Available online at www.sciencedirect.com
SCIENCE DIRECT®
Coordination Chemistry Reviews 249 (2005) 3075–3197
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

The chemistry of binuclear palladium(II) and platinum(II) complexes

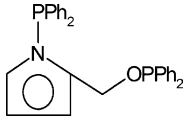
Vimal K. Jain [a,*], Leela Jain [b]

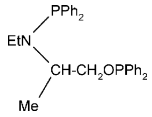
[a] *Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India*
[b] *Department of Chemistry, VES College, Chembur, Mumbai 400076, India*

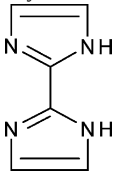
Received 7 December 2004; accepted 24 June 2005
Available online 15 September 2005

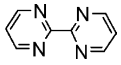
Contents

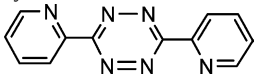
1. Introduction 3076
2. Binuclear complexes containing Group 14 donor ligands 3076
   2.1. Carbon monoxide complexes 3076
   2.2. Alkene and alkyne complexes 3077
   2.3. Isocyanide, carbene and ylide complexes 3082
3. Binuclear complexes containing Group 15 donor ligands 3083
   3.1. Complexes containing Group 15 as bridging ligands 3083
      3.1.1. Amido-, phosphido- and arsenido-bridged complexes 3083
      3.1.2. Pyrazolato-bridged complexes 3085
   3.2. Complexes containing Group 16 as bridging ligand 3088
      3.2.1. Hydroxo-bridged complexes 3088
      3.2.2. Complexes with RE^- bridges 3090
      3.2.3. Complexes with chalcogenido (E^{2-}) bridges 3093
   3.3. Complexes containing Group 17 as bridging ligand 3098
      3.3.1. Classical complexes 3098
      3.3.2. Organometallic (σ bonded) complexes 3104
      3.3.3. Complexes with small bite anionic three-atom bridging ligands 3106
4. Binuclear complexes containing Group 16 neutral ligands 3112

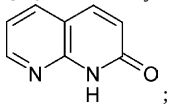
Abbreviations: dmpm, bis(dimethylphosphino)methane; dppm, bis(diphenylphosphino)methane; depm, $Et_2PCH_2PEt_2$; dipm, $Pr^i_2CH_2PPr^i_2$; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppen, *cis*-$Ph_2PCH{=}CHPPh_2$; dppa, 1,2-bis(diphenylphosphino)acetylene; dpm, $Ph_2PCH(Me)PPh_2$; dpam, 1,2-bis(diphenylarsino)ethane; dppam, $Ph_2PCH_2AsPh_2$; dpsm, $Ph_2SbCH_2SbPh_2$; dppet, $Ph_2PCH_2CH_2S$-; pz, pyrazolate; dmpz, 3,5-dimethylpyrazolate; tmpz, 3,4,5-trimethylpyrazolate; $N_3C_2H_2$, 1,2,3-triazolate; az, azaindolate; dpf, diphenylformidinate; gua, guanidine; COD, 1,5-cycloocadiene; nbd, norbornadiene; prolophos, 

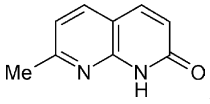
; butaphos, 

; biim, 

; bipym, 

; bptz, 

; bipy, 2,2′-bipyrdine; phen, 1,10-phenanthroline; trpy, 2,2′,2″-terpyridine; py, pyridine; tmeda, $Me_2NCH_2CH_2NMe_2$; en, ethylenediamine; GSH, glutathione; Haccys, *N*-acetylcysteine; pytH, 2-mercaptopyridine; dppf, $(Ph_2PC_5H_4)_2Fe$; np, $N(CH_2CH_2PPh_2)_3$; tht, tetrahydrothiophene; Mes, 2,4,6-$Me_3C_6H_2$; c-Hx, cyclohexyl; Th, 2-thineyl; acacH, acetylcetone; bzacH, benzoylacetone; OxH, 8-hydroxyquinoline; c-Hx_3P, tricyclohexylphosphine; Honp, 

; Hmonp, 

; Pap, cyclometallated azobenzene

* Corresponding author. Tel.: +91 22 25595095; fax: +91 22 25505150.
E-mail address: jainvk@apsara.barc.ernet.in (V.K. Jain).

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2005.06.020

5. Binuclear ionic complexes ... 3113
5.1. Cationic binuclear complexes ... 3113
5.2. Cationic hydrido-bridged complexes ... 3119
5.3. Anionic binuclear complexes ... 3122
6. Binuclear allyl complexes of palladium(II) and platinum(II) ... 3125
6.1. Synthesis involving allyl alcohols/halides and related compounds ... 3125
6.2. Synthesis from palladium(O) and platinum(O) precursors ... 3125
6.3. Synthesis involving olefins ... 3126
6.3.1. Synthesis from mono-olefins ... 3126
6.3.2. Synthesis from diolefins ... 3126
6.4. Synthesis from cyclopropanes ... 3127
6.5. Spectroscopic and structural aspects ... 3128
6.6. Chemical reactivity of binuclear allyl complexes ... 3130
6.6.1. Bridge-cleavage with neutral donor ligands ... 3130
6.6.2. Halide exchange with other anionic ligands ... 3131
6.6.3. Reactions involving allylic carbon ... 3132
6.6.4. Thermal decomposition ... 3134
7. Binuclear cyclometallated complexes ... 3134
7.1. Nitrogen ligands ... 3135
7.2. Phosphorus and arsenic donor ligands ... 3144
7.3. Sulfur ligands ... 3145
7.4. Chemical reactivity ... 3155
8. Binuclear complexes with small bite ligands ... 3160
8.1. Complexes with dppm and related ligands ... 3160
8.2. Lantren type complexes ... 3164
9. Miscellaneous derivatives ... 3166
10. Conclusions and future outlook ... 3170
Acknowledgements ... 3170
References ... 3170

Abstract

The chemistry of binuclear palladium(II) and platinum(II) complexes has been reviewed. This review deals with complexes derived from various classes of ligands and covers various aspects, viz. synthesis, spectroscopic and structural features and chemical reactivity, of these complexes. Applications of these complexes are briefly described in the respected sections.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Binuclear complexes; Palladium; Platinum; Phosphines; Thiolate; Ionic complexes

1. Introduction

The chemistry of binuclear palladium(II) and platinum(II) complexes is of considerable interest. These complexes have a long history, the platinum carbonyl $[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ being the first binuclear compound isolated as early as 1870. The synthetic procedure of $[M_2Cl_2(\mu\text{-}X)_2(PR_3)_2]$ (X = Cl or SR′) complexes emerged in the second quarter of the last century. The progress on binuclear complexes of palladium and platinum was rather slow but steady, with about 100 publications, till 1960. Isolation of allylpalladium and *ortho*-palladated complexes in 1960s gave a new turn to the development of binuclear complexes owing to their relevance in organic transformations. Over a period the chemistry of binuclear palladium and platinum complexes has grown considerably in scope and magnitude. The field has become multidisciplinary in nature encompassing areas like organic synthesis, catalysis, materials science, photo-physical chemistry, chemotherapy, etc. Various aspects of palladium and platinum chemistry have been published in books, monographs and review articles (references appear in the respective sections) [1–9]. It is intended to provide an updated and concise, yet a comprehensive, review on the subject which may further accelerate work on these complexes.

2. Binuclear complexes containing Group 14 donor ligands

2.1. Carbon monoxide complexes

The binuclear chloro-bridged platinum carbonyl complex, $[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ was the first carbonyl complex synthesized as early as 1870 [10]. Carbonylation of MX_2 with CO has been a convenient method to prepare binuclear complexes $[M_2X_2(\mu\text{-}X)_2(CO)_2]$ (M = Pd or Pt). Carbonylation of $PdCl_2$

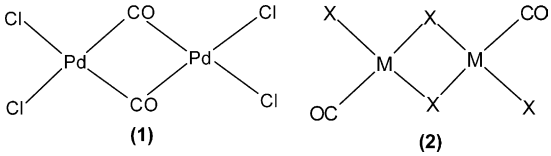
in methanol in the presence of traces of moisture with CO at 20 °C readily affords $[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ [11]. Although water decomposes the product, moisture is essential in the reaction [11–15]. Similarly a bromo-analogue has been prepared [14,15]. In an alternative preparation, CO is passed over solid $PdBr_2$ at 180 °C [16,17]. However, attempts to prepare an iodo derivative employing this method have been futile [17]. The stability of halocarbonyl complexes decreases in the sequence Cl > Br > I.

High pressure carbonylation of $PdCl_2$ in anhydrous thionylchloride affords $[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ [18,19]. The reaction is exothermic with $\Delta H^\circ = -13.6 \pm 0.2$ kcal/mol [19]. Recently, DellAmico and Labella [20] prepared $[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ in nearly quantitative yield from "palladium black", obtained from $Pd(dba)_2$ and CO in toluene, in sulfurylchloride (SO_2Cl_2) under a CO atmosphere. However, similar reaction with platinum yields *cis*-$[PtCl_2(CO)_2]$ [20] which is thermally unstable and loses CO to give $[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ [21]. Carbonylation of PtX_2 or H_2PtBr_6 initially gives $PtX_2(CO)_2$ which loses CO (X = I at room temperature; X = Cl under vacuum) (1) [22–25]. Metathesis of $[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ with appropriate halogen halide yields $[Pt_2X_2(\mu\text{-}X)_2(CO)_2]$ (X = Br or I) [26].

$$PtX_2 \text{ or } H_2PtBr_6 \xrightarrow{CO} PtX_2(CO)_2 \rightarrow \tfrac{1}{2}[Pt_2X_2(\mu\text{-}X)_2(CO)_2] + CO \quad (1)$$

Although carbon monoxide is known to insert across the metal–carbon bond, a few Pt-σ-alkyl carbonyl complexes have been reported. The reaction of CO with $[Pt_2Me_2(\mu\text{-}Cl)_2(ethylene)_2]$ at low temperatures gives $[Pt_2Me_2(\mu\text{-}Cl)_2(CO)_2]$ ($\upsilon CO = 2040\ cm^{-1}$) which is unstable above 0 °C [27]. Li_2PtCl_4 reacts with α-olefins (ethylene, hexene, heptene, octene, dodecene) and formic acid in DMF to afford alkylplatinum carbonyl complexes, $[Pt_2R_2(\mu\text{-}Cl)_2(CO)_2]$ stability of which is independent of alkyl group [28]. In these reactions the intermediate olefinic complex, $[PtCl_2(CO)(olefin)]$, is believed to be reduced by formic acid via a hydrido complex $[PtHCl(CO)(olefin)]$. An acyl complex of the type $[Pt_2(COCF_3)_2(\mu\text{-}Cl)_2(CO)_2]$ has been reported [29].

A low value of υCO ($1967\ cm^{-1}$) for $[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ reported earlier has been attributed to the bridging CO in the palladium dimer (**1**) [30–33]. However, DellAmico and co-workers [18,19] reported υCO absorption at $2167\ cm^{-1}$ and attributed the usual halogen-bridged dimeric structure (**2**) (M = Pd; X = Cl). A steady decrease in the υCO with increasing mass of halogen in platinum complexes, $[Pt_2X_2(\mu\text{-}X)_2(CO)_2]$ (X = Cl; $\upsilon C{=}O$ $2152\ cm^{-1}$; X = Br, $\upsilon CO = 2130\ cm^{-1}$; X = I, $\upsilon CO = 2104\ cm^{-1}$) has been attributed to increased π-back donation from Pt(II) to CO with decreasing electronegativity of halogen [34]. The structures of $[Pt_2X_2(\mu\text{-}X)_2(CO)_2]$ (X = Cl or I), established by X-ray crystallography, reveal a planar centro-symmetric halo-bridged dimer with *trans* configuration [35,36]. However, the corresponding palladium compound $[Pd_2Cl_2((\mu\text{-}Cl)_2(CO)_2]$ adopts a *cis* configuration [36].



The halo-bridged carbonyl complexes, $[M_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ undergo a variety of reactions. They are decomposed by water into palladium/platinum metal and CO_2 [37]. However, a methanolic solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ in the presence of moisture yields a red-violet Pd(I) complex $[PdCl(CO)]_n$ (2) [37]. The latter can also be obtained in 88% yield on treating $[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ with CO in acetic anhydride [19].

$$[PdCl(CO)]_n + HCl + CO_2 \overset{MeOH/H_2O}{\longleftarrow} [Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2] \xrightarrow{H_2O} 2Pd + 2CO_2 + 4HCl \quad (2)$$

$[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ reacts with 1,5-cyclooctadiene or norbornadiene to yield mononuclear diene complexes, $[PdCl_2(diene)]$ [38], whereas with 1,3-cyclohexa- or heptadiene, π-allylic chloro-bridged complexes are formed [38,39]. Treatment of $[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ with olefins (olefin = ethylene, propene, cyclopentene or cyclohexene) results in bridge cleavage yielding olefin carbonyl complexes, *cis*-$[PtCl_2(CO)(olefin)]$ [40]. Such bridge cleavage reactions have been observed with a variety of neutral donor ligands [34,41–43] including CO [24,36]. Mondentate ligands, such as R_2SO (R = Me, Et) [40], *p*-toludine, $AsPh_3$ [34], cleave the bridge symmetrically. In contrast bidentate ligands, such as bipy, diarsine, cleave the bridge unsymmetrically and afford $[PtCl(CO)L\text{–}L]^+[PtCl_3(CO)]^-$ [34,42,44]. With ammonia, complexes **3**–**5** have been isolated (3) [41]. Treatment of $[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ with HCl results in the cleavage of chloride bridge with the formation of anionic complex, $[PtCl_3(CO)]^-$ [21]. Reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ with nitric oxide and sodium cyclopentadienide at 50 °C for a week yields $[Pt(NO)(\eta^5\text{-}Cp)]$ [45]. Treatment of $[Pd_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ with $SnCl_2$ in the presence of HCl and PPh_3 yields a trichlorostannate complex $[\{Pd(SnCl_3)(PPh_3)\}_2(CO)]$ [46].

$$[Pt_2Cl_2(\mu\text{-}Cl)_2(CO)_2] \xrightarrow{2\ NH_3} \underset{\mathbf{3}}{[PtCl_2(CO)(NH_3)]} \xrightarrow{2\ NH_3} \underset{\mathbf{4}}{[PtCl(CO)(NH_3)_2]Cl} \xrightarrow{-CO} \underset{\mathbf{5}}{[PtCl_2(NH_3)_2]} \ldots \quad (3)$$

2.2. Alkene and alkyne complexes

Several reviews dealing with transition metal–alkene/alkyne complexes have been published [47–55]. The Zeise's

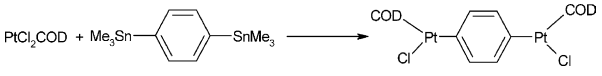
dimer $[Pt_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ (**6**) has been prepared initially by the reaction of $PtCl_2$ with ethanol [56]. Reaction of Zeise's salt, $K[PtCl_3(CH_2{=}CH_2)]$ with HCl affords **6**. Another convenient way to prepare **6** is to pass a solution of *trans*-$[PtCl_2(py)(CH_2{=}CH_2)]$ through a sulfonated cation exchange resin to remove pyridine as pyridinium salt [57]. Reaction of olefin under pressure with solid $PdCl_2$ in a suitable solvent has been used to prepare $[Pd_2Cl_2(\mu\text{-}Cl)_2(olefin)_2]$ [58–60], but the latter can be conveniently prepared by using a soluble precursor, $[PdCl_2(PhCN)_2]$ and appropriate olefin (4) [61]. The reaction is of general nature and can be exploited for the synthesis of a variety of binuclear olefin complexes [62]. The ethylene complexes **6** and $[Pd_2Cl_2(\mu\text{-}Cl)_2(ethylene)_2]$ (**7**) are frequently used as precursors for the synthesis of other olefin (usually less volatile) [61,63–71] and acetylene [72–74] derivatives as volatility of ethylene aids its smooth displacement (5). The reaction is particularly useful for the synthesis of alkyne complexes as alkynes are readily oligomerized by palladium(II). For instance, the reaction of bis(*p*-methoxyphenyl)acetylene with Na_2PdCl_4 in ethanol affords a salt $[Pd_2Cl_3(\eta^4\text{-}C_4Ar_4)_2][Pd_2Cl_6]$ [75]. Displacement of ethylene in **6** by vinyltrimethylsilyl ether yields $[Pt_2Cl_2(\mu\text{-}Cl)_2(RCH{=}CHOSiMe_3)_2]$ which on hydrolysis affords vinylalcohol complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(RCH{=}CHOH)_2]$ (R = H or Me) [76].

$$[PdCl_2(PhCN)_2] + \text{olefin} \rightarrow \tfrac{1}{2}[Pd_2Cl_2(\mu\text{-}Cl)_2(\text{olefin})_2] + 2\text{PhCN} \quad (4)$$

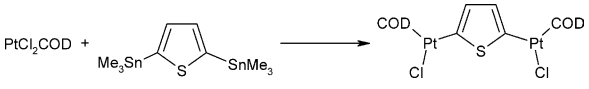
$$[M_2Cl_2(\mu\text{-}Cl)_2(\text{olefin})_2] + 2\text{L} \rightarrow [M_2Cl_2(\mu\text{-}Cl)_2(\text{L})_2] + 2\,\text{olefin} \quad (5)$$

(M = Pd or Pt; L = RCH=CHR′ or cyclic olefin; RC≡CR′)

σ-Bonded binuclear platinum alkene complexes have also been synthesized [27,77–80]. Treatment of K_2PtCl_4 with ethylene at 800 psi in water over a period of 5 days affords $[Pt_2Et_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ [27,81]. Reaction of $[Pt_2Me_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ [27] with Zeise's dimer yields an asymmetric complex, $[Pt_2MeCl(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ [77]. Complexes containing cyclooctadiene have been prepared by the reaction of $PtCl_2(COD)$ with bis(trimethyltin)aryls (6) and (7) [81–83].

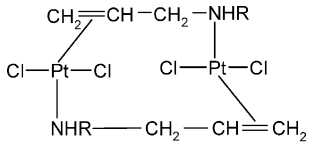


(6)



(7)

Primary and secondary amines of the type $CH_2{=}CH(CH_2)_nNHR$ ($n = 1$ or 3; R = H or *n*-octyl) react with K_2PtCl_4 to form *trans* dimeric compound **8** [84,85] whereas analogous phosphine/arsine ligands $CH_2{=}CH(CH_2)_3EPh_2$ (E = P or As) yield chelate complexes [86,87].



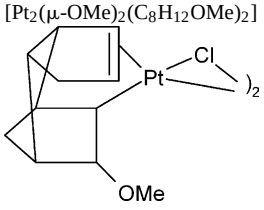
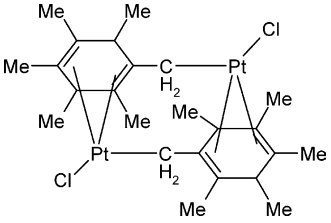
(8)

The molecular weight determination of soluble palladium olefin complexes, $[Pd_2Cl_2(\mu\text{-}Cl)_2(olefin)_2]$ indicates their dimeric nature [65–67]. IR and Raman spectra of several binuclear olefin and acetylene complexes $[M_2Cl_2(\mu\text{-}Cl)_2(L)_2]$ have been reported [73,74,88–91]. The platinum–carbon stretching vibrations have been assigned at ∼490 and ∼400 cm^{-1} while Pt–Cl absorptions have been reported at ∼290 (bridging Cl) and ∼320 cm^{-1} (terminal Pt–Cl) in the platinum olefin complexes [89]. The IR spectra of $[M_2Cl_2(\mu\text{-}Cl)_2(Bu^tC{\equiv}CBu^t)_2]$ display bands at 2005, 2023 (for Pt) and 2050 cm^{-1} (for Pd) due to $\upsilon C{\equiv}C$ stretching vibrations [73,74,91]. The NMR spectra of **6** have been investigated [92,93]. There is a rocking motion perpendicular to the platinum–olefin bond and wagging about the carbon–carbon bond axis [92]. The chemical shift tensor measurements from ^{13}C NMR spectrum of **6** indicate that the C–C bond order is intermediate between single and double bond. The ^1H NMR data on $[Pt_2Cl_2(\mu\text{-}Cl)_2(Me_2C{=}C{=}CMe_2)_2]$ show that the complex is fluxional in solution due to migration of platinum from one double bond to another [94–96].

Dimeric structures have been established by X-ray diffraction studies on several olefin complexes (Table 1) [71,80,97–108]. In general the olefin plane in these complexes lies perpendicular to the metal square-plane and the bridging M–X groups are asymmetrically bound to the metal atoms. The M–X distances *trans* to the olefin are longer than those *trans* to X. Structural analyses of $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_nH_{2n})_2]$ ($n = 5$, 7, 8) reveal a gradual increase in the $Pt\text{–}Cl_{(bridging)}$ distances from cyclopentene to octene [71,103]. This has been attributed to a gradual weakening of the chloride bridge in this order [71]. The complex $[Pt_2Et_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ (Fig. 1) has a planar structure and the ethylene molecules are orthogonal to this plane [27,80]. Although ethylene in **7** could not be located accurately, it is thought to be perpendicular to the Pd_2Cl_4 plane [97,98]. In $[Pd_2Cl_2(\mu\text{-}Cl)_2(PhCH{=}CH_2)_2]$ the olefinic double bond is neither symmetrically disposed about the palladium–olefin bond nor perpendicular to the $PdCl_2Pd$ plane [98]. In $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}pz)(CH_2{=}CH_2)_2]$ both the ethylene molecules are *trans* to the bridging pyrazolate group and are perpendicular to the planar Pt_2ClN_2 plane [105].

Although binuclear olefin complexes of palladium and platinum undergo a variety of reactions, nucleophilic

Table 1
X-ray structures of binuclear olefin complexes of palladium and platinum

Complex	Comments	References
$[Pd_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$	Olefin perpendicular to Pd_2Cl_4	[97]
$[Pd_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CHPh)_2]$	Pd–Pd = 3.46(1) Å monoclinic space group $P2_{1/C}$	[98]
$[Pd_2Cl_2(\mu\text{-}Cl)_2\{\eta^4\text{-}C_4(C_6H_4OMe\text{-}p)_4\}_2]$	Centrosymmetric chloro-bridged dimer, Pd_2Cl_2 ring non-planar	[75]
$[Pt_2Et_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$	Planar and ethylene is orthogonal to this plane	[80]
$[Pt_2(\mu\text{-}OAc)_2(C_8H_{12}OAc)_2]$	Pt · · · Pt = 3.03 Å, acetate is asymmetrically bridged	[110]
$[Pt_2(\mu\text{-}OMe)_2(C_8H_{12}OMe)_2]$	Asymmetric MeO, Pt_2O_2 ring planar, Pt–O = 2.040(9) Å	[107,108]
		[99]
	Monoclinic, $C_{2/C}$, Pt · · · Pt = 3.262(2) Å	[100,101]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(\eta^2\text{-}C_5H_8)_2]$ C_5H_8 = cyclopentene	Orthorhombic, space group Ibam, Olefin perpendicular to Pt_2Cl_2 plane	[103]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(C_7H_{12})_2]$; ($C_7H_{12}$ = tetramethyl allene)	Orthorhombic, space group Pbca, Olefinic bond orthogonal to Pt_2Cl_4 plane	[94,102]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(\eta^2\text{-}C_7H_{12})_2]$; ($C_7H_{12}$ = cycloheptene)	Monoclinic, space group $P2_{1/C}$, Olefinic perpendicular to Pt_2Cl_4 plane	[103]
$[Pt_2(\mu\text{-}Cl)_2(CH_2CH_2COC_6H_4Cl\text{-}p)_2(CH_2{=}CH_2)_2]$	Ethylene perpendicular to asymmetric Pt_2Cl_2 ring,	[104]
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}pz)(CH_2{=}CH_2)_2]$	Pt · · · Pt = 3.717 Å, olefin is planar to the Pt_2ClN_2 ring	[105]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(\text{cyclooctene})_2]$	Pt · · · $Cl_{(bridging)}$ = 3.340(3) Pt · · · $Cl_{(bridging)}$ = 3.371(3) Å,	[71]

attack on coordinated carbon atom has been extensively investigated. Most of the nucleophilic attack has been studied with coordinated dienes $[MX_2(diene)]$ (M = Pd or Pt; X = Cl, Br, I) [102,107–119], the reaction of $[MCl_2(diene)]$ with alkoxide ion being the first report [119] (8). The reaction (8) is reversible and on treatment with HCl yields the parent diene complex. Palladium complexes are more reactive than the corresponding plat-

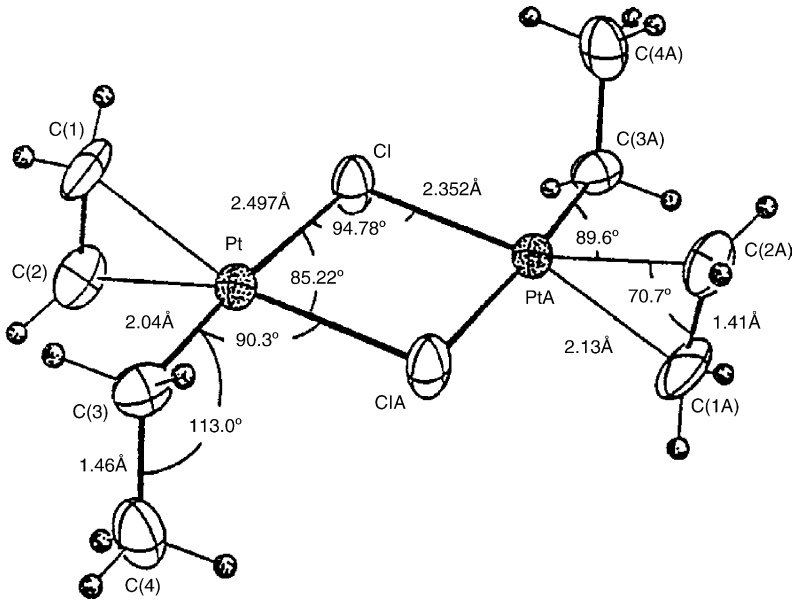
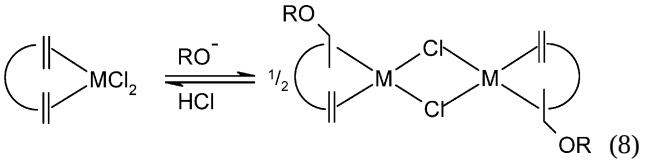
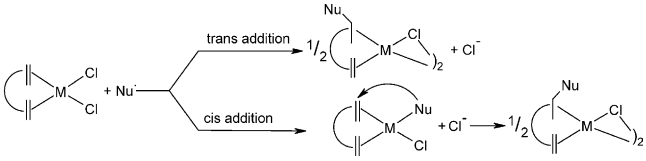


Fig. 1. Molecular structure of $[Pt_2Et_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ (reproduced with permission from ref. [80]).

inum analogues. The stability of diene complexes also depends on diene and halogen and varies in the order: 1,5-cyclooctadiene ≥ dicyclopentadiene > dipentene > 1,5-hexadiene and Cl, Br, I. Nucleophilic attack on coordinated olefin proceeds via two different mechanisms, i.e. *trans* and *cis* additions (9).

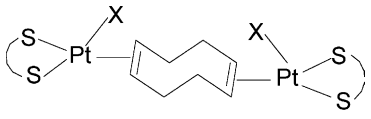


(8)



(9)

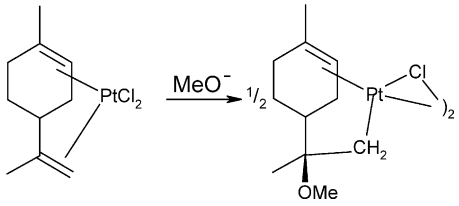
The *trans* addition reactions are very common and usually take place by the hard nucleophiles, such as hydroxide [119,120], alkoxy [109,111,119,121–126], β-diketonates [127,128], malonates [129,130], carboxylates [113,114,125,131,132], amines and ammonia [114,115,128,133–137], azide [133] and chloride [125]. In these reactions, nucleophile attacks one of the double bonds of the diene at the *exo* position (external attack). The *cis* addition is less frequent and is confined to soft nucleophiles like hydride, alkyl or aryl. The nucleophile initially coordinates to the metal atom which migrates intramolecularly at the *endo* position of the double bond leading to the *cis* addition [68,138–141]. Interestingly dithio ligands, such as diethyldithiocarbamates [142], dithiophosphates [143], yield cyclooctadiene bridged complexes (**9**) rather than an addition product. Similarly when [CODPtMe(I)] is treated with $M(C_5Me_4R)$ (R = Me, $CH_2CH_2NMe_2$), the COD bridged complexes, $[\{PtMe(C_5Me_4R\}_2COD]$ are isolated and one of them is structurally characterized by X-ray diffraction ($R = CH_2CH_2NMe_2$) [144].



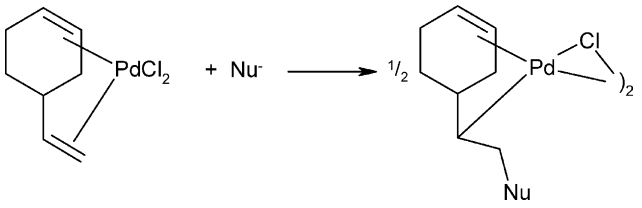
(9)

(S^S = $(RO)_2PS_2^-$; X = Cl or Me)

Preferential nucleophilic attack takes place on coordinated dienes with inequivalent two double bonds [109,111,114,115,125,145]. The acyclic double bond is the preferred site of attack (10) and (11) [111,114,115].

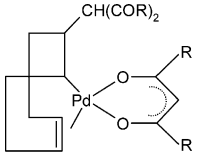


(10)

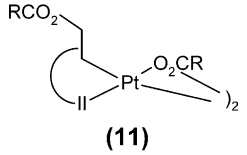


(11)

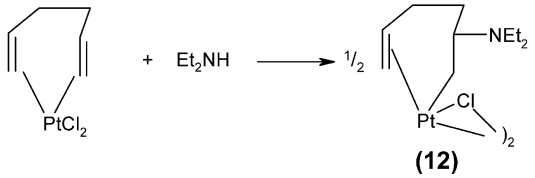
Nucleophilic attack at coordinated carbon and metathesis reactions may proceed simultaneously yielding mono- (**10**) or binuclear (**11**) complexes depending on the nature of nucleophile. For instance, carboxylate ions react with $[PtCl_2(diene)]$ to yield **11** by attack at platinum(II) as well as at alkene carbon [113,131]. Similarly PhS^-, NCS^- undergo both substitution and nucleophilic attack [146]. Reaction of $PdCl_2COD$ with Tl(β-dik) yield **10** [127]. The product of nucleophilic attack by amines on coordinated dienes depends on the rigidity of the diolefin [114–117]. Complexes with flexible olefins in the presence of an excess amine lose HCl to yield chloro-bridged dimmer (12) (**12**). Complexes with rigid olefins lose HCl to form mononuclear derivatives **13** (13). Reactions of MCl_2COD with pyrazoles in the presence of NaOH in methanol afford pyrazolato-bridged complexes $[M_2(\mu\text{-pz})_2(C_8H_{12}X)_2]$ (X = OMe or pz) [147].



(10)

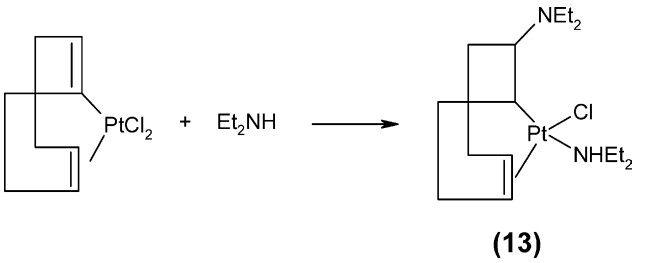


(11)



(12)

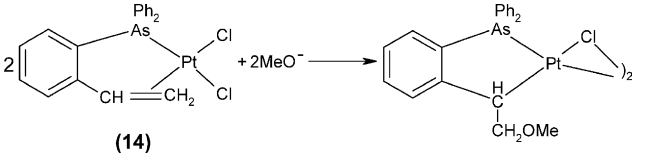
(12)



(13)

(13)

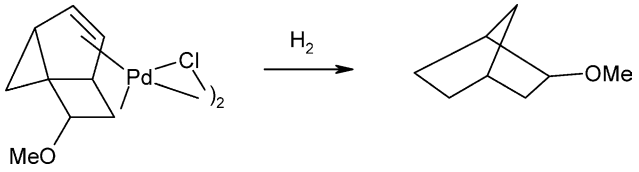
Besides chelating dienes, other internally functionalized chelating ligands are susceptible to nucleophilic attack. Examples of such ligands include diallyl ether, CH_2=C(Me)CH_2NMe_2, RC≡C-CR'_2NMe_2, tertiary phosphines and arsines (14) [148–154]. In **14** nucleophilic attack takes place exclusively at β-carbon atom to form a five membered ring (14) [153].



(14)

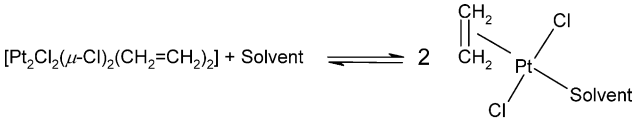
(14)

Binuclear halo-bridged complexes, $[M_2(\mu\text{-}X)_2($ $)_2]$ undergo metathesis reactions as well as bridge cleavage by neutral ligands, e.g. amines, ER_3 (E = P, As, Sb) [72–74,112,120,122,127,136,155]. Cationic complexes, $[MX($ $)L_2]^+$, are formed with bidentate ligands like bipy [146,156–158]. However, a similar reaction with dppp yields $[Pd(dppp)(\eta^3\text{-}C_8H_{12}OMe)]^+$ [158]. The reaction with HCl is much more facile with palladium than platinum yielding the parent diene complex [112,119,145]. Treatment of $[Pt_2(\mu\text{-}X)_2(C_8H_{12}OMe)_2]$ (X = Cl or OMe) with tetrahydroborate in the presence of bulky phosphines affords *trans*-$[PtH_2(PR_3)_2]$ whereas the acetato-bridged (X = OAc) complex yields $[PtH(OAc)(PR_3)_2]$ under similar conditions [106,110,155]. However, the palladium complex on treatment with borohydride [133] or hydrogen [111,114] leads to cleavage of the Pd–C bond (15). Reaction of $[M_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ with TlCp or $acac^-$ yields $[MCp(C_8H_{12}OMe)]$ (M = Pd or Pt) [159] or $[M(acac)(C_8H_{12}OMe)]$ [160,161], respectively. The palladium complex $[Pd_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ on treatment with KO_2 in dichloromethane affords dioxygen bridged compound $[Pd_2(\mu\text{-}O_2)(C_8H_{12}OMe)_2]$ [162]. The chloro-bridge in these complexes is readily cleaved by neutral donor ligands [163].



(15)

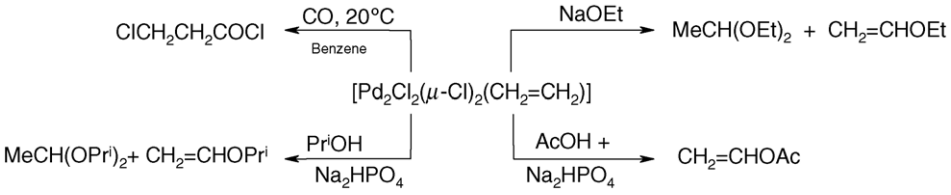
Although the complex $[Pt_2Me_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ undergoes ethylene displacement with other alkenes or alkynes, $CF_3C{\equiv}CCF_3$ yields a Pt–C insertion product. Reaction with monodentate neutral ligands results in bridge cleavage to afford $[PtMeCl(L)(CH_2{=}CH_2)]$ (L = py, $SeMe_2$, $CH_2{=}CH_2$) [27]. Bridge cleavage with neutral bidentate nitrogen ligands yields five coordinate mononuclear complexes, $[PtMeCl(L\text{–}L)(CH_2{=}CH_2)]$ [164]. The mono-olefin complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ readily dissociates in solution where solvent acts as a base (16) [71,165–167]. Reaction in acetone with ethylene at −80 °C yields a yellow crystalline *trans*-$[PtCl_2(CH_2{=}CH_2)_2]$ which isomerizes to a colourless *cis* isomer at room temperature [165]. These mononuclear complexes are thought to be intermediate in the exchange reaction between bonded C_2H_4 and C_2D_4 [166].



(16)

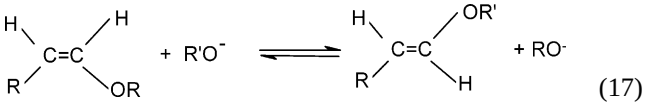
Thermal decomposition of $[M_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ (M = Pd or Pt) has been studied [166,168]. Platinum complex is thermally more stable. These binuclear complexes undergo a variety of reactions [53,169–176], a few of them are depicted in Scheme 1.

Several olefin complexes of palladium and platinum are effective homogeneous catalysts [177–181]. The Zeise's dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ (**6**) not only acts as a hydrosilylation catalyst but is also used for isomerization of terminal olefins, the *cis* olefins are formed predominantly. It also catalyses alkoxide exchange of vinyl ethers which is accompanied by *cis* ⇆ *trans* isomerization (17) [180]. Olefins can be arylated catalytically by aromatic hydrocar-

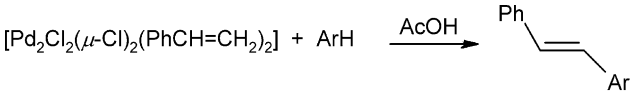


Scheme 1.

bons in the presence of a palladium complex (18) [178,179].



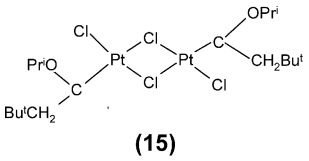
(17)



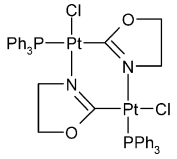
(18)

2.3. Isocyanide, carbene and ylide complexes

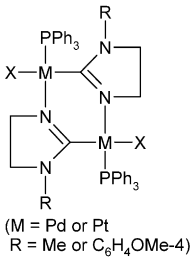
Reaction of $H_2PtCl_6{\cdot}6H_2O$ with $Bu^tC{\equiv}CH$ in isopropanol yields a neutral binuclear carbene complex, $[Pt_2Cl_2(\mu\text{-}Cl)_2\{C(OPr^i)CH_2Bu^t\}_2]$ (**15**) [182,183]. The latter is a centrosymmetric dimer with a planar "Pt_2Cl_2" fragment in which Pt···Pt separation is 3.537(3) Å [183,184]. The carbene ligand lies perpendicular to the coordination plane of platinum at an angle of 113°. Reaction of CODPdMeCl with Ag(carbene) (carbene = 3-methyl-1-(methylacetyl)imidazolin-2-ylidene) yields $[Pd_2Me_2(\mu\text{-}Cl)_2(\text{carbene})_2]$ and in solution equiliberates with a monomeric species containing chelated carbene [185]. Besides **15**, a few other binuclear carbene complexes (**16**–**18**) have been reported [186–188].



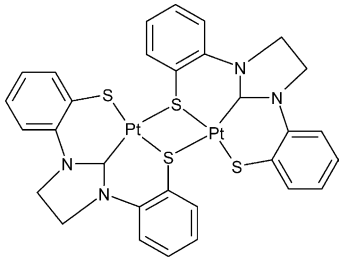
(15)



(16)



(17)



(18)

A few binuclear complexes containing sulfur [189] or phosphorus [190–193] ylides have been synthesized. Proton abstraction from phosphonium salts affords ylide complexes. Thus, complexes, $[Pd_2Cl_2(\mu\text{-}Cl)_2(\text{ylide})_2]$ (ylide = $Bu_3PCHOPh$), characterized by X-ray crystallography, are formed by HX abstraction from phosphonium salts like, $[(Bu_3PCH_2COPh)_2Pd_2Cl_6]$ with bases [190]. Treatment of $Pd(OAc)_2$ with bis(phosphonium) salts, $(Ph_3PCH_2COCH_2PPh_3)Cl_2$ results in the formation of mononuclear palladium complex containing chelating bis ylide, $[PdCl_2\{C(H_2)PPh_3\}_2CO]$ which on chloride abstraction with $TlClO_4$ yields binuclear complex $[Pd_2(\mu\text{-}$

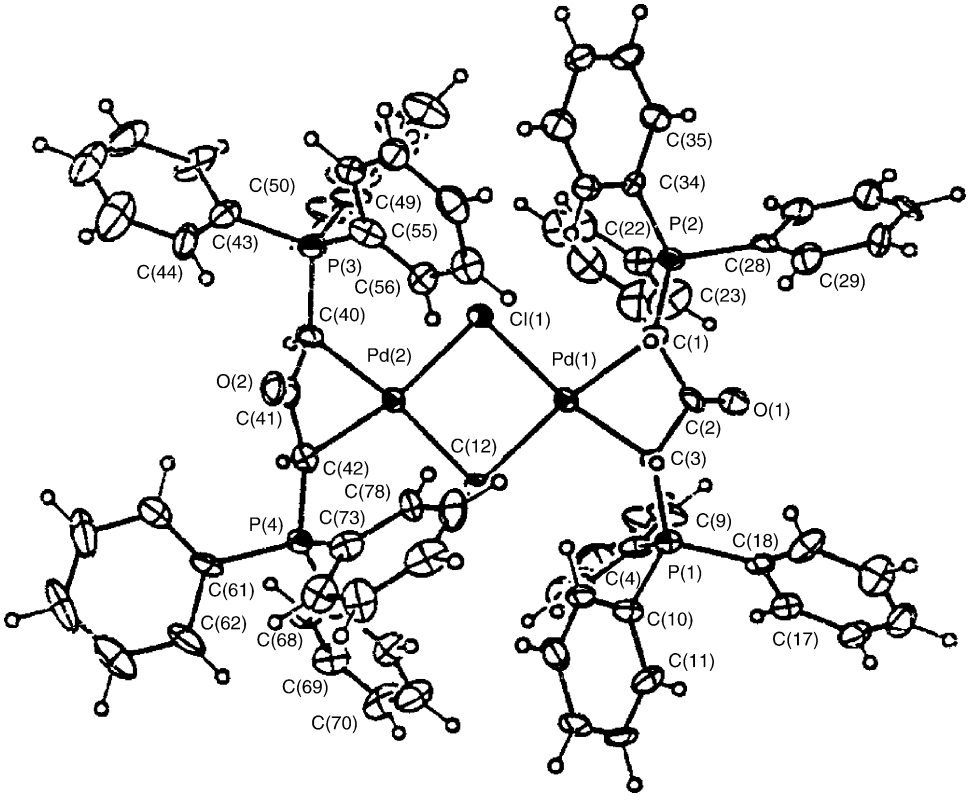
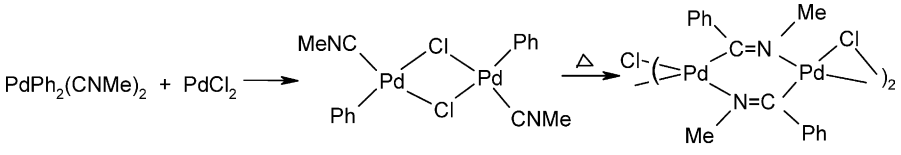


Fig. 2. Molecular structure of $[Pd_2(\mu\text{-}Cl)_2\{CH(PPh_3)CO\}_2]^{2+}$ (reproduced with permission from ref. [191]).



(20)

Cl)$_2${CHPPh$_3$)$_2$CO}$_2$] [191]. The X-ray structure of the latter revealed that bis-ylide ligand is C,C-chelating and the four-membered Pd_2Cl_2 ring is non-planar with dihedral angle between the palladium coordination planes is 145.38(27)° (Fig. 2) [191].

Halo-bridged isocyanide complexes are usually prepared by boiling a benzene solution of [$PdCl_2$(MeCN)$_2$] with [$PdCl_2$(CNR)$_2$] (R = Ph or *p*-tol) [194]. They can also be prepared by oxidative addition of isocyanide chloride on palladium metal (19) [195]. The arylpalladium complexes **19** have been isolated by the reaction of $PdCl_2$ with *cis*/*trans*-[$PdAr_2$(CNMe$_2$)$_2$]. The thermolysis of **19** yields a bridged polymer **20** which is formed by insertion of isocyanide across the Pd–C bond (20) [196,197]. Although PdIR′(PR$_3$)$_2$ reacts with isocyanides in 1:1 molar ratio, when PR_3 = $PMePh_2$ and CNR″ (R″ = Bu^t, c-Hx) affords dimeric complex [Pd_2(μ-I)$_2${CMe(NR″)}(PMePh$_2$)$_2$] (**21**) [198].

$$Pd + RNCCl_2 \xrightarrow{100\,^{\circ}C,\ 2\,days} \tfrac{1}{2}[Pd_2Cl_2(\mu\text{-}Cl)_2(CNR)_2] \qquad (19)$$

3. Binuclear complexes containing Group 15 donor ligands

3.1. Complexes containing Group 15 as bridging ligands

3.1.1. Amido-, phosphido- and arsenido-bridged complexes

There are only a few reports dealing with amido-bridged neutral complexes. They are often prepared by deprotonation of coordinated NH group with a suitable base. Thus, the reaction of cationic amine complexes, *trans*-[PtX(NH$_3$)L$_2$][ClO_4] with a base yields binuclear amido-bridged complexes [Pt_2X_2(μ-NH$_2$)$_2$L$_2$] (X = H or Me) (**21**) which are formed via a monomeric neutral intermediate, *trans*-[PtX(NH$_2$)L$_2$] (21) [199,200]. Similarly deprotonation of chelated secondary amine in [(tol$_2$PCH$_2$CHPr^i-NHC$_6$H$_4$OMe-4}PtCl$_2$] and in **22** (22) with sodium alkoxide afford chiral non-planar diastereomeric amido complexes, [{tol$_2$PCH$_2$CHPr^i-NC$_6$H$_4$OMe-4}PtCl]$_2$ [201] and **23** [202], respectively. In the latter Pt···Pt distance is unusually short 2.875(1) Å and the amido-R

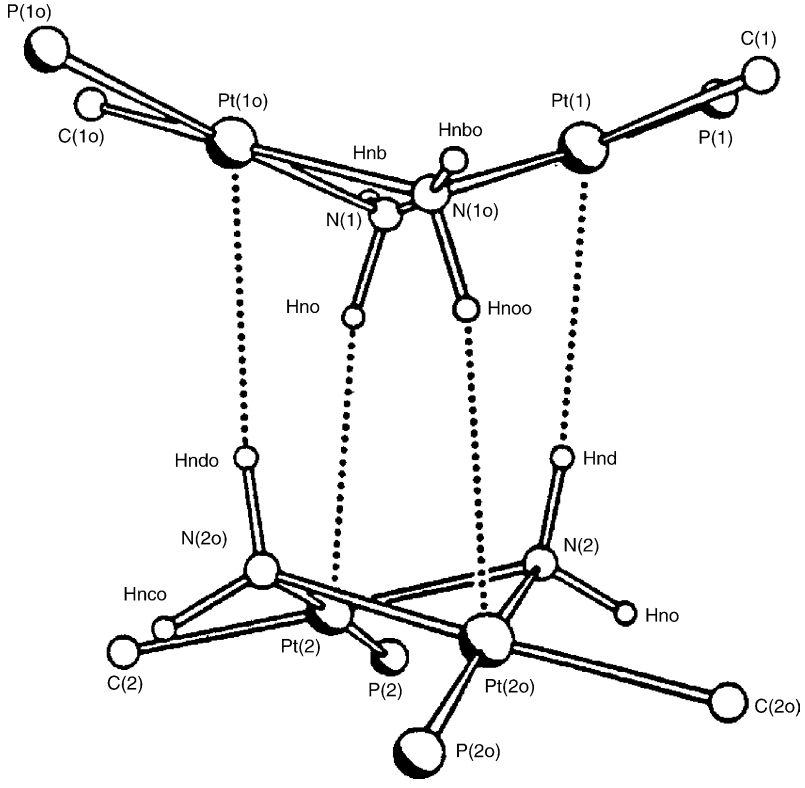
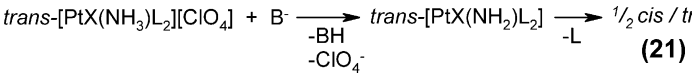


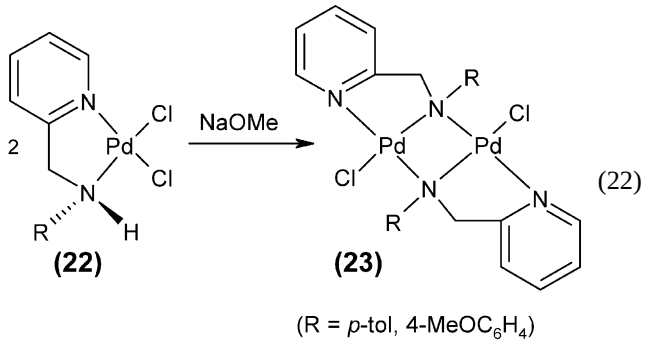
Fig. 3. Molecular structure of Pt_2Me_2(μ-NH$_2$)$_2$(PPh$_3$)$_2$ (reproduced with permission from ref. [200]).

groups are *syn–exo* [202]. Another amido-bridged complex, $[Pt_2(\mu\text{-}NH_2)_2(Ph_2PO)_2(PMePh_2)_2]$ containing a rare diphenylphosphine oxide anion, is isolated in 80% yield in an unexpected manner when $PtCl_2(dppm)$ is treated with an excess of NaOH in liquid ammonia [203,204]. This complex appears to be formed via a hydroxo-bridged intermediate, $[Pt_2(\mu\text{-}OH)_2(dppm)_2]^{2+}$. Treatment of $[Pd_2(C_6F_5)_2(\mu\text{-}Cl)_2(CNBu^t)_2]$ with arylamines in the presence of 20% Bu_4NOH in methanol affords $[Pd_2(C_6F_5)_2(\mu\text{-}NHAr)_2(CNBu^t)_2]$ (Ar = Ph, C_6H_4-X; X = Me, OMe, Cl, Br). The latter has been isolated as *syn* and *anti* isomers [205]. The syntheses and structures of (**24**) [206] and an imido-bridged complex $[Pd_2(\mu\text{-}N{=}CHC_6H_4PPh_2)_2Cl_2]$ [207] have been reported.

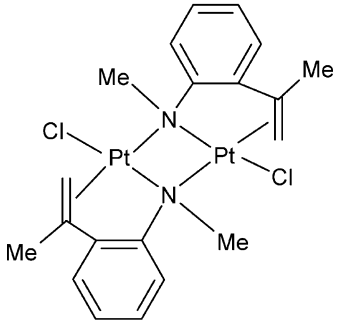


(21)

($B^- = NH_2$ or 4-Me(2, 6-Bu^t)$_2C_6H_2O^-$; X = H or Me; L = PEt_3, $PMePh_2$, PPh_3, or c-Hx_3P)



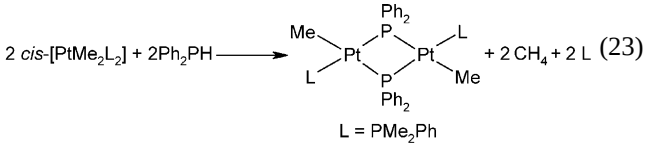
(22)



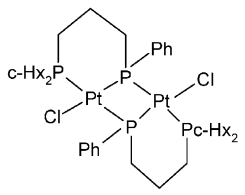
(24)

The amido-bridged complexes usually exist as a mixture of *cis* and *trans* isomers [199,200,203,204]. The bridge can be cleaved by addition of phosphine ligands [200]. The X-ray structural analyses of $[Pt_2Me_2(\mu\text{-}NH_2)_2(PPh_3)_2]$ [199,200] and $[Pt_2(\mu\text{-}NH_2)_2(Ph_2PO)_2(PMePh_2)_2]$ [203,204] revealed that the two platinum square planes have a dihedral angle of 45 and 44° with Pt···Pt separation of ~3.1 and 3.087(1) Å, respectively. The bridging NH_2 hydrogen in the former shows intermolecular agostic interaction with platinum atom of an adjacent molecule (Fig. 3) [200].

Both primary and secondary phosphines have been employed to prepare phosphido-bridged derivatives. Reactions of primary phosphines are quite facile while a base is usually required for secondary phosphines. Accordingly, the reactions of halide-bridged dimers, $[M_2X_2(\mu\text{-}X)_2(PR_3)_2]$ with secondary phosphines (PMe_2H, PEt_2H, PPh_2H, $PcHx_2H$) in the presence of a base (*p*-toludine [208–211] or NaOEt [212]) or with Me_3SiPPh_2 [213] readily afford $[M_2X_2(\mu\text{-}PR'_2)_2(PR_3)_2]$ [208–213]. Treatment of PdX_2 [209,210,214,215] or $PtCl_2(PhCN)_2$ [215,216] with secondary phosphines in benzene or methanol affords dimeric phosphido-bridged complexes, $[M_2X_2(\mu\text{-}PPh_2)_2(PHPh_2)_2]$. The latter (M = Pd; X = I) is formed when $[Pd_2I_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-}PPh_2)]$ is treated with PPh_2H [217]. The reaction of $[PtHCl(PEt_3)_2]$ with PPh_2H in the presence of NaOEt or with Me_3SiPPh_2 yields a hydrido complex $[Pt_2H_2(\mu\text{-}PPh_2)_2(PEt_3)_2]$ [212,218]. Similar hydrido complexes $[M_2H_2(\mu\text{-}PBu_2^t)_2(PBu_2^tH)_2]$ are formed when $[Cp(\eta^3\text{-allyl})M]$ (M = Pd or Pt) is treated with di-*tert*-butylphosphine [219]. The platinum complex is stable whereas the palladium analogue readily loses a molecule of hydrogen to give a palladium(I) dimer $[Pd_2(\mu\text{-}PBu_2^t)_2(PBu_2^tH)_2]$ [219]. The platinum complex $[Pt_2H_2(\mu\text{-}PBu_2^t)_2(PBu_2^tH)_2]$ reacts with tetracyanoethylene in tolune to give a charge transfer complex [220]. The mononuclear complexes $[MX_2(R_2PC_6H_4PRH)]$ loose readily HX to give phosphido-bridged derivatives $[MX(R_2PC_6H_4PR)]_2$ [221] (M = Pd or Pt; X = Cl, Br, I) which are bent at phosphido-bridges with M···M separation of ~3.4 Å. Treatment of $[PtCl_2\{PhHPCH_2CH_2CH_2PcHx_2\}_2]$ with Et_3N yields **25** which is isolated into both meso and dl forms as characterized by X-ray crystallography [222,223]. Cleavage of Pt···Me bond with secondary phosphines and arsines has been reported to give phosphido/arsinido-bridged derivatives [224,225]. The mechanism involves initial coordination of diphenylphosphine followed by intramolecular loss of methane (23) [224].

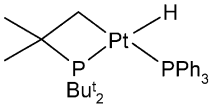


(23)

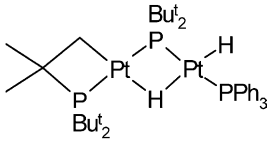


(25)

Platinum induced cleavage of the phosphorus–carbon bond of PBu_3^t under mild conditions has been reported for **26** which on decomposition yields a mixed phosphido- and hydrido-bridged derivative **27** [226]. Reaction of $Pt(C_6F_5)_2(PPh_2H)_2$, $Pt(norborene)_3$ and PPh_3 in 1:1:2 stoichiometry gave a mixture of products from which a platinum(I) $[Pt_2(\mu\text{-}PPh_2)(PPh_3)_3(C_6F_5)]$ and a platinum(II) complex $[Pt_2(\mu\text{-}PPh_2)_2(H)(C_6F_5)(PPh_3)_2]$ ($Pt\cdots Pt = 3.498(1)$ Å) have been isolated [227]. The phosphorus–carbon bond cleavage takes place when a CH_2Cl_2 solution of $[Pt(dppet)_2]$ is left in sunlight with the formation of an insoluble phosphido bridged complex $[Pt_2(\mu\text{-}PPh_2)_2(dppet)_2]$ [228].



(26)



(27)

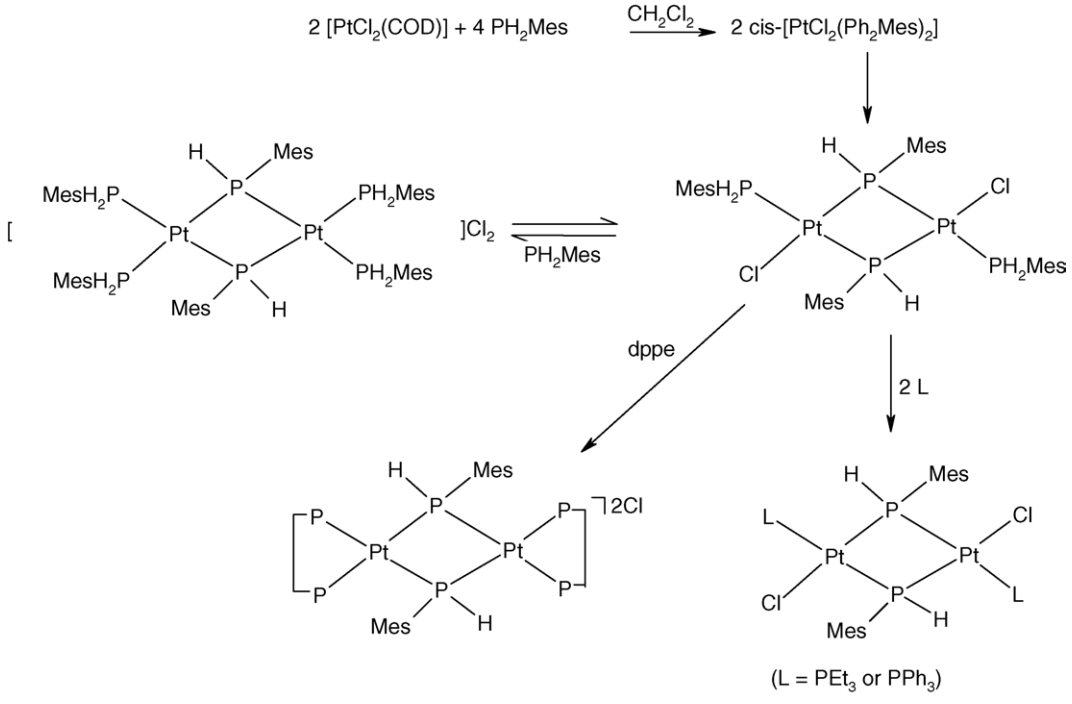
Primary phosphines, such as PH_2Mes [229] or PH_2cHx [214,230], react with MX_4^{2-} or $PtCl_2COD$ to give dimeric complexes $[M_2X_2(\mu\text{-}PHR)_2(PH_2R)_2]$ (X = Cl or Br; R = Mes or c-Hx) (Scheme 2). The latter (M = Pt) reacts reversibly with PH_2Mes affording an ionic complex $[Pt_2(\mu\text{-}PHMes)_2(PH_2Mes)_4][Cl]_2$ [229].

Unlike amido-bridged derivatives, phosphido-bridged complexes are prone to bridge cleavage. Substitution of terminal ligands can also take place. The terminal chloride in $[Pt_2Cl_2(\mu\text{-}PPh_2)(PPr_3^n)_2]$ can be substituted by phenyl groups [212]. The terminal primary or secondary phosphines can be substituted by tertiary phosphines (Scheme 2) [209,229].

The $^{31}P\{^1H\}$ NMR spectra of several $[M_2Cl_2(\mu\text{-}PR_2)_2L_2]$ have been recorded and analysed by computer simulation [216]. The resonances for bridging phosphido groups occur at very high field (δ −267 to −322 ppm) upfield of $P(OMe)_3$ [216]. The X-ray structures of $[Pt_2Cl_2(\mu\text{-}PPh_2)_2(PHPh_2)_2]$ [231], $[Pt_2Cl_2(\mu\text{-}PHMes)_2L_2]$ (L = PEt_3, PPh_3) (Fig. 4) [229] and $[Pt_2(\mu\text{-}PR_2)_2(dppe)_2]Cl_2$ (PR_2 = PPh_2, PHMes) [229,231] have been reported. The four-membered Pt_2P_2 rings are planar with very large platinum–platinum separations (3.585–3.70 Å).

3.1.2. *Pyrazolato-bridged complexes*

Reactions of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ or $[M_2R_2(\mu\text{-}Cl)_2L_2]$ (M = Pd or Pt) [231–236] with pyrazoles in the presence of NaOH in 1:2 stoichiometry in methanol readily yield bis pyrazolato-bridged complexes (24) and (25). The organopalladium complexes, $[Pd_2R_2(\mu\text{-}dmpz)_2(PEt_3)_2]$ (R = Me or Br) can also be prepared by the reaction of $[Pd_2R_2(\mu\text{-}OH)_2(PEt_3)_2]$ with 3,5-dimethyl pyrazole [237]. When reaction (24) is extended to platinum compounds for the preparation of bis-pyrazolato-bridged complexes, only terminal chlorides are replaced (Scheme 3) [238]. However, reaction with one equivalent of pyrazoles yields chloro(methoxo)-pyrazolato-bridged complexes depending on the stochiometry of the base [238,239]. The bis-pyrazolato-bridged platinum complexes are readily obtained by refluxing a dichloromethane



Scheme 2.

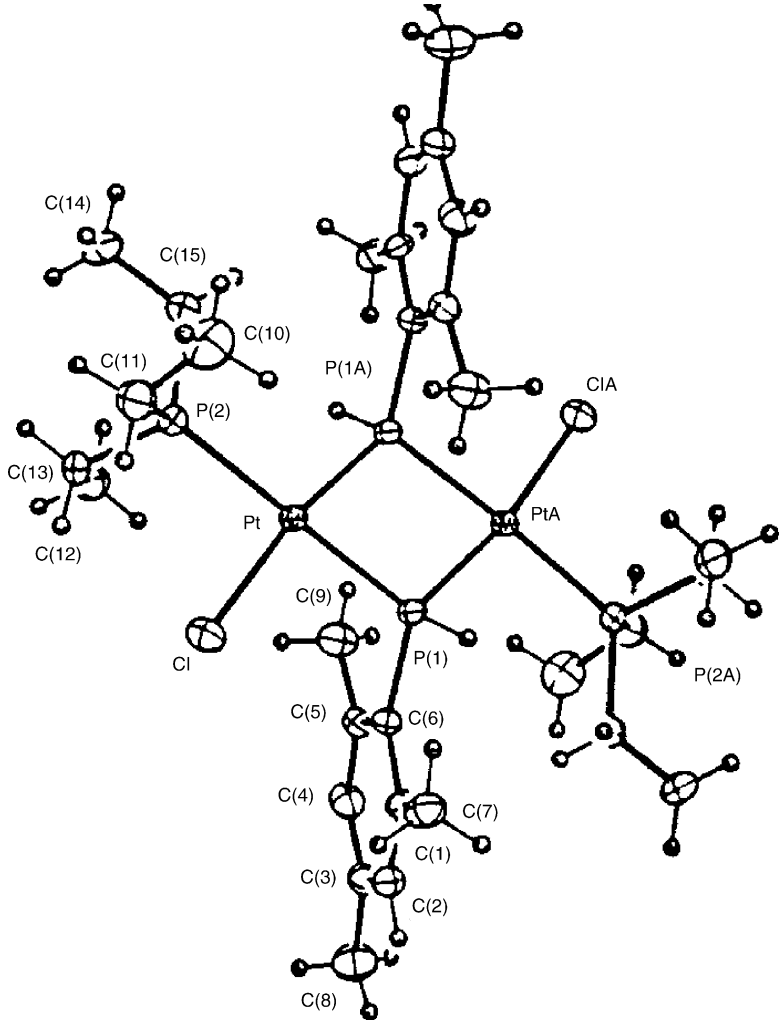
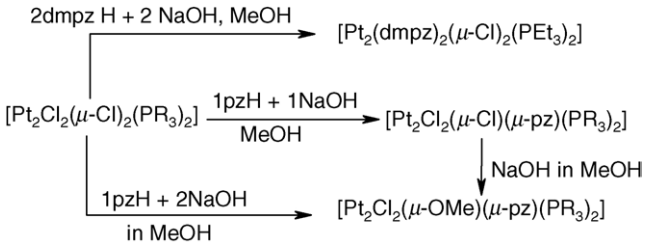


Fig. 4. Molecular structure of $[Pt_2Cl_2(\mu\text{-}PHMes)_2(PEt_3)_2]$ (reproduced with permission from ref. [229]).

solution of $[Pt_2Cl_2(\mu\text{-}OAc)_2(PR_3)_2]$ with pyrazoles (26) [240].

$$[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + 2NNH \xrightarrow{2NaOH} [Pd_2Cl_2(\mu\text{-}NN)_2(PR_3)_2] \quad (24)$$

$$[M_2R_2(\mu\text{-}Cl)_2(PR_3)_2] + 2NNH \xrightarrow{2NaOH} [M_2R_2(\mu\text{-}NN)_2(PR_3)_2] \quad (25)$$



Scheme 3.

$$[Pt_2Cl_2(\mu\text{-}OAc)_2(PR_3)_2] + 2NNH \xrightarrow{-2AcOH} [Pt_2Cl_2(\mu\text{-}NN)_2(PR_3)_2] \quad (26)$$

(M = Pd or Pt; NNH = pzH, dmpzH, tmpzH; R = Me, Ph or tol; PR_3 = tertiary phosphine)

The formation of bis pyrazolato-bridged palladium complexes is so facile that even when the reaction (24) is carried out with one equivalent of pyrazole, only bis derivatives are formed leaving behind 50% unreacted tetrachloro precursors [232]. The reaction (25) for platinum complexes, in contrast, with one equivalent of pyrazole in the presence of a base affords chloro-pyrazolato-bridged derivatives $[Pt_2R_2(\mu\text{-}Cl)(\mu\text{-}pz)(PR_3)_2]$. The latter complexes are invariably isolated as a *cis* isomer with the phosphine ligands *trans* to bridging pyrazolate group as shown by X-ray structural analysis of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$ (Fig. 5) [241]. The bis pyrazolato bridged complexes, $[Pt_2R_2(\mu\text{-}NN)_2(PR_3)_2]$, on the other hand, exist as a mixture of *cis* and *trans* isomers and their relative ratio varies from one

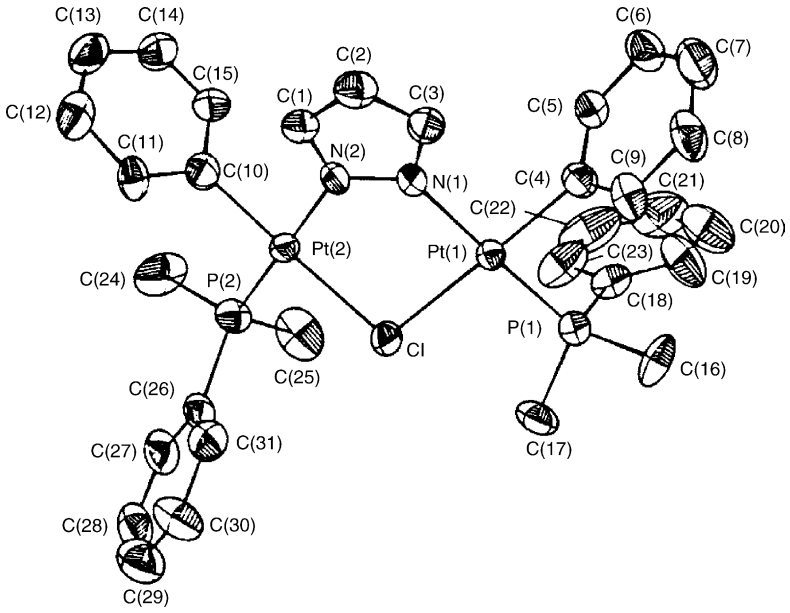


Fig. 5. Molecular structure of $[Pt_2Ph_2((\mu\text{-}Cl)((\mu\text{-}pz)(PMe_2Ph)_2)]$ (reproduced with permission from ref. [241]).

preparation to another [234]. Initially a mononuclear complex $[PtRCl(NNH)(PR_3)]$ forms which during proton abstraction isomerizes rapidly with simultaneous formation of the dimer [234]. The organopalladium complexes, $[Pd_2R_2(\mu\text{-}NN)_2(PR_3)_2]$ and $[M_2Cl_2(\mu\text{-}NN)_2(PR_3)_2]$ adopt a *trans* configuration both in solution (by NMR) and in the solid state (X-ray analyses) (Figs. 6 and 7) [232,240].

Another series of mixed bridged complexes, $[M_2Cl_2(\mu\text{-}ER')(\mu\text{-}NN)(PR_3)_2]$ have been isolated by the reactions (27) and (28) [239,242–245].

$$[M_2Cl_2(\mu\text{-}ER')(\mu\text{-}Cl)(PR_3)_2] + NNH + NaOH \xrightarrow{MeOH} [M_2Cl_2(\mu\text{-}ER')(\mu\text{-}NN)(PR_3)_2] \quad (27)$$

$$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}NN)(PR_3)_2] + L^- \rightarrow [Pt_2Cl_2(\mu\text{-}L)(\mu\text{-}NN)(PR_3)_2] \quad (28)$$

(M = Pd or Pt; R′E = OMe, R′S, R′Se, R′Te;
NN = pz, dmpz; L = Spy, $(R''O)_2PS_2$)

Although these complexes adopt a *cis* configuration, the relative disposition of phosphine ligands differs in palladium and platinum complexes. The phosphine ligands are *trans* to bridging pyrazolate group in palladium complexes as established by X-ray structure of $[Pd_2Cl_2(\mu\text{-}SePh)(\mu\text{-}pz)(PBu_3)_2]$ [244], whereas in the corresponding platinum

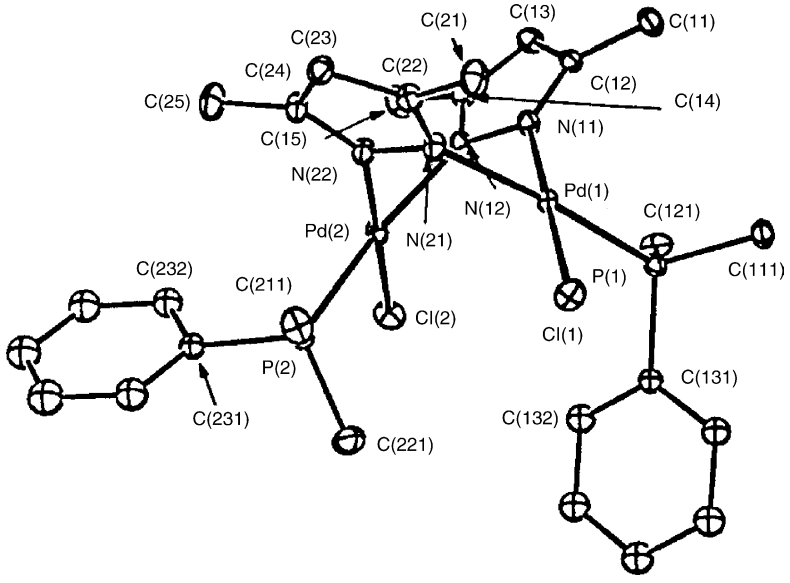


Fig. 6. Molecular structure of $[Pd_2Cl_2(\mu\text{-}dmpz)_2(PMe_2Ph)_2]$ (reproduced with permission from ref. [232]).

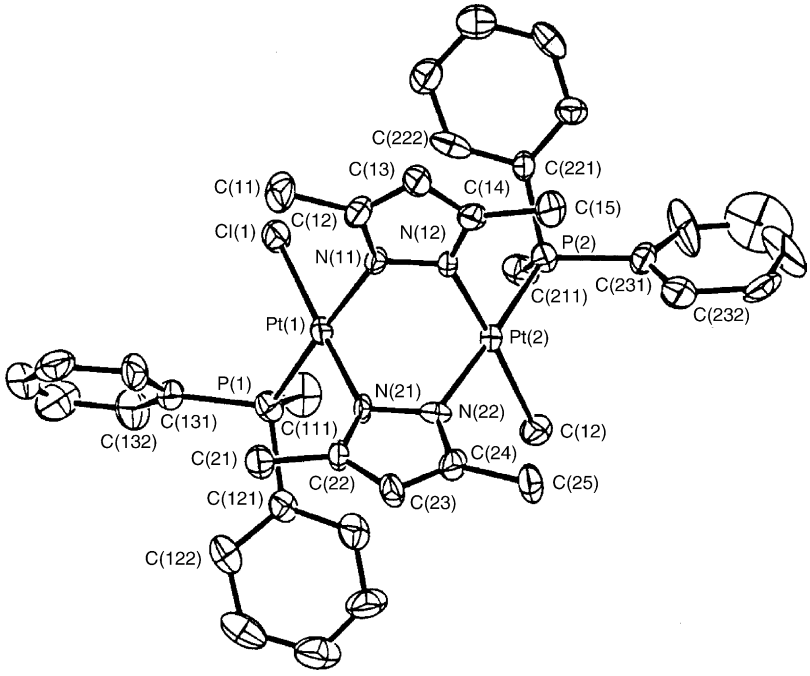
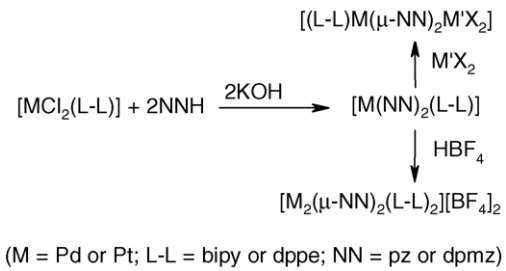


Fig. 7. Molecular structure of $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$ (reproduced with permission from ref. [240]).

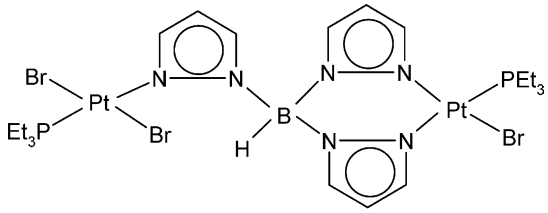
derivatives they are *trans* to bridging ER′ group [239]. The magnitude of ^1J(Pt–P) increases in the following order of ER′: TeR′ < SeR′ ≈ SR′ < OMe [239].

Banditelli and co-workers [246–250] prepared a variety of mononuclear palladium and platinum complexes, $[M(L–L)(NN)_2]$ and used them as a metallo-ligand. Thus, on treatment with metal ions, several homo- and hetero-binuclear complexes are formed. Protonation of the monomer with HBF_4 yields homo-binuclear cationic complexes (Scheme 4).

Treatment of $[Pd(OAc)_2]_3$ with pyrazoles yields *trans*-$[Pd_2(\mu\text{-NN})_2(OAc)_2(NNH)_2]$ (NN = dmpz, 3,5-Ph_2pz) in which the acetate group can be exchanged with other carboxylates [251]. The reaction of $PdCl_2(Hdmpz)_2$ with methanolic KOH in aceton leads to formation of $[Pd_2Cl_2(\mu\text{-dmpz})_2(Hdmpz)_2]$ and $[Pd_2(dmpz)_2(\mu\text{-dmpz})_2(Hdmpz)_2]$ depending on the stoichiometry of the reactants [252]. Reaction of $[Pt_2Br_2(\mu\text{-Br})_2(PEt_3)_2]$ with tris pyrazolyl borate affords **28** as characterized X-ray crystallography [253].



Scheme 4.



(28)

3.2. Complexes containing Group 16 as bridging ligand

3.2.1. Hydroxo-bridged complexes

Several neutral hydroxo-bridged palladium and platinum complexes, $[M_2X_2(\mu\text{-OH})_2L_2]$ have been prepared and characterized [237,254–262]. They are readily prepared by the reaction of $[M_2X_2(\mu\text{-Cl})_2L_2]$ with aqueous Bu_4NOH or KOH [237,254,258] (29). While studying carbonylation of aromatic halides by Pd(II) complexes Grushin and Alper [257] isolated hydroxo-bridged palladium complexes. Thus, refluxing a benzene solution of $PdCl_2L_2$ (L = PPh_3, Pc-Hx_3, PPr_3^i) with aqueous KOH in the presence of aryliodide (ArI, Ar = Ph or *p*-tol) results in the formation of hydroxo bridged complexes (30) [257,260].

$$M_2R_2'(\mu\text{-X})_2(PR_3)_2 \xrightarrow{KOH/Bu_4NOH} [M_2R_2'(\mu\text{-OH})_2(PR_3)_2] \quad (29)$$

$$2PdCl_2L_2 + 2ArI + 6KOH \xrightarrow{C_6H_6/H_2O} [Pd_2Ar_2(\mu\text{-OH})_2L_2] + 2LO + 2KI + 4KCl + 2H_2O \quad (30)$$

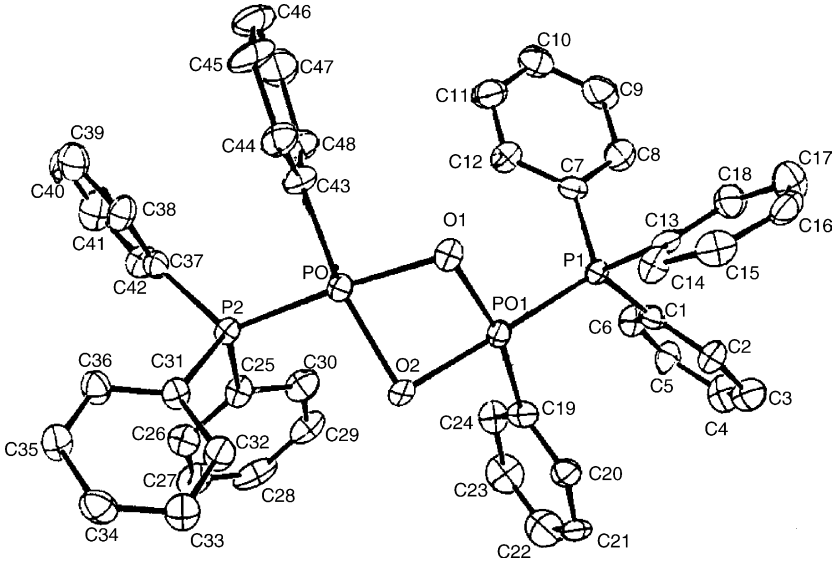


Fig. 8. Molecular structure of $[Pd_2Ph_2(\mu\text{-}OH)_2(PPh_3)_2]$ (reproduced with permission from ref. [257]).

(M = Pd or Pt; R′ = Me, Bz, Ph or tol;

Ar = Ph or tol; $PR_3 = PEt_3$, PPh_3 or PEt_2Ph;

L = PPh_3, Pc-Hx_3, PPr^i)

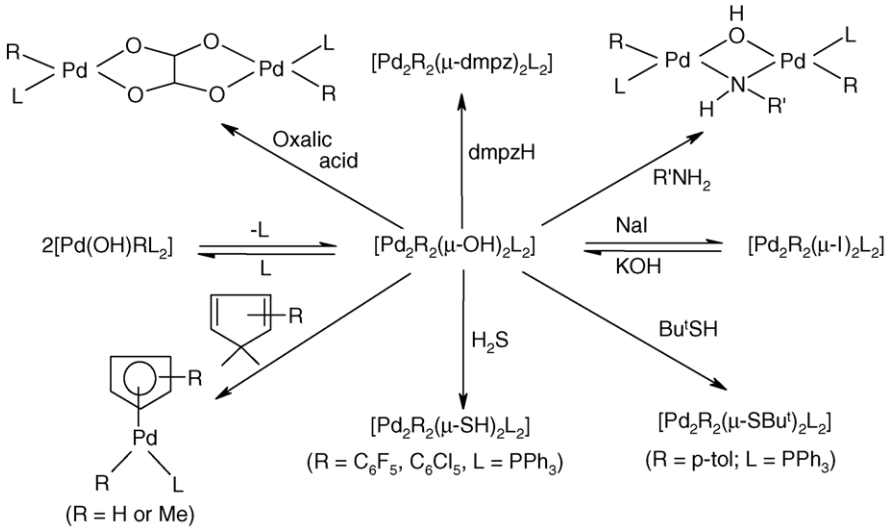
The hydroxo-bridged complexes usually exist as a mixture of *cis* and *trans* isomers, the latter being predominating [237,257]. However, for perhalo-complexes $[Pd_2Ar_2(\mu\text{-}OH)_2(PPh_3)_2]$ (Ar = C_6F_5 or C_6Cl_5), only *trans* isomer is present in solution [255,256]. The hydroxo protons in the ^{1}H NMR spectra are considerably shielded and appear in the region δ −0.3 to −3.4 ppm [237,257,260]. The structure of $[Pd_2Ph_2(\mu\text{-}OH)_2(PPh_3)_2]$, established by X-ray diffraction, reveals a *trans* configuration with non-planar four-membered "Pd_2O_2" metallocyclic ring (Fig. 8). The Pd · · · Pd separation is 2.983(15) Å (Table 2) [257].

Hydroxo-bridged complexes undergo a variety of reactions (Scheme 5) [205,237,257,258,260,262–265]. They can be interconverted to $[Pd_2Ar_2(\mu\text{-}I)_2(L_2)]$ and the hydroxo-bridged complexes by treatment of the latter with NaI in CH_2Cl_2–acetone–water and the former with aqueous KOH [257]. The protonation of $[Pd_2(\mu\text{-}OH)_2(C_6F_5)_2L_2]$ by triflic acid results in th formation of diaqua complexes, $[Pd(C_6F_5)L(H_2O)_2][CF_3SO_3]$ (L = PPh_3, $AsPh_3$) [265]. The hydroxo-bridge is reversibly cleaved with tertiary phosphines to yield mononuclear complexes [Pd(OH)ArL_2], some of which have been isolated in the solid state [237,260]. The bridging hydroxo group is susceptible to various protic electrophiles such as cyclopentadiene, amines, phenols, H_2S, etc. Thus, the reaction of $[Pd_2Ph_2(\mu\text{-}OH)_2L_2]$ (L = PPh_3 or P-cHx_3) with cyclopentadiene or methylcyclopentadiene affords mononuclear complexes $[PdPh(C_5H_4R)(L)]$ (R = H or Me) at room temperature [258]. However, similar reaction with platinum complexes require elevated temperatures (60 °C) [258].

The reaction of $[Pd_2R_2(\mu\text{-}OH)_2L_2]$ with primary amines, aniline or *p*-substituted anilines in 1:1 molar ratio affords μ-hydroxo/μ-amido-bridged palladium complexes $[Pd_2R_2(\mu\text{-}OH)(\mu\text{-}NHR)L_2]$ in 67–80% yield [205,237,262,263]. Initially a mononuclear complex $[PdR(OH)(NH_2R)(L)]$ forms by bridge cleavage of hydroxo-bridge by amines. This mononuclear hydroxo complex after reversible proton transfer gives the amido ligand and coordinated water, [PdAr(NHR)(H_2O)L]. The latter, on recombination with the original hydroxo monomer, affords amido-hydroxo-bridged dimer with concomitant displacement of water and amine [262]. The hydroxo-amido-bridged complexes adopt a *trans* geometry. The two coordination planes are bent as shown by X-ray structural analysis [205,237,262,263].

Table 2
Structure of hydroxo-bridged neutral complexes determined by X-ray diffraction

Complex	Comments	References
$[Pd_2Ph_2(\mu\text{-}OH)_2(PPh_3)_2]$	Bent structure, Pd · · · Pd = 2.983(15) Å	[257]
$[Pd_2Ph_2(\mu\text{-}OH)\ (\mu\text{-}NHBu^t)\ (PPh_3)_2]$	Bent, dihedral angle 56.91°, Pd · · · Pd = 2.905(1) Å	[262,263]
$[Pd_2Ph_2(\mu\text{-}OH)\ (\mu\text{-}NHC_6H_4OMe\text{-}p)\ (PPh_3)_2]$	Bent, dihedral angle 52.5°	[237]
$[Pd_2(C_6F_5)_2(\mu\text{-}OH)\ (\mu\text{-}NHR)\ (PPh_3)_2]$	Bent structure	[205]
$[Pt_2(\mu\text{-}OH)_2\{Ph_2P\text{-}N\text{-}P(O)Ph_2\}(PMe_2Ph)_2]$	Pt · · · Pt = 3.21 Å, Pt–O = 2.096(7) Å	[259]



Scheme 5.

3.2.2. *Complexes with RE^- bridges*

Several methods have been employed to prepare binuclear palladium(II) and platinum(II) complexes containing bridging thiolato- [212,213,266–289], selenolato- [290–299] and tellurolato- [242,292,300–303] ligands (31)–(39), reactions (31)–(34) being the most common routes. Although reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_3)_2]$ with various mercaptans ((31), $PR_3 = PMe_3$) yields binuclear complexes, with cyclohexylmercaptan both bi-, $[Pd_2Cl_2(\mu\text{-}ScHx)_2(PMe_3)_2]$, and tri-nuclear complexes $[Pd_3Cl_2(\mu\text{-}ScHx)_4(PMe_3)_2]$ are formed depending on the reaction conditions [282]. Organometallic complexes, $[M_2R_2(\mu\text{-}ER')_2(PR_3)_2]$, are prepared either by alkylation of $[Pt_2Cl_2(\mu\text{-}SR')_2(PR_3)_2]$ with alkyllithium/Grignard reagent [212,274,278] or more conveniently by treatment of $[M_2R_2(\mu\text{-}Cl)_2(PR_3)_2]$ with NaER′/py·R′SH [285,286]. The mixed bridged complexes, $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')(PR_3)_2]$ are readily obtained in nearly quantitative yields by redistribution reaction (33) [267,279,280]. These reactions are believed to proceed via a tetranuclear intermediate [279]. This reaction has been successfully extended to prepare hetero-binuclear complexes, $[PdPtCl_2(\mu\text{-}X)(\mu\text{-}SR')(PR_3)_2]$ [280]. Treatment of $[Pt(PEt_3)_3]$ with 2-methylbenzothiophene gives a mononuclear complex $[Pt(C,S\text{-}C_9H_8S)(PEt_3)_2]$, via ring opening reaction, in 38% yield which slowly rearranges to a binuclear thiaplatinacycle $[Pt_2(C,\mu\text{-}S\text{-}C_9H_8S)_2(PEt_3)_2]$ [304]. Dimerization of $[Pt(SiMe_3)(TePh)(PEt_3)_2]$ to $[Pt_2(SiMe_3)_2(\mu\text{-}TePh)_2(PEt_3)_2]$ in solution has been reported [305].

$$[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + 2R'SH \rightarrow [M_2Cl_2(\mu\text{-}SR')_2(PR_3)_2] + 2HCl \quad (31)$$

(R′ = Me, Et, Pr^n, Pr^i, Bu^t, Ph, tolyl)

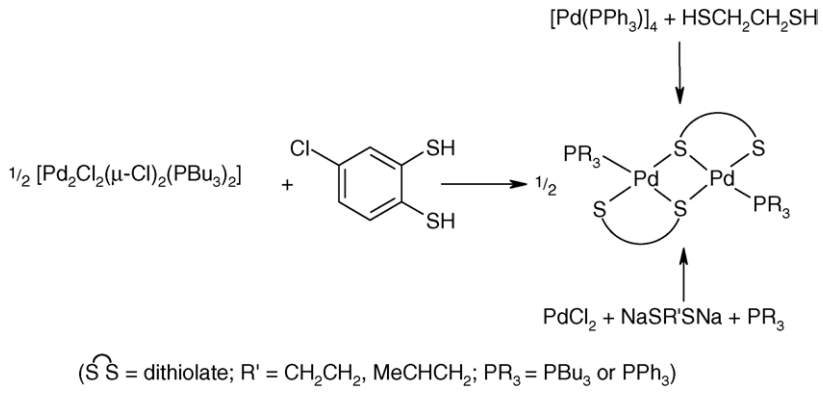
$$[M_2R''_2(\mu\text{-}Cl)_2(PR_3)_2] + 2NaER' \xrightarrow{\text{py}} 2MR''Cl(py)(PR_3) \xrightarrow{2\,R'SH} [M_2R''_2(\mu\text{-}ER')_2(PR_3)_2] \quad (32)$$

(R″ = Cl, Me, Ph, tolyl, etc.; E = S, Se, Te)

$$[M_2Cl_2(\mu\text{-}ER')_2(PR_3)_2] + [M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] \rightarrow 2[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')(PR_3)_2] \quad (33)$$

$$[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + R'SH(NaER') \rightarrow [M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')(PR_3)_2] \quad (34)$$

$$2\,PdCl_2(PPh_3)_2 + 2\,Ph_3SnTePh \rightarrow [Pd_2Cl_2(\mu\text{-}TePh)_2(PPh_3)_2]$$
$$[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2] + 2Ph_3SnTePh \rightarrow [Pd_2Cl_2(\mu\text{-}TePh)_2(PPh_3)_2] \quad (35)$$



Scheme 6.

$$M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2 + 4NaER' \rightarrow [M_2(ER')_2(\mu\text{-}ER')_2(PR_3)_2] \quad (36)$$

$$Pt(SR)_2(PR_3)_2 \xrightarrow{\text{Vacuum fusion}} [Pt_2(SR')_2(\mu\text{-}SR')_2(PR_3)_2] \quad (37)$$

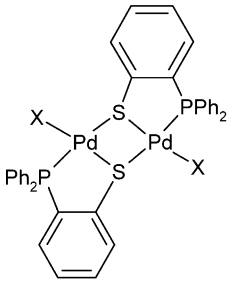
$$Pd(PPh_3)_4 + R_2'E_2 \rightarrow [Pd_2(\mu\text{-}ER')_2(ER')_2(PPh_3)_2] \quad (38)$$

$[ER' = SPh,\ TeR\,(R = C_6H_4OEt\text{-}4, C_4H_3S),\ SeTh]$

$$M'_2MCl_4 + NaER' \rightarrow [MCl(ER')]_n \xrightarrow{L} [M_2Cl_2(\mu\text{-}ER')_2L_2] \quad (39)$$

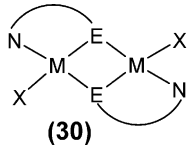
$[L = py, PPh_3, AsPh_3;\ E = S, Se, Te;\ R' = Ph\ or\ C_6H_4OR\text{-}4\,(R = Me\ or\ Et)]$

A few dithiols have also been employed for construction of bi-nuclear palladium complexes (Scheme 6) [266,306,307]. Internally functionalized chalcogenolate ligands containing P or N donor sites have also been used to prepare bi-nuclear complexes of the type **29** [308–312] and **30** [313–320].



X = Cl or I

(29)

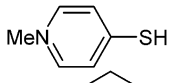


(30)

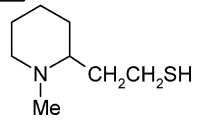
M = Pd or Pt
X = Cl, Br, I or OAc; E = S, Se, Te

E N = $ECH_2CH_2CH_2NMe_2$

4-mecapto-1-methylpiperidine,



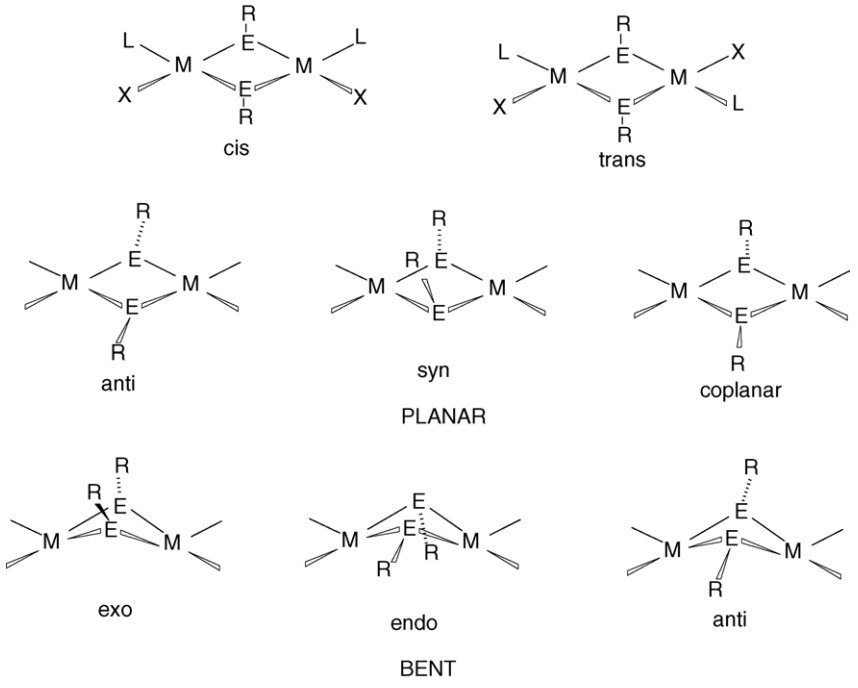
2-(mercaptoethyl)-1-methylpiperidine,



Besides symmetrical organochalcogenido-bridged complexes some asymmetric complexes of the general formula, $[L_2M(\mu\text{-}ER')_2M'X_2]$ have also been reported [272,321,322]. They are prepared by treatment of a mononuclear complex $M(ER')_2L_2$ (ER' = SPh, SC_6F_5, SePh, TePh; L_2 = dppe, dppm, $2PPh_3$] with $PdCl_2(RCN)_2$ (R = Me or Ph) [272,321] or $M'(C_6F_5)_2(THF)_2$ (M′ = Pd or Pt) [322].

Binuclear organochalcogenido-bridged complexes undergo a variety of reactions. Thiolato- and selenolato-bridged complexes are stable in chlorinated solvents, however, tellurolato-bridged complexes react readily, particularly with chloroform leading to decomposition [303]. When terminal chloride is replaced with strong *trans* influencing ligands as in $[Pd_2(SPh)_2(\mu\text{-}SPh)_2(PPh_3)_2]$ [272] and $[Pt_2Me_2(\mu\text{-}SMe)_2(PMe_2Ph)_2]$ [273,274], reaction with methyliodide gives $[Pd_2I_2(\mu\text{-}SPh)_2(PPh_3)_2]$ and $[Pt_2Me_4(\mu\text{-}SMe)_2I_2(PMe_2Ph)_2]$, respectively. The metathesis reaction of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeAr)(PR_3)_2]$ with KBr or KI in acetone yields the corresponding bromo- and iodo-complexes $[Pt_2X_2(\mu\text{-}X)(\mu\text{-}TeAr)(PR_3)_2]$ (X = Br or I) [242]. Complexes, $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-}ER')(PR_3)_2]$ (X = Cl or ER') react with $SnCl_2{\cdot}2H_2O$ in chloroform or dichloromethane via a simple insertion of $SnCl_2$ into terminal Pt–Cl bonds to yield the corresponding trichlorostannate complexes, $[Pt_2(SnCl_3)_2(\mu\text{-}X)(\mu\text{-}ER')(PR_3)_2]$ [242,278,279].

Although the ER' bridge (R' = alkyl) in $[M_2Cl_2(\mu\text{-}ER')_2(PR_3)_2]$ is resistant to cleavage by neutral donor ligands like PR_3 [278], bridge in aryl derivatives (R' = aryl) as in $[Pt_2Cl_2(\mu\text{-}SPh)_2(PBu_3)_2]$ and tetrathiolato derivatives such as $[Pt_2(SR')_2(\mu\text{-}SR')_2(PR_3)_2]$ and $[Pd_2(SCH_2CH_2S)_2(PPh_3)_2]$ is quite facile and can be

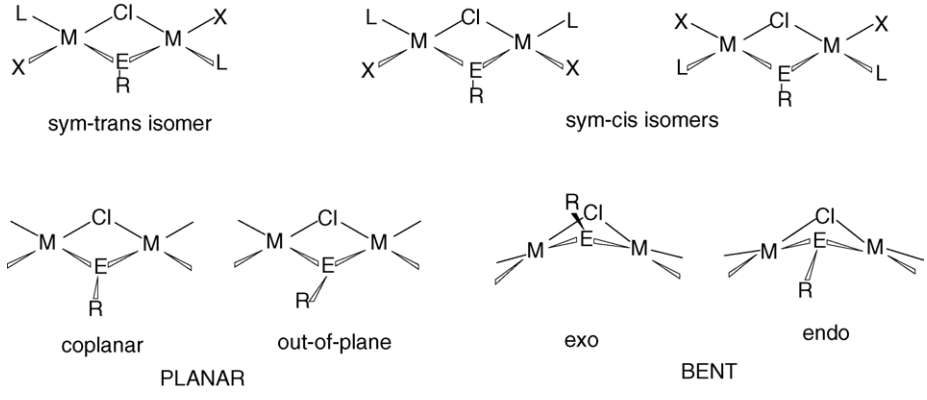


Scheme 7.

cleaved with neutral donor ligands [276,284,306]. However, the hetero-bridge in $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')(PR_3)_2]$ is invariably labile and on cleavage with neutral donor ligands affords various products depending on the ER′ and incoming ligand [267,279,280,284,291,303]. Cleavage reactions with palladium complexes proceeds much faster than the analogous platinum complexes. Reaction of $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')(PR_3)_2]$ with an excess of pyridine affords *cis*/*trans*-$[M_2Cl_2(\mu\text{-}ER')_2(PR_3)_2]$ and $[MCl_2(py)(PR_3)]$. The former is formed from a mononuclear species $[MCl(SR')(py)(PR_3)]$ [284]. Similarly, reaction of triphenylarsine with $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}EPh)(PBu_3)_2]$ initially yields *trans*/*cis*-$[PtCl_2(AsPh_3)(PBu_3)]$ and $[PtCl(EPh)(AsPh_3)(PBu_3)]$, from which the latter species slowly converts to $[Pt_2Cl_2(\mu\text{-}EPh)_2(PBu_3)_2]$ (E = S, Se, Te). Such cleavage reactions with triphenylphosphine give a mixture of products [279,291].

Some of the complexes have been evaluated for homogeneous catalytic hydrogenation of styrene in the presence of $SnCl_2$. The bis-thiolato-bridged platinum complexes $[Pt_2Cl_2(\mu\text{-}SR')_2(PR_3)_2]$ show poor catalytic activity (turnover number 0–94 at 1050 psi of H_2 pressure) [278]. On the other hand the chloro-mercapto bridged complexes give higher turnover number 1322 at 800 psi in the presence of excess $SnCl_2$ [279]. The binuclear complexes like $[Pd_2(SePh)_2(\mu\text{-}SePh)_2(PPh_3)_2]$ are efficient catalysts for catalyzing *cis* addition of R_2E_2 (E = S or Se) to alkynes [296,298].

