NICKEL, PALLADIUM AND PLATINUM, ANNUAL SURVEY COVERING THE YEAR 1979 [*]

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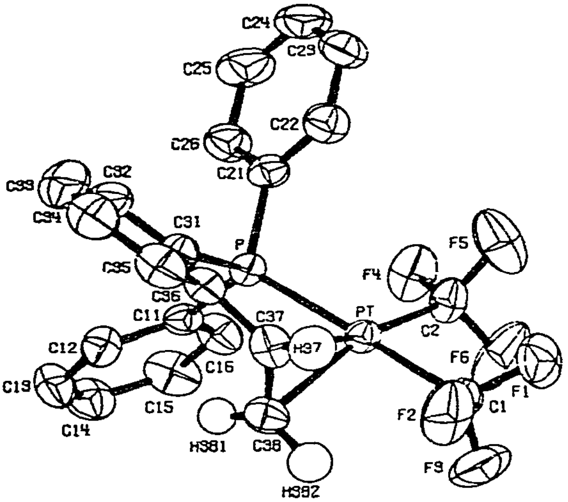
[*] Nickel, palladium and platinum; Annual Survey covering the year 1978 see J. Organometal. Chem., 196(1980) 175-293

I. Metal-carbon complexes

Data have been reported for the content of organometallic nickel in marine samples [1]. The reaction between methylcobalamin and $PtCl_6^{2-}$ gives platinum(II) complexes $PtMeCl_3^{2-}$. Complete demethylation requires 2 equivalents of $PtCl_4$. A second compound is formed which is possibly $PtMe(H_2O)Cl_2^-$ [2].

The ^{31}P nmr spectra of the compounds [cis-M(L)Me(dppe)]PF_6(M=Pd,Pt; L=4-C_5H_4NX; X=Me, H, NMe_2, CO_2Me, COMe, CN) show a regular decrease in $\delta(^{31}P)$ and $J(^{31}P-^{195}Pt)$ as the ρ value of the substituent X on the pyridine decreases. The trends are attributed to decreasing lone pair donation from phosphorus as the electron donating ability of the other ligands on the metal increases [3]. The crystal structures of the platinum(II) complexes trans-$PtClR(PMePh_2)_2$ (R=Me, CF_3, C_2F_5) show respective bond lengths for Pt-C of 2.08, 2.09 and 2.00 (average). The shorter value in the third compound is attributed to the electrostatic effect of a positive charge induced on the ligating carbon atom by the electronegative fluorine atoms. Discussion relating to estimating the trans influence of the C_2F_5 group is presented [4]. In the following paper the crystal and molecular structures of the compounds dimethyl[(2-vinylphenyl)diphenylphosphine] platinum(II) and bis(trifluoromethyl)[(2-vinylphenyl)diphenylphosphine]platinum(II) (1) have been solved [5]. The structure of (1) is shown with the π-bonded vinyl group being coordinated almost normal to the metal coordination plane.



(1)

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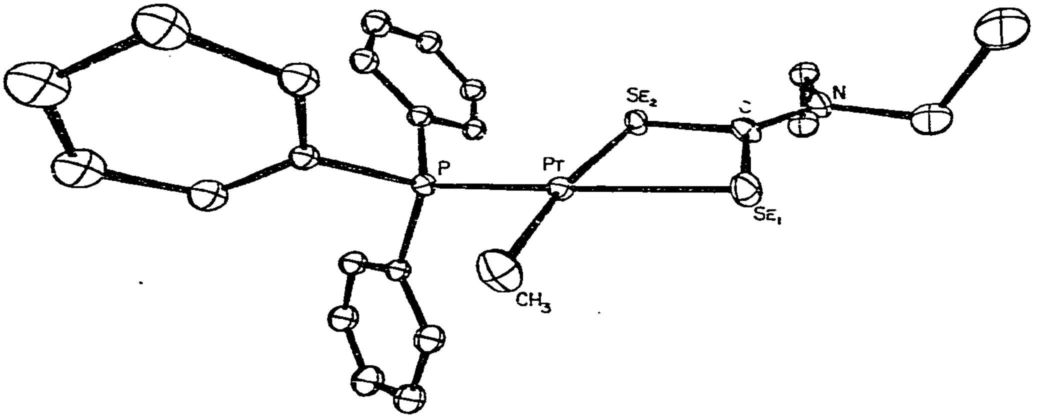
An nmr study has been made of complexes $PtMe_3(AA)L$ and $PtMe_3(AA)_2^-$ (L = MeOH,3,5-lutidine; HAA = amino acid). When the amino acid contains an asymmetric carbon atom diastereomers are formed. The effects of various substituents on the amino acid on the relative proportions of isomers, and on the chemical behavior of the compounds have been investigated [6]. The reaction of $Pt(Se_2CNEt_2)_2$ with $PtMe_2(PPh_3)_2$ gives $Pt(Se_2CNEt_2)Me(PPh_3)$ (2). The compound exists as discrete monomers of an essentially planar $PtSe_2PC$ core. The Pt-Me falls in the usual range [7]. A kinetic study has been made of the biomethylation reaction between platinum and methylcobalamin. An "outer-sphere" complex is formed between charged Pt(II) salts on the corrin macrocycle, which catalytically labilizes the Co-C σ-bond to electrophilic attack [8].



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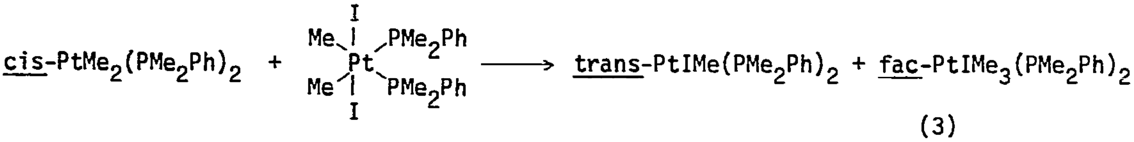
The compound cis-$PtMe_2(PMe_2Ph)_2$ reacts with $PtX_2Me_2(PMe_2Ph)_2$ (X = I, NO_2, NO_3) to give $PtXMe(PMe_2Ph)_2$ and $PtXMe_3(PMe_2Ph)_2$ (3). By labelling studies it is shown that when X = NO_3 the reaction occurs by methyl for nitrate exchange rather than by a redox mechanism [9]. The UV photolysis of methylplatinum complexes has been studied both in the absence and presence of deuterated solvents. The data is in agreement with the formation of free radicals in the reaction [10]. The bond energies ΔH of the reaction of $Pt(PPh_3)_2C_2H_4$ have been found to be -176, -108 and -79 kJ mol^{-1}. The difference in bond energy between Pt-Me and Pt-I is small [11]. The ^{31}P, ^{13}C, and ^{195}Pt nmr spectra of the compounds $PtMe_2[Ph_2P(CH_2)_nPPh_2]$ have been compared with the spectra of the compound cis-$PtMe_2(PMePh_2)_2$ [12]. Irregularities in the nmr parameters can be explained on the basis of the existence.



$$\underline{cis}\text{-}PtMe_2(PMe_2Ph)_2 + PtI_2Me_2(PMe_2Ph)_2 \longrightarrow \underline{trans}\text{-}PtIMe(PMe_2Ph)_2 + \underline{fac}\text{-}PtIMe_3(PMe_2Ph)_2$$

(3)

$$Pt(PPh_3)_2(C_2H_4)\ (s) + I_2\ (g) \longrightarrow \underline{trans}\text{-}Pt(PPh_3)_2I_2(s) + C_2H_4\ (g)$$

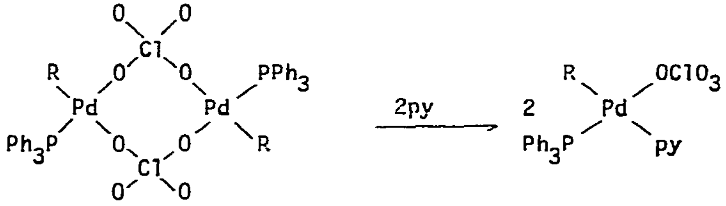
$$Pt(PPh_3)_2(C_2H_4)\ (s) + CH_2ICH_2I\ (g) \longrightarrow \underline{cis}\text{-}Pt(PPh_3)_2I_2\ (s) + C_2H_4(g)$$

$$Pt(PPh_3)_2(C_2H_4)\ (s) + CH_3I\ (g) \longrightarrow \underline{cis}\text{-}Pt(PPh_3)_2MeI\ (s) + C_2H_4\ (g)$$

of angle strain for 4-membered but not for 5-membered rings. Alkyllithium reagents RCH_2Li react with nickelocene to give methylidene trinickel cluster compounds. These compounds $RCNi_3(\eta^5\text{-cp})_3$ (R = Ph, CMe_3, $SiMe_3$) have also been obtained by treating the σ-alkylnickel complexes $(\eta^5\text{-cp})Ni(CH_2R)(PPh_3)$ with n- BuLi in the presence of excess nickelocene [13].

X-ray photoelectron spectroscopy nickel $2p_{2/3}$ binding energies have been measured for a series of trans square planar $Ni(X)(Y)(PEt_3)_2$ complexes and correlated with a calculated "charge parameter" for the nickel atoms. A good correlation for X,Y being chloro, alkyl, vinyl, acyl or phenyl, but not when both X and Y are acetylide. This failure is considered to be due to considerable π-character in the Ni-C bonds and it is suggested that such π-character is minimal in the other compounds [14].

A series of stilbene bromohydrin compounds PhCHBrCHYPh (Y = OAc, OSO_2Me, OMe, SMe) react with $Pd(PPh_3)_4$ with β-elimination to give stilbene. The stereochemistry of the elimination is only selective for the case of the dibromide where anti-selectivity is observed [15]. Dinuclear complexes $[PdX(R)(PPh_3)]_2$ (R = 2-(6-chloropyridyl) containing ClO_4, BF_4^- and PF_6^- as bridging ligands X have been prepared and characterized (4) [16] . Reaction with pyridine converts these anions into the unidentate ligands giving rise to the more stable compounds (5). A palladium alkyl intermediate is postulated in the palladium catalyzed cyclization of α-substituted N-acryloyl-o-bromoanilines to oxindole derivatives [17]. The compounds $MCl(CH_2CN)(PPh_3)_2$ (M = Pd,Pt) react with 8-hydroxyquinoline and 8-mercaptoquinoline to give a single isomer which is given the structure (6)[18]. The reaction of the compounds $MCl(CH_2SR)(PPh_3)_2$ (M=Pd, Pt) with electrophiles has been studied. With methyl iodide there is formation of methyl chloride. A



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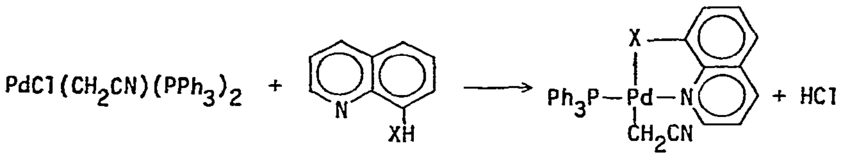
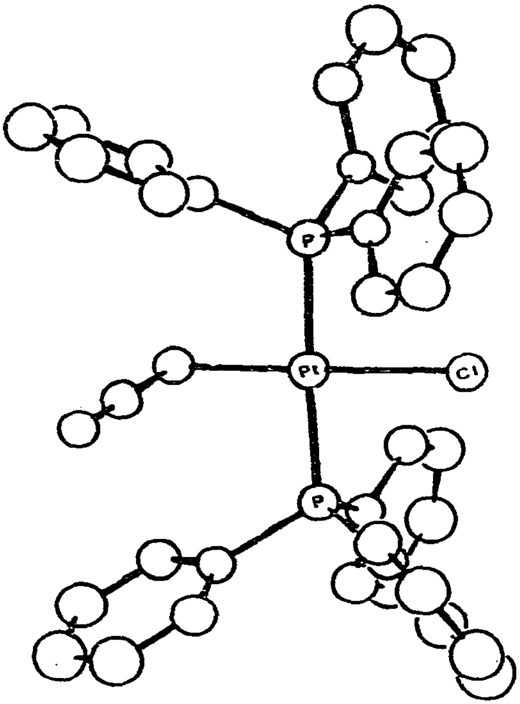


(6)

sequence involving a sulfonium intermediate is shown [19]. The addition of alcohols, thiols, water and amines to the coordinated CN group of cis-[Pd(o-$CH_2C_6H_4CN)L_2](BF_4)_2$ (L= $2PPh_3$, dppe) leads to stable N-bonded iminoether, iminothioether, amide and amidine complexes respectively [20]. The structure of trans-$PtCl(CH_2CN)(PPh_3)_2$ (7) has a Pt-C distance of 2.08 A [21]. The structure of

$$\begin{tikzcd}
\text{trans-}L_2MCl(CH_2SR) + R'X \arrow[r] \arrow[d, shift right, "R'X"'] & L_2MCl(R')X(CH_2SR) \arrow[d] \\
\left[L_2ClM\text{-}CH_2SRR'\right]^{+}X \arrow[r] \arrow[u, shift right] & \text{trans-}L_2M(X)CH_2SR + R'Cl
\end{tikzcd}$$



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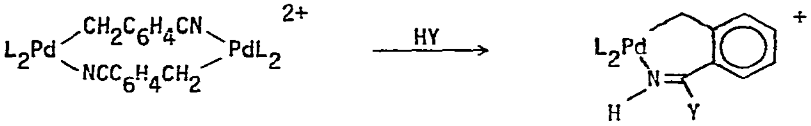
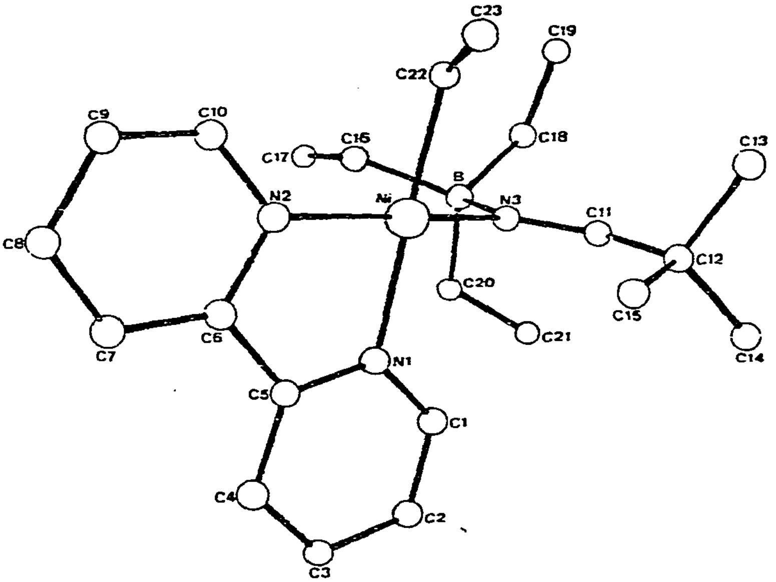


(Y= OH, OMe, SMe, SCH_2Ph, NMe_2)

(bipy)NiEt(N=CHR'BEt_2) (8), prepared from $NiBr_2$ or Ni(acac) and iminoborate compounds in the presence of 2,2'-bipyridine, shows a Ni-C distance of 1.97 Å [22].



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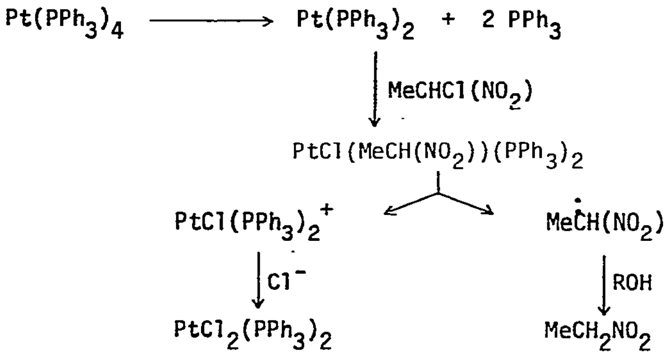
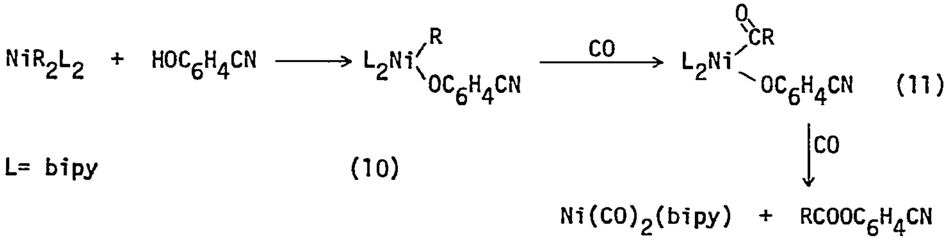
The reaction between K_2PtCl_4 and a variety of tetraorganotin compounds $SnMe_3R$ (R=Me, aryl) in DMSO gives the complexes cis-$PtR_2(DMSO)_2$ and trans-PtR(Cl)$(DMSO)_2$. The reaction conditions are given and the DMSO is bonded via the S atom [23]. In an article describing the reactions of atomic metal ions with alkyl halides and alcohols in the gas phase the number of carbonyls displaced from $Ni(CO)_4$ by RX has been measured as well as the reaction of Ni^+ with CH_3I. The latter reaction gives 100% of MI^+ + Me and no product MMe^+ + I [24]. The oxidative addition of 1-chloro-1-nitroethane with $Pt(PPh_3)_4$ gives nitroethane and cis-$PtCl_2(PPh_3)_2$ as main products. The mechanism of the reaction involves radicals [25]. The reactivity of a series of Ni(0) complexes and $NiEt_2$(bipy) to diethyl malonate shows that only complexes with a high electron density at the central metal atom are able to react under oxidative substitution. From $NiEt_2$(bipy), the complex (9) is formed [26].



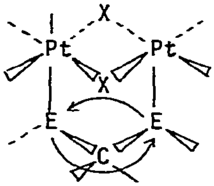
The reaction of $NiR(O\text{-}\underline{p}\text{-}C_6H_4CN)(bipy)$ (R= Et,Me) (10) with one mole of CO yields $Ni(COR)(O\text{-}\underline{p}\text{-}C_6H_4CN)(bipy)$ (R= Et,Me) (11). Esters are formed when (11) is treated with a π-acid such as CO [27]. The VSEPR model has been applied to alkyl transition metal compounds [28]. A rationalization has been developed for the large interbond angles at α-carbon atoms, and for intramolecular non-bonded atomic radii for a series of elements, including platinum.

$$NiEt_2(bipy) + 2\ CH_2(CO_2Et)_2 \longrightarrow Ni[CH(CO_2Et)_2]_2 + 2\ C_2H_6 \qquad (9)$$



^{19}F and ^{31}P nmr data for the series of complexes trans-$PtX(SCF_3)(PEt_3)_2$ (X=Ph,Me,H,CF_3,C_2F_3,CN,NO,SCF_3,N_3,I,NCS,Br,Cl,NO_3); cis-$PtX(SCF_3)(PEt_3)_2$ (X= Me, NO_2, SCF_3, N_3, NCS, NCO, Cl); trans-$PtX(C_2F_3)(PEt_3)_2$ (X= CN, NO_2, SCF_3, N_3, I, Br, Cl, NO_3); trans-$[Pt(C_2F_3)(PEt_3)_2L]ClO_4$ (L= PEt_3, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, PPh_3, CO, py) have been used to establish scales of cis- and trans-influence for X and L. It is concluded that the cis- effect may be much more sensitive to π-bonding, and also to steric effects, than is the trans- influence [29]. The compound $PtMe_3(SMe)$ has been prepared and is tetrameric in solution ($CHCl_3$) and in the vapor state. The synthesis uses $[PtMe_3]_2SO_4$ and NaSMe [30].

In a theoretical paper using MO-SCF-CI calculations it has been found that dimethylnickel should have a linear, high-spin ground state. The nickel-carbon bonds are predicted to be strong. Bending the molecule leads to considerable reduction in bond strength. Only the single state of the bent molecule has the correct symmetry for concerted reductive elimination, which may require thermal excitation to this state [31]. A series of complexes $PtMe_2$(polyphosphine) have been prepared and studied by ^{31}P nmr. The tridentate and tetradentate phosphines function as bidentate ligands at low temperature. Some of these compounds undergo rapid exchange of the terminal phosphine ligands [32]. The binuclear complexes (±)-$(Me_3PtS)_2MeE(CHR)_nEMe$(E=S,Se; X= Cl,Br,I; R= H,Me; n= 0,1) show a series of fluxional phenomena over a range of temperatures. One of these is an intermetallic commutation by the two donor atoms of the bidentate S and Se ligands (12) [33]. A trimethylplatinum complex has been prepared using the theophyllinate ligand. The complex is proposed to have a cyclic trimetallic structure [34]. The tetrameric $(Me_3PtBr)_4$ compound reacts with Me_2Se_2 and Me_2Se to give $(Me_3PtBr)_2MeSeSeMe$ (13) and $Me_3PtBr(Me_2Se)_2$. The structure of (13) shows a novel diselenide bridge [35]. The compound $[Pt_2Me_3(dppm)_2]^+$ has a unique structure involving a previously unpostulated conformation for a dppm bridge binuclear complex (14) [36]. Reaction of the diplatinum(I) complex $Pt_2Cl_2(\mu\text{-dppm})_2$ with CH_2N_2, SO_2, and S_8 gives adducts $Pt_2Cl_2(\mu\text{-X})(dppm)_2$ (15) where X is CH_2, SO_2, or S [37]. The structure of trans-$Pd(CO_2Me)(OCOMe)(PPh_3)_2$ has a unidentate acetate ligand and respective Pd-O and Pd-C distances of 2.116 Å and 1.984 Å.



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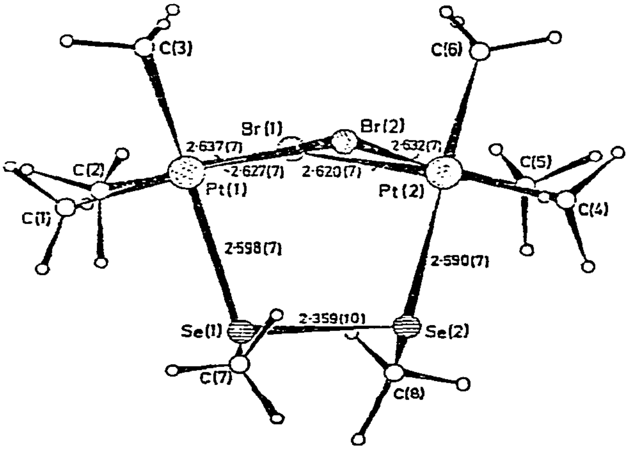

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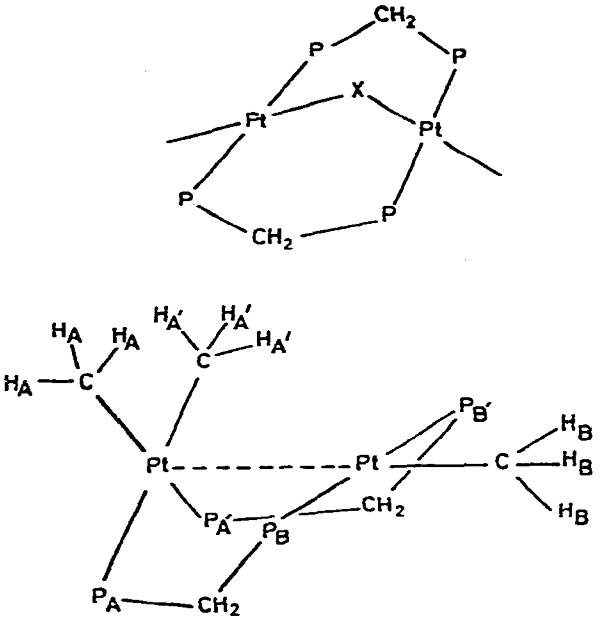

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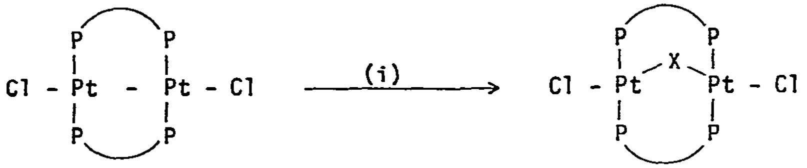
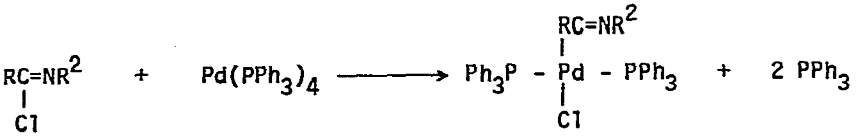
The observance of a monodentate acetate ligand is reported to be unique for acetatopalladium compounds [38].



(15)

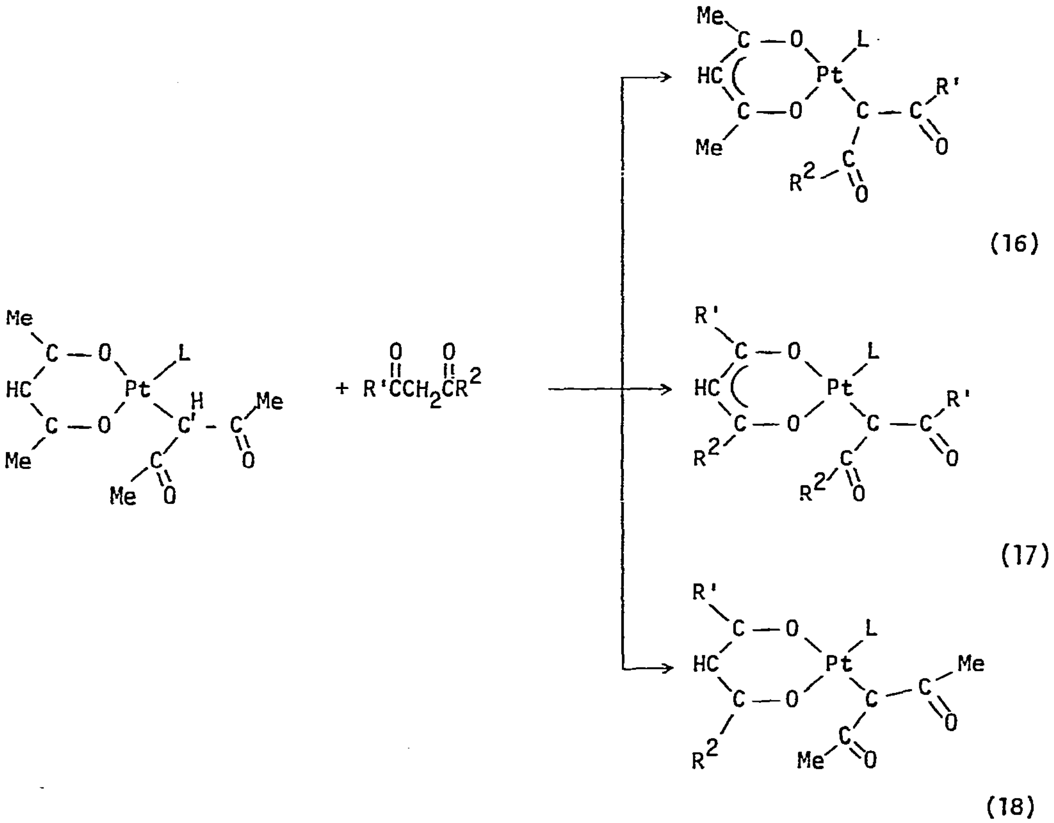
X= CH_2 ; (i)= CH_2N_2
X= (i) = SO_2
X= S ; (i)= S_8

Palladium carbon σ-bonds have been formed by the oxidative addition of imidoyl chlorides to the compound $Pd(PPh_3)_4$ [39]. Carbon bonded acetylacetonato



$$\underset{\displaystyle Cl}{\overset{}{RC{=}NR^2}} + Pd(PPh_3)_4 \longrightarrow Ph_3P - \overset{\displaystyle RC{=}NR^2}{\underset{\displaystyle Cl}{Pd}} - PPh_3 + 2\ PPh_3$$

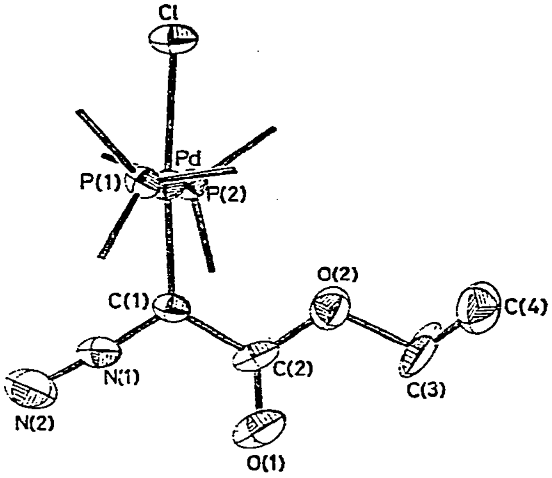
complexes of platinum(II) and palladium(II), M(acac)(γ-acac)(PPh_3) give different types of complexes (16, 17, 18) when reacted with β-dicarbonyl compounds [40].



(16) R'= R^2= OMe; R'=Me, R^2=OMe; R= Me, R^2= OEt
(17) R'= Me, R^2= Ph
(18) R'= Me, R^2= Ph; R'=R^2=Ph

The structure of the first α-diazomethyl group VIII transition metal complexes (19) shows the ligand coordinated to palladium via carbon [41]. A metal carbon bond is also found in the complex $Pt(SPh)(PhSCSO)(PPh_3)_2$. The structure (20) has been verified by X-ray crystallography [42].

A study has been reported on exchange mechanisms involving platinacyclobutanes. The authors conclude that their data are consistent with an intramolecular rearrangement process [43]. The crystal structure of carboxymethylpalladium(triphenylphosphine)pyridine (21) shows the palladium atom is C,O-chelated by an acetic acid to give a 4-membered ring [44]. In a further article on the isomerization of platinacyclobutanes the isomerization has been found to be intramolecular [45]. Skeletal isomerization of platinacyclobutane complexes between (22) and (23) has been investigated. Steric effects are dominant in favoring (23). Isomerization is retarded by added ligand L, and for R= p-tolyl and L= py the approach to



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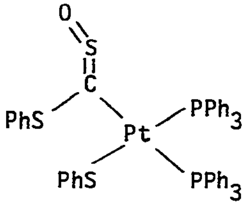

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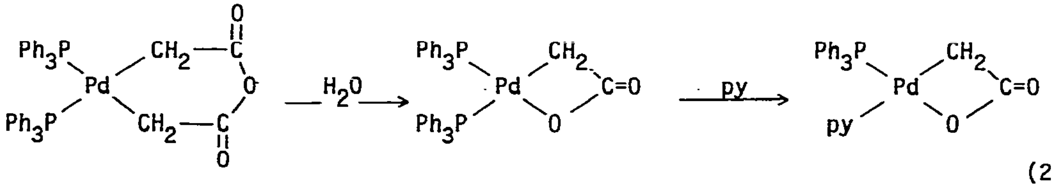
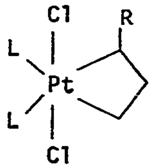


(21)

equilibrium follows first-order kinetics, and a linear correlation between the reciprocal of the observed rate constant and py is demonstrated. A mechanism



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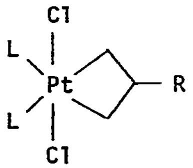
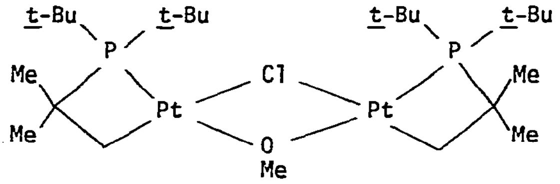


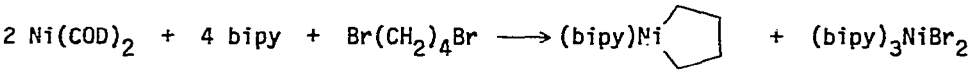
(23)

involving reversible dissociation of ligand L, followed by skeletal isomerization of the resulting five-coordinate platinum(IV) complex is proposed [46]. A methoxyplatinum(II) complex having a metal—carbon σ bond has been prepared. The symmetrical structure (24) has been proposed based on the ^1H and ^{31}P nmr data [47].

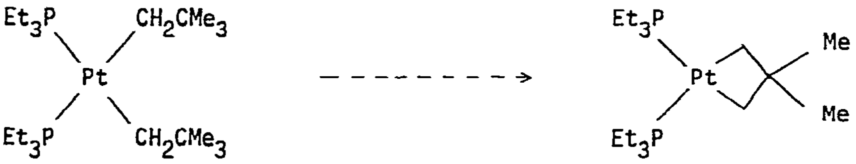


(24)

The compound bipyridylnickelacyclopentane (25) has been prepared from 1,4-dibromobutane and $Ni(COD)_2$ [48]. In a study of the thermal conversion of dineopentylbis(triethylphosphine)platinum(II) (26) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (27) it is found that the cleavage of an unactivated C-H bond proceeds by an oxidative addition to the platinum atom of a reactive trialkylphosphine dialkylplatinum(II) moiety [49].



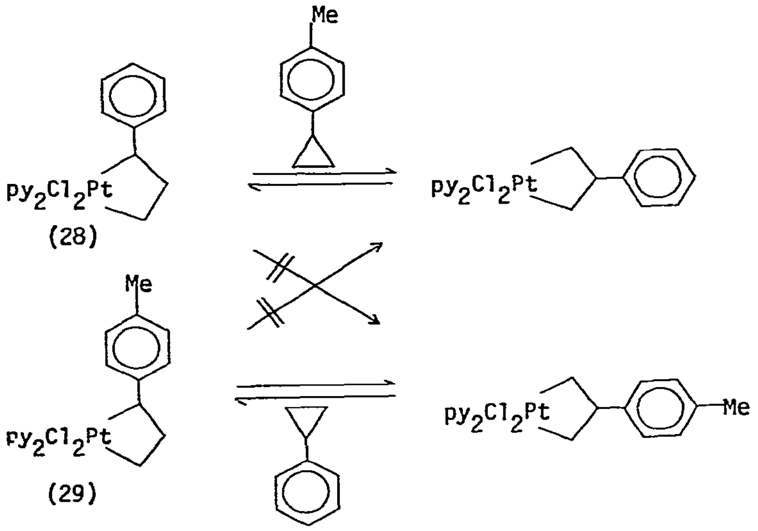
$$2\ Ni(COD)_2 + 4\ bipy + Br(CH_2)_4Br \longrightarrow (bipy)Ni\square + (bipy)_3NiBr_2 \qquad (25)$$



(26) (27)

In a further study on platinacyclobutanes, no crossover products were observed in the rearrangement of (28) to (29) in the presence of p-tolylcyclopropane or p-methylstyrene [50]. Labelling experiments were performed and their stereochemical consequences discussed. Deuterated platinacyclobutanes were decomposed to give deuterium labelled 2,3-dimethylbut-1-enes. The olefins are formed by a β-hydrogen abstraction followed by a reductive elimination, and an α-hydrogen abstraction process is not operative [51]. The thermolysis of metallacycles has been considered from an orbital symmetry approach and a rationalization presented for the effects of other ligands about the metal [52].

