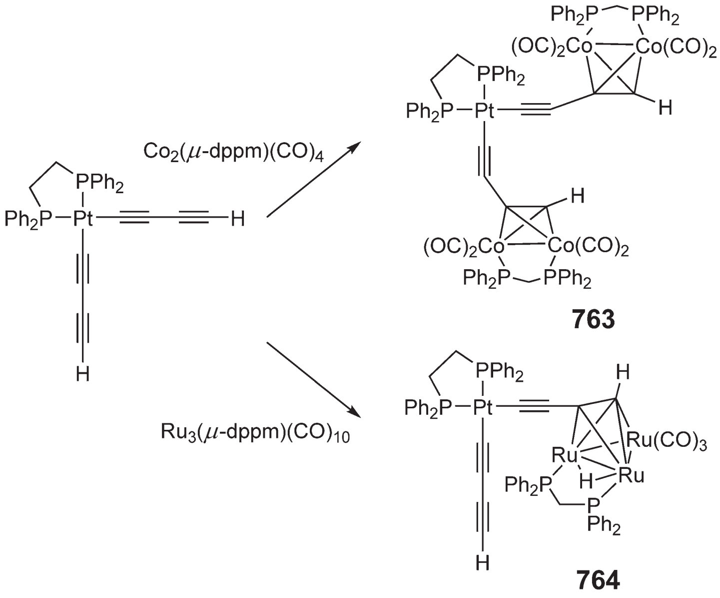
762

A complex with buta–1,3-diynyl ligands and dppe reacts with dinuclear or trinuclear carbonyl complexes of Co and Ru to cause addition of the metal to the CC triple bonds (**763** and **764**, Scheme 103).[596] Theoretical calculations suggest negative charge at the diynyl carbons bonded to Pt, and these carbons actually bind cationic metal centers Ag^+, Cu^+, and Li^+.

Alkynylplatinum(II) complexes with the NCN pincer ligands formed from metallation of the 1,3-diaminobenzene and from 1,3-diiminobenzene have also been reported. The alkynylplatinum complex with the 2,6-bis(dimethylamino)phenyl ligand **765** reacts with $Co_2(CO)_8$ to form the Pt–Co binary complex via addition of two Co centers to the C≡C bond of the ligand (**766**, Equation (149)).[597] Coordination of a CO ligand to Pt also takes place to make the ligand *C*,*N*-chelating bidentate.

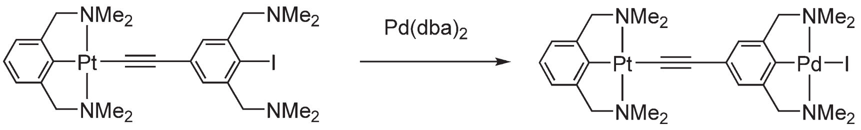


(149)



Scheme 103

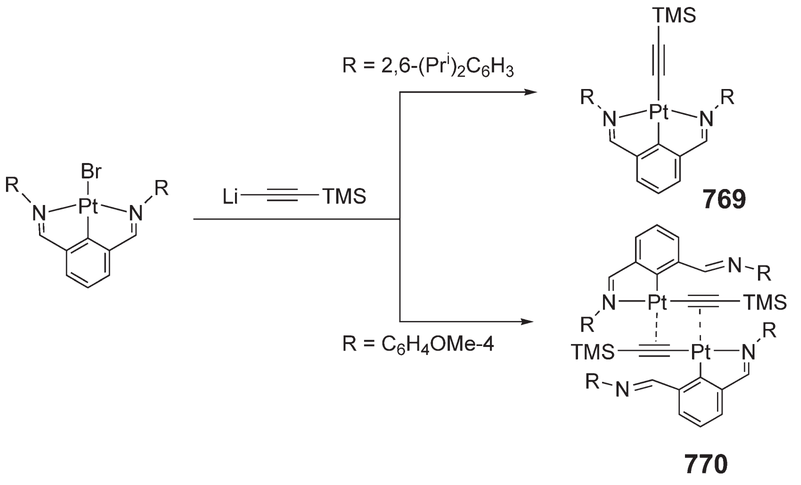
The complex with the alkynyl ligand bound to the iodo derivative of a pincer ligand **767** reacts with a Pd(0) complex to form a Pt–Pd dinuclear complex whose two metal centers are bonded by the π-conjugated spacer (**768**, Equation (150)).[598]



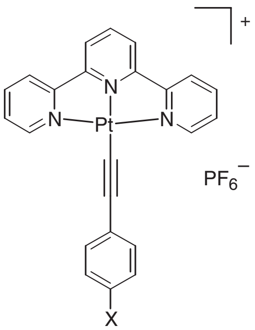
767 **768** (150)

An alkynylplatinum(II) complex with the 2,6-diiminophenyl ligand has a mononuclear structure with *N,C,N*-tridentate ligand **769** or a dinuclear structure with bidentate *C,N*-chelating ligands and the alkynyl ligands binding two Pt centers via σ,π-coordination (**770**, Scheme 104).[599,600] The structures of the complexes are influenced by steric bulkiness of the *N*-substituents of the imino ligand.

Cationic monoalkynylplatinum(II) complexes with aromatic *N,N,N*-tridentate ligands and neutral complexes with *N,N,C*-tridentate ligands were studied in detail because they exhibited interesting physical properties including luminescence and phosphorescence. Crystallography of the complexes with tridentate terpy as the supporting ligand **771–774** shows stacking of the coordination planes in the crystal structures. Emission peak positions of the complexes with arylethynyl ligands are influenced by the substituents at the phenyl groups of the ligand.[601] Electron-withdrawing substituents of the ligand increase emission energy. The complexes with *t*-butyl groups at the terpy ligand **772** are employed to label human serum albumin (HSA).[602] The HSA labeled with the Pt complexes shows emission at 630–650 nm in a buffer solution. Two crystal forms of the complex with buta–1,3-diynyl ligand and terpy **773** show a linear alignment of the Pt centers (Pt–Pt distance = 338.8 pm) and a zigzag alignment formed by a pair of the aggregated complexes (Pt–Pt distances = 339.4 and 364.8 pm), respectively.[603] The complexes with an arylated terpy ligand show long-lived luminescence (>1 μs).[604] Solutions of the complex show a marked solvatochromism and on–off switching of emission, depending on slight differences in solvent composition. An alkynylplatinum complex with terpy as the ligand **774** shows photocatalytic activity for dihydrogen production from 1,4-dihydropyridine.[605]

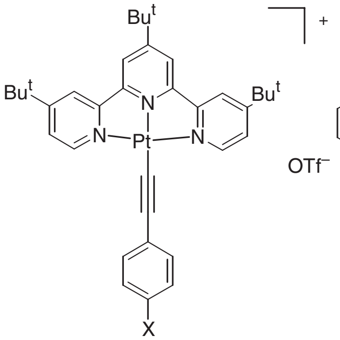


Scheme 104



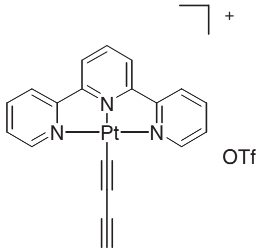
771

(X = H, Cl, Me, OMe, NO$_2$)

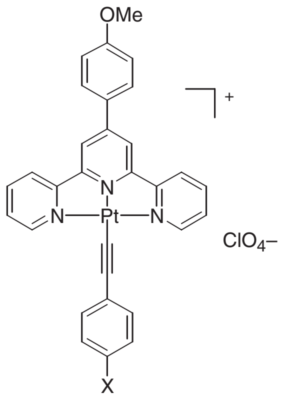


772

(X = NH$_2$, NCS, NHCOCH$_2$I)



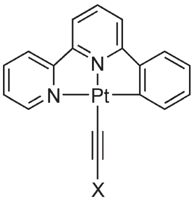
773



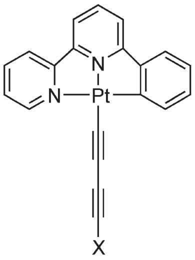
774

(X = CC-Ph)

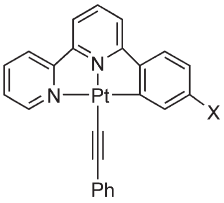
Structures and emission properties of the complexes with aromatic CNN ligands have also been studied.[606] A series of the alkynylplatinum complexes with tridentate CNN ligand 775–778 show emission whose energy is tuned by the kind of substituents of the alkynyl ligands and terdentate ligands; emission color of the complexes ranges from green-yellow to saturated red.[607,608] Crystallographic studies revealed the head-to-tail dimer structure with interaction between the apical sites of two Pt centers.



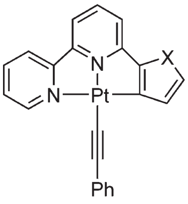
X = TMS, Ph, Tol, C$_6$H$_4$-F
775



X = TMS, –CC–TMS
776

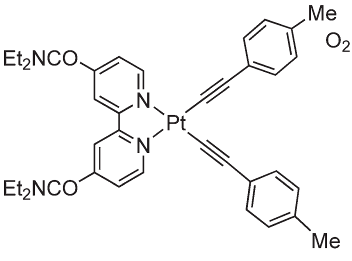


X = F, CF$_3$
777

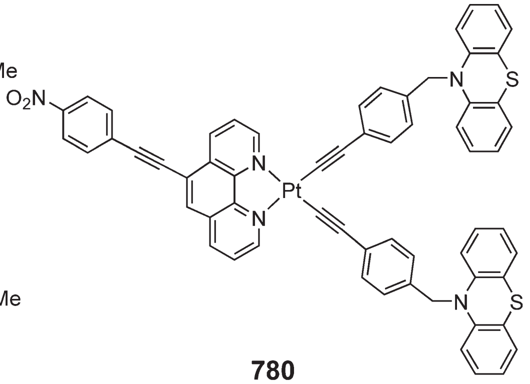


X = O, S
778

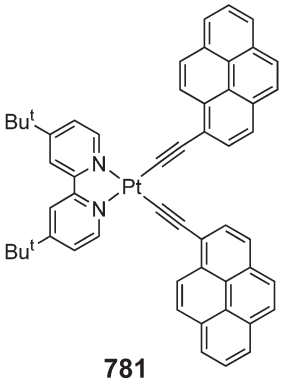
The dialkynyl complexes with chelating bipy and phen ligands also exhibit emission whose intensity can be higher than $[\mathrm{Ru(bipy)_3}]^{2+}$. MLCT absorption is responsible for the bright emission based on the self-quenching data.[609] Arylalkynyl complexes with bipy ligands having various electron-donating or electron-withdrawing substituents at the aryl group of the alkynyl ligand and at bipy have been prepared systematically.[610,611] An amide-substituted bipy ligand has been employed for preparation of the dialkynyl complex **779**. Complexes having phenothiazine as donor at the arylalkynyl ligands and nitrophenyl group at phenanthroline **780** have also been studied.[612,613] A complex with pyrenylalkynyl ligands **781** show phosphorescence at room temperature.[614]



779

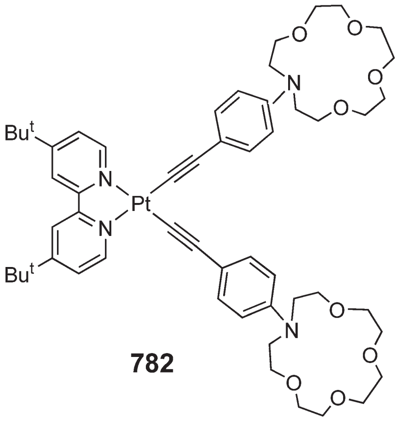


780

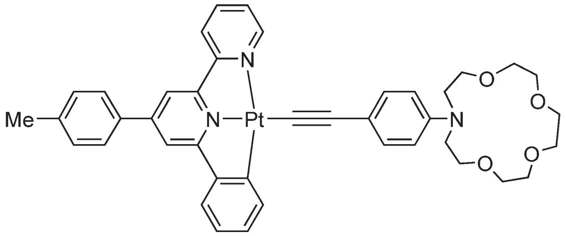


781

The complexes with alkynyl ligands furnished with a crown ether moiety **782 and 783** change the emission properties significantly upon addition of metal cations such as $\mathrm{Mg^{2+}}$ and $\mathrm{Zn^{2+}}$ due to complexation of the cyclic group to the metal cation.[615–617]

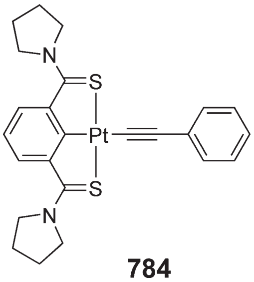


782

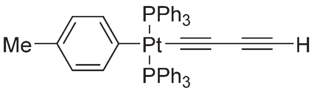


783

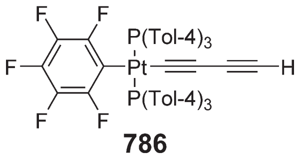
Alkynylplatinum(II) complexes with novel SCS pincer ligands, for example, **784**, have been prepared and fully characterized.[618,619] Not only photoluminescence, but also electroluminescence, are observed and studied in detail for these complexes.



784

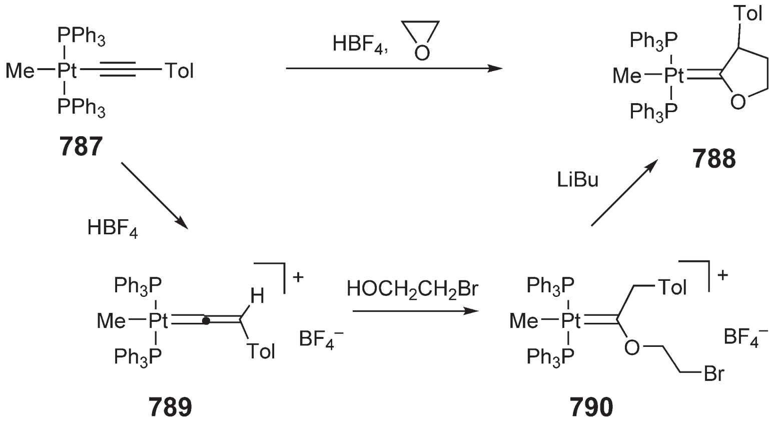


785



786

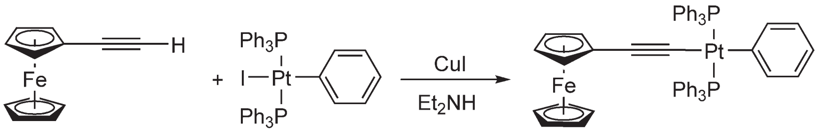
Butadiynylplatinum complexes with 4-Tol **785** and pentafluorophenyl **786** ligands have been prepared.[620] Although reactions of alkynylplatinum complexes involving cleavage of the Pt–C bond are less common



Scheme 105

than those of alkyl and aryl complexes, unsaturated C≡C bonds and acidic ≡CH bonds of the ligands show unique reactivities toward organic compounds. The alkynyl ligand bonded to the Pt–PPh_3 complex **787** reacts with ethylene oxide in the presence of HBF_4 to form the complex with a cyclic Fischer-type carbene ligand (**788**, Scheme 105).[621–624] The product was obtained also by stepwise reactions that involve protonation, addition of bromohydrin to the resulted cationic viniylidene intermediate **789**, and further reaction with base to give the cationic carbene complex **790**. Lithiation of **790** causes cyclization to form **788**.

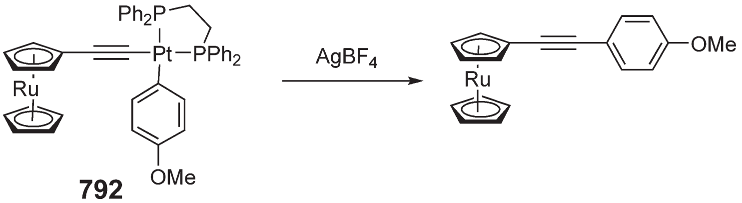
A *trans*-complex with aryl and ferrocenylethynyl ligands **791** has been prepared by a CuI-promoted coupling reaction (Equation (151)).[625] The complex undergoes electrochemical oxidation and chemical oxidation by DDQ to produce the cationic compound, and absorption spectra indicate delocalization of the electron between Fe and Pt.



791

(151)

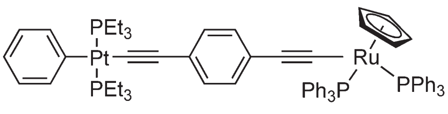
A Pt complex with aryl and ruthenocenylethynyl ligands **792** has been prepared, and its oxidation by $AgBF_4$ results in aryl(ruthenocenyl)acetylene (Equation (152)).[626,627] Oxidation occurs at the Ru center to form ruthenocenium, but electron transfer between Pt and Ru causes partial formation of the cationic Pt(II) species which shows rapid reductive elimination of the two organic ligands.



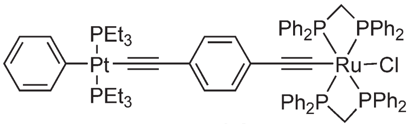
792

(152)

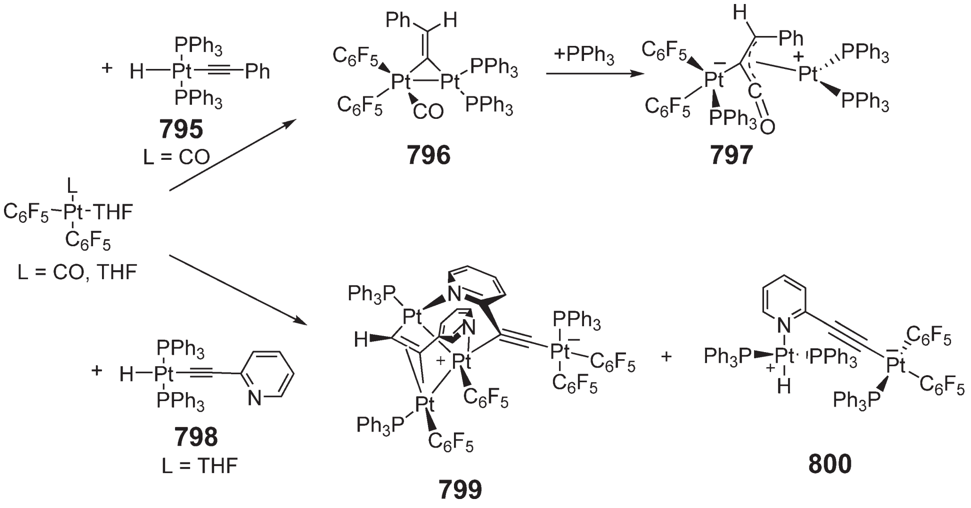
Pt(II)–Ru(II) binary complexes with a bridging benzene–1,4-diethynylene ligand **793** and **794** have been reported.[628]



793



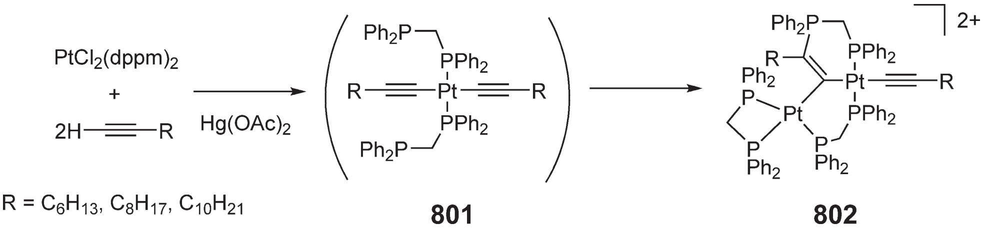
794



Scheme 106

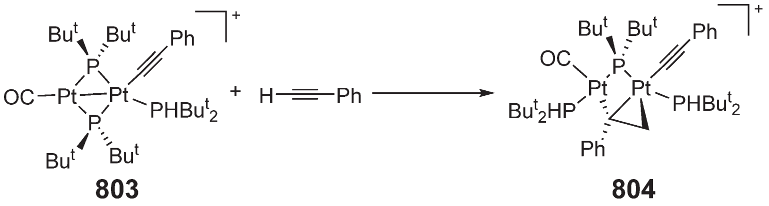
cis-Pt(C_6F_5)$_2$(CO)(THF) reacts with a hydrido(phenylethynyl)platinum complex **795** to form dinuclear Pt complex with a bridging phenylvinylidene ligand **796**.[629] Further reaction with PPh_3 forms the complex with a bridging vinylketenyl ligand **797**. Reaction of *cis*-Pt(C_6F_5)$_2$(THF)$_2$ with hydrido(pyridylethnyl)platinum **798** affords the trinuclear complex **799** and dinuclear complex **800**, with a bridging pyridylacetylide ligand, as the initial and secondary products, respectively (Scheme 106).[630]

Dinuclear Pt complexes with bridging alkenylidene and dppm ligands **802** are prepared by formation of a dialkynylplatinum complex with two dppm ligands **801** and intramolecular addition of an uncoordinated PPh_2 group to the alkynyl carbon (Equation (153)). The product has a structure involving overlap of the coordination plane via a π–π-interaction, and shows emission spectra whose peak shifts vary depending on the substituent at the alkynyl ligand.[631]



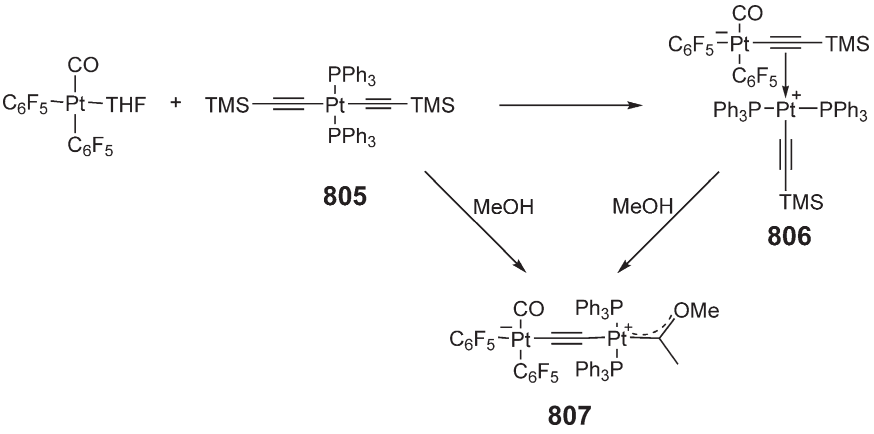
(153)

A cationic dinuclear Pt(I) complex with two bridging phosphido ligands **803** reacts with phenylacetylene to form the Pt(II) complex with a bridging phosphido ligand and a styryl ligand that coordinates to one Pt via a σ-bond and to the other via a π-bond (**804**, (Equation (154)).[632]

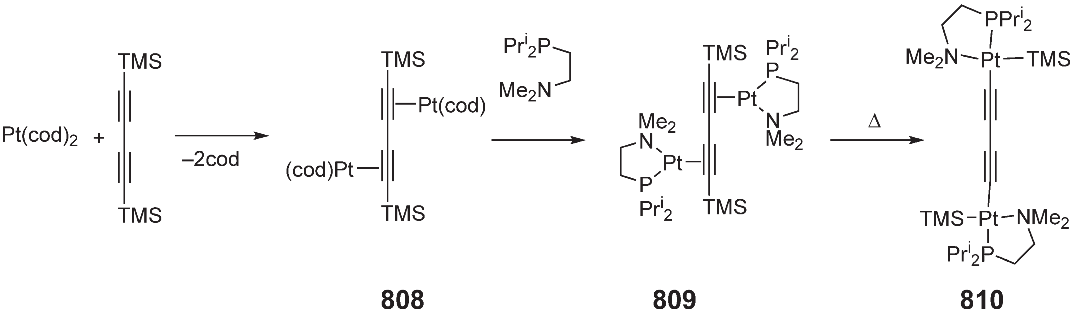


(154)

Dinuclear Pt complexes with bridging ethynediyl and polyynediyl ligands have been prepared by several reactions. The reaction of *cis*-Pt(C_6F_5)$_2$(CO)(THF) with a bis(trimethylsilylethynyl)platinum complex **805** results in transfer of one alkynyl ligand of **805** to produce a dinuclear complex **806** with an alkynyl ligand bonded to two Pt centers via σ- and π-bonds (Scheme 107).[633] The reaction of methanol with **806** and a direct reaction in methanol forms the dinuclear complex with a bridging ethynediyl ligand **807**.



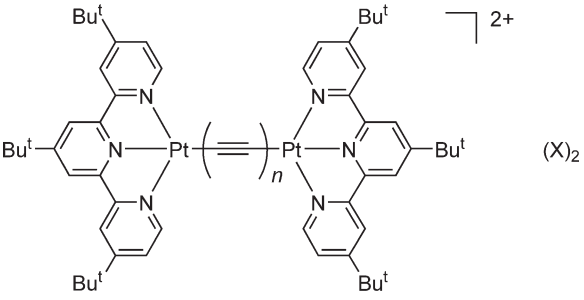
Scheme 107



Scheme 108

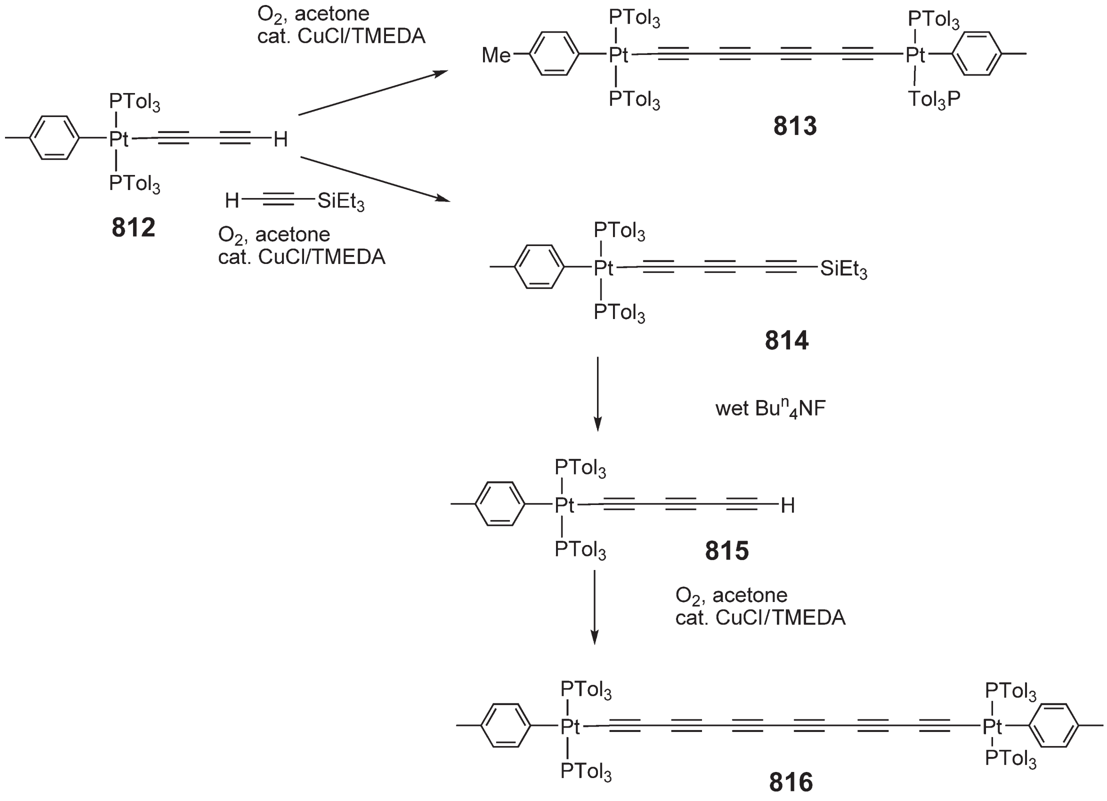
A dinuclear Pt(0)–cod complex with a π-coordinated bis(trimethylsilyl)butadiyne ligand 808 undergoes exchange of the ligand with a chelating aminophosphine to form 809 (Scheme 108).[634] Activation of the Si–C bonds is promoted by the metal center to afford silyl(alkynyl)platinum(II) complex 810.

Dinuclear Pt complexes with a bridging oligoethynediyl ligand 811 have also been prepared. The complexes with C2, C4, and C6 bridging ligands whose peak positions are shifted to longer wavelengths upon elongation of the polycarbyne chain exhibit absorption in the visible region.[635]



811

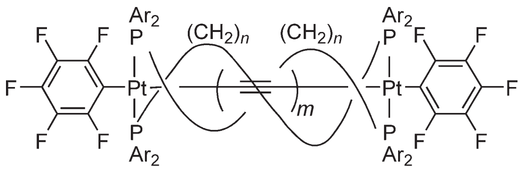
Diplatinum complex 813 whose metal centers are bridged by an octatetraynediyl ligand has been prepared by oxidative coupling of the butadiynyl ligand of 812 (Scheme 109).[636] Coupling of trimethylsilylacetylene with the alkynyl ligand of 812 forms 814 with a C6 ligand. Desilylation of the alkynyl ligand 815 and oxidative coupling of



Scheme 109

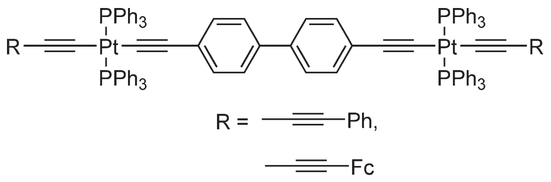
the ≡CH group of the two molecules form 816 having a bridging C12 ligand. The dinuclear complex with a bridging C16 ligand has also been prepared and fully characterized.[637]

Dinuclear complexes with a bridging polyynediyl ligand and diphosphine ligands with long methylene chains between the two P atoms show a structure in which the alkylene chains are double-helixed around the polyyne ligand 817.[638]

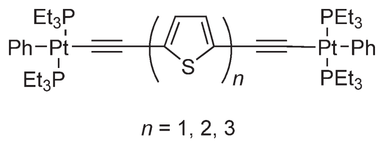


817

Dinuclear Pt complexes with bridging diacetylide ligands containing biphenylene and oligoethienylene groups have been prepared 818 and 819.[639,640]

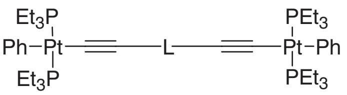


818

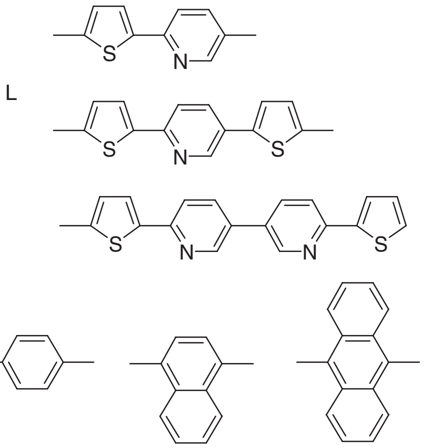


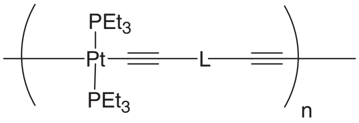
819

Similar complexes with π-conjugated fragments 820 and 821 within the bridging ligand have been prepared and their optical properties studied.[641,642]

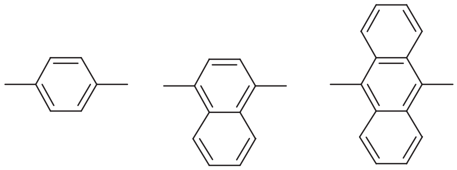


820



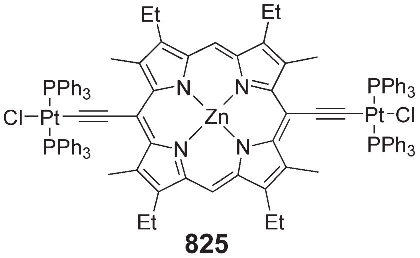


821

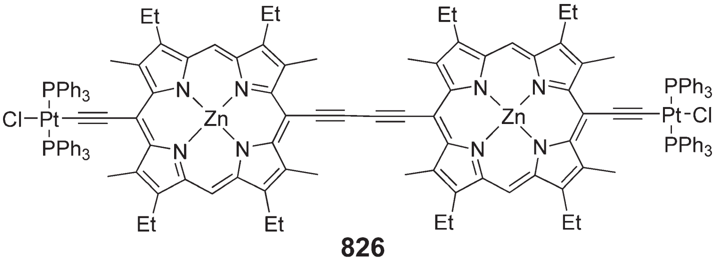


Complexes with ferrocenyl acetylide and diferrocenyl acetylide bonded to $PtPh(PEt_3)_2$ fragments 824 have been prepared, from the reactions of $PtCl(Ph)(PEt_3)_2$ with 822 and 823 together with polymers having biferrocene and alkynylplatinum units (Scheme 110).[643] They have been characterized by X-ray crystallography and by molecular orbital calculations.

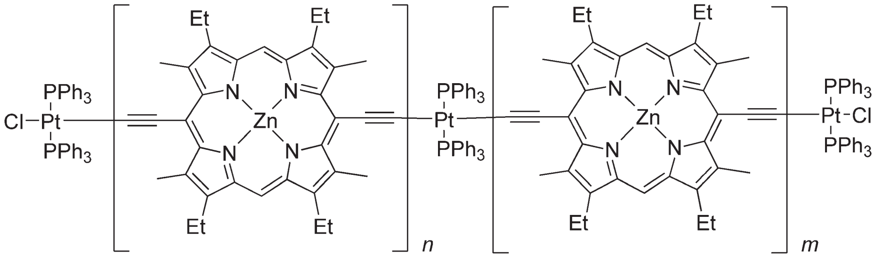
Complexes with Zn–porphyrin have been prepared 825–827 by conventional synthetic methods for alkynylplatinum complexes.[644]



825

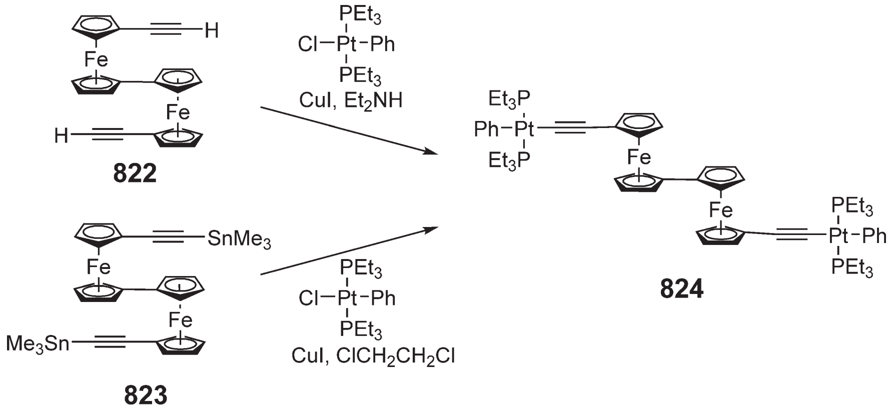


826

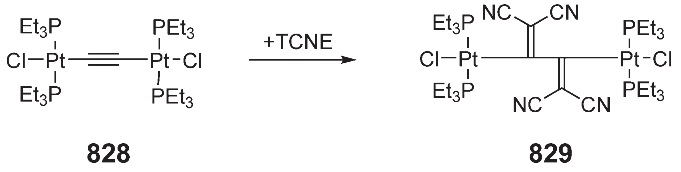


827

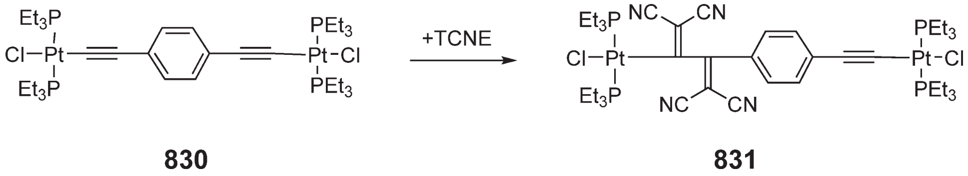
A dinuclear complex with bridging ethynylene 828 reacts with TCNE to afford a complex with dicyanovinylidene groups on the bridging ligand (829, Equation (155)).[645] Cleavage of the C═C double bond of TCNE and addition of the carbene to the alkynyl ligand take place during the reaction. The dinuclear complex with a bridging 1,4-phenylene–ethynylene ligand 830 undergoes similar addition of the dicyanocarbene at a C≡C triple bond to form 831 (Equation (156)).



Scheme 110

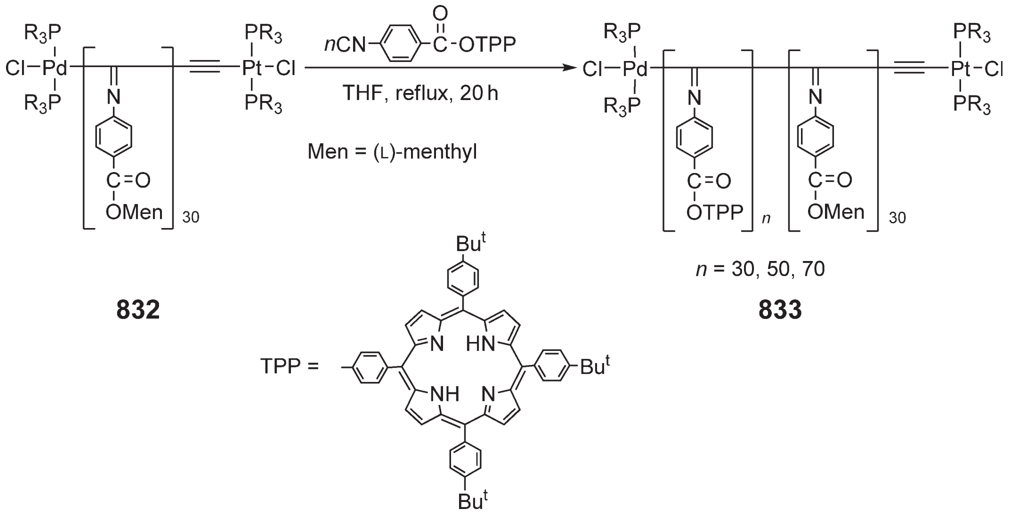


(155)



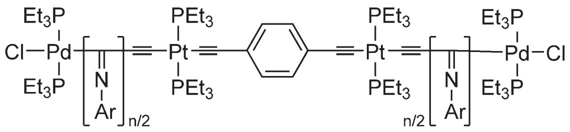
(156)

Palladium–platinum dinuclear complexes with bridging ethynylene ligands undergo multiple insertion of nitriles into the Pd–C bond preferentially.[646] Living homopolymer 832 and the block co-polymers with an AB type 833 are obtained using isonitriles with porphyrin and with a menthyl group in the monomers (Equation (157)). The absolute configuration of the helical chirality can be determined based on CD spectra.

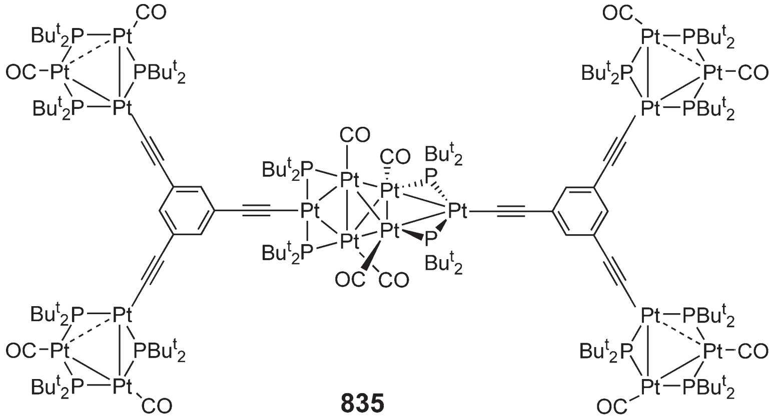


(157)

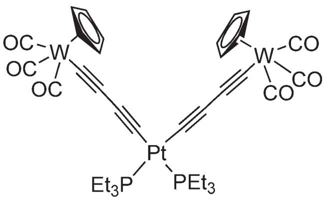
A Pd_2Pt_2 complex with bridging ethynylene and phenylene–diethynylene ligands undergoes multiple insertion of isonitriles to give the polyisonitrile containing these metals 834.[647] A complex with 18 Pt centers 835 has been prepared and fully characterized, where 1,3,5-triethynyl benzene binds two Pt_3 and one Pt_6 fragments;[648] a W_2Pt complex with bridging C4 ligands 836 has been fully characterized.[649]



834

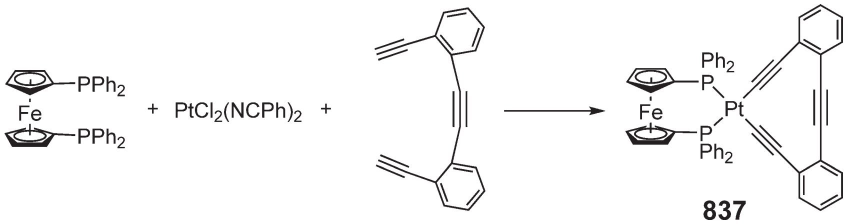


835



836

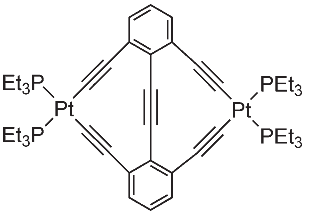
Complexes with macrocyclic dialkynyl ligands have been prepared. Reaction of a dialkynyl compound having a spacer with two *o*-phenylene groups with $PtCl_2(NCPh)_2$ in the presence of dppf affords the complex having an 11-membered chelate ring (837, Equation (158)).[650] Bicyclic diplatinum complex with two fused 11-membered rings 838 has also been formed.



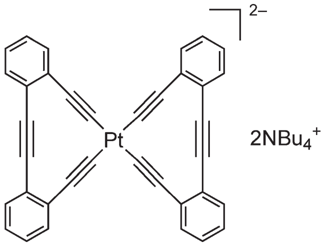
837

(158)

A compound with two *spiro*-rings 839 reacts with $HgCl_2$ to produce its Hg adduct.[651]

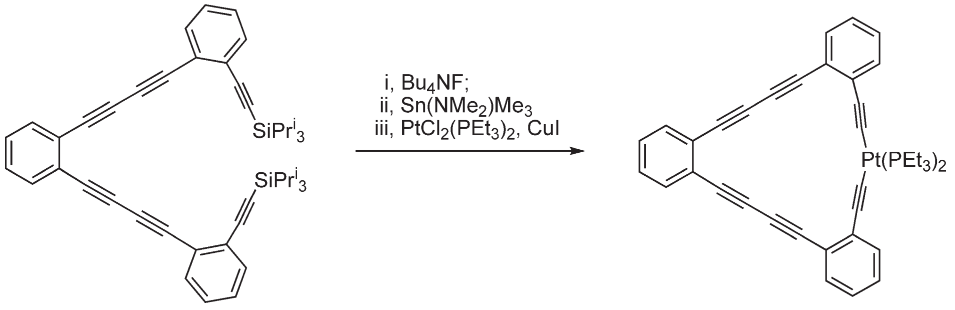


838



839

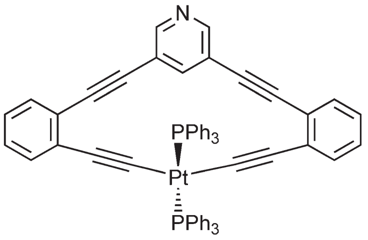
Transmetallation of an alkynylsilane to a Pt complex has been applied for the synthesis of a Pt-containing macrocycle (**840**, Equation (159)),[652] and a complex with a smaller ring **841** has also been prepared.[653]



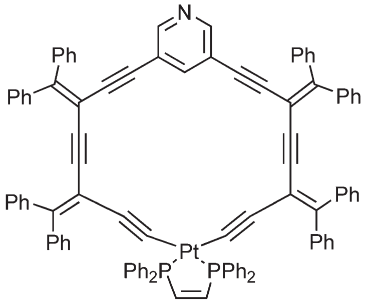
840

(159)

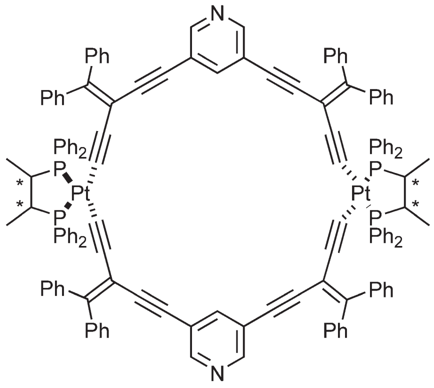
Related macrocyclic complexes with chelating diphosphine ligands **842**,[654] chiraphos **843**,[655] and PPh_3 **844**[656] have been reported.



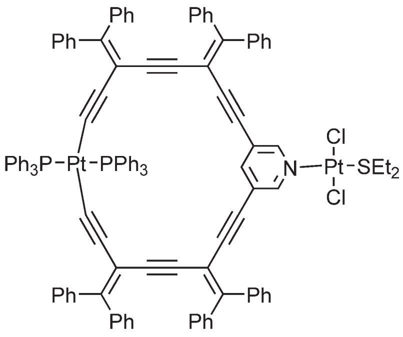
841



842

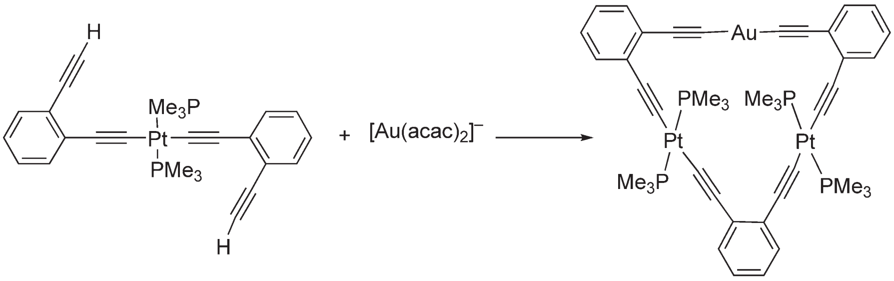


843



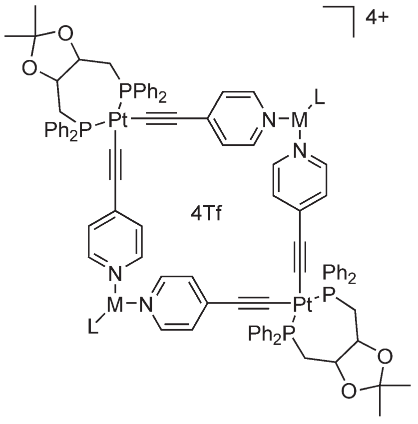
844

A pyridine group in the cyclic ligand of **844** can also serve as a monodentate ligand to coordinate to newly added $PtCl_2(SMe_2)_2$. A macrocycle containing one Au and two Pt centers **846** may be prepared by the reaction of a dialkynylplatinum complex **845** with an aurate having acac ligands (Equation (160)).[657] Exchange of the alkynyl ligand between the Pt complexes takes place during the reaction.



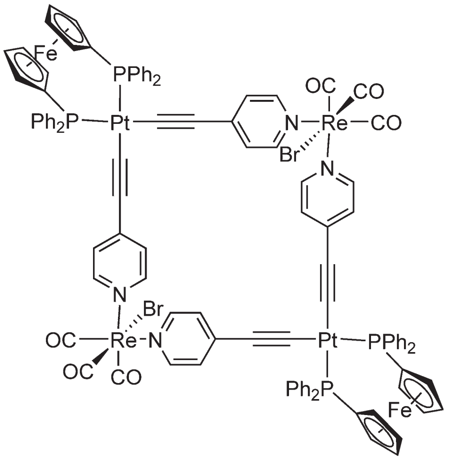
845 **846** (160)

Square-planar macrocyclic Pt_2Pd_2 and Pt_4 complexes **847** whose metal centers are bonded by 4-alkynylpyridine ligands have been isolated;[658] Ag^+ is bonded to the two alkynyl ligands in the pore. The Pt atom is bonded to optically active diphosphine (DIOP) and shows a Cotton effect in the CD spectrum.



M = Pd, Pt; L = DIOP, BINAP, $2PEt_3$

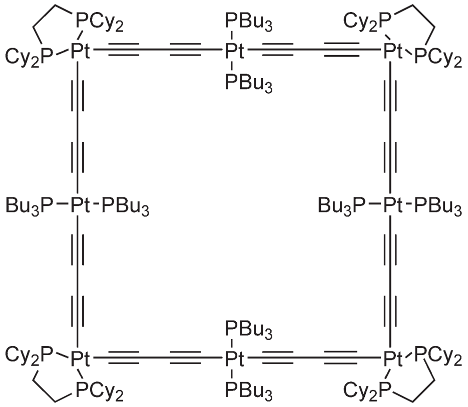
847



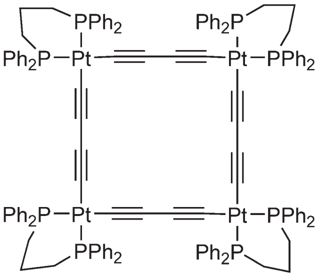
848

A Pt_2Re_2 complex **848** with a square structure has been prepared using bridging alkynylpyridine ligands.[659]

A macrocyclic octanuclear Pt complex **849** has been prepared by using a –C≡C–C≡C– bridging ligand, which binds the $Pt(Cy_2PCH_2CH_2PCy_2)$ and $Pt(PBu_3)_2$ fragments alternatively.[660]



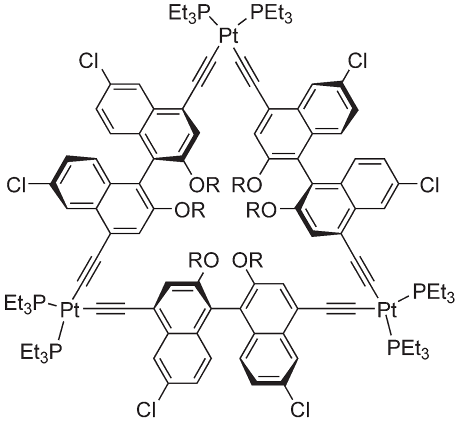
849



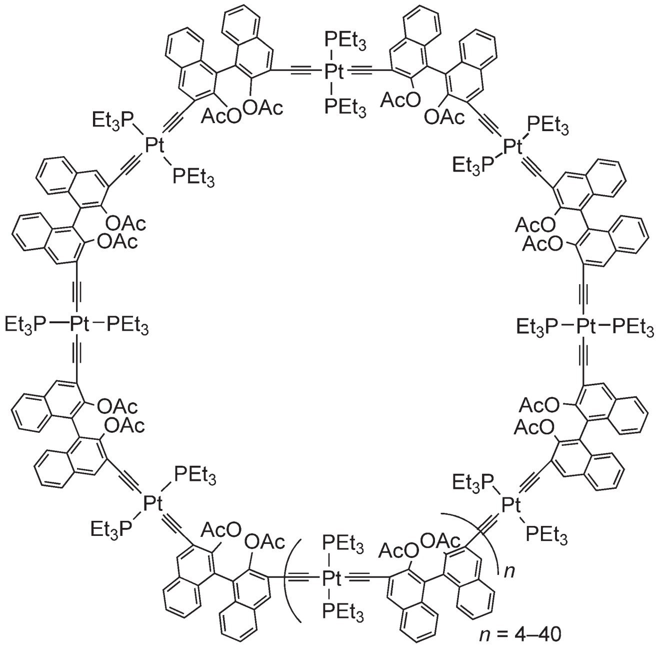
850

A butadienediyl Pt complex with phosphine ligands reacts with $PtCl_2L_2$ in the presence of CuI and amine resulting in coupling to form a tetranuclear planar Pt complex with a C4 spacer **850**.[661] A crystal structure revealed the presence of channels in the crystal lattice and occupation by solvent molecules within the pore of the 20-membered ring.

A macrocyclic triangular trinuclear Pt complex composed of an optically active biaryl group and *cis*-dialkynylplatinum(II) group **851** has been prepared.[662] The macrocycle containing Ti at the binaphthyl group shows high catalytic activity toward asymmetric addition of diethylzinc to aldehydes.



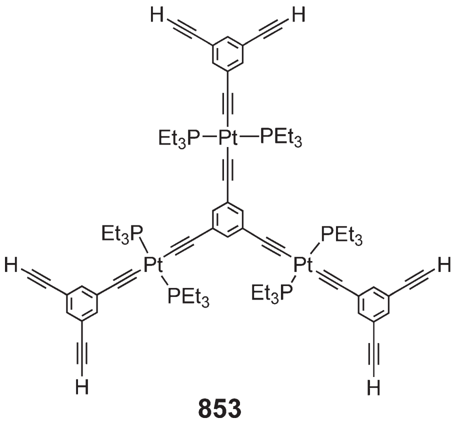
851



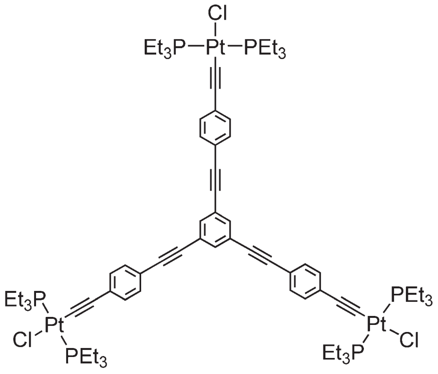
852

Complexes with three to eight Pt atoms, for example, **852**, have been formed and purified by chromatography.[663] Acyclic and cyclic Pt alkynyl polymers with optically active binaphthyl groups have been prepared and separated.[664]

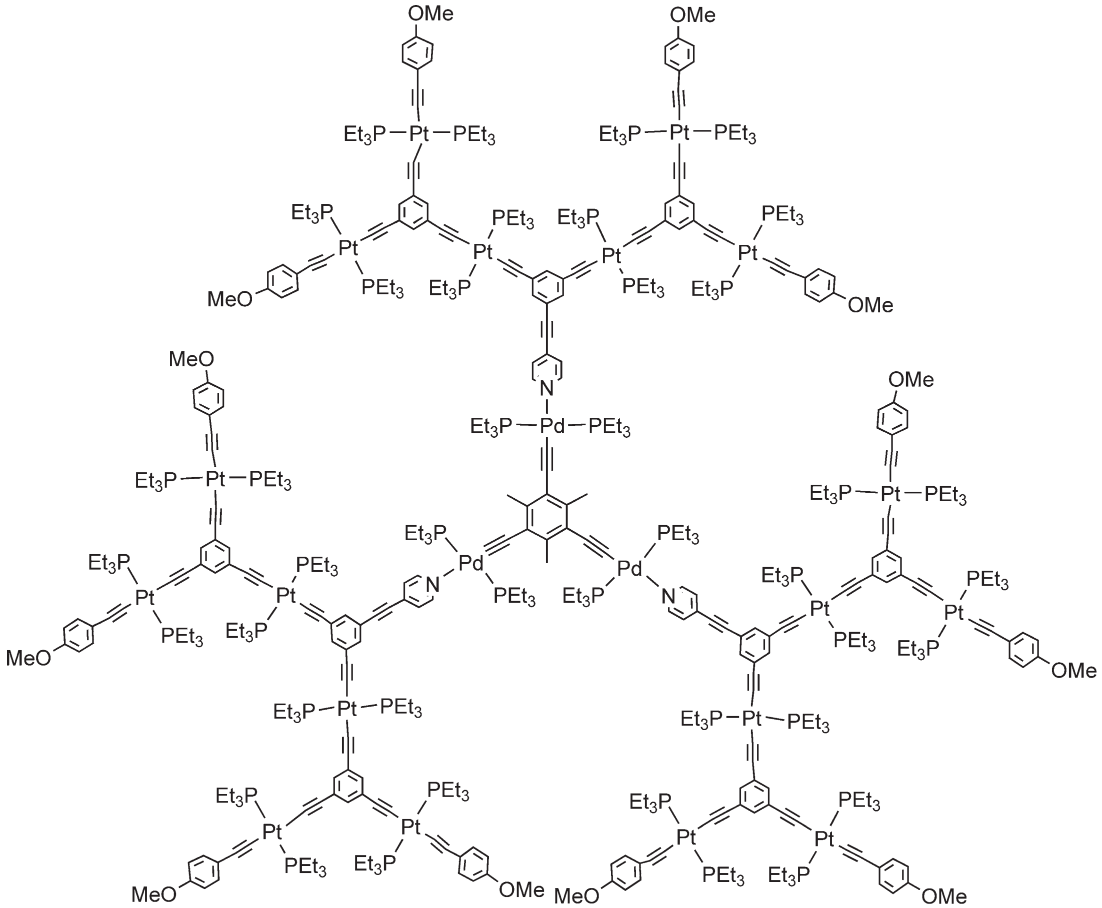
Dendrimers composed of dialkynylplatinum species with two PEt_3 ligands **853** have been prepared by the divergent method.[665] The trinuclear Pt complex whose metal centers are bonded by three alkynyl groups connected to a benzene ring **854** has been prepared, and the complex shows emission around 520 nm.[666] Higher dendrimers, for example, **855**, have been prepared by convergent and divergent methods, and involve both Pd and Pt centers.[667]



853

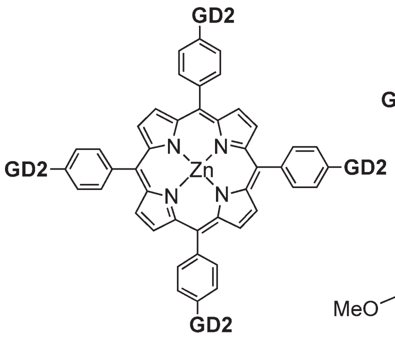


854

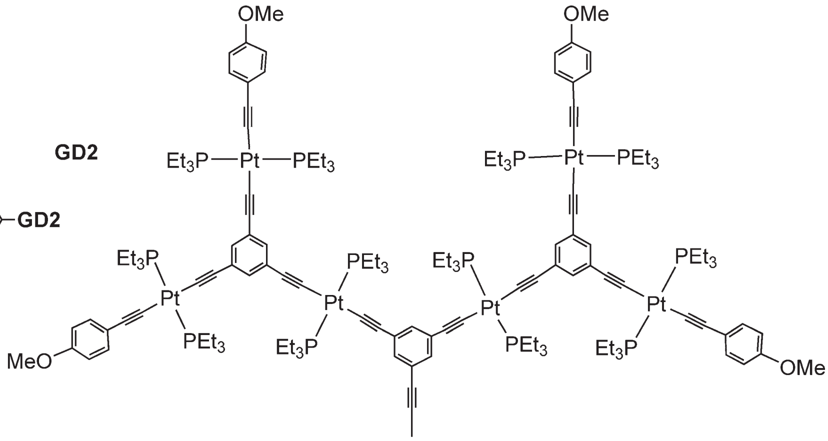


855

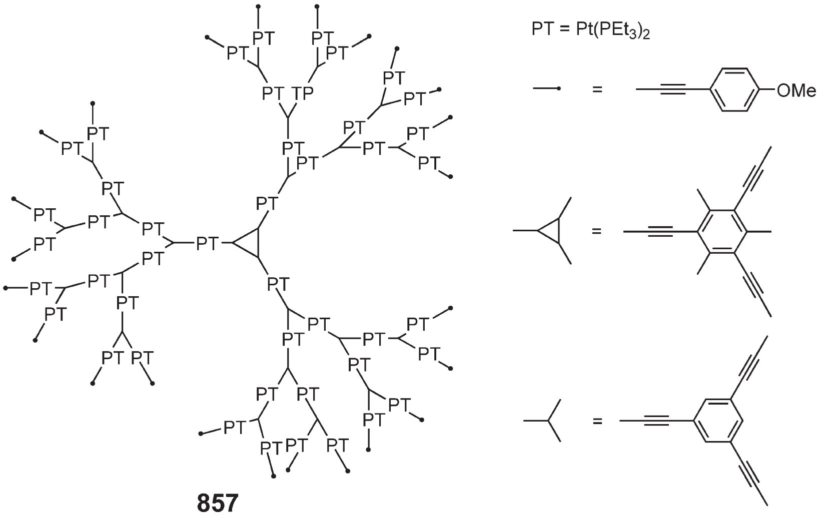
The second-generation Pt dendrimers can be bonded to a Zn–porphyrin to produce a dendrimer with the metallaporphyrin in the core 856,[668] and a large Pt dendrimer involving 1,3,5-trisubstituted benzene closely related to 856 has been reported 857.[669]



856

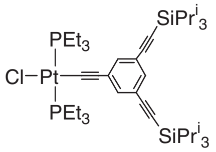


GD2



857

Higher dendrimers including the 46-dendron **862** have been prepared according to the procedure involving repetition of coupling of intermediate lower-generation dendrimers **858–861** and desilylation of the formed dendrimer.[670,671]



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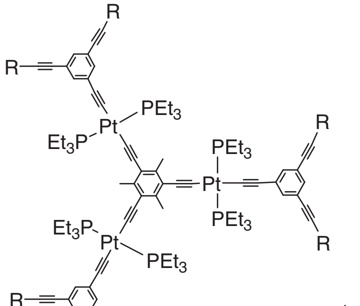
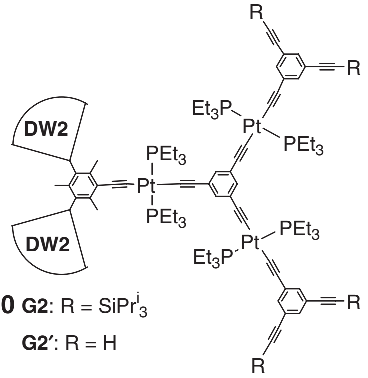


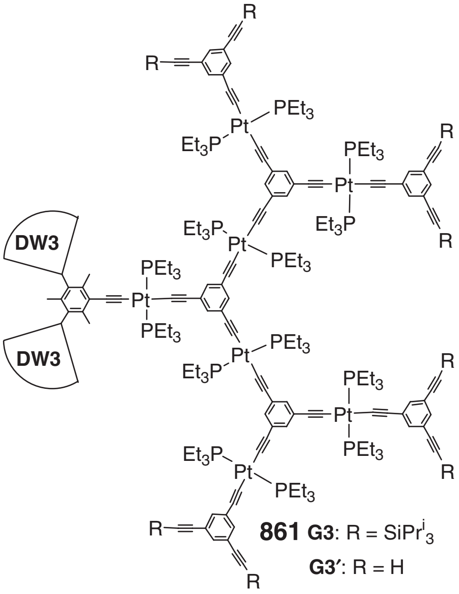
859 **G1**: R = $SiPr^i_3$

G1′: R = H



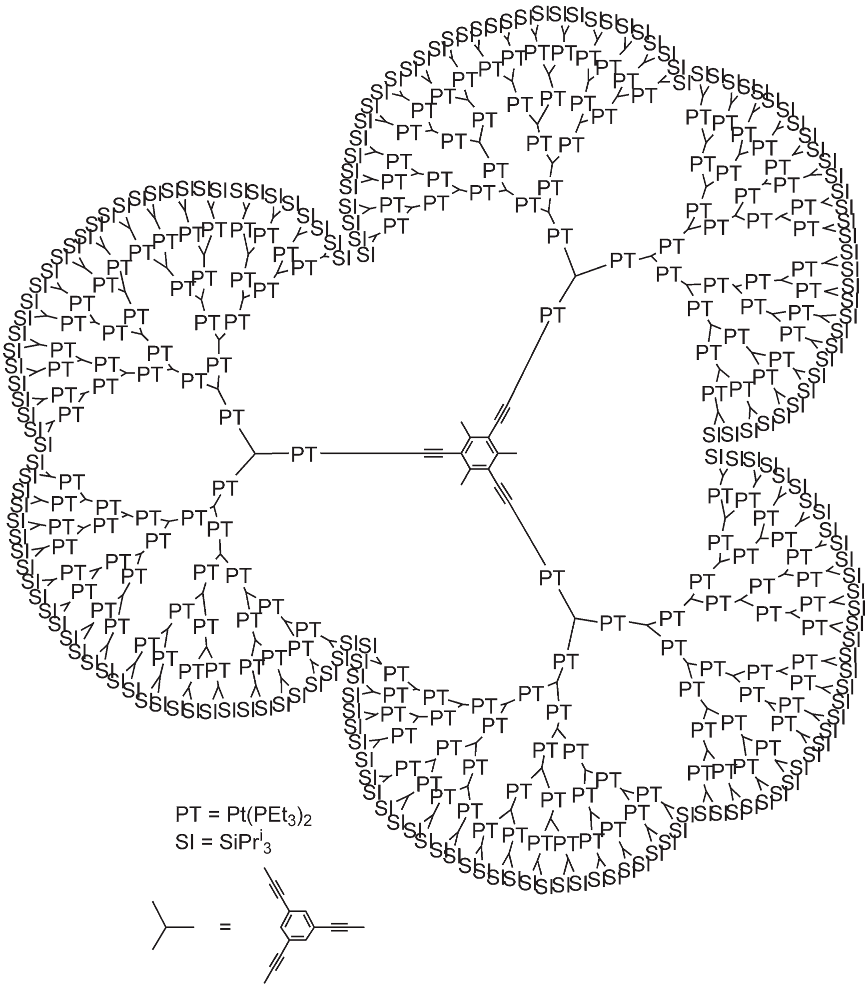
860 **G2**: R = $SiPr^i_3$

G2′: R = H



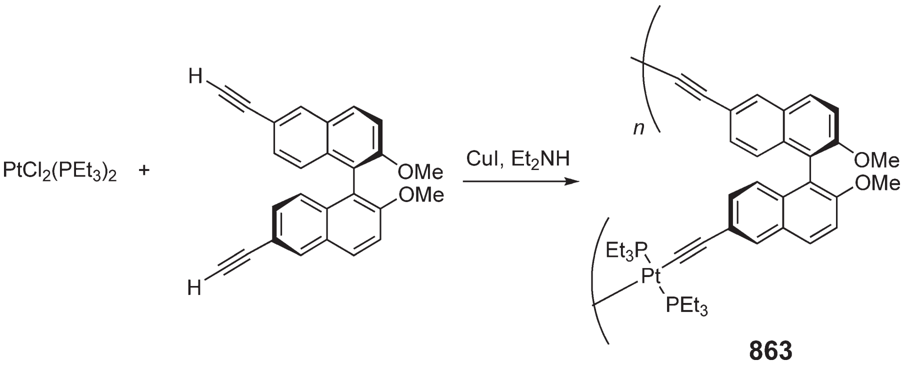
861 **G3**: R = $SiPr^i_3$

G3′: R = H



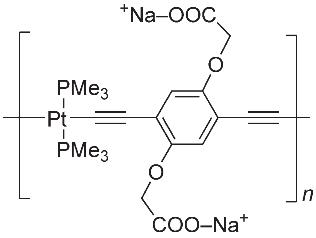
862 G6

Polymeric compounds such as 863 with analogous repeating units have been obtained by using a 5,5′-dialkynylbinaphthol derivative as the starting material (Equation (161)).[672]

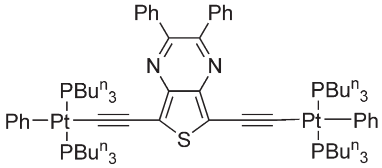


(161)

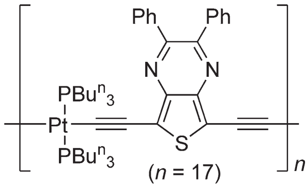
Polynuclear platinum(II) complexes with bridging alkynediyl ligands have been reported, and for some of these, the energy gap for the π-conjugated polymers has been calculated.[673] Luminescent and phosphorescent behavior of a series of the complexes composed of alternating $Pt(PR_3)_2$ and 1,4-phenylene–diethynylene diyl fragments have been studied, for example, 864.[674,675] Dinuclear and polynuclear complexes with bridging diyl ligands containing an electron-accepting 5,7-diphenyl–2,3-thieno[3,4-*b*]-pyrazine group **865** and **866** show low-energy emission behavior.[676]



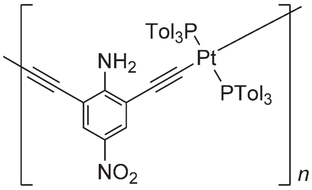
864



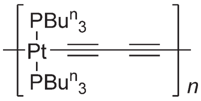
865



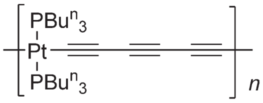
866



867



868



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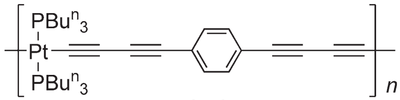
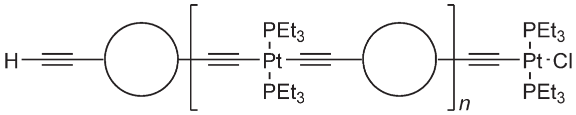
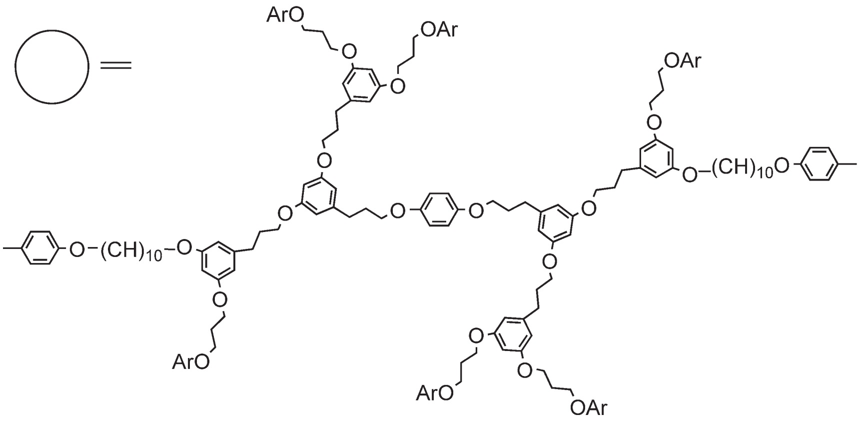


870

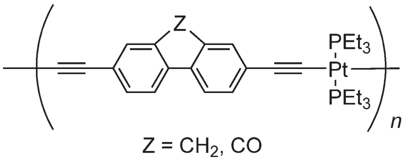
A polymer containing dialkynylplatinum(II) groups and a 1,3-disubstituted phenylene **867** has been revealed to have a helical conformation based on the results of spectroscopic measurements.[677] IR and Raman spectra have been measured for Pt polymers with bridging polyyne diyl ligands **868–870**.[678] The polymer having long branched groups with a dendritic structure **871** has been prepared.[679]



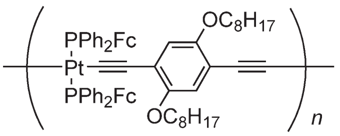
871



Various complexes with briging ethynylene ligands **872–874** are formed as listed below;[680–682] Cr(CO)$_3$-containing arylene ethynylene polymer **875** and a Ge-containing polymer **876** have been prepared and fully characterized.[683,684]



872



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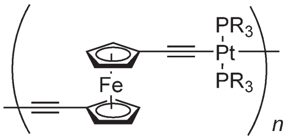
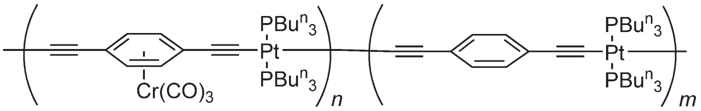


874



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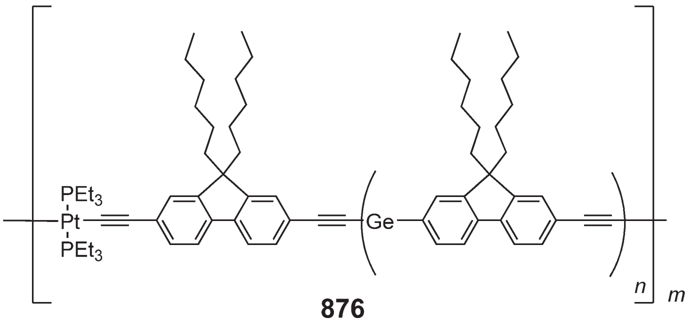
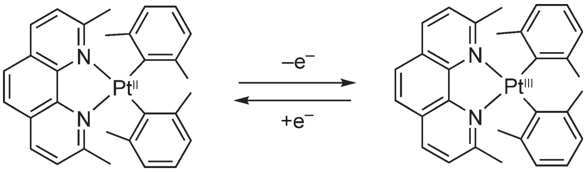


876

8.08.4 Pt(III) Complexes

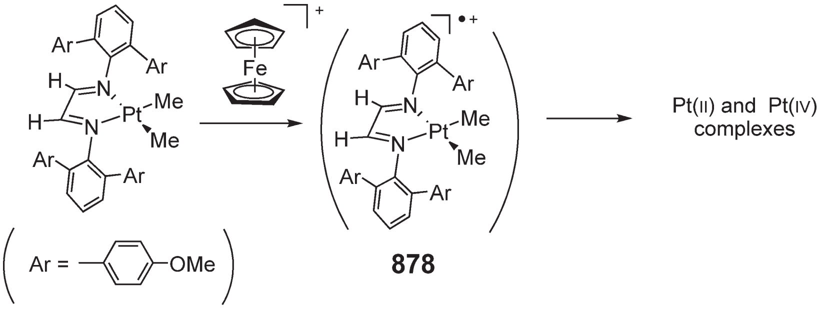
The dimesitylplatinum complex with 2,9-Me_2phen ligand 235 has been prepared, in which the apical site of square-planar coordination is blocked sterically.[232] Electrochemical oxidation affords the cationic Pt(III) complex 877 as a stable species in solution (Equation (162)). The complex is ESR silent, but exhibits an absorption band characteristic of a d^7-metal complex.