The complexes $[M_2X_2(\mu\text{-}ER')_2L_2]$ and $[M_2X_2(\mu\text{-}Cl)(\mu\text{-}ER')L_2]$ can exist into two and three isomeric forms, respectively (Schemes 7 and 8). These isomers can be identified by various physico-chemical data. Initially they were characterized by dipole moment measurements by Chatt and Hart [267,268]. The *trans* isomers of $[Pt_2Cl_2(\mu\text{-}SR')_2(PR_3)_2]$



Scheme 8.

have dipole moments in the range 0–4.68 while the corresponding *cis* isomer has the value falling in the range 10.6–14.8. The *cis* and *trans* isomers of dithiolato-bridged complexes have been separated by thin layer chromatography, the *trans* form being more mobile possessing a higher Rf value than the *cis* form [269]. IR spectra of some $[M_2Cl_2(\mu\text{-}ER')_2L_2]$ and $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')L_2]$ (L = $AsMe_3$, PMe_3, PPh_3, $AsPh_3$) have been reported [270,271,290,301,302]. The υM–Cl terminal and bridging absorptions appear at 310 ± 10 and $\sim 260\,cm^{-1}$, respectively. Organochalcogeno-bridged complexes have been characterized extensively by multinuclear NMR (^{1}H, ^{13}C, ^{31}P, ^{77}Se, ^{125}Te, ^{195}Pt) data [242,271–274,278–281,284–294,303,323]. Some salient NMR features for these complexes can be summarized as follows.

3.2.2.1. $[M_2Cl_2(\mu\text{-}ER')_2(PR_3)_2]$ complexes.

(i) ^{31}P NMR signal for the *trans* isomer is deshielded than that of the corresponding *cis* isomer. Signal is shielded with increasing mass of the chalcogen atom. For example, in the ^{31}P NMR spectra of $[Pt_2Cl_2(\mu\text{-}ER')_2(PBu_3)_2]$ signal appears at 3.1 (SPh), 0.6 (SePh) and −2.4 (TeC_6H_4OMe) ppm.

(ii) The magnitude of ^{1}J(Pt–P) is considerably reduced than that of the corresponding chloro-bridged complexes owing to the strong *trans* influence of the ER′ group. The magnitude of ^{1}J(Pt–P) is greater in the *cis* isomer than that of the *trans* form.

(iii) The values of ^{3}J(Pt–P) and ^{4}J(P–P) for the *trans* isomer ($^{3}J = \approx 50$ Hz, $^{4}J = \sim 12$ Hz) are larger than those for the corresponding *cis* isomers ($^{3}J = 15$–20 Hz, $^{4}J = <2$ Hz). The magnitude of ^{3}J(Pt–P) for the *trans* isomer decreases with increasing mass of the chalcogen atom.

(iv) The magnitude of the ^{2}J(Pt–Pt) coupling constants increases considerably (800–1000 Hz) [291,294,303,323] being greater than the corresponding chloro-bridged dimers $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (140–400 Hz).

(v) The $^{2}J(^{125}Te/^{77}Se\text{-}^{31}P)$ *cis* is small and is not usually resolved whereas the corresponding *trans* values are large (∼150 Hz). Fig. 9 depicts two different types of coupling in the ^{77}Se NMR spectrum of *cis*-$[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr^n_3)_2]$ [294].

3.2.2.2. $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')L_2]$ complexes. The chloro-organochalcogenolate bridged complexes usually adopt a *cis* configuration with phosphine *trans* to the bridging chloride. The ^{1}J(Pt–P) decreases with increasing mass of the chalcogen atom, e.g. ^{1}J(Pt–P) values for $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}EPh)(PBu_3)_2]$ are 3937 (E = S), 3853 (E = Se) and 3802 Hz (E = Te), respectively.

Both *cis* and *trans* isomers of $[M_2X_2(\mu\text{-}ER')_2L_2]$ show another geometrical isomerism (Scheme 7), i.e. *syn* and *anti* forms. In solution these complexes undergo fluxional process. Attempts to detect *syn* and *anti* isomers by variable temperature NMR spectroscopy have been thrawted due to rapid inversion at the chalcogen atom [274,278,285].

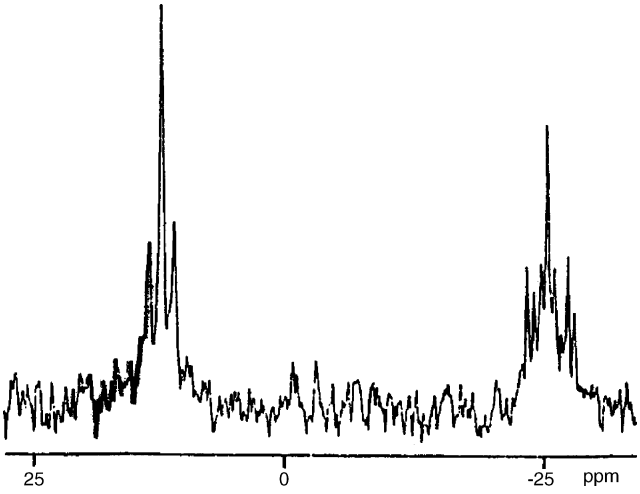


Fig. 9. $^{77}Se\{^{1}H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr_3)_2]$ (reproduced with permission from ref. [294]).

The structures of several $[M_2X_2(\mu\text{-}ER')_2(PR_3)_2]$ and $[M_2X_2(\mu\text{-}Cl)(\mu\text{-}ER')(L_2)]$ have been established by X-ray diffraction methods [242,276,281,283–285,293–295,304,307,308,313,315–317,324–334]. These complexes show considerable structural diversity. The majority structural data on these molecules reveal the following general features.

Both planar and bent (hinged) structures (see Section 3.3.1) are found for the $[M_2X_2(\mu\text{-}ER')_2(PR_3)_2]$ complexes. As is evident from Table 3 that the *trans* isomer has a planar M_2E_2 ring while the *cis* isomer adopts a hinged structure. The folding along the E···E-axis results in shortening of M···M distances than the planar structures. The bridging ER′ groups in general adopt an *anti* configuration with respect to each other. It is believed that alkanethiolates lead to hinged geometries whereas arenethiolates give rise to planar structures [283]. However, the existence of a planar Pt_2Se_2 ring in $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_2]$ [293] suggests that the substituents on E are of little significance in determining the geometry of the M_2E_2 ring (Figs. 10 and 11).

The mixed-bridged complexes $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER')(PR_3)_2]$ invariably have a *sym cis* configuration (Fig. 12) (Scheme 8) in which phosphine ligands are *trans* to the bridging chloride. Structures appear to be influenced by the substituents on E, the aryl substituents prefering a planar structure [242,283] while alkyl substituents leading to a bent configuration with R′ in *exo* orientation [281,283,284,330,333]. The hinge angle varies between 134 and 157°.

3.2.3. Complexes with chalcogenido (E^{2-}) bridges

The oxo-bridged neutral complexes are rare [335–337]. They are usually prepared by deprotonation of hydroxo-bridged cationic complexes. Thus, treatment of $[Pt_2(\mu\text{-}OH)_2L_4][BF_4]_2$ with $NaN(SiMe_3)_2$ yields a white solid, $[Pt_2\mu\text{-}O)_2L_4]$ (L = PPh_3; δ ^{31}P 8.5 ppm, ^{1}J(Pt–P) = 3180 Hz)

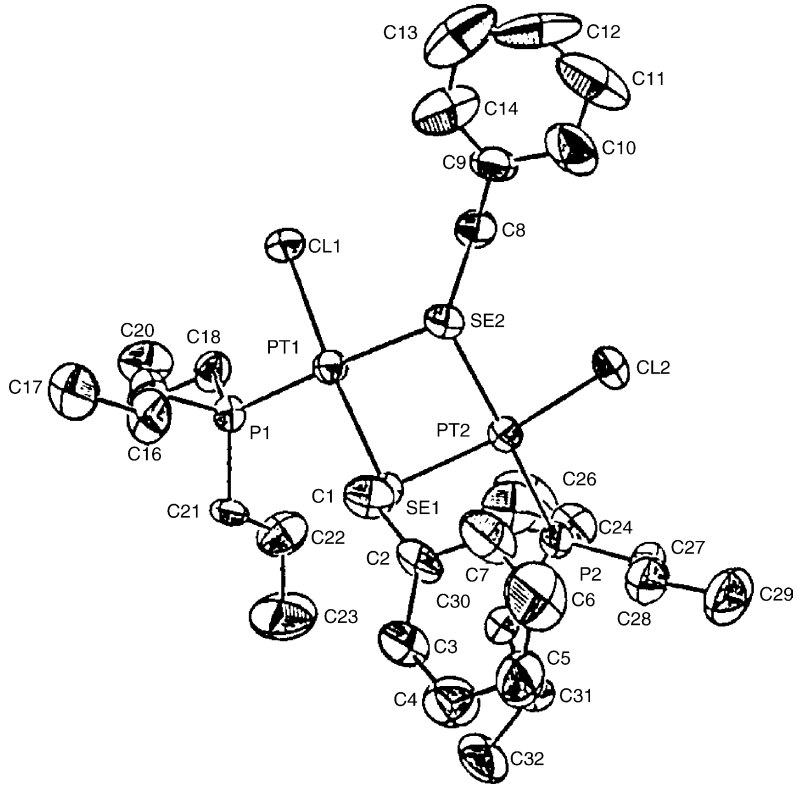


Fig. 10. Molecular structure of $[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr_3)_2]$ (reproduced with permission from ref. [294]).

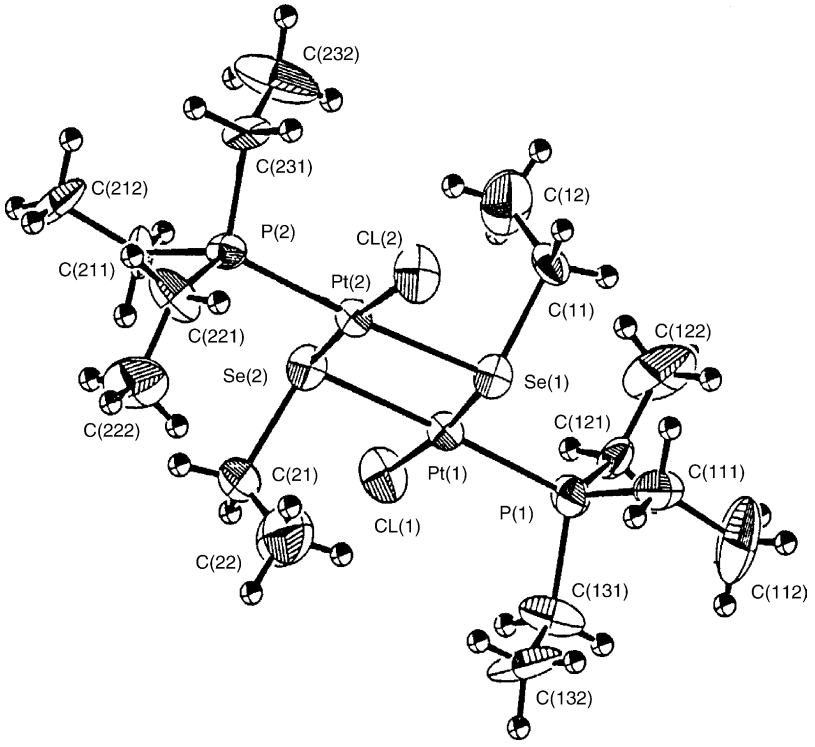


Fig. 11. Molecular structure of $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$ (reproduced with permission from ref. [293]).

Table 3
Structures of chalcogenolato bridged complexes of Pd and Pt determined by X-ray diffraction

Complex	Comment (R′ = organic groups on E)	References
trans-$[Pd_2(SPh)_2(\mu\text{-}SPh)_2(PPh_3)_2]$	Planar Pd_2S_2 ring with *anti* R′, Pd···Pd = 3.506 Å	[330]
trans-$[Pd_2(SC_6F_5)_2(\mu\text{-}SC_6F_5)_2(PPh_3)_2]$	Planar Pd_2S_2 ring with *anti* R′, Pd···Pd = 3.532, 3.552, 3.651 Å	[324,325]
trans-$[Pd_2(SCH_2CH_2S)_2(PPh_3)_2]$	Bent Pd_2S_2 ring with *endo* R′, $\theta = 108.55^\circ$; Pd···Pd = 3.038(2) Å	[307]
cis-$[Pt_2(SBz)_2(\mu\text{-}SBz)_2(PMePh_2)_2]$	Bent Pt_2S_2 ring with *anti* R′, $\theta = 138.8^\circ$; Pt···Pt = 3.348 Å	[276]
trans-$[Pd_2Cl_2(\mu\text{-}SPh)_2(PEt_3)_2]$	Planar Pd_2S_2 ring with *anti* R′, Pd···Pd = 3.463(2) Å	[283]
trans-$[Pd_2Cl_2(\mu\text{-}SC_6H_4OH\text{-}2)_2(PPh_3)_2]$	Planar Pd_2S_2 ring with *anti* R′, Pd···Pd = 3.495(2) Å	[331]
trans-$[Pd_2Cl_2\{\mu\text{-}SC_2H_4CpPPh_2)(FeCp)\}_2]$	Bent Pd_2S_2 ring, Pd···Pd = 3.363 Å	[332]
trans-$[Pt_2(NO_2)_2(\mu\text{-}SMe)_2(PPh_3)_2]$	Bent Pt_2S_2 ring, R′ *anti*, $\theta = 144$, Pt···Pt = 3.341 Å	[327]
cis-$[Pt_2Cl_2(\mu\text{-}SEt)_2(PPr_3)_2]$	Bent Pt_2S_2 ring, R′ *anti*, $\theta = 130^\circ$, Pt···Pt = 3.206 Å	[326]
trans-$[Pt_2Ph_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$	Planar Pt_2S_2 ring, R′ = *anti*, Pt···Pt = 3.570 Å	[285]
trans-$[Pt_2I_2(\mu\text{-}SCH_2CH_2CMe{=}CH_2)_2(PPh_3)_2]$	Planar Pt_2S_2 ring, R′ = *anti*, Pt···Pt = 3.539(1) Å	[328]
trans-$[Pt_2(\mu\text{-}\overline{SC(Me)CH_2C_6}H_4\text{-}2\}_2(PEt_3)_2]x$	Pt–S = 2.372(6), 2.404(5) Å	[304]
trans-$[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$	Planar Pt_2Se_2 ring R′ = *anti*, Pt···Pt = 3.674 Å	[293]
cis-$[Pt_2Cl_2(\mu\text{-}SeBz)_2(PPr_3^n)_2]$	Non-planar Pt_2Se_2 ring and hinge angle 131.1°, Bz groups are *anti*	[294]
cis-$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SMe)(PMe_3)_2]$	Bent "Pd_2SCl", R′ *exo*, $\theta = 140^\circ$, Pd···Pd = 3.294(4) Å	[283]
cis-$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SBu^t)(PMe_3)_2]$	Bent Pd_2SCl, R′ = *exo*, $\theta = 146^\circ$, Pd···Pd = 3.208(1) Å	[283]
cis-$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$	Bent Pd_2SCl, R′ = *exo*, $\theta = 134.3^\circ$, Pd···Pd = 3.234 Å	[281]
cis-$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PMe_3)_2]$	Planar Pd_2SCl, R′ = out-of-plane, Pd···Pd = 3.934(3) Å	[283]
cis-$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SCH_2CH_2CH_2Cl)(PMe_3)_2]$	Bent Pd_2SCl, R′ = *exo*, $\theta = 150, 157^\circ$, Pd···Pd = 3.305, 3.353 Å	[329]
cis-$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$	Bent Pt_2SCl, R′ = *exo*, $\theta = 135.6^\circ$, Pt···Pt = 3.299 Å	[284]
cis-$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMe_2Ph)_2]$	Bent Pt_2SeCl, R′ = *exo*, $\theta = 153^\circ$, Pt···Pt = 3.400 Å	[333]
cis-$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(PBu_3)_2]$	Planar "Pt_2TeCl", R′ = *exo*, Pt···Pt = 3.670 Å	[242]
trans-$[Pd_2I_2(\mu\text{-}SC_6H_4PPh_2\text{-}2)_2]$	Bent "Pd_2S_2", R′ = *endo*, $\theta = 110/107$, Pd···Pd = 2.965/2.915 Å	[308]
trans-$[Pd_2Cl_2(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2]$	Hinged Pd_2Se_2 bridge, $\theta = 105.81^\circ$, thiolato-bridge *syn-endo*, Pd···Pd = 2.9726(7) Å	[334]
trans-$[Pd_2Cl_2(\mu\text{-}SCH_2CH_2CH_2NMe_2)_2]$	Planar Pd_2S_2, R′ = *anti*, Pd···Pd = 3.442 Å	[313]
trans-$[Pd_2Cl_2(\mu\text{-}SCH_2CH_2\text{-}C_5H_9NMe)_2]$	Bent "Pd_2S_2", R′ = *endo*, $\theta = 142.8^\circ$, Pt···Pt = 3.374(1) Å	[315]
trans-$[Pt_2Br_2(\mu\text{-}SC_5H_9NMe)_2]$	Bent Pt_2S_2, R′ = *endo*, $\theta = 127^\circ$, Pt···Pt = 3.142 Å	[316]
trans-$Pd_2(SeTh)_2(\mu\text{-}SeTh)_2(PPh_3)_2$	Planar Pd_2Se_2 ring	[294]
trans-$Pt_2(SeTh)_2(\mu\text{-}SeTh)_2(PPh_3)_2$	Planar Pt_2Se_2 ring	[294]
trans-$[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2CH_2NMe_2)_2]$	Pd_2Se_2 non-planar, Pd–Pd = 3.413(1) Å	[317]
$[Pt_2(SC_6HF_4\text{-}4)_2(\mu\text{-}SC_6HF_4\text{-}4)_2\{PPh(C_6F_5)_2\}_2]$	$Pt\text{–}S_{terminal}$ = 2.327(3) Å, $Pt\text{–}S_{bridging}$ = 2.359(2) $Pt\text{–}S_{bridging}$ = 2.370(2) Å	[289]
$[Pd_2\{(SeC_5H_4)_2Fe\}_2(PBu_3)_2]$	Planar Pd_2Se_2 ring	[299]
$[Pt_2\{(SeC_5H_4)_2Fe\}_2(PBu_3)_2]$	Planar Pt_2Se_2 ring	[299]

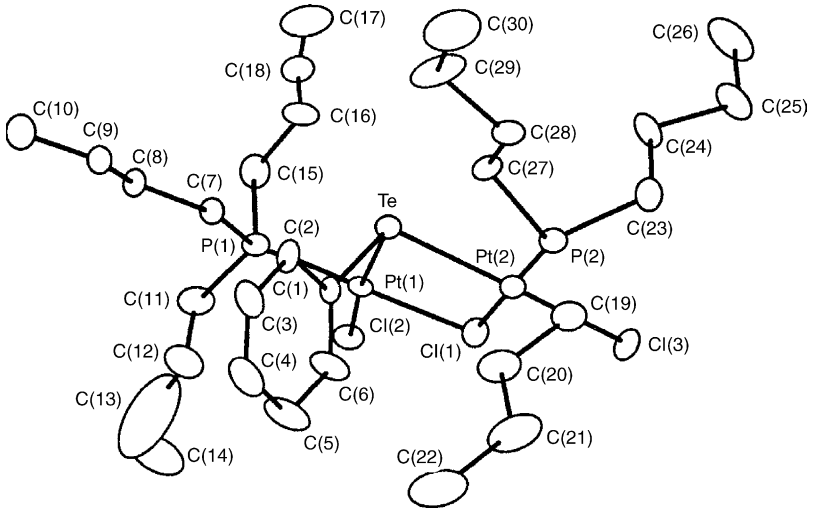


Fig. 12. Molecular structure of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(PBu_3)_2]$ (reproduced with permission from ref. [242]).

$$2\,MCl_2L_2 + 2\,Na_2S \longrightarrow [M_2(\mu\text{-}S)_2L_4] + 4\,NaCl$$

$$2\,Pt(PPh_3)_4 + {}^{3}\!/_{4}S_8 \longrightarrow [Pt_2(\mu\text{-}S)_2(PPh_3)_4] + 4Ph_3PS$$

$$2\,Pt(SH)_2(PPh_3)_2 + NaOEt \longrightarrow [Pt_2(\mu\text{-}S)_2(PPh_3)_4] + 2\,Na_2S + 4\,EtOH$$

$$PtCl_2(Ph_2pyP)_2 + NaSH + Et_3N \longrightarrow [Pt_2(\mu\text{-}S)_2(Ph_2pyP)_4]$$

Scheme 9.

(40) [335]. However, when reaction (40) is carried out with $LiN(SiMe_3)_2$, a $LiBF_4$ adduct, $[Pt_2(\mu\text{-}O)_2(PPh_3)_4{\cdot}LiBF_4]$ (δ $^{31}P = 7.80$ ppm, $^{1}J(Pt–P) = 3286$ Hz) is formed (41). In the latter the bridging *oxo*-ligands are coordinated to a Li atom of $LiBF_4$. The two edge shared platinum centers are folded along the shared O–O edge [fold angle 146.4(1)°] [335,336]. Although reaction (41) with other phosphines proceeds in a similar way, with PMe_2Ph a trinuclear complex, $[\{Pt(PMe_2Ph)_2\}_3(\mu_3\text{-}O)_2][BF_4]_2$ is formed [336].

$$[Pt_2(\mu\text{-}OH)_2(PPh_3)_4][BF_4]_2 + 2NaN(SiMe_3)_2 \rightarrow [Pt_2(\mu\text{-}O)_2(PPh_3)_4] + 2NaBF_4 + 2HN(SiMe_3)_2 \quad (40)$$

$$[Pt_2(\mu\text{-}OH)_2(PPh_3)_4][BF_4]_2 + 2\,LiN(SiMe_3)_2 \rightarrow [Pt_2(\mu\text{-}O)_2(PPh_3)_4{\cdot}LiBF_4] + LiBF_4 + 2\,NH(SiMe_3)_2 \quad (41)$$

Among the chalcogenide-bridged derivatives, chemistry of sulfido-bridged complexes has been explored in considerable detail and has been reviewed recently by Fong and Hor [338]. Several sulfido-bridged platinum complexes, $[Pt_2(\mu\text{-}S)_2(L_4)]$ (L = PMe_2Ph [339], PPh_3 [340], $Ptol_3$ [341], PPh_2py [342], $\frac{1}{2}$dppe [343], $\frac{1}{2}$dppp [344], $\frac{1}{2}$dppf [345], $\frac{1}{2}$dppen) [346] have been prepared. However, the chemistry of analogous palladium complexes, except $[Pd_2(\mu\text{-}S)_2(dppf)_2]$ [347], is little developed [348]. These complexes are usually prepared by a reaction of MCl_2L_2 with Na_2S [339–341,343,345–347,349] or by oxidation of a platinum(O) complex $Pt(PPh_3)_4$ with sulfur in benzene [340]. However, other methods (Scheme 9) have also been employed [342,350].

Because of poor solubility of these complexes in majority of organic solvents, except halogenated one with which they react, NMR data are not well studied. Only recently NMR data for a highly soluble $Ptol_3$ complex, (δ $^{195}Pt = -4417$ ppm, $^{1}J(Pt–P) = 2800$ Hz, $^{3}J(Pt–P) = 39$ Hz) [341] and also for dppen analogue (δ $^{195}Pt = -4336$ ppm, $^{1}J(Pt–P) = 2965$ Hz; $^{3}J(Pt–P) = 50$ Hz) [346] have been reported. The ^{195}Pt NMR chemical shifts and coupling constants can be compared with other dimeric μ-organothiolato bridged complexes. The X-ray structures of some complexes (Table 4) have been reported. These complexes usually show a hinged square planar geometry (Fig. 13) [327,343] with the exception of $[Pt_2(\mu\text{-}S)_2(PPh_2py)_4]$ which has a flat four-membered Pt_2S_2 ring [342].

The bridging sulfur sites in these complexes is susceptible to nucleophilic attack and react with various organic nucleophiles particularly halogenated compounds including HCl [327,339,340,342,344,351,352]. Reaction with HCl followed by metathesis by NH_4PF_6 affords $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4][PF_6]$. Variable temperature NMR data and theoretical calculations provide evidence for fast intramolecular proton exchange between the bridging sulfur atoms in $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(P^{-}P)_2][ClO_4]$ ($P^{-}P$ = dppe, dppp) [353]. Chlorinated solvents such as $CHCl_3$ or CH_2Cl_2 readily alkylate bridging sulfide [351] resulting in ionic complexes, $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4][X]$ (R = $CHCl_2$ or CH_2Cl; X = Cl) [327,352]. Reactions with methyliodide [327,340] and benzylhalide [339,340] proceed similarly, and the structure of one such ionic complex, $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^{+}$ has been determined by X-ray crystallography [327]. Further alkylation of these ionic complexes results in the formation of

Table 4
X-ray structures of chalcogenido-bridged complexes

Complex	Comment	References
$[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$	Pt_2S_2 ring non-planar; $\theta = 121°$, Pt···Pt = 3.175(2) Å, S···S = 3.06(2) Å, Pt–S = 2.340(8) Å	[327]
$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$	Pt_2S_2 ring non-planar; $\theta = 168.2°$, Pt···Pt = 3.17 Å	[404]
$[Pt_2(\mu\text{-}S)_2(dppe)_2]$	Pt_2S_2 ring non-planar; $\theta = 140.2°$, Pt–S = 2.3496(12) Å, Pt···Pt = 3.29 Å	[343]
$[Pt_2(\mu\text{-}S)_2(dppp)_2]$	Pt_2S_2 ring non-planar, 134.80°, Pt···Pt = 3.23 Å	[344]
$[Pt_2(\mu\text{-}S)_2(PPh_2py)_4]$	Pt_2S_2 ring planar, Pt···Pt = 3.555(1) Å, S···S = 3.005(2) Å	[338]
$[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4][PF_6]$	Pt–S = 2.333(1) Å, Pt_2S_2 ring non-planar, $\theta = 135°$	[351]
$[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4][PF_6]$	Pt_2S_2 ring non-planar, $\theta = 138°$, Pt···Pt = 3.10 Å	[327]
$[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]{\cdot}2DMF$	Pt_2Se_2 planar, Pt···Pt = 3.763 Å; Se···Se = 3.136(1) Å; Pt···Se = 2.4651(1), 2.433(1) Å	[396]
$[Pt_2(\mu\text{-}Te)_2(PPh_3)_4]$	Pt_2Te_2 planar, Pt···Te = 2.612(1), 2.628(1) Å	[398]
$[Pt_2(\mu\text{-}Te)_2(PEt_3)_4]$	Pt_2Te_2 planar, Pt–Te = 2.62 Å; Te···Te = 3.263(1) Å	[400]
$[Pd_2(\mu\text{-}Te)_2(PEt_3)_4]$	Pd_2Te_2 planar, Pd–Te = 2.6122(16) Å, Te···Te = 3.0657(21) Å	[399]
$[(np)Pd(\mu\text{-}Te)]_2$	Pd–Te = 2.6381(1), 2.612(1) Å	[401]
$[Pt_2(\mu\text{-}Te)_2(dppe)_2]$	Pt···Pt = 3.96 Å, Pt_2Te_2 planar	[405]

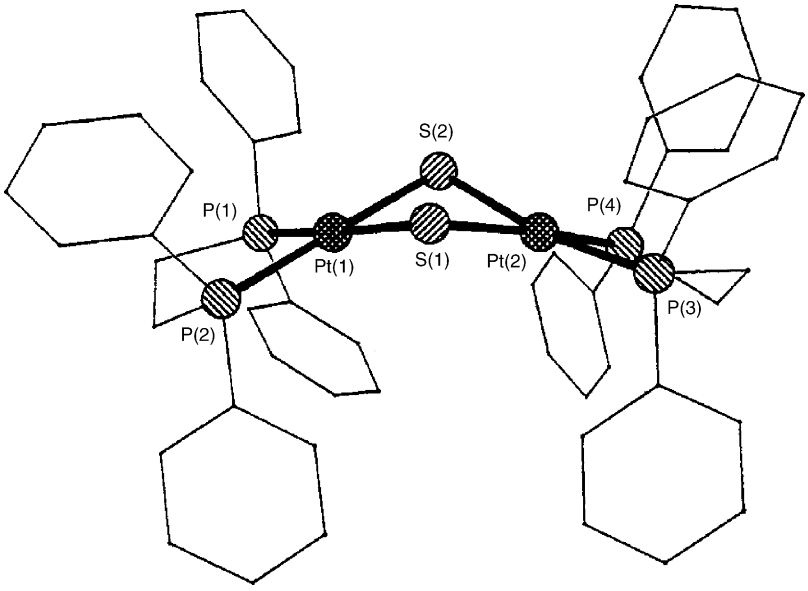
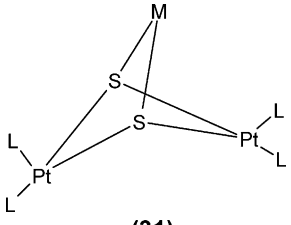


Fig. 13. Molecular structure of $[Pt_2(\mu\text{-}S)_2(dppe)_2]$ (reproduced with permission from ref. [343]).

mono nuclear derivatives, $[Pt(SR)_2(PR_3)_2]$ ($(SR)_2 = S_2CH_2$) [342].

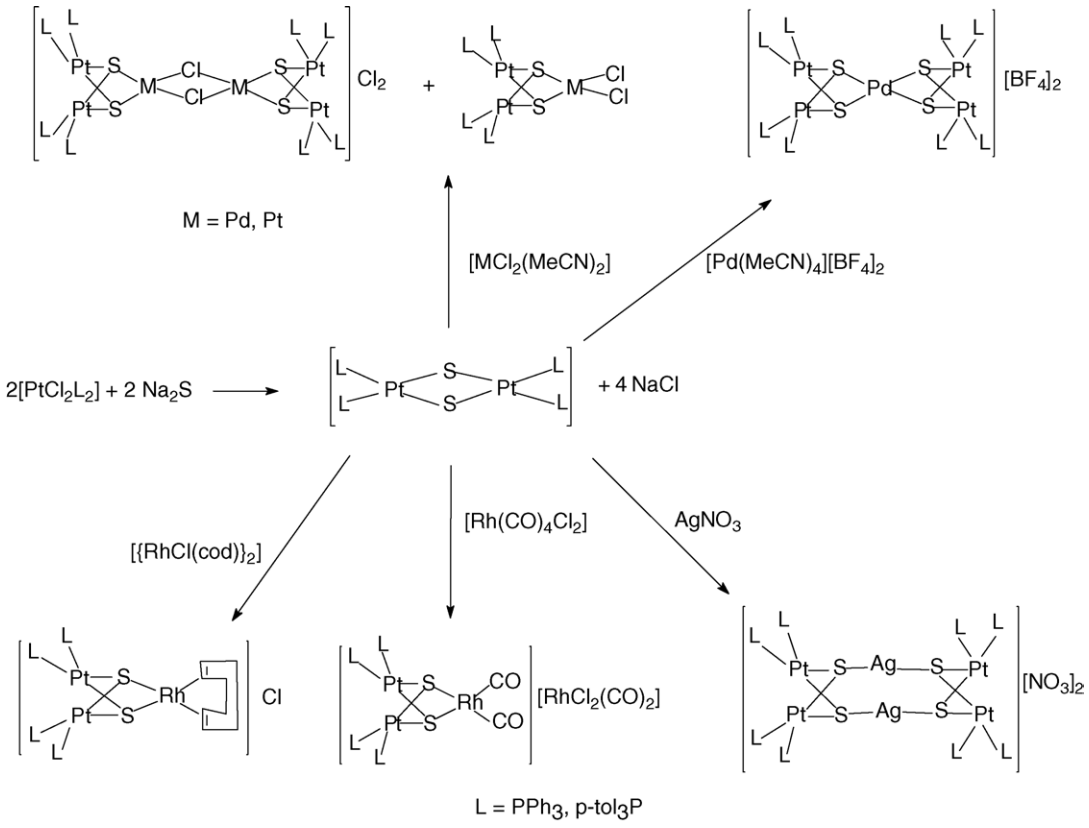
The chalcogen lone pairs of the Pt_2S_2 or Pt_2Se_2 fragment are sufficiently basic and can be compared with bidentate thioethers. Accordingly such molecules can function as a bidentate metallo ligand. This property has been exploited to prepare a variety of coordination complexes both with transition metals ([341,343,354–381] (S); [373,382–385] (Se)) and main group elements [386–395]. Structures of nearly all of them have been established by X-ray crystallography. Several transition metal fragments coordinate with bridging sulfur atoms of $[M_2(\mu\text{-}S)_2L_4]$ (M = Pd or Pt) to give polynuclear aggregates (Scheme 10). Nuclearity of the resulting aggregate is determined by the geometric requirement of the hetero-metal. Thus, tri-, tetra-, penta- and hexa-nuclear complexes are formed in these reactions. Transition metals which have been employed in these reactions include, ruthenium (e.g. $[RuCl(PPh_3)_2\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}]Cl$) [354], rhodium (e.g. $[CODRh\{Pt_2(\mu\text{-}S)_2L_4\}]^+$ (L = PPh_3, $Ptol_3$) [341,355], $[Rh(CO)_2\{Pt_2(\mu\text{-}S)_2L_4\}][Rh(CO)_2Cl_2]$ [341,356], cobalt (e.g. $[CoCl_2\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}]$ [357], nickel (e.g. $[dppeNi\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}]^{2+}$ [358], palladium (e.g. $[Pd\{Pt_2(\mu\text{-}S)_2(L)_4\}_2]^{2+}$ (L = PPh_3 or $Ptol_3$) [341,358,359], platinum [341,357], copper [343,354,357,360] (e.g. $[Cu\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2]^+$ [360], $[CuCl(PPh_3)\{Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ [354], silver [347,354,358,361–364] (e.g. $[AgCl\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}]$ [354], $[Ag_2\{Pt_2(\mu\text{-}S)_2L_4\}_2][NO_3]_2$ (L = PPh_3 or $Ptol_3$) [341,358], gold [365] and mercury [358]. On coordination, the ^{31}P NMR signal for $[Pt_2(\mu\text{-}S)_2(L_4)]$ fragment is shielded and the magnitude of ^1J(Pt–P) increases (170–420 Hz) from uncoordinated precursor. The increase in ^1J(Pt–P) coupling constant has been interpreted in terms of diminished polarizability of the Pt–S bond as a consequence of the non-bonding electron pair donation to the incoming metal atom. The complexes $[Pt_2(\mu\text{-}E)_2(Ph_2pyP)_4]$ (E = S or Se) and their transition metal adducts exhibit luminescence properties [373].

The complexes (**31**) with main group Lewis acids such as $GaCl_3$ [386], $InCl_3$ [386], $Tl(NO_3)$ [387,388], $Pb(NO_3)_2$ [388,389], $BiCl_3$ [390] exhibit some unusual coordination geometries at the main group metal center.



(31)
L = PPh_3 or 0.5 dppf
M = Main group element

Selenido [340,396,397] and tellurido [398–401] bridged complexes have also been prepared and characterized. The selenido-bridged platinum complex, $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ has been isolated as brick-red crystalline solid in 20% yield by the reaction of $PtCl_2(PPh_3)_2$ with $(NBu_4)SeH$ in DMF [396]. The reaction of $PtCl_2(dppe)$ with NaSeH in acetonitrile at 70 °C has been employed to prepare $[Pt_2(\mu\text{-}Se)_2(dppe)_2]$ in 36% yield [382]. Oxidative addition of Se on $Pd(dppe)_2$ gives $[Pd_2(\mu\text{-}Se)_2(dppe)_2]$ [402]. Like the sulfido bridged complex, the selenido-bridged platinum derivative, $[Pt_2((\mu\text{-}Se)_2(PPh_3)_4]$ reacts with various organic halides to yield $[Pt_2(\mu\text{-}Se)(\mu\text{-}SeR)PPh_3)_4]^+$ [403]. Tellurido-bridged complexes have been isolated by oxidative addition of a tellurium reagent on M(O) derivatives. The reaction of $Pt(PPh_3)_4$ with $[NBu_4]_4[Hg_4Te_{12}]$ in DMF affords a tellurido-bridged dimer $[Pt_2(\mu\text{-}Te)_2(PPh_3)_4]$ in



Scheme 10.

~20% yield [398]. Trialkylphosphine telluride has been successfully used as a tellurium transfer reagent [399–401]. Thus, treatment of $[Pt_3(CO)_6]_n^{2-}$ ($n = 3$, 4, 5) with Et_3PTe in THF results in cluster degradation with the formation of primarily red $[Pt_2(\mu\text{-}Te)_2(PEt_3)_4]$ (80% yield) (δ ^{31}P C_6D_6: 1.4, ^1J(Pt-P) = 3031 Hz; ^{195}Pt in acetone d_6 δ: −5380(t); ^1J(Pt-P) = 2935 Hz) and two cationic complexes, $[Pt_2(\mu\text{-}Te_2)(PEt_3)_4]^{2+}$ (2%) and $[Pt_3(\mu\text{-}Te)_2(PEt_3)_6]^{2+}$ (^{31}P in acetone-d_6 δ: 3.7, ^1J(Pt–P) 3238 Hz) [400]. The analogous palladium complex, $[Pd_2(\mu\text{-}Te)_2(PEt_3)_4]$ has been obtained in poor yield (2%) as a dark green crystalline solid when the reaction of $Pd(PPh_3)_4$ with Et_3PTe in the presence of PEt_3 was carried out in heptane-toluene mixture at room temperature [399].

Unlike oxo- and sulfido-bridged complexes [404], heavier chalcogenido-bridged complexes have a planar four-membered M_2E_2 (E = Se or Te) ring [398–400,405] and the E–E distances (3.06–3.26 Å) are much longer than reported for E–E (Se or Te) bonds (Fig. 14).

3.3. Complexes containing Group 17 as bridging ligand

3.3.1. Classical complexes

Binuclear halogen-bridged palladium complexes are readily obtained by the reaction of $PdX_2(ER_3)_2$ with M_2PdCl_4 (M = Li or Na) in refluxing ethanol or chloroform (42) [406,407]. Analogous platinum complexes $[Pt_2X_2(\mu\text{-}X)_2(ER_3)_2]$ require more drastic conditions. They

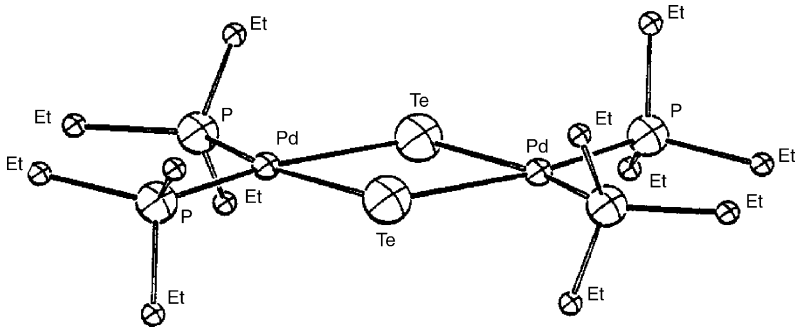


Fig. 14. Molecular structure of $[Pd_2(\mu\text{-}Te)_2(PEt_3)_4]$ (reproduced with permission from ref. [399]).

are obtained by fusing $PtX_2(ER_3)_2$ with PtX_2 (43) [408,409]. However, this method is unsuccessful if either the starting material or the product decomposes before melting, e.g. $[PtCl_2(PMe_3)_2]$. To overcome this problem, a slurry of reactants either in hydrocarbons (e.g. xylene or naphthlene) [410] or tetrachloroethane [411,412] is heated at reflux. The latter solvent is generally preferred as the reactants as well as the final product are often soluble. In certain cases even (e.g. PPh_3) both *cis* and *trans* isomers of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ could be isolated [413]. In an alternative approach, platinum complexes have been synthesized by refluxing platinum chloride with one equivalent of tertiary phosphine in chlorobenzene, (44) [414]. If the reactants of (42) and (43) are interchanged, heterobimetallic complexes are formed [415].

$$[PdX_2(ER_3)_2] + M_2PdX_4 \rightarrow [Pd_2X_2(\mu\text{-}X)_2(ER_3)_2] + 2MX \quad (42)$$

$$[PtX_2(ER_3)_2] + PtX_2 \rightarrow [Pt_2X_2(\mu\text{-}X)_2(ER_3)_2] \quad (43)$$

$$2PtCl_2 + 2PR_3 \xrightarrow{PhCL} [Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] \quad (44)$$

(PR_3 = PEt_3, PBu_3, PMe_2Ph, PPh_3, $Ptol_3$)

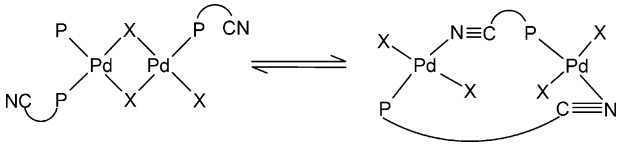
Dimeric platinum complexes with sterically demanding phosphine like P-c-Hx_3 have been prepared by the reaction of phosphine with a dilute acetone solution of $K[PtCl_3(CH_2{=}CH_2)]$ [416]. Reaction of PtX_2COD (X = Cl or I) with various phosphines (PBz_3, P-cHx_3, PPhc-Hx_2, PPh_2cHx, etc.) yields a mixture of products, *cis*-/*trans*-$[Pt_2X_2(\mu\text{-}X)_2(PR_3)_2]$ and $[PtX_2(PR_3)_2]$ depending on the X and phosphine ligand [417,418].

Trialkylstibine complexes, $[Pt_2Cl_2(\mu\text{-}Cl)_2(SbR_3)_2]$ are obtained rather indirectly as reaction (43) yields mainly black decomposition products. Generally, a solution of binuclear olefin complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(olefin)_2]$ is treated with a required quantity of the ligand at -75° which on warning to room temperature affords desired product (45) [408,409]. The reaction of $SbBu_3^t$ with $PtCl_2/MCl_2(PhCN)_2/PdCl_2COD/Na_2PdCl_4$ invariably yields a dimeric complex $[M_2Cl_2(\mu\text{-}Cl)_2(SbBu_3^t)_2]$ (M = Pd or Pt) [419]. Reaction of $AsBu_3^t$ with $Na_2PdCl_4/PdCl_2$ proceeds similarly [420]. However, reaction with $PtCl_2/K_2PtCl_4$ yields either *trans*-$[PtCl_2(AsBu_3^t)_2]$ or $[Pt_2Cl_2(\mu\text{-}Cl)_2(AsBu_3^t)_2]$ depending on arsine to platinum mole ratio [420]. The behaviour of $AsBu_3^t$ and $SbBu_3^t$ is markedly different from that of PBu_3^t which gives internally metallated complexes. Treatment of $PtH_2(AsBu_3^t)_2$ with HI in acetone gives $[Pt_2I_2(\mu\text{-}I)_2(AsBu_3^t)_2]$ [421].

There is no direct method to prepare binuclear complexes with nitrogen donor ligands. The method generally involves slow (several weeks) displacement of weak donors like olefins [409,422–425] or dmso [426] from the mononuclear complexes $[PtCl_2(L)amine]$ (L = olefin or dmso; amine; 2,6-lutidene [418], piperidine, substituted pyridines, *p*-toludine). Irradiation of $PtCl_2(CH_2{=}CH_2)(amine)$ also results in the formation of $[Pt_2Cl_2(\mu\text{-}Cl)_2(amino)_2]$ [422,423]. The iodo-bridged dimers, $[Pt_2I_2(\mu\text{-}I)_2L_2]$ (L = NH_3 or other amines) are synthesized by protonation of PtI_2L_2 with perchloric acid [427].

1,2-bis(Diphenylphosphino)acetylene (dppa) in which the rigidity of the C≡C back bone forces two phosphorus atoms apart, forms binuclear complexes [428–434]. Thus, treatment of $[Pt(C_6F_5)_2(tht)_2]$ or $[Pt(C{\equiv}CR)_2(COD)]$ with dppa in 1:1 molar ratio yields $[Pt_2R_4'(dppa)_2]$ (R′ = C_6F_6 or C≡CR) which have dppa bridges as shown by X-ray analysis. The reaction of MCl_2 or MCl_4^{2-} with dppa affords $[MCl_2(\mu\text{-}dppa)_2MCl_2]$ [428,429]. The terminal chloride can easily be substituted by I [430] or SR′ [431]. Inter-mixing of homo-binuclear complexes readily establish an equilibrium between homo- and hetero-binuclear complexes (46) [432]. Treatment of $[Pd(OOCCF_3)_2]$ with *cis*, *trans*-1,2-$(Pr_2^iPO)_2C_6H_{10}$ in the presence of NaI gives binuclear 16-atom ring chelate complex *trans*-$Pd_2I_4\{cis\text{-}(Pr_2^iPO)_2C_6H_{10}\}_2]$ [435]. Reaction of H_2PdX_4 (X = Cl or Br) with $Ph_2PCH_2CH_2CN$ or $Ph_2PC_6H_4CN$-2 ($P^{\frown}CN$) yields $[Pd_2X_4(P^{\frown}CN)_2]$ which exist in an equilibrium between the halo-bridged and ligand-bridged dimers as revealed by NMR spectroscopy (47) [436]. Several complexes containing bridging phosphine ligands such as *trans*-$Ph_2PCH{=}CHPPh_2$, 1,2,3,4-tetrakis(diphenylphosphino)butane, etc. have been isolated and characterized [437–442].

$$[Pd_2Cl_4(\mu\text{-}dppa)_2] + [Pt_2Cl_4(\mu\text{-}dppa)_2] \rightleftharpoons 2[PdPtCl_4(\mu\text{-}dppa)_2] \quad (46)$$



(47)

Dimeric halogen-bridged complexes have been studied by various physico-chemical techniques. Molecular weight

$$[Pt_2Cl_2(\mu\text{-}Cl)_2(olefin)_2] + 2SbR_3 \xrightarrow{-75^0C} 2[PtCl_2(SbR_3)(olefin)] \xrightarrow{RT} [Pt_2Cl_2(\mu\text{-}Cl)_2(SbR_3)_2] + 2olefin \quad (45)$$

(SbR_3 = $SbMe_3$, $SbEt_3$, $SbPr^n$; olefin = C_2H_4, C_3H_6)

Table 5
υPt–X stretching for $[Pt_2X_2(\mu\text{–}X)_2L_2]$ (in cm^{-1})

X	υPt–$X_{terminal}$	υPt–$X_{bridging\ trans\ to\ X}$	υPt–$X_{bridging\ trans\ to\ L}$
Cl	340–365	310–335	250–295
Br	235–260	210–230	175–190
I	170–200	150–190	135–150

determination of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ in benzene gives normal value, however, in boiling acetone, these complexes dissociate reversibly [443]. Metal-halide stretching absorptions in the IR spectra appear in three different regions [416,419,420,444–447]. These different regions for platinum complexes are given in Table 5 while in Table 6 individual absorptions for selected complexes are summarized. Absorption bands associated with υM–Cl (bridging *trans* to Cl) appear at ~300 cm^{-1} (for Pd) and ~325 cm^{-1} (for Pt). The stretching due to bridging M-Cl (*trans* to phosphine) are observed at lower wave numbers (~250 cm^{-1} for Pd and ~260 cm^{-1} for Pt). This absorption is sensitive to the specific ligand and vary with the *trans* effect of the ligand [313]. The terminal M–X absorptions are generally independent of ER_3. The chloro-derivatives usually show a shoulder on the low frequency side of the υPt–Cl stretch which is due to either heavier chlorine isotope (^{37}Cl) [313] or non-planarity of the four-membered Pt_2Cl_2 ring [444].

The NMR spectra of several binuclear palladium and platinum complexes are reported [323,415,416,418,448–453] and data for a few selected platinum complexes are summarized in Table 7. The ^{31}P NMR spectra of palladium complexes exhibit single resonances which are deshielded than those observed for the corresponding platinum complexes [415]. In the ^{31}P NMR spectra of platinum complexes 19 lines are expected due to the presence of three isotopomers, but in most of the cases only three are reported. Thus, the ^{31}P NMR spectra of platinum complexes are characterized by ^1J(Pt–P), ^3J(Pt–P) (~25 Hz), ^4J(P–P) (5 to <2 Hz) and ^2J(Pt–Pt) (140–400 Hz). The magnitude of ^1J(Pt–P) on going from Cl to I decreases while the magnitude of $^2J(Pt\cdots Pt)$ coupling increases in this order [323,418,449]. The ^{195}Pt NMR spectra of phosphine complexes exhibit doublet due to phosphorus coupling. The ^{195}Pt resonances appear in the region δ −3000 to −4400 ppm [418,452]. When a terminal chloride is replaced by a trichlorostannate ligand ^{195}Pt signal is shielded by ~1000 ppm [452].

The halo-bridged complexes show a dynamic equilibrium in solution. Thus, when an equimolar mixtures of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ and $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ are mixed in solution, a dynamic equilibrium is established between homo- and hetero-bi-nuclear complexes (48) [415,448,453]. A kinetic study of this reaction indicates that the exchange occurs via a tetrameric intermediate [453]. This redistribution reaction can even be extended to prepare hetero-bimetallic rhodium/irridium complexes. Thus, treatment of $[M'Cl_2(ppy)]_2$ (M′ = Rh or Ir; ppy = *o*-metalated 2-phenylpyridine) with $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (M = Pd or Pt; $PR_3 = PEt_3$, PBu_3) yields quantitatively hetero-bimetallic

Table 6
υM–X (cm^{-1}) for some selected $[M_2X_2(\mu\text{-}X)_2(ER_3)_2]$

Complex	υM–$X_{terminal}$		υM–$X_{bridging\ trans\ to\ X}$		υM–$X_{bridging\ trans\ to\ ER_3}$		References
	M = Pd	M = Pt	M = Pd	M = Pt	M = Pd	M = Pt	
$[M_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$	356	351	301	327	249	257	[444]
$[M_2Br_2(\mu\text{-}Br)_2(PEt_3)_2]$	268	249	194	210	185	184	[447]
$[M_2I_2(\mu\text{-}I)_2(PEt_3)_2]$	173	177	166	167	139	149	[447]
$[M_2Cl_2(\mu\text{-}Cl)_2(AsEt_3)_2]$	352	350	300	322	261	261	[444]
$[M_2Br_2(\mu\text{-}Br)_2(AsEt_3)_2]$	273	249	193	209	171	182	[447]
$[M_2I_2(\mu\text{-}I)_2(AsEt_3)_2]$	222	205	161	164	139	149	[447]
$[M_2Cl_2(\mu\text{-}Cl)_2(AsBu^t_3)_2]$	344	338	299	322	260	266	[420]
$[M_2Cl_2(\mu\text{-}Cl)_2(SbBu^t_3)_2]$	345	340	320	315	295	290	[419]

Table 7
$^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR data for some $[Pt_2X_2(\mu\text{-}Y)_2(ER_3)_2]$ complexes

Complex	δ ^{195}Pt (ppm)	δ ^{31}P (ppm)	^1J(Pt-P) (Hz)	^3J(Pt-P) (Hz)	^4J(P-P) (Hz)	^2J(Pt-Pt) (Hz)	References
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$	−3409	9.8	3845	20	–	–	[414,452]
$[Pt_2(SnCl_3)_2(\mu\text{-}Cl)_2(PEt_3)_2]$	−4320	12.2	3480	–	–	531	[452]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(AsEt_3)_2]$	−3069	–	–	–	–	–	[452]
$[Pt_2(SnCl_3)_2(\mu\text{-}Cl)_2(AsEt_3)_2]$	−4231	–	–	–	–	–	[452]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$	–	1.8	3822	23.5	2.8	199	[449]
$[Pt_2I_2(\mu\text{-}I)_2(PBu_3)_2]$	–	–	3528	26.0	5.1	380	[449]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PcHx_3)_2]$	−3467	20.2	3875	20	<2	138	[416,418]
$[Pt_2I_2(\mu\text{-}I)_2(PcHx_3)_2]$	–	22.9	3612	–	–	–	[418]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$	–	4.5	4100	–	–	–	[414]
$[Pt_2(SnCl_3)_2(\mu\text{-}Cl)_2\ (PPh_3)_2]$	–	7.5	3721	–	<2.5	165	[451]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(Ptol_3)_2]$	−3353	3.3	4065	–	–	–	[452]
$[Pt_2(SnCl)_2(\mu\text{-}Cl)_2(Ptol_3)_2]$	−4178	5.0	3721	–	–	–	[452]

complexes $[M'(ppy)(\mu\text{-}Cl)_2MCl(PR_3)_2]$ [453].

$$[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + [Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] \rightleftharpoons 2[PdPtCl_2(\mu\text{-}Cl)_2(PR_3)_2] \quad (48)$$

Although three geometrical isomers are possible for the halo-bridged complexes, the *trans* configuration has been established from several X-ray structural analyses (Table 8) [235,415,418,454–469]. In certain cases, from spectral data, a *cis* configuration has also been reported [413,418], and for $[Pd_2I_2((\mu\text{-}I)_2(Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2)]$ has been extablished by structural analysis [467].

Ab initio calculations on several structurally characterized binuclear d^8 metal complexes have been performed by Alvarez and co-workers [470–475] and others [476,477]. The structural preference between planar and hinged configuration results from an interplay of several factors. Following general patterns have emerged:

(i) Most of the X-bridged compounds are planar whereas hinged configuration is common for XR and XR_2 bridged derivatives.
(ii) The energy difference between the bent and planar form is small (within 10 kcal/mol) [473].
(iii) Attractive metal–metal interaction which results from donor-acceptor interaction between the filled dz^2 and empty pz orbitals of the two metal atoms has been a driving force for folding. The metal–metal interactions are modulated by the nature of metal atom, bridging as well as terminal ligands. The stability for bent form increases in the order O < S > Se > Te and F < Cl < Br < I [473].
(iv) The Pd···Pd distance (∼3.4 Å) in the bent Pd compounds is significantly longer than the Pt···Pt distance in the corresponding platinum complexes (∼3.2 Å) [473].
(v) Good σ donors as terminal ligands lead to a stronger metal–metal interaction favouring bent form. A higher electronegativity for the bridging atom favour the planar form. Compounds having only halides as terminal ligands are planar, so is the case for compounds with two bridging halides and one terminal halogen at each metal atom. This is in accord with that poor σ donors and π-basic ligands hinder the bending.
(vi) Among the complexes of the same metal, the bent forms show a large degree of bending (smaller θ) for bridging S than for bridging O ligands. In the former the M–S distance is longer than M–O thus requiring larger bending to achieve a sufficiently short M···M contact.
(vii) Complexes with two S^{2-} or one S^{2-} and one RS^- bridging ligands are bent [476].
(viii) Complexes with two bridging thiolato groups adopt both planar and hinged configurations depending on the relative orientation of R groups (*syn* or *anti*), nature of terminal ligands and their disposition (*cis* or *trans*). The thiolato group in most cases adopt an *anti* configuration owing to steric demands. With *anti* configuration the through ring antibonding interaction is very weak, in such cases with four equal terminal ligands planar structures are formed (e.g. $Pt_2(\mu\text{-}SC_5H_5NMe)_2(dppe)_2]^{2+}$). In contrast, with *syn* R groups and four equal terminal ligands folding takes place due to stronger through-ring antibonding interaction [476]. Although no correlation between relative position of the terminal ligands or the nature of the R group (alkyl or aryl) and the geometry of the Pt_2S_2 ring has been established, hinged and planar rings correspond to the *cis* (e.g. $[Pt_2(\mu\text{-}SEt)_2Cl_2(PPr^n{}_3)_2]$ $\theta = 130^\circ$ [456] and *trans* (e.g. $[Pt_2I_2(\mu\text{-}SCH_2CH_2CMe{=}CH_2)_2(PPh_3)_2]$ (planar Pt_2S_2 ring) [458], respectively.

The chemical reactions of halogen-bridged binuclear complexes can be grouped into three different categories. One of the reactions is bridge cleavage by a variety of neutral donor ligands (49). This reaction is often used for synthetic purposes.

$$[M_2X_2(\mu\text{-}X)_2(ER_3)_2] + 2L \rightleftharpoons 2[MX_2(L)(ER_3)] \rightleftharpoons MX_2L_2 + [MX_2(ER_3)_2] \quad (49)$$

The nature of the product (mixed ligand or symmetrical derivatives) and the stereochemistry of monomeric complex depend upon the M and the relative *trans* affects of the ligands [X, ER_3 and incoming ligand L (49)]. The rate of the reaction is primarily influenced by L. The bridge cleavage with oxygen donor solvents has been studied. The equilibrium shifts increasingly to left (49) as the solvent varied in the order H_2O < MeOH < cyclopropane < acetone ≪ MeCHO, PhCHO < PhCOPh [478]. The bridge cleavage of palladium complexes with nitrogen donors, CO, olefins, etc. invariably yields, *trans*-$[PdX_2(L)(ER_3)]$ [421,479,480], whereas for platinum complexes both *cis* and *trans* isomers are formed [416,421,427,481–484]. Bridge cleavage of platinum complexes with nitrogen donors (simple amines or pyridines) affords *trans*-$[PtX_2(PR_3)L]$ [416,479,481,482,485–487]. However, the cleavage of *cis*-$[Pt_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ with *p*-toluidine yields *cis*-$[PtCl_2(PPh_3)$(toludine)] [413]. Cleavage with bidentate nitrogen donor ligands [488–490], like $R'N{=}CHCH{=}NR'$, yields yet another series of binuclear complexes of general formula, $[MCl_2(PR_3)(\mu\text{-}R'N{=}CHCH{=}NR')MCl_2(PR_3')]$ [488]. Cleavage with phenylhydrazine or *N*,*N*′-diphenylhydrazine yields *trans*-$[MCl_2(PR_3)(NH_2NPhR')]$ (R′ = H or Ph) in which hydrazine is coordinated to the metal atom through the least substituted nitrogen atom (i.e. NH_2) [491]. Bridge cleavage of $[Pt_2Cl_2(\mu\text{-}Cl)_2(ER_3)_2]$ (ER_3 = PEt_3, $Ptol_3$, PPh_3, $AsMe_3$, $AsEt_3$, $AsPr^i_3$, $Astol_3$, $AsMePh_2$) with 8-methylquinoline, benzoquinoline, quinoline 8-carboaldehyde and pyridyl Schiff bases yields *trans*-$[PtCl_2(ER_3)L]$. The latter show weak Pt ← H–C interactions (agostic interaction) to remote

Table 8
X-ray structural data for $[M_2X_2(\mu\text{-}Y)_2(ER_3)_2]$

Complex	Comments	References
$[Pd_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$	Planar Pd_2Cl_2 ring Pd–Cl = 2.270(1)$_{terminal}$ Å Pd–Cl = 2.314(1)$_{bridging\ trans\ to\ Cl}$ Å Pd–Cl = 2.439(1)$_{bridging\ trans\ to\ P}$ Å	[463]
$[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$	Sym trans configuration Pd–Cl = 2.275(3)$_{terminal}$ Å Pd–Cl = 2.321(2)$_{bridging\ trans\ to\ Cl}$ Å Pd–Cl = 2.428(2)$_{bridging\ trans\ to\ P}$ Å	[464]
$[Pd_2Cl_2(\mu\text{-}Cl)_2(PthEt_2)_2]$	planar Pd_2Cl_2 ring Pd–Cl = 2.282(1)$_{terminal}$ Å Pd–Cl = 2.320(1)$_{bridging\ trans\ to\ Cl}$ Å Pd–Cl = 2.431(1)$_{bridging\ trans\ to\ P}$ Å	[465]
$[Pd_2Cl_2(\mu\text{-}Cl)_2\{P(OPh)_3\}_2]$	Sym trans configuration Pd–Cl = 2.269(3)$_{terminal}$ Å Pd–Cl = 2.309(2)$_{bridging\ trans\ to\ Cl}$ Å Pd–Cl = 2.413(2)$_{bridging\ trans\ to\ P}$ Å	[462]
$[Pd_2Cl_2(\mu\text{-}Cl)_2\{P(CF_3)_2\ N\ N\ NPPh_3\}_2]$	Sym trans configuration Pd ··· Pd = 3.481(1) Å	[461]
$[Pd_2Br_2(\mu\text{-}Br)_2(AsMe_3)_2]$	Centro symmetric dimmer Pd–Br = 2.45$_{terminal}$ Å Pd–Br = 2.45$_{bridging\ trans\ to\ Br}$ Å Pd–Br = 2.50(5)$_{bridging\ trans\ to\ As}$ Å	[454]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(NC_5H_3Me_2\text{-}2,6)_2]$	Lutidine plane perpendicular to the Pt plane; Pt–Cl = 2.272(3)$_{terminal}$ Å Pt–Cl = 2.321(3)$_{bridging\ trans\ to\ Cl}$ Å Pt–Cl = 2.320(3)$_{bridging\ trans\ to\ N}$ Å	[426]
$[PtPdCl_2(\mu\text{-}Cl)_2(PEt_3)_2]$	Centro symmetric dimmer, Pd and Pt site disordered	[415]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$	Centro symmetric dimmer Pt–Cl = 2.282(3)$_{terminal}$ Å Pt–Cl = 2.318(3)$_{bridging\ trans\ to\ Cl}$ Å Pt–Cl = 2.431(3)$_{bridging\ trans\ to\ P}$ Å	[460]
$[Pt_2(SnCl_3)_2(\mu\text{-}Cl)_2(PEt_3)_2$		[457]
$[Pt_2\{CF_3C=C(CF_3)(SnCl_3)\}_2(\mu\text{-}Cl)_2(PEt_3)_2]$		[458]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PPr^n{}_3)_2]$	Planar Pt_2Cl_2 ring Pt–Cl = 2.279(9)$_{terminal}$ Å Pt–Cl = 2.315(8)$_{bridging\ trans\ to\ Cl}$ Å Pt–Cl = 2.425(8)$_{bridging\ trans\ to\ P}$ Å	[455]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu^t_2\text{-}\overline{CH_2CH_2C}H_2)_2]$	Asymmetric Pt_2Cl_2 bridge Pt ··· Pt = 3.618(1) Å	[459]
$[Pt_2Cl_2(\mu\text{-}Cl)_2(AsMe_3)_2]$	Pt ··· Pt = 3.481(2) Å Pt–Cl = 2.268(6)$_{terminal}$ Å Pt–Cl = 2.312(5)$_{bridging\ trans\ to\ Cl}$ Å Pt–Cl = 2.394(6)$_{bridging\ trans\ to\ As}$ Å	[456]
$[Pt_2Cl_2(\mu\text{-}SCN)_2(PPr^n{}_3)_2]$	α- (m.p. 154 °C) and β- (m.p. 172 °C) forms both give monoclinic crystals, space group $P2_{1/c}$ and $P2_{1/n}$	[466]
$[Pd_2I_2(\mu\text{-}I)_2\{Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2\}]$	*cis*-Phosphine	[467]
$[Pd_2I_2(\mu\text{-}I)_2(Ph_2P\{(CH_2CH_2O)_2CH_2CH_3\}_2)_2]$	Anti-isomer	[467]
$[Pd_2Cl_2(\mu\text{-}Cl)_2(Ph_2PPr^n)_2]$	Sym trans isomer	[468]
$[Pd_2Cl_2(\mu\text{-}Cl)_2(Ph_2PCH_2CH=CH_2)_2]$	Sym trans isomer	[468]
$[Pd_2I_2(\mu\text{-}I)_2(Ph_2PCX=CF_2)_2]$, X = Cl or F	Sym trans structure	[469]

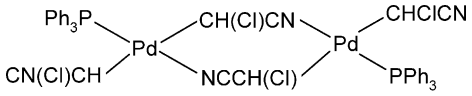
protons as inferred from *J*(Pt–H) coupling constants (8–39 Hz) [489,492–495].

The reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ with PMe_2Ph in $CHCl_3$ at RT yields a mixture of *cis*- and *trans*-$[PtCl_2(PMe_2Ph)_2]$, however, at −60 °C ionic products, $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ are formed, which on warming give a neutral complex. With a high local concentration of phosphine the reaction initially gives $[(PMe_2Ph)_2ClPt(\mu\text{-}Cl)PtCl_2(PMe_2Ph)]$ which reacts with more phosphine to form either *trans*-$[PtCl_2(PMe_2Ph)_2]$ or $[PtCl(PMe_2Ph)_3]^+[PtCl_3(PMe_2Ph)]^-$ [496,497]. The reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ with 2,5-di-*tert*-butyl-1-thia-3,4-diphosphole yields a symmetric *cis* diplatinum complex $[\{PtCl_2(PEt_3)\}_2(P_2SC_2Bu_2^t)]$ in which both the ring phosphorus atoms are coordinated to the "$PtCl_2(PEt_3)$" fragments [498].

Bridge-cleavage reactions of platinum complexes with olefins [499–508], carbon monoxide [411,499,502,509–512], dialkylsulfoxides (R_2SO) [508,513,514], etc. [496,497,513,515,516] have been investigated. In these reactions initially a *trans*-$[PtX_2(PR_3)L]$ forms which isomerizes to a thermodynamically more stable *cis* isomer. The isomerization is autocatalytic and depends on eliminated L from *trans* isomer in solution. The olefin loss from the *trans* product is quite rapid and facile. Volatile olefins (such as $CH_2{=}CH_2$, $MeCH{=}CH_2$) can be removed easily by bubbling nitrogen even at −60 °C [508]. The liberated olefin catalyses isomerization process to give a more stable *cis* derivative, although the latter too loses olefin in solution to give $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$. The olefin complexes are favoured by chloride over bromide and no iodo derivatives are isolated. This is in confirmity of bridge strength sequence of I > Br > Cl. With dialkenes, e.g. 1,3-butadiene, bridge cleavage affords yet another binuclear complexes, $[(PR_3)ClPt(CH_2{=}CH{-}CH{=}CH_2)PtCl_2(PR_3)]$ [506].

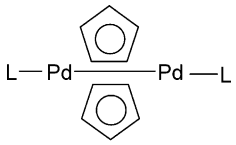
Binuclear platinum complexes, $[Pt_2Cl_2(\mu\text{-}Cl)_2(ER_3)_2]$ react with $SnCl_2$ in halogenated solvents via insertion at terminal chloride to yield trichlorostannate complexes, $[Pt_2Cl(SnCl_3)(\mu\text{-}Cl)_2(ER_3)_2]$ and $[Pt_2(SnCl_3)_2(\mu\text{-}Cl)_2(ER_3)_2]$ depending on platinum to $SnCl_2$ mole ratio [415,451,452,457,517–519]. Reaction in acetone is, however, more complex and yields a mixture of products [451]. The trichlorostannate complexes show high catalytic activity in olefin hydrogenation [517]. Activated acetylenes such as hexafluorobutyne, inserts across the Pt–Sn bonds to give $[Pt_2(CF_3C{=}C(SnCl_3)CF_3)_2(\mu\text{-}Cl)_2(PEt_3)_2]$ in which the chloro-bridge is preserved as shown by X-ray crystallography [458]. Insertion of other reagents, such as $M(NR_2)_2$ (M = Ge, Sn, Pb; R = $SiMe_3$), into the terminal Pt–Cl bond of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ has also been reported, $[Pt_2\{SnCl(NSiMe)_3)_2\}_2(\mu\text{-}Cl)_2(PEt_3)_2]$ [520,521].

The bridging halogen can be substituted with another anionic ligand such as thiocyanate to afford thiocyanato-bridged derivatives, $[M_2Cl_2(\mu\text{-}SCN)_2(PR_3)_2]$ [466,522–525]. Diazoacetonitrile decomposes in the presence of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ with the formation of another binuclear complex **32** [526]. Several other reactions are described in other sections.



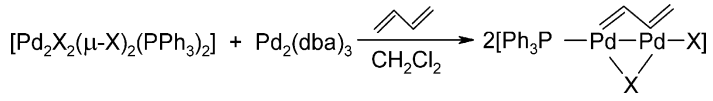
(32)

Treatment of $[Pt_2X_2(\mu\text{-}X)_2(PR_3)_2]$ (X = Cl, Br, I; PR_3 = PEt_3, PMe_2Ph) with mono-substituted acetylenes, RC≡CH (R = Me, Et, Ph), in alcohols (MeOH, EtOH or Pr^iOH) affords alkoxy(organo)carbene complexes, $[PtX_2\{C(OR')(CH_2R)\}(PR_3)]$ [527]. Electron rich olefins react with $Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$ to give monomeric carbene derivatives [528]. Reactions of $[M_2X_2(\mu\text{-}X)_2(PR_3)_2]$ (X = Cl, Br or I) with thallium or mercury cyclopentadienide and Na/Tl salts of substituted cyclopentadiene inTHF yield $[M(C_5H_4R')(X)(PR_3)]$ [529,530]. Reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2\{P(OPh)_3\}_2]$ with four equivalents of TlCp affords a Pd(I) dimer **33** [531].



(33)
(L = $P(OPh)_3$)

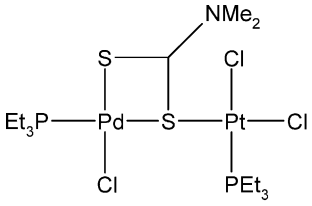
Reaction of $[Pd_2X_2(\mu\text{-}X)_2(PPh_3)_2]$ (X = Cl, Br, I) and $Pd_2(dba)_3$ in the presence of buta-1,3-diene affords a deep-red palladium(I) complexes in 70–82% yield (50) [532].



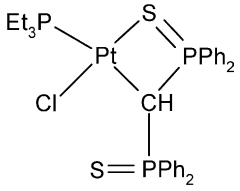
(50)

The rections of $[M_2Cl_2((\mu\text{-}Cl)_2(PR_3)_2]$ with anionic ligands result into ligand substitution as well as bridge cleavage [533]. The dianionic ligands, like 2,3-dihydroxypyridine afford metallomacrocyclic compounds [534]. The reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ with NaS_2CNMe_2 in 1:1 molar ratio yields a rather unexpected product **34** as characterized by X-ray crystallography [535]. The reactions of $[M_2X_2(\mu\text{-}X)_2(PR_3)_2]$ with alkali or ammonium salts of various dithio acid ligands in 1:2 stochiometry yield complexes of the general formula $[MX(S^{\cap}S)(PR_3)]$ (M = Pd or Pt; X = Cl, Br, I; $S^{\cap}S$ = S_2CNR_2, S_2COR, S_2PR_2, $S_2P(OR)_2$; PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3) in which dithio ligand acts in a chelating fashion [536–538]. However, when these reactions are carried out with excess of sodium salts, $M(S_2CNR_2)_2$ or $[M(S_2PMe_2)_2(PR_3)]$ are formed [536]. The difference in reactivity is attributed to higher nucleophilicity of S_2CNR_2

as compared to S_2PMe_2. The chloro-bridged platinum dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$, reacts with $LiCH(Ph_2P{=}S)_2$ to give **35** [539].



(34)



(35)

3.3.2. Organometallic (σ bonded) complexes

Although organolithium and Grignard reagents are powerful alkylating/arylating agents, their reactions with $[M_2X_2(\mu\text{-}X)_2(PR_3)_2]$ (X = halogen) in many cases result in either poor yields or complete decomposition. Reaction of PhLi with $[Pt_2X_2(\mu\text{-}X)_2(PR_3)_2]$ yields $[PtPh_2(PR_3)_2]$ when X = Cl, but with X = Br or I, binuclear complexes $[Pt_2Ph_2(\mu\text{-}X)_2(PR_3)_2]$ (X = Br or I) have been isolated in low yields (20–30%) [212]. Similar reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with MeLi leads to the formation of palladium metal even at −40 °C [540]. However, reaction of benzylmagnesium chloride with $[Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ in THF-ether mixture proceeds smoothly to give $[Pd_2Bz_2(\mu\text{-}Cl)_2(PEt_3)_2]$ in 62% yield [541].

Several milder alkylating/arylating agents, such as organoaluminium, organotin and organomercury, have been used successfully to prepare binuclear organometallic palladium and platinum complexes. The reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ ($PR_3 = PEt_3$, PBu_3, PMe_2Ph) with trimethylaluminium in diethylether affords chloro-bridged dimer, $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ [542]. In these reactions air and moisture sensitive Me_3Al can be replaced with tetramethyltin. Reaction proceeds with a greater ease in benzene at room temperature and completes in 15–90 min depending on the nature of phosphine/arsine [233,235,236] (51). The methyl palladium complexes can be obtained alternatively by treatment of [PdMeCl(COD)] with one equivalent of a neutral donor ligands (52) [543,544].

$$[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + 2Me_4Sn \rightarrow [Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2] + 2Me_3SnCl \quad (51)$$

$$2[PdMeCl(COD)] + 2L \rightarrow [Pd_2Me_2(\mu\text{-}Cl)_2(L)_2] + 2COD \quad (52)$$

(L = PEt_3, $PMePh_2$, PPh_3, PBz_3, $AsPh_3$, 2, 6-lutidine)

The reaction (51) with platinum complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ is rather slow and requires more than 36 h [545]. It was later shown that the reaction proceeds with excessive decomposition (53) [546]. Pure $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ is obtained by passing the reaction mixture, after removal of Me_3SnCl, through a Florisil column and recrystallizing the product several times and separating the colourless crystals mechanically [233].

$$[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2] + \text{excess } Me_4Sn \rightarrow cis,trans\text{-}[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2] + trans\text{-}[PtCl_2(PMe_2Ph)_2] + \text{Pt metal} + Me_3SnCl + \text{unreacted } Me_4Sn \quad (53)$$

Trimethylaryltins (Me_3ArSn) are useful arylating agents. Eaborn et al. [502] have shown that the treatment of $[PtCl_2(CH_2{=}CH_2)(PR_3)_2]$ with Me_3ArSn yields arylplatinum dimers, $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ (54). However, reaction (54) with Me_4Sn does not take place even in refluxing dichloromethane [502].

$$2cis\text{-}[PtCl_2(CH_2{=}CH_2)(PR_3)] + 2Me_3ArSn \rightarrow [Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2] + 2\,Me_3SnCl + 2\,CH_2{=}CH_2 \quad (54)$$

Although organomercury (R_2Hg) compounds have also been employed to prepare binuclear palladium and platinum complexes [547–549], their toxicity and a tedious process to remove the side product (RHgCl) by sublimation poses problems and at times yields are moderate. Thus, reaction of $[Pd_2Cl_2(\mu\text{-}Cl)(PR_3)_2]$ with R_2Hg affords $[Pd_2R_2(\mu\text{-}Cl)_2(PR_3)_2]$ (R = Ph, tol, Bz; $PR_3 = PBu_3$, $PMePh_2$ or PPh_3) in 22–43% yield [547].

Palladium(O) complexes have been used in several palladium catalysed organic transformations. The reactions involving arylhalides often proceed via a binuclear organopalladium complex formed by oxidative addition of an arylhalide on Pd(O) complex. Indeed these dimers have been isolated in several instances (55) [550–557]. The reaction of Pd_2dba_3 with 2-equivalents of $\{(C_6F_5)_2PCH_2\}_2$ in refluxing THF leads to the formation of a phosphido bridged complex, $[Pd_2(C_6F_5)_2\{\mu\text{-}P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}_2]$ [558]. Besides these general procedures, other less commonly used routes have been also employed for the preparation of binuclear complexes [417,559–562]. For instance, terminal phosphine exchange, as in $[PdAr(\mu\text{-}Br)(P\text{-}o\text{-}tol_3)_2]$ by $(C_5H_4PBu^t_2)_2Fe$, has been employed successfully [563].

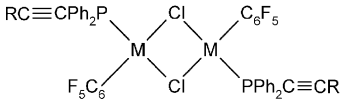
$$2Pd(dba)_2/Pd_2(dba)_3 + 2L + 2ArX \rightarrow [Pd_2Ar_2(\mu\text{-}X)_2L_2] + dba \quad (55)$$

$ArX = PhI, BrC_6H_4R\text{-}4\,(R = Me, OMe, Bu^n, Bu^t)$,

$IC_6H_4R\text{-}4\,(R = Bu^t, Me, OMe;\ L = AsPh_3, Ptol_3\text{-}o)$

Unlike simple organolithiums or Grignard reagents, perhalophenylmagnesium halides (C_6F_5MgBr or C_6Cl_5MgCl) have been successfully used for arylation of $[Pd_2X_2(\mu\text{-}X)_2(PR_3)_2]$ (56) [564]. The organothalium reagent, $[Tl(\mu\text{-}Br)(C_6F_5)_2]_2$ reacts with *trans*-$PdCl_2L_2$ in 2:1 ratio in

refluxing benzene to afford a mixture of $[Pd_2(C_6F_5)_2(\mu\text{-}Cl)_2L_2]$ and $[PdCl(C_6F_5)L_2]$ which are separated by fractional crystallization [565,566]. The chloro-bridged



(36)

perhalophenyl palladium complexes have been prepared conveniently by refluxing an acetone solution of $PdCl_2$ with $Pd(C_6X_5)_2L_2$ (57) [566]. A variety of asymmetric homo- and hetero-binuclear complexes, $[R_2Pd(\mu\text{-}X)_2ML_2]$, has been isolated by the reaction of a labile palladium complex *cis*-$PdR_2(PhCN)_2$ with MX_2L_2 (58) [567,568].

$$[Pd_2X_2(\mu\text{-}X)_2(PR_3)_2] + 2C_6F_5MgBr \rightarrow [Pd_2(C_6F_5)_2(\mu\text{-}X)_2(PR_3)_2] + 2MgBrX \quad (56)$$

(X = Cl, Br)

$$Pd(C_6X_5)_2L_2 + PdCl_2 \xrightarrow{\text{Acetone}} [Pd_2(C_6X_5)_2(\mu\text{-}Cl)_2L_2] \quad (57)$$

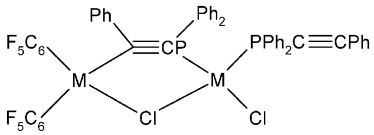
(X = F, Cl; L = py, PPh_3, $AsPh_3$, $SbPh_3$)

$$PdR_2(PhCN)_2 + cis\ MX_2L_2 \rightarrow [R_2Pd(\mu\text{-}X)_2ML_2] + 2PhCN \quad (58)$$

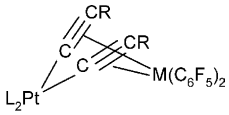
(*R* = C_6F_5; 2, 4, 6-$C_6H_2F_3$; X = Cl, Br, I, SCN; M = Ni, Pd or Pt)

Similarly other labile complexes $[M(C_6F_5)_2(THF)_2]$ or $Pt(C_6F_5)_2(CO)_2$ have been used for the preparation of several homo- and hetero-binuclear complexes [569–571]. Thus, while the reaction of $M(C_6F_5)_2(THF)_2$ with $[Pd(C_6F_5)X(PPh_3)_2]$ readily forms trinuclear complex, $[M(C_6F_5)_2\{XPd(C_6F_5)(PPh_3)_2\}_2]$ (M = Pd or Pt; X = CN or SCN), on the other hand treatment of $Pt(C_6F_5)(CO)_2$ with $[PdX(C_6F_5)(PPh_3)_2]$ affords binuclear derivatives $[(C_6F_5)_2(CO)Pt(\mu\text{-}X)Pd(C_6F_5)(PPh_3)_2]$ (X = CN or SCN) [570].

Reaction of $M(C_6F_5)_2(THF)_2$ with $M'Cl_2(Ph_2PC{\equiv}CR)_2$ (R = Ph or Bu^t) in 1:1 molar ratio yields asymmetric complexes, $[(C_6F_5)_2M(\mu\text{-}Cl)_2M'(Ph_2PC{\equiv}CR)_2]$ which slowly (~1 day) isomerizes to a thermodynamically stable sym *trans* products, **36** [571]. The $Pt(C_6F_5)_2(THF)_2$ reacts with $MCl_2(Ph_2PC{\equiv}CPh)_2$ to give yet another sparingly soluble binuclear complex (**37**) structure of which is established by X-ray crystallography [571]. The reaction of $M(C_6F_5)_2(THF)_2$ with $Pt(C{\equiv}CR)_2L_2$ (L = $Ph_2PC{\equiv}CR'$, PPh_3, ½dppe or ½COD; R′ = Ph or Bu^t) gives doubly alkynyl-bridged binuclear derivatives (**38**) [572,573]. Neutral bimetallic platinum hydride complexes, $[Pt_2(\mu\text{-}X)(\mu\text{-}H)(C_6F_5)_2(PR_3)_2]$ have also been synthesized and characterized [574].



(37)



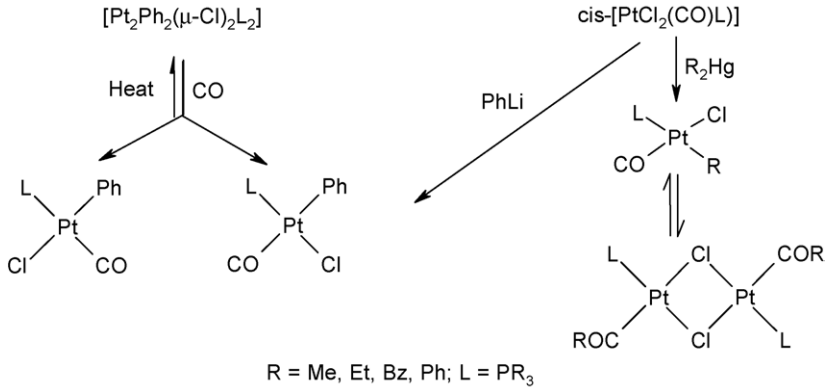
(38)
M = Pd, Pt

Organometallic derivatives, like tetrahalo complexes described in Section 3.3.1, undergo primarily three classes of reactions: (a) substitution of bridging halide with another anionic ligand; (b) insertion reactions; and (c) bridge splitting reactions with neutral donors. The latter reactions give mono-nuclear mixed ligand complexes, *trans*-[MRXLL′] (59) [502,542,543,546,547,567]. With non-chelating bidentate ligand such as 4,4′-bipyridine, a single-bridged binuclear complexes are formed [567]. Although reaction of $[Pd_2Ar_2(\mu\text{-}X)_2(PR_3)_2]$ with tertiary phosphines results in the formation of $[PdArCl(PR_3)L]$, with strongly electron donating phosphines (such as PBu_3^t), reductive elimination of arylhalide takes place with concomitant formation of $Pd(PBu_3^t)_2$ [575].

$$[M_2R_2(\mu\text{-}X)_2(L)_2] + 2L' \rightarrow 2[MR(X)LL'] \quad (59)$$

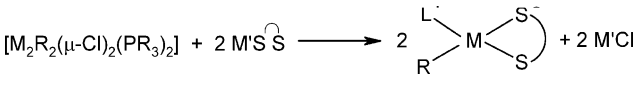
Bridged cleavage with carbon-monoxide is of particular interest. Methyl- and aryl-palladium complexes react with CO to produce acyl or aroyl palladium dimers, $[Pd_2(COR)_2(\mu\text{-}Cl)_2(PR_3)_2]$ [542,543,547]. Similar reaction with the corresponding platinum complexes yield two isomers of [PtR(Cl)(CO)L] which are reluctant to undergo carbonyl insertion [511,568,576] and attempts to promote this either by heating or addition of excess phosphine lead to elimination of CO. The third isomer, in which Ar is *trans* to L, produced by the reaction of *cis*-$PtCl_2(CO)L$ with R_2Hg, readily undergoes carbonyl insertion and yields a chloro-bridged aroyl derivative (Scheme 11) [511,568,576–579]. The monomer ⇌ dimer equilibrium exists in solution. Electron-donating 3- or 4-substituents favours formation of arylplatinum dimer while electron withdrawing group inhibits the process. The aryl groups substituted at 2-position do not undergo insertion possibly due to steric reasons [579]. Although reaction of R_2Hg with *cis*-$[PtCl_2(CO)L]$ yields a dimeric aroyl complex, reaction is influenced by L. When L is *o*-tol_3P, $AsPh_3$ or $AsMePh_2$ only [PtPh(Cl)(CO)L] is formed [417]. Reaction of Me_3ArSn with $[PtCl_2(CO)(PR_3)]$ also affords binuclear aroyl complexes, $[Pt_2(COAr)_2(\mu\text{-}Cl)_2(PR_3)_2]$ [502]. Other alternative methods have also been employed for the preparation binuclear acyl/aroyl derivatives [543,580–582]. These complexes have been used in carbonylation of alkylhalides [582].

Treatment of $[Pd_2Ar_2(\mu\text{-}Br)_2(PR_3)_2]$ with sodium aryloxide affords aryloxide bridged complexes *trans*-$[Pd_2Ar_2(\mu\text{-}OAr')_2(PR_3)_2]$ in which Pd_2O_2 ring is puckered (hinge



Scheme 11.

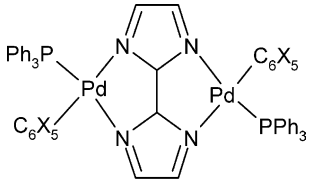
angle 33.3°) [563]. These complexes on thermolysis give diaryl ether. Reactions of $[M_2R_2(\mu\text{-}Cl)_2(PR_3)_2]$ with 2 mol equivalents of sodium/potassium/ammonium salts of a dithio acid afford mononuclear complexes, $[MR(S^{\frown}S)(PR_3)]$ (60) [583–585]. A mononuclear complex $[PtPh(Cp)(PPh_3)]$ is formed in low yields by the reaction between $[Pd_2Ph_2(\mu\text{-}Cl)_2(PPh_3)_2]$ and TlCp [586]. Treatment of $[Pd_2(C_6F_5)_2(\mu\text{-}Cl)_2(PPh_3)_2]$ with thallous 2,2′-biimidazolate, 2,2′-bibenziimidazolate and 4,5,4′,5′-tetramethylbimidazolate affords another series of binuclear complexes **39** [587].



(60)

[M = Pd or Pt; M′ = Na, K, NH_4; R = Me, Ph, tol;

$S^{\frown}S = S_2COEt, S_2CNR'_2, S_2PR'_2, S_2P(OR')_2$]



(39) (X = F or Cl)

IR spectra of acyl and aroyl complexes, exhibit a υCO absorption in the regions 1645–1730 cm^{-1} [542,543,547] and 1600–1650 cm^{-1}, [417,502,511,577,578] for Pd and Pt derivatives, respectively. The υPt–Cl stretching vibrations for Pt–R and PtCOR complexes have been reported in the region 260–280 cm^{-1} and in some cases two absorptions are observed which are assigned to *cis* and *trans* isomers [502].

Except in some cases, $[Pd_2Me_2(\mu\text{-}Cl)_2(PEt_3)_2]$ [543], $[Pd_2(COR)_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (R = Bz or Ph) [547], the palladium complexes exhibit only one ^{31}P NMR signal. A *trans* configuration has been assigned [233,542,547]. The platinum complexes, in contrast, display two closely spaced ^{31}P NMR signals which are attributed to *cis* and *trans* forms [502,546]. The relative concentration of two isomers is solvent dependent [578]. The magnitude of ^1J(Pt–P) for these complexes is larger than those for the corresponding tetrahalo derivatives and fall in the region 3900–5500 Hz [502,511,578]. The large magnitude of ^1J(Pt–P) has been attributed to the *cis* influence of the terminal organo groups [578]. The *cis* and *trans* isomerization in acyl and aroyl complexes is usually rapid on NMR time scale leading to broadening or coalesced signals [511]. There is an exchange of dimers in solution. Thus, when $CDCl_3$ solutions of $[Pd_2Ph_2(\mu\text{-}Cl)_2(PBu_3)_2]$ and $[Pd_2Bz_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ are mixed, a complex of the type $[(PBu_3)PhPd(\mu\text{-}Cl)_2Pd(Bz)(PMePh_2)]$ forms without phosphine exchange between PdPh and PdBz centers [547].

Although these complexes exhibit *cis* and *trans* isomerization in solution, on recrystallization only one isomer, i.e. *trans* is crystallized out. The X-ray structures of $[Pd_2Me_2(\mu\text{-}Cl)_2(AsPr^i_3)_2]$ (Fig. 15) [235] and $[Pt_2(COEt)_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (Fig. 16) [578] have been reported. The four-membered ring M_2Cl_2 adopts a planar conformation. Similar planar skeleton is reported for asymmetric complex $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PEt_3)_2]$ [568].

3.3.3. Complexes with small bite anionic three-atom bridging ligands

A myriad of anionic three-atom ligands (abc^-) incorporating Group 14 (C), 15 (N, P, As) and 16 (O, S, Se, Te) elements is known as there are fairly large permutation and combination possibilities. Examples of such ligands include carboxylate, triazine, amidine, 2-chalcogeno-pyridines, phosphorus based acids. Electronic and steric properties of each group of ligands can be further modified with a suitable choice of organic substituents. The bite size of the ligand is greatly influenced by the nature of ligand core atoms (abc). Bite distance of some common ligands are summarized in Table 9.

The reactions (61) of anionic three-atom (abc^-) ligands with halo-bridged binuclear palladium and platinum complexes yields a variety of products depending on the ligand

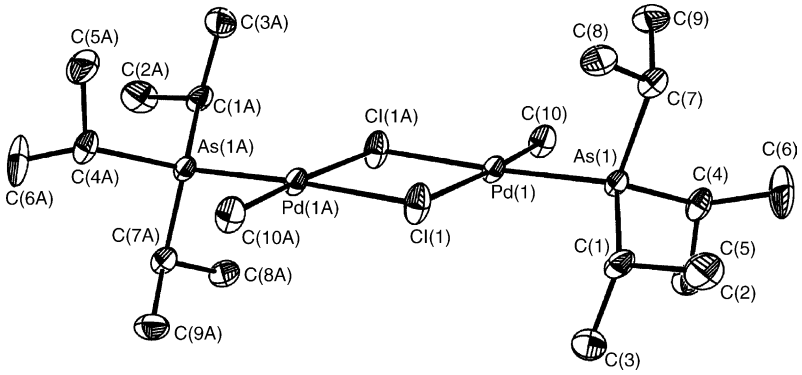


Fig. 15. Molecular structure of $[Pd_2Me_2(\mu\text{-}Cl)_2(AsPr^i{}_3)_2]$.

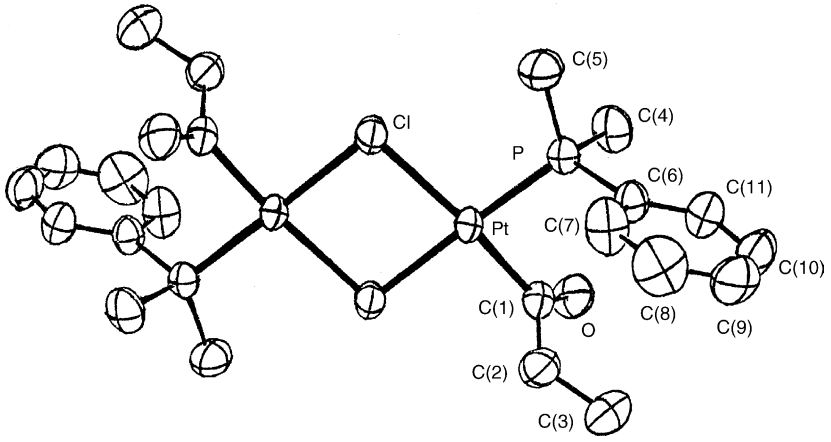


Fig. 16. Molecular structure of $[Pt_2(COEt)_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (reproduced with permission from ref. [578]).

Table 9
Bite distance of some common anionic three-atom ligands

Ligand	Bite (Å)
Diaryltriazene	~2.23
Acetate	2.23–2.26
Diarylformamidine	2.33–2.40
2-Hydroxy pyridinates	~2.34
Sulfate	2.45–2.47
Phosphates	2.52–2.56
2-Mercapto pyridinates	2.71–2.74
2-Seleno pyridinate	2.70
Pyrophosphate ($H_2P_2O_5$)	2.86–2.98
Dithiocarboxylate	2.99–3.11
Dithiophosphate	~3.3

bite and the electronic and steric properties of auxiliary ligands.

$$M_2X_2(\mu\text{-}Y)_2L_2 + 2\ abc^- \rightleftharpoons M_2X_2(\mu\text{-}abc)_2L_2 + 2\ [MX(\eta^2\text{-}abc)L] \quad (61)$$

Treatment of $[M_2X_2(\mu\text{-}X)_2L_2]$ with silver carboxylates in halogenated solvents (61) yields several carboxylato-bridged complexes, $[M_2X_2(\mu\text{-}O_2CR)_2L_2]$ (M = Pd, Pt; X = Cl, Br, I; R = Me, CH_2Cl, CH_2Br, CCl_3, CF_3, CMe_3, CPh_3; L = PEt_3, PPr_3, PBu_3, PMe_2Ph, $PMePh_2$, PPh_3, $Ptol_3$, $AsMe_2Ph$) [588–591]. However, when *trans*-$[Pt_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ is treated with six equivalents of AgOAc, a tetranuclear complex $[Pt(OAc)_3(PPh_3)Ag]_2$ is formed as characterized by X-ray crystallography [591]. The latter complex undergoes a variety of reactions with transition metal chloro complexes. For example, reaction with $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ yields $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}OAc)_2Pt(OAc)(PPh_3)]$ [591] while with $[Re(OAc)Cl_2]_2$ affords $[Pt_2(\mu\text{-}OAc)_2(\eta^1\text{-}OAc)_2(PPh_3)_2]$ **40** (62) [589,591]. The corresponding palladium complex, $[Pd_2(\mu\text{-}OAc)_2(\eta^1\text{-}OAc)(PPh_3)_2]$ **41** has also been prepared [592]. Interestingly the reaction of $[Pd(OAc)_2]_3$ with PPh_3 produces an aryl complex, $[Pd_2Ph_2(\mu\text{-}OAc)_2(PPh_2)_2$ [593]. The **40** reacts with formic acid to give initially a substitution product $[Pt_2(O_2CH)_2(O_2CH)_2(PPh_3)_2]$ which after evolution of CO_2 and benzene converts into a polymeric phosphide cluster $[Pt(PPh_2)]_n$ [589,591]. In contrast the palladium complex **41** under similar conditions gives 60–70% hydrido complex $[Pd_2(PPh_2)H_x]_n$ and about 8–10% $[Pd_2Ph_2(\mu\text{-}O_2PPh_2)_2(PPh_3)_2]$ [591].

$$[Pt(OAc)_3(PPh_3)Ag]_2 \xrightarrow[-2AgCl\ -[Re(OAc)_2Cl]_2]{[Re(OAc)Cl_2]_2.2H_2O} [Pt_2(OAc)_2(\mu\text{-}OAc)_2(PPh_3)_2] \quad (62)$$

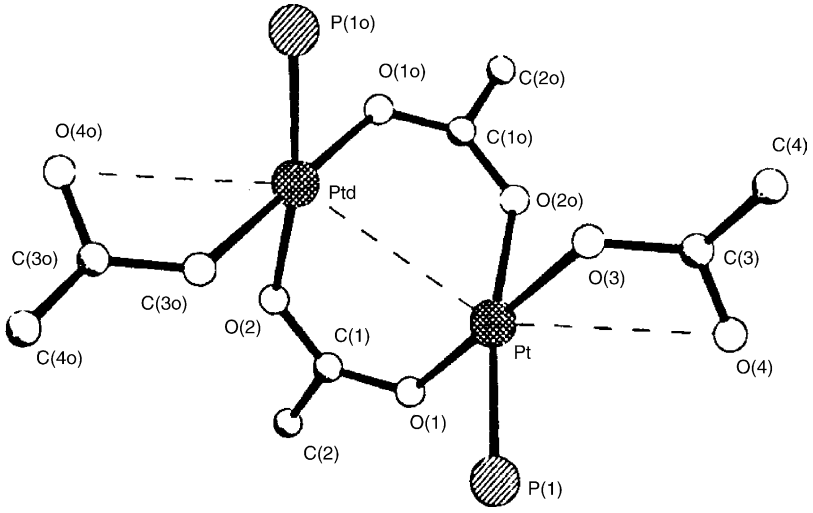
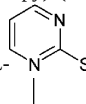
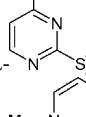
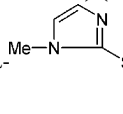
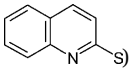


Fig. 17. Molecular structure of $[Pt_2(OAc)_2(\mu\text{-}OAc)_2(PPh_3)_2]$ (reproduced with permission from ref. [591]).

The crystal structures of $[Pd_2Cl_2(\mu\text{-}OAc)_2(PMe_2Ph)_2]$ [594], $[Pd_2Ph_2(\mu\text{-}OAc)_2(PPh_3)_2]$ [593] and $[Pt_2(OAc)_2(\mu\text{-}OAc)_2(PPh_3)_2]$ (Fig. 17) [589,591] have been established by X-ray diffraction. The two metal atoms are bridged by two acetate groups in the *cis* position and the phosphine ligands are mutually *trans*. The metal–metal distances are more than the sum of their covalent radii indicative of the absence of metal–metal interactions (Table 10). Although the X-ray structural data does not support any metal–metal interaction, the ^{31}P and ^{195}Pt NMR data [$J(Pt–P') = \sim 30$ Hz; $J(Pt–Pt') \sim 1000$ Hz)] (Fig. 18) strongly favours direct M–M interactions in a d^8 metal ion configuration [590]. Most of the carboxylato-bridged complexes are dynamic in nature. The exchange process has low activation energies (3–6 kcal/mol) and involves rapid solvolysis of metal carboxylate bond leading to a mono-μ-carboxylato bridged intermediate rather than inversion of the "$M_2(O_2C)_2$" ring [588].