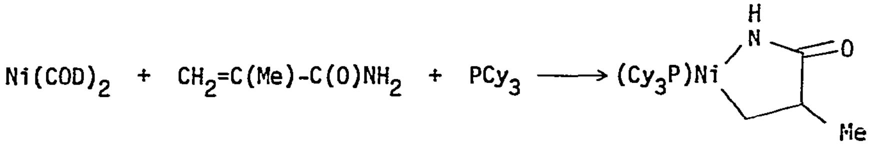
The reaction of $Ni(COD)_2$ with methacrylamine and PCy_3 gives a nickelacyclic amide complex (30) [53]. Reacting equimolar quantities of PtL_4 (L= PPh_3, $AsPh_3$) with indan-1,2,3-trione or 2,2-dihydroxyindan-1,3-dione gives a side-bonded



(28)

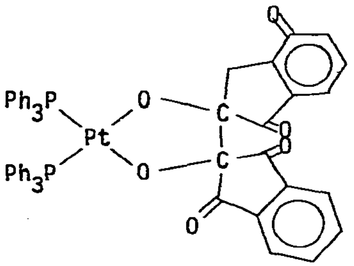
(29)

ketone complex which undergoes ring expansion with indan-1,2,3-trione. This



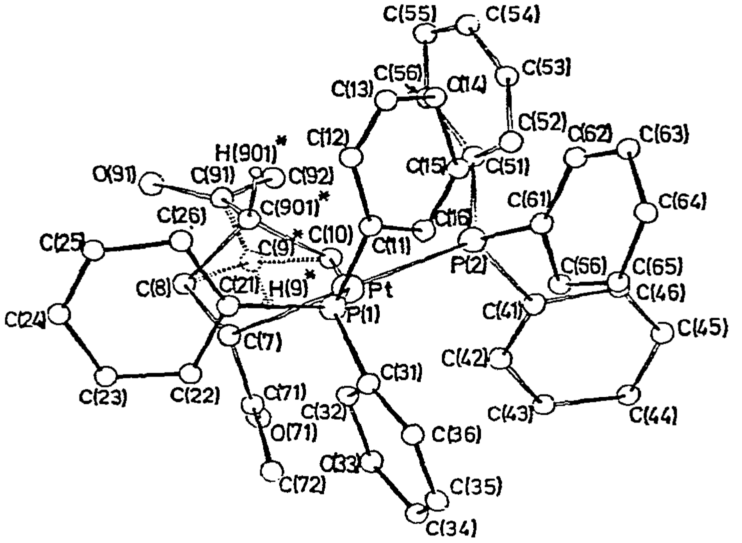
(30)

complex has the structure (31) which has been confirmed by x-ray crystallography [54]. Pt(COD)$_2$ reacts with methylvinyl ketone at -20° to give either



(31)

Pt[η^2-CH$_2$=CHC(Me)=O]$_2$COD or Pt[η^2-CH$_2$=CHC(Me)=O]$_3$. The former isomerizes to a platinacyclopentane Pt[CH$_2$CH(C(Me)=O)CH$_2$CH(C(Me)=O]COD, from which the COD group may be replaced by CNBu-t or PPh$_3$ to give Pt[CH$_2$CH(C(Me)=O)CH$_2$CH(C(Me)=O]L$_2$ (L= CNBu-t, PPh$_3$). The structure of the PPh$_3$ complex (32) has been solved.



(32)

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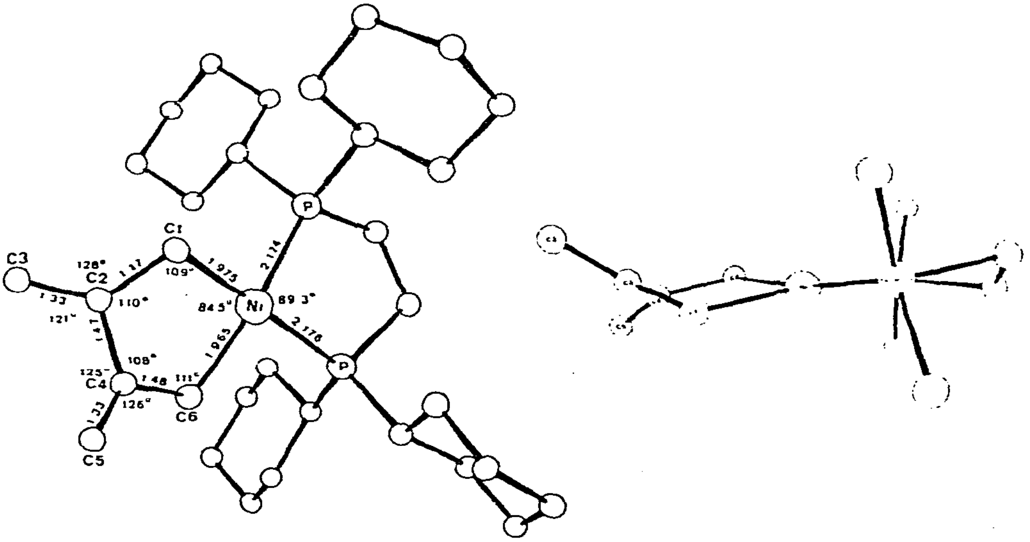
Reactions with O_2, $(CF_3)_2CO$ and $(CF_3)_2C{=}C(CN)_2$ are reported [55]. The reaction between allene, Ni(0) and a chelating phosphine gives a bis-methylenenickelacyclopentane derivative (33), the structure of which has been confirmed crystallographically [56].



(33)

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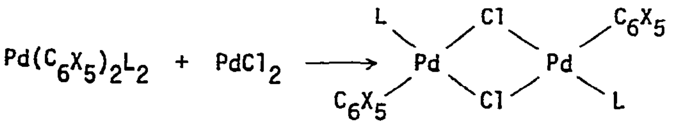
Platinum(IV) phenyl complexes have been detected by ^1H and ^{13}C nmr in reaction mixtures containing benzene with H_2PtCl_6 and Na_2PtCl_4 [57]. Arylnickel complexes are intermediates in the synthesis of heterocyclic compounds using $NiCl_2(PPh_3)_2$ [58]. A series of reactions of $PtCl_2(COD)$ with aryl and alkyl tin complexes have been reported leading to the isolation of the compounds $PtClMe(COD)$, $[Pt(C_6H_4SMe\text{-}\underline{p})_2]_n$, $Pt(COD)(C_5H_4FeC_5H_5)Cl$, $Pt(COD)Cl(C_5H_4FeC_5H_5)Cl(COD)Pt$. The ^{13}C nmr and electronic spectra are discussed [59]. Reactions between $Pt(C_2H_4)(PPh_3)_2$ and organotin halides lead to insertion into either Sn-Cl or Sn-C bonds. Competition experiments indicate an order of reactivity in the oxidative addition reaction: $SnMe_4 < SnPh_4 < SnMe_3Cl < SnMe_2Cl_2 < SnPh_2Cl_2, SnMeCl_3 < SnPhCL_3 < SnCl_4$. The presence of radicals in the reaction mixture was not detected by radical transfer or spin-trapping experiments [60]. The reactions of trans-$[PtCl(CO)(PPh_3)_2]ClO_4$ have been used to prepare a wide range of alkyl and aryl platinum compounds. Reaction pathways are suggested to explain the variety of transformations [61]. Similarly the reactions of cis-$Pt(O_2CCF_3)_2(PMe_2Ph)_2$ with $SnRMe_3$ (R= aryl) have been investigated and a series of platinum-carbon bonded compounds isolated [62].

Palladium aryl complexes have been used in the arylation of vinyl sulfides [63]. The oxidative addition of aryl halides to Ni(0) triethylphosphine complexes gives trans-arylhalonickel(II) compounds, together with paramagnetic nickel(I) halides. The product ratio is dependent on halide, substituent, and solvent polarity. Kinetic and other studies are presented and the mechanisms discussed in relation to concerted or radical-chain processes [64]. The mechanism of the nickel catalyzed coupling of aryl halides to biaryls involves a radical-chain process involving paramagnetic Ni(I) and arylnickel(III) species. The initiation of the catalytic cycle is associated with electron transfer from trans-$ArNiX(PEt_3)_2$ to ArX, and it can be manipulated by choice of initiators and inhibitors [65].

A series of cationic complexes trans-$[C_6Cl_5Ni(PPhMe_2)_2L]X$ (L=CNMe, $C(NMeH)_2$, $C(NMeH)NMe_2$, $C(OMe)NMeH$, $C(OEt)NMeH$, $C(OMe)NMe_2$, $C(OMe)_2$; X= SO_3F, ClO_4, PF_6) and trans-$C_6Cl_5Ni(PPhMe_2)(C(OMe){=}NMe)$ have been prepared. These complexes contain both a pentachlorophenyl and a carbene moiety [66]. Preparative routes and spectra of the complexes are presented. Dimeric compounds are of general formula $[Pd(\mu\text{-}Cl)RL]_2$ ($R{=}C_6F_5$, C_6Cl_5; L is a neutral N,P,As,Sb,S donor ligand). The synthetic route involves the addition of the two mononuclear fragments together to form the bridged product (34) [67]. The Grignard method has been used to prepare

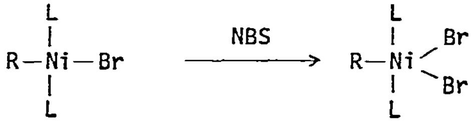


(34)

complexes $NiXR(PEt_3)_2$ ($R=C_6Cl_5$, 2,3,4,5-, 2,3,4,6- and 2,3,5,6-C_6Cl_4H or 2,4,6- and 2,3,6-$C_6Cl_3H_2$). Metathetical replacement has been used to expand the number of new compounds [68]. Similar new compounds $NiX(C_6Cl_5)bipy$ have been isolated. Substitution with PEt_3, PPh_3 and dppe has been studied, and addition of HCl to cis-$Pd(C_6Cl_5)_2(PEt_3)_2$ leads to Pd-C cleavage [69]. Paramagnetic organonickel (III) complexes $RNi(PPhMe_2)_2Br_2$ ($R=CCl_2{=}CCl$ or C_6Cl_5) (35) have been prepared from

$$Pd(C_6Cl_5)_2(PEt_3)_2 + HCl \longrightarrow PdCl(C_6Cl_5)(PEt_3)_2 + C_6Cl_5H$$

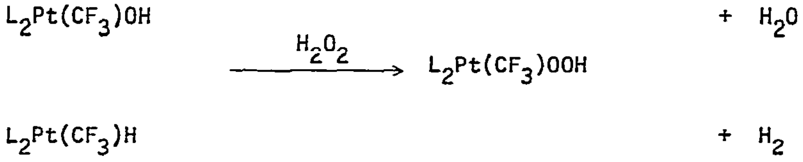
trans-$RNi(PPhMe_2)_2Br$ with N-bromosuccinimide [70]. In the following communication



(35)

the reactions of some diorganonickel(II) complexes with N-bromosuccinimide leads to facile bromine for hydrogen substitution in aromatic, alkynyl or alkenyl substituents, or in addition of NBS to C=C bonds [71].

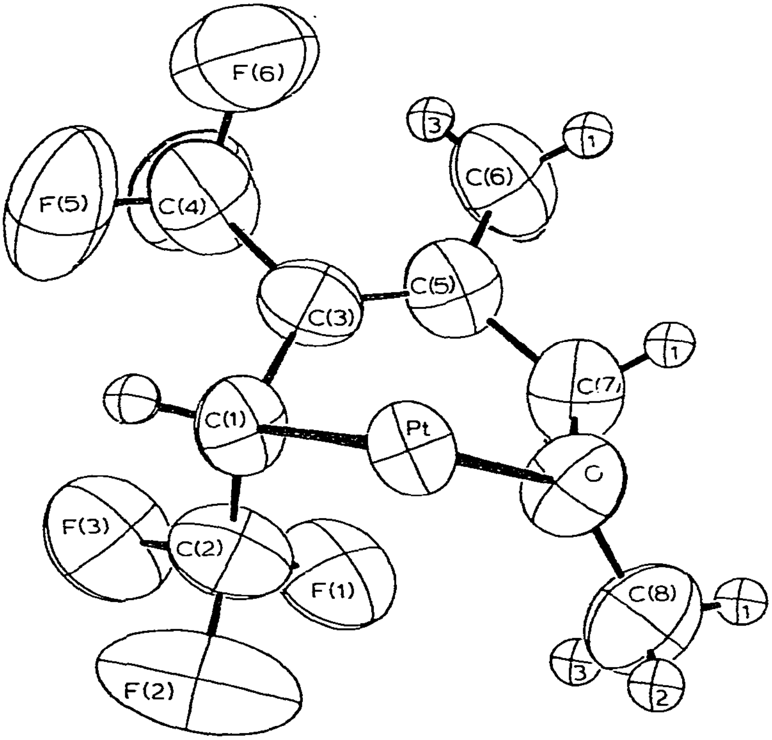
The crystal structure of $PtCl(CF_3)$(cis-$Ph_2PCH{=}CHPPh_2$) has values of 2.275 Å for Pt-P trans to CF_3, and a distance of 2.188 Å for Pt-C. The coordination about Pt is typically square planar [72] . A Pt-CF_3 compound has been reported containing also a coordinated hydroperoxide ligand. The compound (36) is prepared from the reaction of either $L_2Pt(CF_3)OH$ or $L_2Pt(CF_3)H$ with hydrogen peroxide [73].



$$\begin{array}{lcl} L_2Pt(CF_3)OH & & + \ H_2O \\ & \xrightarrow{H_2O_2} L_2Pt(CF_3)OOH & \\ L_2Pt(CF_3)H & & + \ H_2 \end{array}$$

(36)

The reaction of $[Pt\{(CF_3)C{=}CH(CF_3)\}(PEt_3)_2CH_3OH]PF_6$ with allene in methanol yields a metallocyclic complex $[\overline{Pt\{(CF_3)CHC(CF_3){=}C(Me)CH_2O}Me\}(PEt_3)_2]PF_6$ (37) [74]. The structure of (37) is shown. Reaction pathways to the formation of the complex are discussed. Alkyl palladium complexes (38) having an oxo bridge have been obtained using potassium superoxide [75]. The bridge splitting reactions of bis[(2-methoxy-5-cyclooctenyl)iodoplatinum(II)] by ligands leads to an equilibrium mixture of two stereoisomers. The stronger the σ-donor character of L the higher the proportion of the isomer having L in a cis position to the Pt-C σ bond [76].



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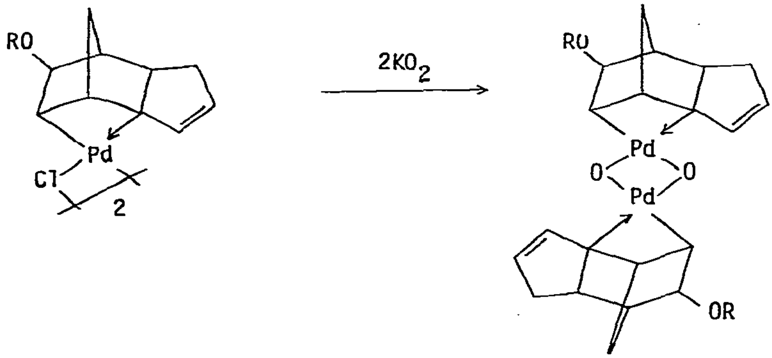
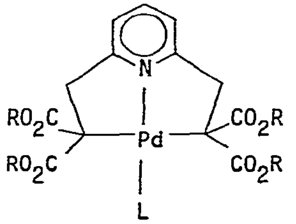
A complex (39) has been reported with two Pd-C σ bonds [77]. Both a methyl and a cyanomethyl complex of Pt have been reported having a chelating triphosphine as additional coordinating groups [78]. The reaction of cyanogen with Ni(acac)$_2$



(38)

has been studied and the products isolated and characterized [79]. A carbon-phosphorus bond cleavage has been found in the reaction of $MCl_2(PR_3)_2$ (M= Ni, Co, Pd; R= Ph, n-C_8H_{17}) with p-tolyllithium, p-tolylmagnesium halide, lithium aluminum hydride or magnesium amalgam. The thermal decomposition of Ni(mesityl)X$(PEt_3)_2$ (X= mesityl or Br) at 30° gives vinyl mesitylene [80]. Treating $Pd(OAc)_2$ in acetic acid at room temperature with PPh_3 in the presence of styrene gives trans-stilbene, H_3PO_4, $PhP(O)(OH)_2$, $Ph_2P(O)(OH)$ and $Ph_3P{=}O$. Phenylpalladium species are considered to be involved in these reactions [81].



R= Me; L= py

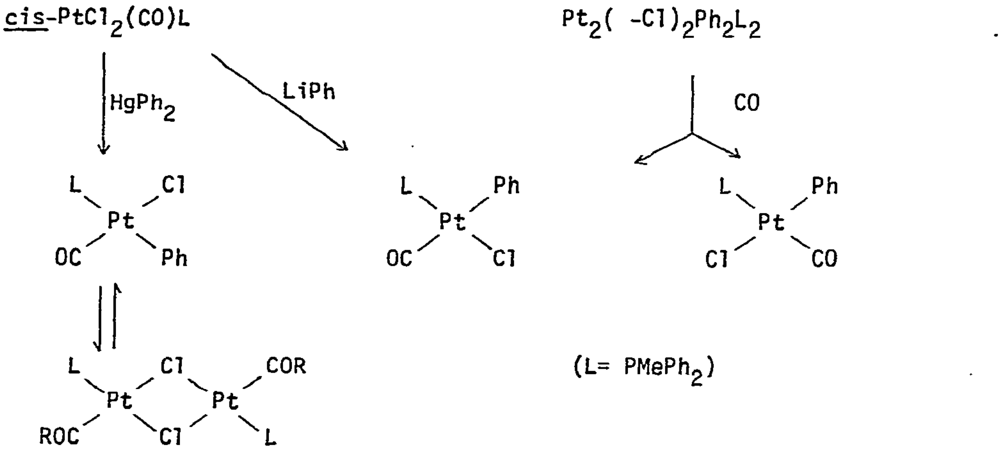
(39)

The pressure and temperature dependencies on the rates of substitution of cis- and trans-$Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)Br$ by I^- and thiourea in methanol show negative volumes of activation. The results are interpreted in terms of an associative process [82]. Substituent effects on the rates of uncatalyzed cis to trans isomerization have been measured along with the methanol solvolysis of arylplatinum complexes. Correlation of rates with Hammett's parameters of the Y substituents in cis-$[Pt(PEt_3)_2(YC_6H_4)X]$, or with the set of Swain and Lupton dual-substituent parameters indicates that σ rather than π interactions are dominant in the aryl-platinum bond [83]. The kinetics of trans-$PtL_2(R)Cl + Y^- \longrightarrow$ trans-$PtL_2(R)Y + Cl^-$ (R= H,Et,m-$CF_3C_6H_4$, C_6F_5; L= PEt_3; Y= Br, I, N_3, NO_2, CN, SCN) fit the usual two-term rate law. It is suggested that the weakening of the Pt-Cl bond trans to strong σ donors R in the ground state is the driving force of the bimolecular reaction with a weak nucleophile (e.g. methanol solvent) which has no π-acceptor ability [84]. Protonolysis of complexes trans-$Pt(PEt_3)_2RMe$ (R= Et,m-MeC_6H_4, o-MeC_6H_4, m-FC_6H_4, p-FC_6H_4, m-$CF_3C_6H_4$, C_6F_5) by HCl in aqueous methanol selectively cleaves the alkyl group [85]. Rate data are given and a

$$\text{trans-}Pt(PEt_3)_2RMe + HCl \longrightarrow \text{trans-}Pt(PEt_3)_2RCl + CH_4$$

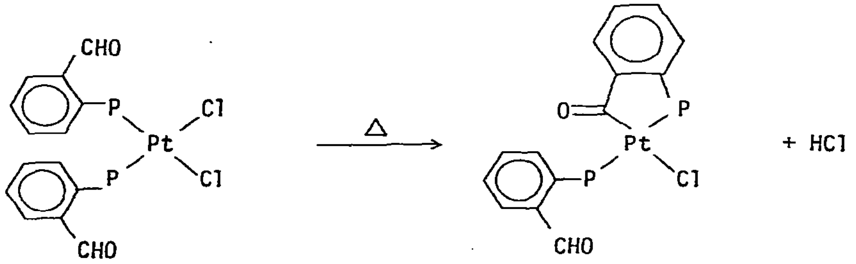
mechanism involving a three-center transition state proposed. The kinetics of the Si-Ar bond cleavages in $Me_3SiC_6H_4X$ (X= H, m-Me, m-OMe, mCl, p-Me, p-Cl) in the presence of Li_2PdCl_4 as catalyst are first order in silane and palladium complex. A mechanism is presented involving intermediate phenylpalladium compounds [86]. In a mechanistic paper dealing with the mechanism of reductive elimination, a series of reactions involving alkyl- and arylpalladium compounds are described. The reductive elimination process is proposed to take place preferentially from Pd(IV) intermediates with retention of configuration at carbon [87].

The three geometric isomers of $PtCl(Ph)CO(PMePh_2)$ have been prepared. Only the isomer with Ph trans to $PMePh_2$ readily undergoes carbonyl insertion, and gives the halo bridged acyl complex $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, with which it equilibrates in solution. The acyl/carbonyl equilibrium is dependent on the R group which replaces phenyl [88]. An acylplatinum(II) compound (41) has been obtained by the



($L= PMePh_2$)

thermolysis of (40) [89]. The structure of trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ has a Pt-C bond length of 1.972 Å. From the Pt-Cl distances, relative to

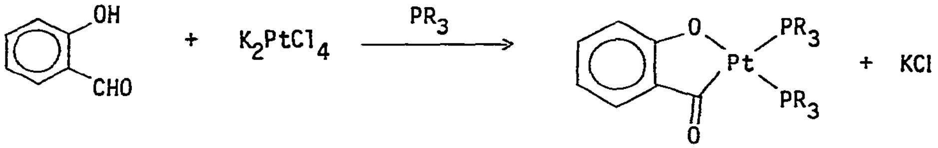


(40)

(41)

($P= PPh_3$)

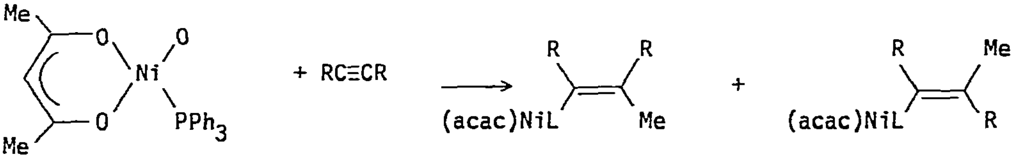
phosphine, σ-carbon donor ligands exert a greater trans influence in binuclear complexes than they do in mononuclear Pt(II) derivatives [90]. Acylplatinum complexes of Pt(II) have been prepared from salicylaldehyde. The compound (42) has both the phenolic oxygen and the aldehyde carbon coordinated to Pt [91].



(42)

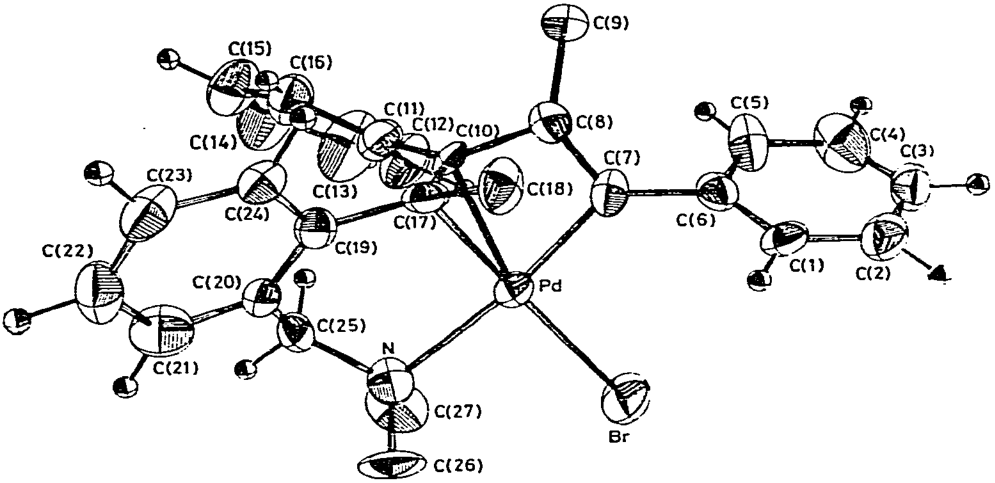
II. Metal complexes formed by insertion and related reactions.

The complexes *cis* and *trans*-$PtH(YCN)(PPh_3)_2$ and *cis*-$PtH(YCN)(L\text{-}L)$ (YCN= C_2H_4CN, *n*-C_3H_6CN, *o*-$CH_2C_6H_4CN$) have been isolated. Insertion of olefin (C_2H_4CN, C_2H_3CN, NBD, allene) into the Pt-H bond of the *trans*-hydride complexes occurs to give *cis*-dialkyl complexes, but the *cis*-hydride complexes are unreactive [92]. Mechanisms are discussed. The insertion of an acetylene into the Ni-Me bond of $(acac)Ni(Me)PPh_3$. The reaction gives different kinetic and thermodynamic ratios of E and Z vinylnickel products (43). The structure of Z has been determined.



(43)

The effects of added phosphine are discussed [93]. Reactions between disubstituted alkynes and $[Pd(N,N\text{-dimethylbenzylamine})X]_2$ gives bis insertion products. The structure of $[Pd\{MeC{=}CPh)_2C_6H_4CH_2NMe_2\}Br]$ (44) shows two acetylenes inserted into the Pd-C bond in a head-to-tail arrangement, the Pd being σ bonded to a carbon bearing a phenyl group [94]. Dimethylacetylene dicarboxylate and hexafluorobut-2-yne add to $Pd_2(dppm)_2Cl_2$ to give adducts $Pd_2(dppm)_2(\mu\text{-acetylene})Cl_2$ where the acetylene has inserted into the Pd-Pd bond. The structure of the compound from $CF_3C{\equiv}CCF_3$ (45) has a C-C bond length of 1.34 Å [95]. Reaction of PtIMe(bipy) with $MeO_2CC{\equiv}CCO_2Me$ gives first a 5-coordinate π-complex $PtIMe(MeO_2CC\ CCO_2Me)(bipy)$, and then the product of insertion into the Pt-I bond, $PtMe(C(CO_2Me){=}C(CO_2Me)I)bipy$ (46) [96]. Formation of (46) may involve nucleophilic attack of I^- on the coordinated alkyne of a cationic intermediate. The reaction of isocyanides with hydroxy and methoxy alkyl complexes of platinum(II) yields insertion products (47) and (48) containing the carboxamido and imidoyl moieties respectively [97].



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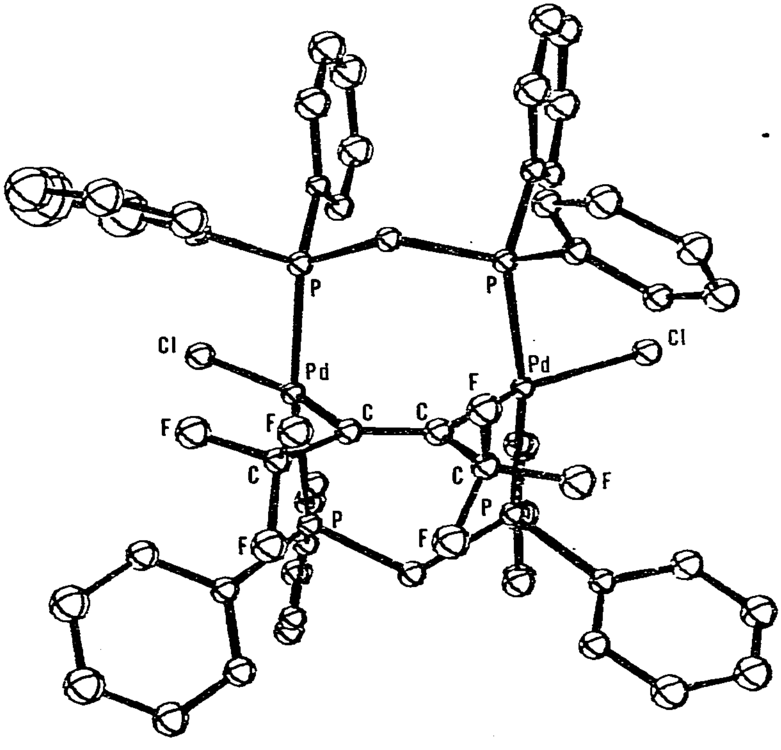

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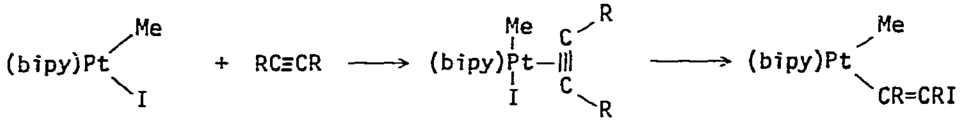
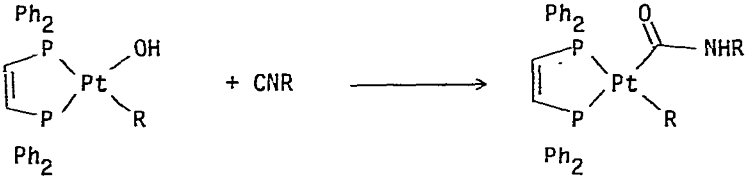

(46)

Hydroxy and alkoxy alkyl complexes used in this study can be prepared by metathesis with NaOR. Insertion reactions with SO_2 and S=C=Y are described [98].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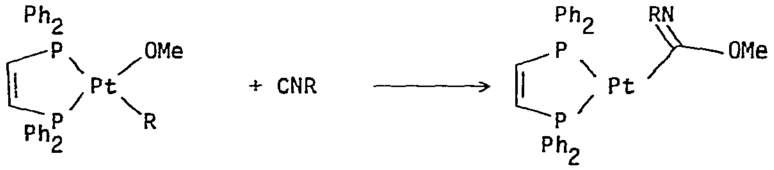
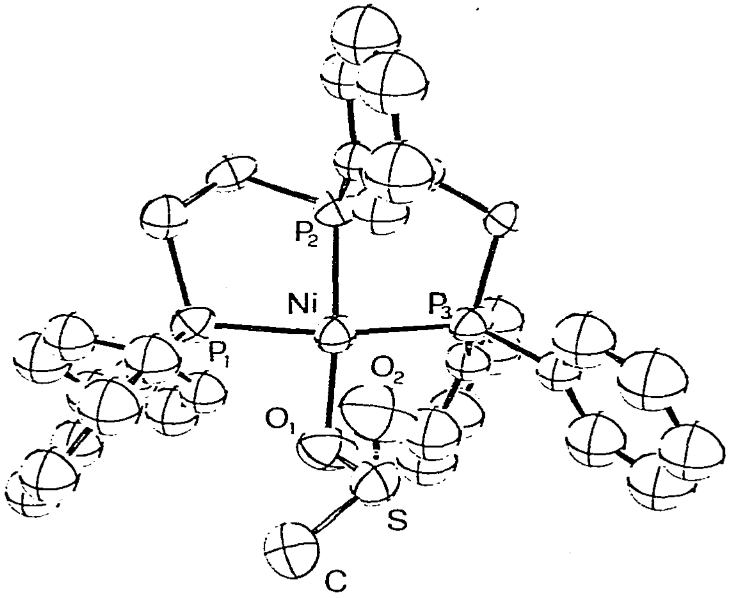

(48)

Nickel(0) will insert into the C-CN bond of acetonitrile to give unstable complexes [99]. Carbamatopalladium complexes (49) have been prepared from $PdMe_2L_2$ and CO_2 [100].

$$PdMe_2L_2 + CO_2 + HNR_2 \longrightarrow PdMe(O_2CNR_2)L_2 + CH_4 \qquad (49)$$

3-Methyl-2-butenoic acid and 3-methyl-3-butenoic acid, and their methallyl esters were obtained by CO_2 insertion into π-allylpalladium complexes [101]. Sulfur dioxide reacts with $[NiMe(ppp)]BPh_4$(ppp=bis(2-diphenylphosphinoethyl)phenylphosphine) to give the O-methylsulfinate complex $[NiOS(O)Me(ppp)]BPh_4$ (50). The structure of (50) is shown [102]. Addition of tin chloride to $Pd_2(dppm)_2Cl_2$ produces $Pd_2(dppm)_2(SnCl_3)Cl$ where the tin chloride has inserted into the Pd-Cl bond. Carbon monoxide will insert into the Pd-Pd bond of this complex to give the carbonyl compound $Pd_2(dppm)_2(\mu\text{-}CO)(SnCl_3)Cl$ [103].



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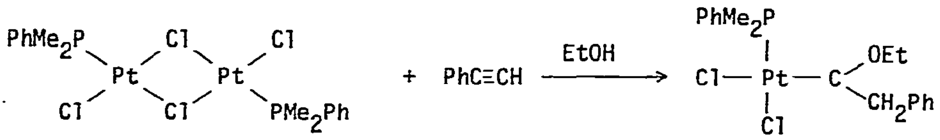
III. Metal carbenes and ylides

Detailed synthetic procedures have been described for the preparation of cis-$PtCl_2(PhNC)(PEt_3)$ and subsequently cis-$PtCl_2[C(OMe)NHPh]$, cis-$PtCl_2[C(NHPh)NHPh]$ and trans-$[PtCl[C(NHPh)NHEt](PEt_3)_2]ClO_4$ [104]. New alkoxycarbene complexes of platinum(II) have been prepared from H_2PtCl_6 and either $Me_3CC{\equiv}CH$ or $Me_3SiC{\equiv}CH$ in i-PrOH [105]. A series of neutral carbene complexes of platinum(II) have been similarly obtained by reaction of the halide bridged dimer $Pt_2X_4L_2$(X= Cl,Br,I; L= PMe_2Ph, PEt_3) with monosubstituted acetylenes $RC{\equiv}CH$(R= Ph,Me, Et) and alcohols R'OH (R'= Me,Et,n-Pr). The crystal structure of the complex cis-$PtCl_2(PMe_2Ph)\{C(OEt)CH_2Ph\}$ (51) shows a Pt····H contact of 2.6 Å to a hydrogen atom of the ethoxy CH_2 group [106]. In the following article the reactions of these compounds are reported. Reaction with chloride yields the acyl. Treatment with tertiary phosphines gives the cationic carbene complex. Halogen abstraction yields chloro bridged cationic carbene complexes [107]. The structures of the two compounds formed from $Me_3CC{\equiv}CH$ and $Me_3SiC{\equiv}CH$ [105] have been solved and been found to be a dimer $Pt_2Cl_4\{C(CH_2CMe_3)OCHMe_2\}_2$ (52) and a monomer $PtCl_2\{C(CH_3)OCHMe_2\}_2$ (53) [108].