235 **877**

(162)

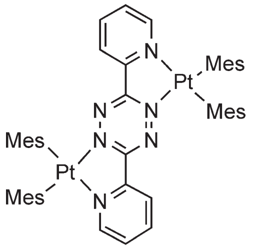
One-electron oxidation of the dimethylplatinum complex with a 1,4-diaza–1,3-butadiene ligand by ferrocenium cation leads to a mixture of cationic Pt(II) and Pt(IV) complexes, where the distribution of the products indicates presence of the Pt(III) intermediate 878 with a radical cation structure (Equation (163)).[37]



878

(163)

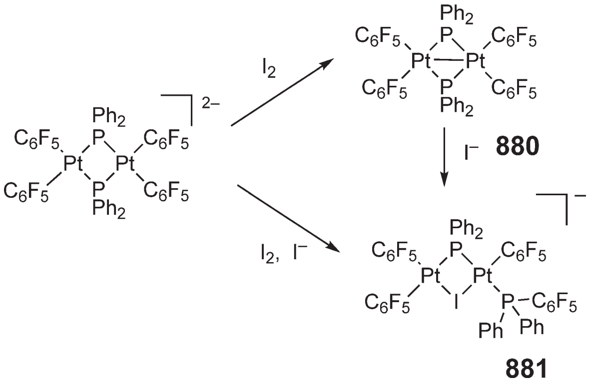
The dinuclear Pt complex with the 3,6-bis(2-pyridyl)–1,2,4,5-tetrazine ligand **879** undergoes one-electron reduction and one-electron oxidation electrochemically.[685] The oxidation product is composed of a Pt^{II}–Pt^{III} mixed-valence state, although the K_c value is small due to the d_σ-orbital character of the redox orbitals.



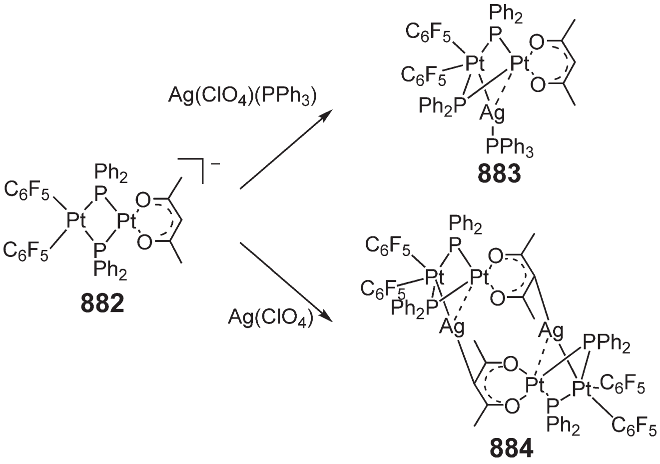
879

An anionic dinuclear Pt(II) complex having bridging PPh_2 ligands and terminal C_6F_5 ligands is oxidized by I_2 to form two kinds of dinuclear complex, depending on the conditions (Scheme 111).[686] Simple oxidation leads to a symmetrical dimer with a Pt^{III}–Pt^{III} bond **880**, while the reaction with I_2 in the presence of I^- affords the dinuclear Pt(II) complex with a $PPh_2(C_6F_5)$ ligand **881**, formed via coupling of the phosphide and aryl ligands at one Pt center. Addition of I^- to **880** also yields **881**.

An attempt to oxidize the anionic dinuclear Pt(II) complex having an acac ligand **882** with Ag^+ forms adducts of Ag(I) with the dinuclear Pt(II) complexes **883 and 884**, rather than Pt(III) complexes (Scheme 112).[687]

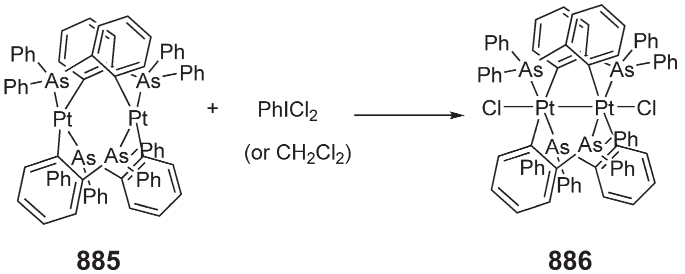


Scheme 111



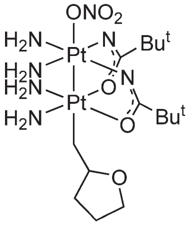
Scheme 112

A lantern-type dinuclear Pt(II) complex with bridging *C,As*-coordinated triphenylarsine ligands 885 undergoes oxidation with $PhICl_2$ or CH_2Cl_2 to afford the $Pt^{III}–Pt^{III}$ complex with chloro ligands (886, Equation (164)).[688]

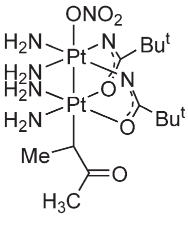


(164)

Dinuclear and tetranuclear complexes containing $Pt^{III}–Pt^{III}$ bonds at the apical sites such as 887 and 888 have been prepared.[689–694] An alkyl ligand bonded to the Pt(III) center undergoes elimination upon reaction with bases such as amine and OH^-.



887

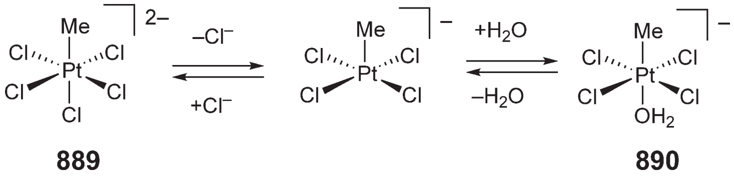


888

8.08.5 Pt(IV) Complexes

Organoplatinum(IV) complexes have mostly an octahedral geometry around the d^6-metal center. Preparation of complexes and their chemical properties have been summarized in review articles.[695–697] Commonly used preparation methods are oxidative addition of organic halides and pseudohalides to dialkylplatinum(II) complexes and addition of ligands to trimethylplatinum(IV) precursors having halide or triflate bridging ligands. Coupling of the two alkyl or aryl ligands from the Pt(IV) center via reductive elimination occurs more easily than that from square-planar Pt(II) complexes, although electron-donating ligands including bidentate and tridentate *N*-ligands stabilize alkyl and arylplatinum(IV) complexes.

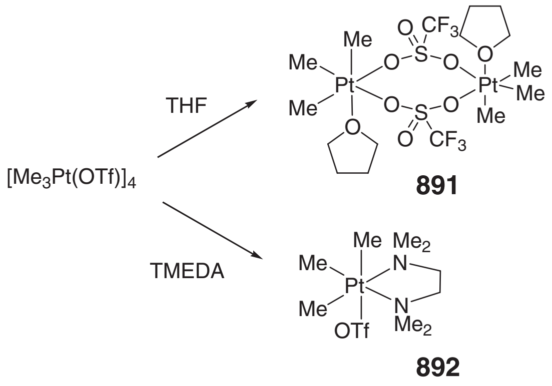
Oxidative addition of MeI to K_2PtCl_4 and exchange of the cation with NMe_4Cl yield the methylplatinum(IV) complex without neutral supporting ligands, $[NMe_4]_2[PtMeCl_5]$ 889.[698] NMR studies of the complex in aqueous solutions show the presence of an equilibrium with methyl(tetrachloro)platinate having an aqua ligand (890, Equation (165)).



(165)

Treatment of K_2PtCl_4 with acetaldehyde and with acetic acid forms the corresponding monoalkylplatinates, $[PtCl_5(CH_2CHO)]^{2-}$ and $[PtCl_5(CH_2COOH)]^{2-}$, respectively, characterized *in situ* by ^1H NMR spectroscopy.[699]

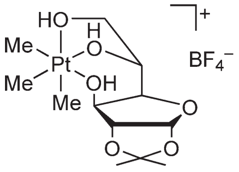
Well-known neutral trimethyl(halo)platinum(IV) complexes have a cubane-type tetrameric structure with the halo ligands bridging three Pt centers. The trimethylplatinum(IV) complex with triflate ligands, with a similar tetrameric



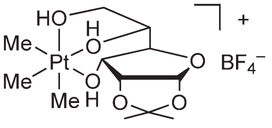
Scheme 113

structure, reacts with THF and TMEDA to produce the corresponding Pt(IV) complexes with the *O*- or *N*-donor as the ligand (**891** and **892**, Scheme 113).[700]

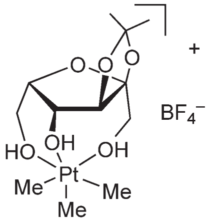
Sugar derivatives are able to occupy three meridional sites of the octahedral cationic trimethylplatinum(IV) complex via coordination by OH groups **893–895**.[701,702] Crystallographic results for **893** and **894** indicate networks composed of the cationic complex and BF_4^- anion linked through O–H···F hydrogen bonding. Glycopyranosides also coordinate as the tridentate ligand for three facial sites of the trimethylplatinum(IV) complexes **896** and **897**.[703] Aminosugar derivatives function as a bidentate chelating ligand to form the trimethylplatinum(IV) complex with an aqua ligand, while the aminosugar alcohol coordinates to trimethylplatinum as a tridentate ligand,[704,705] and bidentate oximate also coordinates to the trimethylplatinum(IV) complex **898**.[706] Methyladenine forms a cyclic trinuclear Pt(IV) complex **899** via μ-κN^1:κN^6,N^7 coordination to the two Pt centers.[707]



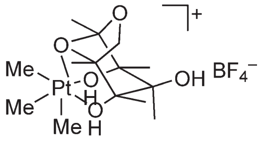
893



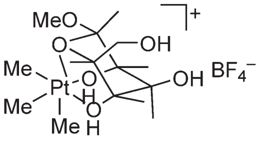
894



895



896



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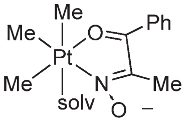
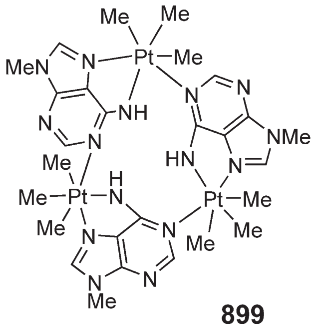
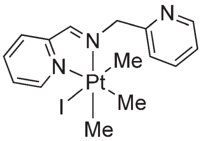


898

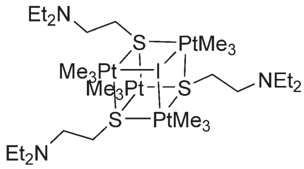


899

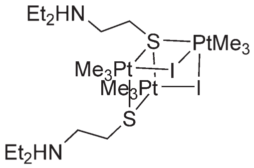
An imine containing two pyridyl groups reacts with $[PtMe_3I]_4$ to form the mononuclear complex with a five-membered chelating ligand **900**.[708] The reaction of 2-aminoethanethiol yields various products, including **901–903**, depending on the reaction conditions.[709] The reaction of a bisthiolatoplatinum(II) complex with $[PtMe_3I]_4$ yields the Pt^{IV}–Pt^{II} dinuclear complex with two bridging thiolato ligands **904**.[710]



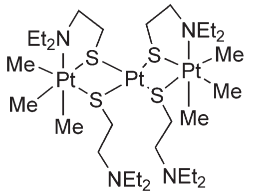
900



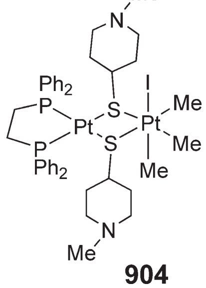
901



902

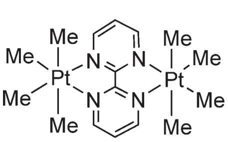


903

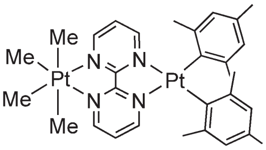


904

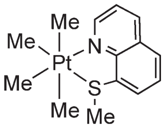
Mononuclear and dinuclear tetramethylplatinum complexes **905–907** have been prepared by using $[PtMe_2(\mu\text{-}SMe_2)]_2$ as the precursor.[711,712]



905

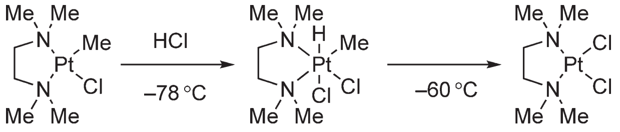


906



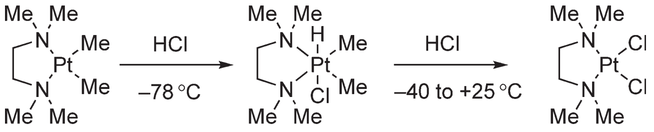
907

Chelating diamine and diimine are the common ligands that stabilize alkylplatinum(IV) species. Hydridoplatinum(IV) complexes have a tendency to decompose in solution at room temperature or below. Protonation of PtClMe(TMEDA) and $PtMe_2$(TMEDA) with HCl at −78 °C forms Pt(IV) complexes with hydride and methyl ligands (**908** and **909**, Equations (166) and (167)).[713] The octahedral complexes have the hydride and chloro ligands at *trans*-positions. The Pt(IV) complexes are converted into the dichloroplatinum(II) complex by warming the solution or further protonolysis with HCl. The complex with a benzyl ligand instead of a methyl ligand is more stable.



908

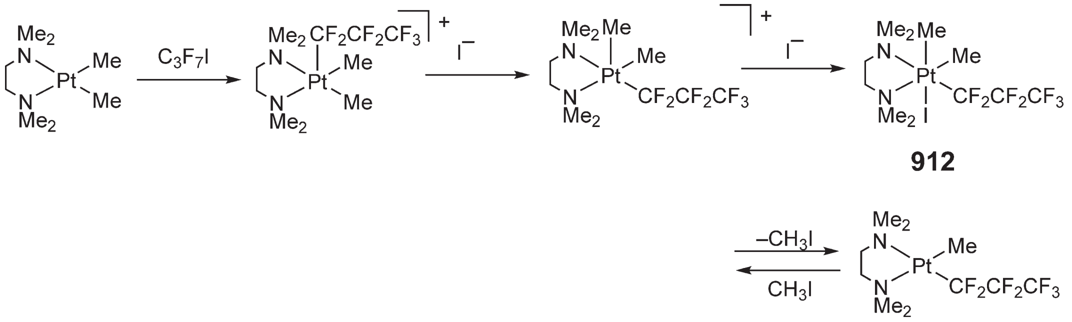
(166)



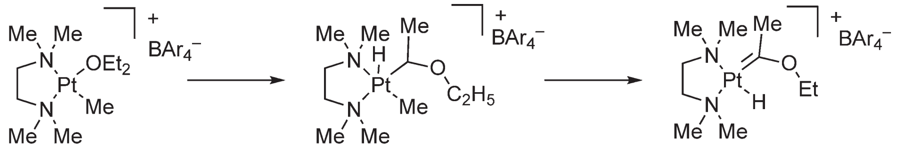
909

(167)

The cationic methylplatinum(II) complex with a $[B(C_6H_3(CF_3)_2\text{-}3,5)_4]^-$ counteranion, and Et_2O and TMEDA as ligands, is converted into the hydrido(carbene)platinum(II) complex **911**, via a Pt(IV) intermediate **910** formed by C–H activation of the Et_2O ligand, and subsequent reductive elimination of methane and transfer of a hydrogen from diethyl ether ligand to Pt(II) (Equation (168)).[714]


912

Scheme 114

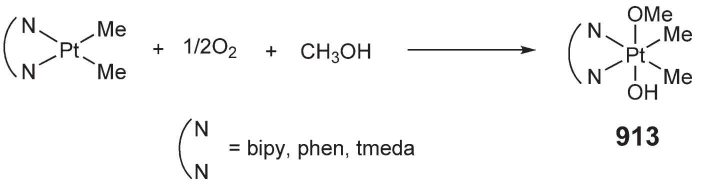

910 **911**

(168)

Ar = $C_6H_3(CF_3)_2$-3,5

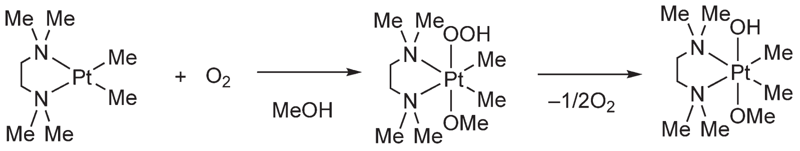
The dimethylplatinum complex with TMEDA as the ligand undergoes oxidative addition of perfluoroalkyl iodide to produce the cationic dimethyl(fluoroalkyl)platinum(IV) complex with iodide counteranion, which is converted to the neutral Pt(IV) complex **912** (Scheme 114). Cationic intermediate Pt(IV) complexes change the coordination geometry during the reaction. Reductive elimination of methyl iodide occurs to form the methyl(fluoroalkyl)platinum(II) complex.[715,716]

Oxidation of the dimethylplatinum(II) complexes of bipy, phen, and TMEDA, by dioxygen in MeOH, produces the dimethyl(methoxido)platinum(IV) complex **913** (Equation (169)).[717]


913

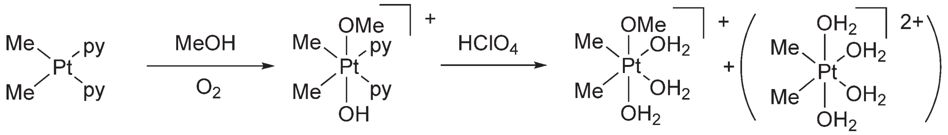
(169)

Oxidation of $PtMe_2$(TMEDA) with O_2 in MeOH produces a platinum(IV) complex with hydroxide and methoxide ligands **915** via an intermediate complex with a hydroperoxo ligand **914** (Equation (170)).[718] The latter complex undergoes slow conversion into the former accompanied by evolution of O_2.


914 **915**

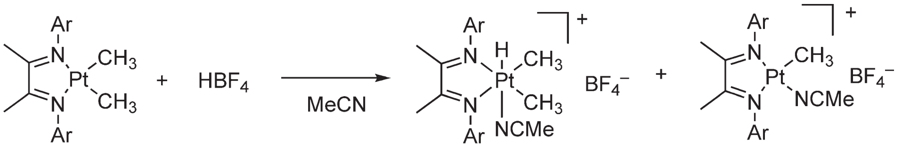
(170)

The complex with supporting aqua ligands **917** has been prepared by oxidation of $PtMe_2(py)_2$ and hydrolysis of the produced Pt(IV) complex with two pyridine ligands **916**, and characterized in solution, although the reaction at higher temperature causes hydrolysis of the Pt–OMe ligand, forming a tetraaqua complex (Equation (171)).[719]


916 **917**

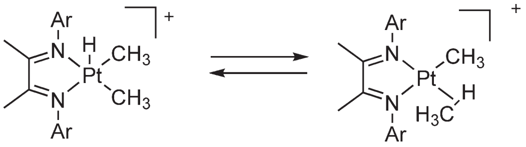
(171)

Protonation of the dimethylplatinum complex having a 1,4-diaza–1,3-butadiene ligand by HBF_4 in MeCN produces a mixture of the cationic hydrido(dimethyl)platinum(IV) **918** and methylplatinum(II) complex **919**, depending on the amount of MeCN used (Equation (172)).[720] The results indicate that protonation occurs at the Pt center rather than the Me ligand. Distribution of the product of the protonation by HOTf is consistent with a mechanism involving an equilibrium between the cationic hydrido(dimethyl)platinum(IV) intermediate and the cationic methylplatinum(II) complex with a coordinated methane molecule (Equation (173)).[721]



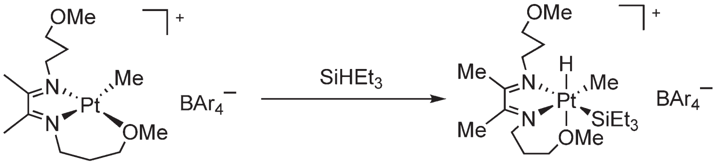
918 **919**

(172)



(173)

The cationic methylplatinum(II) complex with a 1,4-diaza–1,3-butadiene ligand having 3-methoxypropyl pendants reacts with triethylsilane to form a cationic Pt(IV) complex having hydride, methyl, and triethylsilyl ligands (**920**, Equation (174)).[722] The Pt(IV) complex is more stable than the complex without the pendant groups, but does decompose in 20 min at room temperature in solution.

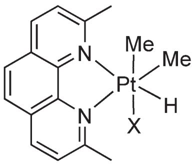


920

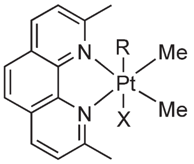
(174)

Ar = 3,5-$(CF_3)_2C_6H_3$

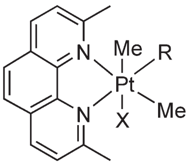
Bipyridine and phenanthroline are employed as auxiliary ligands of the alkylplatinum(IV) complexes, for example, **921–923**, and methyl(iodo)bis(thiolato)–platinum(IV) complexes are obtained as a mixture of the two geometrical isomers **924** and **925**.[723–726] The dimethyl(iodo)phenoxoplatinum(IV) complex **926** has also been prepared.[726] Halogenation of the five-coordinated olefin–platinum(II) complex with a phen ligand affords the Pt(IV) complex with three halides and a halogenoalkyl ligand.[727]



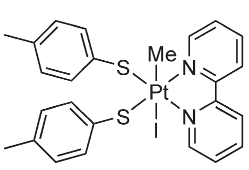
921



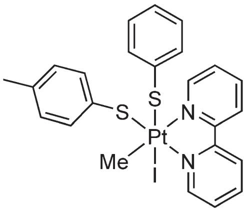
922



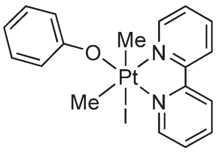
923



924

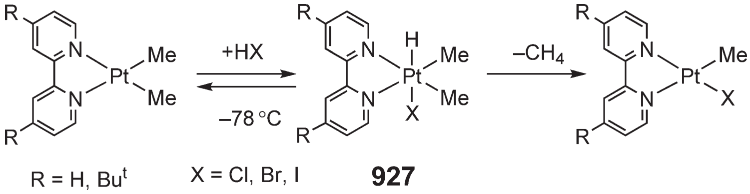


925



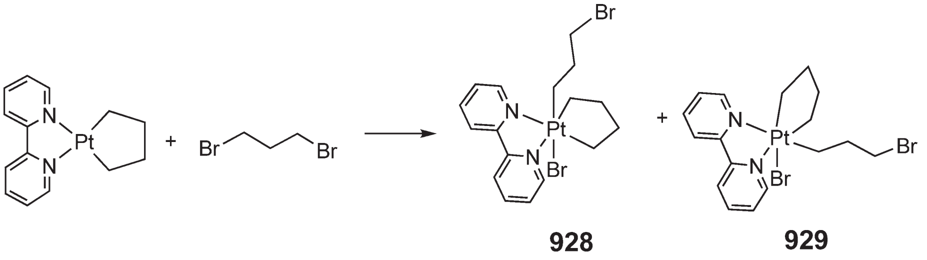
926

$PtMe_2$(bipy) and $PtMe_2$(4,4′-Bu^t_2bipy) react with hydrogen halide to cause oxidative addition to form hydrido(dimethyl)platinum(IV) complexes **927** (Equation (175)).[728] The complexes are stable at −78 °C in solution, and well characterized by NMR spectra. Raising the temperature of the solutions induces reductive elimination of methane to afford Pt(II) complexes with methyl and halo ligands.



(175)

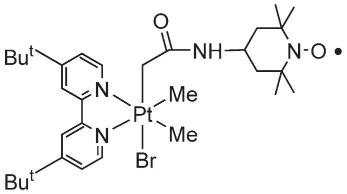
Oxidative addition of 1,3-dibromopropane to platinacyclopentane with a bipy ligand yields a mixture of geometrical isomers of the Pt(IV) complexes with bromo and 3-bromopropyl ligands (**928** and **929**, Equation (176)).[729]



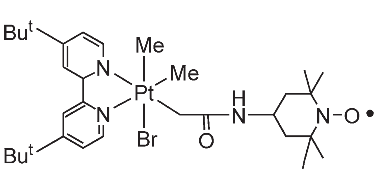
(176)

Oxidative addition of diphenyliodonium salt, Ph_2IOTf, to $PtMe_2$(bipy) produces the Pt(IV) complex with methyl, phenyl, and triflate ligand **930**, and the product reacts with NaI to form a mixture of structural isomers of octahedral Pt(IV) complexes **931** and **932** (Scheme 115). The analogous platinacyclopentane complexes also undergo the oxidative addition to afford Pt(IV) metallacycles with OTf and I ligands **933** and **934**.[730]

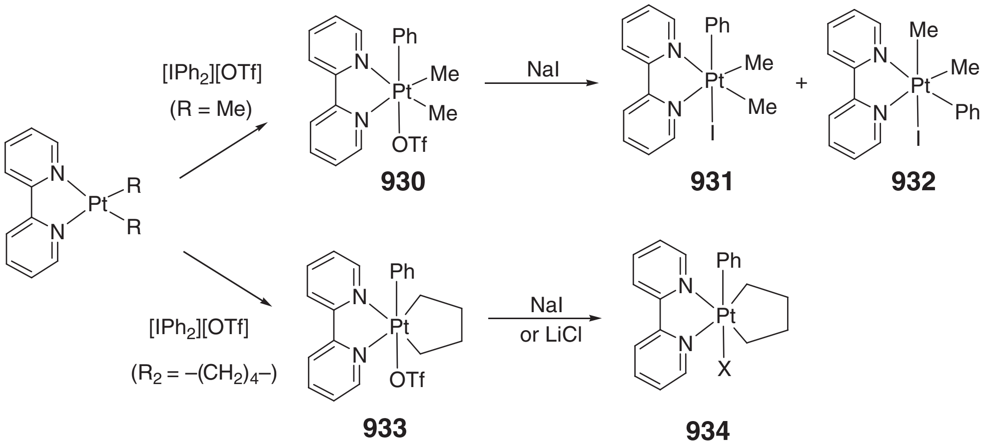
The TEMPO radical has been introduced to the alkyl ligand of a Pt(IV) complex, and characterized by X-ray crystallography and NMR spectroscopy.[731] Two isomeric complexes **935** and **936** have been identified. The ^1H NMR peaks are shifted by 1 ppm compared with related diamagnetic complexes.



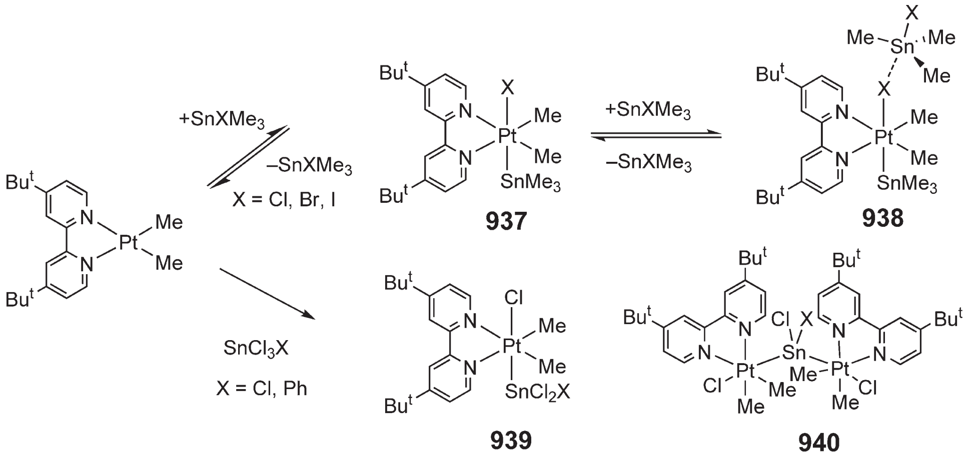
935



936



Scheme 115



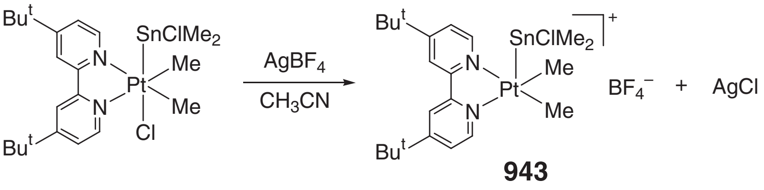
Scheme 116

The reaction of $SnClMe_3$ with $PtMe_2(4,4'\text{-}Bu^t{}_2bipy)$ affords a Pt(IV) complex with an $SnMe_3$ ligand (**937**, Scheme 116), and the produced complex undergoes reductive elimination of $SnClMe_3$ upon heating.[732,733] Further reaction of $SnXMe_3$ results in an adduct of Sn to the X ligand to form a pentacoordinated Sn group **938**. The stepwise reaction takes place reversibly.

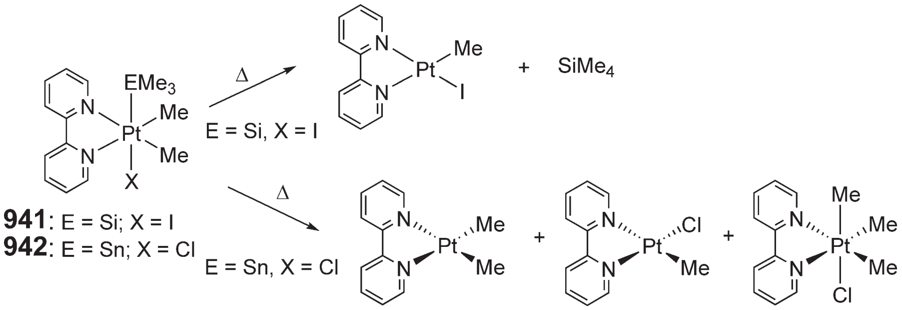
Oxidative addition of $SnCl_4$ and $SnCl_3Ph$ produces mononuclear Pt(IV) complexes **939** and dinuclear complexes with bridging $SnCl_2$ and SnClPh ligands **940**, depending on the reaction conditions.[734]

The dimethyl(trimethylsilyl)iodoplatinum(IV) complex with a bipy ligand **941** undergoes reductive elimination of tetramethylsilane to give a methyl(iodo)platinum(II) complex (Scheme 117).[735] Heating an analogous dimethylplatinum(IV) complex with chloro and $SnMe_3$ ligands **942** leads to several products via reductive elimination reactions of $SnClMe_3$ and of MeCl and via β-elimination of a methyl group from the stannyl ligand.[736] DSC studies of the thermal reactions of a number of related Pt(IV) complexes show the relative stability of the complexes $PtXMe_2(EMe_3)(bipy)$ (X = Cl, Br, I; E = Si, Sn) to be in the order E = Sn > Si and X = I > Br > Cl.

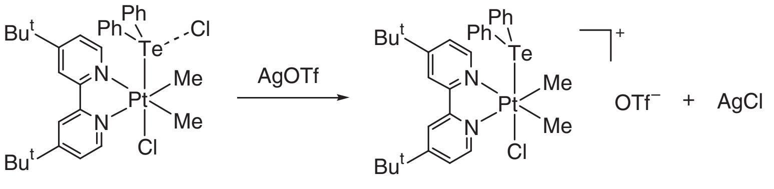
Addition of $AgBF_4$ to Dimethyl(chloro)platinum complex with a chloro(dimethyl)stannyl ligand affords the cationic pentacoordinated Pt(IV) complex formed via abstraction of the chloro ligand **943** (Equation (177)).[737] In the crystal state, there is an intermolecular interaction between the vacant apical coordination site of the Pt center and the Cl of the stannyl ligand. The complex formed by oxidative addition of $TeCl_2Ph_2$ has a $TePh_2$ ligand **944** that is associated with Cl (Ti–Cl 343 pm), and reacts with AgOTf to produce the complex with Cl and $TePh_2$ ligands at *trans*-positions (**945**, Equation (178)).[738]



(177)



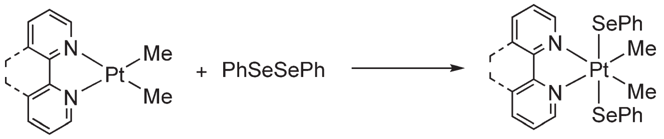
Scheme 117



944 **945**

(178)

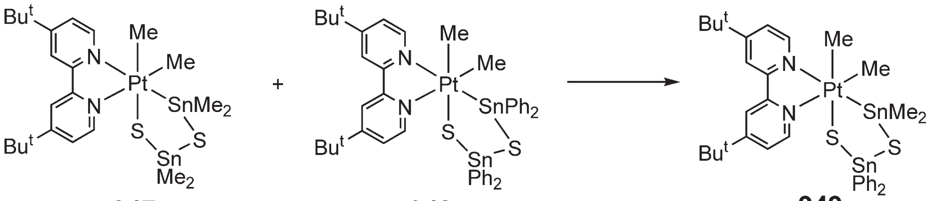
Oxidative addition of Se_2Ph_2 to dimethylplatinum(II) complexes with bipy (or phen) ligand forms the Pt(IV) complex with two SePh ligands at the *trans*-positions (**946**, Equation (179)).[739]



946

(179)

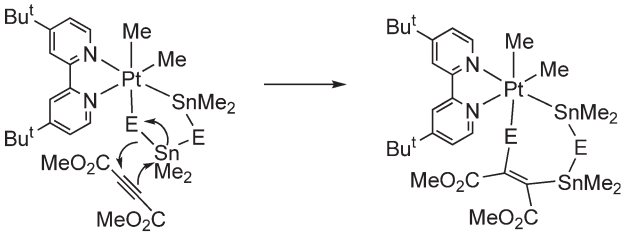
$PtMe_2(4,4'-Bu^t{}_2bipy)$ reacts with $(Me_2SnS)_3$ and $(Ph_2SnS)_3$ to form Pt(IV) complexes with Pt–Sn–S–Sn–S-five-membered metallacyclic structures.[740] The two platinacycles **947** and **948** undergo intermolecular exchange of the $–Me_2S–Sn–$ and $–Ph_2S–Sn–$ fragments to afford the Pt(IV) complex containing $SnMe_2$ and $SnPh_2$ groups (**949**, Equation (180)).[741]



947 **948** **949**

(180)

The Pt(IV) complexes with cyclic $–Pt–SnMe_2—E–SnMe_2—E–$ fragments (E = S, Se, Te) undergo insertion of dimethyl acetylenedicarboxylate into an E–Sn bond to form complexes with a seven-membered ring (**950**, Equation (181)).[742] The Pt–Sn–C═C–Sn metallacycle reacts further with alkyne to produce a vinyl(alkynyl)-platinum complex.

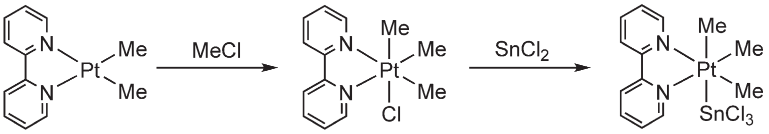


E = S, Se, Te

950

(181)

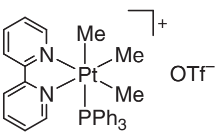
The chloro(trimethyl)platinum(IV) complex with bipy **951** reacts with $SnCl_2$ in CH_2Cl_2 to form the trimethyl-platinum complex with an $SnCl_3$ ligand (**952**, Equation (182)).[743]



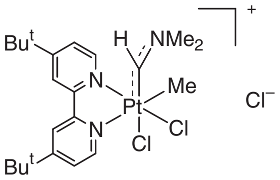
951 **952**

(182)

Exchange of the $SnCl_3$ ligand by PPh_3 forms a cationic complex containing the triflate couteranion, **953**, which may be prepared also from the reaction of methyl triflate with $PtMe_2$(bipy), followed by addition of PPh_3.[744]



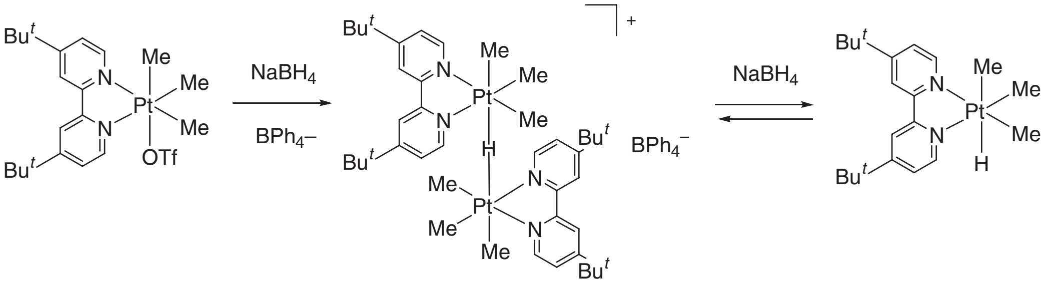
953



954

Complexes with Fischer-type carbene ligands **954** have been fully characterized, and reactions with nucleophiles lead to reductive elimination of an iminium salt.[34]

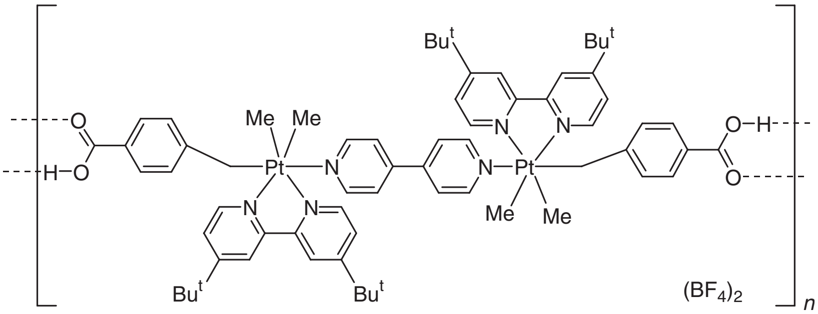
Reaction of $NaBH_4$ with equimolar $PtMe_3(OTf)(4,4'\text{-}\mathrm{Bu^t}_2\mathrm{bipy})$ **955** produces a monocationic dinuclear Pt(IV) complex with a bridging hydrido ligand, and the complex was isolated using BPh_4^- as the counteranion (**956**, Equation (183)).[745,746] Further treatment of the complex with excess $NaBH_4$ gives an equilibrated mixture of the dinuclear complex and a mononuclear Pt(IV) complex with a hydrido and three methyl ligands **957**. The latter complex has been characterized by NMR spectroscopy, although the presence of equilibrium with the dinuclear complex and low stability of it in basic conditions prevented its isolation.



(183)

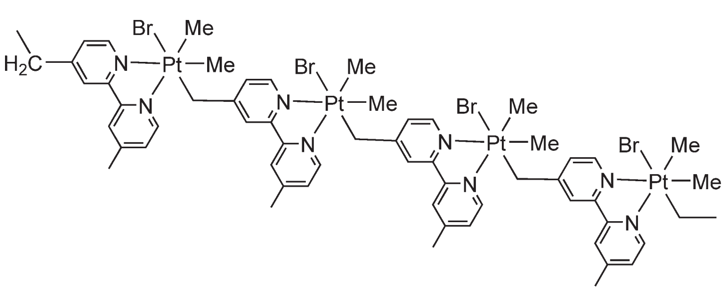
955 **956** **957**

Oxidative addition of functionalized benzyl halides to $PtMe_2(4,4'\text{-}\mathrm{Bu^t}_2\mathrm{bipy})$ affords dinuclear Pt(IV) complexes, which form a molecular assembly, and polynuclear complexes having branched structures. Treatment of bromo(dimethyl)platinum(IV) complex having a 4-carboxylbenzyl ligand with $AgBF_4$ in the presence of 4,4′-bipy leads to the dinuclear complex whose Pt centers are bridged by the bipyridine ligand **958**.[747] X-ray crystallography of the complex indicates a polymeric alignment of the molecules via intermolecular hydrogen bonds between the carboxylic acid groups.

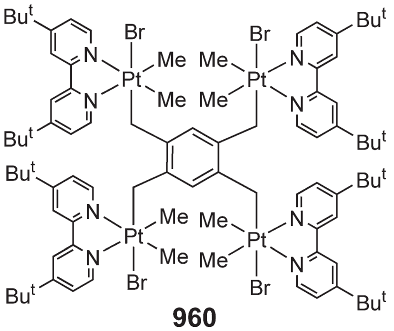


958

Ligand-exchange reactions of $PtMe_2(4,4'\text{-}\mathrm{Bu^t}_2\mathrm{bipy})$ with 4-bromomethyl–4′-methyl–2,2′-bipyridine result in a linear polymer **959** containing Pt(IV) centers, while the reaction with 4,4′-di(bromomethyl)–2,2′-bipyridine forms organoplatinum dendrimers containing Pt(IV) centers.[748]



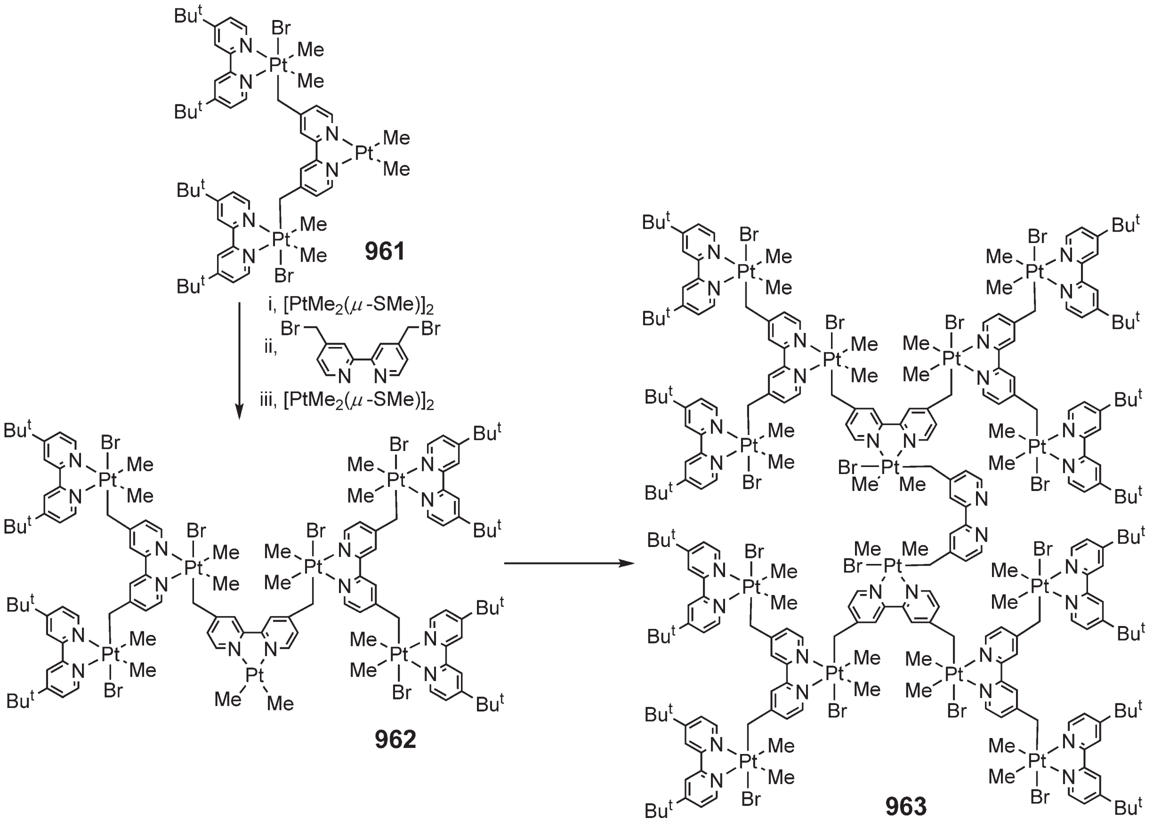
959



960

Growth of the linear oligomer has been monitored by an NMR study of the reaction, involving oxidative addition as the rate-determining step (Scheme 118). The polymer formed is insoluble in solvents. 1,2,4,5-Tetra(bromomethyl)-benzene can be used to generate the Pt(IV) complex **960**, and this reagent can also be employed to generate star-shaped polymers.[748] Thus, the $\mathrm{Pt^{IV}}$–$\mathrm{Pt^{II}}$–$\mathrm{Pt^{IV}}$ trinuclear complex **961**, prepared from the reaction of 4,4′-di(bromomethyl)–2,2′-bipyridine with $\mathrm{PtMe_2(4,4'\text{-}Bu^t{}_2bipy)}$, followed by addition of $\mathrm{[PtMe_2(\mu\text{-}SMe_2)]_2}$,[749] is employed as an $\mathrm{AB_2}$ unit of the dendrimer.[750] Oxidative addition of 4,4′-di(bromomethyl)–2,2′-bipyridine to the Pt(II) complex and introduction of Pt(II) centers leads to the dendrimer with seven Pt centers **962**, which is converted to the 14-Pt dendrimer **963** according to a similar procedure.

Another dendrimer containing Pt(IV) centers has been prepared by a divergent synthetic route, using a bridging bis(2,2′-bipyridine) group **964**.[751] Purification by reprecipitation affords the analytically pure dendrimers in high yields, and related dendrimers containing Pt and Pd are also obtained by a similar procedure.

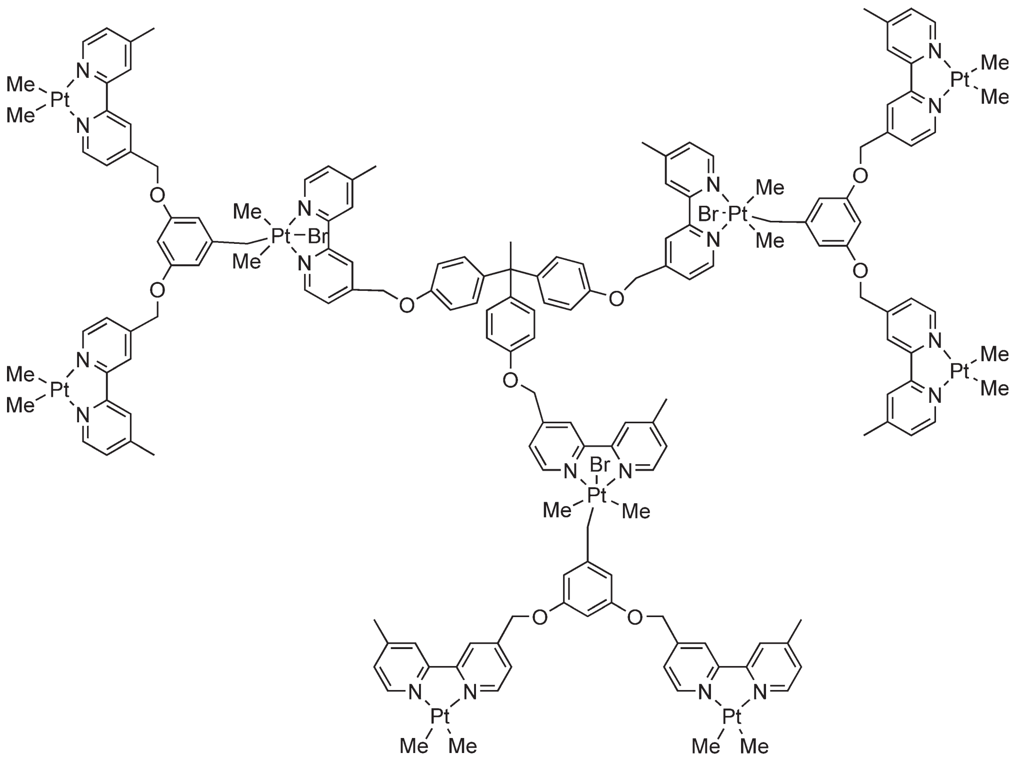


961

962

963

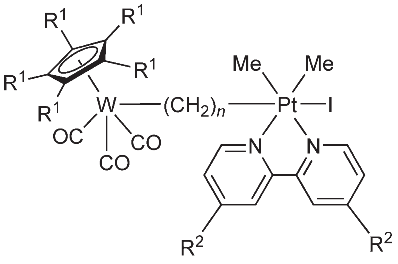
Scheme 118



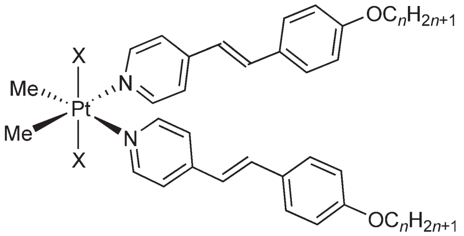
964

A dimethylplatinum(II) complex with an SO_3^- group-equipped dipyridylmethane as a bidentate chelate ligand undergoes protonation to afford the dimethyl(hydrido)platinum(IV) complex **965** accompanied by coordination of the sulfonate group (Scheme 119).[752] Addition of OH^- regenerates the Pt(II) complex. Reaction of the complex with O_2 forms the dimethyl(hydroxide)platinum(IV) complex **966**.

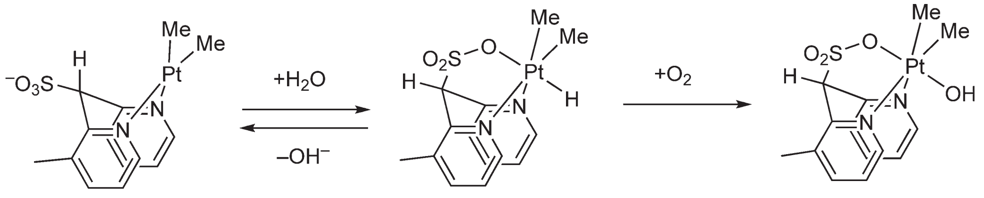
Dinuclear complexes containing W and Pt(IV) centers **967** have been prepared by using a polymethylene bridging ligand.[753] A dimethylplatinum complex with two pyridine ligands containing stilbazole groups **968** has been reported.[754]



967



968

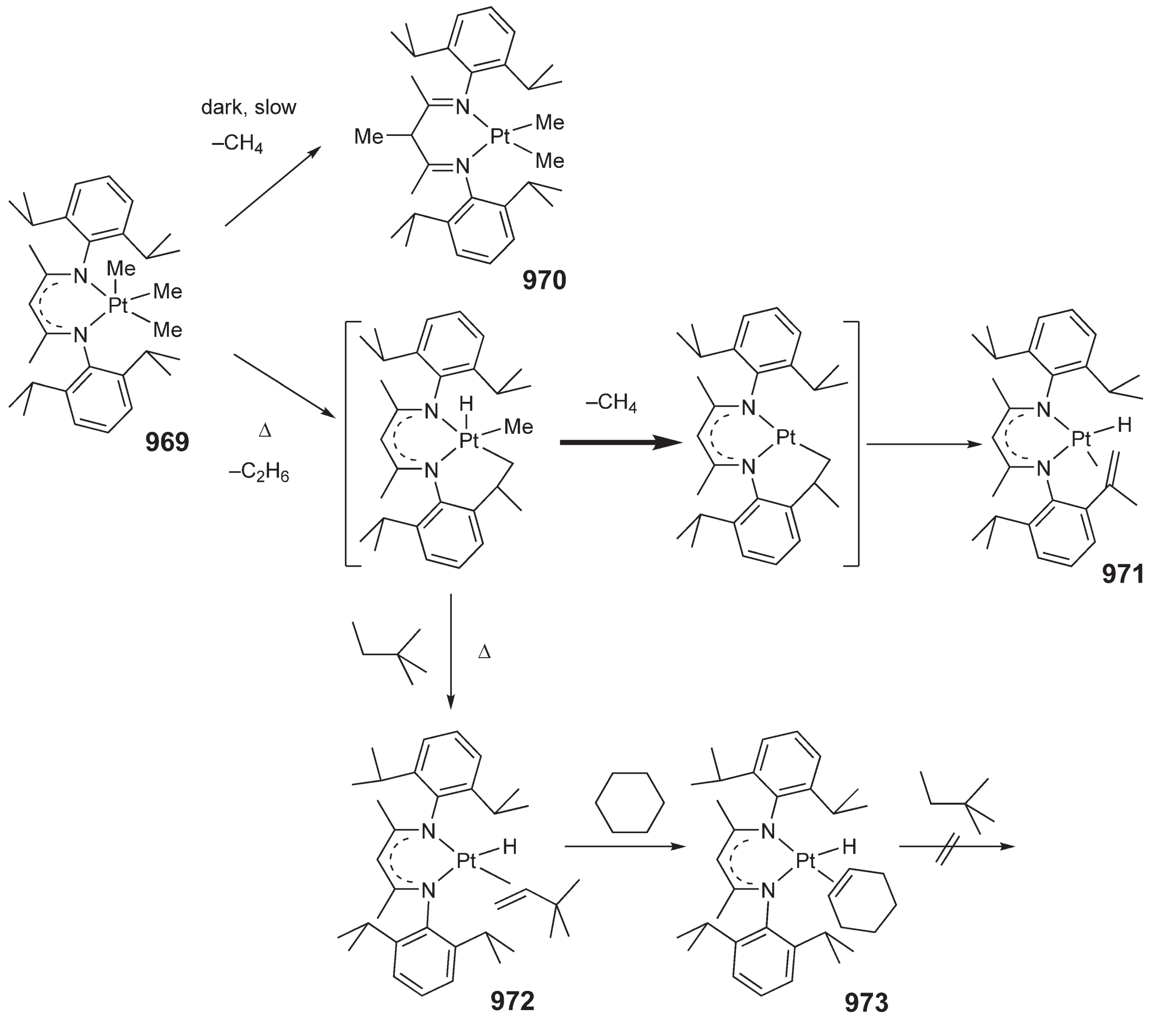


965 **966**

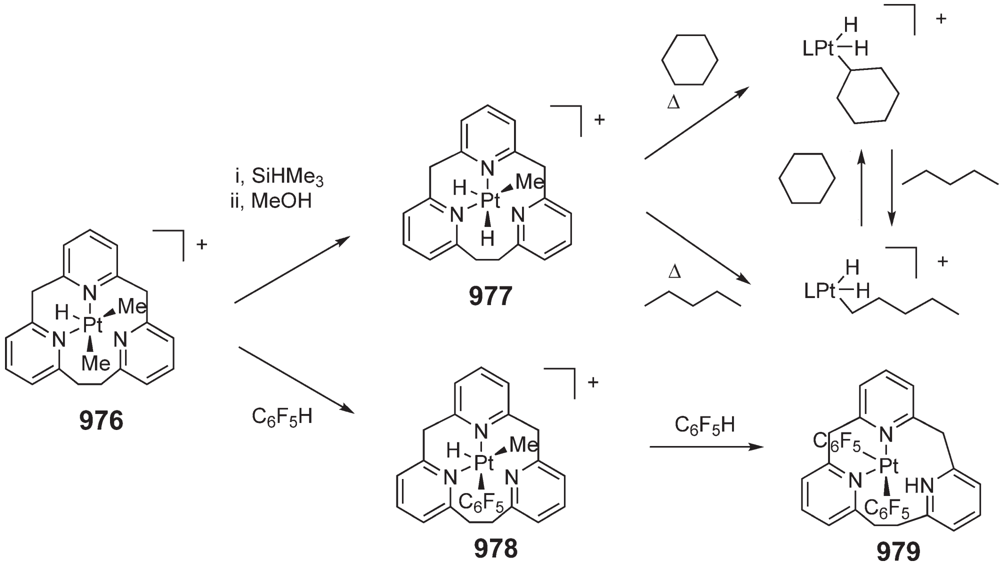
Scheme 119

A pentacoordinated trimethylplatinum(IV) complex **969** has been prepared from the reaction of the potassium salt of the β-diimine having 2,6-isopropylphenyl substituents at N position, with $[Me_3Pt(Tf)]_4$.[755] The square-pyramidal coordination was confirmed by X-ray crystallography. The complex is slowly converted into a dimethylplatinum(II) complex with β-methyl–β-diimine ligand **970**, in the dark, via migration of a methyl ligand at an apical position to the ligand (Scheme 120). Thermolysis of the trimethylplatinum(IV) complex produces a hydridoplatinum(II) complex with a π-coordinated isopropenyl group in the ligand **971**. The reaction proceeds via reductive elimination of ethane from **969**, cyclometallation of the ligand that involves C–H activation of the isopropyl group, reductive elimination of methane from the Pt(IV) center, and β-hydrogen elimination of the cyclometallated ligand.[756] A minor product of thermolysis in hydrocarbon solvents is a hydrido(alkene)platinum(II) complex formed via intermolecular C–H bond activation of the solvent.[757] The complex with neohexene as ligand **972** has been isolated and fully characterized. Exchange of neohexene with cyclohexene is caused by addition of cyclohexane, although the resulting cyclohexene-coordinated complex **973** does not react further with neohexane.

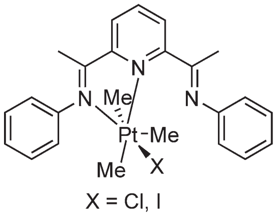
Nitrogen ligands, which tend to coordinate to three meridional coordination sites of five- and six-coordinated transition metal centers, form trimethylplatinum complexes with these ligands as bidentates **974** and **975**.[758,759]



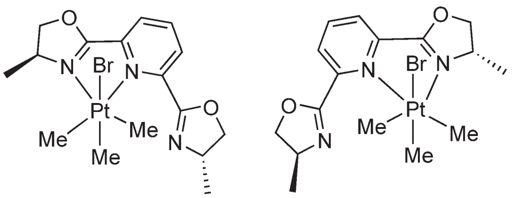
Scheme 120



Scheme 121



974

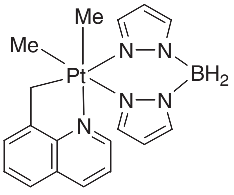


975

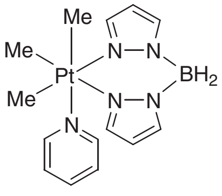
Heating a cationic dihydrido(methyl)platinum(IV) complex of the [2.1.1]-pyridinophane ligand **977**, formed from the reaction of $SiHMe_3$ with **976** in a hydrocarbon solvent, undergoes replacement of the methyl ligand with alkyl and aryl ligands via reductive elimination of methane and C–H bond activation of the solvent (Scheme 121).[157]The resulting dihydrido(cyclohexyl)platinum(IV) and dihydrido(pentyl)platinum(IV) complexes are converted reversibly to each other via C–H bond activation of the solvents. Complex **976** reacts with pentafluorobenzene to produce the cationic hydrido(methyl)perfluorophenyl complex **978** and the neutral diarylplatinum(II) complex with a protonated cyclic ligand **979**.[760]

Tris(pyrazolyl)borates are suitable ligands for organoplatinum(IV) complexes because they stabilize the octahedral complexes by coordination to the three facial coordination sites. The outline of the chemistry of Pd and Pt has been reviewed.[761]

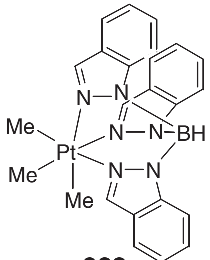
Reaction of 8-(bromomethyl)quinoline with $[PtMe_2(\mu\text{-}SMe_2)]_2$ in the presence of potassium bis(pyrazolyl)borate produces the neutral Pt(IV) complex with a chelating 8-methylquinolinyl ligand **980**.[762] The analogous cationic Pt(IV) complex is obtained by using bipy as the auxiliary ligand. Bis(pyrazolyl)borate forms the trimethylplatinum complex with a pyridine ligand **981**.[763] Tris(indazolyl)borate occupies three coordinating sites of the trimethylplatinum complex **982**.[764]



980

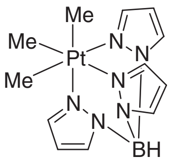


981

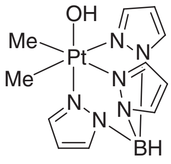


982

Unsubstituted tris(pyrazolyl)borate has been used to stabilize trimethyl, dimethylhydrido, dimethyl(hydroxido), dimethyl(carboxylato), and dimethylthiolato complexes **983–985**.[765–767] The dimethyl(hydrido)platinum(IV) complex **986** was characterized by comparison of the NMR data with the above-related complexes, and theoretical calculations of a tris(iminoamino)borate complex provided reasonable results for the Pt(IV) complex with a hydride ligand **987** rather than a potential Pt(II) hydrogen-bonded species **988**.[768]



983



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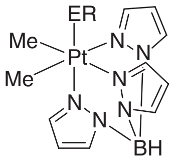
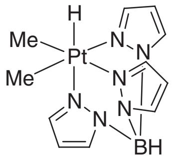
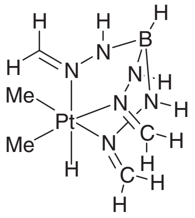


985

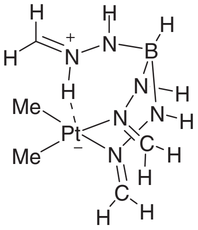
ER = OCOPh, SMe,
SPh, SeMe, SePh



986

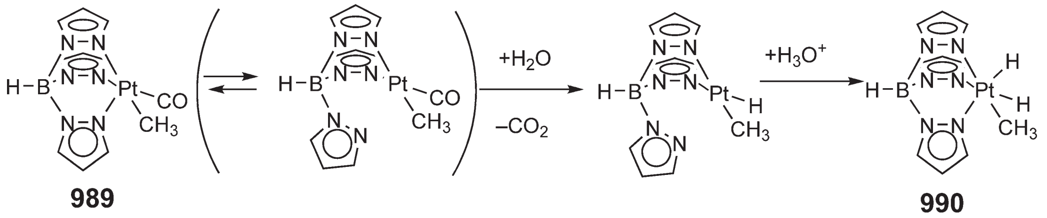


987



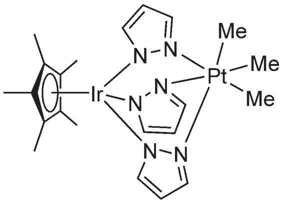
988

A methyl(dihydrido)platinum(IV) complex with the tris(pyrazolyl)borate ligand **990** has been prepared by protonation of the methyl(carbonyl)platinum(II) complex with the chelating tris(pyrazolyl)borate **989** (Equation (184)).[769]



(184)

A Pt-Ir dinuclear complex with trimethylplatinum(IV)- and bridging pyrazolide ligands **991** has been reported.[770]

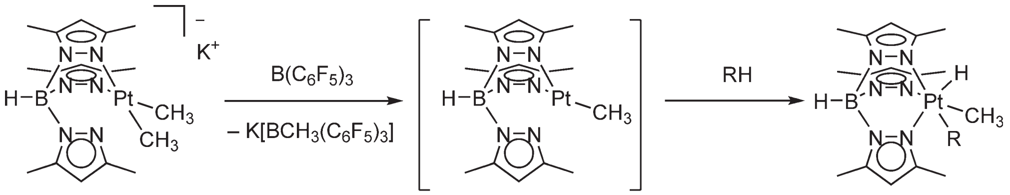


991

The dimethyl(hydrido)platinum(IV) complex with tris(3,5-dimethylpyrazolyl)borate (Tp′) as a ligand **992** can be obtained as a stable complex by protonolysis of the anionic dimethylplatinum(II) complex (Equation (185)).[771] Similar reactions of HCl and MeI with the dimethyl and diphenyl complexes produce trimethyl-, diphenyl(hydrido)-, and diphenyl(methyl)platinum(IV) complexes. Addition of $B(C_6F_5)_3$ to the platinate in hydrocarbon solvents leads to a dialkyl(hydrido)platinum(IV) complex **993**, probably via abstraction of a methyl ligand followed by oxidative addition of the solvent to the Pt(II) center (Equation (186)).[772]

992

(185)



R = Ph, C_5H_{11}, C_6H_{11}

993

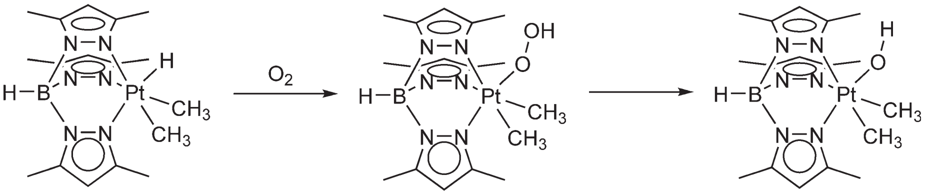
(186)

Complex **992** reacts with oxygen to form the hydroperoxoplatinum(IV) complex **994** (Scheme 122);[773] thermolysis or reduction of the complex with PR_3 forms the complex with an OH ligand **995**.