Another family of small bite anionic three-atom ligands includes triazenes. Several triazenido-bridged palladium and platinum complexes, $[M_2X_2(\mu\text{-}R'NNNR')_2(PR_3)_2]$ (M = Pd or Pt; X = Cl, Me or tol) have been prepared by employing reaction (61) [595,596]. They can also be obtained by substituting bridging acetate in $[Pd_2Cl_2(\mu\text{-}OAc)_2(PMe_2Ph)_2]$ with a triazene (PhNNHNPh or PhNNNHMe) [588,595]. The

Table 10
Binuclear palladium and platinum complexes containing anionic three-atom bridging ligands

Complex	M ··· M distance (Å)	References
$[Pd_2Cl_2(\mu\text{-}OAc)_2(PMe_2Ph)_2]$	2.944(2)	[594]
$[Pd_2Ph_2(\mu\text{-}OAc)_2(PPh_3)_2]$	3.079	[599]
$[(\eta^3\text{-}C_3H_5)Pd(OAc)_2Pt(OAc)(PPh_3)]$	2.89	[589,591]
$[Pt_2(OAc)_2(\mu\text{-}OAc)_2(PPh_3)_2]$	3.10	[589,591]
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PEt_3)_2]$	2.9302(8)	[596]
$[Pd_2Cl_2(\mu\text{-}PhN\,CMe\text{-}NPh)_2(PMe_2Ph)_2]$	2.914(2)	[596]
$[Pt_2Cl_2(\mu\text{-}O_2PPh_2)_2(PMe_2Ph)_2]$	3.22	[599]
$[Pd_2Ph_2(\mu\text{-}O_2PPh_2)_2(PPh_3)_2]$	5.35	[591,600]
$[Pd_2Cl_2(\mu\text{-}Spy)_2(PMe_3)_2]$	2.942(2)	[603]
$[Pd_2Cl_2(\mu\text{-}Spy)_2(PMe_2Ph)_2]$	2.921(2)	[604]
$[Pd_2Cl_2(\mu\text{-}Spy)_2(PMePh_2)_2]$	2.982(3)	[604]
$[Pd_2Cl_2(\mu$-  $)_2(PMe_3)_2]$	2.915(1)	[608]
$[Pd_2Cl_2(\mu$-  $)_2(PMe_3)_2]$	2.924(1)	[608]
$[Pd_2Cl_2(\mu$-  $)_2(PMe_3)_2]$	3.104(2)	[608]
$[Pd_2(\eta'\text{-}qnS)_2(\mu\text{-}qnS)_2(PMe_3)_2]$, (qnS = 	3.224(2)	[607]
$[PdCl_2(PR_3)(\mu\text{-}C_5H_4NSe)PdCl(PPr_3)]$		[606]

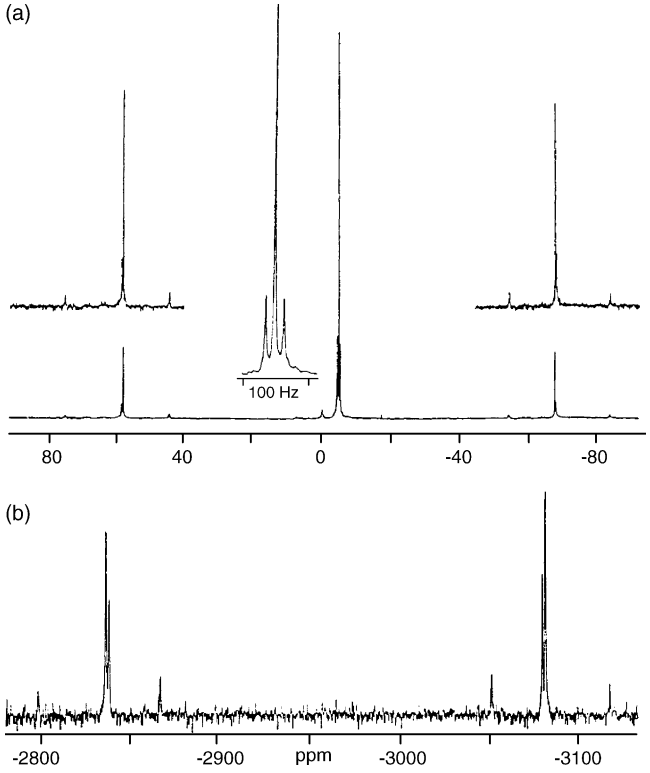


Fig. 18. (a) $^{31}P\{^1H\}$ and (b) $^{195}Pt\{^1H\}$ NMR spectra of $[Pt_2Cl_2(\mu\text{-}OAc)_2(PMe_2Ph)_2]$ (reproduced with permission from ref. [590]).

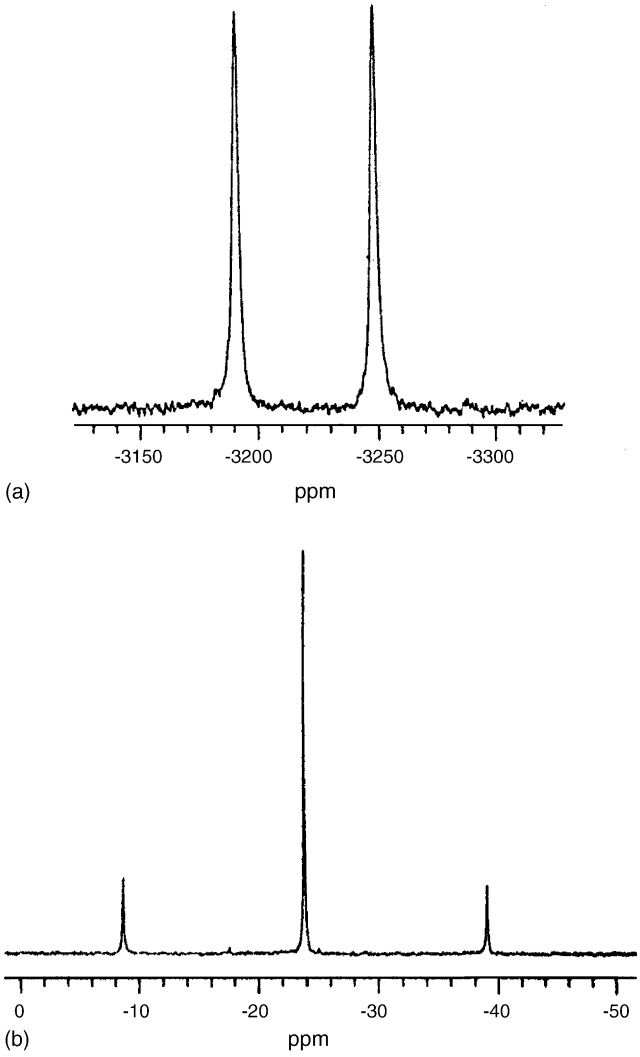


Fig. 19. (a) $^{31}P\{^1H\}$ and (b) $^{195}Pt\{^1H\}$ NMR spectra of $[Pt_2Cl_2(\mu\text{-}PhNCMeNPh)_2(PEt_3)_2]$ (reproduced with permission from ref. [598]).

platinum complexes react reversibly with HCl [595]. The reaction (61) with bulky X ligands, such as 2,4,6-$Me_3C_6H_2$, affords mononuclear palladium complex, $[Pd(Mes)(\eta^2\text{-}PhNNNPh)(PPh_3)]$ [597].

Unlike carboxylato-bridged complexes, the triazinedo-bridged complexes are stereochemically rigid in the temperature range −50 to +50 °C [595]. The ^{31}P and ^{195}Pt NMR spectra exhibit J(Pt–P′) (∼50 Hz) and J(Pt–Pt′) (∼1500 Hz) coupling constants in spite of four-bond separation between two platinum atoms [595]. This has been interpretated in terms of metal–metal interactions, although X-ray structure of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PEt_3)_2]$ reveals that the large separation of two metal atoms (2.93 Å) does not account for any metal–metal interaction [596].

Amidines, another family of anionic three-atom ligands, are isoelectronic and isostructural to carboxylates and triazenes. A series of amidinato and formamidinato-bridged palladium and platinum complexes, $[M_2Cl_2(\mu\text{-}ArN{=}CR'\text{-}NAr)_2(PR_3)_2]$ (M = Pd or Pt; $PR_3 = PEt_3$, PBu_3, PMe_2Ph; $PMePh_2$, PPh_3; Ar = Ph, tol, 4-$MeOC_6H_4$; R′ = H, Me or Ph) [596–598] have been isolated employing reaction (61). In the ^{31}P and ^{195}Pt NMR spectra (Fig. 19) J(Pt–P′) and J(Pt–Pt′) coupling is absent. The absence of such coupling has been interpreted in terms of vanishingly small metal–metal interactions in these complexes which is manifested by the X-ray structure of $[Pd_2Cl_2(\mu\text{-}PhN{=}CMe\text{-}NPh)_2(PMe_2Ph)_2]$ (Pd ··· Pd = 2.914(2) Å [598].

Diphenylphosphinato-bridged complexes, $[M_2Cl_2(\mu\text{-}O_2PPh_2)_2(PR_3)_2]$ (M = Pd or Pt; $PR_3 = PEt_3$, PBu_3, PMe_2Ph, $PMePh_2$) [599] and $[Pd_2Ph_2(\mu\text{-}O_2PPh_2)_2(PPh_3)_2]$ [591,594] have been prepared. The increased bite distance of $Ph_2PO_2^-$ group as compared to acetate is reflected in lengthening of M ··· M separation [3.2212(6) Å] in $[Pt_2Cl_2(O_2PPh_2)_2(PMe_2Ph)_2]$ and 5.35 Å in $[Pd_2Ph_2(\mu\text{-}O_2PPh_2)_2(PPh_3)_2]$, consequently J(Pt–P′) and J(Pt–Pt′) coupling is not observed in their ^{31}P and ^{195}Pt NMR spectra [599]. The large ligand bite also contributes to the conformation of the eight-membered metallocyclic ring "$M_2(O_2P)_2$". The platinum complex, $[Pt_2Cl_2(\mu\text{-}O_2PPh_2)_2(PMe_2Ph)_2]$ has a boat conformation [599] while the palladium complex, $[Pd_2Ph_2(\mu\text{-}O_2PPh_2)_2(PPh_3)_2]$ adopts a chair-like conformation (Fig. 20) [591,600].

Pyridine-2-chalcogenolates (2-$NC_5H_4E^-$; E = O, S, Se, Te) are yet another important class of three-atom ligands in which ligand bite can be varied with a suitable choice of chalcogen atom. While 2-hydroxypyridinate has a compara-

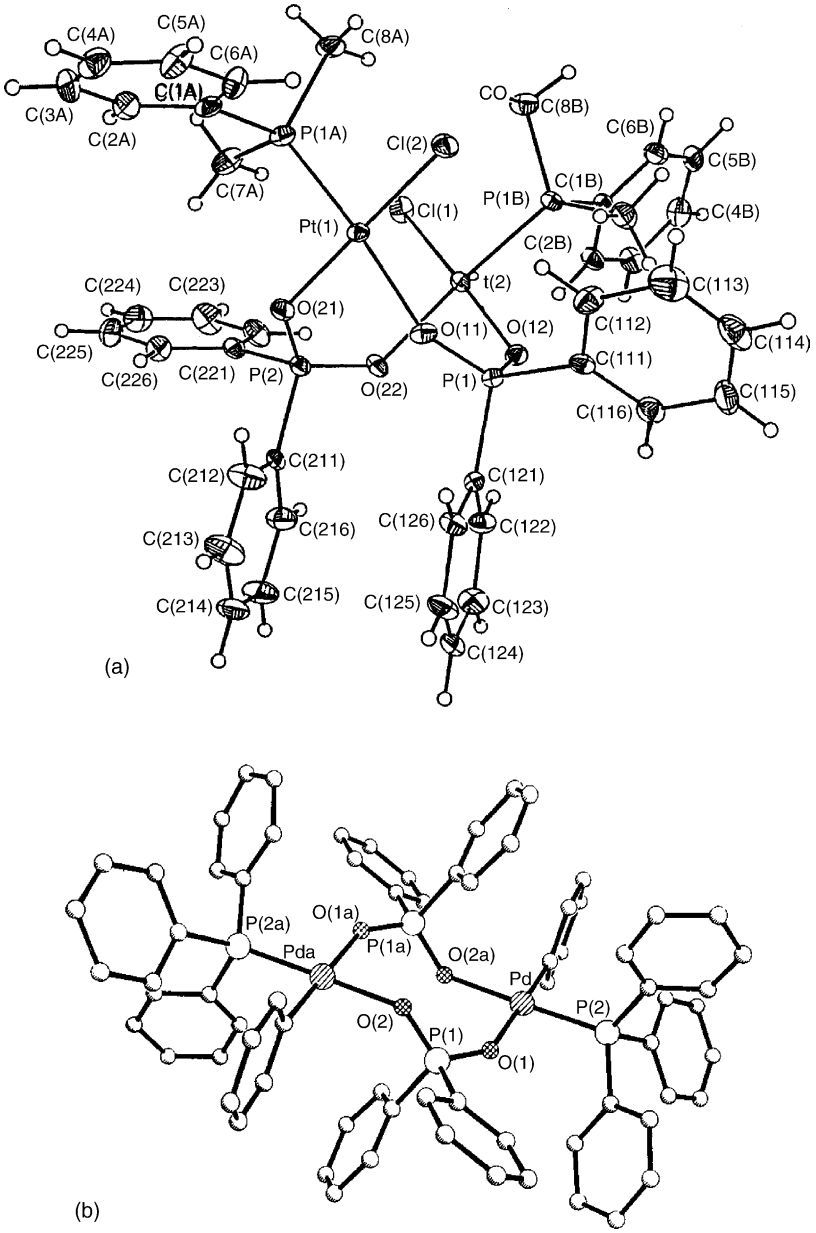
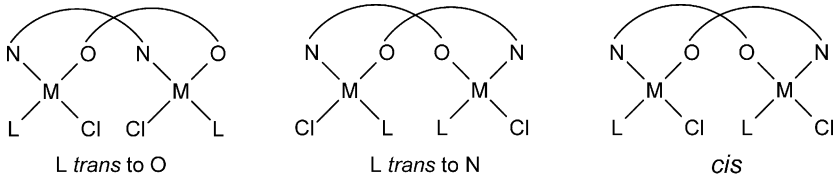


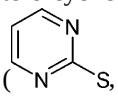
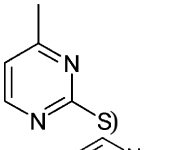
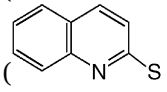
Fig. 20. Molecular structures of (a) $[Pt_2Cl_2(\mu\text{-}O_2PPh_2)_2(PMe_2Ph)_2]$ (reproduced with permission from Ref. [599]) and (b) $[Pd_2Ph_2(\mu\text{-}O_2PPh_2)_2(PPh_3)_2]$ (reproduced with permission from ref. [591]).

ble bite size (∼2.3 Å) to that of amidinates, higher homologs (E = S, Se, Te) have intermediate bites (∼2.75 Å) (carboxylates ∼2.23 Å and $(RO)_2PS_2^-$ ∼3.3 Å).

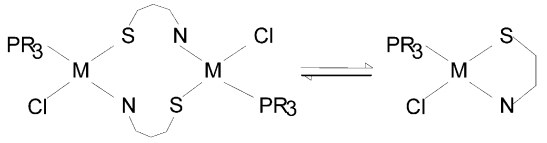
The reaction (61) with 2-hydroxypyridinate initially gives three isomers (**42**–**44**) of binuclear complexes $[Pt_2Cl_2(\mu\text{-}Opy)_2(PR_3)_2]$ (viz. one *cis*-PR_3 and two *trans* isomers:PR_3 *trans* to bridging O/N) which isomerize slowly in solution at room temperature (rapidly in refluxing benzene) to a more stable isomer in which phosphine ligands are *trans* to the bridging oxygen [601]. Like amidinato-bridged complexes, the ^{31}P NMR spectra are devoid of $J(Pt–P')$ coupling [601].



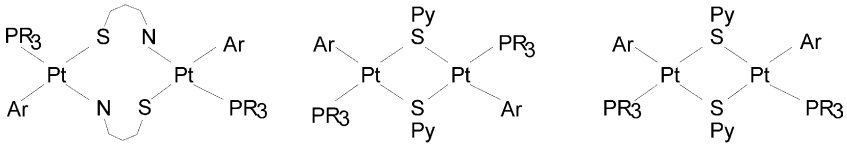
As the bite size in 2-mercapto- or 2-seleno-pyridine increases, ligands behave differently and both mono- and bi-nuclear complexes are isolated [602–606]. The reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3) with pySH in the presence of a base (e.g. NaOR) gives an equilibrium mixture of monomer and dimer [602,603]. The equilibrium shifts from dimer to monomer with increasing phenyl substitution on phosphorus. Thus, with PPh_3 only monomer exists both in the solid state and in solution [602,604] whereas with PMe_3 dimeric species predominates [603]. This dynamic process has been studied by variable temperature ^{31}P NMR spectroscopy. The Pd–N interaction strengthens in the monomeric complex due to decreased donor ability of the *trans* aryl substituted phosphines. The relative ratio of the monomer and dimer is concentration dependent [607], but on crystallization only the dimer crystallizes out for $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$ [603,604]. The X-ray structures of these complexes reveal that the μ-pyS ligands bridge two palladium atoms in a head-to-tail fashion. The terminal chlorine atoms are *trans* to the sulfur atoms while the PR_3 are *trans* to nitrogen [603,604].

Binuclear palladium complexes with other hetero-cyclic thiolates, such as pyrimidine-2-thiolates (), 1-methylimidazole-2-thiolate () [608] and quinoline-2-thiolate () [607] have also been prepared. While the complexes derived from pyrimidine-2-thiolates, $[Pd_2Cl_2(\mu\text{-}S^{\frown}N)_2(PMe_3)_2]$ exhibit monomer ⇌ dimer equilibrium in solution, the corresponding 1-methylimidazole-2-thiolate complex is static in solution in the temperature range −50 to +100 °C. Dimers are isolated only in the solid state [608].

Like palladium complexes with 2-mercaptopyridine, the analogous platinum complexes exhibit monomer ⇌ dimer equilibrium in solution (63) [605]. In contrast to [PdCl(Spy)(PPh_3)], the platinum complex shows a dynamic behaviour and ∼10% dimeric species exists in solution [605]. The arylplatinum complexes $[Pt_2Ar_2(\mu\text{-}Spy)_2(PR_3)_2]$ prepared by reaction (61) have been isolated exclusively as dimers with predominantly $S^{\frown}N$ bridging (**45**). However, with PMe_2Ph, dimers with thiolate bridges (**46**, **47**) also exists in solution (∼5–10%) as shown by ^{31}P and ^{195}Pt NMR spectroscopy [605].

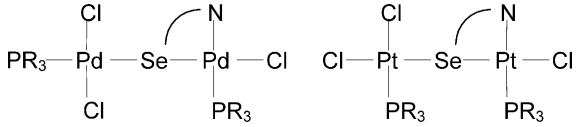


(63)



(45) **(46)** **(47)**

As the chalcogen size increases from sulfur to selenium, i.e. Sepy, the reaction (61) yields predominantly monomeric complexes, [MCl(Sepy)(PR_3)] and even if dimer forms (in case of some alkylphosphines) its concentration is never more than 5% [606]. When these complexes are treated with $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ another series of dimeric complexes can be isolated where the selenium atom of the chelating Sepy ligand coordinates with the $MCl_2(PR_3)$ fragment (**48**, **49**) [606]. Reaction (61) with 2-telluoropyridinate ligand invariably yields monomeric derivatives [609].

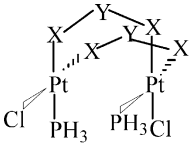


(48) **(49)**

Although bridging mode for the ligands with larger bite such as xanthate, dithiocarbamates, dithiophosphates is known, reaction (61) with all these ligands yields mononuclear complexes exclusively. These reactions are described in Section 3.3.1.

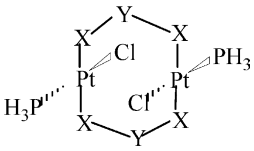
Evidently the metal–metal distance determined for isoelectronic and isostructural carboxylato, triazinedo and amidinato-bridged complexes fall in a narrow range of ∼2.95 Å, yet their ^{31}P and ^{195}Pt NMR spectra differ significantly [590,595,596,598,610]. In order to probe the role of the ligand in mediating metal–metal interactions, EHT calculations have been carried out on model systems [596]. The metal–metal interaction is significantly affected by the nature and relative orientations of the bridging ligand (**50**, **51**) [596].

Metal–metal interaction is observed when the metal planes are in a face-to-face fashion.



cis - trans

(50)



trans - trans

(51)

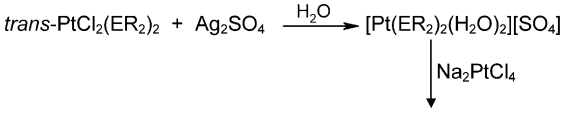
The reaction of $[Pd_2Cl_2(OAc)_2(PR_3)_2]$ with TlCp yields $Pd(\eta^5\text{-Cp})(\eta'\text{-Cp})(PR_3)$ which are fluxional in solution [611].

4. Binuclear complexes containing Group 16 neutral ligands

Binuclear complexes, $[M_2Cl_2(\mu\text{-Cl})_2(R_2SO)_2]$ (M = Pd or Pt; R = Me, Et, Ph) [612–619] and $[Pt_2Ph_2(\mu\text{-X})_2(Me_2SO)_2]$ (X = Br, I, SCN) [620] have been isolated. The former are usually prepared by heating $[MCl_2(MeCN)_2]$ (M = Pt in nitromethane, Pd in acetone) with an equimolar quantity of sulfoxide [616]. The X-ray structures of $[Pt_2Cl_2(\mu\text{-Cl})_2(Et_2SO)_2]$ [616] and $[Pd_2Br_2(\mu\text{-Br})_2(Pr_2SO)_2]$ [617] shows a centro-symmetric chloro-bridged dimeric structure. Sulfoxide is coordinated to platinum through sulfur. The iodo-bridged complexes, $[Pt_2I_2(\mu\text{-I})_2(R_2SO)_2]$, prepared from K_2PtI_4 and sulfoxides, exist in *cis* and *trans* isomeric forms in solution as shown by ^{195}Pt NMR spectroscopy (δ $^{195}Pt = \sim -4933$ and ~ -4827 ppm). However, in the solid state it adopts an iodo bridged structure in which sulfoxides are mutually *trans* disposed [618]. The halo-bridge is readily cleaved by neutral donors (pyridine type ligands) to afford $[PtX_2(L)(dmso)]$ [618,621]. Reaction of $K[Pt(R_2SO)Cl_3]$ with pyrazine and 1,2-diaminocyclobutane yields *trans* $[\{PtCl_2(R_2SO)\}_2(L)]$ (L = pyrazine, 1,2-$(NH_2)_2C_4H_6$; R = Me, Pr^i, Bu^n, Bz, Ph) [622,623].

Organochalcogeno ether-based binuclear palladium and platinum complexes of general formula, $[M_2X_4(R_2E)_2]$ (M = Pd or Pt; E = S, Se, Te) are prepared in several ways (64)–(67) [407,409,624–629] and the one involving reaction of $MCl_2(R_2E)_2$ with Na_2MX_4 in ethanol (64) is commonly employed. A few bidentate ligands such as Bz_2Se_2 [630], $BzSCH_2SBz$ [631] have also been used for the synthesis of binuclear complexes. A complex, $[Pt_2(C_6F_5)_4(\mu\text{-}SPPh_2C_5H_4)_2]$, containing cyclopentadienyldiphenylphosphine sulfide bridge has been reported [632]. The complex $[PdCl_2\{(C_4H_3O)SeMe\}_2]$ (yellow) on recrystallization from acetone affords red crystals of $[Pd_2Cl_2(\mu\text{-}SeMe)_2\{Se(Me)(OC_4H_2)\}_2CMe_2]$ formed by condensation of an acetone molecule followed by dimerization [633]. Binuclear palladium complexes have been reported using α-substituted thio ethers, MeSCHC(O)OR [634].

$$MX_2(ER_2)_2 + Na_2MX_4 \rightarrow [M_2X_4(ER_2)_2] + 2\,NaX \quad (64)$$



(65)

$$2[PtCl_2(ER_2)(\text{alkene})] \rightarrow [Pt_2Cl_2(\mu\text{-Cl})_2(ER_2)_2] + 2\,\text{alkene} \quad (66)$$

$$2Na_2PdCl_4 + 2\,ER_2 \rightarrow [Pd_2Cl_2(\mu\text{-Cl})_2(ER_2)_2] + 4NaCl \quad (67)$$

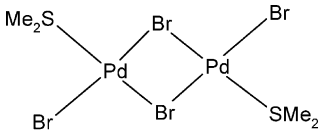
(ER_2 = Me_2S, Et_2S, Pr^n_2S, Bu^n_2S, Oct^s_2S, Et_2Se, Pr^n_2Se, Et_2Te, Pr^n_2Te, $\overline{CH{=}CH{-}CH{=}CHTe}$)

The platinum complexes have higher stability than the analogous palladium complexes. Based on the IR spectral data [444,447,635–638], the palladium complexes have been assigned a halo-bridged structure with terminal thioethers (**52**), whereas analogous platinum complexes

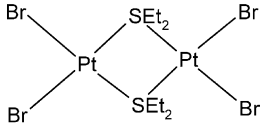
Table 11
X-ray structures established for Group-16 donor complexes

Complex	Comment	References
$[Pd_2Br_2(\mu\text{-}Br_2)(SMe_2)_2]$	Halo-bridged dimmer	[539]
$[Pt_2Br_4(\mu\text{-}SEt_2)_2]$	Thio-ether bridged dimmer	[539]
$[Pd_2Me_2(\mu\text{-Cl})_2(SMe_2)_2]$	Pd_2Cl_2 is almost planar	[642]
$[Pt_2Me_4(\mu\text{-}SEt_2)_2]\cdot C_6H_6$	Thioether bridged dimer, planar four-membered Pt_2S_2 ring, Pt···Pt = 3.610(1) Å	[648]
$[Pt_2tol_4(\mu\text{-}SEt_2)_2]$	Pt···Pt = 3.6315(1) Å, centrosymmetric SEt_2 bridged dimmer	[649]
$[Pt_2(\mu\text{-Cl})_2Cl_2(Et_2SO)_2]$	Chloro-bridged dimer, Pt···Pt = 3.471 Å	[616]
$[Pd_2Br_2(\mu\text{-Br})_2(Pr_2SO)_2]$	Bromo-bridged dimer, Pd···Pd = 3.609 Å	[617]
$Pt_2Me_4(SMe_2)_2$	Thio-ether bridge; Pt···Pt = 3.615(1) Å	[643,650]
$Pt_2Ph_4(SMe_2)_2$	Thio-ether bridge; Pt···Pt = 3.662(1) Å	[650]

have a thioether bridged structure (**53**). However, with arylthioethers, halide–bridged structures have been assigned for both palladium and platinum complexes. X-ray structural analyses (Table 11) of $[Pd_2Br_4(SMe_2)_2]$ [639] and $[Pt_2Br_4(SEt_2)_2]$ [639] reveal that the M–S bond is significantly shorter (2.22(1) Å) in a bridging situation than the one observed for terminal bonding (2.30(2) Å).



(52)



(53)

Several organometallic complexes containing organo chalcogenoethers have also been reported. Treatment of $[M(C_6X_5)_2(tht)_2]$ (M = Pd [566], Pt [640]) with MCl_2 in an appropriate solvent yield $[M_2(\mu\text{-}Cl)_2(C_6X_5)_2(tht)_2]$ [566,640]. The palladium complex is an active precursor for polymerization of methyl acrylate. Polymerization begins with insertion in the Pd-aryl bond to give alkyl complexes $Pd_2(\mu\text{-}Cl)_2\{CH(CO_2Me)CH_2C_6F_5)\}_2(tht)_2]$ [641]. Methylation of $[PdCl_2(SMe_2)_2]$ with methyllithium in diethylether at −60 °C affords *trans*-$[Pd_2Me_2(\mu\text{-}Cl)_2(SMe_2)_2]$ which on halogen exchange with LiX yields the corresponding bromo- and iodo-bridged complexes [642]. Analogous platinum complex, $[Pt_2Me_2(\mu\text{-}I)_2(SMe_2)_2]$ exists as a mixture of *cis* and *trans* isomer in chloroform solution [643]. Tetraorganoplatinum complexes, $[Pt_2R_4'(\mu\text{-}SR_2)_2]$ (R′ = Me or Ar; R = Me, Et, Pr^n, Pr^i) have been isolated from the reaction of $[PtCl_2(SR_2)_2]$ with Me_2Mg or RLi [643–649]. These complexes have thio ether-bridged structures as shown by x-ray analysis [648–650]. However, the complexes $[PtPh_2(SMe_2)]_n$ exists into both di- and tri-meric forms stabilized by SMe_2 bridges [650]. The reaction of 2,2′-dilithiumbiphenyl with *cis*-$PtCl_2(SEt)_2$ at −10 °C affords $[Pt_2(\mu\text{-}SEt_2)_2(bph)_2]$ (bph = dianion of 2,2′-biphenyl) which contains planar bph groups. The latter is also formed by cyclometallation of Hbph (Hbph = monoanaion of 2,2′-biphenyl) in $[Pt_2(\mu\text{-}SEt_2)_2(Hbph)_4]$ [651].

Dimeric thioether complexes, $[M_2Y_2(\mu\text{-}X)_2(R_2E)_2)]$ [479,482,652–655], $[Pd_2Me_2(\mu\text{-}X)_2(SMe_2)_2]$ [656–662] and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**54**) [27,647,648,663–674] are versatile precursors for the synthesis of a variety of complexes. Bridge cleavage reactions of $[M_2X_4(R_2E)_2]$ with monodentate neutral donors, such as amines, chalcogenoethers, yield mononuclear complexes $[MX_2(L)(ER_2)]$. Bridge cleavage of $[Pt_2Me_4(SMe_2)_2]$ with bidentate nitrogen ligands (N∩N = 2,2′-bipyridine, 2,2′-bipyrimidine, 2,2′-bithiazoline) [647,664,665] or COD [671] yield $[PtMe_2(N^{\cap}N)]$ (**55**) or $[PtMe_2COD]$ (Scheme 12). Treatment of **54** with 0.5 mol equivalents of dialkenylchalcogenoether, $E(CH_2CH_2CH{=}CH_2)_2$ (E = S or Se) gives a binuclear complex **56** [663]. Reaction of **54** with thioethers results in to the formation of *cis*-$PtMe_2L_2$, most of them dissociates in solution to establish a monomer ⇌ dimer equilibrium [643–647]. Methyliodide oxidatively adds to **54** affording trimethylplatinum(IV) derivatives [644]. If reaction is carried out in the presence of MeLi, tetramethylplatinum(IV) species, $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ (**57**) is formed [675]. Treatment of **54** with silver acetate [648] or silver salt of hydroxypyridinate [666] in the presence of pyridine generates platinum(III) dimers, $[Pt_2Me_4(\mu\text{-chel})_2(py)_2]$ (**58**) (chel = OAc, 6-XC_5H_3N-O). Activation of aromatic C–X bonds by **54** has been reported [667–670]. Reaction of **54** with imines, $C_6F_5CH{=}NCH_2C_6H_4X$-2 (X = H, Cl, Br) affords a platinum(IV) complex **59** via selective activation of the C–F bond [667]. On the other hand the diimine ligands, $C_6F_5CH{=}NCH_2CH_2NMe_2$ initially forms a organoplatinum(II) complex **60** which reacts further to produce a platinum(IV) complex **61**. In contrast, analogous reactions with the ligands $Me_2NCH_2CH_2N{=}CHAr$ (Ar = 2,3-, 2,4- or 2,6-$C_6H_3F_2$) yields a platinum(II) complex $[PtMe_2(Me_2NCH_2CH_2N{=}CHAr)]$ and subsequently the compound $[Pt^{II}Me(Me_2NCH_2CH_2N{=}CHC_6H_2F_2)]$ in which C–H activation had occurred [668].

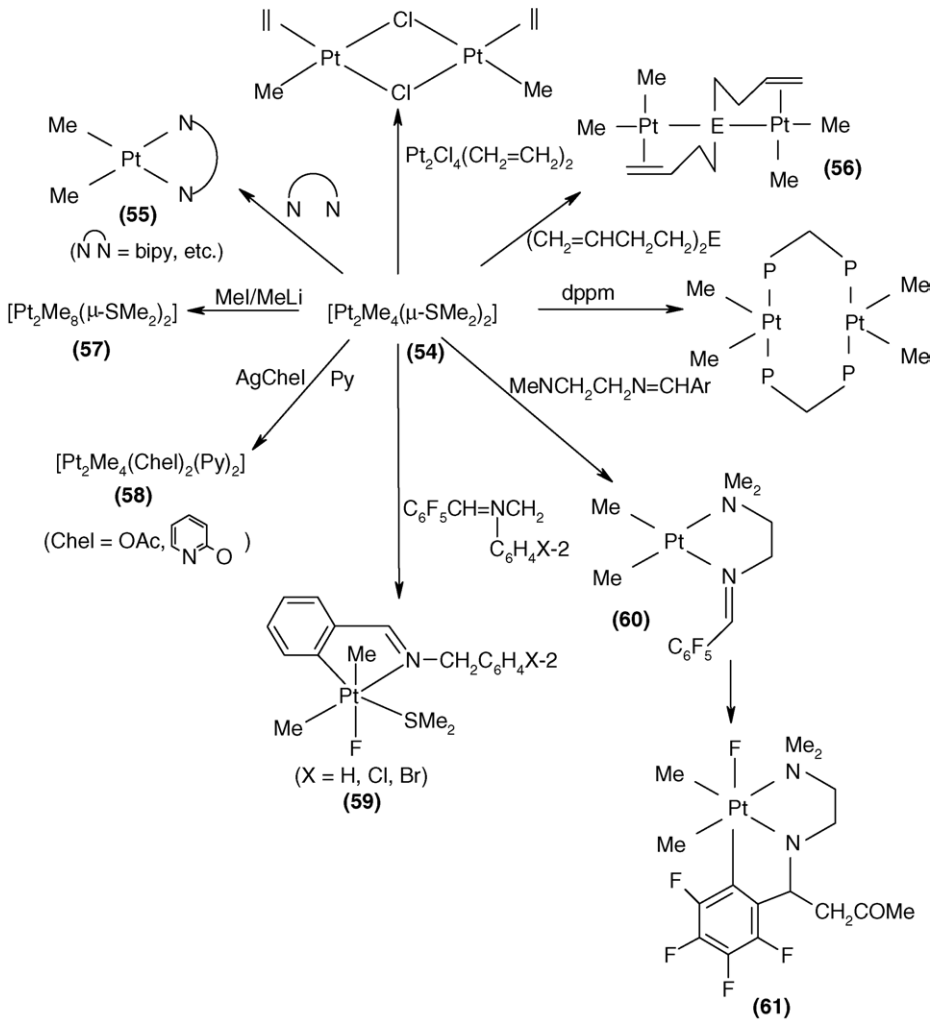
5. Binuclear ionic complexes

5.1. Cationic binuclear complexes

Reaction of $[MX_2(PR_3)_2]$ (M = Pd, X = Cl, R = Et, Ph; M = Pt, X = Cl, Br or I, R = Et or Ph) with BF_3 in chloroform readily yields halogen-bridged cationic complexes $[M_2(\mu\text{-}X)_2(PR_3)_4][BF_4]_2$ (68) [676]. $AgBF_4$ [677–682], $AgClO_4$ [678,683] or $AgPF_4$ [684] is usually employed to abstract chloride from MCl_2L_2 (where L = tertiary phosphine, arsine or stibine [677–681] or a chelating phosphine, $(Ph_2P)_2NC(H)Me(Ph)$, $Ph_2PNCH(Bz)(COOMe)PPh_2$ [683]). Reaction of $Pt(CH_2Cl)_2COD$ with tricyclohexyl phosphine in chloroform followed by addition of $AgPF_6$ results in a cationic platinum complex, $[Pt_2(\mu\text{-}Cl)_2(Pc\text{-}Hx_3)_2\{P^+(CH_2CH_2)(c\text{-}Hx_3\}_2][PF_6]_2$ which is formed by coupling of two methylene moieties of chloromethyl groups [685,686]. The complex exists as a mixture of *cis* and *trans* isomers in solution.

$$2MX_2(PR_3)_2 + 4BF_3 \rightarrow [M_2(\mu\text{-}X)_2(PR_3)_4][BF_4]_2 + 2BF_2X \quad (68)$$

The cationic binuclear complexes, $[Pt_2(\mu\text{-}X)_2L_4]^{2+}$ (L = alkylphosphine; X = Cl, Br or I) show two IR and two Raman active platinum-halogen stretching vibrations [447,680,681,687]. The structure of $[Pt_2(\mu\text{-}I)_2(dppm)_2][BF_4]_2$ shows that the metal coordination planes are coplanar and form Pt_2I_2 rhombus with Pt···Pt separation of 3.881(8) Å [682]. The halo-bridge in these complexes is quite labile and is cleaved by CO to give mono-nuclear cationic complexes $[MX(CO)L_2]^+$ [676,677]. Pyrazoles (NNH = pzH, Me_2pzH, Me_3pzH)

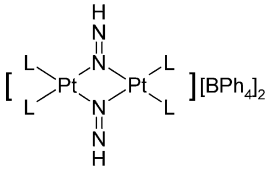


Scheme 12.

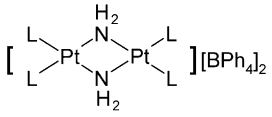
also cleave the chloro-bridge in $[Pt_2(\mu\text{-}Cl)_2(PEt_3)_4][BF_4]_2$ to afford $[PtCl(NNH)(PEt_3)_2][BF_4]$ [688,689]. Similarly, cleavage with phosphadithiatriazine ($Ph_2PS_2N_3$) yields $[PtCl(Ph_2PS_2N_3)(PEt_3)_2][BF_4]$ in which platinum is bound to nitrogen atom adjacent to phosphorus [690]. The $[Pt_2\mu\text{-}Cl)_2(PEt_3)_4][BF_4]_2$ catalytically decomposes formic acid to CO_2 and H_2 with concomitant formation of *trans*-$[PtCl(CO)(PEt_3)_2][BF_4]$ [679].

Azide-bridged, $[Pd_2(\mu\text{-}N_3)_2(PPh_3)_4]X_2$ ($X = ClO_4$, BF_4, PF_6) [691,692] have also been prepared from $Pd(N_3)_2(PPh_3)_2$ and NO^+X^- and characterized. Treatment of $[M(pz)_2(dppe)]$ with HBF_4 affords cationic complexes, $[M_2(\mu\text{-}pz)_2(dppe)_2][BF_4]_2$ (M = Pd or Pt) [248,250].

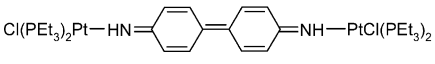
Reduction of platinum phosphine complexes $[PtCl_2(PR_3)_2]$ with hydrazine has been routinely used to prepare $[PtHCl(PR_3)_2]$. The reaction proceeds via various reaction intermediates which after elimination of N_2 yields $[PtHCl(PR_3)_2]$ [693,694]. When $PtCl_2(PPh_3)_2$ is treated with 85% hydrazine in alcohol followed by addition of $NaBPh_4$, a cream coloured crystalline product is separated. The latter has been identified as a mixture of dehydrodiimide- (**62**) and amino- (**63**) bridged species as revealed by X-ray crystallography [693]. The presence of a mixed bridged species, $[Pt_2(\mu\text{-}NH_2)(\mu\text{-}N{=}NH)(PPh_3)_4]^{2+}$ has also been suggested [693]. Treatment of $[PtCl(PhNH)(PEt_3)_2]$ with $AgPF_6$ in propanol gives oxidative dimerization with the formation of weakly paramagnetic *trans*-$[\{PtCl(PEt_3)_2\}_2(\mu\text{-}C_{12}H_{11}N_2)]$ which undergoes reversible dimerization to (**64**). The X-ray structure of **64** shows that the benzidine ligand has quinonoid character [695]. Reaction of 1,3-bis(2-diphenylphosphino)benzylidineaminopropane-2-ol with $Pd(OAc)_2$ in the presence of $NaBF_4$ affords **65** [696]. The Pt···Pt separation in $[Pt_2(O_2CBu^t)_2(NH_3)_4][X]_2$ is influenced by the counter anion, when $X = ClO_4$ it is 3.0928(9) Å but for sulfate ($X = \frac{1}{2}SO_4$) it is much smaller (2.9011(9) Å) [697].



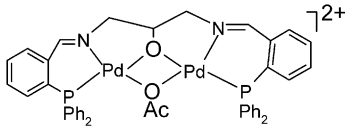
(62)



(63)



(64)



(65)

Several terpyridyl cationic platinum complexes stabilized by anionic bridging ligands, $[Pt_2(trpy)_2(\mu\text{-}L)][X]_3$ (X = PF_6, ClO_4; L = pz; trpy [698], az [699], dpf [700], arginine (arg) [700], SMe [701] and gua [702]) and $[Pt_2(trpy)_2(\mu\text{-}L')]^{2+}$ (L = 2,5-dimethyl-1,4-dicyanamide benzene [703]) have been synthesized [698–703]. Photophysical work on these molecules has revealed that the visible absorption ($\ldots{}^3(d\sigma^*\pi^*)$) moves to lower energy with decreasing Pt–Pt separation [704] (Pt–Pt (in Å) and λ_{max} (in nm): pz = 3.432 (430); az = 3.13 (460); gua = 3.090 (483); dpf = 3.049 (490); arg = 2.998 (488).

Reaction of MCl_2(bipy) with naphthyridines in the presence of LiOH followed by addition of $LiClO_4$ yields binuclear cationic complexes, $[M_2(\mu\text{-}L)_2(bipy)_2]^{2+}$ (L = onp, monp) in which bridging ligand is in a head/tail arrangement. The complexes show short M···M distances in the range 2.794–2.804 Å [705]. Treatment of $PdCl_2$(bipy) with silver nitrate in water yields a nitrate bridged complex $[Pd_2(\mu\text{-}NO_3)_2(bipy)_2]^{2+}$ in which Pd···Pd separation is 2.848(3) Å [706]. The reaction of [Pd(dppp)(solvent)][OTF]$_2$ with 2,2′-biimidazole affords $[Pd_2(biim)(dppp)_2][OTF]_2$ [707]. Several other cataionic complexes containing a variety of nitrogen [708–712] and phosphorus [713] as bridging ligands have been isolated and characterized. The binuclear palladium complexes containing β,δ-triketone and bridging nitrogen ligands, $[Pd_2\{OCRCHC(O)CH\text{-}CR)O)\}(N^{\cap}N)L_2]^+$ show high catalytic activity in oxidation of ketones and α-olefins [714].

Several hydroxo-bridged complexes, $[M_2(\mu\text{-}OH)_2L_4]X_2$ have been prepared usually by the reaction of MCl_2L_2 with 2-equivalents of $AgBF_4$ or $AgNO_3$ in moist acetone or methanol (69) [204,336,715–738a]. The nitrate salts of $Pt(NO_3)_2(PR_3)_2$ (R = Me or Et) in aqueous solution are extensively hydrolysed with the formation of $[Pt_2(\mu\text{-}OH)_2(PR_3)_4]^{2+}$ which is investigated by emf titration and ^{31}P NMR spectroscopy [739].

$$MCl_2L_2 + 2Ag^+ \xrightarrow{OH^-} [M_2(\mu\text{-}OH)_2L_4]^{2+} \quad (69)$$

L = NH_3, PMe_3, PEt_3, PMe_2Ph, PPh_3, $\frac{1}{2}$dppm, $\frac{1}{2}$dppe, $\frac{1}{2}$dppp, $\frac{1}{2}$dppb, $\frac{1}{2}$dppf, $\frac{1}{2}$-4,4′-ditertbutyl-2,2′-bipyridine, prolophos, butaphos, α-diimine, tmeda.

Another method to prepare these complexes involves the use of phase transfer catalysis with crown ethers to facilitate the reaction of KOH with platinum(II) chloro derivatives [254]. Reaction of $[M(O_2)(PPh_3)_2]$ with $NO.BF_4$ in CH_2Cl_2 containing traces of moisture yields hydroxo-bridged complex, $[M_2(\mu\text{-}OH)_2(PPh_3)_4][BF_4]_2$ [722]. Molecular oxygen inserts across the Pt–H bond in $[PtH(solv)(PR_3)_2]^+$ (PR_3 = PEt_3, PMe_2Ph, PPh_3) in THF resulting into the hydroxo bridged complexes, $[Pt_2(\mu\text{-}OH)_2(PR_3)_4]^{2+}$ [740]. The reaction of [PtPhI(COD)] with Bu_4NOH yields $PtPh_2COD$ via a hydroxo bridged complex $[\{PtPh(COD)\}_2(\mu\text{-}OH)]^+$ which is isolated and structurally characterized [741].

The IR spectra show a relatively sharp absorptions at ∼3500 cm^{-1} due to υOH which shift to ∼2600 cm^{-1} on deuteration [336,716,718,742]. The hydroxo-bridged complex $[Pt_2(\mu\text{-}OH)_2(NH_3)_4]^{2+}$ has been studied by normal coordinate analysis, laser Raman spectroscopy and ^{195}Pt NMR data [743–746] Using normal coordinate analysis vibrational bands in $[Pt_2(\mu\text{-}OH)_2(NH_3)_4]^{2+}$ have been assigned [743,744]. The hydroxyl proton in ^{1}H NMR spectra appears either as a broad singlet or pseudo triplet (due to phosphorus coupling) in a region δ −0.4 to 6.50 ppm depending on the phosphine ligand [336,716,729]. The magnitude of ^1J(Pt–P) in the ^{31}P NMR spectra is slightly reduced from the corresponding $PtCl_2L_2$ [729]. The ^{195}Pt resonances are deshielded as compared to those for the corresponding $PtCl_2L_2$. They appear at ∼−3900 ppm as triplet of triplets due to ^1J(Pt–P) and ^3J(Pt–P) (∼10 Hz). The spectra also exhibit ^2J(Pt–Pt) of ∼240 Hz [720]. The third order coupling is not always observed [336]. FAB mass spectra of $[Pt_2(\mu\text{-}OH)_2L_4][BF_4]_2$ (L = prophos, butaphos) exhibits ions due to $[M\text{-}H]^+$ and $[Pt_2(\mu\text{-}OH)_2L_4BF_4]^+$. The appearance of the latter species suggests a strong interaction between the cation and one of the BF_4 ions [729]. Hydrogen bonding interactions between proton and the anion are well illustrated from the X-ray structural analyses of several such derivatives [336,717–720,729,747]. These complexes usually have a planar Pt_2O_2 ring (Fig. 21, [720]) (Table 12) with the exception, $[Pt_2(\mu\text{-}OH)_2(PEt_3)_4][BF_4]_2$ in which two platinum planes

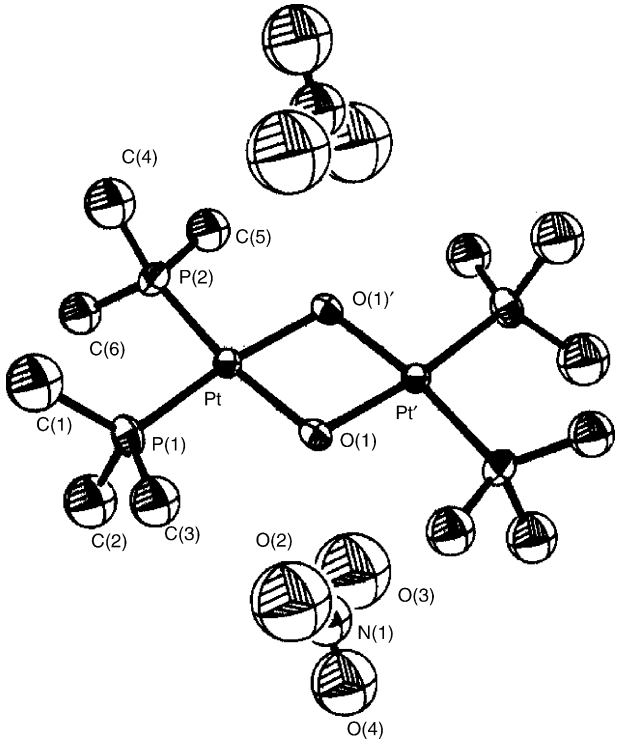


Fig. 21. Molecular structure of *cis*-$[Pt_2(\mu\text{-}OH)_2(PMe_3)_4][NO_3]_2$ (reproduced with permission from ref. [720]).

are hinged at an angle of 36.4° [719]. The Pt···Pt distances are of ~3.2 Å while the O···O distances lie in the range 2.5–2.65 Å [336].

The hydroxyl proton is rather non-labile. Deutration requires prolonged stirring or even a catalyst (piperdine) in D_2O/acetone [716]. Deprotonation of the hydroxyl group needs a strong base like $LiN(SiMe_3)_2$. Thus, the reaction of $[Pt_2(\mu\text{-}OH)_2L_4][BF_4]_2$ with $LiN(SiMe_3)_2$ yields a highly basic neutral oxo-complex (70) [336]. The reaction of amine with $[Pt_2(\mu\text{-}OH)_2L_4][BF_4]_2$ depends on the nature of L and amine [336,728]. When L is PPh_3 or $\frac{1}{2}$dppp, even large amounts of aryl amines afford mono hydroxo substituted product, $[Pt_2(\mu\text{-}OH)(\mu\text{-}NHR)(L_4)][BF_4]_2$, however, with PMe_2Ph, $\frac{1}{2}$dppm, $\frac{1}{2}$dppe and NH_3 or hydrazine a disubstituted product, $[Pt_2(\mu\text{-}NHR)_2(L_4)][BF_4]_2$ forms [204,727,728,732]. Reaction of *N*-methylaniline with $[L_2Pt(\mu\text{-}OH)]_2^{2+}$ ($L_2 = Ph_2PCMe_2PPh_2$) yields a mono-hydroxo-bridged complex $[Pt_2(\mu\text{-}OH)(\mu\text{-}NMePh)L_4]^{2+}$ [748]. The palladium hydroxo complexes $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4[BF_4]_2$ reacts similarly with aromatic amines [726]. The hydroxo-bridged palladium and platinum complexes, $[M_2(\mu\text{-}OH)_2(N^{\cap}N)_2][ClO_4]_2$ [$N^{\cap}N = 2NH_3$, 1,2-diaminocyclohexane, bipyrazolylmethane or bis(3,5-dimethyl pyrazolyl)methane] react similarly with weak protic electrophiles such as pzH, triazole, RSH, R_2NCS_2H, etc. [724,749–751]. The reaction of $[Pt_2(\mu\text{-}OH)_2(PMe_3)_4][NO_3]_2$ with 1-methylcytosine affords another binuclear complex, $[Pt_2(\mu\text{-MeCy(-H)}(PMe_3)_4][NO_3]_2$ in which deprotonated ligand bridges two metal atoms in a head-to-tail (N^3, N^4-) fashion. The two platinum planes form a dihedral angle of 46.2° [720]. The hydroxo-azolate bridged platinum complex $[Pt_2(\mu\text{-}OH)(\mu\text{-}NN)(N^{\cap}N)]^{2+}$ (N–N = pz, triazolate) are effective in vitro on a cisplatin resistant cell line [749–752]. The leaving hydroxo group provides a bifunctional coordination on DNA as shown by the reaction between binuclear platinum complexes and 9-ehtylguanine (9EtG). From these reactions 1:2 complexes $[cis\text{-}\{Pt(NH_3)_2(9EtG\text{-}N7)\}_2(\mu\text{-}N\text{–}N)]^{3+}$ (N–N = pz or triazolate) have been isolated and structurally characterized [749,751]. Reaction of 9-methylaldenine (9-MeAd) with $[Pt_2(\mu\text{-}OH)_2L_4]^{2+}$ yields a trimeric derivative $[Pt_3(\mu\text{-}9\text{-}MeAd)_3L_6]^{3+}$ [753].

$$[Pt_2(\mu\text{-}OH)_2(L_4)][BF_4]_2 + 2LiN(SiMe_3)_2 \rightarrow [Pt_2(\mu\text{-}O)_2L_4]\cdot LiBF_4 \quad (70)$$

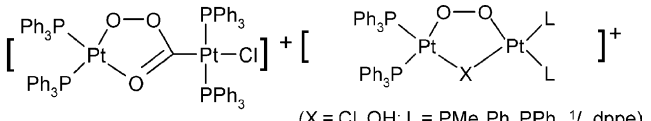
(L = PMe_2Ph, PPh_3, $\frac{1}{2}$dppm, $\frac{1}{2}$dppp)

Table 12
X-ray structures determined for hydroxo-bridged platinum complexes

Complex	Comment	References
$[Pt_2(\mu\text{-}OH)_2(NH_3)_4](CO_3)\cdot 2H_2O$	Pt_2O_2 planar, hydrogen bonding holds two centrosymmetric dimeric units, Pt···Pt 3.085(1) Å	[718,747]
$[Pt_2(\mu\text{-}OH)_2(PMe_3)_4][NO_3]_2$	Pt_2O_2 planar	[720]
$[Pt_2(\mu\text{-}OH)_2(PEt_3)_4][BF_4]_2$	Pt_2O_2 bent, Dihedral angle 36.4^0, Pt···Pt = 3.121(1) Å	[719]
$[Pt_2(\mu\text{-}OH)_2(PPh_3)_4][BF_4]_2$	Pt_2O_2 planar, Pt···Pt = 3.153(2) Å	[336]
$[Pt_2(\mu\text{-}OH)_2(dppm)_2][BF_4]_2$	Pt_2O_2 planar, Pt···Pt = 3.270(1)	[336]
$[Pt_2(\mu\text{-}OH)_2(dppp)_2][BF_4]_2$	Pt_2O_2 planar	[412]
$[Pt_2(\mu\text{-}OH)_2(dppb)_2][BF_4]_2$	Pt_2O_2 planar, Pt···Pt = 3.215(4)	[336]
$[Pt_2(\mu\text{-}OH)_2(dppf)_2][BF_4]_2$	Pt_2O_2 planar, Pt···Pt = 3.227(1) Å	[717]
$[Pt_2(\mu\text{-}OH)\ (\mu\text{-}N_3C_2H_2)(NH_3)_4][NO_3]_2$	Pt···Pt = 3.4411(6) Å	[750]
$[Pt_2(\mu\text{-}OH)\ (\mu\text{-pz})(NH_2C_6H_{10}NH_2)][NO_3]_2$	Pt···Pt = 3.4873(7) Å	[750]
$[Pt_2(\mu\text{-}OH)(\mu\text{-}N_3C_2H_2)(NH_2C_6H_{10}NH_2)]\ [NO_3]_2$	Pt···Pt = 3.3343(2) Å	[750]
$[Pd_2(\mu\text{-}OH)_2L_4][BF_4]_2$, $L_2 = (MeC = NAr)_2$	Pd_2O_2 non-planar, $\theta = 156\,^{\circ}C$	[733]
$[Pt_2(\mu\text{-}OH)_2L_4][BF_4]_2$, $L_2 = (MeC = NAr)_2$	Pt_2O_2 planar	[733]
$[Pd_2(\mu\text{-}OH)_2L_4]^{2+}$, $L_2 = (MeC = NC_6H_3Bu^t_2\text{-}3,5)_2$	Pd···Pd = 2.9706 Å	[738a]
$[Pt_2(\mu\text{-}OH)_2(PMe_2Ph)_4]^{2+}$	Pt_2O_2 planar, Pt···Pt = 3.233(1) Å	[738]
$[Pt_2(\mu\text{-}OH)_2(PMePh_2)_4]^{2+}$	Pt_2O_2 planar, Pt···Pt = 3.174(1) Å	[738]

The hydroxo-bridged complexes are inert towards bridge-cleavage, no reaction takes place even with excess of PPh_3 [716]. However, the terminal ligands in $[Pt_2(\mu\text{-}OH)_2(NH_3)_4]^{2+}$ can be substituted by amines or diamines [746]. Carbon dioxide inserts into the Pd–OH bonds in $[Pd_2(\mu\text{-}OH)_2L_4][BF_4]_2$ to yield mononuclear bicarbonate complexes, $[PdL_2\{OC(O)OH\}_2]$ (L = PPh_3, $PMePh_2$, ½dppe, (c-$Hx_2PCH_2)_2$) [715]. The $[M(\mu\text{-}OH)(P^{\cap}P)]_2^{2+}$ ($P^{\cap}P$ = dppm, dppe, dppp or dppb) are active catalyst in the Baeyer-Villiger oxidation of ketones with H_2O_2 [735,736].

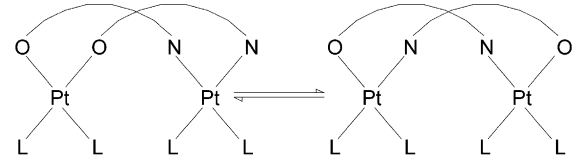
The platinum dioxygen complex $PtO_2(PPh_3)_2$ reacts with various cationic platinum species $[PtCl(CO)(PPh_3)_2]^+$ [754] and $[Pt_2(\mu\text{-}X)_2(L_4)]^{2+}$ [755] to give peroxo complexes **66** and **67**, respectively. The acetato-bridged complexes, $[Pt_2(\mu\text{-}OAc)_2(NH_3)_4)]_n^{2+}[X_2]_n$ (X = ClO_4, NO_3, BF_4, PF_6, SiF_6) form one-dimensional infinite chain stabilized by hydrogen bond formation between the amines and the oxygen atoms of acetates [756].



66 (X = Cl, OH; L = PMe_2Ph, PPh_3, $^1/_2$ dppe)

67

Another series of cationic binuclear complexes of platinum, relevant to anti-tumor activity [757–784], and palladium [785] have been investigated in considerable detail. These complexes are stabilized by various amidate bridging ligands such as α-pyridone [758,765–768,785], 1-methylcytosine [762,775,776], 1-methylthymine [757,759,778], uracil/1-methyl uracil [760–762], 1-methylhydantoin [763], 2-mercaptopyridine [764,779,782,783] and α-pyrrolidene [769,770,773]. These complexes are usually obtained by the reaction of *cis*-MCl_2L_2 (L_2 = NH_3, bipy, en, etc.) and amidate ligands in the presence of halide abstractant or by treatment of $[Pt_2(H_2O)_2L_4]^{2+}$ (L = NH_3 or en) with free ligands. With some ligands such as α-pyrrolidonate [773], succinimidate [777] only head-to-head isomer is formed while in other cases both head-to-head (HTH) (**68**) and head-to-tail (HTT) (**69**) isomers are formed. In most of the cases they have been structurally characterized. These complexes show interesting redox chemistry with Pt···Pt oxidation states varying +2.25, +2.5 and +3.0 [770]. The HTH isomer of $[Pd_2(OC_5H_4N)_2(en)_2][NO_3]_2$ formed initially isomerizes in solution to HTT arrangement [785]. For platinum complexes such as $[Pt_2(OC_5H_4N)_2(en)_2][NO_3]_2$, ^{195}Pt NMR spectroscopy has been employed to study the isomerization between HTH and HTT (71) [765,771]. Treatment of HTT*cis*-$[Pt_2(OC_5H_4N)_2(NH_3)_4]^{2+}$ with nitric acid in the presence of X^- (X = NO_2, Cl, Br) results in oxidative addition and metal–metal bond formation to give Pt(III) dimer [766]. Treatment of $PtCl_2$(bipy) with pyridine-2-thiol in water followed by addition of NH_4PF_6 affords a mixture of *syn* and *anit* isomers of $[Pt_2(pyt)_2(bipy)_2][PF_6]_2$. The crystals of *syn* isomer are dark-red whereas *anti* isomer is orange in colour. The *anti* isomer shows very intense orange luminescence (λ_{max} = 603 nm) even at room temperature [779]. The *syn* isomer has HTH configuration of two bridging pyt while *anti* isomer has HTT arrangement of the pyt ligand. The Pt···Pt separations in *syn* and *anti* isomers are 2.923(1) and 2.997(1) Å, respectively [779]. A similar platinum complex $[Pt_2(pyt)_2(bipyBu_2^t)_2]^{2+}$ shows photoluminescence (λ_{max} = 606 nm), but the corresponding palladium derivative is non-emissive [783].



68 **69**

Head – to – Head (HTH) (Two ^{195}Pt NMR resonances)

Head – to – Tail (HTT) (Only one ^{195}Pt NMR resonance)

(71)

In order to probe the nature of platinum antitumor drugs with sulfur functionalized protein interactions, reactions of several mononuclear platinum complexes, such as $PtCl_2$(bipy) [786] *cis*-$PtCl_2(NH_3)_2$ [772,787], $PtCl_2(PMe_3)_2$ [788], with *N*-acetyl cysteine and glutathione have been investigated [786–788]. In these reactions cationic thiolato-bridged complexes, $[Pt_2(\mu\text{-}SR)_2L_4]^{2+}$ (SR = accys, GS; L = NH_3, PMe_3, $\frac{1}{2}$bipy, $\frac{1}{2}$diene) are generally formed [786–789].

Organochalcogenolato-bridged cationic complexes of the general formula $[M_2(\mu\text{-}ER)_2(PR_3)_4]X_2$ have been isolated employing the following reaction routes (72) and (73) [790–796]. Besides these general routes, when thiaplatinacycles, formed by the reaction of $Pt(PEt_3)_3$ with sulfur heterocycles (thiophene, benzothiophene and dibenzothiophene), are treated with HBF_4, ring opening takes place resulting into dinuclear thiolato dications, $[Pt_2(\mu\text{-}SR')_2(PEt_3)_4][BF_4]_2$ (R′ = CH=CH-CH=CH_2; 2-C_6H_4-CH=CH_2; 2-C_6H_4Ph). Interestingly similar reaction with HCl yields appropriate organic thiol and *cis*-$[PtCl_2(PEt_3)_2]$ [797].

$$[M_2(\mu\text{-}Cl)_2(PPh_3)_4]X_2 + 2AgSCF_3 \rightarrow [M_2(\mu\text{-}SCF_3)_2(PPh_3)_4]X_2 \quad (72)$$

$$M(ER')_2(PR_3)_2 + [M(Solv)_2(PR_3)_2]^{2+} \rightarrow [M_2(\mu\text{-}ER')_2(PR_3)_4]^{2+} \quad (73)$$

(where X = BF_4, ClO_4, BPh_4; E = S, Se, Te;

ER′ = SPr^i, SPh, Stol, SC_5H_9NMe, $SCH_2CH_2NMe_2$;

SePh, TePh, etc.).

Table 13
X-ray structures of thiolato-bridged cationic complexes of palladium and platinum

Complex	Comments	References
$[Pd_2(\mu\text{-}SC_5H_9NMe)_2(dppe)_2][BPh_4]_2$	Pd_2S_2 planar	[792]
$[Pt_2(\mu\text{-}SC_5H_9NMe)_2(dppe)_2][BPh_4]_2$	Pt_2S_2 planar	[792]
$[Pt_2(\mu\text{-}SC_6H_4Ph)_2(PEt_3)_4][BF_4]_2$	Centrosymmetric dimer	[797]
$[Pt_2(\mu\text{-}SC_5H_9NMe)_2(en)_2]^{2+}$	Pt···Pt = 3.452 Å	[798]
$[Pt_2(\mu\text{-}SCH_2CH_2CH_2NMe_2)_2(en)_2]^{2+}$	Pt···Pt = 3.425 Å	[798]
$[Pd_2(\mu\text{-}SCH_2CH_2CH_2NMe_2)_2(dppe)_2]^{2+}$	Pd···Pd = 3.504 Å	[792]
$[Pt_2(\mu\text{-}SCH_2CH_2CH_2NMe_2)_2(dppe)_2]^{2+}$	Pt···Pt = 3.556 Å	[792]
$[Pt_2(\mu\text{-accys})_2(bipy)]^{2+}$	Accys adopt *syn* orientation and are involved in hydrogen bonding with water molecules.	[786]
$[Pd(C_6F_5)(phen)(\mu\text{-}SC_6F_5)Pt(C_6F_5)(dppe)]^{+}$	Pt···Pd = 4.164 Å	[799]

The existence of *syn* and *anti* isomers in $[M_2(\mu\text{-}SCF_3)_2(PPh_3)_4]X_2$ has been demonstrated by ^{19}F NMR spectroscopy [790]. The ^{195}Pt NMR resonances for these complexes appear at ∼−4500 ppm which are deshielded from the corresponding resonances for mononuclear complexes $[Pt(ER')_2(PR_3)_2]$ [792,794]. The ^{77}Se NMR resonances for these complexes appear as a triplet due to coupling with two equivalent *trans* phosphorus nuclei [^2J(Se–P) = 94 Hz] [794] and are shielded relative to the mononuclear complexes.

Structures of several of these molecules have been established by X-ray diffraction (Table 13) [786,792,797–799]. The structure of $[M_2(\mu\text{-}SC_5H_9NMe)_2(dppe)_2][BPh_4]_2$ (M = Pd or Pt) reveal a planar M_2S_2 ring and the piperidine rings adopt an *anti* conformation (Fig. 22) [792].

The SCF_3 bridged complexes undergo bridge cleavage reactions with PR_3, py, *p*-toluidine or Cl^- to give mono nuclear species, $[Pt(SCF_3)(L)(PPh_3)_2]X$ or *cis*-$[PtCl(SCF_3)(PR_3)_2]$ reflecting poor bridging ability of the SCF_3 group [790].

The reaction of $[M(SC_6F_5)(C_6F_5)L_2]$ with $M'X(C_6F_5)L_2'$ (L and L′ = $\frac{1}{2}$bipy, $\frac{1}{2}$phen, and $\frac{1}{2}$dppe; M = Pd or Pt; X = SO_3CF_3 or ClO_4) results in single bridged compounds $[L_2(C_6F_5)M(\mu\text{-}SC_6F_5)M'(C_6F_5)L_2']X$ [799]. The structure of $[Pd(C_6F_5)(phen)(\mu\text{-}SC_6F_5)Pt(C_6F_5)(dppe)]^+$ reveals single thiolato-bridge between two approximately square planar metal centers which are separated by 4.164(2) Å [799].

The ligand $(H_2NCH_2CH_2)_2CHSH$ forms binuclear complexes such as **70**, the structure of the com-

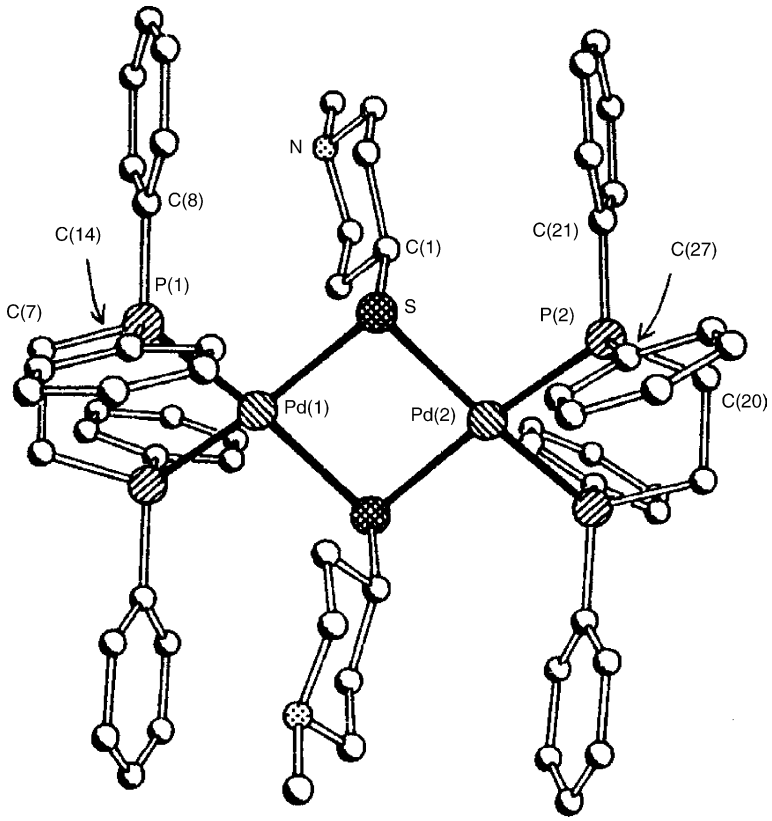
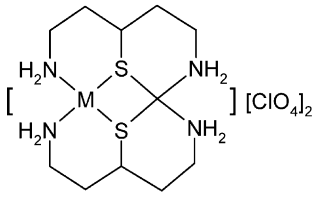
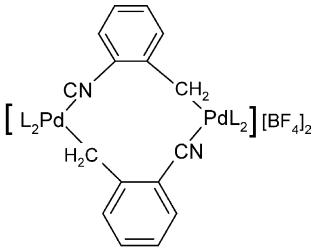


Fig. 22. Molecular structure of $[Pd_2(\mu\text{-}SC_5H_9NMe)_2(dppe)_2][BPh_4]_2$ (reproduced with permission from ref. [792]).

plex is maintained in solution [800]. Similar complexes have been synthesized using 5-*tert*-butyl-2,6-di(aminomethyl)thio/selenophenol [801]. These complexes undergo two irreversible reduction processes in the range −1.5 to −1.0 V (versus SCE) and are ascribed to metal centred reductions [801]. The reaction of 1,2-cyanobenzyl complex, $[PdCl(1,2\text{-}CH_2C_6H_4CN)(PPh_3)_2]$ with $AgBF_4$ affords **71** [802,803] which on treatment with *p*-tolylmercaptan yields $[Pd_2(\mu\text{-Stol})_2(PPh_3)_4][BF_4]_2$ [803]. Some reactions of thiocarbonate derivatives have been described (74) [804].



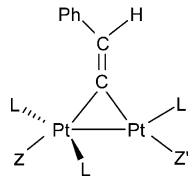
70



71

$$[Pd(C_6F_5)(PR_3)_2(ClO_4)] + [Pd(CS_3)(PR_3)_2] \rightarrow [Pd(C_6F_5)(PR_3)_2(\mu\text{-}CS_3)(Pd(PR_3)_2][ClO_4] \quad (74)$$

Diplatinum complexes **72** containing bridging alkenylidene ligands have been isolated by Lukehart and coworkers [805–811]. The reaction of $[Pt(H)solv(PEt_3)_2]^+$ with $[Pt(C{\equiv}CPh)_2(PEt_3)_2]$ yields a "T-frame" complex, $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4][BF_4]_2$ which reacts thermally or photochemically with halide or pseudohalide to give neutral complexes (Scheme 13) [809]. Diphenylacetylene inserts into alkenylidene group to give an expanded $\mu\text{-}\eta^1{:}\eta^3$-butadienediyl ligand [810].



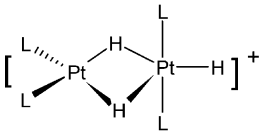
72

Z	Z'
PhC≡C	$PEt_3]^+$
PhC≡C	Cl
PhC≡C	Br
PhC≡C	I
PhC≡C	SPh
Cl	Cl
Br	Br
I	I
SCN	SCN

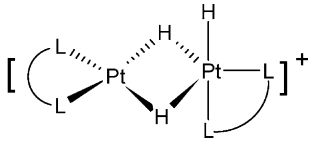
The ^{195}Pt NMR chemical shifts occur in a narrow range of δ −1860 to −2267 ppm and the value of ^1J(Pt–Pt) ranges from 567 to 1604 Hz which could neither be correlated with the Pt–Pt distance nor with the electronegativity of the two substituents [808]. X-ray structures of $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4][BF_4]$, $[Pt_2(C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3X]$ (X = Cl or I) and $[Pt_2(C{=}CHPh)(PEt_3)_3Br_2]$ have been determined [805,807].

5.2. Cationic hydrido-bridged complexes

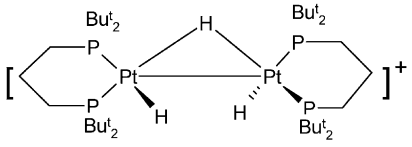
Several singly (μ-H) and doubly $(\mu\text{-H})_2$ hydrido-bridged complexes having structures **73–75** have been reported [721,812–838].



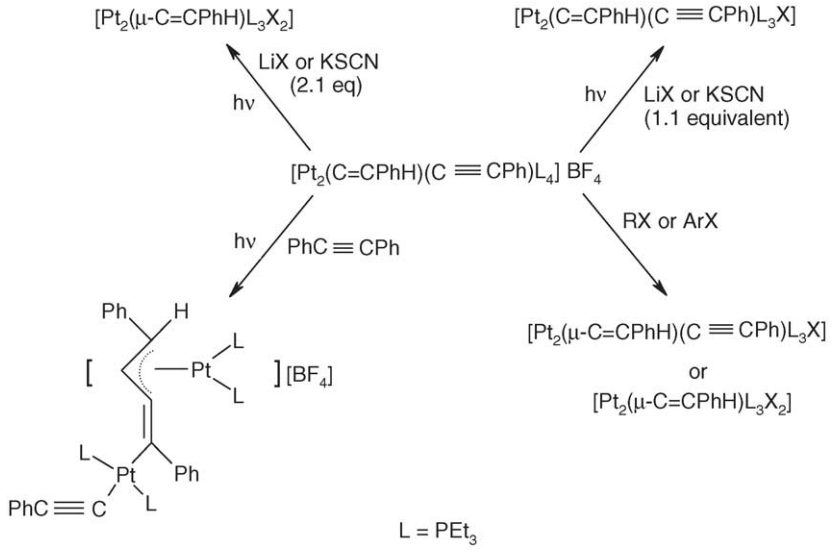
73



74



75



Scheme 13.

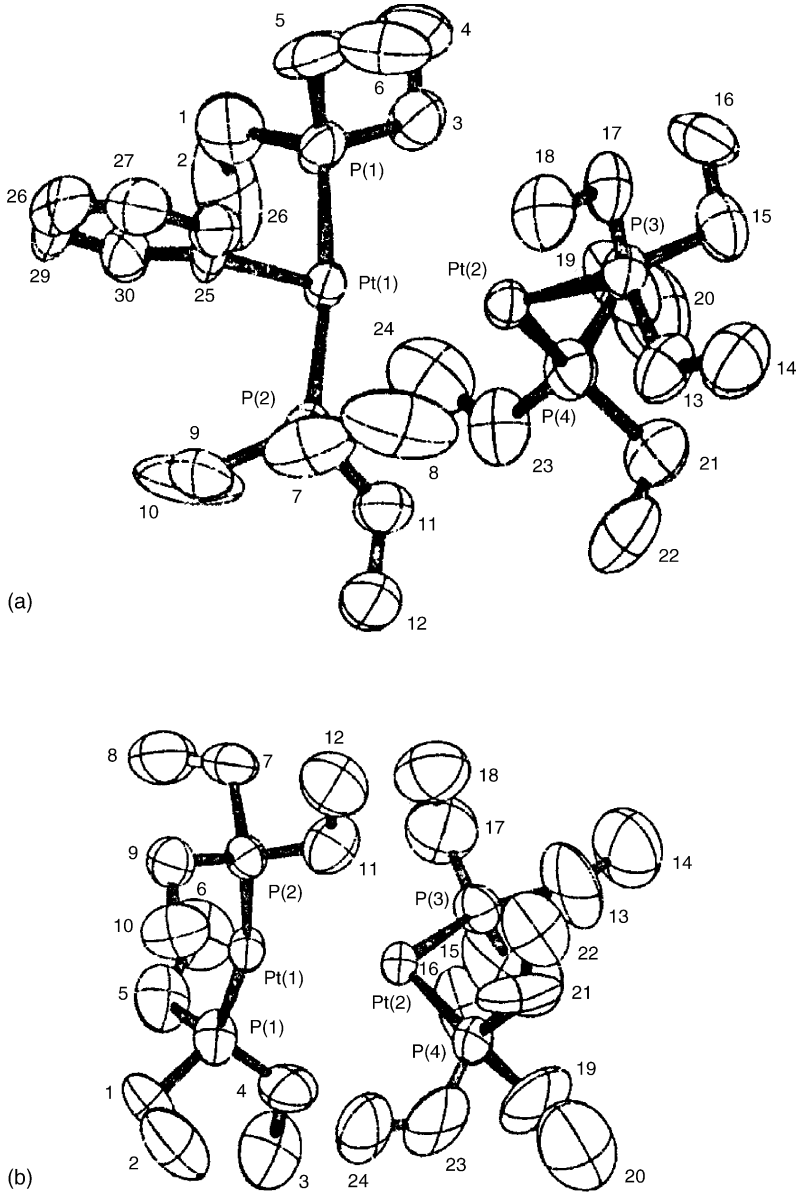
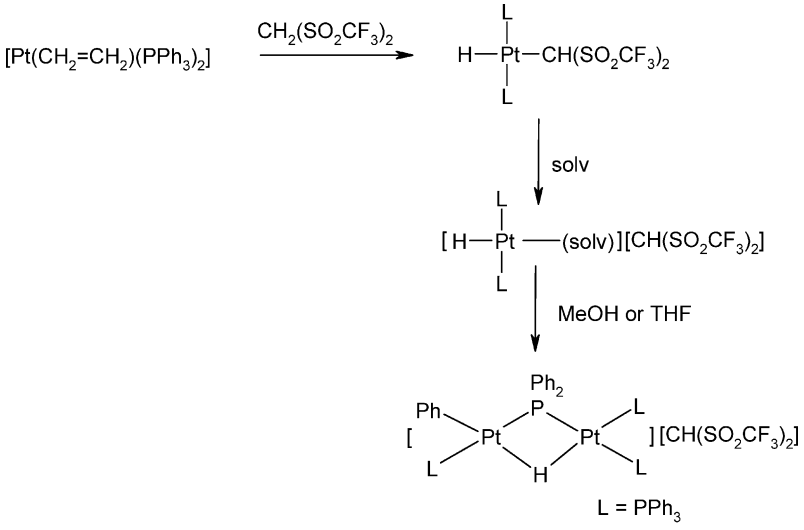


Fig. 23. Molecular structures of (a) $[Pt_2(\mu\text{-}H)_2Ph(PEt_3)_4]^+$ and (b) $[Pt_2(\mu\text{-}H)_2H(PEt_3)_4]^+$ (reproduced with permission from ref. [827]).

The reaction between $[Pt(3,5\text{-}dmpzH)_2(L\text{–}L)][BF_4]_2$ and KBH_4 in methanol or $PtCl_2(L\text{–}L)$ with $AgBF_4$ followed by reduction with KBH_4 in methanol affords doubly hydride bridged complexes, $[Pt_2H(\mu\text{-}H)_2(L\text{–}L)_2][BF_4]$ (L–L = dppe, dppp, dpb, dpet, dpae and dppf [721,812,828]. Venanzi and co-workers [826,827] isolated a series of complexes $[Pt_2(\mu\text{-}H)_2X(PR_3)_4][BF_4]$ (X = H or Ph; R = Et, Ph, c-Hx) by reacting a "hydride intermediate" formed from $Pt(COD)_2$, $2PR_3$ and H_2 with *trans*-$[PtX(acetone)(PR_3)_2][BF_4]$. However, the reaction of $PtH_2(PPh_3)_2$ with $[PtPh(acetone)(PPh_3)_2]^+$ yields a mixed bridged cation, $[Pt_2(\mu\text{-}H)(\mu\text{-}PPh_2)Ph(PPh_3)_3]^+$ formed by cleavage of Ph–P bond, instead of expected product $[Pt_2(\mu\text{-}H)_2Ph(PPh_3)_4]^+$ [827,833]. X-ray structures of $[Pt_2(\mu\text{-}H)_2X(PEt_3)_4][BPh_4]$ (X = H or Ph) (Fig. 23) [827] and $[Pt_2(\mu\text{-}H)(\mu\text{-}PPh_2)Ph(PPh_3)_3]^+$ [833] have been determined. The Pt · · · Pt bond distances in these complexes range 2.82–2.89 Å. Although the hydride ligands in the former are not located, the position of the heavy atom suggests that the $Pt_2(\mu\text{-}H)_2$ bridge is unsymmetrical [827].

The oxidative addition of $CH_2(SO_2CF_3)_2$ to $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ produces first *trans* $[PtH\{CH(SO_2CF_3)_2\}(PPh_3)_2]$ which slowly isomerizes to *cis* form. In the presence of coordinating solvents such as MeCN, DMF, H_2O, MeOH, THF, displacement of $[CH(SO_2CF_3)_2]^-$ anion takes place (75). In MeOH or THF solution cleavage of a Ph–P bond in one of the PPh_3 ligands

occur to produce **76**, structure of which has been established by X-ray diffraction analysis [834].



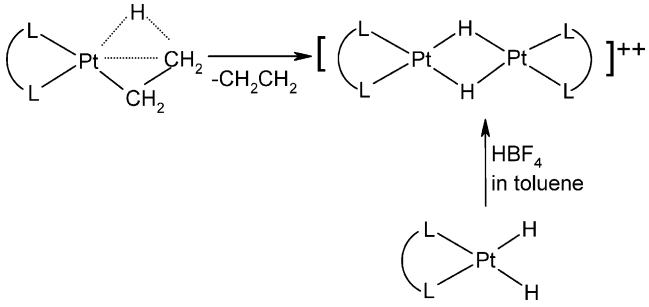
76 (75)

UV irradiation of an acetonitrile solution of $[Pt(C_2O_4)(PEt_3)_2]$ under a hydrogen atmosphere yields $[Pt_2(\mu\text{-}H)_2H(PEt_3)_4][O_2CH]$ with elimination of CO_2 [824]. Initially *trans*-$[PtH(OMe)(PEt_3)_2]$ forms which after β-hydride abstraction generates *trans*-$[PtH_2(PEt_3)_2]$. The latter is trapped by the $[PtH(OMe)(PEt_3)_2]$ to give $[Pt_2(\mu\text{-}H)_2H(PEt_3)_4]^+$. This has been demonstrated by the reaction of methanol with $[PtH_2(PEt_3)_2]$ which via proposed methoxy intermediate yields $[Pt_2(\mu\text{-}H)_2H(PEt_3)_4][OMe]$ [829]. The complex $[Pt_2(\mu\text{-}H)_2H(PEt_3)_4][O_2CH]$ catalyses the decomposition of formic acid at 25 °C [824].

The complexes $[Pt_2(\mu\text{-}H)_2H(L\text{-}L)_2]^+$, in general, are fluxional at room temperature even in certain cases fluxionality exists down to −95 °C. The ^1J(Pt–H) values lie in the range 448–552 Hz [828]. The structures of several complexes have been established by X-ray diffraction, the Pt–Pt distances are rather short and fall in the range 2.73–2.89 Å [814,827,828,833]. The structure of one of the complexes, $[Pt_2(\mu\text{-}H)_2H(dppe)_2][BPh_4]$, has been determined by neutron diffraction [835]. The bridging hydrides, which asymmetrically bridge two platinum atoms show non-bonding H···H distance of 2.399(3) Å.

Reductive elimination of hydrogen takes place when an acetone solution of $[Pt_2(\mu\text{-}H)_2H(L\text{–}L)_2][BF_4]$ is treated with carbon monoxide or isocyanides to yield platinum(I) deriatives, $[Pt_2H(L')(L\text{–}L)_2]^+$ (L′ = CO or CNR (R = *p*-tolyl, Bu^t); L–L = dppe, dpp, dpb, dppf [721,836]. Photochemistry of $[Pt_2(\mu\text{-}H)_2H(PEt_3)_4][BPh_4]$ and $[Pt_2H_2(\mu\text{-}H)(PEt_3)_4][BPh_4]$ has also been investigated using 334 nm light [817]. Highly reactive *trans*-$PtH_2(PEt_3)_2$ and *trans*-$[PtH(solvent)(PEt_3)_2]^+$ are formed in these reactions. Preparation of $[Pt_2(\mu\text{-}H)(\mu\text{-}S)(dppe)_2][PF_6]$ has been reported [837,839].

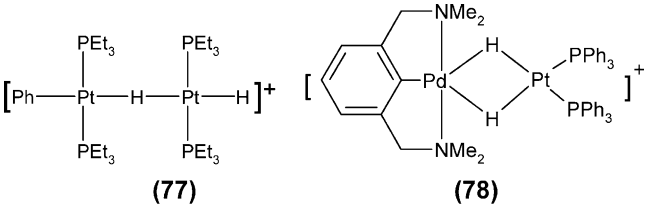
A few dicationic complexes $[Pt_2(\mu\text{-}H)(\mu\text{-}Cl)(L\text{–}L)_2]^{2+}$ (L–L = (c-Hx$_2$PCH$_2$)$_2$] [840] and $[Pt_2(\mu\text{-}H)_2(L\text{–}L)_2][BF_4]_2$ (L–L = $R_2P(CH_2)_nPR_2$ (*n* = 2 or 3; R = c-Hx or Bu^t) [832] have been prepared and characterized. The latter are formed by β-elimination of $CH_2{=}CH_2$ from $[PtEt(L\text{–}L)]^+$. These complexes can also be prepared by protonation of $[PtH_2(L\text{–}L)]$ with excess of $HBF_4{\cdot}Et_2O$ (76) [832]. The structures of $[Pt_2(\mu\text{-}H)_2(R_2PCH_2CH_2CH_2PR_2)_2]^{2+}$ (R = c-Hx or Bu^t) have been determined by X-ray diffraction and the Pt–Pt distances are 2.698 and 2.725 Å, respectively [832]. The dication, $[Pt_2(\mu\text{-}H)_2(Bu^tPCH_2CH_2CH_2PBu^t_2)_2]^{2+}$ on treatment with hydrogen affords a trihydride $[Pt_2H_3(L\text{–}L)_2]^+$ [832].



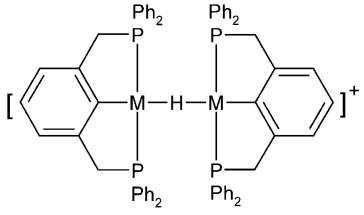
(76)

One or two terminal hydride ligands in $[Pt_2H_3(L\text{–}L)_2]^+$ can be replaced by alkyl or aryl groups to give complexes of the types $[Pt_2(\mu\text{-}H)R(H)(L\text{–}L)_2]^+$ and $[Pt_2(\mu\text{-}H)R_2(L\text{–}L)_2]^+$ [815,826,827]. The reaction of $[PtH(NO_3)(PEt_3)_2]$ with $NaBPh_4$ gives a mono-hydrido bridged complex **77** together with $[PtPh_2(PEt_3)_2]$ [813]. The **77** can also be prepared when *trans*-[PtH(MeOH)(PEt$_3$)$_2$][OTF] is treated with $NaBPh_4$ by transfer of a phenyl group from BPh_4 anion [841]. The structure of **77**, as shown by X-ray diffraction, consists of two inter-locking square planar platinum moieties. Their coordination planes are inclined at a

dihedral angle of 85° around the Pt–Pt vector with Pt–Pt separation of 3.09 Å [813]. Addition of sodium formate to *trans*-[PtAr(MeOH)(PEt_3)$_2$][BF_4], which is prepared in situ from *trans*-[PtClAr(PEt_3)$_2$] with $AgBF_4$ in methanol, followed by anion exchange with $NaBPh_4$ yields [Pt_2Ar_2(μ-H)(PEt_3)$_4$][BPh_4] (Ar = Ph, *p*-tolyl, 2,4-$Me_2C_6H_3$). The Pt-Pt distance (Ar = Ph) (3.238(1) Å) is longer than the related monohydride complex **77** indicating variation in the "donor–acceptor" interactions. Binuclear hydrido-bridged Pd/Pt complexes **78**, **79** have been isolated and characterized [822,842]. The reaction of *trans*-[PtHCl(PPh_3)$_2$] with $AgBF_4$ in moist toluene yields *trans*-[PtH(H_2O)l(PPh_3)]$^+$ which rearranges to hydrido/phosphido-bridged complex, [Pt_2(μ-H)(μ-PPh_2)Ph(PPh_3)$_3$]$^+$ [843]. The phosphido-bridged terminal hydride complexes, [Pt_2H(CO)(μ-PBu_2^t)$_2$(PBu_2^tH)][SO_3CF_3], reacts rapidly with CO to give Pt(I) dicarbonyl complex [Pt_2(μ-PBu_2^t)(CO)$_2$(PBu_2^tH)$_2$][SO_3CF_3] [844].



(77) (78)



M = Pd or Pt

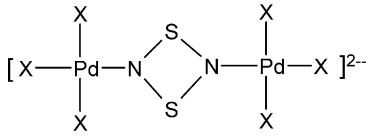
(79)

5.3. Anionic binuclear complexes

Several classical and organometallic anionic binuclear complexes of palladium and platinum have been reported. The anionic halo-bridged complexes, [M_2(μ-X)$_2$X$_4$]$^{2-}$ are usually prepared when an aqueous solution of MX_4^{2-} is treated with bulky cations such as tetraalkyl ammonium (R_4N^+; R = Me, Et, Bu, etc.), phosphonium and arsonium (Ph_4As, Ph_3MeAs) [845–849]. The iodo derivative is obtained by the reaction of MI_2 with R_4NI in alcohol in the presence of NaI [845,850]. The anion, [Pd_2(μ-Cl)$_2$Cl$_4$]$^{2-}$ is an important ion in palladium chloride chemistry in non-aqueous solvents. For example, $PdCl_2$ at low LiCl concentration in acetic acid gives $Li_2Pd_2Cl_6$ which is converted into Li_2PdCl_4 with an excess of LiCl [851]. Similar behaviour is observed for $PdCl_2$–NaCl system in acetic acid [852,853]. The complex $Pd_2Cl_4(MeCN)_2$ formed on dissolution of $PdCl_2$ in acetonitrile, converts into [Pd_2(μ-Cl)$_2$Cl$_4$]$^{2-}$ in the presence of chloride ion [854]. Reaction of [PdX(NO)]$_n$ with Ph_3BzPX yields [Ph_3BzP]$_2$[Pd_2X_4(NO)$_2$] (X = Cl or Br) which on treatment with dioxygen in acetone affords [Ph_3BzP][Pd_2X_4(NO$_2$)$_2$] [855].

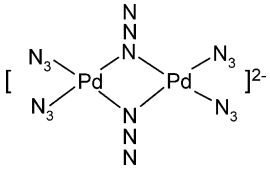
The electronic spectra of [Pt_2(μ-X)$_2$(X$_4$)]$^{2-}$ [856,857] and $Pd_2Cl_6^{2-}$ [858] have been analysed and are consistent with a planar structure. Force constant calculations for the in-plane-vibrations of [Pt_2(μ-X)$_2$X$_4$]$^{2-}$ show that the terminal stretching force constants are larger than the bridging stretching force constants which diminishes for heavier halides [859]. Infra-red spectra are interpreted in terms of planar structures [846,848,860]. The conclusions drawn from spectroscopic studies have been confirmed by X-ray structures of [Bu_4N]$_2$[Pd_2Cl_4(μ-Cl)$_2$] [861], [Et_4N]$_2$[Pt_2Br_6] [862], [Bu_4N]$_2$[Pt_2I_6] [863] and [Ph_3BzP][Pt_2Cl_6] [859]. The M_2X_6 core is planar with slightly distorted square planar coordination around each metal atom [848,862,863].

These anions undergo a variety of reactions. Bridge cleavage of [PPh_4]$_2$[Pd_2X_6] (X = Cl or Br) with S_4N_4 yields a mixture of anions, [PPh_4]$_2$[Pd_2(μ-S_2N_2)X_6] (**80**), [PPh_4]$_2$[Pd_2(μ-S_3N_2)X_4]$^-$. The X-ray structure of **80** has been reported [864].



(80)

Reaction of hydrazine hydrate with [Pr_4^nN]$_2$[Pt_2Cl_6] in DMF affords a yellow crystalline hydrazine bridged complex [Pr_4^nN]]$_2$[Pt_2Cl_6(μ-N_2H_4)] in 60% yield. The complex is stabilized by intramolecular NH···Cl hydrogen bonding [865]. A binuclear azido-bridged complex, [$AsPh_4$][$Pd_2(N_3)_6$] (**81**) has been prepared and characterized [866].



(81)

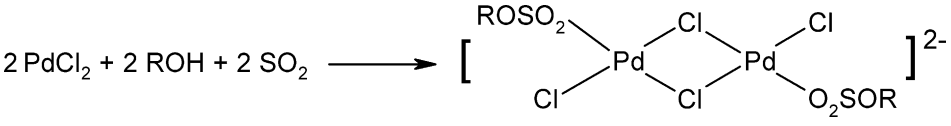
Treatment of [Pd_2(μ-SPh)$_2$Cl$_2$]$_n$ with Ph_4AsCl or Me_4NCl results in the formation of ionic thiolato-bridged complexes, Q_2[Pd_2(μ-SPh)$_2$Cl$_4$] (Q = Me_4N, Ph_4As) [270,867]. The reaction of $Pd(NO_3)_2$ with NaSPh in the presence of Et_4NBr and Ph_4PBr yields air sensitive red crystals of yet another thiolato anion, [PPh_4]$_2$[Pd_2(μ-SPh)$_2$(SPh)$_4$] [868]. The perfluorophenylthiolato derivative [Bu_4N]$_2$[Pd_2(μ-SC_6F_5)$_2$(SC_6F_5)$_4$] have been prepared by the reaction of halide complex with Tl(SC_6F_5) [869]. The structures of [Ph_4As]$_2$[Pd_2(μ-SPh)$_2$Cl$_4$] [867] and [PPh_4]$_2$[Pd_2(μ-SPh)$_2$(SPh)$_4$] [868] have revealed that the Pd_2S_2 ring is planar and the Pd···Pd distances are 3.42 and

3.505(4) Å, respectively. The phenyl groups of the bridging thiolate ligands have *anti* conformation. In the complexes $[Pt_2(\mu\text{-}SR)_2(SR)_4]^{2-}$ (R = C_6F_5, C_6HF_4, $C_6H_4CF_3$-*p*) contains planar $Pt_2(\mu\text{-}S)_2$ rings with an *anti* configuration as shown by X-ray analysis [870]. The variable temperature ^{19}F NMR studies show the occurrence of dynamic processes leading to several stereoisomers. Both inversion of configuration at bridging sulfur and hindered rotation about C–S bond are responsible for various isomeric species in solution [870].

Arene sulfinate complexes $[Pd_2(\mu\text{-}Cl)_2(SO_3R)_2]^{2-}$ (R = Me, Et) containing chloride bridges have been prepared by bubbling SO_2 into a solution of $PdCl_2$ in alcohol (77) [871]. Complexes of the type $[Ph_4As]_2[Pd_2(\mu\text{-}Cl)_2Cl_2(SO_2R)_2]$ (R = Ph or tol) have also been prepared. Sulfur atom is coordinated to palladium in these complexes [872,873]. Diallylsulfide (L) reacts with K_2PtCl_4 to give 1:1 and 1:2 complexes, $[Pt_2(\mu\text{-}L)_2Cl_4]$ and $[Pt_2(\mu\text{-}L)Cl_6]^{2-}$ in which L is bidentate and bridges through sulfur atom. Similar reaction with pyrimidine affords pyrimidine bridged complex $[Pt_2(\mu\text{-pyrimidine})Cl_6]^{2-}$ [874]. Thermolysis of $[Me_3SO]_2[Pt_2I_6]$ in air or helium yields $[Pd_2I_4(dmso)_2]$ and 2 mol of MeI [875].

Reaction of $[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]^{2-}$ (X = Cl or Br) with silver perchlorate in diethylether or with $AgClO_4{\cdot}L$ at −30 °C yields $[Pt_2(\mu\text{-}AgL)(\mu\text{-}X)_2(C_6F_5)_4]^-$ (L = Et_2O, $PMePh_2$, PPh_3) [888]. The analogous reaction with pentachlorophenyl complex, however, yields a hexanuclear complex, $[Bu_4N][\{Pt(C_6Cl_5)\}_4(\mu\text{-}Cl)_4(\mu\text{-}Ag)_2]$ [889]. Treatment of $[Bu_4N]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ with $AgClO_4$ in the presence of $SnCl_2$ affords a trigonal pyramidal species, $[Pt_3(\mu\text{-}Cl)_3(\mu_3\text{-}Sn)(C_6F_5)_6]$ which contains three Pt^{II}–Sn^{II} dative bonds [890]. Reaction of $[Bu_4N]_2[M_2(\mu\text{-}Cl)_2(C_6X_5)_4]$ with $AgClO_4$ in THF yields neutral mononuclear complex *cis*-$[M(C_6X_5)_2(THF)_2]$ (M = Pd or Pt; X = F or Cl) which on treatment with CO produces the carbonyl complexes *cis*-$[M(C_6X_5)_2(CO)_2]$ [891,892].

The halide-bridge can be substituted by various anionic ligands such as I^-, SCN^- [881], SC_6F_5 [869], PPh_2 [893] to yield $[M_2(\mu\text{-}L)_2(C_6X_5)_4]^{2-}$. The chemical oxidation of phosphido-bridged platinum complex $[NBu_4]_2[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ yields binuclear Pt(III) compound $[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ in which Pt-Pt distance (2.7245(7) Å) is reduced significatntly than that of the Pt(II) complex (3.621(1) Å) [894,895]. The phosphido-bridged palladium complex $[Bu_4N]_2[Pd_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ serves as a



(77)

Terminal halides can be substituted with an alkyl or aryl group employing an organolithium or mercury reagent. Thus, the reaction of LiR (R = $CH_2SO_2C_6H_4Me$-4) with $[NBu_4]_2[Pd_2Br_6]$ yields $[Bu_4N]_2[Pd_2(\mu\text{-}Br)_2R_4]$ [876]. Similarly diorganomercury reacts with $[Pd_2Cl_6]^{2-}$ with retention of halogen bridge to give a range of substituted aryl palladium complexes, $[Pd_2(\mu\text{-}Cl)_2Cl_2R_2]^{2-}$ [R = $C_6H_2(NO_2)_3$-2,4,6; C_6H_3Me-2-NO_2-6] [877–880].

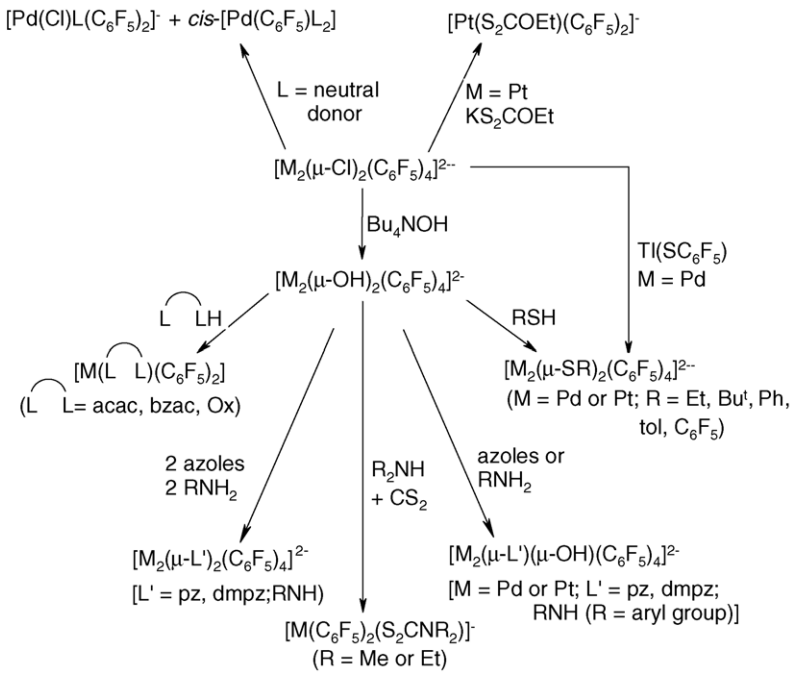
The chemistry of perhalophenyl (C_6X_5; X = F or Cl) complexes has been explored quite extensively. The arylation of $[M_2(\mu\text{-}Y)_2(Y_4)]^{2-}$ with C_6X_5Li/C_6X_5MgY (Y = Cl or Br) yields anions of the type $[M_2(\mu\text{-}Y)_2(C_6X_5)_4]^{2-}$ (M = Pd or Pt) [881,882]. Addition of halide to $[Pt(CF_3)_2(nbd)]$ in acetone generates the halide bridged anion, $[Pt_2(\mu\text{-}X)_2(CF_3)_4]^{2-}$ [883].