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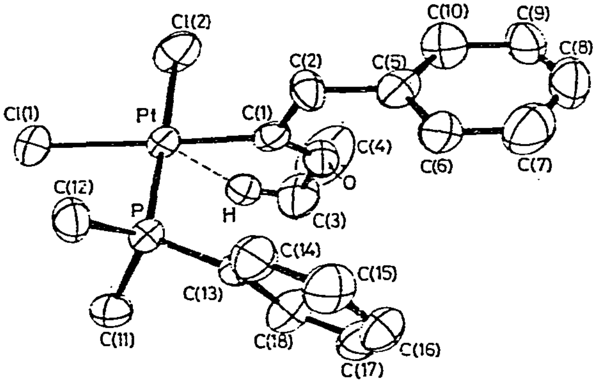

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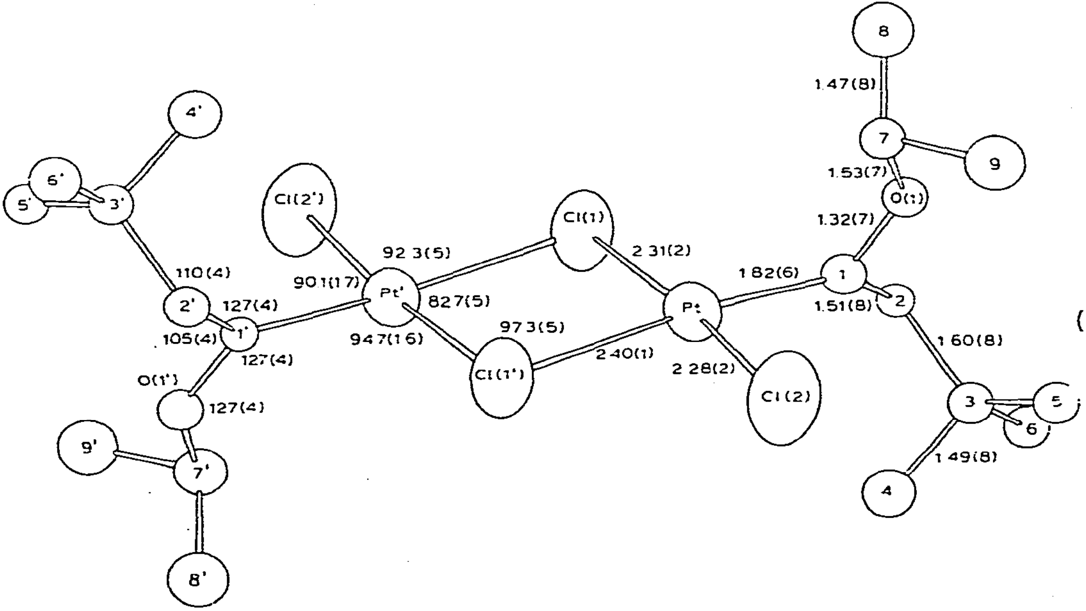

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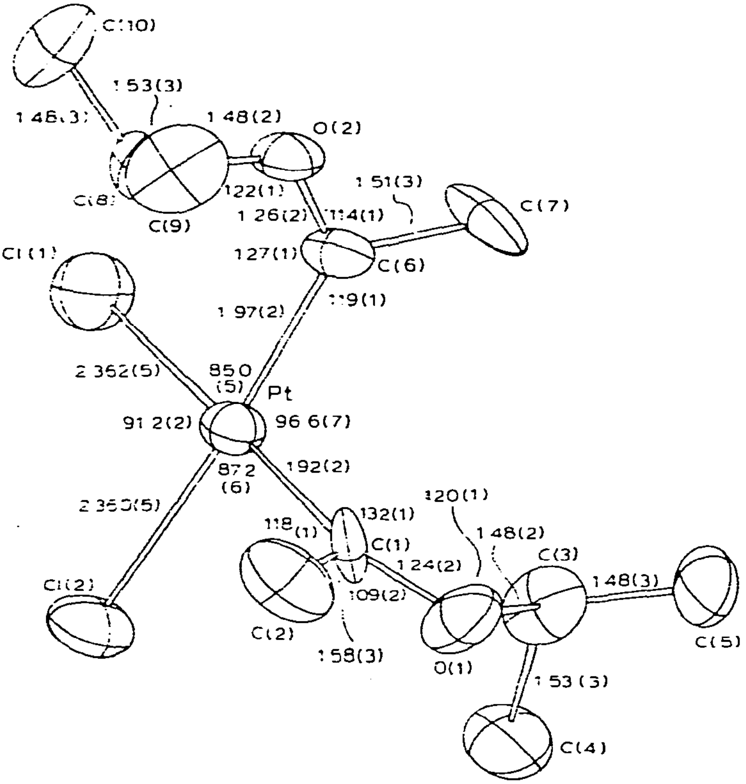

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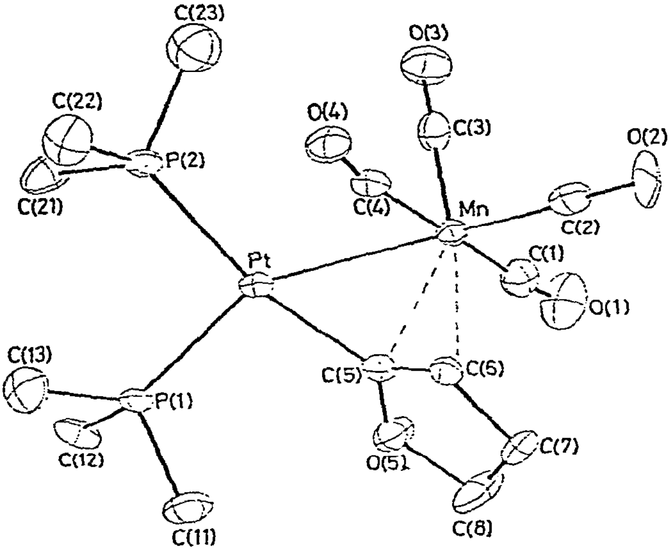
Addition of a solution of η-cpW(CO)$_2$(CR), where R=p-tolyl,to Pt(C_2H_4)(PMe$_2$Ph)$_2$ gives a compound PtW(μ-CR)(CO)$_2$(PMe$_2$Ph)(η-cp). The structure shows the complex to have a Pt-W bond with a bridging carbyne ligand [109]. Similarly these workers have prepared dimetal complexes from metal carbene complexes. The structures of the yellow and red forms of (CO)$_4$Mn{μ-(1-σ, 1-2-η-C=CHCH$_2$CH$_2$O}Pt(PMe$_3$)$_2$ have been solved, the latter being shown below (54) [110]. This group has also prepared complexes [MPt$_2${μ-C(OMe)Ph}(CO)$_6$(PR$_3$)$_2$] (M= Cr, W; PR$_3$= t-Bu$_2$MeP, PCy$_3$) (55). The structure of the complex with M=W and PR$_3$=t-Bu$_2$MeP has been solved. Related reactions forming triangulo Pt$_3$ compounds with bridging μ-C(OMe)Ph groups are described [111]. Bimetallic compounds with an alkylidene bridging Pt-Mn and Pt-Cr bonds have been prepared. Again the structures have been confirmed by x-ray crystallography [112].



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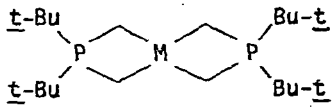
$$Pt(C_2H_4)(PR_3)_2 \quad + \quad M\{C(OMe)Ph\}(CO)_5 \longrightarrow [MPt_2\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2] \qquad (55)$$

Metalating $[Me_3P]_2BH_2{}^+Br^-$ with 2 equivalents of BuLi and reacting with 0.5 equivalents $MCl_2(PMe_3)_2$ (M= Ni, Pd, Pt) gives the phosphonium ylide complexes $H_2B(Me_2PCH_2)_2M(CH_2PMe_2)_2BH_2$. The complexes have been characterized by ^1H, ^{11}B, ^{13}C and ^{31}P nmr spectroscopy, and the structure of the nickel complex shows it to be centrosymmetric with a square planar array of CH_2 carbons around the metal center and a chair conformation for both 6-membered chelate rings [113]. Transylidation has been used to form the ylide chelates $(\underline{t}\text{-}Bu)_2P(CH_2)_2M(CH_2)_2P(Bu\text{-}\underline{t})_2$ (M= Ni, Pd) (56). With platinum only the "half-complex"$[(\underline{t}\text{-}Bu)_2P(CH_2)_2Pt(PMe_3)_2]^+Cl$

$$4(\underline{t}\text{-}Bu)_2P(=CH_2)Me \quad + \quad MCl_2(PMe_3)_2 \longrightarrow$$

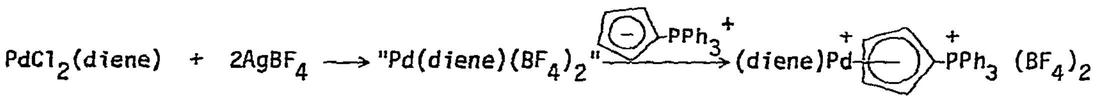


$$+ \quad (\underline{t}\text{-}Bu)_2PMe_2{}^+Cl^- \quad + \quad 2PMe_3 \qquad (56)$$

is formed [114]. The reaction of $\mathrm{MeR_2P{=}CH_2}$ (R= Me, $\mathrm{Me_3C}$) with $\mathrm{(COD)PtMe_2}$ gives $\mathrm{(MeR_2PCH_2)_2PtMe_2}$ [115]. Treating $\mathrm{Me_3Pt^+X^-}$ (X=$\mathrm{PF_6}$, $\mathrm{OSO_2CF_3}$, I) with $\mathrm{Ph_3P{=}C{=}PPh_3}$ gives an *ortho* metalated ylide platinum(II) complex and methane. Structures of the compounds have been deduced from ir and nmr spectroscopy [116]. Nickelocene reacts with methylenetriphenylphosphorane to give the cation $[\mathrm{Ni(CH_2PPh_3)_2(\eta\text{-}cp)}]^+$ (57). The compound can also be prepared from nickel phosphine complexes [117]. The reaction of $\mathrm{Pt(PPh_3)_4}$ with $\mathrm{CH_2ClI}$ yields the cationic ylide complex *cis*-$[\mathrm{Pt(PPh_3)_2(CH_2PPh_3)Cl}]\mathrm{I}$ (58) in high yield [118]. The structure of $[\mathrm{Pd(COD)\{CH(PhMe_2)(SiMe_3)\}Cl}]\mathrm{PF_6}$ shows the chiral ylide bonded to Pd(II) with the trimethylsilyl and dimethylphosphonium substituents oriented above and below the plane of the complex [119]. Cationic η^3-allyl ylide and η^5-cyclopentadienyl ylide complexes of palladium(II) have been prepared from $\mathrm{(R_3P^+CHCRCHR)Pd^-Cl_2}$ or $[\mathrm{(R_3P^+CHCRCHR)_2Pd_2Cl_2}]\mathrm{Y_2}$ with silver salts of non-coordinating anions. Cationic(triphenylphosphonium -η^5-cyclopentadienyl ylide)diene Pd(II) complexes (59) have been obtained from reaction of $\mathrm{PdCl_2(diene)}$ with $\mathrm{AgBF_4}$ followed by triphenylphosphonium cyclopentadienyl ylide [120]. A further article from this group describes the preparation and nmr of these (η^3-allyl)(η^3-allyl ylide)-, (η^3-allyl ylide)(η^5-cyclopentadienyl ylide)-, and (η^3-allyl)(η^5-cyclopentadienyl ylide) palladium(II) complexes [121]. New palladium(II) complexes containing dimethylsulfonium allylide and tetramethylenesulfonium allylide as η^3-allyl ligands have been prepared (60) [122].

$$\mathrm{Nicp_2} + \mathrm{Ph_3PCH_2} \longrightarrow [\mathrm{Ni(CH_2PPh_3)_2cp}]^+ \longleftarrow \mathrm{Ph_3PCH_2} + [\mathrm{cpNi(PBu_3)_2}]^+ \qquad (57)$$

$$\mathrm{Pt(PPh_3)_4} + \mathrm{CH_2ClI} \longrightarrow \textit{cis}\text{-}[\mathrm{Pt(PPh_3)_2(CH_2PPh_3)Cl}]\mathrm{I} + \mathrm{PPh_3} \qquad (58)$$



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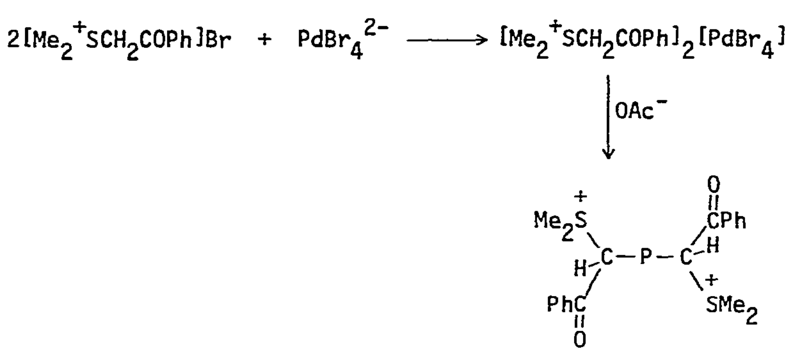
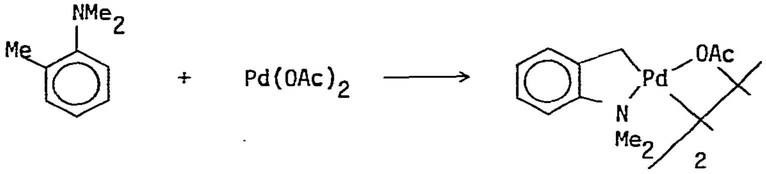


$$2[Me_2{}^{+}SCH_2COPh]Br + PdBr_4{}^{2-} \longrightarrow [Me_2{}^{+}SCH_2COPh]_2[PdBr_4]$$

(60)

IV. Internal metalation reactions

o-N,N-Dimethylaminotoluene reacts with palladium acetate with metalation of the ortho methyl group. The product has the structure shown (61) [123]. A study



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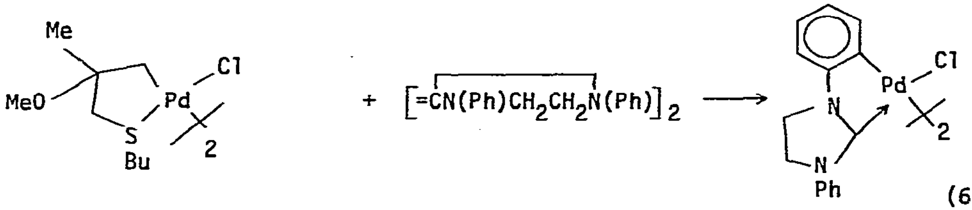
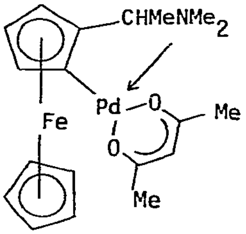
has been made of the potentially bidentate ligands 8-methyl-, 8-ethyl-, 8-isopropylquinoline-2-carboxaldehyde-N-methylimine 8-RC_9H_5N-CH=NMe with Pd, Rh and Ir. In particular the authors have investigated the sites of metalation using ^1H and ^{13}C nmr spectroscopy [124]. The kinetics of azobenzene palladation shows the reaction to be catalyzed by OAc^-, $ClCH_2CO_2{}^-$, OH^- and Et_3N. The reaction mechanism is discussed [125]. A cyclopalladated carbene complex (62) has been prepared from bis(1,3-diphenyl-2-imidazolidinylidene). Transformations of the compound have been made with AgOAc, Tl(acac) and phosphites [126]. o-Palladated complexes of N-phenylbenzaldimine and N-phenyl-p-anisaldiimine react at 150° with methyl acrylate



(62)

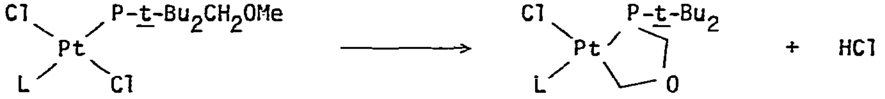
undergoing two successive methyl acrylate insertions followed by cyclization to form tetralin derivatives [127]. The reactions appear to involve vinylic palladation as an intermediate step. Acetylhydrazones of p-methylacetophenone, acetylthiophene, and acetylferrocene are readily cyclopalladated. A Pd-C bond is formed with the ortho positions of phenyl and ferrocenyl rings and with the position 3 of a thienyl ring. Reactions with pyridine are described [128]. Crown ether substituted oximes are cyclopalladated on treatment with Na$_2$PdCl$_4$/NaOac exclusively in the 16 position. The compounds react with PPh$_3$, and spectral data are presented and discussed [129]. Cyclopalladated compounds have been prepared from acetanilides. Coupling reactions of these complexes with olefins gives a variety of 2-substituted acetanilides which will undergo intramolecular cyclization to quinolines [130]. Cyclopalladation has also been used as a route to cationic condensed ring systems containing isothiazole or 1,2-dithiole nuclei [131]. An article has been published describing the asymmetric cyclopalladation of aminoferrocenes [132]. These authors also describe new pathways to enantiomeric 1,2-disubstituted ferrocenes from reactions of these cyclopalladated ferrocene compounds [133]. A crystal structure of the compound (63) shows it to have an R configuration about the chiral C atom and an S configuration at the substituted ferrocenyl moiety [134]. Other workers have treated *o*-palladation products of optically active 1-dimethylaminoethyl1ferrocene with phenylvinyl ketone and CO to give a variety of optically



(63)

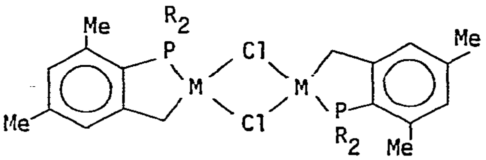
active 1,2-disubstituted ferrocene derivatives [135]. Similarly a σ-bonded palladium(II) complex has been obtained from (dimethylaminomethyl)ruthenocene by treatment with Li$_2$PdCl$_4$ [136].

The reaction of R$_2$PCH$_2$Ph (R= Cy, *t*-Bu) with PdCl$_2$ or PtCl$_2$(PhCN)$_2$ gives cyclometalated compounds. The mechanism of the reaction has been probed with *m*-FC$_6$H$_4$CH$_2$PR$_2$; for Pd(II) an electrophilic pathway is proposed but no conclusion has been drawn for the case of Pt(II)[137]. Heating *trans*-PtCl$_2$(*t*-Bu$_2$PCH$_2$OMe)$_2$ at 125° in 2-methoxyethanol gives the cyclometalated complex $\overline{\text{PtCl}(t\text{-Bu}_2\text{PCH}_2\text{OCH}_2)}$ (*t*-Bu$_2$PCH$_2$OMe) (64). Similarly *trans*-PtCl$_2$(*t*-Bu$_2$POEt) is methylated at the methyl carbon but the reaction rate is slower [138]. Palladium hydride complexes PdHX(*t*-Bu$_3$P)$_2$ (X= Cl,Br, OCOCF$_3$) undergo rapid intramolecular metalation in



(64)

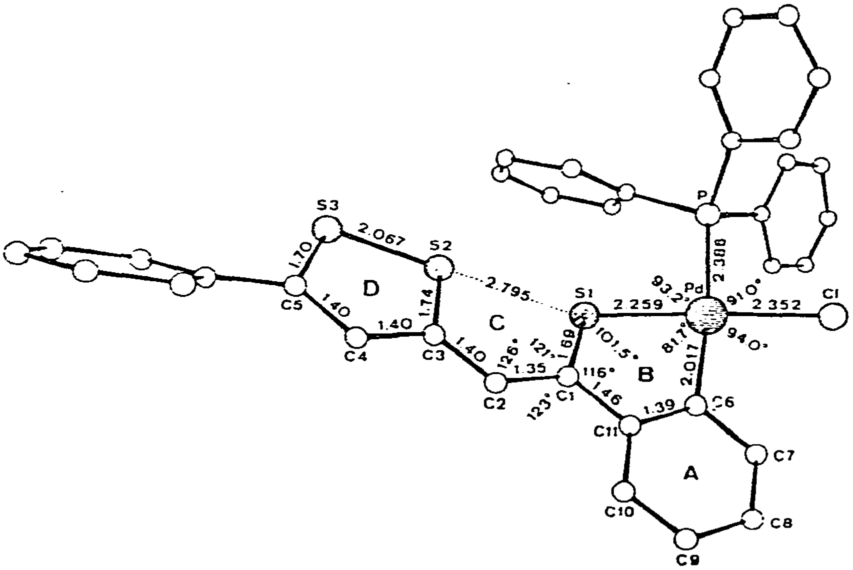
solution under ambient conditions to give complexes of the structure PdX(t-$Bu_2PCMe_2CH_2$)(t-Bu_3P). Reactions of the complexes with $NaBH_4$ are described [139]. The reaction of trimesitylphosphine with $PdCl_2(PhCN)_2$, $PtCl_2(PhCN)_2$ or $PtCl_2$ gives the metalated compound (65). The greater tendency of Pd than Pt to



(R= mesityl; M= Pd,Pt)

(65)

induce cyclometalation, and the greater ease of metalation of trimesitylphosphine over trimesitylarsine suggests a steric dominance in these reactions [140]. An o-palladated complex of 2,5-diphenyl-1,6,6aλ^4-trithiapentalene (66) has been prepared from $PdCl_2$ [141].



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V. Metal carbonyls and thiocarbonyls

A simple low risk nickel carbonyl generator fabricated from a 100ml round-bottom flask has been described. The inexpensive apparatus will yield 0.2 to 0.5g of $Ni(CO)_4$ per hr. [142]. A useful preparative procedure has been developed for the synthesis of $Ni(CO)_2(PPh_3)_2$, $Ni(C_2H_4)(PPh_3)_2$, $Pt(CO)_2(PPh_3)_2$ using zinc dust for the reduction of the M(II) precursor complexes [143]. On a large scale alkaline earth hydroxide scrubbers have been used to purify a $Ni(CO)_4$ stream [144]. The electronic absorption spectra of the metal carbonyls $M(CO)_4$ (M= Ni, Pd, Pt) have been measured. The compounds exhibit $d \rightarrow \pi^*$ CO bands in the UV region. Assignments of the bands are made [145].

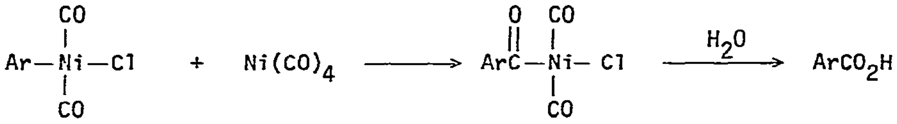
An increased amount of erythrocytes and reticulocytes, and of volume and diameter of erythrocytes are the initial signs of $Ni(CO)_4$ poisoning (at 10 to 100 times greater than the maximum permissible concentration). The changes are further combined with an increase in the number of leukocytes and lympho-eosinopenia [146]. The distribution of $^{63}Ni(CO)_4$ and $Ni(^{14}CO)_4$ has been studied in mice. Radioactivity from $Ni(^{14}CO)_4$ is found almost exclusively in the blood, probably because of CO binding to hemoglobin. After the administration of $^{63}Ni(CO)_4$ the highest level of ^{63}Ni is found in the lung [147]. A resume has been presented on the use of dithiocarbamates for the treatment of persons exposed to $Ni(CO)_4$. The 3 persons who received dithiocarbamate became symptomless and returned to normal activity (work) within 72 hrs after exposure; the 4th man exposed to $Ni(CO)_4$ and who did not receive dithiocarbamate died within 5 days after exposure [148]. In a study on pregnant rats the specificity of $Ni(CO)_4$ for induction of ocular anomalies in rats appears to be unique among known teratogenic agents [149].

The molecular structure of $Ni(CO)_4$ by electron diffraction at room temperature has led to an evaluation of bond distances and amplitudes of vibration. The force constants are in general agreement with those reported from a spectroscopic study [150]. Ultrasoft x-ray spectroscopy has been used to study the electronic structure of $Ni(CO)_4$. The experimental results agree with a calculated ground state from electron d character and energy parameters [151]. The thermodynamics of evaporation of a binary mixture of $Ni(CO)_4$ and $Fe(CO)_5$ obeys Dalton and Raoult laws and thus practical calculations for separation processes of technical carbonyl mixtures by isothermal bubbling can assume equilibrium ratios for ideal mixtures [152].

The reaction of $ArTeCl_3$ and Ar_2TeCl_2 with $Ni(CO)_4$ in DMF followed by aqueous work-up gives the carboxylic acids. The suggested pathway is shown [153]. Nickel carbonyl reacts with 1,10-phenanthroline, o-phenylenebis(dimethylarsine), cis-1,2-bis(dimethylarsino)ethylene and DIARS in two consecutive, first-order reactions. The first is a dissociation of CO to give the intermediate $Ni(CO)_3$ which is rapidly attacked by one of the donor atoms of the chelate. The second reaction is first

$$ArTeCl_3 + Ni(CO)_4 \longrightarrow (ArTe)Ni(CO)_2Cl + NiCl_2$$

$$(ArTe)Ni(CO)_2Cl + Ni(CO)_4 \longrightarrow ArNi(CO)_2Cl + NiTe$$

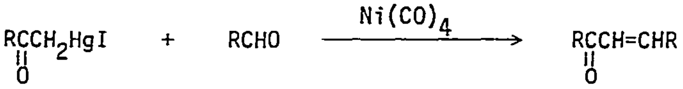


$$Ar{-}\overset{CO}{\underset{CO}{Ni}}{-}Cl + Ni(CO)_4 \longrightarrow Ar\overset{O}{\overset{\|}{C}}{-}\overset{CO}{\underset{CO}{Ni}}{-}Cl \xrightarrow{H_2O} ArCO_2H$$

order but associatively activated and involves the displacement of a second CO ligand by the attached donor atom of the chelating ligand [154]. Nickel carbonyl

$$Ni(CO)_4 + L\text{-}L \xrightarrow{-CO} Ni(CO)_2(L\text{-}L) \xrightarrow{-CO} Ni(CO)_2(L\text{-}L)$$

in DMF has been used in a C-C bond forming reaction with α-iodomercuric ketones [155].



$$R\underset{O}{\underset{\|}{C}}CH_2HgI + RCHO \xrightarrow{Ni(CO)_4} R\underset{O}{\underset{\|}{C}}CH{=}CHR$$

Nickel tetracarbonyl physisorbed onto partially dehydroxylated γ-alumina rapidly reacts to form a yellow complex, probably adsorbed nickel tricarbonyl. Carbon monoxide rapidly reverses this reaction [156]. Thermal treatments of the system are discussed. The crystal structure of tricarbonyl(trimethyl-1-methoxy-4-oxo-1,2-diphenyl-1,2-diphosphacyclopenten-3,3,5-tricarboxylate)nickel has been solved [157]. The preparation of mono and disubstituted mononuclear carbonyls of Ni with the cage ligand $P(NMeCH_2)_3CMe$ are reported. Borane adducts are reported in addition to adducts of $X{=}P(NMeCH_2)_3CMe$ (X= SE, PhN). Discussion of the data obtained for ν(CO) and $^2J(^{31}P\text{-}^{31}P)$ are presented [158]. Trigonal bipyramidal carbonylnickel compounds have been prepared by carbonylation of $NiX_2(PMe_3)_n$ (n= 2,3) and $[NiX(PMe_3)_m]BF_4$ (m= 3,4). The Ni-CO distance (1.73 Å) is the shortest reported Ni-CO distance [159]. The carbonyl is stereochemically located in the equatorial position. The substituted carbonyl compounds $NiL(CO)_3$ and $NiL_3(CO)$ (L= Me_2NPF_2) have been prepared. Boron trifluoride reacts with $NiL_2(CO)_2$ to give $NiL_2(CO)_2\cdot nBF_3$ where n= 1.44 at -128°C. and 1.11 at 2°C. Infrared and nmr spectroscopy indicates that the BF_3 coordinates to the N of the coordinated Me_2NPF_2 ligands [160].

Hartree-Fock-Slater calculations have been carried out on $Ni(CO)_3L$ for a number of ligands L. The order for σ-donation, based on extent of electron transfer, is CS=CO>MeNC>N_2-PF_3; and for back-bonding is MeNC>CS>CO>PF_3>N_2. Calculations on ν(CO) of CO complexed to $Ni(CO)_3$ show that ν(CO) is decreased by the π back-donation but is increased by the steric interaction energy between $Ni(CO)_3$ and CO. Thus the decrease in ν(CO) is not a reliable measure of the extent of π back-bonding in the metal-ligand bond [161]. The compound $[(CO)_2NiPPh_2]_2$ is compared with similar first row transition metal compounds of Fe and Co; the M-M bond lengths are controlled by the electronic influence of the Ph_2P ligands [162]. A comparative study of $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, $Ni(N_2)_4$, $Co(N_2)_4^-$ and $Fe(N_2)_4^{2-}$ by the multiple scattering Xα method has correlated ν(CO) and $\nu(N_2)$ with back donation [163]. In a critical evaluation of an earlier article by others, Larson and Braga have used Xα methods to calculate the extent of "back bonding" in $Ni(CO)_4$. A measure of the back donation is obtained by taking the ratio of 3d charge in the unoccupied level to the total 3d charge in all molecular orbitals of t_2 symmetry. These authors conclude there is significant back donation in $Ni(CO)_4$ as evidenced by their (MSXα) calculation [164]. Extended Hückel theory, modified with the inclusion of two-body repulsion, has been used to reproduce and predict geometries and bond lengths of some first-row transition metal carbonyl compounds, including nickel [165].

The interstitial dihydride anion $[Ni_{12}(CO)_{21}H_2]^{2-}$ is readily converted by CO into the lower carbonyls $Ni(CO)_4$ and $[Ni_2(CO)_6H]^-$ [166]. The structure of $[Ni_2(CO)_6H]^-$ consists of two tetrahedral $Ni(CO)_3$ moieties joined by a Ni-Ni bond

$$[Ni_{12}(CO)_{21}H_2]^{2-} \quad + \quad 23CO \longrightarrow 2[Ni_2(CO)_6H]^- \quad + \quad 8Ni(CO)_4$$

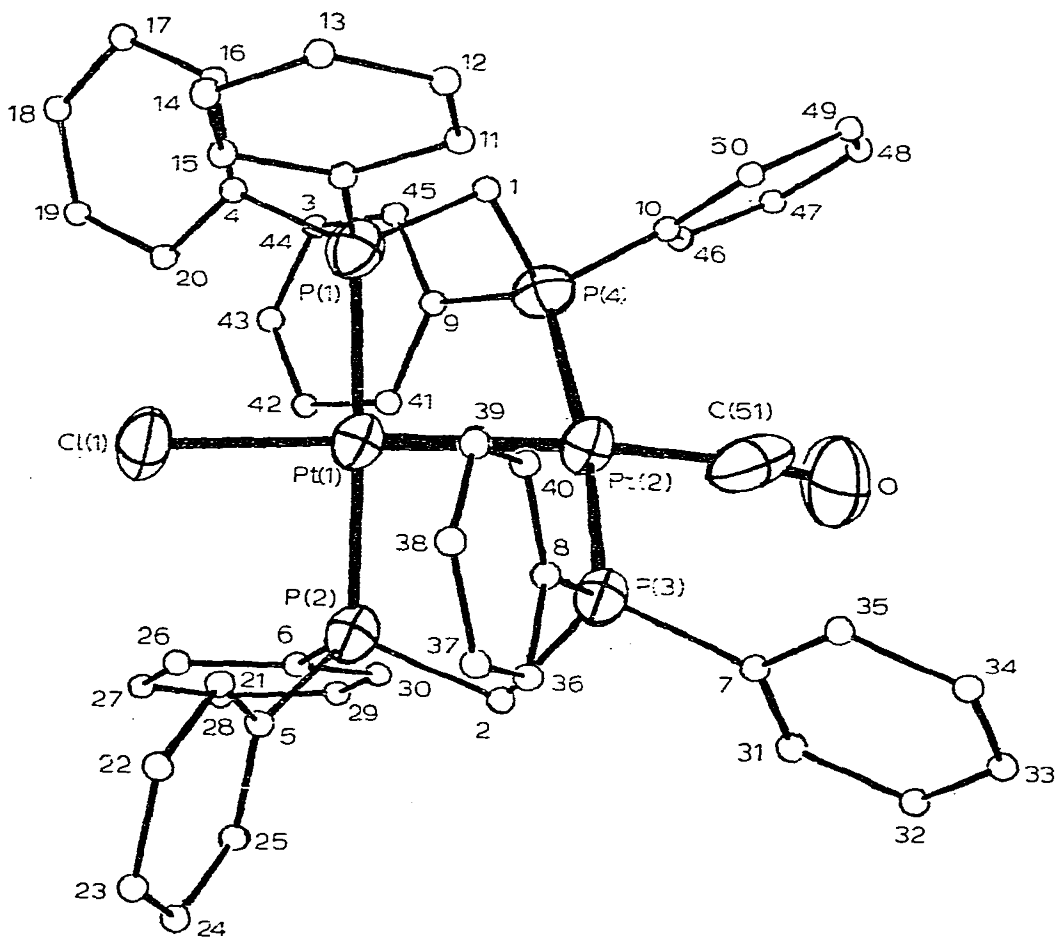
of 2.863 Å and with the carbonyls in an eclipsed conformation. From this structure determination, and in view of the close similarity of the ir spectra of $[Ni_2(CO)_6H]^-$ and $[Ni(CO)_3X]^-$ (X= Cl,Br,I), it is suggested that the latter compounds are best formulated as dimers. The structure of $[Pd_2(OAc)_2(CO)_2]_2$ consists of tetranuclear clusters. The four Pd atoms form a parallelogram with Pd-Pd distances of 2.663, 2.909 Å. Two sides of the parallelogram have bridging acetate groups and the other two sides bridging carbonyls [167]. The adsorption and electrooxidation of CO on palladium shows O-desorption peaks which is interpreted as being due to a CO induced agglomeration of Pd atoms on the alloy surface [168]. The compound $Pd(CO)(PPh_3)_3$ can be isolated from a reaction mixture resulting from cyclohexene hydrocarboxylation by $PdCl_2(PPh_3)_2$. The complex can be prepared from $Pd(PPh_3)_4$ and CO. The ^{31}P and ^{13}C nmr spectra have been interpreted to suggest a rapid dissociation of PPh_3 at room temperature and a tetrahedral structure at -70° in solution [169]. A series of carbonyl palladium compounds have been prepared including some having a polymer bound diphenylphosphino group [170].

$PdCl_2(PhCN)_2 + CO \longrightarrow PdCl_2(CO)(PhCN) + PhCN$

$PdCl_2(PhCN)(PPh_2polymer) + CO \longrightarrow PdCl_2(CO)(PPh_2polymer)$

Force constant calculations have been carried out for $MCl_3(CO)^-$ (M=Pd,Pt). The M-C stretching force constants are proportionately more sensitive than those for CO, but for members of the same transition series the trends correlate with bond order changes. Estimated bond orders are given [171].