Reaction of $SiHEt_3$ with **992** produces dihydrido(silyl)platinum(IV) complex **996** via elimination of methane and $SiMeEt_3$ (Scheme 123).[774] The obtained complex reacts further with MeOH to produce the trihydridoplatinum(IV) complex **997**.

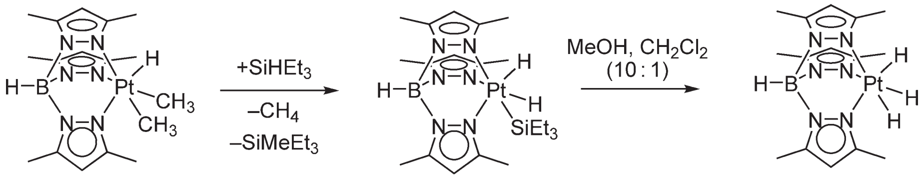
Protonation of the dihydrido(methyl)platinum(IV) complex **998** forms cationic hydridoplatinum(II) complex with the protonated Tp′ ligand **999** (Scheme 124). It is stabilized by addition of ethylene and MeCN to form the complex with these ligands **1000**, while the complex without addition of such ligands tends to form a dinuclear complex with two bridging hydride ligands **1001**.[775] Addition of $SiHEt_3$ to **999** forms the dihydrido(triethylsilyl)platinum(IV) complex **1002**.[776]

Protonation of **992** occurs at a pyrazole group; reductive elimination of methane occurs during this reaction and the square-planar species thus formed can be isolated as a complex with MeCN as a ligand (**1003**, Equation (187)).[777] Deuterium labeling experiments indicate the presence of the intermediate with methane as a ligand.



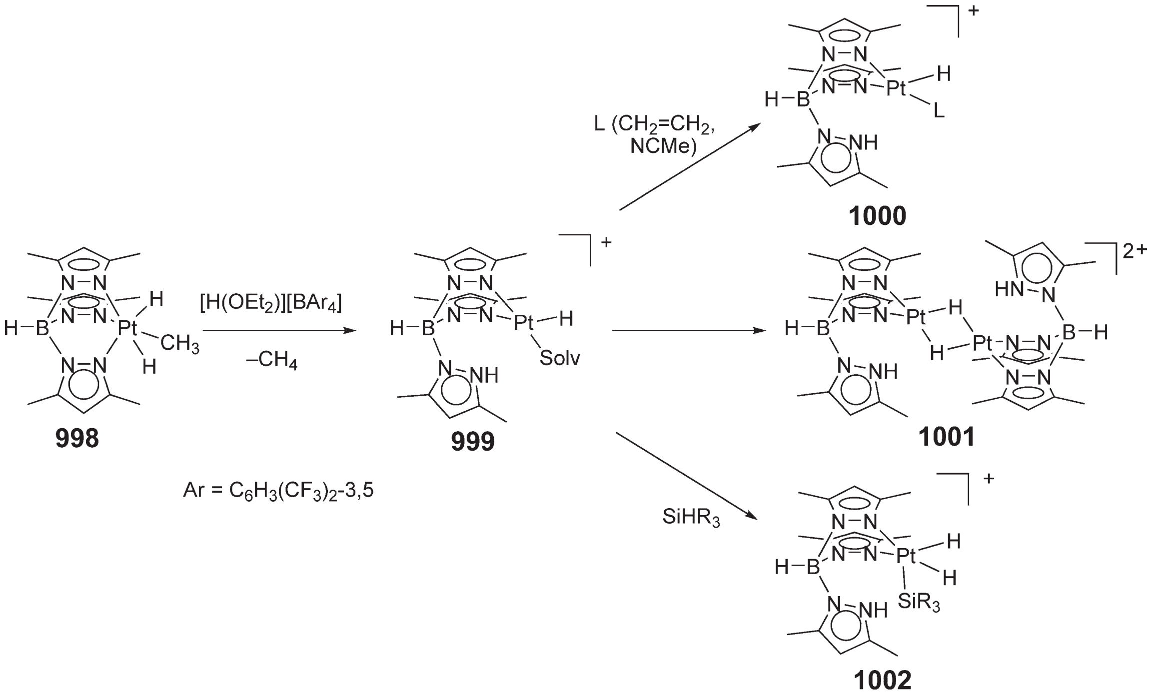
992 **994** **995**

Scheme 122

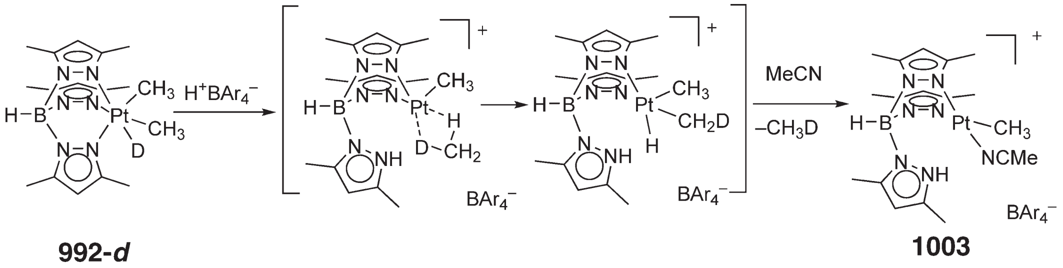


992 **996** **997**

Scheme 123



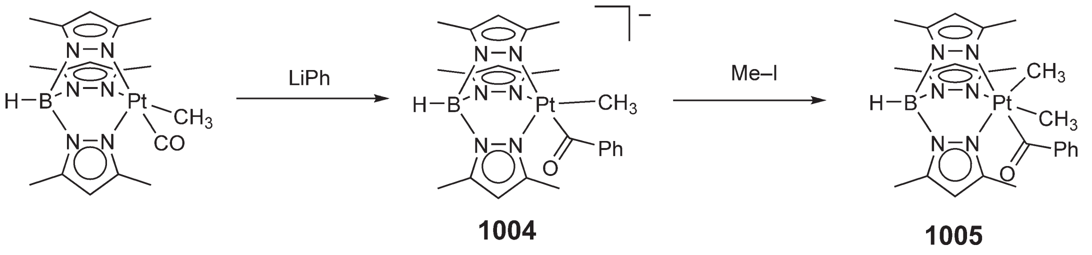
Scheme 124



(187)

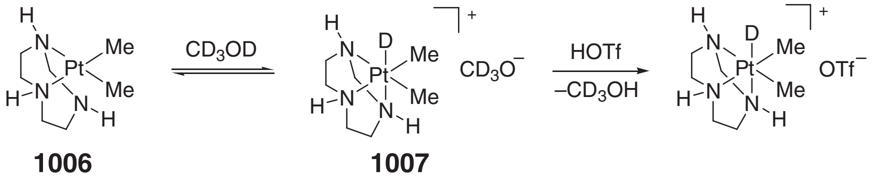
Addition of LiPh to the methyl(carbonyl)platinum(II) complex forms the anionic complex with methyl and benzoyl ligands (**1004**, Scheme 125).[778] The product is methylated upon treatment with MeI to afford the neutral Pt(IV) complex **1005**.

A trimethylplatinum(IV) complex with tris(3,5-bistrifluoromethylpyrazolyl)borate as a ligand has been prepared and studied by H–F two-dimensional NMR spectroscopy; the spectra exhibit long-range C–H–F–C interaction which is evidenced also by IR spectra.[779] 1,4,7-Triazacyclononane coordinates to the Pt(II) center as a bidentate ligand and to the Pt(IV) center as a facial tridentate ligand.[780] Square-planar dimethylplatinum(II) complex **1006** is in equilibrium with the octahedral hydrido (dimethyl)platinum(IV) complex **1007** in MeOH via reversible protonation of the Pt(II)



Scheme 125

complex and elimination of the hydride from Pt(IV) (Equation (188)). The cationic complex is isolated by exchange of the methoxide anion with trifluoromethane sulfonate.

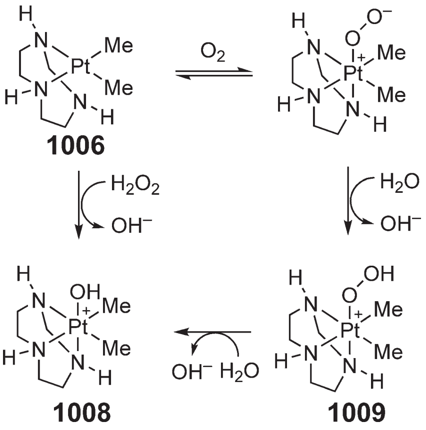


(188)

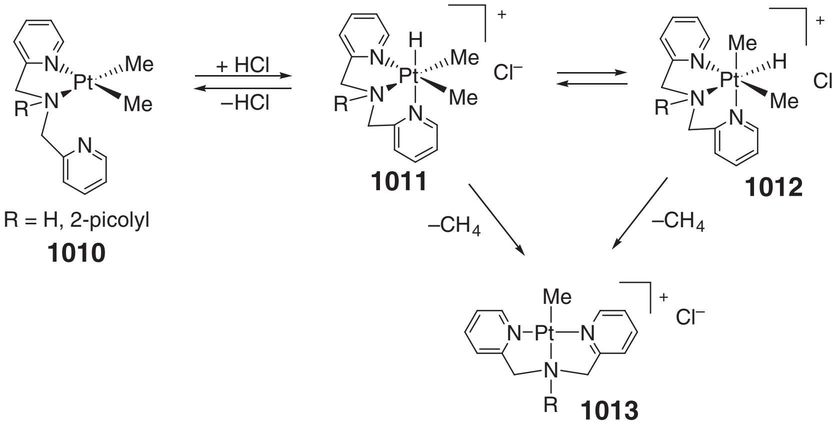
The dimethyl(hydroxo)platinum complex **1008** is obtained from oxidation of **1006** with O_2 followed by hydrolysis of the hydroperoxoplatinum complex **1009** (Scheme 126). Oxidation of **1006** in aqueous media also yields **1008**.

Acyclic tridentate nitrogen donor ligands are able to occupy three facial or meridional coordination sites of Pt complexes.[781,782] Protonation of the dimethylplatinum(II) complex of bidentate bis(2-picolyl)amine **1010** and tridentate tris(2-picolyl)amine by HCl produces the hydrido(dimethyl)platinum(IV) complex with three facial donors as a mixture of geometrical isomers **1011 and 1012** (Scheme 127). Reductive elimination of methane affords the cationic Pt(II) complex with the ligand coordinating to three meridional sites of square-planar complex **1013**.

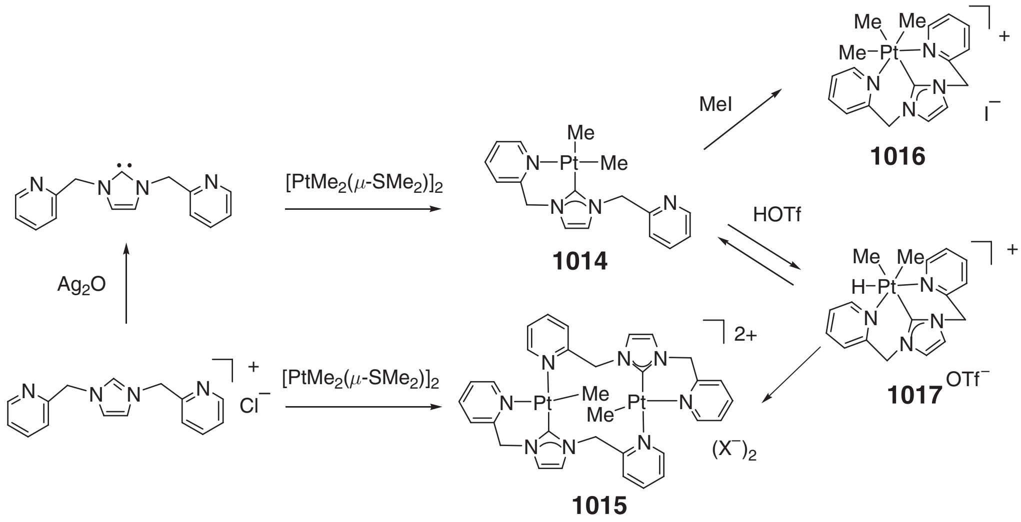
1,3-Di(2-picolyl)imidazoline forms a mononuclear dimethylplatinum complex **1014** with a picolyl carbene ligand, and a dinuclear complex which contains two tridentate ligands **1015** (Scheme 128).[783] Complex **1014** can also be generated from the carbene ligand, and converted to **1016 and 1017** upon treatment with MeI and with HOTf, respectively. The dinuclear complex **1015** is formed also by reductive elimination of methane from **1017** with hydride and methyl ligands.



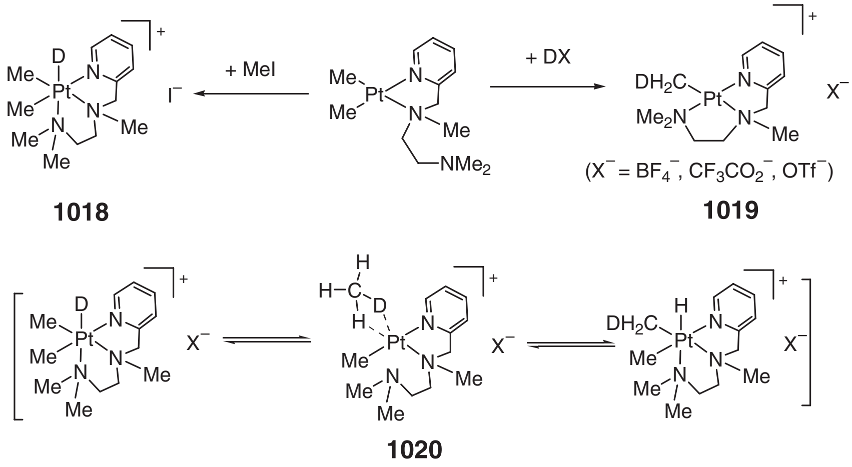
Scheme 126



Scheme 127



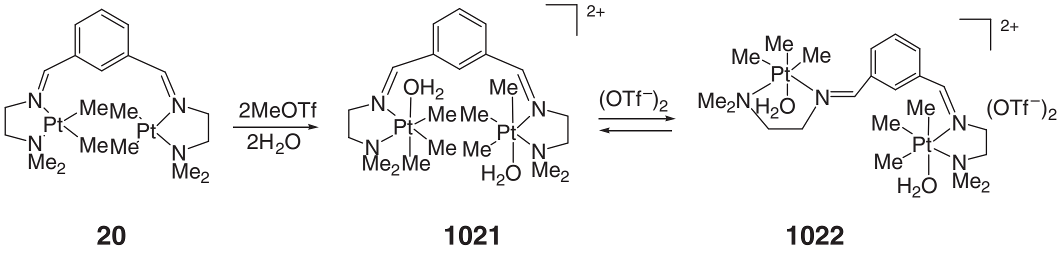
Scheme 128



Scheme 129

The dimethylplatinum(II) complex with a bidentate *N*,*N*,*N*′-trimethyl-*N*′-(2-picolyl)ethylenediamine ligand undergoes methylation by MeI and protonation by several protic acids to produce cationic trimethylplatinum(IV) complex **1018** and methylplatinum(II) complex **1019**, respectively (Scheme 129).[784] The protonation involves an intermediate cationic hydrido(dimethyl)platinum(IV) complex **1020**. Scrambling of hydrogen atoms between hydride and methyl ligands during the reaction indicates an intermediate complex with methane as a ligand.

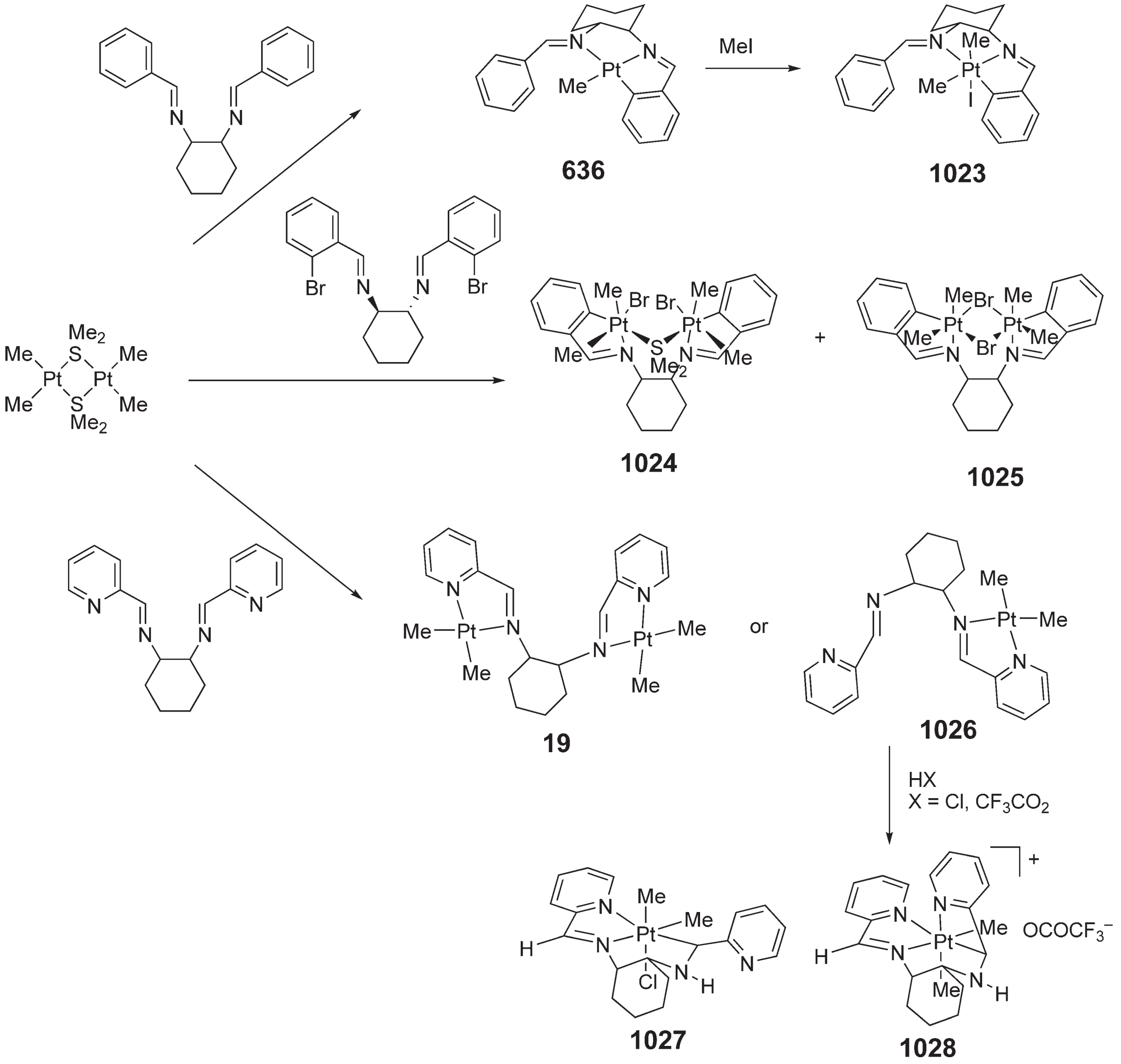
Methylation of complex **20** using MeOTf has afforded dinuclear trimethylplatinum(IV) complexes that exist as an equilibrated mixture of **1021** and **1022** (Equation (189)).[45] The complexes are in equilibrium via rotation of the C–C bonds of the ligand.



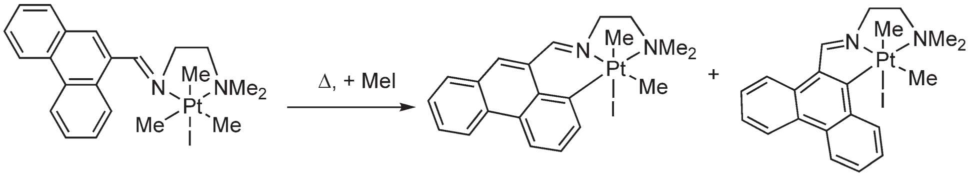
(189)

The diimine prepared from benzaldehyde and *trans*- or *cis*-1,2-cyclohexanediamine reacts with $[PtMe_2(\mu\text{-}SMe_2)]_2$ to produce the methylplatinum(II) complex **636** via cycloplatination of a diimine-coordinated dimethyl complex and loss of CH_4 (Scheme 130).[785] Oxidative addition of alkyl iodide to **636** yields Pt(IV) complexes, for example, **1023**. The reaction of diimines from 2-bromobenzaldehyde and *trans*-cyclohexanediamine produces dinuclear Pt(IV) complexes with a bridging terdentate C_2N_2 ligand **1024** and **1025**, while the *cis* ligand forms a mononuclear Pt(IV) complex.[786] The diimine with 2-pyridyl groups forms dinuclear and mononuclear Pt(II) complex **19** or **1026**, depending on the ratio of the ligand to Pt used in the reaction.[44,787] Complex **19** undergoes oxidative addition of MeI to produce the corresponding dinuclear Pt(IV) complex. Protonation of **1026** occurs at an imine nitrogen of the ligand to afford a neutral complex with a CN_2 terdentate ligand **1027** or cationic complex with a CN_3 tetradentate ligand **1028**.[788–790]

A dimethylplatinum(II) complex having monoimine of ethylenediamine with 9-phenanthraldehyde undergoes oxidative addition of MeI to afford dimethyl(iodo)platinum(IV) complex with terdentate *C*,*N*,*N*-ligand. Complex **1029** with a six-membered cyclometallated imine ring and its isomer with a five-membered ring are obtained as a mixture (Equation (190)).[797]



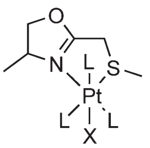
Scheme 130



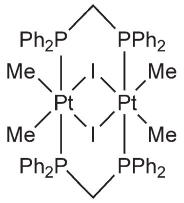
1029

(190)

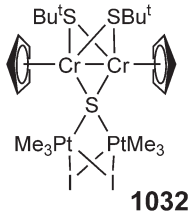
The following scheme summarizes a range of other organoplatinum(IV) complexes **1030–1035**.[791–797]



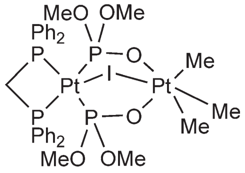
1030



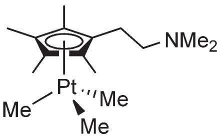
1031



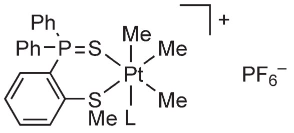
1032



1033



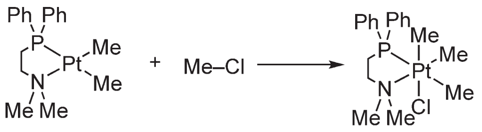
1034



L = PPh_3, py

1035

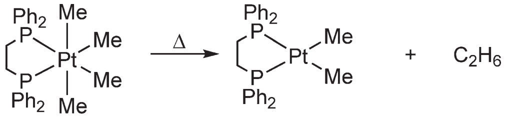
A dimethylplatinum(II) complex with a chelating *N*,*P*-ligand reacts with MeCl to form chloro(trimethyl)platinum(IV) complex **1036** as the oxidative addition product (Equation (191)).[798,799] This contrasts with the fact that $PtMe_2$(dppe) does not undergo oxidative addition of MeCl under the same conditions.



1036

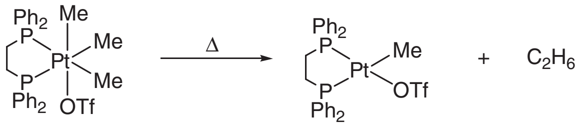
(191)

Alkylplatinum(IV) complexes with phosphine ligands are less stable than those having amine and imine supporting ligands. Chelating diphosphines often enable isolation of complexes although they are unstable at room temperature in solution. Addition of dppe to $PtMe_4(4,4'\text{-}Bu^t{}_2bipy)$ forms the tetramethylplatinum(IV) complex **1037**, and this complex undergoes reductive elimination of ethane in the presence of a methylplatinum(II) triflate complex (Equation (192)).[800] The reaction involves dissociative reductive elimination of ethane from trimethyl(triflate)platinum(IV) complex **1038** and exchange of the triflate and methyl ligands between the Pt(II) and Pt(IV) complexes (Equations (193) and (194)).



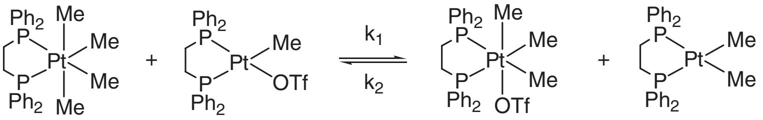
1037

(192)



1038

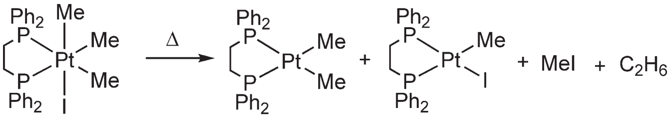
(193)



1037 **1038**

(194)

In contrast, the iodo complex **1039** undergoes reductive elimination of both MeI and ethane (Equation (195)).[801]



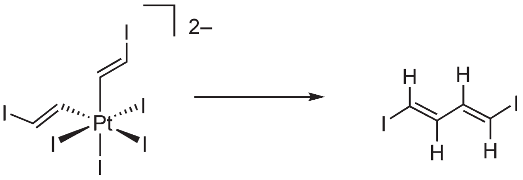
1039

(195)

Elimination of ethane from $PtMe_4(dppe)$ **1037** requires days, even at 165 °C, and is considered to take place predominantly via a five-coordinated intermediate formed by dissociation of one of the phosphine donor atoms, prior to the reductive elimination, rather than direct reductive elimination of ethane (Scheme 131).[802,803]

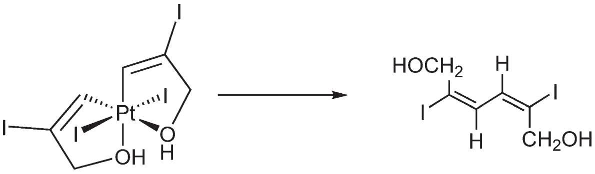
Heating the acetate complex **1040** results in reductive elimination of methyl acetate to form the dimethylplatinum(II) complex or of ethane to form the methyl(acetato)platinum(II) complex, depending on the polarity of solvent.[804] A cationic trimethylplatinum(IV) intermediate is proposed for the former reaction.

Iodoalkynes react with $[PtCl_6]^{2-}$ to form dianionic bis(alkenyl)platinum complexes such as **1041** (Equation (196)).[805–807] Reductive elimination of the two vinyl ligands occurs easily to form dienes, and **1042** decomposes similarly (Equation (197)).



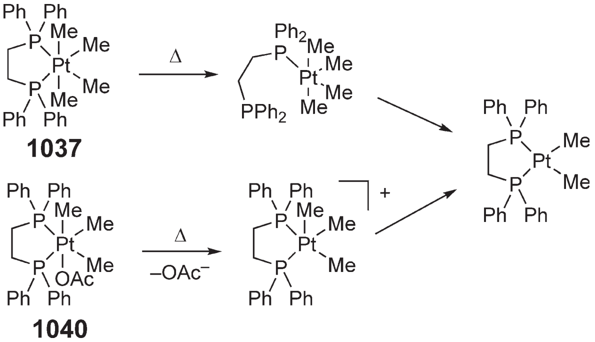
1041

(196)

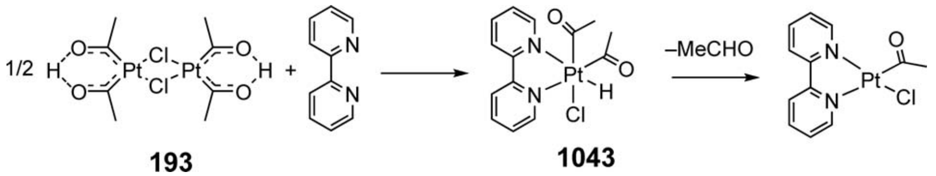


1042

(197)



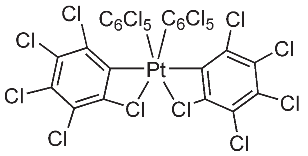
Scheme 131



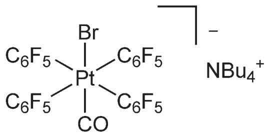
Scheme 132

The dinuclear Pt complex **193** reacts with bipy to afford the bis(acyl)hydrido(chloro)platinum(II) complex, $PtHCl(COR)_2(bipy)$ **1043** which has been fully characterized, and **1043** undergoes reductive elimination of aldehyde to afford a Pt(II) complex (Scheme 132).[808–810]

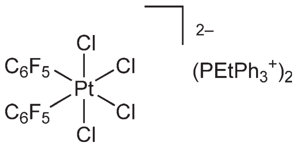
Oxidation of $NBu_4[Pt(C_6Cl_5)_4]$ with Cl_2 in CCl_4 in the presence of $AlCl_3$ produces the homoleptic tetraarylplatinum(IV) complex, $Pt(C_6Cl_5)_4$ **1044**.[811] X-ray crystallography of the complex shows coordination of two *ortho*-chlorine atoms of the aryl ligands, forming octahedral coordination. Oxidative addition of Br_2 to the homoleptic platinate $(NBu_4)_2[Pt(C_6F_5)_4]$, followed by bromo ligand abstraction by $AgClO_4$ in the presence of CO, gives a hexa-coordinated Pt(IV) complex with a CO ligand, $(NBu_4)[PtBr(C_6F_5)_4(CO)]$ **1045**. [812] A dianionic complex with two pentafluoro ligands **1046** has been prepared.[813]



1044

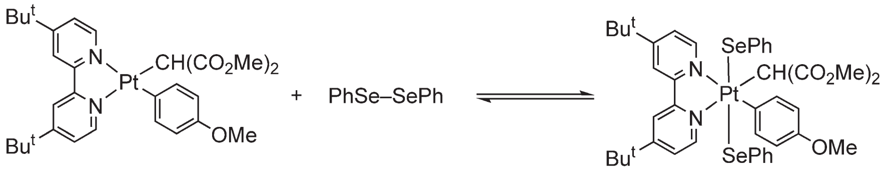


1045



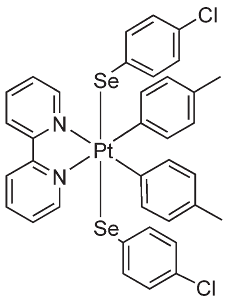
1046

A Pt(II) complex with aryl, alkyl, and 4,4′-Bu^t_2bipy ligands undergoes oxidative addition of diaryl diselenide to form a Pt(IV) complex with two C and two Se donor atoms (**1047**, Equation (198)).[814] The Pt(II) and Pt(IV) complexes are in equilibrium in solution via reversible oxidative addition and reductive elimination of diaryl diselenide.

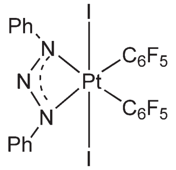


(198)

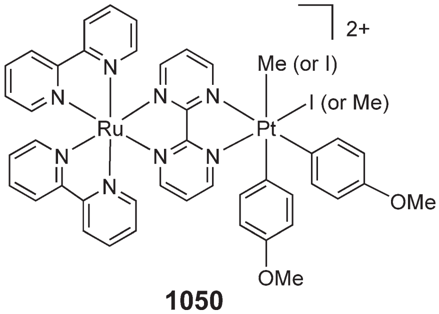
The structure of complex **1048** with two arylselenide ligands at *trans* positions of octahedral Pt(IV) center has been determined by X-ray crystallography.[815] The diiodo(bisperfluorophenyl)platinum(IV) complex with triazenide ligand **1049** is prepared by oxidative addition of iodine to the diarylplatinum complex.[290] Oxidative addition of MeI to a dinuclear Ru(II)–Pt(II) complex with a bridging 2,2′-bipyrimidine ligand forms an Ru(II)–Pt(IV) complex with Me and I ligands at *cis* positions of the Pt(IV) center **1050**.[816]



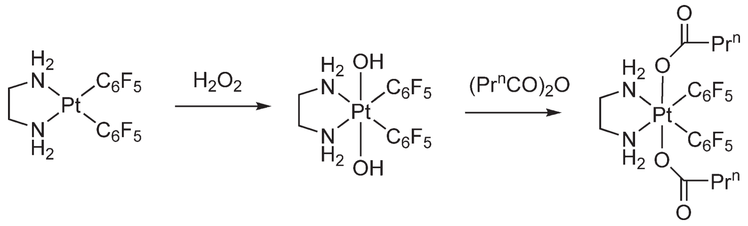
1048



1049



1050

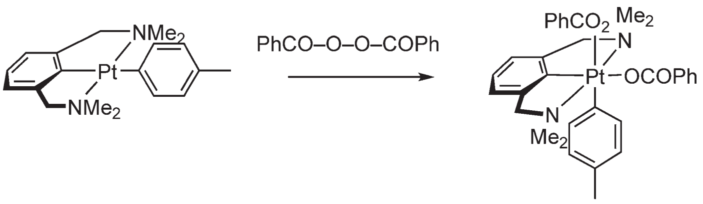


1051 **1052**

Scheme 133

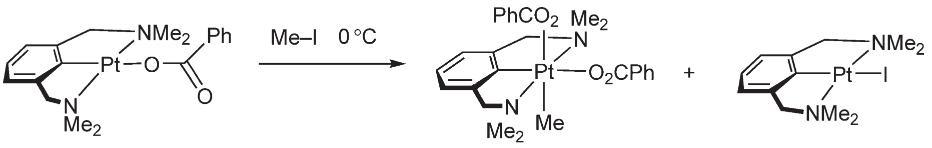
Oxidation of $Pt(C_6F_5)_2(en)$ with H_2O_2 forms the dihydroxo complex **1051** which reacts further with carboxylic anhydrides to produce a complex with two carboxylate ligands at *trans* positions **1052** (Scheme 133).[817]

The tolylplatinum(II) complex with an NCN pincer ligand undergoes oxidative addition of dibenzoyl peroxide to produce a Pt(IV) complex with two benzoate ligands at *cis* positions (**1053**, (Equation (199)).[818] The reaction of MeI with the benzoatoplatinum(II) complex causes oxidative addition and intermolecular exchange of anionic ligands between the Pt(II) and Pt(IV) complexes, leading to a mixture of Pt(IV) complexes with two benzoate ligands and a methyl ligand **1054** and an iodoplatinum(II) complex (Equation (200)). Complex **1054** undergoes reductive elimination of methyl benzoate easily to regenerate the Pt(II) benzoate complex.



1053

(199)

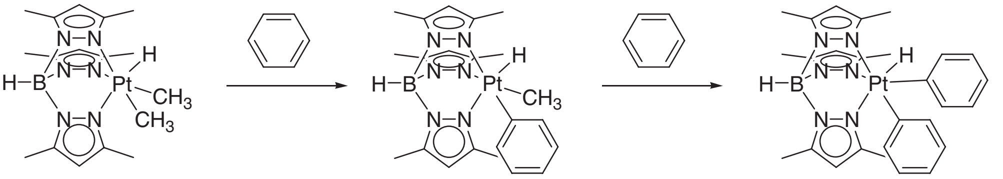


1054

(200)

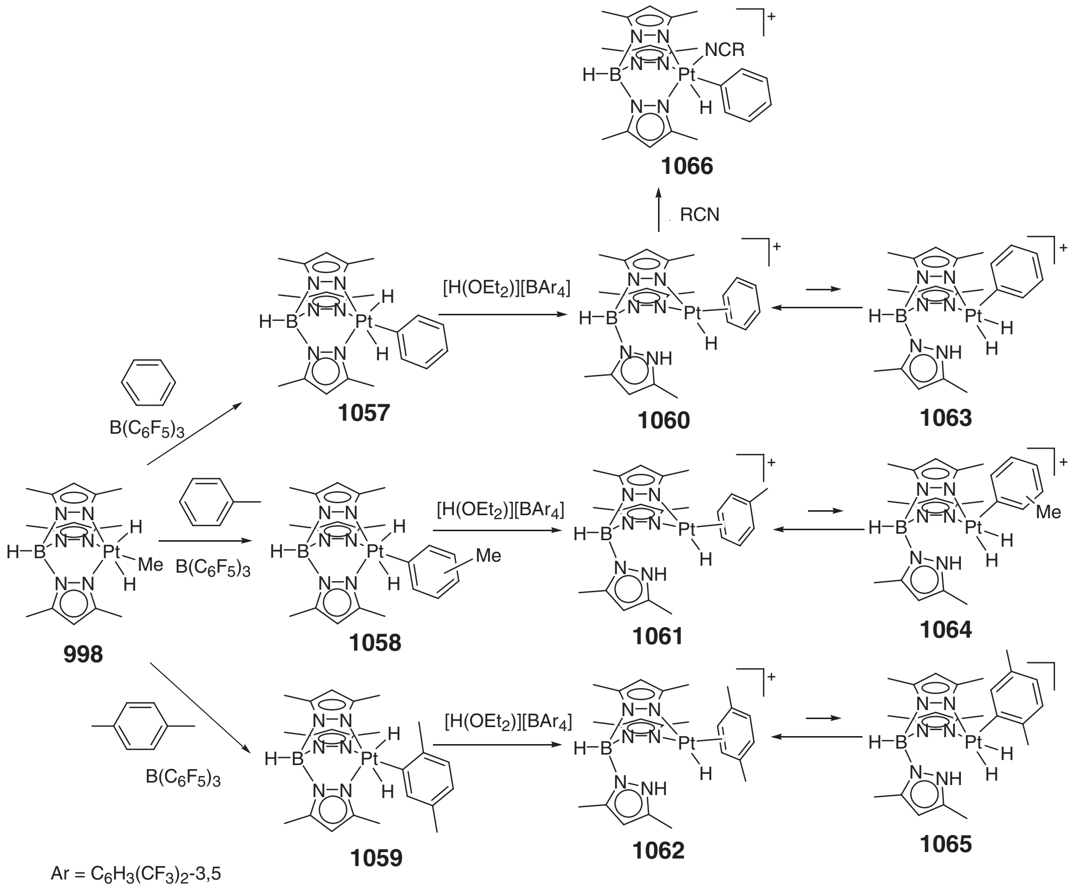
The dihydrido(methyl)platinum(IV) complex with Tp′ as ligand **998** causes aromatic C–H bond activation of benzene, toluene, and *p*-xylene to form the corresponding hexa-coordinated dihydrido(aryl)platinum(IV) complexes (Scheme 134).[820] The reaction in benzene and *p*-xylene forms **1057** and **1059** as the respective product selectively, while toluene yields a mixture of the complexes having a methyl group at 2-, 3-, and 4-positions **1058**. Protonation of the complexes by $[H(OEt_2)_2]^+[B(C_6H_3(CF_3)_2\text{-}3,5)_4]^-$ takes place at a nitrogen of the Tp′ ligand to form hydrido complexes with π-bonded arene ligands and protonated Tp′ ligand **1060–1062**.[821,822] These complexes are equilibrated with cationic dihydrido(aryl)platinum(IV) complexes **1063–1065**, while the Pt(II) complexes are thermodynamically more favored than the Pt(IV) complexes in solution. Complex **1060** (and **1063**) reacts with nitrile to form cationic Pt(IV) complex with hydrido, phenyl, and tridentate Tp′ ligand **1066**, consistent with presence of a five-coordinated intermediate for the reaction.[823]

The hydrido(dimethyl)platinum(IV) complex **992** undergoes stepwise displacement of methyl ligands by phenyl ligands in benzene to form methyl(phenyl)hydrido- and diphenyl(hydrido)platinum(IV) complexes **1055** and **1056** (Equation (201)).[819] The reaction has been proposed to involve intermediates having a methane-coordinated complex and elimination of coordinated methane as the rate-determining step.



992 **1055** **1056**

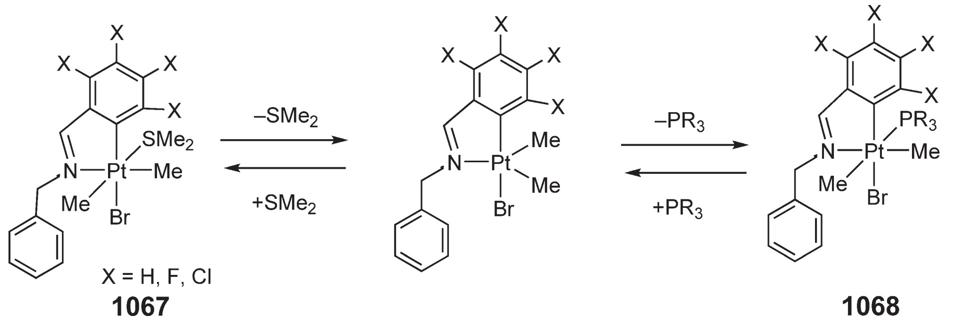
(201)



Ar = $C_6H_3(CF_3)_2$-3,5

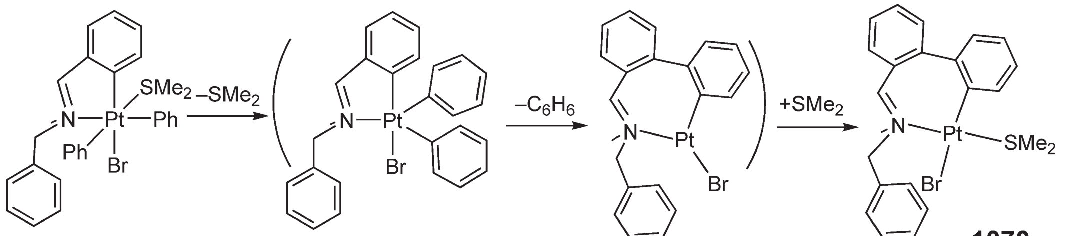
Scheme 134

Dimethyl(bromo)platinum(IV) complexes with *N,C*-chelating aromatic imine and thioether ligands **1067** undergo substitution of the thioether ligand by addition of tertiary phosphines to yield the phosphine-coordinated complexes **1068** (Equation (202)). Kinetic studies of the reaction have revealed a dissociative pathway involving a pentacoordinated intermediate.[824,825] The complexes with fluorinated aromatic imine ligands also proceed via an associative pathway, which has been evidenced by kinetic studies including measurement of the activation volume. [826,827]



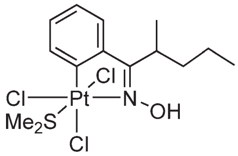
(202)

A bromo(diphenyl)platinum(IV) complex with a similar structure **1069** is converted into a seven-membered metallacycle **1070**, which is induced by elimination of an SMe_2 ligand (Equation (203)).[828] Insertion of a phenyl ligand into the Pt–C bond of the chelating ligand of an intermediate five-coordinated Pt(IV) complex forms a seven-membered chelate ring, and it is involved in the reaction of arylimine with $[PtPh_2(SMe_2)]_2$, giving the Pt(II) complex with a seven-membered chelate ring.[524]

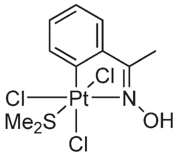


1069 **1070** (203)

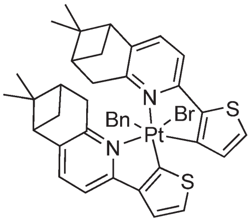
Other cyclometallated Pt(IV) complexes are shown below. *N*,*C*-chelating oximes form trichloroplatinum(IV) complexes **1071** and **1072**.[829,830] Coordination of 2-(2-thienyl)pyridine with optically active substituents forms the Pt(II) complex with helical chirality of the two cyclometallated ligands. Oxidative addition of bromomethylpentafluorobenzene to the complex forms the octahedral Pt(IV) complex **1073**.[831]



1071



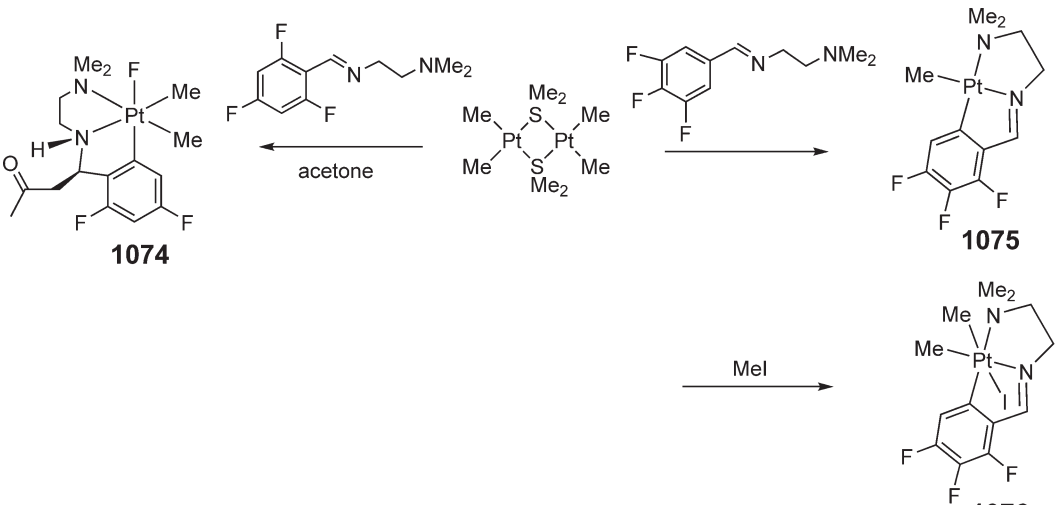
1072



1073

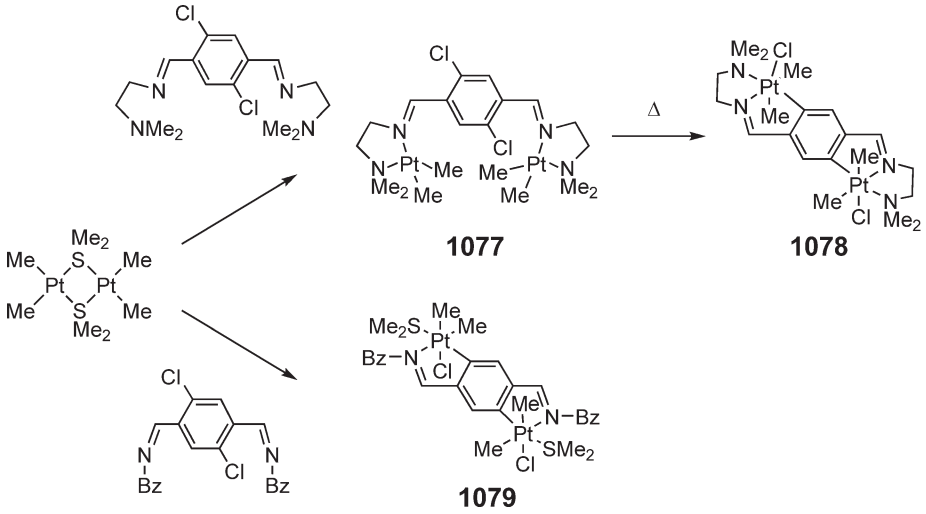
Cyclometallation of the imine of fluorinated benzaldehyde with *N*,*N*-dimethylethylenediamine forms two types of Pt(IV) complex (Scheme 135).[832] The imine with a 2,4,6-trifluorophenyl group reacts with $[PtMe_2(\mu\text{-}SMe_2)]_2$ to afford a Pt(IV) complex with a fluoro ligand **1074**. Activation of a C–F bond at an *ortho* position of the ligand and addition of acetone to the C=N double bond take place during the reaction. The imine with a 3,4,5-trifluorophenyl group undergoes coordination of two nitrogen atoms and cyclometallation involving C–H bond activation, yielding the Pt(II) complex **1075**. Oxidative addition of MeI affords the dimethylplatinum(IV) complex **1076**.

Diimines with 2,5-dichloro-1,4-phenylene groups are able to bridge two Pt(IV) centers. The reaction of bis(*N*,*N*-dimethylethylenediamine)imine forms a dinuclear dimethylplatinum(II) complex **1077**, and **1077** undergoes intramolecular oxidative addition of C–Cl bonds to the Pt(II) centers, giving the Pt(IV) complex **1078** (Scheme 136).[833] The diimine of benzylamine forms dinuclear complexes with Pt(IV) centers bonded to Cl, SMe_2, and two Me ligands **1079**.



1074 **1075** **1076**

Scheme 135

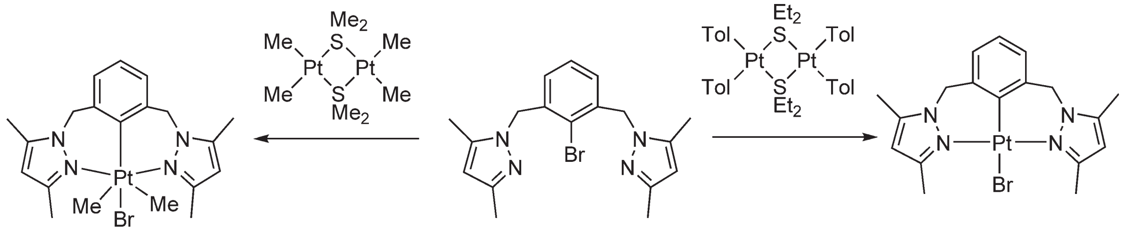


1077

1078

1079

Scheme 136



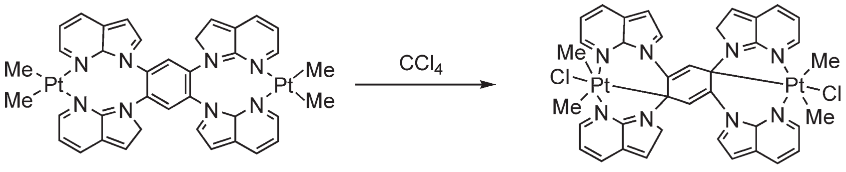
1080

1081

Scheme 137

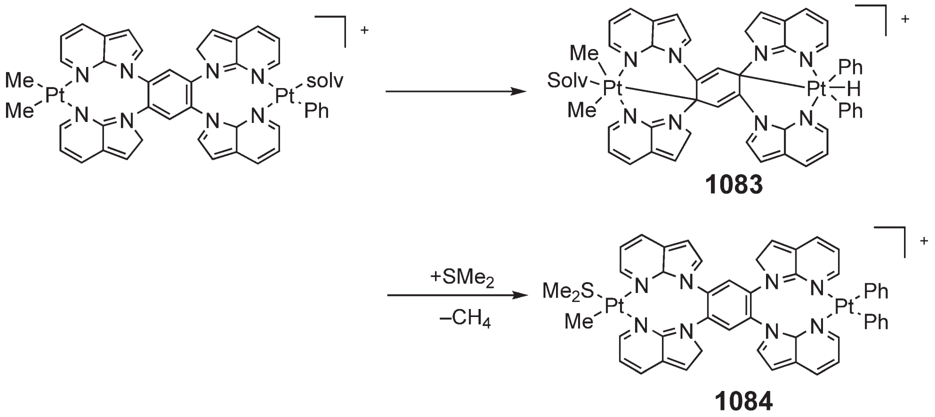
2,6-Bis(3,5-dimethylpyrazolylmethyl)phenyl bromide reacts with $[PtMe_2(\mu\text{-}SMe_2)]_2$ to provide the facially coordinated Pt(IV) complex **1080**, but reaction with $[Pt(4\text{-}Tol)_2(\mu\text{-}SEt_2)]_2$ provides a new pathway for the synthesis of Pt(II) pincer complexes such as **1081** (Scheme 137).[834]

1,2,4,5-tetrakis(1-*N*-7-azaindolyl)benzene is able to bridge two dimethylplatinum(II) fragments by coordination of four pyridine groups. Treatment with CCl_4 causes coordination of chloro ligands to the Pt centers and metallation of carbon atoms of the central aromatic group of the ligand **1082** (Equations (204) and (205)).[835,836] A dinuclear Pt complex containing dimethylplatinum(II) and cationic monophenylplatinum(II) fragments undergoes C–H activation of benzene solvent, and is converted into the cationic Pt(IV) complex **1083**. Reductive elimination of methane forms the cationic dinuclear complex with two phenyl and methyl ligands bonded to two Pt centers **1084**.



1082

(204)

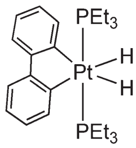


1083

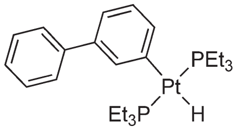
1084

(205)

$Pt(PEt_3)_4$ catalyzes hydrogenolysis of biphenylene in which an intermediate five-membered metallacycle and a biphenylplatinum complex are formed.[837] A dihydido(biphenyl)platinum(IV) intermediate **1085** has been isolated from an independent reaction and fully characterized. Gentle heating of **1085** forms hydridoplatinum(II) complex **1086** which is a stable catalyst precursor in the above hydrogenation reaction. This chemistry is related to Ni complex-promoted reactions, but the stability of organoplatinum complexes renders elucidation of the mechanism possible.



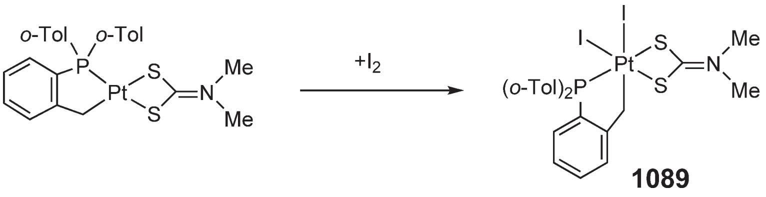
1085



1086

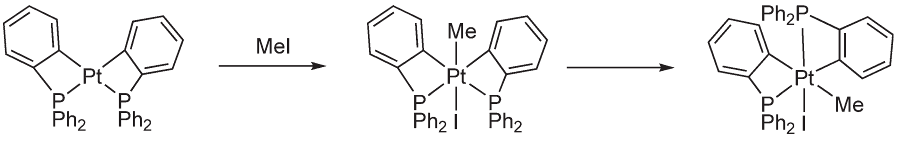
The Pt(II) complex with two cyclometallated PPh_3 ligands undergoes oxidative addition of MeI to produce a stable Pt(IV) complex with an octahedral structure having the Me and I ligands at *trans* positions as the kinetic product **1087** (Scheme 138).[838]

The Pt(IV) complex with a dithiocarbamate ligand and a cyclometallated tris(*ortho*-methylphenyl)phosphine **1089** has been reported (Equation (206)).[839] Complex **1090**, containing a phosphoylide group with a PPh_2 tether, is formed by direct oxidative addition of chlorine to the Pt(II) complex (Equation (207)).[840]



1089

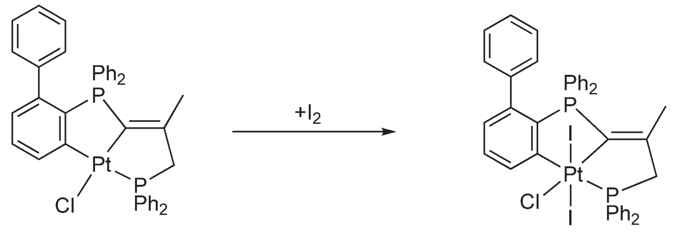
(206)



1087

1088

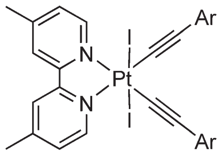
Scheme 138



1090

(207)

Platinum(IV) complexes with alkynyl ligands are rarer than the alkyl and aryl complexes of the metal. A bipy complex with two alkynyl and two iodo ligands **1091** has been obtained, and this complex slowly eliminates $(ArC{\equiv}C)_2$ with formation of $PtI_2(4,4\text{-}Me_2bipy)$.[841]



1091

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8.09

Platinum–Carbon π-Bonded Complexes

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8.09.1 Introduction

This chapter gives an up-to-date report on the development of the area from 1994 to 2005 (in part) with the aim of providing a supplement to the excellent reviews by Hartley in COMC (1982)[1] and Young in COMC (1995).[2] The organization of the chapter follows essentially that used in COMC (1995).

We have used the primary literature as the main source of references; however, since there are several important reviews covering some aspects of the chemistry presented in this chapter, these have been cited appropriately. The catalytic aspects of these types of π-organoplatinum complexes, as well as their application in organic synthesis and several special properties, have not been considered, since these topics will be discussed elsewhere within volumes of this third edition. Since the most important structural details of organometallic platinum-π complexes have been widely presented in COMC (1982) and COMC (1995), and for the sake of saving space yet providing as much information as possible, we have only discussed in detail several selected structural examples which display some special characteristics. In these cases, the interesting structural information has been given in the text.

8.09.2 Alkene and Related Complexes

8.09.2.1 η^2-Monoalkene Complexes (Monodentate)

In this section, complexes with a single C=C bond coordinated to a platinum center will be examined.

8.09.2.1.1 Zerovalent derivatives

In this area, although many complexes continue having phosphines and diphosphines as ancillary ligands, the preparation of derivatives (16-electron structures) with bidentate N,N (or *N*,*N*′) and N,P ligands has been notably developed.

8.09.2.1.1.(i) Preparation

In general, alkene platinum(0) complexes are synthesized by reduction of Pt(II) complexes or by displacement processes starting from Pt(0) precursors.

8.09.2.1.1.(i).(a) Reductive processes

Many complexes of the general formula Pt(η^2-alkene)(diphos) have been prepared by reduction of the corresponding PtCl$_2$(diphos) compounds.[3–7] In complexes with *trans*-stilbene, the reducing agent depends on the diphosphine: Li[BHEt$_3$] (dppe, dppf, (2*S*,3*S*)-(−)-bis(diphenylphosphino)butane ((*S*,*S*)-chiraphos)), NaBH$_4$ (R = Tol–Binap) or Na[BH(OMe)$_3$] [(2*R*,2′*R*,5*R*,5*R*′)-2,2′,5,5′-tetramethyl–1,1′-(*o*-phenylene)diphospholane ((*R*,*R*)-Me-Duphos), (*S*,*S*)-diop].[3] The enantiomeric derivative Pt(*trans*-stilbene){(*S*)-PN} ((*S*)-PN = (4*S*)-2(diphenylphosphinophenyl)–4-isopropyl–1,3-oxazoline), with a chiral diphenylphosphino–oxazoline ligand, was prepared similarly (although as impure material) using Na[BH(OMe)$_3$], showing a moderate enantioselectivity in allylic substitution.[5] NaBH$_4$ has been also shown as an effective reducing agent[4,7] for the synthesis of Pt(η^2-CH$_2$═CHCN)(PCH$_2$CH$_2$CN)$_2$,[7] which is believed to be involved in the Pt(0)-catalyzed P–H addition of PH$_3$ to acrylonitrile.[7] Atwood and Helfer,[8,9] who have studied the aqueous reactions of alkenes with platinum(II, 0) complexes having the TPPTS (P(*m*-C$_6$H$_4$SO$_3$Na)$_3$) ligand, have shown that Pt(TPPTS)$_2$(η^2-C$_2$H$_4$) is formed under basic conditions (pH ≈ 12) starting from [PtCl(TPPTS)$_3$]$^+$ or Pt(TPPTS)$_3$. Another alternative, and simpler, preparation of the versatile homoleptic derivatives Pt(cod)$_2$ and Pt(η^2-nb)$_3$ has been recently reported by reduction of PtCl$_2$(NCPh)$_2$ or PtCl$_2$(cod), in the presence of 2-norbornene (nb) or cod, under mild conditions with the commercially available reducing agent SmI$_2$.[10]

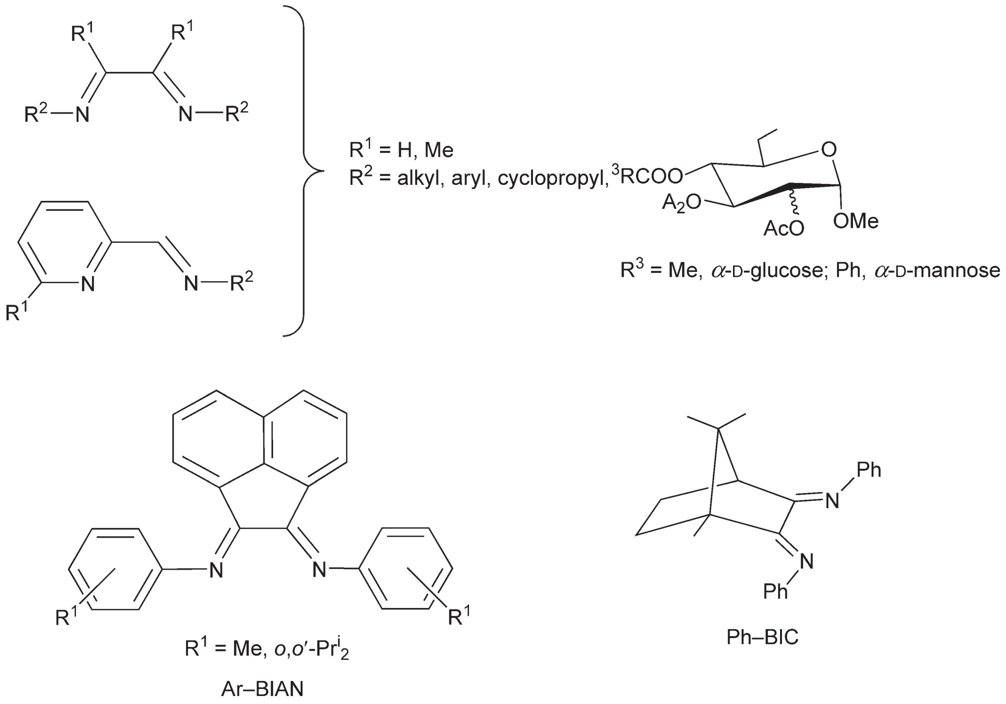
Thermically induced[4] or mild E–H (E = C, N) reductive eliminations[11] have been reported. The complex Pt(dba)(PN)$_2$ (PN = *N*-(2-diphenylphosphino)benzylidene–2-phenylethylamine) is generated quantitatively from the hydride derivative *cis*-[Pt{η^2-OP(Ph$_2$)C$_6$H$_4$C═N(CH$_2$CH$_2$)Ph}H(PN)] and dba.[11] Similar to this latter complex, Pt(η^2-TCNE)L was found to be readily formed from the carbonyl-coordinated hydride complex *trans*-[PtHL]BF$_4$ (L = substituted bis(diphenylphosphinomethoxy)calix[4]-arene) and tetracyanoethylene.[12,13] An interesting reductive elimination of H$_2$ from the diphosphine-hydride bridged complex [Pt(μ-H)(dfepe)]$_2$ in the presence of alkene (C$_2$H$_4$, C$_2$F$_4$) has proved to be a new route to Pt(η^2-alkene)(dfepe) (dfepe = 1,2-bis(dipentafluoroethylphosphino)ethane).[14] However, the analogous reaction of [Pt(μ-H)(dbpp)$_2$]$_2$(BF$_4$)$_2$ and 2,3,3-trimethylbut-1-ene afforded the alkyl derivative [Pt(CH$_2$CHMeBu^t)(dbpp)]BF$_4$, which exhibits a β-C–H agostic interaction (dbpp = 1,3-(di-tert-butylphosphino)propane).[15]

8.09.2.1.1.(i).(b) Preparation from Pt(0) precursors

Ethylene displacement from Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ has continued to be a suitable route to similar complexes with other alkenes. A great variety of alkenes,[16] including propenoate and 2-methylpropenoate esters,[17] displace ethene. Alkene-exchange reactions indicate that the most stable are, as expected, those bearing electron-withdrawing substituents, but steric factors are not negligible.[16,17] The analogous chiral complex containing the *rac*-*cis*-1,2-bis(phenylsufinyl)ethene acting, unusually, as an η^2-ligand has been also prepared similarly.[18] The homologous complexes featuring the highly pyramidalized alkenes tricyclo[3.3.*n*.0^{3,7}]-alk-3(7)enes (n = 1, 2, 3) have been also isolated by this approach,[19] but, in this case, the olefins were generated *in situ* by reducing the corresponding 3,7-diiodo (n = 1) or 3,7-dimesylate (n = 2, 3) tricyclo[3.3.*n*.0^{3,7}]-nonane with sodium amalgam. The tetrathiafulvalene complexes Pt(η^2-L)(PPh$_3$)$_2$ (L = TTF (tetrathiafulvalene), *o*-Me$_2$TTF), which represent the first examples containing these ligands coordinated in a π-fashion, are prepared likewise.[20] Ethene is readily displaced, and the synthesis of new cyclopropene Pt(η^2-cyclopropene)L$_2$ (L = PPh$_3$, ½ dppe) with a variety of bulky substituents on all positions of the cyclopropene employs the same approach.[21] No corresponding complex with 1,2,3-*tert*-butylcyclopropene is formed, probably due to the presence of the bulky *tert*-butyl groups.

The formation of the fumarate complex Pt(η^2-*trans*-Et–fu)(PPh$_3$)$_2$ (Et–fu = diethylfumarate),[22] from Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ and the diazoalkene N$_2$CHCO$_2$Et, has been examined by modern mass spectrometric techniques, suggesting that terminal and bridging carbene species and Pt(N$_2$CHCO$_2$Et$_3$)(PPh$_3$)$_2$ are probably involved in the final formation of the fumarate Pt(0) complex.[23] A range of Pt(η^2-alkene)L^{1}L^2 have been synthesized starting from Pt(η^2-C$_2$H$_4$)$_2$(PR$_3$), with moderately bulky phosphines at low temperature,[24] or by treatment of Pt(η^2-alkene)(PPh$_3$)$_2$ with PCy$_3$, usually as a mixture of regioisomers.[16,17] Complexes of the type Pt(η^2-alkene)(CO)L (L = PPh$_3$, PPh$_2$Bz, PCy$_3$, PBu$^t{}_3$; alkene = CHCN═CHCN, maleic anhydride (ma), maleimide, 1,4-naphtoquinone (nq)) are generated by treating the clusters Pt$_3$(μ-CO)$_3$L$_3$ with an excess of olefin,[25,26] via initial cluster adducts of type Pt$_3$(η^2-alkene)-(μ-CO)$_3$L$_3$ as intermediate species.[25]

The homoleptic derivatives Pt(dba)$_2$, Pt$_2$(dba)$_3$·CHCl$_3$, Pt(η^2-nb)$_3$, or Pt(cod)$_2$ are widely employed to generate zerovalent platinum complexes,[27,28] particularly with chelating (P,P;[29] P,N;[30] P,S;[31] or N,N[32–37]) ligands. Pt(η^2-dba)(P,P) (P,P = dppf or 1,1′-bis(diphenylphosphino)rutenocene (dppr)) were prepared from Pt$_2$(dba)$_3$ and the corresponding metallocenyldiphosphine.[38] The complex Pt(η^2-nb)L$_2$ is formed by reaction of Pt(η^2-nb)$_3$ with 2 equiv. of P(CH$_2$CH$_2$COOEt)$_3$(L), and subsequent reaction with ethylacrylate yields P(η^2-CH$_2$═CHCOOEt)L$_2$. Both complexes are believed to be intermediates in the synthesis of the triester phosphine P(CH$_2$CH$_2$COOEt)$_3$, by addition of PH$_3$ to CH$_2$═CHCOOEt, catalyzed by Pt(0) complexes.[27]



Scheme 1

The family of complexes Pt(η^2-alkene)(N,N′-chelate) has been extensively developed, because they are excellent precursors to several types of 18-electron Pt(II) complexes.[32–37] The synthesis of several 2,9-dimethyl–1,10-phenanthroline (dmphen) derivatives with various alkenes with electron-withdrawing substituents, Pt(η^2-alkene)(dmphen), has been reported by reacting Pt(η^2-nb)$_3$ with dmphen and the appropriate alkene.[39] Novel Pt(η^2-alkene)-(N,N′-diazadiene) derivatives containing various *N*,*N*′-disubstituted 1,4-diaza-1,3-dienes,[33,34] including rigid bidentate ligands (bis(arylimino)acenaphthene (Ar–BIAN), bis(phenylimino)camphane (Ph–BIC)),[35] or based on α-D-glucose[36] or α-D-mannose,[37] and several unsymmetrical pyridine–imine chelating ligands ($R^1 = H$, $R^2 = Bu^t$, 4-MeOC$_6$H$_4$),[31] even hydrophilic ($R^1 = H$, Me; $R^2 = 3\text{-}CO_2HC_6H_4$, 3-CO$_3NaC_6H_4$, 3-SO$_3$Na, 4-SO$_3$Na)[34] (see Scheme 1), have been prepared with the appropriate bidentate ligand (Pt(η^2-nb)$_3$,[33,34,36,37] Pt(cod)$_2$,[33] or Pt(dba)$_2$)[31,35] in the presence of the corresponding alkene. Occasionally, substitution of alkenes has been reported.