The halide-bridged perhalophenyl derivatives undergo a variety of reactions. The halo-bridge can be cleaved with neutral ligands. Bridge cleavage of $[Bu_4N]_2[Pt_2(\mu\text{-}Y)_2(C_6X_5)_4]$ (X = F or Cl; Y = Cl or Br) with neutral ligands affords $[Bu_4N][PtY(L)(C_6X_5)_2]$ [881,882,884] whereas similar reaction with palladium complex, $[Bu_4N]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ yields $[Bu_4N][PdCl(L)(C_6F_5)_2]$ and *cis*-$[Pd(C_6F_5)_2L_2]$ (L = N, P, As or Sb donor ligands) [885]. Bridge cleavage with bis phosphines (e.g. dppa), yields $[\{Pt_2(C_6F_5)_2Cl\}_2(dppa)]$ which has been used for construction of multi metal aggregates [886,887].

precursor for the preparation of high nuclearity derivatives $[Bu_4N]_2[Pd_4(\mu\text{-}PPh_2)_2(\mu\text{-}X)_4(C_6F_5)_4]$ (X = Cl or Br) when treated with MCl_2 [896]. The reaction of $[Bu_4N]_2[Pt_2(\mu\text{-}Cl)_2(C_6X_5)_4]$ with $K(S_2COEt)$ affords a mononuclear complex $[Pt(S_2COEt)(C_6F_5)_2]^-$ in which xanthate ligand acts in a chelating fashion [897]. Complexes containing pyrazolates, indazolates and $[pz_4B]^-$ bridges have also been synthesized and characterized [898–900]. Reaction of dihydroxy benzoquinonate with $[Bu_4N]_2[Pt_2(C_6F_5)_2(thf)_2]$ in 1:2 ratio gives a binuclear complex $[Bu_4N]_2[Pt_2(C_6F_5)_4(\mu\text{-}O_4C_6X_2)]$ [901].

Substitution of bridging chloride in $[M_2(\mu\text{-}Cl)_2(C_6X_5)_4]^{2-}$ by Bu_4NOH affords hydroxo-bridged complexes, $[M_2(\mu\text{-}OH)_2(C_6X_5)_4]^{2-}$ which are important precursors for the synthesis of a variety of derivatives (Scheme 14) [902–906]. The bridging OH in the ^1H NMR spectrum of platinum complex appears at −1.21 ppm indicative of its highly nucleophilic nature [902]. The structures of $[Bu_4N]_2[M_2(\mu\text{-}OH)_2(C_6F_5)_4]$ (M = Pd or Pt) have been established by X-ray diffraction (Fig. 24) [903,904].

The hydroxo-bridged complexes $[Bu_4N]_2[M_2(\mu\text{-}OH)_2(C_6X_5)_4]$ (X = F or Cl) reacts with protic acids to give either mononuclear or binuclear complexes depending on the denticity of the incoming ligand. Thus, the reactions with acacH, bzacH, or OxH ligands afford mononuclear complexes, $[Pt(L^{\frown}L)(C_6X_5)_2]$ [903], while mercaptans [907], pyrazoles [902–904,907–909] and arylamines [910] yield binuclear derivatives. The palladium hydroxo-bridged



Scheme 14.

complexes invariably give bis pyrazolato-bridged complexes $[Pd_2(\mu\text{-NN})_2(C_6X_5)_4]^{2-}$ [902–904,908], while in case of platinum both hydroxo/pyrazolato-bridged, $[Pt_2(\mu\text{-OH})(\mu\text{-NN})(C_6X_5)_4]$ and bis pyrazolato-bridged derivatives, $[Pt_2(\mu\text{-NN})_2(C_6X_5)_4]^{2-}$ are formed depending on the reaction stochiometry and conditions (NN = pz, 3,5-dmpz, 3-Me-pz; indazolate) [909]. The five-membered ring (Pt_2O, NN) in $[Pt_2(\mu\text{-OH})(\mu\text{-pz})(C_6F_{54})]^{2-}$ adopts an envelope configuration [909]. The complex on treatment with RSH yields $[Pt_2(\mu\text{-SR})(\mu\text{-pz})(C_6F_5)_4]^{2-}$ [907].

The reaction of $[Bu_4N]_2[M_2(\mu\text{-OH})_2(C_6F_5)_4]^{2-}$ with arylamines in dichloromethane yields arylamido-bridged complexes, $[M_2(\mu\text{-NHAr})(\mu\text{-X})(C_6F_5)_4]^{2-}$ (X = OH or NHAr; Ar = Ph, C_6H_4R-4 (R = F, Cl, NO_2) or C_6F_5] depending on the arylamine ratio [910]. The X-ray structure of $[Pd_2(\mu\text{-NHC}_6F_5)_2(C_6F_5)_4]^{2-}$ revealed a planar Pd_2N_2 core with Pd···Pd distance of 3.147(2) Å [910]. The diarylamido-bridged complexes on treatment with CS_2 yields mononuclear dithiocarbamates, $[Pd(S_2CNHAr)(C_6F_5)_2]^-$ [910] which can also be obtained by the reaction of $[M_2(\mu\text{-OH})_2(C_6F_5)_4]^{2-}$ with amines in the presence of CS_2 [905].

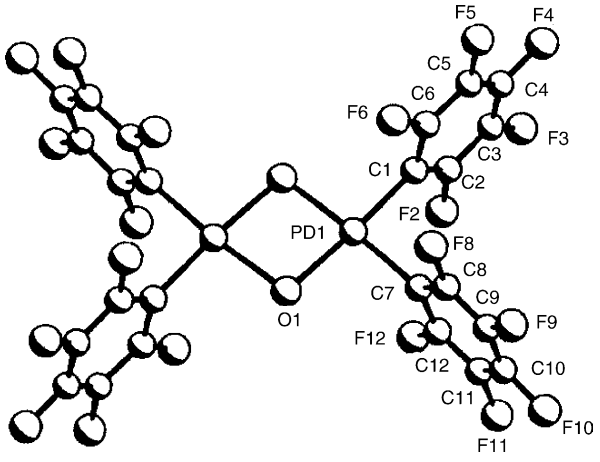
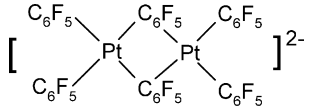


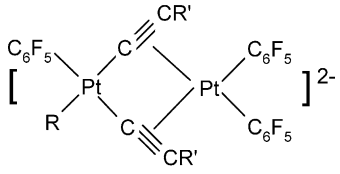
Fig. 24. Molecular structure of $[Pd_2(\mu\text{-OH})_2(C_6F_5)_4]^{2-}$ (reproduced with permission from ref. [904]).

Several aryl or alkenyl-bridged anions have been prepared [573,888,910–914]. The aryl bridged anion $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ (**82**) are prepared by the reaction of *cis*-$[Pt(C_6F_5)_2(THF)_2]$ with $[Bu_4N]_2[Pt(C_6F_5)_4]$, the method can be extended to prepare hetero-metallic complexes [913]. The **82** has alternatively been prepared by the reaction of $[Bu_4N]$ $[PtCl(C_6F_5)_3]$ with $AgClO_4$ [911,912]. However, this reaction in ether yields a trinuclear complex $[Bu_4N]_2[Pt_2Ag(C_6F_5)_6Et_2O]$ [888,911]. The **82** on treatment with bipyridine generates another binuclear complex, $[Bu_4N]_2[Pt_2(\mu\text{-bipy})(C_6F_5)_6]$ in which bipy acts as a bridging ligand. However, similar reaction with 1,10-phenanthroline results in bridge cleavage with the formation of $[Pt(C_6F_5)_2(phen)]$ and $[Bu_4N]_2[Pt(C_6F_5)_4]$ [914]. The dppm bridged complexes, $[NBu_4][Pt(C_6F_5)_3\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-Ph})\}M(C_6F_5)_2]$ could be isolated by treating $[NBu_4][Pt(C_6F_5)_3(dppm)]$ with $[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt) [915].



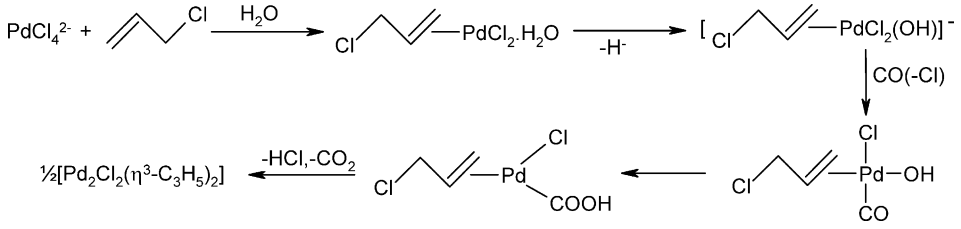
(82)

Treatment of $[Pt(C_6F_5)_2(THF)_2]$ with $[Pt(C_6F_5)R(C{\equiv}CR')_2]^{2-}$ ($R = C_6F_5$; $C{\equiv}CR'$; $R' = Ph$ or Bu^t) results in alkynyl-bridged anions (**83**) [573]. The structure of $[PMePh_3]_2[Pt_2(\mu\text{-}C{\equiv}CPh)_2(C_6F_4)_4]$ has been established by X-ray diffraction [573].



(83)

under conditions employing reducing reagents such as carbon monoxide in methanol in the presence of traces of moisture [927,931–934]. Hydroxo(carbonyl) olefin complexes (**84**) have been proposed as reaction intermediates in these reactions (79) [931]. Several variations of reaction (79) have been explored which involve use of another nucleophile (e.g. primary amine [935]) in place of water or a different reducing agent (e.g. $SnCl_2$ [936]) instead of carbon monoxide. Other variations include the use of chloride complexes of Ti, Zn, Cu in methanol [937] and also ethylene [938]. Complexes contatining functionalized allyl group were prepared in a similar way [939–941]. Activated palladium or platinum, prepared by reduction of MX_2 using lithium in naphthalene, reacts with allylhalides to give $[M_2X_2(\eta^3\text{-allyl})_2]$ [942].



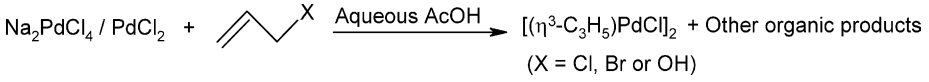
(79)

6. Binuclear allyl complexes of palladium(II) and platinum(II)

The chemistry of transition metal allyl complexes is dominated by allylpalladium derivatives due to their ease of formation and relevance in several organic transformations. Palladium catalysed allylic reactions often proceed under milder conditions than ordinary SN_2 reactions with different chemo-, regio- and stereo-selectivities. The synthesis of allylpalladium complexes was first described in mid 1950s. General chemistry of allyl palladium and platinum complexes has been reviewed earlier [1,2,4,8,48,916,917]. Binuclear allyl palladium and platinum complexes are prepared in several ways which can broadly be classified as follows.

6.1. Synthesis involving allyl alcohols/halides and related compounds

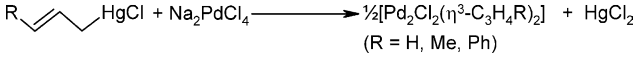
Allylalcohols [918–924] and allylhalides [925–929] have been employed to prepare η^3-allyl complexes usually in aqueous acetic acid at 30–60 °C (78). The reaction of allylalcohol with platinum salts, however, yields olefin complexes [930]. Although the reaction of allyl alcohol with $PdCl_2(PhCN)_2$ in benzene affords allylpalladium chlorodimer, π-olefin complex, $[(HOCH_2CH{=}CH_2)PdCl_2]_2$, also forms [920]. The reaction tends to give propylene, cyclic alcohols and palladium metal as the side products.



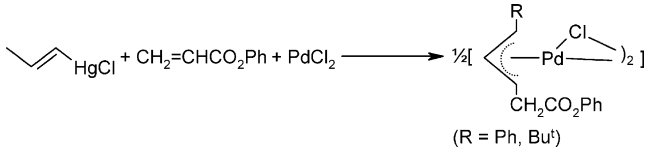
(78)

Reaction (78) genrally gives poor yields of desired allyl complex, $[Pd_2Cl_2(\eta^3\text{-allyl})_2]$. Higher yields are obtained

Transmetallation reactions have been employed to prepare allylpalladium complexes. Allylmercury [943–945] and triallylantimony [946] transfer allyl group to palladium salts affording allylpalladium derivatives (80). Vinyl mercury compounds in the presence of olefin give binuclear allyl palladium complexes (81) [947,948].



(80)

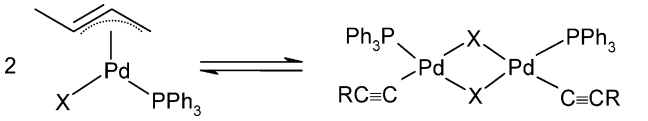


(81)

6.2. Synthesis from palladium(O) and platinum(O) precursors

Reaction of palladium sponge with allylhalide for synthesis of allylpalladium complex has been reported by Fischer and Burger [949]. Reaction is facilitated by ultra sound [950]. Zerovalent palladium/platinum precursors, $Pd_2(dba)_3$, $M(dba)_2$ (M = Pd or Pt), $Pt(\eta^3\text{-norborene})_2$ have been used for the synthesis of allyl complexes [951–956]. Reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ with $RC{\equiv}CCH_2Cl$ in the presence of

PPh_3 affords a monomeric η^3-propargyl complexes which on treatment with NaX (X = Br or I) yields the bromo- and iodo-derivatives. The latter two equilibrates with halide-bridged η^1-propargyl dimer (82) [956].



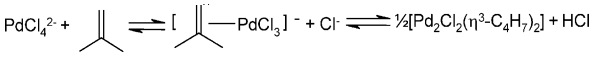
(82)

6.3. Synthesis involving olefins

Both mono- and di-olefins have been extensively employed for the preparation allyl complexes.

6.3.1. Synthesis from mono-olefins

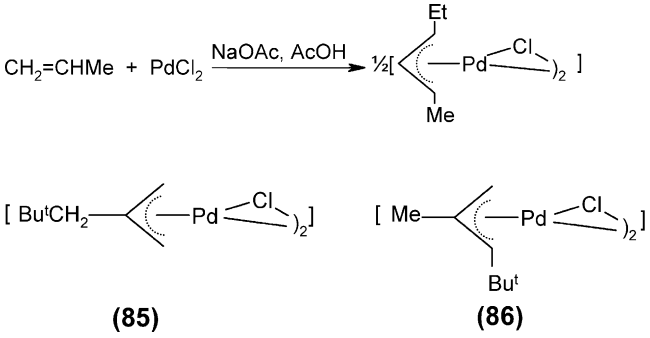
Reaction of palladium salts with olefins in acetic acid in the absence [925,926,957–960] or presence of sodium acetate [961]/sodium carbonate [962]/sodium methoxide [963] yields binuclear allylpalladium complexes (83). Tsuji and co-workers [964,965] used $[PdCl_2(PhCN)_2]$ as the palladium precursor. These reactions proceed in two steps [926,961,966–968]. In the first step a palladium-alkene complex is formed. In the second step oxidative addition of C–H bond to palladium takes place with concomitant removal of HCl. The proton can be removed either by an internal (e.g. chloride ligand) or external (e.g. solvent molecule) base [968]. Reactions in the absence of a base, in addition to the allylic complex, results in precipitation of palladium metal and formation of aldehydes and ketones. These products appear to be formed through oxidation of η^3-allyl complex by $PdCl_2$ [926,958]. Because of stability of platinum–olefin complexes, reaction (83) with platinum salts under similar conditions does not yield platinum allyl complexes [966,969,970]. The platinum-allyl complexes $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ are, however, obtained either by heating binuclear olefin complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(olefin)_2]$ in acetic acid [971] or by treatment of $Pt(allyl)_2$ with dry HCl [972]. The $[PtCl(C_3H_5)]_4$ is tetrameric in nature, consisting of alternating diallyl and dichloro-bridges [973].



(83)

The formation of allyl complexes in reaction (83) is facilitated by olefins containing electron withdrawing substituents [960,964,965,974–980]. Several functionalized olefins (e.g. containing amide functionality) have also been employed to prepare η^3-allyl derivatives [981]. Trimethyl vinyl silane reacts with palladium chloride in DMF in the presence of methanol to yield a *syn* isomer of chloride bridged dimer containing η^3-1-methyl-1-(trimethylsilyl)allyl group. The *syn* isomer is converted into *anti* isomer on heating in chloroform [982]. The reaction of allyltrimethyl silane with $PdCl_2(MeCN)_2$ affords $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ which is formed by nucleophilic attack of chloride ion on the silicon atom. However, in the presence of a base, such as Et_3N, $[Pd_2Cl_2(\eta^3\text{-}C_3H_4SiMe_3)_2]$ is formed in a moderate yield [983]. Optically active allylsilanes yields optically active η^3-allyl palladium complexes. The reaction (83) has been successfully employed to prepare allyl palladium complexes from cyclic mono olefins (e.g. cyclohexane, cycloheptene, 1-methylcycloheptene, cyclodecene) [984–988] and from several natural products such as steroids, terpenes, alkaloids, etc. [978,979,988–994].

Olefin isomerization during the reaction is not uncommon which results in the formation of mixture of allylic complexes [995–998]. For instance, Lukas et al. [996] isolated **85** and **86** from 2,4,4-trimethylpent-2-ene $[Bu^tCH_2C(Me)=CH_2]$. The **85** is formed by isomerization of coordinated olefin followed by loss of HCl whereas **86** is formed by elimination of H_2 from coordinated olefin. Some simple olefins may couple to give allylic complexes where allyl group is formed by di- or tri-merization of olefin (84) [60,999–1002].

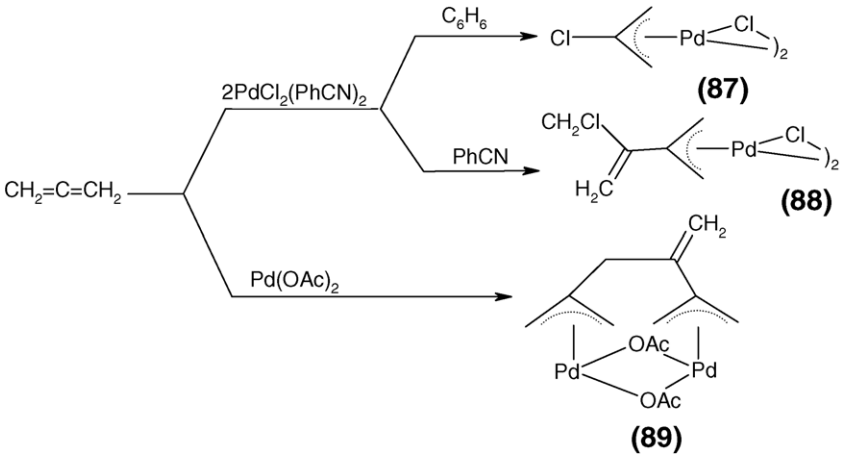


(84)

6.3.2. Synthesis from diolefins

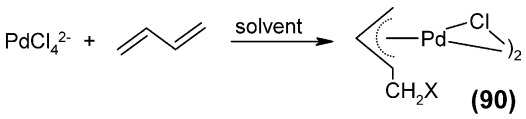
Both acyclic and cyclic dienes (1,2-, 1,3-, 1,4-, 1,5-, 1,6- and 1,7-dienes) react with palladium salts in protic solvents to yield η^3-allylpalladium complexes. The reaction of 1,2-dienes (allenes) with palladium compounds gives various allyl compounds, the nature of which depends on reaction medium and palladium precursors (Scheme 15) [1003–1009]. Thus, reaction of $PdCl_2(PhCN)_2$ with allene in non-polar solvents (e.g. benzene) yields **87** while in polar solvents (e.g. MeOH, PhCN) **88** is isolated. However, reaction of palladium acetate with allene affords an acetato-bridged complex (**89**) which is formed by trimerization of an allene [1007–1009].

The reaction of 1,3-diene with palladium precursors yields η^3-allyl palladium dimers. The nature of allylpalladium complexes depends on the reaction medium and 1,3-diene (85) [1010–1015]. Reaction (85) in alcohol (such as methanol) gives an alkoxo complex (X = OR) while in acetic acid an acetate derivative is formed (X = OAc) [1011,1012]. Configuration of the allyl complex is influenced by the nature of 1,3-diene. Thus, reaction of butadiene with $PdCl_2$ in acetic acid yields the *syn* isomer of **90** (X = OAc) whereas



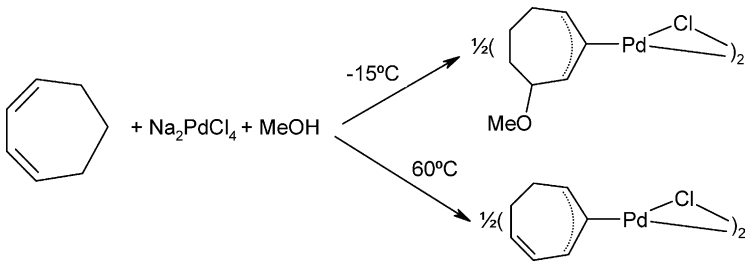
Scheme 15.

with isoprene an *anti* isomer of **90** (X = OAc) is isolated [1014].



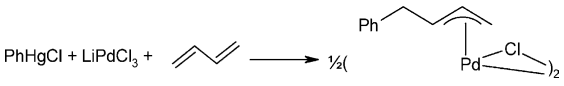
(85)

Cyclic dienes react similarly with palladium salts and the nature of the resulting products depend on the reaction conditions [39,66,984,1016–1020]. An excess of diene is often required to give a high yield of the complex [1020]. 1,3-Cycloheptadiene and 1,3-cyclooctadiene at low temperatures afford an alkoxo derivative but at higher temperatures an unsaturated cyclic allyl complex is formed in which double bond is not conjugated to the allyl group (86). Nucleophilic attack at the coordinated cyclo-1,3-dienes has been reported to yield η^3-allyl palladium complexes [1021–1031].

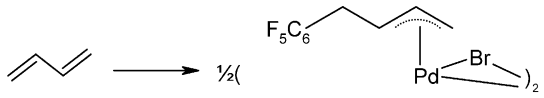


(86)

Both mono- and di-enes react with palladium salts in the presence of organomercury compounds (RHgX) to yield R-substituted allylpalladium complexes (87) [1027,1028,1031–1033]. Reaction with 1,4-dienes is regioselective with attack occurring exclusively on the least substituted double bonds. Organopalladium species, "PdRX", formed by the reaction between palladium precursor and RHgX, has been proposed as an intermediate in these reactions. The proposed "PdRX" has now been stabilized with perfluorophenyl group. Thus, the complex $[PdC_6F_5(Br)(MeCN)_2]$ reacts with acyclic and cyclic 1,3-dienes to give η^3-allyl palladium complexes (88) [1034].



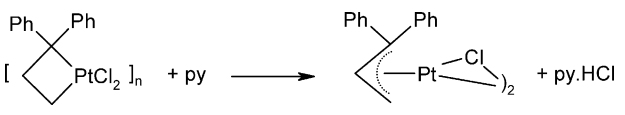
(87)



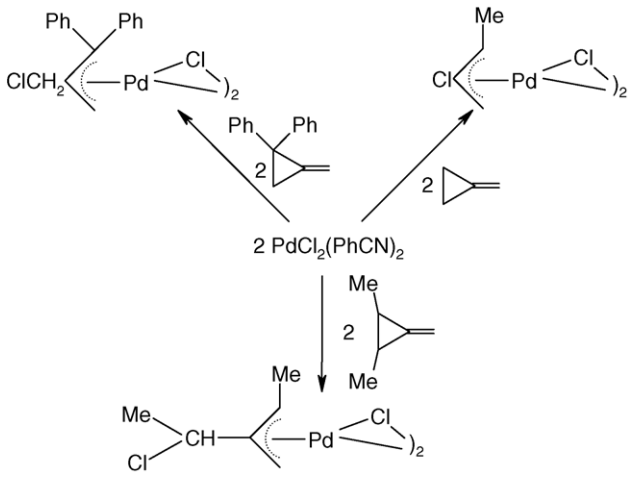
(88)

6.4. Synthesis from cyclopropanes

Reactivity of cyclopropanes with palladium and platinum differ markedly, the former yielding allyl complexes while the latter affording platinacyclobutanes. Sterically crowded platinacyclobutane on treatment with pyridine yields an allyl complex (89) [1035], although sterically non-demanding platinacyclobutanes afford pyridine adducts like $[PtCl_2(CH_2CH_2CH_2)(py)_2]$.



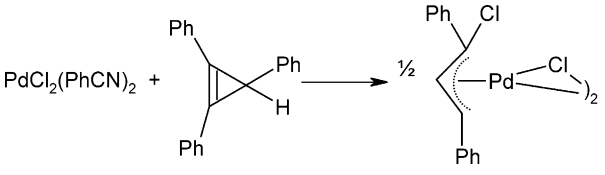
(89)



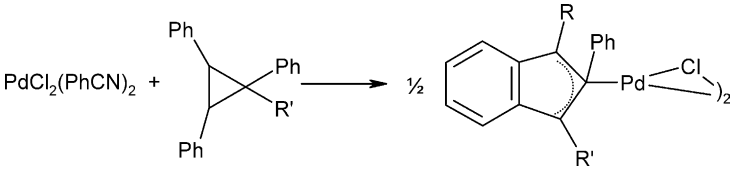
Scheme 16.

Cyclopropanes react with $[PdCl_2(RCN)_2]$ (R = Me or Ph) or $[Pd_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ in organic solvents to give η^3-allyl palladium dimers [173,1036–1042]. Although cyclopropane does not yield η^3-allyl palladium complex, bromocyclopropane reacts with $[Pd_2Cl_2(\mu\text{-}Cl)_2(CH_2{=}CH_2)_2]$ in refluxing benzene to form $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}BrCHCHCH_2)_2]$ [173,1036,1037]. The formation of η^3-allylpalladium complexes from vinylcyclopropanes decreases with the substitution either at olefin or in the ring [1038,1039]. Substituents in methylenecyclopropane greatly influence the direction of ring opening in its reaction with $PdCl_2(PhCN)_2$ resulting in the formation of a variety of η^3-allyl palladium complexes (Scheme 16) [1038,1039]. Spiroalkanes also give allylpalladium complexes [173].

Treatment of $PdCl_2(PhCN)_2$ with triphenylcyclopropene yields an allyl complex (90) [1043], whereas substituted cyclopropane affords an indenyl derivative (91) [1043]. Synthesis of an indenyl complex $[Pd_2Cl_2(\eta^3\text{-indenyl})_2]$ has also been reported [1044].



(90)



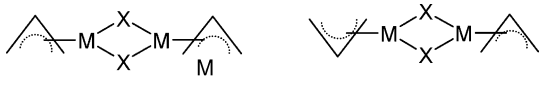
(91)

6.5. Spectroscopic and structural aspects

Electronic spectra of some binuclear allylpalladium complexes have been reported [984,1011,1045–1049]. Initially three bands in the region 20,000–56,000 cm^{-1} have been identified for $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ which were later resolved to five bands. (λ_{max} = 318 (sh, ε = 1600), 285 (sh, 1500), 243 (sh, 6800), 224 (sh, 11,500) and 207 (17,700) nm). The three weak bands (~29,500, 34,000, 40,500 cm^{-1}) have been assigned to d–d transitions while the two strong ones (~44,000 and 46,500 cm^{-1}) have been attributed to charge transfer transitions from Cl_π-Pd and Pd-$allyl_\pi$* [1047,1049]. Although an acetonitrile solution of $[Pd_2Cl_2(\eta^3\text{-allyl})_2]$ is thermally stable, but light sensitive and on photolysis yields colloidal palladium and $PdCl_2(MeCN)_2$ (λ_{max} = 242 (23,800) and 211 (12,600) nm) [1049]. The quantum yield for the formation of the latter is ϕ = 0.008 at λ_{irr} = 366 nm. Several allyl complexes have been characterized by IR and Raman spectral data [963,1050–1053]. Two strong bands are usually observed for Pd–Cl stretching vibrations at ~250 cm^{-1}. A band at 360–405 cm^{-1} has been assigned to the Pd-allyl absorptions [1051]. Although C=C absorption is not observed in the IR spectra, a band at ~1455 cm^{-1} is assigned to ωC–C of the allyl ligand.

Palladium $3d_{5/3}$ core binding energies have been measured by electron spectroscopy for chemical analysis (ESCA) for $[Pd_2X_2(\eta^3\text{-}C_3H_5)_2]$ (X = Cl, Br, I). The observed energies (337.6, 337.7 and 337.9 eV, respectively) are independent of the bridging halide [1054].

The halo-bridged allylpalladium/platinum complexes exist in to two isomeric forms, viz. *syn* (**91**) and *anti* (**92**). These complexes are usually stereochemically non-rigid and interconversion between the two isomers (**91** and **92**) in solution is quite facile at room temperature. However, on crystallization only one isomeric form is crystallized out (see later).



(91) **(92)**

The ^1H NMR spectrum of $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}MeC_4H_3)_2]$ in $CDCl_3$ exhibits three singlets at δ 2.18, 2.14 and 3.66 ppm in a ratio 3:2:2 and are assigned to methyl, *anti* and *syn* protons [971]. Two isomers are identified at −65 °C. Similar pattern is observed for the corresponding palladium complex. ^1H NMR spectrum of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ in $CDCl_3$ displays three resonances at δ 2.95, 4.02 and 5.45 ppm attributable to the *syn*, *anti* and the central carbon protons, respectively [1016,1055]. However, the spectra in coordinating solvents show complex pattern (see later) due to the existence of an equilibrium between the dimeric

and monomeric species. The central carbon proton resonance (δ 5.45 ppm) appears as multiplet due to coupling with two *syn* protons (J_{H-H} = 6.8 Hz) and two *anti* protons (J_{H-H} = <1.0 Hz). The *syn* and *anti* protons appear as a doublet due to coupling with the central carbon proton. The *anti* protons (δ 2.95 ppm) which are close to the metal atom are most shielded and are little influenced by the nature of the bridging ligand. In general substitutents occupy *syn* rather than *anti* positions except when a bulky group is present [996]. From the NMR data of $[Pd_2Cl_2(CH_2CH{=}CHPr^i)_2]$ it has been suggested that torsion around C_2-C_3 bond followed by face exchange of palladium atom in a σ-bonded allyl palladium intermediate takes place [1056]. The *J*-values serve as an important tool in assigning the stereochemistry of allyl complexes [960,996,1010,1057,1058]. The NMR spectra of thiolato/selenolato-bridged allylpalladium complexes, unlike halo-bridged derivatives, reveal that both *syn* and *anti* isomers are present in solution indicative of rigid configuration [286]. In some cases, however, a dynamic behaviour has been noticed which could be arrested at ∼0 °C (Fig. 25). Variable temperature ^{1}H NMR measurements on acetato-bridged allyl palladium derivatives indicate the existence of two conformational isomers [1059].

The structures of several halo-bridged allyl complexes [956,973,982,1025,1040,1044,1060–1076] have been established by single crystal X-ray diffraction analysis (Table 14).

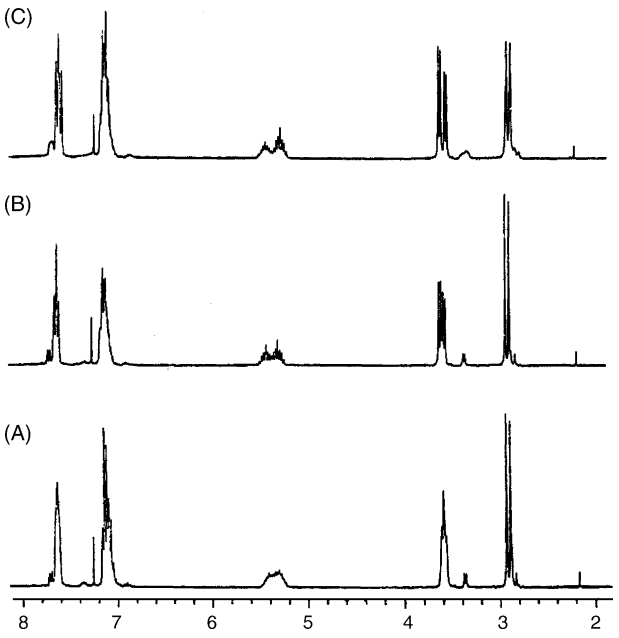


Fig. 25. Variable temperature ^{1}H NMR spectrum of $[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_3H_5)_2]$ in $CDCl_3$ at (A) 25, (B) 0 and (C) –45 °C (reproduced with permission from ref. [286]).

Table 14
Structures of allyl complexes determined by X-ray diffraction analyses

Complex	Comments	References
$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$	Planar Pd_2Cl_2; η^3-allyl are *anti*	[1062,1063,1065,1066]
$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(Me)CH_2)_2]$	Planar Pd_2Cl_2; η^3-allyl are *anti*	[1069,1070]
$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(Bu^t)CH_2)_2]$	Planar Pd_2Cl_2; η^3-allyl are *anti*	[1064,1067]
$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(CH_2Bu^t)CH_2)_2]$	–	[1067]
$[Pd_2(\mu\text{-}Cl)_2(MeCHCHCHMe)_2]$	Pd_2Cl_2 non-planar with dihedral angle 150°, η^3-allyl are *syn*	[1068]
$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}Me_2CCHCMe_2)_2]$	Pd_2Cl_2 non-planar, η^3-allyl are *anti,* Pd–Pd = 3.418(6) Å	[1069,1071]
$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(Me)CHBu^t)_2]$	Pd_2Cl_2 ring, non-planar, θ = 148°	[1074]
$[Pd_2(\mu\text{-}Cl)_2\{\eta^3\text{-}CH_2C(OH)CH(CO_2Et)\}_2$	Pd_2Cl_2 non-planar, η^3-allyl are *anti*	[1060,1061]
$[Pd_2(\mu\text{-}Br)_2\{\eta^3\text{-cycloheptenyl}\}_2$	Pd_2Br_2 non-planar, dihedral angle 139°, allyl in *syn* configuration, Pd ··· Pd = 3.32 Å	[1072]
$[(Ph_4C_4OEt)_2Pd_2Cl_2]$	Pd_2Cl_2 symmetrical, Pd ··· Pd = 3.432(6) Å	[1028]
$[Pd_2(\mu\text{-}Cl)_2\{\eta^3\text{-}C_8H_8Cl\}_2$, C_8H_8Cl = 4, 6-(1-chlorocyclooctatrienyl)	Dihedral angle between Pd and allylic group = 119.8°	[1075]
$[PtCl(CH_2\text{-}CH\,CH_2]_4$	Chloro and olefin-bridged tetramer	[973]
$[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}CH_2C(Me)CH_2)_2]$	Pd_2S_2 non-planar with *syn* allyl groups, Pd ··· Pd = 3.1447(6) Å	[1078]
$[Pd_2(\mu\text{-}SC_6H_4F\text{-}4)_2(\eta^3\text{-}C_3H_5)]_2$	Hinged structure θ = 49.18°, R substituents are *syn-exo*	[1085]
$[Pd_2(\mu\text{-}Me_2pz)_2(\eta^3\text{-}C_3H_5)_2]$		[1082]
$[Pd_2(\mu\text{-}OAc)_2(\eta^3\text{-}C_3H_5)_2]$	Pd ··· Pd = 2.94	[1064]
$[Pd(\mu\text{-}OAc)_2(\eta^3\text{-}C_3H_5)Pt(OAc)(PPh_3)]$	Pd ··· Pt = 2.992(1) Å	[1083]
$[Pd_2(\mu\text{-}OAc)_2(\eta^3\text{-}2\text{-methylallyl-}3\text{-norbonyl})$	Pd ··· Pd = 2.960(1) Å	[1079]
$[Pd_2(\mu\text{-}NHCPhNH)_2(\eta^3\text{-}C_3H_5)_2]$	Pd ··· Pd = 3.128(1) Å	[1084]
$[Pd_2(\mu\text{-}tolNNNtol)_2(\eta^3\text{-}C_3H_5)_2]$	Pd ··· Pd = 2.856(1) Å	[1081]
$[Pd_2Cl_2(C_{10}H_{16}Cl)_2]$	Allyl groups *cis* arrangement	[1040]
$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-indenyl})_2]$	Indenyl groups are *anti*	[1044]
$[Pd_2(\mu\text{-}MeNNNMe)_2(\eta^3\text{-}C_4H_7)_2]$	Pd ··· Pd = 2.75 Å	[1070]
$[Pd_2(\mu\text{-}Cl)_2(C_8H_{11}O_2)_2]$, ($C_8H_{11}O_2$ = *trans*- and *cis*-4-acetoxy {(η^3-(1, 2, 3)-cyclohexenyl)	Pd_2Cl_2 non-planar, with θ = 148.9(2)° *trans* isomer, 148.1(2)° *cis* isomer	[956]
$[Pd_2(\mu\text{-}pzR_2\text{-}3,5)_2(\eta^3\text{-}C_3H_5)_2]$, (R = $C_6H_4OC_{12}H_{25}$)	Pd_2N_4 ring boat conformation, Pd ··· Pd = 3.293 Å	[1086]
$[Pd_2(\mu\text{-}pz(CF_3)_2\text{-}3,5)_2(\eta^3\text{-}C_3H_5)_2]$	Pd ··· Pd = 3.2169 Å	[1087]

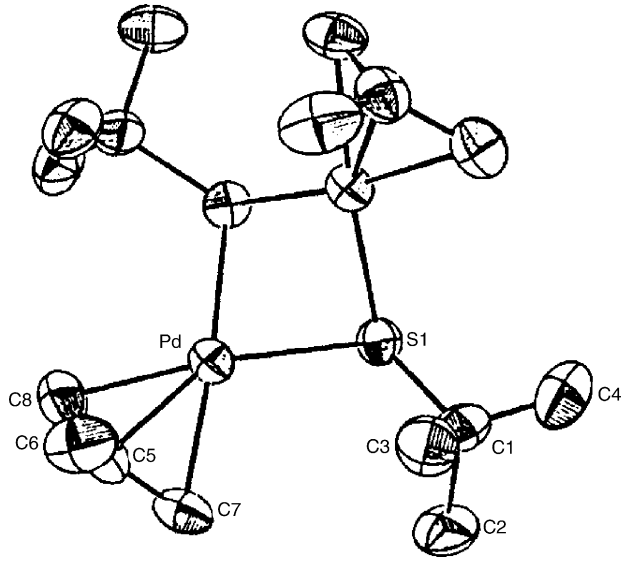


Fig. 26. Crystal and molecular structure of $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$ (reproduced with permission from ref. [1078]).

The allyl group is η^3-bonded. Two coordination site of the metal atom are occupied by the allyl group while the remaining two are occupied by the bridging halide. The square plane of the metal atom and the planar allyl group intersects each other with the dihedral angle varying between 108 and 127°. The two allyl groups adopt either *syn* or *anti* conformation. The four-membered "M_2X_2" ring may have either a planar [1062,1063,1065,1066,1069,1070,1077] or non-planar [956,973,1060,1068,1071,1072,1078] conformation. The bridging M–X distances are generally equal. To minimize thermal vibrations, structure of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ has been determined at −140 °C. All the Pd–C distances (2.108–2.132 Å) are almost equal, but at room temperature central carbon-palladium distance is marginally longer than the other two distances.

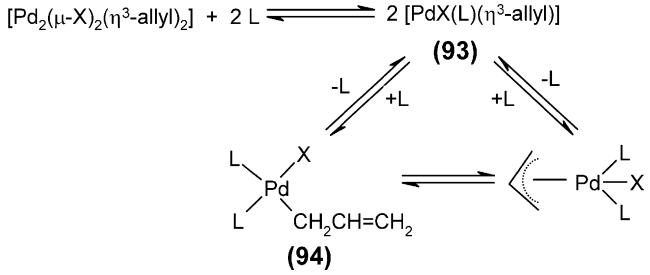
The structures of allylpalladium complexes containing bridging ligands other than halides have been reported [1078–1087]. All the compounds have a bent (non-planar Pd_2X_2 ring) configuration irrespective of the bridging ligands (SBu^t, $pzMe_2$, triazine, formamidine, acetate). The Pd · · · Pd distances in the complexes containing three atom bridging ligands [1064,1079–1081,1083,1084] are significantly shorter than those containing either single atom [Cl or SBu^t (Fig. 26)] or two-atom bridging ligands (e.g. Me_2pz). These distances varies between 2.94 and 3.13 Å and are significantly longer than the metal indicating absence of direct metal–metal bonding.

6.6. Chemical reactivity of binuclear allyl complexes

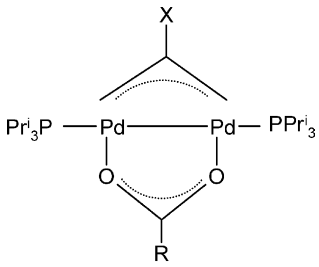
Chemical reactivity of binuclear allyl complexes has been extensively investigated and is dominated by allylpalladium complexes, although allylplatinum derivatives display similar reactivities. These complexes undergo primarily three different classes of reactions, viz.: (a) bridge cleavage with neutral donors; (b) substitution of bridging halide with other anionic ligands; and (c) nucleophilic attack at the allyl carbon. The latter reaction finds numerous applications in organic synthesis.

6.6.1. Bridge-cleavage with neutral donor ligands

The halo-bridged allyl-palladium and -platinum complexes are labile and the bridge is cleaved by a variety of mono- and bi-dentate neutral donor ligands. The resulting complexes quite often show dynamic behaviour which has been investigated by NMR spectroscopy. The NMR spectra are usually complex due to the following equilibria.



Treatment of halo-bridged allyl-palladium and -platinum complexes with monodentate nitrogen donors (e.g. amines, pyridines, triazines, formamidine, pyramidines, purines) [1088–1096], tertiary phosphines [1052,1097–1100], tertiary arsines [1100–1102], triphenylantimony [1100,1102], dmso [1055,1103,1104] and other [1095,1102,1105–1108] ligands (L) yields 1:1 adducts (**93**). The reactions with tertiary phosphines are usually complex yielding species of the types $[PdCl(\eta^3\text{-allyl})(PR_3)]$ (**93**), $[PdCl(\sigma\text{-allyl})(PR_3)_2]$ (**94**), $[Pd(allyl)(PPh_3)_2]Cl$, $Pd(PPh_3)_4$ depending on solvent and stochiometry of the reactants [1052,1097,1098]. For instance, $Pd(PPh_3)_4$ and $[Ph_3Pallyl]Cl$ are formed when $Pd_2Cl_2(\eta\text{-allyl})_2$ is treated with an excess of PPh_3 in aqueous acetone [1007]. The reaction of $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ with $4PPh_3$ or $[PdCl(\eta^3\text{-allyl})(PPh_3)]$ with one equivalent of PPh_3 yields the σ-allyl palladium complex **94** instead of cationic derivative $[Pd(\eta^3\text{-allyl})(PPh_3)_2]Cl$ [1099]. Cleavage with $AsPh_3$ gives 1:1 adduct (**93**) and the formation of any ionic compound $[Pd(allyl)(AsPh_3)_2]Cl$ is negligible. The carboxylate bridged dimers $[Pd_2(\mu\text{-}O_2CR)_2(\eta^3\text{-}2\text{-}XC_3H_4)_2]$ (R = Me, CF_3, Ph; X = H, Me, Pr^i, Bu^t) when treated with PPr^i_3 in hexane yields Pd(I) dimers (**95**) [1109].



(95)

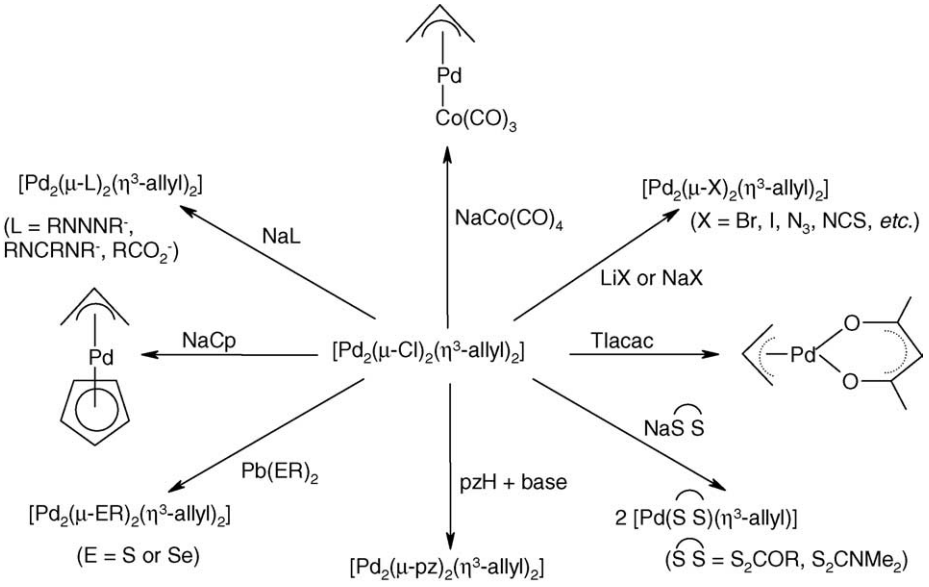
Cleavage with bidentate neutral donor ligands yields cationic complexes which are isolated as the salts of non-coordinating anions. Thus, the complexes of the general formula $[M(\eta^3\text{-allyl})L_2]X$ (M = Pd or Pt; X = NO_3, BF_4, ClO_4, PF_6 or CF_3SO_3; L_2 = PPh_3, PMe_2Ph, PEt_2Ph, $PEtPh_2$, $AsMe_2Ph$, $AsPh_3$, $SbPh_3$, 7,8-benzoquinoline, 8-methylquinoline, tetramethylthiophene, 1,4-dithiane; L_2 = 2,2′-bipyridine, diene, cyclooctatetraene, 2,2′-biimidazole, 2,2′-bibenzimidazole, tmeda, RN=CHCH=NR, RN=CH-C_5H_4N-2) have been isolated [1110–1132]. Treatment of $[PtCl(C_3H_5)]_4$ with $Ph_2PCH_2CH_2SR$ yields a neutral tetracoordinate complex $[PtCl(\eta^1\text{-}C_3H_5)(Ph_2PCH_2CH_2SR)]$ in which allyl is σ-bonded and P∩S ligand is chelated. The complex is stable in non-polar solvents, but in polar solvents (e.g. alcohol) it is rapidly converted in an ionic compound $[Pt(\eta\text{-}C_3H_5)(Ph_2PCH_2CH_2SR)]Cl$ [1120].

6.6.2. Halide exchange with other anionic ligands

The bridging halide, usually chloride, is readily exchanged with a variety of anionic ligands to afford a myriad of complexes (Scheme 17). The chloride in $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ is substituted by bromide, iodide and pseudohalides (e.g. CN, N_3, NCS) by reaction with alkali metal salts in appropriate solvents [963,974,976,1011,1055,1133–1135]. The ^1H NMR spectrum of $[Pd_2(\mu\text{-}SCN)_2(\eta^3\text{-}MeC_3H_4]$ at −61 °C revealed that the thiocyanate is bridged unsymmetrically in solution [1133].

The chloro-bridged allyl palladium/platinum complexes react with Tlacac or acetylacetone in the presence of a base to give mononuclear complexes of the type $[M(acac)(\eta^3\text{-allyl})]$ (M = Pd or Pt) [963,1006,1010,1011,1045,1073,1136,1137], $[Pt(acac)(C_3H_5)]_2$, however, is a dimer [1073,1136]. Similar reactions with monothiodibenzoylmethane [1077], xanthates (S_2COR, R = Me, Et), dithiocarbamates [1057,1138], oxine, picolinolate [1139], salicyaldiimines, salicyaldehyde [1140–1143] and 2-acetylphenolate [1144] afford mononuclear complexes $[M(chel)(\eta^n\text{-allyl})]$ containing chelating ligands. However, with simple phenolate ligands, binuclear complexes $[Pd_2(\mu\text{-}OAr)_2(\eta^3\text{-allyl})_2]$ are isolated from the reaction between $[Pd_2Cl_2(\eta^3\text{-allyl})_2]$ and phenols in the presence of Bu_4NOH in methanol [1145]. Similarly binuclar complexes have been isolated from $[Ph_2P(O)NPPh_2E]^-$ (E = S or Se) [1146]. Treatment of allylpalladium chloro-bridged dimers with sodium or thalium cyclopentadienide yields monomeric $[Pd(\eta^3\text{-allyl})(\eta^5\text{-Cp})]$ [1010,1016,1024,1045,1147,1148]. Stable dimeric aryl-bridged palladium complexes, $[Pd_2(\mu\text{-}Ar)_2(\eta^3\text{-allyl})_2]$ are formed when $[Pd(acetone)_2(allyl)]^+$ is treated with $[NBu_4][Pd(allyl)Ar_2]$. These complexes are fluxional in solution [1149].

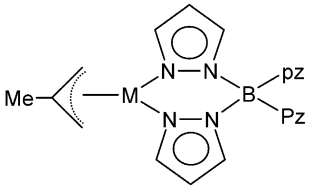
Several binuclear complexes derived from anionic three-atom bridging ligands, such as acetate [1057], triazenido (1,3-diphenyltriazando, 1-methyl-3-phenyltriazenido) [1081,1150,1151], formamidinato (RNCR′NR; R = Ph, tol-*p*, *p*-ClC_6H_4, $SiMe_3$; R′ = H or Me) [1084,1152], have been isolated by treatment of chloro-bridged allyl complex with lithium or sodium salt of an appropriate ligand. The acetato and formamidinato-bridged complexes are fluxional at room temperature whereas the triazenido-bridged derivatives are non-labile and are inert to ligand substitution [1081]. Similarly sulfurdiimine-bridged complexes, $[Pd_2(\mu\text{-}R'NSRNR')_2(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$ (R = Me or Bu^t; R′ = aryl) have been synthesized [1153]. These complexes decompose on heating to azoarenes and thiolato-bridged allylpalladium complexes, $[Pd_2(\mu\text{-}SR)_2(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$. A direct method for the synthesis of the latter molecules and related chalcogenolates involves the reaction of $[Pd_2(\mu$-



Scheme 17.

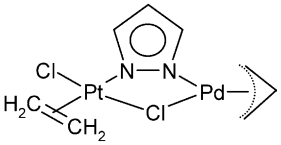
$Cl)_2(\eta^3\text{-allyl})_2]$ with $Pb(ER)_2$ or $Hg(TeR)_2$ [286,1078,1085].

Reaction of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}2\text{-}RC_3H_4)_2]$ (R = H, Me, Ph) with pyrazole/substituted pyrazoles in the presence of a base gives pyrazolato-bridged complexes, $[Pd_2(\mu\text{-}pz)_2(\eta^3\text{-}2\text{-}RC_3H_4)_2]$ (pz = pyrazolate or substituted pyrazolate) [1086,1087,1154]. The reaction between $[M_2(\mu\text{-}Cl)_2(\eta^3\text{-}2\text{-}MeC_3H_4)_2$ (M = Pd or Pt) and $KBpz_4$ affords mononuclear complexes (**96**) [1155] whereas in the reaction of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ with $K_2[pz_3B\text{-}Bpz_3]$ a bridged complex $[\{(\eta^3\text{-}C_3H_5)Pd\}_2\{(\mu\text{-}pz)_2Bpz\}_2]$ is isolated [1156]. A hetero-bridged complex (**97**) is reported by Deese and Johnson [1157]. Reaction between $[MR_2(pz)(pzH)]^-$ (M = Pd or Pt; R = C_6F_5 or C_6Cl_5) and [Pd(acac)(allyl)] (allyl = C_3H_5 or 2-MeC_3H_4) yields bimetallic derivative $[R_2M(\mu\text{-}pz)_2Pd(\eta^3\text{-allyl})]$ [1158].



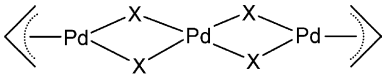
(M = Pd or Pt)

(96)



(97)

Allylpalladium complexes containing extra mole of $PdCl_2$ per dimer have been prepared for which a PdX_2-bridged structure (**98**) has been suggested and later confirmed by X-ray crystallography where $PdCl_2PdCl_2Pd$ framework has a nearly planar arrangement [1159]. A number of carbonyl metallate anions or metal carbonyls react with allylpalladium dimers to give allylpalladium–metal carbonyl complexes [1027,1160–1163]. Treatment of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}2\text{-}MeC_3H_4)]_2]$ with $(Me_3Si)_2Se$ affords a hexanuclear complex $[Pd_6(\mu\text{-}Se)_3(\eta^3\text{-}2\text{-}MeC_3H_4)_6]$ which contains a distorted trigonal prismatic cluster as revealed by X-ray structural analysis [1164]. A few other reactions of chloro-bridged allylpalladium dimers have been described [1165,1166].

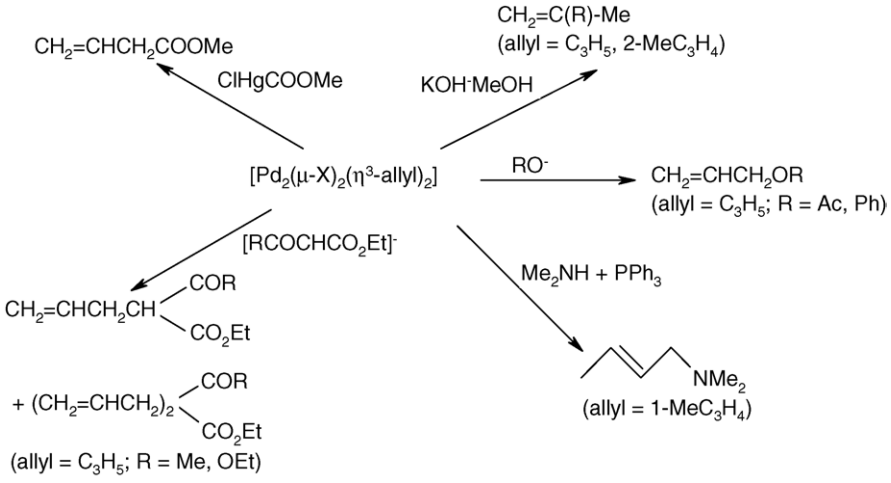


(98)

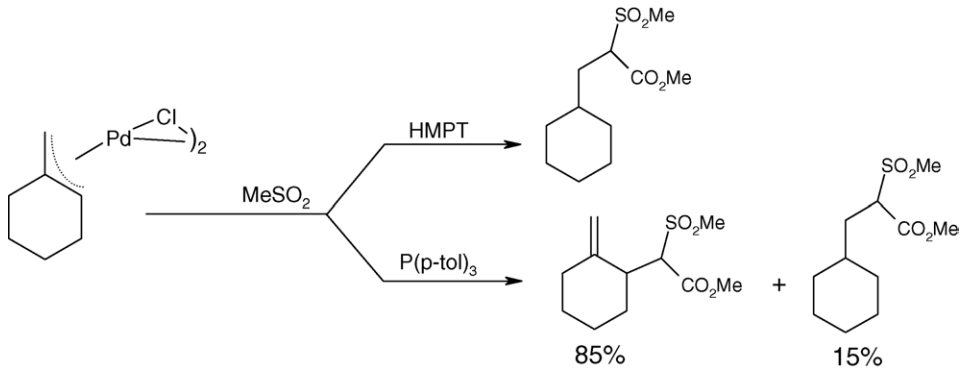
6.6.3. Reactions involving allylic carbon

Nucleophilic attack on allylpalladium complexes find extensive applications in organic synthesis [1167], particularly in natural product chemistry of stereospecific allylations [1168–1171]. Nucleophiles usually attack from *exo* (opposite to the metal) side, preferably at the least hindered site, at C-1 and C-3 carbons of the allyl group. However, in certain cases attack on C-2 carbon has also been reported where palladacyclobutane as an intermediate has been proposed [1172]. Nucleophilic attack results in decomposition of the complex. A variety of nucleophiles, e.g. RO^-, methanolic KOH [926,985,1173–1175], anions of dimethylmalonate and ethylacetoacetate [1176,1177], methoxy, carboxylate [170], amines [1030,1178], etc. attack on the coordinated allyl group to give functionalized olefins (Scheme 18). Stereochemistry of nucleophilic attack on allylpalladium complexes has been investigated. Both inversion and retention of configuration in the final product have been reported. An exo-attack of the nucleophile on the allyl is responsible for the former while for the latter coordination of nucleophile to palladium followed by reductive elimination (*cis* attack) is attributed. Ligands play an important role on regioselectivity (Scheme 19) [1179,1180].

Carbon monoxide and olefins react with allyl-palladium and platinum complexes to give a variety of products depending on the reaction conditions. Initially a 1:1 adduct, similar to other Lewis bases, is formed which are isolated as trichlorostannate complexes $[M(SnCl_3)(L)(\eta^3\text{-allyl})]$ (L = CO or olefin) [1181–1184]. Further reaction of



Scheme 18.

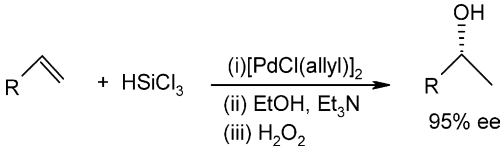


Scheme 19.

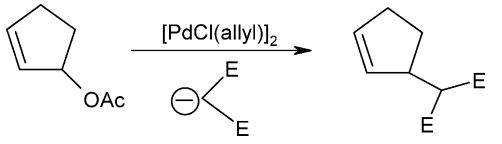
1:1 adduct results in insertion products. Thus, insertion of CO affords an acyl derivative which couples with halogen and extrudes the metal (Scheme 20) [1185]. Thus, acid chlorides are formed in inert solvents whereas an ester is isolated in alcoholic medium and an acid in the presence of water [172,927,960,1186–1192]. These carbonylation reactions are sensitive to ligands, substituents and temperature. For instance, carbonylation is sluggish with the chloro-bridged allyl complexes, but in the presence of carboxylic acid salts it is quite facile and proceeds at low CO pressure at 25 °C [1193].

Unlike carbon monoxide, alkene attacks the most substituted allylic carbon atom [172,1189]. Reactions of mono- and di-enes with allylpalladium dimers have been investigated [172,1007,1194–1196]. Electron withdrawing substituents on allyl group increase the rate of reaction considerably. For instance, chloroallyl palladium complex reacts 10^5 times faster than that of the unsubstituted complex. Methyl substitution both at the allyl group and the olefin retards the rate of reaction. Isocyanides also insert across the allylpalladium bond via a mononuclear intermediate formed by halogen bridge cleavage of $[Pd_2(\mu\text{-}X)_2(\eta^3\text{-allyl})_2]$ [198,1197].

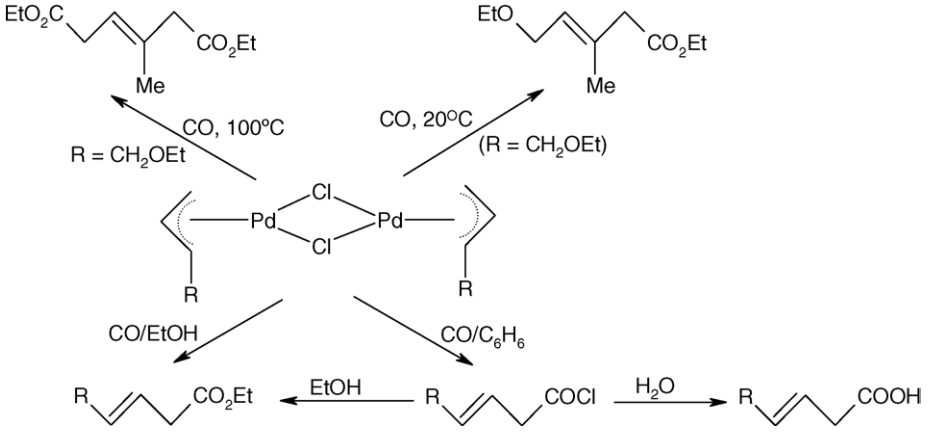
Allylpalladium complexes are used as catalysts in several organic transformations [1044,1171,1192,1198–1211]. These include precatalyst for enantioselective hydrosilylation of olefins, asymmetric alkylation and amination, carbostannylation of alkynes, etc. (92)–(95). The thiolato bridged complexes $[Pd_2(\mu\text{-}SR)_2(\eta^3\text{-}C_3H_5)_2]$ in the presence of phosphines are used as catalyst for the allylic alkylation coupling of (E)-3-acetoxy-1,3-diphenyl-1-propene and dimethylmalonate (95) [1212]. In several organic transformations allylpalladium complexes are believed to be reactive intermediate, in such reactions they are seldom isolated [1201].



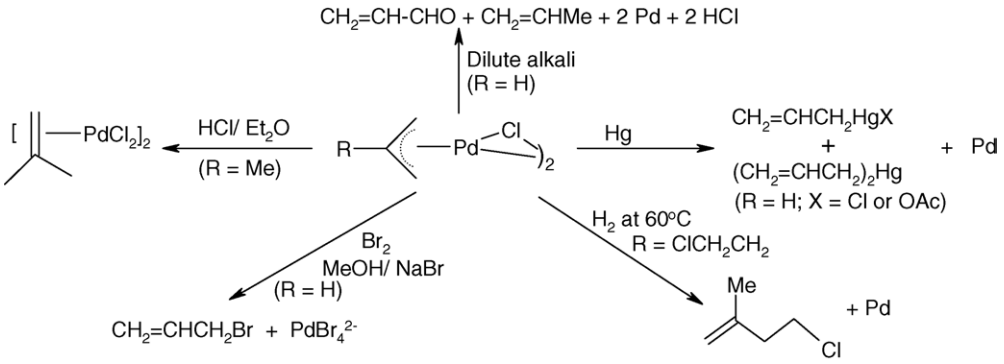
(92)



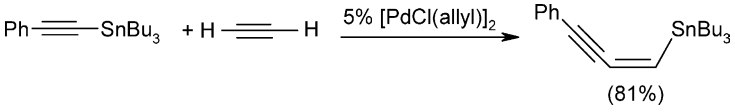
(93)



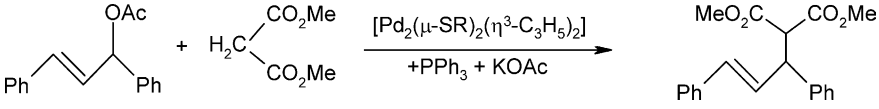
Scheme 20.



Scheme 21.



(94)



(95)

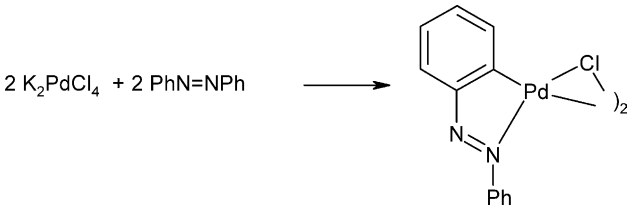
Binuclear allylpalladium complexes undergo a variety of other reactions (Scheme 21) which are relatively less explored. These include halogenation [1000,1213], hydrolysis [1214], oxidation [925,926,958,1175,1214,1215], reduction [91,978,979,1037,1175,1216–1220], reactions with protic acids [926,1221] and allyl group transfer to another metal (e.g. mercury) [1222]. Allyl palladium complex, $[Pd_2(\mu\text{-}Cl_2)(\eta^3\text{-allyl})_2]$ reacts with organic free radicals ($R^\bullet = Ph^\bullet$, $Ph_3C^\bullet$, c-$Hx^\bullet$) which initially attack the palladium center followed by secondary processes converting coordinated allyl ligand preferentially to terminal rather than internal alkenes [1223].

6.6.4. *Thermal decomposition*

Thermal decomposition of a few allylpalladium halides has been investigated [925,926,1224–1227]. The complexes $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ (allyl = C_3H_5, 2-MeC_3H_4) on pyrolysis yields allylchloride (180 °C) [925,1226], 2-methylallylchloride (at 25 °C) [925,926], respectively, besides minor other organic products and palladium metal. Thermogravimetric analysis of allylpalladium halides show an endothermic decomposition in the temperature range 160–200 °C [1224]. The allylpalladium bond dissociation energy has been estimated to be 237 kJ/mol as determined by differential scanning calorimetry [1226]. Allylpalladium acetate on thermal decomposition yields allylacetate, propylene and other unidentified organic products [1058]. Thermal behaviour of organochalcogenolato-bridged methylallyl palladium complexes, $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$ (ER = SBu^t, SPh, SC_6F_5, SePh, TePh) has been investigated by thermogravimetric analysis in the authors group [1078]. These complexes yield Pd_4E (E = S or Se) at moderately low temperatures (∼140 °C) or Pd_3Te_2 at room temperature.

7. Binuclear cyclometallated complexes

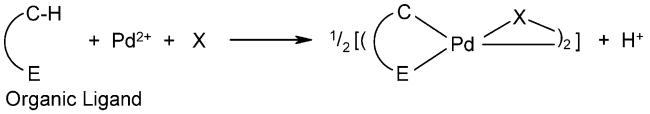
Following the first report on cyclometallation reaction by Kleiman and Dubeck [1228], Cope and Siekman [1229] examined the reaction between K_2PdCl_4 and azobenzene in dioxane and isolated the first cyclopalladated complex (96). Since this early study, cyclopalladation reactions have been extensively studied as is evident from several review articles published time to time (Table 15) [1230–1246]. These compounds find numerous applications in organic synthesis and catalytic processes, characterization of enantiomerically chiral compounds and as metallomesogens.



(96)

A myriad of organic ligands undergoes cyclometallation reactions which can be represented according to general equation (97). In general, cyclometallation is facile with palladium complexes as compared to their platinum analogues. Cyclopalladation reactions are usually carried out at room temperature between a palladium salt [M_2PdCl_4 (M = Li, Na, K), M_2PdCl_4/NaOAc or $Pd(OAc)_2$] and an organic ligand in methanol, ethanol, acetone, dioxane, chloroform, acetic acid or binary mixture of water and organic solvent. The system M_2PdCl_4/NaOAc is usually more effective. An electrophilic reaction mechanism involving Pd···HC interactions in a 14-electron species such as

"[Pd(H-C-E)$(X)_2$]" has been suggested for cyclometallation [1247–1249]. For example, reaction of $[Pd(OAc)_2]_3$ with dimethylbenzylamine initially yields a mononuclear species $[Pd(OAc)_2(PhCH_2NMe_2)_2]$ which reversibly dissociates into amine and a pseudo- three coordinate 14-electron intermediate "$[Pd(OAc)_2(PhCH_2NMe_2)]$". The latter subsequently undergoes rate limiting *ortho*-palladation to form cyclopalladated acetato-bridged dimer $[Pd_2(\mu\text{-}OAc)_2(C^{\frown}N)_2]$. The activation entropy for the rate limiting step, which is electrophilic in character, is negative ($-250\,J\,K^{-1}\,mol^{-1}$) for $PhCH_2NMe_2$ suggesting a highly ordered tight transition state.



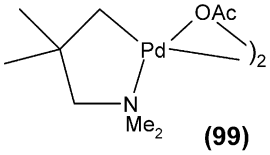
(X = Cl, OAc; E = donor atom; -C- = ≡C-, =CH-, -CH_2-)

(97)

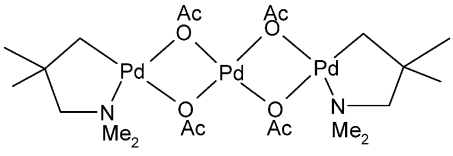
Besides the general synthetic method (97), other routes have also been employed for the preparation of *ortho*-metallated compounds. These include reaction of $Pd_2(dba)_2$ with halogenated organic compound [1250,1251], exchange of cyclopalladated moiety with another organic ligand [1252–1257], use of organomercury compounds [1258,1259].

7.1. Nitrogen ligands

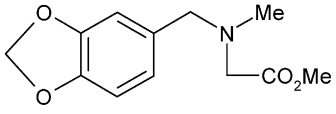
Cyclometallation of several *tert*-aliphatic/aromatic amines has been investigated. Treatment of $Pd(OAc)_2$ with *N*,*N*-dimethylneopentylamine ($Me_2NCH_2Bu^t$) yields both bi- and tri-nuclear cyclopalladated species (**99** and **100**) [1260,1261]. Cyclopalladation of amino ester (**101**) and allylic amines (**102**) takes place regiospecifically to give **103** and **104**, respectively [1262,1263]. *N*,*N*-dimethyl-α-naphthylamine [1264] and 1,3-disubstituted phenylamines [1265] are readily cyclopalladated. In the latter double cyclopalladation occurs at 4- and 6-phenyl positions to give **105**.



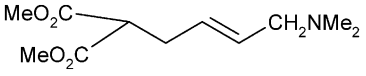
(99)



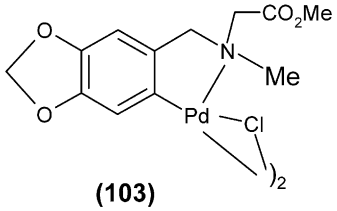
(100)



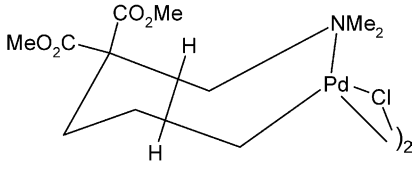
(101)



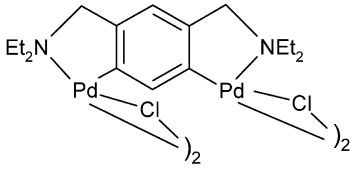
(102)



(103)



(104)

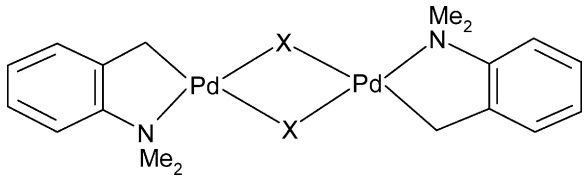


(105)

The reaction of palladium acetate with 2-dimethylamino toluene in acetic acid was initially thought to give cyclometallated dimer **106** (X = OAc) [1266,1267]. However, reinvestigation using field desorption MS and NMR spectroscopy showed the product a trimer. The **106** (X = OAc) is obtained by the reaction of chloro-bridged dimer (X = Cl) with silver acetate [1268]. *N*,*N*-dimethyl-2-phenyl benzene is similarly metallated [1269].

Table 15
Reviews on cyclometallated compounds

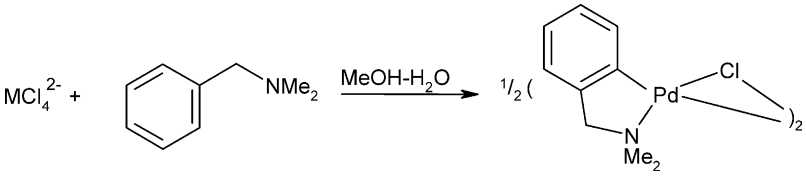
Title	Author(s)	References
Intramolecular aromatic substitution in transition metal complexes	G.W. Parshall	[1230]
Cyclometallated compounds	J. Dehand and M. Pfeffer	[1231]
Cyclometallierungsseaktionen	M.I. Bruce	[1232]
Ortho-metallierungsseaktionen	H.P. Abicht and P. Issleib	[1233]
Cyclometallic intramolecular coordination compounds containing a nitrogen donor ligand	I. Omae	[1234]
Organometallic intramolecular coordination compounds recent aspects in the study of sulfur donor ligands	I. Omae	[1235]
Organometallic intramolecular coordination compounds containing a phosphorus donor ligand	I. Omae	[1236]
Organometallic intramolecular coordination compounds containing a cyclopentadienyl donor ligand	I. Omae	[1237]
Organometallic intramolecular coordination compounds containing a arsine donor ligand	I. Omae	[1238]
Organometall-verbindungen-mit intramolekularer π-olefin-metallkoordination	I. Omae	[1239]
Cyclometallated complexes incorporating a heterocyclic donor atom; the interface of coordination chemistry and organometallic chemistry	E.C. Constable	[1240]
Cyclopalladated complexes in organic synthesis	A.D. Ryabov	[1241]
Cyclometallation of platinum metals with nitrogen and alkyl, alkenyl and benzyl carbon donors	G.R. Newkome et. al.	[1242]
Recent studies on organometallic intramolecular coordination compounds	I. Omae	[1243]
Cyclometallated complexes of 8-methyl quinoline and derivatives with the platinum metals	D.W. Evans et. al.	[1244]
Mechanisms of intramolecular activation of C-H bonds in transition metal complexes	A.D. Ryabov	[1245]
Resolution of tertiary phosphines and arsines with *ortho*-metallated palladium(II) amine complexes	S.B. Wild	[1246]



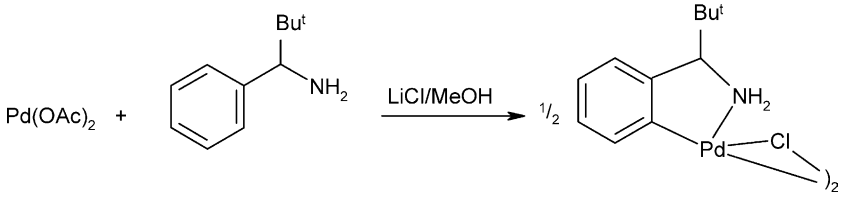
(106)

N,*N*-dimethylbenzylamine readily reacts with $PdCl_4^{2-}$ in water–methanol to give *ortho*-metallated product. Similar reaction with $PtCl_4^{2-}$ is slow (98) [1247]. Metallation is quite sensitive to the substituents on benzene ring as well as on amine. While 4-$MeOC_6H_4CH_2NMe_2$ and 3,5-Me_2-$C_6H_3CH_2NMe_2$ are readily metallated, 4-$NO_2C_6H_4CH_2$-NMe_2 and $PhCH_2NHMe$ yield MCl_2L_2 complexes [1247].

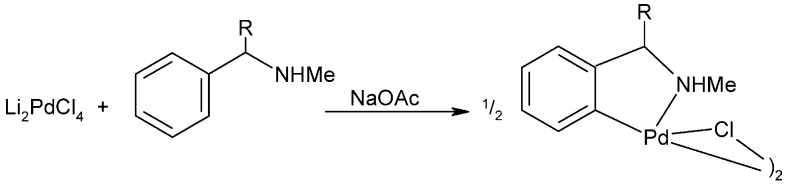
Cyclometallation of several substituted benzylamines has been investigated [1249,1270–1290]. Steric demands of R substituents at α-benzylic position greatly influence *ortho*-palladation reactions. Thus, with sterically crowed substituent (e.g. Bu^t) even a primary amine can be metallated in rather moderate yield (50%) (99) [1291]. The reactions of secondary amines also show similar trend [1292–1296]. The reaction of $PhCH_2NHMe$ with Li_2PdCl_4 gives only $PdCl_2L_2$ [1292] whereas with PhCHRNHMe (R = Me or Bu^t) metallation is observed. Moreover, activation of sp^3 C–H bond (26%) in $PhCHBu^tNHMe$ becomes possible in competition with sp^2 C–H bond activation (60%) to give two possible regio-isomers in ca. 1:3 ratio (100).



(98)



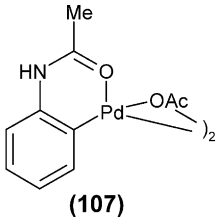
(99)



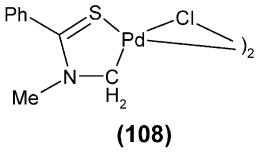
R = Me (47 % yield)
Bu^t (60 % yield)

(100)

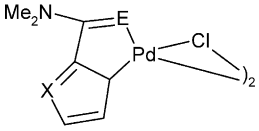
Cyclopalladation of PhNHCOMe with $Pd(OAc)_2$ yields **107** [1297]. *N*,*N*-dimethylbenzothioamide with Li_2PdCl_4 is palladated at *N*-methyl substituent to give **108** [1298]. Contrary to this, *N*,*N*-dimethylaminofuran [1299,1300] or *N*,*N*-dimethylaminothiophene [1301,1302] and carbo-thio (or seleno-) amides are metallated at the heterocyclic ring to yield **109** and **110**.



(107)

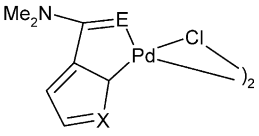


(108)



(109)

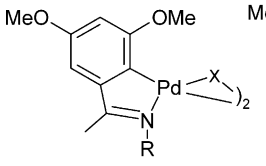
X = O, S
E = S, Se



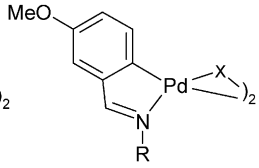
(110)

Cyclometallation of Schiff base ligands has been extensively studied. Most imine complexes are prepared by direct metallation of an aryl ring using $Pd(OAc)_2$ [1226,1305–1335]. The nature of the product formed depends on the reaction conditions as well as on the substituents in the ring. Both *endo*- (C=N included into metallocyclic ring) and *exo*- (C=N outside the metallocyclic ring) cyclic products are formed (Scheme 22). So far five structural motifs for the cyclopalladated organic imines have been identified (Scheme 23).

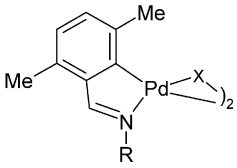
Regioselectivity of cyclometallation for the ligands containing more than one possible metallation sites has been studied [1326,1336,1337]. Methoxy groups at the C-3 and C-5 positions hinder direct metallation by palladium(II) at the C-2 or C-6 positions (**113**); with only one methoxy group in the C-3 position, C-6 is selectively metallated (**114**); whereas less sterically demanding methyl group allows attack of the palladium atom at C-2 positions in **115** and **116** [1336,1337].



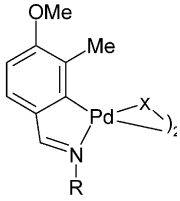
(113)



(114)

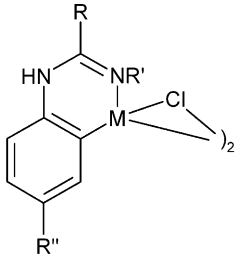


(115)

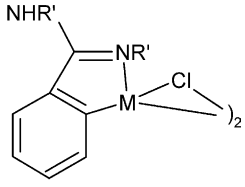


(116)

Reactions of arylamidines, R′NHCRNR′ (formamidines, acetamidines, benzamidines) with K_2MCl_4 (M = Pd or Pt) in refluxing aqueous methanol yields grey-green *ortho*-metallated complexes, **111**, **112** [1303,1304].

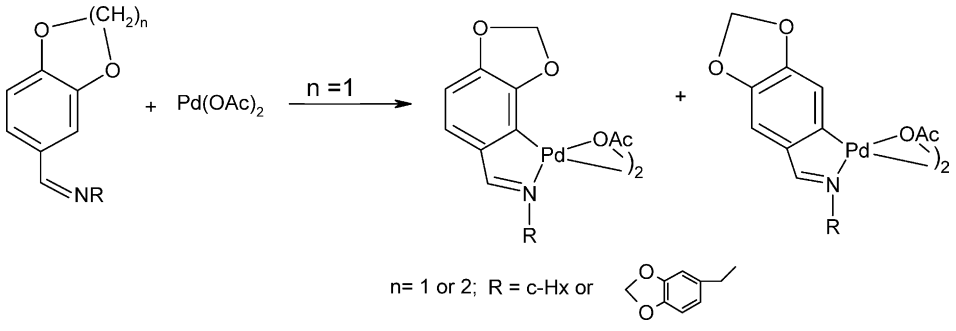


(111)

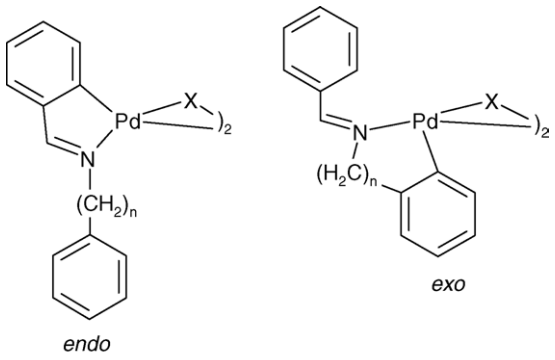


(112)

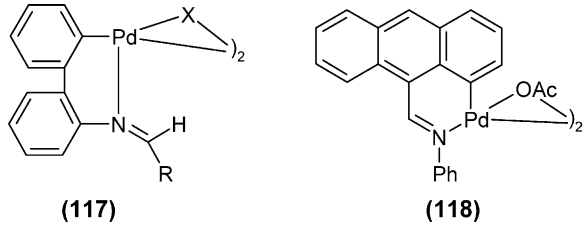
Reactions of $Pd(OAc)_2$ with Schiff bases containing OCH_2O linkage results in a mixture of two products formed by activation of C–H bond either at 2- or 6-position (101) [1338,1339]. However, when $n = 2$, only one product is formed by activation of 6-position [1338]. X-ray structures of all these complexes reveal that the *endo* isomer is present and the cyclometallated moiety is almost planar [1338,1339].



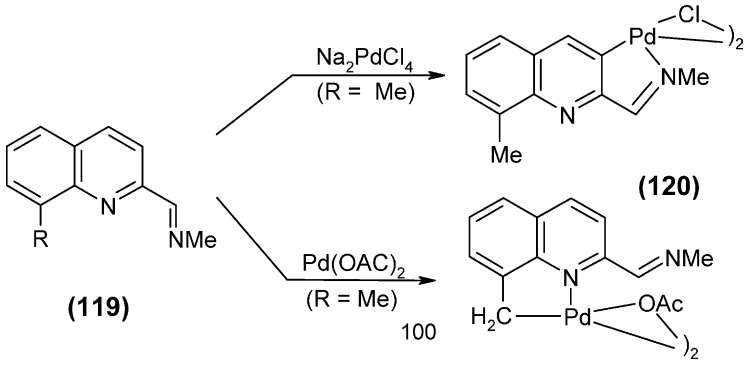
(101)



Scheme 22.



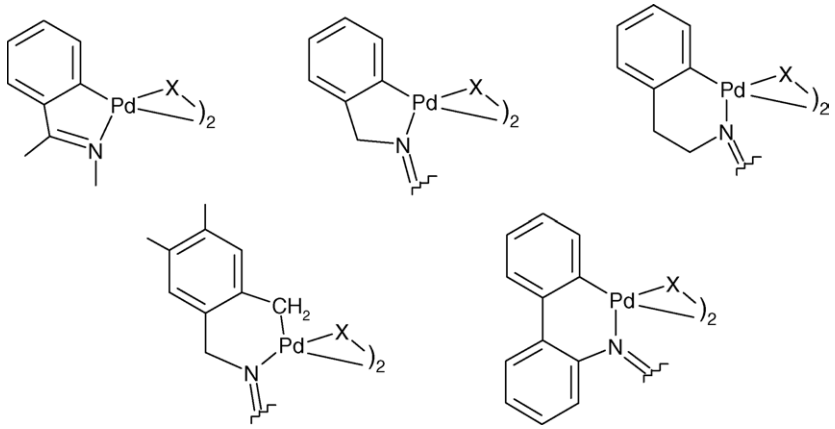
Cyclometallation of **119** with Pd(II) depends on the nature of R group. When R is the methyl group metallation occurs at different positions depending on the ligands on palladium (102). However, with R = Et or Pr^i only the analogue of **120** is formed exclusively [1342,1343].



(102)

N-benzyldene-2-phenylanilines (RCH = NC_6H_4Ph-2; R = 2,6-$Cl_2C_6H_3$, 2,6-$F_2C_6H_3$; 2,4,6-$(MeO)_3C_6H_2$) react with $Pd(OAc)_2$ to give *exo*-cyclic six-membered cyclopalladated dimer (**117**) which on subsequent treatment with LiBr yields corresponding bromo-bridged dimer. The *E*/*Z* composition of these dimers has been evaluated by ^1H NMR spectroscopy [1340]. Cyclopalladation of anthracene-9-ylmethylene-phenylamine with $Pd(OAc)_2$ in acetic acid, however, affords *endo*-cyclic six-membered cyclopalladated complex (**118**) [1341].

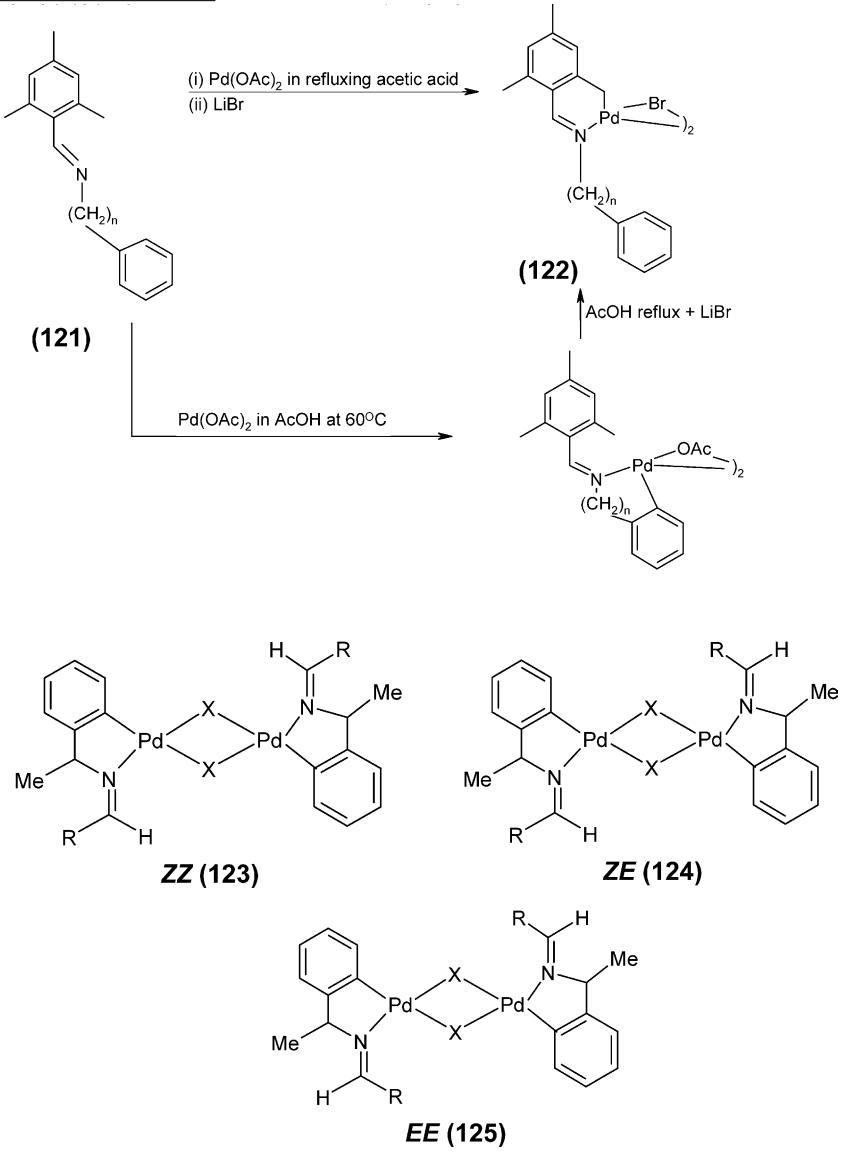
The cyclopalladation of benzyl-benzylidine amines has been investigated in considerable detail [1251,1260,1307, 1313,1314,1338,1344–1365]. A high yield synthesis (85%) of cyclopalladated benzylbenzylidene amine has been reported [1345]. The synthesis involves the reaction of benzylbenzylidene amine with $Pd(OAc)_2$ in 2:1 molar ratio in refluxing acetic acid for 45 min. Cyclometallation reactions of *N*-benzylidene-benzylamines, -anilines and -propylamine (Scheme 24) with $Pd(OAc)_2$ have been investigated in acetic acid [1360] and toluene [1359]. The thermal activation parameters for these metallation reactions cover a wide range of values ($\Delta H^{\pm}$ = 49–73 kJ mol^{-1}; $\Delta S^{\pm} = -52$ J K^{-1} mol^{-1}) as evaluated from UV–vis spec-



Scheme 23.

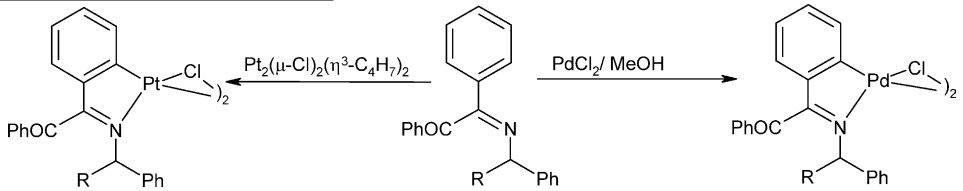
troscopy. Different metallocycles are formed by activation of C–H electrophilic bond. The stability of final metallacycle is in the order: five-membered aromatic *endo* > six-membered aliphatic *endo* > five-membered aromatic *exo* ⋙ five-membered *exo*, four-membered.

Reaction of *N*-benzylidene amines **121** with $Pd(OAc)_2$ in refluxing acetic acid affords cyclopalladated complexes containing aliphatic M–C bond (**122**) rather than an aromatic M–C bond [1314]. The latter compounds are obtained from similar reactions under milder conditions [1314,1366], but isomerization to **122** takes place in refluxing acetic acid (103). The reaction of $Pd(OAc)_2$ with benzylidene-R(1-phenyl ethyl)amines, RCH=NCHMePh (R = 2,6-$Cl_2C_6H_3$; 2,6-$F_2C_6H_3$; 2,4,6-$(MeO)_3C_6H_2$) and subsequent treatment with LiCl, LiBr or KI yields corresponding halo-bridged *exo*-cyclic cyclopalladated dimers. These complexes usually exist as a mixture of ZZ (**123**), ZE (**124**) and EE (**125**) isomers in relation to the Z or E form adopted by the imines [1344].

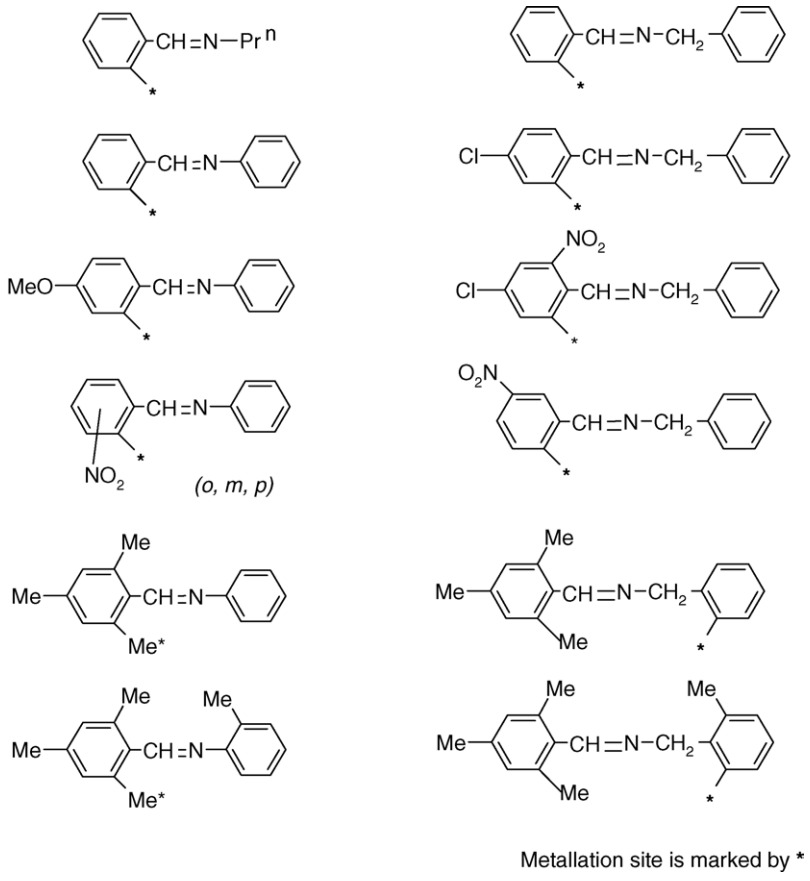


(103)

Cyclometallation of *N*-benzyl- and *N*-(phenyl ethyl)-α-benzoyl benzylidene amines with Pd and Pt yields five-membered metallocycle involving the less activated aromatic rings [1367]. The metallation with palladium is quite facile, but platinum complex could be obtained by the reaction of allyl–platinum complex with the free imine (104) [1367]. The latter route has usually been employed to prepare cycloplatinated Schiff base complexes [1368,1369].

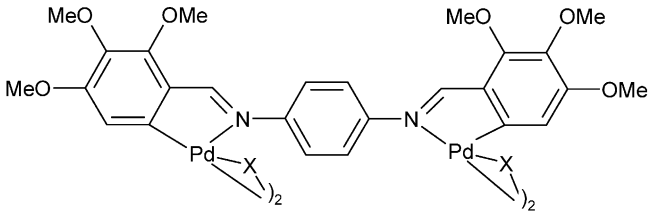


(104)

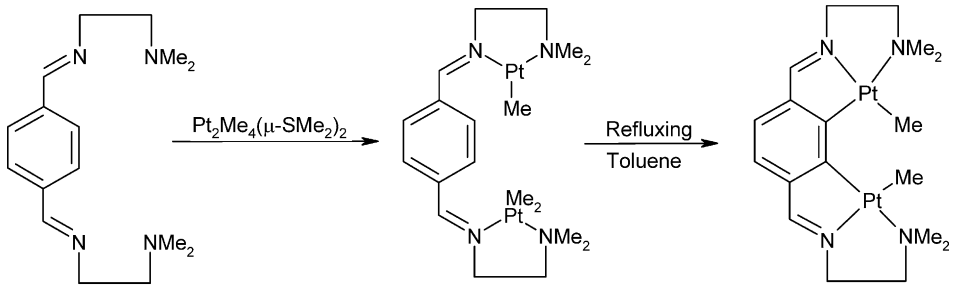


Scheme 24.

Several doubly cyclopalladated species, e.g. **126**, have been isolated by the usual reaction route [1332,1348,1370–1375]. However, doubly cyclometallated platinum complexes are obtained by the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with imine ligands derived from terephthaldehyde in refluxing toluene (105) [1376]. A similar double cyclometallated palladium complex has been obtained by the oxidative addition reaction of $Pd_2(dba)_3$ with 1,4-$\{C{=}NHCH_2CH_2NMe_2\}$-2,5-$Cl_2C_6H_2$ [1377].

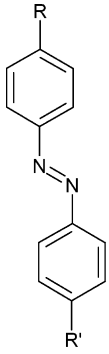


(126)

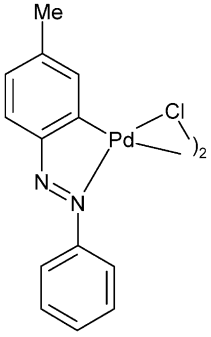


(105)

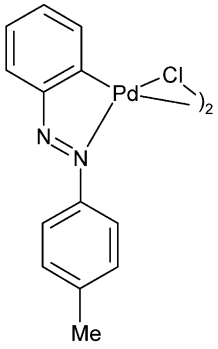
Azoarenes (ArN=NAr) are another important class of ligands for which cyclometallation has been studied quite extensively [1378–1386] ever since the first report of Cope and Siekman [1229]. Palladation of asymmetrically substituted azobenzenes (e.g. **127**) shows regioselectivity and usually occurs preferentially in the ring with higher electron density [1387–1391]. For example, 4-methylazobenzene gives two products **128** and **129** in 3:1 ratio [1387], whereas 1:1 mixture of **130** and **131** is formed with *p*-$ROC_6H_4N{=}NC_6H_4OR'$-*p* [R = $C_{n-1}H_{2n-1}CH_2-$ (*n* = 7, 10, 12 or 14); R′ = , $-CH_2CH_2CH(Me)CH_2CH_2C{=}CMe_2$; $-CHMe(CH_2)_5Me$] [1391].



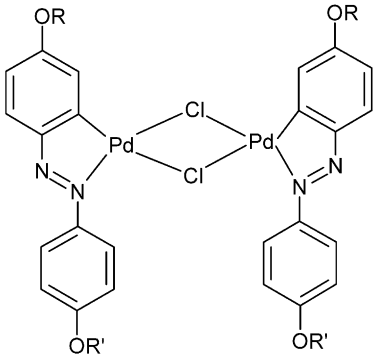
(127)



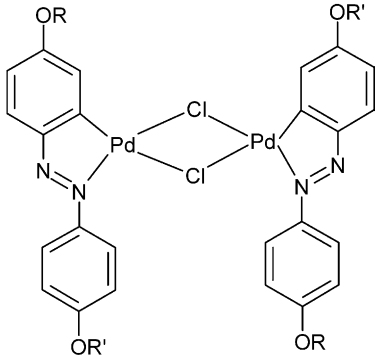
(128)



(129)

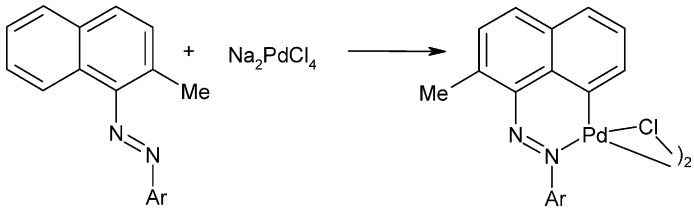


(130)



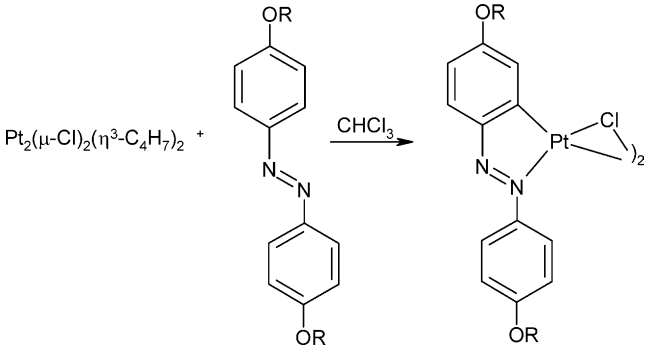
(131)

Cyclopalladation of naphthylphenylazenes also takes place regiospecifically at the naphthyl ring [1383–1385]. Thus, a six-membered rather than the five-membered metallocycle is formed in these reactions (106) which has been studied by ^{15}N NMR spectroscopy [1383].