The structure of $[Pt_2Cl(CO)(dmpe)]PF_6$ (67) shows Pt-Cl and Pt-CO fragments linked together by a bridging dmpe ligand and a Pt-Pt bond. There is a dihedral



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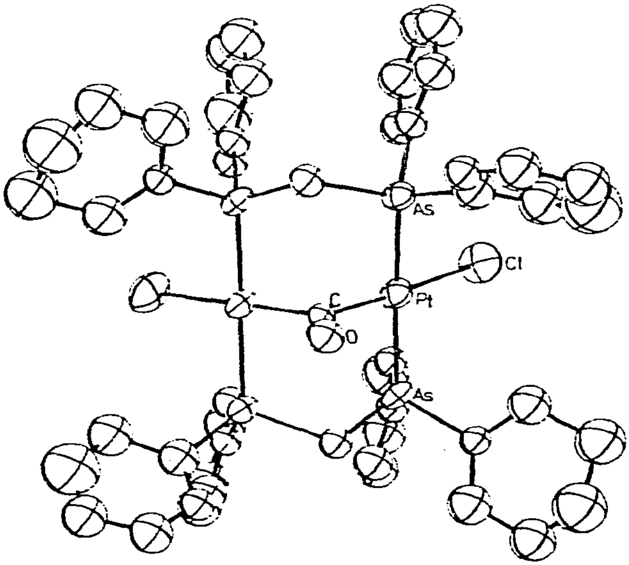
angle between the two coordination planes of 40° [172]. The structure of [$Pt_2Cl_2(CO)dpam$] (68) shows a bridging carbonyl. The structure is thus very similar to that of the Pd analog and discussion is centered on the significant



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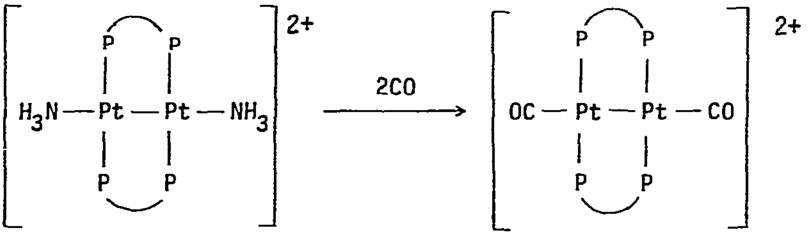
difference between the values of ν(CO) in the two compounds [173] . The carbonyl compound [$Pt_2(CO)_2(\mu\text{-dppm})_2$]($PF_6$)$_2$ (69) and an unsymmetrical complex [$Pt_2(CO)(py)$ $(\mu\text{-dppm})_2$](PF_6)$_2$ (70) have been isolated from the reactions of the amine and pyridine complexes respectively with CO [174]. A series of platinum carbonyl dianion clusters have been studied by x-ray photoemission spectroscopy. These



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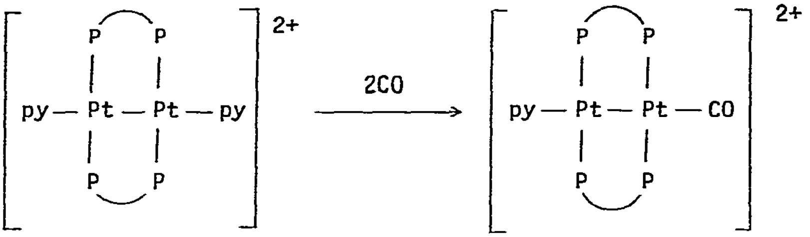
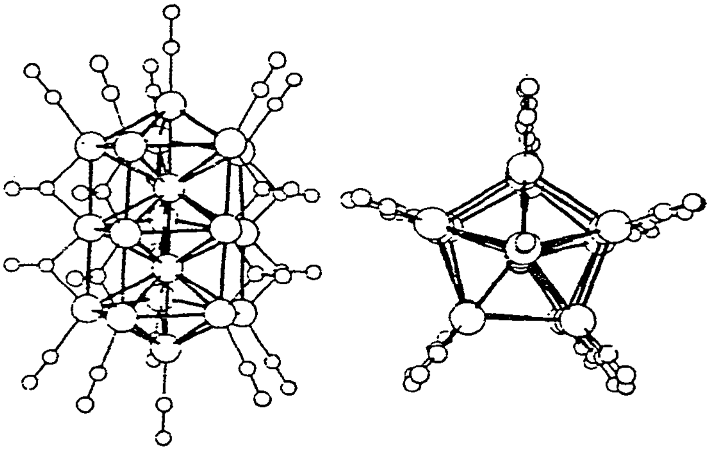


(70)

include $[Pt_3(CO)_6]_n^{2+}$ (n= 2,3,4,5,6,~10). The general structure of all valence spectra, in particular that of the Pt 5d derived bands, are remarkably similar. The authors consider negligible interaction to exist between the $Pt_3(CO)_6$ layers. The binding energies are given and discussed [175]. A comparative discussion is made about metal-metal bonds. Consideration is given to surfaces and clusters and to the forces binding the metals. A section considers carbonyl compounds and particular reference is made to the compounds $M_3(CO)_6^{2-}$ (M= Ni,Pd,Pt) [176]. The one-electron states in the polyatomic transition metal carbonyls $[M_3(CO)_6]_n^{2-}$ (M=Ni, Pt; n= 1,2) were calculated using the chemical pseudopotential method. The main electronic interactions involve metal s and d orbitals and the lone pair 5σ MO's of the ligand. The symmetry-allowed electronic transitions were calculated and compared with experimental results from solution absorption spectroscopy [177]. The synthesis, structure and stereochemical implications of a compound $[Pt_{19}(CO)_{12}(\mu_2\text{-}CO)_{10}]^{4-}$ (71), which is a bicapped triple-decker sandwich, are



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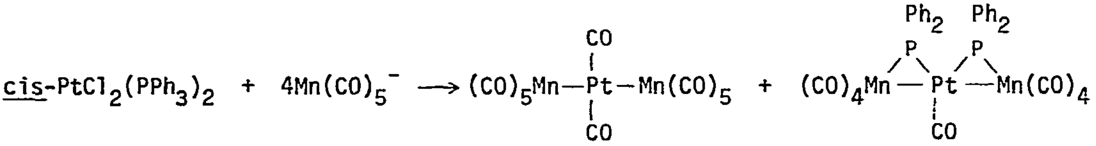
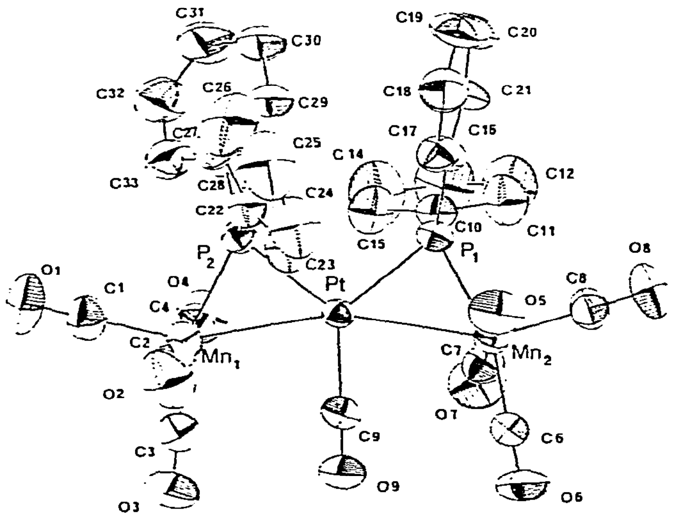
reported and discussed. The compound was prepared by heating the dianion $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_3^{2-}$ in refluxing acetonitrile. The Pt_{19} framework consists of three 5-membered rings stacked in an eclipsed conformation with the other four Pt atoms lying stacked in an eclipsed conformation with the other four Pt atoms lying on the principal fivefold axis, two internally sandwiched between the rings, and two externally capping the two outer pentagons [178]. A detailed article has been published by Chini on the comparison between large anionic carbonyl clusters and small metallic crystallites. The clusters of Pt are included in this discussion [179]. The ^{195}Pt nmr spectra have been measured for the compounds $[Pt_n(CO)_{2n}]^{2-}$ (n= 3,6,9,12,15) and ^{13}C nmr reported for n= 6,9,12 over a range of temperatures. The spectra show intramolecular rotation of the Pt_3 triangles about the principal 3-fold axis, interexchange of Pt_3 triangles, and lack of terminal/edge carbonyl exchange within the $Pt_3(CO)_3(\mu\text{-}CO)_3$ groups. Evidence is presented for the formation of $[Ni_3Pt_3(CO)_{12}]^{2-}$ on mixing $[Pt_6(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ [180].

The cluster compounds $Pt_2M_2(\eta^5\text{-}cp)_2(CO)_6L_2$ (M- Mo, W; L= PEt_3, PPh_3) have been prepared from cis-$PtCl_2L_2$ and $cpM(CO)_3^-$. The compounds have planar, triangular centrosymmetric arrangements of the metal atoms [181]. Treating cis-$PtCl_2(PPh_3)_2$ with $Mn(CO)_5^-$ gives two mixed metal carbonyl complexes, the structure of one (72), having been solved by x-ray diffraction techniques [182]. The preparation and catalytic properties of polymer-and silica-supported bimetallic clusters have



$$\text{cis-}PtCl_2(PPh_3)_2 + 4Mn(CO)_5^- \longrightarrow (CO)_5Mn-\overset{CO}{\underset{CO}{Pt}}-Mn(CO)_5 + (CO)_4Mn-\underset{CO}{Pt}-Mn(CO)_4$$

(72)



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been reported. Infrared data are presented for a number of compounds and the rate of hydrogenation of ethylene by $Fe_2Pt(CO)_8(Ph_2P\text{-}\textcircled{P})_2$ is discussed [183].

The ^{13}C nmr data are reported for a series of carbonyl and acyl complexes of platinum(II). Both the ^{13}C chemical shifts and the magnitudes of $J(^{195}Pt\text{-}^{13}C)$ are markedly affected by changes in the cis ligands, as well as those trans to CO [184]. Furthermore, in this study it is found that the electronic charge on the complexes does not appear to exert a dominating influence on these parameters. A convenient synthesis of $\underline{cis}$-$PtCl_2(CO)_2$ (73) has been published using thionyl chloride. Yields are 72% and the product is indefinitely stable at room temperature when sealed in vials under CO [185]. On the assumption that there is a relationship between the carbonyl force constant and reactivity, the compound $\underline{cis}$-$PtCl_2(CO)_2$

$$PtCl_4{}^{2-}.nH_2O \; + \; 3CO \; + \; nSOCl_2 \longrightarrow 2nHCl \; + \; nSO_2 \; + \; COCl_2 + \underline{cis}\text{-}PtCl_2(CO)_2$$

(73)

predictively reacts with amines to give carbamoyl compounds (74). The structure

$$PtCl_2(CO)_2 \; + \; (\underline{i}\text{-}Pr)_2NH \longrightarrow [(\underline{i}\text{-}Pr)_2NH_2][PtCl_2(CONPr\text{-}\underline{i})CO]$$

of the isopropyl compound has been solved [186].

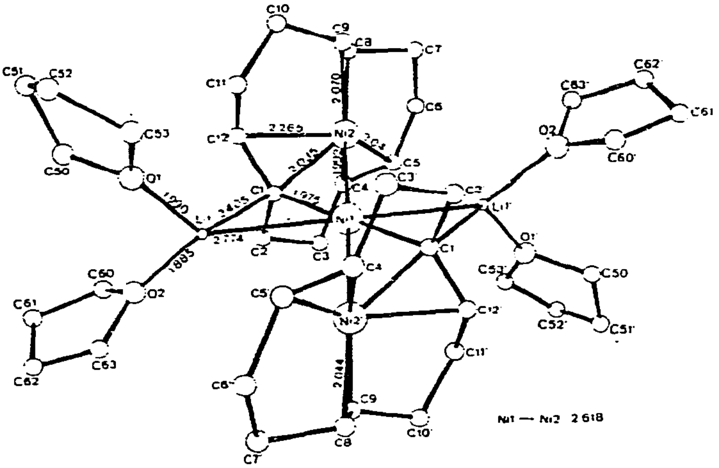
VI. Metal olefins and vinyls

A review has appeared covering the field of Co, Ni and Cu naked metal clusters and olefin chemisorption models. Considerable reference is made to the low temperature spectroscopy of matrix isolated compounds [187].

A novel compound $Ni(C_{12}H_{17}NiLi)_2(THF)_4$ (75) has been obtained by the lithiation of $C_{12}H_{18}Ni$. The complex is prepared at 0° and it is precipitated as red crystals. The structure has been confirmed cyrstallographically [188]. In the following paper this group describes the nickel(0) induced synthesis of ethyllithium from Li, H_2 and C_2H_4 [189]. A detailed synthetic procedure has been

$$C_{12}H_{18}NiLi_2(TMEDA)_2 \xrightarrow[THF]{C_{12}H_{18}Ni} Ni(C_{12}H_{17}NiLi)_2(THF)_4$$

(75)



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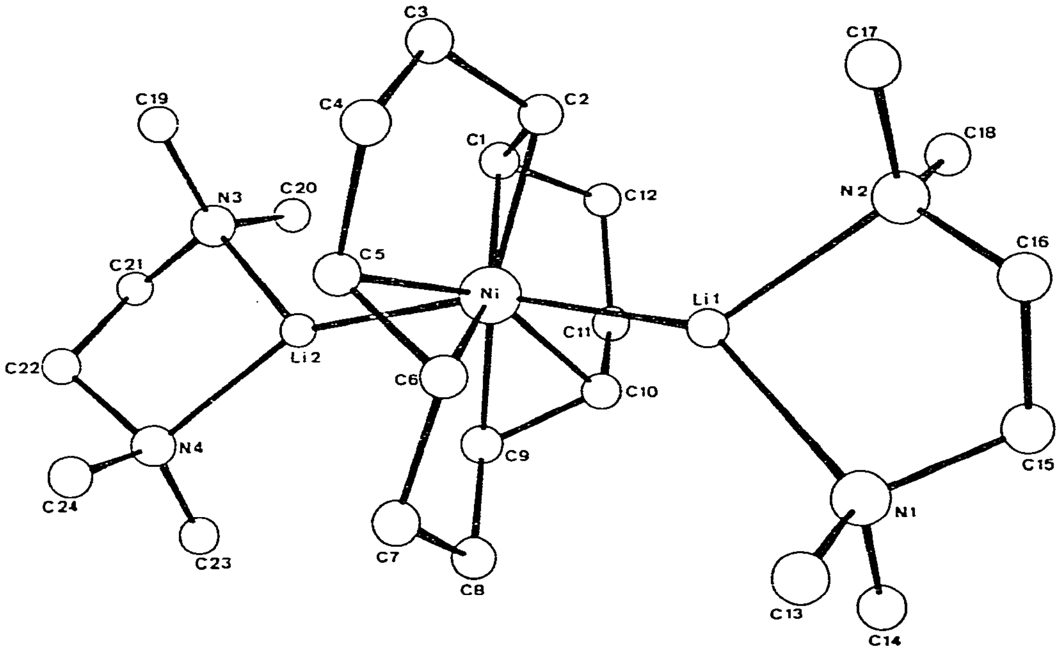
published for (1-3:6-7:10-12-η-2,6,10-dodecatriene-1,12-diyl)Ni using a metal atom reactor [190]. An equilibrium study has been made of ligand concentration control in the system Ni(0)/PPh_3/butadiene[191]. Partial control maps are presented for the distribution of oligomers and dimers in the catalyzed butadiene reaction [191] . The structures of bis(lithium-N,N,N',N'-tetramethylethylenediamine) (all-trans-1,5,9-cyclododecatrienenickel) (76) and tris(N,N,N',N'-tetramethyl-2-butene-1,4-diamine)dilithiumnickel (77) have been solved structurally [192].

New Pd(0) complexes Pd(olefin)$(PMePh_2)_2$ (olefin=styrene, ethyl methacrylate, methyl methacrylate, methyl acrylate, methacrylonitrile and dimethyl maleate) have been obtained from $PdEt_2(PMe_2Ph)_2$ and the olefin. The olefin will dissociate in solution and kinetic parameters were evaluated for this process [193]. Palladium olefin complexes PdX_2L_2 (X= Cl,Br,I; L= styrene, propylene) are prepared from $PdCl_2(PhCN)_2$ and olefin. The reaction with water has been investigated and the reactivity patterns deduced [194]. The interaction of $PdCl_4^{2-}$ with ethylene to form π-complexes has been reinvestigated using a reactor with high efficiency gas-liquid mixing. This has allowed evaluation of the equilibrium constants K_1, K_2 and K_h. Spectra taken at high [Pd(II)] indicate dimeric species are not formed under those conditions [195].

$$PdCl_4^{2-} + C_2H_4 \xrightleftharpoons{K_1} PdCl_3(C_2H_4)^- + Cl^-$$

$$PdCl_3(C_2H_4)^- + H_2O \xrightleftharpoons{K_2} PdCl_2(H_2O)(C_2H_4) + Cl^-$$

$$PdCl_4^{2-} + H_2O \xrightleftharpoons{K_h} PdCl_3(H_2O)^- + Cl^-$$



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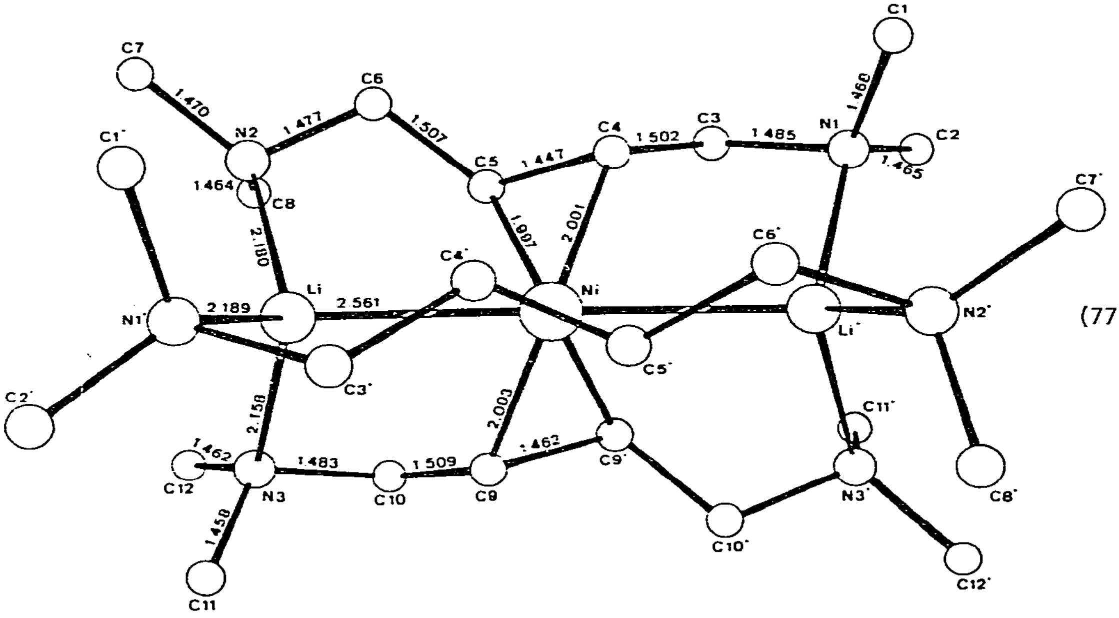

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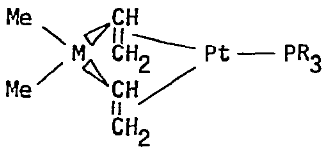
Detailed synthetic procedures have been published for the preparation of $Pt(COD)_2$, $Pt(C_2H_4)_3$ and $Pt(C_2H_4)_2PCy_3$ [196]. The compound $Pt(COD)_2$ reacts with dimethyl or diethyl fumarate or maleic anhydride (olefin) to give complexes Pt(COD)(olefin). Compounds of type $PtL(olefin)_2$ (L= t-BuNC, PPh_3) and $Pt(t\text{-}BuNC)_2$ (olefin) have also been prepared. Using these olefins with $Pt(C_2H_4)_3$ the complexes $Pt(C_2H_4)(olefin)_2$ and $Pt(olefin)_3$ have been prepared [197]. Protonation of Pt(COD)(DMF) with CF_3CO_2H gives selectively the platinum (II) σ-bonded complex $[Pt\{CH(CO_2Me)CH_2(CO_2Me)\}O_2CCF_3(COD)]$. The compounds $Pt(C_2H_4)_2(PR_3)$ (PR_3= P-t-Bu_2Me, PCy_3, PPh_3) react with dimethyldivinylsilane or dimethyldivinyltin to give chelate complexes$[Pt\{(CH_2{=}CH)_2MMe_2\}PR_3]$ (M= Si,Sn) (78). Allyltrimethyltin reacts with diethylene(tertiary phosphine)platinum compounds with cleavage of the allyl group to give complexes $[Pt(SnMe_3)(\eta^3\text{-}C_3H_5)PR_3]$ [198]. A Zeise salt (79) has been prepared with a nitrogen-phosphorus ylide as a chelate ligand. The nmr data suggest a delocalized structure in the ylide [199]. The synthesis and structure of the Bredt olefin complex bicyclo[4.2.1]non-1(8)-enebis(triphenyphosphine) platinum(0) (80) shows the olefin the complex to be in the energetically preferred conformation of the free olefin as deduced by force field calculations [200].



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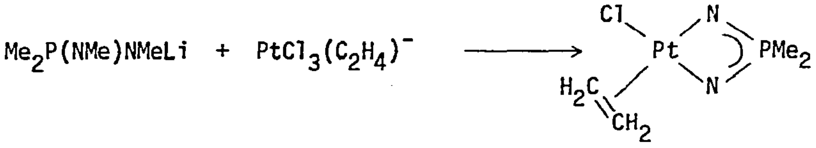

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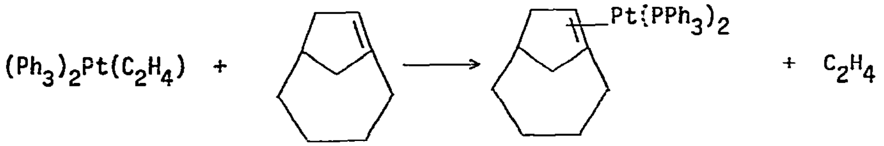
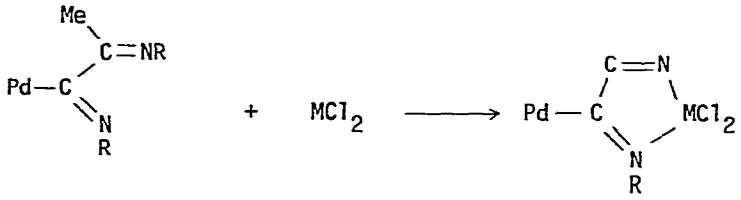


(80)

Catalytic amounts of $Pt(C_2H_4)(PPh_3)_2$ have been used for the isomerization of Bredt olefins [201]. The nature of diastereomeric discrimination in the series of Pt(II) complexes trans(N,olefin)-choro(N-methyl(S)-prolinato)olefin platinum has been studied using ^1H, ^{13}C and ^{195}Pt nmr spectroscopy. The abundant diastereomers have a stronger Pt-olefin bonding, and thus enhanced thermodynamic stability [202]. In a series of complexes the ^{15}N and ^{31}P nmr spectra are reported for the complex cis-$PtCl_2(NH_2(CH_2)_5CH_3)C_2H_4$ [203]. Vibrational and nmr studies on the complexes PtCl(acac)olefin with a series of olefins reveal the σ- and π-back bonding are of comparable importance in the Pt(II)-olefin bond. The bonding is compared for Rh(I) and Ir (I). The σ-bonding of the Pt-olefin bond is stronger for PtCl(acac)(olefin) than for trans-$PtCl_2$(4-Mepy-N oxide)(olefin) [204]. A study has been made of the effect of chain length on the structure and reactivity of $PtCl_2$(diamine)(ethylene) complexes. Comparison is made between 4- and 5-coordinate structures, and in some cases the 5-coordinate structure is found at low temperatures [205]. The crystal structure of $[PtCl(C_2H_4)(Me_2NCH_2CH_2NMe_2)]ClO_4$ shows a long C-C bond and a short metal-C distance. The elongation of the C-C bond is considered due to strong C_2H_4 to Pt σ donation [206]. The structure of trans-$PtCl_2(C_2H_4)$(2,6-dimethylpyridine) has a twofold axis passing through Pt,N, and bisecting the C=C bond [207]. Differences from previous structures center mainly on the increased tilting of the ethylene in this present case. Solvent effects are important in the photochemical behavior of cis- and trans-$PtCl_2$(ethylene)(amine) complexes. Dimeric compounds $Pt_2Cl_4(amine)_2$ are obtained on irradiation in $CHCl_3$ or Et_2O. With MeOH, DME or DMF the cis and trans complexes have a different photochemical behavior, but in all cases photodegradation to $PtCl_3(ethylene)^-$ and $PtCl_3(amine)^-$ is the main reaction [208]. The oxidation of $PtCl_3(C_2H_4)^-$ by Cl_2 in aqueous solution gives $ClCH_2CH_2OH$ and $PtCl_4^{2-}$ and proceeds by a sequence of steps involving a coordinated chloroalkyl complex which is hydrolyzed to the alcohol [209].

Nonempirical molecular electronic structure theory has been applied to the systems $Ni(ethylene)_2$ and $Ni(C_2H_4)_2$. For $Ni(C_2H_4)_3$ the twisted (D_{2d}) and "planar" (D_{2h}) conformation lie energetically within 0.1kcal of each other. For $Ni(C_2H_4)_3$, however, the planar conformation lies ~24kcal lower than the upright form. The lowest D_{2h} triplet state of $Ni(C_2H_4)_2$ is of $^3B_{3u}$ symmetry, and a number of other electronic states have been investigated [210]. An analysis based on the Hartree-Fock-Slater transition state method has been presented of the Pt-C_2H_4 bond in complexes of $PtCl_3^-$ and $Pt(PH_3)_2$. Emphasis is again placed on the contribution to the bonding [211].

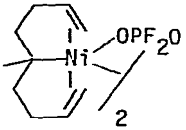
Binuclear complexes have been prepared of 1,4-diaza-3-methylbutadien-2-yl with Pd(II) and Pt(II) chlorides. The complexes have one carbon of the diene bonded to Pd or Pt, and complexation to a second metal can occur (81). Substitution of backbone ligands (dppe, dithiocarbonate, etc.) can be effected to prepare a series of complexes [212]. In the following paper the chemistry of these complexes is discussed where the second metal M is a rhodium [213]. The kinetics of the reaction of alkenes (cis-pentene-2,hexene-1,cyclopentene) with $\overline{PtX_2(CH_2CH_2C}H_2)(THF)_2$



(81)

(X= Cl,Br) or with $PtCl_2(CHPhCH_2CH_2)(THF)_2$ occur with displacement of cyclopropane or phenylcyclopropane to give $PtCl_2$(olefin)THF. The kinetics show first order dependence on both Pt complex and olefin. Mechanistic details are discussed [214]. The compounds 1-, 2-, and 3-methyl-4-pentenylamine cyclize in a reaction mixture containing $PtCl_4^{2-}$ to the corresponding cis- and trans-dimethylpyrrolidines with marked regio- and stereoselectivity effects. The crystal structures of two pyrrolidine compounds are also reported [215].

Treating Ni(allyl)$_2$ with difluorophosphoric acid under addition of 1,5-hexadiene, bis(pentahapto-1,8-nonadiene-5-yl nickel(II) difluorophosphate)(82) can be synthesized. The reaction involves the 1,2-addition of the trihapto-allyl-nickel (II) fragment to the double bond of an α-olefin [216]. An exocyclic dimeric π-enyl complex has been formed from treating trans-$PdCl_2(PhCN)_2$ with 1,3-dimethylenecyclohexane [217].

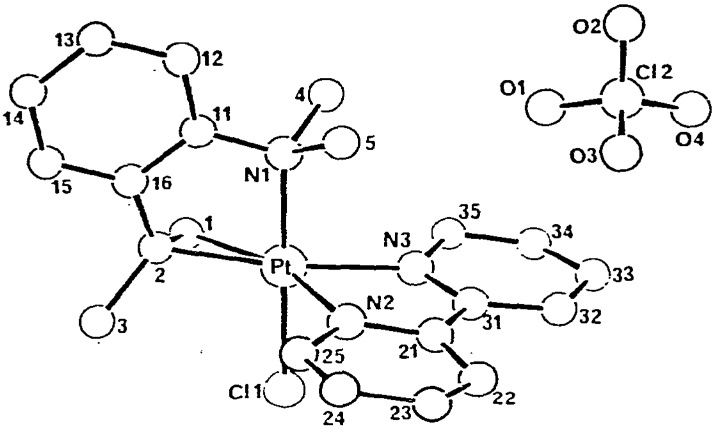


(82)

The compound $Pt(COD)_2$ has been prepared in good yield by reduction of $PdCl_2$(COD) with $Cocp_2$ in the presence of excess COD [218]. Reaction of dichloro(o-isopropenyl-N,N-dimethylaniline)Pt(II) with bipyridine and $NaClO_4$ gives the cationic complex (83). The ligand arrangement about Pt(II) is a very distorted trigonal bipyramidal one with the olefin and the bipyridine groups in the equational plane [219].

$$PtCl_2(COD) + 2Cocp_2 + COD \xrightarrow{-20^\circ} Pt(COD)_2 + 2Cocp_2Cl$$

N,N-diallylaniline and 2,6-diallylaniline form complexes with Pt(II). In the first complex the ligand is coordinated through two double bonds, in the second it is coordinated through the N atom and one of the double bonds [220]. From 2 series of olefin platinum(II) complexes having respectively phenolato and thiophenolato ligands trans to the olefin, the values of $J(^{195}Pt-^{1}H(olefin))$ have been used with ligand pK_a's to show a significant degree of π-acid character in the thiophenolato-sulfur atom [221]. A complex cis-$NiCl_2[CH_2N(CH_2CH=CH_2)_2]_2$ has two



(83)

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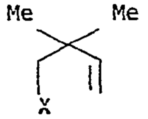
double bonds coordinated and two free, from an ir study in the solid state. From nmr data all four vinylic double bonds are equivalent in solution indicating a rapid "bonded/non-bonded" equilibrium for the double bonds [222].

A series of 1:1 complexes with palladium(II) halides and the substituted halides (84) and (85) have been prepared. In solution the complexes are chelated. Variable temperature ^{1}H nmr studies of two exchange processes, labilization of the metal-olefin bond and, for the sulfur chelates, inversion at sulfur, are discussed [223]. The interaction of $Pt_2Cl_4(C_2H_4)_2$ with polar olefins having 1,1' substitution of OMe or NMe_2 groups leads to both η^1 and η^2 complexes. The complexes have been isolated and characterized, and the bonding is elucidated from the ^{1}H nmr data [224]. The ^{13}C nmr spectra of $PtCl_2(CH_2{=}CHOR)py$ have been used to show that both the CH_2 and CH groups remain essentially sp^2 hybridized. Attempts to correlate ^{1}H and ^{13}C shifts and coupling constants showed little relationship [225]. ^{13}C nmr data have also been given for a series of Ni(0) complexes $Ni(PR_3)_2(CH_2{=}C(Me)CO_2Et)$($PR_3$= PPh_3, $PEtPh_2$, PEt_2Ph, PMe_2Ph, PEt_3). The olefinic carbons move upfield by 71.5-86.5 ppm on coordination, the magnitude of the shift increasing with increase in the basicity of the phosphine ligand. Some



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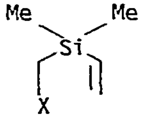


(85)

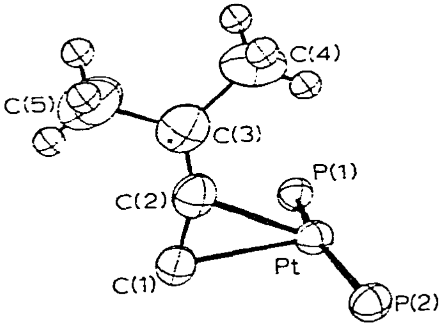
X= NMe_2, SMe

variable temperature ^1H nmr studies show that for the least sterically demanding phosphine ligands, the complexed olefin exchanges with the free compound on the nmr time scale [226]. A series of complexes cis-$PtCl_2(PR_3)$(olefin) (where the olefin is CH_2=CHOAc, CH_2=$CHCH_2OAc$; and PR_3= PMe_3, PMe_2Ph, PEt_3) have been prepared. The structure of cis-$PtCl_2(PMe_2Ph)(CH_2$=CHOAc) has been solved. Variable temperature nmr has been used to study the rotation of the coordinated olefin [227].

The compound trans-$[PtH(MeOH)(PCy_3)_2]PF_6$ reacts with 1,1-dimethylallene to give trans-$[PtH(Me_2C{=}C{=}CH_2)(PCy_3)_2]PF_6$ (86) which has the unsubstituted double bond coordinated to Pt [228]. In an article describing an application of asymmetric hydrogenation a method for obtaining isomerically pure (Z)-ethyl-2-acetoxy-3-deuterioacrylate (87) is described using the corresponding bromo compound. A method is given for recycling the palladium [229].

$$\text{trans-}[PtH(MeOH)(PCy_3)_2]PF_6 \;+\; Me_2C{=}C{=}CH_2 \longrightarrow \text{trans-}[PtH(Me_2C{=}C{=}CH_2)(PCy_3)_2]PF_6$$

(86)



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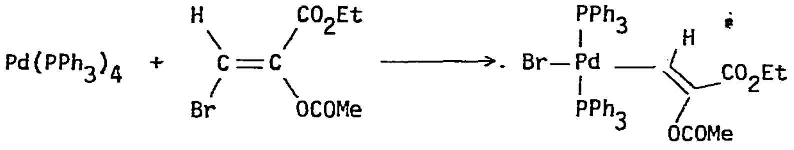
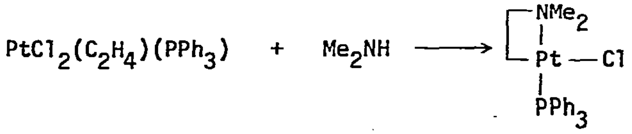


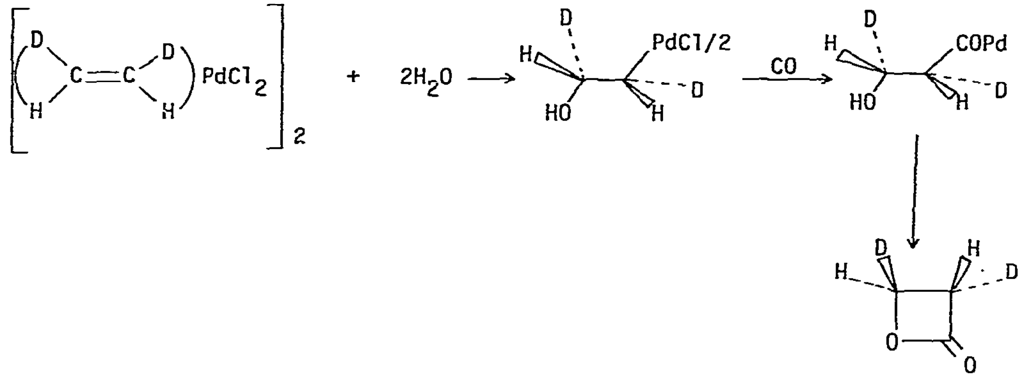
(87)

A cyclization reaction is described upon treating $PtCl_2(C_2H_4)(PPh_3)$ with dimethylamine. The product (88) has been characterized by spectroscopic



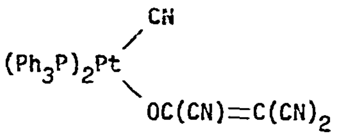
(88)

techniques [230]. The reaction of olefin Pt(II) complexes with amines usually gives products of structure $(\overset{+}{\text{amine}})CH_2CH_2Pt$, and the kinetics and mechanism of such a reaction has been investigated. Steric effects in the amine predominate over electronic effects. With aromatic amines attack will occur at platinum leading to the formation of pentacoordinate π-ethylene complexes [231]. The stereochemistry of hydroxypalladation, the first step in the Wacker oxidation of ethylene to acetaldehyde, has been determined using cis-1,2-dideuterio ethylene by intercepting the intermediate β-hydroxyethylpalladium complex with CO. It is concluded that the hydroxypalladation step proceeds steroespecifically trans [232].