8.09.2.1.1.(ii) Structural aspects

Most of the complexes reported and commented on in the previous section have been characterized from the usual spectroscopic techniques, and, in many cases, by X-ray diffraction studies. Only salient features will be commented upon here. The signs of the coupling constants in Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ have been determined by selective hetero double and triple resonance (^{1}H{^{31}P}, ^{13}C{^{1}H}, ^{31}P{^{1}H}) and HETCOR (^{13}C/^{1}H, ^{195}Pt/^{1}H and ^{31}P/^{1}H) experiments.[40] Similar spectroscopic studies of related derivatives Pt(η^2-alkene)(PPh$_3$)$_2$ containing asymmetric olefins, bearing electron-withdrawing substituents at one end and electron-donating ones at the opposite (push–pull), indicate strong differences between $^1J_{\text{P–Pt}}$ and $J_{\text{Pt–C}}$. These findings, and the trend of ^{195}Pt chemical shifts, confirm the role played by backdonation from Pt(0) in the bonding.[41] Solid-state ^{13}C NMR spectra of double ^{13}C labeling of Pt(*trans*-stilbene–α-β-^{13}C$_2$)(PPh$_3$)$_2$ and the alkene precursor indicate that the olefinic chemical tensors of *trans*-stilbene change dramatically upon coordination. The isotropic carbon chemical shift is shifted from 128 to 68 ppm, and the span of the chemical shift tensor decreases dramatically ($\Omega = 51$ ppm), primarily because of changes to δ_{11} and δ_{12}.[42] Similar solid-state ^{13}C and deuterium NMR studies have also been carried out with isotopically marked Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$, demonstrating that the ethylene ligand is not subject to significant motion.[43]

Kinetic investigations of exchange reactions between Pt(η^2-ol$_1$)(L^{1}L^2) and ol$_2$ (ol$_1$ = dimethylfumarate (Me–fu), nq; L^{1}L^2 = pyridyl methanamine (N^1,N^{2}R^2, $R^2 = Bu^t$, 4-(OMe)C$_6$H$_4$), pyridyl thioether (N-SR; $R = Bu^t$, Ph); ol$_2$ = ma, fumaronitrile (fn), nq, and tetramethylethylenetetracarboxylate (tmetc)) suggest an associative reaction mechanism, and the ensuing reactivity order for electron-poor olefins: ma > fn ≈ nq >> tmetc. The crystal structures of the pyridyl–methanamine derivatives Pt(η^2-ol)(*N*,*N*′-Bu^t) (ol = fn, ma, Me–fu) reveal that the complex with dimethyl fumarate shows the longest Pt–C(olefin) bonds, supporting the experimental observation that the most labile olefin is Me–fu.[31]

Complexes of type Pt(η^2-alkene)(N,N′) (N,N′ = asymmetric ligands (Ar–BIAN, Ph–BIC); alkene = fn, ma, TCNE) are formed as mixture of isomers, and some of the complexes are fluxional in solution as a result of rotation of the olefin around the Pt–alkene bond.[35] Mixtures of diastereomers, differing in their binding of enantiofaces of the prochiral *trans*-stilbene olefin, are observed by NMR and X-ray studies of [Pt(*trans*-stilbene)(diphos)] complexes containing chiral diphosphines (*S*,*S*-chiraphos, (*R*)-(+)-bis-(ditolylphosphino)–1,1′-binaphthalene ((*R*)-Tol–Binap), *R*,*R*-Me-Duphos and *S*,*S*-diop).[3] Complexes with carbohydrate *N*,*N*-chelate ligands based on α-D-mannose or α-D-glucose induce enantioselectivity in the coordination of prochiral olefins.[36,37] The structure of the complex of N,N-diazadiene based on α-D-glucose indicates that the ligand creates a chiral pocket, which is also retained in solution.[36] The X-ray structures of the (PPh$_3$)$_2$Pt complexes with the strained tricyclo[3.3.*n*.0^{3,7}]-alk-3(7)-enes (*n* = 1, 2, 3) show that the degree of pyramidalization at the carbons bonded to Pt increases from *n* = 3 (48.3°) to *n* = 1 (62.3°). This pyramidalization has a marked effect on the chemical shifts and coupling constants observed in the NMR spectra, and shows that the π-retrodonation in the complexes increases as the pyramidalization increases.[19]

8.09.2.1.1.(iii) Reactions

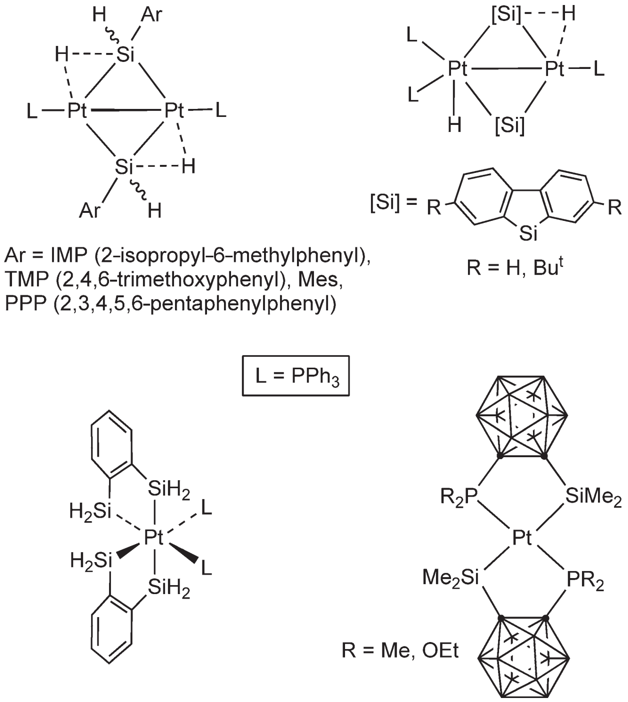
Several aspects of the reactivity of these complexes will appear in other sections, because they are common precursors to other π-organoplatinum species (for instance, formation of pentacoordinate Pt(II) derivatives). They are also precursors, in particular, Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$, for the formation of many bi- or polymetallic derivatives containing Pt–M bonds. In this section, we will remark upon other types of reactivity centered on the coordinated ligand or on the metal center.

8.09.2.1.1.(iii).(a) Protonation and related electrophilic reactions

Some interesting results have been obtained by protonation of complexes Pt(η^2-CH$_2$=CHBu^t)(P,P) (P,P = 1,2-bis(ditert-butylphosphino)ethane (dbpe), dbpp, or Bu$^t_2$PCH$_2$C$_6$H$_4$CH$_2$PBu^t (dppx)) with HBF$_4$·OMe$_2$, affording both the hydride–olefin [PtH(CH$_2$=CHBu^t)(dbpe)]BF$_4$, or the β-C–H agostic alkyl derivatives [Pt(C$_6$H$_{13}$)(P,P)]BF$_4$ (P,P = dppp, dppx), depending on the bite angle and bulkiness of the diphosphine ligand.[15] These complexes are fluxional, and two alternative processes involving a 14-electron species (for all derivatives) or a pentacoordinated transition state (for the alkyl derivatives) have been proposed.[15] Different types of products result from reactions of Pt(η^2-alkene)(N^1,N^2) with HX (X = Cl, BF$_4$), depending on the nature of the N^1,N^2 ligand and the X group, but a general mechanism involving a reversible protonation of the platinum center is suggested.[32] Similar studies of a series of *bis*(triphenylphosphine)(cyclopropene)platinum(0) complexes with HCl or DCl yielding cyclopropane or propene-type molecules have also been suggested to be formed by insertion into transient Pt–H bonds.[44] A remarkable methine proton transfer from 2-pyridylbis(diphenyl)phosphinomethane (NPP) on reaction with Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ to form the hydride complex PtH(NPP–H)(PPh$_3$) has been recently observed.[45] η^2-Enol and enone complexes of platinum(0) react with electrophilic substrates with a variety of interesting results. Thus, η^3-1-hydroxyallyl or η^3-methoxyallyl, [Pt(η^3-CH$_3$OCHCHCH$_2$)L$_2$]Tf, complexes are formed by treatment of Pt(η^2-CH$_2$=CHCRO)L$_2$ (R = H, Me; L$_2$ = 2PPh$_3$, dppf) with CF$_3$SO$_3$H[46] or CF$_3$SO$_3$Me,[47] respectively (Tf = triflate). However, similar reactions with Lewis acid compounds, such as BX$_3$ (X = F, C$_6$F$_5$) or AlMe$_3$, afford simple η^2-vinylketone platinum(0) adducts, formed by the greater preference for coordination of BX$_3$ or AlMe$_3$ to the oxygen atom of the carbonyl group.[48]

8.09.2.1.1.(iii).(b) Oxidative additions

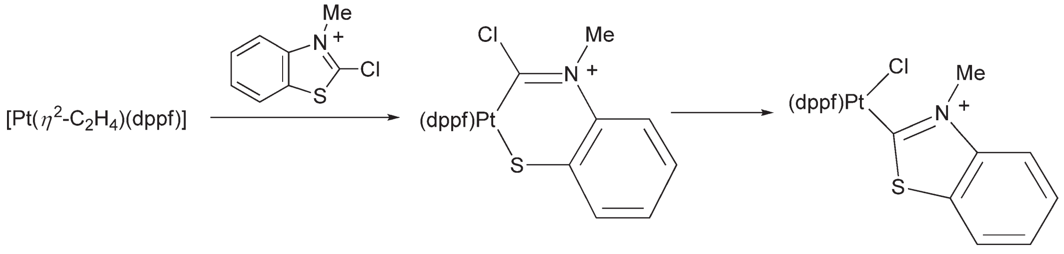
The characteristic feature of many platinum(0) complexes is their pronounced ability to add oxidatively many reagents. Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ has been used in a wide range of oxidative additions involving the formation of mono- and bis(silyl)platinum complexes,[20,49] because they have been implicated as key intermediates in platinum-catalyzed processes, such as hydrosilylation and double silylation of unsaturated organic ligands. The formation of stable transition metal silyl compounds has been recently reviewed.[50,51] Particularly interesting (Scheme 2) are the formation of symmetrical or unsymmetrical diplatinum complexes containing three-center two-electron non-classical Pt···H···Si interactions using sterically hindered arylsilanes[52] or silafluorene,[53] the formation of trans-bis(chelate) Pt(Cab^{P,Si})$_2$ starting from (phosphine-*o*-carboranyl)silanes,[54] or the formation of the first tetrakis(silyl)platinum(IV) by treatment of Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ with 2.2 equiv. of 1,2-bis(silyl)benzene.[55] Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ also undergoes oxidative additions of C–Si and C–Sn bonds with (phosphinoalkyl)silanes[56] or stannanes,[57] Ph$_2$PCH$_2$CH$_2$ER$_3$



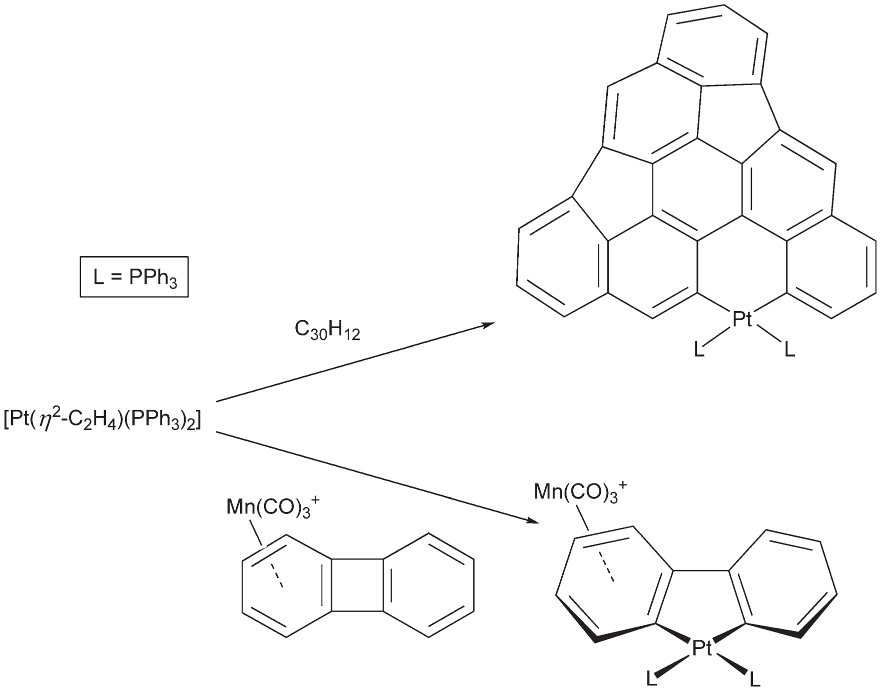
Scheme 2

(E = Si, Sn; R = Ph, Me), showing that E–Ph groups are, in general, more reactive than E–methyl groups. In this category, bis(stannyl)platinum(II) complexes are also formed using organotin compounds, such as Sn_2Me_6 or 1,1,2,2-tetramethyl-1,2-distanna[2]-ferrocenophane.[58]

Oxidative additions to C–C bonds have been observed with strained three-,[59] four-,[60,61] and five-membered rings-[62] (Scheme 3). The reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with semibuckminsterfullerene, $C_{30}H_{12}$, gives, rather than the expected simple η^2-coordination of $Pt(PPh_3)_2$ to a [6 : 6]-carbon bond, an unusual C–C cleavage, probably due to the relief of the strain associated with the five-membered ring.[62] The insertion into the C–C bond of biphenylene occurs, but only facilitated by coordination of the electrophilic $[Mn(CO)_3]^+$ fragment.[60] Similar remote activations of C–S, C–O, and N–H bonds have recently been reviewed.[61] Other common oxidative additions to $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ are the X–B and B–B bonds of haloboranes XBR_2[63] and diborane(4) compounds. These latter include B_2F_4,[64] aryl and alkyloxydiborane(4) species,[63,65–67] as well as $B_2(1,2\text{-}S_2C_6H_4)_2$ or $1,2\text{-}B_2Cl_2(NMe)_2$,[68] giving rise to the corresponding *cis*-bis(boryl)bis(triphenylphosphine)platinum(II) complexes. The chemistry of transition metal–boryl complexes has been also reviewed.[69] Insertions of PtL_2 ($L_2 = 2PPh_3$, dppe) into S–S[70,71] and C–S[72] bonds have also been reported. Facile and regioselective insertion of Pt(dppf) occurs with both 3-methyl and 2,3-dimethylthiazoline salts, as well as with related 3-methylbenzothiazolium salts and $Pt(\eta^2\text{-}C_2H_4)(dppf)$. Interestingly, similar chemistry was initially observed with 2-chloro-3-methylbenzothiazolium BF_4^-, but rearrangement occurs subsequently to give the C–Cl insertion product (Equation (1)).[73]



(1)



Scheme 3

Reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with labile triflate derivatives $M(Tf)_2Cp^*(PMe_3)$ (M = Rh, Ir) causes an effective oxidative addition of the C–H bond of the olefin, yielding bimetallic species (Pt–M) stabilized by a mixed $(\mu\text{-H})(\mu\text{-CH{=}CH_2})$ bridging system.[74]

8.09.2.1.2 Divalent derivatives

Many of these complexes are 16-electron square-planar derivatives, but the number of pentacoordinate (18-electron) compounds has increased notably in the last decade. A remarkable effort has been directed to the preparation and study of reactive cationic 16-electron Pt(II) complexes, which model the discovery that analogous Pd(II) and Ni(II) complexes catalyze the homogeneous polymerization of α-olefins, probably one of the most promising findings concerning the chemistry of d^8-ions.

8.09.2.1.2.(i) Preparation

8.09.2.1.2.(i).(a) Preparations starting from Zeise's salt

Many preparations of mononuclear η^2-alkene platinum(II) derivatives continue using Zeise's anion as precursor. Neutral complexes of general formulation *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)L]$ having active ligands, such as antitumor (1-nitro-9-[(2-dialkylaminoethyl)amino]acridine)[75] or anti-inflammatory (piroxicam (H_2pir), tenoxicam (H_2ten), and meloxicam (H_2mel))[76,77] drugs, *N*-ferrocenylamine $(Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NHR)$; R = alkyl, aryl),[78] ferrocenylimine ((*N*-alkyl-1-ferrocene-1-yl)methanimine),[79] or even various phosphorus and arsenic keto-stabilized ylides, $Ph_3ECHCOR$ (E = P, As),[80] have been prepared by reaction of Zeise's anion with the corresponding ligand. The cationic salts $[PtCl(\eta^2\text{-}C_2H_4)(Me_2dab)]ClO_4$ (Me_2dab = N,N′-dimethyl-2,3-diaminobutane), with *R*,*S*, *R*,*R* and *S*,*S* configurations at the asymmetric carbons, have been also prepared by reaction of Zeise's anion with the diamine in the presence of $LiClO_4$.[81] Equilibration of different diastereomeric species occurs in solution and their stability is dependent not only on the 1,3-diaxial repulsion but also on the flexibility of the ring puckering and interligand repulsions.

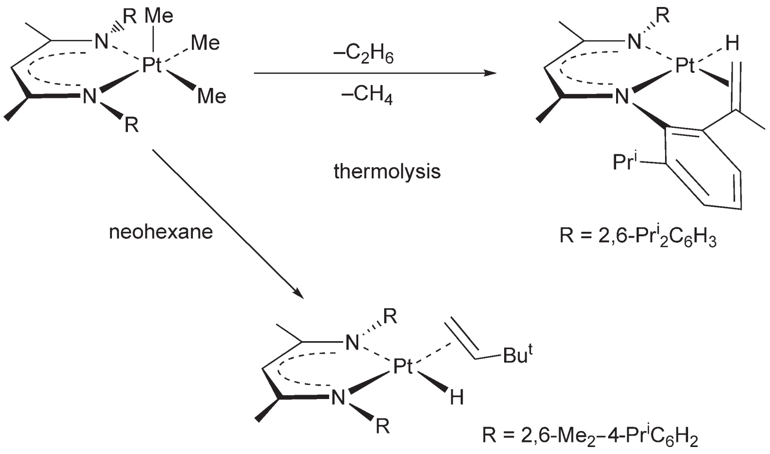
8.09.2.1.2.(i).(b) Preparation via bridge cleavage

A variety of crown ether adducts of type $[K(18\text{-cr-}6)][PtCl_3(\eta^2\text{-alkene})]$ have been prepared by reaction of the diplatinum complex $[K(18\text{-cr-}6)]_2[Pt_2Cl_6]$ with a variety of terminal and internal alkenes,[82] while direct reaction of the dimer $[PtCl_2(\eta^2\text{-}C_2H_4)]_2$ with 2 molar equiv. of $Ph_3PC{=}C{=}O$ gives the unusual η^1-ketenyl-ethylene derivative *trans*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}(\eta^2\text{-}C_2H_4)]$.[83] Ethene is able to split the pentafluorophenyl bridging system in $(NBu_4)_2[M(R_F)_4(\mu\text{-}R_F)_2]$ to afford the organometallic analogs of Zeise's salt, $(NBu_4)[M(R_F)_3(\eta^2\text{-}C_2H_4)]$ (M = Pt, Pd (X-ray)) (R_F = pentafluorophenyl). The related Ni derivative, stable only at low temperature ($<-50\,°C$), has been generated by C_6F_5 abstraction from $(NBu_4)_2[Ni(R_F)_4]$ with $B(R_F)_3$ in the presence of ethylene.[84] Selective formation of neutral orthometallated complexes $PtCl(2\text{-}Me_2NCH_2C_6H_4)(\eta^2\text{-alkene})$ (alkene = C_2H_4, coe (cyclooctene), CH_2CHCH_2OH), containing the olefin *cis* to the aryl group, are formed in a similar way by bridge splitting of $[Pt(\mu\text{-}Cl)(2\text{-}Me_2NCH_2C_6H_4)]_2$ with the olefin.[85] A similar complex $PtCl(\eta^2\text{-}C_2H_4)(N,N)$ is generated by treatment of the potassium salt of 2-(2-pyridyl)indole with Zeise's dimer.[86] A new synthetic procedure for complexes *cis*-$[PtCl_2(\eta^2\text{-alkene})(PPh_3)]$ has recently been reported based on $PtCl_2$ dissolved in DMF.[87] The first imidazole-type carbene–olefin complex *cis*-$[PtCl_2(\eta^2\text{-}C_2H_4)$(1-ethyl-3-methylimidazol-2-ylidene)] has been prepared by reacting $PtCl_2$ and $PtCl_4$ with ethylene in the basic [EMIM]Cl/$AlCl_3$ ionic liquid ($EMIM^+$ = 1-ethyl-3-methylimidazolium).[88]

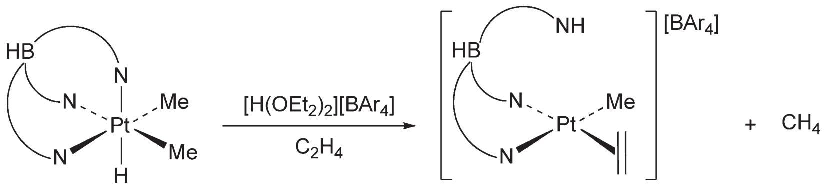
8.09.2.1.2.(i).(c) *Preparation using electrophilic species and/or creating vacant coordination sites*

Unusual cationic complexes with the general formulation $[PtR(\eta^2\text{-alkene})(N,N')]^+$ (R = H, Me, C(sp^2)) have been prepared starting from Pt(0), Pt(II), and Pt(IV) precursors and appropriate electrophilic or acidic species. The simplest strategy involves treatment of the corresponding halo derivative with $AgBF_4$. Thus, cationic complexes $[PtMe(\eta^2\text{-}CH_2{=}CHCOR)(N,N)]BF_4$ (N,N = diacetylbis(di-*i*-propylphenylimine; diacetylbis(diethyl)phenylimine; R = H, NMe_2, Me, OMe) have been prepared by reaction of PtIMe(N,N) with $AgBF_4$ in the presence of the appropriate alkene.[89] Chlorine abstraction from PtClMe(N,N) [N,N = glyoxal-bis((2-α-triisopropyl-siloxymethyl)–4-methylphenyl)diimine, TIPS–6-MPD,[90] *syn*- or *anti*-isomers of bis((2-methoxymethyl)-4,6-di-*tert*-butylphenyl)-diimine,[91] diacetyl-bis(phenylimine) (daph), diacetyl-bis(2,6-diisopropylphenylimine) (daproph), diacetyl-bis(2,6-diethylphenylimine) (daethyph)[92]] with $AgBF_4$ in the presence of the olefin leads to the corresponding compounds $[PtMe(\eta^2\text{-alkene})(N,N)]^+$ (alkene = C_2H_4,[90,91] $CH_2{=}CHCN$,[91] various alkenes[92]). The same cationic complexes $[PtMe(alkene)(N,N)]^+$ can also be prepared by methyl group abstraction from $PtMe_2(N,N)$ using the strong Lewis acid $B(R_F)_3$ in the presence of the olefin.[91] The analogous complex $[PtMe(\eta^2\text{-}C_2H_4)(bu_2bpy)][MeB(R_F)_3]$ is prepared in a similar fashion.[93] In this case, the presence of H_2O in the reaction gives rise to $[PtMe(\eta^2\text{-}C_2H_4)\text{- }(bu_2bpy)][HOB(R_F)_3]$ (bu_2bpy = 4,4′-ditert-butyl-2,2′-bipyridine). It is suggested that the presence of H_2O generates $H_2OB(R_F)_3$, which acts as a strong acid, $H[B(OH)(R_F)_3]$, protonating a Pt–Me bond in the precursor.[93] The chiral complexes $[Pt\{$*cis*/*trans*-1-$(N{=}CHC_6H_4)$–2-$(N{=}CHPh)(C_6H_{10})\}(\eta^2\text{-}CH_2{=}CHR)]BX_4$ (R = H, Me, Ph, 4-$(Me)C_6H_4$; X = F, Ar) result from the treatment of the methyl precursors (*cis* or *trans*) with protic acids HBF_4 or $H(OEt_2)BAr_4$ (Ar = 3,5-$(CF_3)_2C_6H_3$) and $CH_2{=}CHR$.[94] For prochiral alkenes, highly stereoselective olefin coordination is observed. Complexes $[Pt(DPCB\text{–}Y)Me(\eta^2\text{-}C_2H_4)]Tf$ with 1,2-diaryl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutenes (DPCB–Y; aryl = 4-$(OMe)C_6H_4$, Ph, 4-$(CF_3)C_6H_4$) were prepared as oily materials by sequential treatment of the dimethyl precursor with HTf and ethylene.[95] On the other hand, alkylation of the tricoordinate Pt(0) complex Pt(phen)(Me–fu) by Me_3OBF_4 or Et_3OBF_4 is another effective method to the corresponding cationic complexes $[PtR(phen)(Me\text{–}fu)]BF_4$ (R = Me,[96] Et[97]). As expected, displacement of Me–fu by electron-rich olefins ($RCH{=}CH_2$) (R = H, Ph, Me) gives similar complexes.[92,96]

A very elegant method to the chiral complex $[PtMe(\eta^2\text{-}C_2H_4)\{\kappa^2\text{-}(Hpz^*)BHpz^*_2\}]BAr_4$[98] starting from $PtTp'HMe_2$ is shown in Equation (2), and following similar selective protonation at a pyrazole nitrogen atom of $PtTp'H_2Me$, which induces reductive elimination of methane, the corresponding hydride–olefin complex $[PtH(\eta^2\text{-}C_2H_4)\{\kappa^2\text{-}(Hpz^*)BHpz^*_2\}]BAr_4$ has also been prepared (pz^* = 3,5-dimethylpyrazolyl).[99] A related neutral hydride–olefin complex is prepared by thermolysis of the five-coordinate Pt(IV) complex $[Pt(nacnac)Me_3]$, where the olefin is part of a nacnac-type ligand (Scheme 4) (nacnac = $[(o\text{-}Pr^i{}_2C_6H_3NCMe_3)_2CH]^-$). Its formation is suggested to occur through a three-coordinate Pt(II) species Pt(nacnac)Me. In C_6D_6, the corresponding olefin-deuterio d_{27}, with the Pr^i, the hydride, and isopropenyl groups completely deuterated, is generated, and has been characterized by X-ray.[100] This latter strategy has been extended to other five-coordinate complexes with a variety of β-diimate ligands $Pt(diimate)Me_3$, showing that they are useful species for alkane dehydrogenation[101] (Scheme 4). Very unusual dicationic complexes $[Pt(\eta^2\text{-alkene})(PNP)](BF_4)_2$ ($CH_2{=}CHR$, R = H, Me, Et, Ph) have been prepared by abstracting halide in [PtI(PNP)]I with 2 equiv. of $AgBF_4$ in presence of the corresponding alkene (PNP = [2,6-bis(diphenylphosphinomethyl)]pyridine).[102] Related complexes with *Z*,*E*-2-butene and norbornene were generated by displacement of ethylene in $[Pt(\eta^2\text{-}C_2H_4)(PNP)]^{2+}$.



Scheme 4



(2)

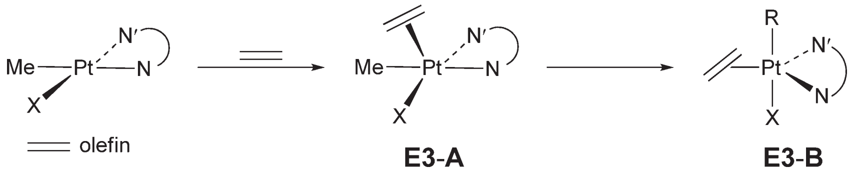
8.09.2.1.2.(i).(d) *Pentacoordinate complexes*

Most of these complexes are neutral trigonal-bipyramidal Pt(II), Pt(A)(B)(N,N)(η^2-alkene) (A, B = halide, hydride, alkyl, aryl, ER (E = O, S, Se, Te), SnR_nX_{3-n}, HgR, GeR_nCl_{3-n}, PbR_2Cl (X = halide; R = alkyl)), or cationic $[Pt(A)L(\eta^2\text{-alkene})(N,N)]^+$ (L = H_2O, *N*-donor, carbene) complexes. A comprehensive review of this type of complexes appeared in 1994,[97] and the most common synthetic strategies (see below) were included in COMC (1995).[2] The stability of these 18-electron Pt(II) complexes is favored usually by the presence, in the trigonal plane, of sterically crowded nitrogen chelates and of a π-acceptor olefin ligand, which draws electron charge from the metal center. Some novel contributions are outlined here.

Ligand displacement. Novel ethylene complexes $PtCl_2(\eta^2\text{-}C_2H_4)(N,N)$ (N,N = 1,10-phenantroline–5,6-dione (phedon), 2,9-dimethyl–1,10-phenantroline–5,6-dione (Me_2phedon),[103] 6,6′-dimethylbipyridyl crown[104]) are prepared from displacement of Cl^- by the corresponding bidentate ligand in Zeise's salt. A similar family of complexes containing the chiral diamine (1,2-diphenyl–N,N'-bis[(2,4,6-trimethylphenyl)methyl]–1,2-diaminoethane (mestien)) and different alkenes has been prepared as a mixture of isomers by reacting the Zeise dimer with the diamine ligand and the corresponding alkene in two steps; with electron-rich olefins, the olefin is added first, while with electron-poor olefins, the Zeise dimer is treated initially with the diamine, giving $PtCl_2(\eta^2\text{-}C_2H_4)$(mestien), and subsequently the ethylene is displaced for the olefin in the second step.[105] Displacement of labile ligands in the cationic $[PtR^1(S)(\eta^2\text{-alkene})(dmphen)]^+$ (S = MeCN, H_2O) with $K[CHR^2R^3]$ or $K[CH_2NO_2]$ affords unusual complexes containing two η^1-C-bonds in axial sites $Pt\{CHR^2R^3\}R^1(\eta^2\text{-alkene})$(dmphen) or $Pt(CH_2NO_2)R^1(\eta^2\text{-alkene})$(dmphen) ($R^2$, R^3 = CO_2Me, COMe, CN; R^1 = Me, CH_2Ph; alkene = dimethylmaleate, C_2H_4).[106]

Alkene addition to a Pt(II) complex. Unstable olefins such as $CH_2{=}CHOH$, 1-propen-ol, 1-buten-1-ol, or (*Z*)-1,2-ethenediol have been stabilized in complexes $PtXY(\eta^2\text{-alkene})$(dmphen) (X = halide; Y = Cl, Me). Their synthesis is based on the uptake of the corresponding trimethylsilyl enol ethers from PtXY(dmphen) and subsequent hydrolysis of the resulting complexes $PtXY(dmphen)(RCH{=}CHOSiMe_3)$.[107] Careful monitoring of the general olefin addition reaction to complexes PtXMe(N,N) (X = Cl, $CH(CO_2Me)_2$) has shown that the olefin uptake occurs in two successive steps (Equation (3)). First, a direct bimolecular addition leads to a bipyramidal trigonal species **E3-A**, in which the axial positions are occupied by the alkyl group and by one nitrogen atom. In most cases, this subsequently rearranges, probably via intramolecular pseudorotations, to give the usual compounds **E3-B**.

The structure of the type **E3-A** species has been confirmed by an X-ray study of the complex PtMe{CH(CO$_2$Me)$_2$}(dmphen)(η^2-(*E*)-NCCH=CHCN).[108] Using a similar methodology, η^2-butadiene complexes PtClR(η^2-butadiene)(N,N) (N,N = dmphen, R = Me, 4-(OMe)C$_6$H$_4$; N,N = 2-methyl–6-[(phenylimino)methyl]pyridin (pimpy), R = Me) have been prepared.[109] Photoreaction ($\lambda > 350$ nm) of Pt(hfacac)$_2$ in the presence of an excess of ethylene gives an unusual five-coordinate tbp adduct Pt(hfacac)$_2$(η^2-C$_2$H$_4$) having symmetrical hfacac ligands (X-ray). Similar products have been detected spectroscopically with propene and 1-hexene but not isolated.[110]



(3)

Oxidative addition to Pt(0) precursors. Three-coordinate complexes Pt(η^2-alkene)(N,N-chelate) readily undergo addition by a variety of electrophiles A–B to give five-coordinate products. Novel hydride–olefin derivatives *trans*-[PtHX(η^2-alkene)(dmphen)] (*Z*,*E*-RCH=CHR; R = CO$_2$Me, CO$_2$Bu^t; X = Cl, Br, I) are obtained by oxidative addition of HX to suitable precursors.[111] Analogous addition of [ClCH=NMe$_2$]Cl yields unusual cationic carbene complexes [PtCl(CHNMe$_2$)(η^2-alkene)(N,N)]Cl (N,N = dmphen, 6,6′-dimethylbipyridine (dmbipy); olefin = *Z*,*E*-MeO$_2$CCH=CHCCO$_2$Me; fn).[112] However, attempts to form similar derivatives with the Pt=CHY unit by reacting [PtR(H$_2$O)(dimethylmaleate)(dmphen)]BF$_4$ with diazoaceto reagents N$_2$CHY (Y = CO$_2$Et, CO$_2$NMe$_2$, CN) leads instead to neutral pentacoordinate complexes PtR{η^1,η^2-CH(Y)O$_2$CCH=CHCO$_2$Me}(dmphen) (R = Ph, Me) containing an η^1,η^2-C,C=C chelating moiety. These are formally derived by a fast nucleophilic attack of H$_2$O to a cationic carbene intermediate.[112] Water-soluble compounds [PtI(η^2-alkene)(py)(N,N)]NO$_3$ are formed by oxidative addition of [I(py)$_2$]$^+$(NO$_3$)$^-$ to suitable precursors containing electron-withdrawing olefins.[113] Activation of C–C, S–S, and C–Cl bonds in (CN)$_2$, (SCN)$_2$, and Cl(CH$_2$)$_n$CO$_2$CH=CH$_2$ ($n = 0, 1$),[114] and more recently E–E bonds in electrophilic RE–ER molecules (E = O; R = H, COPh, COMe; E = S, Se, Te; R = Me, Ph),[115] by suitable Pt(0) precursors Pt(η^2-alkene)(dmphen) (alkene = C$_2$H$_4$,[114] maleic or fumaric ester[115]), have been achieved. A broad range of halo–metal bonds (M = Sn, Pb, Ge, and Hg) in A–B derivatives of type (A–B = X–SnR$_n$X$_{3-n}$,[116] X–HgR,[116] Cl–GeR$_n$Cl$_{3-n}$,[117] Cl–PbR$_2$Cl;[118] X = halides, R = alkyls) have been also added to give complexes of general formula Pt(A)(B)(η^2-alkene)(N,N-chelate). These reactions have been particularly suitable for the study of addition–elimination processes.

Other processes. Novel synthetic strategies have used Pt(IV) precursors. Thus, octahedral PtX$_4$(2,9-Me$_2$-4,7-Ph$_2$phen) complexes react with an excess of C$_2$H$_4$ to give reductive elimination of halogen, which, in turn, reacts with an excess of C$_2$H$_4$ to give 1,2-dihaloethane and formation of PtX$_2$(η^2-C$_2$H$_4$)(2,9-Me$_2$-4,7-Ph$_2$phen).[119] Cationic hydride–olefin complexes [PtH{η^2-R^{1}CH=CHR^2}(η^3-L)]Q (Q = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; L = [2.1.1]-2,6-pyridinophane) are formed by activation of C–H bonds in both acyclic and cyclic saturated hydrocarbons, probably through a 14-electron [PtMe(η^2-L)]$^+$ species generated by elimination of CH$_4$ starting from [PtHMe$_2$(η^3-L)]Q.[120] The complex PtTp′Me(η^2-C$_2$H$_4$) is accessible from PtTp′HMe$_2$ via two sequential steps of protonation in the presence of C$_2$H$_4$ to yield [PtMe(η^2-C$_2$H$_4$){κ^2-(Hpz*)BHpz$^*_2$}]$^+$ and subsequent deprotonation of the pyrazolium ring.[98]

8.09.2.1.2.(ii) Structural aspects

Several aspects of structure and reactivity of η^2-monoalkene complexes have been reviewed,[2,97,121] or treated in part, in several reviews.[122,123] Improvements in technology have facilitated the use of solid-state NMR techniques. ^{13}C (CPMAS) and ^{1}H (SPEDA) NMR studies of K[PtCl$_3$(η^2-CH$_2$CH$_2$)]·xH$_2$O have shown second-order dipolar couplings between ^{13}C and ^{1}H and the quadrupole spins $^{35/37}$Cl of the two chlorine atoms mutually *trans* and ^{195}Pt.[124] Similar deuterium NMR studies of the ethylene–^{2}H$_4$ in Zeise's salt are characterized by long ^{2}H T$_1$s and by quadrupolar coupling comparable to that seen for rigid olefins indicating that the ethylene ligand is not subject to significant motion.[43] CP MAS NMR spectroscopy is particularly useful for complexes which are unstable in solution.[125]

A continuing interest in this area is to obtain more insight into the factors that govern the stereoselectivity of olefin coordination. NMR studies, including NOE and low-temperature experiments, concerning the effect of the olefin structure on the stability and stereoselectivities of a large number of prochiral olefins (CH$_2$=CHR) in the alkene–amino acid chiral complex *cis*-(N,olefin)-(*R*,*S*)[PtX(η^2-2-mb)(sarcosinato)] (2-mb = 2-methyl-3-buten-2-ol; X = Cl$^-$)

provide evidence that the significant stereoselectivity for one rotamer of the *R*, *S* diastereomer requires the presence of a good hydrogen-bond acceptor in the olefin to allow intermolecular hydrogen-bonding interaction with the NH proton of the sarcosinato located *cis* to the alkene.[126] The strong stereoselectivity and rotamer preference is reduced by replacement of X (Cl^-) by H_2O and almost eliminated by furher deprotonation ($X = OH^-$) and notably attenuated by change from CD_3OD to D_2O, emphasizing the importance of hydrogen bonding in these species.[126,127] Similarly, variable-temperature NMR studies on cationic complexes $[PtR(\eta^2\text{-alkene})(N,N)]^+$ (R = Me, Et; N,N = phen, daph, daethyph, daproh; alkene = Me–fu, C_2H_4, propylene, styrene, allyl alcohol, *trans*-2-butene) indicate that these complexes are involved in a dynamic associative exchange process involving the alkene ligand, which is strongly influenced by the steric hindrance of the N,N ligand. This fact also favors selective coordination of α-olefins.[92] Chiral complexes $[Pt(\mathit{cis/trans}\text{-}1\text{-}(N{=}CHC_6H_4){-}2\text{-}(N{=}CHPh)C_6H_{10}\}(\eta^2\text{-}CH_2{=}CHR)]BF_4$, with a diimine-type ligand precluding easy olefin exchange, have been obtained with high stereoselectivity, as demonstrated by NMR spectroscopy. The X-ray structures of complexes $[Pt\{R,S\text{-}\mathit{cis}\text{-}1\text{-}(N{=}CHC_6H_4){-}2\text{-}(N{=}CHPh)C_6H_{10}\}(\eta^2\text{-}CH_2{=}CHR)]BF_4$ (R = H, Ph) reveal that the stereochemistry about the free imine N=CHPh is *cis*, whereas it was *trans* in the precursor, a change which seems to be necessary to allow alkene coordination.[94,128]

The accessibility of a nucleophile to the metal center in related complexes $[PtMe(\eta^2\text{-alkene})(N,N)]BF_4$ ($N,N = 2,6\text{-}(R^1)_2C_6H_3N{=}C(R^2)C(R^2){=}N{-}2,6\text{-}(R^1)_2C_6H_3$; R^1 = H, Me, Et, Pr^i; R^2 = H, Me; alkene = $CH_2{=}CHR^3$ (R^3 = H, Me); COOMe) has been investigated by detecting cation–anion interactions through $^{19}F\{^1H\}$ HOESY spectroscopy. Only when R^1 is H or Me, the BF_4^- interacts with the methyl, R^3, and olefin protons showing that the accessibility to the metal center is not forbidden, and probably takes place from the side of the N,N ligand.[129] By extension of these studies to related cationic complexes with $R^1 = Pr^i$; R^2 = Me; olefin $CH_2{=}CHR^3$ (R^3 = Ph, Tol, 4-$(CF_3)C_6H_4$), an equilibrium between a pseudo-*trans* (PT) and a pseudo-*cis* (PC) ion pair (relating BF_4^- and R^3 substituents) is observed. A preference for the PC, in which a clear interaction of an *ortho*-proton of the R^3 group with the anion occurs, is detected.[130] Neutral complexes $PtMe(\eta^2\text{-alkene})(N,N'\text{-imino–amide})$ (N,N′-imino–amide = NN′-(1,2-dimethyl–1,2-ethanediylidene)bis(2,6-diisopropylaniline)); alkene = $CH_2{=}CHR^3$ (R^3 = H, Me, Ph, CH_2OH, COMe, CO_2Me)), generated by selective deprotonation from the corresponding cationic complexes $[PtMe(\eta^2\text{-alkene})(N,N)]^+$ (N,N = daproph), are formed as only one isomer, whose geometry, *cis* Me and N(amido) and the R^3 group oriented toward the Pt–Me vector, seems to be favored by steric factors and relevant π-backdonation, in agreement with NMR parameters and theoretical calculations.[131] It is worth mentioning that $[PtCl_3(\eta^2\text{-}C_2H_4)](AmH)]^+$ containing chiral secondary amines (Am), such as (1*S*,1′*S*)-bis(1-phenylethyl)amine, (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]amine,[132] and (1*S*,1′*S*)-N-[1′-(1-naphthyl)ethyl]–1-phenylethylamine,[133] show interesting possibilities as chiral derivatizing agents (CDAs) for the enantiomeric composition of unsaturated compounds, including olefins, via ^{195}Pt NMR spectroscopy arising from the exchange of ethylene by the corresponding analyte.[132,133]

Many olefin Pt(II) complexes have been characterized by X-ray diffraction studies. The usual vertical alignment of the olefin to the coordination plane is not observed (tilt angle = 74.5°) in the cation $[PtMe(\eta^2\text{-}C_2H_4)\{\kappa^2\text{-}(Hpz^*)\text{-}BHpz_2^*\}]^+$, probably due to its unfavorable steric interactions with either the protonated pyrazole ring or the Me group of the *cis*-pyrazole ring,[98] and in the neutral deuterido d_{27}-complex shown in Scheme 4, in which the olefin is part of a nacac-type ligand [torsion angle N–Pt–X–C (X = midpoint of the olefin) = 55.5(1)°].[100]

Five-coordinate complexes $Pt(SeMe)_2(\eta^2\text{-alkene})(dmphen)$ (alkene = diisopropylfumarate (Pr^i–fu), Et–fu, Me–fu, di(4-methylphenyl)fumarate (MePh–fu), diphenylfumarate (Ph–fu), di(chlorophenyl)fumarate (PhCl–fu)) partially dissociate in solution indicating reversible addition of MeSe–SeMe (NMR) to $Pt(\eta^2\text{-alkene})(dmphen)$. As expected, the equilibrium constants ($pk_{add} = -3.5$ to -2.5) decrease with increasing electron withdrawing properties of the coordinated olefin due to the lower basicity of the Pt(0) center.[134] In the same way, the higher stability of $PtCl_2(\eta^2\text{-}C_2H_4)(Me_2phedon)$ versus the analogous Me_2phen derivative relative to the release of ethylene can be attributed to the reduced electron donor properties of the oxidized $Me_2phedon$ ligand, which diminishes the electron charge in the trigonal plane.[103] The X-ray crystal structures of most of the five-coordinate tbp complexes do not differ substantially from that collected in COMC (1995), and have been exhaustively discussed.[2,97] Only some examples that exhibit interesting features are outlined here. An unusual bipyramidal structure occurs in the complex $PtMe\{CH(CO_2Me)_2\}(\eta^2\text{-}(E)\text{-}NCCH{=}CHCN)(dmphen)$, which shows the dmphen ligand with an equatorial-axial coordination and the Me group *trans* to the N atom being considered as a frozen point in the uptake of olefins by PtXY(NN) complexes.[108] The stability of this isomer is suggested to be due to the high *trans*-influence of both alkyl groups, which probably would destabilize the expected isomer with biaxial coordination of both anionic ligands. However, complex $PtMe\{\eta^1,\eta^2\text{-}CH(CHCO_2Et)O_2CCH{=}CHCO_2Me\}(dmphen)$ presents a biaxial coordination of both sp^3-carbons, in this case probably favored by the chelate ring ligand connecting equatorial and axial sites.[112]

Hydrogen bonds between axial ligands (Br,[135] H_2O) and equatorial olefins or counterions (Cl^-) contributing to the final stability have been also found.[112,135] Similar axial-equatorial features involving tin (Sn–O 2.677(5) Å) and lead (Pb–O 2.66(1) Å) metal–oxygen contacts are observed in $PtCl(PbPh_2Cl)(\eta^2$-(*Z*)-$MeO_2CCH{=}CHCOOMe)$(dmphen)[118] and $PtCl(SnMe_2Cl)(\eta^2$-Me–fu)(dmphen).[116]

8.09.2.1.2.(iii) Reactivity

8.09.2.1.2.(iii).(a) Olefin-exchange reactions and equilibria in solution

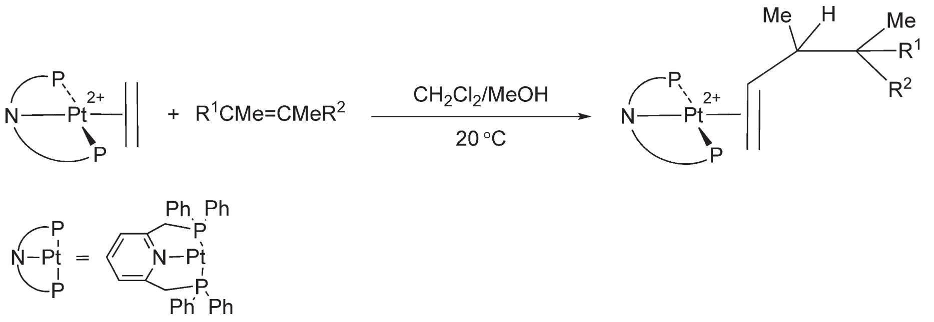
The exchange rate of coordinated alkene in square-planar platinum complexes usually grows from anionic to neutral derivatives. Thus, ethene-exchange rate constants at 298 K for $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$ and *trans*-$PtCl_2(\eta^2\text{-}C_2H_4)(MeOH)$ in methanol-d_4 are $(2.1 \pm 0.1)10^3$ and $(5 \pm 0.2)10^5\ M^{-1}\ s^{-1}$, respectively.[136] The activation process is largely entropy controlled (-117.1 ± 1 and $-102 \pm 2\ J\ K^{-1}\ mol^{-1}$), consistent with an associative pathway involving attack by the entering olefin at the labile site *trans* to ethene.[136] Low-temperature (223 K) studies using stopped-flow spectroscopy of extremely fast substitution processes of chloride *trans* to olefin in complexes $[PtCl_3(\eta^2\text{-olefin})]^-$ (olefin = CH_2CH_2, $CH_2{=}CHCH_2OH$, $CH_2{=}CHSiMe_3$, C_8H_{14}) also indicate an associative pathway, and reveal the following nucleophilicity $MeOH < Br^- < I^- < N3^- < SCN^-$ (1 : 100 : 700 : 2,500 : 12,000) for the ethylene complex.[137] The relative *trans*-effect of the olefins is $C_2H_4 \approx CH_2CHCH_2OH >> CH_2CHSiMe_3 \approx C_8H_{14}$.[137] Kinetic studies of olefin-exchange reactions in $PtCl(2\text{-}Me_2NCH_2C_6H_4)(\eta^2$-alkene) (alkene = C_2H_4, coe, CH_2CHCH_2OH) are compatible with concerted substitution via a turnstile twist pseudo-rotation in a short-lived five-coordinate intermediate involving initial attack on the labile coordination position *trans* to the σ-bonded aryl.[85] In monocationic complexes of type $[PtR(\eta^2\text{-alkene})(N,N)]^+$,[92] the associative olefin-exchange process is fast but can be strongly retarded by steric hindrance.[92,102] NMR measurements of exchange with excess of ethylene in the complex $[PtMe(\eta^2\text{-}C_2H_4)(N,N)]BF_4$ (N,N = glyoxal-bis((2-α-triisopropylsiloxymethyl)-6-methylphenyl)diimine) also suggest the exchange occurs via an associative pathway, and the rate of exchange was estimated as $1.2 \times 10^3\ s^{-1}$ at T_c (>363 K).[90]

Equilibrium measurements of the addition–elimination reactions of MX_nR_m (M = Hg, Sn; X = Cl, Br, I; R = hydrocarbyl group) to platinum(0) derivatives $Pt(\eta^2$-alkene)(N,N′-chelate) (N,N′ = dmphen, pimpy, mphen), yielding five-coordinate adducts $PtX(MR_mX_{n-1})$(N,N′-chelate), can be tuned by the features of each ligand from no appreciable to quantitative formation of the adduct product.[116] The equilibrium constants confirm that a greater donor ability of the olefin is accompanied by a greater stability of the adduct, although steric hindrance or interactions between axial ligands and olefin substituents also play an important role. The reverse holds true for groups on the reduced tin or mercury metal, that is, oxidation equilibrium constants increase along the series Me_3SnCl, Me_2SnCl_2, and $MeSnCl_3$. Finally, it has been shown that the influence of the halide moving onto platinum can be rationalized in terms of the relative softness of the two metals involved in the equilibrium (Hg(II) > Pt(II) > Sn(IV)) and the hardness of the halide ion (I < Br < Cl).[116] In contrast to this behavior, cationic complexes $[Pt(HgMe)(\eta^2$-(*Z*)-$RO_2CCH{=}CHCO_2R)(dmphen)(H_2O)]^+$ (R = Me, Bu^t) demercuriate in solution to $[PtMe(\eta^2$-alkene)-(dmphen)$(H_2O)]BF_4$, while the analogous $[Pt(HgBu^t)(\eta^2$-(*Z*)-$MeO_2CCH{=}CHCO_2Me)(dmphen)(H_2O)]^+$ gives the trinuclear cluster $[\{Pt(\eta^2$-(*Z*)-$MeO_2CCH{=}CHCO_2Me)(dmphen)(H_2O)\}_2Hg](BF_4)_2$.[138]

8.09.2.1.2.(iii).(b) Reactions with nucleophiles

General aspects of this reactivity,[2,97,121,122] including theoretical studies,[139] have been reviewed. Particular attention has been paid to reactions with amines to get more information on metal-catalyzed hydroamination of alkenes. A recent DFT theoretical study has evaluated the hydroamination process for different metals, concluding that nucleophilic attack of amine is thermodynamically and kinetically favorable for group 10 metals.[140]

Markovnikoff addition of amines (aromatic amines) and other nucleophiles (MeOH, H_2O) to alkenes coordinated to a dicationic platinum fragment $[Pt(\eta^2\text{-alkene})(PNP)]^{2+}$ (alkene = CH_2CHR^1 (R^1 = H, Me, Et, Ph); (*Z*)- and (*E*)-2-butene, norbornene) is reported to be very facile, yielding the corresponding β-functionalized complexes $[Pt(CHR^1CHR^2Nu)(PNP)](BF_4)_2$ (R^1 = H, R^2 = H, Me, Et, Ph; $R^1 = R^2$ = Me) even in the absence of base.[102] In the reaction with H_2O, the ethylene complex reacts in the presence of $NaHCO_3$ to give a mixture of $[Pt(CH_2CH_2OH)(PNP)]^+$ and the dinuclear derivative $[\{Pt(PNP)(CH_2CH_2)\}_2O]^{2+}$ (1 : 4), the latter complex probably formed by a further nucleophilic attack of the β-hydroxyalkyl at the precursor $[Pt(\eta^2\text{-}CH_2CH_2)(PNP)]^{2+}$ or by a spontaneous condensation reaction. Related mono-$[Pt(CH_2CH_2NHPh)(PNP)]BF_4$ and bimetallic $[\{Pt(PNP)(CH_2CH_2)\}_2NPh)](BF_4)_2$ complexes are also generated in the reaction with $PhNH_2$.[102] It is worth mentioning that the ethylene complex reacts even with electron-rich alkenes, giving rise to a coupling reaction (Equation (4)), which, in addition, has been shown to be a catalytic hydrovinylation process.[141]



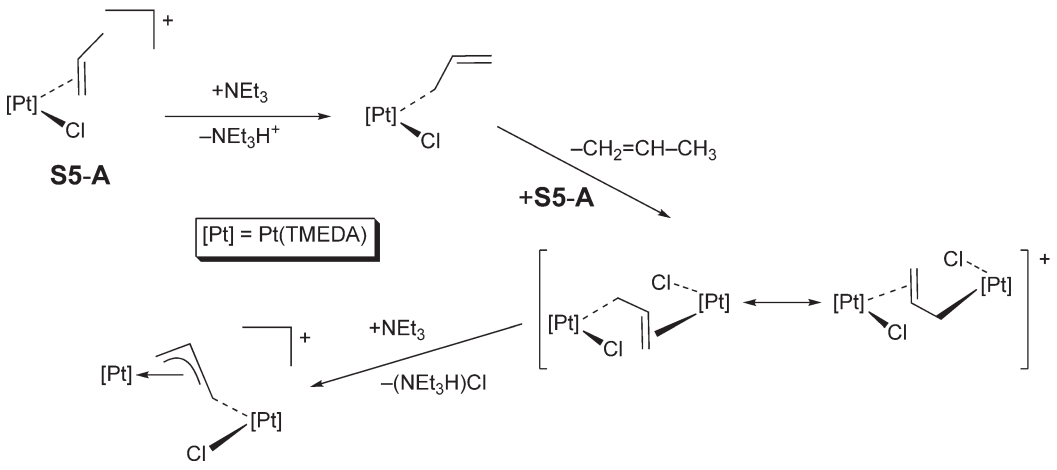
(4)

Low-temperature reactions (−75 °C) of *cis*-[PtCl$_2$(η^2-alkene)(PPh$_3$)] (alkene = CH$_2$CHR (R = H, Me, Et, (*Z*)-2-butene)) with NEt$_2$H show that the addition leads initially exclusively to the *anti*-Markovnikov addition (attack on the least substituted olefinic carbon) products, which slowly rearrange quantitatively to the final Markovnikov addition products.[87] The transformation is suggested to occur without amine dissociation. Similar precursors with higher olefins (1-hexene, 1-octene, and 1-decene) do not react with NEt$_2$H, probably due to increased steric hindrance. It is worth noting that temperature control is essential, because at RT, simple substitution occurs rather than the nucleophilic attack.[87] The acac$^-$ ligand adds to [PtCl(η^2-CH$_2$CHPh)(TMEDA)]$^+$ to afford PtCl{η^1-CH(H,Ph)CH(Ph,H)(*C*-acac)}(TMEDA) as a mixture of Markovnikov (≈75%) and *anti*-Markovnikov isomers in solution,[142] but, in the solid state, slow isomerization to the pure Markovnikov isomer is observed.[143] This isomerization is suggested to occur via detachment of the added carbanion and its subsequent readdition to the thermodynamically more favored site. Further examples such as the slow dissociation of the adduct PtCl(CH$_2$CH$_2$OCOMe)(TMEDA) into its constituent species are in accord with a higher stability of the η^2-olefin and free nucleophile in the solid state versus the η^1-alkyl addition product in solution. This fact is suggested to be due to entropic factors.[143] Cationic complexes [PtCl{CH$_2$CH$_2$CH(PPh$_3$)CO$_2$R}(TMEDA)](ClO$_4$) (R = Me, Et) are generated by *exo*-addition of the carbon nucleophilic ylide Ph$_3$P═CHCO$_2$R to [PtCl(η^2-C$_2$H$_4$)(TMEDA)](ClO$_4$).[144]

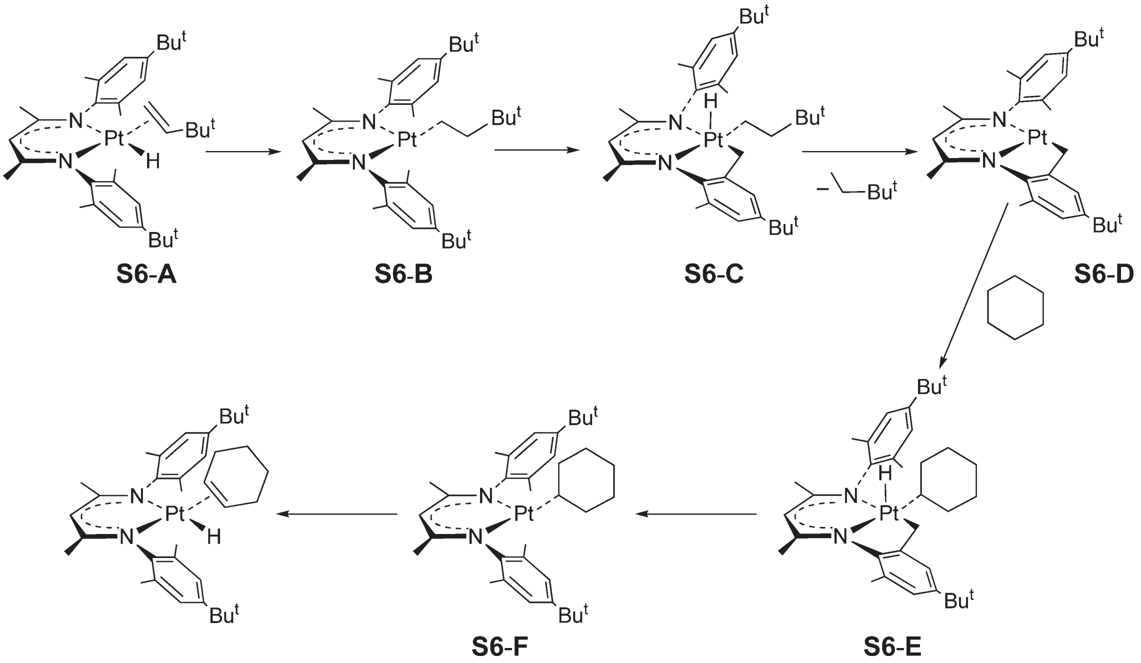
An unusual example of reversible interconversion is provided by the five-coordinate complexes [PtClMe(η^2-RHC═CHOH)(dmphen)] containing vinyl alcohol,[135] 1-propen-1-ol,[107] and 1-buten-1-ol,[107] which react with KOH to afford the square-planar aldehyde complexes PtMe(CHR–CHO)(dmphen). These latter complexes revert reversibly to the precursors on treatment with HCl.[107] However, cationic diimine complexes [PtMe(η^2-alkene)(daproph)]$^+$ (alkene = CH$_2$═CHR (R = H, Me, Ph, CH$_2$OH, COMe, CO$_2$Me)) are selectively deprotonated by treatment with KOH to afford the corresponding neutral derivatives containing the novel N,N′-imino–amide chelate ligand depran (N,N′ = 1,2-dimethyl–1,2-ethanediylidene)bis–2,6-diisopropylaniline).[131] In the same way, deprotonation of one allylic proton is observed in the reaction of cationic complexes [PtCl(η^2-alkene)(TMEDA)](ClO$_4$) (alkene = 1-butene, 1-hexene) with NEt$_3$, affording η^1-allyl species PtCl(η^1-allyl)(TMEDA), which, subsequently, rearrange to form selectively cationic *syn*-[Pt(η^3-allyl)(TMEDA)]$^+$ complexes.[145] In the case of [PtCl(η^2-2-propene)(TMEDA)](ClO$_4$), the reaction gives the final diplatinum complex [{PtCl(TMEDA)}(μ-η^1,η^3-CHCHCH$_2$){Pt(TMEDA)}](ClO$_4$)[145] through the sequence of reactions shown in Scheme 5.

8.09.2.1.2.(iii).(c) Migratory alkene insertion

Two different types of products are generated by insertion of alkenes into the Pt–Ph bond of [PtPh(η^2-CH$_2$CH$_2$)(phen)]$^+$. Thus, in the presence of donor ligands (L = olefin, py, PPh$_3$), 2-phenylethylplatinum(II) complexes [Pt(CH$_2$CH$_2$Ph)L(phen)]$^+$ are generated, while in the absence of them and in the presence of MeCN, a fast rearrangement takes place to form 2-ethylphenylplatinum(II) [Pt(2-EtC$_6$H$_4$)(MeCN)(phen)]$^+$.[146] An unusual cyclometallated complex [$\overline{\text{PtCH}_2\text{CH}_2\text{CH}_2\text{CO}}$OMe(daethyph)]BF$_4$, obtained by refluxing [PtMe(η^2-CH$_2$═CHCO$_2$Me)(daethyph)]$^+$ in CHCl$_3$, is suggested to be formed by insertion of methylacrylate into the Pt–Me bond.[89] In this category, an interesting dehydrogenation reaction takes place by heating the olefin–hydride complex **S6-A**, shown in Scheme 6, in the presence of cyclohexane. The reaction generates the related cyclohexene–hydride derivative, probably through the mechanism depicted in Scheme 6. The reaction is proposed to occur through an initial alkene insertion to generate **S6-B**, followed by internal cyclometallation (**S6-B** → **S6-C**). Successive reductive elimination and oxidative addition reactions lead to **S6-F**, which undergoes a β-hydrogen elimination giving the final complex. In accordance with this mechanism, by using C$_6$D$_{12}$, the corresponding cyclohexene-d_{10} deuteride derivative is formed and *all*-protio neohexane is liberated.[101]



Scheme 5



Scheme 6

8.09.2.1.2.(iii).(d) Oxidative addition

Photoactivated halogenation reactions of very stable five-coordinate complexes $PtX_2(\eta^2$-alkene)(dmphen) (X = Cl, Br, I; alkene = CH_2CHR, R = H, Me, Et) with Cl_2 and Br_2 offer an easy route to unprecedented β-haloalkylplatinum(IV) species $PtX_3(CH_2CHRX)$(dmphen).[147] Treatment of $PtCl_2(\eta^2$-$CH_2CH_2)$(dmphen) with Br_2 affords $PtCl_2Br(CH_2CH_2Br)$(dmphen) with both chloride ions mutually *trans*. This fact, and other experimental data, suggest that the radical $X^{\cdot}$ is responsible for attacking the alkene through a cross-oxidation, involving, simultaneously, the metal center.[147] Novel insights have been obtained about the activation of alkanes in water by platinum salts. It has been demonstrated that Zeise's salt transforms to $[PtCl_5(CH_2CH_2OH)]^{2-}$ in the presence of an excess of $[PtCl_6]^{2-}$. Kinetic studies of this reaction indicate that the attack of water on coordinated ethylene, giving a β-hydroxyethyl species $[PtCl_3(CH_2CH_2OH)]^{2-}$, precedes oxidation of Pt(II) to Pt(IV) rather than the reverse order, and, using labeling experiments (^{195}Pt 97%), it has been demonstrated that $[PtCl_5(CH_2CH_2OH)]^{2-}$ is also generated by oxidation of $[PtCl_3(CH_2CH_2OH)]^{2-}$, probably through an inner-sphere two-electron transfer accompanied by Cl^- transfer.[148,149] In fact, $[PtCl_5(CH_2CH_2OD)]^{2-}$ is also generated by treatment of Zeise's salt with Cl_2 in CD_3OD.[150]

8.09.2.1.2.(iii).(e) Alkene modification

One aldehyde function of the fumaraldehyde PtClMe(η^2-(*E*)-CHR═CHR)(dmphen) (R = CHO) is easily oxidized with H_2O_2 to acid (R = COOH), or both condensed with $PhNH_2$ to yield the complex with R = CH═NPh.[107] The vinyl alcohol in complexes PtXY(η^2-H$_2$C═CHOH)(dmphen) (X = Cl, Br, I; Y = Cl, Me) is functionalized with electrophiles such as MeCOCl or CCl_3NCO to yield the related derivatives with vinyl acrylates (R = OCOMe) or vinyl trichloroacetylcarbamate (R = $OCONHCCl_3$).[135]

8.09.2.1.3 Tetravalent derivatives

Alkene coordination to platinum(IV) remains relatively rare,[2] although it has been suggested as intermediate in the thermolysis of ethylplatinum(IV) complexes.[151] An interesting exception are the mononuclear complexes [PtCp*Me$_2$(η^2-CH$_2$═CHR)](Tf) (R = H, Me), formed by displacement of triflate in Pt(Tf)Cp*Me$_2$.[152]

8.09.2.1.4 Theoretical aspects

Recent reviews about theoretical studies in platinum and palladium chemistry and on the nature of the bonding in transition metal compounds are worth mentioning.[139,153] Numerous theoretical studies aimed at a better understanding of both the nature of the platinum–alkene bond, and its reactivity, have been published in the last decade. Most of these studies are based on quantum chemical calculations, and mainly focusing on geometries and binding energies.[154–160] Geometry optimization of binding of bare Pt to the π-bond in benzene, by an extensive *ab initio* study, leads to a structure in which the Pt atom binds one of the C═C bonds in an η^2-fashion.[154] The role of relativistic effects has been examined by computing the bond energies in M(η^2-C$_2$H$_4$)(PH$_3$)$_2$ (M = Ni, Pd, Pt), using a density functional method. The V-like trend within the triad (Ni >> Pt > Pd) is attributed to relativistic effects, which are very important for the 5*d*-elements.[155,156] The effect of the electron-attracting substituents on complexes M(η^2-C$_2$X$_4$)(PH$_3$)$_2$ (X = H, F, CN; M = Ni, Pd, Pt) have been found, by density functional calculations, in good agreement with crystal structure data, and, in terms of the D–C–D model, the contribution of the π-backdonation was found to dominate over that from σ-donation.[156] Recently, the nature of bonding interactions between the metal and ethene in M(η^2-C$_2$H$_4$)L$_2$ (M = Ni, Pd, Pt; L$_2$ = (PH$_3$)$_2$, (PMe$_3$)$_2$, PH$_2$(CH$_2$)$_n$PH$_2$ (n = 1, 2)) has been investigated with an energy partitioning analysis (EPA), indicating that the metal–carbon bonds have a higher electrostatic (57.8 – 62.3%) than covalent (42.2–37.7%) character.[157] DFT calculations predict that the ethylene ligand is more strongly bonded in complexes with bidentate phosphine ligands, and the EPA reveals that it is due to the smaller preparation energy of the ML$_2$ (L$_2$ = PH$_2$(CH$_2$)$_n$PH$_2$ (n = 1, 2)) fragments that is necessary to deform the metal fragment from the equilibrium geometry to the geometry in the complex.[157] The effect of the R substituents in the bonding energy in complexes Pt(η^2-CH$_2$CHR)(PH$_3$)$_2$ has been also evaluated by DFT/B3LYP calculations.[159] Geometries and binding energies have been calculated with high level theoretical methods for model complexes containing highly pyramidalized tricyclic alkenes Pt(PH$_3$)$_2$(R) (R = $C_{11}H_{16}$, $C_{10}H_{14}$, C_9H_{12}, and C_8H_{10}).[160] Charge-decomposition analyses show that the backdonation increases as the alkene becomes more pyramidal, and the natural-bond analyses reveal an increase in the Pt(6*s*) and C(2*s*) character of the Pt–C bond, in agreement with previous NMR studies.[19] The calculated bond-dissociation energy of $Pt^+(C_2H_4)$ varies from 223 to 261 kJ mol^{-1}, depending on the basis set used, being consistent with the experimental value of 230 kJ mol^{-1} and with a metallocyclopropane structure.[161] The key factors determining the stability of Pt(II) olefin complexes have been also examined by theoretical calculations.[84,162,163] For complexes M(η^2-C$_2$H$_4$)Cl$_x$(NH$_3$)$_{3-x}$ (M = Ni(II), Pd(II), Pt(II); x = 1, 2, 3), the ability to coordinate ethylene is in the expected order Pt > Pd > Ni.[162] The computed bonded energies for [M(R$_F$)$_3$(η^2-C$_2$H$_4$)]$^-$ (Pt = 18.6; Pd = 12.4; Ni = 10.9 kcal mol^{-1}) have been found to match the experimentally established stability, that is, in general, these organometallic species are less stable than the related [MCl$_3$(η^2-C$_2$H$_4$)]$^-$ (Pt = 34.1; Pd = 16.2; Ni = 8.2 kcal mol^{-1}).[84]

Theoretical calculations (HF, MP2, and DFT) predict a very low barrier for the insertion of the alkene into the Pt–H bond of cationic species [PtH(η^2-alkene)(PR$_3$)$_2$]$^+$ (R = H, Me, halide; alkene = C$_2$H$_4$, CH$_2$═CHCH$_3$),[164,165] and, in agreement with the experimental data for propene insertion, the linear propyl groups are favored over the branched ones.[165] Studies (DFT/B3LYP) on the migratory insertion in complexes [PtR(η^2-C$_2$H$_4$)(NH═CH–CH═NH)]$^+$ (M = Pt, Pd, Ni; R = Me, Et) and the subsequent β-hydride elimination process reveal that the barrier for migratory insertion is much higher in the platinum case (R = Me 25.5 vs. 10.4 kcal mol^{-1} for Ni).[163] The β-hydride elimination is exothermic for Pt and less endothermic for Pd than for Ni, which is consistent with $[PdMe(diimine)]^+$ being a polymerization catalyst promoting branched polyethylene.[163] Comparison of the insertion of ethylene into the Pt–H versus Pt–$SiMe_3$ bond for $PtH(SiH_3)(\eta^2\text{-}C_2H_4)(PH_3)$ indicates (HF/MP4SDQ levels) that the insertion into the Pt–SiH_3 bond is more difficult than insertion into the Pt–H bond, although it can be modulated by other factors such as the respective *trans*-influence of the spectator ligands.[166] A similar *trans*-influence has been found by density functional B3LYP calculations in $PtHX(\eta^2\text{-}C_2H_4)(PH_3)_2$ (X = Cl, $SnCl_3$), in which X is *trans* to the migrating hydrogen: the stronger *trans*-directing ligand provides the lower barrier.[167]

Catalytic cycles (or part of them) of some relevant processes such as the hydrosilylation of ethylene[168–170] or the disilylation of alkenes[171] catalyzed by Pt(0) bis(phosphine) complexes have been also the subject of several theoretical studies.[168–171]

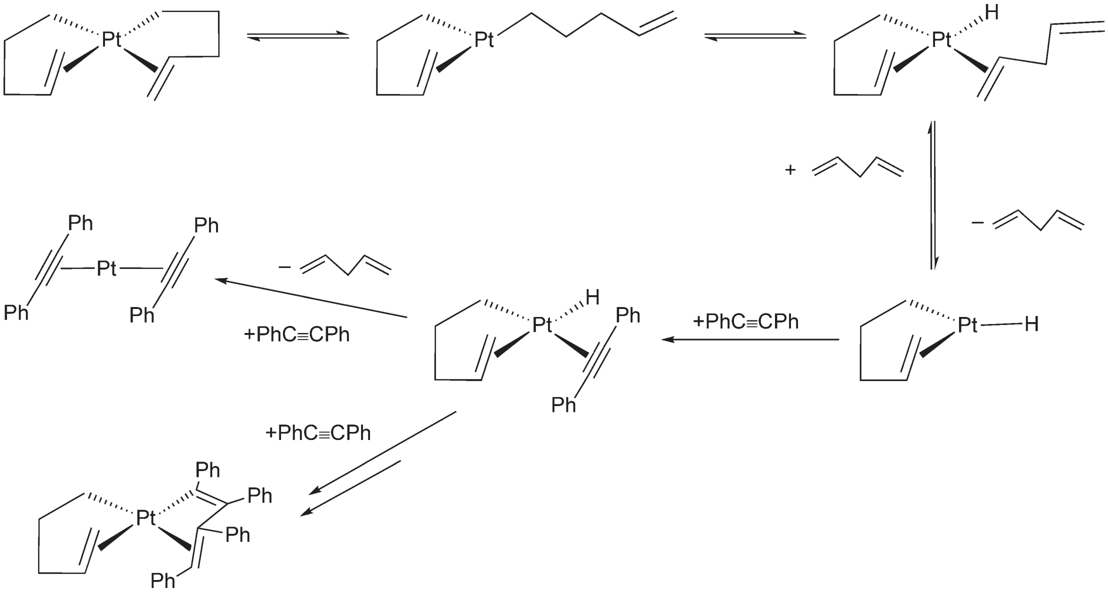
8.09.2.2 η^2-Monoalkene Complexes (Polydentate)

This section refers to mononuclear complexes with ligands having, in addition to a single η^2-alkene interaction, one (or more) additional donor atoms linked to the metal center. Most of the complexes reported are divalent derivatives.