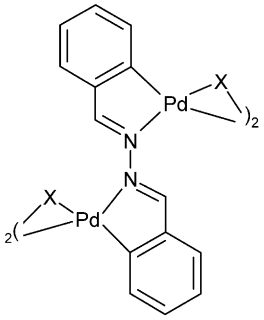
(106)

Unlike cyclopalladated azobenzenes, cycloplatinated chloro-bridged dimers, $[Pt(\mu\text{-}Cl)L]_2$, are prepared by the reaction of $[Pt_2Cl_2(\eta\text{-}C_4H_7)_2]$ with azobenzene is refluxing chloroform (107) [1392].

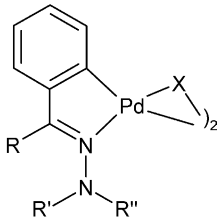


(107)

Cyclopalladation of several benzalazines (ArCH=N–N=CHAr) [1393–1395] and hydrazones [Ar(R)C=N–NR′R″)] [1264,1396–1402] is achieved conveniently to give **132** and **133**, respectively. Metallation of the substituted hydrazone $Bu^t(Me)C{=}N{-}NRR'$ yields a mixture of two binuclear *ortho*-metallated products [1403,1404].

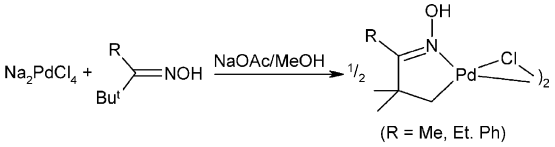


(132)



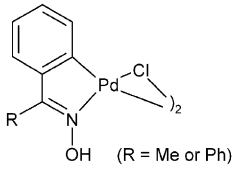
(133)

The cyclopalladation of ketoximes is quite facile [1405–1411]. *Z*-isomer of the *tert*-butylphenylketoxime when treated with Na_2PdCl_4/NaOAc, cyclometallation on a *tert*-butyl group takes place to give **134** (108) [1406,1408]. Oximes of *o*-allylethers undergo palladation on the central carbon of the allyl group with facile nucleophilic addition to the terminus of the double bond. Similarly acetophenone and benzophenone oximes are metallated to yield **135** [1412]. Dioximes of 1,4- and 1,3-diacetylbenzene undergo double cyclopalladation to bridge two palladium atoms [1413]. Cyclopalladated oxime complexes, such as $[Pd(\mu\text{-}Cl)\{C_6H_4(CR{=}NOH)\text{-}2\}]_2$ (R = H, Me, Et, Ph), have been synthesized via ligand exchange reactions between aryloximes and cyclopalladated complexes of *N*,*N*-dimethylbenzylamine, dimethylaminemethylferrocene or benzophenone oxime [1414].



(R = Me, Et. Ph)

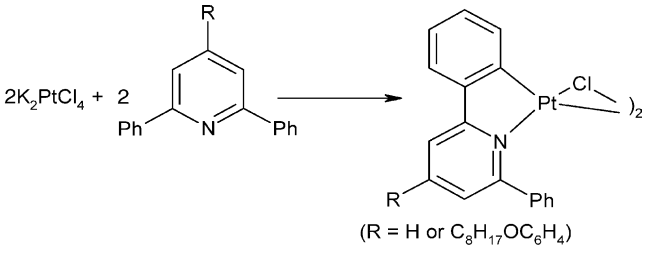
(134) (108)



(R = Me or Ph)

(135)

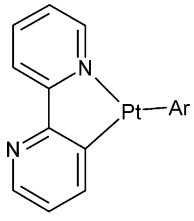
The reaction of 2-phenylpyridine with Na_2PdCl_4 initially yields a N-bonded complex, *trans*-$[PdCl_2(2\text{-}Phpy)_2]$ which on refluxing in toluene or slow evaporation of CH_2Cl_2 solution affords a cyclometallated complex $[Pd_2(\mu\text{-}Cl)_2(py\text{-}C_6H_4\text{-}2)_2]$ [1259,1378]. However, palladation with $Pd(OAc)_2$ is more facile and takes place at the *ortho* position of the aryl group. Thus, refluxing a CH_2Cl_2 solution of $Pd(OAc)_2$ with 2-phenyl pyridine yields the cyclometallated acetato-bridged complex which on treatment of LiCl results in the corresponding chloro-bridged derivative [1259,1415–1419]. Similarly several other arylpyridines [1416,1420–1428], 2-benzylpyridine [1420], 2-*tert*-butylpyridine [1260], 2-pivaloylpyridine [1429] and quinoline derivatives [1248,1342,1378,1380,1430–1432] (Scheme 25) have been *ortho*-metallated. 2,6-Diphenylpyridine and 4-substituted 2,6-diphenylpyridine reacts with K_2PtCl_4 in acetic acid to give monocyclometallated chloro-bridged dimer (109) [1433].



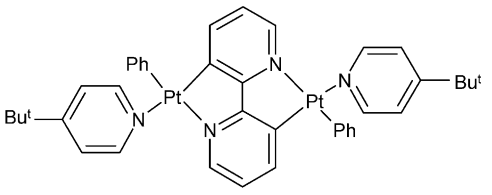
(R = H or $C_8H_{17}OC_6H_4$)

(109)

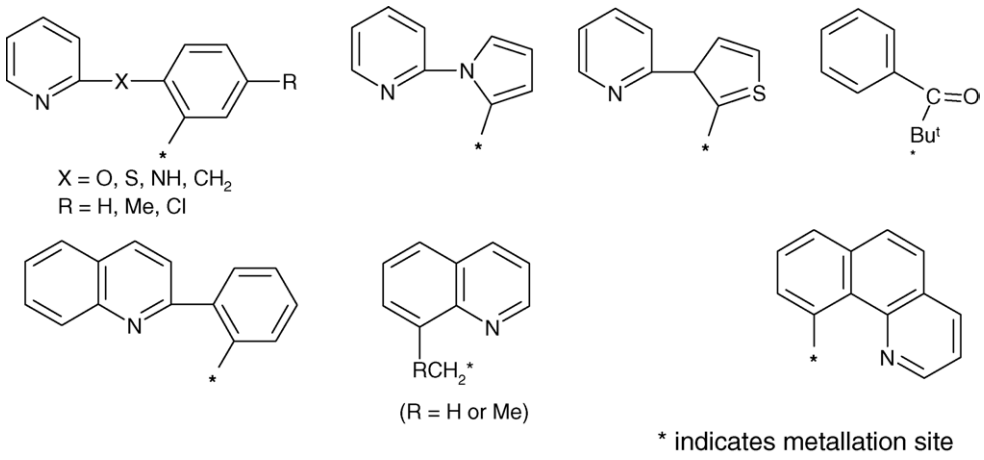
Cyclometallation of 2,2′-bipyridine is fairly facile. The reaction of bipy with $Pd(OAc)_2$ yields a cyclometallated dimer [1434]. Thermolysis of $PtAr_2$(bipy) gives **136** with no significant coupling of the arenes. In the absence of a trapping agent, oligomerization takes place readily. However, in the presence of 4-Bu^{t}py **137** is formed which has been structurally characterized [1435].



(136)

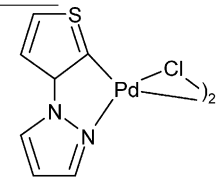


(137)

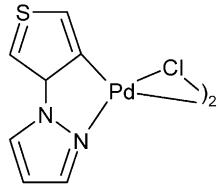


Scheme 25.

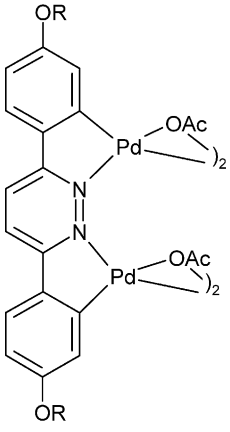
Cyclopalladation of several nitrogen heterocycles, such as pyrazoles (e.g. *N*-phenylpyrazole, *N*-benzylpyrazole, *N*-Bu^t-pyrazole, *N*-(2- or 3-thienyl)pyrazoles) [1436–1442], pyroles [1443], 4-substituted 2-phenyl-2-oxazoline [1444,1445],1-methylphenyl imidazole [1446], 2-substituted-benzoxazoles [1447], benzathiozoles [1447,1448], 2-phenylthiazole [1449], 2-aryl-1,2,3-triazoles [1450,1451], 5,4-disubstituted 2-phenylpyrimidines [1382,1452], ArEPy (Ar = Ph, Nap; E = O or S) [1453–1454], 2-vinylpyridine [1455], etc. [1456–1465] has been investigated. The reaction of 3-thienylpyrazole in 1:1 ratio with $PdCl_2$ gives two isomers, the major and minor species identified by NMR spectroscopy as **138** and **139** [1439]. 3,6-Diphenylpyridazines and related ligands when treated with palladium acetate both mono- and di-cyclopalladated products (**140**) are formed. The first cyclometallation deactivates the system for dicyclometallation [1466–1468]. Similarly, 1,4-bis(benzothiazol-2-yl)benzene undergoes double cyclopalladation of the central benzene ring to form tetranuclear acetato-bridged complex (**141**), structure of which is established by X-ray crystallography [1469].



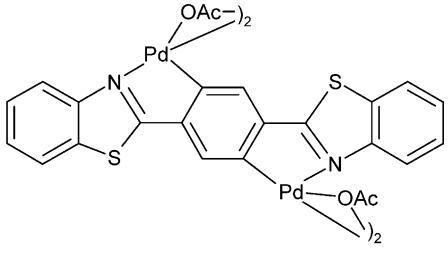
(138)



(139)



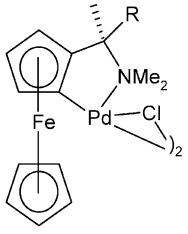
(140)



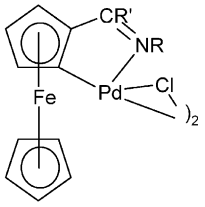
(141)

Many ferrocenyl ligands containing dimethylaminomethyl (**142**), Schiff base functionality (**143**), thioketone (**144**) and tertiary phosphine are readily cyclopalladated [1470–1489]. The reaction of dimethylaminomethyl ferrocene (L) with Na_2PdCl_4 in dioxane yields *trans*-$[PdCl_2L_2]$. However, in the presence of NaOAc in methanol a cyclopalladated species **142** is formed. The **143** (R = H) has been resolved into optically pure enantiomers through its

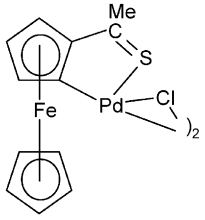
3-proline derivatives [1477]. Cyclopalladation of ferrocenyl Schiff bases of general formula $[(\eta^5\text{-Cp})Fe\{\eta^5\text{-}C_5H_4\}\text{-}CR'{=}NR\}]$ (R′ = H, Me or Ph; R = Ph or Bz) yields a five-membered palladacycle fused with ferrocenyl fragment. However, when R′ = H and R = biphenyl, two products are obtained which are formed by activation of either $\sigma(Csp_{ferrocene}{}^2\text{-H})$ bond (five-membered palladacycle) or $\sigma(Csp_{biphenyl}{}^2\text{-H})$ bond (six-membered palladacyle) (110) [1481].



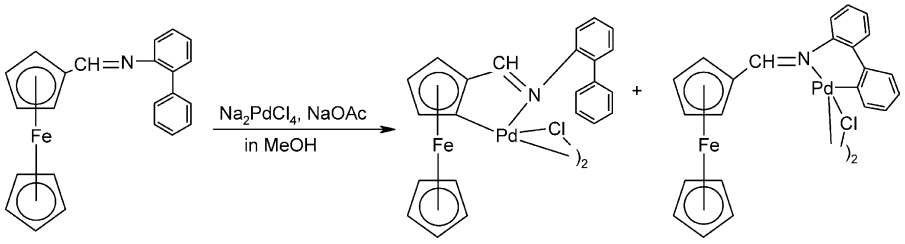
(142)



(143)



(144)



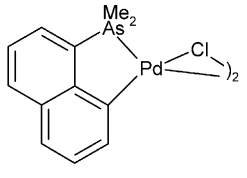
(110)

7.2. Phosphorus and arsenic donor ligands

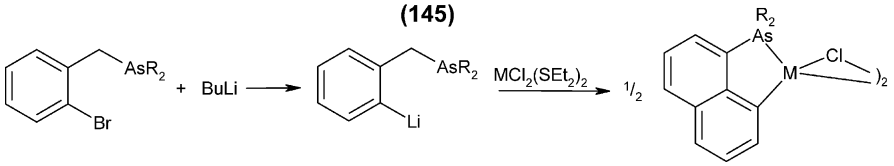
Cyclometallation of a variety of sterically hindered tertiary phosphines [459,1490–1521] and phosphite [1522–1528] ligands (Scheme 26) has been investigated by several workers.

Reactions of $MCl_2(PhCN)_2$ with $PBu_3{}^t$ in dichloromethane readily give metallated binuclear complexes, $[M_2(\mu\text{-Cl})_2\{Bu_2{}^tPC(Me_2)CH_2\}_2]$ (M = Pd or Pt) [1498,1503,1507]. However, similar reaction with $PBu_2{}^tBu^i$ yields a product where metallation of isobutyl group takes place, although reaction with Na_2PdCl_4 initially yields $[Pd_2Cl_2(\mu\text{-Cl})_2(PBu_2{}^tBu^i)_2]$. The latter on prolonged refluxing in 2-methoxyethanol affords a metallated dimer [1510]. Similarly other asymmetric *tert*-butylphosphines, e.g. $Bu_2{}^tPtol\text{-}o$, $Bu^tP(o\text{-tol})_2$ [1510], $Bu_2{}^tPC_6H_4R\text{-}2$ (R = Et or Pr^i) [1493,1509], Ph_2BzP [1529], metallates at the alkyl substituents of the aryl group. However, in the case of $Bu_2{}^tPPh$ [1503], one of the *tert*-butyl groups is metallated. Oxidative addition of HX (X = Cl, Br, I, O_2CCF_3) on $M(PBu_3{}^t)_2$ initially affords a mononuclear complex $[MX(P^{\cap}C)(PBu_3{}^t)]$ which losses a $PBu_3{}^t$ to give the binuclear derivatives, $[M_2(\mu\text{-X})\{PBu_2{}^t(C(Me)_2CH_2\}_2]$ (M = Pd or Pt) [1501,1506,1508]. Treatment of $Pd(OAc)_2$ with P(tol-*o*)$_3$ or P(Mes)$_3$ in toluene affords cyclometallated acetato-bridged complexes [1515–1517].

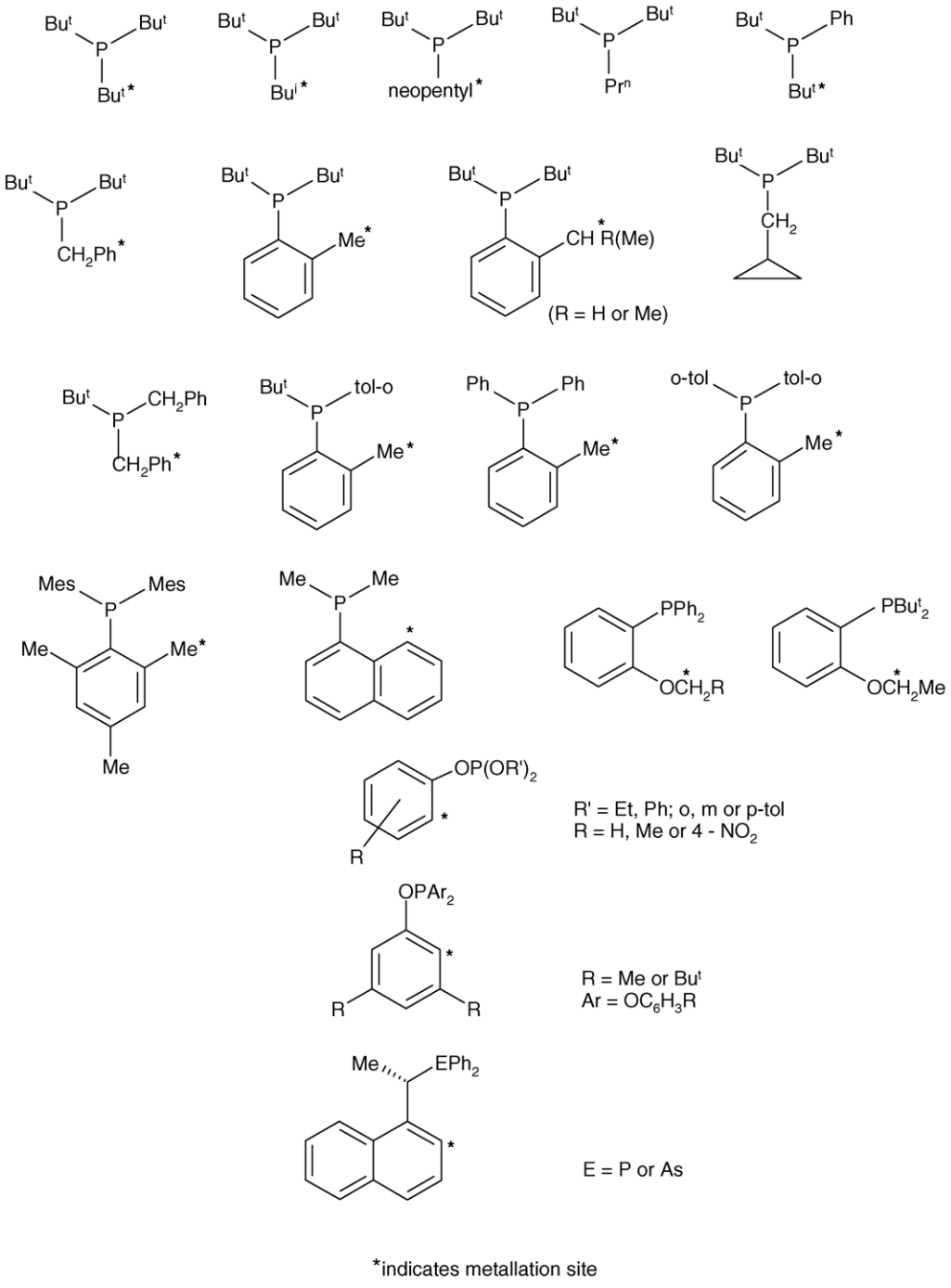
Unlike tertiary phosphines, metallation of arsine ligands is rather sluggish and in most of the cases complexes of the type *trans*-$PdX_2(AsR_3)_2$ (X = Cl; $AsR_3 = Bu_2{}^tAs\text{-}o\text{-tol}$; $Bu^tAs(o\text{-tol})_2$, $AsMe_2Bz$, etc.) are isolated [1501,1530–1535]. Except some hindered arsines where metallation (**145**) takes place directly (though slowly) [1530], metallation of arsines is carried out indirectly. For example, a lithio derivative of an arsine is treated with $MCl_2(SEt_2)_2$ (111) [1534]. Reaction of Na_2PdCl_4 with $AsBu_3{}^t$ in absolute alcohol at RT yields *trans*-$PdHCl(AsBu_3{}^t)_2$ which is stable for several months in the solid state, but in benzene solution cyclometallation slowly takes place with the formation of hydrido-bridged dimer (**146**) (111a) [1533]. This is in contrast to *trans*-$PdHCl(PBu_3{}^t)_2$ which cyclometallates with Pd-H bond cleavage [1501].



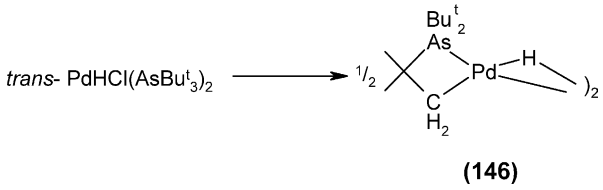
(145)



(111)



Scheme 26.



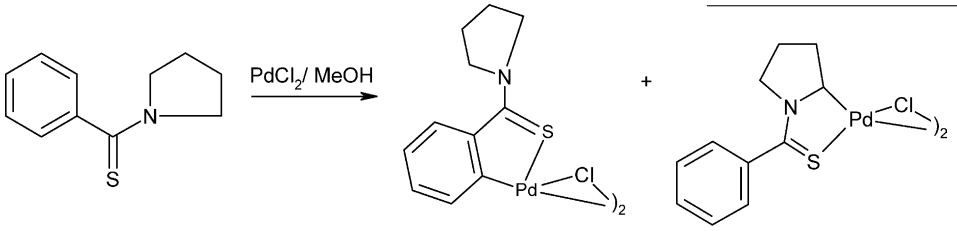
(146)

(111a)

7.3. Sulfur ligands

Cyclometallation of a few sulfur ligands [1257,1536–1544] such as thio ethers [BzSR; R = Me, Bu^i, Bu^t, Ph), 4-tolCH$_2$SCH$_2$C$_6$H$_4$NO$_2$-4] [1257,1538–1540], thio ketones (112) [1541,1542,1544] and thiosemicarbazone [1545] has been investigated. Product of cyclometallation of **147** (112) depends on the conditions of the reaction. The complex **148** is isolated as a mixture of *dl* and *meso* isomers which

could be resolved by addition of chiral ligand in the bridge cleavage reaction and separation of the products [1542, 1544].



(147) **(148)** (112)

The electronic spectra of some of these complexes have been recorded [1389,1418]. Complexes exhibit different absorption spectra (i.e. colour) depending on the nature of bridging ligand as well as metallated species. The low energy absorption band (at 360 nm) in $[Pd_2Cl_2(C_6H_4py\text{-}2)_2]$ and emission band at 460 nm at 77 K are assigned to transitions localized on the metallated 2-phenylpyridine/azobenzene chromophore. Cyclopalladated azo complexes exhibit differntial UV–vis absorption spectra in the presence of α-amino acids with different side chain groups and can be used as the differntial chromogenic probe for amino acids [1546].

Most of these complexes exist into a mixture of *cis* ⇌ *trans* isomers in solution as revealed by variable temperature ^{1}H NMR spectroscopy [1267,1547,1548]. These isomeric forms for metallated phosphine ligands can readily be identified by ^{31}P and ^{195}Pt NMR data at room temperature (e.g. $[Pt_2Cl_2\{PBu_2^t(CMe_2CH_2)\}_2]$ δ ^{31}P = −18.8, ^1J(Pt–P) = 3793 Hz, −18.6, ^1J(Pt–P) = 3757 Hz [1502]). The two isomers remain in equilibrium in solution as shown by 2D ^{31}P NMR spectroscopy [1524]. However, on crystallization only one isomer preferentially crystallizes out from solution. The acetato-bridged complexes derived from metallated P(*o*-tol)$_3$ or P(Mes)$_3$ exhibit monomer ⇌ dimer equilibrium in solution, although a dimeric structure is preserved in the solid state [1516,1517].

The molecular structures of a number of metallated binuclear complexes have been established unambiguously by X-ray crystallography (Table 16) [459,1259,1277,1284,1304,1308,1338,1339,1349,1365–1368,1382,1400,1404,1408,1424,1433,1440,1447,1479, 1496,1504,1507,1511,1514,1516,1540,1549–1564]. These dimers have asymmetric chloro-/acetato-bridges. The asymmetry within the bridges arises due to differing *trans* groups. Thus, the bonds *trans* to carbon are usually longer than those *trans* to the neutral donor (N or P). The four-membered "M_2X_2" ring (M = Pd or Pt; X = Cl, Br, I) are often planar with M–M separation of ∼3.5 Å. However, in some cases, the "Pd_2X_2" ring adopts a non-planar conformation with significant shortening in the M–M separation (∼3.0 Å). The hinge angle in these non-planar molecules may vary between 10.5 and 46.4°. The acetato-bridged complexes have basket shaped eight-membered "$(MOCO)_2$" ring with M. . .M separation of ∼2.9 Å. Both halo- and acetato-bridged complexes are often crystallized out from solution as a *trans* isomer, but the *cis* isomers are not uncommon [1408,1551]. The molecular structure of $[Pd_2(\mu\text{-}Cl)_2(C_6H_4py)_2]$ is unusual in a sense that the two chloro-bridged $[PdClL]_2$ units are weakly associated to form tetramer. Within each unit there are two asymmetric chloride bridges (Fig. 27) [1259]. The Pt · · · Pt distance in $[Pt_2(C^{\cap}N)_2(\mu$-

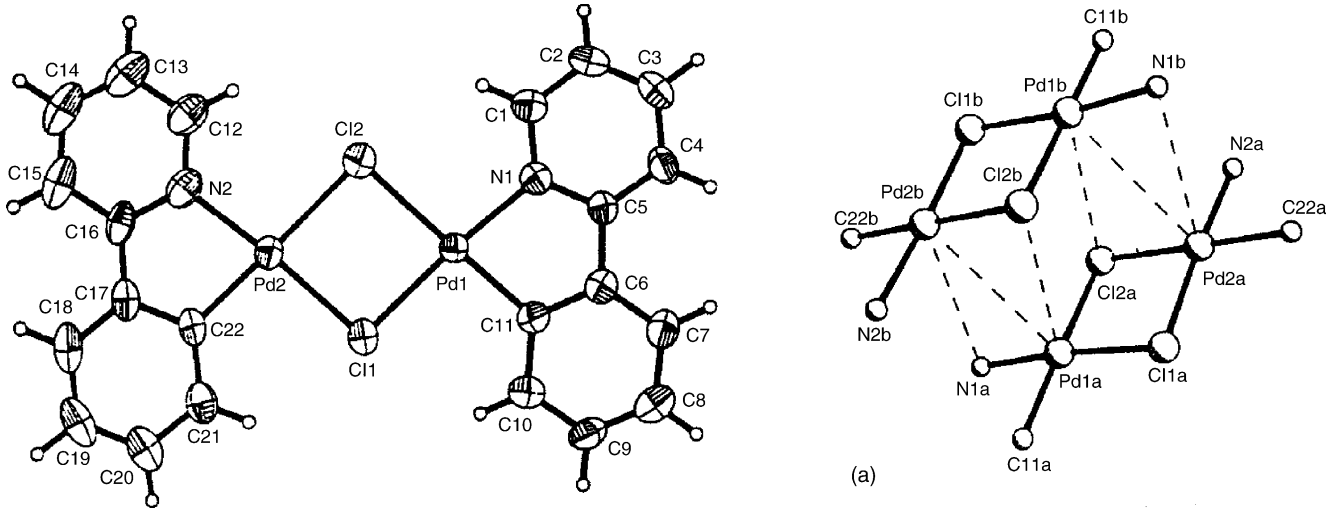


Fig. 27. Molecular structure of $[Pd_2(\mu\text{-}Cl)_2(C_6H_4\text{-}C_5H_3N)_2]$ (reproduced with permission from ref. [1259]).

Table 16
X-ray structural data of metallated binuclear palladium and platinum complexes

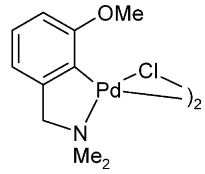
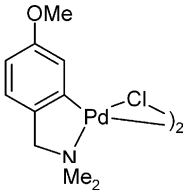
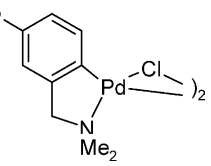
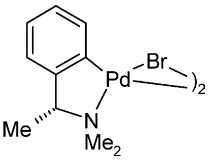
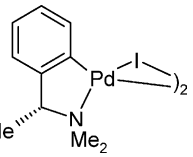
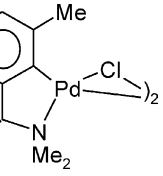
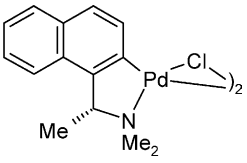
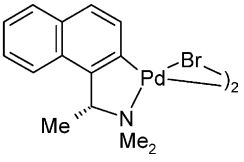
Complex	Comments	References
trans - 	Centrosymmetric dimer, Pd–Cl *trans* to C is longer than *trans* to N, Pd · · · Pd = 3.535(1), five-membered twisted	[1227]
trans - 	Centrosymmetric dimer, Pd–Cl *trans* to C is longer than *trans* to N, Pd · · · Pd = 3.509(1) Å	[1227]
trans - 	Centrosymmetric dimer, Pd–Cl *trans* to C is longer than *trans* to N, Pd · · · Pd = 3.502(2) Å	[1227]
cis - 	Pd_2Br_2 ring non-planar with dihedral angle of 24.7°	[1547]
cis - 	Pd_2I_2 ring non-planar with dihedral angle 16.5°	[1547]
	Pd_2Cl_2 non-planar with dihedral angle 29.8°	[1561]
trans - 	Pd_2Cl_2 non-planar with dihedral angle 17.4°	[1547]
trans - 	Pd_2Br_2 non-planar with dihedral angle 16.9°	[1547]

Table 16 (*Continued*)

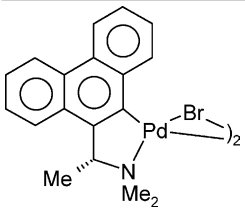
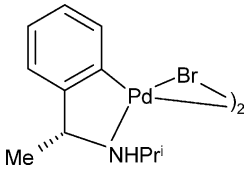
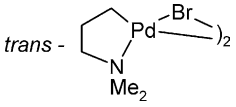
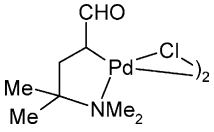
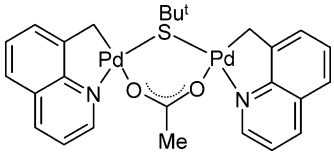
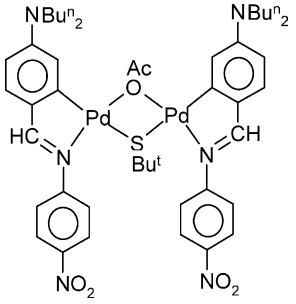
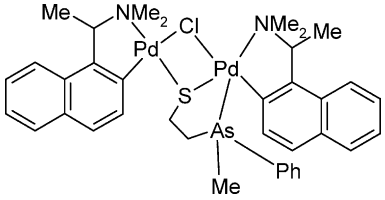
Complex	Comments	References
		[1562]
trans - 	Pd_2Cl_2 non-planar, Pd–Cl *trans* to C is longer, transoid structure, Pd · · · Pd = 2.991(1) Å	[1294]
trans - 	Transoid, Pd_2Cl_2-planar, Pd · · · Pd = 3.501 Å	[1594]
	Transoid, Pd_2Cl_2 planar, Pd · · · Pd = 3.471 Å	[1550]
	C∩N cisoid	[1551]
	Pd · · · Pd = 3.3 Å	[1552]
	Single thiolato-bridge between two non-equivalent square-planar Pd(II). The five-membered rings have asymmetric skew conformations of δ helicity, Pd · · · Pd = 3.726(2) Å; Pd–C = 2.01(1) Å	[1553]

Table 16 (*Continued*)

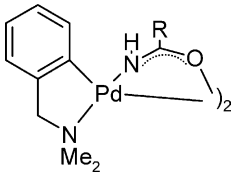
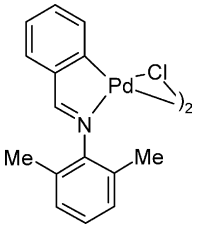
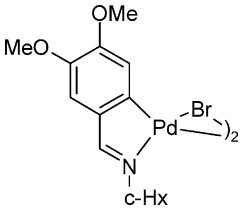
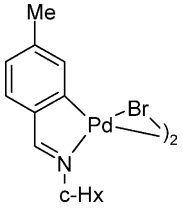
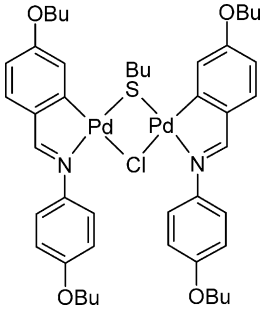
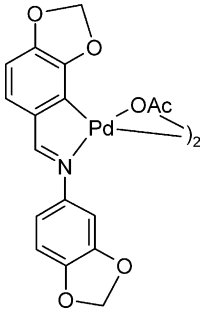
Complex	Comments	References
	Transoid, basket shaped eight-membered ring "$(PdNCO)_2$"	[1554]
	Pd_2Cl_2 non-planar Pd–Pd = 3.425(1) Å	[1366]
	Centrosymmetric dimmer with two asymmetrically bridging bromine atoms, Pd_2Br_2–planar Pd · · · Pd = 3.631(5) Å, Pd–Br = 2.439(3), 2.565(4) Å	[1304]
	Asymmetric bridge, Pd–Br = 2.597(2), 2.449(2) Å Pd_2Br_2 non-planar with hinge angle 46.4° Pd · · · Pd = 3.418(2) Å	[1308]
	A large structure is formed, where molecular long axis is titled with respect to the layer plane Pd · · · Pd = 3.443 Å	[1555]
	*endo*-Isomer Pd · · · Pd = 2.9330(5) Å Pd–C_N = 1.965 Å	[1339]

Table 16 (*Continued*)

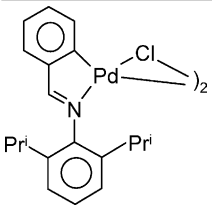
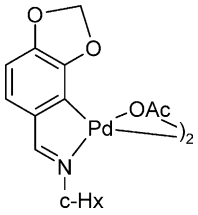
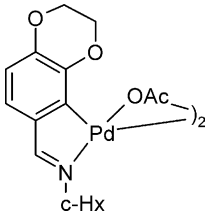
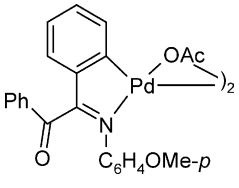
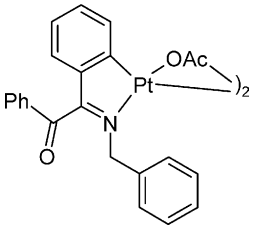
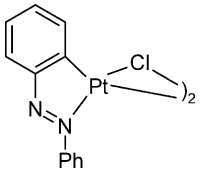
Complex	Comments	References
	Pd · · · Pd = 3.457 Å	[1365]
	μ-Acetate is *cis* to chelating CN Schiff base Pd · · · Pd = 2.8653(3) Å	[1338]
	Pd · · · Pd = 2.8485(10) Å	[1338]
	Open book structure Pd · · · Pd = 3.046(2) Å = 2.927(3) Å	[1556]
	Two cyclometallated rings are planar Pt · · · Pt = 2.925(1) Å	[1367]
	Metallated ligands are mutually trans Pt–Cl = 2.326(6)$_{\text{trans to N}}$ Å Pt–Cl = 2.460(5)$_{\text{trans to C}}$ Å	[1557]

Table 16 (*Continued*)

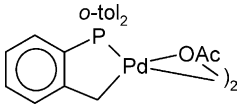
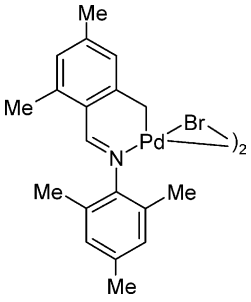
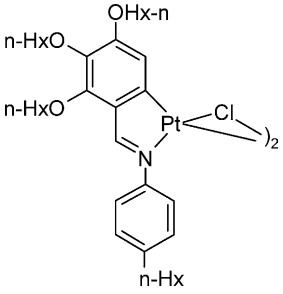
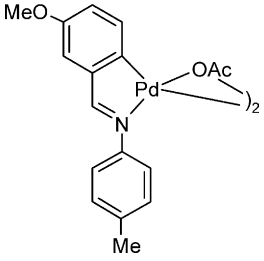
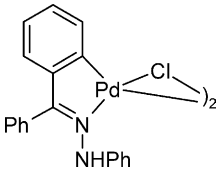
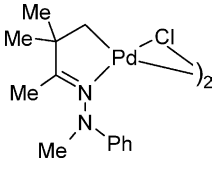
Complex	Comments	References
	Pd · · · Pd = 3.115 Å	[1516]
	Transoid structure, Pd_2Br_2 planar	[1349]
	Transoid structure, anti configuration, Pt–Cl *trans* to C is longer	[1368]
	Transoid structure, Pd · · · Pd = 3.113(1) Å, Pd–O *trans* to C is longer, molecule is bent with hinge angle of 136.2°	[1479]
	Transoid, Pd_2Cl_2 planar, Pd · · · Pd = 3.575(1) Å	[1558]
	Transoid, Pd_2Cl_2 planar, Pd–Cl *trans* to C is longer Pd · · · Pd = 3.511(4) Å	[1404]

Table 16 (*Continued*)

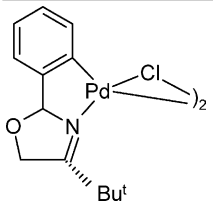
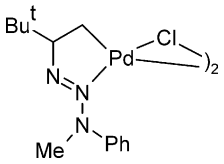
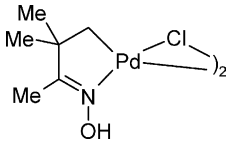
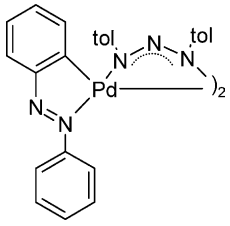
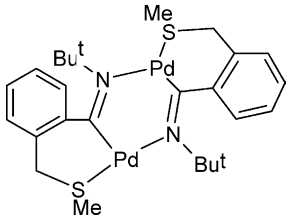
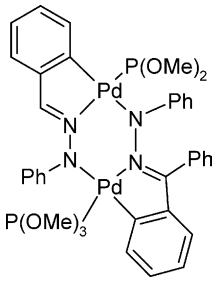
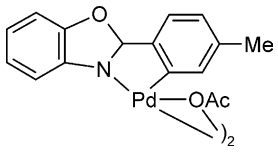
Complex	Comments	References
	Pd_2Cl_2 non-planar, $\theta = 161.1^\circ$	[1444]
	Transoid, Pd_2Cl_2 planar, Pd · · · Pd = 3.434(3) Å, Pd–Cl *trans* to C is longer	[1404]
	Cisoid, Pd_2Cl_2 non-planar, Pd · · · Pd = 2.991(1) Å, Pd–Cl *trans* to C is longer	[1408]
	Transoid, Pd · · · Pd = 2.895(2) Å, five-membered palladacycle is planar	[1559]
	Six-membered cyclopalladated ring adopts a chair conformation, Pd · · · Pd = 2.894(1) Å	[1540]
	Six-membered dipalladacycle has a butterfly shape Pd · · · Pd = 3.788(1) Å, Pd–$C_{(av)}$ = 2.02 Å	[1400]
	Two acetato-groups are mutually *cis* Pd · · · Pd = 2.842(1) Å	[1447]

Table 16 (*Continued*)

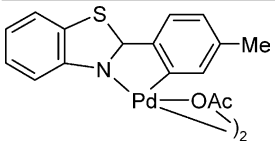
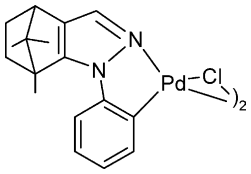
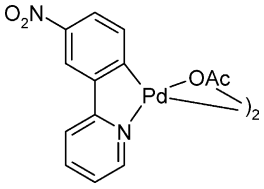
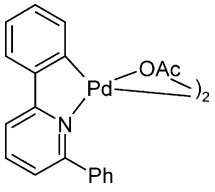
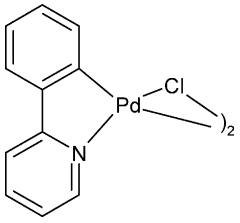
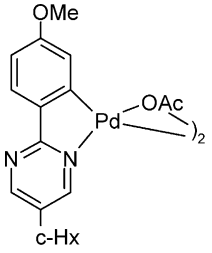
Complex	Comments	References
	Two acetato groups are mutually *cis* Pd · · · Pd = 2.871(1) Å	[1447]
	Pd–Cl is longer *trans* to C, Pd · · · Pd = 3.447(1) Å	[1440]
	Pd–O distance *trans* to C is longer, boat conformation Pd · · · Pd = 2.822(6) Å	[1424]
	Pd–O distance *trans* to C is longer, boat conformation Pd · · · Pd = 2.906(1) Å	[1429]
	Cisoid arrangement asymmetric Pd–Cl bridges, Pd–Cl *trans* to C is longer than the *trans* to N, Pd · · · Pd = 3.48 Å Pd–Cl = 2.426(1), 2.349(2) Å weakly associated tetramer	[1259]
	Pd · · · Pd = 2.871(1) Å	[1382]
[(2,6-Dimethylazobenzeneto)$_2$Pd$_2$Cl$_2$]	Pd_2Cl_2 core is planar, metallated ligands are mutually *trans*	[1563,1564]
[(4-Hydroxy-4′-methylazobenzenato)$_2$ Pd$_2$Cl$_2$]	Pd_2Cl_2 core is bent, metallated ligands are mutually *trans* Pd · · · Pd = 3.554(1) Å	[1563,1564]

Table 16 (*Continued*)

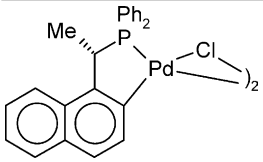
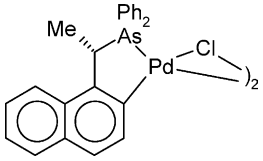
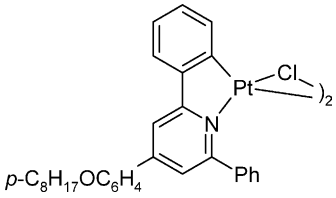
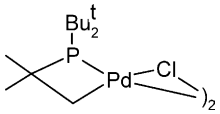
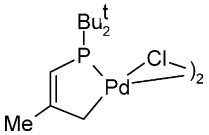
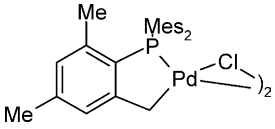
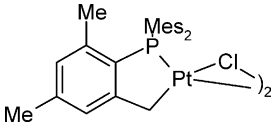
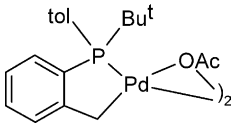
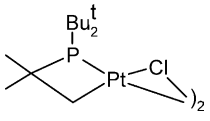
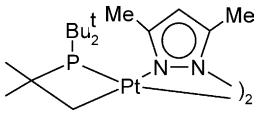
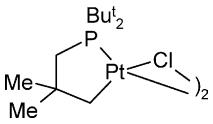
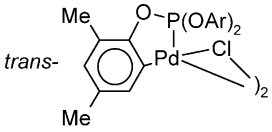
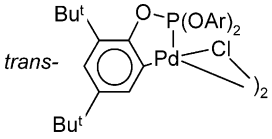
Complex	Comments	References
	Pd · · · Pd = 2.985(1) Å	[1519]
	Pd · · · Pd = 2.990(1) Å	[1519]
	Asymmetric Pt_2Cl_2 unit Pt–Cl *trans* to C is longer	[1433]
	Pd–P–C–C four-membered ring is puckered. Transoid structure Pd · · · Pd = 3.554 Å	[1507,1504]
	Pd · · · Pd = 3.561(1) Å five-membered Pd–PC=C–C is planar	[1511]
	Transoid structure Pd–Cl = 2.488 Å (*trans* to C) Pd–Cl = 2.400 Å (*trans* to P)	[1514]
	Transoid structure Pt–Cl = 2.474 Å (*trans* to C) Pt–Cl = 2.386 Å	[1514]
	Basket of the binuclear complex is not sufficiently larger Pd–O distances 2.137, 2.120 (P and C *trans* influences are comparable), Pd · · · Pd = 3.413(1) Å	[1494]
	Transoid structure, Pt–Cl *trans* to C is longer Pt–P–C–C ring non-planar, Pt · · · Pt = 3.618(1) Å	[1504]

Table 16 (*Continued*)

Complex	Comments	References
	Transoid structure, boat conformation Pt–N = 2.159(18) Å, 2.095(18) Å *trans* P	[1560]
	Transoid structure, Pt–Cl *trans* to C is longer	[1496]
 OAr = $OC_6H_3Me_2$	Transoid structure, Pd–Cl = 2.390(1) Å, 2.408(1) Å	[1527]
 OAr = $OC_6H_3Bu^t_2$	Transoid structure	[1526]

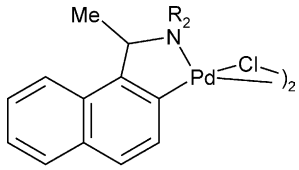
N–N)$_2$] (C∩N = 2-(2,4-difluorophenyl)pyridyl; N–N = pz, dmpz, 3-methyl-5-*tert*-butylpyrazolate and 3,5-di-*tert*-butyl(pyrazolate) decreases with increasing bulk of the bridging ligand and falls in the region 3.3763(7)–2.8343(6) Å [1565].

7.4. Chemical reactivity

Cyclometallated complexes undergo following three general chemical reactions: (i) bridge cleavage reactions with neutral donor ligands; (ii) substitution of the bridging ligands with another anionic ligand; and (iii) reactions at the metal–carbon bond. Besides these several of these derivatives have shown high catalytic activity and also exhibited liquid crystalline behaviour.

The halo-bridged dimeric complexes react with neutral ligands (e.g. pyridine, 4-CNpy, 3-Mepy, 4-Mepy, piperidine, morpholine, PPh_3, $P(OMe)_3$, Ph_2PCH_2COPh, etc.) leading to the formation of the corresponding monomeric complexes [MCl(E∩C)L] [1260,1261,1265,1303,1389,1397,1398,1400,1566–1576]. In the presence of a halide abstractant, such as $AgPF_6$, cationic complexes, $[Pd(L)_2(E∩C)]^+$ are formed [1285,1577]. In the neutral complexes entering ligand L is almost *trans* to E donor atom. The complex $[Pt_2Cl_2(pap)_2]$ reacts reversibly with CO to give a mononuclear complex [PtCl(pap)(CO)] which readily loses CO to yield the parent dimers [1578]. The reactions of halo-bridged binuclear complexes with neutral bidentate ligands (e.g. dppm, diars, α-diimines, etc.), however, yield a variety of complexes viz., $[M(E∩C)(L–L)]^+$ with chelating L–L ligand [1332,1337,1579–1583], $[Pd_2(\mu\text{-}X)(\mu\text{-dppm})(C∩N)_2]^+$ [1332,1582] and $[\{M(E∩C)X\}_2(\mu\text{-L–L})]$ [1584,1585]. With α-diimines, both mono- and bi-nuclear species are isolated. The former, [PdCl(C∩N)(RN=CHCH=NR)], is fluxional due to rapid head to tail exchange of the α-diimine nitrogen functionality [1579].

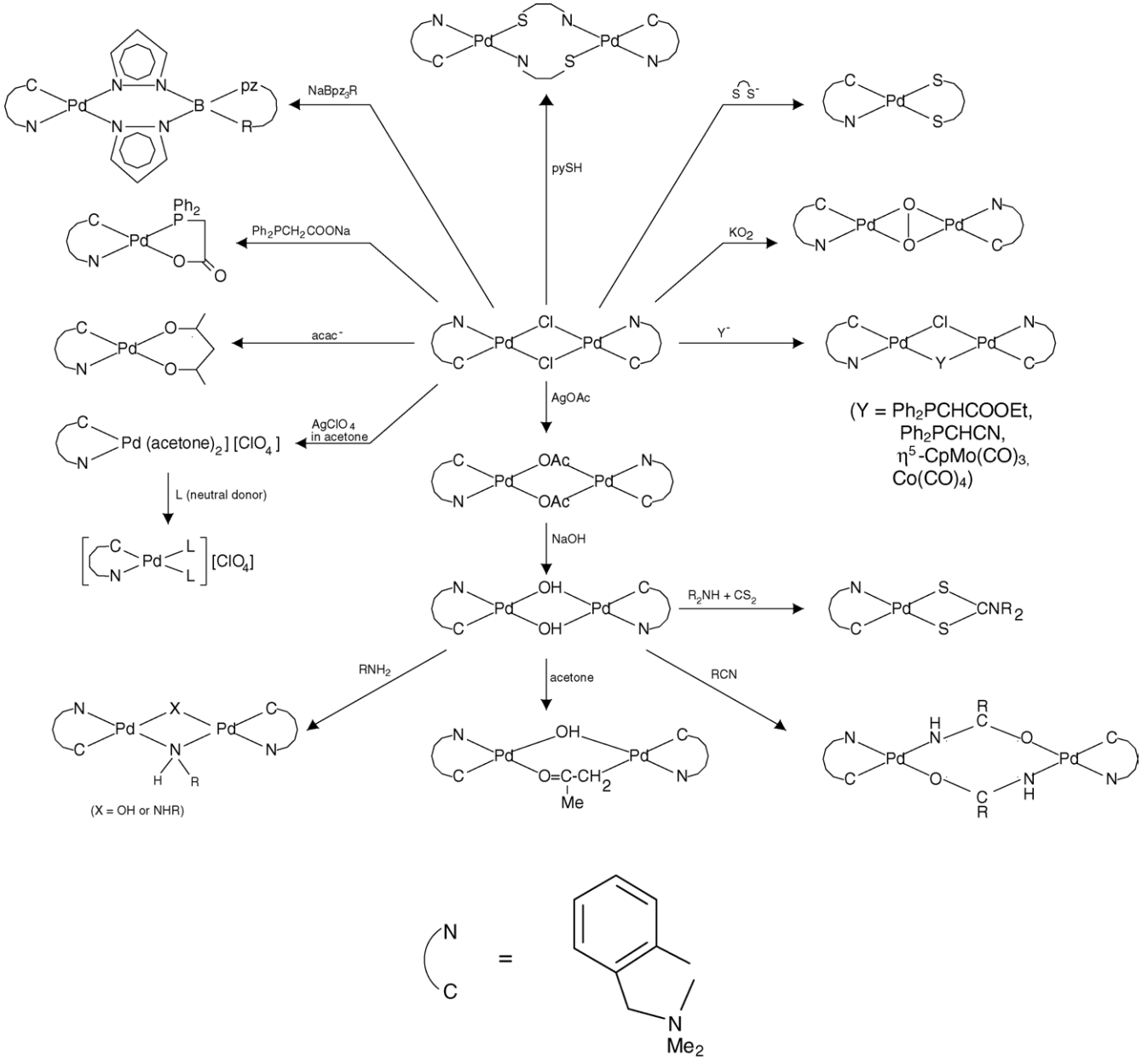
The bridge cleavage reactions have been successfully employed for optical resolution of amine, phosphine, arsine and stibine ligands [1548,1553,1586–1596]. When these ligands are treated with optically active cyclometallated derivatives, such as **149**, diastereomeric monomeric complexes are formed which are separated by either fractional crystallization or by column chromatography.



(R = H or Me)

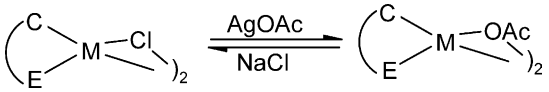
(149)

Substitution of bridging chloride or acetate group by another anionic ligand is an important route to prepare several other *ortho*-metallated complexes. Some of these reactions are depicted in Scheme 27 [1551,1554,1559,1570,1571,1597–1613]. Interconversion of chloride to acetate and vice versa is quite facile and pro-



Scheme 27.

ceeds smoothly (113) [1267,1268]. These bridging ligands can easily be substituted by bromide, iodide, thiocyanate, etc. upon treatment of an acetone solution of the chloro-bridged dimer with LiBr, NaI and NaSCN, respectively [1571].



(113)

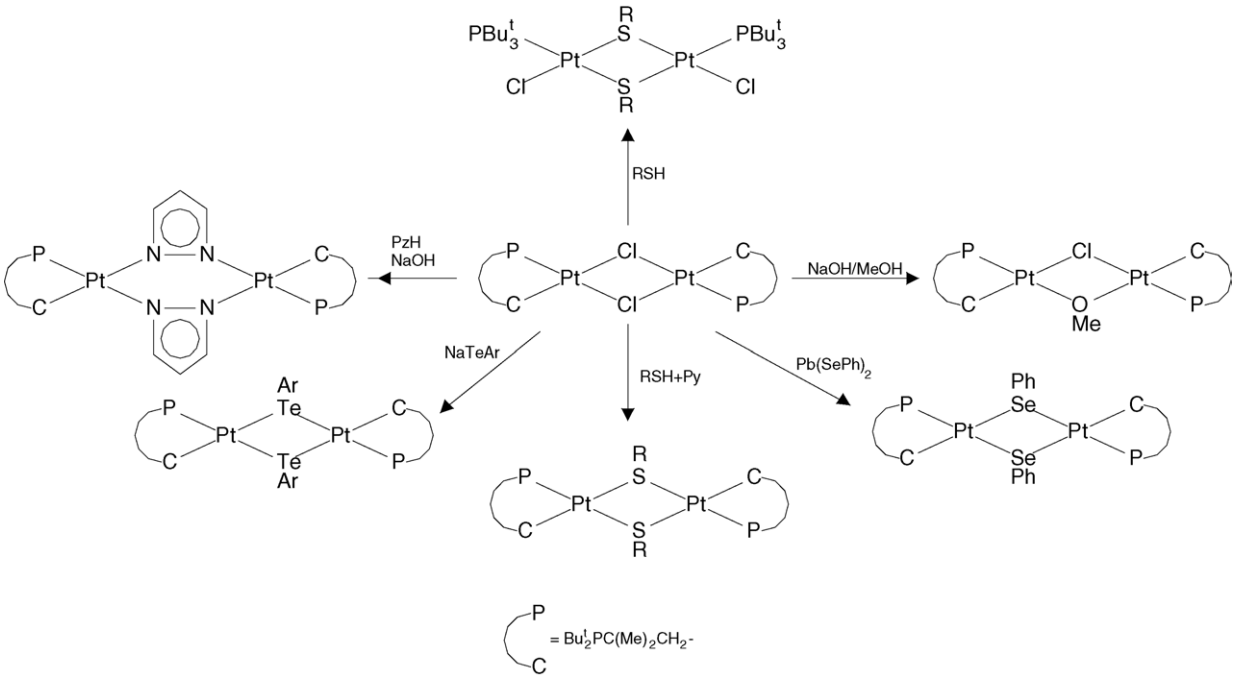
Several functionalized carbon anion Y^- ($Y^- = Ph_2PCHZ^-$ (Z = CN, COOEt) and carbonyl metallate ions ($CpMo(CO)_3^-$, $Co(CO)_4^-$, $Fe(CO)_3NO^-$) have been used to prepare hetero-bridged structures, $[Pd_2(\mu\text{-Cl})(\mu\text{-L})(C^{\frown}N)_2]$ [1431,1599,1600,1603,1604]. However, with metallated azobenzene palladium dimer with some carbonyl metallate ions [$Co(CO)_4^-$, $Mn(CO)_5^-$, $Re(CO)_5^-$] transmetallation takes place with the formation of palladium metal [1597]. Reactions of small bite anionic bidentate ligands, e.g. 2-pyS^-, 6-Me-2-pyS^- [1607], 5-mercapto-1-alkyltetrazole [1614], acetate or triazene [1559], with chloro-bridged metallated derivative yield binuclear complexes (e.g. $[Pd_2(\mu\text{-Spy})_2(C^{\frown}N)_2]$) which are fluxional at room temperature [1607,1614]. However, large bite ligands, such as pyrazolylborate [1615], $R_2NCS_2^-$ $(RO)_2PS_2^-$ [1415,1613], $Ph_2PCH_2COO^-$ [1606], $acac^-$ [1275,1417,1441,1458,1459,1610] and others [1605,1616] afford mononuclear complexes in which the incoming lig-

and is chelated. The reaction of $[Pd(\mu\text{-}Cl)(C^{\cap}N)_2]$ with Li(Fmes), after hydrolysis yields $[Pd(C^{\cap}N)(Fmes)(H_2O)]$ (Fmes = 2,4,6-tris(trifluoromethyl)phenyl; $C^{\cap}N$ = metallated *N*,*N*-dimethyl benzylamine, etc.) [1617].

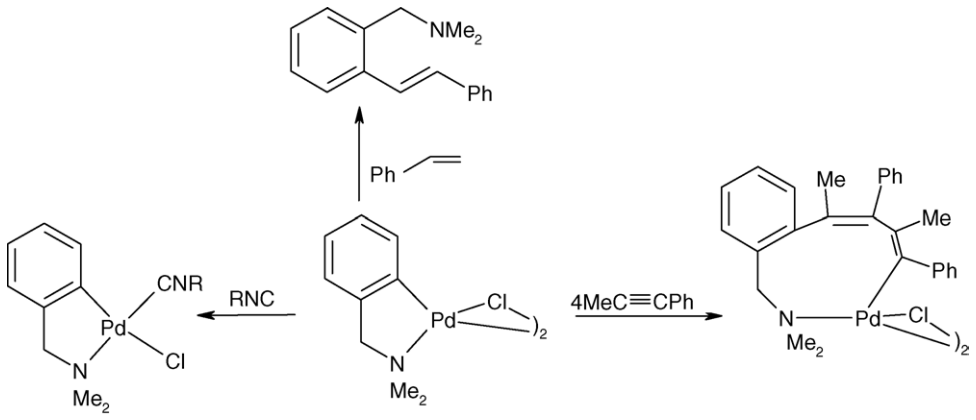
Reactions of acetato-bridged complexes with sodium hydroxide, depending on stochiometry, generate hydroxo-bridged complexes, $[Pd_2(\mu\text{-}OH)(\mu\text{-}X)(N^{\cap}C)_2]$ (X = OH or O_2CR) [1551,1610]. The hydroxo-bridged complexes are quite labile and react with several thiols [1551], primary amines [1551], nitriles [1554] to give another series of binuclear complexes, $[Pd_2(\mu\text{-}X)(\mu\text{-}Y)(N^{\cap}C)_2]$ (X, Y = SR, O_2CR; RNH, O_2CR; RNH, OH; RNH, RNH; NHC(R)ONHC(R)O). The structure of $[Pd_2(\mu\text{-}SBu^t)(O_2CCF_3)(C^{\cap}N)_2]$ ($C^{\cap}N$ =) reveals cisoid arrangement of the cyclopalladated ligands in which oxygen atoms of the O_2CCF_3 group are *trans* to carbon. The molecule adopts a folded conformation [1551]. The reaction of the dihydroxo-bridged complexes with acetone under reflux results in deprotonation of acetone with the formation of OC bound carbonyl complex (Scheme 27). Both mono- and bis-acetonyl complexes can be isolated depending on reaction conditions (30 min and 4 h reflux, respectively) [1612]. The reaction of $[Pd_2(C^{\cap}N)_2(\mu\text{-}OH)_2]$ with CS_2 in octanol results in C–S bond cleavage with the formation of $[(C^{\cap}N)_3Pd_3(\mu_3\text{-}S)(OH)]$ ($C^{\cap}N$ = 4-$ROC_6H_4CH{=}NC_6H_4OR$-4) [1618].

Several substitution reactions of metallated phosphine complexes have also been investigated (Scheme 28) [278,291,303,1560,1610,1619–1621]. A chloro-methoxo-bridged complex with phosphorus *trans* to bridging oxygen is formed when $[Pt_2Cl_2(P^{\cap}C)_2]$ is treated with NaOH in methanol [1619]. Both palladium and platinum complexes react with pyrazole/3,5-dimethyl pyrazole in the presence of NaOH to give $[M_2(N^{\cap}N)_2(P^{\cap}C)_2]$ (M = Pd or Pt; NN = pz or dmpz; $P^{\cap}C$ = metallated PBu_3^t or $PMes_3$) [1560,1621]. The X-ray structure of platinum complex ($P^{\cap}C$ = metallated PBu_3^t) reveals that the two pyrazolate groups are in boat form and the metallated *t*-butylphosphine chelates away from the pyrazolate groups [1560]. Reaction of $[Pt_2Cl_2(P^{\cap}C)_2]$ with mercaptans yields $[Pt_2(\mu\text{-}SR)_2Cl_2(PBu_3^t)_2]$ which is formed by the reaction of liberated HCl on metal–carbon bond [278]. However, when the reaction is carried out in the presence of a base, thiolato-bridged metallated complexes $[Pt_2(\mu\text{-}SR)_2(P^{\cap}C)_2]$ are isolated [278]. The analogous selenolate and tellurolato-bridged derivatives are obtained by treatment of $[Pt_2Cl_2(P^{\cap}C)_2]$ with $Pb(SePh)_2$ or NaTeAr [291,303]. All the organochalcogenolato-bridged complexes are formed as a mixture of *cis* and *trans* isomers.

The metal–carbon bond in metallacycles is expected to be similar to σ-M–C bond. Accordingly several reactions involving M–C bond are observed, and some of them are depicted in Scheme 29. Olefins and acetylenes insert across the palladium–carbon bond to give vinyl derivatives for the former while double insertion takes place with the latter [1268,1269,1427,1622–1631]. One of the first known reactions of cyclopalladated compounds is the formation of indazolone from the azobenzene cyclopalladated compounds (114) [1387]. Reactions of cyclometallated compounds with carbon monoxide are carried out usually in alcohol or amine to give an ester [1346,1479], an amide [1346] or

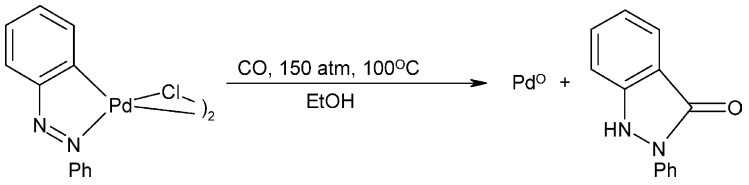


Scheme 28.

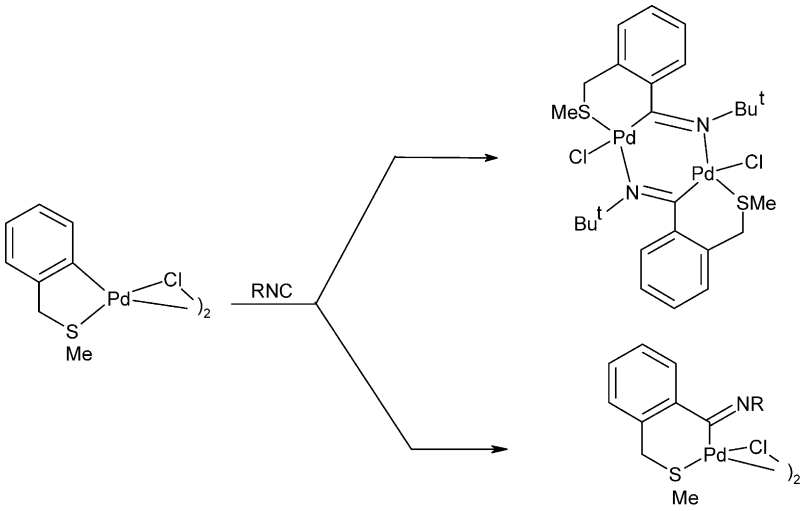


Scheme 29.

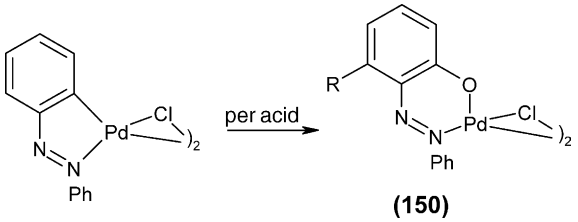
2-aryl-3-indazolinones [1387]. Isocyanides in addition to bridge cleavage reactions [1632], insert into Pd-C bond [1540] affording new imino units (115) [1611,1633–1635]. Metallated azobenzene derivative on oxidation with per acids yields **150** (116) [1636].



(114)

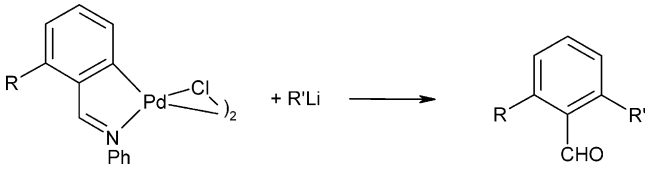


(115)



(116)

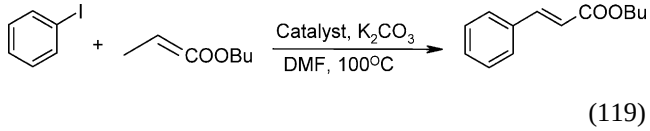
Metal–carbon bond is reductively cleaved with $LiAlH_4/D_4$ or H_2 [1229,1570,1637]. The fused bicyclic palladacycle **104** on hydrogenation yields cyclopentane [1263]. HCl and MeI also react at the metal–carbon bond [1570,1637]. Treatment of *ortho*-metallated Schiff base complex with RLi or RMgX followed by hydrolysis produces *o*-alkyl substituted benzaldehydes in 60–95% yield (117) [1638,1639].



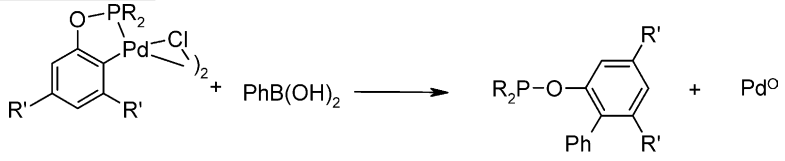
(117)

The use of palladacycles as catalyst and precatalysts in organic synthesis has been a subject of considerable recent research. Cyclometallated palla-

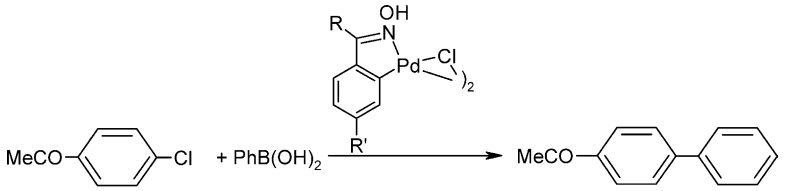
dium [1516,1518,1525,1527,1640–1654] and platinum [1655] complexes have been successfully employed in the Heck, Suzuki and Stille coupling reactions and hydrogenation of various unsaturated functional groups, such as C=C, C=O, C=N, N=N [1641,1655]. The *ortho*-palladated phosphine complex, *trans*- di-(μ-acetato)bis[*o*-(di-*o*-tolyl)phospino)benzyl]dipalladium, $[Pd_2(\mu\text{-}OAc)_2\{P(o\text{-}tol)_2(C_6H_4CH_2\text{-}o)\}_2]$ is an active catalyst for Heck reaction of arenes (118) and shows a very high turnover number (2×10^5 mol products per mol of catalyst). In these reactions Pd(O) species, rather than a Pd(IV) intermediate, is an active intermediate [1642,1647,1656]. Similarly Schiff base palladium complexes catalyse coupling of iodo-benzene with styrene in *N*-methylpyrrolidinone and Pr_3N as a base [1643,1644]. Cyclometallated pyrazole and benzothiazole complexes **151** and **152** have been used as catalyst between iodobenzene and *n*-butylacrylate (119). These complexes show very high catalytic activity (turnover number 10^6 at 70–110 °C) [1645]. A phosphite palladacycle show a very high activity in the Suzuki coupling of both sterically hindered and electronically deactivated aryl boronodes specially in the presence of one equivalent of free ligand (120) [1525,1527]. Oxime palladacycles with hydroxy substituents on the aromatic ring [1412,1657] have been shown to be effective catalyst in Suzuki cross coupling reaction of arylchlorides in water with turnover number as high as 7700 (121) [1657]. Chloro-bridged *ortho*-palladated complexes derived from $ArCHMeNMe_2$ (Ar = Ph, 1-napthyl, 9-phenanthrenyl) have been used as catalyst for asymmetric Calisen rearrangement [1658].



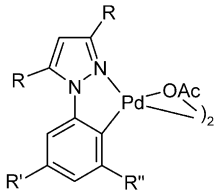
(119)



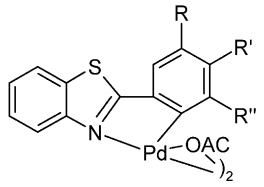
(120)



(121)

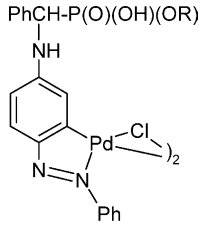


(151)



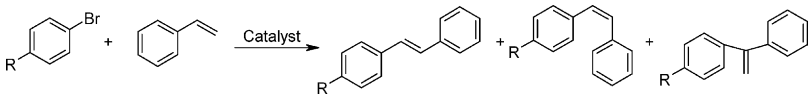
(152)

Cyclometallated azobenzenes with phosphoric acid substituents (**153**) show anti-tumor activity. The concentration of the complex required to inhibit tumour cell growth by 50% was higher than 10^{-5} mol^{-1} [1659]. Cyclometallated palladium complexes derived from 4,5-diphenylimidazole interact with DNA and modify its secondary structure [1660].

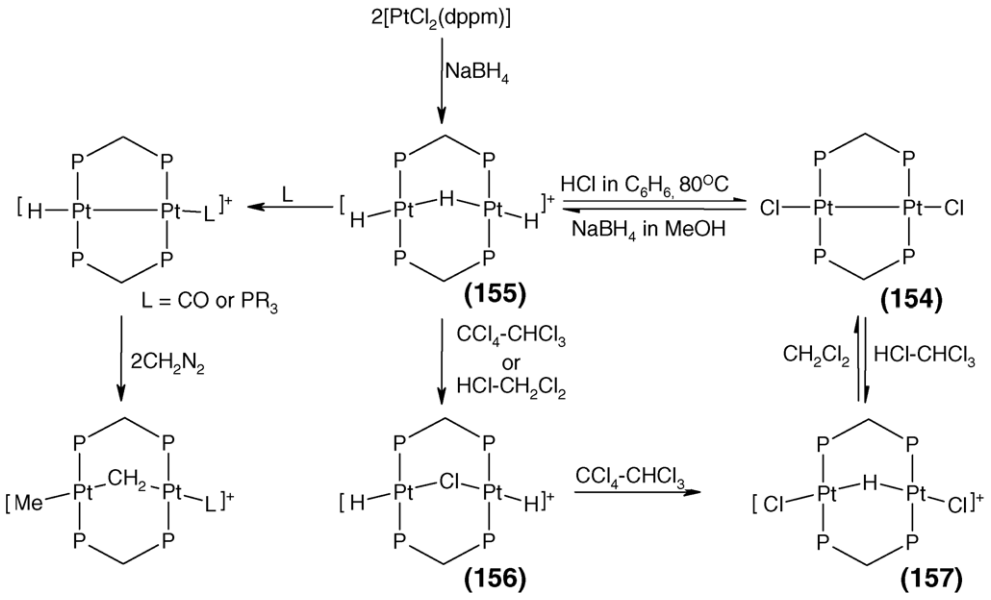


(153)

Since the first report by Ghedini et al. [1661] of *ortho*-palladated mesogens, the area of transition metal based mesogens has grown considerably. A number of binuclear cyclopalladated complexes show thermo-tropic properties [1662–1664]. These complexes are derived from azobenzene [1390,1665–1670], azoxybenzenes [1671], Schiff bases [1368,1555,1672–1681], azines [1376,1395] or phenylpyrimidines [1382,1452,1682]. The metallated ligands bear aliphatic chains in *para* and *para*′ positions



(118)



Scheme 30.

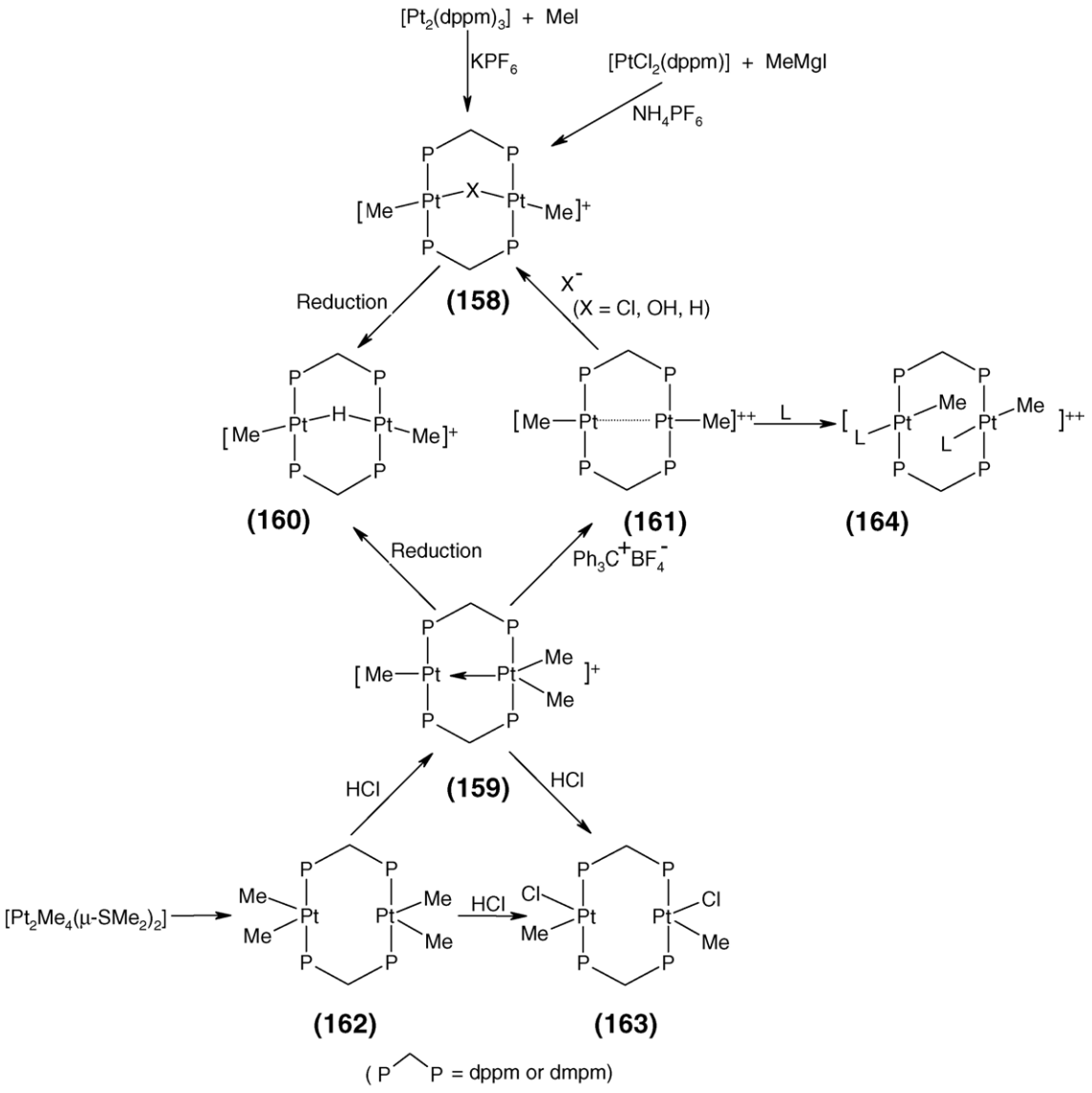
and most of the complexes contain halo or carboxylate groups. The nematic phase appears in the order Cl < Br < I with increasing temperature, while the smectic phases show reverse order [1382,1452,1682]. The nature of bridging ligand changes mesogenic properties of these complexes. Several azobenzene compounds and their bridge cleavage products with neutral ligands show smectic [1388,1391] or nematic [1388] mesophases. N Containing palladacycles have been used for the preparation of ligand free palladium nanoparticles by the reaction between $[(N^{\cap}C)_2Pd_2Cl_2]$ and allenes [1683,1684].

8. Binuclear complexes with small bite ligands

8.1. Complexes with dppm and related ligands

The chemistry of these complexes has evolved primarily from two focal themes, viz. structural diversity of MXY(L–L) complexes and reduction of $PtCl_2$(dppm) by $NaBH_4$. The latter reaction (Scheme 30) yields a platinum(I) dimer $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (**154**) [1685] and proceeds via an electron deficient cationic hydride intermediate, $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (**155**) [1686]. The latter cation adopts an A-frame structure with a long metal–metal bond (2.933 Å) and exhibits a very wide range of reactivity [1687–1697]. The complex **155** undergoes reductive elimination of hydrogen either on photolysis or on treatment with neutral ligands (L) (L = CO or PR_3) with the formation of $[Pt_2HL(\mu\text{-dppm})_2]^+$ [1689–1692]. The **155** acts as a catalyst for the water gas shift reaction at low CO pressure [1694].

Several derivatives of the general formulae $[Pt_2H_nX_{3-n}(\mu\text{-dppm})_2]^+$ (X = H, Cl, Me), $[Pt_2Me_nX_{3-n}(\mu\text{-dppm})]^+$ and $[Pt_2X_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (X = H, halide, alkyl, aryl or alkenyl) have been isolated (Scheme 31) and characterized [1698–1719]. The reaction of $Pt_2(dppm)_3$ with methyliodide in the presence of KPF_6 [1710] yields $[Pt_2Me_2(\mu\text{-I})(\mu\text{-dppm})_2][PF_6]$ (**158**) which can also be isolated by treatment of $PtCl_2$(dppm) with MeMgI [1698,1701,1711]. The reaction between PtRCl(COD) (R = Ph, *p*-tol, *o*-tol, Bz) with one equivalent of dppm affords [PtRCl(dppm)] which are in equilibrium with $[Pt_2R_2(\mu\text{-Cl})(\mu\text{-dppm})_2][Cl]$. The cation can be isolated quantitatively as PF_6 salts by addition of NH_4PF_6 or $TlPF_6$ [1713]. Reduction of $[Pt_2Me_2(\mu\text{-Cl})(dppm)_2]^+$ or $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ (**159**) results in another A-frame complex, $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (**160**). The cation **159** is unusual in a sense that one of the platinums shows *cis* configuration while the other acquires *trans* stereochemistry [1699,1700]. The electron rich $PtMe_2$ center donates electrons from filled $5dz^2$ orbitals to the PtMe center leading to a Pt(II)dz^2 – Pt(II)$dx^2 - y^2$ donor-acceptor metal–metal bond [1699,1700]. Photolysis of **159** in pyridine yields the mononuclear complexes $[PtMe_2(dppm)]$ and $[PtMe(py)(dppm)]^+$ [1705,1709]. Reductive elimination of H_2 from $[Pt_2MeH(\mu\text{-H})(\mu\text{-dppm})_2]^+$, methane from $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (**160**) or ethane from **159** have been reported [1702,1703,1709,1715]. The ethyl derivative $[Pt_2Et_3(\mu\text{-dppm})_2]^+$ undergoes an intramolecular β-hydrogen elimination reaction with the formation of $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ and ethylene [1704]. These complexes often exhibit fluxional behaviour [1707,1708]. Variable temperature ^{31}P and ^{195}Pt NMR data on $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2]$ indicate that the fluxional process corresponds to intramolecular chloride ion transfer [1707]. A correlation between ^1J(Pt–P) and γ(Pt–Pt) has been established by ^{195}Pt NMR spectroscopy for a series of binuclear platinum-dppm complexes [1718]. Hydrido-

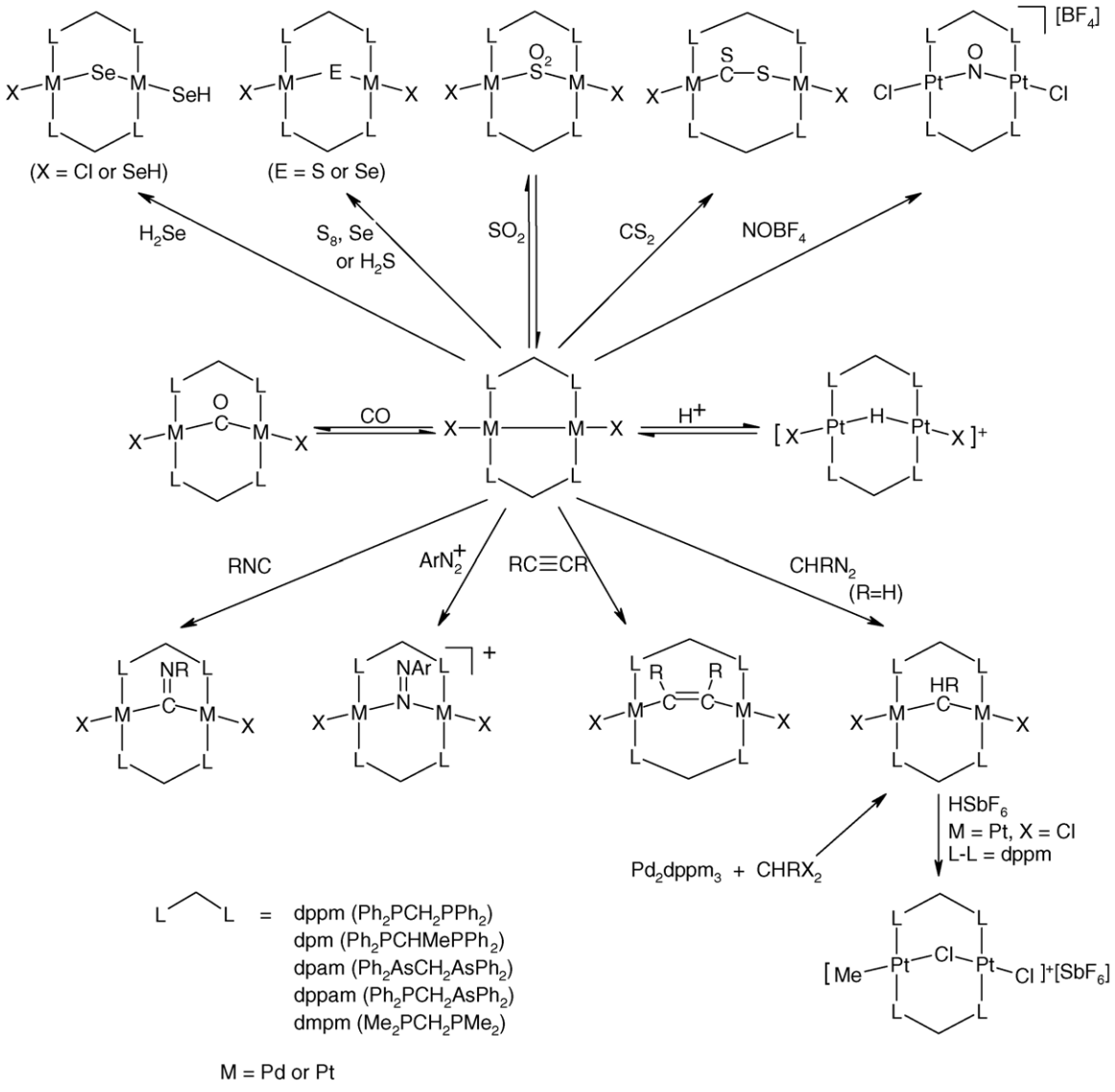


Scheme 31.

bridged palladium complexes, $[Pd_2(H)X_3(dppm)_2]$ [1719] and $[Pd_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ (R = Me, Et, Ar) [1720–1723] have also been isolated and characterized. Although the latter are stable at ambient temperature, undergo reductive elimination of RH at elevated temperatures [1722].

A wide variety of A-frame complexes of palladium [1687,1724–1745] and platinum [1686,1687, 1695,1724,1726,1728,1729,1730,1746–1764] has been prepared by insertion of various substrates into the metal–metal bond of dimeric M(I) complexes, $[M_2X_2(L\text{–}L)_2]$ (Scheme 32). Insertion results in increase of M–M separation by more than 0.5 Å depending on the nature of the entering group. Insertion can be reversible (e.g. addition of CO, SO_2, H^+) [1686,1724,1727,1731,1740,1749,1750] or irreversible as in the case of S, Se, isocyanides, diazonium ions, etc. Reaction of $[Pd_2Cl_2(L\text{–}L)_2]$ (L–L = dppm or $Ph_2PCHMePPh_2$) with H_2Se yields selenido-bridged derivatives $[Pd_2(\mu\text{-}Se)Cl_2(L\text{–}L)_2]$ [1738,1743]. In addition to the latter products, reaction with H_2Se also affords chloride substitution complexes, $[Pd_2X(SeH)(\mu\text{-}Se)(L\text{–}L)_2]$ (X = Cl or SeH). The formation of the latter has been ascribed to higher acidity of H_2Se than H_2S. Similar reaction with H_2S, however, yields only the sulfido-bridged complexes, $[Pd_2Cl_2(\mu\text{-}S)(\mu\text{-}L\text{–}L)_2]$ [1739,1741,1742]. The chloride in the latter can be substituted with NaSH in methanol affording $[Pd_2(SH)_2(\mu\text{-}S)(\mu\text{-}L\text{–}L)_2]$ [1740]. $[Pd_2X_2(\mu\text{-}S)(dppm)_2]$ when treated with halogen leads to the formation of elemental sulfur and PdX_2dppm. Similar to the insertion into the metal–metal bonds of M(I) halo-complexes (Scheme 32), analogous organometallic compounds also undergo insertion reactions [1765–1769].

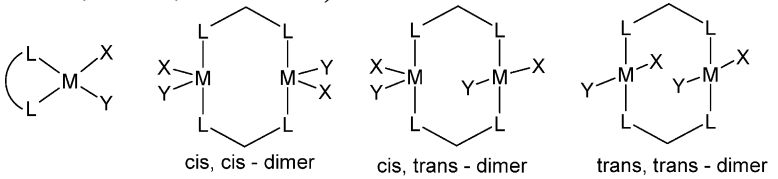
Four structures (**165**–**168**) have been identified for the complexes of the general formula [MXY(L–L)]. The structure is influenced by subtle changes in the nature of anionic



Scheme 32.

ligands (X and Y) and the organic substituents on L–L. The nuclearity of such complexes is believed to be due to steric effects of the R groups on the L–L, bulky R group favouring monomeric structure. Steric hinderance in these complexes follows: *cis*, *cis* dimer (**166**) ≈ *cis*, *trans* dimer (**167**) > *trans trans* dimer (**168**) > monomer (**165**). Accordingly chelation of diphosphinomethanes take place in $[PtX_2(R_2PCH_2PR_2)]$ (X = Cl, R = Et, Pr^i, Ph; X = Me; R = Ph) [1770,1771] whereas *cis*, *cis*-dimer forms in $[Pt_2X_4(R_2PCH_2PR_2)_2]$ (X = Cl, R = Me; X = Me, R = Me or Et).

The reaction of MCl_4^{2-} or MCl_2 with dppm affords monomeric complexes (**165**) $[MCl_2(dppm)]$, although existence of a dimeric species $M_2X_4(dppm)_2$ (X = Cl, Br, I) in solution has been reported [1772]. Similarly other face-to-face compounds have been proposed as reaction intermediates [1689,1732,1773,1774]. Oxidation of $[Pd_2X_2(P^{\cap}P)_2]$ ($P^{\cap}P = R_2PCH_2PR_2$; R = Me, Et; X = Cl, Br, I) by halogens results in the formation of *trans*, *trans*-dimer (**168**) (X = Cl or Br) with exception of X = I for which an ionic



(165) **(166)** **(167)** **(168)**

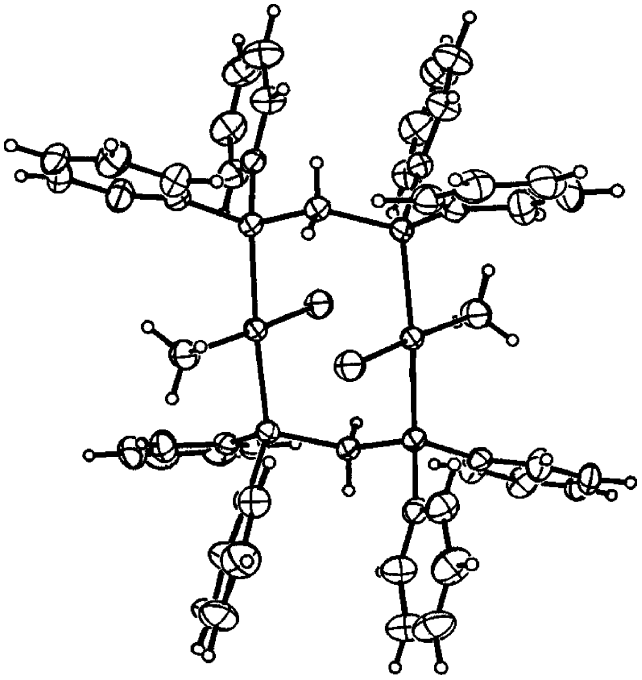
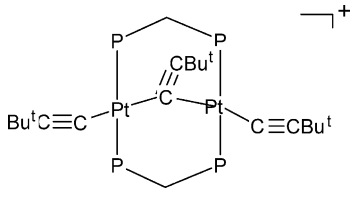


Fig. 28. Molecular structure of $[Pd_2Me_2Cl_2(dppm)_2]$ (reproduced with permission from ref. [1785]).

complex $[Pd_2I_2(\mu\text{-}I)(\mu\text{-}P^{\frown}P)_2]^+$ is formed [1775]. The ligands $Ph_2SbCH_2SbPh_2$ [1776], $BzSCH_2SBz$ [631], $Ph_2PCH_2NEt_2$ [1777] and $Pr^i_2PCH_2PPr^i_2$ [1778] tend to yield face-to-face dimeric complexes (**168**). Although the former ligand was thought to yield **168**, X-ray structural analyses of $[Pt_2Cl_4(dpsm)_2]$ and $[Pd_2Br_4(dpsm)_2]$ confirmed the existance of **167** isomer [1779]. On the other hand treatment of $PtX_2(SMe_2)_2$ or $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with $(RO)_2PCH_2P(OR)_2$, $[CODPtMe_2]$ with $Ph_2AsCH_2AsPh_2$ (dpam) and $PdMe_2$(tmeda) with $Me_2PCH_2PMe_2$ yield *cis*, *cis* dimeric complexes $[M_2X_4(L\text{-}L)_2]$ (**166**) [1780–1782]. The binuclear complex $[Pt_2Me_4(dppm)_2]$ (**162**), prepared from $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and dppm and characterized by X-ray crystallography [1770,1783], breaks down in hot solution in to a monomeric species $PtMe_2$(dppm) [1698]. The reaction of $Pt_2Me_4(dppm)_2$ with HCl yields an ionic A-frame complex $[Pt_2Me_2(\mu\text{-}Cl)(dppm)_2]Cl$ (**158**) [1698], but the similar reaction with $Pt_2Me_4(dmpm)_2$ (dmpm = $Me_2PCH_2PMe_2$) yields neutral derivative $[Pt_2Me_2Cl_2(\mu\text{-}dmpm)_2$ [1770] which does not readily rearrange so is the case for $[Pt_2Me_2I_2(\mu\text{-}dmpm)_2]$ [1784]. In contrast to **158**, the analogous palladium complex, prepared from $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ and $AlMe_3$, is a neutral face to face dimer, $[Pd_2Me_2Cl_2(\mu\text{-}dppm)_2]$ (Fig. 28) in which methyl groups adopt an anti geometry as shown by X-ray structural analysis [1771,1785]. A similar structure is observed for $[Pd_2Me_2Cl_2(PMe_2CH_2PMe_2)_2]$ [1782]. However, the corresponding bromo- and iodo-derivatives as well as $[Pd_2Me_2(\mu\text{-}Cl)(Pr^i_2PCH_2AsR_2)_2]^+$ exist in an ionic structure similar to the platinum counterpart [1773,1786–1788]. The phenyl derivatives, $[Pd_2Ph_2(X_2)(\mu\text{-}dppm)_2]$ (X = Cl or Br), prepared by substitution of $SbPh_3$ in *trans*-$PdPhX(SbPh_3)_2$ by dppm, are similar to the $[Pd_2Me_2Cl_2(dppm)_2]$ [1789].

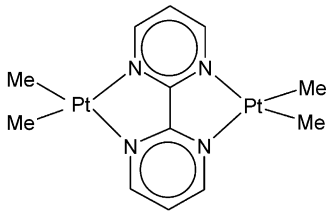
The complexes $[M_2Me_4(\mu\text{-}P^{\frown}P)_2]$ [1701,1733, 1790–1792] and $[MCl_2(P^{\frown}P)]$ are very useful precursors for the synthesis of several binuclear complexes stabilized by bridging diphosphine [643,1793–1806]. Treatment of MCl_2(dppm) with sodium cyanide in boiling ethanol or 2-methoxy ethanol for several hours yields face-to-face dimeric complex (**168**; X = Y = CN) [1798]. Similarly other $[M_2(CN)_4(P^{\frown}P)_2]$ (M = Pd, Pt; $P^{\frown}P$ = c-Hx_2PCH_2Pc-Hx_2, $Me_2PCH_2Me_2$, dppm) have been prepared [1799]. The Pt···Pt distance of 3.301 Å has been attributed to weak Pt···Pt bonding interaction which is further substainated by appearance of a bond at 324 nm (ε_{max} 10,500) (spin allowed $^1A_{1g} \rightarrow {}^1B_{1u}$ transition) [1805]. The reactions of $[PtCl_2(R_2PCH_2PR_2)]$ with alkynylating agents give a variety of products [1793–1796,1798–1804]. Reaction with $Me_2Sn(C{\equiv}CR)_2$ (R = H, Me, Bu^t, Ph) yields $[Pt(C{\equiv}R)_2(dppm)]$ [1796] which in the presence of catalytic amount of free phosphine rearranges to face-to-face dimer (**168**, X = Y = C≡CR; L–L = dppm). The latter (**168**) can also be obtained by the reaction between $PtCl_2$(dppm) and LiC≡CR (R = Me, CF_3, Ph, tol) [1794,1800]. The Pt···Pt distances (3.437(1) 3.250 Å) are considerably longer in $[Pt_2(C{\equiv}CR)_4(\mu\text{-}dppm)_2]$ (R = Ph, $SiMe_3$, $C_6H_4NO_2$-p, C_6H_4Cl-p) than expected for metal–metal bonding [1806,1807]. The electronic absorption spectrum of the complex shows bands at 330 and 370 nm. The former is assigned to a mixed metal-to-alkynyl (MLCT/inter ligand π–π* C≡CPh) transition while the latter is attributed to metal centered $^1[(d_6{*})^2] \rightarrow {}^1[(d\sigma{*})^1(p\sigma)^2]$ transition with substantial mixing of a metal–metal bond to charge transfer MMLCT transition. The complex on excitation at λ 350 nm shows a strong emission band [1806,1807]. Reaction of $PtCl_2$(dppm) with $LiC{\equiv}CBu^t$ in boiling THF yields **169** containing an alkynyl bridge and in no case $[Pt_2(C{\equiv}CBu^t)_4(\mu\text{-}dppm)_2]$ could be isolated [1802]. The **169** and the corresponding other derivatives $[Pt_2(\mu\text{-}C{\equiv}CR)_3(dppm)_2]^+$ (R = Bu^t, Ph, C_6H_4R'-*p*; R′ = Et, OMe, OEt) are fluxional molecules and show a long lived intense broad emission band in th region 570–650 nm [1803]. Reaction of $[PtCl_2(P\text{–}P)]$ (P–P = dppm, depm, dipm) with MeC≡CH and NaOR in ROH affords monomeric $[Pt(C{\equiv}CMe)_2(P\text{–}P)]$ whereas $[Pt_2Cl_4(\mu\text{-}dmpm)_2]$ affords the *cis*, *cis* dimer (**166**; M = Pt, X = Y = C≡CMe; L–L = dmpm) [1800].



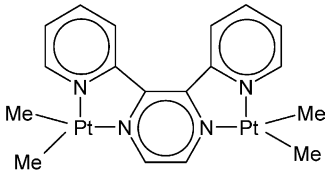
(169)

Nucleophilic attack of pyridine nitrogen of *cis*-$[PtCl_2(dmso)(\eta\text{-}Ph_2Ppy)]$ on coordinatively unsaturated species $[PtMe_2(dmso)_2]$ leads to the formation of a binuclear

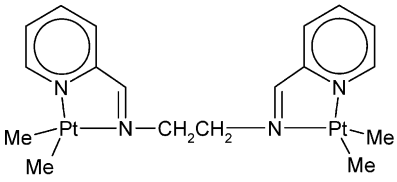
complex [PtMeCl(μ-Cl)(μ-Ph_2Ppy)PtMe(dmso)] [1808]. A few small bite nitrogen ligands have been employed to prepare binuclear complexes **170–173** by their reactions with [Pt_2Me_4(μ-SMe_2)$_2$] [643,1809]. The reaction of the latter with small bite phosphine ligands (dppm, Ph_2Ppy, Ph_2PNHPPh_2) in 1:1 ratio yields, [Pt_2Me_4(μ-SMe_2)(μ-P∩E)] (E = P or N) [1810–1814] which can also be obtained by reation of *cis*-$PtR_2(SMe_2)_2$ with [PtR_2(dppm)] [1815]. The bridging SMe_2 is quite labile and can be substituted readily with other ligands [1812–1814].