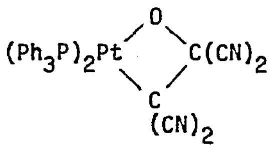


A kinetic study of the reaction of $M(C_{10}H_{12}OMe)(L\text{-}L)^+$ complexes (M= Pd,Pt) with HX follows a pathway with a slow formation of $M(C_{10}H_{12})solv(L\text{-}L)^+$ and then a fast reaction with X^- to give $M(L\text{-}L)X_2$ [233]. The kinetics of the oxidative arylation of substituted styrenes by benzene, naphthalene and phenylmercuric acetate in the presence of $Pd(OAc)_2$ show pathways zero- and first-order in olefin. For the olefin dependent path a π-arene-π-olefin Pd complex is proposed as the reactive intermediate [234].

Carbonato complexes L_2PtCO_3 (L= PPh_3, $AsPh_3$) react with electrophilic olefins liberating CO_2. The reaction with tetracyanoethylene is solvent dependent, and by changing conditions complexes (89),(90), or (91) can be obtained


$(Ph_3P)_2Pt(CN)(OC(CN){=}C(CN)_2)$

(89)



(90)

$(Ph_3P)_2Pt(CN)_2$

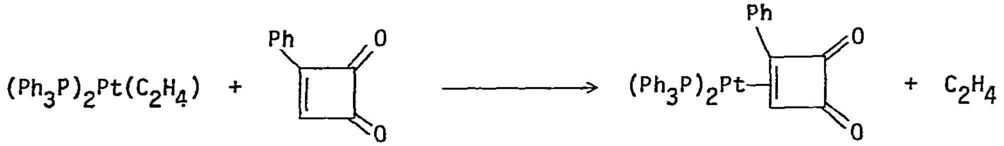
(91)

[235]. The enthalpies of reactions (92) and (93) have been measured and the data used to explain patterns of reactivity of these compounds [236]. Enthalpy

$$\textit{trans}\text{-Pt(PMe}_2\text{Ph)}_2\text{MeCl(s)} + \text{C}_2\text{(CN)}_4\text{(g)} \longrightarrow \text{Pt(PMe}_2\text{Ph)}_2\text{MeCl(C}_2\text{(CN)}_4\text{) (s)} \qquad (92)$$

$$\textit{trans}\text{-Pt(PPh}_3\text{)}_2\text{HCl(s)} + \text{C}_2\text{(CN)}_4\text{(g)} \longrightarrow \text{Pt(PPh}_3\text{)}_2\text{(C}_2\text{(CN)}_4\text{)(s)} + \text{HCl(g)} \qquad (93)$$

studies of the reaction of $Pt(PPh_3)_2(C_2H_4)$ with 3-phenylcyclobutene-1,2-dione to give the complex (94) show that the Pt-olefin bond with the substituted olefin is slightly stronger than that with styrene [237]. The geometries of binding dibenzylideneacetone to Pt has been investigated by nmr spectroscopy for the complexes $Pt_2[(PhCH{=}CH)_2CO]_3$, $Pt_2[(C_6D_5CD{=}CH)_2CO]_3$ and $Pt_2[(C_6D_5CH{=}CD)_2CO]_3$. The three ligands which triply bridge the two Pt atoms are composed of one *s-cis,cis-* ligand which is distant from the Pt atoms and of two *s-cis,cis* ligands which are close to the Pt atoms [238]. A new route to complexes Ni(COD)(duroquinone), Ni(endo-dicyclopentadiene)(duroquinone), $Ni(COD)_2$ and $Ni(tetracyclone)_2$ uses $Ni(allyl)_2$ as starting material [239]. Benzophenonimine can be complexed to Ni(0) by reaction with $Ni(COD)_2$ and bipy (95). In the absence of bipy a complex $Ni(PhC{=}NH)_2$ (96) is formed [240]. A side bonded ketone complex $Pt(PPh_3)_2$(alloxan) has been obtained by treating $Pt(PPh_3)_2$(*trans*-stilbene) with alloxan [241]. The compounds $Ni(C_2H_4)(PR_3)_2$ (R= Ph,Cy) and Ni(COD)(bipy) react with CS_2 to give $[Ni(CS_2)(PR_3)]_x$ and $Ni(CS_2)$(bipy) respectively. The compounds do not react with CO_2 but a compound Ni(COS)(bipy) has been prepared [242].



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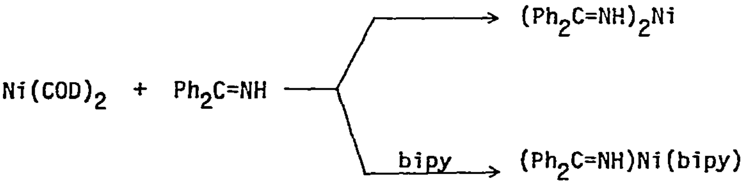
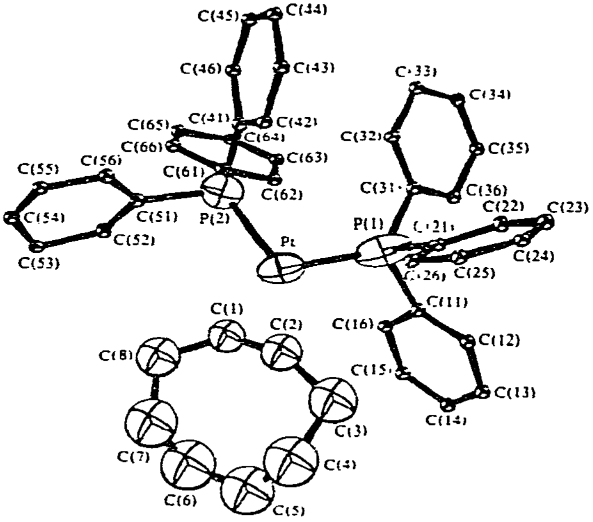


(96)

(95)

VII. Metal acetylenes and acetylides

The structure of $Pt(PPh_3)_2$(cyclooctyne) (97) has a planar unit along C-C-C≡C-C-C in the coordinated cyclooctyne group [243]. Similar π-bonded complexes of $(Ph_3P)_2Pt$ have been formed from the acetylenes RC≡C(R')P(S)SMe (R=Me,Et,Me_3Si; R'= Me, 4-MeOPh) [244]. Acetylene complexes of Ni and Pt have been prepared from the acetylene (98) derived from 15-substituted benzo-15-crown-5 [245]. Treating $PdCl_2$ with acetylenes yields complexes which have been used for the hydrogenation of acetylenes in DMF [246].



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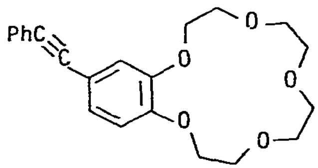
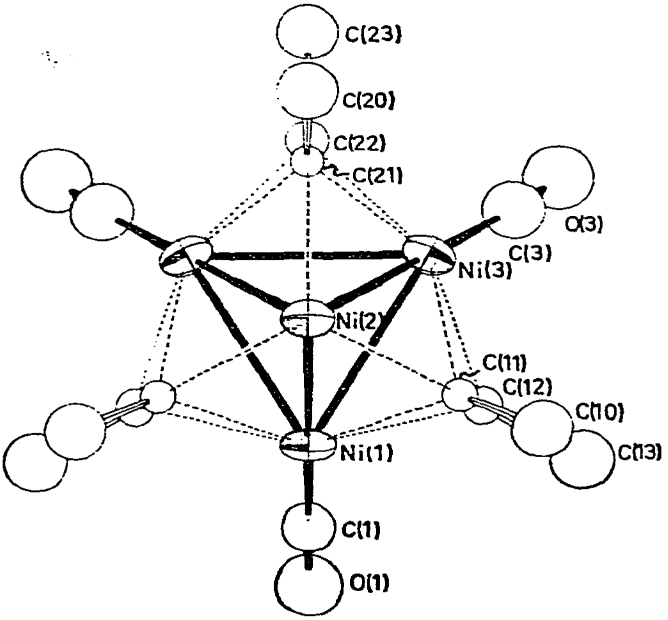


(98)

Methyl *t*-butyl acetylene reacts with $Pd(PhCN)_2Cl_2$ to give the cyclobutadiene complex $[Pd_2(C_4\underline{t}\text{-}Bu_2Me_2)_2Cl_3]_2[Pd_2Cl_6]$ at 20°. At -50° the π-acetylene complex $[Pd_3(C_2Me\underline{t}\text{-}Bu)_2Cl_6(PhCN)_n]$ is formed which rearranges at 0° to give the σ,π-butadienyl complex. The mechanism of the formation of the σ,π-butadienyl complex is discussed and reasons proposed for the acceleration in rate caused by positive charge on the complex and the absence of a detectable σ-alkenylpalladium intermediate [247]. In the following paper some chemistry of the σ-butadienyl complex is described. The acetylenes Ph_2C_2 and t-BuC_2Ph are catalytically carbonylated in the presence of $PdCl_2(PhCN)_2$ to give tetraphenylcyclopentadienone and 3,4-diphenyl-2,5-di-t-butylcyclopentadienone respectively. The σ,π-butadienyl complex $Pd_3(\eta^3\text{-}C(t\text{-}Bu)\text{=}CMeCMe\text{=}C(t\text{-}Bu)Cl)_2Cl_4$ reacts with mono-t-butyl acetylene to give 1,3-dimethyl-2,4,6-tri-t-butylbenzene [248].

Reaction of $Ni(CO)_4$ with $(CF_3)_2C_2$ gives initially $Ni(CO)_2(\eta^2\text{-}CF_3C_2CF_3)$ which decomposes to the cluster compound $Ni_4(CO)_4\{\mu_3\text{-}(\eta^2\text{-}CF_3C_2CF_3)\}_3$ (99). Reaction of the cluster with t-BuNC or dppe gives mononuclear complexes (100) [249].

$$\begin{tikzcd}
Ni(CO)_4 + CF_3C_2CF_3 \arrow[r] & (CO)_2Ni(CF_3C_2CF_3) \arrow[r] & Ni_4(CO)_4\{\mu_3\text{-}(\eta^2\text{-}CF_3C_2CF_3)\}_3 \quad (99) \arrow[d, "L"] \\
 & L= t\text{-}BuNC,\ L_2= dppe & NiL_2(\eta^2\text{-}CF_3C_2CF_3) \quad (100)
\end{tikzcd}$$



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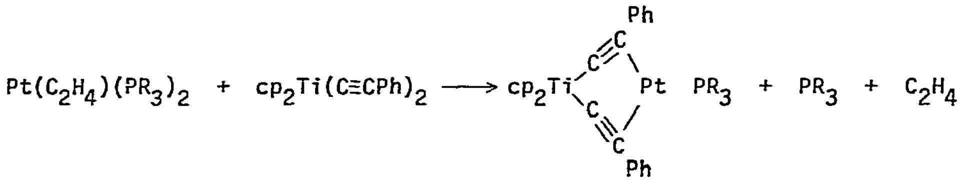
In contrast cyclooctatetraene gives $Ni_3(CO)_3\{\mu_3-(\eta^2-CF_3C_2CF_3)\}\{\mu_3-(\eta^2-C_8H_8)\}$, the structure of which is also reported. Alkynyl complexes *trans*-(mesityl)Ni$(PPhMe_2)_2C\equiv CR$ (R= H,Me,CH_2CH_2OH, Ph,C_6H_4OMe-*p*), *trans*-$(CCl_2{=}CCl)Ni(PPhMe_2)_2C\equiv CR$, and *trans*-$\{(o\text{-}MeO)_2C_6H_3\}Ni(PPhMe_2)_2C\equiv CR$ (R=H,Ph) have been isolated. Reactions with methanol in the presence of $HClO_4$ can give the expected cationic carbene complex [250]. Treating $Pt(C_2H_4)(PR_3)$ (PR_3= PCy_3,PMe_2Ph,$PMePh_2$,PPh_3,P*i*-Pr_2Ph) with $cp_2Ti(C\equiv CPh)_2$ gives compounds $[Pt\{\eta-(PhC\equiv C)_2Ticp_2\}PR_3]$ (101) in which the $PhC\equiv C-Ti-C\equiv CPh$ group acts as a bidentate ligand to platinum. With $Me_2Si(C\equiv CPh)_2$ complexes $[Pt_2(-C\equiv CPh)\{\mu-(1-\sigma:1-2-\eta-C\equiv CPh)(\mu-SiMe_2)(PR_3)_2]$ are formed, and the single crystal structure has been solved for the PCy_3 complex (102) [251]. A general procedure has been reported for the high yield syntheses of $(Ph_3P)_2Pt(C\equiv CR)_2$ (R= Ph,$C(CH_2)Me$, $(CH_2)_6C\equiv CH$, CH_2OH, CH(OH)Me, CH(OH)Ph, $CH_2CH(OH)Me$, $C_6H_{10}OH$, C(OH)(Me)Et, CH_2NHMe, CH_2NHCH_2Ph, CH_2NMe_2, CH_2NEt_2) using dimethylamine and cuprous iodide with the appropriate acetylene and $(Ph_3P)_2PtCl_2$ [252]. When $PtHCl(PPh_3)_2$ and 1-ethynylcyclohexanol are warmed in benzene, addition of ethanol leads to an acetylide platinum complex (103) where the hydroxy group has been converted to an ethoxy group. The structure of the compound (103) has been confirmed by x-ray crystallography. The cyclohexyl ring is in a twisted chair conformation with the Pt-C-C system in an axial position. The acetylene $C\equiv C$ distance is 1.22(2) Å [253]. The mass spectra of complexes *trans*-$(Ph_3P)_2Pt(C\equiv CR)_2$ (R= 2-hydroxy-2-Bu, 2-hydroxy-2-Pr, 2-propenyl, 1-hydroxy-1-cyclohexyl and 1-cyclohexen-1-yl) and of *trans*- and *cis*-$(Ph_3P)_2Pt(C\equiv CPh)_2$ will show dehydration reactions easily under electron impact. For the phenylacetylide compounds the Pt-P bonds are more stable than the Pt-C bonds [254]. In a further mass spectral study of complexes $(Ph_3P)_2PtCl(C\equiv CR)$, again the Pt-P bond is the strongest. Several organic polymers are present in the spectra suggesting a rapid polymerization reaction of protolytic hydrocarbon radicals catalyzed by the platinum containing fragment [255]. The structure of the compound $(Bu_3P)_2Ni(C\equiv CC_6H_4C\equiv CH\text{-}o)_2$ shows a nearly linear $Ni-C\equiv C-C$ moiety with the planar phenylene rings being inclined towards the coordination plane by 56.7° [256].



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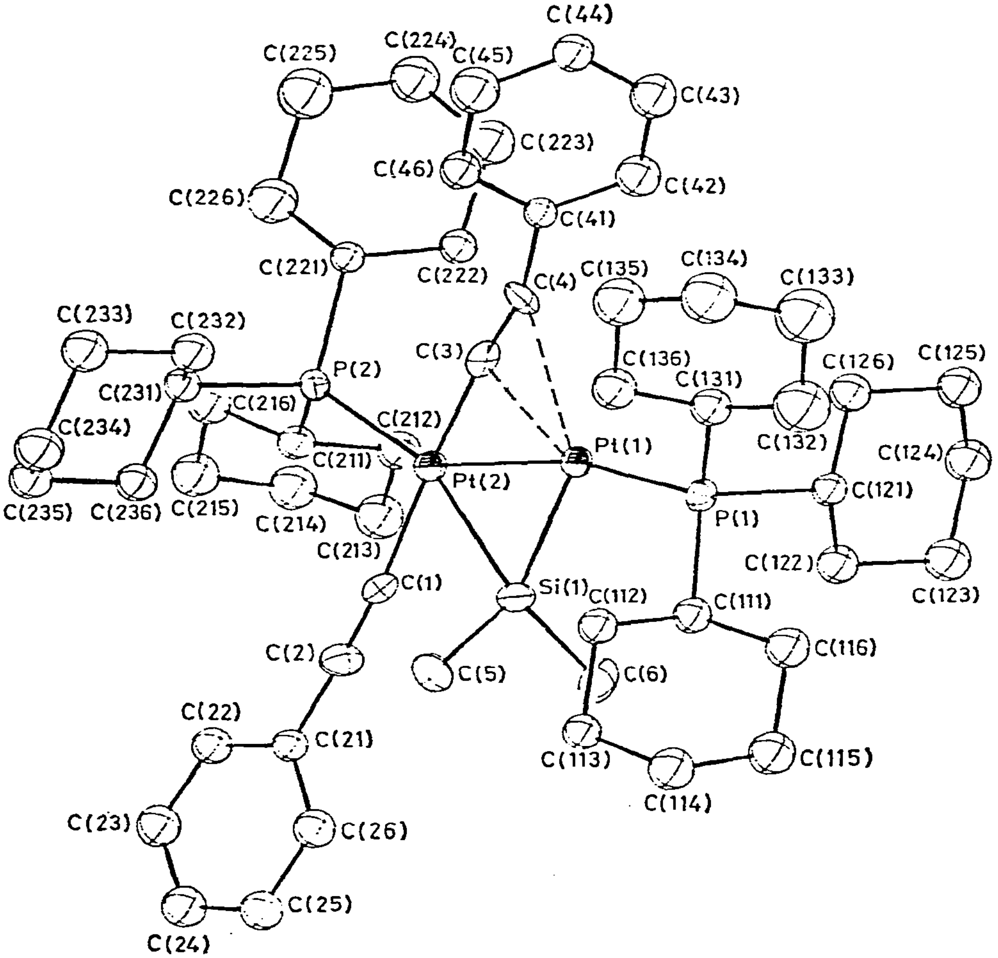
An infrared study has shown that complexes of acetylene with Ni,Pd and Pt are formed when the reactants are condensed on a CsI support at 20K [257].



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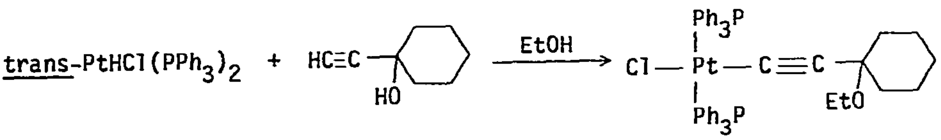
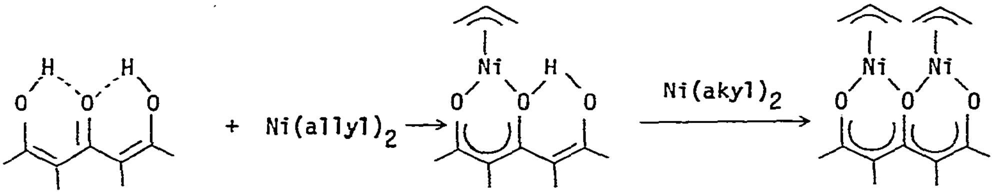


(103)

VIII. Metal allyls

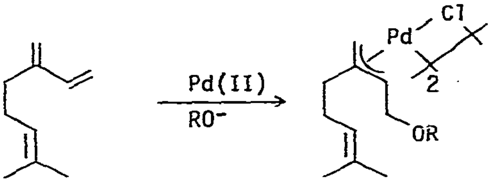
A synthesis of π-allyl nickel complexes using transition metal powders has been described. The powders are made by alkali metal reduction of the transition metal salts and compounds (π-allyl $NiX)_2$ prepared using allylic halides. The work focuses mainly on nickel chemistry but there is some discussion of research on Pd allyls [258].

Using $Ni(allyl)_2$ and 1,8-dihydroxyanthraquinone the mono- (104) and bis (105) allylic complexes have been prepared [259]. Nickel allyls have been used in the synthesis of linear alcohols from their reaction with paraformaldehyde [260]. An allyl complex $(\eta^3\text{-}C_3H_5)(\eta^5\text{-cp})Pd$ (106) has been prepared from $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and sodium cyclopentadienide[261]. Details of the preparation of the synthetic precursor are also given. The complex (106) forms red needles which decompose at 61°. Steroidal π-allyl palladium complexes have been obtained by reacting the following steroidal olefins with $PdCl_2$ in the presence of sodium acetate in acetic acid; 5α-cholest-1-,-2-, and -3-ene; cholest-4- and -5-ene; 3-methyl- and 3-phenyl-5α-cholest-2-ene; 3β-chloro- and 3β-acetoxycholest-5-ene; and 5β-cholest-1-,-2-, and -3-ene [262]. Oxygen nucleophiles (HO^-, EtO^-, i-PrO^-, AcO^-) regioselectively react at the terminal position of β-myrcene in the presence of $PdCl_2$ to give π-allyl complexes (107) [263]. Nickel allyls react



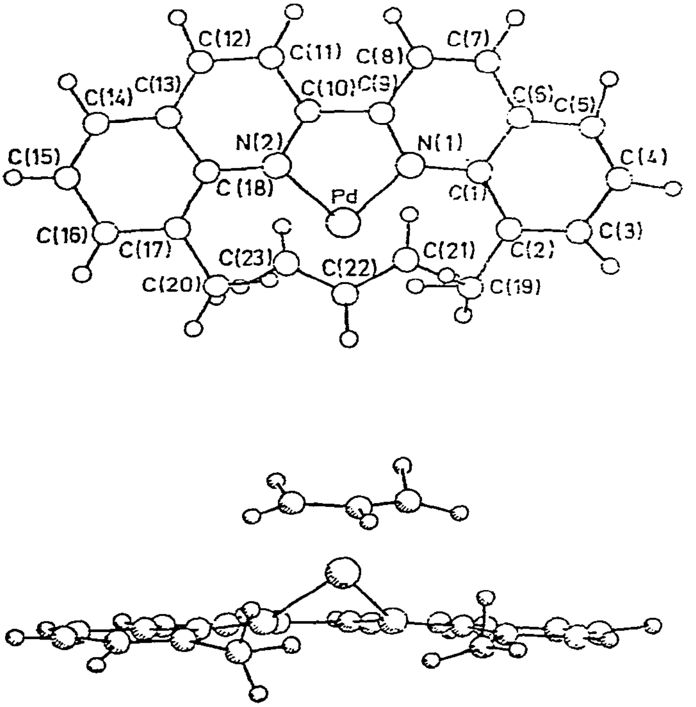
(104) (105)

$$[(\eta^3\text{-}C_3H_5)PdCl]_2 + 2Nacp \longrightarrow 2Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-cp}) + 2NaCl \qquad (106)$$



(107)

with norbornene to give organic products derived mainly from double insertion and ring opening processes. The reaction is catalytic in nickel and can be used for organic synthetic purposes [264]. The crystal structure of di-μ-chlorobis [{2',3'-η-exo-3-allylnorborn-2-yl)palladium](108), prepared from [π-allyl PdCl]$_2$ and norbornene, where the olefin has inserted into the metal-allyl bond, shows a relatively small π component in the metal-olefin bond [265]. Treating [PdCl(allyl)]$_2$ with L(L=P(NEt$_2$)$_3$, trimorpholinophosphine) gives PdCl(allyl)L [266].



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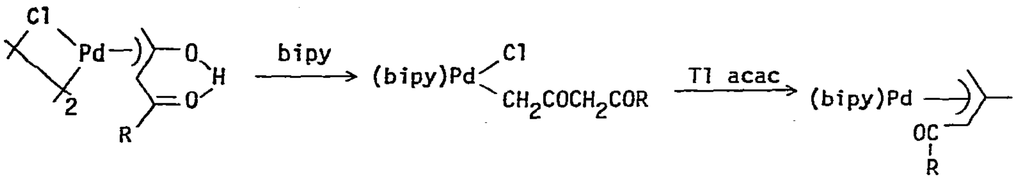
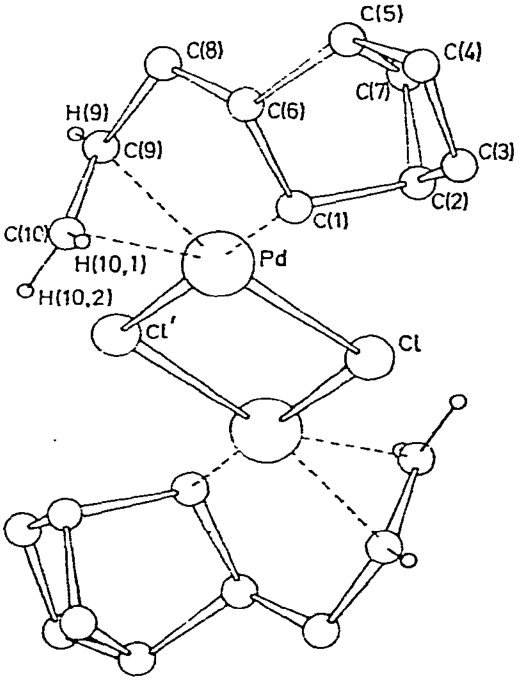
The terminal carbon bonded monoanions of 2,4-pentanedione and ethyl acetoacetate in the [PdCl(β-dik-C')(bipy)] complexes have been deprotonated and converted into the trihapto dianions in the reactions with Tl(acac) [267]. Reactions of β-diketo anions with η^3-allylbis(triphenylphosphine)platinum (II) complexes.



(R= Me,OEt)

or allyl acetates in the presence of triphenylphosphine platinum complexes, gives good yields of allylic alkylation products. Reactions of η^3-allyl(triphenylphosphine)Pt(II) complexes with Tl acac gives stereochemically rigid, thermally stable, σ-allyl acac Pt(II) complexes [268]. The methyl groups in the complex $[Pd(\eta^3\text{-allyl})(8,8'\text{-dimethyl-}2,2'\text{-diquinolyl})]ClO_4$ (109) would be too close together were it not for the Pd atom lying 1.10 Å out of the plane of the bidentate diquinolyl ligand [269]. Reactions of $[(allyl)PdCl]_2$ with neutral



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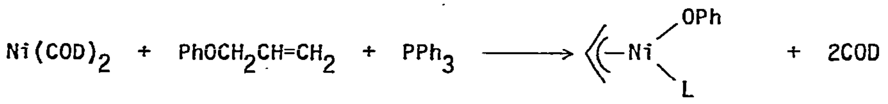
ligands L (L= RN=CHNHR, R=$PhCH_2$, *p*-MeC_6H_4, *p*-ClC_6H_4; L= RN=NNHR, R= *p*-MeC_6H_4, *p*-ClC_6H_4) yield bridge splitting reactions to give Pd(η^3-allyl)ClL. Variable temperature ^{13}C nmr spectra show two dynamic processes. The first one involved dissociation of L, and the second one of lower activation energy is considered to involve Cl-L exchange, probably via a pentacoordinate chloro bridged species [270]. The rates of cleavage of μ-Br and μ-Cl(allyl)Pd by HBr and HCl respectively is proportional to the activity of the complex and H^+, but not to the halide ion concentration [271].

The reaction of allyl phenyl ether with a mixture of $Ni(COD)_2$ and PPh_3

leads to oxidative addition of the ether to give $Ni(\eta^3-C_3H_5)(OPh)PPh_3$ (110). Similar reactions of diallyl ether with $Ni(COD)_2$ in the presence of PR_3(R=Ph,Cy)

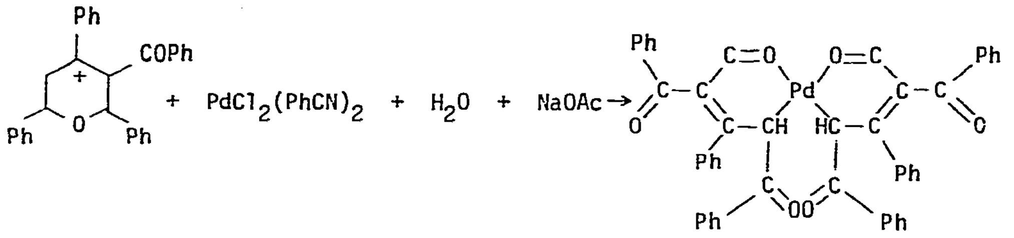


(110)

give uncleaved π-type complexes $Ni(\pi$-allyl ether)(PR_3) [272]. Methylenecyclopropanes having alkyl substituents on the cyclopropane ring undergo addition of the elements Pd-Cl in a 1,3-fashion. The difference in reaction mode showing a preference for 1,3- over 1,2-chloropalladation is caused by substituting a methyl group for a hydrogen on the cyclopropane ring [273]. A mechanism involving a dipolar transition state is proposed. The kinetics and isotope effects for the demetalation of π-allylpalladium chloride by HCl indicate a bimolecular mechanism in which H^+ attacks the π-bond of the complex [274].

2,4,6-Triphenyl-3-benzoylpyrylium perchlorate reacts with $PdCl_2(PhCN)_2$ to give cis-(1,3,3-tribenzoyl-2-phenyl-σ-allyl)Pd(II) (111). The Pd atom is σ-bonded with two carbon atoms and coordinated by two keto-oxygen atoms [275]. The crystal structure of (η^3-allyl)PtCl(tri-p-tolylphosphine) is compared with the t-Bu_3P and PCy_3 analogs [276]. The nmr behavior of PtCl(allyl)(t-Bu_3P) has considered the effect of halide and phosphine on the fluxionality. Distortion effects have been investigated in the solid state by solving the crystal structure of the complex. The structure provides confirmatory evidence of asymmetry of the allyl group and is related to the nmr solution studies [277]. Treating π-allylpalladium complexes with WCl_6/EtOH/$EtAlCl_2$ gives primarily alkylation of the aromatic solvent by the olefin, although C-C sigma bond cleavage in the reactant is also observed [278]. Treating Na_2PdCl_4 in MeOH with allylHgCl gives $[(\pi-C_3H_5)PdCl]_2$. The π-allyl acetato complex was also formed using mercuric acetate [279]. The reductive decomposition of 1-(methoxymethyl)-2-methyl-π-allylpalladium chloride in aqueous HCOOK involves transfer of hydrogen from the formate ion to the allyl ligand of the complex [280]. A similar study has been made in the presence of methoxide ion in methanol [281].

A convenient preparation is described for the conversion of monosubstituted terminal olefins to π-allylpalladium compounds (112) via an in situ allylic chlorination-palladation sequence [282]. Various π-allylnickel halides react with 2-pyridyl carboxylates to give β,γ-unsaturated ketones in good yields [283]. The reaction of 1,3-dienes with $PdCl_2(PhCN)_2$ and Me_2NH gives 4-dimethylamino π-allylic palladium complexes, which on treatment with $AgBF_4$ or PPh_3 are attacked



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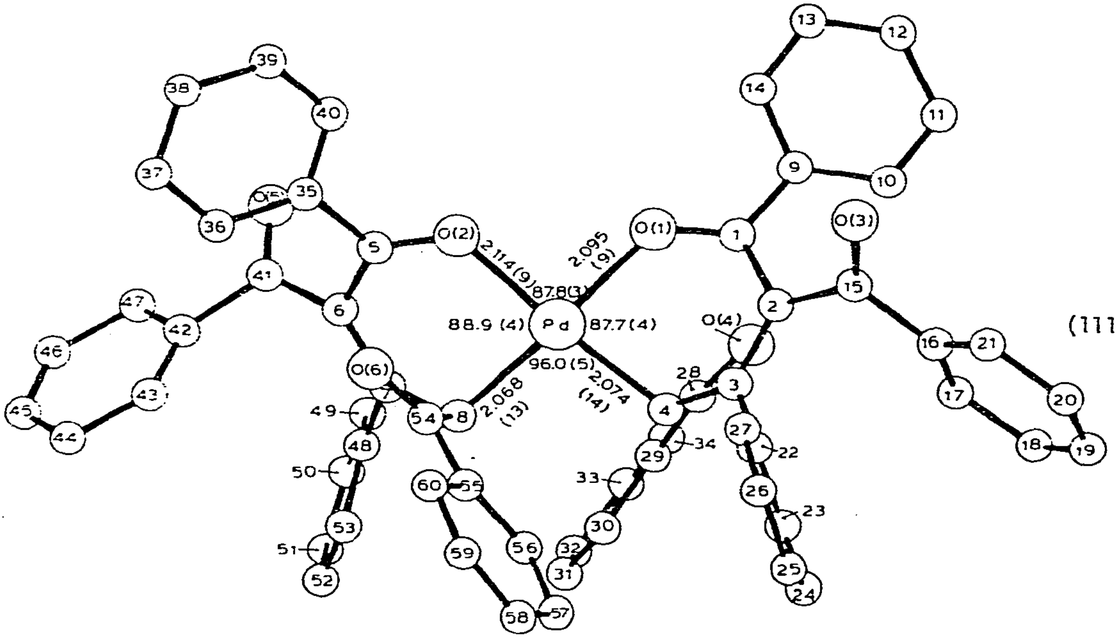

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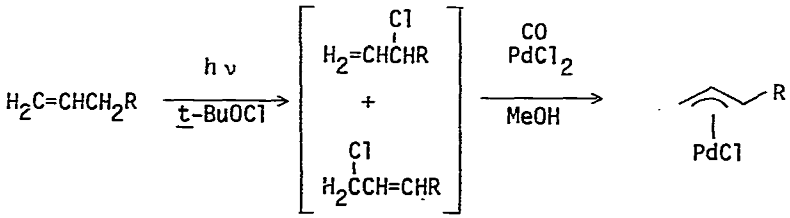
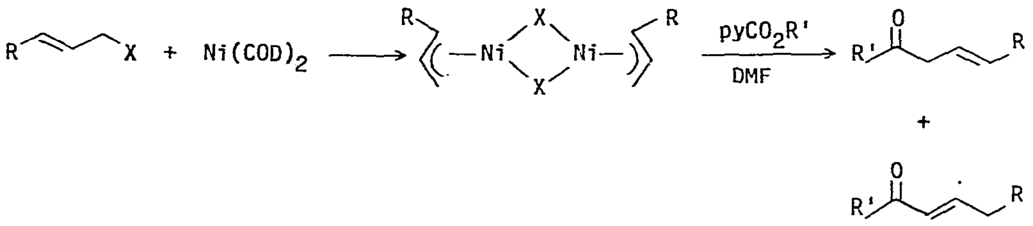
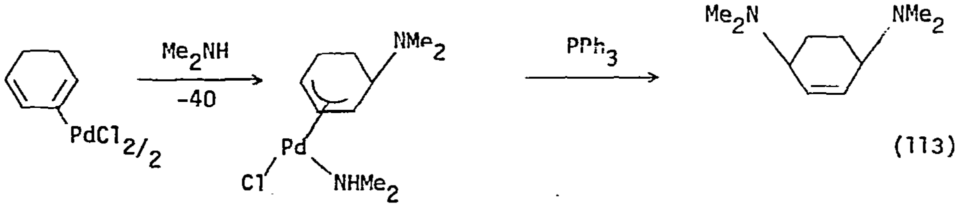


(112)

by excess Me_2NH on the face of the allyl group opposite to that occupied by Pd to give 1,4-diamines (113) [284]. ^1H and ^{31}P nmr spectra of compounds (η^3-allyl) $PtCl(PR_3)$(PR_3= PMe_3, PCy_3, P-t-Bu_3, PPh_3, PPh_2Me, $PPhMe_2$ and P(p-tol)$_3$) suggest there is bonding interaction between the phosphine and the allyl group via the central metal atom. Plots of chemical shifts and coupling constants against phosphine ligand cone angle are given and discussed [285]. The ^{13}C and ^{31}P nmr spectra of $[Pt(\eta^3\text{-allyl})(PCy_3)_2]PF_6$ indicates restricted rotation about the Pt-P bond. Activation parameters have been measured. The compound with i-Pr_3P behaves similarly but the rotation of the $P(CH_2Ph)_3$ complex has not been stopped [286]. Two geometrical isomers of Pd(η-crotyl)(C_6Cl_5)PPh_3 (114,115) undergo uncatalyzed mutual interconversion in benzene at room temperature. The large decrease of the rate on adding free PPh_3 is attributed to occurence of a dissociative isomerization path involving a 3-coordinate





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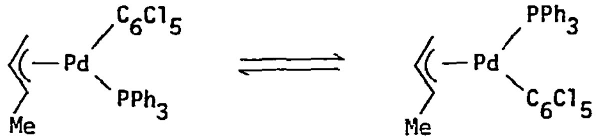
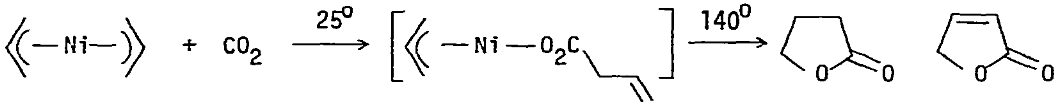
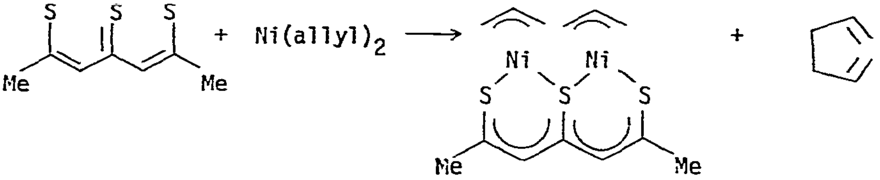


(114) (115)

intermediate [287]. Oxo-π-allylpalladium(II) intermediates are involved in the cyclization of silyl enol ethers to γ,β-unsaturated ketones [288]. γ-Lactones have been obtained by treating π-allylnickel complexes with CO_2. Solvents, yields and temperatures are given for the reaction [289].