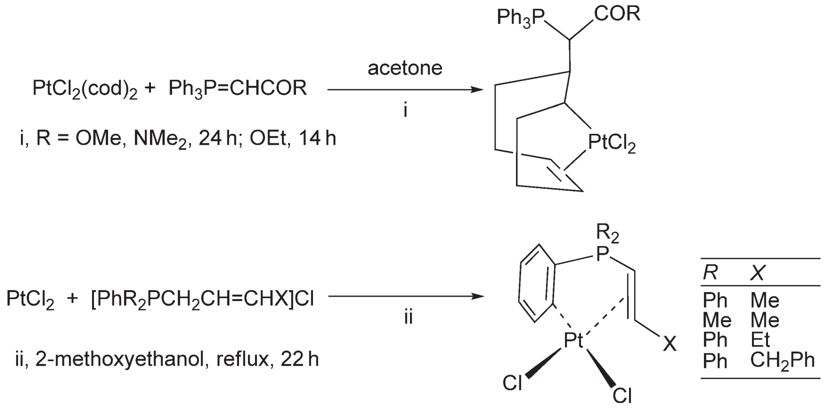
(i) *Group 14 donors* Pentacoordinate complexes $PtR\{\eta^1,\eta^2\text{-}CH(Y)O_2CCH{=}CHCO_2Me\}$(dmphen) (R = Me, Ph; Y = CO_2Et, $CONMe_2$, CN), formally derived from an intramolecular nucleophilic addition to a carbene intermediate, are generated by treatment of $[PtR(H_2O)(\eta^2\text{-}(Z)\text{-}MeO_2CCH{=}CHCO_2Me)(dmphen)]BF_4$ with diazoaceto reagents N_2CHY (Section 9.2.1.2(i)(d)). The structure of these complexes has been confirmed by an X-ray diffraction study (R = Me; Y = CO_2Et), revealing the presence of the new anionic chelating ligand $\{\eta^1,\eta^2\text{-}CH(CO_2Et)\text{-}O_2CCH{=}CHCO_2Me\}$, which spans one equatorial (alkene function) and one axial (alkyl carbon) site in the bipyramid.[112]

Treatment of $PtCl_2$(cod) with pent-4-en-1-ylmagnesium bromide yields *cis*-bis(η^1,η^2-pent-4-en-1-yl)platinum, containing two chelating pentenyl rings with both η^2-bound alkenes oriented *cis* to one another (X-ray). This complex has unusual volatility, which has proved useful for CVD of thin platinum films.[172] Its thermolysis in the gas phase and in aromatic solvents has been thoroughly examined (Scheme 7). Kinetic studies reveal the presence of a platinum hydride complex, which is chemically trapped with PhC≡CPh, to give the novel (η^2,η^1-pentenyl)(1,2,3,4-tetraphenylbuta-1,3-dien-1-yl)platinum(II) complex by successive insertion of two PhC≡CPh molecules, as confirmed by X-ray, and $Pt(\eta^2\text{-}PhC{\equiv}CPh)_2$.[172]

In contrast to the expected, and previously reported, compound $Pt(R_F)_2$(1-5-hexadiene),[173] the reaction of $PtCl_2$ (1-5-hexadiene) with LiC_6F_5 forms the aquo complex $Pt\{\eta^1,\eta^3\text{-}CH(CH_2C_6F_5)CH_2CH_2CH{=}CH_2\}(R_F)(H_2O)$, containing the



Scheme 7



R	X
Ph	Me
Me	Me
Ph	Et
Ph	CH2Ph

Scheme 8

1-pentafluorophenylhex-5-en-2-yl ligand, in low yield, as verified by X-ray diffraction. Its formation implies nucleophilic attack of C_6F_5 on both platinum and one alkene unit (*anti*-Markovnikov), followed by aquation *trans* to the alkyl carbon on hydrolytic workup.[174] New compounds containing η^1,η^2-cyclooctenyl-substituted ligands have been reported.[175,176] Interesting examples containing metallated phosphonium salts result from reaction of $PtCl_2$(cod) with carbonyl-stabilized phosphorus ylides (Scheme 8, i),[176] but attempts to isolate similar complexes with the less basic $Ph_3P{=}CHCOPh$ have proved to be unsuccessful. The mono- and dicationic complexes $[PtCl\{\eta^1,\eta^2\text{-}C_8H_{12}CH(PPh_3)CO_2Et\}(py)](ClO_4)$ and $[Pt\{\eta^1,\eta^2\text{-}C_8H_{12}CH(PPh_3)CO_2Me\}(py)_2](Tf)_2$ were generated by removing one or both chloro ligands with $AgClO_4$ or TlTf, respectively, and treatment with 1 or 2 equiv. of py. X-ray diffraction studies for one neutral complex (R = OMe), and for the dicationic derivative, confirm that the compounds are produced by an *exo*-attack of the carbon nucleophilic ylide to one olefinic unit of the cod ligand, and the NMR data indicate that the attack generates only one enantiomer couple (*RSR*/*SRS*). Extension of these studies to other $PtCl_2$(diene) (diene = 1,5-hexadiene, dicyclopentadiene, 4-vinylcyclohexa-1-ene, nbd) complexes gives rise to related complexes resulting from nucleophilic attack of the ylide ($Ph_3P{=}CHCO_2R$ (R = Me, Et)) at one of the olefinic carbons. Crystal structures of $PtCl_2\{\eta^1,\eta^2\text{-}C_6H_{10}CH(PPh_3)CO_2Et\}$, $PtCl_2\{\eta^1,\eta^2\text{-}C_{10}H_{12}CH(PPh_3)CO_2Me\}$, and $PtCl_2\{\eta^1,\eta^2\text{-}C_8H_{12}CH(PPh_3)CO_2Me\}$ indicate an *exo*-attack in the case of the dicyclopentadiene complex, and *anti*-Markovnikov addition in the other two compounds.[144] Orthometallated vinyl phosphonium complexes (Scheme 8, ii) are formed by reaction of $PtCl_2$ with allylphosphonium salts, as confirmed by an X-ray diffraction study of the complex with R = Ph and X = Me.[177] In the reaction with $[Ph_3PCH_2CH{=}CHPh]ClO_4$, the zwitterionic η^2-olefin complex $Pt^-Cl_3(\eta^2\text{-}CHPh{=}CHCH_2P^+Ph_3)$ is also generated, and has been characterized by X-ray crystallography. The orthometallated vinyl complexes are suggested to be formed starting from a platinum allyl–ylide complex $PtCl_2$ (η^3-$CH_2CHCHPPh_3$), generated by C_α-dehalogenation of the phosphonium salt, followed by C(phenyl)–H bond activation, and final rearrangement to the orthometallated vinyl derivatives.[177]

(ii) *Group 15 and 16 donors* An interesting example in this category (involving a tridentate N,N-olefin) is generated by thermolysis of $Pt(nacnac)Me_3$ in benzene (Section 9.2.1, Scheme 4), which affords an olefin–hydrido platinum(II) complex, where the olefin is part of a nacnac-type ligand. The structure has been confirmed in the analogous olefin–deuterido d_{27}-complex, with the Pr^i groups, the hydride, and the isopropenyl unit, deuterated. It is suggested to be formed by a mechanism involving a reversible sequence between unsaturated five-coordinate Pt(IV) and three-coordinate Pt(II) species.[100] A cationic olefin–hydride intermediate platinum(II) complex, with a generated tridentate N,N-olefin ligand, has been also identified in the total synthesis of the antimicotic Rhazinilam.[178] In the same manner, treatment of $PtCl_2$ with *cis*-1,2-bis-[N,N-(dimethylamino)methyl]cyclohexane affords *cis*-$[PtCl_2(C_7H_{11}CH_2NMe_2)]$, containing a chelating (η^2,η^1N) dimethyl[(2-methylidenecyclohex-1-yl)methyl]amino group arising from a metal-catalyzed intramolecular elimination of NMe_2H.[179] Similar complexes are generated using ligands with alkenyl fragments in the backbone. Thus, reaction of PtX_2(cod) (X = Cl, Me) with 1 equiv. of diallylaminodiphenylphosphine gives *cis*-$PtX_2\{PPh_2N(CH_2CH{=}CH_2)_2\}$, featuring η^2-alkene and η^1-P coordination, as confirmed by an X-ray structure for the related palladium complex $PdCl_2\{PPh_2N(C_3H_5)_2\}$,[180] and with the polydentate tri(1-cyclohepta-2,4,6-trienyl)phosphine $P(C_7H_7)_3$, the related $PtCl_2\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}$ is generated.[181] Treatment of $[PtCl_4]^{2-}$ with di(silaalkenyl)chalcogeno ether ligands $E(CH_2\text{–}SiMe_2\text{–}CH{=}CH_2)_2$ (E = S, Se) yields *cis*-$[PtCl_2L]$ complexes, in which the ligands bind in a bidentate fashion via η^2-alkene and η^1-E (S, Se). Analogous bromo and iodo derivatives are prepared by metathesis of the chloro derivatives. The structure of *cis*-diiodo(3,3,7,7-tetramethyl-5-thia-3,7-disilanona-1,8-diene)platinum(II) has been verified by X-ray crystallography.[182] Similar compounds *cis*-[PtX_2L] (L = Te{$CH_2ER^1{}_2$–C(R^2=CH_2)}$_2$) ($R^1 = R^2 = H$, E = C, Si; R^1 = Me, R^2 = H, E = C), featuring both η^2-alkene and η^1-Te, have been synthesized using $PtX_2(dmso)_2$ as precursor.[183] NMR studies indicate dynamic behavior, involving facile exchange of the alkene moieties.[182,183] Itaconate zwitterionic derivatives Pt(ita)(N,N) (N,N = 2,2-dimethyl–1,3-propanediamine (dmpda), tetrahydro-4H-pyran–4,4-diyl-bis(methylamine) (thpdma), *trans*-(±)-1,2-diaminocyclohexane (dach), en; ita = $O_2CCH_2C({=}CH_2)CO_2{}^{2-}$)[184] have been prepared from reactions between PtX_2(N,N) and barium itaconate. NMR and X-ray data for Pt(ita)(dmpda)(confirm an ethylene–β-O chelating coordination mode for the itaconate ligand, probably favored by the presence of an intramolecular hydrogen bond between the oxygen of dangling carboxylate and a *cis*-atom of the dmpda ligand.[184]

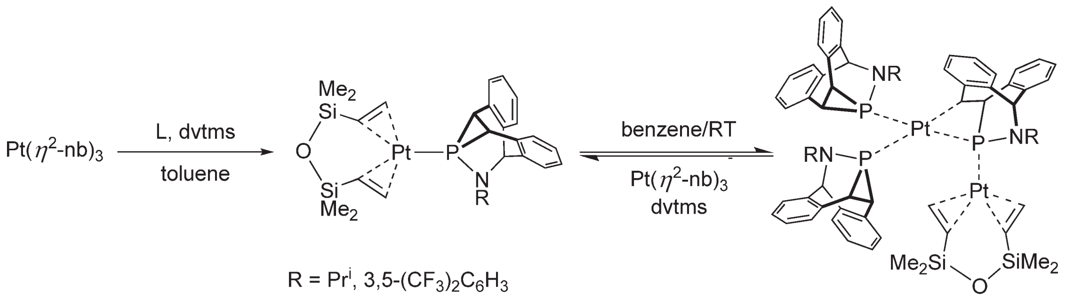
8.09.2.3 η^n-Polyene Complexes (Unconjugated)

8.09.2.3.1 Zerovalent derivatives

Although, in general, studies of η^2-polyene complexes of Pt(0) have continued to involve other unsaturated fragments or phosphines as ancillary ligands, some new examples with carbene ligands have appeared. Most of them display three (16-electron) coordinated structures. Particular attention has been devoted to complexes containing only alkene ligands, because they are useful sources for ligand-free Pt atoms, and have been widely used as catalyst precursors.

8.09.2.3.1.(i) Preparation

A simple method for the synthesis of $Pt(cod)_2$, $Pt(\eta^2\text{-nb})_3$, and the homoleptic $Pt_2(dvtms)_3$ (dvtms = 1,3-divinyl–1,1,3,3-tetramethyldisiloxane) by reduction of $PtCl_2(cod)$ or $PtCl_2(NCPh)_2$ (for the complex with norbornene) with SmI_2, in the presence of the appropriate alkene ligand, have been reported.[10] Reduction of $PtCl_2(cod)$ with Li_2cot in hepta-1,6-diene yields the homoleptic dimer $Pt_2(\eta^2,\eta^2\text{-}C_7H_{12})(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_7H_{12})$, which is employed as a precursor of $Pt(\eta^2,\eta^2\text{-}C_7H_{12})L$ (L = η^2-C_7H_{12}, η^2-C_2H_4, PPh_3, $PPr_3{}^i$, PMe_3) by subsequent treatment with additional L.[185] Similar replacement of the bridging divinylsiloxane in $Pt_2(dvtms)_3$ (Karstedt catalyst solution) with di-, tri-, or tetrasubstituted electron-withdrawing alkenes (Me–fu, dimethylmaleate,[186] fn, Et–fu, TCNE, (*E*)-PhCOCH=CHCOPh, ethylenetetracarboxylate, several naphthoquinones and dihydronaphthoquinones)[186,187] affords novel complexes of type $Pt(\eta^2,\eta^2\text{-dvtms})(\eta^2\text{-alkene})$. Similar reactions with monosubstituted olefins do not yield the desired products.[187] Complexes $Pt(\eta^2\text{-nb})_2(\eta^2\text{-alkene})$ were prepared from $Pt(\eta^2\text{-nb})_3$ and electron-poor alkenes (dimethylmaleate, ma, several fumarates, and fumaric acid),[188] even using an excess of alkene. However, treatment of $Pt(\eta^2\text{-nb})_2(\eta^2\text{-ma})$ with py yields $Pt(\eta^2\text{-nb})(\eta^2\text{-ma})py$.[188] Nitrogen-containing triolefinic 15-membered macrocycles, such as (*E*,*E*,*E*)-1,6,11-tris(arenesulfonyl)–1,6,11-triazacyclopentadeca–3,8,13-triene (L), also form stable complexes with Pt(0) of type $Pt(\eta^2,\eta^2,\eta^2\text{-L})$.[189] $Pt(\eta^2\text{-nb})_3$ reacts with *BABAR*-Phos- (L) type phosphiranes and dvtms or ma to yield $Pt(\eta^2,\eta^2\text{-dvtms})$(*BABAR*-Phos) (see Equation (5)) or $Pt(\eta^2\text{-nb})(\eta^2\text{-ma})$(*BABAR*-Phos) (*BABAR*-Phos = phosphaazabarbaralane).[190] Very stable $Pt(carbene)(\eta^2\text{-Me–fu})_2$ complexes are formed by displacement of cod ligands in $Pt(cod)_2$ with free carbene (carbene = 1,3-dimesitylimidazol–2-ylidene (IMes), 1,3-dimesityldihydroimidazol–2-ylidene) and Me–fu.[191] A related $Pt(IMes)(\eta^2\text{-nb})(\eta^2\text{-ma})$ complex has been reported, by using $Pt(\eta^2\text{-nb})_3$ as precursor and ma.[192] Complex $Pt(\eta^2\text{-}C_2H_4)_2(dppo)$ (dppo = $Ph_2PCH_2CH_2CH_2POPh_2$) is formed from $[Pt(dppp)(\mu\text{-O})]_2(LiTf)_2$ and ethylene, by an unusual oxygen atom transfer to one arm of the bidentate ligand.[193]



(5)

R = Pr^i, 3,5-$(CF_3)_2C_6H_3$

dvtms = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane

R = 3,5-$(CF_3)_2C_6H_3$

8.09.2.3.1.(ii) Structural aspects

As expected, the crystal structures of complexes $Pt(\eta^2\text{-ma})(\eta^2\text{-nb})_2$ and $Pt(\eta^2\text{-Ph–fu})(\eta^2\text{-nb})_2$ indicate a trigonal-planar arrangement of the double bonds.[188] For complex $Pt(\eta^2,\eta^2\text{-dvtms})(\eta^2\text{-Menq})$ the structure confirms that the methylnaphthoquinone ligand is bound by its olefinic double bond and that the divinyldisiloxane ligand adopts a chair conformation.[187] In this complex, the divinyldisiloxane ligand adopts a chair conformation.[187] NMR data of complexes $Pt(\eta^2,\eta^2\text{-}C_7H_{12})L$ indicate that the hepta-1,7-diene also assumes a locally C_s-symmetrical chairlike conformation in the ground state.[185] By contrast, NMR studies of $Pt(\eta^2,\eta^2\text{-dvtms})(PBu^t{}_3)$ suggest that this complex probably undergoes a facile dissociation–reassociation process in solution, involving the alkene fragments.[194] By using $Pt(\eta^2\text{-nb})_2(\text{alkene})$[188] as catalysts in the hydrosilylation of styrene with $HSiEt_3$, it has been suggested that the strength of the Pt–alkene bond decreases in the following order: fumarate $\approx$ maleate $>$ ma $>$ 2-methylnapthoquinone $\approx$ *p*-benzoquinone $>$ nb.

8.09.2.3.1.(iii) Reactions

Zerovalent polyene complexes are mentioned as reagents throughout this chapter, and they are also versatile precursors for the preparation of polymetallic species, being adequate sources, in many instances, of naked platinum centers,[195,196] or Pt(cod) entities[197,198] (see also Sections 9.2.7 and 9.2.8). Their potential for the synthesis of silyl and boryl complexes has been reviewed.[51,69,199] Insertion of platinum into C–Sn,[200,201] C–Si,[202] and Si–Sn[203] bonds yielding stannyl and silyl–stannyl platinum(II) complexes have been also reported. Thus, $Pt(cod)_2$ reacts with tin-bridged [1]ferrocenophane, $Fe(C_5H_4)_2SnBu^t{}_2$, to afford the novel trimetallic 1-stanna-2-platina[2]-ferrocenophane, $Fe(C_5H_4)_2SnBu^t{}_2Pt(cod)$, as confirmed by an X-ray study.[201] 1,2-Diphenyl-3(dicyanomethylene)cyclopropene reacts, via a ring-opening reaction, with $Pt(cod)_2$, yielding a platinacyclobutene complex, $\overline{Pt\{CPh{=}CPhC{=}C}(CN)_2\}(cod)$, or a 1,3-diphenylpropanediylidene-bridging complex, $Pt_2\{\mu\text{-}(PhC)_2C{=}C(CN)_2\}(cod)_2$, depending on the molar ratio.[59] An interesting example of insertion into a P–C bond is given in Equation (5). The binuclear mixed-valent Pt(II)–Pt(0) phosphido-bridged complex $Pt_2(^{3,5CF}{}_3\,\textit{BABAR}\text{-Phos})_2(\mu\text{-}^{3,5CF}{}_3\,\textit{BABAR}\text{-Phos})(\text{dvtms})$ is generated by intermolecular insertion of a platinum fragment into one P–C bond, as has been confirmed by X-ray crystallography. The process is reversible, and the binuclear complex reverts to the mononuclear one on treatment with $[Pt(\eta^2\text{-nb})_3]$ and dvtms.[204]

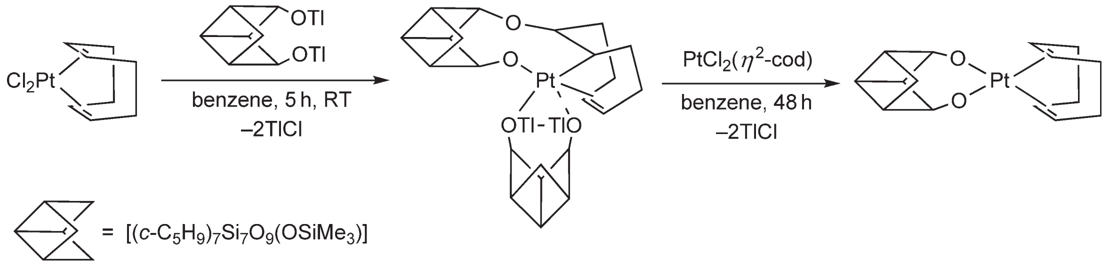
Hydride transfer from metal hydride complexes, such as $ReH_7(\text{dbpe})$[205] or $FeH(SiOMe)_3(CO)_3(\text{dppm-}P)$,[198] to an olefinic unit of $Pt(\eta^2\text{-}C_2H_4)_2L$ ($L = $ phosphine, C_2H_4) or $Pt(\eta^2\text{-nb})_3$, probably through a Pt–H intermediate, yields ethyl and η^1-norbornyl bimetallic derivatives $Re(\text{dbpe})H_6PtR(\text{phosphine})$ or $(CO)_3Fe(\mu\text{-}SiOMe)(\mu\text{-dppm})PtR$ ($R = C_2H_5$, C_7H_{11}).[198,205]

8.09.2.3.2 Divalent derivatives

Most of the complexes reported in this section contain 1,5-cod, probably because this diene is easily displaced in subsequent reactions with other ligands and metalloligands, thus providing an easy entry to novel mono- and polynuclear platinum complexes.

8.09.2.3.2.(i) Preparation

The most frequent preparative route to this type of complex involves halide substitution in appropriate precursors. A standard procedure for the synthesis of the widely employed complex $PtMe_2(cod)$ has been reported.[206] To gain an understanding of Pt-catalyzed hydrosilation processes, the preparation of alkene–silyl complexes is desirable. Bis-silyl complexes $Pt(SiR_3)_2(cod)$ ($SiR_3 = SiCl_3$, $SiMeCl_2$, $SiMe_2Cl$, $SiMe_2Ph$) are formed by direct reaction of $PtCl_2(cod)$ with 4 equiv. of the corresponding hydrosilanes, in the presence of a small excess of cod.[207] These complexes are generated from unusual initial diplatinum species $[Pt(SiR_3)(\mu\text{-}Cl)(\eta^2\text{-cod})]_2$, which are the final products using only 2 equiv. of the corresponding hydrosilanes.[207] The bis(silyl) derivatives are suggested to be formed via pentacoordinate silyl Pt(IV) intermediate species, stabilized by a η^1,η^2-cyclooctenyl ligand. An unusual hydroxo product $Pt(OH)(Me)(cod)$ is generated from the solvento complex $[Pt(Me)(cod)(\text{solvent})]^+$ and KOH.[208] Subsequent reaction of this hydroxo complex with acidic substrates, $PhC{\equiv}CH$, $HC{\equiv}C\text{–}C{\equiv}CH$, or even acetone, leads to $PtR(Me)(cod)$ ($R = C{\equiv}CPh$, CH_2COCH_3) or the diplatinum complex $\{PtMe(cod)\}_2(\mu\text{-}C{\equiv}C\text{–}C{\equiv}C)$.[208] Simultaneous activation of the Pt–I bond and the C–H bond of acetone, leading to the product $PtPh(CH_2COMe)(cod)$, is observed in the reaction of $PtIPh(cod)$ with Ag_2O, as confirmed by an X-ray diffraction study.[209] Partial disproportionation of this complex generates a mixture of $PtIPh(cod)$, $PtPh_2(cod)$, and the bis(acetonyl) product $Pt(CH_2COMe)_2(cod)$ 75 : 13 : 12.[209] Cyclooctadiene complexes containing ureylene ligands $\overline{Pt(NR^1CONR^2})(cod)$ (R^1, $R^2 = $ alkyl, aryl) have been obtained by reaction of $PtCl_2(cod)$ with the appropriate urea and an excess of Ag_2O, as confirmed



Scheme 9

by an X-ray structure of $\overline{\mathrm{Pt(PhNCON}}\mathrm{Ad)(cod)}$ (Ad = 1-adamantyl).[210] Insertion of phenylisocyanate or acetylenedicarboxylate into the Pt–NPh or Pt–NMe linkages of the ureylene fragments have been also reported.[211] The silsesquioxane product $Pt\{(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)O_2\}$(cod) is formed by the reaction of $PtCl_2$(cod) with 1 equiv. of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OTl)_2$, via an unusual $PtTl_2$ trinuclear intermediate containing a siloxo metallacycle, derived from a formal migration of a Pt–O–Si unit to one olefinic function, as confirmed by X-ray (see Scheme 9).[212] This complex together with $Pt(OSiPh_3)_2$(cod)[213] are rare examples of organometallic siloxo complexes of platinum(II). The related complex $Pt(SSiMe_3)_2$(cod), obtained from PtI_2(cod) and $NaSSiMe_3$, has also been reported.[214]

Reaction of the Zeise dimer with ethenoanthracene affords $PtCl_2(\eta^2,\eta^2\text{-}C_{16}H_{12})$, featuring an unusual η^2-(alkene),η^2-(arene) bidentate coordination mode.[215] A bridge-splitting reaction of $[PtCl_2(\eta^2\text{-}C_8H_{14})]_2$ with an excess of coe forms a unique complex *trans*-$[PtCl_2(\eta^2\text{-}C_8H_{14})_2]$.[216,217]

8.09.2.3.2.(ii) Structural aspects

Many derivatives with 1,5-cod have been characterized by X-ray diffraction studies.[207–212,218,219] Only salient features are outlined here. In the complex $Pt(SiMeCl_2)_2$(cod), it is of particular interest to note the longer (by about 0.17 Å) Pt–C(olefinic) bond distances compared with those in $PtCl_2$(cod), due to the strong *trans*-influence of the silicon, which correlates with the NMR data.[207] The crystal structure of $PtCl_2(C_{16}H_{12})$ reveals that the ethenoanthracene ligand coordinates in a bidentate η^2,η^2-fashion through the alkene fragment, which acts as an anchor, and a double bond of one of the arene units.[215] As expected, the Pt–M(arene) distance (2.22(4) Å) is longer than the Pt–M(alkene) distance (1.98 Å) (M = midpoint of the C=C bond), reflecting the stronger coordination of the latter.[215] In the complex *trans*-$[PtCl_2(\eta^2\text{-}C_8H_{14})_2]$, the X-ray structure,[216,217] which confirms the perpendicular coordination of both C=C bonds, shows very long Pt–C(olefin) bonds (av. 2.273(6) Å), reflecting a significant labilization of the coe ligand, in agreement with thermodynamic data.[216]

Principal values of ^{13}C chemical shift tensors have been measured for PtXY(diene) (X = Y = Me, $C{\equiv}CBu^t$, CH_2SiMe_3; X = Me, Y = Cl; diene = cod and X = Y = Me, $(4\text{-}Bu^t)C_6H_4$, CH_2SiMe_3; diene = nbd), showing a very large anisotropy induced by the presence of the chelating diolefin.[220] The spectroscopic and photochemical properties of PtR_2(cod) (R = alkyl, alkynyl, aryl) have been complemented with DFT theoretical calculations, which reveal that the high-lying occupied orbitals are not exclusively located on the Pt atom.[221] For alkyl derivatives, the contribution of the R ligand increases with increasing σ-donor strength of the ligand, and, for the aryl and alkynyl systems, their π-orbitals form to a large extent the high-lying occupied orbitals of the molecule. As a consequence, the complexes are photoreactive, and irradiation of the alkyl derivatives leads to the formation of radicals, whereas the alkynyl complex generates a R–R coupling product by a concerted pericyclic way.[221]

8.09.2.3.2.(iii) Reactions

Two reviews about the chemistry of metallacyclic complexes include reactivity of relevance to this section.[222,223]

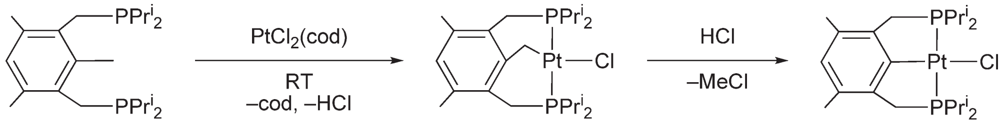
8.09.2.3.2.(iii).(a) Diene displacement

A common feature of diene, in particular 1,5-cod, metal chemistry is substitution; 1,5-cod may be displaced by a range of phosphorus, nitrogen, or mixed P-N donor ligands. For example, stable complexes with secondary phosphine ligands *cis*-$[Pt(C{\equiv}CR)_2(PPh_2H)_2]$,[224] or unstable derivatives with primary phosphines *cis*-$[PtCl_2(PH_2Ar)_2]$ (Ar = $2,4,6\text{-}(Pr^i)_3C_6H_2$, Me)[225] have been prepared from the corresponding cod precursors. However, similar reactions of $Pt(C{\equiv}CR)_2(cod)_2$ with PPh_2OH affords $Pt\{(PPh_2O)_2H\}(C{\equiv}CR)(PPh_2OH)$.[224] Displacement of cod from *cis*-[PtX_2(cod)] by phosphites $P(OR)_3$ (R = (2-OMe)C_6H_4) and *N*-pyrrolidinyl phosphines $P(C_4H_8N)_2R$ (R = C_4H_8N, Ph, Me) exclusively gives the corresponding *cis*-bis(phosphine) derivatives *cis*-[$PtX_2\{P(OR)_3\}_2$][226] and *cis*-[$PtCl_2\{P(C_4H_8N)_2R\}_2$],[227] respectively, although the sterically bulky *tert*-butyldi(pyrrolinyl)phosphine does not give the desired product. The reactions of $PtCl_2$(cod) with the amino-functionalized aminophosphines $Ph_2PN(R)CH_2CH_2NMe_2$ (R = H, Me)[228] yield *cis*-[$PtCl_2L_2$] or *cis*-[$PtCl_2$(L-κ^2*P*,*N*)] (R = Me), depending on the molar ratio 1 : 2 or 1 : 1. However, similar reactions with a variety of tertiary amine-functionalized phosphines give either *cis*- or *trans*-complexes, depending on the cone angle of the phosphines.[229] Displacement of cod in PtR_2(cod) (R = Me, Ph) by the enantiomerically pure P,N ligand (4*S*)-2-(2-(diphenylphosphino)phenyl)–4-isopropyl–1,3-oxazoline affords PtR_2((*S*)-P,N) as single isomers;[230] cod is easily displaced in complexes *cis*-PtR(SnX_3)(cod) (R = Ph, SnX_3 = $SnPh_2Cl$, $SnPhCl_2$; R = Me, SnX_3 = $SnMe_3$) and *cis*-PtCl(SnX_3)(cod) (SnX_3 = $SnMe_3$, $SnMe_2Cl$, $SnCl_3$) by phosphines and diphosphines, giving phosphine complexes, which in some cases are not accessible by other routes.[200] Similar displacements using N,N donor[231] and CN^-[232] ligands have been also exploited. Extension of this reaction chemistry to sulfur[233,234] and phosphorus[235] metalloligands has provided an easy entry to polynuclear platinum complexes.[233–235]

8.09.2.3.2.(iii).(b) *Miscellaneous: nucleophilic additions, insertions, migrations*

Nucleophilic addition reactions to dienes provide a facile synthesis to chelating η^1,η^2-ligands. Several examples have been commented upon in Section 9.2.2 (see Scheme 8), particularly remarkable being the nucleophilic addition of the soft carbon of ylides, yielding products stabilized by a metallated phosphonium salt.[144,176] An interesting example in this category is shown in Scheme 9, $PtCl_2$(cod) reacting with 2 equiv. of the thallium silsesquioxane [(*c*-$C_5H_9)_7Si_7O_9(OSiMe_3)(OTl)_2$] to give a trinuclear $PtTl_2$ product, which is formed by a formal nucleophilic attack from SiO^- to a C=C bond of a coordinated 1,5-cod.[212] Subsequent reaction of this complex with 1 equiv. of additional $PtCl_2$(cod) generates Pt{(*c*-$C_5H_9)_7Si_7O_9(OSiMe_3)O_2$}(cod), implying formal β-elimination of the Si–O^- unit.

Activation of the C–C bond in the pincer ligand P–C–P (Equation (6)) has been achieved with $PtCl_2$(cod). The initial kinetic C–H activation product was quantitatively converted into the C–C activation product, by subsequent treatment with HCl.[236] Complex PtIPh(cod) reacts with TBA^+OH^- (TBA = tetra-*n*-butylammonium) giving $PtPh_2$(cod) via an intramolecular phenyl transfer, involving the hydroxo-bridged diplatinum complex {PtPh(cod)}$_2$(μ-OH) as intermediate, as confirmed by experimental data and X-ray diffraction.[237] Facile rearrangement of $PtPh_2$(cod) and $Pt(CH_2COCH_3)_2$(cod), to form a mixture of both complexes with the mixed monoacetonyl complex $Pt(CH_2COCH_3)Ph$(cod) (17 : 17 : 66), in acetone or benzene is suggested to occur via an intermediate diplatinum complex with bridging Ph and acetonyl groups.[209] The stannyl derivative PtCl($SnMe_3$)(cod) is unstable, even in the solid state, either at room or low temperature, evolving to some extent to the isomeric derivative PtMe($SnMe_2Cl$)(cod) via an unknown intermediate.[200]



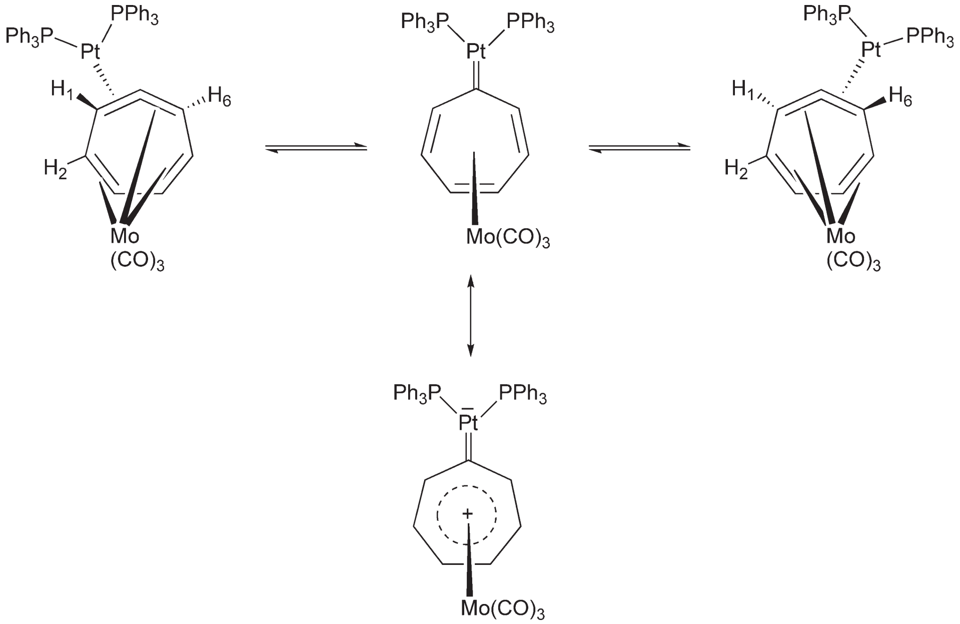
(6)

8.09.2.4 η^2-Allene, η^2-X=CR_2, and Related Complexes

Comprehensive reviews of the chemistry of heavy allenes and cumulenes,[238] heteroaldehyde,[239] heteroketone,[239] phosphaalkene[240,241] and η^1-ketenyl (η^1-C(PPh_3)=CO)[242] complexes, which include platinum complexes, have been published. A review of transition metal complexes of arynes, strained cyclic alkynes, and strained cyclic cumulenes also includes information relative to this section.[243]

8.09.2.4.1 η^2-Allene and cumulene derivatives

Replacement of the ethene ligand in Pt(η^2-C_2H_4)$(PPh_3)_2$ with 1,1-difluoroallene affords selectively Pt(η^2-CH_2=C=CF_2)$(PPh_3)_2$, with the allene coordinated through the double bond containing the hydrogen-substituted carbon, as confirmed by X-ray diffraction.[244] The strength of the Pt–C(allene) bond is reflected in the bend-back angle at the central C atom (138.9(3)°) and in the NMR data, which show that the complex is rigid on the NMR timescale even at 100 °C.[244] Spin saturation transfer has been used to study the fluxionality of Pt(η^2-C_7H_6)$(PPh_3)_2$ (C_7H_6 = 1,2,4,6-cycloheptatetraene) and of the related bimetallic complex $Pt(PPh_3)_2$(μ-η^2 : η^6-C_7H_6)$Mo(CO)_3$.[245] The migration of the platinum fragment between the two cumulene double bonds in the mononuclear complex



Scheme 10

takes place at 80 °C, by both an intermolecular and an intramolecular mechanism. In the Pt–Mo product, the process occurs at lower temperatures, and an intramolecular mechanism via an achiral intermediate with a significant tropylium character (see Scheme 10) has been proposed.[245] Although attempts to obtain the mononuclear complex Pt(η^2-$C^{2,3}$-1,2,3,5–C_7H_6)(PPh_3)$_2$ have proved to be unsuccessful, the related bimetallic complex Pt(PPh_3)$_2${(μ-η^2 : η^6-C_7H_6)Mo(CO)$_3$} containing a butatriene entity has been generated by reduction of the corresponding tropyne complex [Pt(PPh_3)$_2${(μ-η^2 : η^7-C_7H_5)Mo(CO)$_3$}]BF_4.[246]

Anionic divalent platinum(II) derivatives [$PtCl_3$(η^2-$MeR^1C{=}C{=}CHR^2$)]$^-$[(*S*,*S*)-(1-NpMeCH)$_2$$NH_2$]$^+$, prepared from the corresponding [$PtCl_3(C_2H_4)$]$^-$[AmH]$^+$ (Am = *S*,*S*-(1-NpMeCH)$_2$NH) by displacement with chiral trisubstituted allenes, exhibit well-separated ^{195}Pt NMR resonances, thus allowing the determination of the enantiomeric purity.[247] It was found that the signals of the (*R*)-enantiomers appear downfield with respect to those of the (*S*)-enantiomers.[247] Related complexes *trans*-[$PtCl_2${(*S*)-α-phenylethylamine}($R^1R^2C{=}C{=}CHR^3$)] (R^1,R^2 = alkyl; R^3 = alkyl, aryl) are generated from the corresponding *trans*-ethene platinum derivative and the appropriate allene, and the ee of the allenes have been also determined by ^{195}Pt spectroscopy.[248] Similarly, 1,1-dimethylallene reacts with PtClR(N,N) to yield the corresponding pentacoordinate complexes PtClR($Me_2C{=}C{=}CH_2$)(N,N) (R = Me, Et, C_6H_4OMe-4; N,N = dmphen, pimpy) having the allene in the equatorial plane and coordinated through the less-substituted double bond. Chloride abstraction in these pentacoordinate complexes affords cationic allyl derivatives, [Pt(CH_2CRCMe_2)(N,N)]BF_4 (see Section 9.4.1.1), through migratory insertion of R to the coordinated allene.[109]

8.09.2.4.2 Complexes of η^2-X=CR_2 and related derivatives

The chemistry of ketenylidenetriphenylphosphorane $Ph_3P{=}C{=}C{=}O$ has been recently reviewed. Its behavior is typical of ylides forming η^1-ketenyl complexes with Pt(II) and other metals that can be viewed as metal-substituted ketenes.[242]

The ^{31}P and ^{13}C MAS NMR spectra of the bis-ketene complex M(η^2-*C*,*C*′-O=C=C=C=O)(PPh_3)$_2$, as well as theoretical calculations, are in agreement with an η^2-*C*,*C*′ coordination mode confirming the presence of two different M–C bonds.[249] Several (η^2-thiocarbonyl) platinum complexes Pt(η^2-$R_2C{=}S$)(PPh_3)$_2$ (R_2 = Ph_2, C_9H_{14})[250] and Pt(η^2-(1-Ad)$Bu^tC{=}S$)(PPh_3)$_2$[251] (Ad = adamantyl) are accessible by displacement of ethene in Pt(η^2-C_2H_4)(PPh_3)$_2$, but have also been generated by other routes.[250,251] Thus, treatment of dithiirane (Bu^t)(1-Ad)CS_2 with Pt(η^2-C_2H_4)(PPh_3)$_2$ also gives the (η^2-thiocarbonyl) platinum complex in high yield[251] and the reaction 3,3,5,5-tetraphenyl-1,2,4-trithiolane with a twofold excess of Pt(η^2-C_2H_4)(PPh_3)$_2$ gives a mixture of $\overline{\text{Pt(SCPh}_2\text{S}}$)($PPh_3$)$_2$ and Pt(η^2-$Ph_2C{=}S$)(PPh_3)$_2$.[250]

The chemistry of phosphaalkenes,[240,241] phosphaketenes, and phosphaazallenes has been reviewed.[238] Pt{η^2-$Bu^tC(H)=PH$}(dppe), containing the unstable η^2-ligated *tert*-butylphosphaalkene,[252] and Pt{η^2-$Bu^tC(H)=P$–$P=C(SiMe_3)_2$}(dppe),[253] with the η^2-2,3-diphosphabutadiene ligand, have been prepared via initial hydrozirconation of Pt(η^2-$P\equiv CBu^t$)(dppe) with ZrH(Cl)Cp$_2$ to yield the η^2-metallaphosphaalkene (dppe)Pt{η^2-$Bu^tC(H)=PZrClCp_2$}, followed by protonolysis[252] or subsequent treatment with $ClP=C(SiMe_3)_2$[253] respectively. Adducts PtL$_2${η^2-(*P*,*C*)-Mes*P=C=NPh} (L$_2$ = ½ dppe, PPh$_3$, PCy$_3$; Mes* = 2,4,6-(Bu^t)$_3$C$_6$H$_2$) are easily formed starting from the appropriate "PtL$_2$" sources and Mes*P=C=NPh.[254] The complex with dppe is stable and can be isolated, whereas the products with PPh$_3$ and PCy$_3$ are unstable in solution. By contrast, treatment of Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ and Pt(PCy$_3$)$_2$ with the phosphaketene, Mes*P=C=O, gives rise to the diphosphaureylene carbonyl complexes PtL(CO)-(Mes*PCOPMes*) (L = PPh$_3$, PCy$_3$), which result formally from decarbonylation of the phosphaketene and coupling of the resulting phosphinidene intermediate with another molecule of the cumulene.[255]

8.09.2.5 η^2-Polyalkene Complexes (Conjugated)

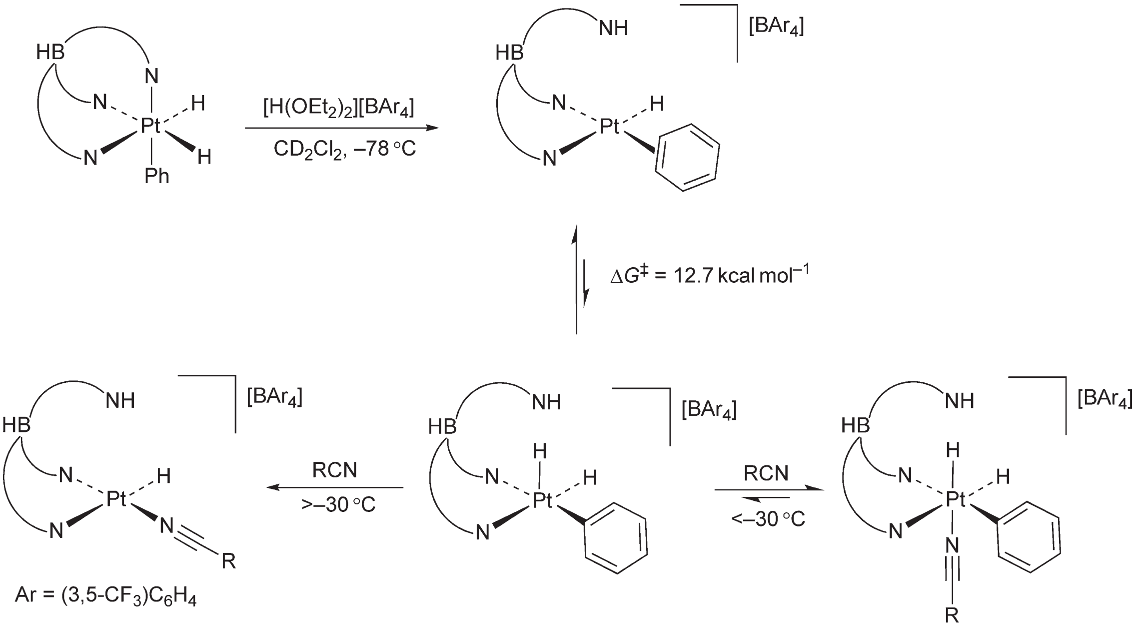
With the exception of the pentacoordinate η^2-butadiene complexes PtClR(η^2-C$_4$H$_6$)(dmphen), which have been previously mentioned[109] (Section 9.2.1.2), the complexes reported in this section feature η^2-cyclic-polyalkene, although $\eta^2:\eta^2$ (or η^4) 1,3-diene–platinum species will be considered in Section 9.5 (complexes with η^4-ligands).

(i) *Zerovalent derivatives:* Ethylene displacement from Pt(η^2-C$_2$H$_4$)(d^{i}ppe) with cot, or treatment of PtCl$_2$(d^{i}ppe) with [Li$_2$(cot)(TMEDA)], affords Pt(η^2-C$_8$H$_8$) (d^{i}ppe), for which solid-state NMR data confirm the presence of a semiaromatic η^2-cot ligand, and reveal fluxional behavior averaging coordinated and uncoordinated C=C bonds (d^{i}ppe = 1,2-bis(diisopropylphosphino)ethane).[256] In solution, the complex equilibrates with a square-planar Pt(II) isomer Pt{(η^2(1,4)-C$_8$H$_8$)}(d^{i}ppe), arising from a formal oxidative 1,4-addition of a cot 1,3-diene subunit to the Pt(0) center.[256]

Pt(dtbpm) generated by thermolysis of PtH(NP)(dtbpm) (NP = neopentyl; dtbpm = di-(*tert*-butylphosphino)-methane) interacts with electron-poor arenes (1,4-(X)$_2$C$_6$H$_4$; 1,3,5-(X)$_3$C$_6$H$_3$) and biphenyls (3,5,4′-(X$_3$)C$_{12}$H$_7$; 3,5,3′,5′-(X)$_4$C$_{12}$H$_6$) (X = CF$_3$) to form η^2-arene complexes.[257] The structures of Pt(η^2-1,3,5-(X)$_3$C$_6$H$_3$)(dtbpm) and both substituted biphenyl complexes confirm the η^2-bonding motif, and reveal a localized diene structure for the non-bound portion of the corresponding complexed ring with a clear lengthening of the η^2-bound C=C. Subsequent thermolysis or photolysis affords thermodynamic (thermal) or apparent kinetic aryl hydride Pt(II) complexes.[257] Curiously, the complex Pt(dtbpm) does not activate benzene, contrasting with the behavior of the analogous Pt(dcpe),[258] and with recent theoretical calculations, which suggest a low energetic barrier for the C–H activation on the Pt(H$_2$PCH$_2$CH$_2$PH$_2$)/C$_6$H$_6$ system.[259]

(ii) *Divalent derivatives:* Extensive research has established that η^2-arene Pt(II) complexes are key intermediates in C–H aromatic activation. This subject has been widely reviewed in the context of the more general topic of hydrocarbon C–H bond activation,[151,260–265] so only the most significant reports will be outlined.

η^2-Arene platinum(II) species have been suggested as intermediates in the course of the reactions of methyl cationic [PtMe(S)(N–N)]$^+$ complexes[266,267] with benzene, or in the protonation of neutral aryl compounds,[268] being in some instances identified by low-temperature NMR techniques.[269] Thus, protonation (HTf) of PtMePh(N–N) (N–N = ArN=CMe–CMe=NAr, Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$) at −69 °C allows the observation of a fluxional η^2-benzene complex [PtMe(η^2-C$_6$H$_6$)(N–N)]$^+$. This complex, also generated by treatment of [PtMe(solv)(N–N)]$^+$ with C$_6$H$_6$, evolves at −23 °C with loss of CH$_4$ and C$_6$H$_6$, to form a mixture of the corresponding [PtPh(solv)(N–N)]$^+$ and [PtMe(solv)(N–N)]$^+$ (82 : 18 ratio, respectively). Kinetic investigations and labeling experiments indicate that the η^2-benzene adduct interconverts reversibly via the Pt(IV) methyl/phenyl/hydride species with a C–H η^2-methane adduct, finally evolving with preferential methane loss.[269] The first complex stable enough to be characterized by X-ray crystallography was [PtH(η^2-C$_6$H$_6$)(κ^2-HTp′)](BAr$_4$) (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$), prepared by protonation of Pt(Tp′)H$_2$Ph (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate)with [H(OEt$_2$)$_2$](BAr$_4$) at low temperature (Scheme 11). The orientation of the benzene plane is almost perpendicular to the metal plane, and Pt–C distances (2.24, 2.21 Å) are in the expected range.[270] Spectroscopic data indicate that this[270] and related complexes [PtR(η^2-HAr)(κ^2-HTp′)]$^+$ (Ar = Ph, Tol, 3,6-(Me)$_2$C$_6$H$_3$, R = H; Ar = R = Ph)[271] equilibrate in solution at low temperature with the five-coordinated platinum(IV) hydride species, via arene C–H activation, increasing the activation barrier with methyl substitution from benzene (12.7 kcal mol^{-1}) to *p*-xylene (14.2 kcal mol^{-1}). Addition of nitrile



Scheme 11

ligands to the η^2-benzene species at temperatures below −30 °C results in trapping of the five coordinate species giving six-coordinate Pt(IV) products, [PtHPhR(nitrile)(κ^2-HTp′)]$^+$ (R = H, Ph). At temperatures above −30 °C, the Pt^{II}/Pt^{IV} equilibrium was perturbed by irreversible displacement of η^2-benzene, to form [PtR(nitrile)(κ^2-HTp′)]$^+$ (Scheme 11).[272] In contrast to this behavior, interaction of the diphosphine solvate cations [PtMe(OEt$_2$)(P–P)]$^+$ (P–P = dcpe, depe) with arenes (benzene, toluene) generates [Pt$_2$(μ_2-η^3 : η^3-biaryl)(P–P)$_2$]$^{2+}$ by intermolecular C–H activation with concomitant C–C coupling, as confirmed by X-ray diffraction.[273] The C–C coupling is suggested to occur through a dinuclear species [Pt$_2$(μ_2-η^1 : η^2-Ph)$_2$(P–P)$_2$]$^{2+}$ as intermediate, having a similar structure to the μ-2-furyl dimer [Pt$_2$(μ-η^1 : η^2-OC$_4$H$_3$)$_2$(dcpe)$_2$]$^{2+}$, synthesized by reacting [PtMe(OEt$_2$)(dcpe)]$^+$ with furan.[273] Several stable neutral Pt(II) complexes featuring the η^2-arene motif as a secondary interaction have been also reported[215,274,275] (see Section 9.2.3.2 for PtCl$_2$(ethenoanthracene)).[215] Displacement of both THF ligands in *cis*-[Pt(R$_F$)$_2$(THF)$_2$] with 1 equiv. of NC$_5$H$_4$Bz-2,[274] NC$_5$H$_4$(CHPh$_2$)-2, or NBz$_3$(L)[275] generates [Pt(R$_F$)$_2$L], in which the nitrogen atom of the ligand serves as an anchor to place the phenyl or one of the phenyl rings in close enough proximity for a η^2-arene interaction.[274,275]

8.09.2.6 η^2-Fullerene and Related Complexes

The chemistry of transition metal complexes of fullerenes has been comprehensively reviewed.[276–281] In mononuclear complexes, fullerenes such as C_{60} and C_{70} (and also functionalized fullerenes) act as electron-deficient polyalkenes, and the metal is attached in an η^2-fashion to the C–C carbon bond at the fusion of two six-membered rings.

For platinum, several synthetic methods have been employed. A standard procedure involves the displacement by the fullerene of a ligand weakly bonded to platinum. Thus, novel Pt(η^2-C$_{60}$)L$_2$ (L = AsPh$_3$,[282] P(OR)$_3$[283]) and Pt(η^2-C$_{70}$)L$_2$ (L = PPh$_3$,[284,285] PEt$_3$[284]) have been prepared from PtL$_4$ or Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ and C_{60} and C_{70}, respectively. The addition of 4 molar equiv. of Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$ to C_{70} results in the formation of C$_{70}${Pt(PPh$_3$)$_2$}$_4$, as confirmed by X-ray crystallography. The product has the C$_{70}$(PtP$_2$)$_4$ core arranged so that it has idealized C_{2v}-symmetry with two Pt centers coordinated by the most pyramidalized C_a–C_b bonds and the other two to C_c–C_c bonds resulting in a effective coverage of the two poles of C_{70} by phenyl groups.[285] The lower adducts C$_{70}${Pt(PPh$_3$)$_2$}$_2$ and C$_{70}${Pt(PPh$_3$)$_2$}$_3$ have been also obtained and characterized by NMR spectroscopy.[285] However, attempts to add more platinum fragments were unsuccessful, in spite of the fact that up to six Pt(PEt$_3$)$_2$ groups may be added to the smaller fullerene C_{60}.[278] Following this procedure, the first organometallic complexes

$Pt(\eta^2\text{-}Ar_5C_{60}H)(PPh_3)_2$ ($Ar = Ph$, $3\text{-}MeC_6H_4$, $4\text{-}MeC_6H_4$) containing penta-arylated [C_{60}] fullerene ligands $Ar_5C_{60}H$ have been prepared as a mixture of several isomers using $Pt(PPh_3)_4$ as precursor.[286] Optically active complexes $Pt(\eta^2\text{-}C_{60})\{(+)\text{-diop}\}$,[287] $Pt(\eta^2\text{-}C_{70})\{(+)\text{-diop}\}$,[287] and $Pt(\eta^2\text{-}C_{60})\{(-)\text{-diop}\}$[288] have been obtained by ligand-exchange process between PPh_3 and diop starting from $Pt(C_x)(PPh_3)_2$ ($C_x = C_{60}$, C_{70}). The geometrical parameters of both enantiomers with C_{60} are similar and, as expected, their CD spectra are mirror images of each other. Similarly, $Pt(\eta^2\text{-}C_x)(L\text{–}L)$ ($C_x = C_{60}$, C_{70}; L–L = dppf, 1,1′-bis(diphenylarsino)ferrocene (dpaf)) have been prepared by direct or *in situ* treatment of $Pt(\eta^2\text{-}C_x)(L_2)$ ($L = PPh_3$, $AsPh_3$) with the appropriate diphosphine.[282] The structure of $Pt(\eta^2\text{-}C_{70})$(dpaf) confirms the coordination of the platinum fragment Pt(dpaf) by one of the 10 Ca–Cb 6 : 6 bonds of C_{70}.[282] Complex $Pt(\eta^2\text{-}C_{60})(PCy_3)_2$ has been obtained quantitatively by an unusual route in which $PtH_2(PCy_3)_2$ reacts with C_{60} eliminating H_2.[289] An interesting approach to this type of complex is the use of, or the *in situ* preparation of, $C_{60}Pt_n$ ($n \cong 1$) species from reaction of $Pt(dba)_2$[290] or $Pt(cod)_2$[291] with C_{60} or by electroreduction of platinum(II) complexes in the presence of C_{60}.[292] These species, which are believed to be formed by a series of $\ldots C_{60}Pt(C_{60}Pt)_nC_{60}Pt\ldots$ units, in which the Pt centers are covalently bonded to the fullerene in an η^2-fashion, react easily with phosphines (PPh_3, PEt_3),[290] phosphites ($P(OMe)_3$),[290] diphosphines (dppe,[291] dppp,[291] $Ph_2PCH_2(CH_2OCH_2)_nCH_2PPh_2$ ($n = 1$–3)[293]) or isocyanides[294] (L_2) to give the corresponding $Pt(\eta^2\text{-}C_{60})L_2$ complexes. Following this procedure, the first homo- and heterobinuclear products $(\eta^2\text{-}C_{60})M(\mu\text{-}L\text{–}L)_2M'(\eta^2\text{-}C_{60})$ (M, M′ = Pt, Pd; L–L = *trans*-$Ph_2PCH{=}CHPPh_2$),[295] $Pt(\eta^2\text{-}C_{60})$(dppr), and $[Pt(\eta^2\text{-}C_{60})(dppc)]PF_6$ (dppc = 1,1′-bis(diphenylphosphino)cobaltocinium)[296] have been recently prepared. Electrochemical studies of $Pt(\eta^2\text{-}C_{60})$(dppr) have revealed three C_{60}-localized sequential reductions,[296] while in complexes $C_{60}\{Pt(PEt_3)_2\}_n$ ($n = 1-4$) the ease of oxidation (metal centered) increases as additional $Pt(PEt_3)_2$ groups are added to the fullerene.[297] It is remarkable that photofragmentation of these metal fullerides $C_{60}Pt_x$ (or films C_{60}/Pt) by laser ablation leads to the formation of novel fullerenes ($C_{58}Pt$, $C_{59}Pt$) that contain Pt atoms as part of the fullerene.[298] In the presence of 2-butene, new species such as $[C_{57}Pt_2(\text{2-butene})]^-$ or $[C_{59}Pt(\text{2-butene})]^+$ have been detected by mass spectrometry.[299]

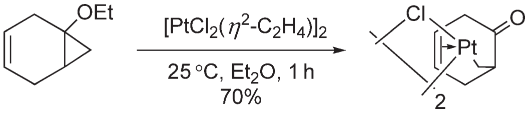
The nature of the bonding in platinum–fullerene complexes has been the subject of many studies.[153,300–302] Recent theoretical calculations (DFT-NL) on $M(\eta^2\text{-}C_{60})(PH_3)_2$ (M = Ni, Pd, Pt) reveal that the metal–fullerene bond-dissociation energies ($Pd < Ni < Pt$) are higher than the corresponding metal–ethylene complexes but lower than those of substituted ethylene (C_2X_4, X = F, CN).[300] Similar studies on a series of complexes $(\eta^2\text{-}C_x)\{Pt(PH_3)_2\}_n$ ($x = 60$, 70, 84; $n = 1$–6) indicate that the binding energy between the $Pt(PH_3)_2$ unit is almost independent of the size of the cage and the number of metals coordinated on the fullerene surface.[301] In the C_{70} species, the most reactive site corresponds to the bond with the most pyramidalized carbon atoms in the free fullerene.[301]

8.09.2.7 Bimetallic Alkene Complexes

8.09.2.7.1 Homobimetallic complexes

A few diplatinum(0) complexes have been reported. The synthesis of $Pt_2(C_7H_{12})_3$ (C_7H_{12} = 1,6-heptadiene)[185] has been previously mentioned (Section 9.2.3.1.). The related complex $Pt_2(\eta^2\text{-nb})_2(\mu\text{-}\eta^2:\eta^2\text{-bq})_2$ (bq = *p*-benzoquinone), displaying two *p*-benzoquinones as bridging ligands, and a very short Pt–Pt separation (2.97 Å), has been prepared by reaction of $Pt(dba)_2$ with an excess of bq and nb (5 equiv.).[303] Similarly, the complex $Pt_2(\eta^2\text{-nb})_2(\mu\text{-}L\text{–}L)_2$ (L–L = *Z*,*Z*-$Ph_2PCH_2CBu^t{=}N\text{–}N{=}CBu^tCH_2PPh_2$) is reported to be formed by treatment of $Pt(\eta^2\text{-nb})_3$ with the azine diphosphine ligand L–L.[304] A mixed valence complex having a cinnamonitrile bridging ligand $[Pt(CF_3)L_2(\mu\text{-}1\kappa N:\eta^2\text{-}NCCH{=}CHPh)PtL_2]BF_4$ ($L = PPh_3$) has been obtained by the reaction of $[Pt(CF_3)L_2(NCCH{=}CHPh)]BF_4$ with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$.[305] *cis*-Chelating coordination to platinum(II) is not favored with N,N ligands such as 2,2′-methylenebis(5-(dimethylamino)aniline),[306] dpf, (1,1′-bis(2-pyridyl)ferrocene)[307] and dpf* (octamethyl-5,5′-bis(2-pyridyl)ferrocene),[308] and their reactions with Zeise's salt affords binuclear $\{PtCl_2(\eta^2\text{-}C_2H_4)\}_2(\mu\text{-N,N})$ complexes.[306–308] X-ray diffraction studies of $\{PtCl_2(\eta^2\text{-}C_2H_4)\}_2(\mu\text{-dpf})$[306] and the analogous μ-dpf*[307] confirm their dimeric formulation with both ethylene ligands in an approximately perpendicular orientation to their respective coordination planes. Diplatinum complexes $\{Pt(\eta^5\text{-}Cp^R)Me\}_2\mu\text{-}(1,2\text{-}\eta^2:5,6\text{-}\eta^2\text{-cod})$ ($Cp^R = Cp^*$, $C_5Me_4CH_2CH_2NMe_2$) with cod-bridged structures are generated by spontaneous dimerization of initially formed η^2-cod species $Pt(\eta^5\text{-}Cp^R)Me(1,2\text{-}\eta^2\text{-cod})$, formed by reaction of $PtXMe(\eta^2:\eta^2\text{-cod})$ (X = halide) with MCp^R (M = Li, K).[175] An X-ray diffraction study ($Cp^R = C_5Me_4CH_2CH_2NMe_2$) confirms the presence of the 1,5-cod bridging group with two pentacoordinate electron-rich platinum(II) centers.[175]

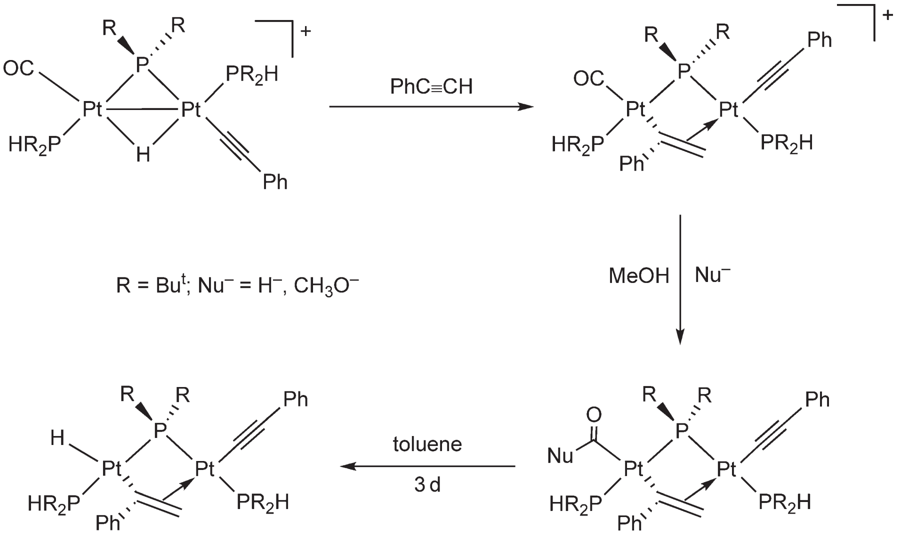
A characteristic complex of this section is the Zeise dimer $[PtCl(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)]_2$, because it is widely employed in many synthetic procedures. Recent studies reveal that this complex is easily split in coordinating solvents (MeOH, THF),[136] making questionable previous studies of ethene exchange only at the dinuclear complex.[309] The insertion of Pt(II) in the form of the Zeise dimer into a C–C bond of substituted three-membered rings has been reviewed,[222] and a similar recent example[310] is shown in Equation (7).