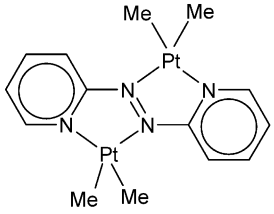
(170)



(171)



(172)



(173)

8.2. Lantren type complexes

Several small bite anionic ligands form complexes of the general formula [M_2(XYZ)$_4$] which have lantren type structures. The ligands giving such structural type are dithiocarboxylate, 2-hydroxypyridinate, triazinate, amidinate, etc. Dithiocarboxylates of palladium(II) and platinum(II) of the type [M(S_2CR)$_2$]$_2$ have been prepared by the reaction between K_2MCl_4 and RCS_2H (R = Me, Pr^i, Ph, C_6H_{13}, etc.) (122) [1816–1823]. Some of these complexes exist in equilibrium between monomer and dimer in solution [1819]. The complex [Pd(S_2CMe)$_2$]$_2$ on recrystallization yields both monomer and dimer [1818,1819], however recrystallization from CS_2 affords only the dimer. It is worth noting that other dithio ligands (S∩S) such as xanthates, dithiocarbamate or dithiophosphate give exclusively monomeric complexes [M(S∩S)$_2$]. The platinum complexes are deep purple in colour. Their crystals show metallic luster and are strongly dichroic in plane polarized light [1820,1821,1823]. The X-ray structural analyses of these complexes have revealed an approximate square antiprism of sulfur atoms containing metal centers in the two square faces with M···M separation varying between 2.72 and 2.86 Å [1819–1826]. The binuclear units of [Pt_2(S_2CPr^i)$_4$] (Fig. 29) are stacked along with *c*-axis of the unit cell. The Pt···Pt distance in the dimer is short 2.79 Å while between adjacent dimers is ∼ 3.08 Å [1821]. The platinum complexes are readily oxidized by halogens (123) to give platinum(III) derivatives [Pt_2X_2(S_2CR)$_4$] (X = Cl, Br, I) [1827], while oxidation with small amount of iodine results in to the formation of mixed valence Pt(II)–Pt(III) complexes [Pt_2I(S_2CR)$_4$]. These mixed valence compounds, often referred as MMX chain are readily obtained by heating [Pt_2(S_2CR)$_4$] with [Pt_2(S_2CR)$_4X_2$] [1827–1829]. The structure of these compounds consists of neutral one dimentsional chains with repeating -Pt–Pt–I unit lying on the crystallographic two-fold axes parallel to the

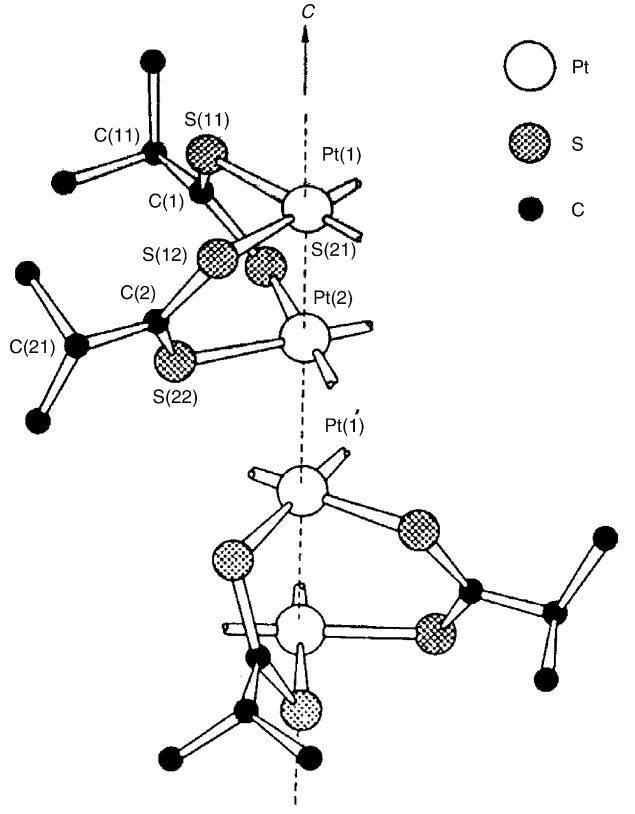
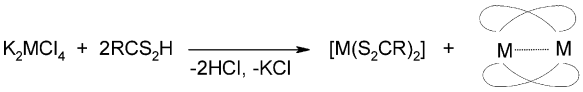
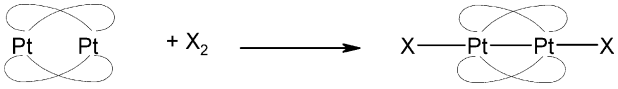


Fig. 29. Molecular structure of [Pt_2(S_2CPr^i)$_4$] (reproduced with permission from ref. [1821]).

b-axis [1828,1830]. The Pt-Pt distance is ~2.68 Å. These compounds show strong intervalence charge transfer (IVCT) absorption, high electrical conductivity (5–30 S cm^{-1}) at room temperature and undergo metal-semiconductor transition [1831–1833].

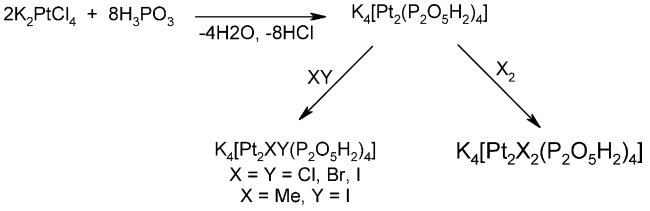


(122)



(123)

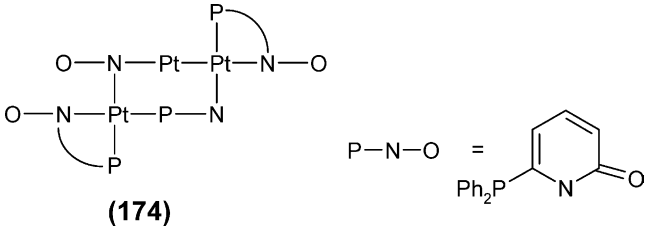
The chemistry of tetrakis(μ-diphosphito)diplatinum(II) $[Pt_2(P_2O_5H_2)_4]^{4-}$, prepared by heating $PtCl_4^{2-}$ with phosphorus acid at 100 °C (124) [1834–1837], has been the subject of considerable research [1838–1841]. The Pt···Pt separation is 2.925(1) Å. The ^{195}Pt NMR spectrum displays a singlet at δ −3411 ppm with a very large J(Pt···Pt) coupling (800 Hz) [1842]. The complex exhibits a strong absorption peak at 368 nm and an intense green phosphoresence at 514 nm. The absorption and emission spectra have been interpreted in terms of transitions between MO levels of platinum atoms [1843–1845]. Several metal ions such as Tl^+, Pb^{2+}, Sn^{2+}, interact with the luminescent Pt–Pt moiety at the vacant axial sites in $^*Pt_2$ [1846,1847]. The complex undergoes one electron (Ir^{IV}, Ce^{IV} or small quantity of halogen) or two electron (excess halogens or MeI) oxidation to yield Pt^{II}–Pt^{III} and Pt^{III}–Pt^{III} dimmers, respectively [1848–1850]. The mixed valent compounds, $A_4[Pt_2(pop)_4X]\cdot nH_2O$ (X = Cl, Br, I) have been investigated recently by single crystal X-ray diffraction, resonance Raman spectra, optical spectra and EPR measurements [1851–1859]. The Pt–Pt distance (2.84 Å) lies between $[Pt_2(pop)_4]^{4-}$ (2.92 Å) and $[Pt_2(pop)_4X_2]^{4-}$ (2.75 Å). These complexes are usually prepared by redistribution reaction between $A_4[Pt_2(pop)_4]$ and $A_4[Pt_2(pop)_4X_2]$. The complexes with X = Cl or Br show charge density wave (CDW) structure (···Pt^{2+}–Pt^{2+}···X–Pt^{3+}–Pt^{3+}–X···). However, when X = I, the cation determines the structure. Thus, for A = Li, Na, K, complexes have spin density wave (SDW) state (–$Pt^{2.5+}$–$Pt^{2.5+}$–X–$Pt^{2.5+}$–$Pt^{2.5+}$–), whereas Cs and Rb derivatives have CDW structure. The NH_4 compound shows a phase transition around 200 K between CDW and SDW states [1851–1853].



(124)

2-Hydroxy or mercapto pyridines and similar other related ligands have been successfully employed to prepare lantern type molecules, $M_2(EC_5H_3RN)_4$ (R = H, Me, Cl) [1860–1868]. The structural analyses reveal that each metal has *trans* square planar coordination and the M_2 unit is tetra bridged by the C_5H_3RNE ligand with M···M separation varying in the range 2.55–2.75 Å. The platinum complex $[Pt_2(pyt)_4]$ (pyt = SC_5H_4N) in chloroform solution converts readily to a Pt(III) dimer $[Pt_2Cl_2(pyt)_4]$ [1863].

The reaction of $PtCl_2COD$ or $PtCl_2(PhCN)_2$ with 6-(diphenylphosphino)2-pyridone yields $PtCl_2(pyphosH)_2$ which on treatment with sodium methoxide in ethanol gives a binuclear complex $[Pt_2(pyphos)_4]$ (**174**) in 84% yield. The two platinum atoms are bridged by two N–P pyphos ligand and are separated from each other by 4.3615(6) Å [1869]. Reaction of 2-Li(C_6H_3Me-4)$AsPh_2$ with $PtCl_2(SEt_2)_2$ in diethyl ether at −30 °C gives two isomeric products of empirical formula $[Pt(Ph_2AsC_6H_3Me)_2]$, one containing all the four bridging C_6H_3-5-Me-2-$AsPh_2$ ligands (a full-lantern derivative) and the other with two chelating and two bridging ligands (a half lantern structure). Both the isomeric forms have been structurally characterized [1870].



(174)

Amidines and triazines are yet another family of small bite anionic ligands employed to prepare lantren type complexes, although their coordination pattern differ markedly with substituents. Thus, bis chelates, bis-bridged dimers and tetra-bridged dimeric species have been isolated and characterized [1871]. Dimeric structures have been found for diaryltriazenido derivatives, $[Pd_2(ArNNNAr)_4]$ [1872]. The reaction of lithium salt of amidines Li(ArNCRNAr) (R = H, Me, Ph) with $MCl_2(PhCN)_2$ yields complexes of the type $[M\{ArNCRNAr\}_2]_n$ (M = Pd or Pt), several of them have been isolated as monomeric bis chelates (R = Me or Ph) [1873,1874], while in certain cases dimeric species, e.g. $[Pd_2(\mu\text{-PhNCPhNPh})_2(\eta^2\text{-PhNCPhNPh})_2]$ and $[Pd_2(\mu\text{-PhNCPhNPh})_4]$ [1875,1876] are formed. The monomer ⇌ dimer equilibrium in solution is not uncommon [1872]. Deprotonation of $PtCl_2(HDArF)_2$ (HDArF = PhNCHNHPh or tolNCHNHtol) with NaOMe in the presence of $TlPF_6$ affords an intermediate binuclear complex $[Pt_2(\mu\text{-DArF})_2(\eta^2\text{-DArF})_2]$ which on heating in weakly coordinating solvents affords a tetra-bridged species $[Pt_2(DArF)_4]$ (Fig. 30) [1877]. The complexes $[M_2(\mu\text{-amidino})(\eta^2\text{-amidino})_2]$ contain two bridging amidine ligands *cis* to each other and two are chelating with each metal atom (Fig. 31). The long M–M separation (~2.9 Å) has been attributed to interligand repulsion between two chelating amidine ligands [1872,1877]. The complexes $[M_2(\mu$-

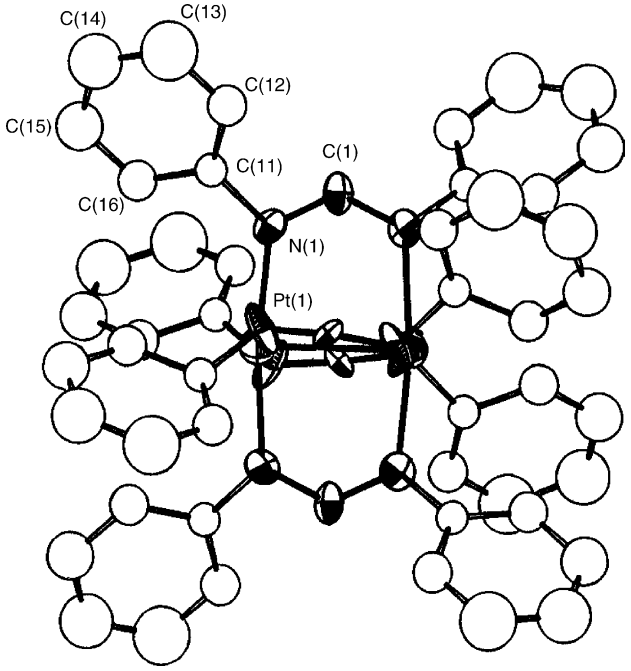


Fig. 30. Molecular structure of $[Pt_2(PhNCHNPh)_4]$ (reproduced with permission from ref. [1877]).

amidino)$_2$(η^2-amidino)$_2$] or [M$_2$(μ-amidino)$_4$] undergo one electron oxidation to yield mixed valent compound [M$_2$(μ-amidino)$_4$]$^+$. In case of platinum Pt–Pt distance is reduced significantly on oxidation while there is slight increase in Pd $\cdots$ Pd distance for palladium complexes [1877].

9. Miscellaneous derivatives

A variety of binuclear complexes stabilized with bridging organic ligands has been designed and synthesized. Among them complexes with ynediyl and aromatic bridges have attracted considerable attention. A number of ynediyl complexes such as **175**–**178** have been prepared (125) and characterized [1878–1897]. Both homo- and hetero-binuclear μ-ethynediyl complexes (**176**) have been prepared employing reaction **175** [1879–1882]. In the complexes of the type **176** the two metal square planes are connected perpendicularly by $-C\equiv C-$ linkage [1880]. Dichloroethylene ($ClC\equiv CCl$) reacts with $Pt(PPh_3)_4$ or $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ to give initially a platinum(O) ethyne complex which on prolonged refluxing in toluene yields an oxidative addition product $[PtCl(C\equiv CCl)(PPh_3)_2]$. The latter complex on further treatment with $Pt(PPh_3)_2(CH_2{=}CH_2)$ affords a binuclear complex $[(PPh_3)_2Pt(Cl)C\equiv C\text{-}Pt(Cl)(PPh_3)_2]$ [1883]. The μ-ethynediyl complexes show novel reactivity based on the mutual interaction of metals through conjugated system. For instance, $[(PR_3)_2(Cl)PtC\equiv CPt(Cl)(PR_3)_2]$ (R = Me or Et) reacts with tetracyanoethylene to initially give a green charge transfer complex and finally a yellow butadiene derivative $[\{PtCl(PR_3)_2C(=C(CN)_2\}_2]$ [1884]. Isocyanides inserts across the Pd–C bond of homo- and hetero-μ-ethynediyl complexes $Cl(PR_3)_2PdC\equiv CM(PR_3)_2Cl$ (M = Pd or Pt) [1880,1881]. Selective double or multiple insertion into only one Pd–C bond takes place. The complex $Cl(PEt_3)_2PdC\equiv CPtCl(PEt_3)_2$ reacts with 10 equivalents PhCN in THF to yield

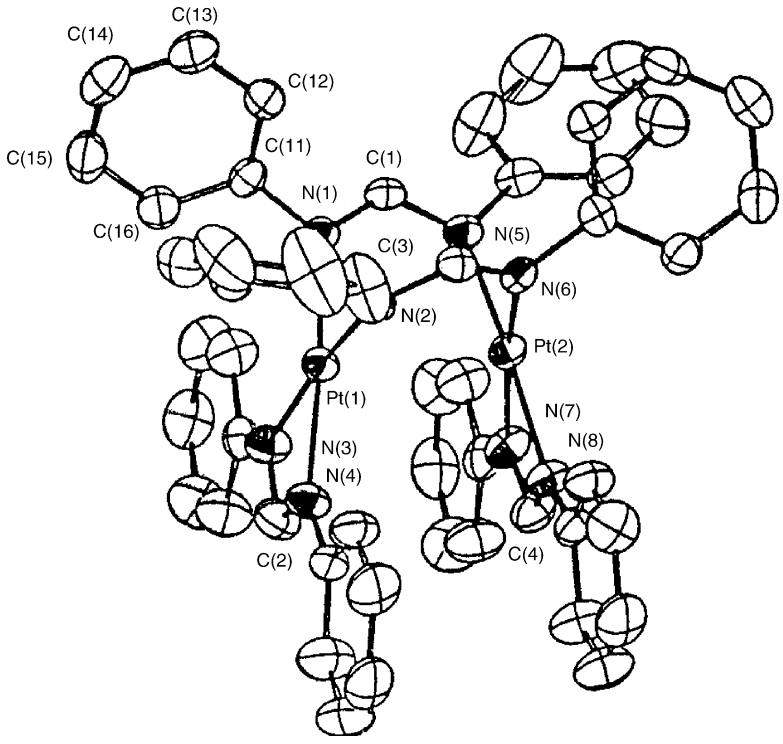
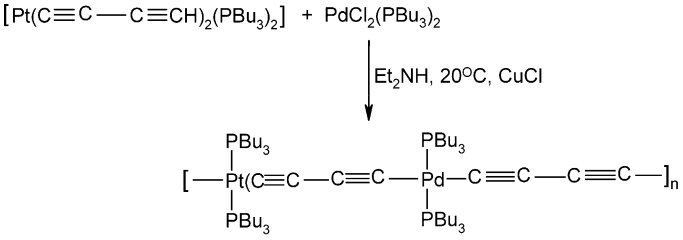


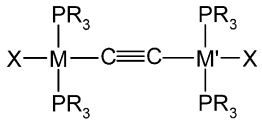
Fig. 31. Molecular structure of $[Pt_2(\mu\text{-}PhNCHNPh)_2(\eta^2\text{-}PhNCHNPh)_2]$ (reproduced with permission ref. [1877]).

$[Cl(PEt_3)_2Pd(C{=}NPh)_{10}(C{\equiv}C{-})PtCl(PEt_3)_2]$ [1881]. Several of the ynediyl-bridged complexes exhibit intense ligand localized absorptions in UV–vis spectra [1892–1897] which become progressively more intense and red shifted as the *sp* carbon chain is lengthened. These absorptions are attributed to alkynyl–platinum ligand-to-metal charge transfer transition (LMCT) [1892]. These complexes show photoluminescence with emission peaks appearing in the range 340–590 nm. The origin of the emission is from triplet states predominantly having intra-ligand character with some mixing of metal-to-ligand charge transfer (MLCT) [1893,1894,1897].

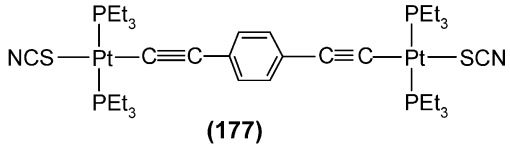


(175)

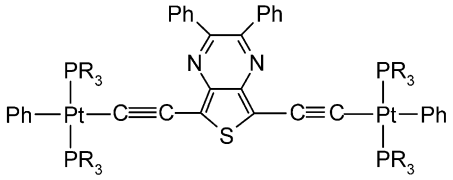
(125)



(176)

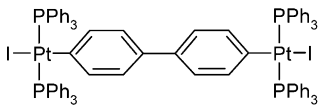


(177)

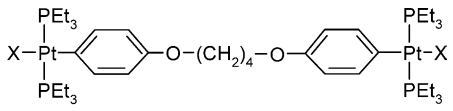


(178)

Oxidative addition of dihaloaryls (such as 1,4-$X_2C_6H_4$, 4,4′-X_2biphenyl, 4,4′-X_2ter-peraphenyl, 4,4′X_2-benzobenzene) to $M(PPh_3)_4$ (M = Pd or Pt) or $Pt(PEt_3)_4$ yields binuclear derivatives of the type **179** [1898–1903]. These complexes are useful precursors for the preparation of nano-scale macrocyclic platinum complexes [1898]. The **180** has been obtained from $PdX_2(PEt_3)_2$ with $Li(C_6H_4O(CH_2)_4OC_6H_4Li$ in 2:1 molar ratio [1904].

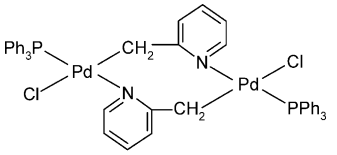


(179)

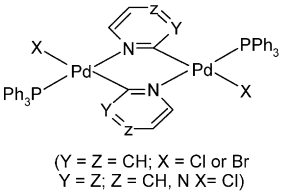


(180)

Binuclear complexes stabilized with ligands which bridge through both C and N atoms have been reported [187,1905–1913]. The reaction of $Pd(PPh_3)_4$ with $pyCH_2Cl$ results in bridging by the picoline group (**181**) rather than halogen [1906–1908,1913]. Halopyridines and related heterocycles (2-chloropyrimidine and 2-chloropyrazine) react similarly to give binuclear complexes (**182**) [1905,1911,1912,1914]. Protonation and methylation of **182** have been investigated. Electrophilic attack involves only the 2-pyridyl nitrogen without cleavage of the N–C bond. The X-ray structures of **182** (Y = 2 = CH; X = Cl [1910], Br [1905]) have been determined. The central six-membered ring adopts a boat conformation and the Pd · · · Pd distance (3.165(3) Å) is rather long for Pd · · · Pd bonding [1910]. UV irradiation of *trans*-$Pd(NCS)_2(PPr_3)_2$ undergoes a stepwise reaction with the formation of **183**, which is characterized by X-ray diffraction. The first step in the reaction appears to be the formation of a linkage isomer [1915].

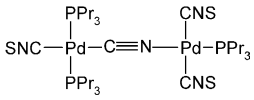


(181)



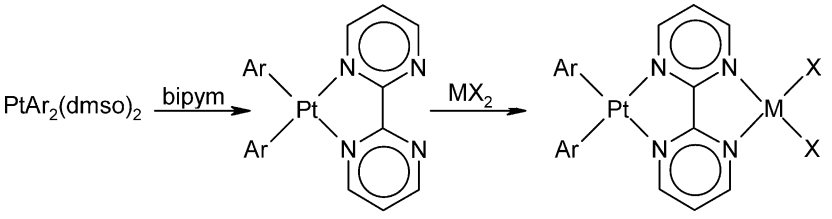
(Y = Z = CH; X = Cl or Br
Y = Z; Z = CH, N X= Cl)

(182)

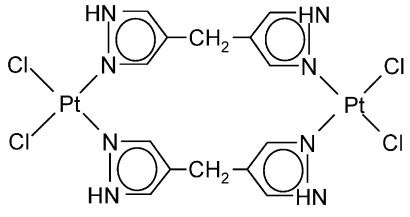


(183)

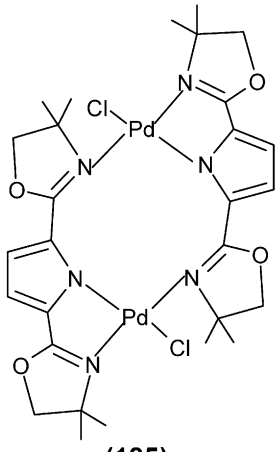
Several neutral polyimine type bridging ligands, such as bipym, bptz, 3,5-bis(dimethylaminomethyl)pyridine, phenazine, etc. have been employed to prepare binuclear complexes (126) [1376,1916–1927]. These complexes undergo two successive one electron reductions. The reduction products have been studied in situ via UV–vis/near IR and EPR spectroscopy [1922]. The first reduction takes place at the heterocyclic ring rather than at the metal center. The bis(pyrazolyl) ligand such as 4,4′-dipyrazolyl methane (dpzm) has been employed to prepare conformational isomers of binuclear platinum complexes α/β/γ-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$.ndmf (α, $n = 1/2$; β, $n = 0$; γ, $n = 2$) (**184**) [1921]. The reaction of $PdCl_2COD$ with the lithium salt of bis{2–4,4′-dimethyl-4,5-dihydroxazolylpyrazole (dmoxpLi) yields a dimeric complex (**185**). The **185** is an active catalyst in the Suzuki cross coupling of phenylboronic acid with activated and non-activated arylbromides [1928].



(126)

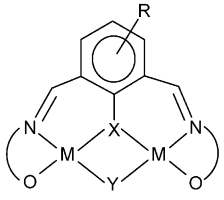


(184)

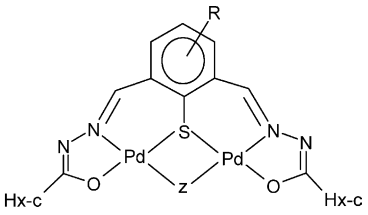


(185)

Complexes of the general structural types **186** and **187** have been prepared and characterized [1929–1937]. If X = O; Y must be a good bridging ligand, although with X = S a weaker bridging ligand Y (e.g., carboxylate) can be accepted [1929–1931]. Reaction of the binuclear complex **187** Z = OAc, with indole results in substitution of acetate group by indole ligand. Similarly other bridging ligands such as amide, amidine [1932], carboxylates [1938], carbamate (HNOCOEt) or urea [1939] in **187** can be employed. The **187** (R = Me) shows high catalytic activity in hydration of nitriles to carboxamides ($RCN + H_2O \rightarrow RCONH$) [1940]. A concerted bimetallic intermediate, in which two different reactants on two metal atoms in close proximity, has been suggested [1940].



(186)

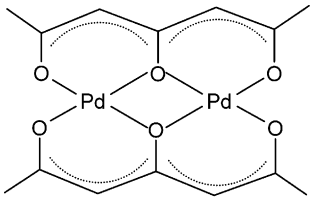


[Z = O_2CR' (R' = H, Me, Et), RCONH, NHNHPh, urea]

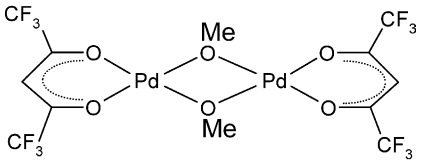
(187)

Binuclear palladium complexes (**188**) with β, δ-triketone and β-ketophenol have been isolated [1941]. Reaction of $Pd(hfacac)_2$ with methanol yields methoxo-bridged complex (**189**) in which Pd_2O_2 ring is folded with hinge angle of 154° and Pd · · · Pd distance of 2.984(1) Å [1942]. However, reaction in the presence of urea affords urea-bridged complex $[Pd(hfacac)(\mu\text{-}NHCONH_2)]_2$ as a yellow powder [1943].

$Pd(acac)_2$ in refluxing toluene reacts with 2-thienylamine yields binuclear complex $[Pd(\mu\text{-}NRH)(acac)]_2$ [1944,1945].

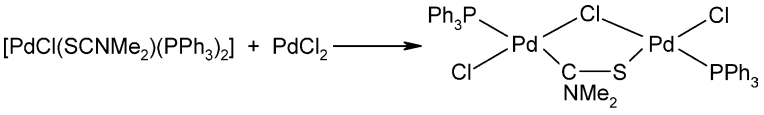


(188)

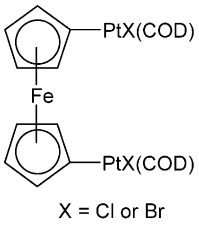


(189)

Reactions of $[MCl(SCNMe_2)(PPh_3)_2]$ with metal chloride have been studied. The X-ray analysis showed asymmetric bridge in palladium complex (127) [1946]. Preparation [1947] and some reactions [1948] of **190** have been described.



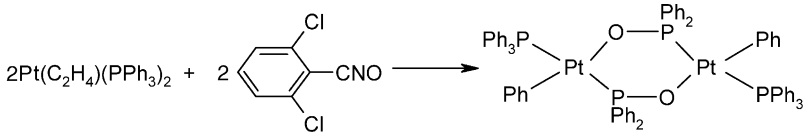
(127)



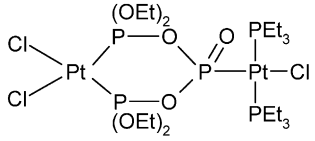
X = Cl or Br

(190)

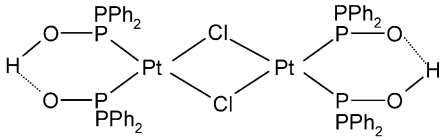
Activation of PPh bonds has been found in the reactions $Pt(C_2H_4)(PPh_3)_2$ or $Pt(PPh_3)_3$ with a series of nitrile oxides (128) [1949]. Reaction of $\{(EtO)_2P\}_2O$ with $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ yields **191** [1950]. Preparation of similar derivative **192** has been reported [1951,1952].



(128)

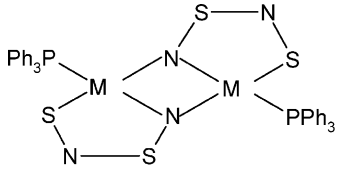


(191)

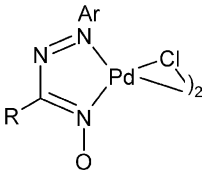


(192)

Reaction of N_4S_4 with $Pt(PPh_3)_3$ and $Pd(PPh_3)_4$ yields **193** which is characterized by X-ray crystallography [1953,1954]. The reaction of triazine with K_2PdCl_4 gives chloro-bridged dimer **194** [1955]. Selective cleavage of **194** with tertiary phosphines involves initial halide-bridge cleavage followed by a bidentate to unidentate transformation. Reaction with HCl results in oxime protonation [1956,1957].

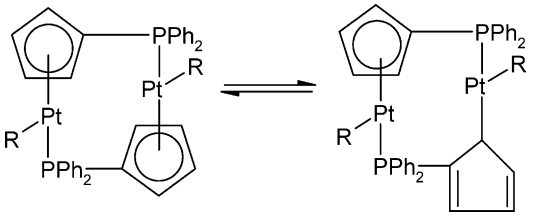


(193)



(194)

Diphenylphosphino cyclopentadienyl (dppc) has been employed to prepare homo- and hetero-binuclear complexes. Thus, reactions of PtRCl(COD) (R = Me, Et, Np, Bz, Ph) with $TlC_5H_4PPh_2$ yield dimeric complexes which exist into two forms and equilibrate in solution (129) [1958–1960]. Treatment of $Pt_2Me_2(\eta^5\text{-}C_5H_4PPh_2)_2$ with CO in CH_2Cl_2 or benzene yields $[Pt_2Me_2(CO)_2(PPh_2C_5H_4\text{-}\eta')_2$ [1959]. Structure of $[Pd(\mu\text{-Br})(\mu\text{-}\eta^3\text{-Cp})(PEt_3)]_2$ has been reported [531]. The synthesis of $[Pd(\mu\text{-Br})(Cp)]_2$ has been described [1072].



(129)

10. Conclusions and future outlook

There has been continuous growth of the subject area since 1960s. A wide variety of binuclear palladium and platinum complexes differing in the nature, structure and chemical reactivity has been reported. The halo-bridged complexes of the type $[M_2Y_2(\mu\text{-}X)_2L_2]$ have proved useful precursors as the halo-bridge can either be cleaved by neutral donor ligands or substituted by other anionic ligands to yield both mono-nuclear mixed ligand complexes and other binuclear derivatives. Substitution of bridging halide by ER′ (E = O, S, Se, Te) leads to the formation of $[M_2Y_2(\mu\text{-}ER')_2L_2]$ which have both planar and hinged structures. The latter molecules provide unique opportunities to study different kinds of isomerism and fluxionality which has been explored by NMR spectroscopy. The reactivity of organometallic complexes (σ, π and allyl-) has been fully exploited in a number of stoichiometric and catalytic organic reactions. Their use in such reactions will continue to grow in the future. Mechanistic aspects of anti-tumor action of platinum drugs have also been explored using α-pyridinate type ligands. Although synthetic aspects of binuclear palladium and platinum complexes and their use in organic reactions are now fairly well demonstrated, their role in materials science, as liquid crystals (e.g., cyclometallated derivatives), preparation of metal chalcgenides and metal (e.g., Pd) films and bio-inorganic chemistry is emerging. The work on binuclear complexes stabilized by single bridging ligands (e.g., **48**, **49**, **75**, **175**, **176**, etc.) can be a subject of further research.

Acknowledgements

The authors are thankful to Drs. T. Mukherjee and S.K. Kulashrestha for encouragement of this work. Help from Mr. A.P. Wadawale is gratefully acknowledged for preparing electronic version of this manuscript and drawing chemical structures. Permission to reproduce figures in this article by the publishers of the respective journals is gratefully acknowledged.

References

[1] P.M. Maitlis, The Organic Chemistry of Palladium, Academic Press, London, 1971.
[2] F.R. Hartley, The Chemistry of Platinum and Palladium, Applied Science Publishers Ltd., London, 1973.
[3] U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, London, 1974.
[4] P.M. Maitlis, P. Espinet, M.J.H. Russel, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 6, Pergamon Press, Oxford, 1982 (Chapter 38.7).
[5] F.R. Hartley, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 6, Pergamon Press, Oxford, 1982 (Chapter 39).
[6] C.F.J. Barnard, M.J.H. Russell, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol.5, Pergamon Press, Oxford, 1987.
[7] D.M. Roundhill, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987 (Chapter 52).
[8] J.A. Davies(Chapter 6), A.J. Canty (Chapter 5), K.R. Dixon, A.C. Dixon (Chapter 4), R.J. Cross (Chapter 7); G.K. Anderson (Chapter 8), G.B. Young (Chapter 9), Comprehensive Organometallic Chemistry. II., vol. 9; R.J. Puddephatt, (volume Ed.), E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Pergamon Press, Oxford, 1995.
[9] E. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, vols. 1 and 2, Wiley Interscience, New York, 2002;
J. Tsuji, Palladium Reagents and Catalysts, John Wiley & Sons Ltd., Chichester, 2004.
[10] R. Schützenberger, Bull. Soc. Chim. 14 (1870) 17;
R. Schützenberger, Bull. Soc. Chim. 17 (1872) 482;
R. Schützenberger, Bull. Soc. Chim. 18 (1872) 148.
[11] W. Manchot, Chem. Ber. 58 (1925) 2518.
[12] W. Manchot, J. Konig, Chem. Ber. 59 (1926) 883.
[13] W. Manchot, A. Waldmüller, Chem. Ber. 59 (1926) 2363.
[14] V.F. Vozdvizhenskii, Yu.A. Kushniov, G.E. Kutyukov, F.B. Fasman, Russ. J. Inorg. Chem. 12 (1967) 798.
[15] Yu.A. Kushnikov, A.Z. Beilina, V.F. Vozdvizhenskii, Russ. J. Inorg. Chem. 16 (1971) 218.
[16] W. Pullinger, Chem. Ber. 24 (1891) 229.
[17] B.P. Adreini, D.B. DellAmico, F. Calderazzo, M.G. Venturi, G. Pellizzi, J. Organomet. Chem. 354 (1988) 369.
[18] F. Calderazzo, D.B. DellAmico, Inorg. Chem. 20 (1981) 1310.
[19] D.B. DellAmico, F. Calderazzo, N. Zandona, Inorg. Chem. 23 (1984) 137.
[20] D.B. DellAmico, L. Labella, J. Organomet. Chem. 593–594 (2000) 427.
[21] D.B. DellAmico, F. Calderazzo, Gazz. Chim. Ital. 109 (1979) 99.
[22] J.M. Lutton, R.W. Parry, J. Am. Chem. Soc. 76 (1954) 4271.
[23] L. Malatesta, L. Naldini, Gazz. Chim. Ital. 90 (1960) 1505.

[24] D.B. DellAmico, F. Calderazzo, C.A. Veracini, N. Zandona, Inorg. Chem. 23 (1984) 3030.
[25] B.P. Andreini, D.B. DellAmico, F. Calderazzo, N. Pasqualetti, Inorg. Synth. 29 (1992) 188.
[26] F. Mylius, M. Foester, Chem. Ber. 24 (1891) 2424.
[27] J.D. Scott, R.J. Puddephatt, Organometallics 5 (1986) 1253.
[28] D. Wright, Chem. Commun. (1966) 197;
E. Lodewijk, D. Wright, J. Chem. Soc. (A) (1968) 119.
[29] S.T. Lin, K.J. Klabunde, Inorg. Chem. 24 (1985) 1961.
[30] R.J. Irving, E.A. Magnusson, J. Chem. Soc. (A) (1958) 2283.
[31] W. Schnabel, E. Kober, J. Organomet. Chem. 19 (1969) 455.
[32] R. Colton, R.H. Farthing, M. McCormick, Aust. J. Chem. 26 (1973) 2607.
[33] M.N. Vargaflik, T.A. Strommova, I.I. Moiseev, Zh. Neorg. Khim. 25 (1980) 236.
[34] R.J. Irving, E.A. Magnusson, J. Chem. Soc. (1956) 1860.
[35] B.P. Andreini, D.B. DellAmico, F. Calderazzo, M.G. Venturi, G. Pellizzi, A. Segre, J. Organomet. Chem. 354 (1988) 357.
[36] F. Bagnoli, D.B. Dell'Amico, F. Calderazzo, U. Englert, F. Marchetti, A. Merigo, S. Ramello, J. Organomet. Chem. 622 (2001) 180.
[37] A. Treiber, Tetrahedron Lett. (1966) 2831.
[38] E.O. Fischer, H. Werner, Chem. Ber. 93 (1960) 2075.
[39] D. Jones, G.W. Parshall, L. Pratt, G. Wilkinson, Tetrahedron Lett. 2 (1961) 48.
[40] H. Alper, Y.J. Huang, D.B. DellAmico, F. Calderazzo, N. Pasqualetti, C.A. Veracini, Organometallics 10 (1991) 1665.
[41] A. Gelman, Ann. Inst. Plat. 18 (1945) 50.
[42] R.J. Irving, E.A. Magnusson, J. Chem. Soc. (1957) 2018.
[43] A. Panunzi, F. Giordano, I. Orabona, F. Ruffo, Inorg. Chim. Acta 358 (2005) 1217.
[44] T. Theophanides, P.C. Kong, Inorg. Chim. Acta 5 (1971) 485.
[45] E.O. Fischer, H.S. Woldan, Z. Naturforsch. 19B (1964) 766.
[46] M.E. Lamberova, A.S. Khramov, V.K. Polovnyak, N.S. Akhmetov, Zh. Obshch. Khim. 60 (1990) 2069;
M.E. Lamberova, A.S. Khramov, V.K. Polovnyak, N.S. Akhmetov, Chem. Abst. 114 (1991) 74085a.
[47] R.N. Keller, Chem. Rev. 28 (1941) 229.
[48] R.G. Guy, B.L. Shaw, Adv. Inorg. Chem. Radiochem. 4 (1962) 77.
[49] M.A. Bennett, Chem. Rev. 62 (1962) 611.
[50] R. Jones, Chem. Rev. 68 (1968) 785.
[51] F.R. Hartley, Chem. Rev. 69 (1969) 799.
[52] U. Belluco, B. Crociani, R. Pietropaolo, P. Uguagliati, Inorg. Chim. Acta Rev. 3 (1969) 19.
[53] H.W. Quinn, J.H. Tsai, Adv. Inorg. Radio Chem. 12 (1969) 217.
[54] J.H. Nelson, H.B. Jonassen, Coord. Chem. Rev. 6 (1971) 27.
[55] F.R. Hartley, Angew. Chem. Int. Ed. 11 (1972) 596.
[56] J.S. Anderson, J. Chem. Soc. (1934) 971.
[57] P.J. Bruce, B. Greene, M. Orchin, Inorg. Synth. 20 (1980) 181.
[58] W.M. MacNevin, S.A. Giddings, Chem. Ind. (Lond.) (1960) 1191.
[59] J.T. van Gemert, P.R. Wilkinson, J. Phys. Chem. 68 (1964) 645.
[60] A.D. Ketley, L.P. Fisher, A.J. Berlin, C.R. Morgan, E.H. Gorman, T.R. Steadman, Inorg. Chem. 6 (1967) 657.
[61] M.S. Kharasch, R.C. Seyler, F.R. Mayo, J. Am. Chem. Soc. 60 (1938) 882.
[62] Y. Wakatsuki, S. Nozakura, S. Murahashi, Bull. Chem. Soc. Jpn. 45 (1972) 3426.
[63] J.S. Anderson, J. Chem. Soc. (1936) 1042.
[64] H.B. Jonassen, J.E. Field, J. Am. Chem. Soc. 79 (1957) 1275.
[65] G.F. Pregaglia, M. Donati, F. Conti, Chem. Ind. (Lond.) (1966) 1923.
[66] M. Donati, F. Conti, Tetrahedron Lett. (1966) 1219.
[67] G.F. Pregaglia, F. Conti, B. Minasso, R. Ugo, J. Organomet. Chem. 47 (1973) 165.
[68] A. Kasaharo, T. Izumi, K. Endo, T. Takeda, M. Ookita, Bull. Chem. Soc. Jpn. 47 (1974) 1967.
[69] P. Ponti, J.C. Baldwin, W.C. Kaska, Inorg. Chem. 18 (1979) 873.
[70] P.J. Ridgwell, P.M. Bailey, S.N. Wetherell, E.A. Kelleg, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1982) 999.
[71] S. Otto, A. Roodt, L.I. Elding, Dalton Trans. (2003) 2519.
[72] J. Chatt, L.A. Duncanson, R.G. Guy, Chem. Ind. (Lond.) (1959) 430.
[73] J. Chatt, R.G. Guy, L.A. Duncanson, J. Chem. Soc. (1961) 827.
[74] J. Chatt, R.G. Guy, L.A. Duncanson, D.T. Thompson, J. Chem. Soc. (1963) 5170.
[75] P.J. Ridgwell, P.M. Bailey, P.M. Maitlis, J. Organomet. Chem. 233 (1982) 373.
[76] Y. Wakatsuki, S. Nozakura, S. Murakashi, Bull. Chem. Soc. Jpn. 42 (1969) 273.
[77] E.J. Parsons, R.D. Larsen, P.W. Jennings, J. Am. Chem. Soc. 107 (1985) 1793.
[78] M.H. Rakowsky, J.C. Woolcock, L.L. Wright, D.B. Green, M.F. Rettig, R.M. Wing, Organometallics 6 (1987) 1211.
[79] V. DeFelice, A. de Renzi, F. Giordano, D. Tesauro, J. Chem. Soc. Dalton Trans. (1993) 1927.
[80] N. Basickes, A.C. Hutson, A. Sen, G.P.A. Yap, R.L. Rheingold, Organometallics 15 (1996) 4116.
[81] W.D. Muller, H.A. Brune, Chem. Ber. 119 (1986) 759.
[82] S. Kotani, K. Shiina, K. Sonogashira, J. Organomet. Chem. 429 (1992) 403.
[83] M. Sato, A. Asami, G. Maruyama, M. Kosuge, J. Nakayama, S. Kumakura, T. Fujihara, K. Unoura, J. Organomet. Chem. 654 (2002) 56.
[84] R.G. Denning, L.M. Venanzi, J. Chem. Soc. (1963) 3241.
[85] D.V. Claridge, L.M. Venanzi, J. Chem. Soc. (1964) 3419.
[86] M.A. Bennett, H.W. Kouwenhoven, J. Lewis, R.S. Nyholm, J. Chem. Soc. (1964) 4570.
[87] D.I. Hall, J.H. Ling, R.S. Nyholm, Struct. Bond. 15 (1973) 3.
[88] D.M. Adams, P.J. Chandler, Chem. Commun. (1966) 69.
[89] J. Pradilla-Sorzano, J.P. Fackler Jr., J. Mol. Spectrosc. 22 (1967) 80.
[90] J. Hiraishi, Spectrochim. Acta 25A (1969) 749.
[91] T. Hosokawa, I. Moritani, S. Nishioka, Tetrahedron Lett. (1969) 3833.
[92] L.W. Reeves, Can. J. Chem. 38 (1960) 736.
[93] Y. Huang, D.F.R. Gilson, I.S. Butler, J. Chem. Soc. Dalton Trans. (1992) 2881.
[94] T.G. Hewitt, K. Anzenhofer, J.J. De Boer, J. Organomet. Chem. 18 (1969) 19.
[95] K. Vrieze, H.C. Volger, P.W.N.M. Van Leeuwen, Inorg. Chim. Acta Rev. 3 (1969) 109.
[96] K. Vrieze, H.C. Volger, A.P. Praat, J. Organomet. Chem. 21 (1970) 467.
[97] J.N. Dempsey, C.N. Baenziger, J. Am. Chem. Soc. 77 (1955) 4984.
[98] J.R. Holden, C.N. Baenziger, J. Am. Chem. Soc. 77 (1955) 4987.
[99] W.A. Whitla, H.M. Powell, L.M. Venanzi, Chem. Commun. (1966) 310.
[100] R. Mason, G.B. Robertson, P.O. Whimp, Chem. Commun. (1968) 868.
[101] R. Mason, G.B. Robertson, P.O. Whimp, J. Chem. Soc. (A) (1970) 535.
[102] T.G. Hewitt, J.J. DeBoer, J. Chem. Soc. (A) (1971) 817.
[103] J. Bordner, D.W. Wertz, Inorg. Chem. 13 (1974) 1639.
[104] K. Ikura, I. Ryu, A. Ogawa, N. Sonoda, S. Harada, N. Kasai, Organometallics 10 (1991) 528.
[105] D.A. Johnson, W.C. Deese, A.W. Cordes, Inorg. Chem. 20 (1981) 1519.
[106] A.B. Goel, D. Vander Veer, Inorg. Chim. Acta 87 (1984) L19.
[107] A.B. Goel, S. Goel, D. Vander Veer, Inorg. Chim. Acta 54 (1981) L169.
[108] F. Giordano, A. Vitagliano, Inorg. Chem. 20 (1981) 633.

[109] J.K. Stille, R.A. Morgan, D.D. Whitehurst, J.R. Doyle, J. Am. Chem. Soc. 87 (1965) 3282.
[110] A.B. Goel, S. Goel, Inorg. Chim. Acta 45 (1980) L85.
[111] J.K. Stille, R.A. Morgan, J. Am. Chem. Soc. 88 (1966) 5135.
[112] M. Green, R.I. Hancock, J. Chem. Soc. (A) (1967) 2054.
[113] C.B. Anderson, B.J. Burreson, J. Organomet. Chem. 7 (1967) 181.
[114] G. Paiaro, A. De Renzi, R. Palumbo, Chem. Commun. (1967) 1150.
[115] R. Palumbo, A. De Renzi, A. Panunzi, G. Paiaro, J. Am. Chem. Soc. 91 (1969) 3874.
[116] R.N. Haszeldine, R.V. Parish, D.W. Robbins, J. Organomet. Chem. 23 (1970) C33.
[117] A. DeRenzi, R. Palumbo, G. Pairo, J. Am. Chem. Soc. 93 (1971) 880.
[118] C.T. Bailey, G.C. Lisensky, J. Chem. Educ. 62 (1985) 896.
[119] J. Chatt, L.M. Vallarino, L.M. Venanzi, J. Chem. Soc. (1957) 2496.
[120] D.A. White, J. Chem. Soc. (A) (1971) 145.
[121] R.G. Schultz, J. Organomet. Chem. 6 (1966) 435.
[122] B. Crociani, P. Uguagliati, T. Boschi, U. Belluco, J. Chem. Soc. (A) (1968) 2869.
[123] H. Reinheimer, H. Dietl, J. Moffat, D. Wolf, P.M. Maitlis, J. Am. Chem. Soc. 90 (1968) 5321.
[124] H. Dietl, H. Reinheimer, J. Moffat, P.M. Maitlis, J. Am. Chem. Soc. 92 (1970) 2276.
[125] W.T. Wipke, G.L. Goeke, J. Am. Chem. Soc. 96 (1974) 4244.
[126] G. Wiger, G. Albelo, M.F. Rettig, J. Chem. Soc. Dalton (1974) 2242.
[127] B.F.G. Johnson, J. Lewis, M.S. Subramanian, J. Chem. Soc. (A) (1968) 1993.
[128] J.K. Stille, D.B. Fox, J. Am. Chem. Soc. 92 (1970) 1274.
[129] J. Tsuji, H. Takahashi, J. Am. Chem. Soc. 87 (1965) 3275.
[130] H. Takahashi, J. Tsuji, J. Am. Chem. Soc. 90 (1968) 2387.
[131] S.J. Betts, A. Harris, R.N. Haszeldine, R.V. Parish, J. Chem. Soc. (A) (1971) 3699.
[132] M.N.S. Hill, B.F.G. Johnson, J. Lewis, J. Chem. Soc. (A) (1971) 2341.
[133] M. Tada, Y. Kuroda, T. Sato, Tetrahedron Lett. (1969) 2871.
[134] C. Agami, J. Levisalles, F.R. Munch, J. Organomet. Chem. 39 (1972) C17.
[135] C. Agami, J. Levisalles, F.R. Munch, J. Organomet. Chem. 65 (1974) 401.
[136] H. Hemmer, J. Rambaud, I. Tkatchenko, J. Organomet. Chem. 97 (1975) C57.
[137] D.J. Evans, L.A.P. Kane Maguire, J. Organomet. Chem. 312 (1986) C24.
[138] A. Segnitz, P.M. Bailey, P.M. Maitlis, J. Chem. Soc. Chem. Commun. (1973) 698.
[139] H. Horino, M. Arai, N. Inoue, Tetrahedron Lett. (1974) 647.
[140] Y. Tamaru, Z. Yoshida, Tetrahedron Lett. (1978) 4527.
[141] Y. Tamaru, Z. Yoshida, J. Org. Chem. 44 (1979) 1188.
[142] M.C. Cornock, T.A. Stephenson, J. Chem. Soc. Dalton Trans. (1977) 683.
[143] S. Chaudhary, V.K. Jain, Polyhedron 15 (1996) 1685.
[144] N. Oberbeckmann, K. Merz, R.A. Fischer, Organometallics 20 (2001) 3265.
[145] J. Chatt, L.M. Vallarino, L.M. Venanzi, J. Chem. Soc. (1957) 3413.
[146] R.N. Haszeldine, R.V. Parish, D.W. Robbins, J. Chem. Soc. Dalton Trans. (1976) 2355.
[147] F. Bonati, H.C. Clark, Can. J. Chem. 56 (1978) 2513.
[148] A.C. Cope, J.M. Kliegman, E.C. Fredrich, J. Am. Chem. Soc. 89 (1967) 287.
[149] M.A. Bennett, W.R. Kneen, R.S. Nyholm, Inorg. Chem. 7 (1968) 556.
[150] T. Yukawa, S. Tsutumi, Inorg. Chem. 7 (1968) 1458.
[151] R.N. Haszeldine, R.J. Lunt, R.V. Parish, J. Chem. Soc. (A) (1971) 3705.
[152] E. Benedetti, A. DeRenzi, A. Panunzi, C. Pedone, J. Organomet. Chem. 39 (1972) 403.
[153] M.K. Cooper, P.J. Guerney, J.H. Ling, R.S. Nyholm, J. Organomet. Chem. 91 (1975) 117.
[154] M.K. Cooper, P.J. Guerney, H.J. Goodwin, M. McPartil, J. Chem. Soc. Dalton Trans. (1982) 757.
[155] H.C. Clark, A.B. Goel, S. Goel, J. Organomet. Chem. 216 (1981) C25.
[156] P. Uguagliati, B. Crociani, U. Belluco, J. Chem. Soc. (A) (1970) 363.
[157] R. Pietropaolo, F. Cusmano, E. Rotondo, J. Organomet. Chem. 155 (1978) 117.
[158] B. Milani, F. Paronetto, E. Zangrando, J. Chem. Soc. Dalton Trans. (2000) 3055.
[159] C.C. Hunt, J.R. Doyle, Inorg. Nucl. Chem. Lett. 2 (1966) 283.
[160] B.F.G. Johnson, J. Lewis, D.A. White, J. Am. Chem. Soc. 91 (1969) 5186.
[161] R.A. Stockland Jr., G.K. Anderson, Organometallics 17 (1998) 4694.
[162] H. Suzuki, K. Mizutani, Y. Morooka, T. Ikawa, J. Am. Chem. Soc. 101 (1979) 748.
[163] L. Garcia, S.I. Shupack, M. Orchin, Inorg. Chem. 1 (1962) 893; L. Garcia, M. Orchin, J. Chem. Soc. (1961) 2254; P. Schmidt, M. Orchin, Inorg. Chem. 6 (1967) 1260.
[164] V.G. Albano, D. Braga, V. DeFelice, A. Panunzi, A. Vitaglano, Organometallics 6 (1987) 517.
[165] J. Chatt, R.G. Wilkins, J. Chem. Soc. (1952) 2622.
[166] A.S. Gow, H. Heinemann, J. Phys. Chem. 64 (1960) 1574.
[167] U. Belluco, M. Nicolini, D.S. Martin Jr., D.G. McMane, Inorg. Chem. 8 (1969) 2809.
[168] J.T. van Gemert, P.R. Wilkinson, J. Phys. Chem. 68 (1964) 645.
[169] J. Tsuji, M. Morikawa, J. Kiji, J. Am. Chem. Soc. 86 (1964) 4851.
[170] T. Saegusa, T. Tsuda, K. Nishijima, Tetrahedron Lett. 8 (1967) 4255.
[171] A.D. Ketley, L.P. Fisher, J. Organomet. Chem. 13 (1968) 243.
[172] D. Medema, R. van Helden, C.F. Kohl, Inorg. Chim. Acta 3 (1969) 255.
[173] A.D. Ketley, J.A. Braatz, J. Craig, Chem. Commun. (1970) 1117.
[174] N.M. Boag, R.J. Goodfellow, M. Green, B. Hessner, J.A.K. Howard, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1983) 2585.
[175] T.W. Hanks, R.A. Ekeland, K. Emerson, R.D. Larsen, P.W. Jennings, Organometallics 6 (1987) 28.
[176] L. Mink, M.F. Rettig, R.M. Wing, J. Am. Chem. Soc. 113 (1991) 2065.
[177] J.F. Harrod, A.J. Chalk, J. Am. Chem. Soc. 86 (1964) 1776.
[178] I. Moritani, Y. Fujiwara, Tetrahedron Lett. (1967) 1119.
[179] Y. Fujiwara, I. Moritani, M. Matsuda, Tetrahedron 24 (1968) 4819.
[180] P. Busse, F. Pesa, M. Orchin, J. Organomet. Chem. 140 (1977) 229.
[181] V. Vybiral, P. Svoboda, J. Heteleis, Collect. Czech. Chem. Commun. 44 (1979) 866.
[182] V.B. Pukhanarevich, S.P. Sushchinskaya, V.K. Voronov, S.M. Ponomareva, B.A. Trofinov, M.G. Voronkov, J. Gen. Chem. (USSR) 42 (1972) 1068.
[183] Yu.T. Struchkov, G.G. Aleksandrov, V.B. Pukhanarevich, S.P. Sushchinskaya, M.G. Voronkov, J. Organomet. Chem. 172 (1979) 269.
[184] V.P. Pukhnarevich, Yu.T. Struchkov, G.G. Aleksandrov, S.P. Suschinskaya, E.O. Tsetlina, M.G. Voronkov, Sov. J. Coord. Chem. 5 (1979) 1195.
[185] D.S. McGuinness, K.J. Cavell, Organometallics 19 (2000) 4918; D.S. McGuinness, K.J. Cavell, Organometallics 19 (2000) 741.

[186] L. Zanotto, R. Bertani, R.A. Michelin, Inorg. Chem. 29 (1990) 3265.
[187] R. Bertani, M. Mozzon, R.A. Michelin, F. Benetollo, G. Bomberi, T.J. Castilho, A.J.L. Pomberio, Inorg. Chim. Acta 189 (1991) 175.
[188] D. Sellmann, W. Prechtel, F. Knoch, M. Moll, Inorg. Chem. 32 (1993) 538.
[189] R.K. Singhal, A.K. Awasthi, N.K. Misra, Indian J. Chem. 23A (1984) 1046.
[190] J.A. Albanese, D.L. Staley, A.L. Rheingold, J.L. Burmeister, J. Organomet. Chem. 375 (1989) 265.
[191] L.R. Falvello, S. Fernandez, R. Navarro, A. Rueda, E.P. Urriolabeitia, Inorg. Chem. 37 (1998) 6007.
[192] L.R. Falvello, S. Fernandez, R. Navarro, A. Rueda, E.P. Urrilabeitia, Organometallics 17 (1998) 5887.
[193] J. Vicente, M.T. Chicote, I.S. Llamas, M.J. Lopez-Munoz, P.G. Jones, J. Chem. Soc. Dalton Trans. (1990) 3683.
[194] T. Boschi, B. Crociani, M. Nicolini, U. Belluco, Inorg. Chim. Acta 12 (1975) 39.
[195] W.P. Fehlhammer, A. Mayer, B. Olgemoller, Angew. Chem. Int. Ed. Eng. 14 (1974) 369.
[196] R. Uson, J. Fornies, P. Espinet, E. Lalinde, P.G. Jones, G.M. Sheldrick, J. Chem. Soc. Dalton Trans. (1982) 2389.
[197] B. Crociani, M. Nicolini, R.L. Richards, J. Organomet. Chem. 104 (1976) 259.
[198] Y. Mamamoto, H. Yamazaki, Bull. Chem. Soc. Jpn. 43 (1970) 2653;
Y. Mamamoto, H. Yamazaki, Inorg. Chem. 13 (1974) 438.
[199] S. Park, D.M. Roundhill, A.L. Rheingold, Inorg. Chem. 26 (1987) 3972.
[200] S. Park, D.M. Roundhill, A.L. Rheingold, Organometallics 10 (1991) 615.
[201] A. Albinati, F. Lianza, H. Berger, P.S. Pregosin, H. Ruegger, R.W. Kunz, Inorg. Chem. 32 (1993) 478.
[202] J.V. Cuevas, G. Garcia-Herbosa, A. Munoz, S. Garcia-Granda, D. Miguel, Organometallics 16 (1997) 2220.
[203] N.W. Alcock, P. Bergamini, T.J. Kemp, P.G. Pringle, J. Chem. Soc. Chem. Commun. (1987) 235.
[204] N.W. Alcock, P. Bergamini, T.J. Kemp, P.G. Pringle, S. Sastero, O. Traveso, Inorg. Chem. 30 (1991) 1594.
[205] J. Ruiz, M.T. Martinez, C. Vicente, G. Garcia, G. Lopez, P.A. Chaloner, P.B. Hitchcock, Organometallics 12 (1993) 4321.
[206] M.K. Cooper, P.V. Stevens, M. McPartlin, J. Chem. Soc. Dalton Trans. (1983) 553.
[207] W.K. Wong, L.L. Zhang, Y. Chen, W.Y. Wong, W.T. Wong, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (2000) 1397.
[208] R.G. Hayter, Nature 193 (1962) 872.
[209] R.G. Hayter, J. Am. Chem. Soc. 84 (1962) 3046.
[210] R.G. Hayter, F.S. Humiec, Inorg. Chem. 2 (1963) 306.
[211] R.G. Hayter, Inorg. Chem. 3 (1964) 301.
[212] J. Chatt, J.M. Davidson, J. Chem. Soc. (1964) 2433.
[213] C. Eaborn, K.J. Odell, A. Pidcock, J. Organomet. Chem. 170 (1979) 105.
[214] H. Goldwhite, A.S. Hirschon, Trans. Met. Chem. 2 (1977) 144.
[215] K. Issleib, W. Wenschuh, Z. Anorg. Allg. Chem. 305 (1960) 15.
[216] J.B. Brandon, K.R. Dixon, Can. J. Chem. 59 (1981) 1188.
[217] M.A. Zhuravel, J.R. Moncraz, D.S. Glueck, K. Lam, A.L. Rheingold, Organometallics 19 (2000) 3447.
[218] M. Itazaki, Y. Nishihara, K. Osakada, Organometallics 23 (2004) 1610.
[219] P. Leoni, M. Sommovigo, M. Pasquali, P. Sabatino, D. Braga, J. Organomet. Chem. 423 (1992) 263;
P. Leoni, S. Manetti, M. Pasquali, Inorg. Chem. 34 (1995) 749.
[220] P. Leoni, M. Pasquali, A. Fortunelli, G. Germano, A. Albinati, J. Am. Chem. Soc. 120 (1998) 9564.
[221] H. Brunner, S. Dormeir, I. Grau, M. Zabel, Eur. J. Inorg. Chem. (2002) 2603.
[222] R. Glaser, D.J. Kountz, J.C. Gallucci, D.W. Meek, Inorg. Chim. Acta 77 (1983) L207.
[223] R. Glaser, D.J. Kountz, R.D. Waid, J.C. Gallucci, D.W. Meek, J. Am. Chem. Soc. 106 (1984) 6324.
[224] R.J. Puddephatt, P.J. Thompson, J. Organomet. Chem. 117 (1976) 395.
[225] D.W. Meek, R. Waid, K.D. Tan, R.M. Kirchner, C.N. Morimoto, Inorg. Chim. Acta 64 (1982) 221.
[226] A.B. Goel, S. Goel, Inorg. Chim. Acta 90 (1984) L33.
[227] E. Alonso, J. Fornies, C. Fortuno, A. Martin, A.G. Orpen, Organometallics 20 (2001) 850.
[228] J. Duran, A. Polo, J. Real, A.A. Larena, J.F. Piniella, Inorg. Chim. Acta. 353 (2003) 280.
[229] I.V. Kourkine, M.B. Chapman, D.S. Glueck, K. Eichele, R.E. Wasylishen, G.P.A. Yap, L.M. Liable-Sands, A.L. Rheingold, Inorg. Chem. 35 (1996) 1476;
I.V. Kourkine, D.S. Glueck, Inorg. Chem. 36 (1997) 5160.
[230] K. Issleib, H.R. Roloff, Z. Anorg. Allg. Chem. 324 (1963) 250.
[231] A.J. Carty, F. Hartstock, N.J. Taylor, Inorg. Chem. 21 (1982) 1349.
[232] V.K. Jain, S. Kannan, E.R.T. Tiekink, J. Chem. Soc. Dalton Trans. (1992) 2231.
[233] A. Singhal, V.K. Jain, J. Chem. Soc. Dalton Trans. (1993) 1515.
[234] A. Singhal, V.K. Jain, S. Kannan, J. Organomet. Chem. 447 (1993) 317.
[235] P.P. Phadnis, V.K. Jain, A. Knoedler, W. Kaim, Z. Anorg. Allg. Chem. 628 (2002) 1332.
[236] H. Mahalakshmi, V.K. Jain, E.R.T. Tiekink, Polyhedron 22 (2003) 549.
[237] J. Ruiz, V. Rodriguez, G. Lopez, P.A. Chaloner, P.B. Hitchcock, J. Chem. Soc. Dalton Trans. (1997) 4271.
[238] F. Bonati, H.C. Clark, C.-S. Wong, Can. J. Chem. 58 (1980) 1435.
[239] V.K. Jain, S. Kannan, Polyhedron 11 (1992) 27.
[240] V.K. Jain, S. Kannan, E.R.T. Tiekink, J. Chem. Soc. Dalton Trans. (1993) 3625.
[241] A. Singhal, V.K. Jain, R.P. Patel, A. Vyas, R. Bohra, J. Organomet. Chem. 479 (1994) 87.
[242] V.K. Jain, S. Kannan, R. Bohra, Polyhedron 11 (1992) 1551.
[243] V.K. Jain, S. Kannan, J. Chem. Res. (S) (1992) 278.
[244] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, J. Chem. Res. (S) (1996) 284.
[245] S. Narayan, V.K. Jain, Trans. Met. Chem. 23 (1998) 435.
[246] G. Minghetti, G. Banditelli, F. Bonati, Chem. Ind. (1977) 123.
[247] A.L. Bandini, G. Banditelli, G. Minghetti, F. Bonati, Can. J. Chem. 57 (1979) 3237.
[248] G. Minghetti, G. Banditelli, F. Bonati, J. Chem. Soc. Dalton Trans. (1979) 1851.
[249] G. Banditelli, A.L. Bandini, F. Bonati, G. Minghetti, Inorg. Chim. Acta 60 (1982) 93.
[250] A.L. Bandini, G. Banditelli, B. Bovio, Polyhedron 20 (2001) 2869.
[251] J. Powell, A. Kuksis, Can. J. Chem. 57 (1979) 2986.
[252] J. Fornies, A. Martin, V. Sicilia, L.F. Martin, Chem. Eur. J. 9 (2003) 3427.
[253] D.L. Reger, J.C. Baxter, L. Lebioda, Inorg. Chim. Acta 165 (1989) 201.
[254] M.E. Fakley, A. Pidcocok, J. Chem. Soc. Dalton Trans. (1977) 1444.
[255] G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J.M. Marti, M.D. Santana, J. Organomet. Chem. 393 (1990) C53.
[256] J. Ruiz, C. Vicente, J.M. Marti, N. Cutillas, G. Garcia, G. Lopez, J. Organomet. Chem. 460 (1993) 241.
[257] V.V. Grushin, H. Alper, Organometallics 12 (1993) 1890.
[258] V.V. Grushin, C. Bensimon, H. Alper, Organometallics 12 (1993) 2737.
[259] V.V. Grushin, C. Bensimon, H. Alper, Organometallics 14 (1995) 3259.

[260] V.V. Grushin, H. Alper, Organometallics 15 (1996) 5242.
[261] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 4567.
[262] M.S. Driver, J.F. Hartwig, Organometallics 16 (1977) 5706.
[263] M.S. Driver, J.F. Hartwig, J. Am. Chem. Soc. 118 (1996) 4206.
[264] J. Ruiz, V. Rodriguez, C. Vicente, J.M. Marti, G. Lopez, J. Perez, Inorg. Chem. 40 (2001) 5354.
[265] J. Ruiz, F. Florenciano, C. Vicente, M.C.R. de Arellano, Inorg. Chem. Commun. 3 (2000) 73.
[266] J.F. Chatt, G. Mann, J. Chem. Soc. (1938) 949.
[267] J. Chatt, F.A. Hart, J. Chem. Soc. (1953) 2363.
[268] J. Chatt, F.A. Hart, J. Chem. Soc. (1960) 2807.
[269] G.B. Kauffman, B.W. Bensen, Inorg. Chem. 6 (1967) 411.
[270] T. Boschi, B. Crociani, L. Toniolo, U. Belluco, Inorg. Chem. 9 (1970) 532.
[271] P.J. Goggin, R.J. Goodfellow, F.J.S. Reed, J. Chem. Soc. A (1971) 2031.
[272] R. Zanella, R. Ros, M. Graziani, Inorg. Chem. 12 (1973) 2736.
[273] R.J. Puddephatt, C.E.E. Upton, J. Organomet. Chem. 91 (1975) C17.
[274] M.P. Brown, R.J. Puddephatt, C.E.E. Upton, J. Chem. Soc. Dalton (1976) 2490.
[275] R. Saleedo, H. Torrens, Trans. Met. Chem. 5 (1980) 247.
[276] P.H. Bird, U. Siriwardane, R.D. Lai, A. Shaver, Can. J. Chem. 60 (1982) 2075.
[277] A. Zschunke, H. Meyer, I. Heidlas, B. Messbauer, B. Walther, H.D. Schadler, Z. Anorg. Allg. Chem. 504 (1983) 117.
[278] H.C. Clark, V.K. Jain, G.S. Rao, J. Organomet. Chem. 279 (1985) 181.
[279] V.K. Jain, G.S. Rao, Inorg. Chim. Acta 127 (1987) 161.
[280] V.K. Jain, Inorg. Chim. Acta 133 (1987) 261.
[281] V.K. Jain, R.P. Patel, K.V. Muralidharan, R. Bohra, Polyhedron 8 (1989) 2151.
[282] E.M. Padilla, C.M. Jensen, Polyhedron 10 (1991) 89.
[283] E.M. Padilla, J.A. Golen, P.N. Richmann, C.M. Jensen, Polyhedron 10 (1991) 1343.
[284] V.K. Jain, R.P. Patel, K. Venkatasubramanian, Polyhedron 10 (1991) 851.
[285] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, J. Organomet. Chem. 468 (1994) 285.
[286] A. Singhal, V.K. Jain, J. Organomet. Chem. 494 (1995) 75.
[287] W. Henderson, J.J. McCaffrey, B.K. Nicholson, J. Chem. Soc. Dalton Trans. (2000) 2753.
[288] A. Romerosa, C.L. Magana, M. Saoud, S. Manas, Eur. J. Inorg. Chem. (2003) 348.
[289] L. Villanueva, M. Arroya, S. Bernes, H. Torrens, Chem. Commun. (2004) 1942.
[290] B.L. Khandelwal, S.K. Gupta, Inorg. Chim. Acta 166 (1989) 199.
[291] V.K. Jain, S. Kannan, J. Organomet. Chem. 405 (1991) 265.
[292] V.K. Jain, S. Kannan, J. Organomet. Chem. 439 (1992) 231.
[293] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, Polyhedron 14 (1995) 3641.
[294] S. Dey, V.K. Jain, B. Varghese, J. Organomet. Chem. 623 (2001) 48.
[295] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgren, J. Organomet. Chem. 587 (1999) 200.
[296] V.P. Ananikov, I.P. Beletskaya, G.G. Aleksandrov, I.L. Eremenko, Organometallics 22 (2003) 1414.
[297] S. Ford, P.K. Khanna, C.P. Morley, M.D. Vaira, J. Chem. Soc. Dalton Trans. (1999) 791.
[298] V.P. Ananikov, M.A. Kabeshov, I.P. Beletskaya, G.G. Aleksandrov, I.L. Eremenko, J. Organomet. Chem. 687 (2003) 451.
[299] M.J. Brown, J.F. Corrigan, J. Organomet. Chem. 689 (2004) 2872.
[300] L.Y. Chia, W.R. McWhinnie, J. Organomet. Chem. 148 (1978) 165.
[301] B.L. Khandelwal, K. Kundu, S.K. Gupta, Inorg. Chim. Acta 148 (1988) 255.
[302] B.L. Khandelwal, K. Kundu, S.K. Gupta, Inorg. Chim. Acta 154 (1988) 183.
[303] V.K. Jain, S. Kannan, J. Organomet. Chem. 418 (1991) 349.
[304] A. Arevalo, S. Bernes, J.J. Garcia, P.M. Maitlis, Organometallics 18 (1999) 1680.
[305] L.B. Han, S. Shimada, M. Tanaka, J. Am. Chem. Soc. 119 (1997) 8133.
[306] T.B. Rauchfus, D.M. Roundhill, J. Am. Chem. Soc. 97 (1975) 3386.
[307] R. Cao, M.C. Hong, F.L. Jiang, H. Liu, Acta Cryst. C51 (1995) 1280.
[308] D.M. Roundhill, S.G.N. Roundhill, W.B. Beaulieu, U. Bagchi, Inorg. Chem. 19 (1980) 3365.
[309] A. Benefiel, D.M. Roundhill, W. Fullz, A. Rheingold, Inorg. Chem. 23 (1984) 3316.
[310] A.H. Eisenberg, F.M. Dixon, C.A. Mirkin, C.L. Stern, C.D. Incarvito, A.L. Rheinglod, Organometallics 20 (2001) 2052.
[311] E. Colacio, R. Cuesta, M. Ghazi, M.A. Huertas, J.M. Moreno, A. Navarrete, Inorg. Chem. 36 (1997) 1652.
[312] E. Cerrada, L.R. Favello, M.B. Hursthouse, M. Laguna, A. Laquin, C. Pozo-Gonzalo, Eur. J. Inorg. Chem. (2002) 826.
[313] X. Solans, M.F. Altaba, J.L. Brianso, J. Sola, J. Suades, H. Barrera, Acta Cryst. C39 (1983) 1653.
[314] H. Barrera, J.C. Bayon, J. Suades, C. Germain, J.P. Declero, Polyhedron 3 (1984) 969.
[315] H. Barrera, J.M. Vimas, M.F. Altaba, X. Solans, Polyhedron 4 (1985) 2027.
[316] J. Ayllon, P. Gonzalez-Duarte, C. Miravitlles, C. Molins, J. Chem. Soc. Dalton Trans. (1990) 1793.
[317] S. Dey, V.K. Jain, A. Knoedler, W. Kaim, Inorg. Chim. Acta 349 (2003) 104.
[318] S. Dey, V.K. Jain, B. Varghese, J. Butcher, Unpublished results.
[319] J.G. Anton, J. Pons, X. Solans, M.F. Bardia, J. Ros, Inorg. Chim. Acta 357 (2004) 571.
[320] J.G. Anton, J. Pons, X. Solans, M.F. Bardia, J. Ros, Inorg. Chim. Acta 355 (2003) 87.
[321] S.K. Gupta, B.L. Khandelwal, Indian J. Chem. 29A (1990) 977.
[322] R. Uson, J. Fornies, M.A. Uson, S. Herrero, J. Organomet. Chem. 447 (1993) 137.
[323] J. Soulie, J.-Y. Lallemand, R.C. Rao, Org. Magn. Res. 12 (1979) 67.
[324] R.H. Fenn, G.R. Segrott, J. Chem. Soc. A (1970) 3197.
[325] R.H. Fenn, G.R. Segrott, J. Chem. Soc. Dalton (1972) 330.
[326] M.C. Hall, J.A.J. Jarvis, B.T. Kilbourn, P.G. Owston, J. Chem. Soc. Dalton (1972) 1544.
[327] C.E. Briant, C.J. Gardner, T.S.A. Hor, N.D. Howells, D.M.P. Mingos, J. Chem. Soc. Dalton Trans. (1984) 2645.
[328] E.W. Abel, D.G. Evans, J.R. Koe, M.B. Hursthouse, M. Mazid, M.F. Mahon, K.C. Molloy, J. Chem. Soc. Dalton Trans. (1990) 1697.
[329] J.H. Yamamoto, G.P.A. Yap, C.M. Jesnson, J. Am. Chem. Soc. 113 (1991) 5060.
[330] I. Nakanishi, S. Tanaka, K. Matsumoto, S. Ooi, Acta Cryst. C 50 (1994) 58.
[331] R. Cao, M. Hong, F. Jiang, B. Kang, X. Xie, H. Liu, Polyhedron 15 (1996) 2661.
[332] A. Albinati, J. Herrmann, P.S. Pregosin, Inorg. Chim. Acta 264 (1997) 33.
[333] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, Unpublished results.
[334] N. Brugat, A. Polo, A. Alvarez-Larena, J.F. Piniella, J. Real, Inorg. Chem. 38 (1999) 4829.
[335] W. Li, C.L. Barnes, P.R. Sharp, J. Chem. Soc. Chem. Commun. (1990) 1634.
[336] J.J. Li, W. Li, P.R. Sharp, Inorg. Chem. 35 (1996) 604.
[337] P.R. Sharp, J. Chem. Soc. Dalton Trans. (2000) 2647.

[338] S.W.A. Fong, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (1999) 639.
[339] J. Chatt, D.M.P. Mingos, J. Chem. Soc. A (1970) 1243.
[340] R. Ugo, G. La Monica, S. Cenini, A. Segre, F. Conti, J. Chem. Soc. A (1971) 522.
[341] S. Narayan, V.K. Jain, Trans. Met. Chem. 25 (2000) 400.
[342] V.W.W. Yam, P.K.Y. Yeung, K.K. Cheung, J. Chem. Soc. Chem. Commun. (1995) 267.
[343] M. Capdevila, Y. Carrasco, W. Clegg, R.A. Coxall, P. Gonzalez-Duarte, A. Lledos, J. Sola, G. Ujaque, Chem. Commun. (1998) 597.
[344] R. Mas-Belleste, M. Capdevial, P.A. Champkin, W. Clegg, R.A. Coxall, A. Lledos, C. Megret, P. Gonzalez-Duarte, Inorg. Chem. 41 (2002) 3218.
[345] M. Zhou, C.F. Lam, K.F. Mok, P.H. Leung, T.S.A. Hor, J. Organomet. Chem. 476 (1994) C32.
[346] W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, C. Langes, A. Rieder, P. Brüggeller, Inorg. Chim. Acta 274 (1998) 143.
[347] G. Li, S. Li, A.L. Tan, W.H. Yip, T.C.W. Mak, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (1996) 4315.
[348] S. Datta, U.C. Agarwal, Indian J. Chem. 20A (1981) 1190.
[349] P. Gonzalez-Duarte, R.M. A-Lledos, Balleste, Eur. J. Inorg. Chem. (2004) 3585.
[350] M. Schmidt, G.G. Hoffmann, Z. Anorg. Allg. Chem. 464 (1980) 209.
[351] S.W.A. Fong, J.J. Vittal, W. Henderson, T.S.A. Hor, A.G. Oliver, C.E.F. Rickard, Chem. Commun. (2001) 421.
[352] R.R. Gukathasan, R.H. Morris, A. Walker, Can. J. Chem. 61 (1983) 2490.
[353] G. Aullon, M. Capdevila, W. Clegg, P. Gonzalez-Duarte, A. Lledos, R. Mas-Balleste, Angew. Chem. Int. Ed. 41 (2002) 2776.
[354] H. Liu, A.L. Tan, K.F. Mok, T.C.W. Mak, A.S. Batsanov, J.A.K. Howard, T.S.A. Hor, J. Am. Chem. Soc. 119 (1997) 11006.
[355] C.E. Briant, D.I. Gilmour, M.A. Luke, D.M.P. Mingos, J. Chem. Soc. Dalton Trans. (1985) 851.
[356] D.I. Gilmour, M.A. Luke, D.M.P. Mingos, J. Chem. Soc. Dalton Trans. (1987) 335.
[357] H. Liu, A.L. Tan, K.F. Mok, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (1996) 4023.
[358] B.H. Aw, K.K. Looh, H.S.O. Chan, K.L. Tan, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (1994) 3177.
[359] C.E. Briant, T.S.A. Hor, N.D. Howells, D.M.P. Mingos, J. Chem. Soc. Chem. Commun. (1983) 1118.
[360] H. Liu, A.L. Tan, Y. Xu, K.F. Mok, T.S.A. Hor, Polyhedron 16 (1997) 377.
[361] C.E. Briant, T.S.A. Hor, N.D. Howells, D.M.P. Mingos, J. Organomet. Chem. 256 (1983) C15.
[362] V.W.W. Yam, P.K.Y. Yeung, K.K. Cheung, Angew. Chem. Int. Ed. Eng. 35 (1996) 739.
[363] H. Liu, A.L. Tan, C.R. Cheng, K.F. Mok, T.S.A. Hor, Inorg. Chem. 36 (1997) 2916.
[364] W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, C. Langes, A. Rieder, P. Brüggeller, Inorg. Chem. Commun. 1 (1998) 185.
[365] W. Bos, J.J. Bour, P.P.J. Schlebos, P. Hageman, W.P. Bosman, J.M.M. Smits, J.A.C. Wietmarschen, P.T. Beurskens, Inorg. Chim. Acta 119 (1986) 141.
[366] J.S.L. Yeo, G. Li, W.H. Yip, W. Henderson, T.C.W. Mak, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (1999) 435.
[367] Z. Li, H. Liu, K.F. Mok, A.S. Batsanov, J.A.K. Howard, T.S.A. Hor, J. Organomet. Chem. 575 (1999) 223.
[368] S.W.A. Fong, W.T. Yap, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (2002) 1826.
[369] M. Capdevila, Y. Carrasco, W. Clegg, R.A. Coxall, P. Gonzalez-Duarte, A. Lledos, J.A. Ranirez, J. Chem. Soc. Dalton Trans. (1999) 3103.
[370] Z. Li, S.H. Loh, S.W.A. Fong, Y.K. Yan, W. Henderson, K.F. Mok, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (2000) 1027.
[371] S.W.A. Fong, W.T. Yap, J.J. Vittal, T.S.A. Hor, W. Henderson, A.G. Oliver, C.E.F. Rickard, J. Chem. Soc. Dalton Trans. (2001) 1986.
[372] P.A. Shapley, H.C. Liang, N.C. Dopke, Organometallics 20 (2001) 4700.
[373] V.W.W. Yam, K.L. Yu, E.C.C. Cheng, P.K.Y. Yeung, K.K. Chenung, N. Zhu, Chem. Eur. J. 8 (2002) 4122.
[374] M. Capdevila, W. Clegg, R.A. Coxall, P. Gonzalez-Duarte, M. Hamidi, A. Lledos, G. Ujaque, Inorg. Chem. Commun. 1 (1998) 466.
[375] H. Brunner, M. Weber, M. Zabel, J. Organomet. Chem. 684 (2003) 6.
[376] Z. Li, K.F. Mok, T.S.A. Hor, J. Organomet. Chem. 682 (2003) 73.
[377] S.W.A. Forg, T.S.A. Hor, W. Henderson, B.K. Nicholson, S. Gardyne, S.M. Devoy, J. Organomet. Chem. 679 (2004) 24.
[378] J. Ruiz, V. Rodriguez, A. Perez, G. Lopez, D. Bautista, J. Organomet. Chem. 689 (2004) 2080.
[379] S.W.A. Forg, T.S.A. Hor, J.J. Vittal, W. Henderson, S. Cramp, Inorg. Chim. Acta 357 (2004) 1152.
[380] S.W.A. Forg, T.S.A. Hor, S.M. Devoy, B.A. Waugh, B.K. Nicholson, W. Henderson, Inorg. Chin. Acta 357 (2004) 2081.
[381] R. Mas-Balleste, W. Clegg, A. Lledos, P. Gonzalez-Duarte, Eur. J. Inorg. Chem. (2004) 3223.
[382] K. Matsumoto, N. Kotoku, T. Shizuka, R. Tanaka, S. Okeya, Inorg. Chim. Acta 321 (2001) 167.
[383] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, Inorg. Chem. 41 (2002) 1194.
[384] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Organomet. Chem. 659 (2002) 92.
[385] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (2002) 328.
[386] M. Zhou, Y. Xu, C.F. Lam, P.H. Leung, L.L. Koh, K.F. Mok, T.S.A. Hor, Inorg. Chem. 33 (1994) 1572.
[387] M. Zhou, Y. Xu, L.L. Koh, K.F. Mok, P.H. Leung, T.S.A. Hor, Inorg. Chem. 32 (1993) 1875.
[388] M. Zhou, Y. Xu, A.M. Tan, P.H. Leung, K.F. Mok, L.L. Koh, T.S.A. Hor, Inorg. Chem. 34 (1995) 6425.
[389] M. Zhou, Y. Xu, C.F. Lam, L.L. Koh, K.F. Mok, P.H. Leung, T.S.A. Hor, Inorg. Chem. 32 (1993) 4660.
[390] M. Zhou, P.H. Leung, K.F. Mok, T.S.A. Hor, Polyhedron 15 (1996) 1737.
[391] M.S. Zhou, A.L. Tan, Y. Xu, C.F. Lam, P.H. Leung, K.F. Mok, L.L. Koh, T.S.A. Hor, Polyhedron 16 (1997) 2381.
[392] Z. Li, X. Xu, S.B. Khoo, K.F. Mok, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (2000) 2901.
[393] X. Xu, S.W.A. Forg, Z. Li, Z.H. Loh, F. Zhao, J.J. Vittal, W. Henderson, S.B. Khoo, T.S.A. Hor, Inorg. Chem. 41 (2002) 6838.
[394] Z. Li, W. Zheng, H. Liu, K.F. Mok, T.S.A. Hor, Inorg. Chem. 42 (2003) 8481.
[395] G. Li, C.K. Lam, S.W. Chien, T.C.W. Mak, T.S.A. Hor, J. Organomet. Chem. 690 (2005) 990.
[396] A. Bencini, M.D. Vaira, R. Morassi, P. Stoppioni, F. Mele, Polyhedron 15 (1996) 2079.
[397] S.J.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (2001) 315.
[398] R.D. Adams, T.A. Wolfe, B.W. Eichhorn, R.C. Haushalter, Polyhedron 8 (1989) 701.
[399] J.G. Brennan, T. Siegrist, S.M. Stuczynski, M.L. Steigerwald, J. Am. Chem. Soc. 112 (1990) 9233.
[400] A.L. Ma, J.B. Thoden, L.F. Dahl, J. Chem. Soc. Chem. Commun. (1992) 1516.
[401] F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini, Inorg. Chem. Commun. 2 (1999) 275.
[402] M.R. Lewtas, C.P. Morley, N. DiVaira, Polyhedron 19 (2000) 751.
[403] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, Organometallics 21 (2002) 2944.

[404] H. Li, G.B. Carpenter, D.A. Sweigart, Organometallics 19 (2000) 1823.
[405] H. Wolkers, K. Dehnike, D. Finske, A. Kassanov, S.S. Hafner, Acta Cryst. C47 (1991) 1627.
[406] F.G. Mann, D. Purdie, J. Chem. Soc. (1936) 873.
[407] J. Chatt, L.M. Venanzi, J. Chem. Soc. (1957) 2351.
[408] J. Chatt, J. Chem. Soc. (1951) 652.
[409] J. Chatt, L.M. Venanzi, J. Chem. Soc. (1955) 2787.
[410] R.J. Goodfellow, L.M. Venanzi, J. Chem. Soc. (1965) 7533.
[411] A.C. Smithies, M. Rycheck, M. Orchin, J. Organomet. Chem. 12 (1968) 199.
[412] A.C. Smithies, P. Schmidt, M. Orchin, Inorg. Synth. 12 (1970) 240.
[413] F.R. Hartley, G.W. Searle, Inorg. Chem. 12 (1973) 1949.
[414] W. Baratta, P.S. Pregosin, Inorg. Chim. Acta 209 (1993) 85.
[415] H.C. Clark, G. Ferguson, V.K. Jain, H. Parvez, Inorg. Chem. 24 (1985) 1477.
[416] G.K. Anderson, H.C. Clark, J.A. Davies, Inorg. Chem. 20 (1981) 944.
[417] G.K. Anderson, H.C. Clark, J.A. Davies, Inorg. Chem. 20 (1981) 3607.
[418] I.M. Al-Najjar, Inorg. Chim. Acta 128 (1987) 93.
[419] R.G. Goel, M.G. Montemayer, J. Coord. Chem. 8 (1978) 1.
[420] R.G. Goel, W.O. Ogini, R.C. Srivastava, Inorg. Chem. 20 (1981) 3611.
[421] R.G. Goel, W.O. Ogini, R.C. Srivastava, Inorg. Chem. 21 (1982) 1627.
[422] P. Courtot, A. Peron, R. Rumin, J.C. Chottard, D. Mansuy, J. Organomet. Chem. 99 (1975) C59.
[423] P. Courtot, R. Rumin, A. Peron, J. Organomet. Chem. 144 (1978) 357.
[424] P.C. Kong, F.D. Rochon, Can. J. Chem. 57 (1979) 682.
[425] R. Pichon, R. Rumin, J.Y. Salaun, J. Organomet. Chem. 282 (1985) C60.
[426] F.D. Rochon, R. Melanson, Acta Cryst. B37 (1981) 690.
[427] F.D. Rochon, P.C. Kong, Can. J. Chem. 64 (1986) 1894.
[428] A.J. Carty, A. Efraty, Inorg. Nucl. Chem. Lett. 4 (1968) 427.
[429] A.J. Carty, A. Efraty, Can. J. Chem. 47 (1969) 2573.
[430] W. Oberhauser, C. Bachmann, T. Stampfl, P. Brüggeller, Inorg. Chim. Acta 256 (1997) 223.
[431] A. Singhal, V.K. Jain, R.J. Butcher, J. Coord. Chem. 46 (1999) 355.
[432] H.C. Clark, G. Ferguson, P.N. Kpoor, M. Parvez, Inorg. Chem. 24 (1985) 3924.
[433] L.R. Falvello, J. Fornies, J. Gomez, E. Lalinde, A. Martin, F. Martinez, M.T. Moreno, J. Chem. Soc. Dalton Trans. (2001) 2132.
[434] D. Xu, H.J. Murfee, W.E. van der Veer, B. Horg, J. Organomet. Chem. 596 (2000) 53.
[435] S. Sjovall, C. Andersson, O.F. Wendt, Inorg. Chim. Acta 325 (2001) 182.
[436] M. Habib, H. Trujillo, C.A. Alexander, B.N. Storhoff, Inorg. Chem. 24 (1985) 2344.
[437] W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, C. Langes, A. Rieder, P. Bruggeller, Polyhedron 17 (1998) 3211.
[438] G.C. Dol, G. Gaemers, M. Hietikko, P.C.J. Kamer, P.W.N.H. van Leeuwen, R.J.M. Nolte, Eur. J. Inorg. Chem. (1998) 1975.
[439] W. Oberhauser, T. Stampfl, C. Bachmann, R. Haid, C. Langes, H. Kopacka, K. Ongania, P. Bruggeller, Polyhedron 19 (2000) 913.
[440] C. Bianchini, H.M. Lee, A. Meli, W. Oberhauser, F. Vizza, P. Bruggeller, R. Haid, C. Langes, Chem. Commun. (2000) 777.
[441] J. Bennet, A.D. Rae, G. Salem, N.C. Ward, P. Waring, K. Wells, A.C. Willis, Dalton Trans. (2002) 234.
[442] P. Nair, G.K. Anderson, N.P. Rath, Organometallics 22 (2003) 1494.
[443] J. Chatt, A.A. Williams, J. Chem. Soc. (1951) 3061.
[444] R.J. Goodfellow, P.L. Goggin, L.M. Venanzi, J. Chem. Soc. (A) (1967) 1897.
[445] R.J. Goodfellow, J.G. Evans, P.L. Goggin, D.A. Duddell, J. Chem. Soc. (A) (1968) 1604.
[446] M.J. Tayler, A.L. Odell, H.A. Raethel, Spectrochim. Acta (A) 24A (1968) 1855.
[447] D.M. Adams, P.J. Chandler, J. Chem. Soc. (A) (1969) 588;
D.M. Adams, M. Goldstein, E.F. Mooney, Trans. Faraday Soc. 59 (1963) 2228.
[448] C. Masters, J.P. Visser, J. Chem. Soc. Chem. Commun. (1974) 932.
[449] A.A. Kiffen, C. Masters, J.P. Visser, J. Chem. Soc. Dalton Trans. (1975) 1311.
[450] J.Y. Lallemand, J. Soulie, J.C. Chottard, J. Chem. Soc. Chem. Commun. (1980) 436.
[451] G.K. Anderson, H.C. Clark, J.A. Davies, Inorg. Chem. 22 (1983) 434.
[452] A. Albinati, R. Naegeli, K.H.A. Ostoja-Starzewski, P.S. Pregosin, H. Ruegger, Inorg. Chim. Acta 76 (1983) L231;
P.S. Pregosin, H. Ruegger, Inorg. Chim. Acta 86 (1984) 55.
[453] K. Polborn, K. Severin, Eur. J. Inorg. Chem. (1998) 1187.
[454] A.F. Wells, Proc. R. Soc. A167 (1938) 169;
F.G. Mann, A.F. Wells, J. Chem. Soc. (1938) 702.
[455] M. Black, R.H.B. Mais, P.G. Owston, Acta Cryst. B 25 (1969) 1760.
[456] S.F. Watkins, Chem. Commun. (1968) 504;
S.F. Watkins, J. Chem. Soc. (A) (1970) 168.
[457] A. Albinati, R. Naegeli, H. Ruegger, P.S. Pregosin, Angew. Chem. 94 (1982) 310.
[458] H.C. Clark, G. Ferguson, A.B. Goel, B.L. Ruhl, Organometallics 3 (1984) 15.
[459] B.L. Simms, M. Shang, J. Lu, W.J. Youngs, J.A. Ibers, Organometallics 6 (1987) 1118.
[460] M.J. Blake, R.O. Gould, A.M. Marr, D.W.H. Rankin, M. Schröder, Acta Cryst. C45 (1989) 1218.
[461] H.G. Ang, Y.M. Cai, W.L. Kwik, A.L. Rheingold, J. Chem. Soc. Chem. Commun. (1990) 1580.
[462] W.J. Grigsby, B.K. Nicholson, Acta Cryst. C48 (1992) 362.
[463] P.A. Chaloner, S.Z. Dewa, P.B. Hitchcock, Acta Cryst. C51 (1995) 232.
[464] A. Singhal, V.K. Jain, T. Manisekaran, Unpublished results.
[465] V.K. Jain, K. Venkatasubramanian, Unpublished results.
[466] U.A. Gregory, J.A.J. Jarvis, B.T. Kilbourn, P.G. Owston, J. Chem. Soc. (A) (1970) 2770;
P.G. Owston, J.M. Rowe, Acta Cryst. 13 (1960) 253.
[467] D.C. Smith Jr., C.H. Lake, G.M. Gray, Chem. Commun. (1998) 2771;
D.C. Smith Jr., C.H. Lake, G.M. Gray, Dalton Trans. (2003) 2950.
[468] S.J. Coles, P. Faulds, M.B. Hursthouse, D.G. Kelly, G.C. Ranger, A.J. Toner, N.M. Walker, J. Organomet. Chem. 586 (1999) 234.
[469] A.A. Barnes, A.K. Brisdon, J.G. Fay, R.G. Pritchard, J.E. Warren, Inorg. Chim. Acta 358 (2005) 2543.
[470] G. Aullon, S. Alvarez, Inorg. Chem. 35 (1996) 3137.
[471] G. Aullon, P. Alemany, S. Alvarez, Inorg. Chem. 35 (1996) 5061.
[472] G. Aullon, S. Alvarez, Chem. Eur. J. 3 (1997) 655.
[473] G. Aullon, G. Ujaque, A. Lledos, S. Alvarez, P. Alemany, Inorg. Chem. 37 (1998) 804.
[474] G. Aullon, G. Ujaque, A. Lledos, S. Alvarez, Chem. Eur. J. 5 (1999) 1391.
[475] G. Aullon, S. Alvarez, Inorg. Chem. 40 (2001) 4937.
[476] M. Capdevila, W. Clegg, P. Gonzalez-Duarte, A. Jarid, A. Lledos, Inorg. Chem. 35 (1996) 490.
[477] U. Fekl, R. van Eldik, C. Richardson, W.T. Robinson, Inorg. Chem. 40 (2001) 3247.
[478] J.R. Briggs, C. Crocker, B.L. Shaw, Inorg. Chim. Acta 40 (1980) 245.
[479] J. Chatt, L.M. Venanzi, J. Chem. Soc. (1957) 2445.
[480] M. Cusumano, A. Giannetto, P. Ficarro, R. Ficarro, S. Tommasini, J. Chem. Soc. Dalton Trans. (1991) 1581.

[481] T.H. Chan, Chem. Commun. (1968) 895.
[482] J. Chatt, L.M. Venanzi, J. Chem. Soc. (1955) 3858.
[483] J. Auffret, P. Courtot, R. Pichon, J.Y. Salaün, J. Chem. Soc. Dalton Trans. (1987) 1687.
[484] G.K. Anderson, R.J. Cross, J. Chem. Soc. Dalton Trans. (1988) 1980.
[485] G. Bruno, M. Cusumano, A. Giannetto, A. Giuffrida, G. Guglielmo, Acta Cryst. C46 (1990) 192.
[486] M.C. Aversa, P. Giannetto, G. Bruno, M. Cusumano, A. Giannetto, S. Geremia, J. Chem. Soc. Dalton Trans. (1990) 2433.
[487] J.F. van Baar, K. Vrieze, D.J. Stufkens, J. Organomet. Chem. 81 (1974) 247.
[488] H.C. Clark, G. Ferguson, V.K. Jain, M. Parvez, Inorg. Chem. 25 (1986) 3808.
[489] A. Albinati, C.G. Anklin, P.S. Pregosin, Inorg. Chim. Acta 90 (1984) L37.
[490] B. Miller, J. Altman, C. Leschke, W. Schunack, K. Sunkel, J. Knizek, H. Noth, W. Beck, Z. Anorg. Allg. Chem. 626 (2000) 978.
[491] A. Singhal, V.K. Jain, J. Chem. Res. (S) (1996) 246.
[492] C.G. Anklin, P.S. Pregosin, Magn. Res. Chem. 23 (1985) 671.
[493] A. Albinati, C.G. Anklin, F. Ganazzoli, H. Ruegg, P.S. Pregosin, Inorg. Chem. 26 (1987) 503.
[494] A. Albinati, C. Arz, P.S. Pregosin, Inorg. Chem. 26 (1987) 508.
[495] A. Albinati, P.S. Pregosin, F. Wombacher, Inorg. Chem. 29 (1990) 1812.
[496] R.J. Cross, I.G. Phillips, Inorg. Chim. Acta 54 (1981) L1.
[497] R.J. Cross, I.G. Phillips, J. Chem. Soc. Dalton Trans. (1981) 2132.
[498] S.E. d'Arbeloff-Wilson, P.B. Hitchcock, S. Krill, J.F. Nixon, L. Nyulaszi, M. Regitz, J. Am. Chem. Soc. 122 (2000) 4557.
[499] J. Chatt, N.P. Johnson, B.L. Shaw, J. Chem. Soc. (1964) 1662.
[500] A. Panunzi, A. de Renzi, R. Palumbo, G. Paiaro, J. Am. Chem. Soc. 91 (1969) 3879;
A. de Renzi, G. Paiaro, A. Ranunzi, Gazz. Chim. Ital. 102 (1972) 413.
[501] J. Ashley-Smith, I. Douek, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans. (1972) 1776.
[502] C. Eaborn, K.J. Odell, A. Pidcock, J. Chem. Soc. Dalton Trans. (1978) 1288.
[503] J.R. Briggs, C. Crocker, W.S. McDonald, B.L. Shaw, J. Organomet. Chem. 181 (1979) 213.
[504] J.R. Briggs, C. Crocker, W.S. McDonald, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1980) 64.
[505] J.R. Briggs, C. Crocker, W.S. McDonald, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1981) 121.
[506] J.R. Briggs, C. Crocker, W.S. McDonald, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1982) 457.
[507] R.J. Cross, M.F. Davidson, M. Rocamora, J. Chem. Soc. Dalton Trans. (1988) 1147.
[508] R.J. Cross, M.F. Davidson, J. Chem. Soc. Dalton Trans. (1987) 139.
[509] P.G. Leviston, M.G.H. Wallbridge, J. Organomet. Chem. 110 (1976) 271.
[510] G.K. Anderson, R.J. Cross, J. Chem. Soc. Dalton Trans. (1980) 1988.
[511] G.K. Anderson, R.J. Cross, J. Chem. Soc. Dalton Trans. (1980) 712.
[512] G.K. Anderson, H.C. Clark, J.A. Davies, Inorg. Chem. 22 (1983) 427.
[513] H. Motschi, P.S. Pregosin, L.M. Venanzi, Helv. Chim. Acta 62 (1979) 667.
[514] J.A. Davies, A. Sood, Inorg. Chem. 24 (1985) 4213.
[515] B. Cetinkaya, P.B. Hitchock, M.F. Lappert, P.L. Pye, D.B. Shaw, J. Chem. Soc. Dalton Trans. (1979) 434.
[516] H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes, C.H. Stam, J. Organomet. Chem. 175 (1979) C21;
H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes, C.H. Stam, Inorg. Chim. Acta 39 (1980) 197.
[517] G.K. Anderson, C. Billard, H.C. Clark, J.A. Davies, C.S. Wong, Inorg. Chem. 22 (1983) 439.
[518] A. Albinati, H. Moriyama, H. Ruegger, P.S. Pregosin, A. Togni, Inorg. Chem. 24 (1985) 4430.
[519] H. Ruegger, P.S. Pregosin, Inorg. Chem. 26 (1987) 2912.
[520] M.F. Lappert, P.P. Power, J. Chem. Soc. Dalton Trans. (1985) 51.
[521] T.A.K. AlAllaf, C. Eaborn, P.B. Hitchcock, M.F. Lappert, A. Pidcock, J. Chem. Soc. Chem. Commun. (1985) 548.
[522] J. Chatt, F.A. Hart, Nature 169 (1952) 673.
[523] J. Chatt, L.A. Duncanson, Nature 178 (1956) 997.
[524] J. Chatt, L.A. Duncanson, F.A. Hart, P.G. Owston, Nature 181 (1958) 43.
[525] J. Chatt, F.A. Hart, J. Chem. Soc. (1961) 1416.
[526] K. Matsumoto, Y. Odaira, S. Tsutrumi, Chem. Commun. (1968) 832.
[527] G.K. Anderson, R.J. Cross, L. Manojlovic-Muir, K.W. Muir, R.A. Wales, J. Chem. Soc. Dalton Trans. (1979) 684.
[528] D.J. Cardin, B. Cetinkaya, M.F. Lappert, L. Manojlovic-Muir, K.W. Muir, Chem. Commun. (1971) 400.
[529] R.J. Cross, R. Wardle, J. Organomet. Chem. 23 (1970) C4.
[530] M. Onishi, K. Hiraki, Y. Ohama, A. Kurosaki, J. Organomet. Chem. 284 (1985) 403.
[531] H. Werner, H.J. Kraus, U. Schubert, K. Ackermann, Chem. Ber. 115 (1982) 2905.
[532] T. Murahashi, N. Kanehisa, Y. Kai, T. Otani, H. Kurosawa, Chem. Commun. (1996) 825.
[533] O. Briel, A. Fehn, K. Polborn, W. Beck, Polyhedron 18 (1998) 225.
[534] T. Brasey, R. Scopelliti, K. Severin, Inorg. Chem. 44 (2005) 160.
[535] A.B. Goel, S. Goel, D. van Derveer, C.G. Brinkley, Inorg. Chim. Acta 64 (1982) L173.
[536] M.C. Cornock, T.A. Stephenson, J. Chem. Soc. Dalton Trans. (1977) 501.
[537] D.L. Reger, J.C. Baxter, D.G. Garza, Organometallics 9 (1990) 16.
[538] K. Panneerselveam, T.H. Lu, S.F. Tung, S. Narayan, V.K. Jain, Acta Cryst. C55 (1999) 541.
[539] J. Browning, G.W. Bushnell, K.R. Dixon, A. Pidcock, Inorg. Chem. 22 (1983) 2226.
[540] G. Calvin, G.E. Coates, J. Chem. Soc. (1960) 2008.
[541] J. Ruiz, V. Rodriguez, G. Lopez, P.A. Chaloner, P.B. Hitchcock, J. Chem. Soc. Dalton Trans. (1977) 4271.
[542] Y. Hayashi, K. Isobe, Y. Nakamura, S. Okeya, J. Organomet. Chem. 310 (1986) 127.
[543] F.T. Ladipo, G.K. Anderson, Organometallics 13 (1994) 303.
[544] J.S. Kim, A. Sen, I.A. Guzi, L.M.L. Sands, A.L. Rheingold, J. Chem. Soc. Dalton. Trans. (2002) 4726.
[545] R.J. Puddephatt, P.J. Thompson, J. Chem. Soc. Dalton (1977) 1219.
[546] H.C. Clark, A.B. Goel, V.K. Jain, K.G. Tyers, C.S. Wong, J. Organomet. Chem. 321 (1987) 123.
[547] G.K. Anderson, Organometallics 2 (1983) 665.
[548] J. Vicente, A. Arcas, M.V. Borrachero, E. Molins, C. Miravitlles, J. Organomet. Chem. 359 (1989) 127.
[549] J. Vicente, A. Arcas, M.V. Borrachero, M.L. deGoicoechea, M. Lanfranchi, A. Tiripicchio, Inorg. Chim. Acta 177 (1990) 247.
[550] F. Paul, J. Patt, J.F. Hartwig, J. Am. Chem. Soc. 116 (1994) 5969.
[551] J.G. Hartwig, F. Paul, J. Am. Chem. Soc. 117 (1995) 5373.
[552] F. Paul, J. Patt, J.F. Hartwig, Organometallics 14 (1995) 3030.
[553] R.A. Widenhoefer, H.A. Zhong, S.L. Buchwald, Organometallics 15 (1996) 2745.
[554] C. Amatore, A.A. Bahsoun, A. Jutand, G. Meyer, A.N. Ntepe, L. Ricard, J. Am. Chem. Soc. 125 (2003) 4212.
[555] J. Vicente, J.A. Abad, E.M. Vivente, M.C.K. Arellano, P.G. Jones, Organometallics 19 (2000) 752.