An allyl complex of nickel has been prepared from 2,5-dimethyl-1,6,6aλ^4-trithiapentalene and $Ni(allyl)_2$. The structure of the complex (116) has been



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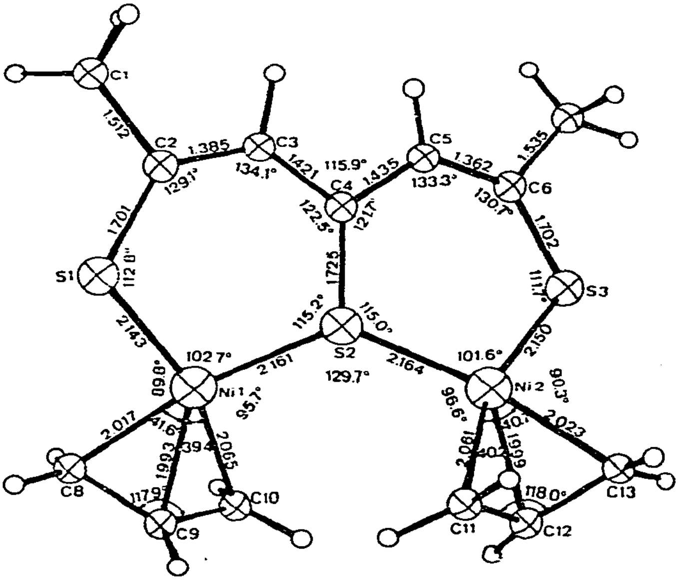

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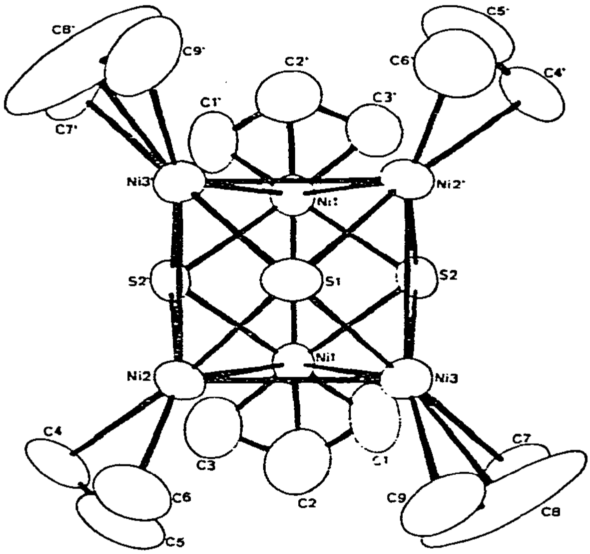
solved [290]. A cluster compound $[(\eta^3\text{-}C_3H_5M)_2S]_3$ (M=Ni,Pd,Pt) has been obtained by treating 2,5-disubstituted-1,6,6a-trithiapentalenes or H_2S with $M(allyl)_2$. The structure of the Ni complex (117) shows the compound to be a fraction of a NiS framework in which peripheral coordination sites are occupied by partial disordered η^3-allyl groups [291].



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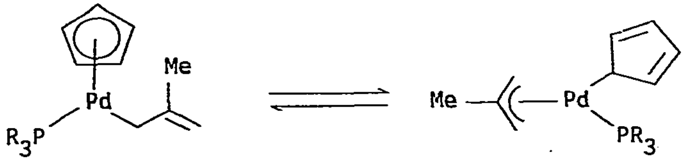
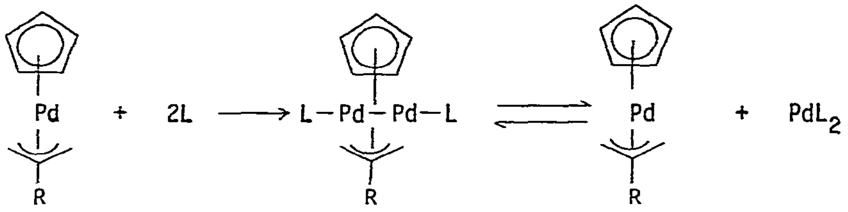
An interesting equilibrium has been investigated by nmr spectroscopy. In solution the isomers (118) and (119) have respectively a pentahapto-bonded cyclopentadienyl and a monohapto-bonded allyl ligand, and a monohapto-bonded cyclopentadienyl and a trihapto-bonded allyl ligand. The respective compounds are 18- and 16-electron molecules. The isomer ratio is temperature dependent



(118) (119)

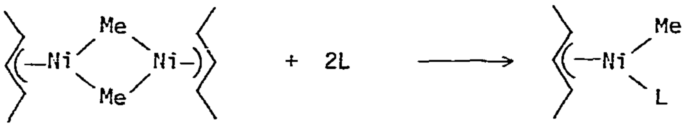
[292]. The binuclear complexes $cpPd_2L_2(2\text{-}RC_3H_4)$ (120) are formed either on reaction of equimolar amounts of $cpPd(2\text{-}RC_3H_4)$ and L (L= tertiary phosphine, phosphite, arsine) or by addition of $cpPd(2\text{-}RC_3H_4)$ and PdL_2. In addition the reactions of the allyl complexes with I_2, HCl and MeI are described [293].



(120)

This method of 1+1 addition has also been applied to prepare (2-Me$_3$H$_4$)XPd$_2$L$_2$ (X- Cl,L=P(*i*-Pr)$_3$, P(*t*-Bu)$_3$, PCy$_3$; X=I, L=P(*i*-Pr)$_3$). Attempts to synthesize similar binuclear complexes with Ni-Ni, Pt-Pt and Ni-Pd bonds fails [294].

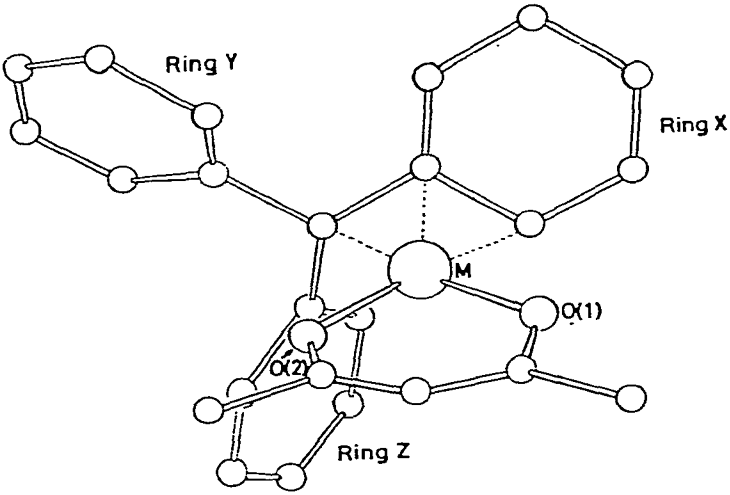
The reaction enthalpies have been measured for the reaction of 22 phosphines and phosphites with the allyl nickel complex (121). A three dimensional representation is plotted of the reaction enthalpies as a function of the electronic and steric parameters. Collectively the calculated enthalpies of association span a range of 82 kJ/mol, of which 48kJ/mole is ascribed to the electronic influence and 34 kJ/mol to the steric influence. It is considered that further analysis may require a "mesomeric effect" to be taken into consideration [295].



(121)

IX. Delocalized carbocyclic systems and carboranes

Papers on CPh$_3$ complexes describe the crystal structures of [M(α,1,2-η^3-CPh$_3$)(acac)] (M=Pd,Pt) (122) which show a η^3-benzylically bonded CPh$_3$ ligand [296]. The complexes have been prepared by treating the zerovalent compounds M$_2$(dba)$_3$ with Ph$_3$CCl, followed by treatment with acac to yield M(CPh$_3$)acac. The Pd complex shows 3 different dynamic nmr processes. These are (a) where the metal moves between the two η^3-positions on a single phenyl via a suprafacial 1,5 -sigmatropic shift; (b) where the metal moves from one phenyl ring to another; and (c) where the ends of the acac ligand become equilibrated. Free energies are measured and discussed where possible, and the effects of phenyl substituent are considered [297]. Palladium compounds are used in the reaction of 2-acetoxymethyl-3-



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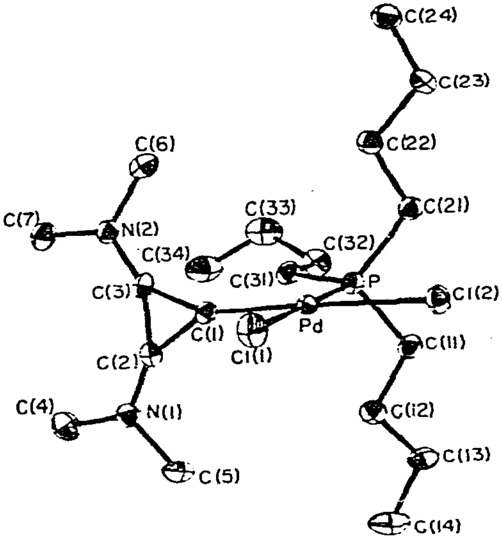
allyltrimethylsilane with olefins having electron-withdrawing groups and the reagent is a useful precursor for trimethylene-metal complexes [298]. The compound $(Ph_3C_3)Ni(CO)Cl$ reacts with ligands L(L=THF, bipy, Ph_2PMe, Ph_2PCl, $PhPCl_2$, $P(OR)_3$) to give 2:1 complexes $(Ph_3C_3)NiL_2Cl$ (123). The compound $(Ph_3C_3)Ni(CO)Cl$ readily loses CO in solution and under these conditions it is an active catalyst for the isomerization of quadricyclane to norbornadiene [299]. The structure of

$$(Ph_3C_3)Ni(CO)Cl \ + \ 2L \longrightarrow (Ph_3C_3)NiL_2Cl \qquad (123)$$

cis-dichloro(tri-n-butylphosphine)(bis(N,N-dimethylamino)cyclopropenylidene palladium(II) (124) is the first precise analysis of the structure of a cyclopropenylidene transition metal complex. The C_3 ring is bonded through the unique carbon atom to the metal center and is roughly perpendicular to the metal square plane [300]. Nickelocene reacts with TCNQ to give $Ni(TCNQ)_2$ [301].

Nonempirical M.O. calculations have been made on a variety of cyclobutadiene metal complexes. For $C_4H_4Fe(CO)_3$ a detailed analysis of the frontier orbitals indicates the molecule is a C_4H_4Fe fragment perturbed by the carbonyls. These ideas are expanded to $C_4H_4Ni(CO)_2$ [302]. The crystal structure of $[(C_4Me_4)NiBr]_2$ (125) shows a π-bonded cyclobutadiene ring in a square with an average C-C distance of 1.464 A. The methyl groups are displaced away from the Ni atom, the average distance between the ring plane and the methyl carbon atoms is 0.20 A [303]. Treating $(Ph_4C_4)NiBr_2$ with 1,2,3,4-tetraphenyl-1,4-dilithiumbutadiene gives $(Ph_4C_4)_2Ni$ (126) [304]. A



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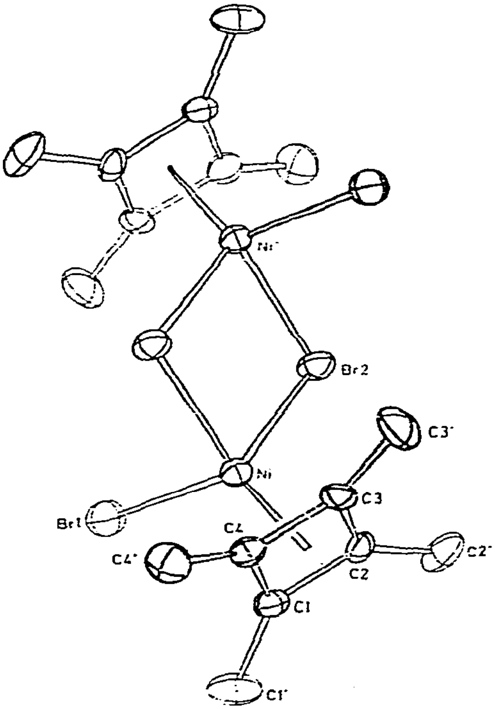

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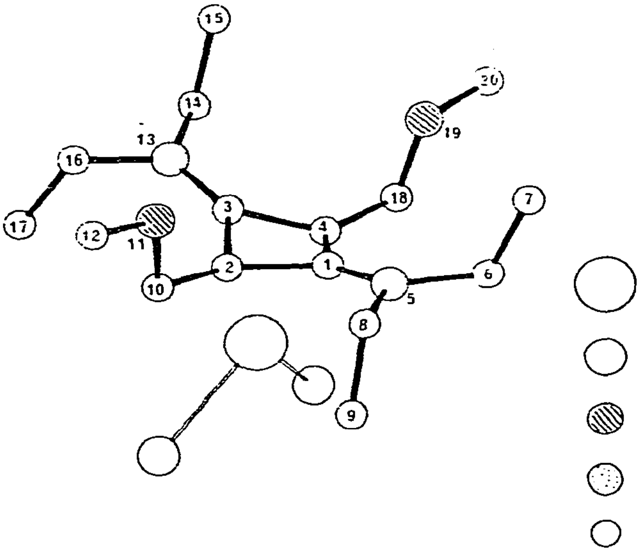
$$(Ph_4C_4)NiBr_2 \quad + \quad [PhC(Li)=CPh]_2 \quad \longrightarrow \quad (Ph_4C_4)_2Ni \quad + \quad 2LiBr \qquad (126)$$

cyclobutadiene palladium complex (127) formed by dimerization of an ynamine has a highly puckered four membered ring. A qualitative M.O. pertubation scheme shows first a rigid arrangement of the $PdCl_2$ unit in a plane containing the C(2) and C(4) atoms of the cyclobutadiene, and second a ring puckering resulting



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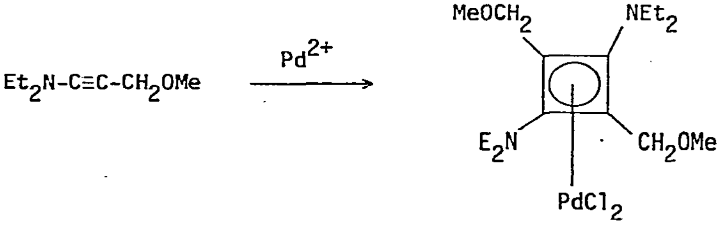


(127)

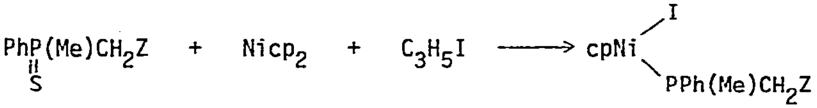
from repulsive interactions between the filled d orbitals of Pd and the p lobes located on both nitrogen atoms [305].

Reaction of Me_5C_5Li with $Ni(CO)_4$ gives $[(\eta^5\text{-}Me_5C_5)Ni(CO)]_2$. Conversions to $(\eta^5\text{-}Me_5C_5)Ni(L)X$ (L=tertiary phosphine) and $(\eta^5\text{-}Me_5C_5)Ni(L)R$ (R=Me,PhC C) are described [306]. Magnetic circular dichroism spectra of cp_2Ni are reported and discussed and comment is made on the striking similarity between the solution and matrix spectra [307]. Vacuum and low-temperature electrochemical techniques on cp_2Ni lead to an electron transfer series of 3 or 4 members. The nickelocene anion is a reduction intermediate stable at -60° in DMF, and $cpNi(\eta_3\text{-}C_5H_7)$ is a minor product of the bulk reduction of nickelocene [308]. Molecular orbital calculations using the all-electron self-consistent-field multiple scattering

$$cp_2Ni^{2+} \overset{+0.7}{\rightleftharpoons} cp_2Ni^{+} \overset{-0.1}{\rightleftharpoons} cp_2Ni \overset{-1.7}{\rightleftharpoons} cp_2Ni^{-}$$

Xα method have been carried out for $Nicp_2$ and $Nicp_2^{+}$. The calculated ionization energies of $Nicp_2$ are in good agreement with photoelectron data [309].

Metalation of $PhP(S)Me_2$ by BuLi followed by reaction with carbonyl derivatives gives functional and chiral phosphine sulfides of general formula $PhP(S)Me(CH_2Z)$ where $Z=Ph_2C(OH)$, PhC(O), HC(O), CO_2Et. These sulfides were reductively complexed to cpNiI (128), and if the free phosphines are required they can be obtained by treatment with $P(OMe)_3$ [310]. The complex $cpNiRu_3(CO)_9\{CC(H)\underline{t}\text{-}Bu\}$ has been

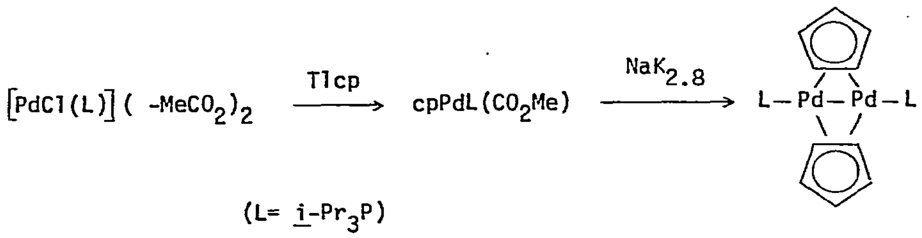


$$PhP(S)(Me)CH_2Z + Nicp_2 + C_3H_5I \longrightarrow cpNi(I)(PPh(Me)CH_2Z)$$

(128)

prepared from $[cpNi(CO)]_2$ and $HRu_3C_2\underline{t}\text{-}Bu$. The structure consists of a "butterfly" arrangement of three Ru and one Ni atoms bonded to nine terminal carbonyl groups, a cp group bonded to Ni, and a rearranged t-butylacetylene group bonded to all the metal atoms [311]. From the reaction of $[cpNi(CO)]_2$ and $HRu_3(CO)_9(C_6H_9)$ the compound $cpNiRu_3(CO)_8(C_6H_9)$ has been prepared. This again has the "butterfly" arrangement of metal atoms and is similar in many respects to the previous structure [312].

Nickel atoms will cause dimerization of fulvalene. The product is a head-to-tail dimer and is formally derivable by a thermally forbidden [6+6] cycloaddition process followed by [1,5]-hydrogen shifts [313]. A new route is described to prepare cyclopentadienyl bridged palladium dimers (129). The method involves treating the acetate bridged complex with sodium-potassium alloy at room temperature. Reactions with Me_3SiCl, PhSH and $PhCO_2H$ are described and the products have one of the cp groups replaced by a Cl, PhS or CO_2Ph bridging ligand [314]. Compounds of type (130) have been isolated and shown to be fluxional in solution. Two dynamic processes occur simultaneously. That with the higher activation energy is a π/σ exchange between the different cp rings; the lower activation energy process is a metallotropic rearrangement [315]. Nickelocene will react with α-bromo acids in the presence of triphenylphosphine to give $cpNiBr(PPh_3)$ [316].



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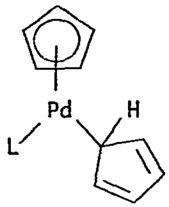


(L= PMe_3, $P(i\text{-}Pr)_3$, PPh_3)

(130)

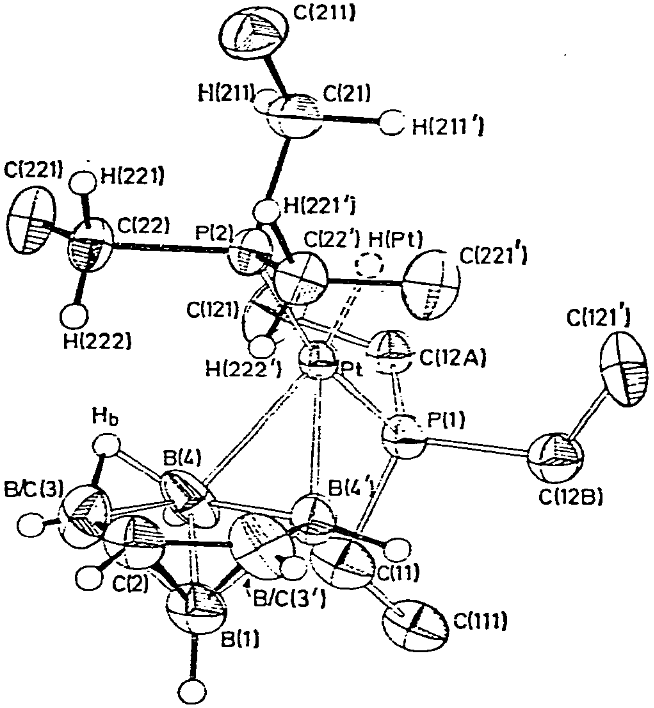
π-Complexes of palladium with benzene have been observed by UV and nmr spectroscopy. Their stability constants have been measured and the oxidative coupling of benzene to terphenyl discussed [317]. A detailed synthetic procedure has been published for the compound $Ni(C_6F_5)_2(\eta^6\text{-toluene})$ (131). The compound is prepared by the codeposition of nickel vapor with a C_6F_5Br and toluene mixture [318]. In a theoretical study of the delocalization in metallocycles of type

$$2Ni + 2C_6F_5Br + MePh \longrightarrow (\eta^6\text{-}MePh)Ni(C_6F_5)_2 + NiBr_2 \qquad (131)$$

$L_nM(C_4R_4)$ the analysis leads to a set of orbital criteria for minimizing delocalization, and to some speculations concerning the possible stability of mononuclear $L_nM(CR)_x$ (x=3,5,6) complexes [319]. Hammett correlations and phosphine dependencies have been plotted for the complexation of benzophenone to Ni(0). The crystal structure of $Ni(Ph_2CO)(PEt_3)_2$ shows sideways bonding of the carbonyl. The length of the C=O bond of 1.335 Å is approximately 0.1 Å longer than that of free benzophenone [320].

The complexes $Pt(PEt_3)_3$, Pt(*trans*-stilbene)$(PR_3)_2$, $M(COD)(PMe_3)_2$ (M=Ni,Pt), $Ni(COD)(PEt_3)_2$ react with *closo*-1,7-R_2-1,7-$C_2B_6H_6$, *closo*-4,5-R_2-4,5-$C_2B_7H_7$ and *closo*-1,6-$C_2B_8H_{10}$ to give carbametallaboranes *closo*-[4,5-R_2-6,6-(PR_3)-4,5,6-$C_2MB_6H_6$], *nido*-[4,5-R_2-7,7-(PR_3)-4,5,7-$C_2PtB_6H_6$], *nido*-[2,8-R_2-10,10-(PR_3)-

2,8,10-$C_2MB_7H_7$] and *nido*-[μ-(6,10)-{Pt(PMe_3)$_2$}-10,10-(PMe_3)$_2$-7,9,10-$C_2PtB_8H_{10}$] respectively. The latter compound with activated charcoal gives the compound *nido*-[10,10-(PMe_3)$_2$-7,9,10-$C_2PtB_8H_{10}$]. The spectra of the compounds are reported and their mechanism of formation and molecular structures discussed [321]. Reaction of Pt_2(μ-COD)(PEt_3)$_4$ with 2,3-dicarba-*nido*-hexaborane(8),2,3-dimethyl-2,3-dicarba-*nido*-hexaborane(8) and monocarba-*nido*-hexaborane(9) gives respectively [*nido*-$\mu_{4,5}$-{*trans*-(Et_3P)$_2$Pt(H)}-$\mu_{5,6}$-H-2,3-CB_5H_6], [*nido*-$\mu_{4,5}$-{*trans*-(Et_3P)$_2$Pt(H)}-$\mu_{5,6}$-H-2,3-Me_2-2,3-$C_2B_4H_4$] and [*nido*-$\mu_{4,5}$-{*trans*-(Et_3P)$_2$Pt(H)}($\mu_{3,4}$-H)($\mu_{5,6}$-H)-2-CB_5H_6]. The structure of the first of these compounds (132) shows both pentagonal B-B links are bridged, one by hydrogen and the other by a *trans*-(Et_3P)$_2$PtH



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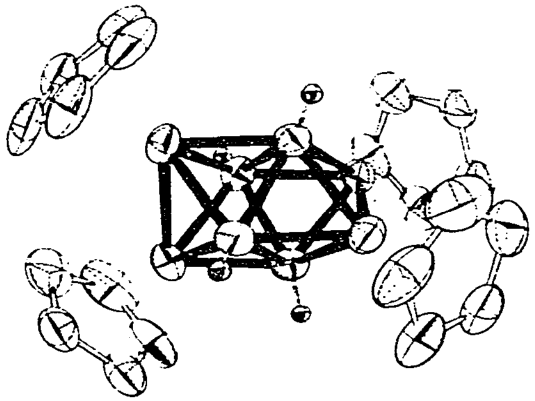
fragment, the latter demonstrating insertion by the metal nucleophile into a bridging B_2H function of the *nido*-carbaboranes [322]. Treatment of NaB_5H_8 with $NiBr_2$ and Nacp generates *closo*-1,6-$cp_2Ni_2B_8H_8$ and *closo*-1,7-$cp_2Ni_2B_{10}H_{10}$ and the reaction of NaB_5H_8 with cp_2Ni and Na/Hg gives *closo*-$cp_4Ni_4B_4H_4$ and *nido*-$cp_4Ni_4B_5H_5$. $Nicp_2$ and $NaMe_2C_2B_4H_5$ yield *closo*-$cp_2Ni_2Me_2C_2B_4H_4$ and *nido*-$cp_2Ni_2Me_2C_2B_5H_5$. The structure of $cp_4Ni_4B_4H_4$ (133) has a *closo*-D_{2d} cage geometry 323 . In an nmr study of compounds [M(B_5H_8)X(dppe)] (M=Ni,Pd,Pt) it is concluded that all the



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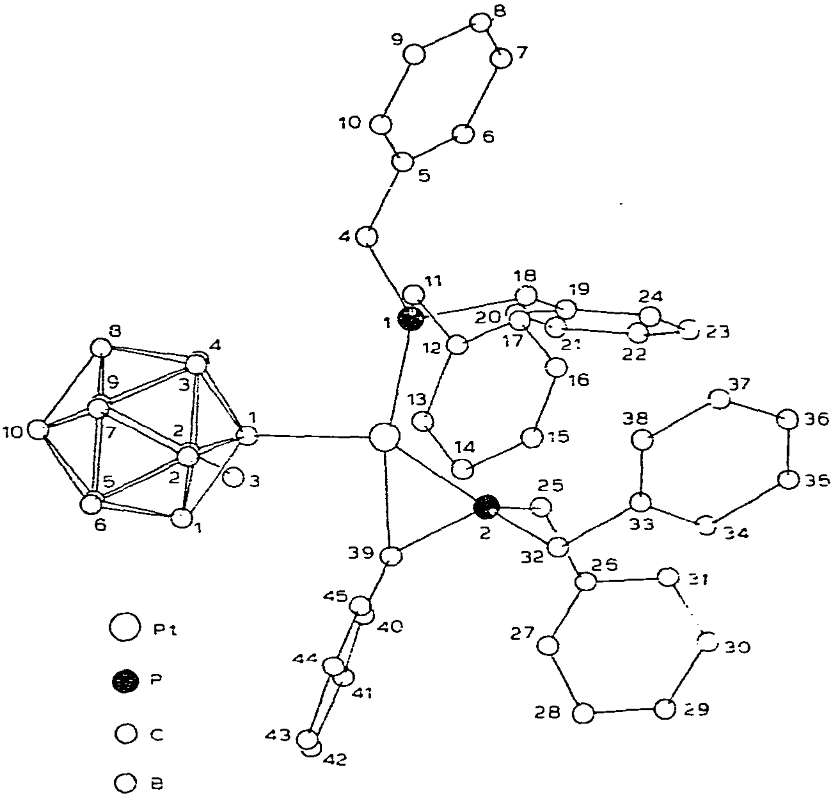
compounds examined have a static metallo-nido-pentaborane structure in which the metal atom occupies a bridging position between two basal boron atoms [324]. Treating $Pt(P(CH_2Ph)_3)_2Cl_2$ with 1-Li-2-Me-1,2-$B_{10}C_2H_{10}$ gives the complex cis-1-$[(PhCH_2)_3P\overline{PtP(C}HPh)(CH_2Ph)_2]$-2-Me-1,2-($\sigma$-$B_{10}C_2H_{10}$) (134). The carboranyl group is σ-bonded to Pt through its C(1) atom. One phosphine is bonded through its P atom and the C atom bonded to phosphorus of one benzyl side group, leading to a three-membered Pt-P-C chelate ring [325]. Platinathiaboranes have been obtained by treating PtL_4(L= PMe_2Ph, PEt_3, PPh_3) with 1-SB_9H_9. The complexes have the stoichiometry $L_2Pt(SB_8H_{10})$. Crystal structures have been solved for 9,9-$(PPh_3)_2$-6,9-$SPtB_8H_{10}$ (135) and 8-OEt-9,9-$(PPh_3)_2$-6,9-$SPtB_8H_9$ (136) [326].

X. Metal hydrides

The ligand $Ph_2PCH_2CH_2SEt$(PSEt) has been used to prepare complexes $Ni(PSEt)_2(BF_4)_2$, $Ni(PSEt)_2$(fumaronitrile), $Ni(CO)_2(PSEt)_2$ and $NiH(PSEt)_2\,BPh_4$. This hydride complex will catalyze the isomerization of 1-pentene. The complex is believed to decompose by loss of H_2 [327]. Addition of hydrogen atoms to

$$NiH(PSEt)_2^{\;+} \rightleftharpoons Ni(PSEt)_2 + H^+$$

$$NiH(PSEt)_2^{\;+} + H^+ \rightleftharpoons Ni(PSEt)_2^{\;2+} + H_2$$



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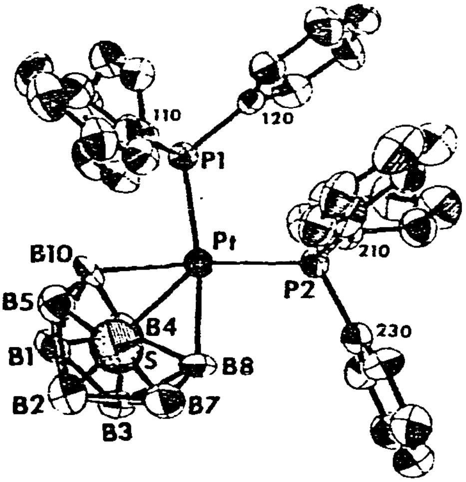
$Ni(CN)_4^{2-}$ ions in various salt hydrates induced by radiolysis gives $HNi(CN)_4^{2-}$ ions in which the σ^* electron is strongly delocalized onto hydrogen [328]. More details on this chemistry is supplied in a full paper [329]. In an article concerning the properties and reactions of organometallic complexes in the gas phase there is a table giving values for proton affinities. Nickel and $Nicp_2$ are included in the list [330].