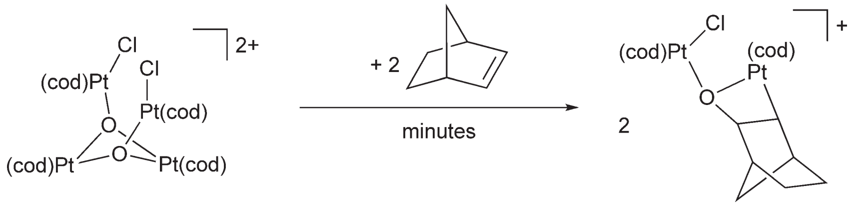
(7)

The reaction of the related *trans*-$[Pt(\eta^2\text{-coe})Cl(\mu\text{-}Cl)_2]_2$ with aminopropylvinylether ($H_2NCH_2CH_2CH_2OCH{=}CH_2$) gives *trans*-$[PtCl_2(\eta^2\text{-coe})(thmo)]$ (thmo = tetrahydro-2-methyl-1,3-ozazine) arising from a metal-catalyzed intramolecular hydroamination of the alkenylamine.[217] New homologs of the Zeise dimer have been also reported. Thus, reaction of ethene with K_2PtCl_4 in H_2O generates acetaldehyde and the ethyl–ethylene complex *trans*-$[Pt(\mu\text{-}Cl)Et(\eta^2\text{-}C_2H_4)]_2$, as confirmed by X-ray crystallography.[311] Insertion of ethylene into a Pt(II)–H bond is suggested to occur as a crucial step in the proposed mechanism. Analogous silyl–alkene complexes $[Pt(SiR_3)(\mu\text{-}Cl)(\eta^2\text{-cod})]_2$ ($R_3Si = SiEt_3$, $SiMe_2Cl$, $SiMeCl_2$, $Si(OEt)_3$, $SiPhMe_2$, $SiMe_2OSiMe_3$) with monodentate η^2-cod ligands are isolated by an unusual route in which $PtCl_2(cod)$ reacts with 2 equiv. of the appropriate silane in the presence of additional cod.[207] In the reaction, coe and cod isomers are also formed suggesting facile H transfer to cod, rather than Si transfer, thus providing additional support for the Chalk–Harrod catalytic cycle.[207] A mixed asymmetric styrene–acetylene complex $Pt_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CHPh)(PhC{\equiv}CPh)$ has been reported to be formed by interaction of $[PtCl(\mu\text{-}Cl)(\eta^2\text{-}CH_2{=}CHPh)]_2$ with 2 equiv. of diphenylacetylene (dpa), this being a model for the equilibria found for the reaction of $PtCl(\mu\text{-}Cl)(\eta^2\text{-}CH_2{=}CHPh)$ with a polymer based on a poly(*p*-phenylene–ethynylene) derivative.[312]

An unusual diplatinum complex featuring a platinaoxenate is generated quantitatively by reaction of $Pt_4(\mu_3\text{-}O)_2Cl_2(cod)_4$ with norbornene (Equation (8)),[313] and a related derivative is proposed as an intermediate in the oxidation of CH_2CH_2 by the tetranuclear complex, giving rise to acetaldehyde together with $PtClEt(cod)$ and $[Pt(\eta^3\text{-}CH_2CHCHCH_3)(cod)]BF_4$.[313] The formation of several phosphido–$\eta^1:\eta^2$-alkenyl species generated by initial insertion of phenylacetylene into the $Pt_2(\mu\text{-}H)$ moiety of $[(CO)(PBu^t_2H)Pt(\mu\text{-}PBu^t_2)(\mu\text{-}H)Pt(PBu^t_2H)(C{\equiv}CPh)]BF_4$ is shown in Scheme 12.[314] Dinuclear phosphido–(μ-$\eta^2:\eta^2$-L)-bridged complexes $[Pt_2(\mu\text{-}PBu^t_2)(\mu\text{-}\eta^2:\eta^2\text{-}L)(PBu^t_2H)_2]CF_3SO_3$ ($L = CS_2$, isoprene), formed by phosphido–hydride coupling, are easily obtained by direct interaction of CS_2 or isoprene with $[(CO)Pt(\mu\text{-}PBu^t_2)_2PtH(PBu^t_2H)]CF_3SO_3$.[315] However, $Pt_2(\mu\text{-}PBu^t_2)_2(PBu^t_2H)CO$ reacts with CS_2, yielding $Pt_2(\mu\text{-}PBu^t_2)_2(PBu^t_2H)(\eta^2\text{-}CS_2)$.[316]



Scheme 12



(8)

Several binuclear complexes *cis*-$[R_F(PPh_3)Pt(\mu\text{-}H)(\mu\text{-}\kappa P:\eta^2\text{-}PPh_3)Pt(R_F)_2]$[317] and $[(R_F)_3Pt(\mu\text{-}1\kappa P:2\kappa P,\eta^2\text{-dppm})M(R_x)_2]^-$ (M = Pd, Pt; $R_x = C_6X_5$ (X = F, Cl)),[318] featuring η^2-arene (phenyl) bonding interactions have been also prepared by reacting the labile THF complexes *cis*-$[M(R_x)_2(THF)_2]$ (M = Pt, Pd) with *trans*-$[PtHR_F(PPh_3)_2]$ or $[Pt(R_F)_3(\text{dppm-}\kappa P)]^-$, respectively.

8.09.2.7.2 Heterobimetallic complexes

The chemistry of bimetallic complexes, in particular species containing hydrocarbyl bridging ligands, has experienced a notable development in recent years.[319–323] Several reviews on the subject have appeared, and therefore only salient examples having η^2-olefinic platinum-bonding interactions will be considered here.

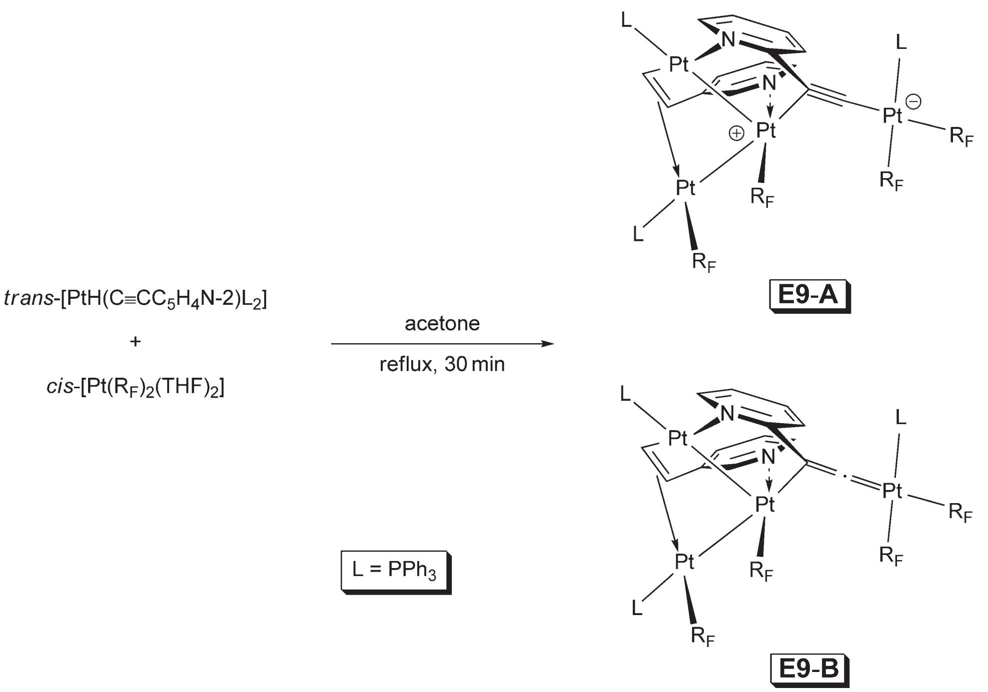
The most common reaction to form heterobinuclear complexes is the complexation of the $Pt(PPh_3)_2$ unit by a free olefinic fragment in the precursor. This strategy has been used in the preparation of $[Rh(PPh_3)_2(CO)(\mu\text{-}\kappa N:\eta^2\text{-}NCCH{=}CHPh)Pt(PPh_3)_2]BF_4$.[305] Binding of $Pt(PPh_3)_2$ to the exocyclic C=C bond in styrene cationic complexes $[Mn(CO)_3(\eta^6\text{-}C_6H_5CR^1{=}CR^2R^3]^+$ ($R^1 = R^2 = R^3 = H$; $R^1 = R^2 = H$, $R^3 = Me$; $R^1 = Me$, $R^2 = R^3 = H$) has been also reported and confirmed by an X-ray diffraction study for the complex $[Mn(CO)_3(\eta^6:\eta^2\text{-}C_6H_5\text{-}CH{=}CH_2)Pt(PPh_3)_2]BF_4$.[324] It is remarkable that although *cis*-β-methylstyrene does not react with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$, precoordination of the $[Mn(CO)_3]^+$ fragment facilitates platinum η^2(C=C) binding. In the same way, $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ does not react with free benzofuran, but $[Mn(CO)_3(\eta^6\text{-}C_6H_8O)]^+$ reacts reversibly to give the adduct $[Mn(CO)_3(\mu\text{-}\eta^6:\eta^2\text{-}C_6H_8O)Pt(PPh_3)_2]^+$, which converts slowly to an oxoplatinacyclic derivative by irreversible insertion into the adjacent O–C(vinyl) bond.[325] Detailed kinetic studies of the reaction of $[Mn(CO)_3(\eta^6\text{-}C_6H_8S)]^+$ with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$, which results in a similar S–C(olefinic) bond activation to give a final thiaplatina-containing cycle, establish that the first step is also the coordination to the thiophenic double bond to give $[Mn(CO)_3(\mu\text{-}\eta^6:\eta^2\text{-}C_6H_8S)Pt(PPh_3)_2]^+$.[326] Spectroscopic evidence suggest that reaction between allenyl complexes $M(CH{=}C{=}CH_2)Cp(CO)_2$ and $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$, yielding heterobinuclear μ-allenyl complexes $Pt(PPh_3)_2(\mu\text{-}\eta^1:\eta^2_{\alpha,\beta}\text{-}(CH{=}C{=}CH_2)MCp(CO)$ (M = Fe, Ru), involve also initial η^2-coordination of the platinum fragment to the C=C bond in the allenyl precursor.[327]

Novel complexes having the Pt(cod) unit have been reported. Transmetallation reactions between $PtCl_2(cod)$ and $Mn(\eta^5\text{-}C_5H_4SnMe_3)(CO)_3$, $RuCp(\eta^5\text{-}C_5H_4SnMe_3)$ or $Ru\{C_5H_4SnMe_3\}_2$ give $\{PtCl(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(cod)\}Mn(CO)_3$[328] or the ruthenocenylplatinum complexes[329] $\{PtCl(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(cod)\}RuCp$ and $\{PtCl(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(cod)\}_2Ru$, respectively. In a similar way, replacement of the chloride ligand in PtClR(cod) (R = alkyl, aryl) by anionic complexes $Na[MCp(CO)_3]$ (M = Mo, W) gives the corresponding heterobinuclear complex PtR(cod)–$MCp(CO)_3$ with an unbridged metal–metal bond, as confirmed by an X-ray structure for complex $PtPh(cod)MoCp(CO)_3$.[330] Ligand-exchange reaction with $PPh_2CH_2CH_2CH{=}CH_2$(P–L) yields PtMe(P–L)-$MoCp(CO)_3$, which is a useful precursor to bimetallic complexes containing a platinacyclobutenone framework η^2-bonded to Mo.[331] Direct reaction of $Pt(cod)_2$ with *mer*-$[Fe(H)Si(OMe_3)(CO)_3(PPh_2H)]$ affords $FeSi(OMe_3)(CO)_3(\mu\text{-}PPh_2)Pt(cod)$, probably by oxidative addition of the P–H bond to Pt(0), resulting in a phosphido-bridged intermediate followed by reductive elimination of H_2.[198] However, reaction with the carbene complex $Cp(OC)_2Re{=}C(OMe)Ph$ results in the heterobimetallic complex $Cp(OC)_2Re\{\mu\text{-}C(OMe)Ph\}Pt(cod)$, and subsequent treatment with Me_3OBF_4, removes the methoxy group giving rise to the complex $[Cp(OC)_2Ru(\mu\text{-}CPh)Pt(cod)]BF_4$ containing a carbyne-bridging ligand.[332] Differences in Pt–olefinic distances indicate a stronger *trans*-influence of the carbene and carbyne ligands relative to a semibridging CO ligand, which is present in both complexes.[332] Complex $(\eta^2\text{-}C_2H_4)ClPt(\mu\text{-}Cl)_2RuCl(\eta^3:\eta^3$-2,7-dimethyloctadienediyl), which is an interesting precursor for the formation of PtRu nanoparticles, is accessible by metal fragment metathesis of the Zeise dimer with $Ru(\eta^3:\eta^3$-2,7-dimethyloctadienediyl)Cl(μ-Cl).[333] Several dimetallic μ-alkenyl complexes featuring a $\eta^1(Pt):\eta^2(M)$ bonding mode have been also reported.[74,331,334]

8.09.2.8 Polymetallic Alkene Complexes

8.09.2.8.1 Homometallic complexes

Interest in this type of complex has grown in recent years. Thus, the 44-electron triplatinum cluster ($Pt^{I}Pt^{I}Pt^{II}$) $[Pt_3(\mu\text{-}PBu^t_2)_3(\eta^2\text{-}CH_2CH_2)(CO)_2]PF_6$ (X-ray) has been obtained by treatment of $Pt_3(\mu\text{-}PBu^t_2)_3H(CO)_2$ with 2 equiv. of $[FeCp_2]PF_6$ in the presence of base (Na_2CO_3) and ethylene.[335] The overall reaction can be seen as a formal oxidation of the hydride to H^+, which is removed by the added base, with concomitant coordination of the ethylene to the resulting unsaturated $[Pt_3(\mu\text{-}PBu^t_2)_3(CO)_2]^+$ cation.[335] In the same way, interaction of activated olefins ((*E*)-CHCN=CHCN, ma) with $Pt_3(\mu\text{-}CO)_3L_3$ ($L = PPh_3$, PPh_2Bz, PCy_3), at low temperature, affords unstable adducts $Pt_3(\mu\text{-}CO)_3(\eta^2\text{-alkene})L_3$, which have been characterized by spectroscopic means.[25] A very unusual tetranuclear complex, which can be described as a formal zwitterionic cationic Pt_3 cluster alkynyl platinate complex $[Pt^-]\text{–}C{\equiv}CC_5H_4N\text{-}2[Pt_3]^+$ **E9-A** (Equation (9)), is generated by a rearrangement reaction between *trans*-$[PtH(C{\equiv}CC_5H_4N\text{-}2)(PPh_3)_2]$ and *cis*-$[Pt(R_F)_2(THF)_2]$.[336] The X-ray structure confirms the presence of a pyridyl–vinyl fragment, which interacts with three metal centers and shows structural details suggesting some degree of participation of the vinylidene neutral form **E9-B**.[336]



(9)

Exchange reactions involving the $PtCl_2(cod)$ precursor have revealed interesting results (see also Scheme 9 in Section 9.2.3.2). Thus, the trinuclear mixed valence complex $Pt^{II}_2Pt^0$, $\{Pt(C{\equiv}CBu^t)(\mu\text{-}C{\equiv}CBu^t)(cod)\}_2Pt$, which contains two $Pt(C{\equiv}CBu^t)_2(cod)$ units linked by a naked Pt atom (X-ray), is formed not only by reaction of $Pt(\eta^2\text{-nb})_3$ with 2 equiv. of $Pt(C{\equiv}CBu^t)_2(cod)$, but also by treatment of $PtCl_2(cod)$ with $HC{\equiv}CBu^t$ in the presence of NaOEt.[337] Similar oxo/chloro exchange reactions using oxogold reagents $[(LAu)_3(\mu_3\text{-}O)]BF_4$ afford, depending on the reactant ratios, unusual oxoplatinum(II) complexes. With a molar ratio 3 : 2, the tetranuclear complex $[Pt_4(\mu_3\text{-}O)_2Cl_2(cod)_4](BF_4)_2$, shown as precursor in Equation (8), is generated.[338] Subsequent hydrolysis affords the novel tetranuclear hydroxo–oxo product $[Pt_4(\mu_3\text{-}O)_2(\mu\text{-}OH)(cod)_4](BF_4)_3$, featuring a distorted tetrahedron of Pt atoms.[338]

High-nuclearity species have been also reported. Reaction of the hexakis(4-cinnamonitrilephenoxy)cyclophosphazene with $Pt(\eta^2\text{-}C_2H_4)L_2$ affords $\{PtL_2\}_6\{N_3P_3(OC_6H_4CH{=}CHCN)_6\}$ ($L = PPh_3$) in which the six olefinic fragments are coordinated to Pt(0), and coordination of six cationic $[Pt(CF_3)L_2(solvate)]^+$ fragments to the six nitrile functions, affords the related $[\{PtL_2\}_6\{N_3P_3(OC_6H_4CH{=}CHCN)Pt(CF_3)L_2\}_6]^{6+}$ having 12 platinum centers coordinated to the phosphazene ring.[305] Organometallic polymers containing trigonal-bipyramidal platinum(II) entities as pendants have been successfully generated using typical synthetic strategies (Section 9.2.1.2).[339] Anchoring of the metal fragment occurs with high regioselectivity in the equatorial or axial position depending on the π- and σ-donor properties of the polymer ligand.[339] A somewhat different type of complex is exemplified in polynuclear unsaturated phosphido bridging clusters featuring η^2-phenyl interaction. Reaction of $[(R_F)_2Pt(\mu\text{-}PPh_2)]_2{}^{2-}$ and $[(R_F)_2Pt(\mu\text{-}PPh_2)_2\text{-}Pt(\mu\text{-}PPh_2)_2Pt(R_F)_2]^{2-}$ with *cis*-$[Pt(R_F)_2(THF)_2]$ yields trinuclear $(Pt_3(\mu\text{-}PPh_2)_2(R_F)_5]^-$ and tetranuclear $(Pt_4(\mu\text{-}PPh_2)_4(R_F)_5]^-$ cluster complexes containing two Pt–Pt metal bonds and an unusual μ_3-PPh_2 ligand which has a η^2-phenyl interaction.[340,341] A similar μ_3-PPh_2 ligand is found in $Pt_4(\mu\text{-}PPh_2)_3(\mu_3\text{-}PPh_2)(R_F)_4$, generated by chloride abstraction from $[Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)(R_F)_2]_2{}^{2-}$ with $AgClO_4$.[342]

8.09.2.8.2 Heterometallic complexes

Many complexes reported contain Pt(cod) units. As noted above, the outcome of the reaction between $PtCl_2$(cod) with oxogold reagents $[(LAu)_3(\mu_3\text{-}O)]^+$ depends on the reactant ratios.[338] By using 1 : 1 and 1 : 2 molar ratios, tetra- and pentanuclear complexes $[Pt(cod)(\mu_3\text{-}O)AuL]_2(BF_4)_2$ and $[Pt(cod)\{(\mu_3\text{-}O)(AuL)_2\}_2](BF_4)_2$, respectively, are formed. Considering the isolobal relationship between LAu^+ and R^+ ($R = H^+$, alkyl$^+$), these platinum–gold complexes can be viewed as aura–hydroxo ($OauL^-$) and aura–aqua $O(AuL)_2$ complexes, respectively, and it is worth noting that the analogous cation $[Pt(\mu\text{-}OR)(cod)]_2{}^{2+}$ seems to be unknown in platinum chemistry.[338] Similar reactions of $PtCl_2$(cod) with $[Fe_2(CO)_6(\mu\text{-}S)_2]^{2-}$ yields $Fe_2(CO)_6(\mu\text{-}S)_2Pt(cod)$.[343] Electrochemical analysis reveals a quasi-reversible two-electron reduction and a fully reversible one-electron oxidation, which are believed to be localized on the $Fe_2(CO)_6(\mu\text{-}S)_2$ fragment.[343] Similarly, reaction of $\{PtCl(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(cod)\}_2Fe$ with HC≡CPh in the presence of a CuI catalyst in NEt_2H affords $\{Pt(C{\equiv}CPh)(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(cod)\}_2Fe$.[344] However, the use of an excess of CuI and HC≡CPh leads to olefin substitution and incorporation of Cu(I) resulting in the formation of $\{PtCu_2(C{\equiv}CPh)_3(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)\}_2Fe$, which contains alkynyl ligands σ-bonded to Pt and η^2-bonded to copper.[344] Reaction of $Pt(cod)_2$ with $Fe(\eta^5\text{-}C_5H_4)_2ER_2$ ($ER_2 = SiMe_2$,[202] $SnBu^t{}_2$[201]) yields novel 2-platina[2]-ferrocenophane complexes $Fe(\eta^5\text{-}C_5H_4)_2Pt(cod)ER_2$ by insertion of Pt into one of the E–C bonds.[201,202] The role of these species as ROP pre-catalysts of metallocenophanes has been examined. Binuclear $Cp(CO)_2Mn(\mu\text{-}C{=}CHPh)PtL^1L^2$ ($L^1 = L^2$; $L^1 \neq L^2$) react with $Fe_2(CO)_9$ to afford new trimetallic species $Cp(CO)Mn(\mu\text{-}CO)Fe(CO)_3(\mu\text{-}\eta^1:\eta^1:\eta^2\text{-}C{=}CHPh)PtL^1L^2$ ($L^2 = CO$, $L^1 = PPh_3$, ½ dppm, phosphite; $L^1 = L^2 =$ phosphite) formulated on the basis of spectroscopy as having η^2-coordination of the vinylidene ligand to the Pt atom.[345]

8.09.3 Alkyne and Related Complexes

Developments in platinum alkyne chemistry have been the subject of a comprehensive survey.[346]

8.09.3.1 η^2-Monoalkyne Complexes

Several reviews of the chemistry of strained cyclic alkynes and arynes[243,347] and *ortho*-arene cyclynes,[348] which include synthesis, structure, and reactivity of platinum complexes, have also appeared. The behavior of 1,4-enynes in the presence of transition metals has been reviewed.[349]

8.09.3.1.1 Zerovalent derivatives

The complexes reported are monoalkyne tricoordinate species although the number of known dicoordinate compounds is growing.

8.09.3.1.1.(i) Preparation

The typical reaction pathways to zerovalent derivatives are included in COMC (1995).[2] These involve: (a) preparation via reduction of higher valent platinum or (b) displacements using a zerovalent precursor.

8.09.3.1.1.(i).(a) Preparations via reduction of higher valent platinum

In a similar way to the synthesis of $Pt(\eta^2\text{-alkene})(dfepe)$,[14] treatment of the hydride dimer $[Pt(\mu\text{-}H)(dfepe)]_2$ with alkynes ($R^1C{\equiv}CR^2$) affords $Pt(\eta^2\text{-}R^1C{\equiv}CR^2)(dfepe)$.[350] In the reaction with propyne, a small amount of the dimer $\{Pt(dfepe)_2\}_2(\mu\text{-}\eta^2:\eta^2\text{-}MeC{\equiv}CH)$ is also formed.[350] Selective hydride transfer in $PtH(dppe)MCp(CO)_3$ ($M = Mo$, W) was induced with disubstituted alkynes to yield $Pt(\eta^2\text{-alkyne})(dppe)$ and $MHCp(CO)_3$.[334,351] With diphenylacetylene, the β-hydrogen elimination is found to be a reversible process.[351] A new synthetic route to $Pt(\eta^2\text{-}PhC{\equiv}CPh)_2$ based on the reduction of *cis*-$[PtCl_2(\eta^2\text{-}PhCH{=}CH_2)_2]$ with $SiHPh_3$ in the presence of PhC≡CPh has been reported.[352] The reaction of *trans*-$[PtHCl(PPh_3)_2]$ with 1,1-diphenyl-2-propynol in the presence of NEt_2H affords a mixture of the expected hydride–acetylide *trans*-$\mathrm{[PtH(C{\equiv}C\text{–}CPh_2OH)(PPh_3)_2]}$ and the η^2-alkyne $\mathrm{Pt(\eta^2\text{-}HC{\equiv}CCPh_2OH)(PPh_3)_2}$ as confirmed by X-ray crystallography.[353] η^2-Acetylene complexes $\mathrm{Pt(\eta^2\text{-}R^1C{\equiv}CR^2)(P\text{–}P)}$ (P–P = dppe, dmpe, depe) have been also shown to be formed by treatment of $\mathrm{Pt(C{\equiv}CR^1)_2(P\text{–}P)}$ with trialkylboranes $\mathrm{BR^2_3}$. Depending on the reaction conditions, $\mathrm{Pt(\eta^2\text{-}R^1C{\equiv}CR^2)(P\text{–}P)}$ and or η^3-alkenylboryl Pt(0) complexes $\mathrm{Pt(\eta^3\text{-}BR^2_2CR^2CR^1C{\equiv}CR^1)(P\text{–}P)}$ are generated.[354]

Direct intramolecular reductive processes may be used to afford η^2-alkyne complexes. Thus, complexes *cis*-$\mathrm{[Pt(C{\equiv}CAr^1)(SiAr^2_3)(PMe_2Ph)_2]}$ bearing a variety of $\mathrm{Ar^1}$ and $\mathrm{Ar^2}$ groups cleanly undergo under mild conditions (30–40 °C) C–Si reductive elimination to give $\mathrm{Pt(\eta^2\text{-}Ar^2_3Si\text{–}C{\equiv}CAr^1)(PMe_2Ph)_2}$.[355] Kinetic studies suggest a concerted reaction process in the precursor involving simultaneous weakening of the Pt–C and Pt–Si bonds with concomitant formation of a C–Si bond via a three-center transition state.[355] Similarly, by thermal activation, $\mathrm{Pt(C{\equiv}CPh)(SiMe_3)(dcpe)}$ affords $\mathrm{Pt(\eta^2\text{-}Me_3SiC{\equiv}CPh)(dcpe)}$, which, in this case, reversibly reverts to the precursor under photochemical conditions.[356] In the presence of internal alkyne promotors ($\mathrm{PhC{\equiv}CPh}$, $\mathrm{MeO_2C\text{–}C{\equiv}C\text{–}CO_2Me}$), *cis*-alkyl(silyl)platinum complexes *cis*-$\mathrm{PtR(SiPh_3)L_2}$ (R = Me,[357] Et, Pr, Bu; L = $\mathrm{PMe_2Ph}$, $\mathrm{PMePh_2}$)[358] also readily undergo C–Si reductive elimination to give $\mathrm{SiRPh_3}$ and $\mathrm{Pt(\eta^2\text{-}alkyne)L_2}$. In this case, experimental data, in agreement with theoretical calculations,[168,359] indicate that the reaction proceeds through the formation of an (η^2-alkyne)platinum(II) intermediate, *cis*-$\mathrm{[PtR(SiPh_3)(\eta^2\text{-}PhC{\equiv}CPh)L]}$ or *cis*-$\mathrm{[PtPh(SiRPh_2)(\eta^2\text{-}PhC{\equiv}CPh)L]}$ (operative for R = Et, Pr, Bu) followed by reductive elimination of $\mathrm{SiRPh_3}$ via a four-coordinate transition state. However, competition between insertion into the Pt–Si bond and alkyl–silyl reductive elimination is found in the reaction of *cis*-$\mathrm{[PtMe(SiPh_3)(PMePh_2)_2]}$ with $\mathrm{HC{\equiv}CPh}$,[360] and only insertion of acetylene ($\mathrm{HC{\equiv}CPh}$, $\mathrm{HC{\equiv}CH}$) is observed with *cis*-bis(silyl) derivatives *cis*-$\mathrm{[Pt(SiR_3)_2(PMe_2Ph)_2]}$.[361] In the same way, the reaction of *trans*-$\mathrm{[PtPh(SR^1)(PPh_3)_2]}$ with $\mathrm{HC{\equiv}CR^2}$ ($\mathrm{R^2} = n\text{-}\mathrm{C_6H_{13}}$) has been shown to form $\mathrm{Pt(\eta^2\text{-}R^2C{\equiv}CH)(PPh_3)_2}$ and (Z)-$\mathrm{C(SR^1)R^2{=}CHPh}$, this latter formed by insertion of the alkyne into the Pt–S bond followed by reductive elimination of the resulting vinyl with the Ph group.[362] The η^2-diyne complex $\mathrm{Pt(\eta^2\text{-}PhC{\equiv}C\text{–}C{\equiv}CPh)(dppe)}$ is unexpectedly formed by alkynyl coupling in the reaction of $\mathrm{Pt(C{\equiv}CPh)_2(dppe)}$ with the cluster $\mathrm{Ru_3(CO)_9(PPh_3)_3}$.[363] However, a similar reaction with $\mathrm{Mn_2(CO)_9(MeCN)}$ affords $\mathrm{Mn_2Pt(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^4\text{-}PhC{\equiv}C\text{–}C{\equiv}CPh)(CO)_6(dppe)}$, in which the resulting diyne acts as a bridging ligand.[363]

8.09.3.1.1.(i).(b) Preparations via ligand displacements

Novel bis(η^2-alkyne)platinum(0) complexes, with substituted alkynols and alkynediols $\mathrm{Pt(\eta^2\text{-}R^1C{\equiv}CR^2)_2}$ ($\mathrm{R^1 = R^2 = CMe_2(OH)}$;[364] $\mathrm{R^1 = Bu^t}$, $\mathrm{R^2 = CMe_2(OH)}$,[364] $\mathrm{C_6H_{10}(OH)}$,[365] $\mathrm{C_5H_8(OH)}$;[365] $\mathrm{R^1}$ = 4-$\mathrm{(NO_2)C_6H_4}$, 2,4-$\mathrm{(NO_2)_2C_6H_3}$, 2,4-$\mathrm{Br(NO_2)C_6H_3}$, 2-$\mathrm{BrC_6H_4}$, 3-$\mathrm{BrC_6H_4}$, $\mathrm{R_2 = CMe_2(OH)}$[366]) have been prepared by treatment of $\mathrm{Pt(cod)_2}$ with 2 equiv. of $\mathrm{R^1C{\equiv}CR^2}$ [364,365] or by using $\mathrm{Pt_2(dmvts)_2}$ as precursor.[366] Related homoleptic $\mathrm{Pt(\eta^2\text{-}alkyne)_2}$ complexes with alkynylphenylsilanes[367] or containing either $\mathrm{NH_2}$ [1,1-$\mathrm{(C{\equiv}CSiMe_3)(NH_2)C_6H_{10}}$, 1,1-$\mathrm{(C{\equiv}CSiPh_3)(NH_2)C_6H_{10}}$)] or $\mathrm{NH_2/OH}$ [$\mathrm{(H_2N)CMe_2\text{–}C{\equiv}C\text{–}CMe_2OH}$, 1,1-$\mathrm{(C{\equiv}C\text{–}CMe_2NH_2)(OH)C_6H_{10}}$, 1,1-$\mathrm{(C{\equiv}C\text{–}CMe_2OH)(NH_2)C_6H_{10}}$, 1,1-$\mathrm{(C{\equiv}C\text{–}C_6H_{10}OH)(NH_2)C_6H_{10}}$)] substituents are accessible using $\mathrm{Pt(cod)_2}$.[368] An unusual cationic product $\mathrm{\{Pt(cod)[\eta^2\text{-}(C{\equiv}CSiMe_3)(NH_3)C_6H_{10}]Cl\}_4}$, in which four molecular units are self-assembled, may also be prepared by reaction of $\mathrm{Pt(cod)_2}$ with the corresponding ammonium salt.[368] Complexes of type $\mathrm{Pt(\eta^2\text{-}alkyne)(P\text{–}E)}$ (E = P, N) may also be prepared from $\mathrm{Pt(cod)_2}$.[356,369] Equimolar mixtures of $\mathrm{Pt(cod)_2}$, the bidentate ligand (PE = $\mathrm{PPr^i_2CH_2CH_2NMe_2}$ (PN), d^{i}ppe, dppf), and the appropriate alkyne, give rise to the corresponding $\mathrm{Pt(\eta^2\text{-}alkyne)(P\text{–}E)}$ (alkyne = $\mathrm{PhC{\equiv}CPh}$,[369] $\mathrm{Me_3SiC{\equiv}CPh}$,[356] P–E = P–N, d^{i}ppe; alkyne = $\mathrm{RC{\equiv}C\text{–}C{\equiv}CR}$, R = Ph, P–E = dppf;[370] R = H, P–E = d^{i}ppe[371]). Addition of 2 equiv. of $\mathrm{PPr^i_2CH_2CH_2NMe_2}$ affords the bis-phosphine complexes $\mathrm{Pt(\eta^2\text{-}PhC{\equiv}CPh)(PN\text{-}\kappa \mathit{P})_2}$ (R = Ph, $\mathrm{SiMe_3}$).[356,369] The η^2-diyne $\mathrm{Pt(\eta^2\text{-}RC{\equiv}C\text{–}C{\equiv}CR)L_2}$[372–374] (L = $\mathrm{PPh_3}$, $\mathrm{PTol_3}$;[373] R = Ph,[372] Me,[373] $\mathrm{SiMe_3}$[374]) or η^2-enyne $\mathrm{Pt(\eta^2\text{-}HC{\equiv}C\text{–}CR{=}CH_2)L_2}$[373,375] (R = Me,[373] n-$\mathrm{C_6H_{13}}$; $\mathrm{L_2 = (PPh_3)_2}$,[373] $(p\text{-}\mathrm{Tol_3})_2$,[373] dppp[375]) have been obtained by treatment of $\mathrm{Pt(\eta^2\text{-}C_2H_4)L_2}$ with the appropriate unsaturated ligand. Similar reactions of $\mathrm{Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2}$ with other alkynes such as $\mathrm{ClC{\equiv}CCl}$,[376] $\mathrm{PhC{\equiv}CCH_2OMe}$,[377] or $\mathrm{HC{\equiv}CR}$ (R = p-$\mathrm{C_6H_4CH_2CH(CO_2Me)NH(COPh)}$)[378] afford the corresponding species $\mathrm{Pt(\eta^2\text{-}alkyne)(PPh_3)_2}$. Further reactions of $\mathrm{Pt(\eta^2\text{-}ClC{\equiv}CCl)(PPh_3)_2}$ with phosphines[376] or phosphites[379] have been described to give phosphine substitution or oxidative addition reactions to form *trans*-$\mathrm{[PtCl(C{\equiv}CCl)(PR_3)_2]}$ (R = Et, $\mathrm{Bu^n}$) or *cis* and *trans*-$\mathrm{[PtCl(C{\equiv}CCl)(PPh_3)_\mathit{n}\{P(OPh)_3\}_{2\text{-}\mathit{n}}]}$.[379] Displacement of ethylene in $\mathrm{Pt(\eta^2\text{-}C_2H_4)(dcpe)}$ by $\mathrm{PPh_2C{\equiv}CMe}$ affords the η^2-alkynylphosphine $\mathrm{Pt(\eta^2\text{-}Ph_2PC{\equiv}CMe)(dcpe)}$, and subsequent oxidation with sulfur or air gives rise to the corresponding complexes $\mathrm{Pt(\eta^2\text{-}Ph_2P(X)C{\equiv}CMe)(dcpe)}$ (X = S, O), as confirmed by X-ray diffraction studies.[380] Cluster fragmentation yielding $\mathrm{Pt(\eta^2\text{-}RC{\equiv}CR)(CO)(PBu^t_3)}$ (R = $\mathrm{CF_3}$, $\mathrm{CO_2Bu^t}$) occurs by treatment of $\mathrm{Pt_3(\mu\text{-}CO)_3(PBu^t_3)_3}$ with an excess of the appropriate alkyne. For R = $\mathrm{CO_2Bu^t}$, its formation takes places through the binuclear alkyne-bridged species $\mathrm{Pt_2(CO)_2(PBu^t_3)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC{\equiv}CR)}$ isolated as an intermediate.[26]

8.09.3.1.1.(ii) Structural Aspects

Single crystal structure determinations of several Pt(η^2-alkyne)$_2$ complexes containing either OH or NH$_2$/OH substituents reveal that the central platinum atom is tetrahedrally coordinated to four *sp*-carbon atoms of the alkyne ligands, and that the resulting units are connected via hydrogen bonds to form a dimer (alkyne = Bu^t–C≡CCMe$_2$OH,[364] 1,1-(C≡CBu^t)(OH)C$_6$H$_{10}$,[365] 1,1-(C≡C–CMe$_2$NH$_2$)(OH)C$_6$H$_{10}$[368]), a polymer-like chain (alkyne = Me$_2$(OH)-C–C≡C–CMe$_2$(OH),[365] (NH$_2$)Me$_2$C–C≡C–CMe$_2$(OH)[368]), or an extended chain of dimers (alkyne = 1,1-(C≡CBu^t)(OH)C$_5$H$_8$[365]), the latter based on additional O–H–O bonds between dimers. In the same way, the X-ray structure of {PtCl[η^2-1,1-(C≡CSiMe$_3$)(NH$_3$)C$_6$H$_{10}$](cod)}$_4$ shows that four molecular units form a cube with four NH$_3^+$ groups and Cl$^-$ at the corners linked by hydrogen bridges.[368] The X-ray crystal structure of the previously elusive dichloroethyne complex Pt(η^2-ClC≡CCl)(PPh$_3$)$_2$ is quite unusual, exhibiting different Pt–C (2.051(11), 1.983(10) Å) and C–Cl (1.644(11) vs. 1.725(11) Å) bonds lengths, which, in agreement with spectroscopic data, suggest some degree of contribution of a carbene-type structure.[376] X-ray and spectroscopic data for some diyne Pt(η^2-RC≡C–C≡CR)L$_2$ (R = Ph, L = PPh$_3$;[372] L$_2$ = dppe,[363] dppf[370]) and enyne Pt(η^2-HC≡CCMe=CH$_2$)(dppp)[375] complexes confirm that complexation occurs through only one C≡C bond or takes place through the alkyne unit. The structures show the expected normal tetragonal coplanar arrangement of the PtP^{1}P^{2}C^{1}C^2 inner core, being remarkable in the enyne complex that all carbon atoms of the enyne moiety are also coplanar with the coordination plane.

8.09.3.1.1.(iii) Reactions

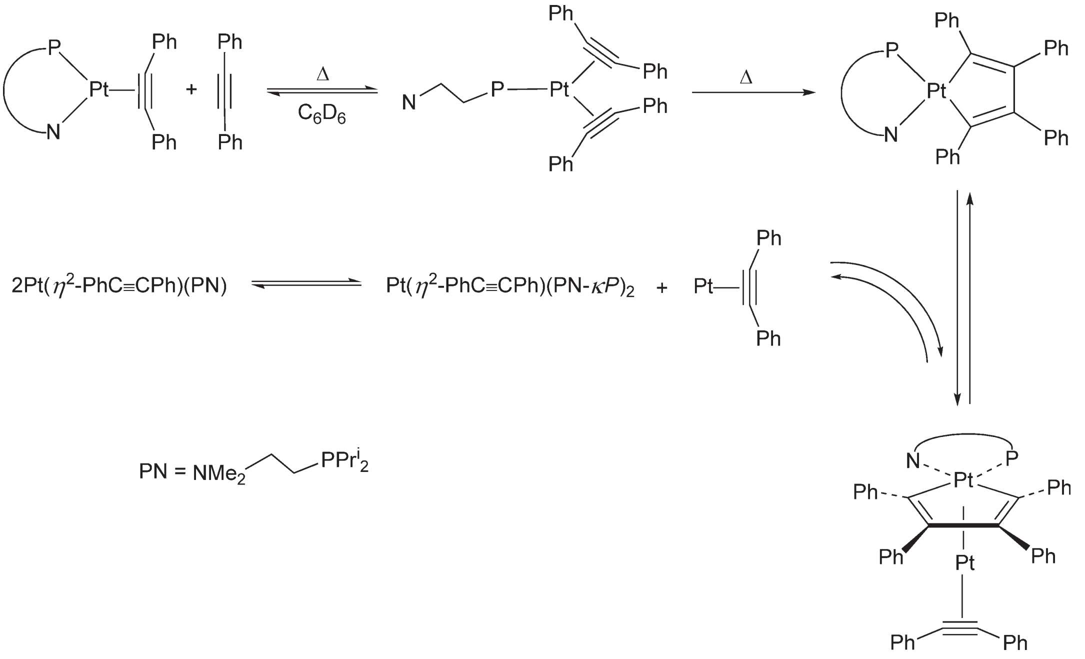
The more common processes are the activation of the alkyne fragment to yield alkynyl derivatives and the interaction with acids (H$^+$) or related electrophilic species.

8.09.3.1.1.(iii).(a) Activation of the alkyne fragment

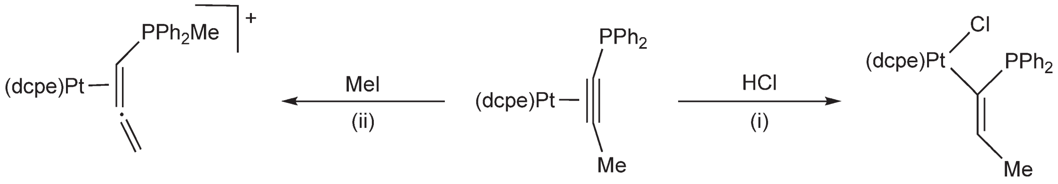
In contrast to the stability of Pt(η^2-Me$_3$SiC≡CPh)(dcpe) in solution, the related derivative Pt(η^2-Me$_3$SiC≡CPh)(PN) (PN = Ph$_2$PCH$_2$CH$_2$NMe$_2$) rearranges at RT to selectively afford Pt(SiMe$_3$)(C≡CPh)(PN) (Si *trans* to N), a behavior that can be attributed to the higher electron density at Pt due to the lower π-acceptor character of the hybrid hemilabile PN ligand.[356] In agreement with this proposal, the analogous Pt(η^2-Me$_3$SiC≡CPh)(PN-κP)$_2$ complex is also thermally robust. In a similar reaction, Pt(η^2-ClC≡CCl)(PPh$_3$)$_2$ undergoes a thermally induced isomerization to *trans*-[PtCl(C≡CCl)(PPh$_3$)$_2$].[376] However, under photochemical conditions, Pt(η^2-Me$_3$SiC≡CPh)(dcpe) is also activated to give Pt(SiMe$_3$)(C≡CPh)(dcpe), which, in this case, reverts thermodynamically on heating to the precursor.[356] Similar photochemically induced oxidative additions occur with both Pt(η^2-PhC≡CPh)(PN) and Pt(η^2-PhC≡CPh)(d^{i}ppe) to yield PtPh(C≡CPh)(PN) and PtPh(C≡CPh)(d^{i}ppe).[381] However, the complex Pt(η^2-PhC≡CPh)(PN) exhibits higher reactivity, and reacts with PhC≡CPh to afford quantitatively the platinacyclopenta-2,4-diene complex Pt(CPh)$_4$(PN) (Scheme 13).[369] This complex is also generated by thermal activation of [Pt(η^2-PhC≡CP)(PN)] being the bis(phosphine) complex Pt(η^2-PhC≡CPh)(PN-κP)$_2$, and the unusual diplatinum compound (PN)Pt(CPh)$_4$Pt(η^2-PhC≡CPh) (X-ray) intermediate species (Scheme 13).[369] Facile C–H activation leading to bimetallic species [Pt(PPh$_3$)$_2$(μ-H)(μ-C≡CPh)MLn]^n (ML$_n$ = MCp*PMe$_3$, n = 2+, Pt(R$_F$)$_2$, n = 0) is promoted by interaction of Pt(η^2-PhC≡CH)(PPh$_3$)$_2$ with labile species such as MCp*(Tf)$_2$(PMe$_3$) (M = Rh, Ir)[74] and *cis*-[Pt(R$_F$)$_2$(THF)$_2$].[382]

8.09.3.1.1.(iii).(b) Interaction with acid (H$^+$) or related electrophilic species

Treatment of Pt(η^2-Ph$_2$PC≡CMe)(dcpe) with HCl (Equation (10), (i)) affords the η^1-vinyl derivative PtCl{C(PPh$_2$)=CHMe}(dcpe), while the analogous reaction with MeI (Equation (10), (ii)) results in the formation of [Pt{η^2-C(=CH$_2$)=CHPPh$_2$Me}(dcpe)]I, in which the alkynylphosphine has rearranged to a phosphonium allene ligand as confirmed by X-ray studies.[380] In the same way, reaction of Pt(η^2-HC≡CMe)(dfepe) with HSO$_3$F (HX), at low temperature, produces instead the double-proton-transfer propene adduct [PtX(η^2-H$_2$C=CHMe)(dfepe)]X without evidence for a propenyl Pt(II) intermediate.[350] However, protonation of diyne complexes Pt(η^2-RC≡C–C≡CR)L$_2$ (R = Me, SiMe$_3$; L = PPh$_3$, PTol$_3$) at low temperature initially gives the corresponding hydride derivatives [PtH(η^2-diyne)L$_2$]$^+$, which subsequently rearrange to the corresponding η^3-propargyl cationic complexes[373] [Pt{η^3-$C^{2,4}$-C(R)H=CCCR}L$_2$]$^+$. An analogous reaction takes place by direct interaction of Pt(η^2-PhC≡C–C≡CPh)(dppf) with the isolobal entity [Au(PPh$_3$)]$^+$, which affords the bimetallic derivative[370] [Pt{η^3-$C^{2,4}$-C(Ph)(AuL)=CCCPh}(dppf)]$^+$. In η^2-enyne complexes Pt(η^2-HC≡C–CR=CH$_2$)L$_2$, protonation occurs exclusively at the triple bond to afford an η^3-butadienyl derivative (R = Me) [Pt{η^3-CH$_2$C(Me)C=CH$_2$}L$_2$]X (X = BF$_4$, CF$_3$CO$_2$; L = PPh$_3$, PTol$_3$)[373] or a neutral σ-dienyl complex PtCl{η^1-C^2-C(=CH$_2$)–CR=CH$_2$}(PPh$_3$)$_2$][75] (R = n-C$_6$H$_{13}$), depending on the counterion.



Scheme 13



(10)

8.09.3.1.2 Divalent derivatives

8.09.3.1.2.(i) Preparation

The number of simple alkyne complexes of Pt(II) remain scarce due to the facility of alkynes to undergo other processes such as oligo- or polymerization of alkynes, deprotonation, insertions or rearrangement, followed by nucleophilic attacks.[346] Examples of *trans*-$[PtCl_2(\eta^2\text{-alkyne})_2]$ with a variety of alkyne triols have been reported by reaction of K_2PtCl_4 with the appropriate alkyne, in which the presence of inter- and intramolecular hydrogen bonds probably play a significant role in their formation.[383] Reaction of *cis*-$[Pt(R_F)_2(\eta^2\text{-RC}\equiv\text{CR})_2]$ with either *cis*-$[Pt(R_F)_2(THF)_2]$ or $(NBu_4)_2[Pt(R_F)_4]$ gives rise to neutral *cis*-$[Pt(R_F)_2(\eta^2\text{-RC}\equiv\text{CR})(THF)]$ (R = Et, Ph) or anionic complexes $(NBu_4)[Pt(R_F)_3(\eta^2\text{-PhC}\equiv\text{CPh})]$, respectively.[384] Further displacement of THF affords related *cis*-$[Pt(R_F)_2(\eta^2\text{-RC}\equiv\text{CR})L]$ (L = py, PPh_3, $SbPh_3$). Internal alkynes react easily with $[K(18\text{-cr-}6)]_2[Pt_2Cl_6]$ to give $[K(18\text{-cr-}6)][PtCl_3(R^1C\equiv CR^2)]$ (R^1, R^2 = Me, Et, Ph, Pr^n, CMe_2OH),[385] but related complexes with terminal alkynes (HC≡CR, R = Ph, Bu^t, Bu^n, Pr^n) are only accessible by displacement of 2-butyne in $[PtCl_3(\eta^2\text{-CH}_3C\equiv CCH_3)]^-$.[386] Unusual cationic derivatives $[PtR(\eta^2\text{-alkyne})(phen)]^+BF_4^-$ (R = Me, Et) are generated by displacement of Me–fu in $[PtR(Me\text{–}fu)(phen)]^+$ with internal electron-rich alkynes (MeC≡CMe, PhC≡CPh, MeC≡CPh).[387] However, the analogous methyl complexes (R = Me) with terminal alkynes, RC≡CH (R = Ph, CH_2Ph, Bu^n), are only detected as transient species evolving in solution to give stable η^3-allyl complexes $[Pt(\eta^3\text{-CH}_2CHCHR)(phen)]BF_4$.[387]

In a similar way to alkene complexes, novel pentacoordinate complexes of the type $PtX_2(\eta^2\text{-R}^1C\equiv CR^2)(dmphen)$ have been prepared by direct uptake of alkynes, $R^1C\equiv CR^2$ (R^1, R^2 = H, Me, Ph, Pr^n), with distorted square-planar complexes $PtX_2(dmphen)$ (X = halide).[388] Furthermore, very stable complexes $PtTpMe(\eta^2\text{-alkyne})$ (Tp = tris-pyrazolylborate) are generated by bridge splitting of the polymer $\{PtTpMe\}_n$ with the corresponding alkyne.[389] The bis(silyl)platinum complex *cis*-$[Pt(SiHPh_2)_2(PMe_3)_2]$ reacts with excess of dimethyl acetylenecarboxylate to afford the pentacoordinate derivative $\overline{\mathrm{Pt(CR{=}CR\text{-}SiPh_2\text{-}CR{=}C}}\mathrm{R)(\eta^2\text{-}RC{\equiv}CR)(PMe_3)_2}$ ($\mathrm{R = CO_2Me}$) having a 5-sila-2-platina-1,4-cyclohexadiene cycle and an η^2-coordinated $\mathrm{RC{\equiv}CR}$ ligand, as confirmed by X-ray crystallography.[390] Its formation probably involves the initial formation of a 4-sila-3-platinacyclobutene complex $\overline{\mathrm{Pt(CR{=}CR\text{-}S}}\mathrm{iPh_2)(PMe_3)_2}$, followed by further insertion of an alkyne molecule into the Pt–Si bond and coordination of another alkyne molecule.[390]

8.09.3.1.2.(ii) Structural Aspects

The structures of several anionic complexes $\mathrm{(NBu_4)[Pt(R_F)_3(\eta^2\text{-}PhC{\equiv}CPh)]}$[384] and $\mathrm{[K(18\text{-}cr\text{-}6)][PtCl_3(R^1C{\equiv}CR^2)]}$ ($\mathrm{R^1 = R^2 = Me}$,[385] Et;[385] $\mathrm{R^1 = Ph}$, $\mathrm{R^2 = D}$[386]) confirm that the alkyne ligand is essentially perpendicular to the tetragonal coordination plane. The small lengthening of the $\mathrm{C{\equiv}C}$ bonds (~0.04 Å), bend-back angles (17°–21.4°) as well as spectroscopic data, with typical $\Delta\nu(\mathrm{C{\equiv}C})$ in the range (140–200 $\mathrm{cm^{-1}}$), are in accord with *ab initio* MO calculations, reflecting the dominance of σ-donation over π-backdonation.[385,386] The structure of $\overline{\mathrm{Pt(CR{=}CR\text{-}SiPh_2\text{-}CR{=}C}}\mathrm{R)(\eta^2\text{-}RC{\equiv}CR)(PMe_3)_2}$ ($\mathrm{R = CO_2Me}$) reveals a trigonal-bipyramidal structure with the two $\mathrm{PMe_3}$ ligands in the apical positions.[390] Spectroscopic, and also crystal data, for the complex $\mathrm{PtI_2(\eta^2\text{-}PhC{\equiv}CPh)(dmphen)}$,[388] suggest that in these tbp complexes (bend-back angles 38°,[390] 25°[388]), the alkyne–Pt interaction is intermediate between those of Pt(0) and square-planar Pt(II) derivatives.

8.09.3.1.2.(iii) Reactions

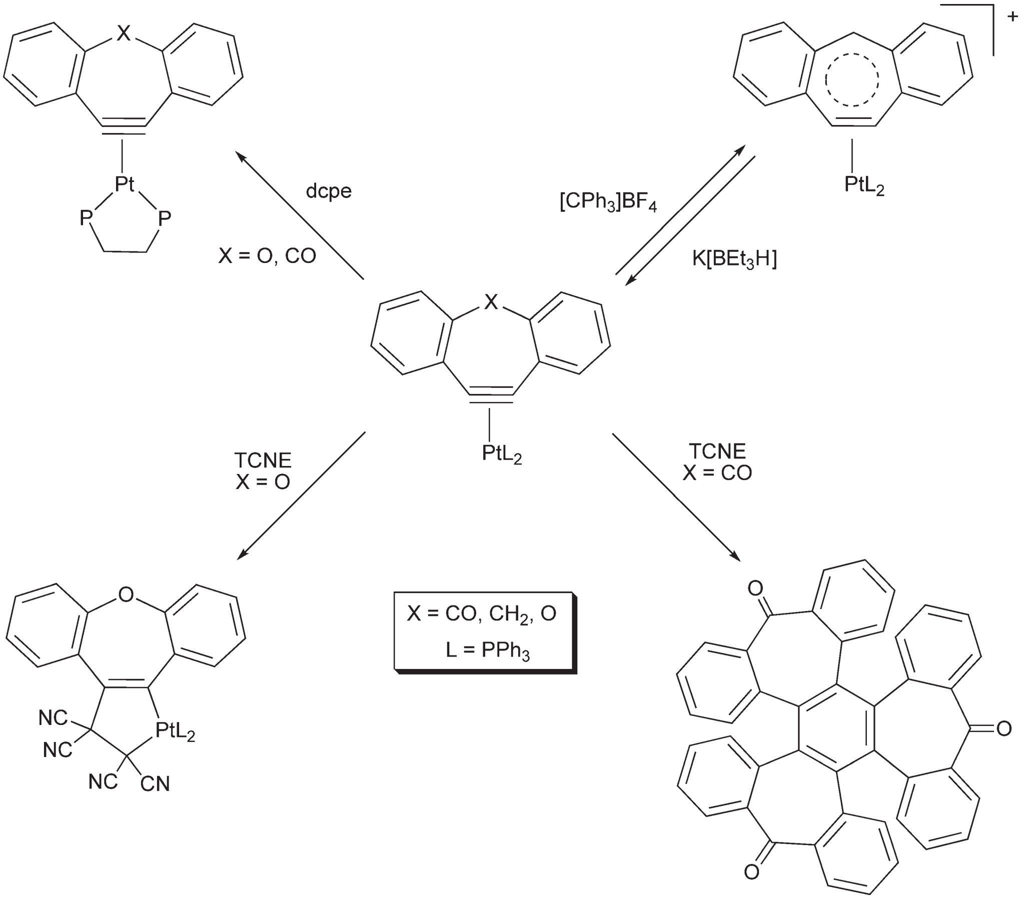
In pentacoordinate complexes $\mathrm{PtTpMe(\eta^2\text{-}alkyne)}$, the (trispyrazolylborate) (methyl)platinum fragment acts as a protecting group allowing further reactions on the alkyne giving polyfunctional acetylenes, which can subsequently be released from the complex by carbon monoxide.[389] As noted earlier, treatment of $\mathrm{[PtMe(\eta^2\text{-}Me\text{–}fu)(phen)]^+}$ with $\mathrm{HC{\equiv}CR}$ gives, through the detected transient η^2-alkyne species, η^3-allyl final products $\mathrm{[Pt(\eta^3\text{-}CH_2CHCHR)(phen)]BF_4}$.[387] The analogous reaction of $\mathrm{[PtEt(\eta^2\text{-}Me\text{–}fu)(phen)]BF_4}$ with $\mathrm{HC{\equiv}CPh}$ affords $\mathrm{[Pt(\eta^3\text{-}CHMeCHCHPh)(phen)]^+}$. Labeling studies suggest a mechanism in which the initial η^2-alkyne complex isomerizes to a vinylidene species as an intermediate.[387] However, the related $\mathrm{[PtMe(\eta^2\text{-}MeO_2C{\equiv}CCO_2Me)(phen)]^+}$, detected only at low temperature, rapidly evolves in the presence of NCMe by insertion into the Pt–Me bond leading to the corresponding σ-vinyl derivative.

8.09.3.1.3 Theoretical aspects

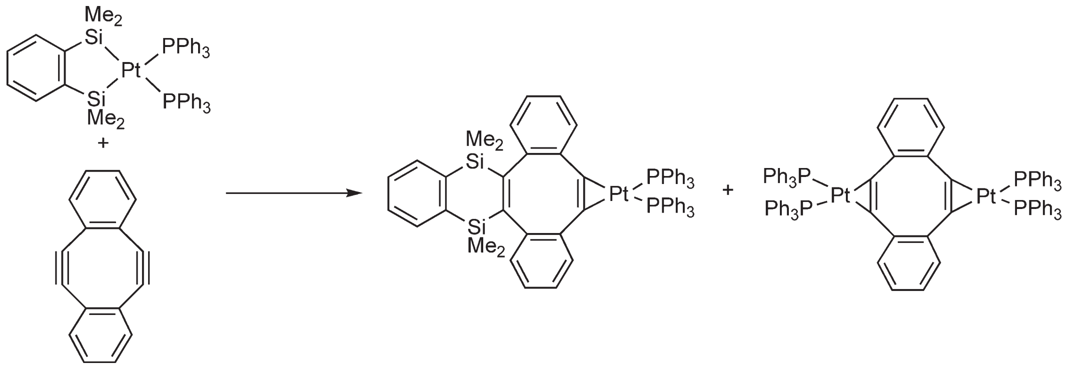
Some of the theoretical studies carried out on alkyne complexes are paralleled by corresponding studies of alkene derivatives (Section 9.2.1.3).[139,153,155,157] A comparison of the bonding interaction in $\mathrm{Pt(\eta^2\text{-}C_2H_2)(PH_3)_2}$ and the analogous $\mathrm{C_2H_4}$ complexes gives a slightly higher bonding energy for the acetylene complex.[155] Recent gradient-corrected DFT calculations on systems $\mathrm{M(\eta^2\text{-}C_2H_2)L_2}$ ($\mathrm{M = Ni, Pd, Pt}$; $\mathrm{L = PH_3, PMe_2}$; $\mathrm{L_2 = H_2P(CH_2)_xPH_2}$ ($x = 1, 2$)) reveal, as in the ethylene complexes, that the $\mathrm{C_2H_2}$ ligand is more strongly bonded in the diphosphine derivatives.[157] The energy partitioning analysis also indicates that the M–C bonds have a higher electrostatic than covalent character, and this latter comes mainly from the in-plane backdonation, suggesting that the ligand should be considered only as a two-electron donor.[157] In the context of the study of the formation of dinuclear platina β-diketones from reaction of hexachloroplatinic acid with $\mathrm{RC{\equiv}CSiMe_3}$, by theoretical calculations, the anionic $\mathrm{[PtCl_3(\eta^2\text{-}HC{\equiv}CMe)]^-}$, $\mathrm{[PtCl_2(OH)(\eta^2\text{-}HC{\equiv}CMe)]^-}$, and neutral $\mathrm{PtCl_2(C{=}CHMe)(\eta^2\text{-}HC{\equiv}CMe)}$ and $\mathrm{PtCl_2(CEt(OH))(\eta^2\text{-}HC{\equiv}CMe)}$ complexes have been examined, leading to the conclusion that π-donation in anionic complexes is slightly larger than in neutral ones.[391] A recent MP2 geometry optimization, of both the perpendicular and planar geometries of $\mathrm{PtH(SiH_3)(\eta^2\text{-}C_2H_2)(PH_3)}$, has been carried out in the framework of the study of acetylene insertion into Pt–X ($\mathrm{X = H, Si}$) bonds, indicating that the planar form is slightly more stable than the perpendicular one and revealing that insertion into the Pt–H bond is favored.[392] Calculations on the thermal and photochemical isomerization of $\mathrm{Pt(\eta^2\text{-}NCC{\equiv}CCN)(PH_3)_2}$ to the acetylide derivative indicate that, in agreement with experimentation, the isomerization can only be induced photochemically through a bisect complex in the singlet excited state and a three-coordinate Pt-complex in the triplet state.[393] Recent DFT calculations have been carried out to optimize and produce the isotopic vibrational frequencies of the products ($\mathrm{PtCCH_2}$, HPtCCH, and $\mathrm{Pt(\eta^2\text{-}C_2H_2)}$) generated by reaction of laser-ablated Pt atoms with $\mathrm{C_2H_2}$.[394] Mechanisms and energetics of several platinum-catalyzed reactions involving alkyne ligands have been also studied.[395–397]

8.09.3.2 η^2-Arynes and Strained Cyclic Alkynes

The chemistry of transition metal complexes of arynes and strained cyclic alkynes have been surveyed in two reviews.[243,347] Special interest has been focused on complexes with the benzyne's next higher homolog ($C_7H_5^+$, tropyne). Thus, the cation $[Pt(\eta^2\text{-}C_7H_5)(PPh_3)_2]^+$ is readily generated by hydride abstraction with Ph_3CBF_4 from the corresponding complex with cycloheptadienyne $Pt(\eta^2\text{-}C_7H_6)(PPh_3)_2$.[398] A series of dibenzametallated complexes (Scheme 14) is generated by base-induced (KOBu^t) dehydrobromination from the corresponding bromoalkenes (X = CO, CH_2, O) in the presence of $Pt(PPh_3)_3$.[399] Some selected reactions of these complexes are shown in Scheme 14. In particular, hydride abstraction from the product with didehydrocycloheptatriene gives the corresponding dibenzotropyne complex.[399] The access to two phenylene platinum derivatives[400] is shown in Equation (11), although the diplatinum complex can be alternatively generated by direct reaction of 5,6,11,12-tetradehydrobenzo-[*a*,*e*]-cyclooctene with 2 equiv. of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ (see section 9.3.4.1).[400] The geometries of the Pt centers in both complexes are typical of trigonal platinum alkyne complexes with a fold angle at the central eight-membered ring smaller in the diplatinum complex (ca. 20° vs. 40°).[400] Effective reduction of 1,2-dibromo[2,2]-paracyclophane-1-ene with sodium amalgam in the presence of $Pt(PPh_3)_3$ or $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ yields the $Pt(PPh_3)_2$ η^2-complex of [2,2]-paracyclophane-1-yne, whose structure has been solved by X-ray methods.[401] Both the benzyne, $Pt(\eta^2\text{-}C_6H_4)(PPh_3)_2$, and the cyclohexyne, $Pt(\eta^2\text{-}C_6H_8)(PPh_3)_2$, complexes have been reported to undergo isomerization by unusual H-transfer from the PPh_3 to the alkyne fragment, yielding the orthometallated phenyl, $[Pt\{C_6H_4(PPh_2)\text{-}2\}(C_6H_5)(PPh_3)]$, and η^1-cyclohexenyl, $Pt\{C_6H_4(PPh_2)\text{-}2\}(\eta^1\text{-}C_6H_9)(PPh_3)$ complexes, respectively, as confirmed by X-ray diffraction methods.[402]



Scheme 14



(11)

8.09.3.3 η^2-X≡CR and Related Complexes

The coordination chemistry of phosphaalkynes has been summarized in several reviews.[241,403–405] The preparation of novel stable phosphaalkynes $P\equiv CR$ has allowed the synthesis of new mononuclear complexes $Pt(\eta^2\text{-}P\equiv CR)(PPh_3)_2$ ($R = NPr^i_2$,[406] Mes[407] (X-ray)), generated using $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ as precursor. In a similar way, the first arsaalkyne $Pt(\eta^2\text{-}As\equiv CR)(PPh_3)_2$ ($R = 2,4,6\text{-}(Bu^t)_3C_6H_2$) has been isolated and characterized by X-ray crystallography.[408] Treatment of the diphosphaalkyne $P\equiv C\text{–}C(C_6H_4)_3C\text{–}C\equiv P$ with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ (1 : 2) causes complexation of both $C\equiv P$ triple bonds to afford the bis-platinum complex $\{(PPh_3)_2Pt\}_2(\mu\text{-}\eta^2:\eta^2\text{-}P\equiv C\text{–}C\text{-}(C_6H_4)_3C\text{–}C\equiv P)$, as confirmed by X-ray diffraction.[409] In general, side-on coordination of these ligands results in a remarkable elongation of the $X\equiv C$ bond lengths (8–10%) and bend-back angles in the range (37.4–48°), providing strong evidence for π-backbonding.

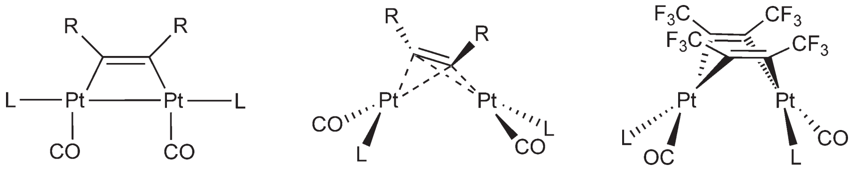
Examples with cyaphide ($C\equiv P^-$) bridging ligands have been also reported. Thus, reaction of the η^1-phosphavinyl complex, *trans*-$[PtCl(CCl{=}PR)L_2]$ ($R = N(SiMe_3)_2$, $L = PEt_3$) with $PtCl_2(PEt_3)_2$ in the presence of sodium benzophenone as reductant gives rise to the bridging $\eta^1:\eta^2$-cyaphide binuclear complex $ClL_2Pt(\mu\text{-}\eta^1:\eta^2\text{-}C\equiv P)PtL_2$, characterized by X-ray difraction.[410,411] The terminal electron pair on phosphorus has also been used to coordinate different ML_n fragments ($ML_n =$ *trans*-$PtCl_2L$, $W(CO)_5$), affording trinuclear cyaphide-bridging complexes $ClL_2Pt(\mu\text{-}\eta^1:\eta^1:\eta^2\text{-}C\equiv P)\{ML_n\}PtL_2$ ($L = PEt_3$), as confirmed by X-ray for the complex with $ML_n = W(CO)_5$, or alkylated by MeTf to give the cationic isocyaphide compound, $[ClL_2Pt(\mu\text{-}\eta^1:\eta^2\text{-}C\equiv PMe)PtL_2]Tf$.[411]

8.09.3.4 Polymetallic Alkyne Complexes

The chemistry of polymetallic complexes featuring bridging alkyne and alkynyl ($M\text{–}C\equiv CR$) ligands has been an intense area of study in recent years, which has also been expanded to polyynes and polyynyl moieties linking the metal centers. Recent developments in the chemistry and also materials properties of these complexes have been the subject of several reviews and highlight articles.[321,346,348,412–423] In this section, we only present complexes featuring η^2-alkyne–platinum bonding interactions.