[556] A.H. Roy, J.F. Hartwig, Organometallics 23 (2004) 194;
A.H. Roy, J.F. Hartwig, Organometallics 23 (2004) 1533.
[557] W.J. Marshall, R.J. Youg Jr., V.V. Grushin, Organometallics 20 (2001) 523.
[558] R.H. Heyn, C.H. Gorbitz, Organometallics 21 (2002) 2781.
[559] P. Fitton, J.E. McKeon, B.C. Ream, J. Chem. Soc. Chem. Commun. (1969) 370.
[560] R. Ros, M. Lenarda, T. Boschi, R. Roulet, Inorg. Chim. Acta 25 (1977) 61.
[561] P. Zanello, R. Seeber, A. Cinquantini, R. Ros, J. Inorg. Nucl. Chem. 43 (1981) 1095.
[562] E. Gretz, A. Sen, J. Am. Chem. Soc. 108 (1986) 6038.
[563] G. Mann, C. Incarvito, A.L. Rheingold, J.F. Hartwig, J. Am. Chem. Soc. 121 (1999) 3224;
G. Mann, Q. Shelby, A.H. Roy, J.F. Hartwig, Organometallics 22 (2003) 2775.
[564] R. Uson, J. Fornies, F. Martinez, J. Organomet. Chem. 132 (1977) 429.
[565] R. Uson, P. Royo, J. Fornies, F. Martinez, J. Organomet. Chem. 90 (1975) 367.
[566] R. Uson, J. Fornies, R. Navarro, M.P. Garcia, Inorg. Chim. Acta 33 (1979) 69.
[567] R. Uson, J. Fornies, R. Navarro, A. Gallo, Trans. Met. Chem. 5 (1980) 284.
[568] G.K. Anderson, R.J. Cross, J. Chem. Soc. Chem. Commun. (1978) 819.
[569] R. Uson, J. Fornies, M. Tomas, B. Menjon, A.J. Welch, Organometallics 7 (1988) 1318.
[570] R. Uson, J. Fornies, M.A. Uson, M.L. Mas, Inorg. Chim. Acta 168 (1990) 59.
[571] J. Fornies, E. Lalinde, A. Martin, M.T. Moreno, A.J. Welch, J. Chem. Soc. Dalton Trans. (1995) 1333.
[572] I. Ara, L.R. Falvello, S. Fermandez, J. Fornies, E. Lalinde, A. Martin, M.T. Moreno, Organometallics 16 (1997) 5923.
[573] J. Fornies, M.A. Gomez-Saso, E. Lalinde, F. Martinez, M.T. Moreno, Organometallics 11 (1992) 2873.
[574] I. Ara, L.R. Falvello, J. Fornies, E. Lalinde, A. Martin, M.T. Moreno, Organometallics 16 (1997) 5392.
[575] A.H. Roy, J.F. Hartwig, J. Am. Chem. Soc. 123 (2001) 1232.
[576] G.K. Anderson, R.J. Cross, J. Chem. Soc. Dalton Trans. (1979) 1246.
[577] R.J. Cross, R. Wardle, J. Chem. Soc. (A) (1970) 840.
[578] G.K. Anderson, R.J. Cross, L. Manojlovic-Muir, J. Organomet. Chem. 170 (1979) 385.
[579] R.J. Cross, J. Gemmill, J. Chem. Soc. Dalton Trans. (1981) 2317.
[580] J. Collin, D. Commereue, Y. Chauvin, J. Mol. Catal. 14 (1982) 133.
[581] J.S. Brumbaugh, S. Sen, J. Am. Chem. Soc. 110 (1988) 803.
[582] Y.S. Lin, A. Yamamoto, Organometallics 17 (1998) 3466.
[583] V.K. Jain, S. Chaudhury, J. Organomet. Chem. 468 (1994) 279.
[584] V.K. Jain, S. Chaudhury, A. Vyas, R. Bohra, J. Chem. Soc. Dalton Trans. (1994) 1207.
[585] S. Narayan, V.K. Jain, S. Chaudhury, J. Organomet. Chem. 530 (1997) 101.
[586] G.K. Anderson, Organometallics 5 (1986) 1903.
[587] R. Uson, J. Gimeno, J. Fornies, F. Martinez, Inorg. Chim. Acta 50 (1981) 173.
[588] J. Powell, T. Jack, Inorg. Chem. 11 (1972) 1039.
[589] N.Yu. Kozitsyna, M.V. Surashskaya, T.B. Larina, P.A. Kozmin, A.C. Kotelnikova, I.I. Moiseev, Izv. Akad. Nauk. SSSR Ser. Kim. 8 (1989) 1894.
[590] S. Kannan, V.K. Jain, Magn. Reson. Chem. 28 (1990) 1007.
[591] I.I. Moiseev, N.Yu. Kozitsyna, D.I. Kochubey, V.N. Kolomijchuck, K.I. Zamaraev, J. Organomet. Chem. 451 (1993) 231.
[592] A.S. Berenblyum, A.G. Knizhnik, S.L. Mund, I.I. Moiseev, J. Organomet. Chem. 234 (1982) 219.
[593] M.B. Hursthouse, O.D. Sloan, P. Thornton, N.P.C. Walker, Polyhedron 5 (1986) 1475.
[594] W.W. Ng, P.T. Cheng, V. Kocman, H. Lüth, S.C. Nyburg, Inorg. Chem. 18 (1979) 2620.
[595] A. Singhal, V.K. Jain, Polyhedron 14 (1995) 285.
[596] A. Singhal, V.K. Jain, M. Nethaji, A. Samuelson, D. Jayaprakash, R.J. Butcher, Polyhedron 17 (1998) 3531.
[597] M. Gomez, G. Muller, J. Sales, Polyhedron 12 (1993) 1171.
[598] A. Singhal, V.K. Jain, Can. J. Chem. 74 (1996) 2018.
[599] V.K. Jain, R.J. Butcher, Polyhedron 17 (1998) 1317.
[600] N. Yu Kozitsyna, A.M. Ellern, M.Yu. Antipin, Yu.T. Struchkov, I.I. Moiseev, Mendeleeve Commun. 3 (1991) 92.
[601] V.K. Jain, Trans. Met. Chem. 21 (1996) 494.
[602] Y. Nakatsu, Y. Nakamura, K. Matsumoto, S. Ooi, Inorg. Chim. Acta 196 (1992) 81.
[603] J.H. Yamamoto, W. Yoshida, C.M. Jensen, Inorg. Chem. 30 (1991) 1353.
[604] M. Gupta, R.E. Cramer, K. Ho, C. Pettersen, S. Mishina, J. Belli, C.M. Jensen, Inorg. Chem. 34 (1995) 60.
[605] S. Narayan, V.K. Jain, Trans. Met. Chem. 24 (1999) 409.
[606] S. Narayan, V.K. Jain, B. Varghese, J. Chem. Soc. Dalton Trans. (1998) 2359.
[607] E.M. Padilla, J.H. Yamamoto, C.M. Jensen, Inorg. Chim. Acta 174 (1990) 209.
[608] G.P.A. Yap, C.M. Jensen, Inorg. Chem. 31 (1992) 4823.
[609] S. Dey, V.K. Jain, J. Singh, V. Trehan, K.K. Bhasin, B. Varghese, Eur. J. Inorg. Chem. (2003) 744.
[610] V.K. Jain, International Symposium on Metalloorganic Chemistry at the Dawn of 21st Century, Rajasthan University, Jaipur, 16–18 March 1998.
[611] H. Werner, H.J. Kraus, U. Schubert, K. Ackermann, P. Hofmann, J. Organomet. Chem. 250 (1983) 517.
[612] Yu.N. Kukushkin, I.V. Pakhomova, Zh. Neorg. Khim. 15 (1970) 1882.
[613] P.C. Kong, F.D. Rochon, Inorg. Chim. Acta 37 (1970) L457.
[614] I.V. Pakhomova, Yu.N. Kukushkin, I.V. Knonvalov, V.V. Strukov, Zh. Neorg. Chim. 29 (1984) 1000.
[615] G. Annibale, M. Bonivento, L. Canovese, L. Cattalini, G. Michelon, M.L. Tobe, Inorg. Chem. 24 (1985) 797.
[616] V.Yu. Kukushkin, V.K. Belsky, V.E. Konovalov, R.R. Shifrina, A.I. Moiseev, R.A. Vlasova, Inorg. Chim. Acta 183 (1991) 57.
[617] I.A. Krol, V.M. Agre, V.K. Trunov, E.G. Morozova, G.G. Gorovoi, Russ. J. Inorg. Chem. 33 (1988) 80.
[618] F.D. Rochon, G. Masserweh, N. Nedelec, Inorg. Chim. Acta 346 (2003) 197.
[619] J.A. Davies, Adv. Inorg. Radiochem. 24 (1981) 116.
[620] C. Eaborn, K. Kundu, A. Pidcock, J. Chem. Soc. Dalton (1981) 933.
[621] G. Annibale, M. Bonivento, L. Cattalini, M.L. Tobe, J. Chem. Soc. Dalton Trans. (1992) 3433.
[622] J.R.L. Priqueler, F.D. Rochon, Inorg. Chim. Acta 357 (2004) 2167.
[623] D.J. Altken, H.P. Husson, D.N. Huy, S. Ongeri, F. Vergne, B. Viossalt, Inorg. Chem. Commun. 1 (1998) 314.
[624] L.A. Tshugaev, W. Subbotin, Chem. Ber. 43 (1910) 1200.
[625] Jensen, Z. Anorg. Chem. 225 (1935) 115.
[626] K. Ofele, E. Dotzauer, J. Organomet. Chem. 42 (1972) C87.
[627] S.G. Murray, F.R. Hartley, Chem. Rev. 81 (1981) 365.
[628] T.S. Lobana, K. Sharma, Trans. Met. Chem. 7 (1982) 333.
[629] H. Morita, J.C. Bailar, Inorg. Synth. 22 (1983) 128.
[630] W. Baratta, P.S. Pregosin, A. Bacchi, G. Pelizzi, Inorg. Chem. 33 (1994) 4494.
[631] Y. Fuchita, H. Maruyama, M. Kawatani, K. Hiraki, Polyhedron 10 (1991) 561.
[632] E. Delgado, E. Hernandez, E. Lalinde, H. Lang, N. Mansilla, M.T. Moreno, G. Rheinwald, F. Zamora, Inorg. Chim. Acta 315 (2001) 1.

[633] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgren, Chem. Commun. (1999) 585.
[634] M. Basato, C. Bertani, M. Zecca, A. Grassi, G. Valle, J. Organomet. Chem. 575 (1999) 163;
M. Basato, A. Cardinale, M. Zecca, G. Valle, Inorg. Chim. Acta 303 (2000) 100.
[635] J.R. Allkins, P.J. Hendra, J. Chem. Soc. (A) (1967) 1325.
[636] P.L. Goggin, R.J. Goodfellow, D.L. Sales, J. Stokes, P. Woodward, Chem. Commun. (1968) 31.
[637] P.L. Goggin, R.J. Goodfellow, S.R. Haddock, F.J.S. Reed, J.G. Smith, K.M. Thomas, J. Chem. Soc. Dalton (1972) 1904.
[638] P.L. Goggin, R.J. Goodfellow, F.J.S. Reed, J. Chem. Soc. Dalton (1974) 576.
[639] D.L. Sales, J. Stokes, P. Woodward, J. Chem. Soc. (A) (1968) 1852.
[640] R. Uson, J. Fornies, P. Espinet, G. Alfranca, Synth. React. Inorg. Met. Org. Chem. 10 (1980) 579.
[641] A.C. Albeniz, P. Espinet, R.L. Fernandez, Organometalics 22 (2003) 4206.
[642] P.K. Byers, A.J. Canty, L.M. Engelhardt, A.H. White, J. Chem. Soc. Dalton Trans. (1986) 1731.
[643] J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643.
[644] J. Kuyper, R. van der Laan, F. Jeanneaus, K. Vrieze, Trans. Met. Chem. 1 (1976) 199;
J. Kuyper, R. van der Laan, F. Jeanneaus, K. Vrieze, Trans. Met. Chem. 1 (1976) 3116.
[645] B.R. Steele, K. Vrieze, Trans. Met. Chem. 2 (1977) 140.
[646] R.J. Puddephatt, M.A. Thomson, L. Manojlovic-Muir, K.W. Muir, A.A. Frew, M.P. Brown, J. Chem. Soc. Chem. Commun. (1981) 805.
[647] G. Alibrandi, D. Minniti, L. Scolaro, R. Romeo, Inorg. Chem. 28 (1989) 1939.
[648] D.P. Bancroft, F.A. Cotton, L.R. Falvello, W. Schwotzer, Inorg. Chem. 25 (1986) 763.
[649] M.A.C. Lacabra, A.J. Canty, M. Lutz, J. Patel, A.L. Spek, H. Sun, G. van Koten, Inorg. Chim. Acta 327 (2002) 15.
[650] D. Song, S. Wang, J. Organomet. Chem. 648 (2002) 302.
[651] M.R. Plutino, L.M. Scolaro, A. Albinatti, R. Romeo, J. Am. Chem. Soc. 126 (2004) 6470.
[652] J. Chatt, L.A. Duncanson, L.M. Venanzi, J. Chem. Soc. (1955) 4461.
[653] J. Chatt, L.A. Duncanson, L.M. Venanzi, J. Chem. Soc. (1958) 3203.
[654] R. Uson, J. Fornies, R. Navaro, P. Espinet, C. Mendivic, J. Organomet. Chem. 290 (1985) 125.
[655] G. Sanchez, J.L. Serrano, F. Momblona, F. Ruiz, J. Garcia, J. Perez, G. Lopez, P.A. Chaloner, P. Hitchcock, Polyhedron 20 (2001) 571.
[656] P.K. Byers, A.J. Canty, B.W. Skelton, A.H. White, J. Organomet. Chem. 336 (1987) C55.
[657] A.D. Renzi, G. Morelli, A. Panunzi, A. Vitagliano, Gazz. Chim. Ital. 117 (1987) 445.
[658] P.K. Byers, A.J. Canty, B.W. Skelton, A.H. White, J. Organomet. Chem. 393 (1990) 299.
[659] P.K. Byers, A.J. Canty, Organometallics 9 (1990) 210.
[660] V.G. Albano, C. Castellari, M.E. Cucciolito, A. Panunzi, A. Vitagliano, Organometallics 9 (1990) 1269.
[661] K.J. Cavell, H. Jin, J. Chem. Soc. Dalton Trans. (1995) 4081.
[662] H. Jin, K.J. Cavell, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1995) 2159.
[663] E.W. Abel, D.G. Evans, J.R. Koe, M.B. Hursthouse, M. Mazid, J. Chem. Soc. Dalton Trans. (1992) 663.
[664] S. Lanza, E. Rotondo, Inorg. Chim. Acta 146 (1988) 205.
[665] M.C. Aversa, P. Bonaccorsi, M. Cusumano, P. Gainnetto, D. Minniti, J. Chem. Soc. Dalton Trans. (1991) 3431.
[666] D.P. Bancroft, F.A. Cotton, Inorg. Chem. 27 (1988) 1633.
[667] M. Crespo, M. Martinez, J. Sales, J. Chem. Soc. Chem. Commun. (1992) 822.
[668] C.M. Anderson, M. Crespo, G. Ferguson, A.J. Lough, R.J. Puddephatt, Organometallics 11 (1992) 1177.
[669] M. Crespo, M. Martinez, J. Sales, X. Solans, M. Font Bardia, Organometallis 11 (1992) 1288.
[670] C.R. Baar, G.S. Hill, J.J. Vittal, R.J. Puddephat, Organometallics 17 (1998) 32.
[671] R. Bassan, K.H. Bryars, L. Judd, A.W.G. Platt, P.G. Pringle, Inorg. Chim. Acta 121 (1986) L41.
[672] J.D. Scott, R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (1984) 193.
[673] D. Song, K. Sliwowski, J. Pang, S. Wang, Organometallics 21 (2002) 4978.
[674] C. Anderson, M. Crespo, J. Organomet. Chem. 689 (2004) 1496.
[675] M. Lashanizadehgan, M. Rashidi, J.E. Hux, R.J. Puddephatt, S.S.M. Ling, J. Organomet. Chem. 269 (1984) 317.
[676] H.C. Clark, K.R. Dixon, W.J. Jacobs, Chem. Commun. (1968) 93;
H.C. Clark, K.R. Dixon, J. Am. Chem. Soc. 91 (1969) 596.
[677] W.J. Cherwinski, H.C. Clark, Can. J. Chem. 47 (1969) 2665.
[678] J.A. Davies, F.R. Hartley, G.S. Murray, Inorg. Chem. 19 (1980) 2299.
[679] K.R. Dixon, D.J. Hawke, Can. J. Chem. 49 (1971) 3253.
[680] D.A. Duddell, P.L. Goggin, R.J. Goodfellow, M.G. Norton, Chem. Commun. (1968) 879.
[681] P.M. Treichel, K.P. Wagner, W.J. Knebel, Inorg. Chim. Acta 6 (1972) 674.
[682] F. Neve, A. Crispini, M. Ghedini, G.D. Munno, Inorg. Chem. Acta 176 (1990) 23.
[683] A. Badia, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 554 (1998) 105.
[684] U. Schmidt, K. Hg, H. Werner, J. Chem. Soc. Dalton Trans. (2000) 1005.
[685] R. McCrindle, G.J. Arsenault, A. Gupta, M.J. Hampden-Smith, R.E. Rice, A.J. McAlees, J. Chem. Soc. Dalton Trans. (1991) 949.
[686] R. McCrindle, G. Ferguson, G.J. Arsenault, M.J. Hampden-Smith, A.J. McAlees, B.L. Ruhl, J. Organomet. Chem. 390 (1990) 121.
[687] D.A. Duddell, P.L. Goggin, R.J. Goodfellow, M.G. Norton, J.G. Smith, J. Chem. Soc. (A) (1970) 545.
[688] G.W. Bushnell, K.R. Dixon, D.T. Eadie, S.R. Stobart, Inorg. Chem. 20 (1981) 1545.
[689] J.L. Atwood, K.R. Dixon, D.T. Eadie, S.R. Stobart, M.J. Zaworotka, Inorg. Chem. 22 (1983) 774.
[690] T. Chivers, R.W. Hilts, I.H. Krouse, A.W. Cordes, R. Hallford, S.R. Scott, Can. J. Chem. 70 (1992) 2602.
[691] W.P. Fehlhammer, W. Beck, P. Pollmann, Chem. Ber. 102 (1969) 3903.
[692] W. Beck, P. Kreutzer, K. Werner, Chem. Ber. 104 (1971) 528.
[693] G.C. Dobinson, R. Mason, G.B. Robertson, R. Ugo, F. Conti, D. Morelli, F. Bonati, Chem. Commun. (1967) 739.
[694] M. Keubler, R. Ugo, S. Cenini, F. Conti, J. Chem. Soc. Dalton Trans. (1975) 1081.
[695] N.W. Alcock, R.D. D'Sullivan, A.W. Parkins, J. Chem. Soc. Chem. Commun. (1980) 1216.
[696] E.K. vanden Beuken, N. Veldman, W.J.J. Smeets, A.L. Spek, B.L. Feringa, Organometallics 17 (1998) 636.
[697] K. Sakai, E. Ishigami, K. Yokokawa, T. Kajiwara, T. Ito, Acta Cryst. E59 (2003) m1178.
[698] J.A. Bailey, H.B. Gray, Acta Cryst. C48 (1992) 1420.
[699] J.A. Bailey, V.M. Miskowski, H.B. Gray, Acta Cryst. C49 (1993) 793.
[700] E.M.A. Ratilla, B.K. Scott, M.S. Moxness, N.M. Kostic, Inorg. Chem. 29 (1990) 918.

[701] G. Annibale, P. Bergamin, V. Bertolasi, M. Cattabriga, A. Lazzaro, M. Marchi, G. Vertuani, J. Chem. Soc. Dalton Trans. (1999) 3877.
[702] H.K. Yip, C.M. Che, Z.Y. Zhou, T.C.W. Mak, J. Chem. Soc. Chem. Commun. (1992) 1369.
[703] M.C. DeRosa, F. Almutlaq, R.J. Crutchley, Inorg. Chem. 40 (2001) 1406.
[704] J.A. Bailey, V.M. Miskowski, H.B. Gray, Inorg. Chem. 32 (1993) 369.
[705] B. Oskui, M. Mintert, W.S. Sheldrick, Inorg. Chim. Acta 287 (1999) 72.
[706] S.Y. Yu, M. Fujita, K. Yamaguchi, J. Chem. Soc. Dalton Trans. (2001) 3415.
[707] A. Maiboroda, G. Rheinwald, H. Lang, Inorg. Chem. Commun. 4 (2001) 381.
[708] S.J. Berners-Price, M.S. Davies, J.W. Cox, D.S. Thomas, N. Farrell, Chem. Eur. J. 9 (2003) 713.
[709] N.J. Wheate, A.I. Day, R.J. Blanch, A.P. Arnold, C. Cullinane, J.G. Collins, Chem. Commun. (2004) 1424;
N.J. Wheate, B.J. Evison, A.J. Herlt, D.R. Phillips, J.G. Collins, Dalton Trans. (2003) 3486.
[710] B.A.J. Jansen, P. Wielaard, H. den Dulk, J. Brouwer, J. Reedijk, Eur. J. Inorg. Chem. (2002) 2375;
G.V. Kalayda, S. Komeda, K. Ikeda, T. Sato, M. Chikuma, Reedijk, Eur. J. Inorg. Chem. (2003) 4347.
[711] W.M. Teles, N.L. Speziali, C.A.L. Filgueiras, Polyhedron 19 (2000) 739.
[712] M. Janka, G.K. Anderson, N.P. Rath, Inorg. Chim. Acta 357 (2004) 2339.
[713] M.A. Zhuravel, D.S. Glueck, C.D. Incarvito, A.L. Rheingold, Organometallics 18 (1999) 4673;
W. Oberhauser, T. Stampfl, C. Bachmann, R. Haid, C. Langes, H. Kopacka, K.H. Ongania, P. Bruggeller, Polyhedron 19 (2000) 913.
[714] A. El Qisairi, P.M. Henry, J. Organomet. Chem. 603 (2000) 50; A.K. Al Qisairi, H.A. Qaseer, J. Organomet. Chem. 659 (2002) 50;
A.K. Qisairi, H.A. Qaseer, P.M. Henry, J. Organomet. Chem. 656 (2002) 168.
[715] S. Ganguly, J.T. Mague, D.M. Roundhill, Inorg. Chem. 31 (1992) 3831.
[716] G.W. Bushnell, K.R. Dixon, R.G. Hunter, J.J. McFarland, Can. J. Chem. 50 (1972) 3694.
[717] B. Longato, G. Pilloni, G. Valle, B. Corain, Inorg. Chem. 27 (1988) 956.
[718] R. Faggiani, B. Lippert, C.J.L. Lock, B. Rosenberg, J. Am. Chem. Soc. 99 (1977) 777.
[719] G.W. Bushnell, Can. J. Chem. 56 (1978) 1773.
[720] G. Trovo, G. Bandoli, U. Casellato, B. Corain, M. Nicolini, B. Longato, Inorg. Chem. 29 (1990) 4616.
[721] A.L. Bandini, G. Banditelli, M.A. Cinellu, G. Sanna, G. Minghetti, F. Demartin, M. Manassero, Inorg. Chem. 28 (1989) 404.
[722] D.A. Phillips, M. Kubota, J. Thomas, Inorg. Chem. 15 (1976) 118.
[723] A.J. Deeming, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans. (1973) 1848.
[724] G. Sanchez, J.L. Serrano, M.C. Ramirez de Arellano, J. Perez, G. Lopez, Polyhedron 19 (2000) 1395.
[725] J.J. Li, P.R. Sharp, Inorg. Chem. 33 (1994) 183.
[726] S. Kannan, A.J. James, P.R. Sharp, Inorg. Chim. Acta 345 (2003) 8.
[727] A. Xia, P.R. Sharp, Inorg. Chem. 40 (2001) 4016.
[728] J.J. Li, W. Li, A.J. James, T. Holbert, T.P. Sharp, P.R. Sharp, Inorg. Chem. 38 (1999) 1563.
[729] A.L. Bandini, G. Banditelli, E. Cesarotti, G. Minghetti, B. Bovio, Inorg. Chem. 31 (1992) 391.
[730] G. Sanchez, A. Sanmartin, J. Garcia, G. Lopez, Trans. Met. Chem. 22 (1997) 545.
[731] G. Sanchez, J.L. Serrano, J. Garcia, G. Lopez, J. Perez, E. Molins, Inorg. Chem. Acta 287 (1999) 37.
[732] U. Anandhi, T. Holbert, D. Lueng, P.R. Sharp, Inorg. Chem. 42 (2003) 1282.
[733] S. Kannan, A.J. James, P.R. Sharp, Polyhedron 19 (2000) 155.
[734] A.D. Getty, K.I. Goldberg, Organometallics 20 (2001) 2545.
[735] R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, Organometallics 17 (1998) 661.
[736] R.A. Michelin, E. Pizzo, A. Scarso, P. Sgarbossa, G. Strukul, A. Tassan, Organometallics 24 (2005) 102.
[737] S. Kannan, A.J. James, P.R. Sharp, Inorg. Chim Acta 345 (2003) 8.
[738] B. Longato, G. Bandoli, A. Dolmella, Eur. J. Inorg. Chem. (2004) 1092;
(a) L.J. Ackerman, J.P. Sadighi, K.M. Kurtz, J.A. Labinger, J.E. Bercaw, Organometallics 22 (2003) 3884.
[739] K. Hara, M. Taguchi, A. Yagasaki, Polyhedron 20 (2001) 1903.
[740] G. Strukul, R. Ros, R.A. Michelin, Inorg. Chem. 21 (1982) 495.
[741] Y. Suzaki, K. Osakada, Organometallics 23 (2004) 5081.
[742] S. Wimmer, P. Castan, F.L. Wimmer, N.P. Johnson, J. Chem. Soc. Dalton Trans. (1989) 403.
[743] A.J.P. Alix, M. Manfait, O. Krug, T. Theophanides, Can. J. Chem. 60 (1982) 2222.
[744] M. Manfait, A.J.P. Alix, J.D. Zeches, T. Theophanides, Can. J. Chem. 60 (1982) 2216.
[745] M. Clikuma, R.J. Pollock, J. Magn. Reson. 47 (1982) 324.
[746] D.S. Giel, B. Rosenberg, J. Am. Chem. Soc. 104 (1982) 4598.
[747] B. Lippert, C.J.L. Lock, B. Rosenberg, M. Zvagulis, Inorg. Chem. 17 (1978) 2971.
[748] U. Anandhi, P.R. Sharp, Inorg. Chem. 43 (2004) 6780.
[749] S. Komeda, H. Ohishi, H. Yamane, M. Harikawa, K. Sakaguchi, M. Chikuma, J. Chem. Soc. Dalton Trans. (1999) 2959.
[750] S. Komeda, M. Lutz, A.L. Spek, M. Chikuma, J. Reedijk, Inorg. Chem. 39 (2000) 4230.
[751] S. Komeda, M. Lutz, A.L. Spek, Y. Yamanaka, T. Sato, M. Chikuma, J. Reedijk, J. Am. Chem. Soc. 124 (2002) 4738.
[752] S. Komeda, H. Yamane, M. Chikuma, J. Reedijk, Eur. J. Inorg. Chem. (2004) 4828.
[753] B. Longato, L. Pasquato, A. Mucci, L. Schenetti, E. Zangrando, Inorg. Chem. 42 (2003) 7861;
B. Longato, L. Pasquato, A. Mucci, L. Schenetti, Eur. J. Inorg. Chem. (2003) 128.
[754] M. Kubota, F.S. Rosenbert, M.J. Sailar, J. Am. Chem. Soc. 107 (1985) 4558.
[755] H. Kurosawa, T. Achiha, H. Kajimaru, I. Ikeda, Inorg. Chim. Acta 190 (1991) 271.
[756] K. Sakai, M. Takeshita, Y. Tanaka, T. Ue, M. Yangisawa, M. Kosaka, T. Tsubomura, M. Ato, T. Nakano, J. Am. Chem. Soc. 120 (1998) 11353.
[757] C.J.L. Lock, H.J. Peresie, B. Rosenberg, G. Turner, J. Am. Chem. Soc. 100 (1978) 3371.
[758] J.K. Barton, S.J. Lippard, Ann. N. Y. Acad. Sci. 313 (1978) 686.
[759] B. Lippert, D. Neugebauer, U. Schubert, Inorg. Chim. Acta 46 (1980) L11.
[760] R. Faggiani, C.J.L. Lock, R.J. Pollock, B. Rosenberg, G. Turner, Inorg. Chem. 20 (1981) 804.
[761] B. Lippert, Inorg. Chem. 20 (1981) 4326.
[762] R. Faggiani, B. Lippert, C.J.L. Lcok, R.A. Speranzini, J. Am. Chem. Soc. 103 (1981) 1111.
[763] J.P. Laurent, P. Lepage, P. Dahan, J. Am. Chem. Soc. 104 (1982) 7335.
[764] I. Kinoshita, Y. Yasuba, K. Matsamoto, S. Ooi, Inorg. Chim. Acta 80 (1983) 13.
[765] L.S. Hollis, S.J. Lippard, Inorg. Chem. 22 (1983) 2600.
[766] L.S. Hollis, S.J. Lippard, Inorg. Chem. 22 (1983) 2605.

[767] T.V. O'Halloran, S.J. Lippard, J. Am. Chem. Soc. 105 (1983) 3341.
[768] L.S. Hollis, S.J. Lippard, J. Am. Chem. Soc. 105 (1983) 3494.
[769] K. Matsumoto, Chem. Lett. (1984) 2061.
[770] K. Matsumoto, N. Matoba, Inorg. Chim. Acta 120 (1986) L1.
[771] T.V. O'Halloran, S.J. Lippard, Inorg. Chem. 28 (1989) 1289.
[772] T.G. Appleton, J.W. Conner, J.R. Hall, P.D. Prezler, Inorg. Chem. 28 (1989) 2030.
[773] K. Matsumoto, H. Miyamae, H. Moriyama, Inorg. Chem. 28 (1989) 2959.
[774] D. Min, R.D. Larsen, K. Emerson, E.H. Abbott, Inorg. Chem. 29 (1990) 73.
[775] M. Krumm, E. Zangrando, L. Randaccio, S. Menzer, B. Lippert, Inorg. Chem. 32 (1993) 700;
M. Krumm, I. Mutikainen, B. Lippert, Inorg. Chem. 30 (1991) 884.
[776] C. Mealli, F. Pichierri, L. Randaccio, E. Zangrando, M. Krumm, D. Holtenrich, B. Lippert, Inorg. Chem. 34 (1995) 3418.
[777] Y. Dehta, M. Kodaka, T. Okada, K. Okamoto, H. Okuno, Inorg. Chim. Acta 252 (1996) 5.
[778] H. Schoelhorn, U. Thewalt, B. Lippert, Inorg. Chim. Acta 93 (1984) 19.
[779] M. Kato, A. Mura, A. Toshikawa, S. Kishi, Y. Sugimoto, Angew Chem. Int. Ed. 41 (2002) 3183.
[780] M.J. Rauterkus, I. Puscasu, B. Kerbs, Inorg. Chim. Acta 339 (2002) 438.
[781] J.A.R. Navarro, M.A. Romero, J.M. Salas, M. Quiros, Inorg. Chem 36 (1997) 3277;
M.A. Haj, M. Quiros, J.M. Salas, J. Chem. Soc. Dalton Trans. (2002) 4740.
[782] J. Umakoshi, I. Kinoshita, Y. Yasuba, K. Matsumoto, S. Ooi, H. Nakai, H. Shiro, J. Chem. Soc. Dalton Trans. (1989) 815.
[783] B.C. Tzeng, W.F. Fu, C.M. Che, H.Y. Chao, K.K. Cheung, S.M. Peng, J. Chem. Soc. Dalton Trans. (1999) 1017.
[784] B. Oskui, W.S. Sheldrik, Eur. J. Inorg. Chem. (1999) 1325.
[785] K. Matsumoto, H. Moriyama, K. Suzuki, Inorg. Chem. 29 (1990) 2096.
[786] K.A. Mitchell, K.C. Streveler, C.M. Jensen, Inorg. Chem. 32 (1993) 2608.
[787] E.L.M. Lampers, K. Inagaki, J. Reedijk, Inorg. Chim. Acta 152 (1988) 201.
[788] K.S. Wyatt, K.N. Harrison, C.M. Jensen, Inorg. Chem. 31 (1992) 3867.
[789] E.L.M. Lempers, J. Reedijk, Inorg. Chem. 29 (1990) 217.
[790] K.R. Dixon, K.C. Moss, M.A.R. Smith, J. Chem. Soc. Dalton Trans. (1974) 971.
[791] M. Capdevila, P. Gonzalez-Duarte, C. Foces-Foces, F. Cano, M. Martinez-Ripoll, J. Chem. Soc. Dalton Trans. (1990) 143.
[792] M. Capdevila, W. Clegg, P. Gonzalez-Duarte, B. Harris, I. Mira, J. Sola, I.C. Taylor, J. Chem. Soc. Dalton Trans. (1992) 2817.
[793] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, J. Chem. Soc. Dalton Trans. (1993) 1509.
[794] A. Singhal, V.K. Jain, B. Varghese, E.R.T. Tiekink, Inorg. Chem. Acta 285 (1999) 190.
[795] J. Ruiz, J. Giner, V. Rodriguez, G. Lopez, J. Casabo, E. Molins, C. Miravitlles, Polyhedron 19 (2000) 1627.
[796] J. Fornies-Camer, A.M. Masdeu-Bulto, C. Claver, Inorg. Chem. Commun. 5 (2002) 351.
[797] J.J. Garcia, A. Arevalo, V. Montiel, F.D. Rio, B. Quiroz, H. Adams, P.M. Maitlis, Organometallics 16 (1997) 3216.
[798] M. Capdevila, W. Clegg, P. Gonzalez-Duarte, I. Mira, J. Chem. Soc. Dalton Trans. (1992) 173.
[799] R. Uson, M.A. Uson, S. Herrero, L. Rello, Inorg. Chem. 37 (1998) 4473.
[800] I. Murase, S. Ueno, S. Kida, Bull. Chem. Soc. Jpn. 56 (1983) 2748;
G.A. Lawrance, J. Chem. Soc. Dalton Trans. (1990) 2491.
[801] B. Kersting, Eur. J. Inorg. Chem. (1998) 1071.
[802] L. Calligaro, Polyhedron 3 (1984) 117.
[803] R. Ros, R.A. Michelin, T. Boschi, R. Roulet, Inorg. Chim. Acta 35 (1979) 43.
[804] R. Uson, J. Fornies, M.A. Uson, M.A. Orta, Inorg. Chim. Acta 89 (1984) 175.
[805] D. Afzal, P.G. Lenhert, C.M. Lukehart, J. Am. Chem. Soc. 106 (1984) 3050.
[806] D. Afzal, C.M. Lukehart, Organometallics 6 (1987) 546.
[807] E. Baralt, E.A. Boudreaux, J.N. Demas, P.G. Lenhert, C.M. Lukehart, A.T. McPhail, D.R. McPhail, J.B. Myers Jr., L.A. Sacksteder, W.R. True, Organometallics 8 (1989) 2417.
[808] E. Baralt, C.M. Lukehart, Inorg. Chem. 29 (1990) 2870.
[809] E. Baralt, C.M. Lukehart, Inorg. Chem. 30 (1991) 319.
[810] E. Baralt, C.M. Lukehart, A.T. McPhail, D.R. McPhail, Organometallics 10 (1991) 516.
[811] L. Sacksteder, E. Baralt, B.A. DeGraff, C.M. Lukehart, J.N. Demas, Inorg. Chem. 30 (1991) 3955.
[812] G. Minghetti, G. Benditelli, A.L. Bandini, J. Organomet. Chem. 139 (1977) C80.
[813] G. Bracher, D.M. Grove, L.M. Venanzi, F. Bachechi, P. Mura, L. Zambonelli, Angew. Chem. Int. Ed. Eng. 17 (1978) 778.
[814] T.H. Tulip, Y. Yamagata, T. Yoshida, R.D. Wilson, J.A. Ibers, S. Otsuka, Inorg. Chem. 18 (1979) 2239.
[815] D. Carmona, R. Thouvenot, L.M. Venanzi, F. Bachechi, L. Zambonelli, J. Organomet. Chem. 250 (1983) 589.
[816] D. Carmona, S. Chaloupka, J. Jans, R. Thouvenot, L.M. Venanzi, J. Organomet. Chem. 275 (1984) 303.
[817] P. Bergamini, S. Sostero, O. Traverso, L.M. Venanzi, Inorg. Chem. 29 (1990) 4376.
[818] F. Bachechi, Acta Cryst. C49 (1993) 460.
[819] F. Bachechi, P. Mura, L. Zambonelli, Acta Cryst. C49 (1993) 2072.
[820] D.J. Schwartz, R.A. Anderson, J. Am. Chem. Soc. 117 (1995) 4014.
[821] A. Albinati, S. Chaloupka, J. Eckert, L.M. Venanzi, M.K. Wolfer, Inorg. Chim. Acta 259 (1997) 305.
[822] D.M. Grove, G. van Koten, H.J.C. Ubbels, J. Am. Chem. Soc. 104 (1982) 4285.
[823] R.S. Paonessa, W.C. Trogler, J. Am. Chem. Soc. 104 (1982) 3529.
[824] R.S. Paonessa, W.C. Trogler, Inorg. Chem. 22 (1983) 1038.
[825] A.L. Bandini, G. Banditelli, G. Minghetti, J. Organomet. Chem. 595 (2000) 224.
[826] G. Brachor, D.M. Grove, P.S. Pregosin, L.M. Vensnzi, Angew. Int. Ed. Eng. 18 (1979) 155.
[827] F. Bachechi, G. Bracher, D.M. Grove, B. Kellenberger, P.S. Pregosin, L.M. Venanzi, L. Zambonelli, Inorg. Chem. 22 (1983) 1031.
[828] C.B. Knobler, H.D. Kaesz, G. Minghetti, A.L. Bandini, G. Banditeli, F. Bonati, Inorg. Chem. 22 (1983) 2324.
[829] D.L. Packett, A. Syed, W.C. Trogler, Organometallics 7 (1988) 159.
[830] D. Carmichael, P.B. Hitchock, J.F. Nixon, A. Pidcock, J. Chem. Soc. Chem. Commun. (1988) 1554.
[831] S. Aime, R. Gobetto, A.L. Bandini, G. Banditelli, G. Minghetti, Inorg. Chem. 30 (1991) 316.
[832] L. Mole, J.L. Spencer, S.A. Litster, A.D. Redhouse, N. Carr, A.G. Orpen, J. Chem. Soc. Dalton Trans. (1996) 2315.
[833] J. Jans, R. Naegeli, L.M. Venanzi, A. Albinati, J. Organomet. Chem. 247 (1983) C37.
[834] A.R. Siedle, R.A. Newmark, W.B. Gleason, J. Am. Chem. Soc. 108 (1986) 767.
[835] M.Y. Chiang, R. Bau, G. Minghetti, A.L. Bandini, G. Banditelli, T.F. Koetzle, Inorg. Chem. 23 (1984) 122.
[836] G. Minghetti, A.L. Bandini, G. Banditelli, F. Bonati, R. Szostak, C.E. Strouse, C.B. Knobler, H.D. Kaesz, Inorg. Chem. 22 (1983) 2332.

[837] M. Capdevila, P. Gonzalez-Duarte, I. Mira, J. Sola, W. Clegg, Polyhedron 11 (1992) 3091.
[838] A.L. Bandini, G. Banditelli, M. Manassero, A. Albinati, D. Cologneri, J. Eckert, Eur. J. Inorg. Chem. (2003) 3958.
[839] W. Clegg, M. Capdevila, P. Gonzalez-Duarte, J. Sola, Acta Cryst. B52 (1996) 270.
[840] N. Carr, B.J. Dunne, L. Mole, A.G. Orpen, J.L. Spencer, J. Chem. Soc. Dalton Trans. (1991) 863.
[841] C. Sorato, L.M. Venanzi, Inorg. Synth. 26 (1989) 134.
[842] H. Rimml, L.M. Venanzi, J. Organomet. Chem. 260 (1984) C52.
[843] A.W. Parkins, C.J. Richard, J.W. Steed, Inorg. Chim. Acta 358 (2005) 2827.
[844] V. Cittadini, P. Leoni, L. Marchetti, M. Pasquali, A. Albinati, Inorg. Chim. Acta 330 (2002) 25.
[845] C.M. Harris, S.E. Livingstone, N.C. Stephenson, J. Chem. Soc. (1958) 3697.
[846] D.M. Adams, P.J. Chandler, R.G. Churchill, J. Chem. Soc. (A) (1967) 1272.
[847] V.Yu. Kukushkin, A.I. Moiseev, Koord. Khim. 15 (1989) 419.
[848] V.Yu. Kukushkin, V.M. Tkachuk, I.A. Krol, Z.A. Starikova, B.V. Zhadanov, N.P. Kiseleva, Zh. Obsch. Khim. 61 (1991) 51.
[849] S. Bouquillon, A.Du.M. D'Hardemare, M.T. Averbuch-Pouchot, F. Henin, J. Muzart, Polyhedron 18 (1999) 3511.
[850] L.F. Olsson, Inorg. Chem. 25 (1986) 1697.
[851] P.M. Henry, O.W. Marks, Inorg. Chem. 10 (1971) 373.
[852] N.R. Davies, Aust. J. Chem. 17 (1964) 212.
[853] R.M. Alcock, F.R. Hartley, D.E. Rogers, J.L. Wagner, J. Chem. Soc. Dalton (1975) 2189.
[854] I.I. Volchenskova, Russ. J. Inorg. Chem. (Eng. Trans.) 19 (1974) 1540.
[855] S.S. Kurasov, N.N. Troyan, N.K. Eremenko, V.A. Miklvaitov, Izv. Sib. Old. Akad. Nauk, SSSR (1980) 31.
[856] C.D. Cowman, J.C. Thibeautt, R.F. Ziolo, H.B. Gray, J. Am. Chem. Soc. 98 (1976) 3209.
[857] D.S. Martin Jr., R.M. Rush, T.J. Peters, Inorg. Chem. 15 (1976) 669.
[858] C.M. Harris, S.E. Livingstone, I.H. Reece, J. Chem. Soc. (1959) 1505.
[859] P.L. Goggin, J. Mink, Inorg. Chim. Acta 26 (1978) 119.
[860] P. Day, M.J. Smith, R.J.P. Williams, J. Chem. Soc. (A) (1968) 668.
[861] S. Bouquillon, A.du.M. d'Hardemore, M.T.A. Pouchot, F. Henin, J. Muzart, Polyhedron 18 (1999) 3511.
[862] D.R. Russell, P.A. Tucker, C. Whittaker, Acta Cryst. 31B (1975) 2530;
N.C. Stephenson, Acta Cryst. 17 (1964) 587.
[863] R.B. Rogers, H. Isci, W.R. Mason, J. Cryst. Spectr. Res. 14 (1984) 383.
[864] V.C. Ginn, P.F. Kelly, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1992) 963.
[865] L.L. Nguyen, J. Kozelka, C. Bois, Inorg. Chim. Acta 190 (1992) 217.
[866] W. Beck, K. Feldl, E. Schuierer, Angew. Chem. Int. Ed. Eng. 4 (1965) 439.
[867] G.B. Karet, N.M. Kostic, Inorg. Chem. 37 (1998) 1021.
[868] I. Nakanishi, K. Matsumoto, S. Ooi, Acta Cryst. C47 (1991) 2073.
[869] R. Uson, J. Fornies, M.A. Uson, J.A. Apaolaza, Inorg. Chim. Acta 187 (1991) 175.
[870] G. Rivera, S. Bernes, C. Rodriguez de Barbarin, H. Torrens, Inorg. Chem. 40 (2001) 5575.
[871] M. Graziani, R. Ros, G. Carturan, J. Organomet. Chem. 27 (1971) 19.
[872] I.P. Lorenz, E. Lindner, W. Reuther, Z. Anorg. Allg. Chem. 414 (1975) 30.
[873] C.W. Dudley, C. Oldham, Inorg. Chim. Acta 3 (1969) 3.
[874] N. Nedelec, F.D. Rochon, Inorg. Chem. 40 (2001) 5236.
[875] Yu.N. Kukushkin, V.N. Demidov, J. Gen. Chem. USSR 53 (1983) 1286.
[876] P. Espinet, J.M. Martinez-Ilarduya, C. Perez-Briso, J. Organomet. Chem. 447 (1993) 145.
[877] J. Vicente, A. Arcas, M.V. Borrachero, M.B. Hurthouse, J. Chem. Soc. Dalton Trans. (1987) 1655.
[878] J. Vicente, A. Arcas, M.V. Borrachero, E. Molins, C. Miravitlles, J. Organomet. Chem. 359 (1989) 127.
[879] J. Vicente, A. Arcas, M.V. Borrachero, E. Molins, C. Miravitlles, J. Organomet. Chem. 441 (1992) 487.
[880] J. Vicente, J.A. Abad, P.G. Jones, Organometallics 11 (1992) 3512.
[881] R. Uson, J. Fornies, F. Martinez, M. Tomas, J. Chem. Soc. Dalton Trans. (1980) 888.
[882] R. Uson, J. Fornies, F. Martinez, M. Tomas, I. Reoyo, Organometallics 2 (1983) 1386.
[883] T.G. Appleton, R.D. Berry, J.R. Hall, D.W. Neale, J. Organomet. Chem. 364 (1989) 249.
[884] G. Lopez, J. Ruiz, C. Vicente, J.M. Marti, G. Garcia, P.A. Chaloner, P.B. Hitchcock, R.M. Harrison, Organometallics 11 (1992) 4090.
[885] R. Uson, J. Fornies, P. Espinet, F. Martinez, M. Tomas, J. Chem. Soc. Dalton (1981) 463.
[886] L.R. Falvello, J. Fornies, J. Gomez, E. Lalinde, A. Martin, F. Martinez, M.T. Moreno, J. Chem. Soc. Dalton Trans. (2001) 2132.
[887] J. Fornies, J. Gomez, E. Lalinde, M.T. Moreno, Chem. Eur. J. 10 (2004) 888.
[888] R. Uson, J. Fornies, M. Tomas, J.M. Casas, F.A. Cotton, L.R. Falvello, Inorg. Chem. 26 (1987) 3482.
[889] R. Uson, J. Fornies, M. Tomas, J.M. Casas, Angew. Chem. Int. Ed. Eng. 28 (1989) 748.
[890] R. Uson, J. Fornies, M. Tomas, I. Uson, Angew. Chem. Int. Ed. Eng. 29 (1990) 1449.
[891] R. Uson, J. Fornies, M. Tomas, B. Menjon, Organometallics 4 (1985) 1912.
[892] R. Uson, J. Fornies, M. Tomas, B. Menjon, Organometallics 5 (1986) 1581.
[893] J. Fornies, C. Fortuno, R. Navarro, F. Martinez, A.J. Welch, J. Organomet. Chem. 394 (1990) 643.
[894] E. Alonso, J.M. Casas, F.A. Cotton, X. Feng, J. Fornies, C. Fortuno, M. Tomas, Inorg. Chem. 38 (1999) 5034.
[895] N. Chaouche, J. Fornies, C. Fortuno, A. Kribii, A. Martin, P. Karipidis, A.C. Tsipis, C.A. Tsipis, Organometallics 23 (2004) 1797.
[896] E. Alonso, J. Fornies, C. Fortuno, A. Martin, G.M. Rosair, A.J. Welch, Inorg. Chem. 36 (1997) 4426.
[897] R. Uson, J. Fornies, L.R. Falvello, M. Tomas, I. Ara, I. Uson, Inorg. Chim. Acta 232 (1995) 35.
[898] J. Ruiz, F. Florenciano, M.A. Sanchez, G. Jopez, M.C.R. deArellano, J. Perez, Eur. J. Inorg. Chem. (2000) 943.
[899] J. Ruiz, F. Florenciano, V. Rodriguez, C. deHaro, G. Lopez, J. Perez, Eur. J. Inorg. Chem. (2002) 2736.
[900] R. de da Cruz, P. Espinet, A.M. Gallego, J.M. Martin-Alvarez, J.M. Martinez-Ilarduya, J. Organomet. Chem. 663 (2002) 108.
[901] J.M. Casas, L.R. Falvello, J. Fornies, G. Mansilla, A. Martin, Polyhedron 18 (1998) 403.
[902] G. Lopez, G. Garecia, J. Ruiz, G. Sanchez, J. Garcia, C. Vicente, J. Chem. Soc. Chem. Commun. (1989) 1045.
[903] G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J.M. Marti, J.A. Hermoso, A. Vegas, M. Martinez-Ripoll, J. Chem. Soc. Dalton Trans. (1992) 53.
[904] G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J. Casabo, E. Molins, C. Miravitlles, Inorg. Chem. 30 (1991) 2605.
[905] G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J.M. Marti, V. Rodriguez, J. Organomet. Chem. 436 (1992) 121.
[906] G. Lopez, G. Garcia, G. Sanchez, M.D. Santana, J. Ruiz, J. Garcia, Inorg. Chim. Acta 188 (1991) 195.

[907] J. Ruiz, C. Vicente, V. Rodriguez, G. Lopez, Polyhedron 17 (1998) 1503.
[908] G. Lopez, J. Ruiz, G. Garcia, J.M. Marti, G. Sanchez, J. Garcia, J. Organomet. Chem. 412 (1991) 435.
[909] G. Lopez, J. Ruiz, G. Garcia, C. Vicente, V. Rodriguez, G. Sanchez, J.A. Hormoso, M. Martinez-Ripoll, J. Chem. Soc. Dalton Trans. (1992) 1681.
[910] J. Ruiz, V. Rodriguez, G. Lopez, J. Casabo, E. Molins, C. Miravitlles, Organometallics 18 (1999) 1177.
[911] R. Uson, J. Fornies, M. Tomas, J.M. Casas, F.A. Cotton, L.R. Falvello, J. Am. Chem. Soc. 107 (1985) 2556.
[912] R. Uson, J. Fornies, M. Tomas, J.M. Casas, F.A. Cotton, L.R. Falvello, R. Llusar, Organometallics 7 (1988) 2279.
[913] R. Uson, J. Fornies, M. Tomas, J.M. Casas, R. Navarro, J. Chem. Soc. Dalton Trans. (1989) 169.
[914] R. Uson, J. Fornies, M. Tomas, J.M. Casas, C. Fortuno, Polyhedron 8 (1989) 2209.
[915] J.M. Casas, J. Fornies, F. Martinez, A.J. Rueda, M. Tomas, A.J. Welch, Inorg. Chem. 38 (1999) 1529.
[916] M.L.H. Green, P.L.I. Nagy, Adv. Organomet. Chem. 2 (1964) 325.
[917] P.W. Jolly, Angew Chem. Int. Ed. Eng. 24 (1985) 283.
[918] J. Schmidt, W. Hafner, Angew Chem. 71 (1959) 284.
[919] I.I. Moiseev, E.A. Fedorovskya, Ya.K. Syrkin, Russ. J. Inorg. Chem. 4 (1959) 1218.
[920] I.A. Zakharova, I.I. Moiseev, Izv. Akad. Nauk. SSSR (Eng. Trans.) (1964) 1826.
[921] W. Hafner, H. Prigge, J. Smidt, Justus Liebigs Annu, Chem. 693 (1966) 109.
[922] A. Bright, B.L. Shaw, G. Shaw, Am. Chem. Soc. Div. Petrol Chem. Prepr. 14 (1969) B81.
[923] R. Pietropaolo, P. Uguagliati, T. Boschi, B. Crociani, U. Belluco, J. Catal. 18 (1970) 358.
[924] T. Hosokawa, T. Tsuji, Y. Mizumoto, S.I. Murahashi, J. Organomet. Chem. 574 (1999) 99.
[925] R. Hüttel, M. Bechter, Angew. Chem. 71 (1959) 456.
[926] R. Hüttel, J. Kratzer, M. Bechter, Chem. Ber. 94 (1961) 766.
[927] W.T. Dent, R. Long, J.A. Wilkinson, J. Chem. Soc. (1964) 1585.
[928] R. Jira, J. Sedlmeier, Tetrahedron Lett. (1971) 1227.
[929] V.A. Golodov, E.O. Fischer, Zh. Obshch Khim. 42 (1972) 2685.
[930] J. Chatt, R.G. Guy, L.A. Duncauson, D.T. Thompson, J. Chem. Soc. (1963) 5170.
[931] J.K. Nicholson, J. Powell, B.L. Shaw, Chem. Commun. (1966) 174.
[932] G.A. Gray, W.R. Jackson, J.J. Rooney, J. Chem. Soc. (C) (1970) 1788.
[933] A.N. Nesmeyanov, A.Z. Rubezhov, L.I. Voronchikina, S.P. Gubin, Izv. Akad. Nauk. SSSR, Ser. Khim. (1972) 2538.
[934] Y. Tatsuno, T. Yashida, S. Otsuka, Inorg. Synth. 19 (1979) 220.
[935] J. Tsuji, N. Iwamoto, Chem. Commun. (1966) 828.
[936] M. Sakakibara, Y. Takahashi, S. Sakai, Y. Ishii, Chem. Commun. (1969) 396.
[937] J.H. Lukas, J.E. Blom, J. Organomet. Chem. 26 (1971) C25.
[938] F.R. Hartley, S.R. Jones, J. Organomet. Chem. 66 (1974) 465.
[939] H. Nishiyama, J. Organomet. Chem. 165 (1979) 407.
[940] K. Pannell, M.F. Lappert, K. Stanley, J. Organomet. Chem. 112 (1976) 37.
[941] P.A. van der Schaaf, J.P. Sutter, M. Grellier, G.P.M. van Mier, A.L. Spek, G. van Koten, M. Pfeffer, J. Am. Chem. Soc. 116 (1994) 5134.
[942] R.D. Rieke, A.V. Kavaliunas, L.D. Rhyne, D.J.J. Fraser, J. Am. Chem. Soc. 101 (1979) 246.
[943] A.N. Nesmanyanov, A.Z. Rubezhov, S.P. Gubin, N. Ivanov, L.J. Voronchikhina, Izv. Akad. Nauk. SSSR, Ser. Khim (1971) 235.
[944] W. Kitching, T. Sakakiyama, Z. Rappoport, P.D. Sleezer, S. Winstein, W.G. Young, J. Am. Chem. Soc. 94 (1972) 2329.
[945] A.N. Nesmeyanov, A.Z. Rubezhov, J. Organomet. Chem. 164 (1978) 259.
[946] P.P. Phadnis, V.K. Jain, A. Klein, T. Schurr, W. Kaim, New J. Chem. (2003) 1584.
[947] R.C. Larock, M.A. Mitchell, J. Am. Chem. Soc. 98 (1976) 6718.
[948] R.C. Larock, M.A. Mitchell, J. Am. Chem. Soc. 100 (1978) 180.
[949] E.O. Fischer, G. Burger, Z. Naturforsch B 16 (1961) 702.
[950] Y. Inoue, J. Yamashita, H. Hashimoto, Synthesis (1984) 244.
[951] T. Ukai, H. Kawazura, Y. Ishi, J.J. Bonnet, J.A. Ibers, J. Organomet. Chem. 65 (1974) 253.
[952] A. Sonoda, B.E. Mann, P.M. Maitlis, J. Organomet. Chem. 96 (1975) C16.
[953] A. Vitaglino, B. Akermark, S. Hansson, Organometallics 10 (1991) 2592.
[954] H. Kurosawa, H. Kajimaru, S. Ogoshi, H. Yoneda, K. Miki, N. Kasai, S. Murai, I. Ikeda, J. Am. Chem. Soc. 114 (1992) 8417.
[955] K. Tsutsumi, S. Ogoshi, S. Nishiguchi, H. Kurosawa, J. Am. Chem. Soc. 120 (1998) 1938.
[956] C. Jonasson, M. Kritikos, J.E. Backvall, K.J. Szabo, Chem. Eur. J. 6 (2000) 432.
[957] R. Hüttel, H. Christ, Chem. Ber. 96 (1963) 3101.
[958] R. Hüttel, H. Christ, Chem. Ber. 97 (1964) 1439.
[959] R. Hüttel, M. McNiff, Chem. Ber. 106 (1973) 1789.
[960] J. Tsuji, S. Imamura, J. Kiji, J. Am. Chem. Soc. 86 (1964) 4491.
[961] H.C. Volger, Am. Chem. Soc. Div. Petrol Chem. Prepr. 14 (1969) B72.
[962] A.D. Kettley, J. Braatz, Chem. Commun. (1968) 169.
[963] B.L. Shaw, G. Shaw, J. Chem. Soc. (A) (1969) 602.
[964] J. Tsuji, S. Imamura, Bull. Chem. Soc. Jpn. 40 (1967) 197.
[965] T. Susuki, J. Tsuji, Bull. Chem. Soc. Jpn. 46 (1973) 655.
[966] D. Morelli, R. Ugo, F. Conti, M. Donati, Chem. Commun. (1967) 801.
[967] D.R. Chrisope, P. Beak, J. Am. Chem. Soc. 108 (1986) 334.
[968] D.R. Chrisope, P. Beak, W.H. Saunders Jr., J. Am. Chem. Soc. 110 (1988) 230.
[969] G.W. Parshall, G. Wilkinson, Chem. Ind. (Lond.) (1962) 261.
[970] G.W. Parshall, G. Wilkinson, Inorg. Chem. 1 (1962) 896.
[971] B.E. Mann, B.L. Shaw, G. Shaw, J. Chem. Soc. (A) (1971) 3536.
[972] S. O'Brien, J. Chem. Soc. (A) (1970) 9.
[973] G. Raper, W.S. McDonald, J. Chem. Soc. Chem. Commun. (1970) 655.
[974] A. Kasahara, K. Tanaka, K. Asamiya, Bull. Chem. Soc. Jpn. 40 (1967) 351.
[975] R. Hüttel, H. Schmid, Chem. Ber. 101 (1968) 252.
[976] Y. Tezuka, T. Ogura, S. Kawaguchi, Bull. Chem. Soc. Jpn. 42 (1969) 443.
[977] S. Okeya, T. Ogura, S. Kawaguchi, Inorg. Nucl. Chem. Lett. 5 (1969) 713.
[978] I.T. Harrison, E. Kimura, E. Bohme, J.H. Fried, Tetrahedron Lett. (1969) 1589.
[979] K. Dunne, F.J. McQuillin, J. Chem. Soc. C (1970) 2196.
[980] S. Baba, T. Sobata, S. Kawaguchi, Inorg. Nucl. Chem. Lett. 8 (1972) 605.
[981] M. Mori, Y. Ban, Chem. Pharm. Bull. 24 (1976) 1992.
[982] T. Ohta, T. Hosokawa, S.I. Murahashi, K. Moki, N. Kasai, Organometallics 4 (1985) 2080.
[983] S. Ogoshi, W. Yoshida, K. Ohe, S. Murai, Organometallics 12 (1993) 578.
[984] R. Hüttel, H. Dietl, H. Christ, Chem. Ber. 97 (1964) 2037.
[985] R. Hüttel, H. Dietl, Chem. Ber. 98 (1965) 1753.
[986] B.M. Trost, P.E. Strege, Tetrahedron Lett. (1974) 2603.
[987] B.M. Trost, P.E. Strege, L. Weber, T.J. Fullerton, T.J. Dietsche, J. Am. Chem. Soc. 100 (1978) 3407.
[988] B.M. Trost, P.J. Metzner, J. Am. Chem. Soc. 102 (1980) 3572.
[989] R.W. Howsam, F.J. McQuillin, Tetrahedron Lett. (1968) 3667.
[990] D.J. Collins, W.R. Jackson, R.N. Timms, Aust. J. Chem. 33 (1980) 2663.

[991] C. Mahe, H. Patin, M.T. van Hulle, D.H.R. Barton, J. Chem. Soc. Perkin Trans. I (1981) 2504.
[992] A.A. Danopoulos, S.M. Paraskewas, Inorg. Chim. Acta 71 (1981) 259.
[993] P. Hütter, T. Butters, W. Winter, D. Handschuh, N. Voelter, Liebigs Ann. Chem. (1982) 1111.
[994] C.A. Horiuchi, T. Takayama, Y. Koike, M. Tanaka, J.Y. Satoh, Chem. Lett. (1989) 277.
[995] M. Donati, F. Conti, Inorg. Nucl. Chem. Lett. 2 (1966) 343.
[996] J. Lukas, S. Coren, J.E. Bolm, J. Chem. Soc. Chem. Commun. (1969) 1303.
[997] B.T. Heaton, D.J. McCaffrey, J. Organomet. Chem. 43 (1972) 437.
[998] J. Lukas, Inorg. Synth. 15 (1974) 75.
[999] I.I. Moiseev, A.P. Belov, Ya.K. Syrkin, Izv. Akad. Nauk SSSR (Eng. Trans.) (1963) 1395.
[1000] A.P. Belov, M.V. Vargaftik, I.I. Moiseev, Izv. Akad. Nauk. SSSR (Eng. Trans.) (1964) 1465.
[1001] A.P. Belov, G.Yu. Pek, I.I. Moiseev, Izv. Akad. Nauk. SSSR (Eng. Trans.) (1965) 2170.
[1002] I.I. Moiseev, A.P. Belov, G.Yu. Pek, Russ. J. Inorg. Chem. 10 (1965) 180.
[1003] R.G. Schultz, Tetrahedron Lett. (1964) 301.
[1004] R.G. Schultz, Tetrahedron 20 (1964) 2809.
[1005] M.S. Lupin, B.L. Shaw, Tetrahedron Lett. (1964) 833.
[1006] M.S. Lupin, J. Powell, B.L. Shaw, J. Chem. Soc. (A) (1966) 1687.
[1007] T. Okamoto, Chem. Commun. (1970) 1126.
[1008] T. Okamoto, Y. Sakakibara, S. Kunichika, Bull. Chem. Soc. Jpn. 43 (1970) 2658.
[1009] T. Okamoto, Bull. Chem. Soc. Jpn. 44 (1971) 1353.
[1010] B.L. Shaw, Chem. Industry (Lond.) (1962) 1190.
[1011] S.D. Robinson, B.L. Shaw, J. Chem. Soc. (1963) 4806.
[1012] J.M. Rowe, D.A. White, J. Chem. Soc. (A) (1967) 1451.
[1013] A. Kasahara, T. Izumi, Bull. Chem. Soc. Jpn. 41 (1968) 516.
[1014] O.G. Levanda, G.Y. Pek, I.I. Moiseev, Zh. Org. Khim. 7 (1971) 217.
[1015] S. Ogoshi, K. Ohe, N. Chatani, H. Kurosawa, S. Murai, Organometallics 10 (1991) 3813.
[1016] B.L. Shaw, N. Sheppard, Chem. Industry (Lond.) (1961) 517.
[1017] C. Agami, J. Levisalles, F. Rose-Munch, J. Organomet. Chem. 35 (1972) C59.
[1018] T. Hosokawa, Y. Imada, S.I. Murahashi, Tetrahedron Lett. 23 (1982) 3373.
[1019] S.S. Hall, B. Akermark, Organometallics 3 (1984) 1745.
[1020] S. Imaizumi, T. Matsuhisa, V. Senda, J. Organomet. Chem. 280 (1985) 441.
[1021] R. Criegee, F. Foerg, H.A. Brune, D. Schoenleber, Chem. Ber. 97 (1964) 3461.
[1022] P.M. Maitlis, M.L. Games, Can. J. Chem. 42 (1964) 183.
[1023] R. Hüttel, H.J. Neugebauer, Tetrahedron Lett. (1964) 3541.
[1024] P.M. Maittis, A. Efraty, M.L. Games, J. Am. Chem. Soc. 87 (1965) 719.
[1025] L.F. Dahl, W.E. Oberhansli, Inorg. Chem. 4 (1965) 629.
[1026] P.M. Maitlis, D.F. Pollock, M.L. Games, W.J. Pryde, Can. J. Chem. 43 (1965) 470.
[1027] R.F. Heck, J. Am. Chem. Soc. 90 (1968) 317.
[1028] R.F. Heck, J. Am. Chem. Soc. 90 (1968) 5542.
[1029] S.H. Taylor, P.M. Maitlis, J. Am. Chem. Soc. 100 (1978) 4700.
[1030] B. Akermark, J.E. Backvall, A. Lowenborg, K. Zetterberg, J. Organomet. Chem. 166 (1979) C33.
[1031] F.G. Stakem, R.F. Heck, J. Org. Chem. 45 (1980) 3584.
[1032] R.C. Larock, K. Takagi, Tetrahedron Lett. 24 (1983) 3457.
[1033] R.C. Larock, K. Takagi, J. Org. Chem. 49 (1984) 2701.
[1034] A.C. Albeniz, P. Espinet, C. Foces-Foces, F. Cano, Organometallics 9 (1990) 1079.
[1035] W.J. Irwin, F.J. McQuillin, Tetrahedron Lett. (1968) 1937.
[1036] A.D. Kettley, J.A. Braatz, J. Organomet. Chem. 9 (1967) P5.
[1037] A.D. Ketley, J.A. Braatz, Chem. Commun. (1968) 959.
[1038] R. Noyori, H. Takaya, Chem. Commun. (1969) 525.
[1039] R.P. Hughes, D.E. Hunton, K. Schumann, J. Organomet. Chem. 169 (1979) C37.
[1040] J.E. Backvall, E.E. Bjorkman, J. Chem. Soc. Chem. Commun. (1982) 693.
[1041] E.E. Bjorkman, J.E. Backvall, Acta Chem. Scand., Ser. A 37 (1983) 503.
[1042] D. Wilhelm, J.E. Backvall, R.E. Nordberg, T. Norin, Organometallics 4 (1985) 1296.
[1043] P. Mushak, M.A. Battiste, J. Organomet. Chem. 17 (1969) P46; R.A. Fiato, P. Mushak, M.A. Battiste, J. Chem. Soc. Chem. Commun. (1975) 869.
[1044] K. Nakasuji, M. Yamaguchi, I. Murata, K. Tatsumi, A. Natamura, Organometallics 3 (1984) 1257;
E. Samuel, M. Bigorgne, J. Organomet. Chem. 19 (1969) 9;
G.D. Enright, D. Zargarian, Organometallics 23 (2004) 1236.
[1045] S.D. Robinson, B.L. Shaw, J. Chem. Soc. (1964) 5002.
[1046] B.L. Hegarty, W. Kitching, J. Organomet. Chem. 6 (1966) 578.
[1047] F.R. Hartley, J. Organomet. Chem. 21 (1970) 227.
[1048] A.P. Klyagina, I.F. Golovaneva, E.P. Sizova, S.P. Gubin, Russ. J. Inorg. Chem. 45 (2000) 1379.
[1049] H. Kunkely, A. Vogler, Inorg. Chem. Acta 344 (2003) 262.
[1050] M.S. Lupin, J. Powell, B.L. Shaw, J. Chem. Soc. (A) (1966) 1410.
[1051] M.J. Grogan, K. Nakamoto, Inorg. Chim. Acta 1 (1967) 228.
[1052] J. Powell, B.L. Shaw, J. Chem. Soc. (A) (1967) 1839.
[1053] D.M. Adams, A. Squire, J. Chem. Soc. (A) (1970) 1808.
[1054] G.B. Petrov, L.M. Markovich, A.V. Ryabtser, A.P. Belov, Zh. Strukt. Khim 24 (1983) 113.
[1055] K.C. Ramey, G.L. Stalton, J. Am. Chem. Soc. 88 (1966) 4387.
[1056] C.W. Alexander, W.R. Jackson, R. Spratt, J. Am. Chem. Soc. 92 (1970) 4990.
[1057] S.D. Robinson, B.L. Shaw, J. Organomet. Chem. 3 (1965) 367; H.K. Cotton, R.C. Verboom, J. Johansson, B.J. Plietker, J.E. Backvall, Organometallics 21 (2002) 3367.
[1058] H.C. Dehm, J.C.W. Chien, J. Am. Chem. Soc. 82 (1960) 4429.
[1059] J. Powell, J. Am. Chem. Soc. 91 (1969) 4311.
[1060] K. Oda, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, Y. Tezuka, T. Ogura, S. Kawaguchi, Chem. Commun. (1968) 989.
[1061] K. Oda, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, Bull. Chem. Soc. Jpn. 43 (1970) 362.
[1062] V.F. Levdik, M.A. Porai-Koshits, Zh. Strukt. Khim. 3 (1962) 472; V.F. Levdik, M.A. Porai-Koshits, Chem. Abstr. 58 (1963) 7452e.
[1063] M. Rowe, Proc. Chem. Soc. (1962) 66.
[1064] M.R. Churchill, R. Mason, Nature 204 (1964) 777.
[1065] W.E. Oberhansli, L.F. Dahl, J. Organomet. Chem. 3 (1965) 43.
[1066] A.E. Smith, Acta Cryst. 18 (1965) 331.
[1067] M.K. Minaysan, S.P. Gubin, Y.T. Struhkov, Zh. Strukt. Khim. 8 (1967) 1108.
[1068] G.R. Davies, R.H.B. Mais, S. O'Brien, P.G. Owston, Chem. Commun. (1967) 1151.
[1069] R. Mason, A.G. Wheeler, Nature 217 (1968) 1253.
[1070] R. Mason, A.G. Wheeler, J. Chem. Soc. (A) (1968) 2549.
[1071] R. Mason, A.G. Wheeler, J. Chem. Soc. (A) (1968) 2543.
[1072] B.T. Kilbourn, R.H.B. Mais, P.G. Owston, Chem. Commun. (1968) 1438.
[1073] G. Raper, W.S. McDonald, J. Chem. Soc. Dalton Trans. (1972) 265.
[1074] J. Lukas, J.E.R. Bolm, T.G. Hewitt, J.J. DeBoer, J. Organomet. Chem. 46 (1972) 167.
[1075] N.C. Baenziger, C.V. Goebel, B.A. Foster, J.R. Doyle, Acta Crystallogr. B34 (1978) 1681.
[1076] P. Hendriks, K. Olie, K. Vrieze, Cryst. Struct. Commun. 4 (1975) 611.
[1077] S.J. Lippard, S.M. Morehouse, J. Am. Chem. Soc. 91 (1969) 2504.

[1078] A. Singhal, V.K. Jain, R. Mishra, B. Varghese, J. Mater. Chem. 19 (2000) 1121.
[1079] M. Zocchi, G. Tieghi, A. Albinati, J. Chem. Soc. Dalton Trans. (1973) 883.
[1080] M. Zocchi, G. Tieghi, A. Albinati, J. Organomet. Chem. 33 (1971) C47.
[1081] S. Candelero de Sanctis, N.V. Pavel, L. Toniolo, J. Organomet. Chem. 108 (1976) 409.
[1082] G.W. Henslee, J.D. Oliver, J. Cryst. Mol. Struct. 7 (1978) 137.
[1083] N.Yu. Kozitsyna, L.M. Dikareva, V.I. Andrianov, S.V. Zinchenko, V.A. Khutoryanskii, F.K. Shmidt, M.A. Porai-Koshits, I.I. Moiseev, Izv. Akad. Nauk. SSSR, Ser. Khim. (1988) 1894.
[1084] F.T. Edelmann, W. Ziegler, U. Behrens, J. Organomet. Chem. 426 (1992) 261.
[1085] R. Redon, R. Cramer, S. Bernes, D. Morales, H. Torrens, Polyhedron 20 (2001) 3119.
[1086] M.C. Torralba, M. Cano, S. Gomez, J.A. Campo, J.V. Heras, J. Perles, C. Ruiz-Valero, J. Organomet. Chem. 682 (2003) 26.
[1087] Z. Wang, C.D. Abernetty, A.H. Cowley, J.N. Jones, R.A. Jones, C.L.B. Macdonauld, L. Zhang, J. Organomet. Chem. 666 (2003) 35.
[1088] P. Corradini, G. Maglio, A. Musco, G. Pariro, Chem. Commun. (1966) 618.
[1089] F. DeCandia, G. Maglio, A. Musco, G. Paiaro, Inorg. Chim. Acta 2 (1968) 233.
[1090] P. Ganis, G. Maglio, A. Musco, A.L. Segre, Inorg. Chim. Acta 3 (1969) 266.
[1091] J.W. Faller, M.J. Incorvia, M.E. Thomsen, J. Am. Chem. Soc. 91 (1969) 518.
[1092] J.W. Faller, M.J. Incorvia, J. Organomet. Chem. 19 (1969) 13.
[1093] J.W. Faller, M.E. Thomsen, J. Am. Chem. Soc. 91 (1969) 6871.
[1094] T. Boschi, U. Belluco, L. Toniolo, R. Favez, R. Roulet, Inorg. Chim. Acta 23 (1979) 37.
[1095] G. Maglio, A. Musco, R. Palumbo, Inorg. Chim. Acta 4 (1970) 153.
[1096] A. Guerrero, F.A. Jalon, B.R. Manzano, A. Rodriguez, R.M. Claramunt, P. Cornago, V. Milata, J. Elguero, Eur. J. Inorg. Chem. (2004) 549.
[1097] J. Powell, S.D. Robinson, B.L. Shaw, Chem. Commun. (1965) 78.
[1098] J. Powell, B.L. Shaw, J. Chem. Soc. (A) (1968) 774.
[1099] C. Amatore, A. Jutand, M.A. M'Barki, G. Meyer, L. Mottier, Eur. J. Inorg. Chem. (2001) 873.
[1100] K. Vrieze, P. Cossee, A.P. Praat, C.W. Hilbers, J. Organomet. Chem. 11 (1968) 353.
[1101] K. Vrieze, A.P. Praat, P. Cossee, J. Organomet. Chem. 12 (1968) 533.
[1102] K.A. Holder, P. Powell, J. Organomet. Chem. 122 (1976) 275.
[1103] G.L. Statton, K.C. Ramey, J. Am. Chem. Soc. 88 (1966) 1327.
[1104] J.C.W. Chien, H.C. Dehn, Chem. Ind. (Lond.) (1961) 745.
[1105] L.A. Leites, V.T. Aleksanyen, S.S. Bukalov, A.Z. Rubezhov, Chem. Commun. (1971) 265.
[1106] E.A. Kelley, G.A. Wright, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1979) 178.
[1107] A.T. Teleshev, N.K. Kuznetsova, I.D. Rozhdestvenskaya, E.E. Nifant'ev, Zh. Obsch. Khim. 49 (1979) 752.
[1108] C. Facchin, R. Bertani, M. Calligaris, G. Nardin, M. Mari, J. Chem. Soc. Dalton Trans. (1987) 1381.
[1109] H. Berner, H.J. Kraus, Chem. Ber. 113 (1980) 1072.
[1110] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 93 (1971) 3089.
[1111] B.F.G. Johnson, J. Lewis, D.A. White, Synth. React. Inorg. Met. Org. Chem. 1 (1971) 235.
[1112] D.A. White, Inorg. Synth. 13 (1972) 55.
[1113] A.J. Deeming, I.P. Rothwell, Inorg. Chim. Acta 31 (1978) 271.
[1114] G.A. Kukina, V.S. Sergienko, Yu.L. Gaft, I.A. Zakharova, M.A. Poraikoshits, Inorg. Chim. Acta 45 (1980) L257.
[1115] I.A. Zakharova, Yu.L. Gaft, N.T. Kuznetsov, Ya.V. Salyn, L.A. Leites, A.P. Kurbakova, M.M. Kayansky, Inorg. Chim. Acta 47 (1981) 181.
[1116] B. Crociani, T. Boschi, P. Uguagliati, Inorg. Chim. Acta 48 (1981) 9.
[1117] L.S. Hegedus, B. Akermark, D.J. Olsen, O.P. Anderson, K. Zetterberg, J. Am. Chem. Soc. 104 (1982) 697.
[1118] R. Uson, J. Gimeno, L.A. Oro, J.M. Ilarduya, J.A. Cabeza, A. Tiripicchio, M.A. Camellini, J. Chem. Soc. Dalton Trans. (1983) 1729.
[1119] R. Ciajolo, M.A. Jama, A. Tuzi, A. Vitagliano, J. Organomet. Chem. 295 (1985) 233.
[1120] M. Bressan, A. Morvillo, J. Organomet. Chem. 304 (1986) 267.
[1121] H. Kurosawa, A. Tsuboi, Y. Kawasaki, M. Wada, Bull. Chem. Soc. Jpn. 60 (1987) 3563.
[1122] D.P. Grant, N.W. Murrall, A.J. Welch, J. Organomet. Chem. 333 (1987) 403.
[1123] B. Crociani, F. DiBianca, A. Giovenco, T. Boschi, Inorg. Chim. Acta 127 (1987) 169.
[1124] B. Akermark, B. Krakenberger, S. Hansson, A. Vitagliano, Organometallics 6 (1987) 620;
N.W. Murral, A.J. Welch, J. Organomet. Chem. 301 (1986) 109.
[1125] B. Akermark, S. Kansson, A. Vitagliano, J. Am. Chem. Soc. 112 (1990) 4587.
[1126] H. Ruegger, R.W. Kunz, C.A. Amman, P.S. Pregosin, Magn. Reson. Chem. 29 (1991) 197.
[1127] E. Cesarotti, M. Grassi, L. Prati, F. Demartin, J. Chem. Soc. Dalton Trans. (1991) 2073.
[1128] M. Sawmura, H. Nagata, H. Sakamoto, Y. Ito, J. Am. Chem. Soc. 114 (1992) 2586.
[1129] P.S. Pregosin, H. Rugger, R. Salzmann, A. Albinate, F. Lianza, R.W. Kunz, Organometallics 13 (1994) 83.
[1130] P.S. Pregosin, R. Salzmann, Magn. Reson. Chem. 32 (1994) 128.
[1131] T. Hayashi, H. Iwamura, M. Naito, Y. Matsumoto, Y. Uozumi, M. Miki, K. Yanagi, J. Am. Chem. Soc. 116 (1994) 775.
[1132] R.F. Galan, B.R. Manzano, A. Otero, M. Lanfranchi, M.A. Pellinghelli, Inorg. Chem. 33 (1994) 2309.
[1133] D.L. Tibbetts, T.L. Brown, J. Am. Chem. Soc. 91 (1969) 1108.
[1134] B.L. Shaw, G. Shaw, J. Chem. Soc. (A) (1971) 3533.
[1135] L. Bussetto, A. Palazzi, R. Ros, Inorg. Chim. Acta 13 (1979) 233.
[1136] W.S. McDonald, B.E. Mann, G. Raper, B.L. Shaw, G. Shaw, J. Chem. Soc. Chem. Commun. (1969) 1254.
[1137] P.T. Cheng, T.R. Jack, C.J. May, S.C. Nyburg, J. Powell, J. Chem. Soc. Chem. Commun. (1975) 369.
[1138] J. Powell, A.W.L. Chan, J. Organomet. Chem. 35 (1972) 203.
[1139] E. Ban, A. Chan, J. Powell, J. Organomet. Chem. 34 (1972) 405.
[1140] P.F. Swanton, G. Zannoni, R. Rampone, Spectrosc. Lett. 5 (1972) 307.
[1141] B.E. Reichert, B.O. West, J. Organomet. Chem. 36 (1972) C29.
[1142] B.G. Ragachev, A.S. Astakhova, O.S. Roschchutskina, M.L. Khidekel, Izv. Akad. Nauk. SSSR Ser. Khim (1972) 1855.
[1143] I.D. Rae, R.E. Reichert, B.O. West, J. Organomet. Chem. 81 (1974) 227.
[1144] M. Beller, T.H. Riermeir, W. Magerlein, T.E. Muller, W. Scherer, Polyhedron 17 (1998) 1165.
[1145] J. Ruiz, J.M. Marti, F. Florenciano, G. Lopez, Polyhedron 18 (1999) 2281.
[1146] P. Bhattacharya, A.M.Z. Slawin, M.B. Smith, J. Chem. Soc. Dalton Trans. (1998) 2467.
[1147] W.R. McClellan, H.H. Hoehn, A.N. Cripps, E.L. Muetterties, B.W. Howk, J. Am. Chem. Soc. 83 (1961) 1601.
[1148] R. Rienschneidler, E. Hoerner, F. Herzel, Monatsh. Chem. 92 (1961) 777.
[1149] A.C. Albeniz, P. Espinet, L.C. Cimas, B.M. Ruiz, Chem. Eur. J. 11 (2005) 242.
[1150] T. Jack, J. Powell, J. Organomet. Chem. 27 (1971) 133.

[1151] S.C. deSanctis, L. Toniolo, T. Boschi, G. Deganello, Inorg. Chim. Acta 12 (1975) 251.
[1152] T. Toniolo, T. Boschi, G. Deganello, J. Organomet. Chem. 93 (1975) 405.
[1153] P. Henriks, J. Kuyper, K. Vrieze, J. Organomet. Chem. 120 (1976) 285.
[1154] S. Trofimenko, Inorg. Chem. 10 (1971) 1372.
[1155] K. Ohkita, H. Kurosawa, T. Haregawa, T. Shirafuji, I. Ikeda, Inorg. Chim. Acta 198–200 (1992) 275.
[1156] C.P. Brock, M.K. Das, R.P. Minton, K. Niedenzu, J. Am. Chem. Soc. 110 (1988) 817.
[1157] W.C. Deese, D.A. Johnson, J. Organomet. Chem. 232 (1982) 325.
[1158] J. Ruiz, F. Florenciano, M.A. Sanchez, G. Lopez, M.C.R. deArellano, J. Perez, Eur. J. Inorg. Chem. (2000) 943.
[1159] P.M. Bailey, E.A. Kelley, P.M. Maitlis, J. Organomet. Chem. 144 (1978) C52.
[1160] A.N. Nesmeyanov, S.P. Gubin, A.Z. Rubezhov, J. Organomet. Chem. 16 (1969) 163.
[1161] T.J. Henly, S.R. Wilson, J.R. Shapley, Inorg. Chem. 27 (1988) 2551.
[1162] P. Braunstein, M. Knorr, H. Piana, U. Schubert, Organometallics 10 (1991) 828.
[1163] V.N. Kalinin, I.A. Cherepanov, S.K. Moiseev, A.S. Batsanov, Yu.T. Struchkov, Mandeleev Commun. (1991) 77.
[1164] D. Fenske, A. Hollnagel, K. Merzweiler, Z. Naturforsch. 43B (1988) 634.
[1165] W. Keim, R. Appel, A. Storeck, C. Krueger, R. Goddard, Angew. Chem. 93 (1981) 91.
[1166] B. Crociani, R. Bertani, T. Boschi, G. Bandoli, J. Chem. Soc. Dalton Trans. (1982) 1715.
[1167] L.S. Hegedus, in: M. Schlosser (Ed.), Palladium in Organic Synthesis in Organometallics in Synthesis, John Wiley & Sons Ltd., 1994.
[1168] D.J. Collins, W.R. Jackson, R.N. Timms, Tetrahedron Lett. (1976) 495.
[1169] D.J. Collins, W.R. Jackson, R.N. Timms, Aust. J. Chem. 30 (1977) 2167.
[1170] P.S. Manchand, H.S. Wong, J.F. Blount, J. Org. Chem. 43 (1978) 4769.
[1171] B.M. Trost, Acc. Chem. Res. 13 (1980) 385.
[1172] L.S. Hegedus, W.H. Darlington, C.E. Russell, J. Org. Chem. 45 (1980) 5193.
[1173] H. Christ, R. Hüttel, Angew. Chem. 75 (1963) 921.
[1174] R. Hüttel, P. Kochs, Chem. Ber. 101 (1968) 1043.
[1175] T.A. Schenach, F.F. Caserio, J. Organomet. Chem. 18 (1969) P17.
[1176] J. Tsuji, H. Takahashi, M. Morikawa, Tetrahedron Lett. (1965) 4387.
[1177] W.R. Jackson, J.U.G. Strauss, Tetrahedron Lett. (1975) 2591.
[1178] B. Akermark, K. Zetterberg, Tetrahedron Lett. (1975) 3733.
[1179] B.M. Trost, L. Weber, P.E. Strege, T.J. Fullerton, T.J. Dietsche, J. Am. Chem. Soc. 100 (1978) 3416.
[1180] B.M. Trost, L. Weber, P. Strege, T.J. Fullerton, T.J. Dietsche, J. Am. Chem. Soc. 100 (1978) 3426.
[1181] M. Grassi, S.V. Meille, A. Musco, R. Rontellim, A. Sironi, J. Chem. Soc. Dalton Trans. (1989) 615.
[1182] A. Musco, R. Pontellini, M. Grassi, A. Sironi, S.V. Meille, H. Rüegger, C. Ammann, P.S. Pregosin, Organometallics 7 (1988) 2130.
[1183] C. Ammann, P.S. Pregosin, H. Rüegger, M. Grassi, A. Musco, Magn. Reson. Chem. 27 (1989) 355.
[1184] M. Grassi, S.V. Meille, A. Musco, R. Pontellini, A. Sironi, J. Chem. Soc. Dalton Trans. (1990) 251.
[1185] H.C. Volger, K. Vrieze, J.W.F.M. Lemmers, A.P. Praat, P.W.N.M. van Leeuwen, Inorg. Chim. Acta 4 (1970) 435.
[1186] J. Tsuji, J. Kiji, M. Morikawa, Tetrahedron Lett. (1963) 1811.
[1187] J. Tsuji, J. Kiji, S. Hosaka, Tetrahedron Lett. (1964) 605.
[1188] R. Long, G.H. Whitfield, J. Chem. Soc. (1964) 1852.
[1189] J. Tsuji, T. Susuki, Tetrahedron Lett. (1965) 3027.
[1190] J. Tsuji, S. Hosaka, J. Am. Chem. Soc. 87 (1965) 4075.
[1191] T. Susuki, J. Tsuji, Bull. Chem. Soc. Jpn. 41 (1968) 1954.
[1192] J. Tsuji, J. Kiji, S. Mamura, M. Morikawa, J. Am. Chem. Soc. 86 (1964) 4350.
[1193] D. Milstein, Organometallics 1 (1982) 888.
[1194] Y. Takahashi, S. Sakai, Y. Ishii, J. Organomet. Chem. 16 (1969) 177.
[1195] J. Kiji, Y. Miura, J. Furukawa, J. Organomet. Chem. 140 (1977) 317.
[1196] A.M. Lazutkui, A.I. Lazutkina, V.M. Mastikhima, V.I. Prozorova, Zh. Obsch. Khim. 46 (1976) 2625.
[1197] T. Kajinoto, H. Takahashi, J. Tsuji, J. Organomet. Chem. 23 (1970) 275.
[1198] A.C. Albeniz, P. Espinet, B. Martin-Ruiz, Chem. Eur. J. (2001) 2481.
[1199] W.T. Dent, R. Long, G.H. Whitfield, J. Chem. Soc. (1964) 1588.
[1200] E.J. Smutny, J. Am. Chem. Soc. 89 (1967) 6793.
[1201] Y. Masuyama, Y. Nimura, Y. Kurusu, Tetrahedron Lett. (1991) 225;
J.P. Takahara, Y. Masuyama, Y. Kurusu, Chem. Lett. (1991) 879.
[1202] B.M. Trost, R.C. Bunt, J. Am. Chem. Soc. 116 (1994) 4089.
[1203] B.M. Trost, R.C. Bunt, Angew. Chem. Int. Ed. 35 (1996) 99.
[1204] E. Shirakawa, H. Yoshida, T. Kurahashi, Y. Nakao, T. Hiyama, J. Am. Chem. Soc. 120 (1998) 2975.
[1205] C. Jonasson, A. Horvath, J.E. Backvall, J. Am. Chem. Soc. 122 (2000) 9600.
[1206] K. Itami, T. Koike, J. Yoshida, J. Am. Chem. Soc. 123 (2001) 6957.
[1207] S.L. You, Y.G. Zhou, X.L. Hou, L.X. Dai, Chem. Commun. (1998) 2765.
[1208] E. Shirakawa, T. Kurahasi, H. Yoshida, T. Hiyama, Chem. Commun. (2000) 1895.
[1209] M. Feurstein, D. Laurenti, C. Bougeant, H. Doucet, M. Santelli, Chem. Commun. (2001) 325.
[1210] S. Dalili, A. Caiazzo, A.K. Yudin, J. Organomet. Chem. 689 (2004) 3604.
[1211] T. Tu, X.L. Hou, L.X. Dai, J. Organomet. Chem. 689 (2004) 3847.
[1212] R. Redon, H. Torrens, Z. Wang, D. Morales-Morales, J. Organomet. Chem. 654 (2002) 16.
[1213] S.M. Ali, S. Tanimoto, T. Okamoto, J. Org. Chem. 53 (1988) 3639.
[1214] F.R. Hartley, M.D. Higgs, J. Organomet. Chem. 44 (1972) 197.
[1215] D.N. Jones, S.D. Knox, J. Chem. Soc. Chem. Commun. (1975) 166.
[1216] D.N. Jones, S.D. Knox, J. Chem. Soc. Chem. Commun. (1975) 165.
[1217] G.A. Razuvaev, G.A. Domrachev, V.T. Bychkov, S.N. Titova, I.V. Lomakova, Izv. Akad. Nauk. SSSR Ser. Khim. (1976) 2120.
[1218] G.M. Bogdanov, A.P. Belov, Dokl. Akad. Nauk SSSR 232 (1977) 814.
[1219] M. Takahashi, H. Suzuki, Y. Morooka, T. Ikawa, Chem. Lett. (1979) 53.
[1220] G. Carturan, G. Strukul, J. Organomet. Chem. 157 (1978) 475.
[1221] A.P. Belov, I.I. Moiseev, N.G. Satsko, Y.K. Syrkin, Izv. Akad. Nauk. SSSR (1969) 2573.
[1222] A.N. Nesmeyanov, A.Z. Rubezhov, L.A. Leites, S.P. Gubin, J. Organomet. Chem. 12 (1968) 187.
[1223] S.J. Reid, N.T. Freeman, M.C. Baird, Chem. Commun. (2000) 1777.
[1224] L.M. Zaitsev, A.P. Belov, M.N. Vargaftik, I.I. Moiseev, Russ. J. Inorg. Chem. 12 (1967) 203.
[1225] G.B. Kazarinov, G.A. Domrachev, Zh. Obsch. Khim. 39 (1969) 2155.
[1226] S.J. Ashcroff, C.T. Mortimer, J. Chem. Soc. (A) (1971) 781.

[1227] G.A. Domrachev, K.G. Shal'nova, S.N. Titova, I.A. Teplova, Zh. Obsch. Khim. 45 (1975) 319.
[1228] J.P. Kleiman, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 1544.
[1229] A.C. Cope, R.W. Siekman, J. Am. Chem. Soc. 87 (1965) 3272.
[1230] G.W. Parshall, Acc. Chem. Res. 3 (1970) 139.
[1231] J. Dehand, M. Pfeffer, Coord. Chem. Rev. 18 (1976) 327.
[1232] M.I. Bruce, Angew Chem. Int. Ed. Engl. 16 (1977) 73.
[1233] H.P. Abicht, P. Issleib, Z. Chem. 17 (1977) 1.
[1234] I. Omae, Chem. Rev. 79 (1979) 287.
[1235] I. Omae, Coord. Chem. Rev. 28 (1979) 97.
[1236] I. Omae, Coord. Chem. Rev. 32 (1980) 235.
[1237] I. Omae, Coord. Chem. Rev. 42 (1982) 31.
[1238] I. Omae, Coord. Chem. Rev. 42 (1982) 245.
[1239] I. Omae, Angew. Chem. Int. Ed. Engl. 21 (1982) 889.
[1240] E.C. Constable, Polyhedron 3 (1984) 1037.
[1241] A.D. Ryabov, Synthesis (1985) 233.
[1242] G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kifer, Chem. Rev. 86 (1986) 451.
[1243] I. Omae, Coord. Chem. Rev. 83 (1988) 137.
[1244] D.W. Evans, G.R. Baker, G.R. Newkome, Coord. Chem. Rev. 93 (1989) 155.
[1245] A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[1246] S.B. Wild, Coord. Chem. Rev. 166 (1997) 291.
[1247] A.C. Cope, E.C. Friedrich, J. Am. Chem. Soc. 90 (1968) 909.
[1248] A.J. Deeming, I.P. Rothwell, J. Organometal. Chem. 205 (1981) 117.
[1249] A.D. Ryabov, I.K. Sakodinskaya, A.K. Yatsimirsky, J. Chem. Soc. Dalton Trans. (1985) 2629.
[1250] P.W. Clark, S.F. Dyke, J. Organomet. Chem. 276 (1984) 421.
[1251] P.W. Clark, S.F. Dyke, J. Organomet. Chem. 259 (1983) C17.
[1252] A.D. Ryabov, G.M. Kazankov, J. Organomet. Chem. 268 (1984) 85.
[1253] J. Granell, D. Sainz, J. Sales, X. Solans, M. Font-Altaba, J. Chem. Soc. Dalton Trans. (1986) 1785.
[1254] A.D. Ryabov, Inorg. Chem. 26 (1987) 1252.
[1255] R.M. Ceder, M. Gomez, J. Sales, J. Organomet. Chem. 361 (1989) 391.
[1256] A.D. Ryabov, A.V. Eliseev, E.S. Sergeyenko, A.V. Usatov, L.I. Zakharhin, V.N. Kalinin, Polyhedron 8 (1989) 1485.
[1257] J. Dupont, N. Beydoun, M. Pfeffer, J. Chem. Soc. Dalton Trans. (1989) 1715.
[1258] R.J. Cross, N.H. Tennent, J. Organomet. Chem. 72 (1974) 21.
[1259] E.C. Constable, A.M.W. Thompson, T.A. Leese, D.G.F. Reese, A.D. Tocher, Inorg. Chim. Acta 182 (1991) 93.
[1260] Y. Fuchita, K. Hiraki, T. Uchiyama, J. Chem. Soc. Dalton Trans. (1983) 897.
[1261] Y. Fuchita, K. Hiraki, Y. Matsumoto, J. Organomet. Chem. 280 (1985) C51.
[1262] N. Barr, S.F. Dyke, S.N. Quessy, J. Organomet. Chem. 253 (1983) 391.
[1263] R.A. Holton, J.R. Zoeller, J. Am. Chem. Soc. 107 (1985) 2124.
[1264] B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans. (1973) 404.
[1265] S. Chakladar, P. Paul, A.K. Mukherjee, S.K. Dutta, K.K. Nanda, D. Podder, K. Nag, J. Chem. Soc. Dalton Trans. (1992) 3119.
[1266] C. Mutet, M. Pfeffer, J. Organomet. Chem. 171 (1979) C34.
[1267] M. Pfeffer, E. Wehman, G. van Koten, J. Organomet. Chem. 282 (1985) 127.
[1268] J. Dehand, C. Mutet, M. Pfeffer, J. organomet. Chem. 209 (1981) 255.
[1269] J. Dupont, M. Pfeffer, M.A. Rotteveel, A. De Cian, J. Fischer, Organometallics 8 (1989) 1116.
[1270] K. Selvakumar, S. Vancheesan, Polyhedron 15 (1996) 2535.
[1271] A.J. Deeming, I.P. Rothwell, M.B. Hursthouse, L. New, J. Chem. Soc. Dalton Trans (1978) 1490.
[1272] P.W. Clark, H.J. Dyke, S.F. Dyke, G. Perry, J. Organomet. Chem. 253 (1983) 399.
[1273] A.D. Ryabov, V.A. Polyakov, K.A. Yatsimirsky, J. Chem. Soc. Perkin Trans II (1983) 1503.
[1274] A.D. Ryabov, V.A. Polyakov, K.A. Yatsimirsky, J. Chem. Soc. Perkin Trans. II (1983) 1511.
[1275] P.W. Clark, S.F. Dyke, J. Organomet. Chem. 281 (1985) 389.
[1276] T.C. Jones, A.J. Nielson, C.E. Rickard, Aust. J. Chem. 37 (1984) 2179.
[1277] N. Barr, S.F. Dyke, G. Smith, C.H.L. Kennard, V. McKee, J. Organomet. Chem. 288 (1985) 109.
[1278] B.J. Brisdon, P. Nair, S.F. Dyke, Tetrahedron 37 (1981) 173.
[1279] A.D. Ryabov, N.A. Polyakov, A.K. Yatsimisrsky, Inorg. Chim. Acta 91 (1984) 59.
[1280] M. Pfeffer, Inorg. Synth. 26 (1989) 211.
[1281] S. Affolter, P.S. Pregosin, J. Organomet. Chem. 298 (1990) 197.
[1282] N. Beydoun, M. Pfeffer, A. DeCian, J. Fischer, Organometallics 10 (1991) 3693.
[1283] E.I. Karpeiskaya, et al., Bull. Acad. Sci. USSR 33 (1984) 73; E.I. Karpeiskaya, et al., Izv. Akad. Nauk. SSSR, Ser. Khim. (1984) 85.
[1284] V.M. Titov, A.D. Ryabov, Russ. J. Inorg. Chem. 30 (1985) 1072.
[1285] J. Fournies, R. Navarro, V. Sicilia, F. Martinez, A.J. Welch, J. Organomet. Chem. 408 (1991) 425.
[1286] A.W. Kleij, R.J.M.K. Gebbink, P.A.J. van den Nieuwenhuijzen, H. Kooijman, M. Lutz, A.L. Spek, G. van Koten, Organometallics 20 (2001) 634.
[1287] J. Albert, J. Granell, R. Tavera, Polyhedron 22 (2003) 287.
[1288] Y. Fuchita, H. Tsuchiya, Polyhedron 12 (1993) 2079.
[1289] Y. Fuchita, H. Tsuchiya, A. Miyafuji, Inorg. Chim. Acta 233 (1995) 91.
[1290] Y. Fuchita, K. Yoshinaga, T. Hanaki, H. Kawano, J.K. Nagaoka, J. Organomet. Chem. 580 (1999) 273.
[1291] V.V. Dunina, L.G. Kuzmina, M.Yu. Kazakova, O.N. Gorunova, Y.K. Grishin, E.I. Kazakova, Eur. J. Inorg. Chem. (1999) 1029.
[1292] V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, J. Gen. Chem. USSR (Eng. Trans.) 54 (1984) 347.
[1293] V.V. Dunnia, O.A. Zalevskaya, J.P. Smolyakova, V.M. Potapov, J. Gen. Chem. USSR (Eng. Trans.) 56 (1986) 599.
[1294] L.G. Kuzmina, O.Yu. Burtseva, K.A. Porai-Koshits, V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, J. Gen. Chem. USSR (Eng. Trans.) 59 (1989) 2259.
[1295] V.V. Dunina, N.S. Gulyukina, E.B. Golovan, I.Yu. Nalimova, A.A. Koksharova, I.P. Beletskaya, Organomet. Chem. USSR (Eng. Trans.) 6 (1993) 36.
[1296] V.V. Dunina, J.S. Gulyukina, I.V. Byakova, Yu.F. Oprunenko, I.P. Beletskaya, Russ. J. Org. Chem. (Eng. Trans.) 30 (1994) 1497.
[1297] S.J. Tremont, H.U. Rahman, J. Am. Chem. Soc. 106 (1984) 5759.
[1298] T.J. Grinter, D. Leaver, R.M. O'Neil, Inorg. Nucl. Chem. Lett. 16 (1980) 145.
[1299] M. Nonoyama, Inorg. Chim. Acta 157 (1989) 9.
[1300] M. Nonoyama, K. Nonoyama, Polyhedron 10 (1991) 2265.
[1301] H. Mizuno, M. Kita, J. Fujita, M. Nonoyama, Inorg. Chim. Acta 202 (1992) 183.
[1302] H. Mizuno, M. Nonoyama, Polyhedron 9 (1990) 1287.
[1303] J. Barker, N.D. Cameron, M. Kilner, M.M. Mahmoud, S.C. Wallwork, J. Chem. Soc. Dalton Trans. (1991) 3435.
[1304] J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernandez, M. Thornton-Pett, J. Organomet. Chem. 401 (1991) 385.
[1305] R.L. Bennett, M.I. Bruce, B.L. Goodall, M.Z. Iqbal, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1972) 1787.
[1306] R. Bosque, J. Granell, J. Sales, M. Font-Bardia, X. Solans, J. Organomet. Chem. 453 (1993) 147.
[1307] A. Albert, M. Gomez, J. Granell, J. Sales, X. Solans, Organometallics 9 (1990) 1405.
[1308] J.M. Vila, M. Gayoso, M.T. Pereira, J.M. Ortigueira, A. Fernandez, N.A. Bailey, H. Adams, Polyhedron 12 (1993) 171.
[1309] P.S. Pregosin, R. Ruedi, J. Organomet. Chem. 273 (1984) 401.