The structure of trans-PtH_2(t-$Bu_3P)_2$ shows the Pt-P distance of 2.277 Å. A ligand profile diagram is shown outlining the van der Waals spheres. Such a diagram can be used in conjunction with the cone angle concept [331]. The platinum hydrides $PtH_2(PR_3)_2$ (PR_3= PCy_3, i-Pr_3P, t-Bu_2-n-BuP, t-$BuPh_2P$) react with CO to give trinuclear cluster compounds (137) [332]. Palladium(II) hydrides (trans-PdHX(P-t-$Bu_3)_2$), formed by addition of HX to Pd(P-t-$Bu_3)_2$, undergo facile intramolecular metalation in solution giving complexes PdX(P-t-$Bu_2CMe_2CH_2$)(P-t-Bu_3). These complexes will change into the bridged dimeric complexes [PdX(P-t-$Bu_2CMe_2CH_2$)$]_2$. This chloride bridge can be cleaved by a variety



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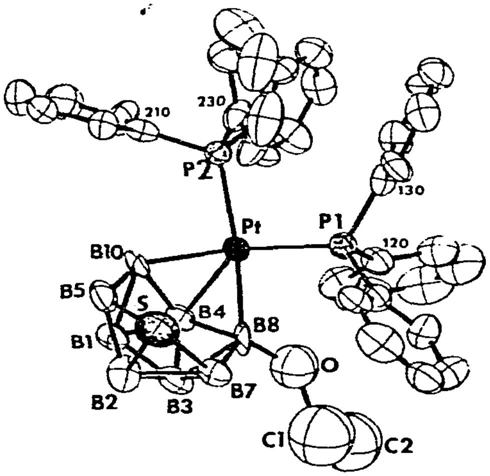

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$$\begin{tikzcd}
PtH_2(PR_3)_2 \arrow[rr, "CO", "H_2"'] \arrow[dr, "CO"] & & Pt(PR_3)_2 \arrow[dl, "CO"'] \\
& {[Pt(PR_3)(CO)]_3 + PR_3} &
\end{tikzcd}$$

(137)

of ligands to give the mononuclear complexes [333]. The mutual influence of ligands in trans-$PtHX(PPh_3)_2$ and trans-$PtX(SnX_3)(PPh_3)_2$ shows a trans influence for X of $Cl<Br<<SnBr_3<SnCl_3$. A qualitative estimate of the σ-donor and π-acceptor properties of the $SnCl_3$ ligand has been proposed from the relative change in the isomer shift ($\Delta\delta$) and quadrupole splitting ($\Delta\varepsilon$) in the Mössbauer spectra of the complexes [334]. The complexes trans-$PtH(SnR_3)L_2$ (L= PCy_3, $P(\underline{i}\text{-}Pr)_3$, $P(\underline{t}\text{-}Bu)Ph_2$, $P(\underline{t}\text{-}Bu)_2Me$; R=Ph) (138) have been prepared from PtH_2L_2 and $HSnR_3$, PtL_2 and $HSnR_3$, and PtH_2L_2 and $ClSnR_3$ [335]. Addition of water to complexes PtL_3 (L=PEt_3, $P\text{-}i\text{-}Pr_3$) gives platinum(II) hydrides $PtHL_3$ OH or $PtH(S)L_2$ OH, depending on

$$PtH_2L_2 \quad + \quad HSnR_3(ClSnR_3) \longrightarrow PtH(SnR_3)L_2 \longleftarrow PtL_2 \quad + \quad HSnR_3 \qquad (138)$$

the ligand L. The compound $PtH(OH)(P(i\text{-}Pr)_3)_2$ has also been obtained. The equilibria involved have been investigated by conductometric techniques. The reactions are shown. The hydration of the nitrile and double bonds of RCH=CHCN,

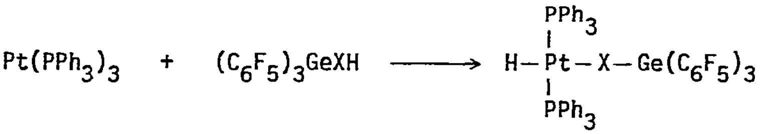
$$PtL_3 \xrightleftharpoons{K_L} PtL_2 + L \qquad\qquad L= P(\underline{i}\text{-}Pr)_3$$

$$PtL_2 + H_2O \xrightleftharpoons{K_o} PtH(OH)L_2$$

$$PtH(OH)L_2 + S \xrightleftharpoons{K_s} PtH(S)L_2\ OH$$

$$PtH(S)L_2\ OH \xrightleftharpoons{K_d} PtH(S)L_2^{\ +} + OH^-$$

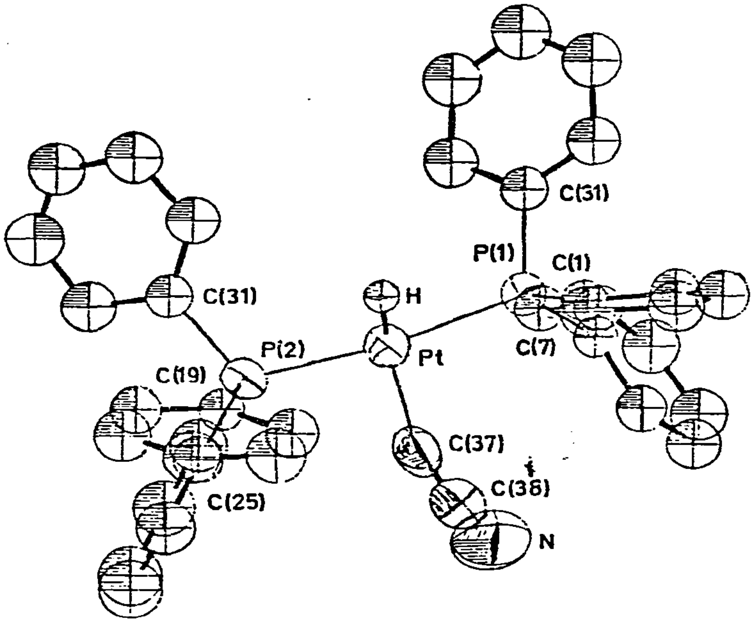
catalyzed by $[PtHL_3]OH$ or $[PtH(S)L_2]OH$ and trans-$Pt(OH)R(PPh_3)_2$ occurs in excellent yield [336]. The kinetics of hydrogen evolution in the reaction of $Pd(PPh_3)_4$ with HCl in dioxane solution has been studied. The importance of the $Pd(PPh_3)_4$ reaction with CF_3CO_2H with respect to liquid phase conversion of CO is discussed [337]. The electronic structure of a series of compounds trans-$PdXY(PH_3)_2$ (X and Y= H,Cl,OH,OCOMe) have been calculated by the CNDO method [338]. Treating $Pt(PPh_3)_3$ with $(C_6F_5)_3GeH$ gives PtH $(C_6F_5)_3Ge$ $(PPh_3)_2$. Using the same procedure the complexes $PtH\{(C_6F_5)_3GeX\}(PPh_3)_2$ (X=S, Se) (139) have been isolated [339]. The crystal structure of trans-$PtH(CF_3)(PPh_3)_2$ shows



$$Pt(PPh_3)_3 \quad + \quad (C_6F_5)_3GeXH \longrightarrow H-\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}-X-Ge(C_6F_5)_3$$

(139)

considerable steric crowding at the platinum atom [340]. The structure of trans-$PtH(CH_2CN)(PPh_3)_2$ (140) shows an angle PPtP of 169.6 [341]. The protonolysis of the Pt-C bond in trans-$PtH(CH_2CN)(PPh_3)_2$ in methanol/dichloroethane



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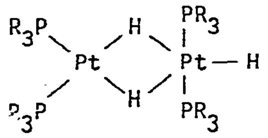
involves oxidative addition to the metal center followed by reductive elimination of MeCN and the formation of trans-$PtHCl(PPh_3)_2$. Activation parameters are given [342]. For the complexes trans-$PtH(SnCl_3)L_2$ (L= PPh_3, PPh_2Bz) there is an

$$\begin{tikzcd}
\text{trans-PtH(CH}_2\text{CN)L}_2 \quad + \quad H^+ \arrow[r, phantom, "\rightleftharpoons"] & {[PtH_2(CH_2CN)(S)L_2]^+} \arrow[dd] \arrow[dr, dash] & \\
(L = PPh_3) & & PtH(S)L_2^+ \arrow[dl] \\
& \text{trans-PtHClL}_2 &
\end{tikzcd}$$

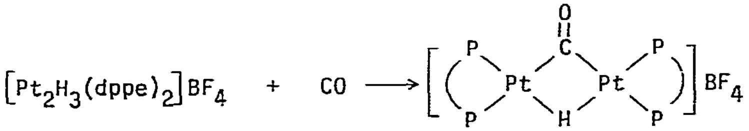
unusually large coupling constant for $^2J(Sn,H)$. The values are in the 1650-1750 Hz range [343]. When a solution of $Pt(COD)_2$ and PPh_3 at 0° is added to a separate solution of trans-$[PtH(Me_2CO)(PPh_3)_2]BF_4$ saturated with H_2, and the whole saturated with H_2, the dihydro bridged complex (141) is obtained. Details of the



(R= Ph, Et, Cy)

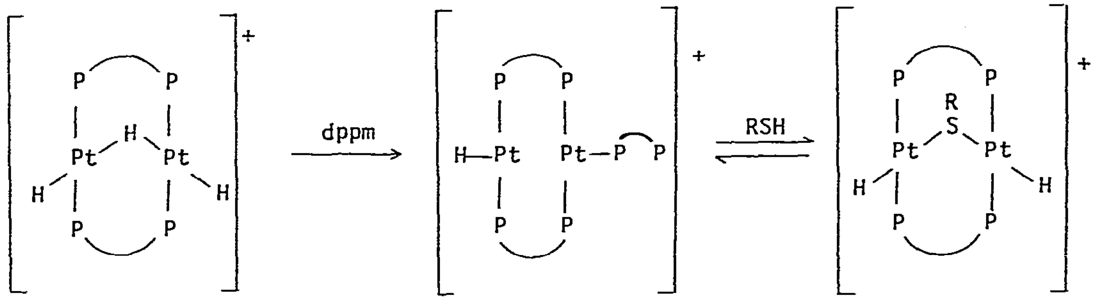
(141)

nmr spectra are given [344]. A series of complexes of bis(diphosphine)Pt_2H_3 have been prepared from the PtH_2(L-L) or Pt_2(L-L)$_2$ compounds. The ir spectra show bridging and terminal hydride ligands but the nmr data suggest rapid exchange on that time scale. The crystal structure of $[Pt_2H_3\{(\underline{t}\text{-Bu})_2P(CH_2)_3P(\underline{t}\text{-Bu})_2\}]BPh_4$ shows a Pt-Pt separation of 2.768 Å [345]. Treating $[Pt_2H_3(dppe)_2]BF_4$ with CO or RNC gives the dinuclear hydrides $[Pt_2H(CO)(dppe)_2]X$ (142) and $[Pt_2H(CNR)(dppe)_2]X$ (R= Me, p-tolyl, t-Bu) [346]. The reaction of $[Pt_2H_3(\mu\text{-dppm})_2]PF_6$ with dppm

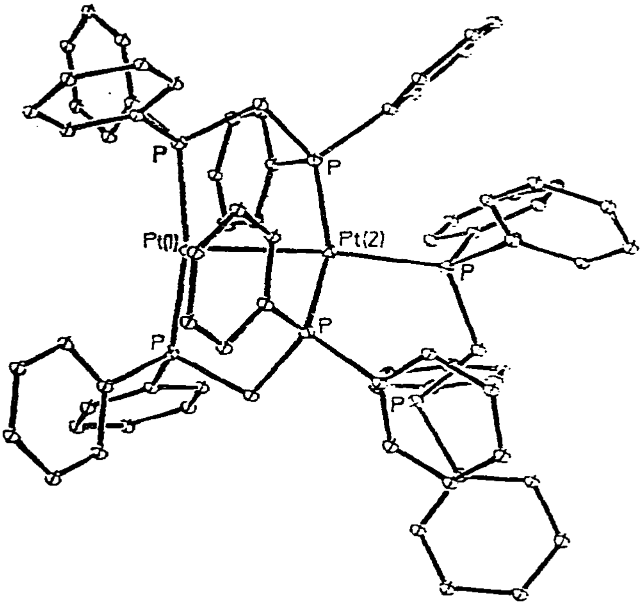


(142)

proceeds by reductive elimination of H_2 to give $[Pt_2H(dppm)(\mu\text{-dppm})_2]PF_6$ (143) which has both bridging and terminal dppm ligands. The compound undergoes a reversible reaction with RSH to give (144). The structure of (143) confirms



(143) (144)



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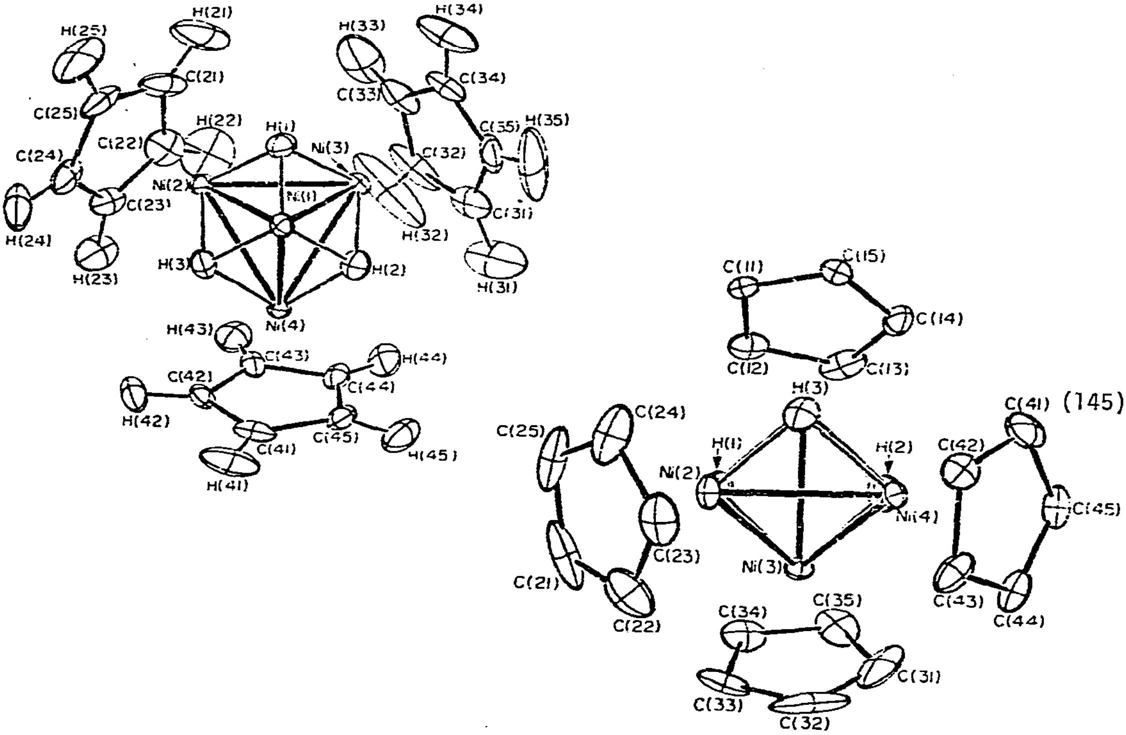
the proposed stoichiometry and bonding [347].

A neutron diffraction analysis of the structure of $Ni_4H_3cp_4$ (145) shows the Ni_3H linkages to be unsymmetrical. The H atoms are slightly displaced away from the unique apical Ni atom. The Ni-H distances involving the apical Ni atom average to 1.716 Å while those involving the basal Ni atoms average to 1.678 Å [348]. The structures of $Ni_6(CO)_{12}^{2-}$, $Pt_{12}(CO)_{24}^{2-}$ and the distribution of CO groups in $Ni_{12}(CO)_{21}H_{4-n}^{n-}$ (n= 2,3,4) are given. The importance of the interstitial positions of hydrogen atoms in metal carbonyls is discussed [349].

XI Metal isocyanides

The crystallographic parameters of $[Pt(CNEt)_4][Pt(CN)_4]$ have been determined from x-ray powder data [350]. Nitrogen 1s binding energies for bridging methyl isocyanide in $Pd_2(dppm)_2(\mu\text{-}CNMe)Cl_2$ and $Pd_2(dppm)_2(\mu\text{-}CNMe)(CNMe)_2\ PF_6$ have been measured and are ~1 eV lower than those for terminal MeNC. For comparison XPS data are also presented for $[Pd_2(CNMe)_6](PF_6)_2$, $[Pd(CNMe)_4](PF_6)_2$, $Pd(CNME)_2I_2$ and $[Pt_2(CNMe)_6](BF_4)_2$ [351].

The compound Pt_3(t-BuNC)$_6$ reacts with SiR_3H (SiR_3= $SiMe_3$, $SiEt_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, $Si(OEt)_3$) to give compounds Pt(CH=N-t-Bu)(SiR_3)(t-BuNC)$_2$ (145) arising from insertion of an RNC ligand into the formed Pt-H bond. The structure of (146) shows the platinum bridged by HC=N-t-Bu ligands to give a six-membered



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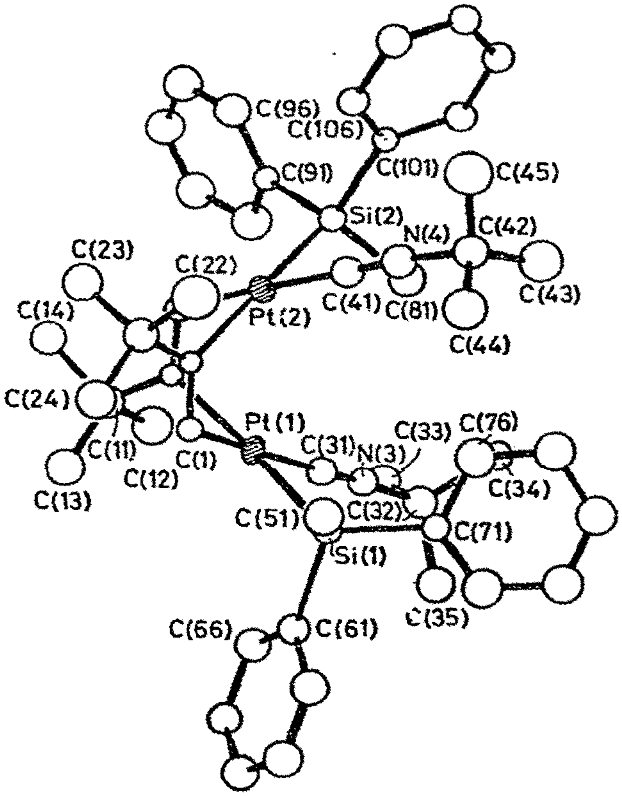
ring of boat conformation [352]. Reduction of $PtCl_2$(2,6-xylyl isocyanide)$_2$ with Na/Hg gives Pt_7(2,6-xylyl isocyanide)$_{12}$ which has both bridging and terminal isocyanide groups. The molecule contains a metal atom cluster derived from the distorted trigonal bipyramidal unit to which two extra Pt atoms have been attached in the bridging position between one basal platinum atom and each apical one [353]. The isocyanide derived complex trans-$PtCl(PEt_3)_2(CH{=}NC_6H_4Me\text{-}p)$ gives 1:1 complexes with $CdCl_2$, $HgCl_2$ and AuCl, and 1:2 trans adduct with $PdCl_2$ [354]. Similar mixed metal complexes have been prepared from the complexes $L_2Pt\ C(OMe){=}NR_2$ [355]. A linear trimetallic compound trans-Pt(CyNC)(CyNHCOEt)$\{cpMo(CO)_3\}_2$ (147) has been obtained from cis-$PtCl_2$(CyNC){C(OEt)(NHCy)} and Na[cpMo$(CO)_3$]. The structure is confirmed by x-ray crystallography. The molecule is a mixed trimetallic having both coordinated carbene and isocyanide groups [356].



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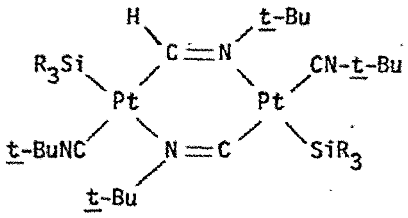

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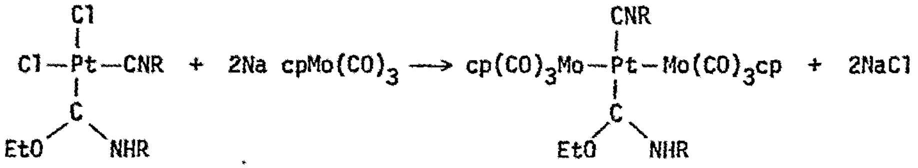
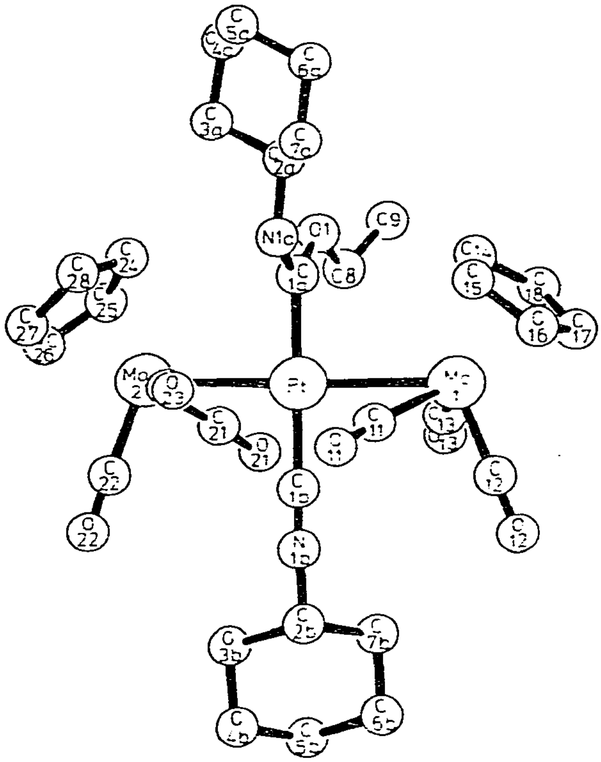


$$\mathrm{Cl{-}Pt(Cl)(CNR)\{C(OEt)NHR\}} + 2\mathrm{Na\ cpMo(CO)_3} \longrightarrow \mathrm{cp(CO)_3Mo{-}Pt(CNR)\{C(OEt)NHR\}{-}Mo(CO)_3cp} + 2\mathrm{NaCl}$$

(147)



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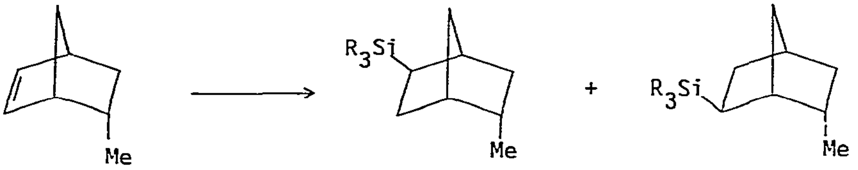
XII Catalytic reactions involving complexes

A review has been published comparing catalytic activities of complexes in homogeneous systems and in fixed states [357]. The complex trans-$PtH(NO_3)(PEt_3)_2$ is an active catalyst for the hydrogenation of olefins. While it is active towards both internal and terminal olefins it is ineffective towards olefins with electron-withdrawing substituents. The most effective conditions are 60° and 600 psi in methanol solvent. Reaction pathways are presented and discussed with respect to the role of methanol in the system [358]. Hydrogenation of 1,5-COD; 1,3-COD; 1,4-octadiene and 1,7-octadiene to the corresponding monoenes has been carried out under mild conditions using different allyl palladium(II) derivatives in DMA solution. Nonconjugated dienes are isomerized prior to hydrogenation. The selectivity is suggested to result from an intrinsic property due to formation of π-allylic intermediates [359]. The hydrogenation of 1,5,9-cyclododecatriene with $NiI_2(PPh_3)_2$ as catalyst involves initial formation of a π-complex with

$NiHI(PPh_3)_2$ and its subsequent conversion to a σ,π complex[360]. The compound $NiX_2(dppe)$ (X= Br,I) catalyzes the catalytic hydrogenation of 1,5,9-cyclodecatriene with 95% conversion at 150°/50 atmosphere. The activity of the catalysts decreases in the order I>Br>Cl [361]. The semihydrogenation of 15 acetylenes to olefins has been studied synthetically and mechanistically. The catalyst is a polymer-bound Pd(II) complex. Isolated bonds give selectivities of 92% or better whereas conjugated acetylenes fall in the range of 71-85%. Solvents such as DMF, THF, DMSO and EtOH give high activity. The catalytic activity is affected more strongly by the π-acidity of acetylenes than their steric factor. Kinetics and mechanism are discussed. The polymer-bound catalyst is comparable in selectivity to cationic rhodium and the Lindlar catalysts [362].

Hydrosilylation of endo- and exo-cyanonorbornenes, endo-methylnorbornene and camphene by $SiHCl_3$ on a catalyst composed of $Ni(acac)_2$ and PPh_3 shows that hydrosilylation occurs as stereoselective exo-addition to the double bond [363] .

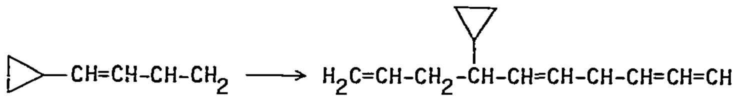


The mixture of $Ni(acac)_2$ and R_3Al (R= Et,i-Bu) catalyzes the hydrosilylation of 1,3-butadiene, isoprene, piperylene and CH_2=CHCHMeCH=CHCH=CH_2. With the first two olefins appreciable quantities of 1,4-disilylated olefins were formed [364]. The rate constants for the hydrosilylation of 4-RC_6H_4CH=CH_2 by $MeSiCl_2H$ increases in the order R=Cl<H<Me<MeO for the catalyst $Pt(PPh_3)_4$. The effects of solvents and added PPh_3 are discussed [365]. The catalyzed hydrosilylation of styrene by platinum phosphine complexes and of 1-octene by nickel phosphine complexes was exmained kinetically and by ir spectroscopy. It is proposed that coordination of the silyl weakens but does not break the Si-H bond [366].

The activity of the $PtCl_2(PPh_3)_2$-$SnCl_3$ catalyst system for catalyzed hydroformylations is dramatically enhanced by the use of diphosphine ligands of type $Ph_2P(CH_2)_nPPh_2$ (n= 1,2,3,4,5,6,10). The optimum ligand has n=4 which yields hexanals (n/iso=99/1) from pentene-1 with a much higher reaction rate than is found with $RhH(CO)(PPh_3)_3$ [367].

Racemic 1-olefins are isomerized by the homogeneous (R)-N,N-dimethyl-1-phenylethylamine/i-Bu_3Al/Ni(N-methylsalicylideneamine)$_2$ catalytic system. Both the unchanged 1-olefins and the (E)-2 olefins formed are optically active [368]. The dimerization of diquinoethylene to tetraquinocyclobutane is catalyzed by $Ni(CO)_2(PPh_3)_2$ and $Ni(CO)_2(dppe)$, and also by a mixture of $Ni(COD)_2$ and PPh_3. The reaction is catalyzed by PPh_3 alone but the dimerization proceeds more slowly

[369]. The compound N-hydroxymethylmorpholine is an efficient H-donor molecule in the hydrodimerization of butadiene catalyzed by Ni(0) complexes mixed with triphenylphosphine. The product distribution of coupled products is given and a mechanism presented involving nickel allyl complexes [370]. The oligomerization of 1-cyclopropyl-1,3-butadiene is effected using a Ni(0)-triphenylphosphine catalyst. The product (148) has the head-to-head structure which has been proven by deuterium labelling [371]. The new complexes (π-4-cyclooctene-1-yl)(trifluoroacac)Ni and (π-4-cyclooctene-1-yl)(hexafluoroacac)Ni oligomerize olefins such as ethylene, propylene, butene-1, hexene-1 and octene-1 to predominantly linear products in the absence of cocatalyst. The reactivity rate drops with increasing chain length. Mechanistic schemes are proposed and MO calculations made for the binding of olefin to the complexes [372]. In the catalytic cyclodimerization of norbornadiene by reaction with nickel atoms, nickelacyclopentane derivatives are formed in the presence of bipy. The compound α,α'-bipyridyl-exo-trans-endo-3-nickelapentacyclo 9.2.1.^{5,8}0.^{2,10}0^{4,9}-pentadeca-6,12-diene is the major component. By contrast the catalytic dimerization leads predominantly to the exo-trans-exo isomer of pentacyclo 8.2.1.1.^{4,7}0.^{2,9}0^{3,8} tetradeca-5,11-diene [373]. The complex (π-allyl NiCl)$_2$ on γ-alumina catalyzes the oligomerization of ethylene in the presence of CF_3CO_2H, $AlCl_3$, $AlBr_3$ and $TiCl_4$. Addition of benzene to the reaction mixture decreases the oligomerization rate and increases the yield of trimers [374]. The mixture of Ni(acac)$_2$ and i-Bu$_3$Al does not polymerize 2,4-dimethyl-pentadiene-2,3, but leads to its reduction and isomerization to 2,4-dimethylpentene-1 and -2. A possible mechanism is discussed which involves nickel hydrides and allyls as intermediates [375]. The compounds $[NMe_4]_2[Ni_5(CO)_{12}]$, $[NMe_4]_2[Ni_{12}(CO)_{21}H_2]$ and $[NEt_4]_3[Ni_{12}(CO)_{21}H]$ in acetone are efficient catalysts for the polymerization of acetylene. The product is insoluble and air sensitive and has not been characterized fully [376].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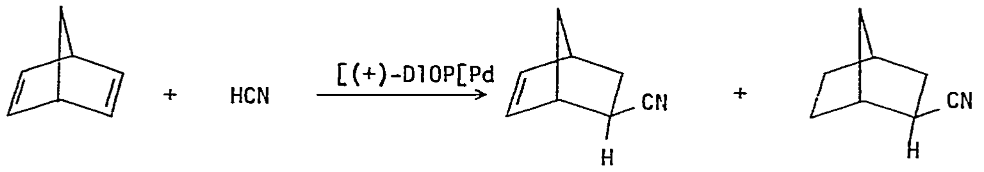
The asymmetric addition of HCN to alkenes has been catalyzed by Pd(DIOP). The catalyst has been prepared by reduction of $PdCl_2$ with hydrazine in the presence of (+)-DIOP or by reduction of [(+)-DIOP]$PdCl_2$ with $NaBH_4$. The optical induction is 28% [377]. The catalytic hydrocyanation of acetylenes using $Ni(CN)_4^{2-}$ has been achieved in the absence of HCN. The reaction is carried out in ethylene glycol or water solvent in the presence of $NaBH_4$ or Zn. A pathway



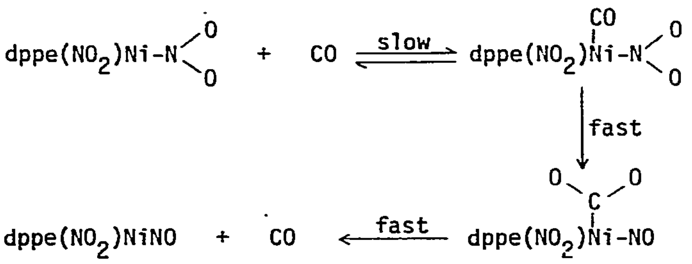
is proposed where the acetylene inserts into the Ni-H bond of $NiH(CN)_3^{2-}$ [378].

Comments are made on a previous paper and experimental evidence is given to show that DCl, which can be formed from the chloro platinum group catalysts, is also a catalyst in the hydrogen isotope exchange reaction between naphthalene and D_2O-AcOD [379]. Chloroplatinate (II) and (IV) salts have been used to catalyze the exchange of hydrogen for deuterium in methyl nonanoate. The incorporation has been followed by nmr spectroscopy using shift reagents [380].

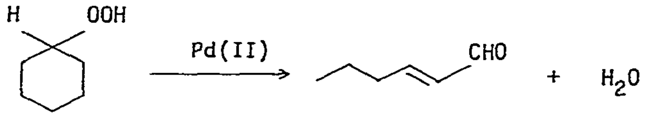
A review has been published on catalyzed oxidations using platinum group metals. The review includes the use of complexes and covers the gas and liquid phase oxidation of olefins and complex olefins, oxidative combination and acetoxylation [381]. Complexes of platinum have been used as catalysts for the cooxidation of benzaldehyde and cyclohexene. Infrared data indicate surprisingly that when $Pt(PPh_3)_4$ is used as a catalyst that no oxygen adduct is formed. The activation energy for formation of cyclohexene oxide in the presence of $Pt(PPh_3)_4$ is 25 kcal/mol [382]. In the oxidative acetoxylation of toluene using Pd complexes the active species are found to be palladium clusters having a low oxidative state [383]. A mechanistic study has been made of the oxidation of CO to CO_2 by $NiNO_2$ complexes. Kinetic data for the reaction of $Ni(NO_2)_2$dppe with CO to form $Ni(NO)(NO_2)$dppe (149)

$$Ni(NO_2)_2dppe + CO \longrightarrow Ni(NO)(NO_2)dppe + CO_2 \qquad (149)$$

and CO_2 shows a rate law first order in both $Ni(NO_2)_2$dppe and CO. The reaction is associative and shown below [384]. Cyclohexyl hydroperoxide is catalytically decomposed by Pd(II) complexes to yield an α,β-unsaturated linear aldehyde (150). The



generality of the reaction is shown by the use of other hydroperoxides. A mechanism is proposed involving initial electron transfer followed by the formation of alkyl, olefin and hydro palladium compounds. Plots are made of the influence of ligands in the palladium(II) complexes and on the yield of products with time [385].



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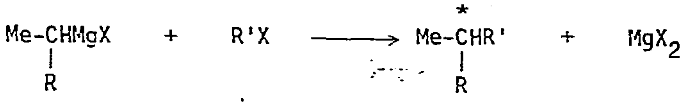
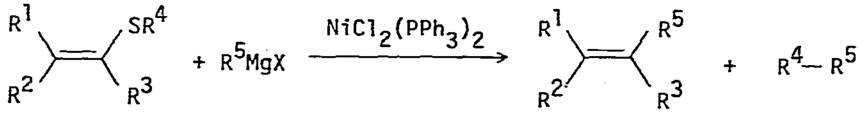
Addition of $Ni[P(OPh)_3]_4$ and $EtAlCl_2$ to the WCl_6-$EtAlCl_2$ catalytic system causes the formation of internal olefins. Through the process of cross- and homometathesis a series of olefinic products are formed [386]. Allylic alcohols $RCH{=}CHCH_2OH$ (R=H,Me,Et) are converted into corresponding alkenes RCH=CHMe, α,β-unsaturated aldehydes RCH=CHCHO and water by the interaction with $Ni(COD)_2$ and PPh_3. A mechanism is proposed involving oxidative addition of the alcohol to Ni(0) via either O-H or C-OH bond cleavage [387]. The reaction of acetylenes and allyl halides with palladium complexes selectively gives 1,4-diene codimers. The compound $PdX_2(PhCN)_2$ is the most active catalyst. A mechanism is proposed involving insertion to form the palladium vinyl followed by insertion of an allylic halide into this bond. Yields are given for a wide range of substitutes [388].