8.09.3.4.1 Homobimetallic complexes

Interaction of diynes such as 1,4-*para*-diethynylbenzene or 5,6,11,12-tetrahydrodibenzo[*a*,*e*]-cyclooctene with 2 equiv. of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ affords $\{Pt(PPh_3)_2\}_2(\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv C\text{–}C_6H_4\text{–}C\equiv CH)$[353] and $\{Pt(PPh_3)_2\}_2(\eta^2:\eta^2\text{-}C_{16}H_8)$,[400] respectively. The phenylene complex has been crystallographically characterized.[400] A related diplatinum complex of [2.2]-paracyclophane-1,9-diyne $\{Pt(PPh_3)_2\}_2(\eta^2:\eta^2\text{-}C_{16}H_8)$ is generated by treatment of 1,2,9,10-tetrabromo[2.2]-paracyclophanediene with sodium amalgam and $Pt(PPh_3)_3$.[401] Binuclear zerovalent complexes $\{Pt(cod)\}_2(\mu\text{-}\eta^2:\eta^2\text{-}Me_3SiC\equiv C\text{–}C\equiv CSiMe_3)$,[356] $[Pt\{Ph_2Si(C\equiv CBu^t)_2\}]_2$,[367] and $[Pt\{SiPh(C\equiv CBu^t)_3\}]_2$[367] are generated by reaction of $Pt(cod)_2$ with bis(trimethylsilyl)butadiyne or (alkynyl)phenylsilanes in appropriate molar ratios. The molecular structure of $[Pt\{SiPh(C\equiv CBu^t)_3\}]_2$ reveals the presence of two uncoordinated alkynyl fragments and a central eight-membered ring comprising two silicon, four alkyne carbon, and two platinum atoms with an approximate chair conformation.[367] The cod is relatively labile, and treatment of $[\{Pt(cod)\}_2(\mu\text{-}\eta^2:\eta^2\text{-alkyne})]$ with the P,N chelating ligand $PPr^i_2PCH_2CH_2NMe_2$ generates the related $\eta^2:\eta^2$-diyne complex $\{Pt(P,N)\}_2(\mu\text{-}\eta^2:\eta^2\text{-}Me_3SiC\equiv C\text{–}C\equiv CSiMe_3)$, in which both Si–C(*sp*) bonds can be thermally activated to give the Pt(II)–Pt(II) complex

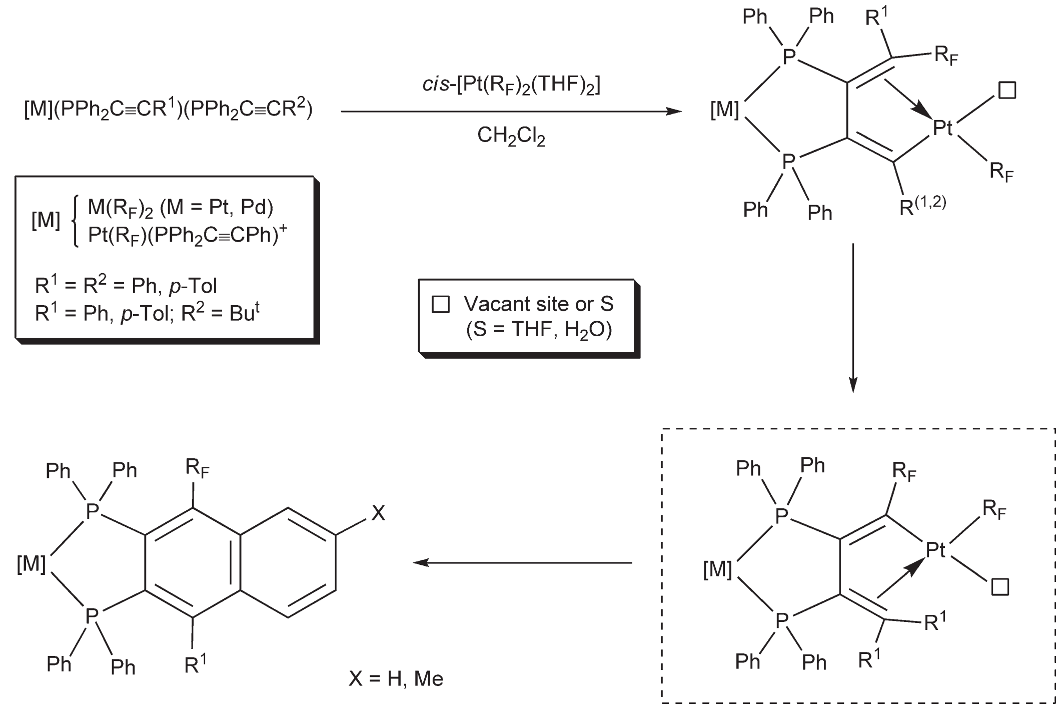


S15-A **S15-B** **S15-C**

Scheme 15

$(P,N)(Me_3Si)Pt–C{\equiv}C–C{\equiv}C–Pt(SiMe_3)(P,N)$.[356] Aromatic dialkynols $Ar(C{\equiv}C\text{-}Me_2OH)_2$ have been also successfully employed to form dinuclear species $Pt_2(\eta^2:\eta^2\text{-}ArC{\equiv}C–Me_2OH)_2$. The structure of $Pt_2\{C_6H_3(C{\equiv}CMe_2OH)_2\text{-}(NO_2)\text{-}1,2,4\}_2\}$ confirms that both Pt(0) centers are connected through two diacetylenic ligands by their acetylenic bonds.[366] Triangulo clusters $Pt_3(\mu\text{-}CO)_3L_3$ (L = tertiary phosphine) react with electron-poor alkynes, $RC{\equiv}CR$ ($R = CO_2Me$, CO_2Bu^t, CF_3),[424–426] to give stable binuclear complexes having the acetylenic C–C axis coplanar with the Pt–Pt bond (type **S15-A**, Scheme 15), $Pt_2(CO)_2L_2(\mu\text{-}\eta^1:\eta^1\text{-}RC{\equiv}CR)$ ($R = CO_2Me$, $L = PPh_3$, PCy_3;[426] $R = CO_2Bu^t$, $L = PPh_3$, PPh_2Bz)[424], or perpendicular to the Pt–Pt axis (type **S15-B**, Scheme 15), $Pt_2(CO)_2L_2(\mu\text{-}\eta^2:\eta^2\text{-}RC{\equiv}CR)$ ($R = CO_2Bu^t$, $L = PCy_3$, P^iPr_3; $R = CF_3$, $L = PPh_3$, PPh_2Bz, PCy_3, P^iPr_3),[424,425] as has been established by spectroscopic means and confirmed by X-ray crystallography for complexes $Pt_2(CO)_2L_2\text{-}(\mu\text{-}\eta^1:\eta^1\text{-}RC{\equiv}CR)$ ($R = CO_2Bu^t$, $L = PPh_2Bz$)[424] and $Pt_2(CO)_2L_2(\mu\text{-}\eta^2:\eta^2\text{-}RC{\equiv}CR)$ ($R = CO_2Bu^t$, $L = PCy_3$;[424] $R = CF_3$, $L = PPh_3$,[425] PCy_3[425]), respectively. These complexes are formed via initial unstable and fluxional 1:1 cluster adducts $Pt_3(CO)_3L_3(\mu\text{-}RC{\equiv}CR)$, identified at low temperature,[424,426] which undergo cluster fragmentation on warming to RT. Subsequent treatment of type **S15-B** complexes ($R = CF_3$; $L = PPh_3$, PPh_2Bz) with a large excess of hexafluoro-2-butyne, slowly affords the diplatinum(II) complexes $Pt_2(CO)_2L_2(\mu\text{-}\eta^1:\eta^1\text{-}CF_3C{\equiv}CCF_3)_2$ having two planar acetylenic bridges (**S15-C**, Scheme 15).[425] The Pt–Pt separation increases on going from complex **S15-A** to **S15-C** (**S15-A** ~2.6 Å; **S15-B** (3.03–3.09 Å; **S15-C** ~3.22 Å).[424,425]

A parallel mode of μ-alkyne coordination has been found in $Pt_2Cl_2(\mu\text{-}dppm)_2(\mu\text{-}RC{\equiv}CH)$, formed by reaction of the diplatinum(I) complex $Pt_2Cl_2(\mu\text{-}dppm)_2$ with $HC{\equiv}CR$ (R = Ph,[427] Fc[428]). Complexation of $Pt(PPh_3)_2$ to the remote alkyne fragment in *trans*-$[PtH(C{\equiv}CR)(PPh_3)_2]$ ($R = (CH_2)_5C{\equiv}CH$, $C_5H_3N(C{\equiv}CH)\text{-}2$, $C_6H_4–C{\equiv}CH$) yields very stable mixed-valent hydride–alkynyl–alkyne $Pt^{II}–Pt^0$ complexes, which are emissive in frozen solution.[353] A somewhat different type of complex is generated with alkynyl phosphines $PPh_2C{\equiv}CR$, which can be easily *P*-bonded to a platinum(II) center. Further coordination of the alkyne fragment to another platinum center, as well as the type of the resulting product, are usually determined by the nature of the precursor, the R group, and the electronic nature of the acceptor platinum fragment (Pt(II) or Pt(0)). Thus, mixed valence $Pt^{II}–Pt^0$ complexes containing only one bridging alkynyl phosphine η^2-coordinated to a $Pt(PPh_3)_2$ fragment are generated by reaction of platinum(II) complexes having either one, *cis*-$[Pt(R_F)_2(tht)(PPh_2C{\equiv}CR)]$[429] and $[Pt(CN)(R_F)_2(PPh_2C{\equiv}CR)]^-$,[430] or two, *cis*-$[Pt(R_F)_2(PPh_2C{\equiv}CR)_2]$[429] (R = Ph, Tol), *P*-bonded phosphines with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$. Structural confirmation is provided in $(tht)(R_F)_2Pt(\mu\text{-}\kappa P:\eta^2\text{-}PPh_2C{\equiv}CPh)Pt(PPh_3)_2$ and in the related $Pd^{II}–Pt^0$ derivative $(PPh_2C{\equiv}CPh)(R_F)_2Pd(\mu\text{-}\kappa P:\eta^2\text{-}PPh_2C{\equiv}CPh)Pt(PPh_3)_2$.[429] Similar dinuclear alkynyl-phosphine bridging complexes $(PPh_2C{\equiv}CR^1)(R^2C{\equiv}C)_2Pt(\mu\text{-}\kappa P:\eta^2\text{-}PPh_2C{\equiv}CR^1)Pt(PPh_3)_2$ ($R^2 = Bu^t$, Ph; $R^1 = Ph$, Tol) are formed by using *cis*-bis(alkynyl)platinum complexes, *cis*-$[Pt(C{\equiv}CR^2)_2(PPh_2C{\equiv}CR^1)_2]$, as precursors revealing that the $PC{\equiv}CR$ entity has stronger η^2-bonding capability toward the basic Pt(0) center than the alkynyl group does.[431] However, attempts to coordinate the $Pt(PPh_3)_2$ fragment to *P*-bonded $PPh_2C{\equiv}CBu^t$ ligands were unsuccessful, pointing to a lower η^2-bonding capability of this ligand. Preferential η^2-complexation to the remote alkyne fragment is observed with the diynylphosphine precursors $[\{Pt\}(Ph_2PC_2–C_6H_4–C_2Ph)]^{n-}$ ($\{Pt\}$ = *cis*-$Pt(R_F)_2(tht)$, $n = 0$; *cis*-$Pt(CN)(R_F)_2$, $n = 1$), but, in solution, the complex $\{Pt\}(\mu\text{-}\kappa P:\eta^2\text{-}C^{5,6}–PPh_2C_2–C_6H_4–C_2Ph)Pt(PPh_3)_2$ slowly isomerizes to the thermodynamically more stable complex having the Pt(0) fragment coordinated to the inner alkyne function, as has been confirmed by X-ray crystallography.[430] Diplatinum hetero- $(\mu\text{-}X)(\mu\text{-}PPh_2C{\equiv}CR)$ bridged $Pt^{II}–Pt^{II}$ complexes $(R_F)_2Pt(\mu\text{-}tht)(\mu\text{-}PPh_2C{\equiv}CR)Pt(R_F)_2$ ($R = Ph$, Bu^t, Tol, $C_6H_4C_2Ph$[430])[429,430] and $(PPh_2C{\equiv}CPh)Pt(\mu\text{-}\kappa E\text{-}o\text{-}C_6H_4E_2)\text{-}(\mu\text{-}PPh_2C{\equiv}CPh)Pt(R_F)_2$ (E = O, S)[432] are obtained by treatment of *cis*-$[Pt(R_F)_2(tht)(PPh_2C{\equiv}CR)]$[429,430] or $Pt(o\text{-}C_6H_4E_2)(PPh_2C{\equiv}CPh)_2$[432] with the bis-solvento complex *cis*-$[Pt(R_F)_2(THF)_2]$.[432] However, attempts to coordinate two alkynyl *P*-bonded phosphines using as precursors complexes such as *cis*-$[M(R_F)_2(PPh_2C{\equiv}CR)_2]$ (M = Pt, Pd) or $[Pt(R_F)(PPh_2C{\equiv}CR)_3]^+$[432] resulted, as shown in Scheme 16, in an unprecedented sequential insertion reaction into the robust $Pt–C_6F_5$ bond, giving rise to binuclear complexes containing a butadienyldiphosphine ligand bridging the



Scheme 16

metal centers, as has been confirmed by several X-ray diffraction studies.[432–434] The structure of $Pt(R_F)\{CBu^t{=}C(PPh_2)–C(PPh_2){=}C(Tol)(C_6F_5)\}Pt(R_F)_2$ confirms that the initial insertion process takes place with the aryl alkynyl phosphine, and, in addition, the presence of an unusual T-shaped three-coordinated Pt(II) center stabilized by the steric crowding of the diphenylbutadienyl ligand. In solution, the labile solvento complexes are unstable, evolving to give 1-C_6F_5-2,3-bis(diphenylphosphine)-4-arylnaphthalene products,[432–434] presumably via intermediate isomeric derivatives (Scheme 16), as confirmed by X-ray diffraction on complex $Pt(R_F)(H_2O)$-$\{\mu$-$C(C_6F_5){=}C(PPh_2)–C(PPh_2){=}CPh_2\}Pt(R_F)_2$,[434] by annulation of a phenyl or tolyl group.

8.09.3.4.2 Heterobimetallic derivatives

The bimetallic complex $(CO)_3Fe(\mu\text{-dppm})(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C{\equiv}CCF_3)Pt(CO)$, containing the alkyne coordinated in a μ-$\eta^1{:}\eta^1$ mode (Scheme 15 **S15-A**), is generated by treatment of $(CO)_2Fe\{Si(OMe)_3\}(\mu\text{-dppm})PtH(PPh_3)$ with $CF_3C{\equiv}CCF_3$.[435] The reaction occurs by initial insertion of the alkyne into the Pt–H bond yielding $(CO)_3$-$Fe\,\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})Pt(CF_3C{=}CHCF_3)$, which slowly evolves in solution by $SiH(OMe)_3$ loss and CO migration to the final alkyne-bridging complex. The structures of the σ-vinyl intermediate and that of the final dimetallaolefin complex have been confirmed by X-ray crystallography.[435] Displacement of CO by $P(OMe)_3$ and XylNC gives similar complexes. Interaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with the diyne complex $W(C{\equiv}C–C{\equiv}CH)$-$Cp(CO)_3$ affords $(CO)_3CpW(\mu\text{-}\eta^1{:}\eta^2\text{-}C^{3,4}–C{\equiv}C–C{\equiv}CH)Pt(PPh_3)_2$ with the Pt(0) fragment attached to the outer alkyne unit, as confirmed by X-ray methods.[436] However, related reactions with terminal propargyl complexes $MCp(CH_2C{\equiv}CPh)(CO)_3$ ($M = Ru$, Fe) give μ-allenyl complexes $(PPh_3)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C^{\alpha,\beta}–CPh{=}C{=}CH_2)MCp(CO)_3$ featuring an η^1-Pt–hydrocarbyl bridging mode and a Pt–M bond.[327] Spectroscopic evidence suggests a mechanism involving an initial intermediate with the Pt fragment coordinated to the C≡C triple bond.[327] In contrast to this behavior, by using the propargylpalladium complex $Pd(\eta^3\text{-}Bu^tC{\equiv}CCH_2)(R_F)(PPh_3)$ as precursor, the bimetallic product $(PPh_3)_2Pt(\mu\text{-}\eta^2{:}\eta^3\text{-}Bu^tCCH_2)Pd(R_F)(PPh_3)$ having a remarkable structure with a μ-η^2(Pt)$:\eta^3$(Pd) propargyl bridging group with no Pt–Pd bond is generated.[437] Pt/Mo complexes with cycloheptadienynes connecting the metal centers, $(PPh_3)_2Pt(\mu\text{-}\eta^2{:}\eta^6\text{-}C_7H_6)Mo(CO)_3$ (two isomers), have been prepared by $Mo(CO)_3$ transfer from $Mo(\eta^6$-p-xylene$)(CO)_3$ to $Pt(\eta^2\text{-}C_7H_6)(PPh_3)_2$, or by hydride reduction of the tropyne-bridging complex $[(PPh_3)_2Pt(\mu\text{-}\eta^2{:}\eta^7\text{-}C_7H_5)Mo(CO)_3]^+$, previously generated by reacting $[Pt(\eta^2\text{-}C_7H_5)(PPh_3)_2]^+$ with $Mo(\eta^6$-*p*-xylene$)(CO)_3$.[246] Heterobridged $(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CR)M(d^6)–Pt(d^8)$, neutral $(\eta^6$-*p*-cymene$)ClRu(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CR)Pt(R_F)_2$,[438]

$(PPh_2C{\equiv}CPh)Cp^*Ru(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)Pt(R_F)_2$,[439] or cationic $[(\eta^6\text{-}p\text{-cymene})(PPh_2C{\equiv}CR)Ru(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CR)Pt(R_F)_2](Tf)$[438] and $[(PPh_2C{\equiv}CPh)Cp^*M(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)Pt(R_F)_2](Tf)$ (M = Rh, Ir)[439] complexes are generated by reactions of the appropriate *P*-bonded $M(d^6)$ alkynylphosphine complexes with *cis*-$[Pt(R_F)_2(THF)_2]$. Facile migration of the $Pt(R_F)_2$ unit is observed in solution in neutral $(\eta^6\text{-}p\text{-cymene})ClRu(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CR)Pt(R_F)_2$, which exists in solution in slow equilibrium with the corresponding doubly chloride-bridged complexes $(\eta^6\text{-p-cymene})(PPh_2C{\equiv}CR)Ru(\mu\text{-}Cl)_2Pt(R_F)_2$.[438]

8.09.3.4.3 Polymetallic derivatives

Insertion of electron-deficient alkynes $R^1C{\equiv}CR^2$ (R^1, $R^2 = CO_2Me$, CO_2Et; $R^1 = H$, $R^2 = CO_2Me$) into one of the Pt–Pt bonds of the linear triplatinum complex $[Pt_3(\mu\text{-dpmp})_2(CNXyl)_2](PF_6)_2$ (dpmp = bis((diphenylphosphino)methyl)phenylphosphine) affords $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}\eta^1:\eta^1\text{-}R^1C{\equiv}CR^2)(CNXyl)_2](PF_6)_2$ having an asymmetrical A-frame structure with the alkyne coordinated in a parallel fashion (X-ray for $R^1 = H$, $R^2 = CO_2Me$).[440] In the same way, electron-poor alkynes insert selectively into the Pt–Pd bond of the related complex $[Pt_2Pd(\mu\text{-dpmp})_2(CNXyl)_2](PF_6)_2$, but in this case, yielding $[Pt_2Pd(\mu\text{-dpmp})(\mu\text{-}Ph_2PCH_2P(Ph)CH_2P(Ph)_2\text{-}CR^1CR^2)(CNXyl)_2](PF_6)_2$ due to a subsequent insertion into a Pd–P bond, as has been confirmed by X-ray diffraction studies.[441]

Several triangular clusters $MPt_2(CO)_5(PPh_3)_2(\mu\text{-}\eta^1:\eta^1:\eta^2\text{-}R^1C{\equiv}CR^2)$ ($R^1 = R^2 = Ph$, M = Fe, Ru, Os;[442] $R^1 = Ph$, $R^2 = C{\equiv}CPh$, M = Fe, Ru[372]), which can be considered as $M(CO)_3$ complexes of the diplatinacyclobutadiene having the alkyne parallel to the Pt–Pt bond, have been generated by reaction of $Pt(\eta^2\text{-}R^1C{\equiv}CR^2)(PPh_3)_2$ with $Fe(CO)_5$, $Ru_3(CO)_x$ ($x = 10$, 12) or $Os(CO)_5$. The reaction of $Pt(\eta^2\text{-}PhC{\equiv}CPh)(PPh_3)_2$ with $Ru_3(CO)_{10}$ also generates $Ru_2Pt(CO)_7(PPh_3)_2(PhC_2Ph)$, in which the triple bridging alkyne is parallel to one of the Ru–Pt bonds.[442] Interaction of the diyne cluster $Os_3(CO)_{10}(\mu_3\text{-}FcC_2\text{–}C{\equiv}CFc)$ with $Pt(cod)_2$ yields $PtOs_3(CO)_9(\mu_4\text{-}FcC_2\text{–}C{\equiv}CFc)$ and $Pt_2Os_3(CO)_{10}(\mu_5\text{-}FcC_2\text{–}C{\equiv}CFc)$, respectively.[197] The tetranuclear cluster shows a butterfly metal core bonded to one of the two C≡C alkyne units, while the pentanuclear cluster adopts a bow tie structure with both triple bonds involved in bonding to both triangular metal groupings (μ-‖) to the Os_2Pt and μ-⊥ to the $OsPt_2$).[197]

High-nuclearity clusters $PtRu_5(CO)_{13}(\mu\text{-}RC{\equiv}CR)(\mu_3\text{-}RC{\equiv}CR)(\mu_5\text{-}C)$ are formed by irradiation of the hexanuclear cluster $PtRu_5(CO)_{16}(\mu_6\text{-}C)$ with RC≡CR (R = Ph, Et). X-ray diffraction studies reveal a central square pyramid of Ru atoms with the carbido atom in the center of the square face and the Pt atom capping one Ru_3 triangle having one of the alkyne groups bridging the Pt–Ru(apex) bond and the other one the $PtRu_2$ face.[443,444] In the reaction with 3-hexyne, the octanuclear cluster $Pt_2Ru_6(CO)_{17}(\mu_3\text{-}EtC{\equiv}CEt_3)(\mu\text{-}\eta^5\text{-}C_5Et_4)(\mu_6\text{-}C)$ is also isolated in low yield. Its structure shows a central Ru_5PtC octahedron with additional Ru and Pt atoms bonded to the Pt atom of the central cluster core, but not each other. The alkyne shows a $\mu_3\text{-}\eta^1(Ru):\eta^1(Ru):\eta^2(Pt)$ bonding mode, whereas the formed C_5Et_4 ligand is bonded to the Pt_{cap} and η^5-bonded to the Ru spike.[444]

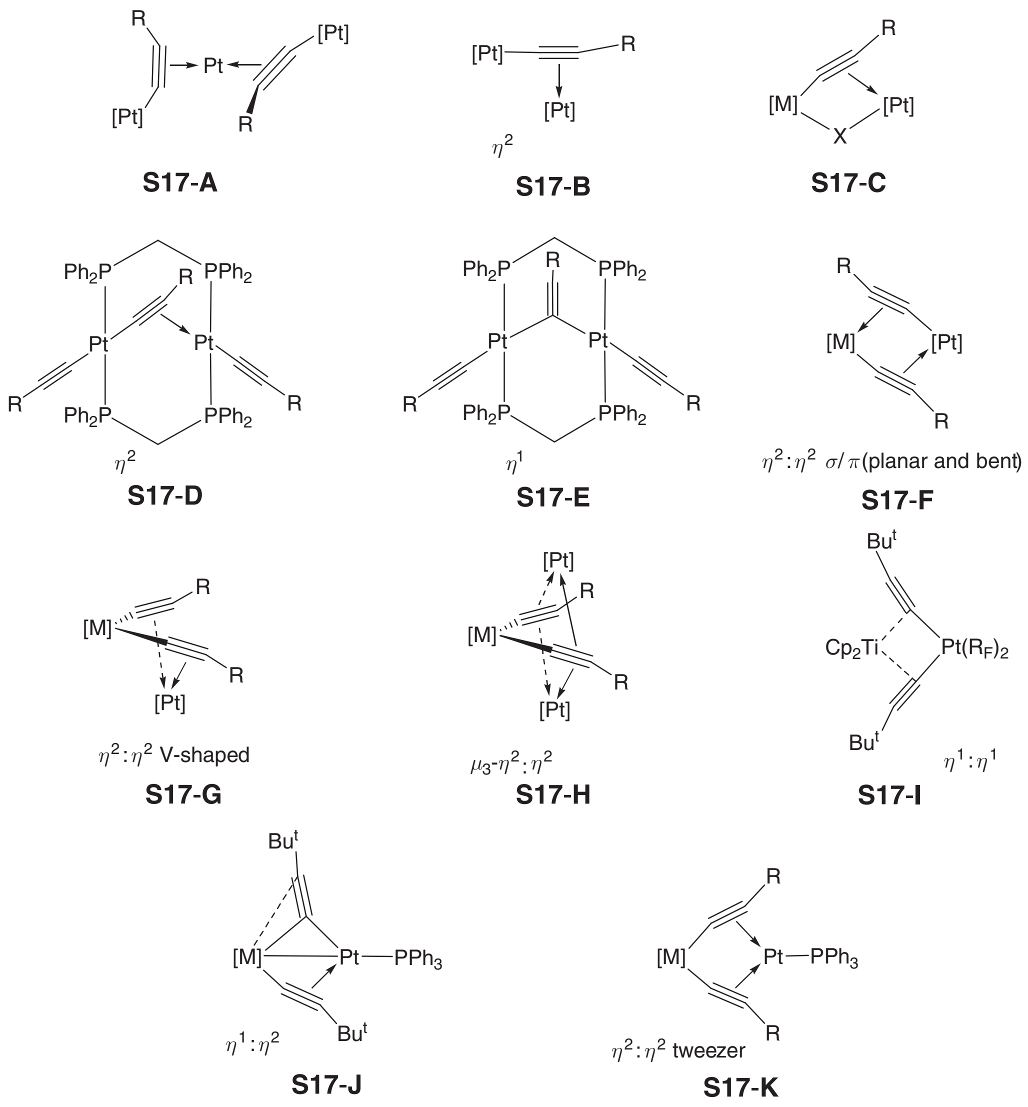
8.09.3.5 η^2-MC≡CR Complexes

The ability of the MC≡CR entity to model the alkyne ligand is well documented. Its structural properties have been used in the preparation of many di- and trinuclear complexes and also in the construction of supramolecular architectures (see Section 9.3.4). In the case of platinum chemistry, this area has grown steadily since the initial report by Stone *et al.*[445] of the first homo- and heterobimetallic platinum complexes containing μ-C≡CR ligands. Many examples of complexes having metal centers other than platinum complexed by Pt–C≡CR units have been examined in different reviews[321,346,412,417,418,423] and, therefore, they are not included in this section. Polymetallic platinum complexes having μ,σ^n-alkyne–diide or polyide and functionalized (with pyridyl or polypyridyl) fragments have been a topic of intense interest.[346,414,418,446,447] However, in this section, only complexes featuring η^2(Pt) M–C≡CR will be considered; η^2-homo- and heteropolynuclear platinum complexes containing mono- or double alkynyl bridging systems of types **S17-A–S17-K** shown in Scheme 17 are known.

8.09.3.5.1 Homometallic complexes

Generally, the preparation of these species is achieved by (i) reaction of a platinum σ-alkynyl complex with a platinum substrate containing labile ligands and (ii) chloride–alkynide exchange reactions.

Platinaalkynyl complexes of Pt(0) are very rare. An interesting exception is found in the complex $\{(cod)(Bu^tC{\equiv}C)Pt(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CBu^t)\}_2Pt$ (Scheme 17 **S17-A**), considered to model bis(η^2-alkyne)platinum(0), generated by reaction of $Pt(\eta^2\text{-nb})_3$ with $Pt(C{\equiv}CBu^t)_2(cod)$ (1 : 2 molar ratio).[337] This complex is also formed in low yield in the synthesis of $Pt(C{\equiv}CBu^t)_2(cod)$ from the system $PtCl_2(cod)/HC{\equiv}CBu^t/NaOEt$.[337] η^2-Complexation of $Pt(PPh_3)_2$



Scheme 17

to *trans*-[Pt(C≡CCl)Cl(PEt$_3$)$_2$] has been detected as an intermediate species (type **S17-B**, Pt(II)–Pt(0)) in the reaction of the ethylene Pt(0) precursor, Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$, with the chloroethynyl complex to give a final μ-ethynediyl complex, *trans,cis*-[(PEt$_3$)$_2$ClPt–C≡C–PtCl(PPh$_3$)$_2$].[376] By contrast, complexation of a platinum(II) metal fragment to platinaalkynyl entities is more frequent. Thus, trinuclear zwitterionic divalent platinum complexes of type **S17-B** *trans,trans,trans*-[{Pt^{-2}(R$_F$)$_2$(μ-$\eta^1:\eta^2$-C≡CR)$_2$}{Pt$^+$HL$_2$}$_2$] (R = Ph, Bu^t, SiMe$_3$; L = PPh$_3$, PEt$_3$)[448] are formed by reaction of *trans*-[Pt(R$_F$)$_2$(C≡CR)$_2$]$^{2-}$ with 2 equiv. of the hydride cationic solvento (hydrido) complex *trans*-[PtHL$_2$(acetone)]$^+$. A crystal structure of the complex with R = Ph and L = PEt$_3$ confirms that the dianionic precursor metal fragment acts only as a 3-platina-1,4-diyne bridging ligand of two identical cationic [PtH(PEt$_3$)$_2$]$^+$ units.[448] In contrast to this behavior, neutral bis(alkynyl)platinum complexes such as *trans*-[Pt(C≡CR)$_2$L$_2$] (R = Ph, Bu^t, SiMe$_3$,[449] C(OH)EtMe, C(OMe)EtMe′, C(OH)Ph$_2$),[449–451] *cis*-[Pt(C≡CBu^t)$_2$L$_2$],[450] (L = PPh$_3$, PEt$_3$), or Pt(C≡CR)$_2$(dppe) (R = Bu^t, SiMe$_3$)[450] react with the solvento (carbonyl) complex *cis*-[Pt(R$_F$)$_2$(CO)(THF)] to give, after alkynyl transfer to the neutral fragment "*cis*-Pt(R$_F$)$_2$(CO)," the μ-$\eta^1:\eta^2$-acetylide-bridged zwitterionic compounds (CO)(R$_F$)$_2$Pt$^-$(μ-$\eta^1:\eta^2$-C≡CR)Pt$^+$(C≡CR)L$_2$ (L = phosphine, (1/2)dppe). The crystal structures of the complexes *cis,trans*-[(CO)(R$_F$)$_2$Pt$^-$(μ-$\eta^1:\eta^2$-C≡CR)Pt$^+$(C≡CR)(PPh$_3$)$_2$] (R = Ph,[450] C(OH)EtMe[451]) show that the PtC≡CR unit is oriented essentially perpendicular to the local coordination plane of the cationic Pt center. The complexes *cis,trans*-$[(\text{CO})(\text{R}_\text{F})_2\text{Pt}^-(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CSiMe}_3)\text{Pt}(\text{C}{\equiv}\text{CSiMe}_3)\text{L}_2]$ ($\text{L} = \text{PPh}_3$, PEt_3) interact easily with alcohols (EtOH, MeOH) to afford unusual (μ-ethynediyl)(methylalcoxycarbene)diplatinum complexes *cis,trans*-$[(\text{CO})(\text{R}_\text{F})_2\text{Pt}^-\text{–C}{\equiv}\text{C–Pt}^+\{\text{C(Me)OR}\}\text{L}_2]$ ($\text{L} = \text{Me}$, Et).[449] Their formation is presumed to proceed by an initial desilylation of the alkynyl bridging ligand, and probably via μ-ethynediyl vinylidene species, which can undergo addition of ROH to give the final carbene products.[449] The complex *cis*-$[\text{Pt}(\text{R}_\text{F})_2(\text{THF})_2]$ reacts with *trans*-$[\text{PtH}(\text{C}{\equiv}\text{CPh})\text{L}_2]$ ($\text{L} = \text{PPh}_3$) to give, by a ligand-redistribution process, a mixed (μ-H)(μ-C$\equiv$CPh) diplatinum complex *trans*-$[(\text{R}_\text{F})\text{LPt}(\mu\text{-H})(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CPh})\text{PtL}(\text{R}_\text{F})]$ (type **S17-C**), having a very short Pt–Pt separation ($\sim$2.82 Å), in agreement with a total valence electron count of 30 electrons.[317] The diplatinum isomer *gem*-$[\text{L}_2\text{Pt}(\mu\text{-H})(\mu\text{-C}{\equiv}\text{CPh})\text{Pt}(\text{R}_\text{F})_2]$ is accessible via direct C–H activation of HC$\equiv$CPh when $\text{Pt}(\eta^2\text{-HC}{\equiv}\text{CPh})\text{L}_2$ interacts with the solvento complex *cis*-$[\text{Pt}(\text{R}_\text{F})_2(\text{THF})_2]$.[382] Extension of both processes to the dihydride diplatinum complex *trans-trans*-$[\text{HL}_2\text{Pt–C}_2\text{–C}_6\text{H}_4\text{C}_2\text{–PtL}_2\text{H}]$, and the isomeric diyne $\{\text{PtL}_2\}_2(\mu\text{-}\eta^2:\eta^2\text{-HC}_2\text{–C}_6\text{H}_4\text{–C}_2\text{H})$ precursor, and 2 equiv. of *cis*-$[\text{Pt}(\text{R}_\text{F})_2(\text{THF})_2]$ affords the corresponding tetranuclear bis(μ-hydride)(μ-diethynylbenzene) complexes.[382] The crystal structure of $[\{$*trans*-$\text{PPh}_3(\text{R}_\text{F})\text{Pt}(\mu\text{-H})\text{Pt}(\text{R}_\text{F})(\text{PPh}_3)\}_2(\mu_4\text{-C}{\equiv}\text{C–C}_6\text{H}_4\text{–C}{\equiv}\text{C})]$ confirms the presence of the central *p*-diethynylbenzene, which is attached to two diplatinum units via the alkynyl fragments (σ-bonded to one Pt and η^2-bonded to the other).[382] A more general synthetic method based on the treatment of $[\text{Pt(dppm)}_2]\text{Cl}_2$ with HC$\equiv$CR in the presence of Hg(OAc)_2 in refluxing ethanol has been developed for the synthesis of arylacetylide A-frame complexes $\text{Pt}_2(\text{C}{\equiv}\text{CR})_2(\mu\text{-C}{\equiv}\text{CR})(\mu\text{-dppm})_2$ (type **S17-D**: $\text{R} = \text{Ph}$, 4-(OMe)C_6H_4, 4-(OEt)C_6H_4, 4-(Et)C_6H_4, biphenyl (Bp), Bu^t; or type **S17-E**: $\text{R} = 4\text{-(Bu}^\text{n}\text{)C}_6\text{H}_4$), containing one bridgehead alkynyl ligand.[419,452] These complexes exhibit luminescence properties (^{3}MMLCT) and are fluxional in solution involving both an $\eta^1:\eta^2$-alkynyl exchange and a pseudo-boat inversion.[419,452] Neutral double-bridged acetylide-type **S17-F** complexes, *trans*-$[\text{Pt}(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CR})(\text{R}_\text{F})\text{L}]_2$ ($\text{L} = \text{PPh}_3$, $\text{R} = \text{Ph}$, Bu^t, SiMe_3, C(OH)EtMe, (*Z*)-CMe=C(H)Me; C(OMe)EtMe, C(OH)Ph_2),[451,453] are formed by a ligand-rearrangement process between *trans*-$[\text{Pt}(\text{C}{\equiv}\text{CR})_2\text{L}_2]$ and *cis*-$[\text{Pt}(\text{R}_\text{F})_2(\text{THF})_2]$. X-ray studies reveal a central dimetallacyclic planar PtC_4Pt core for the complex with $\text{R} = \text{Ph}$,[453] whereas derivatives with $\text{R} = \text{C(OH)Ph}_2$ and C(OMe)EtMe display non-planar cores.[451] In solution, the $\eta^1:\eta^2$ pairwise intramolecular exchange and fast inversion of the central ring (for bent structures), probably via intermediate η^1,η^1 (type **S17-I**)[454] and/or unsymmetrical η^1,η^2 (type **S17-J**)[455] species, are common features for this type of complex.[456] The η^2-alkynyl interaction is displaced by PPh_3 to give bridge-cleavaged mononuclear complexes.[451,453] However, treatment of *trans*-$[\text{Pt}\{(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{C(OH)EtMe}\}(\text{R}_\text{F})\text{L}]_2$ with HSPh leads to the formation of the novel thiolate/cyclobutenediylidene-bridged complex *cis*-$[\text{L}(\text{R}_\text{F})\overline{\text{Pt}\{\mu\text{-C=C(OH)EtMe=C}}(\text{C=CEtMe})\}(\mu\text{-SPh})\text{Pt}(\text{R}_\text{F})\text{L}]$, formed by a formal [2 + 2]-cycloaddition process.[457] A similar bimetallic neutral complex $[\text{Pt}(\sigma^2\text{–N,C,N})(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CSiMe}_3)]_2$ (type **S17-F**, bent) ($\text{N,C,N} = 2,6\text{-(C=NR)}_2\text{C}_6\text{H}_3$, $\text{R} = 4\text{-(OMe)C}_6\text{H}_4$), containing a chelating C,N bis(imino)aryl ligand, is obtained by reaction of $\text{Pt}(\sigma^3\text{–N,C,N})\text{Br}$ with $\text{Li}[\text{C}{\equiv}\text{CSiMe}_3]$.[458] In this case, the η^2-alkyne interaction displaces one Pt–N bond in the expected $\text{Pt}(\sigma^3\text{–N,C,N})(\text{C}{\equiv}\text{CSiMe}_3)$. Homoleptic complexes $[\text{Pt}(\text{C}{\equiv}\text{CR})_4]^{2-}$ react with *cis*-$[\text{Pt}(\text{R}_\text{F})_2(\text{THF})_2]$ acting as mono-alkynylating agents to afford type **S17-F** complexes $[(\text{R}_\text{F})_2\text{Pt}(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CR})_2\text{Pt}(\text{C}{\equiv}\text{CR})_2]^{2-}$. The migration of one of the alkynyl ligands decreases the alkynylating capability of the Pt center, and these bimetallic complexes interact with a second "$\text{Pt}(\text{R}_\text{F})_2$" unit by simple complexation to give $[(\text{R}_\text{F})_2\text{Pt}(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CR})_2\text{Pt}(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CR})_2\text{Pt}(\text{R}_\text{F})_2]^{2-}$ ($\text{R} = \text{Ph}$, Bu^t, SiMe_3) having both a σ/π- and a chelating V-shaped (type **S17-G**) double alkynyl-bridging systems (X-ray, $\text{R} = \text{Ph}$).[459] However, no alkynyl-migration process is found in the reaction of *cis*-$[\text{Pt}(\text{R}_\text{F})_2(\text{C}{\equiv}\text{CSiMe}_3)_2]^{2-}$ with $[\text{PtCl}(\text{C}_3\text{H}_5)]_4$ in a 4 : 1 molar ratio, which affords a zwiterionic anionic type **S17-G** complex $[\{\text{Pt}(\text{R}_\text{F})_2(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CSiMe}_3)_2\}\text{Pt}(\eta^3\text{-C}_3\text{H}_5)]^-$, as confirmed by an X-ray diffraction study for the related heterobimetallic Pt–Pd complex.[460] The final outcome of the interaction of mixed alkynyl–phosphinoalkynyl complexes *cis*-$[\text{Pt}(\text{C}{\equiv}\text{CR}^1)_2(\text{PPh}_2\text{C}{\equiv}\text{CR}^2)_2]$ (R^1, $\text{R}^2 = \text{Ph}$, Bu^t) with *cis*-$[\text{Pt}(\text{R}_\text{F})_2(\text{THF})_2]$ depend on the molar ratio.[431] In a 1 : 1 ratio, exclusive coordination of the "$\text{Pt}(\text{R}_\text{F})_2$" unit to the alkynyl ligands with formation of 1 : 1 type **S17-G** adducts takes place. However, in 1 : 2 molar ratio, the results depend on the R^1 and R^2 substituents. Variable mixtures of trimetallic type **S17-H** complexes *cis*-$[\{\text{L}_2\text{Pt}(\mu_3\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CPh})_2\}\{\text{Pt}(\text{R}_\text{F})_2\}_2]$ with the alkynyl entities acting as six-electron μ_3-η^2 bridging ligands and symmetrical *cis*-$[\{\text{Pt}(\mu\text{-PPh}_2\text{C}{\equiv}\text{CPh})(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CR})_2\}\{\text{Pt}(\text{R}_\text{F})_2\}_2]$ having two mixed-type **S17-C** systems are formed, as confirmed by spectroscopic means and X-ray diffraction studies.[431] The η^2-bonding capability to Pt(II) is suggested to be Pt–C$\equiv$CR > $\text{PPh}_2\text{PC}{\equiv}\text{CR}$ and C$\equiv$CPh fragments > $\text{C}{\equiv}\text{CBu}^\text{t}$.

8.09.3.5.2 Heterometallic complexes

Metalloalkynyl complexes of Pt(0) are rather scarce.[412,445] Reactions of the diyne complex $\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}{\equiv}\text{C–C}{\equiv}\text{CEt})_2$ with $\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2$ affords a tweezer complex (type **S17-K**), in which the $\text{Pt}(\text{PPh}_3)_2$ moiety is suggested to be complexed by the inner C$\equiv$C triple bonds, as confirmed by X-ray crystallography in the analogous

Ti–Pd complexes.[461] However, interaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with $WCp(CO)_3(C{\equiv}C\text{–}C{\equiv}CH)$ causes complexation of the low-valent $Pt(PPh_3)_2$ moiety to the outer alkyne fragment,[462] and its reaction with $TiCp_2(C{\equiv}CBu^t)_2$ yields $Cp_2Ti(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CBu^t)(\mu\text{-}\eta^1\text{-}C{\equiv}CBu^t)Pt(PPh_3)$ (**S17-J**, Scheme 17), which can be formally considered as the result of the oxidative addition of a Ti^{IV}–C bond to a Pt(0) substrate to give a binuclear Ti^{III}–Pt^{I} complex.[455]

An unusual double alkynyl-transfer processes occurs when the homoleptic σ-bonded ions $[Pt(C{\equiv}CR)_4]^{2-}$ react with the solvento dicationic $[MCp^*(PEt_3)(acetone)_2]^{2+}$ to give neutral type **S17-G** complexes $(PEt_3)Cp^*Ir(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2$ ($R = Ph$, Bu^t, $SiMe_3$), in which the organometallic *cis*-$Pt(C{\equiv}CR)_2$ unit is stabilized by η^2-bis(alkyne) interactions, as confirmed by X-ray diffraction.[463] Similar reactions of the solvento d^6-complexes with *cis*-$[Pt(R_F)_2(C{\equiv}CR)_2]^{2-}$ ($R = Ph$, $SiMe_3$) reveal that a double alkynylation process takes place with the iridium fragment to give $(PEt_3)Cp^*Ir(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CR)_2Pt(R_F)_2$ (V-shaped).[464,465] The presence of two C_6F_5 ligands increases the preference of platinum for σ-coordination, and the reactions with $[RhCp^*(PEt_3)(acetone)_2]^{2+}$ afford formally zwitterionic σ/π- (type **S17-F**) complexes $(PEt_3)Cp^*Rh^+(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CR)_2Pt^-(R_F)_2$, resulting from a single alkynyl migration.[465] These mixed d^6–d^8 complexes are alternatively obtained starting from the neutral precursor $MCp^*(C{\equiv}CR)_2(PEt_3)$ and *cis*-$[Pt(R_F)_2(THF)_2]$, indicating that the observed thermodynamic site preference for σ-coordination is mainly due to the electronic effect of the metal fragments.[465] *Ab initio* theoretical calculations suggest that the alkynyl-transfer processes can proceed with low energetic barrier through intermediate species of type **S17-J**, with η^1- and η^2-bridging ligands.[456] Interaction of $MCp^*(C{\equiv}CR)X(PEt_3)$ ($M = Rh$, $R = Ph$, Bu^t, $SiMe_3$, $X = Cl$; $M = Ir$, $R = Ph$, $SiMe_3$, $X = Cl$, I) with *cis*-$[Pt(R_F)_2(THF)_2]$ occurs with retention of the σ-M (Rh, Ir) coordination of the alkynyl ligand yielding heterobridged type **S17-C** complexes, as confirmed by an X-ray structure for $(PEt_3)Cp^*Rh(\mu\text{-}Cl)(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CSiMe_3)Pt(R_F)_2$.[465] In the same way, the course of the reaction of $[PtX_2(C{\equiv}CR)_2]^{2-}$ ($X = C_6F_5$,[466] $C{\equiv}CR$[467]) with the chloride-bridged $[M(\mu\text{-}Cl)(cod)]_2$ ($M = Rh$, Ir) or $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ strongly depends on the metal and substituents. Only the reactions of $[Ir(\mu\text{-}Cl)(cod)]_2$ with $[PtX_2(C{\equiv}CSiMe_3)_2]^{2-}$ ($X = C_6F_5$, $C{\equiv}CSiMe_3$) evolve with monoalkynyl transfer processes, yielding heterobimetallic σ/π-anionic complexes $[X_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Ir(cod)]^-$. Both anions show bent PtC_4Ir central cores and asymmetric η^2-metal acetylenic linkages with $M\text{–}C_\beta$-bond distances slightly shorter (0.1–0.12 Å) than the corresponding $M\text{–}C_\alpha$, suggesting a considerable vinylidene contribution to the bonding mode of the alkynyl ligands. The reactions with the rhodium and palladium substrates afford binuclear (PtM),[460,466,468] trinuclear (PtM_2)[466,468] or pentanuclear ($PtRh_4$),[469] formally zwitterionic, complexes, in which the alkynyl groups remain σ-bonded to Pt and are η^2-bonded to M (Pd, Rh), indicating a clear σ-site alkynyl preference of Pt(II) relative to the second row metals (Pd(II), Rh(I)). In fact, the complex $[(cod)Ir(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(C{\equiv}CSiMe_3)_2]^-$, $\{Ir\text{–}Pt\}^-$, having two terminal alkynyl ligands σ-bonded to Pt, has been used successfully to chelate neutral and cationic d^8- (Pd, Rh) metal fragments yielding heterotrimetallic complexes $[\{Ir\text{-}Pt\}(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CSiMe_3)_2ML_n]^x$ ($ML_n = M(R_F)_2$, $M = Pt$, Pd, $x = -1$; Rh(cod), $Pd(\eta^3\text{-}C_3H_5)$, $x = 0$). The structure of $\{Ir\text{–}Pt^-\}(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CSiMe_3)_2Rh^+(cod)$ confirms the presence of two different bridging systems (σ/π **S17-F** and V-shaped **S17-G**).[467] However, the reaction of the dianionic molecular squares $[cyclo\{cis\text{-}[Pt(C{\equiv}CPh)_2(\mu\text{-}CN)_2][M(cod)]\}_2]^{2-}$ ($M = Rh$, Ir) with *cis*-$[Pt(R_F)_2(THF)_2]$ (2 equiv.) affords hexanuclear complexes $[\{(R_F)_2Pt(\mu\text{-}C{\equiv}CPh)_2(\mu\text{-}CN)_2\}_2\{M(cod)\}_2]^{2-}$, formed by a simultaneous σ-alkynyl migration from each platinum in the square to both "*cis*-$Pt(R_F)_2$" units, as confirmed by an X-ray structure for the Pt_4Rh_2 complex.[232] Kinetic studies of σ-alkynyl ligand transfer from mononuclear palladium complexes to platinum (in many cases catalyzed by copper) suggest that these types of processes probably occur via a bimetallic state with alkynyl bridging between Pt and Pd centers.[420]

8.09.4 Allyl and Related Complexes

In this section, complexes having unsaturated hydrocarbon ligands that bind the platinum in a η^3-form will be considered. The chemistry of η^3-allyl complexes has grown, including extensively studied η^3-(2-heterosubstituted)-allyl derivatives, generated by addition processes to η^3-propargyl/allenyl $C_3R_3^-$ complexes. Several recent reviews have covered the chemistry of both types of ligands.[320,470–474]

8.09.4.1 η^3-Allyl Complexes

8.09.4.1.1 Preparation

The most common routes to η^3-allyl complexes have been reviewed.[122] Many preparative methods use platinum(II) precursors, the most frequently used being tetrameric $[Pt(\mu\text{-}\eta^1:\eta^2\text{-}C_3H_5)(\mu\text{-}Cl)]_4$, dimeric $[PtX(\eta^3\text{-}C_3H_4R\text{-}2)]_2$, and propargyl/allenyl species $[Pt(\eta^3\text{-}CH_2CCR)L_2]^+$ (R = H, Ph, Me). Preparations starting from Pt(0) derivatives have also been reported.

8.09.4.1.1.(i) Preparation from Pt(II) precursors

8.09.4.1.1.(i).(a) Transmetallation and insertion processes

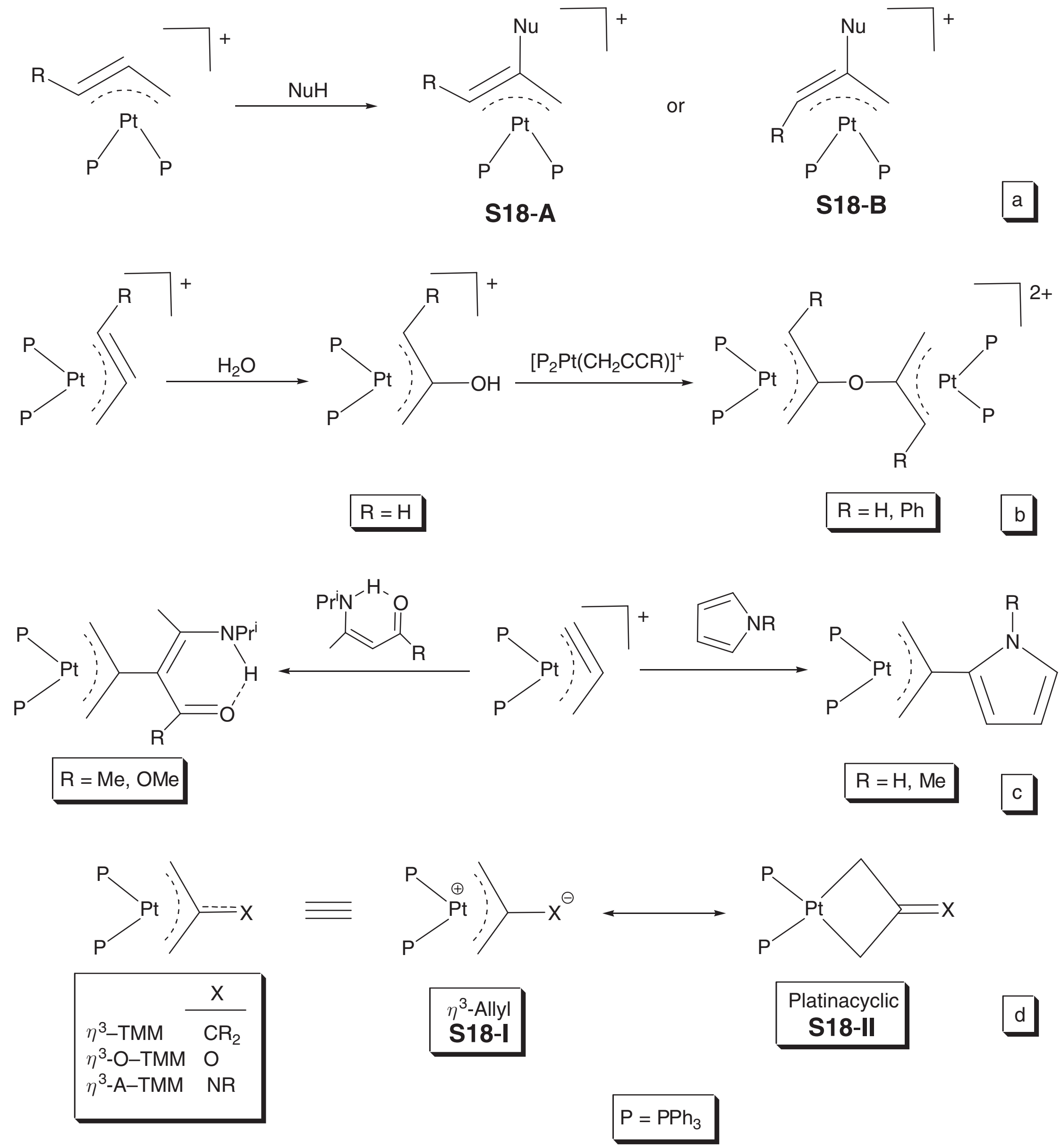
Transmetallation reactions between $[Pt(\eta^3\text{-}CH_2CMeCH_2)(\mu\text{-}Cl)]_2$ and the potassium salt $K[\eta^5\text{-}C_{60}R_5]$ (R = Ph, Me) yield the corresponding neutral complexes $Pt(\eta^5\text{-}C_{60}R_5)(\eta^3\text{-}CH_2CMeCH_2)$, containing unusual η^5-cyclopentadienide $C_{60}R_5$ ligands, as confirmed by X-ray structures of several palladium analogs.[475] Similarly, the anionic allylic carborane species $[Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]^-$ is generated by treatment of $[Pt(\eta^3\text{-}C_3H_5)Br]_2$ with Na_2[*nido*-7,8-Me_2–7,8-$C_2B_9H_9$], and isolated as $NEt_4{}^+$ and $N(PPh_3)_2{}^+$ salts.[476] The diplatinum hydride complex $[Pt_2(\mu\text{-}H)_2(DPCB)](Tf)_2$ undergoes insertion of 1,3-cyclohexadiene and 1-phenylbutadiene into the Pt–H bond, to yield η^3-allyl complexes $[Pt(\eta^3\text{-}C_6H_9)(DPCB)]^+$ and $[Pt(\eta^3\text{-}CHMeCHCHPh)(DPCB)]^+$, respectively.[477] Similar reactions with allylic alcohols ((*E*)-$CRH{=}CHCH_2OH$) (R = H, Me, Ph) occur with C–O bond cleavage, affording $[Pt(\eta^3\text{-}CRHCHCH_2)(DPCB)](Tf)$.[477] Facile insertion of allenes into Pt–R bonds, to yield η^3-allyl complexes, have been also reported. Thus, reaction of phenylallene with $[PtPh(bipy)(acetone)]^+$ produces $[Pt(\eta^3\text{-}CH_2CPhCHPh)(bipy)]$ as a mixture of *syn*- and *anti*-isomers. Recrystallization gives simple crystals of the *syn*-isomer, which have been characterized by X-ray crystallography.[478] Similarly, chloride abstraction from $PtCl(R)(\eta^2\text{-}CH_2{=}C{=}CMe_2)(NN)$ with $AgBF_4$ causes the migratory insertion of R, yielding cationic η^3-allylic complexes $[Pt(\eta^3\text{-}CH_2CRCMe_2)(NN)](BF_4)$ (NN = dmphen, R = Me, 4-(OMe)C_6H_4; NN = pimpy, R = Me, Et, 4-(OMe)-C_6H_4,CH_2Ph; NN = 2-[(methylimino)methyl]pyridine (mipy), R = 4-MeC_6H_4; NN = 2-methyl–6-[(methylimino)-methyl]pyridine (mimpy), R = 4-MeC_6H_4; NN = phen, R = COMe), which are also alternatively generated by reaction of $[PtR(NN)(NCMe)]^+$ with $CH_2{=}C{=}CMe_2$.[109]

8.09.4.1.1.(i).(b) Bridge-splitting reactions

Treatment of $[Pt(C_3H_5)Cl]_4$ with carbonyl-stabilized ylides, $Ph_3PCHCOR$ (R = Me, Ph, OMe),[479] or with ketenylidenetriphenylphosphorane, Ph_3PCCO,[480] affords selectively *C*-coordinated derivatives $PtCl(\eta^3\text{-}C_3H_5)\{C(PPh_3)\text{-}HCOR\}$ (2 : 3 mixture of isomers)[479] and $PtCl(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)CO\}$,[480] respectively. Chloride abstraction in the presence of a further equivalent of Ph_3PCCO leads to $[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)CO\}_2]^+$, which is stable only at low temperature.[481] In the same way, reaction of $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)(THF)](BF_4)$ with Ph_3PCCO gives the mixed ligand complex $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)\{\eta^1\text{-}C(PPh_3)CO\}](BF_4)$, whose molecular structure has been solved by X-ray diffraction.[481] Further reaction of these η^1-ketenyl derivatives with ROH[480] or Me_2NH[481] gives the corresponding ester species[480] or the amide derivative $[Pt(\eta^3\text{-}C_3H_5)\{C(PPh_3)HC(O)NMe_2\}(PPh_3)](BF_4)$ (as a mixture of two diasteromeric forms),[481] respectively. Reaction of $[PtCl(C_3H_5)]_4$ with *o*-$Ph_2PNHC_6H_4P(S)Ph_2$ (PS) affords $PtCl(\eta^3\text{-}C_3H_5)(PS)$, containing the difunctional ligand acting as a *P*-bonded monodentate, and subsequent chloride abstraction with $AgClO_4$ gives $[Pt(\eta^3\text{-}C_3H_5)(PS)](ClO_4)$, in which the ligands is κ-*P*,*S*-bound.[482] However, addition of $Ph_2PNHC_6H_4PPh_2$ (P^1P^2) in toluene gives the ionic derivative $[Pt(\eta^3\text{-}C_3H_5)(P^1P^2)]Cl$ directly.[483] Similarly, addition of the N^1N^2 redox active ligand, 3-(ferrocen-1-yl)-1-(pyridin-2-yl)pyrazole, and NH_4PF_6 yields $[Pt(\eta^3\text{-}C_3H_5)(N^1N^2)](PF_6)$, which is static on the NMR timescale.[484] Related cationic complexes with chiral ligands, such as *exo*-8-((*o*-diphenylphosphino)benzyl)thioborneol (PS)[485] or (+)-11*S*,12*S*-bis[(2,2′-(diphenylphosphino) benzanilido]-9,10-ethanoantracene (P^1P^2),[486] have been prepared in a similar way.[485,486] Bridge-splitting reactions of $[Pt(\mu\text{-}Cl)(\eta^3\text{-}CH_2CMeCH_2)]_2$ with the chiral monophosphines H–MOP and MeO–MOP (MOP = (*S*)-2-diphenylphosphino-1,1′-binaphthyl) give neutral $PtCl(\eta^3\text{-}CH_2CMeCH_2)L$ (L = H–MOP, MeO–MOP), containing monodentate *P*-chiral ligands.[486] Chloride abstraction affords cationic complexes $[Pt(\eta^3\text{-}CH_2CMeCH_2)L]^+$, featuring the naphthyl backbone also interacting with the platinum center (*P*,η^1 for H–MOP and *P*,η^2 for MeO–MOP).[486]

8.09.4.1.1.(i).(c) Addition reactions to propargyl/allenyl or trimethylenemethane complexes

Interaction of η^3-allenyl/propargyl platinum(II) complexes $[Pt(\eta^3\text{-}CH_2CCR)(PPh_3)_2]^+$ (R = H, Ph, Me) with nucleophiles NuH leads selectively to the formation of β-substituted η^3-allyl complexes $[Pt\{\eta^3\text{-}CH_2C(Nu)CHR\}(PPh_3)_2]^+$ (Scheme 18, a). The complex $[Pt(\eta^3\text{-}C_3H_3)(PPh_3)_2](BF_4)$ reacts with H_2O to give the hydroxyallyl species $[Pt\{\eta^3\text{-}CH_2C(OH)CH_2\}(PPh_3)_2]^+$ (X-ray) and a diplatina-η^6-diallyl ether dication $[\{(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCH_2)\}_2O]^{2+}$, generated by further interaction of the hydroxyallyl with the precursor.[487] The related $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]^+$ ion only produces the diplatinadiallyl ether complex (Scheme 18, b).[488] η^3-2-Chalcogenoxyallyl complexes $[Pt\{\eta^3\text{-}CH_2C(ER^1)CHR^2\}(PPh_3)_2]^+$ (R^2 = H,[489] E = O, S, R^1 = Me, Et, Pr^i, Bu^t, Ph; E = Se, R^1 = Ph (isomer *syn* or *endo*, Scheme 18, a, **S18-A**); R = Ph, Me, E = O, R^1 = Me;[377] R^2 = Ph,[488] E = O, R^1 = Et, Pr^i, CH_2CMe_3, $CH_2CH{=}CH_2$,



Scheme 18

CMe$_3$, CMe$_2$Et)[377,488,489] are generated by treatment of $[\mathrm{Pt}(\eta^3\text{-}\mathrm{CH_2CCR^2})(\mathrm{PPh_3})_2]^+$ with the appropriate EOH. According to competitive experiments, the orders of reactivity are $\mathrm{R^1SeH} > \mathrm{R^1SH} > \mathrm{R^1OH}$[489] and $\mathrm{MeOH} > \mathrm{EtOH} > \mathrm{Pr^iOH} > \mathrm{Bu^tOH} > \mathrm{PhOH}$.[377] Selective addition of weak acids such as $\mathrm{HSO_4}^-$ or $\mathrm{H_2PO_4}^-$ affords neutral η^3-2-sulfatoallyl $\mathrm{Pt}\{\eta^3\text{-}\mathrm{CH_2C(OSO_3)CH_2}\}(\mathrm{PPh_3})_2$ and η^3-2-hydrogenophosphatoallyl complexes $\mathrm{Pt}\{\eta^3\text{-}\mathrm{CH_2C(OPO_3H)CH_2}\}(\mathrm{PPh_3})_2$, respectively.[490] Addition of ammonia, and a broad spectrum of primary and secondary amines, is also successful, affording η^3-aminoallyl complexes $[\mathrm{Pt}\{\eta^3\text{-}\mathrm{CH_2C(NR^1R^2)CHR^3}\}(\mathrm{PPh_3})_2]^+$,[377,487,491–493] which are obtained as *exo*- (or *anti*-) isomers (Scheme 18, a, **S18-B**) when using the phenyl-substituted η^3-allenyl/propargyl precursor.[377,492,493] Complexes $[\mathrm{Pt}\{\eta^3\text{-}\mathrm{CH_2C(NR^1R^2)CH_2}\}(\mathrm{PPh_3})_2]^+$ can also be obtained in a slower reaction starting from *trans*-$[\mathrm{PtBr}(\eta^1\text{-}\mathrm{CH{=}C{=}CH_2})(\mathrm{PPh_3})_2]$.[491] Complex $[\mathrm{Pt}(\eta^3\text{-}\mathrm{C_3H_3})(\mathrm{PPh_3})_2]^+$ is more reactive than the complex with R = Ph, being able even to activate C–H bonds.[2] Its reaction with enamines $\mathrm{(ROC)HC{=}CMe(NHPr^i)}$[494] (R = Me, OMe), pyrrole, *N*-methylpyrrole, indole, or 3-methylindole, with hydroalkenylation[494] or hydropyrrolylation[495] (Scheme 18, c) yields the corresponding η^3-2-C(substituted)allyl complexes by selective C–C bond formation.[495] The addition of a neutral nucleophile (Nu = $\mathrm{PPh_3}$ or $\mathrm{NEt_3}$) generates platinacyclobutene adducts $[\overline{\mathrm{Pt\{CH_2C(Nu)C}}\mathrm{H\}(PPh_3)_2}]^+$, which in the presence of acid ($\mathrm{H^+}$) evolve to form η^3-allyl species $[\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(Nu)CH_2\}(PPh_3)_2](BF_4)_2}$.[496] In contrast, $[\mathrm{Pt(}\eta^3\text{-}\mathrm{C_3H_3)(PPh_3)_2]^+}$ selectively activates a *p*-phenyl C–H bond of $\mathrm{NMe_2Ph}$ affording $[\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(4\text{-}NMe_2C_6H_4)CH_2\}(PPh_3)_2](BF_4)}$, and similar hydroarylation reactions are observed with electron-rich arenes such as dimethoxy- or trimethoxybenzene, to yield $[(\eta^3\text{-}\mathrm{CH_2C(Ar)CH_2)(PPh_3)_2]^+}$ (Ar = 2,4-$\mathrm{(OMe)_2C_6H_3}$, 2,4,6-$\mathrm{(OMe)_3C_6H_2}$).[495] A mechanism, involving an electrophilic aromatic substitution of the arene to give a metallacyclobutene intermediate, followed by protonation, has been suggested by crossover labeling experiments.[495]

Alternative precursors to β-substituted η^3-allyl derivatives are η^3-trimethylenemethane (TMM) and related (O–TMM, N–TMM) complexes, which exhibit a resonance structure between zwitterionic η^3-allyl and a platinacyclic structure (Scheme 18, d), being prone to interact with organic electrophiles. Thus, protonation ($\mathrm{NEt_3H^+}$) of $\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(C(CO_2Me)_2)CHPh\}(PPh_3)_2}$ leads to the central carbon-substituted η^3-hydrocarbylallyl cation $[\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(CH(CO_2Me)_2)CH_2\}(PPh_3)_2]^+}$.[497] Similarly, electrophilic addition of acid halides or organic halides XR (X = Cl, R = C(O)Me, C(O)Ph, $\mathrm{C(O)CH_3SO_2}$, Ts, $\mathrm{CH_2OCH_2Ph}$, $\mathrm{P(O)(OPh)_2}$; X = Br, R = Bz, C(O)Me, C(O)Ph, $\mathrm{CH_2CH{=}CH_2}$; X = I; R = Et, $\mathrm{Pr^i}$)[498,499] and ionic electrophiles ($\mathrm{Me_3SiTf}$, $\mathrm{Ph_3CBF_4}$)[499] to the η^3-O–TMM complex $\mathrm{Pt\{(}\eta^3\text{-}\mathrm{CH_2C(O)CH_2)\}(PPh_3)_2}$, or alkylation ($\mathrm{Me^+}$, $\mathrm{Et^+}$) of $\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(O)CHPh\}(PPh_3)_2}$[488] leads to the corresponding η^3-2-alcoxy, -acyloxy, -siloxy, or -trityloxyallyl cationic complexes $[\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(OE)CH_2\}(PPh_3)_2]^+}$ (E = alkyl, acyl, $\mathrm{SiMe_3}$, $\mathrm{CPh_3}$)[498,499] and $[\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(OE)CHPh\}(PPh_3)_2]^+}$ (E = Me, Et),[488] respectively. η^3-Aminoallyl complexes[491,492] are also alternatively generated by protonation or alkylation of aza–trimethylenemethane (η^3-A–TMM) complexes $[\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(NR^1)CHR^2\}(PPh_3)_2}]$ ($\mathrm{R^1 = NSO_2Ph_2}$, $\mathrm{R^2}$ = H;[491] $\mathrm{R^1}$ = *p*-$\mathrm{MeC_6H_4NH_2}$, *p*-$\mathrm{O_2NC_6H_4NH_2}$, $\mathrm{R^2}$ = Ph[492]).

8.09.4.1.1.(ii) Preparation from Pt(0) precursors

An alternative method[2] for the synthesis of cationic complexes of type $[\mathrm{Pt(}\eta^3\text{-}\mathrm{CH_2CR^1CR^2R^3)(PPh_3)_2]^+}$ has been developed, based on the oxidative allyl transfer from $[\mathrm{NEt_3(CH_2CR^1{=}CR^2R^3)]X}$ (X = $\mathrm{ClO_4}$, $\mathrm{BF_4}$) to $\mathrm{Pt(}\eta^2\text{-}\mathrm{C_2H_4)(PPh_3)_2}$.[500] For $\mathrm{R^2}$ = H and $\mathrm{R^3}$ = Me, Et, a mixture of *syn*- and *anti*-isomers are formed, with the *syn*-geometry always favored. Related complexes $[\mathrm{Pt(}\eta^3\text{-}\mathrm{CH_2CR^1CR^2{}_2)(cod)]^+}$ ($\mathrm{R^1}$ = H, $\mathrm{R^2}$ = H, Me; $\mathrm{R^1}$ = Me, $\mathrm{R^2}$ = H) are generated by using $\mathrm{Pt(cod)_2}$ as precursor.[500] Oxidative addition of $\mathrm{CH_2{=}CClCH_2CO_2Z}$ (Z = OEt, $\mathrm{NEt_2}$) to $[\mathrm{Pt(}\eta^2\text{-}\mathrm{C_2H_4)(PPh_3)_2}]$, followed by decarboxylation, gives η^3-2-ethoxy or (diethylamino)allyl complexes $[\mathrm{Pt\{}\eta^3\text{-}\mathrm{CH_2C(Z)CH_2\}(PPh_3)_2]Cl}$.[501] The reaction has been suggested,[501] and supported by theoretical calculations, to take place in three steps, formation of $\{[\mathrm{Pt(}\eta^3\text{-}\mathrm{CH_2CClCH_2)(PPh_3)_2]OCOOEt}\}$ followed by nucleophilic substitution at the central carbon to yield a platinametallacyclobutane, which subsequently converts to the final η^3-2-ethoxyallyl complex.[502]

8.09.4.1.2 Structural aspects

General structural aspects of transition metal allyl complexes have been reviewed.[470] A variable-energy photoelectron study of $\mathrm{M(}\eta^3\text{-}\mathrm{C_3H_5)_2}$ (M = Ni, Pd, Pt) using He(I), He(II), and monochromatized synchrotron radiation has been carried out, allowing a more confident assignment of the orbital energies (supported by MS-X_α calculations),[503] mainly based on the presence of *trans*-isomers.