[1310] A. Suarez, J.M. Vila, E. Gayoso, M. Gayoso, Rev. Port. Quim. 26 (1984) 21;
A. Suarez, J.M. Vila, E. Gayoso, M. Gayoso, Chem. Abst. 101 (1984) 72931f.
[1311] A. Suarez, J.M. Vila, M.T. Pereira, J. Filgueira, E. Gayoso, M. Gayoso, Acta Cient Cimpostelana 20 (1983) 45;
A. Suarez, J.M. Vila, M.T. Pereira, J. Filgueira, E. Gayoso, M. Gayoso, Chem. Abst. 103 (1985) 37585r.
[1312] A. Suarez, J.M. Vila, M.T. Pereira, J. Filgueira, E. Gayaso, M. Gayoso, Acta Cient Compostelana 20 (1983) 55;
A. Suarez, J.M. Vila, M.T. Pereira, J. Filgueira, E. Gayaso, M. Gayoso, Chem. Abst. 103 (1985) 71468q.
[1313] J. Albert, J. Granell, J. Sales, J. Organomet. Chem. 273 (1984) 393.
[1314] J. Albert, R.M. Ceder, M. Gomez, J. Granell, J. Sales, Organometallics 11 (1992) 1536.
[1315] H. Onoue, I. Moritani, J. Organomet. Chem. 43 (1972) 431.
[1316] D.P. Lydon, G.W.V. Cave, J.P. Rourke, J. Mater. Chem. 7 (1997) 403.
[1317] G.W.V. Cave, D.P. Lydon, J.P. Rourke, J. Organomet. Chem. 555 (1998) 81.
[1318] S. Murahashi, Y. Tamba, M. Yamamura, N. Yoshimura, J. Org. Chem. 43 (1978) 4099.
[1319] S. Tollari, S. Cenini, C. Tunice, G. Palmisano, Inorg. Chim. Acta 272 (1998) 18.
[1320] M.T. Pereira, J.M. Vila, A. Suarez, E. Gayoso, M. Gayoso, Gazz. Chim. Ital. 118 (1988) 783.
[1321] J.M. Villa, A. Suarez, M.T. Pereira, E. Gayoso, M. Gayoso, Synth. React. Inorg. Met. Org. Chem. 18 (1988) 47.
[1322] V.A. Dorokhov, K.L. Cherkasova, A.I. Lutsenko, Inz. Akad. Nauk. Ser. Khim. (1987) 2351.
[1323] J. Albert, J. Granell, J. Sales, X. Solans, M. Font-Altaba, Organometallics 5 (1986) 2567.
[1324] J. Albert, J. Granell, J. Sales, Polyhedron 8 (1989) 2725.
[1325] R.M. Ceder, J. Granell, J. Sales, J. Organomet. Chem. 307 (1986) C44.
[1326] M. Hugentobler, A.J. Klaus, H. Mettler, P. Rys, G. Wehrle, Helv. Chim. Acta 65 (1982) 1202.
[1327] M.C. Navarro-Ranninger, A.A. Valdes, M.J. Camazon, J. Roman, R. Lozana, J. Organomet. Chem. 331 (1987) 107.
[1328] J.L. Garcia-Ruano, I. Lopez-Solera, S.R. Masaguer, G.N. Ranninger, S.M. Carrera, Organometallics 11 (1992) 3013.
[1329] M.J. Barrera, P. Espinet, M.B. Ros, J.L. Serrano, Angew. Chem. Int. Ed. Engl. 30 (1991) 711.
[1330] S.F. Dyke, S.N. Quessy, Trans. Met. Chem. 7 (1982) 233.
[1331] R. Grigg, J. Delvin, J. Chem. Soc. Chem. Commun. (1986) 631.
[1332] J.M. Vila, J.M. Ortigueria, E. Gayoso, M. Gayoso, A. Castineiras, W. Hiller, J. Strähle, Inorg. Chim. Acta 179 (1991) 171.
[1333] J.M. Vila, M. Gayoso, M.T. Pereira, M. Lopez, G. Alonso, J.J. Fernandez, J. Organomet. Chem. 445 (1993) 287.
[1334] A. Fernandez, D.V. Garcia, J.J. Fernandez, M.L. Torres, A. Suarez, S.C. Juiz, J.M. Vila, Eur. J. Inorg. Chem. (2002) 2389.
[1335] M.L. Torres, A. Fernandez, J.J. Fernandez, A. Suarez, S.C. Juiz, M.T. Pereira, J.M. Vila, J. Organomet. Chem. 655 (2002) 127.
[1336] J.M. Vila, A. Suarez, M.T. Pereira, E. Gayoso, M. Gayoso, Polyhedron 6 (1987) 1003.
[1337] J.M. Vila, M.T. Pereira, E. Gayoso, M. Gayoso, Trans. Met. Chem. 311 (1986) 342.
[1338] B. Teijido, A. Fernandez, M. Lopez-Torres, S. Castro-Juiz, A. Suarez, J.M. Ortigueira, J.M. Vila, J.J. Fernandez, J. Organomet. Chem. 598 (2000) 71.
[1339] S. Castro-Juiz, M. Lopez-Torres, A. Ferandez, R. Mosteiro, A. Suarez, J.M. Vila, J.J. Fernandez, Polyhedron 20 (2001) 2925.
[1340] J. Albert, J. Granell, A. Luque, M. Font-Bardia, X. Solans, J. Organomet. Chem. 545 (1997) 131.
[1341] J. Albert, R. Bosque, J. Granell, R. Tavera, J. Organomet. Chem. 595 (2000) 54.
[1342] A.J. Deeming, J.P. Rothwell, M.B. Hursthouse, K.M. Abdul Malik, J. Chem. Soc. Dalton Trans. (1979) 1899.
[1343] A.J. Deeming, I.P. Rothwell, Pure Appl. Chem. 52 (1980) 649.
[1344] J. Albert, J. Granell, J. Sales, M. Font-Bardia, X. Solans, Organometallics 14 (1995) 1393.
[1345] J. Albert, R. Bosque, J. Granell, R. Tavera, Polyhedron 20 (2001) 3225.
[1346] J.M. Thompson, R.F. Heck, J. Org. Chem. 40 (1975) 2667.
[1347] P.W. Clark, S.F. Dyke, G. Smith, C.H.L. Kennard, J. Organomet. Chem. 330 (1987) 447.
[1348] S. Chakladar, P. Paul, K. Venkatasubramanian, K. Nag, J. Chem. Soc. Dalton Trans. (1991) 2669.
[1349] J. Barro, J. Granell, D. Sainz, J. Sales, M. Font-Bardia, X. Solans, J. Organomet. Chem. 456 (1993) 147.
[1350] J. Albert, J. Granell, R. Moragas, J. Sales, M. Font-Bardia, X. Solans, J. Organomet. Chem. 474 (1995) 95.
[1351] J. Albert, J. Granell, R. Moragas, M. Font-Bardia, X. Solans, J. Organomet. Chem. 522 (1996) 59.
[1352] K. Hiraki, S. Ibaraki, M. Onishi, Y. Ono, J.K. Kawashima, M. Ando, J. Organomet. Chem. 547 (1997) 199.
[1353] M. Gomez, J. Granell, M. Martinez, Eur. J. Inorg. Chem. (2000) 217.
[1354] G. Wu, A.L. Reingold, R.F. Heck, Organometallics 5 (1986) 1992.
[1355] G. Wu, S.J. Geib, A.L. Reingold, R.F. Heck, J. Org. Chem. 53 (1988) 3238.
[1356] J. Albert, J. Granell, J. Sales, X. Solans, J. Organomet. Chem. 379 (1989) 177.
[1357] J. Albert, J. Granell, D. Sainz, M. Font-Bardia, X. Solans, Tetrahedron Asymmetry 6 (1995) 325.
[1358] J. Albert, J. Granell, J. Minguez, G. Muller, D. Sainz, P. Valerga, Organometallics 16 (1997) 3561.
[1359] M. Gomez, J. Granell, M. Martinez, Organometallics 16 (1997) 2539.
[1360] M. Gomez, J. Granell, M. Martinez, J. Chem. Soc. Dalton Trans. (1998) 37.
[1361] G. Zhao, Q.G. Wang, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (1998) 1241.
[1362] A. Fernandez, D.V. Garcia, J.J. Fernandez, M.L. Torres, A. Suarez, R. Mosteiro, J.M. Vila, J. Organomet. Chem. 654 (2002) 162.
[1363] J. Albert, J.M. Cadena, A. Gonzalez, J. Granell, X. Solans, M. Font-Barida, J. Organomet. Chem. 663 (2002) 277.
[1364] J. Albert, J. Gravell, R. Tavera, J. Organomet. Chem. 667 (2003) 192.
[1365] C.L. Chen, Y.H. Liu, S.M. Peng, S.T. Liu, J. Organomet. Chem. 689 (2004) 1806.
[1366] A. Crispini, G. DeMunno, M. Ghedini, F. Neve, J. Organomet. Chem. 427 (1992) 409.
[1367] C. Navarro-Ranninger, I. Lopez-Solera, A. Alvarez-Valdes, J.H. Rodriguez-Ramos, J.R. Masaguer, J.L. Garcia, X. Solans-Ruano, Organometallics 12 (1993) 4104.
[1368] K. Praefcke, B. Bilgin, J. Pickardt, M. Borowski, Chem. Ber. 127 (1994) 1543.
[1369] K. Praefcke, B. Bilgin, J. Pickardt, M. Borowski, J. Organomet. Chem. 592 (1999) 155.
[1370] K.K. Nanda, K. Nag, K. Venkatsubramanian, P. Paul, Inorg. Chim. Acta 196 (1992) 195.
[1371] J.M. Vila, M. Gayoso, M.T. Pereira, M.C. Rodriguez, J.M. Ortigueira, M. Thornton-Pett, J. Organomet. Chem. 426 (1992) 267.
[1372] J.L. Casas, E. Gayoso, J.M. Vila, M.T. Pereira, M. Gayoso, Synth. React. Inorg. Met. Org. Chem. 21 (1991) 263.
[1373] J. Granell, J. Sales, J. Vilarrasa, Trans. Met. Chem. 9 (1984) 203.
[1374] P. Espinet, J. Perez, M. Marcos, M.B. Ros, J.L. Serrano, J. Barbera, A.M. Levelut, Organaometallics 9 (1990) 2028.
[1375] D.P. Lydon, J.P. Rourke, Chem. Commun. (1997) 1741.

[1376] M. Crespo, C. Grande, A. Klein, J. Chem. Soc. Dalton Trans. (1999) 1629.
[1377] A. Fernandez, J.J. Fernandez, M.L. Torres, A. Suarez, J.M. Ortigueira, J.M. Vila, H. Adams, J. Organomet. Chem. 612 (2000) 85.
[1378] A. Kasahara, Bull. Chem. Soc. Jpn. 41 (1968) 1272.
[1379] A.L. Balch, D. Petridis, Inorg. Chem. 8 (1969) 2247.
[1380] G.E. Hartwell, R.V. Lawrence, M.J. Smas, J. Chem. Soc. Chem. Commun. (1970) 912.
[1381] M.I. Bruce, B.L. Goodall, G.L. Sheppard, F.G.A. Stone, J. Chem. Soc. Dalton (1975) 591.
[1382] M. Ghedini, D. Ricci, G. DeMunno, D. Viterbo, F. Neve, S. Armentano, Chem. Mater. 3 (1991) 65.
[1383] K. Gehrig, M. Hugentobler, A.J. Klaus, P. Rys, Inorg. Chem. 21 (1982) 2493.
[1384] K. Gehrig, A.J. Klaus, P. Rys, Helv. Chim. Acta 66 (1983) 2603.
[1385] M. Hugentobler, A.J. Klaus, P. Ruppen, P. Rys, Helv. Chem. Acta 67 (1984) 113.
[1386] M. Ghedini, S. Morrone, U. Caruso, A. Roviello, Inorg. Chim. Acta 292 (1999) 163.
[1387] H. Takahashi, J. Tsuji, J. Organomet. Chem. 10 (1967) 51.
[1388] M. Ghedini, S. Licoccia, S. Armentano, R. Bartolino, Mol. Cryst. Liq. Cryst. 108 (1984) 269.
[1389] Y. Wakatsuki, H. Yamazaki, P.A. Grutsch, M. Santhanam, C. Kutal, J. Am. Chem. Soc. 107 (1985) 8153.
[1390] M. Ghedini, S. Armentano, F. Neve, S. Licoccia, J. Chem. Soc. Dalton Trans (1988) 1565.
[1391] M. Ghedini, D. Pucci, E. Cesarotti, P. Antogniazza, O. Francescangeli, R. Bartolino, Chem. Mater. 5 (1993) 883.
[1392] M. Ghedini, D. Pucci, A. Crispini, G. Barberio, Organometallics 18 (1999) 2116.
[1393] J. Granell, J. Sales, J. Vilarrasa, J.P. Declercaq, G. Germain, C. Miravitlles, X. Solans, J. Chem. Soc. Dalton Trans. (1983) 2441.
[1394] R.M. Ceder, J. Sales, J. Organomet. Chem. 276 (1984) C31.
[1395] P. Espinet, E. Lalinde, M. Marcos, J. Perez, J.L. Serrano, Organometallics 9 (1990) 555.
[1396] P. Braunstein, J. Dehand, M. Pfeffer, Inorg. Nucl. Chem. Lett. 10 (1974) 521.
[1397] P. Braunstein, J. Dehand, M. Pfeffer, Inorg. Nucl. Chem. Lett. 10 (1974) 581.
[1398] J. Dehand, M. Pfeffer, M. Zinsius, Inorg. Chim. Acta 13 (1975) 229.
[1399] M. Nonoyama, Trans. Met. Chem. 8 (1983) 121.
[1400] P. Espinet, G. Garcia, F.J. Herrero, Y. Jeannin, M. Philoche-Levisalleo, Inorg. Chem. 28 (1989) 4207.
[1401] J. Granell, R. Moragas, J. Sales, M. Font-Bardia, X. Solans, J. Organomet. Chem. 431 (1992) 359.
[1402] J.M. Vila, M.L. Torres, A. Fernandez, M.T. Pereira, J.M. Ortigueira, J.J. Fernandez, Inorg. Chim. Acta. 342 (2003) 185.
[1403] B. Galli, F. Gasparrini, L. Maresca, G. Natile, G. Palmieri, J. Chem. Soc. Dalton Trans. (1983) 1483.
[1404] B. Galli, F. Gasparrini, B.E. Mann, L. Marsca, G. Natile, A.M. Manotti-Lanfredi, A. Tiripicchio, J. Chem. Soc. Dalton Trans. (1985) 1155.
[1405] B.A. Grigor, A.J. Nielson, J. Organomet. Chem. 132 (1977) 439.
[1406] A.G. Constable, W.S. McDonald, L.C. Sawkins, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1978) 1061.
[1407] B.L. Shaw, I. Shepherd, J. Chem. Soc. Dalton Trans. (1979) 1634.
[1408] A.G. Constable, W.S. McDonald, L.C. Sawkins, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1980) 1992.
[1409] J.E. Baldwin, C. Najera, M. Yus, J. Chem. Soc. Chem. Commun. (1985) 126.
[1410] V. Rocherolle, J.C. Lopez, A. Olesker, G. Lukacs, J. Chem. Soc. Chem. Commun. (1988) 513.
[1411] A.P. Wells, W. Kitching, Organometallics 11 (1992) 2750.
[1412] H. Onoue, K. Minami, N. Nakagawa, Bull. Chem. Soc. Jpn. 43 (1970) 3480.
[1413] I.G. Phillips, P.J. Steel, J. Organomet. Chem. 410 (1991) 247.
[1414] A.D. Ryabov, G.M. Kazankov, A.K. Yatsimirsky, L.G. Kujmina, O.Y. Burtseva, N.V. Dvortsova, V.A. Polyakov, Inorg. Chem. 31 (1992) 3083;
E.Y. Bezsoudnova, A.D. Ryabov, J. Organomet. Chem. 622 (2001) 38.
[1415] M.A. Gutierrez, G.R. Newkome, J. Selbin, J. Organomet. Chem. 202 (1980) 341.
[1416] J. Selbin, M.A. Gutierrez, J. Organomet. Chem. 214 (1981) 253.
[1417] P.J. Steel, G.B. Caygill, J. Organomet. Chem. 327 (1987) 101.
[1418] C.A. Craig, R.J. Walts, Inorg. Chem. 28 (1989) 309.
[1419] I. Aiello, A. Crispini, M. Ghedini, M.L. Deda, F. Barigellitti, Inorg. Chem. Acta 308 (2000) 121.
[1420] K. Hiraki, Y. Fuchita, K. Takechi, Inorg. Chem. 20 (1981) 4316.
[1421] M. Nonoyama, S. Kajita, Trans. Met. Chem. 6 (1981) 163.
[1422] M. Nonoyama, Trans. Met. Chem. 7 (1982) 281.
[1423] Y. Fuchita, K. Hiraki, Y. Kage, Bull. Chem. Soc. Jpn. 55 (1982) 955.
[1424] J. Selbin, K. Abboud, S.F. Walkins, M.A. Gutierrez, F.R. Fronczek, J. Organomet. Chem. 241 (1983) 259.
[1425] M. Nonoyama, J. Organomet. Chem. 262 (1984) 407.
[1426] A.J. Canty, N.J. Minchin, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1986) 2205.
[1427] F. Maassarani, M. Pfeffer, G.L. Borgne, Organometallics 9 (1990) 3003.
[1428] E.C. Constable, L.R. Sausa, J. Organomet. Chem. 427 (1992) 125.
[1429] K. Hiraki, M. Nakashima, T. Uchiyama, Y. Fuchita, J. Organomet. Chem. 428 (1992) 249.
[1430] A.J. Deeming, I.R. Rothwell, J. Chem. Soc. Chem. Commun. (1978) 344.
[1431] M. Pfeffer, D. Grandjean, G.Le. Borgne, Inorg. Chem. 20 (1981) 4426.
[1432] J. Selbin, M.A. Gutierrez, J. Organomet. Chem. 246 (1983) 95.
[1433] G.W.V. Cave, F.P. Fanizzi, R.J. Deeth, W. Errington, J.P. Rourke, Organometallics 19 (2000) 1355.
[1434] E.C. Constable, J. Chem. Soc. Dalton Trans. (1985) 1719.
[1435] A.C. Skapski, V.F. Sutcliffe, G.B. Young, J. Chem. Soc. Chem. Commun. (1985) 609.
[1436] S. Trofimenko, Inorg. Chem. 12 (1973) 1215.
[1437] M.I. Bruce, B.L. Goodall, I. Matsuda, Aust. J. Chem. 28 (1975) 1259.
[1438] M. Nonoyama, H. Takayangi, Trans. Met. Chem. 1 (1976) 10.
[1439] M. Nonoyama, J. Organomet. Chem. 229 (1982) 287.
[1440] A.A. Watson, D.A. House, P.J. Steel, J. Organomet. Chem. 311 (1986) 387.
[1441] G.B. Caygill, P.J. Steel, J. Organomet. Chem. 327 (1987) 115.
[1442] M.T. Alonso, O. Juanes, J. deMendoza, J.C. Rodriguez-Ubis, J. Organomet. Chem. 430 (1992) 349.
[1443] M.E.K. Cartoon, G.W.H. Cheeseman, J. Organomet. Chem. 234 (1982) 123.
[1444] D.L. Peterson, K.J. Keuseman, N.A. Kataeva, L.G. Kuzimina, J.A.K. Howard, V.V. Dunina, I.P. Smoliakova, J. Organomet. Chem. 654 (2002) 66.
[1445] M. Kim, Q. Liu, F.P. Gabbai, Organometallics 23 (2004) 5560.
[1446] A. Saurez, J.M. Vila, M.T. Pereira, E. Gayoso, M. Gayoso, Synth. React. Inorg. Met. Org. Chem. 20 (1990) 1425.
[1447] M.R. Churchill, H.J. Wasserman, G.J. Young, Inorg. Chem. 19 (1980) 762.
[1448] K. Hiraki, Y. Fuchita, M. Nakashima, H. Hiraki, Bull. Chem. Soc. Jpn. 59 (1986) 3073.
[1449] K. Hiraki, Y. Fuchita, S. Takahura, J. Organomet. Chem. 210 (1981) 273.
[1450] J.A.C. Allison, H.S. Elkhadem, A.C. Wilson, J. Heterocyclic Chem. 12 (1975) 1275.
[1451] M. Nonoyama, C. Hayata, Trans. Met. Chem. 3 (1978) 366.
[1452] M. Ghedini, D. Pucci, J. Organomet. Chem. 395 (1990) 105.

[1453] D.J. de Geest, B.J. O'Keefe, P.J. Steel, J. Organomet. Chem. 579 (1999) 97.
[1454] B.J. O'Keefe, P.J. Steel, Inorg. Chem. Commun. 2 (1999) 10.
[1455] G.R. Newkome, K.J. Theriot, B.K. Cheskin, D.W. Evans, G.R. Baker, Organometallics 9 (1990) 1375.
[1456] K. Hiraki, Y. Fuchita, H. Nakaya, S. Takahura, Bull. Chem. Soc. Jpn. 52 (1979) 2531.
[1457] M. Nonoyama, Trans. Met. Chem. 12 (1984) 1.
[1458] A. Suarez, J.M. Villa, E. Gayoso, M. Gayoso, W. Hiller, A. Castineiras, J. Strahle, Z. Anorg. Allg. Chem. 535 (1986) 213.
[1459] G.B. Caygill, R.M. Hartshorn, P.J. Steel, J. Organomet. Chem. 382 (1990) 455.
[1460] D.J. de Geest, P.J. Steel, Inorg. Chem. Commun. 1 (1998) 358.
[1461] S.W. Lai, M.C.W. Chan, K.K. Cheung, S.M. Peng, C.M. Che, Organometallics 18 (1999) 3991.
[1462] B. Neumann, T. Hegmann, R. Wolf, C. Tschierske, Chem. Commun. (1998) 105.
[1463] M. Lousame, A. Fernandez, M.L. Torres, D.V. Garcia, J.M. Vila, A. Suarez, J.M. Ortigueira, J.J. Fernandez, Eur. J. Inorg. Chem. (2000) 2055.
[1464] A. Zucca, A. Doppiu, M.A. Cinellu, S. Stoccoro, G. Minghetti, M. Manassero, Organometallics 21 (2002) 783;
A. Zucca, M.A. Cinellu, G. Minghetti, S. Stoccoro, M. Manassero, Eur. J. Inorg. Chem. (2004) 4484.
[1465] G. Carvotto, F. Demartin, G. Palmisano, A. Penoni, T. Radice, S. Tollari, J. Organomet. Chem. 690 (2005) 2017.
[1466] J.W. Slater, D.P. Lydon, N.W. Alcock, J.P. Rourke, Organometallics 20 (2001) 4418.
[1467] J.W. Slater, D.P. Lydon, J.P. Rourke, J. Organomet. Chem. 645 (2002) 246.
[1468] J.W. Slater, J.P. Rourke, J. Organomet. Chem. 688 (2003) 112;
M.L. Torres, P. Juanatey, J.J. Fernandez, A. Fernandez, A. Suarz, R. Mosteiro, J.M. Ortigueira, J.M. Vila, Organometallics 21 (2002) 3628.
[1469] B.J. O'Keefe, P.J. Steel, Organometallics 17 (1998) 3621.
[1470] H. Alper, J. Organomet. Chem. 80 (1974) C29.
[1471] J.C. Gaunt, B.L. Shaw, J. Organomet. Chem. 102 (1975) 511.
[1472] A. Kasahara, T. Izumi, M. Maemura, Bull. Chem. Soc. Jap. 50 (1977) 1878.
[1473] L.L. Troitskaya, V.I. Sokolov, O.A. Reutov, Dokl. Akad. Nauk. SSSR 236 (1977) 371;
L.L. Troitskaya, V.I. Sokolov, O.A. Reutov, Chem. Abst. 88 (1978) 7023.
[1474] S. Kamiyama, T. Kimura, A. Kasahara, T. Izumi, M. Maemura, Bull. Chem. Soc. Jap. 52 (1979) 142.
[1475] A. Kasahara, I. Izumi, H. Watabe, Bull. Chem. Soc. Jap. 52 (1979) 957.
[1476] V.I. Sokolov, L.L. Troitskaya, O.A. Reutov, J. Organomt. Chem. 182 (1979) 537.
[1477] T. Komatsa, M. Nonoyama, J. Fujita, Bull. Chem. Soc. Jap 54 (1981) 186.
[1478] V.I. Sokolov, B.S. Khruscheva, L.L. Troitskaya, O.A. Reutov, Dokal. Chem. 274 (1984) 15.
[1479] A. Albinati, P.S. Pregosin, R. Rüedi, Helv. Chim. Acta 68 (1985) 2046.
[1480] J.C. Kotz, E.E. Getty, L. Lin, Organometallics 4 (1985) 610.
[1481] M. Benito, C. Lopez, X. Morvan, Polyhedron 18 (1999) 2583.
[1482] P.R.R. Bandarage, N.W. Duffy, S.M. Hohnston, B.H. Robinson, J. Simpson, Organometallics 13 (1994) 511.
[1483] G. Zhao, Q.G. Wang, T.C.W. Mak, Polyhedron 18 (1998) 577.
[1484] Y.J. Wu, X.L. Cui, C.X. Du, W.L. Wang, R.Y. Guo, R.F. Chen, J. Chem. Soc. Dalton Trans. (1998) 3727.
[1485] G. Zhao, Q.G. Wang, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (1998) 3785.
[1486] G. Zhao, Q.C. Yang, T.C.W. Mak, Organometallics 18 (1999) 3623.
[1487] V.V. Dunina, O.N. Gorunova, M.V. Livantsov, Y.K. Grishin, L.G. Kuzmina, N.A. Kataeva, A.K. Churakov, Inorg. Chem Commun. 3 (2000) 354.
[1488] F.X. Roca, C.J. Richards, Chem. Commun. (2003) 3002.
[1489] F.X. Roca, M. Motevalli, C.J. Richards, J. Am. Chem. Soc. 127 (2005) 2388.
[1490] A.J. Cheney, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1972) 860.
[1491] D.F. Gill, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1972) 65.
[1492] A.J. Cheney, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1972) 754.
[1493] D.G. Gill, B.E. Mann, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1973) 270.
[1494] G.J. Gainsford, R. Mason, J. Organomet. Chem. 80 (1974) 395.
[1495] B.L. Shaw, M.M. Truelock, J. Organomet. Chem. 102 (1975) 517.
[1496] R. Mason, M. Textor, J. Chem. Soc. Chem. Commun. (1976) 292.
[1497] R.G. Goel, R.G. Montemayor, Inorg. Chem. 16 (1977) 2183.
[1498] H.C. Clark, A.B. Goel, R.G. Goel, S. Goel, W. Ogini, Inorg. Chim. Acta 31 (1978) L441.
[1499] H.C. Clark, A.B. Goel, R.G. Goel, W.O. Ogini, J. Organomet. Chem. 157 (1978) C16.
[1500] H.C. Clark, A.B. Goel, S. Goel, Inorg. Chem. 18 (1979) 2803.
[1501] H.C. Clark, A.B. Goel, S. Goel, J. Organomet. Chem. 166 (1979) C29.
[1502] H.C. Clark, A.B. Goel, R.G. Goel, S. Goel, Inorg. Chem. 19 (1980) 3220.
[1503] H. Werner, H.J. Kraus, J. Organomet. Chem. 204 (1981) 415.
[1504] A.B. Goel, S. Goel, D. Vanderveer, Inorg. Chim. Acta 54 (1981) L267.
[1505] A.B. Goel, S. Goel, H.C. Clark, Synth. React. Inorg. Met. Org. Chem. 11 (1981) 289.
[1506] R.G. Goel, W.O. Ogini, R.C. Srivastava, J. Organomet. Chem. 214 (1981) 405.
[1507] J.D. Oliver, D.F. Mullica, W.O. Milligan, Inorg. Chem. 21 (1982) 3284.
[1508] R.G. Goel, W.O. Ogini, R.C. Srivastava, Organometallics 1 (1982) 819.
[1509] R.G. Goel, W. Ogini, Organometallics 1 (1982) 654.
[1510] A.R.H. Bottomley, C. Crocker, B.L. Shaw, J. Organomet. Chem. 250 (1983) 617.
[1511] W.J. Youngs, J. Mahood, B.L. Simms, P.N. Swepston, J.A. Ibers, S. Maoyu, H. Jinling, L. Jiaxi, Organometallics 2 (1983) 917.
[1512] A.L. Rheingold, W.C. Fultz, Organometallics 3 (1984) 1414.
[1513] E.C. Aleya, J. Malito, J. Organomet. Chem. 340 (1988) 119.
[1514] E.C. Aleya, G. Ferguson, J. Malito, B.L. Ruhl, Can. J. Chem. 66 (1988) 3162.
[1515] E.C. Aleya, G. Ferguson, J. Malito, B.L. Ruhl, Organometallics 8 (1989) 1188.
[1516] W.A. Herrmann, C. Brossmer, K. Ofele, C.P. Reisinger, T. Preiermeier, M. Beller, H. Fischer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1844.
[1517] W.A. Herrmann, C. Brossmer, C.P. Reisinger, T.H. Riermeier, K. Ofele, M. Beller, Chem. Eur. J. 3 (1997) 1357.
[1518] B.L. Shaw, S.D. Perera, E.A. Staley, Chem. Commun. (1998) 1361.
[1519] J.K.P. Ng, G.K. Tan, J.J. Vittal, P.H. Leung, Inorg. Chem. 42 (2003) 7674.
[1520] O. Clot, M.O. Wolf, B.O. Patrick, J. Am. Chem. Soc. 122 (2000) 10456;
O. Clot, M.O. Wolf, B.O. Patrick, J. Am. Chem. Soc. 123 (2001) 9963.
[1521] V. Dura-Vila, D.M.P. Mingos, R. Vilar, A.J.P. White, D.J. Williams, Chem. Commun. (2000) 1525.
[1522] N. Ahmad, E.W. Ainscough, J.A. James, S.D. Robinson, J. Chem. Soc. Dalton Trans. (1973) 1151.
[1523] C.E. Jones, B.L. Shaw, B.L. Turtle, J. Chem. Soc. Dalton (1974) 992.
[1524] A. Albinati, S. Affolter, P.S. Pregosin, Organometallics 9 (1990) 379.

[1525] R.B. Bedford, S.L. Welch, Chem. Commun. (2001) 129.
[1526] D.A. Albisson, R.B. Bedford, S.E. Lawrence, P.N. Scully, J. Chem. Soc. Chem. Commun. (1998) 2005.
[1527] R.B. Bedford, S.L. Hazelwood, M.E. Limmert, D.A. Albisson, S.M. Draper, P.N. Scully, S.J. Coles, M.B. Hursthouse, Chem. Eur. J. 9 (2003) 3216.
[1528] V.I. Sokolov, L.A. Bulygina, O.Y. Borbulevych, O.V. Shishkin, J. Organomet. Chem. 582 (1999) 246.
[1529] K. Hiraki, Y. Fuchita, T. Uchiyama, Inorg. Chim. Acta 69 (1983) 187.
[1530] J.M. Duff, B.E. Mann, B.L. Shaw, R.M. Slade, J. Chem. Soc. (A) (1971) 3833.
[1531] B.L. Shaw, R.E. Stainbank, J. Chem. Soc. Dalton Trans. (1973) 2394.
[1532] S.A. Dias, E.C. Aleya, Trans. Met. Chem. 4 (1979) 205.
[1533] R.G. Goel, W.O. Ogini, Inorg. Chim. Acta 44 (1980) L165.
[1534] H.P. Albieht, Z. Chem. 24 (1984) 387.
[1535] P.P. Prasad, V.K. Jain, A. Klein, M. Weber, W. Kaim, Inorg. Chim. Acta 346 (2003) 119.
[1536] Y. Takahashi, A. Tokuda, S. Sakai, Y. Ishii, J. Organomet. Chem. 35 (1972) 415.
[1537] B. Bogdanovic, C. Krüger, P. Locatelli, Angew. Chem. 91 (1979) 745;
B. Bogdanovic, C. Krüger, P. Locatelli, Angew. Chem. Int. Ed. Eng. 18 (1979) 684.
[1538] K. Hiraki, Y. Fuchita, T. Maruta, Inorg. Chim. Acta 45 (1980) L205.
[1539] K. Hiraki, Y. Fuchita, Y. Kage, J. Chem. Soc. Dalton Trans. (1984) 99.
[1540] J. Dupont, M. Pfeffer, J.C. Daran, Y. Jeannin, Organometallics 6 (1987) 899.
[1541] H. Alper, J. Organomet. Chem. 61 (1973) C62.
[1542] V.V. Dunia, O.A. Zalevskaya, I.P. Smolyakova, V.M. Potapov, Dokl. Akad. Nauk. SSSR 278 (1984) 628.
[1543] S.J. Loeb, G.K.H. Shimizu, J.A. Wisner, Organometallics 17 (1998) 2324.
[1544] V.V. Dunia, O.A. Zalevskaya, I.P. Smolyakova, V.M. Potapov, Zh. Obshch. Khim. 54 (1984) 2290.
[1545] J. Martinez, M.T. Pereira, I. Buceta, G. Alberdi, A. Amoedo, J.J. Fernandez, M.L. Torres, J.M. Vila, Organometallics 22 (2003) 5581.
[1546] S.H. Li, C.W. Yu, J.G. Xu, Chem. Commun. (2005) 450.
[1547] N. Gül, J.H. Nelson, Organometallics 19 (2000) 91.
[1548] K. Tani, L.D. Brown, J. Ahmed, J.A. Ibers, M. Yokota, A. Nakamura, S. Otsuka, J. Am. Chem. Soc. 99 (1997) 7876.
[1549] J.W. Suggs, K.S. Lee, J. Organomet. Chem. 299 (1986) 297.
[1550] E.C. Alyea, S.A. Dias, G. Ferguson, A.J. McAlees, R. McCrindle, P.J. Roberts, J. Am. Chem. Soc. 99 (1977) 4985.
[1551] J. Ruiz, N. Cutillas, J. Torregroso, G. Garcia, G. Lopez, P.A. Chaloner, P.B. Hitchcock, R.M. Harrison, J. Chem. Soc. Dalton Trans. (1994) 2353.
[1552] J. Buey, S. Coco, L. Diez, P. Espinet, J.M.M. Alvarez, J.A. Miguel, S.G. Granda, A. Tesouro, I. Ledoux, J. Zyss, Organometallics 17 (1998) 1750.
[1553] P.H. Leung, G.M. McLaughlin, J.W.L. Martin, S.B. Wild, Inorg. Chem. 25 (1986) 3392.
[1554] J. Ruiz, N. Cutillas, V. Rodriguez, J. Sampedro, G. Lopez, P.A. Chaloner, P. Hitchock, J. Chem. Soc. Dalton Trans. (1999) 2939.
[1555] J. Buey, G.A. Diez, P. Espinet, S. Garcia-Granda, E. Perez-Carreno, Eur. J. Inorg. Chem. (1998) 1235.
[1556] J.L. Garcia-Ruano, I. Lopez-Solera, J.R. Masagner, C. Navarro-Ranninger, J.H. Rodriguez, S. Martiney Carrera, Organometallics 11 (1992) 3013.
[1557] R.C. Elder, R.D.P. Cruea, R.F. Morrison, Inorg. Chem. 15 (1976) 1623.
[1558] P.W. Clark, et al., Cryst. Struct. Commun. C 41 (1985) 1742.
[1559] G. Garcia-Herbosa, N.G. Connelly, A. Munoz, J.V. Cuevas, A.G. Orpen, S.D. Politzer, Organometallics 20 (2001) 3223.
[1560] A.B. Goel, S. Goel, D. Vanderveer, Inorg. Chim. Acta 82 (1984) L9.
[1561] Y.L.S. Selvaratnam, J.J. Vittal, P.H. Leung, Inorg. Chem. 42 (2003) 3229.
[1562] Y. Li, K.H. Ng, S. Selvaratnam, G.K. Tan, J.J. Vittal, P.H. Leung, Organometallics 22 (2003) 834.
[1563] S. Arementano, A. Crispini, G. DeMunno, M. Ghedini, F. Neve, Acta Cryst. C47 (1991) 966.
[1564] S. Arementano, A. Crispini, G. DeMunno, M. Ghedini, F. Neve, Acta Cryst. C47 (1991) 2545.
[1565] B. Ma, J. Li, P.I. Djurovich, M. Yousufuddin, R. Bau, M.E. Thompson, J. Am. Chem. Soc. 127 (2005) 28.
[1566] D.L. Weaver, Inorg. Chem. 9 (1970) 2250.
[1567] B. Crociani, T. Boschi, R. Pietropaolo, W. Belluco, J. Chem. Soc. (A) (1970) 531.
[1568] H. Onoue, K. Nakagawa, I. Moritani, J. Organomet. Chem. 35 (1972) 217.
[1569] G. Gerguson, A.J. McAlees, R. McCrindle, B.L. Ruhl, Acta Cryst. B38 (1982) 2253.
[1570] E.L. Weinberg, B.K. Hunter, M.C. Baird, J. organomet. Chem. 240 (1982) 95.
[1571] R. McCrindle, A.J. McAlees, J. Organomet. Chem. 244 (1983) 97.
[1572] A.B. Goel, S. Goel, Inorg. Chim. Acta 82 (1984) 41.
[1573] S.E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt, D. Nobel, Inorg. Chem. 25 (1986) 3765.
[1574] P. Espinet, M.Y. Alonso, G. Garcia-Herbosa, J.M. Ramos, Y. Jeannin, M. Philoche-Levisalles, Inorg. Chem. 31 (1992) 2501.
[1575] J.F. Ma, Y. Yamamoto, Inorg. Chim Acta 299 (2000) 164;
P. Stepnika, Inorg. Chem. Commun. 7 (2004) 426.
[1576] E.R. Falvello, S. Fernandez, M.M. Garcia, R. Navarro, N.P. Urriolabeitia, J. Chem. Soc. Dalton Trans. (1998) 3745.
[1577] J. Dehand, M. Pfeffer, M. Zinsius, J. Organomet. Chem. 118 (1976) C62.
[1578] R.J. Cross, N.H. Tennent, G.M. Warden, J. Chem. Soc. Dalton Trans. (1986) 1059.
[1579] H. Vander Poel, G. van Koten, J. Organomet. Chem. 217 (1981) 129.
[1580] H. Adams, N.A. Bailey, T.N. Briggs, J.A. McCleverty, H.M. Colqushoun, J. Chem. Soc. Dalton Trans. (1982) 1521.
[1581] G. Salem, S.B. Wild, Inorg. Chem. 22 (1983) 4049.
[1582] J.M. Vila, M. Gayoso, J.J. Fernandez, J.M. Ortigueira, A. Suarez, Polyhedron 9 (1990) 2741.
[1583] G. Sanchez, J.L. Serrano, M.A. Moral, J. Perez, E. Mollins, G. Lopez, Polyhedron 18 (1999) 3057.
[1584] R. Ares, M.L. Torres, A. Fernandez, S.C. Jiuz, A. Suarez, G. Alberdi, J.J. Fernandez, J.M. Vila, Polyhedron 21 (2002) 2309;
J.M. Vila, G. Alberdi, M.T. Pereira, M. Marino, A. Fernandez, M.L. Torres, R. Ares, Polyhedron 22 (2003) 241.
[1585] R. Ares, M.L. Torres, A. Fernandez, M.T. Pereira, A. Suarez, R. Mosteiro, J.J. Fernandez, J.M. Vila, J. Organomet. Chem. 665 (2003) 87.
[1586] N.K. Roberts, S.B. Wild, J. Chem. Soc. Dalton (1979) 2015.
[1587] D.G. Allen, G.M. McLaughlin, G.B. Robertson, W.L. Steffen, G. Salem, S.B. Wild, Inorg. Chem. 21 (1982) 1007.
[1588] J.W.L. Martin, J.A.L. Palmer, S.B. Wild, Inorg. Chem. 23 (1984) 2664.
[1589] P. Gugger, A.C. Willis, S.B. Wild, J. Chem. Soc. Chem. Commun. (1990) 1169.
[1590] N.W. Alcock, J.M. Brown, D.J. Hulmes, Tetrahedron Asymmetry 4 (1993) 743.
[1591] N. Gabbitas, G. Salem, M. Sterns, A.C. Wills, J. Chem. Soc. Dalton Trans. (1993) 3271.
[1592] S.Y. Chooi, S.Y. Siah, P.H. Leung, K.F. Mok, Inorg. Chem. 32 (1993) 4812.

[1593] M. Pabel, A.C. Wills, S.B. Wild, Angew. Chem. Int. Ed. Engl. 33 (1994) 1835.
[1594] C.E. Barclay, G. Deeble, R.G. Doyle, S.A. Elix, G. Salem, T.L. Jones, S.B. Wild, A.C. Wills, J. Chem. Soc. Dalton Trans. (1995) 57.
[1595] J. Albert, J.M. Cadena, J. Granell, G. Muller, D. Panyella, C. Sanudo, Eur. J. Inorg. Chem. (2000) 1283.
[1596] J. Kurita, F. Usuda, S. Yasuike, T. Tsuchiya, Y. Tsuda, F. Kiuchi, S. Hosobi, Chem. Commun. (2000) 191.
[1597] R.F. Heck, J. Am. Chem. Soc. 90 (1968) 313.
[1598] P.J. Chung, H. Suzuki, Y. Morooka, T. Ikawa, Chem. Lett. (1980) 63.
[1599] M. Pfeffer, J. Fischer, A. Mitschler, L. Ricard, J. Am. Chem. Soc. 102 (1980) 6338.
[1600] P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler, L. Ricard, J. Am. Chem. Soc. 103 (1981) 5115.
[1601] V.A. de Neta, A.E. Mauro, A.C.F. Cairas, S.R. Ananias, E.T. De Almeida, Polyhedron 18 (1998) 413.
[1602] P.J. Chung, Gakujutsu Ronbunshu Chosen Shogakkai 9 (1979) 226;
P.J. Chung, Chem. Abstr. 94 (1981) 84269.
[1603] P. Braunstein, J. Fischer, D. Matt, M. Pfeffer, J. Am. Chem., Soc. 106 (1984) 410.
[1604] M. Pfeffer, J. Fischer, A. Mitschler, Organometallics 3 (1984) 1531.
[1605] M. Onishi, K. Hiraki, A. Iwamoto, J. Organomet. Chem. 262 (1984) C11.
[1606] P. Braunstein, D. Matt, D. Nobel, S.E. Bouaoud, D. Grandjean, J. Organomet. Chem. 301 (1986) 401.
[1607] A.J. Deeming, M.N. Meah, P.A. Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1988) 2193.
[1608] J. Fornies, R. Navarro, V. Sicilia, M. Tomas, Inorg. Chim. Acta 168 (1990) 201.
[1609] A. Crispini, D. Pucci, I.A. Aiello, M. Ghedini, Inorg Chim. Acta 304 (2000) 219.
[1610] A. Ara, L.R. Falvello, J. Fornies, V. Sicilia, P. Villarroya, Organometallics 19 (2000) 3091.
[1611] L. Diez, P. Espinet, J.A. Miguel, J. Chem. Soc. Dalton Trans. (2001) 1189.
[1612] J. Ruiz, V. Rodriguez, N. Cutillas, M. Pardo, P. Chaloner, P.B. Hitchcock, Organometallics 20 (2001) 1973.
[1613] N. Naryan, V.K. Jain, R.J. Butcher, J. Organomet. Chem. 549 (1997) 73.
[1614] Y.J. Kim, X. Chang, J.T. Han, M.S. Lim, S.W. Lee, Dalton Trans. (2004) 3699.
[1615] M. Onishi, Y. Ohama, K. Sugimura, K. Hiraki, Chem. Lett. (1976) 955.
[1616] M. Ghedini, F. Neve, D. Pucci, E. Cesarotti, M. Grassi, J. Organomet. Chem. 438 (1992) 343.
[1617] C. Bartolome, P. Espinet, L. Vicente, F. Villafane, J.P.H. Charmant, A.G. Orpen, Organometallics 21 (2002) 3536.
[1618] P. Espinet, C. Harnandez, J.M. Martin-Alvarez, J.A. Miguel, Inorg. Chem. 43 (2004) 843.
[1619] H.C. Clark, A.B. Goel, J. Organomet. Chem. 178 (1979) C27.
[1620] A.B. Goel, S. Goel, Trans. Met. Chem. 5 (1980) 125.
[1621] E.C. Aleya, S.A. Dias, F. Bonati, Trans. Met. Chem. 6 (1981) 24.
[1622] R.A. Holton, R.A. Kjonaas, J. Am. Chem. Soc. 99 (1977) 4177.
[1623] A. Bahsoun, J. Dehand, M. Pfeffer, M. Zinsius, S.E. Bouaoud, G. Le Borgne, J. Chem. Soc. Dalton Trans. (1979) 547.
[1624] C.H. Chao, D.W. Hart, R. Bau, R.F. Heck, J. Organomet. Chem. 179 (1979) 301.
[1625] M.A. Andrews, C.W.F. Cheng, J. Am. Chem. Soc. 104 (1982) 4268.
[1626] A.K. Yatsimirskü, A.D. Ryabov, I.K. Sakadynskaya, I.V. Berezin, Dokl. Akad. Neuk SSSR 270 (1983) 150.
[1627] C. Arlen, M. Pfeffer, O. Bars, D. Grandjean, J. Chem. Soc. Dalton Trans. (1983) 1535.
[1628] A.D. Ryabov, R. van Eldik, G. LeBorgne, M. Pfeffer, Organometallics 12 (1993) 1386.
[1629] M. Benito, C. Lopez, Y. Moravan, X. Solans, M. Font-Bardva, J. Chem. Soc. Dalton Trans. (2000) 4470.
[1630] G. Zhao, Q.G. Wang, T.C.W. Mak, J. Organomet. Chem. 574 (1999) 311.
[1631] S. Perez, C. Lopez, A. Caubet, A. Pawelczyk, X. Solans, M. Font-Bardia, Organometallics 22 (2003) 2396.
[1632] Y. Yamamoto, H. Yamazaki, Inorg. Chim. Acta 41 (1980) 229.
[1633] J.F. van Baar, J.M. Klerks, P. Overbosch, D.J. Stufkens, K. Vrieze, J. Organomet. Chem. 112 (1976) 95.
[1634] J. Dupont, M. Pfeffer, J. Chem. Soc. Dalton Trans. (1990) 3193.
[1635] J. Vicente, I.S. Llamas, C. Grunwald, C. Alvarez, P.G. Jones, D. Bautista, Oragnometallics 21 (2002) 3587.
[1636] A.K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, J. Chem. Soc. Chem. Commun. (1984) 999.
[1637] R.A. Holton, R.A. Kjonaas, J. Organomet. Chem. 142 (1977) C15.
[1638] M. Yamamura, I. Moritani, S.I. Murahashi, Chem. Lett. (1974) 1423.
[1639] S.J. Murahashi, Y. Tanba, M. Yamamura, I. Moritani, Tetrahdron Lett. (1974) 3749.
[1640] V.I. Sokolov, L.L. Troitskaya, O.A. Reutov, J. Organomet. Chem. 202 (1980) C58.
[1641] A. Bose, C.R. Saha, Indian J. Chem. 29A (1990) 461.
[1642] M. Beller, H. Fischer, W.A. Herrmann, K. Ofele, C. Brossmer, Angew. Chem. Int. Ed. Eng. 34 (1995) 1848.
[1643] M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357.
[1644] M. Nowotny, U. Hanefeld, H. van Koningsveld, T. Maschmeyer, Chem. Commun. (2000) 1877.
[1645] X. Gai, R. Grigg, M.I. Ramzan, V. Sridharan, S. Collard, J.E. Muir, Chem. Commun. (2000) 2053.
[1646] J.M. Brund, M. Hirlemann, A. Heumann, G. Buono, Chem. Commun. (2000) 1869.
[1647] V.P.W. Bohm, W.A. Herramann, Chem. Eur. J. 7 (2001) 4191.
[1648] F. Yang, Y. Zhang, R. Zheng, J. Tang, M. He, J. Organomet. Chem. 651 (2002) 146.
[1649] I.P. Beletskaya, A.N. Kashin, N.B. Karlstedt, A.V. Mitin, A.V. Cheprakov, G.M. Kazankov, J. Organomet. Chem. 622 (2001) 89.
[1650] R.B. Bedford, C.S.J. Cazin, M.B. Hursthouse, M.E. Light, V.J.M. Scordia, Dalton Trans. (2004) 3864.
[1651] S. Gibson, D.F. Foster, G.R. Eastham, R.P. Tooze, D.J. Cole Hamilton, Chem. Commun. (2001) 779.
[1652] S.G. Fiddy, J. Evans, M.A. Newton, T. Neisius, R.P. Tooze, R. Oldman, Chem. Commun. (2003) 2682.
[1653] H. Weissman, D. Milstein, Chem. Commun. (1999) 1901.
[1654] P. Espinet, A.M. Echavarren, Angew Chem. Int. Ed. 43 (2004) 4704.
[1655] R. Rumin, J. Organomet. Chem. 247 (1983) 351.
[1656] L.F. Tietze, T. Nobel, M. Spescha, J. Am. Chem. Soc. 120 (1998) 8971.
[1657] L. Botella, C. Najera, Angew. Chem. Int. Ed. Engl. 41 (2002) 179.
[1658] P.H. Leung, K.H. Ng, Y. Li, A.J.P. White, D.J. Williams, Chem. Commun. (1999) 2435.
[1659] L. Tusek-Bozic, M. Komac, M. Curic, A. Lycka, M. D'Alpaos, V. Scarcia, A. Furlani, Polyhedron 19 (2000) 937.
[1660] F. Zamora, V.M. Gonzalez, J.M. Perez, J.R. Masaguer, C. Alonso, C.N. Ranninger, Appl. Organomet. Chem. 11 (1997) 591.
[1661] M. Ghedini, M. Longieni, R. Bartolino, Mol. Cryst. Liq. Cryst. 84 (1982) 207.
[1662] C.C. Veraace, R. Bartolino, M. Ghedini, F. Neve, S. Armentano, M. Petrov, N. Kirov, Liq. Cryst. 8 (1990) 481.
[1663] P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215.

[1664] A.P. Polishchuk, T.V. Timofeeva, Russian Chem. Rev. 62 (1993) 291.
[1665] N. Hoshino, H. Hasegawa, Y. Matsunaga, Liq. Cryst. 9 (1991) 267.
[1666] A.M. Lanfredi, F. Ugozzoli, M. Ghedini, S. Licoccia, Inorg. Chim. Acta 86 (1984) 165.
[1667] M. Ghedini, S. Armeritano, F. Neve, Inorg. Chim. Acta 134 (1987) 23.
[1668] M. Ghedini, S. Armentano, R. Bartolino, F. Rustichalli, G. Torquati, N. Kirov, M. Petrov, Mol. Cryst. Liq. Cryst. 151 (1987) 75.
[1669] V. Formoso, M.C. Pagnotta, P. Mariani, M. Ghedini, F. Neve, R. Bartolino, M. More, G. Pepy, Liq. Cryst. 11 (1992) 639.
[1670] M. Ghedini, D. Pucci, A. Crispini, I. Aiello, F. Barigelletti, A. Gessi, O. Francescangeli, Appl. Organomet. Chem. 13 (1999) 565;
A. Crsipini, M. Ghedini, S. Morrone, D. Pucci, O. Francescangeli, Liq. Cryst. 20 (1996) 67.
[1671] M. Ghedini, S. Morrone, G. DeMunno, A. Crispini, J. Organomet. Chem. 415 (1991) 281.
[1672] M. Marcos, M.B. Ros, J.L. Serrano, Liq. Cryst. 3 (1988) 1129.
[1673] M.A. Ciriano, P. Espinet, E. Lalinde, M. Ros, J.L. Serrand, J. Mol. Struct. 196 (1989) 327.
[1674] M.B. Ros, N. Ruiz, J.L. Serrano, P. Espinet, Liq. Cryst. 9 (1991) 77.
[1675] B.B. Eran, D. Singer, K. Praefcke, Eur. J. Inorg. Chem. (2001) 111.
[1676] J. Barbera, P. Espinet, E. Lalinde, M. Marcos, J.L. Serrano, Liq. Cryst. 2 (1987) 833.
[1677] M. Ghedini, S. Armentano, G. deMunno, A. Crisptni, F. Neve, Liq. Cryst. 8 (1990) 739.
[1678] M.T. Pereira, J.M. Vila, E. Gayoso, M. Gayoso, J. Coord. Chem. 18 (1988) 245.
[1679] R. Mosteiro, E. Perille, A. Fernandez, M.L. Torres, J.M. Vila, A. Suarez, J.M. Ortigueira, M.T. Pereira, J.J. Fernandez, Appl. Organomet. Chem. 14 (2000) 634.
[1680] L. Diez, P. Espinet, J.A. Miguel, M.P. Rodriguez-Medina, J. Organomet. Chem. 690 (2005) 261.
[1681] M.J. Baena, J. Buey, P. Espinet, C.E. Garcia-Prieto, J. Organomet. Chem. 690 (2005) 998.
[1682] M. Ghedini, S. Morrone, D. Gatteschi, C. Zanchini, Chem. Mater 3 (1991) 752.
[1683] C. Sirlin, J. Chengebroyen, R. Konrath, G. Ebeling, I. Raad, J. Dupent, M. Paschaki, F. Kotzyba-Hibert, C. Harf-Monteil, M. Pfeffer, Eur. J. Org. Chem. (2004) 1724.
[1684] C.C. Cassol, A.P. Umpierre, G. Machado, S.I. Wolke, J. Dupont, J. Am. Chem. Soc. 127 (2005) 3298.
[1685] M.P. Brown, R.J. Puddephatt, M. Rashidi, K.R. Sedden, J. Chem. Soc. Dalton Trans. (1977) 951.
[1686] M.P. Brown, R.J. Puddephatt, M. Rashidi, K.R. Seddon, J. Chem. Soc. Dalton Trans. (1978) 516;
M.P. Brown, R.J. Puddephatt, M. Rashidi, K.R. Seddon, Inorg. Chim. Acta 23 (1977) L27.
[1687] M.P. Brown, A.N. Keith, L. Manojlovic Muir, K.W. Muir, R.J. Puddepahtt, K.R. Seddon, Inorg. Chim. Acta 34 (1979) L223.
[1688] R.J. Puddephatt, M.A. Thomson, Inorg. Chim. Acta 45 (1980) L281.
[1689] R.H. Hill, R.J. Puddephatt, Inorg. Chim. Acta 54 (1981) L277.
[1690] M.P. Brown, J.R. Fisher, R.H. Hill, R.J. Puddephatt, K.R. Seddon, Inorg. Chem. 20 (1981) 3516.
[1691] H.C. Foley, R.H. Morris, T.S. Targos, G.L. Geoffroy, J. Am. Chem. Soc. 103 (1981) 7337.
[1692] R.H. Hill, P. deMayo, R.J. Puddephatt, Inorg. Chem. 21 (1982) 3642.
[1693] J.R. Fisher, A.J. Mills, S. Sumner, M.P. Brown, M.A. Thomson, R.J. Puddephatt, A.A. Frew, L. Manojlovic Muir, K.W. Muir, Organometallics 1 (1982) 1421.
[1694] A.A. Frew, R.H. Hill, L. Manojlovic Muir, K.W. Muir, R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (1982) 198.
[1695] R.J. Puddephatt, M.A. Thomson, Inorg. Chem. 21 (1982) 725.
[1696] K.A. Azam, A.A. Frew, B.R. Lloyd, L. Manojlovic Muir, K.W. Muir, R.J. Puddephatt, Organometallics 4 (1985) 1400.
[1697] A.J. McLennan, R.J. Puddephatt, Organometallics 5 (1986) 811.
[1698] T.G. Appleton, M.A. Bennett, B. Tompkins, J. Chem. Soc. Dalton Trans. (1976) 439.
[1699] A.A. Frew, L. Manojlovic-Muir, K.W. Muir, J. Chem. Soc. Chem. Commun. (1980) 624.
[1700] M.P. Brown, S.J. Cooper, A.A. Frew, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, K.R. Seddon, M.A. Thomson, Inorg. Chem. 20 (1981) 1500.
[1701] S.J. Cooper, M.P. Brown, R.J. Puddephatt, Inorg. Chem. 20 (1981) 1374.
[1702] K.A. Azam, R.J. Puddephatt, M.P. Brown, A. Yavari, J. Organomet. Chem. 234 (1982) C31.
[1703] M.P. Brown, S.J. Cooper, A.A. Frew, L. Manojlovic Muir, K.W. Muir, R.J. Puddephatt, M.A. Thomson, J. Chem. Soc. Dalton Trans. (1982) 299.
[1704] K.A. Azam, M.P. Brown, S.J. Cooper, R.J. Puddephatt, Organometallics 1 (1982) 1183.
[1705] R.H. Hill, R.J. Puddephatt, Organometallics 2 (1983) 1472.
[1706] A.T. Hutton, B. Shabanzadeh, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1983) 1053.
[1707] R.J. Puddephatt, K.A. Azam, R.H. Hill, M.P. Brown, C.D. Nelson, R.P. Moulding, K.R. Seddon, M.C. Crossel, J. Am. Chem. Soc. 105 (1983) 5642.
[1708] M.C. Crossel, R.P. Moulding, K.R. Seddon, J. Organomet. Chem. 247 (1983) C32.
[1709] K.A. Azam, R.H. Hill, R.J. Puddephatt, Can. J. Chem. 62 (1984) 2029.
[1710] K.A. Azam, M.P. Brown, R.H. Hill, R.J. Puddephatt, A. Yavari, Organometallics 3 (1984) 697.
[1711] F.S.M. Hassan, D.M. McEwan, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1985) 1501.
[1712] C. Xu, G.K. Anderson, Organometallics 15 (1996) 1760;
C. Xu, G.K. Anderson, Organometallics 13 (1994) 3981.
[1713] M. Janka, G.K. Anderson, N.P. Rath, Organometallics 19 (2000) 5071.
[1714] M.P. Brown, J.R. Fisher, A.J. Mills, R.J. Puddephatt, M.A. Thomson, Inorg. Chem. Acta 44 (1980) L271.
[1715] M.P. Brown, S.J. Cooper, A.A. Frew, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, M.A. Thomson, J. Organomet. Chem. 198 (1980) C33.
[1716] L. Manojlovic-Muir, K.W. Muir, J. Organomet. Chem. 219 (1981) 129.
[1717] R.J. Puddephatt, M.A. Thomson, Inorg. Chem. 21 (1982) 725.
[1718] M.C. Grossel, R.J. Batson, R.P. Moulding, K.R. Seddon, J. Organomet. Chem. 304 (1986) 391.
[1719] B.S. Haggerty, C.E. Housecroft, A.L. Rheingold, B.A.M. Shaykh, J. Chem. Soc. Dalton Trans. (1991) 2175.
[1720] R.U. Kirss, D.A. Forsyth, M.A. Plante, J. Organomet. Chem. 688 (2003) 206.
[1721] R.A. Stockland Jr., G.K. Anderson, N.P. Rath, Inorg. Chim. Acta 259 (1997) 173.
[1722] R.A. Stockland Jr., G.K. Anderson, N.P. Rath, J. Am. Chem. Soc. 121 (1999) 7945.
[1723] R.A. Stockland Jr., G.K. Anderson, N.P. Rath, Inorg. Chim. Acta 300 (2000) 395.
[1724] M.M. Olmstead, H. Hope, L.S. Benner, A.L. Balch, J. Am. Chem. Soc. 99 (1977) 5502.
[1725] R. Colton, M.J. McCormick, C.D. Pannan, J. Chem. Soc. Chem. Commun. (1977) 823.
[1726] L.S. Benner, M.M. Olmstead, H. Hope, A.L. Balch, J. Organomet. Chem. 153 (1978) C31.
[1727] L.S. Benner, A.L. Balch, J. Am. Chem. Soc. 100 (1978) 6099.

[1728] A.D. Rattray, D. Sutton, Inorg. Chim. Acta 27 (1978) L85.
[1729] A.L. Balch, C.H. Lee, C.H. Lindsay, M.M. Olmstead, J. Organomet. Chem. 177 (1979) C22.
[1730] P. Brant, L.S. Benner, A.L. Balch, Inorg. Chem. 18 (1979) 3422.
[1731] A.L. Balch, L.S. Benner, M.M. Olmstead, Inorg. Chem. 18 (1979) 2996.
[1732] A.L. Balch, C.T. Hunt, C.L. Lee, M.M. Olmstead, J.P. Farr, J. Am. Chem. Soc. 103 (1981) 3764.
[1733] M.L. Kullberg, C.P. Kubiak, Organometallics 3 (1984) 632.
[1734] C.L. Lee, B.R. James, D.A. Nelson, R.T. Hallen, Organometallics 3 (1984) 1360.
[1735] C.L. Lee, G. Besenyei, B.R. James, D.A. Nelson, M.A. Lilga, J. Chem. Soc. Chem. Commun. (1985) 1175.
[1736] M.L. Kullberg, F.R. Lamke, D.R. Powell, O.P. Kubiak, Inorg. Chem. 24 (1985) 3589.
[1737] M.L. Kullberg, C.P. Kubiak, Inorg. Chem. 25 (1986) 26.
[1738] G. Besenyei, C.L. Lee, B.R. James, J. Chem. Soc. Chem. Commun. (1986) 1750.
[1739] C.L. Lee, Y.P. Yang, S.J. Rettig, B.R. James, D.A. Nelson, M.A. Lilga, Organometallics 5 (1986) 2220.
[1740] G. Besenyei, C.L. Lee, J. Gulinski, S.J. Rettig, B.R. James, D.A. Nelson, M.A. Lilga, Inorg. Chem. 26 (1987) 3622.
[1741] A.F. Barnabas, D. Sallin, B.R. James, Can. J. Chem. 67 (1989) 2009.
[1742] C. Besenyei, C.L. Lee, Y. Xie, B.R. James, Inorg. Chem. 30 (1991) 2446.
[1743] G. Besenyei, L. Parkanyi, K.I. Siman di, B.R. James, Inorg. Chem. 34 (1995) 6118.
[1744] T.Y.H. Wong, A.F. Barnabas, D. Sallin, B.R. James, Inorg. Chem. 34 (1995) 2278.
[1745] T.Y.H. Wong, S.J. Rettig, B.R. James, Inorg. Chem. 38 (1999) 2143.
[1746] R. Colton, M.J. McCormick, C.D. Pannan, Aust. J. Chem. 31 (1978) 1425.
[1747] M.P. Brown, R.J. Puddephatt, M. Rashidi, K.R. Seddon, J. Chem. Soc. Dalton Trans. (1978) 1540.
[1748] M.P. Brown, J.R. Fisher, R.J. Puddephatt, K.R. Seddon, Inorg. Chem. 18 (1979) 2808.
[1749] P.G. Pringle, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1982) 81.
[1750] G. Besenyei, L. Parkanyi, E.G. Baitz, B.R. James, Inorg. Chim. Acta 327 (2002) 179.
[1751] C.L. Lee, C.T. Hunt, A.L. Balch, Inorg. Chem. 20 (1981) 2498.
[1752] T.S. Cameron, P.A. Gardner, K.R. Grundy, J. Organomet. Chem. 212 (1981) C19.
[1753] S. Muralidharan, J.H. Espenson, Inorg. Chem. 22 (1983) 2786.
[1754] K.A. Azam, R.J. Puddephatt, Organometallics 2 (1983) 1396.
[1755] M.C. Grossel, R.P. Moulding, K.R. Seddon, Inorg. Chim. Acta 64 (1983) L275.
[1756] K.R. Grundy, K.N. Robertson, Organometallics 2 (1983) 1736.
[1757] P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1983) 889.
[1758] A.L. Balch, R.R. Guimerans, J. Linehan, F.E. Wood, Inorg. Chem. 24 (1985) 2021.
[1759] S. Muralidharan, J.H. Espenson, S.A. Ross, Inorg. Chem. 25 (1986) 2557.
[1760] M. Ghedini, F. Neve, C. Mealli, A. Tiripicchio, F. Ugozzoli, Inorg. Chim. Acta. 178 (1990) 5.
[1761] F. Neve, M. Ghedini, G. DeMunno, A. Crispini, Inorg. Chem. 31 (1992) 2979.
[1762] R. Huang, I.A. Guzei, J.H. Espenson, Organometallics 18 (1999) 5420.
[1763] I. Foch, G. Besenyei, L.I. Simandi, Inorg. Chem. 38 (1999) 3944.
[1764] J.H.K. Yip, J. Wu, K.Y. Wong, K.P. Ho, L.L. Koh, J.J. Vittal, Eur. J. Inorg. Chem. (2004) 1056.
[1765] P. Espinet, J. Fornies, C. Fortuno, G. Hidalgo, F. Martinez, M. Tomas, A.J. Welch, J. Organomet. Chem. 317 (1986) 105.
[1766] R. Uson, J. Fornies, R. Navarro, J.I. Cebollada, J. Organomet. Chem. 304 (1986) 381.
[1767] J. Fornies, F. Martinez, R. Navarro, A. Redondo, M. Tomas, A.J. Welch, J. Organomet. Chem. 316 (1986) 351.
[1768] R. Uson, J. Fornies, P. Espinet, C. Fortuno, J. Chem. Soc. Dalton Trans. (1986) 1849.
[1769] R. Uson, J. Fornies, J. Martinez, R. Navarro, M.C. Frias, Inorg. Chim. Acta 132 (1987) 217.
[1770] S.S.M. Ling, R.J. Puddephatt, L. Manojlovic Muir, K.W. Muir, Inorg. Chim. Acta 77 (1983) L95.
[1771] S.J. Young, B. Kellenberger, J.H. Reinbenspies, S.E. Himmel, M. Manning, O.P. Anderson, J.K. Stille, J. Am. Chem. Soc. 110 (1988) 5744.
[1772] C.T. Hunt, A.L. Balch, Inorg. Chem. 20 (1981) 2267.
[1773] C.L. Lee, C.T. Hunt, A.L. Balch, Organometallics 1 (1982) 824.
[1774] N.A. AlSalem, H.D. Empsall, R. Markham, B.L. Shaw, B. Weeks, J. Chem. Soc. Dalton Trans. (1979) 1972.
[1775] C.B. Pamplin, S.J. Rettig, B.O. Patrick, B.R. James, Inorg. Chem. 42 (2003) 4117.
[1776] W. Levason, C.A. McAulliffe, J. Coord. Chem. 4 (1974) 47.
[1777] R. Turpin, J. Casteran-Baumassy, P. Dognac, J. Chem. Res. (S) (1979) 164;
P. Dognac, R. Turpin, R. Poilblanc, J. Organomet. Chem. 253 (1983) 123.
[1778] W.R. Paryzek, A.J. McLennan, R.J. Puddephatt, Inorg. Chem. 25 (1986) 3097.
[1779] T. Even, A.R.J. Genge, A.M. Hill, N.J. Holmes, W. Levason, M. Webster, J. Chem. Soc. Dalton Trans. (2000) 655.
[1780] L. Manojlovic-Muir, I.R. Jobe, B.J. Maya, R.J. Puddephatt, J. Chem. Soc. Dalton Trans. (1987) 2117.
[1781] G.B. Jacobsen, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1987) 151.
[1782] M.K. Richmond, S.L. Scott, G.P.A. Yap, H. Alper, Organometallics 21 (2002) 3395.
[1783] R.J. Puddephatt, M.A. Thomson, L. Manojlovic Muir, K.W. Muir, A.A. Frew, J. Chem. Soc. Chem. Commun. (1981) 805;
R.J. Puddephatt, et al., organometallics 7 (1988) 2257.
[1784] L. Manojlovic Muir, S.S.M. Ling, R.J. Puddephatt, J. Chem. Soc. Dalton Trans. (1986) 151.
[1785] B. Kellenberger, S.J. Young, J.K. Stille, J. Am. Chem. Soc. 107 (1985) 6105.
[1786] D. Evrard, M. Drouin, Y. Mugnier, P.D. Harvey, Inorg. Chim. Acta 350 (2003) 442.
[1787] U. Schimdt, K. Ilg, C.D. Brandt, H. Werner, J. Chem. Soc. Dalton Trans. (2002) 2815.
[1788] R.A. Stockland Jr., M. Janaka, G.R. Hoel, N.P. Rath, G.K. Anderson, Organometallics 20 (2001) 5212.
[1789] A. Mentes, R.D.W. Kemmitt, J. Fawcett, D.R. Russeli, Polyhedron 18 (1999) 1141.
[1790] L. Manojlovic-Muir, K.W. Muir, A.A. Frew, S.S.M. Ling, M.A. Thomson, R.J. Puddephatt, Organometallics 3 (1984) 1637.
[1791] S.S.M. Ling, N.C. Payne, R.J. Puddephatt, Organometallics 4 (1985) 1546.
[1792] M. Rashidi, S. Jamali, M. Hashemi, J. Organomet. Chem. 633 (2001) 105.
[1793] P.G. Pringle, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1982) 581.
[1794] R.J. Puddephatt, M.A. Thomson, J. Organomet. Chem. 238 (1982) 231.
[1795] C.R. Langrick, D.M. McEwan, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1983) 2487.
[1796] A. Sebald, B. Wrackmeyer, Z. Naturforsch, Teil B 38 (1983) 1156;
A. Sebald, B. Wrackmeyer, Z. Naturforsch Teil B 40 (1985) 148.
[1797] C.R. Langrick, R.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1984) 1233.

[1798] F.S.M. Hassan, D.P. Markham, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1985) 279;
G.R. Cooper, A.T. Hulton, C.R. Langrick, D.M. McEwan, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans (1984) 855.
[1799] C.M. Che, V.W.W. Yam, W.T. Wong, T.F. Lai, Inorg. Chem. 28 (1989) 2908;
H.K. Yip, T.F. Lai, C.M. Che, J. Chem. Soc. Dalton Trans (1991) 1639;
B.H. Xia, C.M. Che, D.L. Phillips, K.H. Leung, K.K. Cheung, Inorg. Chem. 41 (2002) 3866;
B.H. Xia, C.M. Che, Z.Y. Zhou, Chem. Eur. J. 9 (2003) 3055.
[1800] A.J. McLennan, R.J. Puddephatt, Organometallics 4 (1985) 485.
[1801] C.R. Langrick, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1985) 1015.
[1802] N.W. Alcock, T.J. Kemp, P.G. Pringle, P. Bergamini, O. Traverso, J. Chem. Soc. Dalton Trans. (1987) 1659.
[1803] V.W.W. Yam, P.K.Y. Yeung, L.P. Chan, W.H. Kwok, D.L. Phillips, K.L. Yu, R.W.K. Wong, H. Yan, Q.J. Meng, Organometallics 17 (1998) 2590.
[1804] X.L.R. Fontaine, S.J. Higgins, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1988) 1179.
[1805] C.M. Che, V.W. Yam, W.T. Wong, T.F. Lai, Inorg. Chem. 28 (1989) 2908.
[1806] V.W.W. Yam, K.L. Yu, K.M.C. Wong, K.K. Cheung, Organometallics 20 (2001) 721.
[1807] V.W.W. Yam, C.K. Hui, K.M.C. Wong, N. Zhu, K.K. Cheung, Organometallics 21 (2002) 4326.
[1808] C.G. Arena, G. Bruno, G. DeMunno, E. Rotondo, D. Drommi, F. Faraone, Inorg. Chem. 32 (1993) 1601.
[1809] J.D. Scott, R.J. Puddephatt, Organometallics 5 (1986) 2522.
[1810] M. Rashidi, S. Jamali, M. Hashemi, J. Organomet. Chem. 633 (2001) 105.
[1811] M. Rashidi, M. Hashemi, M.K. Motlagh, R.J. Puddephatt, Oranometallics 19 (2000) 2751.
[1812] S. Jamali, M. Rashidi, M.C. Jennings, R.J. Puddephatt, Dalton Trans. (2003) 2313.
[1813] M. Rashidi, M.C. Jennings, R.J. Puddephatt, Organometallics 22 (2003) 2612.
[1814] M. Rashidi, K. Kamali, M.C. Jennings, R.J. Puddephatt, J. Organomet. Chem. 690 (2005) 1600.
[1815] M. Hashemi, M. Rashidi, J. Organomet. Chem. 690 (2005) 982.
[1816] M. Bonamico, G. Dessy, J. Chem. Soc. Chem. Commun. (1968) 483.
[1817] J.P. Fackler Jr., J. Am. Chem. Soc. 94 (1972) 1009.
[1818] O. Piovesana, L. Sestili, C. Bellitto, A. Flamini, M. Tomassini, P.F. Zanazzi, A.R. Zanzari, J. Am. Chem. Soc. 99 (1977) 5190.
[1819] O. Piovesana, C. Bellitto, A. Flanini, P.F. Zananzzi, Inorg. Chem. 18 (1979) 2258.
[1820] C. Bellitto, A. Flamini, O. Piovesana, P.F. Zanazzi, Inorg. Chem. 19 (1980) 3632.
[1821] C. Bellitto, G. Dessy, V. Fares, A. Flamini, J. Chem. Soc. Chem. Commun. (1981) 409.
[1822] T. Kawamura, T. Ogawa, T. Yamabe, H. Masuda, T. Taga, Inorg. Chem. 26 (1987) 3547.
[1823] C. Bellitto, M. Bonamico, G. Dessy, V. Fares, A. Flamini, J. Chem. Soc. Dalton Trans. (1987) 35.
[1824] J.M. Burke, J.P. Fackler Jr., Inorg. Chem. 11 (1972) 3000.
[1825] K.W. Browdl, T. Bursh, L.V. Interrante, J.S. Kasper, Inorg. Chem. 11 (1972) 1800.
[1826] M. Bonamico, G. Dessy, V. Fares, J. Chem. Soc. Dalton Trans. (1977) 2315.
[1827] C. Bellitto, A. Flamini, L. Gastaldi, L. Scaramuzza, Inorg. Chem. 22 (1983) 444.
[1828] M. Mitsumi, T. Murase, H. Kishida, T. Yoshinari, Y. Ozawa, K. Toriumi, T. Sonoyama, H. Kitagawa, T. Mitani, J. Am. Chem. Soc. 123 (2001) 11179.
[1829] H. Kitagawa, N. Onodera, T. Sonoyama, Y. Yamashita, T. Fukawa, T. Mitani, M. Seto, Y. Maeda, J. Am. Chem. Soc. 121 (1999) 10068.
[1830] M. Mitsumi, K. Kitamura, A. Morinaga, Y. Ozawa, M. Kobayashi, K. Toriumi, Y. Iso, H. Kitagawa, T. Mitani, Angew Chem. Int. Ed. 41 (2002) 2767.
[1831] J. Ohara, S. Yamamoto, Condensed Matter (2004) 15.
[1832] M. Mitsumi, S. Umebayashi, Y. Ozawa, K. Toriumi, H. Kitigawa, T. Mitani, Chem. Lett. (2002) 258.
[1833] S. Yamamoto, Condensed Matter (2001) 1.
[1834] M.A.F.D.R. Pinto, P.J. Sadler, S. Neidle, M.R. Sanderson, A. Subbiah, J. Chem. Soc. Chem. Commun. (1980) 13.
[1835] C.M. Che, L.G. Butler, P.J. Grunthaner, H.B. Gray, Inorg. Chem. 24 (1985) 4662.
[1836] K.A. Alexander, S.A. Bryan, M.K. Dickson, D. Hedden, D.M. Roundhill, Inorg. Synth. 24 (1986) 211.
[1837] T. Yamaguchi, Y. Sasaki, T. Ikeyama, T. Azumi, T. Ito, Inorg. Chim. Acta 172 (1990) 233.
[1838] A.P. Zipp, Coord. Chem. Rev. 84 (1988) 47.
[1839] D.M. Roundhill, H.B. Gray, C.M. Che, Acc. Chem. Res. 22 (1989) 55.
[1840] R.I. Sweeney, E.L. Harvey, H.B. Gray, Coord. Chem. Rev. 105 (1990) 23.
[1841] I.V. Novozhilova, A.V. Volkov, P. Coppens, J. Am. Chem. Soc. 125 (2003) 1079.
[1842] C. King, D.M. Roundhill, M.K. Dickson, F.R. Fronczek, J. Chem. Soc. Dalton Trans. (1987) 2769.
[1843] W.A. Fordyce, J.G. Brummer, G.A. Crosby, J. Am. Chem. Soc. 103 (1981) 7061.
[1844] C.M. Che, L.G. Butler, H.B. Gray, J. Am. Chem. Soc. 103 (1981) 7796.
[1845] S.F. Rice, H.B. Gray, J. Am. Chem. Soc. 105 (1983) 4571.
[1846] S.A. Clodfelter, T.M. Doede, B.A. Brennan, J.K. Nagle, D.P. Bender, W.A. Turner, P.M. LaPunzina, J. Am. Chem. Soc. 116 (1994) 11379.
[1847] D.P. Bender, J.K. Nagle, Inorg. Chim. Acta 225 (1994) 201.
[1848] C.M. Che, W.P. Schaefer, H.B. Gray, M.K. Dickson, P.B. Stein, D.M. Roundhill, J. Am. Chem. Soc. 104 (1982) 4253.
[1849] C.M. Che, F.H. Herbstein, W.P. Schaefer, R.E. Marsh, H.B. Gray, J. Am. Chem. Soc. 105 (1983) 4604.
[1850] S.A. Bryan, M.K. Dickson, D.M. Roundhill, J. Am. Chem. Soc. 106 (1984) 1882.
[1851] M. Yamashita, S. Miya, T. Kawashima, T. Manabe, T. Sonoyama, H. Kitigawa, T. Mitani, Synth. Metals 103 (1999) 2164.
[1852] M. Yamashita, S. Miya, T. Kawashima, T. Manabe, T. Sonoyama, H. Kitigawa, T. Mitani, H. Okamoto, R. Ikeda, J. Am. Chem. Soc. 121 (1999) 2321.
[1853] T. Kawashima, S. Miya, T. Manabe, M. Yamashita, K. Takizawa, T. Ishii, H. Mastuzaka, T. Sonoyama, H. Kitigawa, T. Mitani, H. Matsuzaki, H. Kishida, H. Okamoto, R. Ikeda, Mol. Cryst. Liq. Cryst. 342 (2000) 145.
[1854] S. Yamamoto, Condensed Matter (2001) 5.
[1855] S. Yamamoto, J. Physical Soc. Jpn. 70 (2001) 1198.
[1856] K. Marumota, H. Tanaka, S. Kozaki, S. Kuroda, S. Miya, T. Kawashima, M. Yamashita, Solid State Commun. 120 (2001) 101.
[1857] H. Mastuzaka, T. Matsuoka, H. Kishida, K. Takizawa, H. Miyasaka, K. Sugiura, M. Yamashita, H. Okamoto, Physical Rev. Lett. 90 (2003) 046401.
[1858] H. Mastuzaki, H. Kishida, K. Takizawa, M. Yamashita, H. Okamoto, Synt. Metals 135–136 (2003) 607.
[1859] H. Mastuzaki, H. Kishida, H. Okamoto, K. Takizawa, S. Matsunaga, S. Takaishi, H. Miyasaka, K. Sugiura, M. Yamashita, Angew Chem. Int. Ed. 44 (2005) 2.
[1860] W. Clegg, C.D. Garner, M.H. AlSamman, Inorg. Chem. 21 (1982) 1897.
[1861] M. Kubiak, Acta Crystallogr. C41 (1985) 1288.

[1862] D.P. Bancroft, F.A. Cotton, L.R. Falvello, W. Schwotzer, Inorg. Chem. 25 (1986) 1015.
[1863] K. Umakoshi, I. Kinoshita, A. Ichimura, S. Ooi, Inorg. Chem. 26 (1987) 3551.
[1864] W. Micklitz, J. Riede, B. Huber, G. Muller, B. Lippert, Inorg. Chem. 27 (1988) 1979.
[1865] K. Umakoshi, A. Ichimura, I. Kinoshita, S. Ooi, Inorg. Chem. 29 (1990) 4005.
[1866] J. Jolly, W.I. Cross, R.G. Pritchard, C.A. McAuliffe, K.B. Nolan, Inorg. Chim. Acta 315 (2001) 36.
[1867] K. Umakoshi, T. Yamasaki, A. Fukuoka, H. Kawano, M. Ichikawa, M. Onishi, Inorg. Chem. 41 (2002) 4093.
[1868] M.A. Haj, M. Quiros, J.M. Salas, Polyhedron 23 (2004) 2373.
[1869] K. Mashima, M. Tanaka, K. Tani, H. Nakano, A. Nakamura, Inorg. Chem. 35 (1996) 5244.
[1870] M.A. Benett, S.K. Bhargava, A.M. Bond, A.J. Edwards, S. Guo, S.H. Priver, A.D. Rae, A.C. Willis, Inorg. Chem. 43 (2004) 7752.
[1871] K. Umakoshi, Y. Sasaki, Adv. Inorg. Chem. 40 (1993) 187.
[1872] M. Corbelt, B.F. Hoskins, N.J. McLeod, B.P. O'Day, Aust. J. Chem. 28 (1975) 2377.
[1873] J. Barker, N. Cameron, M. Kilner, M.M. Mahmoud, S.C. Wallwork, J. Chem. Soc. Dalton Trans. (1986) 1359.
[1874] J. Barker, M. Kilber, R.O. Gould, J. Chem. Soc. Dalton Trans. (1987) 2687.
[1875] F.A. Cotton, M. Matusz, R. Poli, X. Feng, J. Am. Chem. Soc. 110 (1988) 1144.
[1876] C.L. Yao, L.P. He, J.D. Krop, J.L. Bear, Inorg. Chem. 27 (1988) 4389.
[1877] F.A. Cotton, J.H. Matonic, C.A. Murillo, Inorg. Chem. 35 (1996) 498.
[1878] R. Nast, J. Moritz, J. Organomet. Chem. 117 (1976) 81;
U. Behrens, K. Hoffman, J. Kopf, J. Moritz, J. Organomet. Chem. 117 (1976) 91.
[1879] H. Ogawa, T. Joh, S. Takahashi, K. Sonogashira, J. Chem. Soc. Chem. Commun. (1985) 1220.
[1880] H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto, H. Yamazaki, Organometallics 7 (1988) 2257.
[1881] K. Onitsuka, T. Joh, S. Takahashi, Angew Chem. Int. Ed. Engl. 31 (1992) 851.
[1882] K. Onitsuka, T. Joh, S. Takahashi, Bull. Chem. Soc. Jpn. 65 (1992) 1179.
[1883] K. Sünkel, U. Birk, C. Robl, Organometallics 13 (1994) 1679.
[1884] K. Onitsuka, S. Takahashi, J. Chem. Soc. Chem. Commun. (1995) 2095.
[1885] M. Younus, A. Kohler, S. Cron, N. Choudhury, M.R.A. Al-Mandhary, M.S. Khan, J. Lewis, J.J. Long, R.H. Friend, P.R. Raithby, Angew. Chem. Int. Ed. Engl. 37 (1998) 3036.
[1886] K. Campbell, C.A. Johnson II, R. McDonald, M.J. Ferguson, M.M. Haley, R.R. Tykwinski, Angew Chem. Int. Ed. 43 (2004) 5967.
[1887] M.V. Russo, C.L. Sterzo, P. Franceschini, G. Biagini, A. Furlani, J. Organomet. Chem. 619 (2001) 49.
[1888] T.B. Peters, Q. Zheng, J. Stahl, J.C. Bohling, A.M. Arif, F. Hampel, J.A. Gladysz, J. Organomet. Chem. 641 (2002) 53.
[1889] W.Y. Wong, C.K. Wong, G.L. Lu, K.W. Cheah, J.X. Shi, Z. Lin, J. Chem. Soc. Dalton Trans. (2002) 4587.
[1890] I. Fratoddi, C. Battocchio, A. Furlani, P. Mataloni, G. Polzonetti, M.V. Russo, J. Organomet. Chem. 674 (2003) 10.
[1891] Q. Zheng, F. Hampel, J.A. Gladsysz, Organometallics 23 (2004) 5896.
[1892] H. Zhang, A.W.M. Lee, W.Y. Wong, M.S.M. Yuen, J. Chem. Soc. Dalton Trans. (2000) 3675.
[1893] V.W.W. Yam, L. Zhang, C.H. Tao, K.M.C. Wong, K.K. Cheung, J. Chem. Soc. Dalton Trans. (2001) 1111.
[1894] V.W.W. Yam, C.H. Tao, L. Zhang, K.M.C. Wong, K.K. Cheung, Organometallics 20 (2001) 453.
[1895] M.S. Khan, M.R.A. Al Mandhary, M.K. Al Suti, N. Feeder, S. Nahar, A. Köhler, R.H. Friend, P.J. Wilson, P.R. Raithby, J. Chem. Soc. Dalton Trans. (2002) 2441.
[1896] F. Zhuravlev, J.A. Gladysz, Chem. Eur. J. 10 (2004) 1647.
[1897] C.H. Tao, N. Zhu, V.W.W. Yam, Chem. Eur. J. 11 (2005) 1647.
[1898] J. Manna, J.A. Whiteford, P.J. Stang, D.C. Muddiman, R.D. Smith, J. Am. Chem. Soc. 118 (1996) 8731.
[1899] J. Manna, C.J. Kuehl, J.A. Whiteford, P.J. Stang, Organometallics 16 (1997) 1897.
[1900] Y.J. Kim, S.W. Song, S.C. Lee, S.W. Lee, K. Osakada, Y. Yamamoto, J. Chem. Soc. Dalton Trans. (1998) 1775.
[1901] Y.J. Kim, S.C. Lee, M.H. Chao, S.W. Lee, J. Organomet. Chem. 588 (1999) 268.
[1902] M.G. Crisp, S.M. Pyke, L.M. Rendina, J. Organomet. Chem. 607 (2000) 222.
[1903] P. Teo, L.L. Koh, T.S.A. Hor, Inorg. Chem. 42 (2003) 7290.
[1904] L.C. Sawkins, B.L. Shaw, B.L. Turtle, J. Chem. Soc. Dalton Trans. (1976) 2053.
[1905] K. Nakatsu, K. Kinoshita, H. Kanda, K. Isobe, Y. Nakamura, S. Kawaguchi, Chem. Lett. (1980) 913.
[1906] M. Onishi, K. Hiraki, K. Maeda, T. Itoh, J. Organomet. Chem. 188 (1980) 245.
[1907] K. Nakatsu, K. Kafuku, H. Yamaoka, K. Isobe, Y. Nakamura, S. Kawaguchi, Inorg. Chim. Acta 54 (1981) L69.
[1908] M. Onishi, K. Hiraki, T. Itoh, Y. Ohama, J. Organomet. Chem. 254 (1983) 381.
[1909] H. Tanaka, K. Isobe, S. Kawaguchi, S. Okeya, Bull. Chem. Soc. Jap 57 (1984) 456.
[1910] T.A. Anderson, R.J. Barton, B.E. Robertson, K. Venkatasubramaian, Acta Cryst. 41C (1985) 1171.
[1911] B. Crociani, F. DiBianca, A. Giovenco, A. Sorivanti, J. Organomet. Chem. 291 (1985) 259.
[1912] R. Bertani, A. Berton, F. DiBianca, B. Crociani, J. Organomet. Chem. 303 (1986) 283.
[1913] K. Isobe, Y. Nakamura, S. Kawaguchi, Bull. Chem. Soc. Jap. 62 (1989) 1802.
[1914] C.C.H. Chin, J.S.L. Yeo, Z.H. Loh, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (1998) 3777.
[1915] G. Bomberi, G. Bruno, M. Cusumano, G. Guglielmo, V. Ricevuto, Polyhedron 4 (1985) 1365.
[1916] S. Lanza, Inorg. Chim. Acta 75 (1983) 131.
[1917] J.D. Scott, R.J. Puddephatt, Inorg. Chim. Acta 89 (1984) L27.
[1918] V.F. Sutcliffe, G.B. Young, Polyhedron 3 (1984) 87.
[1919] A.R. Siedle, K.R. Mann, D.A. Bohling, G. Filipovich, P.E. Toren, F.J. Palensky, R.A. Newmark, R.W. Duerst, W.L. Stebbings, H.E. Mishmash, K. Melancon, Inorg. Chem. 24 (1985) 2216.
[1920] W. Beck, E. Ambach, U. Nagel, Chem. Ber. 118 (1985) 444.
[1921] J.A. Broomhead, L.M. Rendina, M. Sterns, Inorg. Chem. 31 (1992) 1880.
[1922] P.S. Braterman, J.I. Song, C. Vogler, W. Kaim, Inorg. Chem. 31 (1992) 222.
[1923] A. Klein, S. Hasenzahl, W. Kaim, J. Fiedler, Organometallics 17 (1998) 3532.
[1924] M.C. Lagunas, R.A. Gossage, W.J.J. Smeets, A.L. Spek, G. van Koten, Eur. J. Inorg. Chem. (1998) 163.
[1925] F. Zhang, M.C. Jennings, R.J. Puddephatt, Organometallics 23 (2004) 1396.
[1926] W. Kaim, A. Dogan, M. Wanner, A. Klein, I. Tiritiris, T. Schleid, S.J. Stufkens, T.L. Snoeck, E.J.L. Mcinnes, J. Fiedler, Z. Zalis, Inorg. Chem. 41 (2002) 4139.
[1927] A. Satake, H. Koshino, T. Nakata, J. Organomet. Chem 595 (2000) 208.
[1928] C. Mazet, L.H. Gade, Organometallics 20 (2001) 4144.
[1929] W.D. McFadyen, R. Robson, H.A. Schaap, J. Coord. Chem. 8 (1978) 59.
[1930] J.G. Hughes, R. Robson, Inorg. Chim. Acta 35 (1979) 87.
[1931] J.G. Hughes, R. Robson, Inorg. Chim. Acta 36 (1979) 237.

[1932] M. Louey, P.P. Nichols, R. Robson, Inorg. Chim. Acta 47 (1980) 87.
[1933] P. Krautil, R. Robson, J. Coord. Chem. 10 (1980) 7.
[1934] C. Paolucci, P.A. Vigato, G. Rossetto, U. Casellato, M. Vidali, Inorg. Chim. Acta 65 (1982) L71.
[1935] R. Robson, Inorg. Chim. Acta 57 (1982) 71.
[1936] B.F. Hoskins, I.A.S. McDonald, Aust. J. Chem. 37 (1984) 1395.
[1937] B.F. Hoskins, I.A.S. McDonald, Aust. J. Chem. 37 (1984) 725.
[1938] M. Louey, C.J. McKenzie, R. Robson, Inorg. Chim. Acta 111 (1986) 107.
[1939] B.F. Hoskins, C.J. McKenzie, J.A.S. MacDonald, R. Robson, J. Chem. Soc. Dalton Trans. (1996) 2227.
[1940] C.J. McKenzie, R. Robson, J. Chem. Soc. Chem. Commun. (1988) 112.
[1941] V. Casellato, S. Tamburini, P.A. Vigato, A. DeStefani, M. Vidali, D.E. Fenton, Inorg. Chim. Acta 69 (1983) 45.
[1942] A.R. Siedle, L.H. Pignolet, Inorg. Chem. 21 (1982) 3090.
[1943] S. Okeya, S. Koshino, M. Namie, I. Nagasawa, Y. Kushi, J. Chem. Soc. Chem. Commun. (1995) 2123.
[1944] M. Kita, M. Nonoyama, Polyhedron 12 (1993) 1027.
[1945] S. Okeya, H. Yoshimatsu, Y. Nakamura, S. Kawaguchi, Bull. Chem. Soc. Jap. 55 (1982) 483.
[1946] G. Tresoldi, G. Bruno, P. Piraino, F. Faraone, G. Bombieri, Inorg. Chim. Acta 51 (1981) 263.
[1947] Z. Dawoodi, C. Eaborn, A. Pidcock, J. Organomet. Chem. 170 (1979) 95.
[1948] T. Yoshida, S. Tanaka, T. Adachi, T. Yoshida, K. Onitsuka, K. Sonogashira, Angew Chem. Int. Ed. Engl. 34 (1995) 319.
[1949] W. Beck, M. Keubler, E. Leidl, U. Nagel, M. Schaal, S. Cienini, P.D. Buttero, E. Licandro, S. Maiorana, A.C. Villa, J. Chem. Soc. Chem. Commun. (1981) 446.
[1950] D.E. Berry, G.W. Bushnell, K.R. Dixon, A. Pidcock, Inorg. Chem. 22 (1983) 1961.
[1951] E.H. Wong, F.C. Bradley, Inorg. Chem. 20 (1981) 2333.
[1952] E.E. Nifantev, T.S. Kukhareva, M.Yu Antipin, Yu.T. Struchkov, J. Gen. Chem. USSR 52 (1982) 2413.
[1953] R. Jones, P.F. Kelly, D.J. Williams, J.D. Woollins, J. Chem. Soc. Chem. Commun. (1985) 1325.
[1954] C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, J. Organomet. Chem. 286 (1985) 419.
[1955] K.C. Kalia, M. Singla, A. Kumar, Trans. Met. Chem. 7 (1982) 151.
[1956] P.K. Mascharak, A. Chakravorty, Indian J. Chem. 18A (1979) 471.
[1957] P.K. Mascharak, A. Chakravorty, J. Chem. Soc. Dalton Trans. (1980) 1698.
[1958] G.K. Anderson, M. Lin, M.Y. Chiang, Organometllics 9 (1990) 288.
[1959] G.K. Anderson, M. Lin, N.P. Rath, Organometallics 9 (1990) 2880.
[1960] M. Lin, K.A. Fallis, G.K. Anderson, N.P. Rath, M.Y. Chiang, J. Am. Chem. Soc. 114 (1992) 4687.