The asymmetric cross-coupling reaction between phenyl halides and *sec*-butyl magnesium halides has been carried out in the presence of [(+)(R)-dppp] $NiCl_2$. The optical purity and absolute configuration of the 2-phenylbutane (151) is



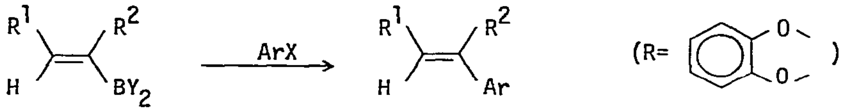
$$\underset{\displaystyle R}{\underset{|}{Me\text{-}CHMgX}} \quad + \quad R'X \quad \longrightarrow \quad \underset{\displaystyle R}{\underset{|}{Me\text{-}\overset{*}{C}HR'}} \quad + \quad MgX_2 \qquad (151)$$

dependent on the halogen in the organic and on the organometallic moieties [389]. It has been found that alkenyl or aryl sulfides can be used as substrates in the $NiCl_2(PPh_3)_2$ promoted coupling reaction (152). Yields and reaction times are given for a range of vinyl compounds with BuMgBr and PhMgBr. The formation of



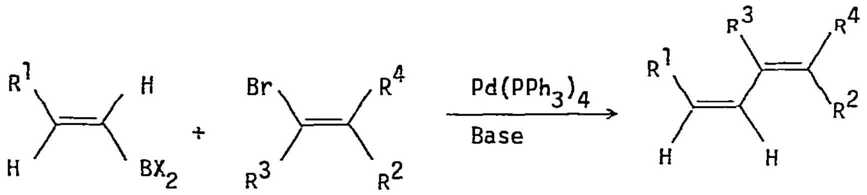
(152)

H_2S was confirmed after quenching the reaction with dilute acid [390]. Allylic sulfides also couple with Grignard reagents in the presence of Ni(II)-phosphine complexes as catalysts to give the corresponding unsaturated compounds in good yields [391]. Dichloro 1,1'-bis(diphenylphosphino)ferrocene palladium(II) is an effective catalyst for the cross-coupling reaction of sec-butylmagnesium chloride with bromobenzene, β-bromostyrene and 2-bromopropene to give the corresponding sec-butyl derivatives [392]. The reaction of aryl halides with alk-1-enyl boranes is a useful method for the stereoselective synthesis of



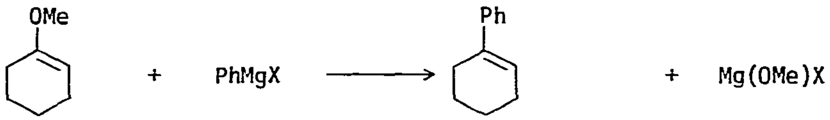
(153)

arylated (E)-alkenes (153) in high yield. The reactions are catalyzed by $Pd(PPh_3)_4$ and bases such as NaOEt [393]. The reaction has also been used for the stereospecific cross-coupling of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides (154) [394]. Arylation of $BrZnCH_2CO_2Et$ by aromatic halides



(154)

gives a fair yield when catalyzed by soluble nickel and palladium complexes. Yields are given and some consideration of the reaction mechanism is discussed [395]. The reaction of the phenylmagnesium and methylmagnesium bromides with enol and aryl ethers in the presence of $NiCl_2(PPh_3)_2$ leads to the replacement of the alkoxy group by arylation or alkylation to give the olefin (155) [396]. Styrene will couple with halopyrazines in the presence of palladium acetate as

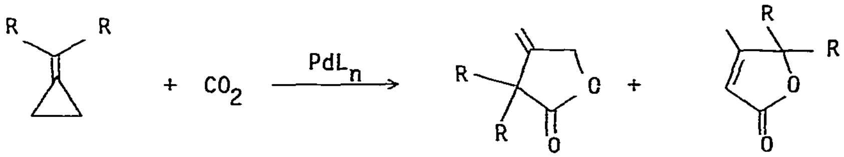


(155)

catalyst [397]. The complex $Pt(PPh_3)_4$ can be used as a catalyst for the rearrangement of allyloxy pyridines (156) to the enones (157). A mechanism is proposed involving allyl platinum intermediates [398]. 2-Acetoxymethyl-3-allyltrimethysilane for methylenecyclopentane annelations are catalyzed by Pd(0) compounds [399]. A stereocontrolled approach to the synthesis of acyclic systems has been described using organopalladium templates [400]. The palladium(II) catalyzed cyclocarbonylation of acetylenic alcohols to methylene lactones proceeds via carboalkoxypalladium intermediates, followed by intramolecular cis addition to the triple bond. These intermediates have been synthesized and shown to undergo this chemistry. A PdI_2-PBu_3-MeCN catalyst gives rates first order in CO pressure, with the rate-determining step being complexation of CO by Pd. The reaction products and rate data are used to test mechanistic postulates [401]. Palladium(0) phosphine complexes catalyze the cyclodimerization of methylenecyclopropanes and CO_2 with opening of the three-membered ring to give five-membered lactones (158) [402]. In the catalytic oxidative cyclization of 2-(butenyl-2)phenol by (+)-[(3,2,10-η-pinene)Pd(OAc)]$_2$ in the presence of $Cu(OAc)_2$ and O_2 (159) the η^3-pinene ligand remains attached to palladium throughout the reaction [403]. The insertion of CO into various 2-bromo-3-aminopropene derivatives in the

R_1= H,R_2=Me
R_1= Me,R_2=H

(156) (157)



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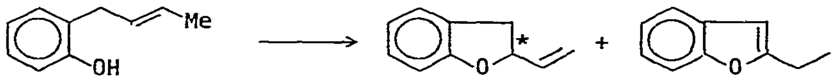
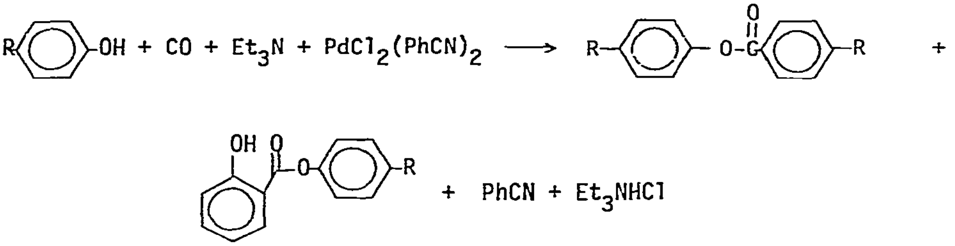


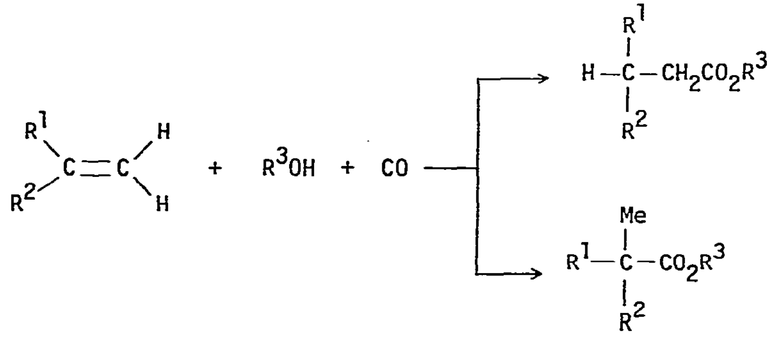
(159)

presence of catalytic amounts of $Pd(OAc)_2$ and PPh_3 gives the corresponding α-methylene-β-lactams in fairly good yields [404]. Kinetic data for the arylation of styrene by $Pd(OAc)_2(PPh_3)_2$ suggest aryl transfer from phosphorus to palladium to give a σ-phenylpalladium compound. The trans cis isomerization is a first order process with an activation enthalpy of 16 kcal/mol and an activation entropy of -21eu [405]. The carbonylation of methanol to dimethyl oxalate and dimethyl carbonate in the presence of $Pd(OAc)_2$ is affected by ligands, CO pressure and base. A mechanism is presented involving methanol attack at a coordinated carbonyl. Methoxide or CO reaction with this product leads to the formation of MeOCOOMe or MeOCOCOOMe respectively [406]. The reaction of phenols with CO in the presence of CO and a tertiary amine produces, in the presence of $PdCl_2$, diaryl carbonates and aryl salicylates (160). Only diaryl carbonates are obtained when palladium carbonyl chloride is substituted for palladium chloride



(160)

[407] The hydrocarboxylation of propene with $PdCl_2(PPh_3)_2$ as catalyst precursor gives high yields in lower alcohol solvent at 90-130 °and pressures of CO in the 40-120 atmosphere range (161) [408]. The catalytic activity of the compound $Pd[P(OR)_3]_2X_2$, with R=Me,Et,i-Pr and X= Cl,Br,I,SCN, for the acetylene

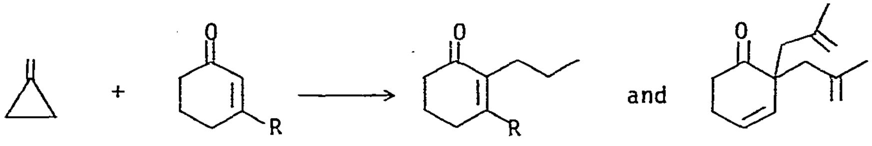


(161)

carbonylation reaction shows a difference in activity with R and X. The selectivity for monoester formation depends on the ligands and the kinetics of the reaction are discussed [409]. The selectivity to $PhCH{=}CHCO_2Me$ approaches 80% in the palladium catalyzed synthesis of methyl cinnanate from styrene, CO and methanol.

The compound MeOCuCL is reoxidant [410]. Dialkyloctadienylamines are formed selectively and in high yields upon reacting secondary amines with butadiene in the presence of catalytic amounts of $Ni(acac)_2$, PPh_3 and Et_3Al. Cationic allylic nickel complexes are proposed as intermediates. Details of the experimental conditions are given, especially the temperature [411].

Methylenecyclopropane and cyclohex-2-en-1-ones react in the presence of an in situ mixture of Pd(dibenzylideneacetone)$_2$ and tertiary phosphine to give 2-alkylated enones (162) [412]. C_9-Carboxylic acids have been obtained by the catalyzed reaction of CO_2 and butadiene in the presence of PhONa. Complexes $Pd(PPh_3)_4$ are effective catalysts. Carboxylated products are not obtained using solely $Pd(OAc)_2$ as catalyst [413]. The nickel catalyzed cyanation of aromatic halides (163) under phase-transfer conditions improves yields and catalyst turnover. The proposed mechanism involves a pentacoordinate cyanoaryl nickel complex [414]. The coupling of tetraorganotin compounds with benzyl and aryl halides is catalyzed by palladium(II) complexes, preferably benzylchlorobis (triphenylphosphine)palladium(II). The reaction is accelerated by oxygen but not by triphenylphosphine. A catalytic cycle is proposed and the generality of the reaction investigated. Electron-withdrawing groups on the bromobenzenes accelerate the reaction but a simple Hammett plot is not observed [415].



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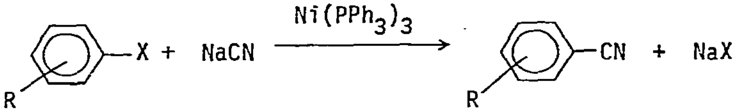
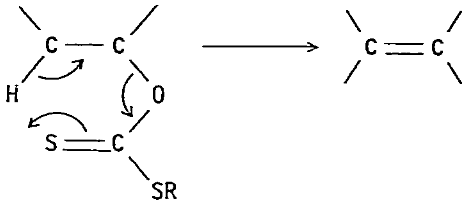


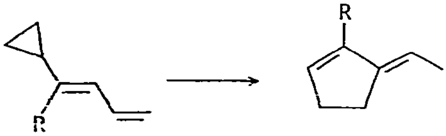
(163)

The reactions of alkenyl sulfides, benzenethiols and aryl sulfides with methylmagnesium- and arylmagnesium bromides using $NiCl_2(PPh_3)_2$ gives olefins (predominantly with retention of configuration), toluenes, and biphenyls in acceptable yields [416]. The mechanism by which Ni(II) complexes catalyze the stoichiometric reaction between terminal aliphatic alkynes and $\underline{i}$-Bu_3Al is considered. Deuteriolysis experiments show the occurrence of hydride nickel and nickelole species as intermediates. The proposed mechanism involves the formation of alkyl, hydride and Ni(0) species still containing the ligand. These catalytic species can yield products by reductive elimination or alkyl exchange reactions with the excess organoaluminum compound [417]. Reactions of O-alkyl and O-cycloalkyl S-methyl xanthates with $M(PPh_3)_4$ (M=Pd,Pt) give olefinic products resulting from 1,2-bond shift skeletal rearrangements in alkyl intermediates (164). These rearrangements are analogous to several of those occurring in hydroisomerization of cycloalkanes and alkanes at elevated



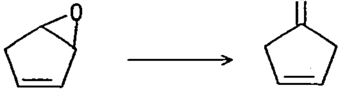
(164)

temperatures on transition metal surfaces [418]. A 1:1 mixture of $Ni(COD)_2$ and PBu_3 catalyzes the vinylcyclopropane-cyclopentene rearrangement (165). Allyl nickel intermediates are proposed and only such vinycyclopropanes as those being capable of complexing with the catalyst will react [419]. The cyclopropanation of



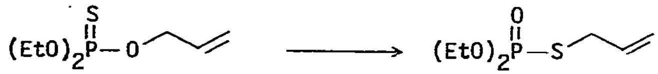
(165)

electron-deficient olefins with gem-dibromides is catalyzed by Ni(0) phosphine or COD complexes [420]. The complex $Pd(PPh_3)_4$ will catalyze the transformation of 1,3-diene epoxides into ketones (166) [421]. Allylic intermediates are



(166)

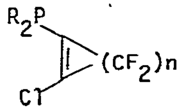
proposed. The complex $Pd(PPh_3)_4$ will also catalyze the thiono-thiolo allylic rearrangement of O-allyl phosphoro- and phosphorothionates (167) [422].



(167)

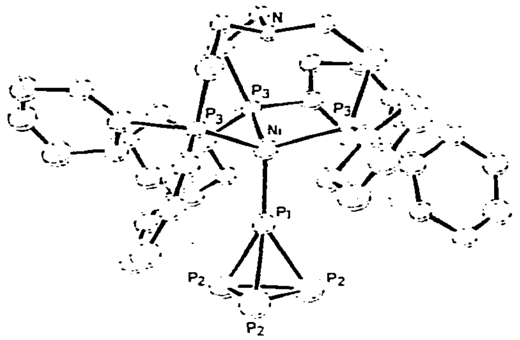
XIII. Complexes and reactions of general interest

In a detailed synthetic series of papers [423,424,425] the preparative procedures for the following compounds have been described; $Pd[PPh(t\text{-}Bu)_2]_2$, $Pd[PCy_3]_2$, $Pd[P(t\text{-}Bu)_3]_2$, $Pt[PPh(t\text{-}Bu)_2]_2$, $Pt[PCy_3]_2$, $Pt(PEt_3)_3$, $Pt[P(i\text{-}Pr)_3]_3$, $Pt(PEt_3)_4$. The structure of $Pt[P(t\text{-}Bu)_3]_2$ has Pt-P distances of 2.249 Å and a P-Pt-P angle of 180° [426]. Nickel(0) complexes with fluorophosphine ligands have been formed from sulfide-activated nickel [427]. In the following paper [428] the compound $Ni(PF_2H)_4$ has been prepared using metal atom-ligand cocondensation techniques. The compound is a colorless liquid (f_p-50°C) which decomposes slowly at room temperature. No compound $Ni(PH_3)_4$ has been identified. The phosphines (168) where R= Ph, Cy and n= 2-4 form P-bonded complexes with



(168)

Pd and Pt [429]. The structure of a 20-membered ring binuclear complex bis[μ-1,7-heptanediylbis(di-t-butylphosphine)bis(dichloropalladium)] has bulky $t\text{-}Bu_2P$ group in the four corner positions and the trans-P-Pd-P linkages and extended $(CH_2)_7$-chains forming the sides. The macrocycle has an elongated boat ("barge") conformation [430]. A series of large chelate rings and cyclometalated products of Pd and Pt are reported with the ligands $t\text{-}Bu_2P(CH_2)_nPBu_2\text{-}t$ (n=5-8) and $Ph_2P(CH_2)_5PPh_2$. Factors affecting the stability and conformation of large chelate rings are discussed [431]. The single crystal ESR spectra of halo 1,1,1-tris(diphenylphosphinomethyl)ethane nickel(I) at 4.2K are interpreted in terms of an orbitally degenerate ground level [432]. The complex tris(2-diphenylphosphinoethyl)amine nickel tetraphosphorus (169) has been prepared by additions of elemental phosphorus to the chelate complex in THF solvent [433]. The complex is bonded to P_4 via a single Ni-P bond. Principal paramagnetic susceptibilities of single crystals of $NiX_2(PPh_3)_2$ (X= Cl,Br) have been used as evidence for π-acid behavior for these ligands because of the observation of large nephelauxetic effects in these systems [434]. A diamagnetic compound (170) has been formed by the displacement of triphenylphosphine. The Ni compound is air stable but the Pd and Pt complexes are very air sensitive. The nature of the Ni compound has been established by x-ray crystallography [435]. The crystal structure of the complex cis-$PtCl_2(Ph_2PC{\equiv}CPPh_2)$.2MeCN (171) does not have the triple bonds coordinated to Pt but they interact with each other [436]. The synthesis and ^{31}P nmr spectroscopy of unsymmetrical cis-diphosphino alkenes (172) from the coordinated alkyne phosphine and a secondary phosphine has been described. Data



(169)

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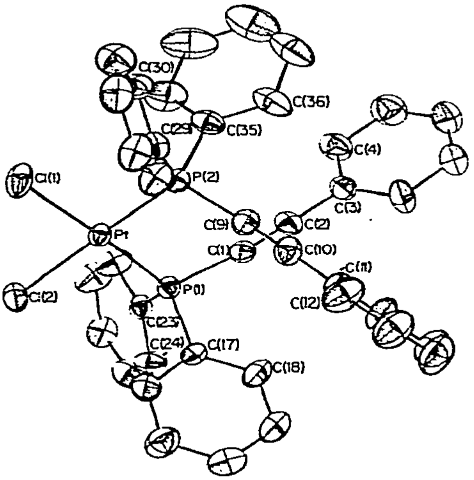

(171)

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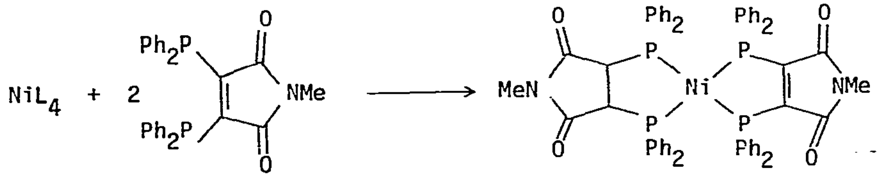
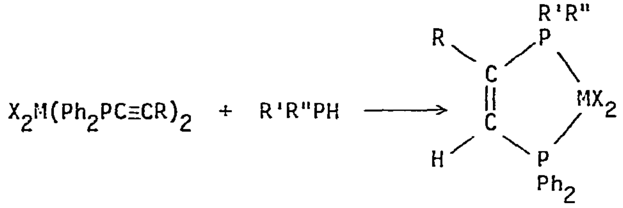


L= PPh_3

(170)

are given for a large number of complexes having differing functional groups [437]. The dissymmetric chelating agent (RR,SS)-o-phenylenebis(methylphenylarsine) has been resolved into its enantiomers by fractionally crystallizing internally diastereomeric palladium complexes containing the ditertiary arsine and optically active o-metalated dimethyl(α-methylbenzyl)amine [438]. These authors also describe the preparation of the phosphine ligand and the fractional separation of the (RR,SS) and (RS)-diphos portions using the nickel complex [439]. A comment has been made that vertical ionization potentials are not a reliable guide to the donor abilities of tertiary phosphines nor to the electronic tendencies of tertiary phosphine Pt complexes to undergo oxidative addition. The note stresses the change in geometry of the phosphine on coordination and the non-bonded interactions between an ortho hydrogen and the coordinatively unsaturated metal center [440].

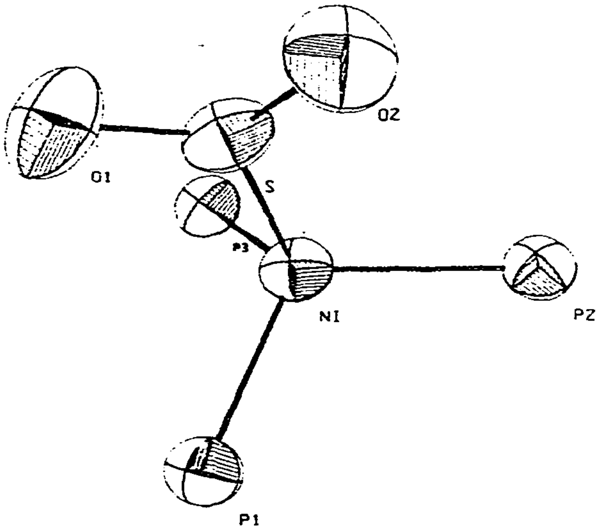
The crystal structure of $[PtCl(\mu\text{-dppm})]_2$ shows distances Pt-Pt and Pt-Cl of 2.651 Å and 2.401, 2.408 for the latter. The angle between the coordination planes is 38.6° [441]. Treating the compounds $M(PR_3)_4$ (M= Pd,Pt) with secondary phosphine sulfides and selenides at room temperature gives chalcogenophosphinito bridged metal(I) complexes (173). The paper describes a series of compounds and data for ν(PS) and the ^{31}P nmr shifts are reported [442].



(172)

$$2M(PR_3)_4 \quad + \quad 2R'_2P(X)H \longrightarrow \left[(R_3P)M(XPR'_2)\right]_2 \quad + \quad H_2 \quad + \quad 6PR_3 \qquad (173)$$

The ^{13}C nmr spectrum of $(PPh_3)_2Pt(n\text{-}CS_2)$ shows an AXX' pattern due to coupling of the CS_2 carbon to both cis and trans PPh_3 ligands. This rigid configuration is consistent with the solid state structure. These couplings do not collapse in the presence of either excess PPh_3 or CS_2 [443]. The compound N_4S_4 reacts with $Pt(PPh_3)_4$ to give $Pt(N_4S_4)(PPh_3)_2$ or $Pt(N_2S_2)(PPh_3)_2$ depending on conditions. Similar compounds are obtained from $Pt[P(OPh)_3]_4$. The compound $S_4(NH)_4$ reacts with $Pt(PPh_3)_4$ to give $Pt(S_2N_2H_2)(PPh_3)_2$. The complexes of S_2N_2 and $S_2N_2H_2$ are considered to be square planar Pt(II) with those of S_4N_4 being 4-coordinate Pt(0) [444]. Platinum and palladium supported on silica have been obtained by the heat of treatment of $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$. The metal dispersion has been determined as a function of thermal treatment [445]. The structures of $Ni(SO_2)(PPh_3)_3$ and $Ni(SO_2)_2(PPh_3)_2$ (174,175) show the SO_2 to be S-bonded to the nickel. For (174) the two SO_2 groups are nearly coplanar with each other, the dihedral angle between them being 25.3°. In both complexes the angles about the nickel atoms are close to tetrahedral [446]. Reactions of $Pt(PPh_3)_4$ with the sulfines XYC=S=O (X,Y= aryl, S-aryl, S-alkyl, Cl) yield complexes of type $Pt(XYCSO)(PPh_3)_2$. In each case the sulfine ligand is coordinated side-on via the C=S π-bond. The compounds $Pt(XYCSO)(PPh_3)_2$ containing reactive C-X and/or C-Y bonds (X,Y= S-aryl, S-alkyl, Cl) undergo a rearrangement in solution to give complexes of the type $PtX(PPh_3)_2(YCSO)$ [447]. Catecholatebis(triphenylphosphine)platinum(II) compounds can be oxidized by $AgOCOCF_3$, $CuCl_2$, or $FeCl_3$ to give paramagnetic compounds. From EPR evidence the unpaired electron is localized essentially on the paramagnetic o-semiquinolate ligand [448]. The reaction of $(PPh_3)_2PtO_2$ with o-diamines and o-diols gives complexes containing the diamido and phenolate groups complexed to platinum (II) (176) [449]. The



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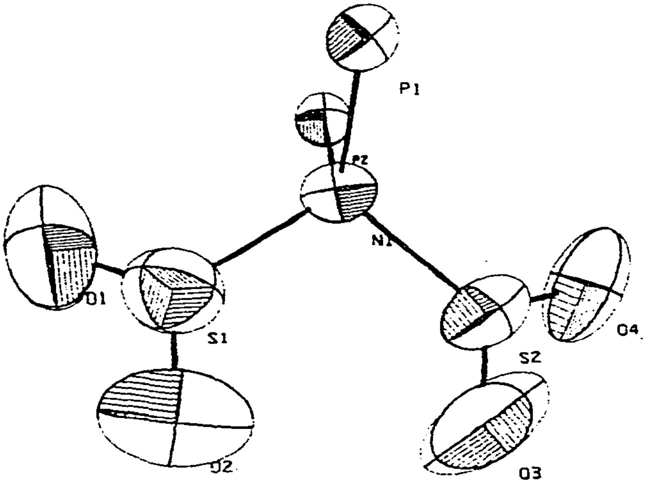

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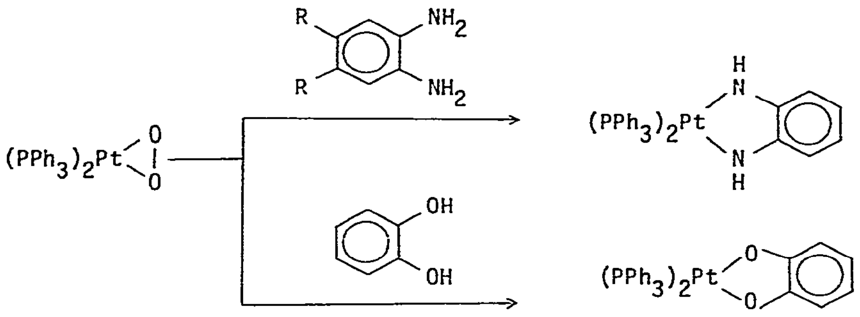
diamido complexes can be reversibly protonated to give cationic diamino complexes. Binuclear complexes $[Pt_2(O_2)(OH)(PPh_3)_4]$ X(X= ClO_4, BF_4, PF_6, NO_3) and $[Pt_2(OH)_2(PPh_3)_4]X_2$ have been prepared by the stepwise reaction of $Pt(O_2)(PPh_3)_2$ with HX (177). The reaction gives H_2O_2. The presence of peroxo- and hydroxo-bridges between the two Pt atoms in $Pt_2(O_2)(OH)(PPh_3)_4$ has been confirmed by x-ray crystallography [450] Chelate compounds $Ni(SH)_2$(dppe) and $Pd(SH)_2$(dppe)(178) have been obtained by treating the corresponding cis-dichloro compounds with NaSH. The yields are greater than 60% [451].



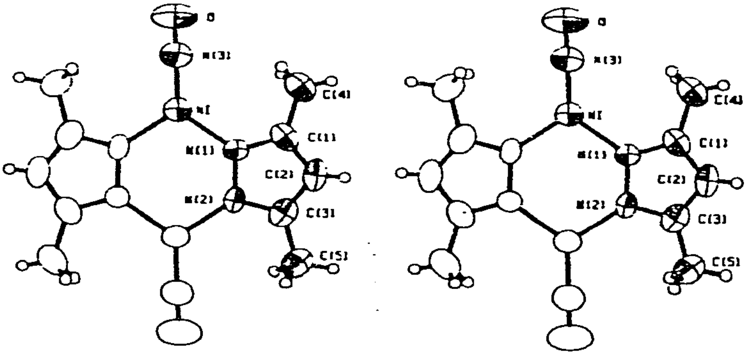
(176)

$$Pt(O_2)(PPh_3)_2 \;+\; HX \dashrightarrow Pt_2(O_2)(OH)(PPh_3)_4\,X + [Pt(OH)_2(PPh_3)_4]X \qquad (177)$$

$$\underline{cis}\text{-}NiCl_2(dppe) \;+\; 2NaSH \longrightarrow \underline{cis}\text{-}Ni(SH)_2(dppe) \;+\; 2NaCl \qquad (178)$$

Liquid-solid chromatography has been used for the separation and analysis of pentafluorophenyl organometallic groups containing Pt-Hg, Pt-Ge, Pt-Cd and Pt-Sn bonds. The technique has been used to monitor the synthesis of the compounds. In addition its use in the investigation of the reactivities of these compounds allows one to determine the direction of the reactions, and also the detection of intermediate formation [452].

In a series of papers the pyrazolyl nitrosyl complexes of nickel are described. The articles describe the syntheses and reactivity along with the crystal structures of $[Ni(NO)(\mu\text{-}N_2C_5H_7)]_2$ (179), $[(NO)Ni(\mu\text{-}I)(\mu\text{-}N_2C_5H_7)_2Ni(NO)]^-$ (180) and $[Me_2Ga(N_2C_5H_7)(OCH_2CH_2NMe_2)]$ Ni(NO) (180) [453,454,455]. The reaction of trans-$Ni(NO_2)_2(PEt_3)_2$ with CO gives CO_2 and $Ni(NO_2)(NO)(PEt_3)_2$. An ^{18}O labeling study using $Ni(N^{18}O_2)_2(PEt_3)_2$ establishes NO_2^- as the oxygen source in CO_2 The extent of ^{18}O enrichment in the CO_2 product indicates that the intermediate(s) involved must be sufficiently long lived to undergo appreciable, but not statistical, oxygen scrambling between carbon and nitrogen atoms prior to the irreversible loss of CO_2 [456]. The structures of MO_2L_2 (M= Pd,Pt; L= PPh(t-Bu)$_2$ have been solved. The O-O distances are given as 1.37(2) and 1.43 (2) Å in the Pd and Pt complexes respectively. Total energies, bond indices (M-O and M-P), and π-orbital population of dioxygen have been calculated on compounds $MO_2(PH_3)_2$ (M=Ni,Pd) by a modified INDO MO method as functions of the interligand angle P-M-P ($90^\circ \leq a \leq 150^\circ$). A minimum in energy is found at =108°. This geometrical effect in MO_2L_2 appears to be an important factor governing the coordination bond strength of dioxygen to a metal. The structures of the compounds Pd (182) and Pt (183) are shown [457].



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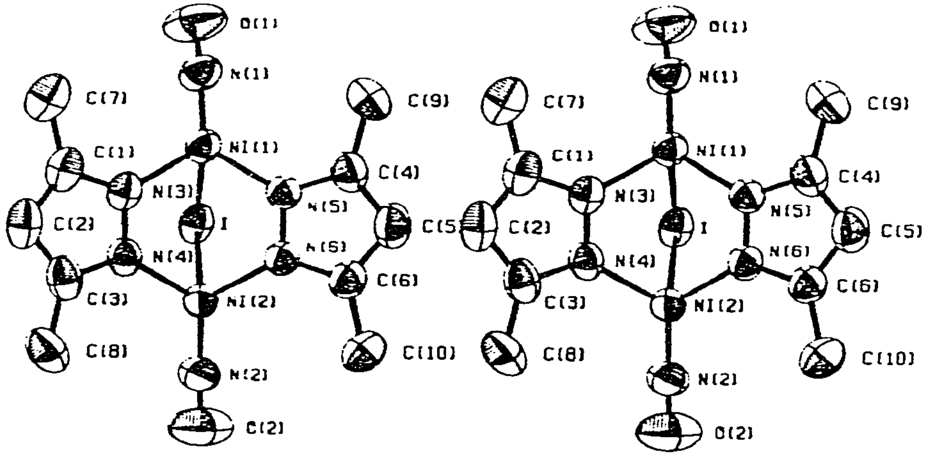

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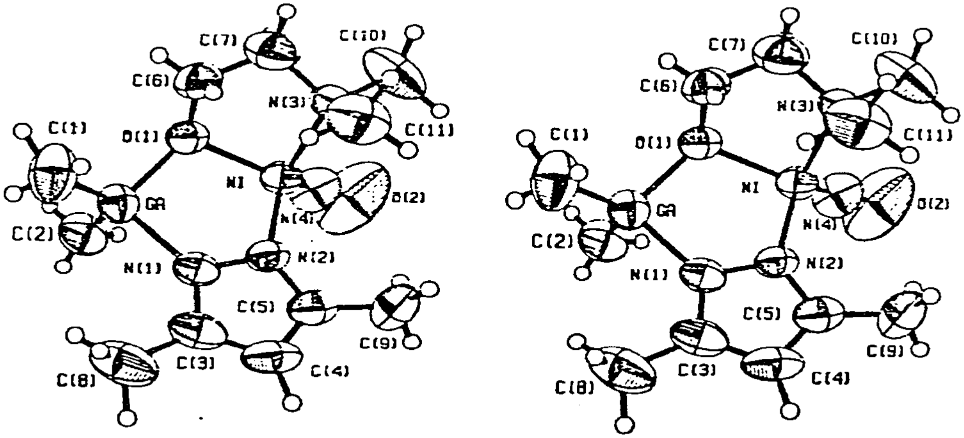

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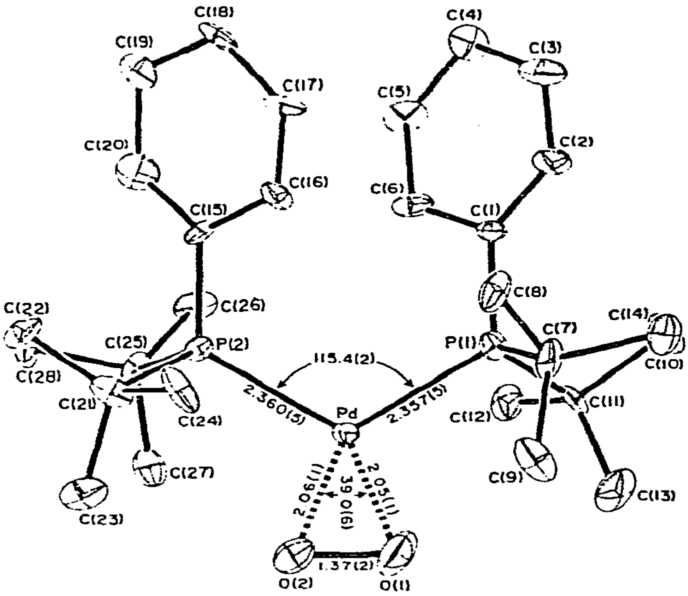

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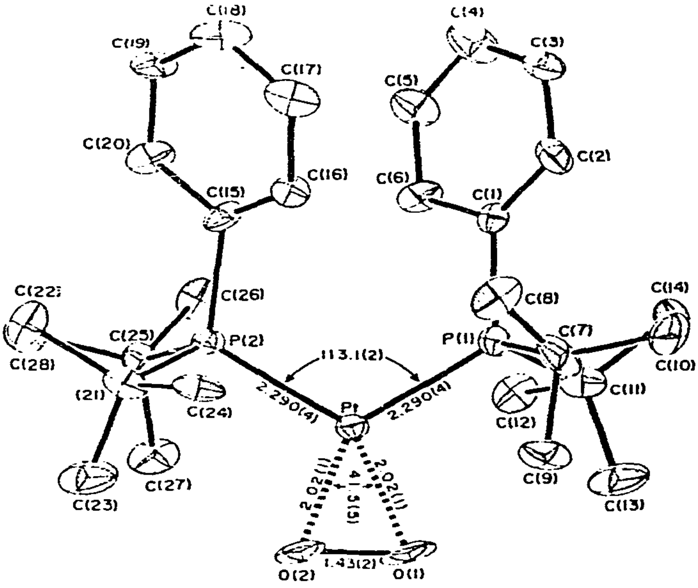
(182)



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(183)

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