The structures of many platinum complexes have been confirmed by X-ray diffraction analyses; therefore, only salient features will be outlined. For $[\mathrm{Pt(}\eta^3\text{-}\mathrm{CH_2CPhCHPh)(bipy)]^+}$, the structure confirms the presence of the *syn*-isomer, having the central and the terminal Ph groups perpendicular and coplanar, respectively, with the allylic plane.[478] However, this complex isomerizes in solution to an equilibrated mixture of *syn*- and *anti*-isomers (52 : 48). The structure of $[\mathrm{Pt(}\eta^3\text{-}\mathrm{C_3H_5)(PS)]^+}$ (PS = *exo*-8-((*o*-diphenylphosphino)benzyl)thioborneol] shows the presence of a mixture of the *exo*- and *endo*-isomers (3 : 1 ratio), with the six-membered chelate ring taking up a boat conformation, and the chiral ligand featuring a chiral pocket with respect to the allyl ligand.[485] Detailed NMR studies indicate that in solution both allylic species are in a relatively slow exchange, even at 323 K, but at 233 K four isomers with similar, but not quite equal populations, are resolved, which are suggested to arise from the stereogenic sulfur atom.[485] Mass spectrometry studies of $\mathrm{Pt(}\eta^3\text{-}\mathrm{C_3H_5)(}\eta^5\text{-}\mathrm{MeC_5H_4)}$[504] (see Section 9.6.1), widely used as an MOCVD precursor, show the facile formation of platinum clusters, containing $\mathrm{MeC_5H_4}$ groups, and this has been related to the incorporation of carbon-containing species in the final films.

The molecular structures of several alcohoxy-, thioxy-, and selenoxy–allyl cationic complexes $[Pt\{\eta^3\text{-}CH_2C(ER)CH_2\}(PPh_3)_2]^+$ (ER = OH,[487] OCH_2OCH_3,[505] OEt, OPh, SEt, SPh, SePh)[489] reveal similar characteristics to other substituted η^3-allyl complexes. The heterosubstituted allyl entity is η^3-bound to platinum, with C_t–C_c bond distances (1.21–1.45 Å) within the double bond range, and a C_t–C_c–C_t angle in the 115–127° range. The Pt–C_c bond length (2.18–2.25 Å) is slightly longer than the Pt–C_t distances (2.16–2.20 Å), and the dihedral angle between the planes C_t–C_c–C_t and C_t–Pt–C_t (θ) is found to be in the range 61–67°. The most salient feature is the C_c–E bond. With the exception of the η^3-hydroxyl cation (R = OH),[487] which exhibits a C–O length of 1.52 Å, the C–O (1.33–1.36 Å), C–S (1.74–1.76 Å) and C–Se (1.88 Å) distances are relatively short in the remaining complexes, suggesting a significant $p\pi$–$p\pi$ interaction, and pointing to some degree of participation of the resonance structure $Pt\{CH_2C{=}E^+(R)CH_2\}(PPh_3)_2$, having the positive charge on the heteroatom.[489,505] Spectroscopic data for related η^3-2-aminoallyl complexes $[Pt\{\eta^3\text{-}CH_2C(NR^1R^2)CHR^3\}(PPh_3)_2]^+$ (R^3 = H, Ph) clearly evidence the presence of a C=N double bond. The rotational energy barrier along the C–N bond has been estimated for several complexes ($R^3 = R^1$ = H, R^2 = Et 15.9, Pr^i 14.6; R^3 = Ph, $R^1 = R^2$ = Me 13.5 kcal mol^{-1}).[491,492] Crystallographic analyses for several cations ($R^3 = R^1$ = H, R^2 = H, Pr^i, Ph, C_2H_4OH; R^3 = H, $R^1 = R^2$ = Et, *c*-C_3H_6)[491] show that the lengths of both C_t–C_c bonds and the C_c–N bond are within the double bond range. The angle C_t–C_c–C_t (111–116°) and the dihedral angle (θ) (56–62°) are slightly smaller than those typical for the η^3-allyl group, suggesting that these cations have resonance structures between η^3-2-aminoallyl and metallacyclobutaniminium $Pt\{\eta^2\text{-}CH_2C{=}N^+(R^3_2)CH_2\}(PPh_3)_2$.

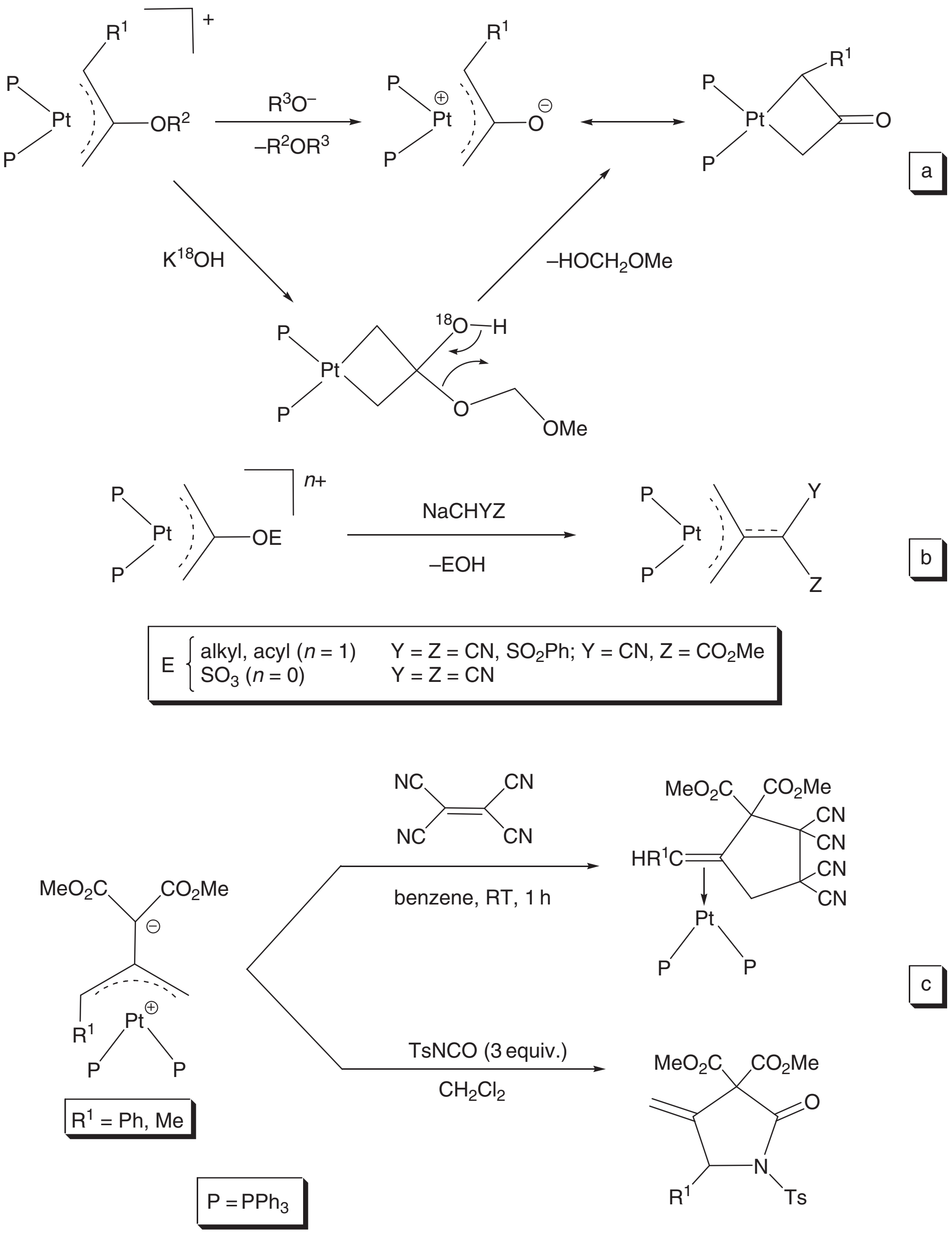
8.09.4.1.3 Reactions

The complex $[Pt(\mu\text{-}Cl)(\eta^3\text{-}C_3H_4Me\text{-}2)]_2$ has been widely used as one of the most suitable reagents to form cycloplatinate complexes under mild conditions.[506–508] In the same way, protonation of $[Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]^-$ in the presence of HC≡CPh yields the bimetallic complex $Pt_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2(\mu\text{-}\eta^1,\eta^1:\eta^4\text{-}CHCPhCHCPh)$, in which the alkyne units have coupled in a head-to-tail manner, to give a platinacyclopentadiene η^4-bonded to the second Pt.[476] However, reaction of $Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}Cp)$ with $PBu^t{}_2H$ gives, at low temperature, $[Pt(PBu^t{}_2H)_3]$, which subsequently evolves to $[Pt(\mu\text{-}PBu^t{}_2)(H)(PBu^t{}_2H)]_2$ by dissociation of one phosphine and oxidative addition of the P–H bond to the Pt center.[509] Nucleophilic attack by aniline at the terminal carbon of the allyl ligand in $[Pt(\eta^3\text{-}C_3H_5)(DPCB)](Tf)$ gives an aminopropyl chelate complex $[Pt(CH_2CH_2CH_2NHPh\text{-}\kappa\text{-}C,N)(DPCB)](Tf)$, probably through the formation of Pt(H)(Tf)(DPCB) as an intermediate, followed by insertion of the resulting allylamine, $H_2C{=}CH{-}CH_2NHPh$, into the Pt–H bond.[477] Similarly, nucleophilic addition of H^-, PhS^-, or $(SO_2Ph)_2CH^-$ to $[Pt\{\eta^3\text{-}CH_2C(R)CH_2\}(PPh_3)_2]^+$ (R = 2,4,6-$(OMe)_3C_6H_2$) results in the formation of vinylarenes, $CH_2{=}C(R)CH_2Nu$.[495]

Deprotonation of $[Pt\{\eta^3\text{-}CH_2C(OH)CH_2\}(PPh_3)_2]^+$ or treatment of the binuclear cations $[\{(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCHR)\}_2O]^{2+}$ with OH^- or OMe^- leads to the corresponding (η^3-O–TMM) neutral complexes $Pt\{\eta^3\text{-}CH_2C(O)CHR\}(PPh_3)_2$ (R = H,[2,487] Ph[488,492]), which are also generated by treating η^2-alkoxyallyl cationic complexes with strong bases (OH^-, OMe^-)[488,492,505] (Scheme 19, a). Labeling studies of this latter reaction (R^1 = H, $R^2 = CH_2OCH_3$) using $K^{18}OH$ suggest that the first step is a nucleophilic attack at the central carbon, to generate a η^2-metallacyclobutane (Scheme 19, a), followed by proton (^{18}O–H) transfer to the ((methyloxy)methyl)oxy group.[505] However, soft carbon nucleophiles react with 2-substituted allyl derivatives, causing unusual substitution at the central carbon,[473,490,499] providing an entry to η^3-TMM complexes (Scheme 19, b). A similar reaction with $Na[NHSO_2Ph]$ gives the η^3-N–TMM complex $Pt\{\eta^3\text{-}CH_2C(NSO_2Ph)CH_2\}(PPh_3)_2$.[499]

8.09.4.1.4 Theoretical aspects

As noted in Section 9.4.1.2, orbital energies for $M(\eta^3\text{-}C_3H_5)_2$ (M = Ni, Pd, Pt) have been assigned, mainly based on the presence of *trans*-isomers in the gas phase.[503] More recent theoretical calculations (DFT) on the molecular and electronic structure of these species have shown very small binding energy preferences between the *cis*- and *trans*-isomers (<0.2 kcal mol^{-1}), slightly favored for the *trans*-isomer[510] in the case of Pd and Pt. A new assignment of the orbital energies from previous variable-energy photoelectron spectra[503] is proposed by assuming a *trans–cis* ratio in gas phase close to one.[502] The electronic and molecular properties of both isomers of *cis*-$[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)(CO)_2\}_2]^+$ have been found essentially isoenergetic, on the basis of a QR-DF study.[511] The results of MO calculations on the reaction of $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)_2]^+$ with hard and soft nucleophiles suggest that both processes are orbital controlled, the metal being the preferred site of attack.[512] However, steric constraints favor the attack of soft nucleophiles to the middle carbon of the allyl ligand.[512] The η^3–η^1 interconversion and reductive elimination from $MH(\eta^3\text{-}C_3H_5)(PH_3)$ (M = Pd, Pt) have been also investigated using *ab initio* calculations.[513] Asymmetric bonding is observed due to the large *trans*-influence of the hydride on the η^3-isomers, which are much



Scheme 19

more stable than the corresponding η^1-allyl forms, the energy difference being greater in the Pt complex. The C–H reductive elimination requires a higher E_a (20.9 vs. 5.4 kcal mol^{-1}) in the platinum model complex.[513]

8.09.4.2 Related η^3-Hydrocarbyl Complexes

8.09.4.2.1 η^3-Butadienyl complexes

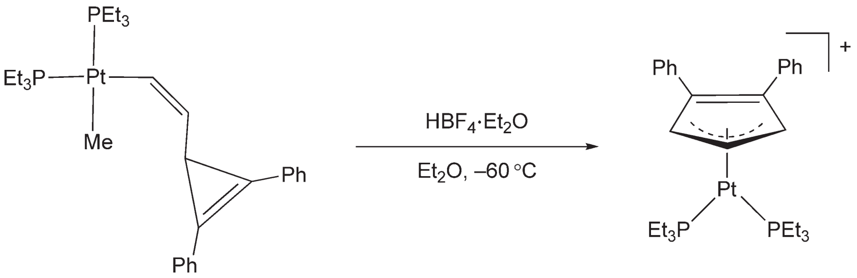
(1–3)-η-*trans*-Butadienylplatinum complexes $[Pt\{\eta^3\text{-}CH_2C(R)C{=}CH_2\}L_2](PF_6)$ (R = H, Me, Et; $L_2 = 2PPh_3$, dppf) are easily obtained by chloride abstraction from 2-η^1-butadienyl precursors, $PtCl\{\eta^1\text{-}C(CH_2)\text{-}C(R){=}CH_2\}L_2$, with $TlPF_6$.[514] The precursors are generated by direct reaction of 4-chlorobuta-1,2-dienes $CH_2{=}C{=}CRCH_2Cl$ with

$Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ or $Pt(\eta^2\text{-}C_2H_4)(dppf)$.[514] The cation $[Pt\{\eta^3\text{-}CH_2C(Me)C{=}CH_2\}(PPh_3)_2]^+$ is alternatively formed by protonation of $Pt\{\eta^2\text{-}HC{\equiv}CC(Me){=}CH_2\}(PPh_3)_2$ with $HBF_4{\cdot}Et_2O$.[373] However, using an excess of CF_3CO_2H, the resulting η^3-butadienyl cation reacts with further CF_3CO_2H, which is added across the *exo*-double bond to give a final 1,1,2-trisubstituted allyl complex $[Pt\{\eta^3\text{-}MeC(CF_3CO_2)C(Me)CH_2\}(PPh_3)_2]CF_3CO_2$.[373]

The complex $[Pt\{\eta^3\text{-}CH(Ph)C(Ph)C{=}CH_2\}(PPh_3)_2](BF_4)$ has been generated via a ring-opening reaction coupled with a hydrogen shift, by the simple reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with the cyclopropenyl cation $[C_3Ph_2Me](BF_4)$.[515] Remarkably, a similar reaction of $[C_3Ph_3](PF_6)$ with $Pt(\eta^2\text{-}C_2H_4)$(triphos) gives the η^3-triphenylcyclopropenyl complex $[Pt(\eta^3\text{-}C_3Ph_3)(\text{triphos})](PF_6)$, whose structure has been confirmed by X-ray diffraction,[516] contrasting with the structure previously found for $[Pt(\eta^2\text{-}C_3H_3)(PPh_3)_2]^+$, which displays an asymmetrical η^2-linkage.[517]

8.09.4.2.2 η^3-Cyclobutadienyl complexes

Protonation of the *cis*-methylvinylcyclopropene complex *cis*-$[PtMe((Z)\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)(PEt_3)_2]$ (Equation (12)) with HBF_4 results in selective splitting of the Pt–Me bond to give the η^3-diphenylcyclopentadienyl cationic complex $[Pt(\eta^3\text{-}C_5H_3Ph_2)(PEt_3)_2]BF_4$.[518] A mechanism involving the participation of a platinabenzvalene or platinabenzene in the vinylcyclopropene–cyclopentadienyl rearrangement could be suggested (see Section 9.6.1), but no spectroscopic evidence was found. The cation can be alternatively generated by chloride abstraction from *cis*-$[PtX((Z)\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)(PEt_3)_2]$ ($X = Cl$) with $TlPF_6$, or by slow rearrangement of the related trifluoroacetate ($X = CF_3CO_2^-$) precursor. The X-ray crystal structure of the cation confirms the formation of the 1,2-diphenylcyclopentadienyl ligand, which is coordinated in η^3-fashion with Pt–(CH) distances (2.252–2.319 Å) distinctly shorter than Pt–(CPh) (2.508, 2.587 Å).[518]



(12)

8.09.4.2.3 η^3-Propargyl/allenyl complexes

The chemistry of these complexes, including detailed NMR data, has been widely reviewed.[320,472–474] The synthetic strategies for the preparation of cationic $[Pt(\eta^3\text{-}CHR^1CCR^2)(PPh_3)_2]^+$ ($R^1 = R^2 = H$; $R^1 = H$, $R^2 = Ph$; $R^1 = Me$, $R^2 = Me$, Bu^n, Bu^t, TMS) complexes are included in COMC (1995).[2] Cationic complexes $[Pt(\eta^3\text{-}CH_2CCR^2)(PPh_3)_2]^+$ ($R^2 = Ph$, Me, H) are obtained by the reaction of *trans*-$[PtBr(\eta^1\text{-}CH_2C{\equiv}CR^2)(PPh_3)_2]$ ($R^2 = Ph$, Me)[377] with AgTf or *trans*-$[PtBr(\eta^1\text{-}CH{=}C{=}CH_2)(PPh_3)_2]$ with $AgBF_4$.[487] Alternatively, the cations with $R^2 = Ph$, Me are formed by treatment of $Pt(\eta^2\text{-}PhC{\equiv}CCH_2OMe)(PPh_3)_2$ with $BF_3{\cdot}OEt_3$ or addition of $R^2C{\equiv}CCH_2OTs$ to $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$.[377] The molecular structures of $[Pt(\eta^3\text{-}CHMeCCBu^t)(PPh_3)_2]^+$[519] and $[M(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]^+$ ($M = Pd$, Pt)[377] show that the unsaturated ligand is severely bent (152.2°–154.7°), and that it is coplanar with the metal center. The M–C distances follow the order $M\text{–}C_c \leq M\text{–}CHR^1 < M\text{–}CR^2$ ($R^1 = H$, Me; $R^2 = Ph$, Bu^t) with the $C_c\text{–}C_t(HR^1)$ (~1.39–1.40 Å) and $C_c\text{–}C_t(R^2)$ (1.23–1.27 Å) lengths in the range of long double and triple bonds, respectively, confirming the η^3-allenyl/η^3-propargyl nature of coordination. Theoretical calculations suggest that the main bonding interaction of the ligand with the platinum occurs through the terminal carbon atoms, despite the observed short Pt–Cc distance.[520] These complexes have demonstrated an unusually high propensity to undergo addition of nucleophilic reagents of the general form NuH (see Section 9.4.1.1) to afford η^3-2-substituted allyl complexes via formation of novel C–E (E = O, S, Se, N, C) bonds. These compounds are also precursors of η^3-TMM and η^3-N–TMM complexes (Section 9.4.3). On the basis of recent theoretical calculations, the addition to the C_c is assumed to occur through a charge-controlled mechanism assisted by the availability of a low-lying acceptor orbital on C_c, leading to a metallacyclobutene intermediate along the reaction pathway.[520] Nucleophilic addition to the metal with a change in hapticity is also observed. Thus, $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]^+$

interacts with py to yield the corresponding η^1-allenyl complex *trans*-$[Pt(\eta^1\text{-}CPh{=}C{=}CH_2)(py)(PPh_3)_2]^+$,[521] whereas the reaction with CO[521] or RNC (R = Bu^t, CH_2Ph)[522] affords a mixture of both *trans*-$[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)L(PPh_3)_2]^+$ and *trans*-$[Pt(\eta^1\text{-}CPh{=}C{=}CH_2)L(PPh_3)_2]^+$ (L = CO (1 : 1), RNC (6 : 1)). Remarkably, regioselective addition of NEt_3, PPh_3, or py to the central carbon of the more reactive cation $[Pt(\eta^3\text{-}C_3H_3)(PPh_3)_2]^+$ leads to new platinacyclobutene species $[\overline{Pt(CH_2CNuC}H_2)(PPh_3)_2]^+$ (Nu = NEt_3, PPh_3, py), which in the case of py evolves to the more stable η^1-allenyl species *cis*-$[Pt(\eta^1\text{-}CH{=}C{=}CH_2)py(PPh_3)_2]^+$.[496] Kinetic studies indicate that five-coordinate $PtX(\eta^3\text{-}CH_2CCPh)(PPh_3)_2$ is a common intermediate in the spontaneous isomerization of *trans*-$[PtX(\eta^1\text{-}CH_2C{\equiv}CPh)(PPh_3)_2]$ to *trans*-$[PtX(\eta^1\text{-}C(Ph){=}C{=}CH_2)(PPh_3)_2]$ (X = halide, $C{\equiv}CPh$).[471,523]

8.09.4.3 η^3-Trimethylenemethane and Related Complexes

In this section, η^3-TMM, η^3-O–TMM, and η^3-A–TMM will be considered (Scheme 18, d). Some of the preparative methods use as precursors cationic η^3-2-alkoxy or acyloxyallyl complexes (Section 4.3.1.3, Scheme 19), in which the OR can be replaced by a soft carbon nucleophilic Na(CHYZ), or by $NaNHSO_2Ph$ to yield the corresponding η^3-TMM and η^3-A–TMM complexes, respectively.[499] The first zwitterionic η^3-TMM complex $Pt\{\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh\}(PPh_3)_2$ has been synthesized by adding $Na[CH(CO_2Me)_2]$ to $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2](Tf)$,[497] but the source of hydrogen in the CHPh group has not been ascertained. This and the related complex $Pt\{\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHMe\}(PPh_3)_2$ can be alternatively obtained in "one-pot" syntheses by reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with $RC{\equiv}CCH_2OTs$ (R = Ph, Me) and $Na[CH(CO_2Me)_2]$.[493,497] Spectroscopic and X-ray data for the complex $\{Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh)\}(PPh_3)_2$ confirm the η^3-coordination of the ligand with a resonance structure (Scheme 18, d) between zwitterionic η^3-allyl and alkenic metallocyclobutane forms and the *anti*-orientation of Ph relative to the $C(CO_2Me)_2$ group.[497] Reaction of these complexes with very strong electrophiles (TCNE,[497] TsNCO[493]) leads to [3 + 2]-coupling of the electrophile to the η^3-TMM ligand, which are isolated or complexed to the metal (Scheme 19, c). By using olefins with lower electrophilic character (Et-fu, fn), head-to-tail [3 + 3]-coupling of two η^3-TMM ligands with concomitant formation of a Pt(0)(olefin) (olefin = Et-fu, fn) is observed.[493] The synthesis of η^3-O–TMM complexes of the type $Pt\{\eta^3\text{-}CH_2C(O)CHR\}(PPh_3)_2$ (R = H, Ph) can be accomplished by direct treatment of $[Pt(\eta^3\text{-}CH_2CCR)(PPh_3)_2]^+$ with an excess of KOH[472] or by reaction of η^3-alkoxyallyl complexes with strong bases (see Section 9.4.1.3, Scheme 19, a). Alternatively, $[Pt\{\eta^3\text{-}CH_2C(O)CH_2\}(PPh_3)_2]$ is generated by mixing alkyl allyl carbonates or an allylammonium chloride, $ClNMe_3\{CH_2\text{–}C{=}(CH_2)\text{–}OR\}$ (R = $CMe(H)O(CH_2)_3CH_3$), with $Pt(PPh_3)_4$.[524] Spectroscopic and X-ray crystallographic analysis of $M\{\eta^3\text{-}CH_2C(O)CH_2\}(PPh_3)_2$ (M = Pd,[525] Pt[526]) reveal that the platinum complex has a lower contribution of the η^3-allylic zwitterionic form than the palladium complex, both in solution and in the solid state. The contribution of this canonical form (Scheme 18, d, **S18-I**) increases with the polarity of the solvent, and the addition of protic solvent probably due to the formation of hydrogen bonding.[525] These complexes are precursors to η^3-allyl cationic complexes $[Pt\{\eta^3\text{-}CH_2C(OE)CH_2\}(PPh_3)_2]^+$ (see Section 9.4.1.1). On the other hand, reaction of $Pt\{\eta^3\text{-}CH_2C(O)CH_2\}(PPh_3)_2$ with TsNCO affords the η^3-A–TMM complex $Pt\{\eta^3\text{-}CH_2C(NTs)CH_2\}(PPh_3)_2$.[501] A more direct entry to η^3-A–TMM (or η^3-iminoallyl complexes) $Pt\{\eta^3\text{-}CH_2C(NR)CHPh\}(PPh_3)_2$ is based in the deprotonation of η^3-aminoallyl complexes $[Pt\{\eta^3\text{-}CH_2C(NRH)CHPh\}(PPh_3)_2]^+$ (R = $4\text{-}MeC_6H_4$, $4\text{-}NO_2C_6H_4$) by LiPh.[492,527] The addition of the amide $NaNHSO_2Ph$ to *trans*-$[Pt(OAc)(\eta^1\text{-}CH{=}C{=}CH_2)(PPh_3)_2]$ affords $Pt\{\eta^3\text{-}CH_2C(NSO_2Ph)CH_2\}(PPh_3)_2$ via *trans*-$[Pt(NHSO_2Ph)(\eta^1\text{-}CH{=}C{=}CH_2)(PPh_3)_2]$.[491] The reaction of $Na[NHSO_2Ph]$ with $PtCl(\eta^1\text{-}CH{=}C{=}CH_2)(dppe)$ also gives $Pt\{\eta^3\text{-}CH_2C(NSO_2Ph)CH_2\}(dppe)$ via an η^1-allenyl–amido intermediate.[491] The crystal structure of $Pt\{\eta^3\text{-}CH_2C(NC_6H_4NO_2)CHPh\}(PPh_3)_2$[527] and $Pt\{\eta^3\text{-}CH_2C(NSO_2Ph)CH_2\}(PPh_3)_2$[491] confirm the η^3-coordination bonding mode, with structural details between the resonance structures zwitterionic η^3-2-amidoallyl and neutral metallacyclobutanimine (Scheme 18 d, **S18-I** and **S18-II**).

8.09.4.4 Bimetallic Complexes

Dicationic complexes $[\{Pt(PPh_3)_2(\eta^3\text{-}CH_2CCHR)\}_2O]^{2+}$ (R = H, Ph), generated from interaction of $[Pt(\eta^3\text{-}CH_2CCR)(PPh_3)_2]^+$ with H_2O, have been mentioned in Section 9.4.1.1 (Scheme 18, b).[487,488] Compounds $[Pt_2(\mu\text{-}\eta^3:\eta^3\text{-}C_6H_5Ph)(P\text{–}P)_2](BAr_4)_2$ (P–P = dcpe, depe; Ar = $3,5\text{-}(CF_3)_2C_6H_3$) containing a dianionic biphenyl ligand with a μ-$\eta^3:\eta^3$-bis-allyl bonding mode (X-ray for the dcpe complex) are generated by simple interaction of $[PtMe(OEt)_2\text{-}(P\text{–}P)]^+$ with benzene through an intermolecular C–H activation with concomitant C–C coupling.[273] Deprotonation of $[PtCl(\eta^2\text{-}CH_2{=}CH\text{–}CH_3)(TMEDA)]ClO_4$ with NEt_3 gives a diplatinum complex

$[\{PtCl(TMEDA)\}(\mu\text{-}\eta^1:\eta^3\text{-}CHCHCH_2)\{Pt(TMEDA)\}]ClO_4$, according to the sequence of reactions shown in Scheme 5.[145] A similar Ru–Pt complex containing a $\mu\text{-}\eta^1(Ru):\eta^3(Pt)$, $[(OC)_2CpRu(\mu\text{-}\eta^1:\eta^3\text{-}C(Ph)CHCH_2)Pt(PPh_3)_2](BF_4)$ has been reported to be formed by the addition of $RuHCp(CO)_2$ to the η^3-allenyl/propargyl complex $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]BF_4$.[493] Complexes containing $Pt(\eta^3\text{-allyl})^+$ fragments are also reported. Thus, reaction of $[Fe(CO)_3Si(OSiMe_3)_3(dppm\text{-}P)]^-$ with $[PtCl(C_3H_5)]_4$ affords $(OC)_3\{(Me_3SiO)_3Si\}Fe(\mu\text{-}dppm)Pt(\eta^3\text{-}C_3H_5)$ whose structure shows a short Fe–Pt distance (2.675(3) Å) indicative of a metal–metal bond. Further interaction with RNC ($R = Bu^t$, 2,6-$(Me)_2C_6H_3$) gives $(OC)_3\{(Me_3SiO)_3Si\}Fe(\mu\text{-}dppm)Pt(\eta^1\text{-}C_3H_5)(CNR)$ in equilibrium with the η^3-allyl precursor due to facile RNC dissociation.[528] A similar η^3-cyclooctenyl Fe–Pt complex is formed by treatment of *mer*-$[FeH\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]$ with $Pt(cod)_2$, presumably via a platinum hydride intermediate generated by addition of the Fe–H bond, followed by hydride transfer to the coordinated cod ligand.[198] The X-ray structure shows that the Pt–C(cyclooctenyl) bond *trans* to P is significantly longer than Pt–C *trans* to Fe due to the higher *trans*-influence of the phosphorus atom.[198] A mixed Pt–Pd complex $PtPd\{\mu\text{-}\eta^3\text{-}CH_2C(CO_2Me)CH_2\}(\mu\text{-}Br)(PPh_3)_2$ with a Pt–Pd bond distance of 2.68 Å is produced from the reaction of $[Pt\{\eta^3\text{-}CH_2C(CO_2Me)CH_2\}(PPh_3)_2]Br$ with $Pd_2(dba)_3$. The X-ray structure reveals that the terminal carbons of the allyl ligand lie almost on the Pt–Pd–Br plane with the central carbon leaning towards the Pt–Pd bond.[529]

The neutral propargyl complex $Pd(\eta^3\text{-}CH_2CCBu^t)(R_F)(PPh_3)$ is stable toward reagents such as MeOH or NEt_2H; however, its treatment with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ provides $(Ph_3P)_2Pt(\mu\text{-}\eta^2:\eta^3\text{-}CH_2CCBu^t)Pd(R_F)(PPh_3)$ having a propargyl bridging ligand without a metal–metal bond.[437] Reaction of the diyne Pt(0) complexes $Pt(\eta^2\text{-}PhC{\equiv}C\text{–}C{\equiv}CPh)(dppf)$ or, alternatively, the di(alkynyl) complex $Pt(C{\equiv}CPh)_2(dppf)$ with $[Au(PPh_3)]^+$ generates the η^3-propargyl dinuclear complex $[Pt\{\eta^3(C^{2\text{–}4})\text{–}C(Ph)(AuPPh_3){=}CCCPh\}(dppf)]^+$.[370] An unusual complex $(Ph_3P)(R_F)_2Pt\{\mu\text{-}\eta^1:\eta^3\text{-}CHPhCCO\}Pt(PPh_3)_2$ containing a benzylideneketene bridging ligand is produced by a reductive coupling (CO, μ-C=CHPh) on the reaction of $(OC)(R_F)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2$ with PPh_3. The structure confirms that the CHPhCCO ligand is coordinated η^1 through the central carbon atom to the $Pt(R_F)_2(PPh_3)$ fragment and η^3 to the $Pt(PPh_3)_2$ unit, giving a complex formally zwitterionic.[530]

8.09.5 Platinum Complexes with η^4-Ligands

This section includes compounds with η^4-cyclobutadiene ligands or featuring η^4- (or $\eta^2:\eta^2$)-1,3-diene fragments.

8.09.5.1 η^4-Cyclobutadiene Complexes

The most common routes to this type of complex, cyclodimerization of alkynes on a platinum template or ligand substitution, are included in COMC (1995).[2]

Novel 16-electron platinum cyclobutadiene complexes $Pt(\eta^4\text{-}C_4R^1{}_2R^2{}_2)Cl_2$ ($R^1 = R^2 = Me$, Et; $R^1 = Me$, $R^2 = Pr$, Et) (*cis-/trans*-isomers 1 : 1) are obtained by reduction of $H_2PtCl_6{\cdot}6H_2O$ in *n*-butanol in the presence of alkynes ($R^1C{\equiv}CR^2$).[531,532] The reaction is suggested to occur through $H[PtCl_3(\eta^2\text{-}CH_2{=}CHCH_2CH_3)]$, which is isolated as the PPN salt.[531] The molecular structures of complexes $PtCl_2(\eta^4\text{-}C_4R_4)$ (R = Et,[531] Me[533]) show planar C_4 rings with symmetrical Pt–C distances (2.08(2)–2.10(2) Å). These complexes react with neutral ligands L to give 18-electron derivatives $PtCl_2(\eta^4\text{-}C_4R_4)L$ (R = Me, Et; L = py, NH_2Tol, PPh_3, $AsPh_3$, $SbPh_3$).[532] An asymmetric coordination of C_4Me_4 group is found in the complex $PtCl_2(\eta^4\text{-}C_4Me_4)(SbPh_3)$ having two shorter (ca. 2.106(4) Å) and two longer (av. 2.188(5) Å) Pt–C bonds.[534] An unexpected 18-electron complex formed by discrete molecules $[K(18\text{-}cr\text{-}6)][PtCl_3(C_4Me_4)]$ with close cation–anion contacts[535] (K⋯Cl 3.097–3.482 Å) has been obtained as a byproduct in low yield in the displacement reaction of 2-butyne in $[K(18\text{-}cr\text{-}6)][PtCl_3(MeC{\equiv}CMe)]$ by 1-pentyne.[385] The Pt–C distances (2.12(2) ± 0.04 Å)[535] are in the typical range for this type of complex (2.08(2)–2.214(8) Å).

An unusual labile triple-decker dication $[(\eta^4\text{-}C_4Me_4)Pt(Cp)Fe(Cp^*)]^{2+}$, stable only at low temperature, has been generated at 0 °C from the reaction of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}Cp^*)$ with the reactive electrophile $[Pt(\eta^4\text{-}C_4Me_4)(solv)_3]^{2+}$ [536] in $MeNO_2$.[537]

8.09.5.2 η^4-1,3-Diene Complexes

K_2PtCl_4 reacts with C_5Me_5H, in the presence of $SnCl_2$/HCl as catalyst, to produce $PtCl_2(\eta^4\text{-}C_5Me_5H)$ as a mixture of *endo*-H and *exo*-H isomers (75 : 25).[538] However, an attempt to obtain similar η^4-bonded complexes with $C_5Me_4(CF_3)H$ unexpectedly resulted in the formation of $PtCl_2(\eta^4\text{-}C_5Me_4H_2)$.[539] Its X-ray structure is similar to that of $PtCl_2\{\eta^4\text{-}C_5Me_5(Pr^i)\}$,[540] with the diene cycle characterized by the envelope conformation and $Pt\text{–}C_{in}$ bond distances shorter (2.140 Å) than $Pt\text{–}C_{ex}$ (2.187 Å).[539] The expected complex $PtCl_2(\eta^4\text{-}C_5Me_4(CF_3)H)$ is generated in high yield as the *exo*-(CF_3) isomer, by using the Zeise dimer $[PtCl_2(\eta^2\text{-}C_2H_4)]_2$ as precursor.[539] Related η^4-bonded diplatinum complexes $[\{Cl_2Pt\}\{(\eta^4\text{-}C_5Me_5(CH_2)_xSiMe_2\}\text{–}]_2O$ ($x = 1$, 3) have been prepared following a similar synthetic route.[541]

Highly reactive cations $[Pt(\eta^4\text{-}C_5Me_5H)(acetone)_x]^{2+}$ (*endo-/exo*-isomers) are generated from $PtCl_2(\eta^4\text{-}C_5Me_5H)$ by chlorine abstraction with $AgBF_4$ at low temperature (−78 °C). In the presence of dienes (C_5H_6, C_5Me_5H, 1,3-C_6H_8, 1,5-cod), spontaneous and selective deprotonation takes place to give $Pt(\eta^5\text{-}Cp)(\eta^4\text{-}C_5Me_5H)$ (*endo-/exo*-isomers) or $[Pt(\eta^5\text{-}Cp^*)(\eta^4\text{-}diene)]BF_4$ (diene = C_5Me_5H, 1,3-C_6H_8, 1,5-cod),[538] which have been spectroscopically and electrochemically[542] characterized. In the same manner, $[Pt(\eta^5\text{-}Cp)\{\eta^4\text{-}C_5Me_4(CF_3)H\}]BF_4$ and $[Pt(\eta^5\text{-}C_5Me_4CF_3)\text{-}\{\eta^4\text{-}C_5Me_4(CF_3)H\}]BF_4$ are obtained by the reaction of $PtCl_2\{\eta^4\text{-}C_5Me_4(CF_3)H\}$ with $AgBF_4$ in the presence of the dienes C_5H_6 and $C_5Me_4(CF_3)H$, respectively.[539] The structure of the cation $[Pt(\eta^5\text{-}Cp)\{\eta^4\text{-}C_5Me_4(CF_3)H\}]^+$ confirms the *exo*-orientation of the CF_3 group and exhibits different Pt–C distances for the η^4-diene (2.132–2.166 Å) and η^5-Cp (2.219–2.329 Å) ligands.[539]

Two diplatinum complexes having a very similar platinacyclopentadiene entity acting as η^4-ligand to a second platinum fragment have been reported. Complex $(PN)Pt(\mu\text{-}\eta^1,\eta^1:\eta^4\text{-}C_4Ph_4)Pt(\eta^2\text{-}PhC{\equiv}CPh)$ (Scheme 13), generated by reaction of $Pt(\eta^2\text{-}PhC{\equiv}CPh)_2$ with 0.5 equiv. of $PPr^i{}_2CH_2CH_2NMe_2$ (PN),[369] and $Pt_2\{\mu\text{-}\eta^1,(\eta^1:\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2$. This latter is formed by treatment of phenylacetylene with the formally Pt(0) fragment $Pt(Me_2C_2B_9H_9)$ generated *in situ* by protonation of the allyl complex $[Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{–}7,8\text{-}C_2B_9H_9)_2]^-$.[476] The structural details of the platinacyclobutadiene ligand are rather similar in both complexes, but the structure of the latter complex reveals that the two $HC{\equiv}CPh$ molecules have coupled in a head-to-tail manner and the presence of a short (2.782 Å) Pt–Pt bond separation.

8.09.6 Cyclopentadienyl and Related Complexes

8.09.6.1 η^5-Cyclopentadienyl Complexes

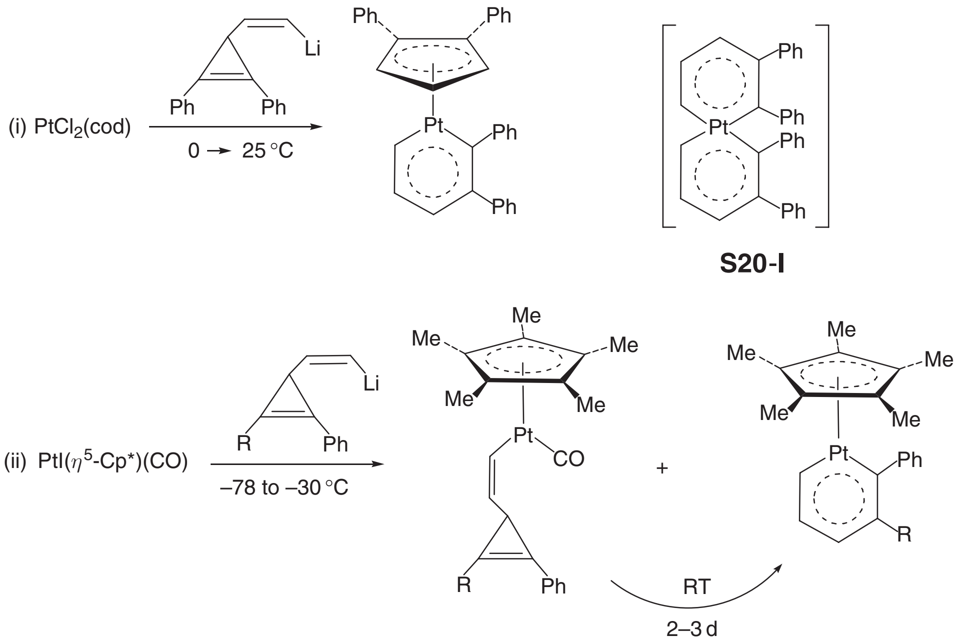
The research area of transition metal complexes stabilized by inter- or intra-side-chain-functionalized cyclopentadienyl ligands has attracted very much attention in recent years due to interesting structural aspects as well as catalytic applications. Recent developments on the chemistry of η^5-cyclopentadienyl compounds bearing hard (NR_2, OR) or soft (ER_2, ER (E = P, As, S), alkenyl) coordinated pendant donors have been the subject of several reviews,[543–545] but there is surprisingly no example in platinum chemistry. Pt(II) and Pt(IV) compounds containing Cp, Cp*, or partially substituted cyclopentadienyl ligands coordinated in an η^5-fashion have continued to be of interest in the last decade. The most common routes to this type of complex have been reviewed[122] and the chemistry of diplatinum complexes with $\mu\text{-}C_5H_4PPh_2$ groups has also been examined.[546,547]

8.09.6.1.1 Divalent derivatives

Cationic complexes $[Pt(\eta^5\text{-}Cp)(\eta^4\text{-}C_5Me_5H)]^+$, $[Pt(\eta^5\text{-}Cp^*)(\eta^4\text{-}diene)]^+$, $[Pt(\eta^5\text{-}Cp)\{\eta^4\text{-}C_5Me_4(CF_3)H\}]^+$, and $[Pt\{\eta^5\text{-}C_5Me_4(CF_3)\}\{\eta^4\text{-}C_5Me_4(CF_3)H\}]^+$ (see Section 9.5.2) are accessible by treatment of $PtCl_2(\eta^4\text{-}C_5Me_5H)$[538] or $PtCl_2\{\eta^4\text{-}C_5Me_4(CF_3)H\}$[539] with 2 equiv. of $AgBF_4$ in the presence of the appropriate diene (HCp, 1,3-C_6H_8, 1,3-cod, or $C_5Me_4(CF_3)H$). Under similar conditions, both $PtCl_2\{\eta^4\text{-}C_5Me_4(CF_3)H\}$[539] and $PtCl_2(\eta^4\text{-}C_5Me_5H)$[538] react with $AgBF_4$ and HCp* to afford $[PtCp^*(\eta^4\text{-}C_5Me_5H)]BF_4$. It is suggested that $C_5Me_4(CF_3)H$ is probably substituted for HCp* in dicationic intermediate species $[Pt\{\eta^4\text{-}C_5Me_4(CF_3)H\}(solvate)_x]^{2+}$ or $[Pt\{\eta^4\text{-}C_5Me_4(CF_3)H\}\{\eta^4\text{-}C_5Me_5H\}]^{2+}$, followed by deprotonation of the resulting dication $[Pt(\eta^4\text{-}C_5Me_5H)_2]^{2+}$.

In the same way, NMR experiments monitoring Diels–Alder reactions catalyzed by $Pt(Tf)_2(P\text{–}P)$ (P–P = dppe, (*R*)-(+)-bis-(diphenylphosphino)–1,1′-binaphthalene ((*R*)-Binap), biphep (biphep = 1,1′-bis(diphenylphosphino)biphenyl)) reveal that these catalysts react with HCp to give the catalytically inactive species $[Pt(\eta^5\text{-}Cp)\text{-}(P\text{–}P)]Tf$.[548,549] The (*R*)-Binap complex was alternatively prepared by reaction of $[Pt(\mu\text{-}Cl)((R)\text{-}Binap)]_2(Tf)_2$ with TlCp,[548] and the structure of $[Pt(\eta^5\text{-}Cp)(biphep)]^+$ (δ, cation) has been solved by X-ray diffraction.[549] Mechanistic studies indicate that a second equivalent of HCp is required to form $[Pt(\eta^5\text{-}Cp)(dppe)]^+$, presumably to deprotonate the proposed intermediate $[Pt(\eta^4\text{-}HCp)(dppe)]^{2+}(Tf)_2{}^-$, generating an acidic HTf/HCp species.[548] A very stable cationic complex $[Pt(\eta^5\text{-}Cp)\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]^+$ has been generated starting from $PtCl_2\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}$ with $AgBF_4$ and TlCp.[181] The complex, which has been thoroughly characterized by multinuclear NMR spectroscopy, contains one of the cyclohepta-2,4,6-trienyl substituents symmetrically η^2-coordinated, as confirmed by X-ray in the related palladium compound, and remains intact in the presence of an excess of $P(C_7H_7)_3$.[181] Chloride abstraction with $Ag[SO_3CF_3]$ from $PtCl(\eta^1\text{-}C_5H_5)(CO)(PPh_2Me)$ (C_5H_5 *trans* to P) affords $[Pt(\eta^5\text{-}Cp)(CO)(PPh_2Me)]^+$, which reverts to the precursor on treatment with NEt_4Cl.[550] Derivatives bearing η^3-allyl as co-ligands and containing the unusual $R_5C_{60}^-$ cyclopentadienyl ligands, $Pt(\eta^5\text{-}R_5C_{60})(\eta^3\text{-}CH_2CMeCH_2)$ (R = Me, Ph) are generated by transmetallation of $[Pt(\eta^3\text{-}CH_2CMeCH_2)Cl]_2$ with KR_5C_{60}.[475] Related $Pt(\eta^5\text{-}C_5H_4Me)(\eta^3\text{-}C_3H_5)$, prepared as an oil from $[PtCl(C_3H_3)]_4$ and $Tl[C_5H_4Me]$, has been shown to be an effective precursor for vapor deposition (MOCVD) of platinum films due to its high volatility.[551] Mass spectrometry studies (see Section 9.4.1.2) reveal the weakness of the Pt–allyl bond and the high stability of $[Pt(C_5H_4Me)]^+$, in agreement with the facile formation of platinum clusters under E.S. conditions.[504] Reaction of PtXMe(cod) (X = Cl, I) with modified cyclopentadienyl anions, C_5Me_4R (R = Me, $CH_2CH_2NMe_2$, $(CH_2)_xCH{=}CH_2$ ($x = 2, 3$)), generates monomeric species $PtMe(\eta^5\text{-}C_5Me_4R)(1,2\text{-}\eta^2{:}5,6\text{-}$cod), in which the cod ligand, on the basis of NMR data (^1H, ^{13}C, ^{195}Pt), is strongly η^2-coordinated to the platinum center.[175] The chelating effect of the side chain in the cyclopentadienyl ring is not strong enough to cause its displacement. Derivatives with Cp* and $C_5Me_4CH_2CH_2NMe_2$ groups dimerize, resulting in cod-bridged dinuclear complexes $\{Pt(\eta^5\text{-}C_5Me_4R)Me\}_2\{\mu\text{-}(1,2\text{-}\eta^2{:}5,6\text{-}\eta^2\text{-cod})\}$, confirmed by an X-ray study of the $C_5Me_4(CH_2)_2NMe_2$ complex. The dimerization is probably driven by entropic effects.[175] The orthometallated complex $Pt(\eta^5\text{-}Cp)$(C–N) (HCN = 4,4′-bis[4-(*n*-octyloxy)benzoyloxy]), obtained from $[Pt(C\text{–}N)(\mu\text{-}Cl)]_2$ and TlCp, is the first 18-electron Pt(II) complex exhibiting liquid crystal behavior.[552]

An interesting route to the first platinabenzene $(1,2\text{-}Ph_2C_5H_3Pt)(\eta^5\text{-}1,2\text{-}Ph_2C_5H_3)$[553] is shown in Scheme 20, (i). The complex contains two different rearrangements of the vinylcyclopropene ligand and is suggested to be formed through a bisplatinabenzene intermediate **S20-I**, which isomerizes into the diphenylcyclopentadienyl ligand by extrusion of the metal fragment.[553] The apparent preference for the formation of a CpPt fragment relative to a platinabenzene has been recently corroborated by DFT calculations, with the process classified as a carbene migratory insertion.[554,555] However, the formation of a second Cp ligand from $(C_5H_5Pt)Cp$ as model complex was found to have a high energetic barrier in agreement with experimentation.[554] Treatment of $PtI(\eta^5\text{-}Cp^*)(CO)$ with (*Z*)-3-(2-lithiovinyl)cyclopropenes (Scheme 20, (ii)) provides a more rational synthesis to platinabenzene complexes $(1,2\text{-}PhRC_5H_3Pt)(\eta^5\text{-}Cp^*)$ via σ-vinyl intermediates, which are also isolated from the reaction mixtures.[556] X-ray structures for $(1,2\text{-}Ph_2C_5H_3Pt)(\eta^5\text{-}1,2\text{-}Ph_2C_5H_3)$ and $(1,2\text{-}PhBu^tC_5H_3Pt)(\eta^5\text{-}Cp^*)$ confirm that the platinabenzene entity is strictly planar with similar $Pt\text{–}C_{ortho}$ (range 1.929(4)–1.972(5) Å) and C–C bonds (av. 1.382–1.387 Å), typical



Scheme 20

of aromatic systems.[553,556] In contrast to that found in $[Pt(\eta^3\text{-}1,2\text{-}Ph_2C_5H_3)(PEt_3)_2]^+$ (Section 9.4.2.2, Equation (12)),[518] the 1,2-diphenylcyclopentadienyl ligand formed is coordinated in an η^5-fashion (Pt–C_{Cp} 2.30 ± 0.05 Å).[553] The aromaticity[555,557] and electronic structure[555] of $(1,2\text{-}Ph_2C_5H_3Pt)(\eta^5\text{-}Cp)$ have been examined, pointing to a formally Pt(IV) complex with the $1,2\text{-}Ph_2C_5H_3$ fragment acting as a vinyl alkylidene six-electron $[Ph_2C_5H_3]^{3-}$ ligand. Dimeric complexes of general formulas $Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2$ (R = Ph, Me, Et, CH_2CMe_3, Bz), accessible from the reaction of PtClR(cod) with $Tl[C_5H_4PPh_2]$, have been shown to exist in solution as an equilibrium mixture of symmetrical $Pt_2R_2(\mu\text{-}\kappa P:\eta^5\text{-}C_5H_4PPh_2)_2$ and unsymmetrical $Pt_2R_2(\mu\text{-}\kappa P:\eta^5\text{-}C_5H_4PPh_2)(\mu\text{-}\kappa P:\eta C^1\text{-}C_5H_4PPh_2)$ isomers, with the latter being the major component. Both isomers (symmetrical, R = Ph, and asymmetrical, R = Me) have been characterized by X-ray crystallography[558] and react with L (CO, Bu^tNC)[559,560] to yield symmetrical face-to-face dimers $Pt_2R_2(\mu\text{-}\kappa P:\eta C^2\text{-}C_5H_4PPh_2)_2L_2$, in which the cyclopentadienyl rings are 1,2-substituted by platinum and phosphorus. At suitable temperatures, the dicarbonyl derivatives undergo carbonyl insertion followed by reductive elimination of the appropriate ketone to produce the platinum(I) dimer $Pt_2(CO)_2(\mu\text{-}\kappa P:\eta^1C^1\text{-}C_5H_4PPh_2)$.[559] Analogous reactions with phosphorus ligands give either related dimers $Pt_2(PR_3)_2(\mu\text{-}\kappa P:\eta C^1\text{-}C_5H_4PPh_2)_2$ (by reductive elimination of R–R) or zwitterionic species $PtR^1(PR^2{}_3)_2(C_5H_4PPh_2\text{-}P)$, in which the cyclopentadienyl ring is not coordinated to platinum, depending on the ligand and solvent.[560]

A Cp transfer to a double bond of the cod ligand (see Section 9.2.3.2) to yield an $\eta^1:\eta^2$-cyclooctenyl ligand is observed by treatment of $[Pt(\eta^5\text{-}Cp)(cod)]Cl$ with $K[Fe(\eta^3\text{-}C_7H_7)(CO)_3]$, which furnishes a bridged cycloheptatrienyl complex *syn*-$[(OC)_3Fe(\mu\text{-}\eta^3:\eta^2\text{-}C_7H_7)Pt(\eta^1:\eta^2\text{-}C_8H_{12}Cp)]$ with an Fe–Pt bond.[561] In contrast to other related Cp migrations, featuring $C(sp^3)$–$C(sp^3)$ bonding,[2,122] the cyclopentadienyl unit is linked to the C_8H_{12} ring in this Fe–Pt complex through a $C(sp^2)$ as confirmed by an X-ray diffraction study.[561] According to quantum chemical calculations, the cyclopentadienyl platinum(II) fragments PtClCp[562] and $[PtCp(CO)]^+$[563] can undergo exothermic oxidative addition with alkanes to give hydride–alkyl complexes of cyclopentadienyl platinum(IV).

8.09.6.1.2 Tetravalent derivatives

As mentioned before, the chemistry of cyclopentadienyl complexes has been recently reviewed.[122] Halogeno(cyclopentadienyl) platinum(IV) chemistry was also included in a more general review.[564]

An extensive series of complexes $Pt(\eta^5\text{-}Cp^4)R^1R^2R^3$ ($Cp^4 = C_5H_5$, C_5H_4Me, Cp^*, $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$, $C_5H_4(SiMe_2Ph)$; R^1, R^2, R^3 = Me, Et, Pr^n, Bu^n, Ac, $CH_2CH{=}CH_2$) have been prepared by reaction of $[PtIMe_3]_4$, $[PtIMeR^1R^2]_4$, or $[Pt(Ac)ClR^1R^2]_4$ and appropriate cyclopentadienyl transfer reagents, and these complexes have been the subject of a detailed ^{195}Pt NMR study.[565] The influence of the substituents, solvent, temperature, and concentration on the ^{195}Pt chemical shift have been examined.[565] The infrared spectrum of $Pt(\eta^5\text{-}Cp)Me_2Ac$ in the gas phase suggests that the complex exists as an equilibrium mixture of two rotational conformers.[566] Similarly, the reaction of $[PtIMe_3]_4$ with $Li[C_5Me_4CH_2CH_2NMe_2]$ ($LiCp^N$) affords $Pt(\eta^5\text{-}Cp^N)Me_3$, which, upon treatment with HBF_4, gives the corresponding protonated amino complex $[Pt(\eta^5\text{-}C_5Me_4CH_2CH_2NHMe_2)Me_3]BF_4$.[567] Halogeno(cyclopentadienyl)–Pt(IV) derivatives have been also reported. Thus, treatment of $[PtBr_2Me_2]_n$ with $MgClCp^*\cdot THF$ affords $PtBr(\eta^5\text{-}Cp^*)Me_2$, which reacts with Br_2 leading to $PtBr_2(\eta^5\text{-}Cp^*)Me$, both having typical "piano-stool" geometries as confirmed by diffractometric methods.[568] However, a similar reaction of $[PtI_2Me_2]_n$ with TlCp gives the expected $PtI(\eta^5\text{-}Cp)Me_2$ together with $Pt(\eta^5\text{-}Cp)Me_2(\eta^1\text{-}Cp)$ and $Pt(\eta^5\text{-}Cp)Me_3$ as secondary products.[569] $Pt(\eta^5\text{-}Cp)Me_3$ reacts with substituted arenes, ArMe, thermally (150 °C) or photochemically (RT) to afford $Pt(\eta^5\text{-}Cp)Me_2(CH_2Ar)$ (Ar = Ph, $4\text{-}MeC_6H_4$, $3,5\text{-}Me_2C_6H_3$) in low yields.[569] One Me group in $Pt(\eta^5\text{-}Cp^*)Me_3$ can be protonated with HTf to yield $Pt(Tf)\ (\eta^5\text{-}Cp^*)Me_2$ containing the labile triflate group, which is displaced by other anionic ($X = I^-$, $N_3{}^-$, $TolS^-$) or neutral ligands (L = CO, C_2H_4, $CH_2{=}CHMe$, NH_3, NH_2Bu^t), forming neutral $PtX(\eta^5\text{-}Cp^*)Me_2$ or cationic $[Pt(\eta^5\text{-}Cp^*)Me_2L]Tf$ derivatives. Related $PtCl(\eta^5\text{-}Cp^*)Me_2$ is generated by reaction of $Pt(\eta^5\text{-}Cp^*)Me_3$ with HCl.[570] The crystal structure of $Pt(STol)(\eta^5\text{-}Cp^*)Me_2$ shows little variation among the five C–C bond lengths (1.421(6)–1.446(6) Å) in the Cp^* ligand,[152] while the analogous chloride derivative exhibits some diene contribution to the bonding.[570]

The first platinocenium dications $[Pt(\eta^5\text{-}Cp^*)\ (\eta^5\text{-}C_5R_5)]^{2+}$ (R = H, Me) have been prepared by interaction of $[Pt_2(\mu\text{-}Br)_3(\eta^5\text{-}Cp^*)_2]Br_3$ with 6 equiv. of $AgBF_4$ in the presence of HCp or HCp^*, respectively.[542,571] The decamethylplatinocene $[Pt(\eta^5\text{-}Cp^*)_2]^{2+}$ can alternatively be generated by electrolysis (1.7 V) of $[Pt(\eta^5\text{-}Cp^*)(\eta^4\text{-}HCp^*)]^+$, presumably through the unstable 17-electron dication radical $[Pt(\eta^5\text{-}Cp^*)(\eta^4\text{-}HCp^*)]^{\cdot 2+}$, which undergoes C–H bond scission at the $C(sp^3)$–H of HCp^*.[542] The η^4-pentamethylcyclopentadiene Pt(II) precursor can be regenerated by electrochemical reduction (−0.80 V) of $[Pt(\eta^5\text{-}Cp^*)_2]^{2+}$, in this case, via the 19-electron monocation radical $[Pt(\eta^5\text{-}Cp^*)_2]^{\cdot +}$, followed by hydrogen abstraction from the medium.[542] The crystal structure[572] of $[Pt(\eta^5\text{-}Cp^*)_2]^{2+}$ shows an eclipsed disposition of both rings with a Pt–C_5Me_5 ring distance (1.84(1) Å), slightly longer than in related isoelectronic species $[M(\eta^5\text{-Cp}^*)_2]^{n+}$ (M = Ir, n = 1 (1.82 Å);[572] M = Os, n = 0 (1.81 Å)[573]).

Due to its low melting point (30 °C), complex $Pt(\eta^5\text{-}C_5H_4Me)Me_3$ has been widely employed as a precursor for platinum thin films using both chemical-vapor deposition (CVD)[574,575] and atomic layer deposition (ALD) techniques.[576] This complex also exhibits high values of absolute photochemical efficiency (Φ_{cr}) (0.34 methylcyclohexane; 0.41 n-pentane) following excitation at 313 and 366 nm, and even higher in the presence of $SiHEt_3$ (0.79–0.85), and its efficiency as an effective photoinitiator for hydrosilylation reactions in vinyl/hydride silicone mixtures has been demonstrated.[577]

8.09.6.2 η^5-Heterocyclopentadienyl Complexes

The complexes reported in this section feature boron–carbon rings or cages as ligands. There have been a large number of reviews and monographs[578–581] concerned with this type of ligand, and the number of platinum-containing complexes is growing. The X-ray structure of $PtCl\{(HR^1{}_2R^2{}_2P(Me)C_5)\}(PPh_3)$ ($R^1 = SiMe_3$, $R^2 = Ph$) shows that the phosphahexadienyl anion is coordinated in an η^2-fashion through the P–C bond with the Cl lying *cis* to the C-atom.[582] NMR data indicate that the $PtCl(PPh_3)$ fragment exchanges between both P–C bonds in solution, presumably through a transition state with the ligand acting as η^1-*P*.[582]

8.09.6.2.1 η^5-Boron–carbon ligands

Reaction of $Na_3[nido\text{-}CB_{10}H_{11}]$ with $PtCl_2L_2$ gives rise to monocarborane anionic complexes $[PtL_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ ($L = PEt_3$,[583] PMe_2Ph[584]), which in turn react with $MClL_n$ ($ML_n = AuPPh_3$, $CuPPh_3$, HgPh) to yield dimetal compounds $PtM(PEt_3)(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})$.[583] The X-ray structures of these bimetallic complexes confirm the pentahapto coordination of the open pentagonal face of the $CB_{10}H_{11}$ cage. Protonation studies of $[PtL_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ allow the synthesis of mono-$PtXL_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})$ (X = H, $L = PEt_3$, PMe_2Ph; X = Cl, $L = PMe_2Ph$) and novel diplatinum complexes $Pt_2\{\mu\text{-}\eta^1,\eta^5:\eta^{1\prime},\eta^{5\prime}\text{-}8,9'\text{-}(7\text{-}CB_{10}H_{10})_2\}(PMe_2Ph)_4$ and $Pt_2\{\eta^5:\eta^{5\prime}\text{-}9,9'\text{-}I(H)\text{-}(7\text{-}CB_{10}H_{10})_2\}(PEt_3)_4$, whose structures have been also confirmed by X-ray diffraction.[584] A related anionic dicarborane species $[Pt(\eta^5\text{-}7,8\text{-}Me_2\text{–}7,8\text{-}C_2B_9H_9)(\eta^3\text{-}C_3H_5)]^-$, isolated as its $NEt_4{}^+$ or PPN^+ salt, has been obtained similarly from $Na_2[nido\text{-}7,8\text{-}Me_2\text{–}7,8\text{-}C_2B_9H_9)]$ and $[Pt(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ (see Section 9.4.1.1).[476] Its protonation ($HBF_4{\cdot}Et_2O$, −78 °C) in the presence of CO or Bu^tCN (L) produces neutral derivatives $Pt(\eta^5\text{-}7,8\text{-}Me_2\text{–}7,8\text{-}C_2B_9H_9)L_2$, while in the presence of $HC{\equiv}CPh$ affords the dimetal species $Pt_2\{\mu\text{-}\eta^1,\eta^1:\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{–}7,8\text{-}C_2B_9H_9)_2$ (see Section 9.5.2), in which two alkyne molecules have coupled to give a C_4 ligand.[476]

A series of *closo*- mono- $1\text{-R–}3,3\text{-}L_2\text{–}3,1,2\text{-}PtC_2B_9H_{10}$ (R = Ph,[585] $L = PMe_2Ph$; $R = C_4H_3S$,[586] L_2 = cod, dppe, $(PMe_2Ph)_2$) and $1\text{-Ph-}2\text{-Me-}3,3\text{-}L_2\text{-}3,1,2\text{-}PtC_2B_9H_9$ ($L = PMe_2Ph$, PEt_3, PPh_3, $PTol_3$)[587] -substituted dicarbaplatinaboranes have been prepared from the reaction of $Tl_2[7\text{-R–}7,8\text{-}nido\text{-}C_2B_9H_{10}]$ or $Tl_2[7\text{-Ph–}8\text{-Me–}7,8\text{-}nido\text{-}C_2B_9H_9]$, and the appropriate *cis*-$[PtCl_2L_2]$. Crystallographic studies for complexes with R = Ph[585] ($L = PMe_2Ph$)[585] and $R = C_4H_3S$ (L_2 = cod, $(PMe_2Ph)_2$)[586] show typical distorted half-sandwich slipped structures, with the platinum fragment located away from one of the carbon atoms of the C_2B_3 face of the carborane (Pt–$C_{\text{ring cage}}$ 2.326(10)–2.620(6) Å) ($\eta^4\text{-}CB_3$ distortion). In the disubstituted carbon derivatives $1\text{-Ph–}2\text{-Me–}3,3\text{-}L_2\text{–}3,1,2\text{-}PtC_2B_9H_9$ ($L = PEt_3$, PPh_3), the intramolecular crowding leads to a significant lateral slippage with the Pt moving toward the three boron atoms and Pt–C_{cage} distances (2.834–3.003(6) Å) essentially non-bonding ($\eta^3\text{-}B_3$ distortion).[587] A similar distortion ($\eta^3\text{-}B_3$) is observed in $1,2\text{-}Ph_2\text{-}3,3\text{-}(PMe_2Ph)_2\text{–}6\text{-Et–}3,1,2\text{-}PtC_2B_9H_8$ formed with the labeled carborane ligand $[3\text{-Et-}7,8\text{-}Ph_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^{2-}$.[588] In some cases, these complexes are generated as the kinetic products and undergo skeletal rearrangement, moving out one of the carbons of the C_2B_3 ring to give less crowded products, with the platinum fragment bonded to CB_4 rings.[585,586,588] Thus, $1,2\text{-}Ph_2\text{–}3,3\text{-}L_2\text{–}6\text{-Et–}3,1,2\text{-}PtC_2B_9H_8$ isomerizes to $1,8\text{-}Ph_2\text{–}2,2\text{-}L_2\text{–}4\text{-Et–}2,1,8\text{-}PtC_2B_9H_8$, a process that can be explained by a simple rotation of a CB_2 face.[588] Both isomers $3,3\text{-}L_2\text{–}3,1,2\text{-}PtC_2B_9H_{11}$ and $[2,2\text{-}L_2\text{–}2,1,8\text{-}PtC_2B_9H_{11}]$ have been prepared with the unsubstituted $Cs[nido\text{-}7,8\text{-}C_2B_9H_{12}]$ reagent and *cis*-$[PtCl_2L_2]$ ($L = PMe_2Ph$) in the presence of NEt_3, being characterized by spectroscopic and diffractometric means. A relatively low free energy barrier for the rotation of the PtL_2 fragment has been measured (<30 kJ mol^{-1}) for the non-isomerized derivative, $3,3\text{-}L_2\text{–}3,1,2\text{-}PtC_2B_9H_{11}$, which crystallizes as a 1 : 1 mixture of two different rotational conformers. In one, the Pt-to-C_2B_3 cage bonding is essentially $\eta^4\text{-}CB_3$, and in the other, the interaction is more typical of a distorted $\eta^3\text{-}B_3$, with weaker interactions to both carbon atoms.[589,590]

8.09.7 Arene and Related Complexes

Most platinum complexes with arene ligands show coordination of the Pt atom to two adjacent C–C bonds (η^2), and have been examined in Sections 9.2.5 and 9.2.6. Theoretical calculations on benzene (Bz)–Pt/Pt$^+$ [154] and higher benzene–platinum complexes (Bz_xPt_y: $x = 1$–3; $y = 1,2$) also indicate that all these species prefer low-symmetry equilibrium structures.[591] The absorption of benzene and higher aromatic molecules has been the subject of several experimental and theoretical studies[592,593] but lie outside the scope of this review. Recently, a species formulated as $[Pt(\eta^6\text{-}C_6H_6)(dfepe)]^{2+}$ has been shown to be formed by protonolysis of $Pt(OCOCF_3)Ph(dfepe)$, or on addition of benzene to a solution of $[Pt(OCOCF_3)_2(dfepe)]$.[594] However, the spectroscopic data do not allow exclusion of more conventional fluxional η^4 or $\eta^2\text{-}C_6H_6$ bonding modes.

8.09.7.1 Complexes with η^6-Heteroarenes

Reaction of 9,10-dihydro–9,10-dimethyl–9,10-diboraanthracene (L) with $Pt(cod)_2$ leads to the 18-electron complex $Pt(cod)(\eta^6\text{-}C_{12}B_2Me_2)$, with the diboraanthracene ligand η^6-coordinated through the central dimethyldiboracycle, as confirmed by an X-ray structure of the related $Pd(cod)(\eta^6\text{-}C_{12}B_2Me_2)$ complex.[595] The platinacarborane complex 1,2-$(CH_2)_3$–4,4-L_2–4,1,2-*closo*-$PtC_2B_{10}H_{10}$ ($L = PMe_2Ph$), with an asymmetric docosahedral cage structure, has the Pt center bonded to two carbon atoms and four boron atoms (2.265(7)–2.322(8) Å), and has been prepared by reduction of 1,2-$(CH_2)_3$–1,2-*closo*-$C_2B_{10}H_{10}$ with Na/naphthalene, followed by treatment with $PtCl_2L_2$.[596]

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